Selenium Removal from Refinery Wastewater
Using Immobilized Cell Bioreactor Technology

Lori Donovan, Account Manager
William Sheridan, Operation Manager
UOP LLC. A Honeywell Company

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Why is selenium an issue for oil refineries?

• Present in crude oil ~1:1000 ratio to Sulfur
  – Se level varies based on crude source

• Increasing regulatory limits on selenium discharges typically at ppb level
  – USA EPA Mandate
  – Levels vary from refinery to refinery and impacted by NPDES permit
  – Fish toxicity
  – Waterfowl deformation and mortality

• Difficult and expensive to remove from water using conventional water treatment technologies

• Distributed amongst various water sources and process units
  – Highest concentration in sour water stripper

EPA Recommended Biological Treatment as Best Available Technology (BAT)
Selenium originates from the crude, 
\(~ 1:1000\) Se: Sulfur
## Contaminants Removable by UOP Xceed™ Bioreactor Technology

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influent (mg/l)</th>
<th>Effluent (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenium</td>
<td>0.295</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Copper</td>
<td>0.35</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>76</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>TOC</td>
<td>2600</td>
<td>286</td>
</tr>
<tr>
<td>BOD₅</td>
<td>925</td>
<td>13-21</td>
</tr>
<tr>
<td>Phenol</td>
<td>345</td>
<td>0.005</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.4</td>
<td>0.003</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.8</td>
<td>0.001</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.7</td>
<td>0.001</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>23.0</td>
<td>0.005</td>
</tr>
<tr>
<td>Phenols</td>
<td>305</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.7</td>
<td>0.008</td>
</tr>
<tr>
<td>COD</td>
<td>1327</td>
<td>290</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>204</td>
<td>6</td>
</tr>
<tr>
<td>NO₃⁻-N</td>
<td>3000</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>
Biological Selenium Reduction

SeO$_4^{2-}$ + Org. C $\xrightarrow{\text{bacteria}}$ SeO$_3^{2-}$ + Org. C $\xrightarrow{\text{bacteria}}$ Se$_0$ + CO$_2$ + H$_2$O

Decreasing Energy Yield

Organic Carbon

Bacterial Cell

CO$_2$

O$_2$, NO$_3$, SeO$_4^{2-}$, SO$_4$, CO$_2$

H$_2$O

N$_2$

Se

H$_2$S

CH$_4$
Advantages of Biological Treatment of Selenium

• Selenate is difficult to remove from wastewater using physical-chemical processes
  – Iron precipitation does not meet ppb levels and has high sludge volume
  – Readily reduced to insoluble elemental selenium by microbial reduction.

• The rapid reduction of Selenate and Selenite to elemental Selenium is higher where there is a diverse flora of bacterial.
  – XCeed technology has a diverse microbial flora with a very high concentration of immobilized biomass.

• Biological systems can be configured to convert various Selenium compounds to elemental Selenium.
  – XCeed technology can be configured with combined aerobic/anaerobic sections to treat all forms of soluble Selenium species
XCeed™ Bioreactor

- Fixed film bioreactor incorporating layered packing
- Combines high concentration of active biomass with good mass transfer characteristics
- Drives removal of selenium to low concentrations
- Promotes high rates of organic contaminant removal in other refinery applications

https://www.youtube.com/watch?v=cVBlpyLvBzA
Selenium Removal from Refinery Wastewater Using Immobilized Cell Bioreactor Technology

Typical Biological Treatment Process

1. Industrial Wastewater
2. Clarifier or DAF
3. Biological Treatment
4. Solid/Liquid Separation
5. Adsorbent, RO Membranes
6. Bulk Treatment
7. Discharge or Reuse

UOP XCeed Bioreactor Technology

- High Density Biomass Provides Robustness, Compact Design and Low OPEX

Influent

Effluent

Aeration (if needed)

Air Diffusers

Effluent to Water Treatment
Refinery Case Study

Customer Needs:

• Achieve total selenium <50 µg/l (50 ppb) in refinery waste water without post-treatment prior to discharge
• Cost effective treatment
• Easy to operate system with low labor and maintenance requirements
• Small footprint
• Ability to scale up treatment as refinery grows
• Customer Evaluation & Implementation
  – Achieved total selenium <50 ppb via Pilot plant evaluation

Cost effective Low level Se removal
Project Evaluation & Implementation

1. Inquiry
2. Evaluate existing facility & treatment goals
3. Conduct Treatability study
4. Optional pilot study
5. Develop Cost estimate
6. Deliver turnkey Modular system
7. Conduct system commissioning & handover to site operator
8. Ongoing training & support

UOP Provides Complete Evaluation, Delivery, and Support

Lab Treatability Study
Optional Field Demo
Installation, Start-up & Operation
Refinery Pilot Scale Selenium Removal

Refinery Pilot Scale Selenium Removal

Effect Se Below Customer Target

Selenium Removal from Refinery Wastewater Using Immobilized Cell Bioreactor Technology

Effluent Se Below Customer Target
NO₃ removal must occur for Se removal to proceed
Refinery Pilot Scale ORP Profile

KPIs – measured to ensure optimal performance
Refinery Case Study Conclusions

- Consistent removal of selenium levels below 50 µg/l demonstrated in the pilot demonstration to meet discharge requirements
  - Stable effluent quality independent of influent variations
  - Pilot results were used for full-scale design
  - Commercial system under construction for 2016 start-up
- UOP XCeed is a cost effective solution relative to conventional water treatment technologies
- UOP XCeed provides ease of operation with minimal maintenance requirements Anoxic configuration specifically designed to remove selenium
- UOP XCeed has ability to expand to meet future capacity increases

UOP XCeed Biological Treatment Demonstrated to be Effective for Se Removal
Mining Wastewaters

Seepage & Run-off

- Selenium
- Copper
- Cobalt
- Cadmium
Metals Removal Process

- Bacteria remove many metals from water by changing their redox state converting the metal from a soluble to an in-soluble species
- Bacteria can do this directly through enzymatic means or indirectly by producing sulfide which captures some metals as insoluble metal sulfides

<table>
<thead>
<tr>
<th>Redox Couple</th>
<th>Representative Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(V) → As (III)</td>
<td>$\text{AsO}_4^{3-} + 2\text{SO}_4^{2-} + 24\text{H}^+ + 17\text{e}^- \rightarrow \text{AsS}_2(\text{s}) + 12\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Cr(VI) → Cr (III)</td>
<td>$2\text{CrO}_4^{2-} + 10\text{H}^+ + 6\text{e}^- \rightarrow \text{Cr}_2\text{O}_3(\text{s}) + 5\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Se(VI) → Se (0)</td>
<td>$\text{SeO}_4^{2-} + 8\text{H}^+ + 6\text{e}^- \rightarrow \text{Se}^0 + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>U(VI) → U (IV)</td>
<td>$\text{UO}_2(\text{CO}_3)_2^{2-} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{UO}_2(\text{s}) + 2\text{HCO}_3^-$</td>
</tr>
</tbody>
</table>
Mine Seepage Case Study

Customer Challenge:
A mine in a sensitive environmental area in Western North America was required to remove toxic metals from wastewater prior to discharge to mountain stream.

Contaminant Profile:
Se, Cd, and sulfate – target contaminants for removal.
Mine Seepage Case Study – UOP Solution

Solution:
Anaerobic and aerobic XCeed bioreactor systems were installed for removal of target contaminants.

System Components:
(2) Anaerobic bioreactors with Biogas H₂S Filters
Aerobic Bioreactor Polisher with low HP Blowers
Mine Seepage Case Study – Se Results

Se (mg/L)

Met the Customer’s 12 ppb limit
Types of Installations by UOP

- Pre-fabricated modular design
  - Ease of installation
  - Four Standard Sizes plus field erected
  - Easily Expandable for Future
- On-site concrete or tanks for larger installations
- Retrofit to existing aeration basins
  - Ease of upgrading existing infrastructure

UOP can provide a variety of installations to meet your needs
# XCeed™ Bioreactor Technology for Selenium Removal

<table>
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<tr>
<th>Features</th>
<th>Benefits</th>
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<tbody>
<tr>
<td>Reduces selenium levels up to 99%</td>
<td>Meets regulatory requirements for selenium discharge</td>
</tr>
</tbody>
</table>
| High Density Fixed Film Biomass              | • Smaller footprint  
                                        | • Lower capital investment                        |
| Increased microbial sludge retention time    | • Less sludge generation  
                                        | • Lower disposal costs                            |
| • Stable microbial population  
  • Consistent performance                     | • Resistant to load swings  
                                        | • Faster recovery to upsets                       |
| No backwashing requirement                   | • Ease of operation  
                                        | • Lower operating expense                         |

High Density Biomass Provides Robustness, Space & OPEX Savings
Conclusion

Selenium presents challenges to various industrial operations:

- Oil refineries: Se in crude oil ends up in wastewater
- Power plants: Se in coal ends up in flue gas water
- Mining operations

US EPA requires significant reduction to protect the environment.

Reduction to ppb levels is difficult (and expensive) with chemical precipitation.

Biological treatment with UOP XCeed Bioreactor Technology removes Se in a cost effective manner.

- Demonstrated in refinery wastewater and mining run off applications by UOP to low ppb levels.

UOP Can Help You with Your Selenium Removal Application.
Questions