

RESTRICTED

80889

TECHNICAL REPORT NO.

-45

SYNTHESIS GAS PURIFICATION PROCESSES IN GERMANY

Summary

This report records information obtained by technical investigators on processes for the purification of gases in Germany for their subsequent use in chemical and synthetic fuel production purposes. It covers those processes which are in commercial use for the purification of large volumes of gas such as are employed in the production of ammonia, hydrogen, methanol and synthetic oils.

The report describes the several processes studied and the factors controlling them. The emphasis has been on those parts of the processes which are not commonly known in the United States, the more common elements having been omitted for sake of brevity. The appendix contains flow diagrams, equipment drawings and copies of original German technical documents pertinent to the subject, which serve to elaborate on the chemical engineering, mechanical design, and development phases of the processes.

AUGUST 1945

U.S. NAVAL TECHNICAL MISSION IN EUROPE

RESTRICTED

80890

TABLE OF CONTENTS

	<u>Page</u>
1. Introduction	1
2. Dusts and Tar Removal	1
3. I. G. Alkaid Process for Gas Purification	2
4. I. G. Claus Process for Recovery of Sulphur from H <sub>2</sub> S.	5
5. H <sub>2</sub> S Removal from Gas with Iron Oxide (Grobreinigung)	6
6. Removal of Organic Sulphur from Gases (Feinreinigung)	7
7. Gas Purification by Activated Carbon (Feinstreinigung)	9
8. Removal of CO <sub>2</sub> from Gases.	10
9. Removal of CO from Gases.	11
10. Conclusions	11

# SYNTHESIS GAS PURIFICATION PROCESSES

## INTRODUCTION

80891

Since the gases manufactured in Germany for chemical and synthetic fuel production purposes are put to use in chemical reactions that employ sensitive catalysts, it has been necessary to clean the gases of both their entrained solid and liquid materials and also to remove by physical or chemical means the deleterious components such as sulphur bearing gases and carbon dioxide.

This report covers the purification of feed gases for synthesis purposes, and describes the processing of these gases between their production and their utilization in the synthesis. It does not describe purification and separation of product gases by the Linde fractionation, adsorption of hydrocarbons on activated carbon, and absorption processes.

The many gases manufactured in Germany for hydrogen production or for production of synthesis gases for the Fischer-Tropsch, Oxo-synthesis, Synol-synthesis, Methanol-synthesis, Isobutanol-synthesis, ammonia-synthesis, Buna rubber synthesis, etc., invariably contained contaminating materials. The principal contaminants in the feed gases are usually one or more of the following: tar, aromatic compounds, dust, hydrogen sulfide, ammonia, carbon monoxide, carbon dioxide, hydrogen cyanide, and nitrogen, the type and quantity of contamination depending on the source of the gas. The degree of purification required depends of course upon the purpose for which the gas is to be used and the purification process is selected with that in mind. The object of this report is to present briefly the various processes that were used in Germany during the war to accomplish the desired purification of gas for these purposes.

For the purpose of presenting several processes in a logical manner in this report they are classified as follows:

1. Dusts and Tar Removal
2. I.G. Alkacid Process for Gas Purification
3. Claus Process for Recovery of Sulphur from  $H_2S$
4.  $H_2S$  removal from Gas with Iron Oxide (Grobreinigung)
5. Removal of Organic Sulphur from Gases (Feinreinigung)
6. Gas Purification by Activated Carbon (Feinstreinigung)
7. Removal of  $CO_2$  from Gases
8. Removal of CO from Gases

## 2. DUSTS AND TAR REMOVAL

Nearly all manufactured gas contains some dust as it leaves the production unit. In addition, gas made from coal in coke-ovens or coal gasifier units (as differentiated from that made from hard coke) also often contains small amounts of tar or resins. In most cases where the gas contains both contaminants, the tar is removed along with the dust. Some of the German installations, however, include a separate electrostatic tar precipitator installation which operates in the conventional manner well known in the United States.

Three methods of dust and tar removal are in general use in Germany as follows: mechanical separators such as cyclone separators, baffled separators, traps (both wet and dry) and filters; (2) Electrostatic precipitators; and (3) Water washing methods.

The mechanical separators used in Germany are of various designs and were made in Germany by several companies. A good description of the methods usually employed is given in a report dated December 12, 1936 by Dr. Geister of I.G. Farbenindustrie entitled "Entstaubung", or translated, "Dust Removal." A copy of this report is contained in the Appendix of this report and is not described further here.

A special filter found to be in use which is claimed to have particular advantages as a mechanical separator for gas cleaning is the "Oppauer Schachtfilter" in which the filter medium is a slowly moving bed of granulated coke installed in a vertical cylindrical chamber and resting on a movable grate. The gas enters the bottom and flows to the top. The coke is shaken from the grate into water, agitated and washed, then returned to the top of the bed by an hydraulic conveyor, which also serves to keep the filter bed wet. The process is described in a report by Dr. Sachsso entitled "Removal of Carbon Black and Dust from Gases with the Oppauer Schacht-filter" attached in the appendix.

Other filters that may be mentioned in passing are the Viscin air filter frequently used on the air inlet of the oxygen plants, the synthetic silk bag filters used in the separation of carbon black from gases cracked in the electric arc, and the many ordinary filters packed with metal turnings, wood shavings, and fibre glass either dry or saturated with an oil or adhesive material.

The principle of the electrostatic process is well known so details of construction were not obtained.

When electrostatic precipitation is not used, the last traces of dust in the gases are usually removed by a water wash. This water wash may be carried out in a spray tower, an ordinary packed column, may be combined with an absorption purification system for removal of  $H_2S$ ,  $CO_2$ ,  $NH_3$  etc. or may be performed in a mechanically agitated washer-cooler such as the patented Theissen unit. Where a gas absorption-purification system such as the Alkazid unit is also used for dust removal, a filter is included in the process through which either continuously or intermittently a part of the circulating absorption solution is passed to remove the accumulated sludge.

### 3. I.G. ALKAZID PROCESS FOR GAS PURIFICATION

Chemical purification is employed where the contaminants are not removable by mechanical means. Gas impurities of a slightly acid nature such as hydrogen sulphide, carbon dioxide and hydrocyanic acid were sometimes removed from gases by basic substances such as alkali hydroxides and possibly sodium or potassium carbonate solutions that can be regenerated. However the process developed by the Girdler Corporation employing the alkylol amines especially the mono-, di-, and triethanolamine and later diaminopropanolite to absorb hydrogen sulphide and carbon dioxide was not found in use. Amines are strong bases and water soluble

substances which readily absorb  $H_2S$  and  $CO_2$  at normal temperatures and liberate them when heated to  $100^\circ C$ , and absorb several times as much  $CO_2$  and  $H_2S$  per unit of volume as do the potassium or sodium carbonate solutions.

The Alkazid process was developed by I.G. Farbenindustrie to remove  $H_2S$  or mixtures of  $H_2S$  and  $CO_2$ . Gas purification units of this type have been constructed in many countries all over the world. The process is used primarily to treat gas of high sulfur content before it goes to other steps for more complete purification. It also claimed the advantage of yielding hydrogen sulfide of quite high concentration, e.g., under favorable conditions up to about 90%  $H_2S$ . This unit is probably used more often in Germany to treat gases from hydrogenation or cracking operations than it is used to treat manufactured gas, but it is satisfactory for either service.

A description of the unit as applied to hydrogenation product gas treatment is given in U.S. Naval Technical Mission in Europe Report No. 87-45 "The Wessling Synthetic Fuel Plant" and is not repeated here.

A simplified general flow sheet is shown on drawing M 2028 (Item 3 in the appendix of this report). In this sketch the raw gas enters the bottom of one or both absorber columns (labelled "Abstreifer") which can be operated in parallel or in series. The purified gas ("Reingas") leaves the unit from the top of the absorber or absorbers. The cold lean caustic solution passes countercurrent to the gas down the columns, out the bottom through a screen and is pumped through a heat exchanger countercurrent to the hot lean caustic from the bottom of the stripper. From the heat exchanger the rich caustic is fed to the top of the stripper column. The stripped gas ( $H_2S$  and  $CO_2$ ) leaves the top of the stripper, passes through a condenser and separator to remove condensate, thence out of the system to the Claus Unit or other disposal. The steam to heat the kettle of the stripper is distributed between direct and indirect heating in order to hold the specific gravity of the caustic between 1.16 and 1.20. The stripped caustic leaves the bottom of the absorber through a screen, passes through the countercurrent heat exchange mentioned above, through a water cooler and to the top of the absorber.

There are two types of solutions used in the Alkazid process. "DIK Caustic", the solution most commonly used, is a solution of potassium dimethyl or diethyl alpha aminoacetate and is used to remove  $H_2S$  from gases containing  $CS_2$ . "M-Caustic" is a solution of potassium methyl alpha aminopropionate. It will absorb both  $H_2S$  and  $CO_2$  but is used only in the absence of  $CS_2$ . The normal effective gas charge of the solutions ranges from 10-15 volumes per volume of caustic for best removal of  $H_2S$  but can be increased to as much as 30-35 volumes per volume by the use of mechanical contacting devices and longer contact time, or by permitting a higher sulfur content in the outlet gas.

The process has been used to treat gas containing up to 10%  $H_2S$ , and will remove the  $H_2S$  to 0.07 to 0.10%. Absorption and stripping are at substantially atmospheric pressure. The optimum absorption temperature is about  $5^\circ C$ , but temperature up to  $30^\circ C$  can be satisfactorily used. The relative absorption of  $CO_2$  by DIK-caustic increases with

increased absorption temperature, and with increased time of contact over the normal one minute.

80894

The stripper kettle temperature is maintained at about 105°C.

A new development of this process, which has not yet been put into commercial operation, absorbs at 8-10 atmospheres and strips at 1 atm without the addition of heat to the kettle except for the direct steam necessary to control caustic gravity. The effective loading of the caustic under these conditions is only 4-5 volumes/volume, but it is claimed that the extra pumping and compression cost is more than compensated by the economy of steam.

The process is also used for low pressure CO<sub>2</sub> removal where sulfur is not present or is present in small quantities.

A cost comparison made by the I.G. Farbenindustrie shows the Alkazid process to be cheaper than water wash, Girbotol, Koppers, Shell and several other processes; however, even if the figures are accepted, altered conditions in the U.S. may well change the results and no positive statement can be made of the superiority, of the process for all conditions. The main advantage of the process over the ethanolamine process is the lower volatility of the salute.

Many operating difficulties have been experienced with the unit. The principal trouble has been with corrosion of the steel and aluminum used in the equipment. The Germans combat this corrosion by close control of the caustic gravity, control of the temperature in the aluminum equipment, careful exclusion of air from the system, and by "passifying" the aluminum through circulation of dilute sodium silicate solution through the equipment before operation. No mercury or mercury salts are used where they can possibly enter the system. The direct steam to the stripper must be maintained dry and free from impurities. Attached is a report of visit made to the Alkazid Plant in Lutzkendorf in regard to the corrosion.

Foaming of the solution occasionally causes trouble, but the I.G. have developed an antidote known as Schaumbekämpfungsmittel "I" (Foam-attacking agent "I") in the Louna plant.

Any oxygen that enters the system during operation forms thiosulfates in the solution, destroying its effectiveness. Special precautions are taken to prevent air entering the system at pump packings, or in the solution storage vessels, etc. This difficulty limits the use of the process to oxygen-free gases.

If the gravity of the solution gets too high or the solution gets too cold, solids will settle out. Corrective measures are heating and/or dilution of the solution.

For more complete information on operating and supervision methods for the Alkazid process two reports are included in the appendix as follows:

1. "Betriebsverfahren und Hinweise zum Alkaidverfahren"
2. "Richtlinien für den Betrieb und Überwachung von Alkaid-Waschanlagen."

80895

A more complete flowsheet which includes a NaOH wash following the Alkaid absorption is shown on drawing No. M3200-1, included in the appendix. A comprehensive technical article on both this process and the Claus process was published in the June 1958 issue of the Refiner and Natural Gasoline Manufacturer pages 237-244 and many of the details given there are not repeated here.

#### 4. I.G. CLAUS PROCESS FOR RECOVERY OF SULPHUR FROM H<sub>2</sub>S

The I.G. Claus process is a method for converting gaseous hydrogen sulfide into molten elementary sulfur. This process is often used as a supplementary process in connection with the Alkaid H<sub>2</sub>S removal process. The reaction basis of the Claus process is shown by the following equations:



Drawing Zo 1416-2 in the appendix of this report presents a flowsheet of the process. In this flowsheet the H<sub>2</sub>S comes from Gasometer Unit 14 through a blower to the two Claus "kessels" in parallel. Here it is partially burned with a controlled amount of air to yield a ratio of SO<sub>2</sub> to H<sub>2</sub>S of 1:2.) This mixture then passes over the bauxite catalyst in the first Claus "ofen" at a temperature of about 300° to 400°C where the second reaction takes place. The gas from the first "ofen" passes through an "aufhitzer" where fuel gas is burned to heat the gases further before they pass through the second Claus "ofen" to complete the second reaction. Molten sulfur is drawn from the bottom of each "ofen". The tail gases from the second "ofen" consist principally of nitrogen, water vapor, and carbon dioxide (from hydrocarbon gases) with about 3.5 g/m<sup>3</sup> of unreacted SO<sub>2</sub> and H<sub>2</sub>S. This gas passes through a cyclone or electrostatic separator to remove entrained elemental sulfur, then to the "Nachbrennungsofen" where a pilot flame burns the remaining H<sub>2</sub>S over bauxite before passage to the atmosphere.

Drawings FZA1b and FZA4-a show the Claus ofen and Nachbrennungsofen respectively. A catalyst bed of 3m diameter and 7m high will produce about 6 tons of sulfur per day at 80% recovery. The inlet H<sub>2</sub>S content can vary from 40% to 100%. Drawing 4A34210 shows the arrangement of equipment and piping.

The catalyst life is indefinite unless overheating causes sintering in which case only the upper layer is ordinarily affected. When this happens, the upper layer of catalyst is replaced.

The equilibria, experimental and calculated, are presented in an "Aktennotiz" dated July 11, 1941 by Dr. Orlicek under the title "Untersuchungen über die Lage des chemischen Gleichgewichtes beim Clausprozess."

Complete operating data for the Louna Plant are presented in a translation "Claus Ofen Operation" in the appendix.

### 5. H<sub>2</sub>S REMOVAL FROM GAS WITH IRON OXIDE (GROBREINIGUNG)

80896

The removal of H<sub>2</sub>S from gases by iron oxide mixtures is well known in the United States in the manufactured gas industry and no new information was obtained on this process. Briefly, the process is to pass the raw gas at low pressure and at atmospheric temperature through a vessel containing beds of wood shavings covered with crude iron oxide, beds of pelleted crude iron oxide or iron oxide mixtures. The H<sub>2</sub>S reacts with the iron oxide to form iron sulfide and water. The Germans ordinarily add air to the inlet gas in an amount sufficient to supply about half of the theoretical oxygen to convert the iron sulfide back to the oxide and to precipitate the elemental sulfur in the bed. When the H<sub>2</sub>S has been previously reduced by Alkzid or other process to 0.1% or less in the gas entering the oxide box, this air usually amounts to 4-6 m<sup>3</sup>/per 1000 m<sup>3</sup> of gas. The hydrogen sulfide in the outlet gas is nil, the organic sulfur is not diminished. When a gas with a high sulfur content is sent to the oxide boxes, the removal may be less complete and the life of the mass is naturally proportionately shorter. The outlet sulfur is, however, rarely over 1 gram per 1000m<sup>3</sup>, because three to four boxes are usually operated in series, with the freshest mass in the last box.

Under proper operating conditions the mass will hold 40-55% of its dry weight in sulfur before excessive H<sub>2</sub>S break through or excessive pressure drop occur. Most plants use a continuous addition of 0.1% to 0.2% oxygen to the inlet gas to react and precipitate the sulfur, but batch regeneration by circulating inert gas with 1% to 4% O<sub>2</sub> has been carried out by some concerns. When the maximum sulfur loading is attained the catalyst is removed, the sulfur burned for recovery of SO<sub>2</sub> and the residue is discarded.

The purifying agent is usually bought under the trade name Luxmasse which is the iron oxide residue from the refining of aluminum ore, or a mixture of Luxmasse and bog iron ore. A newer agent is called Lautamasse, which is the same general type of material containing 3-4% alkali as NaOH, Na<sub>2</sub>CO<sub>3</sub> and/or NaHCO<sub>3</sub>. A typical analysis of Lautamasse is as follows:

Apparent density	0.657 Kg/L.
Water	54.00%
Fe <sub>2</sub> O <sub>3</sub>	22.88%
Al <sub>2</sub> O <sub>3</sub>	16.45%
Ca O	1.03%
Mg O	Trace



$\text{Na}_2\text{CO}_3$	3.15%	
Na OH	0.49%	80897
Si O <sub>2</sub>	1.92%	

To conserve iron oxide, used Feinreinigung mass containing about 5-10% sulfur and 30%  $\text{Na}_2\text{CO}_3$  is sometimes mixed with the fresh charge. It was stated that if too much of this material is mixed in, trouble is experienced with fusing of the carbonate due to the wet operating condition.

## 6. REMOVAL OF ORGANIC SULFUR FROM GASES (FEINREINIGUNG)

The previously discussed iron oxide purification process removes only the inorganic or  $\text{H}_2\text{S}$  sulfur from the gas. The organic sulphur compounds are untouched. If they are present, and must be removed, it is necessary to subject the gases to further purification.

In Germany organic sulfur in synthesis gas is ordinarily removed by a process called "Feinreinigung". After the gas has passed through the final  $\text{H}_2\text{S}$  removal it goes to this "Feinreinigung" process at approximately atmospheric temperature and pressure. Here it passes through the tubes of a heat exchanger and of a direct fired preheater to raise the temperature to 150-300°C, this temperature increasing with the age of the catalyst. The gas then goes to the catalyst chamber where it passes from the center of the chamber to the outside through an annular bed of catalyst at a velocity of about 0.25 meters per second, from the chamber through the shell side of the heat exchanger mentioned above, then through one or two more catalyst chambers similar to the first.

The catalyst is composed of 60-70% crude iron oxide and 30-40% sodium carbonate. The organic sulfur in the gas is cracked to  $\text{H}_2\text{S}$  and reacts with the oxygen present in the inlet gas, (or oxygen added before the catalyst chambers) to form  $\text{Na}_2\text{SO}_4$ ,  $\text{FeSO}_4$ , and some elementary sulfur.

A new method of catalyst manufacture produces a much lighter, more porous mass. The method of preparation for a small batch based on 100kg of Lautarasse is as follows:

100 Kg of Lautarasse with 2% alkali content and 50% water is divided into two parts. One portion is dried, mixed with 5 Kg of  $\text{Na}_2\text{CO}_3$ , and then added to the remainder of the charge. This mixture containing 25% water is then wetted with a fine spray to proper consistency, is pressed to the desired grain size and dried. The drying is carried out first at 60-80°C until the mass is hard and then is completed at a temperature over 100°C. The resulting product is compared to the older catalyst in the table below:

	<u>OLD</u>	<u>NEW</u>
Apparent Specific Gravity, Kg/ liter	0.7	0.5
Grain strength, Kg/ cm <sup>2</sup>	6-7	3-4
$\text{Na}_2\text{CO}_3$ content %	30	15

	<u>OLD</u> 36	<u>NEW</u> 44
Fe <sub>2</sub> O <sub>3</sub> , %		
Porosity, %	50	70
To fill chambers, tons	100.8	76
Alkali in chambers, tons	29.5	12.5
Iron in chambers, tons	36.7	33.8
Organic Sulfur Loss, g/100 m <sup>3</sup>	1.0	0.1
Organic sulfur conversion, %	70	96.8

80898

The catalyst grains should be coarse (8-10mm) and all dust should be removed. The catalyst dust cannot be reworked as it reduces the porosity of the finished catalyst.

A gas volume of 100,000 Nm<sup>3</sup>/hr with 12-15 mg total sulfur in the gas entering the unit will use an average of about 4.8 tons per day of catalyst. Each unit will process 10,000 to 22,000 cbm/hr of gas depending on the age of the catalyst, and contains about 65 tons of catalyst in two chambers. Typical operating conditions for this process are as follows:

Inlet Gas	20,000 m <sup>3</sup> /hr
H <sub>2</sub> S in Inlet Gas	0.3g/100Nm <sup>3</sup>
H <sub>2</sub> S in Outlet Gas	nil
Organic S in inlet	15.0 g/100 Nm <sup>3</sup>
Organic S in outlet	0.20 g/100 Nm <sup>3</sup>
Temp in 1st chamber	230°C
" out 1st "	220°C
" in 2nd "	190°C
" out 2nd "	180°C

Several operating difficulties are encountered in this process. The worst difficulty is the formation of resinous coatings on the catalyst. This is prevented by the installation of an activated carbon absorption process before the unit to remove the resin-forming materials. Excessive H<sub>2</sub>S in the inlet gas overloads the unit and permits sulfur to break through. This is usually traced to poor operation of the previous H<sub>2</sub>S removal unit. Excessive temperature sinters the catalyst. Poor catalyst sizing or charging causes unequal distribution of the gas or excessive pressure drop, and also causes sulfur to break through and appear in the outlet gas.

In spite of these difficulties the "Feinreinigung" process is almost without competition in Germany for general use in the removal of organic sulfur from gas.

## 7. GAS PURIFICATION BY ACTIVATED CARBON (FEINSTREINIGUNG)

80899

There are two activated carbon processes used in Germany for the purification of synthesis gas. One is the so called "Feinstreinigung" of the Lurgi Company, which consists of the absorption of hydrocarbons on activated carbon. This process is used to remove the aromatics and resin forming hydrocarbons whenever gas is obtained from coal instead of from coke, not only to purify the gas but also to protect the catalyst used in the organic sulfur removal process (Feinreinigung). The other activated carbon purification process is that of the I.G. Farbenindustrie and is used to remove hydrogen sulfide. When this process is used it replaces both Alkacid and Grobreinigung wherever the inlet  $H_2S$  concentration is less than 7 grams/ $m^3$ . These processes are described below.

In the "Feinstreinigung" process of Lurgi the raw gas from the Alkacid purification unit or other source enters the Lurgi carbon chambers saturated with water at about  $30^\circ C$ . The water inhibits adsorption so that instead of a possible 80 hours on-stream absorption cycle time, a period of 20 hours is used. After the adsorption period the chamber is steamed for two hours, dried with heated gas for one hour, cooled for one hour and then put back into the adsorption cycle. An understanding of the process can be better obtained from the following concrete example of a Lurgi installation.

90,000  $m^3$ /hr of gas generated from coal is passed over 75,000 Kg of activated carbon located in five parallel chambers of 5m. diameter. A sixth chamber is in the regeneration cycle. After a chamber has been in service 20 hours, it is put into the regeneration cycle and the freshly regenerated chamber put back into adsorption. The regeneration requires a total of 4-1/2 tons of dry steam at 2-1/2 atm. pressure per chamber. The recovery of hydrocarbons amounts to about 0.4g/ $m^3$  of inlet gas and this material is added to the coke-oven gasoline. The drying cycle removes about 1500 kg of water.

One kilogram of carbon will process about 10,000  $m^3$  of gas before reactivation is necessary. The reactivation is carried out in a rotary kiln at  $800^\circ C$  with steam.

The I.G. Farbenindustrie process for hydrogen sulfide removal over activated carbon is an old process that dates from 1928, but it is still considered very satisfactory for gases containing a relatively small amount of sulfur. Drawing S92 in the appendix shows a schematic diagram of this process. The drawing shows that the raw gas goes through a blower then to a water separator, next a water cooler, and then more separators. Next a small amount of ammonia air mixture is added to it. The mixed gases then pass over an activated carbon bed at 800mm water pressure and  $20-40^\circ C$  temperature where the reaction:



takes place with the ammonia acting as an intermediate or catalyst. The H<sub>2</sub>S removal is substantially complete. The ammonia leaves the absorber along with the gas and is subsequently washed out in the water absorption process for removal of the CO<sub>2</sub> in the gas.

The sulfur found in the reaction is precipitated in the carbon bed, and when the bed is loaded the sulphur is washed out with a 20% ammonium sulfide solution in the form of ammonium polysulfide. Ammonium carbonate is also formed in the carbon and it is washed out at the same time. The ammonium carbonate must be removed from the wash solution and this is done by adding Ca Cl<sub>2</sub> solution to give the reaction:



The Ca CO<sub>3</sub> sludge is removed from the wash solution in a Dow type thickener. Sodium sulfide is added and the following reaction takes place in the solution:



The solution goes to a column operating at 2 atm. and 130° kettle temperature where it is distilled. The ammonium sulfide and part of the water go overhead; the sulfur in molten form and the sodium chloride solution are withdrawn from the two liquid phases of the kettle.

A concrete example of the use of this process is the treatment of 6000 m<sup>3</sup>/hr of gas containing 3.5g/m<sup>3</sup> of H<sub>2</sub>S and 0.2g/m<sup>2</sup> of organic sulphur. In this case about 12-13 liters of air plus 0.2g NH<sub>3</sub> are added per cubic meter of gas and the mixture is passed over a 20m bed (7 tons) of activated carbon. This bed will take a "loading" of 6 tons of sulfur before sulfur removal becomes necessary. The regeneration is accomplished by filling the bed 3 times with a total of 200m<sup>3</sup> of ammonium sulfide solution and allowing each of the washes to stand for 1 to 2 hrs. The solution remaining after the third draining is steamed out, the bed is then dried and cooled and put back into service.

### 8. REMOVAL OF CO<sub>2</sub> FROM GASES

The removal of carbon dioxide from the gas is usually performed, if not a part of the alkazid process, in the final step of the synthesis gas preparation, after it is under pressure. Carbon dioxide is readily soluble in water at elevated pressure and the gas is absorbed by passing the CO<sub>2</sub> containing gas in direct countercurrent contact with water in absorption columns. The absorbed CO<sub>2</sub> is released in a discharge system by passing the outlet water at about 200 to 300 lbs. per square inch (the usual absorption pressure) into a Pelton water turbine whose outlet is at atmospheric temperature and pressure. The jet action of the water impinging on the pelton wheel breaks the stream into a fine spray for quick release of the absorbed CO<sub>2</sub> and at the same time produces power to assist in driving a centrifugal pump which recycles the cold water back into the spray tower. About half of the power required to drive the centrifugal pump can be obtained from the pelton water turbine. This water absorption system also removes the last traces of any ammonia that may be present. However, the CO<sub>2</sub> thus produced is usually substantially pure and in Germany is recovered, compressed and sold as commercially pure CO<sub>2</sub>.

## 9. REMOVAL OF CO FROM GASES

80901

In the preparation of synthesis gas for the ammonia process the hydrogen is obtained from CO-H mixtures by the shift reaction changing the  $\text{CO} + \text{H}_2\text{O}$  into  $\text{CO}_2 + \text{H}_2$  and then removing the  $\text{CO}_2$  by water absorption as previously described. However some unreacted CO is carried through and remains in the gas. In the ammonia synthesis carbon monoxide is a catalyst poison and it is therefore necessary to purify the gas to remove the last traces of CO.

This is done by subjecting the gas to direct contact in a counter current absorption tower with a refrigerated copper ammonia carbonate or carbonate solution at 1800 to 3500 pounds per square inch, it having been found that in that pressure range carbon monoxide is readily soluble in a cold ammonia copper salt solution.

A second method of eliminating carbon monoxide by converting it to a hydrocarbon in the Fischer-Tropsch process as a detoxification process is covered in another technical report and is not repeated here.

## 10. CONCLUSIONS

Gases produced in Germany for subsequent utilization in synthesis processes invariably required purification for the removal of impurities and deleterious components.

Dust and tar were removed by (1) mechanical processes, usually cyclones, (2) electrostatic methods, and (3) water washing.

Hydrogen sulfide was removed by (1) Alkazid process, (2) Carbon adsorption with subsequent  $(\text{NH}_4)_2\text{S}$  wash and (3) Iron oxide process. Organic sulfur was generally removed by the "Feinreinigung" which consisted of cracking and removal of the sulfur as  $\text{H}_2\text{S}$  over iron oxide-alkali catalyst at temperatures from 150 to 300°C.

Aromatic and resin-forming compounds were removed by activated carbon.

Carbon dioxide was removed by (1) Alkazid process at low pressure (a) Water washing at high pressure and (3) Caustic solution for removal of final traces for special purposes.

Carbon monoxide was removed from hydrogen for high pressure hydrogenation by high pressure absorption with copper ammonium carbonate or formate solution.

Various other gas purification processes had been developed but were not in large scale use. Some of these processes are described in documents included in the appendix to the report.

W. H. Lyon  
Lt., USNR

R. M. Crawford  
Technician

LIST OF GERMAN DOCUMENTS ON  
SYNTHESIS GAS PURIFICATION PROCESSES

80902

1. Report dated Dec. 12, 1936 by Dr. Goister of I. G. Farbenindustrie entitled "Entstaubung" (Dust Removal)
2. Report by Dr. Sachsse entitled "Removal of Carbon Black and Dust from Gases with the Oppauer Schachtfilter."
3. M 202-8 - a simplified general flow-sheet showing the operation of the Alkazid Process.
4. Report by Drs. Jeltsch, Sommer and Bungor of visit made to the Alkazid Plant in Lutzkendorf, in regard to corrosion.
5. Confidential Reports (2) on the operating and supervision methods for the Alkazid process, entitled:
  - (a) "Betriebs Erfahrungen und Hinweise zum Alkazidverfahren"
  - (b) "Richtlinien für den Betrieb und die Überwachung von Alkazid-Waschanlagen".
6. M3200-I - Flowsheet - showing an NaOH wash following the Alkazid absorption.
7. Zo 1416-2 - Flowsheet showing Claus process of converting hydrogen sulfide to molten elementary sulfur.
8. F.Z.A.1 b - Flowsheet showing the Claus Ofen.
9. F.Z.A.4 a - Flowsheet showing the Nachvorbrunnungssofen.
10. "Clausofen Operation", translated data covering complete operation of the Leuna Plant.
11. S-92 - A drawing which shows a schematic diagram of the I. G. process of hydrogen sulfide removal over carbon.
12. Drawing No. 711496 - A flow sheet of a "Grob- and Feinreinigung" sulfur removal unit.
13. Drawing No. 4A34210 - Piping and Equipment arrangement of Claus plant.
14. Several short reports from Sept. 30, 1942 to May 25, 1943 on the subject of dust removal in multi-cyclone units.
15. Reports by Herr Keinko dated Dec. 29, 1931 on "Vorbrunnen von H<sub>2</sub>S zu Schwefel im Claus-Ofen" and by Dr. Hanisch dated Jan. 11, 1933 "Notiz über Versuche zur Gewinnung von elementarem Schwefel aus Gasen mit niedrigen Schwefelwasserstoffgehalt." Early data on the Claus process.

16. A report by Dr. Braus dated Jan. 21, 1935 on "Berechnung der Vorbronnungstemperaturen von Schwefelwasserstoff - Kohlensäuregemischen", giving theoretical data on combustion temperature of  $H_2S$  mixtures.
17. Tables of data dated Nov. 11, 1933 on requirements of Alkazid process for utilities, equipment, solutions, operating personnel, etc.
18. Analysis results and methods for gas purification catalysts. 80903
19. Report by Dr. Bähr dated Oct. 2, 1936 on "Weiterentwicklung des Alkazid - und Claus Ofen - Verfahrens," reporting late developments in the Alkazid and Claus processes.
20. Report by Dr. Orlicak, dated July 11, 1941 on "Untersuchungen über die Lage des chemischen Gleichgewichtes beim Clausprozess", on the calculated and experimental chemical equilibrium in the Claus process.
21. Drawings A-1030-4 and U 1878-1, flowsheets on carbon monoxide removal.
22. Folder containing numerous short reports and drawings on the Alkazid process.
23. Four curves on CO -  $CO_2$  wash costs.
24. Drawing S IV 3, Flowsheet of a pressure water wash process.
25. Folder containing report and several drawings concerning the removal of carbon oxy sulfide ( $CO_2S$ ) from gases.
26. Report by Dr. Bartholome' dated Nov. 26, 1941 on "Über die Umsetzungsgeschwindigkeit des CO an Braunoxyd-Kontakt bei hohen Drucken" giving data on reaction velocity over "Brown oxide" catalyst for the shift reaction.
27. Patent announcement dated June 27, 1939 on a process for catalytic recovery of S from gases containing  $H_2S$ .
28. Report by Dr. Kuhbier dated April 24, 1939 on "Entschwefelungs-Vorfahren der Sachtleben A.G." covering data on a process reacting  $H_2S$  and  $SO_2$  in thiosulfate solution to produce sulfur.
29. Report on a meeting to exchange information on gas purification processes, dated Nov. 17, 1939.
30. Drawing 240-8 on layout plan for a Claus unit.
31. Report by Dr. Mengdohl dated August 22, 1938 "Ein neues Verfahren zur Trennung von Ammoniak und Kohlensäure bzw. Schwefelwasserstoff" describing a new process for separation of  $NH_3$  -  $CO_2$  -  $H_2S$  mixtures.

80904

- 32. Patentschrift No. 388857 dated 21 January 1924 to Firm Eduard Theisen in Miinchen entitled "Stufen - Gas - O. dgl. Wascher", german patent on the Theisen washer for the purification of gases.
- 33. Patentschrift No. 513288 dated 25 November 1930 to Firm Eduard Theisen in Miinchen entitled "Verfahren zum Reinigen Von Gasen, Luft, Dämpfen u. dgl., german improvement patent on the design of the blades of the Theisen washer presented in the above patent No. 388857.