

# New Improved Dust Protection Catalyst

RESEARCH | TECHNOLOGY | CATALYSTS



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## 1. Introduction

The introduction in the seventies of the first dust protection catalyst, VK38 in the shape of 20 mm rings, provided invaluable savings for sulphuric acid plants suffering from pressure drop build-up as a result of dust present in the feed gas.

Industrial experience from more than 60 installations shows prolonged production campaigns by minimum 50-75%, and thereby reduction of time-consuming and expensive shutdowns for catalyst screening, as well as significant savings in blower energy over time.

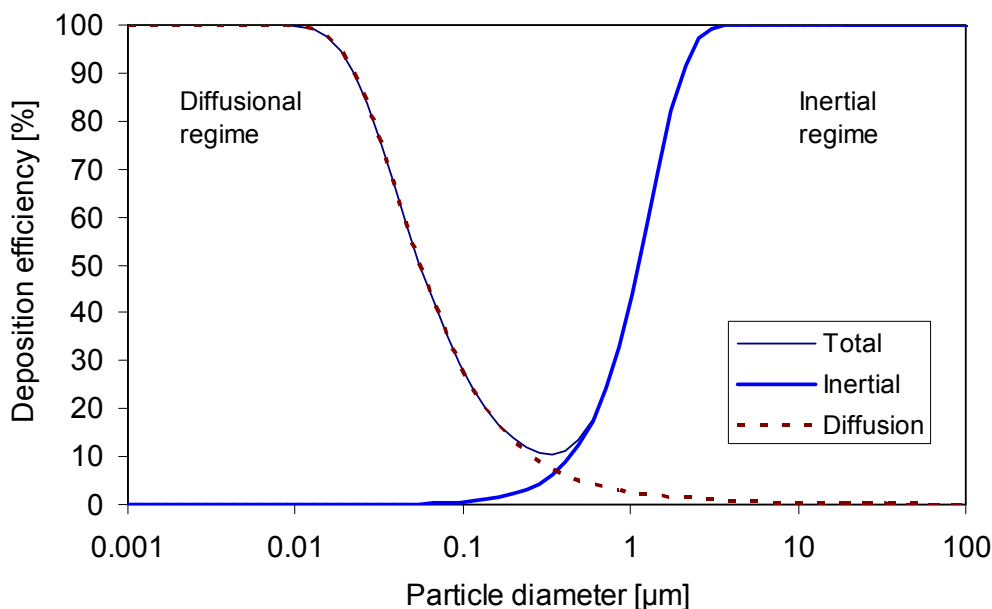
Topsøe now introduces a new, improved dust protection catalyst in the size of 25 mm Daisy, which provides 30-35% longer production campaigns due to the larger size and the higher void fraction compared with the 20 mm rings, without sacrificing catalyst activity.

## 2. Dust deposition in a fixed bed

Dust present in feed gases in sulphuric acid plants typically deposits and accumulates within the top 10-15 cm (4-6 inches) of catalyst in the 1<sup>st</sup> bed of the SO<sub>2</sub> converter [1, 2]. Depending on the dust concentration, particle size and catalyst loading this leads to a pressure drop build-up over time which eventually may cause a costly shutdown of the plant in order to screen the catalyst.

The dust typically originates from the sulphur feed in case of sulphur burning plants or from the roasting operation in case of metallurgical acid plants, but corrosion products from the cold end of the feed gas preheating will also deposit in the 1<sup>st</sup> bed. Under operating conditions the active phase of the sulphuric acid catalyst is a vanadium-containing alkali pyrosulphate melt distributed over the internal surface of the porous silica support. The efficient capture of dust in the catalyst layer is due to the stickiness of the catalyst surface resulting from the melt. Due to the capillary forces of the dust, some of the catalytic melt will also be extracted from the catalyst, and a crust may form at high dust loads in combination with possible acid carryover. Chemical analysis for e.g. Fe, Zn, Cu and Si in the dust may reveal its origin.

The two main mechanisms for deposition of dust particles in a packed bed are inertial impaction and diffusion [3-5]. Large particles deposit by interception or impaction due to their inertia which prevents them from following the tortuous path of the gas through the catalyst bed. Very small particles follow the gas streamlines but similarly to gas molecules they are transported by combined Brownian diffusion and turbulent diffusion. The latter arises from the turbulent eddies present in the catalyst bed, which is operating at Reynolds numbers 50-200. A theoretical prediction of the deposition efficiency for dust particles in a 1<sup>st</sup> bed is presented in Figure 1. Inertial forces remove practically all particles larger than 2 µm, while particles smaller than 0.03 µm are captured as a result of diffusion. The low removal efficiency in the intermediate size range shows that packed beds cannot generally be used for efficient dust or aerosol filtration, which is also known from the poor capture of fine acid mist (typically in the 0.1-1 µm range) in packed absorption towers.



**Figure 1.** Particle deposition efficiency in a packed bed of 10 mm catalyst pellets. Bed height: 1 m, Superficial velocity: 0.4 Nm/s (ref. 1 atm, 0°C), Temperature: 420°C

The size of dust particles in SO<sub>2</sub> gases depends completely on their origin. Mechanical abrasion, fragmentation and entrainment of inorganic dust (fly ash) or corrosion products in the gas flow tend to form particles larger than 10 µm that will be captured at the top of the 1<sup>st</sup> catalyst bed. Impurities present in liquid sulphur feeds, e.g. sulphur or spent alkylation acid, also end up as fly ash particles where the size is determined by the droplet size distribution in the spray combustion, since it can be assumed that each droplet leaves one residual ash particle. For example, if a spent acid feed containing 20 wt ppm Fe is atomized into 40 µm droplets, the resulting iron oxide particles will be about 1 µm and, consequently, penetrate much deeper into the catalyst bed. Very small particles <0.1 µm are typically formed from metals or metal oxides vaporized in high-temperature upstream processes and subsequently condensed by homogeneous nucleation caused by gas phase reaction or gas cooling. Since it is the dust volume that fills up the void for gas passage, the small particles, although sometimes present in high number concentration, will not contribute as much to the pressure drop build-up.

The theoretical prediction in Figure 1 assumes that once deposited the particles stay on the catalyst pellet corresponding to a zero particle concentration in the gas at the pellet surface. This assumption may be valid for the sticky sulphuric acid catalyst but not for dry and smooth pellets from which the dust may be rebound or deposited dust may be reentrained. This effect is clearly observed for industrial catalyst beds where the dust readily penetrates the ceramic bodies, often placed on top of the bed and deposits in the catalyst layer beneath.



Dust deposited in a 1<sup>st</sup> bed loaded with Topsøe 12 mm Daisy catalyst.

### 3. A predictive model for pressure drop build-up

For both inertial and diffusional deposition, the flux of particles to the catalyst surface is proportional to the particle concentration and to the specific external surface area of the catalyst bed  $S_A$  [ $\text{m}^2/\text{m}^3$  bed]. The change in dust concentration in the gas phase may accordingly be described by a 1<sup>st</sup> order differential equation

$$\frac{dw}{dx} = -k \cdot \frac{S_A}{u_s} \cdot w \quad (1)$$

where  $w$  is the gas phase dust concentration [ $\text{mg}/\text{Nm}^3$ ],  $x$  is the position from the top of the bed [m] and  $u_s$  is the superficial linear velocity based on empty reactor [ $\text{Nm}/\text{s}$ ]. The rate constant  $k$  [ $\text{m}/\text{s}$ ] depends on dust particle size, temperature and gas velocity.

If we assume that  $k$  is proportional to the linear gas velocity and inversely proportional to the void fraction and integrate (1), it leads to the dust concentration profile

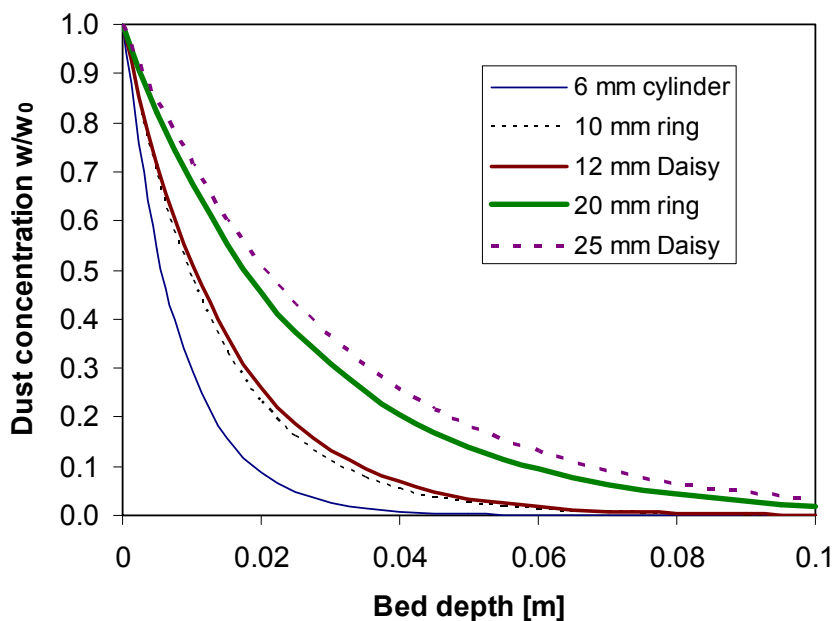
$$w = w_0 \cdot \exp\left(-k_g \cdot \frac{S_A}{\varepsilon} \cdot x\right) \quad (2)$$

where  $w_0$  is the dust concentration of the feed gas [ $\text{mg}/\text{Nm}^3$ ] and  $\varepsilon$  is the fractional voidage of the bed. The new rate constant  $k_g$  depends on dust particle size, catalyst stickiness, and dust

load in the bed. For the present study,  $k_g$  has been fitted to typical industrial observations of penetration depths for sulphuric acid catalyst beds. The dust capture for various catalyst sizes and shapes is determined by  $S_A/\epsilon$ , which is given in Table 1, and shown in terms of gas phase dust concentration profiles in Figure 2. The dust may be distributed over a greater depth by choosing larger pellets.

**Table 1.** The rate of dust deposition depends on  $S_A/\epsilon$  according to (2).  $d_{eq}$  is the equivalent pellet diameter.

Catalyst size	Relative $S_A$	Void fraction $\epsilon$	Relative $S_A/\epsilon$	$d_{eq}$ mm
6 mm cylinder	130	0.35-0.40	188	6.5
10 mm ring	100	0.48-0.52	110	7.1
12 mm Daisy	100	0.54-0.56	100	6.2
20 mm ring	53	0.48-0.52	58	13
25 mm Daisy	52	0.54-0.56	52	12



**Figure 2.** Gas phase dust concentration profiles in a 1<sup>st</sup> bed at 420°C

For more practical purposes it may be assumed that all dust in the gas is captured and distributed evenly in a top layer of catalyst of the height  $H_{dust}$  [m] calculated from (2) as the height in which 90% of the dust is deposited:

$$H_{dust} = \frac{\epsilon}{S_A \cdot k_g} \cdot \ln(10) \quad (3)$$

The pressure drop over a catalyst bed [Pa] can be calculated from

$$\Delta P = k_p \cdot \frac{1}{d_{eq}} \cdot \frac{1 - \varepsilon}{\varepsilon^3} \cdot H_{bed} \quad (4)$$

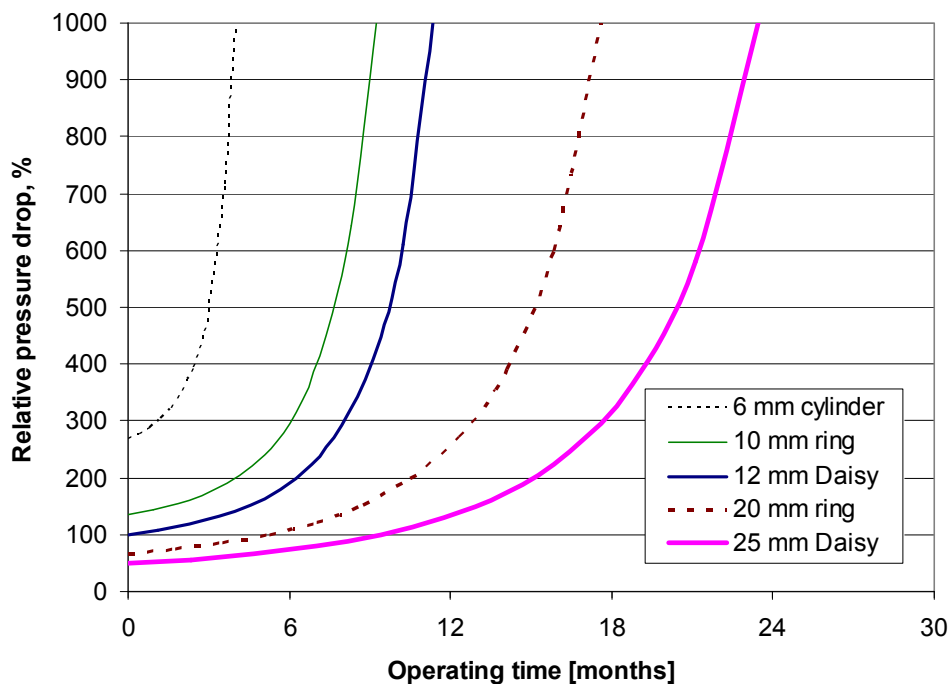
where  $d_{eq}$  is the equivalent pellet diameter [m] and  $H_{bed}$  is the bed height [m]. The proportionality constant  $k_p$  [Pa] depends on the velocity and properties of the gas. As dust deposits in the top layer, the void fraction is reduced according to

$$\varepsilon = \varepsilon_0 - \frac{u_s \cdot w_0 \cdot t}{\rho_{dust} \cdot H_{dust}} \quad (5)$$

where  $t$  is the time from last screening [s] and  $\rho_{dust}$  is the dust density [ $\text{kg}/\text{m}^3$ ]. The total pressure drop over the 1<sup>st</sup> bed is the combined pressure drops of the dust loaded layer (time-dependent) and the clean catalyst layers below.

#### 4. Development of a new dust protection catalyst

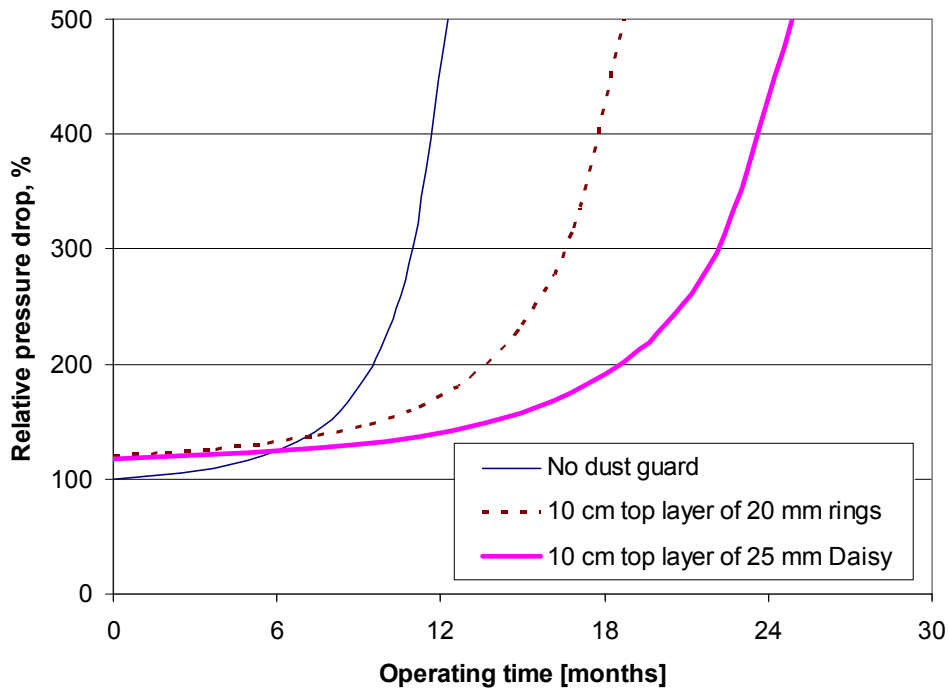
The desire to prolong production campaigns in sulphuric acid plants even beyond the possibilities offered with the 20 mm ring-shaped dust protection catalyst set the goals for development of a new improved Topsøe catalyst product. As a starting point, the model described above was validated against industrial experience for existing catalysts, for which good agreement between the model and industrial measurements of pressure drop development for the 1<sup>st</sup> bed was found. The rapid increase of pressure drop over the top 15 cm (6 inches) of a 6 mm cylindrical catalyst operating at high dust concentration is due to the high specific surface area and low initial void of the 6 mm pellets, cf. Figure 3. The delaying of pressure drop increase observed for 10 mm rings and more pronounced for the 12 mm Daisy is primarily caused by their higher initial void fraction. For larger pellets such as the 20 mm ring, the dust penetrates deeper into the bed, thus, postponing pressure drop build-up even further. The 90% and 55% longer production campaigns calculated for the 20 mm ring compared to the 10 mm ring and the 12 mm Daisy, respectively, are confirmed by feedback from more than 60 industrial installations of the 20 mm ring.



**Figure 3.** Pressure drop increase within the top 15 cm catalyst due to dust deposition.  $u_s=1500$  Nm/h,  $w_0=0.8$  mg dust/Nm<sup>3</sup>,  $\rho_{\text{dust}} = 800$  kg/m<sup>3</sup>

A number of new improved catalyst sizes and shapes were subsequently evaluated by the model, and it was found that a new 25 mm Daisy in an excellent way combines the advantages of a large sized pellet and a high-voidage shape, cf. Figure 3. The effect of installing a 15 cm (6 inches) dust protection catalyst layer on top of 0.6 m 12 mm Daisy is illustrated in Figure 4. The initial pressure drop is a bit higher due to the extra 15 cm catalyst but as the dust accumulates, the 25 mm Daisy shows its superior dust capacity enabling 30-35% longer production campaigns when compared with 20 mm rings or a doubling when compared with 12 mm Daisy. The typical dust loading capacity per m<sup>2</sup> reactor cross section, before the pressure drop reaches a critical limit, is around 10 kg/m<sup>2</sup> for the 12 mm Daisy, 16 kg/m<sup>2</sup> for the 20 mm ring, and 20 kg/m<sup>2</sup> for the new 25 mm Daisy.

The manufacture of the 25 mm Daisy was finally demonstrated and optimised in a full-scale production in our factory. Compared to the 20 mm ring, the new dust protection catalyst has the same catalytic activity and mechanical strength measured by side crush strength, drop test and attrition loss as the 20 mm ring, however, the initial pressure drop is 25-30% lower. This new product is now ready for industrial installation.



**Figure 4.** Effect of installing a top layer of the 25 mm Daisy dust protection catalyst.  $u_s=1500$  Nm/h,  $w_0=0.8$  mg dust/Nm<sup>3</sup> and  $\rho_{dust} = 800$  kg/m<sup>3</sup>

## 5. Conclusion

The sensitivity to plugging and pressure drop build-up in a catalyst bed depends on the bed void and how the dust is distributed. The penetration depth increases with the size of the catalyst particles because the specific surface area is lower. Topsøe has developed a new, improved dust protection catalyst in the shape of a large 25 mm Daisy. This new super Daisy catalyst combines the effect of a larger void fraction for higher dust capacity and the effect of a lower specific surface area for improved dust distribution. Installation of a 10-15 cm (4-6 inches) top layer in the 1<sup>st</sup> bed results in 30-35% longer production campaigns when compared with 20 mm rings, or a doubling when compared with 12 mm Daisy. Yet catalytic activity and mechanical strength are the same as for the classical 20 mm rings.



The 25-mm super Daisy is the third member of Topsøe's Daisy family which also includes the well-known 12 mm and 9 mm mini Daisy.

## References

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