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DEVELOPMENT, PRODUCTION AND USE OF FERTILIZER CATALYST IN INDIA[1]/

by

P. S. Sen

The Fertiliser Corporation of India Ltd.
Sindri, Bihar   India

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not affect the activi.. ... . .w even for
intensive applicators the nickel content in the reformation
catalysts is less than in other commercial varieties. In
case of L.T.Shift catalyst intensive search was made to fix
the optimum copper content[4]. Some of the results are given
in Fig. 4. In our latest version, the five component catalyst
system contains 23.5% CuO.

16.   Some catalysts need very high degree of selectivity.
In such cases, we are to rely much on fundamental studies.
In case of naphtha reformation catalyst for example, before
attempting formulation we carried out extensive studies on
acidity of the possible carriers, inter-action between
carrier-impurities and active component to form spinels,
characteristics of α- and γ -Al_2O_3 in modifying the crystal
habits of compounding medium, barriers for arresting the
growth of nickel crystallites, doping of **rare** earths etc.
Some of the findings led us to conclude that correct formu-
lation of naphtha reformation catalyst is possible without
potash[47].

17.   A catalyst may have all the desired physico-chemical
characteristics of an efficient one, yet can fail in a commer-
cial reactor. The criteria of identification of an industrial
catalyst remains a puzzle to be resolved. No doubt, only by
testing the catalyst under actual running condition one can
verify its industrial worthiness. It is however, not possible
particularly in the developing stages to put all the batches
of catalyst in service test to evaluate it's life. It is
therefore, necessary to rely on some indirect method of
testing.[5,6,15]

18.   Obviously, therefore, the subject of assessing the
surface and bulk characteristics and overall efficiency of the
catalyst will require the services of varied and refined
tools, in addition to test rigs for evaluation of activity.

19.   In our institution, the typical physical and physico-
chemical methods applied are: BET technique, selective adsorp-
tion, helium and mercury density, pressure porosimetry,

magnetic balance, X-ray, electron microscopy, spectroscopy, electrical conductivity, thermogravimetry, quartz microbalance, chromatography, differential thermal analysis (DTA), electron spin resonance (ESR) etc.

20.   The physico-chemical appliances are extensively used at various stages of development[7,8] quality control of the intermediate stage and for the end product as well. Changes occuring in the catalyst species at different stages of production are of specific nature and the physico-chemical appliance are utilized to study such changes. The interpretation of results bring **out** the intricacies of catalytic phenomena and help in assessing the correct route to generation of process know-how. The instruments and equipments, wherever needed are suitably modified to study a catalyst under actual service condition. This route provides us with valuable informations in predicting catalyst life.

21.   The field of application of different techniques is so vast that discussions have been limited to some typical ones. We do not, however, claim that ours is the best approach. Nevertheless, our mode of approach will bring into light the present stature of our institute as a catalyst manufacturer, and may create **interest** in the minds of those who intend to embark on the project of catalyst development and manufacture.

Adsorption Measurements and BET Technique:

22.   Physical adsorption constitutes an important means of investigating the surface properties of heterogeneous catalysts. It can be put to good advantage in the study and assessment of the nature[9,12] of the catalyst surface.

     The estimation of surface area of solids is made by the low temperature gas adsorption using BET equation. For reasons mentioned before, measurements are done with samples before initial activation and after, and at different **intervals** of actual run. Physical adsorption also forms the basis of analysis of modification of pore structure of carriers[10] brought by chemical and thermal methods.

23.   Like physical adsorption, chemisorption is **inextricably** related to heterogeneous catalysis, and that an understanding of mechanism of adsorption is a prelude to the understanding of mechanism of catalysis.

24.   For the surface area measurement and chemisorption studies, conventional BET apparatus as **well** as adsorptomat' and vacuum micro-balance are used. The surface area values in combination with either pore **volume** or pellet density is further utilized[3,9] in determining average pore size and average particle diameter of a catalyst. Reference may also be made to a new method[11] developed for the measurement of surface areas of catalyst carriers, like, silica gel.

25.   <u>Pressure Porosimetry</u> — Pore size distribution has not a significant control[12] over transport of reactive gases to the interior of the catalyst. If the pore diameters are **very** narrow, the active sites located on the finer pore walls may not be utilized at all in a flow system. From analysis of pore size distribution data of the catalyst used in commercial plant, we have seen that fall in activity in some cases are due to elimination of desired pores. We employ pressure porosimeters having ranges upto 5000 lbs/sq. in as well as 15000 lbs/sq.in. The **distribution** data can also be computed for the **evaluation** of surface area[13].

26.   <u>Magnetic Balance</u>:- We utilize the magnetic balance for monitoring dispersion of the active **component** of a supported catalyst during development and production as well as changes in crystal size while in actual **operation**. This **technique** can account for the unpaired electron in the catalyst **species** the valency state, phase transformation, the size of the crystallite. Fig. 5 shows two typical applications of magnetic technique in evaluating the dispersion and the state of oxidation of nickel as a function of Ni concentration in nickel-alumina catalyst. Fig. 5A shows the variation in magnetic susceptibility with increasing nickel concentration, while Fig. 5B shows the changes in magnetic moment and **Weiss** constants as a function of nickel percentage which is **related** to the nickel particle size build-up. It may be mentioned

here that as a part of the accelerated test for catalyst
stability the sample after treatment under the plant operating
condition for different period of time, are tested for growth
in size of the crystallites of the active components.

27.   X-ray :- X-ray is one of the oldest techniques applied
in catalyst science. In a particular chemical formulation it
is required to identify which specific phase composition
contributes to activity and which are the phases necessary
for stability. Identification of essential phases helps a
lot in the formulation of a catalyst as well as process steps
for its preparation. X-ray analysis is apolied by us in gen-
eration[14,15] of know-how and quality control work with
particular reference to phase composition and crystallite
size. X-ray technique is also used to reveal the picture of
transformations taking place under reaction conditions.

28.   Electrical Conductivity and ESR:- The catalytic acti-
vity of a semiconductor is determined by the position of
the fermilevel at the surface of the crystal. In course of
the the reaction, concentration of reacting and product
molecules in adsorbed phase change. This causes a change in
electrical conductivity yielding valuable information on
the mechanism of the surface reaction. The change in elec-
trical conductivity of a semiconductor is related with
catalytic activity. A typical result of the work[16] done
with CuO/ZnO catalyst is represented in Fig.6.

29.   We apply E.S.R. technique for understanding the mecha-
nism through which heterogeneous catalytic reactions occurs
as well as prediction for catalyst formulation[17]. While
selecting the active component for a particular reaction,
the state of its electron levels are examined to asses it's
capacity for surface interaction with reactant molecules
as well as with carrier. Both electrical conductivity and
E.S.R. studies help us in selecting proper catalytic compo-
nents.

30.   **Thermogravimetry:-** The thermogravs' are utilised for studying the mechanism of reduction[5], carbon laydown, gasification of deposited carbon in naphtha steam system etc. The equipments in use are having a working temperature upto 1600^oC, and has facilities for testing under controlled atmosphere, thereby simulating the actual reaction condition of a plant, these help in assessing the stability of a catalyst.

31.   Thermograv is also utilized for studying the mechanism of decomposition of salts like nitrate, carbonate etc. of the active catalyst components for proper setting of temperature programming for heat-treatment in catalyst manufacture.

32.   **D.T.A:-** We are having a battery of such units for studying the mechanism of release of volatile from the surface of porous solid and appearance of new phases in the course of catalyst preparation. Almost every batch of catalyst we produce are tested to examine the uniformity of drying, curing and grinding, in different stages of preparation of catalyst. Some typical DTA curves for CO-conversion catalyst **have been** presented in Fig. 7.

33.   **Quartz Microbalance:** The instrument finds application in studying the mechanism of reduction[18,19] and for direct measurement of carbon liberation from hydrocarbon steam mixture under limiting conditions, of steam/carbon ratio and temperature. This makes the instrument very useful for development of efficient reformation catalyst. It is also used for the assessment of selectivity of a catalyst surface by applying the process of gradual poisoning.

34.   **Chromatography:-** Gas chromatography is widely used as an analytical tool for the separation, detection and estimation of various components involved in a chemical reaction. This technique is applied in studying catalytic processes in pulse reactors for understanding the mechanism and kinetics[20] of catalytic reactions and **as well as** for initial assessment of catalyst formulations.

35.   Activity Test:- In view of the fact that all the eleven varieties of catalyst manufactured by us are by batch process and that each batch is to be tested for its performance characteristics, elaborate facilities for performance test have been developed. We entered in this field in the year 1951, when we had 6 numbers of 1000 ml. capacity bench scale test units deployed in measurement of activity. Thereafter, the testing facilities were increased in stages. At present, there are 125 bench scale units, 30 semi-pilot units housed in 4 bays at different locations in the factory and central laboratory. Besides these, a number of units are located in different plants. Also there are composite pilot plants, where naphtha purification, primary reformation, secondary reformation, high and low temperature CO-conversion are hooked-up in series. This the institution is in possession of testing facilities of all conceivable sizes starting from pulse to pilot reactors.

III. GENERATION OF KNOW-HOW AND ITS TRANSFER TO PRODUCTION:

36.   We have already iscussed in brief the basic requirements of industrial catalysts and techniques and tools employed for their assessment. A catalyst know-how can only be considered complete when the material produced in commercial scale can show sustained performance for the period guaranteed.

37.   One engaged in development and manufacture of catalyst not just overlook all the steps of operation adopted in catalyst making because individually and collectively they modify[21] the surface and bulk properties of the solid. It is, therefore, a necessity to study the effect of all individual process steps on the surface property of the finished catalyst. To cite an example we can take the grinding operation. Grinding is one of the very common steps in catalyst preparation. In laboratory this is done in mortar-pestle or pot mill. With the time of grinding along with the reduction of size the grinding impact induces some electronic changes. Now, when this grinding operation is to be done in commercial

scale we generally employ equipments like ball mill, attrition mill, reymond mill, colloid mill etc. The operation in such equipments can lead to a higher degree of lattice distortion, besides changing the fermilevel in the crystal of the active component.[22,23] Such changes will modify the property of the finished product.

38.   The unit operations involved in catalyst production are in general precipitation, filtration, drying, grinding, mixing, extrusion, granulation, tabletting, soaking, curing etc. It is necessary to study each of these unit operations to understand to what extent it is likely to influence the quality of the product and also to assess the possible deviation of the commercial product from the laboratory one. Detailed discussions on all the variables and their effect on surface and bulk properties of finished catalyst, is beyond the scope of the present paper.

39.   __Drying:-__ Strict control of drying operation in laboratory with small quantity of material can give a reproducible product but it is difficult to attain such control in a large scale operation. In commercial production, actual equipment used and factors like thickness of the material put in the dries, the ratio of the volume of the charge to the volume of the driers, rate of recirculation of air, partial pressure of water vapour in the system, rate of rise of temperature etc. are much different from laboratory practice. So, the operation of commercial units to produce the end product close to that of laboratory can be operated only through a number of trials.

40.   __Grinding:-__ We have already discussed in what way the grinding operation in laboratory and production plant differ. Also we have pointed out how this difference can modify the surface properties of the solid. The energy content[22-24] of a solid state may be expressed as $Es = (\delta a/a \; \eta x)$. On grinding the lattice distortion $\delta a/a$ may increase from 0.05% to 0.91% in case of iron oxide, while lattice defects

μ x increases at the beginning and then decreases. The nature and extent of changes[8,21,25] will depend on the type of equipment and on the time of operation. A typical thermogram of a $Fe_2O_3-Cr_2O_3$ type shift catalyst ground for different time in a ball mill is shown Fig. 7. The splitting up of first endothermic peak amounts to probability of formation of new species; shifting of the second endothermic peak to higher temperature represents delayed dehydration of goethite $(FeO.OH \rightarrow Fe_2O_3)$ and appearance of a new exothermic peak at certain stage of grinding is a phase transformation.

41.   Tabletting:- In laboratory scale this operation is carried out in a hand operated hydraulic press. But in production plants automatic machine which can produce tablets of uniform size and shape and mechanical strength are used. Apart from the performance of the machine uniformity of strength of the tablets depends on particle size distribution nature of lubricant and its mixing with the granules, moisture content, grain strength, compression load etc. In Fig.8 the effect of moisture and grain size on the strength of tablet has been shown. It can be understood that the conditions adopted in laboratory cannot provide any useful guidance in selecting optimum condition for getting uniform product with pre-requisite level of crushing strength. This can only be set after giving a series of trial runs in large scale.

42.   Soaking:- Soaking operation is frequently adopted for incorporating promoters and active ingredients to the semifinished catalyst. The efficiency of soaking operation depends on concentration, impurity level[26] of the solution, temperature, the ratio of the solution to the material and time of soaking. In laboratory operation, the quantity taken for soaking is normally between 100-500 gms, whereas in our production plant the capacity of the soaking basket is 500 Kg On account of this difference in quantity of the solid and soaking solution, quality is likely to change and requires standardisation in large scale operation.

43. <u>Curing</u>:- In catalyst production controlled thermal treatment is necessary at different stages of production either to decompose the salt of the active component of promoter, while in other cases to impart appropriate mechanical strength and for bringing in some new phases.[15,21,27-30] Heat treatment operation in any of the stages has great influence on activity, selectivity and stability of the catalyst. It is not possible to simulate the laboratory conditions in industrial furnace handling material of the order of 1000 to 2000 Kg. per charge. With recirculation of gas in the commercial furnace, which is generally done for attainment of uniformity in temperature the curing atmosphere is laden with gases and vapours formed by decomposition of the salt present in the catalyst. We have seen in case of reformation catalyst that if oxides of nitrogen are present in the recirculation atmosphere and curing operation is long, the material under process is non-uniform in colour, strength and activity. In case of final curing, which imparts mechanical strength, a compromise between time of curing and upper limit of temperature is to be reached, so that the particular phase identified as active is not eliminated and loss of surface area and change in pore size distribution are minimum.

44. In operation of curing furnace the ratio of the volume of the material to be charged to that of the furnace will depend on the amount of the volatile expected from the material under curing and to be ascertained by giving trial runs. For suitable programming of temperature rise particularly when nitrate or carbonate are to be decomposed, it is **recommended that TGA** investigations are carried out first. A composite DTA-TGA apparatus has been developed to study the heat treatment operation.[31] Results of some typical TGA experiments are shown in Fig.9.

45.   It can be concluded that developmental work should start with preparation of samples in prototype of standard equipments employed in commercial manufacture. This will eliminate the wide time gap between the generation of know-how in the laboratory and its implementation for commercial production. No doubt, apparently this will involve higher cost mainly because of higher consumption of raw material in trial formulations of a catalyst, but this will be more than compensated by speedy achievement of the process know-how for commercial production. In fact, most of our know-hows have been generated following this critical path. To cite an example we can mention the development of know-how for autothermal reformation catalyst which went into full commercial production the day generation of know-how was completed. We started the work with reaction tank of 1M diameter and 1M height, steam tray dryer having 500 Kgs. capacity, electrically heated curing furnaces of 2M deep, 1M wide and 0.7M height, ball mill of 0.75M x 0.75M size, extrusion press having 100 Kg/hr. capacity tabletting machine having a capacity of 50 Kg/hr. etc. All these equipments utilized are prototype of the commercial units and therefore, generation of know-how for catalyst formulation and manufacturing process could be completed simultaneously, Following this route this particular catalyst could be manufactured in commercial scale within 18 months of taking up the project.

IV. COMMISSIONING:

46.   It is known to both catalyst manufacturer and users that initial activation step and loading the reactor upto designed level are tricky jobs. There are several instances when catalyst failed due to careless and rapid loading. Similar situation threatening the catalyst life may arise during restart of a plant after long shutdown when the catalyst was kept in isolation in partially or fully oxidised condition.

47.   It can be said that responsibility of catalyst scientists and engineers does n t end in development and production; they must have adequate knowledge about the problems of commissioning and running the commercial catalytic reactors so that the catalyst developed by them can find application. A catalyst supplied to a customer must be accompanied by a commissioning schedule in general comprising of charging, activation and loading with precautions to be taken to safeguard the catalyst life.

48.   Charging:- If the charging of a catalyst is not properly done there may be channeling and the catalyst may not function at its optimum. Charging procedure is comprised of cleaning of the converter internals, checking of the supporting grate, sieving and hand picking of the broken tablets, placement of catalyst avoiding fall of the tablets from a height which may lead to breaking, levelling the catalyst layers, blowing air after boxing up to get rid of the catalyst dust. In case of reformer charging certain additional steps like, pressure drop measurement of each tube is necessary. Also for assuring uniform packing, shaking device should be in operation while charging the catalyst in primary reformer.

49.   Activation:- It is this step which imparts life to the catalyst by bringing into existence the reduced catalytic components in the fine state of division. The activation step is also responsible for bringing in the changes in texture and desired phase composition.[32-35] So, the reduction operation is very critical, and activity and stability both depend on the conditions under which this operation is carried out. In general, it is desirable to carry out the reduction at a very slow rate. But it is not always safe to keep the temperature of the catalyst too low to account for slow reduction rate. It is preferred to fix up the temperature at a point where the rate of reaction is measurable and to keep the level of reducing gas flow low.

50.   A catalyst supplier in general stipulates opening of 5 to 10 mole percent of reducing gas is initial dose. However in most of the plants the reducing gas is admitted by crack opening of the inlet valve. How much gas is going is left to any body's guess. Besides, these problems, the non-availability of sufficient inert gas or steam for maintaining the minimum required linear velocity through the catalyst bed poses additional problem. In view of these uncertainties, we have adopted the practice of sending our specialists to the plant for examining the facilities for reduction operation before entering into committment for supply of catalyst. Yet another problem which catalyst manufacturers are likely to face is the attitude of the users. In a plant shutdowns may be forced due to break down of machines, power failure and other eventualities. The plant authorities are more worried in hastening up the commissioning than anything else. Even when there is real necessity to extend the reduction period beyond what is specified, the plant people are mostly reluctant to agree to it. Such approach may not in every case show adverse effect; but there are also instances where such short-cut procedures have led to catalyst failure forcing long shutdowns. But it is a good sign that there is a change in the trend.

51.   In modern single stream plants there are adequate provisions for metering the small quantities of reducing gas to be dosed for reduction and the plant people try to adhere to the suggestions of the specialists supervising the entire commissioning operation. Provision of adequate supply of inert gas however continues to remain a problem.

52.   Loading:- After completion of reduction the unit has to be loaded up to the design level. This is to be performed in steps and the system should be allowed to stabilise before next increment of feed. The specialists on the job must have the idea about the temperature shock the particular catalyst can withstand without adverse effects, while reco-

mmending increment of the feed in each step.

53.   While commissioning, certain specific problems may arise requiring on the spot decision for suitable action. We are citing here a particular problem we faced while commissioning a primary natural gas reformation catalyst in a plant. The plant employs 4 M^3 catalyst in 60 tubes of 10.5M length each. At plant site there was no provision for synthesis gas and reduction had to be carried out with natural gas. The normal reduction schedule with hydrogen did not work when natural gas was used. After reviewing the whole situation, the specialists on the spot made changes in normal procedure. The condition was made drastic by increasing the pressure and flow of natural gas and the catalyst got reduced. This happened nearly 4 years ago and even to-day that batch of catalyst is at its optimum activity at 100% load. Capacity to assess the problem and taking appropriate on the spot decision for over-coming the problem is possible for those who have matching fundamental back-ground alongwith plant experience.

V.   DEVELOPMENT OF EXPERTISE:

54.   The planning and development division has got a catalyst commissioning group comprising of well experienced scientists and engineers. They have got wide experience to operation of catalytic units and are fully conversant with plant problems. Coupled with these qualities they have acquired thorough knowledge about the fundamentals involved in the process of commissioning. Each and every member of the specialist group performs several investigation to characterise the reduction operation with different catalyst in the central laboratory. Typical experimental results on reducibility of NiO dispersed on Al_2O_3 is shown in Fig. 10. It can be seen that the coprecipitated sample appears to be more resistant to reduction operation. This suggests that if necessary the reduction operation of the coprecipitated batch may be done at higher temperature with greater concentration

of reducing gas without harmful effect on activity and life
of the catalyst. Other typical reduction curves with high
and low temperature shift conversion catalysts are presented
in Fig. 11A and 11B. The curves indicate that at the initial
period, hydrogen is chemisorbed at the reduction temperature
employed. The information helps us in avoiding the danger of
introducing higher concentration f reducing gas on the bas
of hydrogen consumption just at the commencement of reducti
operation.

55.   All these studies are conducted to make our specialist
fully equipped with fundamental background necessary for
successfull commissioning. We believe, without this expertis
the know-how for catalyst development and production will
be meaningless because there will be no outlet of the
product we can manufacture.

56.   In our organisation all new hands are first sent to
commercial units to understand the problems associated with
running of converters. After completion of plant training
they are sent to different catalytic units in the country
using our catalysts to collect plant data and to understand
the behaviour of the catalyst since the date of commissionir
till discharge, and examine the physical and physico-chemica
parameters before and after use. During this period they are
to feed the scientists engaged in fundamental work with
plant data and problems, After completion of this study whic
normally extends for 2 years they are absorbed in research
programme. Almost equal number of staff go for plant study
and discussion with the users. This process works in cyclic
order. In the last two decades this procedure has yielded
sufficient number of specialists having adequate experi-
ence in taking up the full responsibility of commissioning.

VI.   USE:

57.   Fertilizer Catalysts in general are used in such
process steps as, (A) desulphurisation, (B) high and low
temperature shift conversion, (C) primary and secondary

reformation, (D) methanation, (E) synthesis, (F) ammonia oxidation, (G) sulphuric acid.

58.   Of all the catalytic processes the steps leading to ammonia synthesis is considered for the present.

A)   <u>Desulphurisation:-</u>

59.   Sulphur compounds are catalyst poison and desulphurisation of feed stock is invariably a part of catalytic process scheme. Upto 1967, we were concerned with purification of semi-water and coke-oven gas employing alkali scrubbing and dry box purification. From 1953 onward we are using hydrated iron oxides of our own make as substitute of imported bogore and luxmasse.[36-38] Our product CDM-12 is being used in both atmospheric and pressure operating plants.

60.   With change in the feed stock to naphtha very rigorous purification steps are installed due to inclusion of highly sulphur sensitive catalysts in the process. The process employs a hydrodesulphurisation step in presence of either cobalt-molybdenum or nickel-molybdenum catalyst to convert organic sulphur compounds to H_2S followed by ZnO at $350-400^0C$ to retain the H_2S. Considering nonavailability of costly ingrediants in our country we are developing[39] suitable alternative of conventional hydrodesulphurisation catalysts and the formulation at hand is 80% active.

61.   For retention of H_2S our product CDZ-6 finds wide application. The efficiency of ZnO depends to a great extent on particle size and pore geometry. According to us the pores in the region of 300-500 Å are most effective[40]. CDZ-6 can retain its initial activity upto 20% fouling. Our formulation CDZ-7 is used as guard catalyst.

B)   <u>Water Gas Shift Reaction:</u>

(a)   <u>High Temperature:</u>

62.   Carbonmonoxide is a potential source of hydrogen. It reacts with steam ($CO + H_2O \longrightarrow CO_2 + H_2$) in presence of a catalyst. From the time of our appearance in the field in 1951 we had to improve through various investigations,[41-43]

the specific reactivity and stability to cope with the demand of changing process technology for high space velocity, low steam to gas ratio and high operating pressure. At present we are manufacturing 3 types namely CDC-63, 63-A, 63-B and meeting the demand of 18 fertilizer factories in the country and also abroad.

(b) Low Temperature:

63. Whereas in old plants copper liquor and liquid nitrogen wash are used to remove CO from synthesis gas in the new plants purification is effected by methanation.

64. Methanation could be included in the process technology because of L.T.Shift catalyst whose low working temperature permits to bring down the level of CO to 0.2%. This is one of the most sophisticated and critical among catalysts. It is highly sensitive to sulphur and its fall in efficiency due to poisoning or thermal sintering leads to high purge loss. Besides efficient sulphur removal to assure life of this catalyst the question of improving it for greater sulphur resistivity can not be ignored. The improved variety CD-LT-21A which we are manufacturing has the percentage composition Cu-23, ZnO-20, Fe_2O_3-8, Al_2O_3-42 and TiO_2-5. This catalyst is characterised for its high sulphur tolerance and high activity. Fig. 12 shows tolerance of new formulation compared to other proven catalysts.

C) Reformation:

65. The reformation operation is broadly classified into primary and secondary. The primary reformation again is of specific nature for natural gas and liquid hydrocarbon. The family of reformation catalysts is comprised of refractory based NiO systems.[44-46]

66. Primary:- For natural gas reformation we employ CDR-66A. Our first production batch employed in primary reformation at Namrup is in line for nearly 4 years. It's excellent service behaviour has attracted many of its users from within the country and abroad.

67.   The naphtha reformation process had a very long spell in laboratories before it came to be applied in industry. Some of the elementary steps as indicated below show the mechanism through which the reformation takes place as well as liberation of carbon over the contact mass under certain conditions.

1. $CnHm + nH_2O \longrightarrow nCO + (\frac{2n + m}{2}) H_2$

2. $CO + H_2O \longrightarrow CO_2 + H_2$

3. $2CO \longrightarrow CO_2 + C$

4. $CnHm \longrightarrow nC + \frac{m}{2} H_2$

5. $CnHm \longrightarrow Coke.$

68.   The carbon deposition through steps 3, 4 and 5 can lead to increase in pressure drop, change in catalyst function and sometime crumbling of the catalyst.[15,33,46] Even to-day the catalyst in use still have the problem of carbon lay down but a suitable working span could be established by incorporation of alkali and alkaline-earth oxides for accelerating gasification of the deposited carbon[47]. Our line of approach has resulted in formulation of a catalyst which possesses a high degree of selectivity and does not permit liberation of carbon on catalyst surface[33]. In our formulation there is no potash or any other component which will volatilize and force a shutdown by depositing on down stream equipments. Depending on t e quality of feed stock we market two different varieties, namely CIRN-33A and 33B.

69.   Secondary:- Gas from primary reformer is received by the secondary along with calculated volume of air to give required nitrogen content in the synthesis gas. Oxygen reacts with a part of CH_4 and H_2 as -

$(CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O; 2H_2 + O_2 \longrightarrow 2H_2O)$
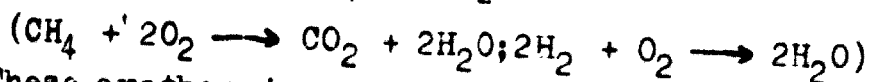
70.   These exothermic reactions results in development of very high temperature particularly at the top of the units and the catalyst in use must have high thermal stability.[29] No

doubt in secondary reformer the conditions are predominently under thermal control[48] but the requirement of very close equilibrium approach to assure low methane content at the exit, brings in the necessity for good catalytic factor as well.

71.   CDR-66B of our make is now in commercial use in various plants and the one in Namrup is running for about 4 years. Customer's choice for this catalyst arise out of its high thermal resistance and low methane leakage. Besides these, for reformation of methane rich gas in one stage, we make the autothermal reformation catalysts containing 2.5, 5.0 and 10.0% Ni to be used in series. These catalysts are in commercial use since 1965.

D)   Methanation:

72.   Exposure of synthesis catalyst even to traces of oxide of carbon for long time causes deactivation. In new plants liquid purification is replaced by methanation. The high throughput per volume of catalyst and the service condition for bringing $CO + CO_2$ from a level of 0.3% to few p.p.m. demands high intrinsic activity. At the same time temperature shock due to surge of $CO+CO_2$ on account of fall in activity of L.T. or trouble in CO_2 scrubbing may upset the temperature So a commercial catalyst must have adequate thermal stability All the qualities combined in our product CDM-15 makes it a successful catalyst.

E)   Synthesis:

73.   Since the time of Haber and Bosch the principal constituent of the catalyst used for ammonia synthesis has been Fe_3O_4 with some promoters. Modern practices of utilising high capacity synthesis converters and lowering of operational pressure made it necessary to increase the activity and thermal stability of the catalyst. Keeping the primary component Fe_3O_4 the same improvements could be effected through altering the sequence of addition of promoters in the melt and changing in the formulation of promoters. The know-how generated for a four promoted catalyst CDS-23 completely meets the present day requirement.

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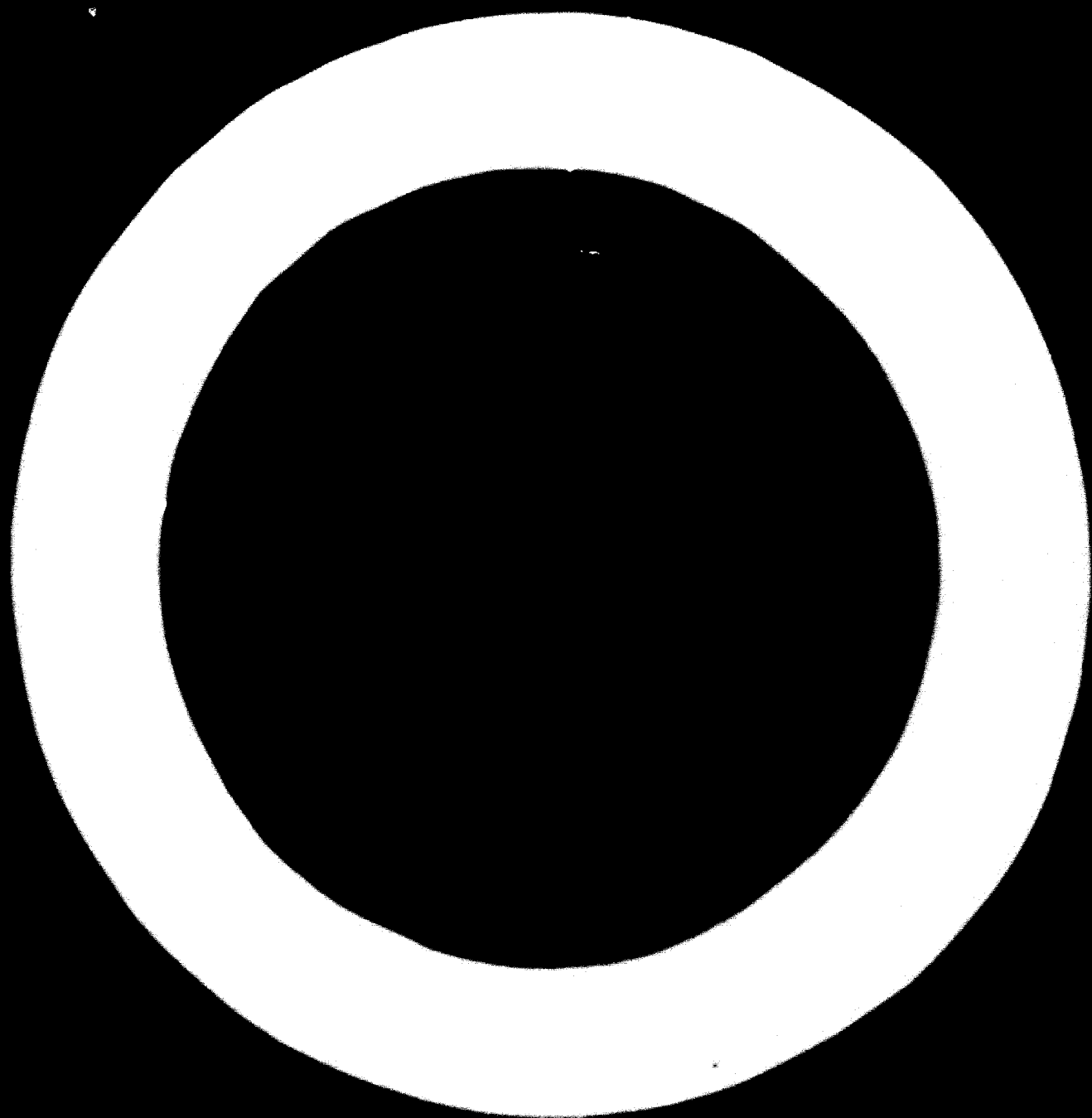
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TABLE - I

Operating Conditions Of Plants Where P.C.I. Catalyst Has Been Supplied

SECONDARY DESULPHURISATION AND GUARD CATALYST

Plants	Process	Feed Rate	Press-ure. (kg/cm^2)	Inlet H_2S. (ppm)	av.bed Temp. C	Outlet H_2S. (ppm)	Cat. vol. (m^3)	Catalyst size (mm)
I.	Secondary desulphuri-sation of Naphtha.	4900 Kg/hr	21.8	3 - 5	350-370	0.5-Max.	4	3 - 5 Spherical balls.
II.	Secondary desulphuri-sation of Naphtha.	1490 "	15.0	5 -10	360-380	0.15-0.2	3.26	3 - 5 Spherical balls.
III.	Secondary desulphuri-sation of Naphtha.	2418 "	14.5	10	350-371	Trace	1.2	3 - 5 Spherical balls.
IV.	Guard for L.T.CO-conversion catalyst.	95000 NM^3/hr.	23.0	0.5	200-250	Traces	9	3 - 5 Spherical balls.

TABLE - II

Operating Condition Of Plants Where I.C.I. Catalyst Has Been Supplied

PRIMARY REFORMATION

Plants	Nature of feed stock	Feed Rate	Steam/Carbon ratio	Press-ure. Kg/cm²	No. of tubes	Temp. °C In/Out	Heat-ed le-ngth. (r)	Press., drop. Kg/cm²	Cat. vol. (m³)	Metha-ne exit. (%)
I.	Naphtha	2418 Kg/hr	6.50	14.5	176	333/880	3.0	2.7	4.0	0.7
II.	Natural gas	2400 NM³/hr	6.50	17.0	60	400/730	10.7	1.7	4.16	7.0
III.	Natural Gas	6800 NM³/hr	3.00	25.0	132	410/800	10.2	2.0	7.0	10.0

TABLE - III

Operating Conditions of Plants Where P.C.I. Catalyst Has Been Supplied

SECONDARY REFORMATION

Plants	Feed Rate NM^3/hr.	Steam/gas Ratio	Press-ure. Kg/cm^2	Temp. °C In /Out	Catalyst volume. (M^3)	Methane Exit. (E)	Catalyst size (mm)
I.	11250	1.30	17.0	733/876	3.30	0.30	9-10 x 15-20 Extrusion.
II.	28100	1.40	23.0	800/960	7.00	0.30	16 x 6 x 16
III.	43000	0.87	28.0	67C/940	14.25	0.28	16 x 6 x 16
IV.	47157	0.70	21.0	810/910	12.70	0.20	16 x 6 x 16
V.	61494	0.75	24.0	774/960	19.40	0.40	16 x 6 x 16
VI.	55795	1.26	30.5	880/976	15.52	0.25	16 x 6 x 16

TABLE IV

Operating Conditions of Plants Where F.C.I.

Catalyst Has Been Supplied

H.T. CO-CONVERSION.

Plants	Dry Gas Rate (NM³/Hr.)	Steam:Gas Ratio	Pressure (kg/cm²)	Inlet Gas Composition(%)				Temperature °C:beds						Catalyst Volume (M³)	CO-leakage(%):beds			Catalyst Size (mm)
				CO	CO₂	H₂	Rest (N₂+A+CH₄)	1st In/Out		2nd In/Out		3rd In/Out			1st	2nd	3rd	
I.	7500	0.80	13.0	27.0	8.6	58.0	6.40	390	420	360	335	-	-	9.1	6.0	3.0	-	10 x 10
II.	13600	0.90	15.0	9.0	11.3	57.7	22.00	400	437	335	350	-	-	24.0	3.0	0.7	-	6 x 6
III.	11000	1.50	16.5	46.0	14.0	37.0	3.00	400	530	395	410	-	-	18.0	7.0	2.6	-	10 x 10
IV.	16000	1.30	28.7	45.9	2.6	50.7	0.80	372	482	404	449	388	399	22.0	14.0	10.0	3.0	10 x 10
V.	41381	0.70	18.0	17.0	8.0	52.5	22.50	380	450	-		-		9.2	3.5	-	-	6 x 6
VI.	17047	1.20	29.5	46.0	4.4	48.7	0.75	395	500	415	470	340	345	30.0	9.0	5.0	3.3	6 x 6
VII.	85570	0.70	23.0	15.0	11.4	51.3	22.20	360	432	-		-		58.0	3.2	-	-	6 x 6
VIII.	64255	0.90	21.0	15.4	10.8	51.7	21.50	400	450	400	420	-		34.4	4.0	2.0	-	6 x 6
IX.	23666	0.90	16.0	11.7	16.2	64.5	7.50	350	470	-		-		12.2	3.0	-	-	6 x 6
X.	45670	0.67	29.5	14.2	10.7	53.0	22.10	360	430	-		-		19.25	3.0	-	-	6 x 6
XI.	86050	0.67	23.5	13.2	12.6	52.1	22.10	360	432	-		-		58.5	3.2	-	-	6 x 6
XII.	80607	0.60	30.2	13.1	8.60	55.4	22.90	360	424	-		-		45.0	3.1	-	-	6 x 6
XIII.	8780	1.40	28.0	43.3	3.6	52.6	0.50	410	520	441	463	-		11.2	3.0	-	-	10 x 10
XIV.	710	2.60	13.5	12.9	14.2	72.5	0.60	371	488	-		-		1.4	0.8	-	-	6 x 6

TABLE - V

Operating Conditions Of Plants Where F.C.I. Catalyst Has Been Supplied

L.T.CO-CONVERSION

Plants	Gas Rate NM3/hr	Steam/gas ratio.	Press-ure. Kg/cm 2	% CO Inlet	Temp. °C In/Out	Catalyst volume (M3)	CO Exit %	Catalyst size (mm)
I.	52400	0.60	18.0	3.56	220/240	16.6	0.20	6 x 6
II.	95385	0.58	21.4	3.20	200/220	53.0	0.29	6 x 6
III.	94520	0.56	21.6	3.10	200/220	53.0	0.30	6 x 6
IV.	1500	1.40	15.9	1.10	232/237	0.7	0.23	6 x 6

TABLE - VI

Operating Conditions Of Plants Where P.C.I. Catalyst Has Been Supplied

METHANATION

Plants	Gas Rate NM^3/hr.	Pressure Kg/cm^2	Inlet CO_2/CO %	Temp. °C In/Out	Catalyst volume (m^3)	Outlet $CO+CO_2$ ppm	Catalyst size (mm)
I.	37500	17.0	0.20/0.20	350/380	7	10	6 x 6
II.	75000	22.5	0.10/0.38	367/402	16	10	6 x 6
III.	73523	27.0	0.10/0.37	316/348	15	10	6 x 6

TABLE VII
TYPICAL OPERATING DATA OF STEAM NAPHTHA REFORMING PILOT PLANT

1. No. of reformer tube = 2
2. Dia. of the tube (o.d x i.d.)(mm) = 107.9 x 90.4
3. Total length of the tube (mm) = 6005.
4. Heated length (mm) = 4267.
5. Volume of the catalyst (litre) = 39.33
6. Size of the catalyst (mm) = 16 x 6 x 16 (ring)
7. Hours of run = 500
8. Operating Pressure (Kg/cm²) = 12.0

Naphtha liq.space velocity Kg/lit.of cat./hour	Steam/Carbon Ratio	Naphtha + Steam inlet temp.(oC)	Reformed gas temperature exit reformer (oC)	Flue Gas temperature exit reformer furnace (oC)	Tube skin temp.(oC) Top	Tube skin temp.(oC) Bottom	Pressure Drop Across the former tube (kg/cm²)	Methane exit (%)
0.60	4.20	470	810	870	870	890	0.42-0.49	1.30
0.68	3.77	475	840	875	870	890	0.42-0.49	1.40
0.72	3.60	470	810	875	865	885	0.35-0.42	1.60
0.77	3.44	470	810	875	866	890	0.35-0.42	1.80
0.80	3.31	465	800	870	870	890	0.35-0.42	2.00
0.85	3.05	450	800	870	870	885	0.35-0.42	2.10
0.85	3.05	450	795	870	875	890	0.35-0.42	2.60
0.85	3.05	450	790	870	875	885	0.35-0.42	2.70
0.90	3.00	450	790	870	875	885	0.35-0.42	2.80

NITROGEN PRODUCTION IN INDIA

CATALYST IN USE

FIG. 1.

C O N T E N T S
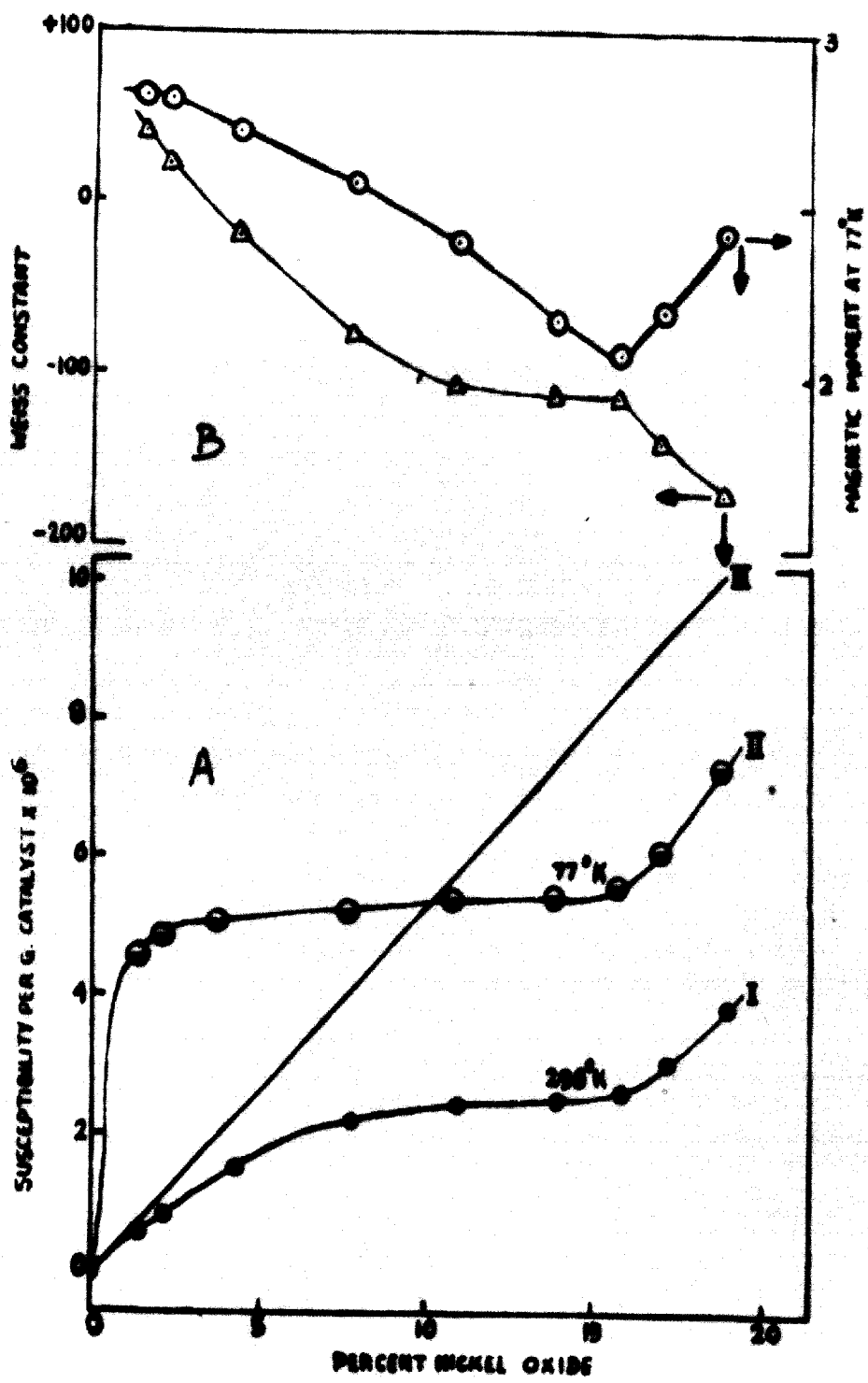
FIG. 3.

FIG. 4. CHANGE IN THE COPPER PARTICLE SIZE WITH CuO CONCENTRATION.

FIG. 5

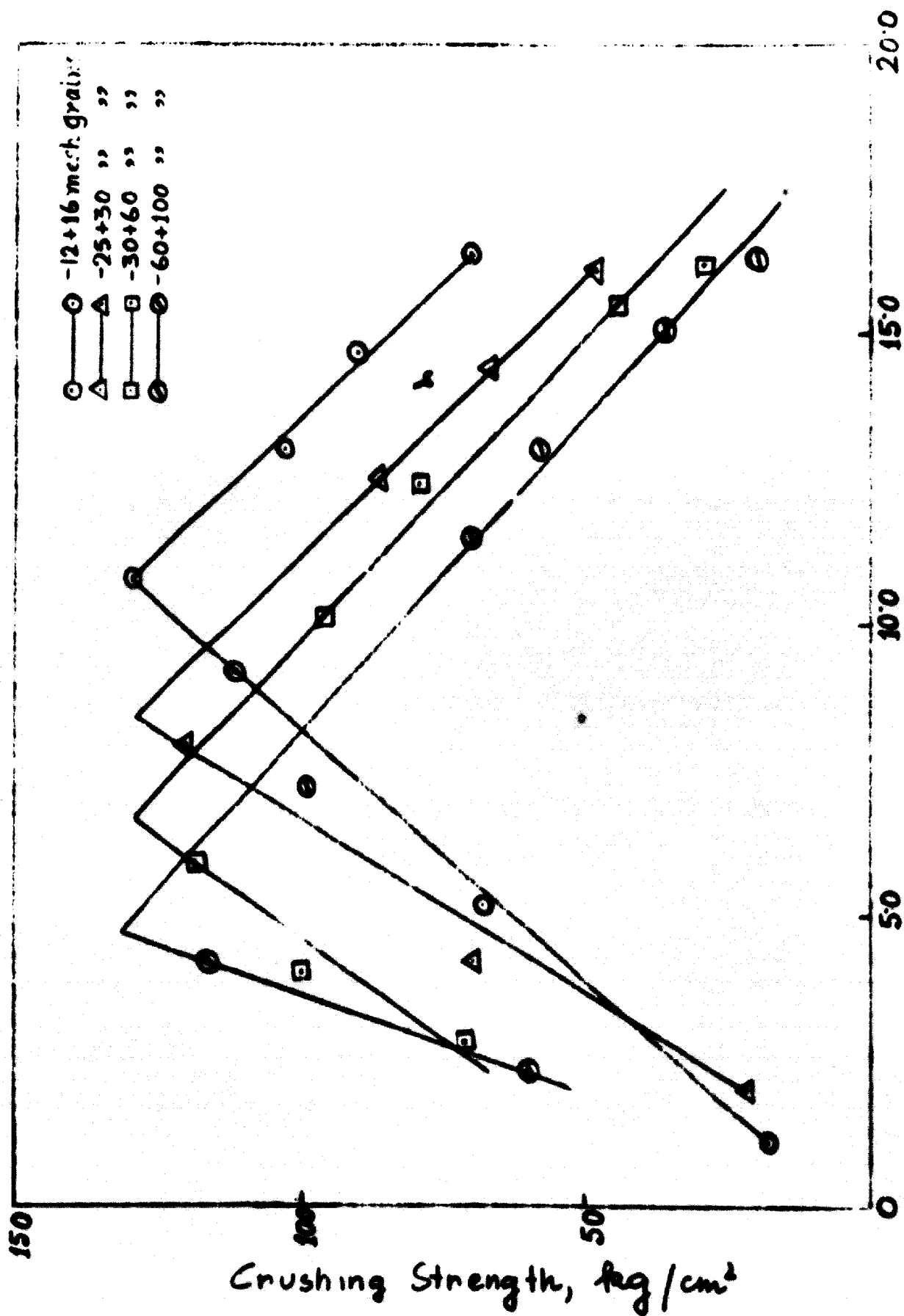FIG.6. TIME IN MTS →
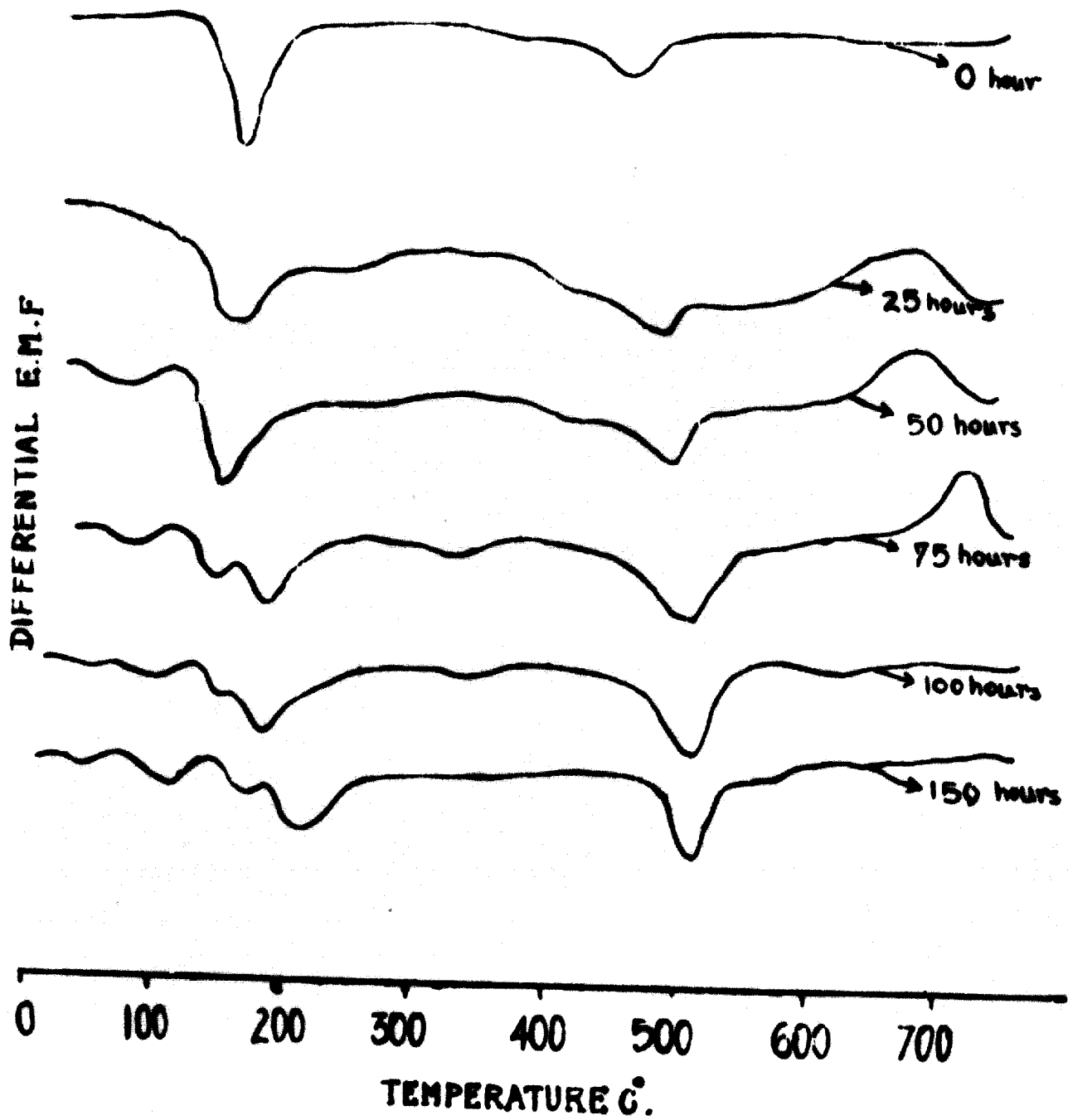
FIG.7. . D.T.A THERMOGRAMS OF $Fe_2O_3-Cr_2O_3$
SAMPLES GROUND FOR DIFFERENT HRS.

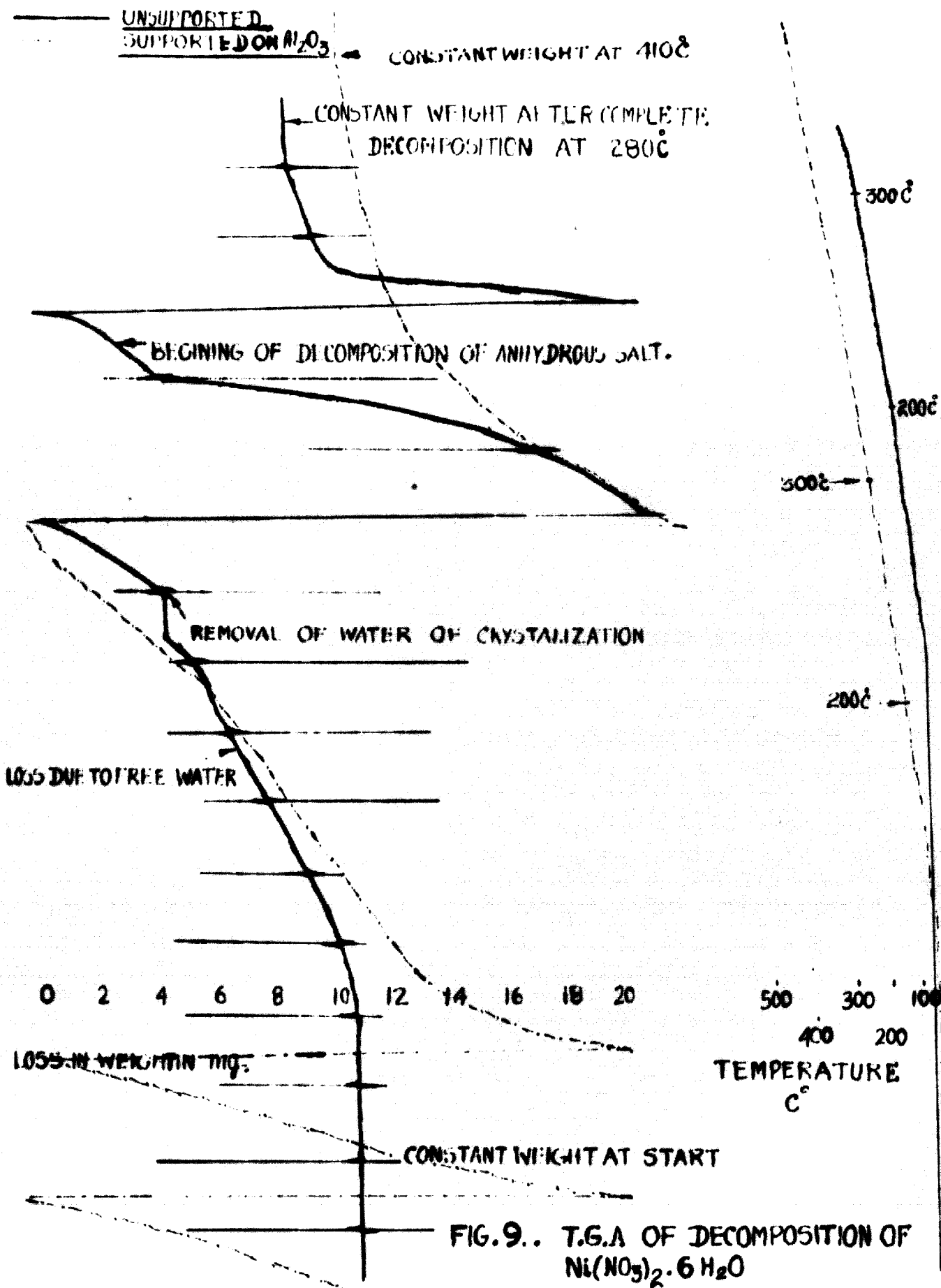Fig-8. Effect Of Moisture And Grain Size
On Tablet Strength
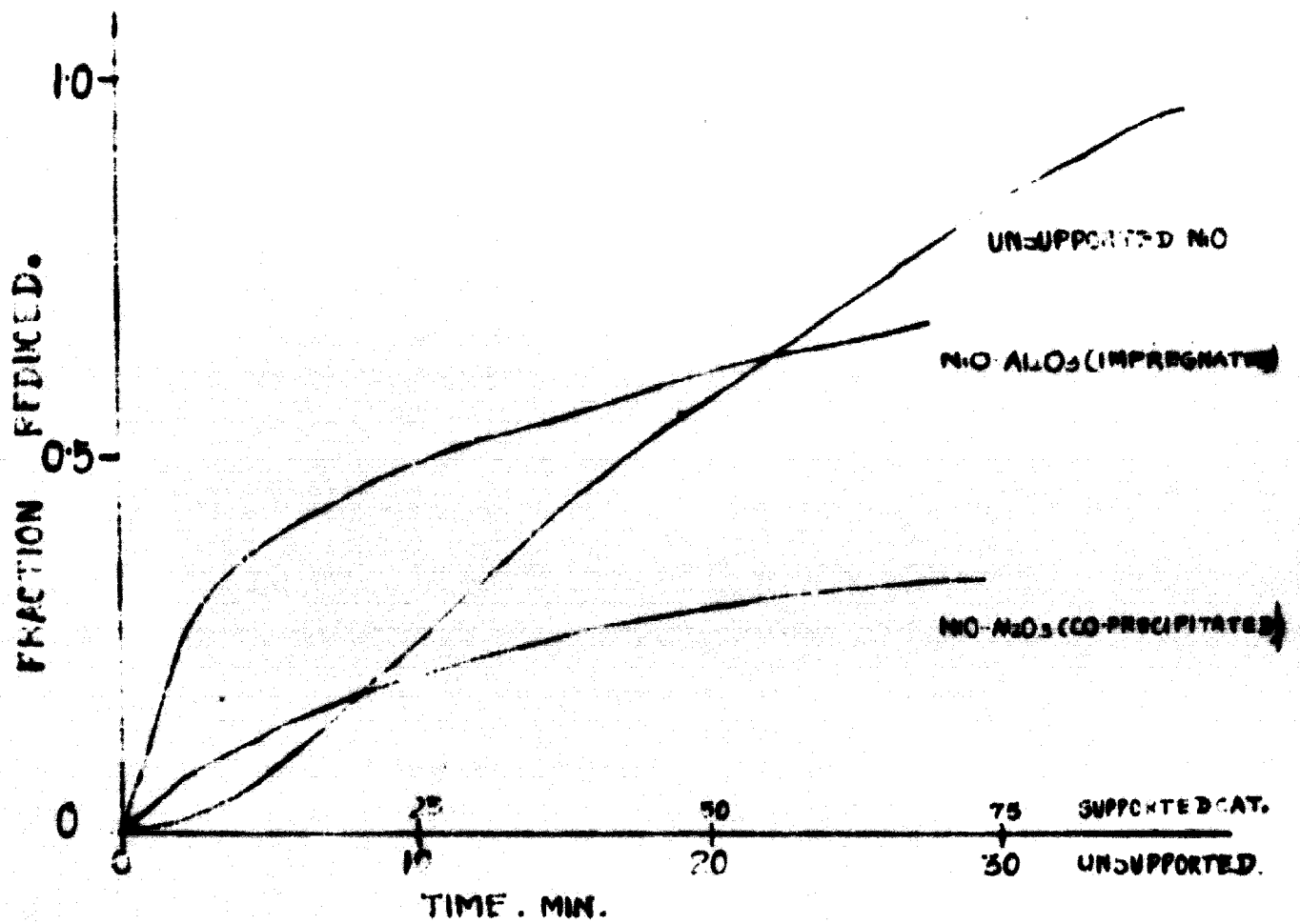
FIG. 9.. T.G.A OF DECOMPOSITION OF
$Ni(NO_3)_2 . 6 H_2O$

FIG. 10. REDUCIBILITY CURVES FOR SUPPORTED AND
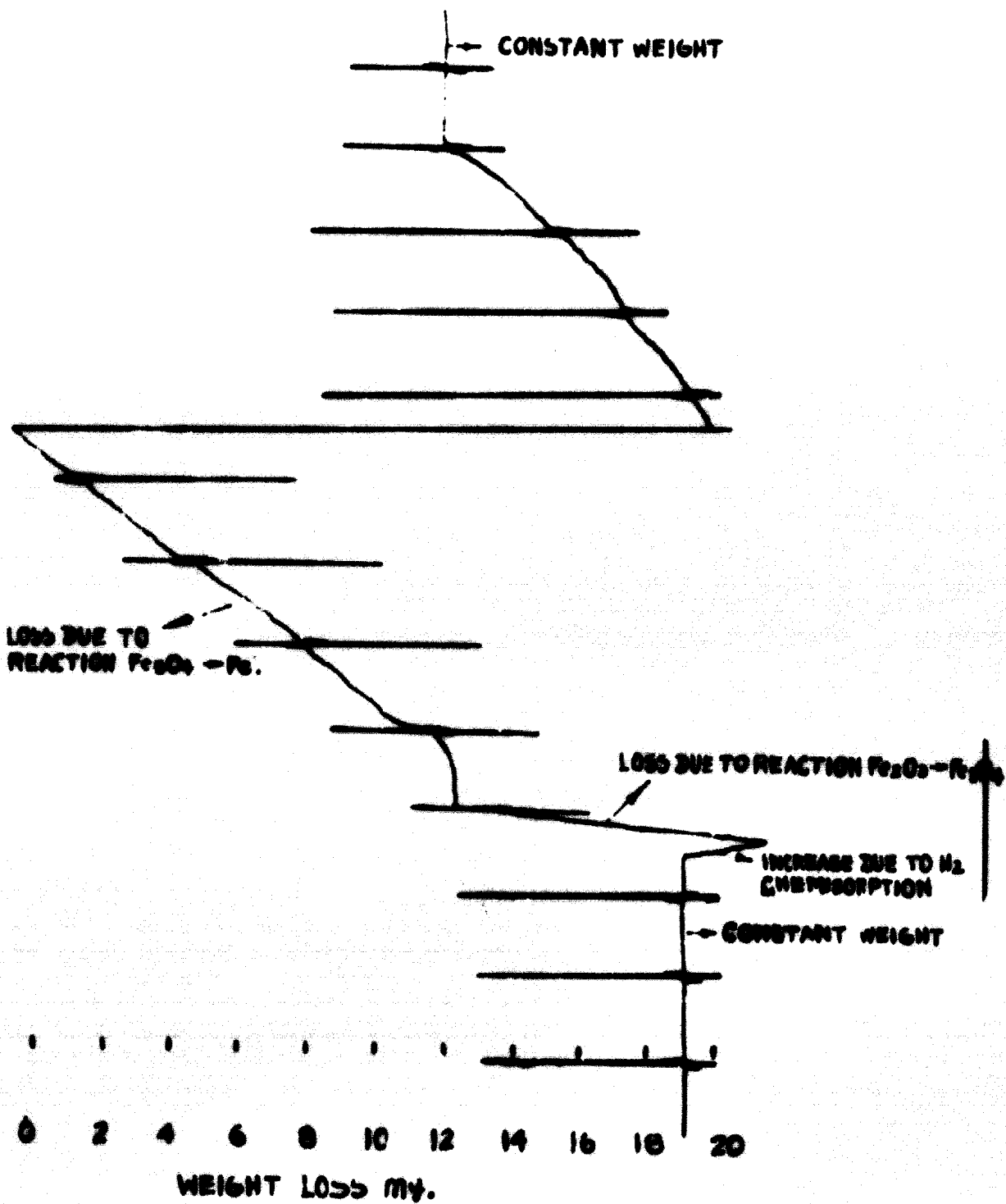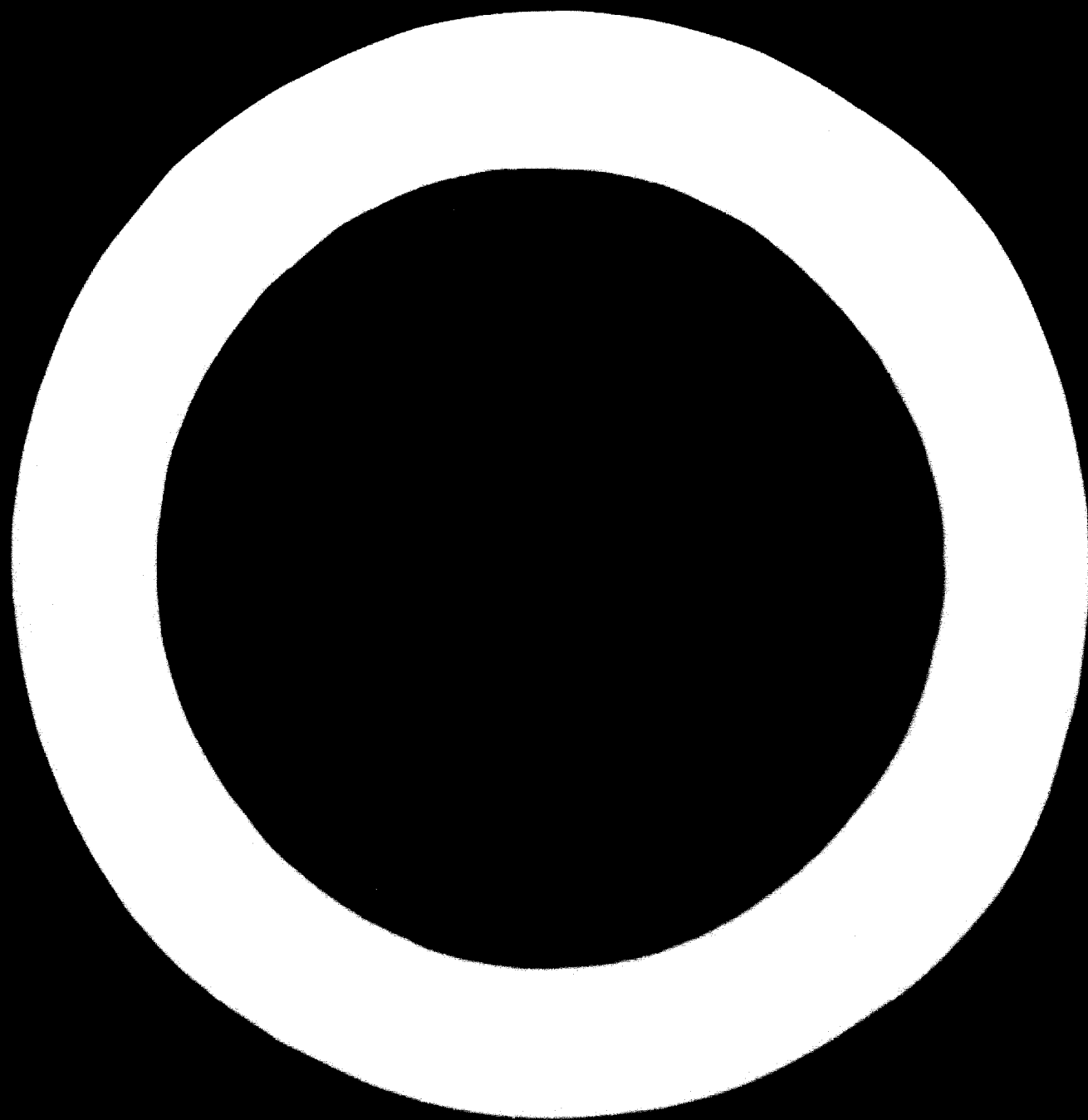UNSUPPORTED NiO AT 400°C UNDER H₂ ATMOSPHERE.

FIG. 11 A. THERMOGRAM OF REDUCTION OF $Fe_2O_3-Cr_2O_3$
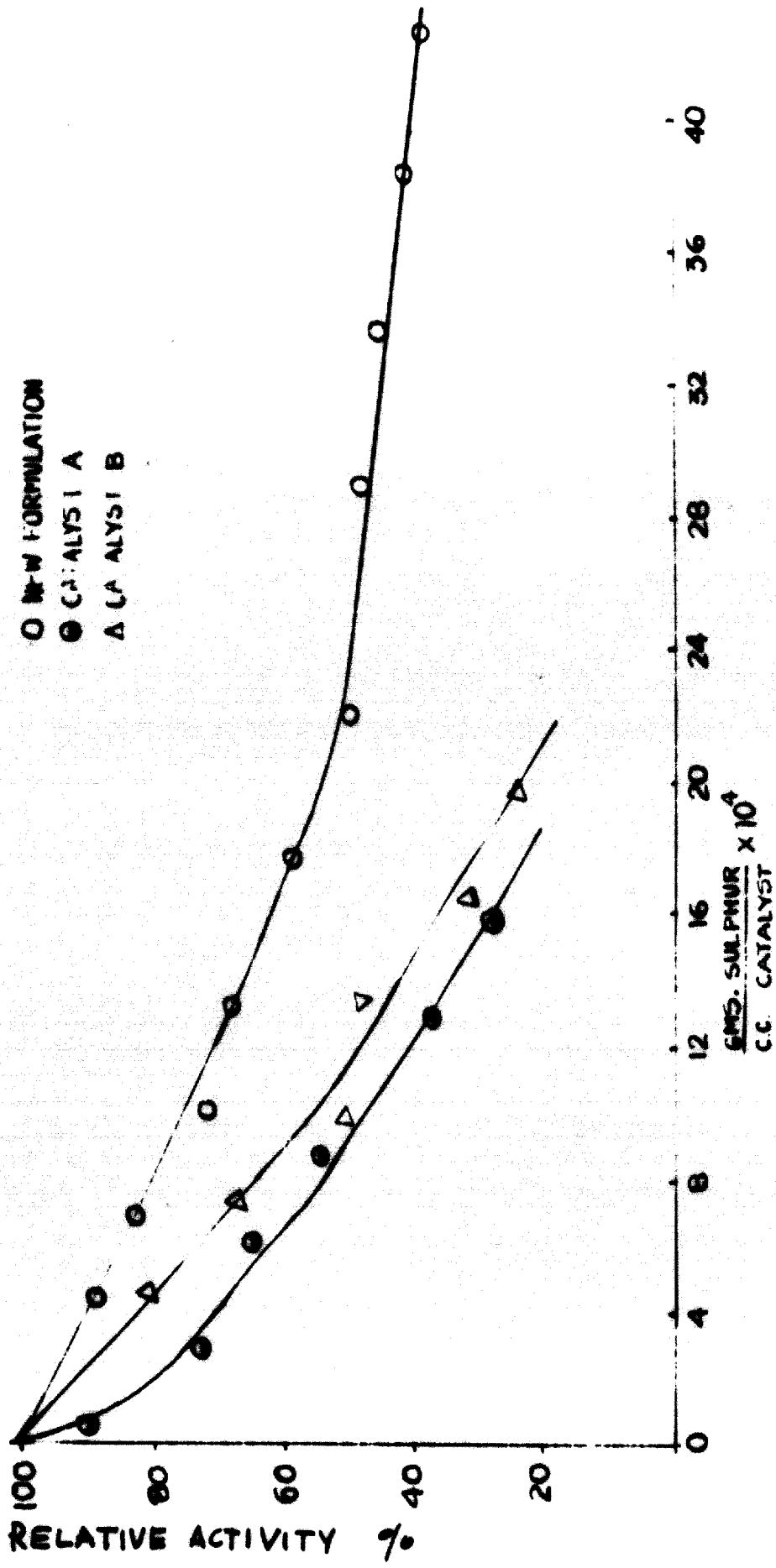CATALYST AT 400°C IN H_2 ATMOSPHERE.

FIG. 48. COMPARISON BETWEEN VARIOUS REDUCTION RATES OF CuO-ZnO CATALYST at 200°C.

FIG.12. SULPHUR POISONING OF L.T. CATALYST.

CO - CONVERSION

CASE I →

DESIGN CONDITIONS
DRY GAS FLOW – 13600 NM³/hr.
INLET S/G – 0.9
GAS COMP – CO–9.07, CO₂–11.3, H₂–57.7, REST – 22.0%
PRESSURE (Kg/cm²) – 15.4
INLET TEMP°C – 400
OUTLET CO% – 2.0
CATALYST VOLUME (m³) – 56

CASE II →

DESIGN CONDITIONS
DRY GAS FLOW – 17047 NM³/hr.
INLET S/G – 1.2
GAS COMP – CO–44.7%, CO₂–4.36, H₂–48.72, REST – 0.75%.
PRESSURE (Kg/cm²) – 29.5, INLET TEMP°C – 335
OUTLET CO% – 3.2, CATALYST VOLUME (M³) – 30

CASE III →

DESIGN CONDITIONS
DRY GAS FLOW – 16500 NM³/hr.
INLET S/G – 1.3
GAS COMP – CO–45.9, CO₂–2.57, H₂–50.7, REST– 0.8%
PRESSURE Kg/cm², – 28.7, INLET TEMP°C – 37
OUTLET CO% – 3.8, CATALYST VOLUME (M3) – 22

TIME ON STREAM, MONTHS

EXIT CO PERCENT

FIG. 13A. PLANT PERFORMANCE OF F.C.I. CATALYST

CO - CONVERSION

DESIGN CONDITIONS
DRY GAS FLOW - 11000 Nm³/hr. INLET S/G - 1·5
GAS COMP - CO - 44·9%, CO₂-14·0%, H₂-37·0% REST -5%?.
PRESSURE (kg/cm²) - 16·5, INLET TEMP°C - 400
OUTLET CO %. - 2·6, CATALYST VOLUME (m³) - 15

CASE IV

DESIGN CONDITIONS
DRY GAS FLOW - 7500 Nm³/hr. INLET S/G - 0·8
GAS COMP - CO - 27·0, CO₂ - 8·6, H₂-58·0, REST - 6·4 %
PRESSURE (kg/cm²) - 13·0, INLET TEMP°C - 400
OUTLET CO % - 3·2
CATALYST VOLUME (m³) - 9·2

CASE V

EXIT CO₂ PERCENT

EXIT CO PERCENT

MONTHS OF RUN

FIG.138. PLANT PERFORMANCE OF F.C.L CATALYST

FIG. 14. PLANT PERFORMANCE OF F.C.I. CATALYST
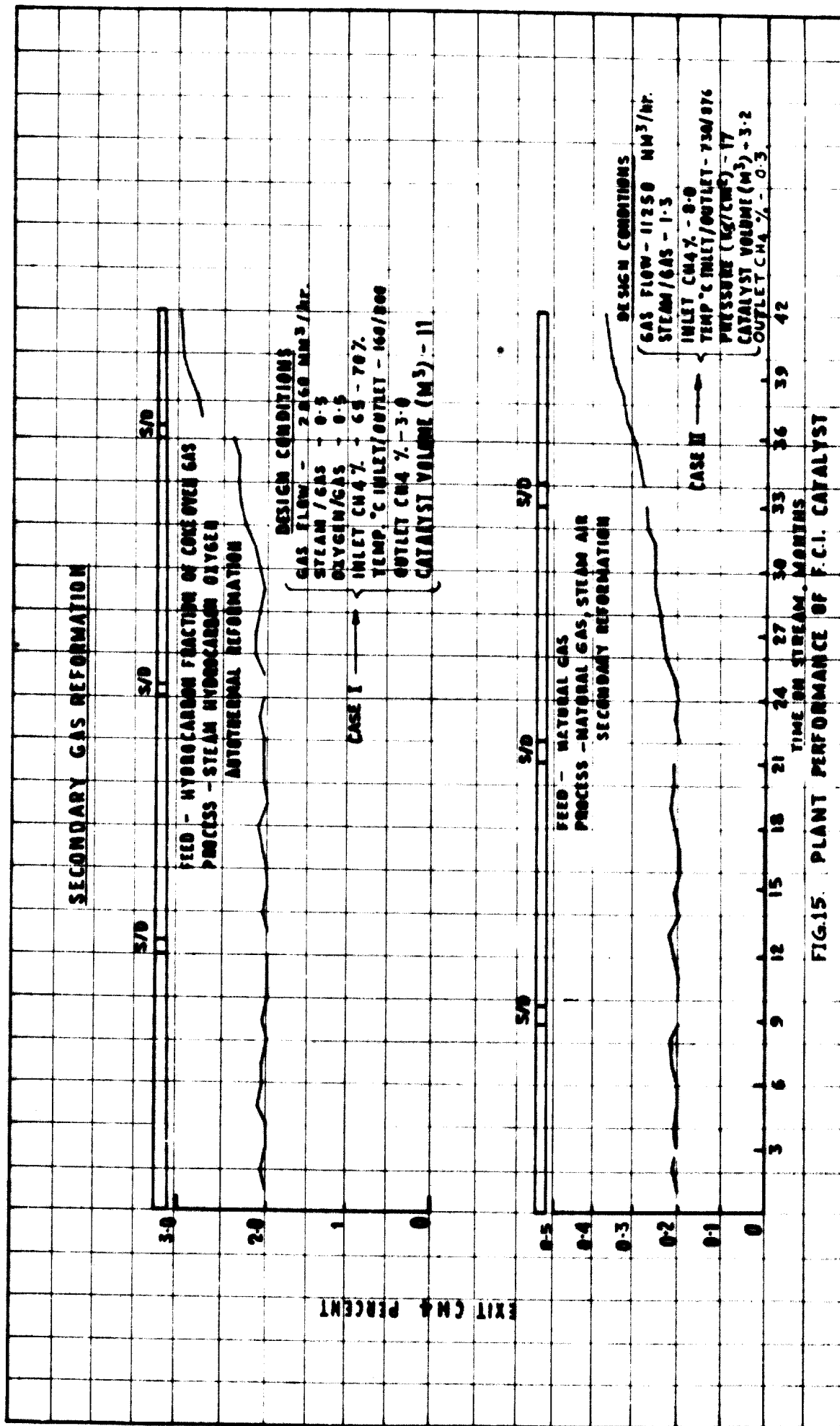
FIG.15. PLANT PERFORMANCE OF F.C.I. CATALYST

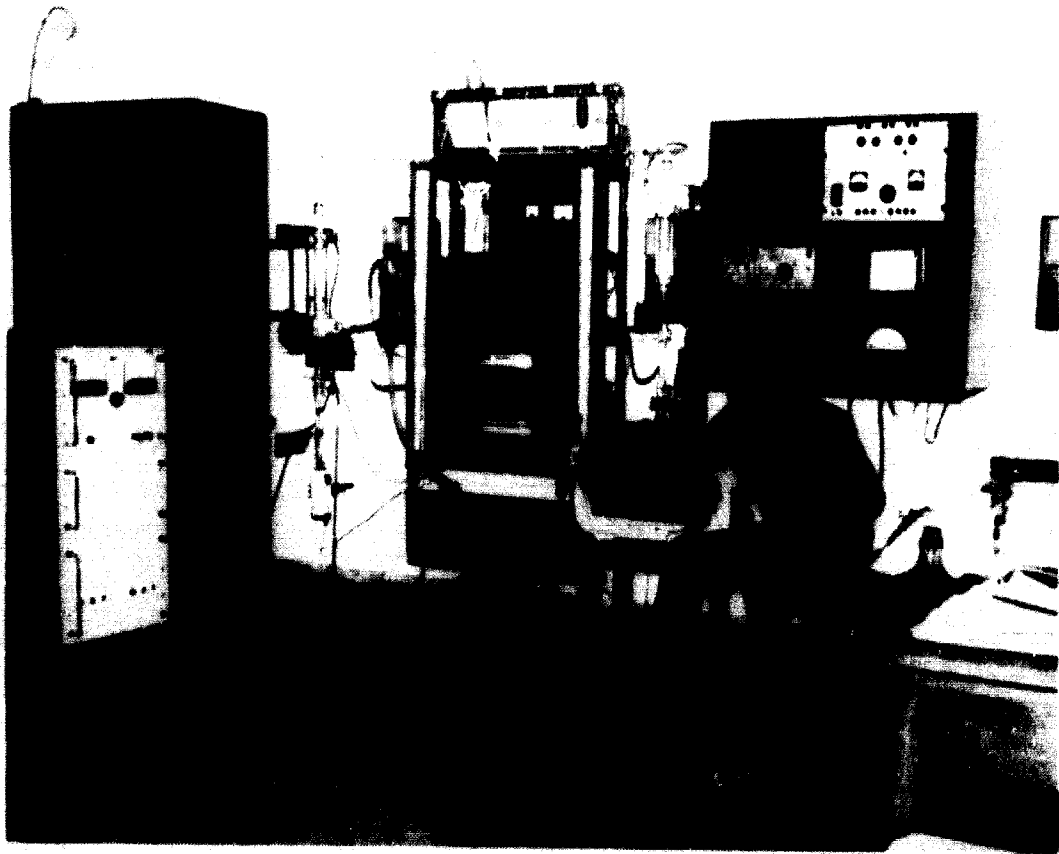Figure: 16: High vacuum laboratories
-one of many-

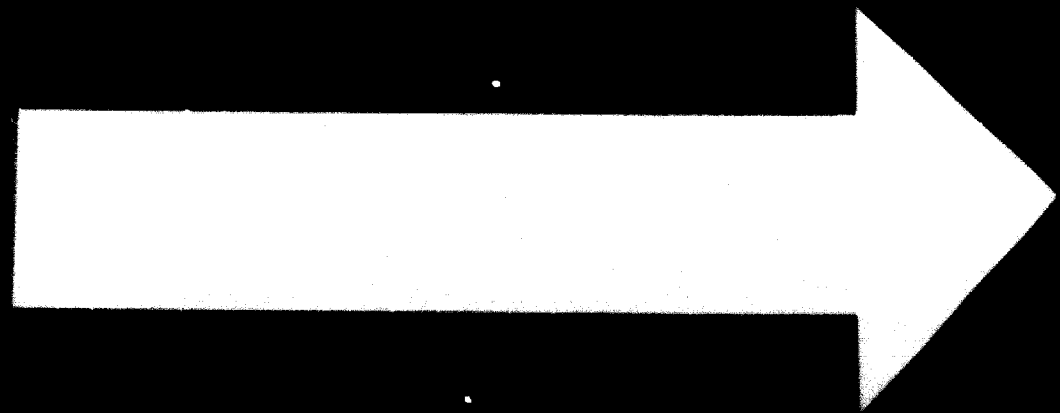Figure 17: Magnetic balance in use
—accelerated test—

IG. 7.   74

I. INTRODUCTION

1.   Over the last few years there has been a spectacular
world wide increase in Ammonia production for intensifying
land productivity. Refinement in process and equipment tech-
nology has kept in step with the increasing demands for
Ammonia. With changing technology, catalysts have also been
improved to secure better on-stream efficiency. In India
production of Nitrogen has shown a steep upward trend, ten-
ding towards 3-4 million tonnes a year by 1975. This will have
an obvious impact on catalyst requirement. In Fig. 1, the
nitrogen production in India and the corresponding figure of
catalyst in use have been shown.

2.   India made its maiden appearance in the field of
fertilizer catalyst in the year 1951. Starting from a scratch
the Planning and Development Division, of F.C.I. is now in
possession of its own generated know-how for production and
utilization of nearly the entire range of fertilizer catalysts.
The development, production and use of the first of its own
series of catalysts is, the typical response of our R&D
Organisation to a crisis which developed when Sindri Ferti-
lizer factory was commissioned. Within a few weeks of the
first trial runs, all the 8 CO-conversion units of our unit at
Sindri, employing 280 tonnes catalyst got de-activated and
plant had to be put out of commission on account of high
CO-leakage. Spare charges were not readily available and
at the same time it was a prestige issue for our government
to get this first state-owned chemical complex firmly on
its feet at the earliest. It was a real crisis for a deve-
loping country as India was in 1951. The nucleus of the
present day P&D Division known as "Technological Department"
rose to the occasion and took up the challenge and developed
a highly sophisticated technique for renovation of the
catalyst. The entire quantity could be regenerated and put
back in line reducing CO-leakage to less than the design
limit.

3.   This single big effort resulted in a direct saving of
Rs.2.8 million in terms of foreign exchange and consequential
prevention of substantial loss in production. This was the
take-off point of our activities in the field of catalyst
development.

4.   In the next 2 years, a break-through was achieved by
developing indigenous know-how for the production of impro-
ved CO-conversion catalyst. In 1953 large scale production of
this catalyst was started in a plant based on our design,
engineering and know-how. The process know-how for the pro-
duction of highly active desulphurization oxide mass as a
substitute for imported bogore and Luxmasse was also generated
as a side line. With the commencement of production of the
oxide mass a target of 400 tonnes per annum could be achieved.

5.   The development indicated above, inspired in the sci-
entists and engineers of this organisation tremendous confi-
dence in their own activities to improvise and to understand
the vital role of catalysts in large chemical plants, and to
realise the risk involved in depending entirely on import of
this commodity from abroad.

6.   Invention of new and improved catalysts has greatly
changed the complexion of fertilizer technology. In 1951 for
CO-conversion catalyst a space velocity of only 500 was consi-
dered safe. In 1957 the operational demand in Sindri's expan-
sion was for a space velocity of 1000 and in modern plants
it is of the order of 4000. Continuous improvement in intrin-
sic activity of the catalyst to cope with this tremendous
increase in space velocity is a real index of advancement of
catalyst technology.

7.   Even at the very early stages it was realised that
unless implements available for fundamental studies are
applied judiciously to have a deep insight of the subject,
it would be difficult to cope with the growing need for
improved varieties of different fertilizer catalysts to keep
pace with the changing process demands. The expertise

generated and fundamental concepts developed during those
early days helped us to conceive of those equipments and
implements which are even to-day considered as modern.
Physical and physico-chemical equipments as will be described
hereinafter came to be applied extensively in our institution
as early as 1960.

8.   One of the primary requirement for creative work in
catalyst technology is knowledge of fundamental sciences
Each catalyst research institution has its own typical appro-
ach to investigations and may have also its own theory of
catalysis. The theory and the fundamental concepts which have
guided most of our activities leading to generation of know-
how in this field is based on the one postulated by
Chakravorty[1,2].

9.   With changes in process technology and adoption of
new processes different catalysts made their appearance in
our country in different phases. We developed the know-how
for each catalyst in such a manner that our own catalyst
could be put to service whenever the imported stock received
along with the particular plant got exhausted.

10.   In this way, we entered the field of pressure CO-
conversion catalyst and autothermal reformation of gaseous
hydrocarbons in 1965. Within another 2 years, we could produce
our own catalyst for primary and secondary reformation
suitable for natural gas. These catalysts were successfully
put to commercial use in 1967. Again in 1969 there was a
break-through when we could put our naphtha reformation cata-
lyst into commercial operation.

11.   The know-how for ammonia synthesis catalyst was genera-
ted in 1965. Almost at the same time our formulations for
low temperature shift and methanation catalysts were employed
for regular commercial production. By 1967 generation of
know-how for other catalysts were complete and in 1969 we
exported the entire range of fertilizer catalysts excepting
ammonia-synthesis. Our concept of application of modern tools
and techniques in physico-chemical studies and approach to

generation of know-now through plant scale studies right from the beginning, resulted in speedy realisation of manufacturing programmes.

12.　　The present day status can be judged from the design data of the plants given in Tables **I-VI**,, and from some typical plant performance data presented in Figs. 13-15, where we have supplied our catalysts. Figures 2 & 3 showing the capacity of the various unit operation can give an idea of our catalyst manufacturing potentiality. In recent years the institute has blended its design and engineering know-how in use of its own catalyst in two large scale plants with rated capacity of 600 T/day Nitrogen designed on the basis of characteristics of our catalyst.

II.　FORMULATION　AND EVALUATION

13.　　A catalyst for its commercial exploitation has to fulfill certain norms, the vital are being its capacity to run at sustained load for the period the supply is guaranteed. The general requirements for an industrial catalyst are: (a) highly developed surface, (b) appropriate size of the pores (c) high mechanical strength, (d) adequate intergranular binding (e) predictable conversion efficiency, and (f) in some cases, selectivity.

14.　　All the above requirements can not be held at optimum because of the opposing factors. For example, the demand for high mechanical strength can be fulfilled[3] only by sacrificing a part of the surface area, and while doing so there may be growth in crystal size of the active component and elimination of favourable pores. These factors in their turn will account for a fall in activity. An efficient catalyst can come out of a suitable compromise between these opposing factors.

15.　　While formulating a new catalyst we always try to manage with indigenous raw materials, The objective is often to find a suitable replacement for the imported constituent, where such complete substitution is difficult, we try to fix a minimum level of the imported component which would

DO

3653

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1.1

1.25

2 8

3 2

3 6
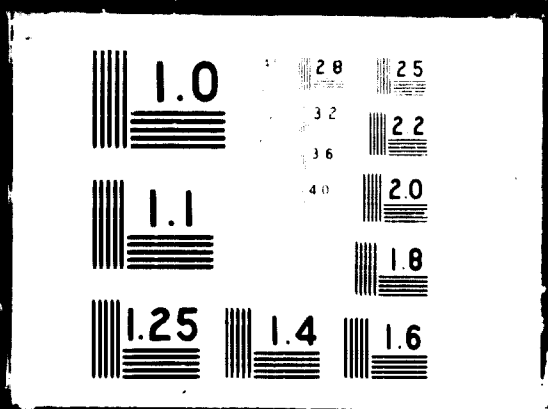
4 0

2 5

2.2

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1.8

1.4

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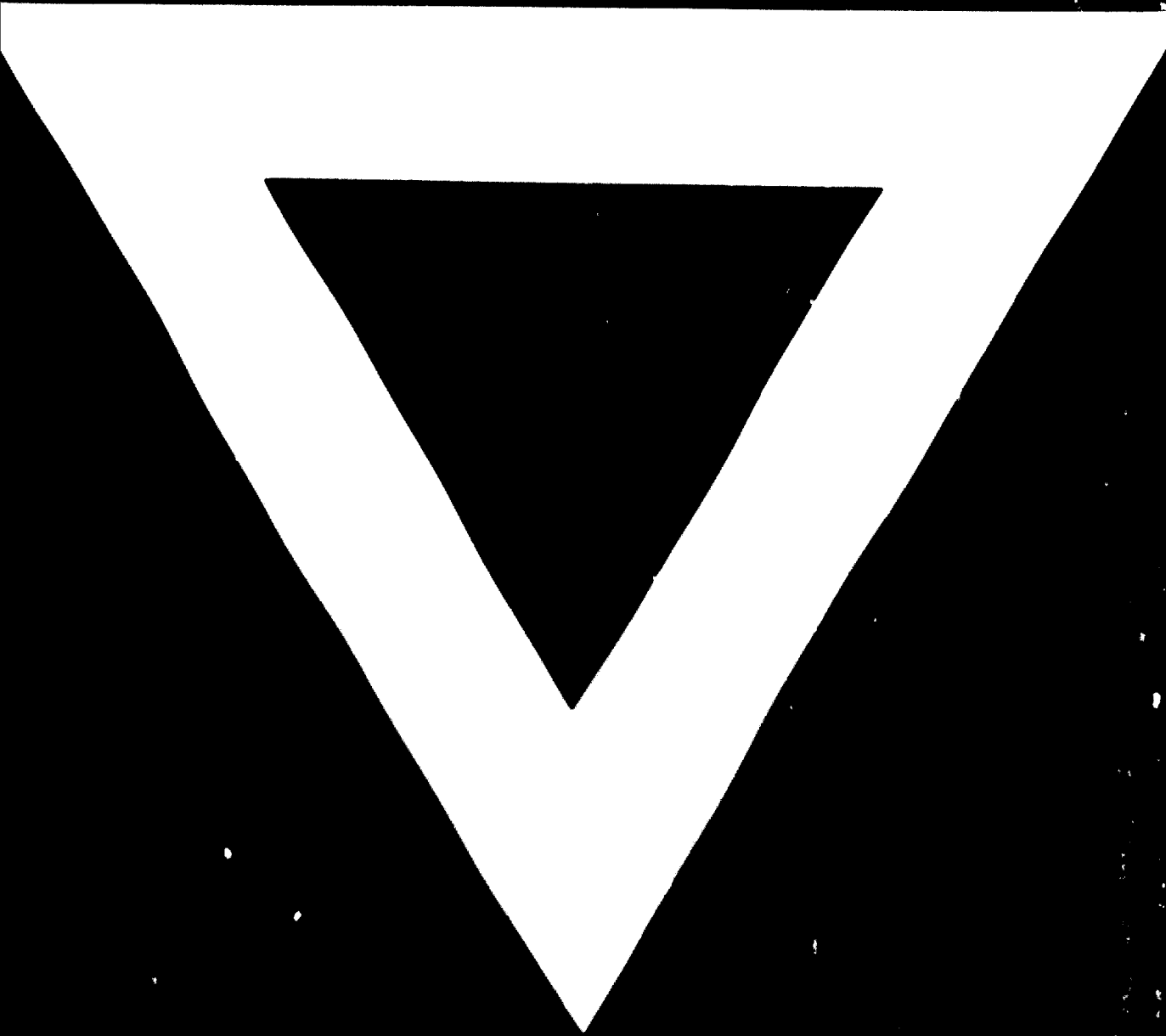Figure 18: Bay of testing units in operation
-L.T. co-conversion-

Figure 19: Bench scale catalyst testing
—extension of facilities—

Figure 20: Pilot plant for catalyst evaluation
—a composite one—

16. 7. 74

16. 7. 74