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**INDUSTRIAL CAPACITY UTILIZATION
REHABILITATION OF THE COSSMIL'S SULPHURIC ACID PLANT
AT EUCALIPTUS**

TERMINAL REPORT

ON

CATALYST AND SULPHUR TESTING ANALYSIS

prepared for UNIDO

by

the Institute of Inorganic Chemistry

Gliwice, Poland

Research and Processing Division

at Lubon, Poland

under the Subcontract

between

the UNIDO, Purchase and Contract Service

Vienna, Austria

and

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1. Introduction

On the basis of the contract no. 78000/5/0114 negotiated between TKP Consultants Ltd. and UNIDO in Vienna an order was received to perform an expertise of delivered samples of sulphur and catalyst for the sulphuric acid installation, Cossmil, in Bolivia. The results of the accomplished order are presented in the report.

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2. Expertise of sulphur quality from the Cossmil installation

Estimation of sulphur quality with respect to its usability for producing sulphuric acid includes the determination of the following content:

- the sum of inorganic substances i.e. ash,
- the impurities decreasing the efficiency of the catalysis process and other unit operations,
- the impurities deteriorating the quality of the produced sulphuric acid product.

The quantity of the basic component of sulphur in sulphur is determined depending on the sulphur content:

- above 95% of S by subtracting the content of some impurities from 100,
- below 95% of S by producing thiosulphate from S, which is titrated with iodine.

In the present control of sulphur quality the range of performed determinations depends on the applied process for generating sulphuric acid. The basic determinations in sulphur analysis include determination of the ash content, which is decisive in gas dustiness after burning sulphur.

Besides the above also the content of H_2O , H_2SO_4 , As, Se, Te, C, Fe, Al, Ca and Mn, Cu and others is determined.

2.1. Determination of ash content

2.1.1. Description of method

The determination was performed according to the international standard ISO 3425 - Sulphur for industrial use -

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Determination of ash at 850-900°C.

This method includes melting, combustion and calcinating of sulphur sample in 900°C. The residue remaining after calcination is expressed as a percentage with respect to the mass of sulphur.

2.1.2. Results of the determination

The arithmetic mean of four results is 0.129%.

2.2. Determination of acid content

2.2.1. Description of method

Acidic components are extracted by distilled water and then titrated with sodium hydroxide solution against phenolphthalein until pink colour is obtained.

The determination was performed according to the international standard ISO-3704 - Sulphur for industrial use - Determination of acidity.

2.2.2. Results of the determination

Acidity expressed in the form of sulphuric acid is 0.003%
 H_2SO_4 .

The result is the arithmetic mean of two parallel determinations differing by 0.0002%.

2.3. Determination of volatile substances content

2.3.1. Description of determination method

The method determines the loss of mass of sample during drying in $80 \pm 2^\circ C$ for 16 hours.

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The analysis was performed according to the international standard ISO-3426 - Sulphur for industrial use - Determination of loss in mass at 80°C.

2.3.2. Results of the determination

The loss in mass is expressed in percents and is 0.015%.

2.4. Determination of organic substances content

2.4.1. Description of method

The method determines the difference of mass of sample after combustion at 200°C and 900°C, according to the international standard ISO-3425.

2.4.2. Result of determination 1

The arithmetic mean of two results is 0.12% of organic substances with regard to the mass of sulphur.

2.4.3. Description of method 2

Sulphur was extracted with chloroform and the residue was determined after the solvents were evaporated.

The sample of sulphur was digested in sodium sulphide solution and the residue, after filtering and drying, was extracted with chloroform. The solvent was evaporated and the residue was dried at 70±2°C until constant mass was obtained.

2.4.4. Result of determination 2

The arithmetic mean of two determinations differing by 0.003% expressed with regard to the mass of sulphur is 0.125% and

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corresponds to the content of organic substances.

2.5. Determination of arsenic content

2.5.1. Description of method 1

Arsenic compounds reduced to gaseous AsH_3 with hydrogen are absorbed in a pyridine solution of silver diethyldithiocarbamate. The intensity of the red colour is determined photometrically by comparison with appropriately prepared reference solutions of arsenic trioxide.

The determination according to the international standard ISO-3705.

Sulphur for industrial use - Determination of arsenic content
- Silver diethyldithiocarbamate photometric method.

2.5.2. Result of determination 1

The arithmetic mean was calculated on base of two determinations differing by 5% of the higher result.

The content of arsenic is expressed with regard to the mass of sulphur and is 0.0018% As_2O_3 .

2.5.3. Description of method 2

Arsenic compounds are reduced with hydrogen in statu nascenti to AsH_3 and absorbed on filter paper saturated with arsenic bromide until a yellow compound $As/HgBr/3$ is obtained.

The intensity of the filter paper is compared with a colour scale obtained in comparable conditions from a reference arsenic compound.

2.5.4. Result of determination 2

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The content of arsenic with regard to the mass of sulphur is 0.0019% As_2O_3 .

2.6. Determination of selenium content

2.6.1. Description of method

It was determined photometrically utilizing the yellow colour of the tetravalent selenium complex with 3,3'-diaminobenzidine.

Sulphur was digested by a mixture of bromine with carbon tetrachloride and then by nitric acid. After complete decomposition and oxidation of sulphur excess bromine and tetrachloride are expelled until SO_3 vapours are seen.

After ammonium chloride and disodium versenate are added pH 2.5 is reached with ammonia solution.

Then formic acid and 3,3'-diaminobenzidine hydrochloride solution is added. The colour complex after pH 5-7 is reached with ammonia solution, is extracted with toluene. The organic phase is subjected to colorimetry and compared with the analytical curve prepared in comparable conditions.

The determination was performed according to standards ST SEW 1417-78 Sulphur and Pn-81/C-84084.

2.6.2. Result of determination

The selenium content is expressed in percentage with regard to the mass of sulphur. An arithmetic mean of two determinations differing by 0.0001% was accepted.

The selenium content is 0.0008% SeO_2 .

2.7. Determination of tellurium content

2.7.1. Description of method

An extraction-photometric determination method of tellurium with diethyldithiocarbamate was used.

A sample of sulphur was digested in sodium hydroxide, and then oxidized by hydrogen peroxide, boiling away its excess. The solution is neutralized by hydrochloric acid against phenolphthalein until the disappearance of the red colour. After this a defined excess of HCl is added what is then reduced by hydrazine monochloride and stannous chloride. The selenium and tellurium residue is separated and then on a filtering paper is digested in acids. After tartaric acid is added pH 8.2-8.4 is reached, then sodium diethyldithiocarbamate is added and extraction with carbon tetrachloride is conducted. The organic phase was subjected to photometry and then compared with appropriately prepared reference samples.

2.7.2. Result of determination

No tellurium content was found. It can be smaller than a hundredthousandth percent with regard to the mass of sulphur /below 0.00001/.

2.8. Determination of antimony content

2.8.1. Description of method

An extraction-photometric method with methyl violet was applied.

A sample of sulphur was dissolved in nitric acid. Antimony

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was separated with manganese dioxide in a nitric acid medium. An association complex with methyl violet in the presence of ceric sulphate and hydroxylamine hydrochloride was extracted with trichloroethylene and compared with reference solutions of antimony prepared in comparable conditions. The organic phase was subjected to photometry.

2.8.2. Result of determination

No antimony content was found.

The bottom limit of the determination was 0.00002% Sb.

2.9. Determination of silica content

2.9.1. Description of method

A weighed sample of grinded sulphur was melted and burnt, the residue was digested in acids. The precipitate dissolved in hydrochloric acid solution and the remainder was filtered off and constituted the undissolved part.

The silica content is determined in the nonsoluble parts of the roasted precipitate by evaporation with HF in the form of volatile SiF_4 . After the remainder is converted into sulphates and then roasted to form oxides, the SiO_2 content is calculated from the loss of mass.

The filtrate after the nonsoluble parts are filtered off, and the precipitate after SiF_4 is expelled are left for Fe, Al, Ca, Mg determinations.

2.9.2. Result of determination

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The silica content in sulphur is 0.10%.

The difference between results of parallel determinations is 0.005%.

2.10. Determination of iron and aluminium content

2.10.1. Description of method of iron determination

Iron content is determined by compleximetry method, by titration with sodium versenate against sulfosalicylic acid at pH 2 until the violet-pink colour disappears.

Determination is conducted after burning the sulphur sample, after digestion of the residue and after filling up to a defined volume. In case of parallel determination of silica content, the iron may be titrated in a combined solution obtained in point 2.9. after the precipitate remaining after SiF_4 is digested. The filtrate, after the nonsoluble parts are separated, is also digested. A part of the solution filled up to a defined volume is sampled.

2.10.2. Result of Fe determination

The content of iron compounds in sulphur is expressed in the form of Fe_2O_3 and is 0.0053%.

The difference between parallel determinations is 0.00005%.

2.10.3. Description of method of aluminium determination

After titrating iron with versenate by the method described in point 2.10.1. aluminium is also determined by a compleximetry method against 3,3-dimethylnaphthydine. An excess of versenate solution and acetic buffer solution is added in order to obtain an aluminium complex. It is then titrated with zinc solution

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against ferricyanide and potassium ferrocyanide and naphthidine until a pink colour is seen.

2.10.4. Result of Al determination

The content of aluminium compounds in sulphur is expressed in the form of Al_2O_3 and is 0.0038%.

The differences between determinations are 0.00005%.

2.11. Determination of calcium and magnesium content

2.11.1. Description of method

The calcium and magnesium content was determined by compleximetry methods in part of the solution obtained in point 2.9.1.

The titration was conducted with disodiumversanate in an ammonium buffer solution against eriochromic black until the change of colour from red to blue.

The volume of used versanate corresponds to overall content of calcium and magnesium.

In order to determine the calcium content in a separate portion of the solution titration with versanate against calces in sodium hydroxide solution was conducted. The volume of versanate used in this titration corresponds to the quantity of calcium

The magnesium content is calculated from the difference of versanate used against ET and calces.

2.11.2. Result of the determination

The quantity of calcium compounds after conversion to CaO is 0.0140 with regard to the mass of sulphur.

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The quantity of magnesium compounds is expressed in the form of MgO and is 0.0017.

Differences between parallel determinations are 0.0002.

2.12. Determination of manganese content

2.12.1. Description of method

The intensity of the brown-red colour of the tetravalent manganese complex with formaldoxime was determined by photometric method by comparison with appropriately prepared reference solutions.

The content was determined in ash obtained after combustion of sulphur and decomposition with acids. The determination range was 0.01-0.05 mg Mn.

Manganese content was also determined in solutions of applied solutions by a comparison method.

2.12.1. Result of the determination

The arithmetic mean of two parallel determinations is 0.0001% MnO₂.

The results differed by 0.00001.

2.13. Determination of copper content

2.13.1. Description of method

A photolorimetry method was applied to measure the brown colour of the diethylditiocarbamate complex of copper in chloroform

It was determined in acidic solution of ash obtained after sulphur combustion. The determination range was 0.001-0.02 mg Cu.

2.13.2. Result of the determination

0.00008% of CuO was determined with regard to the mass of sulphur.

Parallel results differed by 8% in comparison with the larger one.

2.14. Determination of sulphur content

In sulphur of over 95% of sulphur content the basic impurities are determined, and also ash, organic substances, acids, arsenic and selenium are determined by way of subtracting their content from 100 accepting that it corresponds to the sulphur content.

The sulphur content determined by this method is:

$$S = 100 - /ash/ - /org.subst./ - /H_2SO_4/ - /As_2O_3/ - /SeO_2/$$
$$S = 100 - 0.129 - 0.12 - 0.003 - 0.0019 - 0.0008 = 99.7453\%$$

The content of sulphur was calculated by subtracting the results of determinations of impurities given in other points /in brackets/ from 100. The content of sulphur thus calculated is 99.745% S.

Independent of these calculations the sulphur content was determined by the iodometry method by converting sulphur into its sodium tiosulphate.

The arithmetic mean of ten determinations is 99.8% S.

2.15. Compilation of results of sulphur analysis

The content of components in the received sample of sulphur is expressed in percents and is calculated with regard to the compounds given in the list:

mass losses at temperature 80°C	0.015
ash	0.129
organic substances -C	0.12
acidity - H ₂ SO ₄	0.003
As ₂ O ₃	0.0019
SeO ₂	0.0008
TeO ₂	0.00000
SiO ₂	0.10
Fe ₂ O ₃	0.0053
Al ₂ O ₃	0.0038
CaO	0.0140
MgO	0.0017
MnO ₂	0.0001
CuO	0.00008
Sb ₂ O ₃	0.00000

In case of summarizing individual components possible errors should be accounted for. These can be caused by parallel addition of eg. ash, SiO₂, Fe₂O₃, Al₂O₃ and others, which are enclosed in the component.

For correct interpretation of results ash analysis has been given.

The individual basic components are expressed in percents

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with regard to the mass of ash calculated with respect to the compounds listed below:

SiO ₂	83.3
Fe ₂ O ₃	3.9
Al ₂ O ₃	2.6
MgO	1.2
CaO	8.6

Silica is the main component of ash and can originate from impurities accompanying mined sulphur or it can be introduced during its refining process.

2.16 Estimation of usability of sulphur for sulphuric acid production

Sulphur received for testing is in piece form and is of yellow colour.

Presuming that the sample is representative of the bulk, it is found that ash is the main impurity of sulphur and this disqualifies sulphur for direct use in sulphuric acid installations.

Sulphur containing a tenth percent part of ash should be filtered before it is burnt to SO₂ in order to decrease the dustiness of gases directed to catalytic oxidation of SO₂ to SO₃.

Assuming that the content of ash in sulphur is 0.13% and the production of sulphuric acid in the installation in Bolivia is 100 t H₂SO₄/24 hrs, the mass of dust accumulated in the catalytic reactor will amount to about 15 t/year.

The dust will mainly accumulate in the first layer of the catalyst noticeably lowering its activity and the efficiency of

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H₂SO₄ production. Also it will increase the resistance of flow of production gases in the catalysis process.

The main destructive activity of dust is caused by blocking the access of SO₂ to the active mass of the catalyst. Besides this, accounting for the large filtration efficiency of the catalyst layer accumulation of dust takes place in a small surface layer what additionally with corrosion products inside the apparatus can form impermeable crusts for gases.

Limitation of ash content in sulphur used for sulphuric acid production is connected with the stability of parameters and indicators of further unit processes.

The 0.001% content of ash in sulphur does not disturb the work of the installation. Such a degree of sulphur purification can be obtained in industrial conditions in a candle filter with a carbon barrier as well as in a frame filter with a layer of metal fabric. Such filters are applied in sulphuric acid installations in Poland and in the world. After considering the economical aspects and the necessity for periodical repairs of the installation the optimum ash content is a few thousandth of a percent and usually amounts to 0.005%.

On the basis of appearance of the sulphur sample and its chemical composition it can be assumed that the sulphur is already purified and filtered, mainly with bentonite in order to obtain pale yellow colour, but the effect of lowering the ash content is inadequate.

It should be underlined that such colour changes of sulphur do not influence its quality as a raw material for sulphuric

acid production.

The colour changes of sulphur are caused by two reasons:

- structural conversions
- content of some admixtures.

Changes which take place in melted sulphur are responsible for colour changes in solidified sulphur.

Pale yellow chemically clean sulphur, after melting at temperature above 160°C in defined conditions may change colour to brown, green, blue and even black and red. This proves that colour changes of sulphur do not have to be connected with an increase of impurities. These colour changes do not influence in any way the quality of sulphur as the raw material for sulphuric acid production.

Filtration of sulphur with bentonites, only in order to obtain a pale yellow colour is not technologically and economically justified for sulphuric acid and other productions.

The second factor causing a change of sulphur colour is connected with the content of organic substances i.e. bitumens and some other inorganic substances.

The technical requirement for the quality of sulphur concerning the content of organic substances is usually defined at 0.1% at the most for higher raw materials brands.

Limitation of organic substances in sulphur results from the possibility of oxidizing hydrogen contained in them to water. Excess quantities of water hinder the melting process of sulphur sometimes causing foaming, thus increasing the use of heat and increasing the content of water and fog in production gases, what in turn complicates further processes of sulphuric acid

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production. The quantity of water in sulphur destined for sulphuric acid production should not exceed 0.2%.

The requirements concerning the allowed arsenic content in sulphur used in sulphuric acid production is usually defined as 0.0005% As. In the obtained sulphur sample the content of arsenic is three times as large. Arsenic compounds in sulphur hinder the oxidation process of SO_2 and increase the vanadium catalyst consumption with regard to the produced sulphuric acid.

Losses of active substances are possible as a result of formation of volatile complexes of $\text{V}_2\text{O}_5 \cdot \text{As}_2\text{O}_5$ at temperatures above 480°C or at lower temperatures due to sublimation condensation of this compound blocking the contact surface.

The remaining impurities determined in the obtained sulphur do not impend the production of sulphuric acid in the aspect of possible lowering of process efficiency and decrease of quality of the obtained sulphuric acid product.

2.17. Propositions for improvement of sulphur quality

The ash content in sulphur can be decreased by filtration of the melted raw material or by filtration hot gases obtained after burning sulphur.

In the case of a comparatively small Bolivian installation modernization of the existing filtration process of sulphur is economically most justified. However it is not known if this process is conducted by the sulphuric acid producer or by the sulphur supplier.

It would be aimless to filter the sulphur twice. The

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modernization of the existing filtration process of liquid sulphur concerns mainly the change of type and quantity of filtration aids and filtration technology and the choice of a filtration barrier of the appropriate porosity.

The only parameter describing the filtration efficiency should be the lowering of ash content.

When the filtration aids of bentonite type are changed, /they brighten the sulphur colour/ to silica and cellulose type not giving colour effects a decrease of aid consumption with regard to the mass of filtrated sulphur, increase of the filtration process efficiency, decrease of the ash content in the filtrate and the decrease of sulphur loss in the filtrate waste can be assumed. Therefore there is a possibility of decreasing the content of arsenic compounds in the filtration process.

The choice of an optimal filtration barrier depends on the type of the filter. For filters with a porosity barrier, in order to determine the quality of sulphur, the indicated size of pores should be about 100-150 microns. However when a metal grid barrier is applied a rep weave of metal fibre of thickness of the groundmass wire of 0.5 and and thread of 0.2 microns is optimal.

With an optimum choice of filtration aid and barrier in industrial conditions filtrated sulphur containing 0.001%-0.005% of ash can be obtained for direct combustion in sulphuric acid installations.

In case of interest in improving the efficiency of sulphur purification or gas which is directed to the catalysis a process project for a given installation can be elaborated.

3. Estimation of the chemical composition of the catalyst from the H₂SO₄ Cossmil installation

3.1. Applied analytical methods

3.1.1. Determination of vanadium compounds content

A manganometry method of analysis was applied. The catalyst was digested in sulphuric acid and this solution was used to oxidate the reducing substances. Then the vanadium compounds were reduced by ferrous-anionic sulphate the excess of which was oxidized by ammonium persulphate. Tetravalent vanadium compounds were oxidized by titration with KMnO₄ solution to pentavalent compounds and then the vanadium content was determined by expressing it in the form of V₂O₅.

3.1.2. Determination of potassium compounds content

Potassium was determined by flame photometry in an air-acetylene flame.

The catalyst was digested in acids, the solution was subjected to photometry analysis and then compared with a reference curve of intensity dependance of potassium radiation vs. its concentration in solution, expressed as K₂O.

Content of sodium compounds was determined by similar methods.

3.1.3. Determination of loss of mass during roasting

Grinded weights of catalysts were roasted at temperatures 500-600°C. The loss of mass at different temperatures were

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related to the catalyst weights.

3.1.4. Determination of sulphates content

It was determined by the gravimetric method as BaSO_4 after the catalyst was digested in hydrochloric acid.

3.1.5. Determination of iron, aluminium, calcium and magnesium content

The content of individual components was determined by complexometric methods presented during the analysis of sulphur after separation from vanadium compounds.

3.2. Chemical composition of the catalyst

The content of components in the received sample of the catalyst is expressed in percents and is calculated with regard to compounds given in the list below:

Vanadium compounds	-	V_2O_5	6.4
Potassium "	-	K_2O	9.4
Sodium "	-	Na_2O	0.2
Silica "	-	SiO_2	50.7
Sulphate "	-	SO_3	25.3
Iron "	-	Fe_2O_3	1.45
Aluminium "	-	Al_2O_3	2.4
Arsenic "	-	As_2O_3	0.15
Selenium "	-	SeO_2	0.0000
Calcium "	-	CaO	2.4
Magnesium "	-	MgO	0.2
Lead "	-	PbO	0.005

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Copper compounds	- CuO	0.003
Phosphorous compounds	- P ₂ O ₅	1.1

The catalyst during drying and burning shows the following losses of mass expressed in percents at different temperatures:

at 100°C	1.9%
at 500°C	9.6%
at 600°C	16.0%

3.3. Analysis of the fine fraction accompanying the catalyst packing

The catalyst grains in the form of cylinders of 6mm diameter and 5-15mm length contained some liquids and a fine fraction which was separated and analysed.

The chemical composition of the accompanying impurities in percents is given below:

Vanadium content	- V ₂ O ₅	3.8
Potassium "	- K ₂ O	6.5
Iron "	- Fe ₂ O ₃	16.4
Silica "	- SiO ₂	35.1
Sulphate "	- SO ₃	32.1
Arsenic "	- As ₂ O ₃	0.21
Calcium "	- CaO	2.9
Aluminium "	- Al ₂ O ₃	2.1

The fine fraction contains catalyst components and an increased content of iron and arsenic sulphates with respect to the composition of the packing.

Corrosion products inside the catalytic reactor and ash components from the burnt sulphur constitute the impurities.

3.4. Estimation of the catalyst system with respect to its usability in the catalysis of SO_2 to SO_3

The basic components of the oxidation catalyst of SO_2 ; vanadium, potassium, sulphates and silica are found in the tested sample in the following molar ratios $\text{V}_2\text{O}_5 \cdot 2.9 \text{K}_2\text{O} \cdot 9 \text{SO}_3 \cdot 24.1 \text{SiO}_2$.

The vanadium content, 6.4%, is within the limit 6-8% V_2O_5 accepted for oxidation catalysts of SO_2 . The molar ratio $\text{K}_2\text{O}/\text{V}_2\text{O}_5$ and the vanadium content enable the application of the catalyst on all shelves of the catalytic reactor.

The presence of phosphates suggests the possibility of increasing the catalytic activity at low temperatures and through the formation of heteropolyacids the stabilization of vanadium at a higher degree of oxidation. A relatively small content of P_2O_5 does not indicate any significant effects in this respect.

The content of calcium compounds with regard to other components shows a possibility of obtaining good mechanical resistance of the catalyst packing at higher temperatures.

The presence of arsenic compounds in the catalyst requires more detailed discussion. It is a fact that As_2O_5 impurities catalyze the oxidation of SO_2 already at 300°C , however the application of this is hindered by the volatility of As_4O_6 , which forms during thermic dissociation of As_2O_5 .

Arsenic compounds form volatile $\text{V}_2\text{O}_5 \cdot \text{As}_2\text{O}_5$ at $480-600^\circ\text{C}$ and decrease the vanadium content in the catalyst, what can lead to loss of catalytic activity.

In temperatures below 480°C sublimation condensation V_2O_5

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As_2O_5 can take place in the catalyst layers thus blocking the catalytic surface.

Poisoning of the catalyst with arsenic compounds leads to a change in its chemical composition and porous structure.

Accepting as the degree of the catalyst poisoning, the lowering of the oxidation velocity constant of SO_2 by introducing 1g of As_2O_3 per $1dm^3$ of vanadium catalyst, the coefficient value is 0.01.

The ratio of the arsenic and vanadium content in the received catalyst is 2.3% and on the basis of research conducted so far it should not influence any changes of the catalytic activity. The boundary value for the presence of arsenic is usually 4% with respect to the V_2O_5 content in the catalyst.

On assuming a constant value of V_2O_5 content during catalytic exploitation, the limiting arsenic content not influencing the activity is 0.25% As_2O_3 .

When the As_2O_3 content is 0.38%, the oxidation velocity constant of SO_2 with regard to such contaminated catalyst decreases twice over.

Assuming that there is a possibility of decreasing the vanadium content during industrial exploitation, a safe limiting content of arsenic will move towards values smaller than 0.25% As_2O_3 .

Analysing the quality of the received sulphur and catalyst it can be said that the main impendence in industrial exploitation conditions will be the ash content in the raw material blocking the catalytic surface during catalytic oxidation of SO_2 , when sulphur is subjected to combustion directly without improvement

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purity /point 2.16/.

Considering the physicochemical properties of the tested catalyst it is possible to periodically regenerate it by separating the accompanying dust and decreasing the arsenic content by 50%. Additional lowering of the content of arsenic compounds is possible by thermal treatment of the contaminated catalyst.

On the basis of the conducted research over 95% of arsenic compounds can be removed from the catalyst by mechanical and heat treatment, what is optimum forecast for the liveliness of the catalyst.

In case of interest we offer an elaboration of detailed parameters of the catalytic regeneration process.

4. Testig analysis of catalyst obtained from COSSMIL, Bolivia

4.1. The aim of the work

Tests of the received catalyst include:

- tests conducted on special apparatus,
- determination of bulk density of the catalyst,
- determination of mechanical strength..

Discussion of general recommendations concerning the application of this catalyst in the oxidation process of SO_2 anticipated.

4.2. Test research of the catalyst

4.2.1. Description of apparatus for determining the differential degree of conversion /fig.1./

The apparatus for determining the degree of conversion is universal and it can be used for catalytic activity determinations of different catalysts using any type of gases.

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It consists of the following appliances and devices:

- devices drying the air /2/,
- devices for dosing, measurement and regulation and for appropriate mixing of components of the gaseous mixture /1,3,4,5,6/,
- reactors for obtaining an initial degree of conversion /7/,
- gas stove /8/,
- right reactor for testing oxidation kinetics of SO_2 to SO_3 /9/.

4.2.2. Description of the course of tests conducted on the received catalyst

In order to test the oxidation kinetics of SO_2 to SO_3 , the catalyst sample is placed in the right reactor. A gas characteristic for an installation working on SO_2 obtained from burning elementary sulphur, roasting ores containing sulphur or from mixing gaseous SO_2 with air was passed through a layer of the catalyst. As it is thought that the tested catalyst will be used for SO_2 oxidation in gases obtained from burning sulphur it was tested in a mixture of gaseous SO_2 with air. The tests were conducted in an apparatus assembled according to the scheme given in Fig.1. The air from the compressor /1/ was divided into two streams, one after heating was used for regenerating silica-gel, and the other was passed through a previously regenerated silica-gel column and then directed to a gas mixer /6/ through a rotameter /5/. Sulphur dioxide and nitrogen were directed to the gas mixer /6/ from vessels /3/ and /4/. The quantities of these gases were measured by rotameter /5/. Air, SO_2 and N_2 were so adjusted that the composition of the gaseous mixture leaving the mixer /6/

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corresponded to the composition of the gases obtained from burning sulphur in an industrial installation oven. The linear velocity of gases in the measuring reactor /9/ was $0.4 \text{ Nm}\cdot\text{s}^{-1}$, counted according to the diameter of an empty reactor. The gas from the mixer /6/ was directed to the initial reactors /7/ where it was partially reacted. In case of performing measurements without initial conversion reactors /7/ were switched off. Gas after initial reactors /7/ was then directed through stove /8/ to the proper reactor /9/, in which the required reaction temperature was regulated by thermoregulators controlled by thermocouples T_5 , T_6 , T_7 . Gas for determining the SO_2 concentration was taken from reactor /9/. /Measuring point A_3 /.

4.2.3. Determination of the velocity of the oxidation reaction of SO_2 to SO_3

Gas was analyzed for the content of SO_2 in measuring points A_1 , A_2 , A_3 .

On the basis of the SO_2 content determined at these points, the degree of initial and final conversion was determined. The velocity of the reaction was calculated.

The SO_2 concentration determination included the absorption of SO_2 contained in the gas in a defined volume of titrated iodine solution according to the equation /iodometric method/:



The following were used for analysis:

- titrated iodine solution - 0.1n
- aqueous solution of starch - 0.5%

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The percentage content of SO₂ in the analyzed gas was calculated according to the equation:

$$\%SO_2 = \frac{0.5 V_{J_2} \cdot n_{J_2} \cdot 21.89 \cdot 100}{0.5 V_{J_2} \cdot 21.89 \cdot n_{J_2} \times \frac{V_{H_2O} \cdot 273}{273 + t} \cdot \frac{P}{760 - P_{H_2O}}}$$

where:

V_{J_2}	- volume of solution in washer	/ml/
V_{H_2O}	- volume of gas measured in the aspirator	/ml/
n_{J_2}	- normality of iodine solution in washer	/b.w./
t	- solution temperature in aspirator	/C/
P	- atmospheric pressure	/mm Hg/
P_{H_2O}	- water vapour pressure at measurement temperature	/mm Hg/

Knowing the SO₂ concentration before and after the reactor the degree of conversion was calculated according to equation:

$$x = \frac{A - B}{100 - 1.5B}$$

where:

x	- degree of conversion	/%/
A	- SO ₂ concentration in gas before the reactor	/vol %/
B	- SO ₂ concentration in gas after the reactor	/vol %/

The reaction velocity is defined by equation:

$$r = \frac{V_{SO_2} \cdot 100}{21.89 M} / x_1 - x_2 /$$

where:

r	- reaction velocity	$/\text{mol}\cdot\text{s}^{-1}\cdot\text{kg}^{-1}/$
V_{SO_2}	- flow intensity of SO_2	$/\text{m}^3\cdot\text{s}^{-1}/$
M	- mass of the catalyst in the reactor	$/\text{kg}/$
X_1	- degree of conversion before the reactor	$/\%/$
X_2	- degree of conversion after the reactor	$/\%/$

4.2.4. Measurement conditions

SO_2 concentration in gas - 10.5%

O_2 concentration in gas - 10.3%

N_2 concentration in gas - 79.2%

Flow intensity:

SO_2 - $2.316\cdot 10^{-5}$ $/\text{Nm}^3\cdot\text{s}^{-1}/$

N_2 - $8.921\cdot 10^{-5}$ $/\text{Nm}^3\cdot\text{s}^{-1}/$

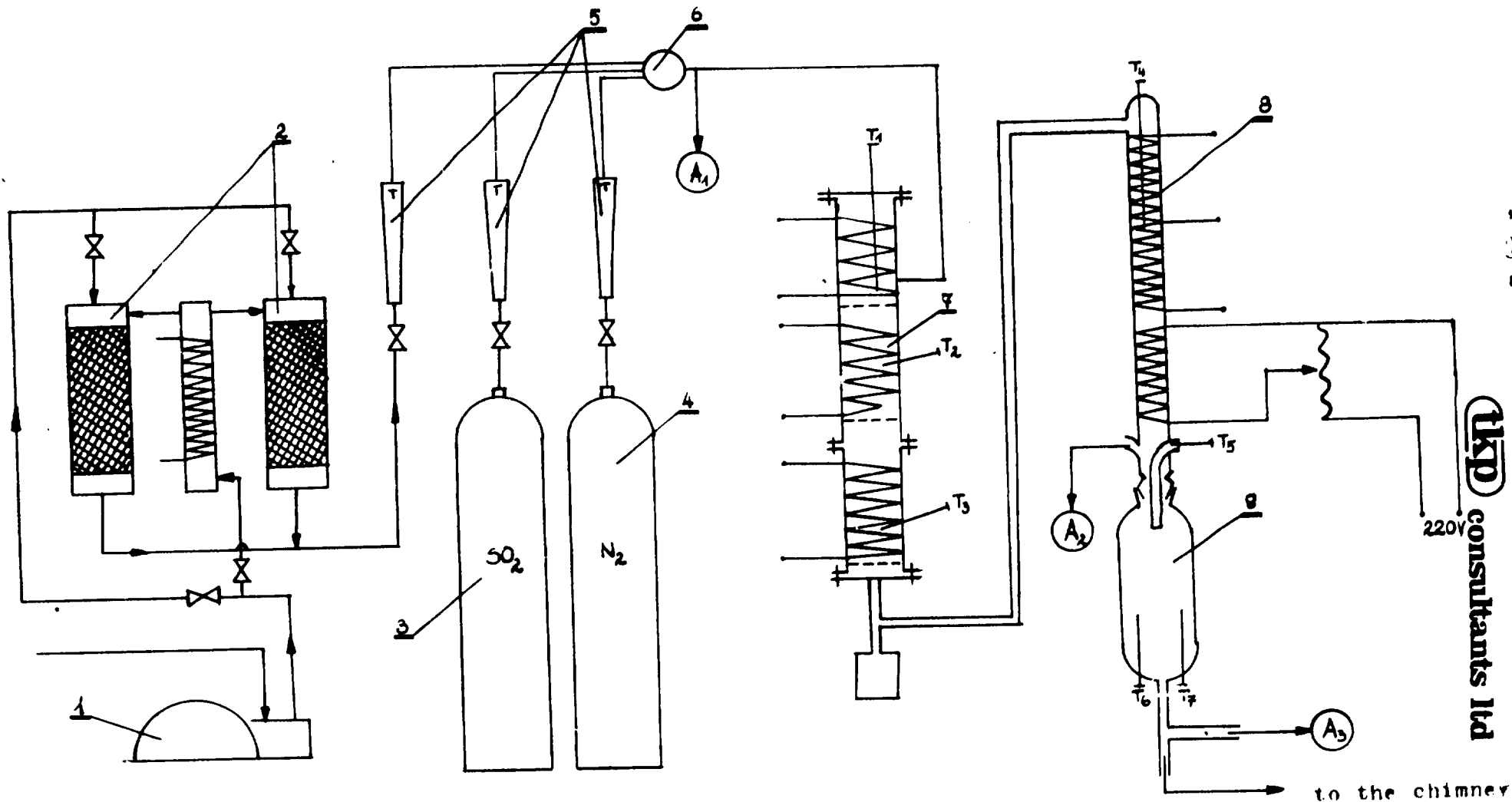
O_2 - $1.082\cdot 10^{-4}$ $/\text{Nm}^3\cdot\text{s}^{-1}/$

Linear velocity of gas - 0.4 $/\text{Nm}\cdot\text{s}^{-1}/$

Mass of catalyst sample - 0.04 $/\text{kg}/$

SO_2 concentration in gas after the right reactor /9/ was determined for reaction temperatures from 400 to 620°C /673.15 - 893.15K/ every 20 degrees.

Fig.1. Scheme of the apparatus for determining catalytic activity



4.2.5. Calculating the height of the catalytic layers and its decomposition

4.2.5.1. Determining the equilibrium curve and equilibrium conversion

The maximum degree of conversion in a given temperature is defined by the equation:

$$x_p = \frac{P_{SO_3}}{P_{SO_2} + P_{SO_3}} \quad /I/$$

Because the reaction velocity constant in equilibrium $/K_p/$ according to the law of mass action is defined by equation:

$$K_p = \frac{P_{SO_3}}{P_{SO_2} \cdot \sqrt{P_{SO_2}}} \quad /II/$$

Equilibrium conversion can be defined from equation $/I/$ and $/II/$ by equation:

$$x_p = \frac{x_p}{K_p + \sqrt{P_{O_2}}} \quad /III/$$

If the equilibrium partial pressure of oxygen is expressed by initial concentration of oxygen and sulphur dioxide by equation:

$$P_{O_2} = \frac{b - 0.5 ax_p}{100 - 0.5 ax_p} \cdot p \quad /IV/$$

then the equilibrium conversion can be calculated from equation:

$$x_p = \frac{K_p}{K_p + \sqrt{\frac{100 - 0.5 ax_p}{b - 0.5 ax_p} / P}} \quad /V/$$

where:

a - initial SO₂ concentration in gas /vol %/

b - initial O₂ concentration in gas /vol %/

K_p - degree of conversion in equilibrium /b,w./

P_{SO₂}, P_{O₂}, P_{SO₃} - partial pressures SO₂, O₂, SO₃

With reference to equation /V/ equilibrium conversions were determined - table 1.

TABLE 1

Temperature	Equilibrium conversion
400 ^o	99.5
420 ^o	98.45
440 ^o	97.55
460 ^o	96.35
480 ^o	94.6
500 ^o	92.35
520 ^o	89.45
540 ^o	85.8
560 ^o	81.5
580 ^o	76.65
600 ^o	71.25
620 ^o	65.5

4.2.5.2. Calculating the layers of the catalyst

Because the known kinetic equations are burdened with extremely large errors, in order to calculate the layers of the catalyst, even for comparison, we use another catalyst with other catalysts, kinetic data of the whole conversion area and temperature for precisely defined parameters and heat and material balance equations

$$\lambda_{cf} = \left(\frac{\partial^2 t}{\partial z^2} + \frac{\partial^2 t}{\partial R^2} + \frac{1}{R} \frac{\partial t}{\partial R} \right) + C_p G \frac{\partial t}{\partial z} - r_c \Delta H \rho_B = 0 \quad /1/$$

$$- \frac{\partial(uc)}{\partial z} + \frac{D_{ef}}{u} \left(\frac{\partial^2(uc)}{\partial R^2} + \frac{1}{R} \frac{\partial(uc)}{\partial R} \right) - r_c \rho_B = 0 \quad /2/$$

Because the analytical solution of these equations is complicated they are solved in a simplified way according to method where the differentials are substituted by finite increases according to the following equations:

$$t_{N,L+1} = t_{n,L} + \frac{\Delta z}{(\Delta R_0)^2} \frac{\lambda_{cf}}{G \cdot C_p} \left[\frac{1}{n} (t_{n+1,L} - t_{n,L}) + t_{n+1,L} - 2t_{n,L} + t_{n-1,L} \right] - \frac{\Delta H (c)_{av} \rho_B}{G C_p} \Delta z \quad /3/$$

Similarly, if in equation 2 the differentials are substituted by finite increases and c , c_0 and u_0 /gas velocity/ are introduced the following equation is received:

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$$x_{n,L+1} = x_{n,L} + \frac{\Delta z}{(\Delta t_0)^2} \frac{D_{ef}}{u} \left[\frac{t}{n} (x_{n+1,L} - x_{n,L}) + x_{n+1,L} - 2x_{n,L} + x_{n-1,L} \right] + \frac{(r_c)_{av} \cdot \rho_B^M \cdot \Delta z}{G_{y1}} \quad /4/$$

As this work limits itself only to stating on which shelves the catalyst can be used, the reactor has been recalculated accepting the diameter of the catalytic reactor as 3.4m and 0.2m for the external insulation. Therefore the heat losses to the environment are not big.

The calculations have been done with reference to standard heights of layers for good catalysts

The used notations:

R	- reactor radius	/m/
L	- number of segments along the axis	/m/
n	- number of segments along the reactor radius	/m/
R,Z	- dimensions of these segments	/m/
t_n	- average temperature for these segments	/deg/
x_n	- average conversion	/b.w./
G	- mass velocity	/kg.m ⁻² .m ⁻¹ /
λ_{cf}	- conduction coefficient of the layer	/J.m ⁻¹ .deg ⁻¹ /
C_p	- specific heat of gas	/J.kg ⁻¹ /
ΔH	- reaction heat	/J.mol ⁻¹ /
v_c	- reaction velocity	/mol.kg ⁻¹ .s ⁻¹ /
ρ_B	- bulk density of the catalyst	/kg.m ⁻³ /
P	- effective coefficient of diffusion	/m ² .s ⁻¹ /

Kinetic data were prepared on the basis of laboratory tests /Fig.2/ and then were used in order to calculate the degree of

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conversion of SO_2 to SO_3 for different shelves of the catalytic reactor with the assumed layer heights /Table 2,3,4,5/.

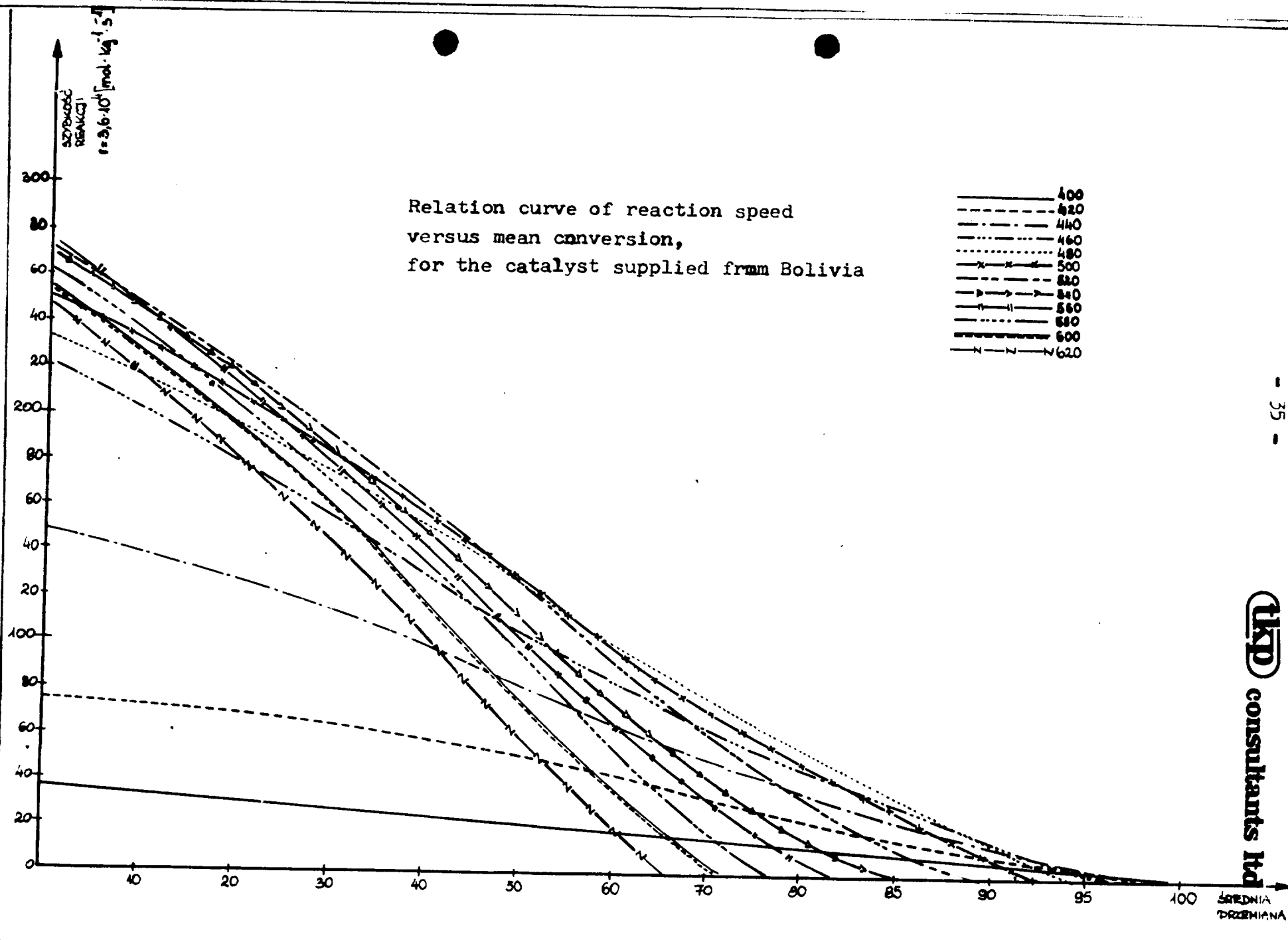


TABLE 2
1st LAYER OF CATALYST
CALCULATING THE HEIGHT OF THE CATALYTIC LAYER
/WITH OVERHEATING/

No of segment Depths in layer	temp.=400 mean conver.temp.	temp.=410 mean conver.temp.	temp.=420 mean conver.temp.	temp.=430 mean conver.temp.	temp.=440 mean conver.temp.
L= 0	0.0050 430.00	0.0050 430.00	0.0050 430.00	0.0050 430.00	0.0050 430.00
L= 1	0.0050 430.00	0.0050 430.00	0.0050 430.00	0.0050 430.00	0.0050 430.00
L= 2	0.0050 430.00	0.0050 430.00	0.0050 430.00	0.0050 430.00	0.0050 430.00
L= 3	0.0050 430.00	0.0050 430.00	0.0050 430.00	0.0050 430.00	0.0050 430.00
L= 4	0.0050 430.00	0.0050 430.00	0.0050 430.00	0.0050 430.00	0.0050 430.00
L= 5	0.0074 430.71	0.0115 431.94	0.0137 432.57	0.0179 433.31	0.0230 435.02
L= 6	0.0100 431.67	0.0184 434.00	0.0234 435.46	0.0321 438.04	0.0435 450.48
L= 7	0.0147 432.92	0.0257 436.02	0.0342 438.67	0.0479 442.72	0.0593 456.18
L= 8	0.0192 434.25	0.0325 438.22	0.0462 442.25	0.0653 447.35	0.0799 462.11
L= 9	0.0239 435.66	0.0405 440.60	0.0595 449.20	0.0836 453.26	0.1010 468.33
L= 10	0.0289 437.16	0.0492 443.20	0.0742 445.54	0.1026 458.30	0.1222 474.56
L= 11	0.0347 438.99	0.0589 446.08	0.0903 449.31	0.1231 464.91	0.1434 480.78
L= 12	0.0403 440.72	0.0697 449.28	0.1076 450.44	0.1435 470.94	0.1645 486.98
L= 13	0.0471 442.66	0.0816 452.82	0.1257 455.78	0.1640 476.95	0.1856 493.16
L= 14	0.0539 444.64	0.0947 456.71	0.1444 461.31	0.1844 482.95	0.2065 499.28
L= 15	0.0611 446.75	0.1091 460.97	0.1642 467.15	0.2047 488.91	0.2271 505.32
L= 16	0.0685 448.99	0.1248 465.61	0.1840 472.97	0.2249 494.32	0.2471 511.15
L= 17	0.0757 451.43	0.1416 470.59	0.2037 478.77	0.2448 500.65	0.2664 516.78
L= 18	0.0827 453.11	0.1591 475.76	0.2233 484.52	0.2644 506.58	0.2850 522.19
L= 19	0.0906 457.06	0.1772 481.10	0.2428 490.22	0.2833 511.90	0.3029 527.40
L= 20	0.1004 459.28	0.1963 486.74	0.2620 495.85	0.3015 517.21	0.3199 532.37
L= 21	0.1133 463.80	0.2154 492.36	0.2809 501.40	0.3190 522.31	0.3363 537.12
L= 22	0.1312 467.65	0.2343 497.93	0.2995 506.83	0.3358 527.19	0.3519 541.66
L= 23	0.1457 471.83	0.2531 503.46	0.3174 512.05	0.3518 531.35	0.3663 546.00
L= 24	0.1604 476.31	0.2717 508.92	0.3345 517.06	0.3671 536.30	0.3811 550.16
L= 25	0.1764 481.04	0.2901 514.31	0.3510 521.85	0.3817 540.56	0.3948 554.15
L= 26	0.1935 486.10	0.3092 519.61	0.3667 526.43	0.3957 544.63	0.4079 557.97
L= 27	0.2111 491.30	0.3280 524.81	0.3817 530.80	0.4090 548.51	0.4205 561.63
L= 28	0.2291 496.60	0.3463 529.83	0.3961 534.98	0.4218 552.22	0.4326 565.14
L= 29	0.2471 501.90	0.3656 534.64	0.4094 538.97	0.4340 555.73	0.4441 568.51
L= 30	0.2650 507.18	0.3844 539.24	0.4228 542.77	0.4457 559.19	0.4551 571.71
L= 31	0.2829 512.43	0.4034 543.62	0.4353 546.39	0.4569 562.44	0.4655 574.72
L= 32	0.3006 517.64	0.4224 547.80	0.4471 549.84	0.4677 565.50	0.4755 577.56
L= 33	0.3181 522.77	0.4414 551.78	0.4585 553.15	0.4780 568.39	0.4844 580.24
L= 34	0.3351 527.80	0.4605 555.58	0.4694 556.32	0.4879 571.47	0.4931 582.75
L= 35	0.3521 532.73	0.4789 559.20	0.4798 559.36	0.4972 574.18	0.5012 585.11
L= 36	0.3681 537.49	0.4958 562.65	0.4898 562.28	0.5060 576.72	0.5089 587.34
L= 37	0.3841 542.07	0.4670 565.94	0.4994 565.07	0.5141 579.10	0.5161 589.44
L= 38	0.3990 546.45	0.4773 569.06	0.5086 567.73	0.5117 581.31	0.5229 591.42
L= 39	0.4133 550.63	0.4880 572.05	0.5172 570.25	0.5209 583.40	0.5294 593.31
L= 40	0.4270 554.62	0.4979 574.92	0.5254 572.63	0.5297 585.37	0.5355 595.09
L= 41	0.4400 558.42	0.5073 577.66	0.5331 574.86	0.5422 587.24	0.5413 596.76
L= 42	0.4525 562.04	0.5163 580.29	0.5402 576.95	0.5482 589.01	0.5467 598.32
L= 43	0.4647 565.50	0.5249 582.78	0.5470 578.91	0.5540 590.69	0.5513 599.86
L= 44	0.4756 568.79	0.5330 585.15	0.5534 580.76	0.5595 592.28	0.5565 601.18
L= 45	0.4864 571.92	0.5407 587.39	0.5594 582.51	0.5647 593.80	0.5610 602.49
L= 46	0.4960 574.91	0.5480 589.50	0.5651 584.17	0.5697 595.24	0.5652 603.71
L= 47	0.5064 577.76	0.5548 591.49	0.5705 585.73	0.5743 596.60	0.5692 604.86
L= 48	0.5157 580.43	0.5612 593.36	0.5756 587.22	0.5787 597.87	0.5729 605.94
L= 49	0.5240 583.08	0.5673 595.12	0.5804 588.64	0.5829 599.07	0.5764 606.96
L= 50	0.5321 585.56	0.5730 596.78	0.5851 589.93	0.5867 600.19	0.5797 607.92

TABLE 3
IIInd LAYER OF CATALYST
CALCULATING THE HEIGHT OF THE CATALYTIC LAYER
/WITH OVERHEATING/

No of segment Depths in layer	temp.=440 mean conver.temp.	temp.=450 mean conver.temp.	temp.=460 mean conver.temp.	temp.=470 mean conver.temp.
l= 0	0.6000 440.00	0.6000 450.00	0.6000 460.00	0.6000 470.00
l= 1	0.6000 440.00	0.6000 450.00	0.6000 460.00	0.6000 470.00
l= 2	0.6000 440.00	0.6000 450.00	0.6000 460.00	0.6000 470.00
l= 3	0.6000 440.00	0.6000 450.00	0.6000 460.00	0.6000 469.99
l= 4	0.6000 440.00	0.6000 450.00	0.6000 459.99	0.6000 469.99
l= 5	0.6038 441.13	0.6077 452.29	0.6086 462.54	0.6095 472.79
l= 6	0.6088 442.60	0.6155 454.59	0.6173 465.09	0.6138 475.52
l= 7	0.6150 444.45	0.6233 456.91	0.6259 467.65	0.6278 478.18
l= 8	0.6213 446.31	0.6312 459.23	0.6346 470.21	0.6366 480.77
l= 9	0.6276 448.18	0.6391 461.56	0.6433 472.78	0.6451 483.28
l= 10	0.6346 450.27	0.6470 463.89	0.6519 475.30	0.6534 485.71
l= 11	0.6417 452.36	0.6549 466.22	0.6602 477.74	0.6614 488.07
l= 12	0.6488 454.46	0.6628 468.56	0.6682 480.12	0.6692 490.36
l= 13	0.6559 456.57	0.6707 470.89	0.6760 482.41	0.6768 492.57
l= 14	0.6630 458.68	0.6786 473.23	0.6836 484.64	0.6841 494.71
l= 15	0.6702 460.79	0.6864 475.52	0.6910 486.80	0.6911 496.76
l= 16	0.6773 462.91	0.6939 477.75	0.6981 488.88	0.6978 498.74
l= 17	0.6845 465.03	0.7013 479.90	0.7050 490.91	0.7043 500.64
l= 18	0.6917 467.14	0.7084 481.98	0.7117 492.88	0.7106 502.48
l= 19	0.6988 469.25	0.7152 484.01	0.7182 494.79	0.7166 504.25
l= 20	0.7060 471.36	0.7219 485.98	0.7245 496.61	0.7225 505.95
l= 21	0.7131 473.46	0.7284 487.89	0.7305 498.44	0.7281 507.59
l= 22	0.7200 475.51	0.7348 489.75	0.7364 500.11	0.7335 509.17
l= 23	0.7268 477.52	0.7409 491.55	0.7420 501.76	0.7386 510.68
l= 24	0.7335 479.47	0.7469 493.30	0.7474 503.34	0.7436 512.13
l= 25	0.7399 481.37	0.7527 495.00	0.7526 504.86	0.7484 513.53
l= 26	0.7462 483.21	0.7583 496.64	0.7576 506.31	0.7530 514.86
l= 27	0.7523 485.01	0.7636 498.21	0.7623 507.71	0.7573 516.14
l= 28	0.7582 486.75	0.7688 499.73	0.7669 509.06	0.7615 517.36
l= 29	0.7640 488.44	0.7737 501.18	0.7713 510.34	0.7655 518.52
l= 30	0.7696 490.08	0.7785 502.57	0.7756 511.58	0.7693 519.62
l= 31	0.7750 491.67	0.7831 503.90	0.7796 512.76	0.7729 520.67
l= 32	0.7802 493.22	0.7874 505.18	0.7835 513.89	0.7764 521.68
l= 33	0.7854 494.72	0.7916 506.41	0.7872 514.97	0.7797 522.64
l= 34	0.7903 496.16	0.7957 507.58	0.7908 516.01	0.7828 523.56
l= 35	0.7950 497.55	0.7995 508.71	0.7942 517.00	0.7858 524.43
l= 36	0.7996 498.88	0.8033 509.81	0.7974 517.95	0.7887 525.27
l= 37	0.8039 500.15	0.8070 510.90	0.8005 518.86	0.7914 526.06
l= 38	0.8081 501.38	0.8107 511.97	0.8035 519.76	0.7941 526.83
l= 39	0.8122 502.57	0.8143 513.03	0.8067 520.65	0.7966 527.56
l= 40	0.8161 503.73	0.8180 514.10	0.8097 521.52	0.7990 528.25
l= 41	0.8200 504.85	0.8216 515.17	0.8126 522.36	0.8013 528.93
l= 42	0.8237 505.96	0.8253 516.25	0.8154 523.19	0.8036 529.58
l= 43	0.8275 507.05	0.8291 517.33	0.8182 523.99	0.8057 530.21
l= 44	0.8312 508.14	0.8327 518.39	0.8208 524.76	0.8078 530.82
l= 45	0.8349 509.22	0.8361 519.40	0.8234 525.50	0.8098 531.40
l= 46	0.8386 510.31	0.8395 520.37	0.8258 526.22	0.8118 531.96
l= 47	0.8424 511.41	0.8426 521.29	0.8282 526.91	0.8136 532.49
l= 48	0.8462 512.53	0.8457 522.17	0.8305 527.56	0.8154 533.00
l= 49	0.8499 513.61	0.8485 523.01	0.8326 528.19	0.8171 533.49
l= 50	0.8535 514.65	0.8511 523.76	0.8347 528.79	0.8187 533.95
l= 51	0.8568 515.63	0.8535 524.45	0.8367 529.36	0.8202 534.39
l= 52	0.8599 516.54	0.8557 525.09	0.8385 529.90	0.8216 534.81
l= 53	0.8628 517.37	0.8577 525.67	0.8403 530.41	0.8230 535.21
l= 54	0.8654 518.13	0.8596 526.21	0.8419 530.89	0.8243 535.59
l= 55	0.8677 518.80	0.8613 526.72	0.8435 531.34	0.8256 535.94
l= 56	0.8698 519.42	0.8629 527.18	0.8450 531.77	0.8267 536.28
l= 57	0.8717 519.97	0.8644 527.62	0.8464 532.16	0.8278 536.59
l= 58	0.8735 520.47	0.8658 528.02	0.8476 532.54	0.8289 536.89
l= 59	0.8750 520.94	0.8671 528.39	0.8488 532.88	0.8298 537.17
l= 60	0.8765 521.36	0.8683 528.74	0.8500 533.21	0.8308 537.44

TABLE 4
IIIrd LAYER OF CATALYST
CALCULATING THE HEIGHT OF THE CATALYTIC LAYER
/WITH OVERHEATING/

No of segment Depths in layer	temp.=430 mean conver.temp.	temp.=440 mean conver.temp.	temp.=450 mean conver.temp.
1= 1	0.8500 430.00	0.8500 440.00	0.8500 450.00
1= 2	0.8500 430.00	0.8500 440.00	0.8500 450.00
1= 3	0.8500 430.00	0.8500 440.00	0.8500 450.00
1= 4	0.8500 430.00	0.8500 440.00	0.8500 450.00
1= 5	0.8520 430.64	0.8524 440.71	0.8527 450.79
1= 6	0.8541 431.21	0.8540 441.41	0.8553 451.56
1= 7	0.8561 431.81	0.8571 442.10	0.8570 452.32
1= 8	0.8581 432.40	0.8594 442.78	0.8604 453.07
1= 9	0.8600 432.99	0.8619 443.45	0.8629 453.80
1= 10	0.8620 433.57	0.8637 444.11	0.8653 454.52
1= 11	0.8639 434.15	0.8660 444.76	0.8677 455.23
1= 12	0.8658 434.72	0.8682 445.39	0.8700 455.92
1= 13	0.8677 435.28	0.8707 446.02	0.8723 456.59
1= 14	0.8696 435.84	0.8724 446.63	0.8745 457.26
1= 15	0.8715 436.39	0.8744 447.23	0.8767 457.91
1= 16	0.8733 436.93	0.8764 447.83	0.8789 458.53
1= 17	0.8751 437.46	0.8783 448.41	0.8809 459.13
1= 18	0.8769 437.99	0.8803 448.98	0.8828 459.69
1= 19	0.8786 438.51	0.8822 449.53	0.8846 460.23
1= 20	0.8803 439.02	0.8840 450.08	0.8863 460.73
1= 21	0.8820 439.53	0.8859 450.62	0.8880 461.22
1= 22	0.8837 440.03	0.8875 451.14	0.8895 461.69
1= 23	0.8853 440.54	0.8893 451.66	0.8911 462.13
1= 24	0.8869 441.04	0.8910 452.17	0.8925 462.56
1= 25	0.8885 441.56	0.8927 452.66	0.8939 462.96
1= 26	0.8901 442.07	0.8944 453.14	0.8952 463.36
1= 27	0.8916 442.57	0.8959 453.62	0.8965 463.73
1= 28	0.8931 443.07	0.8975 454.08	0.8977 464.09
1= 29	0.8946 443.56	0.8990 454.54	0.8989 464.44
1= 30	0.8960 444.04	0.9004 454.98	0.9000 464.77
1= 31	0.8974 444.51	0.9020 455.41	0.9011 465.10
1= 32	0.8988 444.97	0.9035 455.84	0.9022 465.41
1= 33	0.9002 445.42	0.9049 456.26	0.9032 465.71
1= 34	0.9015 445.87	0.9063 456.66	0.9042 466.00
1= 35	0.9028 446.31	0.9076 457.06	0.9051 466.27
1= 36	0.9041 446.74	0.9089 457.44	0.9060 466.56
1= 37	0.9054 447.17	0.9102 457.82	0.9069 466.83
1= 38	0.9067 447.59	0.9114 458.19	0.9078 467.10
1= 39	0.9079 448.00	0.9126 458.55	0.9086 467.29
1= 40	0.9091 448.41	0.9138 458.90	0.9094 467.53
1= 41	0.9102 448.81	0.9150 459.24	0.9101 467.75
1= 42	0.9114 449.21	0.9161 459.57	0.9109 467.97
1= 43	0.9125 449.60	0.9171 459.89	0.9116 468.19
1= 44	0.9136 449.99	0.9181 460.18	0.9123 468.38
1= 45	0.9147 450.37	0.9191 460.47	0.9130 468.58
1= 46	0.9157 450.75	0.9201 460.75	0.9136 468.78
1= 47	0.9168 451.12	0.9211 461.02	0.9143 468.96
1= 48	0.9178 451.49	0.9221 461.27	0.9149 469.15
1= 49	0.9188 451.85	0.9227 461.52	0.9155 469.32
1= 50	0.9198 452.21	0.9235 461.76	0.9161 469.49
1= 51	0.9207 452.57	0.9242 461.99	0.9167 469.66
1= 52	0.9217 452.92	0.9251 462.22	0.9172 469.82
1= 53	0.9226 453.27	0.9259 462.43	0.9178 469.98
1= 54	0.9234 453.61	0.9265 462.64	0.9183 470.14
1= 55	0.9242 453.95	0.9270 462.85	0.9188 470.29
1= 56	0.9250 454.29	0.9275 463.04	0.9193 470.43
1= 57	0.9258 454.62	0.9280 463.23	0.9198 470.57
1= 58	0.9266 454.95	0.9284 463.42	0.9202 470.71
1= 59	0.9273 455.28	0.9292 463.59	0.9207 470.85
1= 60	0.9280 455.61	0.9297 463.77	0.9211 470.99
1= 61	0.9287 455.94	0.9300 463.93	0.9216 471.10
1= 62	0.9294 456.27	0.9304 464.09	0.9220 471.23
1= 63	0.9300 456.59	0.9310 464.25	0.9224 471.35
1= 64	0.9307 456.91	0.9315 464.40	0.9228 471.47
1= 65	0.9314 457.23	0.9319 464.55	0.9232 471.59
1= 66	0.9320 457.55	0.9323 464.70	0.9236 471.70
1= 67	0.9327 457.87	0.9327 464.84	0.9240 471.81
1= 68	0.9333 458.19	0.9331 464.97	0.9244 471.92
1= 69	0.9339 458.51	0.9335 465.10	0.9247 472.02
1= 70	0.9345 458.83	0.9338 465.23	0.9251 472.13

4.3. Mechanical strength tests of the catalyst

The mechanical strength tests of catalysts were conducted on a ripper-compressor, type 11-15, Instron. This apparatus consisted of a mechanical part equipped with a tensometric indicator and a steering part equipped with a recorder describing the compression or ripping of the tested subject. The mechanical part consisted of a lever moved on two screws with a piston. A set of tensometric indicators was found in the bottom part, and it transfers the pressure force measured in kg. In case of testing a catalyst the applied measuring range was 0-100kg. In order to perform the measurement 10 granules from the catalyst batch were chosen at random. The granules were mechanically processed so that the height of each one would be exactly 10 mm and the cross-sections would be parallel to each other and would be smooth. The mechanical strength results of the tested catalyst are shown in Fig.3 .

kg/granul

100

90

80

70

60

50

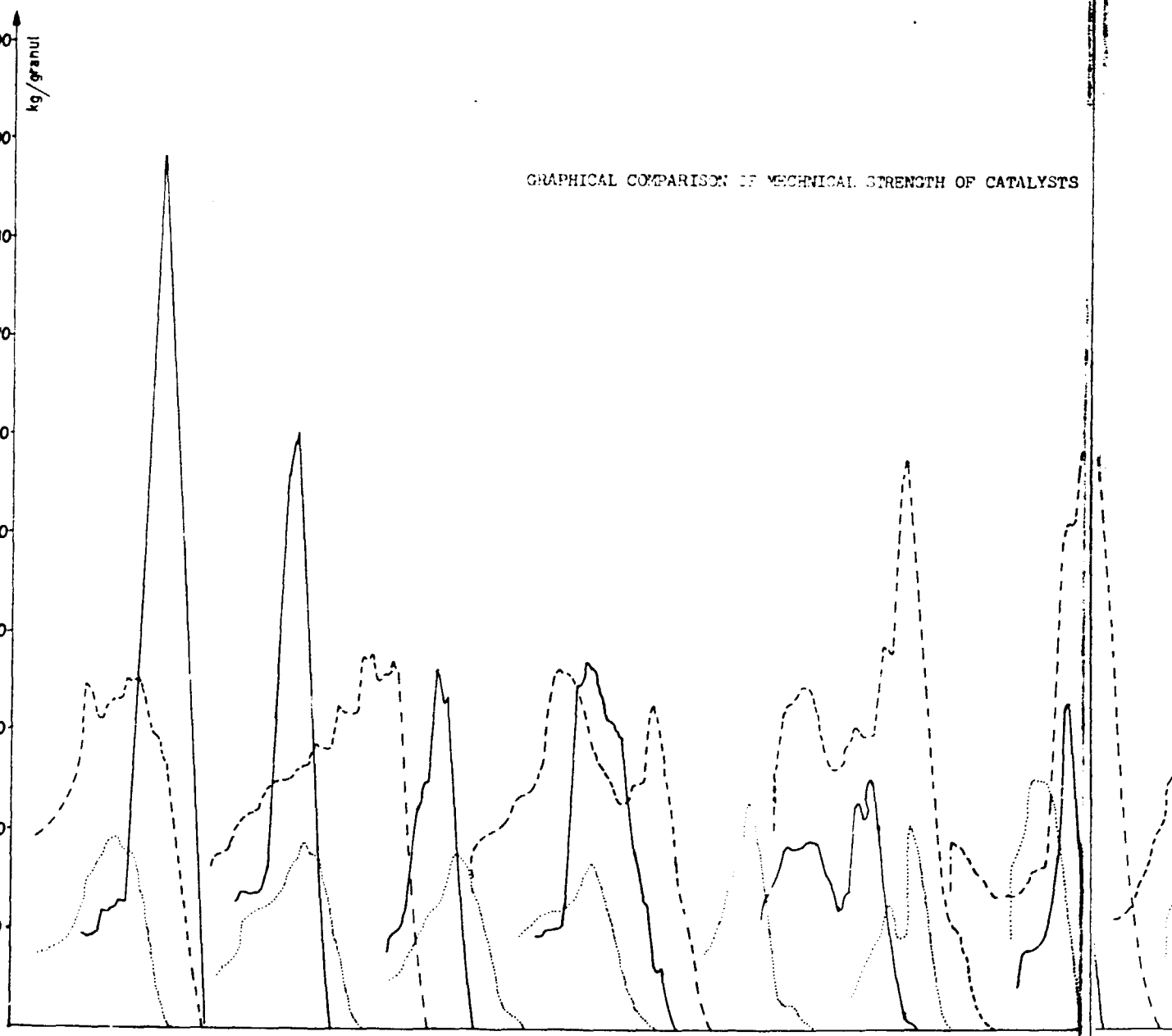
40

30

20

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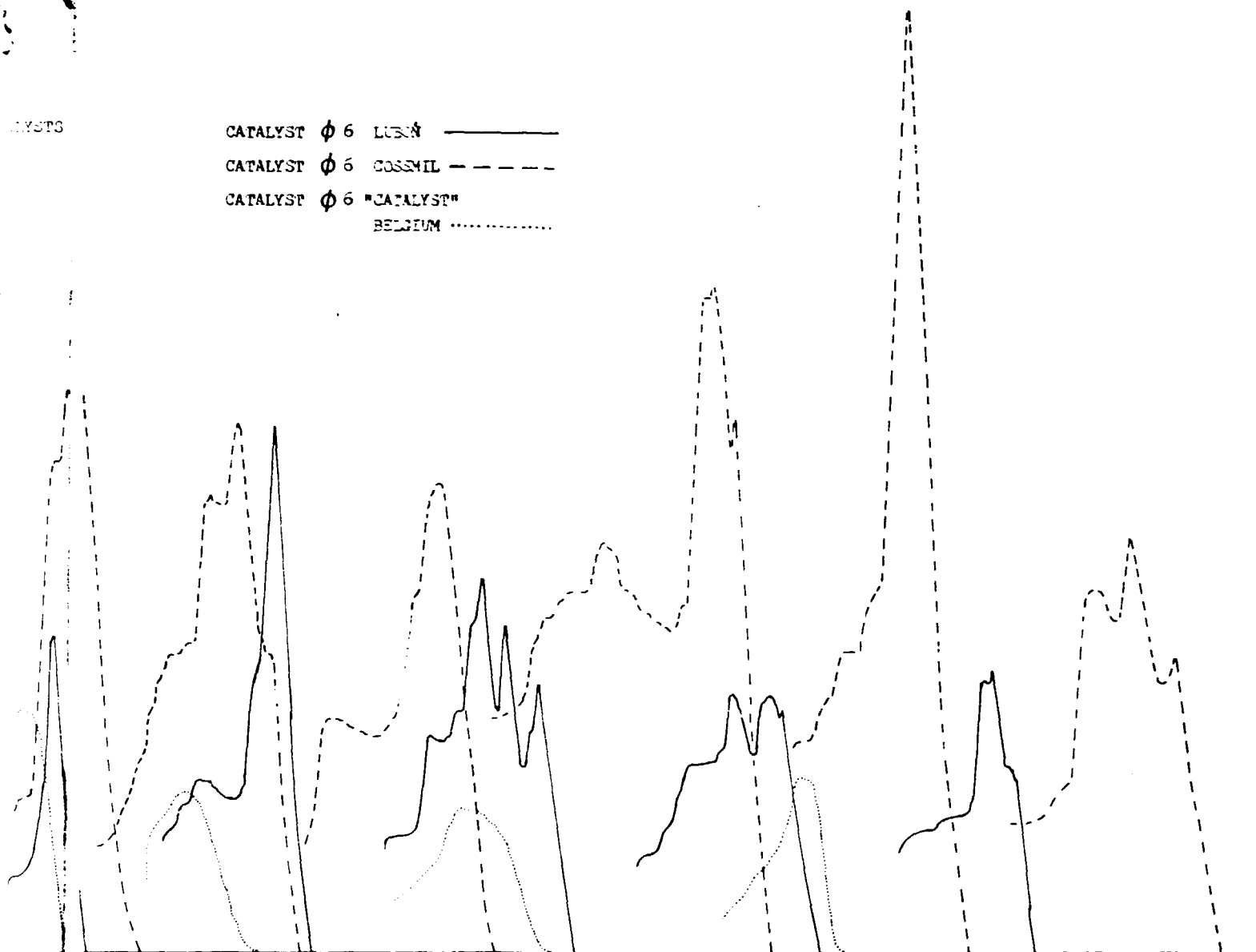
GRAPHICAL COMPARISON OF MECHANICAL STRENGTH OF CATALYSTS



SECTION 1

XYSTG

CATALYST ϕ 6 LUBON —————
CATALYST ϕ 6 COSSMIL - - - - -
CATALYST ϕ 6 "CATALYST"
BELGIUM ·······



SECTION 2

4.4. Determination of the bulk density

Determination of the bulk density of the catalyst according to the polish standard PN-GF/6062-01.

The bulk density was calculated according to the equation:

$$B = \frac{m}{V} \quad /kg.m^{-3}/$$

where:

m - mass of the tested catalyst /kg/

V - volume of cylinder /m³/

The bulk density of the tested catalyst is 0.66 kg.m⁻³.

4.4.1. Work parameters of the catalytic reactor with reference to the research tests

With reference to research tests and complimentary tests the following work parameters of a three shelf catalytic reactor with the discussed catalyst are settled.

	Load	
Ist shelf od catalytic reactor	normal	30% of normal
SO ₂ concentration in gas	6% by vol.	2% by vol.
Height of catalytic layer	0.60 m	0.60 m
Temperature of inlet gas	430 ^o C/703 15K/	430 ^o C
Conversion of SO ₂ to SO ₃	69% by vol.	72% by vol.
Temperature of outlet gas from shelf /excluding heat losses/	549.4 ^o C/822. 53K/	473.2 ^o C/746 35K/
IIInd shelf of catalytic reactor		
Height of catalytic layer	0.65 m	0.65 m
Temperature of inlet gas	440 ^o C /713.15K/	440 ^o C
Conversion of SO ₂ to SO ₃	88% by vol.	92% by vol.
Temperature of outlet gas /excluding heat losses/	473 ^o C /746.15K/	452 ^o C /725.15K/
IIIrd shelf of catalytic reactor		
Height of catalytic layer	0.8 m	0.8 m
Temperature of inlet gas	440 ^o C /713.15K/	440 ^o C
Conversion of SO ₂ to SO ₃	95.5%	97%
Temperature of inlet gas /excluding heat losses/	453 ^o C 726.15K/	443 ^o C /716.15K/

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The presumed working time of the catalyst with sulphur of
99.999% S purity 5 years

General recommendations concerning catalyst application

- I. The catalyst should be stored according to the advice of the producer.
- II. When reloading the catalytic reactor with the catalyst mechanical grinding should be avoided.

4.5. Discussion concerning catalyst tests

Within the tests the oxidation kinetics of SO_2 to SO_3 on the received catalyst has been determined.

The customer did not supply the basic data concerning the working parameters of the installation, such as:

- intensity of gas flow,
- gas composition,
- diameter of catalytic reactor,
- the allowed working height of individual shelves of the catalytic reactor,
- the required complete conversion degree of SO_2 to SO_3 ,
- the thickness of heat insulation of the catalytic reactor.

This made precise calculations of technological parameters for industrial catalytic reactor impossible. Therefore performing kinetic research and calculating catalyst distribution and conversion of SO_2 to SO_3 on individual shelves of the catalytic reactor was limited to testing conditions enabling a comparison of this catalyst with other generally used in sulphuric acid industry. Kinetic research was conducted in more rigorous condi-

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tions, i.e. increased SO_2 concentration in gas /10.5% by vol./, small content of O_2 /10.3% by vol./ and big linear velocity of gas flow through the reactor /0.4 Nm.s^{-1} /. For test calculations of the degree of conversion of SO_2 to SO_3 the heights of the catalyst layers on individual shelves were so chosen as to obtain the following conversions using a good catalyst:

Shelve I	58-60% by vol
Shelve II	85% by vol
Shelve III	94% by vol
Shelve IV / at single conversion/	'97% by vol

The research showed that the catalyst has quite good catalytic properties.

In the working conditions of the first shelve of the catalytic reactor, at temperature of 430°C /703.15K/ of the inlet gas a 58% by vol. conversion of SO_2 to SO_3 can be obtained, on a catalyst layer of 0.45m /Table 2/.

A satisfactory conversion can be obtained on the second shelve of the catalytic reactor. From results of calculations it is found that conversion of 87.65% by vol. can be obtained at temperature of inlet gas of 440°C /713.15K/ on a catalyst layer of 0.55 m /Table 3/. It proves the catalyst to be of great use for work in conditions of the second shelf of the industrial catalytic reactor. No limitations are found to use this catalyst on the third shelf of the catalytic reactor as at the temperature of 440°C /713.15K/ the conversion of SO_2 to SO_3 is 93.58% on a layer 0.65 m thick /Table 4/.

The biggest objections arise when it is considered to use

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this catalyst on the fourth shelf of the catalytic reactor, especially when the installation is working by the method of single conversion.

From mathematical calculations it is seen, that the possible conversion which can be obtained in these conditions is 96% by vol, at temperature of inlet gas 430°C /703.15K/ and height of catalyst layer 0.75 m /Table 5/.

From analysis of mathematical calculations it results that catalyst has good catalytic properties and can be used on the first, second, and third shelf in all types of catalytic reactors working by the method of single conversion.

Additional tests and calculations should be considered in case of applying other, then conditions assumed in this elaboration for the work of industrial installation.

The heights of the catalyst layers accepted for calculations should be considered as test values and should not be used for designing industrial installations.

The received catalyst does not show any limitations concerning its mechanical strength what is shown in the comparison figure /Fig.3/.

The bulk density of the catalyst is 0.66 kg.m⁻⁵ and does not differ from any generally used catalysts chemically formed by gaseous SO₂.

The sample of the received catalyst is too small to determine the hydraulic resistance of the layer in comparable conditions, i.e. at layer height of 0.45 m. Size reduction of the granules shows, that the hydraulic resistance of the layer may be very high and can rapidly increase, especially on the first shelf of the

catalytic reactor, with exploitation time of the installation, with badly conducted sulphur filtration.

In the polish sulphuric acid installations a new type of low-resistance catalyst KGK 12/5 T in the shape of rings is applied. This catalyst has very good catalytic properties and three times as small hydraulic resistance of the layer and is produced by the Poznań Chemical Factory in Luboń near Poznań.

5. Conclusions

5.1. The lumped sulphur received from Bolivia, although filtered and of pale yellow colour contained 0.129% of ash, and can be used, after the ash content is decreased to at least 0.005% for sulphuric acid production.

The most economically justified is to improve the existing purification and filtration process of sulphur by choosing a filtration aid and barrier and by changing the technology.

5.2. During sulphur combustion of sulphur of the presented quality the possibility of dustiness of the first catalyst layer, about 15 t of dust per year, should be assumed, if the established size of the Cossmil installation production is to be maintained.

The resistnace of gas flow will greatly increase, the efficiency of the catalytic oxidation process of SO_2 will fall and the exploitation costs will rise.

5.3. The sulphur although refined contains 0.0015% As, what is three times as much as that allowed for the raw material burnt in sulphuric acid installations without purification processes.

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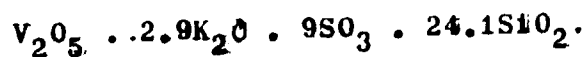
This is connected with catalyst impurities /arsenic compounds of the order of a tenth part of a percent.

The content of arsenic compounds in the catalyst during exploitation can be higher, because the samples come from the Cosmil installation not working for a couple of years now.

5.4. Refinement of bolivian sulphur in order to obtain a pale yellow colour is not justified technologically or economically in the aspect of needs for sulphuric acid production. The main criterium for filtration effectiveness is the lowering of ash content in sulphur.

Also a decrease of arsenic and organic substances content in sulphur is suggested.

5.5. The vanadium catalyst obtained from Bolivia contains the following basic substances in molar ratios:



The chemical composition of the catalyst containing 6.4% V_2O_5 suggests a possibility of applying it on all shelves of the catalytic reactor

Assuming the received samples to be representative and that the determined ratio of the arsenic and vanadium contents is constant and is 2.3%, due to results of recent research, the arsenic content should not influence the catalytic activity during exploitation /point 3.4./.

5.6. With increase of arsenic compounds content in the catalyst, there is a possibility of its regeneration by mechanical and heat processing. Over 95% As can be removed.

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5.7. In case of interest we offer an elaboration on:

- the regeneration process of the catalyst,
- the sulphur filtration process with a decrease in ash content to 0.001 - 0.005%,
- filtration process of hot gases after sulphur combustion.

5.8. The received catalyst shows very good catalytic activity.

5.9. The catalyst can be used on the first, second and third shelf of a four-shelf catalytic reactor, where gas of a larger concentration than 8% SO₂ is directed.

5.10. The catalyst can be applied in a three-shelf catalytic reactor on the condition that the applied gas contains no more than 6% of SO₂ content using technological parameters in accordance with point 4.4.1.

5.11. The catalyst is mechanically resistant and can be used in industrial installations.

5.12. Test were conducted on pure gas not containing such impurities as As, Sb and Pb.