Mercury absorbent's ability to air-load

We consider the air loading capability of an absorbent as a means for improved mercury removal operation

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Elemental mercury is a very toxic compound that affects the human nervous system and kidneys, and bioaccumulates in the surrounding ecosystems. In addition, mercury can compromise plant equipment integrity through liquid metal embrittlement (causing cracks) and amalgams (alloys with metals like aluminium). The latter can cause very severe safety incidents in gas processing plants, with risk to life and extensive financial implications.

It is thus a requirement that mercury is removed from natural gas before it is converted into LNG or transported via a pipeline. With the lowest carbon footprint of all fossil fuels, LNG is a critical enabler towards a decarbonised world, and this is reflected in its on-going growth in demand.

The most effective technology to remove mercury utilises copper sulfide (CuS) absorbents via an irreversible chemical reaction as follows:

$Hg + 2CuS \rightarrow HgS + Cu_2S$

The high reactivity of CuS gives rise to the fastest mercury removal kinetics and the highest absorbent capacities of all technology options. This combination allows for the longest bed lifetimes and the smallest mercury removal unit vessel footprints. The technology also offers a sustainable solution for mercury removal, reducing the overall environmental footprint as part of well-designed flowsheets.

Once the mercury is captured by CuS-based absorbents, the mercury is locked away into the absorbent structure as safe, chemically inert, and non-volatile mercury sulfide. At the end of the lifetime of the charge, the spent absorbent can be safely handled and sent for the responsible disposal of the captured mercury.

Conventional loading of CuS-based mercury removal absorbent

Conventionally, mercury removal absorbents are loaded under inert conditions. High-purity nitrogen is required during loading to prevent self-heating reactions due to CuS oxidation. Run-away exotherm caused from an uncontrolled oxidation could lead to very significant damage to the plant and hazards to personnel. While loading under inert atmosphere is well-established industry practice, gas processors often talk about the difficulties and risks associated with the use of high-purity nitrogen. Using over 30 years of experience of supplying mercury removal absorbents, Johnson Matthey challenged itself to develop a CuS absorbent with high performance and no self-heating potential, allowing for loading in an oxygen- containing atmosphere.

PURASPEC™ 1193 and 1194 were launched at the start of 2023 as high-performance mercury absorbents that also offer the capability to be air-loaded. This new technology has been made possible by advancements in the understanding of how to enhance mercury removal kinetics while inhibiting oxidation kinetics.

The product launch was carried out following an extensive safety and performance testing. An important customer in Japan has already successfully loaded **PURASPEC** 1194 under air. The absorbent charge has been in operation for more than six months and continues to operate as designed.

Why is the ability to air load important to operators?

Safety

Loading under air atmosphere removes the potential danger of nitrogen asphyxiation to personnel. Nitrogen will displace oxygen in enclosed spaces, potentially leading to asphyxiation if appropriate precautions (such as personal protective equipment, training etc.) are not taken.

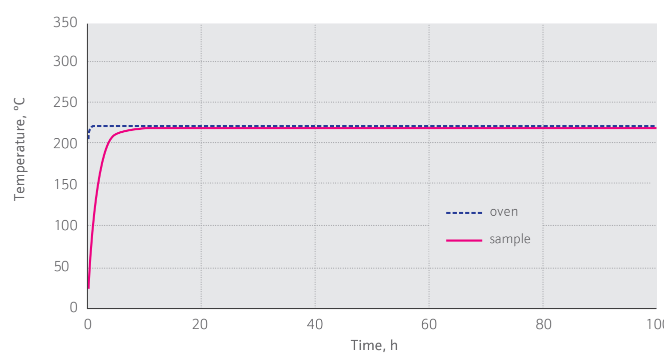

Figure 1. 1 l wire basket self-heating testing at 220 °C, with humidified air for **PURASPEC** 1194.

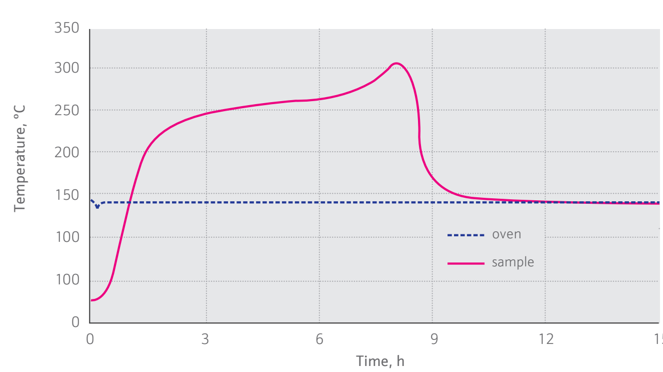

Figure 2. 1 l wire basket self-heating testing at 140 °C for a conventional CuS-based mercury absorbent.

Flexibility

Loading under an oxygen-containing atmosphere provides the flexibility to choose between air or plant-grade nitrogen. Operators can select the approach that best aligns with their established procedures and safety guidelines regarding handling hazardous material.

Availability

Availability of high-purity nitrogen or, more often, liquid nitrogen can be challenging in remote or offshore locations. Using ambient air for loading the absorbent simplifies the logistics and reduces the reliance on specialised nitrogen supply infrastructure.

Cost

Safe handling of nitrogen during absorbent loading requires specialist catalyst handling crews. Contacting such crews adds an extra layer of complexity and cost to the loading process. This is in addition to the cost of liquid nitrogen that can be high depending on location and minimum tanker size. Therefore, loading under air atmosphere allows for a more streamlined and cost-effective approach, reducing the overall operational expenses.

Self-heating testing

The self-heating characteristics of **PURASPEC** 1193 and 1194 absorbents were thoroughly evaluated by the company's own technical experts working in conjunction with a world-leading third-party testing and certification company. Tests were designed based on widely recognised methodologies for classification of hazards of goods for transportation. Further, the conditions of these tests were made more challenging to ensure that risks specifically associated with air loading of the absorbent were appropriately considered and tested for. The experimental work was conducted by the third-party testing and certification company using **PURASPEC** 1194 material – this product grade was expected to be more prone to oxidation if any was to occur.

The 1l wire basket test is based on the standard test for substance self-heating classification, according to UN DG Code and CLP/GHS.[1] The sample is exposed in air while being heated for 72 hr, and the exit temperature of the sample is continuously recorded. If the sample temperature increases more than 60 °C above the set temperature of 140 °C, the sample material is classified as 'self-heating' within GHS and for Transport (Class 4.2).

Under these test conditions, no exotherm was observed. As it is known that high humidity in certain geographical regions can increase the exotherm potential, an additional test was carried out using (i) water saturated air (at 70 °C) and (ii) set temperature of 220 °C. Figure 1 shows the results.

The results clearly show that the **PURASPEC** 1194 exhibits no exotherm due to self-heating at 220 °C, and humidified air as the sample temperature did not deviate from the oven temperature for the full duration of the test.

To eliminate any concerns about the sensitivity of this method, a standard (140 °C) test was run on a reference sample, which represents a conventional copper sulfide-based mercury absorbent (Figure 2).

Significant exotherm of 130 °C was recorded on the reference sample, which was broadly independent on the level of humidity of the air. While this is a strong re-assurance of the accuracy of the test results, three additional testing methodologies were utilised by the third-party company to re-afirm the inertness of **PURASPEC** 1194 towards self- heating during air loading operations. All of these results showed no evidence of self-heating for **PURASPEC** 1194.

Mercury removal performance testing

A mercury removal testing programme was carried out to ensure that the exposure to air during the loading does not negatively impact the inherent performance of the absorbent. Typically, absorbents' performance is characterised in terms of capacity and kinetics as each of these directly impacts the life cycle utilisation and cost of the absorbent.

Figure 3 shows the results for cumulative mercury absorption in a long term (205 days online) gas phase mercury removal test. **PURASPEC** 1194 retains the long- term mercury removal capacity of traditional Johnson Matthey's CuS-based absorbents, allowing for direct replacement with no process changes or equipment modifications.

Accelerated performance tests were also carried out to probe any changes in kinetics that could occur following an air loading process. Firstly, samples of commercially produced **PURASPEC** 1194 absorbent were taken from drums which had been stored for three months to account for typical transportation and storage time prior to loading at customer sites. These were then placed into open dishes where the material was well-spread to ensure very high contact with air and left for 14 days (Figure 4).

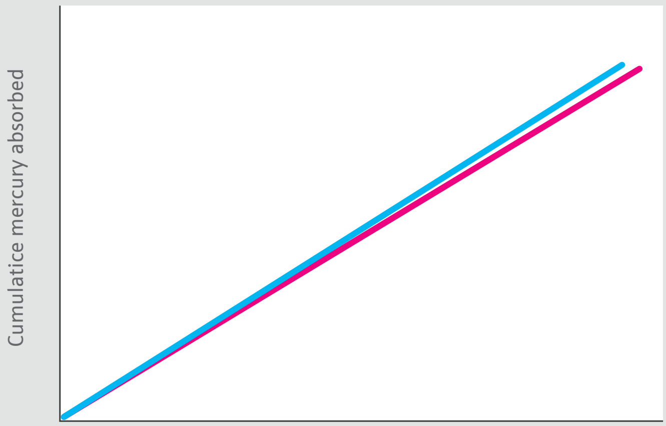

Figure 3: A plot of cumulative mercury absorbed vs cumulative mercury passed over the absorbent. Blue & green = **PURASPEC** 1194. Pink and purple (partly obscured) = conventional high performance CuS product.

Figure 4: **PURASPEC** 1194 spread on an open dish.

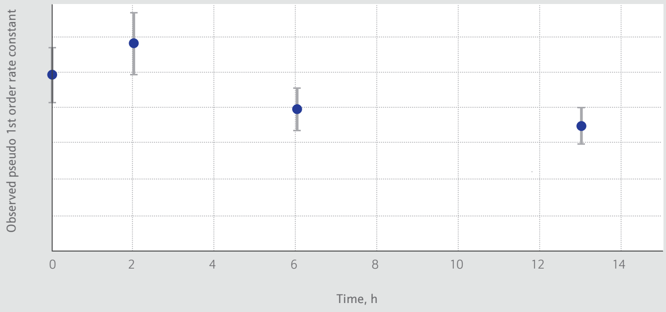

Figure 5: The mercury removal kinetic performance of samples of **PURASPEC** 1194 which had been continuously exposed to air (oxygen and moisture) for various time periods.

This treatment would exacerbate any deactivation due to exposure in air following a typical plant start-up.

Figure 5 shows the changes in rate constant of **PURASPEC** 1194 with time of sample exposure in air starting from when the drum was first opened. The results show that there is no notable change in the mercury removal kinetics of **PURASPEC** 1194 in an accelerated air exposure simulating the air loading process.

Summary

The increasing demand for natural gas/LNG and the stringent safety and quality regulations require purification solutions that are efficient in removing mercury to very low levels in a cost-effective and easy to operate manner. Air loading is an important capability to supplement the high inherent performance of an absorbent.

PURASPEC 1194 has been proven to retain its high capacity and fast kinetics, following safe loading of the absorbent in an oxygen-containing atmosphere. This has also been demonstrated at a full-scale plant environment at Johnson Matthey's customer in Japan.

The absorbent does not undergo any exothermic reactions or generate heat when exposed to air or oxygen-containing nitrogen. This inert behaviour towards self-heating ensures the stability and integrity of the absorbent, providing a secure environment for handling and transportation. Laboratory testing under accelerate conditions showed excellent performance in the removal of mercury following exposure to air, which combined with its inherent high water carry-over resistance would ensure a long and reliable life of the absorbent. Eliminating the requirement for high purity nitrogen loading makes the overall operation safer, more cost-effective and logistically easier to manage especially in remote and offshore locations.

References

1. UNECE: Recommendations on the Transport of Dangerous Goods – Model Regulations (Rev. 21) and CLP Regulation (EC) No 1272/2008 on the classification, labelling and packaging of substances and mixtures.

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