## THE PROCESS

4.

# A. DESCRIPTION OF THE FLOW

#### 1. Process Flows

This section of the manual should give the reader a clearer understanding of the operation and process principles of the unit. The description of the process flows through the unit can be more readily understood if the Process Piping, Auxiliary and Utility Instrumentation Flow Sheets are referred to during study of this section. These are drawing numbers 62-Dl through 62-D7, 63-Dl and 64-Dl through 64-D6 located in Section V of the manual.

The ensuing discussion will describe in detail the main process flow through the unit. All auxiliary systems that are pertinent to the process will be described separately under a separate subsection "2. Auxiliary Flows" in this section of the manual. The auxiliary flows will include the steam, boiler feed water, and etc, systems. The process and operating principles are discussed in detail in the second portion of this section under "B. Process and Operating Principles".

Complex instrumentation is subsequently described under a separate subsection (C. Special Equipment) in Section II of the manual.

#### a. Raw Synthesis Feed Gas Preparation System

#### (1) Feed Gas Desulfurizing and Oil-Removal

Natural gas, of the composition indicated in the Material Balance tabulation, will be supplied at the battery limit at sufficient pressure to letdown to the KO drum 120-F. The feed gas is expected to be saturated with a hydrocarbon oil. The flow is from battery limit through line NG-1 to PRCV-101 (control valve of PRCa-101) which maintains pressure on the feed gas KO drum 120-F. The flow is metered by FRa-101, and then continues to one of the two hydrocarbon and sulphur removal reactors (101-Da, 101-Db.).

Each reactor has two packed zones: (1) a hydrocarbon oil removal zone, and (2) a desulphurization zone. Between beds is a pan and chimney assembly for the purpose of collecting oily condensate and water. The upper or hydrocarbon-oil removal zone contains 100 cu. ft. of activated charcoal. The lower desulphurization zone contains 300 cu. ft. of activated carbon impregnated with metallic oxides. These vessels are each capable of handling the design amounts of heavy hydrocarbon and sulphur in the feed gas.



The natural gas charge is fed to the upper charcoal bed. As the gas passes through the bed, the heavy hydrocarbon constituents are adsorbed. A condition is finally reached where the bed is saturated with heavy hydrocarbon. The vessel is then taken out of service for regeneration.

Following removal of heavy hydrocarbon components, the feed gas flows to the lower (desulphurization) zone where it is treated for removal of mercaptan sulphur and H<sub>2</sub>S.

As soon as the packed beds become saturated with heavy hydrocarbons and/or sulphur, the feed gas is switched to the second vessel to permit regeneration of the bed (or beds) in the first vessel. It is anticipated that each of the vessels will operate for about one week before regeneration is required.

The vessel to be reactivated is taken out of service and depressured to 25 to 50 psig by venting to atmosphere. Superheated steam is then admitted to the upper section of the vessel at a rate of about 2000 #/hr, as measured on FI-101, until the temperature reaches about 600°F at the outlet of the bed. Saturated steam is then injected to the lower bed at a rate of about 3000 #/hr, measured on FI-102, until the temperature leaving this bed approaches 400°F. The steam and vapors from the regeneration operation are vented to atmosphere. As shown on the flow sheet 62-Dl, a small amount of ammonia is injected during regeneration to neutralize sulphur compounds that might otherwise cause corrossion. This ammonia injection flow is measured on FIr-101.

The reactors are also equipped with temperature indicators (TI) thermometer indicators (ThI) and pressure gauges (PI) as necessary to observe process conditions in and around the reactor systems. Each reactor is pressure protected with RV's 101-Da and 101-Db, respectively.

## (2) Feed Gas Compression

Two 55% motor-driven multiple-service compressors are provided with twelve cylinders on each compressor. These cylinders provide the following services. One for feed gas, four for process air, three for synthesis gas, one for recycle and three for ammonia refrigeration.

The feed gas compressors (102-Ja and 102-Jb) raise the pressure level of the desulphurized feed gas for injection into the process. The compressors are reciprocating type that take suction on the outlet of the desulphurizer reactors and discharge through and oil separator to the primary reformer (101-B) via the feed preheat coils. The flow of gas through the compressor is controlled by FRRCa-101, pressure at the discharge is held



constant with PRCa-102. To satisfy minimum flow requirements, the compressors are provided with means to "kickback" or recycle a gas flow from the discharge back to the suction.

At the outlet of the feed preheat coil the feed is joined and mixed with process steam, flow controlled by FRCa-101. The combined stream (gas and steam) passes through the mixed feed preheat coil to the primary reformer via an eight inch distribution header.

## (3) Primary Reforming

From the main eight inch inlet header the process flow is distributed to two six inch sub-headers. Each of the sub-headers distribute the flow downward through 42 parallel (catalyst packed) tubes in the radiant section of the primary reformer heater (101-B). These catalyst packed tubes are, in fact, the "Primary Reforming Reactor".

The bottom of each row of 42 catalyst packed tubes terminate in collection headers located near the floor of the primary reformer heater. There are two risers (centrally located) on these collection headers that return the flow to a transfer line located over the top of the heater (101-B). The transfer line directs the flow from the primary to the process inlet of the secondary reformer (102-B).

The primary reformer has various pressure gauges, temperature indicators and temperature recorders (TR) to observe process conditions. There is also a pressure differential indicator (Pdia-102) for observing the pressure drop across the tubes.

## (4) Secondary Reforming

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The process flow enters a chamber at the top of the secondary reformer reactor (102-B) and is directed downward through a diffuser ring to enter the combustion zone of the reactor. Preheated air is introduced to the process through a nozzle located just below the diffuser ring. Leaving the combustion zone of the reactor the flow passes through the catalyst bed to enter the chamber at the bottom of the reactor.

From the outlet chamber of the reactor the flow passes through the tube side of the waste heat boiler (101-C). The flow through the shell side of the waste heat boiler is boiler feed water. From the tube side outlet of the waste heat boiler the flow continues on to the high temperature shift converter (102-D).

The secondary reformer and waste heat boiler described above have ample pressure gauges, temperature indicators, temperature recorders and a pressure differential indicator to observe process conditions

through the system. The process inlet temperature to the high temperature shift converter is controlled by varying the flow of process gas through the "hot" and "cool" tubes of the waste heat boiler. This is done by manipulation of butterfly valves on the tube outlets under control of MIC-101 and TRCa-101.

The primary as well as the secondary reforming systems (including the waste heat boiler) are pressure protected at the outlet of 101-C by RV-101-C. As added safety protection on the secondary reformer it is provided with metal temperature indicators (MTE) and a level alarm (LA) on the cooling water jacket.

## (5) Shift Converter (high and low temperature)

The shift converter (102-D) is in reality two reactor systems (high and low temperature), so constructed with internal dished heads to separate one from the other. The upper reactor being the high temperature converter and first in the process flow from the secondary reformer.

The flow through the high temperature shift converter is axial (downward) and passes out the side of the reactor via internal piping in the reactor. The flow then enters the tube side inlet of the primary shift effluent waste heat boiler (103-C) to give up heat to the boiler water from 101-F. This exchanger is equipped with a hot line by-pass to give flexibility of temperature control to the inlet of the low temperature shift converter. This temperature is automatically controlled by TRCa-102 located in the hot line process by-pass of the primary shift effluent waste heat boiler (103-C).

The flow then passes through the tube side of the methanator feed heater (104-C) to preheat the methanator reactor (103-D) feed. The cooled process flow re-enters the side of the reactor and enters the low temperature shift converter via internal piping. The flow through the reactor is axial (downward) and leaves the reactor through an outlet nozzle located at the bottom of the low temperature shift converter.

From the outlet of the low temperature shift converter the process flow passes through a reactor effluent desuperheater station (diagram 4D5-6 on drawing 64-D5). The desuperheater outlet temperature is controlled by injecting process condensate from the raw gas separator (102-F). The quench water to the desuperheater is supplied by a quench pump (110-J), with the flow controlled by FICa-101.

From the outlet of the desuperheater the process stream is first cooled in the shell side of the reactor effluent/MEA reboiler exchanger (105-C), giving up heat to reboil the MEA solution. Total condensation of the process steam in the reactor effluent is accomplished in the LT shift effluent/methanator feed exchanger (106-C) and air cooler 107-C. The flow then continues to the raw gas separator (102-F).



The process flow that enters the raw gas separator (102-F) is split into two streams leaving the drum. The raw synthesis feed gas passing overhead continued to the MEA absorber, which is the first step in the synthesis feed gas purification step. Condensed process steam from the bottom of the gas separator is used to quench the reactor effluent at the desuperheater station utilizing quench pump (110-J). Process condensate not required for quench is disposed of by LC control (LC-101) to the battery limits.

The system described above has all the pressure gauges, temperature indicators, temperature recorders and temperature controllers required to observe and control the desired operating conditions. The entire system is normally pressure protected via the relief valve (RV-102-F) located at the outlet of the raw gas separator (102-F).

## b. Synthesis Feed Gas Purification System

## (1) Carbon Dioxide (CO2) Removal

In this section, raw synthesis gas at about 345 psig and 150°F is processed for removal of carbon dioxide (CO<sub>2</sub>) to yield a hydrogen/nitrogen synthesis gas in a very high state of purity (less than 10 ppm of CO plus CO<sub>2</sub>). The bulk of the carbon dioxide is removed by preferential absorption using a 20 wt. % aqueous solution of MEA.

Gas from the raw gas separator, 102-F, is introduced to the bottom of the CO2 absorber, 101-E. Regenerated lean MEA solution, pumped from the CO2 stripper by pumps lll-J and JA, is introduced over the top tray of the absorber and flows down over the twenty-one trays counter-current to the upflowing gas. Pump lll-J is a hydraulic helper turbine pump, which utilizes the absorber bottoms flow as a source of power to drive the pump. The tower will be operated with the MEA level above the gas inlet. The liquid release from the bottom is controlled by a signal proportional to the differential pressure developed across the tower. The level controller, LRC-101, measures the tower bottom liquid head plus the differential pressure across the tower.

Rich MEA (i.e., loaded with the absorbed CO2) leaving the bottom of the absorber is heated by heat exchange with hot stripper bottoms in heat exchangers 109-C. Part of the cold stream is diverted through a slip-stream filter to remove suspended solids. The absorber level controller (LRC-101) throttles the rich MEA after the heat exchange in the 109-C bundles in order to minimize the gas release in these exchangers. The hot, rich MEA then flows to the top tray of the strippers operating at 8.0 psig at the bottom of the tower. Reboiler heat is partly provided by the quenched gas-steam mixture from the shift converter passing through the



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reboiler as described earlier. The remainder of the reboiler service is provided from the 45# steam system in lll-C. Carbon dioxide and water stripped from the MEA passes overhead and through the overhead condenser 110-C where water and a little MEA is condensed out and accumulates in the CO2 stripper reflux drum (103-F). The bulk of the CO2 is released to the atmosphere through the CO2 vent. Condensate accumulating in the reflux drum is returned to the stripper tower by the reflux pump (112-J), which operates to maintain a constant level in the reflux drum, regulated by the level controller LC-105. Water lost from the MEA solution with the CO2 is replaced by the addition of process condensate.

A portion of the CO2 stripper bottoms may be continuously taken off to a kettle type reboiler (113-C) where the MEA solution is redistilled (vaporized). The contamination products will accumulate in the reboiler and will be discharged to waste. The purified MEA returns to the stripper beneath the 25th tray in the bottom section of the tower. The reboiler 113-C utilizes 200 psig steam to purify the MEA solution.

The CO<sub>2</sub> stripper bottoms level is indicated on the control board (LRCa-105) and a high-low level alarm (LA-113) that is furnished to warn of high or low levels in the CO<sub>2</sub> stripper bottoms.

Process gas, from which essentially all of the CO<sub>2</sub> will have been removed, passes overhead from the absorber to the knockout drum 122-F. This drum is provided with a demisting pad designed to remove any entrained moisture, which will accumulate in the drum and will be drained to the MEA sump periodically. The drum is provided with a gauge glass and a high warning alarm, LA-136.

The process gas flows to the methanation system from the KO drum. Analyzer-recorder AR-101 monitors the CO2 content of the gas stream and will be arranged to sound an alarm if the CO2 content should exceed a preset maximum value.

Prior to methanation the gas must be heated to the temperature required for the methanator reactions. This is accomplished by heat exchange against methanator effluent in exchanger 106-C followed by exchange against hot shift converter effluent in exchanger 104-C.

# (2) Methanator (CO Conversion)

The preheated process flow leaving the tube outlet of 104-C enters the top inlet of the methanator reactor (103-D). The flow through the reactor is axial (downward) and leaves the reactor at the bottom outlet.

From the reactor the flow is first cooled in the tube side of the reactor effluent/boiler feed water exchanger (ll4-C). Final cooling of the

flow is achieved in the shell side of synthesis feed gas cooler (115-C). From the shell side outlet of this cooler the flow goes to the synthesis gas suction drum (104-F). The compressors (103-Ja & Jb) taking suction on this drum is the first step in the ammonia production step of the process.

The synthesis feed gas purification part of the system is also equipped with all instruments necessary to control and observe process conditions. The methanator in this system has provision for automatic cutout of feed under certain emergency situations. This system will be described in detail later in the manual.

The purification part of the system is pressure protected by RV's 102-F and 104-F. These relief valves are located at the raw gas separator (102-F) and synthesis gas suction drum (104-F) respectively.

## c. Ammonia Production System

## (1) Compression of Synthesis Feed Gas

The synthesis gas compressors (103-Ja & Jb) are the first step in the liquid ammonia production part of the system. These compressors take suction on the synthesis gas suction drum (104-F) and increase the pressure in the "first stage" compressor case, and discharges to the "second stage" case, thence to the "third stage" case of the machine via a series of inter-coolers and an oil separators drum (105-F).

The flow of synthesis gas is through the tube side of the synthesis feed gas compressor inter-coolers (116-Ca & Cb, 117-Ca & Cb, and 120-Ca & Cb) and is cooled with cooling water. From the last intercooler (120-Ca & Cb) the flow enters the oil separator drum (105-F) where oil and carbomate are drained to the sewer. Before entering the oil separator drum (105-F) the synthesis gas stream is joined with a flow of recycle gas from the discharge of the recycle compressors (104-Ja & Jb).

The ammonia concentration in the recycle gas is reduced when the fresh feed and recycle are combined. This stream, from the oil separator, is passed through an ammonia refrigerated chiller (121-C) to a secondary separator (106-F) where liquid ammonia is removed at 25°F and is delivered to the product flash drum (109-F). This ammonia removes with it water of saturation carried by the fresh feed portion of the gas. This is an essential purifying function for the ammonia synthesis feed since all oxygen compounds, including water vapor, are deleterious to the synthesis catalyst.

The gas from the secondary separator (106-F) passes through the tube sides of exchangers 122-C and 123-C where it is heated to approximately 250°F, by exchange with ammonia converter (104-D) effluent before entering the converter.



The synthesis feed gas and recycle compressors are equipped with pressure recording controllers (PRCa), flow indicators, pressure gauges, temperature indicators and level alarms to provide proper control, and to observe process conditions through the compressors.

The discharges of the synthesis gas compressors are pressure protected by RV's 120-Ca and 120-Cb. The discharges of the recycle compressors are pressure protected by RV-104-Ja and RV-104-Jb.

## (2) Synthesis (Conversion) of Feed Gas to Ammonia

The synthesis converter consists of a high pressure shell containing a catalyst section and a heat exchanger 124-C. The catalyst section is a cylindrical basket which fits inside the vessel, leaving an annulus between the shell and the basket. There are five catalyst beds, each supported on a screen-covered grid. In order to maintain all the catalyst at optimum temperature for maximum yield, provision is made to inject cold feed gas (via MIC's 105 to 109) as quench in the spaces between the beds. Approximately 190 cubic feet of catalyst is contained in the converter. The catalyst zones are arranged so that the top bed contains the smallest quantity of catalyst, to limit the temperature rise before the first quench point. Since the temperature gradient is flatter in succeeding zones, the bed sizes are graduated with the largest at the bottom. Located beneath the catalyst section is the heat exchanger to preheat fresh inlet gas against hot reacted gas from the last catalyst bed.

The normal point of entry for the feed is at the top of the converter, via MICV-104. The gas flows downward between the pressure shell and the wall of the catalyst section; it serves as a cooling medium for the shell and is thus preheated ration to entering the exchanger. The stream enters the exchanger at the bottom of the catalyst section; it serves as a cooling medium for the shell and is thus preheated against the exchanger at the bottom of the catalyst section; it serves as a cooling medium for the shell and is thus preheated against the exchanger at the bottom of the catalyst section; it serves as a cooling medium for the shell and is thus preheated against the exchanger at the bottom of the catalyst section; it serves as a cooling medium for the shell and is thus preheated against the exchanger at the bottom of the catalyst section; it serves as a cooling medium for the shell and is thus preheated against the exchanger. The stream enters the exchanger at the bottom of the catalyst section; the catalyst section is the catalyst section; it serves as a cooling medium for the shell and is thus preheated against the exchanger.

For temperature control of the top bed, a portion of the cold feed gas may be introduced to the top directly (by-passing the exchanger). The combined stream flows downward through the catalyst with a rapid temperature rise as the ammonia reaction proceeds. The stream passes through a grid supporting the catalyst, into a space between the bottom of the first and top of the second bed. At this point, the temperature may be reacted and the ammonia content diluted by the injection of some cold feed gas. This quenching arrangement permits control throughout the catalyst beds to obtain optimum temperature for maximum yields. In like manner, the gas flows downward through the other four beds.

In the presence of the iron oxide catalyst, a portion of the hydrogen and nitrogen combines at a temperature of approximately 900°F and a pressure



of 4765 psig to yield ammonia in a concentration of about 16 percent in the effluent from the last catalyst bed. The hot effluent passes downward through the exchanger (in the converter bottom) giving up heat to the upflowing fresh feed. From the exchanger, the reacted gas leaves the bottom of the converter at 578°F.

The flow leaving the converter enters the tube side inlet of the ammonia converter/boiler feed water exchanger (125-C) to give up heat to the boiler feed water. Then to the shell side inlet of the ammonia converter feed/reactor effluent exchanger (123-C). The flow from the shell side outlet of 123-C cooler goes to the tube side of water cooler 126-C and then receives final cooling in converter feed/reactor effluent exchanger 122-C before entering the primary ammonia separator (107-F) to complete the synthesis gas loop ("Syn. Gas Loop").

The "syn gas loop" is kept free of inerts by a continuous purge of gas from the system to fuel via the purge gas cooler (128-C) and purge gas separator (108-F). Liquid (NH3) that is knocked back in the purge gas separator goes to the product flash drum (109-F) under LC control (LC-109).

The syn gas loop has all the temperature indicators (and recorders), pressure differential indicators and control valves (MIC) to observe and control process conditions within the "loop".

The entire syn gas loop (including converter 104-D) is pressure protected by RV-104-D and RV-107-F.

The ammonia synthesis converter is equipped with a start-up heater (103-B). This heater is used to heat the converter up to reaction temperature during the start-up and will be described later in the manual.

# (3) Ammonia Product Purification (Removal of Light Ends)

The ammonia product that is separated from the syn loop in the secondary separator drum (106-F) was cooled to 25°F for maximum ammonia condensation. This cooling at the 4700 psig pressure level of the syn gas loop will cause a degree of light gas (hydrogen/nitrogen) to be absorbed by the liquid and results in a contaminated ammonia product.

To remove the absorbed light ends from the ammonia product, it is first flashed in the product flash drum (109-F) that operates at about 58°F and 222 psig pressure. The flash gas that leaves the product flash drum is further chilled in 128-C, to condense any flashed ammonia, and is then released to the fuel gas system for disposal via PRC-105, that is set to hold about 222 psig back-pressure on 109-F and will prevent over-flash.



The liquid leaving the primary separator drum (107-F) also flows to the product flash drum 109-F. Flash gas from the primary separator drum is split in two streams. One stream going to the suction of the recycle gas compressors (104-Ja & Jb) to complete the synthesis loop and the second stream going to the H. P. purge separator (108-F).

The gas leaving the primary separator drum is chilled to 25°F in chiller 127-C before entering the H. P. purge gas separator (108-F). Flashed gas (argon/methane) is released to the fuel gas system via PRC-107 that is set to hold about 4500 psig back-pressure on 107-F. Liquid under LC control (LC-109) leaves the H. P. purge gas separator and joins the product stream from the primary and secondary separators going to 109-F.

The product liquid from 109-F under LC control (LC-114) flows to the ammonia refrigerant second stage and first stage flash drums (112-F and 113-F respectively) before being pumped to storage with product pump 114-J. The progression of the ammonia product through the various pressure levels of 109-F, 112-F, and 113-F chills the product from approximately 58°F to about -30°F.

The flash gas that is released from the first, second and third stage refrigerant flash drums is compressed by the refrigerant compressors (105-Ja and Jb) that operate with a suction pressure of about 0.1 psig on the first stage, 20 psig on the second stage and 78 psig on the third stage. The suction of the machines is on pressure control (PIC-105) at 0.1 psig to satisfy the pressure requirement on the first stage refrigerant flash drum 113-F.

The flash gas (ammonia plus inerts) that leave the ammonia compressors (at about 190°F and 220 psig pressure) are sub-cooled to 100°F in the refrigerant condenser (129-C). The second stage of the ammonia compressor is also equipped with an after-cooler (130-C) that removes most of the heat of compressor from the second stage of the machine. This after-cooler allows the third stage of the machine to run at a lower temperature, resulting in a lower final discharge temperature than would otherwise be possible.

From the outlet (tube side) of the refrigerant condenser the subcooled ammonia (100°F) flows to the ammonia refrigerant receiver (110-F). The inerts that flash from the ammonia in this drum in excess of pressure control requirements are vented to fuel gas via PRC control (PRC-106) for disposal.

The refrigeration system has all the temperature indicators and pressure controls to observe and control the system at required conditions.



The refrigeration compressor is also equipped with alarms and automatic shutdown devices necessary for full protection of the machine.

The entire refrigeration system is equipped with RV's for overpressure protection of equipment in the event of emergency conditions.

## 2. Auxiliary Flows

## a. Steam Systems

The steam systems along with the chemical treating and deaeration auxiliaries to the steam system, compose a major portion of the plant. Saturated steam at 500 psig pressure is produced from 101-F steam drum. This 500 pound steam is used to drive steam turbines and in the process. Low pressure steam is provided from the exhaust of certain steam turbines. The operator will find it necessary to study in detail drawings 64-Dl and 64-D2 which will be found in the appendix of this manual. Simplified diagrams entitled "Start-up Steam Balance" will also be found in the appendix. These sketches can be very helpful in understanding the steam distribution system.

A discussion of the steam systems follows:

# (1) 500 psig Steam System (HS)

Boiler feed water is pumped from the deaerator 105-L to the steam drum 101-F by boiler feed water pump 115-J. This water is preheated enroute to 101-F in passage in parallel through 114 and 125-C. The major flow is through 125-C. The flow of B. F. W. to the steam drum is under LC control (LL 1-102) at the discharge of the B. F. W. pump 115-J. Control of this valve will be discussed under "C. Special Equipment", located in Section II of this manual.

Somewhat over 81,000 #/hr. of 450 psig steam will be produced from 101-F. About 56,000 # is produced as a by-product of cooling process gas streams in 101-C and 103-C. The remainder is produced in four convection coils of 101-B reformer furnace (coils D through G).

The 450 psig steam leaves the steam drum at about 472°F and is used in various services as delineated on the steam balance drawing. These services include driving all turbines, process steam to the primary and secondary reformer, heating lll-C and ll3-C, and for regeneration of the desulphurizers. In addition, steam is arranged to automatically open to a steam ring in the 101-B stack in the event of a failure of the 101-BJ fan motor. This is accomplished by tripping a solenoid (VS-105) which must be manually relatched after the difficulty has been corrected. Warning is given in the control room by the alarm MA-101 in the event of fan motor failure.

During normal operation, approximately 25,700 #/hr of steam will be exported to the refinery via the 500 psig header.

## (2) 125 psig Steam System (FS)

The 125 psig fire steam system is made up through a pressure let-down valve (PIC-102) from the 450 psig pressure system. Fire steam is used as snuffing steam for furnaces 101-B and 103-B, snuffing steam to the compressor house, building heating and various service connections throughout the unit.

## (3) 55 psig Steam System (LS)

The 55 psig steam system is made-up from the turbine exhausts and is chiefly used as heat medium on the MEA stripper reboiler and as stripping and heating steam on the boiler feed water deaerator 105-L. Normally there will be no excess steam from the 55 pound header. In the event there is an excess (during start-up or shutdown) facilities have been provided to vent this excess to atmosphere via PC-107.

## (4) Steam Condensate System (SC)

First of all, the reader must differentiate between "steam condensate" and "process condensate". The process condensate, although it is actually condensed steam, has been exposed to the process stream and contains impurities which would be intolerable in the steam system. Therefore the process condensate is largely discarded (going to battery limits from 102-F). A small amount is used for make up to the MEA system and for flushing the MEA filter. The process condensate is therefore not considered part of the steam condensate system.

The steam condensate system consists of steam condensate formed by the condensation of steam used in heating services (hot condensate) and the condensate from various steam traps throughout the unit.

The steam condensate from heating services is returned directly to the deaerator. There are two streams of this hot condensate. One originates from the MEA vaporizer 113-C and is called HP steam condensate since it originates from 500 psig steam. The other hot condensate steam system originated from the 55 psig steam system and is therefore called LP steam condensate.

The hot condensate from the MEA vaporizer and reboilers (113 and 111-C) returns directly to the deaerator (105-L). From the deaerator the water is pumped as boiler feed water to the steam drum (101-F), and as quench for the steam de-superheater stations for the 55 psig steam system.



## (5) The Steam Drum 101-F

This item is, of course, part of the 500 # steam system but a discussion of the drum and the auxiliary piping associated with it is here presented separately. Dwg. 64-Dl shows the piping to and from the steam generators, the steam outlet and superheater, and blowdown piping. The drum contains steam scrubbing cyclones and demisters to insure a dry steam product. The reader should refer to the vendors drawings and literature for particular details of the steam drum.

Blowdown connections are provided to permit "blowing down" sediments from the low points of the drum and the steam generators. A continuous blowdown mounted within the steam drum is located at what is designed to be the interface between the water level and the steam space. Impurities tend to concentrate at this junction of steam and water and the continuous withdrawl of a small amount of water and steam from this point provides the most efficient removal of accumulated dissolved solids.

#### b. Boiler Feed Water Deaeration

Boiler feed water is supplied from offsites to the deaerator 105-L. The rate of flow is regulated by the deaerator level controller LRC-104 which throttles the incoming water stream. The design anticipates about 2/3 makeup and 1/3 recycled condensate (total of hot and cold condensate).

Dissolved oxygen is stripped from the boiler feed water in the traytype deaerator as the water is sprayed into a steam space in the deaerator. 50# steam is introduced as the stripping medium. The hot condensate streams are separately introduced to the deaerator. The total of these waters accumulate in the storage section, from which the water is pumped to the boiler as previously described.

The boiler feed pumps are provided with low flow by-passes which return a controlled amount of water to the deaerator in order to avoid damage to the pumps if the steam drum level controller should shut completely.

# c. Reformer Cooling Water Jackets

The secondary reformer vessel is enveloped in a water jacket.

Water is supplied to the secondary water jacket from the boiler feed water pump 115-J and is cooled by a cooling water flow in an in-line cooler before entering the jacket. The secondary reformer jacket over-flows to the 101-C jacket which in turn overflows to the sewer. The quantity of 1 take-up is indicated locally (FI-103) and a flow alarm (FA-103) gives warning in the control room if the flow should fail.



Drains are provided at the jacket low points. These are to be opened occasionally (briefly) to insure that sludge does not accumulate in the jacket bottoms. There is also an emergency cooling water supply to the jacket to be used only when it is necessary.

A gauge glass and a low level alarm are provided with the jacket.

It is imperative the water jackets be maintained water filled, when heat is applied to the primary or secondary reformers. Failure to maintain adequate water levels in the water jackets, could possibly cause rupturing of the jacketing by uneven expansion. Loss of water from the jacketing could also cause undue stress in the transfer line piping to the secondary reformer. In event of failure of the jacketing and loss of cooling water, it is recommended the reformers be taken out of service, until water jackets are again serviceable, and water levels may be maintained.

NOTE: The "emergency cooling water" should never be used for jacket cooling except in an emergency. Excessive use of "cooling water" can quickly lead to corrosion (or fooling) problems in the jacket cooling system. Heavy blowdown should be used to displace the solids formed during the use of the emergency cooling water, after returning to the normal BFW flow.

# B. PROCESS AND OPERATING PRINCIPLES

1. Raw Synthesis Feed Gas Preparation System

# a. Feed Gas Hydrocarbon Removal and Desulphurization

The feed gas entering the plant contains small quantities of heavy hydrocarbons (0.5 gal. of kerosene per MM SCF of gas) and sulphur compounds (0.6 grains/100 SCF) which must be removed before entering the primary reformer. This is done by passing the gas down-flow over two catalyst beds located in the same vessel. The top bed consists of type BPL activated charcoal for the hydrocarbon removal and the lower desulphurizing bed contains CCI-type C-8-4 activated carbon promoted with metallic oxides.

The quantity and type of these materials is given below:

Service	Type	Density		Quantity	
Hydrocarbon Removal	PCC-Type BPL	4x10 mesh 6x16 mesh	30#/cu.ft.	200 cu. ft.	
Desulfurizer	CCI-C-8-4 CCI-C-8-4	4 - 10 mesh 12 - 30 mesh	40#/cu.ft.	600 cu. ft.	



Two vessels have been supplied, each with the capacity to remove the entrained hydrocarbons and sulphur compounds for about seven days at the design feed gas rate.

## (1) Desulphurizer Absorbent

The gas if fed to the reactors from offsites at 60° to 105°F. As the gas passes through the top bed, all the entrained hydrocarbons are absorbed by the charcoal. The feed gas then continues on to the lower or desulphurizing bed.

The service life of the activated carbon may be from three to five years in "clean" service. However, higher sulfur than the amounts anticipated in the feed will shorten the ultimate service life. Some other materials detrimental to long activated carbon life are:

- (1) Gum forming substances such as dienes and oxides of nitrogen.
- (2) Amine solutions.
- (3) Dust and compressor lube oils.
- (4) Admission of air during regeneration.
- (5) Benzene or other aromatic compounds.
- (6) Introduction of alkaline constituents which convert organic sulfur compounds to un-regenerable sulfate, or elemental sulfur.

Indications are that the rate of absorption of the sulfur compound from the feed gas is very rapid so a wide range of gas flow is possible. The loading (or saturation) of the carbon with contaminant proceeds through the bed (from top to bottom) in the form of a wave. The contaminate gradient at the wave front is rather sharp; with the carbon directly up stream being fairly well saturated with sulfur compounds, while that downstream is little affected until the wave front moves down. The sulfur that remains in the reactor effluent after absorption is normally nil; however, the increase in the sulfur content in the effluent is quite rapid when sulfur "break-through" once starts. Although the normal run cycle is expected to be about seven stream days; the run cycle should be terminated before a break-through actually starts. The maximum allowable sulfur level at the reactor sample point is 0.5 ppm total sulfur. This maximum allowable sulfur at the sample point should always terminate a run-cycle (regardless of time) to insure a sulfur free feed gas.



sulfide (H2S). If the H2S level in the feed gas exceeds about 0.74 grains/100 SCF (or 20 grains/100 SCF for a total of eight hours) during any run, early "break-through" will result. This will in turn shorten time available for regeneration and will result in problems in trying to keep a "fresh" reactor on stream for desulfurization.

A detailed catalyst loading procedure is located in Section V of this manual.

# (2) Desulfurizer Operation

The desulfurizer reactor normally "floats" on the feed gas compressor (102-J) suction at feed gas line pressure. The feed gas line pressure is expected to be about 182 psig (minimum) with a normal temperature range of 60-105°F.

The feed gas compressor is on FRRCa control of the feed gas rate to the primary reformer. This in turn establishes the rate of flow through the "on-stream" desulfurizer that is floating on the feed gas compressor suction.

Normally the temperature and pressure of the on-stream reactor are not considered as operating variables. However, under certain conditions (such as high feed gas line pressure at excessively low temperature) it may be advisable to slightly restrict the feed gas inlet valve to the desulfurizer in operation. This will reduce the operating pressure on the desulfurizer to help insure that temperatures within the reactor are above the "dew point" of the feed gas. Caution: Never allow the desulfurizer pressure to drop below design as the capacity of the feed gas compressor will be affected to limit flow, especially at design rates.

When samples taken at the on-stream desulfurizer indicate that sulfur at the sample point is about 0.5 ppm (maximum); place the fresh stand-by desulfurizer in parallel flow, then take the spent desulfurizer out of service for regeneration. This will insure an un-interrupted flow of sulfur free feed gas to the primary reformer. The regeneration of the desulfurizer procedure is in Section IV, subsection "B".

#### b. Feed Gas Compression

In order to introduce the desulphurized feed gas to the next process step (Primary Reforming) the feed gas has to be compressed to about 520 psig. This is done with meter driven reciprocating compressors (102-Ja & Jb). The process flow is controlled by FRRC-101 located in the discharge line from the machine. Pressure on the discharge is controlled by PRC-102, from upstream of FRRC-101 and, releasing back to the suction.



The operation and control of this compressor will be discussed in

detail under subsection "C. SPECIAL EQUIPMENT", located in Section II of this manual.

# c. Primary Reforming

After the sulfur compounds have been removed; it is desired to reform the feed gas under conditions that will produce hydrogen (H2) in an economical manner. This is done by contacting the feed gas on nickel catalyst in a steam atmosphere at elevated temperature and pressures to promote (and favor) to desirable reactions. The reaction is endothermic and requires constant heat in-put from the primary furnace to maintain the desired temperature level for proper primary reforming.

The following discussion on reforming conditions should be thoroughly understood for the successful operation of the plant. Improper, or maloperation at the front end of the unit can be (and is) reflected throughout the plant.

## (1) Reforming Reactions

The catalysts promote two simultaneous equilibrium reactions in the primary and secondary reformers. These reactions are the steammethane reaction,

and the carbon monoxide shift reaction:

It would be preferable if these reactions went to completion to give an overall reaction:

$$CH_4 + 2H_2O \longleftrightarrow CO_2 + 4H_2$$

but this is not the case and considerable CO occurs in the secondary reformer effluent. Most of this unshifted CO is oxidized to CO2 in the shift converter thus increasing hydrogen yield.

#### (2) Reforming Conditions

Temperature - The overall effect of increasing reforming temperature on the effluent gas composition is to reduce the methane and carbon dioxide content, and increase carbon monoxide and hydrogen content. On decreasing reforming temperatures, the effects are reversed.



Pressure - The pressure of the system is so nearly fixed that reforming pressure should be considered invariable. However, increasing pressure has an effect similar to reducing temperatures and reformer designs always represent a compromise in economics.

Steam Rate - Beyond the vital consideration of sufficient steam to prevent cooling the catalyst, increasing steam-to- carbon ratio will shift both above equilibrium reactions to the right with a net effect of decreased methane and carbon monoxide and increased carbon dioxide and hydrogen in the reformed gas. At the same time, however, utilities consumption will increase. For other than minor deviations, the unit operation is usually most economical at conditions closely approaching design steam-to-carbon ratio of 3.5:1.0.

Whenever there is any doubt about the true steam-to-carbon ratio entering the furnace, the steam rate should be verified with a wet test meter to determine the true conditions. Too much steam could contribute to condensation at the inlet to the LT shift. It is of prime importance that the steam-to-gas ratio to the primary reformer is maintained at a value to insure a steam-to-carbon ratio of 3.5:1.0 at all times.

Should an operating or mechanical accident cause minor coke deposition on the reforming 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, it may be necessary to oxidize the catalyst with steam, or steam and air, and shut down the unit for replacement of the catalyst.

## (3) Primary Reformer Catalyst

The primary reformer tubes are packed with a nickel catalyst, CCI type C-11-25, in the form of 5/8 x 3/8 inch cylinders with a 1/4 inch hole through the center. The tubes in the primary reformer are uniformly loaded to assure equal pressure drops that will result in equal flow distribution through each of the eighty-four tubes in the furnace. If a tube has abnormal pressure differential, overheating or insufficient reforming may occur, thus giving improper operation. A total of 120 cu. ft. of catalyst is contained in the reformer tubes. The catalyst is 5/8" x 3/8" x 1/4" rings with a density of 54 #/cu. ft.

Any sulfur compounds that break through the desulfurizer to enter the primary reformer will reduce catalyst activity; however, this poisoning is temporary and activity may be recovered by stripping the catalyst with sulfur-free gas. The catalyst itself may contain traces of sulfur as it is delivered from the manufacturer, but this sulfur is removed during early phases of the unit start-up.



Section I

might occur.

The catalyst is shipped in the oxidized state. It is pre-shrunk at temperatures higher than those usually encountered in operation and shrinkage in service should be negligible. Wetting of new catalyst does not damage it; however, if water or wet steam should suddenly cool hot catalyst, breakage

A detailed catalyst loading procedure is located in Section V of this manual.

Note: Reforming catalyst that have been activated are placed in operational use in the reduced state and must not be exposed to oxidizing atmospheres at elevated temperatures except under carefully controlled conditions. During the shutdown of the reforming equipment the catalyst should be kept under a steam atmosphere until the temperature of the catalyst has been reduced to  $450^{\circ}$ F 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. This operation is described under subsection "B. Special Procedures" located in Section IV, of this manual.

## (4) Furnace Operation

In order to obtain the tube outlet temperature required (about 1560°F) for the primary reforming, a furnace radiant section temperature of about 1700°F will probably be necessary. The firing must be carefully regulated to avoid "cold" banks of tubes and/or local overheating.

The hot flue gases pass downward through the radiant section box and enter ducts at the floor level. These ducts form the transition between the radiant and convection sections of the furnace and serve to keep the hot flue gases in efficient contact with the catalyst tubes, eliminating stagnant areas in the radiant section.

The draft necessary to cause the flue gases to flow is inducted by the furnace stack fan located in the base of the stack. The flue gases enter the convection section of the furnace at a temperature of about 1700°F and give up heat, successively, to these coils:

- (1) The mixed feed preheater
- (2) The process air (and steam) preheater
- (3) The steam superheater
- (4) The four steam production coils
- (5) The process gas preheater
- (6) The fuel gas preheater

The cooled flue gases leave the convection section at a temperature of about 500°F and are discharged through the stack to atmosphere by the induced draft fan. The draft fan is regulated by manual adjustment of the



damper, to maintain 0.2 or 0.3 inches (water) draft within the firebox.

An alarm (MA-101) is on the induced fan motor. Failure of power to the motor will de-energize a solenoid valve (VS-105); which opens a valve to admit full steam flow to an aspirating jet ring in the furnace stack, to induce a draft. This jet and alarm arrangement is provided to insure adequate draft in the furnace in case of mechanical failure of the stack fan.

The furnace has been designed to operate with excess air of about 20%. A run-around chart for the determination of excess air has been included in Section V of this manual. This chart may be used in conjunction with occasional flue gas analyses as a check on firing efficiency.

Observations of catalyst-tube skin temperatures should be made on a regular schedule using an optical pyrometer. Hot or brightly-colored spots sometimes indicate voids in the catalyst column, or carbon deposits on the catalyst. The gas burners must be operated to avoid flame impingement on the tubes, as such mal-operation could result in early tube failure. A little experience and experimentation will indicate the optimum draft and air register adjustment to provide stable flame patterns and good heat distribution through out the height of the fire box.

# d. Secondary Reforming

The partially reformed gas from the primary reformer enters the secondary reformer (102-B) inlet chamber tangentially via a water jacketed transfer line. The temperature at the reactor inlet will be about 1560°F.

The flow of the is downward around a centrally located air-inlet pipe and passes through a fixed director. Preheated process air (and steam, ter the combustion zone of the reactor. Preheated process air (and steam, ter the combustion zone of the through a nozzle located just below the diffuser ring. This has the effect flow intimately mixing the swirling process stream and air for rapid combustion and distributing the heat (about 2200°F in the combustion zone) over the entire surface of the catalyst bed.

At reduced capacites the pressure drop across the nozzle orifices of the secondary reformer burner-mixer is considerably lower than normal design and as a result mixing of air and reformer effluent may be impaired. To avoid exposing the nozzle to extremely high temperature it will be necessary to inject larger quantities of steam into the secondary reformer air inlet circuits to maintain the gas velocity and pressure drop at a level consistent with good performance.

To minimize the problem of obtaining the desired velocity at the burner, when running at reduced air rates, without making lengthy calculations, a chart



for determining the steam flow has been included in Section V of this majual.

For this unit, the steam flow normally (at 100% capacity) is 1,200 #/hr. This figure should be used for calculating the necessary flow after obtaining the multiplication factor from the chart.

From the combustion zone of the secondary reformer the flow passes through a bed of nickel catalyst to complete the reforming reaction.

## (1) Secondary Reformer Catalyst

The catalyst bed consists of 256 cubic feet of CCI type C-11-4 and C-11-2 nickel catalyst and the effect of change is the same as noted for the primary reformer. The catalyst is supported on two layers of alumina balls. The lower layer of alumina balls are two inches in diameter and the upper layer is one inch in diameter. The alumina balls are supported by an arched brick dome located over the disengaging section of the secondary reformer. The lower portion of the catalyst bed contains 206 cubic feet of the C-11-4 catalyst which is 1" x 0.6" raschig ring type with a density of 54 #/cu. ft. The upper portion of the bed contains the C-11-2 catalyst which is 3/4" x 3/4" in size.

A detailed catalyst loading procedure is located in Section V of this manual.

## (2) Secondary Reforming Operation

Maximum efficiency of the overall reforming operation requires that as much reforming as possible be done in this partial-combustion step. Utilization of combustion energy reduces the fuel gas requirement in the reforming furnace. However, the amount of air charged to the secondary reformer is set by the nitrogen requirements, and the degree of overall reforming will be regulated by variation of primary reformer temperatures.

Close control will be required on the ratio of hydrogen to nitrogen. If it gets very much out of line, difficulties will be encountered at the ammonia converter as will be discussed under the Converter heading below. Gas analyzers are provided to keep a running check on the synthesis gas to the synthesis gas compressor, and on the gas being circulated through the synthesis loop. These instruments are normally a major reference for operation of the primary and secondary reformers.

Whenever the secondary air flow is altered, temperatures in the secondary reformer should be watched and compensating changes made as necessary. Increasing the air flow will raise the temperature and either a decreased firing rate in the primary reformer furnace or the addition of



steam to the inlet of the secondary reformer should be used to compensate as conditions dictate. When conditions are at an optimum and a change in feed gas flow is necessary, a proportional change (in the same direction) of the air rate will be required to maintain the  $H_2/N_2$  balance of 3.0:1.0.

A water jacket envelops the Secondary Reformer, in order to keep the metal temperatures low if heat leak develops. Water for the jacket is supplied from the boiler feed water pump and is regulated by manual adjustment of a valve controlling the supply of condensate to the jacket inlet. An emergency jacket water connection is provided to supply water from the cooling water system when condensate is not available. This is manually controlled by a valve at grade and should never be used except in an emergency. Excessive use of "cooling water" can quickly lead to corrosion (or fouling) problems in the jacket cooling system.

## (3) Waste Heat Boiler 101-C

Raw synthesis gas with process steam at about 1805°F passes from the bottom of the secondary reformer and passes through the tubes of the waste heat boiler (101-C). The process flow is cooled to about 750°F leaving the 101-C and enters the H. T. section of the shift converter (102-D). The overall temperatures drop across the waste heat boiler (101-C) (1805° to 750°F), is reflected as heat in-put to the boiler feed water that is thermo-circulating on the shell side of the exchanger. This waste heat exchanger (boiler) is a major source of the steam required by the process and equipment operation.

The 101-C waste heat exchanger is equipped with TRC control (TRCa-101) located in a "hot line" by-pass for flexibility of temperature control at the inlet to the H. T. section of the shift converter.

# e. Shift Converter 102-D (High and Low Temperature)

The shift converter is constructed as a single vessel having two separate sections. The upper section (hereafter referred to as the high temperature of H. T. section) consists of two beds of high temperature shift catalyst, each catalyst bed is supported by a screen-covered grating. The beds contain about 300 cubic feet of CCI type C-12-1 iron oxide catalyst,  $1/4 \times 1/4$ " with a density of 30-40 #/cu. ft.

The lower section of the shift converter (hereafter referred to as the low temperature or L. T. section) contains two dissimilar catalysts. The top bed of this section is composed of zinc oxide (ZnO) catalyst to absorb any trace amounts of H2S that might break through from the H. T. section. The lower bed in this section of the shift converter contains the low temperature shift catalyst. Each of the above beds in this section contain about 100 and 300 cubic feet of catalyst respectively. The top bed is CCI type C-7-1, zinc oxide and the lower bed contains CCI type C-18-1

CO-precipitated metal oxides. The C-7-1 catalyst is 1/4" x 1/4" tabular with a density of 30-40 #/cu. ft. The C-18-1 catalyst is 1/4" x 1/8" tabular with about the same density.

The first bed in the H.T. section is made shallow in order to minimize the catalyst replacement costs in the event that it is necessary to renove the top bed because of plugging, catalyst deterioration, or catalyst damage due to mal-operation. Provision is made for steaming below each shift catalyst bed to enable exclusion of air, and for maintenance of temperature during a shut-down.

## (1) High Temperature Shift Converter Operation

The gas-steam process flow enters the H. T. section of the shift converter at about 750°F to enter the catalyst beds where a large percentage of the CO content will be oxidized in accordance with the following reaction:

This reaction is a reversible one, with "shifting" of the carbon monoxide (CO) favored by low temperature. However, the rate of reaction is favored by high temperature. To attain a specified CO conversion, the principal operating variables are temperature and steam-to-gas ratio. It is customary to maintain the operating temperature at design level (750°F) or lower. With new catalyst, it may be possible to obtain satisfactory conversion at a temperature inlet of 650 to 675°F to the H.T. section.

The steam-to-gas ratio is usually maintained constant. However, in the event that L. T. shift converter is by-passes, and acceptable conversion has to be accomplished in the H. T. section of the converter; it will be necessary to reduce the feed gas rate to bring the steam-to-carbon ratio to the primary reformer to 7.0:1.0.

Temperature -- If the reaction is near equilibrium, a decrease in temperature will likely improve conversion, and if it is not near equilibrium a temperature decrease will reduce the shifting reaction. Conversely, if the reaction is near equilibrium, an increase in temperature will result in a loss of conversion.

The temperature conditions selected for the shift converter are based on a higher temperature for the H. T. section to take advantage of the higher reaction rate for the high CO content of the inlet gas; and comparatively lower temperature for the L. T. section, to take advantage of favorable equilibrium conditions for the lower CO concentrations in this section of the converter.

Note: The shift catalyst is highly porous and should never be heated to temperatures above 1050°F, as activity for low temperature con-



version may be impaired. In addition, the design temperature for the H. T. and L. T. shift converters is 850 and 490°F respectively. The design temperatures of the converters should never be exceeded.

Steam -- Increasing the steam flow results in an increase of CO shifting if conversion is already near equilibrium, and a loss if not near equilibrium. It is important that at least 20% steam to present in the gas passing over the catalyst when at a temperature above 250°F, otherwise, dehydration or change in the structure of the catalyst (with a loss of physical strength) may occur. Normal steam flows to the reforming section usually insure this minimum steam flow to the shift converters, so should not pose a problem.

## (2) Low Temperature Shift Converter Operation

As previously noted, the L. T. shift converter contains a top bed of zinc oxide (ZnO). This zinc oxide bed is provided to remove the sulfur that may evolve from the H. T. shift catalyst as hydrogen sulfide (H<sub>2</sub>S). This H<sub>2</sub>S sulfur would have a deleterious effect on the L. T. shift catalyst. Most of the H<sub>2</sub>S from the H. T. converter will be evolved during the first week of operation. Indeed, the bulk of the H<sub>2</sub>S is evolved during the first four to six hours at operating temperature. Therefore, the start-up procedure proposed in Section III of this manual recommends venting the H. T. shift effluent from two to three days, or until the sulfur content is less than 1 ppm before going to the L. T. shift converter. This will insure a "clean" bed of zinc oxide to act as a "guard" for the L. T. shift catalyst in the event of a sulfur break-through from the feed gas desulfurizers during subsequent operations.

The L.T. shift converter will normally be operated with an inlet temperature of 460°F. However, lower temperature is permissible and desirable for initial operation, but care must be taken not to operate too close to the dew point of the steam/gas mixture. For this reason 400°F is the lowest recommended inlet temperature. Operating temperatures will be raised as the catalyst ages to sustain reaction, and to hold the CO level down. The maximum temperature to which the L.T. shift catalyst should be exposed is 550°F.

The CO conversion in the L. T. shift converter responds in the same direction as the H. T. converter to changes in temperature and steam-to-gas ratio. However, (as previously noted) the L. T. converter is run at a lower temperature level. This will insure an effluent that is low in CO content and reduce the load on the methanator.

The temperature at the inlet of the L. T shift converter is controlled by TRCa-102 located in the hot line by-pass around the primary shift

effluent waste heat boiler (103-C). This waste heat boiler reduces the temperature to about 630°F in giving up heat to the waste heat boiler (103-C) to generate 500 psig steam. The temperature is finally cooled to the desired 460°F in giving up heat to the methanator feed in 104-C.

A panel-mounted push button operates valves to enable rapid by-passing of the L.T. shift converter in the event of conditions that may lead to excessive operating temperatures. The use of this emergency by-passing of the L.T. shift converter will require immediate reduction of feed gas (to about 50%) and firing rate to the primary reformer, this insures that the CO conversion will be brought to a satisfactory level in the H.T. shift converter. Caution: Do not fail to make a corresponding reduction in the combustion air rate to the secondary reformer. If the reduction in feed rate is not made immediately after by-passing the L.T. shift converter; a high level of carbon monoxide (CO) will break through to the methanator, resulting in excessive temperatures in this reactor.

A detailed catalyst loading procedure for both the H.T. and L.T. shift converters is located in Section V of this manual.

## (3) Shift Converter Catalyst Precautions

Start-up with the new, unreduced catalyst will follow the procedure outlined in Section III of this manual, using hot air for heating the catalyst initially to 225°F to minimize the formation of condensate, then continuing the heating with steam to normal operating temperature.

For subsequent start-ups, under no circumstances will air be used for preheating, unless an entirely new charge of catalyst has been installed. After shift catalysts have been exposed to reducing gases (i.e., hydrogen, carbon monoxide) they are 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 catalyst and/or vessel damage. The oxidation procedure for both H. T. and L. T. shift converters will be found in Section IV - B of the manual.

# (4) Waste Heat Recovery From H. T. and L. T. Shift Converters (103, 104, and 105-C's)

Effluent from the H. T. shift converter at about 850°F is directed through the tube side of the waste heat boiler 103-C where heat is given up to the 500 # steam system. A temperature-controlled bypass (on the process gas side) allows regulation of the quantity of heat given up to the boiler system in order to provide a constant inlet temperature to the L. T. section of the shift converter.



methanator feed preheater 104-C and provides the necessary preheat for the methanator feed stream. Note that the sensing point for the 103-C bypass controller is located after 104-C, in order to provide accurate control of the inlet temperature of the L. T. shift section, 104-C is designed to withstand the "flow through the shell side only" condition that occurs during startup.

The effluent gas from the L.T. section of the shift converter will be quenched to the dewpoint of the gas/steam mixture at the pressure existing (about 344°F at design conditions) before the effluent stream enters the CO2 stripper reboilers. Excessively high temperatures cause degradation of the MEA solution flowing through the reboilers and thus are to be avoided.

## 2. Synthesis Feed Gas Purification System

## a. Carbon Dioxide (CO2) Removal

The cooled raw synthesis gas, containing about 18.0% CO<sub>2</sub>, is fed to the bottom of the CO<sub>2</sub> absorber. The carbon dioxide contained in the gas stream is removed by absorption in aqueous monoethanolamine (MEA) solution at relatively high pressure and low temperature. The carbon dioxide so absorbed is subsequently stripped from the MEA solution at higher temperature and lower pressure.

MEA solution is basic (alkaline) and will rapidly react with the hydrogen ion in acidic solution (such as CO2 in water). Hence, the presence of MEA is very effective in promoting solution of CO2 in water in the absorber, by moving the following reaction to the right.

The CO2 may then be removed by bringing the charged (rich) solution to a boil in the stripper. The release of the gas is accelerated and made more complete by the steam-stripping action in the stripper system (at low pressure). The stripped (lean) solution is thus reactivated, ready for another pass through the absorber. Below are discussions of the factors influencing efficiency and control of the CO2 removal system.

#### (1) MEA Absorbent Characteristics

In the initial phase of CO2 absorption (at the MEA inlet to the top of the absorber) the solution must be lean enough to reduce the CO2 content of the purified gas stream to the desired level. The CO2 content in the lean solution will retard CO2 absorption; in addition, the corrosive tendency of the solution is increased by the presence of excess carbon dioxide. Normally, poor solution regeneration is responsible for the presence of excess CO2 in



the lean solution, and the more probable causes of poor regeneration are insufficient CO2 stripper reboiler heat, or solution contamination. The most desirable regeneration situation is to furnish adequate stripping vapor to the stripper tower so that essentially all of the CO2 is removed from the solution before it drops into the reboiler. Low carbon dioxide concentration in the reboiler will give a low reboiler corrosion rate. The residual CO2 in the lean solution is expected to be less than 1.5 cu. ft. per gallon.

Ampel absorbent must be circulated to remove a given quantity of CO2 without approaching saturation of the solution. High CO2 concentrations make the rich solution more corrosive. This condition is aggravated as the rich solution proceeds through heat exchanger to higher temperature, with pressure reduction at the same time. It is for this reason that the absorber level control throttle valve is located down-stream of the MEA exchanger. It is anticipated that the CO2 loading will be 5.0 to 6.0 scf per gallon of rich 20 wt. % MEA solution.

Concentration of MEA in the lean solution may be varied to suit unit requirements; the range is usually 20 to 22%. However, the lower the solution strength, the greater must be the circulation rate to accomplish equal purification of the process gas stream.

Assuming a constant circulation rate, a constant gas rate to the absorber and a constant level (differential) in the absorber, the level in the stripper bottom should be almost a constant, except for water loss overhead with the CO2. Most of this water is condensed and returned as reflux, entering the stripper on the top tray with the rich MEA. However, there is a slow but constant loss of water to the CO2 stream leaving 103-F reflux drum. This water loss is made up by addition of process condensate under level control (LRCa-105).

## (2) MEA CO<sub>2</sub> Absorber Operation

Changes in process gas rate, especially increases, require proportional changes in absorbent rate and perhaps cooling water rate on the lean MEA cooler (108-Cb). When an increase in process gas rate is anticipated, it is wise to increase circulation rate a small amount, prior to each small gas rate change. During and following changes in flow rates, the purified gas from the absorber should be watched carefully to avoid low-grade purification. Considerable time may elapse before conditions reach a firm equilibrium again.

In general, absorption is favored by low temperatures and high pressure. These factors are subject to very little variation because of the limitations of design and equipment. At reduced rates there may be a little flexibility in temperature control. However, for consistency, the absorber



MEA inlet temperature should be kept fairly close to the design  $110^{\circ}$ F. Previous experience seems to indicate little increase in absorption efficiency at temperatures below  $110^{\circ}$ F, and no great change in absorptive capacity at high temperatures up to as much as  $130^{\circ}$ F.

Another factor influencing the efficiency of absorption is the contact time of the process gas with the MEA. To increase the contact time, the absorber is designed for partially flooded operation. The level control of the absorber is not of the displacement type but uses a differential pressure cell and actually measures, and will maintain, a given differential across the whole absorber. Increasing the set differential pressure (at a constant gas rate) increases the hold-up of MEA in the absorber, and thus the contact time with the gas. This usually gives improvement in absorption. However, if the differential pressure is increased by an increase in gas rate, the level controller will compensate to return the differential to the original value, and the net result will be a reduction in absorber MEA hold-up and a higher stripper level. In normal practice the MEA hold-up (the setting of LRC-101) will be just a little more than the minimum required to give satisfactory CO2 absorption.

If it is desired to circulate the absorbent when there is a major change, or no gas flow through the absorber tower, it is usually necessary to regulate the level controller manually to maintain a level in the stripper gauge glass, returning the control to automatic after the normal gas flow is re-established.

The maximum liquid level to be carried in the stripper is one foot below the reboiler return. However, a normal mid-glass level should ordinarily be maintained; volume above the mid-glass level acts as a surge capacity to avoid submerging the reboiler return line in the event of a drop in the CO2 absorber level, while continued operation at an abnormally low stripper level may accelerate wear on the MEA circulating pumps.

## (3) MEA Absorbent Contamination

Various undesirable contaminants tend to accumulate in the working MEA solution; these must be removed as they tend to cause foaming, corrosion, or loss of absorptive capacity. The contaminants are generally in the form of suspended solids, non-volatile acids, heat-stable salts and high-boiling MEA delradation products.

Two equipment systems are included in the MEA circuit expressly to remove contaminants. The first of these systems is a slip-stream filter arrangement taken off the rich MEA that is leaving the CO2 absorber tower. This system is a Nugent bag-type pressure filter, 101-L, with removable cotton bags. The bags should be removed and replaced after the pressure drop across the filter approaches 18 psig. The system removes finely divided solids, iron,



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organic impurities all of which would contribute to foaming and corrosion problems.

This slip-stream filter arrangement re-enters the system in the CO2 absorber bottoms circuit to the CO2 stripper tower. The flow is controlled manually.

The second solution-cleaning system is the MEA vaporizer, 113-C, an adjunct of the stripper tower. This item is a sidestream redistillation apparatus and is usually operating in a continuous manner. Generally speaking, most of the contaminants found in used MEA solution are either high-boiling or non-volatile. Proper use of the vaporizer will remove almost all of the fouling materials. These may include very fine suspended solids, inorganic salts and high-boiling amine conversion products.

A sidestream of lean absorbent is taken by gravity flow on vaporizer level control, so that its tubes are kept submerged. The vaporizer uses 160 psig steam. The steam rate will be controlled manually. Given constant stripper conditions, which is normally the case, a constant steam rate will induce a constant flow of MEA to the vaporizer. The level control will maintain a constant level in the vaporizer as the MEA is boiled off. When first put into operation, the temperature of the vapors leaving the vaporizer will be about the same as those leaving the stripper reboiler. However, as high-boiling contaminants accumulate in the vaporizer, the exit vapor temperature will tend to rise. When the vaporizer outlet temperature reaches about 290°F, the accumulated contaminants are ready for removal. Operating the vaporizer above 300°F vapor temperature is not recommended, as such temperatures can cause redistillation of contaminants, thus returning them to the circulating MEA solution.

The length of each vaporizer operating cycle depends on the condition of the MEA solution and on the steam rate. When the absorbent is in good condition, build-up of contaminants will be slow. If the steam rate is low, the MEA rate through the vaporizer will be slow and the accumulation of contaminants will be slow. Chemical analyses of the lean circulating solution and its behavior (i.e., absorptivity, and foaming tendencies) will ultimately establish the operating requirements for the vaporizer.

A caustic injection line to the vaporizer is provided to neutralize acids and release MEA inactivated as monoethanolammonium oxalate and formate. When about ready to isolate and dump the vaporizer, shut off the MEA inlet, add 5 or 10 gallons of 10% caustic solution to the vaporizer and boil until the vapor outlet temperature stabilizes, but do not exceed the 290°F vapor outlet limit. The steam may then be shut off, the vaporizer isolated and drained, then filled, flushed and drained, using a mildly alkaline water. A gallon or two of 10% caustic solution should be put in the vaporizer after the flushing. Lean absorbent may be fed again if another

cycle is to be started. It is recommended that the alkali used be a low-salt caustic to reduce the possibility of chloride attack on the vaporizer internals.

Proper use of the above contaminant removal facilities should prevent foaming difficulties. However, if foam appears it may be helpful to use an antifoam agent to minimize MEA losses and permit continuation of operations while measures are taken to eliminate the contaminants. The most commonly used anti-foam agents are long-chain aliphatic alcohols, silicones and phosphate esters. Experimentation may be necessary to determine the best agent, as a product that works well for one plant may be ineffective in another.

A recently devised test for corrosive quality of MEA solutions is as follows:

- (1) Make a 10 wt. % copper sulphate solution.
- (2) Add a standard amount of solution (experience will dictate quantity) to an 8 oz. sample of MEA solution.
- (3) If the MEA is:
  non-corrosive, it turns dark navy blue,
  slightly corrosive, (oxalic acid), it turns light green,
  very corrosive (glycine & high M. W. compounds), it
  turns grass green.

There are a number of corrosion inhibiting additives which may be used to supplement the clean-up equipment provided.

#### b. Methanation

Process gas, containing only 100 ppm of CO2 and about 0.6 mol % CO flows from the top of the absorber through the absorber overhead knockout drum (122-F) where any entrained moisture will be removed in passage through the de-misting pad contained there-in. The gas then flows, in normal operation, to the methanator 103-D via the methanator feed heaters 106 and 104-C and is preheated to 600°F. The gas temperature is regulated by by-passing cold gas around 104-C, under control of TRCa-103.

The aforementioned de-misting section is provided an an additional protection for the catalyst in the methanator. The hot methanator catalyst would be damaged if contacted with liquid. Therefore, the methanator feed gas should occasionally be checked to ascertain that liquid carry-over is not excessive. Should the prospect of liquid carry-over develop, steps should be taken to vent the methanator feed gases and to close the methanator inlet valve. This can be done by use of the emergency push-button provided. Excessive carry-over may be the result of attempting to hold an excessive differential across the absorber or to an excessive circulation rate of MEA.



valve pressure differential. The methanator design metal temperature is 850°F. This temperature must not be exceeded under any circumstances.

The methanator contains 130 cubic feet of CCI type C-13-3 nickel oxide base catalyst, tabular " $1/4 \times 1/4$ " in size with a density of 58 #/cu. ft.

Loading procedures are discussed in Section V of this manual. Once the catalyst has been placed in operation or reduced it should not be exposed to air or to oxidizing atmospheres. In a plant shutdown where methanator entry is not anticipated, it should always be blocked in under an atmosphere of hydrogen or nitrogen. For removal of catalyst, an oxidation procedure, as described in Section IV should be followed.

Under certain conditions, carbon monoxide and nickel may react to form nickel carbonyl, Ni (CO)4, which is highly toxic, and is a gas at temperatures over 110°F. Whenever men are going to enter or open the methanator, tests should be made to assure that carbonyls are not present.

The most likely time for nickel carbonyl formation is during startup or shut-down, since these procedures involve the temperatures range favorable for carbonyl formation. A few simple precautions will suffice:

Shutting down: The catalyst should never be permitted to cool down to ambient temperature in the presence of CO. When the process gas contains CO, the methanator should be flushed with a CO-free gas before the temperature drops to 200-400°F. At moderate pressure, and when the CO concentration is low, temperature in excess of 250°F will prevent carbonyl formation, while 400°F should be considered the safe limit at high pressure and/or high CO concentration.

Starting up: The pressure on the methanator should be kept as low as practicable when heating up on process gas, until the bed temperatures are above 250°F.

#### 3. Ammonia Production System

## a. Compression of Synthesis Feed Gas and Water Removal

The purified gas is compressed to about 4767 psig pressure in three stages of the synthesis feed gas compressors (103-Ja and Jb). The gas is cooled with inter-coolers and an after-cooler (120-C) before entering the oil trap (105-F). After leaving the oil trap, the stream is chilled by ammonia refrigeration in chiller 121-C. This chiller cools the feed gas to about 25°F and drops out most of the water in the secondary separator 106-F.



The low moisture content synthesis gas leaving the secondary separator is reheated to about 250°F by exchange with the ammonia converter effluent before entering the converter 104-D.

## b. Synthesis (Conversion) of Feed Gas to Ammonia

The synthesis converter (105-D) contains about 190 cubic feed (about 34,200 pounds) of promoted iron catalyst. The catalyst is contained in an internal basket that is so designed to have five separate catalyst beds within the reactor. The top bed is the smallest of the five beds, with each succeeding bed containing a greater volume of catalyst. This tends to limit the exothermic heat of reaction in the upper beds (where reaction is sharpest) so the converter can be kept at the desired temperature level. The use of converter inter-cooler (122-C) by-pass and quench gas flows to the inlets the catalyst beds is the means of controlling the converter temperature once a self-sustaining heat of reaction has been established.

The distribution of the catalyst in the five beds of the converter are as follows:

Bed No.	Bed Volume/cu. ft.		Weight/lbs.		Bed Depth
1	22		3960	e de la companya de l	3'4"
2	28		5040	Acres 100	4'2"
3	34	•	6120	•	5'0''
4	42		7560	5.200	6' 1''
5	64	e jag	11520		9' 1''
TOTAL	190		34, 200	*	

With the converter temperature level at about 900°F and a pressure of about 4700 psig a portion of the synthesis gas (hydrogen/nitrogen) passing through the catalyst will convert to ammonia. The concentration of ammonia in the converter effluent will be about 16% leaving the last bed.

The converter effluent is cooled by heat exchange giving up heat to boiler feed water and the converter feed before returning to the recycle gas compressors (104-Ja & Jb) to be recycled back to the converter. Before the recycle gas (plus fresh feed) re-enters the converter it is chilled to 25°F to condense out the net ammonia make produced on its previous pass through the converter. In operation at expected conditions the ammonia level in the syn. gas loop will be about 16% in the converter effluent, 5.0% after fresh feed and recycle gas have combined, and 2.9% at the converter inlet after condensing out the net ammonia make.

A continuous vent or high pressure purge is used to remove excess



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inerts (mainly methane and argon) from the syn. gas loop. This purge gas flow is chilled to 25°F for recovery of ammonia and then passes to the fuel gas system for disposal. If these inerts were allowed to build to too high a level they would ultimately reduce ammonia production. However, excessive venting is to be avoided as a loss of yield by excessive loss of hydrogen/nitrogen synthesis gas will result.

The following are discussions of factors affecting the operation of the synthesis converter:

## (1) Conditions Influencing the Converter Reaction

The Synthesis Reaction, which is promoted by the catalyst, may be illustrated by the following equation:

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

The equilibrium point for this reaction is such that, at the proposed operating conditions, the ammonia content of the reactor effluent will be about 12 mol per cent. The unconverted gases are recycled back through the reactor to get the ultimate production. It will be noted that one molecule of nitrogen plus three of hydrogen produce two molecules of ammonia (not four).

Temperature: The effect of a change in temperature on the ammonia synthesis reaction is a double one, as it affects both equilibrium percentage and reaction rate. As the synthesis reaction is exothermic, a rise in temperature lowers the equilibrium percentage of ammonia and at the same time accelerates the reaction. This means that under conditions far from equilibrium temperature rise will lead to higher conversion, while on the other hand, for a synthesis system giving a conversion near the equilibrium percentage a rise in temperature will lead to a lower conversion. Efficiency always varies directly with temperature when catalyst deterioration is not taken into account. Conversion efficiency is defined as the ratio of the actual percent NH3 in the converted gas to that theoretically possible under the conditions in question.

Pressure: As the synthesis of ammonia involves a decrease in volume (decrease in the number of molecules), the equilibrium percentage of ammonia will increase with pressure. At the same time the reaction rate is accelerated by increasing the pressure; hence the conversion will improve with higher pressure.

Space Velocity: At higher process gas rates (higher space velocity in the converter) the synthesis reaction has less time to operate and does not produce as high a concentration of ammonia in the converter effluent as is produced when the gas is moving through more slowly. However, the reduction in yield is far less than proportional to the per cent increase in space velocity.



The increased production of ammonia, due to the greater amount of gas put through the reaction zone, more than offsets the tendency toward decreased production due to less complete reaction (less residence time). Therefore, at normal or less than normal throughputs, an increase in gas rate to the converter (other conditions unchanged) will give increased production.

The usual method of changing space velocity is by altering the recycle (circulation) rate. With more circulation (if available) the temperatures will tend to drop in the converter beds, due to less conversion per pass; pressure will tend to drop because of more total production of ammonia.

Hydrogen-to-Nitrogen Ratio: The fresh synthesis gas feed (excluding recycle) to the synthesis section should usually have a hydrogen-to-nitrogen ratio of about 3.0:1.0. This is the case because the combining of hydrogen with nitrogen to form ammonia is in the ratio of 3.0:1.0. However, it should be recognized that the hydrogen to nitrogen ratio within the ammonia converter can be other than 3.0:1.0. It has been found that maximum conversion percentage is obtained at a 2.5 to 3.0:1 ratio of hydrogen-to-nitrogen in the converter. The ratio in the fresh gas feed may be altered slightly from 3.0:1.0 to obtain the optimum H2:N2 ratio in the combined gas feed to the converter.

Inert Gases: A continuous bleed of gas will be maintained from the recycle compressor suction header to the purge gas system. This purge stream is required to control the concentration of methane and other inert gases which would otherwise build up in the synthesis circuit, resulting in lower conversion and reduced production capacity.

Synthesis Gas Rate: Increasing the synthesis feed gas rate, alone produces more ammonia and has these effects upon the conditions discussed above:

- (1) The system pressure will increase.
- (2) The catalyst bed temperature will increase.
- (3) The inert gas content will rise.
- (4) The H2:N2 ratio may change.

Conversely, decreasing the synthesis gas rate will have the reverse effects.

Under normal operating conditions, the synthesis gas rate is determined by production requirements. An increase in gas feed to the synthesis section usually will be obtained by more production of gas from the front end of the plant.

# (2) Control of the Synthesis Reaction

The synthesis system essentially rides on the line from the discharge



of the synthesis gas booster compressor. Gas (H<sub>2</sub> and N<sub>2</sub> mixture 3:1) is consumed as determined by the operating conditions, catalyst activity, and resultant capacity of the synthesis loop. The gas from the compressor keeps replacing the removed or converted gas. If excess synthesis gas is available, the pressure on the converter increases to the limit of the compressor, then raw synthesis gas is vented before the first stage of compression at the 104-F suction drum. If there is insufficient gas, the compressor kick-back opens (PIC-103) to maintain the system pressure.

There are several variables, one or more of which may be changed to alter synthesis loop operation. The more important controlling variables are listed below:

Synthesis gas rate
Circulation rate
Inert purge gas rate
Converter bed temperature level

Converter feed temperature Hydrogen -to-nitrogen ratio Purity of feed gas

It will be noted that system pressure is not listed as a variable which is available for control. The pressure frequently changes as a result of the manipulation of other conditions, but it is rare that a change would be made for the sole purpose of raising the pressure, to the exclusion of all other effects. The system is usually so operated that the pressure remains reasonably well below limits, while minimizing the purge rate and while maintaining converter temperatures low enough to assure long catalyst life. Lower pressures usually indicate good operation, provided feed and purge rates are normal and the converter temperatures are satisfactory.

Following are the factors affecting each of the synthesis loop conditions that the operators watch to detect changes or abnormalities in the process. If these factors are known, it is easier for an operator to explain a change in operating conditions. He can then manipulate one or more variables to make necessary corrections.

Converter Pressure: The main factors which individually or collectively contribute to an increase in the synthesis loop pressure are:

- (1) An increase in the synthesis feed gas rate.
- (2) A decrease in converter temperature level.
- (3) A change in gas composition away from the optimum of 2.5 to 3.0:1.0 ratio of hydrogen-to-nitrogen in the syn. gas loop.
- (4) An increase in the ammonia content of the recycle gas.
- (5) An increase in the inert gas (fixed gas) content of the circulating gas.
- (6) A decrease in recycle gas circulation rate.
- (7) Poisoning of the catalyst due to impure synthesis gas.
- (8) Aging of the catalyst.



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Conversely, a decrease in the pressure is caused by the reverse of the actions above.

Catalyst Temperature Level: The main factors which individually or collectively contribute to an increase in the catalyst temperatures are:

- (1) An increase in the synthesis feed gas rate.
- (2) A decrease in recycle gas circulation rate.
- (3) A closer approach to the optimum 2.5 to 3.0:1 hydrogen-to-nitrogen ratio.
- (4) A decrease in the ammonia content of the circulating recycle gas.
- (5) An increase in converter system pressure.
- (6) A reduction in the cold gas by-pass (quench) rate to the converter.
- (7) A decrease in the inert gas content in the circulating syn. gas.
- (8) An increase in catalyst activity, following a temporary poisoning due to impure synthesis gas.

Conversely, the factors causing a decrease in the catalyst temperatures are the reverse of those mentioned above.

The best temperature for steady operation is the lowest temperature which will give the maximum yield of ammonia product, yet high enough to provide stability in case of pressure surges. Excessive temperatures will age the catalyst and cause rapid reduction in catalyst activity.

Hydrogen-to-Nitrogen Ratio: The main factors which individually or collectively contribute to a change in the H2:N2 ratio of the circulating gas are:

- (1) A change in the composition of the synthesis gas from the reforming and purification systems.
- (2) A change in the synthesis feed gas rate.
- (3) A change in the ammonia content of the circulating recycle gas.
- (4) A change in the inert (fixed) gas content of the circulating gas.

The hydrogen-to-nitrogen composition of recycle gas to the converter is controlled to maintain about 2.5 to 3.0:1 ratio. A rapid change of ratio will cause a rapid temperature change.

Ammonia Content of the Circulating Gas: Factors which individually or collectively contribute to a change in the ammonia content of the gas entering the converter are:

(1) A change in cooling in the converter effluent coolers 122-C, 123-C, 125-C and 126-C.



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- (2) Over loading of chiller 121-C.
- (3) An excessively high level in the primary or secondary separators (107-F or 106-F respectively).

It is anticipated that the ammonia concentration of about 16% in the converter effluent will become 5.0% when the recycle and fresh feed gases are combined. After chilling and separation in 106-F, it is expected that the ammonia concentration in the combined gas stream entering the converter will be about 2.9%.

Inert Gas Content of Circulating Gas: The principal constituents which contribute to the inert content of the circulating gas are argon and methane. These gases tend to build up and raise pressure in the system, thus reducing the effective synthesis gas partial pressure. This is reflected in lower conversion per pass. The inert concentration in the system is controlled by withdrawing a stream of purge gas via 127-C and the purge gas separator 108-F. Design is based on an inert gas (methane and argon) content of about 1.3 mol % in the feed gas. However, it may be found by experience that at higher concentrations overall ammonia production can be increased by conserving hydrogen which would otherwise be removed from the system by excessive purge gas rates from the syn. gas loop.

From the preceding discussion of the ammonia synthesis operation it can be seen that the efficiency is affected by the controllable variables listed at the beginning of this subsection "(2)". All of these factors are interdependent and a change in one will have an effect on the others. Consequently, good operation will be a combination of operating experience and a recognition of the factors affecting the operation of the system. Thus if a drastic change in one of the operating conditions occurs, experience will dictate what steps should be taken to compensate for the change, so that the system will remain in good control. Any changes should be made slowly when possible, so as to avoid major disturbances.

### (3) Converter Catalyst Characteristics

Catalyst Activation: The synthesis catalyst is made from fused iron oxides containing potassium, calcium and aluminum oxides as stabilizers and promoters, and is charged to the ammonia converter in either prereduced or the oxidized state. The catalyst must be activated before production of ammonia will take place. The activation requires reduction of the iron oxide to practically pure elemental iron.

The reduction takes place during a period when hydrogen is passes over the oxidized catalyst at progressively higher pressures and temperatures. The hydrogen combines with the oxygen from the iron oxide and forms water. The water is removed (as much as possible) before the gas is recycled over the catalyst. The amount of water produced during the activation period is

a good indication of the progress of the catalyst reduction. At the start of the reduction period, a small amount of water is formed and as reduction of the catalyst progresses, water formation increases. The reduction of the catalyst is aided by fairly high temperatures and controlled pressures. The water formation will reach a peak and then gradually taper off near the end of the reduction period.

The reduction temperature should always be kept below that at which the catalyst is going to operate, so as to avoid deactivation due to the following: One, high concentrations of water vapor in the circulating gas. Two, excessive heat. However, too low a temperature will cause catalyst reduction to move slowly; if temperatures drop low enough, reduction will stop.

The effect of pressure and/or pressure change during catalyst reduction can be critical. If each catalyst bed is not activated uniformly as reduction moves downward, an increase in pressure may cause channeling. That is, the more reduced catalyst areas will promote the reaction of hydrogen and nitrogen to form ammonia in local sections of the bed. This reaction gives off heat and will cause catalyst bed temperatures to become higher and difficult to control in these localized areas. The pressure during catalyst reduction should be maintained at a point where reduction is symmetrical and temperatures in a horizontal section of the bed do not spread beyond a small range. Increasing the pressure will promote ammonia formation; lowering the pressure will retard ammonia formation.

The catalyst can be reduced at fairly low gas rates; however, the higher the velocities through the catalyst the shorter will be the reduction period, and channeling through the beds may diminish at higher rates.

Synthesis gas is recycled through the converter during catalyst reduction. When the reaction has started, it is very important that the circulating gas be cooled as much as possible (without risking the danger of freezing water in the equipment) to condense and remove the water vapor from the gas before recharging to the converter. Otherwise, gas with a high concentration of water vapor would enter the catalyst beds which are already reduced. Water vapor will cause deterioration or poisoning of the reduced catalyst. As soon as ammonia synthesis has started, the ammonia produced will lower the freezing point and permit water removal from the gas stream at lower temperatures.

Careful control of conditions during catalyst activation will result in uniform reduction which will promote longer catalyst service.

Reduction of the synthesis catalyst will be accomplished during the initial start-up of the plant. The recommended procedure, to be used as a guide, is described in Section III.

Catalyst Thermal Resistance: Even when operated on pure synthesis gas, ammonia catalysts do not retain their activity indefinitely. Some data indicate that when purge gas is being used, temperatures below 1022°F do not affect the catalyst, whereas higher temperatures will harm the catalyst. These data also show that catalyst which has suffered slightly from excessive temperatures may show a loss of activity when tried out at 75. °F, whereas the activity at 932°F may be unchanged. It should, however, be emphasized that no definite temperature limit exists below which the catalyst is unaffected. At a fixed temperature level but under more severe conditions of pressure and space velocity, the deterioration of the catalyst should be expected to develop more rapidly.

Degradation of the catalyst will first be apparent in reduced efficiency during operation at lower temperature, higher pressures and/or higher gas rates. It has been observed that the more the catalyst activity has declined from the initial value, the more prolonged or severe will be the treatment required to produce further injury.

Catalyst Poisons: Compounds which (when present in the synthesis gas) are capable of reducing catalyst activity and/or life, are called poisons. Such substances normally form more or less stable compounds with the active materials of the catalyst. There are permanent poisons which cause lasting irreversible lowering of catalyst activity. They form stable surface compounds with active parts of the catalyst. Other poisons may cause only temporary decrease in activity; the initial effectiveness is restored in a relatively short time after removal of the poison compound from the gas.

The most important group of poisons of ammonia synthesis catalyst are oxygen compounds. These cannot be classified as temporary poisons; neither are they permanent poisons. When an oxygen compound such as carbon monoxide is present in small quantities in the synthesis gas, some active areas of the catalyst combine with oxygen thus reducing catalyst activity. When the oxygen compound is removed from the synthesis gas, the catalyst again is fully reduced, but all the regenerated centers do not revert completely to the initial state or regain their initial activity. So the oxygen compounds cause a strong temporary and a small permanent decline in catalyst activity. The usual oxygen compounds which poison the catalyst are water vapor, carbon monoxide, carbon dioxide, and molecular oxygen. Other significant poisons are hydrogen sulfide (permanent) and oil spray deposits, which are not real poisons as this term is used here, but which are capable of lowering the activity of the catalyst by clogging the surface.

Catalyst Mechanical Strength: The synthesis catalyst is mechanically strong; however, the operator should not expose it to excessive abuse. Maloperation may cause very rapid temperature fluctuations, resulting in catalyst breakage. During the reduction period any fast temperature changes should be carefully avoided; during this interval the catalyst is thought to be



particularly sensitive to mechanical crushing and quick temperature variation.

The synthesis catalyst reduction is carried out during the unit startup after the front end of the unit has been brought up to design (or near design) conditions and rates. A step by step reduction procedure is presented in the start-up section (Section III) of this manual.

A detailed catalyst loading procedure for the synthesis converter is presented under subsection "B. CATALYST LOADING PROCEDURES", located in Section II of this manual.

### c. Separation of Anhydrous Liquid Ammonia from Syn. Gas Loop

The ammonia that is produced in the synthesis reactor would quickly build to a level to interfere with the reaction so has to be continuously removed from the synthesis recycle gas stream going to the converter. This is done by chilling the recycle stream via a series of coolers or chillers to condense the net ammonia product that is produced in each pass through the converter. The temperature of the recycle gas stream is 25°F by the time it reaches the secondary ammonia separator. Condensing and sub-cooling the ammonia in the syn. gas loop to 25°F at the 4700 psig pressure level will reduce the ammonia in the recycle gas stream from 12 to 2%. The resulting chilled ammonia liquid collects in the secondary ammonia separator (106-F) which is under LC control (LC-107). The liquid ammonia leaving the 106-F is the feed to the final product purification step of the process.

#### d. Ammonia Product Purification

The purpose of the refrigerant system in the product purification step is twofold; first, flash and reflash of ammonia at successively lower pressure levels to flash out light ends and concentrate them in the ammonia refrigerant receiver (110-F). From this receiver they are vented to the fuel gas system. Second, as an integral part of the refrigerant system, the process chiller that removes heat from the synthesis gas in the syn. gas loop to sub-cool the recycle gas to 25°F for the satisfactory separation and removal of the net ammonia make from the synthesis loop.

The ammonia refrigeration system is somewhat complex by nature, however, once the system is fully understood its operation is straight forward and should operate very steady. The following are descriptions of various items of equipment in the system; what they do, and how conditions are adjusted to give the desired results.

### (1) Product Flash Drum (109-F)

This flash drum receives its feed from the secondary ammonia



separator (106-F) where the net ammonia make has been separated from the synthesis gas loop. The drum does not have any means to adjust the condition at which it operates except in an indirect manner.

The temperature is fixed at the temperature of the product leaving the secondary ammonia separator (106-F). The pressure is fixed at the pressure level at which the product flash drum (109-F) is being operated. If the pressure on 109-F is being held too low there may be degree of over-flash with resulting loss of ammonia to the fuel gas system.

## (2) First Stage Refrigerant Suction Drum (113-F)

This flash drum is in the system to lower the temperature of the ammonia product to that required for low temperature storage. The pressure on the drum is reduced to about 0.5 psig by the refrigeration compressors (105-Ja & Jb), pressure is controlled by PIC-105 by returning some vapors from the second stage discharge. The temperature in the drum will be about -31°F as a result of the evaporating ammonia at 0.5 psig pressure. The level in 113-F is held constant by letting down to storage via product pump 114-J under LC control (LC-115).

#### (3) Second Stage Refrigerant Suction Drum (112-F)

This flash drum is in the system to supply the refrigeration requirements of 121-C. Product ammonia from 109-F is also flashed into the drum to lower its temperature. The pressure on the drum is reduced to about 21.4 psig by the refrigeration compressors. Pressure is controlled by PIC-106 admitting gas from the 3rd stage of compression in the event the flash gas does not supply the compressor demand. The temperature in the drum will be about 5°F as a result of the evaporating ammonia at 21.4 psig pressure. The level in 112-F is held constant by letting ammonia down to 113-F by LC control (LC-110).

The ammonia circulation through 121-C is thermo-syphon and the heat in-put from the synthesis gas loop to this chiller sets its own ammonia circulation rate.

#### (4) Refrigerant Receiver (110-F)

All ammonia that has been flashed in the system, compressed by 105-J's and sub-cooled to about 100°F in the ammonia condenser 129-C collects in this receiver.

The pressure on this drum is controlled at about 210 psig by PRC-106 which vents light end gases to the fuel gas system for disposal. The vent gas from this drum passes through a vent gas chiller to condense out ammonia and return the liquid to 110-F via a seal loop arrangement.

The level of the receiver is held constant by LC control (LC-112) that lets down excess ammonia to the third stage suction drum.

### (5) Third Stage Refrigerant Suction Drum (111-F)

All ammonia let down from the refrigerant receiver (110-F) is reflashed in this drum. The pressure (and the resulting temperature) of the second stage suction drum (111-F) is not a variable, as it "floats" on the second stage of the ammonia compressors (105-J's). This pressure is expected to be about 80 psig, and the temperature of the evaporating ammonia in the flash drum will be about 52°F.

The level of the receiver is held constant by LC control (LC-lll) that lets down excess ammonia to the second stage suction drum (112-F).

Under-pressure protection is provided by PIC-107 which allows hot vapors from the third stage discharge to enter the drum.

This drum supplies ammonia refrigerant to three chillers: 127-C purge gas chiller, 128-C flash gas chiller and 131-C refrigerant purge gas chiller. All three of these chillers are on hand control.

### (6) Refrigeration Compressors (105-J's)

All the ammonia that has been flashed or reflashed to achieve effective light ends removal, and flashed to maintain the proper temperature required for chilling (heat removal) of the process flow in the syn. gas loop amounts to about 19,000 # per hr. The ammonia refrigeration compressors are used to recover this ammonia and keep it in the system.

The refrigeration compressors (105-J's) operate to serve the system in two ways; First, to maintain the desired pressures in the first, second, and third stage flash drums (113, 112, and 110-F). This will insure proper removal of heat and separation of light ends from the product stream. Second, to elevate the pressure of all flashed ammonia to 210 psig so the ammonia may be condensed and slightly sub-cooled with cooling water in the ammonia condensers 129-C.

The condensing ammonia in 129-C is only sub-cooled 4°F below the normal condensing temperature of ammonia (104°F) at 210 psig. This will insure that pressure control of the compressor discharge is maintained by the release of light ends to fuel gas via PRC-106. Sub-cooling the condensing ammonia below 100°F at 210 psig operating pressure on 110-F will result in excessive light ends in the product stream. On the other hand, sub-cooling too close to 104°F will over-load the purge gas cooler (131-C), which in turn could result in excessive loss of ammonia product with the purge gas stream.



## 4. Boiler Feed Water System

Steam systems operating at a relatively high pressure (and temperature) of 500 psig require feed water of high quality. Operating of the 101-C even for a few hours with contaminated water could possibly result in the failure of this item of equipment. Therefore, it is of the utmost importance that a continuous supply of acceptable feed water be supplied to the unit.

The system provided includes a deaerator and chemical injection facilities to obtain the desired quality of feed water for the steam system.

The water furnished as boiler feed water is expected to be supplied from the Shamrock main condensate system or from the central boiler plant feed water when condensate is not available.

# a. B. F. W. Deaeration (105-L)

Warm boiler feed water from offsites (combined with ammonia plant condensate) flows to the preheating section of the deaerator. Oxygen of the water can be reduced to 0.005 c.c./liter or less are:

Harring one water at the saturation condition; i.e., at boiling temperature for the existing pressure.

Providing deaerator design that secures intimate contact between steam and water.

Continually venting the mixture of gases and steam from the system.

The deaerator design provides the intimate contact of steam and water required. It is a tray type, wherein the combined stream of makeup and condensate is sprayed into the steam compartment. The water is spread out in a thin film as it flows down over the trays in continual contact with the steam and is heated to approximately saturation conditions. A continual surplus of steam is used so that steam and the desorbed gases can be continually vented. This is accomplished by injection of sufficient steam under control of PC-102 which maintains the desired 10 psig operating pressure on the deaerator. The vent rate is set manually, it is sufficient that a moderate plume of steam be maintained from the vent, since the volume of noncondensible gases desorbed in normally minute. The vent valve is drilled so that is may never be closed off completely.

The deaerator water flows down from the deaeration section into the storage section of the unit. The storage section holds water sufficient for about 10 minutes normal operation. A level clarm (LA-133) will warn of a



high or low level.

## b. Chemical Treating of B. F. W.

There will be slight (perhaps immeasureable) oxygen content from even the most efficiently operated deaerator. The presence of oxygen in boiler feed water will cause pitting in the boiler and related equipment. For this reason, sodium sulphite is added to the storage section of the deaerator.

Under proper conditions sulphite will react with dissolved oxygen to form sulphate, thus removing the dissolved oxygen from the system. In order for this reaction to proceed rapidly and completely, it is necessary to maintain an excess sulphite concentration at an elevated temperature. An excess of about 20 ppm is generally maintained in the boiler water.

Sodium sulphite reacts with oxygen according to the following equation:

2 parts sodium sulphite + 1 part oxygen = 2 parts sodium sulphate 2Na<sub>2</sub>SO<sub>3</sub> + O<sub>2</sub> = 2Na<sub>2</sub>SO<sub>4</sub>

Scale, in a steam system, is caused primarily by the presence of calcium and magnesium salts, silica and oil in the boiler feed water.

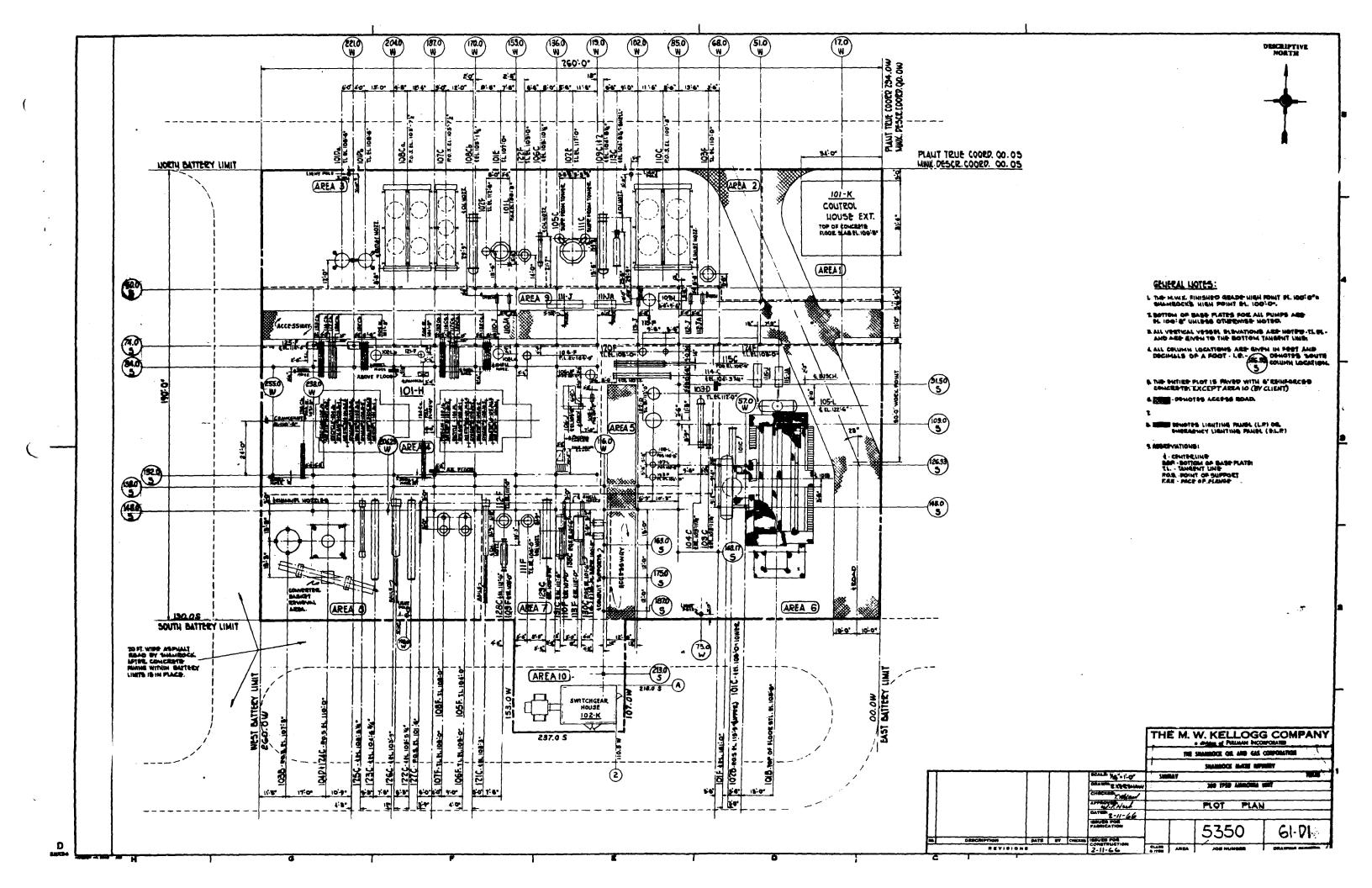
Disodium Phosphate is added to the steam drum to reduce the calcium hardness of the water. Disodium phosphate converts to tri-sodium phosphate, upon coming in contact with water, and as such reacts with calcium to form a flocculent precipitate. In order for this reaction to take place, sufficient alkalinity (over 9.5 Ph) must be present in the boiler water.

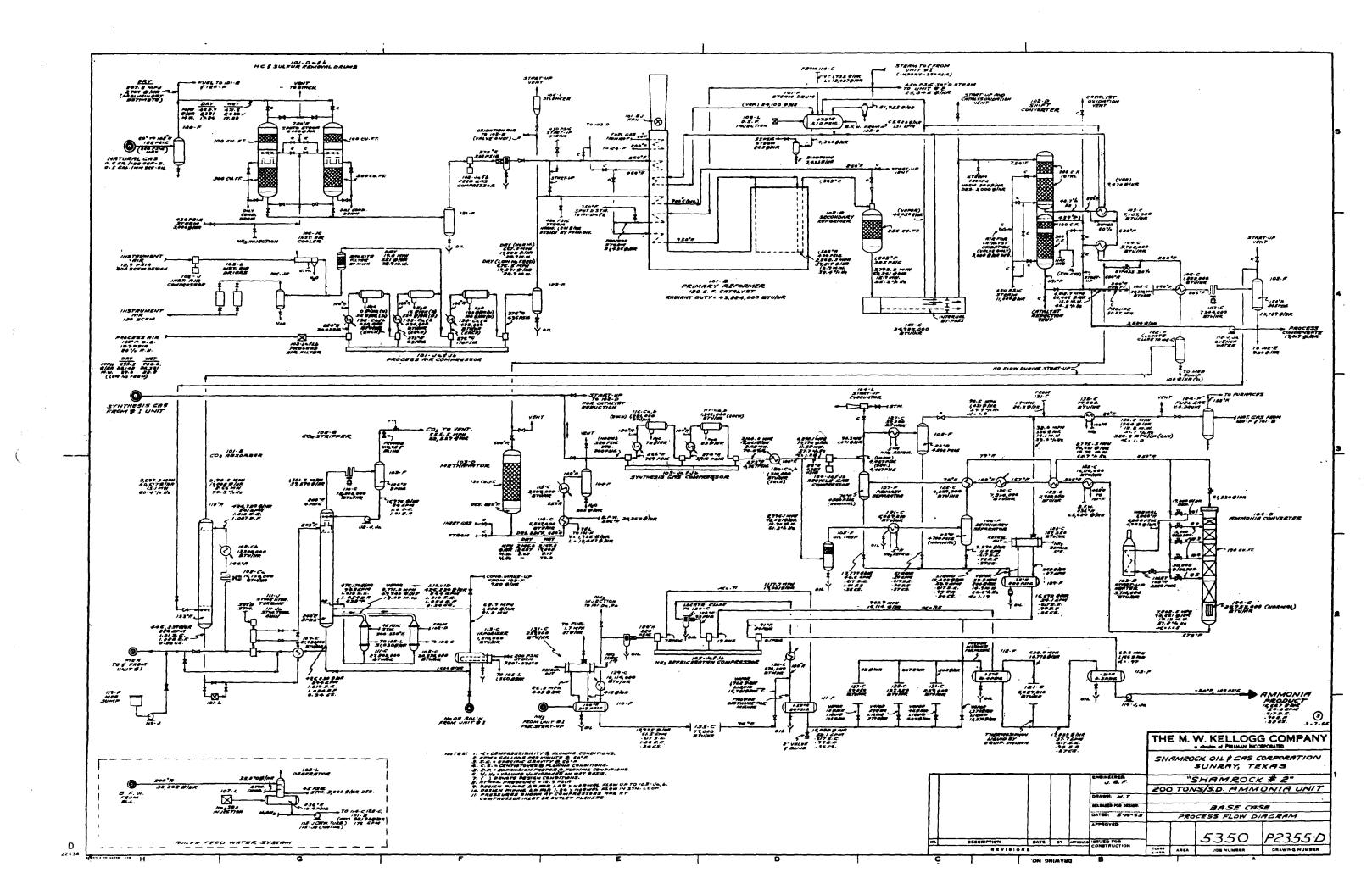
Magnesium salts are precipitated by the alkalinity of the boiler feed water to form magnesium hydroxide sludge. A Ph of about 9.7 is desirable for the removal of the magnesium salts.

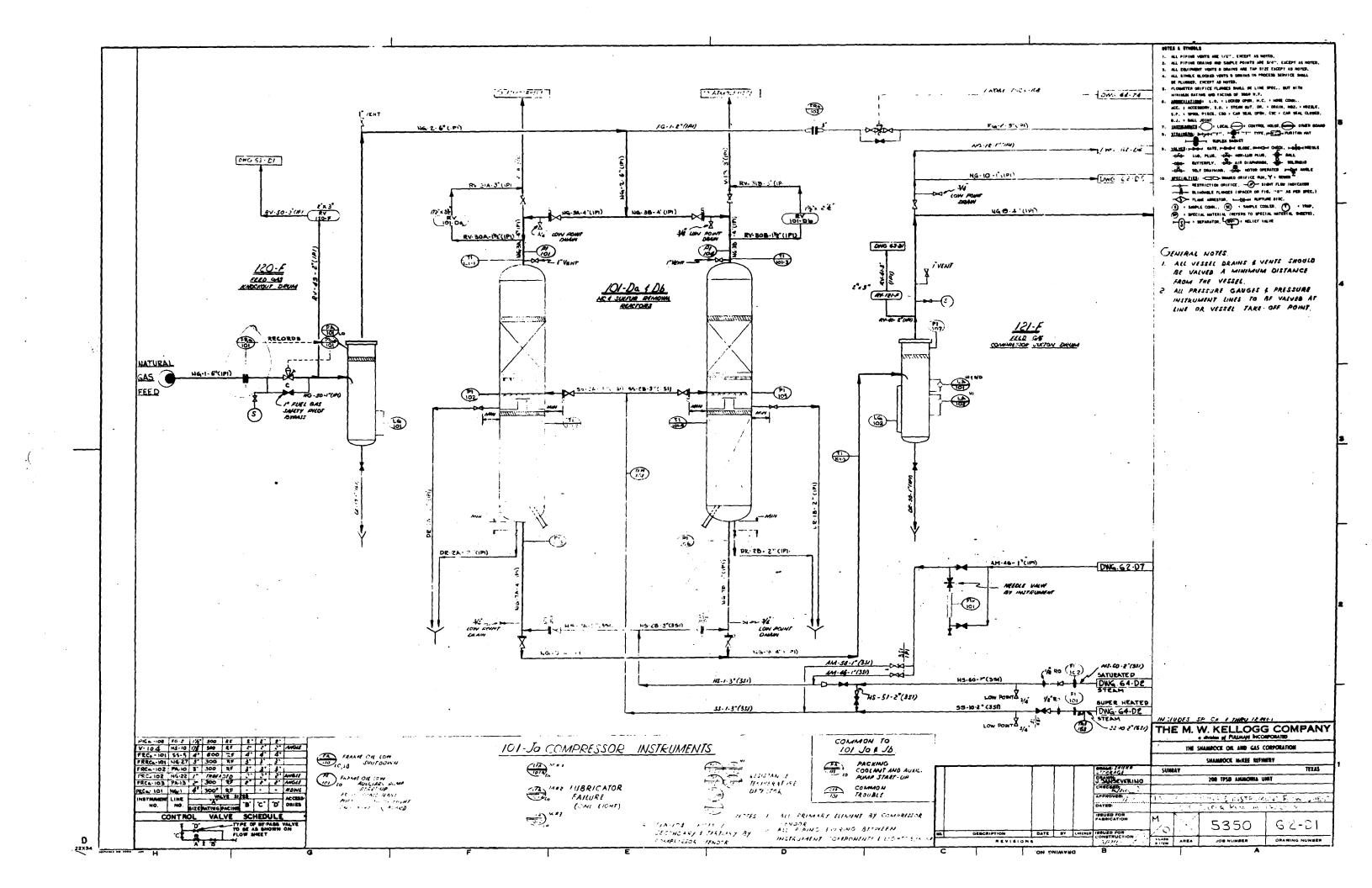
In order to control the Ph and alkalinity of the boiler feed water, caustic is injected into the discharge of the boiler feed water pump 115-J. Injection should be adjusted to control the Ph in vicinity of 10.3 as a Ph of 10.1 aids in the removal of silica.

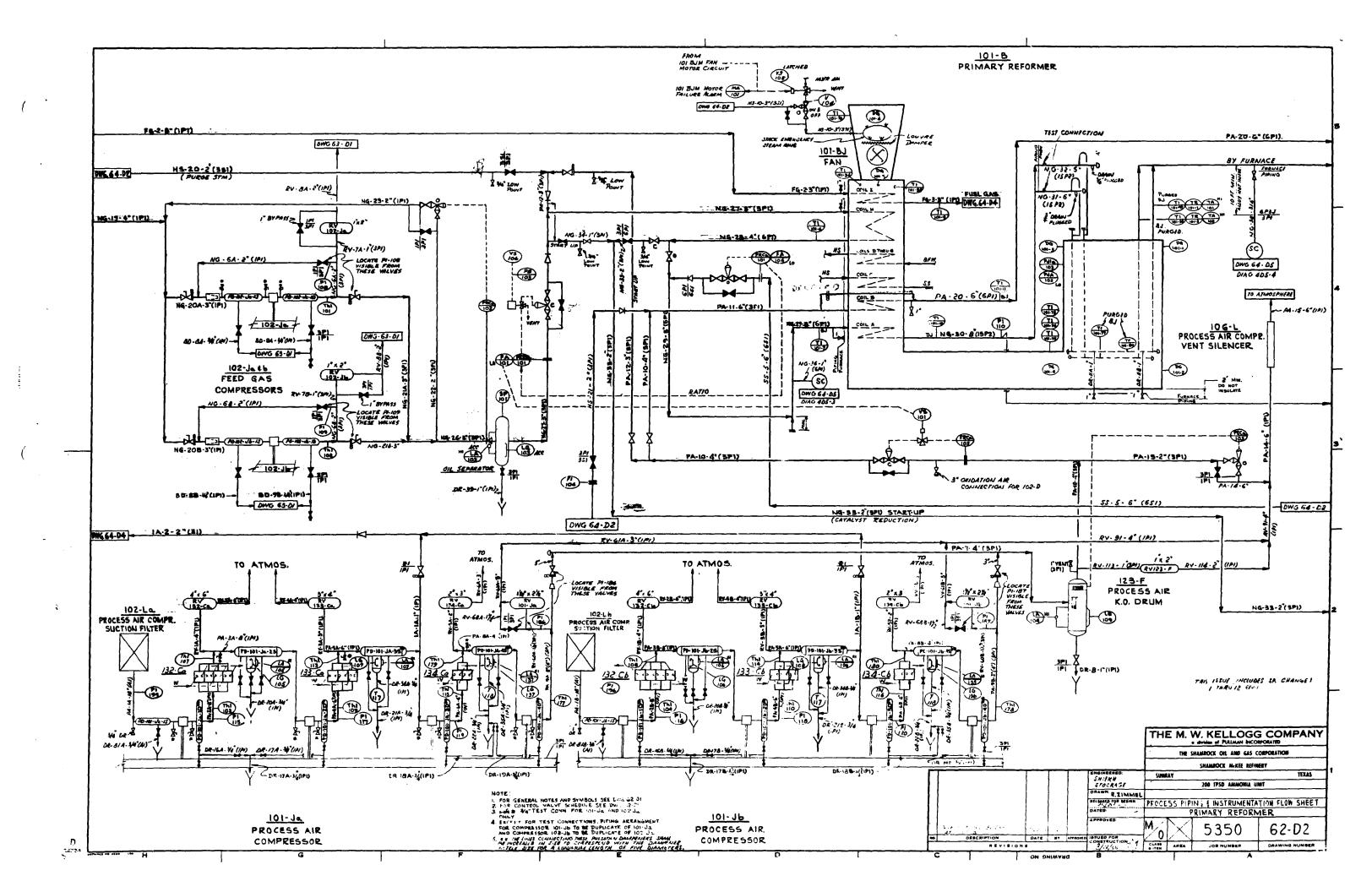
Continuous and intermittent blowdowns are provided to remove the sludge formed and to keep the solids content of the boiler water at the desired level.

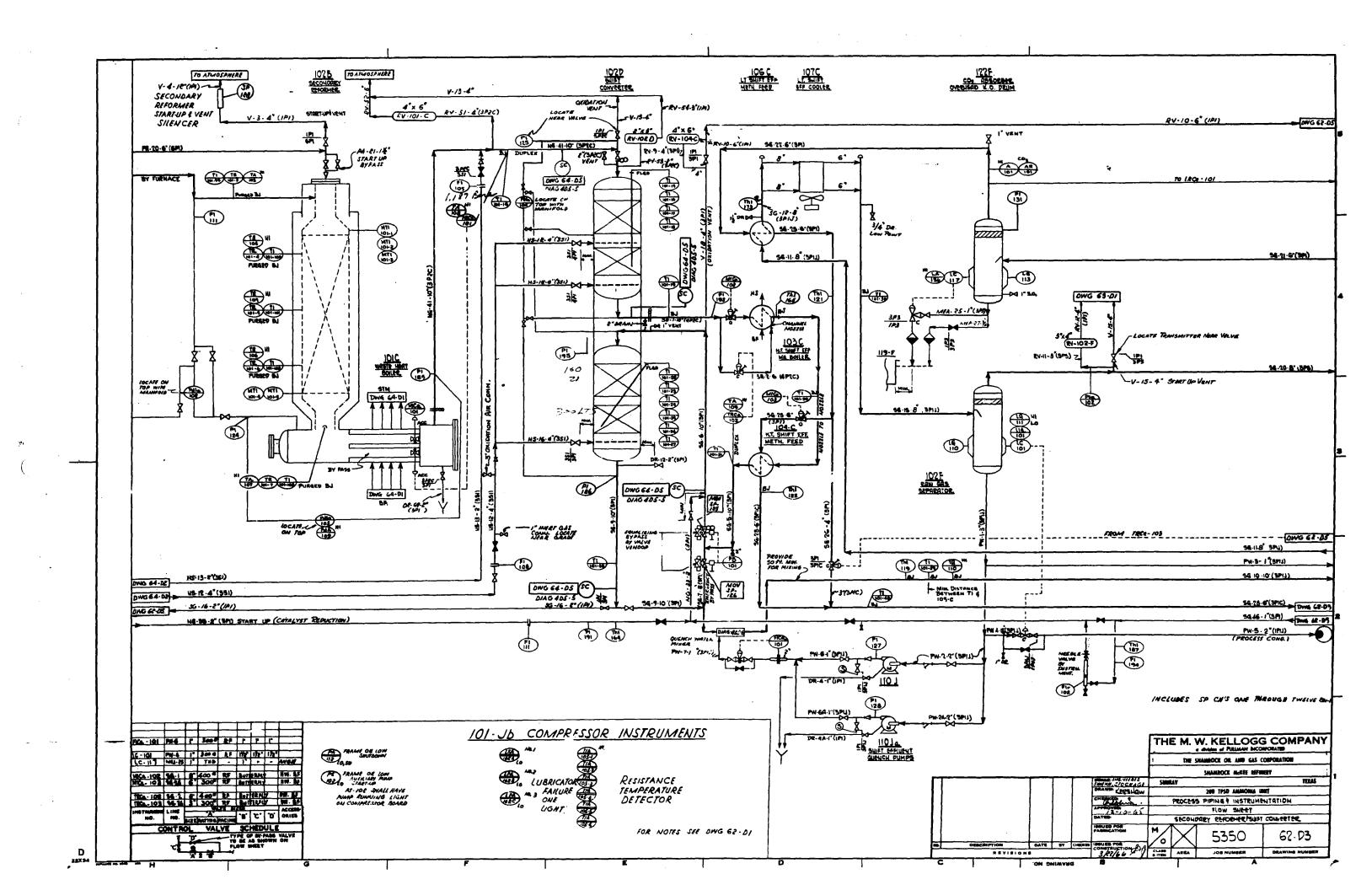


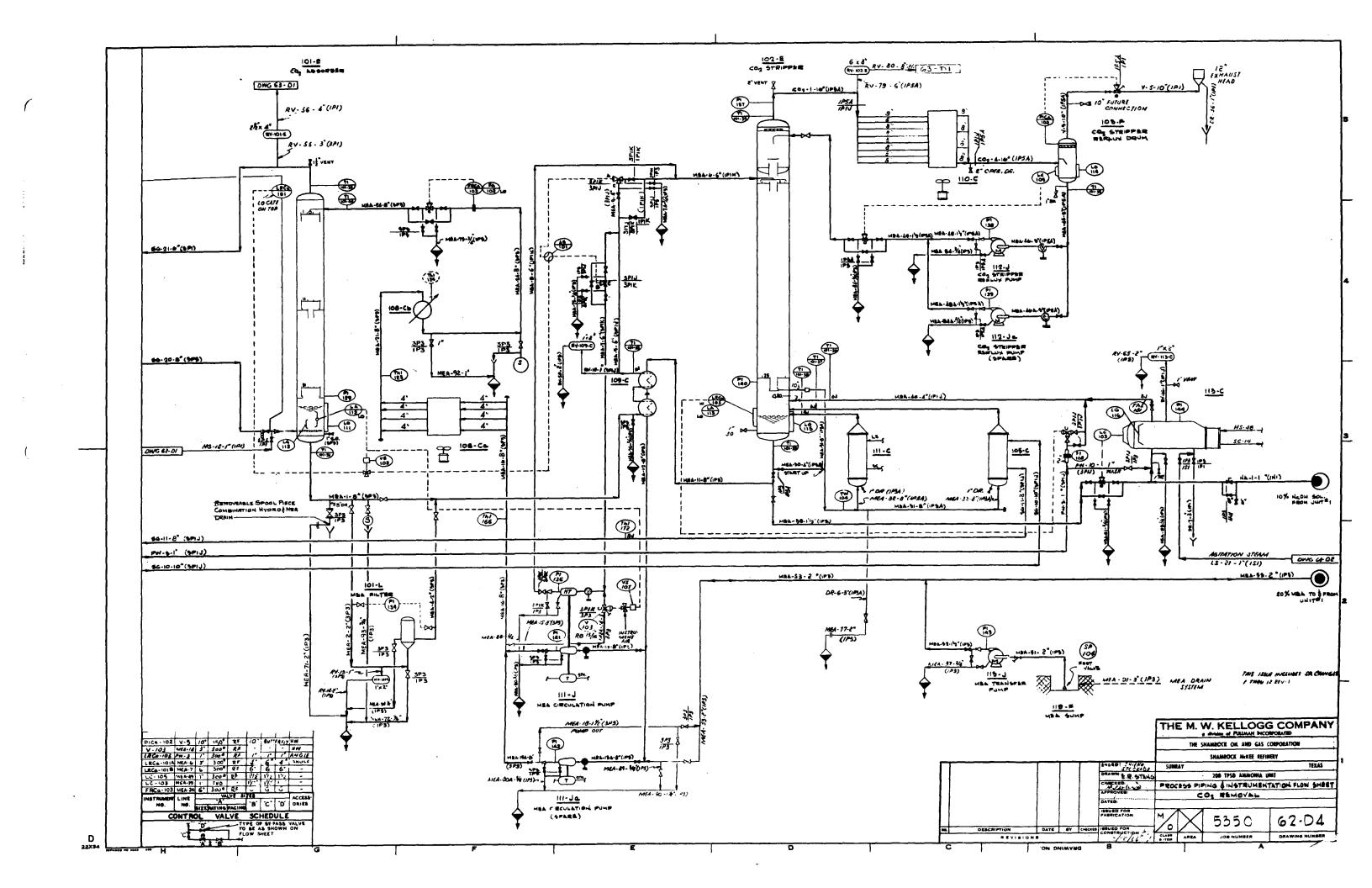


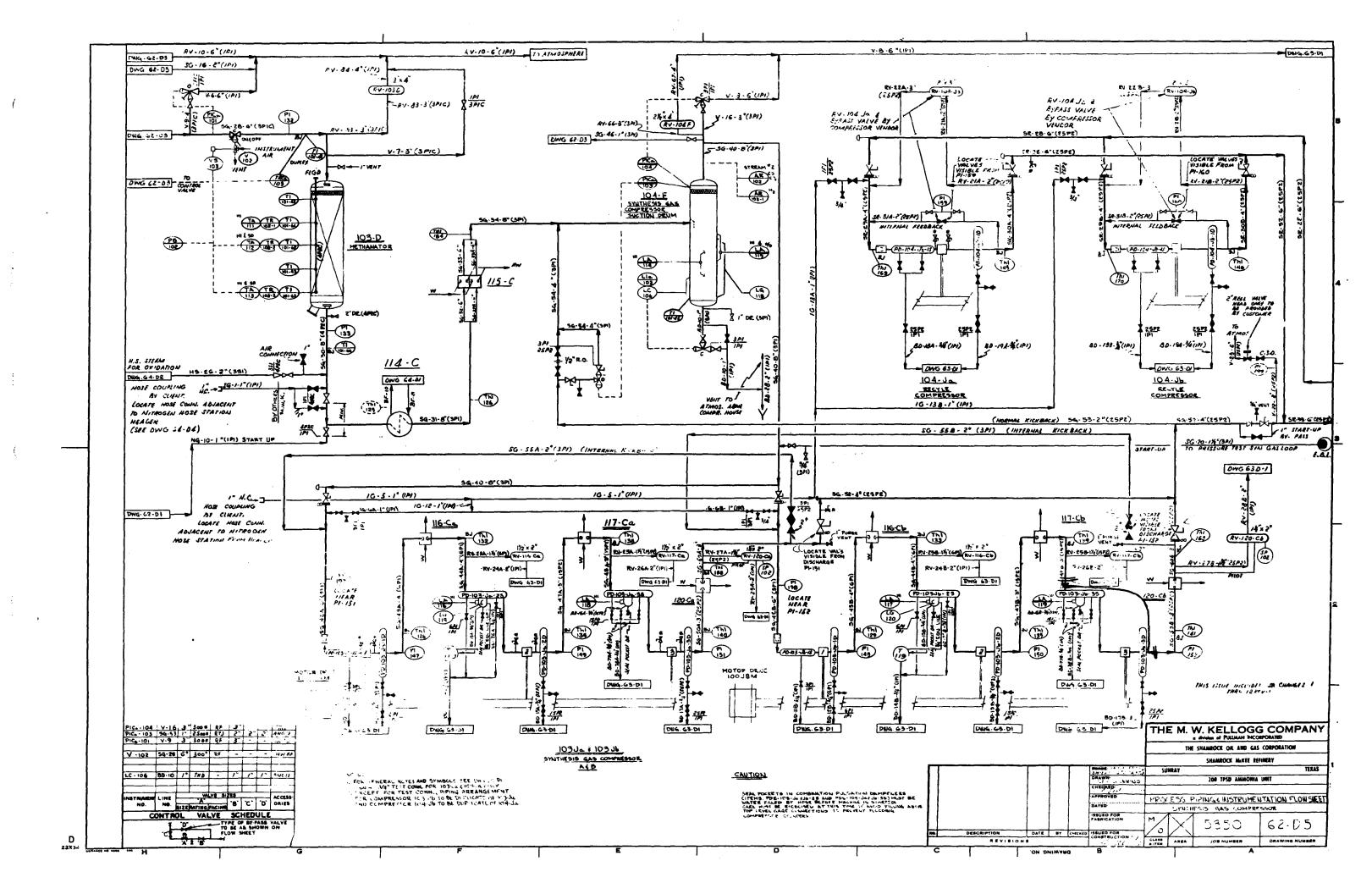


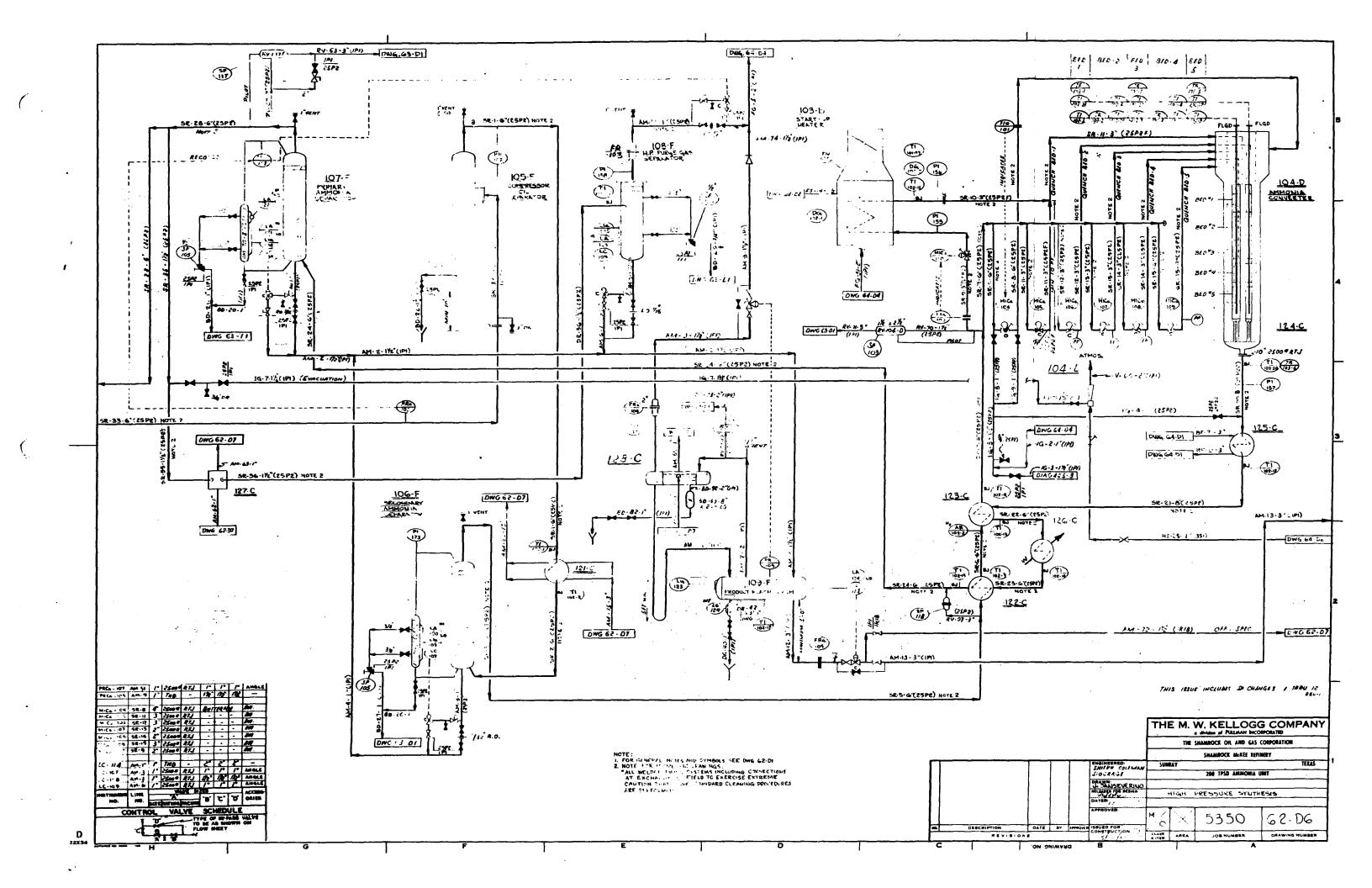


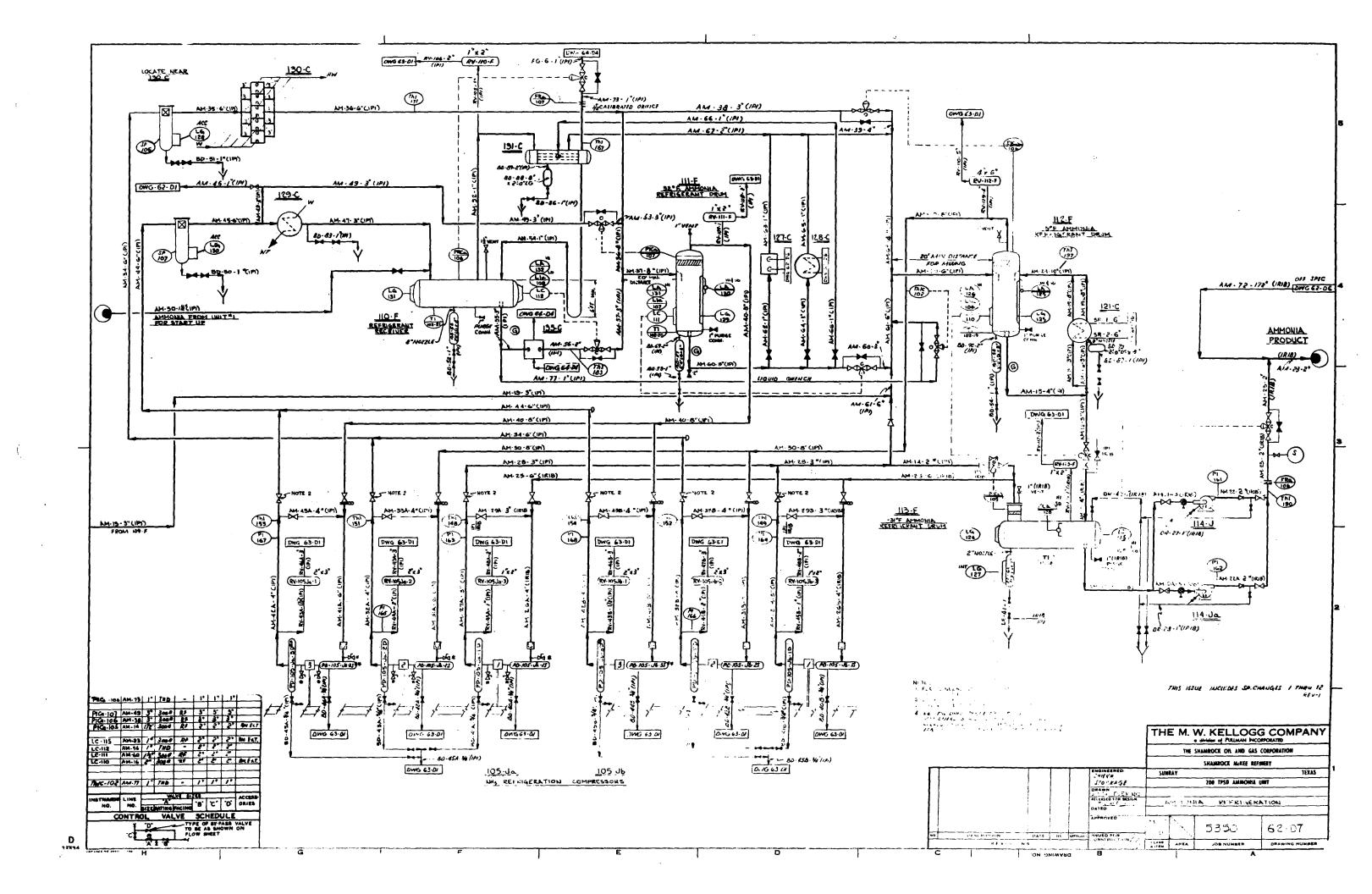


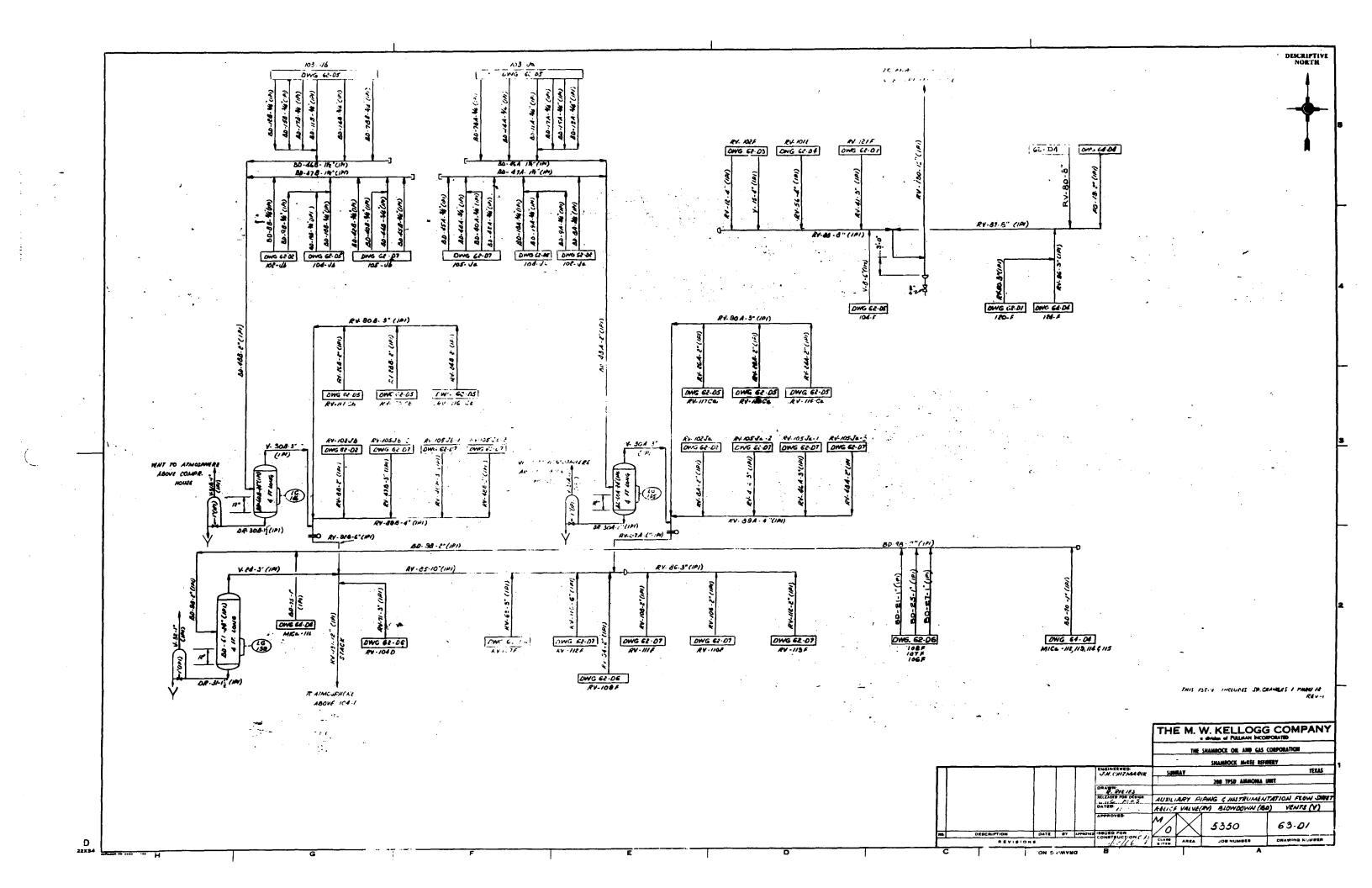


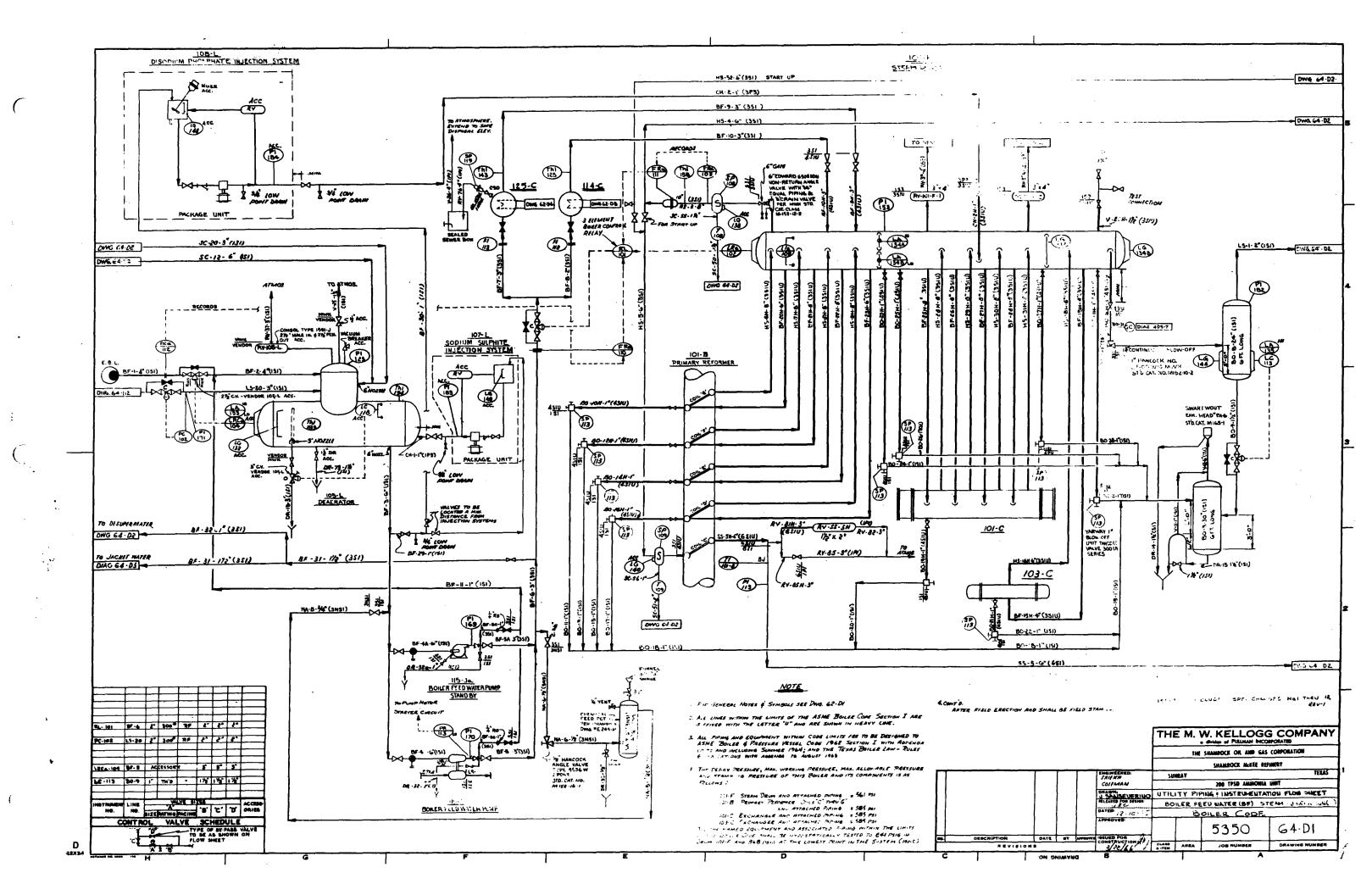


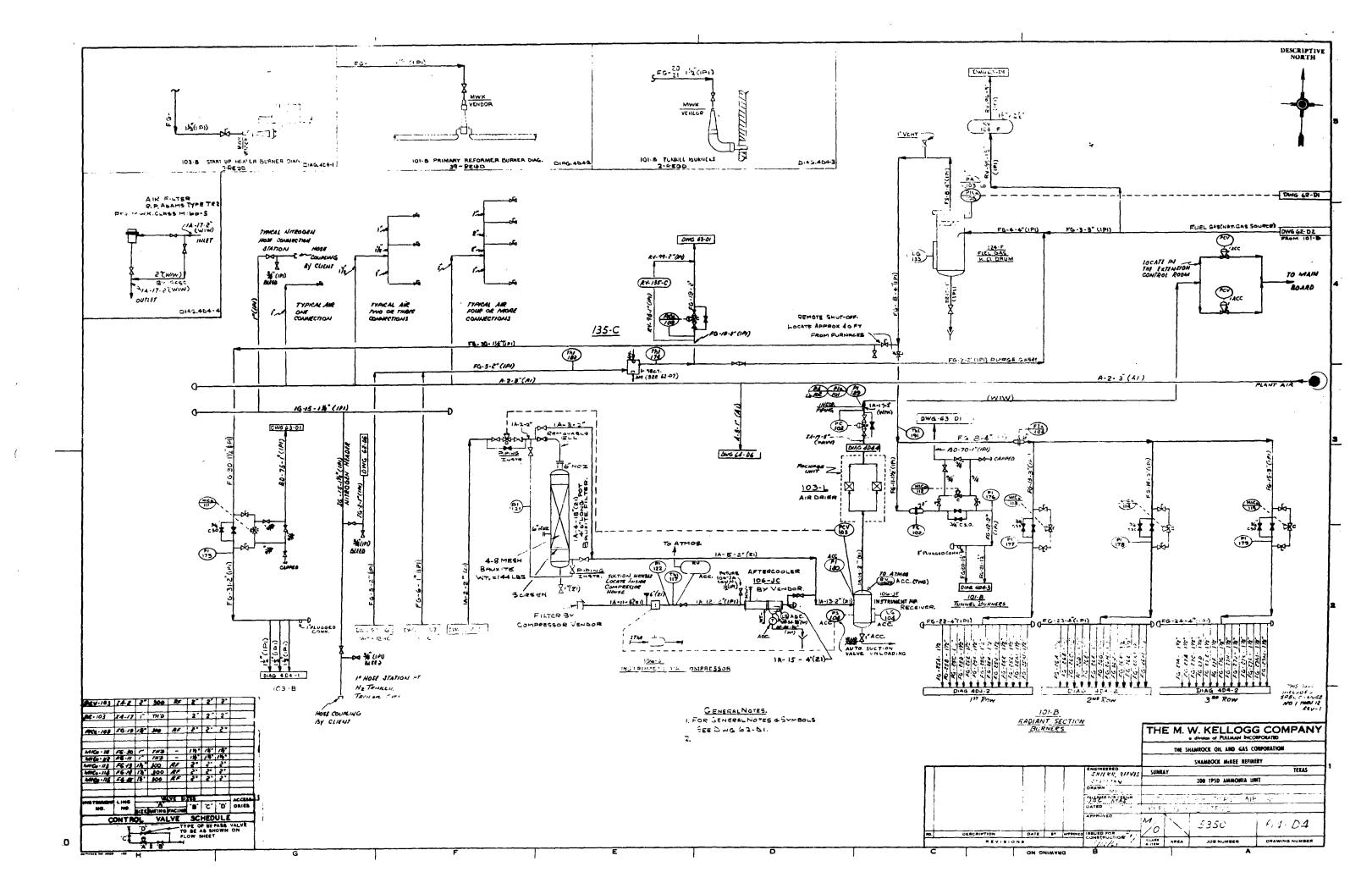


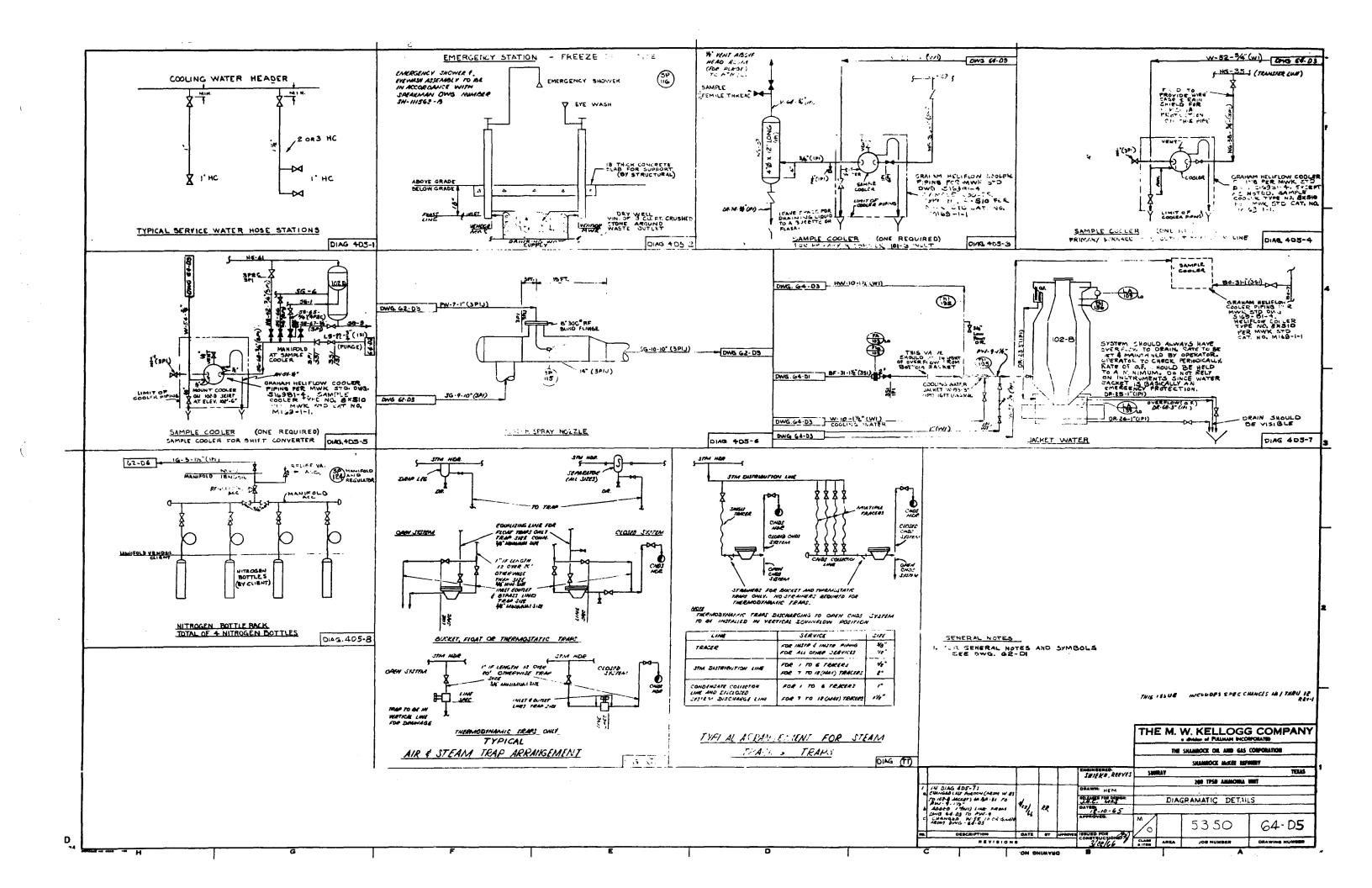


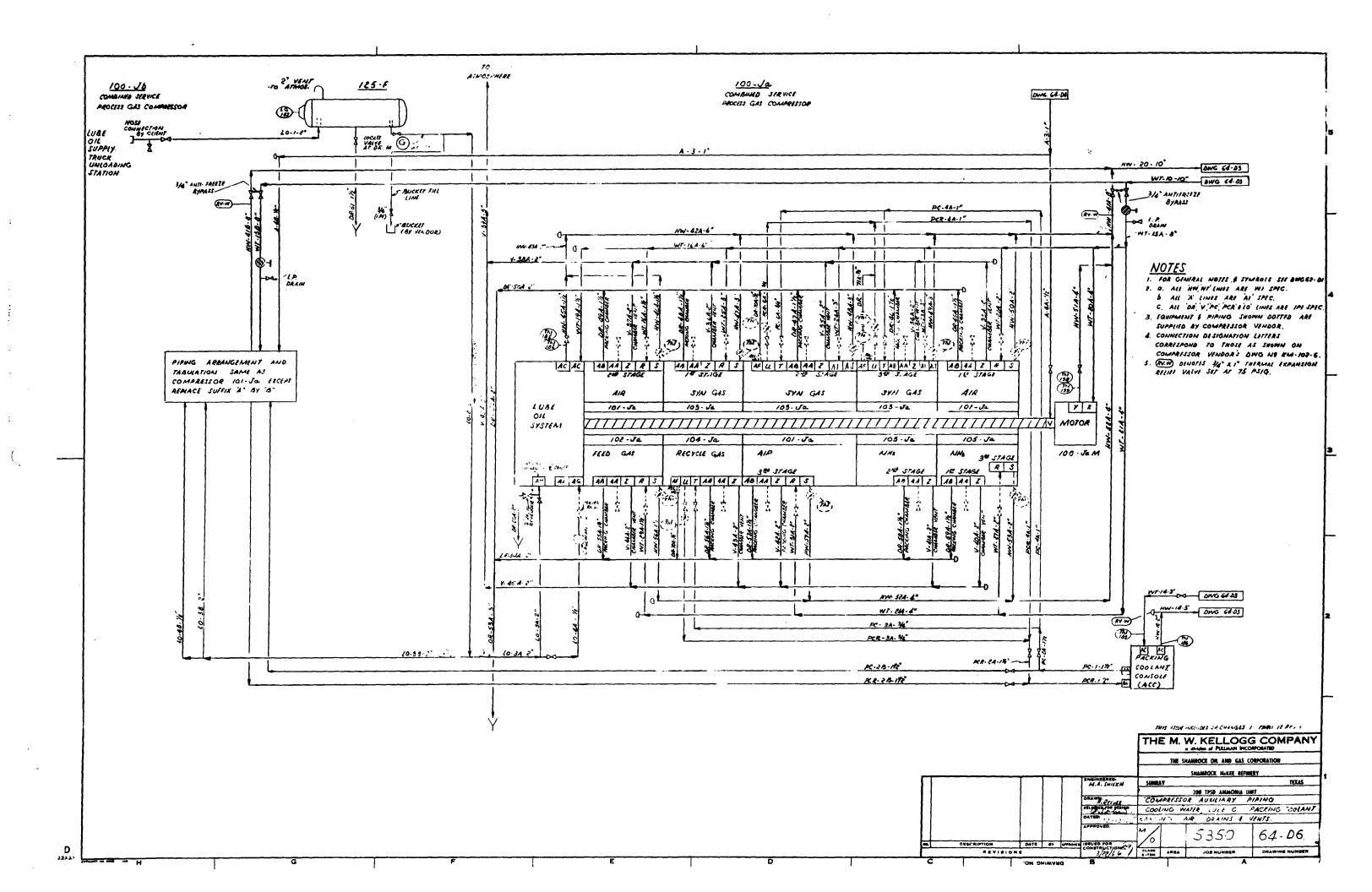


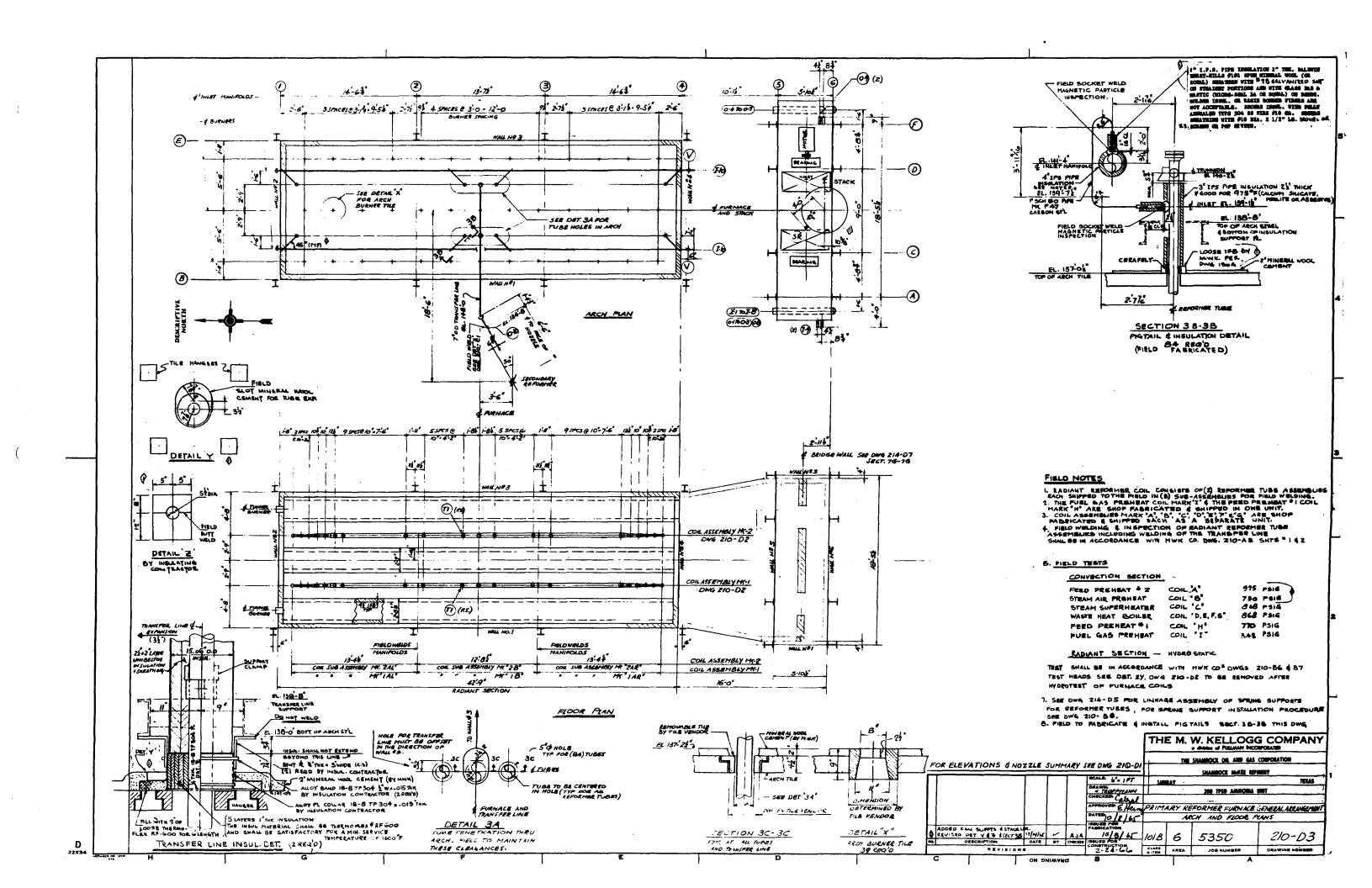


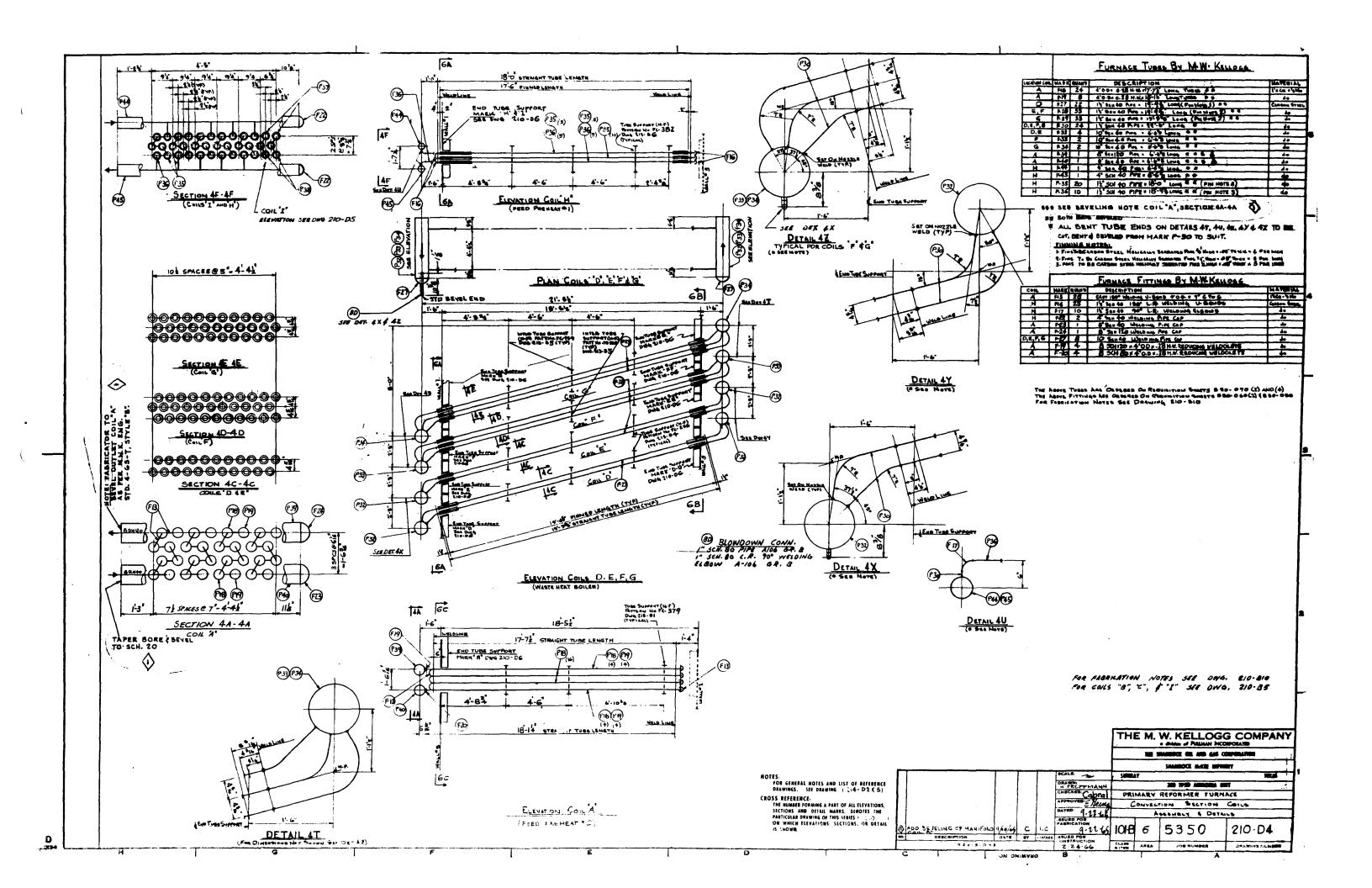


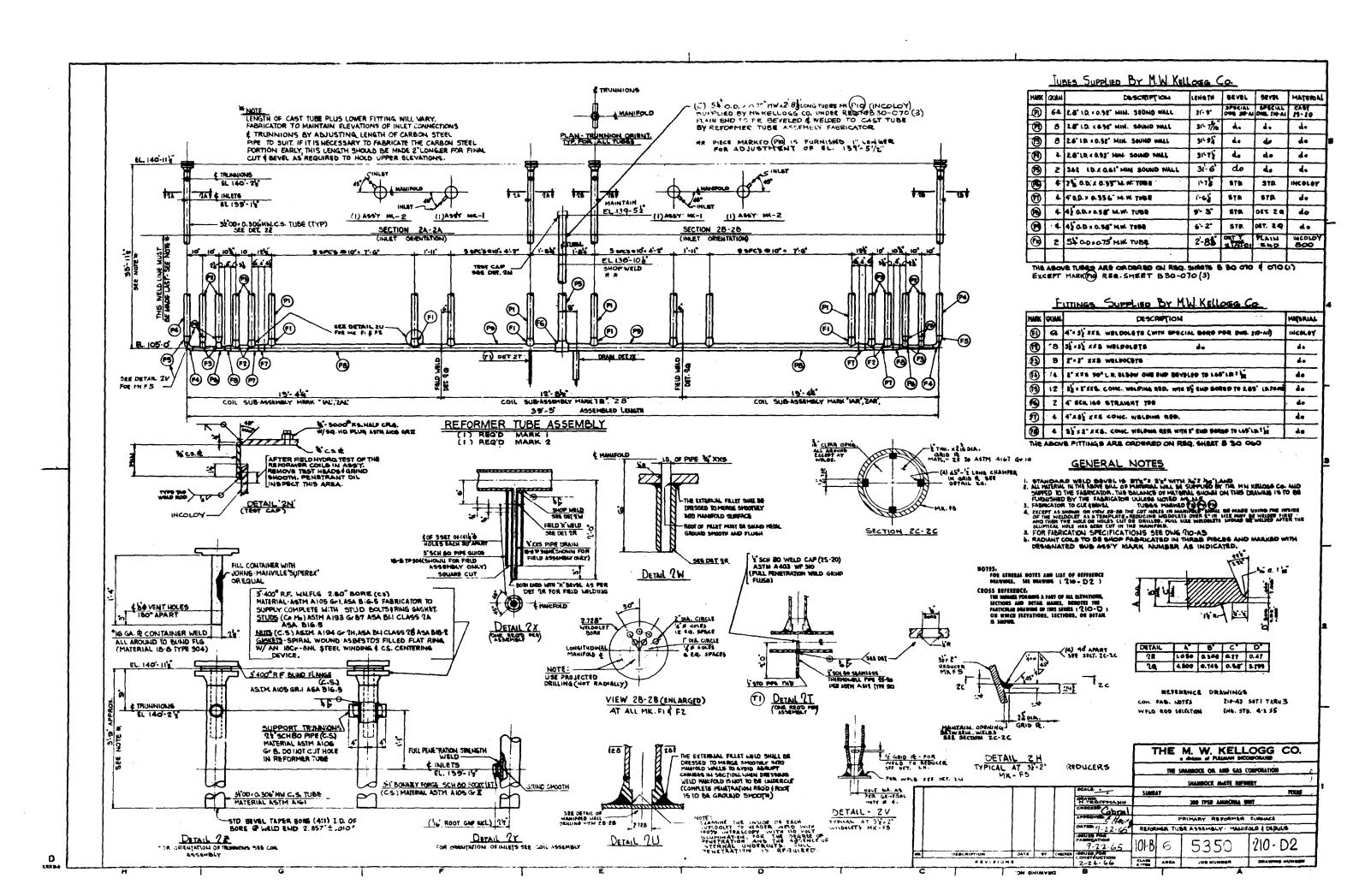


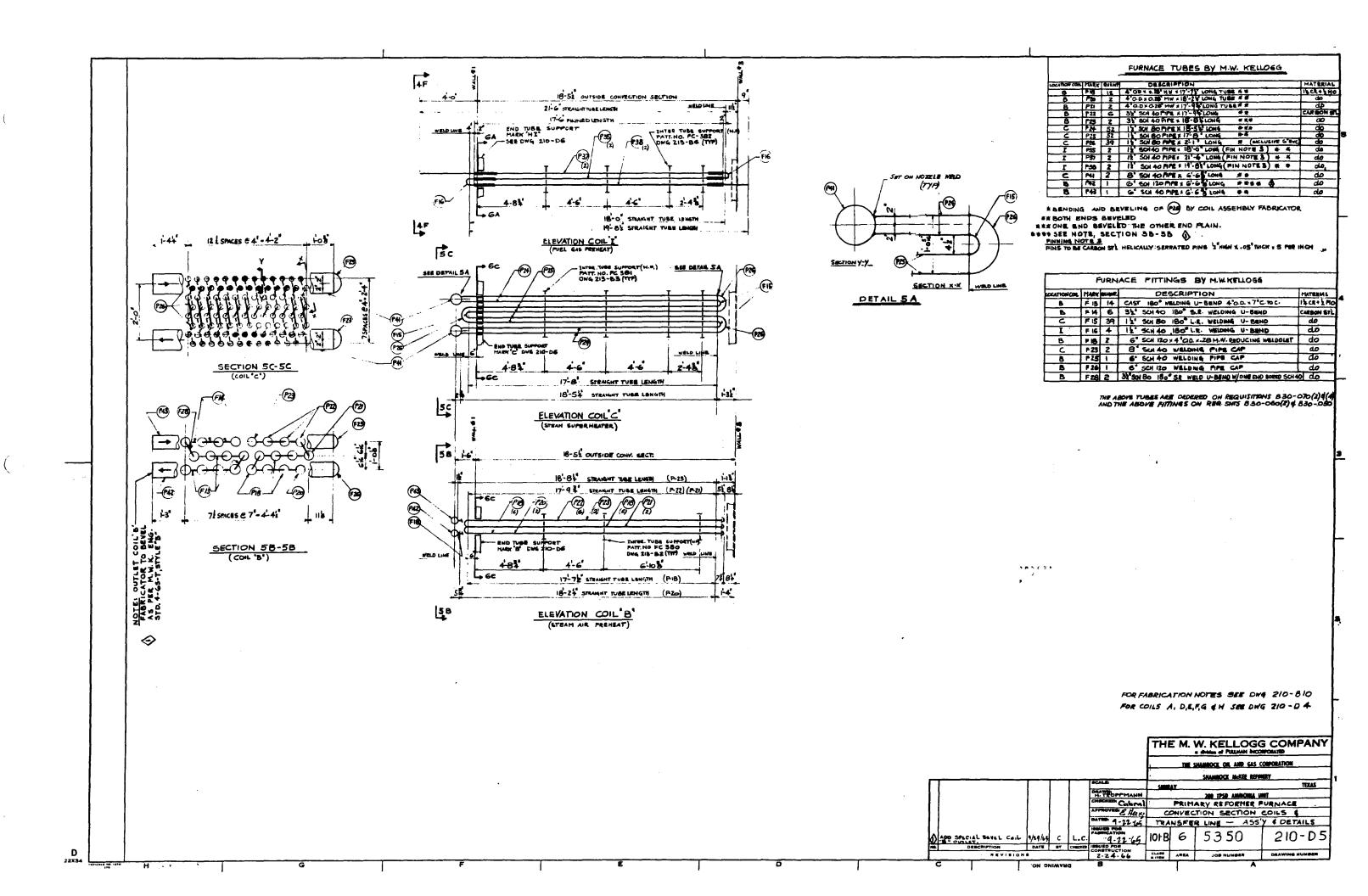


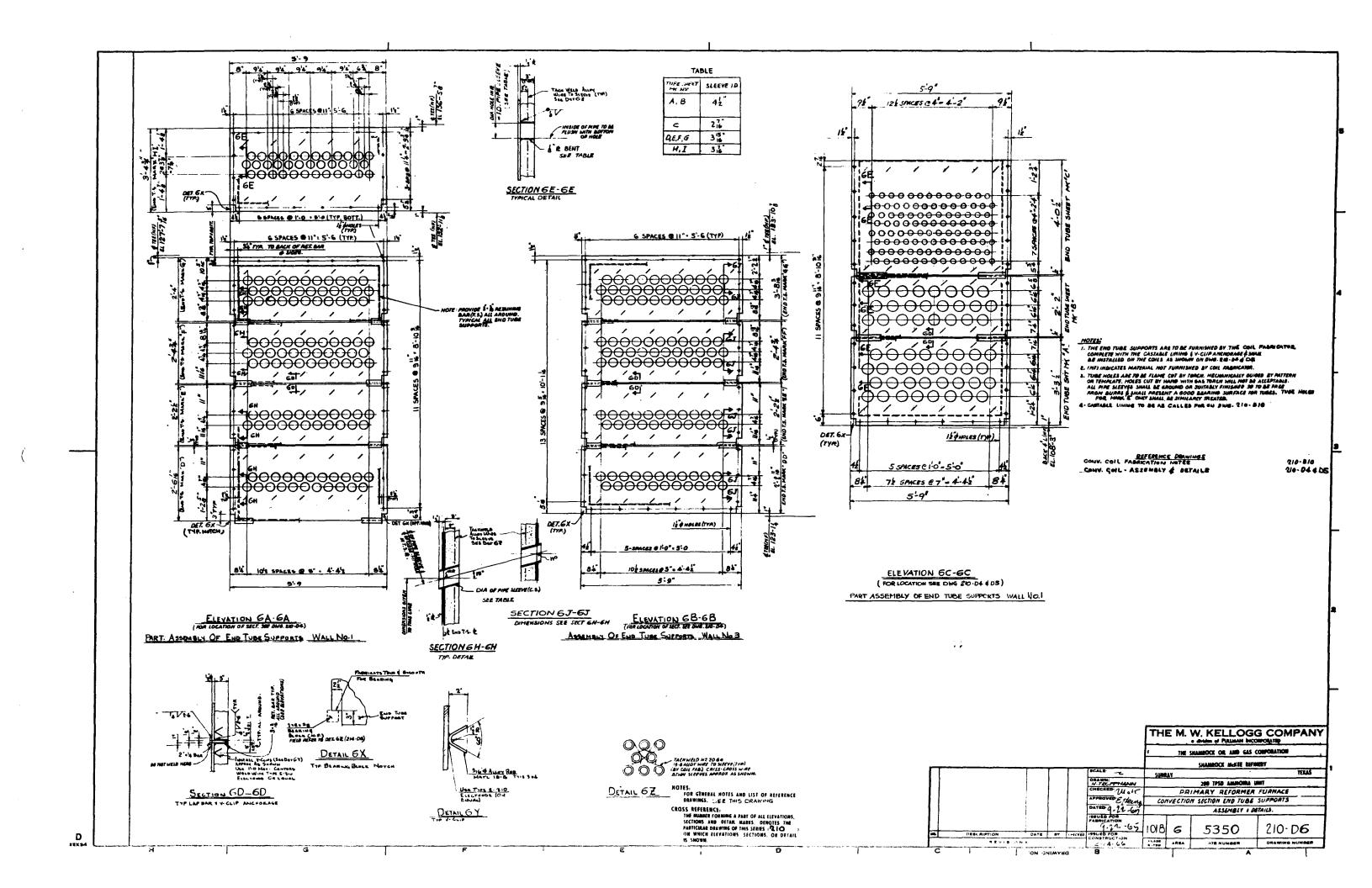


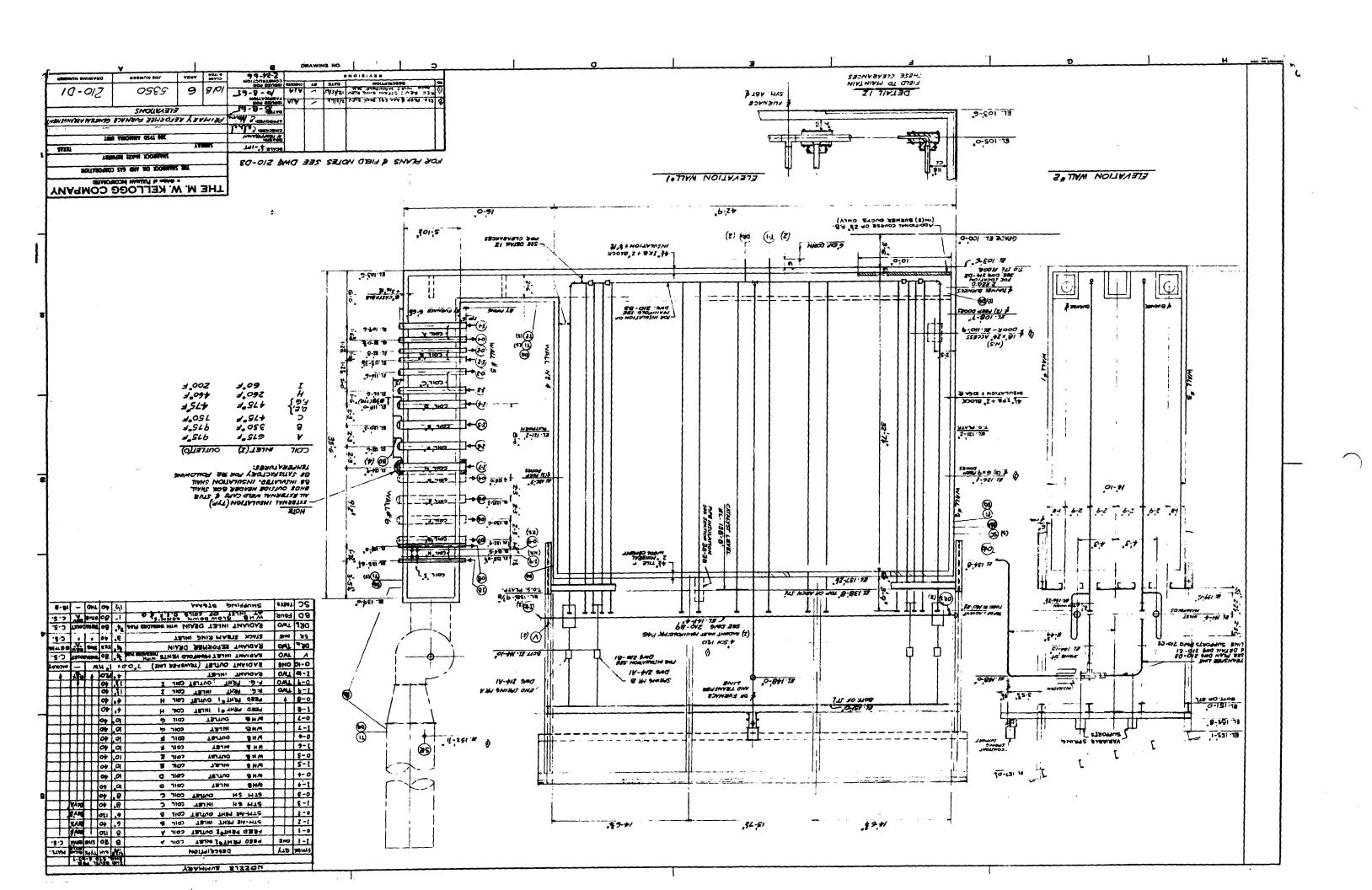












GENERAL NOTES. 1. START, STOP, PB-102, PB-103 AND ANN. TEST
PUSHBUTTONS TO HAVE NORMALLY OPEN CONTACTS (
ANN. ACKNOWLES AT BUTTON HORMALLY LISSED CONTACTS. -MOV-EMERGENCY SWITCH, ZPOLE SINGLE THROW, OPEN-NORMALLY CLOSED-ON EMERG, SAMP, Z+994. 3-POSITION SELECTOR SWITCH WITH TWO SINGLE POLE DOUBLE THROW CONTACTS SPRING RETURN TO HIBBLE OFF POSITION, IN AN EXPLOSION PROOF ENCLOSURE G.E.CO. TYPE SE-1 OR EQUAL. 4-0 7 PANELS @ 4'-0" - 28'-0" 109 (L) H0V-1- 5P-178— SWITCH CABINET T1-101 TRST (ACK. Pla (Pla (Pla (Pla (G) 9" 9" 9" 9" 9" 6"
PICA PICA PICA PICA
104 105 106 107 o PICA FREA TREA TREA FREA 102 103 102 101 753 [RC.] 194 FRA PRCA (67) TRCA (91Ca) MISA MICA MICA MICA POCA EXCITER FIELD LIGHTS 301-IT TIA O O ANMETED AR-IOI COL 8r 8r FRRCA MIC 4
101
11,4
11,4
PICA 101 101 MC2 MICA FRCA FR. FR. MIC. IRC. START-STOP TR-102 AR-108 E01-84 - SELECTOR SWITCHES 15,4 12% 23" 1294 FLOOR LINE FRAME ALL FLOOR LINE FRONT ELEVATION COMPRESSOR CONTROL BOARD FRONT ELEVATION DISTRIBUTION PANEL CIRCUIT DIRECTORY NOTES FOR COMPRESSOR BOARD LOAD NO TI-IOI I, COMPRESSOR PANEL SHALL CONFORM TO ALL SPECIFICATIONS APPLICABLE TO MAIN INSTRUMENT BOARD. INSTRUMENT BOARD.

2. AIR SUPPLY, AND ALL TUBING AND WIRING CONNECTIONS TO COMPRESSOR BOARD TO BE LOLATED IN LOWER PORTION AT PANEL. 2 TI-102 3 TR-101, 102, 103 PANEL 4 TRCs-101, 102, 103 (CONVERTERS) 5 MINIATURE RECORDER CHART DRIVES -®H L®+ 6 SPARE
7 AR-IOL IOZ 4 103 RECORDERS NSHOE PANEL <u>-@</u>-**-**⊚-AL-001 100-16 CEL - PTO LRTHIUIA-V 8 AR-HOLIOZ E 103 ANALYZERS — 🔅 9 SPARE 100-JB IO ANNUNCIATOR 'A' ERS HOIRIV II ANNUNCIATOR 'B' 12 RELAYS E HORN 15 SOLENOID VALVES EMERG. MOV-Z MOV-1 14 TIA-104 (105 (COMPRESSOR BOARD) WIKING DIAGRAM - PANEL +1 15 ANNUNCIATOR 'C' (COMPRESSOR BOARD) FRA 10-FROM FRANCET TIA-10+ T.A-105 16 SPARES 17 18 FROM ERSONIET D - FROM PR. 10 TO DISTRIBUTION PHE → TO RL-ICHV COMPRESSOR BOARD WIRING DIAGRAM THE M. W. KELLOGG COMPANY Lks. FR M UF 100 1 LEVEL SONTROL RELA AND SELISION STA. division of PULLMAN INCORPORATED THE SHAMROCK OIL AND GAS CORPORATION TA\_ PEHN. SHAMBOCK MIKEE REFINERY - FROM DRAWN LEIVAN FRCA-10. 200 TPSD AMMONIA UNIT INSTRUMENT BOARD ARRANGEMENT DATED G- +TO FRM THUS'S ISSUED FOR 5350 315-14 STOR LAND S DETAILS DRAWING NUMBER JOB NUMBER 22X34