REINHOLD ENVIRONMENTAL Ltd.

2014 APC Round Table & Expo Presentation

July 14-15, 2014, in Louisville, KY / Hosted by LG&E/KU

Achieving Cost-Effective MATS Compliance for WFGDs Through the Lens of Hg Absorption

Reinhold Environmental 2014 APC Roundtable
Galt House – Louisville, KY

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Hg and WWT Product Line Manager
July 14, 2014

OUTLINE

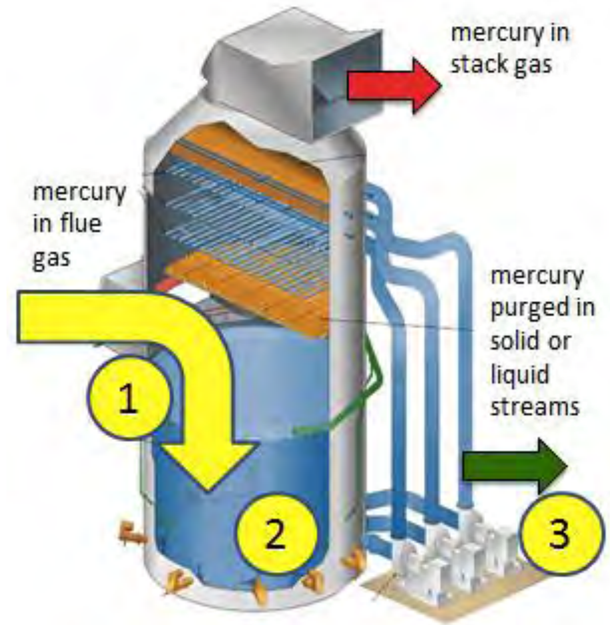
Elemental Mercury Solubility

Hg Re-emission

WFGD Hg Absorption

Field Testing Results

What Does it Mean To You?



Hg^0 Solubility

$10^7 m_{Hg}$/mol kg^{-1}

Table 4. Tentative Values of the solubility of mercury in water.

Temperature T/K	Mercury Solubility: Molality $10^7\ m_{Hg}$/mol kg^{-1}	Mercury Solubility: Mol Fraction $10^9\ x_{Hg}$	Henry's Constant[b] K/atm	Henry's Constant[c] K/bar
273.15	1.36	2.45	108	109
278.15	1.58	2.84	151	153
283.15	1.83	3.30	208	211
288.15	2.12	3.83	282	286
293.15	2.46	4.43	376	381
298.15	2.85[a]	5.14	495	502
303.15	3.30	5.95	642	651
308.15	3.82	6.89	823	834
313.15	4.42	7.97	1040	1054
318.15	5.11	9.21	1310	1327
323.15	5.91	10.6	1620	1641
328.15	6.82	12.3	1980	2006
333.15	7.87	14.7	2400	2432
338.15	9.08	16.3	2890	2928
343.15	10.5	18.8	3450	3495
348.15	12.0	21.7	4.07×10^3	4.12×10^3
353.15	13.8	24.9	4.77×10^3	4.83×10^3
358.15	15.9	28.6	5.56×10^3	5.63×10^3
363.15	18.3	32.9	6.42×10^3	6.51×10^3
368.15	21.0	37.7	7.36×10^3	7.46×10^3
373.15	24.0	43.3	8.39×10^3	8.50×10^3
[illegible]	[illegible]	[illegible]	[illegible]	9.63×10^3
[illegible]	[illegible]	[illegible]	[illegible]	10.84×10^3
[illegible]	[illegible]	[illegible]	[illegible]	12.16×10^3
[illegible]	[illegible]	[illegible]	[illegible]	13.48×10^3

The Solubility of Mercury in Water
J. Phys. Chem. Ref. Data, Vol. 14, No. 3, 1985
www.nist.gov/data/PDFfiles/jpcrd274.pdf

- **Molality = Moles of solute per mass of solvent**
- **MW Hg = 200**
- **Hg^0 solubility = ~120 ppb**

Hg^0(liq)–Hg^0(solution) Equilibrium and Solubility of Elementary Mercury in Water

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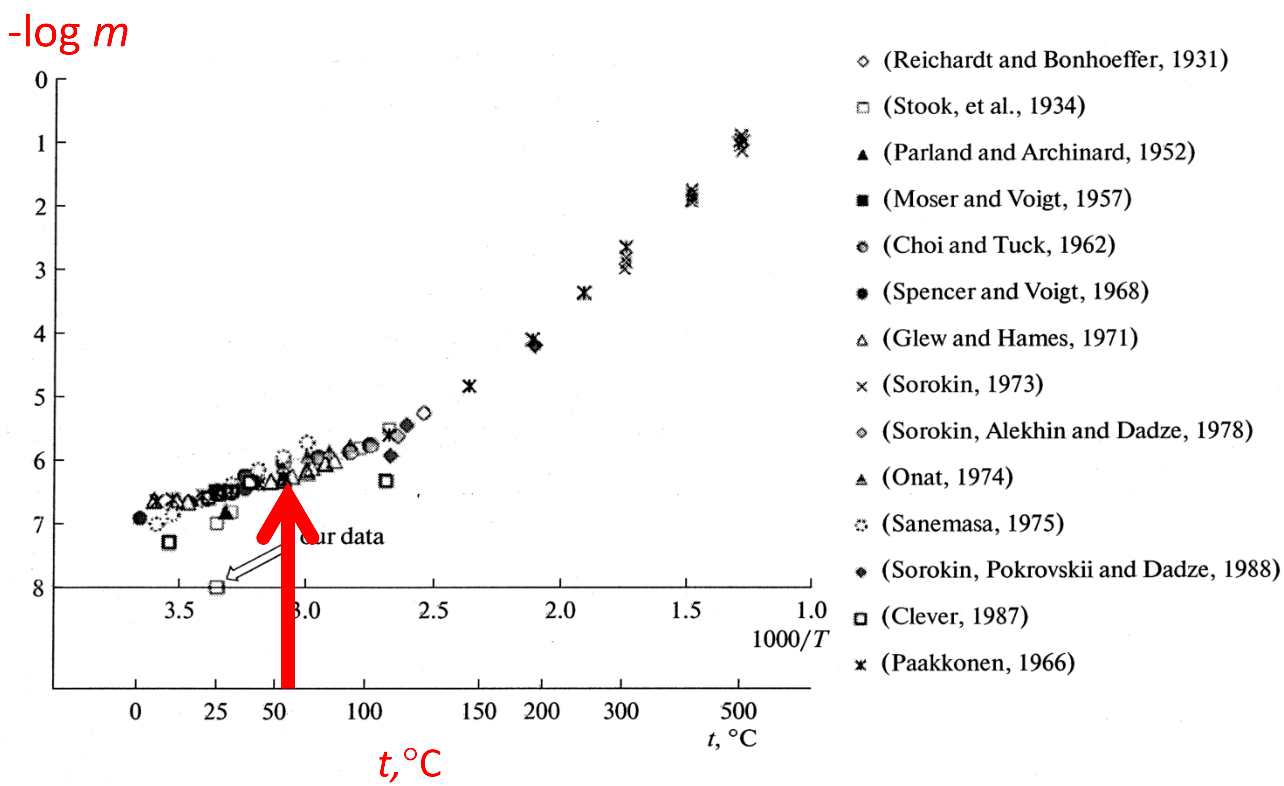
Received May 25, 2011

Abstract—The solubility metallic mercury in water and its dominating forms were studied. The prevalence of the Hg^0_{aq} form in the high-temperature range was confirmed and the reaction constant $Hg^0_{liq} \rightleftharpoons Hg^0_{aq}$ ($\log K = \log m = -8.01$) at 25°C with the predominance of oxidized forms of mercury for the 20–80°C area of low temperatures was found.



The solubility of mercury in water as an inverse temperature function. The initial experimental data of various authors are given from (Sorokin, Pokrovskii, and Dadze, 1988).

Hg^0 Solubility

It has been experimentally studied for 80+ years.

Hg^0 has a finite, non-zero, positive solubility.

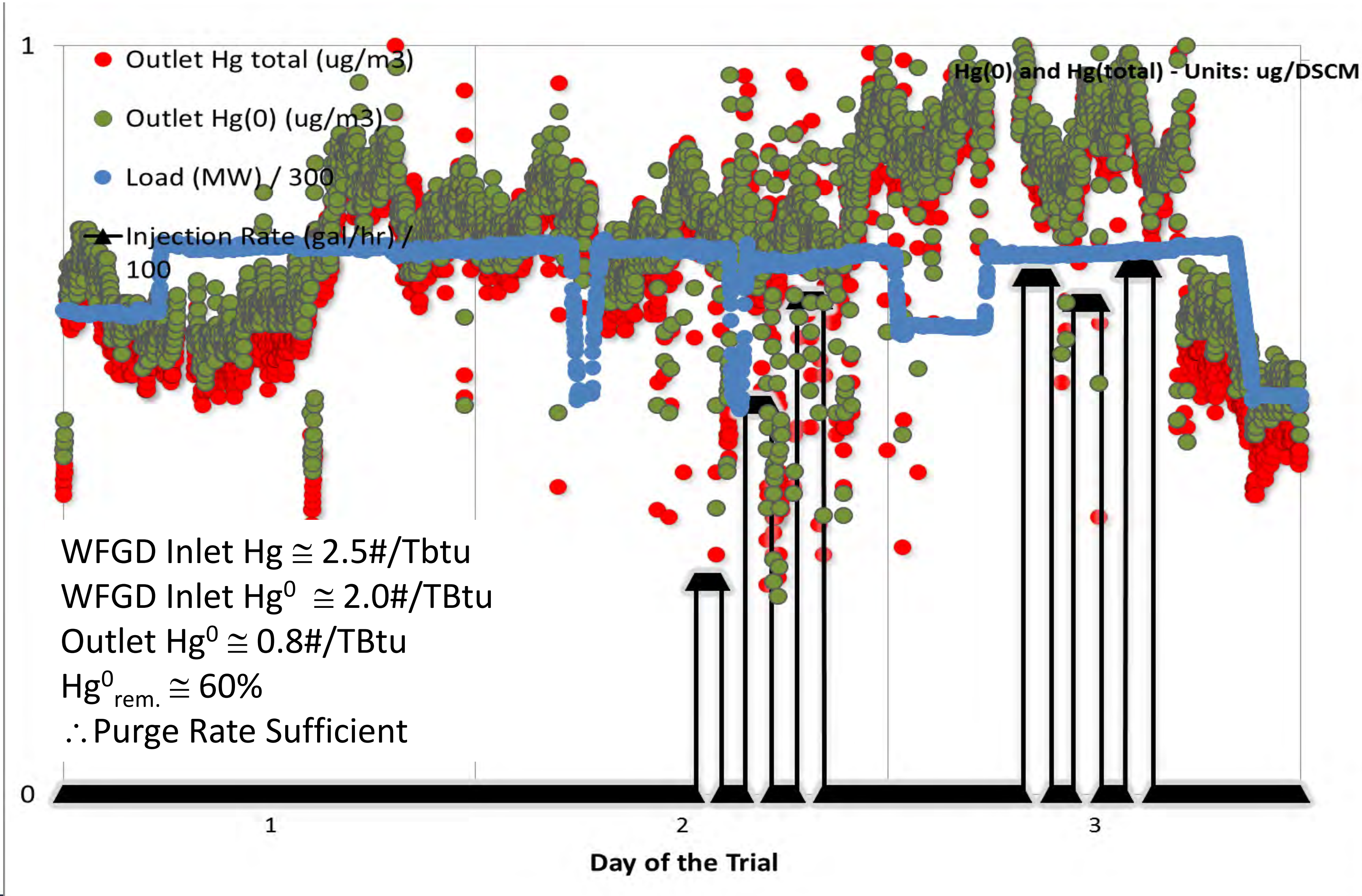
In the context of WFGD SO_2 Absorbers and Hg MATS compliance, it is significant.

After 30 – 50 years of operation, Hg^0 saturation is likely.

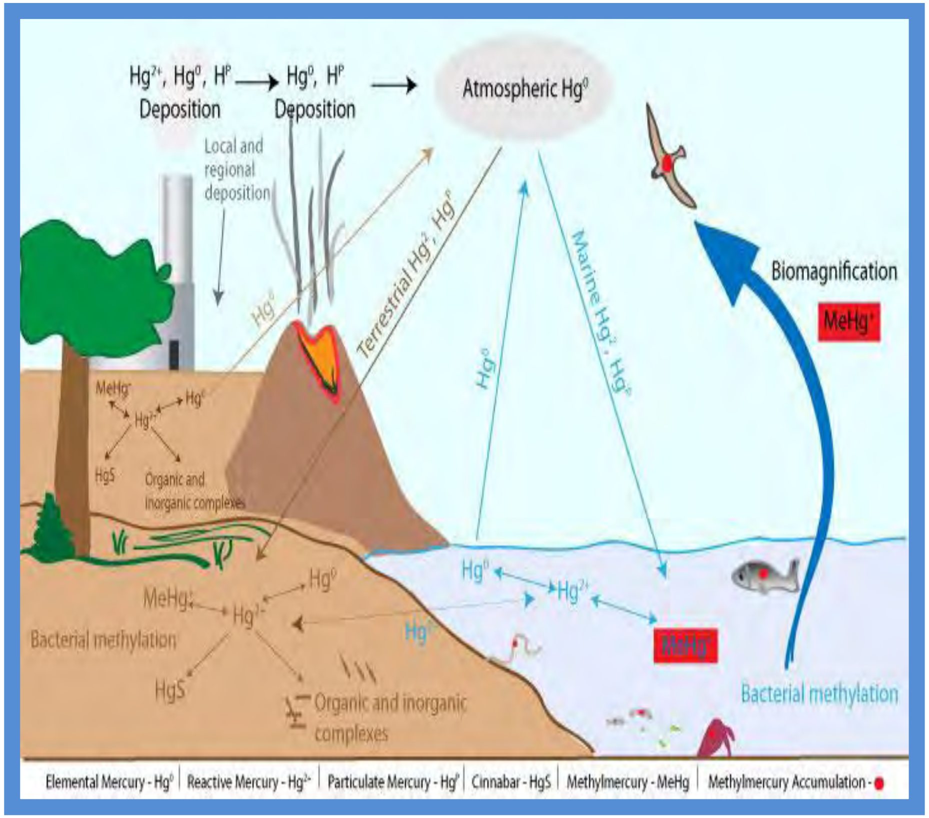
It's not just the inlet flue gas that contains Hg^0.

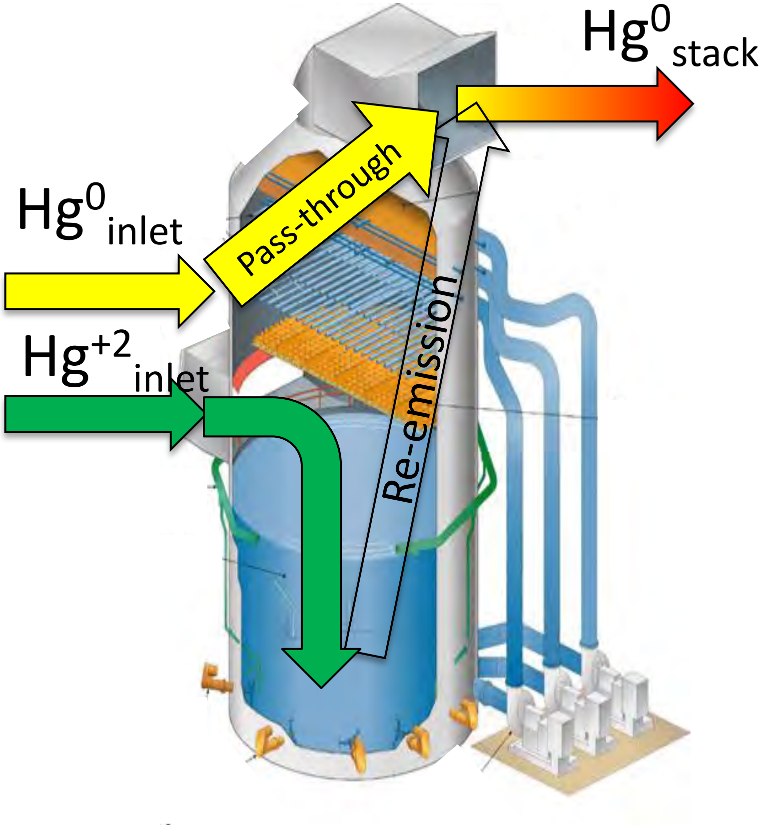
Mercury solubility approach provides greater insight into controlling the re-emission effect.

Western Fuel – Na-based WFGD



Hg Re-emission





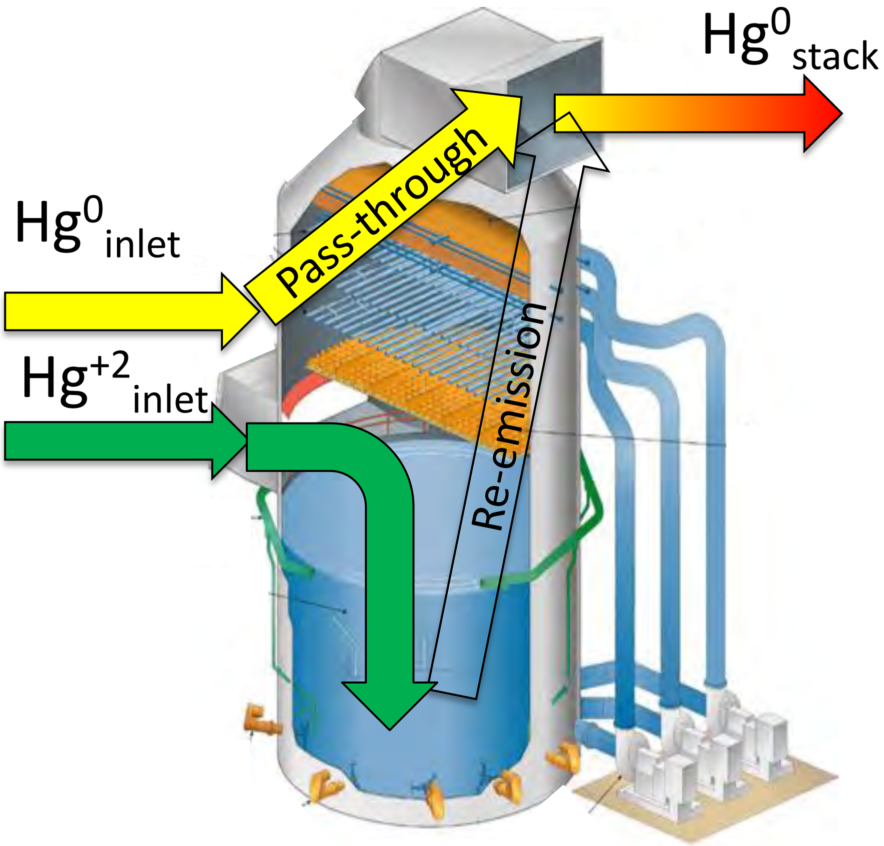
Mercury Emission Control Via Mercury Re-emission Suppression…

Definition of Re-emission:

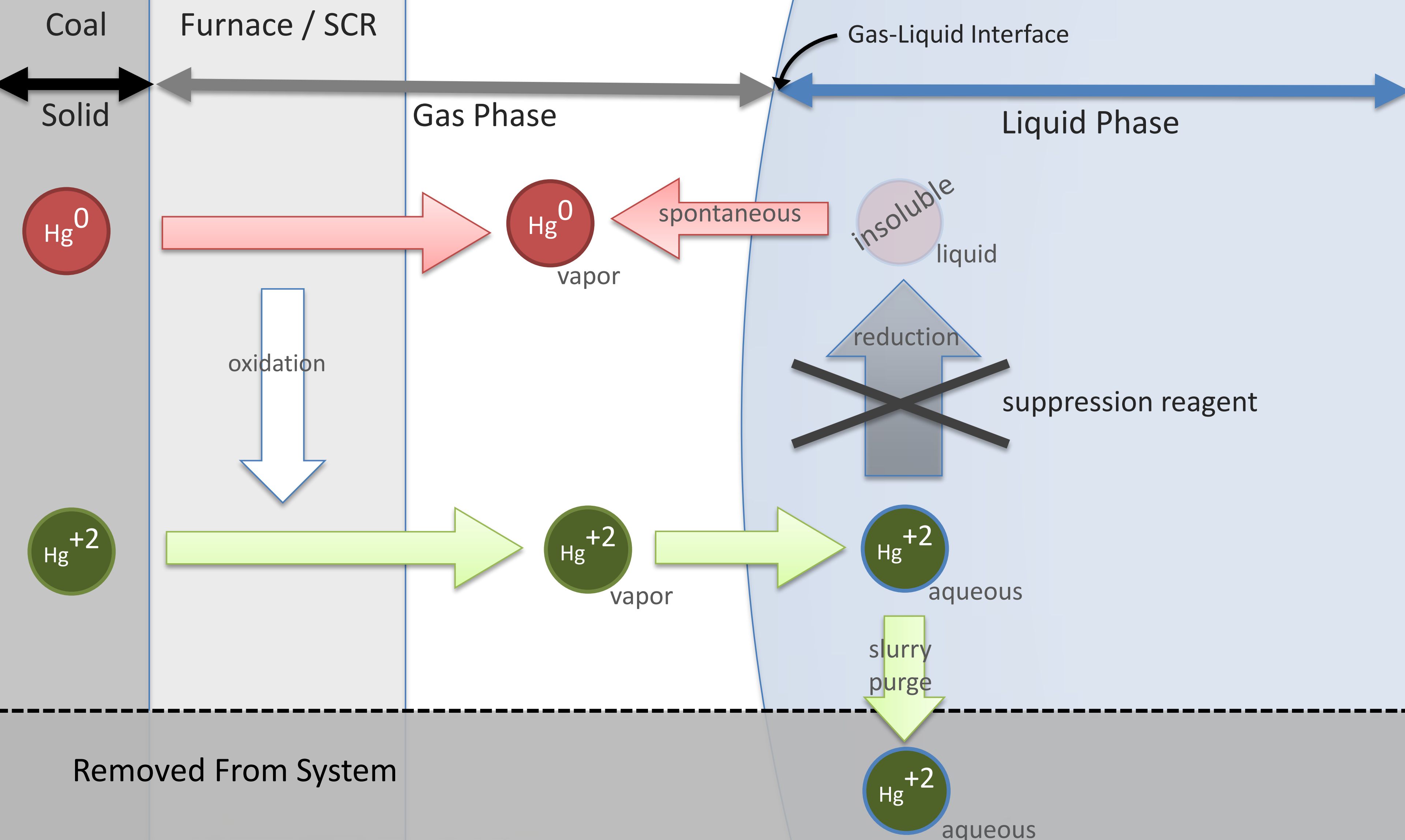
elemental Hg at stack > elemental Hg at scrubber inlet

Objective:

Suppress the re-emission mechanism with additives or adjustments to scrubber chemistry.

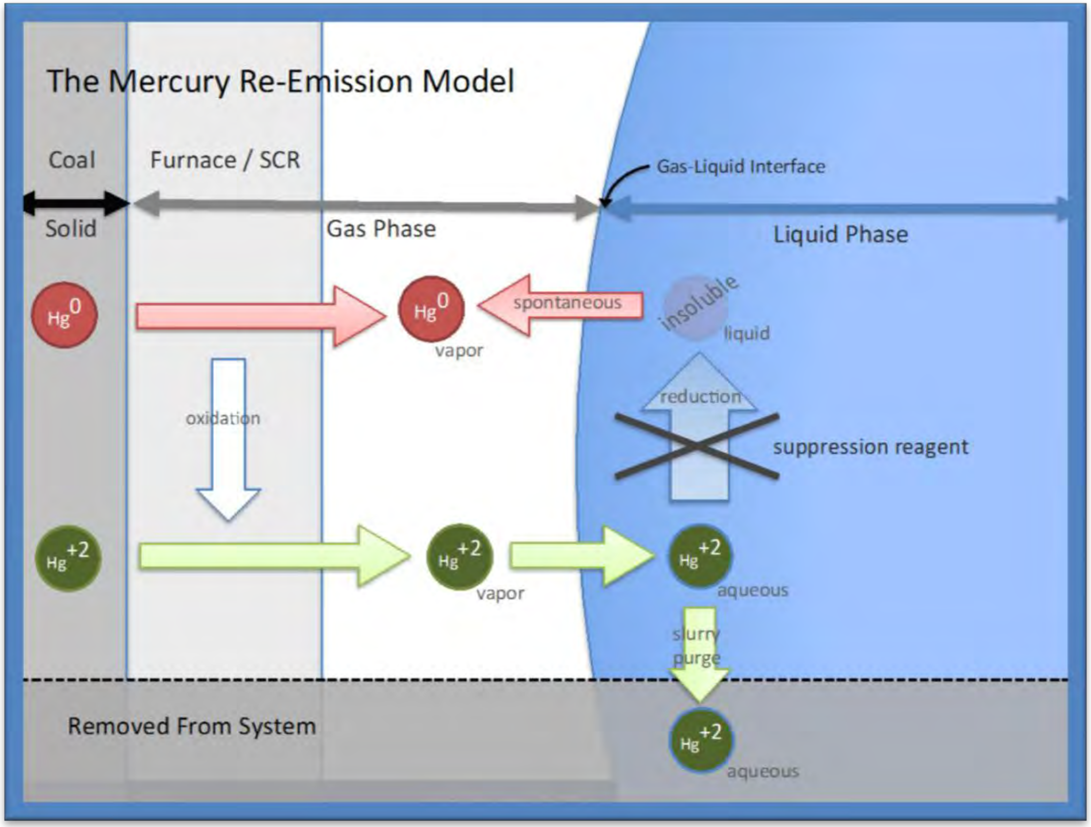


The WFGD Mercury Re-Emission Model



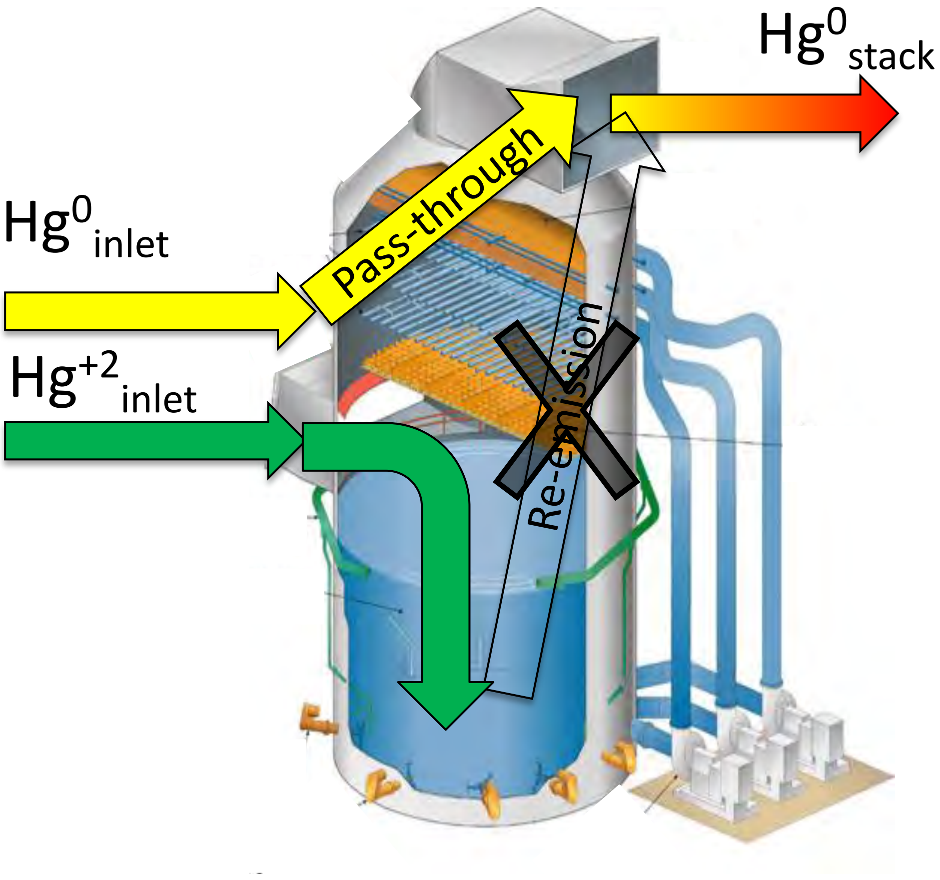
The Mercury Re-Emission Model for a Wet FGD

- Hg^0, Hg^{2+}, and Hg^p are components of combustion gas.
- Some Hg^0 is oxidized to Hg^{2+} in furnace / SCR.
- Hg^{2+} and Hg^p are readily captured in FGD scrubber liquid or particulate control device.
- Hg^{2+} and Hg^p → Hg^0 and then re-emits.
- Hg^0 is insoluble in water.



Mercury Re-emission Suppression -- Chemistry Adjustments

The general understanding has been that "blocking" the chemical pathway of re-emission will lead to a reduction or elimination of the excess mercury emissions in the stack.



WFGD Hg Re-emission – Suggested Causes

"Sulfite causes re-emission"

"Sulfite inhibits re-emission"

"Transition metals cause re-emission"

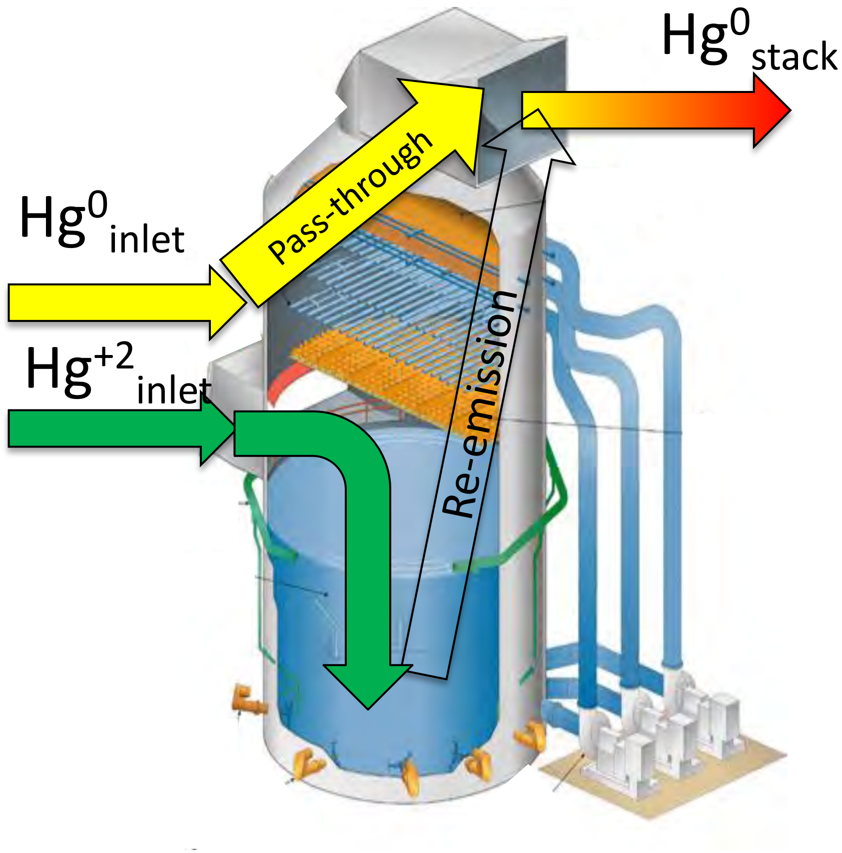
"ORP changes cause re-emission"

"pH can affect re-emission"

"S(IV) reduces Hg^{2+}"

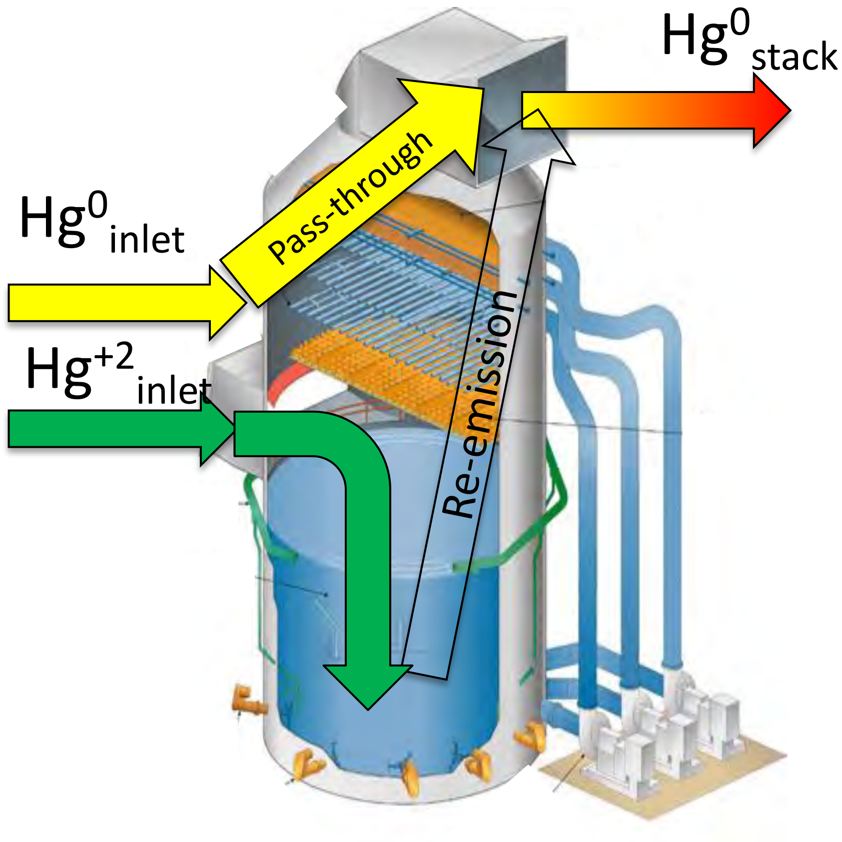
For 20+ years the focus has been suppression through chemistry.

Is it finally time to focus on absorption?

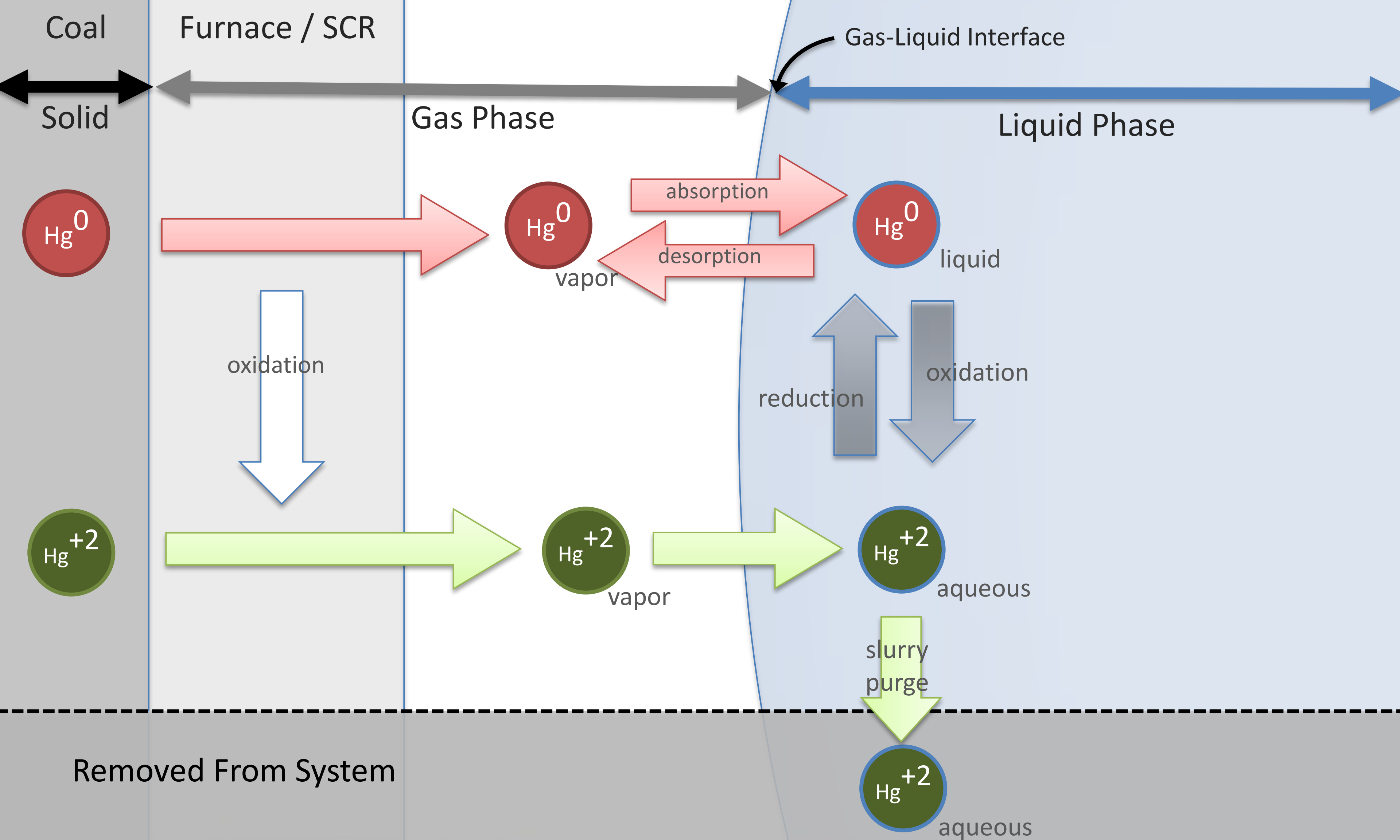


WFGD Hg Re-emission – Our Position

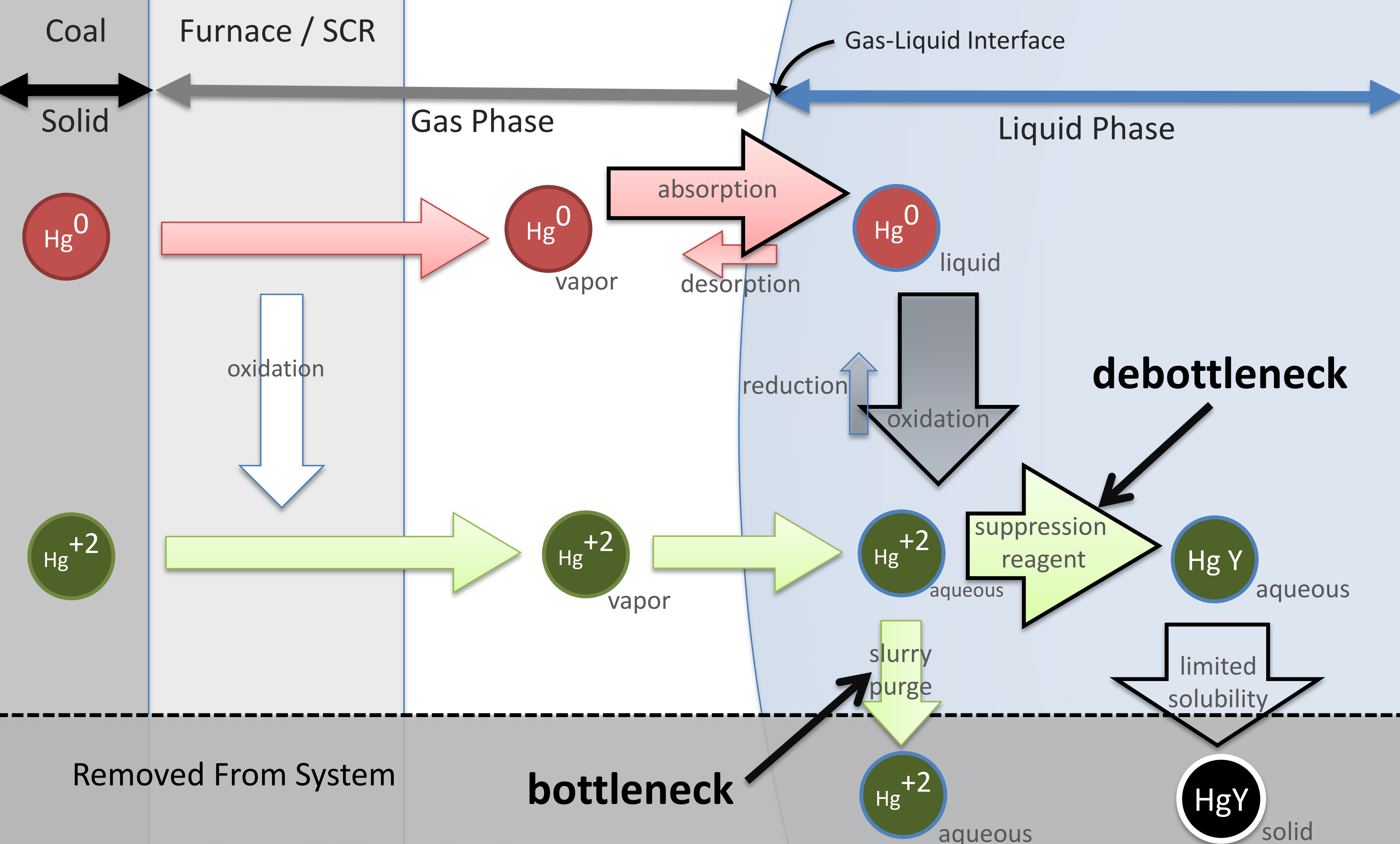
WFGD Hg re-emission is caused by the stripping or desorption of elemental Hg from the liquid phase due to saturation. Sub-saturate the liquid phase, and re-emission is eliminated.



The Mercury Absorption Model



The Mercury Absorption Model



Cost Effective Control via Hg Absorption

Encourage discussion based on Chem. Eng. principles

Hg re-emission is an effect, not a cause

In the context of MATS compliance, this solubility is significant, and therefore relevant

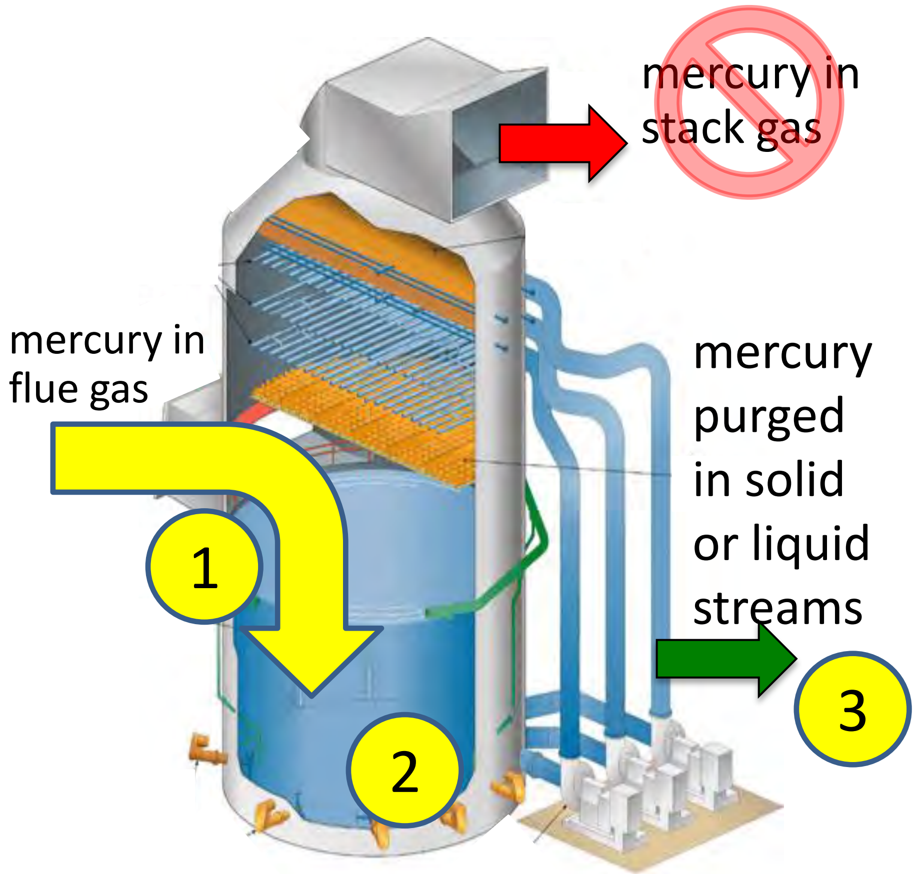
Hg re-emission is caused by the stripping or desorption of aqueous Hg from a saturated slurry or solution

Focusing on the Hg mass balance sheds light on the Hg inventory

ACI and sulfide additives work via Hg sub-saturation

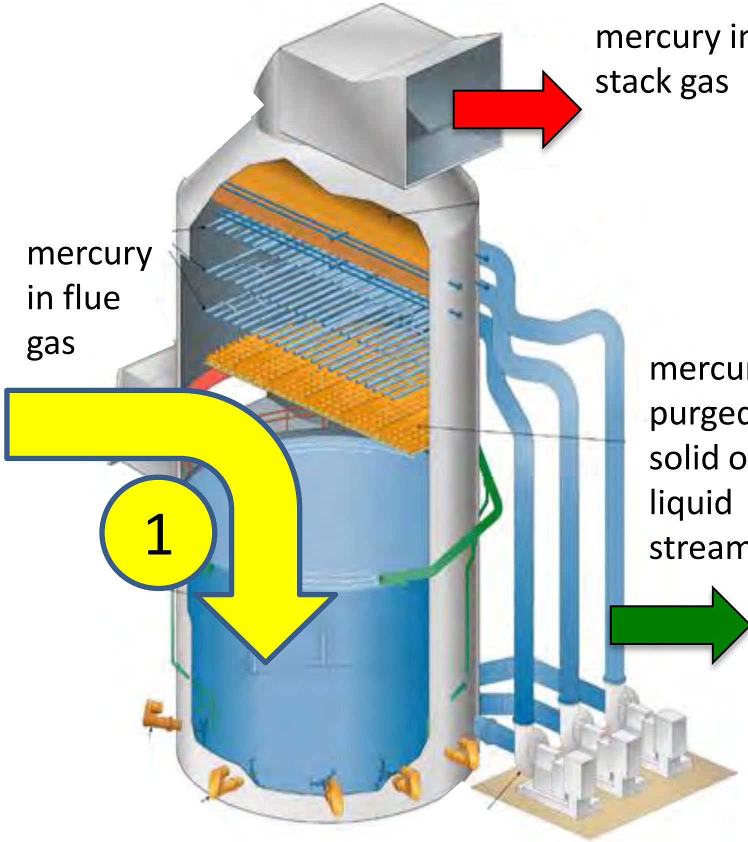
Cost-Effective Mercury Removal -- Through the Lens of Absorption…A 3-step process

1. Mass transfer of mercury from gas to liquid
2. Elemental mercury sub-saturation of the circulating liquid
3. Addressing water treatment requirements of FGD liquid.



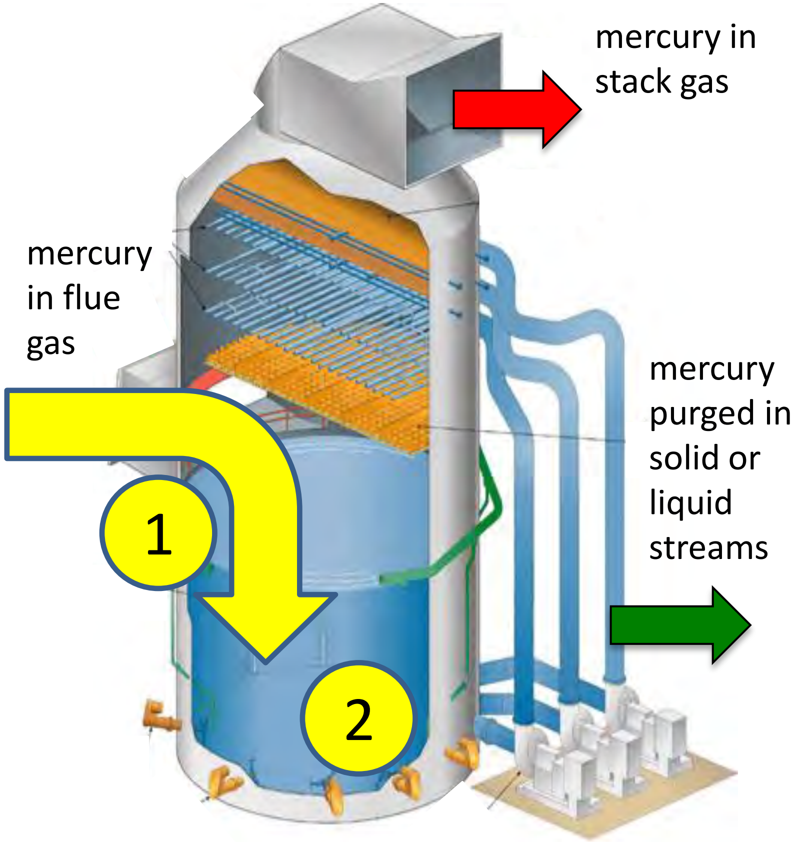
Step 1 Mass Transfer of Mercury From Gas to Liquid

- **Mass transfer is affected by mercury speciation due to differing solubilities of the various mercury species.**
- **Oxidized mercury (as $HgCl_2$, $HgBr_2$ or HgO) is very soluble in aqueous phase of scrubber slurry.**
- **Increased oxidation of mercury is achieved through**
  - **DeNOx SCR catalytic oxidation**
  - **halogen addition to coal**



Step 2 Sub-saturation of the Liquid via Mercury Removal

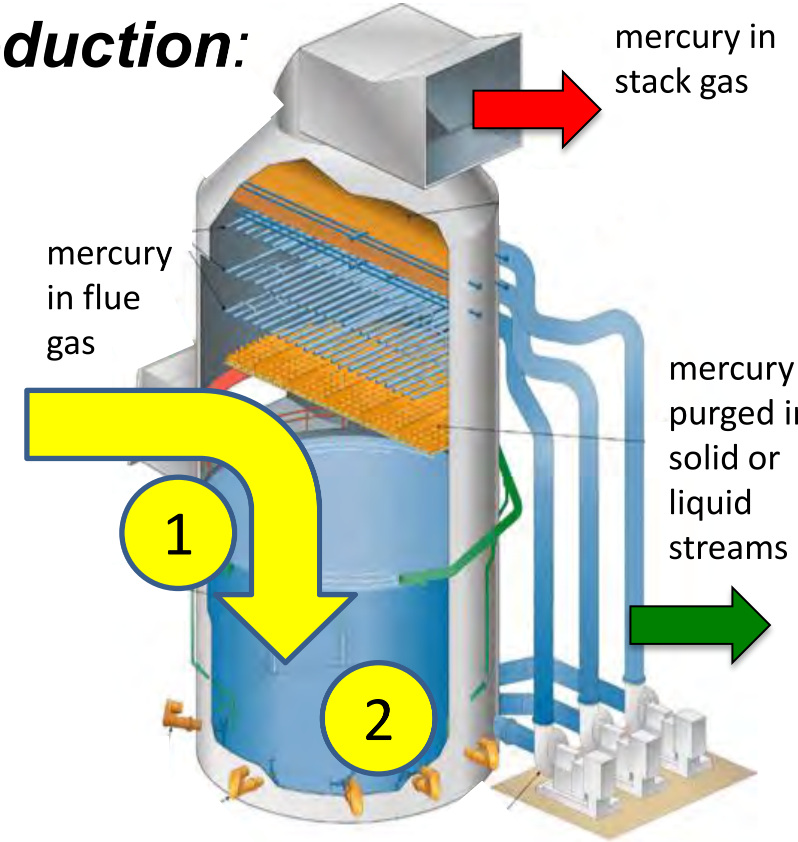
- **Due to its low solubility, elemental mercury saturates in slurry liquid before oxidized mercury compounds.**
- **Due to its high vapor pressure, elemental mercury accounts for nearly all mercury in the stack.**



Step 2 Sub-saturation of the Liquid by Mercury Removal

Strategy for mercury emission reduction:

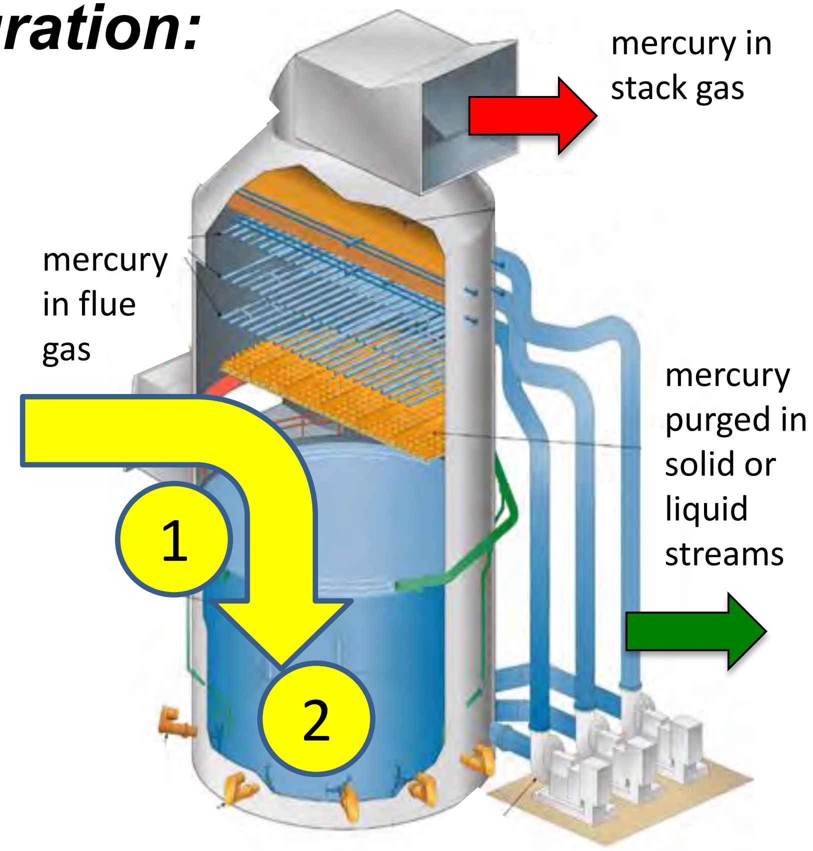
- **Reduce concentration of oxidized mercury in the slurry liquid.**
- **Below a threshold concentration of oxidized mercury, elemental mercury becomes sub-saturated due to redox chemistry of the system (by Le Chatelier's principle).**



Step (2) Sub-saturation of the liquid by mercury removal

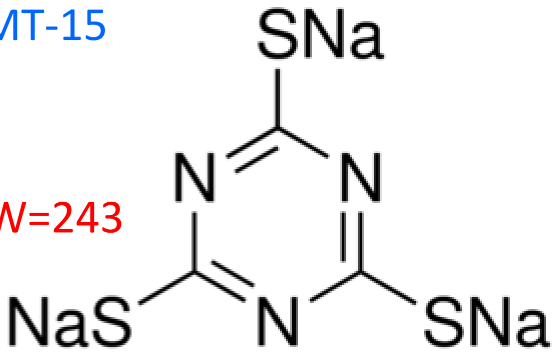
Technologies for mercury sub-saturation:

- precipitation with organic sulfides
- carbon adsorption in scrubber slurry
- precipitation with inorganic sulfides



Sulfide Precipitating Agents

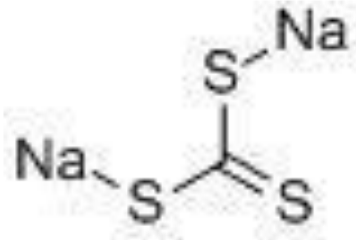
TMT-15



MW=243

1,3,5-Triazine-2,4,6-trithiol trisodium salt, or
2,4,6 – Trimercapto-s-triazine trisodium salt

534-18-9



MW=154

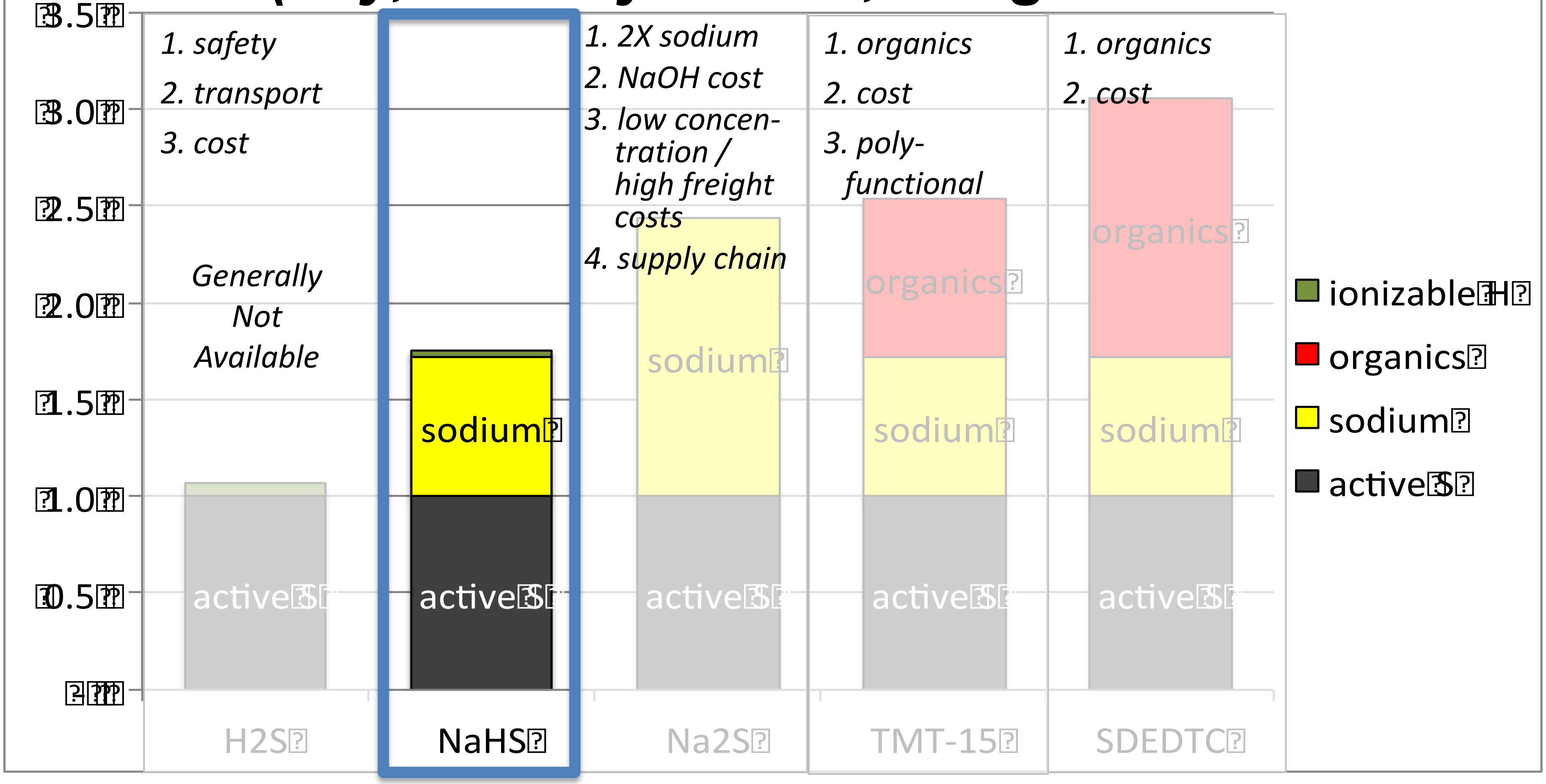
Sodium trithiocarbonate

Absorption Plus

MW=56 HS-Na

Sodium hydrosulfide

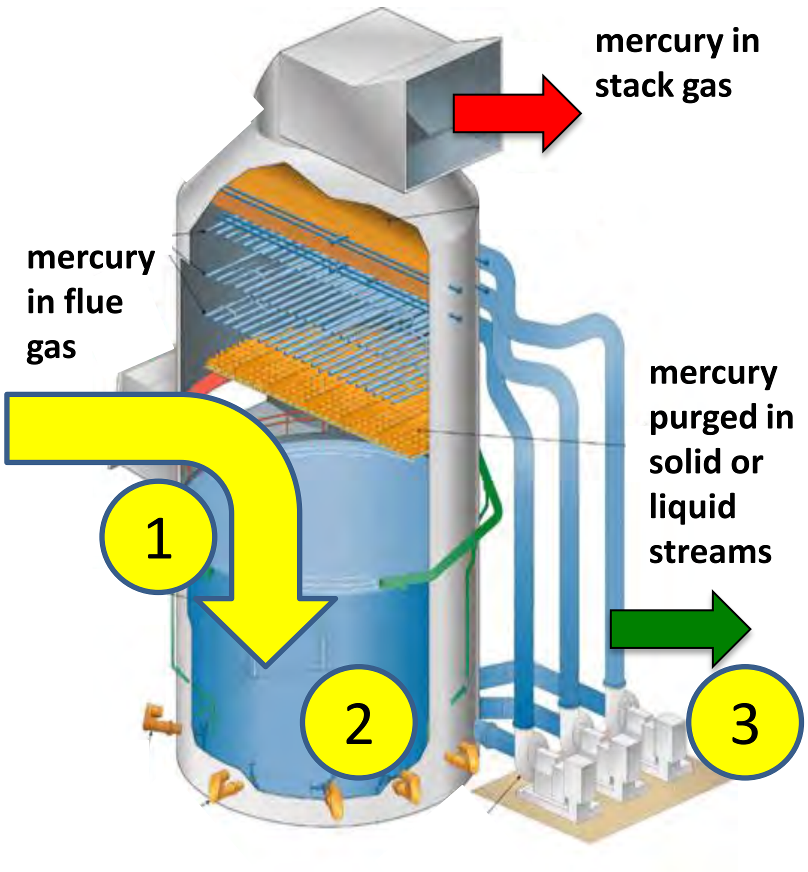
Relative Compositions Of Mercury Precipitants (Dry, Non-Hydrated , Weight Basis



To compare efficacy of reagents, refer to "Study of elemental mercury re-emission in a simulated wet scrubber", Fuel 91 (2012) 93-101 (Elsevier)

Step (3) Addressing Water Treatment Requirements of FGD purge liquid

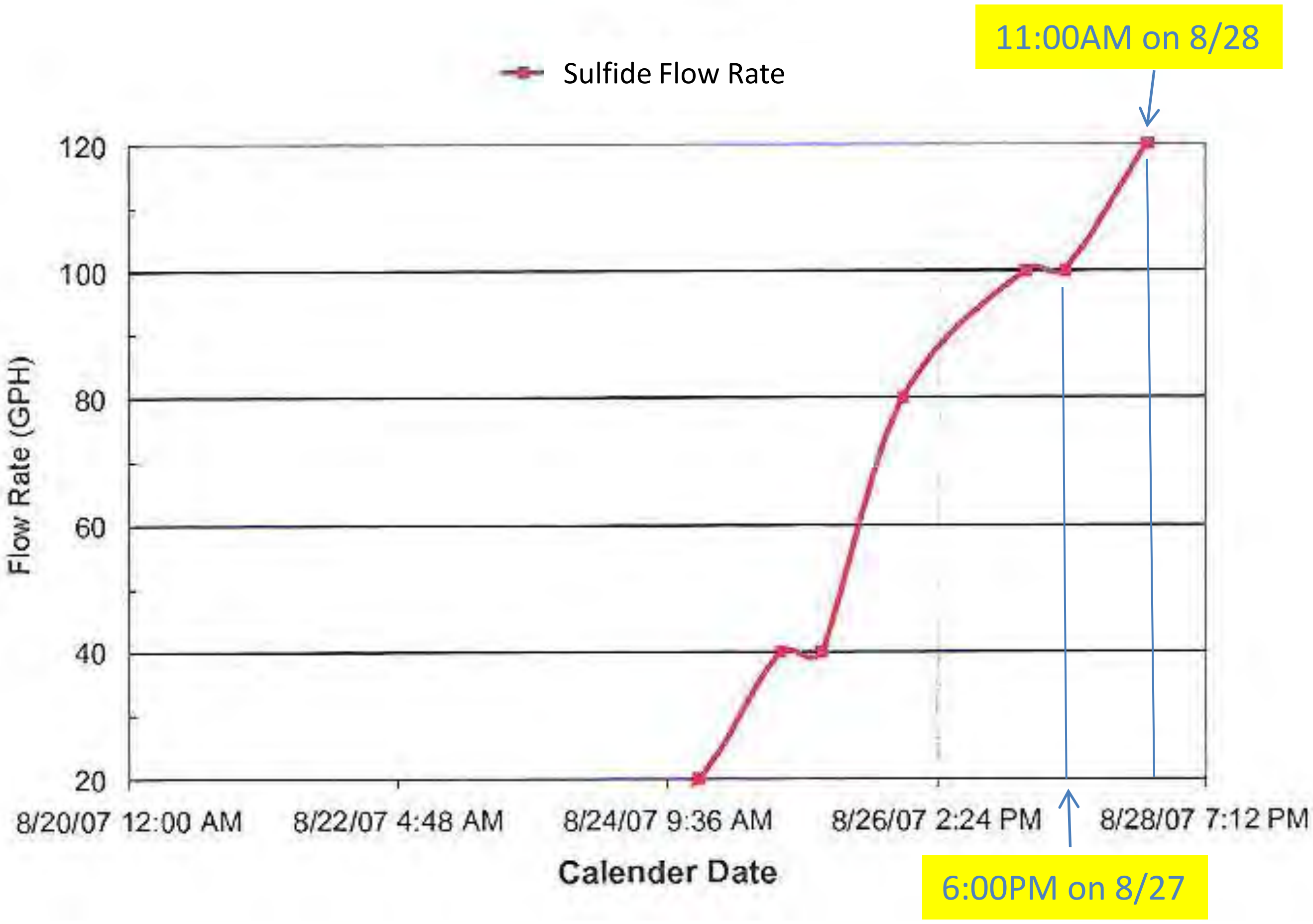
- Water treatment options are often identified by vendors. Limitations in vendor perspectives can result in overlooking generic options.
- Owner/operators need comprehensive options for simultaneously meeting all water criteria compatible with options selected for steps (1) and (2) above.
- Recent InorgS sulfide-based field tests suggest possible co-benefits for As(III) and Se(VI).



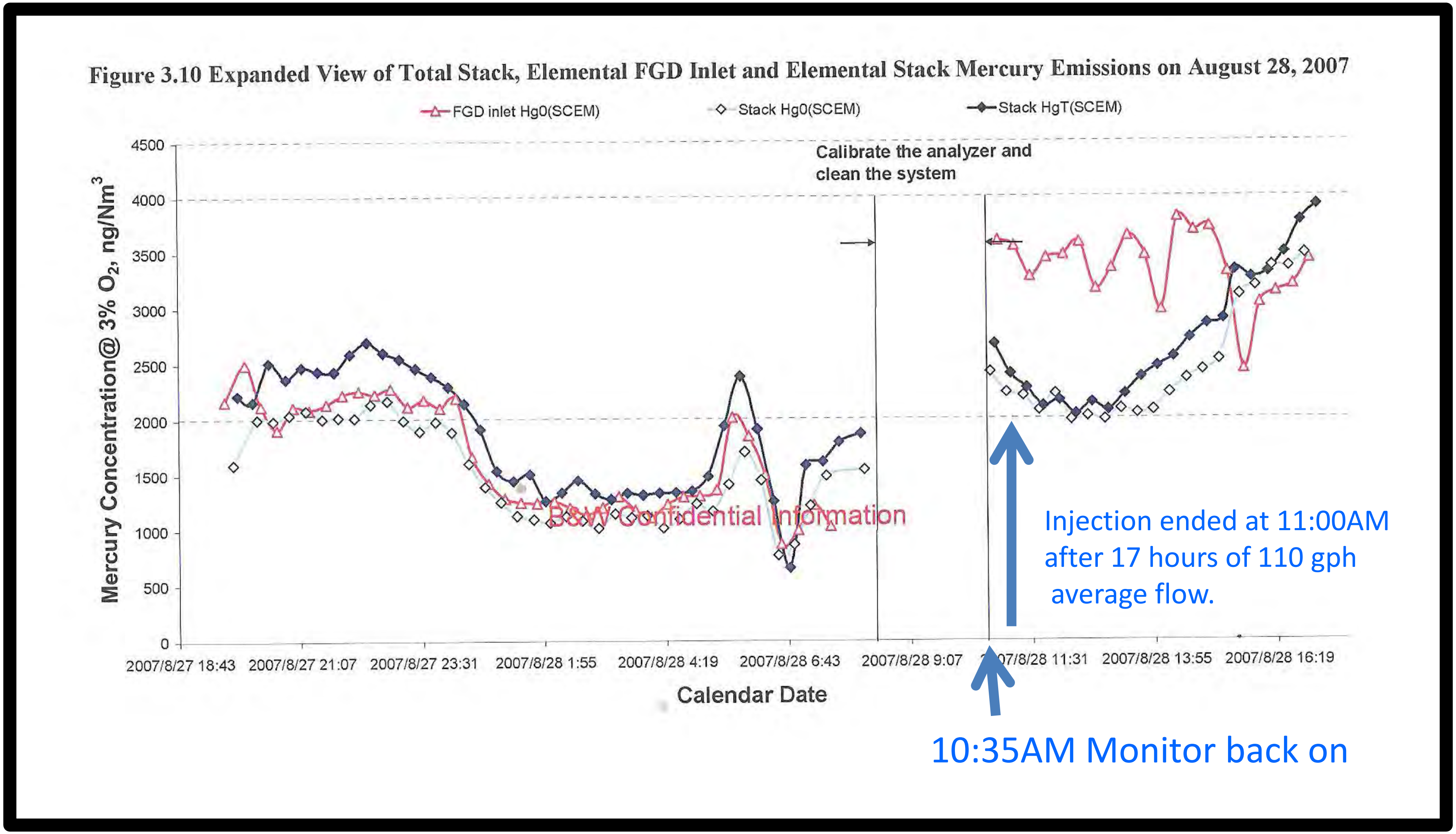
Hiking through old Trials

Re-visiting Prior Testing

MSCPA – 2007 Testing by Western Kentucky Univ.

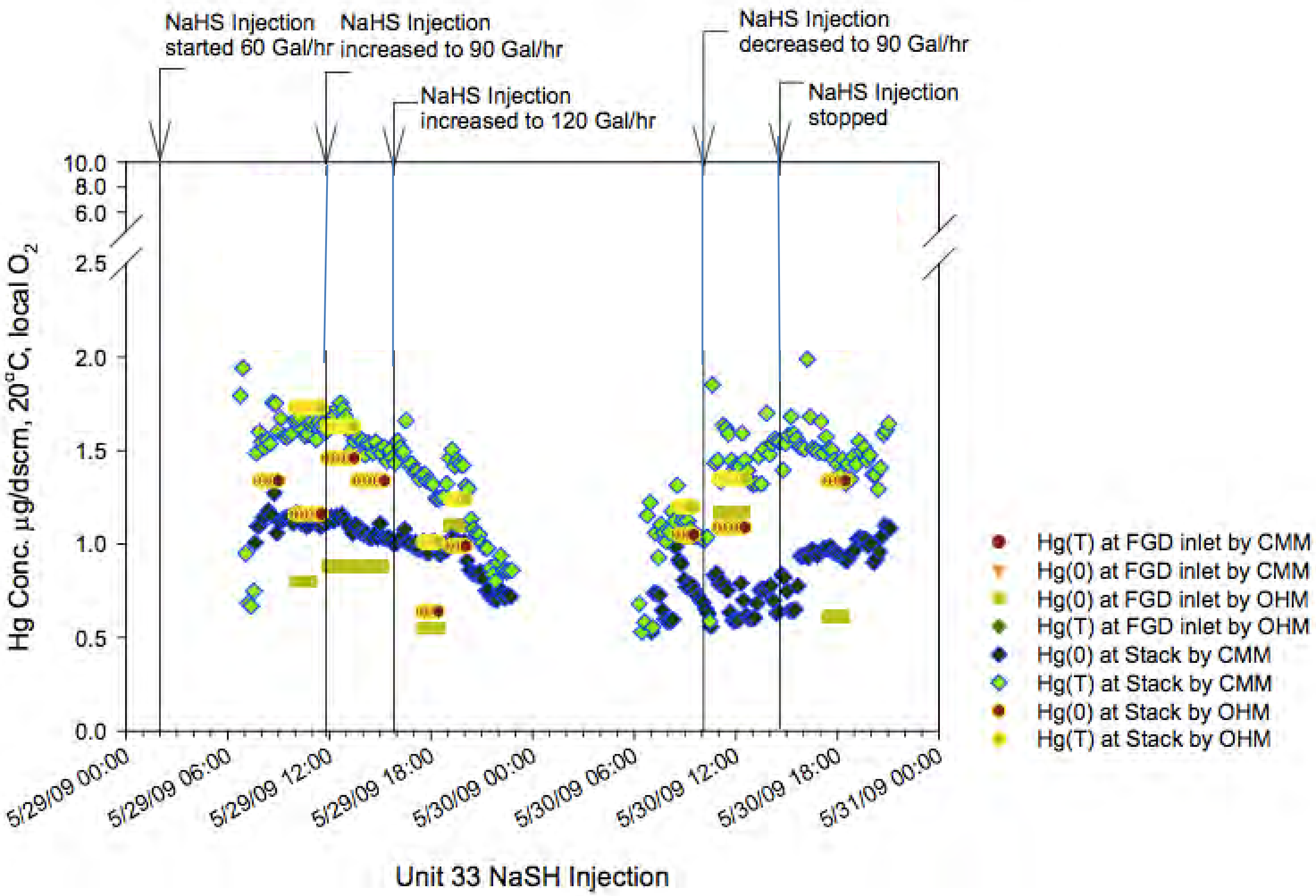


Re-visiting Prior Testing



Re-visiting Prior Testing

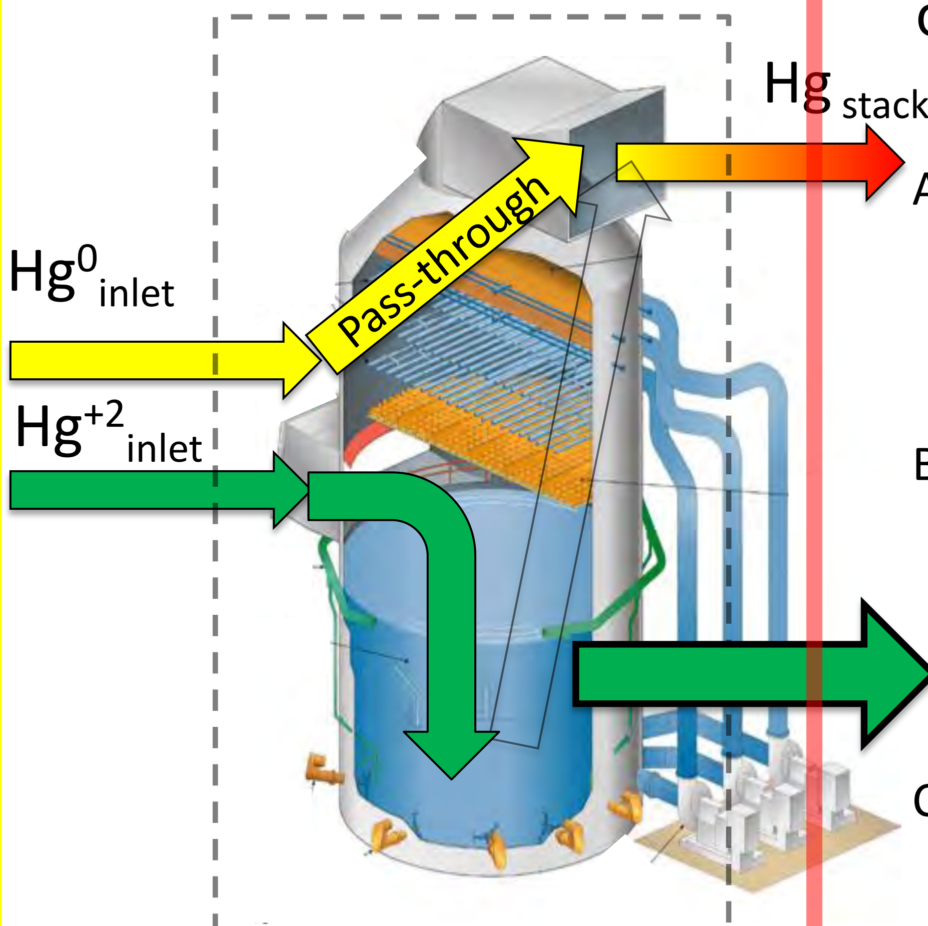
2009 Testing by Western Kentucky University at CWLP – Dallman #33 (~200MW)



Why Does Hg Absorption Matter?

How to Meet the MATS Requirement on Your Wet FGD?

1. **Manage the Hg^0 flow rate at FGD inlet**
   - A. SCR catalyst
   - B. SCR operating conditions
   - C. halogen technologies
   - D. activated carbon injection
   - E. UBC as a sorbent
   - F. other sorbents
   - G. fuel composition or blend

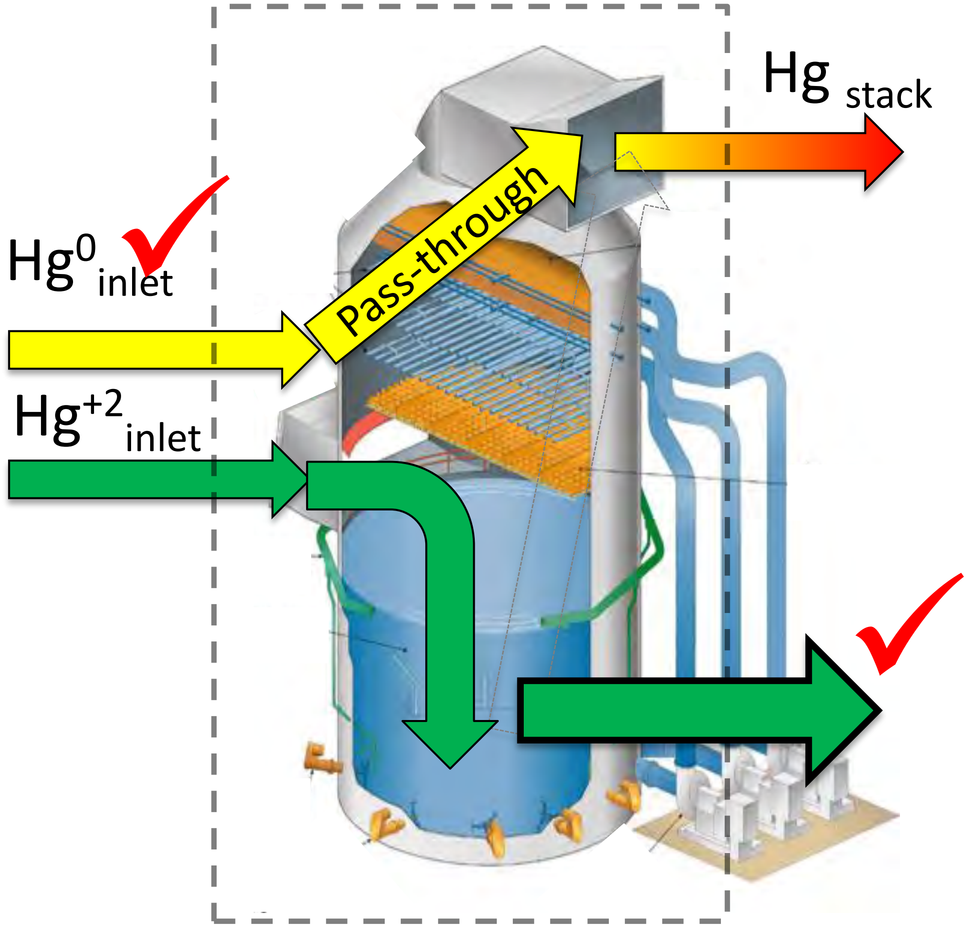


2. "Unplug the drain" for Hg^{+2}
   - A. shift equilibrium of Hg^{+2}/Hg^0 in the slurry liquid
   - B. chemical reactants (sulfides or sulfide-like compounds)
   - C. sorbents

Example 1. Wet FGD, Limestone, Forced Oxidation, Greater Than 95% Oxidized Hg at Inlet

- **Step #1, getting the inlet Hg^0 below the MATS target for stack Hg^{total} is already achieved.**

- **Step #2, sulfide addition, should drop the stack Hg^{total} down to match the inlet Hg^0 thereby achieving MATS compliance.**

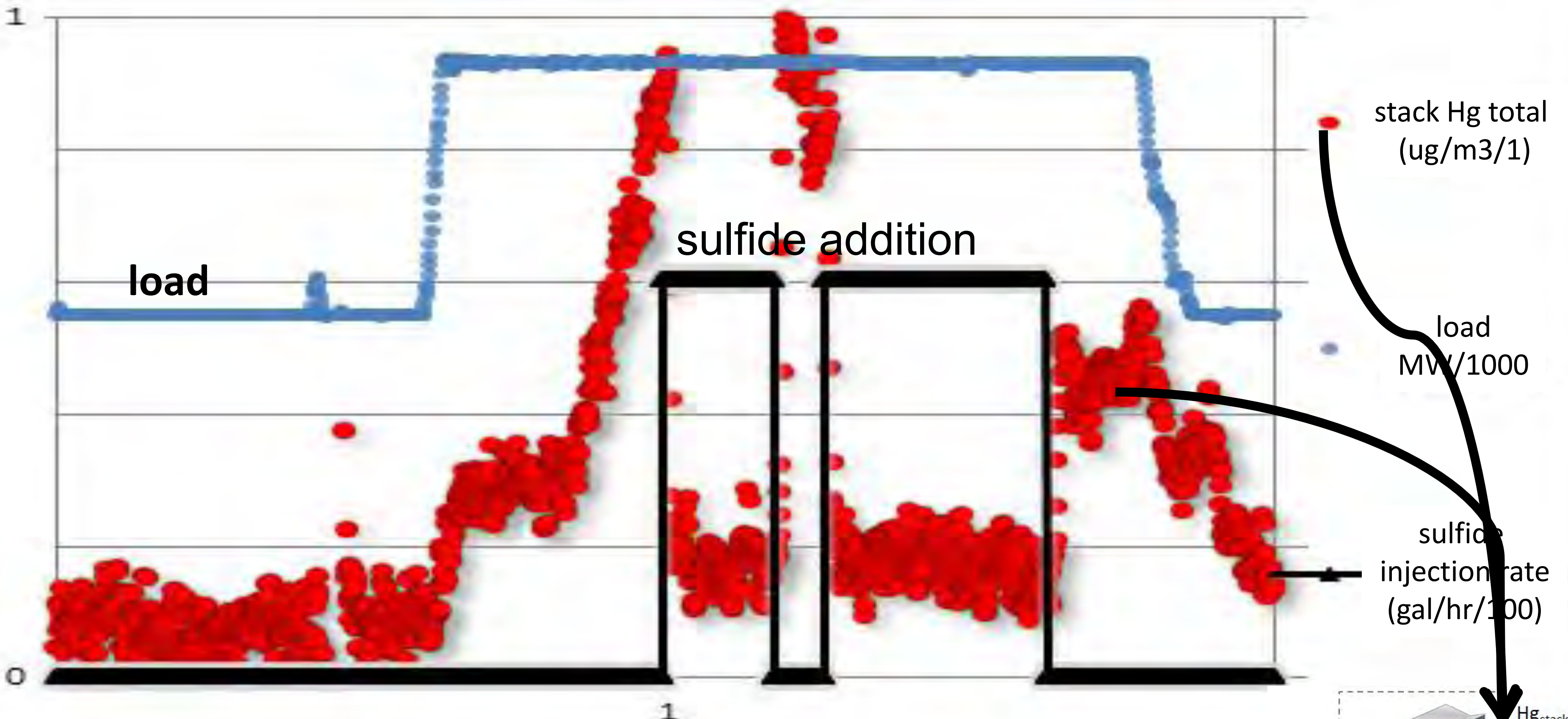


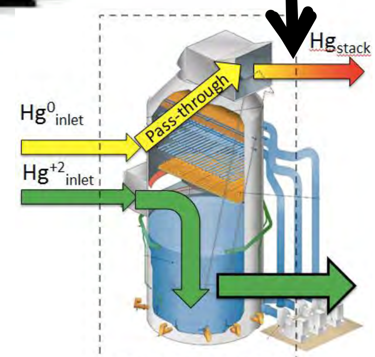
limestone, forced oxidation, SCR, high degree (95+%) Hg oxidation

Example 1.

☑ **Step 1: Hg^0 at Inlet < MATS target (complete)**

☐ **Step 2: Directly effect stack $Hg^{(total)}$ with sulfide (tested below)**





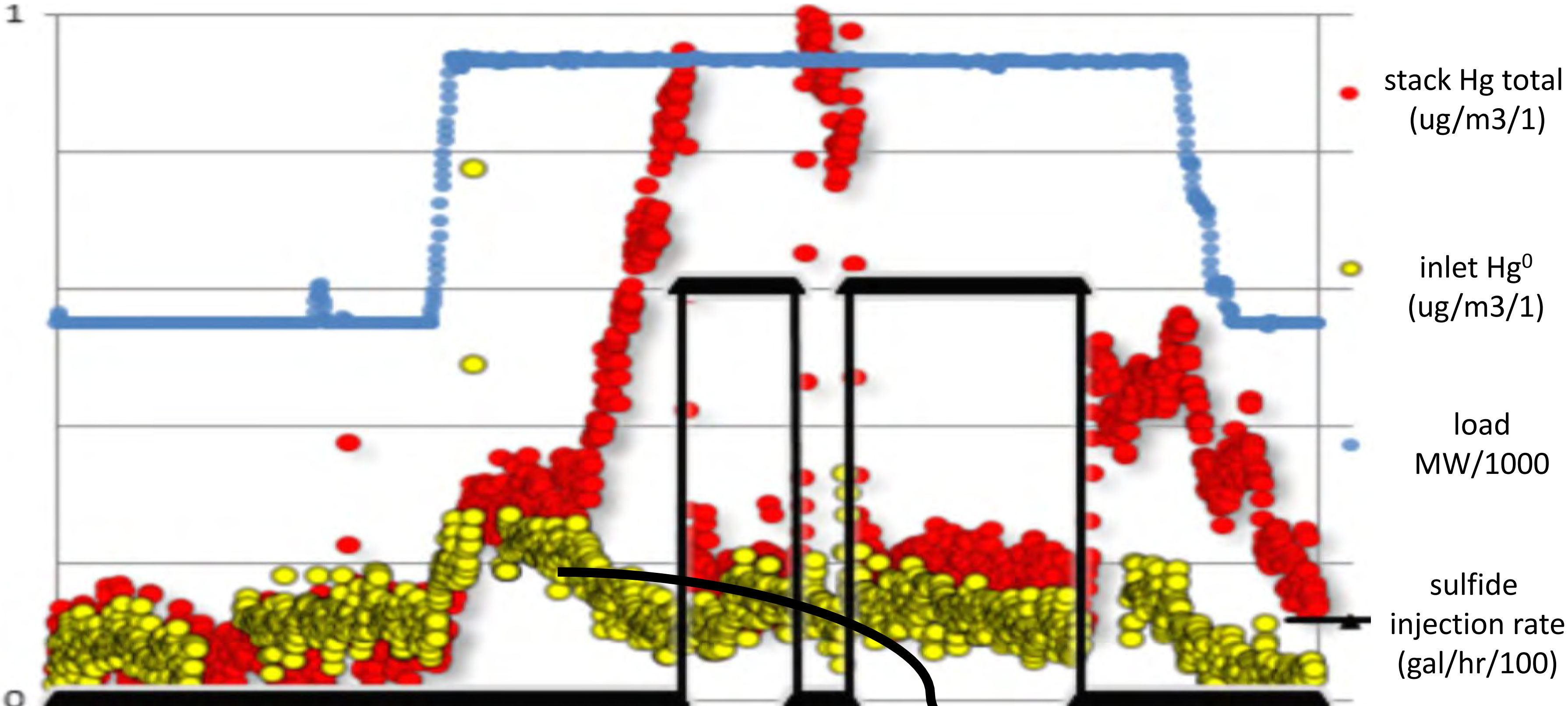
Red points on graph match red arrow on diagram – total stack Hg.

limestone, forced oxidation, SCR, high degree (95+%) Hg oxidation

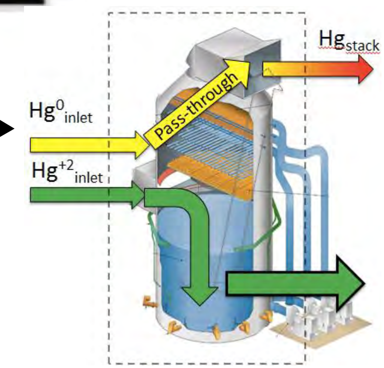
Example 1.

☑ ***Step 1: Hg^0 at Inlet < MATS target*** ***(complete)***

☑ ***Step 2: Directly effect stack $Hg^{(total)}$ with sulfide*** ***(tested below)***



One can see what is happening by overlaying the scrubber inlet Hg^0 data in yellow.

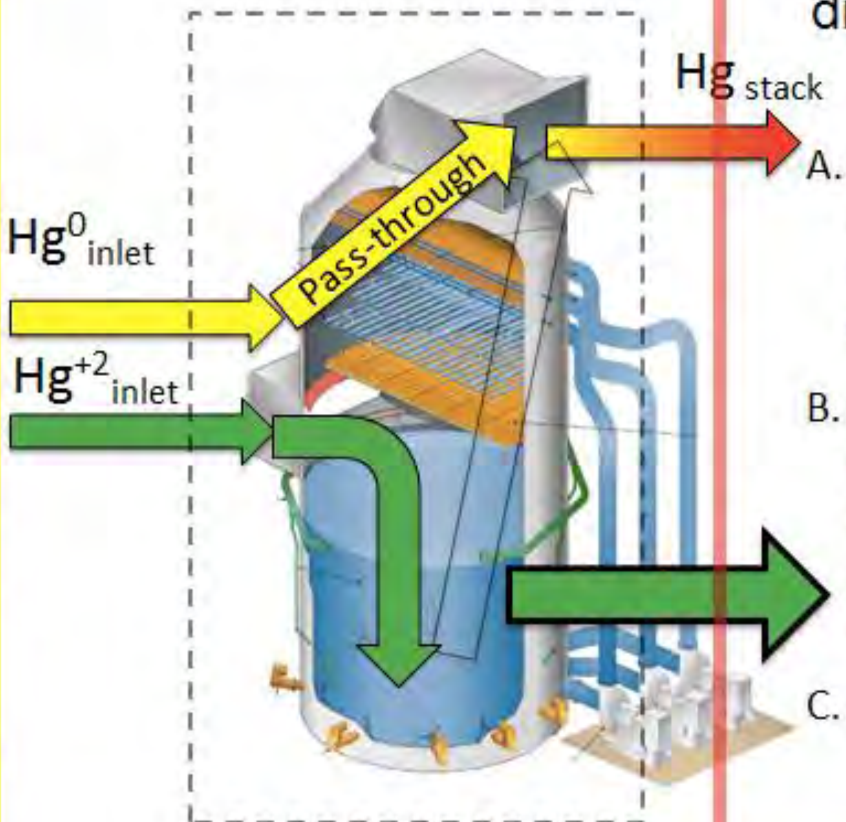


A simple way to look at this is...

Sulfide addition pulls the stack Hg^{total} (in red) down to the inlet Hg^0 (in yellow).

Example 1: Limestone, SCR, forced oxidation
Why is this case successful?

1. Manage the Hg^0 flow rate at FGD inlet
   - ✓ A. SCR catalyst
   - ✓ B. SCR operating conditions
   - C. halogen technologies
   - D. activated carbon injection
   - E. UBC as a sorbent
   - F. other sorbents
   - ✓ G. fuel composition or blend



2. "Unplug the drain" for Hg^{+2}
   - A. shift ✓ equilibrium of Hg^{+2}/Hg^0 in the slurry liquid
   - B. chemical ✓ as needed reactants (sulfides or sulfide-like compounds)
   - C. sorbents

Example 2: Wet PS/FGD, mag-lime, inhibited oxidation, SCR, High Sulfur East. Fuel

1. Manage the Hg^0 flow rate at FGD inlet
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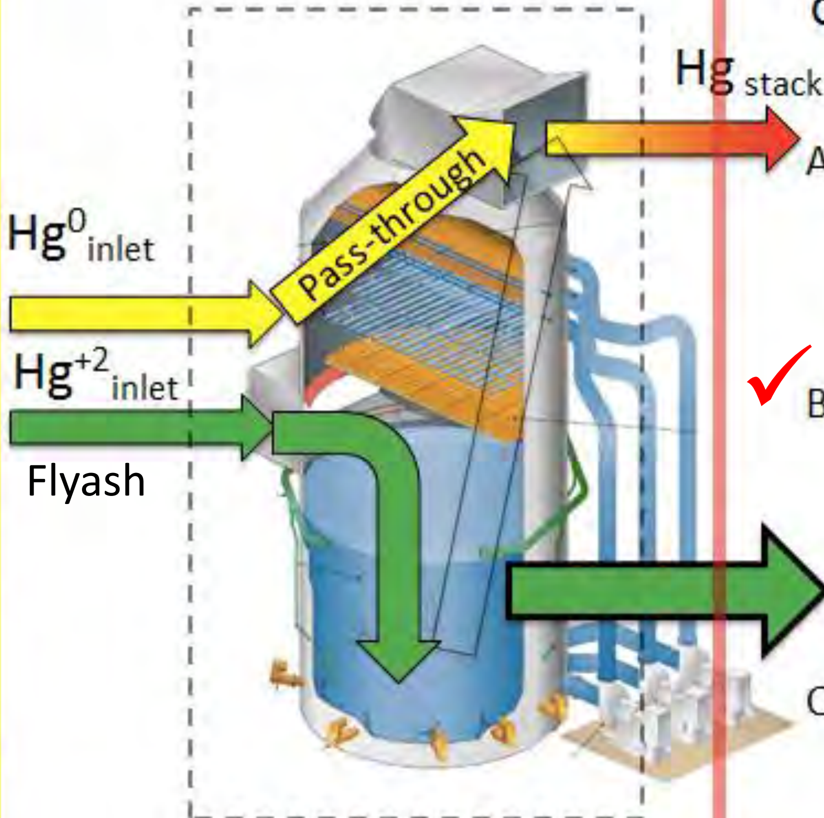

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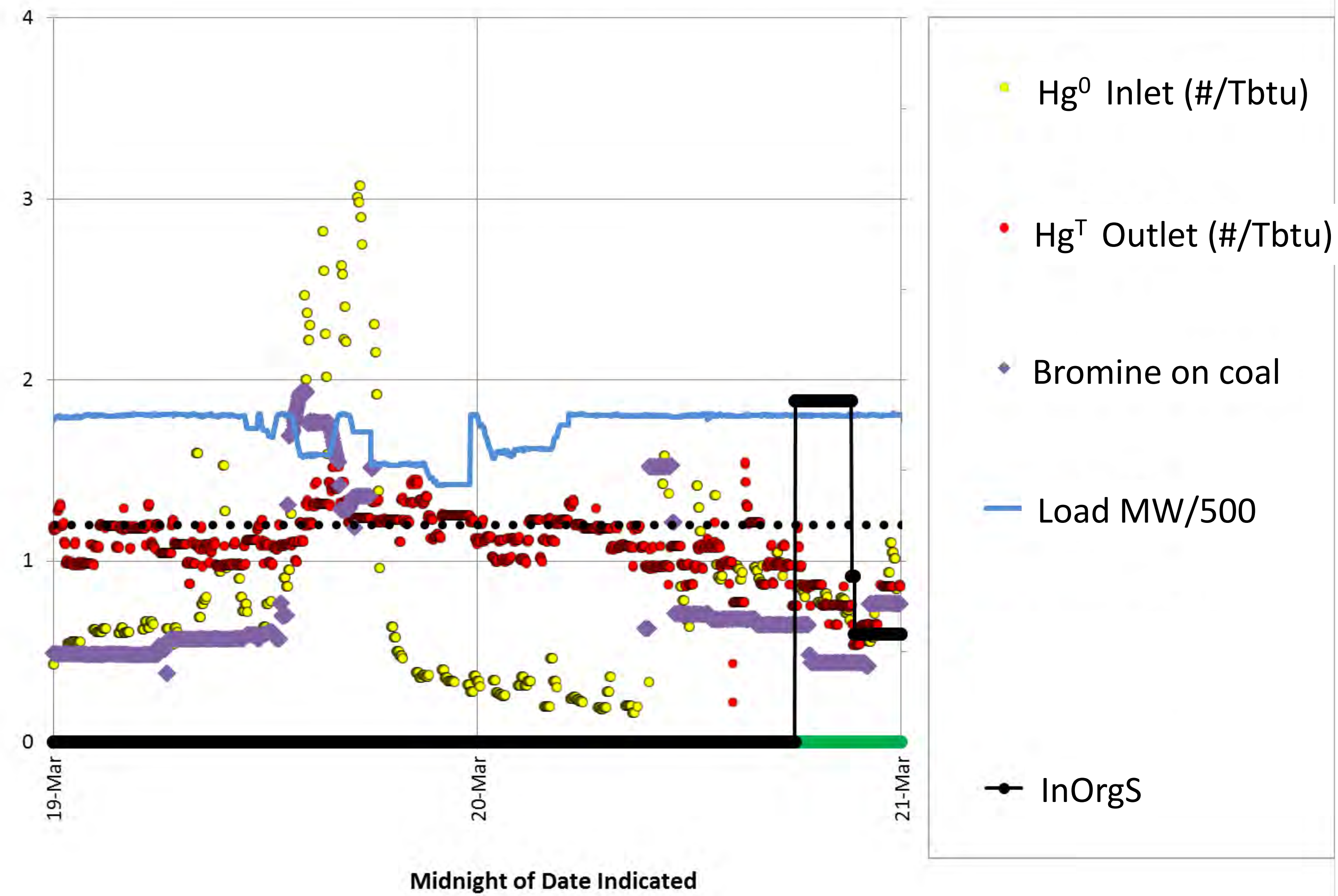
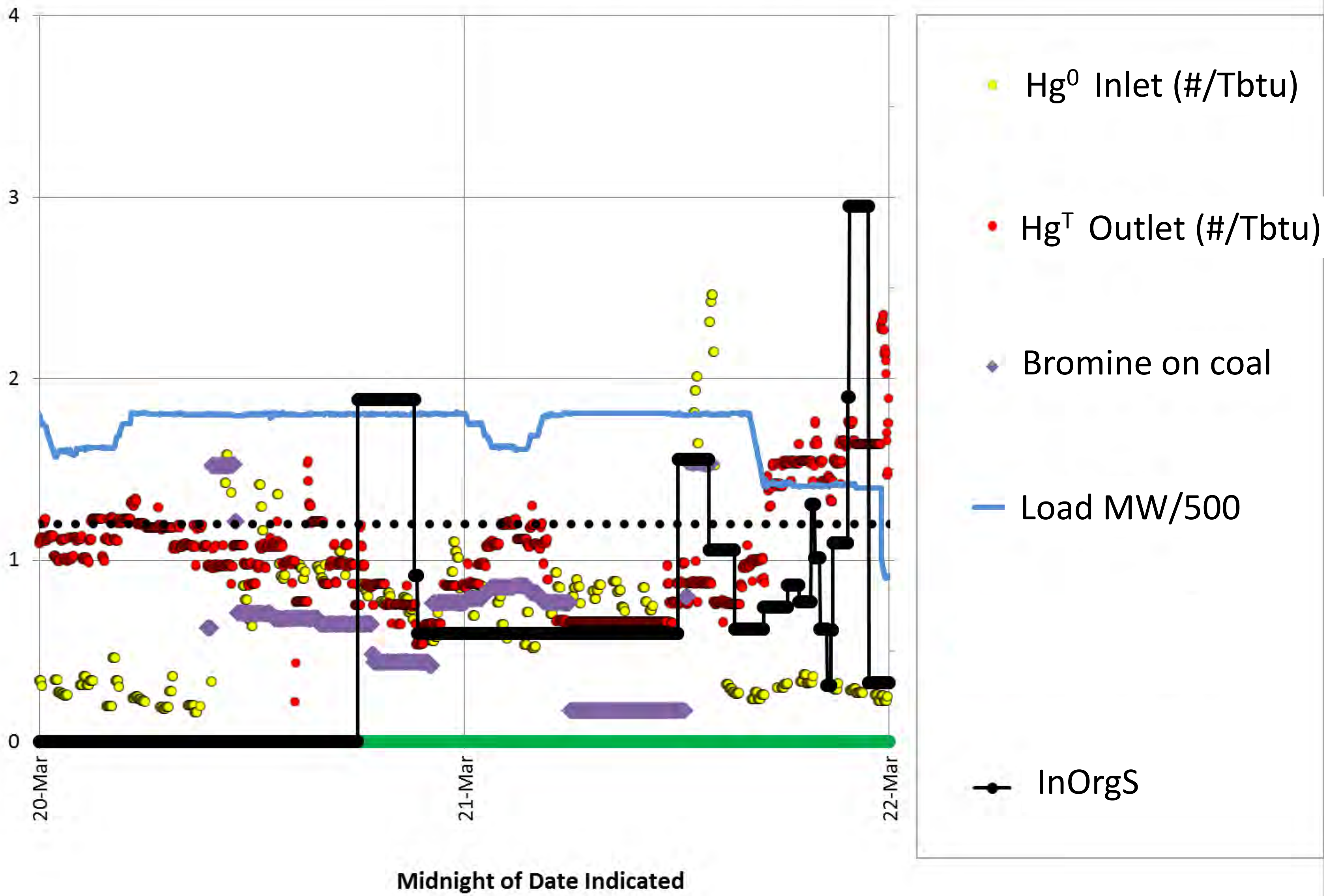


Example 2. **Wet PS/FGD, mag-lime, inhibited oxidation, SCR, High Sulfur East. Fuel**



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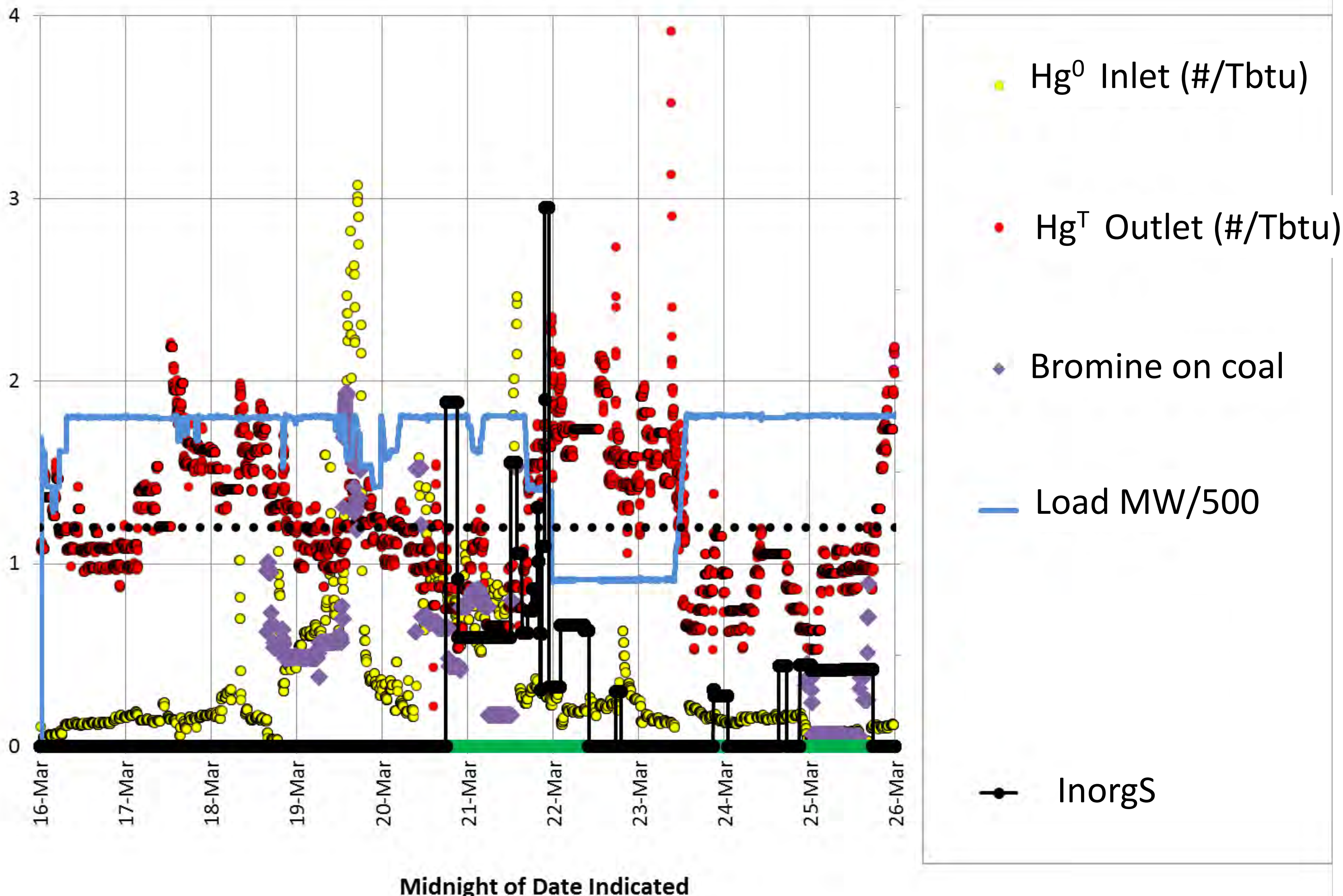

The Lens of Hg Absorption - SUMMARY

Solubility, saturation, mass balance

Hg WFGD Absorption – View as a three-step process

- **1 – Mass Transfer of Hg from gas to liquid.**
- **2 – Hg^0 sub-saturation of the liquid**
- **3 – Treatment of HgS solids in Absorber blowdown stream**

Change the re-emission narrative – Absorption

Through the lens of Hg absorption, you can properly analyze your WFGD system to meet the Hg MATS limit.