



Sulfur Guard Catalysts

OOO «ТИ-СИСТЕМС» ИНЖИНИРИНГ И ПОСТАВКА ТЕХНОЛОГИЧЕСКОГО ОБОРУДОВАНИЯ Интернет: www.tisys.ru www.tisys.kz www.tisys.by www.tesec.ru www.ти-системс.рф Телефоны для связи: +7 (495) 7774788, 7489626, 5007154, 55, 65 Эл. почта: info@tisys.ru info@tisys.kz info@tisys.by

INTRODUCTION

Filtra Catalysts & Chemicals Ltd., offers a wide range of catalysts, adsorbents and bed supports for various applications in chemical process industries including Refineries, Petrochemical Plants, Fertilizer, Steel Plants & Speciality chemicals

FCCL'S Catalysts & adsorbents are well established in numerous applications, such as Desulphurization & Chloride Removal catalysts for feedstock treatment in Syngas Processes, Hydrogenation-Dehydrogenation, De-Oxo, Gas Purification, Volatile Organic Combustion, Ammonia Cracking & Catalyst Bed Support. FCCL is also in Claus Catalysts, Reforming Catalysts, Bio-Diesel Catalysts & Catalysts for Customer Specific Applications. All our catalysts are developed in our in-house R&D centre in India

This bulletin covers our range of desulphurisation / Sulfur guard catalysts (DS Series). The Product Bulletin (PART - A) and the Operating Instructions (PART - B) for DS Series Catalysts have been prepared with specific care to serve as a guidance for users of catalysts from **FCCL**

While the Product Bulletin will serve the purpose of understanding various physico-chemical properties and the related kinetic data in regard to the catalyst, the Operating Instructions have been tailored to provide optimum plant performance. Even though great care has been taken in putting through as much data as is required, the information provided is general in nature and if a customer has any specific query regarding product data or operating guidance, FCCL shall be glad to provide clarifications to such specific queries on written requests from users.

The operating instructions provided herein are of general nature and can be modified by the client to suit their requirements of plant conditions keeping the safety aspects in mind.

FCCL shall be pleased to answer any queries relating to its catalysts, such queries may pleas

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PART-A

PRODUCT BULLETIN

I. ADSORPTION CHARACTERISTICS OF ZnO CATALYSTS

Zinc Oxide adsorbents are used for removal of Sulphur either by using down-stream of hydro-treating catalysts or as main sulphur adsorption catalyst for gas purification and other process applications depending on the demands of process engineering design requirements.

FILTRA offers their unique **DS** Series Catalysts which are ideally suited for these applications.

The main features are

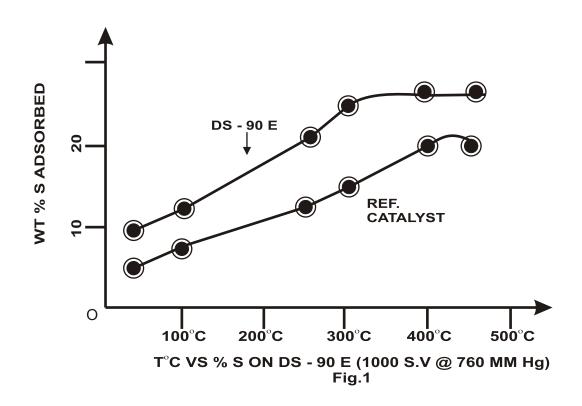
- 1. High Sulphur adsorption capacity. Due to excellent diffusion characteristics and high available surface area, the sulphur adsorption takes place layer by layer and break through is noticeable clearly after the useful life is achieved.
- 2. The **DS** catalyst is supplied in extrusion form as opposed to the conventional spherical form of catalyst which has much higher attrition loss due to low crush strength. **DS** Series catalysts have much higher retained crush strength and thereby exhibit much lower pressure drops during the useful life of the catalyst.
- 3. As such the demands on Zinc Oxide Catalyst apart from sulphur adsorption capacity defined largely by surface area, good crush strength and low attrition loss, also should have sufficient resistance when steam partial pressure is raised in the gas stream or if there is direct impingement of water which generally tend to powder the catalysts. By its superior characteristics, **DS** Series catalysts have exhibited much better retained strength even when liquid water directly contacts the catalyst leave alone rising of partial pressure of steam in the gas.

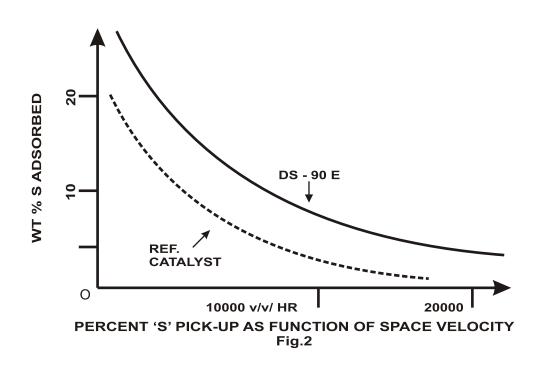
II. ADSORPTION CAPACITY Vs. OPERATING PARAMETERS

In Fig. 1 & 2 enclosed, we have plotted weight % sulphur adsorbed, Vs. temperature and space velocity respectively for one of our standard **DS-90 E** catalyst to show the effect of these parameters on the catalysts.

For the desulphurisation of "Off gases" containing reactive 'S' compounds like H_2S , FILTRA's 'DS-90 E' Catalysts can be used. In case of desulphurisation of gases—with—increased—steam content, adsorption capacity of sulphur removal catalysts is adversely reduced.

TEST DATA ON DS-90 E ZINC OXIDE CATALYST





III. TYPES OF 'S' COMPOUNDS AND ADSORPTION LEVELS

There are many types of sulphur compounds to be treated with Zinc Oxide in which some types are not reactive.

The sulphur compounds commonly met are H_2S , RSH, RSR, COS, RSSR, S, SO₂ and thiophenes etc. Generally, Zinc Oxide beds are designed for optimum performance in relation to sulphur adsorption capacity somewhere between 350 - 450° C. There is no limit on the inlet sulphur levels even though maximum experienced in the industry is of the order of 1500 ppm by weight. The outlet / inlet sulphur levels can be tailored depending on the requirement and outlet sulphur level can be upto < 0.05 ppm or to as required to protect the downstream catalyst.

IV. THE SULPHUR ADSORPTION PROCESS

In feed stock used for steam reforming the outlet sulphur concentration from the desulphurisation unit should be less than 0.1 ppm. The main part of the Sulphur is present as H_2S but some sulphur may be in the form of COS, RSH, CS_2 , R_2S_2 and thiophenes. H_2S reacts at ambient temperature

$$ZnO + H_2S \rightleftharpoons ZnS + H_2O$$

whereas much higher temperatures are required for reaction of the higher sulphur compounds.

The 'S' concentration downstream of the DS-90 E bed in most cases is determined by the chemical equilibrium concentration for the reaction between ZnO and H₂S at operating conditions.

The chemical equilibrium concentration is equal to the ratio of the partial pressure of water vapour and H_2S . Therefore when the temperature and the humidity of the gas is known the equilibrium concentration of H_2S is easily determined. This shows how sensitive the equilibrium H_2S concentration is to the humidity of the gas. The actual H_2S concentration exit the DS-90 E bed will be typically even lower because chemisorption of H_2S on ZnO can lower the H_2S level below a concentration predicted by chemical equilibrium. After some time of operation the axial distribution of sulphur in DS-90 E bed will ideally have sulphur profile as illustrated in Fig. 3.

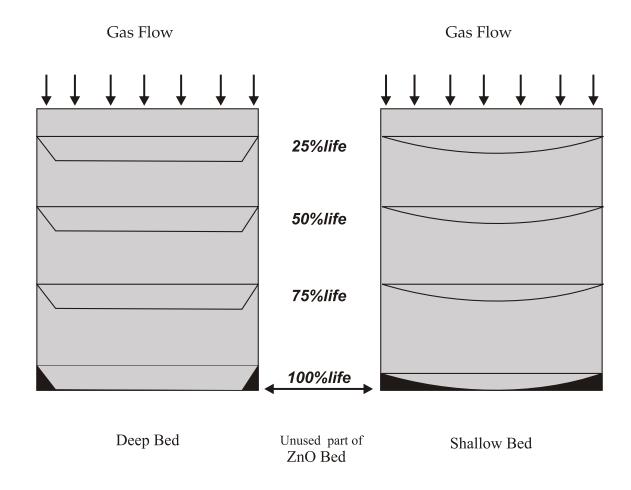


Fig. 3

General Pattern of Sulphur Adsorption over DS-90 E Bed under standard Operating Conditions

^{*}It may be noted that near plug flow condition exists for the usual space velocities in a deep bed resulting in a very small portion of the ZnO bed remaining unused at the end of its life span.

V. SULPHUR ADSORPTION CATALYSTS FOR VARIOUS APPLICATION BY FCCL

FILTRA, with its extensive catalyst and adsorbent experience, offers a range of sulphur removal Zinc Oxide & Mixed Metal Oxide based catalysts for high & low temperature (upto ambient conditions) and other specific applications of H₂S, mercaptans and COS removal from hydrocarbon, gas and liquid streams.

FILTRA's Desulphurisation range of Catalysts have following advantages -

- 1. Low pressure drop due to excellent physical properties.
- 2. High efficiency of Sulphur removal upto very low ppm levels.
- 3. Longer on-stream periods.
- 4. Better overall cost effectiveness.

Various grades of desulfurization / S - guard catalysts supplied by Filtra are briefly discussed In **Table - 1**

'DS-90E-HSM'/'DS-90 E-HS' Catalyst developed for low temperature applications are most suited and widely recommended for Sulphur removal from natural gas streams at ambient temperature. These catalysts are superior in performance than competitor's catalysts for similar conditions. For e.g. DS - 90 - E - HS has adsorption capacity of 12% wt/wt while DS - 90 - EHSM is an improved version of DS - 90 - EHS with minimum adsorption capacities of 20% wt/wt at ambient temperature.

FILTRA also offers '**DS-LHS**' a proprietary mixed metal oxides catalyst for removal of H₂S and trace levels of mercaptans and COS from hydrocarbon and liquid hydrocarbon streams. Based on the feed stream composition, impurities and operating conditions, suitable grades are recommended.

TABLE-1

DS-SERIES OF FCCL				
GRADE	COMPOSITION	APPLICATION		
DS-90-E	Zinc oxide catalyst with proprietary binders. This catalyst is available as extrudates as 3,4 and 5 mm diameter size range. White / off-white in colour.	This grade is suitable for removal of H ₂ S from hydrocarbon feedstock from 250 to 400° C. Typical applications are in hydrogen plants prior to reforming of feedstock to manufacture the hydrogen.		
DS-90-E-HS	High activity Desulfurisation Catalyst with 90% ZnO & mixed metal oxides and binders in extruded form size; 3,4 and 5 mm dia. White / off-white in colour.	Removal of trace levels of H ₂ S & Mercaptans from various gas streams from ambient temperature and above. Most suitable for purification of Natural gas streams.		
DS-90-EHSM	Mixed metal oxide catalyst; Proprietary Composition	Very High Capacity adsorption, for ambient temperature application for H ₂ S,mercaptan & COS removal. Specially suitable for Natural Gas purification		
DS-90-T	90% ZnO with suitable binder in tablet form sizes of 5mm dia. & 7.5 mm dia. and 5mm height.	Removal of trace levels of H ₂ S and Mercaptans from gas streams above operating temperature of 120° C upto 400° C suited for Natural gas streams Superior physical properties.		
DSF-50	Specially prepared high activity Iron Oxide with binders in tablet form in sizes ranging from 5 mm dia.to 7.5mm dia. and 5mm height.	Removal of H ₂ S from hydrocarbon feed stock or gas streams from around ambient temperature with very high adsorption capacities.		
DS-LHS	Mixed Metal Oxides, proprietory composition in extruded form size 3 to 5 mm dia.	Removal of H ₂ S / COS / mercaptans. Desulfurization of liquid hydrocarbon streams to meet copper / silver strip test. Operating temperature from ambient to 230° C.		
DS-85-E	Zinc oxide catalyst with proprietary binders. This catalyst is available as extrudates as 3,4 and 5 mm diameter size range. White / off-white in colour.	Removal of H ₂ S from hydrocarbon feedstock from 250 to 400° C. Typical applications are in hydrogen plants. This catalyst is suitable for low sulphur removal		

^{*} Catalysts can also be made available in specific size / shapes as per requirement

VI. TECHNICAL SPECIFICATIONS OF DS - SERIES

DS-90 E

FUNCTION : DESULFURISATION CATALYST

APPLICATION : Sulphur removal from

hydrocarbon / process

gas streams.

PHYSICAL PROPERTIES

FORM : Extrusions

SIZE** : 4mm, 5mm dia. ± 0.2 mm

(L/D = 1:1 to 3:1)

CRUSH STRENGTH (kg) : > 7

(Min. DWL average side crush)

BULK DENSITY (kg/L) : 1.3 ± 0.05

SURFACE AREA (m^2/g) : 24 ± 5

PORE VOLUME (cm $^{3}/g$) : 0.22 ± 0.03

CHEMICAL ANALYSIS

% **ZnO** : 90 Min.

Mixed Oxides & Proprietary : Balance

Binders

It can be noted that DS-90 E type Catalyst has high Zinc Oxide content per unit volume, at the same time offering high surface area with rugged physical characteristics thereby making it a much superior catalyst.

^{**} The size can be made available as per specific requirement of customer.

DS-90 E-HS

FUNCTION: HIGH ACTIVITY DESULFURISATION CATALYST

APPLICATION : Removal of trace levels of H₂S, and

mercaptans from various gas streams from ambient temp. and above. Most suitable for

purification of Natural gas streams.

PHYSICAL PROPERTIES

FORM : Extrusions

SIZE** : 4mm, 5mm dia. ± 0.2 mm

(L/D = 1:1 to 3:1)

CRUSH STRENGTH (kg) : >7

(Min. average side crush)

BULK DENSITY (kg/L) : 1.15 ± 0.05

SURFACE AREA (m^2/g) : 40 - 55

PORE VOLUME (cm 3 /gm) : 0.22 ± 0.03

CHEMICAL ANALYSIS

% **ZnO** : 90 Min.

Mixed Oxides & Proprietary : Balance

Binders

^{**} The size can be made available as per specific requirement of customer.

DS-90 E-HSM

FUNCTION: HIGH ACTIVITY SULFUR REMOVAL CATALYST

APPLICATION : Removal of H₂S, mercaptans, trace levels of COS &

Mercury from various gas streams from ambient temp. & above. Most suitable from purification of Natural

gas streams.

PHYSICAL PROPERTIES

FORM : Extrusions

SIZE** : 4 mm, 5 mm dia. $\pm 0.2 \text{ mm}$

(L/D = 1:1 to 3:1)

BULK DENSITY (kg/L) : 1.15 ± 0.10

CRUSH STRENGTH (kg) : > 5

(Min. avg. side crush)

CHEMICAL ANALYSIS

% Mixed Metal Oxides : 90 Min.

Balance : Suitable Proprietary binders.

^{**} The size can be made available as per specific requirement of customer.

DS-90 T

FUNCTION DESULFURISATION CATALYST

APPLICATION Removal of trace levels of H₂S

> and Mercaptans from gas streams above operating temperature of 120°C; H₂S removal upto 400°C. Suited for Natural gas

streams and hydrogen plants. Superior

abrasion Resistance and very low pressure Drop.

PHYSICAL PROPERTIES

Tablets FORM :

SIZE 5 mm x 7.5 mm

CRUSH STRENGTH (kg) > 7

(Min. average side crush)

BULK DENSITY (kg/L) 1.15 ± 0.05

SURFACE AREA (m^2/g) 40 - 55

PORE VOLUME (cm³/g) 0.25 0.05

CHEMICAL ANALYSIS

% ZnO 90 Min.

Mixed Oxides & Proprietary: Balance

Binders

Note: DS-90 T, due to its ability to adsorb H₂S to high efficiency even at ambient (20°, 30°C) temperatures, it is recommended for services where fail-safe performance is required at lower temperatures than 350°C upto Ambient.

DSF-50

FUNCTION : DESULFURISATION CATALYST

APPLICATION : Removal of reactive sulphur compounds

such as H₂S and COS from hydrocarbon feed stock or gas streams from ambient

temperature with very high adsorption capacities.

PHYSICAL PROPERTIES

FORM : Cylindrical Pellets

SIZE : $5 \text{ mm dia } \times 7.5 \text{ mm ht.} /$

5 mm dia x 5mm ht.

CRUSH STRENGTH (kg) : > 10

(Min. average side crush)

BULK DENSITY (kg/L) : 1.15 ± 0.05

SURFACE AREA (m^2/g) : 40 - 55

PORE VOLUME (cm^3/g) : 0.25 0.03

CHEMICAL ANALYSIS

Specially prepared high activity Iron Oxide with suitable binders

DS-LHS

FUNCTION : DESULFURISATION CATALYST

APPLICATION : Removal of H₂S / COS / mercaptans,

Desulphurisation of liquid hydrocarbon streams to meet copper/silver strip test. Operating temperature from ambient to

230°C.

PHYSICAL PROPERTIES

FORM : Extrusions

SIZE : 4 mm, $5 \text{ mm dia} \pm 0.2 \text{mm}$

(L/D 1:1 to 4:1 long)

CRUSH STRENGTH (kg) : > 7

(Min. average side crush)

BULK DENSITY (kg/L) : 1.15 ± 0.05

SURFACE AREA (m^2/g) : 40 - 55

PORE VOLUME (cm^3/g) : 0.22 0.03

CHEMICAL ANALYSIS

Mixed Metal Oxides + Binders, proprietary compositions.

^{**} The size can be made available as per specific requirement of customer.

DS-85 E

FUNCTION : DESULFURISATION CATALYST

APPLICATION : Sulphur removal from

Hydrocarbon / Process gas

Streams.

PHYSICAL PROPERTIES

FORM : Extrusions

SIZE** : 5mm dia. \pm 0.2 mm

(L/D 1:1 to 3:1 long)

CRUSH STRENGTH (kg) : > 7

(Min. DWL average side crush)

BULK DENSITY (kg./Lt) : 1.3 ± 0.05

SURFACE AREA (m^2/g) : 24 ± 5

PORE VOLUME (cm^3/g) : 0.22 ± 0.03

CHEMICAL ANALYSIS

% **ZnO** : 85 Min.

Mixed Oxides & Proprietary : Balance

Binders

^{**} The size can be made available as per specific requirement of customer.

PART-B

OPERATING INSTRUCTIONS

I. LOADING AND UNLOADING OPERATIONS

The catalyst is supplied in stabilised condition and can be sock-loaded following standard procedure. Standard precautions of goggles, gloves and nose mask are sufficient for dust exposures during loading and unloading. Respirator and life-line rope are necessary for any person entering the process vessel and safety permit is required for man entry in the process vessel.

II. CHARGING OF THE REACTOR

Before loading the catalyst the reactor should be checked and cleaned and the grids inspected. Generally it is not necessary to screen the catalyst before loading. However, the drums should be examined for any possible damage suffered in shipping and handling. The catalyst may be charged either directly from the drums or by using a chute or filling pipe. In either case the free-fall of the catalyst of more than one meter should be avoided. Wooden boards should be placed on the catalyst for protection if it is necessary to walk on it. Generally it is not recommended that the top of the catalyst bed should be covered with a wire screen or inert material in order to prevent loss of catalyst by blowing or turbulence at high gas velocities that may occur during start-up or shut down of the plant. However, in case such an inert material is installed it should be resistant to the operating conditions.

III. START-UP / SHUT DOWN REQUIREMENTS

DS type catalysts do not require any pre-treatment or activation before start up. Usual precautions of purging the reactor free of air are required before any combustible gas is introduced. This catalyst can be heated upto operating temperatures with process gas (@ 50° C/hr) and condensation may be avoided. Uniform heating of process gas should be carried out and temperature difference between top and bottom bed should not be not more than 80° C. Since DS type Catalysts do not need any special precaution, it can be dumped after use only taking care that the reactor is freed of combustible gases by proper purging. While the catalyst is unloaded, care may be taken not to allow any personnel to enter the vessel without safety precaution especially because of presence of H_2S .

The unloaded catalyst can be stored in steel drums for dumping / disposal in licensed facility.

IV. STORAGE & HANDLING

FCCL's Catalyst is very durable. Prolonged exposure of catalyst to high humidity can lead to a significant decline in catalyst strenght. To guard this the catalyst is stored in ployethlyene lined airtight MS drums. If storage is required then it is advised that the drums to be kept in dry building. During storage it is strongly recommended that the drums are not stacked one above other.

Catalyst handling should be minimal since this lead to generation of catalyst fines. Operator should wear full face respirator and high protection to protect them from catalyst dust while loading. If contact is made with the skin, wash with soap and water.

V. START UP OF USED CATALYST

Used catalyst is always in a partially sulphided form i.e. as Zinc Sulphide and hence it is not recommended to use oxygen containing gases or air for heating of the catalyst.

VI. REGENERATION

Regeneration of Zinc Oxide Catalyst is not recommended since it is un-economical.

VII. PRESENCE OF STEAM IN 'S' BEARING GASES AND POISONS TO DS TYPE CATALYSTS

Presence of steam in gases will tend to bring down the sulphur adsorption capacity of Zinc Oxide catalyst. Zinc Oxide Catalyst has no known poison except that any sooty carbon carried into the catalyst can accumulate and cause high pressure-drops or channelling. Very low space velocity is some time harmful especially when the CO levels are very high in hydrogen which could cause methanation.

The rugged physical properties of DS type catalysts make it ideally suitable for systems where any excess pressure drops can be detrimental to plant operations and hence cannot be tolerated. In the same way, high pressure plants and plants having gases containing copious quantity of steam can also benefit from the rugged physical properties of DS type Catalysts.

If the feed gas contains chlorides, it is recommended to install a special chlorine guard upstream of the DS type Catalyst reactor. **Filtra** recommends its **FCR-91** Chloride Guard catalyst for such application.

VIII. STORAGE

FILTRA's DS type catalysts are delivered in 200 litre capacity Mild Steel drums with Polythene liner and having lock rim lids. This packing allows overseas shipment as well as storage for many years in a clean and dry atmosphere.

Excellence

through

Research...

FILTRA CATALYSTS & CHEMICALS LTD.