REINHOLD ENVIRONMENTAL Ltd.

2018 APC & Wastewater Round Table & Expo Presentation

July 23 & 24, 2018 in Lexington, KY / Hosted by East Kentucky Power Coop

FLUE GAS DESULFURIZATION WASTEWATER POLLUTANT REMOVAL

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24 JULY 2018

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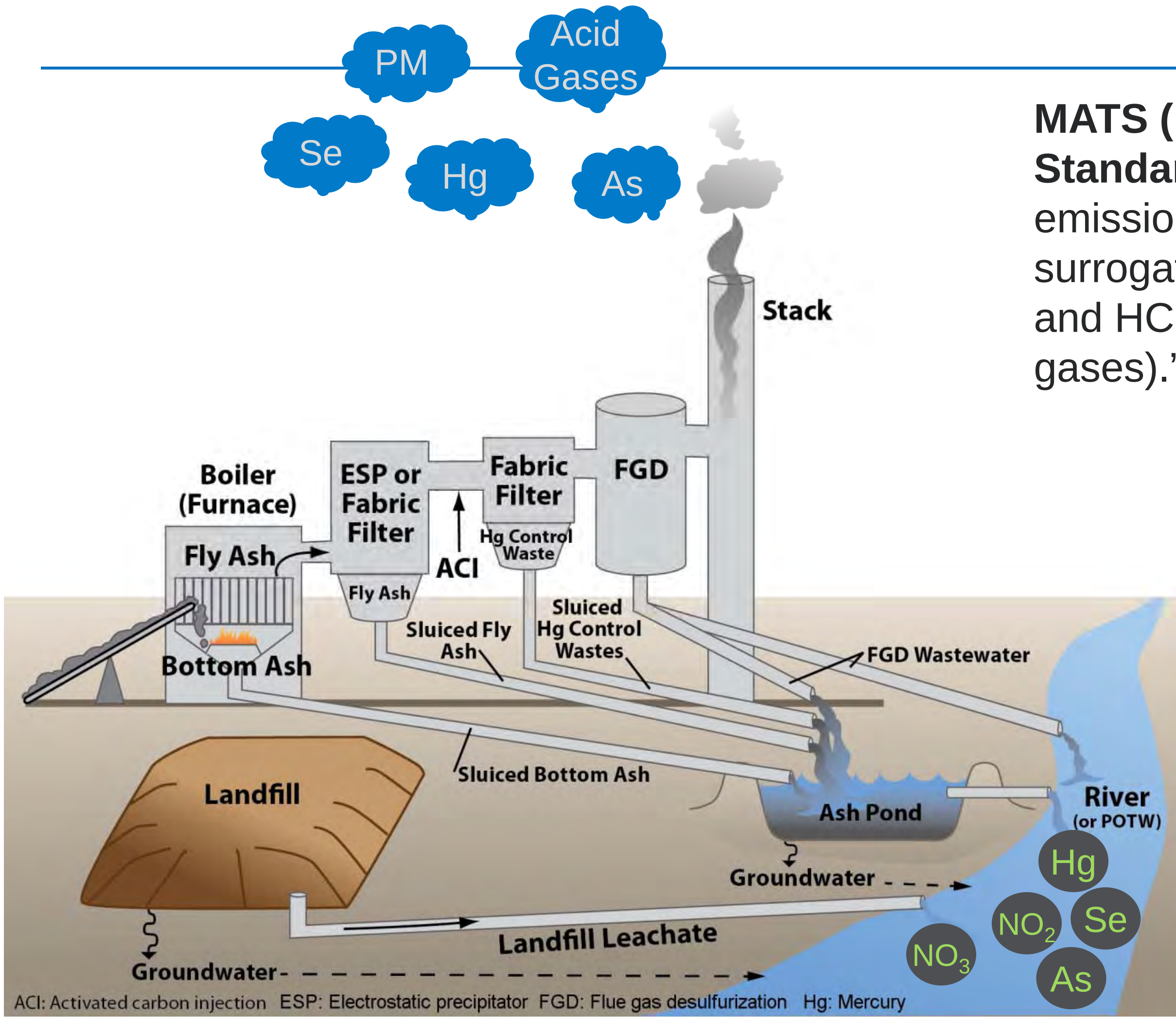
Agenda

- MATS and ELG Compliance
- Pollutant Removal Strategies
- Trace Elements Mass Balance – Holistic Approach
- Physical-Chemical Process
  - Liquid/Solids Separation
  - Sedimentation by Gravity
  - Filtration
- Mercury and Arsenic Removal
  - Precipitation/Co-precipitation
  - Adsorption
- Selenium and Nitrogen Removal
  - Biological

MATS and ELG Compliance

MATS and ELG compliance



Gabe Ravin Duke Energy Required to Pay Towns, Cities for Degraded Water. *North Carolina Health News. www.northcarolinahealthnews.org/2015/06/19/duke-energy-required -to-pay-towns-cities-for-deraded-water/*

MATS (Mercury and Air Toxic Standards) : "…establishes numerical emission limits for **mercury**, PM (a surrogate for toxic non-mercury metals), and HCL (a surrogate for all toxic acid gases)." **Compliance:** April 16, 2015.

ELG (Effluent Limitations Guidelines) : Establishes minimum permitting standards for discharges. **Final Rule:** Published November 3, 2015 (40 CFR Part 423 Part II) Federal Registry Vol.80 No.212.

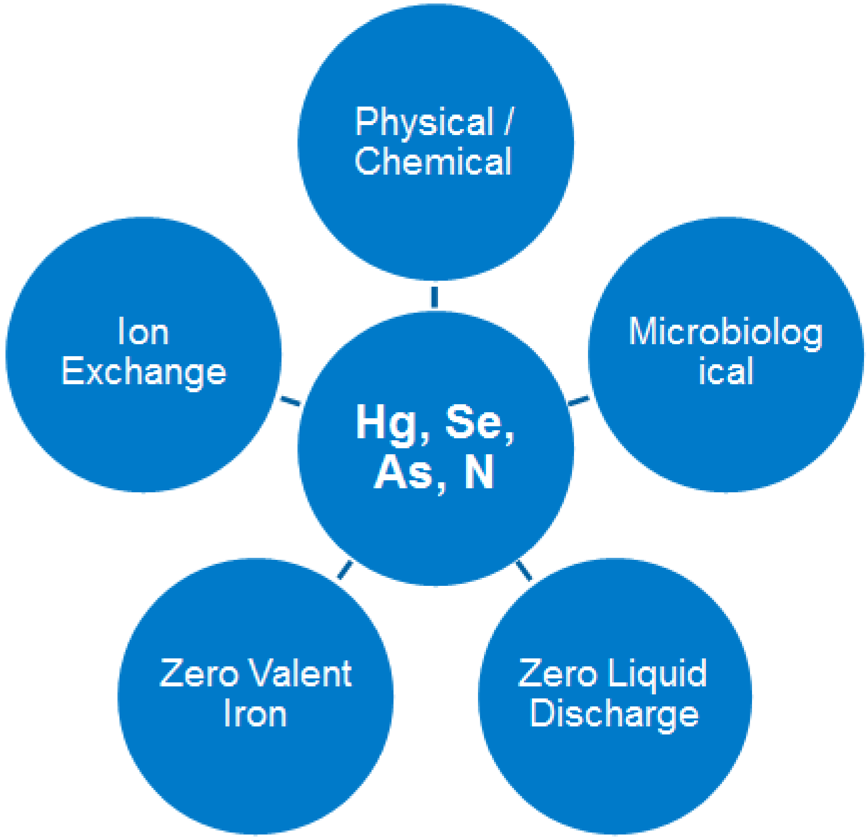
EPA Effluent Limit Guidelines (ELG)

Existing FGD Plants	Final ELG Limits[1]		
Limits	Design Avg[2]	Daily Max	Monthly Avg
As, µg/L (ppb)	5.98	11	8
Hg, ng/L (ppt)	159	788	356
NO_3^-/NO_2^- as N mg/L (ppm)	1.3	17	4.4
Se, µg/L (ppb)	7.5	23	12
Technology Based	Physical/Chemical Precipitation + Biological Treatment		

- Compliance runs from 2018 through 2023 based on state permitting.
- Becomes effective 60 days after publication.
- Two year extension for bottom ash transport water and FGD wastewater.
- Federal guidelines representing maximum discharge limits as guidance to regional regulators.

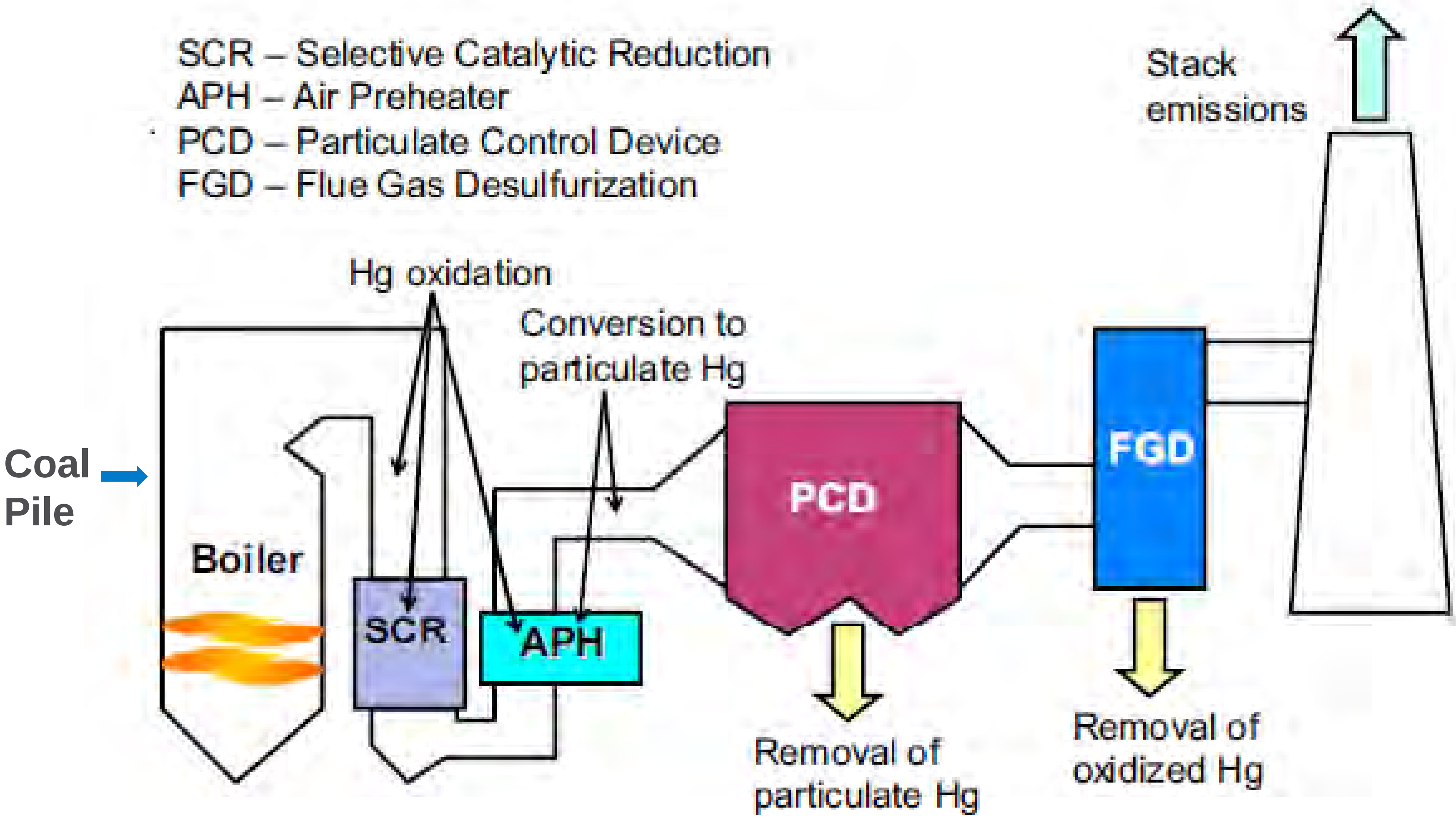
1. Federal Register, Vol. 80, No. 212. November 3, 2015. “Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category; Final Rule”
2. Suggested EPA design target for each pollutant to ensure meeting regulations due to routine variability.

Pollutant Removal Strategies



There is not one solution for all ELG pollutants.
BAT economically feasible

Trace Elements Mass Balance – Holistic Approach



Trace Elements Mass Balance – Some “Typical” Results

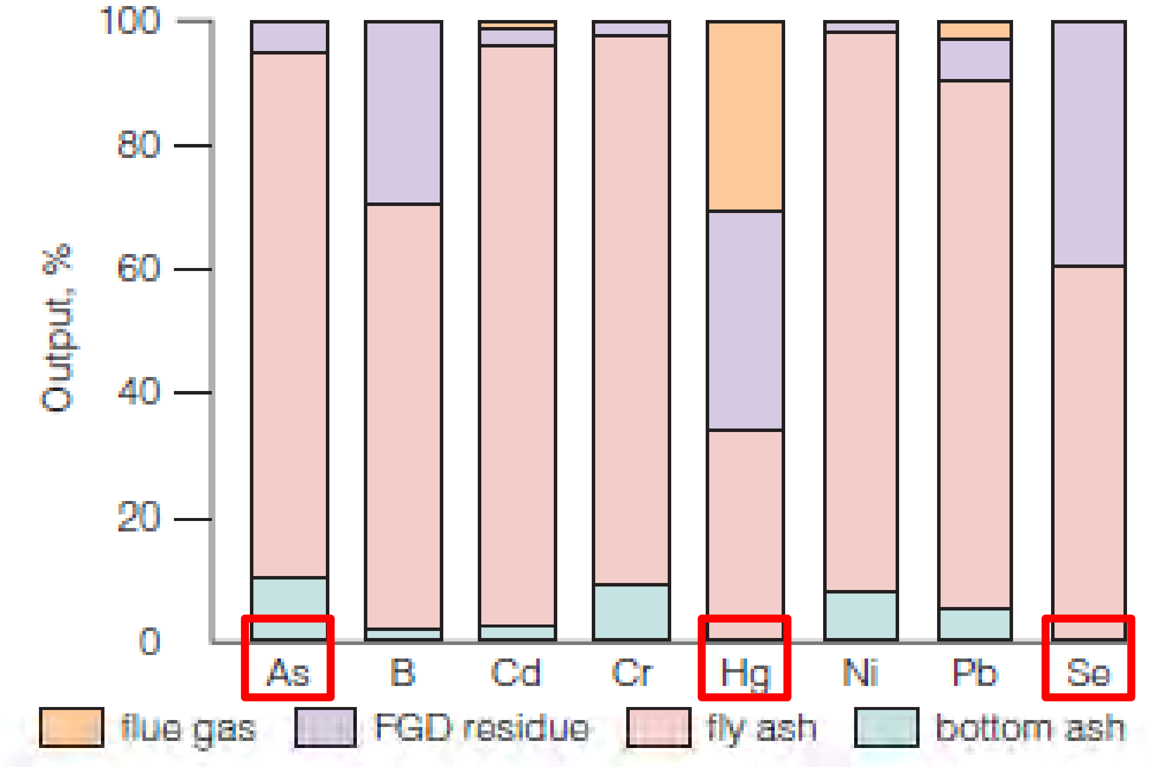


Figure 9 Trace element partitioning at a Danish pulverised coal combustion plants (Studstrup 3) (Zevenhoven and Kilpinen, 2001)

Distribution of selected TEs from a unit burning bituminous coal with an ESP and wet FGD.

Nalbandian, H. Trace element emissions from coal. *CCC/203* IEA Clean Coal Centre, September 2012, ISBN 978-92-9029-523-5.

Cost of Compliance: ELG

As and Hg Compliance in ELG	Physical and Chemical
Capital Costs	1-5X GPD in Dollars
Operating Costs	<1X GPD in Dollars
Se and N Compliance in ELG	**Biological/ Traditional**
Capital Costs	20-40X GPD in Dollars
Operating Costs	1X GPD in Dollars

Holistic approach – minimize influent of trace elements (TEs) and flow to wastewater

Physical-Chemical Process Solid/Liquid Separation

Contaminant Loading in Water

Dissolved Solids

Inorganic

- Mercury
- Arsenic
- Selenium
- Nitrate/Nitrite
- Heavy Metals
- Phosphate
- Ionic Species
- TDS
- Alkalinity
- Hardness

Organic

- BOD
- Chelants
- Aromatics
- Oils
- Greases

Suspended Solids

Inorganic

- Metals
- Mineral Scale
- Silt
- Mud

Organic

- Biosolids
- Greases
- Oils

Settleable Solids

Nonsettleable Solids

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Sedimentation/Clarification

Relative Settling Velocities vs. other particles in STILL water

Particle Size (mm)	Order of Magnitude	Time Required to Settle 1 Foot
10.0	Gravel	0.3 Seconds
1.0	Coarse Sand	3 Seconds
0.1	Fine Sand	38 Seconds
0.01	Silt	33 Minutes
0.001	Bacteria	35 Hours
0.0001	Clay Particles	230 Days
0.00001	Colloidal Particles	6.3 Years

FGD Characteristics

Flow (gpd)	50,000 - 1,000,000
pH	5.0 - 9.0
TSS (mg/L)	2,000 - 100,000
TDS (mg/L)	5,000 - 40,000
Temperature (degree F)	100 -140
Chloride (mg/L)	5,000 - 50,000
Calcium (mg/L)	1,000 -20,000
Magneium (mg/L)	1,000 - 10,000
Mercury (mg/, pptL)	5,000 - 1,000,000
Selenium (mg/L)	0.1 - 6.0
Arsenic (mg/L)	0.002 -0.2
Boron (mg/L)	10 - 700
Copper (mg/L)	0.1 - 7.0

FGD effluent - bituminous coal fired units

Summary of available WFGD liquor "soluble" composition.

	Mercury (ppt)	Selenium (ppb)	Arsenic** (ppb)	Nitrite/Nitrate (ppm as N)
Average	57,192	1,280		41
Std Dev	52,253	741		116
Max	200,000	2,250		440
Min	2,450	300		1
ELG*	356	12		4.4

*ELG = 30 day average
**Arsenic information is not yet available.

FGD effluent = Wastewater Influent

"soluble" = concentration determined on 0.45μ filtered liquor.

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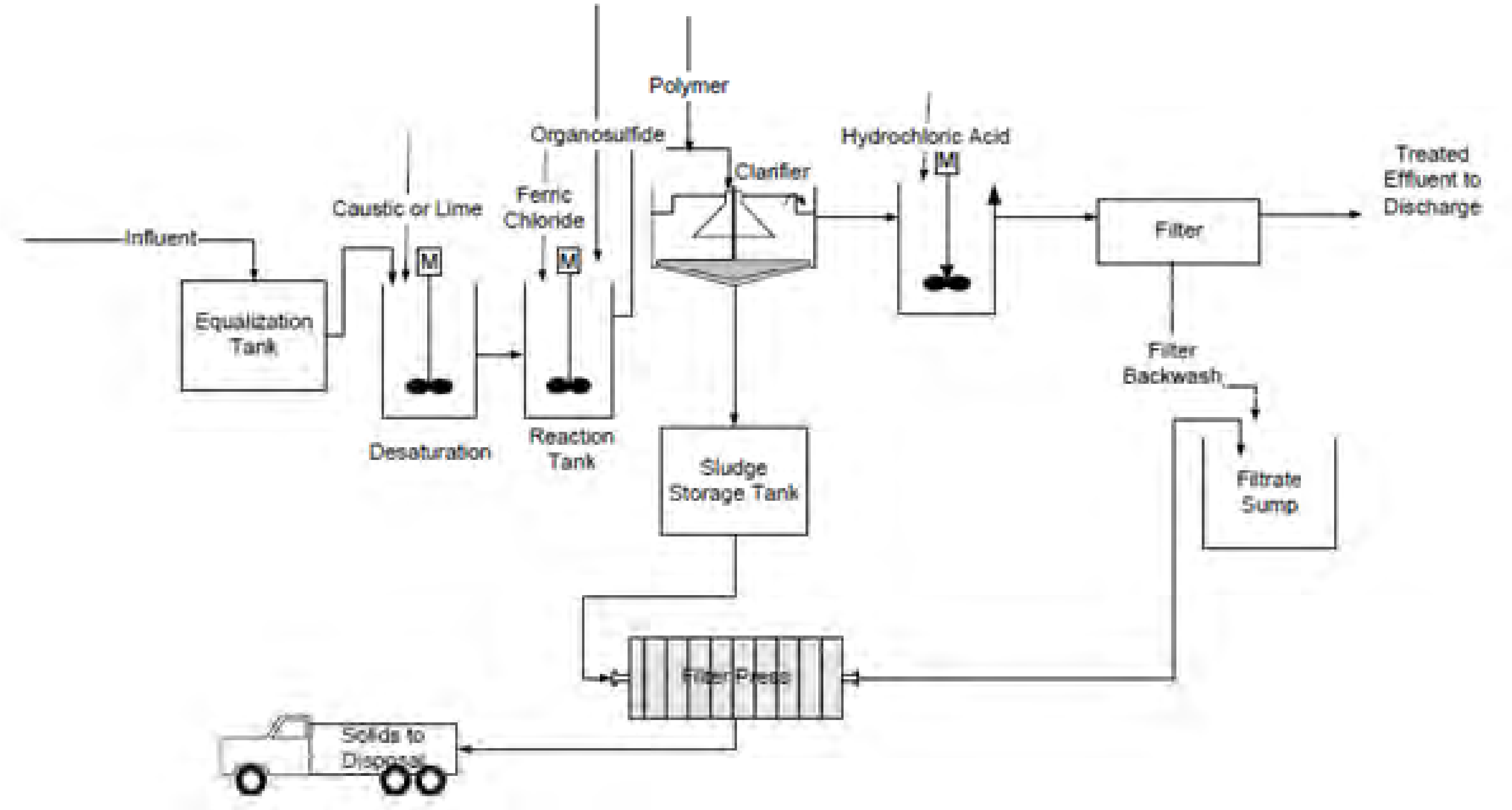
Wastewater Treatment Objectives

- Remove contaminants from wastewater
  - Mass balance and speciation
  - Suspended solids (clay, sand, silt, mud, organic compounds, insoluble BOD/COD)
  - Dissolved ions, (Ca^{+2}, Mg^{+2}, SO_4^{-2}, SeO_3^{-2}, SeO_4^{-2}, Se^{-2}, $HAsO_4^{-2}$, $H_2AsO_4^{-}$, AsO_3^{-3}, PO_4^{-3}, NO_2^{-}, NO_3^{-}, etc.)
  - Heavy metals, dissolved (Hg^{+2}, Hg^{+}, Cu^{+2}, Cr^{+3}, Zn^{+2}, Cd^{+2}, etc.) and suspended
  - Oil and grease
- Target water quality parameters for plant discharge to receiving water or process

Process

- Apply mechanical, operational and chemical process to remove contaminants
- Remove contaminants to meet National Pollutant Discharge Elimination System (NPDES), EPA, State, ORSANCO, Great Lakes Initiative, etc. discharge limits
- Use chemical precipitation, adsorption, coagulation and flocculation to enhance the capability for removing contaminants
  - Coagulation and flocculation accomplished by using organic, inorganic, or blend type coagulants and flocculants (polymers)

FGD Wastewater Treatment



Heavy Metal Removal Methods – Chemical Precipitation

$$M^{+n} \quad + \quad X^{-m} \underset{K_{sp}}{\rightleftharpoons} M_m X_n$$

Insoluble precipitate

M^{+n} = Hg^{+2}, Cu^{+2}, Ni^{+2}, Zn^{+2}, Cd^{+2}, Cr^{+3}, etc

X^{-m} = OH^{-}, CO_3^{-2}, Organosulfur compds/S^{-2}

- High conductivity enhances the solubility of precipitated metal complexes due to greater attraction of the precipitated metal complex ions to the ions (SO_4^{-2}, Cl^{-}, etc) in solution.
- Chelants (EDTA, DBA) form stable metal complexes with soluble metals that can make metal precipitation more difficult.

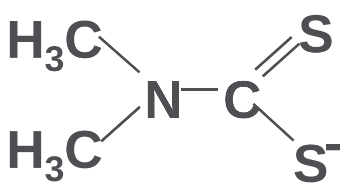
Heavy Metal Removal Methods

- Chemical precipitation

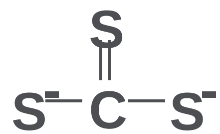
$$K_{eq} = \frac{[A^{Y+}]^{Z} \bullet [B^{Z-}]^{Y}}{[A_Z B_{Y(s)}]} = K_{sp}$$

  - Form low solubility metal complexes
    - Solubility product constant (K_{sp}), lower value for the metal complex gives increased metal precipitation
  - Target conditions that form insoluble metal complexes (pH, temperature, contact time, dosage)
  - Hydroxide precipitation cannot achieve ppt mercury level
  - Sulfur containing organic compounds can achieve ppt mercury level
    - K_{sp} mercury sulfide complex << K_{sp} mercury hydroxide/carbonate complex
    - Good precipitation at a wide pH range

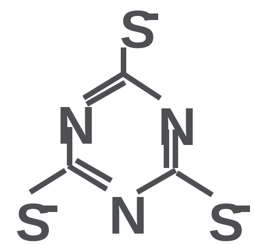
Organic Sulfides/Precipitants



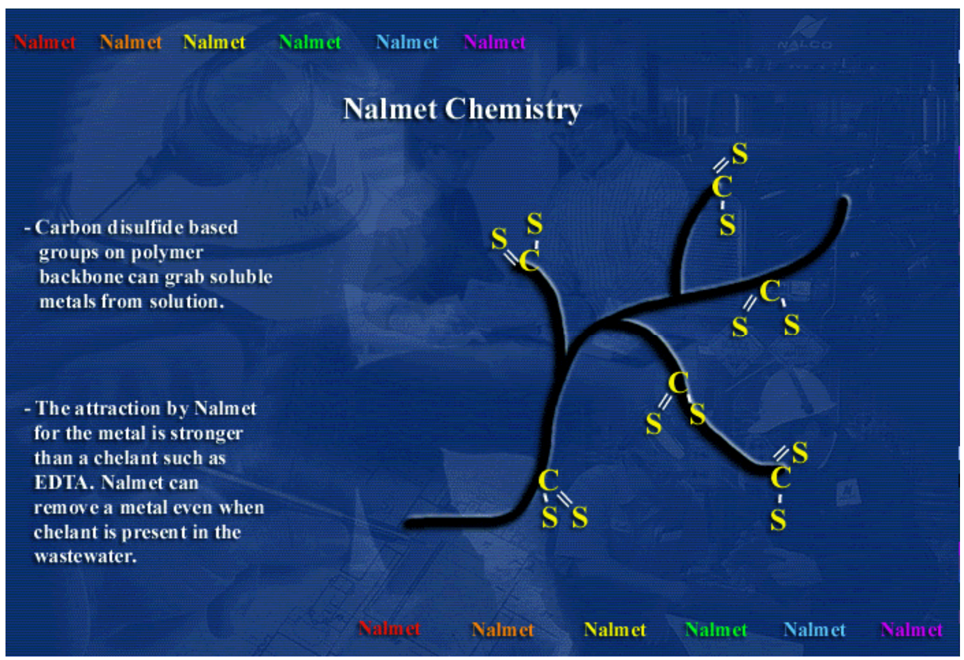
DTC



TTC



TMT



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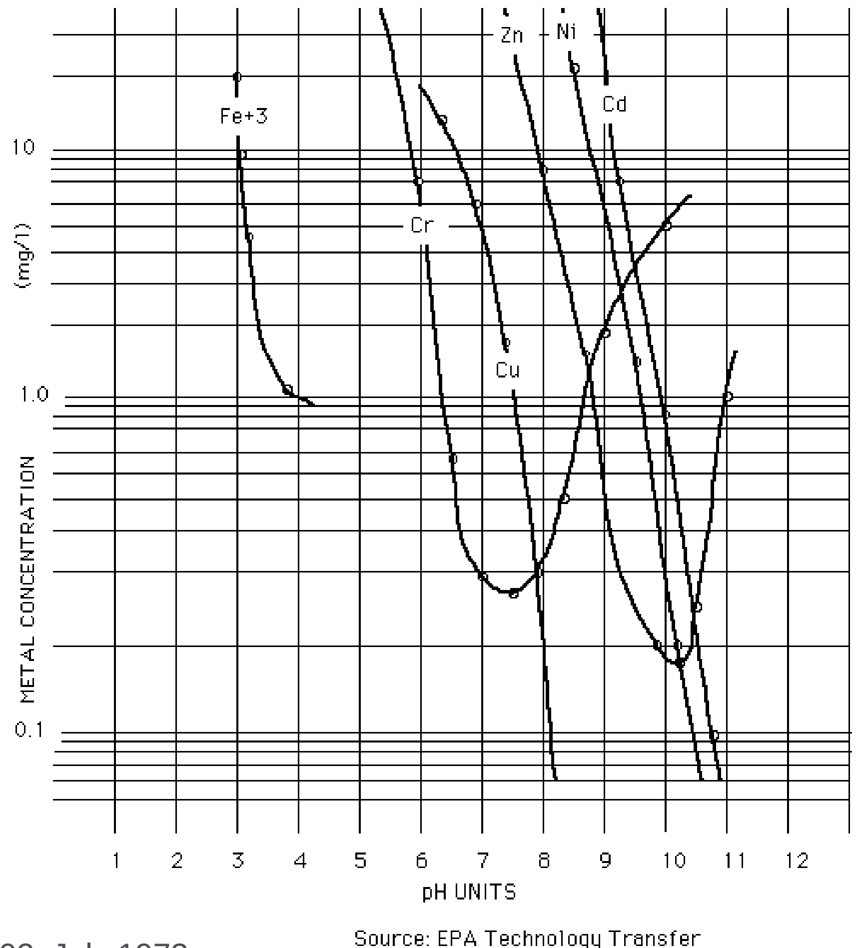
NALMET® vs. DTC

- Considerations
  - Particle size
  - Solid/liquid separation optimization
  - Function as metal precipitant and coagulant
  - Toxicity (DTC - high, TMT - low)

Metal Hydroxide Solubility vs pH



EPA 625/3-73-002, July 1973

R. Weiner, Die Abwasser der Galvanotechnik und Metallindustrie, 4th Edition, Eugen G. Leuze Verlag, 1973.

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Metal Hydroxide Solubility vs pH

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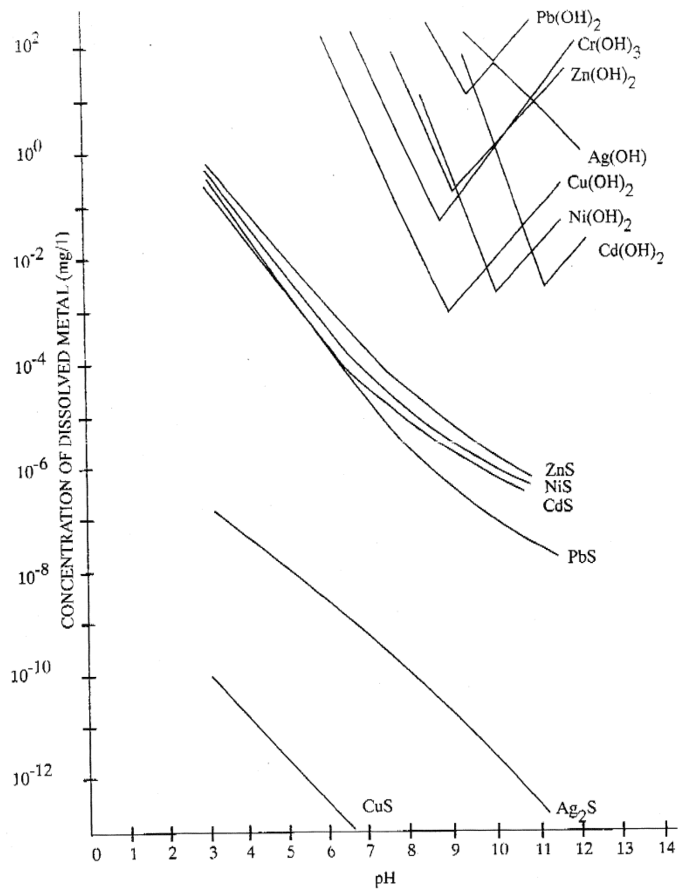
Solubility of Metal Hydroxides and Sulfides as a Function of pH



(Source: EPA publication, EPA-600/2-82-011C, 1981)

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Heavy Metal Removal Methods – Co-Precipitation/Adsorption

- Incorporation/entrapment of soluble metals into iron or aluminum hydroxide matrix as it forms
  - Mechanical entrapment
  - Mixed metal/pollutant complex
- Adsorption of soluble metals unto iron or aluminum hydroxide matrix
  - Surface
  - Internal

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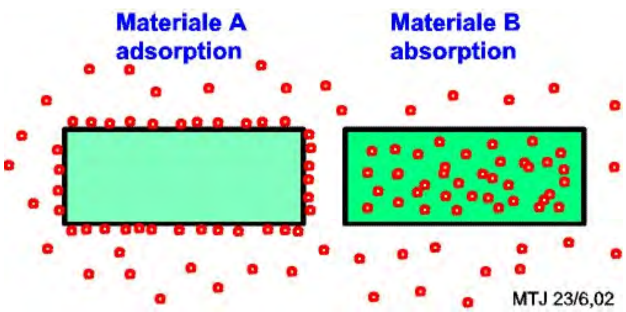
Heavy Metal Removal Methods – Co-Precipitation/Adsorption

- Compounds used for co-precipitation/ adsorption processes
  - ferric chloride/sulfate, ferric blends
  - alum, polyaluminum chloride, aluminum chlorohydrate, aluminum blends, alumina

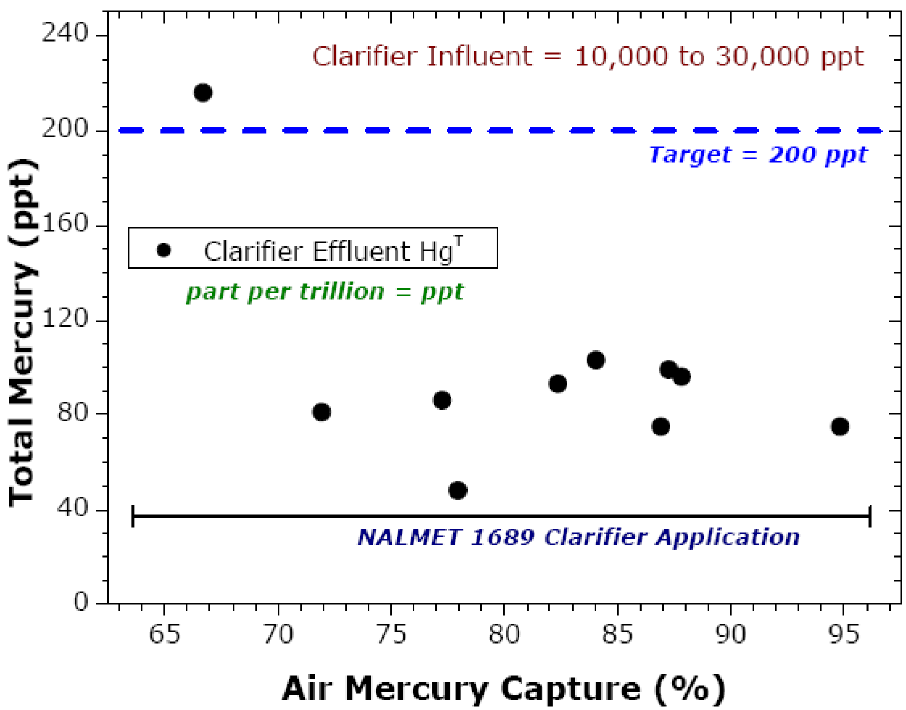


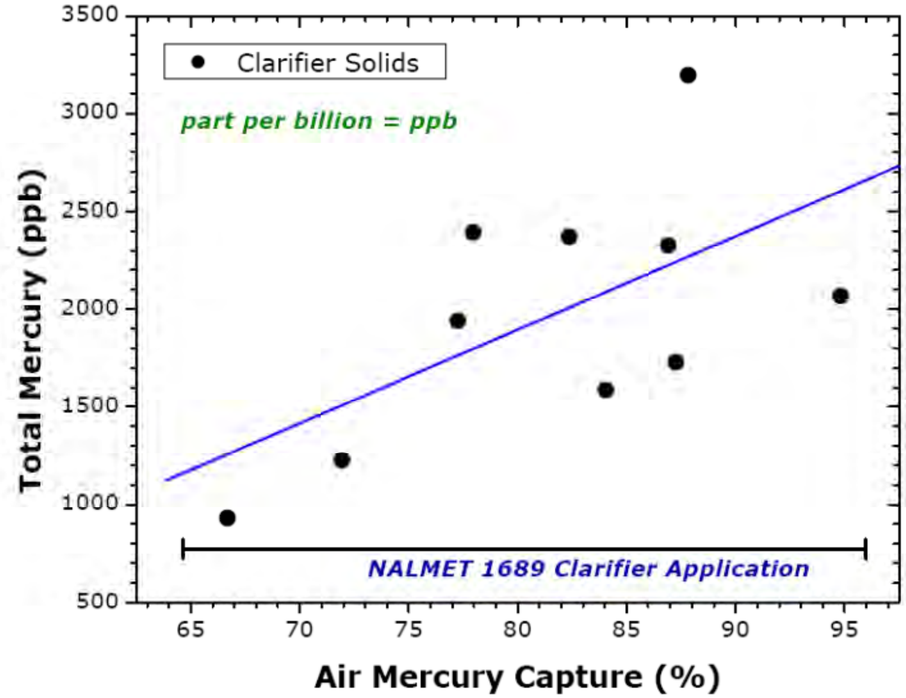
- Effectiveness and efficiency of co-precipitation depends on
  - pH
  - dose of ferric or aluminum compound
  - concentration of heavy metals/pollutants
  - concentration of other species that compete for the adsorption sites

Mercury and Arsenic Removal

- Generally a physical and chemical process
- Precipitation/Co-precipitation
  - Arsenite may require oxidation
  - pH adjustment (lime, caustic, soda ash)
  - Organosulfur compounds
  - Inorganic/Blend coagulants
  - Flocculant
- Liquid Solids Separation
  - Clarification
  - Filtration
  - Adsorption

Mercury MATS and Wastewater ELG

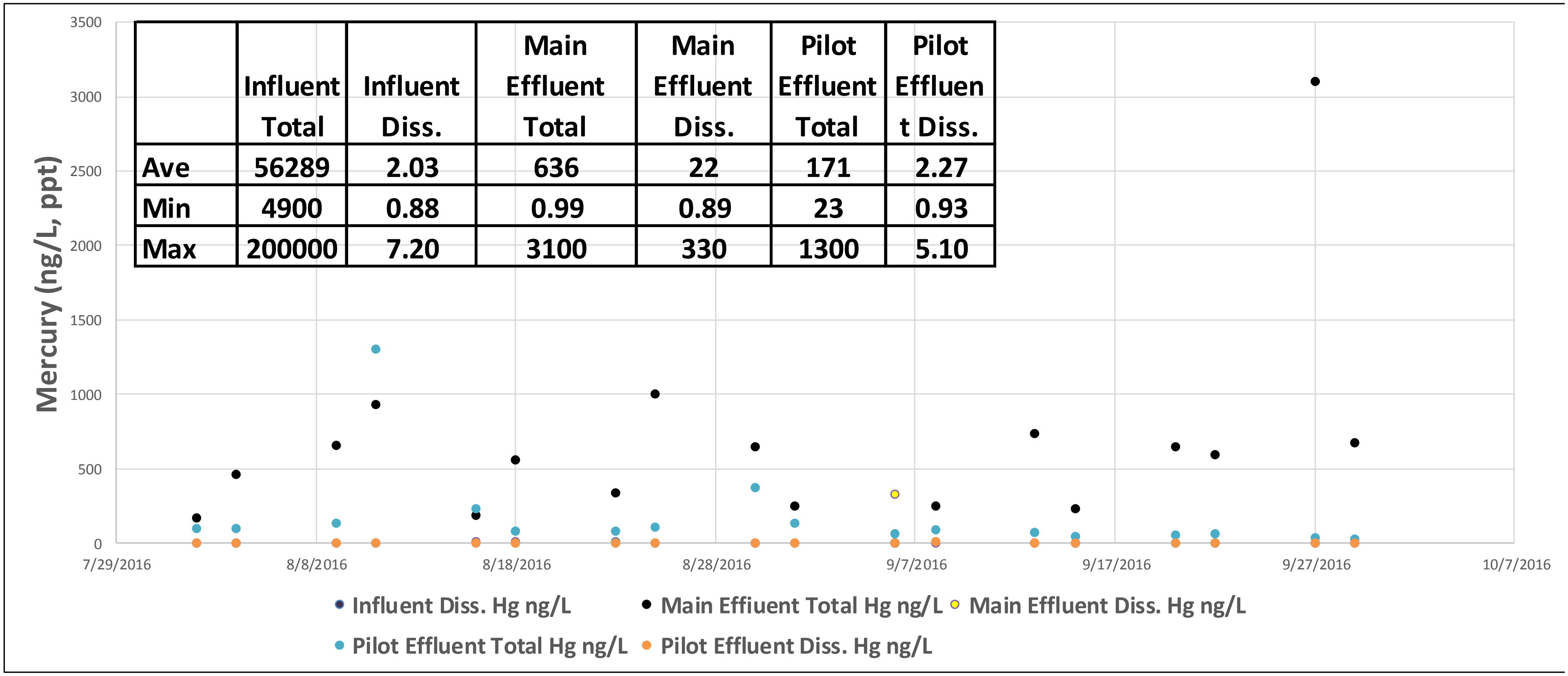




- FGD Purge/Blow-down = WWTP Influent.
- Increased mercury capture ≠ Increased effluent mercury concentration.
- Physical/chemical treatment for WWTP effluent ELG mercury compliance.

[2]Meier, J., Lu, J.V., Shah, J., & Keiser, B. (2010). Mercury Emissions: Demonstration of Air and Water Quality Management. Paper presented at MEGA Symposium 2010, August 30-September 2, 2010, Baltimore, MD. USA.

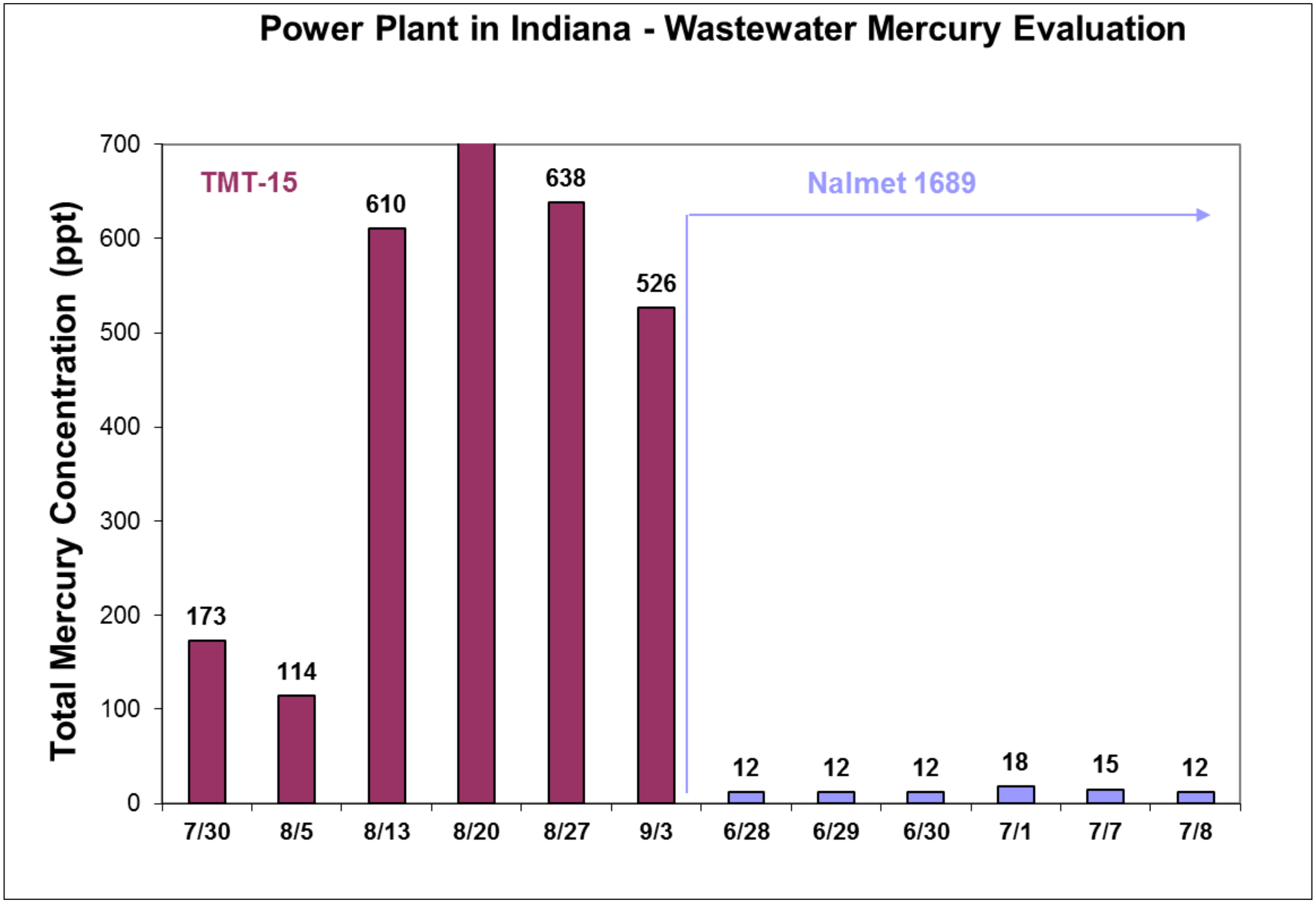
Mercury Removal



	Influent Total	Influent Diss.	Main Effluent Total	Main Effluent Diss.	Pilot Effluent Total	Pilot Effluent Diss.
Ave	56289	2.03	636	22	171	2.27
Min	4900	0.88	0.99	0.89	23	0.93
Max	200000	7.20	3100	330	1300	5.10

- ELG compliance can be achieved by physical-chemical treatment with best practice mechanical, operational, chemical process

Mercury Removal



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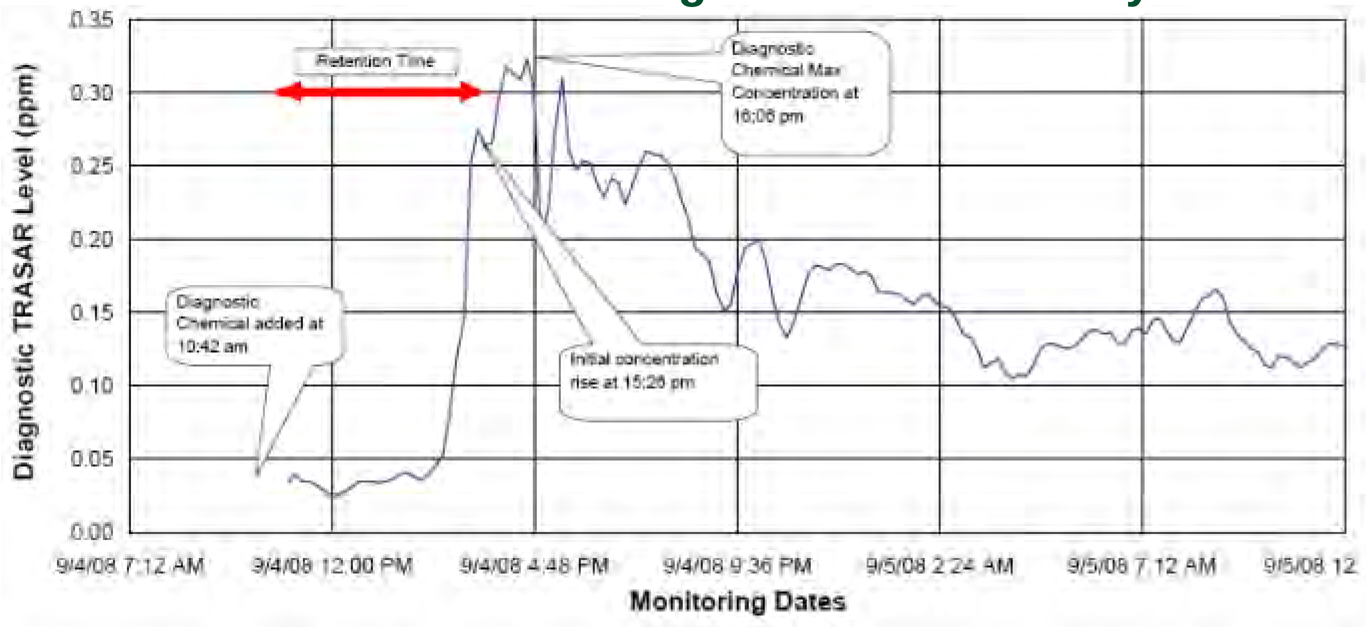
Mercury Removal Across Bottom Ash Pond

Discharge Limit: 9 ppt - no dilution

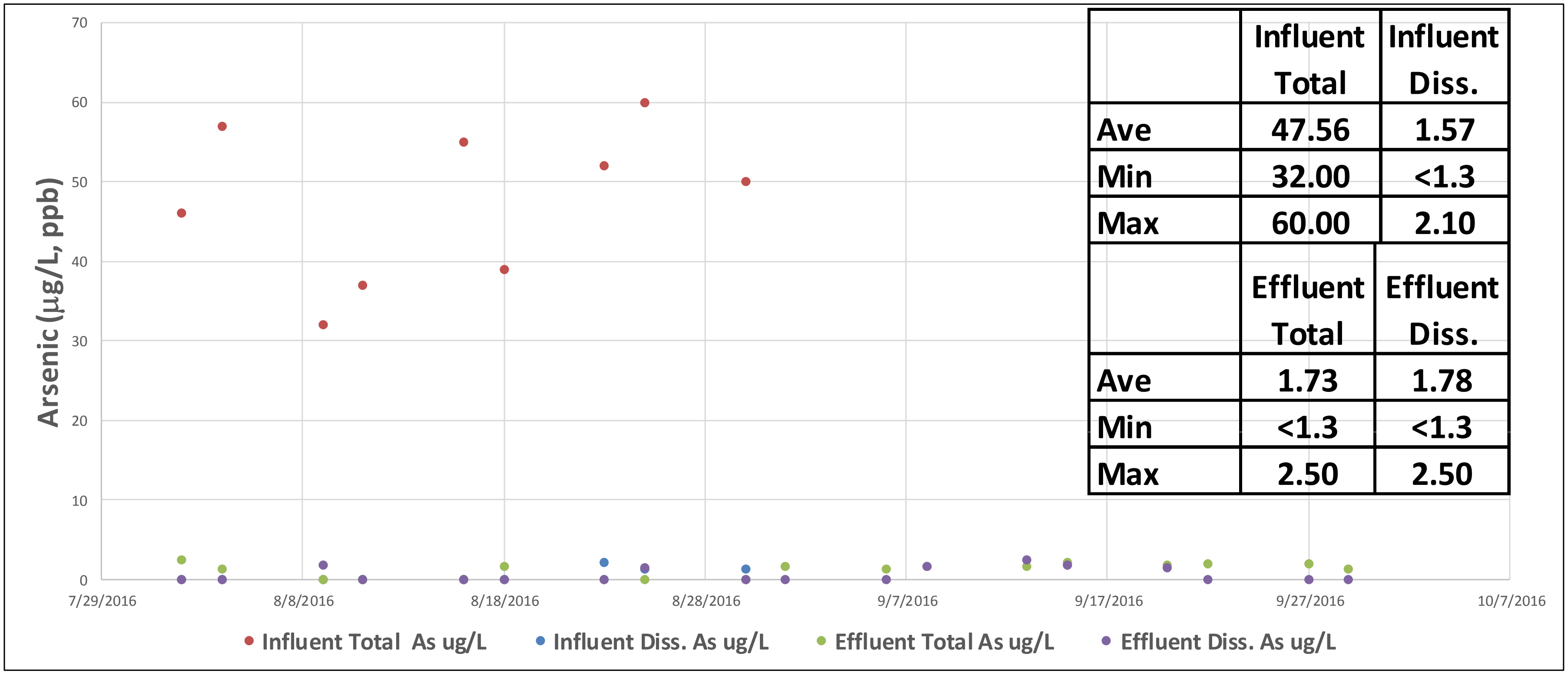
Mercury **influent** to pond (after FGD Wastewater treatment) = 50 to 100 ppt

Mercury **effluent** from pond with Nalco treatment = 4 to 8 ppt

Ash Pond Diagnostic Trasar Study



Arsenic Removal

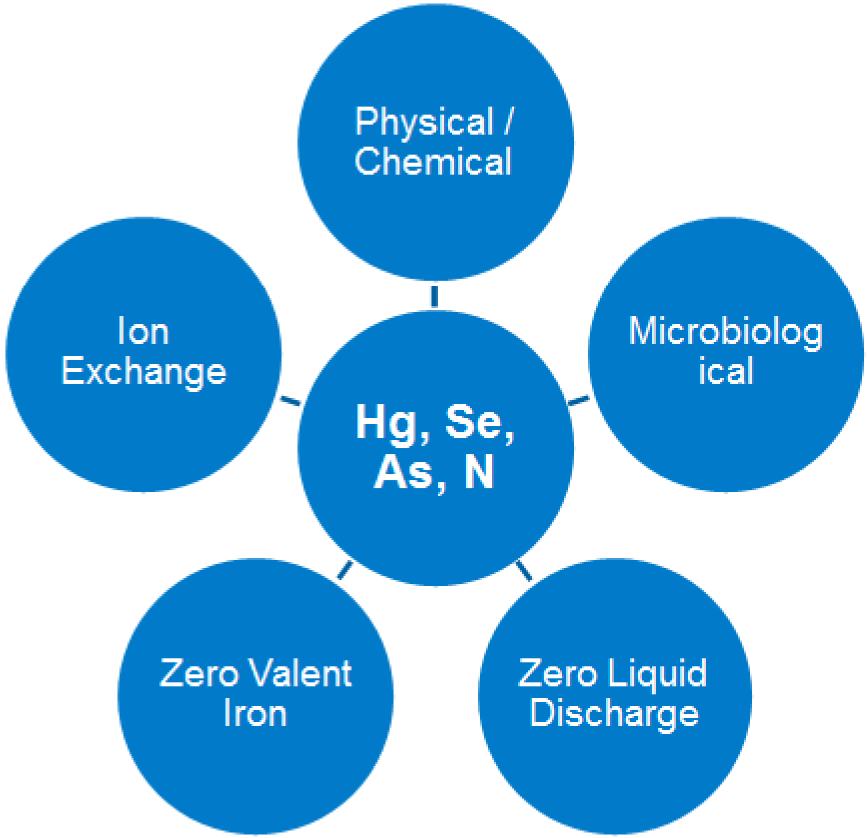


	Influent Total	Influent Diss.
Ave	47.56	1.57
Min	32.00	<1.3
Max	60.00	2.10
	Effluent Total	**Effluent Diss.**
Ave	1.73	1.78
Min	<1.3	<1.3
Max	2.50	2.50

- Insoluble arsenic can be removed by physical-chemical treatment

Selenium and Nitrogen Removal-ELG Compliance

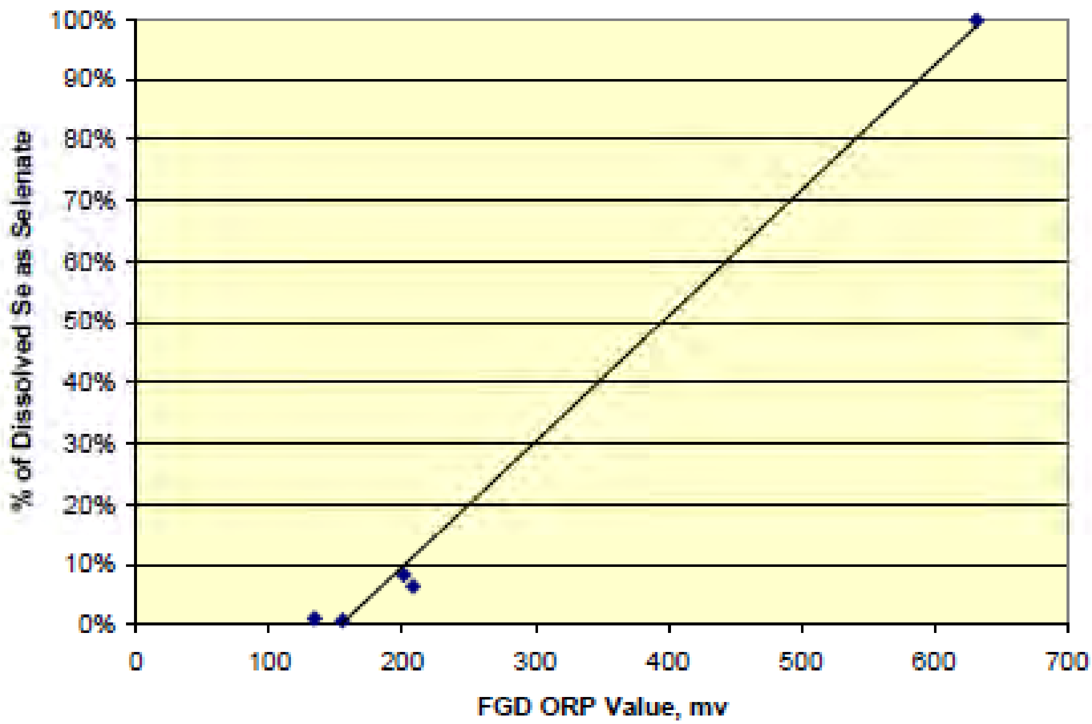
End of Pipe Treatments



Selenium and Nitrogen Removal

- Engineer controls
  - Minimize selenium contribution from FGD bleed
  - Minimize fly ash carryover
  - Minimize ammonia slip
- Treatment options
  - Biological
  - Ion Exchange/RO
  - Valence Reduction
  - Very expensive options
- Zero Liquid Discharge technologies

WFGD Liquor ORP and Selenium



Lower scrubber liquor ORP would favor selenite over selenate.

Recall it enters liquor as the 'ite'.

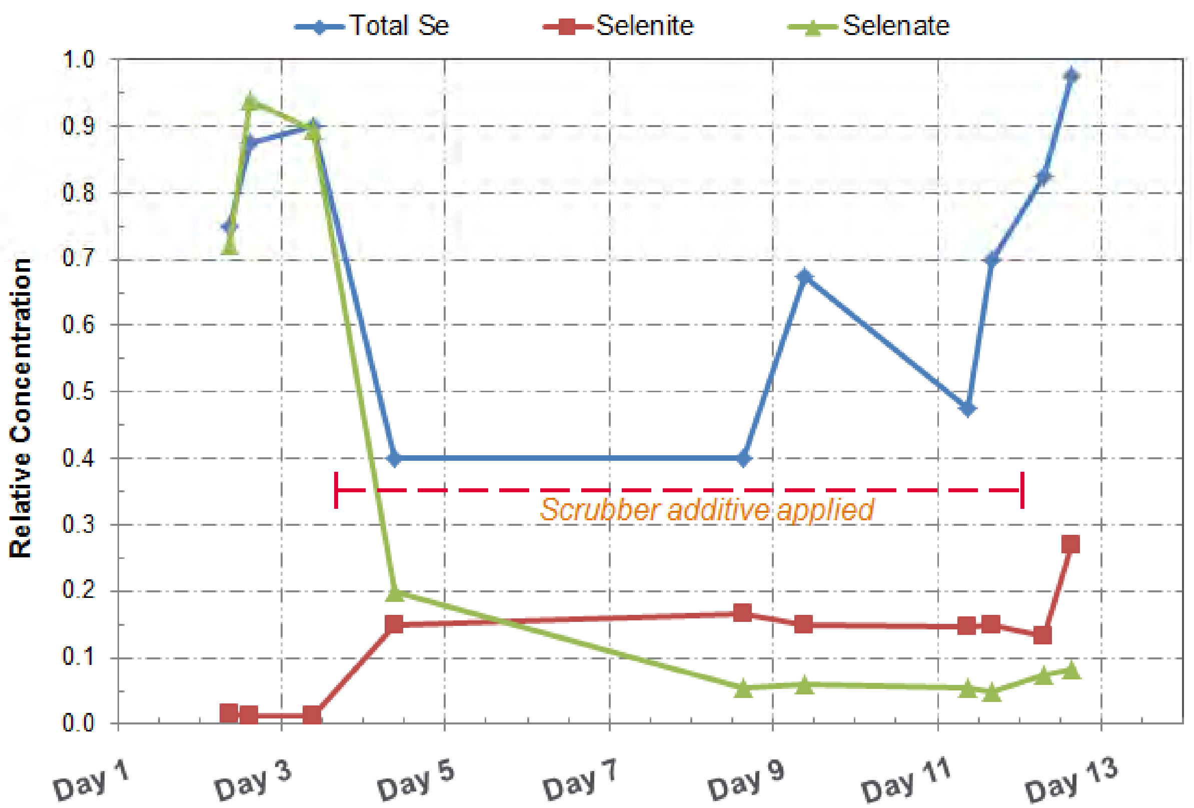
Selenium: $[Se^T] = [Se^{4+}] + [Se^{6+}] + [Se]_{organic}$

Total *Selenite* (SeO_3^{2-}) *Selenate* (SeO_4^{2-}) *Organoselenium*

G. Blythe, M. Richardson, C. Acharya, and C. Dene "Effects of Mercury Control Technologies on FGD Wastewater," IWC 2015.

Scrubber Additives: Selenium in liquor

MerControl 8034 Plus = Scrubber Additive



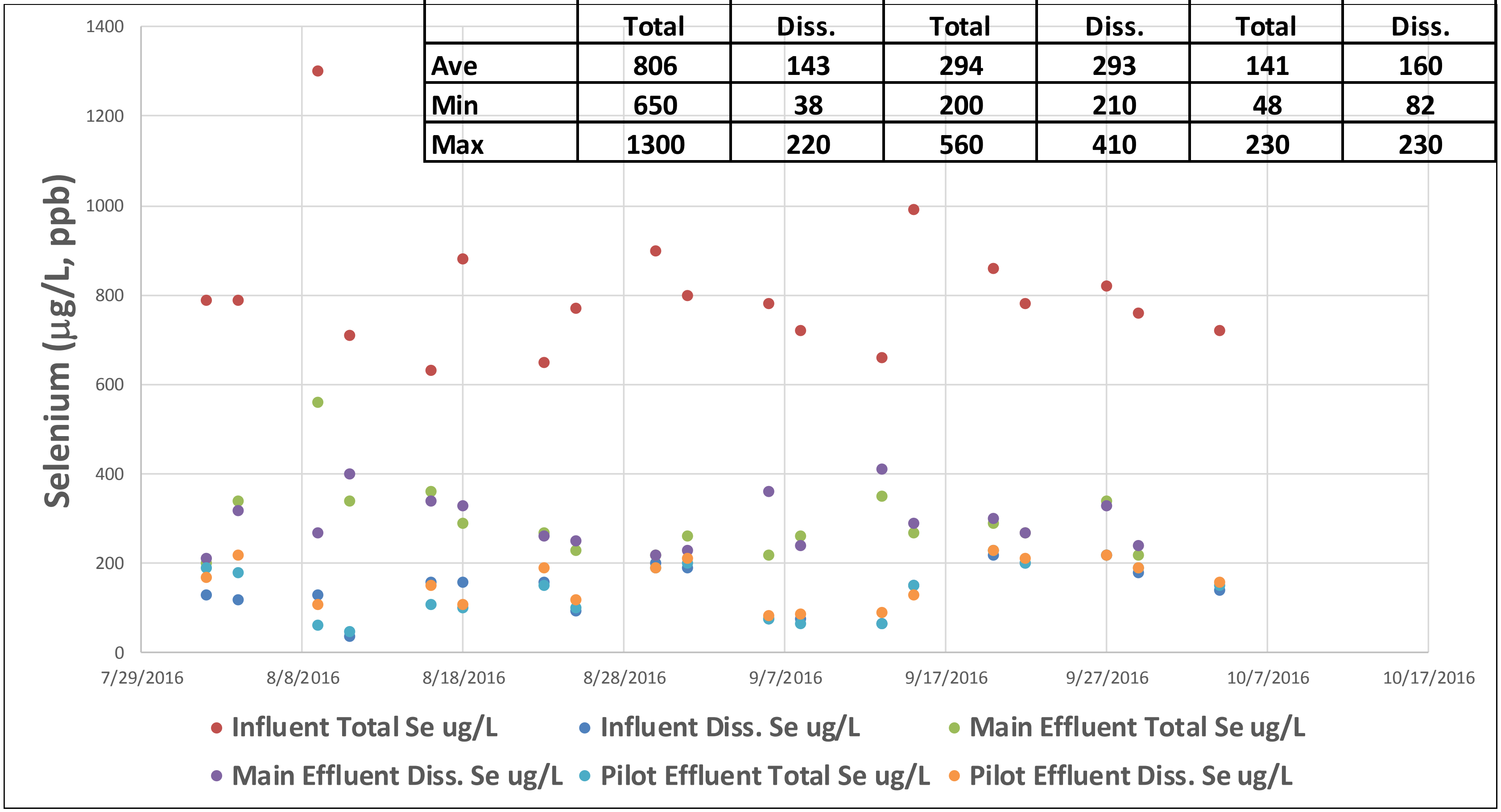
Data with 100 ppm bromide in scrubber liquor.

Lower soluble selenium concentrations result.

Shift from selenate to selenite documented.

Selenium Removal

	Influent Total	Influent Diss.	Main Effluent Total	Main Effluent Diss.	Pilot Effluent Total	Pilot Effluent Diss.
Ave	806	143	294	293	141	160
Min	650	38	200	210	48	82
Max	1300	220	560	410	230	230



- Selenium can be removed by physical-chemical treatment and biological treatment

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Selenium Removal

	Influent Total (ug/L)	Influent Diss. (ug/L)	Effluent Total (ug/L)	Main Effluent Diss. (ug/L)	Effluent Total (ug/L)	Pilot Effluent Diss. (ug/L)	Biological Influent Total (ug/L)	Biological Effluent Total (ug/L)*
Ave	806	143	294	293	141	160	75.6	3.7
Min	650	38	200	210	48	82	10	<0.56
Max	1300	220	560	410	230	230	190	17
*After Ultrafilration								

- Selenium can be removed by physical-chemical and biological treatment
  - Biological treatment by Frontier Water Systems (Luke Halverson and Tim Pickett)

Thank you

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