OCCASION

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

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

DO3662

Expert Group Meeting on Transfer of Know-how
in Production and Use of Catalysts

Bucharest, Romania, 26 - 30 June 1972

ACTIVITY AND LIFE OF CATALYSTS FOR

THE PRODUCTION OF AMMONIA [1]

by

S. P. S. Andrew

Agricultural Division
Imperial Chemical Industries Limited
Billingham, Teesside, United Kingdom

---

[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 paper has been reproduced without formal editing.

id.72-3377

CONTENTS

Preface

The ammonia plant manager is more concerned about the life and reliability of the catalysts which form the heart of modern plants than he is about their initial activity, provided this is adequate. Yet there is no aspect of the technology of catalysis less quantified than life and the factors which determine it, and no phenomenon more open to being dismissed with the pseudo-explanation that the catalyst was 'poisoned' than an undesirably early loss of activity of a plant catalyst. In this paper many of the catalysts which are required in modern ammonia plants will be considered with particular reference to their activity and life, with the aim of showing how the catalyst manufacturer, through a knowledge of the structural changes which take place in catalysts over long periods of time in use, can so formulate his products and recommend to the plant operator the optimum conditions for their use that they are better able to retain their activity over years of ammonia production.

I. CATALYSTS FOR AMMONIA PRODUCTION

1. The process unit sequence employed in ammonia synthesis (Fig 1) consists essentially of three synthesis reactions, each preceded by the appropriate gas purification operations which are designed to reduce greatly the concentration of components which would otherwise cause rapid deactivation of the synthesis catalysts.

Fig 1 The Modern Ammonia Synthesis Route
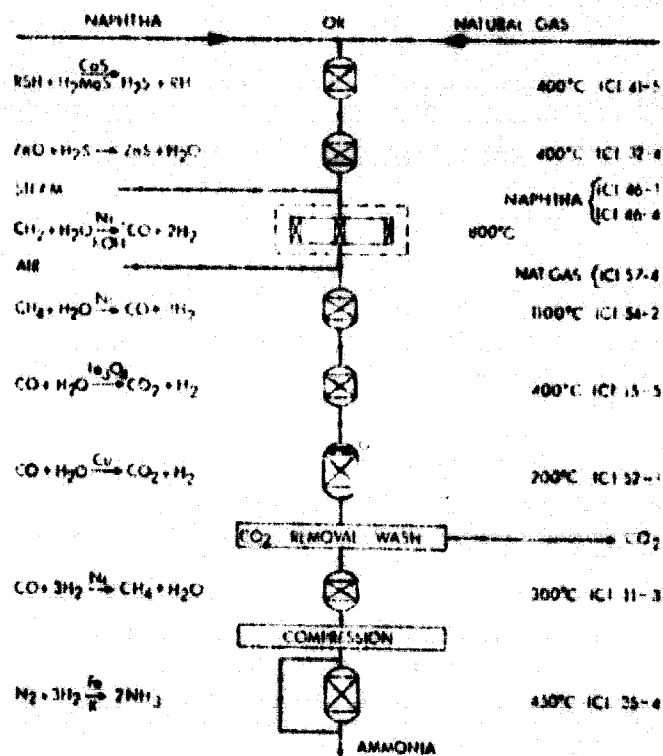
2. Thus the production of CO and H_2 from naphtha in the primary and secondary reformers is preceded by feedstock desulphurisation. During desulphurisation sulphur is liberated as H_2S by hydrogenolysis of the sulphur-containing species in the feedstock using hydrodesulphurisation

catalyst, followed by removal of this H_2S by reaction with solid ZnO to form ZnS. The efficacy of this removal crucially affects the performance of the primary reforming catalyst, so that the duty of the desulphurisation section is determined by the sensitivity to sulphur of the reforming catalyst.

3. It has been recently discovered that the life of the low temperature shift catalyst, used for converting CO to H_2, is markedly influenced by the presence of halogens in the gas stream. A halogen guard absorbent is therefore, on modern plants, often inserted before the low temperature shift catalyst.

4. It has long been known that oxygen-containing compounds, if in excess, cause rapid loss of activity of the ammonia synthesis catalyst. The methanation stage immediately preceding ammonia synthesis is the means by which CO_2, and even more important, CO are removed.

5. Because of these relations between synthesis catalysts and purification operations this paper will consider each of the synthesis catalysts in turn and the manner in which its activity and life are affected by poisons. The requirements of the appropriate purification operations, and the catalysts used in them, are then sketched with particular emphasis on recent developments in both stages. Naturally in a paper as short as this only highlights can be included, chosen from the vast quantity of information accumulated over the decades by the author's organisation whilst both making and using catalysts for ammonia production.

II. STEAM NAPHTHA REFORMING

6. **The discovery** that a sufficient addition of potash in an available form enabled a supported nickel catalyst to be capable of steam reforming naphtha at low steam ratios was made in 1959 and revolutionised the gas-making stage in ammonia production for localities where natural gas was not available. The mode of action of this catalyst (ICI 46-1) is shown in a simplified manner in Fig 2. The ability of this catalyst to operate without carboning up is obtained not so much by inhibiting the carbon-forming reaction (thought the non-acidic support used does not promote carbon formation)

Fig 2 Dual function action in Steam Naphtha Reforming Catalyst (ICI 46-1) required to suppress deactivation by carbon formation
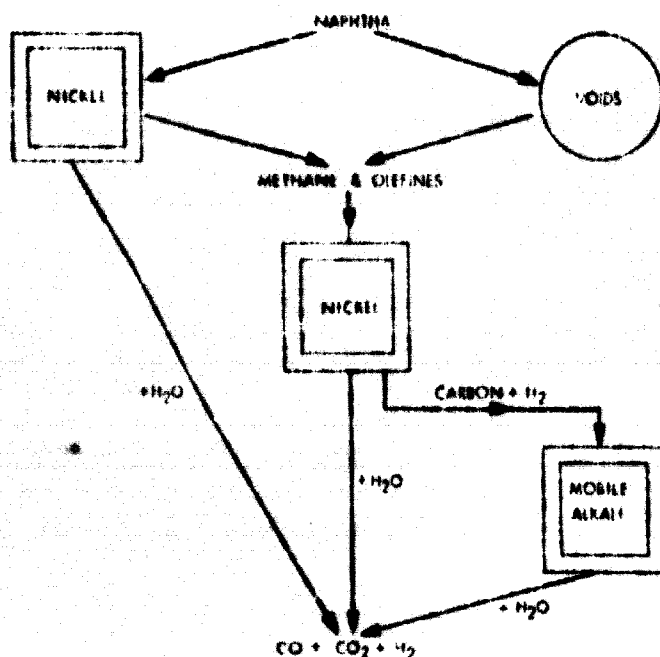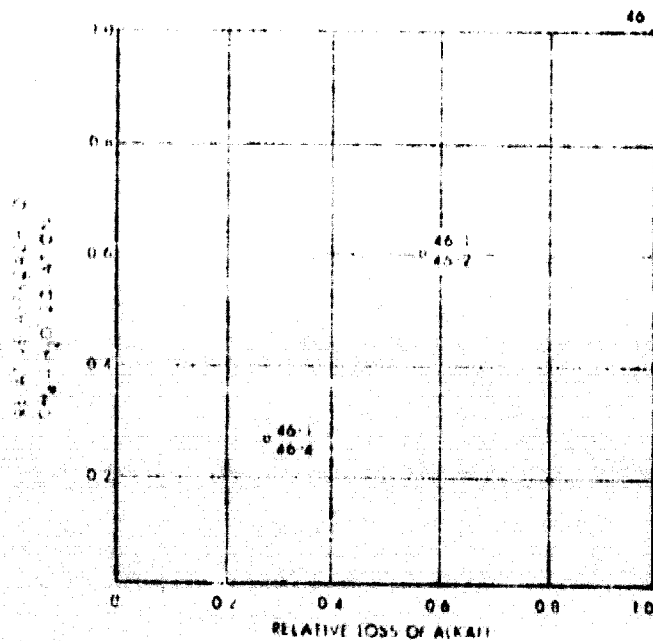

but rather by introducing a second active component into the catalyst formulation, mobile alkali, which serves to catalyse the steam oxidation of any carbon that does form. Although both alkalies and alkaline earths have been shown to be capable of catalysing the steam oxidation

of carbon when they are intimately mixed prior to reaction, the alkaline earths are refractory and are not capable of self mixing, by diffusion, with carbon forming on a nickel surface. Potash, at the temperature of steam reforming, is, however, able to do so. This is the likely cause of its unique efficacy.

7. The necessary mobility of potash in two dimensions unfortunately results in some mobility in three dimensions. The potash slowly vaporises and passes out of the reformer, on occasions depositing in the waste heat boiler or the inlet of the high temperature shift catalyst and in time reducing the performance of these units so that ultimately they must be cleaned. The potash also tends, by obscuration, to reduce somewhat the activity of the nickel surface for methane reforming. During the past ten years, means have therefore been sought of overcoming these disadvantages without losing the proven good abilities of 46-1 in steam naphtha reforming. A dual catalyst system employing catalyst 46-1 in the top (inlet) part of the reformer tube and a non potash-evolving catalyst in the lower part of the tube has been shown to be the preferred method. A combination of ¾ tube of 46-1 and ¼ tube of 46-2 has been used for several years for this purpose. Recently, as a result of further research, a combination of ½ tube of 46-1 and ½ tube of 46-4 has been developed. Fig 3 shows that as a result of these innovations it is now possible to reduce potash evolution to about one quarter of that for 46-1 alone, whilst at the same time reducing the approach to the methane-steam equilibrium at the exit of the reformer tube by about a factor of four.

The hydrocarbon pyrolysis reactions have a markedly higher activation energy than the uncatalysed steam gasification reaction, in consequence high temperatures favour carbon build-up. This feature is illustrated on Fig 4, which very roughly indicates the relative rates of carbon formation and carbon removal for a range of hydrocarbons as a function of temperature for both uncatalysed and potash catalysed carbon removal reactions at low steam ratios. The addition of potash, it will be seen, increases the carbon removal rate at temperatures above $525^{\circ}C$ at least one thousand fold. Below $475^{\circ}C$ the effect of potash rapidly decreases and is small at $400^{\circ}C$ because of its low mobility at these lower temperatures.

9. For methane reforming the formation rate line intersects the uncatalysed removal rate line at about $660^{\circ}C$ showing that provided the methane concentration is reduced in the steam reforming below the carbon-methane equilibrium partial pressure before the reforming gas mixture reaches $660^{\circ}C$ then carbon build-up should not occur on a non-potash containing catalyst. With higher boiling point hydrocarbons this critical temperature is, as can be seen from Fig 4, lower, and the requisite reforming activity is so difficult to obtain at the lower temperatures particularly in view of sulphur poisoning that a potash containing catalyst must be employed if long catalyst life is required.

Fig 4 Carbon formation and removal in the steam reforming of
hydrocarbons at low steam ratios
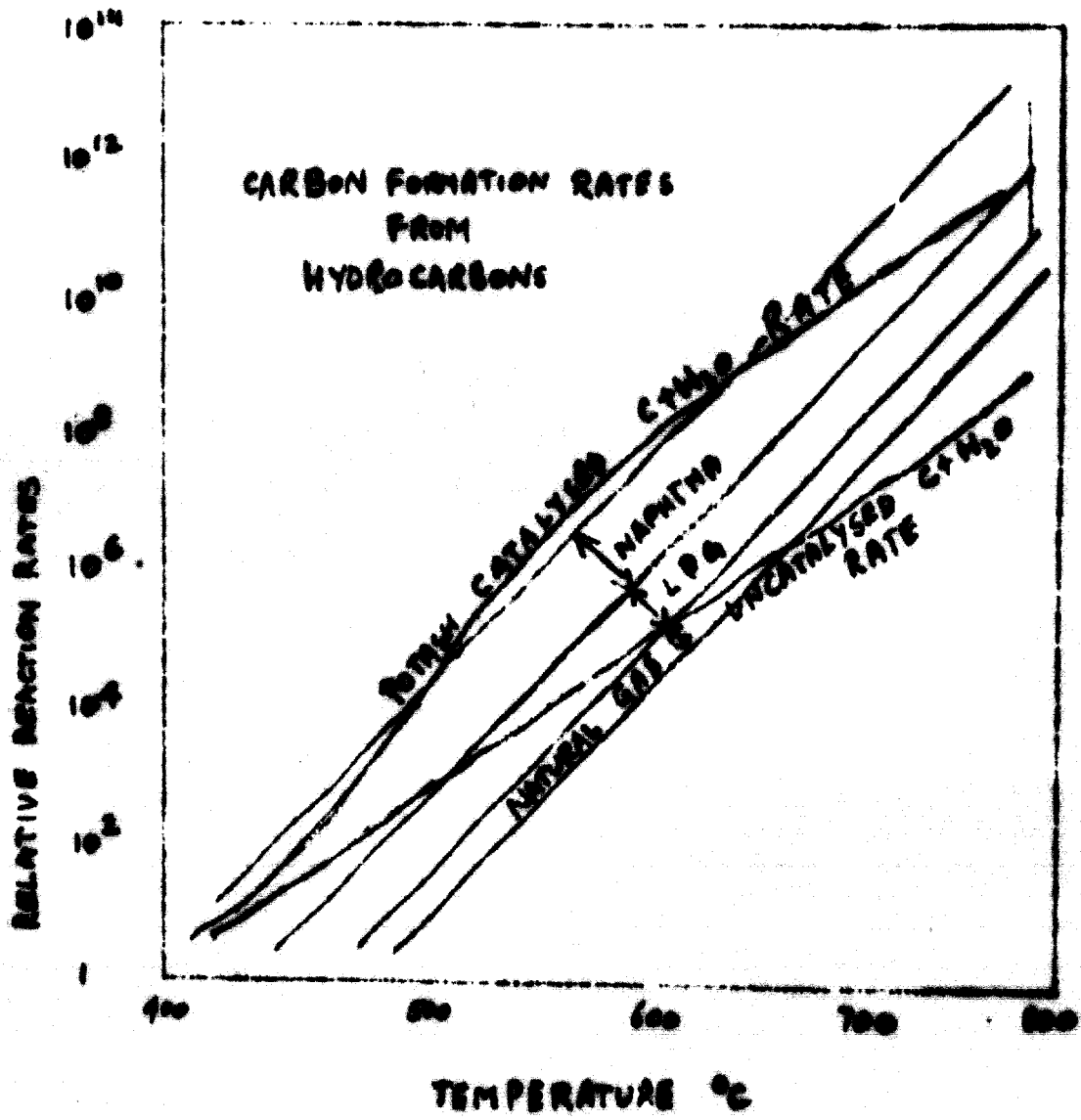
10. The necessity for using a steam reforming catalyst having a good low temperature activity when reforming natural gas or methane in the absence of potash catalyst is readily seen from Fig 5 which is plotted to demonstrate why 'hot bands' occur in reformer tubes when the catalyst is insufficiently active. Fig 5 is based on the methane pyrolysis equilibrium, $CH_4 \rightleftharpoons C + 2H_2$ plotted as a function of temperature, and the equal rate line where carbon deposition rate equals removal rate. If gas compositions anywhere in the reformer fall in the right-hand bottom corner of Fig 5 as defined by these two lines then carbon will be formed and will accumulate. With an inactive reforming catalyst the composition-temperature sequence down the reformer shown by the right-hand broken line is followed. Carbon formation occurs between $660^{\circ}C$ and $675^{\circ}C$ and a 'hot band' is visible on the reformer tube where the carbon acts as an internal insulant. With an active catalyst the composition-temperature sequence follows the left-hand broken line being well clear of the carbon formation region and hence no 'hot band' is formed.

Fig 5   Formation of a hot band in a methane reformer
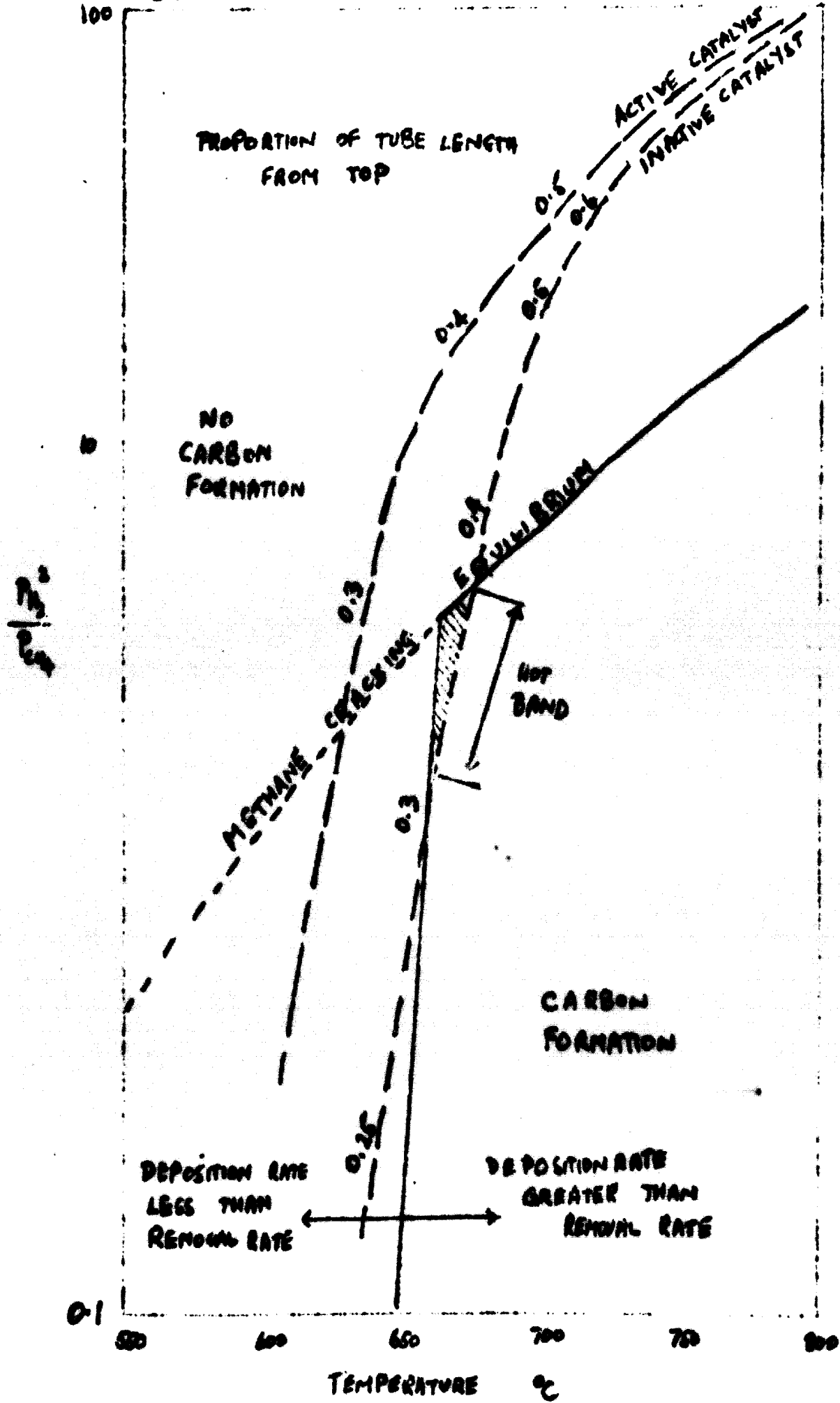
IV. DESULPHURISATION

11. Sulphur, either in the form of H_2S, COS or organic sulphur compounds is normally present in all hydrocarbon feedstocks for steam reformers and must be removed down to low levels as it poisons the nickel catalyst. The extent of nickel poisoning for two different sulphur levels is shown in Fig 6 as a function of temperature. Used in conjunction with Fig 4 which requires substantial removal of hydrocarbons by steam reforming before the steam/hydrocarbon mixture attains a temperature of about 650°C (whether reforming natural gas over a non-potash catalyst or naphtha over a potash containing catalyst) then it is evident that the nickel must have substantial activity in the temperature range 550 - 650°C. Fig 6 therefore indicates that sulphur must not be present in the feedstuck to an extent greater than about 0.5 ppm.

Fig 6 Sulphur poisoning of nickel in hydrocarbon steam reforming

12. In order to attain the almost complete removal of sulphur required by the reforming stage a sulphur removal unit is necessary for prior processing of the hydrocarbon. The form of this unit depends on the type and amount of sulphur compounds in the feedstock and these are primarily dependent on the feedstock boiling points. Thus naphthas contain substantial quantities of thiophenic compounds which must be treated with an active hydrodesulphurisation catalyst (typically a cobalt molybdate catalyst) in order to liberate H_2S to be subsequently absorbed in zinc oxide, whereas natural gas may contain sulphur compounds such as H_2S. COS, RSH or RSR and very occasionally small quantities of a stenching agent such as tetrahydrothiophene. Active carbon is used on many plants to remove sulphur from natural gas, but its capacity for H_2S and COS is limited. The system, however, often proves unreliable due to uncertainties in regeneration or because of the presence of higher hydrocarbons in the natural gas. This can lead to premature sulphur break-through. A more efficient and reliable system uses a cobalt molybdate catalyst with recycle hydrogen to convert all the sulphur to H_2S which is absorbed by zinc oxide. If only H_2S and COS are present zinc oxide alone is adequate for sulphur removal.

13. As with most catalysts operating on hydrocarbon systems, cobalt molybdate catalysts can become deactivated in time due to carbon deposition. The formulation of the catalyst support and the operating temperature are most important factors in determining the rate at which carbon deposition occurs. Alumina silicates are acidic and promote cracking and carbon deposition. Even alumina is somewhat acidic, and the more basic a support is, the less the rate of carbon formation at a given temperature of operation. Typical data from accelerated laboratory tests in which an acidic alumina-supported cobalt molybdate was compared with a non-acidic-support cobalt molybdate (ICI 41-5) with respect to carbon deposition are

shown in Fig 7.   With suitable formulation both these catalysts have
the same initial activity (at a fixed temperature of operation) but the
non-acidic supported catalyst takes longer to become carboned up.

Fig 7   Influence of composition of support on rate of carbon deposition
on Cobalt Molybdate Hydrodesulphurisation Catalysts
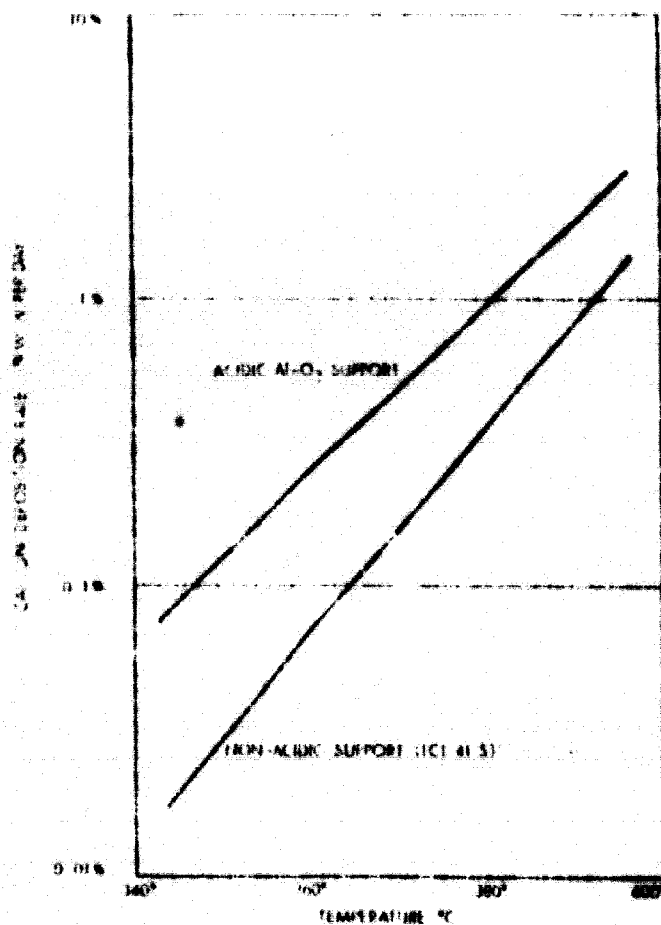
14. The rate of carbon deposition is, of course, also markedly dependent
on the feedstock.   In general, heavier feedstocks tend to carbon up
the catalyst more readily and hence should be hydrodesulphurised using
non-acidic supported catalysts whereas lighter feedstocks can be
satisfactorily treated with more acidic supports.

15. The requirements for efficient absorption of the H_2S liberated sets a severe duty on an H_2S absorbent. ZnO is the preferred absorbent, as the equilibrium H_2S over ZnS is only about one-hundredth of that for Fe_3O_4 as can be seen from Fig 8.

Fig 8   Equilibrium Sulphur as H_2S in treated Naphtha for Fe_3O_4 & ZnO Absorbents
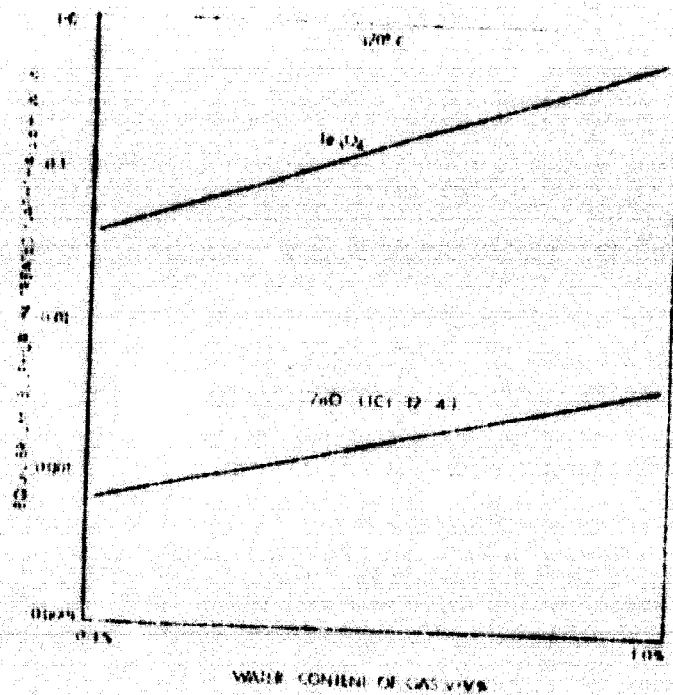
V. WATER GAS SHIFT REACTION

16. The material efficiency of the conversion of naphtha into ammonia in a
modern ammonia plant is markedly dependent on the ability of the low
temperature water gas shift reactor to replace CO by H_2. Every molecule
of CO slipping past this reactor represents a loss of four molecules of
hydrogen in the make-up gas to ammonia synthesis, together with a further
loss of hydrogen in the synthesis loop purge required to remove the
additional methane formed by methanating this CO.   Reliable behaviour
in use of the low temperature shift catalyst is, therefore, most desirable.
Experience has shown that two factors which are most important in securing
freedom from rapid loss of activity of copper-containing low temperature
shift catalysts are firstly, correct formulation, and secondly, the
absence of chlorine poisoning.   Fig 9 shows clearly how important is the
correct choice of preparation conditions in securing life, as two catalysts
of identical chemical compositions have very different die-off curves.

Fig 9   Influence of method of formulation on the life of
Low Temperature Shift Catalyst
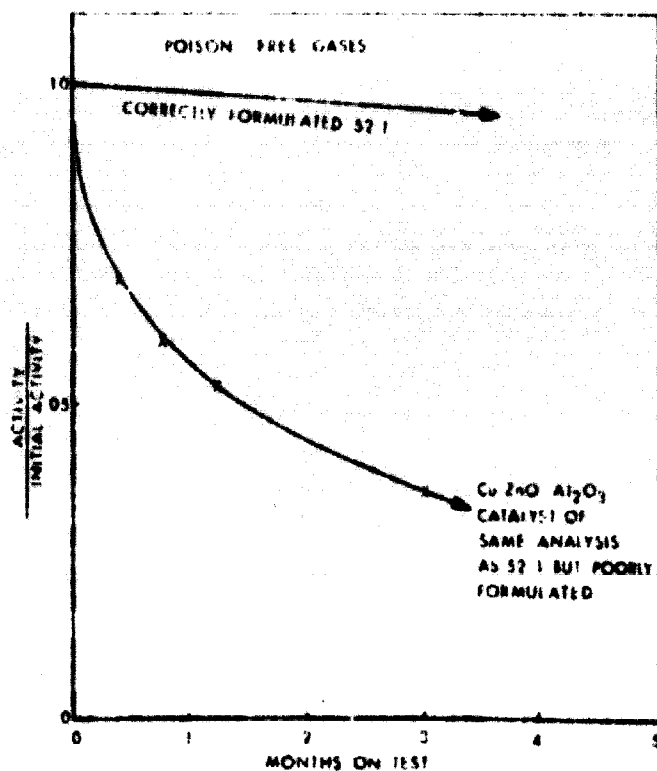
The reason for this difference can best be understood by reference to the sketch in Fig 10, which has been drawn up as a result of X-ray diffraction, electron microscopy, surface area and other physical investigations of the structure of these types of catalyst. Essentially, in order to secure long life the metal crystals must be separated from one another by small refractory oxide crystals.

Fig 10 Hypothetical picture of a metal + refractory catalyst prepared by precipitation and reduction
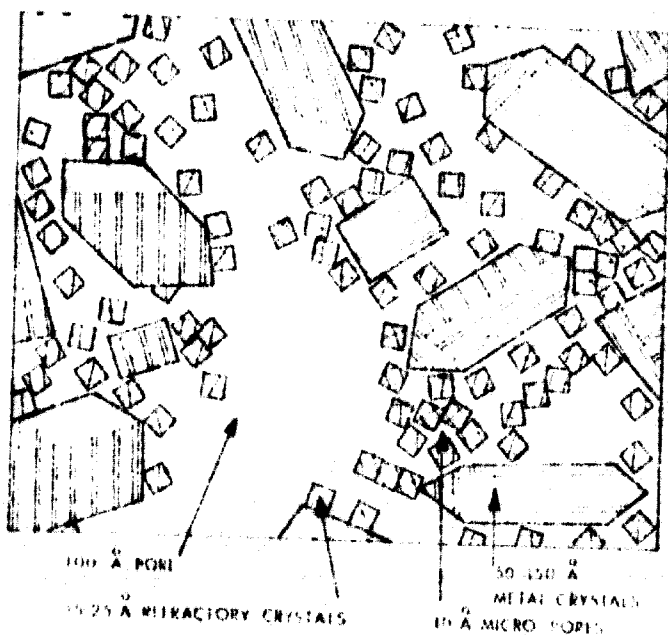
17. Furthermore, in order to secure high activity the scale of this geometry must be very small. The copper crystals in ICI 52-1 are only about 100 Å (10^{-6} cm) in diameter. The refractory crystals are even smaller, only some 20 Å in diameter. Provided a small but even separation of the metal crystals is produced, by a suitable catalyst preparation procedure, then even over-heating of the catalyst does not produce sintering of the copper and loss of activity, provided halogens such as

chlorine are absent.   In the presence of halogens, however, the structure
of the catalyst is rendered mobile and recrystallisation takes place,
driven by the thermodynamic differences in chemical potential between
small and large crystals.   The rate at which this phenomenon takes place
is, for a given formulation, primarily a function of the halogen level.
Typically this recrystallisation process, which is similar in principle
to Ostwald ripening of precipitates, follows the law indicated in Fig 11.

Fig 11   Loss of activity due to metal crystal growth in a
supported copper catalyst
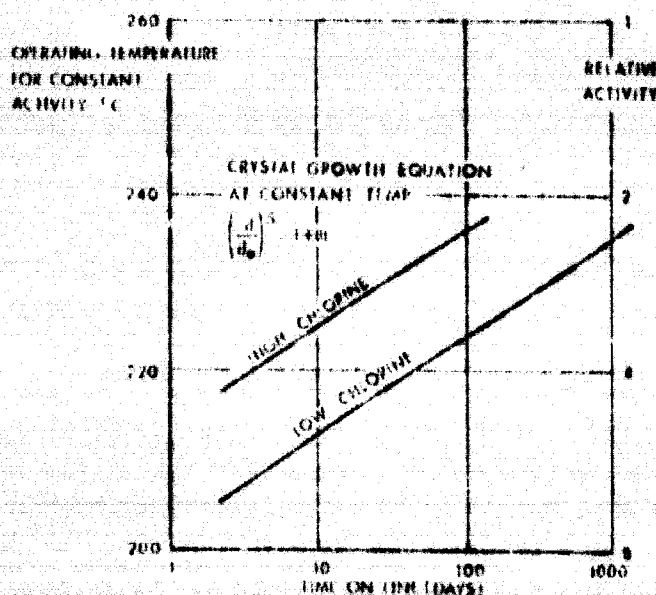
Fig 1.2 Relative activities & pressure drops as a function of particle size for NH_3 Synthesis Catalyst (ICI 35-4)
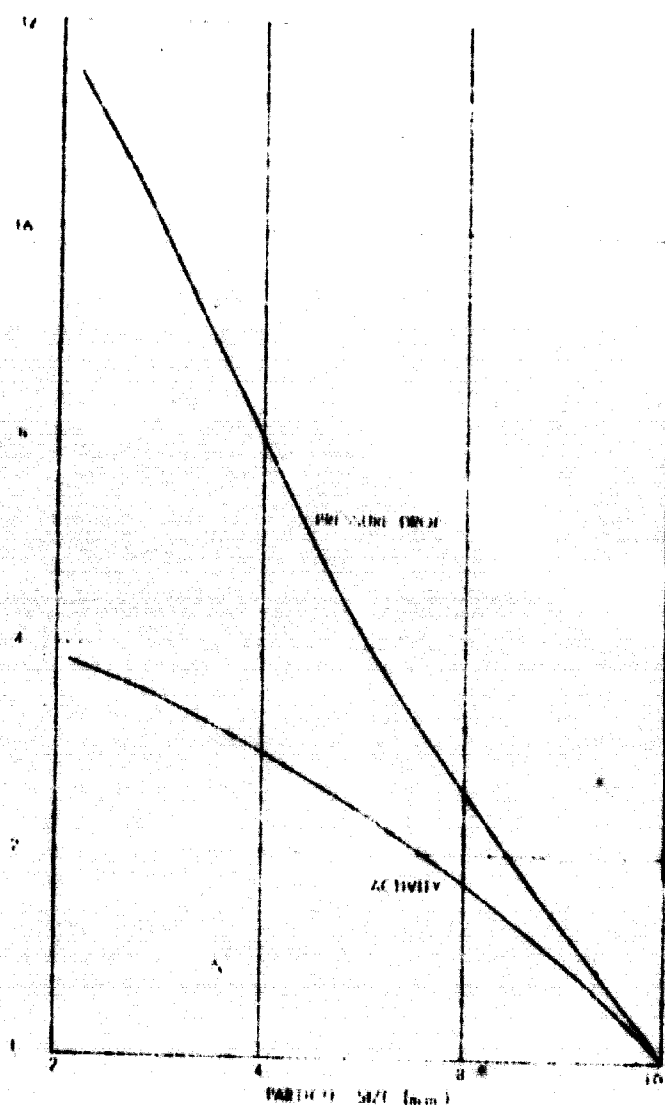
This type of plot of log activity against log time is very useful for predicting life from relatively short term data.   Chlorine 'poisoning' of the above type is, of course, not a true poisoning but an acceleration of the structural collapse of the catalyst.   It is necessarily irreversible and the only method of preventing it is to stop chlorine from reaching the catalyst by the use of a guard absorbent.

Levels of chlorine greater than 0.01 ppm in the gas can have a serious effect on the catalyst life. Two types of guard have been devised by ICI. One (ICI 59-1) is for use where chlorine contamination is liable to be heavy, the second (ICI 52-1G) is for use where chlorine is less plentiful. The second type also has high shift catalytic activity and is not simply an absorbent as is the first type.
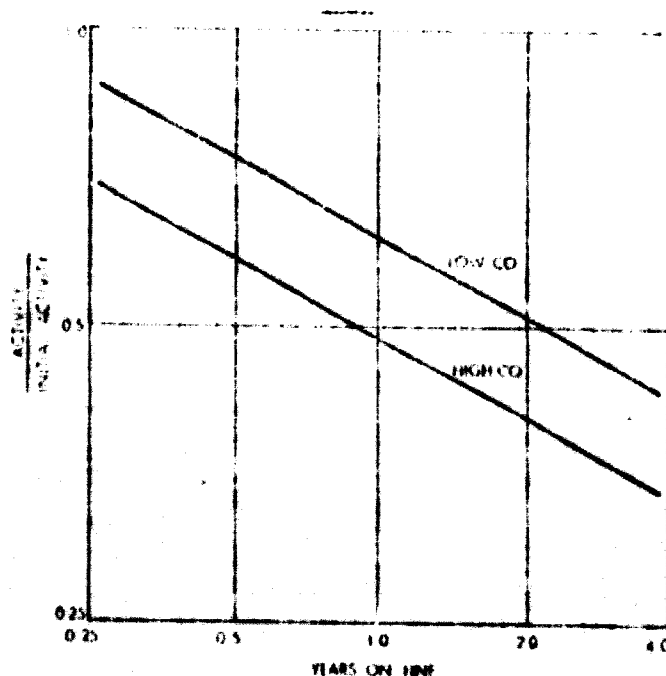
VI. AMMONIA SYNTHESIS

18. Very much has been written on the kinetics of ammonia synthesis from the standpoint of the chemist. Rather less has been written from the point of view of the catalyst user and the subject of catalyst life is very little discussed in a quantitative manner. Unlike most other catalysts, ammonia synthesis catalyst is available in a wide range of particle sizes, derived by different degrees of crushing and sieving of the frozen iron oxide-promoters melt. The smaller the particle size, the greater the catalyst activity (Fig 12). This increased activity is only secured, however, at the expense of an inherently higher pressure drop, which increases more rapidly with decrease in particle size than does the activity. The plant operator should choose an optimum size range bearing in mind the restrictions obtaining on his plant.

19. The rate of loss of activity of ammonia synthesis catalysts in modern ammonia plants should be much less than those in old plants because of the greater purity of the make-up gas to the synthesis loop. Catalyst life should also be longer, although the plant designer anxious to economise on capital cost will no doubt have partly offset the advantage gained by lower die-off rate by reducing the volume of catalyst in the converter.

Oxygen-containing compounds are the primary cause of loss in activity in modern plants. In particular, CO slipping the methanator passes straight to the synthesis catalyst. In the modern synthesis loop both H_2O and CO_2 are finally removed by passing the make-up gas along with converted gas through the ammonia separation section of the synthesis loop. The condensing ammonia then effectively scrubs both these species from the gas stream.

20. Oxygen compounds have both a temporary and a permanent effect on the synthesis catalyst. The temporary effect is due to chemisorption which is greater at lower catalyst temperatures. The permanent effect is more significant, as it results in an accelerated destruction of the catalyst surface due to crystal growth. Typical die-off plots for high and low CO in the gas entering the synthesis converter (not the make-up gas) are shown in Fig 13. This figure has been plotted in the same manner as Fig 11 for low temperature shift catalyst, as both die-off phenomena are the result of accelerated recrystallisation. In modern plants it is desirable to reduce CO to 1 ppm or less, which corresponds to between 3 and 5 ppm exit the methanator, depending on the recirculation ratio in the loop.

Fig 13   Poisoning of Ammonia Synthesis Catalyst

VII. METHANATION

21. **Consideration of the effects** of oxygen-containing compounds, in particular
CO, on the life of the ammonia synthesis catalyst thus define a required
performance of the methanator.   Choice of catalyst formulation for
methanation in order to secure high activity is important.   Even more
important is a uniform charging of the catalyst in the reactor so that the
catalyst bed has a uniform density.   Usually methanators have a single
adiabatic bed of catalyst.   Gas enters containing some 3000 ppm of CO and
should leave at only 3 ppm CO, a thousand-fold reduction in concentration.
Under these circumstances it is most important that the catalyst charge has
a uniform voidage across the reactor cross section.   The consequences of
non-uniform voidage in reducing the performance of the methanator may be
seen from Fig 14, which has been calculated for a methanator designed to
give an exit concentration of the total carbon oxides of 10 ppm.   Differences
in voidage of 15% are surprisingly easy to achieve if the catalyst is weak
or is charged in an asymetric manner.

VIII. THE COST OF UNRELIABILITY

22. The modern ammonia plant process sequence, indicated in Fig 1, reveals clearly how dependent the operation of this plant must be on the satisfactory performance of each of the catalysts or absorbents employed in sequence. No duplication of the major process items is normal, so that the failure of one catalyst results in the shut-down of the whole plant. It is therefore most important that, as all catalysts inevitably lose activity in time and therefore must be replaced, this loss of activity must proceed slowly and at a predictable rate, so that catalyst changes can be synchronised and unscheduled shut-downs for catalyst changes are minimised. Unscheduled shut-downs, if at all numerous, severely reduce plant availability and, in effect, increase the capital cost of the ammonia plant per ton of ammonia produced. Their economic effects are even more serious if, in addition, they reduce the output of the whole fertilizer plant through shortage of ammonia. Shut-downs and start-ups are also occasions of greater process and engineering hazard than is steady running. Shut-downs thus are liable to lead to further shut-downs. Even ignoring the indirect effects on the output of other dependent plants or the hazards associated with shut-downs, the major effect of catalyst unreliability can easily be appreciated from Fig 15.

Fig 14   Influence of uneven packing of catalyst on performance of a
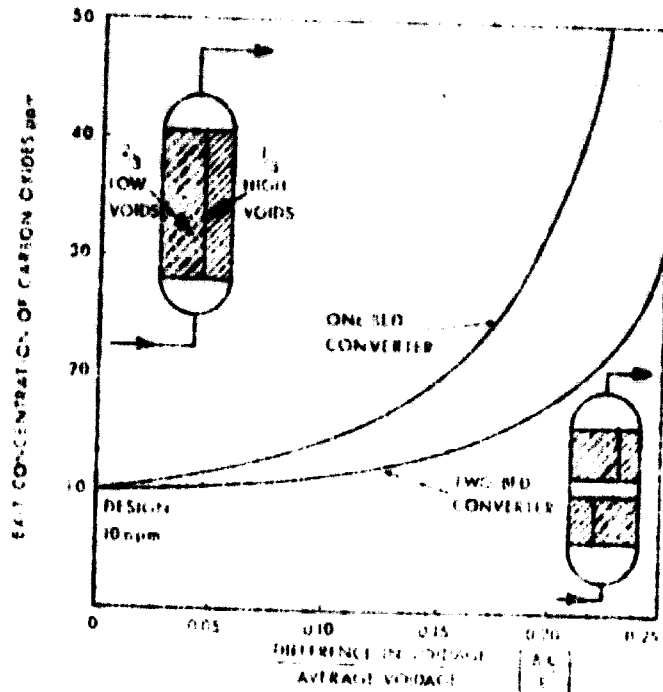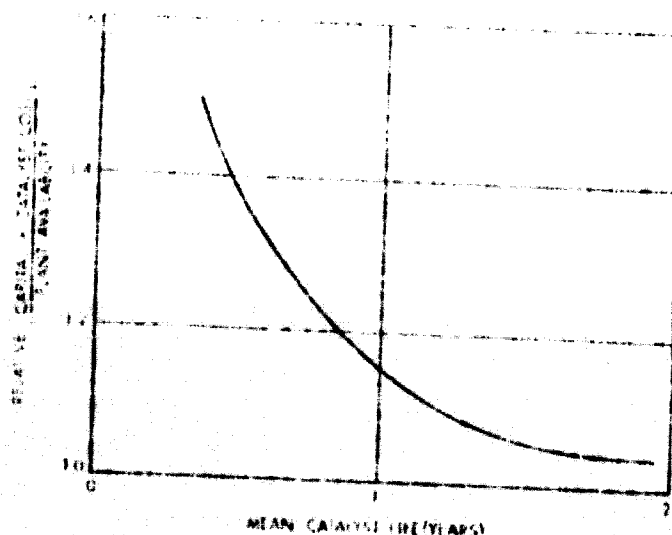   Methanator

Fig 15 Real cost of 'free' unreliable catalysts relative to
reliable purchased catalysts for ammonia production

23. In this figure a comparison is made between the capital + catalyst cost
per ton of ammonia produced for unreliable free catalysts and for reliable
normal purchase price catalysts. Thus, taking a mean life of 1 year as an
example, the free unreliable catalyst, it is assumed, might fail at any time
between the first day on line and the end of the second year on line. The
reliable catalyst fails at the end of 1 year, and it has to be purchased at
the normal price.   Because of the number of catalysts in sequence,
unreliability leads to frequent shut-downs with the economic consequences
evident from Fig 15.   Even when the mean life of both types of catalyst
is as long as two years, the free unreliable catalyst is, in reality,
more costly to the plant manager than is the purchased reliable catalyst.
Reliability is worth purchasing, unreliability is expensive even if
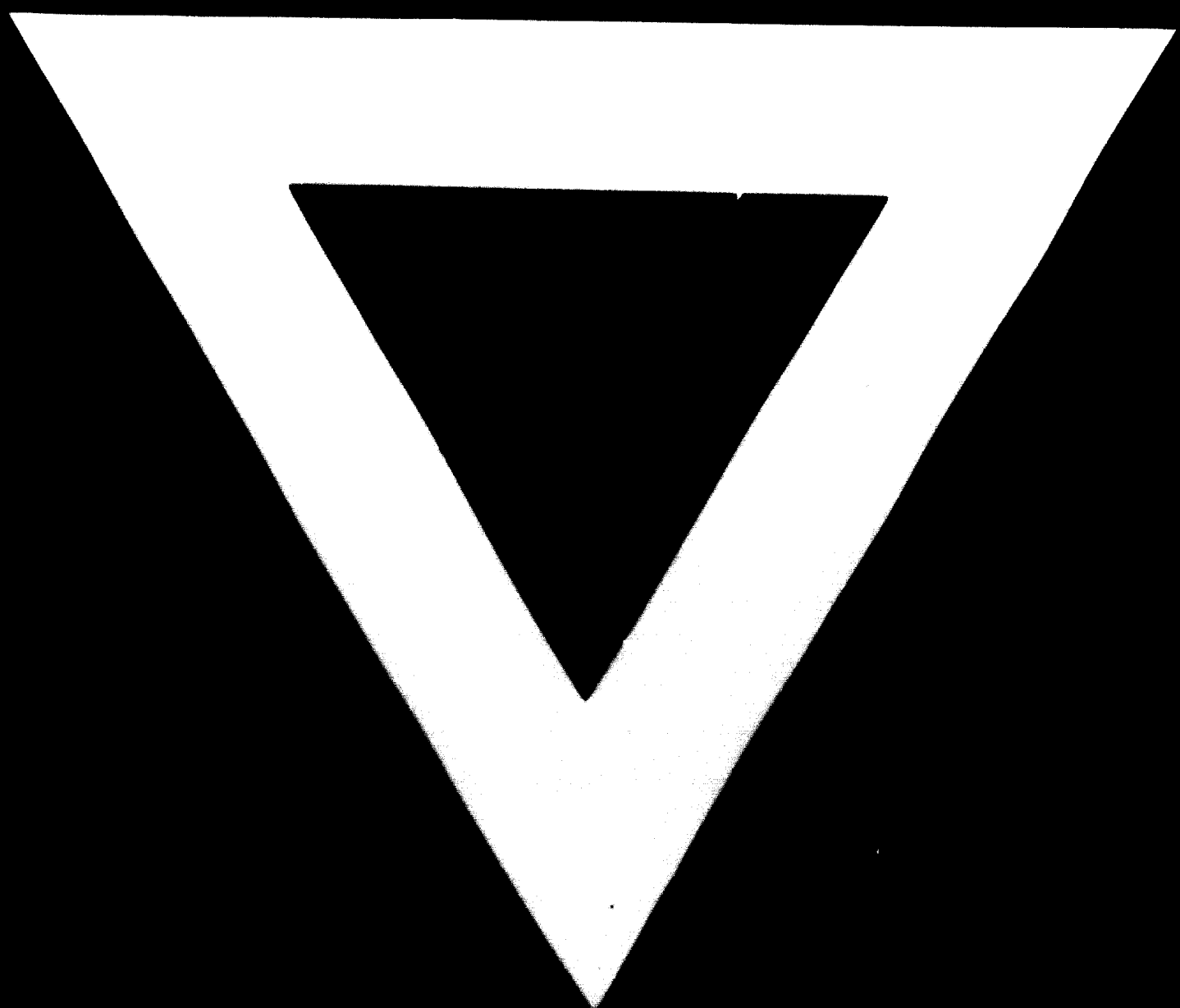apparently free!

24. The consequences of relatively small amounts of sulphur entering the naphtha reforming catalyst, of chlorine entering the low temperature shift catalyst and of carbon monoxide entering the ammonia synthesis catalyst have been outlined above. It is worthwhile noticing that these levels of poison in the gas streams are not easy to measure. Frequently the plant manager only learns of the excessive levels of these poisons when it is too late and his catalyst has lost its activity and has been discharged and examined. His first defence against such a calamity must be an assurance that the appropriate purification systems, hydrodesulphurisation plus zinc oxide, low temperature shift guard and the methanator have reliable catalysts in them, charged correctly, and operated in the correct manner. Poisons are not the only reasons for loss of activity of the reforming, shift and ammonia synthesis stages. Poor formulation of the reforming catalyst can lead to carbon laydown, poor formulation of the shift catalyst can lead to structural collapse with loss of copper surface area and activity, poor formulation of the ammonia synthesis catalyst leads to lack of stability relative to thermal sintering. These catalysts may also be damaged by mal-operation. The only sure course for the plant manager must therefore be both to choose reliable catalysts for all stages in ammonia synthesis and, having learnt the necessary conditions for optimum operation of these catalysts, to initiate operating routines which ensure, so far as is possible, that these conditions are adhered to.

IX. IMPLICATIONS FOR DEVELOPING COUNTRIES

25. The arguments put forward in this paper apply to all ammonia plants whatever their location. The ammonia plant operator in a developing country is, however, under greater pressure to operate his plant well because of the important place his plant occupies in the industrial sector of his country's economy. The fertilizer it produces is vital to the

agricultural industry and the quality of life of his fellow countrymen. Equally, while his country's technical infra-structure is developing, the plant manager is less likely to have as many highly qualified technicians and technical organisations ready to assist him in time of operating difficulties. His plant operators are often less experienced than those in an industrial country and spare parts and catalysts may not be so freely available.

26. Because of all these factors the greatest care must be taken in selecting catalysts to be used in the ammonia plant. The choice must be made on the grounds of catalyst quality and reliability and the temptation to merely buy the cheapest catalyst must be resisted. It is the responsibility of management (and Government) to ensure that adequate funds are available for plant managers to buy the quality of catalyst they require. Any extra cost involved will be rapidly recovered in improved plant operation.

16. 7. 74