

REINHOLD ENVIRONMENTAL Ltd.



**2015 APC Round Table
& Expo Presentation**

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Meeting Part-per-Trillion Mercury Limits and Impacts of MACT Changes

July 13, 2015

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Outline

- Mercury regulation
- Mercury treatment
- Treatability variables
- Scrubber operation impacts
- Approach to evaluate scrubber/APC changes
- Case study example
- Summary



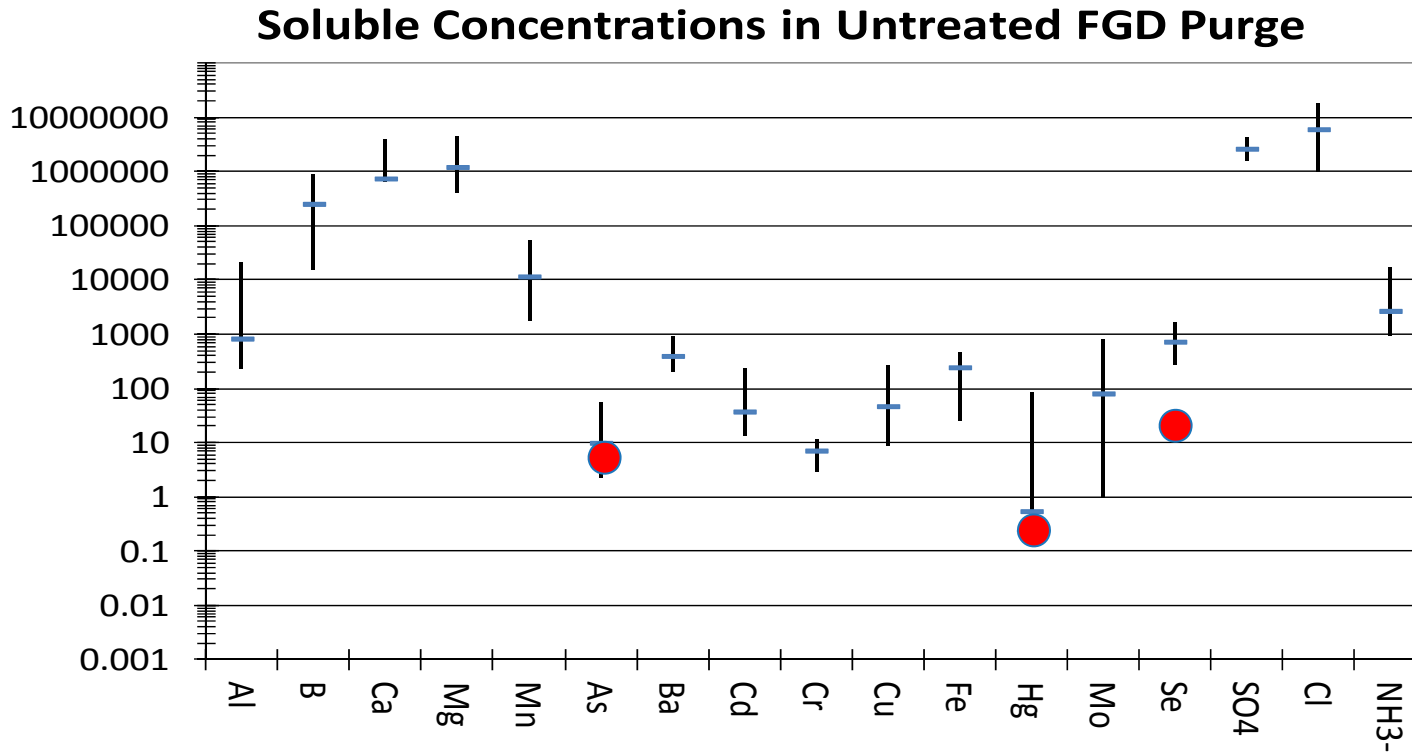
Mercury Regulation

Mercury in water regulations



- Technology based effluent limitation guideline for steam electric utilities – draft set at 119 ng/L average on FGD blowdown
- Water quality based – based on water quality standard, receiving stream designated uses, and impairment, set at the end of pipe
 - Great Lakes Initiative – 1.3 ng/L (1.3 part per trillion)
 - ORSANCO (Ohio River Valley Sanitary Water commission) – 12 ng/L
 - State of Kentucky standard – 51 ng/L

Characteristics of FGD Blowdown Soluble Concentrations (ug/L)



Dot (●) = Proposed Effluent Limitation Guideline
 Dash (—) = Median. Range is 5th to 95th percentile.

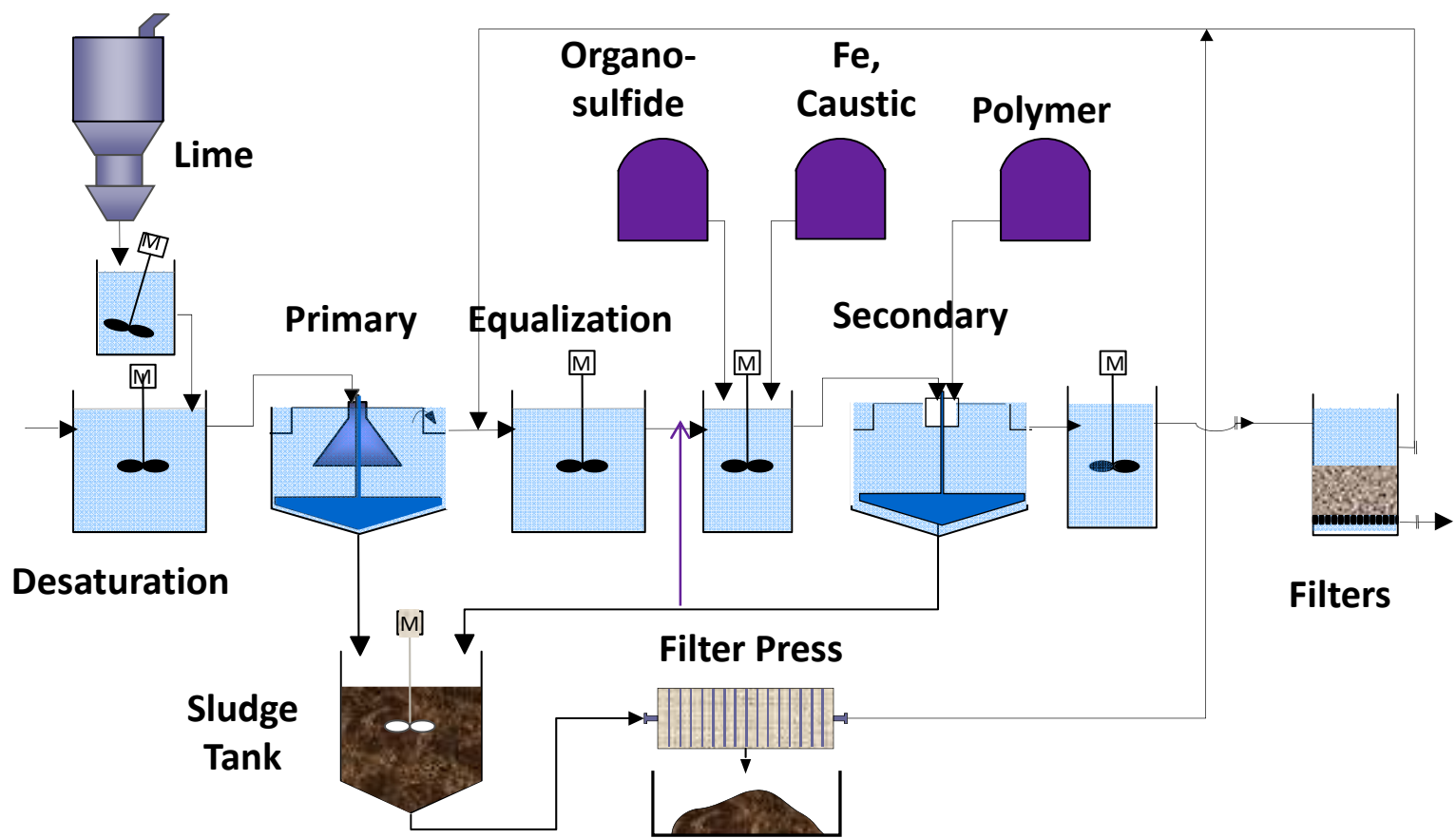
* Information from EPRI funded research



Mercury Treatment

DESIGN CONSIDERATIONS

TYPICAL PHYSICAL/CHEMICAL TREATMENT



Metals Removal Evolved From Hydroxide Precipitation...

- Limited to ppb to ppm limits
- High pH required
- Different optimal pH for different metals

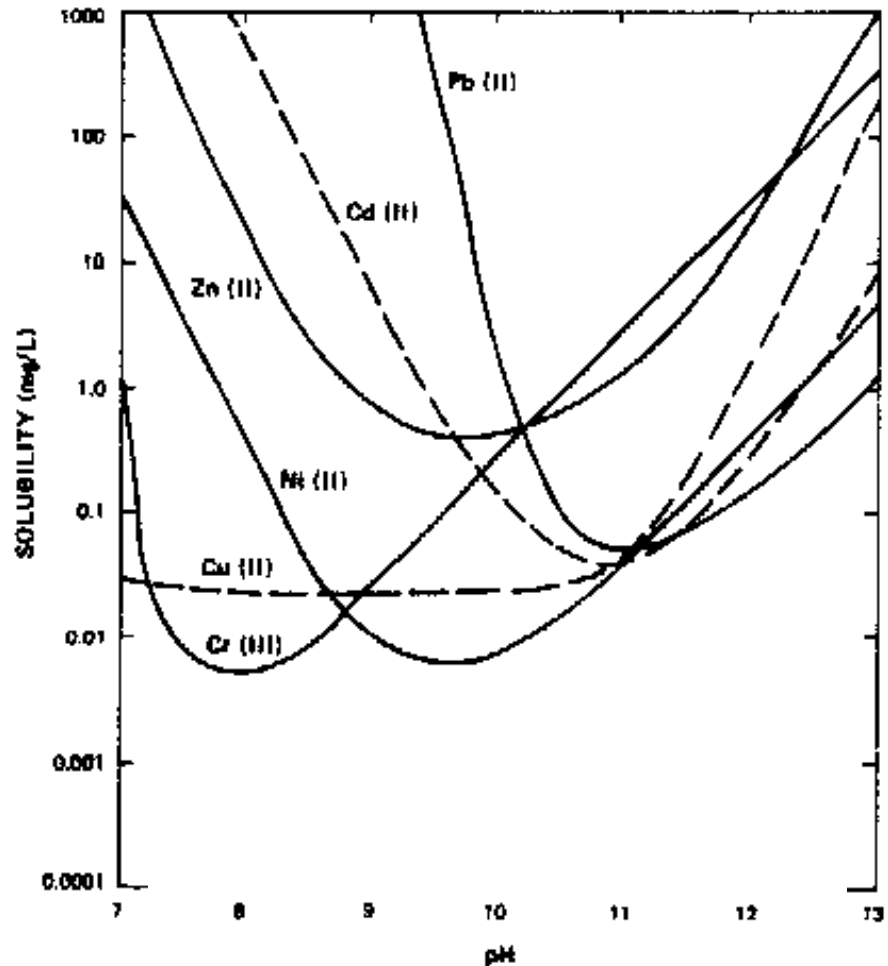


FIGURE 1. Solubilities of metal hydroxides as a function of pH.

.....To Sulfide Precipitation

- Low solubility
- Theoretically - 330 liters of water needed to dissolve 1 molecule of HgS
- Precipitation is rapid
- Broad pH range
- Precipitates colloidal
- Sulfides toxic

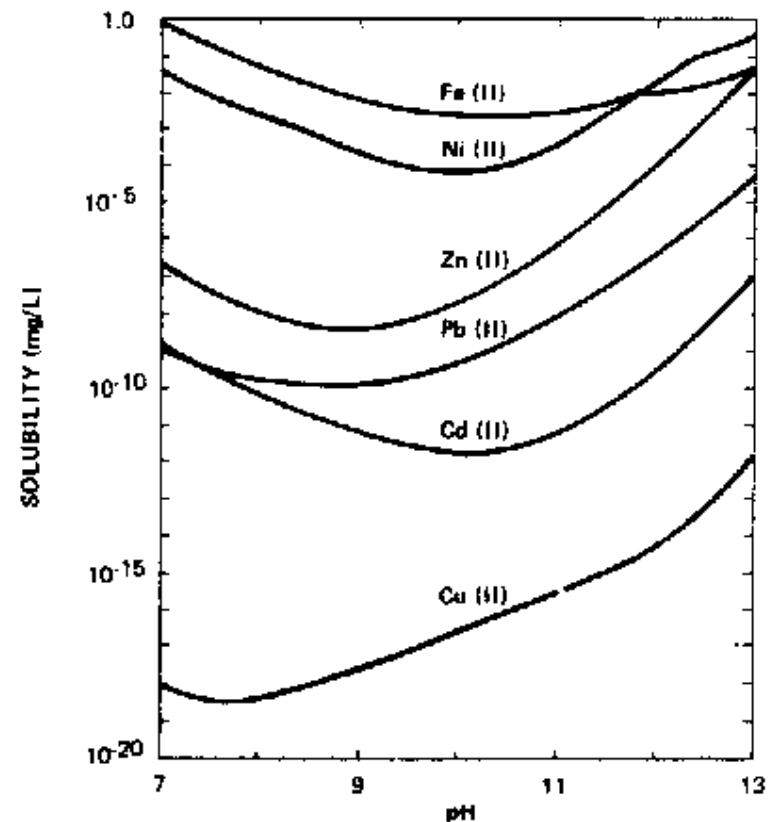
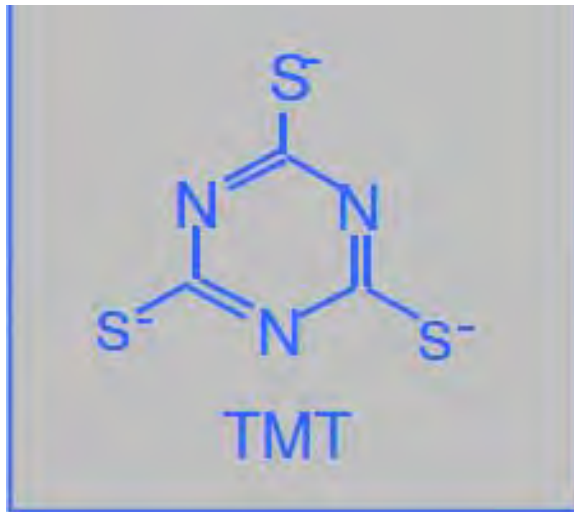


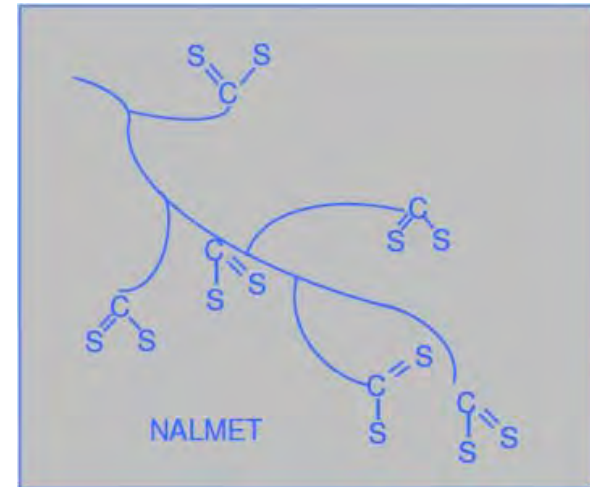
FIGURE 2. Metal solubilities with 10⁻⁶ molar sulfides as a function of pH.

.....To Organosulfide Precipitation

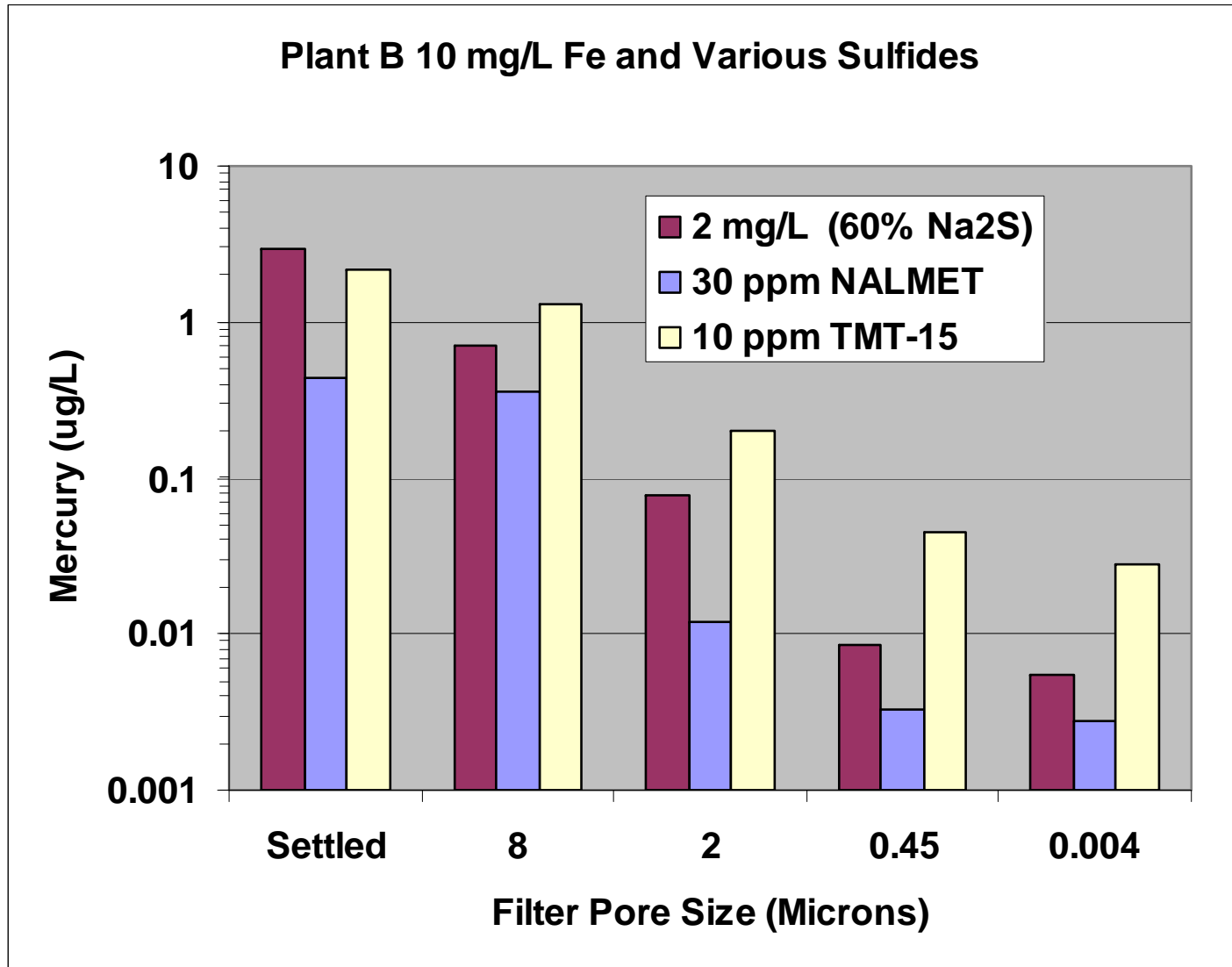


- TMT-15
 - Small molecule
 - Dependent on coagulation

- Nalmet 1689, 1691, Metclear
 - Larger molecule (5,000 MW)
 - Less dependent on coagulation



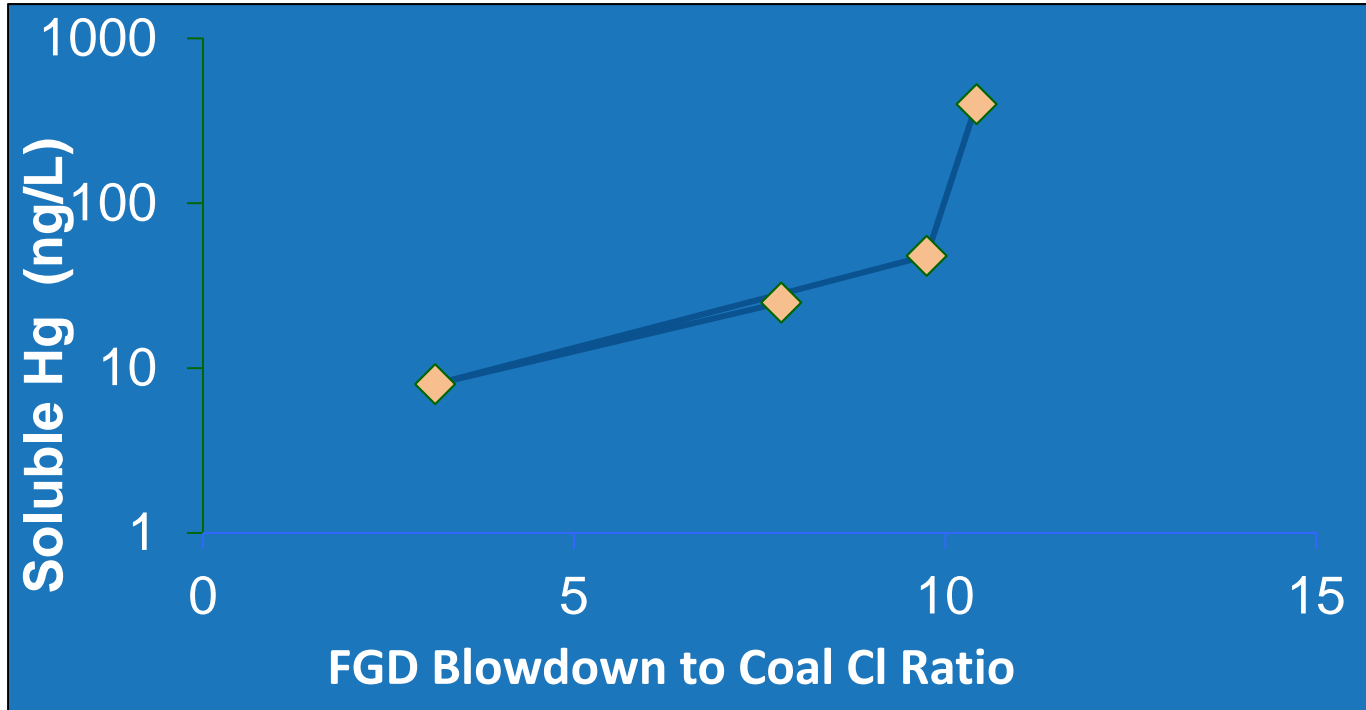
Comparison of Sulfide Addition Chemicals



Variables Affecting Treatment

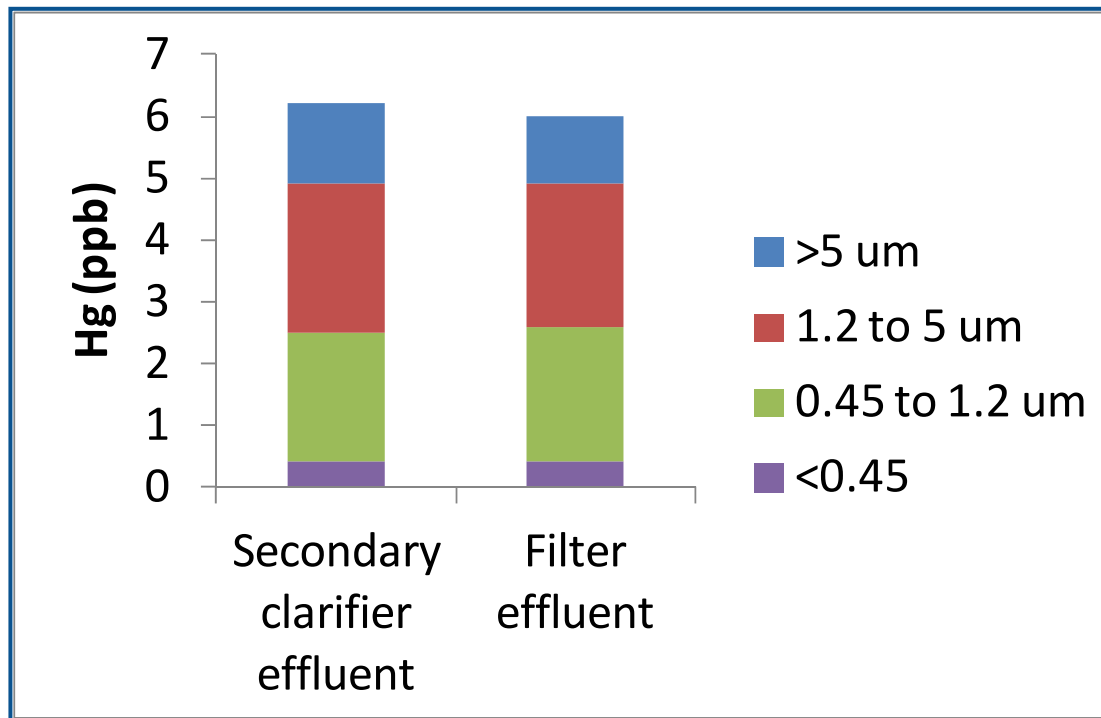
Physical / Chemical Treatment Mercury Removal

Long absorber hydraulic residence times adversely impact mercury solubility



Physical / Chemical Treatment Mercury Removal

Mercury precipitation can form colloidal particles not removed by sand filtration



Physical / Chemical Treatment Mercury Removal

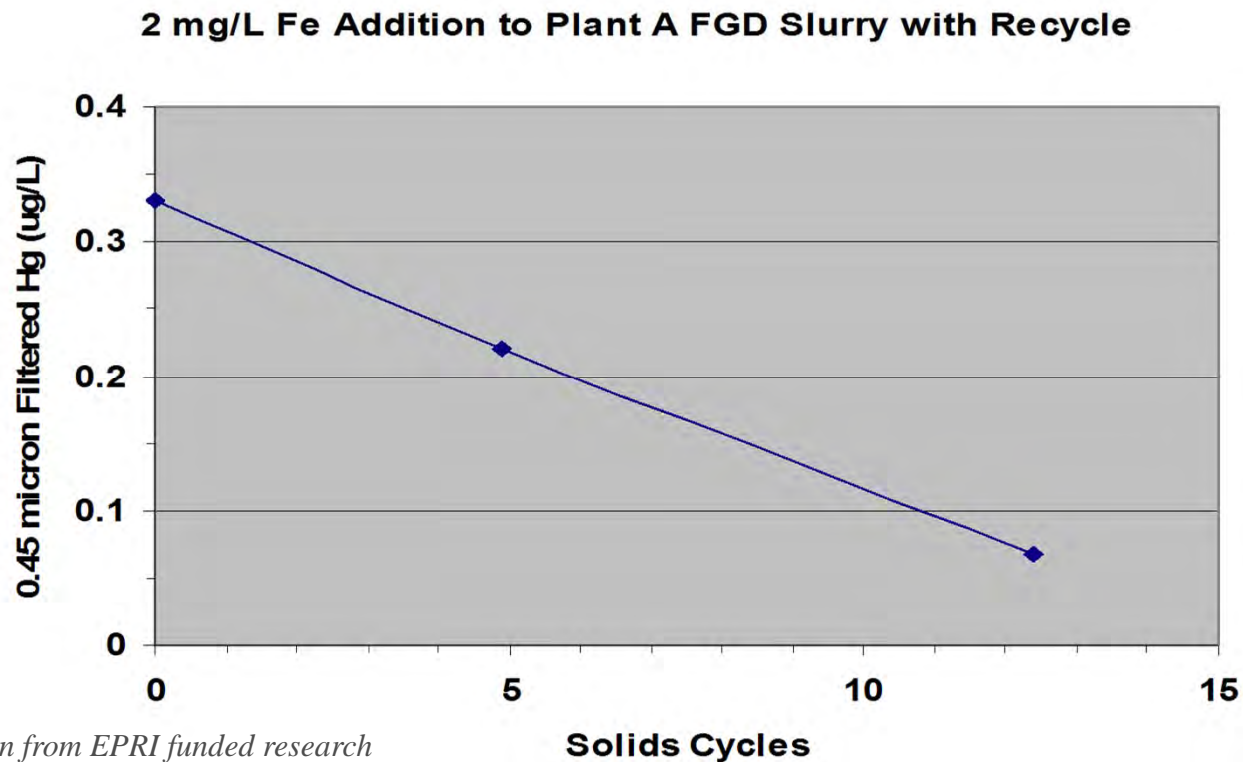
**Despite membrane filtration – mercury can
sometimes resist treatment**

**Mysterious yellow color –
result 10 ppb Hg**



Physical / Chemical Treatment Design

Iron reduces mercury solubility when solids are recycled

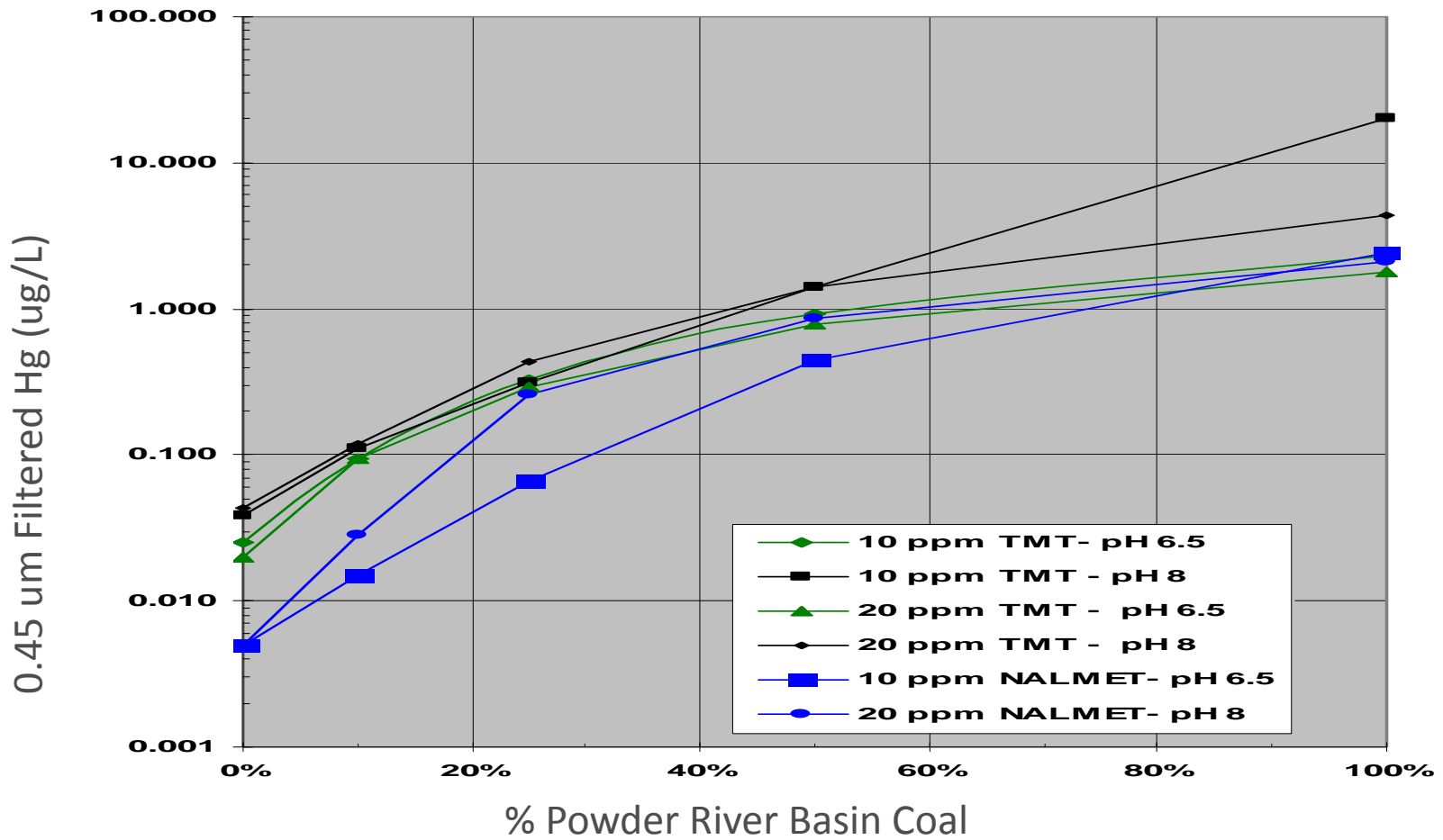


**Information from EPRI funded research*

SCRUBBER CONSIDERATIONS

SOURCE OF COAL IMPACTS TREATABILITY

EASTERN BITUMINOUS VS POWDER RIVER BASIN

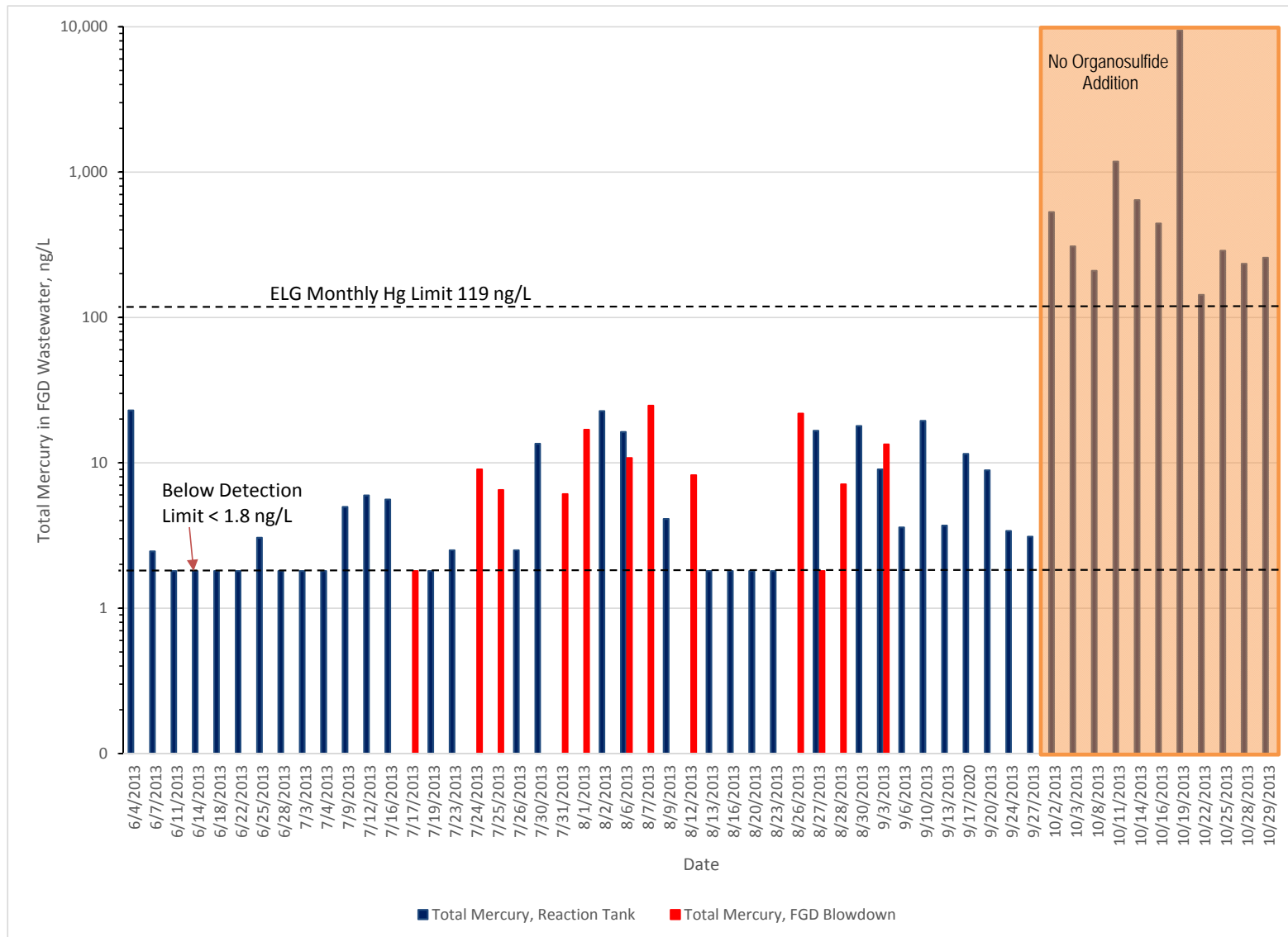


Case study – Mercury control scrubber additive

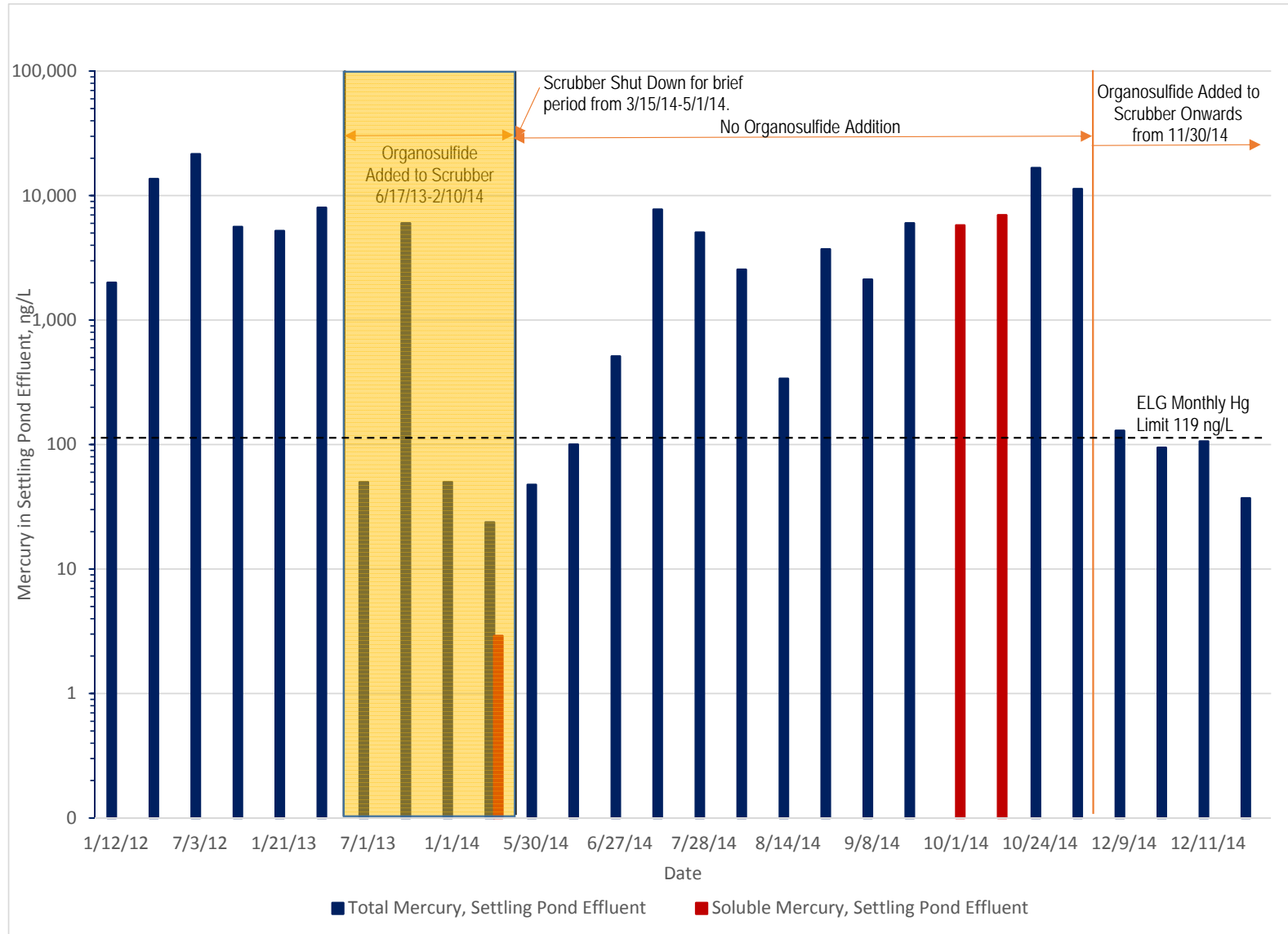
Organosulfide Case Study: Addition in Wet Scrubber

- Sampling for Effluent Limitation Guideline showed low mercury concentrations in settled FGD wastewater
- Multiple Plants(s) at southeast Utility add a Nalco organosulfide product to FGD Make-up Supply Tank to meet Mercury air limits (MerControl).
- Organosulfide addition to at least one scrubber at each site - the blowdowns show a reduction in mercury in the settled samples.
 - Soluble mercury converted to particulates, which are captured and stabilized in gypsum solids.
- Based on the operation of the scrubber, the additive could reach concentrations as high as 900 ppm in the blowdown, assuming no other losses.
 - Other water quality considerations- whole effluent toxicity.

MerControl Case Study 1 (Lower Baseline Mercury): Reduction Significant



Organosulfide Case Study 2 (Higher Baseline Mercury)



Case Study #2 – Evaluation of Iodide Additive Trial

Evaluation of APC changes LGE-KU

- Trial addition of potassium iodide to coal to improve Hg capture
- Sampling objectives were to evaluate
 - fate of elemental iodide
 - changes in coal combustion residuals
 - FGD wastewater changes
 - toxicity
 - mercury treatability



Coal Additive Case Study

- Mercury concentrations decreased in the scrubber wastewater over the trial.
 - Observed decreases in mercury for the FGD wastewater and gypsum solids – may be due to experimental variability.
- Mercury increased in fabric filter fly ash
- Mercury content decreases slightly in coal feed during this time period.

Observed Change in Mercury Concentrations

Sample	Mercury
Day 0 ESP Fly Ash (µg/kg)	120
Day 8 ESP Fly Ash (µg/kg)	57
ESP Increase/Decrease (µg/kg)	-63
Day 0 PJFF Fly Ash (µg/kg)	180
Day 8 PJFF Fly Ash (µg/kg)	490
PJFF Increase/Decrease (µg/kg)	310
Day 0 Gypsum (µg/kg)	920
Day 8 Gypsum (µg/kg)	410
Gypsum Increase/Decrease (µg/kg)	-510
Day 0 Bottom Ash (BA) (µg/kg)	15 J
Day 8 Bottom Ash (µg/kg)	33
BA Increase/Decrease (µg/kg)	18
Day 0 Coal Feed (µg/kg)	46
Day 8 Coal Feed (µg/kg)	38
Coal Increase/Decrease (µg/kg)	-8
Day 0 FGD Blowdown (µg/L) ^a	0.050
Day 8 FGD Blowdown (µg/L) ^a	0.016
FGD Increase/Decrease (µg/L)	-0.034
a. Mercury represents soluble (<0.45 µm) analysis.	

Coal Additive Case Study

Observed Change in Iodine Concentrations

Sample	Iodine	Iodide
Day 0 ESP Fly Ash (µg/kg)	40	--
Day 8 ESP Fly Ash (µg/kg)	150	--
ESP Increase/Decrease (µg/kg)	110	--
Day 0 PJFF Fly Ash (µg/kg)	290	--
Day 8 PJFF Fly Ash (µg/kg)	280	--
PJFF Increase/Decrease (µg/kg)	-10	--
Day 0 Gypsum (µg/kg)	200	--
Day 8 Gypsum (µg/kg)	170	--
Gypsum Increase/Decrease (µg/kg)	-30	--
Day 0 Bottom Ash (BA) (µg/kg)	580	--
Day 8 Bottom Ash (µg/kg)	200	--
BA Increase/Decrease (µg/kg)	-380	--
Day 0 Coal Feed (µg/kg)	<10	--
Day 8 Coal Feed (µg/kg)	<10	--
Coal Increase/Decrease (µg/kg)	NA	--
Day 0 FGD Blowdown (µg/L) ^a	ND	1200
Day 8 FGD Blowdown (µg/L) ^a	ND	4400
FGD Increase/Decrease (µg/L)	--	3200

a. Iodide represent soluble (<0.45 µm) analysis.

- In contrast, the majority of the salts (i.e. iodide) end up in the FGD wastewater.
- This is also supported by mass balances.
- Iodine (oxidant) was non-detect.

Coal Additive Case Study: Decreased Toxicity and Reduced Effluent Hg Concentration

Acute Toxicity Results (Ceriodaphnia)

Parameter	Day 0 Simulated Outfall Effluent	Day 8 Simulated Outfall Effluent
LC50 (%)	25%	>50%
Iodine (µg/L)	<4.3	<4.3
pH	6.8	6.9
Conductivity (µS/cm)	6360	5700
TSS (mg/L)	158	123
Ammonia (mg/L as N)	3.45	1.40
Chloride (mg/L)	1300	1357
LC50 - Lethal Concentration to 50% of test organisms.		

- Daphnia Toxicity reduced in FGD Blowdown /cooling tower blowdown mixture.

- Mercury concentration reduced in FGD blowdown and organosulfide treated effluent.
- Starting Hg low due to organosulfide addition in the scrubber.

Results from Chemical Precipitation Jar Tests

Parameter	Day 0 FGD Untrt	Day 0 FGD Trt	Day 8 FGD Untrt	Day 8 FGD Trt
pH (s.u.)	6.3	8.5	6.8	8.5
Iodide, soluble (µg/L)	1200		4400	
Mercury, soluble (ng/L)	50	11	16	7.71 J
TSS (mg/L)	7	2.2 J	4.40 J	3.6 J
TDS (mg/L)	7,670		7,030	
COD (mg/L)	326		176	

Summary

- Mercury discharges are being limited to parts per trillion levels in some regions
- Soluble Hg in FGD blowdown 1-100 ppb
- Treatment performance is dependent on coal, APC, additives, treatment chemical, formation of colloidal particles
- Operation of FGD scrubber and upstream APC system can impact Hg treatability
- Planned trials offer opportunity to evaluate impacts on wastewater treatment, and evaluate based on air quality as well as water quality impacts