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

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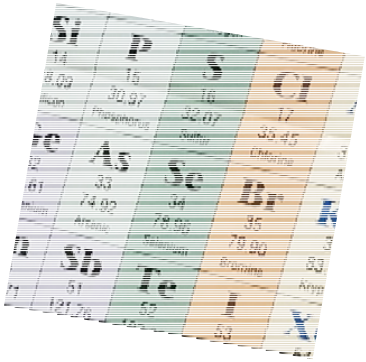
# Selenium Basics



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

# 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)

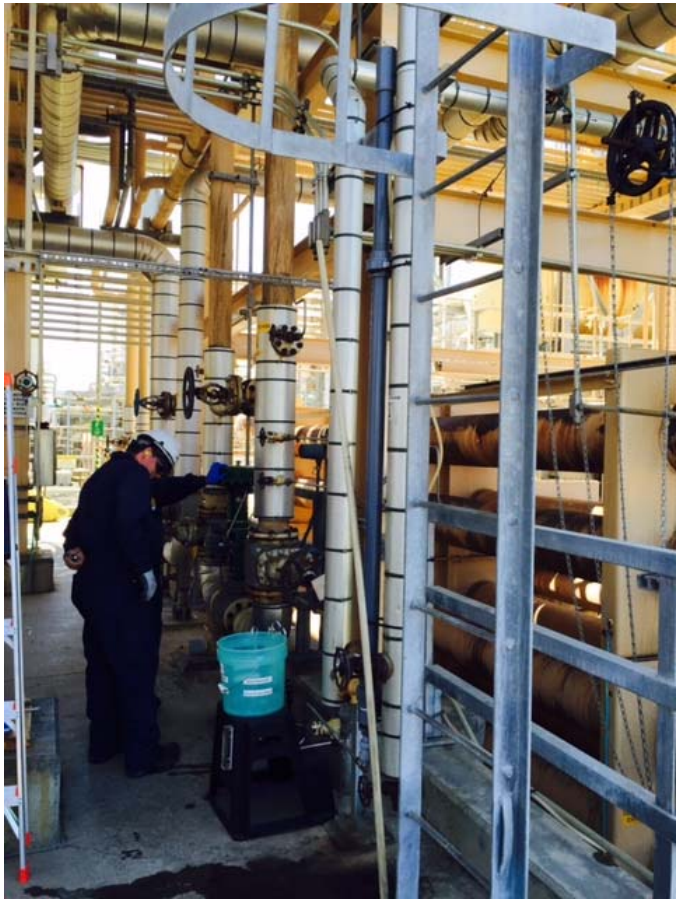
| Analyte | Units | Influent | Effluent |
|---|---|---|---|
| Selenium | | | |
| dissolved | mg/L | n.m. | < 0.010 |
| total | mg/L | 0.92 | < 0.010 |
| pH | -- | 7.0 | 5.7 |
| Color | -- | Pink/orange | Pale yellow |

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, µg/L | 650 – 1,200 |
| Effluent Se, µg/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)

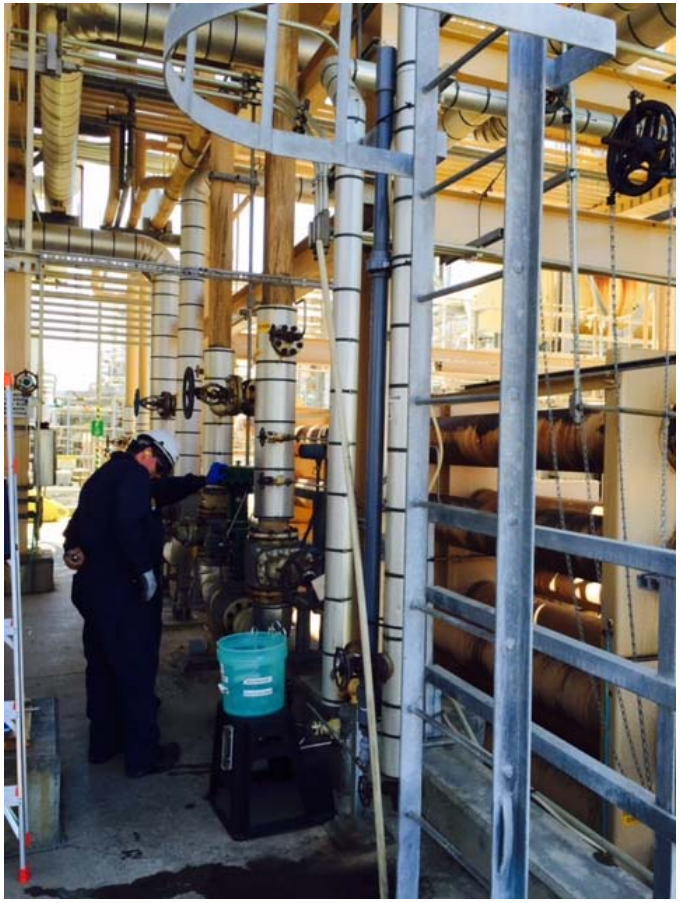
| Analyte | Units | Influent | Effluent |
|---|---|---|---|
| Selenium (total) | mg/L | 0.64 | < 0.010 |
| Iron (total) | mg/L | < 0.60 | 12 |
| pH | -- | 9.1 | 6.2 |
| Color | -- | Light brownish orange/slightly cloudy | Brownish yellow |

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, μg/L | 850 |
| Effluent Se, μg/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

Contact Info

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