Mercury Contamination in Crude Oil Drilling Operations

Presented to:
Crude Oil Quality Association

New Orleans, 27th February, 2013
Peter A. Spitz
Intertek Singapore Technical Center
Content

• Introduction
• What are we measuring
• Barite
  • Typical Concentrations – amounts of mercury Hg°
• Wellbore Circulation
  • Temperature and Energy
• Thermal Liberation
  • Mercury loss in drilling

Conclusion and Discussion
The Intertek Global Network

• FTSE 100 company in the Support Services sector
• Market capitalization at £5.0 (USD 7.6) billion
• Revenue generation of over £2 (USD3) billion in 2012

More than 100 countries

More than 1,000 laboratories and offices

35,000 people
Energy Services overview

Serving the World’s Energy Markets

- Upstream oil and gas
- Petrochemical
- Nuclear power
- Biofuels
- Refining and distribution
- Power generation
- Solar
- Wind
Measuring Mercury
What Are We Measuring

1 ppm = 1 second in 12 days

1 ppb = 1 second in 32 years or 1 drop of Macallan Whiskey in 50000 liters.

1 ppt = 1 second in 320 centuries

1 drop of water in twenty Olympic swimming pools.
Olympic pool defined by Fédération Internationale de Natation (FINA)
Length: 50 m
Width: 25 m
Depth: 2.0 m minimum

The metric drop is a 1/20 mL. This means it take 20 drops to make one milliliter.

50x25x2x1000x1000 = 2,500,000,000 ml or 50,000,000,000 drops
So twenty Olympic pools is 1 trillion drops

ONE DROP IN TWENTY OLYMPIC SWIMMING POOLS IS A PPT
The Fish Story

1: 538 ppb
2: 41 ppb
3a: 190 ppb
3m: 294 ppb
4: 159 ppb
5: 122 ppb
6: 1055 ppb
Mercury Fish Story

• CH$_3$Hg is one of the most toxic forms of Mercury
  • All mercury in fish is Methyl Mercury (CH$_3$Hg)
• Tuna 1055 ng/gm CH$_3$Hg
  • Bad?
• Salmon 41 ng/gm CH$_3$Hg
  • Very healthy – high omega3 fatty acids
• Methyl mercury in fish is nearly 100 per cent absorbed into the human system
Mercury Fish Story

• 250 grams Salmon = 10000 ng CH$_3$Hg
• 250 grams Tuna = 260000 ng CH$_3$Hg

• One is healthy and one is not?

• Note: EPA guideline for mercury intake per week 55 kg person is 38500 ng.
Mercury Exposure

- A 15 gram standard solution of 50 ng/g CH3Hg
- 750 ng exposure possibility
- If totally injected into the body
  - 7.5% of a salmon dinner
  - 0.3% of a tuna dinner
Labile Colloids (Agglomerates) of Mercury
the beginning (Once Upon A Time)

Understanding Thermal Sensitivity of Mercury

• The temperature dependence of thermally labile mercury “particulates” has long been known based on study of particulate mercury at various temperatures in high mercury Gulf of Thailand crude oil.

• Knowledge of what portion of particulate mercury is stable will indicate what may end up as bottom sediments in crude oil tankers, barges and in production and process systems. This is critical to knowledge for mercury management and mitigation.
Thermally Sensitive Mercury Colloids (Agglomerates)

Testing Development

• A system was devised at the INTERTEK Singapore Technical Center (STC) with guidance from research scientists to study the thermal mercury profile.

• When our client had mercury alarms at surface while drilling through shale we were asked to assist in understanding – we applied our thermal liberation experiment to drilling fluid additives (Barite).

THIS IS THE STORY
Barite is Used in Virtually All Oil and Gas Drilling Operations

• Barite is BaSo4, 85 – 95 %, and may have As, Cd, Pb, Hg, Cr, Se, Ag

• Mercury concentrations range from low to very high on various Barites (ppb)
  • 305
  • 2680
  • <10
  • 9500
  • 757
  • 7500
How Much Mercury Are We Talking About

• Typical Well may use 2000 tons of Barite.

• If the barite is 3000 ppb Hg you have potential of releasing

5-6 kg of mercury
## Mercury in Barite Loss Upon Heating

### Barite 1

<table>
<thead>
<tr>
<th></th>
<th>run 1</th>
<th>run 2</th>
<th>average</th>
<th>Hg Loss</th>
<th>% Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>THg original (normal condition), ppb</td>
<td>746</td>
<td>769</td>
<td>757.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>THg after 100°C heating, ppb</td>
<td>674</td>
<td>688</td>
<td>681</td>
<td>76.5</td>
<td>10.1</td>
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<tr>
<td>THg after 150°C heating, ppb</td>
<td>642</td>
<td>644</td>
<td>643</td>
<td>114.5</td>
<td>15.1</td>
</tr>
<tr>
<td>THg after 200°C heating, ppb</td>
<td>626</td>
<td>622</td>
<td>624</td>
<td>133.5</td>
<td>17.6</td>
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<tr>
<td>THg after 310°C heating, ppb</td>
<td>84</td>
<td>84</td>
<td>84</td>
<td>673.5</td>
<td>88.9</td>
</tr>
</tbody>
</table>

Heating time = **12 hours**

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<td>688</td>
<td>678</td>
<td>683</td>
<td>74.5</td>
<td>9.8</td>
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<td>THg after 150°C heating, ppb</td>
<td>447</td>
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<td>45.2</td>
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<td>THg after 200°C heating, ppb</td>
<td>153</td>
<td>151</td>
<td>152</td>
<td>605.5</td>
<td>79.9</td>
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</tbody>
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Heating time = **24 hours**
# Mercury in Barite
## Loss Upon Heating

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<td><strong>THg original (normal condition), ppb</strong></td>
<td>9160</td>
<td>9390</td>
<td>9275</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>THg after 100°C heating, ppb</strong></td>
<td>9020</td>
<td>9020</td>
<td>9020</td>
<td>255</td>
<td>2.7</td>
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<td><strong>THg after 150°C heating, ppb</strong></td>
<td>7480</td>
<td>7520</td>
<td>7500</td>
<td>1775</td>
<td>19.1</td>
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<tr>
<td><strong>THg after 200°C heating, ppb</strong></td>
<td>5820</td>
<td>6110</td>
<td>5965</td>
<td>3310</td>
<td>35.7</td>
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<td><strong>THg after 310°C heating, ppb</strong></td>
<td>76</td>
<td>74</td>
<td>75</td>
<td>9200</td>
<td>99.2</td>
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Heating time = **12 hours**

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<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>THg after 100°C heating, ppb</strong></td>
<td>8620</td>
<td>9190</td>
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<tr>
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<td>7090</td>
<td>7105</td>
<td>2170</td>
<td>23.4</td>
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<tr>
<td><strong>THg after 200°C heating, ppb</strong></td>
<td>702</td>
<td>607</td>
<td>654.5</td>
<td>8620.5</td>
<td>92.9</td>
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</tbody>
</table>

Heating time = **24 hours**
## Mud Gas Analysis versus Formation Gas Analysis

<table>
<thead>
<tr>
<th>Date</th>
<th>Depth</th>
<th>Sample</th>
<th>C2H4 ppm</th>
<th>C3H6 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/12/2013</td>
<td>2150m</td>
<td>Drilling Fluid Gas</td>
<td>1290</td>
<td>228</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Mud Gas)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/12/2013</td>
<td>2150m</td>
<td>Formation Gas</td>
<td>n/d</td>
<td>n/d</td>
</tr>
</tbody>
</table>
MERCURY THERMAL PROFILING
Summary

- Total Mercury analysis prior to thermal evolution
- Total Particulate Mercury (if liquid asset)
- Mercury vapor during controlled heating (to 250-300°C)
- Mercury loss analysis versus temperature profile
- Mercury analysis in cuts <240°C (if liquid asset)
- Mercury analysis in the residue
Real Time Mercury Evolution

Controlled Heating –

File name: D:\BARITE STUDY\Premier Oil Vietnam\131009.dat

- 193°C
- 75°C
- 310°C
Real Time Mercury Evolution
Controlled Heating –

185°C
Mercury
Thermal
Liberation

75°C

310°C
What Does This Mean

• There is an analytical tool for understanding mercury in your drilling and production operations

• Optimizing Materials Selection for Drilling Fluids

• Hg can be released into the drilling fluid affecting the well bore
  • Filter cake, formation invasion and metallurgy contamination

• Formations can be analyzed for mercury content
Conclusion

• This is a new tool in understanding mercury in drilling operations.

• Implications for drilling additive selection, interpretation of DST data and HSE of drilling operations is clear.

• Intertek thanks all the contributing companies for permission to discuss the phenomenon observed in demonstrating this technique.
The End

QUESTIONS?