Mercury Removal – Oil & Gas

PURASPEC$_{JM}^{TM}$ Technology Solutions

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Johnson Matthey – Then & Now

• British company – 200 years of history
  • 1817: Mr Johnson established gold assaying business in London
  • 1852: Mr Matthey joined to form partnership
    • Gold, platinum, palladium refining
    • Global speciality chemicals company

• World class technology in fine chemicals, precious metals and catalysts
  • ~ 13,000 employees in 30+ countries
Divisional structure

Emission Control Technologies
- Light Duty Catalysts
- Heavy Duty Catalysts
- Stationary Emissions Control

Process Technologies
- Chemicals
  - JM Davy Technologies
  - Syngas
  - Chemical Catalysts (including Formox)
- Oil and Gas
  - Upstream
  - Downstream

Precious Metal Products
- Services
  - Platinum Marketing and Distribution
  - Refining
- Manufacturing
  - Noble Metals
  - Colour Technologies
  - Chemical Products

Fine Chemicals
- Active Pharmaceutical Ingredient (API) Manufacturing
- Catalysis and Chiral Technologies

New Businesses
- New Business Development
- Water Purification
- Battery Technologies
- Fuel Cells
- Advanced Packaging
What is Hg and why do we need to remove it?
Including natural gas, crude oil, coal and other hydrocarbons
Mercury in oil & gas

Naturally occurring trace element in fossil fuels

Predominantly present in the metallic (elemental) form but can be present in the form of inorganic salts and organic species

Typical levels in crude oil range from <1 ppb w/w to 1000's of ppb w/w depending on field and well. Some refiners are starting to impose limits on feedstock's in the single ppb range.

Solubility and volatility of elemental, inorganic and organic species varies largely. This affects the species present in each stream and the removal technologies required.
Mercury Species

- Volatile Mercury (elemental) follows the lighter streams:
  - Gas, Propane, Butane
  - Inorganic & organic mercury rarely seen in these streams
- Heavier hydrocarbon streams can contain all Hg forms.
Mercury belt and global hot spots for mercury in oil and gas reserves

- **South America**
  - Hg (gas) = 50-120 µg/m³**
  - Hg (cond.) = 26-40 ppb*

- **North Africa**
  - Hg (gas) = 50-80 µg/m³**
  - Hg (cond.) = 26-40 ppb*

- **SE Asia, Australia**
  - Hg (gas) = 200-300 µg/m³
  - Hg (cond.) = 10-800 ppb

- **Northern Europe**
  - Hg (gas) = 180 µg/m³∗

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* Mercury Hot spots
** Global Mercuriferous Belts

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Why Do We Need To Remove Hg?

- Causes liquid metal embrittlement of some alloys
- Causes corrosion of aluminium heat exchangers
- Equipment contamination
- Increases hazards of equipment maintenance / operator exposure
- Environmental emission limits to land, air & water
- Poisons precious metal catalysts
- Product specifications
LME - Moomba explosion

Serious financial and safety implications

- Losses:
  - Leading insurers put the insured loss at A$320 million ($US245 million)

- Energy crisis in NSW & South Australia
  - Supplies were limited to 30-40% capacity
  - Cutbacks by major industrial customer
  - Job layoffs
Mercury Amalgam Corrosion
Mercury and occupational health

- Mercury can be absorbed through the skin, by inhalation and if swallowed through digestion
- Volatility combined with lack of smell makes Hg very dangerous
- The Environmental Protection Agency (EPA) limit on drinking water is 2 µg/L (ppb)
- Acceptable levels in workspace air – 50 µg/m³
  - Propane and butane specs ~ 5 µg/m³ !!
  - Natural sales gas specs as low as < 0.01 µg/m³ !!
- Methyl mercury is a very toxic form of mercury found in aquatic systems where it concentrates in predatory fish
  - Food and Drug Administration (FDA) recently set limit of 1 mg/kg (ppm) in seafood
PURASPEC$_{\text{JM}}^{\text{TM}}$ Hg Removal Absorbents
Mercury distribution – GP Plant

- **Acid Gas Removal (Amine/Membrane)**
  - Regen / Permeate
  - 65% Hg

- **Gas Dehydration (Glycol/Mol Sieve)**
  - Dehydration Regen Gas
  - 5% Hg

- **Al Heat-Exchanger**
  - 20% Hg

- **Separation**
  - Fuel Gas
  - 4% Hg

- **NGL Export**
  - 19% Hg

- **Gas Export**
  - 15% Hg

- **Produced Water**
  - 2% Hg

- **Oil Export/Storage**
  - 8% Hg

- **Multiphase Flow**
  - 100% Hg

- **Export/Storage**
  - 90% Hg

- **Export**
  - 2% Hg

- **Export**
  - 25% Hg

- **Export**
  - 8% Hg

- **Export**
  - 65% Hg

- **Export**
  - 5% Hg

- **Export**
  - 20% Hg

- **Export**
  - 19% Hg

- **Export**
  - 15% Hg

- **Export**
  - 4% Hg
PURASPEC\textsubscript{JM}™ Technology

- **PURASPEC\textsubscript{JM}™ Process**
  - fixed bed, solid absorbents
  - non regenerable
  - highly selective
  - no operator involvement
  - proven technology
    - gas and liquid duties
  - co-removal of H2S and Hg possible
  - re-processable spent material

- **PURACARE Services**
  - Design Guidance
  - Loading & Discharge Services
  - Operational Support
  - Reprocessing Services

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PURASPEC\textsubscript{JM} – Hg removal reactions

- Gas & liquid duties

- Sulphur removal by reaction with metal oxide
  \[
  MO + H_2S \rightarrow MS + H_2O
  \]
  \[
  MO + COS \rightarrow MS + CO_2
  \]

- Elemental Mercury removal by reaction with metal sulphide
  \[
  MS + Hg \rightarrow M_2S + HgS
  \]

- Sulphur & mercury become bound in the structure of the absorbent pellet
  - Liberation back into the process can not occur
Porosity in the right place

- It is not as simple as the bulk porosity and copper content (active phase) of the material

- It is the way the active material is produced and the porosity around it as it is generated

- **PURASPEC**\textsubscript{JM} has, and always will have sufficient copper and bulk porosity, and most importantly also porosity associated with the active material not just the binder / support material

- This is only achieve by engineering this into the particle from the first manufacturing step
### PURASPEC$\textsubscript{JM}$ fixed bed performance

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Effect</th>
<th>Benefits</th>
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<tbody>
<tr>
<td>Unique formulation</td>
<td>Highest capacity (kg Hg/m$^3$ absorbent)</td>
<td>Long life</td>
</tr>
<tr>
<td>Right porosity in the right place</td>
<td>Fast Hg Removal Kinetics</td>
<td>Long life before Hg slip</td>
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<tr>
<td></td>
<td>Sharp absorption profile down the bed</td>
<td>Smallest bed/longest life</td>
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<tr>
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<td>Better protection</td>
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Hg Removal Efficiency –
Hg Capacity

- Hg capacity and Hg removal kinetics must be assessed together

- $\text{PURASPEC}_{\text{JM}}$ products have extremely high Hg capacities
  - > 20wt%
Hg Removal Efficiency – Mass Transfer Kinetics

- Mass transfer kinetics are important because they control the time required, (i.e. CT required) for a fixed bed process
- Fast kinetics implies a sharp Hg removal profile
  - Smaller bed volumes
- Slow kinetics leads to an extended removal profile
  - Larger bed volumes
  - Reduced flowrate per m3 of absorbent
Absorbent Vessel Designs
Vessel Arrangement / Configuration

- Vessels can be arranged in multiple configurations:
  - Single
  - Parallel
  - Series
  - Duty / Standby
  - Lead-lag

Lead-Lag optimises material capacity.

Most mercury removal designs are limited by reaction kinetics – therefore single vessel usually advised due to long bed lives.
Loading and Discharge
Loading and Discharge

JM strongly recommends the use of experienced reputable contractors for vessel loadings and discharges, especially when vessel entries are required.

JM would advise against vessel entries from a safety standpoint.
Discharge

Vacuum

Gravity
Safe Handling and Operating

- **PURASPEC**\textsubscript{JM} absorbents can be supplied in the unsulphided or sulphided form and both have been handled safely and effectively by many customers throughout the world – onshore and offshore.

- In the sulphided form (MS), the material is **self-heating**, i.e. it can heat up if air or oxygen is blown through it. Contact with air should be minimised and purging gas must have oxygen content of <0.1mol%.

- Standard PPE is recommended for PURASPEC\textsubscript{JM} changeouts: Hard hat, protective overalls, gloves, boots, safety glasses.
  - Dust masks should be worn when handling the material

- **Other Considerations:**
  - The hazards of nitrogen / inert gases
  - Safe working from heights
  - The hazards of vessel entries / confined spaces
Services
Mercury Removal Onshore

UK GP plant using PURASPEC$_{JM}$ H$_2$S & Mercury guards
Co-removal
Mercury Removal Offshore

Gas Platform

FPSO

Puraspec
Thank you for listening

Questions?