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Increasing profit in hydrocracking and diesel hydroprocessing

A drop-in catalyst for hydrocracking pretreat and distillate hydrotreating raises activity with heat management savings

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Increasing profitability is a key question addressed regularly by refiners, particularly in recent times. In hydroprocessing terms, and recognising that energy transition will mean limited scope for new build, increasing profitability will focus on a simple question: "How can we do more with the facilities we already have?" An answer to this question will certainly focus on selecting the right catalyst solutions for use in an existing refinery kit. Including Celestia catalyst in a catalyst system is a drop-in opportunity to improve unit profitability.

A refinery's net profitability is determined from a balance of controlling opex in several dimensions: feed costs, energy use, and use of utilities. The goal is to drive to the highest margin for the amount of energy use. Older refineries may be processing feeds that are substantially different in quality from the original design. This can lead to units operating at lower utilisation, or at higher energy use to meet a sub-optimal product slate. The choice to include new capital to improve the operating efficiency is rarely justified, particularly in the current environment, thereby leaving the refinery margin also at sub-optimal levels. What if there is another way to unlock performance in existing equipment?

Celestia catalyst is a novel bulk-metal catalyst co-developed by Albemarle and ExxonMobil. The goal of the catalyst design was to drive catalyst activity to new heights to enable new use of existing equipment in ExxonMobil's refineries. This continues a trend from 2000s with the Nebula bulk metal catalyst. Celestia catalyst was first commercialised in 2015 in a light feed hydrocracker and improved the unit profitability via a number of captured margin advantages. The catalyst has since been deployed in 15 process units in North America, Europe, and Asia Pacific, demonstrating outstanding hydroprocessing activity on light and heavy feeds, implemented across a range of hydroprocessing platforms, and providing in each case a clearly defined opportunity for increased profitability.

This article describes the Celestia catalyst, reviews three case studies where Celestia catalyst was deployed successfully, and illustrates how its applications can contribute to significantly improve economic outcomes from a hydroprocessing unit or hydrocracker. The case studies illustrate how application of Celestia technology in distillate hydrotreating, and light cycle oil (LCO) and vacuum gasoil (VGO) hydrocracker pretreat applications has yielded exceptional margin and operating expense returns.

Celestia catalyst

The catalyst's performance is brought about by increased hydrodesulphurisation (HDS), hydrodenitrogenation (HDN) activity achieved through a unique design. The catalyst is a bulk-metal design synthesised almost entirely from the active metals needed for hydroprocessing activity. This enables much higher activity than conventional catalyst, more than twice the volumetric activity of leading NiMo catalysts. Moreover, Celestia catalyst's advantage arises from strong hydrodearomatisation (HDA) activity that has been demonstrated at over 2.5 times the level expected from leading NiMo catalysts. Adding Celestia catalyst to a catalyst load brings a high degree of activity improvement and will improve performance significantly even where it forms less than 10% of the reactor volume.

Defining the opportunity

Profitability can have many dimensions, and examples where Celestia catalyst provides value include:

- Improve margin via feed basis change: increase feed rate, process less expensive and more refractory feed components.
- Improve margin via improved product quality and yield: lower product sulphur or nitrogen, lower product total aromatics, increase volume swell, improve cetane and cloud properties, and improve conversion.
- Reduce operating expense: stretch a unit cycle length, eliminate a unit shutdown to coordinate with refinery wide shutdown planning.
- Reduce energy consumption: change the reactor temperature profile to reduce inlet temperature, or/and increase outlet temperature, leading to reduced energy consumption.

Heat release management and energy sparing

Adding significant activity to the reactor does come with additional considerations. Hydroprocessing reactions are generally exothermic in nature and lead to temperature rises in the reactor catalyst beds. Celestia catalyst is certainly more exothermic than other catalysts and the catalyst temperature rise needs to be managed to ensure process and product quality control, and to minimise catalyst deactivation.

ExxonMobil has developed mitigation strategies to manage safely the operation of the catalyst. Mitigations used to control catalyst temperature rise include:

- Splitting the Celestia catalyst load between beds to limit the temperature rise per bed.
- Increasing inter-bed quench gases. Cold quench gases are introduced between catalyst beds and mix with the hot liquid and vapour exiting the bed above.
- Changing the reactor temperature control strategy to increase the ascending temperature rise axially in the reactor, accomplished by reducing the reactor inlet temperature, or increased outlet temperature, or both.
- Limiting the start-of-run operation to lower reactive feeds over one or two weeks during the catalyst line out period.

Placement of Celestia catalyst is a critical component to the catalyst stacking design, and typically it would be loaded in mid to lower catalyst beds. This strategy allows the catalyst to work efficiently, removing the more refractory sulphur and nitrogen species, and enhancing aromatic saturation.

A hydroprocessing unit configuration (hydrocracker or hydrotreater) and design will vary with core business purpose. While Celestia catalyst is an enabling influence to improve profitability, the extent of the gain in opportunity will depend on the unit configuration and facilities design.

Implementation pathways and case studies

Considering the above, the approach taken to achieve opportunities for profitability in 15 applications to date has broadly fallen into one of the two implementation pathways:

1. Optimising Celestia catalyst load to predefined equipment limitations: in this case, the catalyst load is maximised within the unit facilities capability and design. Improved outcomes created by Celestia catalyst will also be variable but generally complementary to the process unit's economic targets, and also can generate value across the site's business.
2. Optimising Celestia catalyst load to achieve a predefined process objective: in this case, the load is prioritised, determined to achieve process advantage and economic objectives. The application may require limited investment to fully mitigate heat release, heat integration, or hydraulics impacts.

Each of the value creation opportunities illustrated has been realised by incorporating Celestia catalyst into a reactor load. They are illustrated by the three following case studies.

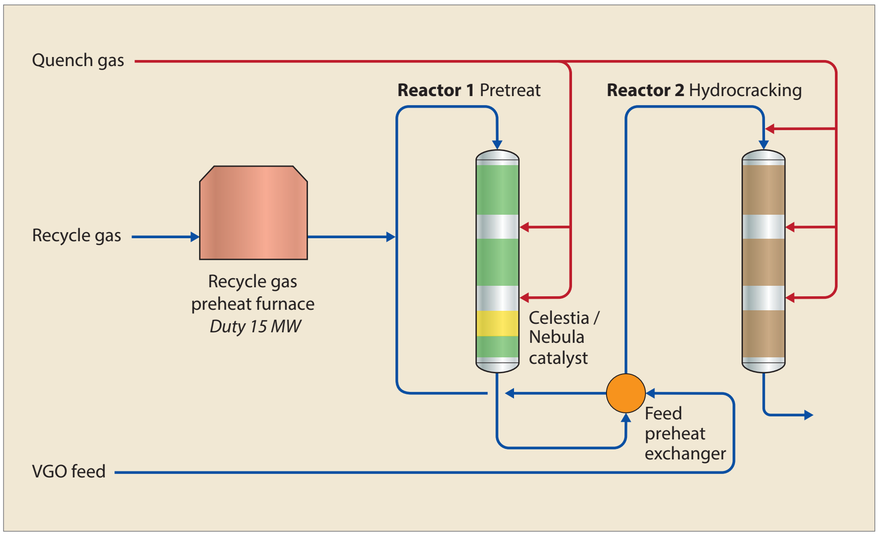

Figure 1 Once-through hydrocracker configuration

Case 1: Increased feed margin and reduced energy consumption in a VGO hydrocracker

The first case study begins with a once-though VGO hydrocracker application that converts a heavy VGO feed to clean fuels and steam cracker feed. The unit comprises a two-series reactor system (pretreat and cracking reactors), with recycle gas and hydrogen make-up gas. The reactor feed is preheated against cracking reactor effluent in several heat exchangers, with the final shell preheating against the inter-reactor stream. This exchanger is bypass controlled to achieve the cracking reactor inlet temperature required for the unit conversion. A furnace provides external energy to preheat the combined hydrogen gas stream which is blended with the feed prior to entering the pretreat reactor (see **Figure 1**). The reactor inlet temperature controls the degree of furnace firing required.

A 1:1 Celestia/Nebula catalyst system was loaded into bed 3 of a three-bed pretreat reactor. This replaced a Nebula/NiMo catalyst load used in the prior cycle. The process objective achieved by the Celestia catalyst addition was to increase margin by maximising the rate of a refractory heavy coker gasoil processed in the mixed VGO feed. The Celestia catalyst load met the economic objectives, more than doubling the heavy coker gasoil feed processed compared with the prior cycle while reducing the nitrogen slip to the hydrocracking catalyst beds. Celestia catalyst improved product qualities and demonstrated high aromatic saturation and HDN, which boosted the cracking catalyst's functionality and led to sustained conversion levels. Celestia catalyst also improved the density of the export unconverted oil stream, providing economic credit to a partner refinery steam cracker.

An energy consumption credit was not originally included in the economic forecast for deployment of Celestia/Nebula catalysts, but the Celestia catalyst's impact enabled significant value to be captured from reduced furnace firing. The reactor operates an ascending temperature profile; the reactor inlet temperature and the beds 1 and 2 temperature profiles were similar to the prior cycle. Loading Celestia catalyst increased the bed 3 exotherm from 8°C in the prior cycle to 15°C when processing a similar feed rate. The higher temperature rise was mitigated by increasing quench flow above the catalyst bed such that the inlet temperature to bed 3 was lowered by 4°C, and the reactor outlet temperature increased by 4°C. The inter-reactor exchanger hot side (total reactor effluent) has a higher mass flow than the cold side (feed only). Increasing the hot side exchanger inlet temperature by 4°C increased the feed side outlet temperature by 7°C, and the exchanger duty by 1.7 MW. With Celestia catalyst loaded, the furnace duty reduces from 16.7 MW to 15 MW, a net reduction of 10% firing and energy consumption.

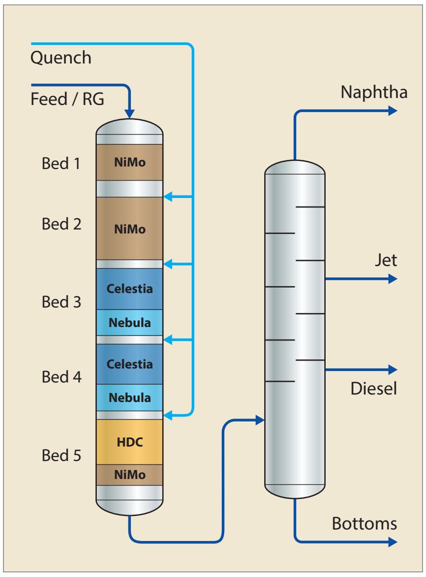

Figure 2 VGO hydrocracker reactor configuration

Celestia catalyst's stability in a challenging VGO service has been proven to be outstanding, and the exotherm advantage at start of run has been maintained throughout the run, allowing sustained energy cost savings throughout the cycle.

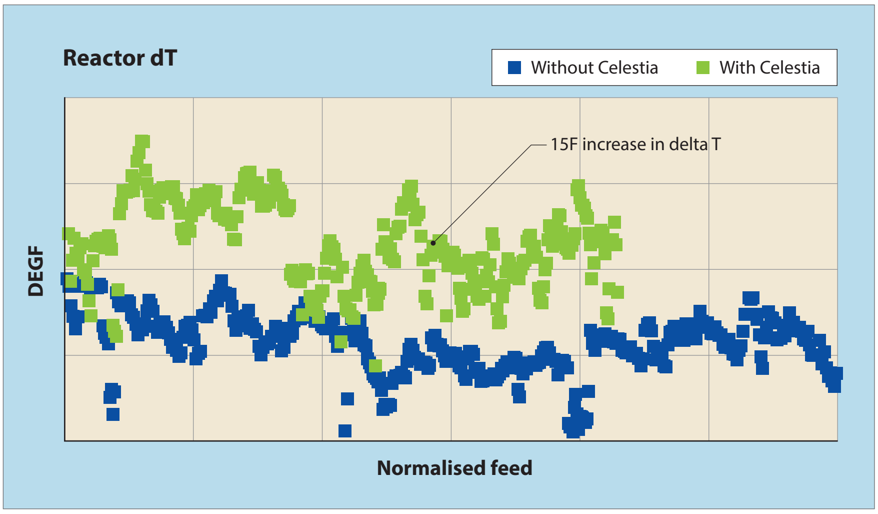

Figure 3 VGO hydrocracker reactor exotherm

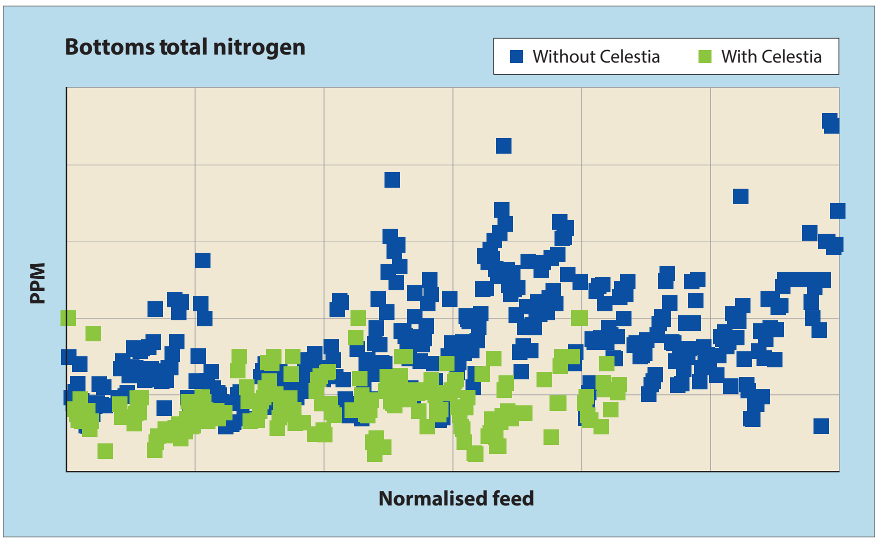

Figure 4 VGO hydrocracker product nitrogen

Case 2: Stretched VGO hydrocracker cycle length and improved product qualities

The second case study focuses on another VGO hydrocracker where the unit had been previously debottlenecked to nearly twice the original design capacity. The refinery identified a significant opportunity to extend the cycle length and coordinate with other units' shutdown planning, and avoid derating unit capacity at end of run.

Celestia catalyst was loaded in a split configuration with Nebula catalyst in two catalyst beds in a five-bed VGO hydrocracker pretreat reactor (see **Figure 2**). The catalyst load replaced a Nebula/NiMo catalyst load in the prior cycle to achieve a process objective of stretching the unit cycle length by 60% and, in doing so, eliminating a planned full hydrocracker shutdown and catalyst change that would be required to coordinate with the wider plan for refinery unit shutdown, equivalent to a 25% reduction in annualised operating expense.

To achieve these goals, a significant amount of Celestia catalyst was needed to boost the overall pretreat activity by about 130%. Load optimisation required detailed kinetic and process modelling to define the load plan accurately, and to carefully plan the increased temperature rise in the catalyst beds to achieve multiple process objectives. Optimisations and mitigations were applied in the Celestia catalyst load design, including increasing the ascending temperature profile to achieve product quality and run length target:

- Balanced the Celestia catalyst and Nebula catalyst load in two separate beds to provide the additional activity required, and limit the temperature rise in each bed.
- Lowered the reactor inlet temperature by 12°C, while maintaining the reactor outlet temperature constant compared to the prior cycle.
- Adjusted the quench gas supply to manage the reactor temperature

profile and lower the overall reactor weighted average bed temperature (WABT) by 10°C, to meet the target of run length extension (see **Figure 3**).
- Set the quench gas supply to the catalyst beds to allow an overall 8.5°C higher temperature rise and simultaneously matching the interface temperature required into the hydrocracking catalyst in bed 5.

The key impact of the combined load of Celestia/Nebula catalysts was to drive increased aromatic saturation and lower product nitrogen (see **Figure 4**) at lower reactor WABT (see **Figure 5**). The lower nitrogen slip to the hydrocracking beds improved cracking catalyst functionality and drove higher volume swell with a 1 vol% yield improvement compared to the prior cycle.

The significant reduction in reactor inlet temperature, while maintaining similar outlet temperature, improves the heat integration system and results in 5% lower furnace firing energy requirement. This advantage is sustained for most of the cycle; capturing the energy credit is a critical component in assessing the opportunity for extra value.

Minor modifications to debottleneck the reactor quench gas supply and off-gas purge capacity were implemented during the unit catalyst change; this was required to manage catalyst temperature control to process quality and cycle length targets.

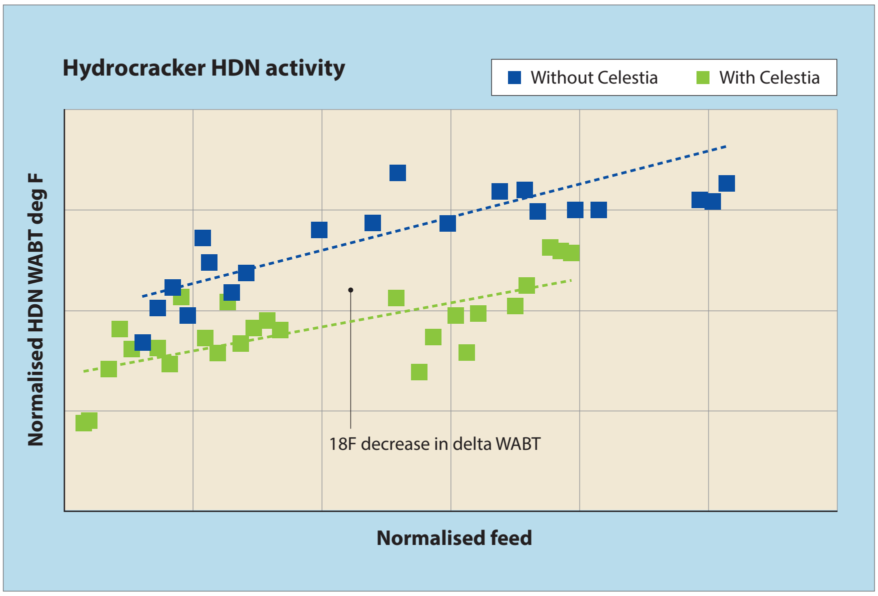

Figure 5 VGO hydrocracker normalised WABT

Case 3: Increased distillate hydrotreater feed rate and improved product qualities

The third case study focuses on a high pressure distillate unit, one of three distillate units in the refinery that supply product to a 10 ppm ULSD combined diesel pool.

Celestia catalyst was loaded in stack with NiMo catalyst in bed 4 of the four-bed high pressure distillate hydrotreater. The unit operates as two parallel reactors processing equal feed rate and quality (see **Figure 6**). The distillate products from each reactor are combined prior to stabilisation and blending into the site diesel pool. The Celestia/NiMo catalysts load replaced an all-NiMo catalyst load in the previous cycle. The process incentive achieved by Celestia catalyst included 14% feed rate creep, coupled with feed heavy-up, while generating improved product quality and maintaining a cycle length of 2.5 years. A key benefit achieved was the net lower sulphur in the ULSD product, which created a blending opportunity.

Celestia catalyst load design was optimised by detailed process modelling to fit within the existing unit's capability for heat release management. Celestia catalyst was determined to be 25% of bed 4's volume, and 8% of the total active catalyst load. Optimisations and mitigations applied in the catalyst load design included the following:
- Detailed modelling was completed to set the maximum Celestia catalyst load that could be accommodated without investment in compression and/or hydraulics.
- The feed heavy-up and increased feed rate led to an overall reduction in the reactor start of run exotherm. The reactor inlet temperature and WABT remained approximately constant compared to the prior cycle.
- Overall quench flow also remained constant compared to the prior cycle, but the quench gas split was redistributed with increased quench rates to beds 3 and 4 to counter the higher heat release generated by Celestia catalyst in bed 4. As a result, the bed 4 temperature rise increased by 5°C compared to the prior cycle, and the reactor outlet temperature increased by 6°C compared to the prior cycle (see **Figure 7**).

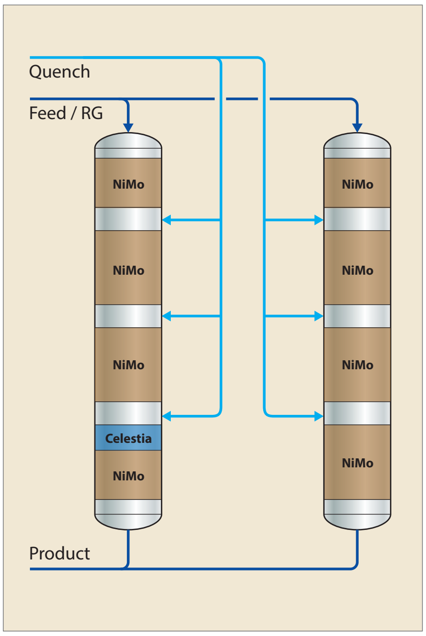

Figure 6 Celestia catalyst application in a distillate hydrotreater

Celestia catalyst improved the unit HDS activity (see **Figure 8**) and drove a sharp reduction in diesel product sulphur, from 9 ppm to 3.5 ppm. The margin impact of Celestia catalyst was realised via the diesel blend pool, enabling a more challenged hydroprocessing unit to relax severity and increase run length by operating a higher sulphur product into the pool blend.

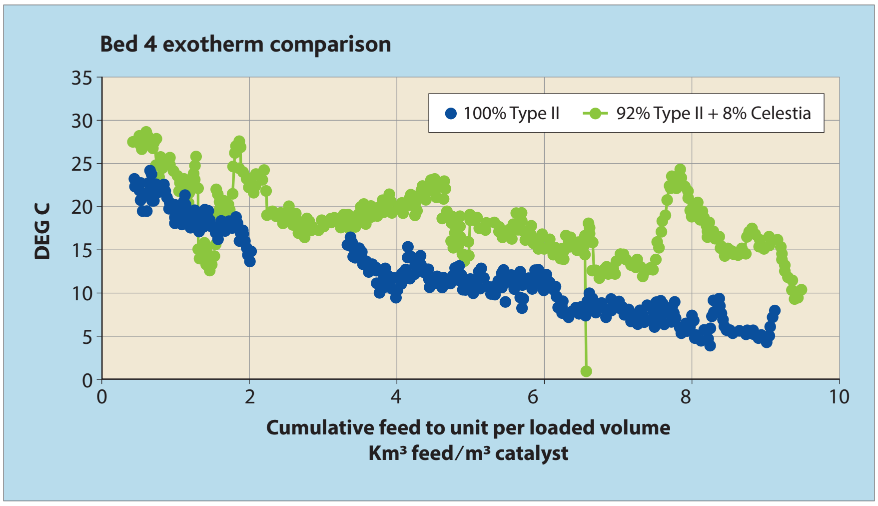

Figure 7 Distillate unit exotherm comparison after Celestia catalyst load

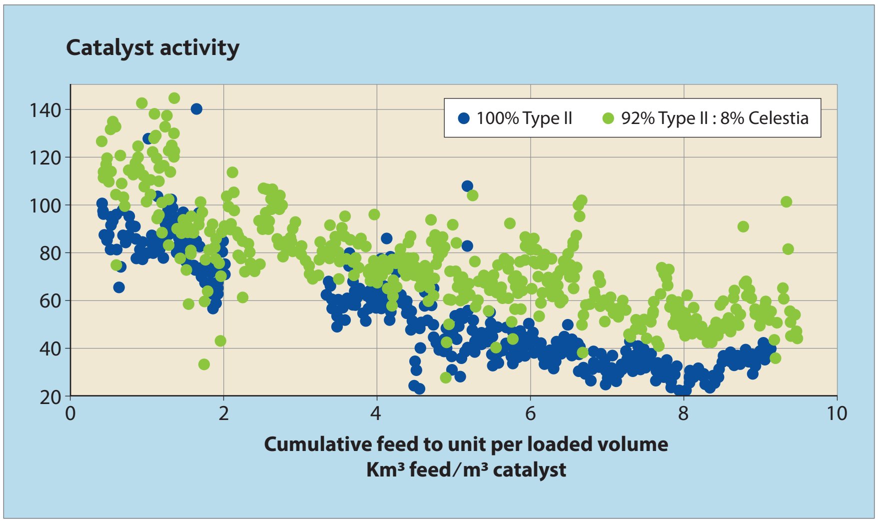

Figure 8 Distillate unit activity comparison after Celestia catalyst load

Increasing feed rate with a lower reactor exotherm increases the external energy input required. However, this was offset by an increased heat release in the Celestia catalyst bed which created an advantage for heat integration, with higher outlet temperature offsetting the higher energy input required to support an increased feed rate.

The Celestia catalyst's stability in this service has proven to be outstanding. Despite the higher feed rate and heavier feed, the temperature rise in bed 4 has deactivated at a lower rate and held the delta T for longer than the all-NiMo load used in the prior cycle.

Conclusion

In five years since its initial commercialisation in November 2015, Celestia catalyst has demonstrated applicability in several types of units, shown high catalyst activity, and contributed to improved profitability in 15 applications to date. The high activity which the catalyst provides does require a different approach on deployment. The first approach is to look at value differently. High activity enables multiple benefits to be achieved directly from the unit, and also from adjacent units and blend plant. Secondly, the high activity needs to be evaluated for safe operation. In most cases, heat release and other issues can be managed effectively at no cost by utilising different operating practices, and employing optimal catalyst stacking designs. Case studies presented in this article demonstrate how Celestia catalyst can be applied in three separate units to yield three very different value propositions, each having a significant impact for the refineries concerned.

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