INORGANIC PROBLEMS IN DCU HEATERS:

LESSONS LEARNED

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Petrobras heavy crude production is constantly increasing.
Heavy crudes reserves volume is increasing.

Domestic Proven Reserves as of Dec/2006 (SPE): 13.75 billion boe

Production Mbpd
Petrobras DCU Overview

- Petrobras is an important player in coker units design, operation and high quality anode grade coke production.
- Petrobras (CENPES), has designed 7 DCU and 3 are under basic design, so new capacity increase is forecast from 2011 on.
- Today, there are 6 operating units and 3 already under engineering or construction phases and will be operating by 2010.
- The importance of DCU: Brazilian fuel gas demand increases while fuel oil demand decreases.

Petrobras design unit. Start up in 1994

Data presented in plot refer to design capacity

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Historical Aspects of Inorganic Problems

- In 1999, the first evidence of inorganic deposits in Petrobras coker heaters was observed in RPBC refinery.
- Deposits appeared in some of the top tubes of the radiation section after heater decoking.
- After 2003 deposits frequency clearly increased.

Decoking history (in months)

<table>
<thead>
<tr>
<th></th>
<th>Before 2003</th>
<th>After 2003</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heater Run Length</td>
<td>7 - 8</td>
<td>4 - 6</td>
</tr>
<tr>
<td>Hydroblasting Cleaning Frequency</td>
<td>18</td>
<td>12</td>
</tr>
</tbody>
</table>
Inorganic Deposits Composition

XRD Analysis

- Sodium Titanium Silicate (NaTiSi₂O₆)
- Silicon Oxide (SiO₂)
- Iron Titanate (Fe₂TiO₄)
- Iron Oxide (Fe₃O₄ and Fe₂O₃)
- Sodium Silicate (Na₈Si₂O₇)

Deposits Qualitative Analysis

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Deposits Location

DCU-1: Design by LUMMUS
Start-up in 1973

Heater Coil - Oil Temperature Profile

Deposits appeared in temperature range:
370 - 480°C (700 - 900°F)
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Effect on Heaters Run Length

\[ T_{\text{WALL}} = T_{\text{FLUID}} + \Delta T_{\text{FILM}} + \Delta T_{\text{METAL}} + \Delta T_{\text{CORE}} \]

Skin-Points Temperature Tendency

Heaters Run Length Target

100 °C (180 °F)

42 hr

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Searching for Causes

What were inorganic deposits possible causes?

Fact: high Silicon content found

No problems reported as to desalters. Chlorides analysis were under control.

Immediate conclusion: new crudes produced by E&P (Upstream) caused deposits !!!
**Possible Silicon Sources**

- **Silicon**
  - **Organic**
    - Antifoam agent used in oilfield is the source of silicon
  - **Inorganic**
    - Colloidal silicon in water co-produced with petroleum
  - n-pentane soluble
  - n-pentane insoluble

*Silicon was inorganic!*

**Causes and Possible Solutions**

The cause of inorganic deposits could be "filterable solids" present in crude, not removed by desalters.

Would wetting agents solve the problem?
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Causes and Possible Solutions

Wetting agents employed in refinery desalters in order to minimize "filterable solids" were not effective.

"Filterable solids" concentration was low!

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**Samples Analysis Complete Table**

Main Elements in Deposits, wt % (XRF Analysis)

<table>
<thead>
<tr>
<th>Tag</th>
<th>DCU-2</th>
<th>DCU-2</th>
<th>DCU-1</th>
<th>DCU-1</th>
<th>Heaters B</th>
<th>Heaters A</th>
<th>Heaters A</th>
<th>Heaters A</th>
<th>Heaters A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Heater A</td>
<td>Heater B</td>
<td>(Layer 1)</td>
<td>(Layer 2)</td>
<td>Refin B</td>
<td>Refin B</td>
<td>Refin C</td>
<td>Refin C</td>
<td>Refin C</td>
</tr>
<tr>
<td>Decoking</td>
<td>SA</td>
<td>SA</td>
<td>SA</td>
<td>SA</td>
<td>SA</td>
<td>SA</td>
<td>SA</td>
<td>SA</td>
<td>SA</td>
</tr>
<tr>
<td>Na</td>
<td>13</td>
<td>6.7</td>
<td>9.9</td>
<td>7.7</td>
<td>2.6</td>
<td>0.2</td>
<td>11.1</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>5.2</td>
<td>5.1</td>
<td>7.2</td>
<td>5.6</td>
<td>11.8</td>
<td>16.4</td>
<td>3.0</td>
<td>14.2</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>5.7</td>
<td>4.7</td>
<td>3.4</td>
<td>4.4</td>
<td>4.2</td>
<td>6.4</td>
<td>2.8</td>
<td>9.9</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>8.7</td>
<td>6.8</td>
<td>3.9</td>
<td>3.5</td>
<td>4.9</td>
<td>2.3</td>
<td>1.4</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
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<td>n.d.</td>
<td>2.1</td>
<td>2.8</td>
<td>2.1</td>
<td>1.6</td>
<td>76.0</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>2.9</td>
<td>1.6</td>
<td>0.8</td>
<td>0.6</td>
<td>n.d.</td>
<td>1.1</td>
<td>n.d.</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>n.d.</td>
<td>0.7</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.2</td>
<td>0.3</td>
<td>n.d.</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>1.1</td>
<td>0.5</td>
<td>0.6</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.5</td>
<td>n.d.</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>n.d.</td>
<td>n.a.</td>
<td>n.d.</td>
<td>1.5</td>
<td>1.4</td>
<td>6.4</td>
<td>n.d.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SA - Steam-Air, PG - Pigging, n.d. - Not determined
Samples Analysis Normalized Plot

Refinery: C

Coke Sample (before steam air)

“In Natura”
Sample thermal gravimetric analysis

Sodium vanishes above
700 °C (1,292 °F)

✓ Steam-air decoking is responsible for NaCl vanishing!

Searching for Causes...Again

Inorganic deposits origins still needed to be evaluated

Misleading conclusion: crudes received from E&P caused the deposits !!!

Since first assumption was not verified, what really caused inorganic deposits?
Sodium Effects on Heaters Run Length

Back to classroom: it is a known fact that there is a correlation between sodium feedstock concentration and its effect on run length decrease.

Investigative Method

Next step - Investigating sodium salts sources.
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**Salt Contents Analytical Methods**

ASTM D-6470

\[ \text{Cl}^{-\text{(aq)}} + \text{Ag}^{+\text{(aq)}} \rightarrow \text{AgCl}_{(s)} \]

(white deposit)

Chloride is expressed as equivalent sodium chloride in mg/liter NaCl.

Method not applicable for other salts such as sulfates and carbonates.

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**Cause Identification**

- May 04, 2006 06:00 pm: sudden increase in heater coil skin temperature
- May 04, 2006 07:00 pm: FCC's stripped sour water injection was discontinued
- May 05, 2006 07:00 am: wall temperature tends to reduce
- This same pattern was observed other times

![Graph showing time vs. temperature or similar data]
FCC stripped sour water is used as dilution water for the desalters;
FCC SWTU receives water from the FCCU, Cokers and from the SSNU;
FCC SWTU is a two-towers unit and does not use soda in NH₃ stripper,
SSNU uses sulfuric acid for neutralizing soda from LPG and gasoline treatments.

Abbreviations:
SWTU: Sour Water Treatment Unit
SSNU: Spent Soda Neutralizing Unit

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Sodium content during test run

Reference: March to April 2006
Control Actions Effectiveness

<table>
<thead>
<tr>
<th>UNIT</th>
<th>Start-up date</th>
<th>Before mitigating actions (*)</th>
<th>After mitigating actions (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCU 1</td>
<td>1973</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>DCU 2</td>
<td>1986</td>
<td>4</td>
<td>6</td>
</tr>
</tbody>
</table>

(*) Periods in months

Remarks:

- 8 to 10 months run lengths were normal before inorganic deposits.
- Petrobras new designs are for higher than 10 months run lengths.

Lessons Learned

1. Old lessons should never be forgotten: a limit for sodium concentration in the charge for Delayed Coking Units shall be established.

2. It is important to be aware, understand and control all sodium sources in order to guarantee that the limit will always be respected.

   Remark: Are we sure our fired heater run length is really optimized under the limit we established above?

4. Multidisciplinary effort is fundamental for the solution of complex problems in a refinery.

5. Criterious methodology should be applied to analyse a complex problem. Do not overlook any possibility, since root cause could be the one neglected first and solution can be simpler than expected.

"The problem solution may not be so far that you need a telescope nor so close that you might need a microscope."
Thank you

Weimar Lázaro

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