REINHOLD ENVIRONMENTAL Ltd.

2013 APC Round Table & Expo Presentation

July 8-9, 2013, in St. Louis, MO / Hosted by Ameren

 

Mercury and Selenium

Rich Marsan
July 8th, 2013

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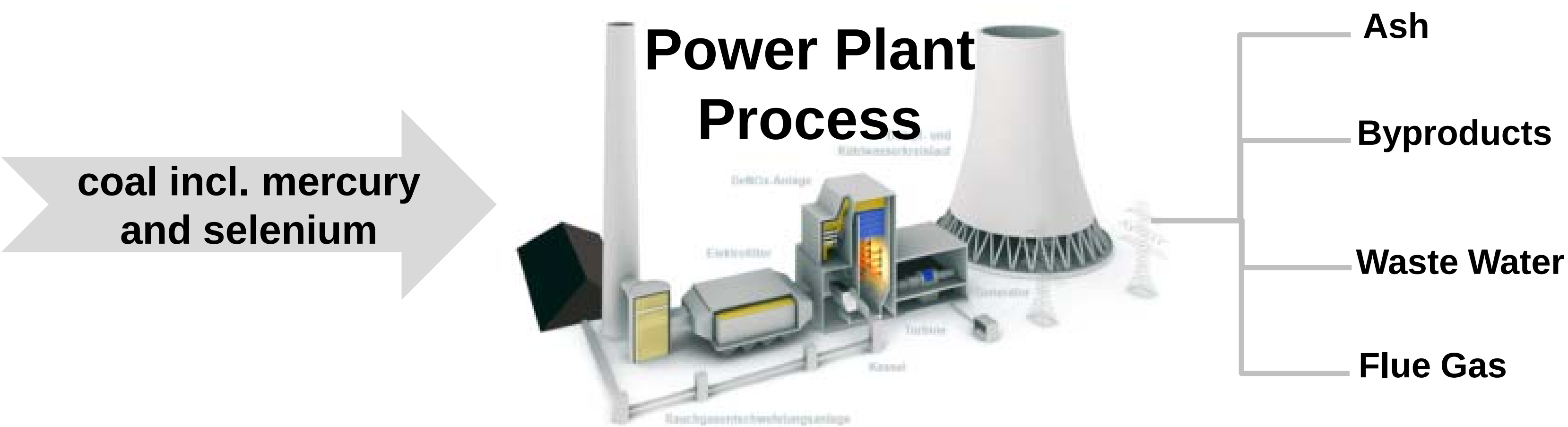
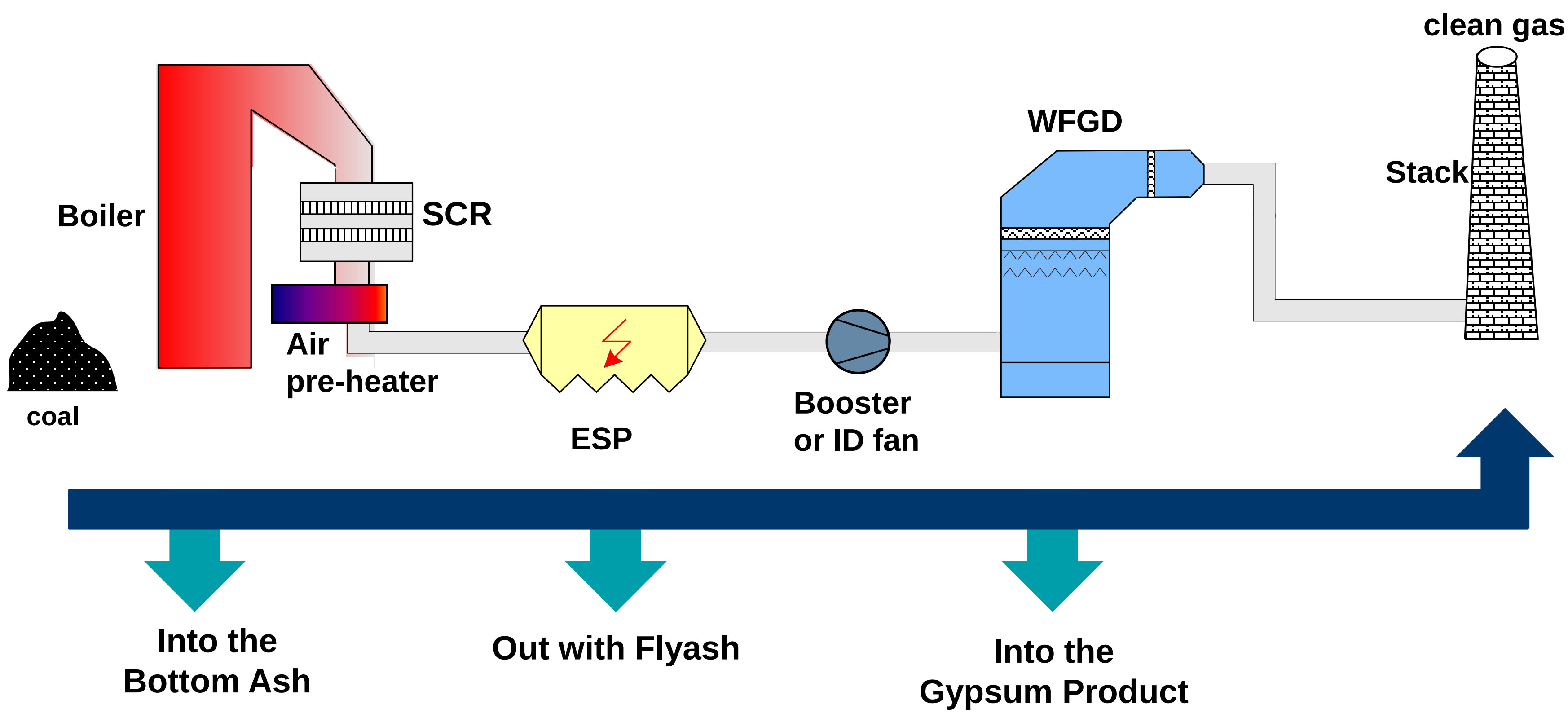
The Path of Mercury and Selenium

This diagram shows, that the ways to influence the mercury and selenium concentration are limited.

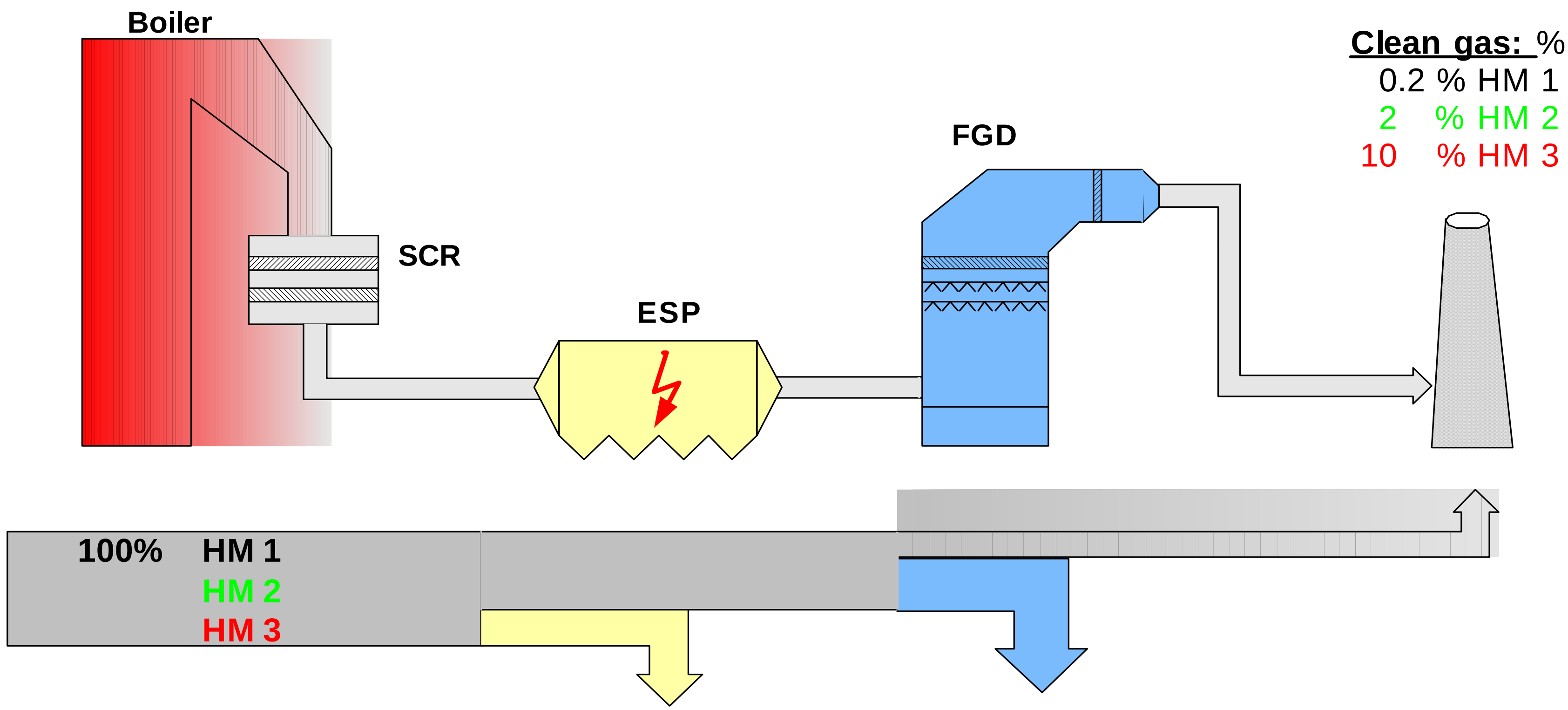


Mercury and Selenium can either be prevented from entering the process or has to be removed from the process via ash, waste water, flue gas or byproducts (e.g. gypsum).
If byproducts are sold the amount of mercury and selenium in them is limited. Regulation limits the amount of mercury and selenium discharged via flue gas and waste water.

What is the fate of the Mercury and Selenium?



“Typical” Mass Balance



Ash:
97 % HM 1
68 % HM 2
5 % HM 3

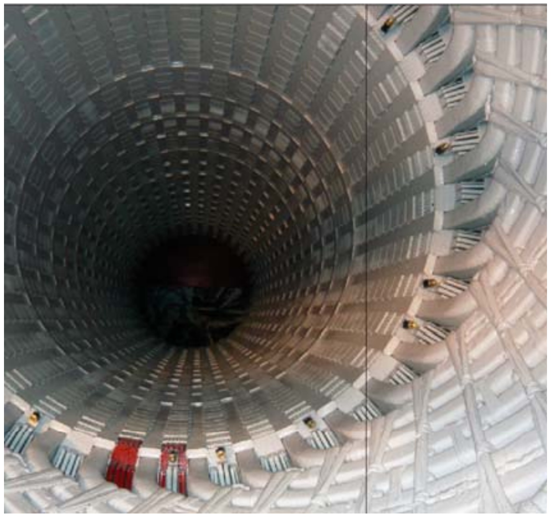
Gypsum slurry:
2.7 % HM 1
30 % HM 2
85 % HM 3

HM 1 = As, Ag, Ba, Be, B, Cd, etc.
HM 2 = Se
HM 3 = Hg

Mercury Regulations

•Mercury and Air Toxics Standards (MATS)

- EPA finalized the Mercury and Air Toxics Standards (MATS) rule in December 2011, covering mercury and hazardous air pollutants (HAPs) like selenium, arsenic and others
- Existing coal- and natural gas-fired plants face a compliance date of April 2015, with a 'broadly available' one-year extension
- First time mercury has been regulated at a national level for power plants, although ~16 states were already phasing in limits roughly similar to MATS



	Filterable PM[a]	HCl[b]	SO_2[c]	Mercury
Existing units (higher grade coals)	$3*10^{-2}$ lb/MMBtu (~45 mg/Nm^3)	$2*10^{-3}$ lb/MMBtu (~3 mg/Nm^3)	0.20 lb/MMBtu (~300 mg/Nm^3)	1.2 lb/TBtu (~1.8 ug/Nm^3)
Existing units (lignite)	$3*10^{-2}$ lb/MMBtu (~45 mg/Nm^3)	$2*10^{-3}$ lb/MMBtu (~3 mg/Nm^3)	0.20 lb/MMBtu (~300 mg/Nm^3)	4.0 lb/TBtu (6 mg/Nm^3)

[a]Surrogate for non-mercury HAP metals
[b]Surrogate for acid gas HAP
[c]Surrogate for acid gas HAP for plants operating FGDs

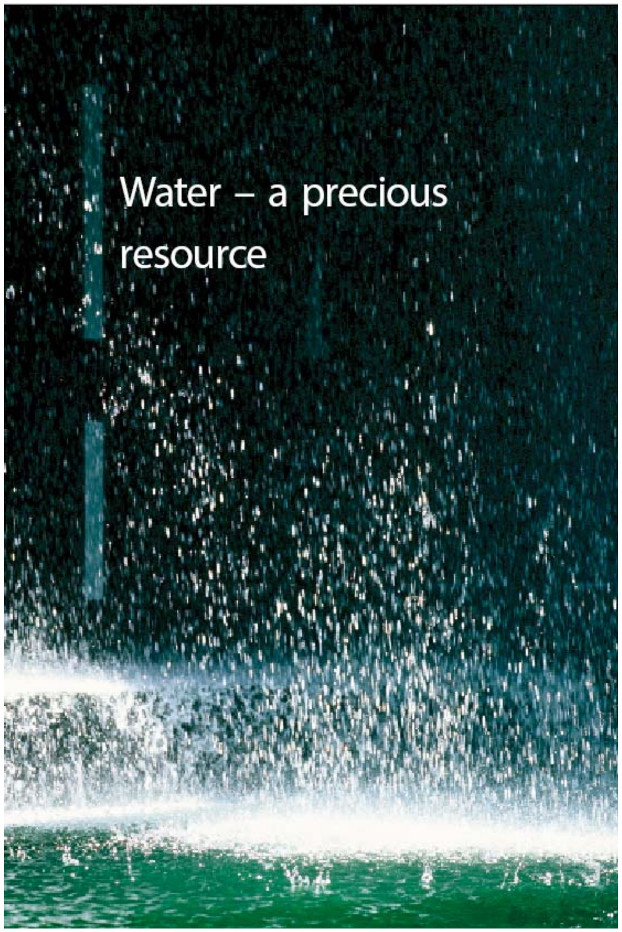
Water Regulations

•The Clean Water Act

- Passed in 1972 on a wave of environmentalism
- Technology-based law
  - Performance standards defined by Best Available Control Technology (BAT), Best Practicable Control Technology Currently Available (BPT), Best Conventional Pollutant Control Technology (BPT), etc.
- Operates on a permit system, National Pollutant Discharge Elimination System (NPDES)
  - Delegated to states in most cases

•Effluent Limitation Guidelines

- Set for individual industries
- Electric steam generating facility ELG was last updated in 1982
- Administered through NPDES permits



Water Regulations

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•Effluent Limitation Guidelines

- New standard proposed April 19th, 2013 with four ‘preferred options’
- ELGs have not kept up with new environmental equipment (FGDs, SCRs, mercury control devices)
- As the air has gotten cleaner, pollutants have been diverted to liquid waste
- EPA is most concerned with mercury and selenium

Treatment Technology	Pollutant	Daily Limintation	Monthly Limination
Chemical Precipitation and Biological Treatment for FGD	Mercury	242 ng/L	119 ng/L
	Selenium	16 µg/L	10 µg /L
Chemical Precipitation and Evaporation for FGD	Mercury	39 ng/L	24 ng/L
	Selenium	5 µg/L	[Detection limit]

Water Regulations

•Safe Drinking Water Act

- Passed in 1974
- Requires EPA to set limits on contaminants in drinking water
- Uses both Maximum Contaminant Levels (MCLs), which are legally enforceable, and Maximum Contaminant Level Goals (MCLGs), which are optional health goals

Mercury

- MCL and MCLG are equal, set to 0.002 milligrams per liter (2 ppb)

Selenium

- MCL and MCLG are equal, set to 0.05 milligrams per liter (50 ppb)

Combustion Process Relevant Reactions

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Formation of Mercury Oxide in the Furnace

$$2\,Hg + O_2 \rightleftharpoons 2\,HgO$$

Formation of Elemental Chlorine in the Furnace

$$4\,HCl + O_2 \rightleftharpoons 2\,H_2O + 2\,Cl_2$$

Oxidation of Mercury

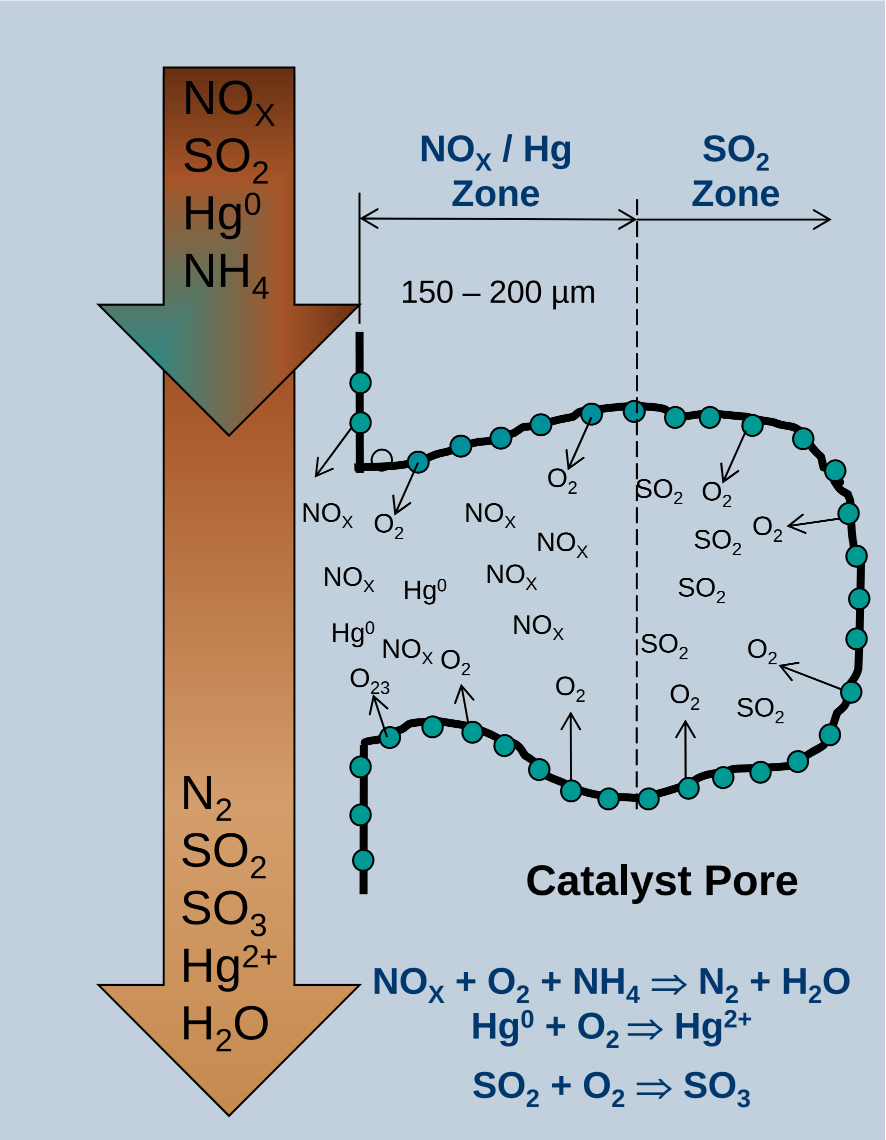
$$Hg + Cl_2 \rightleftharpoons HgCl_2$$

Selenium: No relevant chemical reactions are seen during combustion

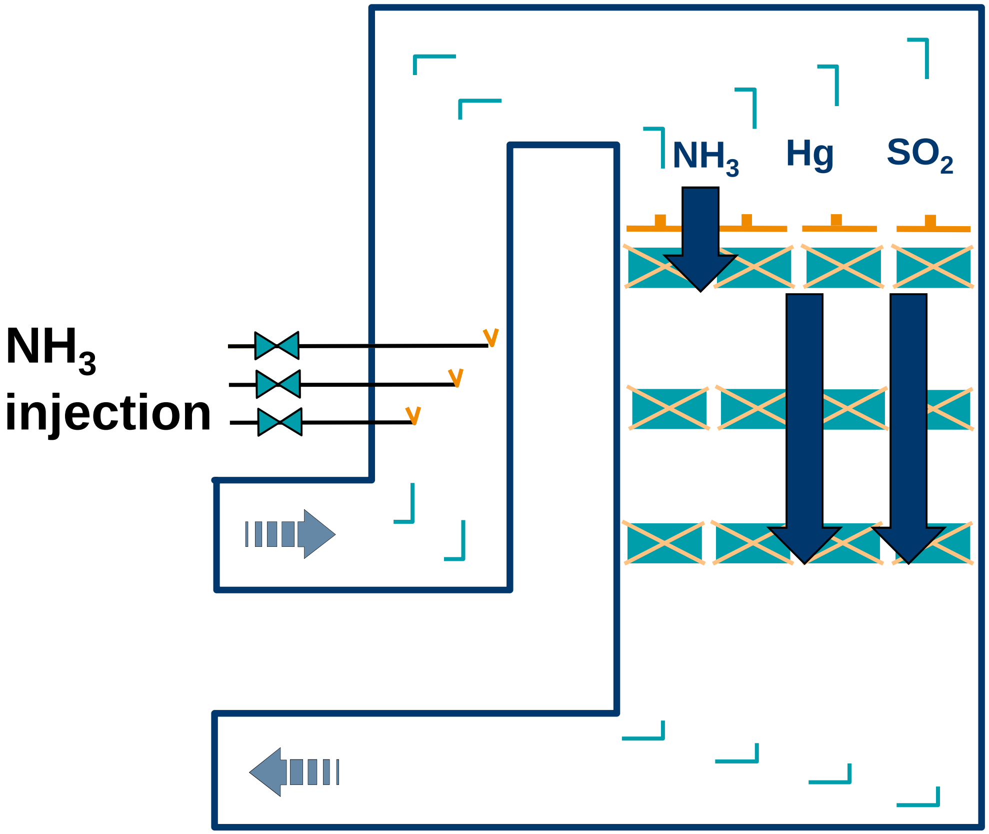
➡ **These reactions are important for the oxidation of elemental mercury in the furnace and boiler, which influences the generation of Cl_2 and subsequent formation of ionic mercury.**

The SCR Oxidation Reaction

- **The Vanadium Pentoxide (V_2O_5) releases oxygen (O_2)**
- **The fluegas stream contains the following constiuents; Nitrous Oxide (NO or NO_2), Sulfur Dioxide (SO_2) and Mercury (Hg) which compete for the oxygen**
- **The preference for the oxygen is;**
  - **1st – Nitrogen,**
  - **2nd – Sulfur Dioxide**
  - **3rd – Mercury**
- **The presence of Ammonia (for the NOx reaction) inhibits the Mercury reaction**



SCR Catalyst Arrangement
New Layer of catalyst on Top Layer



- **Results:**
  - Ammonia is consumed in the SCR top layer
  - Lower 2 elevations will produce oxygen for Mercury Oxidation (also SO_2 to SO_3 conversion rate)

High levels of Mercury Oxidation should occur with an active SCR!

SCR Catalyst Arrangement
Depleted Catalyst Reactor

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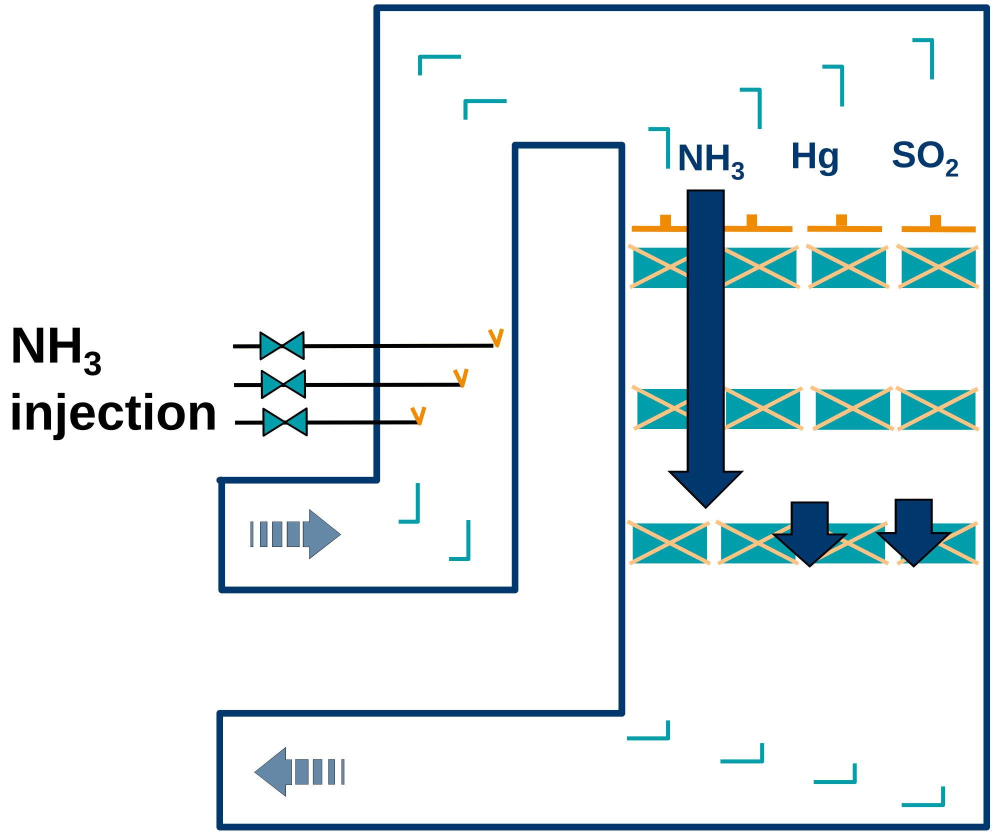
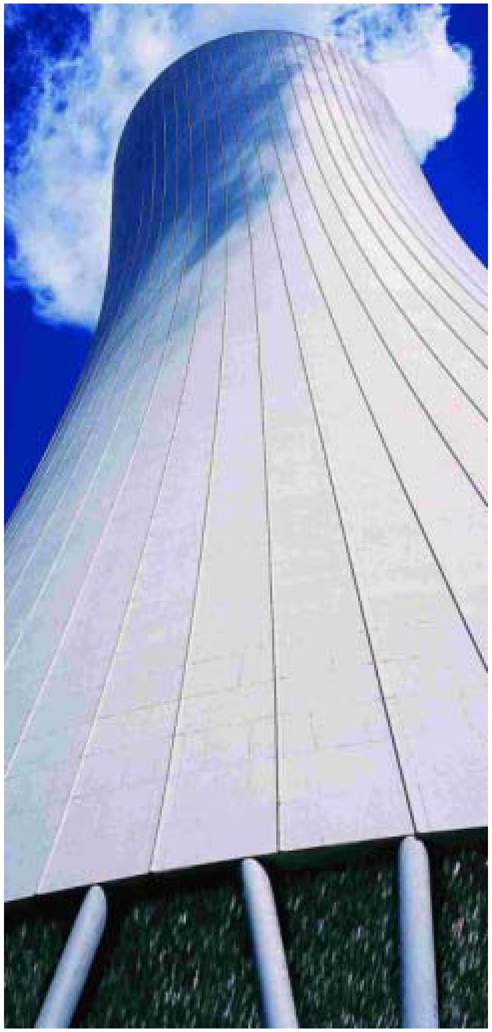
- **Results:**
  - Ammonia consumption for NOx removal takes most of the catalyst surface
  - Lower levels are the only effective surface areas for Mercury Oxidation (also SO_2 to SO_3 formation conversion rate)

Low levels of Mercury Oxidation should occur with this arrangement!



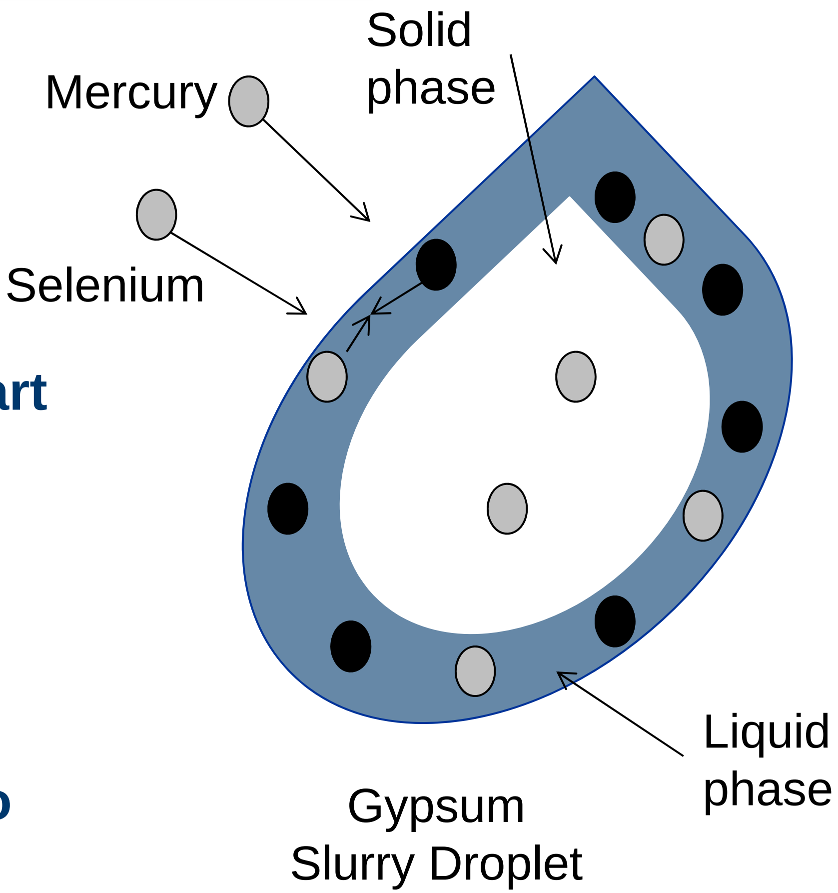
The STEAG Metal (Hg & Se) Approach

- **This is a 3 Phase Approach**
  - **Phase 1 – <u>Oxidized</u> Mercury captured in a wet FGD system – liquid phase**
  - **Phase 2 – Disposition of the Mercury - several options**
  - **Phase 3 – Se deposition**
- **STEAG Approach Requirements**
  - **The Mercury <u>must</u> be in the oxidized state (Hg2+)**
  - **Wet FGD System with injection points**
  - **Power Activated Carbon (PAC) added to wet FGD System via Recycle Pump**
  - **Mercury and Selenium can be removed from the process by:**
    - Hg/Se into the gypsum/dewatered solids
    - Hg/Se into the waste water filter press
    - Hg/Se/metals further chemically reduced then removed from system

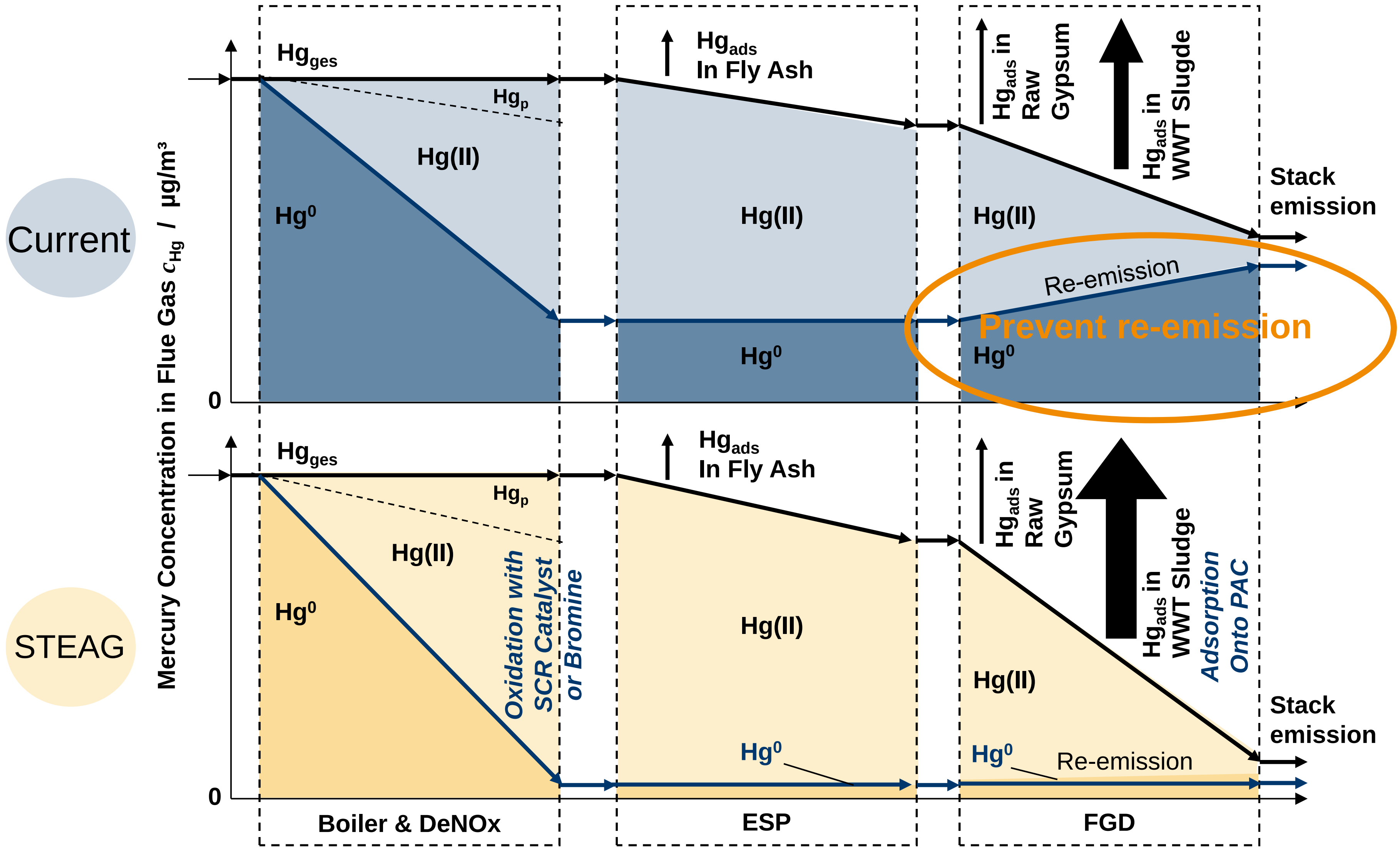


How is the it Sequestered?

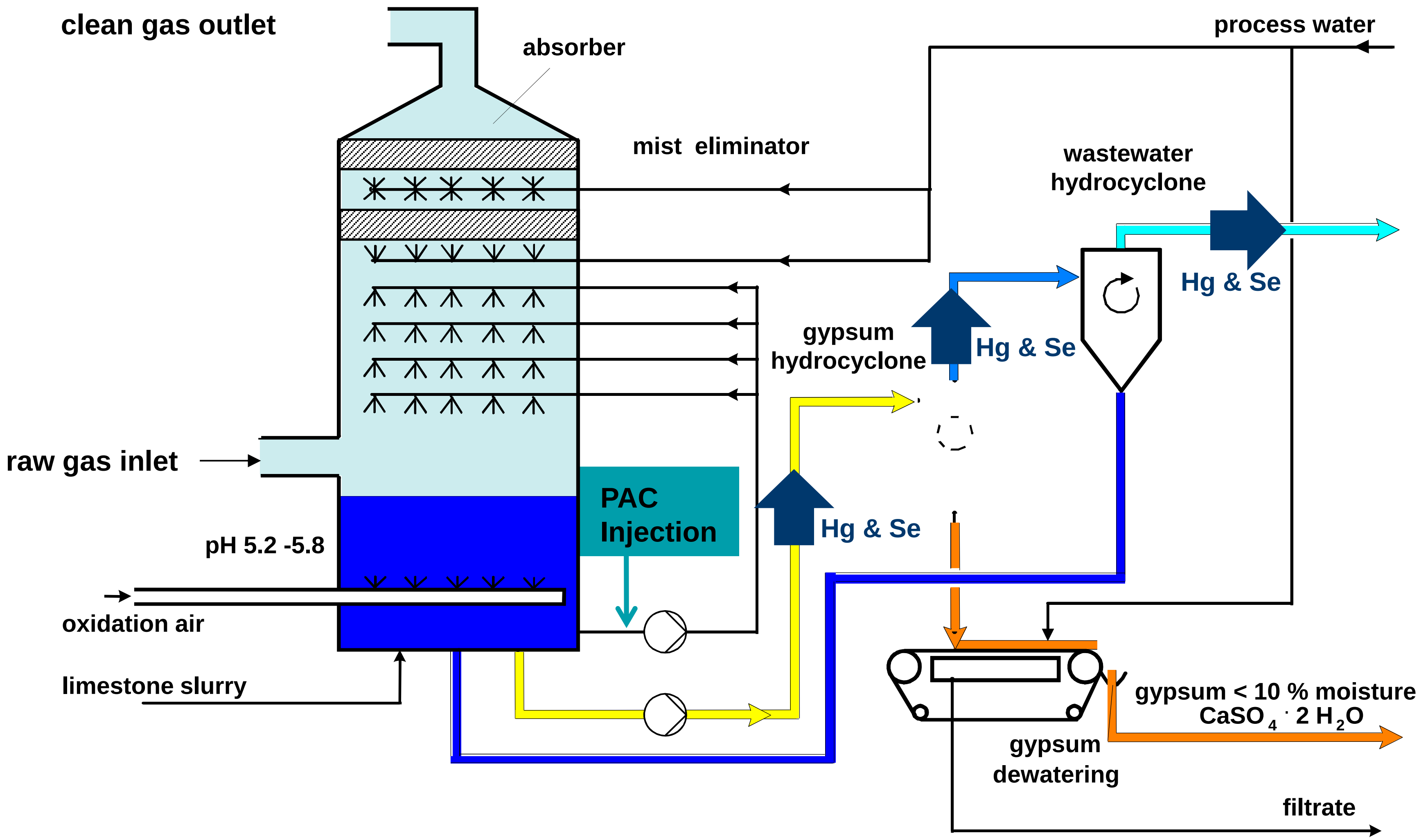
- The FGD does the mercury capture process
- STEAG adds carbon which resides in droplet liquid phase
- The Hg/Se moves to the solid part and remains captured
- The Hg/Se / carbon in the liquid phase is the important mercury capture requirement
- Once the mercury bonds to the carbon it cannot convert back to elemental state (reduction)



Current vs. STEAG Technique–Hg focus



Simplified wFGD Process without Hydroclones



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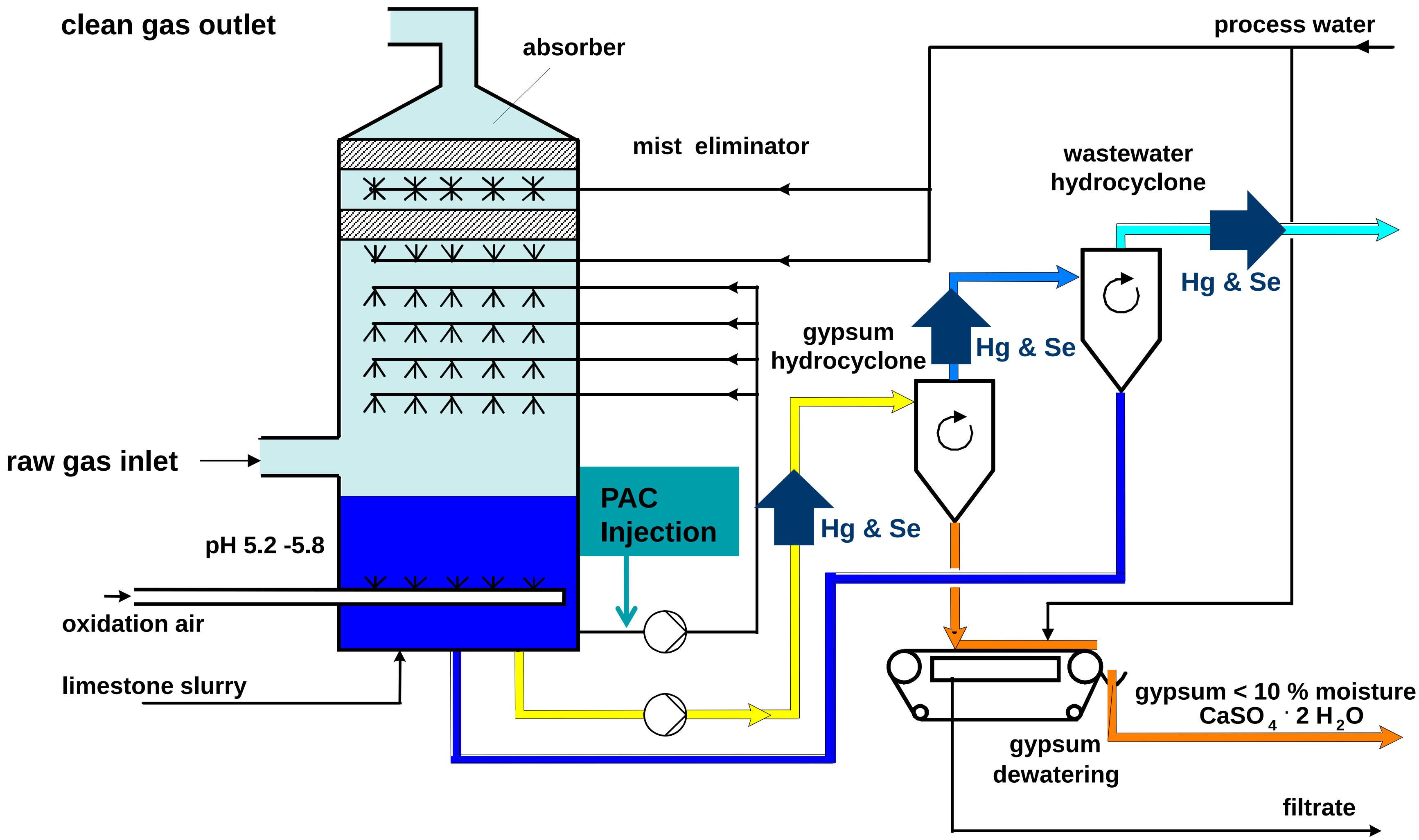


Utilization of PAC in a Wet FGD

Test Dosing Skid for PAC:

- Gravity influenced and reliable dosing of PAC from Super Sacks
- Injection of PAC upstream of FGD recycle pump
- PAC consumption depends on FGD blow-down & concentration desired

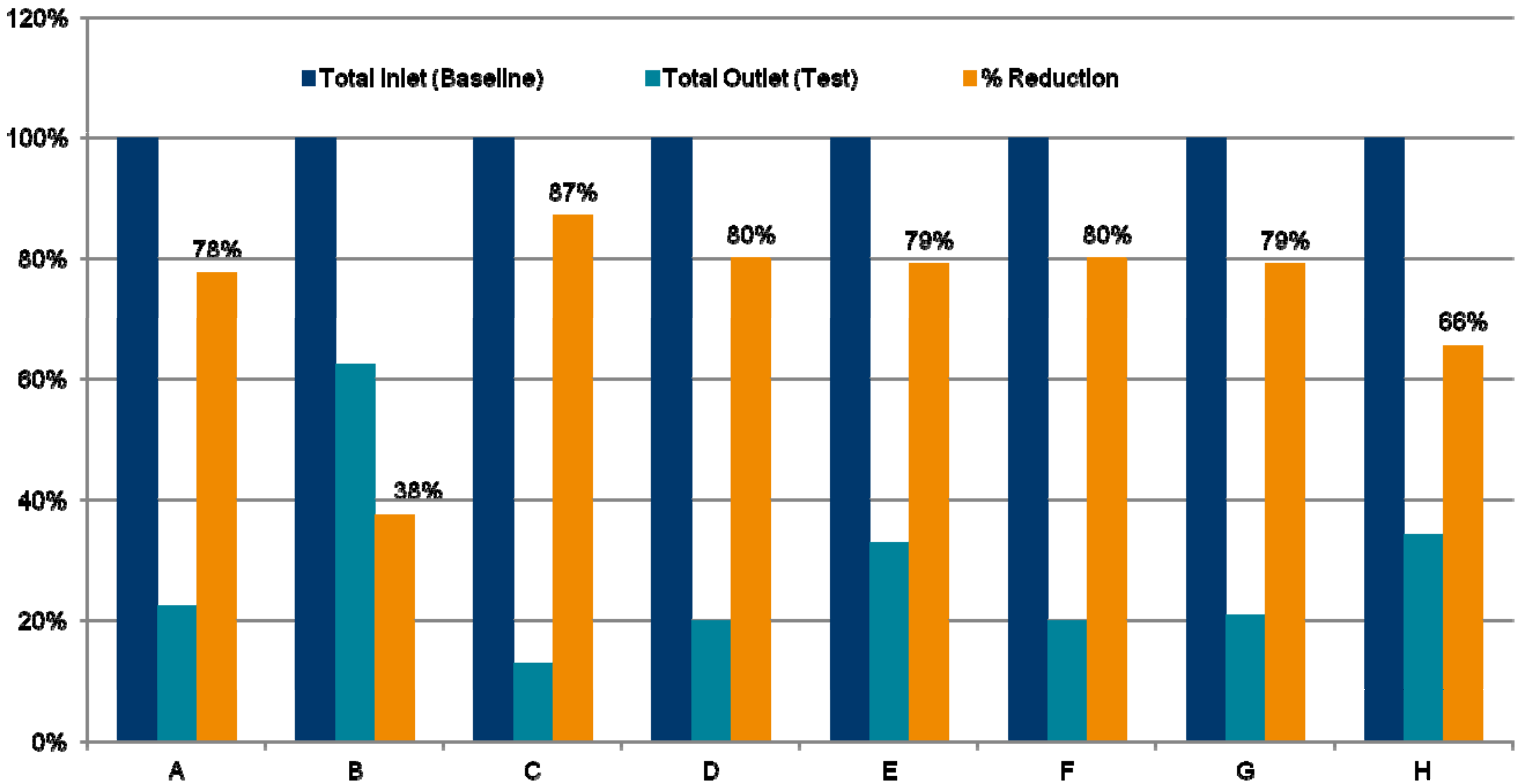
Alternative option:

- Manual interval dosing of PAC from smaller bags

Different Injection Points

Summary Chart

Mercury reduction in % at various test sites



Removal of the Mercury

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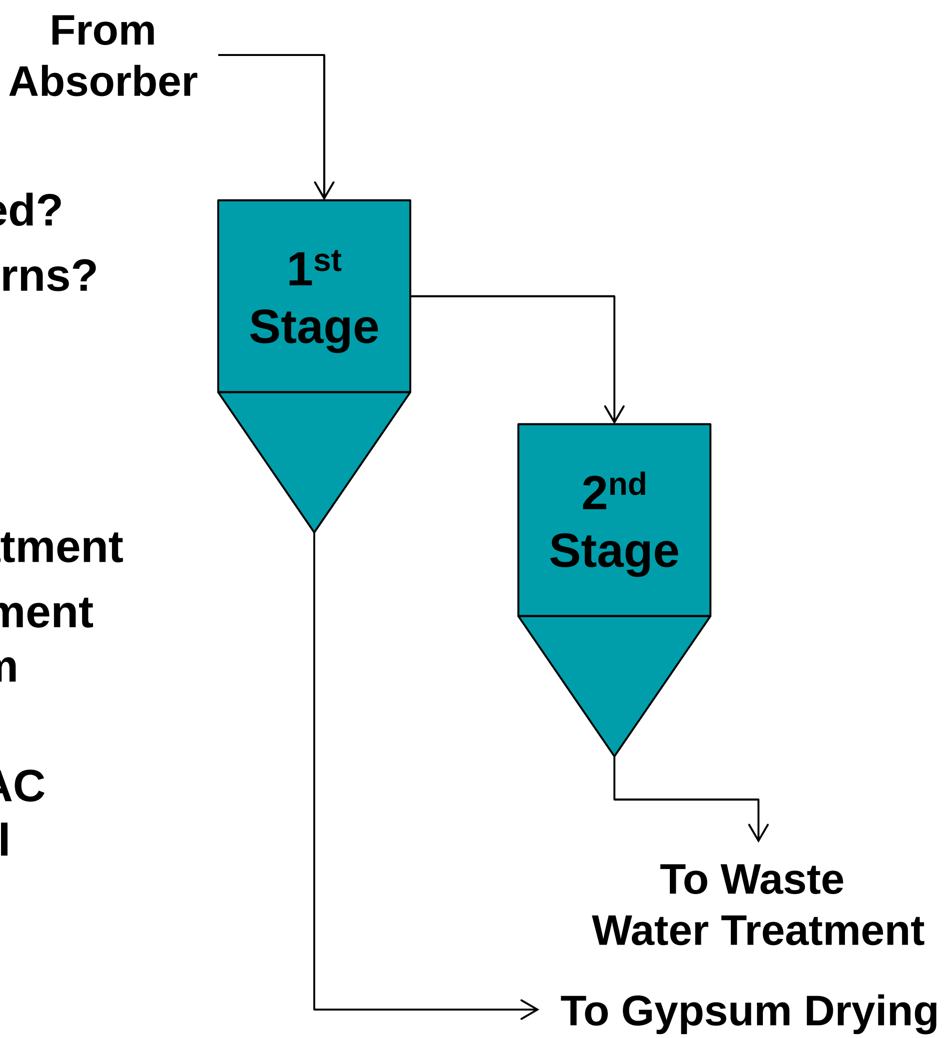
- **Decision Cycle**
  - Is the Gypsum being sold?
  - Does Mercury need to be removed?
  - Landfill / Product Liability Concerns?

- **Hydro-cyclones are the primary Mercury Separation System**
  - Mercury to the Waste Water Treatment
  - Hydro-cyclone separation equipment can be 2 stage separation system
  - Adjustments in the separation equipment may be needed for PAC recovery or further solids control

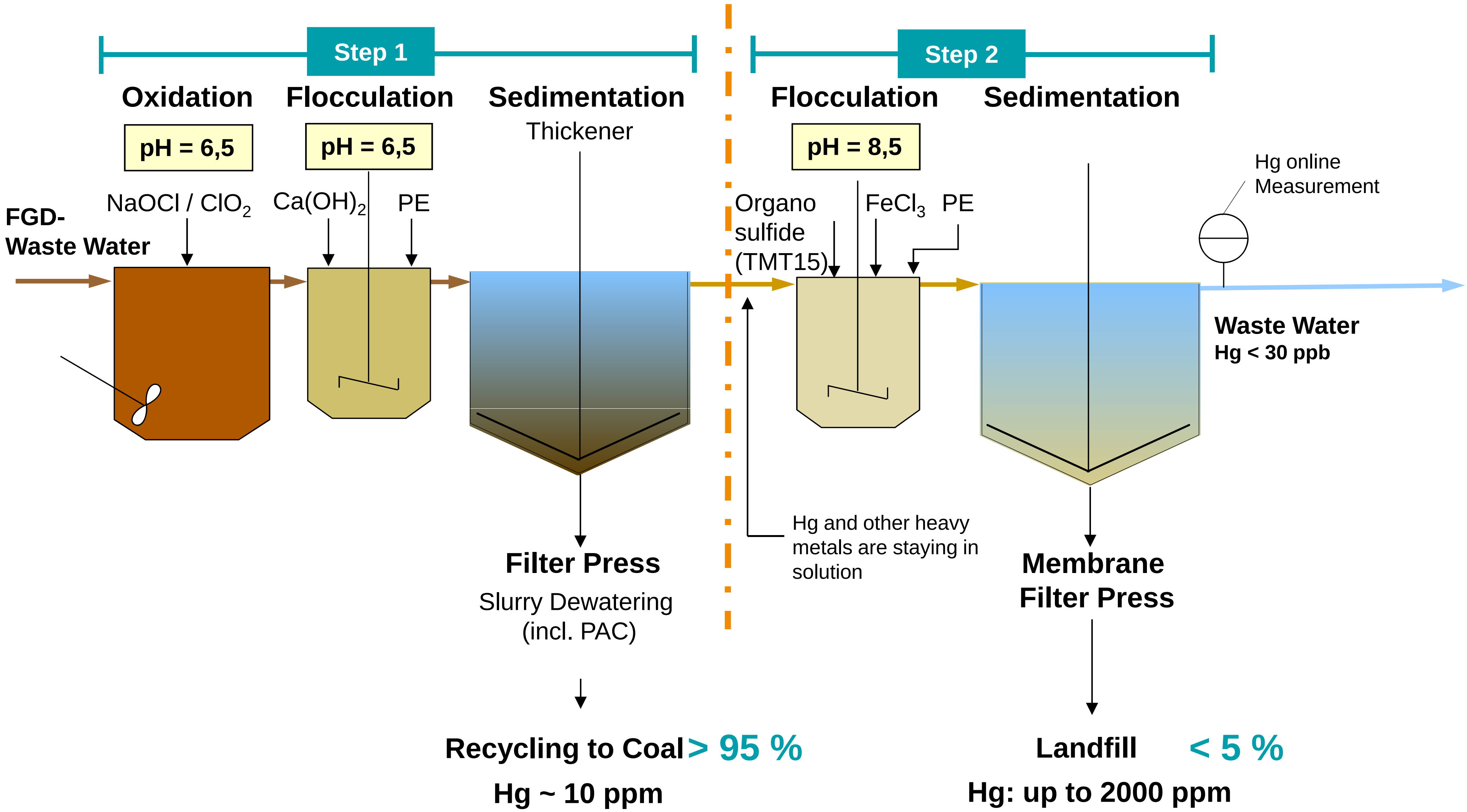


What is the driver to do anything?

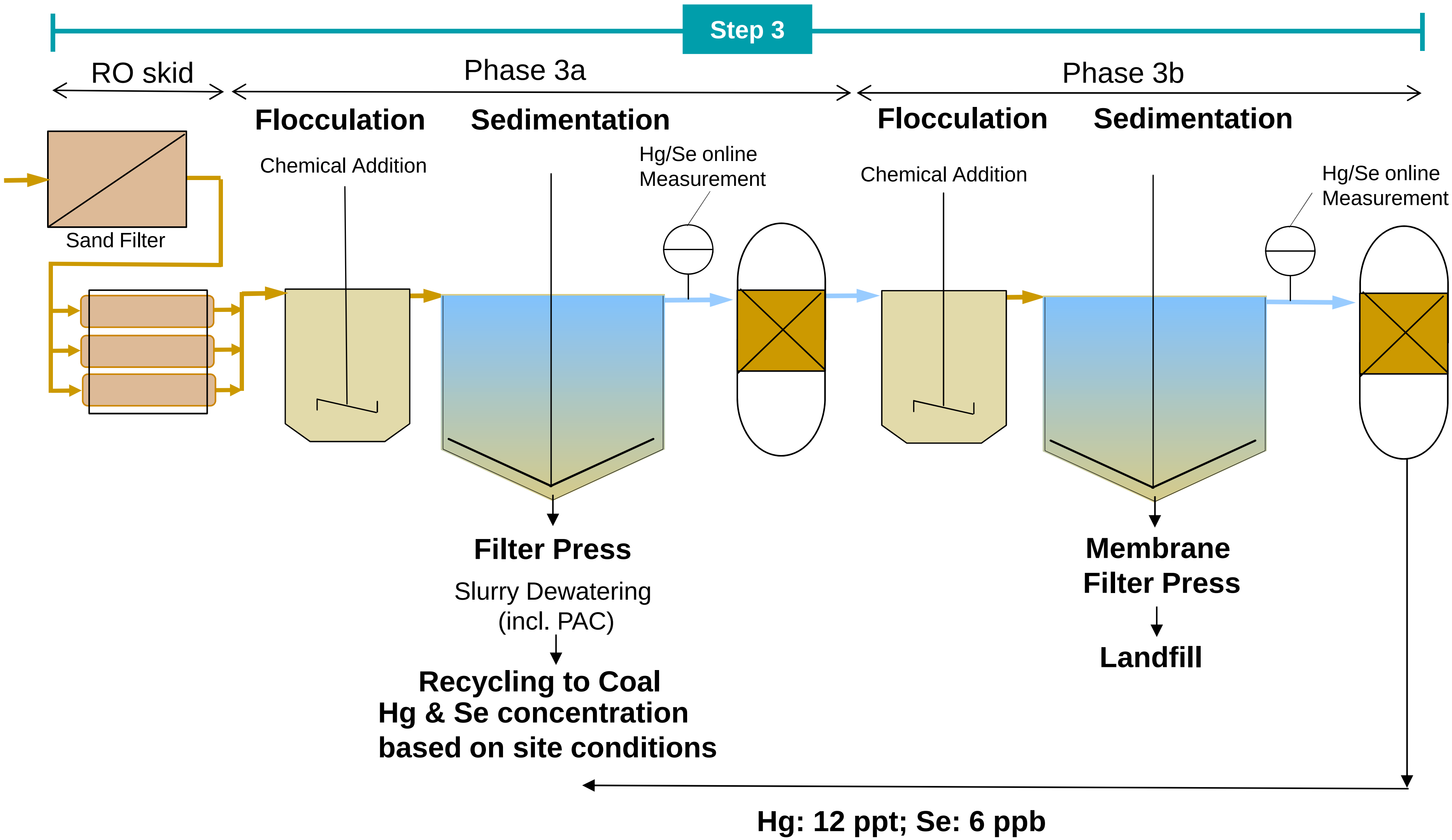
What is Driving the New WWT Technology?

- **Effluent Discharge Limits of:**
  - Hg: 12 ppt (2 ppb – Drinking Water)
  - Se: 6 ppb (50 ppb – Drinking Water)
- **Mercury cannot be removed with typical precipitation WWT**
- **Selenium is extremely water soluble and must be dealt with**
- **$Se_{IN} = Se_{OUT}$ for Typical Waste Water**

FGD Waste Water Treatment Details



FGD Waste Water Treatment Details



Hg and Se Pilot at Herne Power Plant

- **After successful laboratory test**
- **First pilot at Herne**
  - November 2012 – March 2013
  - Operating continuously with FGD treated effluent which is normally discharged.
- **Hg: 1- 6 ppt**
- **Se: Approaching 6 ppb**

	Concentrate	After Phase 1	After Phase 2	After Phase 3
- SO_4^{2-} (mg/L)	2400 – 2600	25	-	-
- Hg (ng/L)	< 5000*	-	1 – 6	-
- Se (µg/L)	950	-	-	< 5*

* Value are below the detectable limits of the analytical instrument used

Why STEAG's Technology?

- **Mercury Must be Oxidized for Effective Capture:**
  - No SCR: Calcium Bromide Addition to Coal
  - SCR: Catalyst will do most of the oxidation
- **The PAC/gypsum mixture can be separated using hydro-cyclones to control gypsum whiteness**
- **Ammonia Oxidation and Mercury Oxidation are SCR Competing Reactions**
- **Mercury Oxidation in SCR decreases over Time – Regular SCR Regeneration addresses**
- **Annual Operating Costs:**
  - Investment cost of PAC dosing station: TBD/site specific
  - Operating costs: based on blow down rate and cost of PAC

Why STEAG's Technology?

- **Take it out of the air – where is it going?**
- **Selenium is highly water soluble**
  - Desirable to safely concentrate as impermeable as possible
- **High concentrations can be toxic**
  - May influence drinking water quality
- **Chemistry of mercury considerably different than selenium:**
  - Approaching 6 ppb
- **Site specific risks are to be assessed**
- **First pilot at Herne**

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