Effective Stack Mercury Emission Control In the Power Industry

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Overview

- Regulatory Perspective
- Overview of Mercury Detection and Measurement
- Typical APC Configurations Important to Hg Control
- Primary Hg Control Technologies
- Advantages / Disadvantages of Various Hg Control Technologies
- Hg Re-Emissions
- REDOX Hg^{RPC} Re-emission Control

Technology Driver: EPA Regulation

NESHAPS from Coal and Oil-Fired Electric Utility Steam Generating Units and Standards of Performance for Fossil-Fuel Fired Electric Utility, Industrial/Commercial/Institutional, and Small Industrial-Commercial-Industrial Steam Generating Units

(40 CFR 63, Subpart UUUUU)

MATS = Mercury Air Toxics Standard

EPA Regulations

Primary Target: Power Generating Industry, Regulation Final February 16, 2012

Emission Standards: (New and Existing Units. Includes emission standards for metals, halogens, and mercury)

Example: Existing Generating Stations – 1.2 lb/TBtu or 1.3E-2 lb/GWhr Total Hg emissions

EPA Justification for MATS Regulations

EPA Basis for MATS

- Value to society $37 to $90 billion per year
- Total economic benefit outweighs cost 9 to 1
- Create 28,000 to 158,000 jobs through 2015
- Prevent 1,300 asthma attacks
- Prevents 5,700 hospital visits per year
- Prevents 11,000 premature deaths per year
- Prevents 4,700 heart attacks per year

Emission Perspective

Standard: 1.2 lb/TBtu

Bull Run Steam Plant: 1,000 MW

Assume: 100% OSF

Coal Feed Rate: 1,000,000 lb/hr (500 tons/hr) or 4 rail cars/hr

Emissions = $\frac{\text{1,000 MW x 3,413,000 Btu/MW x 8760 hr/yr}}{\text{0.3 efficiency x 1E12 Tbtu/Btu}}$ = **120 lb/yr (0.014 lb/hr)**

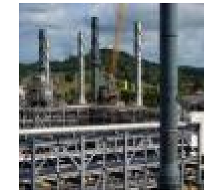
Typical Coal Hg Content

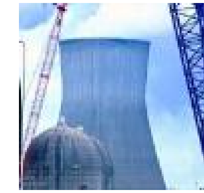
Coal Type	Typical Hg Range lb/TBtu (ppm)	Typical Total Hg (lb/Tbtu)	Required Hg Control[1]
Sub-Bituminous (e.g. PRB)	7.06-9.97 (0.06-0.09)	8	85%
Bituminous (KY coal)	2.87-26.58 (0.04-0.33)	10	88%
Lignite	17.87-29.81 (0.12-0.19)	25	84%

Note 1: To meet standards for existing non low rank coal.

Mercury Speciation

- **Elemental** (Hg^0) - Predominant combustion product (not desired for APC)
- **Oxidized** (Hg^{2+}) – Desired form for wet scrubber capture (has affinity for ash)
  - $HgCl_2$, Hg_2Cl_2 – High fraction (70-90%) if high-chlorine coal is fired
  - $HgBr_2$, Hg_2Br_2 – Not normally present at high concentrations (other halogens negligible)
- **Particulate Bound** (Hg_p)



Methods for Measuring Hg Emissions

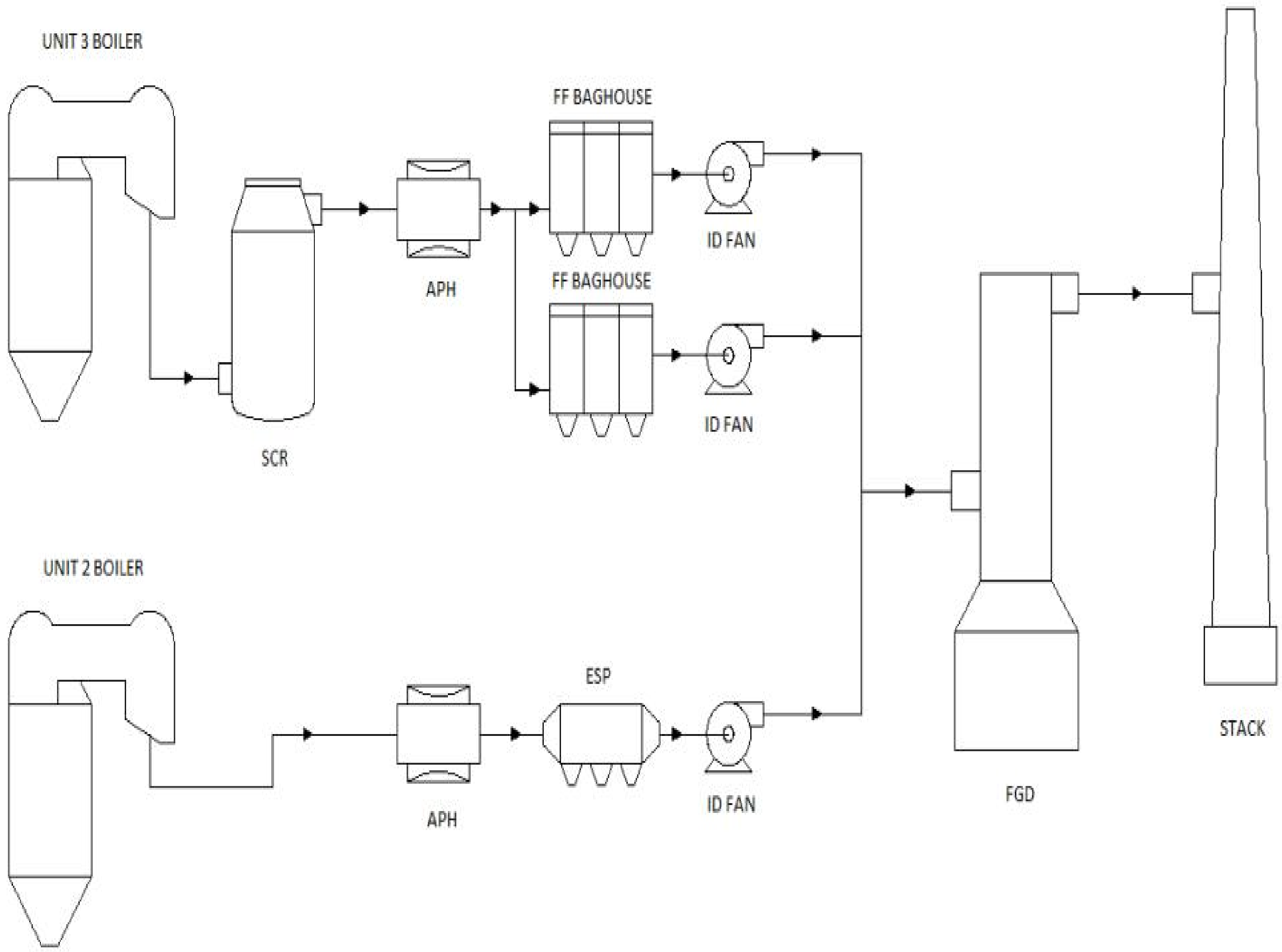
Method	Allows Speciation	Drawbacks	Method	Sampling Time
Hg CEMS	YES	Expensive, maintenance intensive	40 CFR 60, Appendix F	Continual, periodic purges of gold amalgam
Method 30B (RATA)	YES	Limited to short-term testing	Method 30B, 40 CFR 60, Appendix B	30 min to 8 hr typical
Appendix K	YES	Tube plugging	40 CFR 75, Appendix K	Days to over a week
Ontario Hydro	YES	Wet Chemistry, long analytical TAT	ASTM D6784	Typically 4 hr
Method 29	NO	Wet Chemistry, long analytical TAT	EPA Method 29, CFR 60, Appendix A	Typically 4 hr

Method 30B Sampling System

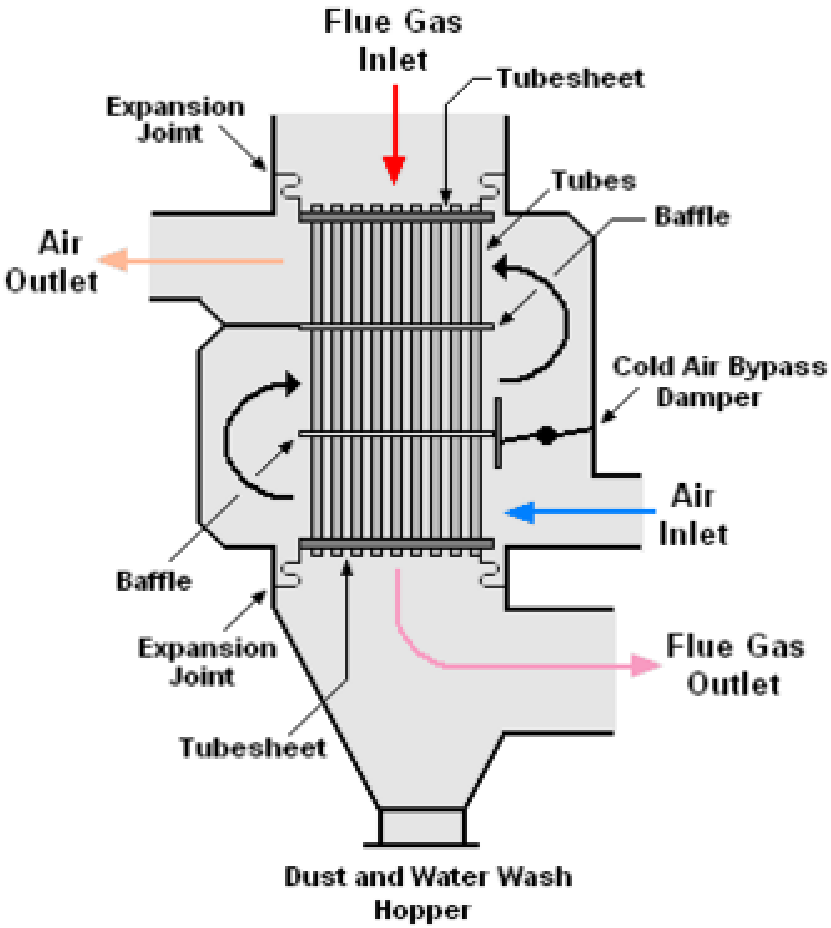
Typical Power Plant Air Pollution Control (APC) Equipment Important to Hg Removal

- Cold Side Electrostatic Precipitator (ESP)
- Hot Side Electrostatic Precipitator
- Wet Electrostatic Precipitator (WESP)
- Fabric Filter Baghouse (FFBH)
- Flue Gas Desulfurization (FGD)
- Spray Dryer Absorber (SDA)
- Air Preheater – (tubular, rotating regenerative)

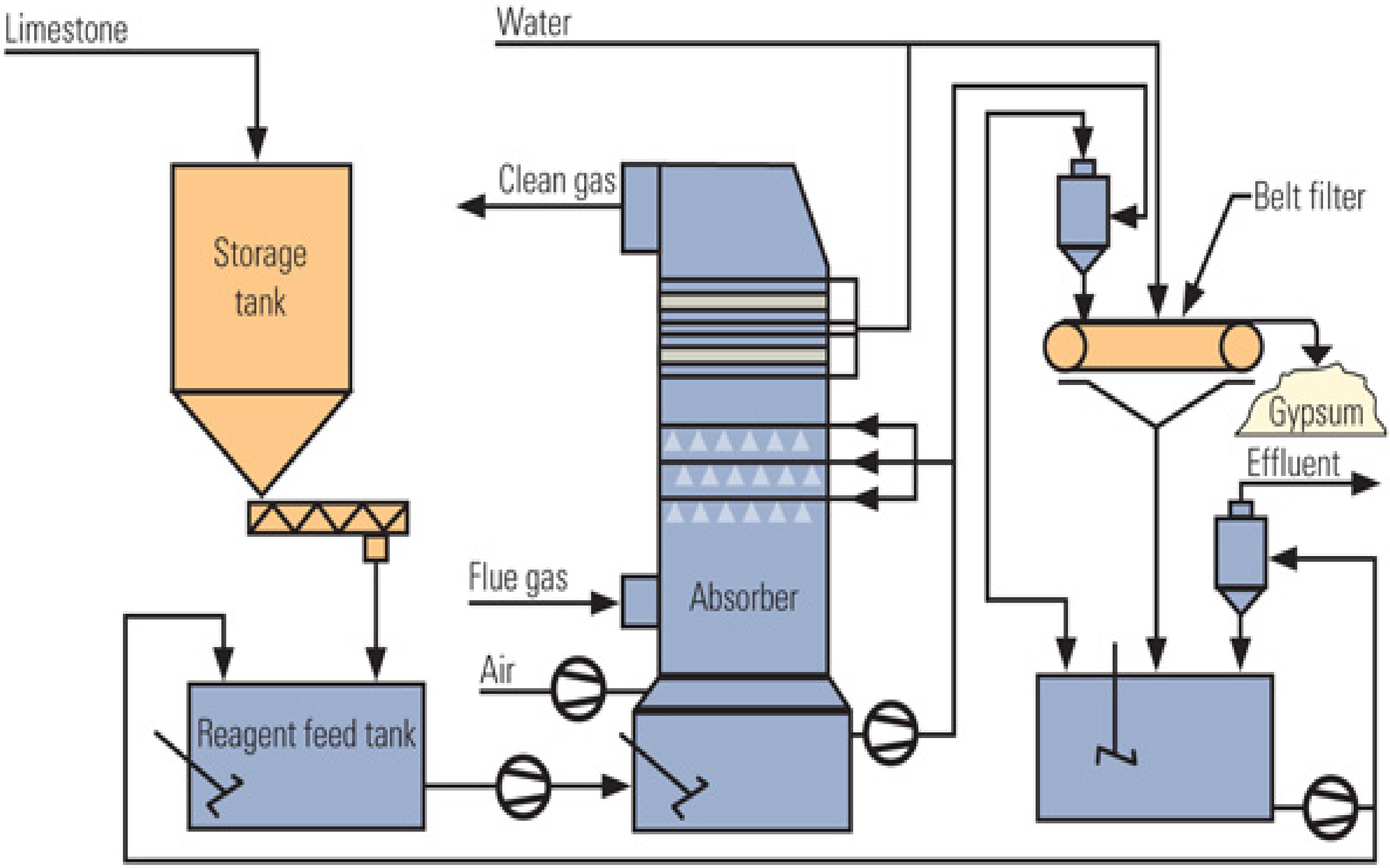
Typical Power Plant APC Configuration



Air Preheater (Fixed Tube and Regenerative)



Typical Limestone FGD Unit



Example of Operational FGD System

Key APC Considerations Affecting Hg Control and Hg Control Equipment Selection

- Selective Catalytic Reduction (SCR)
- Dry Versus Wet collection
- Hg Content of Coal
- Halogen (Chlorine) Content of Coal
- Sulfur Content of Coal
- Ash Loss On Ignition

Primary Hg Control Technologies

- **Carbon Injection (ACI)**
  - Brominated (B-PAC)
  - Non-brominated
  - Requires Dry Collection
- **Oxidation**
  - Inorganic bromides
  - Hydrogen bromide (CB&I EMO®)
- **Combinations/Other**
  - EMO + PAC
  - Amended Silicates

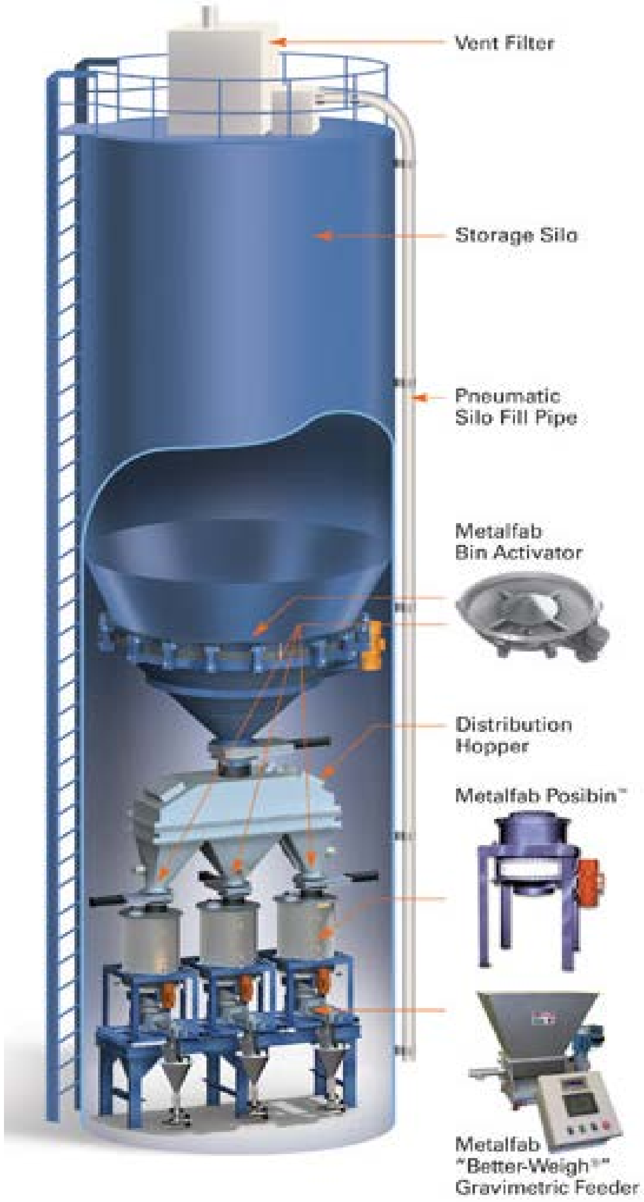
No Universal Control Solution

EACH FACILITY IS UNIQUE

CB&I provides various sizes of portable systems and routinely conducts site-specific testing

Powdered Activated Carbon (PAC) Systems

- Off Loading
- Storage Silo
- Mass Feeder
- Pneumatic Conveyance
- Lances
- Control System
- Primary and Secondary Solids Collection



IBS (Various Trade Names)

- Tanker Offloading
- Chemical Storage
- Injection Pump Skid (typically added at coal pulverizer)
- Controls

EMO® Injection System Features

- Tanker Offloading Skid
- Storage Tank
- Mixing/Dilution Module
- Control System
- Injection Lances

  (Economizer Outlet - typical)

Pros and Cons – PAC Systems (ACI)

Advantages

- Low cost
- Considerable industry experience
- Effective

Disadvantages

- Carbon surface fouling at high SO_2 levels
- Carbon surface fouling by other species
- PAC contaminates ash, limiting resale potential – landfill $$
- Abrasive
- May require secondary FFBH
- Difficulty in troubleshooting pluggage issues

Pros and Cons – EMO®

Advantages

- Low Overall Cost
- Highly effective in oxidizing Hg
- Concurrent EMO® and ACI very cost effective
- Best performance with both FFBH + FGD
- Br much more effective oxidation than Cl

Disadvantages

- Limited applications for ESP-only
- Additional safety requirements for HBr

Typical Flue Gas Composition (PRB Coal)

Component	Units	Combustion Outlet	Economizer Outlet	Stack
Ash	gr/dscf	3.7	3.7	0.004
SO_2	ppmdv	< 900	< 900	< 1
HCl	ppmdv	< 10	< 10	< 0.01
Hg	lb/Tbtu	8	8	<1.2
HBr	ppmdv	0	**5-10**	**0.005-0.01**

Note: PRB Coal 50 ppm Cl, Bitmuminous Coal 50- 2,100 ppm Cl

Pros and Cons - Inorganic Bromide

Advantages

- Least expensive feed system
- Simple addition to coal during feed process

Disadvantages

- Partial availability of Br (NaBr, $CaBr_2$)
- High effective cost (higher reagent cost than competing technologies)
- Limited maximum dosing

Potential for Serious Problems

- Can cause degradation of APH baskets (Regenerative type)
- Boiler tube compatibility issues (Ca, Na) – low melting salts

Inorganic Bromide ($CaBr_2$, NaBr)

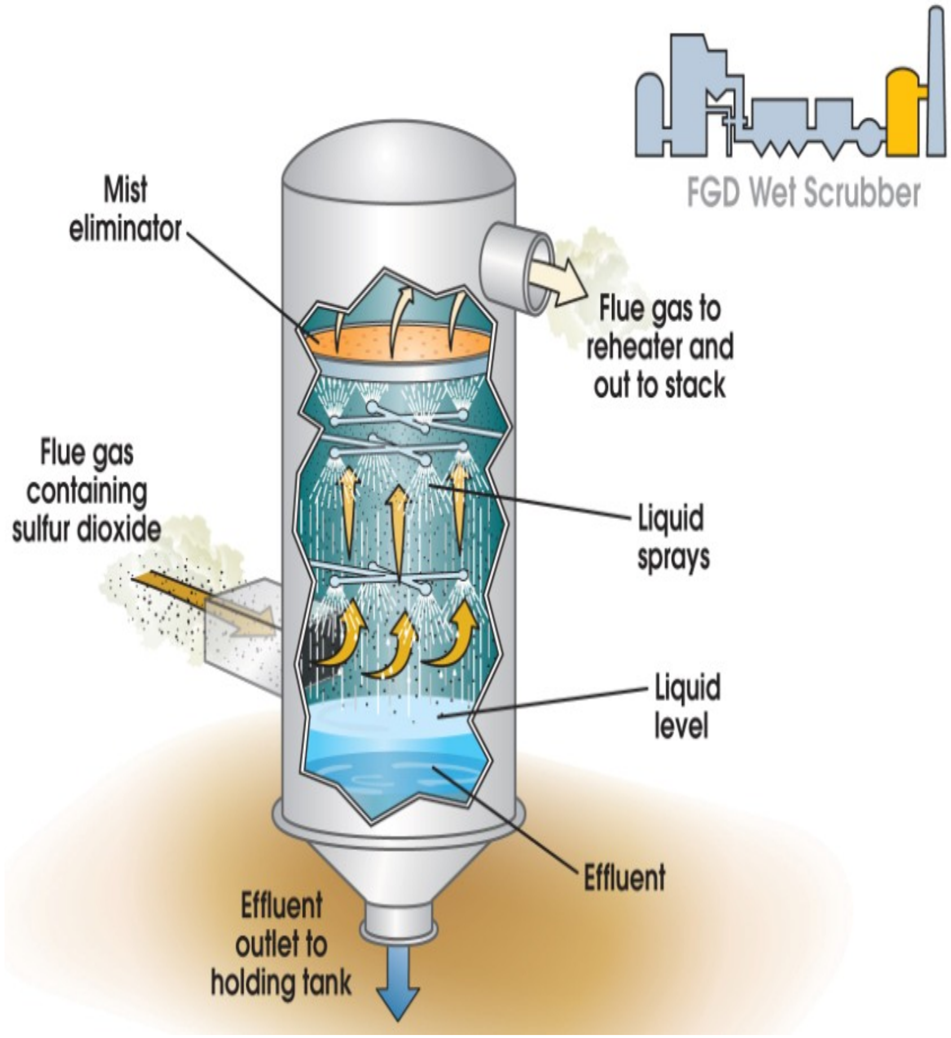
Corrosion

- Primarily affects regenerative APHs
- When heat storage medium “baskets” rotate to heat the incoming air, a small fraction of the basket is briefly below H_2SO_4 dew point (280-300 °F, typical)
- $CaBr_2$, NaBr solids collect on basket mix with condensed H_2SO_4 and react to form HBr, Br_2 mixed with H_2SO_4
- Problem is exacerbated if baskets are purged with steam to remove accumulated ash
- Vapor phase HBr has not been shown to contribute to this type of chemical attack (HBr dew point 60-100°F)

Mercury Re-emission Control

Mercury re-emission occurs across a wet FGD when oxidized (or ionic) mercury converts back to its elemental form and subsequently returns to the process stream, increasing total mercury in stack emissions.

FGD Mercury Re-Emission



Across the FGD:

- **$CaCO_3$ + SO2 → CaSO3**
  (Inhibited Oxidation)
- **$CaCO_3$ + O2 +SO2 → CaSO4**
  (*Forced Oxidization)*

Predominant form of oxidized Hg in the flue gas is HgCl, HgCl2, Hg2Cl2

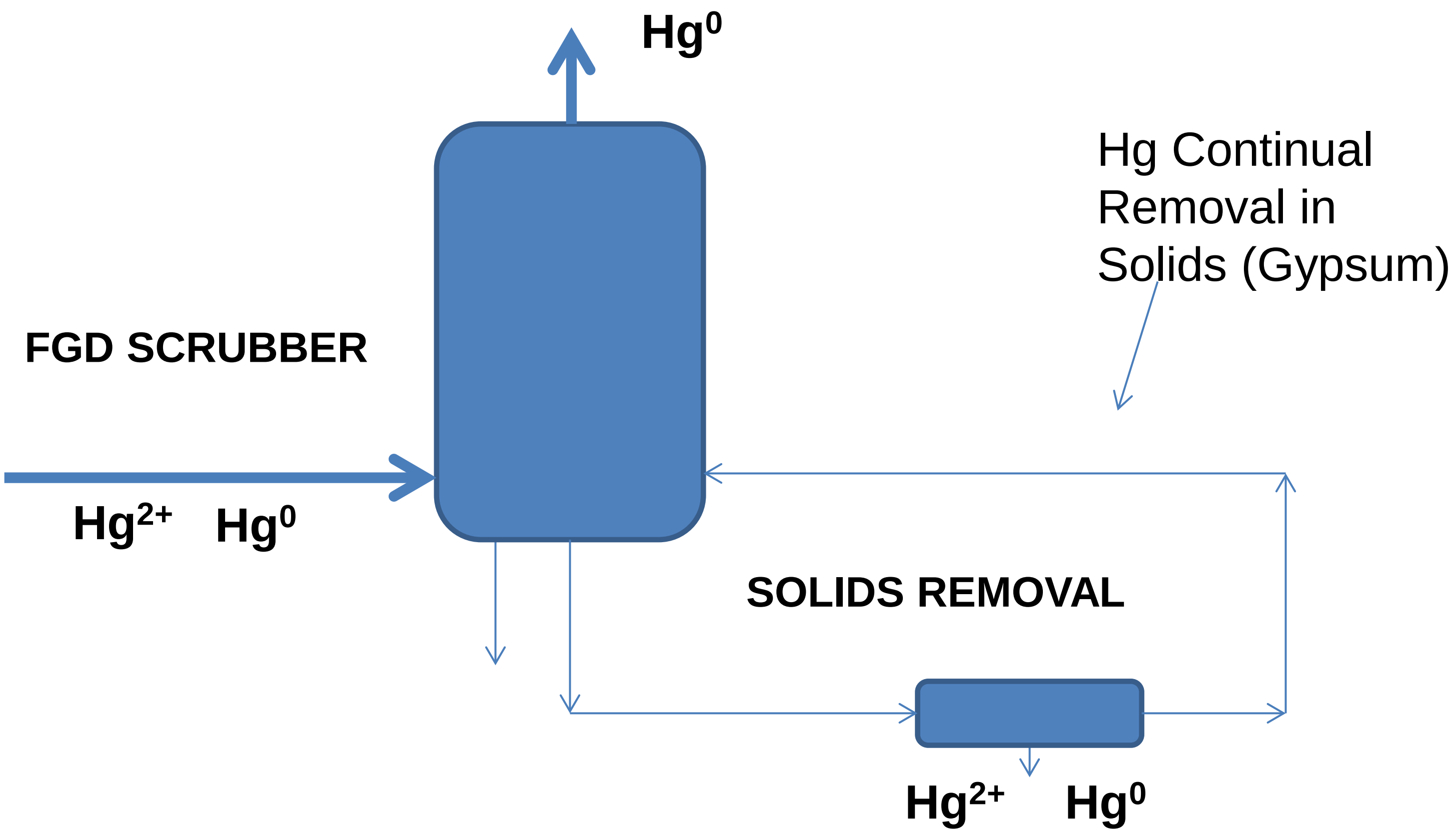
- **HgCl, HgCl2, Hg2Cl2 → $Hg^{(0)}$**

(Reducing Reaction – Hg Reemission)

Hg Re-Emission: The Chemical reduction of Hg^{+} and Hg^{2+} to Hg^{0} within a scrubber system (e.g., FGD scrubber)

$$Hg^{2+} + 2e^{-} \rightarrow Hg^{0}$$

Soluble Volatile



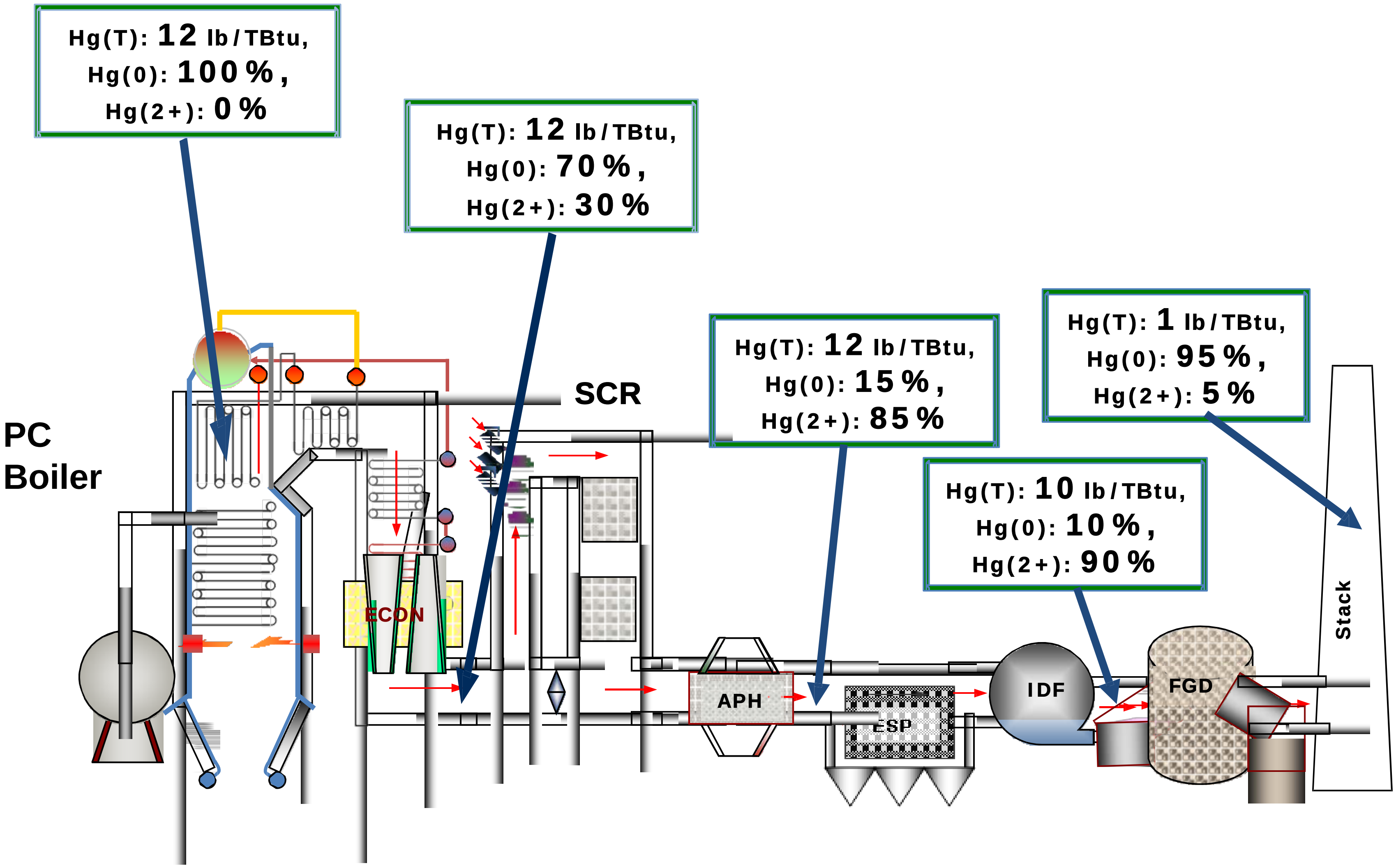
How Significant is Hg Re-Emission

- Highly facility-specific
- Routine FGD process adjustments can influence re-emission
- Can be transient
- Large hold-up volumes complicate evaluation

EPA Study of Factors Affecting Re-Emission

- Degree of oxidation (forced air rate)
- Halogen content
- pH
- ORP
- Type of FGD (lime, limestone, dual alkali, etc.)
- Complex chemical interactions

FGD Re-Emissions



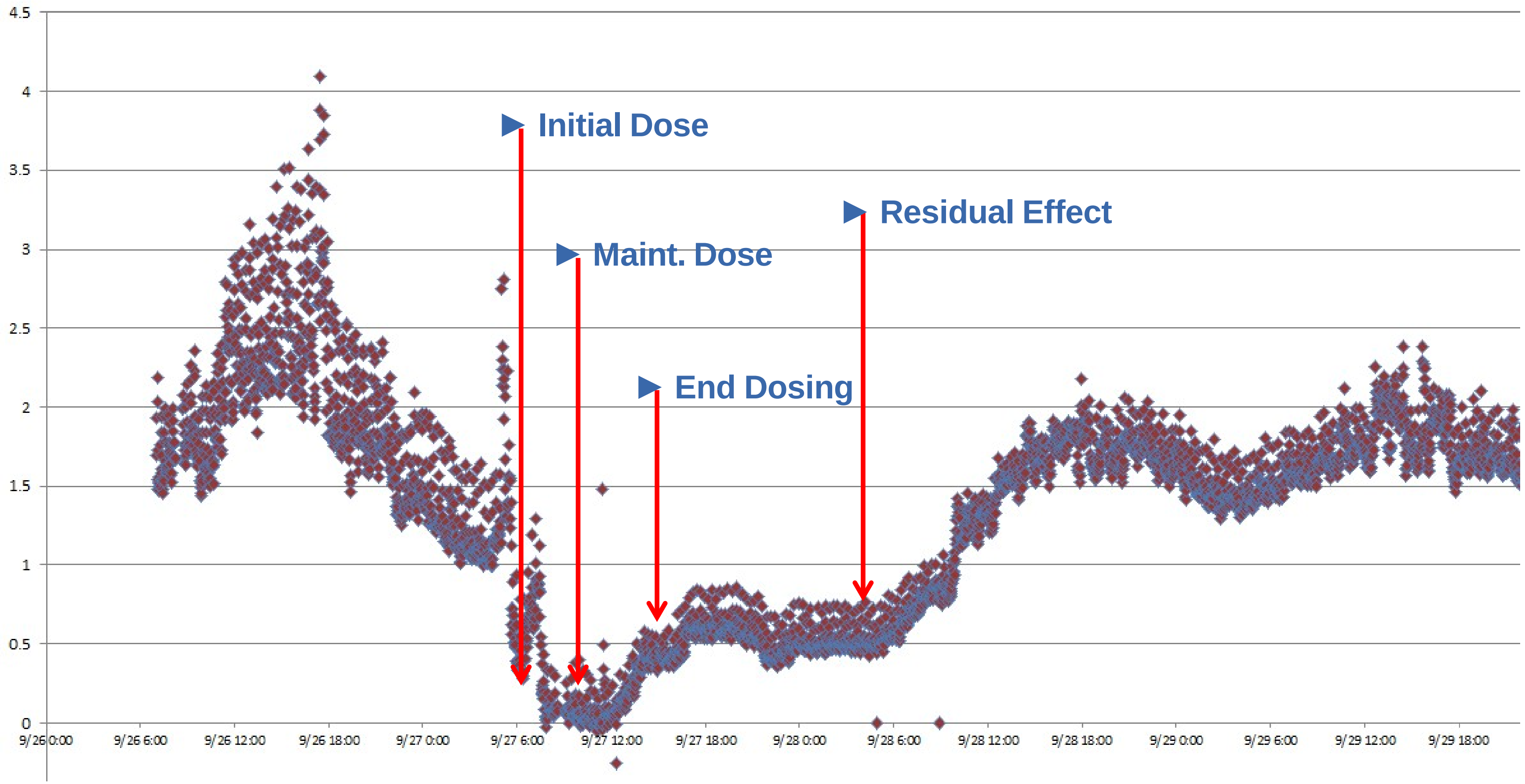
If more than 1.0 lb/TBtu of stack Hg emission is observed, there is Hg re-emission across the FGD.

REDOX Hg^{RPC} is a slurry consisting of insoluble sulfides and other proprietary constituents

- Provides Hg control through a chemical reaction within FGD slurry sump
- Produces a highly stable solid product
- Hg^{2+} (aq) + S^{2-} → HgS (s)

stabilizers, catalysts

Redox-Hg^{RPC} Preliminary Test



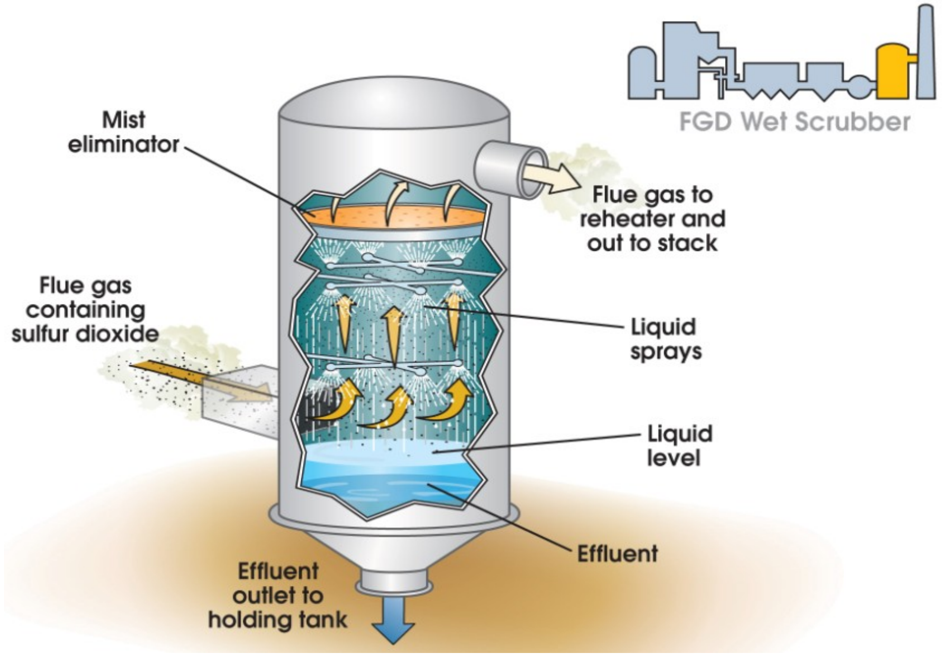
Baseline Stack Hg(T) varied between **0.87** lb/TBtu and **4.09** lb/TBtu, averaged at **1.82** lb/TBtu

Redox-HgRPC initial dosing started at 8:36 on 9/27/2013 at **~500** GPH for 30 minutes, stack Hg(T) reduced down to **0.50** lb/TBtu on average

Redox-HgRPC maintenance dosing started at 11:36 on 9/27/2013 at **~80** GPH for 6 hours, stack Hg(T) reduced down to **0.10** lb/TBtu on average

Redox-HgRPC maintenance dosing stopped at 16:30 on 9/27/2013, the memory effect lasted for 10 hours before the stack Hg recovered

Redox- Hg^{RPC} Parametric Test



Date (2013)	Test	Hg in Coal Blend lb/TBtu	Dose/Scrubber Redox-Hg^{RPC} GPH	FGD Inlet Hg^0 lb/TBtu	FGD Inlet Hg^T lb/TBtu	FGD Inlet % Hg Oxidization	Stack Hg^0 lb/TBtu	Stack Hg^T lb/TBtu	Stack % Hg Re-emission	System % Overall Hg Removal
7/11	Baseline	6	0	0.68	3.13	88.7%	1.06	1.41	56%	76.5%
7/25	Baseline	9	0	0.15	5.91	98.3%	1.95	2.25	1200%	75.0%
11/11	Baseline	12	0	0.36	6.72	97.0%	1.21	1.46	236%	87.8%
11/12	Parametric	12	40	0.90	10.99	92.5%	0.40	0.59	0%	95.1%
11/19	Parametric	12	20	1.08	9.60	91.0%	0.30	0.46	0%	96.2%
11/19	Parametric	12	10	0.93	8.55	92.3%	0.23	0.33	0%	97.3%
11/20	Parametric	12	5	0.84	9.88	93.0%	0.31	0.50	0%	95.8%

Impacts of Redox- Hg^{RPC} on FGD Slurry

Hg in FGD slurry solid

Conditions	Hg Concentration (mg/kg)
Baseline	0.12
LD Hg RPC	0.16
MD Hg RPC	0.15
HD Hg RPC	0.20

LD = low dose (10 GPH)

MD = low dose (20 GPH)

HD = low dose (40 GPH)

Hg in FGD slurry liquid

Conditions	Hg Concentration (mg/L)	Det. Limit (mg/L)
Baseline	0.0029	0.0002
LD Hg RPC	BDL	0.0002
MD Hg RPC	BDL	0.0002
HD Hg RPC	BDL	0.0002

BDL = below detection level

Pros and Cons of Redox-Hg[RPC]

Advantages

- Effectively prevents Hg re-emission across the FGD
- Maintains gypsum quality for re-use of ash
- Significantly more cost-effective when compared to other available Hg re-emission chemicals (110% to 150%)
- Demobilizes Hg through creation of thermodynamically stable compound (in nature as mineral vermillion)

Disadvantages

- Difficulty in providing real-time slurry process feedback for control (typically ratio controlled based on unit load, and coal Hg content).

Other Applications

Applications in gaseous, sludge, wastewater and solids treatment:

- REDOX Hg^{RPC}
- Ferroblack®

FerroBlack - applications treating plating waste sludges with high chromium, nickel, copper concentrations. Reduce environmental mobility.

- Stabilization of plating waste soils
- Stabilization of Hg sludges

FerroBlack – applications in wastewater treatment to remove and stabilize heavy metals

EMO®

Mercury Oxidation Technology

REDOX Hg^{RPC}

Mercury Re-Emission Control