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INORGANIC PROBLEMS IN DCU HEATERS:

LESSONS LEARNED

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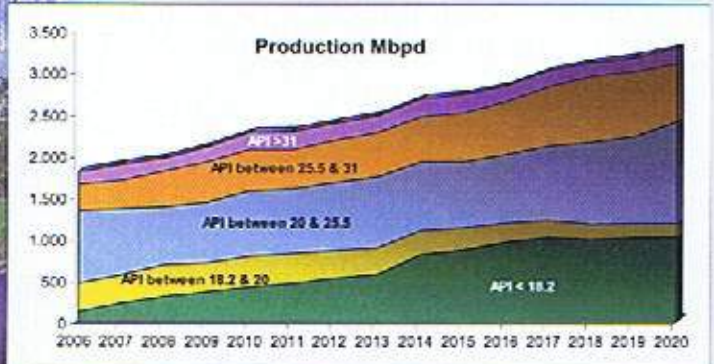
Heavy oils production increase

- ✓ 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



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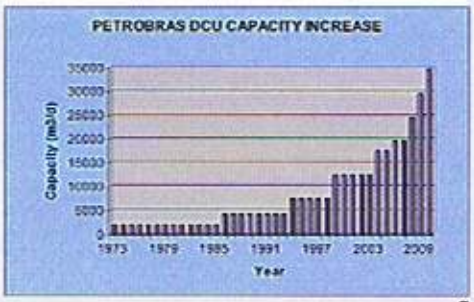
Petrobras DCU Overview

- ✓ 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)	Before 2003	After 2003
Heater Run Length	7 - 8	4 – 6
Hydroblasting Cleaning Frequency	18	12

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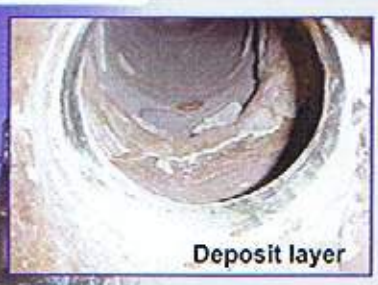
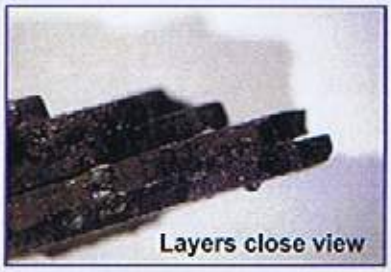
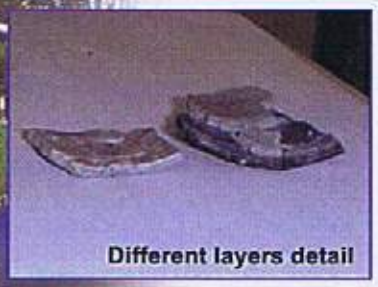
Deposits Evidences



Deposit layer



Layers close view



Different layers detail

Layer inside tube section

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Deposits Evidences

Deposits removed after heater decoking

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Inorganic Deposits Composition

XRD Analysis

- ✓ Sodium Titanium Silicate ($NaTiSi_2O_6$)
- ✓ Silicon Oxide (SiO_2)
- ✓ Iron Titanate (Fe_2TiO_4)
- ✓ Iron Oxide (Fe_3O_4 and Fe_2O_3)
- ✓ Sodium Silicate ($Na_6Si_2O_7$)

Deposits Qualitative Analysis

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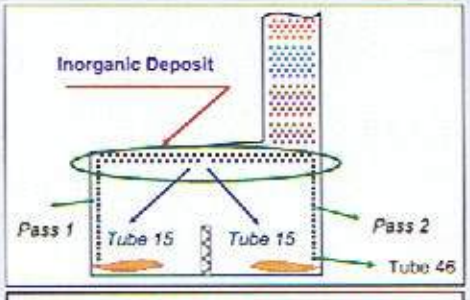
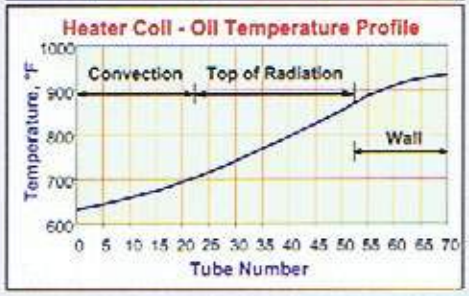
Deposits Location





DCU-1: Design by LUMMUS

Start-up in 1973

Deposits appeared in temperature range: 370 – 480°C (700 – 900°F)

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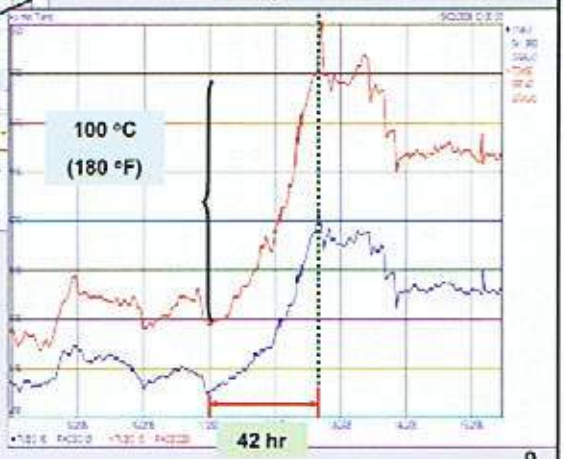
Effect on Heaters Run Length

$$T_{WALL} = T_{FLUID} + \Delta T_{FILM} + \Delta T_{METAL} + \Delta T_{COKE}$$

Heaters Run Length Target

Skin-Points Temperatute Tendency



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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.

<u>Immediate conclusion</u>: new crudes produced by E&P (Upstream) caused deposits !!!

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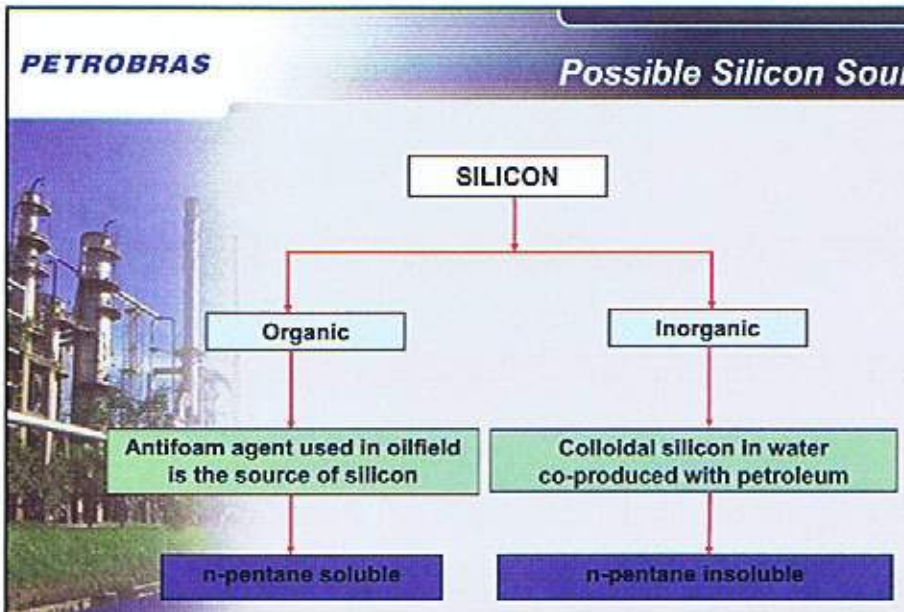
Possible Silicon Sources



Silicon was inorganic !

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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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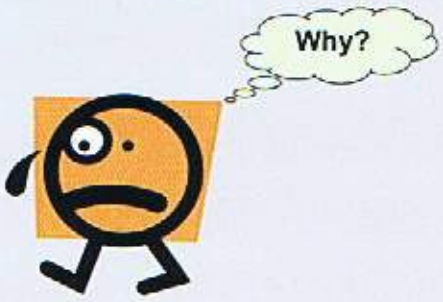
Causes and Possible Solutions

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)

Tag	DCU-2 Heater A	DCU-2 Heater B	DCU-1 (Layer 1)	DCU-1 (Layer 2)	Heater B	Heater A	Heater A	DCU-2
Refinery	RPBC	RPBC	RPBC	RPBC	Refin B	Refin B	Refin C	RPBC
Decoking	SA	SA	SA	SA	SA	SA	PG	SA
Year	2001	2001	2004	2004	2001	2003	2004	2004
Si	21	16	19.0	14.1	16.9	19.7	12.5	30.7
Na	*13*	*6.7*	*9.9*	*7.7*	*2.6*	*0.2*	*11.1*	*16.6*
Fe	8.2	5.1	7.2	6.8	11.8	18.4	3.5	14.2
Ca	5.7	4.7	4.4	4.4	4.2	6.4	2.8	9.9
Mg	8.7	6.8	3.9	3.6	4.9	2.3	1.4	6.7
Cl	*n.d.*	*n.d.*	*2.1*	*2.8*	*2.1*	*1.6*	*16.0*	*n.d.*
Ti	2.9	1.6	0.8	0.6	n.d.	1.1	n.d.	0.8
Al	n.d.	0.7	n.d.	n.d.	1.2	0.3	n.d.	n.d.
V	1.1	0.5	0.6	n.d.	n.d.	1.5	n.d.	0.8
S	n.d.	n.a.	n.d.	1.8	1	n.d.	6.4	n.d.

SA – Steam-Air PG – Pigging n.d. – Not determined

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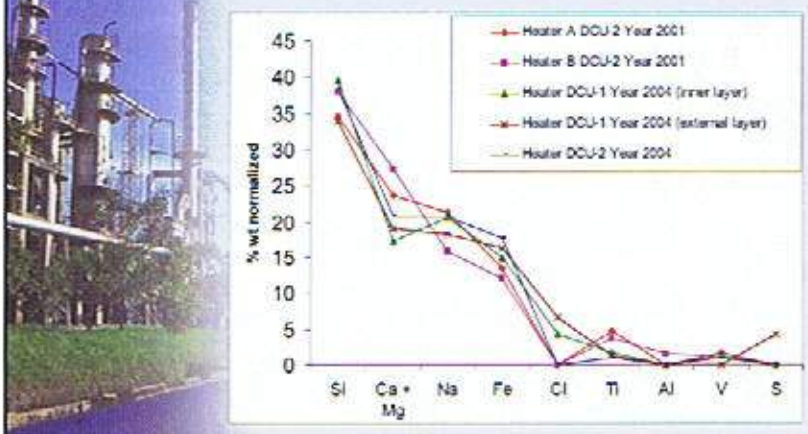
Samples Analysis Normalized Plot



Refinery: RPBC

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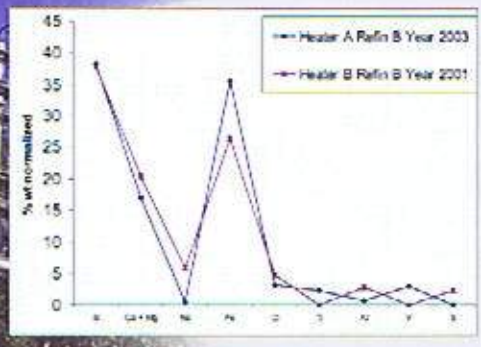
Samples Analysis Normalized Plot



Refinery: B

40% ashes from refinery B

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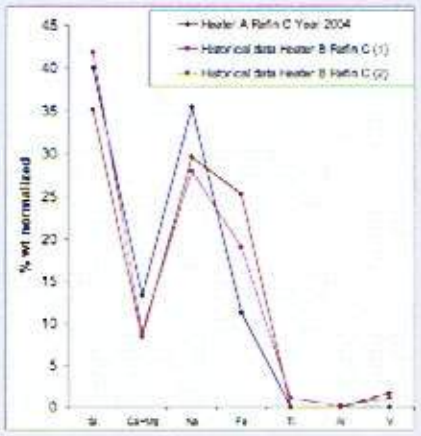
Samples Analysis Normalized Plot



Refinery: C

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Coke Sample (before steam air)

"In Natura"

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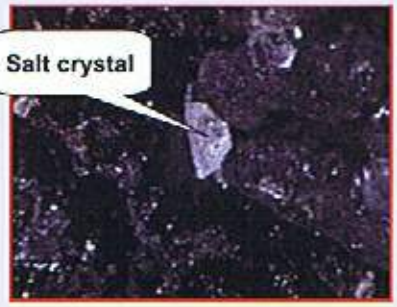
Coke Sample (before steam air)

"In Natura"

Zoom

Electronic Microscope



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Coke Sample (before steam air)

XRF Analysis

Element	wt %
Na	22
Cl	78

Semi Quantitative Analysis

Electronic Microscope

Crystal → Halite (NaCl)

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Coke Sample (before steam air)

"In Natura"

800 °C

After Calcination

65% wt inorganic

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Coke Sample (before steam air)

XRF Analysis

Element	wt %
Na	*12*
Si	*25*
Cl	*1.6*
Fe	5.4
Ca	4.7
Ti	0.6
S	1.2
Mg	6.3

Semi Quantitative Analysis

After Calcination

65% wt inorganic

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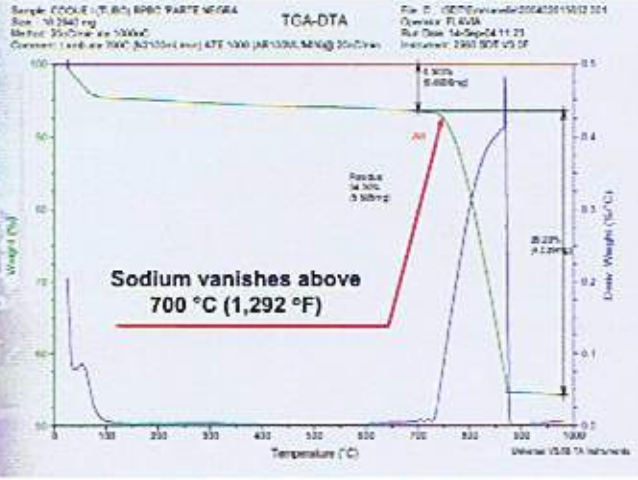
Theoretical Thesis Confirmation

Sample thermal gravimetric analysis



✓ *Steam-air decoking is responsible for NaCl vanishing !*

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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 ?

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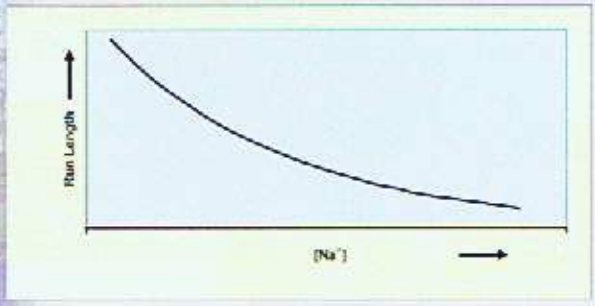
Sodium Effects on Heaters Run Length

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



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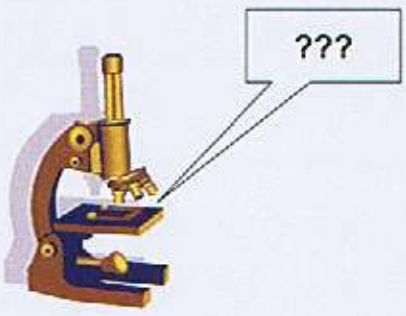
Investigative Method



Next step - Investigating sodium salts sources.

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Salt Contents Analytical Methods

ASTM D-6470

$$Cl^-_{(aq)} + Ag^+_{(aq)} \rightarrow \underbrace{AgCl_{(s)}}_{\text{(white deposit)}}$$

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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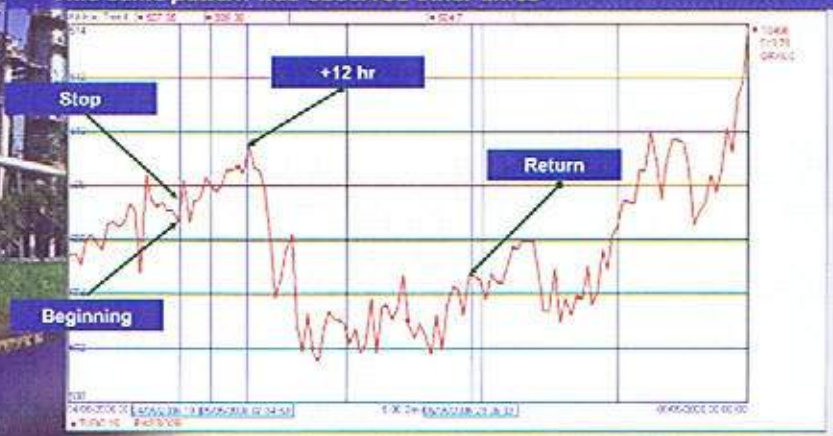
Cause Identification

- ✓ 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*



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Cause identification details

- 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 NH_3 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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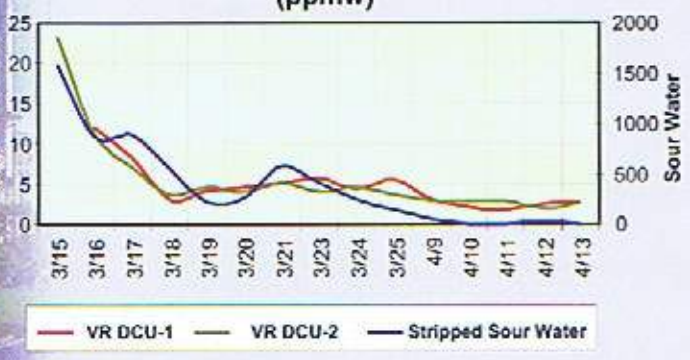
Desalters Stripped Sour Water

Sodium content during test run

(ppmw)



Reference: March to April 2006

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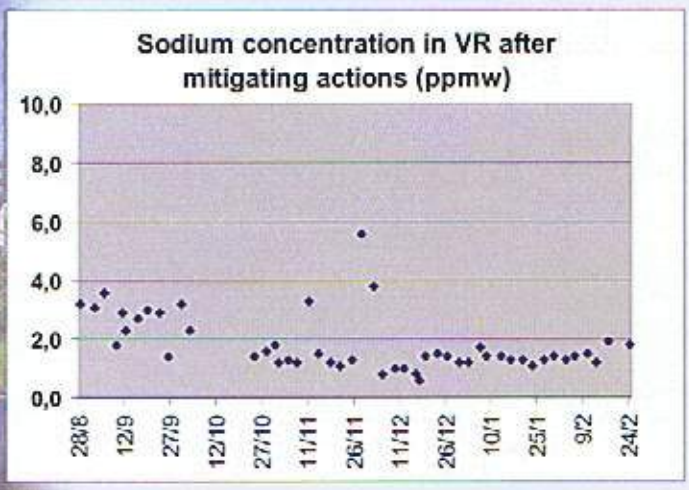
Follow up

Vacuum Residue – DCU-1



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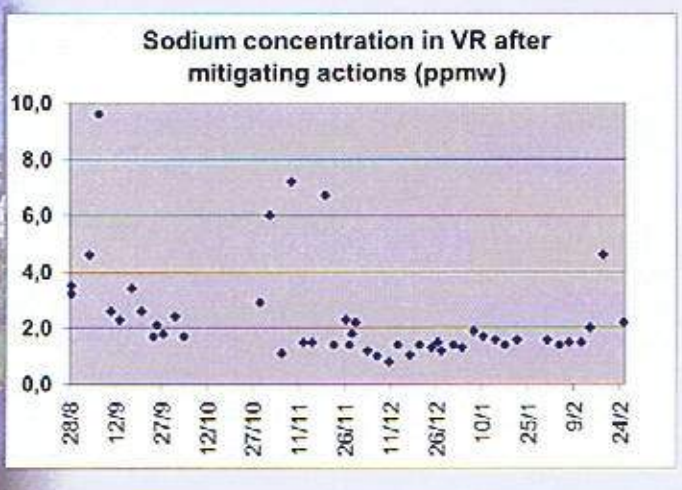
Follow up

Vacuum Residue – DCU-2



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Control Actions Effectiveness

UNIT	Start-up date	Before mitigating actions (*)	After mitigating actions (*)
DCU - 1	1973	3	8
DCU - 2	1986	4	6

(*) *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.**

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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".

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THANK YOU

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