



TOGETHER
for a sustainable future

OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.



TOGETHER
for a sustainable future

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as “developed”, “industrialized” and “developing” are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org



06712



Distribution
LIMITED

ID/WG.221/1
9 November 1975

Original: ENGLISH

United Nations Industrial Development Organization

UNIDO/FAI Interregional Meeting on Safety in
the Design and Operation of Ammonia Plants

New Delhi, India,
20 - 24 January 1976

Industrial safety

SAFETY IN THE DESIGN CONSIDERATIONS OF AMMONIA PLANTS
FACT EXPERIENCES AT COCHIN AND UDYOGAMANDAL PLANTS

(1975)

by

J. Chidambaram*

* Sr. Process Engineer, FAI Engineering and Design Organisation, Udyogamandal
Via. Cochin, India

1/ The views and opinions expressed in this paper are those of the author and do
not necessarily reflect the views of the Secretariat of UNIDO.
This document has been reproduced without formal editing.

We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards even though the best possible copy was used for preparing the master fiche.



06712



Distribution
LIMITED

ID/WG.221/1/SUMMARY
5 November 1975

United Nations Industrial Development Organization

Original: ENGLISH

UNIDO/FAI Interregional Meeting on Safety in
the Design and Operation of Ammonia Plants

New Delhi, India,
20 - 24 January 1976

SAFETY IN THE DESIGN CONSIDERATIONS OF AMMONIA PLANTS
FACT EXPERIENCES AT COCHIN AND UDYOGAMANDAL PLANTS 1/

SUMMARY

by

S. Chidambaram*

Some of FACT experiences in Cochin and Udyogmandal Naphtha reforming ammonia plants are listed as checklists of safety for future modern plants in India.

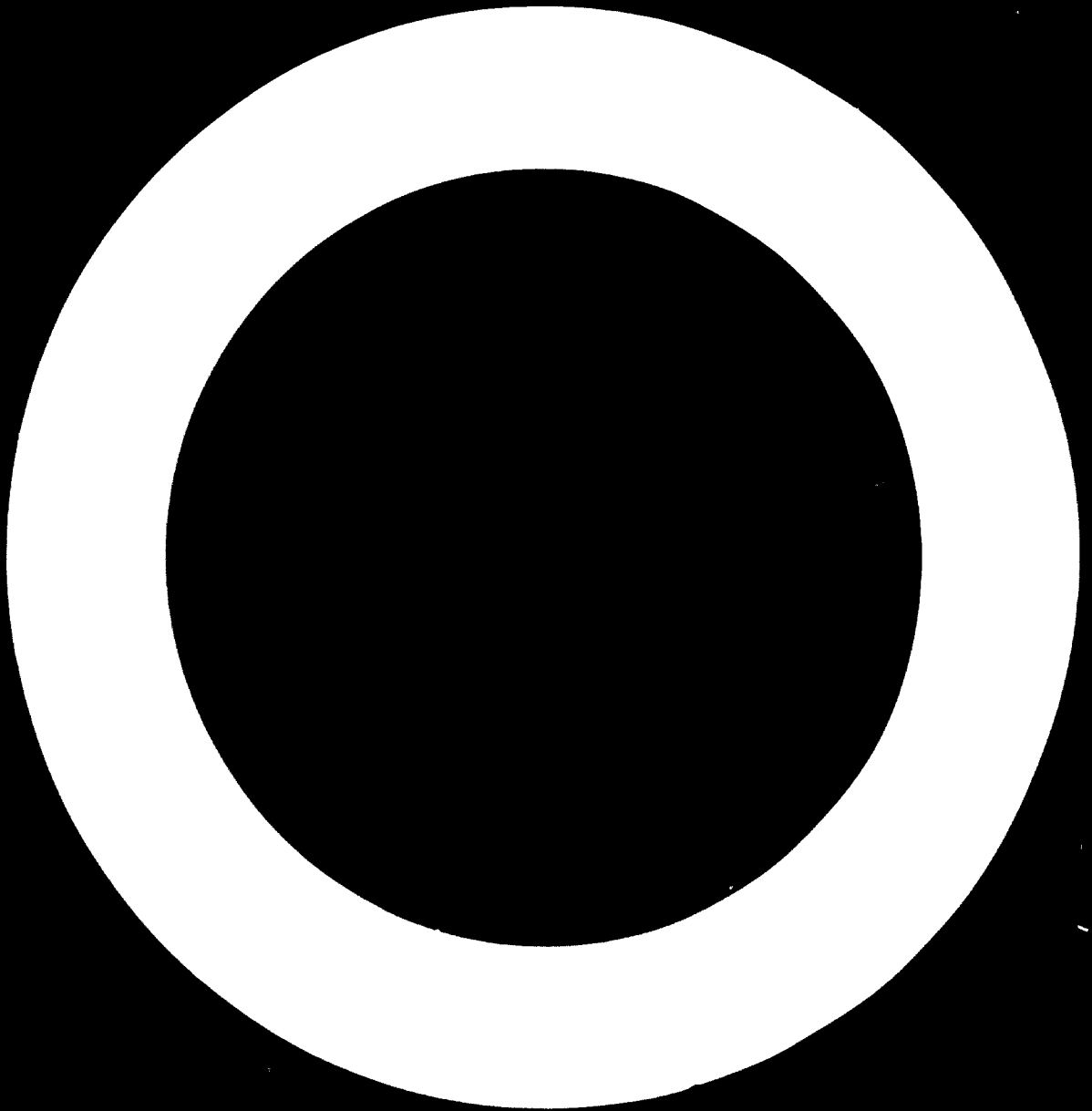
Due to improved high heat flux designs in superheater and boiler, Indian Boiler Regulations arbitrary design temperature basis of steam temperature - fixed constant was discussed as inadequate. The effect of wide turn down demanded from waste heat boilers, and silica migration with water carry over are mentioned for necessity of silica wash with feed water.

Reformer manifold material with cast instead of wrought high temperature steel is brought in the topic for safe substitution. The importance of using the layer refractory lining for hydrogen service is reproduced from IPI reports as many plants have experienced hot spots. Cochin experiences of burner performance in a high turbulent furnace, low steam production in synthesis loop due to insufficient insulation, NH_3 contamination in hydrofining, recycle hydrogen by the centrifugal compressor anti-surge water and cavitation in CO_2 solution pumps by dissolved gas RICH requirement are mentioned as consultation topics. A small suggestion to design reformer with steam/carbon ratio of 3.5 instead of 3 is made considering naphtha specification, LT activity and Benfield steam requirement.

* Sr. Process Engineer, FACT Engineering and Design Organization, Udyogmandal Via. Cochin, India

1/ The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the secretariat of UNIDO.

This document has been reproduced without formal editing.



1.0 INTRODUCTION.

Based on long experience in design, we have two operating Ammonia plants with 60,000 and 120,000 capacities. The latter plant was designed, constructed and equipped with some very advanced equipment. The 120,000 plant was engineered by Mitsui with Jeler - ICI. The experience gained in these plants has been below mentioned for safety in the process design of Ammonia plants in our country.

2.0 HIGH PRESSURE STEAM AND POWER RECOVERY.

The total energy concept with power recovery (1) has been found to reduce operating cost by implant steam generated at pressures between 100-135 kg/cm². This type of high pressure steam net work is of very specialised nature and are ordered with reputed boiler manufacturers. The only consideration, owner boilers is its statutory acceptance by Indian Boiler Regulations. Unfortunately Indian rules for waste heat boilers are inadequate in many respects and failures are not uncommon in the system if the owner does not pay attention to various emergency conditions and cross-check with other codes.

A typical example is the present free supply natural draft direct fired steam superheater for Cochin plant improvement. Figure 1 and Table 1 explain clearly that the design temperature as stipulated by I.B.R. in relation with steam temperature does not necessarily mean to be a safe condition for the equipment. It can be argued that API RP530 - 1 design code for direct fired heaters - gives correspondingly a lower thickness when $p = \frac{2.49t}{D}$ is compared with I.B.R. formula of $t = \frac{2.5(p - 0.6)}{S + 0.6}$ when S the allowable stress value is same. However, API RP530 limits the application to only above 50 mm dia and below this API or I.B.R. 301 gives much safer thickness when calculated with metal temperature as the basis of design conditions.

For convective type superheaters mounted in primary reformer flue gas duct, different type of problem arises. Normal NH₃ plants have the following heat recovery sources either as boilers or economisers:

- a. ...
- b. ...
- c. ...
- d. ...

However, to ensure reliability, care should be given to any means by which plant steam generating is lowered considerably, but to have a plant which can or to be back on stream quickly, various relief or operation is not considered, with this to ensure that in the emergency condition, as that of full operating conditions. The anticipated full temperature is to be calculated for the steam side and material thickness safety must be assured for this type of emergency. Simply designing for normal steam temperature may be a very dangerous condition to consider. Some of all some experience in this, would be able to estimate the risk involved with a reasonable probability and basic design on this (16).

In emergency, hollow out condition must be checked and avoided by suitably sizing the gas side heat exchanger for the production condition unless with process side condition more or less maintained.

Widespread 100% average stress to rupture at 10,000 hours as allowable stress at the design temperature. Babcock & Wilcox article (2) disagrees about this limit and considers from metallurgical point of view, a conservative design criteria must be used as an allowance.

3.0 BOLLER PERFORMANCE AND SILICA DEPOSIT IN TURBINE.

Wohin synthesis turbine performance visibly deteriorated due to silica deposits and washing with H₂ steam and condensate was necessary to restore its original performance. Figures 2 & 3 (3) and table 2 give data on silica solubility in steam and VBI specification on boiler water. For the operating pressure of 134 kg/cm² Wohin has boiler water quality in silica as 0.4 ppm and for this, silica volatility in steam should be limited to 0.01 ppm only. The high silica deposit was attributed to water carry over from different drums. The wide turn down demand and various operating conditions may probably be one reason for ineffective separation and water carry over. In such regular operation at low level was found necessary in the drums.

Another condition that may contribute to higher silica in steam may be pH lower range operation in the stipulated 9-10. Without caustic injection, it was found not possible to operate at high pH. Its use is still disputed even though the supplier has recommended it for pH adjustment. Synthesis gas drum supplier recommend NH₃ injection, but its quantity and proportional loss with steam will affect turbine condensing parts and hence could not be tried.

We can only conclude that in selecting the high pressure waste heat boiler between 10-134 kg/cm², silica problem must be given due importance unless feedwater silica wash is incorporated in the drum as a mandatory item.

4.0

It is suggested that some of the following other items are more and more important in the reports for proposed data.

Reformer materials: Most of the refractory alloys are offered as cheaper alternatives to wrought steels (ASTM A 213 (2.5) for semi-old material). However, they are still to be used in silicon burners. The following are the main points to be considered: Variation of surface area, porosity, etc. due to the variation in embrittlement and the use of the same material for different cross-sections of high temperature. The material should be of the method of test and will vary. The maximum allowable stress should not be the stress of the material. The material should be Miller process. The refractory material should be of the thickness (10) with allowances for expansion. The material should contain only 7% of the metal impurities.

CO has used 1/2% of the total gas for H₂ hydrogen plant and this has caused a number of operational difficulties and many shutdowns.

Refractory lining: According to the report, the boiler, pool place and transfer lines are the weak points in the system, which have caused many shutdowns due to frequent hot spots. There are many variations and methods of lining with each one of them to the responsibility of the consulting firms. It is worthwhile to adapt the report of the lining as minimum requirement. It is highly recommended that the selection must give suitable attention to CO's recommendations.

A typical pool place data is given in Table 19. It is reproduced as Figure 4 & in Cochran. Modifications in these lines are being carried out.

5.0 FURNACES

Cochran has an auxiliary combustion chamber after primary reformer coffins to satisfy the steam network heat balance. This type of furnaces are to be compact to ensure those remaining for completing the combustion, are to have high turn-over, firing flexibility and are to withstand the high hurricane wind loading from primary coffins.

For most of the services with 80% mechanical/air atomized combustion, normal test book firing volume of 2.5 x 10⁶ kcal/h.m² are found quite adequate, but in this service, furnace effective volume is determined by the type of burner and other aerodynamic considerations (15).

Cochran has 80% burner fitted with air side swirlers for spread out flame to confine in effective volume. But due to the heavy eddies, the whole combustion chamber is turned to have flame box with severe damage to burner tips, swirler, quartz block, refractory and mortar. Presently it is planned to be replaced with jet flame characteristic burner with increased length of flame for its resistance against

high inside turbulence. This is a problem for 600 mm. For after combustion studies the results are not satisfactory by other suppliers.

Correct specification of furnace conditions must be prepared for this type of combustion burner for finding the suitable burners.

6.0 LT CATALYST FOR DET. OF

Most of the catalysts contain sulphur, chlorine and arsenic. These poisons here in catalysts are not a detriment on of LTS is noted due to these poisons and will request next stage. The effect of activity deterioration as reported by Topsoe (14) is given below:

	20% approach to design librium conversion	S/C	
		Ar.	CH ₄
Design case	40	0,29	1,60
LTS 75% active	70	0,29	1,12
LTS 50% active	100	0,29	1,47

In a typical kinetic study for deciding allowance of LT volume, it was found that it is worth to base primary steam/gas ratios at 3,5 instead of 3,0 for the following reasons:

1. Naphtha feedstock specification given by refinery always for worst crude derivative like heavy oil. These 2,0% HPI naphthas have increased specific gravity and aromatics before and after hydrofining and stripping by dehydrogenation of naphthanes. Thus PCMA analysis on aromatics will be minimum 26,5% Vol. for which reformer catalyst loading need be reduced from 1 to 0,7 Tn naphtha/hr.m³ catalyst (15). Thus the number of reformer tubes are controlled by catalysts volume and not for heat flux consideration. The investment difference between S/C of 3 & 3,5 will not be appreciable.
2. Incorporation of quench vessels for increasing steam/gas ratio at downstream has given many mechanical problems and failures due to 'wind and water' interface (15).
3. LTS catalyst cost constitutes approximately 35% of total catalysts in NH₃ plant. For a typical 2,8% to 0,3% CO conversion, operation at S/C 3,5 requires 7,27 m³/100 TPD NH₃ and S/C 3,0 require 8,1 m³/100 TPD NH₃ (15). LT Catalysts.
4. For a typical split flow single stage regeneration (with no flash cooling) Benfield system, operation with S/C of 3,5 alone will satisfy the regeneration efficiency of 0,45 Nm³ CO₂/Kg steam.

It is noted that modern plants on a similar basis, with 100% liquid ammonia, will probably allow the plant performance to be 10% better.

7.0 AMMONIA PURIFICATION

Ammonia purification is a significant factor in the higher ammonia content of the gas, and is particularly important when the gas is used for the synthesis of urea. The purification of ammonia is a well-known process, and is described in detail in the literature. The ammonia purification process is described in detail in the literature, and is particularly important when the gas is used for the synthesis of urea. The ammonia purification process is described in detail in the literature, and is particularly important when the gas is used for the synthesis of urea.

8.0 ANTI-SURGE CONTROL OF AMMONIA SYSTEM

Urea has a single anti-surge system for combined synthesis and recycle compressor similar to ref. (16), with a small cushion of manual loading station between the synthesis and recycle discharge lines. As these gases are to go to chillers combined for stripping carbon oxides, it was considered that they can be connected at compressor discharge itself, after anti-surge tripping. However, such an arrangement caused NH₃ to seep into the low pressure stages and to recycle hydrogen through anti-surge line during compressor unloading operations. A double anti-surge system is ideal or an isolation loading valve may be an alternative to avoid this problem.

9.0 NH₃ CONVERSION LOSS

A brief sketch of Uoshin NH₃ converter is shown in Fig. 5. The internal boilers are designed to recover 1.58 lb steam/lb NH₃ with feed water at 200°C. But in actual operation, 1.1 is the maximum attained figure and any attempt to reduce the converter exit temperature by boiler valves resulted only in thermal level adjustment in catalyst beds with no effect in steam production recovery.

It is attributed to insufficient insulation over the Recuperator exchanger as shown in Fig. 6 as the cause of this problem. As a part of plant operation improvement, for example, another gas to gas exchanger in series outside mounted is proposed, so that the design steam production rate can be achieved.

Another interesting disparity noted is the equilibrium NH₃ vapour content and dew point. This gives a higher figure than used by the process designer. Uoshin operation and load on refrigeration loop suggest that literature data is more reliable. It is noted to note each factor in sizing the refrigeration loop so as to avoid ending with a very tightly designed loop.

10.0 CONCLUSION

A brief sketch of Urea plant design, in the points listed by UNIDC/IAS experts, with 100% experience is attempted in this article.

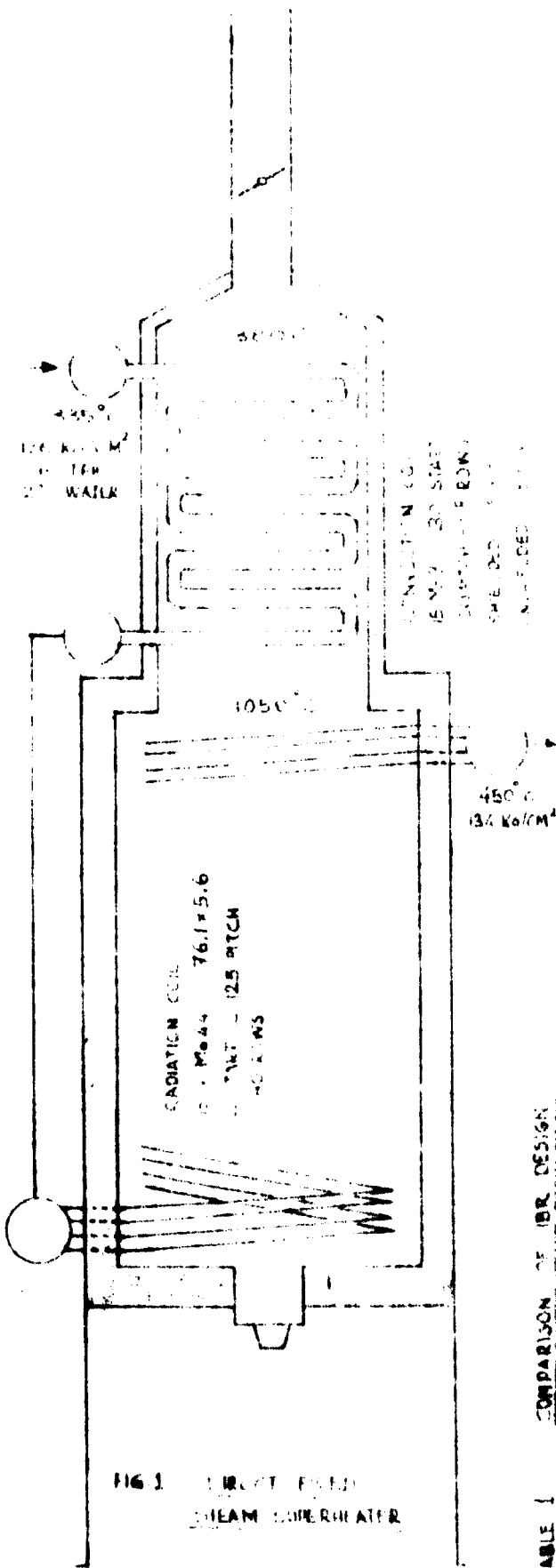


FIG. 1. PROJECT FILED
STEAM SUPERHEATER

TABLE I. COMPARISON OF IBR DESIGN
WITH ACTUAL PERFORMANCE

POSITION	STEAM TEMP.	IBR DES. DESIGN TEMP.	CALCULATED METAL TEMP. AT DESIGN PRESSURE	APPROXIMATE % REDUCTION IN ALLOWABLE STRESS VALUE
SHIELDED COILS	325	315 + 39 = 374	352 + 55 = 407	4
UNSHIELDED COILS	355	355 + 50 = 405	404 + 50 = 509	26
RADIATION COILS	450	450 + 50 = 500	470 + 55 = 531	22

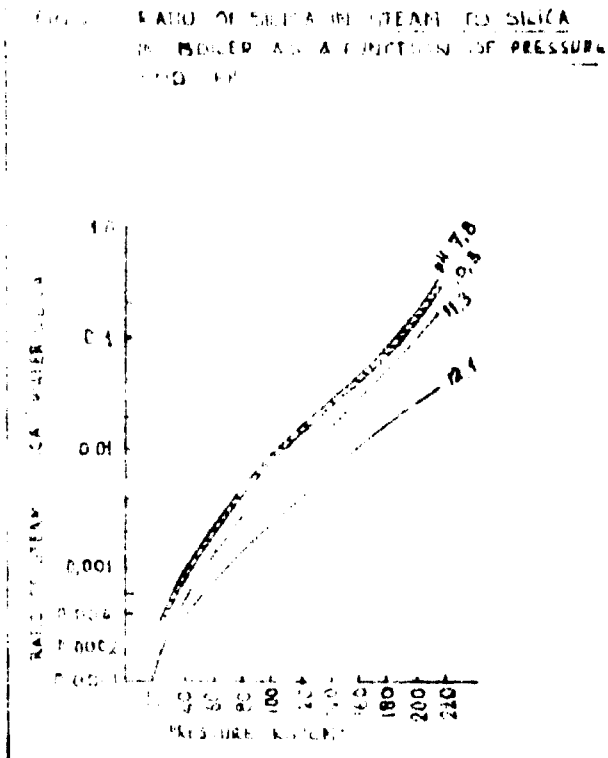


TABLE 1: GERMAN BOILER WATER SPECIFICATION

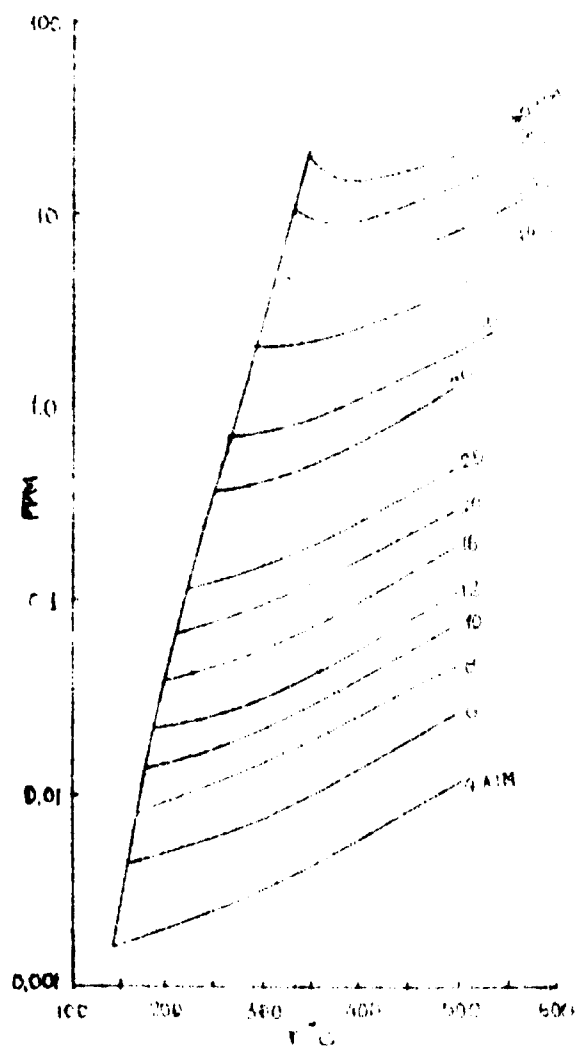


TABLE 2: GERMAN BOILER WATER SPECIFICATION

PRESSURE BAR	64	80	110	125	716.0
CONDUCTIVITY AT 25°	<2500		300		<50
P VALUE $\mu\text{val/lit}$	0.1 to 1.0				4.0
PH VALUE AT 25°C	10-11	9-10.5			10.5
SiO ₂ mg/kg	<9		<1.8	<1.2	1.3
PO ₄ mg/kg	<15		2 To 7		

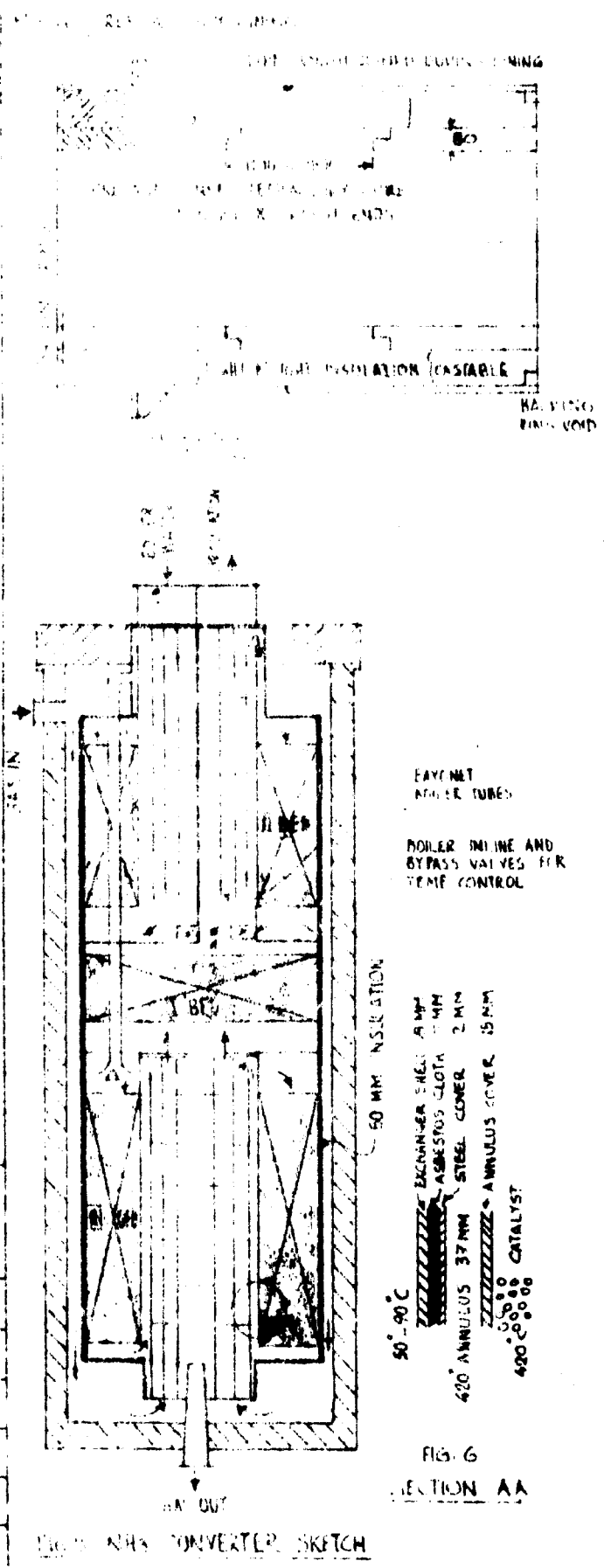
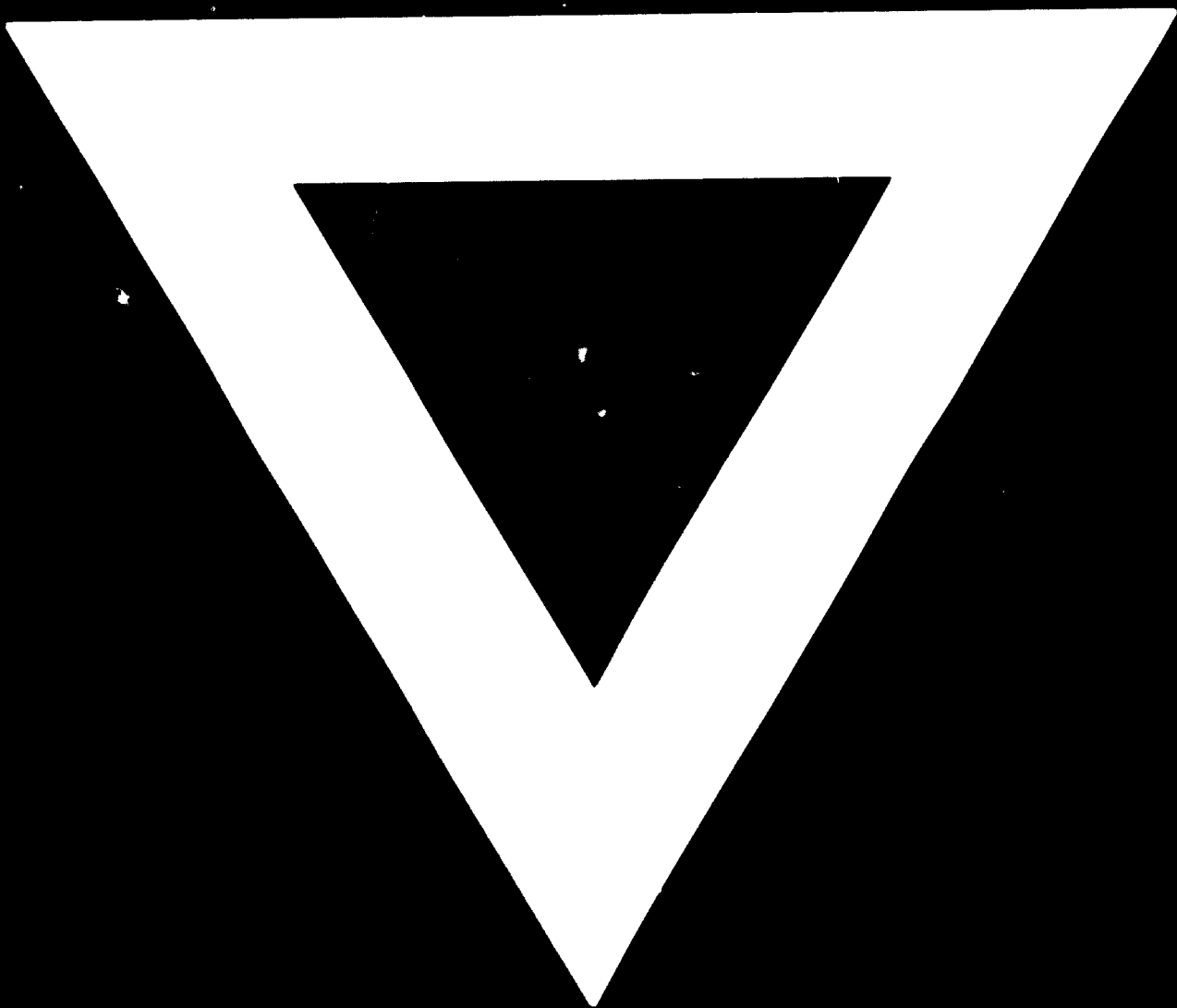


FIG. 6 NH₃ CONVERTER SKETCH

- 1 -

REFERENCES

1. Energy Recovery in NH₃ synthesis plants - Mr. Nimzo - Davy Power Gas - The Chemical Engineer - London July/Aug. 1967.
2. New creep rupture data on furnace tubes - Fr. Thomas W. Krebs - Babcock & Wilcox - HCP & PR - Aug. 1962.
3. Causes and cures for silica deposits in steam turbines - Mr. John S. Schre - HCP & PR - Dec. 1972.
4. New materials of construction for steam hydrocarbon reforming service - Mr. S.N. Anant Narayan - Fertiliser News - June 1975.
5. Thermalloys' - Lloyds brochure book.
6. High pressure hydrogen with special reference to material of construction - Chemical Engineer - Nov. 1975.
7. Case history - Failure of steam CH₄ reformer furnace - wrought material recommendation - Shell Oil Co. - HCP & PR - May 1971.
8. Reformer manifold cracking - CEP - March 1969.
9. API Report - Piping design for hydrogen service - Esso Research And Engg. Co. - HCP & PR - May 1967.
10. Catalyst tubes in primary reformer furnace - Kellogg - CEP July '70.
11. API Report - H₂ plant shut down reduced - HCP & PR - May 1972.
12. Preventing flange fires - ICI - CEP - August 1969.
13. Airoil brochure EE/00/02 on furnace effective volume.
14. Catalytic processes and Ammonia plant - Topsoc - CEP Oct. 1967.
15. Private communications with various catalyst manufacturers and recommendations for HACP plants.
16. The use of centrifugal compressors in ammonia production plants - QuisJerni Pignone 9 - Dec. 1967.
17. Find NH₃ recycle gas equilibrium - Snam Progetti - HCP & PR Dec. 1970.
18. Furnace rating procedure - Oct. 1963 - HCP & PR - R.N. Winbress - C. F. Braun.



76.01.16