

JM

H₂S removal in challenging CO₂ streams

Non-regenerable fixed bed absorbent technology for the removal of hydrogen sulfide, its strengths and disadvantages in carbon dioxide purification, and the impact of oxygen presence.

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Achieving global sustainability targets requires a multipronged approach to the prevention and reduction of harmful emissions. Carbon capture, utilisation, and storage (CCUS) is a very important technological solution to reduce carbon dioxide (CO₂) – the most abundant greenhouse gas.

CO₂ is generated from a wide variety of operations and at various scales. Broadly, the CO₂ sources are split into industrial (post-combustion), and biogenic. The composition of the CO₂ streams directly reflects the processes by which these streams are generated, but also how they have been handled. In some cases, the CO₂ sequestration or utilisation is done at the point of generation, but the more likely approach is combining these streams and transporting them to CCUS hubs. The latter reduces the investment and risk for individual CO₂ producers.

Purification of CO₂ streams prior to liquefaction or pipeline transportation is a firm requirement; however, there are no agreed industry wide specifications. One of the most specified contaminants by transportation operators or downstream users is hydrogen sulfide (H₂S) as it is harmful to human health and the environment, causes equipment corrosion, and is a poison to many catalysts in utilisation applications. H₂S is most commonly present in pre-combustion CO₂ capture.

There are a number of well-known technologies to remove H₂S from hydrocarbon streams – these are transferable to CO₂ streams; however, the full impurity composition needs to be considered as this is likely to impact their performance. One possible concern for efficiency of the H₂S removal system is oxygen. Some of the streams where H₂S and O₂ are expected to be co-present include:

- CO₂ from the fermentation process.
- CO₂ from biogas upgrading.
- CO₂ captured/removed from O₂-containing natural gas, i.e.:
 - Natural gas from fracking.
 - Natural gas from recently commissioned pipelines depending on the length of pipeline network, residual oxygen may be present in the feed gas for a long time (years).
 - O₂ ingress in the process gas, typically during compression at well gas gathering / boosting stations.
- Pipeline CO₂ from multiple sources, e.g. pre and post-combustion CO₂.

Non-regenerable fixed bed absorbent technology

Non-regenerable fixed bed absorbents are the most common solution for H₂S polishing duties. H₂S absorbents are simple to install and operate, require little intervention, and can achieve an outlet specification in the ppb range. The removal occurs via a stoichiometric chemical reaction with the active components in the absorbent. This prevents any re-release into the stream or the environment in contrast to adsorbents which use physical interaction as their main removal mechanism. The absorbent removes the H₂S until they reach full saturation or they breakthrough H₂S at the bed outlet.

There are three families of metal-based absorbents that are most commonly used for H₂S removal in CO₂ streams – their features are described considering their techno-commercial applicability.

ZnO-based absorbents

ZnO absorbents have been used in natural gas and syngas purification applications to remove sulfur for many years. While they can remove H₂S to very low levels, they suffer from some operational limitations:

- Their capacity to remove H₂S is low at near ambient conditions – they only reach their optimum capacity at temperatures higher than 300 °C.
- ZnO can react with CO₂ forming ZnCO₃; the latter will block access of H₂S to the active ZnO and will impact performance severely. This means the operation needs to be carried out outside the temperatures where ZnCO₃ can be formed.

ZnO-based absorbents are therefore not the first choice for the removal of H₂S from CO₂ streams.

Iron oxide-based absorbents

Iron oxide-based absorbents are also a well-established H₂S removal solution in natural gas and CO₂. There are many commercially-available iron oxide-based products which can contain a combination of iron oxide phases, such as Fe₂O₃, FeO, and Fe(OH)₂.

The iron oxide-based absorbents are designed to have a very high capacity, however, the achieved capacity in CO₂ streams is often significantly lower for several reasons:

- Iron oxide absorbents have slow kinetics, meaning that very long residence times are required when a low H₂S outlet specification is required. This means that bed volumes tend to be much larger compared to other technologies.
- The chemistry behind iron oxide absorbents means that they require the feed stream to be fully water saturated to maximise the H₂S removal capacity. Therefore, steam injection or a water spray system is normally required if the stream is not continuously at water saturation conditions.
- Under these conditions, the absorbents can suffer from severe agglomeration if the water condenses onto the absorbent bed leading to progressive pressure drop (dP) increase (and premature changeout) and difficult and time-consuming discharge.
- Depending on the formulation, certain iron phases can react with CO₂ to form carbonates which have a similar impact as ZnCO₃.

Iron-based absorbents are often the preferred choice when the upfront cost is the primary decision driver and the feed stream is already water saturated. Their cost is significantly lower compared to other metal-based absorbents.

Other metal oxide-based absorbents

Metal oxides absorbents usually contain transition metals such as copper, manganese, or iron. Copper is the most active metal for H₂S removal. These types of absorbents have been used in both natural gas and CO₂ purification for many decades.

Metal oxide absorbents can reach very high sulfur capacities at low/ambient temperatures due to their inherently fast kinetics and high affinity for H₂S. This allows the operator to reach low H₂S outlet specifications using much smaller bed volumes and/or to extend the life of the absorbent, making the lifecycle cost for this technology the most attractive.

Metal oxide-based absorbents may not reach the expected capacity in water-saturated streams if they are exposed to continuous water dropout. The free water would generate a diffusion barrier, blocking the active sites and making the H₂S reaction more difficult. It is thus commonly recommended to pre-heat the stream above dewpoint by a few degrees to prevent water condensation.

Enabling metal oxides to reach their true potential requires extensive knowledge and experience in materials science and chemistry. Johnson Matthey (JM) has over 40 years of experience in this area and has optimised the formulation and manufacturing process of **PURASPEC**[™] absorbents throughout the years. The resulting solutions have the optimum properties required to reach maximum sulfur capacity and to withstand the demands of loading and operating conditions. The absorbents are robust with high crush strength until end of bed life, meaning no pressure drop increase is typically observed and are free flowing upon discharge.

JM offers a range of copper-based and ZnO-based absorbents to remove H₂S from natural gas and CO₂ streams. For the purpose of this article, the following references to **PURASPEC** absorbents assume copper-based products.

The performance of **PURASPEC** products is not dependent on operating temperature, pressure or the nature of the feed, reaching their maximum capacity (i.e. complete copper active site utilisation) in the proven operating range:

- Temperature: 0 °C – 150 °C.
- Pressure: Atmospheric – 150 barg.

Under these conditions, H₂S is removed to non-detectable levels using the company's absorbents.

H₂S removal from CO₂ streams, even when O₂ is present

At first glance, it might be thought that low-cost iron oxide absorbents would be the choice option for H₂S removal from captured CO₂ when O₂ is present as there is precedence of use in such systems. However, this has been associated with reduced performance under these conditions, increasing the size of the beds and the associated investment.

Copper-based absorbents' capacity for H₂S removal is not impacted by pure CO₂. If oxygen is found to be 'benign' in the removal of H₂S, then this technology should be preferentially considered from both a technical and commercial perspective.

It is important to note that removal of oxygen prior to removing CO₂ is not economical as the most commonly used technology utilises precious metal catalysts which are highly sensitive to H₂S.

JM carried out extensive research and testing on various copper-based formulations to evaluate the effect of O₂ on H₂S removal. **PURASPEC** 2058 has been found to have the right combination of chemical and physical properties to remove H₂S efficiently in the presence of oxygen.

Testing and comparison to iron oxide-based absorbents

The experimental conditions for the H₂S removal tests using **PURASPEC** 2058 and an iron oxide absorbent are shown in Table 1. 30 ml of absorbent material was charged to a fixed bed tubular reactor. A carrier gas mix of 0.35% O₂, balance CO₂ was dosed with 500 ppm/0.05% H₂S.

For the tests carried out with the iron oxide-based absorbent, the carrier gas was first diverted through a water bubbler before mixing with H₂S and passing over the reactor. This was done to give the iron oxide materials the best chance to reach its full potential in the test.

The gas exiting the reactors was analysed using a magnetic sector mass spectrometer to determine the H₂S concentration. The test was set up using the rig software to automatically stop the flow of the H₂S and carrier gases when the outlet H₂S concentration was at 95% of the inlet concentration (475 ppm). An automatic purge using 100% N₂ was then carried out for a minimum of six hours until the material was safe to remove from the reactors for post-mortem analysis (combustion analysis to determine sulfur content of the discharged material).

The comparative testing results are shown in Figure 1. The performance comparison between the two products is based on two main factors:

- Breakthrough time: when a clear deviation from the H₂S baseline is detected. Figure 1. Graph showing the H₂S reactor exit breakthrough profiles of **PURASPEC** 2058 vs an iron oxide-based product.
- Sulfur saturation capacity: the total sulfur content of the absorbent when it reaches 95% H₂S breakthrough and the experiment is stopped.

PURASPEC 2058 showed first signs of deviation from the baseline after more than 4800 min, i.e. 34% through the run length. In contrast, the iron oxide-based absorbent breakthrough was after 4% of the experimental run length. This indicates that **PURASPEC** 2058 has a much sharper reaction profile i.e. better absorbent utilisation which results in higher capacity. The experimental results show that JM's copper-based absorbent had five times higher capacity than the iron-oxide-based material.

In addition, the spent samples were analysed using a Soxhlet extraction technique which uses n-hexane to extract and quantify any elemental tubular reactor. A carrier gas mix of 0.35% O₂, balance CO₂ was dosed with 500 ppm/0.05% H₂S.

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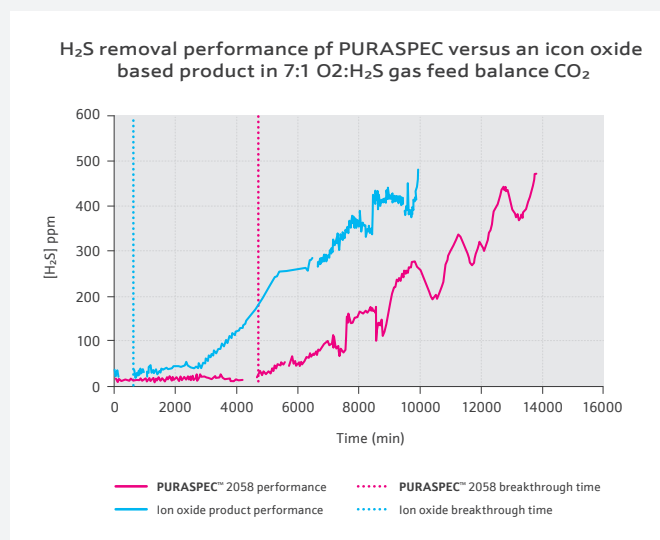


Figure 1. Graph showing the H₂S reactor exit breakthrough profiles of **PURASPEC** 2058 vs an iron oxide-based product.



Figure 2. Soxhlet extraction in hexane solution. **PURASPEC** 2058 (right) and iron oxide (left).

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The comparative testing results are shown in Figure 1. The performance comparison between the two products is based on two main factors:

- Breakthrough time: when a clear deviation from the H₂S baseline is detected.
- Sulfur (S8) which may have formed on the product during the sulfur removal reaction. S8 in the CO₂ stream can lead to corrosion (by forming sulfuric acid if the stream is water saturated) or depositions and blockage in the narrow flow paths in the downstream systems. With time, S8 can be also accumulated in the pipeline network and can be even found in the end user delivery points due to its high solubility in CO₂ streams at every pressure.

For the iron oxide-based absorbent, a significant amount of S8 precipitate was observed (Figure 2, left), whereas there was no visual indication of S8 for the **PURASPEC** 2058 sample (Figure 2, right).

To explore this observation further, the sulfur content of the spent absorbents was re-analysed after the extraction process. The reduction in sulfur content was found to be 95% for the iron oxide-based material compared to 10% for the **PURASPEC** absorbent, clearly indicating that the former had converted much of the H₂S to S8. Another important observation was the condition of the absorbents on discharge. **PURASPEC** 2058 was found to be free flowing whereas the iron oxide-based product was agglomerated and difficult to discharge from the testing reactor.

Conclusions

A non-regenerable fixed bed absorbent technology comparison has shown that copper and iron-based absorbents are technologically and economically suitable for the removal of H₂S from CO₂ streams. In the presence of oxygen, copper-based absorbent technology, i.e. JM **PURASPEC** 2058 absorbent, has much faster sulfur removal kinetics, demonstrated by a much longer breakthrough time and five times higher sulfur capacity.

It was also determined that 95% of the sulfur removed by the iron oxide product was in the form of S8 compared to only 10% for the **PURASPEC** absorbent product. Therefore, most of the sulfur removed by the JM **PURASPEC** absorbent is permanently locked into the absorbent structure and cannot be released back in the feed.

Therefore, by selecting a copper-based absorbent, the operator will not only achieve much higher sulfur capacities i.e. smaller bed and/or longer bed lives but they will also minimise any S8 released into the CO₂.

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