# Grading & Guard Materials

**MAXIMUM CATALYST PROTECTION AND OPTIMUM PRESSURE DROP MANAGEMENT**

## INTRODUCTION

With the increased levels of heavy and non-conventional crude oils in the refinery diets, state-of the art catalysts need state of the art Grading and Guard Materials to create the best working environment mitigating pressure drop and eliminating contaminants.

Cycle length of a Hydroprocessing unit is typically controlled either by the catalyst activity (*maximum allowable working temperature*) or by the reactor pressure drop (*maximum allowable pressure drop*). Therefore, optimum Grading and Guard Materials system is definitely part of the success of a catalyst load allowing its maximum usage.

Based on its large experience and expertise, Axens has developed a large portfolio of products that address complex issues from dramatic pressure drop build-up to the severe catalysts poisoning. Axens has also developed enhanced diagnosis tools that allow proposing cost-effective solutions to our clients.

## PRESSURE DROP MANAGEMENT

In Hydroprocessing reactors, pressure drop is mainly induced by particulates build-up and gum formations. Pressure drop not only affect the capacity of the unit but can also have detrimental impact on the distribution.

Particulates have various origins:
- Iron scales
- Iron sulfides
- Coke fines (from coker products…)
- Catalyst fines (from FCC products…)
- Sediments
- Salts, etc.

Proper feed filtration system should be able to remove most of these particulates contained in the feed. However, scales from the unit equipment or particulates formed within the unit itself (iron sulphide, coke and in some cases clays) have to be handled by a dedicated grading.

This grading must be designed to ensure the maximum retention while minimizing the pressure drop. Therefore a proper arrangement of high void fraction materials with decreasing size, various porosities and surfaces, increased activities must be put in place.
The key challenge is to ensure that the refiners will be able to minimize the catalyst activity give away due to pressure drop build-up (*Figure 1*).

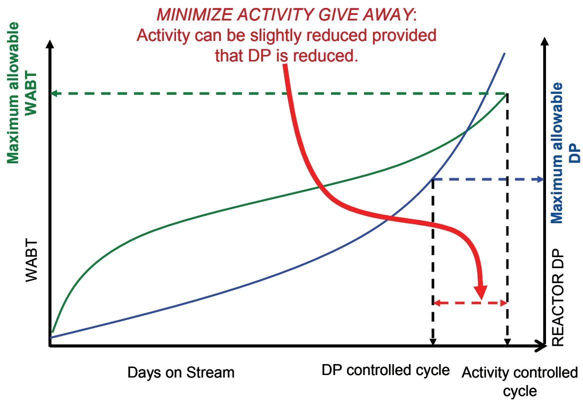



*Figure 1 - Catalyst activity give away due to pressure drop build-up*

Based on Axens' expertise and customer feedback from previous runs, a customized grading system has been proposed to refiners to handle the high levels of particulates that were mining the operation of this specific unit (CFHT / VGO HDS). This new grading system allowed increasing the unit cycle by **30% at** constant feed rate and quality while taking the full benefits of the catalyst activity (*Figure 2*).

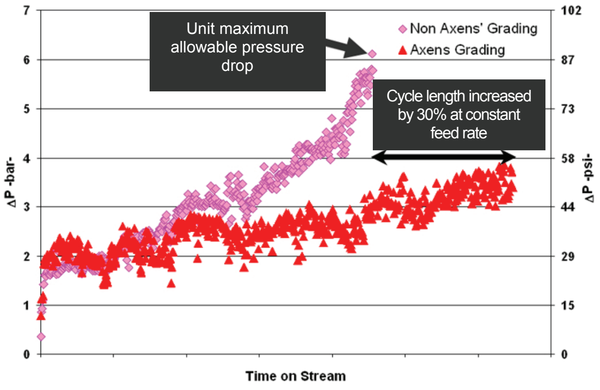



*Figure 2 - Unit performance improvement with Axens' grading - CFHT*

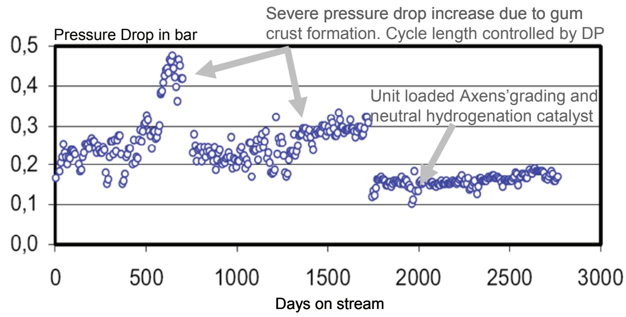



*Figure 3 - Example of unit operation improvement with Axens' grading (NHT co-processing 25% of Coker Naphtha)*

### *Iron sulfides removal*

For iron sulfides removal, Axens has developed a dedicated grading that allows a large trapping of the micronic iron sulfide particles.

As an additional tool to solve pressure drop problems, for the most difficult services where levels of particulates in the feed are extremely high and cycles short, Axens can offer reticulated ceramics. These reticulated ceramics have a significant tortuosity and a high internal volume which result in a high trapping efficiency as well as a very large storage capacity.

### *Gums management*

Pressure drop induced by gum formation is frequently encountered in unit processing some cracked feedstock derived from various conversion processes. The olefins and mainly the diolefins contained in these streams tend to polymerize and get oxidized forming a crust which deposit in the upper layers of the reactor.

Axens has developed specific gradings, with neutral support and medium activity, to ensure the full hydrogenation of the olefins and diolefins while minimizing the risk of polymerization.

| Product | Main Characteristics |
|---|---|
| ACT 068-069-070-072 | Pentarings |
| ACT 077 | Fluted ring – Macroporous Alumina Iron Trap |
| ACT 078 | Fluted ring – Ceramic |
| ACT 108 | Ring – Ceramic |
| ACT 139 | Macroporous Alumina beads Iron Trap |

*Table 1 – Inert grading and Scale Traps*

| Product | Main Characteristics |
|---|---|
| ACT 935 | Active alumina ring.<br>Scale trap and diolefins & olefins saturation |
| ACT 945 | Active beads on neutral support.<br>Dedicated to PYGAS service |
| ACT 955 | Active extrudate on neutral support.<br>Diolefins & olefins saturation – Shape Grading |

*Table 2 – Active grading – Gum formation prevention*

## CATALYST CONTAMINANTS MANAGEMENT

Due to the more and more stringent product specifications, the decline of the "good old" sweet crude, the increased numbers of cokers and other conversion processes in the refineries, hydroprocessing is no more an easy game.

While hydroprocessing resembles more and more to fine chemistry with in some cases level of sulfur conversion above 99.5%, the feeds contain more and more contaminants. To achieve this high level of performance, the latest generations of catalysts are required. The most severe services need dedicated Guard Material designed to remove and trap the contaminants (Ni, V, As, Si, Na …) that are detrimental to catalysts performance.

Catalyst pollution is easily manageable provided that information on the nature of poisons in the feed is well known (which is often a difficult issue). Detailed spent catalyst analysis (along with accurate sampling) is of the utmost importance when developing strategies to control contaminants and extend catalyst life. Axens has also developed analytical tools that allow precise analyses of the species present in the feed.
Proper protection of the catalyst is mandatory not only to extend cycle length but also to ensure that most of the main Hydrotreating catalyst can be fully regenerated.

Catalysts contaminants are mainly in the form of organo-metallic compounds. They can be present in the crude itself or can be introduced during the crude production, transportation or processing in the refinery.

| | | | |
|---|---|---|---|
| **Silicon** | Coker products & Flow | Mainly coker Naphtha. Found also in Heavier | + |
| **Arsenic** | Crude Oil | Mainly in VGO+ and in derived products | +++ |
| **Nickel & Vanadium** | Crude Oil | VGO+ | ++ |
| **Sodium, Calcium** | Mainly desalters upsets | All cuts | ++ |
| **Iron** | Corrosion products | All cuts | + |

*Table 3 – Most common catalysts contaminants*

### *Arsenic Management*

Arsenic is by far the most severe poison. Arsenic is present naturally in some crudes.

Arsenic, if present, is mainly found in the heavier fractions (VGO ~ 25 to 350 wppb; Residue > 300 wppb) and in the lighter fractions of the cuts issued from heavy oil conversion units (up to 100 wppb). To some extent Arsenic can also be found in LPG and Gas Condensates.

The maximum allowable content on hydroprocessing catalysts during operation, depending upon the service, is in the range of hundreds of wppm. The maximum allowable level of Arsenic on catalyst after regeneration is 1,000 wppm.

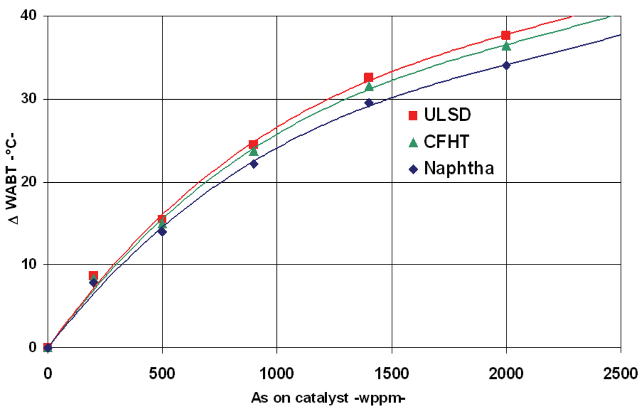



*Figure 4- Impact of Arsenic on Hydroprocessing catalysts (typical)*

Arsenic organic compounds are very reactive. They interact mainly with the active phase. In fixed bed reactors, under normal hydroprocessing conditions, a steep gradient is usually observed.
The key features for arsenic trap are:

| | |
|---|---|
| **Dedicated Support** | Maximum Arsenic Retention |
| **Dedicated Active Phase** | Maximum Arsenic removal activity (hydrogenolysis) while maintaining high HDS & HDN activity. |
| **High Density** | Maximum Volumetric retention |

*Table 4 – Arsenic trap key features*

Axens' arsenic traps, ACT 979 and ACT 989, have been developed to meet these key properties.

| Product | Application | Main Characteristics |
|---|---|---|
| **ACT 979** | FCC Naphtha | High Retention & Low Olefins saturation Activity |
| **ACT 989** | All other HDT applications | High Retention & High Hydrotreating Activity |

*Table 5 – Axens' Arsenic Trap Portfolio*

The following example show the benefits in terms of reduction of the deactivation rate brought by Axens' arsenic trap in a Naphtha HDT unit contaminated by arsenic originated from Ural crudes (*figure 5*).

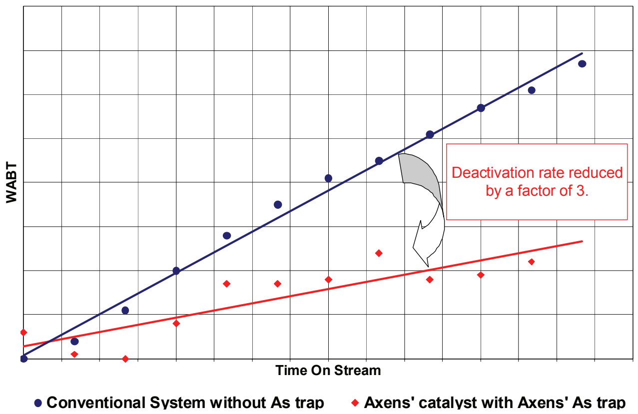



*Figure 5 – Cycle length improvement with Axens' arsenic trap*

The second example demonstrates the high level of protection reached with ACT 989 in a Diesel HDT unit (20 wppb arsenic in the feed) that allowed full regeneration and reuse the main catalyst (*Table 6*).

| Catalyst | Arsenic, w% |
|---|---|
| ACT 989 | > 4 w% |
| ACT 955 | 1,000 wppm |
| HR 626 – Main Catalyst | < 500 wppm |

*Table 6 – Main catalyst protection with Axens' arsenic trap*

### *Silicon Management*

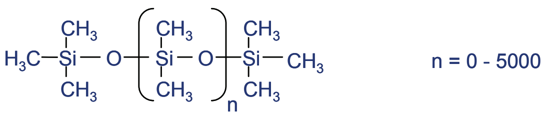
Thanks to its unique properties, silicones are used from upstream to downstream. In upstream their properties make them suitable for use as drilling fluids, flow improvers whereas in refining, silicones are used as antifoaming agents in delayed cokers, solvent desalphalting units and solvent extraction units.

The benefits of silicones end at the Hydrotreater battery limit.

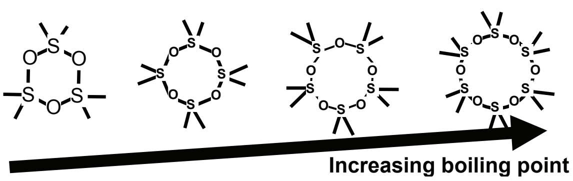
Silicon is a well known widespread poison for hydroprocessing catalysts. The main contributor to silicon is the Delayed Coker (this becomes a key issue with the increased number of cokers in operation). Also, there is a general tendency in the oil production industry to use more silicon based flow improvers.

Silicon is found in the form of:

- **Polydemethylsiloxane – PDMS**




- **Cyclic siloxanes** (thermal decomposition products in the coker)




- **Clays** (mainly when dealing with Oil sands – not harmful for the catalyst but significant source of pressure drop)

| Streams | Typical Silicon level |
|---|---|
| Coker Naphtha | Up to 10 wppm |
| Light Coker Gas Oil & Heavy Coker Gas Oil | Up to 5 wppm (when high viscosity antifoaming agent is used) |
| VGO & Heavier | Up to 10 wppm (when flow improver is used in the crude transportation) |
| Waste lube oils | Up to 100 wppm |
| FCC Gasoline | Up to 1 wppm |
| Pyrolysis Gasoline | ~ 0.1 wppm |

*Table 7 – Typical level of Silicon in Hydrocarbon streams*

Deposition of silicon on catalysts is temperature dependent. Whereas silica fragments condense on the catalyst alumina surface in a kinetically controlled way, temperature increase also promotes the hydrogenolysis of Si-C carbon bonds present in the feed on active phase and as a result, silicon is dispersed throughout the catalyst surface but also on the active sites. Silicon builds-up on the catalyst, leads to decrease of access to the active sites and by extent to a cycle reduction.

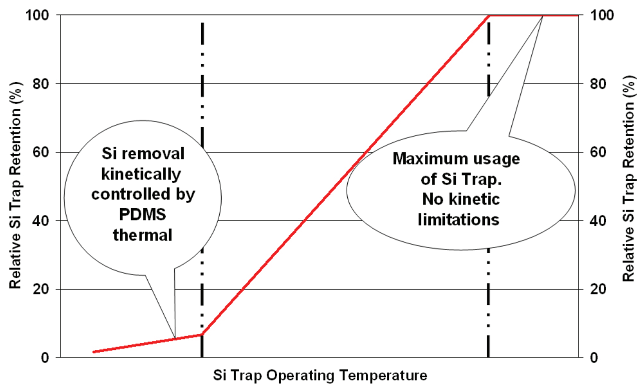



*Figure 6 – Si trap operating window*

Silicon poisoning is not only an issue for hydrotreating catalysts. Contamination of reforming catalysts may also occur as silicon breakthrough from naphtha hydrotreaters. Axens can propose specific strategies to control this contamination.

The key features for silicon trap are:

| | |
|---|---|
| **High Surface Area** | Maximum Si retention |
| **High Density** | Maximum Volumetric retention |
| **Optimized active phase** | Trade-off between Si pick-up & HDS activity |
| **Tuned pores structure** | Minimum diffusional limitations |

*Table 8 –Silicon Trap key features*

Axens' portfolio of silica traps (ACT 971, ACT 981, ACT 991) meet all these stringent requirements.

| Product | Application | Main Characteristics |
|---|---|---|
| **ACT 971** | Naphtha & Diesel | Very High Retention / Medium Activity |
| **ACT 981** | Naphtha & Diesel | High Retention / High Activity |
| **ACT 991** | VGO & DAO | Optimized pores structure for heavy feeds |

*Table 9 – Axens Silicon Trap Portfolio*

In terms of performances, the following canister data clearly demonstrates that in Naphtha & Diesel service, Axens' ACT 971 and ACT 981 outperform the market reference.

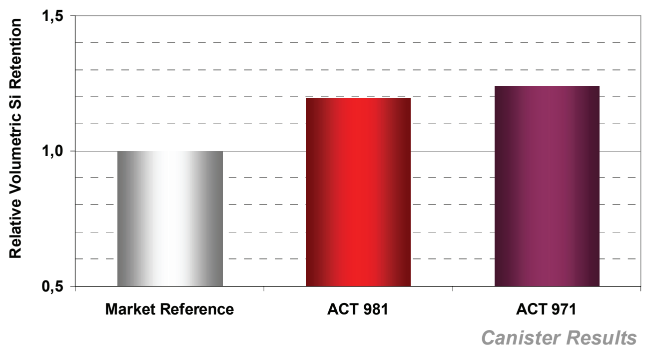



*Figure 7 – ACT 981 & 971 relative performance*

### *Nickel & Vanadium Management*

Nickel and vanadium are naturally present in Crude Oil and usually in fractions boiling over 500°C. Nickel and vanadium poisoning affect only VGO and resid hydrotreaters and hydrocrackers. Specific systems (Hyvahl™, PRS™) and catalysts have been developed by Axens for years to handle metal contamination in residues.

Typically, the maximum level of nickel and vanadium allowable on VGO hydrotreating catalysts is in the range of 3 to 5 wt%.

Because of the specific structure of the large molecules (porphyrin) containing nickel and vanadium specific demetalization catalyst must be used.
Axens' demetalization catalyst, HF 858, is the catalyst of choice to extend cycle length in VGO hydrotreaters as shown in this example where unit cycle length have been considerably extended following the loading of Axens' demetalization catalyst.

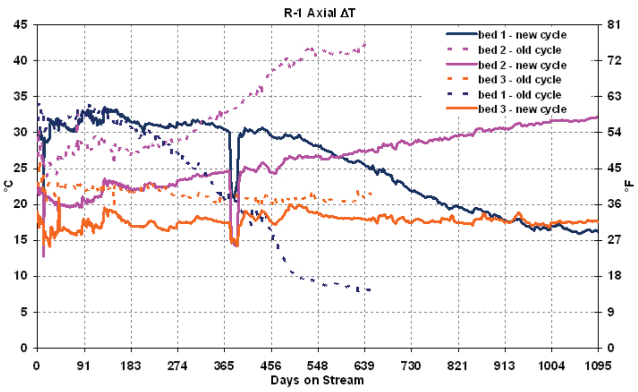



*Figure 8 – Si trap operating window*

In the case of resid hydroprocessing, the HF 858 catalysts combined with other products from the HF and HM series enable very high metal removal activity and very high metal retention. The maximum uptake of nickel + vanadium allowable on the hydrodemetalization catalyst can excess 100 wt%.

## HIGH EFFICIENCY DISTRIBUTOR TRAY EQUIFLOW®

Optimum usage of grading and catalyst in the reactor requires an even distribution of the fluids. EquiFlow distributor trays and quench boxes are industrially proven solutions enabling a nearly perfect distribution within the reactors.

Optimum grading arrangements downstream of distributor trays have been studied through extended pilot plant experiments.