

Report 3. Investigation of Catalyst Manufacture
and Recovery

Date of Investigation: April 6 and 7, 1945.

Personnel conducting Investigation:

Dr. V. Haensel, U.S., Petroleum Administration for War
Capt. J.H.G. Plant, British, Ministry of Fuel and
Power

Capt. C.C. Hall,

Personnel Interrogated:

Dr. Blöschel
Dr. Herbke

Reported by: Capt. C.C. Hall, British, Ministry of Fuel
and Power.

The Preparation and Reduction of Cobalt Catalyst.

Dr. Gehrke, who was in charge of the Ruhrchemie catalyst factory, was not available for interview but Dr. Blöschel who was in charge of cobalt catalyst manufacture and recovery and Dr. Herbke, in charge of catalyst reduction, were present and gave full information in their respective fields.

The composition of the standard cobalt catalyst prepared at Sterkrade and supplied to all Western-German Fischer-Tropsch plants was given as 100:5:8:180-200 cobalt; thorium:magnesia:kieselguhr. This catalyst had been in use since 1938 and replaced the former 100:15:200, cobalt; thorium:kieselguhr catalyst.

To be suitable for catalyst preparation, the kieselguhr must contain less than 1% of iron (as tested by refluxing a sample for 1 hour with 25% HNO₃) otherwise excessive methane production occurs during the synthesis. It must also contain less than 0.4% Al₂O₃ in the raw, uncalcined state, otherwise the catalyst tends to 'gel'. To avoid the necessity for acid-washing, the kieselguhr used at Sterkrade is selected to meet the above conditions. The present material is obtained from deposits near Hanover and is calcined before use, at Sterkrade, at 600-700°C. After this treatment the total volatile matter, including water, must not exceed 1%.

Due to slight variations in the density of various batches of kieselguhr, the proportion used in the catalyst is varied over the range indicated above in order to maintain a constant cobalt content of 80 gm./litre unreduced catalyst granules.

The various steps in the catalyst preparation are indicated in the diagram (fig. 5). 750 l. of a solution of the nitrates in the desired proportions, 100 Co : 5 ThO₂ : 10 MgO (2 parts MgO are left unprecipitated) containing 40/41 gm. Co./l. are heated to 100°C. in an overhead, stainless-steel tank (1). The contents are run into the precipitating tank (2) fitted with a direct-drive twin-screw stirrer and containing 750 l. of a solution containing 104 gm. Na₂CO₃/l. also maintained at 100°C. The mixture is stirred for $\frac{1}{2}$ minute and then dry kieselguhr is added through the hopper (3) and stirring continued for a further 1 minute. The slurry is pumped to a standard-type filter-press (4) and the cake washed with distilled water until the wash-water is neutral as tested by the addition of nitrophenol to 100 ml. wash water + 5 ml. 1/10 N.H₂SO₄. Catalyst equivalent to 64 Kg.Co requires ca. 10m³ wash-water and the washing occupies 14-15 minutes.

The washed cake is then dropped into a "masher" (5) situated below the press and is mixed with dust from the screening plant. (64 kg. total Co gives 45 Kg. Co as dust). The resulting cream is then pumped to a rotating suction filter (6). The thin cake scraped off the filter drum contains approximately 70% water and falls into the extruder (7) where rotating arms force the paste through 3 mm. diameter holes whence it falls into the drying chamber (8). The dryer is a cylindrical vessel 7 m. in diameter and comprises 20 super-imposed stages 20 cm. apart. The catalyst is swept round each stage by rotating arms and falls down the vessel from stage to stage during a period of 1 $\frac{1}{2}$ -2 hours. Drying is effected by steam heat and an air blast.

From the final stage of the dryer the rough granules containing 10% moisture are carried by a conveyor to the vibrating screens (9) and separated into over 3 mm., 1-3 mm. (the desired size), fines, and a dust which is sucked away in an air current. The air stream is filtered through a cloth filter (10) and then scrubbed with water and steam (11). The fine catalyst recovered from the scrubber is not returned to the masher for inclusion in the final catalyst because oxidation tends to convert carbonate to oxide which renders reduction more difficult and because

dirt and dust are apt to become concentrated in this fraction. This material, which only represents 0.1 - 0.2% of the whole, is therefore sent to the catalyst regeneration plant and treated as spent catalyst.

The fines from the screens and cloth filters are returned to the masher.

The particles above 3 mm. pass to a further set of screens (12) where rotating arms force the granules through the 3 mm. screen. The dust and fines from this process are returned to the masher and the 1-3 mm. grade is blended with the stream from the original screens (9) and is bagged for transport to the adjacent reduction plant via a telfer conveyor.

The bulk density of the granules is 320-350 gm./l. The maximum daily output of the plant is equivalent to 4 tonnes of cobalt.

The flow-scheme for catalyst reduction is shown in Fig. 6, which is based on a diagram prepared by Dr. Herbke. The reduction vessel comprises a central compartment of square cross-section containing the catalyst in a bed 30-35 cm. deep and 2.1 m² in area, with top and bottom fittings in the form of truncated pyramids. A sheet-iron grille (15 cm. cubes) is placed on top of the catalyst bed and sinks into it to a depth of about 10 cm. This device serves to break up the gas stream entering the top of the reduction vessel. One charge of catalyst weighs 200-250 kg. and occupies 800 l. There are 6 of these reduction vessels. (See Fig. 7)

The reduction is effected by passing downwards through the catalyst a rapid stream of ammonia synthesis gas (75% H₂ + 25% N₂) which is preheated to 460°C. in a tubular heater fired with coke-oven gas. The effluent gas is re-heated to 300°C. and the CO₂ present (ca. 2 gm./m³) is converted to methane by passage through a bed of synthesis catalyst in another reduction vessel. The gas is then cooled, dried by refrigeration and passage through silica gel and is returned to the preheater for the reduction where it meets fresh make-up gas.

The recycle and fresh gas enter the reducer at about 7000 m³/hr. (S.V. 8800). The period of reduction varies from 40 to 60 minutes, depending on the exact gas velocity which varies according to the number of reduction vessels in use. The temperature is varied according to the time and gas velocity as shown below :

<u>Time</u>	<u>Temperature at inlet to reducer</u>	<u>Gas Velocity</u>
40 mins.	435°C	8000 m ³ /hr.
60 mins.	428°C	6000 m ³ /hr.

The temperature is controlled to within $\pm 2^{\circ}\text{C}$. After reduction is complete the catalyst is cooled to room temperature in a stream of nitrogen, the nitrogen then displaced by CO₂ and the contents of the reduction vessel discharged into a kübel by removing the top cover plate and inverting the vessel. The vessels were so balanced that this inversion could be accomplished by a hand-operated mechanism.

A total of 16 reduction charges are required to fill one kübel.

In the reduction process 50-60% of the cobalt is reduced to metal. If over 60% is so reduced a less suitable catalyst results. The extent of the reduction is determined by measuring the volume of hydrogen evolved when the reduced catalyst is treated with acid.

The exact reduction conditions were said to depend on the nature of the kieselguhr used in the catalyst preparation. Dense catalysts caused difficulties in the reduction.

Regeneration of Spent Cobalt Catalysts

This subject was not discussed in detail but Dr. Blöchel prepared a diagrammatic flow sheet (Fig. 8) for the recovery of cobalt and thorium. The regeneration plant had been almost entirely destroyed by bombing.

The Preparation of Other Catalysts

Nickel catalyst for the methanisation of coke-oven gas, chromium-aluminium catalysts for dehydrocyclisation of heptane, water-gas shift catalyst and Feinreinigungsmasse were also prepared in the catalyst factory, but as these did not come under Blöchel's control no further information was obtained.

Plant similar in general design to the cobalt catalyst plant was being erected for large-scale manufacture of iron catalysts. So far these catalysts had only been prepared on pilot-plant scale.

The iron catalyst preparation was carried out directly under Dr. Gehrke's supervision but Blöchel understood that the catalyst which was to have been prepared on a large scale had the composition :-

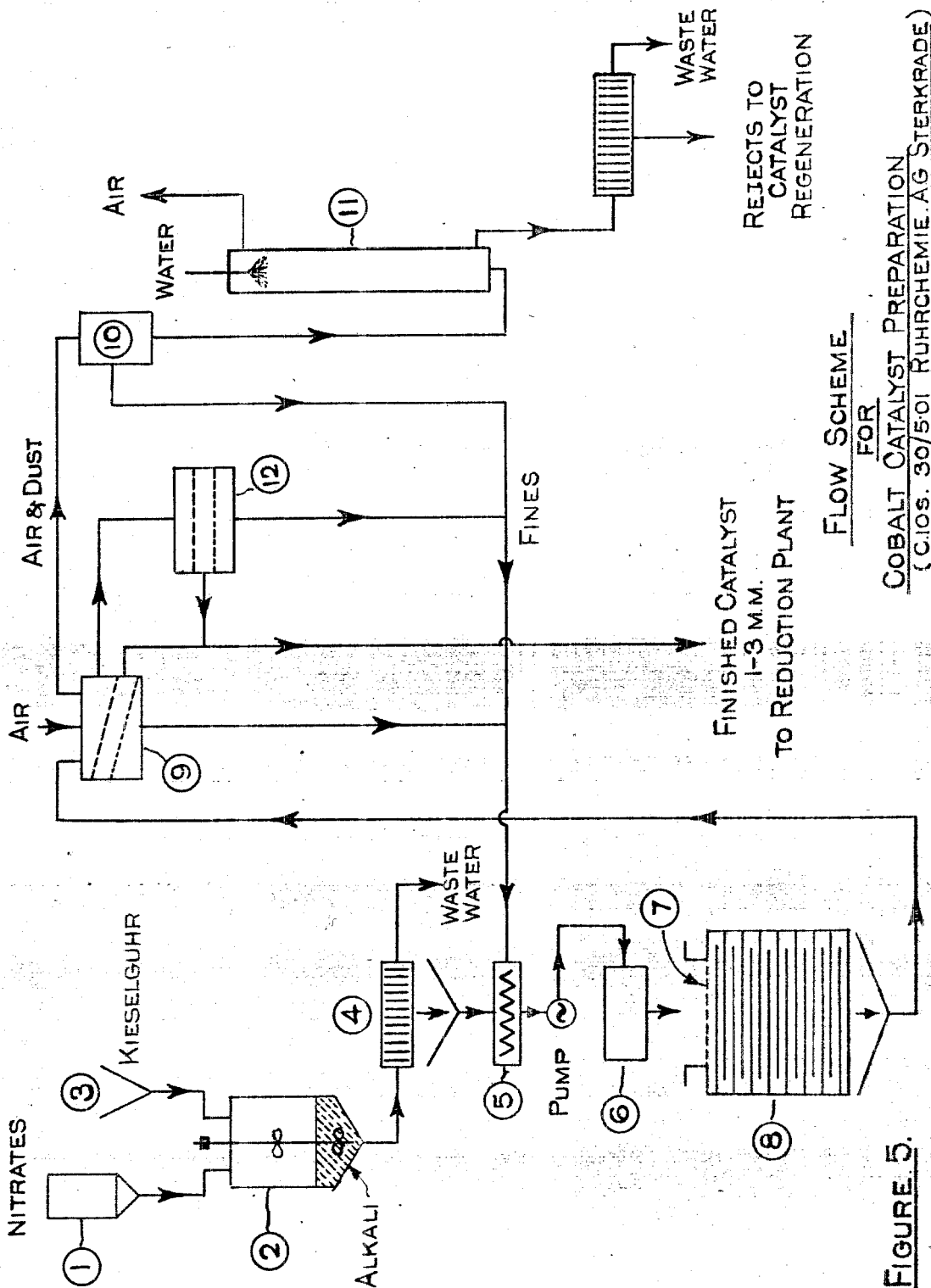
100 Fe : 2.5 Cu : 10 CaO : 15 kieselguhr

The precipitation was carried out with KOH and the nitrates under conditions generally similar to those used for cobalt. Blöchel believed that the precise details of the precipitation were most important but he was not acquainted with them. He understood that the best reduction conditions were not fully established, but believed that H₂ was used at 300°C. under conditions generally similar to those used for cobalt.

Samples

Small samples (2-5 lb.) of tested and approved unreduced and reduced cobalt catalyst and kieselguhr were obtained (under Blöchel's guidance) from the sample room. A bulk sample (28 lb.) of kieselguhr was taken from the store adjacent to the feed hopper on the top floor of the cobalt-catalyst plant.

Samples of reduced and unreduced iron catalyst were removed from Dr. Gehrke's laboratory.



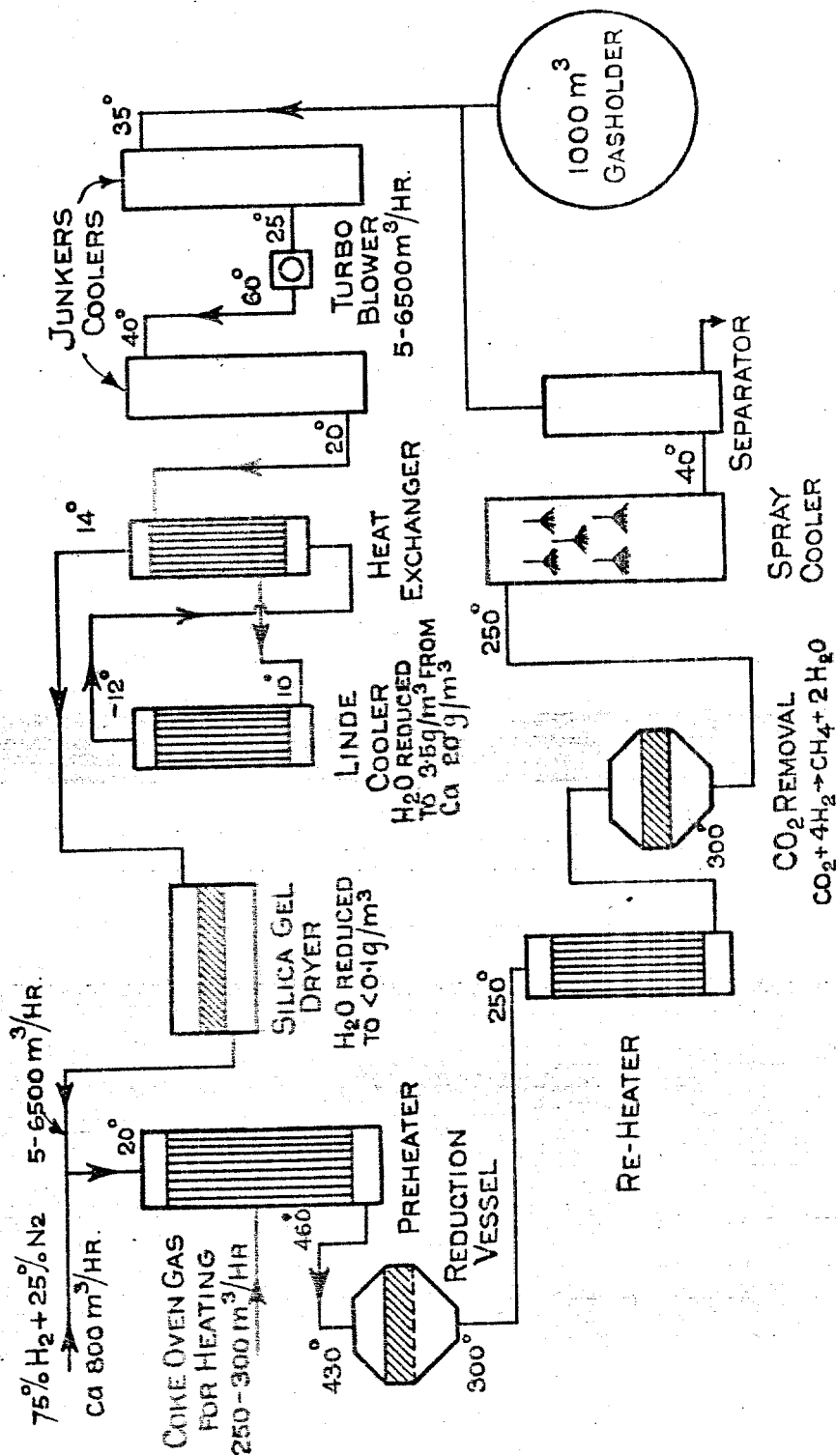


FIGURE 6. FLOW-SCHEME FOR COBALT CATALYST REDUCTION
 (C.I.O.S. 30/5-01 RUHRCHEMIE A.G., STERKRADE.)

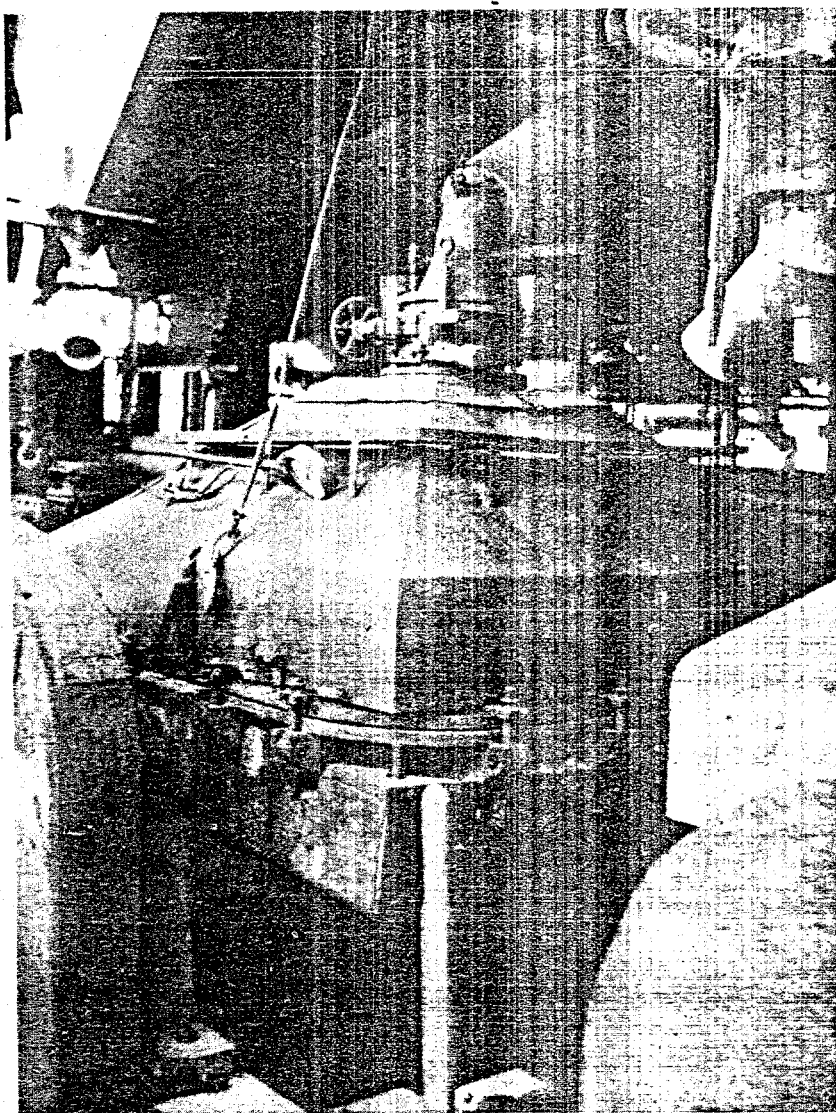


Fig.7. Catalyst reduction vessel.
(30/5.01, Ruhrchemie A.G., Sterkrade-Holten)

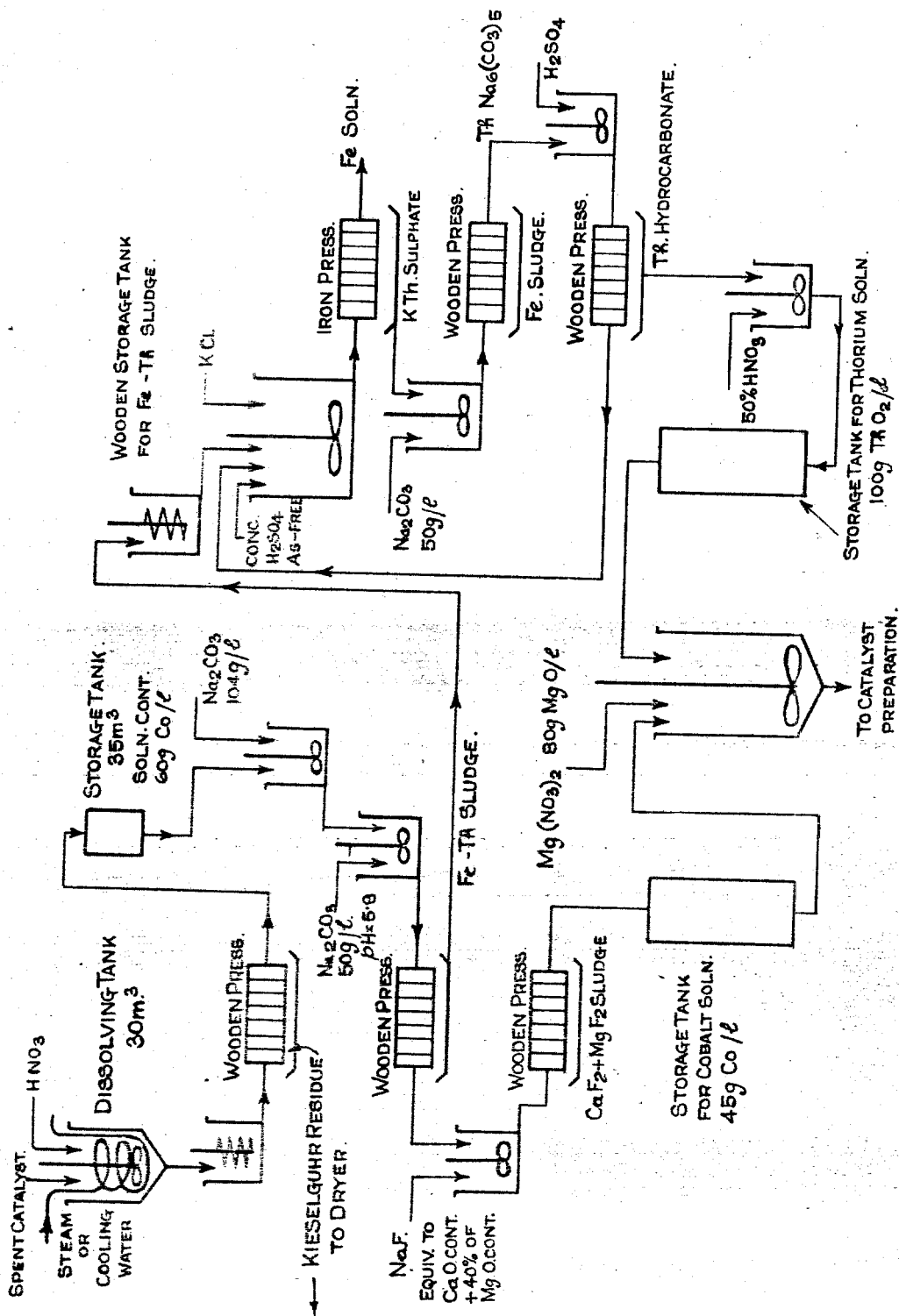


FIG. 8. FLOW SCHEME FOR RECOVERY OF COBALT AND THORIUM.

C.I.O.S. 30/5-01 RUHRCHEMIE A.G. STERKRADE.