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Natural gas fuels the energy transition

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Abstract

Natural gas usage is forecast to rise over the next ten years as part of global efforts to move away from coal to reduce CO₂ emissions. Natural gas contains hydrogen sulphide and mercury impurities which are damaging to health, the environment, and to downstream processes, so it is essential that these are removed as part of gas processing.

Johnson Matthey's **PURASPEC**[™] range of absorbents are 'fit and forget' fixed bed solutions for hydrogen sulphide and mercury removal. The latest step-out technology in the **PURASPEC** range is presented.

PURASPEC 1065 for sulphur removal offers a 25% improvement in capacity for hydrogen sulphide removal over the previous product. This improvement has been achieved through an increase in the density of the reactive copper phase, and an increase in the product's geometric surface area giving rise to faster kinetics.

For mercury removal the latest generation products include **PURASPEC** 1198/1199 which offers a 25% improvement in capacity for mercury removal. This is achieved through improvements in the mercury removal kinetics which allows for higher utilisation of the active copper component. **PURASPEC** 1193/1194 in the latest generation is also presented, which offers the best water tolerance of all **PURASPEC** mercury absorbents..

Natural gas place in the energy transition

Natural gas is an important intermediate on the path to global decarbonisation. Natural gas offers the lowest CO₂ footprint from all fossil fuels, and coupled with carbon capture and sequestration, emissions can be up to 90% lower than when using coal ^[1].



Figure 1: The reduction in CO₂ emissions achievable when moving away from coal.

It is widely acknowledged that demand for natural gas is going to increase over the next ten years. Beyond 2030 demand modelling depends on the success of countries net-zero pledges. Gas usage is present as a stepping-stone in many countries' policies relating to reduction in greenhouse gas emissions.

It is hugely important that this increased utilisation of gas does not cause other environmental and health issues through increased hydrogen sulphide and mercury emissions.

This paper focusses on **PURASPEC** science and technology, Johnson Matthey's absorbent product range which is employed around the world to remove these contaminants as part of natural gas processing.

Why remove mercury and sulphur?

Sulphur and mercury must be removed from natural gas during processing for many reasons. Firstly, and most importantly, these contaminants are hazardous to health.

Sulphur in the form of hydrogen sulphide (H₂S) is a very toxic and corrosive compound which needs to be removed from natural gas before it can be safely used by businesses and homes.

Some sources of natural gas contain significant amounts of sulphur. Upon the combustion of sulphur containing gas, sulphur dioxide can be formed which can lead to health issues such as respiratory and cardiovascular disease.

In addition, environmental issues arising from SO_x emissions include the formation of acid rain that adversely affects ecosystems, as well as technical issues such as pipework corrosion or downstream catalyst poisoning, costing industry billions of dollars per year as a result of catalyst replacement and process shutdowns.

If sulphur impurities in gas are not effectively reduced to a very low concentration before use in other chemical processes, it irreversibly poisons - metal catalysts i.e. reducing their activity, selectivity and lifetime. This is especially detrimental to those used for both catalytic reforming and fuel cells electrodes.

Elemental mercury is also a well-known toxin which is particularly hazardous to the brain where it can accumulate leading to neurological dysfunction ^[2]. Other forms of mercury (e.g. mercurous and mercuric salts and organomercury) are also dangerous toxins to many of the body's organs. Elemental mercury in sea water can be converted by microorganisms into organic mercury, which bio-accumulates as it works its way up through the food chain. Mercury must therefore be removed from natural

gas at source not just for occupational safety reasons but also to protect the wider public.

A second concern is elemental mercury is known to be capable of causing liquid metal embrittlement, with cryogenic aluminium heat exchangers used in LNG plants being particularly vulnerable [3]. There have been several high profile cases where embrittlement has led to sudden and catastrophic loss of containment at gas processing plants. For this reason, absorbents to remove mercury are ubiquitous in LNG plants.

There are also economic reasons for sulphur and mercury to be removed from natural gas during processing, e.g. to meet pipeline specifications to avoid fines & penalties, extending assets life (CAPEX) and reducing downtime (OPEX).

What are PURASPEC absorbents?

PURASPEC products are high performance fixed bed absorbents for sulphur and mercury removal which are attractive to customers for many reasons including their straightforward "fit and forget" operation. PURASPEC is in the form of small spherical granules with the typical appearance as shown in Figure 2.

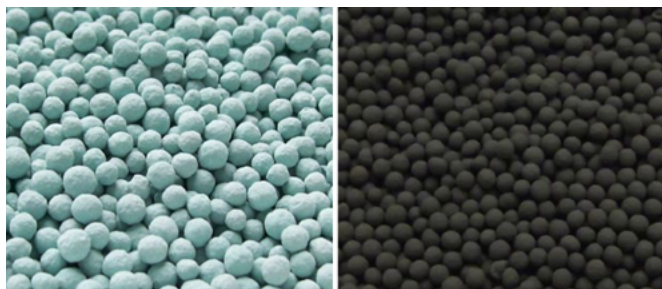


Figure 2: Typical appearance of PURASPEC for sulphur removal (left) and mercury removal (right).

To manufacture PURASPEC, the active copper compounds are combined with binders before the product is granulated into a form suitable for fixed bed absorption. The granulation technology is optimised to ensure the product acquires the desired characteristics, such as strength, porosity, density and activity.

Due to the inherent porosity and strength characteristics combined with ability to incorporate high loadings of active material, granulation was chosen by Johnson Matthey as the preferred and optimum forming technique for all purification products and the company have decades of experience in this area.

The resulting PURASPEC products have an exceptionally high capacity for sulphur and mercury in addition to fast rate of reaction at low temperatures.

The high strength and low attrition of the granulated product has several benefits for the customer including reduced risk of pressure drop increase, easy handling during changeouts and increased resistance to abnormal operation.

PURASPEC for long bed life and small footprint

PURASPEC's high removal capacity and fast kinetics gives rise to long bed lives and small footprint for the sulphur and mercury removal units.

The total sulphur capacity is strongly linked to concentration of active metal in the granule. The kinetic activity of the product is influenced by factors such as particle size and porosity of the product and this has an effect on the Mass Transfer Zone (MTZ).

The MTZ is the difference between the initial sulphur breakthrough in the exit gas and end saturation of bed. This indicates the efficiency of the rate of reaction and sulphur removal i.e. the lower this value and the closer together these two points are, the better. A long initial breakthrough time as well as short MTZ suggests the product is being utilised efficiently and for longer which is what is seen for JM's new product, PURASPEC 1065.

For mercury removal, fast mercury removal kinetics are a critical requirement to achieve high capacity and a long bed life. The illustration in Figure 3 explains the strong link between mercury removal kinetics and capacity. Three cases are illustrated, which show the absorbent mercury content vs bed depth profiles at the end of the life of the charge (when changeout is required).

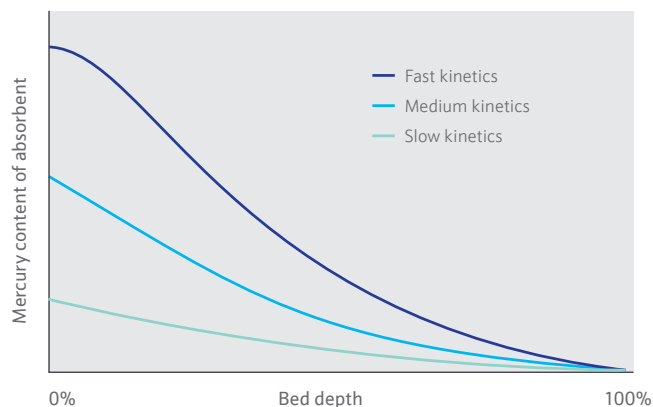


Figure 3: An illustration showing the link between mercury removal kinetics and typical mercury content profiles at the end of the lifetime of the charge.

In the case of the red line (shallow gradient), the mercury removal kinetics are slow. While the theoretical maximum capacity of the absorbent may be high, the observed true capacity of the absorbent is low because a long contact time is required to remove the mercury. The effect of this is that the charge will have a short lifetime, as slip occurs early and the absorbent would be underutilised at the point of breakthrough.

In the case of the absorbent's mercury removal kinetics being fast (green line, steep gradient), the absorbent has a short contact time requirement, so the absorbent can stay online for much longer (equivalent to the difference in the areas under the curves) before slip is observed. The observed real-world capacity of this absorbent is high.

Fast kinetics in combination with high maximum capacity are required to give the highest real-world absorbent bed capacities. **PURASPEC** offers both of these qualities, which translates to longer bed lives and smaller footprints for the mercury or sulphur removal units, and ultimately this translates to **PURASPEC** being the most overall cost-effective technology for contaminant removal.

PURASPEC is available in different size ranges with the smaller granule size offering the highest contaminant removal kinetics, and the larger size range offering the lowest differential pressure (DP).

Sulphur removal - **PURASPEC 1065** advancements

PURASPEC 1065 is JM's new high-capacity high activity sulphur removal product. It is an extension of our current offering and encompasses:

- An increase in the amount of active phase in the product
- An increase in the product density

The product also has a smaller particle size compared to the previous generation products in order to increase the geometric surface area and reduce potential diffusion limitations. As a result, **PURASPEC 1065** has fast removal kinetics and low MTZ, ensuring a high sulphur pick up per volume of absorbent.

PURASPEC 1065 has a 25% improvement in H₂S pickup over its predecessor. This directly translates into a 25% reduction in the required bed volume of material (lower cost per kg of sulphur removed) or 25% increase in bed life for equivalent bed volume (less frequent vessel changeouts).

Performance evaluations on JM's bespoke test rig have clearly shown the benefit of **PURASPEC 1065** in terms

of total sulphur capacity and also impressive kinetics. The initial H₂S breakthrough at the exit of the bed for **PURASPEC 1065** occurs at a much later time, alongside a sharp H₂S exit profile and short MTZ.

Comparative performance of **PURASPEC 1065** versus **PURASPEC 1039** and **PURASPEC 1038A** in our accelerated laboratory testing can be seen in Figure 4. The H₂S removal profiles show that despite having the highest density, **PURASPEC 1065** has the lowest MTZ which is slightly better than P1038A and around 15 - 20% lower than P1039.

The improvement in performance and reduction in OPEX/CAPEX also offers positive environmental, health and safety benefits. The use of smaller vessels to give the same bed life compared to the predecessor materials or a reduced change out frequency of existing vessels yields a reduced carbon footprint from transportation of products. Less frequent change out means fewer inherently hazardous operations being required to maintain continuous sulphur removal from a process.

JM have developed this product over the past few years through rigorous lab, pilot and full-scale manufacturing trials and subsequent characterisation and performance testing. It has been designed with the needs of our customers in mind, with the intention to resolve problems such as increased sulphur content of their hydrocarbon feedstock and high OPEX due to change out frequency. The product was launched in 2019 and since then it has been utilised in significant quantities by several customers in the gas processing field.

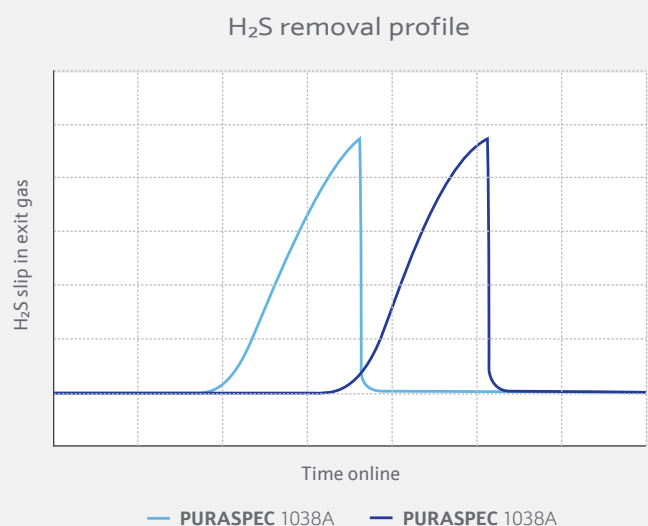


Figure 4: Graph showing the comparative performance between JM's sulphur guard absorbent products demonstrating the shorter and sharper MTZ for **PURASPEC 1065** v **PURASPEC 1039**.

PURASPEC sulphur removal absorbents – key points

The main upstream process for bulk sulphur removal in the sweetening of natural gas is the amine process where sour gas containing up to % levels of sulphur is passed through a vessel containing an amine solution typically MEA where H₂S is absorbed by the amine solution. However, it is difficult for this type of technology alone to achieve the level of purity required for most hydrocarbon feedstocks.

JM's absorbent products are more suited to the polishing stage of natural gas processing working at relatively low inlet concentration levels and also at ambient conditions and having the ability to remove H₂S down to sub ppm levels (Figure 5).

The CAPEX and OPEX costs for our **PURASPEC** absorbents are low with little operator intervention required. As fit and forget technology, once the product is loaded into vessels it can be left with the exit gas monitored over time.

JM's absorbents can be used in processes that have been designed to deal with large variations in flow, pressure, and temperature and impurity level and are extremely robust with respect to plant upsets.

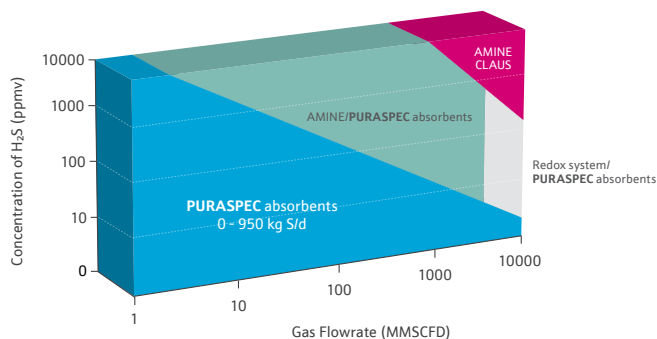


Figure 5: Operating windows for PURASPEC and bulk sulphur removal

Mercury removal – latest PURASPEC offers

JM have offered products for natural gas mercury removal for over three decades, leading to a deep understanding of mercury removal science and technology within the company. This understanding has led to the latest generation of mercury removal products which offer a step change in JM's **PURASPEC** mercury removal offer. The new products include **PURASPEC 1198/1199** which offers a 25% improvement in observed (real world) capacity for mercury removal. This is achieved through improvements in the mercury removal kinetics and better utilisation of the active copper component.

This latest generation of products require no process changes or equipment modifications at customer sites; they are a drop-in replacement for previous generation products which offer the same handling and physical characteristic while greatly improving mercury removal performance.

Figure 6 shows gas phase test data on the latest generation **PURASPEC 1198/1199** with the mercury slip from the bed plotted against run day. In this test, a very short contact time and high inlet mercury concentration is used which forces premature observable slip in the test.

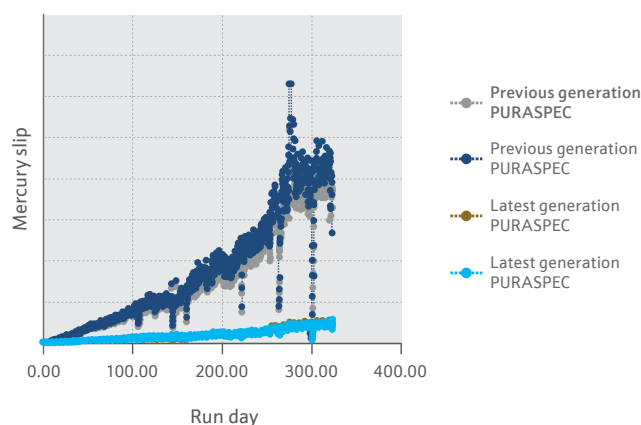


Figure 6: Gas phase test data on PURASPEC products

The data shows that the mercury slip from the latest generation **PURASPEC 1198/1199** product is significantly lower than for the previous generation product. This would translate for the customer into a higher capacity for mercury removal and a significantly longer lifetime for the charge than would be achieved with the previous generation **PURASPEC**.

Several different testing methods have been employed during the development of the latest generation **PURASPEC** mercury removal absorbents. In the test shown in Figure 7, a longer contact time was used which is closer to typical contact times used in real duties. The plot shows the cumulative mercury absorbed by the bed plotted against the cumulative mercury passed over the bed.

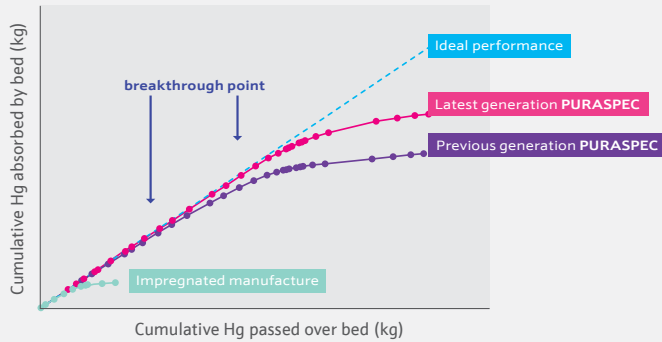


Figure 7: Further gas phase test data on **PURASPEC** products

In this test, both generations of **PURASPEC** were seen to achieve ideal performance (100% removal) at the start of the test. After some time online, deviation away from ideal performance starts to be observed which allows performance to be differentiated. As shown by the indicative 'breakthrough point' arrows, the latest generation **PURASPEC** was observed to run for around twice as long before the slip threshold was crossed.

Similarly to JM's newest sulphur absorbent, **PURASPEC** 1198/99 performance allows the customer to run with significantly longer change out cycle, or design much smaller mercury removal units, ultimately reducing the OPEX, CAPEX and footprint of their operation.

Tolerance to intermittent water wetting

All **PURASPEC** products in the current generation and the previous generation are tolerant of intermittent water upsets, but **PURASPEC** 1193/1194 in the latest generation offers the best water tolerance of all **PURASPEC** mercury absorbents, both in terms of physical robustness and maintenance of mercury removal performance.

It is important that absorbent products are physically robust, as breakage can lead to increased pressure drop during operation, more frequent change-outs, more time-consuming discharge, hazardous non-routine tasks for personnel during discharge, and potential to damage process equipment. Physical robustness has been demonstrated for the latest generation **PURASPEC** 1193/1194 product through a test where discharged mercury-laden granules were wetted at ambient temperature (Figure 8, left) and then tumbled for 10 mins in a Pascal mixer (Figure 8, right).



Figure 8: Photos of mercury-laden **PURASPEC** after exposure to water (left) and after subsequent tumbling in a Pascal mixer (right).

The images in Figure 8 show that the physical integrity of **PURASPEC** is unaffected by intermittent water wetting during operation, with the product form being unchanged even after 10 mins of tumbling following the water wetting. Crush strength measurements confirm that the product crush strength is maintained after exposure to water.

Performance is also maintained after intermittent water exposure. In another test, to simulate a water upset in a mercury removal unit containing **PURASPEC**, the inlet 25% of one bed was saturated with water prior to the run commencing while another bed was run under identical conditions but left dry for comparison. The beds were run in a liquid phase duty (mercury saturated hydrocarbon), and after 750 h online, the absorbent was discharged, dried, and then the Hg content of the absorbent at different positions down the bed was analysed. The results are shown in Figure 9.

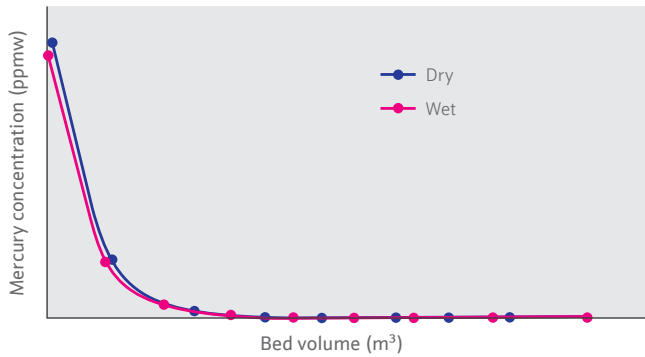


Figure 9: The mercury content on discharged absorbent as a function of bed volume in the 'water upset' test.

The results show that the mercury content of the absorbent and absorption profile at the end of the test was similar in both the wet and dry cases, showing that the performance of the absorbent recovers after a temporary water upset.

PURASPEC mercury removal absorbents – key points

PURASPEC latest generation products offer a step-change in performance. The improvements and benefits are summarised as follows;

- PURASPEC 1198/1199 offers a very significant enhancement of kinetics and capacity (60% increase in pseudo-first order rate constant in liquid phase and lasts over twice as long for a given slip in gas phase testing), while maintaining very high physical robustness and tolerance to upsets.
- PURASPEC 1193/1194 is the most robust PURASPEC ever developed to plant upsets including water upsets while maintaining very high mercury removal capacity and kinetics

Conclusion

Natural gas is critical in the energy transition to low-carbon fuels as a direct energy source or as a basis for blue hydrogen production. The increase in production will come from different geographies and fields with different gas characteristics and impurity levels. In order to bring the quality of the gas in line with regulative and environmental legislation, removal of hydrogen sulphide and mercury to very low levels is required.

PURASPEC products are designed to perform such contaminant removal in way that makes the operation effortless and economical both from CAPEX and OPEX perspective. PURASPEC latest generation products offer step improvements in their bed lifetimes, capacity, kinetics and tolerance to upsets while maintaining excellent physical integrity.

References

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