VEOLIA

Selenium Removal

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WATER TECHNOLOGIES

Selenium in the Environment

Environmental Science & Technology | Feature

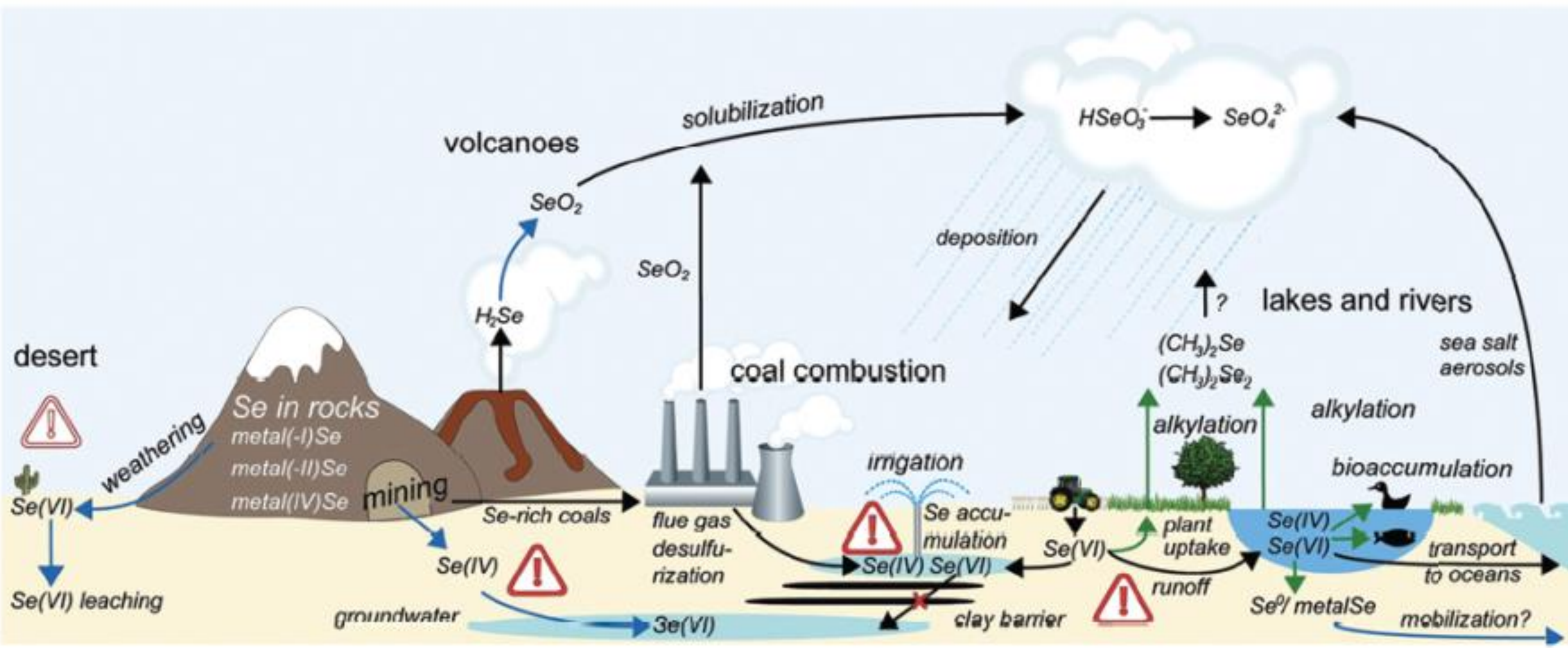


Figure 1. Schematic global cycle of Se with main focus on the terrestrial environment. Blue arrows indicate processes that involve oxidation of Se species and green arrows indicate processes that involve reduction of Se species. Warning symbols indicate specific environmental settings that are at risk of either developing Se deficiency (open warning symbol) or Se excess (shaded warning symbol).

Environmental Concerns

- *Listed as a “Priority” Toxic Pollutant*
- *No Human Health Based Criteria Available*
- *U.S. EPA regulates selenium in WW under Clean Water Act through*
  - *NPDES permits and TMDL (Total Maximum Daily Limits)*
- *Recently issued NPDES Permits: very strict*
  - *total Selenium < 5µg/L*

Phys-Chem Treatment Methods

Selenite Se(IV)

Easy to remove Selenite Se (IV)

Se (IV) removal to ppb level:

- *Iron coprecipitation and adsorption followed by Solid/liquid Separation (Actiflo/Multiflo)*
- *Fixed-bed adsorption onto Iron Oxide media*
- *MetClean Technology*
- *Activated Alumina*
- *Membrane [RO]*

Selenate Se(VI)

Much more difficult than Se (IV)

Adsorption onto Iron oxide: not efficient

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 an issue

Sulfate interference

SeleniumZero® adsorption media

SeleniumZero® - New Technology for Selenate Removal

- Adsorption media with high affinity for selenium (VI) and selenium (IV)
- Upflow column
  - *5-10 minutes of contact time*
  - *2 to 4 gpm/sqft hydraulic loading.*
- Once media is saturated, it is sent for disposal (no regeneration)
- Not impacted by other ions such as sulfate, chloride, calcium, magnesium
- Veolia has an exclusivity agreement with supplier of SMI media for US in mining applications.

SeleniumZero®: Results

- Tested on coal mine effluent

  26 µg/l Selenate (Se^{+6})

  1 µg/l Selenite (Se^{+4})

  300 mg/l SO_4

  75 mg/l Ca

- Approx 80 000 bed volumes before media became saturated

- Effluent Se conc < 2 µg/l

Spent media passes the US EPA TCLP and CA WET test : nonhazardous disposal

The media cannot be regenerated (at least at this time)

SeleniumZero: Operation

- Pre-filtration required to maintain the column free of solids
- Optimal pH between 6.0 and 6.5
- Daily backwash of approx 15 minutes
- The media can be used as a polishing unit to remove selenate or selenite after biological reduction processes, if necessary.
- Some leaching of iron from the column, post treatment required
  (aeration+filtration)
- On-going development : potentially can be used for Arsenic, Hexavalent Chromium (Cr^{+6}), Mercury and Nitrate removal

Biological Selenium Reduction

Denitrification vs. Selenium removal

Denitrification

NO_3^- --(Heterotophs, COD (40%))--> NO_2^- --(Heterotophs, COD (60%))--> N_2

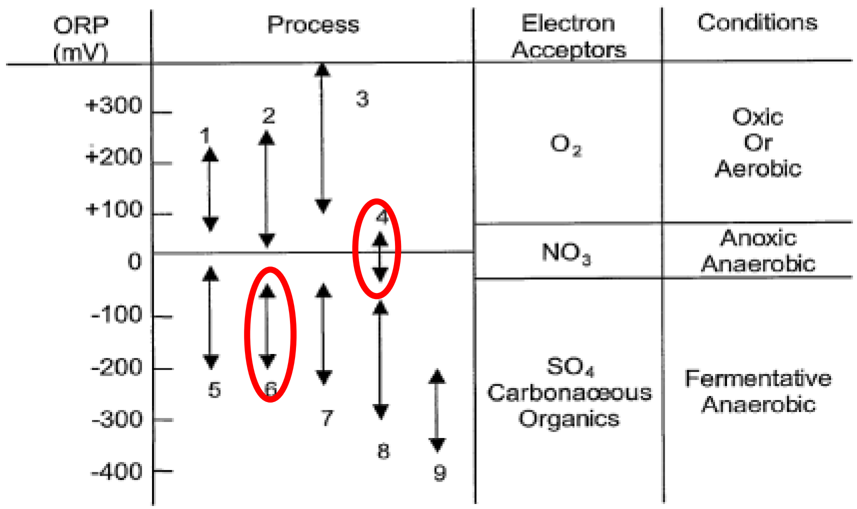
under anoxic conditions

Selenate and selenite reduction

SeO_4^{2-} --(Heterotophs, COD)--> SeO_3^{2-} --(Heterotophs, COD)--> Se

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
- A 2 stage system may be required depending on influent characteristics

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

- Se is reduced to elemental Se which is a solid, a solid separation step is therefore also required

The MBBR process
(Moving Bed Biofilm Reactor)

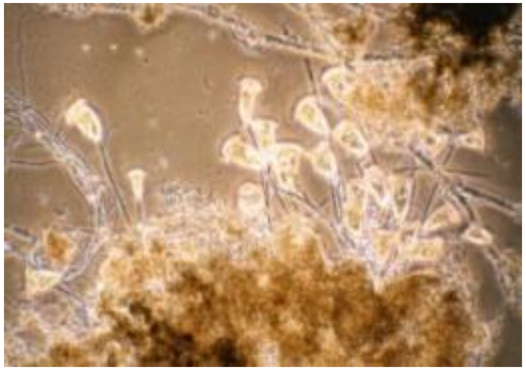
- Process was developed in Norway in the 1980's. First full scale plant built in 1989, still in operation today.

- 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.

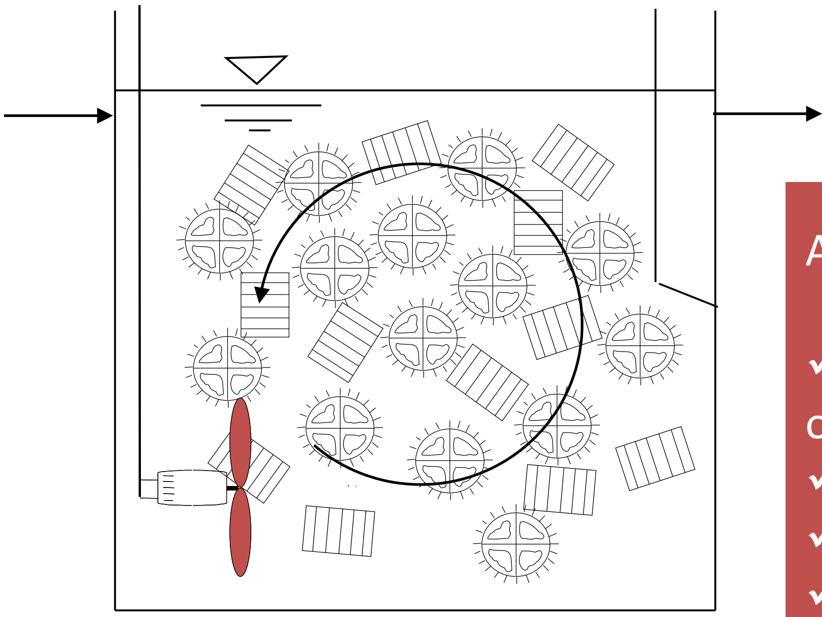
- The carriers are designed to provide a large protected surface for bacteria development (800 m^2/m^3)

- Carriers are maintained in continuous motion within the reactor, using the aeration system or mechanical mixers

- Continuous sloughing of excess biomass



MBBR for denitrification > 20 years of experience



Advantages of MBBR process

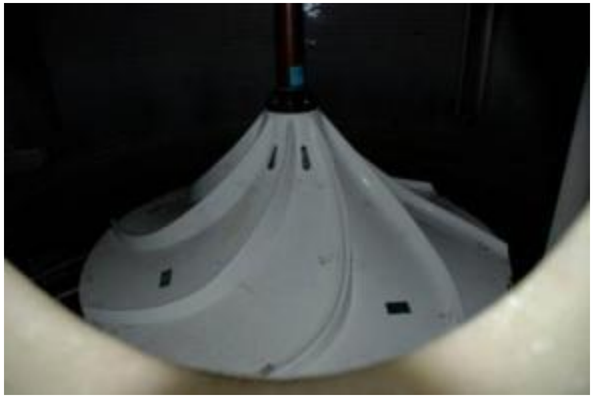
✓ Can operate with the same support material for over 20 years
✓ No backwashing requirements
✓ No issues with gas entrapment (N_2, CO_2)
✓ Can tolerate high TSS concentrations in the feed
✓ Can tolerate large hydraulic variations

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

Key Elements

Sieve

Biomedia



Mixers

VEOLIA

West Virginia Mine

Project Background

3 sites (same client)

Engineering and Process Design undertaken by CH_2MHill

Equipment supply by Veolia Industrial Project Group

Design Basis

Design Parameters		Units	site1		site2		site3	
			Average	Peak	Average	Peak	Average	Peak
General	Feed Flow	gpm	200	300	265	310	860	1400
		m3/d	1090	1635	1445	1690	4688	7631
	Influent Nitrate-N	mg/l	1	2	18.6	30	15	18
	Influent Total Se	µg/l	6	10	29	39	22	27
	Influent Temperature	C	7	7	7	7	7	7
Anoxic Reactor	MBBR Diameter	m	4.88		8.84		15.24	
	MBBR Operating Depth	m	4.57		4.88		4.88	
	MBBR Volume	m3	85		299		890	
	Media Surface Area	m^2/m^3	800		800		800	
	Hydraulic Retention Time (HRT)	hrs	1.9	1.3	5.0	4.3	4.6	2.8
Anaerobic Reactor	MBBR Diameter	m	6.10		8.84		15.24	
	MBBR Operating Depth	m	4.57		4.88		4.88	
	MBBR Volume	m3	133		299		890	
	Media Surface Area	m^2/m^3	800		800		800	
	Hydraulic Retention Time (HRT)	hrs	2.9	2.0	5.0	4.3	4.6	2.8

Discharge Requirements

Guaranteed Parameters

	Monthly Average	Daily Max
N-NO_3 - mg/l	1	
TSS- mg/l	10	15

Permitted Discharge Limits

	Monthly Average	Daily Max
Total Se - µg/l	4.7	8.2
Total Al - mg/l	0.44	
Total Fe - mg/l	1.42	

Site 3

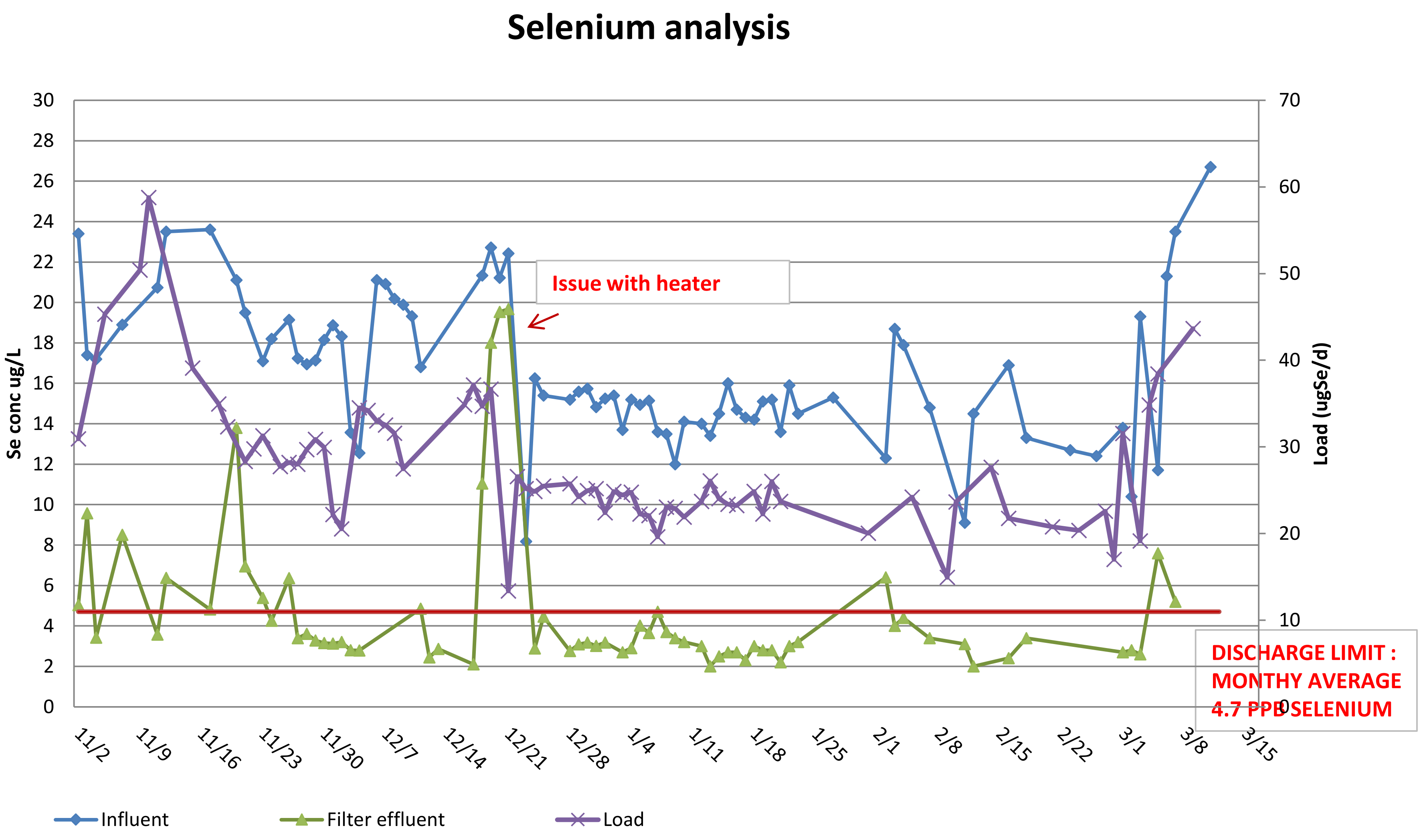
Site 3 was commissioned in September 2014

MBBR were seeded with sludge from site 2

Operating at 400 gpm (average design flow 860 gpm)

Flow limited by heater in the winter – currently ramping up

Site 3 Selenium Profile



Lessons Learned (so far….)

Seeding the MBBR allows for a reasonable start up period (4 - 6 weeks)

Carbon dosing is critical to ensure complete Se reduction

Post-treatment chemistry needs to be considered if SO_4 are present (formation of colloidal metal sulfide in Actiflo)

Selenium analyses on a mine effluent matrix (containing nitrate and sulphate) to low ppb is EXTREMELY difficult. MUST use known spike dosing to ensure reliability of the analysis

Conclusions

Biological treatment of mine effluents with MBBR technology is a viable solution to meet stringent discharge limits

In combination with SeleniumZero®, complete selenium removal can be achieved, even at very low temperature

Thank you