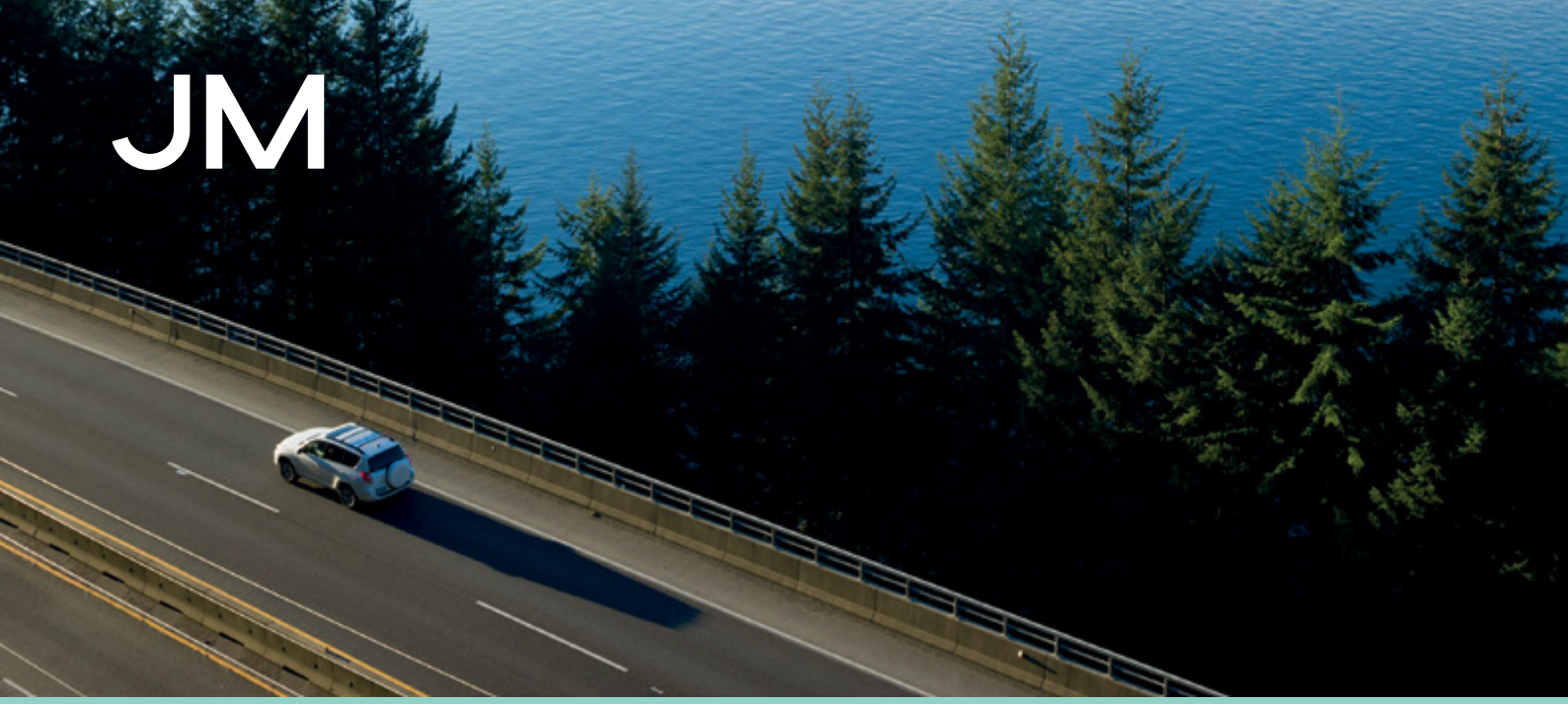


JM

INTERCAT FCC additives and catalyst handling technologies

Johnson Matthey
Inspiring science, enhancing life

Introduction

Most refiners now find it essential to use catalytic additives to supplement the host FCC catalyst in order to achieve the desired unit performance, product quality, and environmental emissions targets that must be met.

Johnson Matthey (JM) is the foremost supplier of FCC additives and addition systems, specializing in the development, manufacture, sale, and technical support of both additives and addition systems for the refining industry. Our **INTERCAT**™ range of FCC additives and addition systems allow refiners to make the most of the synergies that exist in the FCC unit so that they may continually optimise yields and minimise emissions. Our additives afford refiners the ability to tailor the selectivity of the FCC, boost LPG yield at the expense of LCO and HCO, decrease bottom yields, and reduce regenerator SOx, NOx and CO emissions.

INTERCAT additives can be broken down into two groups, Performance and Environmental Additives. Performance Additives include propylene, butylene and octane improvement FCC additives while Environmental Additives include SOx and NOx reduction, gasoline sulphur reduction and CO promotion additives.

Performance additives

Propylene, butylene and octane improvement additives

Refinery profitability can be maximised by selectively choosing the proper ZSM-5 type additive. When propylene demand is high, JM's **INTERCAT** ZSM-5 based additives, **PROPYL MAX™**, **SUPER Z™**, **SUPER Z EXCEL**, and **SUPER Z EXCEED**, are highly selective for cracking low octane gasoline range molecules to C_3 and C_4 olefins with no increase in coke or C_2 and lighter gases. ZSM-5 isomerises straight chain C_4–C_{10} molecules to more highly branched molecules. The cracking of low octane components out of the gasoline, together with isomerization, result in increased gasoline octane (RON and MON). In addition, the isobutane yield also increases via secondary hydrogen transfer of some of the isobutene formed on ZSM-5 on the RE-USY in the base catalyst. Isobutane and n-C_4 olefins are valuable as feeds for alkylation units, isobutene is valuable as feed to etherification units such as ETBE.

When butylene production is the primary goal, our **ZMX™** additive, **ZMX-B-HP**, allows the refiner to increase FCC gasoline octane and LPG yields, but primarily at the expense of LCO instead of gasoline. This additive also significantly increases the C_4:C_3 ratio of the incremental LPG produced vs. standard ZSM-5 additives. These additives may be used at very high concentrations to provide a simple and effective route for adjusting FCC LPG olefin production to meet changing market demands.

For refiners who require higher gasoline octane, but are wet gas compressor or gas plant limited or do not desire higher LPG yields, JM offers the **ISOCAT™** product. This additive is based on ZSM-5 with much higher Silica to Alumina Ratio (SAR) than those grades used to increase propylene selectivity. Higher SAR ZSM-5 results in lower selectivity towards cracking gasoline to LPG while maintaining high isomerization activity that boosts gasoline octane.

Bottoms upgrading additive

Reducing the heavy fuel oil (bottoms or slurry) make from an FCC unit is a challenge that has faced refiners for many years. In general, the components in the FCC feed boiling above 800°F (427°C) cannot be cracked by the zeolite component of an FCC catalyst. Their molecular diameters are too large to pass through the openings in the zeolite crystal. These high molecular weight compounds must first be cracked on the catalyst matrix (mesoporous acidic alumina) before the pre-cracking molecules are small enough to enter the zeolite for further cracking to gasoline and LPG. Most commercial FCC catalysts have sufficient matrix activity to provide some cracking of high boiling point materials, however, this matrix activity is very quickly lost by the metal poisons in the feed. JM's **INTERCAT** bottoms cracking additive, **BCA-105**™, selectively cracks the heaviest portion of the feedstock not otherwise converted by the base catalyst to lighter, more valuable, products. As crudes being processed by refiners become increasingly heavier and more sour in composition, the heaviest liquid stream, or 'bottoms' increases. **BCA-105** provides an important means to help solve this problem and has the added advantage of enabling the refiner to respond quickly and dynamically to changes in crude type, product pricing, and demand, by addition of the additive as needed, rather than changing out the base catalyst.

Catalyst enhancement additives

CAT-AID™, JM's **INTERCAT** catalyst enhancement additive, is designed to overcome many of the shortcomings related to deactivation of base catalyst from metal contaminants such as vanadium, nickel, iron, calcium, sodium, and potassium.

Vanadium and iron poisoning can have an especially devastating effect on FCC catalyst performance. Vanadium attacks the Y-zeolite in the base catalyst causing permanent destruction and consequent loss in activity and coke selectivity. Whereas iron, at added levels from just +0.3 wt%, forms a glassy/nodular shell on the catalyst surface which seals off the catalyst interior prohibiting hydrocarbon diffusion into and out of the catalyst particle. **CAT-AID** traps vanadium and iron (and other feed contaminants) thereby protecting the base catalyst from their detrimental effects. In addition, these contaminant metals promote undesired dehydrogenation reactions which when left uncontrolled increase the hydrogen yield and delta coke. **CAT-AID** traps and passivates vanadium and iron thereby decreasing the hydrogen (relieving wet gas compressor constraints) and delta coke (lowering the regenerator temperature and increasing catalyst circulation).

SOx is well known to compete with vanadium for metal trapping sites, rendering most so-called vanadium traps ineffective in the real world. As part of the fundamental design of **CAT-AID** its metals trapping component is protected by sites designed to capture SOx and preserve them for the function they are intended to perform – trapping metals. As a consequence, **CAT-AID** also acts as a SOx capturing agent. Use of **CAT-AID** decreases caustic consumption in units running with wet gas scrubbers.

With the use of **CAT-AID** refiners will experience decreased fresh catalyst addition requirements and often eliminate the need for flushing equilibrium catalyst additions. **CAT-AID** provides the refiner with a 'delta coke credit' that may be used to increase unit severity, feed rate, and/or increase resid processing.

Environmental additives

SOX reduction additives

Government agencies worldwide are adopting ever more stringent legislation regulating the levels of sulphur oxide (SOx) emissions from oil refineries. While FCC feedstock desulphurization and flue gas scrubbing are both proven methods for FCC flue gas SOx emission control, many refiners find that the use of an in-situ SOx reduction additive is the most cost effective means of meeting these regulatory requirements.

SOx reduction additives are added directly to the FCC catalyst inventory where they adsorb sulphur oxides in the regenerator and release the sulphur as hydrogen sulfide in the riser. Hydrogen sulfide is routinely processed in the refinery sulphur recovery unit (SRU) where it is converted to elemental sulphur. The incremental hydrogen sulfide production is relatively low and can usually be handled by existing sulphur recovery facilities..

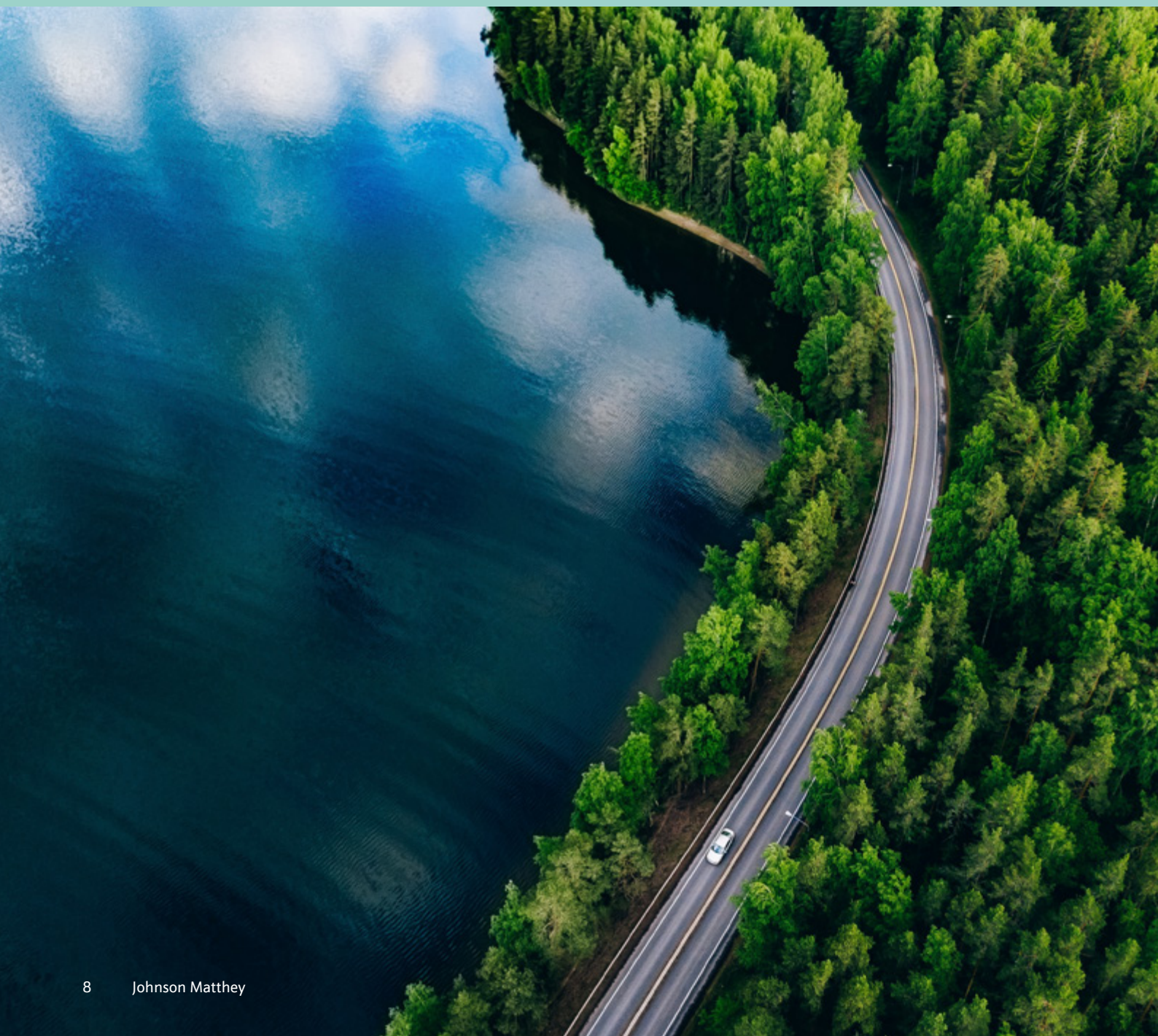
JM's **INTERCAT SUPER SOXGETTER™** and **LO- SOX PB™** families of SOx reduction additives have been developed to decrease the cost of removing SOx from the FCC flue gas in full burn, partial burn and two-stage regenerators. These additives are based upon hydrotalcite- like compounds that maximise the accessibility of sulphur containing regenerator gases to the reactive magnesium containing sorbate phase in the additive. The high magnesium content of these additives allows them to outperform products based on all other sorbate technologies and have been proven commercially to be the most effective additives in the marketplace. Our SOx additives can easily achieve and maintain SOx reduction levels of over 95% with no negative impact on unit operation yields, or process equipment.

NOx reduction additives

As concern grows over atmospheric pollution, government agencies worldwide have become focused on regulating the level of nitrogen oxide (NOx) emissions from oil refineries. NOx emissions from an FCC are extremely unit specific and can vary with changes in feed and other process parameters. Potential sources of NOx include nitrogen compounds from coke in the feed and nitrogen from air in CO boilers. Most of the nitrogen present in FCC feeds ends up in the coke being burned in the regenerator. When this is combusted the nitrogen forms N_2, NOx and other nitrogen species depending on specific regenerator conditions, type of CO-promoters used, etc.

Under full burn conditions NOx usually correlates well with flue gas excess oxygen, whereas under partial burn conditions much of the nitrogen in coke is only partially combusted to reduced species which go on to form NOx in the CO boiler.

The latest development in NOx reduction is **INTERCAT NONOX™** technology. This formulation focuses on selectively converting the precursors that go on to form NOx to N_2. **NONOX** is also effective in partial burn regenerators because these precursors are present in abundance under partial burn conditions.



Sulphur reduction in gasoline additives

A refiner's ability to reduce the sulphur content of FCC gasoline may be limited by the molecular species that are present in the FCC unit. Numerous sulphur containing species including mercaptans, sulphides, disulphides, thiophenes, and benzothiophenes are present in the gasoline. Their concentration varies depending upon the original crude source, the boiling ranges of feedstocks, and their historical treatment.

To reduce gasoline sulphur, the refiner has a number of options in which to choose. Most options involve trade-offs between high capital costs and gasoline yield loss. However the use of sulphur reducing additives, such as **INTERCAT LGS**™ additives, offer an economically attractive alternative. These additives can provide the refiner with a capital free option to reduce gasoline sulphur upwards of 40% without the loss of gasoline yield.

CO oxidation additives

Combustion promoters are required to ensure smooth regenerator operation, control of afterburning and reduction of CO emissions. Afterburning occurs when carbon monoxide reacts exothermically with oxygen in the regenerator dilute phase. Because of the lack of catalyst to absorb the heat of CO combustion the dilute phase experiences a large increase in temperature – the most common constraint in FCC unit operations. A CO promoter is used to accelerate this reaction in the regenerator dense phase (catalyst bed) where the heat of reaction is readily absorbed by catalyst particles leading to much lower temperature rises.

CO promoters employ platinum group metals as their active component supported on high surface area alumina to ensure high dispersion for maximum activity and retard deactivation via sintering.

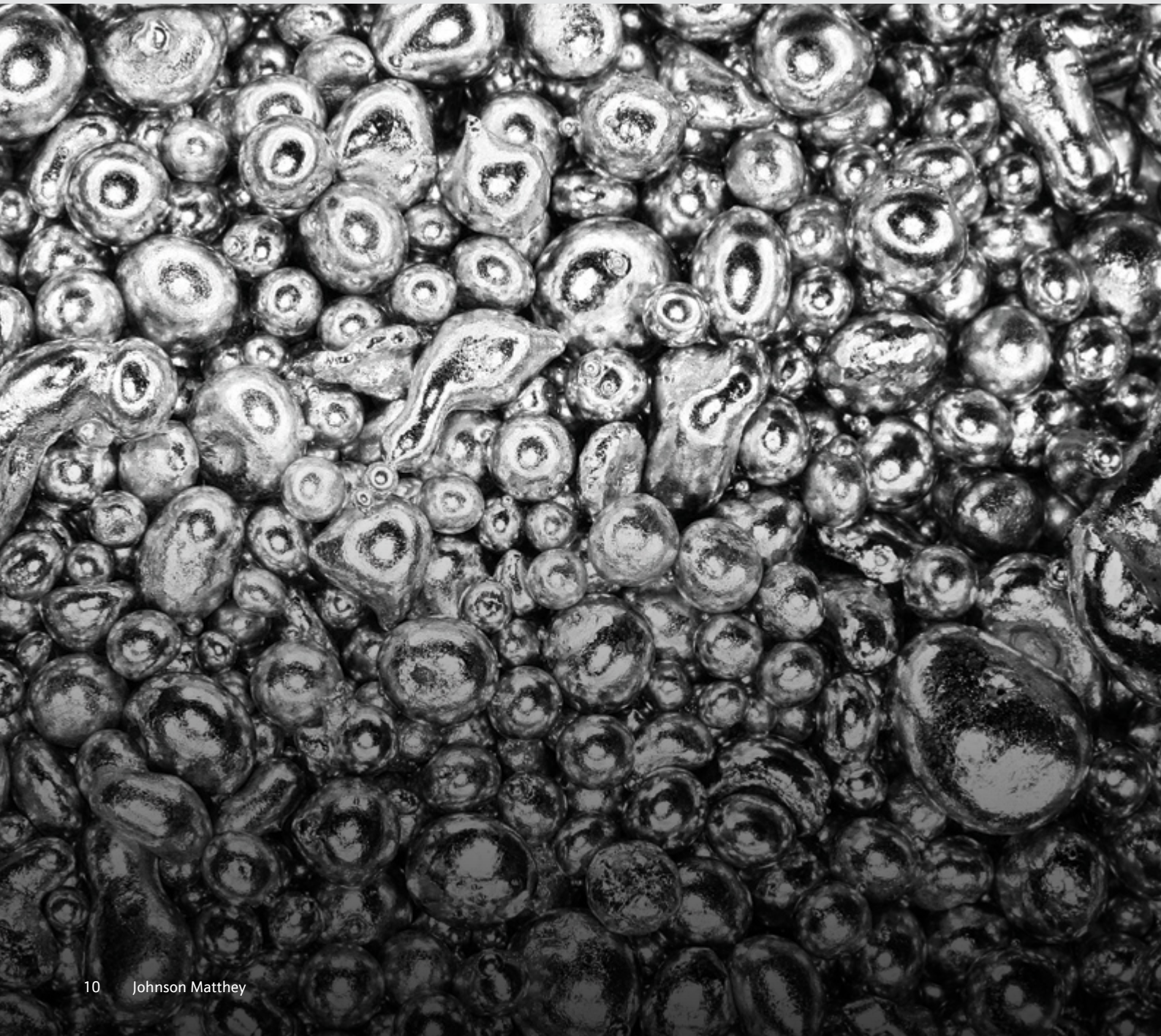
The physical properties of JM's **INTERCAT** CO promoters, including particle size distribution, attrition resistance and bulk density, have been optimised to be fully compatible with all commercially available FCC unit designs and catalyst technologies. Independent testing has shown that **INTERCAT** CO promoters have the highest CO conversion efficiency on the market.

Platinum based promoters

Platinum based combustion promoters, **COP™-250**, **375**, **550**, and **COP-850**, containing various levels of platinum provide a range of additives with varying activity. For units requiring higher levels of promotion the higher activity grades are recommended. For refiners requiring very little promotion it is usually more effective to add a greater amount of a lower activity additive for optimal control of afterburning.

Non-platinum based promoters

An undesired side effect of platinum based CO promoters is that they may increase the formation of NOx in some FCC regenerators. For this reason non-platinum CO promoters were developed. In cases where platinum based promoters lead to increased NOx their substitution with non-platinum CO promoters reduces NOx emissions at comparable levels of CO oxidation. **COP-NP™** is an EPA approved non-platinum CO promoter that is commercially proven to effectively promote CO oxidation and control afterburn while reducing NOx emissions by over 70% relative to platinum based CO promoters.



Research and development

JM's state-of-the-art R&D facility in Savannah, GA, USA, is a comprehensive research center focused on the development and advancement of fluid catalytic cracking additives and technologies for the refining industry. Expertise in advanced materials technology and applications allows for the creation of innovative products that benefit the planet while bringing value to our customers.

Continued investment in R&D is vital to remain at the forefront of the industry and provide cutting edge products. Research and Development consists of approximately 13% of Johnson Matthey's total workforce and is comprised of the world's top scientific talent and engineers. JM's R&D team works hand- in-hand with the Sales and Technical Service groups to provide a full service customer experience; from assessment of the FCC operation, product proposal and evaluation, trial monitoring and analysis, to performance evaluation.

Addition systems

INTERCAT addition systems have been in widespread use on the FCC process since the mid 1980's, and today there are over 300 units installed in refineries throughout the world.

These addition systems come in a variety of configurations, for adding additives from a few kilograms per day to fresh catalyst systems at tens of tons per day. Our fresh catalyst addition systems are recommended for new FCCs by licensors TechnipFMC, Axens, UOP and CBI Lummus.

The advantages of an **INTERCAT** addition system include:

- **Reliable and precise additions**. Allows for improved control of unit severity.
- **The ability to control e-cat activity**. Permits higher throughputs, higher severities or the processing of a greater range of feed stocks.
- **The ability to add additives separately from the fresh catalyst**. Allows the refiner the flexibility to quickly respond to changing market conditions.
- **More stable and efficient FCC operation**. Adding small shots of additive over a 24 hour period is up to three times more efficient than adding large quantities at the end of each shift.

The basic **INTERCAT** addition system consists of a storage vessel for the additive or catalyst, associated piping and equipment to load the vessel and a control system which controls the supply of catalyst to the FCC unit.

The flow of the catalyst from the hopper is precisely controlled by the **INTERCAT** Management System (IMS), the heart of the addition system. The IMS is a self-contained, digital, electronic controller which controls and tracks the catalyst or additive loaded into the regenerator. The operator enters the amount of catalyst or additive to be added daily to the process as a set point. By reading the vessel load cell output directly, the IMS automatically adjusts the periods between fixed shot additions to control catalyst addition rates precisely to refinery requirements, automatically spreading the additions out over a full 24 hour period each day. The IMS then controls, monitors and logs the catalyst or additive additions. It also provides graphical displays which show current and historic additions and how these compare with set points. The IMS can be interfaced with the plant's distributed control system (DCS) via a digital interface (MODBUS) and/or using 4-20 mA signals.

The hopper is mounted on three load cells. Any change in weight is detected by means of these load cells allowing the IMS to precisely monitor and control catalyst and additive additions.

The catalysts flow through a patented control valve, the Everlasting Valve, located below the outlet of the vessel, into the catalyst feed line. The Everlasting Valve is the only moving part of the system in frequent contact with catalyst during normal operation.

When refilling, carrier air is usually vented to atmosphere. To prevent any fines escaping, the **INTERCAT** loader is fitted with a sintered metal filter (SMF). This is a stainless steel mesh self-cleaning system which prevents any powder escaping the addition system during refill. There is a back pulse system that cleans the filter while in operation and blows back the fines into the vessel.

These SMF's are also available for retrofitting to existing addition systems, and refinery main catalyst storage hoppers to eliminate dust emissions.

To simplify additive and catalyst inventory management and save valuable supervisory resources, JM's patented **AIM TECHNOLOGY**™, Automatic Inventory Management system, automatically tracks the onsite inventory of FCC catalyst and additives. The **AIM** database continually tracks the number of days of inventory remaining on site and can automatically schedule the next delivery or alert the refiner of the need to reorder. **AIM** tracking provides complete and accurate auditable data collection to ensure compliance with government mandated testing protocols. For inventory updates and information **AIM** clients can access through the secure JM **AIM** site.

Technical service

JM employs technical service staff with a depth of industry experience. All of our technical service engineers and professional consultants have over twenty years of refining industry experience that is predominantly FCC related. Our technical service staff is augmented by R&D and manufacturing personnel for conducting analysis and FCC additive performance evaluations.

Technical Service representatives readily support

- Additive selection
- Addition system design, installation, and servicing Test protocol development
- On-site testing
- Product evaluation

JM maintains ongoing relationships with the refinery process engineers, FCC operations supervisors, and economics and planning personnel with frequent visits to understand any potential opportunities for FCC additive usage as well as to assess the performance of any additives in use. Recommendations for FCC additive usage and performance estimates for establishing economic justification are also provided.

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For further information on Johnson Matthey, please contact your local sales representative or visit our website.

Billingham, UK
Tel +44 (0) 1642 553601
www.matthey.com

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