Worldwide Pollution Control Association

WPCA-Southern Company Wastewater Treatment Seminar

April 16 & 17, 2013

WPCA

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Mercury and Mercury Oxidation

Rich Marsan
April 16, 2013 – WPCA WWT Conference

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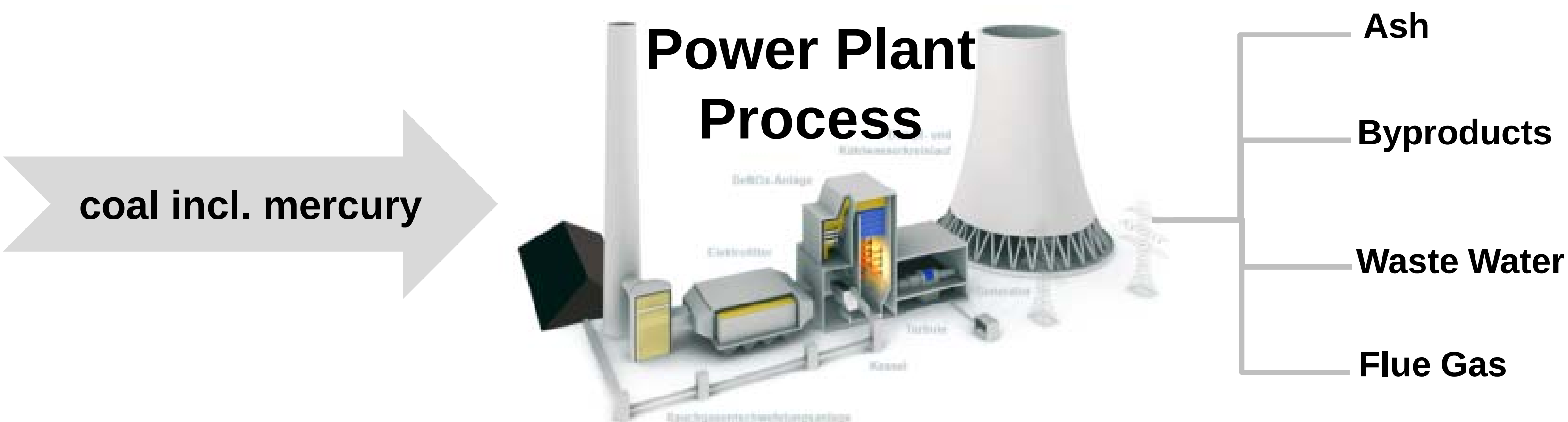
The Path of Mercury

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

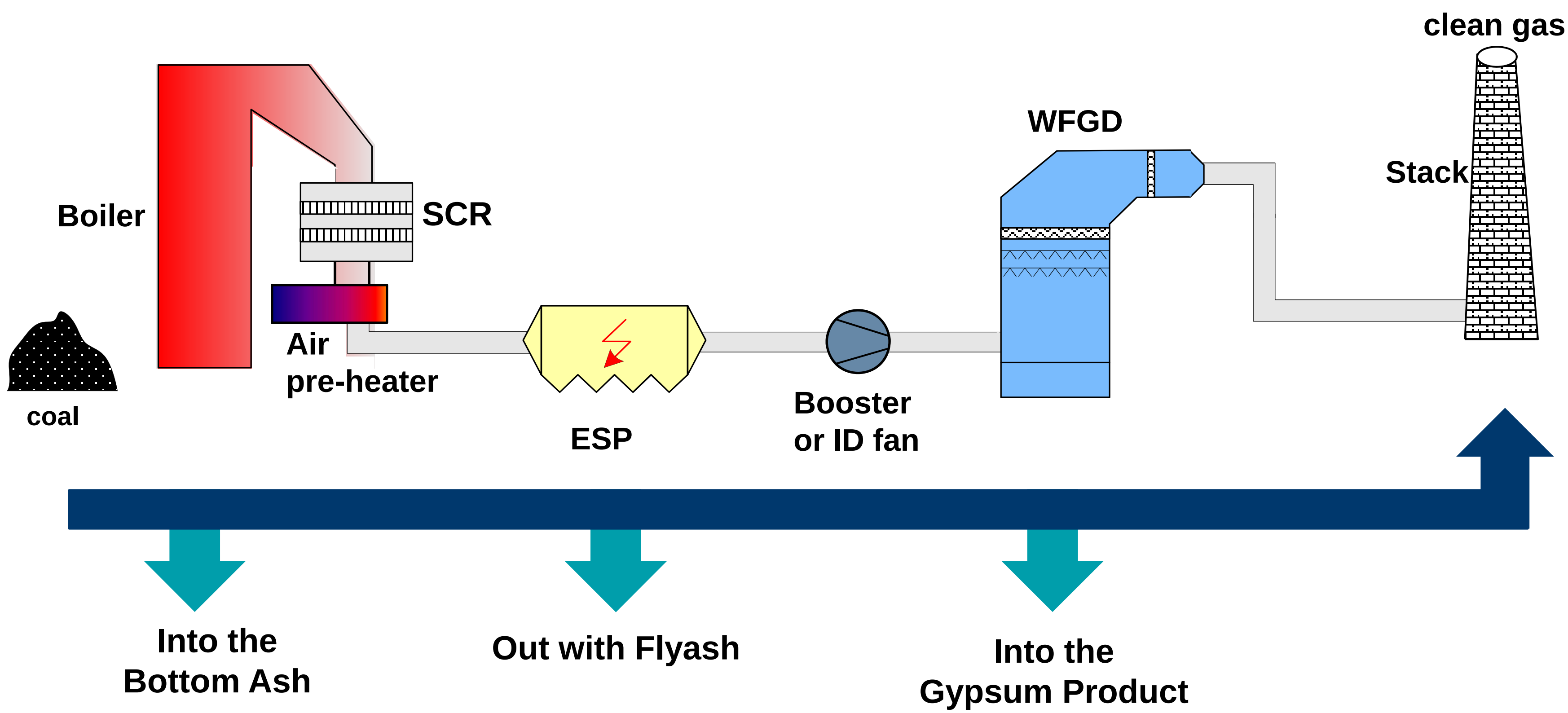


Mercury can either be prevented from entering the process or has to be removed from the process via ash, waste water, flue gas or byproducts (e.g. gypsum).

If byproducts are sold the amount of mercury in them is limited.

Regulation limits the amount of mercury discharged via flue gas and waste water.

What is the fate of the Mercury?



“Typical” Mass Balance for Mercury

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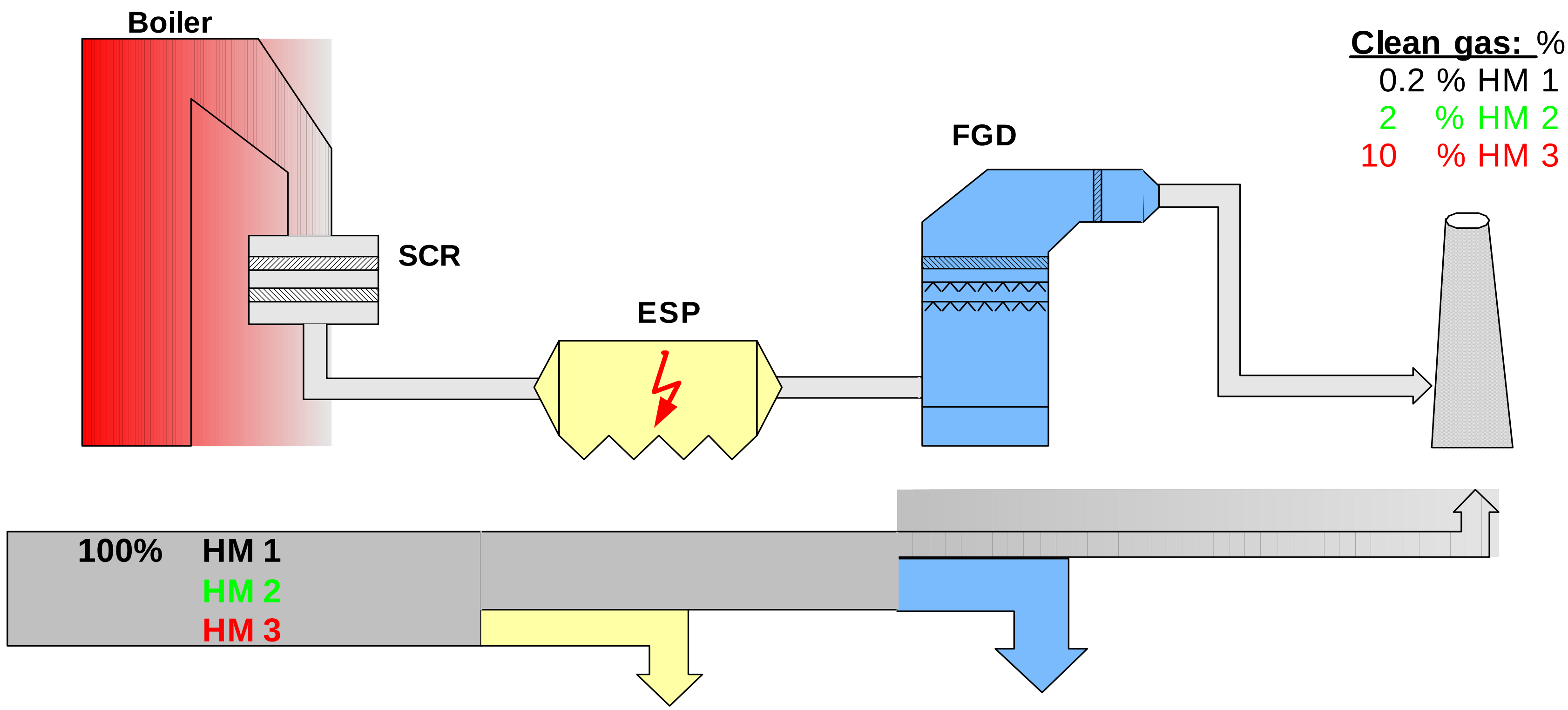

Ash:
97 % HM 1
68 % HM 2
5 % HM 3

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

What is the Utility drivers?

What is Driving the New Technology’s?

- **Effluent Discharge Limits of:**
  - Hg: 12 ppt
  - Se: 6 ppb
- **Mercury cannot be removed with typical precipitation**
- **Selenium is extremely water soluble**
  - $Se_{IN} = Se_{OUT}$ for Typical Waste Water

Combustion Process Relevant Reactions

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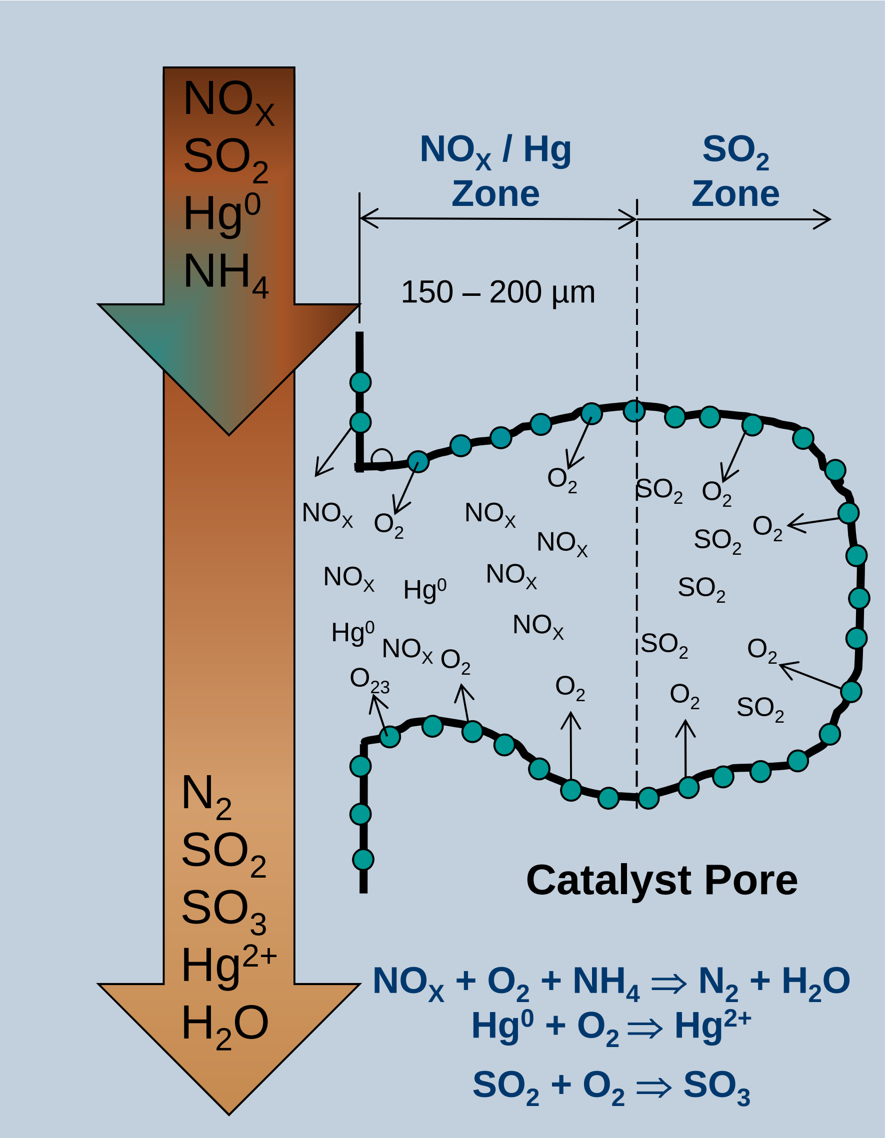
Formation of Mercury Oxide in the Furnace	$2\,Hg + O_2 \rightleftharpoons 2\,HgO$
Formation of Elemental Chlorine in the Furnace	$4\,HCl + O_2 \rightleftharpoons 2\,H_2O + 2\,Cl_2$
Oxidation of Mercury	$Hg + Cl_2 \rightleftharpoons HgCl_2$

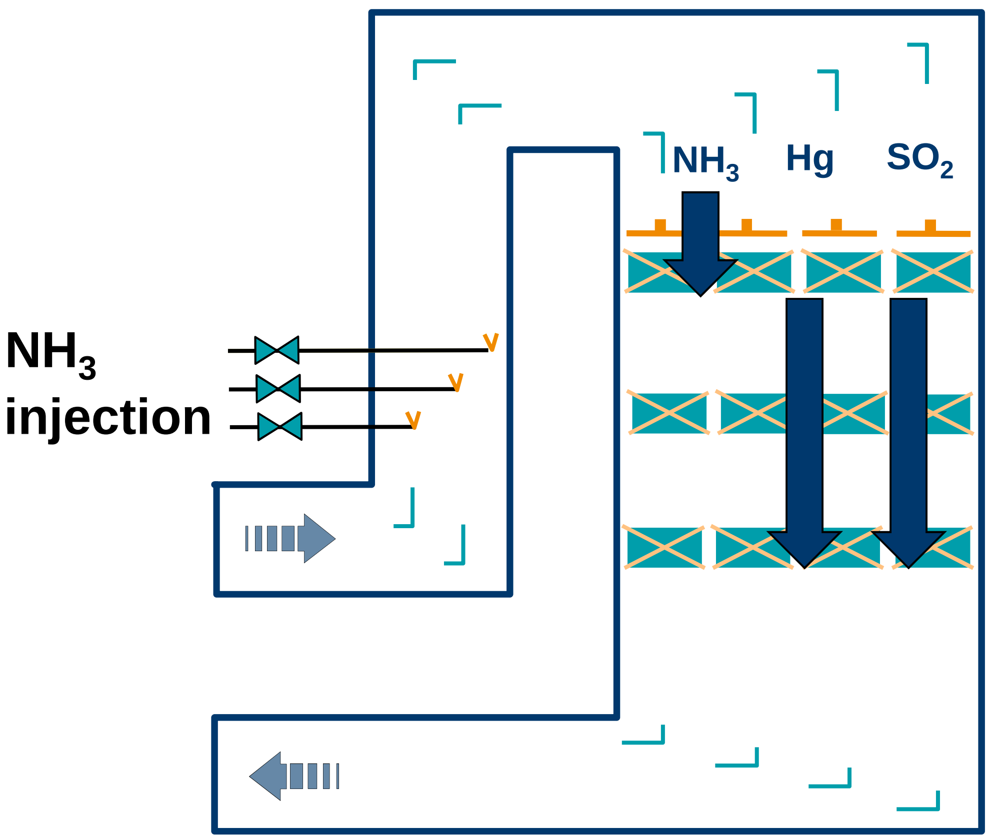
→ **These reactions are important for the oxidation of elemental mercury in the furnace and boiler, the generation of Cl_2 and subsequent formation of ionic mercury.**

The SCR Oxidation Reaction

- **The Vanadium Pentoxide (V_2O_5) releases oxygen (O_2)**
- **The flue gas stream contains the following constituents; 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



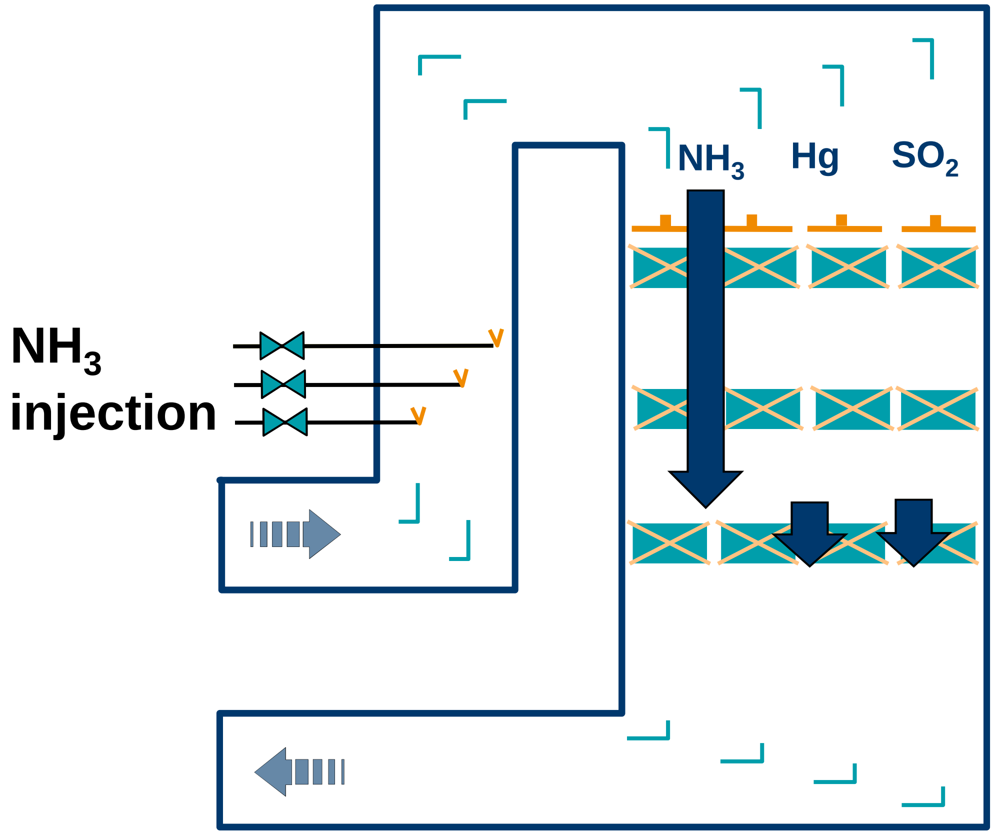
- **Results:**
  - Ammonia is consumed in the top layer.
  - Lower 2 elevations will produce the oxygen for Mercury Oxidations (also SO_2 to SO_3 conversion rate)

High levels of oxidation should occur with the Mercury!

SCR Catalyst Arrangement
Depleted Catalyst Reactor

- **Results:**
  - Ammonia consumption for NOx removal takes most of the catalyst surface.
  - Lower level is the only effective surface for Mercury (also SO_2 to SO_3 conversion rate).

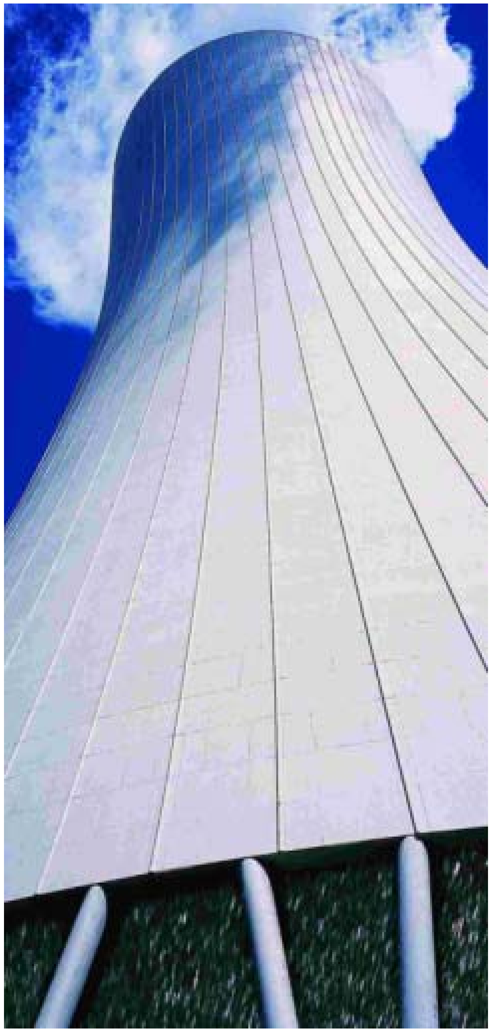
Low levels of oxidation should occur with this arrangement!



The STEAG Mercury Approach

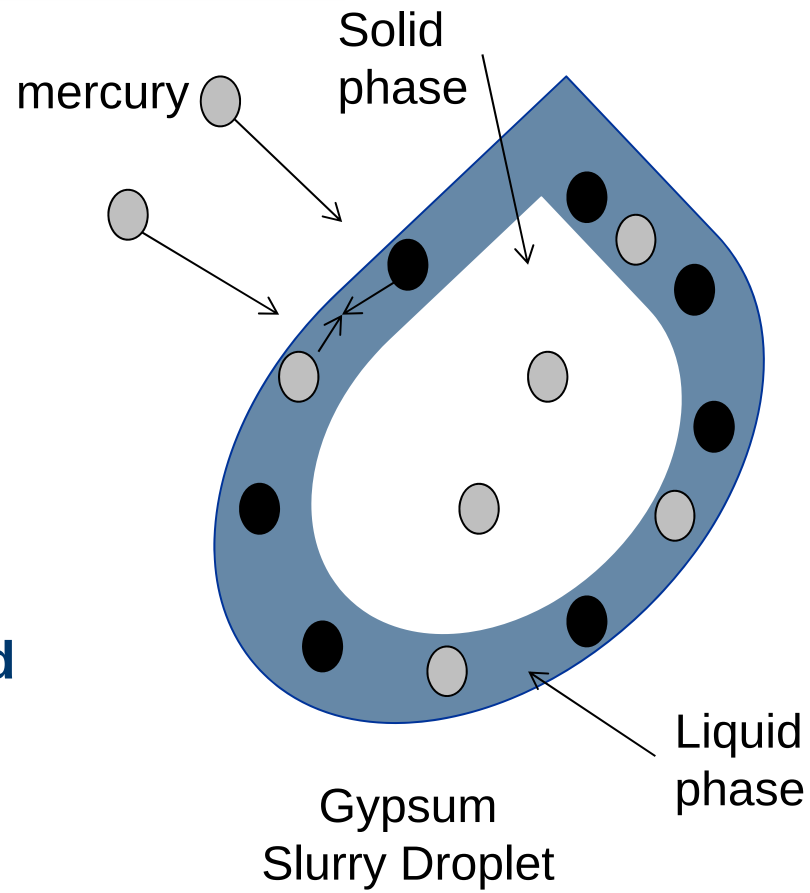
- **This is a 2 Phase Approach**
  - **Phase 1 - <u>Oxidized</u> Mercury captured in a wet FGD system**
  - **Phase 2 – Disposition of the Mercury. There are several options.**

- **STEAG Approach Requirements**
  - **The Mercury <u>must</u> be in the oxidized state (Hg^{2+})**
  - **Wet FGD System**
  - **Power Activated Carbon (PAC) is added to Wet FGD System**
  - **Mercury can be removed from the process by:**
    - Mercury in the gypsum/dewatered solids
    - Mercury into the waste water filter press
    - Mercury / metals reduced and then removed from system

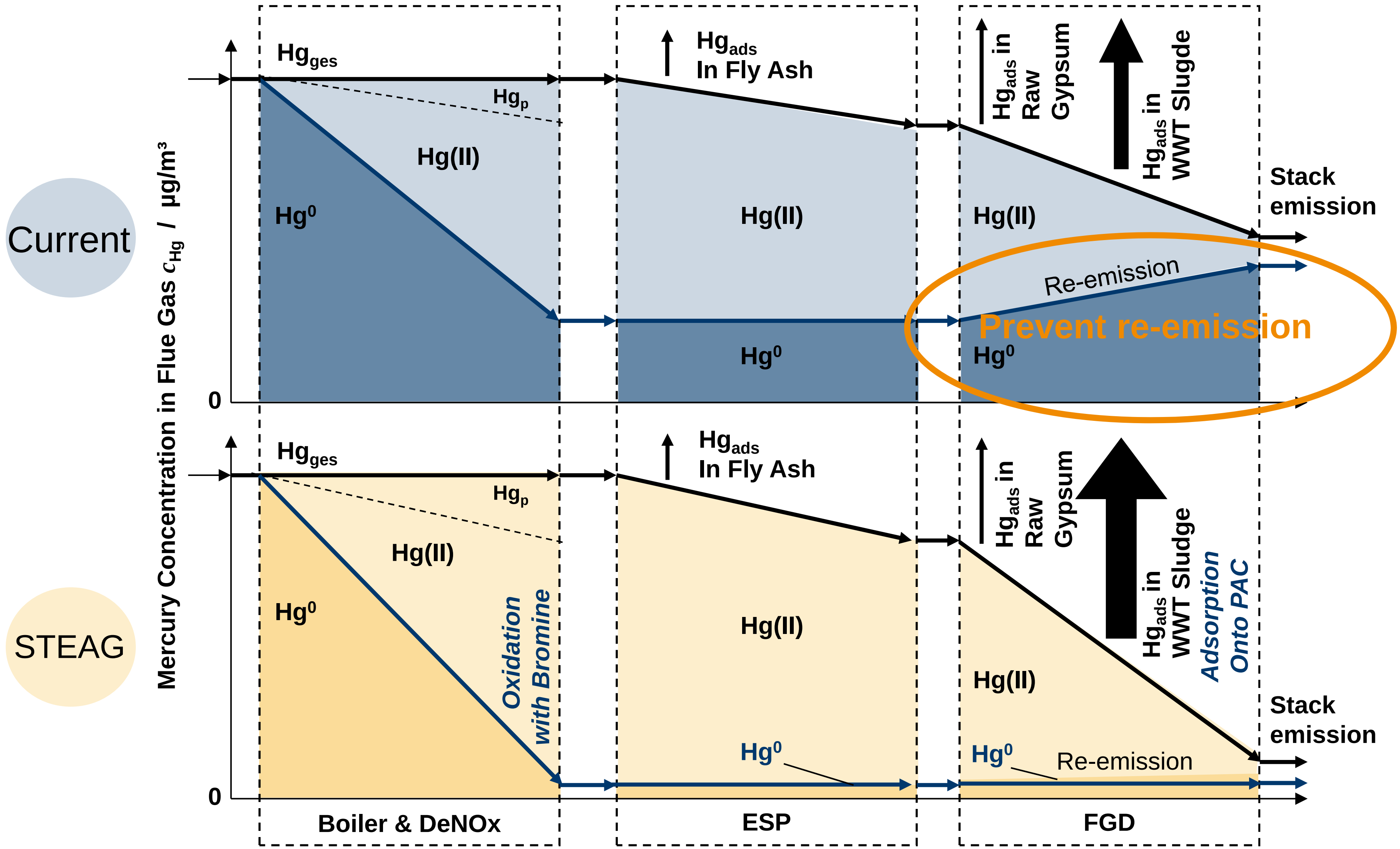


How is the Mercury Sequestered?

- **The FGD liquid does the mercury capture process. Oxidized Mercury is very soluble and**
- **STEAG adds carbon to the liquid phase of the droplet.**
- **The mercury the moves into the solid part of the particle remains captured.**
- **The mercury / carbon in the liquid phase is the important mercury capture.**
- **Once the mercury bonds to the carbon it cannot convert back to elemental state.**



Current vs. STEAG Technique



Utilization of PAC in a Wet FGD

Dosing Skid for PAC:

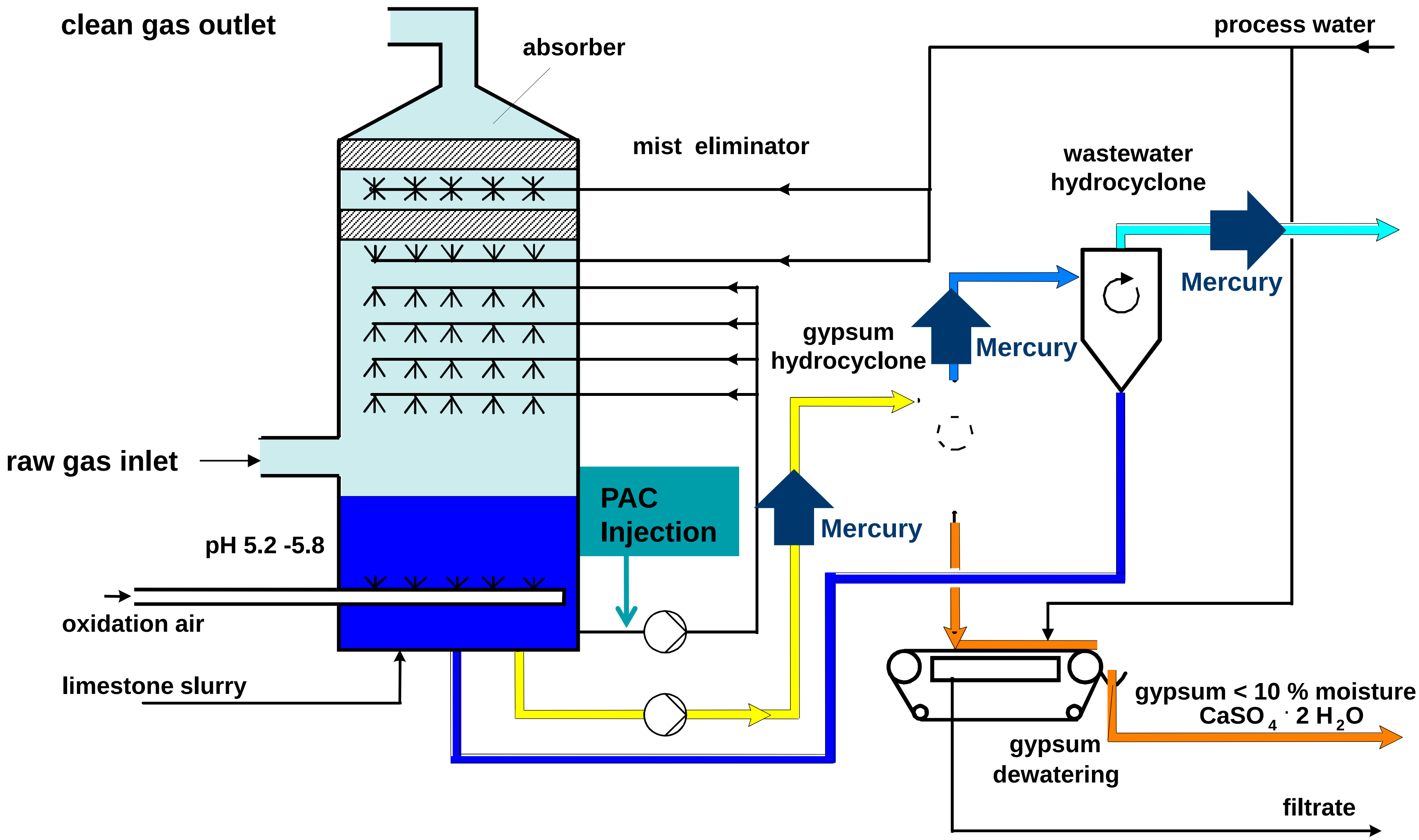
- Gravity influenced and reliable dosing of PAC from Super Sacks
- Injection of PAC upstream of FGD recycle pump
- PAC consumption depends on FGD blow
- down, approx. < 50 kg (100 lbs) per day

Alternative option:

- Manual interval dosing of PAC from bags

Different Injection Points

Simplified wFGD Process without Hydroclones



Simplified wFGD Process with Hydroclones

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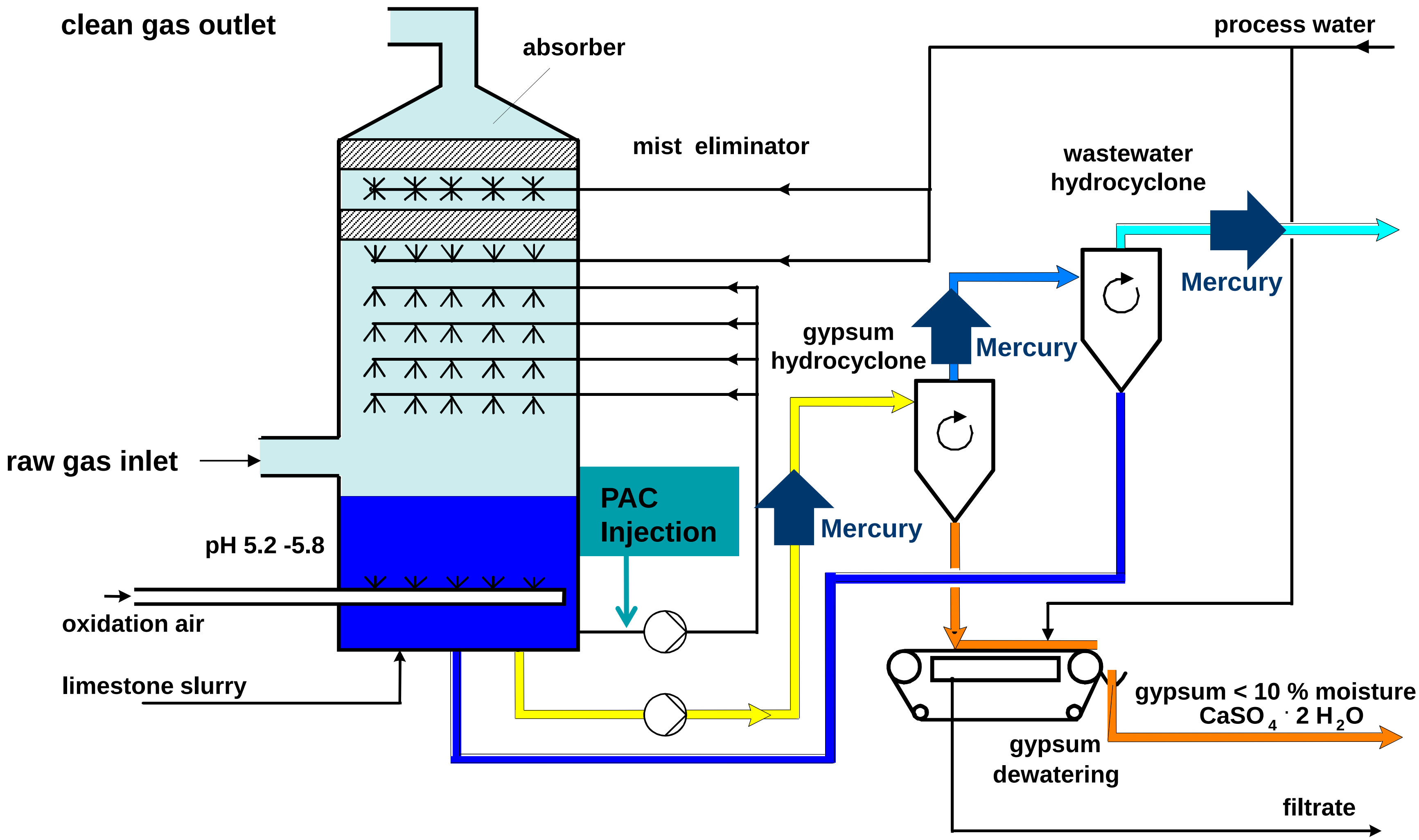

Testing Results

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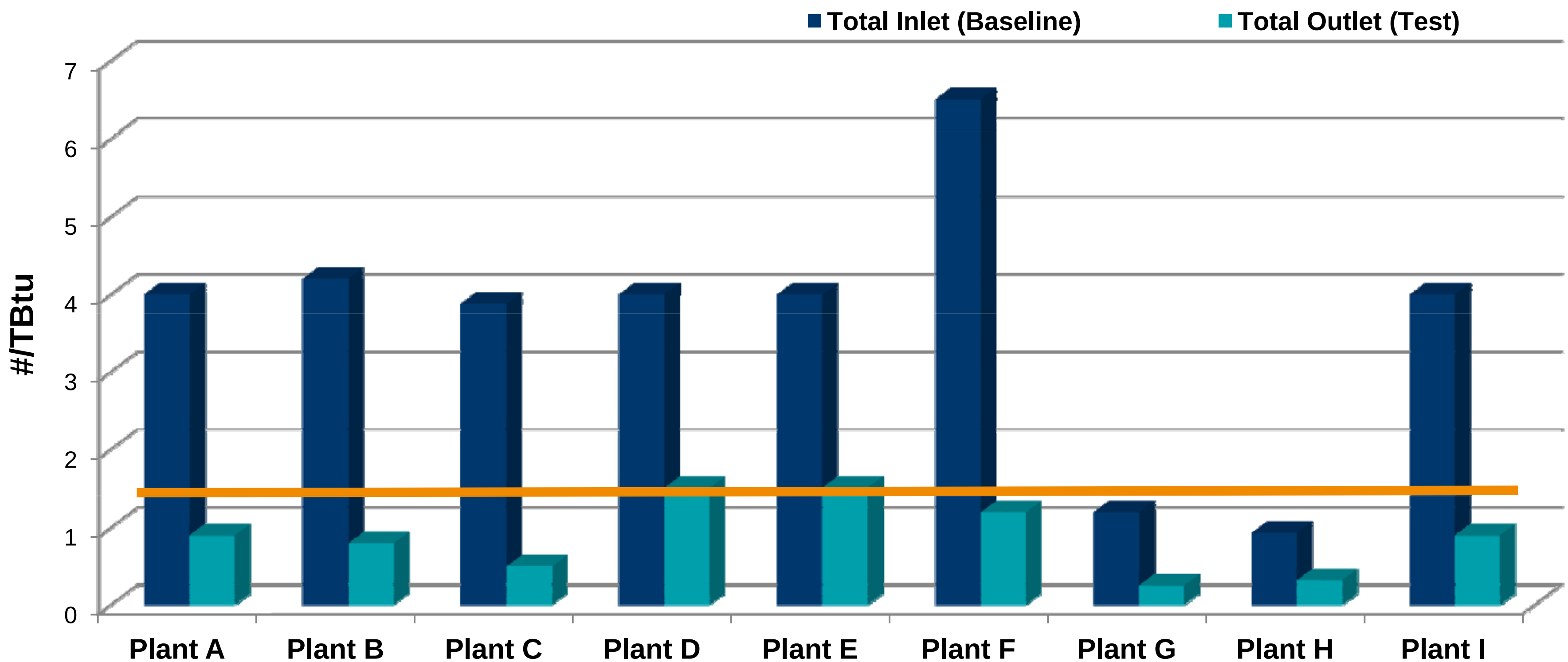

	Plant A	Plant B	Plant C	Plant D	Plant E	Plant F	Plant G	Plant H	Plant I
Fuel Type	Western Bit.	PRB	PRB	Western Bit.	Western Bit.	Eastern Bit.	Eastern Bit.	Eastern Bit.	Eastern Bit.
SCR / SNCR	No	SCR	SCR	SNCR	SNCR	No	SCR	No	SCR
Halogen Addition	CaBr2	CaBr2 Addition (OD)	None	CaBr2 Addition	CaBr2 Addition	CaBr2 Addition	None	None	None
FGD	W-Sodium	LSFO	LSFO	LSFO	LSFO	LSFO	LSFO	LSFO	LSFO

Need for Immediate Compliance

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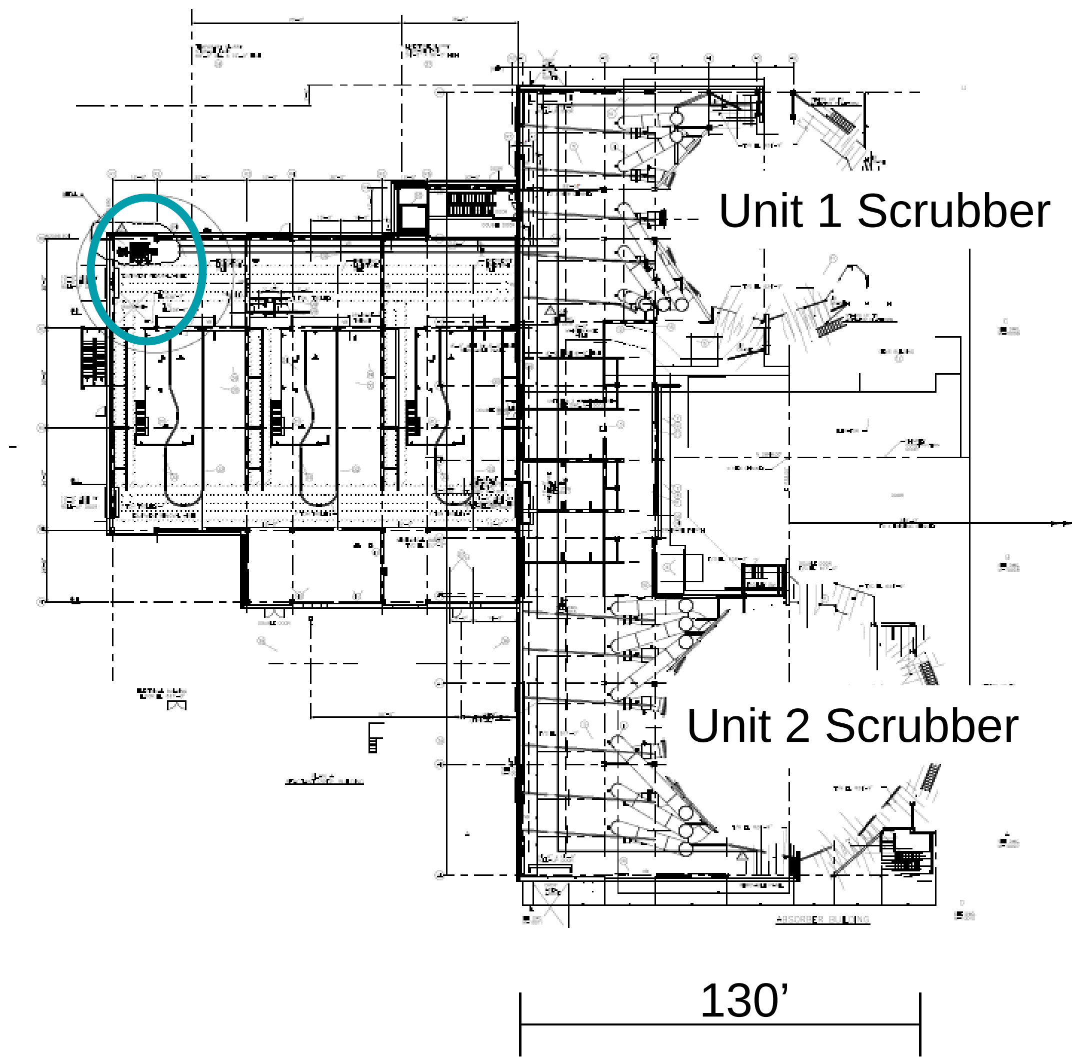
- **Accepted by State compliance.**
  - **By State requirements - Injection at 850 #/hr (5 #/ million acfm)**
- **Unit sizes 365 MW / 590 MW.**
- **Temporary PAC Injection System.**
- **Inject Rate is 6 # / Hr – both units.**
- **30 min. per week feed once a week.**
- **Operational since September 2012.**

**Savings to this utility for this station is $ 6.6 million per year.
System payback is in less than 2 months!**

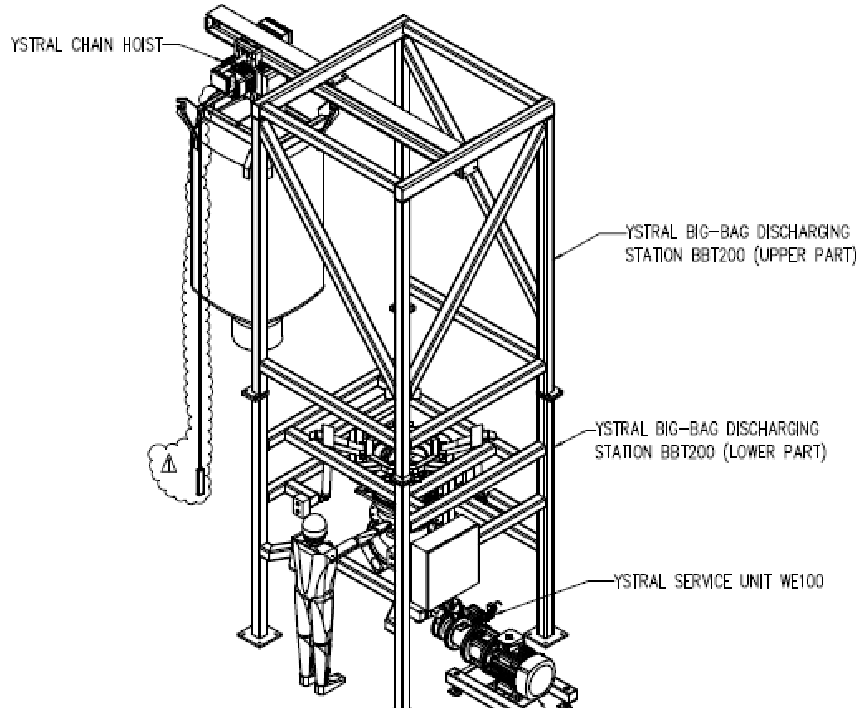
First US Commercial System

- Mid-Western Utility
- 2 units dosed w/1 PAC addition system
- Feed to each unit less than 30 min. per day
- About 300 ft of piping
- PLC control system.
- Injection direct into units
- Back-flush system



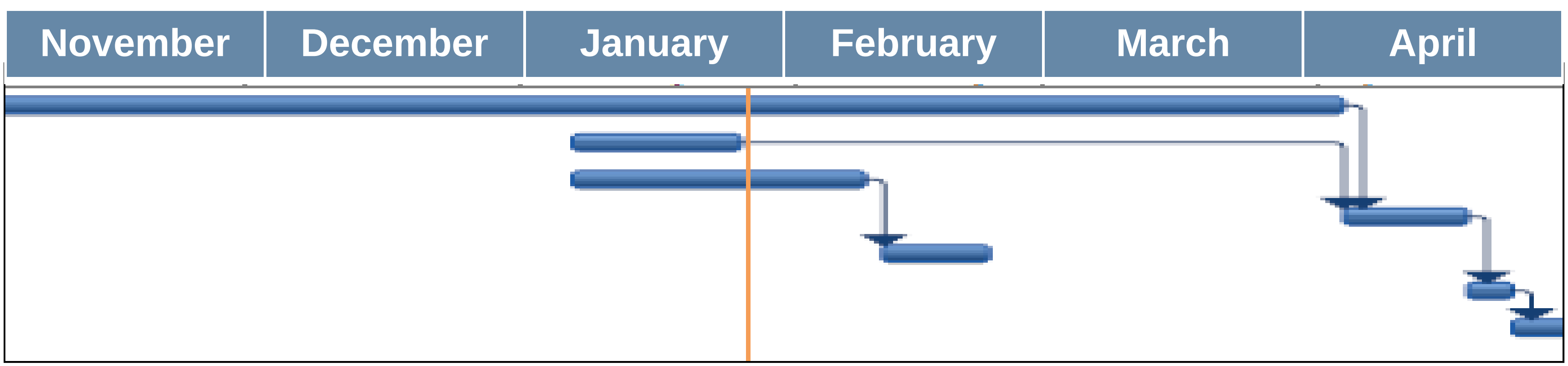
Equipment Selection

- **Option Chosen: Conti TDS Skid for high throughput dosing**
- **Super-sack based System – 900#**
- **Change bag once per week**
- **Both units dosed in about ½ hr.**
- **Silo based system available for higher PAC volume users**



Typical Schedule

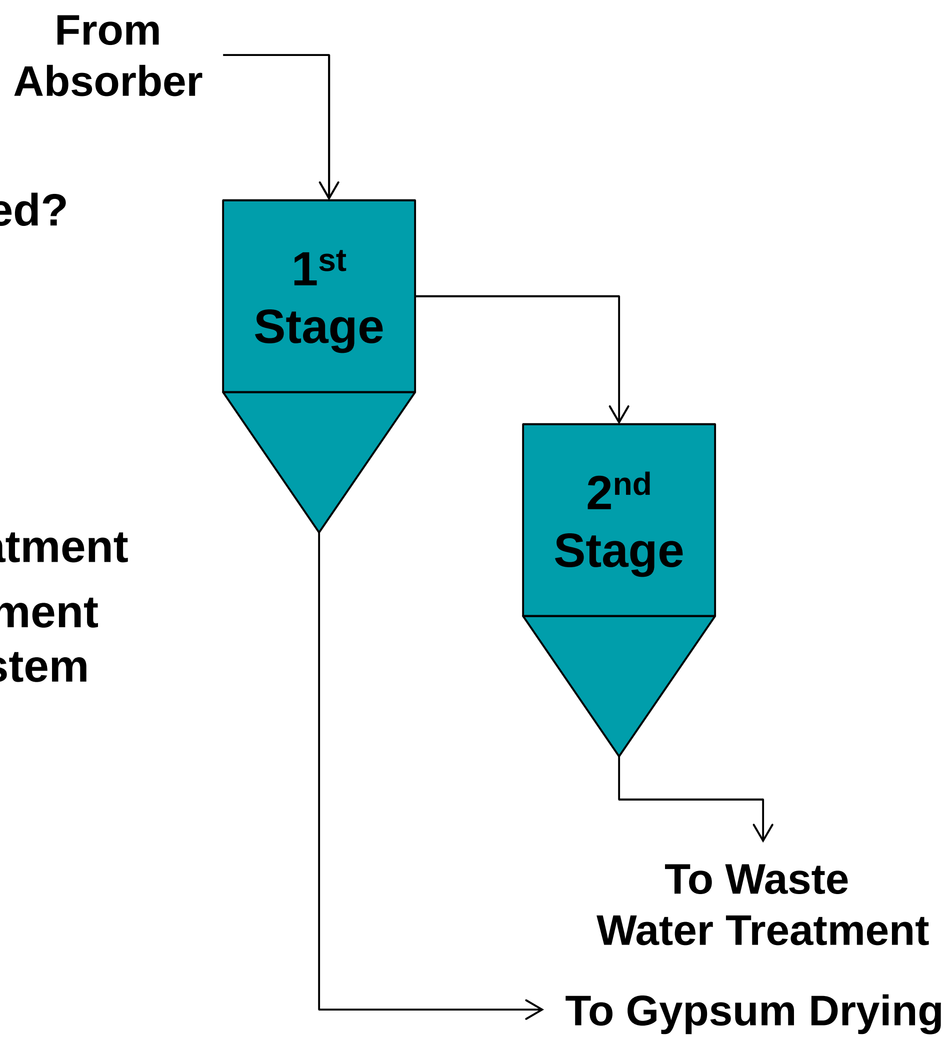
	Task Name	Duration	Start	Finish	Predecessors
1	Skid Fabrication	22 wks	11/1/2012	4/3/2013	
2	Controls Engineering	3 wks	1/7/2013	1/25/2013	
3	Piping Engineering	5 wks	1/7/2013	2/8/2013	
4	Controls Installation	2 wks	4/4/2013	4/17/2013	2,1
5	Piping Installation	3 days	2/11/2013	2/22/2013	3
6	Skid Installation	1 wk	4/18/2013	4/22/2013	4
7	Commissioning and Startup		4/23/2013	4/29/2013	6



Removal of the Mercury

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

- **Hydro-cyclones is the Mercury Separation System**
  - Mercury to the Waste Water Treatment
  - Hydro-cyclone separation equipment may need 2 stage separation system
  - Adjustments in the separation equipment may be needed



FGD Waste Water Treatment Details

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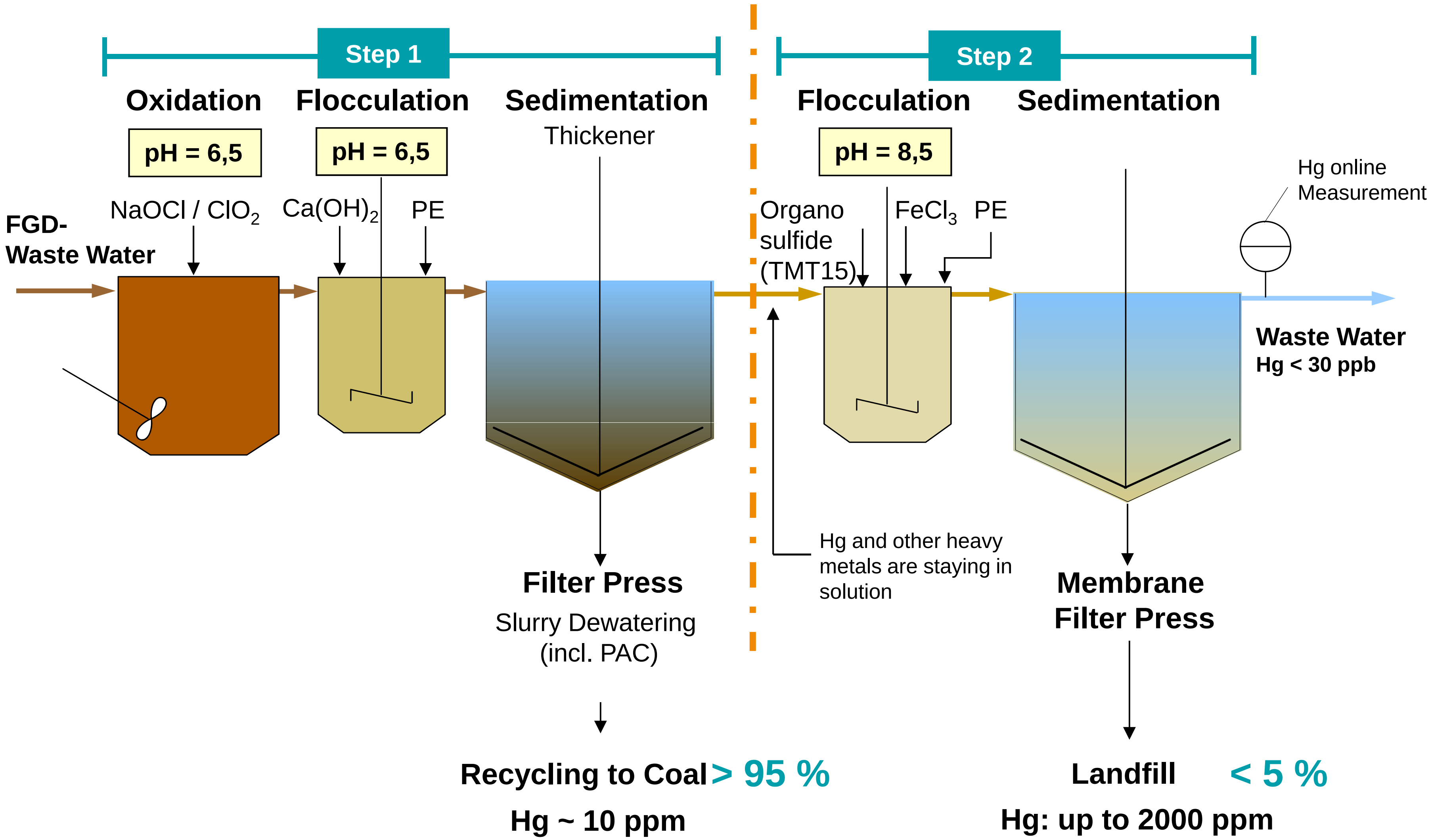
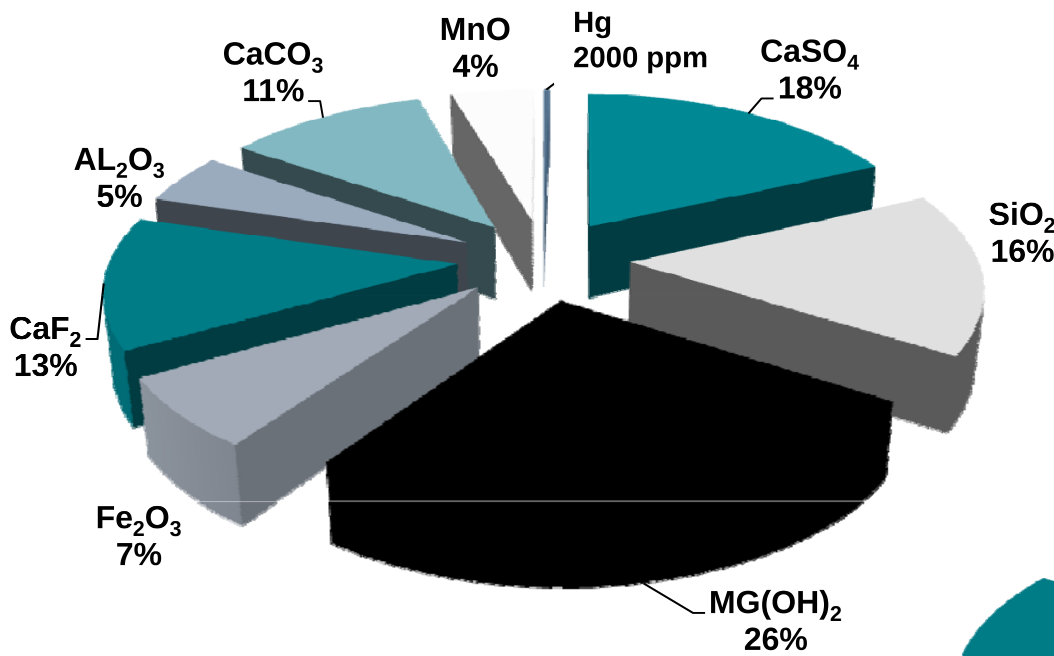
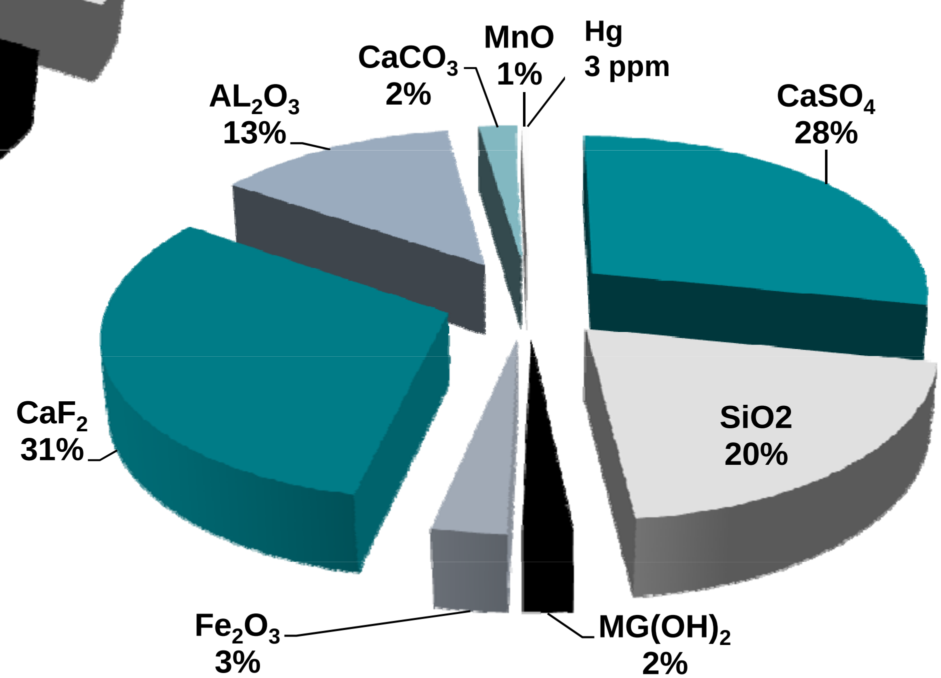


Waste Characterization

Waste minimization



Hg- containing sludge to landfill
<5%



Hg- free sludge to combustion
>95%

Why STEAG's mercury technology?

- **Mercury Must be Oxidized for Effective Capture:**
  - No SCR: Calcium Bromide Addition (e.g. Alstom KNX)
  - SCR: Catalyst will do the oxidation
- **The PAC/gypsum mixture can be separated completely using hydrocyclones (gypsum whiteness unaffected).**
- **Ammonia Oxidation and Mercury Oxidation are Competing Reactions**
- **Mercury Oxidation decreases over Time**
- **Costs:**
  - Investment cost of PAC dosing station: TBD/site specific
  - Operating costs: based on blow down rate and cost of PAC

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