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Elemental Sulphur Deposition Mitigation Evaluation for Offshore Natural Gas Reservoir

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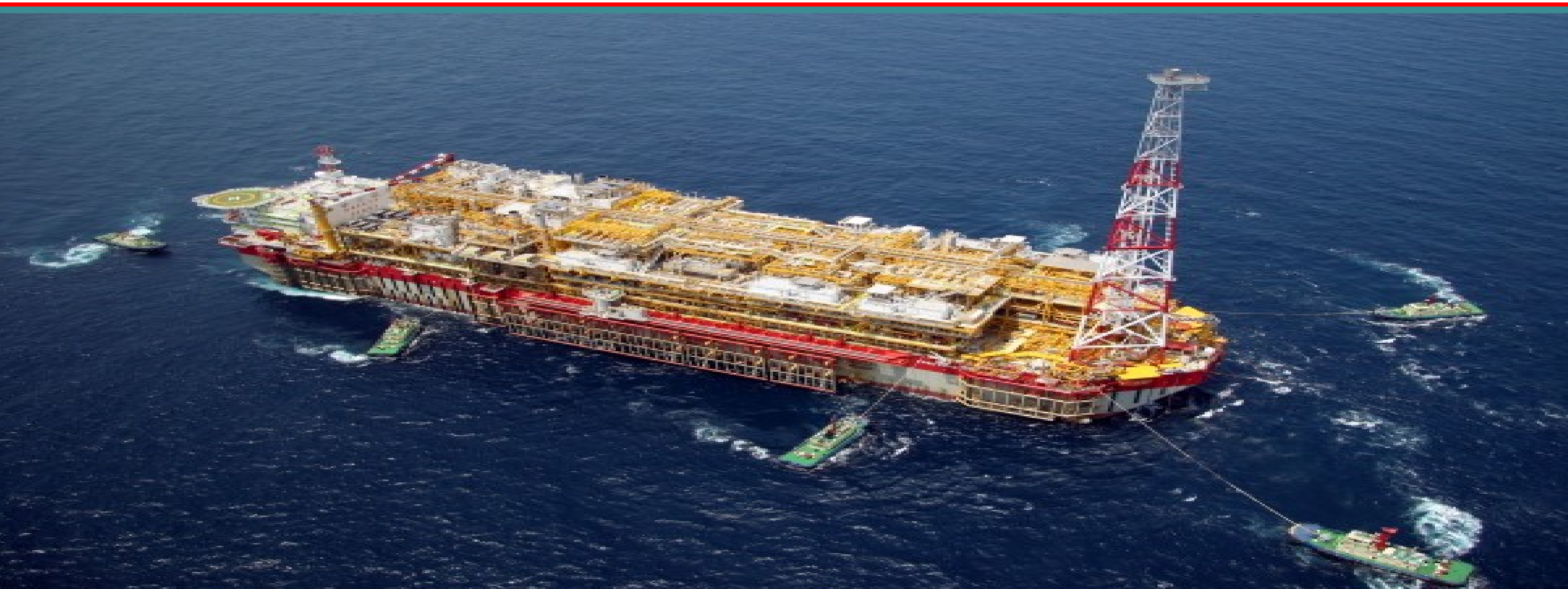


Overview

- Sour gas contaminants
  - Elemental sulphur
  - Mercury
  - Heavy hydrocarbons
  - Organic sulphur – such as COS/CS2
  - Particulates
- Staged SRU co-firing
  - Lean feed, BTEX
  - Extreme Turndown
- NH3 buildup in Regenerator
  - Often overlooked in gas plants?

Dealing with Impurities

- Gas Preconditioning Upstream or Downstream of Gas Treating are become essential
- Feed Gas Compositions, Pressure & Temp
- Sales Gas Specifications, SRU Efficiency, Stack Emission
- Process Configuration: Solvent, New, Revamp
- Ease of Operation or Flexibility
- Safety, Reliability, Low Energy Consumption
- Capital & Operating Costs

Elemental Sulphur Removal

- The objectives for the solvent selection would be based on
  - No corrosion with the well fluid
  - Sufficient sulphur solubility
  - No irreversible reactions with precipitated sulphur
  - Stability under conditions
  - Low vapor pressure
  - Corrosion prevention
  - Ability to separate from water
  - Suitable uniform quality
  - Suitable viscosity
  - Ability to be regenerated and recirculated if applicable
  - Simple recovery of the absorbent sulphur if applicable

Elemental Sulphur

- Throughout sour gas gathering systems
  - Formation
  - Production tubing
  - Pipeline
  - Surface equipment
- Deposits quantified basis gas
  - Composition
  - Temperature
  - Pressure

Alternative to disulfide Solvents

- Non Regenerable solvents
- Alternate to disulfide:
  - Commercially proven
  - Less odor
  - Much larger quantities require supply lines to each Wellhead Platform
  - Potential MEG emulsions if commingled

Elemental Sulphur Removal

Disposal Solvents

- Dimethyl Disulfide (DMDS)
  - 150% of its weight of sulphur at 20°C
- Diaryl Disulfide (DADS)
  - 25% of its weight of sulphur at 20°C
  - Less volatile, more easily recoverable
  - Less odor (but still stinks)
- CS2 is another chemical solvent that could be used to establish a reaction with the elemental sulphur in the well which requires H2S for chemical reaction – this is not a common method.
- Using different type of crude oil from refineries

Elemental Sulphur Removal Cont'd…

Recoverable Solvents

- Sulphur scrubbing by such chemical solvent as alkyinaphthaiene diluted in mineral oil solvent (recoverable solvent)
- The elemental sulphur removal is achievable by using absorption oil as a sulphur solvent in sour gas wells to control sulphur deposition.

Other methods

- Water wash scrubber & settling storage tank
- Slug catchers
- Filter separation with special media
- Inline separator
- Membranes

Elemental Sulphur – Using Physical Solvents

- Using physical solvents HCs with high aromatics
  - Physical solvents are generally hydrocarbons with high aromatic content – e.g. Naphthalene, benzene, toluene, xylenes

- Considerations
  - Common in down-hole, tubing due to increased sulphur solubility with temperature
  - Down-hole flashing with lean sour gas
  - Re-precipitation at cooler downstream temps
  - Higher volumes required, but field condensates possible source
  - Easier to handle, regenerate

Disulfide Chemistry

Catalysis

- $H_2S + R_1R_2NH \rightarrow R_1R_2NH_2 + HS^-$

Sulphur Uptake

- $HS^- + RSSR \rightarrow RS^- + RSSH$
- $RS^- + S_8 \rightarrow RSS_8$
- $RSS_8^- + RSSR \rightarrow RSS_8SR + RS^-$

Overall

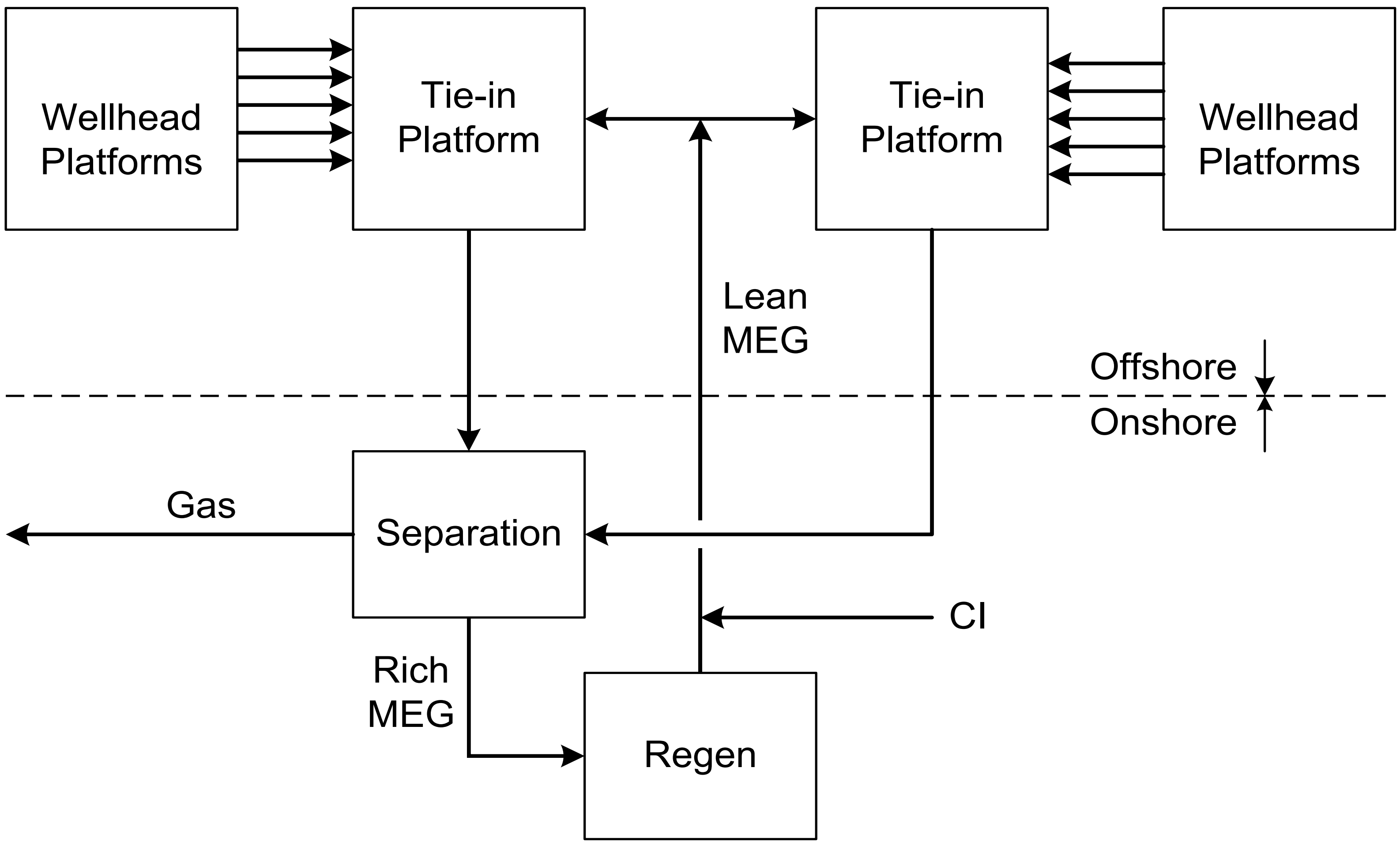
- $RSSR + S_8 \rightarrow RSS_xSR$

First Class Design for Protection of the Environment

Disulfide Corrosion

- Corrosion a problem
  - Filming corrosion inhibitors only marginally effective
- Other Observations:
  - Only corrosive in presence of H_2S and water (brine worse)
  - Corrosion increases with temperature, dissolved sulphur
- Recommendations:
  - Only inject at depth sulphur predicted
  - Never at > 115°C (liquid sulphur)

Sulphur Mitigation Case Study



First Class Design for Protection of the Environment

Sulphur Solubility

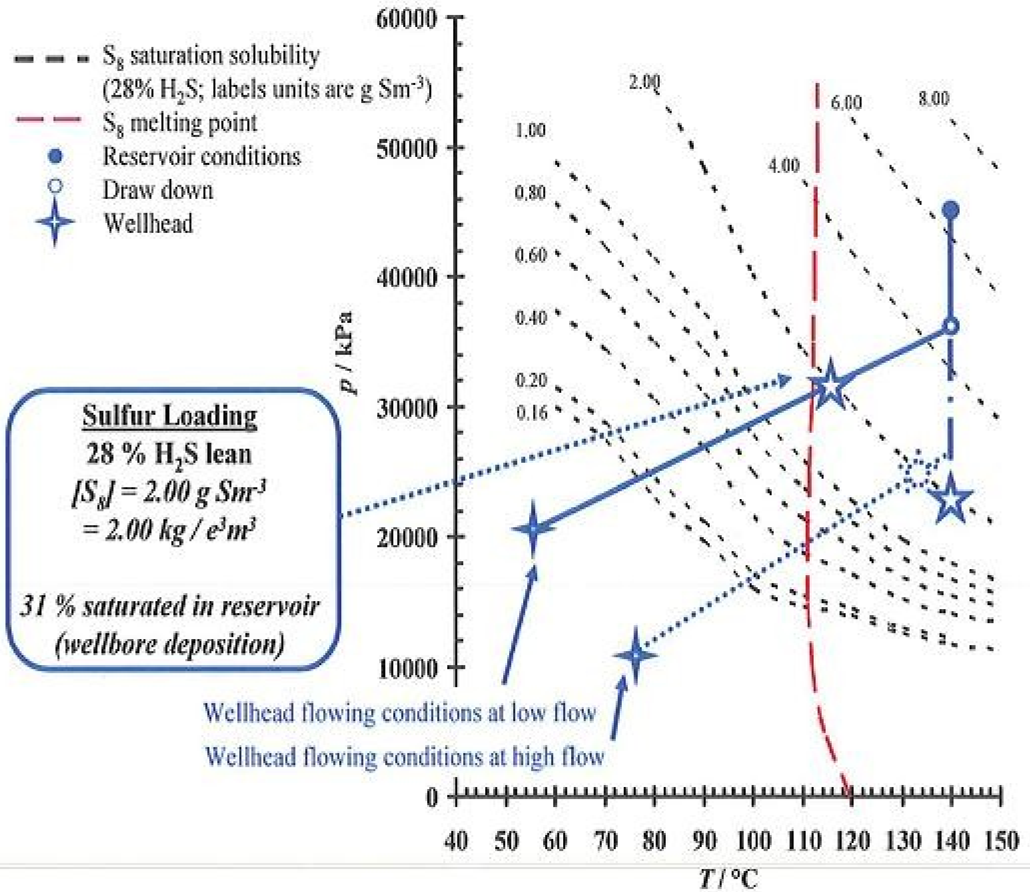


Figure 4. The Sulfur Solubility Phase Diagram for Hypothetical Well Producing 28% H_2S Lean Sour Gas.

Treatment Options

Regenerable Solvents

- Mobil Erdgas-Erdoel GmbH (Germany) – alkylnaphthalene and mineral oil carrier
- Shell Canada, Bearberry – similar to Mobil process
- Crystatech process still under development not ready for commercialization
- In general not common, particularly offshore
- More common in downhole applications
- Supply piping required to Wellhead Platforms

Treatment Options

- Non Regenerable solvents - Once-through solvents
  - DMDS / DSO
    - Catalyzed with base such as ethylamine
    - DMDS, ICTC SS2000
    - DSO, local Merox byproduct
  - Naphthalene
    - ICTC Sulpha-Max with CI
  - Amine based with methanol
    - Baker Hughes
  - Alkylnaphthalene (aromatic)
    - Baker Hughes

Survey of Other Operations

- Mobil Erdgas-Erdoel GmbH (Germany)
  - Sour gas reservoirs date to 1960s
  - No HC condensate
  - Substantial formation water
  - Aqueous ethylamine, severe carbonate precipitation
  - Alkylnaphthalene (tar oil distillates)
  - Mineral oils (cyclic with double bonds)
  - Regenerable
  - Low boiling range (240-300°F)
  - Injected downhole

Heavy Hydrocarbons Removal

- Silica gel, mole sieves remove gas phase C6+
- HCs condensed from regen gas and stabilized
- BASF/Engelhard Sorbead™ oil drop silica gel
  - Adsorption capacity directly related to MW, BP (except water)
- When only dehydration of sweet gas req'd
  - Small-pore zeolites (3A or 4A) avoid BTEX coking
- Heavy HCs accumulate at membrane inlet
  - Condensed liquids are potential membrane solvent
  - At best, liquids inhibit permeation
- Carbon filter upstream of multicyclone separator & coalescing filter upstream of amine unit

Organic Sulphur Removal

- The most common type are COS / CS2
- Some of the chemical and physical solvents are capable of removing COS / CS2 at some level
- The molecular sieves process could be used for COS / CS2
- The amine reclaimer system is an alternative for COS / CS2 Reclaimer operation is a semi-continuous batch operation for removal of degradation product from the solution and removal of suspended solids and impurities.
- The best solution is to be removed in the amine unit and to be routed to the SRU for destruction

Mercury Removal

- Aluminium embrittlement
- Hg in sour gas: 0.01 µg/Nm^3 – 5000 µg/Nm^3
  - OSHA limit in air: 50 µg/Nm^3
  - Required: < 0.01 µg/Nm^3 (1 pptv)
  - Hg not consumed – essentially a catalyst
- Contaminated steel a safety hazard
  - Hot work
  - Scrap, recycling

Mercury Adsorbents

- Activated carbon impregnated with sulphur
  - HgS stable to 450°C
  - Non-regenerable (but long life)
  - Downstream of dehydration, dew point control
- Johnson Matthey mixed-oxide Puraspec H2S scavenger
  - Preferred upstream of acid gas removal
  - Minimizes downstream equipment contamination
  - Abundant H2S to form HgS

Mercury Adsorbents Cont'd…

- UOP regenerative HgSIV
  - Simultaneous dehydration
  - Mole sieves with elemental silver to form amalgam
  - Convention regeneration with hot sales gas
- Stand alone
  - Simultaneous dehydration
  - Regen Hg and water condensed, separated
- When acid gas removal plant exists
  - Upstream carbon for bulk Hg removal
  - Downstream HgSIV polishing step
  - Regen gas recycled to carbon after water condensation

Impact of Impurities on Solvents

- Surface active HCs cause foaming
  - Amines, glycol, physical solvents
- Carbon filtration of solvent
  - Heat soak fresh carbon
- Surface active HCs cause emulsions

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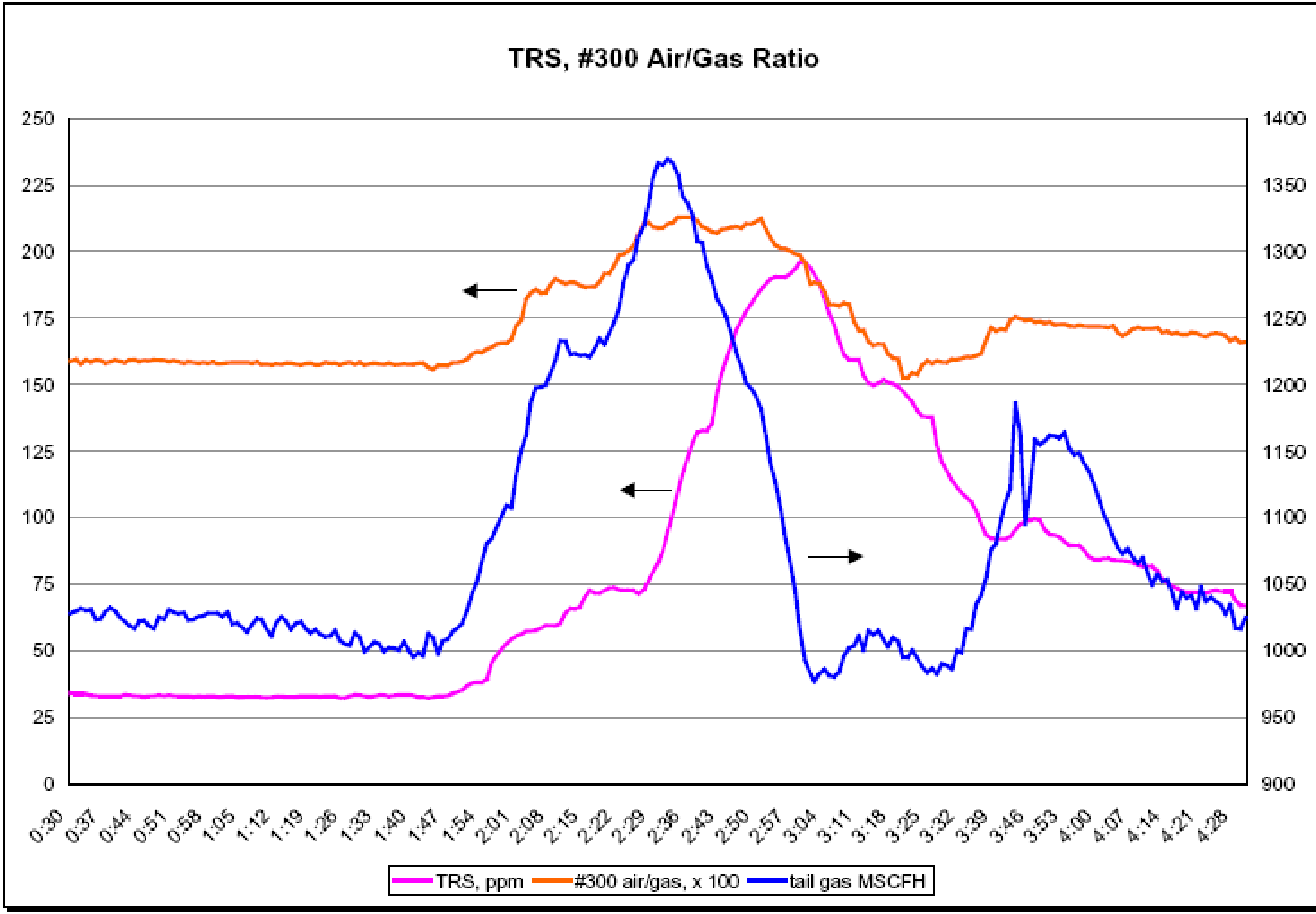
Case History – DCU Aromatics



Case History – DCU Aromatics Cont'd…

- Claus impact
  - Potential catalyst fouling, deactivation
  - 30% increase in air demand
  - 30% increase in TGU tail gas
  - TGU TRS emissions increased from 30 to 200 ppm
  - 1100-1200°C for BTEX destruction
- Saudi Aramco – Several activated carbon on acid gas

Sub-micron FeS

- Case History – J. P. Herrin, LRGCC, 1994
- 25 years of FeS deposits re-dispersed with new upstream glycol dehydration
- Trial – two packed glycol bubble towers in series
  - All FeS captured in 1st stage
- Permanent solution – trayed tower with glycol recirculation
  - Glycol filtration only partially effective
  - Solvent replaced after 3-4 months due to viscosity

SRU Co-Firing

- Lean feed, BTEX
  - Below 50% H_2S, Claus Furnace below 1100-1200°C req'd for BTEX destruction
  - Below 30% H_2S, Claus Furnace below 1800°C req'd for stable destruction, even with split-flow (in absence of BTEX)
- Operators invariably resort to co-firing natural gas
  - Soot = fouled / deactivation catalyst
  - CS_2 = high emissions

Staged Combustion

- 2-zone furnace
  - Zone 1 – natural gas, excess air
  - Zone 2 – acid gas
  - Conventional combustion air control
  - Outlet for poor quality fuel gas
  - Convenient maintenance of spare SRU in hot standby
- Potential downside
  - Reduced SRU capacity, efficiency
  - Long-term cost of surplus steam

Extreme SRU Turndown

- RATE guarantees operation at 20-25% of design
- At progressively lower rates, ambient heat loss greater share of process heat
  - 900-1000°C recommended for flame stability
  - Converters become sub dew point, activity loss
  - sulphur fogging
  - Frozen Condenser tubes – MP steam sparge, LP steam condensation

Future Turndown

- Example – new gas field with high depletion rate
- Design SRU based on O_2 enrichment
  - Future turndown improved on reduced % O_2
  - 100% O_2 doubles SRU capacity

NH_3 Buildup in ARU Reflux

- NH_3 absorbed in amine due to water solubility
  - Concentrates in reflux
  - Increases reboiler duty
  - Can result in under-stripping
- At 2½ wt-% NH_3
  - NH_3 breakthough with acid gas
  - NH_4^+ salts deposit at < 70°C
  - Under-deposit corrosion
  - Plugged instrument taps first sign

NH3 Buildup in ARU Reflux Cont'd…

- Higher pH promotes emulsification of surfactants conducive to foaming
  - Visual: hazy → cloudy → milky
- As dissolved NH3 approaches saturation, co-absorbed H2S / CO2 becomes very corrosive
- Simple reflux test
  - M alkalinity
  - H2S by iodine-thiosulfate back-titration
  - Purge to limit NH3 to 1 wt-%

The Point?

- Experience suggests gas plant design, operation often overlook potential NH_3 buildup due to absence in gas
- However
  - NH_3 is a product of amine degradation
  - Increased reboiler duty can increase tube skin temperatures
  - Hence, increased degradation, particularly if fired reboiler

Conclusions

- The impurities in Sour Gas Field Developments have to be analyzed by taking samples from the well
- Each application requires a complete evaluation and study to select the impurities processes:
- In order to meet an stable operation, prevent plugging, prevent foaming, prevent frequent shut down, increase the life of the plant, Select the proper equipment material and finally to meet the product the impurities has be removed
- The common methods for removing elemental sulphur, mercury, heavy hydrocarbon are discussed
- The selection of the option depends on the quantity of the impurities and the impact on the operation