



Testing to Meet Low Mercury Limits in FGD Purge Water at a Coal-Fired Plant

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I.1 Wastewater Management



Seminole Mercury Pilot Project

Acknowledgements

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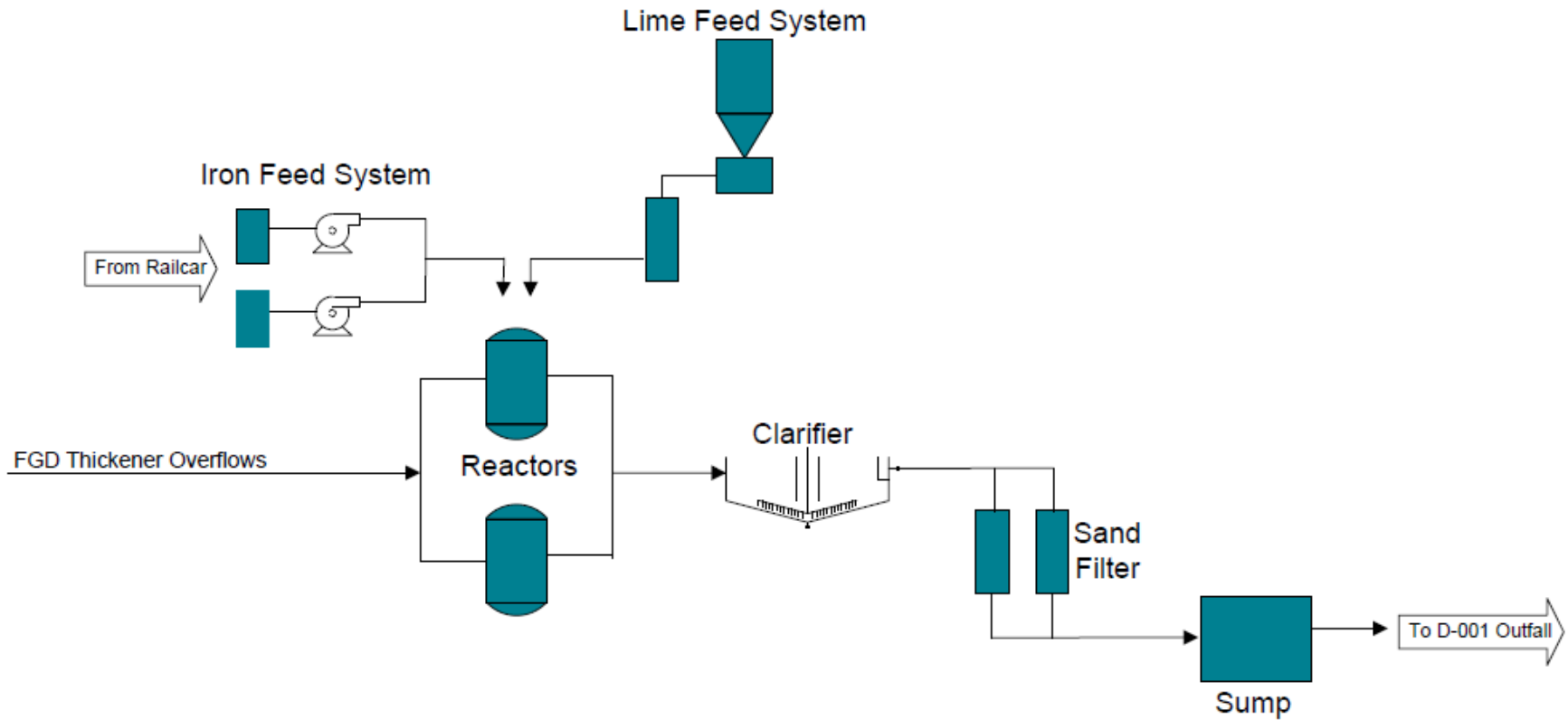


Seminole Generating Station Profile

- 1,500 MW Coal-Fired Plant near Palatka, Florida
- 2 – 750 MW Units with Wet Flue Gas Desulfurization (FGD) Systems
- FGD Produces Gypsum – Supplied to Co-Located Wallboard Plant
- FGD Purge Water Treatment System (PWTS)
 - Gypsum Desaturization
 - Iron Reduction for Selenium Removal
 - Coincident Mercury Removal
- Discharge to St. John's River with Other Low-Volume and Cooling Tower Blowdown Wastewaters at Outfall D-001
- Mercury Sometimes Exceeds Limit at D-001



Existing PWTs





Project Goals

- Study a PWTs Modification for Improved Mercury Removal to Meet NPDES Permit Limit at D-001
- Provide a Path Forward for Compliance with a Florida Department of Environmental Protection Order for Mercury
- Study PWTs Modification to Meet Draft EPA Effluent Limitation Guidelines (ELGs) for PWTs effluent –
 - Mercury – 119 nanograms per liter (ng/L)
 - Selenium – 10 micrograms per liter (ug/L)



Project Approach

- Bench-Scale Treatability Testing and Conceptual Analysis of Alternatives
 1. Single-Stage Organosulfide/Iron Precipitation and Filtration for Mercury Removal
 2. Two-Stage Iron and Organosulfide Precipitation and Filtration for Mercury and Selenium Removal

- Next Step – Pilot Testing of Either or Both Alternatives

Then...

- EPA delayed issuance of Steam Electric Effluent Guidelines



Seminole Pilot Test Decision

- Primary Focus on FDEP Order Compliance - Mercury
- Regulatory Uncertainty of EPA ELG Promulgation Date and Final Regulatory Option to be Selected
- Seminole Selected Alternative 1 and a 4-Week Pilot Test Period
 - ❖ Single-Stage Mercury Removal with Organosulfide/Ferric Iron Precipitation and Sand Filtration
- Pilot Testing Occurred in April and May 2014, immediately after an Outage on 1 Generating Unit



Pilot Testing Objectives

- Primary Objective: Pilot effluent Mercury concentration < 225 ng/l to assure compliance with NPDES effluent limit at D-001
- Secondary Objective: Pilot effluent Mercury concentration < 40 ng/l for ELG compliance (1/3 of Draft Guideline)
- Determine the dosages of organosulfide, ferric chloride, and polymer
- Demonstrate whether the TSS loading generated by chemical treatment can be handled by the existing sand filter units



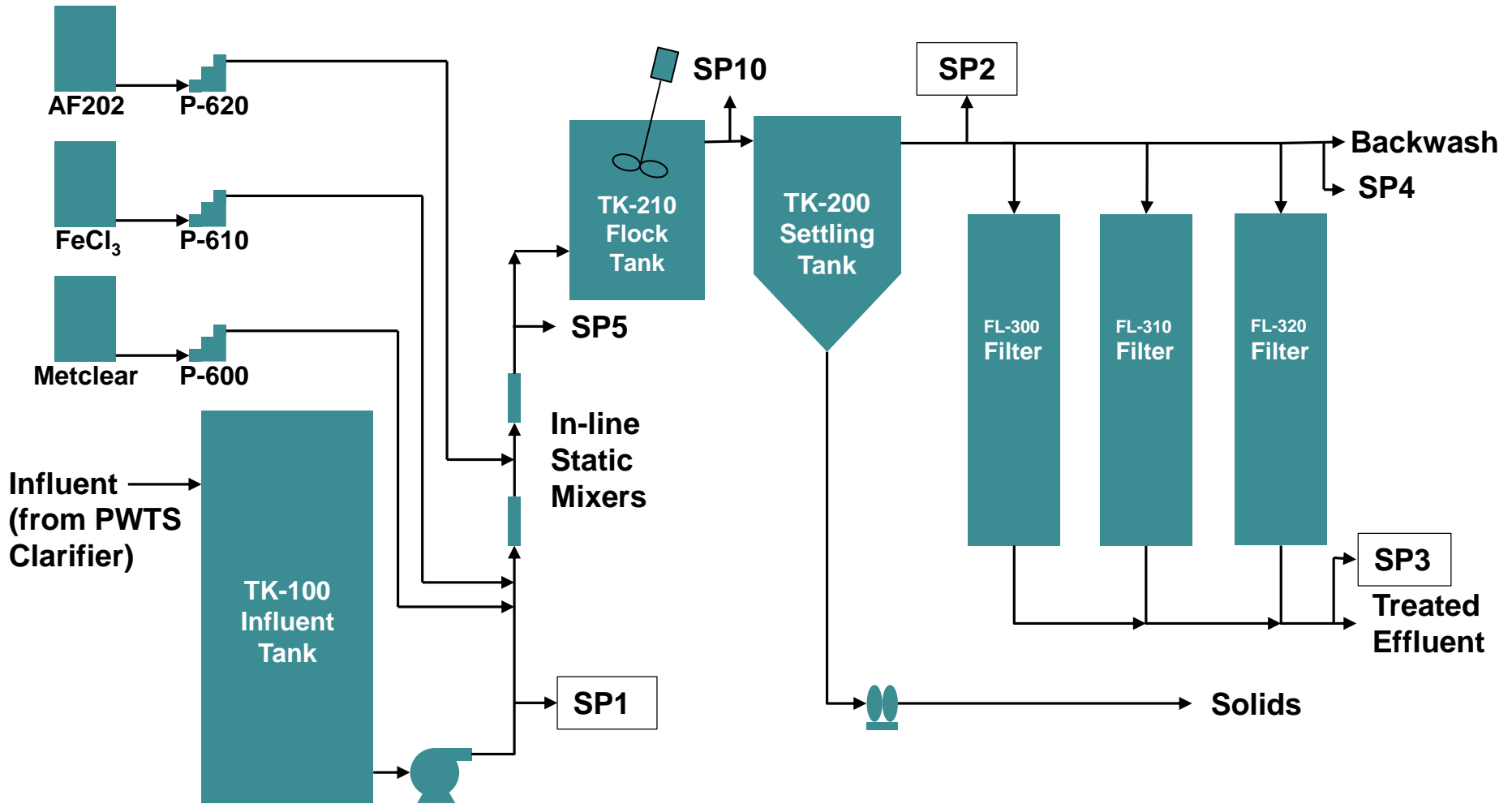
Key Pilot System Design Criteria

- Design flow rate = 5.5 gpm (1% of PWTS flow rate)
- Chemical-physical treatment process for enhanced mercury removal
 - Metclear MR2405 (Organosulfide)
 - FeCl₃ (Ferric Chloride)
 - Hychem AF202 (Anionic Polymer)

<u>Equipment Name</u>	<u>Design Criteria</u>
Reaction Tank (plus Settling)	20 minute HRT 60° cone bottom
Reaction Tank Mixer	Low shear
Sand filters	2.33 gpm/ft ² hydraulic loading rate 8-inch minimum diameter 3 filters operated in parallel



Simplified BFD with Added Flock Tank





Sampling Locations

Sample Port	Sample Location
SP1	PWTS clarifier effluent/Pilot influent
SP2	Pilot sand filter influent
SP3	Sand filter effluent/Pilot effluent

Note: Additional sample IDs were assigned for tracking solids content and laboratory QA samples



Mercury Pilot Installation



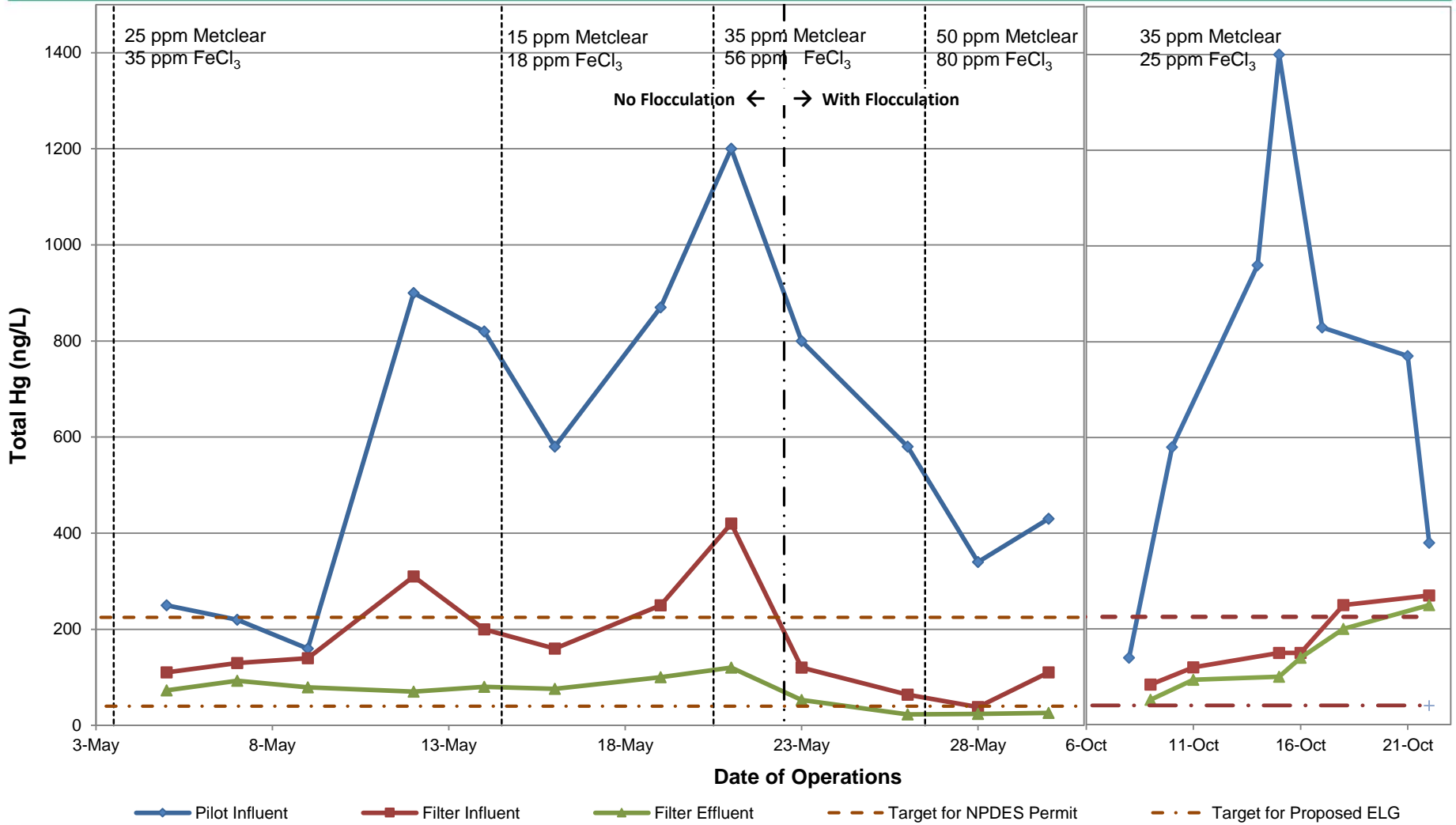


Pilot Influent Water Quality (May)

Parameter	Unit	Average	Minimum	Maximum
Total Mercury	ng/l	586	160	1200
Dissolved Mercury	ng/l	247	96.0	500
Temperature	° C	31.2	24.0	39.3
Conductivity	µS	34,888	23,743	41,408
DO	mg/l	0.90	0.22	3.02
pH	s.u.	9.08	8.80	9.43
ORP	R. mV	0.4	-299.7	127.0
TSS	mg/l	38.4	ND	100.0

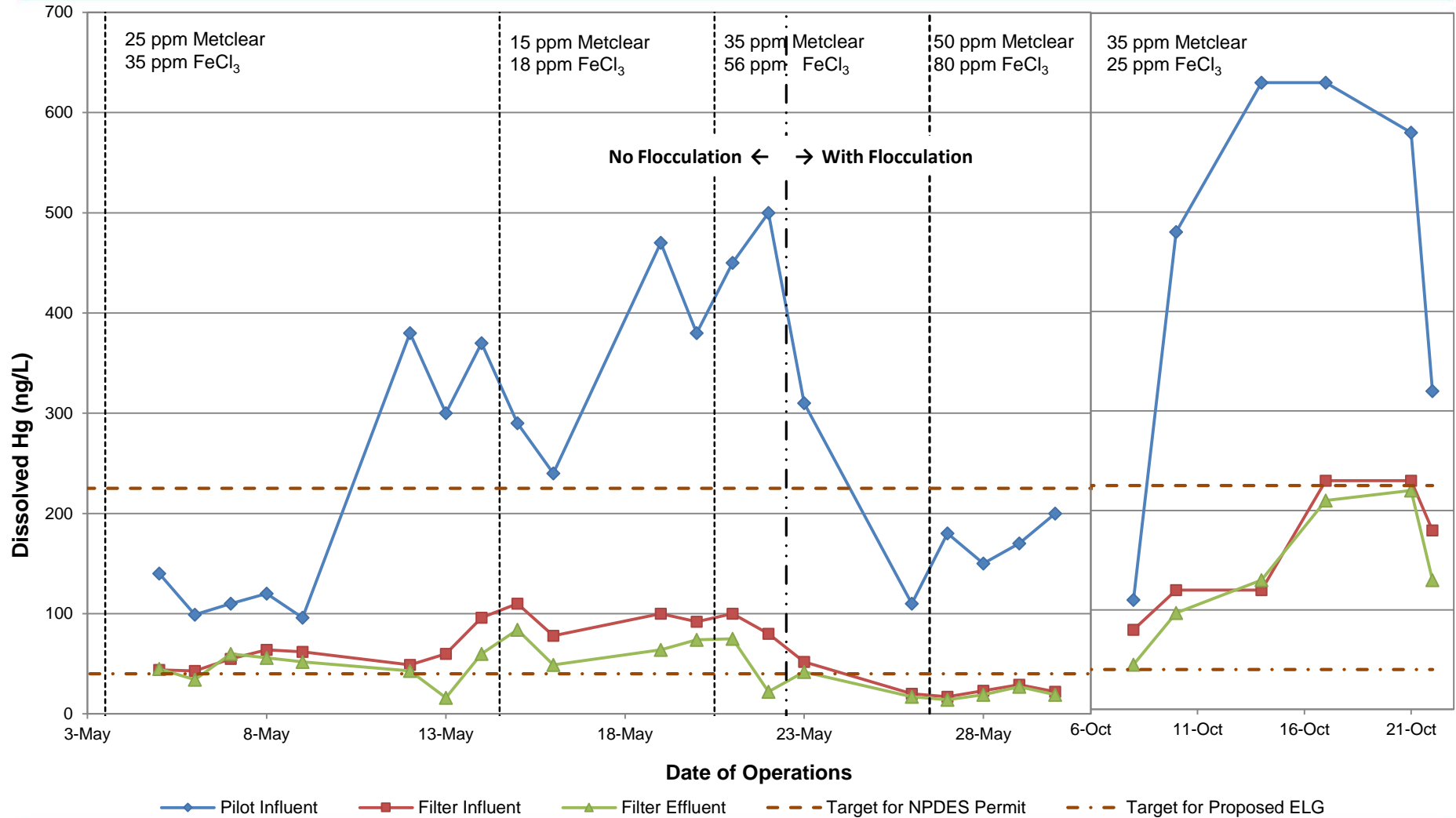
- Total Hg range: 160 ng/l to 1200 ng/l
- 50% of influent dissolved Hg samples < 225 ng/l target
- On average, 44% influent Hg was dissolved or colloidal (passed through 0.45 µm filter)

Total Mercury



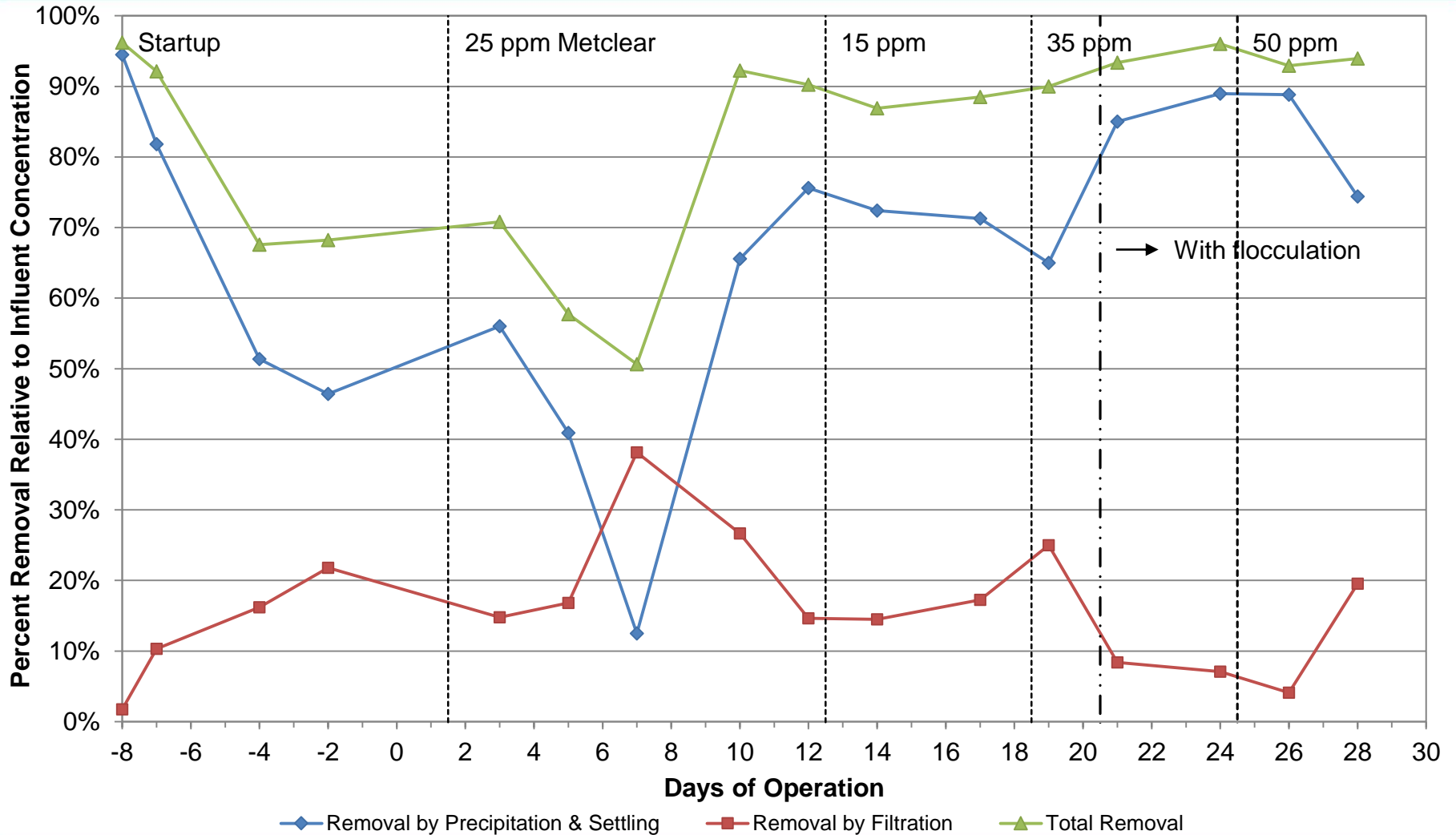


Dissolved Mercury





Mercury Removal





Effluent Water Quality (May)

Parameter	Unit	Average	Minimum	Maximum
Total Mercury	ng/l	70.4	22.0	120
Dissolved Mercury	ng/l	44.0	14.0	84.0
Temperature	° C	28.6	23.1	34.7
Conductivity	µS	31,394	9,998	39,711
DO	mg/L	1.11	0.36	2.92
pH	s.u.	8.74	8.37	9.04
ORP	R. mV	22.3	-225.6	156.4
TSS	mg/l	24.2	3.4	52.0



Effluent Mercury Concentrations

- Average effluent concentration (total Mercury)
 - Before Flock Tank Installation: 70.4 ng/l
 - After Flock Tank: 31.5 ng/l
- Effluent total and dissolved Mercury concentrations tended to be independent of the Metclear dose
 - Similar effluent concentrations over a range of doses prior to the addition of flocculation tank
- Effluent total and dissolved Mercury concentrations appeared to vary slightly with the influent concentration
 - If present, the effect of influent concentration on effluent concentration was weak
- 33% of effluent samples had **dissolved** Mercury < 40 ng/l
 - Ability to remove insoluble Mercury critical to achieve secondary treatment goal



Sequential Filtration

Mercury Fraction	Concentration (ng/l)	% of Total Mercury
Pilot Influent		
Total mercury (no filtration)	220	100%
After 0.45 µm filter (“dissolved”)	110	50%
Pilot Sand Filter Effluent		
Total mercury (no filtration)	77.2	100%
After 0.45 µm filter (“dissolved”)	64.9	84.1%
After 0.10 µm filter	42.9	55.6%
After 30 kDa MW filter	10.5	13.6%
After 10 kDa MW filter	8.21	10.6%

- 1 sample collected May 7, 2014
- At time of sample collection, pilot was more effective at removing particulate mercury than dissolved/colloidal mercury
- Average effluent dissolved mercury without flocculation was 64% of total mercury. After flocculation was installed, dissolved portion increased to 76% of total



Selenium Removal

Location	Units	5/7/14	5/16/14	5/21/14	5/28/14*
FeCl ₃ dose	ppm	35 FeCl ₃	18 FeCl ₃	56 FeCl ₃	80 FeCl ₃
Pilot influent	µg/L	7.1	13.7	14.5	10.9
Pilot effluent	µg/L	6.8	12.9	12.1	7.2
Percent removal	%	4.2%	5.8%	16.6%	33.9%

* After Flocculation Tank Installation

- Remember: Draft Selenium ELG is 10 ug/L
- Some removal may have occurred during pilot treatment
 - Larger data set required to prove removal is statistically significant
 - Better removal observed during higher iron dosing periods
 - Better removal after flock tank was added.



Typical Solids Settling Tests During Pilot

Earlier – Lower Dosing



Later – Higher Dosing





Solids Characteristics

- Settled Solids Volume (SSV) in reaction/flocculation tank influent increased with increasing chemical dose
- Addition of separate flocculation tank reduced SSV in sand filter influent
- Filter backwash interval doubled after flock tank installation, even though chemical dosing was higher than prior to flock tank
- Solids passed TCLP for RCRA metals
 - Arsenic and barium were detected at less than RCRA limits
 - No other metals were detected





Conclusions – Mercury Removal

- Pilot testing successfully reduced effluent Mercury concentrations to < 225 ng/l.
 - Pilot influent concentrations were lower than historical maximums
- Pilot test process reduced effluent Mercury to < 40 ng/l after flocculation and settling unit operations were improved.
 - Results obtained in October 2014 (higher effluent Mercury) need further review (ratio of organosulfide:ferric iron may be a key)
- Substantial colloidal fraction of Mercury was present
 - Effective chemical addition, flocculation and settling are necessary so that sand filters (current Seminole polishing process) can be utilized.
 - Tighter membrane filtration might be needed



Conclusions – Solids Removal

- Visual observations indicated less turbid, higher quality water was produced after the flocculation step was added.
- Filter operation times increased after the addition of flocculation.
- Flocculation and settling appeared to play a larger role than chemical dosing in minimizing solids loading on the sand filters.
- Sand filters hydraulic loading rate of 2.33 gpm/ft² recommended for use during pilot operations should result in filter operations similar to current PWTS conditions.



Path Forward: Mercury Removal at Seminole

- After ELGs are issued for FGD wastewater, check ability of existing PWTS plus Organosulfide Mercury Polishing to provide reliable compliance for Mercury AND Selenium
- Conduct additional Mercury Polishing testing for:
 - Repeatable Mercury results
 - Check Selenium removal
 - Assess need for better filtration
- If another process would be needed for Selenium, consider optional technologies that may achieve both Mercury and Selenium removal in one process



Seminole Mercury Pilot Project



Questions?