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CHIMCO CATALYSTS
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RESUME

CHIMCO a commencé la fabrication des catalyseurs en 1980 après de longues recherches scientifiques pour créer nos propres technologies et l'acquisition d'une expérience pratique par l'application dans nos propres unités d'ammoniac. Les catalyseurs CHIMCO pour la conversion de CH₄ et H₂O (CP-02 et CP-03) ont été créés en fonction de besoins en porosité du support, des conditions de procédé, de la résistance mécanique et de l'acidité. On utilise comme support, avec traitement au calcium, du corindon ou un alliage aluminium-magnésium. Dans le premier cas, on réalise la précipitation de NiO avec le stabilisateur, dans le second la coprecipitation complète.

La dernière variante de ce catalyseur BRC (CP-03) a de grandes activités et sélectivités, une faible densité apparente et un long cycle opératoire en raison de la grande résistance mécanique du support de corindon modifié. Le catalyseur CK-03 de CHIMCO à moyenne température est à base d'oxyde ferreux, stimulé par le cuivre, et est fabriqué par une technologie unique avec modification de la valence du métal principal. La caractéristique principale est sa grande résistance pour une acidité généralement élevée pour ce genre de surface spécifique du catalyseur - plus de 90 m²/g, faible température d'entrée - 300-320°C et faible rapport vapeur/gaz 0,3. Il ne contient pratiquement pas de soufre. Son application dans les unités d'ammoniac conduit immédiatement à une augmentation du rendement énergétique.

Pour un catalyseur à basse température, la fabrication repose sur l'idée d'une synthèse du précurseur avec grande dispersion et homogénéité du produit assurant une grande stabilité thermique du principe actif dans des conditions de procédé normales et extrêmes. L'emploi d'une solution cuivre-ammoniac comme agent de précipitation dans des conditions convenables conduit à la formation d'aurihalcitum comme phase dominante du précurseur. Les principales spécifications de cette dernière modification sont - activité et sélectivité élevées à faible température d'entrée - 180-190°C, résistance au poison, stabilité mécanique et thermique.

Le catalyseur de purge fin est fabriqué en deux variantes : classique, fonctionnant à une température d'entrée de 320°C, et à faible température à une température d'entrée de 270°C. La dernière modification est liée à l'augmentation du rendement énergétique de l'unité mais nécessite la reconstruction de celle-ci.



The modern ammonia plants use eight catalytic processes characterized by different combinations of pressures, but mainly of temperatures, and these processes determine to a great extent the ammonia production energy efficiency.

Three are catalytic processes that have the most significant influence on the economic efficiency:

- The steam conversion of the natural gas;
- The two-stage shift conversion of CO with water vapour;
- The fine CO and CO₂ removal from the synthesis gas by methanation.

The steam quantity limitation for the ammonia plants could be achieved by decreasing the steam/carbon ratio, but this requires, first of all, a specific quality of the steam conversion catalysts for the natural gas and CO conversion - i.e. high catalytic activity, providing industrially acceptable conversion and selectivity for the relevant reaction, that prevents the formation of by-products. The influence of the last is expressed not only in the decreased main product, but also in the aggravation of the catalyst operation. The precipitation of carbon on the primary reformer catalyst influences not only the conversion rate, but also the life-cycle of the active pipes. The Fisher-Tropsch reactions including hydrogen consumption increase the production costs.

With many other ammonia plants which have exhausted all the possible means for process reconstructions, or such reconstructions are not economically proven under the existing conditions, the application of highly active shift catalysts is the unique possibility for achieving of significant natural gas and energy savings respectively, and that with limited investments.

This is the main reason for the companies to direct their investigation activities towards developing catalysts, operating within lower temperature range and limiting the steam/carbon ratio.

CHIMCO, on the basis of its thirty years production experience in its own ammonia plants and its investigation activities, created highly active, thermally stable and poison resistant catalysts, primarily for the mentioned above main catalytic processes, the discussion of which is the subject of the present report.

PRIMARY REFORMER CATALYSTS

The primary reformer is the first stage of synthesis gas production, which is also the basic and the most expensive equipment in the majority of the current operating plants.

The specific conditions of the reaction of natural gas conversion with water vapour- increased pressure, high temperatures of about 800-850°C, high process endothermality and relatively low reaction rate, determine the primary reformer plant construction. The primary reformer is modeled as an aggregate of a lot of pipes with relatively small diameter and big length, providing maximum geometrical surface for the heat transfer and for the conversion course at the desired rate, determined by the process conditions.

The low steam/ carbon ratio at high temperatures, typical for the primary reformer, could result in carbon precipitation on the catalyst and decreasing of its activity. The reaction course is retained due to its reduced temperature consumption, as the wall temperature of the pipes increases, strongly decreasing their life-cycle. The pipes could be completely blocked under heavier process conditions.

The desired natural gas conversion rate at the lowest possible pipes wall temperature, the lowest resistance and lowest possible steam/carbon ration is determined by the main catalysts characteristics- activity, thermal stability, selectivity, poison resistance, and mechanical strength.

CHIMCO produces two types of catalysts for natural gas conversion- CP-02 and CP-03. Normally, the active component for those catalysts is nickel, applied on suitably modified, hard meltable support or homogenous co-deposited with highly-meltable oxides or modifying agents.

The technical data for catalysts CP-02 and CP-03 are presented in Figure 1.

The CP-02 catalyst is produced by co-depositing of ingredients and has the following chemical composition:

NiO- 18%wt.; Al₂O₃- 62% wt.; MgO- 20% wt.

After the catalyst heat treatment, the support is magnesium aluminate with fine homogeneously dispersed nickel oxide, nickel after the reduction respectively. The magnesium oxide is completely bonded with the aluminium oxide.

The catalyst reduction is implemented after the catalyst charging in the pipes, by feeding of steam and natural gas. Small quantities of hydrogen by heat decomposition of the raw material are obtained in the hot part of the pipe, which provokes the beginning of the reduction. The produced hydrogen increases further more the reduction rate to the top of the pipes. The presence of sulphur compound hydrogenerator in most of the plants, in which the hydrogen is fed, is a sufficient condition for the reduction of the catalyst together with the temperature increase in the reactor at the course of the gas within the plant.

The CP-03 catalyst is on corundum support, modified by calcium compounds. The application of the active component nickel is achieved with a soluble nickel salt, and by homogenous precipitation with the stabilizer in a suitable homogenous organic reagent. The unreacted homogenous precipitant at the next heat treatment is completely decomposed with the emission of carbon dioxide and water.

As can be seen in Figure 1, the modification CP-02 is intended for softer operating conditions - lower temperature, lower volume rate and higher steam/carbon ratio, that in most cases are typical for the plants producing ammonia synthesis gas. CP-03 is particularly suitable for methanol plants mainly due to the high thermal resistance.

The influence of the conventional nickel catalysts poison, sulphur, is equal for both catalyst modifications and depends mainly on the temperature. The allowable sulphur content in the outlet raw material at a temperature up to 850°C is 3-5 mg/m³ and 0.5-3 mg/m³ at 750°C.

The catalysts are ring-shaped with different sizes, determined by the specific operating conditions typical for the plant- inlet and outlet temperature, steam/carbon ratio and allowable resistance.

HIGH-TEMPERATURE SHIFT CONVERSION CATALYST

The reaction for carbon monoxide conversion with water vapour is used to transform the carbon monoxide into carbon dioxide. This is applied in order to obtain increased carbon content in the synthesis gas and improved plant performance. Two-stage CO conversion is used in the conventional ammonia plants. The basic conversion on iron catalyst takes place at a temperature of 340-450°C in the first stage. The second stage decreases the carbon oxide content to 0.3-0.5% vol.

The active group of the high temperature catalysts is magnetite Fe_3O_4 which is promoted by chrome oxide.

The continuous exploitation of this type of catalyst has shown some disadvantages. Under more severe reduction conditions with increased content of reducing components- hydrogen and carbon oxide, the magnetite could be reduced to iron oxide or elementary iron.

The reduction of magnetite results in the catalyst crystal changes and destruction of the original geometrical form. The metal iron catalyzes the Fisher-Tropsch hydrocarbons synthesis process. The total result of this undesirable process, most repeatedly appearing during plant start-up operations at low gas/carbon ratio, is the destruction of the catalyst and plant productivity reduction as a consequence of the hydrogen consumption for side reactions. The modification of the conventional ferrous-nickel catalyst with copper eliminates the above mentioned disadvantage. The copper inclusion in the catalyst composition prevents the Fisher Tropsch synthesis and any reduction possibilities.

The technical data of Chimco copper-modified catalyst are given in Figure 2.

Figure 3 shows the change of the temperatures of CK-03 and conventional ferrous-nickel catalyst over the time in Kellogg production plant with 960 tpd ammonia capacity.

CK-03 shows higher stability, as it remains highly active for a long lasting period at significantly lower inlet temperature of 300-330°C, compared to the non-promoted catalysts.

Both catalysts data are compared for a period of 12 months from the initial start-up at equal plant capacities.

The relatively low space velocity in the production reactor defines the character of the correlation of the temperature change at catalyst inlet and outlet and the residual content of carbon monoxide on the time, as shown in Figure 4.

Considering both figures one finds decreased activity over the first 2 to 4 months. That fact could be explained by the initial crystals agglomeration of the most active component (copper). After this period it a catalyst stabilization and stable activity is established for a long time.

Figure 5 shows the same dependence established in a reactor with doubled space velocity for a period of 36 months.

The lower temperature level of CK-03 catalyst improves the operation of carbon monoxide two-stage conversion. The reduced content of it in the gas downstream the reactor allows the low-temperature catalyst inlet temperature to decrease and its life cycle to be indirectly increased.

Figure 6 shows the decrease of the low-temperature catalyst inlet temperature from 218°C to 203°C after implementing of the catalyst CK-03 in operation. As a consequence of this temperature decrease, the CO residual content at low-temperature catalyst outlet decreases from 0.22% vol. to 0.15% vol. The reduction of the carbon monoxide content is significant in the big production units with a capacity of more than 1000 tpd of ammonia, having in mind that the change of the carbon monoxide by 0.1% vol. changes the plant performance by 10 tpd.

Figure 7 shows the qualitative characteristic of the two-stage conversion with conventional ferrous-chrome catalyst and CK-03 catalyst.

CK-03 catalyst is produced by original technology, guaranteeing complete absence of sulphur. That allows direct implementation of the low-temperature catalyst in operation, as the sulphur removal operation, that is

obligatory for the ferrous-chrome catalysts, is eliminated. Depending on the specific conditions, the natural gas and energy savings for the initial start-up could reach 70% of the catalyst cost.

In some cases, there is another more radical solution for the main problems with the ferrous-chrome catalysts utilization, than the discussed hereabove. Such a solution could be the usage of a catalyst operating in the high-temperature stage without iron or chrome.

CK-11 CHIMCO catalyst is based on cuprous oxide promoted and stabilized with oxides of transitional and non-transitional metals.

It operates at inlet temperatures of 220-350°C, space velocity of 3000h⁻¹ and steam/gas ratio of 0.6.

The catalyst provides residual content of monoxide of 0.3-0.5%, at carbon monoxide content in the inlet gas of 12-15% and under the above mentioned process conditions.

Depending on the process conditions and the specific plant, the catalyst CK-11 has the following potential advantages:

- Increased steam production in the main boiler downstream the secondary reformer plant;
- More than doubled life-cycle of the low-temperature catalyst;
- Complete blockage of Fisher-Tropsch hydrocarbon synthesis.

The last advantage is particularly important for the usage of purge gases from the ammonia synthesis plant for krypton, xenon and argon production through cryogenic separation.

LOW-TEMPERATURE SHIFT CONVERSION CATALYST

The creation of the low-temperature shift conversion catalysts in 1960s allowed simplifying of the synthesis gas plant, eliminating the expensive process of copper-ammonia removal of CO and the implementation of a new catalytic process - CO and CO₂ methanation as the last stage of gas production.

The best advantage of the low-temperature catalysts is that they reduce the residual CO content to a level, at which its reciprocal conversion to methane is economically beneficial and technically possible.

Over the last years, the low-temperature catalysts producers have perfected to a great extent the production technology, and along with the increased activity of the catalyst, they improved its thermal and mechanical strength and the poison stability and resistance. Thanks to that fact the catalyst life-cycle has been extended from 1 year at the beginning to more than 5 years with our up-to-date catalysts.

The technical data of the latest CHIMCO low-temperature catalyst modification, called CK-22 are presented in Figure 8.

The catalyst has the traditional chemical composition of CuO, ZnO, Al₂O₃. The very strict requirements towards that catalyst are achieved through high dispersity of the active component (copper) which provides its activity at low temperature and stabilization of the same temperature, which mainly determines the thermal resistance.

The technology is based on simultaneous co-sedimentation of the three ingredients of the oxide system. As a sedimental reagent is used one of the ingredients of the system (the copper in the form of copper-ammonia solution).

The process conditions determine the formation of precursor with phase composition, in which the phase of the aurihalcite (Cu Zn₅ /CO₃/2 /OH/6) prevails. The correlation of the quantity of the phase and the activity, and mainly the thermal stability, respectively the catalyst life-cycle under equal process conditions was experimentally established. The zinc oxide appears to be not only an absorbent of the sulphur but also a stabilizer of the cuprous crystals, preventing their agglomeration.

CK-22 catalyst operates in a temperature range of 180°C to 260°C. The lower limit of the temperature range is determined by the pressure and the steam/gas ratio, and in any case it initial process conditions should be selected in such a way as to prevent the condensation of water vapour on the catalyst.

The upper limit of the temperature range is determined by the capabilities of the specific plant.

As the catalyst does not undergo any changes in the course of the catalytic reaction, theoretically the operation period is not limited. However, in reality, most industrial catalysts change their mechanical and catalytic properties as a result of different physical and chemical processes.

The physical processes are connected with the mechanical destruction and caking, phenomena leading to increased hydraulic resistance.

The chemical processes are related with changes of the chemical nature of the catalyst surface. The reduction of the catalytic activity is a result of the interaction of the catalyst with the reaction environment or of the absorption upon the surface of stable compounds, contained in the reaction mixture or lateral reactions products.

These two processes lead to changes of the surface chemical nature - reduction of the active centers number, and the activity respectively.

The conversion catalysts, based on copper, are very sensitive, even at low concentrations to sulphur and chlorine which are always present in the gas.

The possible sources of gas contamination with sulphuric compounds are as follows:

- The hydrocarbonic raw-material - the sulphur content in the utilized hydrocarbons could be reduced, using the known methods, to less than 0.2 ppm and at low-temperature converter inlet to less than 0.05 ppm.
- The fresh high-temperature catalysts (containing sulphur) are another source for catalyst poisoning. The sulphur content in them is approximately 0.05-0.1 weight %. Due to that reason the fresh high-temperature catalysts are treated through desulphurization to obtain approximately 0.2 ppm S in the synthesis gas.

The sources of synthesis gas contamination with chlorine compounds are as follows:

- The chemically treated water;
- The air to the secondary reformer;
- The hydrocarbons;
- The compressor oil.

CHIMCO has developed a modification called CK-30, as a protective layer for the low-temperature catalysts under conditions of chlorine presence in the gas.

The catalyst CK-22 contains ZnO as a free phase. That's why it is self-protected against the sulphur poisonous effect.

Apart from sulphur and chlorine, the processing possibility for water vapor condensation can also influence the exploitation cycle of the catalyst.

Figures 9 and 10 show the industrial data about the effect of the method of catalyst inlet gas cooling - indirect and direct. The condensation of water vapor upon the catalyst, especially when start-up operations are carried out, has a considerable effect on the activity.

The minimum life-cycle of CK-22 is 4 years.

CATALYST FOR FINE CO AND CO₂ REMOVAL FROM THE SYNTHESIS GAS USING METHANATION

The fine CO and CO₂ removal from the hydrogen-containing gases can be done by using catalysts or by physical methods. With the old schemes such kind of removal is done by absorption with copper-ammonia solution or by flush with liquid nitrogen. In the contemporary plants the recovery of hydro-nitrogen mixture is based on the tubular conversion of hydrocarbons, the low-temperature conversion of CO and the absorption of CO₂. The concentration of CO and CO₂, downstream the low-temperature conversion of CO and CO₂ removal from the gas, is of such rate that the complete removal it is most appropriate to be done by using the process of methanation.

CHIMCO developed several technologies for the production of catalysts for methanation - CM-01, CM-02, CM-03, considering the contemporary requirements concerning these catalysts. The catalyst CM-01 operates within the temperature interval of 350-450°C and its technical characteristics is given in Figure 11. The other two modifications are low-temperature and operate with inlet temperature of 280-290°C.

The process of methanation is carried out at 280-350°C in an adiabatic duty with a considerable excess of hydrogen (73-74%) which is valid for the production of synthesis gas for ammonia, comparatively dry gas blend (1-2% H₂O) and pressure of 2.0-4.0 MPa.

Before operation, the catalyst is reduced, which causes nickel oxide conversion into metal nickel. The reduction passes quickly, practically at the same time with the heating of the methanator and proceeds not more than 6-8 hours. Process gas is used for the reduction. The process starts at about 200°C and ends at 380-400°C, usually at operating pressure and space velocity of 3000-5000 h⁻¹.

Because of the fact that in a reduced state the catalyst is pyrophoric, it is necessary that it be stabilized by controlled oxidation before its taking out of the reactor.

As far as the process of methanation is carried out after the low-temperature conversion of CO, the gas is completely cleared of sulphur and chlorine, which are poisonous for the nickel catalysts. That is why the most probable poisons for the catalyst are the compounds which could be contained in the gas after the separation for CO₂ removal. These are:

- K₂CO₃, which blocks the surface (the pores)
- As₂O₃ in the Giamarco-Vetrokoke system.

Only MEA and Rectisol system does not generate danger of poisoning the methanation catalyst.

The catalyst CM-02 and CM-03 (Nickel-aluminium) are characterized with improved strength and thermal stability (600-650°C), improved mechanical properties and poison resistance.

The minimum life-cycle of the modified CM-01 is 5 years, modified CM-02 and CM-03 - 7 years.

Figure 12 shows the correlation of the residual content of CO and CO₂ on the time for modification CM-01.

TECHNICAL DATA of Catalyst CP- 02 and CP- 03

Indices	CP- 02	CP- 03
Chemical content	homogeneous	of carrier NiO with promoters
NiO, %	18	7- 11
Bulk weight, kg/l	0,75- 1,1	0,75- 1,1
Form	rings	rings
Rings dimension D x d x h, mm	16 x 8 x 12 16 x 8 x 10 20 x 8 x 8	15 x 7 x 12 15 x 7 x 10 16 x 8 x 12 16 x 8 x 10 18 x 8 x 12 18 x 9 x 16
Compressive strength, axial, kg/cm ² radial, kg	> 320 > 20	800 > 45
Specific surface, m ² /g		> 27
Operating temperature, °C	650- 900	600- 1100
Pressure, MPa	up to 4,5	up to 4,5
Volume velocity, h ⁻¹	up to 1500	3000
Steam/ gas ratio	2,5 - 4,0	> 2,0

Figure 2

TECHNICAL CHARACTERISTIC OF CK- 03

Chemical content:

The high shift temperature catalysts is iron chromic catalyst with the following chemical content:

- FeO₃ - 87% wt.
- Cr₂O₃ - 10% wt.
- CuO - 3% wt.
- Sulphur - absence

The high catalytical activity of NBTK is due to the suitable physical-chemical content and structure of the catalyst.

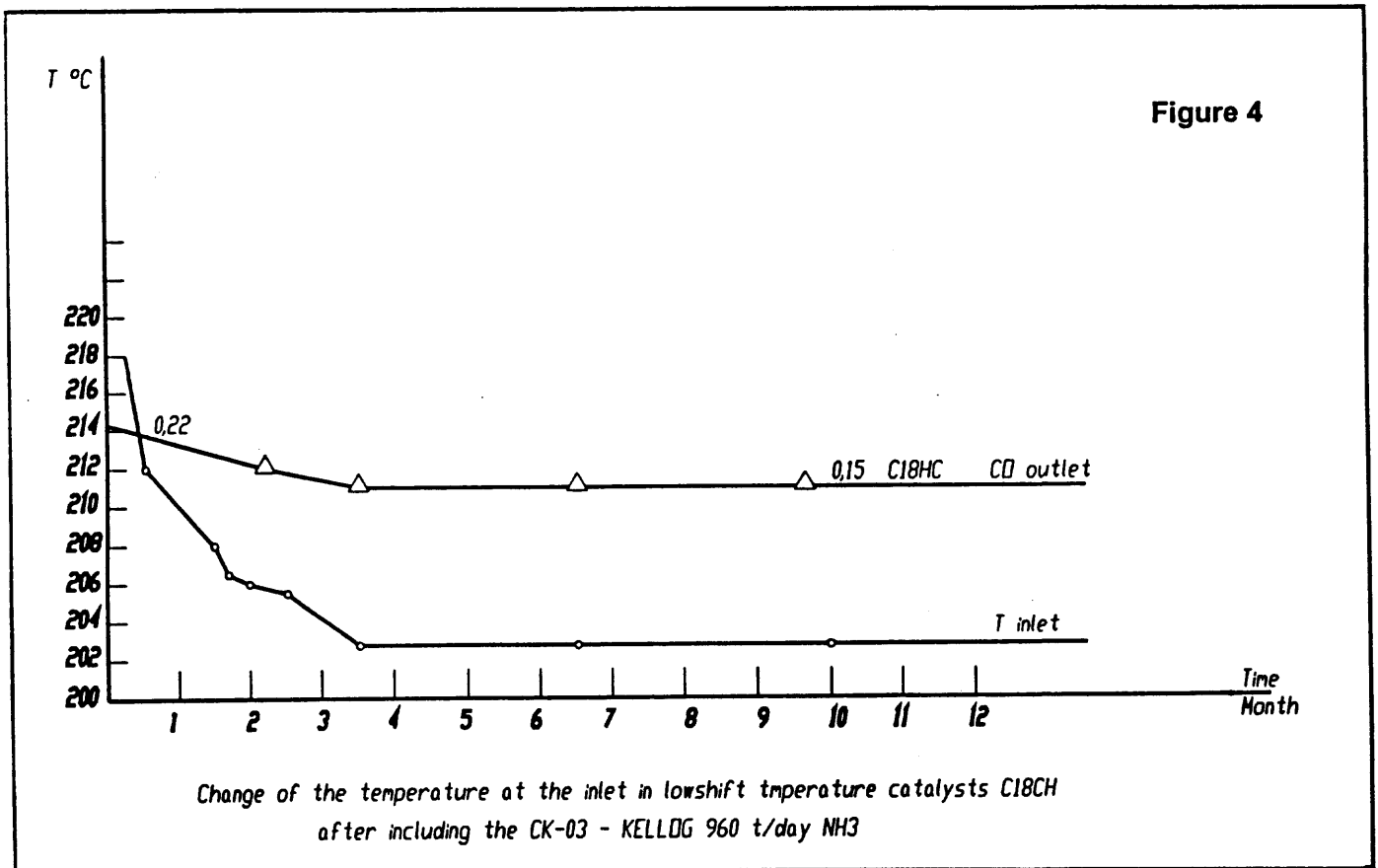
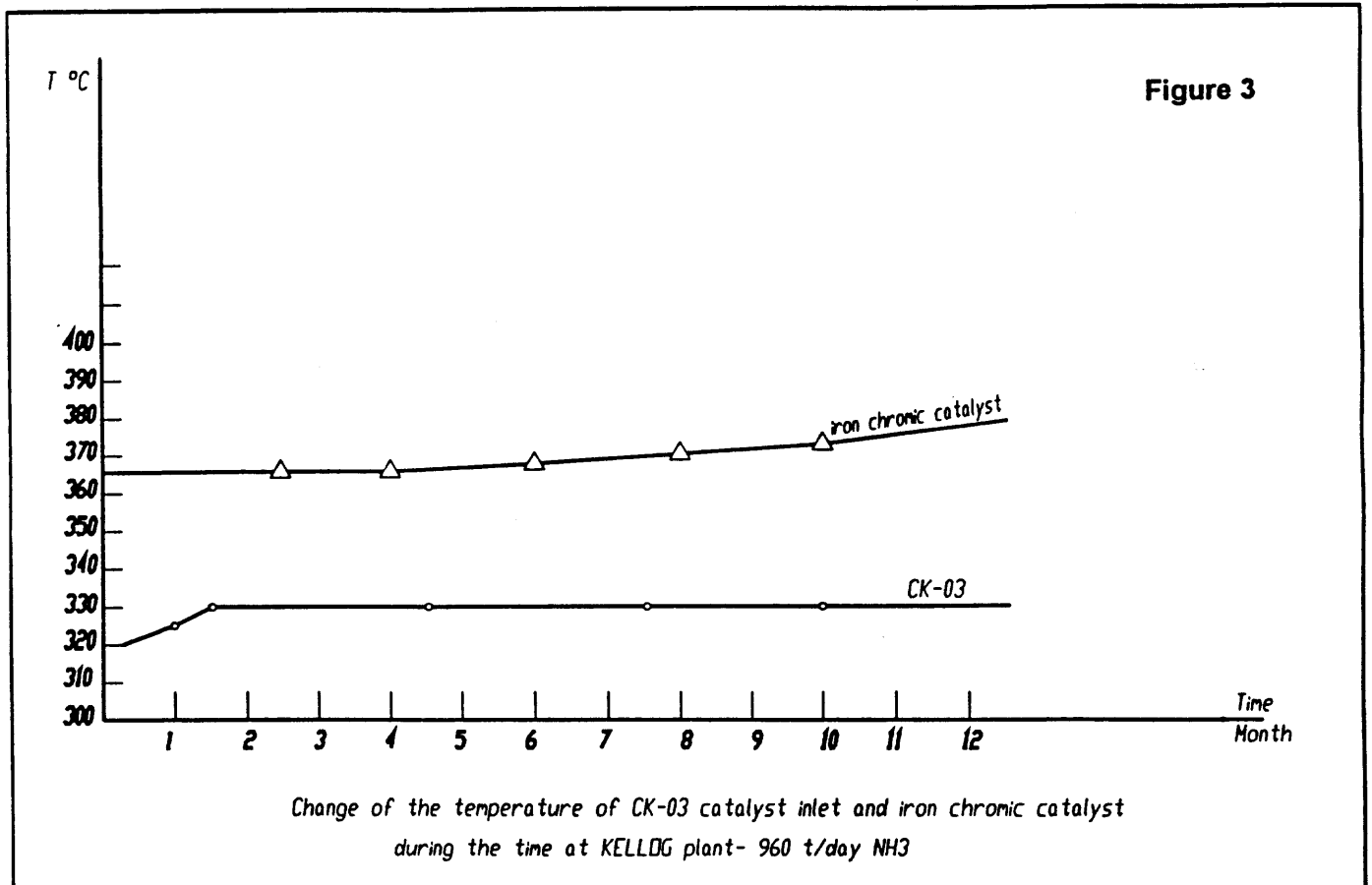
Physical- mechanical indications:

1. Bulk weight, kg/l - 1,2
2. Specific surface, m²/g - not less than 80
3. Mechanical strenght axial not less than 150 kg/cm²
4. Form- cylindrical tablets
5. Dimensions- in mm
 - diameter - 6,8 and 10 mm
 - height - 3, 4, 5, 6, 7, 8, 10 mm

Operating conditions:

1. Operating temperature, °C 300- 480
2. Operating pressure, kg/cm² - up to 50
3. Volume velocity, hour - up to 10000
4. Steam/ gas ratio - 0,3- 1,0
5. Gas content

- H₂ - 56% vol.
- CO - up to 10% vol
- CO₂ - up to 22%, vol



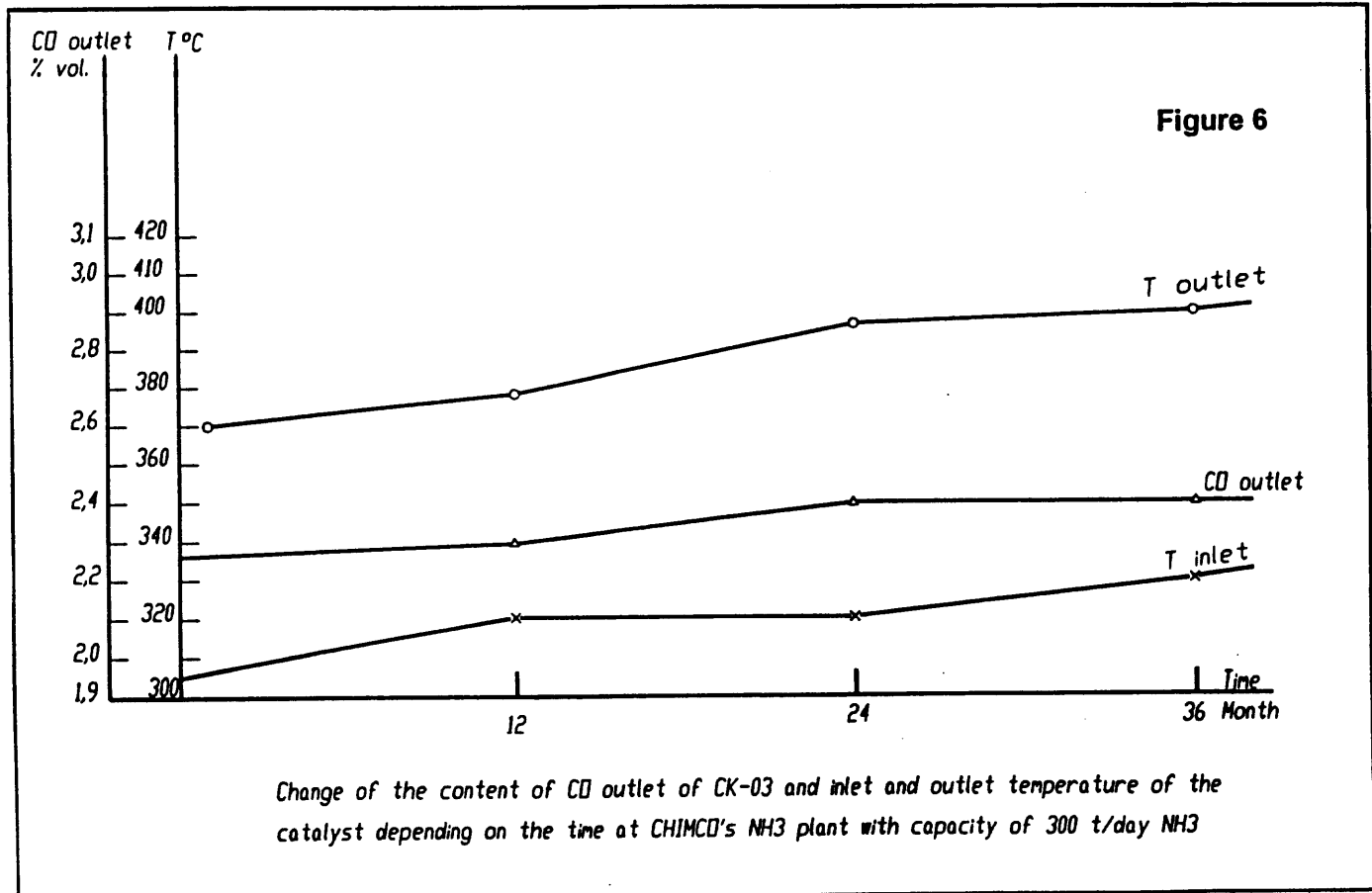
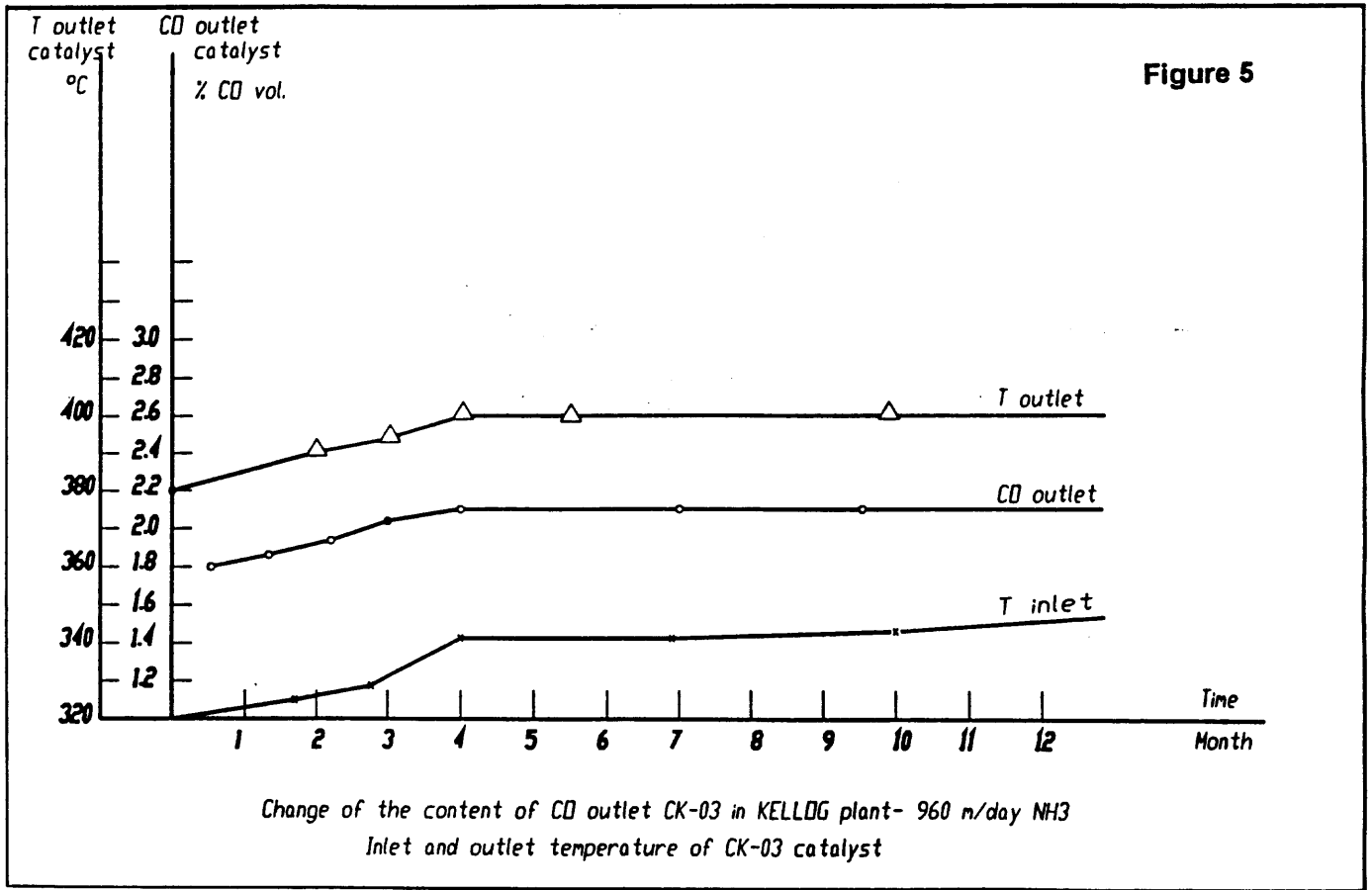


Figure 7

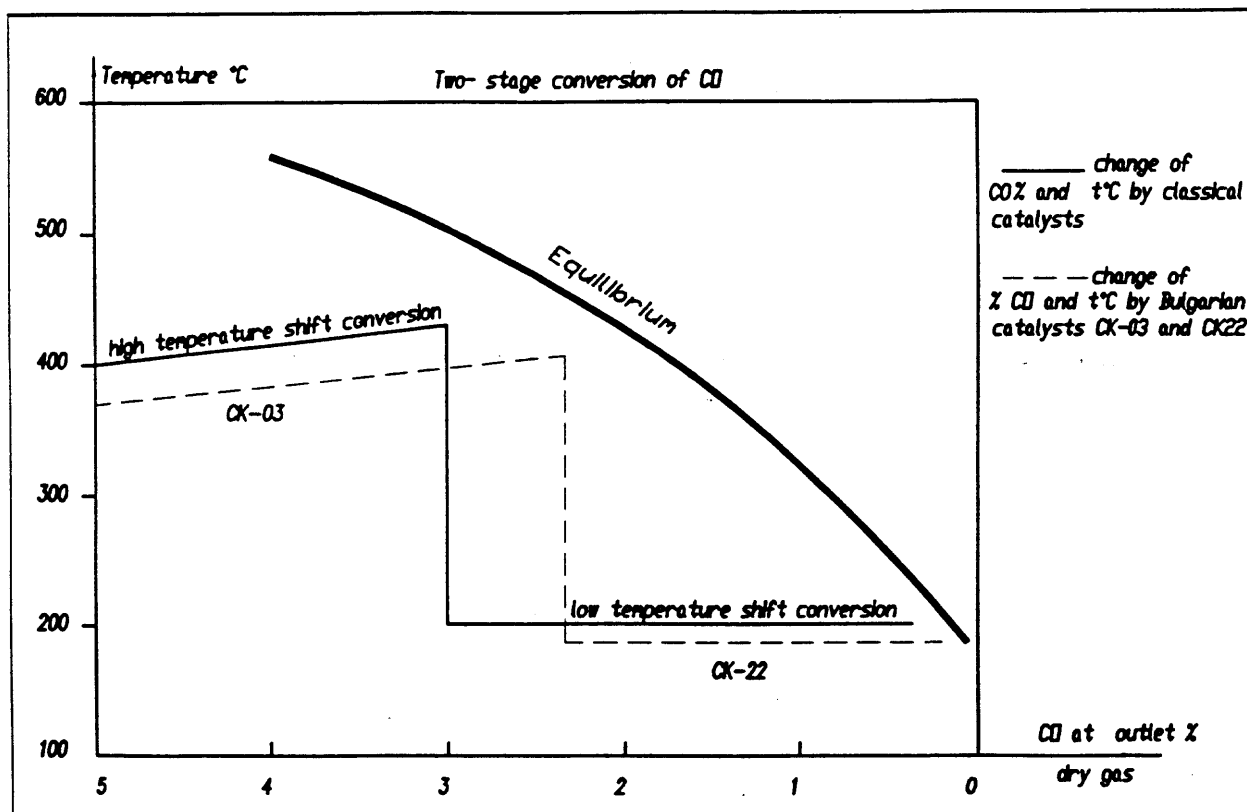


Figure 8

TECHNICAL CHARACTERISTIC OF CK- 22

Chemical content:

The Bulgarian low temperature shift catalyst is copper- oxide catalyst with the following chemical content:

- CuO - 37% wt.
- Al₂O₃ - 10% wt.
- ZnO - 53% wt.

Physical- mechanical indications:

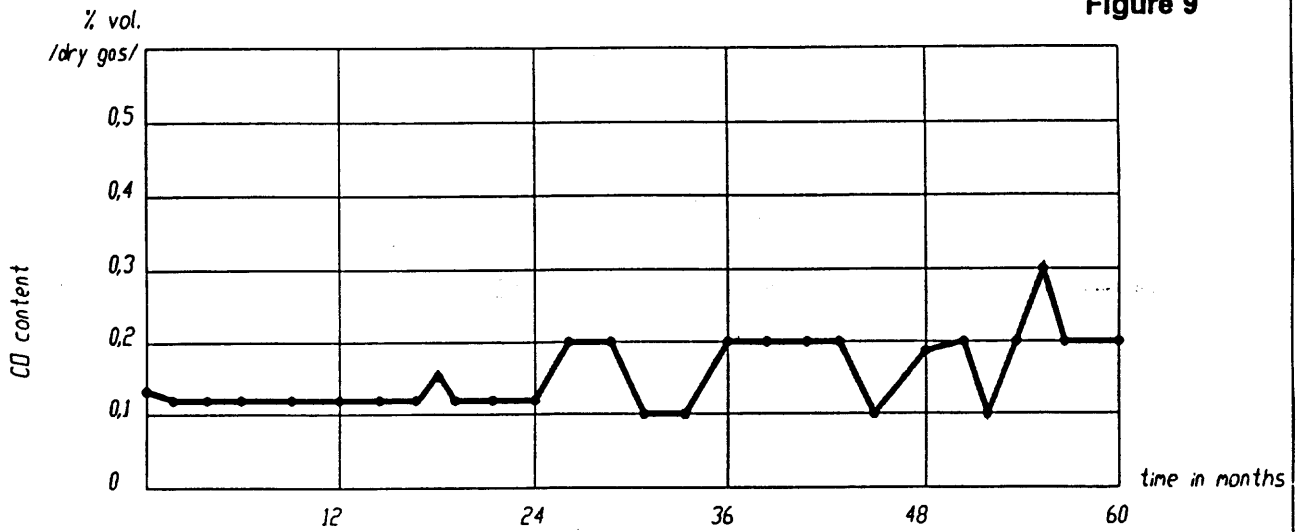
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|--|------------------------------|
| 1. Bulk weight, kg/l | - 1,2 |
| 2. Specific surface, m ² /g | - not less than 60 |
| 3. Mechanical strenght axial not less than | 200 kg/cm ² |
| 4. Form- cylindrical tablets | |
| 5. Dimensions | |
| - diameter | - 6,8 and 10 mm |
| - height | - 3, 4, 5, 6, 7, 8, 9, 10 mm |

Operating conditions:

- | | |
|---|-------------------------------|
| 1. Operating temperature, o C | 180- 260 |
| 2. Operating pressure | - up to 50 kg/cm ² |
| 3. Volume velocity, hour | - up to 6000 |
| 4. Steam/ gas ratio | - 0,3- 1,0 |
| 5. Content of inlet gas in the catalyst, volume % (dry gas) | - 0,3- 1,0 |

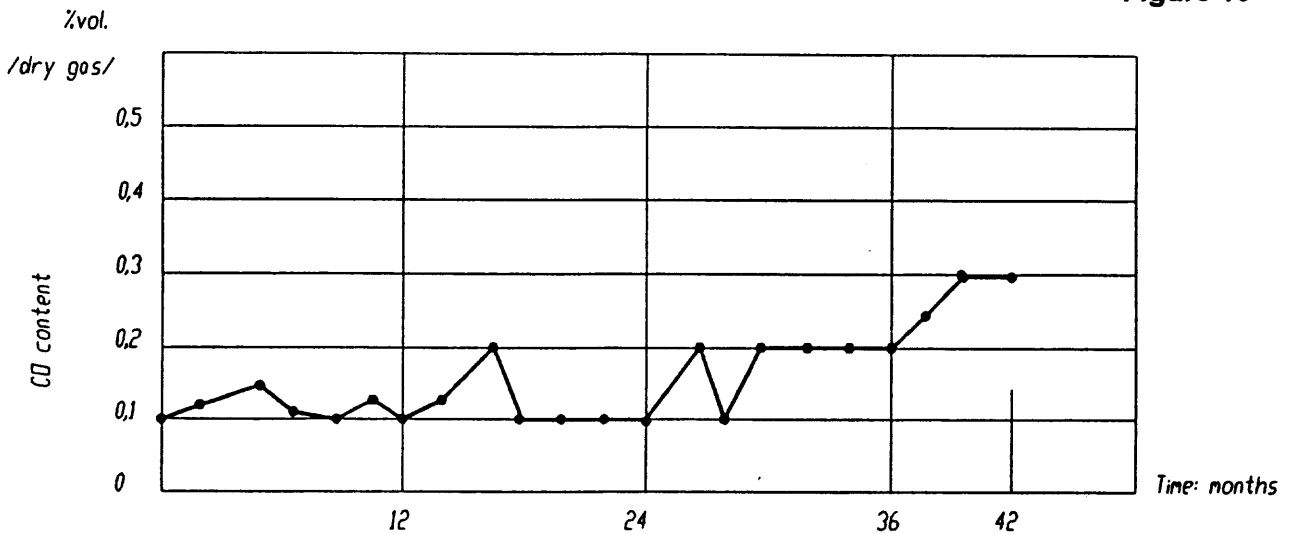
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| H ₂ | - ~60,0 |
| CO | - up to 8,0 |
| CO ₂ | - ~16,0 |

Figure 9



Change of the CO content at Bulgarian lowshift catalyst outlet during one exploitation cycle in ammonia plant with indirect cooling of the gas (CHMCO)

Figure 10



Change of the content of CO at outlet of Bulgarian lowshift temperature catalyst during one exploitation cycle in ammonia plant by direct /by injection/ gas cooling with water /CHMCO/

TECHNICAL CHARACTERISTIC OF CATALYST FOR FINE PURIFICATION OF SYNTHESIS GAS FROM CARBON OXIDE AND CARBON DIOXIDE BY METHANATION CM-01

Chemical content:

- NiO	- 40% wt.
- Al ₂ O ₃	- 53% wt.
- Cr ₂ O ₃	- 7% wt.

Physical- mechanical indications:

1. Bulk weight, kg/l	- 1,1
2. Specific surface, m ² /g	- not less than 80
3. Mechanical strenght axial not less than	200 kg/cm ²
4. Form- cylindrical tablets	
5. Dimensions	
- diameter	- 6, 8 and 10 mm
- height	- 3, 4, 5, 6, 7, 8, 9, 10 mm

Operating conditions:

1. Operating temperature, °C	300- 450
2. Operating pressure	- up to 30 kg/cm ²
3. Volume velocity, hour	- up to 10000
4. Content of inlet gas in the catalyst, volume % (dry gas)	- 0,3- 1,0

H ₂	- ~72,0
N ₂	~ 24
CO + CO ₂	- up to 1%
CH ₄	- ~1%

5. Adiabatic increase of the temperature in the reactor, °C:

for 1% vol. CO	74
for 1% vol. CO ₂	60

Figure 12

