IEA Greenhouse Gas R&D Programme

# Mercury (Hg) in Oxy-Coal Fired Power Plant with $CO_2$ Capture

## What is the Real Score???


*by*

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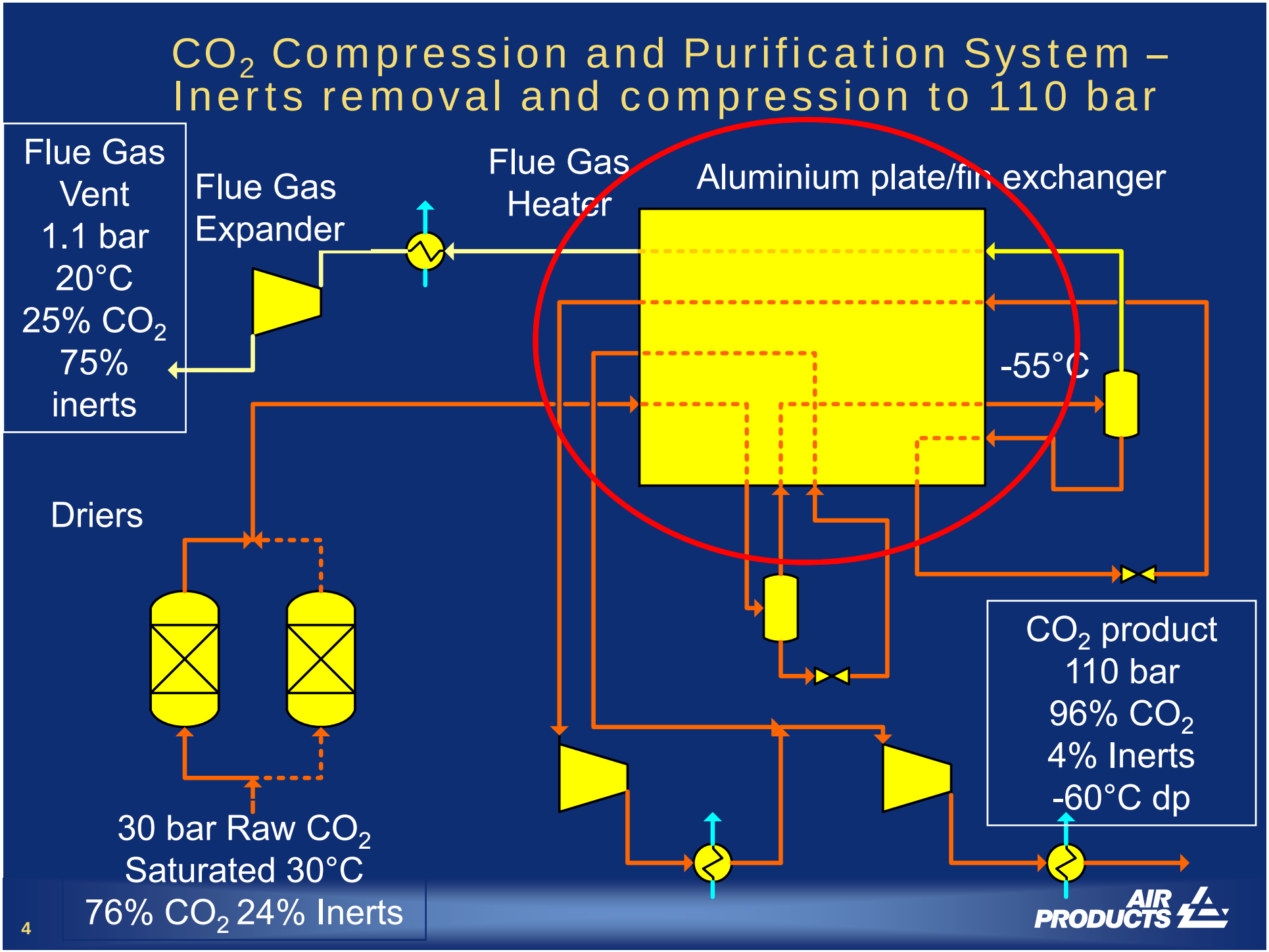
# Objectives of this Presentation

- To provide awareness the impact / risk of ignoring Hg in any Oxy-Coal Combustion Power Plant with $CO_2$ Capture
- To initiate discussion on the issue of Mercury in Oxy-Coal Combustion Power Plant
- To initiate a review on the different factors to reconsider on the design of coal power plant in the perspective of Hg.

# $CO_2$ Compression and Purification System – Inerts removal and compression to 110 bar



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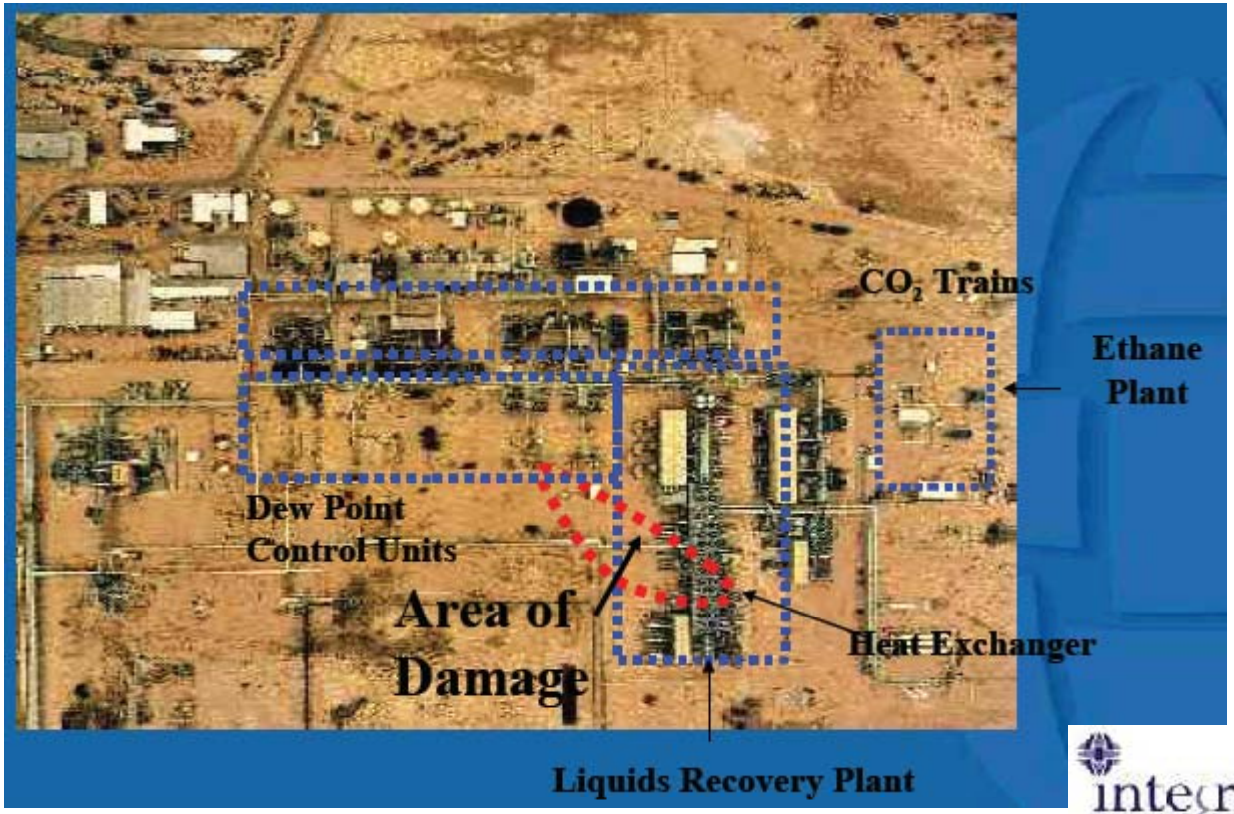
**Case Study:**

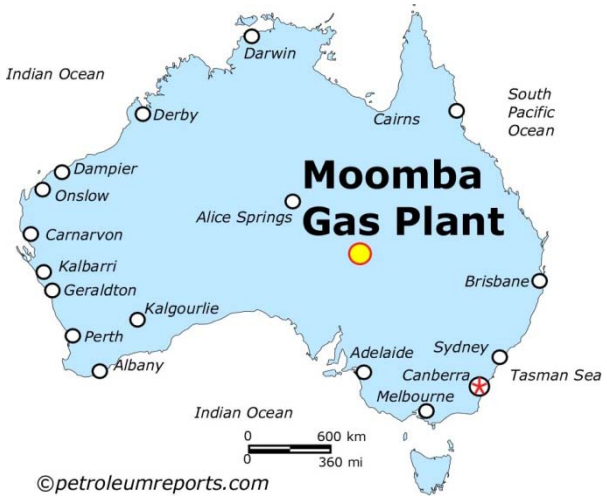
# Moomba Gas Processing Plant Fire Incident (01 January 2004)

# Safety Incident

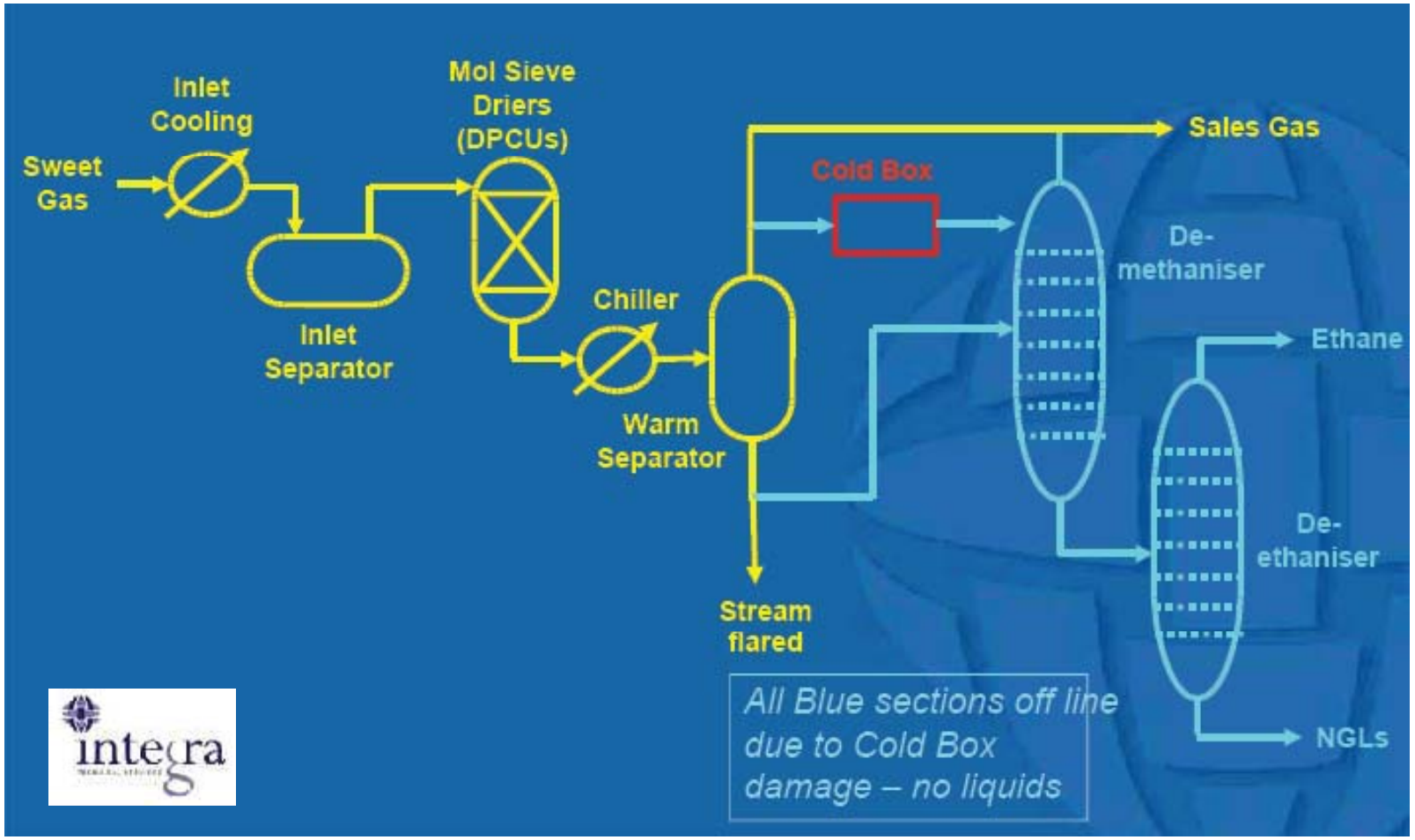
- Moomba Gas Processing Plant owned by Santos is the main supplier of natural gas to South Australia and New South Wales
  - Liquids separated from raw natural gas via 2 trains of LRP (Liquids Recovery Plant)
  - Liquids (condensate and LPG) sent to Port Bonython for export (about 650Km south of Moomba)
- About 02.43 in the morning, 1st January 2004 – an explosion & fire occurred at Train A of the LRP section.
  - The fire incident also damaged Train B.
- Effect: liquids production interrupted for 8 months

# Moomba Gas Processing Plant (Layout)

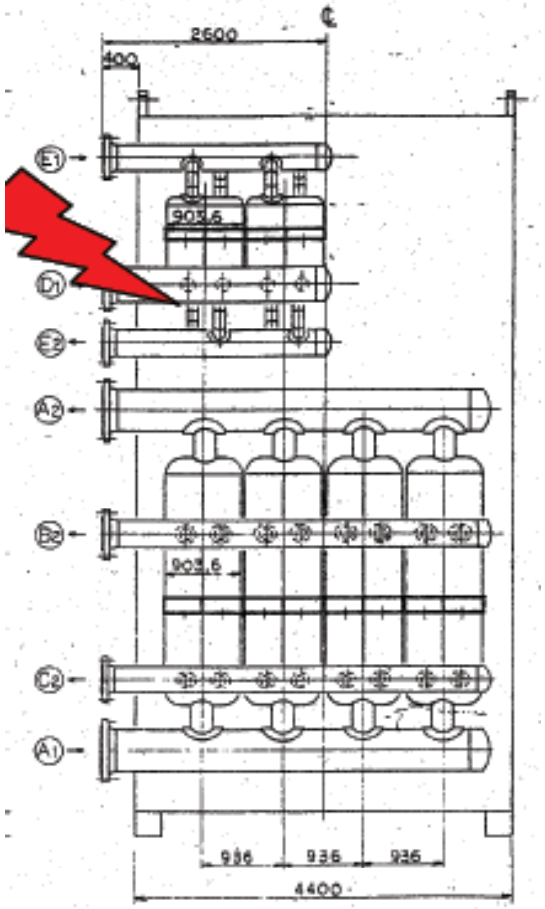


# Process Scheme of Liquid Recovery Plant



# Location of the Failure

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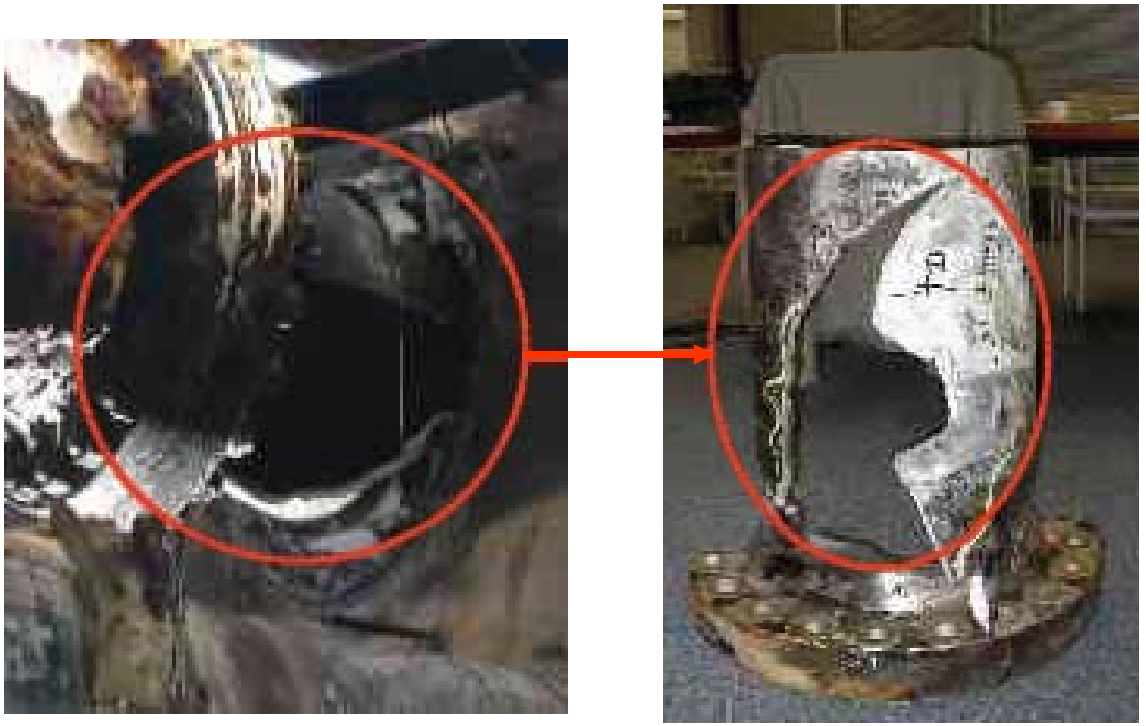
# Failure Location



- Failure occurred at the base (6 o'clock) of the gas nozzle
- Evidence of de-lamination consistent with Liquid Metal Embrittlement (LME) caused by mercury in contact with aluminium

# Other potential failure caused by Hg


Further inspection of the cold box after the incident showed evidence of pitting to the aluminium surface in several parts of the heat exchanger.

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# This is How Mercury attacks the Aluminium


Figure 1: A small amount of mercury attacking an aluminium beam in less than an hour [courtesy of Popular Science website].

# Discussion Points

# Understanding Failure Mechanisms

- Failure Mechanisms
  - Amalgamation
  - Amalgam Corrosion
  - Liquid metal embrittlement
  - Galvanic Corrosion

- Factors that could increase the probability of failure are:
  - Hg accumulation (i.e. due to shut down and process upsets)
  - In addition to the presence of mechanical and thermal stress, and
  - moisture

- Accumulation would not occur under normal operating condition (i.e. -40$^{o}$C and below)

# Understanding Failure Mechanisms

- **Statement from ALPEMA:**
  In general, mercury will not react with aluminium unless it is allowed to exist in contact with the heat exchanger in its liquid state and there is water present. If these conditions exist within a heat exchanger, then mercury contamination can result in problems. This attack is most severe when coupled with another corrosion process.

- QUESTION #1: How dry do we need to go?

# Understanding Failure Mechanisms

- **Known failures of BAHX due to mercury attack (i.e. Algeria, Thailand, Australia) are random events!!!**

- **Statement from UOP Background Paper:**

  Since the level of mercury that can be tolerated is not established, most operators want to remove it “all.” That is, remove it to a level where it can not be detected with the available analytical capability. Currently, this means reducing the mercury to less than 0.01 µg/$Nm^3$.

- QUESTION #2: Is the 0.01 µg/$Nm^3$ to be used as well in the oxy-coal combustion power plant?

# What are the Concerns???

- Mercury from LNG plant are mostly elemental Hg and some organo-Hg species.
  - There are no technical barrier in removing mercury. This is achieved by using Activated Carbon Bed or other adsorbent.
- In Coal Fired Case, Hg will come in the form of elemental Hg (as particulates or vapour) or $Hg^{2+}$ (mostly in the form of $HgCl_2$)
- QUESTION #3: What is the speciation of Hg in an oxy-coal combustion cases?

# Fate of Mercury During Oxy-Combustion

## Possibility of most mercury dumped in the $CO_2$ clean up process

**Table 1: Potential Impact on Mercury Emissions During Oxy-Combustion**

| | Air Fired Case | Oxy-Fired Case |
|---|---|---|
| FF or ESP FGD/SCR | In a coal fired power plant equipped with FF or ESP, FGD and SCR would experience reduction of up to 90% in mercury emissions. | For oxy-coal combustion firing low sulphur coal, both FGD and SCR may not be needed. Thus, the co-benefit of removal of mercury from these flue gas treatment plants would not be realised. |
| ESP / FF performance | Under normal operation, FF and ESP could be operated with high level of particulate capture efficiency | Under oxy-combustion mode, capture efficiency of FF and ESP might have slight performance drop due to operating at higher temperature because of high dew point temperature of the flue gas.<br><br>This could have indirect consequences of lower capture efficiency of mercury in the FF or ESP. |
| Carbon in Ash | It has been reported that firing at a slightly higher carbon in ash could provide a natural capture of mercury. | In an oxy-coal combustion boiler (especially for retrofit), the carbon in ash is reported to be lower as compared to air fired case. Thus it is highly possible that co-benefits of reducing mercury by the natural capture by the ash will not be realised. |
| Sulphation in ash | It has been reported that higher sulphation in ash will compete with adsorption of mercury in the ash. | A higher sulphation in ash was reported in several studies done by IHI, B&W, ANL study and K. Okazaki. This could also indicate that lower mercury adsorption could be observed. |

# Conversion of Hg to $Hg^{2+}$

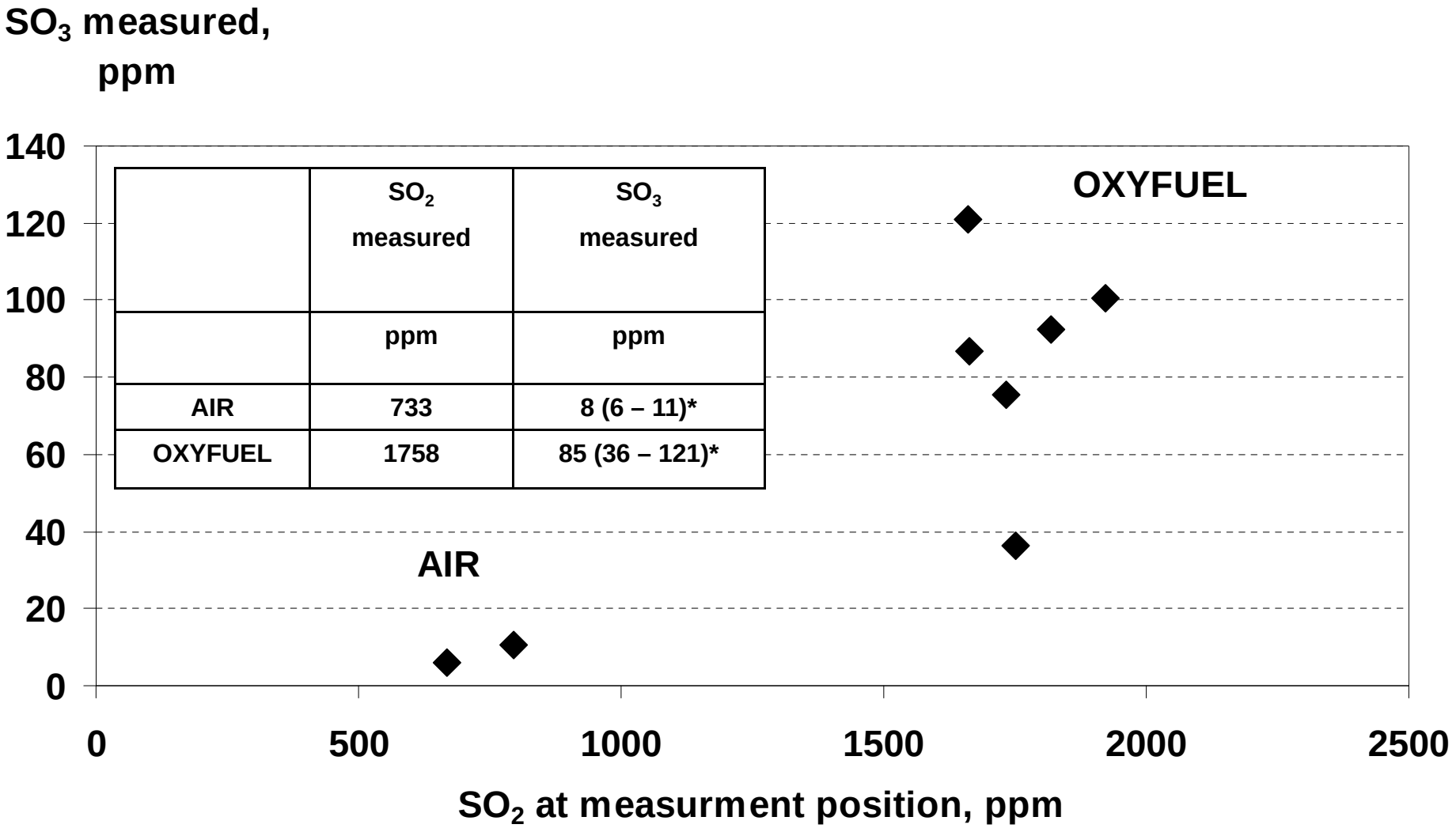
- Clearly established in Air Fired Cases that the benefits of co-removal of Hg with FGD and SCR are due to conversion of Hg (elemental) to $Hg^{2+}$
- Correlation with Cl content of the coal is well established – this promote conversion to $Hg^{2+}$
- Question #5: What will be the rate of conversion from Hg to $Hg^{2+}$ in oxy-combustion case?

# Impact of $SO_3$
## Data from ANL Studies (1980s) - Black Thunder Coal

| Coal | Load ($10^6$ Btu/hr) | Recycle Condition/ $(CO_2+H_2O)/O_2$ | $SO_2$ (ppm, dry @ 3.5% $O_2$) | $SO_2$ lb/$10^6$ Btu | $SO_3$ (ppm, dry @ 3.5% $O_2$) | S in Ash (wt. %) |
|---|---|---|---|---|---|---|
| Black Thunder | 10.10 | Air | 338 | 0.65 | 0.03 | 0.96 |
| | 9.72 | Wet/2.25 | 1160 | 0.28 | - | 4.13 |
| | 9.89 | Wet/2.30 | 1640 | 0.55 | - | - |
| | 9.78 | Wet/2.66 | 1060 | 0.36 | - | 4.43 |
| | 10.05 | Wet/2.72 | 1240 | 0.42 | - | 4.65 |
| | 9.95 | Wet/3.00 | 1025 | 0.35 | 0.76 | - |
| | 9.89 | Wet/3.23 | 1000 | 0.34 | - | 4.40 |
| | 6.10 | Air | 280 | 0.55 | - | - |
| | 5.97 | Wet/3.29 | 600 | 0.20 | - | - |
| | 9.88 | Dry/1.52 | - | - | - | - |
| | 9.90 | Dry/1.82 | - | - | - | 1.15 |
| | 9.90 | Dry/2.15 | 550 | 0.18 | - | - |
| | 9.88 | Dry/2.27 | - | - | - | 2.78 |
| | 9.93 | Dry/2.66 | 560 | 0.14 | 0.23 | 1.14 |
| Utah | 10.00 | Air | 460 | 0.90 | - | 0.88 |
| | 9.91 | Wet/3.11 | 1500 | 0.50 | - | 0.87 |

# Measured $SO_3$ concentrations for Lausitz coal at AIR and OXYFUEL combustion conditions

Universität Stuttgart

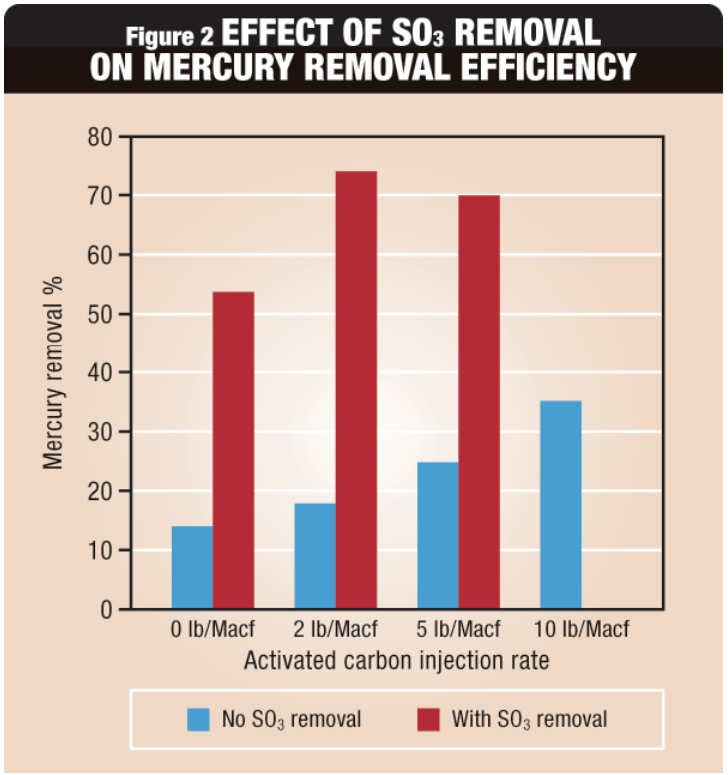



| | $SO_2$ measured | $SO_3$ measured |
|---|---|---|
| | ppm | ppm |
| AIR | 733 | 8 (6 – 11)* |
| OXYFUEL | 1758 | 85 (36 – 121)* |

* ... min. / max. value measured

# Impact of SO3 on Hg Removal Efficiency

## Air Fired Case (CODEN Study)




## Oxy Fired Case

?

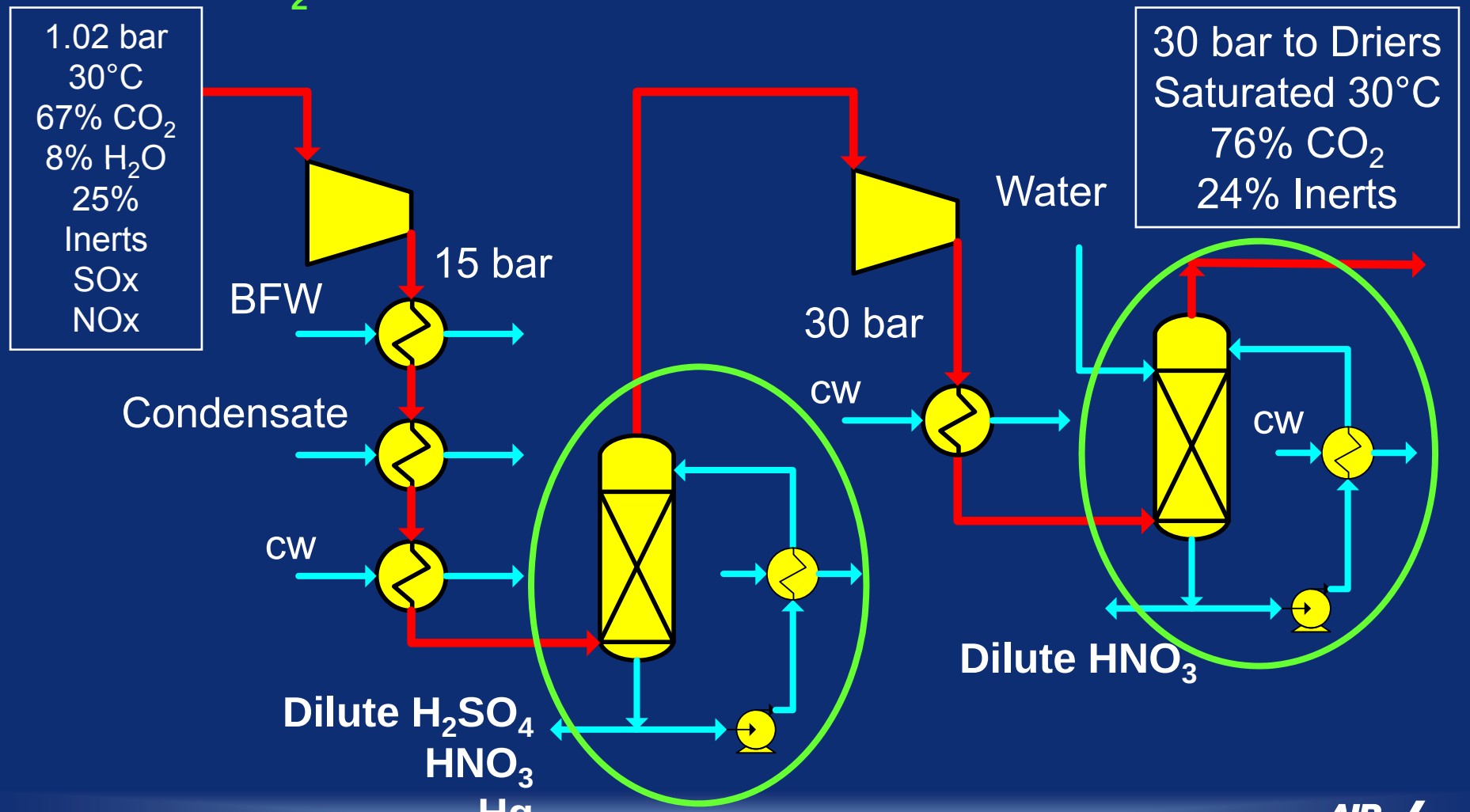
# Mercury Management in the CO2 Processing Plant

- No technical barrier in removing Hg. This has been done in LNG industry. The consideration of cost is the main question!

- There are 3 levels where Hg (both elemental and ionic) could be captured in the $CO_2$ processing plant.
  - Compression stage
  - Moisture Removal stage
  - Activated Carbon Guard bed

# $CO_2$ Compression and Purification System – Removal of $SO_2$, NOx and Hg

- **$SO_2$ removal: 100%  NOx removal: 90-99%**



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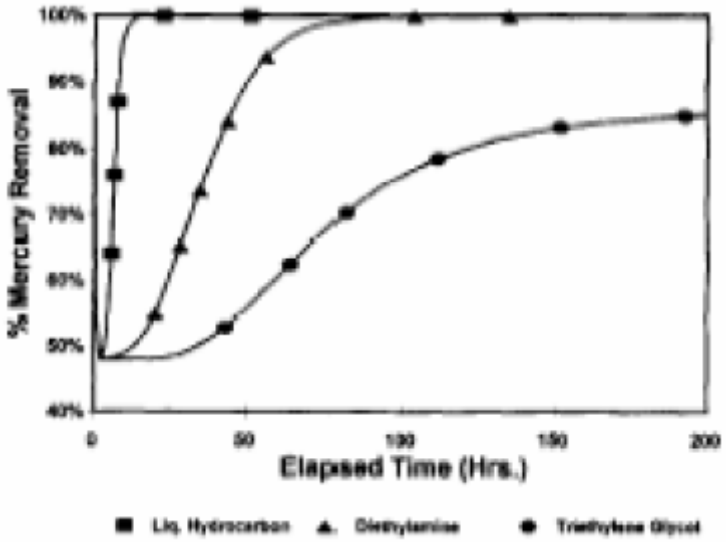
# NG Industry Practice

## (Data from Calgon 1996)

- Activated Carbon bed is generally employed. This is expected to be applied to oxy-combustion oxy-PC as well.

- It is important to be aware with regard to short term performance drop of the activated carbon bed during shut down or process upset.



# Mercury Sorbent Technologies

(From M. Wilhelm, 1995 – Mercury Technology Services)

| REACTANT | SUBSTRATE | COMPLEXED FORM | APPLICATION |
|---|---|---|---|
| Sulfur | Carbon | HgS | Gas ($Hg^o$) |
| Metal Sulfide | $Al_2O_3$ | HgS | Gas ($Hg^o$) |
| $I^-$ | Carbon | $HgI_2$ | Gas, Condensate |
| $I^-$ | $Al_2O_3$ | $HgI_2$ | Condensate |
| Hydrogenation | | | |
| Redox/ Ion Exchange | Resin | $Hg^{2+}$ | Gas |

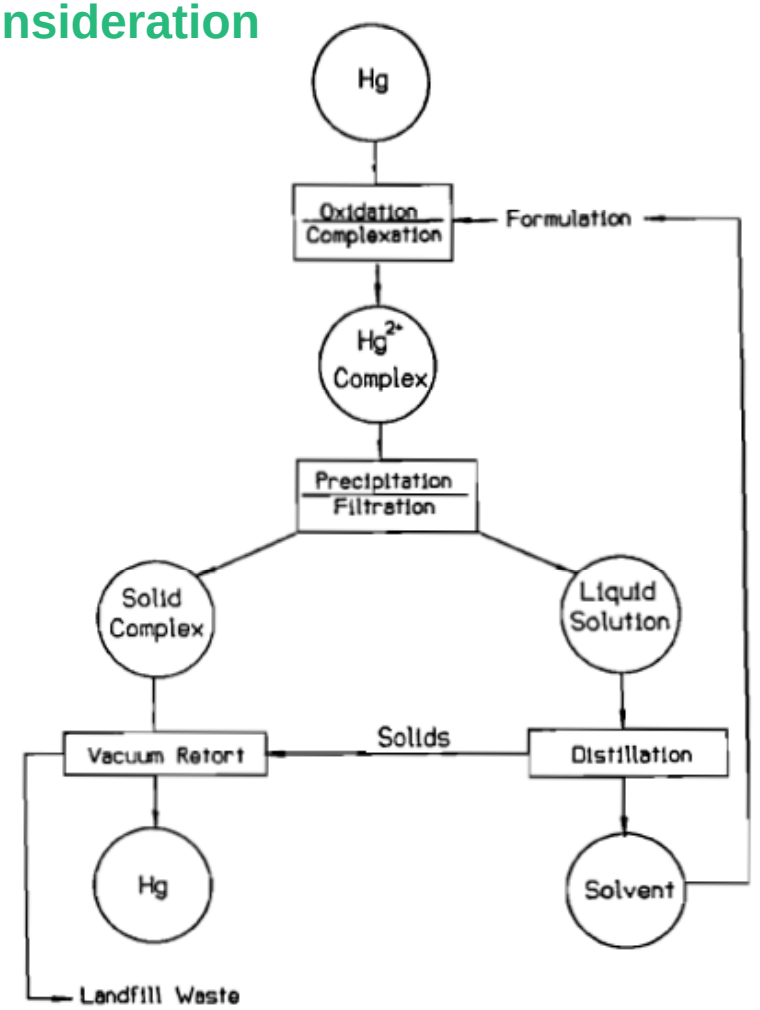
Question 7: What are possible impact of NOx and Oxygen to these substrates?

# Hg Cleaning Process

## Environmental Consideration

- It should be expected that future environmental regulation would require recovery of Hg and back to the commercial cycle!

- Question #8: Can we recover Hg from the wastewater sludges, ash bin and other sink etc...




(M. Wilhelm, 1995)

# Mercury Analysis Method

(From M. Wilhelm, 1995 – Mercury Technology Services)

| | | |
|---|---|---|
| • Colorimetric | 2000 | ng |
| • X-Ray Flourescence | 10 | ng |
| • Neutron Activation | 2 | ng |
| • Gold Film | 0.5 | ng |
| • Differential Pulse Voltametry | 0.04 | ng |
| • Cold Vapor Atomic Absorption | 0.01 | ng |
| • Cold Vapor Atomic Flourescence | 0.0001 | ng |

Question #9: Can we really measure mercury at the very low level?

# The Real Score…

- **What is the real issue?**
  - **The real issue is how much Hg we are delivering to the $CO_2$ processing unit**
  - **What type of Hg species we are introducing to the $CO_2$ processing unit?**
  - **What is the most cost effective way of Hg removal process to be included in the power plant?**