BSR-050 – A Novel, High Capacity H_2S Removal Media

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Gas purification processes employing iron sponge suffer from low H_2S removal capacity and inconsistent performance (especially under conditions involving limited O_2), with the spent media being difficult to remove from the vessels. Further, the low reactivity associated with iron sponge can result in low-level H_2S bleed. BSR-050 was developed to address shortcomings associated with iron sponge often employed in the removal of H_2S from landfill and other natural gas sources. H_2S removal processes are not tightly controlled. Rather, the operating conditions such as the composition of the process stream (i.e.; concentration of H_2S, O_2, H_2O) and temperature vary over time and change with the season. In this presentation, H_2S reaction chemistry is first discussed. In light of the reaction chemistry, the effects of process conditions on H_2S removal using BSR-050 is illustrated. The presentation concludes with a case study involving BSR-050 employed in the purification of landfill gas.

Reaction Chemistry: H_2S will react with metal oxides and hydroxides to yield the corresponding sulfide. O_2, present in the process stream, regenerates the sites and leads to the formation of elemental sulfur plus water. The reaction is catalytic; however, once the pores of the media become filled with sulfur, the reaction is halted, as H_2S is unable to access reactive sites. The role of water is not fully understood; however, water is postulated to hydrate the metal oxide/hydroxide, with the hydrated form being the active site. A highly reactive H_2S removal media is desired, as said media will yield a small "reaction zone" in the bed. A small reaction zone will mitigate low-level H_2S breakthrough until such a time that the media in the bed is nearly completely spent.

BSR-050 Development: BSR-050 was developed by Guild Associates, Inc. to address shortcomings associated with iron sponge and other H_2S removal media. BSR-050 is a highly porous mixed metal oxy-hydroxide supplied as 4x12 mesh granules with a bulk density of 23-26 lbs/ft^3. The high metal content of BSR-050 facilitates rapid reactions involving H_2S, even under conditions unfavorable to other H_2S removal media. BSR-050 significantly out-performs iron sponge. When tested side-by-side, BSR-050 achieved an H_2S loading greater than 1.1 lbs H_2S removed per lb of media – nearly 10 times that of iron sponge!

BSR-050 Evaluation – Oxygen: BSR-050 was evaluated versus simulated landfill gas for its ability to remove H_2S over a range of process conditions. As noted from reaction chemistry, O_2 is necessary for the reaction to proceed. In the absence of O_2, BSR-050 will remove H_2S to a capacity on the order of 0.22 lb/lb. The capacity is reduced because there is no mechanism for the regeneration of the active sites. Consequently, once all the reactive sites are converted to the corresponding sulfide, the reaction is halter and H_2S elutes through the bed. Under conditions of stoichiometric oxygen (1,000 ppm H_2S and 500 ppm O_2), the H_2S removal capacity is greatly improved (to 0.67 lb/lb). At twice stoichiometric O_2 (1,000 ppm H_2S and 1,000 ppm O_2), the full capacity of BSR-050 is achieved. Further increasing the concentration of oxygen does not alter the performance. These results demonstrate the ability of BSR-050 to achieve a high H_2S removal capacity under conditions of low O_2.

BSR-050 Evaluation – Temperature: The temperature over which H_2S is removed can vary significantly based on changes in ambient conditions. This is because vessels employing H_2S removal media may not be well insulated or insulated at all and thus subject to seasonal temperature changes. Because of its high reactivity, BSR-050 is able to achieve a high H_2S removal capacity, even when operated as low as 50°F. At low temperatures, low-level bleed may occur; however, the low-level bleed will be eliminated once the temperature increases. The low-level bleed would be captured in the lag vessel associated with the lead-lag process.

Response to Transients: H_2S removal is not a steady state operation but rather a transient process. As a result, the media must be able to function effectively over a wide range of conditions, plus have sufficient capacity to get through periods where operating conditions are not ideal. One example is when the media is operated at a low temperature with minimal O_2 (1,000 ppm, 1,000 ppm O_2 and 50°F), which may occur when a cold front passes. Under these conditions, the reactivity of BSR-050 is reduced and H_2S bleed through the bed will occur. The bleed will be captured in a lag vessel or in a polishing bed. However, once the bed is returned to normal operating temperature (i.e., the cold front passes), H_2S bleed is eliminated and the full capacity of BSR-050 is achieved.

Effects of Water: Water is necessary for BSR-050 to remove H_2S, and this is true for almost all media employed in natural gas purification processes. For BSR-050, the relative humidity of the process stream needs to be between about 30% and 100% in order for the media to effectively function. Prolonged exposure of BSR-050 to supersaturated gas should be avoided. This is because water will fill the pores of BSR-050 and coat the granule, preventing access to reactive sites within the granule. Under supersaturated conditions, the reactions will occur at or near the external surface of the granule, effectively "egg-shelling" the granule with sulfur and/or metal sulfide. The performance of said media will be greatly reduced. BSR-050 can; however, be periodically exposed to supersaturated gas, as the bed will dry as the water content is reduced to below saturation.

Continuous exposure to supersaturated gas also has additional effects. Specifically, BSR-050 will clump. Referred to as "bricking" in the trade, the impact of continuous operation under supersaturated conditions will be reduced H_2S removal capacity and increase the difficulty in removing the spent media from the vessel. Otherwise, BSR-050 will be relatively free flowing and can be readily removed using suction. Preventing water from condensing in the bed can be achieved through the use of a water knock-out located just before the vessel.

Field Operation Results – Iron Sponge: A customer utilized 110,000 lbs iron sponge in each vessel of a lead-lag process to treat 5,600 scfm of landfill gas. Because of the low H_2S removal capacity of iron sponge, the media in the lead vessel was replaced every 3-4 weeks. This became an expensive endeavor for the customer.

Field Operation Results – BSR-050: The 110,000 lbs of iron sponge was replaced with 35,000 lbs of BSR-050. Due to the improved performance of BSR-050, the customer introduced stranded gas (normally delivered to the flare) – increasing the flow from 5,600 scfm to 6,500 scfm. BSR-050 lasted 4 months in the process before change-out was required, achieving an H_2S removal capacity greater than 1.2 lbs/lb. The customer realized additional revenue due to the increased gas being processed, and reduced costs associated with H_2S removal and change-out/disposal costs. Further, the customer decreased the logistics burdens associated with keeping a significant inventory of iron sponge on site.

Summary: BSR-050 represents an alternative to iron sponge and other H_2S scavenger media. High H_2S removal efficiency can be achieved over a wide range of process conditions. The media has demonstrated field performance at several landfill sites throughout the US and is commercially available in 1,000 lb sacks.

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Background

Hydrogen Sulfide – H_2S – is present in landfill and bio-gases and must be removed, often prior to gas purification

H_2S is often removed using scavenger media that reduces the H_2S to elemental sulfur plus H_2O

Iron Sponge is used in the majority of H_2S removal applications related to gas purification

- 20,000 to 100,000+ lbs of iron sponge is loaded into vessels
- Once H_2S in the effluent exceeds target level (e.g. 4 ppm), bed is taken off-line and iron sponge is removed

Issues with iron sponge include:

- Low H_2S removal capacity
- Slow to react
- Reduced effectiveness versus elevated H_2S concentrations, low O_2 concentration and low temperatures
- "Bricks" – media agglomerates – greatly increasing difficulty of removal
- Inconsistent operational performance

Objectives

Introduce BSR-050 as an alternative to iron sponge in removing H_2S from landfill and bio-gas

Illustrate effects of process conditions on the removal of H_2S using BSR-050

- Temperature
- Concentration of oxygen, $[O_2]$
- Concentration of H_2S, $[H_2S]$
- Role of water

Report field operation results for BSR-050

- Capacity
- Media removal

H_2S Removal Chemistry

Two reactions:

- Metal sulfide formation reaction: $H_2S + M\text{-}O \rightarrow M\text{-}S + H_2O$
- Site regeneration reaction: $M\text{-}S + \frac{1}{2} O \rightarrow M\text{-}O + S$

  Overall: $H_2S + \frac{1}{2} O_2 \rightarrow S + H_2O$

Reaction is catalytic – active sites regenerated with O_2

- O_2 necessary to complete catalytic cycle
  - Metal oxide (M-O) reacts with H_2S to form a metal sulfide (M-S)
  - Metal sulfide is regenerated with O_2 to yield the metal oxide plus elemental sulfur
- Elemental sulfur is deposited in the pores of the material
- Reaction is halted once pores become filled with sulfur (active sites can no longer be accessed)

BSR-050 Development

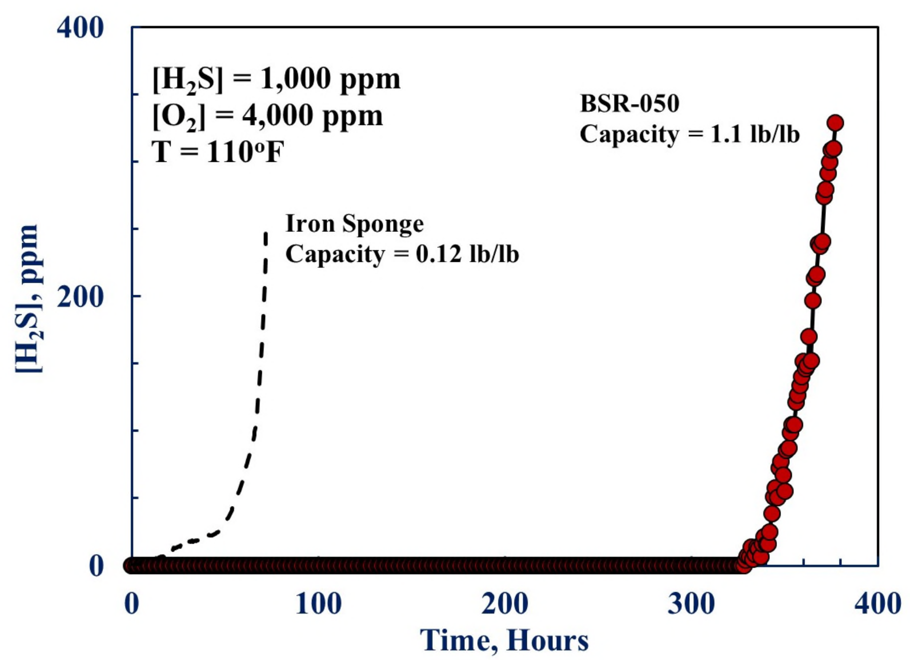
BSR-050 is a highly porous mixed metal oxide comprised of metals that facilitate reactions leading to the removal of H_2S

- BSR-050 designed with a large number of reaction sites to facilitate rapid chemical reactions, even under unfavorable operating conditions
- Porosity results in high H_2S removal capacity that exceeds 1 lb H_2S removed per lb of BSR-050
- BSR-050 out-performs iron sponge

Granular Form – 4x12 mesh

Density – 23-26 lbs/ft^3

Excellent Hardness and Crush Strength



H_2S Removal – Iron Sponge vs BSR-050

BSR-050 Evaluation

BSR-050 evaluated in the laboratory using simulated landfill gas in order to assess the impact of process conditions – namely [H_2S], [O_2], [H_2O] and temperature – on media performance

Employed media manufactured at the production scale

Reaction vessel located within environmental chamber to control humidity and temperature

Gas chromatograph used to measure feed and effluent concentrations of H_2S

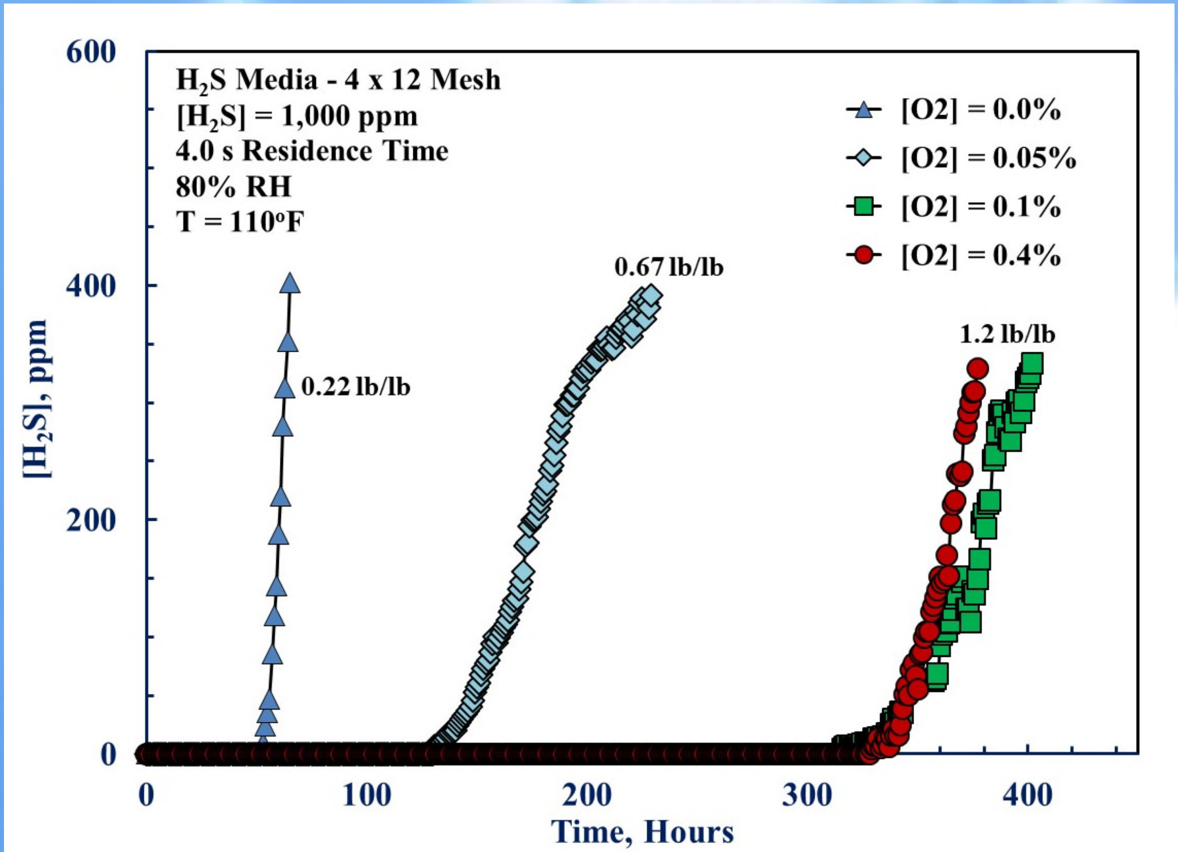
Residence time of 3-5 seconds typically employed in testing

Effects of Oxygen

Oxygen is necessary to maximize H_2S removal efficiency

High reactive site density allows BSR-050 to effectively remove H_2S under conditions where very little O_2 – down to 0.1% – is present in the gas

Operation at higher O_2 contents presents no issues



Effects of Temperature

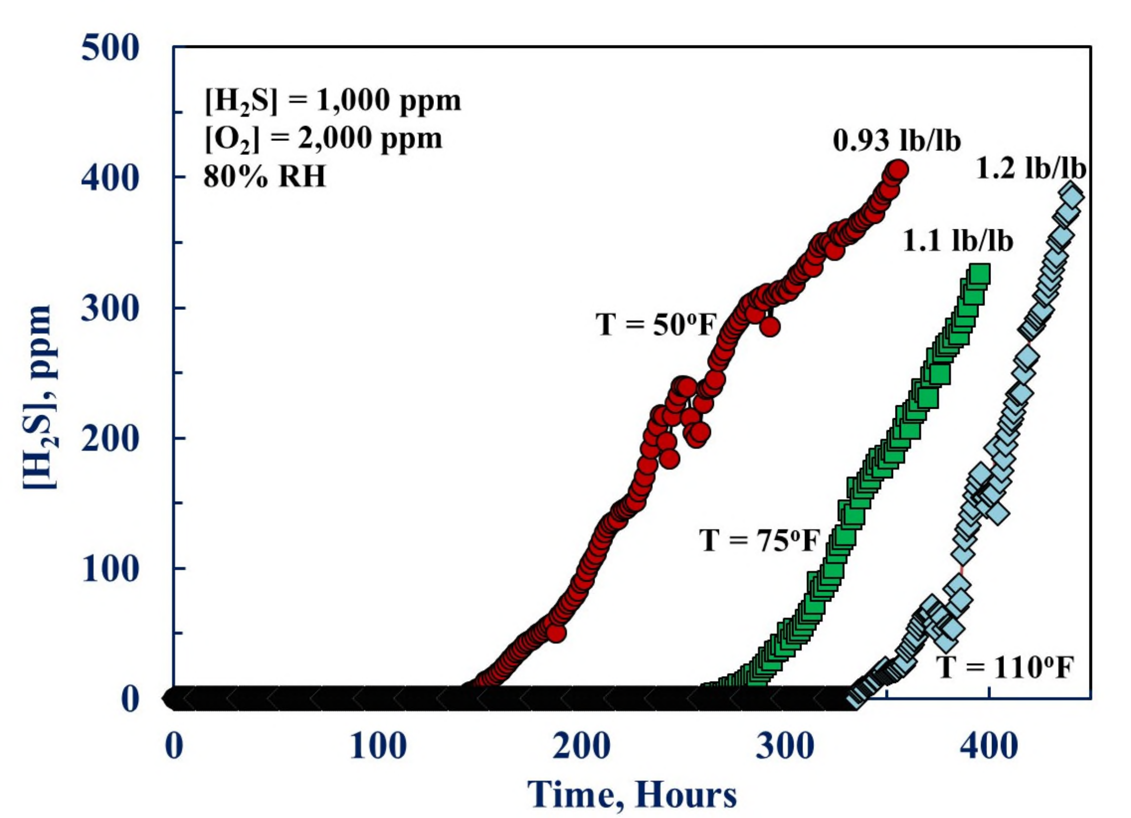
H_2S is most effectively removed at increased temperatures.

- Decreasing the temperature increases the depth of the "reaction zone"
- Operation at reduced temperatures will not decrease the capacity of BSR-050 to remove H_2S but may result in low-level bleed from the bed.

BSR-050 achieves high H_2S removal capacity, even at temperatures as low as 50°F (beneficial during operation in cold climates).

H_2S bleed at 50°F attributed to reduced reaction rate

Removal capacity reported to 400 ppm H_2S in effluent. Allowing media to run longer will increase capacity, especially at 50°F.



Response to Transients

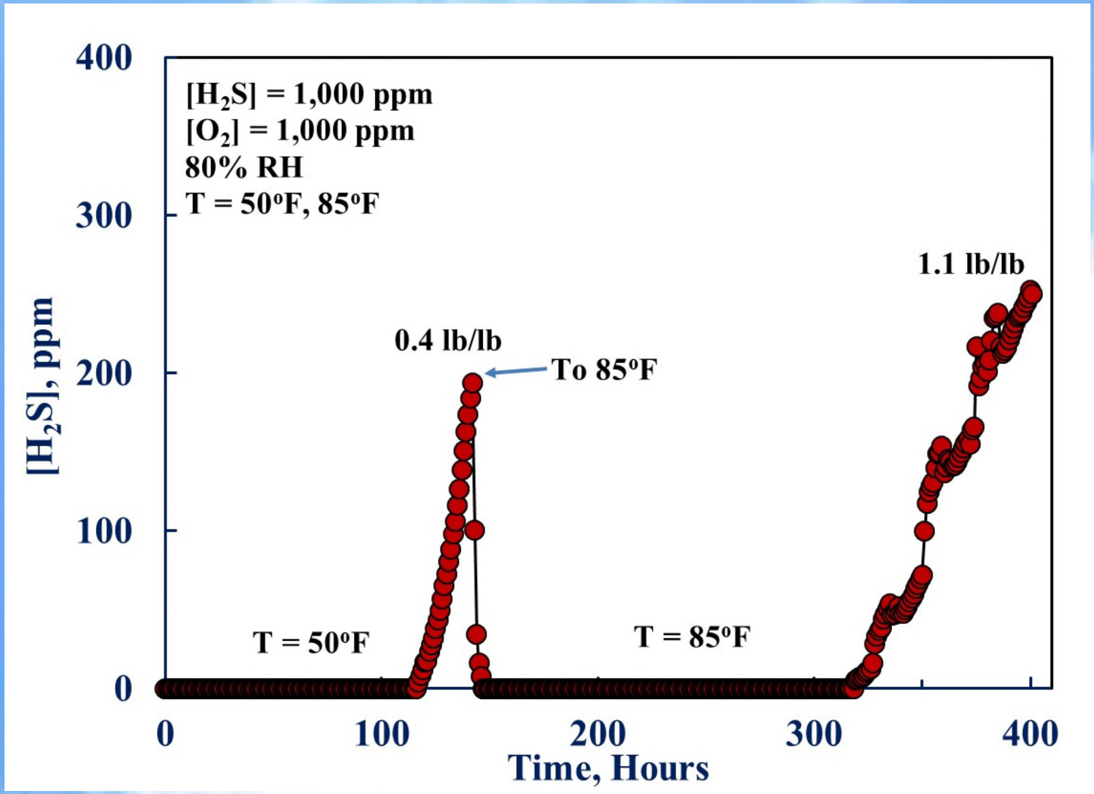
Landfill gas streams are not stable

- $[H_2S]$ will vary based on well heads and landfill composition
- $[O_2]$ will vary based on draw and well heads “sealing” during rain
- Temperature will vary based on ambient conditions

When temperature is cold, media reactivity is reduced, most notably under conditions with limited O_2, and H_2S is present in effluent early on.

As bed returns to higher temperature – 85°F – reactivity and high capacity return

Without high capacity, effluent $[H_2S]$ would exceed threshold and media would have to be replaced



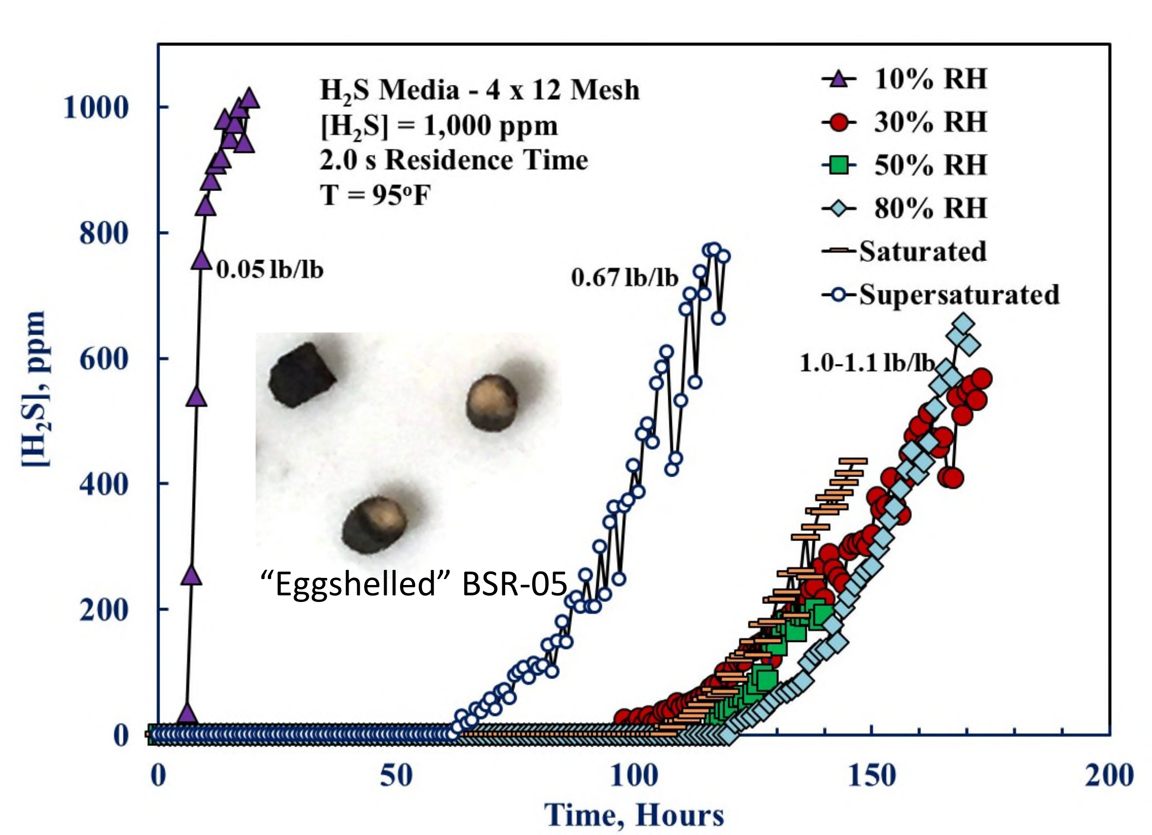
Effects of Water

Water is necessary for the removal of H_2S – activated site believed to be a hydrated metal oxide.

- Absence of water will prevent reactivity
- Excessive water will be problematic

If significant amounts of water are condensing in the bed:

- Pores of media fill with water, preventing H_2S from accessing active sites within media – leading to decreased capacity
- Reaction occurs primarily at external surface, leading to "bricking" and clumping of media
- Media becomes "eggshelled" with sulfur and/or sulfide and must be replaced



Effects of Water

Spent BSR-050 removed from vessel where water significantly condensed.
H_2S removal capacity = 0.78 lb/lb

Spent BSR-050 from process where water condensation was minimized.
H_2S removal capacity = 1.15 lb/lb
Media free-flowing for easy removal!

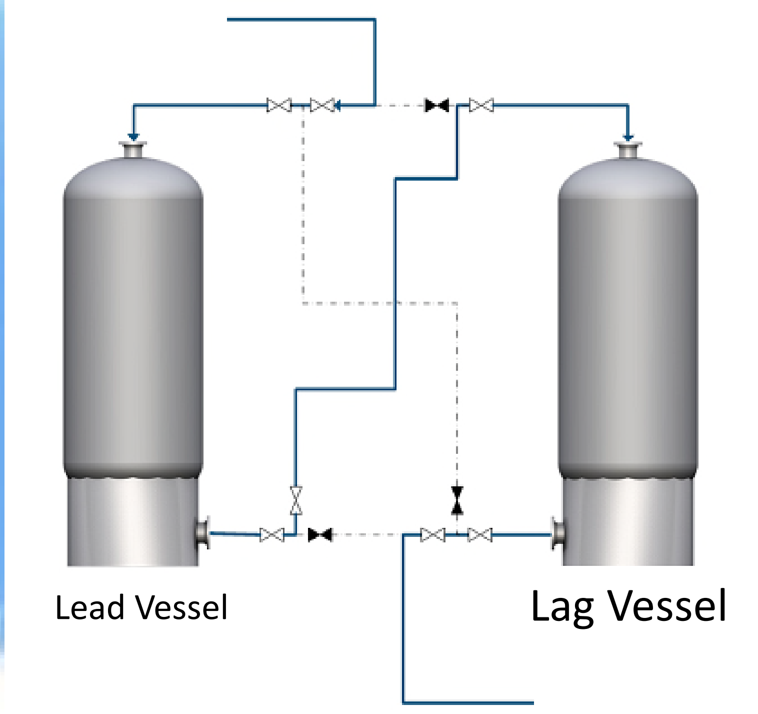
Field Operation Results – Iron Sponge

Customer utilized iron sponge in lead-lag process to remove H_2S from landfill gas (5,600 scfm)

- Vessels filled with 110,000 lbs of iron sponge
- Process opeated with 800 ppm H_2S, 1,000 ppm O_2
- Media replaced every 3-4 weeks in service

<u>Lead-lag process – operation</u>

- Gas enters lead vessel, exits and enters top of lag vessel.
- Once H_2S in lead vessel exceeds threshold, lead vessel taken off line and media replaced
- Lag vessel now becomes lead vessel
- Configuration maximizes utilization of media and prevents operation shutdown during media change-out



Field Operation Results – BSR-050

Customer replaced 110,000 lbs of iron sponge with 35,000 lbs of BSR-050

- Due to performance of BSR-050, customer introduced stranded gas from additional cells – flow increased from 5,600 scfm to 6,500 scfm
- Media lasted 4 months

<u>Cost Savings Realized</u>

- Additional profit due to increased gas flow
- Reduced cost to remove H_2S
- Reduced change-out costs – less frequent change-outs
- Reduced disposal costs – less change-outs and reduced media weight
- Reduced logistics – need to stockpile media on site eliminated

Summary

- BSR-050 is able to remove H_2S from process gas over a wide range of conditions
- The concentration of O_2, H_2S and H_2O will impact the ability of BSR-050 to remove H_2S.
- BSR-050 is able to effectively remove H_2S under conditions where the ratio of [O_2] to [H_2S] is on the order of unity
- Prolonged periods of water condensation in the bed is detrimental to the performance of BSR-050. Prolonged water condensation may lead to “bricking”, reducing media performance and may make removal more difficult
- BSR-050 offers economic advantages including
  - Increased gas flow
  - Reduced change-out and disposal costs
  - Reduced H_2S treatment costs