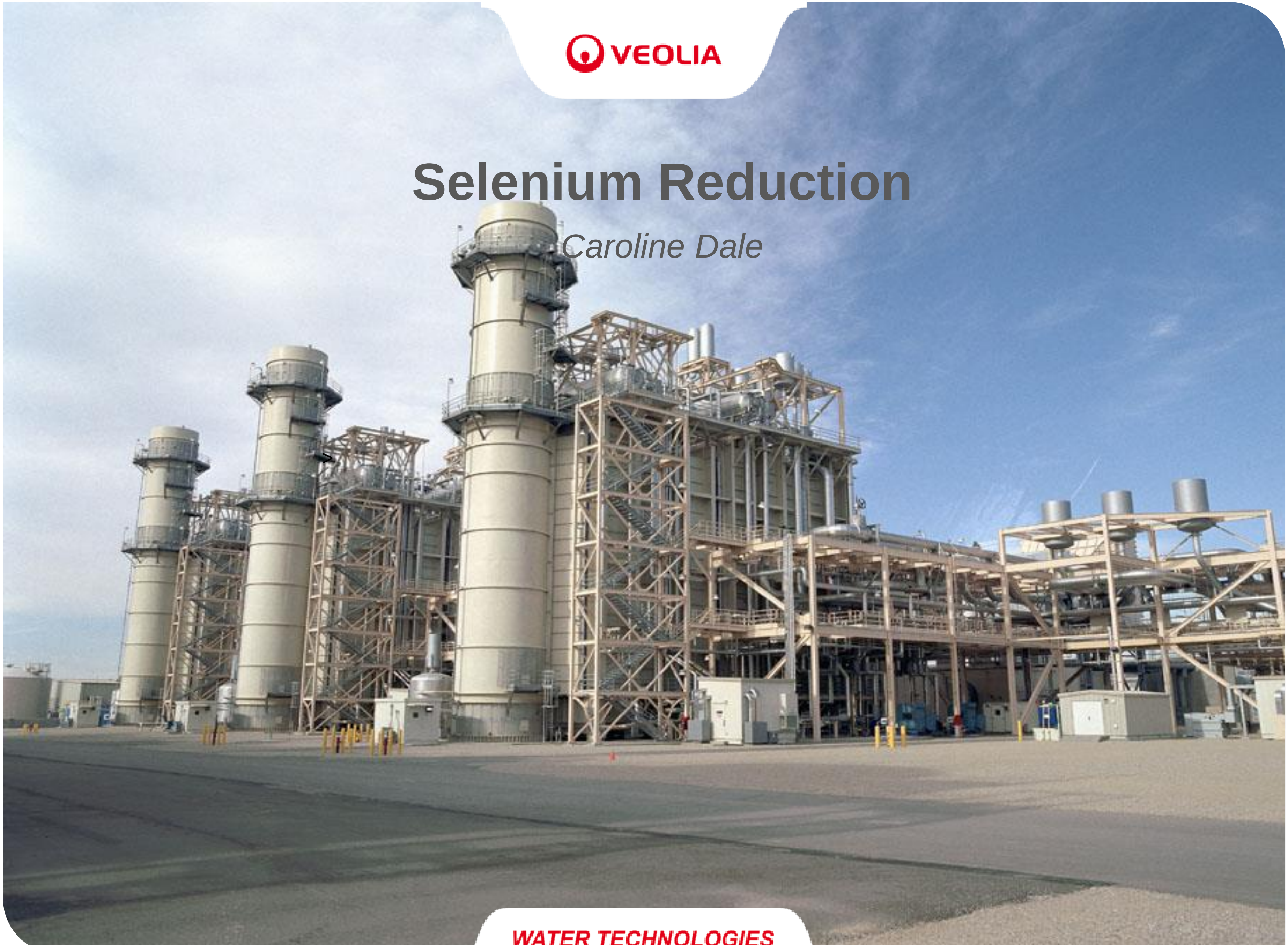
# Selenium Reduction

*Caroline Dale*



WATER TECHNOLOGIES

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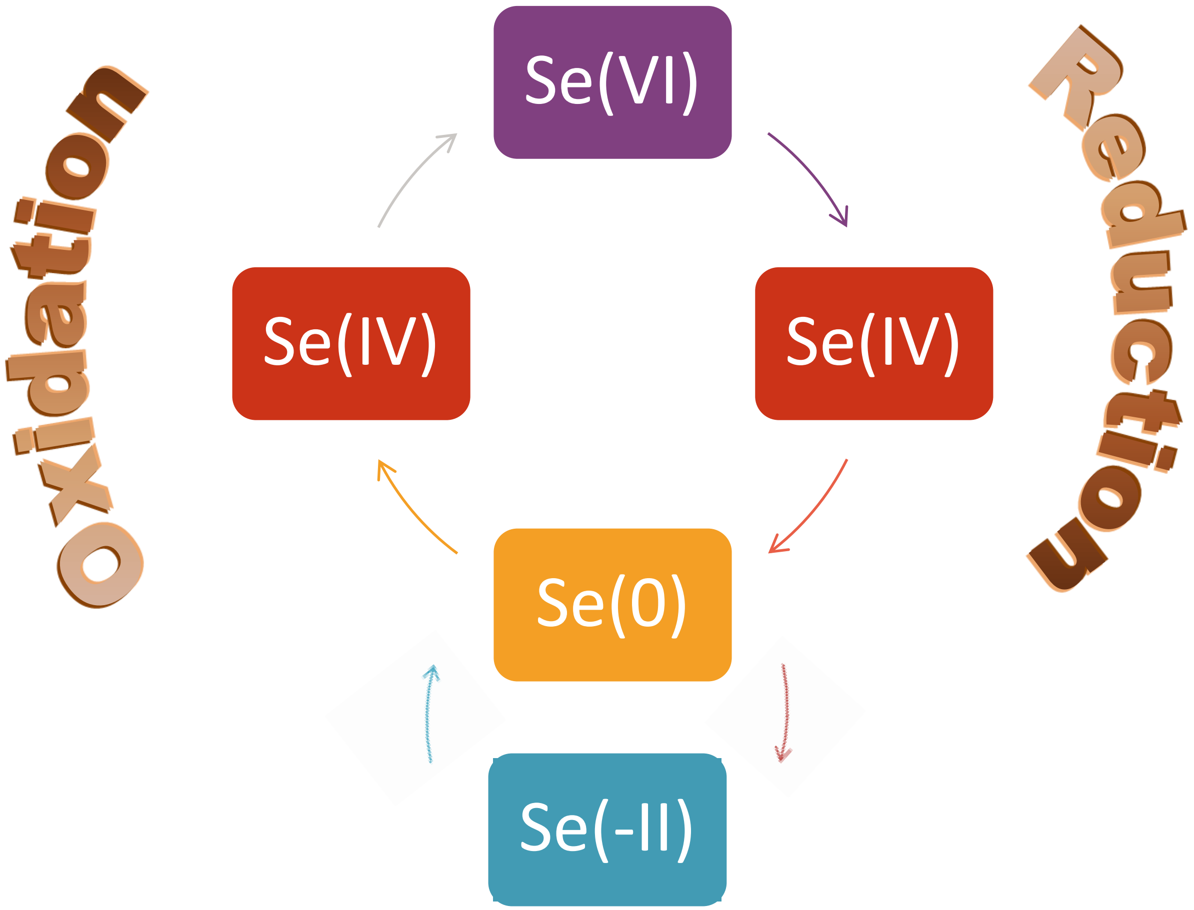
# Selenium Cycle



# Selenium is present in coal , hence FGD effluent

- Selenium mainly present as :
  - *Selenate ($SeO_4^{2-}$)* *can be as high as 10 mg/l*
  - *Selenite ($SeO_3^{2-}$)*
  - *but also SeCN*
  - *Organic complex?*

# Biological Reduction of Selenium :Quick Review

## Selenate and selenite reduction

$$SeO_4^{2-} \xrightarrow[\text{COD}]{\text{Heterotophs}} SeO_3^{2-} \xrightarrow[\text{COD}]{\text{Heterotophs}} Se \downarrow$$

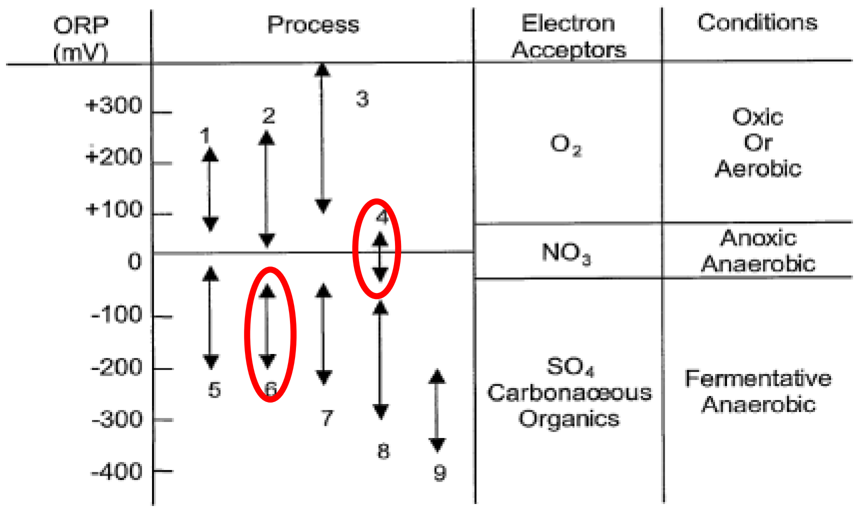
under anoxic conditions

## Denitrification

$$NO_3^{-} \xrightarrow[\text{COD (40\%)}]{\text{Heterotophs}} NO_2^{-} \xrightarrow[\text{COD (60\%)}]{\text{Heterotophs}} N_2 \uparrow$$

under anoxic conditions

# Redox




1 – Organic Carbon Oxidation
2 – Polyphosphate Development
3 – Nitrification
4 – Denitrification
5- Polyphosphate Breakdown
6 – Selenium Reduction
7 – Sulfide Formation
8 – Acid Formation
9 – Methane Formation

- **Redox potential for denitrification and selenium reduction have small overlap**
- **Both reactions can occur in the same reactor**
- **Selenium reducers may be outcompeted by denitrifiers**
  - ***depending on influent characteristics, 2 stage reactor systems may be required***

# Providing the right environment….

- Energy gained from respiration of Se compounds is approx ½ of what can be gained from using dissolved oxygen
    - Selenium reducers have lower growth rates than other heterotrophs

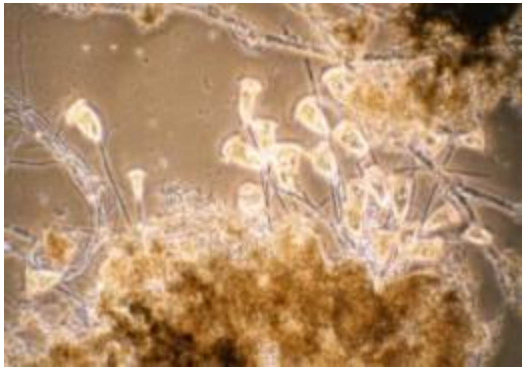
- Fixed film processes for Se reduction have been the most successful

# The MBBR process

# The MBBR process
## (Moving Bed Biofilm Reactor)

- The process is based on the biofilm principle. The core of the process is the biofilm carrier elements made from polyethylene with a density slightly below that of water.

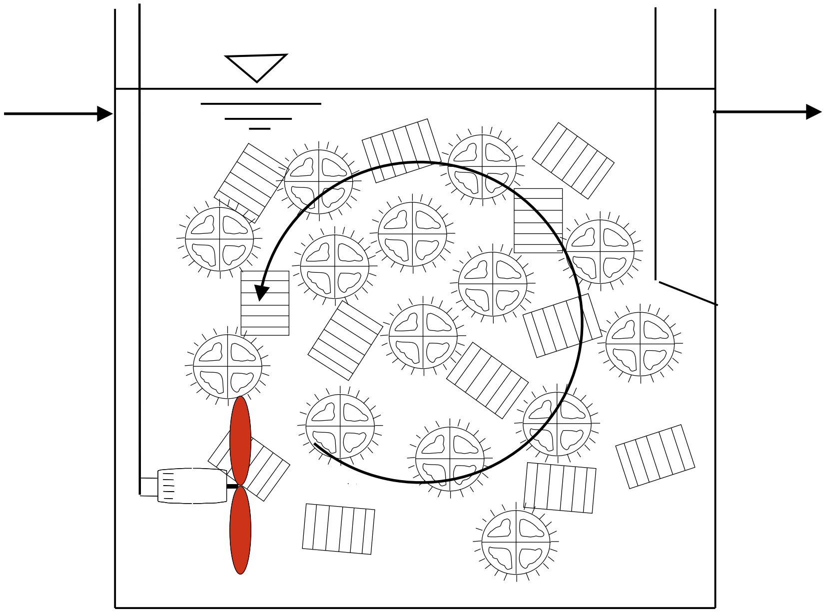
- The carriers are designed to provide a large protected surface for bacteria development (800 $m^2/m^3$)



### Advantages of MBBR process

✓ Can operate with the same support material for over 20 years
✓ No backwashing requirements
✓ No issue with gas build up ( $N_2$ or $CO_2$)
✓ Can tolerate high TSS concentrations in the feed
✓ Can tolerate large hydraulic variations

# MBBR for denitrification > 20 years of experience

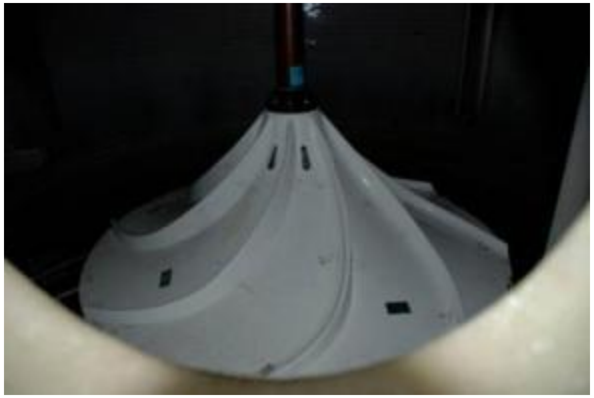


**The carriers are kept in suspension and continuous movement in the water by mechanical mixers**

# Key Elements

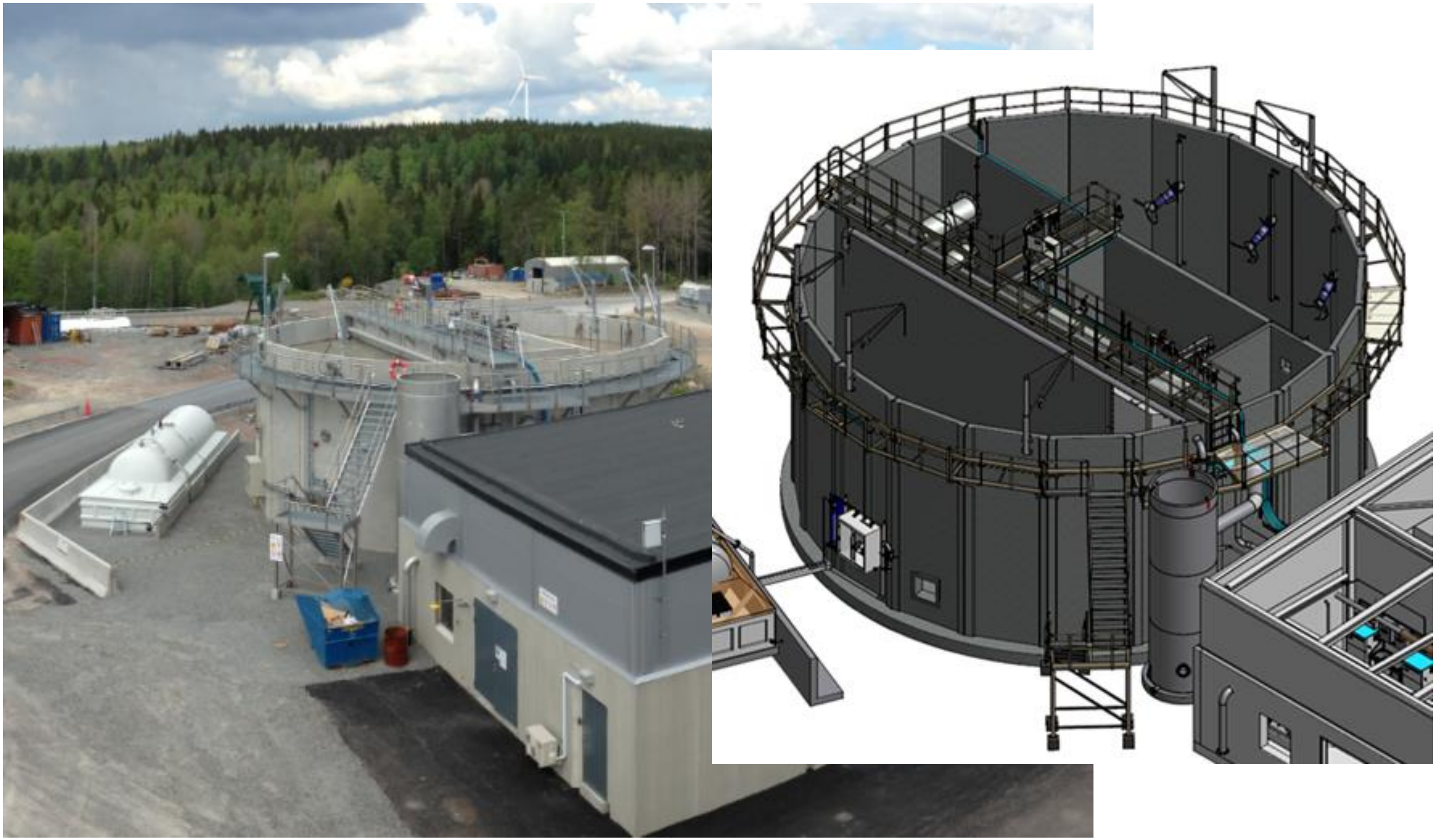
Sieve

Biomedia



Mixers

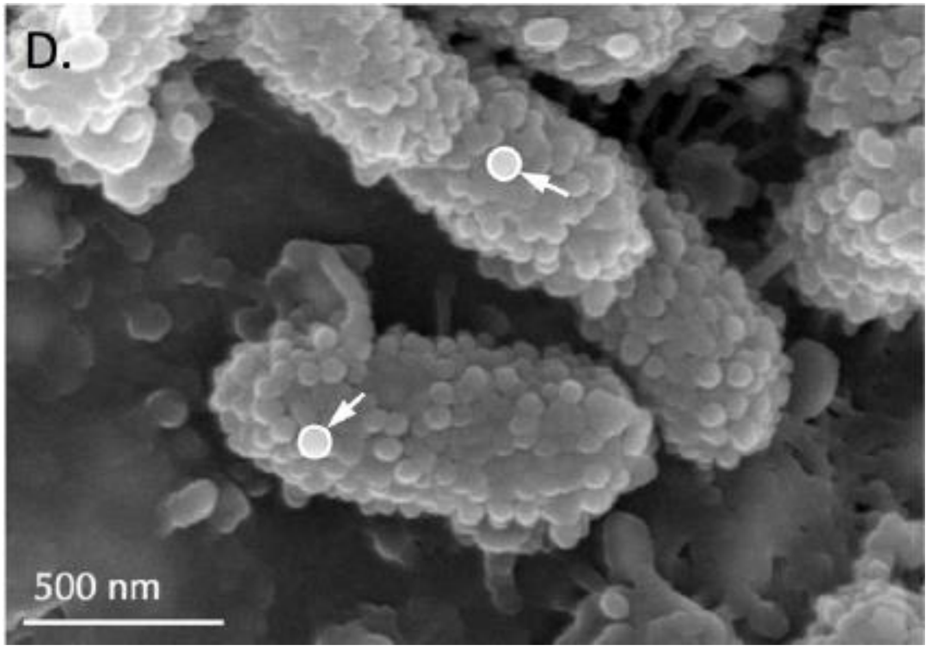
# Full scale MBBR



# Solids separation step

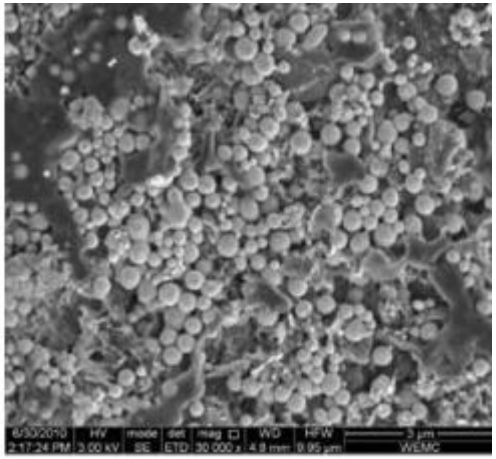
Small Se-particles formed during biological reduction:

Precipitates 50-60 nm = 0.05-0.06 µm




*Williams Et Al. Env. Microbiological Reports, 2013*

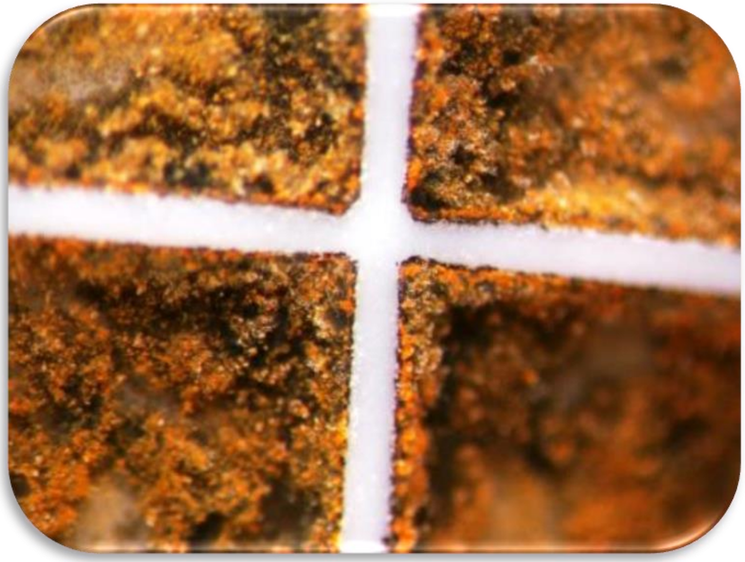
As long as these are stuck to the biomass/biofilm they can be separated from the effluent.



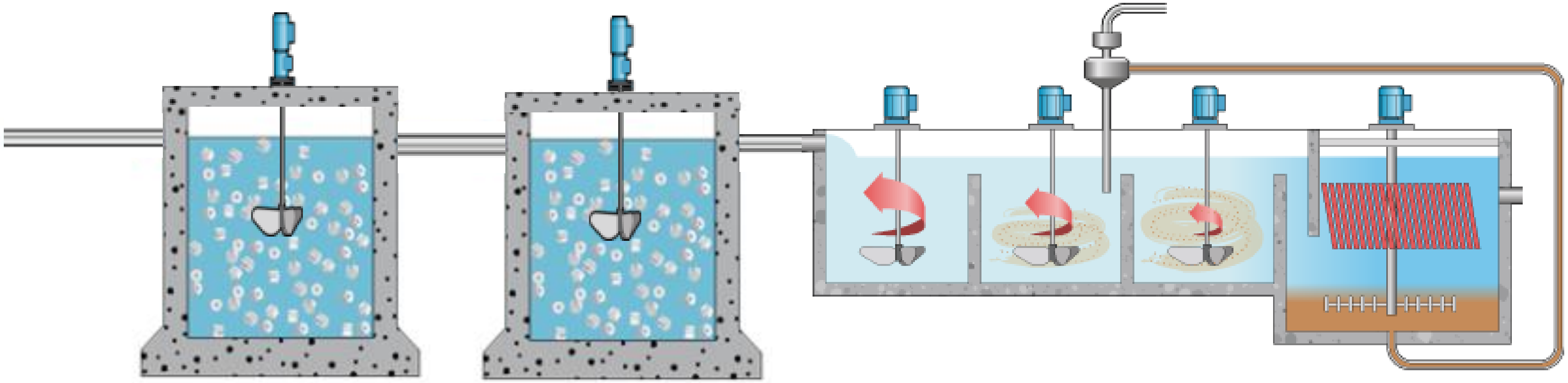
*Hageman et Al, Proceedings of EMC, 2011*

# Solids Separation Step

- Solids removal post MBBR
  - *Actiflo*
  - *Multimedia filters*
  - *UF*



# Process configuration



First Stage
Denitrification
Partial Se
reduction

Second Stage
Se reduction

Solids
separation step

# Operating experience treating FGD effluent

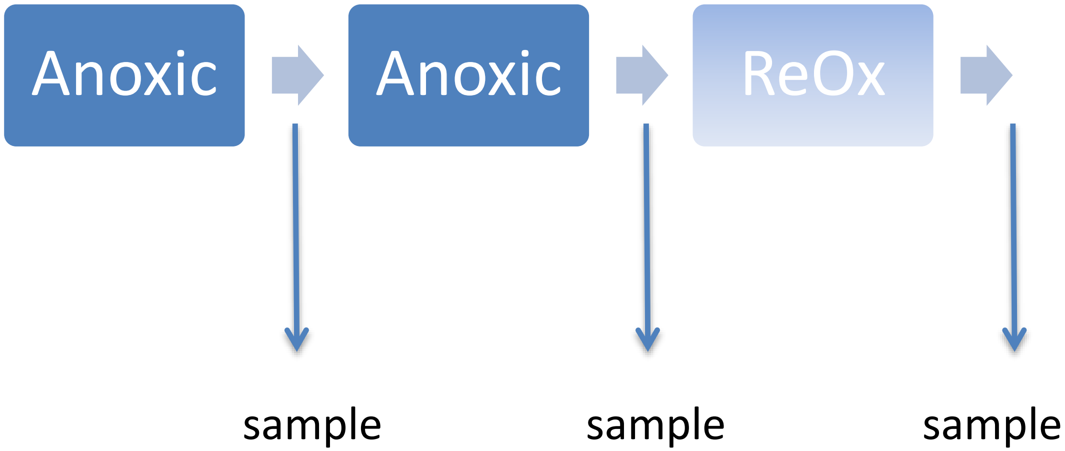
# Selenium Removal Trials

- Bench scale reactors have been operating at AnoxKaldnes for about 1 year
  - *Effluent from a Danish FGD effluent*
  - *Effluent from a US FGD effluent*

Reactors are :

- Continuous flow
- Temperature controlled
- Nutrient & external carbon dosing
- Redox monitoring

# 3 reactors in series

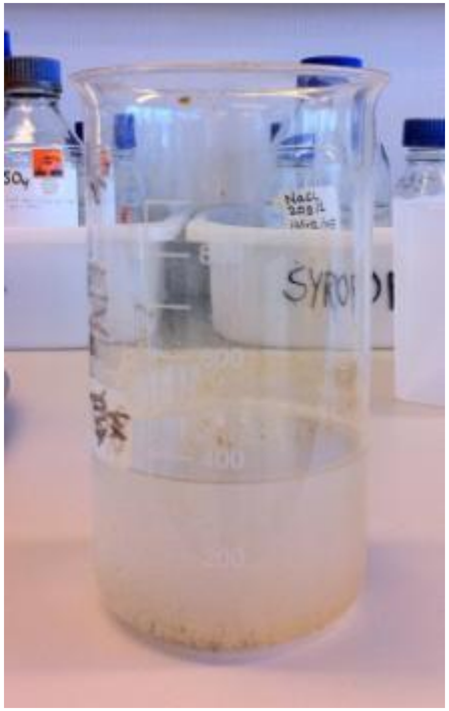


# Selenium Analyses

Performance followed by measurements of total Selenium and selenium speciation (Se (VI) and Se(IV)) on

- Filtered effluent (0.2 um)
- Chemically treated effluent (no filtration)

Coagulation and flocculation using $FeCl_3$ and polymer



# Methods

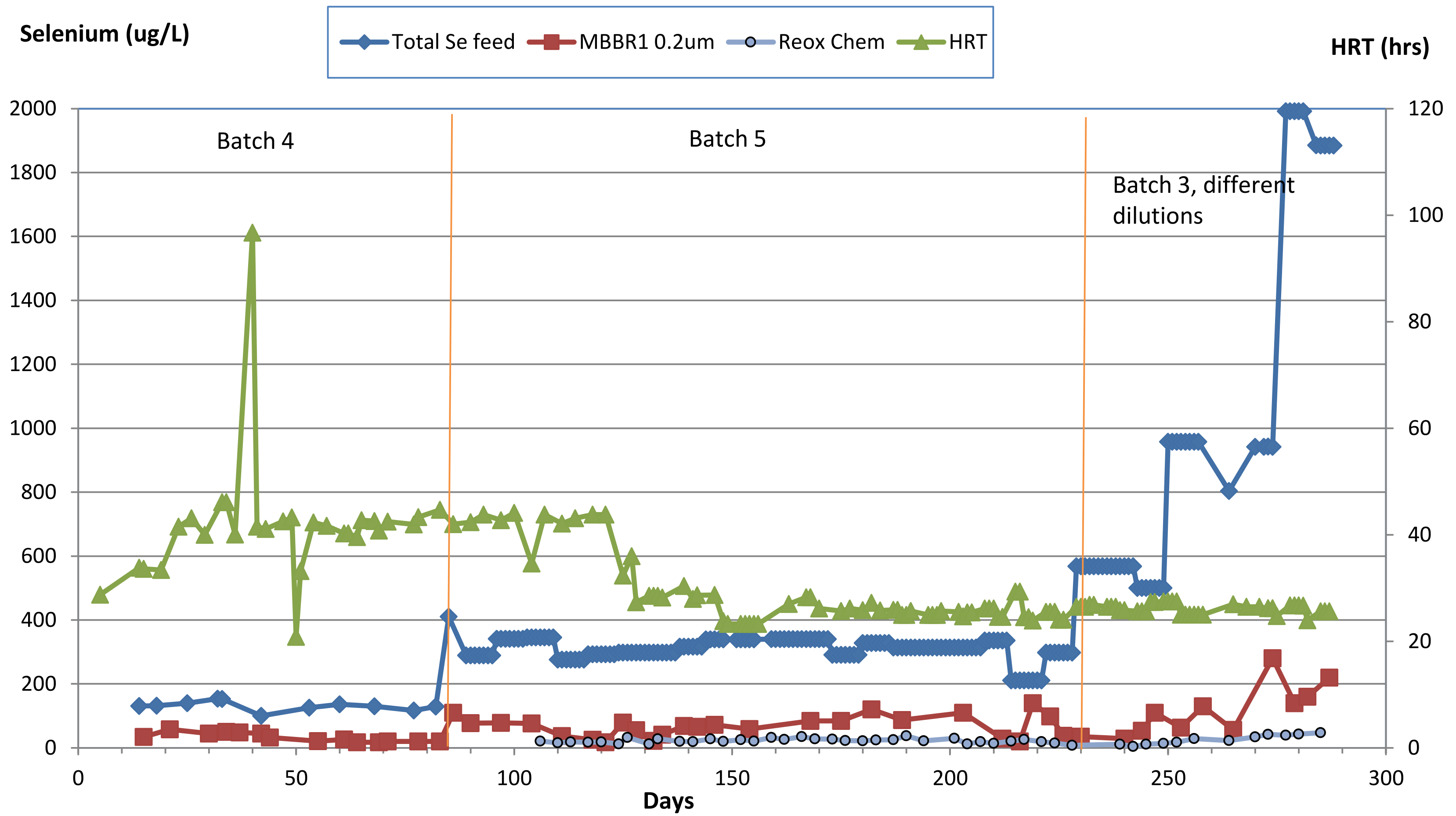
- Total selenium using ICP-MS/AES
- Selenium speciation of selenite ($Se^{4+}$) and selenate ($Se^{6+}$) done occasionally using HPLC-ICP/MS
- Characteristics of studied wastewaters:

| Parameter | FGD Effluent 1 | FGD Effluent 2 |
|---|---|---|
| Selenate (µg/l) | 311* | 129 |
| Selenite (µg/l) | <10 | 57 |
| Total Selenium (µg/l) | 340 | 197 |
| SCOD (mg/l) | 142 | 80 |
| $NO_3$-N (mg/l) | 80 | 35 |
| $NO_2$-N (mg/l) | 0.7 | 2.4 |
| Sulphate (mg/l) | 4000 | 8500 |
| Chloride (mg/l) | 4000 | 1600 |
| $PO_4$-P (mg/l) | 0.1 | 0.03 |
| $NH_4$-N (mg/l) | 3.3 | 0.8 |

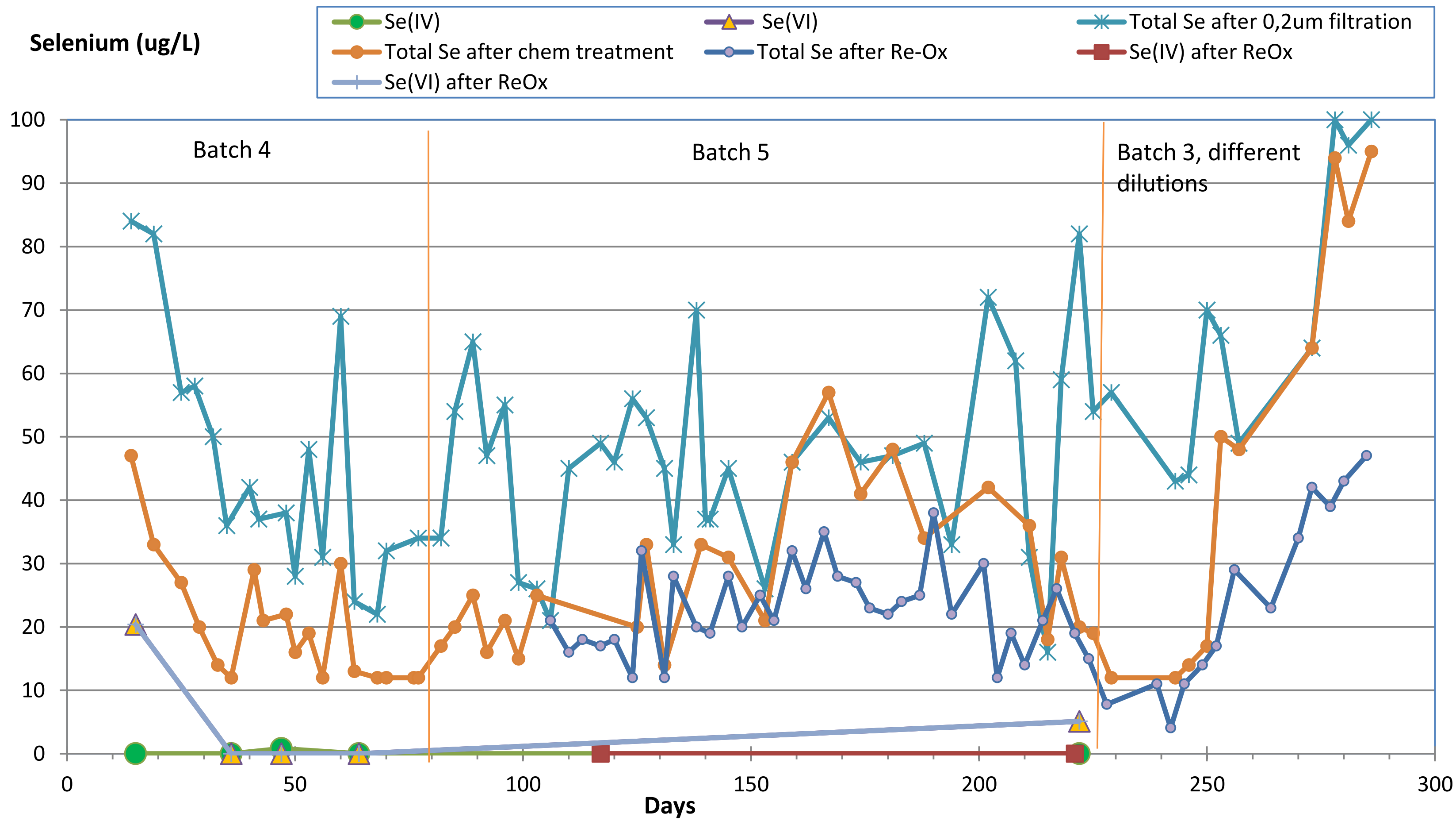
NH4 and PO4 added

*Batch 3 of this effluent contained 4100 µg/l

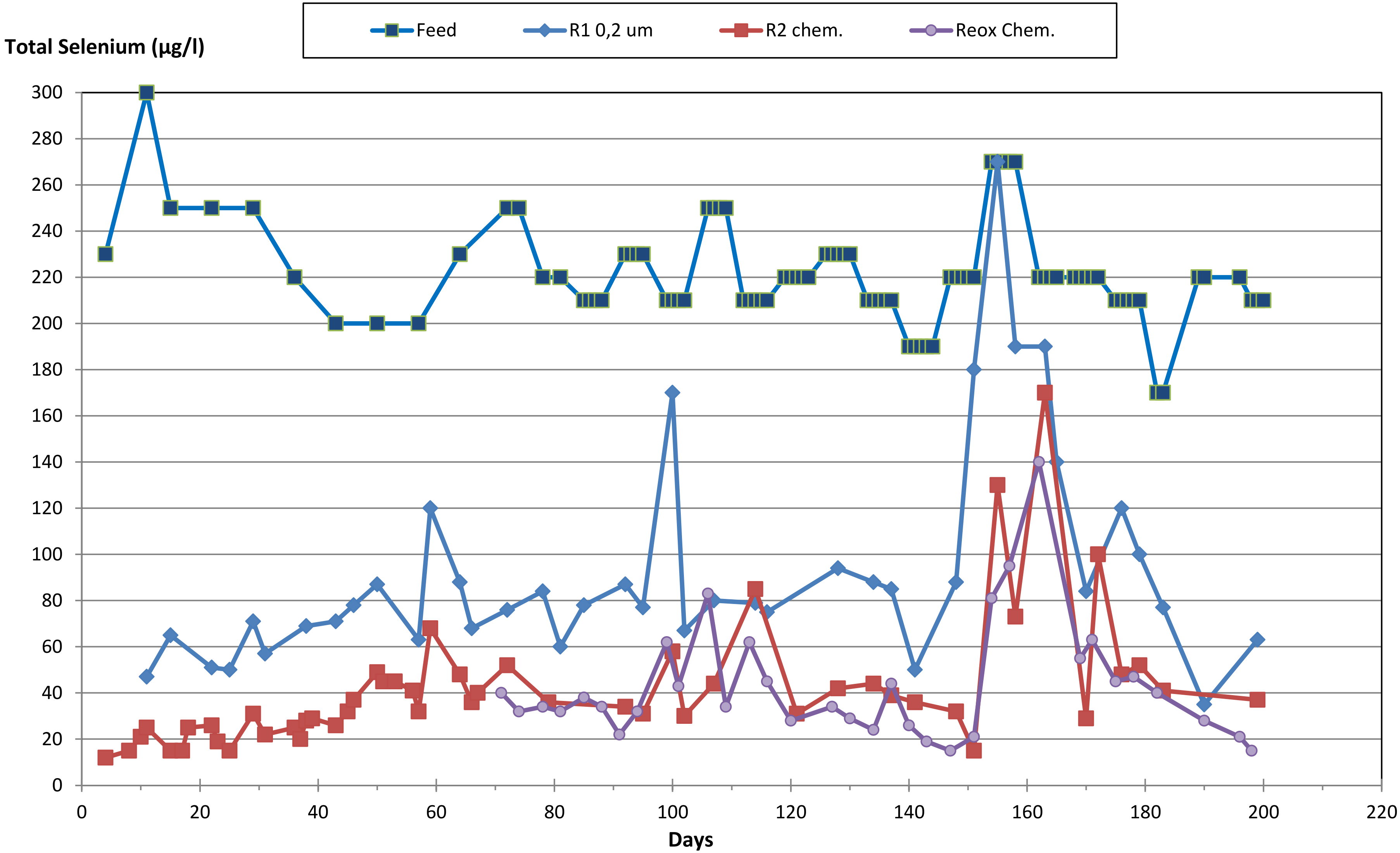
# Results : FGD effluent 1



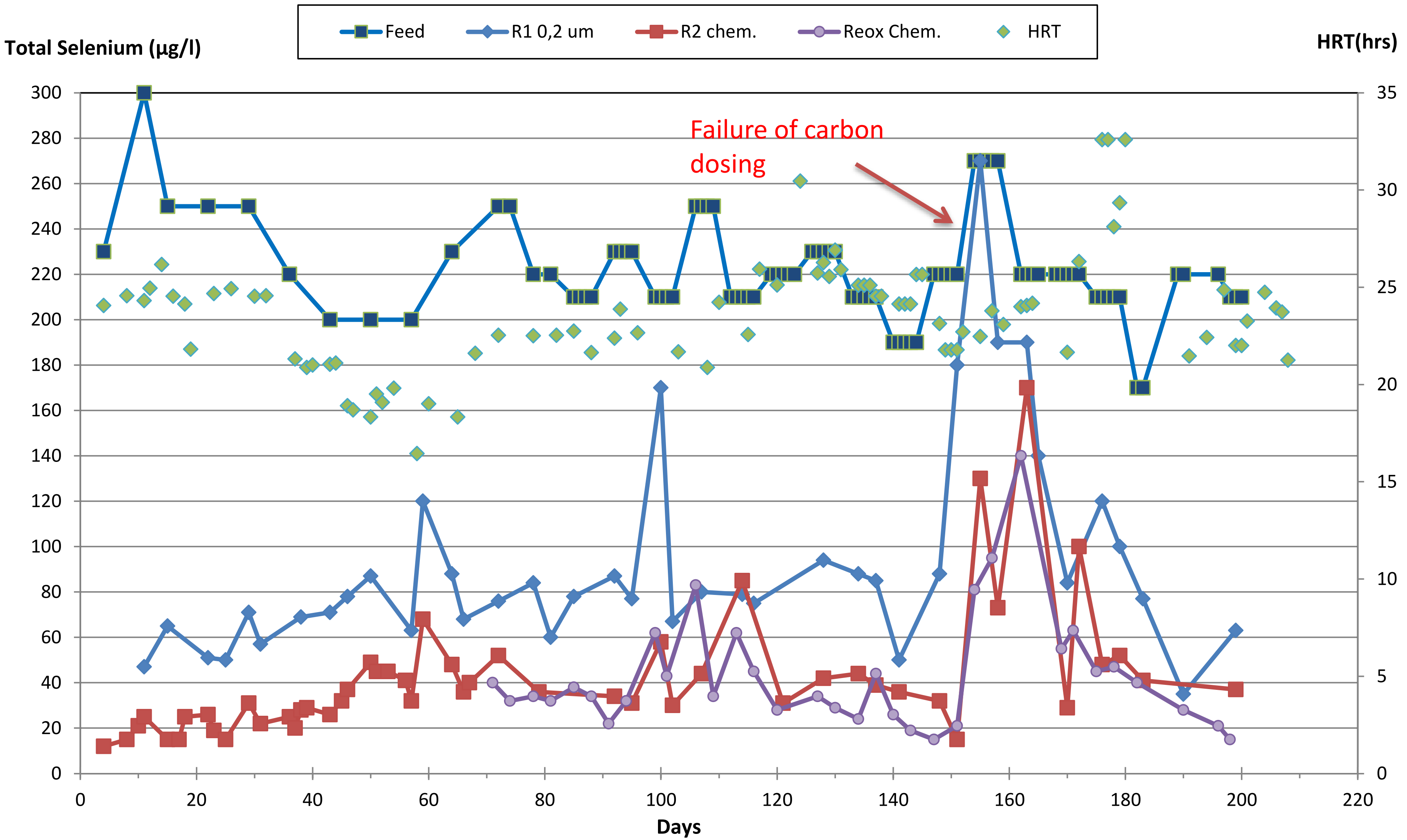
# Results : FGD effluent 1



# Results : FGD effluent 2



# Results : FGD effluent 2



# Selenium Removal and SeleniumZero®

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# Selenite Treatment Technologies

- Easy to remove Selenite, Se(IV)
- Se (IV) removal to ppb level
  - *Iron co-precipitation and adsorption followed by solid/liquid separation (ACTIFLO®/MULTIFLO™)*
  - *Fixed-bed adsorption onto iron oxide media*
  - *MetClean™ Technology*
  - *Activated alumina*
  - *Membrane (RO)*

# Selenate Treatment Technologies

- Selenium (VI) removal to ppb level
  - *Much more difficult than Se (IV)*
  - *Adsorption onto iron oxide: not efficient*
  - *Severe impact of pH and sulfate*
  - *Ion Exchange: reliable process*
    *[High Selectivity for Se (VI)]*
    - $\alpha Se_{(VI)} = 17$; $\alpha SO_4 = 9.1$; $\alpha Se_{(IV)} = 1.3$
    - Regenerant handling is the key issue
    - High sulfate concentrations are a concern with IX
  - *SeleniumZero®*

# Selenate Removal

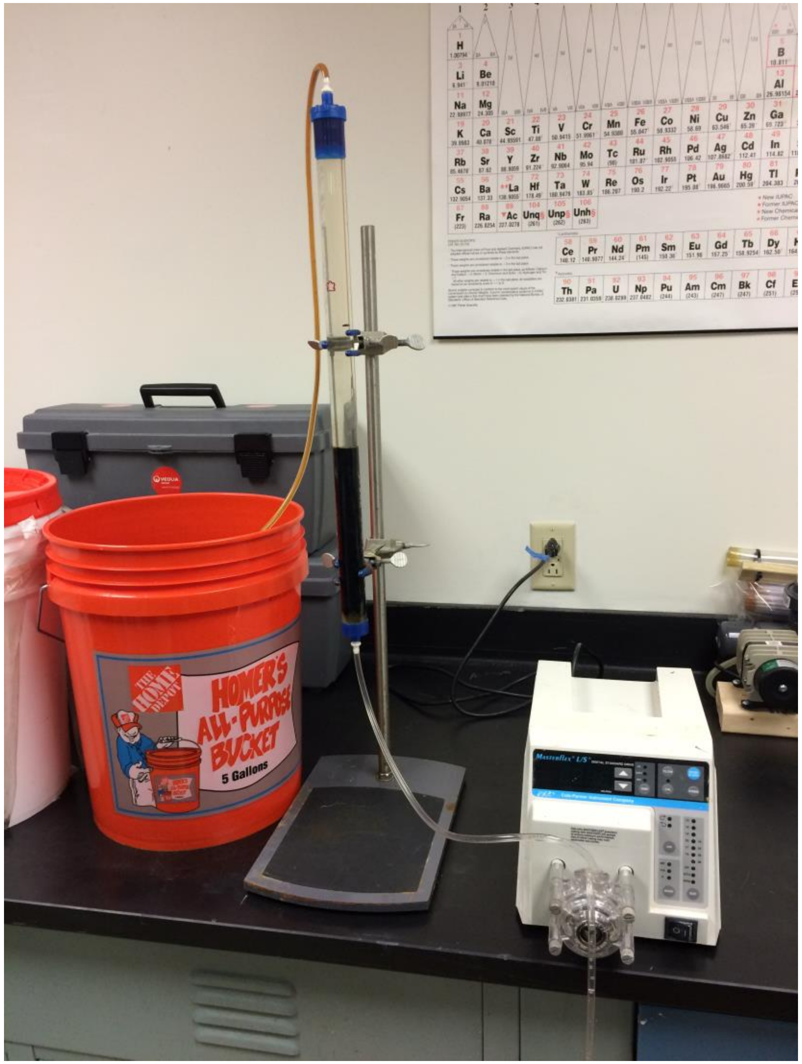
- Reduction of Se(VI) to Se(IV)
- Reaction:
  - *Se (VI) reduced to Se (IV); Fe(II) is oxidized to Fe (III) and forms Hydrous Ferric Oxide (HFO)*
  - *Se (IV) is adsorbed onto HFO at pH 6.5 - 7.5*
- Reducing Agents:
  - *ZVI ($Fe^0$), $Fe^{2+}$, metabisulfite etc*
    - Kinetics is very slow without catalyst
    - Kinetics is pH dependent
    - ZVI best at lower pH +/- 4.5

# SeleniumZero® - New Technology for Selenate Removal

- Se(VI) removal with chemically treated iron based adsorption media
- Conducted 6 months of lab studies with actual wastewater from a coal plant
- Sample contained about 20 ppb of Se (VI) with sulfate, some TSS, and other cations and anions
- Sample was filtered prior to adsorption column

# SeleniumZero®: Operating Conditions

- Column operated in up-flow mode
- Contact time: 5 min
- Influent Se(VI): 100 ppb (sample spiked)
- Breakthrough Se(VI): <5ppb
- Column operated 24x7 for 6 months



# SeleniumZero: Results & Observations

- No significant ΔP across the column
- No impact of $Ca^{2+}$ and $SO_4^{2-}$ on Se (VI) removal capacity
- pH increased only 0.5 unit
- Spent media passed TCLP test (Se in TCLP extract: <0.1 mg/L which is below the TCLP limit of 1 mg/L)
- Some iron leaching was observed from the column

# Conclusions

- Final effluent Se concentration (economically) achievable using MBBR is highly dependent on the influent Se concentration
- FGD effluents have complex / variable matrices – adaptation of the biomass does take time however biological treatment using MBBR is a viable treatment solution – potential for combining with SeleniumZero
- Carbon dosing control required to minimize sulfate reduction
- Solids separation step is critical for capture of small Se particles
- On-going testing of MBBR for different operating conditions and effluents

# Thank you

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