

REINHOLD ENVIRONMENTAL Ltd.



**2014 Wastewater-Ash Round Table
& Expo Presentation**

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Selenium Removal Technologies

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September 22, 2014*



Selenium Removal Background

Selenium Chemistry

- Selenium Treatment Depends on Valence State
- Valence/Oxidation State:
 - (-II); 0; (IV); (VI)
- Exists as Water Soluble Selenium Complex
- Principal Aqueous Forms of Inorganic Selenium:
 - Selenite (IV)
 - Selenate (VI)
 - Se (VI) Predominates Under Oxidizing Environment as SeO_4^{2-}
 - Se (IV) Presents Under Moderately Reduced Condition as SeO_3^{2-}

Selenium Sources

Power Industry;

- Wet FGD
- Fly Ash Sluice Water and Ash Pond Water
- Coal Pile Runoff
- Leachate

Primarily Exists as Selenate [SeO_4^{2-}]: Up to ppm level (1 to 10 ppm)

Wastewater Characteristics

Table 1. Typical properties of waste water from mining, FGD, and agricultural runoff.

	Mining (ppm)	FGD (ppm)	Agricultural (ppm)
Boron		100- 600	
Calcium	130-1,000	300 – 10,000	550
Magnesium	89-174	1000 - 4000	300
Potassium		45	
Sodium	160-1,260	500	2285
Chloride	3.6-481	10,000 – 25,000	1500
Nitrate	1	1 - 400	
Selenium	0.015-0.050	1 - 10	0.35
Sulfate	525-6837	3,000 – 20,000	5000
Alkalinity	10	10 - 250	300
pH	2,1-6.6	4.5 - 5.5	8.1

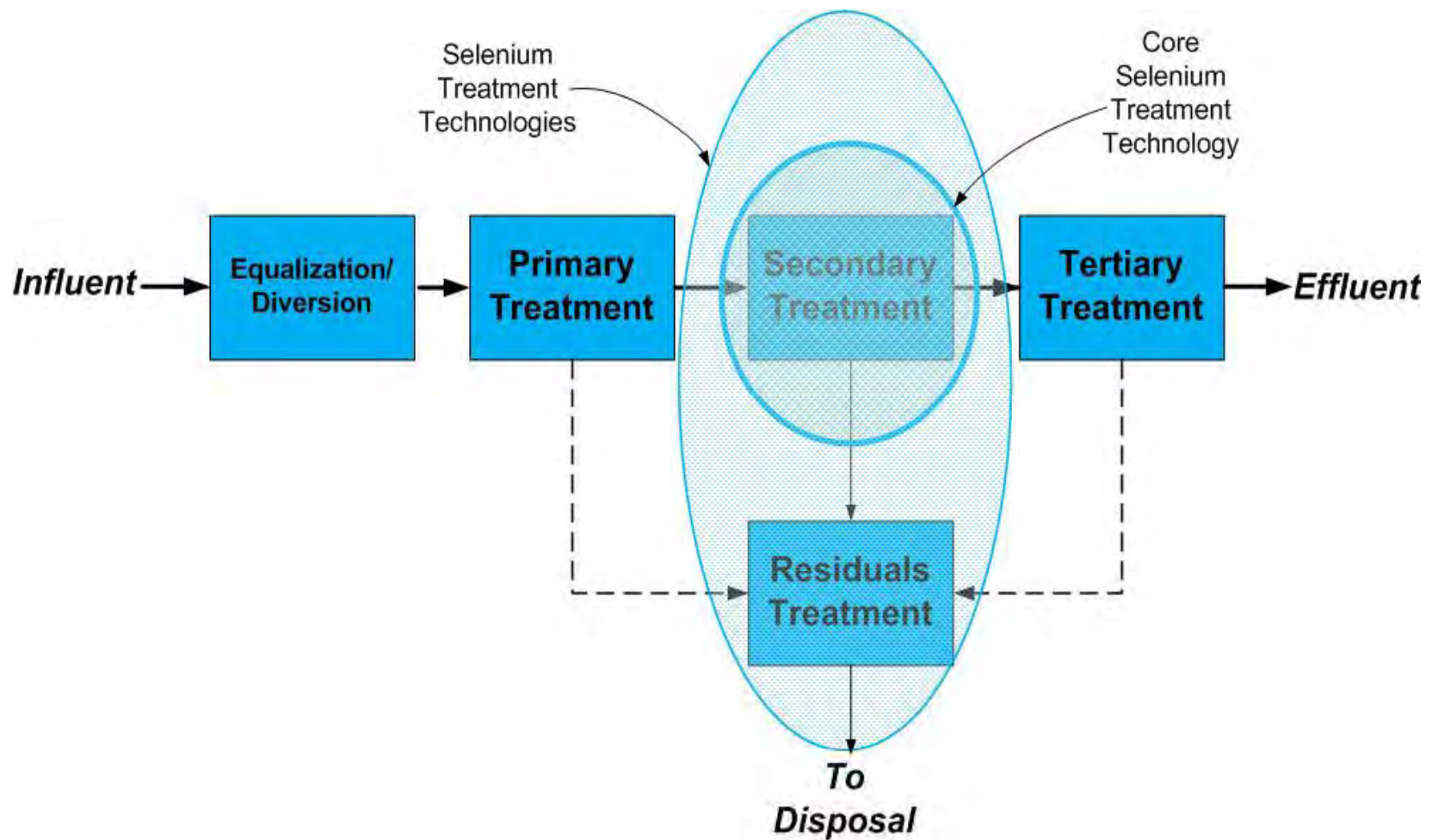
US: Regulatory Background

- The **US National Primary Drinking Water Standard** Maximum Content Level (MCL) is 50 µg/L for Selenium.
- US EPA regulates selenium in WW under Clean Water Act through NPDES (National Pollution Discharge Elimination System) permits and **Total Maximum Daily Loads** (TMDL) Allocations
- The **National Fresh Water Quality Standard** is 5 µg/L for Selenium.
- The U.S. Fish **Treatment of Selenium-Containing Coal Mining Wastewaters** 3 Wildlife Service has recommended that the National Fresh Water Quality Standard be lowered to 2 µg/L to protect fish, waterfowl, and endangered aquatic species.
- In Canada, permits may require stakeholders to monitor levels in water or biota, or to comply with **Canadian Water Quality Guidelines** of 1 - 2 µg/L in surface waters.

Proposed US EPA ELG Limits

<u>Contaminant</u>	<u>Monthly Ave</u>	<u>Daily Max</u>
Arsenic, ug/l	6	8
Mercury, ug/l	0.191	0.242
Selenium, ug/l	10	16
Nitrate/Nitrite as N, mg/l	0.13	0.17

Basic Flow Diagram



Selenium Removal Physical Chemical Treatment

Selenite Removal

- Easy to Remove Selenite (Se IV) to ppb levels;
 - Iron Coprecipitation and Adsorption followed by Solid/Liquid Separation.
 - Fixed-Bed Adsorption onto Iron Oxide Media.
 - RO: Se (VI) & Se (IV).

Difficult to Remove Selenate (Se VI) and Soluble Complex Selenium

Selenate Reduction – Physical/Chemical

- Reducing Agents:
 - Zero Valent Iron (Fe^0),
 - Ferrous Iron (Fe^{2+}),
 - Meta bisulfite, etc
 - Kinetics are very slow at neutral pH
 - Kinetics are pH dependent
- Reaction:
 - Se (VI) Reduced to Se (IV); Fe is Oxidized to Fe (III) and forms HFO
 - Se (VI) is adsorbed onto HFO at pH 6.5 and 7.5

Selenate Removal – Physical/Chemical

- Selenate (VI) Removal to ppb Levels
 - Ion Exchange
 - Zero Valent Iron
 - Adsorption
 - Iron Oxide
 - Activated Alumina
 - Sulfur Modified Iron
 - Reverse Osmosis

Zero Valent Iron

- Can be a powder, granular or fibrous forms
- Acts as a reducing agent – iron acts as electron donor
- Reacts with any oxygen present in the water, as well as, nitrates, sulfates, phosphates, etc.
- Best pH - typically 6.0 – 6.5 S.U.
- Will release soluble iron – which requires removal and disposal.

Ion Exchange

Ion Exchange

- Reliable Process - High Selectivity for Se (VI):
 - $\alpha_{\text{Se}_{(\text{VI})}} = 17$; $\alpha_{\text{SO}_4} = 9.1$; $\alpha_{\text{Se}_{(\text{IV})}} = 1.3$
- Severe Impact of pH and Sulfate
- Regenerant Handling is the Key Issue

Fixed Bed Adsorption

- Activated Alumina – likely expensive to operate.
- Granular Ferric Hydroxide – not likely a good media for Se removal.
- Sulfur Modified Iron – potentially a very good polishing technology.

SMI

- Selenate Adsorption Capacity: 0.75 – 1.0 mg/g
- Also removes Arsenic, Nitrate and Mercury
- No significant ΔP across the column.
- No impact of Ca and SO₄ on Se (VI) removal capacity.
- Column Feed Water ORP: 275 mv & effluent ORP: (-) 50 and (-) 15 mv
- Spent media passed TCLP test (Se in TCLP extract: <0.1 mg/L which is below the TCLP limit of 1 mg/L).
- Iron (Fe²⁺) in the effluent: 1 and 5 mg/L

Biological Removal of Selenium

Key Terminology Review

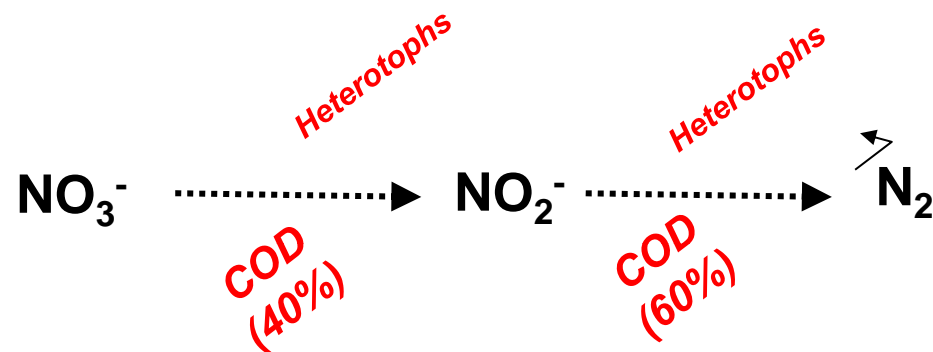
- Biological Oxidation and Reduction
 - *Oxidation - Removal of electrons*
 - *Reduction - Addition of electrons*
- Electron Donor and Acceptors
 - *Electron Donor - Material being oxidized*
 - *Electron Acceptor - Material being reduced*

Key Wastewater Constituents

- Electron donors (food for biomass)
 - *Organic Matter or Carbon Source Measured and expressed as degradable COD*
 - *CO₂ and biomass are the products*
- Electron acceptors
 - *Oxygen (aerobic environment)*
 - Preferred acceptor
 - Reduced product: H₂O
- **ORP Driven**

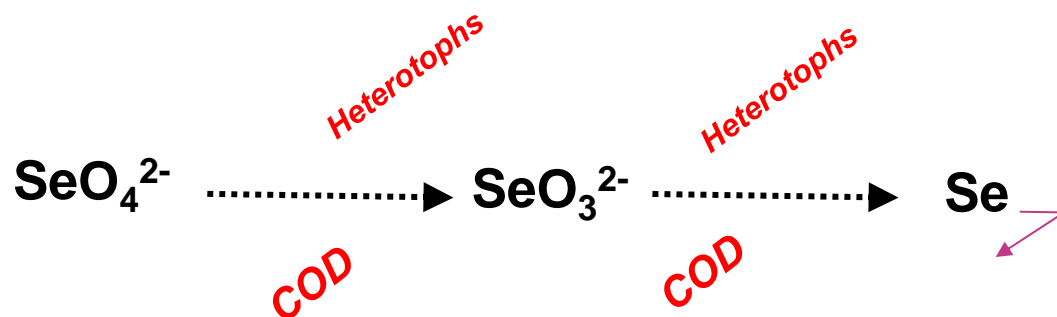
Denitrification and Selenium removal

Denitrification



under anoxic conditions

Selenate and Selenite Reduction



under anoxic conditions

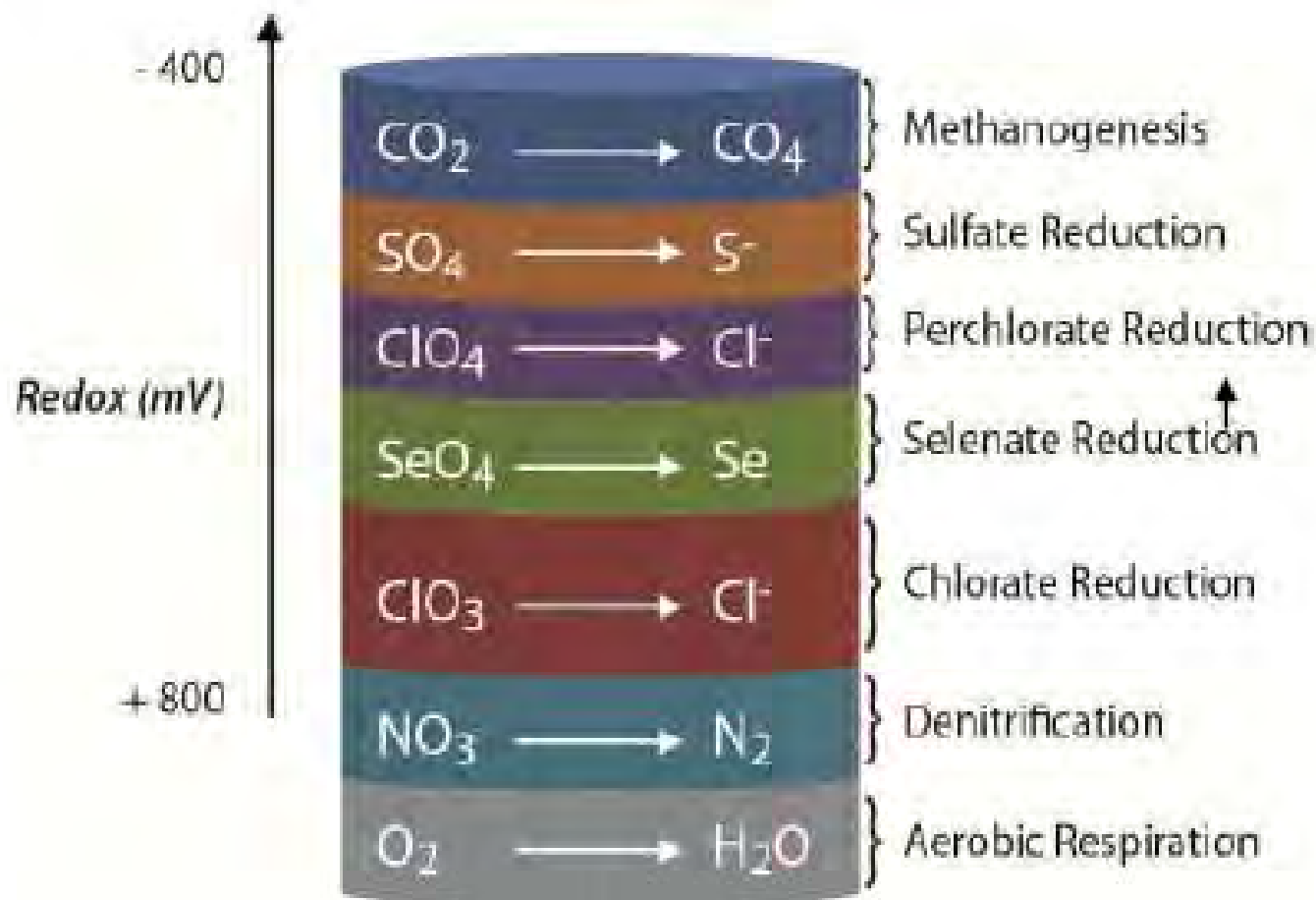
Selenium Removal by Biological Treatment

- Reduction of Selenium by Microbes



- Anoxic Conditions
 - *Heterotrophic bacteria*
 - *Organics + Selenite/Selenate + N + P*
 - *New Cells + CO₂ + H₂O + Se⁰*
- Attached Growth Biological Process

Redox, ORP



External Chemicals Needed for Selenium Treatment Processes

- Readily degradable organic carbon
- Phosphorus (if needed)
- Micronutrients (if needed)
- Ammonia nitrogen (nutrient) for aerobic polishing
- Note: if excess Nitrate is present it will need to be degraded in the biological process.

Attached Growth Systems

- Fluidized Bed Reactor (FBR)
- Fixed Bed or Packed Bed Reactor (PBR)
- Moving Bed Biological Reactor (MBBR)

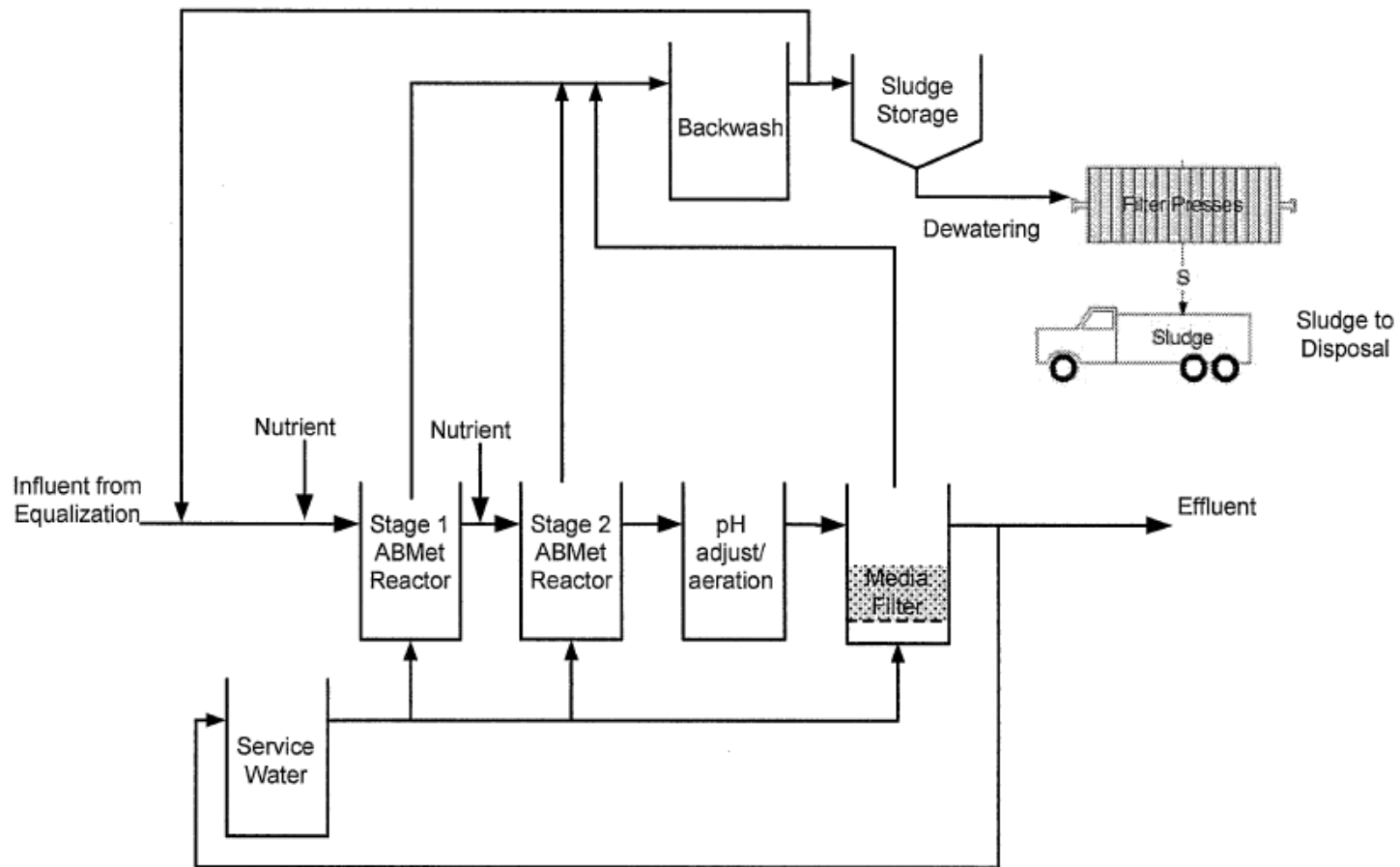
Attached Growth Systems (cont.)

- For low Se concentration wastewater, attached growth system is best suited to grow sufficient biomass.
- Biomass grows as a biofilm on a solid support.
- Some attached growth processes contain fixed media over which the wastewater flows.
- Other attached growth processes contain mobile media kept in suspension by fluid flow.

Fixed Bed Reactor

- Down flow system
- Granular Activated Carbon (GAC)
- Typically, two reactors in series – Nitrate reduction → Selenium reduction
- EBCT – 2 to 6 hours
- ORP -250 to -350 mV
- Hydraulic Loading Rate – 0.3 to 1 gpm/sqft
- Requires periodic backwashing to remove TSS

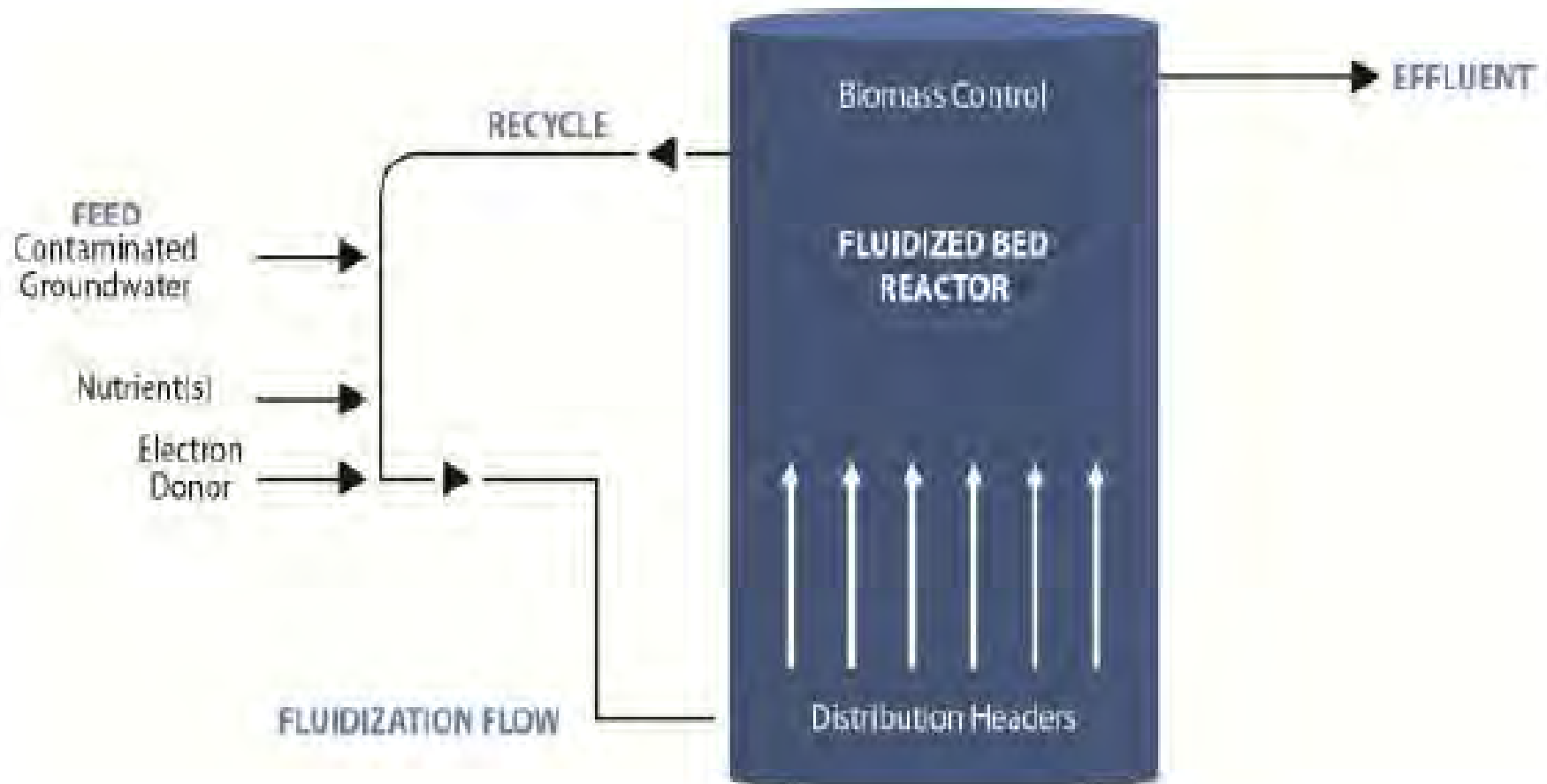
Fixed Bed Reactor



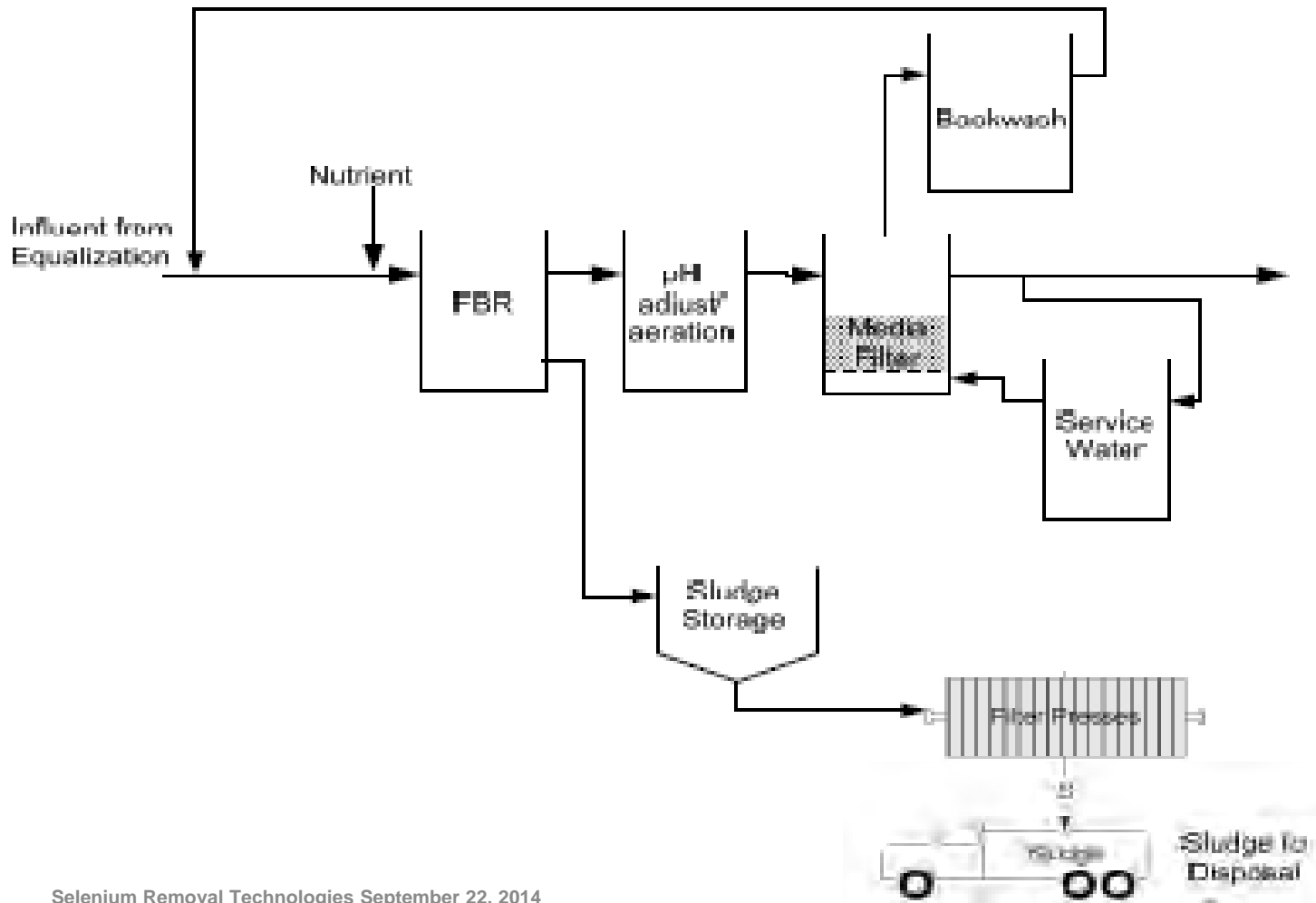
Fluidized Bed Reactor (FBR)

- An up-flow attached growth system – plug flow
- Wastewater is passed through a granular solid media to suspend the media to behave as a fluid.
- Fluidization keeps the media with attached biomass in suspension and expanded to provide good contact of water with biomass.
- Uses sand or GAC as a media for biomass attachment.
- Typically two stage.
- HRT – 1 to 2 hours.
- No backwashing required.

Fluidized Bed Reactor



Fluidized Bed Reactor



Attached Growth Systems (cont.)

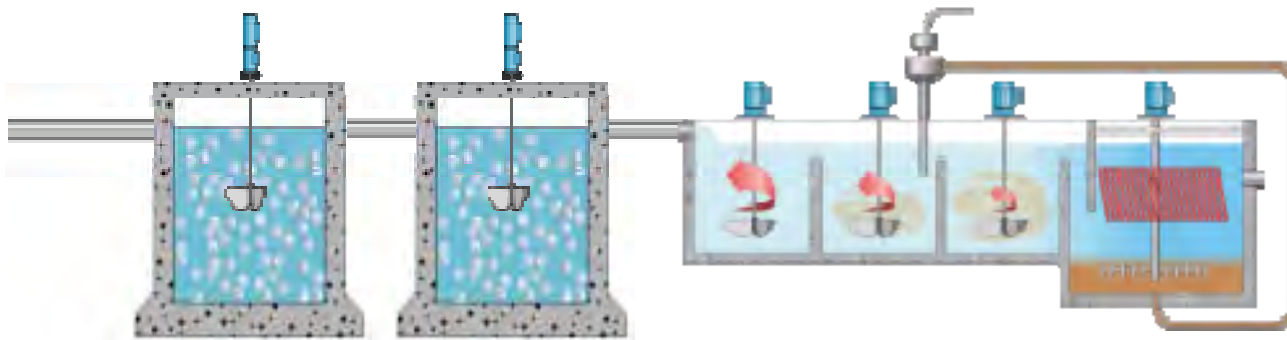
MBBR

- Fluidized bed Anoxic treatment system.
- Uses a proprietary high surface area media



MBBR Process Configuration

- Two-stage MBBR for denitrification and selenium removal.
- Coagulation and flocculation for removal of biomass and elementary selenium.



Costs and Concerns

Typical System CAPEX and OPEX

Typical costs for 1 MGD - 700 gpm (160 m³/hr) system

<u>System</u>	<u>CAPEX (\$M)</u>	<u>OPEX (\$M/year)</u>
Fixed Bed	\$30 to \$40	\$1.5 - \$2.5
Fluidized Bed	\$25 to \$35	\$1.5 - \$2.5
MBBR	\$30 to \$40	\$1.5 - \$2.5
Ion Exchange	\$30 to \$40	\$4 - \$5
ZVI	\$25 to \$35	\$4 - \$5
SMI (polishing)	\$5 to \$7	\$0.5 to \$1

Concerns

- Inability to meet the proposed US EPA ELG Selenium limits.
- TSS removal after the treatment process;
 - *Higher Selenium feed concentrations → more small Se particles that are difficult to remove.*
 - *May require membrane technologies for removal of reduced selenium particles.*
- Tertiary treatment may be needed for removal of other contaminants.
- More work is needed.

C1

Slide 35

C1

Not sure I agree - what we believe the problem with high influent Se to be is that there is more selenium particles associated with effluent TSS hence to achieve very low Se concentration, we need to reduce TSS to very low levels which is being the ability of actiflo so that membrane may be required. but this is just speculation- from the lab tests, it looks as though we get some unidentified Se compounds with these FGD effluents

Dale, 9/19/2014



Thank you

