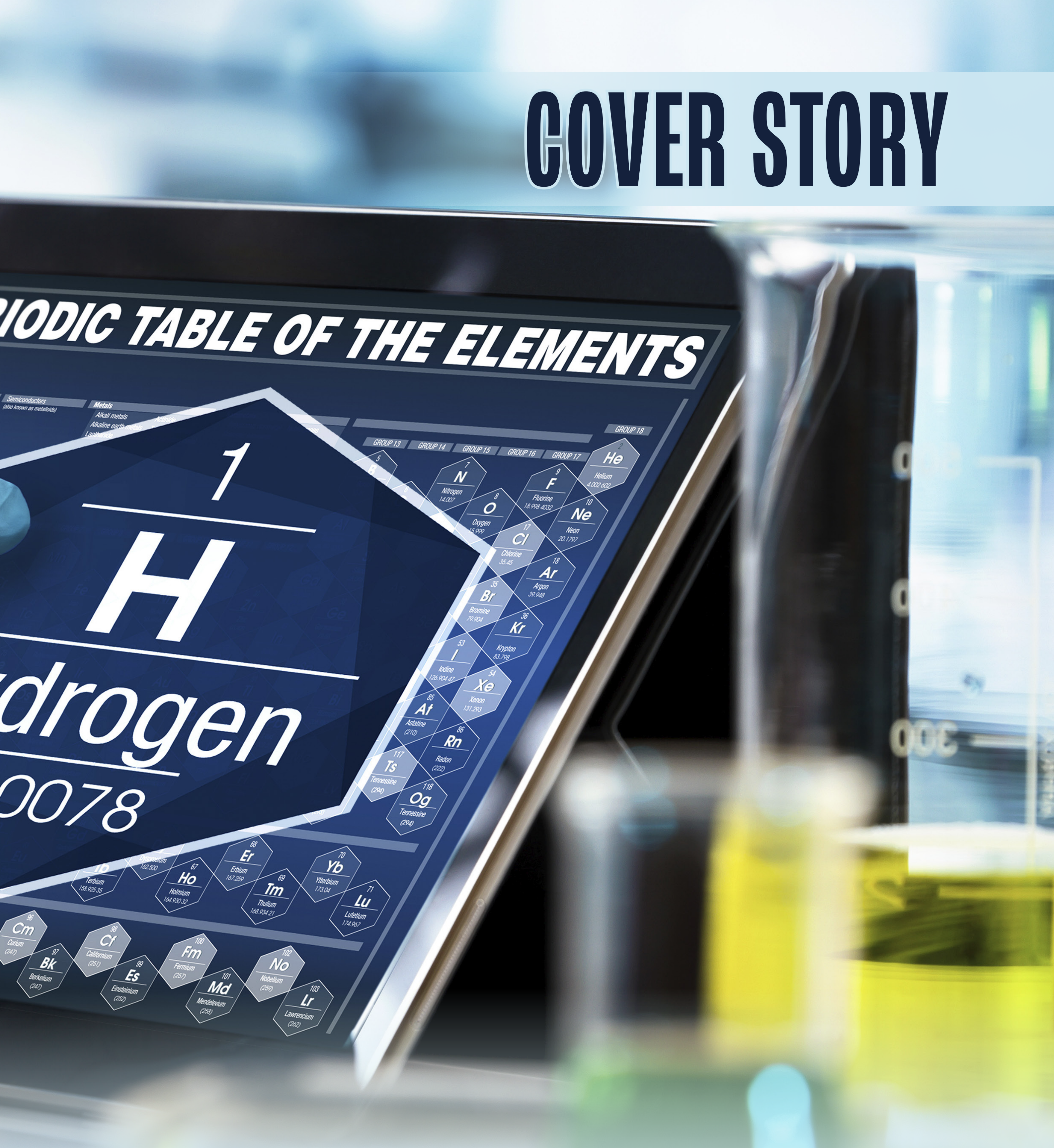
WANT MORE HYDROGEN?

A top five US refiner uses steam methane reforming (SMR) catalysts to increase hydrogen production. **Gary Bennington, UNICAT & Magma Group, and Tom Ventham, UNICAT & G. W. Aru LLC**, discuss the efficacy of this solution in supporting the hydrogen economy, whilst reducing fuel requirements and emissions.

The key to unlocking further refinery efficiencies is the ability to improve the ways in which hydrogen is generated. In addition to this, in order to support alternative fuel developments and enhanced fuel standards, absolute increases in the quantities of hydrogen produced also require consideration. Catalyst technology for steam methane reforming (SMR) is traditionally based on active nickel placed on a shaped support. Alternative manufacturing methods that focus on the catalyst support to unlock further benefits and capacities from existing and new-build SMR equipment have been developed. This novel Magcat® SMR catalyst is fully commercialised, and data from one industrial case study will be discussed in this article.

Background

Hydrogen is considered mainly as an important future fuel and vital chemical building block for sustainable industries. Two-thirds of the world's hydrogen production is consumed by petroleum refineries, fertilizer producers, and other



syngas or hydrogen processes. To support these industries, SMR units generate 96% of the hydrogen that is produced worldwide. In the case of refineries, hydrogen supply and demand dynamics will depend on individual plant configurations. On average, 65% of global refinery hydrogen demand is satisfied by reforming and cracking processes, and 32% provided by on-purpose units. Refinery on-purpose SMR units characteristically process imported natural gas (that is sometimes mixed with refinery fuel gas, LPG, or naphtha streams) with water gas shift units employed to maximise hydrogen composition. Importantly, refineries with on-purpose hydrogen facilities can operate these units for swing capacity in order to meet instantaneous demand, whereas byproduct hydrogen generation can be determined by more complex product quality and demand requirements.

Alternative fuel processes, such as fatty acid conversion to diesel, catalytic upgrading of biofeeds to gasoline, and upgrading of pyrolysis oils derived from organic material, can require several times the mass of hydrogen to produce a barrel of final product compared to conventional fossil-derived processes. As hydrogen requirements ramp up, it is vital that on-purpose units have the capacity to operate above nameplate capacity in order to handle stretch demand without the need for capital intensive retrofit. In addition to this, life cycle sustainability demands that hydrogen used in alternative fuel production must be generated in the most efficient way possible. This is an inherent challenge, as steam reforming of hydrocarbon feeds is highly endothermic, with high activation energies and conversion limited by equilibrium.

Novel technology

Magcat steam reforming catalysts (see Figure 1) comprise active nickel on an innovative spherical, textured ceramic carrier, which results in improved heat transfer capabilities, higher structural strength, and lower pressure drop from a loaded reformer tube. It is compatible with all tubular steam reformers (primary reformers) used for SMR, and is installed in over 25 hydrogen plants worldwide. Building on well-understood nickel catalysis chemistry, but modifying support geometric characteristics in profound and radical ways, changes the fluid dynamic, thermodynamic, and heat transfer properties of packed tube systems, unlocking new capabilities for existing and newly-designed reformers by removing common operational bottlenecks.

Figure 1. Examples of an SMR catalyst in traditional cylindrical shapes (left), alongside a Magcat textured sphere (right).

Magcat has been shown to increase hydrogen production in ways that are easily implemented and avoid equipment investment costs. The first aspect to consider when attempting to increase hydrogen production is the technology's ability to demonstrate lower pressure drop than previous charges, which in turn facilitates higher process gas flows. Traditionally, SMR pressure drop is reduced by moving to larger catalyst pellet sizes. Larger pellets provide more voidage, which translates to lower pressure drop. However, the trade-off of larger size pellets is lower total bed surface area, which results in higher methane slip, particularly late in cycles. The use of externally-textured and internally-porous spherical supports decouples these concerns, with additional surface area and porosity providing significant activity advantages, and the low-drag 3D shape offering baseline pressure drop reduction.

This premise is supported by SMR operating data (see Figure 2) from a site that installed Magcat in early 2022. It is demonstrated that, for fixed conditions, the technology generates 10 psi (0.7 bar) lower pressure drop at all corresponding feed rates compared with previous installations of conventional, cylindrical SMR catalyst. Counterintuitively, Magcat of smaller size than the previous catalyst was loaded to this

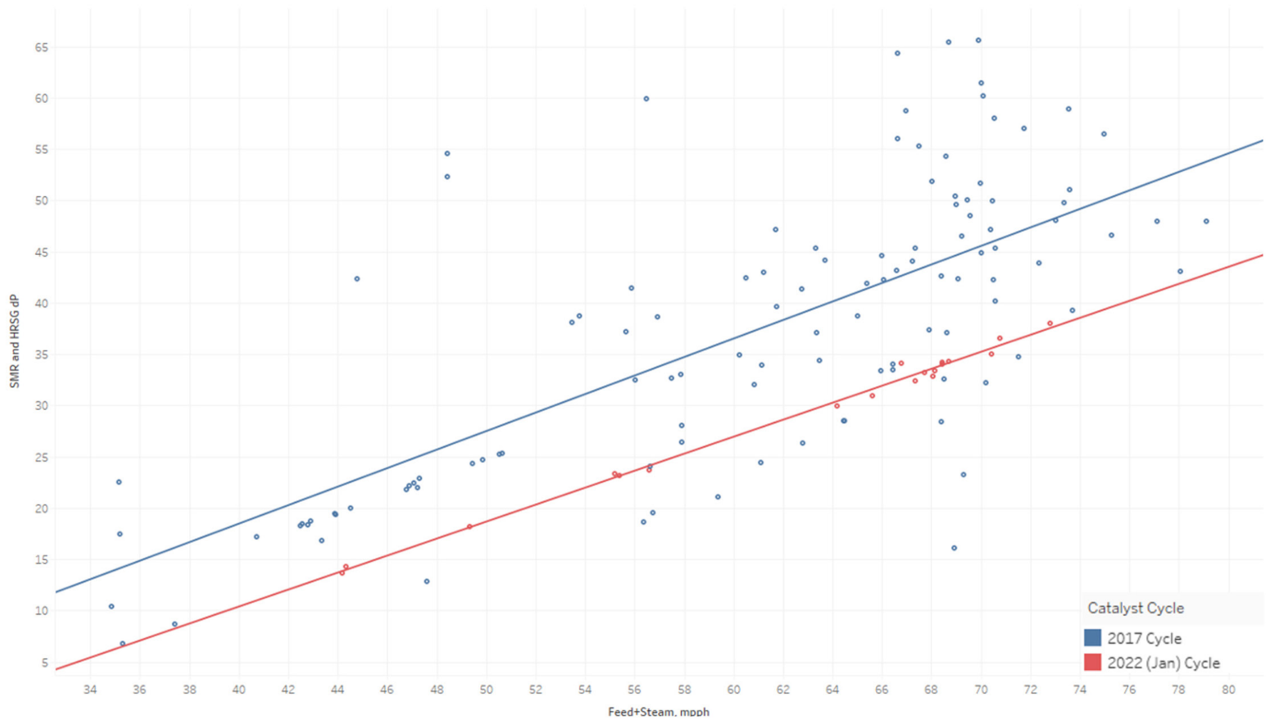


Figure 2. Operating data from a top five US refiner, comparing throughput to unit pressure drop with different SMR catalysts.

reformer, proving the advantage of spherical shaped catalyst in promoting uniform flow. To make use of this benefit, total feed to the reformer (feed gas plus steam, at constant or lower steam-to-carbon ratio) can be increased by 10% at constant pressure drop or observed hydraulic limit. Operating at constant feed rate, this pressure drop benefit significantly offloads feed gas compressor duty at fixed reformer outlet pressure, reducing unit power consumption. Magcat's flexibility allows operators to take advantage of peak hydrogen demand periods by processing more feed, and also make energy savings at times of lower demand and throughputs.

Significant pressure drop improvements derive from Magcat's spherical shape. Introducing an infinitely symmetrical shape with no straight edges into a packed bed reduces excessive pressure drag associated with bluff objects including cylindrical pellets. As well as maintaining a regular surface flow over the sphere (see Figure 3), adding symmetrical spheres into a tube naturally generates repeatable and predictable packing patterns not otherwise associated with random loadings of cylindrical pellets.

The effects on fluid flow from uniform packing vs chaotic packing are profound. Gases entering tubes filled with Magcat divide evenly to flow around full hemispheres of each sphere. The uniformity of spherical packing creates unbiased and equal flow paths for the entire cross-section. Upon exiting the initial layer of spheres, via regular and homogeneous voidage apertures between adjacent spheres, reactant gas flow immediately encounters the next layer of uniformly-packed spheres, over which it will again divide and reconnect with contiguous flow paths. This 'snaking' fluid flow across spheres encourages good mixing and intimate gas-to-surface contact. More crucially, lateral movement promotes heat collection from the tube wall and transportation of heat energy to the core of the tube to satisfy endothermic reforming reactions and equilibrium conditions favouring conversion to hydrogen at high temperatures.

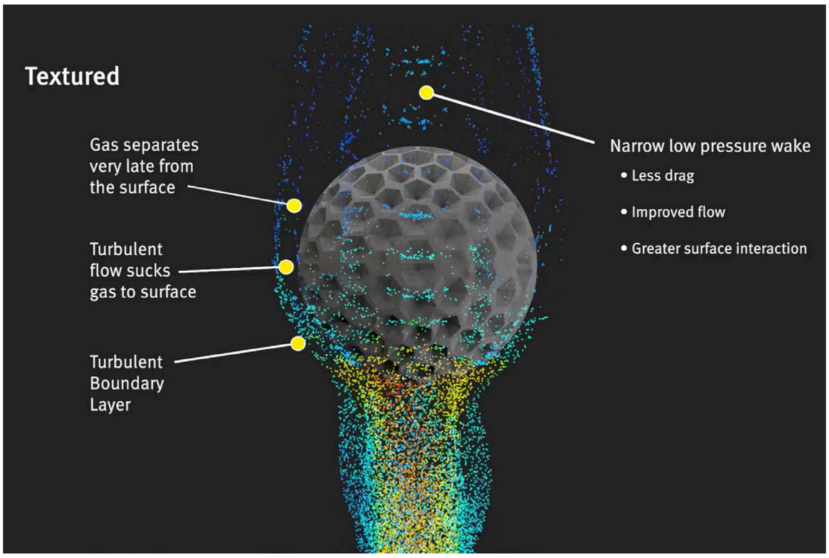


Figure 3. Flow simulation of gas passing over a single static Magcat textured spherical catalyst (gas moving from bottom to top).

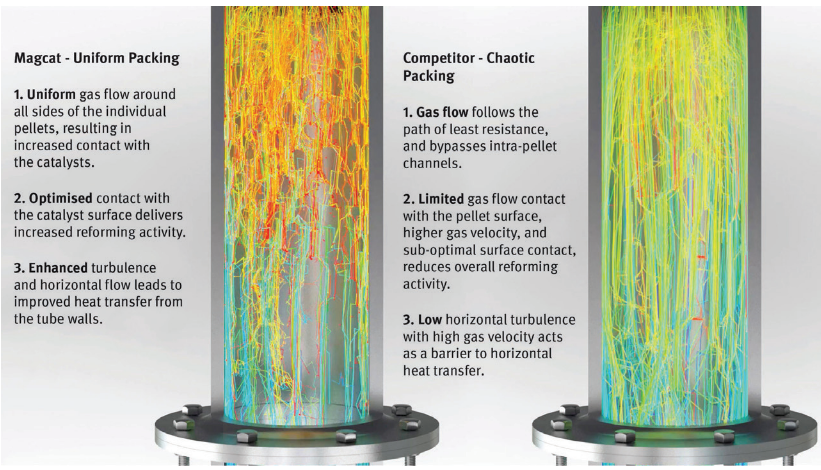


Figure 4. Simulation of gas flow in packed tubes with Magcat (left) and cylindrical catalyst (right), emphasising preferential flow path differences.

In comparison, as well as inducing high-pressure drag over bluff bodies, in most aspects tubes packed randomly with cylinders generate chaotic fluid flow paths resulting in dead spots; back-eddies; bypassing; and hosing through catalyst holes when vertically-orientated, thus diminishing lateral movement that is critical for effective radial heat transfer. Non-uniformity of loading, as well as obstructions to flow paths, cause gases to primarily flush against the wall as the route of least resistance. This results in minimal gas contact with the catalyst bed, and limited lateral movement to carrying heat into the bed. Spherical Magcat generates numerous predictable pellet-wall contacts that disturb convectional boundary layer thickness along the wall and redirect heated flows into the bed (see Figure 4).

By observing Figure 4, it can be noticed that Magcat's SMR catalyst does not incorporate holes. Literature lists the following advantages of multiple holes in cylindrical pellets: increased voidage (associated with lower pressure drop in conventional loadings), and increased active surface area. Magcat is not limited in either of these areas, due to expanses of surface area from external texturing and internal porosity, and substantial and regular voidage between particles when packing solid spheres. Furthermore, lower inherent pressure drop imparted by spheres in comparison to other common SMR catalyst shapes, and observed voidage increases during bed movement of textured sphere packing during heat up, allows smaller Magcat sizes to be selected than would be traditionally expected for an application.

Smaller Magcat spheres further increase surface area, wall contact points, and the

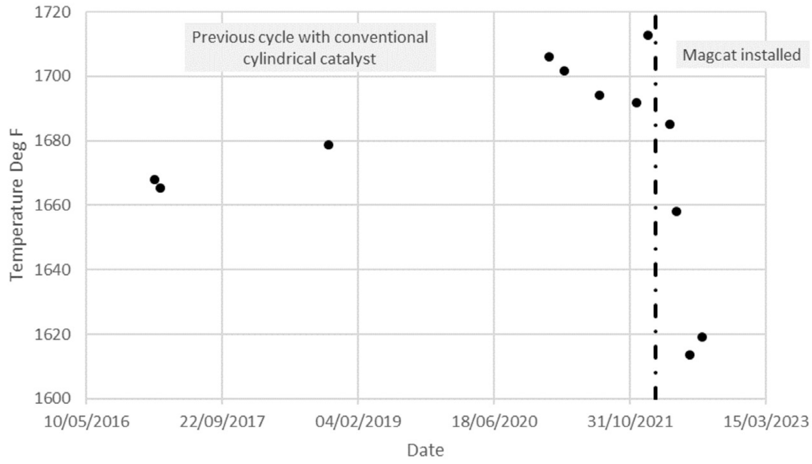


Figure 5. Increases in reformer outlet temperature throughout an operating cycle using a conventional SMR catalyst, compared to low outlet temperature with Magcat installed.

the same methane slip could be achieved at significantly lower combustion outlet temperature at constant other conditions as a result of heat transfer improvements discussed (see Figure 5).

As well as energy efficiency and tube life improvements in constant throughput cases, radial heat transfer tendencies are also important when increasing throughput to increase total hydrogen production. As fluid flow increases, gas residence time decreases. As a result, the transfer of furnace heat needs to take place more rapidly in order to satisfy energy demands through the tube, and meet methane slip specifications. As such, as well as overcoming hydraulic limitations associated with reformer pressure drop profile, and ensuring availability of sufficient active surface area, the catalyst system also needs to be capable of providing sufficient radial heat transfer for acceptable ATE, whilst remaining within furnace capacity and tube metallurgy limits (maximum temperature driving force). It is this unlocking of constraints, particularly the most challenging and most limiting factor of improved radial heat transfer, that allows Magcat users to increase hydrogen production above nameplate capacity, and historical maximums via increased throughput. Once hydrogen production has been increased with the Magcat SMR catalyst, industrial users can also work with UNICAT to uprate their PSA units with advanced absorbents, and PLC upgrades to capture and utilise additional useful product yields.

promotion of radial flow, without compromising overall system pressure drop compared to loading of larger cylinders. The disadvantages of holes that are listed in literature are particle weakness and reduced radial flow. Additionally, holes will not offer the proposed gains unless available to flow by being orientated vertically or near-vertically. Random packing results in the proportions of pellets that are not oriented in ways that are beneficial. Without strength, surface area, or pressure drop concerns, Magcat focuses on maximising the variable which most benefits steam reformers – radial heat transfer – by excluding holes from the support.

Radial heat transfer is key to efficient hydrogen production in SMR. Energy movement from externally-heated tube surfaces to the inner bed core replenishes energy debts generated by net endothermic reforming reactions. Without sufficient heat movement into the bed through radial gas movement (convective heat transfer) and reactant contact with catalytic surfaces at required temperatures, conversion to hydrogen will not achieve expected equilibrium. This will be observed as high approach temperature to equilibrium (ATE). Temperature gradient drives heat movement from the tube wall, perpendicular to bulk flow. More efficient radial heat transfer requires a lower temperature driving force. Magcat applications demand lower tube wall temperatures (TWT) in order to achieve desired ATE and methane slip targets at constant throughput for this reason. Lower TWT implies both reduced furnace firing (reduced fuel consumption and CO_2 emissions) as well as enhanced tube life. Further to the latter point, hot spots and red bands are less likely in Magcat loadings as uniform packing with spheres minimises bridging; increased particle strength minimises crushing, coupled with lower observed level fluctuations through thermal cycles, high intrinsic catalyst activity, and enhanced anti-carbon mechanisms, all defending susceptible tube sections from carbon deposition, as well as avoiding dead spots prone to hot spots. This means further increased tube lifetimes and the avoidance of common points of failure.

Operationally, reformer operators increase reformer outlet temperature by ramping up fuel firing to achieve targeted methane slip. Reformer outlet temperature typically climbs through cycles to compensate catalyst activity reductions. The same industrial user observed that after switching to Magcat,

Conclusion

Magcat is demonstrating excellent performance in refinery SMR plants, as shown in the aforementioned example of a top five refiner in the US. These benefits can be clearly understood from underlying effects on fluid dynamics, thermodynamics, and heat transfer of the textured sphere support, pioneered by Magma Group to produce the Magcat catalyst.

Energy efficiency, lower CO_2 emissions, increased hydrogen production, and extended tube life are just some of the advantages of Magcat that have been discussed in this article. UNICAT and Magma are ready to support all reformer operators to further optimise their plant and understand how Magcat, alongside other catalysts and absorbents, can be best deployed to benefit their operations.

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