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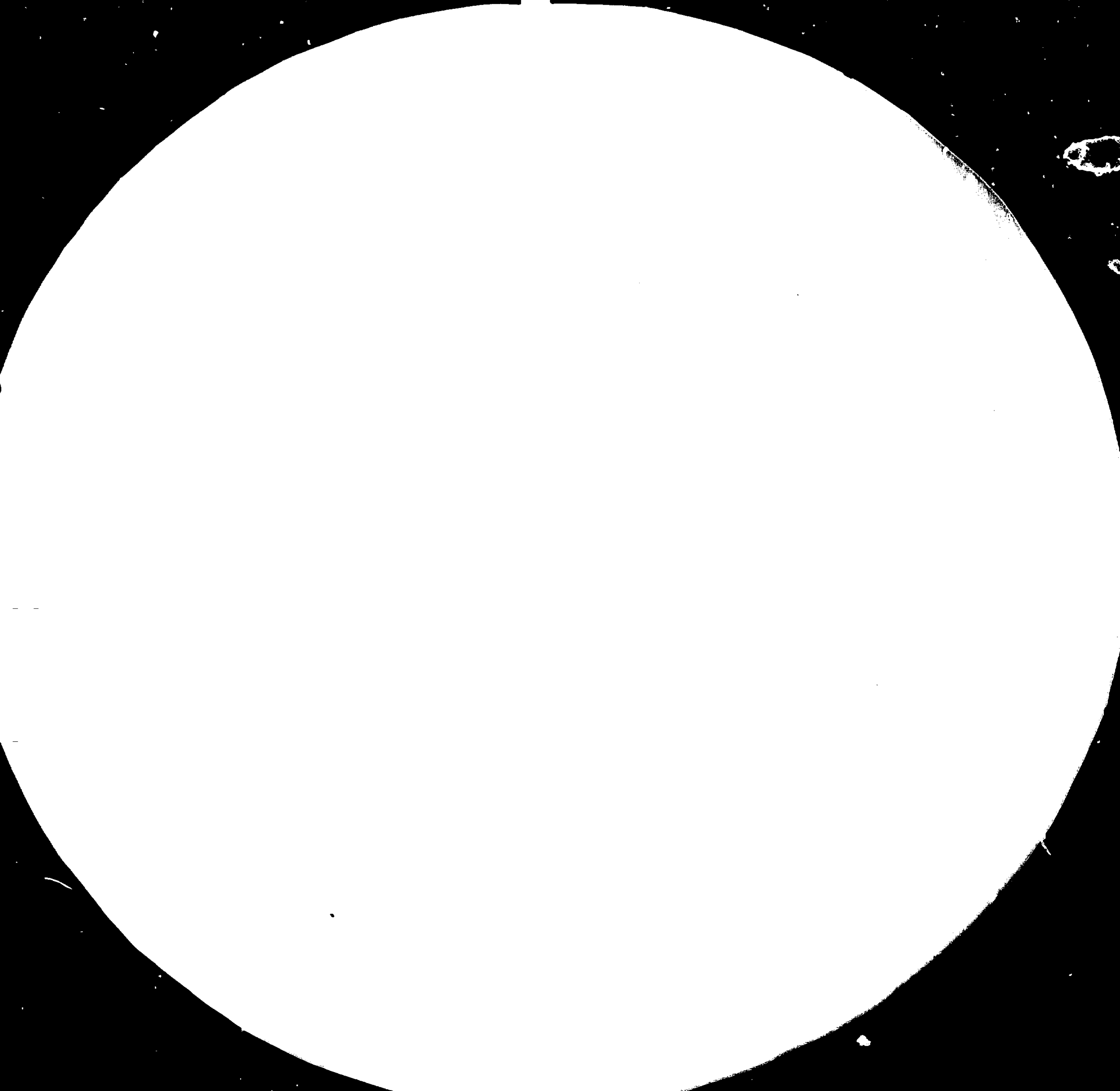

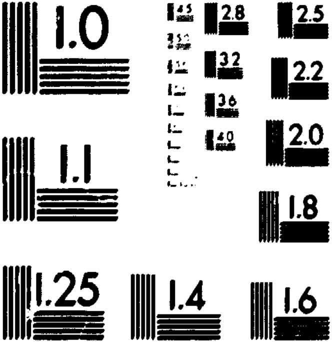

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)

FINAL REPORT

ASSISTANCE TO RESEARCH LABORATORIES IN FERTILIZER PLANTS IN SYRIA

PROJECT No SI/SYR/82/804

This Report is based on the work of UNIDO-team

Dr Marcela Šafaříková
ing Jozef Jankovič
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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
VIENNA
/ June - December 1984 /

GENERAL FERTILIZERS COMPANY

P.O.BOX 280 HOMS SYRIA
CABLE:FERTILIZERS HOMS.
PHONE :(20515)(20535)(23332)
TELEX:FERT (41005) SY

Our ref.................................. Your ref.................................. Date Dec.5th,1984

RE : UNIDO CONTRACT NO. SI/SYR/82/11/32.1

Attention : Dr. Marcela Safarikova / UNIDO Team Leader

Dear sirs,

With reference to above mentioned contract, we would like to express our thanks to you and all your team in this mission and for all efforts made by you toward solving some of our problems that we are facing in production, such like Calnitro fertilizer caking, and ammonia catalyst testing unit (pilot plant) as well.

We hope to be able to realize and implement your ideas .

Looking forward for further assistence from you; and remain.

Yours faithfully

Eng. Ahmed [illegible]

G.FC General Director

ABSTRACT

The task of UNIDO - team assistance to GFC was to investigate:

- the usefulness of a pilot plant installation for testing catalysts for ammonia production
- the possibility of decreasing the existing Calcium Ammonium Nitrate /CAN/ caking tendency

Catalyst Pilot Plant:

The existing system of Ammonia Production Plant catalysts processing, maintenance planning, recharging, and suppliers selection does not answer requirements. A study of a simple and cheap system which would solve the most urgent needs was compiled. This system employing a microprocessor evaluates control data from the process catalysts and combines it with research data obtained from small testing reactors thus getting complex information on the actual needs of the ammonia manufacturer.

Calcium Ammonium Nitrate

Because the CAN quality is determined during the production step, an investigation of the process and its control was carried out and a brief idea of necessary improvements, either in the form of simple reconstruction of individual production machinery, or possible future revamping of the Unit, was carried put.

Secondly a short laboratory research program for caking tendency decrease possibilities through anticaking agents application was worked out and the tests were realized at the GFC laboratories.

The main aim of the whole project was to demonstrate the necessity for research method introduction and economical results are to be achieved.

CONTENTS:

Technical Report:

INTRODUCTION

The Syrian Government has established a Fertilizer Complex at Homs called the General Fertlizer Co /GFC/ under the directorate of the General Establishment of Chemical Industries /GECI/.

This complex consists of the following three subcomplexes

- Calcium Ammonium Nitrate complex /start up 1972/
    - Ammonia 150 t/day - stopped 1982
    - Nitric Acid 280 t/day
    - CAN 110 tN/day
- Ammonia Urea /Naphta Based/ complex /start up 1981/
    - Ammonia 1 000 t/day
    - Urea 1050 t/day
- Triple Phosphate /TSP/ complex/ start up 1981, not yet commissioned/
    - Sulphuric Acid 1950 t/day
    - Phosphoric Acid 533 t P_2O_5/day
    - TSP 1400 t/day
    - Aluminium Fluride 9 t/day

The Homs area was a famous agricultural area where fertilizer distribution and use were mandatory if agricultural production was to be increased. On the other hand experience in heavy chemical production was lacking.

The above list of Production Complexes at GFC Homs indicates that the chemical production is widely based, relatively young, and growing. These were the reasons why GFC and the Syrian Government asked UNIDO for the assistance of experts in the field of ammonia production catalysts and a decrease in the CAN caking tendency.

JOB DESCRIPTION

The original job descriptions are in Appendix 1. of this Report.

In regard to some vagueness in the actual job demand, the mission to Syria was divided into two parts - a 14 days' informative visit of the team leader and a 10 weeks' mission of the team when the body of the job was compiled.

The revised job description left out the demand for decreasing the urea caking tendency, as the caking tendency of urea was low and GFC felt no necessity for assistance on this point.

Secondly the work on a catalyst pilot plant had not yet been started and so it had to be considered wheter such a pilot plant could be useful for GFC and to what extent. A plan for such a pilot plant was worked out and approximate costs were stated.

The work was completed on December 10th, 1984.

SUMMARY AND RECOMMENDATIONS

1.0 Ammonia Catalyst Pilot Plant

Tho Ammonia Plant 1 000 t per day at GFC Homs was put into operation in the year 1981. After three years of ammonia production the catalysts for primary reforming and HT Shift CO conversion had to be replaced due to their low activity and increased pressure drop. The front section of the unit is planned to be reconstructed in the 1987 after naphta feedstock will have been changed to natural gas feed. According to the contractor´s request all the catalysts downstream the primary reformer to be replaced before the reconstructed plant is put into operation. Expenses for the purchase of spent to date and those to be paid in the near future are abnormally high.

As more than 12 competitive world suppliers are ready to offer first-grade catalysts for the ammonia industry, GFC has to consider very carefully which make and which suppliers are to be chosen. To be prepared for this actual task as well as for the future optimation of catalytic processes by means of long-life and highly efficient catalysts, a Catalyst Testing Project has been suggested.

Taking into consideration the specific situation at GFC Homs a 0,8 mil. $ program based on catalyst monitoring procedures is preferred. A classical testing laboratory project /estimated investment costs 15 mil. $ / a laboratory project of reduced scope /estimated investment costs 5 mil. $ / have also been studied but they have not been recommended.

To speed up the realization and to obtain the most urgently needed results before the start-up of the natural gas feed system, the program has been divided into three stages, the first one with a 1987 deadline.

The main aim of the first period /estimated costs lower than 250 000 $ / is to introduce the monitoring and testing of the primary reformer, HTS, and LTS CO conversion catalysts at GFC with the aid of inexpensive but effective installations. Monitoring and evaluation will be carried out with a microprocessor. Time schedules for the organization and training of GFC personnel in catalyst testing, monitoring and the evaluation of results have been worked out. Close operation with the Technical University at Homs has been embodied into the program.

In the second stage the scope of catalyst evaluation will be increased to all nickel based catalysts and desulphurization adsorptives if necessary, and in the third stage the program will be completed so that all reactors and catalysts will be evalutted by monitoring system.

Software for catalyst monitoring by thermodynamic evaluation was demonstrated on a Teleputer Microprocessor 128 kbytes which was brought by the UNIDO team. Software relating to actual operational problems at GFC was compiled and presented to the technical personnel of the Ammonia Plant.

2.0 Caking of Calcium Ammonium Nitrate

The quality of the produced CAN 30 was checked by evaluating the existing results of laboratory tests and it was stated that:

- the moisture content was often too high
- the size range of the prills was unsatisfactory /high content of fine particles/

These results were completed by testing the crushing strength - low hardness, and high plasticity were found. The shape of the individual prills was prolonged. According to these results an inspection of the individual process production steps was carried out at the Plant.

It was found that:

- the feed flow was unstable
- the neutralizator capacity was often exceeded
- the temperature control of the prilling process was often insufficient
- the prilling system was not adequate
- the capacity and efficiency of screening, drying, and cooling systems were low
- anticaking agent application was not situated in a suitable place and the spraying was not efficient enough
- samples for laboratory analysis were not taken at the end of the production line but upstream and did not represent the final CAN 30 quality.

Therefore a proposal for minor improvements in the Plant as well as a suggestion for possible future revamping were compiled.

Because there exists a limited possibility of improvement of the CAN 30 caking tendency by application of a suitable anticaking agent, a short laboratory research program was demonstrated on laboratory equipment which was brought along and handed over to GFC, The purpose of this activity was to demonstrate to the GFC technicians how through well-planned laboratory researchwork results can be obtained which solve both technical and economic problems. The tests were carried out with anticaking agents which were brought but it was emphasized that for making final decisions a more widely based laboratory research program world have to be compiled.

In addition to the mentioned points, the suggestion for producing liquid fertilizers and its future prospects was embodied to this Report.

1. TESTING OF AMMONIA PRODUCTION CATALYSTS

1.0 TESTING OF AMMONIA PRODUCTION CATALYSTS

1.1 Project of Catalyst Testing

ANNEXES TO CHAPTER 1.0

1.1 Project of Catalyst Testing

1.1.1 Purpose of the Project

- Prevention of catalyst collapse breakdown due to catalyst malfunction/
- Objective, technically founded planning of maintenance and catalyst replacement
- Selection of catalyst types /suppliers/ in accordance to catalyst activity/life and mechanical strength
- Postgraduate training of technical staff at GFC and increasing the average technical standard.

1.1.2 Scope of the Project

The Catalyst testing project has to be organized in well-planned steps to ensure sffectiveness and economy.

- The first step should help solve the known operation problems and help the start up after reconstruction of the 1 000 t/day ammonia plant from naphta to natural gas feed.
- The second step should improve maintenance planning, catalyst recharging and optimize catalyst processing .
- The third step should bring the general knowledge and experience of the GFC team to such a level that they are self-sufficient in the field of catalyst application, and to make them a leading group in this field for this gegraphical area.

To bring the above mentioned tasks to life it is necessary:

- To embody catalyst testing and general study into the GFC organization structure.

- To bring to life and develop the catalyst testing project.
- To reserve in the GFC budget means for catalyst testing.
- To instal necessary equipment step by step and to organize its implementation and further application.
- To select personnel.
- To ensure personnel training.
- To organize official contacts with sister ammonia plant manufacturers in the above field.
- To find contractors for design, deliveries, software and hardware.

Catalyst testing project time schedule has one fixed time limit:

- the ammonia plant start up on natural gas feed i.e. 3/1987.

Before the start up date the recharging of all catalysts has to be undertaken. Catalyst delivery time may take approx. 6 weeks and catalyst testing and comparison up to 3 months. All tests have to be started not later than 10/1986.

The terms of the second step are more or less optional and depend on GFC needs and financial possibilities. The second half of the year 1988 is tentatively suggested. However, the second step deadline and program should be set with regard to the realization of the first step during the reconstruction for natural gas.

The third step should be planned later when the 1st and 2nd steps have been realized.

1.1.3 List of Main Equipment

Item	No of pcs
- Crushing strength apparatus 0 - 100 kg	1
- Attrition loss apparatus	1
- Screen shaker with one set of screens 0,1 to 3 mm	1
- Sulphur adsorption apparatus for active surface of nickel catalyst measurement	1
- Bypass reactor for shift catalyst testing	3 - 4
- Processor 128 kbytes /minimally/ for evaluation of catalyst activity based on thermodynamic calculation, operating in real time consisting of: - processor - contact unit for on-line data collection - CRT colour display - keyboard - printer - external memory	
- Piping for bypass reactors and for gas sampling	1 set
- Instruments for bypass reactors	3 - 4 sets
- Instrumentation for catalyst monitoring in 102 - D, 104 - D and 106 - D reactors	1 set for each

1.1.4 Services List

- Manual for mechanical and adsorptive testing, personnel training, commissioning
- Bypass reactor documentation, manual, commissioning, training

- Catalyst monitoring documentation manual commissioning, training
- Microprocessor software
- Training of GFC staff at sister ammonia plants, research organizations and catalyst manufacturers

1.1.5 Labor Needs

It is probably necessary to name one chemical engineer in charge of catalyst processes in general in the first step. However, thorough knowledge and experience in the field of catalysts is indispensable for the ammonia plant technical management to train a good catalyst monitoring team.

Besides the catalyst engineer, 2 engineers from the ammonia plant should be trained in the testing of mechanical and adsorption properties of catalysts and minimally 3 engineers should be trained in the passive and active operation of the microprocessor.

Catalyst monitoring should be carried out on day shifts by the ammonia personnel, and evaluating results should belong to catalyst engineer´s responsibilities. The final decision on catalyst type/supplier selection should be made with the ammonia plant manager and the catalyst engineer. The catalyst engineer should contact catalyst suppliers and specialists in sister ammonia plants.

In the second step of the project, the team of engineers trained in catalyst monitoring should be enlarged.
A catalyst assistant should be named for continuity in the generation problem at GFC and to cover the increasing demand on work and responsibilities.

1.1.6 Training of GFC Personnel

Duty	No. of eng.	Days
- Training at an independont catalyst testing laboratory	2	20
- Training at the manufacturers´	2	15
- Training with microprocessor practice at a manufacturer´s or software developing organization /Basic Programming/	2	30
- Training at sister ammonia manufacturers		
- manufacturer A	2	10
- manufacturer B	2	10

1.2 Catalyst Testing Methods

1.2.0 Introduction

A modern ammonia plant based on steam reforming of hydrocarbons comprises eight catalytical operations:

- Hydrogenation of organic sulphur compounds of hydro carbon feed
- Desulphurization of hydrocarbon feed by hydrosulphide adsorption
- Primary reforming of hydrocarbons by steam
- Secondary reforming of reformed gas by steam and air
- First stage of CO-conversion /high temperature shift conversion/
- Second stage of CO-conversion /low temperature shift conversion/
- Methanation of final traces of carbon oxides
- Ammonia synthesis

All the above operation steps are homogenous reactions in gaseous phase promoted by heterogeneous catalysts, most of them selective ones.

Heterogeneous catalysis is a complicated process normally modelled in the following steps:

- Surface diffusion of reactants into catalyst particles. from the gas stream
- Pore diffusion of reactants into catalyst active centers
- Chemical reaction /generally stepwise/
- Pore diffusion of reaction products from the active catalyst centers
- Surface diffusion of reaction products from the catalyst particles into the gas stream

For an ammonia producer /i,e. for a catalyst user/ the most important factor is the total reaction mechanism in the reactor and the life of the randomly packed catalyst shift.

However, from the research point of view it is important to study all the above described processes of heterogeneous catalysis in all discrete operation steps.

Catalyst manufacturers and reactor designers have to follow the same methods used in research.

1.2.1 Laboratory Testing

Practically all testing methods were developed for either research work or for the needs of catalyst manufacturers and not for the use of ammonia producers. Basic research, used testing methods, and apparatuses are as follows:

- Individual chemical reactions /diffusion influence is reduced/ are tested in microreactors where particle size

0,1 - 0,5 mm is used. Catalyst volume of a reactor is 0,5 - 10 cm^3.

- Chemical reactions and diffusion in pores are tested in similar apparatuses. Grain size is 1 to 2 mm. Reactor volume is slightly increased.
- For surface diffusion study it is necessary to test commercial catalyst particles 3-20 mm in reactors of 500 to 2 000 cm^3 volume.
- In case of tube reactors heat transfer between reaction zone and tube wall beside the mentioned reaction steps is to be taken into consideration.

Reaction mechanism is tested and evaluated in the above reactors under defined conditions /exact rate and composition of gas, temperature and pressure conditions/ and the catalyst activity is calculated on the basis of indicated changes.

The reaction rate is calculated on the basis of test results as a function of pressure, temperature, concentration, space velocity, particle size, and relation to the thermodynamic equilibrium.

$$R = \exp(- E/RT) \;.\; f1/KT, comp, T, P/ \;.\; f2/SV, PS, D, PV/ \qquad 1.2.1/1$$

comp	gas composition
D	catalyst particle size
E	activation energy
f1,f2	mathematical functions
KT	thermodynamic equilibrium constant
P	pressure
PS	porosity of catalyst shift
PV	catalyst pore volume
R	reaction rate

SV ....space velocity
T ....temperature

For test evaluation purposes, instead of absolute reaction rates relative reaction rates /fig 1.2.1/1, 1.2.1/2/ or concentration of reaction products /fig 1.2.1/3, 1.2.1/4/ are used.

Absolute reaction rates for HTS CO-conversion are given in tab. 1.2.1.

TABLE 1.2.1

t °C	Gas Composition mol rate				reaction rate
	CO	H_2O	CO_2	H_2	mol CO/g catalyst/min
360	.277	.445	.048	.048	.00112
	.198	.24	.22	.209	.00060
381	.234	.197	.076	.076	.00173
	.167	.446	.188	.044	.00105
404	.263	.123	.144	.144	.00338
	.277	.136	.234	.24	.00299

Reaction rates for HTS conversion tested under atmospheric pressure. Catalyst Fe-Cr, grain size 0,13-1 mm, tested samples up to 1 g. /See Podolski, Kim; IEC Process, Vol 13, No 4 1974/.

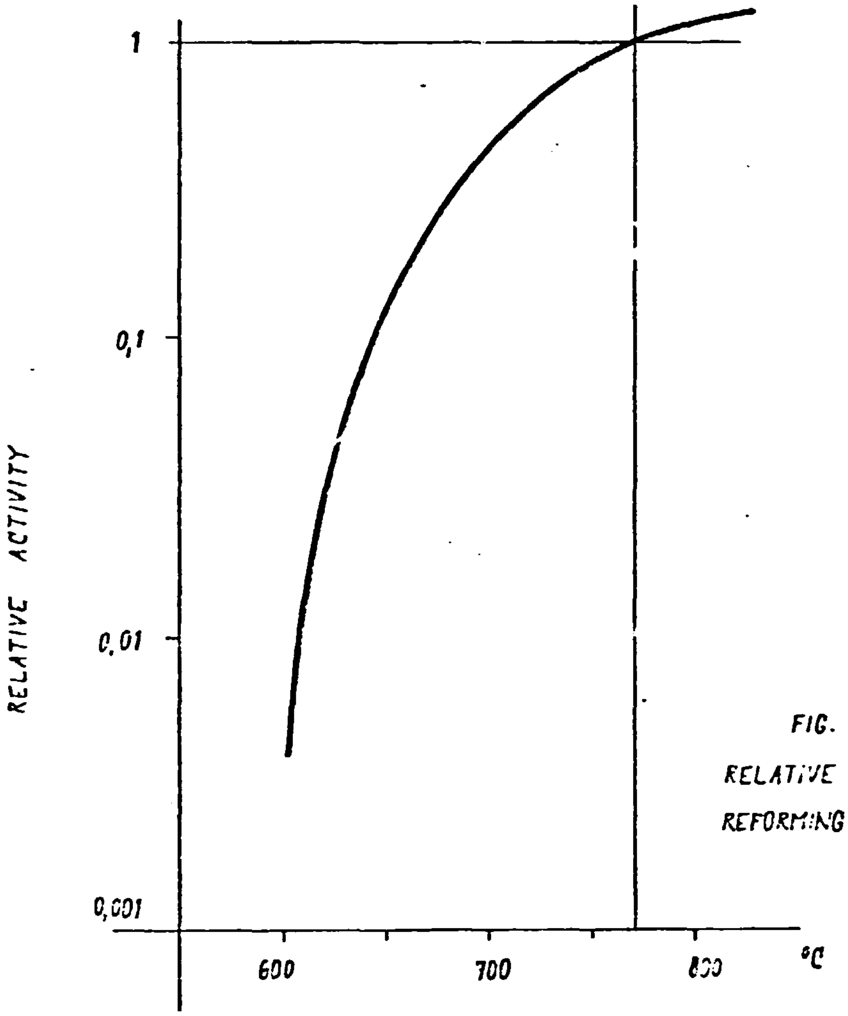


FIG. 1.2.1/1
RELATIVE ACTIVITY OF PRIMARY REFORMING CATALYST

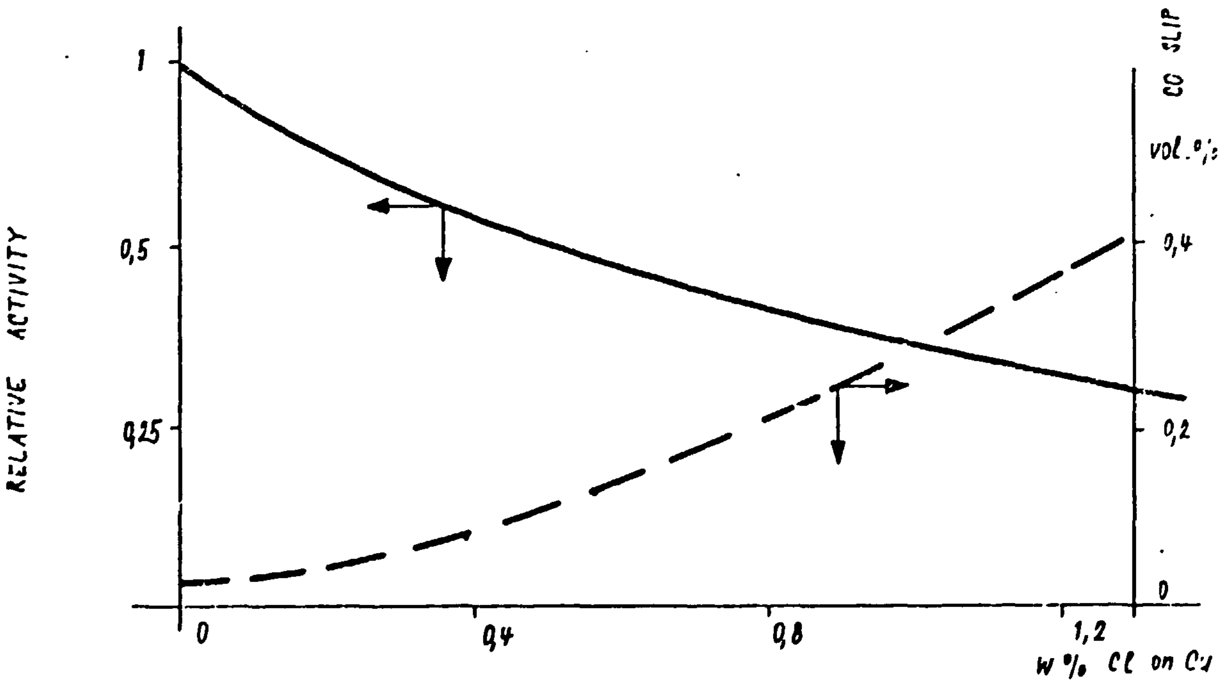


FIG. 1.2.1/2
LTS CATALYST ACTIVITY EXPRESSED AS CO. SLIP OVER REACTOR — — AND AS RELATIVE ACTIVITY ——

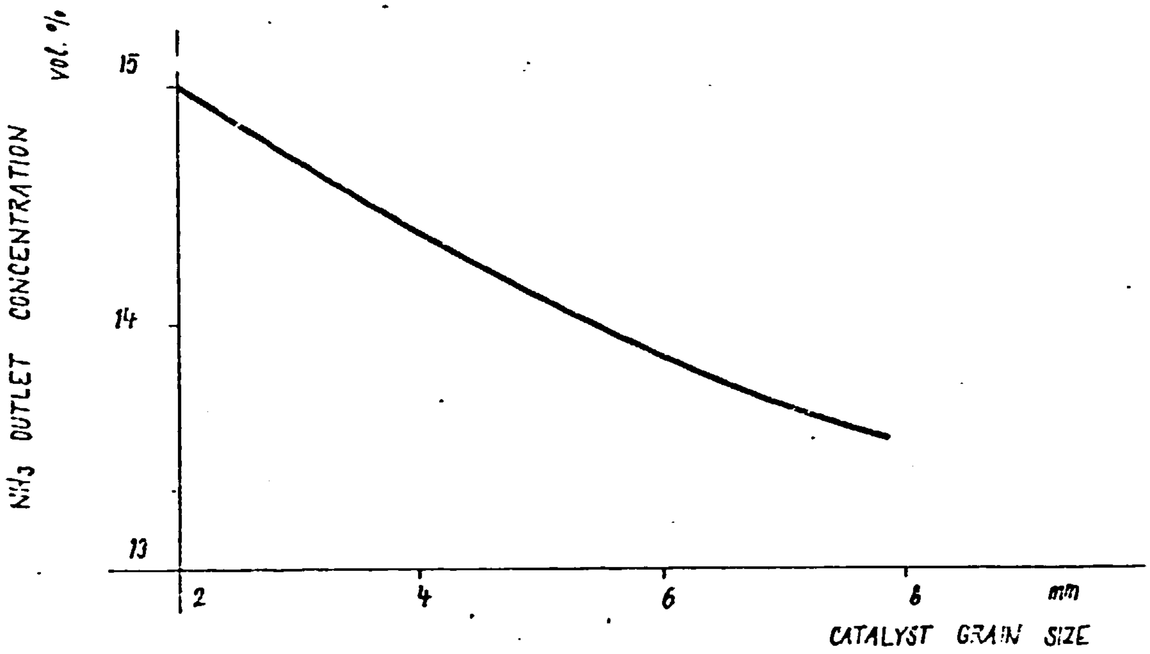


FIG. 1. 2. 1 /3 NH$_3$ SYNTHESIS CATALYST ACTIVITY EXPRESSED AS TOTAL CONVERSION
S.V. 15000 Nm^3 / m^3 / h 150 B

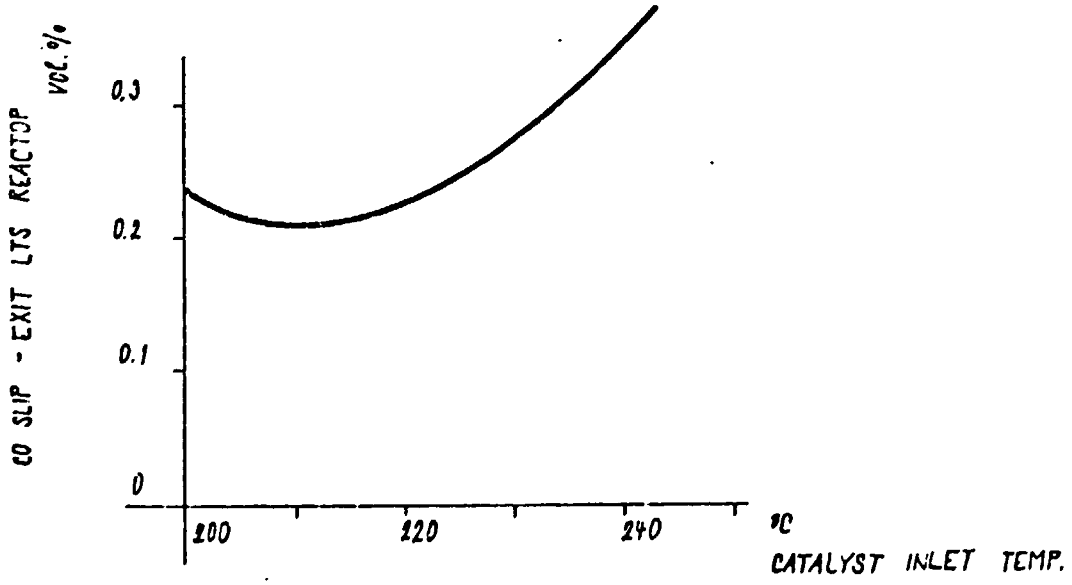


FIG. 1.2.1/4 LTS CATALYST ACTIVITY EXPRESSED AS CO SLIP OVER

Reaction rates calculated from data obtained in test reactors are valid for specific conditions of individual tests. If utilizing them for full scale reactor design or operation purposes, different conditions like the geometry and size of the reactor are to be taken into consideration.

Test results must be scaled up geometrically:

Test reactor volume	Commercial reactor volume	Scaling up ratio
0,1 - 10 cm^3	10 - 100 m^3	10^6 - 10^9
1 - 10 dm^3	10 - 100 m^3	10^3 - 10^5

For laboratory tests poison free gases are generally used. This is the main reason why laboratory results are to be modified before their practical application.

Moreover, laboratory test accuracy is limited according to the instrumentation tolerances /volumetric measurement ± 2 - 3 %, gas analysis ± 2 - 6 %/.

Modelling to full scale reduces the above accuracy dramatically. Generally correction factors 0,1 to 0,7 are introduced if laboratory test results are applied for commercial purposes.

1.3.2. Catalyst Monitoring

To reduce scaling up problems, the testing of full scale reactors is preferred. If full scale reactors are equipped by contact thermocouples /see ANNEX I/1 inserted into a catalyst layer, accuracy higher than ± 1°C and a time delay of less than 1 sec are achieved. In such a way it is possible to evaluate the activity of commercial catalysts with relatively high accuracy as most reactions in the ammonia plant are

strongly exo - or endo - thermic.
Processes in reactors are thus evaluated an a thermodynamic basis only and troublesome sampling and analysis of reactants are not necessary.

If exo - or endothermic reactions /i.e. secondary reformer, HT and LT shift conversion, methanation, ammonia synthesis/ run in adiabatic reactor layers, temperature difference is proportional to the change of composition /fig 1.2.2/1/. Each catalyst shift in the ammonia convertor is adiabatic and can be evaluated in the same way.

However, evaluation of the primary reformer is more complicated. If only radiation heating and heat transfer are considered, catalyst activity for operation purposes has to be calculated on a thermodynamic basis exclusively.

Large scale reactor testing /monitoring/ is an engineering job introduced into the ammonia industry in the last decade. If a decision on the best of competitive catalyst suppliers or a new catalyst supply is to be made, monitoring realized in a single plant has a limited value only. It should be accomplished by analyzing representative data from other similar plants available /monitoring results exchange program/.

But if the exchange of catalysts and the preventive maintenance program of reactors is to be carried out in an economic way, catalyst monitoring is the only objective method. Savings in the range of 100 000 $ were proved in ammonia plants where the monitoring program was professionally realized /a two years maintenance cycle is one of the results/.

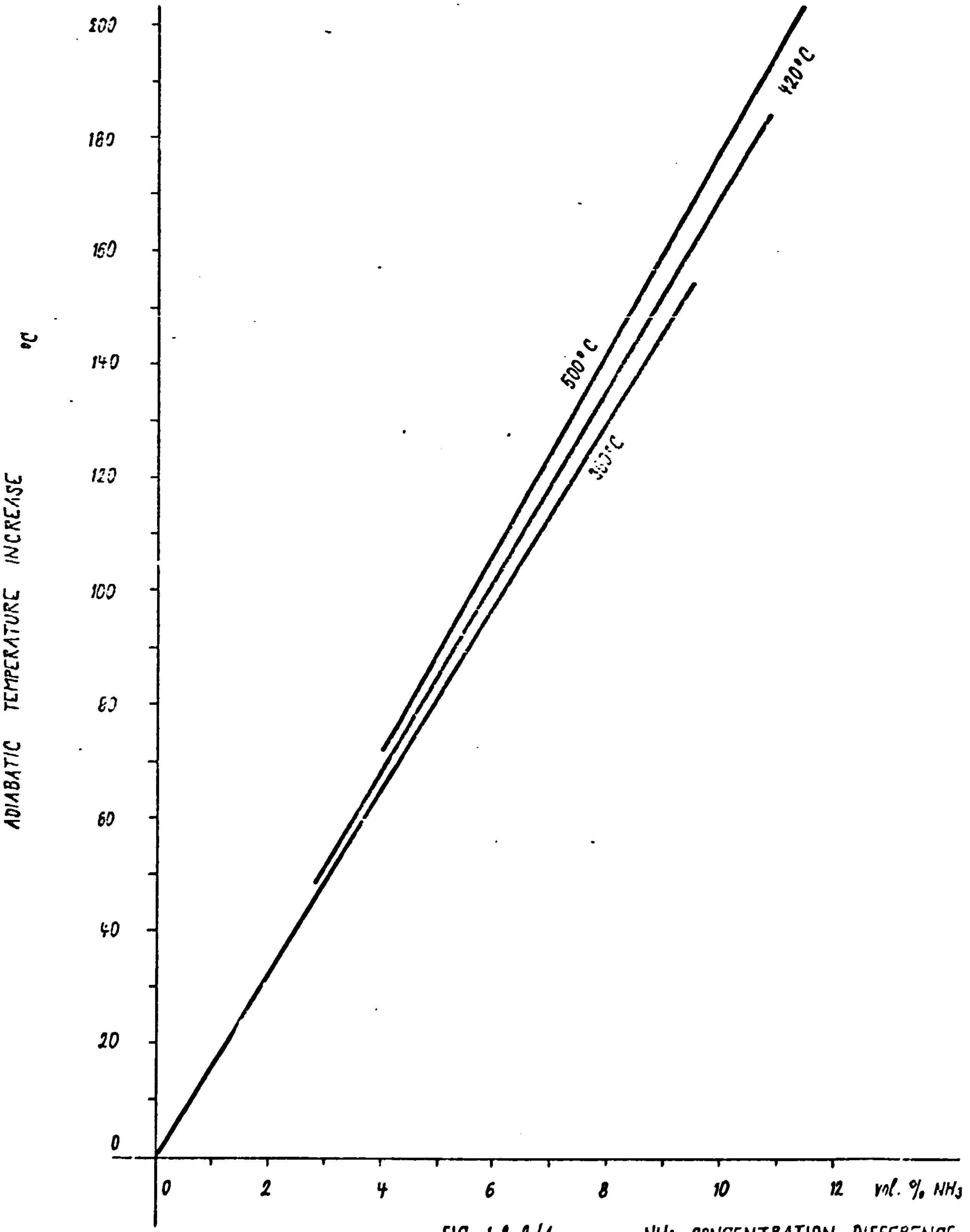


FIG. 1.2.2/1 NH3 CONCENTRATION DIFFERENCE IN AN ADIABATIC CATALYST LAYER

Examples:

- The economic service life of a sulphur adsorbent can be determined in advance if the total sulphur load is monitored /see fig 1.2.2/2/
- CO slip over from the LTS convertor due to catalyst aging and poisoning is not linear /see fig 1.2.2/3/. It is hardly possible to forecast the economic catalyst exchange times without thermodynamic analysis.
- Planning of methanation catalyst recharging is usually inexact. If movement of the active zone downstream the catalyst layer is monitored, it is possible to avoid $CO + CO_2$ breakthrough and to achieve the full use of the catalyst filling /fig 1.2.2/4/
- The long term monitoring of two different catalysts in ammonia convertors can discover the high activity but short life of a catalyst /fig. 1.2.2/5/.

This example shows the importance of international cooperation in monitoring, namely with those ammonia manufacturers operating two or more identical units, as for instance:

- Indian Eyplosives, India: 3 H+G units 440 t/day each
- SCHK Vraca, Bulgaria : 6 H+G units 300 t/day each
- ICI Billingham, England : 3 Kellog units 1000 st/day each

VEB Piesteritz, GDR : 2 Kellog/Toyo units 1360 t/day each

1.2.3 Laboratory Reactor Types

The reaction rate R (see eq. 1 2.1/1) depends strongly on temperature and in most cases on gas composition as well /in relation to the approach to the thermodynamic equilibrium/. If catalyst volume W is specified as:

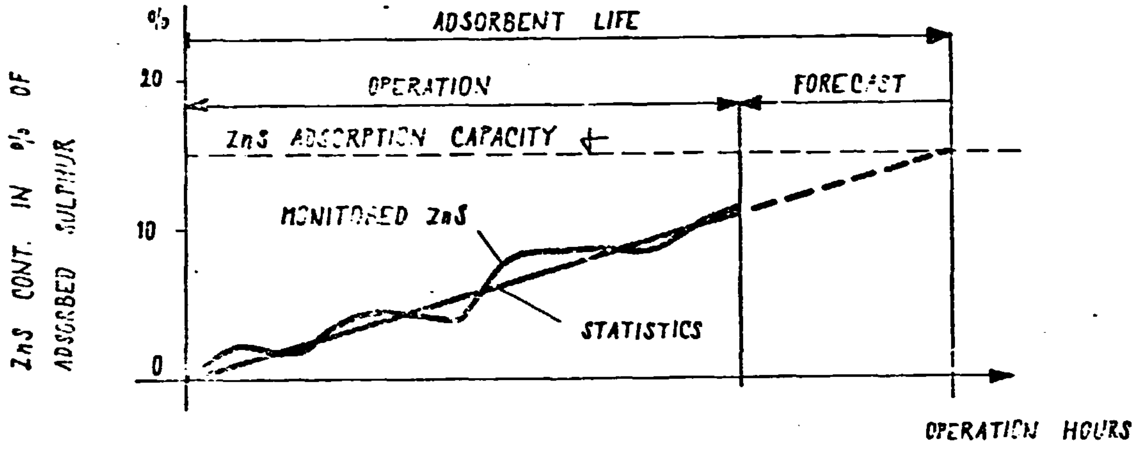


FIG. 1.2.2/2 FORECAST FOR ZnO LIFE

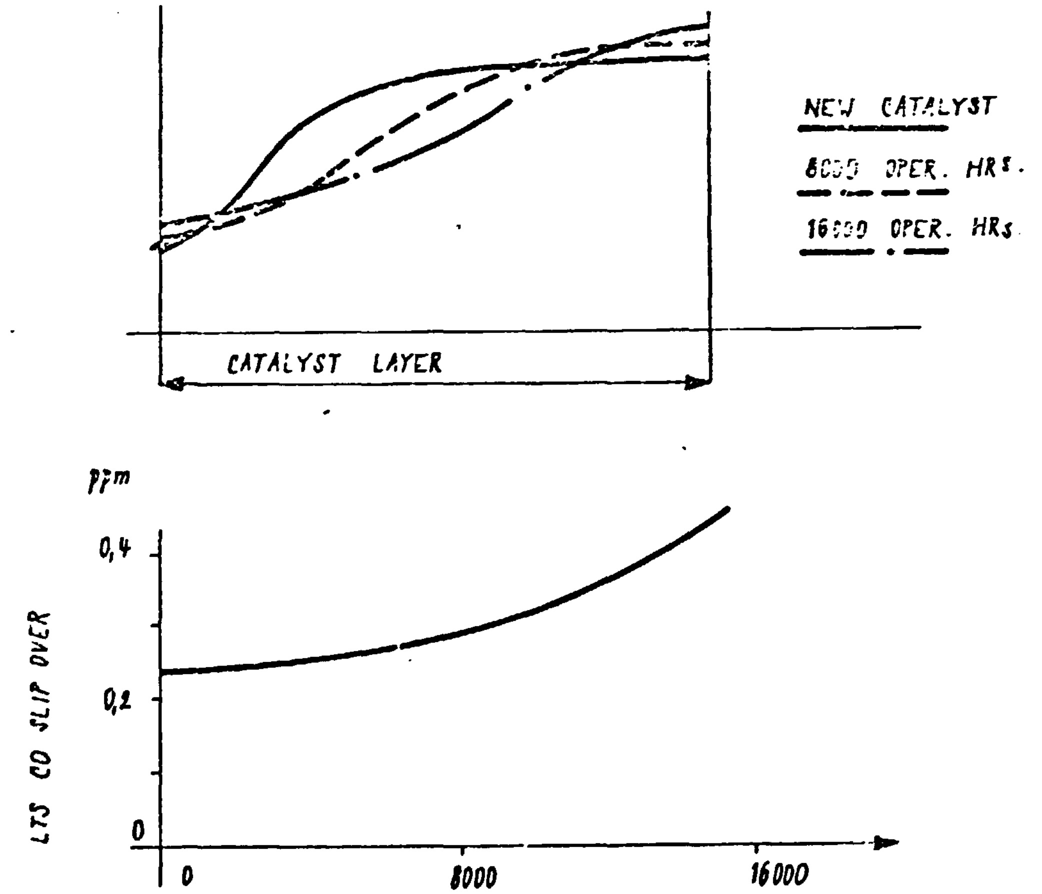
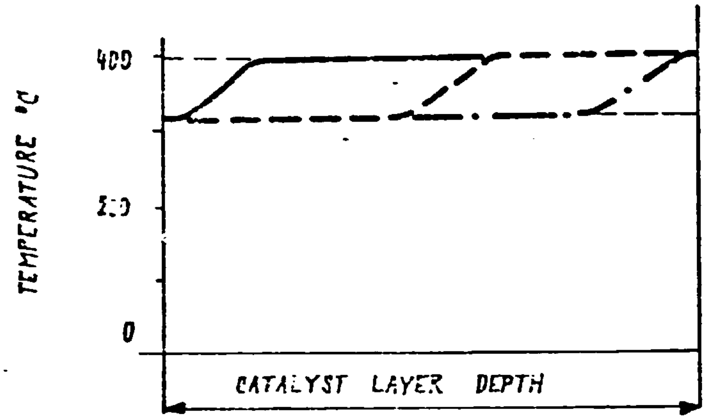


FIG. 1.2.2/3 LTS CATALYST MONITORING



METHANATOR TEMPERATURE PROFIL

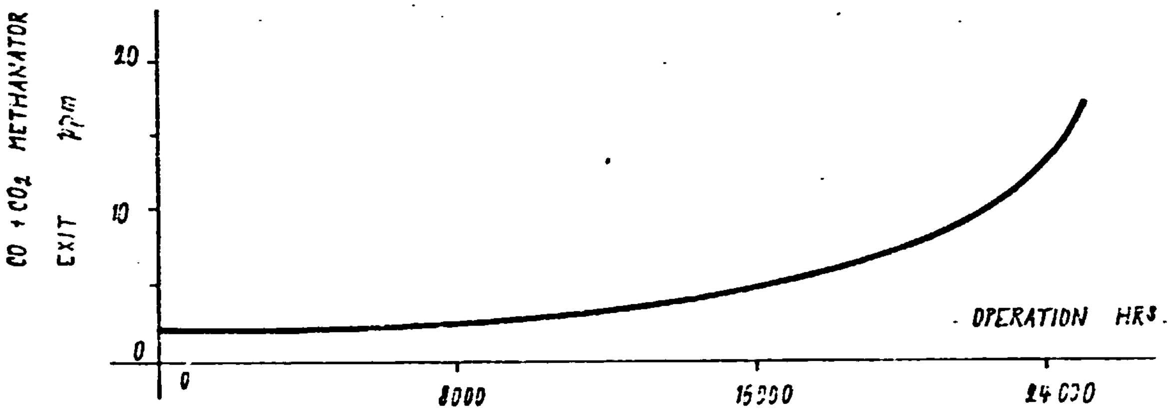


FIG. 1.2.2/4 CO + CO_2 LEAKAGE DOWNSTREAM METHANATOR

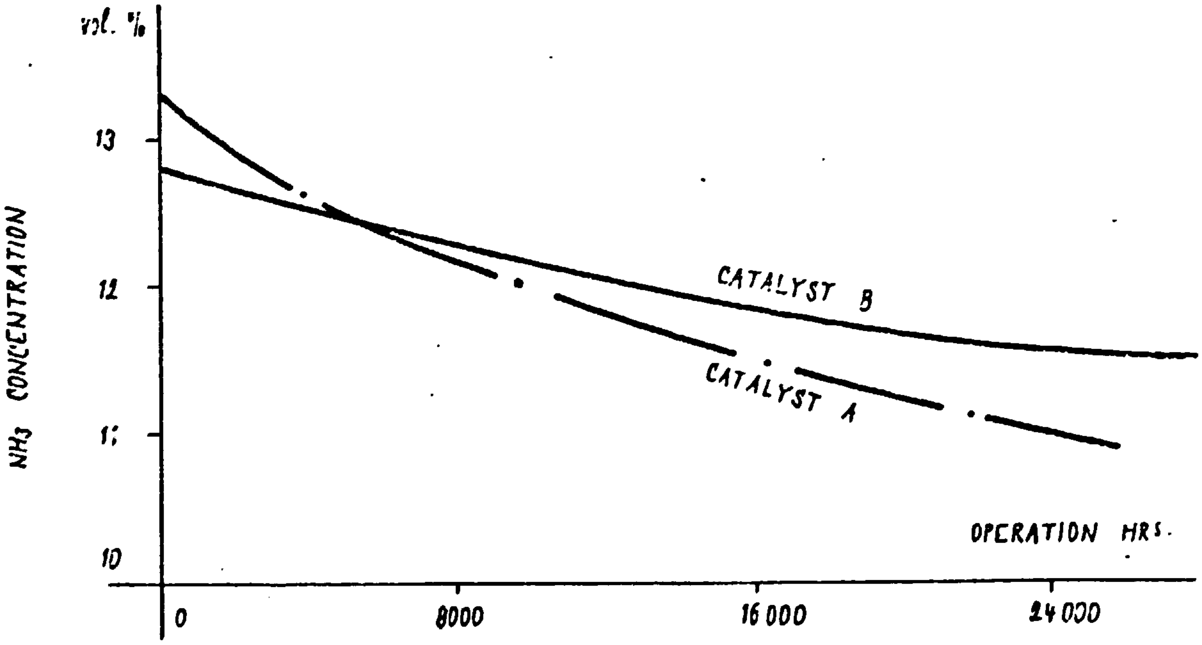


FIG. 1.2.2/ NH_3 CATALYST ACTIVITY

$$W = \frac{\pi D^2}{4} \cdot L \qquad 1.2.3/1$$

differential volume

$$dW = \frac{\pi D^2}{4} \cdot dx, \qquad 1.2.3/2$$

and the constant feed rate is defined as F/kg/hr/, than the longitudial concentration profile along the reactor is expressed in a simplified way as follows:

$$\frac{1}{F} \cdot \int_{y=0}^{y=1} = \int_{x_1}^{x_2} \frac{1}{R} \cdot dx \qquad 1.2.3/3$$

where R .... reaction tate $\frac{\text{kg gas feed}}{\text{kg catalyst . hr}}$

x .... concentration $\frac{\text{kg product}}{\text{kg catalyst}}$

1.2.3.1 Integral Reactors

Reaction rate is estimated on the basis of measured gas concentrations by means of eq. 1.2.3/3. If the reaction rate equation is known, principles of mathematical statistics are applied. The borderline conditions are evaluated for reactor inlet /$y = 0$, x_1 / and outlet /$y = L$, x_2/.

1.2.3.2 Differential Laboratory Reactors

Are designed for discrete reaction rate specification /under given pressure, temperature, concentration, space velocity/. If reaction product concentration difference x caused by presence of catalyst differential volume W at given gas feed rate F is found analytically, the reaction rate for specific conditions is defined as follows:

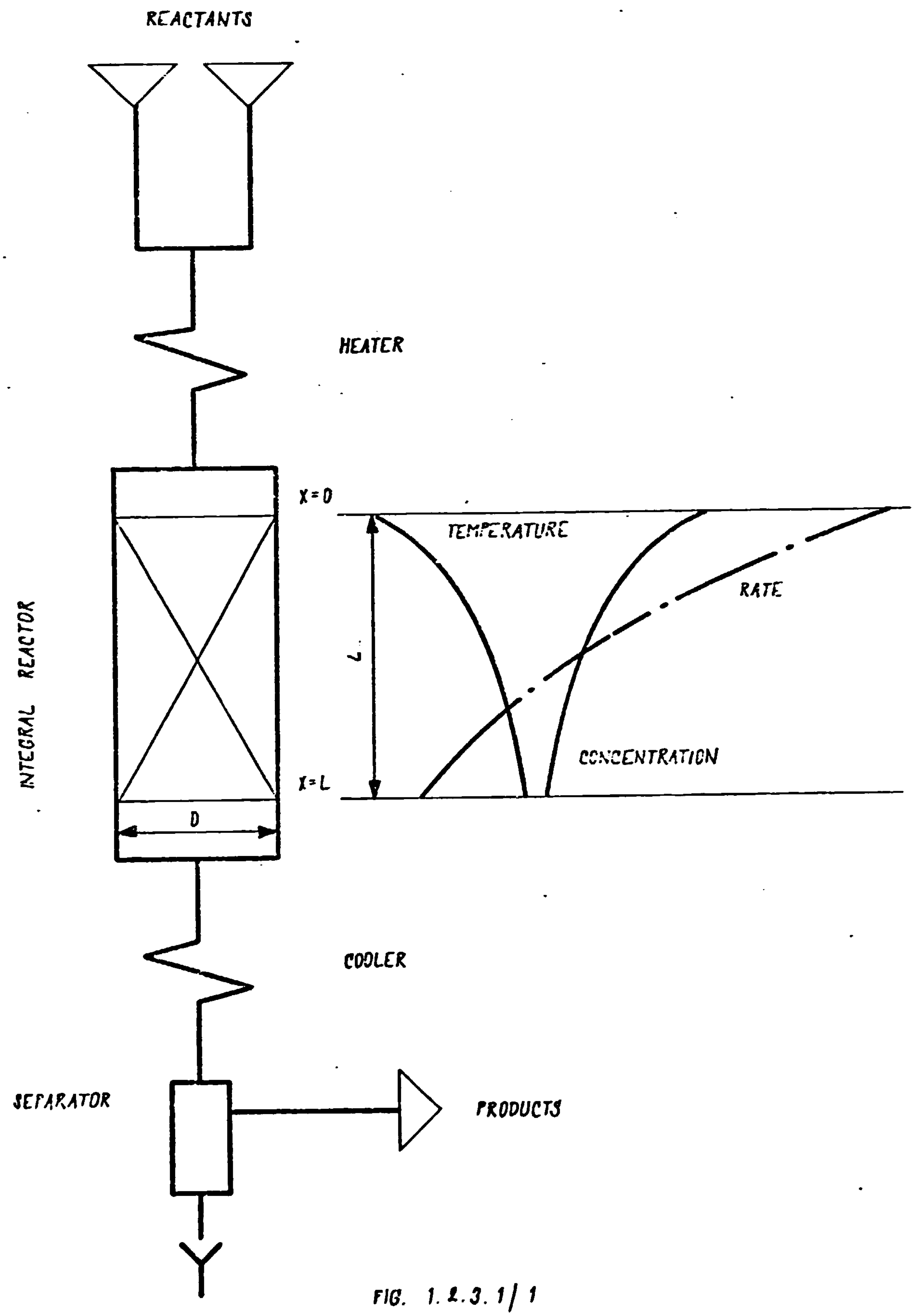

REACTANTS
HEATER
INTEGRAL REACTOR
X = 0
TEMPERATURE
RATE
L
CONCENTRATION
X = L
D
COOLER
SEPARATOR
PRODUCTS

FIG. 1.2.3.1/1

$$R_{/p,t,x,F/} = F \cdot \frac{\Delta x}{\Delta W} \qquad 1.2.3/4$$

For research purposes the differential reactors are realized as circulation reactors /see fig.1.2.3.2/1/. They enable to find the discrete reaction rate in a wide concentration interval. Differential reactor is preferably used in research, it has a limited importance for operational practice only.

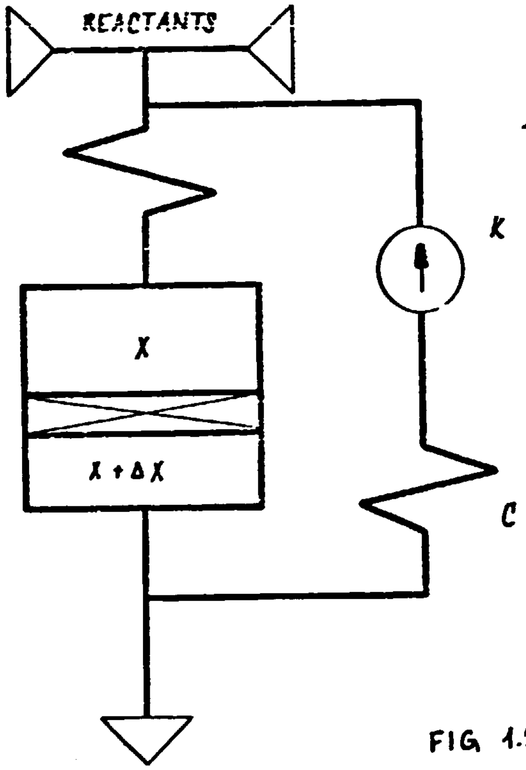


FIG 1.2.3.2/1

K .... circulating compressor
C .... gas cooler
R .... test reactor

1.2.4 Testing of Catalysts Used for Homogenous Reactions in Gaseous Phase

Generally there are three types of catalyst testing plants used for

- Basic research /new processes and catalyst research/
- Applied research /development of catalysts for commercial processes/
- Operational purpose /research/ commercial catalysts evaluation, process optimation/ - field testing

Catalyst testing plants for the first mentioned purpose are generally micro- and mini- scale apparatuses/ tested volume 0,1 cm^3 - 1000 cm^3/ designed universally for wide pressure/temperature and gas load ranges. Up - to - date units are fully computerized, automatically controlled and programmed. Catalyst testing plants for basic research are combined with very sophisticated analytical and instrument systems. Such plants are operated by graduated engineers and results are evaluated by scientists. Both outlay and operating costs are very high.

These reactors are used for thermodynamic recognoscation when new processes are studied.

The second type of catalyst testing plants is used for the development and improvement of commercially manufactured catalysts as well as for the evaluation of kinetic data needed for reactor design and process optimation. Mini scale test units /50 cm^3 - 2000 cm^3 catalyst samples/, designed for one purpose or for sets of processes /e.g. HT shift, LT shift, methanation/ fully computerized and automated need sophisticated analyzers and instrumentation. Plants have to be operated

by highly skilled laboratory personnel, graduated engineers for maintenance, and scientists are needed for evaluation. Both initial and operating costs are very high and they may be financially favourable for large catalyst manufacturers and/or world wide active licensors. For example a plant testing a full range of catalysts active in ammonia production based on natural gas costs about 14 - 18 million $, the cost of a preparation plant for gases not included.
Operation purpose and/or operation research reactors field testing/ are generally directly connected to a full scale plant /e,g. bypass reactors - fig. 1.2.4/1 or side stream reactors - fig.1.2.4/2/.

Using real process gas these reactors operate under real operation conditions. For the results, evaluation thermodynamic methods are preferred to chemical analysis. For example for a running reaction according to the equation

$$M_A + M_B \longrightarrow M_C \qquad 1.2.4/1$$

the conversion increment M_C is calculated in a simplified way from the thermodynamic function H^{T}_{UO}

$$M_A \cdot H^{T1}_{ACO} + M_B \cdot H^{T1}_{BCO} = /M_A - \Delta M_C/\, H^{T2}_{ACO} +$$

$$+ /M_B - \Delta M_C/\, H^{T2}_{BCO} + /M_C - \Delta M/\, H^{T2}_{CCO} \qquad 1.2.4/2$$

If the above thermodynamic evaluation of conversion step and reaction rate is possible with the existing full scale instrumentation, The initial cost of a testing unit is substantially reduced.

These reactors can be used for the comparison of different catalyst types and the selection of competitive catalyst suppliers if the initial cost as well below the cost of one catalyst charge, as a rule. The upper price limit for such a reactor in the ammonia industry is 90 000 - - 130 000 $.

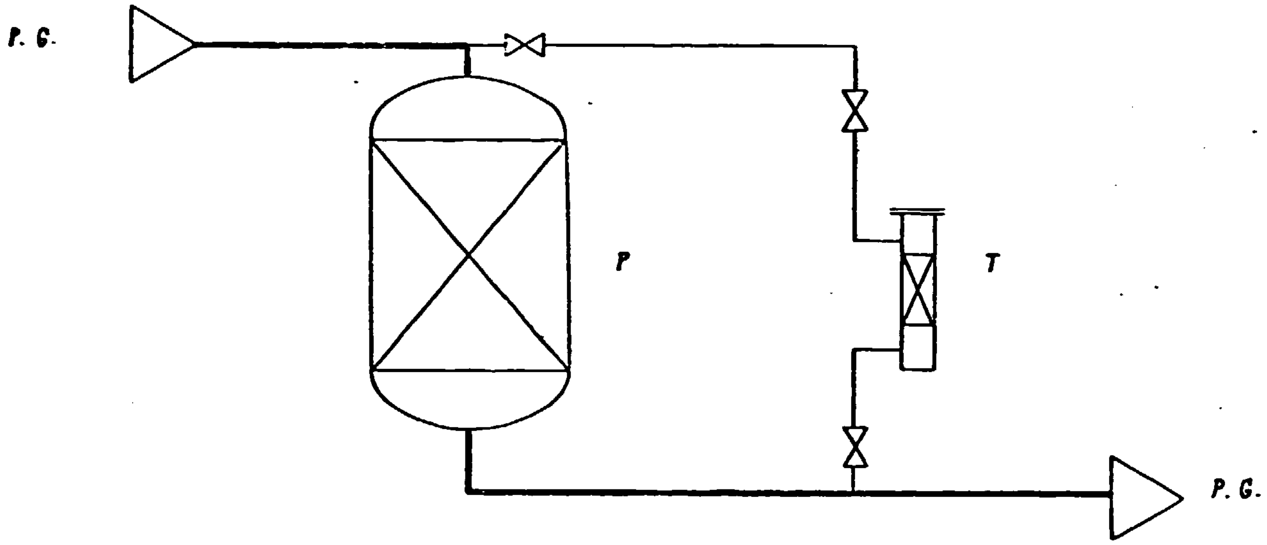


FIG. 1.2.4 / 1

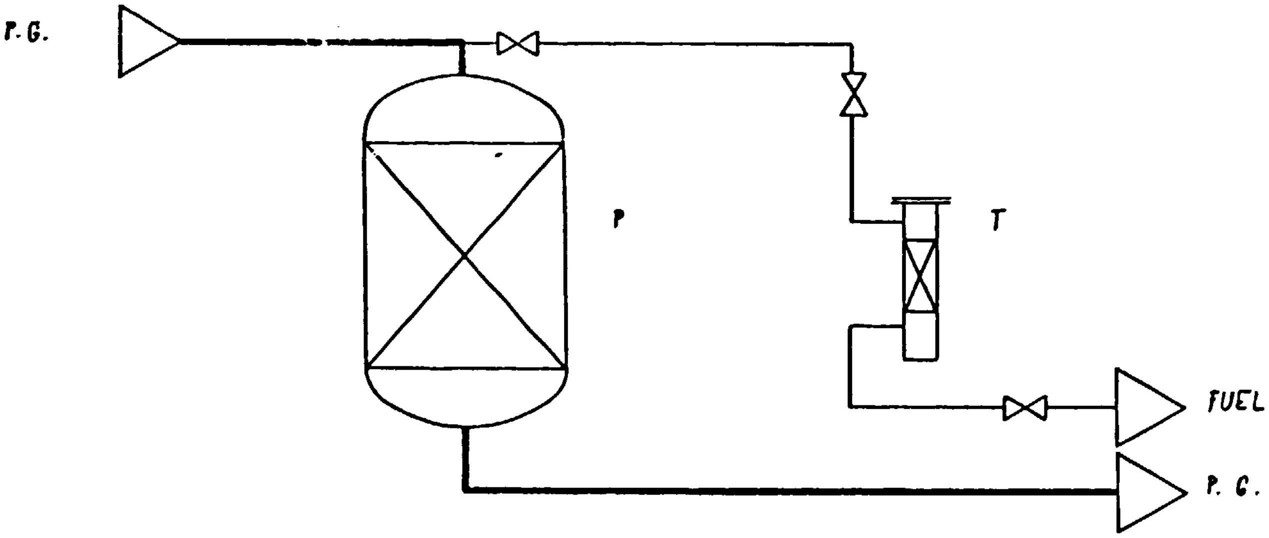


FIG. 1.2.4 / 2

P PROCESS REACTOR

T TEST REACTOR

P.G. PROCESS GAS

1.3 Catalyst Testing at GFC Homs

The construction of a classical catalyst testing laboratory is not recommended for of the following reasons:
- High total investment costs 14 - 18 million $ in full scope and 4 - 5 million $ in reduced scope. Catalyst testing has not been carried out at GFC Homs to date. Lack of experience and tradition in this field would influence the work, that means that the first effective results could be expected in 3 - 4 years after installation. In the meantime GFC would be oblidged to solge the main catalyst problems in a different way.

Howev r, to help overcome the difficulties connected with the temporary short life of primary reformer - and high temperature shift catalysts, to avoid expected future problems with low temperature shift catalysts and to achieve the universal technical standard at GFC ammonia plant, it is recommended to introduce less expensive but more powerful catalyst testing systems consisting of:
- Bypass test reactors /field testing/ connected to the HTS reactor; other bypass reactors can be connected to LTS and eventually to the methanator
- Equiument for the mechanical testing of fresh, reduced and aged catalysts.
- Devices for catalyst life evaluation and the activity monitoring system

It is necessary to make an agreement on effective cooperation with the Technical University at Homs on catalyst testing. /primary reformer, possibly a secondary reformer, and catalyst testing in general/

Cooperation with technical staff in sister ammonia plants /catalyst monitoring results, testing methods and results comparison and exchange of experience/.

The above measures are suggested to be realized according to the time schedule attached in ANNEX 1/II. The necessary staff for catalyst testing should be embodied into the organization scheme of ^{G}FC.

1.3.1 Hydrotreating and Sulphur Hydrogenation

Catalyst types:

Cobalt-molybden oxides or nickel molybdenum oxide based catalysts are used in addition to the ammonia industry also in refineries and in the petrochemical industry for the hydrogenation or organic sulphur compounds in gaseous or liquid phase according to these equations:

$$RSH + H_2 \longrightarrow RH + H_2S$$

$$RS + 3/2\ H_2 \longrightarrow RH + H_2S$$

Laboratory Testing Methods

Once through reactors /electrically heated/ operating under elevated pressures /min. 10 B/ are used. Feed gas free of sulphur compounds and O_2, CO, CO_2 / e.g. desulphurized natural gas or nitrogen/ is mixed with controlled quantities of hydrogen and thiophene. Tiophene as the most stable organic sulphur compound is used for testing in the ratio 1 : 10^5. Hydrogen sulphide as a product of hydrogenation is determined analytically.

Field Testing /Operation Research/

Three or more test reactors /vol. 2 - 3 litres are operating in paralel to the large-scale reactor under exactly the same conditions. If a gas cooler is installed upstream the group of test reactors it is possible to compare the activities of tested catalyst samples at lowered temperatures too. The catalyst activity is evaluated using the results of hydrogen sulphide and total sulphur analyzers. As the hydrogenation heat is negligible due to low sulphur concentration, thermodynamic evaluation is not possible.

Possibility of Catalyst Testing at GFC

Testing of hydrotreating catalysts is not probable in the future because GFC is expected to change the feed stock and to use natural gas instead of naphtha in the near future.

Low sulphur content specified as hydrogen sulphide present in the natural gas which is to be used as feed for the ammonia plant starting in 1987 predetermines the hydrogenation reactor 101 - D to be used as catalyst guard only.

1.3.2. Hydrogen Sulphide Adsorption

Catalyst type /adsorbent/:

Zincoxide. In case of organic sulphur free natural gas processing /which is reckoned with GFC/ it is possible to use the less expensive active carbon adsorbent instead of zincoxide which has been used for the quantitative removal of hydrogen sulphide and mercaptans in ammonia production as well as in related processes like the production of hydrogen, methanol, carbon monoxide, oxoalcohols etc:

$$H_2S + ZnO \longrightarrow ZnS + H_2O$$

Laboratory Testing Methods

The same apparatuses are used as for sulphur hydrogenetion /see 1.3.1/ but instead of thiophene, hydrogen sulphide or methylmercaptan from compressed gas cylinders is used. Sulphur removal properties /desulphurization degree and total sulphur hold-up/are evaluated by continous analysis up and downstream of the reactor and are compared with the total content of adsorbed sulphur in the adsorbent after finishing the test run.

Field Testing

It is possible to install 3 - 5 test adsorbers operating in parallel to 102 - D adsorber and to compare the hydrogen sulphide break - through points. To get results within a relatively short time, it is necessary to operate the adsorbers at relatively high space velocities. /3 - 5 000 $Nm^3/m^3/h$/. To avoid the danger of the hydrogen sulphide slipping over, the effluent gas pipe has to be connected to the fuel system.

Monitoring

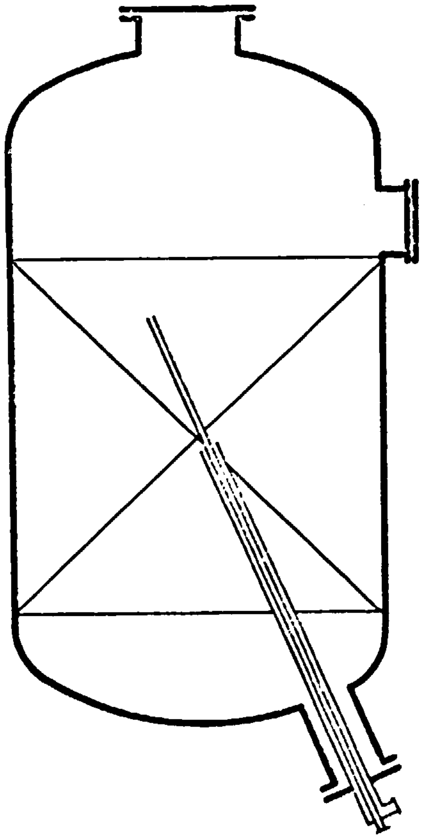
There are two monitoring procedures for H_2S adsorption:
- Quantitative analysis of hydrogen sulphide content in the natural gas feed
- Installation of gas sampling tubes in the ZnO layer /3 at least, preferably more/ to monitor the movement od ZnO zones loaded with sulphur

Application Possibilities at GFC Homs

Because of the expected low hydrogen sulphide level in natural gas, zincoxide consumption after ammonia plant reconstruction is expected to be 10 - 20 tons/year, which in the ammonia production costs represents 0,1 $ /t NH_3 approx.. From this point of view laboratory testing seems not to be important.

However, in case of a hydrogen sulphide break - through, operation losses in the magnitude of 1 000 000 $ are inevitable. Therefore desulphurization monitoring is strongly recommended, i.e. it is worth while:

- to analyze continuously the total sulphur level in feed gas
- to calculate the total weight of adsorbed sulphur in zincoxide and to forecast the term for recharging the catalyst statistically /see fig. 1.2.2/2/
- to install a sampling tube at the lower part of the zincoxide layer in 102 - D /see sketch/. Continuous indicating analyzers of hydrogen sulphide will signalize the danger of a hydrogen sulphide break - through one month in advance at a minimum.

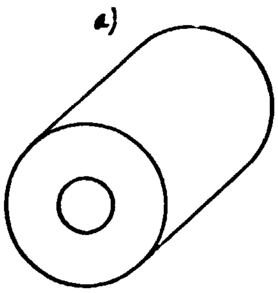


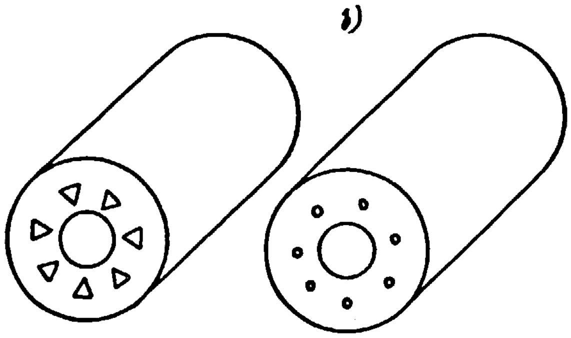
After finishing the ammonia plant reconstruction the use of active carbon for desulphurization may become economically favourable. It depends on the natural gas specification to decide whether active carbon would be sufficient for desulphurization. Active carbon adsorption tests should be realized on laboratory scale first and verified by testing on bypass reactors afterwards.

1.3.3 Primary Reformer Catalyst

Catalyst Types

Supported nickel oxides in the form of Raschig rings /a/ or Rasching rings with enlarged surface /be/.





Reduced pressure drop, good mechanical strength and better gas diffusion conditions are the main features of the ad b/ types. Total savings of 200 kW for a 1 000 t ammonia plant were attained if the ad b/ types replaced the ad a/ ones.

General Use of Reforming Catalysts

The above catalysts are used for hydrocarbon steam reforming reactions only

$$C_nH_m + nH_2O \longrightarrow nCO + /\frac{m}{2} + n/\ H_2 \qquad /1.3.3/1/$$

$$C_nH_m + 2nH_2O \longrightarrow nCO_2 + /\frac{m}{2} + 2n/\ H_2 \qquad /1.3.3/2/$$

Detailed catalyst composition and formulation differs in accordance to hydrocarbon feed type, steam: carbon ratio and final product /ammonia, methanol, hydrogen, town gas, CO + H_2 make-up gases, reducing atmospheres/.

Similar catalysts /supported NiO/ are used for secondary and autothermal reformers and for methanation.

Catalyst Testing

Activity and activity/life tests needed for the ammonia plant operation are difficult to carry out

- under normal operating temperatures /i.e. above 650 °C/, the limiting factor in the complex mechanism of the steam reforming operation is the radiant heat transfer into tubes and not the catalyst activity. This was proved for all catalyst types.
- for long, trouble free operation the most important section of the reaction tube is the upper one. Hydrocarbon/steam mixture is preheated here from 500 °C approx. to operating temperatures /above 700 °C/. In this zone hydrocarbons are preheated and cracked into radicals which are reformed immediatelly afterwards. Carbon formation and coking can eventually take place in this preheating zone /fig. 1.3.3 /1/

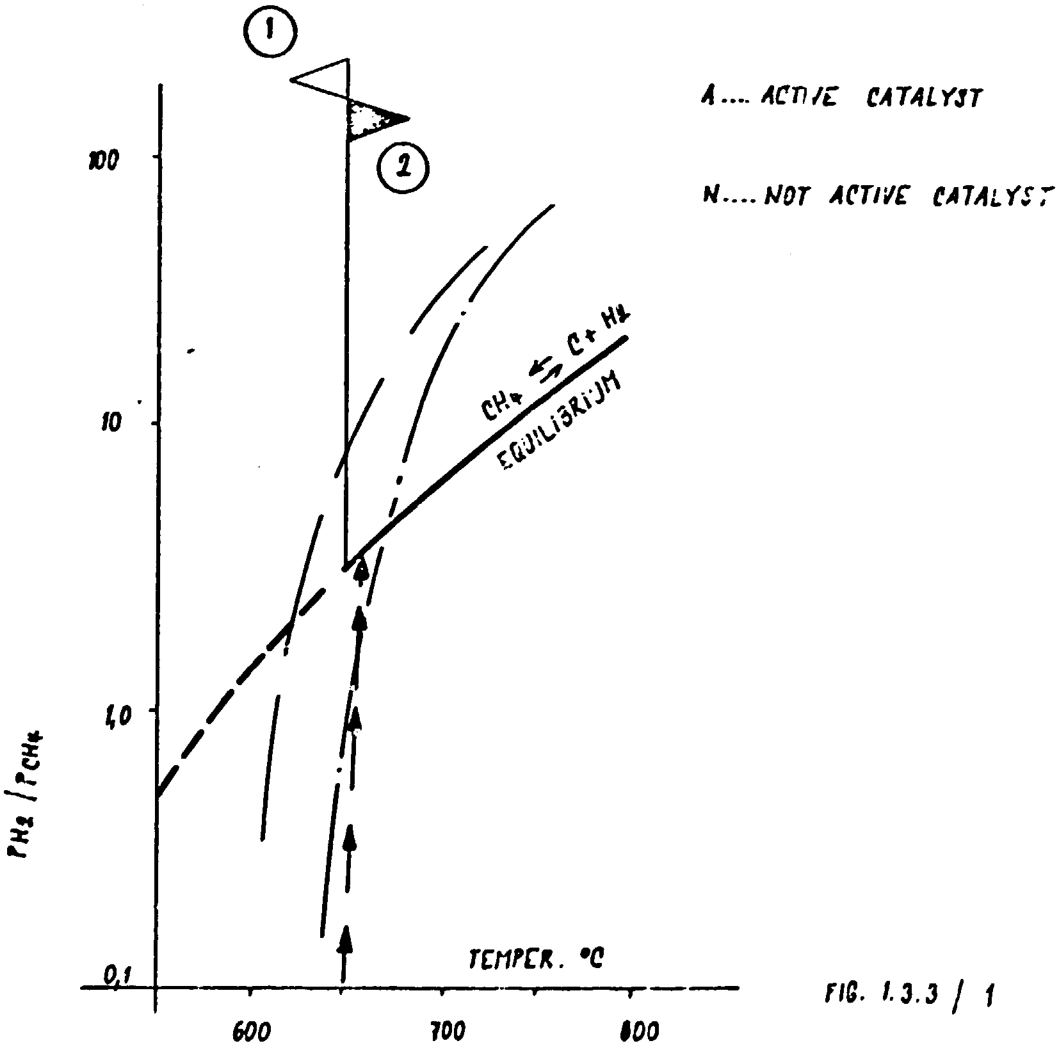
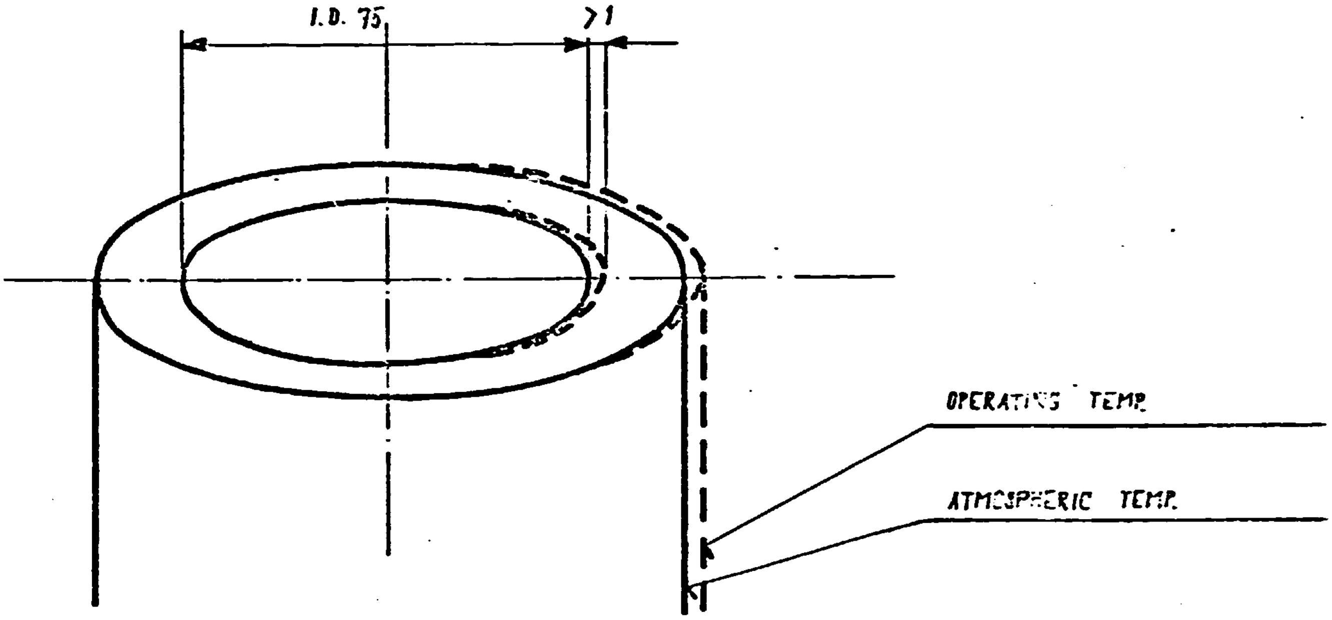


FIG. 1.3.3 / 1

- reaction tube internal diameter difference between the hot and cold states is 1 mm approx.



Random packed catalyst particles are compressed and off-loaded by each shut down/start up operation and they are crushed step by step and worn out. Repeated shut down/start ups perform higher mechanical loads, and catalyst breaking,resulting in increased pressure drop.

Each of the 322 tubes having 0,59 m^3 of catalyst operates as an independent reactor. The scaling up factor for test reactors therefore is relatively low /1:5 000 - 1:60 000/ and reaction mechanism modelling seems to be easy.

In case of tube reactors, the reaction mechanism described in 1.2.1 has to be completed with heat transfer into tube to obtain a representative reactor model. However, due to the completely different nature of chemical reaction mechanism and heat transfer, The primary reformer process can not be tested on a laboratory scale.

Nevertheless, laboratory reactors can be used efficiently for the modelling of specific important parts of complex processes:

- Modelling and comparison of competitive catalysts under preheating zone conditions
- Evaluation of the catalyst reduction conditions /comparison of reducing atmospheres: steam only, steam/nitrogen and steam/nitrogen/hydrogen mixtures/ on the final catalyst activity namely in the preheating zone.

Laboratory Testing

Laboratory testing of primary reformer catalysts is not described here, as a mini scale reactor is available at the Technical University at Homs and it is recommended to make these tests there.

Field Testing

A full scale single catalyst reformer tube installed in paralel to a 101 B primary reformer /fig. 1.3.3/2/ is the only procedure which presents reproducable results for the objective comparison of competitive catalysts. The high installation costs /min. 250 000 $ / will hardly pay off. As each competitive catalyst has to be tested in sequence, catalyst evaluation is time consuming and expensive.

Note: For the general comparison of reaction activity of all nickel based catalysts. The Nielsen adsorption method is used. Analysis of the quantity of adsorbed sulphur on samples of catalysts presents good primary information on the tested catalyst. Relatively cheap apparatus for general use is available.

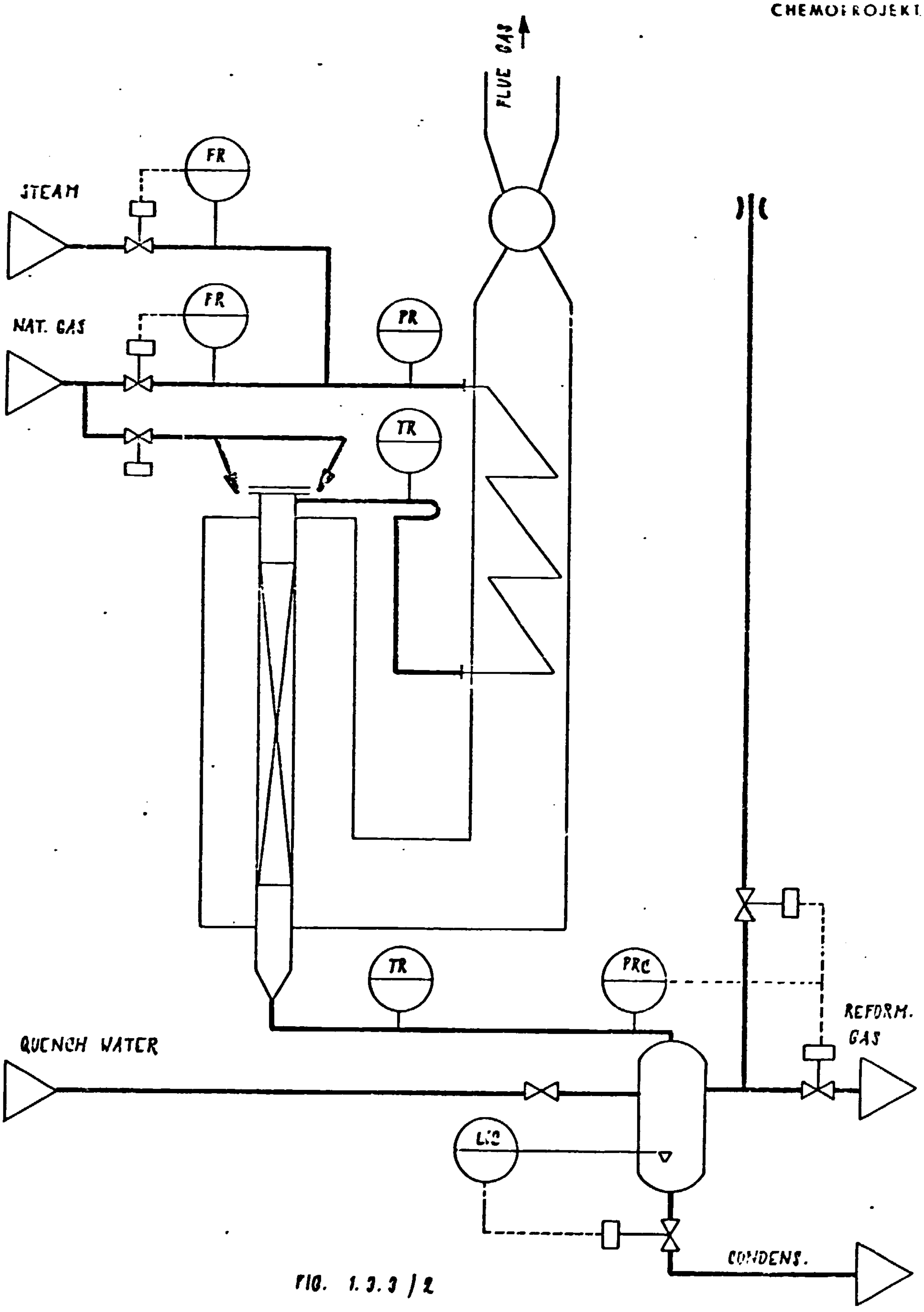


FIG. 1.3.3 / 2

SINGLE TUBE FULL SCALE
TEST REACTOR

Primary Reformer Catalyst Testing at GFC

Primary reformer catalyst life at GFC Homs presents one of the main operation problems. Therefore the above catalyst testing should be preferred.

Natural gas reformer catalyst testing seems to be the only with prospects for GFC /min. 12 competitive catalyst manufacturers are known.

As the primary reformer catalyst at GFC is unfavourable influenced by a small quantity of steam and by an increased number of shut downs/start ups, it is recommended to install a crushing strength measuring apparatus.

For the comparison of catalyst activities in the preheating zone, it is recommended to realize activity tests at the laboratories of Technical University Homs in the temperatures between 600 - 750 °C. For the above test it is necessary to deliver natural gas in compressed gas cylinders. The testing is time consuming. To compare the properties of 5 catalyst types a half year period is usually needed and it is necessary to provide technically trained personnel /1 graduate + 1 technician/.

For general comparison of all the Ni based catalysts /primary and secondary reformers, methanation/ it is recommended to install a simple measuring instrument of sulphur adsorption on nickel.

In tho future a program of catalyst activity testing should be compiled to evaluate and compare different catalyst reduction methods /reduction in superheated steam, nitrogen/steam and nitrogen/steam/hydrogen mixtures/.

Full Scale Testing

Because of the high investment and operating costs of a single scale reformer /see fig. 1.3.3.2/ this alternative is recommended. However, it is suggested to use an ammonia cracking unit - B for primary reformer catalyst testing.

The above mentioned furnace, having 12 tubes, is in operation during ammonia plant start up only/hydrogen production for desulphurization/.

During the normal operation of the ammonia plant up to 12 catalyst types may be tested in parallel providing that temperature monitoring along each testing tube and gas sampling downstream catalyst tubes will be installed.

In such a way GFC would have the opportunity to compare under exactly the same conditions up to 12 competitive catalysts at minimum expense. The operation regime is not too different from operation conditions in the primary reformer furnace 101 - B.

The above tests could present the most objective comparison of competitive catalysts and the risk of misleading results is kept at a minimum. Besides long time activity measurements, resistance to breaking tendency can be tested. Several planned shut downs and restarts can be monitored during the test run.

In case of the reconstruction of the ammonia cracker to the semiscale multitube test reactor, GFC Homs would lose the the hydrogen source for ammonia plant start up. The reconstruction furnace would produce instead of a hydrogen/nitrogen mixture, a hydrogen/carbon oxides/methane mixture.

As carbon oxides should not be used for sulphur hydrogenation to prevent methanation reactions on a CoMox catalyst

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

$$CO + 4H_2 \longrightarrow CH_4 + 2H_2O$$

it is necessary to minimize the above effect by:

- a plant start up with high nitrogen circulation/ to dilute $CO + CO_2$ below 1 % vol./. I.E. 25 to 35 times more nitrogen than hydrogen
- cracked gas could be washed out by means of water, The carbon monoxide content can be reduced and the nitrogen: hydrogen ratio could be kept at the value of approx. 15.
- start up of the ammonia plant with nitrogen recirculation only. Cracked gas can be injected upstream HT shift converter 102 - D it temperature in HTS catalyst reaches 300 °C. Both CO and CO_2 would be reduced in HTS and LTS convertors and in the Carsol plant.

Economic Results of Primary Reformer Catalyst Testing

- less time consuming start up and reduction procedure /in accordance to existing operation manual/ should be developed in future. Every hour saved during the start up and catalyst reduction operations mean 5 000 $ approx. on extra ammonia production and save half of the above sum on utilities and hydrocarbon losses
- life of catalyst up to 5 years may be predicted with a reasonable probability if its mechanical stability and activity in the preheating zone were proved by testing and adequate results were obtained

Rebuilding of the 105 - B ammonia craker to a semiscale multitest reformer may provide an excellent opportunity for precise comparative testing of competitive catalysts under precisely defined conditions.

1.3.4. Secondary Reformer Catalyst

Catalyst types

Supported nickle oxide resistant to high temperatures.

General Use of Reforming Catalysts

Above catylysts are used for hydrocarbon reforming in the presence of air /oxygen/. Steam reforming reactions /1.3.3/1, 1.3.3/2/ follow partial oxidation of the secondary reformer feed. Similar catalysts are used for autothermal reformers.

Catalyst Testing

Due to relatively high operation temperatures in the secondary reformer catalysts, the influence of gas diffusion on the reaction rate is reduced, which is the reason why the test results obtained on crushed catalysts not differ considerably from test results obtained on uncrushed catalysts.

For laboratory testing the same apparatuses are used as for primary reformer testing with appropriate methods.
The test reactor has to be heat resistant up to 1350 °C.

Field test reactors are not realized due to extremely high operation temperatures /namely because of pipe connections/. Even air/gas mixing of field test scale is difficult to design and to operate safely.

Secondary catalysts generally suffer from high operation temperatures /upper part of the laser is heated up to 1 300 °C/, migration of silica from steam and refractories and alcalis from primary reformer catalys s. Most often cracks have been found on catalyst particle bodies resulting from overheating, which has led to the destruction of the particles later.

Secondary Reformer Testing at GFC

No important problems have been discovered to date on the secondary reformer at GFC. The testing of this catalyst, if necessary, should be planned for the second stage of the GFC catalyst testing program, when more serious catalyst problems would have been solved and when GFC technical staff would have more experience in the field of catalyst testing.

If in the meantime a new catalyst charge is needed and an appropriate catalyst supplier is to be selected it is recommended to test the mechanical strength and sulphur adsorption capability of reduced and aged catalysts.

The reduction of catalysts could be carried out in a tube connected to the reformed gas upstream the HT shift reactor. Overheating can be arranged in a laboratory furnace. Besided the crushing strength the most instructive parameter for selecting a catalyst is the optical inspection of cracks which appear on the catalyst surface after repeated overheating to 1350°C.

1.3.5 Shift Conversion Catalysts /High and Low Temperatures/

Catalyst types

For high temperature shift conversion /HTS/

$$CO + H_2 \longrightarrow CO_2 + H_2 \qquad /1.3.5/1/$$

iron and chromium oxides are generally used. Side reaction

$$N_2 + 3H_2 \longrightarrow 2NH_3 \qquad /1.3.5/2/$$

should be suppressed. Operation temperatures are
340 - 450 °C.

Low temperature shift conversion catalysts LTS / see eq. 1.3.5/1/ are supported copper and zincoxides or copper, zinc, and chromium oxides. Operation temperatures are 200 - 260 °C. Side reactions produce methanol and products of methanol oxidation generally expressed as methanol

$$CO + 2H_2 \longrightarrow CH_3OH \qquad /1.3.5/3/$$

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O \qquad /1.3.5/4/$$

Side stream reactions should be minimized in order to decrease hydrogen losses and to avoid corrosion and pollution problems /formic acid is one of the methanol oxidation products/.

Besides HTS and LTS catalysts there are two types of medium temperature shift conversion catalysts available operating from 250 to 400 °C. The first one based on cobalt molybdenum oxides is not applicable at GFC as it operates in sulphidized form only.

The other type is a differently formulated HTS catalyst but even this catalyst should not be applied at GFC due to operation regime /102 - C boiler downstream temperature would have to be decreased below 300 °C, and 103 - C, 104 - C, and 112 - C exchangers would be heavily off-loaded/.

Generally, the activity of the HTS catalyst is inversely proportional to the crushing strength /fig, 1.3.5/1/.

HTS catalysts always contain sulphur. During catalyst reduction sulphur migrates in the form of H_2S downstream to the LTS reactor.

The active component in the LTS catalyst is copper. Very fine particles of copper present the highest activity centres. As copper tends to sinter at temperature above 250 °C, it is important to operate at temperatures up to 250 °C. Operating above 250 °C reduces catalyst life, LTS catalyst is extremely sensitive to chlorides and hydrogen sulphide. Even silica could block the active centres and under the existing conditions high quality steam can not be guaranted before 1987 at GFC. Up to this time a risk of LTS catalyst poisoning through silica, chloridies and other inpurities from process steam cannot be avoided.

HTS catalyst life is unfavourably influenced in a similar way and moreover HTS catalyst can be destroyed by wet steam during start ups without nitrogen. Short life and decreased activity of the HTS catalyst result in increased CO content upstream the LTS convertor. The LTS convertor operates at higher CO content. Higher CO conversion results in higher exotermic heat evolved and the LTS catalyst may be overheated.

GFC has experienced low HTS catalyst life. As indicated above it is necessary to expect limited LTS catalyst life under existing conditions.

These are the reasons why besides primary reforming and HTS catalysts, GFC has to test and evaluate LTS catalysts initially.

Laboratory Testing Methods

Both HTS and LTS catalysts are similar, with the exception of different operation temperatures. Integral /one through/ glass reactors operating at a parallel /up to 4 reactors/ are generally used. Conversion is measured analytically. Reformed gas can be used.

Field Test Reactors

Bypass adiabatic reactors joined to the 102 - C reactor can be installed. The conversion degree can be easily measured by thermocouples as CO conversion is quantitatively proportional to the reaction heat - i.e. to the temperature difference. It is not necessary to install expensive gas analyzers with high requirements on maintenance, however as conversion calculation based on temperature difference measurement is time consuming, it is recommended to use either a programmable calculator or microprocessor.

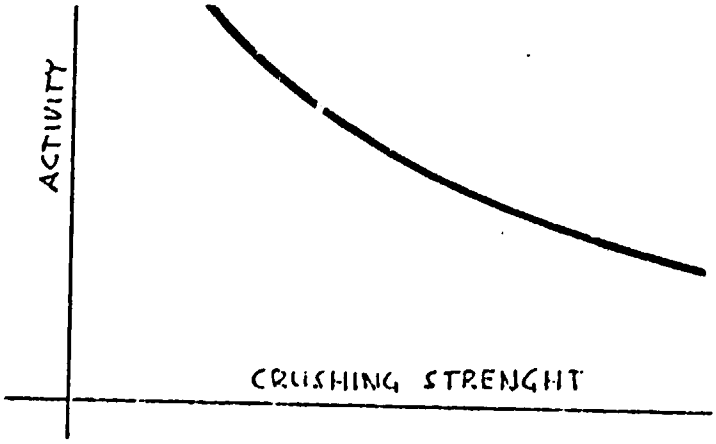


FIG 1.3.5/1

Shift Conversion Catalyst Testing at GFC Homs

In modern ammonia plants the HTS catalyst and the ammonia synthesis catalyst are the most reliable . Quite different is the situation with LTS catalysts. LTS catalysts normally show the shortest life.

Under local conditions the HTS catalyst has an extremely short life and so it is necessary to introduce HTS catalyst testing.

In ANNEX 1/III the field testing of CO catalyst is specified. Bypass reactors can be operated by operation and maintenance personnel. Test evaluatiln /preferably computerized/ can be carried out by engineers in the ammonia plant or by a specialist for the development team of GFC. The above expensive method can be realized within few months and can present the objective comparison of catalyst properties exactly for the GFC present operating needs.

Laboratory reactors for shift conversion are relatively not expensive and can present reasonable results in catalyst testing, based on comparison of their properties, however it is necessary to install them in a special gas laboratory /near the ammonia plant to avoid problems with gas transport/ and to provide staff for keeping the laboratory in operation /1 university graduate, 1 operator, 1 man for maintenance/.

Both bypass reactors and laboratory reactors may be used even for LTS, this will probably be necessary in the near future.

In parallel to catalyst activity testing it is necessary to test the crushing strength /aged catalyst/ namely under present operating conditions of HTS/ low quality steam, possible catalyst wetting during start ups/.

1.3.6 Methanation Catalyst

Catalyst Types

Supported nickle oxides, operating at medium temperatures /250 - 450°C/ for methanation of final traces of carbon oxides

$$CO + 3H_2 \longrightarrow CH_4 + H_2O \qquad /1.3.6/1/$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \qquad /1.3.6/2/$$

Generally, there are three types of methanation catalysts for different operational temperatures:

- low temperature /200 - 250 °C methanation of CO in the presence of oxygen which is simultaneously hydrogenated to water/
- medium temperature /250 - 450 °C used in the ammonia industry/
- high temperature /SNG production/

Low temperature catalysts can contain even chromium oxide besides nickle oxide.

As the reactions 1.3.6/1 and 1.3.6/2 are extremely exothermic it is necessary to prevent the catalyst charge and the methanator to be preheated which may happen if the carbon oxide level exceeds the above safe limit /for the ammonia plant 1 to 1,5% $CO + CO_2$/.

Catalyst Testing

In principle it is similar as reforming catalyst testing. Laboratory reactors are usually designed for atmospheric pressure and for temperatures up to 500 °C. Hydrogen/nitrogen mixture free of carbon oxides is mixed with CO_2 and/or CO, They are purified and tested. CH_4 content and CO, CO_2 traces are indicated downstream teactor. As the methanation of CO_2 has the lowest reaction rate, catalyst testing with CO_2 only is preferred.

Field Testing

Side stream reactors may be installed at a parallel to the plant methanator. Temperature increase can be registred and by means of thermodynamic calculations transformed to the reaction rate /analysis of gas components is not necessary/. Side stream reactors prevent CO, CO_2 leakage to ammonia synthesis system in case of maloperation.

Besides the ammonia synthesis catalyst, the methanation catalyst has the longest life among catalysts used in an ammonia plant. This results from the high purity of the downstream methanator and relatively mild operating conditions. Only if flooding in CO_2 absorbers occurs, drifted droplets of carsol solution may have a harmful effect on catalyst activity.

Reactions 1.3.6/1 and 1.3.6/2 are relatively fast and in case of fresh catalysts they are finished in the upper part of the catalyst layer. During catalyst aging, the reaction zone moves slowly downstream the reactor without noticable CO, CO_2 leakage /see fig 1.2.2/4/. When the reaction zone reached the end of the catalyst layer, CO_2 leakage followed by CO leakage appears a few days later, which results in an unplanned shut down for catalyst recharge. To prevent unexpected shut downs methanation catalyst monitoring is important, and more useful than the common testing of catalyst activity.

Methanation Catalyst Testing at GFC

As there are no serious reasons for the deactivation of the methanation catalyst it is proposed to introduce testing of the methanation catalyst in a later stage after problems with shift conversions and reforming catalysts will be settled. For activity evaluation based on sulphur adsorption the testing equipment installed at the Technical University Homs can be used. But catalyst monitoring should be introduced at GFC as soon as possible as the methanation catalyst has geen under operation for nearly 4 years and so it has entered the second half of its life.

1.3.7 Ammonia Synthesis Catalyst

Catalyst types

Promoted magnetite catalysts reduced to α- iron are generally used for the reaction.

$$N_2 + 3H_2 \longrightarrow 2NH_3 \qquad /1.3.7/1/$$

The conversion is limited, concentration below 16 % NH_3 in the gas leaving the reactor at operating pressure 150 bar. Catalyst reduction procedure is extremely important and essentially influences its final activity. For the ideal reduction of the catalyst enormous space velocities such as 100 000 $Nm^3/m^3/h$ are needed, applicable on a laboratory scale but not in full scale practice. If in laboratories the catalyst is reduced at high space velocities /above 30 000 $Nm^3/m^3/h$/, test results obtained for commercial catalyst types comparison are of little practical value.

In modern ammonia plants with centrifugal compressors and very pure make up gas as at GFC, ammonia synthesis catalyst life is 6 - 12 years and therefore it is more economical to order a new catalyst charge from a traditional highly experienced catalyst supplier even for a higher price than to install a test reactor. The catalyst supplier may be selected on the basis of experience exchanged with foreign

ammonia

producers where more convertors are operating at a parallel.

Laboratory reactors are very expensive because they work under high operation pressures /100 bar min./. Before testing the catalyst is crushed down to the size 0,5 - 1,5 mm. As the ammonia synthesis reaction is controlled by gas diffusion
/see fig. 1.3.7/1 / scaling up of results is problematic.

Installation of bypass reactors is complicated due to the use of high pressure.

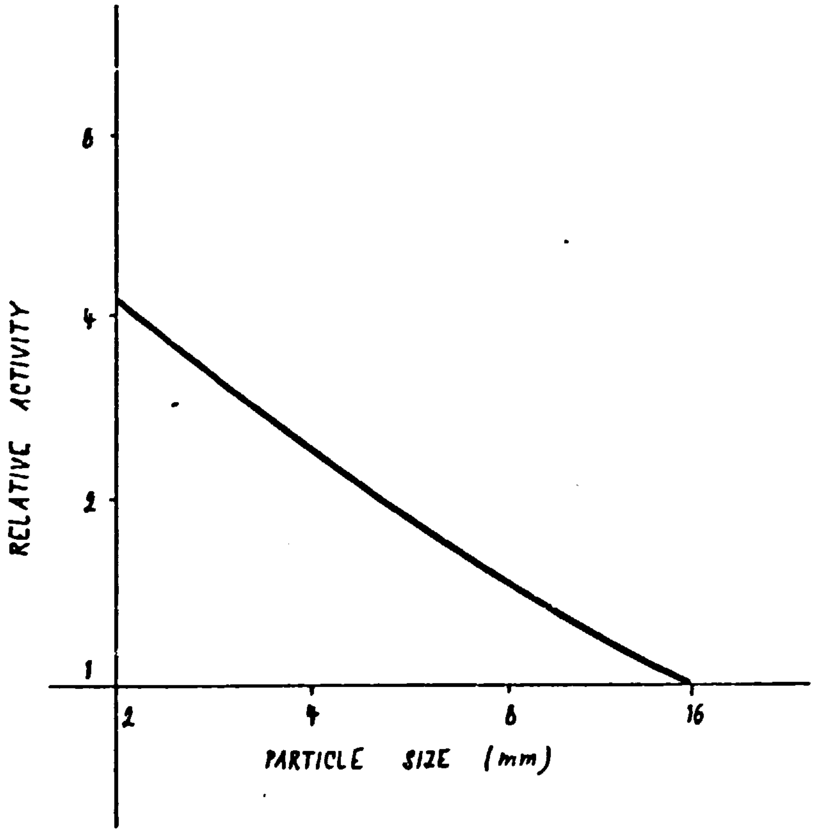


FIG. 1.3.7/1

Conclusions

High investment costs for a fully equipped catalyst testing laboratory 14 - 18 mil $ and operating costs 0,6 - 0,7 mil $ per year would increase costs of produced ammonia by 10 - 12 $ per ton of ammonia. Even a minimalized catalyst testing plant /5 mil $/ is not economic.

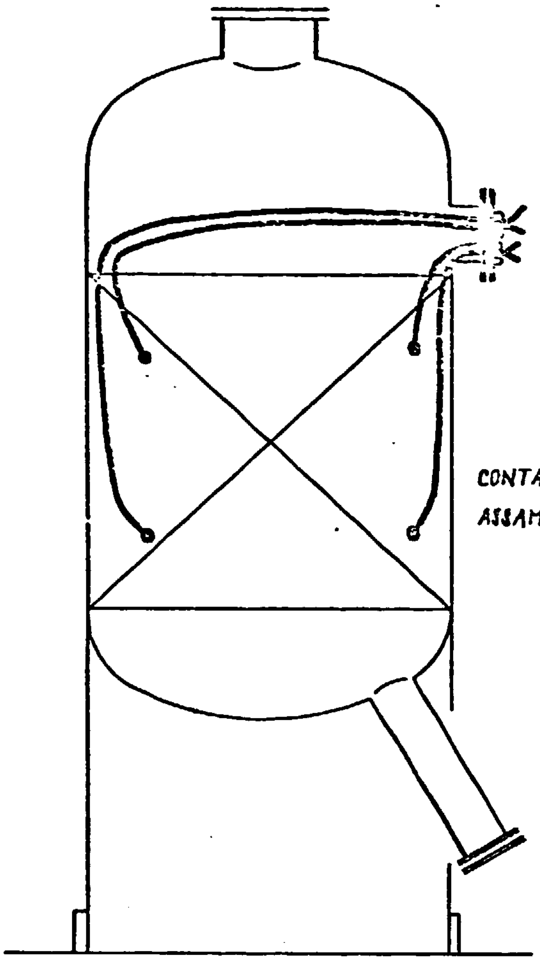
GFC has experience with catalyst life of the primary reformer and HTS conversion catalysts only.

As operation difficulties are to be solved step by step, it is not advisable to install a catalyst testing plant for all the eight catalysts used in the ammonia plant at the same time. The testing of primary reformer and HT-CO conversion catalysts is to be realized as the first step. The above-mentioned low life of the primary reformer catalyst was evidently connected with the high contamination of processed steam.

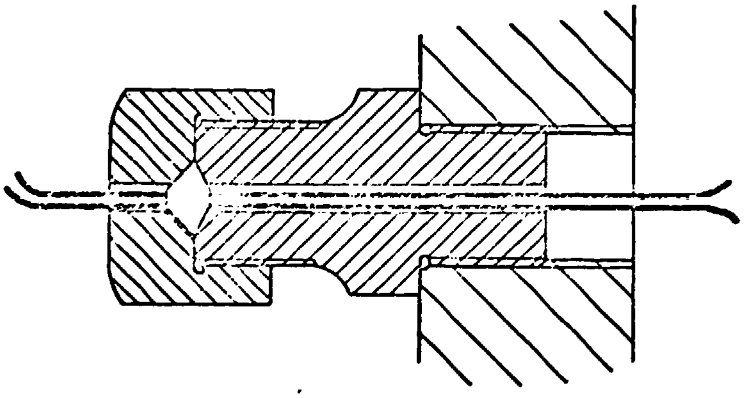
HT-CO catalyst was spoiled by wett steam during start ups and catalyst reduction due to the absence of nitrogen. The low quality of the steam will influence the catalyst degradation until high quality steam /as per boiler codes for 120 - 130 B/ and nitrogen for the start up will be secured. Existing problems of primary reformer and HTS catalysts will be caused by insufficient mechanical strength than by low catalyst activity.

For the decision which of the more than dozen existing catalyst suppliers should be chosen, relatively cheap bypass reactors for HT conversion will give sufficient information.

As far as the preheating zone of primary reformer catalysts is concerned, the existing laboratory reactor at GFC may be used for testing.



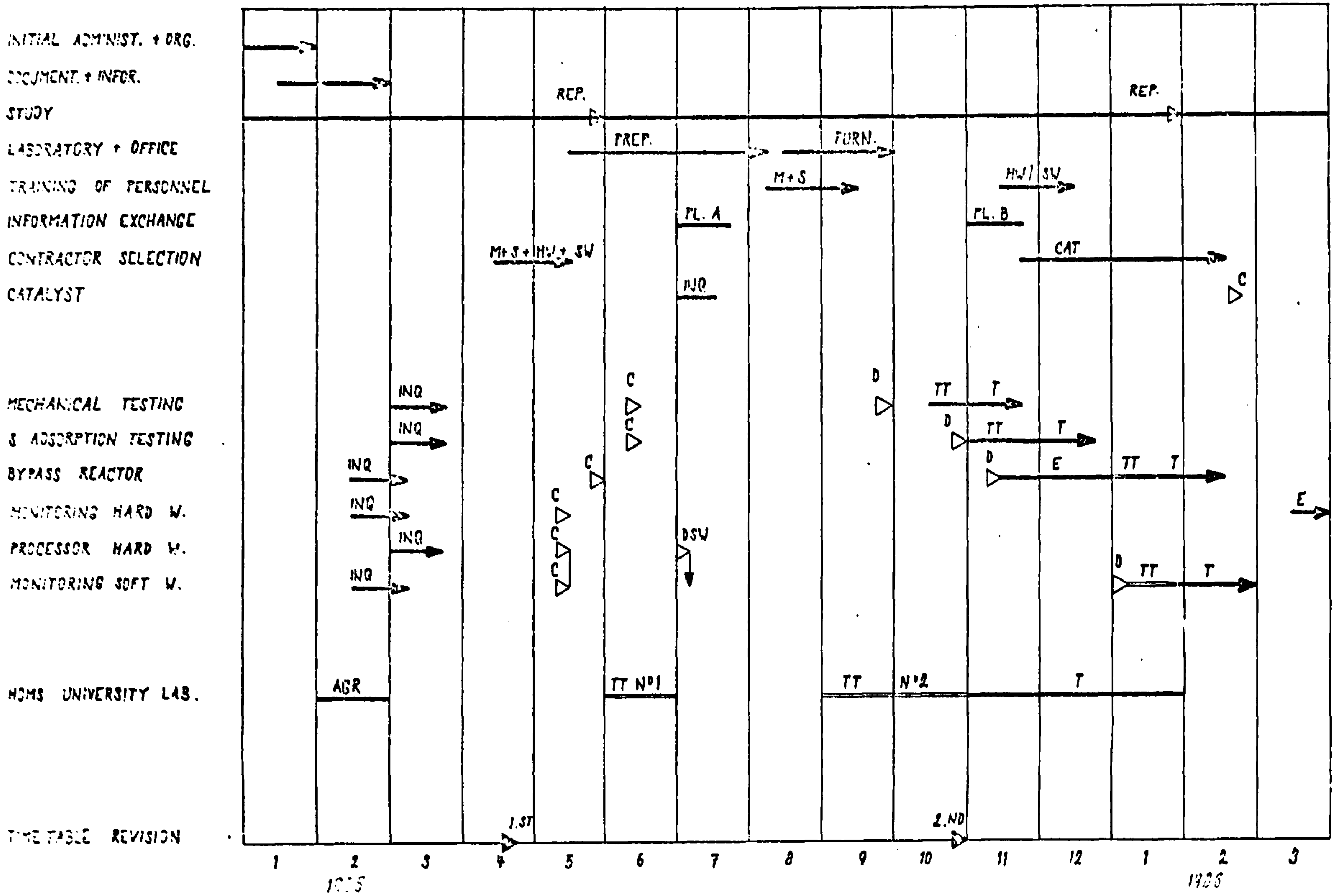
CONTACT THERMOCOUPLES
ASSAMBLE



MULTIPLE THERMOCOUPLE
GLAND

CONTACT THERMOCOUPLES

ANNEX 1/II

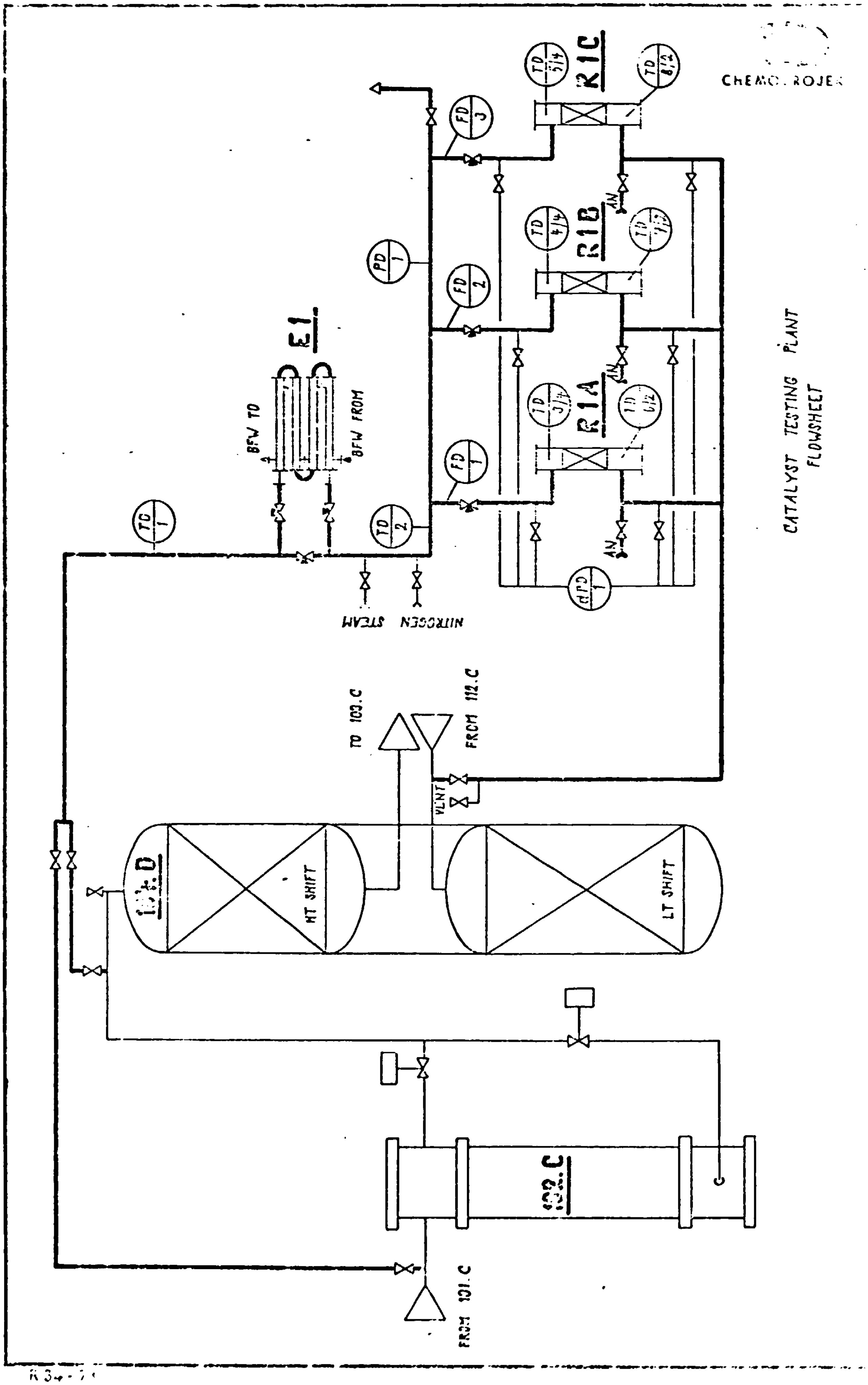


CHEMOPROJEKT

Annex 1/II

Abbreviations used :

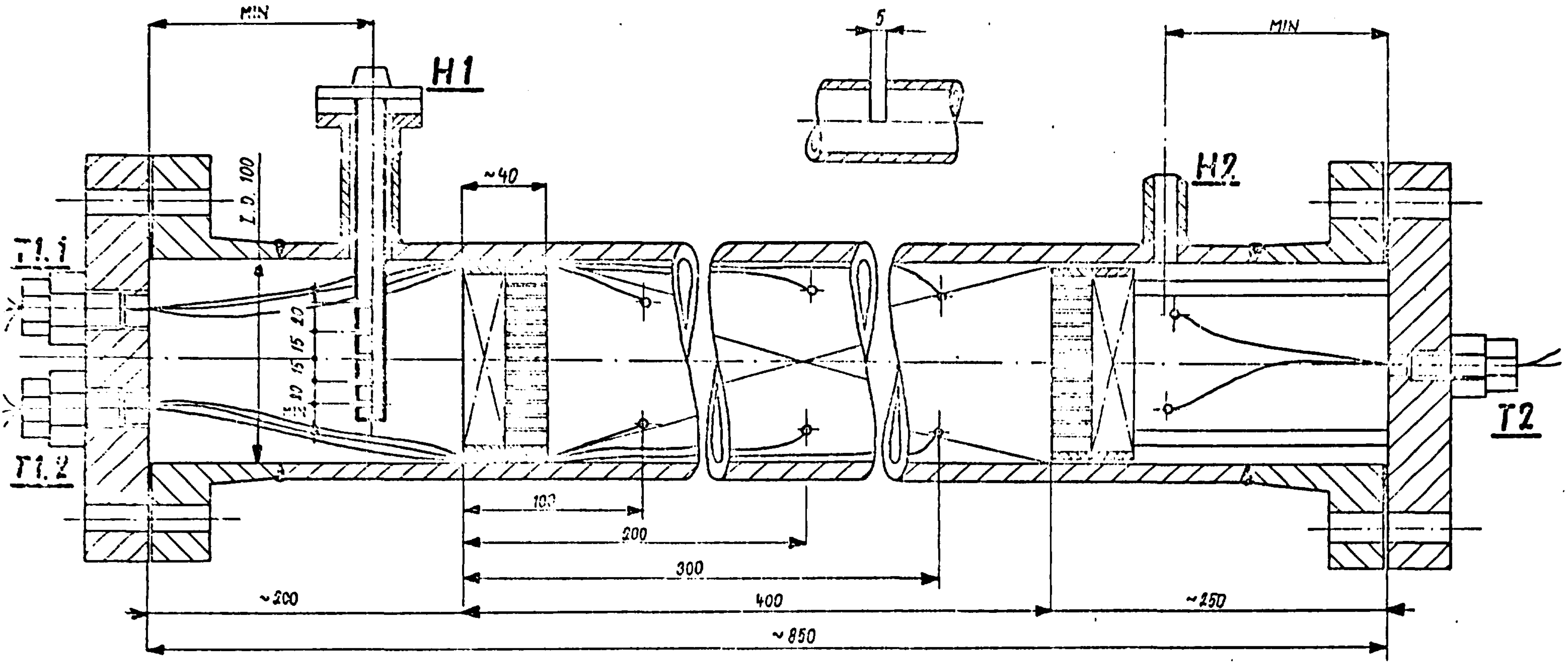
Rep.	Report
Prep.	Preparation
Furn.	Furnishing
Inq.	Inquiry
Agr.	Agreement
C	Contract day
D	Supply
TT	Trial test
T	Test
E	Erection
Dsw	Supplied to sw contractor
Hw	Hard-ware
Sw	Soft-ware
PL.A	Plant "A"
PL.B	Plant "B"
CAT	Catalyst
M	Mechanical testing eq.
S	Sulphur ads. tester



CATALYST TESTING PLANT
FLOWSHEET

ANNEX 1/III

GAS DISTRIBUTOR - DETAIL



OPERATING PRESSURE :
TEMPERATURE :

DESIGN PRESSURE :
TEMPERATURE :

INSULATION : MIN. 50 MM
[MINERAL WOOL IN Al. SHEET]

MATERIAL :

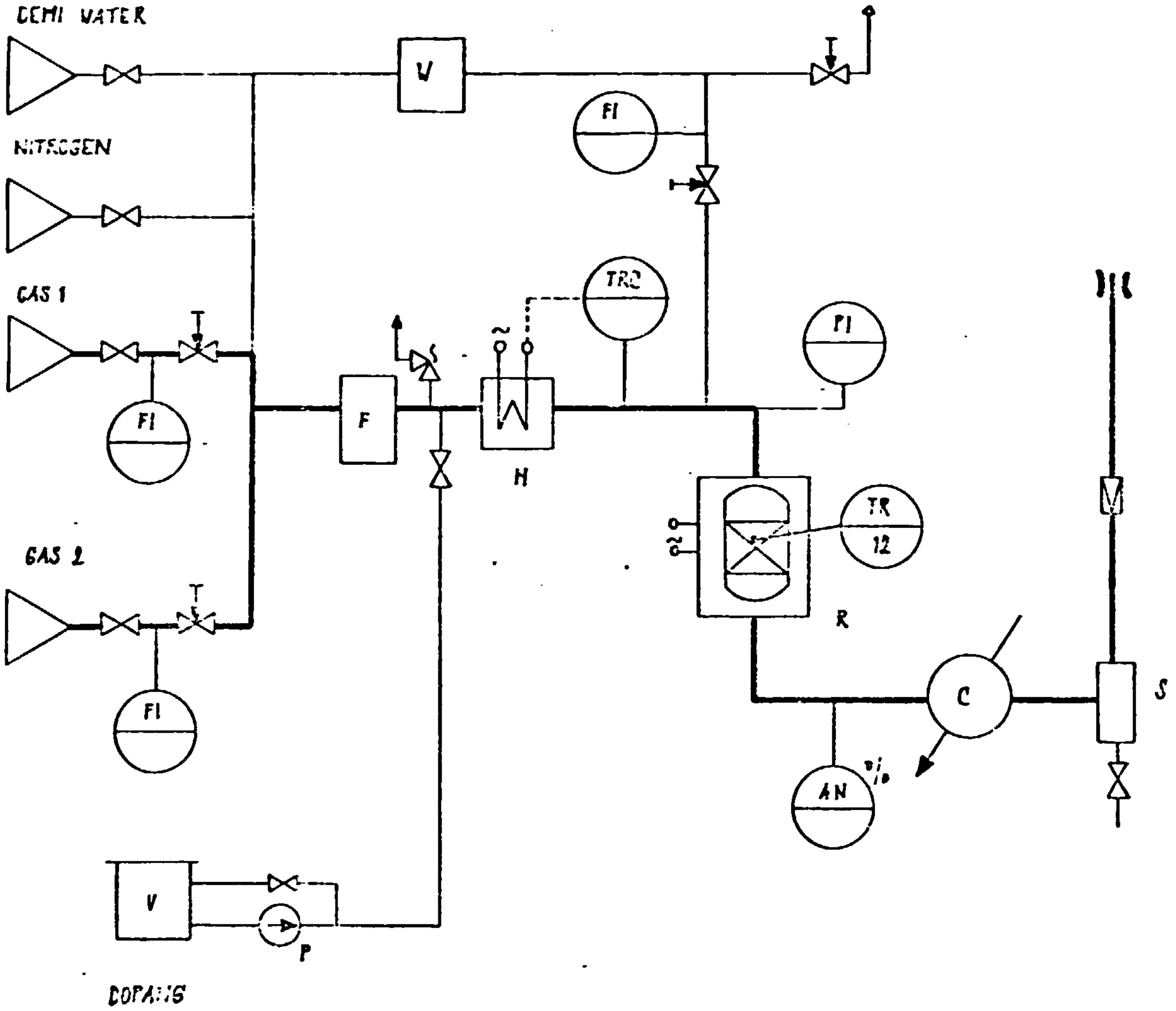
CATALYST Vol. ≐ 2,8 LITERS

T2	1	TERMOCOUPLE	G ½"		CONAX [illegible]
T1.1 T1.2	2	TERMOCOUPLES	G ½"		-"-
H2	1	OUTLET GAS	15		
H1	1	INLET GAS	25/1.5		
[illegible]	[illegible]	DUTY	SIZE	RATING	NOTE

GFC HOMS

PILOT REACTOR

CHEMOPROJEKT



C . . . . . . COOLER

F . . . . . . FILTER

H . . . . . . HEATER

R . . . . . TEST REACTOR

S . . . . . SEPARATOR

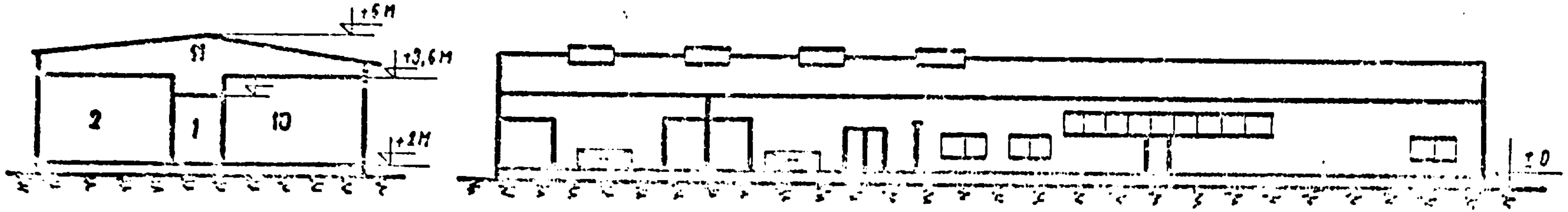
V . . . . . DOPANT RESERVOIR

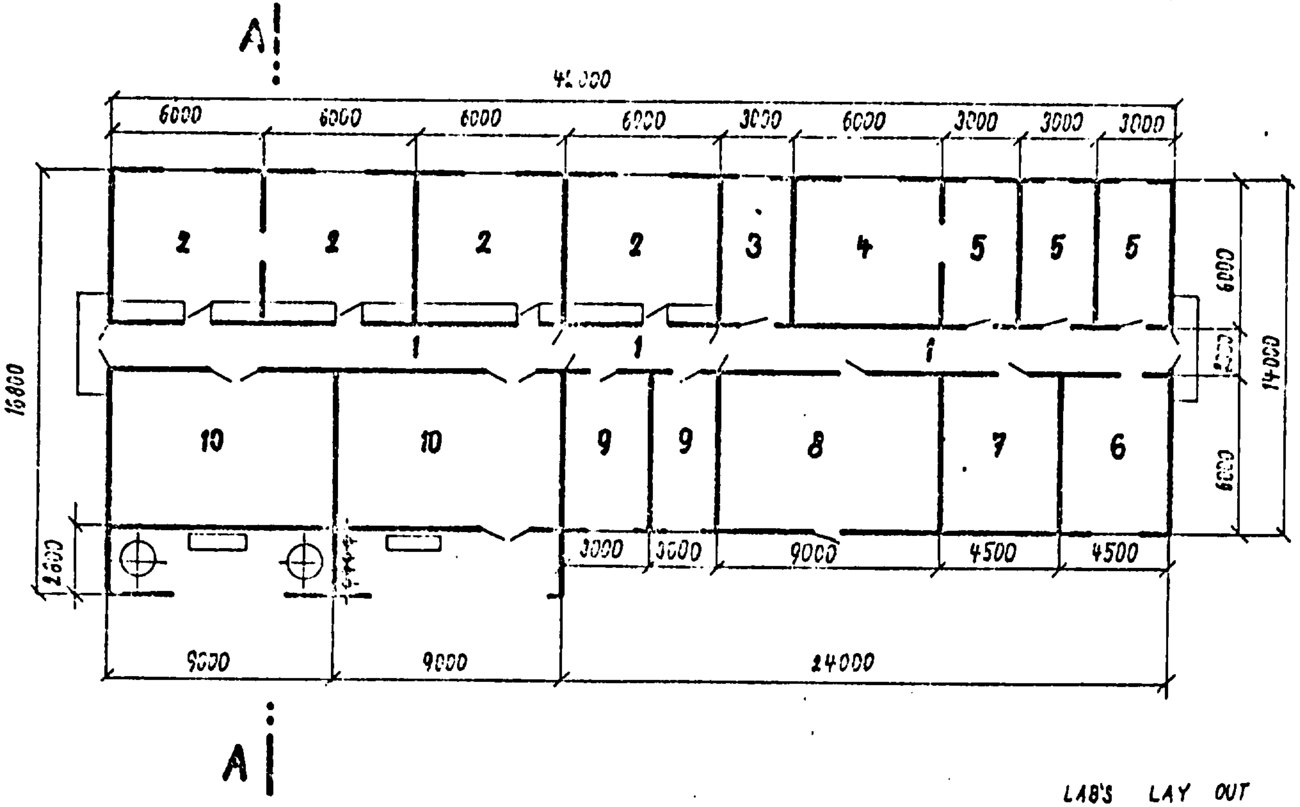
W . . . . . STEAM GENERATOR

CATALYST TESTING UNIT

SECTION A-A

ANNEX 1/IV





11	CABLES, GAS + VENT. PIPING
10	STORE
9	WC, SHOWERS
8	VENTILATION, AIR CONDITION
7	ELECTRIC SUBSTATION
6	CLEAN ROOM
5	OFFICE
4	COMPUTER
3	MECHANICAL LAB
2	CATALYST TESTING LABS
1	CORRIDOR
Nº	SERVICE

SCALE 1:200

LAB'S LAY OUT

CFC HOMS

CATALYST TESTING PLANT

CHEMOPROJEKT

ANNEX I/V

Microprocessor for Catalyst Testing Project

Laboratory tests and/or field tests as well as process units monitoring data have to be evaluated by means of a computer. Hundreds of items of input data for each evaluation have to be collected and dozens of calculation procedures have to be carried out. One evaluation per day for all reactors and test reactors is considered a minimum.

To demonstrate thermodynamic evaluation of catalyzed processes in case of catalyst monitoring or laboratory test evaluation, a computer program was developed. As hardware, Teleputer microprocessor 128k bytes manufactured by Redifussion was used.

Similar not expensive hardware is suggested for GFC according to the catalyst testing project. Two or three units /one operation, one stand by, one for training and program booting/ are recommended as optimum.

The catalyst testing program even if applied to its full extent, may load one microprocessor for less than four hours per day. For the rest of time the microprocessor may be used for other engineering and economic calculations and training purposes.

Brief description of software developed by the UNIDO team during their stay at GFC Homs:

Thermodynamic Evaluation of Shift Convertor Reactors

HT and LT shift conversion reactors /full scale for monitoring field of laboratory reactors for catalyst comparison/ function and activity /reaction rate/ evaluation.

Software consists of:

- Data bank for 25 chemical compounds containing thermodynamic data
- Mass balance for all make up gas plant train /i.e. mass balance for desulphurization, primary and secondary reformers, HTS and LTS conversions, Carsol CO_2 wash out and methanation/.
- Heat balance /enthalpy balance/ for any of the above steps
- Shift conversion reaction process simulation. Reaction rate for selective chemical reactions and thermodynamic approach to the equilibrium are calculated

Calculation of Ammonia Production Cost

On the basis of plant investment, maintenance, and catylyst costs, overhead, labor, feed, fuel, and utilities consumption, the production cost of ammonia is calculated.

Lower efficiency at turn down ratio /load below 100 %/ as well as losses during start up, emergency shut downs, unplanned maintenance and catalyst recharging are respected.

Software consists of:

Simple technical/economic equations for the calculation of:

- Production cost
- Turn down operation losses
- Start up losses
- Unplanned maintenance and catalyst recharge cost.

Boiler Blow Down Calculation

General balance of contaminants in the steam system for an ammonia plant.

Software consists of the following calculations:

- Partial pressure of contaminants in steam
- Balance of contaminants in the steam system

ANNEX 1/VI

Literature :

1/ H. Bohlbro : An Investigation on the Kinetics of Carbon Monoxide with Water Vapour over Iron Oxide Based Catalysts Gjellerup 1966

2/ Catalyst Handbook , Wolfe 1970

3/ Rostrup Nielsen : Steam Reforming Catalysts Copenhagen 1975

4/ Chemoprojekt Internal Manuals for Design and Development of Catalysed Processes

ANNEX 1/VII

Computer Print - Outs

```
1.12.1984                                              Chemoprojekt Praha

KELLOG TYPE AMMONIA PLANT

   HEAT & MASS BALLANCE

G.F.C. HOMS 1000 mt/d NH3 Plant.


     List of process streams :

 1   Low Boiling Naphtha
 2   M.U.G. Recycle
 3   Feed + Recycle
 4   Desulphurised Feed
 5   Primary Reformer In
 6   Primary Reformer Out
 7   Secondary Reformer Out
 8   H.T. Shift Out
 9   L.T. Shift Out
10   Carsol Wash Out
11   Methanator Outlet
12   M.U.G. to NH3 Synthesis
13   CO2
14   Proces Condensate
15   Carsol Solution
16   M.U.G. Condensate
17   Proces Air
18   CO2 Absorber In
```

1.12.1984 Chemoprojekt Praha

STREAM : 1 Low Boiling Naphtha

Pressure	37.05 B		
Temperature	25.00 C		
Composition	kMol/hr	St.m3/hr	molal %
C_nH_m	+199.89440	4018	100.00 %
Total Dry :	+199.89440	4018	100.00
Total Watt :	+199.894	4018	
Total in kgs		22635.480	

STREAM : 2 M.U.G. Recycle

Pressure 36.05 B
Temperature 45.00 C

Composition	kMol/hr	St.m3/hr	molal %
H2	+15.99155	359	74.54 %
N2	+5.21532	117	24.31 %
A	+0.06271	1	0.29 %
H2O	+0.05513	1	0.00 %
CH4	+0.18314	4	0.85 %
Total Dry :	+21.45273	481	100.00
Total Wett :	+21.508	482	

Total in kgs 184.768

Gas Temperature +45.0 C Enthalpy = +40 766 kcal/hr

```
STREAM :   3 Feed + Recycle

Pressure                      37.55 B
Temperature                  400.00 C

Composition                 kMol/hr  St.m3/hr      molal %

H2                        +15.99155       359       7.22 %
N2                         +5.21802       117       2.36 %
A                          +0.06274         1       0.03 %
H2O                        +0.05514         1       0.00 %
CH4                        +0.18372         4       0.08 %
CnHm                     +199.89440      4018      90.31 %
Total Dry  :             +221.35050      4499     100.00
Total Wett :             +221.406        4500

Total in kgs                       22820.350

Gas Temperature   +400.0 C    Enthalpy =        +94 616 kcal/hr
```

```
STREAM :   4 Desulphurised Feed

Pressure                          36.60 B
Temperature.                     400.00 C

Composition                  kMol/hr   St.m3/hr      molal %

H2                         +15.99155        359       7.22 %
N2                          +5.21802        117       2.36 %
A                           +0.06274          1       0.03 %
H2O                         +0.05514          1       0.00 %
CH4                         +0.18372          4       0.08 %
CnHm                      +199.89440       4018      90.31 %
Total Dry   :             +221.35050       4499     100.00
Total Wett  :             +221.406         4500

Total in kgs                          22820.350

Gas Temperature  +400.0 C    Enthalpy =        +94 616 kcal/hr
```

STREAM : 5 Primary Reformer In

Pressure	35.50 B		
Temperature	510.00 C		

Composition	kMol/hr	St.m3/hr	molal %
H2	+15.99155	359	7.22 %
N2	+5.21802	117	2.36 %
A	+0.06274	1	0.03 %
H20	+5533.71400	124033	0.00 %
CH4	+0.18372	4	0.08 %
CnHm	+199.89440	4018	90.31 %
Total Dry :	+221.35050	4499	100.00
Total Watt :	+5755.064	128532	

Total in kgs 122514.800

Gas Temperature +510.0 C Enthalpy = -279 850 400 kcal/hr

```
1.12.1984                                                    Chemoprojekt Praha

STREAM :   6 Primary Reformer Out

Pressure                          32.70 B
Temperature                      812.00 C

Composition               kMol/hr   St.m3/hr      molal %

H2                   +2737.76700     61400      63.05 %
CO                    +513.66420     11510      11.83 %
CO2                   +669.47300     14904      15.42 %
N2                      +5.21802       117       0.12 %
A                       +0.06274         1       0.00 %
H2O                  +3681.10400     82508       0.00 %
CH4                   +416.20200      9315       9.58 %
Total Dry  :         +4342.36700     97248     100.00
Total Wett :         +8023.490      179756

Total in kgs                    122516.300

Gas Temperature  +812.0 C    Enthalpy =  -221 127 000 kcal/hr
```

```
STREAM :   7 Secondary Reformer Out

Pressure                      31.85 B
Temperature                  985.00 C

Composition              kMol/hr    St.m3/hr      molal %

H2                   +3239.68500       72656      52.54 %
CO                    +889.07820       19922      14.42 %
CO2                   +689.10390       15342      11.17 %
N2                   +1310.71700       29367      21.25 %
A                      +15.78963         354       0.26 %
H2O                  +4162.13000       93290       0.00 %
CH4                    +21.15734         474       0.34 %
Total Dry  :         +6166.67200      138114      99.98
Total Wett :        +10327.660        231404

Total in kgs                     174439.500

Gas Temperature   +985.0 C    Enthalpy =  -221 155 400 kcal/hr
```

```
1.12.1984                                                    Chemoprojekt Praha

STREAM :   8 H.T. Shift Out

Pressure                       30.80 B
Temperature                   371.00 C

Composition              kMol/hr     St.m3/hr      molal %

H2                   +3902.58300       87523       57.14 %
CO                    +225.40130        5051        3.30 %
CO2                  +1352.78100       30117       19.81 %
N2                   +1310.45700       29361       19.19 %
A                      +15.78963         354        0.23 %
H2O                  +3498.45400       78414        0.00 %
CH4                    +21.15734         474        0.31 %
NH3                     +0.51962          11        0.01 %
Total Dry  :         +6530.34900      152890       99.98
Total Wett :        +10327.140        231305

Total in kgs                     174439.500

Gas Temperature  +371.0 C    Enthalpy =  -282 601 700 kcal/hr
```

```
1.12.1984                                              Chemoprojekt Praha

STREAM :   9 L.T. Shift Out

Pressure                        30.20 B
Temperature.                   214.00 C

Composition              kMol/hr    St.m3/hr      molal %

H2                  +4106.43600       92095      58.38 %
CO                    +21.10105         473       0.30 %
CO2                 +1556.93200       34662      22.14 %
N2                  +1310.19800       29355      18.63 %
A                     +15.78963         354       0.22 %
H2O                 +3294.30200       73838       0.00 %
CH4                   +21.15734         474       0.30 %
CH3OH                  +0.14905           3       0.00 %
NH3                    +0.51962          11       0.01 %
Total Dry  :        +7033.68200      157427      99.98
Total Wett :       +10326.580        231265

Total in kgs                     174432.300

Gas Temperature  +214.0 C    Enthalpy =  -297 713 800 kcal/hr
```

```
STREAM : 10 Carsol Wash Out

Pressure                      29.90 B
Temperature                   65.00 C

Composition             kMol/hr   St.m3/hr      molal %

H2                  +4083.87600      91589      74.91 %
CO                    +20.99284        470       0.39 %
CO2                    +3.81627         85       0.07 %
N2                  +1306.35600      29269      23.96 %
A                     +15.70863        352       0.29 %
H20                   +47.11540       1056       0.00 %
CH4                   +21.06369        471       0.39 %
Total Dry   :       +5451.81400     122237     100.00
Total Watt  :       +5498.929       123293

Total in kgs                     47402.250

Gas Temperature    +65.0 C    Enthalpy =    +8 787 245 kcal/hr
```

STREAM : 11 Methanator Outlet

Pressure 29.50 B
Temperature 40.00 C

Composition	kMol/hr	St.m3/hr	molal %
H2	+4005.63200	89834	74.54 %
N2	+1306.35600	29269	24.31 %
A	+15.70863	352	0.29 %
H2O	+75.74075	1698	0.00 %
CH4	+45.87279	1027	0.85 %
Total Dry :	+5373.56900	120482	100.00
Total Wett :	+5449.310	122179	

Total in kgs 47402.250

Gas Temperature +40.0 C Enthalpy = +5 999 619 kcal/hr

STREAM : 12 M.U.G. to NH3 Synthesi

Pressure 82.00 B
Temperature 40.00 C

Composition	kMol/hr	St.m3/hr	molal %
H2	+3989.61600	89475	74.54 %
N2	+1301.13700	29152	24.31 %
A	+15.64583	350	0.29 %
H2O	+13.75501	308	0.00 %
CH4	+45.68944	1023	0.85 %
Total Dry :	+5352.08800	120000	100.00
Total Wett :	+5365.844	120308	

Total in kgs 46101.540

Gas Temperature +40.0 C Enthalpy = +9 892 531 kcal/hr

STREAM : 13 CO2

Pressure 1.10 B
Temperature 40.00 C

Composition	kMol/hr	St.m3/hr	molal %
H2	+22.00045	493	1.40 %
CO	+0.10551	2	0.01 %
CO2	+1550.69000	34523	98.35 %
N2	+3.74395	84	0.24 %
A	+0.07895	2	0.01 %
H2O	+116.39480	2609	0.00 %
CH4	+0.09069	2	0.01 %
Total Dry :	+1576.70900	35106	100.00
Total Wett :	+1693.104	37715	

Total in kgs 70501.180

Gas Temperature +40.0 C Enthalpy = -148 344 400 kcal/hr

```
STREAM  :  14  Proces  Condensate

Pressure                           27.20 B
Temperature                         0.00 C

Composition                 kMol/hr    St.m3/hr       molal %

H2                         +0.56450          13       15.01 %
CO                         +0.00271           0        0.07 %
CO2                        +2.42562          54       64.48 %
N2                         +0.09606           2        2.55 %
A                          +0.00203           0        0.05 %
H2O                     +2611.74900       58540        0.00 %
CH4                        +0.00233           0        0.06 %
CH3OH                      +0.14905           3        3.96 %
NH3                        +0.51962          11       13.81 %
Total  Dry   :             +3.76190          84      100.00
Total  Wett  :          +2615.511         58624

Total  in  kgs                    47177.680
```

```
STREAM : 15 Carsol Solution

Pressure                      30.30 B
Temperature                    0.00 C

Composition              kMol/hr   St.m3/hr      molal %

H2                     +22.00045        493       1.40 %
CO                      +0.10551          2       0.01 %
CO2                  +1550.69000      34523      98.35 %
N2                      +3.74395         84       0.24 %
A                       +0.07895          2       0.01 %
H2O                  % 65150.1      % 1.46027E+06          0.00 %
CH4                     +0.09068          2       0.01 %
Total Dry   :        +1576.70900      35106     100.00
Total Wett  :       +66726.760       % 1.49538E+06

Total in kgs                  1242148.000
```

STREAM : 16 M.U.G. Condensate

Pressure	26.50 B
Temperature	0.00 C

Composition	kMol/hr	St.m3/hr	molal %
H2	+0.02417	1	84.26 %
N2	+0.00420	0	14.66 %
A	+0.00009	0	0.31 %
H2O	+61.93064	1388	0.00 %
CH4	+0.00022	0	0.77 %
Total Dry :	+0.02869	1	100.00
Total Wett :	+61.959	1389	

Total in kgs 1115.916

STREAM : 17 Proces Air

```
Pressure                               36.70 B
Temperature                            25.00 C

Composition                kMol/hr    St.m3/hr      molal %

H2                        +0.16731           4        0.01 %
CO2                       +0.50192          11        0.03 %
N2                     +1305.49900       29250       78.03 %
A                        +15.72689         352        0.94 %
H2O                       +0.77236          17        0.00 %
O2                      +351.17810        7864       20.99 %
Total Dry. :           +1673.07300       37481      100.00
Total Watt :           +1673.846         37498

Total in kgs                        48477.160
steam inj.                   +3469.400 kgs     proces air blanket

Gas Temperature    +25.0 C     Enthalpy =     +3 374 887 kcal/hr
```

1.12.1984 Chemoprojekt Praha

Gas Temperature +381.0 C Enthalpy = -275 664 400 kcal/hr

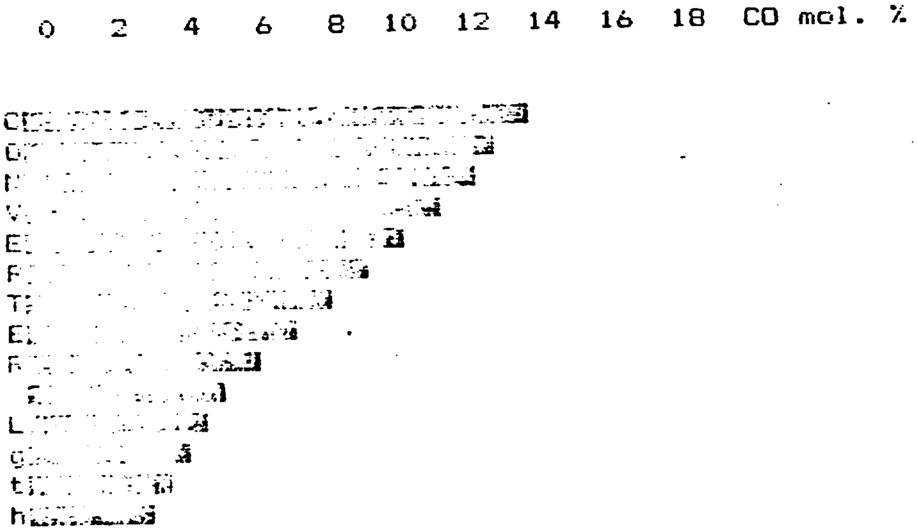
H.T. Shift Conversion Reaction :

Step	Temperature C	CO Content mol. %	Reaction Rate	Equilibrium Temperature	Equilibrium Approach
1	+381.0	14.420	+61488	+970.9	+589.9
2	+383.8	13.950	+61651	+941.4	+557.6
3	+386.5	13.483	+63064	+913.2	+526.7
4	+389.4	13.009	+64410	+885.8	+496.5
5	+392.3	12.530	+65696	+859.2	+466.9
6	+395.2	12.044	+66897	+833.2	+438.0
7	+398.2	11.554	+67986	+807.9	+409.7
8	+401.2	11.061	+68931	+783.2	+382.0
9	+404.3	10.565	+69693	+759.1	+354.8
10	+407.4	10.068	+70230	+735.7	+328.3
11	+410.5	9.572	+70494	+712.8	+302.3
12	+413.7	9.078	+70433	+690.6	+276.9
13	+417.0	8.589	+70097	+669.0	+252.0
14	+420.1	8.107	+69283	+648.0	+228.0
15	+423.0	7.635	+67847	+627.7	+204.7
16	+426.0	7.176	+65887	+608.2	+182.3
17	+428.8	6.735	+63370	+589.5	+160.8
18	+431.5	6.313	+60285	+571.8	+140.3
19	+434.1	5.916	+56648	+555.0	+120.9
20	+436.5	5.545	+52505	+539.2	+102.7
21	+438.8	5.203	+47938	+524.7	+85.9
22	+440.8	4.893	+43063	+511.3	+70.5
23	+442.6	4.616	+38025	+499.2	+56.6
24	+444.3	4.373	+32907	+488.5	+44.3
25	+445.7	4.163	+28109	+479.2	+33.5
26	+446.9	3.984	+23537	+471.1	+24.3
27	+447.9	3.836	+19384	+464.3	+16.5

1.12.1984

Chemoprojekt Praha

CO Concentration Profile :



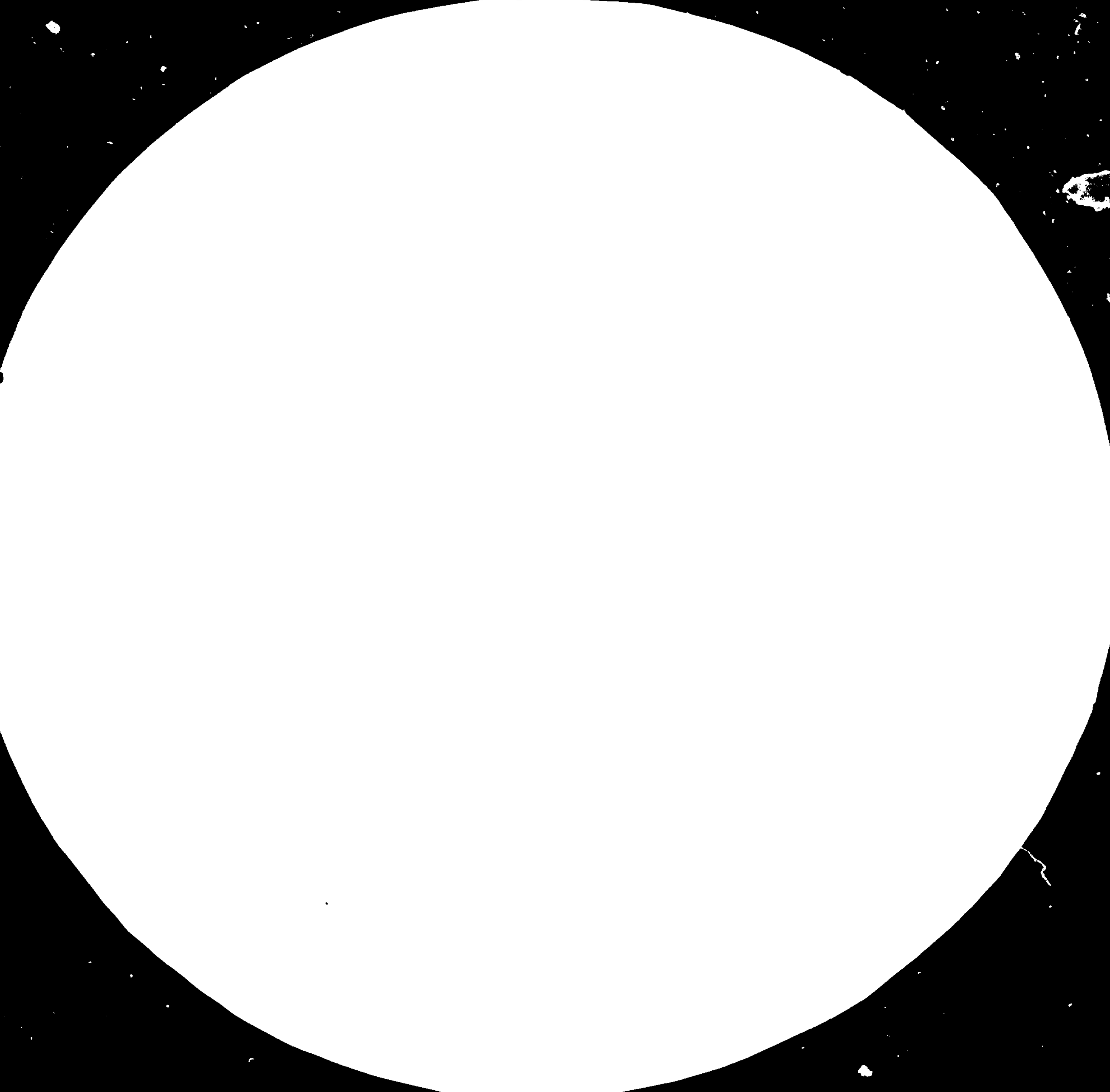
2. CALCIUM AMMONIUM NITRATE

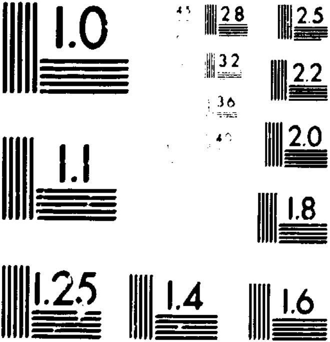
CONTENTS

Page

2. CALCIUM AMMONIUM NITRATE

<u>ANNEXES to chapter 2:</u>





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)

Explanation of Abbreviations

AA	anticaking agent
AN	ammonium nitrate
CAN	calcium ammonium nitrate
CAN 30	Calcium ammonium nitrate, nitrogen content 30 % b.W.
d_{50}	average diameter of particles /mm/
F	fertilizer
GFC	General Fertilizer Co. Homs
HP	hygroscopic point /%/
NP	ammonium phosphate
RHA	relative humidity of air /%/
SA	separating agent /powder conditioner/
UAN	urea and ammonium nitrate solution

2. Calcium Ammonium Nitrate

2.1. Short Characteristics of CAN - Production at GFC Hons

The CAN - plant was designed in the sixties for the capacity of 110 000 mtpa calcium ammonium nitrate expressed on nitrogen basis, i.e. approx. 4,6 tons N/h. The nominal capacity of the production unit of 17,7 tons/h of prilled CAN with 26,0 % N b. W. has been maintained till the year 1984.

At the beginning of September 1984 measures were taken for increasing the nitrogen concentration in the final product in order to cut down handling, storage and transport costs. Since 1/10/84 calcium-ammonium nitrate with 30 % N b. has been produced.

The change of technological conditions has been achieved without any significant change of the existing equipment with the exception of the dosing of dolomite into the mixers. The consumption of dolomits has been adequately decreased.. This resulted in increased specific consumptions of nitric acid form 580 kg /100 %/ t CAN /26 % N/ to 680 kg /100 %/ t CAN /30 % N/ and of ammonia from 160 kg /100 %/ t CAN /26 % N/ to 185 kg /100 %/ t CAN /30 % N/.

The present caking properties of the commercial product do not meet the requirements of customers, In close cooperation with the technicians of GFC appropriate methods for testing the caking tendency have been introduced and steps for decreasing the caking of CAN have been studied.

2.2 Caking of CAN - General review

Nitrogen fertilizers when stored, have the tendency to form hard lumps and crystal agglomerates. The mechanism of their caking has lately been thoroughly investigated. Although different theories exist it has been generally accepted that one of the most important factors in caking is the formation of crystal bridges at the points where individual granules contact each other.

Caking is however a very complex phenomenon. The intensity as well as the speed of caking is affected by various factors both internal and external. Examples of internal factors are: constituent moisture content, particle size, shape, hardness and plasticity, continuing chemical reactions, capillary adhesion. External factors include handling and storage conditions such as storage pressure, time, temperature, humidity of atmosphere etc.

For the most caking mechanisms the presence of moisture in the form of a saturated solution is essential. Therefore, the amount of residual water that remains in the fertilizer at the time of tis manufacture has a great effect on its tendency to cake in storage. The higher the degree of drying at the production stage, the less active the caking mechanism will be.

When a fertilizer is stored in moistureproof bags /and that is the case at GFC Homs/ the effect of atmosphere humidity in the storage is excluded and caking, when it occurs, is related to other factors.

Production of relatively large spherical fertilizer granules with a low content of fine ones reduces the number of contact points between particles and thus reduces the caking. On the other hand, mechanical weakness, high porosity and plasticity, bad shape of granules promote excessive caking. Under the pressure of high bag stacks in storage, weak granules tend to be deformed and destroyed and relative large areas of contact arise among the granules.

Up to date mechanization in farming leads to increasing demands on the freeflowing properties of fertilizers. To meet the requirements of customers, the conditioning of commercial grade fertilizers has been widely introduced. Most conditioners used on granular fertilizers are either very fine powders that adhere to granules or liquids that are sprayed on to their surfaces.

Powder anticaking agents create mechanical barriers between granules and absorb, spread and inactive the solution phase on granule surfaces. Solid conditioning agents such as diatomaceous earth /kieselguhr/, kaolin, talk, chalk, clays - untreated or hydrophobized with fatty amines - are applied usually in the range of 1 % - 4 % b. w. The adherence of conditioners can be improved by spraying the fertilizer with a small amount of oil /usually only 0,2 - - 0,5 % b.w./.

Liquid organic conditioners are surface active agents /surfactants/ that change the interfacial tension between solid and liquid phase and function as crystal modifiers inhibiting or weakening crystal growth among the granules. A surface active molecule comprises a non-polar hydrophilis group. For the CAN - conditioning cationic surfactants are widely used, the most important of which are the long -

- chained fatty amines. The fatty alkyl chain /with 8 - 18 carbon atoms/ gives them a high hydrophobic power, which grows with the number of carbon atoms. The polar radical NH_2 provides the molecule with a great affinity to the surface. Formation of hydrophilic coating on the surface of granules, improved water repellency, reduced capillary adhesion between particles, inhibited or reduced crystal nucleation are the main features of conditioner application. Fatty amines and their derivates are effective at low concentrations /200 - 1000 g per ton of fertilizer/, therefore their presence does not influence the quality grade of the commercial product. Fatty amines may also be used in combination with hydrophobic mineral oils.

In the case of ammonium nitrate fertilizers, internal conditioners may be used to improve physical properties and modify the effects of crystal phase inversions that result from temperature cycling during storage. The inversion of crystal modifications IV. → III. that occurs at 32 °C, in particular, can cause uninhibited ammonium nitrate prills to disintegrate and subsequently to cake.

To achieve the optimum effect when anticaking agents are applied, the selection of appropriate conditioner and the treatment procedure must be properly performed. Extensive preinvestigations and caking tests must be carried out to find the best way as to efficiency and economy. The recommended testing methods described in this report have been introduced at GFC Homs by the UNIDO - team.

2.3 Operational Problems in the CAN - Plant at GFC Homs

2.3.1 Introductory Comment

In respect to the fact that the caking tendency of the product results from operational conditions, a brief investigation of the CAN - plant was also embodied into the program of the UNIDO team assistance to Research Laboratories at GFC Homs, Essential operational problems are discussed in the following chapters. Except for the contamination of waste condensate all described problems are connected with caking directly or indirectly.

2.3.2 High Losses of AN in Vaste Condensate

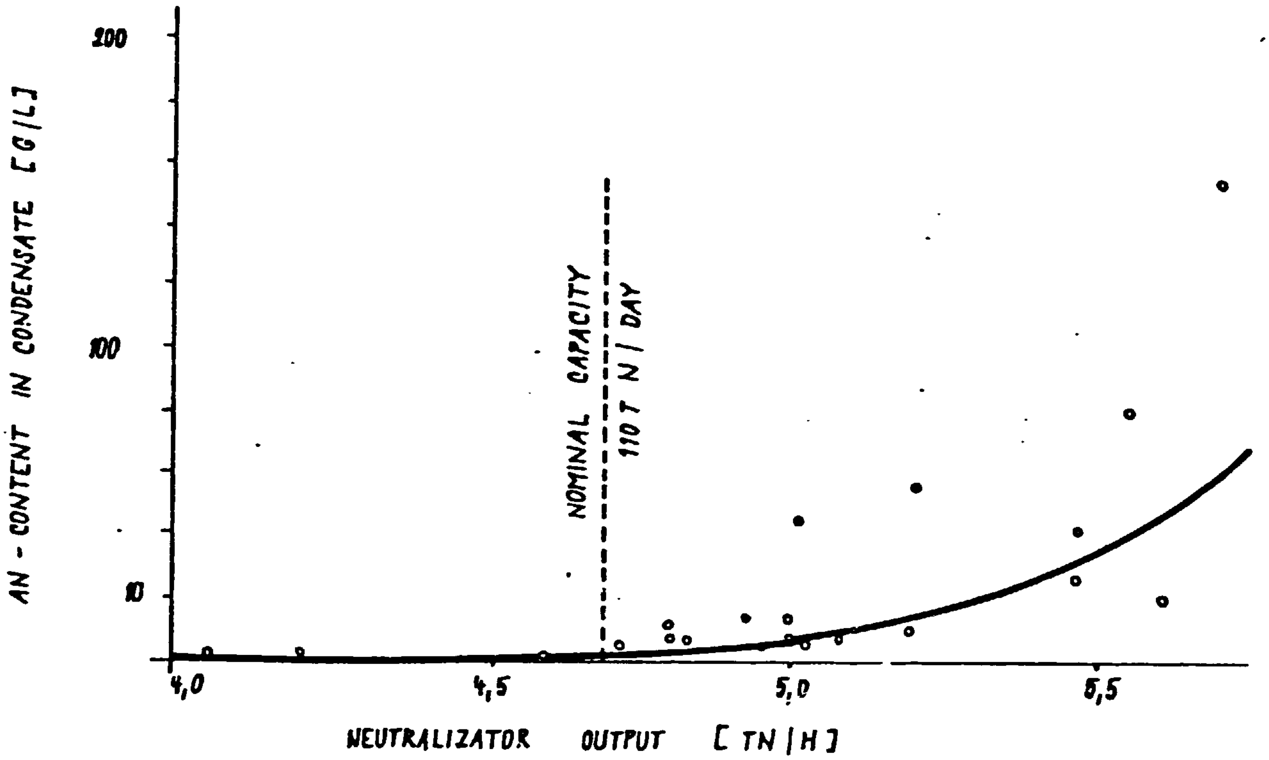
1.3.2.1 Analysis of Present Situation

From the neutralization reactor of ITN - type small droplets of AN - solution are drifted away with the stream of vapor and occur finally in the condensate at the outlet of the 1st stage evaporator. The AN - concentration in the waste condensate should be kept lower than 1 g AN/l.

In the last two months - after the technology had been changed - great differences in the AN - content were observed, with peak concentrations exceeding even 100 g AN/l.

The daily operational reports that cover the pertinent period of time were evaluated. It was found that the losses of ammonium nitrate remain within reasonable limits when the nominal capacity of the neutralizator 4,6 t N/h is maintained or only slightly exceeded up to 5,0 t N/h maximum/ see fig. 2.3/1/.

FIG. 2.3 / 1



(SELECTED POINTS SHOW MAX. AND MIN. VALUES ONLY)

Under the previous operating conditions, when CAN with only 26 % N was produced, it was not possible to surpass the nominal capacity of the neutralizator substantially because of limitations given in the "dry" rear part of the unit. As the same nutrient output can now be reached by a reduced quantity of the final product 30 % N/ the decrease is about 13%/, the bottle-neck at the rear part disappeared and moved to the "wet" front part.

2.3.2.2 Conclusions and Recommendations

It is necessary to hold the mass-flow through the neutralizator in a steady state and not to surpass the designed capacity of the neutralizator 4,6 - 5,0 t N/h.

If allowable AN - concentration in waste condensate is surpassed the proper function of waste water treatment plant may be seriously endangered. Therefore devices for the automatic design of inlet streams into the neutralizator and for ammonia pressure control should be installed.

As the separator of droplets in the neutralizator head was heavily corroded a new one has to be installed.
The proposal for the manufacture of the pertinent spare parts and their assembly has been presented to GFC Homs.

After any unscheduled shut-down of the CAN - plant the effort is evidently made to compensate for the production losses as soon as possible. As no excess capacity in the neutralization section is available, an extra storage tank for AN-solution could be installed adjacent to the existing storage tanks 03 - 10 A and 03 - 10 B. In case that the rear part of the unit has to be put out of operation for about 2 hours /but no longer/, the neutralization section could be kept in operation without interruption and the three storage tanks 03 - 10 A,B,C would be able to receive and store the produced lean AN-solution.

The actual value of AN-content in the waste condensate is checked by the AN-plant personnel. As this indication is important also for the control of the waste water treatment plant an operative link between these two departments has to be assured.

2.3.3 Prilling

2.3.3.1 Analysis of Present Situation

Acoording to the indications of existing measurement devices the AN - melt leaving the vacuum evaporator /580 - 600 mm Hg vacuum/ has the AN - concentration 98 % b.w. max. and temperature 165 °C max. The temperature of CAN - melt at the centrifuge exit is 155 - 160 °C. It is necessary to point out that the temperature difference between the real solution temperature and the real crystallization point has to be consistently and carefully controlled. A low temperature difference results in the bad shape of the granules /prolonged, ellipsoid, needles, the tails developed on granules break off and increase the rate of undersize fraction, a high temperature difference results in variably formed prills due to the extenxive contractions during solidifying. A high temperature of the melt also causes caking on the ground of the prilling tower because the time of fall is not sufficient for intensive cooling. The optimum temperature difference should be traced through long-term results. Generally 6 - 9 °C difference is recommended. New temperature measurement devices at GFC have been installed and will shortly be in operation. However, for a long time period before, the operators were not able to control the prilling temperature in the requested range as the measurement devices were out of order. For optimizing the prilling process, reliable temperature control is absolutely necassary.

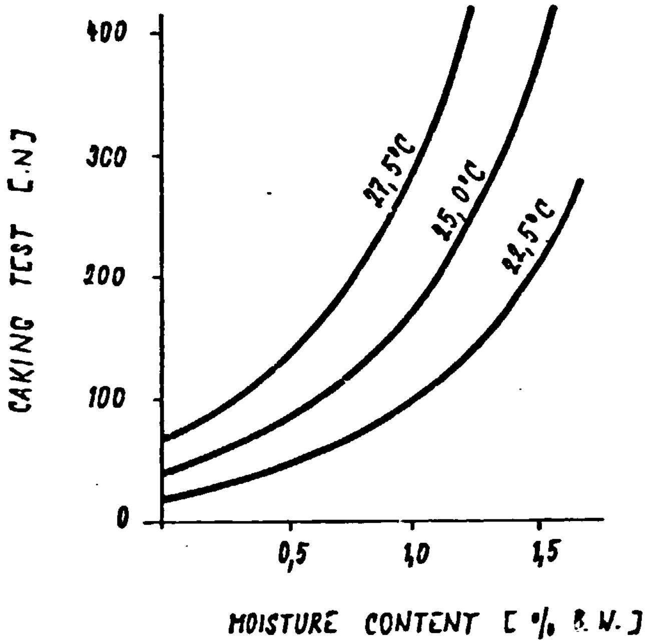
To improve the physical properties of commercial products internal conditioners are generally applied before prilling. At GFC internal conditioning is applied in limited range only. Ammonium sulphate is added to suppress the hygroscopicity of

CAN due to the inversion of $Ca/NO_3/_2$ to insoluble $CaSO_4$ but no sicative component and no hardness promoter are introduced into the process. Let us mention the example of Fisons technology /however using drum granulation instead of prilling/ where additives $/NH_4/_2\ SO_4$ and $FeSO_4$ are succesfully used in the rates 2 % and 1,4 % respectively. Ammonium sulphate besides the mentioned conversion of calcium nitrate to calcium sulphate forms also low soluble complex salts and ferrous sulphate effects as internal sicative because one molecule of $FeSO_4$ is able to bind up to 7 molecules of water. The presence of $FeSO_4$ promotes the increased crushing strength of granules and simultaneously suppresses their plasticity. Not only sulphates, also phosphates may be used as internal conditioners.

To obtain hard, well-shaped, and non-porous prills the water content of the CAN melt before prilling operation should be reduced and AN-concentration 98,5 % should be achieved at least. High moisture content results in a high rate of plastic granules in the product. High plasticity increases the caking tendency.

For information a typical relation between caking tendency of CAN 30 % b.w. /of Czechoslovak origin/ and its moisture content evaluated experimentally by the Research Institute of Inorganic Chemistry Ústí nad Labem /5/ is shown in fig 2.3/2. When CAN 30 /on dolomite basis/ was tested, the slope of curves for water content over 0,8 % was found even more steep /3/.

FIG. 2.3/2.



2.3.3.2 Conclusions

The measurement devices for the control of the prilling process, particularly temperature control, have to be perfectly maintained. The possibility of internal conditioning has to be thoroughly investigated and introduced in practice.

In case of future revamping or extension a proper design of prilling tower height countercurrent cooling air flow has to be carried out. The elevation of the prilling tower would help improve the physical properties of granules including moisture content, granulometric homogenity and mechanical strength. The height of prilling tower should be designed for an exit temperature of 90 - 100 °C. Revamping should comprise the system of vacuum evaporator and spreading bucket. As reported, in up-to-date types of LUWA film evaporators water content of AN melt under 0,1 %

evaporators water content of AN melt under 0,1 % is reached /1/. In case of a radical reconstruction of the whole unit the technology of final treatment of CAN-melt has to be revised with respect to recent progress in this field /fluidized bed on the bottom of prilling tower, granulation drum instead of prilling tower etc./.

2.3.4 Screeinng

2.3.4.1 Analysis of Present Situation

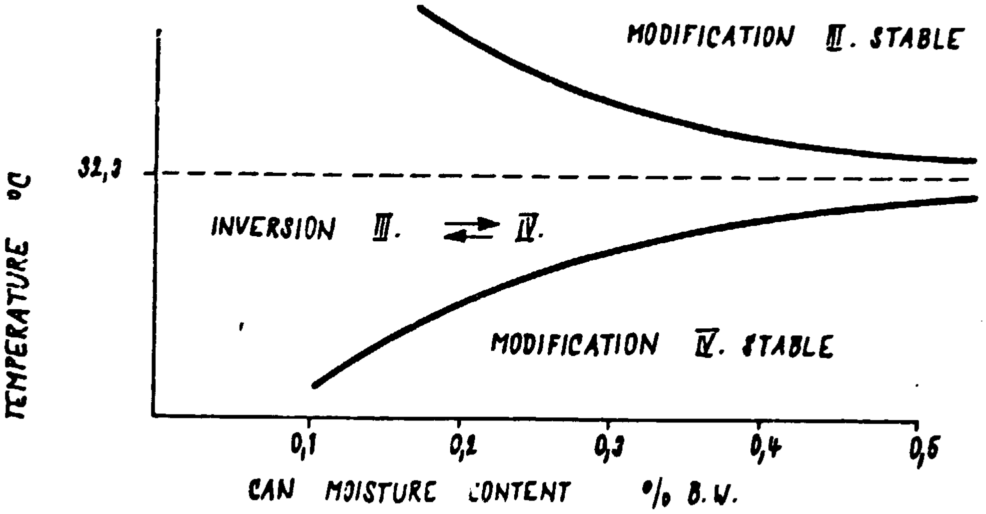
Prilled CAN /temperature 100 - 110 °C/ is transported from the bottom of the prilling tower to a screener 03 - 37. About 30 % of the material is bypassed without screening as the capacity of the screener is said not to be sufficient. This screener is equipped with one mesh-screen only. The undersized fraction is recycled to the mixers 03 - 26 A,B, the separated main fraction joins the bypassed material and enters the drier that operates actually as a cooler only.

During the screening process an undesirable crushing effect upon treated CAN prills has been observed. Low hardness of prills and their unsufficient resistance to sloughing and abrasion in addition to improper function and reduced capacity of the screener are the cumulative reasons for the crushing of prills that finally results in a higher ratio of fines in the screened fraction than in the feed.

The CAN-prills after cooling to 60 - 70 °C are transported by a bucket elevator to two parallel fluidization coolers 03 - 41 AB /one of which is under operation and the second stands by. To prevent the lumps and greater conglomerates of CAN entering the fluidization cooler and to protect it form being blocked, a fix grid with gaps of 1,5 cm was installed at the inlet. The separation of the grid seems to be dubious. Unfortunatelly this device causes 25 - 30 % of the whole production that is not to be subjected to final cooling. Temperature gradients between the cool /30 °C/ and non-cooled bypassed stream /60 - 70 °C/ cause temperature fluctuations in the critical region of the transient temperature. The changes of the III-rd and IVth types of crystal modifications weaken and destroy CAN-prills and result finally in a low anticaking capability of the commercial product.

The described detrimental effect of recrystallization is often increased by higher moisture content 0,5 - 0,9 % /even 1 % was exceeded when the efficiency of the vacuum pump was lowered, peak values over 1,7 % were found/. In these higher ranges of moisture critical transition temperature limits are very narrow /7/ and can easily be surpassed several times in both directions in the course of mixing the cold and hot materials /see fig. 2.3/3/.

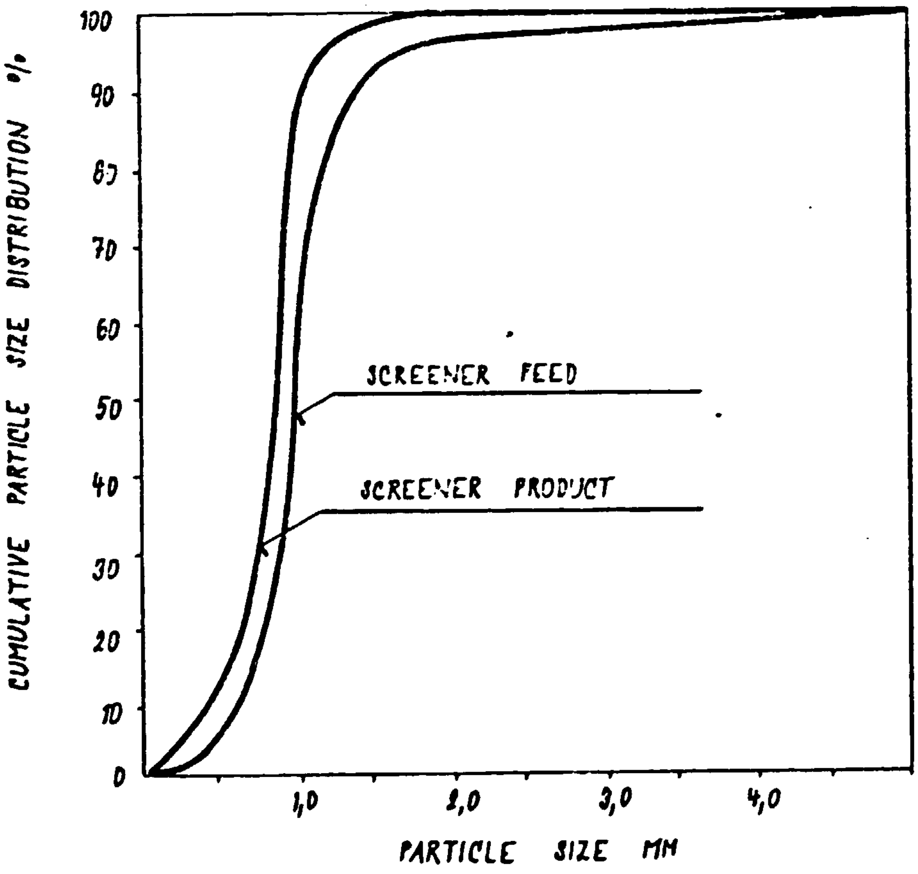
FIG. 2.3 /3



NOTE : INFORMATIVE SKETCH ONLY FOR EXACT DATA SEE LIT. (7)

The above described technological regime was illustrated by the sieve analyses of individual streams which were carried out in Oct./Nov. 1984:

FIG. 2.3/4



Tab. 2.3/1

Size Distribution /in % b. w./

Mesh	mm	>4,0	4,0-2,8	2,8-2,0	2,0-1,0	<1,0
Sample	Date					
Screenor feed	19/10	2,3	5,5	33,7	56,9	1,6
	24/10	3,7	8,8	38,9	44,4	4,2
	28/10	-	2,8	32,4	62,2	2,6
screened product	19/10	0,7	1,3	19,5	66,6	11,9
	24/10	0,9	2,1	23,6	63,4	10,0
	28/10	0,2	1,4	16,9	66,2	15,3
fluid-cooler in	28/10	1,1	2,5	29,8	52,5	14,1
fluid-cooler out	28/10	0,3	2,0	23,4	63,0	11,3
conditioner out	28/10	1,4	4,2	36,6	54,6	3,2

Tab. 2.3/2

Size Distribution of the Fluid-Cooler Bypass /4/11/84/

Mesh	mm	>10	5-10	4-5	2,8-4	2-2,8	1-2	<1
% b. W		1	1	1,4	5,9	44;3	38,7	2,8

From the plot in fig. 2.3/4 it is evident, that the result of screening is adverse to that expected. /higher ratio of fine particles in product than in feed.

2.3.4.2 Recommendations

An up-to-date type of screener of adequate capacity must be installed instead of the existing unsuitable screener 03 - 37.

The present permanent bypass of unscreened material has to be completely avoided.

The screener has to be equipped with two mesh-screens /instead of the present one/ for three fractions to be obtained - product, undersize and oversize. The oversize fraction is to be crushed and recycled back into the screener.

Installation of a new screener before the fluid-cooler 03 - 41 /instead before the drier-cooler 03 - 43/ was recommended as a more adventageous alternative that has been proved in practice abroad. The range of optimum size of granules which is necessary for fluidization will be guaranteed because freshly screened CAN-prills will be directly fed into the fluid-cooler. The range of granulometric size of the product is to be 1 - 4 mm and no particles under 0,6 mm should be present.

The whole production has to be subjected to final cooling in fluid-coolers. No bypassing of uncooled material is acceptable. Exit temperature from the fluid cooler is to be 30 °C max. Conditioning of air used for cooling is discussed in the next chapter.

2.3.5 Cooling and Drying

2.3.5.1 Impact of Cooling and Drying Conditions on the Moisture Content in the Product

The driving force for evaporation of the residual moisture from the surface of the granule to the stream of air used for drying and/or cooling is given by the difference of partial pressures of water vapor in the air stream and at the partical surface. Partial pressure of water vapor in the air must always be kept lower then partial pressure corresponding to the critical humidity of CAN-prills at given temperature to prevent the prill absorbing moisture from the air. When not only cooling but also drying is the aim of the treatment this difference of partial pressures has to be large enough. It is evident that the temperature and relative humidity of used air has to be carefully controlled. If necessary the air used for drying and cooling has to be conditioned.

2.3.5.2 Principles of Cooling and Drying Control

2.3.5.2.1 Critical Humidity

All salts, including fertilizer salts have characteristic critical humidities. Generally speaking, the critical humidity of a fertilizer may be defined as that humidity of atmosphere above which the material will spontaneously absorb moisture and below which it will become dry.
To be precise, the critical humidity of a fertilizer is that humidity of air at which the partial vapor pressure of water in the air equals the equilibrium water vapor pressure above a saturated solution of the fertilizer at any given temperature. When fertilizer is exposed and handled under

more humid atmospheric conditions it is considered hygroscopic, becomes wet and non-flowable. The increasing water content promotes later caking.

Critical humidity of a fertilizer is usually given as critical relative humidity defined as actual water content of air expressed as a percentage of that content required to saturate the air with water vapor at a given temperature.

The knowledge of this characteristic physical property of fertilizer is important for the correct control of drying and cooling of the prilled product to eliminate the fertilizer becoming wet during treatment. If necessary the air used for cooling has to be conditioned.

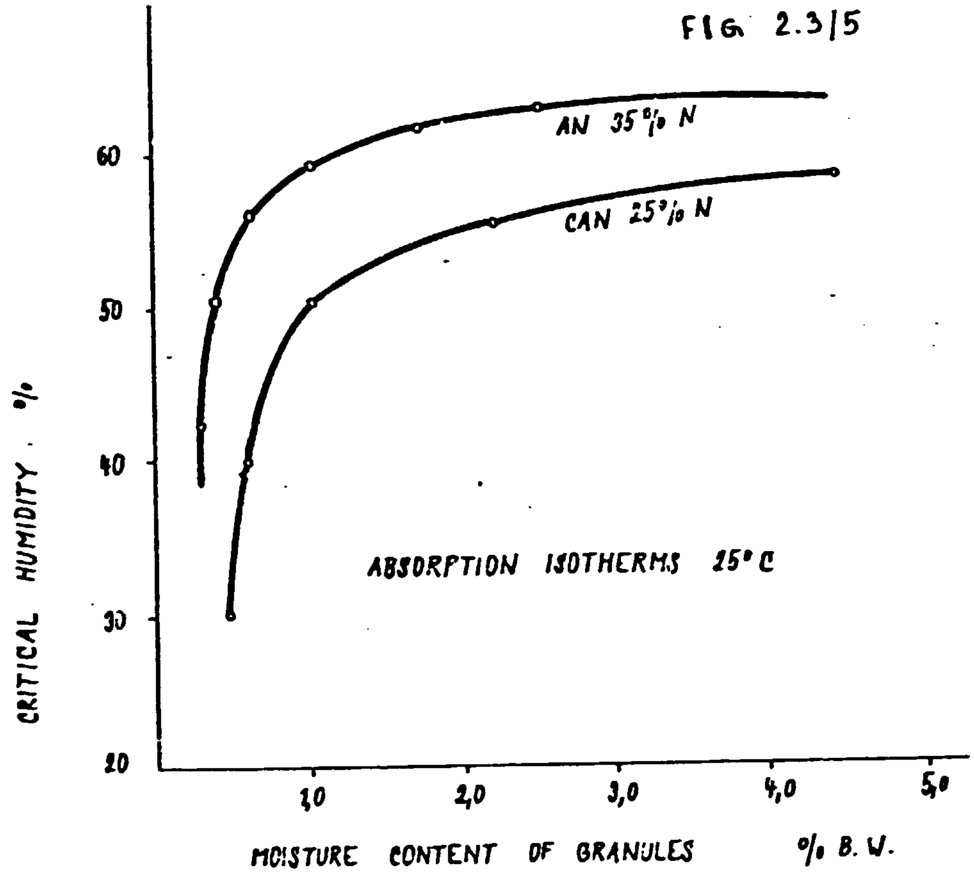
2.3.5.2.2 Critical Humidity of CAN - Hygroscopic Point

In the course of the CAN production process the last controlled reaction step runs in mixers, where AN-melt comes in contact with dolomite powder. During the retention time in mixers ammonium nitrate is in principle converted according to the following summary equation:

$$2\ NH_4NO_3 + CaCO_3 \longrightarrow Ca/NO_3/_2 + 2NH_3 + CO_2 + H_2O$$

When the critical humidity of CAN-product is to be determined, the ternary mixture NH_4NO_3 - $Ca/NO_3/_2$ - H_2O with minute amounts of various impurities has to be taken into account. It means that the critical humidity must be found for the specific type of CAN individually in a laboratory. The measured data is evaluated in the form of an absorption isotherm /usually for the standard temperature 25 °C/ like in the following chart /fig. 2.3/5/ which is valid for CAN 25 % N of Czechoslovak origin and may represent a type of fertilizer of medium quality /6/. For information an absorption isotherm for pure AN /35 % N/ is given too.

FIG 2.3/5



From fig 2.3/5 it may be easily ascertained that the critical relative moisture of air /called Hygroscopic Point - HP/ at 25 °C is 30 %, if CAN with moisture content 0,5 b. w. is to be produced. It is necessary to point out that any absorption isotherm is valid for a specific type of fertilizer with fixed content of water soluble CaO /in case of fig. 2.3/5 0,4 % b. w./. When the content of water soluble CaO increases, the absorption isotherm is shifted to the right.

2.3.5.2.3 Methods Applied for Measuring of Critical Relative Humidities and Absorption Isotherms

The simplest method is based on exposing a sample of fertilizer to various controlled humidities of air at the standard temperature 25 °C /or other fixed temperatures/. The appropriate hygroscopic point is found when the sample gains significant weight increment /caused by moisture absorption/. The curve of absorption isotherm is a set of hygroscopic points for various moisture contents of the sample. For easy evaluation of absorption isotherms laboratory measurement devices were developed using either spiral or tenzometric weighing elements /4/.

Other relevant more sophisticated methods use electric hygrometers or gas chromatographs for the evaluation of absorption isotherms .

2.3.5.3 Design of Proper Cooling Conditions

On the basis of principles given in the previous chapter a graphic chart has been calculated /6/ and is presented on the next page /fig 2.3/6/. Practical use is illustrated in the two following examples:

Example 1: CAN with FP 30 % /25 °C/ is to be cooled as low as 30 °C. Find the temperature and relative humidity of air /RHA/ which may be used for cooling to be certain that the moisture content of the fertilizer will not be increased during cooling.

Solution: Follow the characteristic curve for CAN with HP 30 % /25 °C/ and find, that for the requested outlet temperature 30 °C the partial pressure of water vapor in used air must not exceed 1,20 kPa. With the aid of air curves plotted in the diagram we easily find the temperature limit of air in relation to its actual relative humidity, for instance:

For relative humidity /RHA/	%	40	60	80
temperature limit /max/	°C	24,0	17,5	13,0

Example 2: Find the lowest temperature of CAN /defined as in example no. 1/ we can achieve at the cooler exit when air with relative humidity 60 % and temperature 15 °C is available.

Solution: This temperature limit is 27 °C/min/.

2.3.5.4 Example of Foreign Practice

In the SCHZ Works in Czechoslovakia a high content of residual moisture in the commercial product was caused by incorrect physical properties of air used for the final cooling in the fluid coolers. Since the early eighties air conditioning has been used successfully. For Czechoslovak conditions the following optimum parameters of cooling air were evaluated: relative moisture 50 %, temperature 17 °C. To guarantee these limits, atmospheric air is now cooled in exchangers where liquid ammonia is evaporated. At the outlet of the air cooler the air temperature is 5 °C and relative moisture 100 %, which corresponds to the requested relative humidity of 50 % at the temperature level 17 °C. Air Conditioning has recently been successfully introduced at the occasion of CAN unit revamping at the Chemical Works Borsod in Hungary /2/.

Fig. 2.3/6

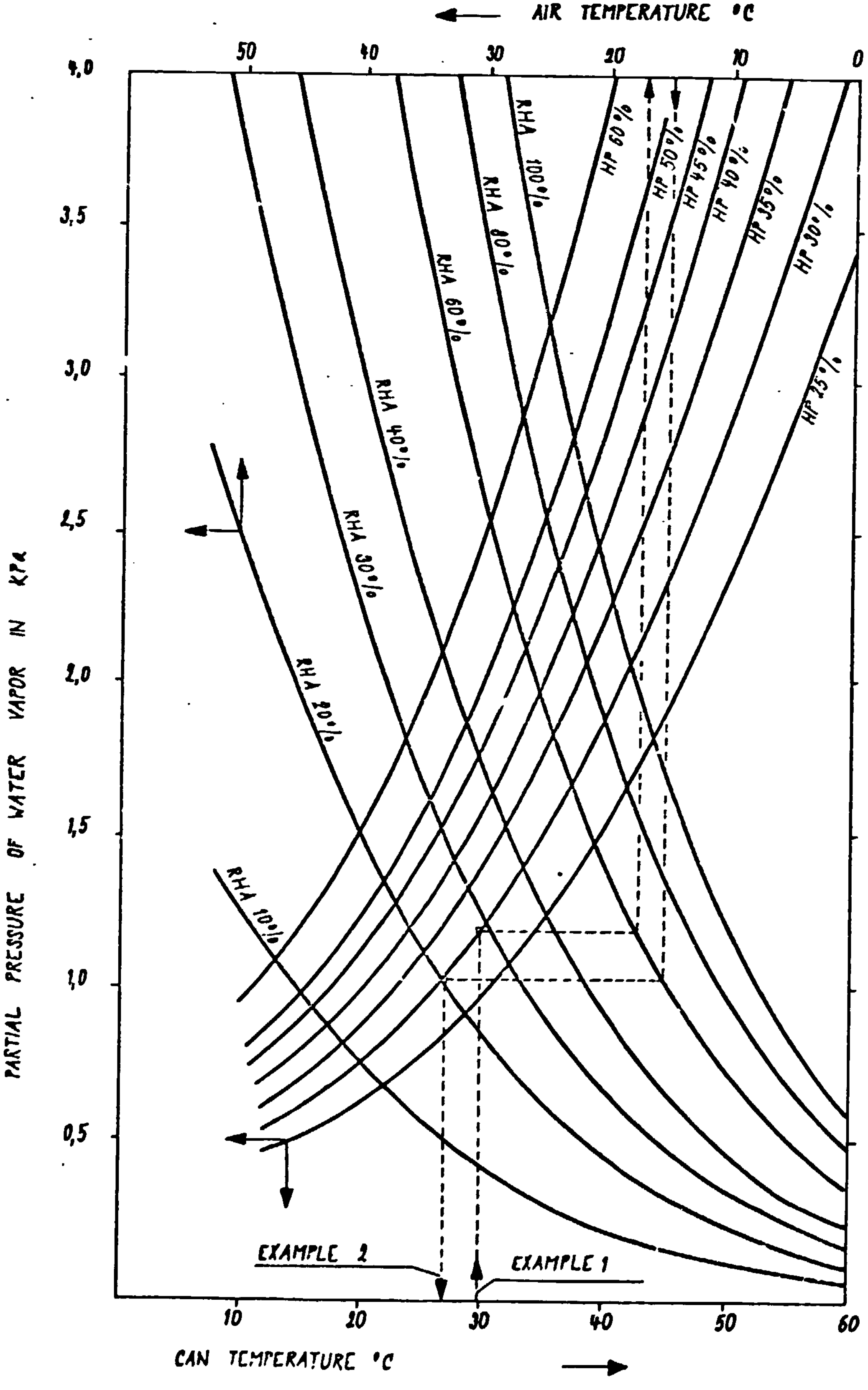


FIG. 2.3 | 6

2.3.5.5 Present Situation at GFC Homs

For preliminary cooling a horizontal rotating cooler/drier ø 3 000 x 18 000 mm is used. Cooling air flows co-currently with the cooled material and is exhausted from the cooler/drier by a suction fan. Low ratio between the cooling and cooled streams /1 300 Nm^3 air per ton CAN/, low residence time of CAN in the cooler /13 - 14 min/ and parallel flow arrangement result in low efficiency of drying and cooling. The exit temperature of CAN is about 60 - 70 °C.

The system of final cooling of the product was described in the chapter 2.3.4.1 in connection with the analysis of screening operation.

2.3.5.6 Conclusions and Recommendations

The further recommended measures are to be considered in accordance with the proposals for the reconstruction of screening system as stated in chapter 2.3.4.2.

A counter-current air flow /instead of co-current/ in the drier/cooler is to be adopted. The specific rate of cooling air is to be increased to 1 900 - 2 000 Nm^3 per ton of CAN. A new fan of higher capacity is to be installed.

Bypassing of the fluid cooler has to be avoided. The new screening system /as recommended in chapt 2.3.4.2/ and conditioning of cooling air will eliminate the possibility of fluid cooler blocking. The use of conditioned air prevents the CAN prills getting wet in the course of their final treatment.

The exit temperature of CAN-prills from the fluid cooler is to be maintained at 30 °C.

Air conditioning in ammonia evaporators is recommended. For information, the specification of the air cooler may be as follows:

cooling capacity	1,6 GJ/h
air in - quantity	30 000 NM^3/1
- temperature	30 °C
air out - temperature	5 °C
refrigerant	ammonia at boiling point - 20 - - 15 °C
heat exchange surface	3 600 m^2 in 15 sections each section comprises 50 pieces of finned tubes ø 38/3 mm, diameter of fin 118 mm, length of tube 3 000 mm, ammonia in tubes

2.3.6 Conditioning

2.3.6.1 Present Situation

The caking of CAN is a complex phenomenon depending on various factors, e. g. moisture content, the hardness and plasticity of individual granules, size-homogenity and size-distribution of the product, store and handling conditions and technical level of used facilities, etc. Caking in general has been discussed in chapter 2.2.

The final operation which may help improve the commercial quality of the product is conditioning achieved by application of powder and/or liquid anticaking agents.

In GFC Homs liquid fatty amines of commercial mako ARMOFLO 66 - S /product of Armour Hess Chem. Lim., G.B./

have been used for conditioning. The nozzle for spraying the liquid anticaking agent was installed at the outlet of the conditioning drum. The short residence time left for the homogenization of coated granules and the relatively narrow spraying angle achieved by the existing spreading system are hardly sufficient to guarantee that all granules are coated perfectly.

To the AN-melt /NH_4/SO_4 is added to suppress the concentration of hygroscopic Ca/NO_3/$_2$. Coating of CAN by powder dolomite in the conditioning drum was used in the past, At present it is used no more.

2.3.6.2 Recommendations

The nozzle should be removed from the outlet and installed at the inlet of the coating drum. Care is to be taken to attain as wide a spraying angle as possible /by modifying the nozzle and raising the outlet pressure of the feeding pump/. More detailed information concerning the quality and selection of appropriate conditioners and anticaking agents is inparted in further chapters of this report.

2.3.7 In conclusion

The CAN-plant at GFC Homs was built in the years 1968 - 71 and has been running for nearly 15 years. It is logical, that the original design applied at GFC does not correspond to the up-to-date progress achieved in the CAN - technology. In the last two decades new systems have been developed /pressure neutralization, granulation in drums, perfect automation of process, internal conditioning resulting in high level of commercial grade product etc./ and consequently the approach to the design of modern units has been basically changed.

It is to be considered carefully if a moderate stepwise revamping, or a long term shut-down for radical reconstruction or an erection of a completely new plant without interruption of fertilizer deliveries to customers is to be preferred. The final decision depends on economic evaluations, and investment feasibility with respect to the present investment policy in SAR.

It should be mentioned that in a similar case in Czechoslovakia it was decided for a new plant to be built rather than revamp the old one although the CAN quality produced at the old plant had been higher than the one produced at GFC at present. The new plant with the capacity 90 000 mtpa N has been running for several years in Duslo Works in Šaľa.

2.4 CAN 30 - Testing

2.4.1 Analytical Control Laboratories

2.4.1.1 Present Practice at GFC Homs Analytical Laboratory

Control of granulated CAN is carried out at the CAN Plant laboratories and at the Central Laboratories,.Samples of CAN are taken from a belt conveyor downstream the prilling tower for both laboratories together. These samples are analysed at the Plant Laboratory every 3 - 4 hours and at the Central Laboratory one analysis of one average 24-hours sample is carried out. That means that neither at the Plant Laboratory nor at the Central Laboratories are samples of the final product analysed because CAN downstream the prilling tower undergoes significant changes especially in its granullmetric composition and moisture content.

At the Plant Laboratory following analyses are carried out:
- ammonia nitrogen content
- moisture content /drying for 3 hours at 100 °C/
- screen analysis /<1 mm, < 2 mm, $< 2,8$ mm, < 4 mm, >4 mm/
- nitric acid concentration /density/
- condensate analysis form the 1. neutralization stage, 2. evaporator stage and their mixtures /N_{NH_3} , NH_4NO_3, free HNO_3 /

At the Central Laboratories following analyses of CAN are carried out:
- moisture content
- ammonia nitrogen content
- total nitrogen
- screen analysis

Laboratory personel of both laboratories is well skilled in the existing laboratory practice. As for laboratory equipment,it is recommendable to fill up the number of screens in both laboratories especially with screen mesh size 0,5 mm and with further screen mesh sizes, as a more detailed granulometric analysis is needed occasionally.

CAN moisture content determination is carried out by drying only. Alternatively, it is recommended to use the well known and used K. Fisher method.

At the Central Laboratories samples of the final product are to be analysed, which means samples taken at a suitable point downstream the coating drum.

At the Plant Laboratory samples taken downstream the prilling tower and the fluid cooler should be analyzed. Both these analyses are important - by the first prilling can be controlled, the second one serves for CAN mechanical strength determination and the dry rear part machinery impact on the CAN quality.

Tests of melted CAN upstream the centrifuge as well as the sulphate content in prilled CAN should be carried out at the Plant Laboratory. These parameters influence CAN quality significantly.

Prill hardness testing with a simple instrument like that from the firm Pfitzer /see ANNEX No 2/IX/ and organic conditioner content determination are advisable. /Crushing strength of granules gran. size 1,6 - 2,0 mm should reach 15 N min./.

CAN caking tendency testing should be carried out at the Central Laboratories. For these tests analytical equipment which was partly brought foom Czechoslovakia and partly furniched at the GFC Workshop following UNIDO - - team specification could be used.

This equipment which was handed to GFC can be used for research purposes as well.

2.4.2 Quality of CAN 30 Produced at GFC Homs

Surveys of average daily analyses carried out at the CAN-Plant Laboratory and at the GFC Central Laboratory are enclosed in ANNEXES II - III. and in ANNEX IV respectively.

As may be seen from the survey the average moisture contents fluctuate usually in the range 0,5 - 0,9 % and in some cases exceed substantially 1 % b. w. Furthermore, these values were obtained on the basis of drying that gives results about 0,2 - 0,4 % lower than the exact K. Fischer method acknowledged generally as a representative way of moisture testing. As explained in chapter 2.2 the moisture content of the prills is the prime cause od caking. Present prilling and drying systems do not assure the moisture content of the product to be permanently mainatained under the commonly recommended level 0,5 % b. W. /0,2 % is considered as the optimum/.

As described in chapter 2.3 the existing bottle-necks as well as low efficiency of some equipment result in the low quality of the product. Differently formed, prolonged or needle-shaped prills possess insufficient mechanical stability and tend to disintegrate during handling and form dust. Fines in the product are prone to caking. Furthermore, the high ratio of the granulometric fraction below 1 mm results in a large contact area among particles of CAN and hence promotes caking.

To obtain representative data for quality control /size distribution spectrum particularly/ samples for testing are to be taken downstream the fluid-cooler and not upstream the screener as it is practised today. The sampling point should be chosen in a place where the easy taking of a homogeneus sample is possible such as the transporter belt overflow.

2.4.3 Anticaking Agents /AA/ Testing

The original idea of the GFC request for UNIDO - team assistance was to introduce methods for decreasing the caking tendency of CAN through anticaking agents application. Therefore great attention was paid to the introduction of laboratory methods for testing the caking tendency of CAN and to the evaluation of these results in order to select the most suitable AA for CAN 30 at GFC Homs.

All the tests were carried out by GFC laboratory personnel under UNIDO - team supervision.

2.4.3.1 Analytical Program

This short-term analytical program was based on the experience of Czechoslovak fertilizer research in the field of the conditioning and caking tendency decrease of granulated fertilizers, particularly of CAN. It was influenced by the present practice at GFC, where the fatty amine

ARMOFLO 66 - S has been used as anticaking agent. This amine was tested in all the series of laboratory test s which were carried out during the UNIDO - team mission to GFC.

The mentions program consistes of seven series of laboratory tests, in each of which untreated CAN was always examined and served as the basis for caking tendency comparison. Freshly taken samples of CAN, one sample for a whole series of tests, were used. In each series of tests the quality of used CAN differed, especially in the quality of moisture content, screen analysis and prill size average.

Individual results of all tests are to be found in tables 2.4/1 - 2.4/

Table 2.4./1

Analytical Program

the quantity of different anticaking agents used for conditioning is given in g/kg of CAN 30

Serie No	1	2	3	4	5	6	7
raw CAN 30	0	0	0	0	0	0	0
Armoflo 66 S	0,9	0,9	0,48	0,9	0,36 0,90 1,50	1,02	0,6
Armoflo + oil J2				0,3 + 0,27 1,0 + 0,8		0,3 + 2,7	
Armoflo + oil Syr							0,3 + 2,7
Armoflo + Kaolin	0,9 + 4,0						
Armoflo + Bento.		0,9 + 4,0					
Armoflo + SiO_2			0,48 + 4,0				
SK F20A	0,9	0,9	0,48	0,9		0,36 0,84	
SK F20A + Kaolin	0,9 + 4,0						
SK F20A + Bento.		0,9 + 4,0					
SK F20A + SiO_2			0,48 + 4,0				
SK F20A + oil J2 + Kaoline				0,3 + 2,7 + 4,0			
SK F20A + oil J2				0,3 + 2,7			

Table 2.4./1 /continued/

Serie No	1	2	3	4	5	6	7
Flotigam 1677	0,9	0,9	0,48				
Flot.1677 + Kaol.	0,9 + 4,0						
Flot.1677 + Bento.		0,9 + 4,0					
Flot.1677 + SiO_2			0,48 + 4,0				
Flot.1677 + oil J2				0,3 + 2,7			
Flot.1677 + oil J2 + Kaolin				0,3 + 2,7 + 4,0			
Flotigam S			0,48		0,6 1,2	0,36 0,84	0,6
Flot. S + SiO_2			0,48 + 4,0				
Flot. S + oil J2				0,3 + 2,7		0,3 + 2,7	
Flot. S + oil Syr							0,3 + 2,7
Romonta 68	0,9	0,9	1,2		0,42 1,08	0,36 0,84	
Rom. + Kaolin	0,9 + 4,0						
Rom. + Bento.		0,9 + 4,0					

As stated preciously the quality of the used CAN differed in each series which was the reason of repeated tests with pure anticaking agents. The quality variations were considered an advantage as the caking tendency decrease caused by individual agents was to be examined under different conditions.

On principle the used agents were fatty amines /Armoflo 66 S, Flotigam 1677, Flotigam S, Sk FERT F 20A/, with the exception of Romonta 68 which was a mineral wax.

All of these anticaking agents have been widely used by fertilizer manufacturers in the world. These commercial anticaking agents were also tested when diluted with low viscose oils /one of Czechoslovak oil J2, the second one was a Syrian oil/, or in combination with inorganic powders having separating properties /Kaolin, Bentonite, and SiO_2/.

2.4.3.2 Anticaking Agents Specifications

Table 2.4./2

Used Anticaking Agents /AA/ Specification

AA type	Armoflo 66 S	Flotigam S	Flotigam 1677	SK FERT F20A	Romonta 68
Origin	AKZO Chemie+	Hoechst+	Hoechst+	Sinor - Kao+	Chemiewerke Werdau+
Appearance 20 °C	Paste	Wax/powder	Paste	Paste	Paste
Melting p. °C	35	not stated	not stated	25 - 35	not stated
Viscosity 60 °C mPa.s	18,4	4	9	10,8	not stated
Density 60 °C g/cm^3	0,8	0,8	0,9	0,9	not stated
Flash p. °C	150	160	185	not stated	not stated
Recommended appl. temp. °C	60 - 70	60 - 70	60 - 70	not stated	not stated

+ For addresses of AA Suppliers see ANNEX No. 2/X

Table 2.4./3

Used Inorganic Anticaking Agents Specification

AA TYPE			Kaolin	Bentonite	SiO_2
Origin			Horní Bříza+	SZ Hnůšťa+	Calofrig Borovany+
Appearance			Powder	Powder	Powder
Colour			White	Green	White
Water Cont.		%	1	3	0,5
Mn cont. in H_2O eluate		%	0,02	not stated	not stated
Cu "		%	0,01	not stated	not stated
Fe "		%	0,05	not stated	not stated
Al_2O_3	approx.	%	39,5	23	not stated
SiO_2	approx.	%	46,5	53	not stated
Fe_2O_3	approx.	%	0,315	7,5	not stated
CaO	approx.	%	not stated	2	not stated
MgO	approx.	%	not stated	3	not stated
Size		mm	0,315	not stated	not stated

Table 2.4./4

Used Dilution Oils Specification

1	Imported oil	
	Type	oil J2
	Origin	Slovnaft, Bratislava ČSSR
	Viscosity at 50° C	14 - 18 mPa . s
	Aniline point	70 °C
	Freezing point	6 °C
	Ash content	0,02 %
	Acidity point /mg KOH/g/	0,05 %
	ASTM colour	3
2	Syrian oil	a low viscisity oil

2.4.3.3 Laboratory Methods and Equipment Description

For each testing series 10 kg of fresh samples of untreated CAN 30 were taken downstream the fluid cooler, 30 - 60 minutes before starting the tests. These samples were tested on moisture content, ammonia nitrogen content and granulometry. From each of the samples 0,75 kg doses were taken, they were treated with anticaking agents in a laboratory coating drum and they were tested together with the untreated blanc sample on their caking tendency. The anticaking agents were heated previously to their application to 65 - 70 °C as their viscosity was to be decreased to a suitable degree.

With Komonta 68, the viscosity of which was higher, had to be heated up to 70 - 80 °C. In the first series Komonta 68 was heated to 60 - 70 °C only, its viscosity was too high and fertilizer clumps were formed.

The CAN 30 used for tests in series VI was dried and screened in the laboratory in order to improve the fertilizer caking parameters.

In series I. anticaking agents were applied with a syringe but in all following tests a spraying nozzle operated with compressed nitrogen was used.

For a detailed description of the used laboratory methods and equipment, see ANNEX No. IV. - VII.

2.4.3.4 Survey of Experimental Results

All experiments results have been worked out in table form /Tables 2.4./5 - 2.4./11/. In every table the series number, CAN 30 quality, the quantities of used CAN 30 and anticaking agents, and caking tendency in absolute and relative numbers are stated. For easier orientation all the results are also scaled up for 1 kg samples of CAN 30. In the case of Romonta 68 tests with 1 kg samples were carried out. In all series all tests were duplicated and average results were used for the final evaluation.

SERIE I.

Table 2.4./5

Caking Tendency Testing

CAN - Date of Production:	31/10/84	CAN Quality Spec.:		Screen Anal.:	
Test Start:	31/10/84	N_{NH_3}	15,30 % b. w.	2,8mm	11,6 %
Caking Tendency Meas.:	1/11/84	H_2O	0,93 % b. w.	2,0mm	49,2 %
CAN Quantity:	1 kg	d_{50}	1,7 mm	1,0mm	32,5 %
				1,0mm	6,7 %

No	AA Tested	AA Dose		Caking N		ΔN	ΔN/1gAA/1 kg F
		g/1 kg	g_0/1 kg	Abs.	Average		
1	Raw CAN	0,0	0,0	190	185	-	-
2	"			180			
3	Armoflo	0,9	0,9	126	125,5	-59,5	- 66,1
4	"			125			
5	Armoflo + Kaolin	0,9+4,0	0,9	210	222,5	+37,5	+ 33,7
6	"			210			
7	Flot. 1677	0,9	0,9	97	83,5	-101,5	- 112,8
8	"			70			
9	Flot. 1677 + Kaolin	0,9+4,0	0,9	175	162,5	-22,5	- 25,0
10	"			150			
11	Sinor	0,9	0,9	54	40,5	-144,5	- 160,5
12	"			27			
13	Sinor + Kaolin	0,9+4,0	0,9	160	150	-35	- 38,9
14	"			140			

No	AA Tested	AA Dose g/1 kg	 g_o/1 kg	Abs.	Caking N Average	ΔN	ΔN/1gAA/1 kg F
15	Romonta 68	0,9		218	223	+ 38	+34,2[++]
16	"			228			
17[+]	Romonta 68 + Kaolin	0,9+4,0		255	243,5	+ 58	+52,2[++]

[+] Low temperature of Romonta resulted in clump formation

[++] N/1 g Romonta 68/1 kg fertilizer

<u>Note:</u> g_o/1 kg ..... gram of organic AA

Average N ... average result of two analyses [N]

ΔN/1 gAA/1kg F caking tendency scaled up to 1 g of AA per 1 kg fertilizer

SERIE II.

Table 2.4./6

Caking Tendency Testing

CAN - Date of Production: 3/11/84
Test Start: 3/11/84
Caking Tendency Meas.: 4/11/84
CAN Quantity: 0,75 kg

CAN Quality Spec.:
N_{NH_3} 15,40 % b. w.
H_2O 0,47 % b. w.

Screen Anal.:
2,8mm 4,2 %
2,0mm 47,2 %
1,0mm 41,6 %
1,0mm 7,0 %

No	AA Tested	AA Dose g/1kg	g_0/1 kg	Caking N Abs.	Averag	ΔN	ΔN/1gAA/1 kg F
1	Raw CAN	0,0	0,0	250	245	-	-
2	"			240			
3	Armoflo	0,9	0,9	165	185	-60	- 66,6
4	"			206			
5	Armoflo + Bentonite	0,9+4,0	0,9	260	262	+17	+ 15,3
6	"			264			
7	Flot. 1677	0,9	0,9	175	185	-60	- 66,6
8	"			195			
9	Flot. 1677+Bentonite	0,9+4,0	0,9	280	260	+15	+ 13,5
10	"			240			
11	Sinor Kao	0,9	0,9	165	167,5	-78,5	- 87,22
12	"			170			
13	Sinor Kao+Bentonite	0,9+4,0	0,9	236	249	+4,0	+ 3,6
14	"			262			

Table 2.4./6 /continued/

No	AA Tested	AA Dose		Caking N		ΔN	ΔN/1gAA/1 kg F
		g/1 kg	g_o/1 kg	Abs. N	Averag.N		
15+	Romonta	0,9	-	282	288,5	+43,5	+ 39,15
16+	"			295			
17+	Romonta + Bentonite	0,9+4,0	-	345	348,5	+103,5	+ 93,15
18+	"			352			

+Low temperature of Romonta resulted in clump formation

SERIE III.

Table 2.4./7

Caking Tendency Testing

CAN - Date of Production:	4/11/84	CAN Quality Spec.:		Screen Anal.:	
Test Start:	4/11/84	N_{NH_3}	14,5 % b.w.	2,8mm	3,14 %
Caking Tendency Meas.:	5/11/84	H_2O	1,1 % b.w.	2,0mm	42,83 %
CAN Quantity:	0,75 kg	d_{50}	1,5 mm	1,0mm	52,05 %
				1,0mm	2,06 %

No	AA Tested	AA Dose			Caking N	ΔN	ΔN/1gAA/1 kg F
		g/1 kg	g_0/1 kg	Abs.	Average		
1	Raw CAN	0,0	0,0	275	263,5	-	-
2	"			252			
3	SK FERT F 20 A	0,48	0,48	140	142,5	-121	- 252,1
4	"			145			
5	SK FERT F 20 A+SiO_2	0,48+4,0	0,48	280	252,5	-11	- 23
6	"			225			
7	Armoflo	0,48	0,48	145	162,5	-101	- 210
8	"			180			
9	Armoflo + SiO_2	0,48+4,0	0,48	235	255	-8,5	- 17,7
10	"			275			
11	Flot. 1677	0,48	0,48	135	135	-128,5	- 267,7
12	"			135			
13	Flot. + SiO_2	0,48+4,0	0,48	290	290	+26,5	+ 12,7
14	"			290			

Table 2.4./7 /continued/

No	AA Tested	AA Dose		Caking N		ΔN	ΔN/1gAA/1 kg F
		g/1 kg	g_o/1 kg	Abs.	Average		
15	Flot. S	0,48	0,48	115	106	-157,5	- 328,1
16	"			97			
17	Flot. S + SiO_2	0,48+4,0	0,48	246	246	-17,5	- 36,4
18	"			-			
19	Romonta	1,2	-	90	100	-163,5	- 340,6
20	"			100			

SERIE IV.

Table 2.4./8

Caking Tendency Testing

CAN - Date of Production: 5/11/84
Test Start: 6/11/84
Caking Tendency Meas.: 7/11/84
CAN Quantity: 0,75 kg

CAN Quality Spec.:
N_{NH_3} 14,85 % b.w.
H_2O 1,4 % b.w.
d_{50} 1,3 mm

Screen Anal.:

2,8mm	3,76 %
2,0mm	27,76 %
1,0mm	62,43 %
1,0mm	6,04 %

No	AA Tested	AA Dose		Caking N		ΔN	ΔN/1gAA/1 kg F
		g/1 kg	g_0/1 kg	Abs.	Average		
1	Raw CAN	0,0	0,0	330	300	-	-
2	"			270			
3	SK FERT F 20A+iol J2	0,3+2,7	0,3	202	199,5	-100,5	- 335
4	"			197			
5	SK FERT+oil J2+Kaol.	0,3+2,7+4	0,3	225	250	- 50	- 166,6
6	"			275			
7	Flot.1677+oil J2	0,3+2,7	0,3	230	242,5	-57,5	- 191,6
8	"			255			
9	F1677+oil J2+Kaol.	0,3+2,7+4	0,3	320	320	+20	+ 6,0
10	"			-			
11	Flot. S+oil J2	0,3+2,7	0,3	185	182,5	-117,5	- 391,6
12	"			180			
13	Armoflo + oil J2	0,3+2,7	0,3	215	222,5	-77,5	- 258,3
14	"			230			

Table 2.4./8 /continued/

No	AA Tested	AA Dose		Caking N		ΔN	ΔN/1gAA/1 kg F
		g/1 kg	g_o/1 kg	Abs.	Average		
15	SK FERT F20A	0,9	0,9	200	200	-100	- 111,1
16	"			200			
17	Armoflo	0,9	0,9	230	232	- 68	- 75,5
18	"			234			
19	Armoflo + oil J2	1+0,8	1	195	207,5	-92,5	- 92,5
20	"			220			

SERIE V.

Table 2.4./9

Caking Tendency Testing

CAN - Date of Production: 7/11/84
Test Start: 7/11/84
Caking Tendency Meas.: 8/11/84
CAN Quantity: 0,75 kg

CAN Quality Spec.:
N_{NH_3} 14,78 % b.w.
H_2O 0,54 % b. w.
d_{50} 1,40 mm

Screen Anal.:
2,8mm 2,26 %
2,0mm 39,21 %
1,0mm 54,30 %
1,0mm 3,37 %

No	AA Tested	AA Dose		Caking N		ΔN	ΔN/1gAA/1 kg F
		g/1 kg	g_0/1 kg	Abs.	Average		
1	Raw CAN	0,0	0,0	275	285	-	-
2	"			295			
3	Armoflo	0,9	0,9	169	163	-122	- 135
4	"			157			
5	"	0,36	0,36	178	173	-113	- 311
6	"			168			
7	"	1,50	1,50	123	119,5	-165,5	- 110
8	"			116			
9	Romonta	-	0,42	242	245	-40	- 95
10	"		0,42	248			
11	"	-	1,08	160	164	-121	- 112
12	"			168			
13	Flotigam S	0,60	0,60	35	40	-245	- 408
14	"			45			
15	"	1,20	1,20	35	36,5	-248,5	- 206
16	"	1,20	1,20	38			

SERIE VI.

Table 2.4./10

Caking Tendency Testing

CAN - Date of Production: 8/11/84
Test Start: 10/11/84
Caking Tendency Meas.: 11/11/84
CAN Quantity: 0,75 kg

CAN Quality Spec.:
N_{NH_3} 14,75 % b.w.
H_2O 0,16 % b.w.
d_{50} 1,7 mm

Screen Anal.:

2,8mm	12,06 %
2,0mm	46,88 %
1,0mm	39,15 %
1,0mm	1,9 %

No	AA Tested	AA Dose		Caking N		ΔN	ΔN/1gAA/1 kg F
		g/1 kg	g_o/1 kg	Abs.	Average		
1	Raw CAN	0,0	0,0	135	142	-	-
2	"			149			
3	Armoflo + oil J2	0,3+2,7	0,3	93	96,5	-45,5	- 151
4	"			100			
5	Armoflo	1,02	1,02	40	47	-95	- 93,1
6	"			54			
7	Flot. S	0,36	0,36	33	31,5	-110,5	- 306,9
8	"			30			
9	"	0,84	0,84	10	12,5	-129,5	- 154,1
10	"			15			
11	Flot. S + oil J2	0,3+2,7	0,3	112	106	-36	- 120
12	"			100			
13	Sinor Kao	0,36	0,36	100	92,5	-49,5	- 137,5
14	"			85			

Table 2.4./10 /continued/

No	AA Testing	AA Dose		Caking N		ΔN	ΔN/1gAA/1 kg F
		g/1 kg	g_o/1 kg	Abs.	Average		
15	Sinor Kao	0,84	0,84	45	30	-112	- 133,3
16	"			15			
17	Romonta	0,36	-	75	77,5	-64,5	- 179,1
18	"			80			
19	"	0,84	-	42	38,5	-103,5	- 123,2
20	"			35			

SERIE VII.

Table 2.4./11

Caking Tendency Testing

CAN - Date of Production: 10/11/84
Test Start: 11/11/84
Caking Tendency Meas.: 12/11/84
CAN Quantity: 0,75 kg

CAN Quality Spec.:
N_{NH_3} 14,83 % b.w.
H_2O 0,7 % b.w.
d_{50} 1,30 mm

Screen Anal.:	
2,8mm	2,61 %
2,0mm	30,52 %
1,0mm	62,78 %
1,0mm	3,6 %

No	AA Tested	AA Dose g/1 kg	g_o/1 kg	Caking N Abs.	Average	ΔN	ΔN/1gAA/1 kg F
1	Raw CAN	0,0	0,0	250	245	-	-
2	"			240			
3	Armoflo	0,6	0,6	110	97,5	-148,5	-247,5
4	"			85			
5	Armoflo + oil GFC	0,3+2,7	0,3	125	127,5	-118,5	-395,0
6	"			130			
7	Flot. S	0,6	0,6	30	39,5	-206,5	-344,1
8	"			49			
9	Flot. S + oil GFC	0,3+2,7	0,3	65	50,5	-194,5	-648,3
10	"			36			

2.4.3.5 Results Evaluation

In the following Tables 2.4./12 - 2.4./19 the influence of individual anticaking agents on CAN 30 caking properties is evaluated. The agents were used undiluted.

See Tables 2.4./12 - 2.4./16

In the first column the serias and the test numbers are introduced. The last column gives the influence of the agent on caking tendency decrease in numbers.

Table 2.4./12

Flotigam´s Influence on CAN 30 Caking Properties

Test No	AA Dose g/1 kg	Fert Caking N	Red. Caking N	ΔN	Effectivity %	ΔN/1 g AA
III/15-16	0,48	263,5	106	-157,5	59,8	-328
V/13-14	0,60	285,0	40	-245	85,9	-408
V/15-16	1,20	285,0	36,5	-248,5	87,19	-307
VI/7-8	0,36	142,0	31,5	-110,5	77,81	-306,9
VI/9-10	0,84	142,0	12,5	-129,5	91,19	-154,16
VII/7-8	0,60	245,0	39,5	-206,5	84,28	-344,1

Table 2.4./14

SK FERT F 20 A Influence on CAN 30 Caking Properties

I/11-12	0,9	185,0	40,5	-144,5	78,1	-160,5
II/11-12	0,9	245,0	167,5	- 78,5	32,0	- 87,22
III/3-4	0,48	263,5	142,5	-121	46,0	-252,0
IV/15-16	0,9	300,0	200	-100	33,3	-111,1
VI/13-14	0,36	142,0	92,5	-49,5	34,8	-137,5
VI/15-16	0,84	142,0	30,0	-112	78,8	-133,3

Table 2.4./12

Flotigam's Influence on CAN 30 Caking Properties

Test No	AA Dose g/1 kg	FERT Caking N	Red. Caking N	ΔN	Effectivity %	ΔN/1 g AA
III/15-16	0,48	263,5	106	-157,5	59,8	-328
V/13-14	0,60	285,0	40	-245	85,9	-408
V/15-16	1,20	285,0	36,5	-248,5	87,19	-207
VI/7-8	0,36	142,0	31,5	-110,5	77,81	-306,9
VI/9-10	0,84	142,0	12,5	-129,5	91,19	-154,16
VII/7-8	0,60	245,0	38,5	-206,5	84,28	-344,1

Table 2.4./14

SK FERT F 20 A Influence on CAN 30 Caking Properties

I/11-12	0,9	185,0	40,5	-144,5	78,1	-160,5
II/11-12	0,9	245,0	167,5	- 78,5	32,0	- 87,22
III/3-4	0,48	263,5	142,5	-121	46,0	-252,0
IV/15-16	0,9	300,0	200	-100	33,3	-111,1
VI/13-14	0,36	142,0	92,5	-49,5	34,8	-137,5
VI/15-16	0,84	142,0	30,0	-112	78,8	-133,3

Table 2.4./13

Armoflo 66 S Influence on CAN 30 Caking Properties

Test No	AA Dose g/1 kg	Fert Caking N	Red. Caking N	Δ N	Effectivity %	Δ N/1 g AA
I/3-4	0,9	185,0	125,5	-59,5	32,1	- 66,1
II/3-4	0,9	245,0	185,0	-60,0	32,4	- 66,6
III/7-8	0,48	263,5	162,5	-101,0	38,33	-210,4
IV/17-18	0,9	300,0	232,0	-68,0	22,66	- 75,0
V/3-4	0,9	285,0	163,0	-122,0	42,80	-135,0
V/5-6	0,36	285,0	173,0	-112,0	39,29	-311,0
V/7-8	1,50	285,0	119,5	-165,5	58,07	-110,0
VI/5-6	1,02	142,0	47,0	- 95,0	66,90	- 93,1
VII/3-4	0,6	245,0	97,5	-148,5	60,61	-247,5

Table 2.4./15

Romonta 68 Influence on CAN 30 Caking Properties

Test No	AA Dose g/1 kg	Fert Caking N	Red. Caking N	ΔN	Effectivity %	ΔN/1 g AA
III/19-20	1,2	263,5	100,0	-163,5	62,04	-135,8
V/9-10	0,42	285,0	145,0	- 40,0	14,0	- 95,0
V/11-12	1,08	285,0	164,0	-121,0	42,4	-112,0
VI/17-18	0,36	142,0	77,5	- 64,5	45,4	-179,1
VI/19-20	0,84	142,0	38,5	-103,5	72,88	-123,2

Table 2.4./16

Flotigam 1677 Influence on CAN 30 Caking Properties

I/7-8	0,9	185,0	83,5	-101,5	54,8	-112,8
II/7-8	0,9	245,0	185,0	- 60,0	24,5	- 66,6
III/11-12	0,48	263,5	135,0	-128,5	48,8	-267,7

Table 2.4./17

Comparison of Anticaking Properties of the Tested Agents

AA	AA Dose g/1 kg	Fert Caking N	Red. Caking N	ΔN	Effectivity %	ΔN/1 g AA
Flotigam S	0,690	227,0	44,33	-182,8	81,03	-264,9
SK FERT F20A	0,73	212,8	112,0	-100,8	50,5	-138,1
Romonta 68	0,79	223,5	125,0	- 98,5	47,34	-124,7
Armoflo 66 S	0,84	248,3	145,0	-103,4	43,69	-123,1
Flotigam 1677	0,76	231,0	134,3	- 96,66	42,7	-127,1

Table 2.4./18

The Quality of CAN 30 Used for the Tests

Production Date		5/11/84	7/11/84	4/11/84	10/11/84	3/11/84	31/10/84	8/11/84
Serie No		4	5	3	7	2	1	6
H_2O cont.	%	1,4	0,54	1,1	0,8	0,5	0,93	0,16
Undersize 1 mm	%	6,04	3,37	2,06	3,6	7,0	6,7	1,9
N_{NH_3} cont.	%	14,85	14,78	14,5	14,85	15,40	15,30	14,75
d_{50}	mm	1,3	1,4	1,50	1,35	1,5	1,7	1,7
Raw fert. caking	N	300	285	263	245	245	185	142

Note: The sequence of individual samples was arranged according to quality parameters

Table 2.4./19

Anticaking Properties of Fatty Amines with Inorganic Powders

Serie No	AA	Caking ΔN_1 with AA	Caking ΔN_2 with AA+SA	$\Delta N_2 - \Delta N_1$
I.	Armoflo + Kaolin	- 59,5	+ 37,5	97,0
II.	" + Bentonite	- 60,0	+ 17,0	77,0
III.	" + SiO_2	-101,0	- 8,5	92,5
I.	Flot. 1677 + Kaolin	-101,5	- 22,5	79,0
II.	" + Bentonite	- 60,0	+ 15,0	75,0
III.	" + SiO_2	-128,5	+ 26,5	155,0
I.	SK FERT F20A + Kaolin	-144,5	- 35,0	109,5
II.	" + Bentonite	- 78,5	+ 4,0	82,5
III.	" + SiO_2	-121,0	- 11,0	110,0
I.	Flot. S + SiO_2	-157,5	-17,5	140,0

Note: + caking was increased as compared with unconditioned CAN

- caking was decreased as compared with unconditioned CAN

$\Delta N_2 - \Delta N_1$ caking increase if SA + AA is used as compared with the caking when only AA is used

2.4.3.6 Discussion of Results

In all series of tests the influence of anticaking agents on the caking tendency of CAN 30 produced at GFC Homs was examined, but the primary idea was to test especially cation active substances, the fatty amines. The only exception is the wax type Romonta 68. The final evaluation of the influence of these anticaking agents on CAN 30 caking tendency can be found in Tables 2.4./12 - 2.4./16, and mainly Table 2.4./17.

2.4.3.6.1 Flotigam S

Influence on CAN 30 caking properties /see table 2.4./12/. In this case doses of Flotigam S in the interval 0,36 - 1,2 g/1 kg CAN were applied. The range of CAN 30 quality fluctuations was 0,16 - 1,1 % b. w. of water, average prills dia /d_{50}/ 1,35 - 1,7 mm, caking tendency 142 - 285 N. The influence of Flotigam S on CAN 30 caking tendency was high /59,8 - 91,19 %, 84,28 % in average/ which could be derived from the ΔN values /caking tendency decrease/ which were found in the range 110 - 248,5; 206,5 N in average. This average value of N if compared with the original untreated CAN 30 caking tendency value was very good. That means that the caking tendency of CAN 30 treated with Flotigam S can be classified as good.

Flotigam S quantity

The quantity of Flotigam S which is needed for the successful treatment of CAN 30 of different quality, can be determined from the results of the above discussed tests.

When the caking tendency of CAN 30 is lower than 200 N, doses of Flotigam S 0,4 g/1 kg may be sufficient. When zhe CAN 30 caking tendency fluctuates in the range of 200 - 300 N, Flotigam S doses 0,6 g/1 kg max are to be used. But anyway it is to be mentioned that the moisture content of the CAN 30 used for the test series III/15 - - 16 was too high /1,1 % H_2O b. w-/ and that the caking tendency decrease was small. It is to be emphasized again that the moisture content of CAN 30 is to be kept on the level 0,4 - 0,5 % H_2O b. w.

This fact is even more important if the produced CAN 30 is not cooled sufficiently /under 32° C/ as happens frequently at the GFC CAN 30 Plant.

2.4.3.6.2 Armoflo 66 S

Armoflo 66 S has been used at CAN 30 Plant at GFC in Homs and that was the reason why this anticaking agent was tested most thoroughly. This agent without separating agents or diluting oils was tested in all series, that means its efficiency was examined with 7 different CAN 30 qualities. Doses of Armoflo 66 S were tested in the range 0,30 - 1,5 g/1 kg CAN 30, and within series V. that means with one defined CAN 30 quality, 3 different Armoflo 66 S doses /0,36; 0,90; 1,50 g/1 kg/ were examined. The raw CAN 30 caking tendency in all tests was in the range 142 - - 300 N, 248,3 N in average. When the above doses of Armoflo 66 were used the average decrease of CAN 30 caking tendency was 103,4 N, that means 43,7 %. The caking decrease N fluctuated in the range 59,5 - 165,5 N which depended on the Armoflo 66 S dose quantity, original CAN 30 caking tendency, its moisture content and other quality parameters.

Armoflo 66 S quantity

From the above results it can be stated that the agent's efficiency is sufficient in the case that the untreated CAN 30 caking tendency is not larger than 150 N. In this case doses of 1 g/1 kg CAN 30 are to be applied.

When testing Armoflo 66 S the best results were attained in series VI. when the used CAN 30 was of a very good quality /0,16 % H_2O b. w., 1,6 % prills <1 mm; average prills dia $d_{50} = 1,7$ mm/ good results were reached also in series V., when 1,5 g AA/1 kg CAN 30 were applied. The caking tendency decrease in this case was 165,5 N, and this can be supposed sufficient in the case of CAN 30 caking tendency being less than 230 N. Anyway it has to be emphasized that the applied Armoflo 66 S dose was extremely high. If the test results of series V. are approximated to the dose 1 g/1 kg /V/3,4; V/5,6; V/7,8/ the caking tendency decrease figure is 135 N. That means that the application range of Armoflo 66 S can be extended to CAN 30 caking tendency limit 200 N under the condition that the moisture content will be less than 0,55 % H_2O b. w., undersize prills fraction <1 mm will be less than 3,5 % and $d_{50} < 1,4$ mm.

2.4.3.6.3 SK FERT F 20 A

This anticaking agent was tested in all series except series V. and the doses used were 0,36 - 0,9 g AA/1 kg CAN 30. The caking tendency of the untreated CAN 30 was in the range 142 - 300 N, which means that both extremely good and not good CAN 30 qualities were examined.
The average anticaking tendency decrease 50,5 % is better than that of Armoflo 66 S in spite of the fact that the used average dose 0,73 g AA/1 kg CAN 30 is by 0,11 g/1 kg

CAN 30 smaller. Caking tendency average decrease ΔN 100,8 N is by 2,6 N less than the one attained with Armoflo 66 S, which can be explained as a result of the lower average caking tendency of CAN 30 used for these tests. The specific caking tendency decrease of SK FERT F 20 A if compared with the specific caking tendency of Armoflo 66 S is higher

ΔN/1 g SK FERT F 20 A/1 kg CAN 30 ....138 N
ΔN/1 g Armoflo 66 S/1 kg CAN 30 ....123 N

SK FERT F 20 A Quantity

Good results with SK FERT F 20 A were attained in the following tests:

- VI/16, 16, application of 0,82 g AA/1 kg CAN 30 resulted in the caking tendency 30 N
- Application of the low dose 0,36 g AA/1 kg CAN 30 resulted in caking tendency 92,5 N which scaled up to 1 g/1 kg means that the final caking tendency would be between 40 - 50 N
- I/11, 12 dose 0,9 g AA/1 kg CAN resulted in decreasing the original caking tendency 185 N to the very good figure of 40,5 N
- Test III/3, 4 by scaling up the used dose 0,48 g AA/1 kg CAN 30 the caking tendency 40 - 50 N will be attained.

Finally it can be stated that SK FERT F 20 A can be successfully used with the application of doses 0,9 - 1,0 g AA/1 kg CAN 30 if the original CAN 30 caking tendency doesn't exceed 200 N.

2.4.3.6.4 Romonta 68

Because of the too low temperature of the applied Romonta 68 the tests in the first two series weren´t successful /< 70 °C, the results of these tests weren´t taken into consideration. When the applied temperature was increased to 70 - 80 °C than the results attained with this anticaking agent coudd be compared with the results attained with Armoflo 66 S and Flotigam 1 677.

Romonta 68 Quantity

If the caking tendency of untreated CAN 30 is below 150 N a very good anticaking result can be attained with this agent, e. i. 35 - 45 N. In case CAN 30 caking tendency will be in the range 150 - 200 N, a dose 1 g/1 kg CAN 30 will prove sufficient if the resulting caking tendency is supposed to be 70 - 75 N.

2.4.3.6.5 Flotigam S 1677

was tested in three test series only. The specific caking tendency decrease /Δ N/ 1 g Flotigam 1677/1 kg CAN 30/ was higher than was attained with Armoflo 66 S and Romonta 68 but it was by 11 N lower than attained with SK FERT F 20 A and much lower than with Flotigam S.

2.5. Future Prospects in Fertilizers Production

Should the planning of investments and future commercial activity at GFC Homs be discussed, liquid fertilizer production should be taken into account.

In many countries liquid fertilizers have been succesfully introduced into modern agricultural technology and their importance and popularity have been growing steadily.

When compared with granulated fertilizers the following advantages of liquid fertilizers are evident:

- production cost related to one ton of nutrient in commercial product is essentially lower and provides high investment returns
- caking does not exist
- no problems with bagging
- the stable and precisely defined quality of the product is easily maintained
- handling, transport and storage losses are negligible
- application cost in agriculture is reduced
- liquid fertilizers may be spread on soil uniformly with respect to high economy and to agricultural needs
- a high degree of automation and mechanization makes the application to soil easy, labour demand is reduced substantially, hard work is eliminated
- conditions for enviromental protection at the production, storafe, transport and application stages are improved essentially /dusty operations are excluded, no liquidation of used bags etc./
- the nutrient in liquid solution is assimilated by the agricultural plants more efficiently
- liquid fertilizer may be applied both before and during the vegetation period, the water solution of nutrient is effectively assimilated by leaves, this fact may be important in arid areas or during long periods without rainfall.
- low specific consumption of energy for production

However, some problems arise when liquid fertilizers are introduced into practice. Farmers have to be prepared for the application of liquid fertilizers which is basically different from granulated ones and relevant machines have to be available.

Taking in consideration the existing production program of GFC Homs, two basic types of liquid fertilizers may be of interest:

UAN - urea ammonium nitrate solution
NP - ammonium phosphate solution of formulation 8-27-0 /N - P_2O_5 - K_2O expressed in % b. w./ or more concentrated types.

UAN is a colourless liquid fertilizer which is produced by mixing ammonium nitrate and urea water solutions /75 %/ in the ratio 1 : 1 . The final product contains 29 - 32 % of nitrogen, which is present in amid /57 %/, nitrate /21,5 %/, and ammonium forms /21,5 %/ but derivations form this composition are acceptable.

In principal two ways of technology are possible, either solid components - prilled urea and prilled ammonium nitrate - are dissolved in water or intermediate products are upstreamed form production units in relevant concentrations /approx. 75 %/ and mixed together. The latter possibility is evidently more economical in case both production units are situated in one place as is the fact at GFC Homs.

In Czechoslovakia a plant with the capacity 150 000 mtpa of UAN /Czechoslovak make DAM-390/ is in operation in Duslo Šaľa and smaller capacities are installed in other localities.

UAN has been used for more than ten years in Czechoslovak agriculture and the present output is not able to cover the needs of the domestic market.

Liquid NP - fertilizer is produced by neutralization of phosphoric acid /concentration 32 % P_2O_5 or higher/ with liquid or gaseous ammonia. At present only limited quantities are produced on Czechoslovakia because of the lack of phosphoric acid. To meet the demand of agriculture a project has been prepared with the following technical specification:

Capacity/ NP-fertilizer 8-24-0/	220 000 t/year
Consumptions:	
Phosphoric acid 32 % P_2O_5	53 000 t P_2O_5/year
Gaseous ammonia 100 % NH_3	21 000 t/year
Electricity - production unit	2 160 MWh/year
- storage facilities	80 MWh/year
Clarified feed water	40 000 m^3/year
Cooling water	2 880 000 m^3/year

If necessary some emulsifying agent may be used /for instance in Czechoslovakia fine ground bentonite of domestic source is applied/.

Both above described technological processes have been developed in Czechoslovakia, the plants referred to have proven in industrial practice.

ANNEX 2/I

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ANNEX 2/II

Survey of CAN - Quality Tested by CAN - Plant Laboratory
Period 1/11/84 - 4/11/84

Date	Moisture content % min-max	Undersize 1 mm % min-max	N_{NH_3} % min-max
1/10	0,55-0,98	0,5-3,0	14,34-15,78
2/10	0,72-0,82	1,5-2,0	14,28-15,51
3/10	0,45-0,90	0,5-2,0	14,27-14,84
4/10	0,50-0,90	0,2-2,0	14,50-15,62
5/10	0,60-0,97	0,8-2,1	14,56-15,68
6/10	0,60-0,84	0,6-2,0	14,50-16,41
7/10	0,54-0,80	0,5-4,4	14,10-15,73
8/10	0,50-0,90	0,5-2,6	14,00-15,60
9/10	0,92-1,00	0,5-1,5	14,11-15,40
10/10	0,57-0,82	1,0-2,2	14,73-15,60
11/10	0,48-0,78	1,0-3,3	14,17-15,60
12/10	0,60-0,72	1,2-8,4	14,00-15,62
13/10	0,60-0,98	0,5-3,0	14,62-15,60
14/10	0,80-0,80	1,5-1,5	14,56-15,11
15/10	0,86-0,86	1,5-3,5	14,15-16,48
16/10	0,55-1,38	0,2-2,2	13,72-15,11
17/10	0,66-1,43	0,3-2,5	14,23-15,22
18/10	0,70-0,99	1,5-5,1	14,65-15,45
19/10	0,60-0,96	0,5-2,1	14,15-15,62
20/10	0,51-0,91	1,0-4,5	14,50-16,10
21/10	0,56-0,94	0,5-2,1	14,52-15,17
22/10	0,65-0,70	3,0-3,0	14,33-14,95
23/10	0,73-0,96	0,8-2,7	14,11-15,96
24/10	0,65-0,85	1,0-11,3	14,56-15,11
25/10	0,73-1,20	2,1-4,5	14,45-15,11
26/10	0,63-0,98	0,5-3,0	14,17-15,17
27/10	0,51-1,09	0,5-3,5	14,84-15,34
28/10	0,60-0,98	2,0-5,5	14,45-15,44
29/10	0,51-1,3	1,0-5,0	14,11-15,57
30/10	0,62-0,96	1,2-6,5	14,17-15,68
31/10	0,50-1,0	0,5-1,0	14,58-16,48
1/11	0,62-0,91	2,5-4,5	14,56-15,79
2/11	0,72-1,32	1,1-6,2	14,17-15,90
3/11	0,47-1,14	1,5-7,0	14,62-15,62
4/11	0,63-1,31	1,5-4,5	14,00-15,51

Survey of Individual Analyses Made at Plant Laboratory GFC During the Period 1/10 - 14/10/84

Date	Hour	Nitrogen Total % b. w.	H_2O % b. w.	Size Distribution in % b. w. Sizes in mm > 4	> 3	> 2	> 1	< 1
1/10	7	15,68	0,55	2,5	4,1	43,7	48,2	1,5
	9	14,56	0,57	3,5	5,5	30,0	58,0	3,0
	12	14,34	-	5,1	6,0	38,2	47,7	3,0
	15	15,17	0,54	2,0	5,0	38,5	54,0	0,5
	17	15,06	0,62	2,0	5,5	41,0	51,0	0,5
	23	15,78	0,98	3,0	5,0	42,0	49,5	0,5
8/10	2	14,82	0,86	0,5	1,2	49,5	48,0	0,5
	5	14,15	-	2,0	2,5	47,0	47,0	1,5
	7	14,57	0,50	5,5	7,5	52,0	33,5	1,5
	10	14,73	0,54	0,5	2,5	32,5	62,2	2,3
	13	14,56	-	4,2	5,0	35,2	53,4	2,2
	15	14,56	0,9	4,0	4,5	39,0	51,0	1,0
	21	15,06	-	1,6	4,2	35,1	56,5	2,6
	23	15,11	0,88	3,0	5,0	47,1	49,5	1,5
13/10	2	15,01	0,62	1,2	5,2	42,0	49,2	2,4
	5	15,01	-	2,1	4,2	42,6	50,11	1,2
	7	15,01	0,80	2,0	5,5	40,0	51,6	1,5
	15	15,01	0,80	0,5	4,0	51,0	51,5	2,0
	17	15,17	0,70	3,0	5,5	49,0	47,0	0,5
	19	15,06	-	1,2	3,5	43,0	50,6	1,7
	23	14,67	0,98	1,0	2,5	42,1	53,0	1,4

Survey of Average Daily Analyses Made at Central Laboratory GFC During the Period 4/9 - 9/10/84

Date	Nitrogen Total % b. w.	NH_4NO_3 Content % b. w.	Size Distribution in % b. w. Sizes in mm >4	>3	>2	>1	<1	H_2O % b.w.
4/9	30.12	86,08	0	5,5	48,2	42,8	3,5	0,63
5/9	30,01	85,76	0	5,0	48,0	43,0	3,5	0,72
8/9	29,00	82,88	0	6,4	50,0	42,0	1,2	0,85
10/9	29,34	83,84	0	15,7	54,8	29,0	0,5	0,44
14/9	29,23	83,52	0	10,5	56,3	32,5	0,7	0,80
16/9	30,35	86,72	0	10,8	44,5	43,0	1,7	0,87
19/9	29,34	83,84	0	7,5	55,6	35,7	1,2	0,73
2[illegible]/9	30,46	85,04	0	8,5	43,2	47,8	0,5	0,60
23/9	29,45	84,16	0	11,2	55,5	32,3	1,0	0,43
25/9	29,30	84,16	0	10,8	50,1	37,4	1,7	0,73
29/9	30,57	85,36	0	12,8	52,0	32,5	2,7	0,70
1/10	29,90	85,49	0	10,7	39,7	48,1	1,5	0,63
7/10	30,01	85,76	0	6,5	46,7	46,1	0,8	0,46
8/10	29,45	84,16	0	6,2	47,7	47,8	2,3	0,70
9/10	30,68	87,68	0	14,0	47,0	34,5	4,5	0,65

Measurement of the Caking Tendency of Fertilizers

Method 1

Scope: This method covers the determination of the caking tendency of fertilizers

Summary: A sample of the tested fertilizer is pressed under the pressure of 0,16 MPa for 17 hours. The hardness of the cake is measured by the means of a penetrating needle instrument.

Apparatus: Fertilizer press, Penetrating needle instrument

Procedure::Samples of fertilizers are filled into stainless steel cylinders up to the rim. The cylinders are placed into small PP bags in order to eliminate the influence of the atmosphere. The PP bags are closed on the side of the cylinders not on top. Then place the lids on the cups and apply pressure on them. This pressure is to be maintained for 17 hours at an ambient temperature of 25 °C./See Fertilizer press - Figure No 3/.

After 17 hours take the cylinders out of the PP bags carefully and place one after another on the supporting frame of the penetrating needle instrument. /See figure 1/. Point the needle of the penetrating needle instrument to the center of the upper opening of the cylinder and apply pressure. On the scale of the instrument read the pressure /N/ at the moment when the fertilizer cake is punched. /See fig. 2/. The hardness of the fertilizer cake is proportional to the measured punch pressure.

Note: Do not forget to take out the fertilizer remains from the penetrating needle collecting vessel, as it might influence further measurements.

Calculation: The caking tendency of the fertilizer is calculated as the average pressure of three parallel tests.

Fertilizer Press - Fig. No 1

The fertilizer press consists of the following principal parts:

1 ....support
2 ....cylinder
3 ....cylinder lid
4 ....lid buttons, where the actual press is applied
5 ....lead weight
6,7,8.............frame

Penetrating Needle Instrument - Fig. 2,3

1 ......fertilizer cake in the cylinder
2 ......supporting frame
3 ......fertilizer collecting vessel
4 ......penetrating needle
5 ......piston
6 ......pressure chamber
7 ......compressed air inlet
8 ......pressure scale

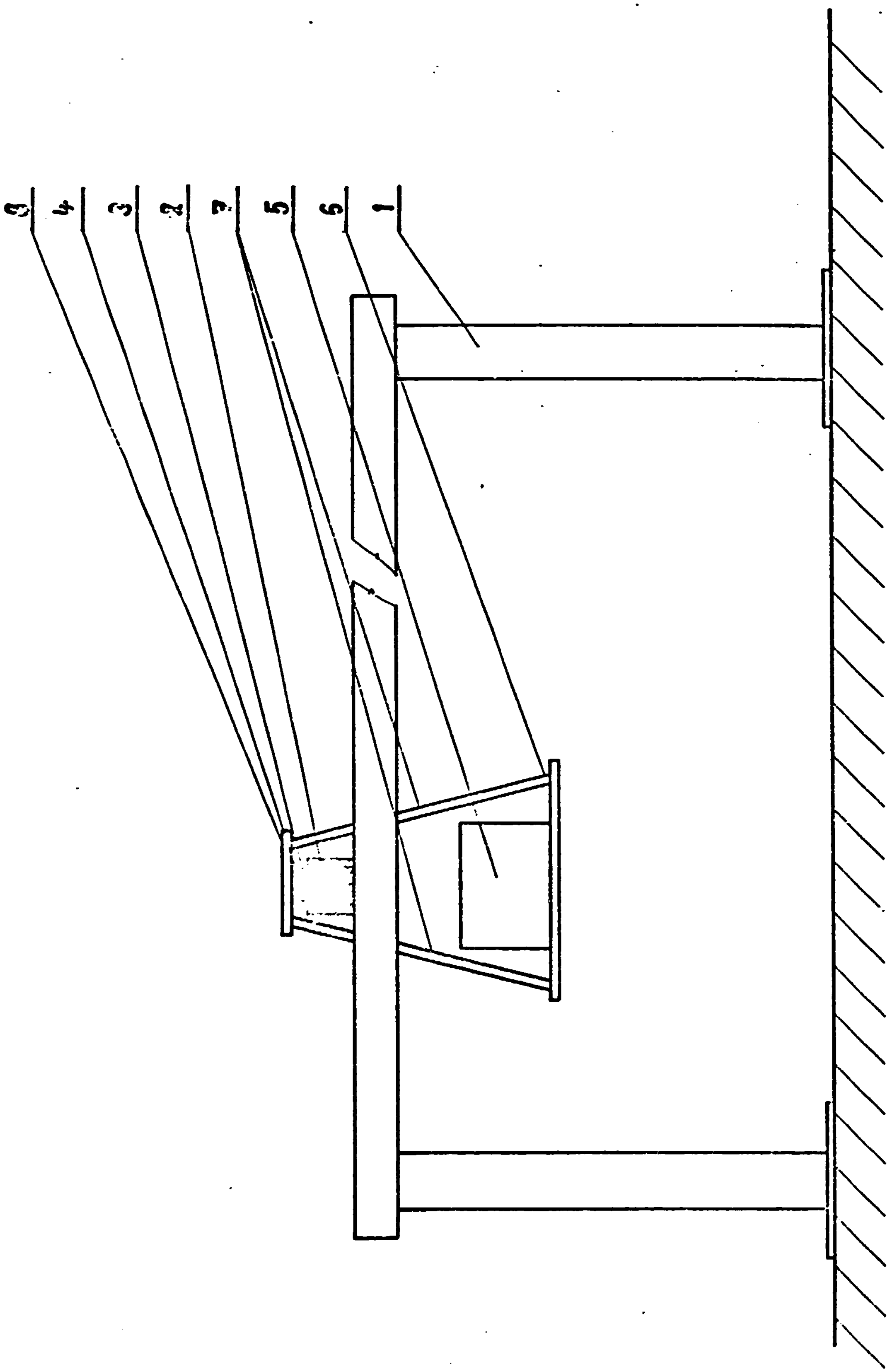


FIG. 1

FIG. 2

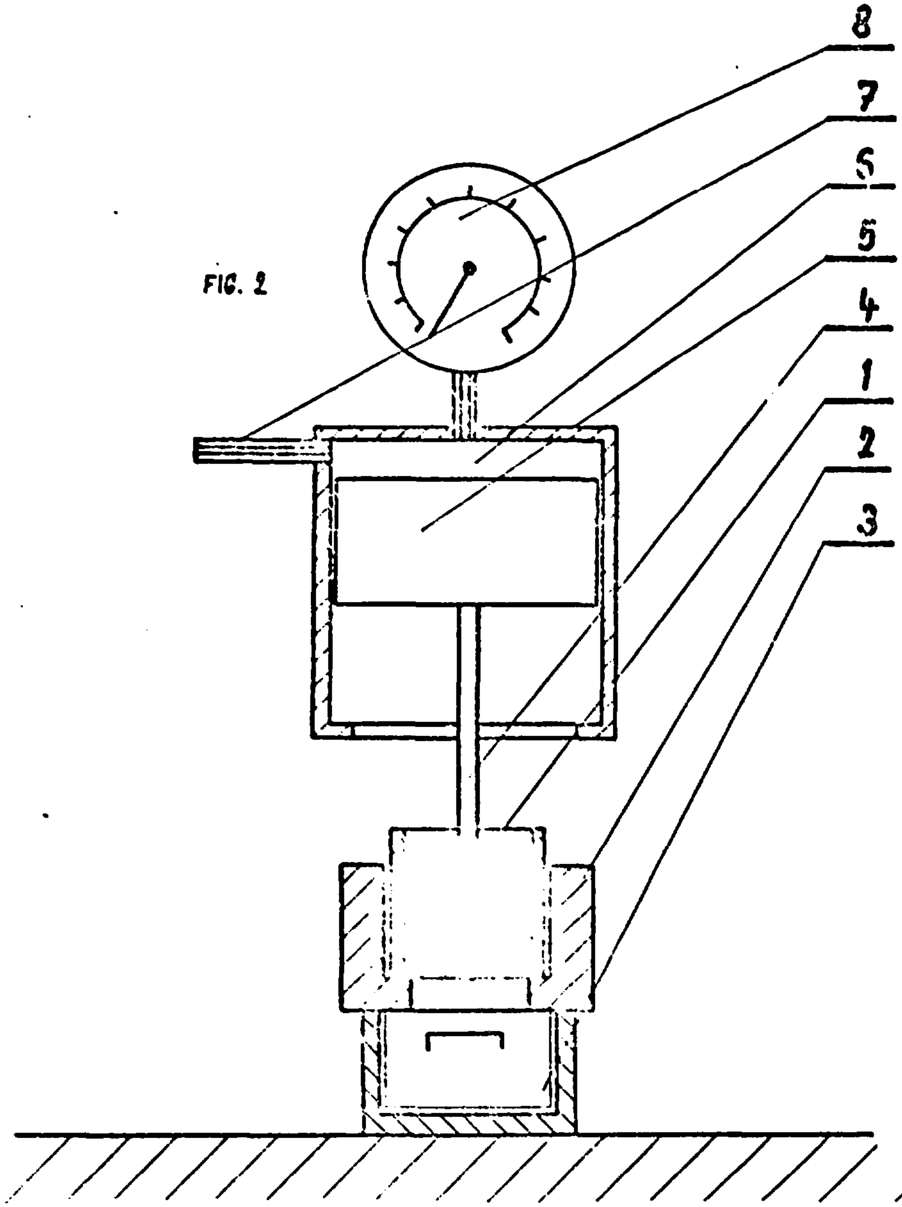
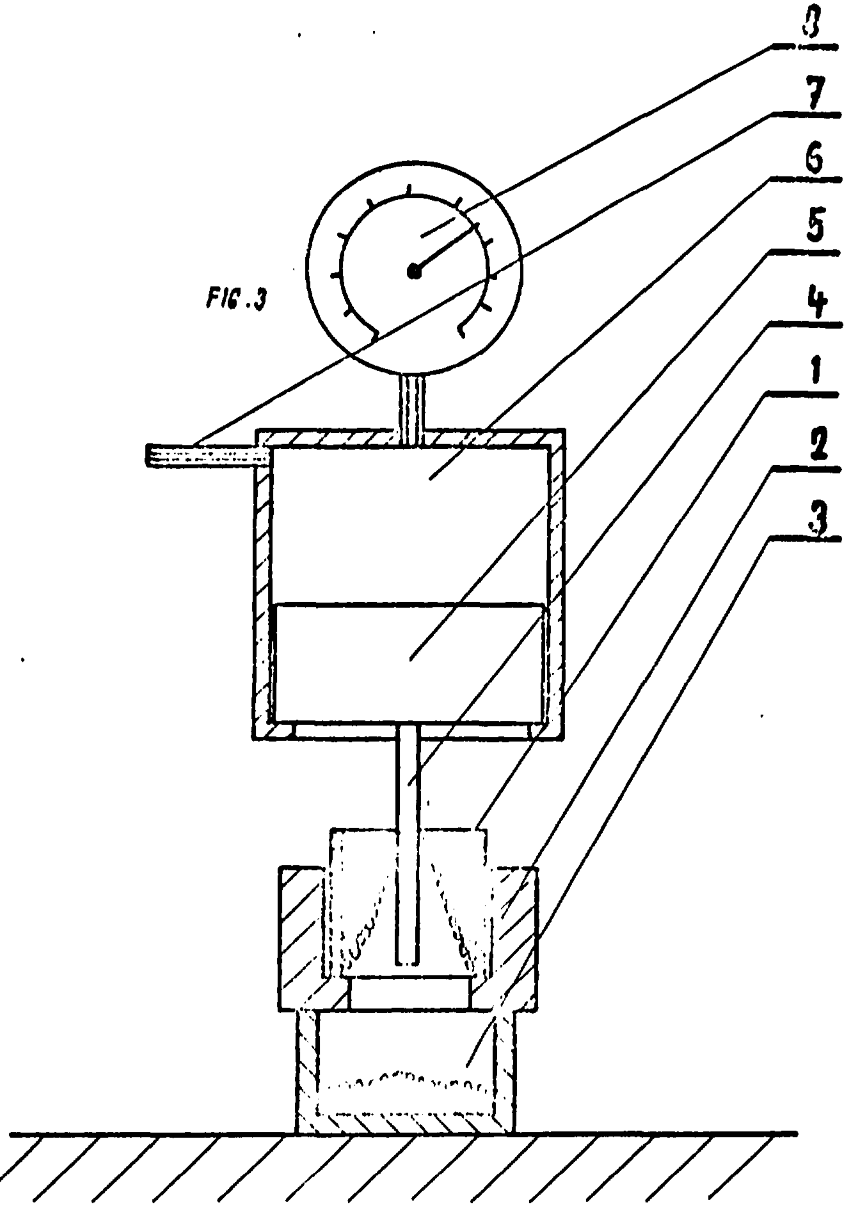


FIG. 3



Evaluation of Results

The value of penetrating pressure of the tested fertilizer is indicated on the above instrument. It is advised to repeat the test with several identical samples to obtain a reliable average value. This result is proportional to the anticaking tendency of the tested fertilizer.

This method is generally used to compare the quality of various fertilizers, As local climatic, storage, transport and handling conditions may vary substantially, the general view on the adequate degree of anticaking tendency is not uniform. However, as a universal guide for CAN quality testinf the following data may be used:

Table

Quality class relating to anticaking tendency	Measured Pressure in N
<u>I. CAN 30 - unconditioned</u>	
- excelent or good	120 - 150
- lower but still satisfactory [1/]	150 - 220
- low or bad	220
<u>II. CAN 30 - conditioned /AA applied/</u>	
- high	20 - 70

1/ <u>Note:</u> Lower quality may occur also when deviation from technological regulations resulted in a higher content of constituent moisture in the tested fertilizer.

When evaluation of the effect of used anticaking agents should be the main aim of testing, the efficiency of conditioning /EF/ is calculated on the basis of pressures measured before conditioning /PBC/ and after conditioning /PAC/ according to the following equation

$$EF = \frac{PBC - PAC}{PBC} \cdot 100$$

The effect of the used anticaking agent is
- very good for EF ....70 - 80 %
- acceptable ....70 - 50 %

When EF < 50 % the use of the tested anticaking agent is not recommendable for economical reasons.

Measurement of the Influence of Different Anticaking Agents on the Caking Tendency of Fertilizers

Method 2

Scope: To minimize the caking tendency of fertilizers different anticaking agents are recommended, The suitability of individual agents is to be tested for fertilizers produced in different plants.

Summary: A measured quantity of raw fertilizer is filled into a small laboratory coating drum. The fertilizer is coated with a known quantity of anticaking agent. The treated fertilizer is homogenized in the drum for 3 minuted and its caking tendency is measured afterwards /See ANNEX 2/ V Measurement of Caking Tendency of Fertilizers/.

Apparatus: Coating drum - a rotating cylinder 30 cm long and 20 cm wide is used. The cylinder is closed at one side, on the other side ther is an orifice 8 cm in dia. This orifice is used for filling in the fertilizer and the application of anticaking agents, On the inner wall of the drum 3 longitudinal shoulders are situated to enable the thorough mixing of the fertilizer. The drum is rotated at the speed of 30 rpm. A special syringe or nozzle for the application of anticaking agents in the form of a fine mist is used.

Chemicals: Samples of the fertilizer and samples of the tested anticaking agents.

Procedure: Insert 0,5 - 1 kg of fertilizer into the drum and start to rotate it. The quality of the fertilizer is expected to be well defined /sieve analysis, moisture content, nitrogen content, possibly soluble calcium content/. During one minute apply a known quantity of the tested anticaking agent. Rotate the drum for 3 minutes and then take samples to measure the caking tendency of the fertilizer.

Note:

- If the tested anticaking agent is highly viscose, it is to be heated to a suitable temperature, so that it can be applied in the form of a fine mist.
- If anticaking and separating agents are applied, the anticaking agent is applied first, than the rotation of the drum is stopped, the separating agent is added, the orifice is closed by means of a PP bag and the drum is rotated for 3 minutes. The caking tendency is measured afterwards.

Calculation: Anticaking properties of different anticaking agents are evaluated from the values of the measurement of the Caking Tendency of Fertilizers /see ANNEX 2/V/.

ANNEX 2/VII

Determination of Organic Anticaking Agent Content in CAN and Combined Fertilizers

Method 3

Scope: This method covers the determination of organic matter, especially of organic anticaking agents in CAN and combined fertilizers.

Summary: The organic anticaking agent in fertilizers is determined by repeated extraction with chloroform; this is distilled off and the organic residue is determined gravimetrically.

Apparatus: Soxhlet apparatus /100 ml capacity/
Flat bottom dist. flask /250 ml capacity/
Water bath
Dissicator

Chemicals: Chloroform redistilled

Procedure: Weigh 100 grams of fertilizer into an extraction thimble of the Soxhlet apparatus. Place the thimble into the extraction apparatus carefully. The apparatus must be thoroughly clean, rinsed with distilled water and dried. Take a distillation flask, clean and dry, put it into a dissicator and leave it there to reach the ambient temperature / /1 hour approx./. Weigh it then with the accuracy of 5 decimals. Place 100 ml of chloroform into this flask, join it to the Soxhlet apparatus and place the water cooler into position. The extraction apparatus is heated by means of a water bath. Repeat the extraction 10 times.

After finishing the extraction, with all chloroform back in the distillation flask, disconnect the cooler, take out the thimble carefully, assemble the apparatus for distillation and distill off the chloroform. Clean the distillation flask containing the organic residue from the outer side carefully /as it was situated in a water bath/ and dry it for 16 hours in an oven at 50°C. Take the flask out of the oven, place it into a dissicator to cool and after it has reached the ambient temperature, weigh it with the accuracy of 5 decimals.

Chloroform which was distilled off can be used for further tests.

Blanc Test

Take a sample of fertilizer which wasn´t treated with the anticaking agent and analyse its contents of organic matter by the same procedure as described above.

Calculation

Calculate the anticaking agent of the sample as follows:

$$\text{anticaking agent \% b. w.} = / \frac{V}{n} \cdot 100 / - \text{blanc test \%}$$

where:

V ....weight of organic matter in grams

n ....weight of the sample in grams

ANNEX 2/VIII

Determination of Water Soluble Calcium Content in CAN

Method 4

Scope: This method covers the determination of water soluble calcium content, which is present in the CAN fertilizer in the form of $Ca/No_3/_2$. Its content is one of the parameters which indicates the CAN tendency to form cakes.

Summary: A sample of CAN is dissolved in methanol and filtered. Ammonia buffer soln. and Zn EDTA are added to the filtrate, which is titrated with 0,1 M soln of EDTA, using Eriochrom black T as indicator. End of the titration is indicated by the violet colour changing into blue. The calcium content is directly proportional to EDTA consumption.

Apparatus:	Volumetric flask 100 ml	- 1 pc
	Volumetric flask 1 000 ml	- 2 pcs
	Volumetric flask 2 000 ml	- 3 pcs
	Beaker 2 000 ml	- 1 pc
	Beaker 500 ml	- 1 pc
	Watch glass	
	Funnel	
	Burette 10 ml	
	Pipette 25 ml	
	Shaking machine	

Chemicals: EDTA
Zinc metal 99,9 %
Hydrochloric acid 36 % A R
Ammonium chloride A R

Ammonia 25 %
Zinc sulphate crystallic A R
Methanol low in water A R

<u>0,1 M EDTA soln.</u> - weigh 37,52 g EDTA, transfer into 1 litre volumetric flask and fill up with distilled water.

<u>EDTA soln. - factor determination</u> - pipette 10 ml of the EDTA soln., add 10 ml of ammonia buffer, Eriochrom black T, and titrate by 0,1 M Zn soln. from blue to red colour

$$f = \frac{V_{Zn} \cdot f_{Zn}}{10} \quad , \text{ where}$$

V_{Zn} ....consumption of 0,1 M Zn soln. in ml
f_{Zn} ....factor of the Zn soln.

<u>0,1 M Zinc soln.</u> - weigh 6,5435 g of Zinc /99,9 %/ into a 1 litre flask, add 33 ml of hydrochloric acid /33 - 37 %/ A R. Cover the neck of the flask with a funnel covered by a watch glass and cool the flask during Zn dissolving. The Zn dissolving procedure is finished in 16 - 20 hours, rinse the watch glass and the funnel with distilled water which is added to the soln. Transfer the soln. into 1 litre volumetric flask and fill up to the mark. If the real weight of the dissolved zinc differs for the above mentioned 6,5435 g, a factor is to be used:

$$f_{Zn} = \frac{\text{Zn weight /g/}}{6,5435}$$

Ammonia Buffer -dissolve 108 g of ammonia chloride in distilled water, add 700 ml of ammonia /25 %/, transfer into a volumetric flask of 2 litre capacity and fill up to the mark.

Zn EDTA - weigh 9,4 g EDTA, transfer into a volumetric flask of 2 litre capacity, add 1 200 ml dist. water. Disslove 7,2 g $ZnSO_4 \cdot 7 H_2O$ in a beaker /500 ml/ in 250 ml. dist. water. This soln. if not turbid, transfer to the EDTA soln., add 5 ml of ammonia soln. concentrated and fill up to 2 litres with dist. water.

Testing of the Zn EDTA soln. - pipette 20 ml of Zn EDTA soln. and titrate it with soln. of Zn.and EDTA. The consumption of either of these standards shouldn´t exceed one drop.

Methyl alcohol soln. - mix 35,3 ml of ammonia /25 %/ and 19,5 ml of dist. water and fill up with methanol in a 2 litre volumetric flask.

Procedure. A 10 g sample of the fertilizer transfer into a weighed volumetric flask /100 ml/, add the ammonia methanol soln., and shake vigorously 30 min. on a laboratory shaking machine. Fill up with dist. water 100 ml. Filtrate the soln. through filter paper /blue rigbon/. Pipette 25 ml into a titration flask /not with a mouth!/, add 10 ml ammonia buffer, 5 ml Zn EDTA soln., Eriochrom black T indicator and titrate with 0,1 M EDTA soln. from red violet to blue. Repeat this analysis twice for each fertilizer samplo.

Calculation - calculate the water soluble calcium content:

$$\text{Ca water soluble \% b.w.} = \frac{A \cdot f_{EDTA} \cdot 0,4008}{B}$$

$$\text{CaO water soluble \% b.w.} = \frac{A \cdot f_{EDTA} \cdot 0,5608}{B}$$

where

A ....EDTA soln. cosumption ml

B ....sample weight g

f_{EDTA} ....titration factor of EDTA

ANNEX2/IX

Granule Strength Testing

Method 5

Scope: A quick determination of the crushing strength of individual granules is carried out with the aid of a simple, hand-operated device /supplied for instance by the firm Pfizer, 62 Wiesbaden, Schöne Aussicht 41, Federal Republic of Germany/. Indicated crushing strength or plastic behaviour of granules are important factors with respect to the caking tendency of fertilizers.

Summary: A sample of fertilizer is to be screened to obtain the granulometric fraction 1,6 - 2,0 mm. Granules of approximately equal size should be compared only, because crushing strength increases significantly with increase in particle size. To obtain an average evaluation it is necessary to crush at least 20 and preferably more granules. Individual granules are crushed between movable jaws of the testing device and the crushing strength is indicated by manometric scale readings at the time when the granule fractures. Some granules do not crush but are plastically deformed. The percentage of plastic granules defines the plasticity of the fertilizer. High plasticity and/or low crushing strength promote the caking tendency of fertilizers.

Apparatus: Testing device-measuring tongs, the movable jaw of which is fitted with a manometer working in the range 0 - 25 kp/cm^2.

Chemicals: No chemicals needed

Procedure: A granulometric fraction 1,6 - 2,0 mm obtained by screening a 0,5 kg sample is put into a polythene bag to protect it against the influence of the enviromental atmosphere. Individual prills are taken with tweezers and put on the lower jaw of the testing device. The upper jaw is pressed down and pressure indicated at the scale in time of crushing is measured.

Calculation:

CS_F ....crushing strength of fertilizer
CS_I ....crushing strength of individual non-plastic granules
m ....number of non-plastic granules
n_T..........total number of tested granules
p ....plasticity of fertilizer

$$CS_F = \frac{\sum CS_I}{n} \qquad /N/$$

$$p = \frac{n}{n_T} \cdot 100 \qquad /\%/$$

ANNEX 2/X

List of Anticaking Agents Tested:

Armoflo 66 S - Armour Hess Chem. Lim.
Victoria Avenue, Harrogate
HC 1 5RR, Great Brittain
Flotigam 1677 - HOECHST AG
D 6230 Frankfurt/Main 80
Federal Republic of Germany
Flotigam S - HOECHST AG
D 6230 Frankfurt/Main 80
Federal Republic of Germany
Romonta 68 - VEB Chemiewerke Werdau
Johannisstrasse 28
Werdau, German Democratic Republic
SK FERT F2CA - Sinor - kao/sa
Aragon, 383, atico
Barcelona - 13
Spain

After the testing program was closed the following AA was delivered to GFC:
Raisamin MPK - Rasio Tehtaat
OY KASVIOLJY
21 200 RAISIO
Finland

APPENDIX I

We gratefully acknowledge the help of :

UNIDO

1. Mr. S. E. SAZONOV
   Industrial Development Officer
   Chemical Industries
   Industrial Operation Division
   UNIDO - Vienna
2. Dr. A. S. SALEM
   SIDFA, UNIDO, DAMASCUS, SYRIA

UNDP

3. Dr. YAHYA KASSAB
   Representative UNDP
   DAMASCUS

GOVT of SYRIA - GECI/GFC

4. Mr. ZEIF AL HARIRI
   Deputy Gen. Director of GECI
5. Mr. A. TURK
   General Director
   GFC HOMS
6. Mr. M. ALI ALHUSSEIN
   Counterpart
   GFC HOMS
7. Special Thanks are due to the Heads, Chiefs and all the GFC staff in the units for their help and cooperation

UNITED NATIONS

Contract No. 84/17 - Annex E

APPENDIX II

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

UNIDO

19 October 1983

JOB DESCRIPTION

Post title Expert in Designing Catalyst Testing Pilot Plant

Duration

Date required

Duty station Homs, Syrian Arab Republic

Purpose of project To assist the General Fertilizer Company in detailed designing of a pilot plant for testing catalysts for ammonia production.

Duties The expert will be assigned to the General Fertilizer Company and will be expected to:

- Evaluate the present status of design work for the construction of a pilot plant to test catalysts for ammonia production;
- Assist in elaboration of technological scheme to be applied for testing catalysts and make recommendations on it;
- Assist in choosing appropriate equipment to be ordered for the construction of the pilot plant;
- Consult on specific requirements to equipment to be applied at the above pilot plant;
- Consult on working out an order list of equipment to be purchased or constructed;
- Assist in elaboration of commissioning scheme for the pilot plant to be built and recommend on different equipment testing;
- Train counterpart specialists;
- Make a report along with the other expert on his achievements and findings upon the completion of the project.

UNITED NATIONS

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

UNIDO

19 October 1983

JOB DESCRIPTION

Post title Expert in prevention of Nitrogen Fertilizers Caking Tedency, with research capability.

Duration

Date required

Duty station Homs, Syrian Arab Republic

Purpose of project To assist the General Fertilizer Company in conducting research work at a pilot plant and laboratories to reduce caking tendency of CAN and urea.

Duties The expert will be assigned to the GFC and will be expected to:

- Evaluate the present status of research work on CAN and urea caking tendency prevention and its results;
- Recommend on elaboration of a research work plan and a list of measuring instruments for controlling CAN and urea caking level;
- Advise on elaboration of the scheme for testing different means of caking tendency prevention;
- Consult on the choice of possible anti-caking agents to be tested and recommend on compiling a list of such agents to be supplied by the contractor in small quantities;
- Recommend on possible schemes and regimes of anti-caking treatment of CAN and urea;
- Assist in conducting experiments on anti-caking treatment;
- Consult on the final decision to be made;
- Train counterpart specialists:
- Make a report on his findings and achievements along with the other expert.

..../

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