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Distribution LIMITED 1D/W0.221/4

2 December 1975

Original: ENGLISH

# United Nations Industrial Development Organization

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

New Delhi, India 20 - 24 January 1976

# SAFETY CONSIDERATION IN THE DESIGN OF AMONIA SYNTHESIS LOOPS 1/

by

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# TAPETY CONSIDURATOR IN THE ISSIGN OF AMMONIA STAPHESIS LOOPS

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L. Mand\* L. Sunderland\*\*

The paper will be about 2 000 words in length and will consist of the following sections:

Introduction

This section will mugaly define the operation conditions of unmonia loops and mertion a recent survey on the causes of annumbia plant shutdowns.

Process Description

Sketches of a typical ammonia synthesis loop and a modern converter lesign will be attached to the paper. This section will give a prief description of the process and will indicate the differences between loops based on synthesis gas from a reformer and these from a Partial Oxidation Plant.

Safety Considerations

This section will give suggestions and recommendations on the safety aspects of design of ammonia synthesis loops. Subjects covered will be - process design, specifications, instrumentation, trip system etc.

Summary - A brief summary will be given • Lependal Chemical Industries Limited, Eillingham, United Kingdom

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### INTRODUCTION

The ammonia synthesis loop is potentially a very hazardous section of the ammonia plant. Besides containing a highly combustible hydrogen rich gas, the loop is operated at high pressure (from 150 to 330 atmospheres) and at a wide band of temperatures ranging from 500°C in the converter down to -20°C in the catchpot. Despite these formidable process conditions, serious accidents are rare on ammonia synthesis loops and the loop is only a minor contributor to downtime on a large modern ammonia plant. (1) There is, of course, still room for improvement on this relatively good past record and this can be accomplished by continuing critical analysis of operation techniques, maintenance procedures and - the subject of this paper - synthesis loop design.

### PROCESS DESCRIPTION

Before proceeding to consider the safety aspects of the synthesis loop design, a brief description of the process will be given. A typical flowsheet is shown in Fig.1 and a modern converter design

Synthesis gas containing 75% hydrogen and 25% nitrogen may be produced by a number of different processes. The most common of these is the steam reforming route but more recently, due to shortage and cost of suitable feedstocks, partial oxidation of fuel oil and coal gasification are becoming more widely used. The type of "front end" process used has little effect on the basic arrangement of the synthesis loop but may influence selection of process conditions and also the type of ammonia recovery system to be used.

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Reverting to Fig.1 (which shows a flowsheet developed for a partial oxidation plant) it can be seen that synthesis gas is first compressed in the synthesis gas compressor and then mixed with circulating gas at the suction of the circulator. The circulator is an integral part of the synthesis gas compressor and forms the last wheel of the final casing of the compressor. From the circulator, the combined gas is fed to the converter after being proheated is a paylos interclination.

The converter illustrated in Fig.11 is an 101 quench type converter. Gas enters the converter at the top and flows downwards through the annulus between the cartridge and the converter shell. The gas is then preheated in an internal exchanger before passing through a central tube to the top of the catalyst bed. As the gas flows down through the catalyst bed the synthesis gas reacts to form ammonia. Cold synthesis gas is introduced at two points in the catalyst bed by means of patented lozenge type distributors. The hot gas passing from the catalyst bed exchanges heat with incoming converter feed gas before leaving the converter.

The converter effluent gas is a source of useful heat and, in the flowsheet illustrated, is used to raise steam and preheat high pressure boiler feedwater. After this stage, heat is transferred to the cold converter feed gas in two gas interchangers. The residual heat cannot be usefully employed and is removed by, firstly, cooling in a water cooler and then by heat exchange with eveporating ammonia in a chiller.

The ammonia which has condensed during the cooling process is separated in a catchpot and then let down in two stages before passing to storage. One major difference between the loop lilustrated in Fig. 1 and a loop based on purified reformed gas is that the very low inert level of the

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synthesis and computed to confidence voluntary purge is not required from the confidence is maintained by passage of constructions to cooperath the asmonia product.

SAFETY CONSIDERATIONS

This section of the paper ontains suggestions and recommendations on the safe design of amounta synthesis loops. It is recognised that there are effect a provide agreements, even between memours of the same company, on requirements for safe design. It must be stressed that the advice given here reflects the personal opinions of the authors and is not necessarily the view of their companies or of the sections of the basiness in which they work.

Safety in its widest sense will be considered in this section. This will include prevention of downtime as well as employee and equipment safety.

### A. PROCESS DESIGN

Modern annonia plants, using centringal compressors, have used a number of different and prim loop designs ranging from low pressure loops with extensive use of refrigeration to non-refrigerated loops working at high pressure and relying on water or a combination of air and water cooling. The choice of loop pressure for annonia plants using the steam reforming route has not been influenced by safety considerations and, indeed, there is no evidence to show that selection of either low or high pressure has any effect on plant safety for this type of plant. For the new generation of partial oxidation plant, however, there do appear to be grounds for using moderate loop pressures. This is because the combination of very low inert content systemetic ges and high pressure can result in high

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temperature in the first bed of the ammunia converter and potential consequent damage to catalyst and converter incornals.

On steam reforming based plants the point of addition or make-up gas is an important consideration in the design of the toop. The preferred point of entry is the liquid ammonia containing region between the second interchanger and the chiller. This is to prevent the formation of solid argonium carbanate "chokes" which can occur under certain conditions in the presence of moisture, CO<sub>2</sub> and gaseous ammonia. Ammonium carbamate is a stress corrodent towards certain steels and particular care should be taken to avoid formation in compressors, particularly those having impellers of rivetted construction. (2) For partial oxidation plants, when the gases have been through methanol wash and nitrogen wash plants, carbon dioxide and moisture should be absent from the synthesis gas and consideration may then be given to make-up gas addition at the inist to the circulator (which is the best point from process design considerations). This is the scheme illustrated in Fig.i.

### B. SPECIFICATIONS

When preparing equipment specifications it is essential to lay down a safe and consistent set of design conditions for the loop and ascoclated equipment. Some suggestions concerning design conditions are given below:

 All equipment in the loop should be designed for the same design pressure regardless of the fact that there may be an appreciable pressure drop around the loop.

- b) The low pressere units in the refrigeration system should be designed for an apple sample above no mail operating pressure. This is because there units work at subumblent temperatures and, on stoppage of the refrigeration compressor, pressures can use fairly rapidly due to heat gain from the atmosphere. The margin between operating and discharge pressure will allow some time to take action to prevent reflef valves fifting and, if annonia has to be vented, will cut down the venting rate due to the lower evaporation rate at the higher pressure.
- c) When specifying design temperatures it is important to consider the consequences of upstream exchanges (such as boiler feedwater heaters) operating at different loads to design. It is not sufficient to simply add a standard margin to normal operating temperatures.

Besides the specification of safe design conditions for equipment the vetting of vendor design and selection of material of construction is of prime importance. One serious failure of an ammonia loop exchanger has been attributed to material selection and defective heat treatment.<sup>(3)</sup>

# C. INSTRUMENTATION, TRIP SYSTEM, PIPING AND VALVES

This is an extensive area for discussion with regard to safety. Some of the more important safety considerations are discussed below for selected process areas of the ammonia synthesis plant. a) Catchpot/Letdown System

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It is essential to safeguard the low atcours letdown vessel against overpressure doe to plow through of gas from the catchpot. The relief value on the letdown vector base be capable of passing a all possible gas from all exits on the catchpot. Some companies have a level trip on the catchpot which closes the letdown values? on low level. If this is the case, this must be regarded as an additional precaution and must not affect the basis for relief value slzing given above. It should be stressed that the relief values are sized to deal with a maximum gas rate; the/will not deal with liquid displaced by the gas. It is advisable to include a high level alarm on the flash vessel.

It is recommended that the bypass value around the catchpot level control value should have the same characteristics as the main control value. In fact, our preference is to have two switchable level control values in parallel rather than a manual bypass value. One of the advantages of this arrangement is that it makes complete on line trip testing of this important safety system possible.

The catchpot should have a high level trip to protect the circulator against carryover of liquid ammonia. The level trips on the catchpot should be completely separate from the level controller.

Regarding the piping between the catchpot and the letdown vessel, it is recommended that this is all to high pressure specification, as it is not possible to predict with any accuracy how the pressure falls in this two phase flow region.

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b) Start-up Heater

Although this is only used occasionally and is sometimes designed for a shorter life than continuously operating heaters, it must be equipped and instrumented to the standards of continuously used heaters. For example, the heater must be protected by low flow or pressure trips on the fuel supply together with flame failure detection on main and pilot burners etc.

c) Synthesis Gas Compressor/Elrculator

It is understood that this machine is the subject of another paper but two points are worth noting here.

The machine must be tripped and automatically isolated and blown down on failure of seal oil supply so that gas blow from potentially failed seal does not enter compressor house.

The suction and interstage relief values must be able to accommodate gas passing back through the machine and through the antisurge bypass lines. The position of auxiliary equipment such as oil supply tanks, oil pumps, control lines and cables should be examined in relation to fire hazards.

### d) Refrigeration System

If the refrigeration compressor should trip out, it is advisable to trip the circulation flow around the loop. If this is not done, heat will continue to be transferred to the loop chillers and this may result in chiller relief values blowing and the loss of an appreciable amount of ammonia from the refrigeration system. It is however possible to design an ammonia loop to operate at part rate without the refrigeration system in operation.

The refrigeration system RV's must be able to handle chiller tube failures.

# e) Loop Cooler/Condenser

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if a water cooler exchanger is used in the loop it is ecommended that the low pressure side of the cooler is protected by bursting discs. These discs should be sized for the cooling water displaced by the flow of gas through both ends of a broken tube. The size based on water displaced is much greater than that calculated from gas flow alone.

## f) Loop Blowdown

To cope with emergencies such as leaks which have fired, a loop blow off should be provided sufficiently large to blow down the loop to the available purge nitrogen pressure as quickly as possible. When operating the blow off valve care should be taken not to depressurise so rapidly that the allowable differential pressures for the converter and other equipment are exceeded.

For circumstances such as loss of loop circulation, it is advisable to guard against possible overheating of the converter shell by maintaining a slow flow of gas through the converter annulus. This can be accomplished by depressurising slowly through the normal purge line.

### g) General

- i) Liquid ammonia lines which can be "blocked in" should be protected against overpressure due to thermal expansion by the installation of relief values. The possibility of ammonia hammer initiated by the too rapid closing of control or trip values should also be considered.
- ii) Vents from the ammonia synthesis section should not be combined with vents containing carbon dioxide to prevent the blockages due to the formation of ammonium carbamate. If the vent system is purged then steam should not be used as the purge medium for vents

containing ammenta. Trouble ammonia must not be introduced into the vent system as accumulation will undoubtedly occur followed by displacement of slugs of the bacuid into the atmosphere. Care should therefore to taken in the design that pump priming lines for example are returned to a liquid system or to a liquid ammonia dump vessel or other safe location in which evaporation can take place.

- III) In general the number of flanges in the loops should be minimised because if a leak does occur there is a good change that it will fire and production will have to be stopped. (4)
- Iv) Flange leakage can be largely prevented by steady operation of the loop and the avoidance of rapid temperature fluctuations.
- Quench converters of the type shown are generally stable and the instrumentation required is relatively simple by dynamic models do exist (5) in which loop stability can be examined.

### SUMMARY

Reliability and safety are of prime importance to all parties concerned in the design and operation of annonia synthesis loops. Surveys have shown that the standard is reasonably high in existing large annonia plants. However, efforts are being made and must be made towards further improvement. The purpose of this paper has been to give some indication of measures which can be taken at the design stage to further this aim.

### REFERENCES

- 1 G.P.Williams and J.G. Sawyer "What Causes Ammonia Plant Shutdowns?" Chemical Engineering Progress (February 1974)
- 2 Process and Catalyst News No.3 ICL Agricultural Division (June 1972)
- 3 H K Kurinen "Brittle Fracture of an Ammonia Synthesis Heat Exchanger" Ammonia Plant Safety - A C E P Technical Manual, Vol.13

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- R.A. Watkins "Preventing Ammonia Plant Fires" Amer. Inst. Chem. Eng. Safety in Air and Ammonia Plants Volume II.
- 5. A.D. Stephens Cambridge University Control Eng. PhD Thesis (1970).

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