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in Fertilizer Plants

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COUNTRY PAPER BY MAURITIUS

CORROSION PROBLEMS ENCOUNTERED AT THE

MAURITIUS CHEMICAL AND FERTILIZER INDUSTRY*

by

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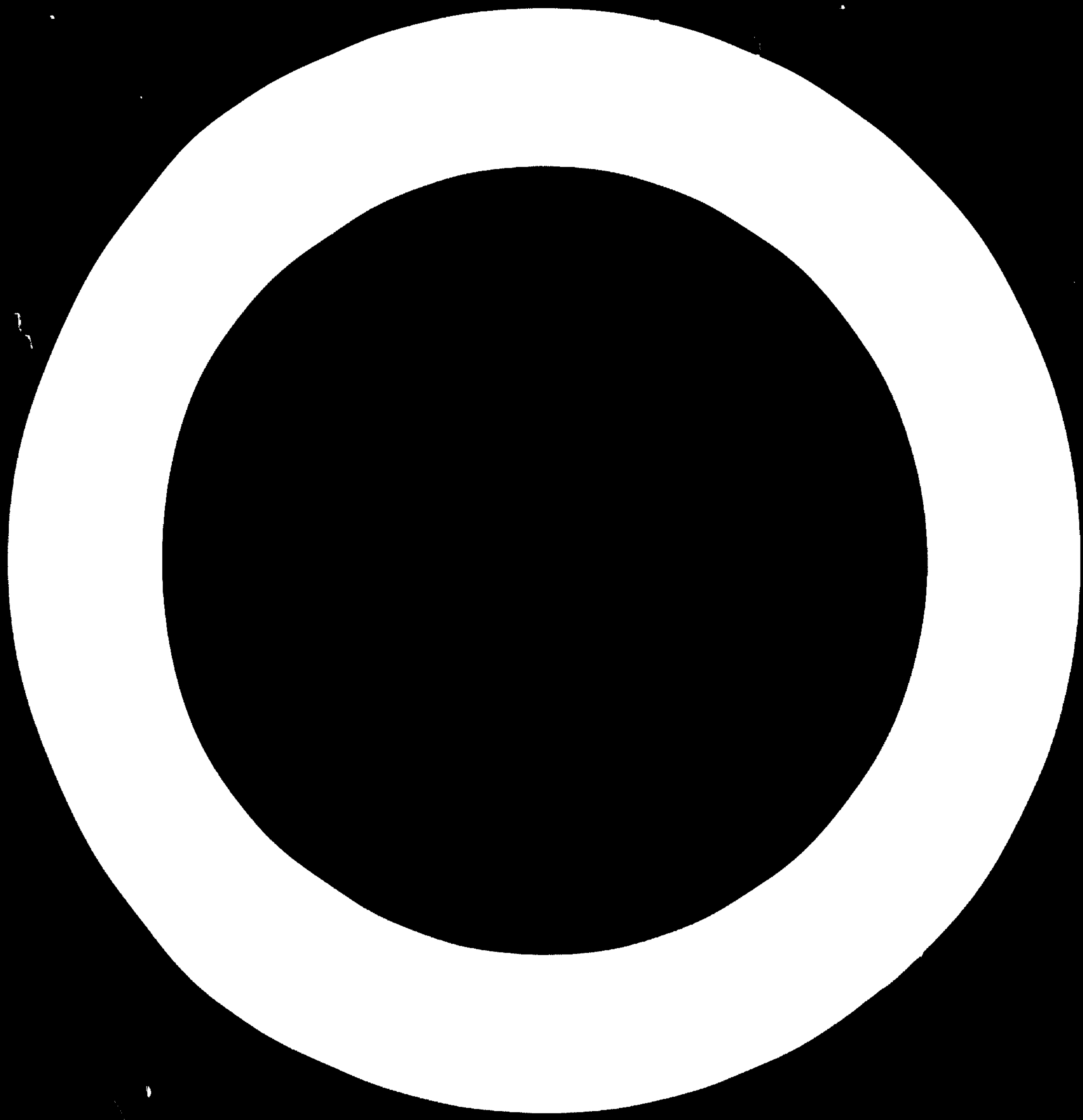


CORROSION PROBLEMS: MCFI CASE STUDY

Corrosion problems encountered at MCFI and relevant to this seminar are described below.

A. NITRIC ACID PLANT

The Ammonia Oxidation Process (AOP) plant makes use of the high-pressure, mono-stage Dupont Process (see flow diagram).

(a) Tail Gas Reheater

(i) Description & Operation

At MCFI the reaction train (converter and tail gas reheater) is constructed as one integrated unit using Type 321 Stainless Steel (18/8).

The reheater portion utilises a vertical U-tube design as shown in Fig 1. With this design, there is a significant thermal gradient across the tube-sheet which is thought to have led to continual tubesheet cracking.

The thermal gradient results when tail gas from the absorption column at 40°C, preheated to 90°C by steam in the tail gas tempering heater and to 150°C by process gas inside the preheater and further heated through the outerjacket of the tail gas is channelled out into the bottom header at 250°C. The resulting thermal gradient is quite steep (T = 650-250 = 400°C) on the cold side of the tubesheet and nearly the same across the pass-plate (T = 340°C).

(ii) Corrosion Problem

Stresses developed by these thermal gradients are believed to cause cracking of the tubesheet across tube ligaments (see photographs).

Furthermore, frequent start-ups and shutdowns of the nitric acid plant submit the tube plate to severe alternating stresses with high tensional and compressional forces.

Heating up and cooling down curves illustrate the problem (curves (a) & (b)): after the catalyst is lit, the plant is on line in about 30 minutes. (curve A). On shutdown, cooling to normal temperature is achieved in about 60 minutes, but with a steep temperature gradient at the beginning. (curve B).

It has been claimed that the problem of cracked tubesheets has been solved successfully by insulating the cold inlet to the reheater tube bundle with an acid resistant refractory to decrease the thermal gradient and by reducing the tubesheet thickness to reduce stresses.

After the cracking of the original 2" tubesheet (October 1976), the latter was reduced to 1½" and insulation placed at the cold inlet in a new equipment. But again cracking occurred (August 78), this time on the hot side where the temperature gradient is not significant (50°C).
Another 1½" tubesheet, without insulation on cold side, also experienced cracking on the hot side (May 79).

(iii) Comments

Stresses due to thermal gradients provide only a partial explanation of the cracking of tubesheets. It appears that we are probably in presence of CORROSION FATIGUE. Adding to the stresses developed by the thermal gradient are severe alternating stresses at start-ups and shutdowns.
Furthermore, the equipment undergoes stresses in a corrosive medium (NO_x gases, nitric acid) and under a small pressure difference of 2 Kg/cm^2 which is the pressure drop of process gas across the system.

Indeed, at S/U but mainly during S/D, there is acid condensation inside the system. Blowing the system with hot air causes "revaporization" of this acid. Especially, on emergency shutdowns (for example caused by power failures) when the air compressor trips, blowing of the system after some time (after power is restored) causes acid vaporization at the tube plate. Power failures or power dips occur frequently in Mauritius.

No satisfactory solution has been found to this problem of cracked tubesheets and the reheater has now been replaced three times at MCFI.
Being given that no modifications can be brought to the design, except for minor details, and that "tripping" conditions are bound to repeat themselves, it seems that the solution lies in the choice of a suitable material for the tubesheet which will better support the alternating stresses* and thus extend the lifetime of the reheater.
Otherwise, the existing tubesheet could probably be protected inside/outside by overlay welding of strip steel.

Suggestions are most welcomed.

* It should be noted, however, that in order to reduce alternating stresses at S/U & S/D, the plant is now brought on line in 90 minutes (instead of 30 minutes) by gradually increasing the amount of reaction and at shutdown, reaction is slowly decreased to avoid sudden cooling.

(b) Tail gas Tempering Heater

(i) Description & Operation

This vertical shell and tube heat exchanger is intended to preheat tail gas from the absorption column from 40°C to 90°C before admission into the preheater where it is further heated to 160°C. Steam at 15 Kg/cm^2 and 202°C circulates inside the carbon steel shell and tail gas in the S.S 304L tubes (Fig 2).

(ii) Corrosion Problem

At the vicinity of the steam inlet to the exchanger, the tube metal temperature is hot enough to boil off droplets of acid carried over from the absorption column and the mist separator. This results in severe corrosion of the tubes at the inlet, immediately at the backface of the tubesheet. Leaking tubes at the top of the tempering heater have caused severe damage to the carbon steel shell which has been eaten up by the acid spray. (see photograph).

(iii) Solution

The tubes protrude through the bottom tubesheet in order to protect the tube plate and welds from any remaining acid droplet at the outlet.

It has been suggested that Teflon sleeves could be used to protect the tubes at the inlet of the heat exchanger to move the area of corrosion so that the tubesheet could be reused when the unit must be retubed. The damaged unit at MCFI has been replaced by a new one, where the 304L tubes have been replaced by SANDVIK 3RE60. SANDVIK 3RE60 - which is ferritic austenitic - is somewhat less resistant to acid and oxidising medium than austenitic steel 304L and problems are expected to crop up in the near future.

SANDVIK 2RE10, which is reported to be more resistant under similar operating conditions, would have probably been a much better choice.

(c) Cooler Condensers

(i) Description & Operation

In the cooler condenser, hot process acid gases are cooled on the tube side prior to absorption in the absorption column from 195°C to 40°C with chemically treated cooling water on the shell side. Shell side material is carbon steel; the tube bundle and tubesheet are made of S.S. Type 430.

(ii) Corrosion Problem

Usually, this type of condenser undergoes severe corrosion at the hot tube inlets just past the tubesheet in a region where condensed-acid formation and revaporization is believed to occur.

This does not appear to be the case at MCFI where inlet gases are at relatively moderate temperatures (185°C) compared to 300-315°C in other types of process.

However, 21 tubes out of 295 had to be plugged on one condenser due to leakages.
A few tubes were extracted for inspection and found to be badly corroded at the extreme end where the tubes fit into the tubesheet. The tubes were found to be brand new with their full thickness all along their length.

(iii) Comments

The type of corrosion in this case can be best described as CREVICE CORROSION. Badly expanded tubes into the tubesheet allowed for crevices which were slowly replenished with the inhibitive chemical used from water treatment.

No futher problems arose with this equipment; what happened should be imputed to bad workmanship.

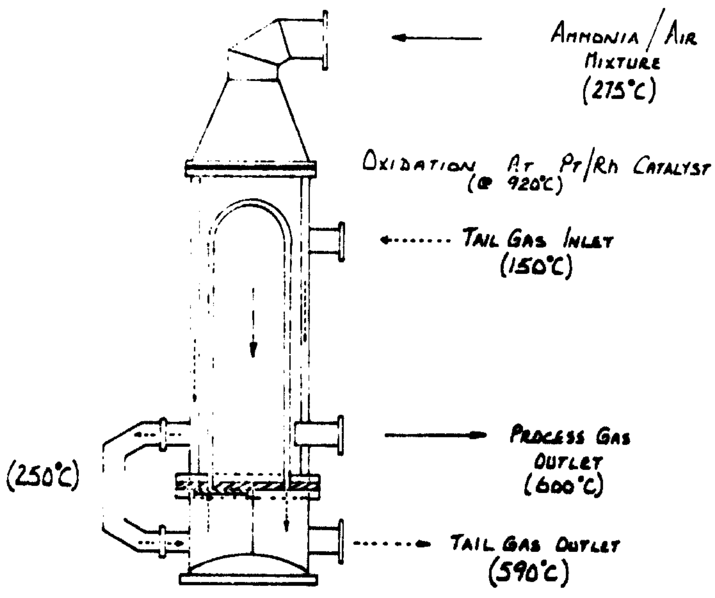


Fig. I

Tail Gas Reheater

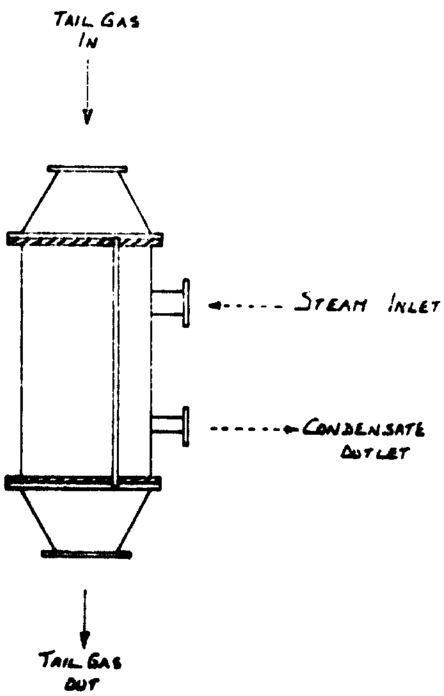
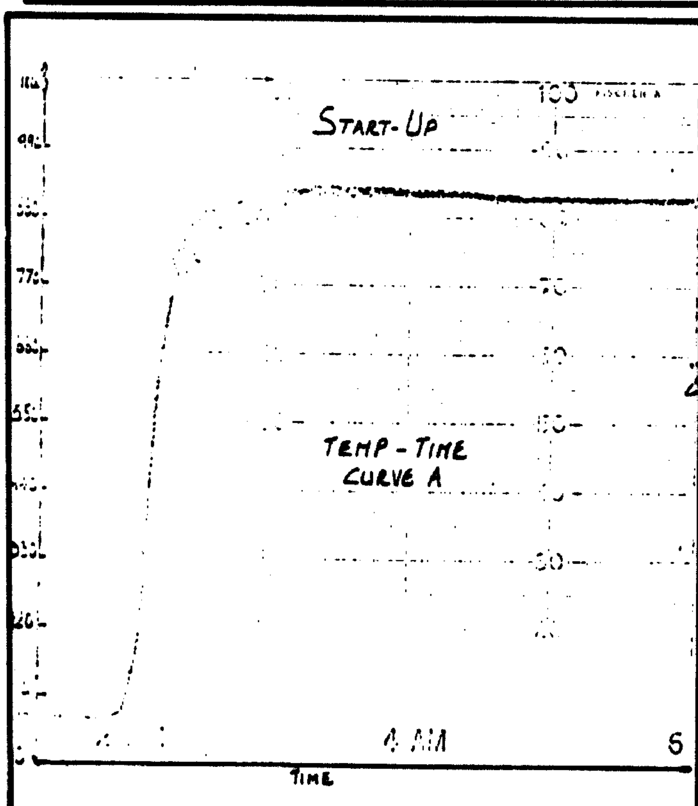
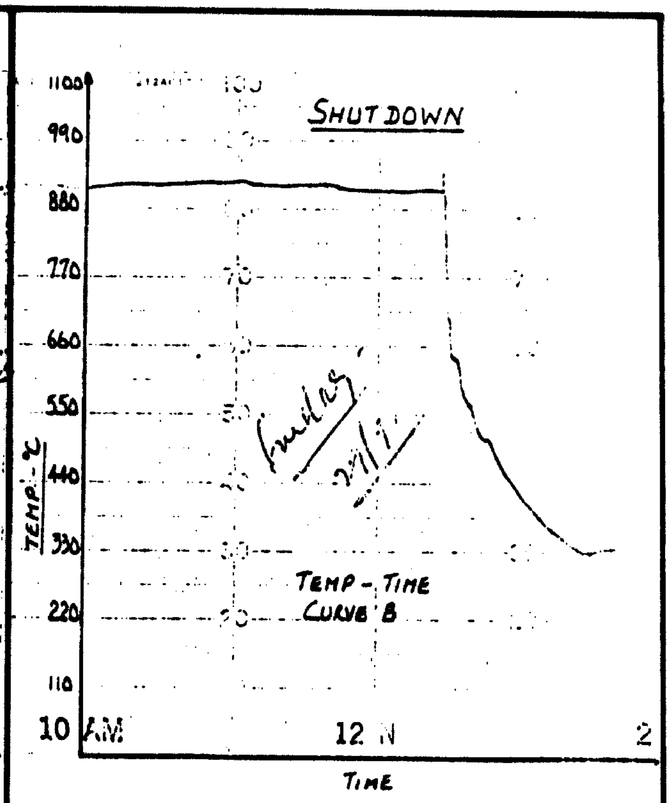


Fig II

Tailgas Tempering Heater





B. AMMONIA STORAGE AREA

The ammonia storage facility at MCFI is designed to store 10,000 MT of liquid ammonia at atmospheric pressure.
Liquid ammonia offloaded from ships is stored in the tank at -33°C (-28°F) and atmospheric pressure.
As the pressure in the tank tends to increase, due to heat gain from the tank's surroundings, the ammonia vapour is withdrawn, compressed in two-stages, condensed and returned in the storage tank.
When required, liquid ammonia from the storage tank is admitted into the transfer pumps which transfer ammonia to the ammonia burn tanks via the Ammonia Heater.

(a) The Ammonia Heater (and Ammonia Condenser)

(i) Description & Operation

The ammonia heater is a horizontal shell and tube heat exchanger with a remouvable U-tube bundle. Cooling water on the shell side is used to heat liquid ammonia from the storage tank to 16°C before admission in the Burn Tank.

The shell material is carbon steel A-106 "Gr B" and the tubes are constructed from carbon steel ASTM A179.

(ii) Corrosion Problem

The outside of the tubes, in contact with cooling water, have undergone heavy pitting at localized spots causing tubes to leak badly. The pitting occurred under sediment deposits on the tubes.

The Ammonia Heater is situated at the end of the cooling water loop where the pressure drop is a maximum. Furthermore, a large number of baffles closely-spaced increase the resistance to water flow. Consequently, the designed water velocity inside the heater is not attained.

Raw water at MCFI is filtered in a gravity sand filter. When both AOP and NPK plants are on, it may happen that the filter is not able to cope with the water requirements of both plants. (make-up to compensate blow-down). Water is then by-passed directly into the Cooling Tower. The result is that settlement of solid materials occur in the cooling system especially at spots where the required velocity is not achieved, causing severe pitting.

The same type of corrosion is experienced with the Ammonia condenser where cooling water on tube side is used to condense ammonia vapours from the second stage of compression on the shell side. Construction material is carbon steel ASTM A285 Gr C for the shell and ASTM A179 for the tubes.

Corrosion is most probably due to some electrochemical action perhaps coupled with microbiological action favoured by the slow replenishment of oxygen under the deposits. Presence of anaerobic bacteria has been detected.

(iii) <u>Solutions</u>

Since it is believed that the muddy deposits are responsible for corrosion in this area, a mixed-media pressure filter has been ordered to replace the gravity sand filter.

Meanwhile, the ammonia heater tube bundle is removed every three months for cleaning. This preventive action has doubled the life time of the tube bundle which confirms the noxious action of deposits.

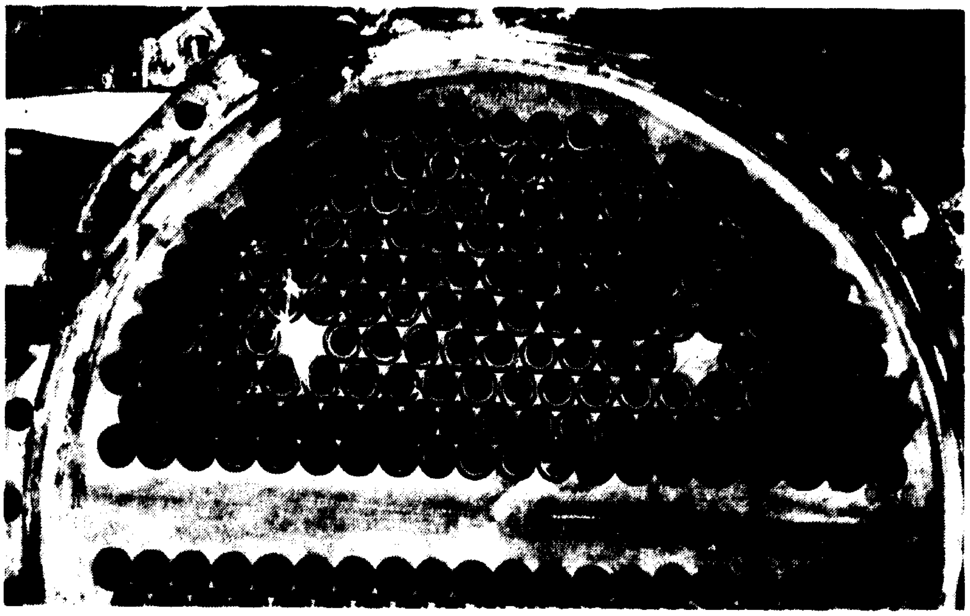
As regards the Ammonia condenser, when the pressure differential across the heater is higher than expected, the tubes are flushed by hosing with high pressure water in order to remove the sediments.

(b) <u>Miscellaneous Problems</u>

Other corrosion problems in this area result from rusting.

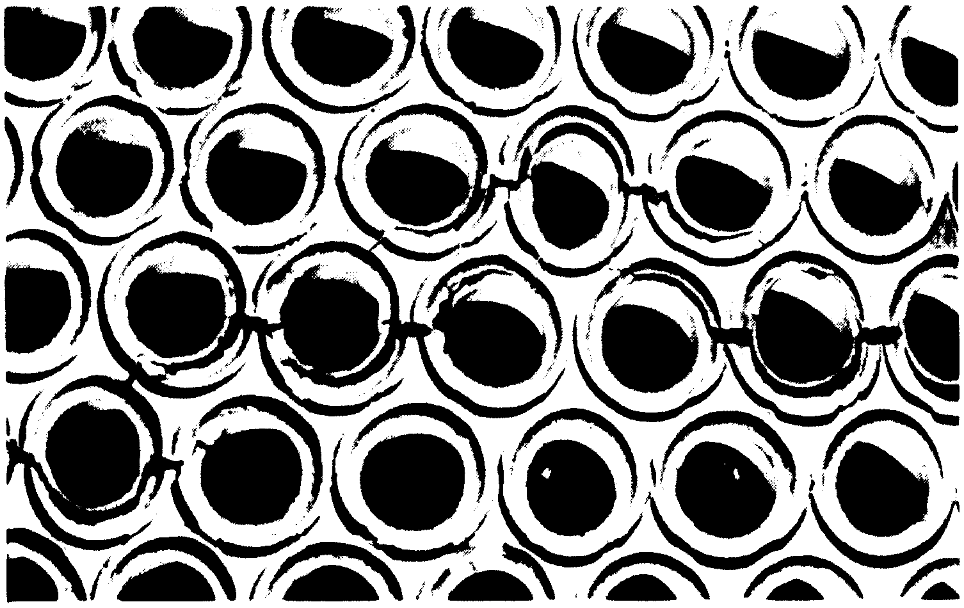
Being given the low temperature of liquid ammonia, there is ice-formation wherever valves or piping are not properly insulated. Dry ice would not be a problem. But during shutdowns the ice melts and the wet surfaces undergo heavy rusting. Problems are futher aggravated by the proximity of the sea.

However, these problems are more relevant to the choice of proper protective coatings than of materials.

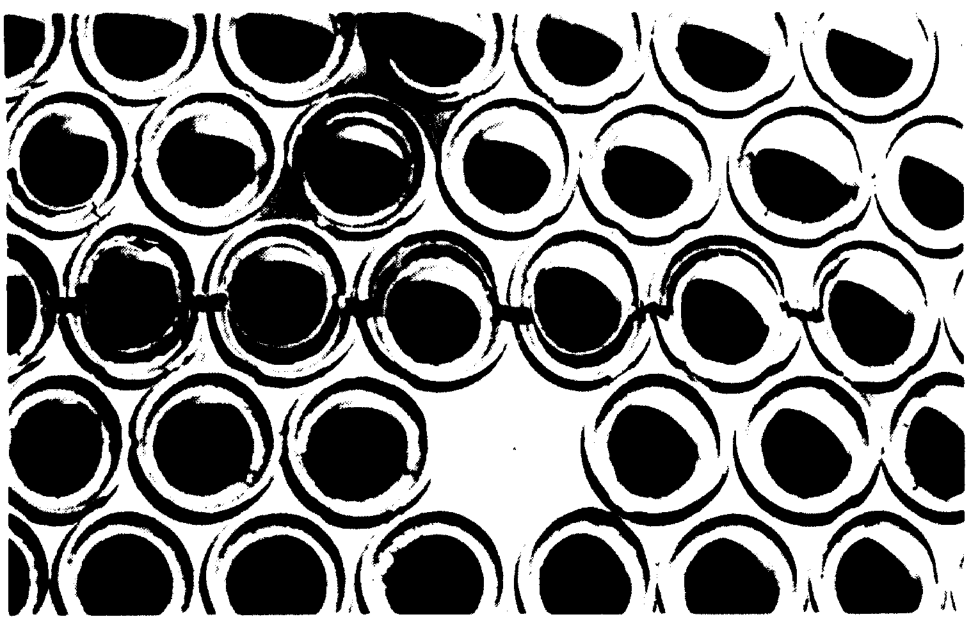


Cracked tube sheet of Tail Gas Reheater

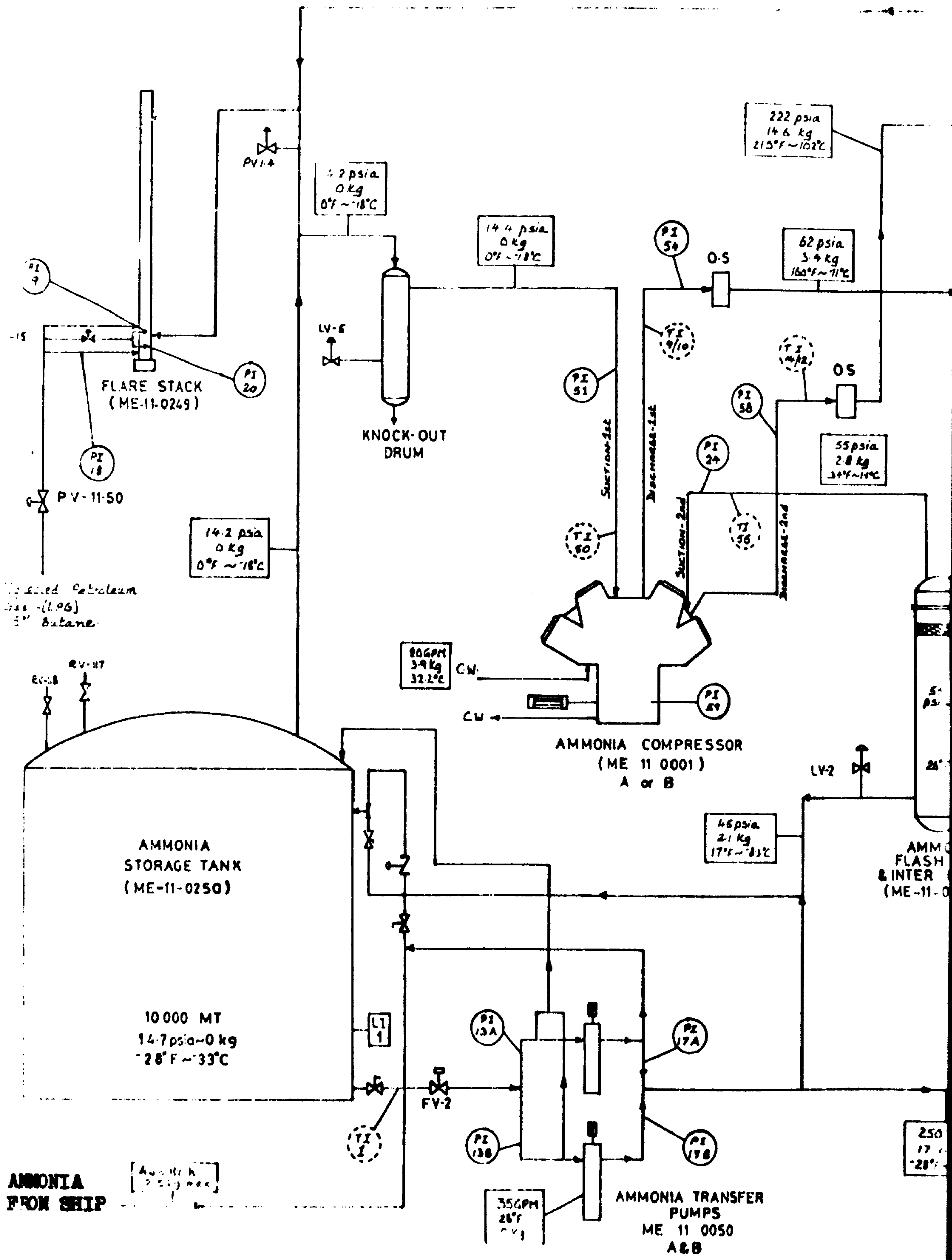
Tail Gas Tempering Heater: Holed Shell



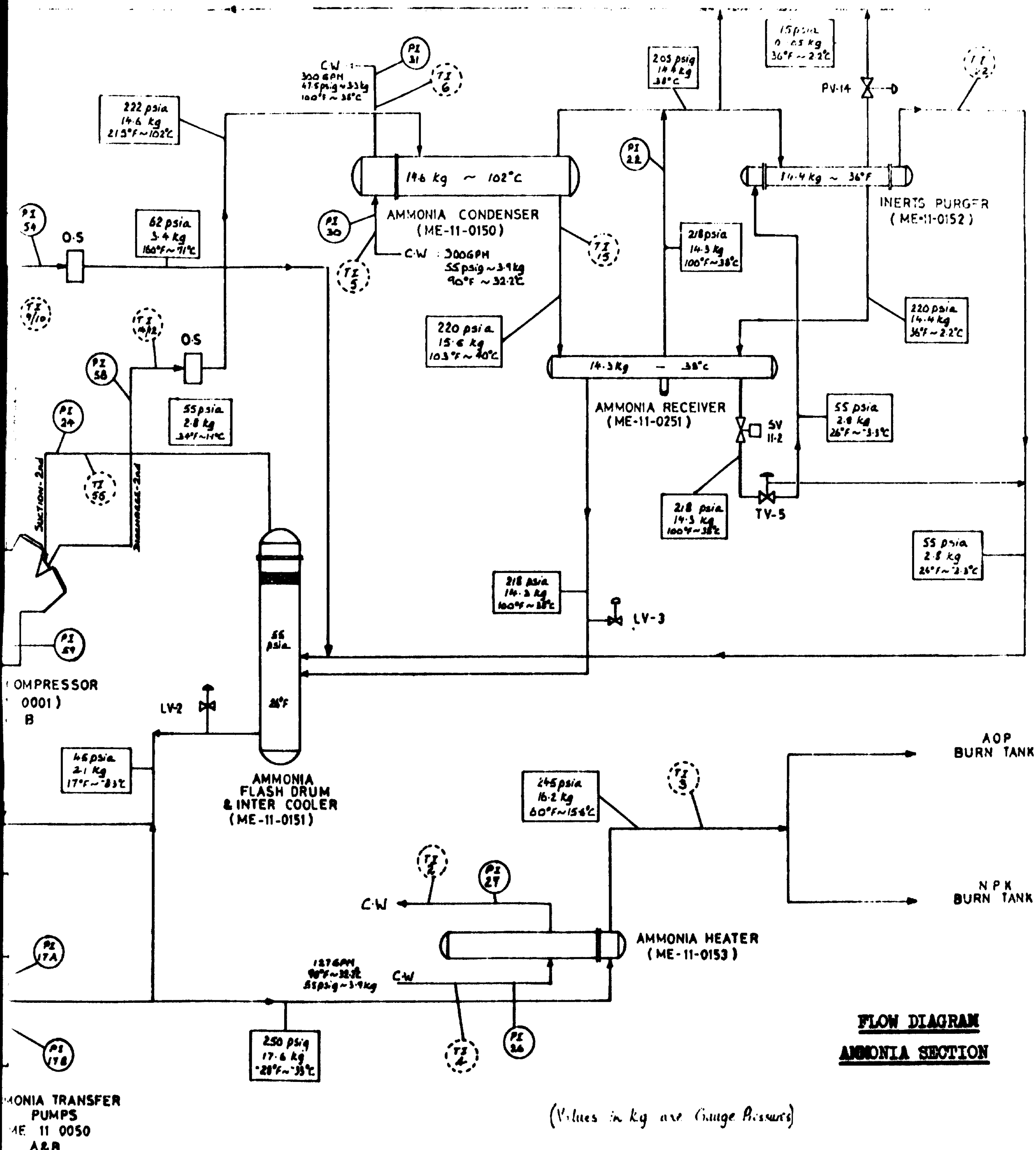
Cracked tube sheet of Tail Gas Reheater



Cracked tube sheet of Tail Gas Reheater


FLARE STACK
(ME-11-0249)
PV-14
PV-11-50
LV-6
KNOCK-OUT DRUM
14.2 psia
0 kg
0°F ~ -18°C
14.4 psia
0 kg
0°F ~ -18°C
222 psia
14.6 kg
215°F ~ 102°C
62 psia
3.4 kg
160°F ~ 71°C
55 psia
2.8 kg
O.S
OS
Suction-1st
Discharge-1st
Suction-2nd
Discharge-2nd
AMMONIA COMPRESSOR
(ME 11 0001)
A or B
C.W.
CW
LV-2
46 psia
2.1 kg
17°F ~ -8.3°C
Butane
AMMONIA
STORAGE TANK
(ME-11-0250)
10 000 MT
14.7 psia ~ 0 kg
-28°F ~ -33°C
FV-2
AMMONIA TRANSFER
PUMPS
ME 11 0050
A&B
35GPM
AMMONIA
FROM SHIP

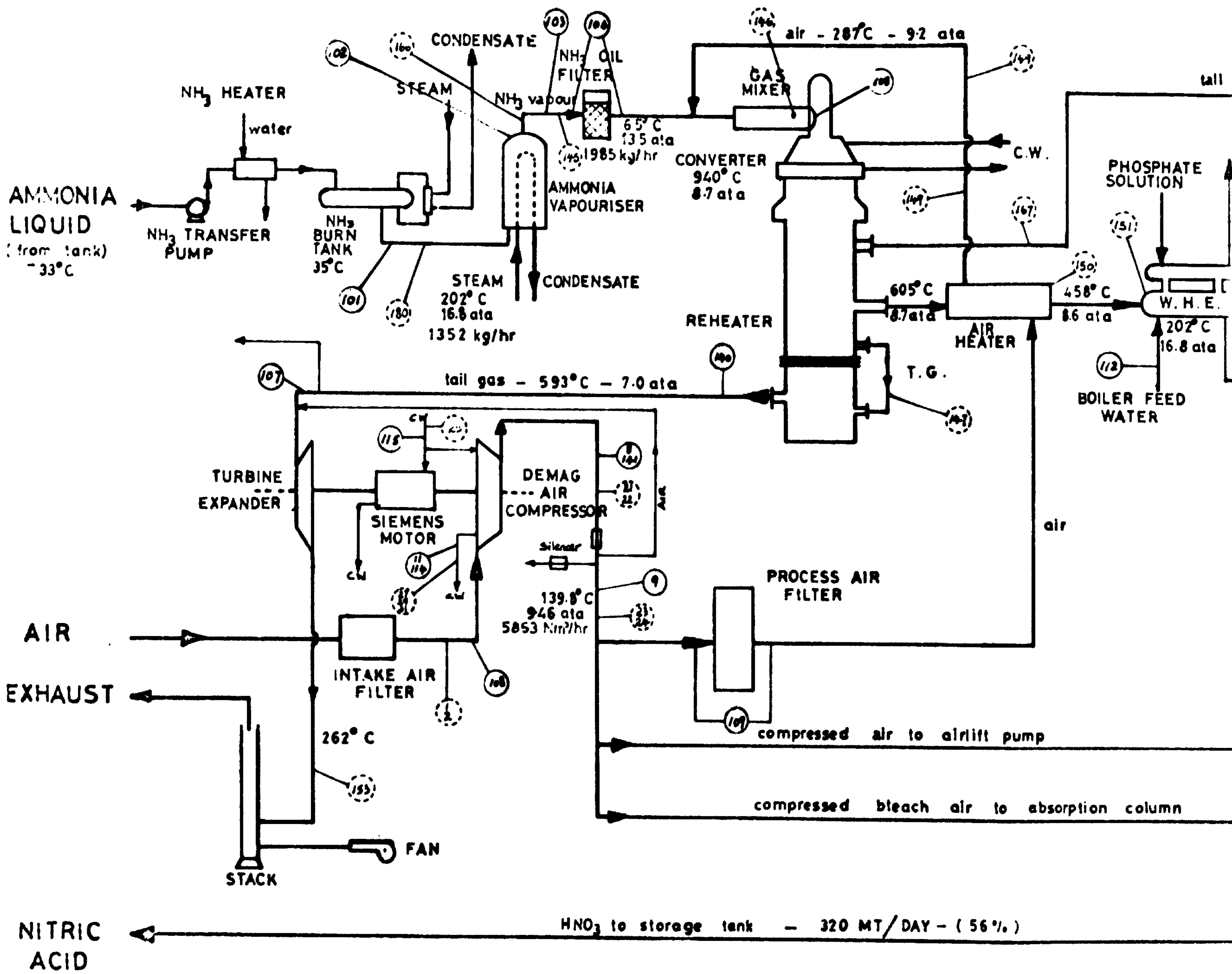
SECTION 1



FLOW DIAGRAM
AMMONIA SECTION

(Values in kg are Gauge Pressure)

SECTION 2

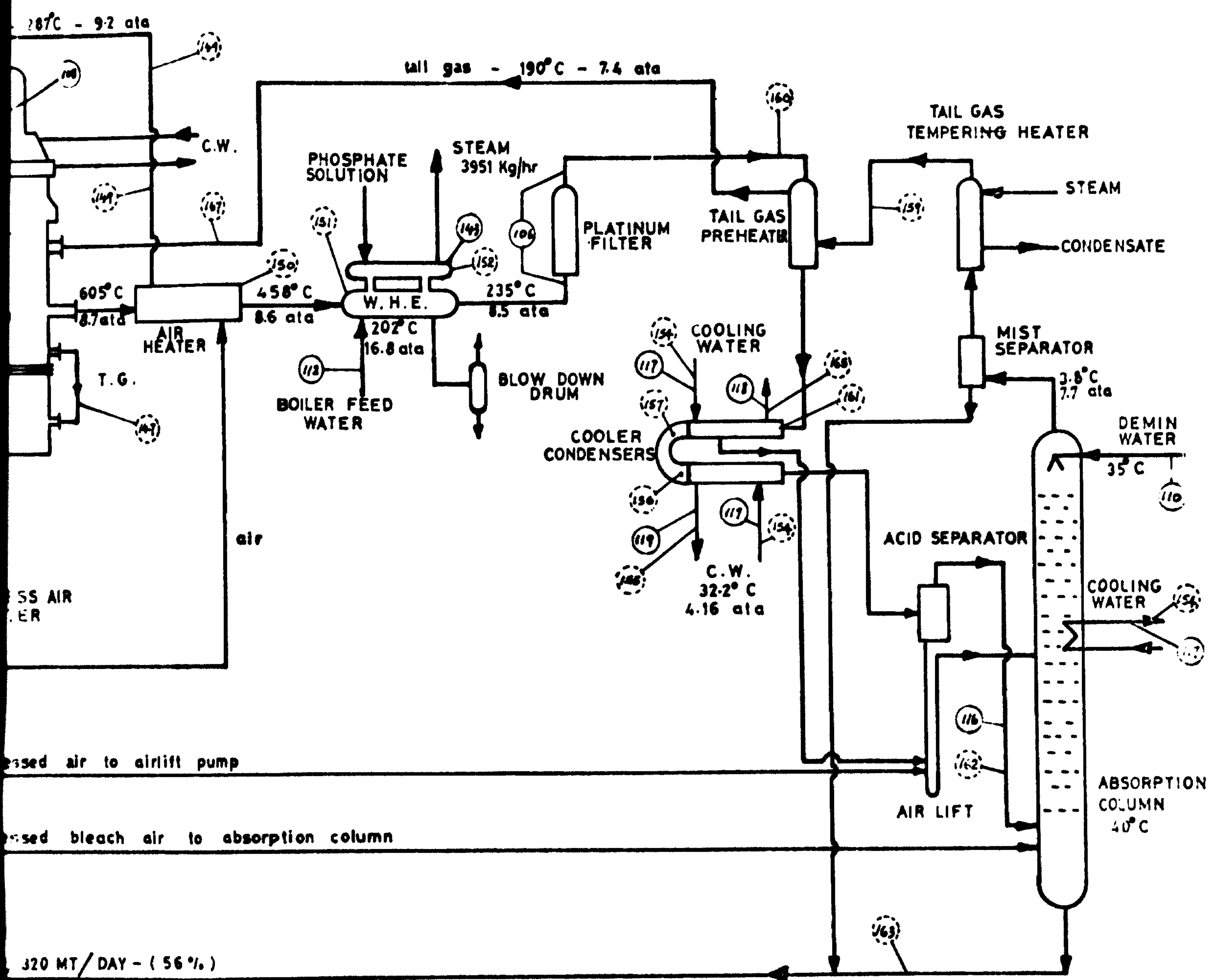


Notes: Converter Panel
1. Pressure Gauges: PIC 140
PIC 141
2. Temperature Gauges: TR 169
TIS 176
TIS 174
TR 175
TR 176
TR 177-178
3. Oil Cooler : C.W. In : TI 25
C.W. Out : TI 33-34

○ PRESSURE GAUGES

◌ TEMPERATURE GAUGES

SECTION 1



FLOW DIAGRAM

NITRIC ACID PLANT

(180 ST/D HNO_3)
165 MT

SECTION 2

A-151

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