

Removal of Selenium from Refinery Wastewater Using Sulfur-Modified Iron (SMI)

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Selenium Basics

- Metalloid; common forms:
 - Selenite, Se(IV): SeO_3^{2-}
 - Selenate, Se(VI): SeO_4^{2-}
- **Essential nutrient** in small amounts (10-75 $\mu\text{g}/\text{day}$)
- **Toxic** at higher levels
- Federal MCL **0.05 mg/L**
- Sources in drinking water
 - Discharge from refineries or mines
 - Natural deposits

Si 14 Silicon	P 15 Phosphorus	S 16 Sulfur	Cl 17 Chlorine
Fe 26 Iron	As 33 Arsenic	Se 34 Selenium	Br 35 Bromine
Sn 50 Tin	Sb 51 Antimony	Te 52 Tellurium	I 53 Iodine

Selenium and Refineries

- Present in sour crude oil
- Carried through refining process; sour water stripper conc. ~ 1 mg/L
- Existing removal methods
 - Iron co-precipitation
 - Bioremediation
 - Evaporation
- Existing methods often \$\$\$, difficult to operate, generate sludge, or require space

SMI®-III Basics

- Granular, iron-based media
 - Patented
 - NSF certified
 - Around for > 20 years
- Removes As, Se, Cr(VI), Hg, nitrate
- Removal occurs through adsorption and/or chemical reaction
- Used ex situ
- Spent media can be recycled



Using SMI

- Shipped dry
- Once wet, must remain wet
- Flow is upflow
- Must be “fluffed” periodically to prevent cementation
- Iron may be released
- Complete systems available



Screening Level Column Tests

- 60 mL syringe
- 50 mL (~ 100 g) SMI
- EBCT 10-20 min
(2.5-5 mL/min)
- Upflow
- Measure Se and other parameters after ~ 100 bed volumes



Waters Tested

- Sour water stripper (SWS) effluent
 - Non-phenolic
 - Phenolic / oily
- Oily water sewer
- Chemical sewer
- Mixed sources
- As Received pH: 6-12
- Contains selenate, selenite, selenocynate



Pre-treatment Options

- None
- pH adjustment (to ~ 6)
- Removal of oil (via polymer)
- Oxidation of Se (via peroxide)

Selenium Removal – Screening

Site	Water Type/Source	Pre-treatment	EBCT	Total Selenium, mg/L		% Removed
			min	Influent	Effluent	
Site A	SW-A	none	10	0.92	< 0.010	100
Site A	SW-B	oil removal	10	1.5	0.43	71
Site A	SW-B	oil removal	10	1.4	0.64	54
Site A	SW-B	oil removal	10	2.1	1.1	48
Site A	SW-B	oil removal	10	2.1	1.1	48
Site A	SW-B	Oil removal + oxidation	10	2.1	0.73	65
Site B	SW-A	none	10	0.25	0.28	-12
Site B	SW-B	none	10	0.64	< 0.010	100
Site B	SW-C	none	10	1.6	0.58	64
Site B	SW-C	pH adjust	10	1.4	0.54	61
Site B	SW-C	none	20	1.3	0.18	86
Site C	pond infl.	none	10	0.076	0.015	80
Site C	sewer	none	10	0.1	0.063	37
Site D	chem sewer	pH adjust	15	0.82	0.52	37
Site D	mixed sources	pH adjust	10	0.86	0.73	15
Site D	mixed sources	none	20	0.9	0.51	43

Site A, SW-A (100% Removal)

Analyte	Units	Influent	Effluent
Selenium			
dissolved	mg/L	n.m.	< 0.010
total	mg/L	0.92	< 0.010
pH	--	7.0	5.7
Color	--	Pink/orange	Pale yellow

No pretreatment; 10 min EBCT

- Complete As removal
- As removal due to adsorption within the bed, not co-precipitation with iron
- pH change atypical



Site A – SW-A Field Pilot

Parameter	Value
Diameter, in (cm)	2 (5.1)
Bed height, in (cm)	40 (102)
EBCT, min	5
Influent Se, $\mu\text{g/L}$	650 – 1,200
Effluent Se, $\mu\text{g/L}$	< 5 (no breakthrough)
Backwash frequency	24-48 hrs
Duration	6 months
Capacity	> 12 mg Se / g SMI
Next Steps	60 gpm unit to be delivered Spring 2018



Site B, SW-B (100% Removal)

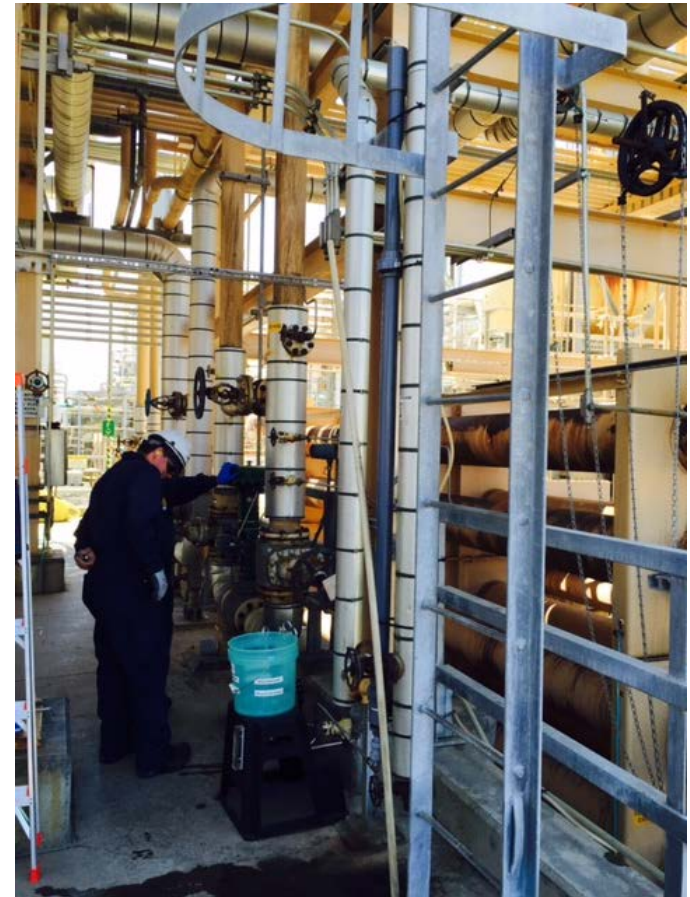
Analyte	Units	Influent	Effluent
Selenium (total)	mg/L	0.64	< 0.010
Iron (total)	mg/L	< 0.60	12
pH	--	9.1	6.2
Color	--	Light brownish orange/slightly cloudy	Brownish yellow

No pretreatment; 10 min EBCT

- SMI effective at elevated pH
- As removal due to adsorption within the bed, not co-precipitation with iron
- Post-treatment iron removal may be required

Site B – SW-B Field Pilot

Parameter	Value
Diameter, in (cm)	2 (5.1)
Bed height, in (cm)	40 (102)
EBCT, min	5
Influent Se, $\mu\text{g/L}$	850
Effluent Se, $\mu\text{g/L}$	< 5 (no breakthrough)
Backwash frequency	24 hrs
Duration	3 weeks
Next Steps	Studying full size system



Summary / Conclusions

- Screening level tests demonstrated SMI can remove Se from refinery waste streams.
- Pre-treatment may be needed to achieve complete removal
- Iron removal may be needed post-treatment, but no other sludge formed
- Long-term effectiveness of SMI borne out in 6 month field pilot
- Capacity > 12 mg Se/g SMI

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