Hydrogen Sulfide in Petroleum

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Hydrogen Sulfide

- Toxic, Colorless Gas
- Rotten Egg Odor
  - Detectable at >10 ppb
  - Paralyzes olfactory system
  - LC50 = 713 ppm
- Weak Acid, Air Oxidized, Absorbs On Metals
- Solubility Depends On Temperature, Fuel, & Henry's Law

Hydrogen Sulfide Toxicity

Concentration (ppm)	Health Effect
< 0.02	Olfactory Detection Limit
10	8 Hr Exposure Limit
15	15 Min. STEL
100	Common Ship Headspace Spec.
300	Considered Immediately Hazardous
713	LC50 Concentration
1000	Common Tank, Ship Headspace Concentration

Hydrogen Sulfide Concerns

- Toxic
  - Employee exposure
    - Storage tanks
    - Barges, ships
- Corrosive
  - Fuel specs.
  - Tank roof
  - Pipelines
- Odor Control
  - Storage tank vents
  - Sewers

Odor Issues

Detection Limits for Common Odorants

ODORANT	DETECTION LIMIT (PPM V/V)
ETHYL MERCAPTAN	0.0003
METHYL MERCAPTAN	0.0008
HYDROGEN SULFIDE	0.002
DIMETHYL SULFIDE	0.002
PHENOL	0.05
P-XYLENE	0.05
TOLUENE	2.0
BENZENE	5.0
AMMONIA	50

Hydrogen Sulfide

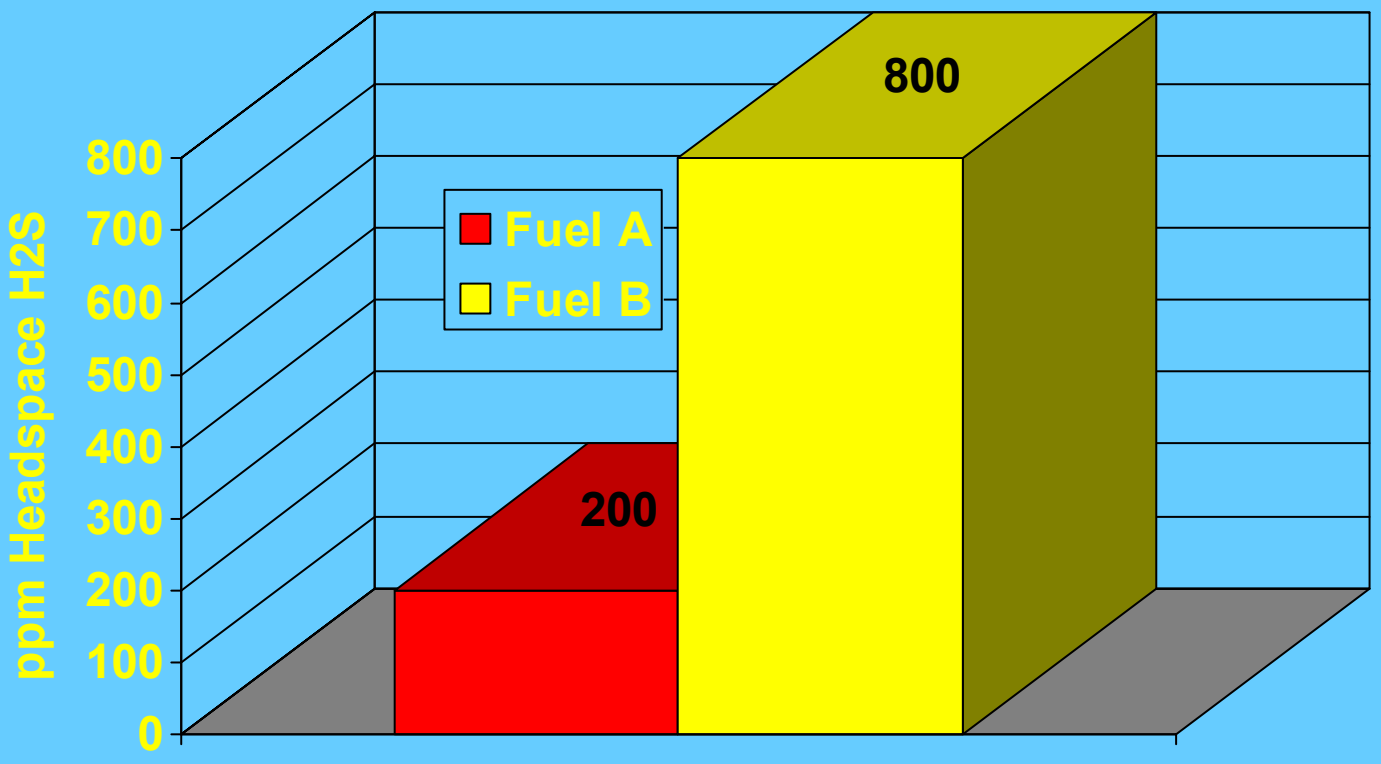
Petroleum Streams Where H_2S Found

- **Crude Oil**
- **Asphalt**
- **Residual Fuel & Components**
- **Mid-Distillates & Blend Components**
- **Gasoline & Blend Components**
- **Natural Gas, Propane, LPG**

Crude Oil

- High Sulfur Crudes
  - Mexico
    - Maya 100ppm liquid
    - Olmeca 116ppm liquid
  - Middle East
    - Eocene 90ppm liquid
    - Ratawi 80ppm liquid
  - Africa
    - Soyo 16ppm liquid

H2S Partitioning



2 ppm liquid phase H2S content
60 F with sample mixing

Partition Coefficients

- Crude Oil
  - 80-300 vppm per 1lppm
- Residual Oil
  - 80-400 vppm per 1lppm
- Gas Oil
  - 30-150 vppm per 1lppm
- Gasoline
  - 50-200 vppm per 1lppm

Partitioning of H_2S

- 1 ppm in liquid can equate to > 50 ppm in vapor space
- 100 ppm in liquid can equate to 20,000 ppm in vapor space

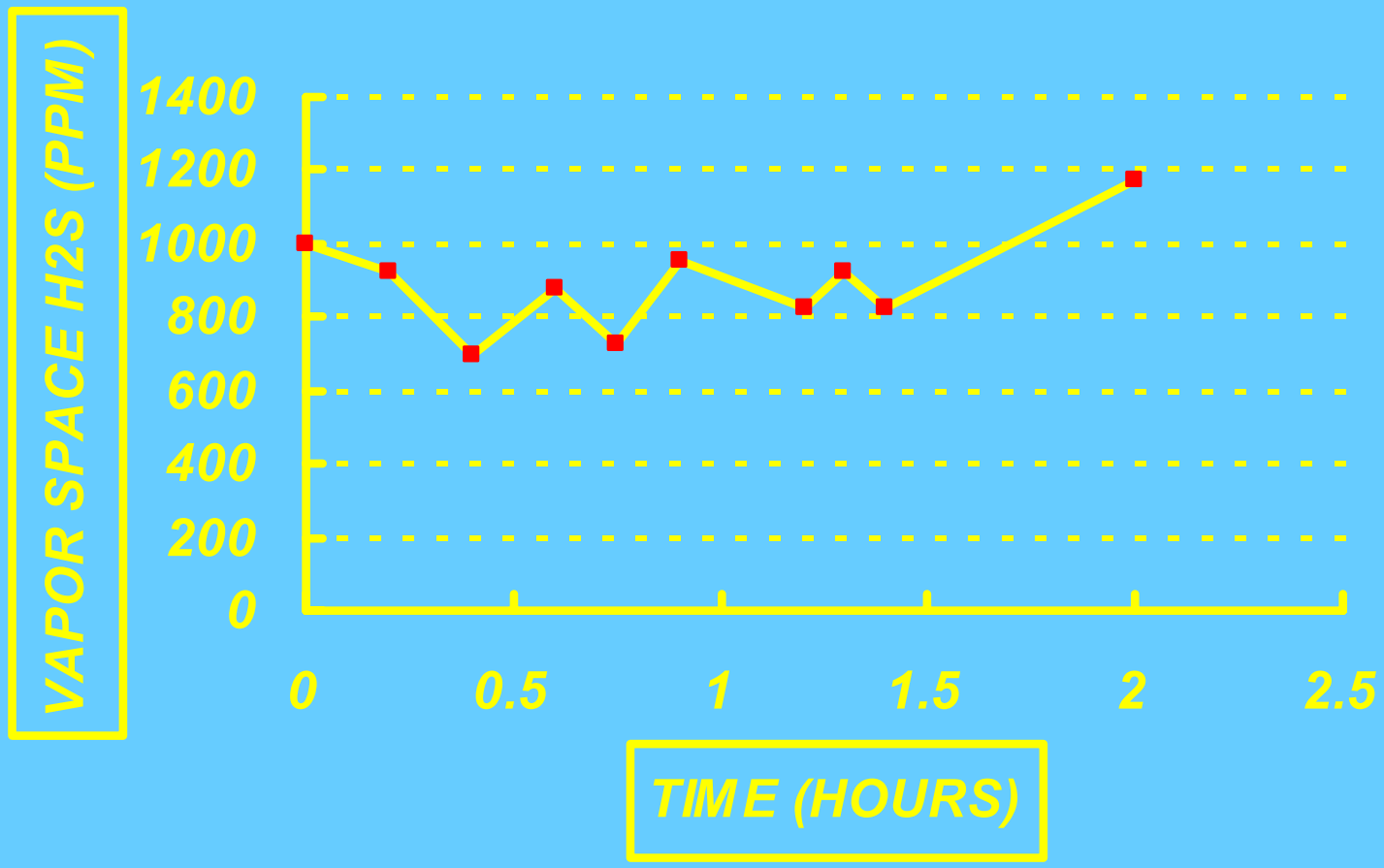
Hydrogen Sulfide Concentrations

- Levels of H2S Can be Extremely High if Cargoes Are Over Heated
- Eocene Crude H2S Production After Heating 1 Hour @ Specified Temperature
  - 100 Deg. F — 400 ppm
  - 200 Deg F — 16,000 ppm
  - 300 Deg F — >80,000 ppm

Factors Affecting Partitioning

- Temperature
- Viscosity
- Pressure
- Agitation
- Basic compound in oil

HEAD SPACE H2S VARIATION WITH TIME



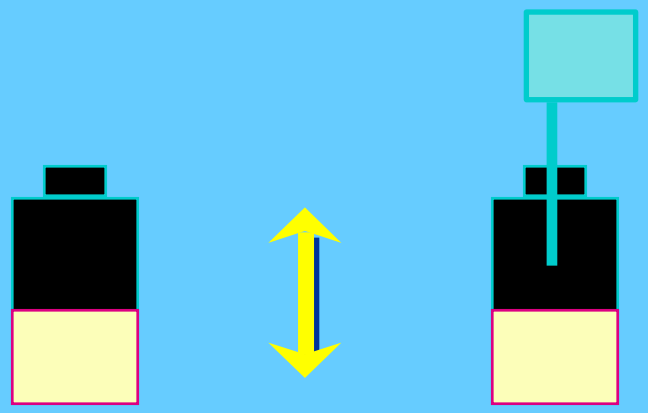
H_2S Specifications

- Regulatory Bodies
  - LA harbor, < 70 ppm in liquid
- Terminals
  - Variable
  - None to 0 ppm
  - 50-200 ppm in vapor typical
- Processing Facilities
  - Variable
  - < 50 ppm in Can Test to None
- Pipelines
  - Only one encountered, < 50 ppm in can test

Hydrogen Sulfide Test Methods

- Vapor Space
  - Gas detection tubes
  - Monitor Electronically
- Fuel Sample
  - ASTM D-5705 “Can Test”
- Liquid
  - Sparge test,
  - ASTM D-3227, UOP-163
  - New ASTM method

"Can Test" Method



Step 1

Add 500 ml Sample to can

Step 2

Equilibrate Temp. Agitate

Step 3

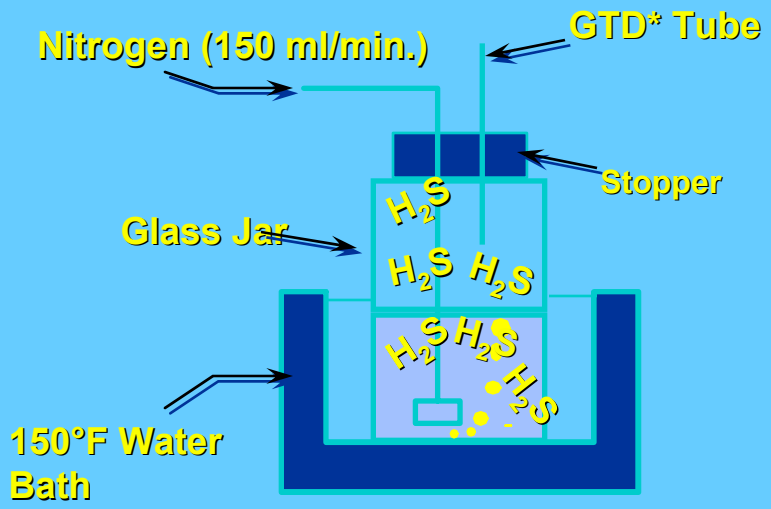
Measure H_2S With Gas Detection Tube

- Advantages
  - Quick & easy
  - 1 - 80,000 ppm
  - Industry standard
- Disadvantages
  - Loss of H_2S
  - Poor repeatability & reproducibility
  - Results influenced by temp. & shaking

Hydrogen Sulfide Scavengers D-5705 Test Conditions

- 140 F Test Temp
- 1/2 Full Liter Bottle
- 3 Minutes @ 150 RPM on Orbital Shaker
- Drager Tube Detection

Liquid Phase Sparge Test



Total H_2S = (GDT* Reading x 1.42) / Sample wt.

- Multi-step Procedure
- Advantages
  - Results not dependent on temp., vol., etc...
  - Field method
  - Works with a variety of hydrocarbons
- Disadvantages
  - Wet chemistry analysis

*Gas Detection Tube with n=10 scale

Hydrogen Sulfide Scavengers Additional Test Methods

- Vapor Space Methods
  - Esso Can Test
  - Shell Can Test
  - Baker Petrolite Can Test
- Liquid Test Methods
  - UOP 163
  - ASTM D-3227
  - ASTM D-6021 (New Method)

H2S Analysis

- Good sampling critical for good results
  - Common mistakes
    - cooling of samples before analysis
    - excessive pouring, transfer of samples
    - storage of oil before analysis
- Test influences
  - Vapor phase test
    - agitation, temperature, vapor/liquid ratio
  - Liquid phase test
    - coating of electrodes, interferences

Hydrogen Sulfide Scavengers

Hydrogen Sulfide Scavengers
Additive Treatments

- Chemistry
  - Oxidizers
  - Neutralizers
  - Reactants
- Process Considerations
  - Temperature gradients
  - Weathering
  - Additive mixing

Hydrogen Sulfide Scavengers
Organic Bases

Typically Amines (e.g. MEA)

H_2S + Neutralizer $\rightleftharpoons$ Salt

- **Advantages:**
  - Fast reaction
  - No sodium
  - Oil soluble/dispersible
- **DISADVANTAGES:**
  - Reaction is Reversible
  - Weak acid/base equilibrium
  - Not specific for H_2S

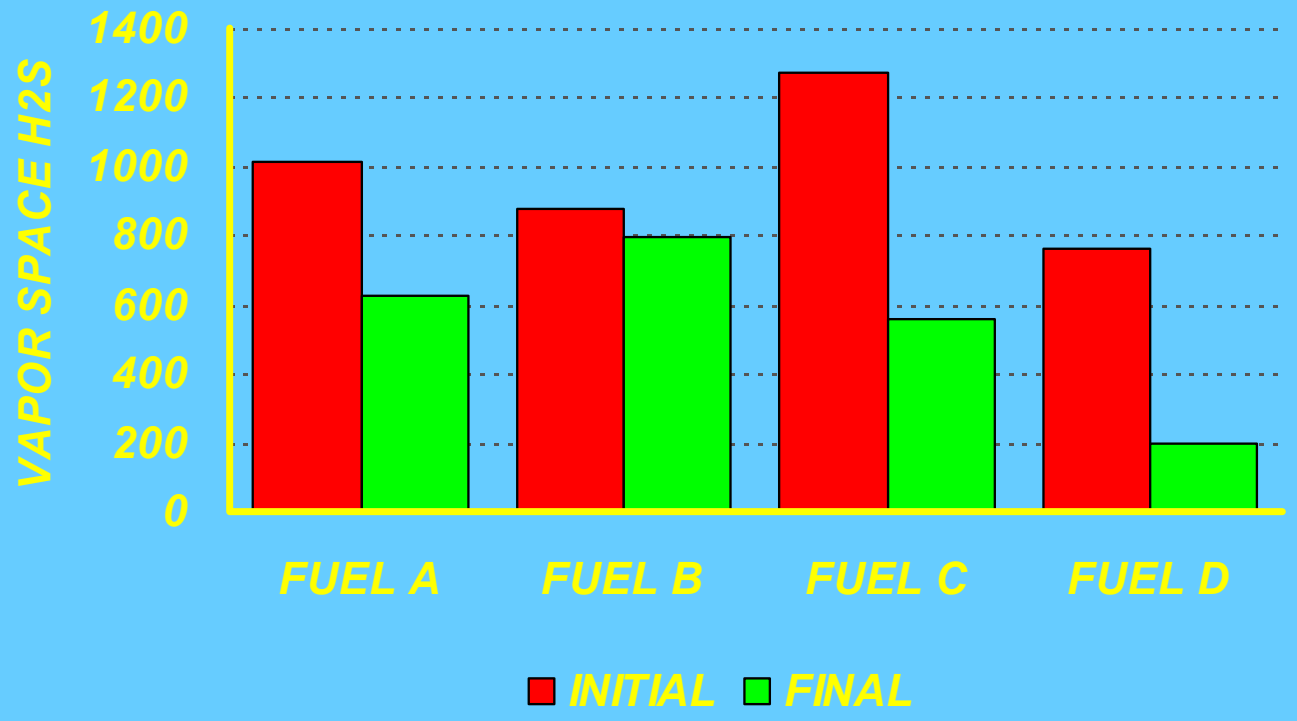
Hydrogen Sulfide Scavengers
Inorganic Neutralizers

Inorganic Bases: NaOH, KOH Or Blends

$H_2S + NaOH \longrightarrow Salt$

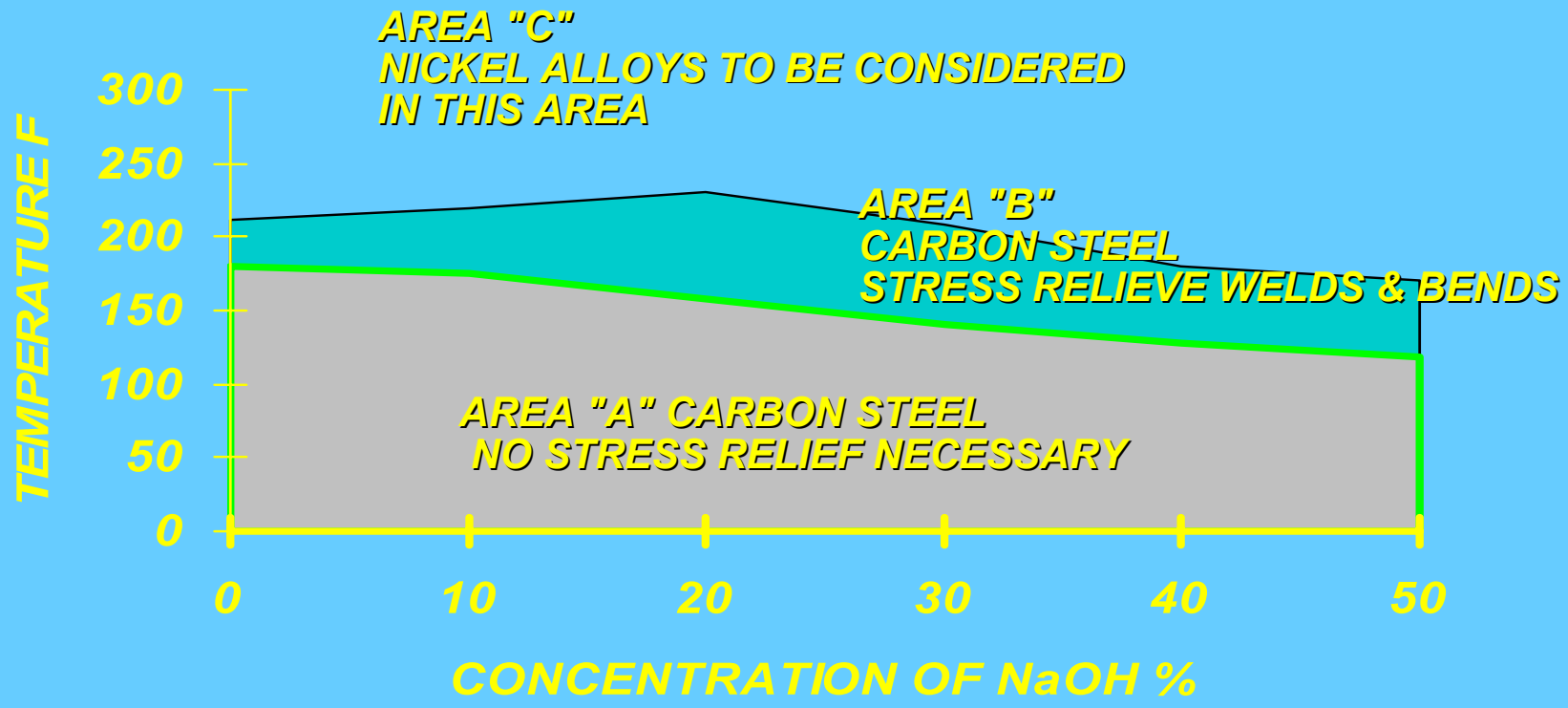
- **Advantages**
  - Fast reaction, cheap
  - Use alone or in combination
  - Thermally stable products (NaHS)
- **Disadvantages**
  - Non-selective for H_2S
    - Ash forming
  - Increases fuel Na content . Reversible
  - Limited Safe Injection Temperature

H2S REDUCTION WITH CAUSTIC, 50 PPM NaOH



60 MIN REACTION TIME

EFFECT OF TEMPERATURE AND CONCENTRATION ON CAUSTIC SODA SERVICE APPLICATION



CORROSION DATA SURVEY; NACE, 1968, p 4

H_2S Scavengers
Reactive/Conversion Additives

Organic Compounds

H_2S + Sulfix product ⟶ alkyl sulfides (RSR)

- **Advantages:**
  - Non-reversible
  - Selective for H_2S
  - Oil Soluble Additives & Rxn. Products
  - May be used at high temperature & with caustic
  - Rapid reaction
  - Wide range of fuels

H2S Scavenger Application

- Scavenger/hydrocarbon mixing important
  - Injection quill
  - Injection up-stream of sample point
  - Continuous injection
  - Storage tank mixing, blending
- Transportation vessel effects
  - Steam coils, temperature
  - Compartment seals
  - “Soda bottle” effect