AMMONIA SYNTHESIS UNITS

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1.0 SCOPE

This data sheet covers two main types of industrial ammonia synthesis units: 1) units producing ammonia from hydrocarbon feed, mostly natural gas, and steam and air; and 2) units producing ammonia directly from nitrogen and hydrogen. In the second type, the nitrogen is obtained from an air fractionating unit contained within the system, and the hydrogen is usually a byproduct of other processes (e.g., electrolytic chlorine or acetylene-producing processes, etc.).

The objective of this data sheet is to aid in better understanding the hazards of the process, and the most probable and the possible causes of system failures. Although this data sheet covers ammonia synthesis specifically, many comments and recommendations are applicable to other petrochemical and chemical processes.

1.1 Changes

September 2010. Minor editorial changes were made for this revision.

2.0 LOSS PREVENTION RECOMMENDATIONS

2.1 Introduction

The recommendations in this data sheet pertain to the entire system rather than to its components. Recommendations presented in various data sheets cover specific subjects (e.g., compressors, turbines, reformers, waste heat boilers, construction, control houses, flow gas and liquid piping, process furnaces, air separation plants, etc.) and should also be considered.

2.2 Operation and Maintenance

2.2.1 Experience indicates that the average time period between a plant's turnaround is approximately one year. Such a time period is suggested for subsequent inspections of the entire system and its components. Recommended time periods for particular equipment items should also be taken in consideration.

2.2.2 During regeneration of the desulfurizer (activated carbon), precautions should be taken to ensure that at no time condensation occurs in the catalyst beds, or condensate is directed therein; otherwise, the promoter in the catalyst could be leached out and deposited on downstream equipment when the desulfurizer is placed back on line leading to tube failure.

2.2.3 If an operating or mechanical accident causes minor coke depositions on the primary reformer catalyst, the deposit may be removed and the catalyst activity restored by increasing steam-to-gas ratio somewhat above normal for a period of time. If the catalyst coking is considerable, the catalyst should be regenerated with steam, or it may be necessary to shut down the unit for replacement of the catalyst. Coking can also lead to tube failure.

2.2.4 During the shutdown of the reforming equipment, the catalyst should be kept under a steam atmosphere until its temperature has been reduced to 450°F (232°C) or less. If the secondary reformer is to be opened or subjected to an air stream, the catalyst should be carefully oxidized before the steam is shut off.

2.2.5 In case of sudden mechanical failure of the reformer stack fan assembly, adequate draft in the furnace should be maintained to allow slow cooldown. One method that can be used is to install a low pressure differential switch between the flue gas duct and atmosphere and connected in such a manner that a valve opens to admit full steam flow to an aspirating jet ring in the furnace stack upon loss of fan.

2.2.6 Observations of primary reformer catalyst tube skin temperatures should be made on a regular schedule using an optical pyrometer. Hot or bright-colored spots indicate voids in the catalyst column, or carbon deposits on the catalyst.

2.2.7 The gas burners must be operated in a proper manner to avoid flame impingement on the primary reformer catalyst tubes, as such improper operation could result in tube failures.

2.2.8 Gas analyzers should be provided to ensure a continuous checking of the composition of the synthesis gas flowing to the synthesis gas compressor, and also of the gas being circulated through the synthesis loop.

2.2.9 The design temperature values for the shift converter are as follows: for the high temperature section 900°F (482°C); for the low temperature section 575°F (302°C). Those values should never be exceeded because the shift catalyst is highly porous and, if overheated, its activity for low temperature conversion may be impaired. High temperatures could also make the vessel more susceptible to cracking.

2.2.10 If shift catalysts have been exposed to reducing gases (i.e., hydrogen, carbon monoxide), they become pyrophoric and must not be exposed to oxygen (air) except under controlled conditions. Excessive temperatures resulting from too rapid oxidation of the reduced catalyst may cause damage to the catalyst and/or the vessel.

2.2.11 If the shift catalyst is to be removed from the vessel, or if the vessel is to be entered, the catalyst should be first subjected to a controlled oxidation procedure in order to render it nonpyrophoric. It should be borne in mind, however, that even though the procedure is followed carefully, some ‘‘dead spots’’ may be left where the oxidation was incomplete, and some overheating may occur upon exposure to air, thus creating hazardous conditions.

2.2.12 When preparing to stop operations or expose reduced shift catalyst, the general procedures should be as follows:

a) If the process gas flow is to be interrupted for only a brief period of time, the shift converter may be isolated under process gas pressure, or under a positive steam pressure, keeping any condensate drained out of the vessel.

b) If the shutdown is to be prolonged but the vessel is not to be entered or exposed at any time to oxygen, it should be isolated and maintained under a positive pressure with inert gas. Desulfurized feed can be used if the shift converter is first cooled below 400°F (204°C).

c) If the catalyst is to be inspected by looking into a top manhole only, it may be cooled with steam to about 250°F (121°C). The steam should be purged out with inert gas at this point and the vessel thus further cooled if desired. While maintaining a slight positive bleed of inert gas, the manhole can be opened for inspection. Only a slight flow of inert gas is required to limit air diffusion.

2.2.13 The methanator should never be depressurized below normal operating pressure while normal pressure exists upstream of the methanator inlet valves. Depressurizing can cause extremely high temperatures in the methanator. The block valve upstream should be closed during venting to prevent gas from entering the methanator. The vessel design temperature value of 850°F (455°C) should not be exceeded under any circumstances.

2.2.14 External in-service inspections of all pressure vessels should be made on a regular basis. Furnaces and tubes should be carefully viewed through the inspection ports for evidence of defects. Bulges and small wisps of blue flame emanating from the tubes and indicating cracks in tube walls permitting process gas leakage should be noted, so that this area may be carefully inspected during the internal inspections. Pyrometers of the visual type may be used to determine the approximate temperatures of the tubes’ or other parts’ surfaces.

2.2.15 Reviews of the recording charts and discussions with plant operating personnel of any difficulties, outages, or failures should be held regularly to help in evaluation of the overall plant conditions.

2.2.16 During internal inspections of pressure vessels, all areas noted for follow-up during external inspections should be examined. The tubes and welded connections should be carefully checked for cracks in the weld areas. Any suspect area should be subjected to appropriate nondestructive tests. Provisions for expansion and contraction should be examined. Any bendings, worn parts, defects, etc., should be corrected.

2.2.17 All repairs, tests, and maintenance of the pressure vessels should be made in strict accordance with all pertinent requirements of the *ASME Boiler and Pressure Vessel Code* (Section VIII), and with the requirements of authorities having jurisdiction.

2.2.18 All controls and instruments should be properly maintained and inspected on a regular basis. The alarms, interlocks, and trip-offs should be provided with suitable means of simulation tests, making it possible to verify their proper performance without any interruptions of the process.

2.2.19 Services of a qualified contractor or laboratory should be retained to ensure adequate and reliable boiler feedwater treatment.

2.2.20 Operating instructions for the entire plant and for every major equipment item should be displayed in appropriate places, describing necessary start-up, operation, and shutdown (regular and emergency) procedures, with references to pertinent flow diagrams. A complete set of operating instructions should be placed in the control room, easily accessible for current references. The instructions should be kept up-to-date, and properly replaced when necessary.

2.2.21 Operating records should be maintained thoroughly and regularly, as they might be an important source of information in tracing down any accident or failure.

2.3 Equipment and Processes

2.3.1 In the event of air failure, the following recommended action should be taken:

Feed Gas Control Valve:	*Close.*
Steam Control Valve:	Open (to flood reformer tubes and compressed air line).
Air Control Valves:	Open the vent valve to prevent surging in centrifugal compressor. Close the control valve for air supply line to process.
Fuel Control Valve:	Close.

In addition to the main supply, a reliable emergency source of compressed air and/or electrical power should be provided to ensure prolonged services in case of electric power or air compressor failure.

2.3.2 In the case of the feed gas controller failure, loss of feed gas should activate the same shutdown procedures as in any other case of feed gas failure. A failure causing an increase of feed gas is not likely to be hazardous.

2.3.3 A failure of the steam controller causing loss of steam should bring about an orderly shutdown with the instrumentation provided. A failure causing an increase of steam flow is not likely to be hazardous.

2.3.4 A failure of the air controller causing a loss of compressed process air should activate the quick acting block valves to shut off the compressed air line and inject steam into the air line to the secondary reformer. Instrumentation should be extended to shut down the compressor in this instance, and open the vent (antisurge protection).

2.3.5 A failure causing an excess of air flow will result in hazardous overheating at the secondary reformer. This contingency can be accommodated by instrumentation arranged to signal for compressor shutdown or opening of the vent valve when secondary reformer temperature reaches a predetermined level.

Multiple controllers for fuel gas are sometimes used in parallel; the minimum number per reforming furnace is three. Therefore, failure causing an excess of flow will not be particularly hazardous, and can be easily detected by the furnace operator.

2.3.6 In case of loss of boiler feedwater supply (leading to loss of steam that will disrupt the plant operation and can result in potentially dangerous situations), the first step is to take all practical measures to ensure continuous supply of boiler feedwater. This should include a parallel pumping arrangement with automatic start-up of the spare pump. The second step is to supply sufficient reserve of water in or ahead of the system to provide for an orderly shutdown of the plant, thus minimizing the danger to that of overheating the generation system through loss of water while still absorbing residual heat from equipment. A combination of steam turbine-driven and electric motor-driven feedwater pumps is recommended to ensure operation if the electrical power or steam supply fails.

2.3.7 Low level in the steam drum and low flow in the feedwater supply should be signaled to the operator. Reduction of process steam should initiate shutdown of the reforming section, etc.

2.3.8 Controls and instruments regulating the flows and monitoring critical parameters, such as reaction temperatures and/or pressure, etc., should be of the fail-safe type, providing safe and reliable handling of situations arising during feed flow, steam, air and/or electric power failures.

2.3.9 Safe light-off and operation of fuel-fired boilers, heaters, and fuel process furnaces is achieved by procedures outlined in Data Sheet 6-10, *Process Furnaces,* and Data Sheet 7-46/17-11, *Chemical Reactors and Reactions*. In addition the following should be incorporated into the control and instrumentation system of the primary reformer:

a) Feed loss (indicated by low feed stream flow) should shut off feed stream, fuel valves, and process air; it can also shut off (optionally) air and/or feed gas compressors, primary steam, synthesis gas compressor, and methanator.

b) Steam loss (indicated by low steam flow) should shut off feed stream, process air, and fuel valves.

c) Boiler feedwater supply loss (indicated by low BFW flow) should shut off the entire plant, if no spare BFW pump is available or if that pump, when activated, fails.

d) Loss of steam drum level should shut off the entire plant.

e) Loss of boiler circulation flow should shut off the entire plant.

It should be noted that although the protection arrangements listed under c) through e) do not belong directly to the primary reformer, the malfunctions which they indicate affect this component first.

2.3.10 Loss of air to the secondary reformer (indicated by low air flow) should shut off air valve and steam injection to air line. It can also (optionally) unload or shut off air and synthesis gas compressors, close methanator inlet, and bypass low temperature shift converter.

2.3.11 High temperature in the secondary reformer (indicated either by high bed temperature or by high exit temperature) should shut off air valve, steam injection to air line, and air compressor.

2.3.12 Loss of CO_2 removal solution flow should start up the spare solution pump; if the pump fails, the solution valve and methanator should shut off.

2.3.13 Loss of CO_2 absorber level should shut off solution pump(s), methanator, synthesis gas compressor, rich solution flow, and air to regenerator.

2.3.14 High temperature in the methanator (indicated either by high bed temperature or by high exit temperature) should shut off the methanator inlet valve, and unload or shut off the synthesis gas compressor.

2.3.15 Loss of process flow to the ammonia converter startup heater should shut down the heater.

2.3.16 High temperature in the ammonia converter startup heater (indicated either by high stack temperature or by high process outlet temperature) should shut down the heater.

2.4 Contingency Planning

2.4.1 A set of spare parts of critical nature should be continuously stored to ensure the shortest possible interruptions to production in case of accident. These spare parts and materials should include (but not be limited to) the following: compressor and turbine rotors; pumps and/or pump impellers; waste heat boiler and major heat exchanger tube bundles; shift converter catalyst (zinc oxide, ZnO); alarm and trip-off control devices and instruments; and a regular stock of maintenance and repair parts and materials.

3.0 SUPPORT FOR RECOMMENDATIONS

3.1 Loss History

3.1.1 Boiler and Machinery Losses

The majority of industrial ammonia synthesis plants with large capacities (600 STPD and up) are of a single-train design. This type of arrangement, while highly advantageous in various engineering and economic aspects, possesses one distinct disadvantage at the same time. A failure of a major component often leads to complete and lengthy shutdown of the entire plant, which results in heavy production and, ultimately, financial losses.

There are three basic categories of failures that lead to such shutdowns:

1. Principal process component failures;
2. Auxiliary process component failures;
3. Operation and protection control and instrument failures.

Industrial experience gained through years of operation of large single-train ammonia synthesis plants indicates that about 50% of all shutdowns are caused by major equipment failures, that is by causes falling into category (1) or (2). The number of downtime days per year per plant varies from 10 to 100 days, amounting to some 50 days per year per ‘‘average’’ plant. The average yearly number of such shutdowns appears to be about 10 per year per plant. Thus downtime caused by failure averages about 25 days per year per plant, and the average number of such shutdowns is about 5 per year per plant. If the average plant capacity is assumed to be 800 STPD (a low figure), and the price per ton is $80 (as given in the 1979 *Chemical and Engineering News* magazine), then the average production losses per year per plant are about $1,600,000 (or $320,000 per one average failure). In addition to this, failures bring about substantial property damage losses (costs of damaged equipment and parts repairs and/or replacements).

3.1.2 Fire Losses (General Information)

The most fire hazardous locations within an ammonia synthesis manufacturing system are the following:

1. Tubes, risers, and manifolds contained within the primary reformer furnace;

2. Gasketed joints and valve packings, especially those containing hydrogen-rich effluents; specific equipment items with the most gasket leaks causing fires are the high temperature shift effluent/methanator feed heat exchangers, waste heat boilers, and the ammonia converter; flange leaks can be expected mainly from primary reformer catalyst tube flanges protruding above or below the furnace;

3. Steam heated surfaces which can come into contact with leaking oil, the latter coming mostly from oil-saturated turbine insulation.

Most fires occur as direct leaks of flammable process gas to the atmosphere. Fires can also originate where synthesis gas leaks into cooling water, as in synthesis gas compressor aftercoolers, cooling towers, etc. Fires might be caused by leaks in fuel gas piping, by sight glass failures, etc.

4.0 REFERENCES

4.1 FM Global

Data Sheet 6-10, *Process Furnaces*.

Data Sheet 7-43, *Loss Prevention in Chemical Plants*.

Data Sheet 7-45, *Instrumentation and Control in Safety Applications*.

Data Sheet 7-46, *Chemical Reactors and Reactions*.

Data Sheet 7-50, *Compressed Gases in Cylinders*.

Data Sheet 7-52, *Oxygen*.

Data Sheet 7-91, *Hydrogen*.

4.2 Other

ASME Boiler and Pressure Vessel Code (Section VIII)

Chemical and Engineering News magazine, 1979.

APPENDIX A GLOSSARY OF TERMS

This document does not have any defined terms.

APPENDIX B DOCUMENT REVISION HISTORY

September 2010. Minor editorial changes were made for this revision.

January 2000. This revision of the document has been reorganized to provide a consistent format.

APPENDIX C DESCRIPTION

C.1 General

Ammonia (NH_3) is the principal source of nitrogen for fertilizers. Its usage as such accounts for 80% of all the ammonia being used in the United States. The remainder is used mostly for polymer products (fibers, elastomers, plastics, resins, and explosives, etc.). Some commercial and industrial refrigeration units use ammonia as a refrigerant.

The manufacturing process consists of three basic steps: synthesis gas preparation, purification, and ammonia synthesis proper. The first two steps involve generation of hydrogen, introduction of nitrogen in the stoichiometric proportion, and removal of reaction byproducts and catalyst poisons, namely oxides of carbon and water. The synthesis comprises a catalytic reaction of one molecule of nitrogen and three molecules of hydrogen at elevated temperatures and pressures, and recovery of ammonia. Although conditions vary greatly, this chemistry of ammonia synthesis is the primary basis of all commercial processes.

The basic differences among those processes lie in the following: 1) sources of hydrogen, and 2) methods of introducing nitrogen from the air into the synthesis process.

The main sources of hydrogen are natural gas, coal, petroleum, and water. Of these, the first and the last are (CH_4 and H_2O) the principal source in commercial practice. The two basic generation techniques for processing are steam reforming and partial oxidation. Partial oxidation is usually employed where steam-reformable feeds are not available, or if very favorable economic conditions exist. This technique is rarely applied commercially, and is not further discussed in this data sheet.

Two basic methods of introducing nitrogen into the synthesis process are commercially employed: 1) secondary reforming of the synthesis gas with introduction of sufficient air containing the required amount of nitrogen for syntheses; and 2) air fractionation, basically into oxygen and nitrogen, followed by introducing the nitrogen into the syntheses part of the unit.

The steam reforming method is most frequently used in industry. Therefore, a description and analysis of this method is presented rather extensively. A brief description of a process using nitrogen from air fractionation is also given in this data sheet.

C.2 Ammonia Synthesis from Natural Gas Feed

The bulk (75-80%) of worldwide ammonia production is obtained by hydrocarbon steam reforming operations, and approximately 60-65% of this amount is produced from natural gas feed. The most typical process in this group is represented by large, single-train units. A large unit can be from 600 to 1200 STPD (standard tons per day) (about the same metric tons/day) or more. This process flow diagram is shown in Figure 1, and is hereafter referred to as the principal process system. The steam and boiler feedwater system flow diagram is also shown in Figure 2, and is referred to as the auxiliary process system. Protection control and instrumentation arrangements (sometimes called *trip-off* controls) are briefly described (see Section C.2.5) as part of the unit protection. No other systems pertaining to the described process, such as instrumentation and operation controls, electric power supply, etc., are discussed herein, as such subjects are beyond the scope of this data sheet. (See other data sheets concerning these subjects.)

The principal process system as shown in Figure 1 comprises three basic subsystems: a) raw synthesis feed gas preparation; b) synthesis feed gas purification; and c) synthesis ammonia production. Each of these subsystems is described below in detail.

C.2.1 Subsystem (a): Raw Synthesis Feed Gas Preparation

The first step in the feed gas preparation is the purification of the initial hydrocarbon feed, that is, removal of sulfur. Purity of the process streams is of particular importance for steam reforming operations. The nickel catalyst used in the reformers is quite susceptible to poisoning by sulfur, even by as little as a few tenths of a ppm (parts per million). This also pertains to low-temperature shift catalysts, where the poisoning is irreversible.

The most commonly used method of removing sulfur, especially when natural gas is the feed material, is adsorption by activated carbon at about 59°-122°F (15°-50°C). Reaction with zinc oxide (ZnO) which is used for natural gas feeds containing large amounts of hydrogen sulfide (H_2S).

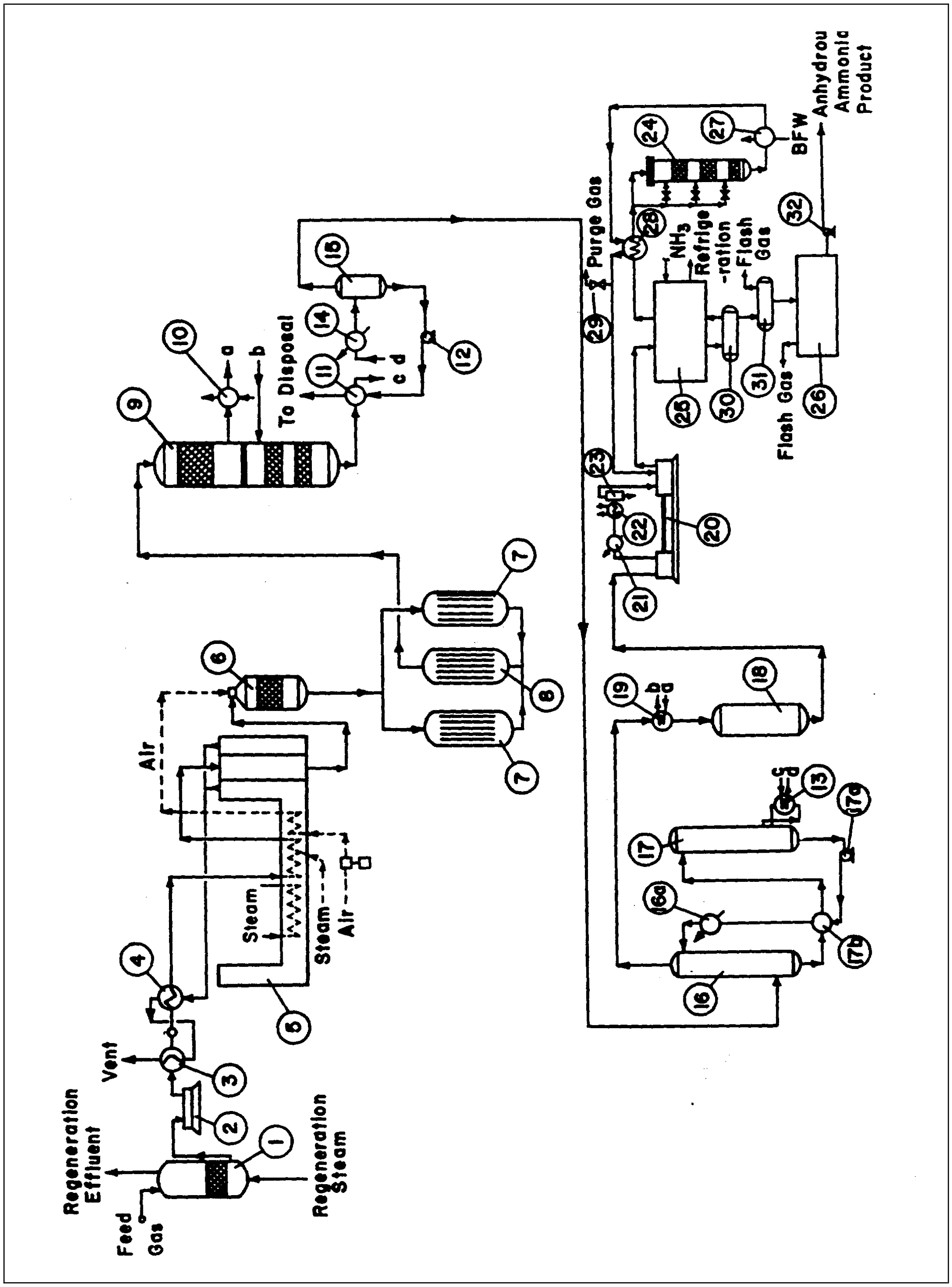

Fig. 1. Principal process flow diagram.

For the majority of natural gas feeds used in the industry, adsorption by activated carbon is most commonly applied. The process is as follows (Fig. 1):

Natural gas from the feed source is delivered to desulfurizer(s) (1). There the gas flows through a bed of activated carbon. After sulfur is removed, the gas goes to the feed gas compressor (2). Activated carbon is regenerated by steam. Regeneration effluent leaving the adsorber is exhausted to the atmosphere or to sulfur recovery equipment. (See Data Sheet 7-43/17-2, *Loss Prevention in Chemical Plants*.)

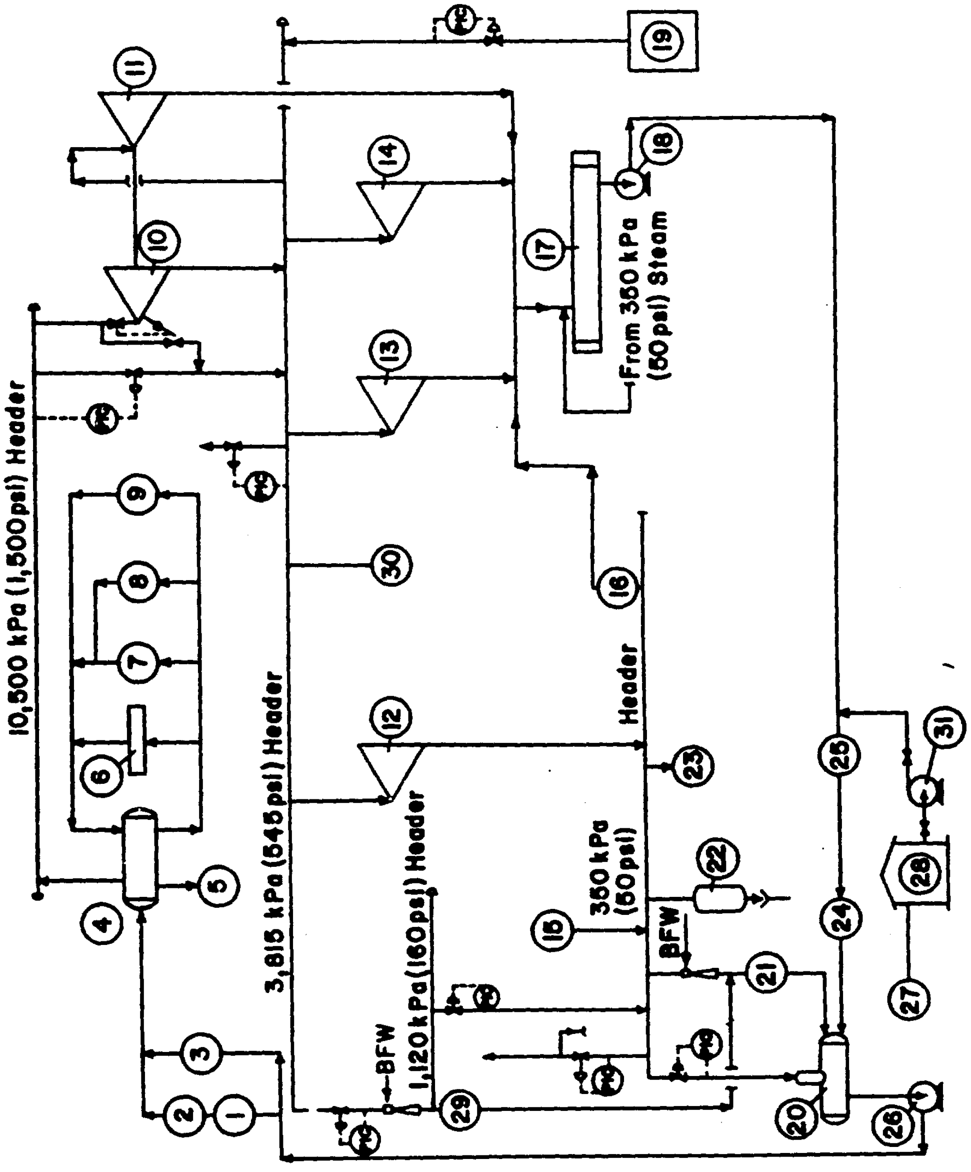

Fig. 2. Auxlliary process flow diagram.

The feed gas compressor (2) discharges pressurized desulphurized gas to the feed preheat coils (3). The heat is supplied by flue gases produced in the furnace of the primary reformer (5). The feed is then mixed with process steam, and is then directed through mixed feed preheat coils (4) to the distribution header of the primary reformer (5). Here the flow is uniformly distributed through catalyst-packed tubes and directed downward to the bottom collection header. From there the flow is manifolded through centrally located risers to a transfer line which directs the flow to the process inlet of the secondary reformer (6). Here the process flow enters a chamber at the top and is directed downward through a diffuser ring to enter the combustion zone of the reformer where it mixes with air.

The purpose of primary and secondary reforming is to obtain a hydrogen and nitrogen mixture from desulfurized natural gas, water (steam), and air. This is achieved by mixing those ingredients in the proper order and ratio and carrying out the reforming reaction in three stages, two of which are catalytically assisted. Unpurified synthesis gas is of the following approximate composition (in mole percent): nitrogen (N_2) 22.8%; hydrogen (H_2) 56.%; methane (CH_4) 0.3%; argon (Ar) 0.3%; carbon dioxide (CO_2) 6.%; and carbon monoxide (CO) 14.6%. The principal chemical reactions involved in reforming are the following:

1. The methane and water reactions in the catalystfilled tubes of the primary reformer:

$CH_4 + H_2O + (heat) \rightarrow CO + 3H_2$;

$CO + H_2O \rightarrow CO_2 + H_2 + (heat)$;

2. Oxidation reactions in the upper part of the secondary reformer:

$CH_4 + O_2 + 3.78\ N_2 \rightarrow CO + H_2 + H_2O + 3.78\ N_2 + (heat)$

$2CO + O_2 + 3.78N_2 \rightarrow 2CO_2 + 3.78N_2 + (heat)$

3. Reducing reaction in the catalyst bed of the secondary reformer (same as in Reaction 1. (See Data Sheet 7-46/17-11, *Chemical Reactors and Reactions*.

The amounts of hydrogen, methane, and carbon oxides in the reformer effluent are determined by reforming conditions, i.e., temperatures, pressures, and steam-to- natural gas (or steam-to-carbon) and air-to-natural gas ratios. Typically 1.33 volumes of air per volume of natural gas and 2.0 volumes of steam per volume of natural gas will yield unpurified synthesis gas of the desired composition.

The secondary reformer (6) is a refractory-lined vessel containing a nickel catalyst on a rugged ceramic base with good physical strength and thermal resistance. Air is preheated or left with heat of compression to facilitate the reactions.

Leaving the combustion zone of the secondary reformer (6), the flow passes the catalyst bed and then enters the outlet chamber at the bottom of the reformer. From here the flow passes through the shell sides of waste heat boilers (7); the most commonly used are the *bayonet* type. Boiler water from the main steam drum flows through the tube side (Fig. 2). From the shell side outlets of the primary waste heat boilers (7), the flow recombines to enter the tube side of a secondary waste heat boiler (8). The flow through its shell side is also boiler water from the steam drum. Other types of combinations of waste heat boilers may be used. The process flow then continues to the shift converter (9).

The intent of the shift converter is to convert CO into CO_2 so that it can be easily removed from the process gas feed. This is achieved by water-gas shift reaction (commonly termed *shift* conversion):

$CO + H_2O \rightarrow CO_2 + H_2 + heat$.

This reaction produces valuable hydrogen in addition to conversion of carbon monoxide (CO) into easily removable carbon dioxide (CO_2). The reaction is exothermic, reversible, and the equilibrium is favored by lower temperatures. However, the reaction rate increases with temperature increase. Therefore, the bulk of CO is shifted to CO_2 in the high temperature section of the converter, where the steam flows downward through a bed of high temperature shift catalyst, supported by a screen-covered grating. The flow then enters the tube side of the primary shift effluent waste heat boiler (10), to give up heat to the boiler water in the steam drum (lines marked ''a'' and ''b''). The flow passes through the tube side of the methanator feed heater (19) to give up heat to the methanator feed. After being cooled to about 464°F (240°C), the flow proceeds to the low temperature section of the shift converter (9), where most of the remaining CO is shifted to CO_2, by passing through two dissimilar catalysts. The first catalyst at the top bed is composed of iron with zinc oxide (ZnO) serving as a guard for removal of any hydrogen sulfide (H_2S) that might enter. The bottom bed, low temperature shift catalyst, is composed of copper.

From the outiet of the low temperature section of the shift converter, the process flow passes through the converter effluent desuperheater exchanger (11). The cooling water (condensed steam from raw gas separator (15)) is supplied to the desuperheater (12), a pump.

From the outlet of the desuperheater, the steam contained in the converter effluent is first cooled in the shell side of the converter effluent/monoethanolamine (MEA) reboiler exchanger (13), giving up heat to reboll the MEA solution (see below). (See lines ''c'' and ''d''.) Final condensation of this steam is accomplished in the converter effluent/demineralized water exchanger (14). The flow then continues to the separator (15), where the raw synthesis feed gas passes overhead to the CO_2 absorber (16), and condensed steam from the bottom of the separator is used to cool the converter effluent at the desuperheater exchanger. Process condensate not required for cooling of recycle is disposed to the sewer via a gas-disengaging pot that is vented to the atmosphere (not shown in Fig. 1).

C.2.2 Subsystem (b): Synthesis Feed Gas Purification

The overhead effluent gases from the separator contain about 17-19% (by volume on a dry basis) of carbon dioxide. This must be removed as completely as possible, otherwise the ammonia synthesis catalyst will be poisoned. To reduce it to a few ppm, two purification stages are used. The first is the bulk carbon dioxide removal, and the second, final purification stage, is usually converting the unremoved carbon dioxide to methane (methanation).

A commonly used CO_2 removal method is scrubbing with an aqueous solution (15-20 wt %) of monoethanolamine (MEA).

The cooled raw synthesis gas flowing from the separator (15) is fed to the bottom of the CO_2 absorber (16) where an aqueous MEA solution which absorbs CO_2 at relatively high pressure and low temperature. The MEA solution regenerated by subsequent degassing CO_2 from the solution in the (17) stripper at higher temperature and lower pressure. The regenerated lean MEA solution is recycled from the stripper (17) by the pump (17a) to the top of the absorber through water-cooled exchanger. From there it flows down the trays counter-current to the upflowing gas. Rich MEA, with absorbed CO_2, leaving the bottom of the absorber is heated before stripping to approximately 210°F (99°C) by heat exchange with hot stripper bottoms (17b).

Accumulation of undesirable contaminants in the working MEA solution is prevented with a mechanical strainer filter that removes finely divided solids, iron, and organic impurities, which would contribute to foaming and corrosion problems. An MEA vaporizer is also used, which distills MEA from almost all of the fouling materials (very fine suspended solids, inorganic salts, and high boiling amine conversion products). This equipment is not shown in Figure 1.

The next purification stage is methanation. Methanation reactions are the reverse of the reforming reactions:

$CO + 3H_2 \rightleftarrows CH_4 + H_2O + \text{heat}$

$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O + \text{heat}$

(See Data Sheet 7-46/17-11, *Chemical Reactors and Reactions*.)

The objective of these reactions is to complete the removal of the oxides of carbon which will position the synthesis catalyst. The methane formed is a nonreactive gas in the ammonia converter; the water formed is removed before synthesis.

Process gas, containing only 100 ppm of CO_2 and about 0.6 volume % CO, flows from the top of the MEA absorber (16), through the absorber overhead demisting section where any entrained moisture is removed. The demisting section of the absorber is provided as an additional protection for the catalyst in the methanator, as the latter could be damaged if in contact with liquid. The gas then flows to the methanator (18) via the methanator feed heater (19), where it is preheated to 600°F (315°C).

Since the methanation reactions are strongly exothermic, the working temperatures of the apparatus should be carefully monitored and controlled in order to avoid damage to the catalyst and to the reactor itself.

Most commercial methanator catalysts contain nickel supported on alumina, kaolin, or calcium aluminate cement. Sulfur and arsenic are catalyst poisons.

After final purification, the typical composition of the synthesis gas on a dry basis is as follows:

N_2: 24.2 volume %
H_2: 73.3 volume%
CH_4: 0.3 volume %
Ar: 0.3 volume %
CO_2 and CO: Less than 10 ppm

C.2.3 Subsystem (c): Synthesis Ammonia Production

After hydrogen production, the addition of nitrogen, and the purification of raw gas, the synthesis gas is ready for compression and ammonia manufacture in the synthesis loop. Contemporary synthesis loops operate under pressures of 5000-6000 psi (14-45 mPa) (140-420 bar). If the capacity exceeds 1,000 STPD, the normal pressure range is 3,000-5,000 psi (20,685-35,000 kPa) (207-350 bar). The synthesis process is as follows:

The purified gas is compressed to about 1000 psi (7 mPa) (7 bar) in the first stage case of the synthesis feed gas and recycle compressor (20) (Modern ammonia plants employ centrifugal compressors for this service.) It is then chilled by cooling water in the synthesis gas compressor interstage cooler (21) and by ammonia refrigeration in the synthesis gas compressor interstage chiller. This cools the feed gas to about 46°F (7.5°C) and condenses most of the water, which is eliminated in the first stage separator (23).

The low moisture content synthesis gas leaving the first stage separator goes to the second stage case (24), where the pressure is increased to about 2,200 psi (15,170 kPa) (152 bar). The gas then enters the synthesis gas loop.

There can be three types of synthesis loops. One type recovers the ammonia product after makeup and recycle gases are compression mixed, and another recovers the ammonia product before recycle compression. The third is a combination. The recycle gas usually joins the feed gas at the midpoint of the second stage case of the compressor (20) as shown in Figure 1.

The main component of the synthesis gas loop is the synthesis ammonia converter (24). The gas enters the converter after chilling and refrigeration recovery (25) which is provided by condensation of ammonia from the synthesis gas. Thus, the plant refrigeration system (26) is one of the basic parts of the synthesis gas loop. Typically it uses some part of the ammonia product as a refrigerant.

The two classes of ammonia converters most commonly used by industry are the tubular and multiple bed. The tubular applications are limited in size to a maximum of about 544 STPD. The multiple-bed reactors usually quench the gas between beds with a side stream of cold syn gas; or remove the heat between catalyst beds either by generating steam or by preheating incoming feed gas by the use of internal heat exchangers.

Promoted iron catalyst is contained in the catalyst cartridge which is the inner part of the converter. The shell is maintained at a low temperature thus reducing the possibility of hydrogen embrittlement which can occur at normal synthesis pressures.

At the converter temperature of about 900°F (482°C) and pressure of 2,000-2,100 psi (13,785-15,170 kPa) (138-152 bar), a portion of the synthesis gas passing through the catalyst converts to ammonia. The concentration of NH_3 in the converter effluent leaving the last bed is usually about 12%.

The ammonia content after fresh feed (make-up) and recycle gas combination will be about 10%; at the converter inlet, after condensing out the ammonia, the concentration will be about 2%.

The converter effluent is cooled by giving up heat to the boiler feedwater exchanger (27) and to the converter feed exchanger (28). It then returns to the compressor (20) to be combined with fresh feed to the converter.

In the synthesis gas loop, a slipstream of the cooled converter effluent passes to a continuous vent or high pressure purge (29) to remove inerts (mainly methane and argon) from the loop.

Ammonia produced in the synthesis converter would quickly build up to a level which would interfere with the reaction. Therefore, it must be continuously removed from the recycling synthesis gas stream going to the converter. This is accomplished by the chilling and refrigeration recovery unit (25). The condensed ammonia flows from this unit to a high pressure ammonia separator (30) at a temperature of about -10°F (-23°C) and a pressure of about 2,150 psi (15,530 kPa) (155 bar). This operation reduces the amount of ammonia in the recycle gas stream from 12 to 2%. The resulting chilled ammonia liquid is collected in the product flash drum (31). This liquid is the feed to the final product purification step of the process. Because it contains a certain amount of absorbed light ends that would result in a contaminated product, it must be purified. This purification is provided by the plant refrigeration system (26).

This system is a three-stage ammonia refrigeration system which provides refrigeration for ammonia condensation in the synthesis gas loop, recovery of ammonia from vented gases, gas compressor interstage chilling, and refrigeration of the anhydrous liquid ammonia product.

The flow from the product flash drum (31) is first chilled by the third stage of the refrigeration system (26) to -28°F (-33°) and 60-65 psi (415-450 kPa) (42-45 bar), and is then directed to storage via a pump (32).

The ammonia gas that has been flashed in the product flash drum and in the system is compressed and subcooled to about 108°F (42°C) in the ammonia condensers. This flash gas has been chilled under pressure at about 235 psi (1,620 kPa) (16 bar). This vents light end gases to the fuel gas (or low pressure purge gas) system for disposal.

The condensed ammonia from the flash gas chiller returns to the system to work as a refrigerant.

The respective pressures and evaporation temperatures in all stages are provided by steam turbine-driven centrifugal three-stage refrigeration ammonia compressor(s) with condensers and subcoolers (not shown in Fig. 1).

C.2.4 Auxiliary Process System

The auxiliary process system (Fig. 2) comprises the following subsystems: (a) steam, (b) steam condensate, and (c) boiler feedwater.

C.2.4.1 Subsystem (a): Steam

The steam subsystem provides process steam of different pressure ranges, for driving steam turbines which serve as prime movers of compressors, pumps, and fans.

Saturated steam at 1,500 psi (10,500 kPa) (105 bar) is produced from a steam drum (4). The drum contains steam-scrubbing cyclones and demisters to ensure a dry steam product. Connections are provided for proper steam and water circulation, and also for blowdown of sediments from the low point during startup. A continuous blowdown mounted within the steam drum is located at a point which is designed to be the interface between the water level and the steam space. Because impurities tend to concentrate at this junction, continuous withdrawal of a small amount of water and steam from this point provides the most efficient removal of accumulated dissolved solids.

Boiler feedwater is pumped from a deaerator (20) to the steam drum (4) by the high pressure boiler feedwater (HP BFW) pump (26). This water is preheated enroute to the drum by flowing in two parallel streams through preheaters: the major flow stream passes through the ammonia converter BFW exchanger (1) and the primary reformer BFW heater (2). The smaller flow stream passes through the methanator effluent BFW heater (3).

About 85% of the 1,500 psi (10,500 kPa) (105 bar) steam from the steam drum is produced as a byproduct of the cooling process streams in the primary (7) and secondary (8) waste heat boilers (both utilizing heat of the secondary reformer effluent), and in the primary shift effluent waste heat boiler (9). The remainder is produced from the primary reformer generating section (6) (sometimes referred to as the auxiliary boiler section of the primary reformer furnace). This section is individually fired in response to a signal from a device sensing the 1,500 psi (10,500 kPa) (105 bar) steam pressure, when the latter drops below the design value.

The 1,500 psi (10,500 kPa) (105 bar) steam leaves the steam drum at about 597°F (315°C) and flows through two sets of superheater tubes arranged in series in the convection section of the primary reformer furnace. The steam leaves the superheater section at a temperature of 825°F (440°C) and flows to the high pressure steam turbine (10) of the synthesis gas compressor. This steam flows through the turbine and is exhausted to the 545 psi (3,815 kPa) (38 bar) header at about 610°F (320°C).

The 545 psi (3,815 kPa) (38 bar) steam is used for driving the synthesis gas low pressure steam turbine (11), the high pressure BFW pump steam turbine (12), the refrigeration compressor steam turbine (13), and the air compressor steam turbine (14). It is used for the synthesis compressor steam turbine glands (15) and for feeding the surface condenser air ejector steam jets (16). This steam is also introduced into the processes in the primary and secondary reformers, and in the shift converter (line marked 30). This steam is sometimes used to drive the induced draft fan turbine of the primary reformer furnaces. It also can be arranged to flow directly through a steam ring in the stack, in case the differential pressure across the fan drops below the predetermined level.

The 160 psi (1,120 kPa) (11 bar) steam is supplied to the unit as necessary by letdown from the 545 psi (3,815 kPa) (38 bar) subsystem via a pressure reducing control arrangement. This steam is usually desuperheated and then introduced into the MEA vaporizer (29). It is also used for warming the portions of 545 psi (3,815 kPa) (382 bar) steam used in the high temperature shift converter section and as regeneration steam for the desulfurizers.

The 50 psi (350 kPa) (3.5 bar) steam is mainly used as a heating medium for the MEA stripper steam reboiler (21) and as stripping and heating steam in the boiler feedwater deaerator (20). It is also used intermittently in the lube oil heaters (23) and more or less continuously in the condensate polishing tank heating coils (25). Normally, there is no excess steam, as a steady amount of makeup is required from the 160 psi (1,120 kPa) (11 bar) subsystem to satisfy all of the 50 psi (350 kPa) (3.5 bar) steam requirements.

C.2.4.2 Subsystem (b): Steam Condensate

The steam condensate as applied herein is distinctly different from the process condensate. The latter, although actually condensed steam, has been exposed to the process stream and therefore contains impurities which would be intolerable in the steam subsystem. The process condensate is largely disposed of, going to the sewer from the shift converter effluent preheat exchanger. Also, a small amount is used for makeup to the MEA components, and for quenching the process stream. It should be emphasized that *the process condensate is not a part of the steam condensate subsystem.*

The subsystem herein described contains condensate formed by condensation of steam used in heating services and condensate formed by the condensation of turbine exhaust steam in the surface condenser (17).

The steam condensate from heating service is returned directly to the deaerator (20). There are two streams of this hot condensate. One originates from the MEA vaporizer (29) and is called high pressure steam condensate; the other originates from the 50 psi (350 kPa) (3.5 bar) steam subsystem and is therefore called low pressure steam condensate.

Condensate formed in the surface condenser is pumped by the condensate pump (18), to the deaerator via the condensate polishing tank (25) and shift converter effluent preheater (24), where it takes up heat from raw synthesis gas going to the raw gas separator. (See Fig. 1.)

The hot condensate from the MEA vaporizer and reboiler returns directly to the deaerator. From there, water is pumped as boiler feedwater to the steam drum (4) and as quench for the steam desuperheter stations employed for the 50 psi (350 kPa) (3.5 bar) and 160 psi (1,120 kPa) (11 bar) steam subsystems. Small amounts of surface condensate are also diverted to the reformers’ cooling jackets as make-up water and to the sealing medium for the relief valves on the vacuum exhaust lines of the surface condenser air ejector steam jets (16).

C.2.4.3 Subsystem (c): Boiler Feedwater (BFW)

Clarified water is typically supplied from offsite to the demineralization section which consists of three cation exchangers, three anion exchangers, a water booster pump (all of these not shown in Fig. 2), a mixed bed polisher (27), and a demineralized water storage tank (28) with turbine- or motor-driven pump(s) (31).

All make-up demineralized water to the deaerator is preheated in the heat exchanger (24) to about 212°F (100°C) by heat exchange with a process stream. Dissolved oxygen is stripped from the BFW in the tray type deaerator (20) as the water is sprayed into the steam space, and 50 psi (350 kPa) (3.5 bar) steam is introduced as a stripping medium. This water accumulates in the storage section, from which it is then pumped to the boilers by the high pressure BPW pump(s) (26).

Considerable auxiliary equipment is used for regeneration of the demineralization facilities, but a discussion of this subject is not included in this data sheet.

C.2.5 Protective Controls and Instrumentation

The objective of ammonia plant protective controls and instrumentation is to protect equipment and inventory. See Data Sheet 7-45, *Instrumentation and Control in Safety Applications*. In order to accomplish this objective, the protective control arrangements provide continuous or intermittent monitoring of all significant variables and alarm or automatically take corrective action when predetermined limits are exceeded. Certain controls and instruments (C & I) are provided as safeguards during shutdown and/or start-up phases; others are used during normal operation. Some C & I's must function continuously, from startup through normal operation until final shutdown.

Their output functions also differ. One function of controls and instruments is to provide an alarm that indicates abnormal deviations of variables, which can be corrected by proper actions of the operator. The second function is to shut down or to block in a certain subsystem or apparatus and activate certain auxiliary bypassing lines so that the remaining part of the plant is kept in operation. The third function controls critical variables which require complete shutdown of the entire system in the event of abnormal deviations from established settings. Some C & I perform only one function; often they perform all three.

Actual protective control and instrumentation arrangements vary from one particular unit to another. The description presented herein is more or less typical and is limited to protective instrumentation as applied to the most important components of the entire process, where automatic protection is paramount. Standard control arrangements for compressors, pumps, and turbines are not described herein, as these descriptions can be found in their respective data sheets.

The protection means recommended involve certain shutdown (trip-off) action. Other instruments are provided to monitor critical process parameters along all product and media streams and in the reactors. These instruments activate alarm devices in case those parameters deviate abnormally, thus indicating a need for operator involvement and adjustment. These instruments and their associated alarms are usually concentrated on the plant's control panel, located in the control room. The process parameters include temperature and pressure in various apparatus and in some points of connecting (transfer) lines; liquid levels; and process stream, water, fuel, and air flows. Usually all control points are listed and displayed on the control panel.

Sometimes several protection arrangements with a ''shutdown'' (*trip-off*) output incorporate time delay between detection of the abnormal condition and the shutdown action. Such a setup is used primarily for the reformer trip systems because the processes there are more inertial and allow for some time delay to correct the abnormal conditions. The majority of the protection means recommended actuate the shutdown procedures at the moment an abnormal parameter deviation is detected, thus effectively protecting the entire ammonia synthesis unit.

C.3 High Pressure Ammonia Synthesis (Fig. 3)

The high pressure ammonia synthesis described here is known as the *Casale process* for producing anhydrous ammonia. Nitrogen for this synthesis is generally obtained from an air separation unit which is part of the entire system. (See Data Sheet 7-52/17-13, *Oxygen*.) Hydrogen for the synthesis is supplied from other processes, not part of the synthesis system. See Data Sheet 7-50, *Compressed Gases in Cylinders,* and Data Sheet 7-91, *Hydrogen.*

The Casale process differs from most other ammonia synthesis processes in two major respects: 1) it uses substantially high operating pressures, in the range of 9,000-12,000 psi (64,800-86,400 kPa) (648-846 bar); and 2) it recirculates unconverted gases by an ejector recirculating device, which is an exclusive feature of the Casale process. The main advantage of these features is elimination of the recirculating compressor and of refrigeration, which simplifies the system's handling and sufficiently reduces contamination of the synthesis gas and catalysts. On the other hand, increased operating pressures require stronger and thus more expensive equipment, and also increase the probability of accidents caused by overpressurization.

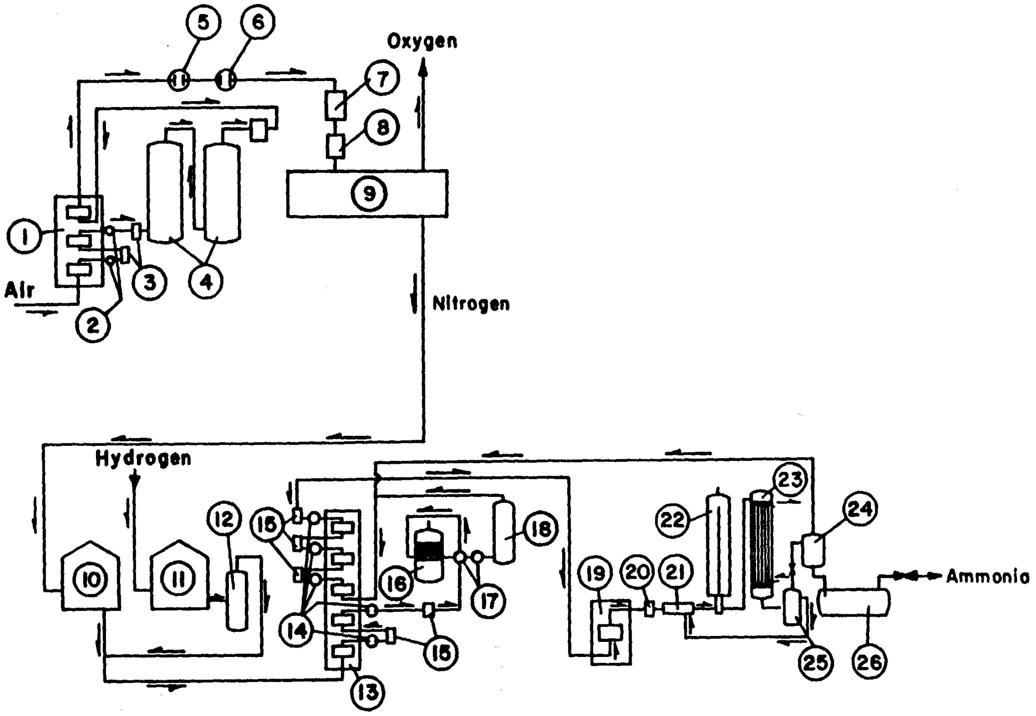

Fig. 3. The Casale process flow diagram.

The system works as follows (Fig. 3):

Air entering the process is compressed in a three-stage air compressor (1). At the discharge of each stage, the air is cooled in water coolers (2) and entrained moisture is trapped in separators (3). After discharge from the second stage, the air flow passes through a cooler and then through sodium hydroxide (NaOH) scrubbing devices (4) which remove carbon dioxide. This, along with water trapping, minimizes deposition of solids in the switch exchangers where the air is cooled to the liquefying temperature.

The air then enters the third compression stage, and from there it is discharged through a water cooler (5) and a Freon-refrigerant chiller (6), to an air dryer (7), and separator (8), after which it enters the liquefied air plant (9) proper.

The oxygen, as a substance not part of the ammonia synthesis process, is vented to atmosphere or used in other processes. Pure nitrogen is directed to the nitrogen gas holder (10). Hydrogen for the process is held in the hydrogen gas holder (11). Before introduction to the main process, stream hydrogen is cooled in a water cooler (12), after which it is mixed in the required proportion with the nitrogen flowing from its gas holder (10).

The mixture enters a five-stage mixed gas compressor (13). As it discharges from each stage, the compressed mixture is cooled by water in coolers (14), and entrained water is trapped in separators (15). After the second stage the cooled gas enters the deoxidation reactor (16), where some residual oxygen and traces of chlorine react with hydrogen in the presence of a metallic catalyst, and form water and hydrogen chloride. The reaction requires a temperature of about 650°F (343°C), which is provided by a heat exchanger and electric heater.

After leaving the deoxidizer (16), the process stream is cooled in water coolers (17), after which it is introduced into a NaOH scrubbing device (18). Here the last traces of carbon dioxide and converted hydrogen chloride are removed. From the scrubbing device, the process gas reenters the compressor third stage (13), and passes through each successive stage as previously described. It leaves the last stage under a pressure of about 5,645 psi (39,515 kPa) (395 bar). The flow then enters a hypercompressor (19), which boosts the pressure to the required converter range, i.e., from 9,000 psi (64,800 kPa) (648 bar) to 12,000 psi (86,400 kPa) (864 bar).

From the hypercompressor, the process gas is directed to an oil filter (20), and after traces of oil are removed, it enters the patented Casale ejector (21). This device draws unconverted gases and some ammonia vapor from the low pressure separating drum (25), and recirculates them with the feed gases into the Casale reactor (22).

The process of ammonia synthesis is exothermic, but it requires sufficient amount of heat to raise the synthesis gas mixture to the desired reaction temperature. This temperature is attained by heat exchange passages in the Casale reactor (converter) (22), where incoming cold gas is heated by outgoing hot gases. For startup purposes, the Casale reactor contains an electric heater.

Ammonia and unconverted gases at a temperature of about 500°F (260°C) flow to a water cooler (condenser) (23), where the high pressure ammonia is condensed. Afterwards, the mixture of liquefied ammonia and unconverted (non-condensing) gases is directed into a separating drum (24). There the gases are separated from ammonia and directed to the reactor for recycling. During this step, the liquid ammonia pressure is reduced to 1,100 psi (7,600 kPa) (76 bar). The flow enters a low pressure separating drum (25), where unconverted gases absorbed in the liquid ammonia and any ammonia vaporized through pressure reduction are released and recycled back to the third stage of the mixed gas compressor (13).

The liquid ammonia from the low pressure separating drum is further reduced to the required storage pressure and released to the storage facilities. (26).