

REINHOLD ENVIRONMENTAL Ltd.



## **2016 APC-Wastewater Round Table & Expo Presentation**

July 18 & 19, 2016 in Dearborn, MI / Hosted by DTE Energy

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# WFGD OPTIMIZATION FOR IMPROVED WASTEWATER TREATMENT

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Joel Citulski

Date: July 19, 2016 – APC and Wastewater Roundtable

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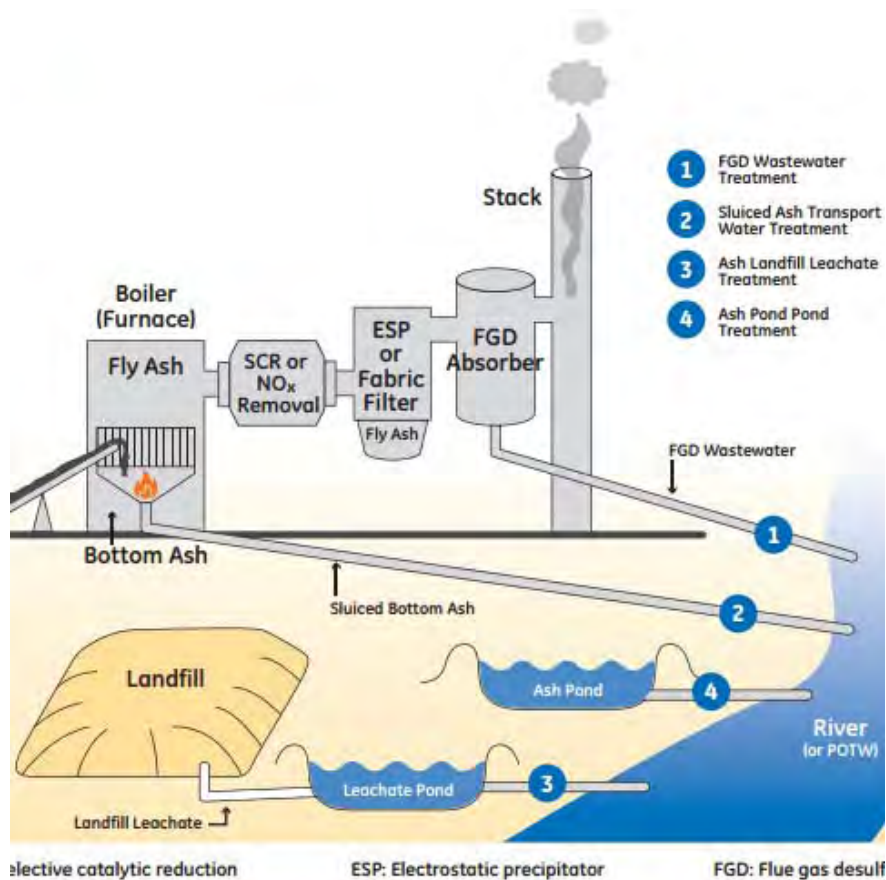
Summary



# Solutions to the FGD Wastewater Challenge



# Discharges at Coal-Fired Power Plants Impacted by New Regulations



- New challenge to manage the overall water balance of the plant
- FGD wastewater treatment is a significant challenge
- Variability due to type of coal, scrubber, operating regime, additives, load, etc
- Robust solution required



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# Federal Regulations for FGD Discharges

## ELG Discharge Limits for FGD Discharges

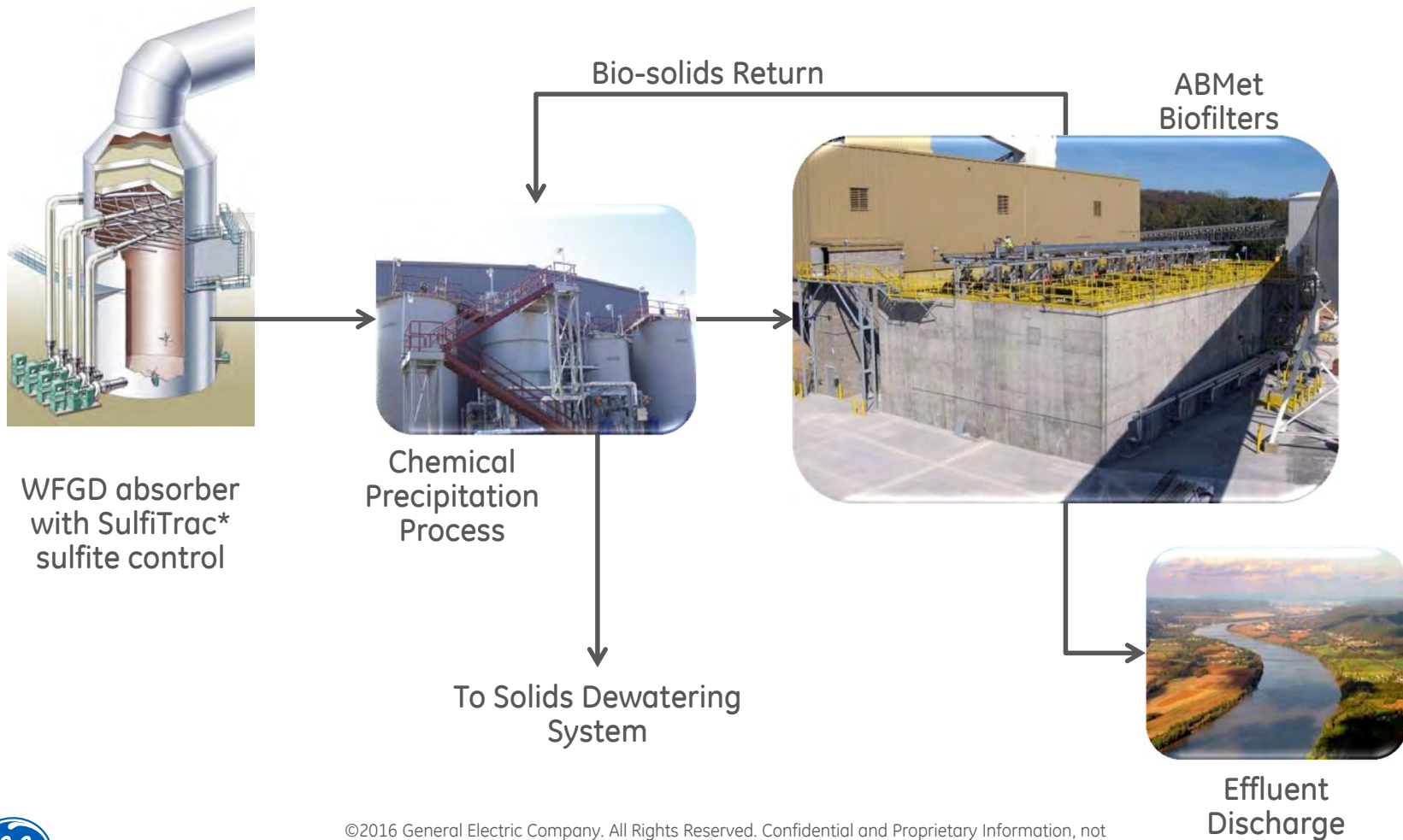
<u>Constituent</u>	<u>units</u>	<u>30-day avg.</u>	<u>1-day max</u>
Arsenic (total)	µg/L	8	11
Mercury (total)	ng/L	356	788
Selenium (total)	µg/L	12	23
Nitrate + nitrite as N	mg/L	4.4	17

## Local Regulators can Require Additional Limits

- Lower limits on arsenic, mercury, selenium and nitrate
- Limits on other constituents, e.g. chlorides, TDS, or boron



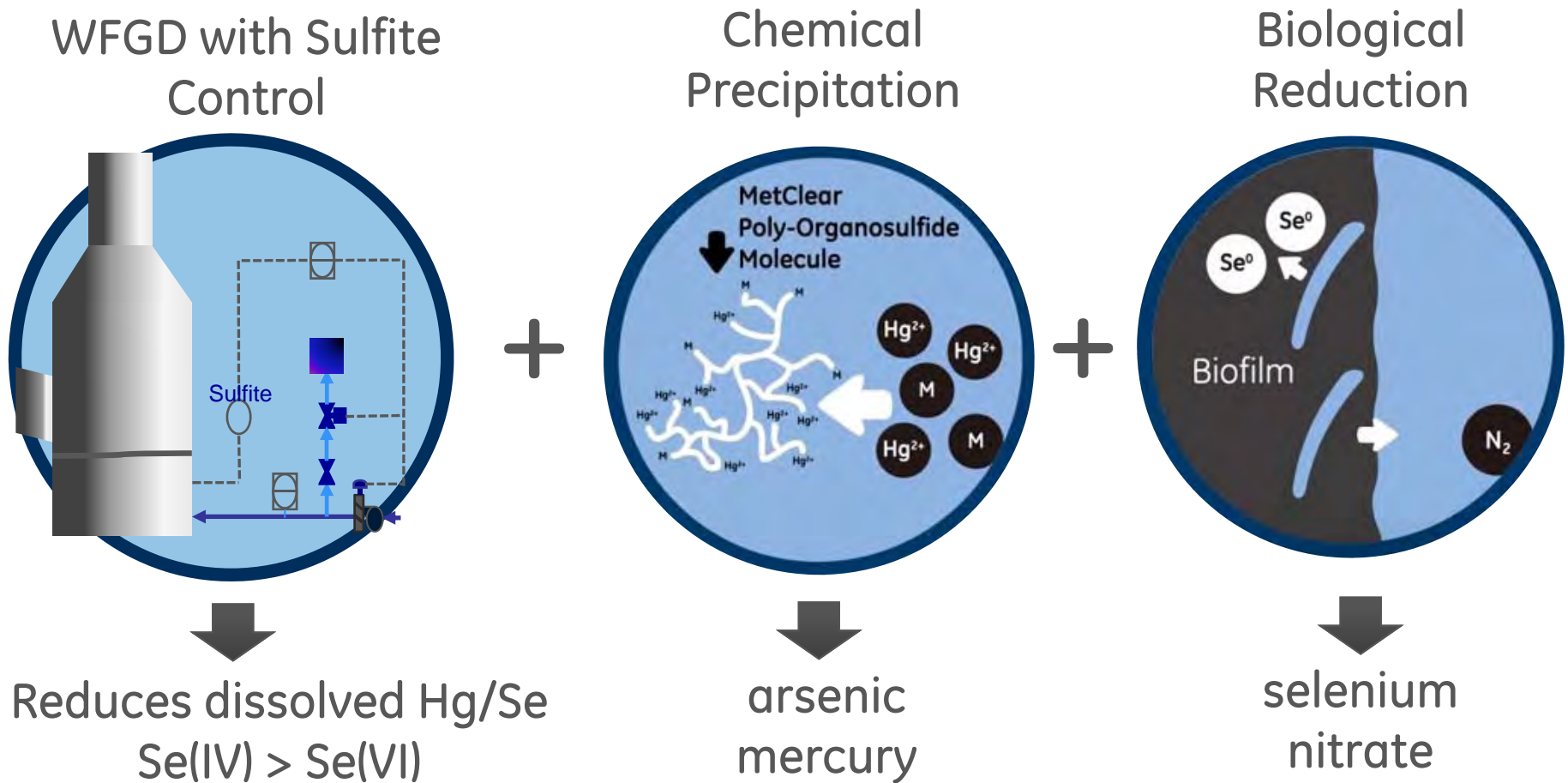
# Integrated Chemical Precipitation + Biological Treatment Flow Sheet



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# Treat & Discharge Solution – BAT for Existing Sources



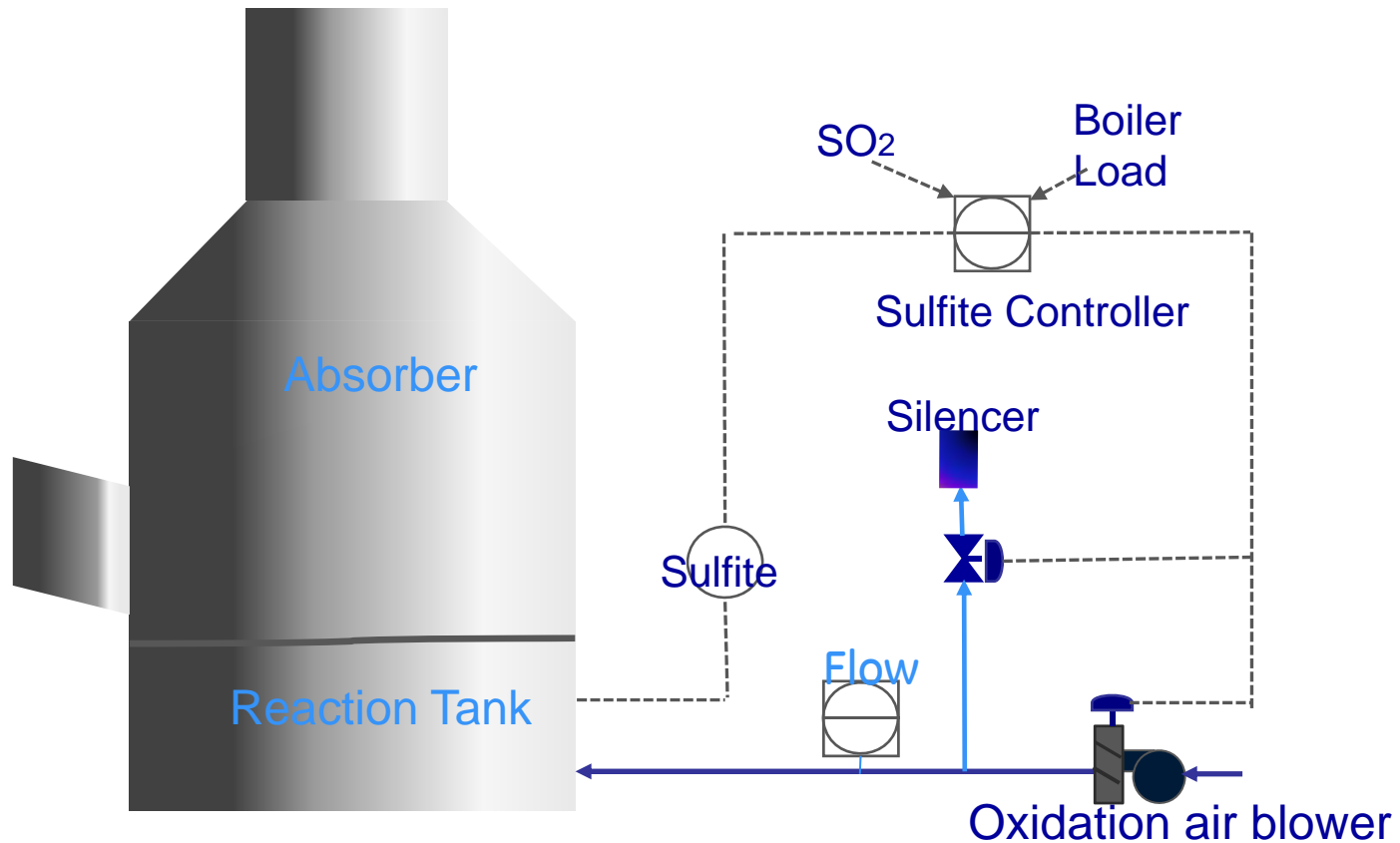
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# WFGD Optimization with Sulfite Control



# Efficient Oxidation Air Control with Sulfite Control



Air flow modulated to maintain sulfite set-point



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# Sulfite Analyzer Installation

- WFGD slurry, 20 to 50 gpm, to analyzer in sample sink
- Calibrated annually using standard analytical method
- Low maintenance
  - Recommend weekly to monthly cleaning
  - Ring electrode replacement approximately every 1-2 years



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# GE SulfiTrac\* Sulfite Analyzer

## Product Specification

<b>Physical Size</b>	Approximately 12" diameter x 44"H
<b>Weight</b>	50 lbs.
<b>Casing</b>	C-PVC, Stainless steel
<b>Control Box</b>	NEMA 4 rated
<b>Mounting Flange</b>	C-PVC, 150 psig rating
<b>Scraper Assembly</b>	C-PVC/Zirconium/Stainless steel
<b>Probe Surface</b>	Platinum
<b>Operating Temperature</b>	15°F to 160°F (-10°C to +70°C)
<b>Ambient Temperature</b>	40°F to 150°F (5°C to +65°C)
<b>Power Supply</b>	24 VDC, ~25 W
<b>Output Signal</b>	4-20 mA, RTD



**Robust construction for industrial applications**



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# Recent Sulfite Control Testing and Data

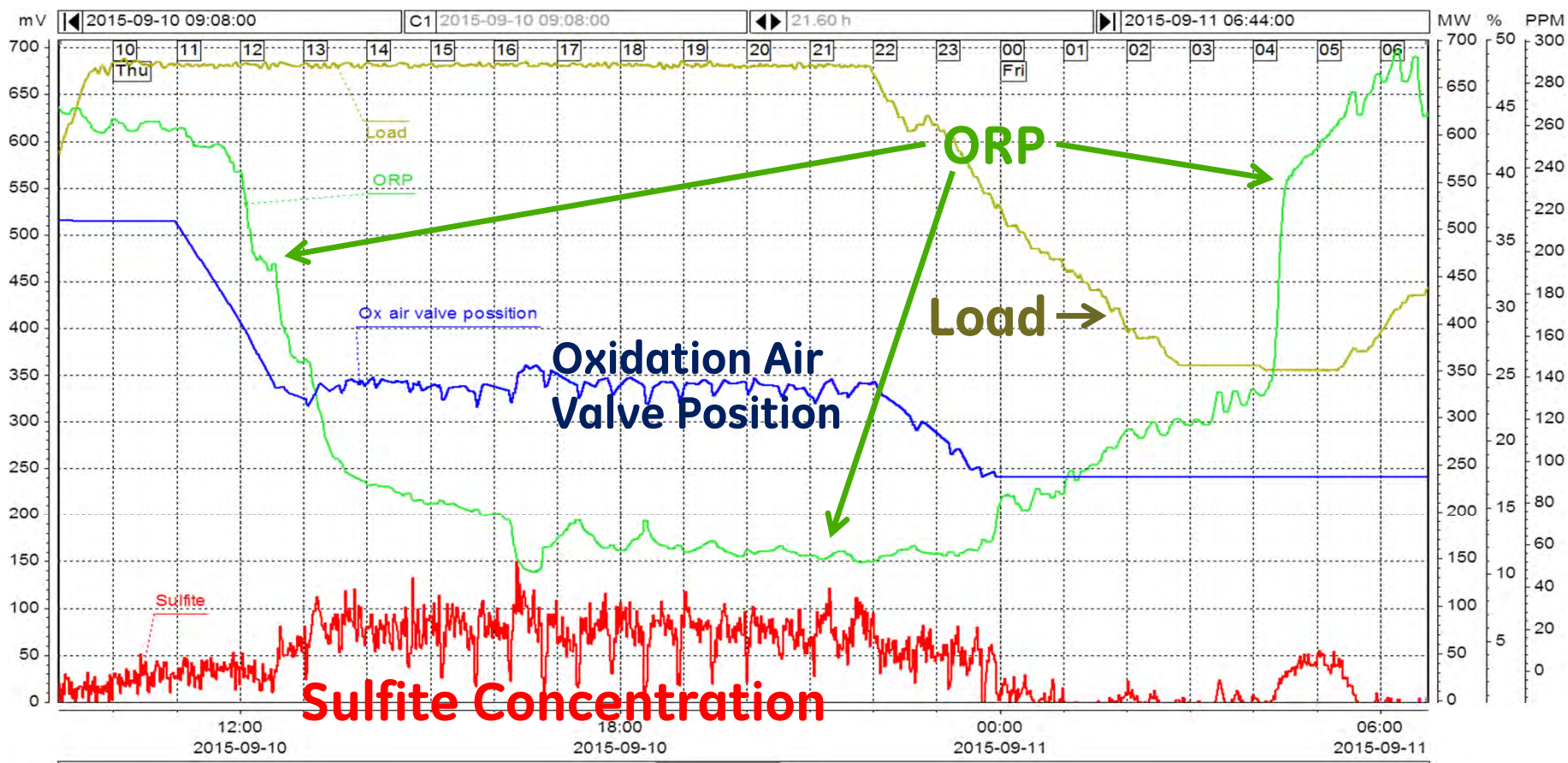
- 2 x 650 MW plant with multiple WFGD absorbers
- 1 of 8 absorbers tested sulfite control
- 7 day test program
  - Baseline (full-oxidation) tested for 2 days
  - Sulfite control at 20 ppm for 4 days
  - Sulfite control with 200 ppm for 1 day
- Sparger system limited air turndown – sulfite control for 12 to 14 hours/day
- Common dewatering system, supernate returned to all absorbers
- Non-ideal testing scenario



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# Operation with Sulfite Control



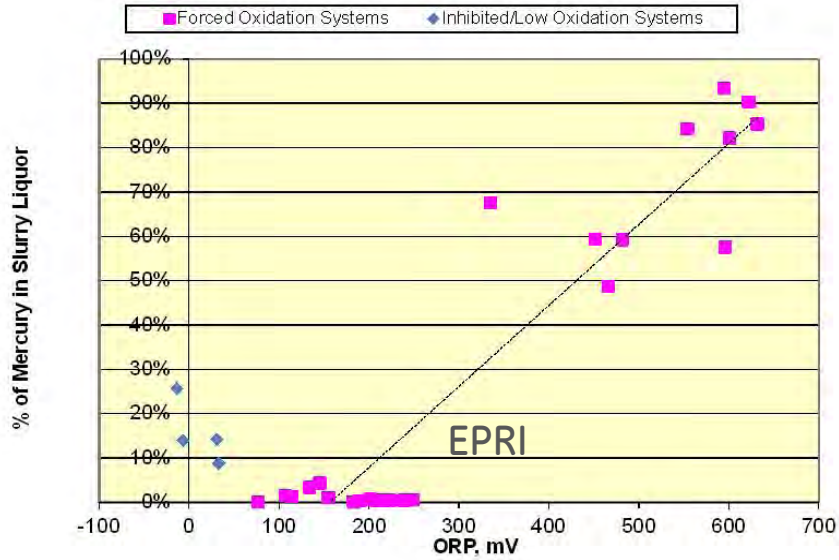
ORP lowered from  $> 500$  mV to  $< 200$  mV



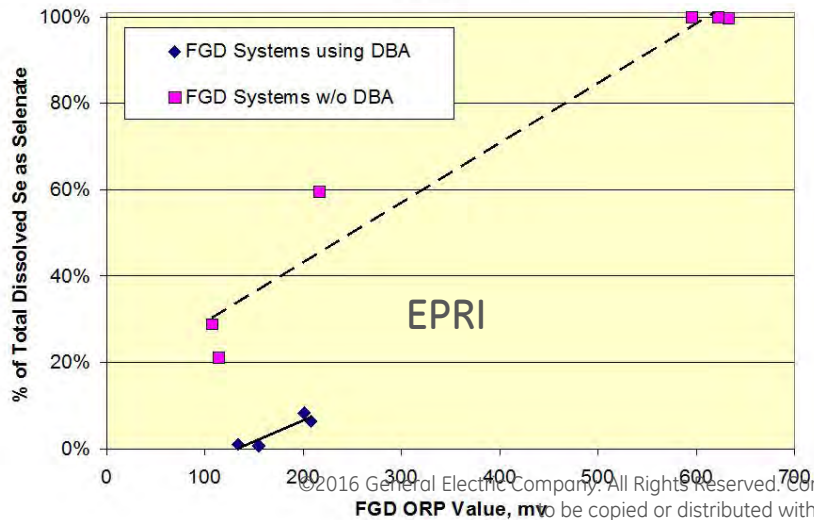
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# EPRI Results for Mercury and Selenium Speciation Impacts with Change in ORP



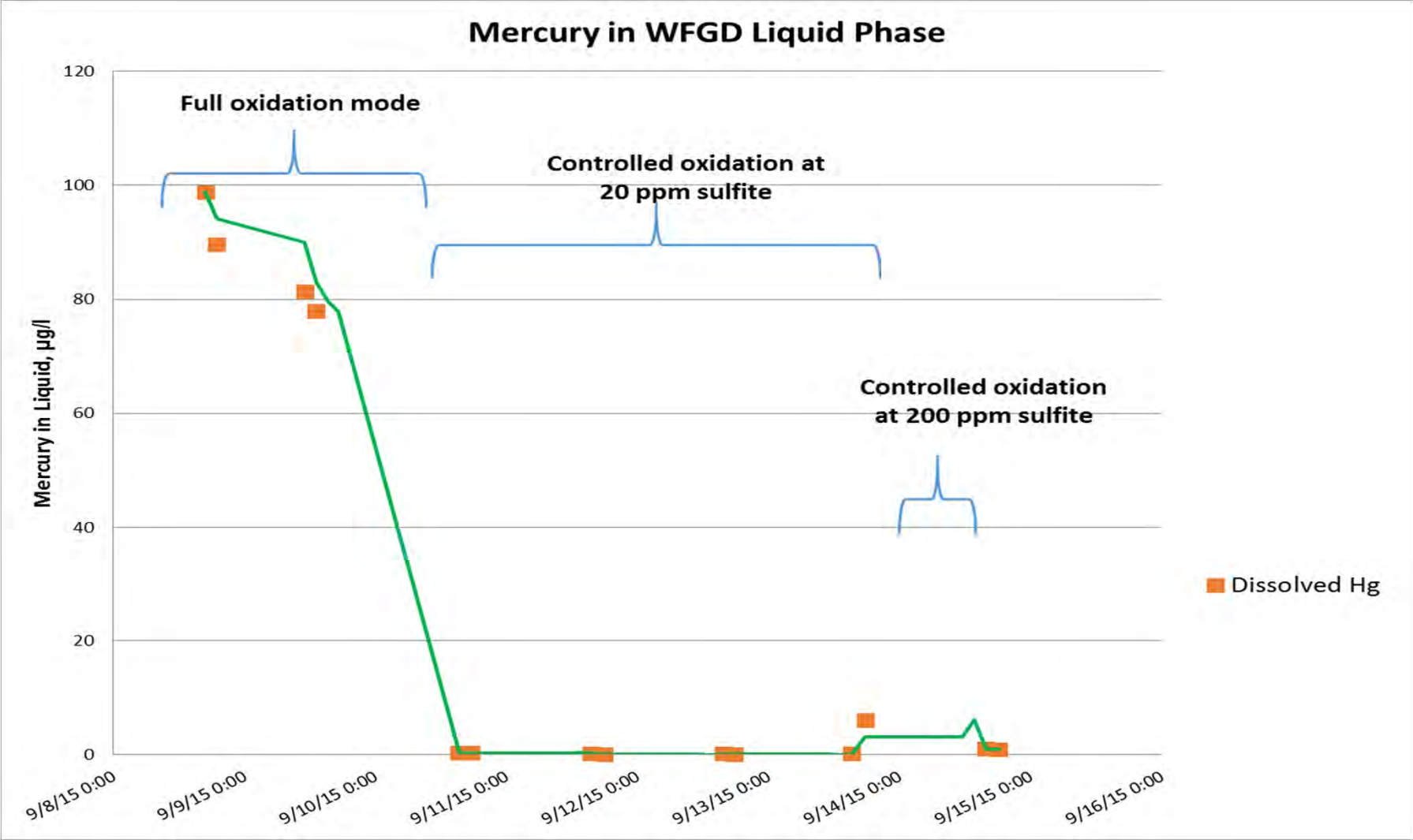
Lower mercury in WFGD liquor with lower ORP



Lower fraction of selenate in WFGD liquor with lower ORP



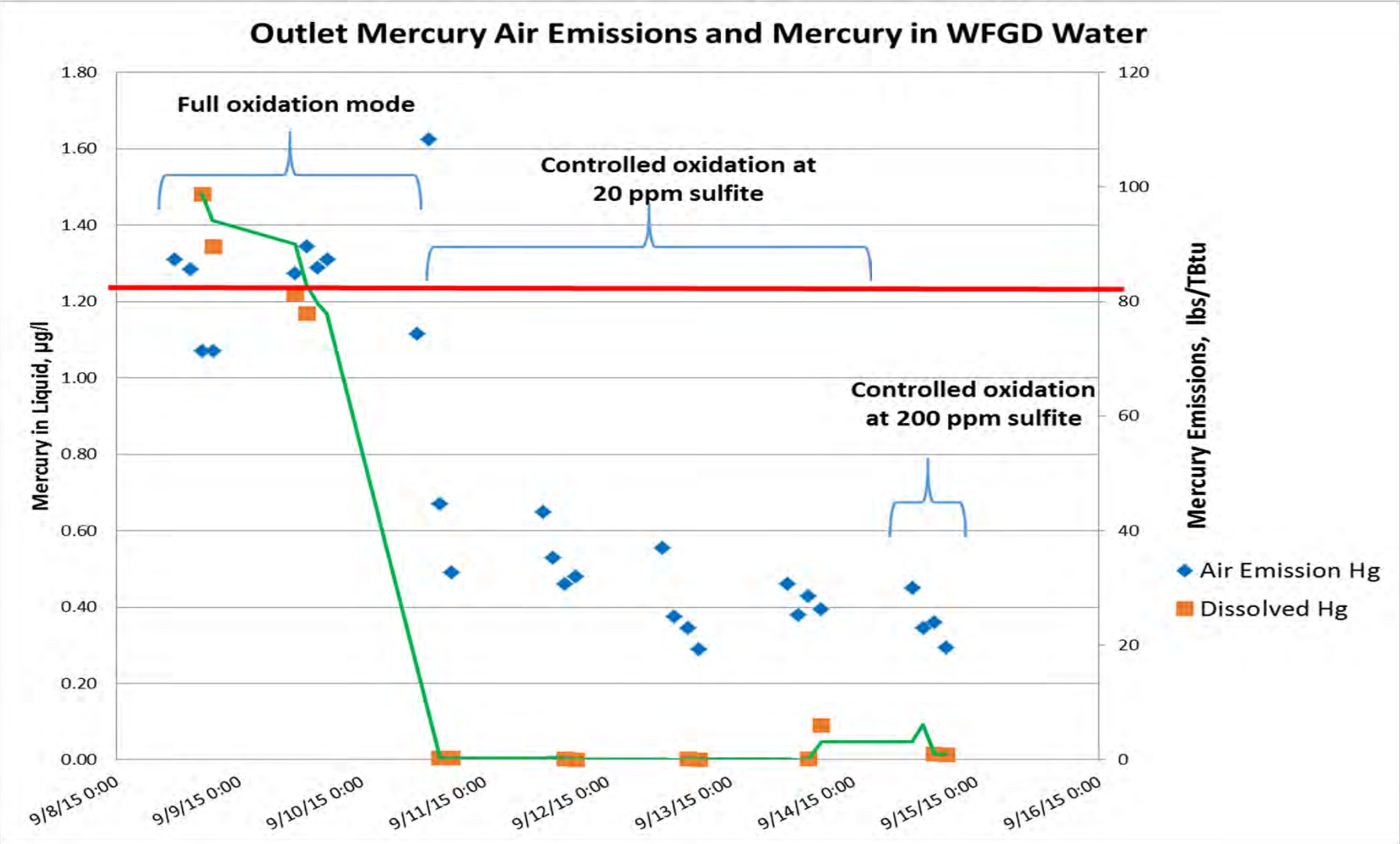
# Mercury changes with sulfite control



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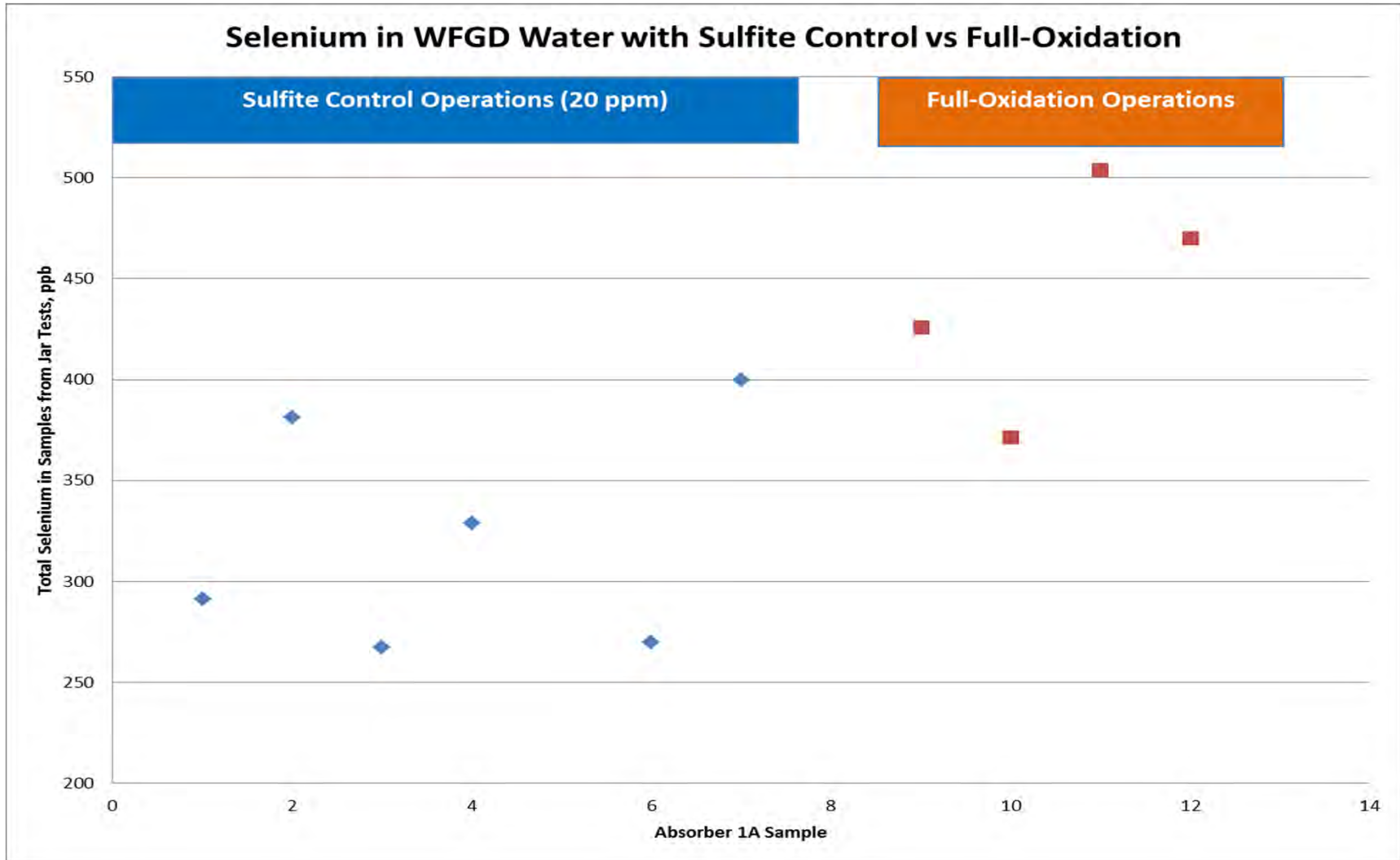
# Mercury changes with sulfite control



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# Total selenium changes with sulfite control



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# Benefits of Operation with Sulfite Control

- Reduce variability in scrubber chemistry, lower oxidants in WW
- Hg level in WFGD WW reduced from  $> 50 \mu\text{g/l}$  to  $<1 \mu\text{g/l}$
- Total selenium in WFGD WW reduced, selenium speciation shifted away from selenate
- Reduce mercury air emissions,  $>80\%$  reduction in re-emissions
- OpEx\$ savings, lower power consumption
- Operate with confidence in sulfite concentration to prevent sulfite blinding and maintain gypsum quality
- Reduce manganese precipitation that contributes to scale formation and corrosion potential

WFGD sulfite control optimizes WFGD purge for improved treatment in WWTS



# Treat & Discharge

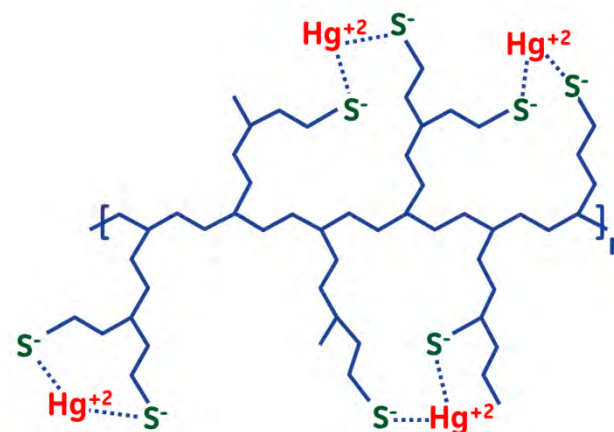
Physical-chemical (P/C) Treatment



# Chemical products for P/C

Objective: precipitation of metals & separation of TSS

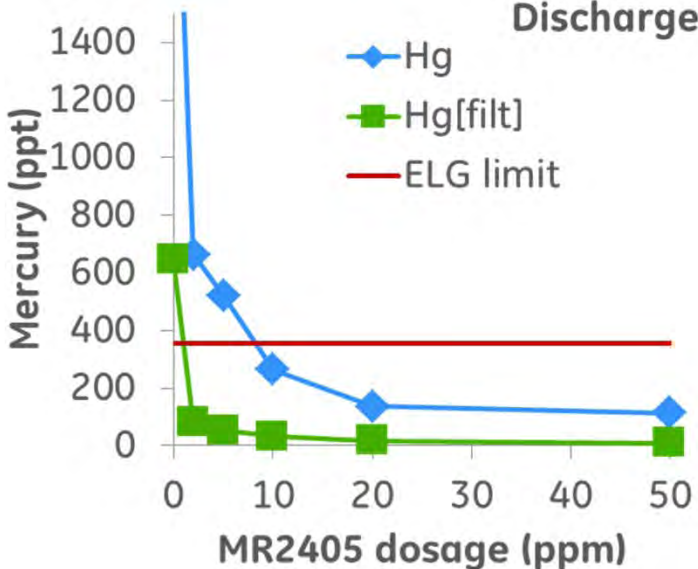
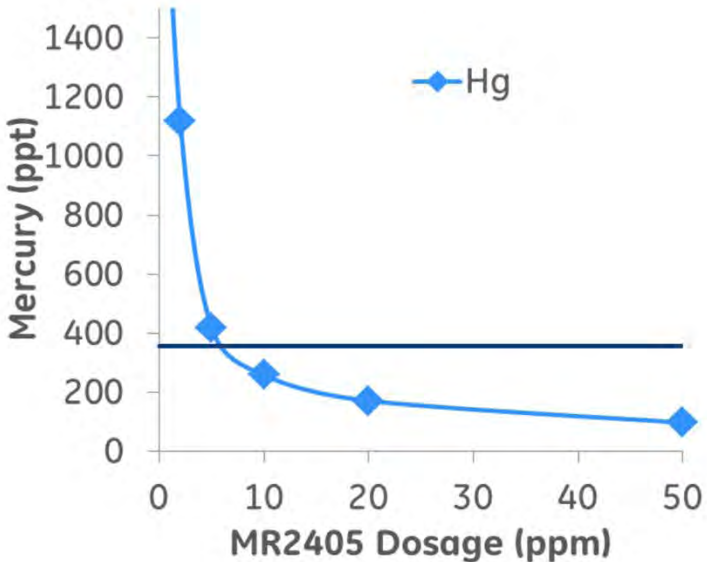
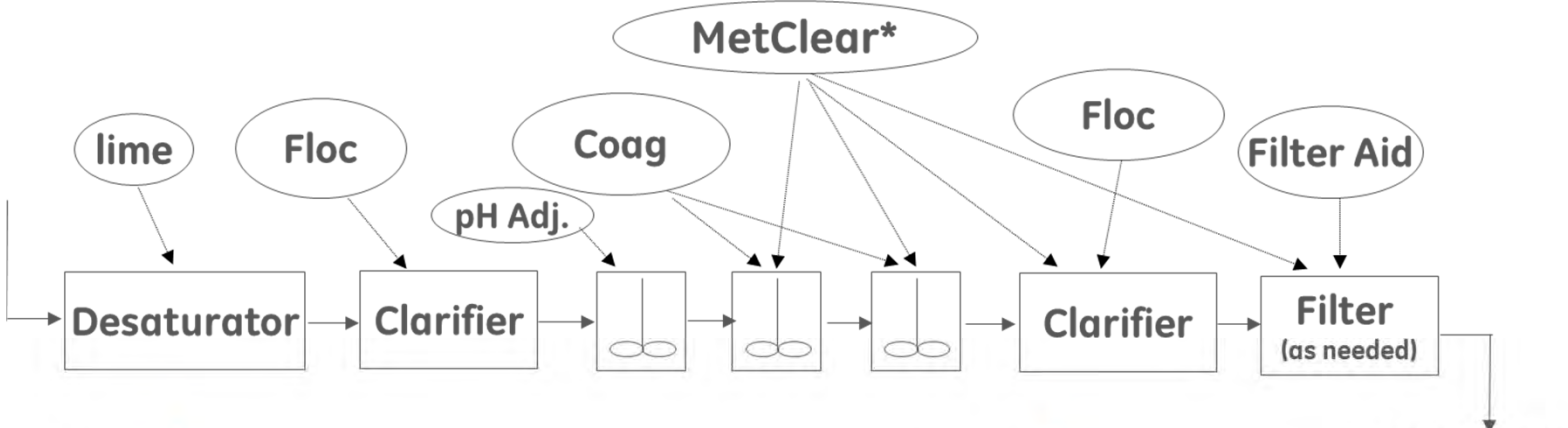
- MetClear\*
  - selective Hg removal chemistry
  - effective for Se precipitation
- PolyFloc\* & Novus\* – anionic and cationic flocculants
- KlarAid\* – complete line of coagulants



Reducing agents & organic molecules susceptible to oxidation



# Hg removal with P/C treatment



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# Se removal with P/C treatment

Example: northeast coal-fired power plant

- 650 MW unit, Eastern bituminous w/ high Se, LSFO wFGD

## Selenium Issue

- Highly variable (2-20 ppm) dissolved Se in purge water
- Challenged to meet environmental permit
- Limited previous success w/ ferric or ferrous chemical treatments
- New chemical program implemented to remove Se

## Se speciation:

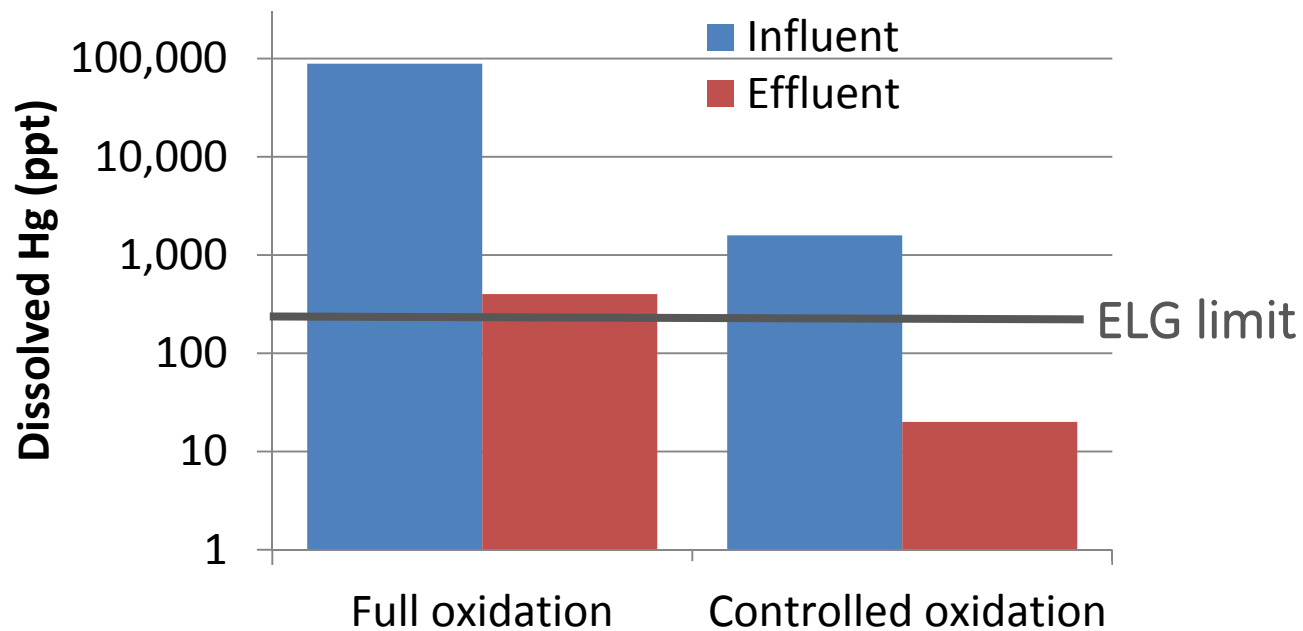
Selenite	Selenate	SeCN	MeSe (IV)	Unknown Se Species
73%	3%	5%	1%	18%

## Se removal:

Selenite	Selenate	SeCN	MeSe (IV)	Unknown Se Species
88 - 92%	50 -70%	60%	0%	85% - 98%



# Sulfite control benefits to P/C Hg removal

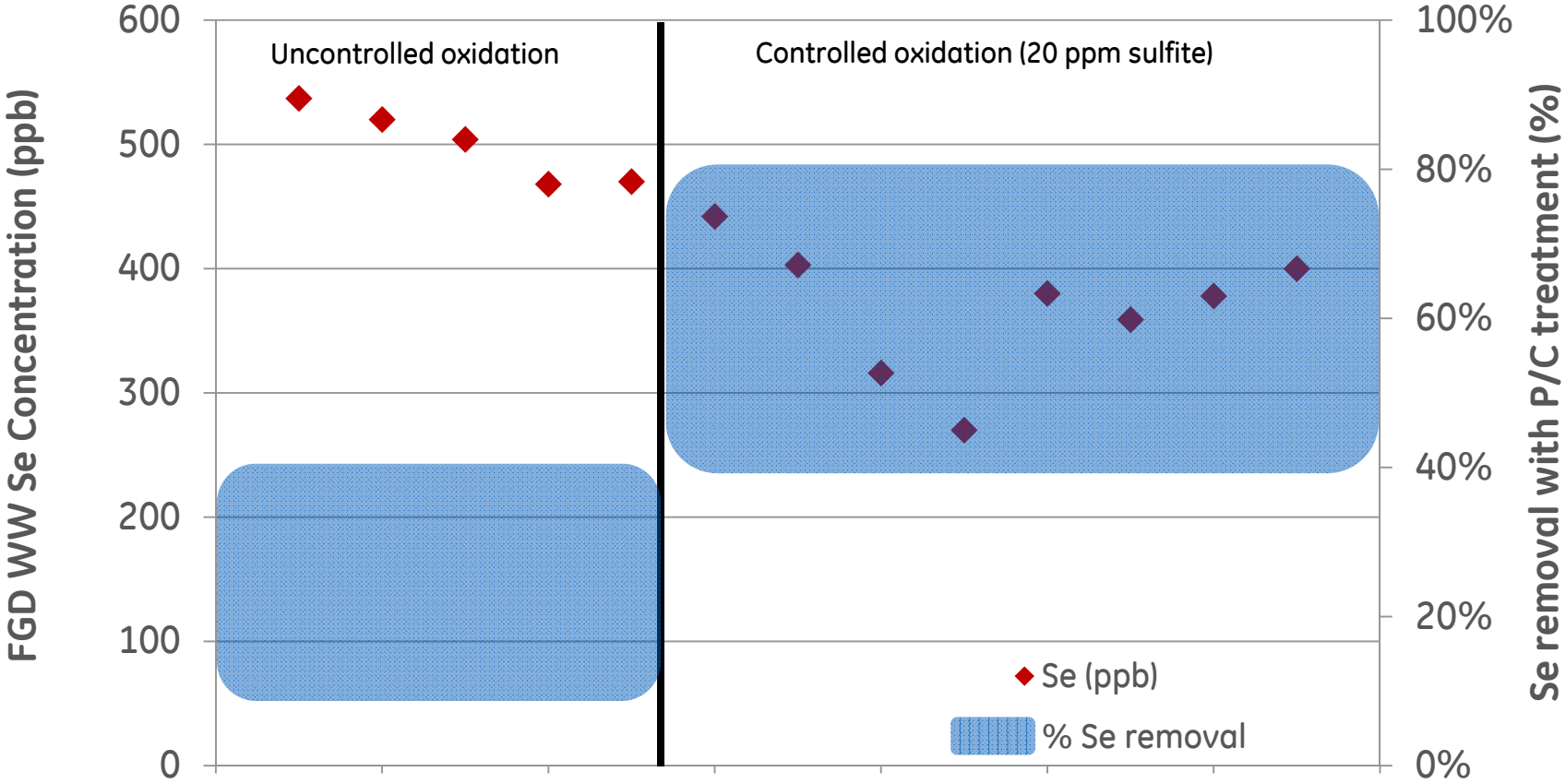


## WFGD w/ sulfite control:

- Significant reduction of WWTP influent Hg
- Reduced variability
- Reduced oxidant loading



# Improved P/C Se removal with sulfite control



**Influent Se concentration reduced while P/C removal more effective**



# Benefits to P/C treatment with sulfite control

- Reduced Hg and Se influent concentrations
- Se: complete oxidation to selenate avoided
  - P/C removal more effective
- Reduced oxidizing species entering WWTP
  - P/C chemicals not consumed/oxidized
- Reduced variability
  - Jar testing more representative

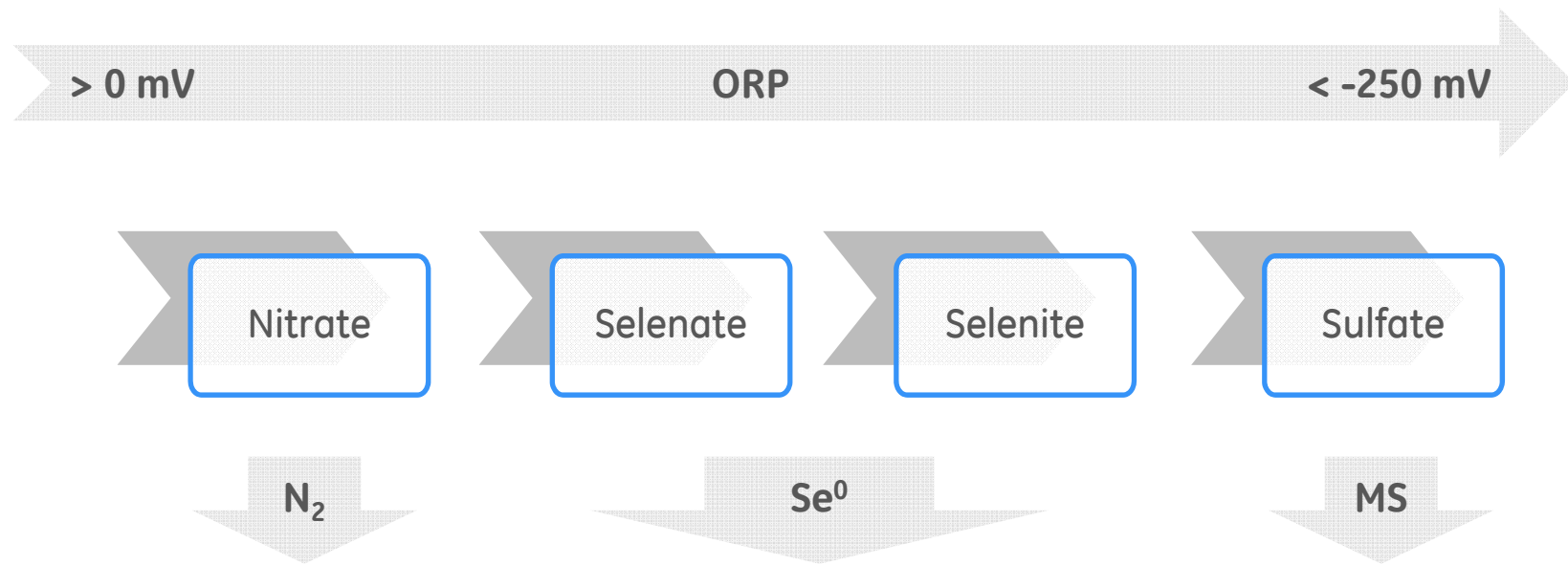


# Treat & Discharge

ABMet\* Biological Treatment



# Biological Reduction of Key Constituents in FGD Wastewaters

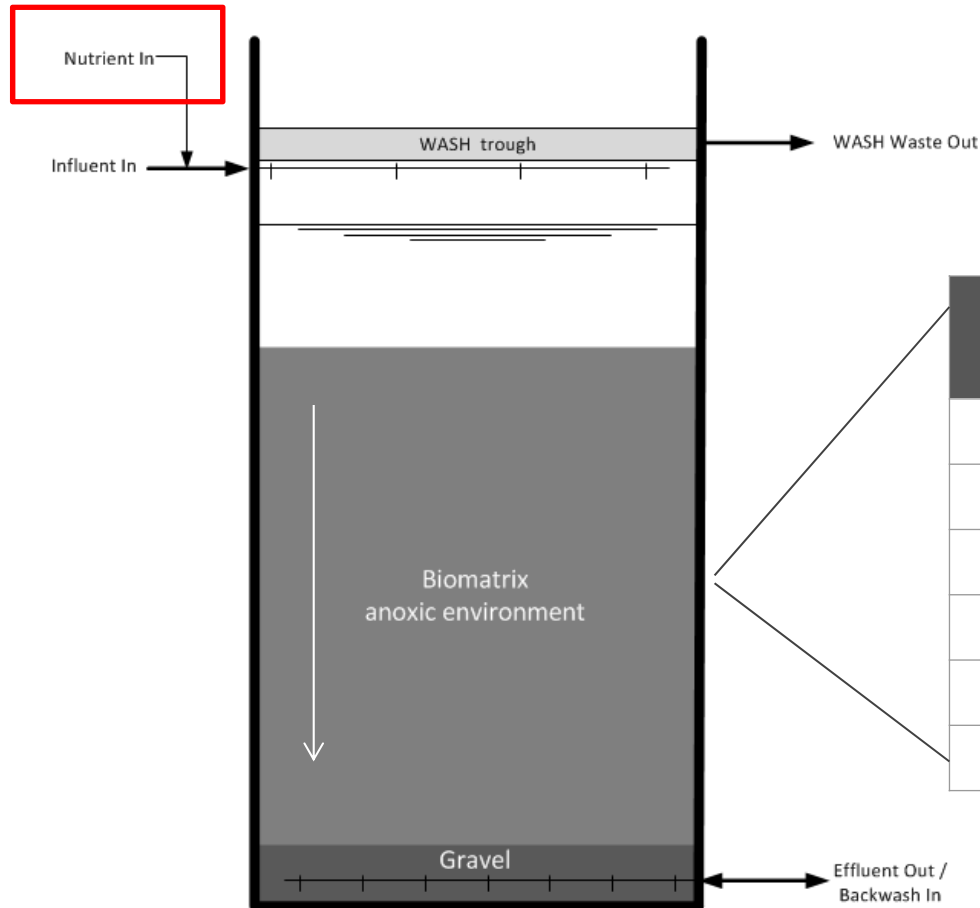


Single-Step Process Without Post-Treatment Required



# Control of Conditions within Biofilter to Optimize Selenium Removal

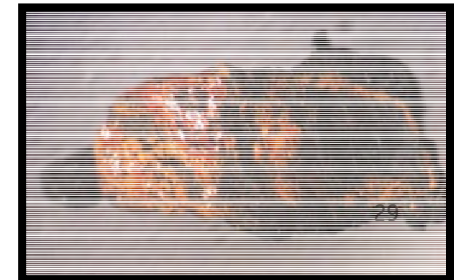
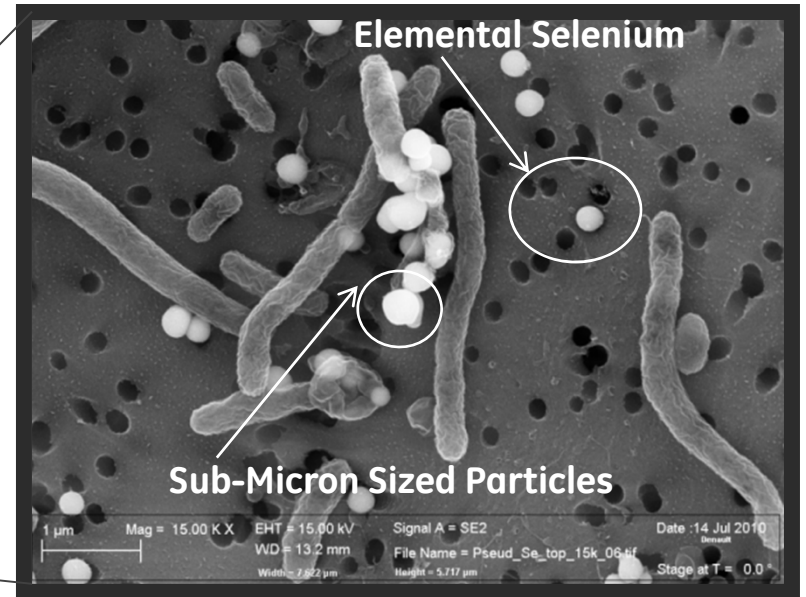
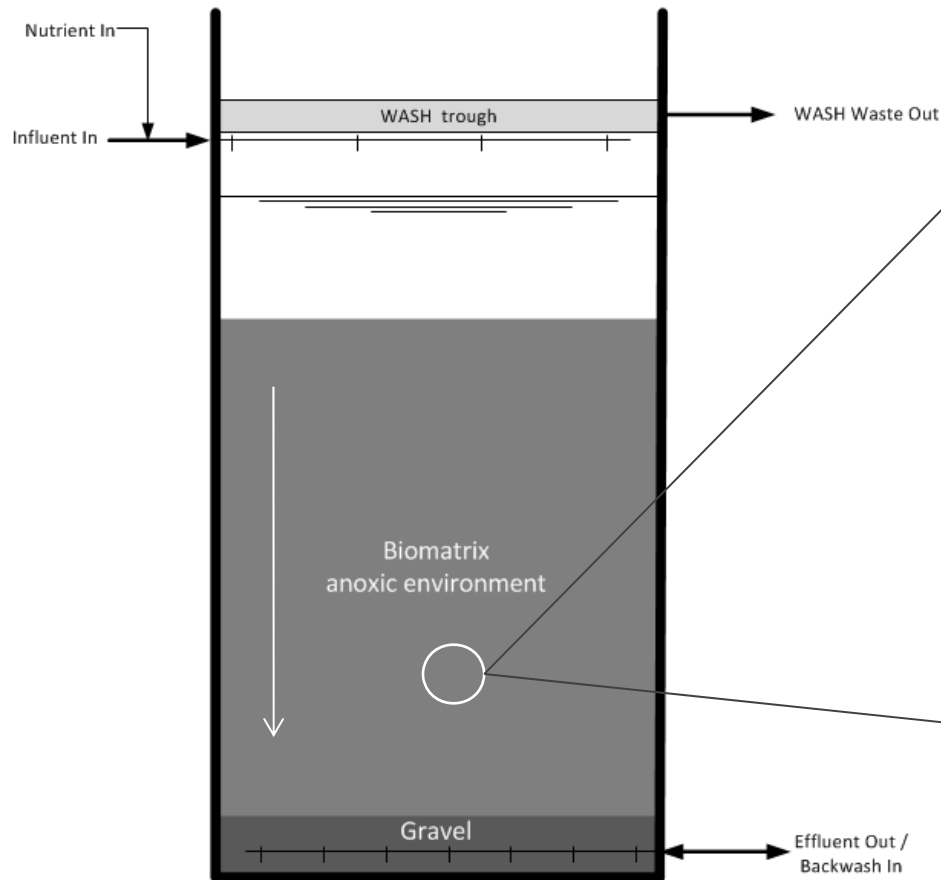
Maintaining a stable, moderate influent ORP reduces the gap to hitting “sweet spot” ORP for nitrate and selenium removal = smaller reactor volume



Electron Acceptor	Approximate ORP
Oxygen	>0 mV
Nitrate	< 0 mV
Nitrite	< -50 mV
Selenate	< -100 mV
Selenite	< -150 mV
Sulfate	< -200 mV



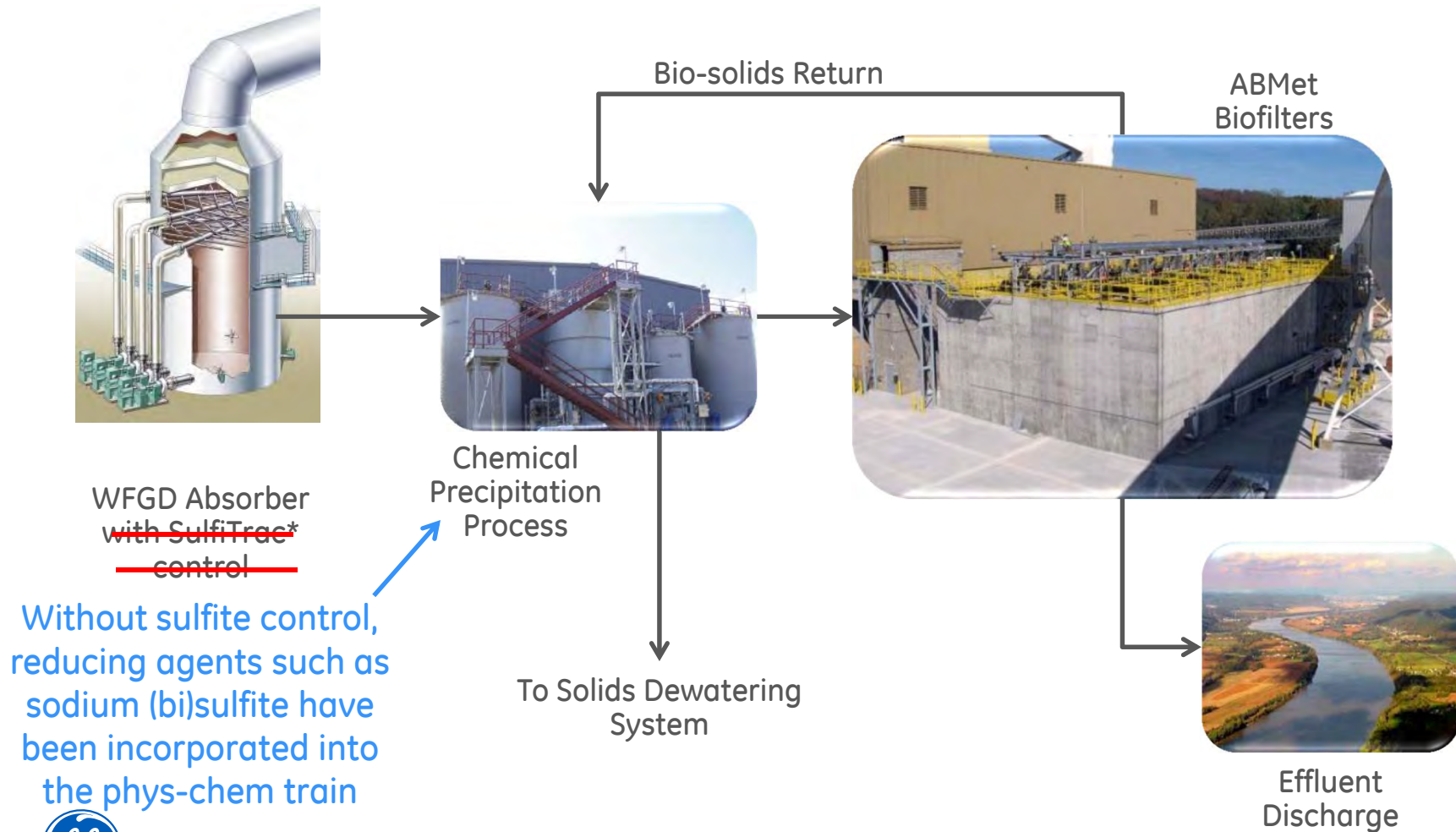
# Biofilter Design Retains By-Products to Product and Effluent Ready for Discharge



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# Integrated Chemical Precipitation + Biological Treatment Flow Sheet



# Oxidant generation in the scrubber

In addition, dithionate ( $S_2O_8^{2-}$ ) by adding excess oxidant  $S_2O_8^{2-}$  would degrade and require to be treated or

Unlike some measurements, it is a measurement based on oxidizers could increase the main oxidizers within the solution, it may react to a certain amount in the process. For example, it may react with slurry containing hypochlorite



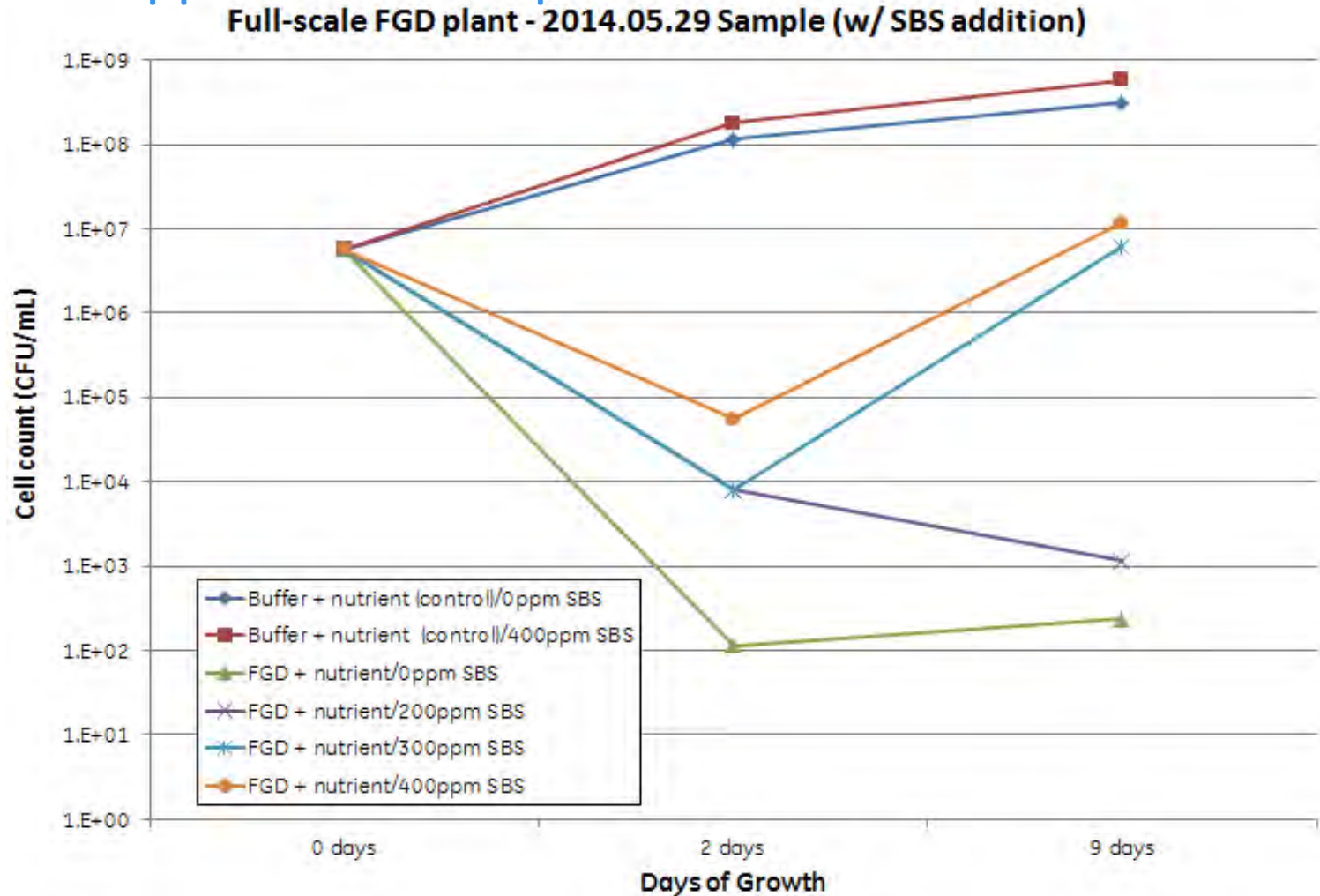
be formed in the scrubber, which is not easily treatable. These compounds would be treated in Japan.

Specific chemical species are formed as a whole. As such, many acids are thought to be the main oxidizers brought into contact with a scrubber, which are produced by a corresponding reaction with scrubber slurry, it may, in turn, react with the



# Impact of oxidants & reducing agents

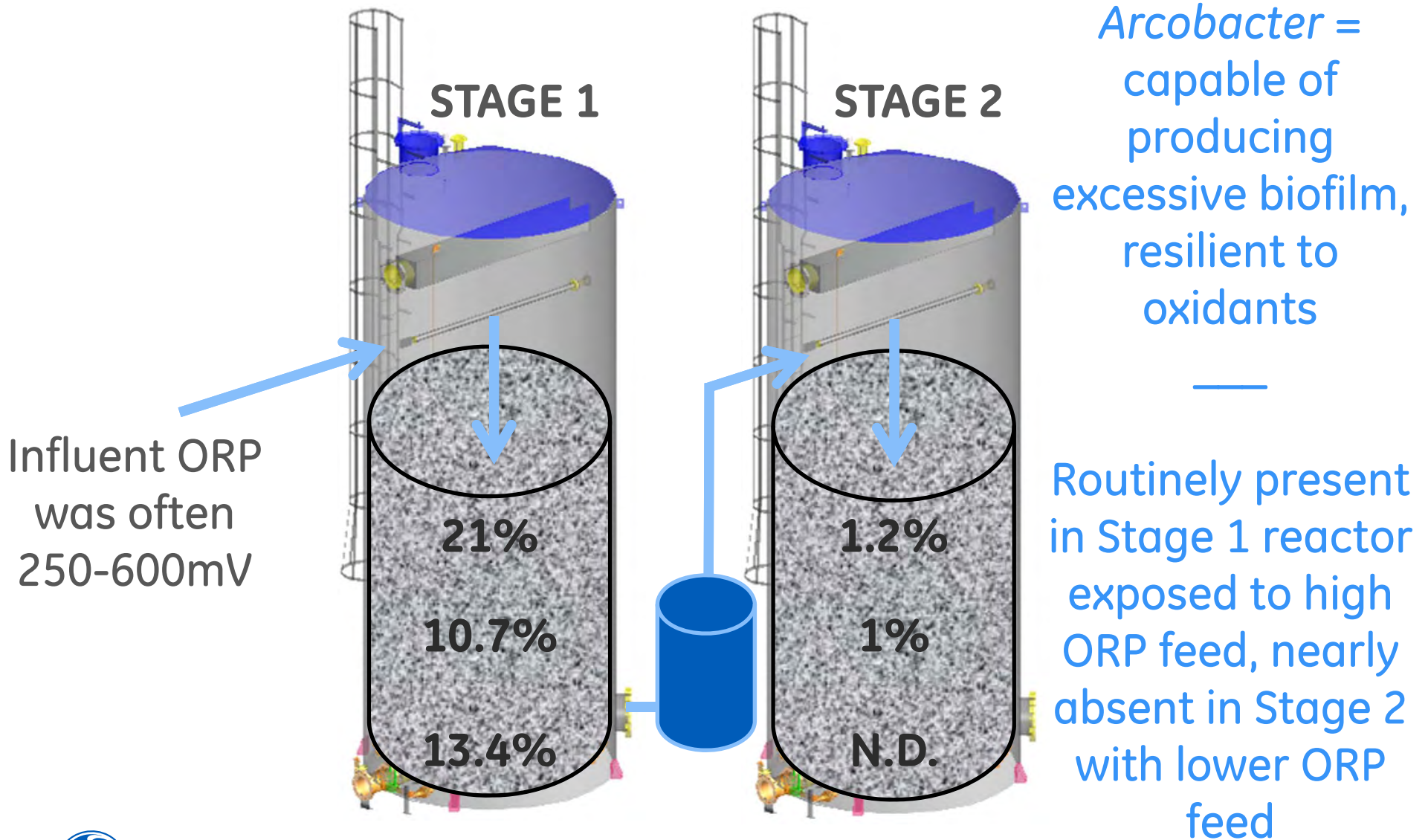
Sodium Bisulfite (SBS) Addition + Cell Growth (plant in USA, total oxidant of 25ppm chlorine-equivalent)



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# “Nuisance” bacteria can persist in high-ORP feed



# Summary



# WFGD Optimization for Improved WW Treatment

## Reduced variability

- Actively controlled oxidation negates ORP swings observed in WFGD operation

## Reduced oxidizing species in WW stream

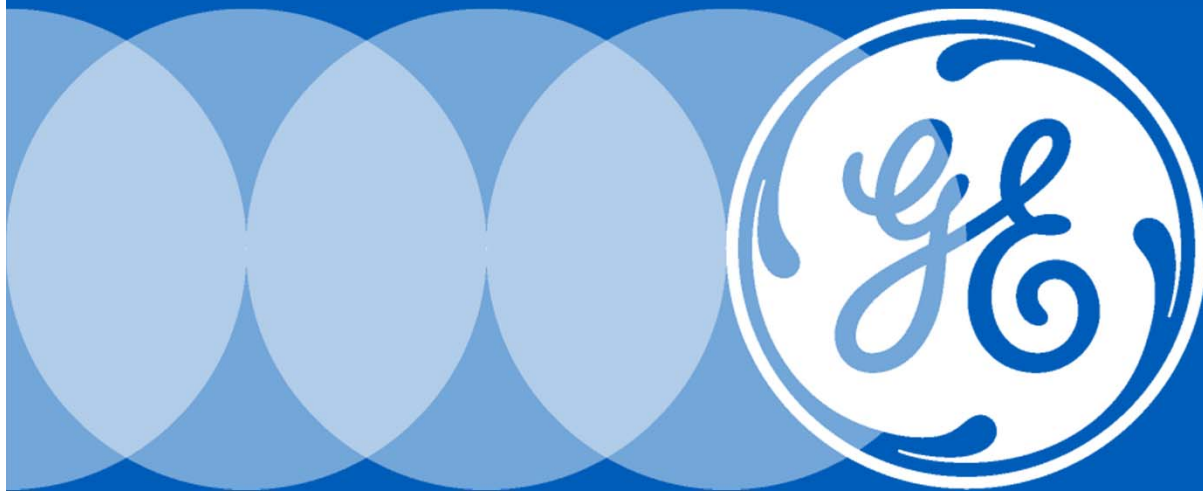
- Protects both WWT chemicals & biological system
- Removes requirement to add reducing agent for optimum WWT
- Maintains desired bacteria for nitrate/selenium removal

## Decreased dissolved contaminant loading on WWTP

- Significant reduction in WW Hg concentration
- Reduction in WW Se concentration
- Avoid complete oxidation of Se to selenate form

**WFGD sulfite control optimizes WFGD purge for improved treatment in WWTS**





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