Passive Treatment Systems for the Removal of Selenium: Barrel Substrate Studies, Design, and Full-Scale Implementation




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CH2MHILL®

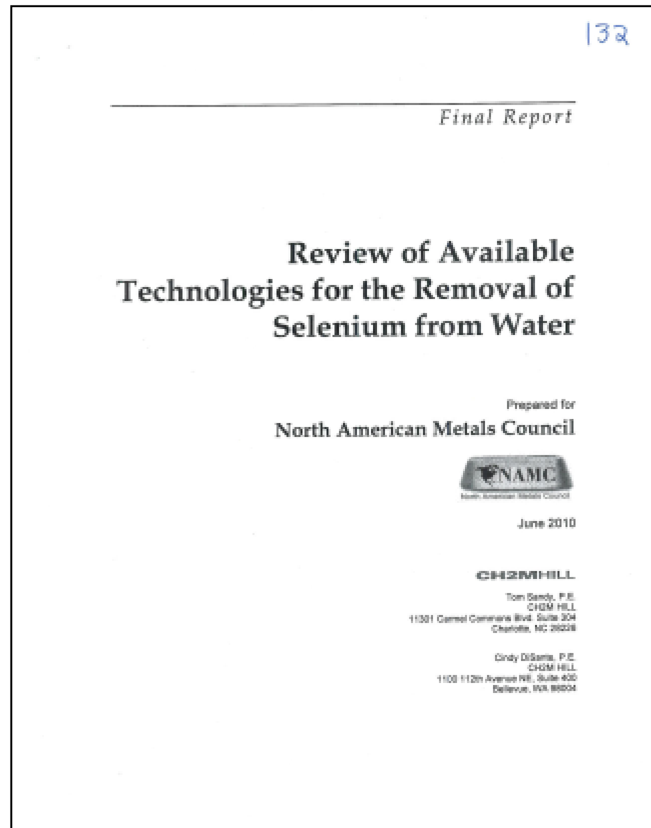
June 3 2013

Overview of Presentation

Outline

- Selenium Issues
- Mechanisms of Selenium Removal
- Historical Systems
- New Full Scale Systems
- Non-mining Examples
- By-Product Treatment
- Conclusions

NAMC Selenium Report 2010



132

Final Report

Review of Available Technologies for the Removal of Selenium from Water

Prepared for

North American Metals Council

NAMC

June 2010

CH2MHILL

http://www.namc.org/docs/00062756.PDF

Key Points about Selenium Control

- Se control can be critical to agriculture runoff, power generation, and mining industries
- Includes active and passive control technologies
- Passive treatment:
  - Uses natural processes to reduce and capture Se
  - Requires less operational effort and management
  - Demonstrated as a viable option for Se treatment

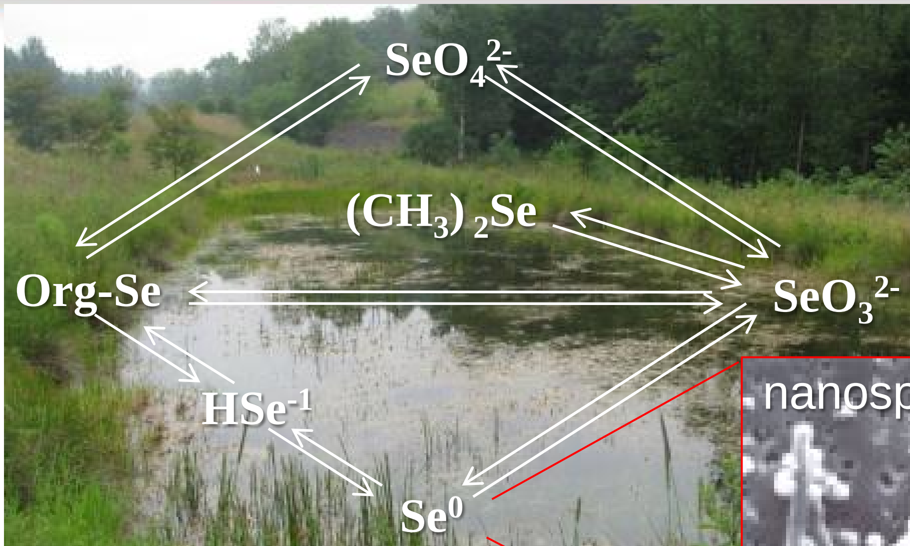
Selenium Chemistry and Toxicity

- **Trace concentrations are essential for diet**
- **Large concentrations can be toxic**
  - Bioaccumulates; aquatic bird egg hatchability, fish larval deformities
- **Oxidation state determines bioavailability, toxicity**

– Elemental (Se^0)	Not toxic, unavailable
– Inorganic selenide (Se^{2-})	Less bioavailable
– Selenate (SeO_4^{2-}, Se^{6+})	Soluble, bioavailable, less toxic
– Selenite (SeO_3^{2-}, Se^{4+})	Soluble, bioavailable, more toxic
– Organic selenide (org-Se)	Most bioavailable, most toxic

- **State NPDES effluent limits**
  - 4.7 µg/L average month; 8.2 µg/L daily max

Wetland Processing and Storage of Selenium



Dissimilatory Reduction

$SeO_4^{2-} \rightarrow SeO_3^{2-} \rightarrow Se^0 \rightarrow Se^{2-}$

- Anaerobic process (Eh -200 mV, DO<2)
- Distribution in wetland sediments:
  - 0:13:41:46
- *Wetlands*: 90% reduction 10 - 16 days
- *Bioreactors*: 90% reduction <1 - 2 days

Volatilization

- Organic + $SeO_3^{2-} \rightarrow (CH_3)_2Se$
- Volatilized from plant tissues
- 5-30% cumulative loss from sediments and plants

Sorption

- Selenite sorbs to sediments and soil constituents: Fe^-, Mn^- or Al^- oxyhydroxides and organic matter

Plant Uptake

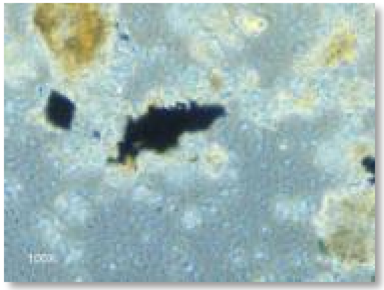
- Rapid uptake
- Tissue concentrations increase but not detrimental
- No long term storage in plants; Se transferred to sediments

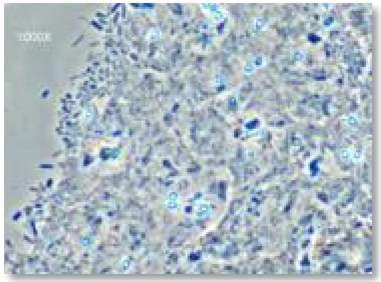
Biological Selenium Treatment

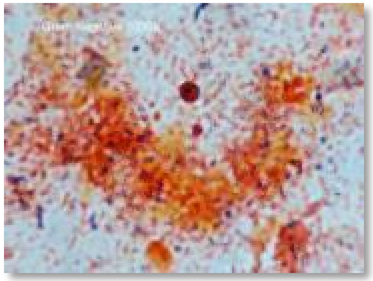
- Organics + Selenite/Selenate + N + P $\longrightarrow$ New Cells + CO_2 + H_2O + Se^0

- Order of reduction:

$DO \rightarrow NO_2^- \rightarrow NO_3^- \rightarrow SeO_3^{2-} \rightarrow SeO_4^{2-} \rightarrow ClO_4^{2-} \rightarrow SO_4^{2-}$







Selenium Passive Treatment Systems: Free Water Surface Wetlands Provide Starting Point

Hansen et al, 1998

Area:	36 ha
Flow:	~6,540 m^3/d
Date:	since 1991
HRT:	7-10 days
Se reduction:	89%
Se in:	20-30 µg/L
Se out:	<5 µg/L
Volatilization:	10-30%

Early Passive Treatment Data

Site/ Date	GPM	pH	Influent Se ug/L	Effluent Se ug/L	Percent Removal
NV Gold Tailing (Aerobic) 1994	10	7.5	40	16	60%
NV Waste Rock (BCR) 1994	6	2.7	22	<5	>78%
Brewer Mine (BCR) 1995	1	2	1,500	50	97%

Source: Gusek (2013)
CLU-IN Bioreactor Overview

Great Recent Progress in Bioreactor Design

www.sdcornblog.com

Denitrifying Bioreactors for Agricultural Wastewater Treatment

Bob Nairn

www.nps.gov

Bioreactors for Minewater Treatment

Case History
Anaerobic "Bioreactor" Wetland Demonstration Showed High Efficiency in Minimal Area

■ Source:	gravel pit seep
■ Volume:	4,380 ft^3
■ Flow:	2-24 gpm
■ Date:	9/08-10/09
■ HRT:	2.4 d
■ Se in flow	1-34 µg/L
■ Se reduction:	98% (90% winter)
■ Se removal rate:	16 $mg/d/m^3$
■ Se out:	0.5 µg/L
■ TCLP	<1 µg/L Se

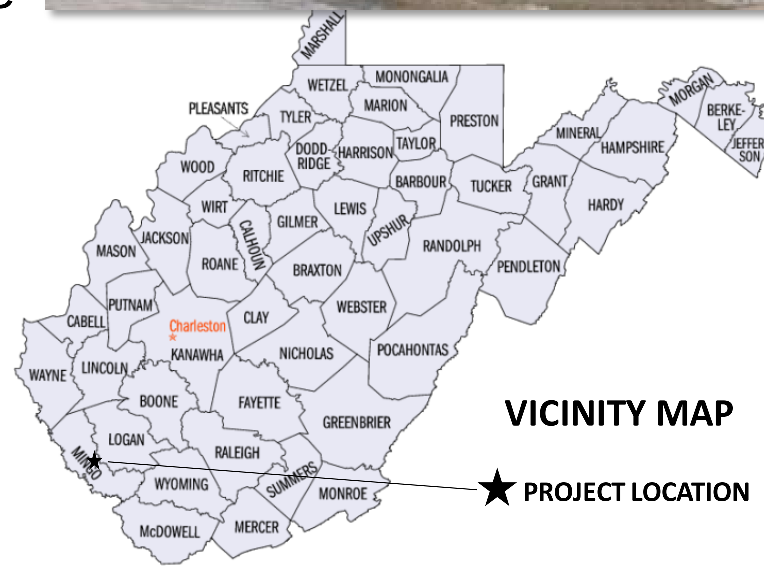
Walker and Golder. 2010. US Bureau of Reclamation

Case Histories:
Pilot and Full-Scale Passive Treatment in WV

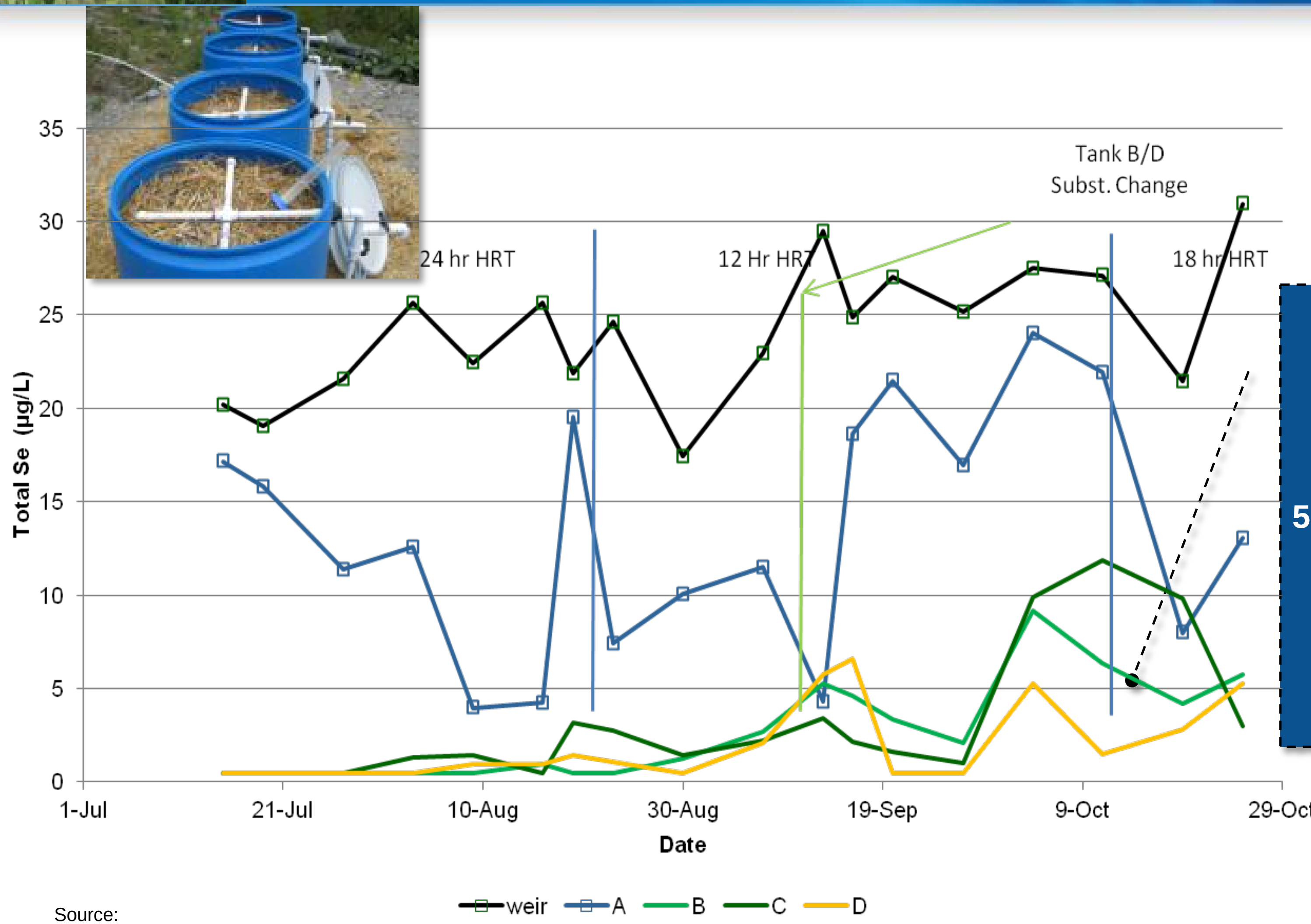
Overview

- Two outlets assigned stringent selenium discharge standard:
  - **4.7** ug/L monthly mean
  - **8.2** ug/L daily max
- Conducted barrel studies to formulate substrate, calibrate model
- Designed two distinct systems based on landscape, space, treatment
- First system July 2011
- Second system November 2011

Location



Case History (2010)
Pilot Study of BCR for Coal Mine Drainage



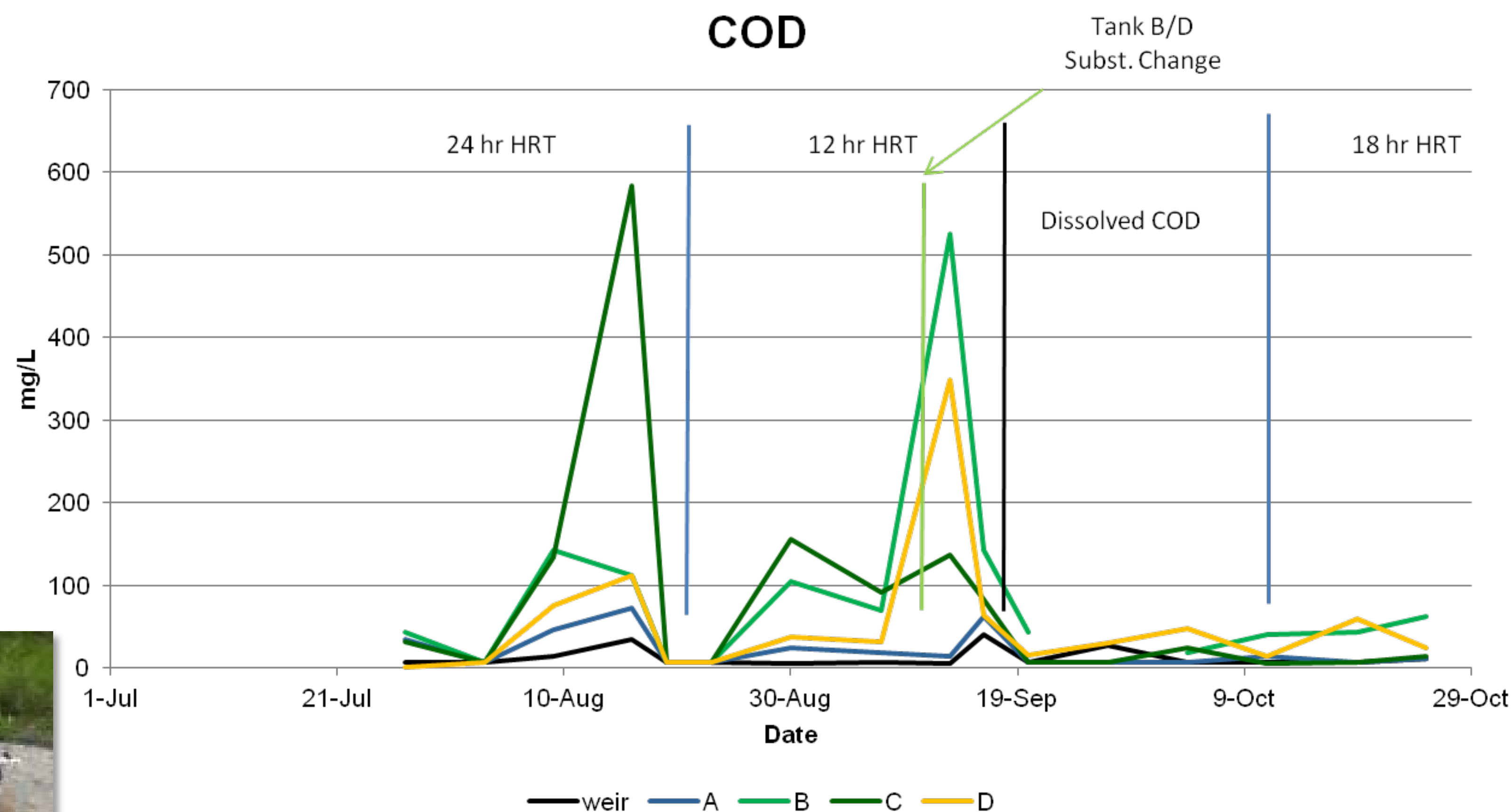
20% woodchips
35% sawdust
10% peat moss
5% limestone sand
25% hay,
5% composted manure

24 hr HRT
~ 17 mg/d/m^3 media

k_{20} ~1700 m/yr

Source:
CH2MHILL (2010)

Barrel Study Confirmed Significant Post-Startup "Byproduct" Discharges



Barrel Study Conclusions

- High strength substrate can remove Se at 12-hour HRT (24- to 48-hour HRT for typical design)
- High strength substrate initially generates elevated concentration of secondary parameters (BOD, COD, low DO, etc.)
- Low strength substrate = lower Se removal rates *but also* lower secondary parameters
- Initial Se removal is largely as weakly adsorbed selenite with minor amounts removed as elemental Se
- Recommend additional long-term investigation


100 m
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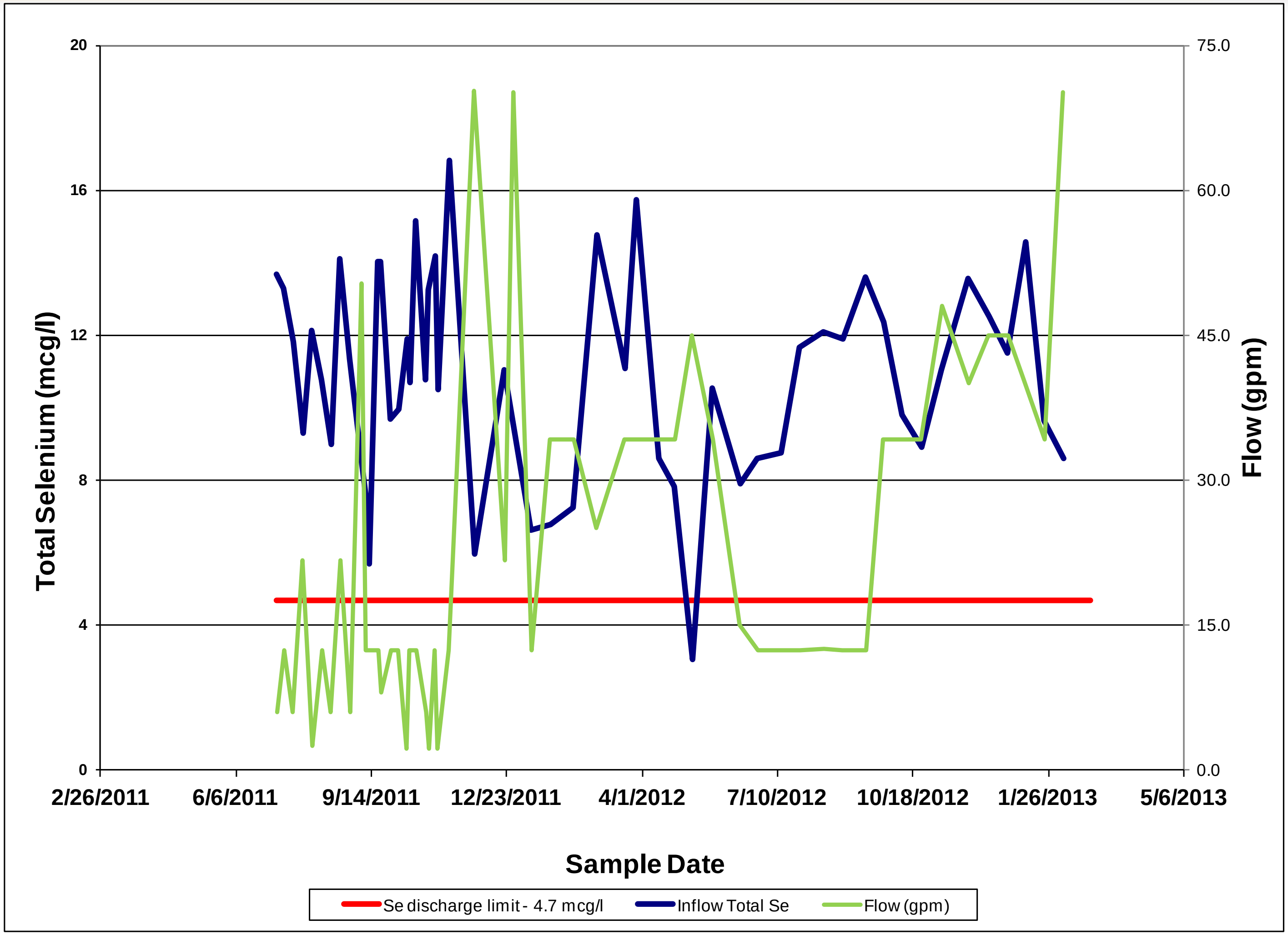
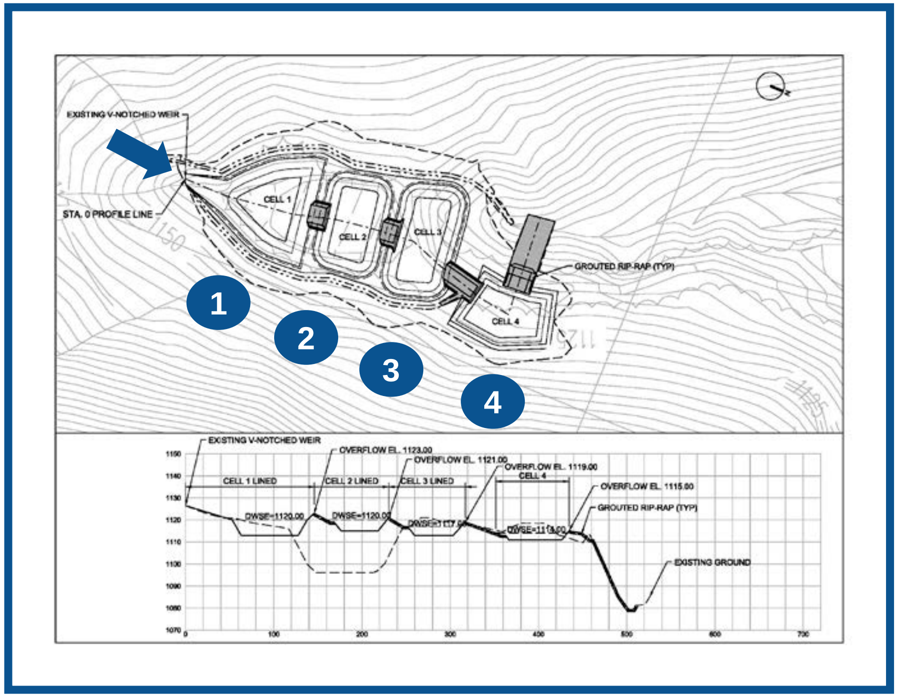
System A: Design Flow Set to Capture Load and Account for Inter-annual Variation



Case History (2011-present) Two Full-Scale BCR Systems for Coal Mine Drainage Treatment



- 60 gpm base flow
- 100 gpm max
- 12 µg/L mean Se to <4.7

- Replace existing sed pond
- Four cells-in-series:
  1. 0.13 ac Downflow BCR

     Barrel "B" mix
  2. 0.14 ac Anaerobic upflow bed

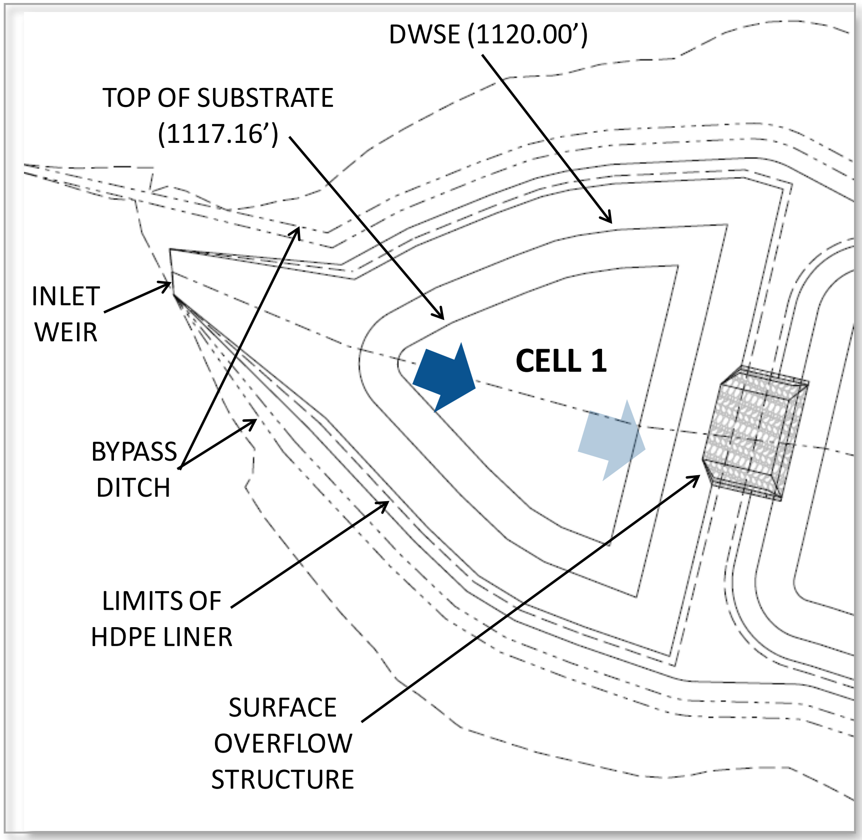
     Barrel "A" peat
  3. 0.16 ac Fill-and-drain wetland

     Gravel; siphon level control
  4. 0.11 ac Surface flow marsh

Source:
CH2MHILL (2912)

Cell 1: Downflow Biochemical Reactor (BCR)

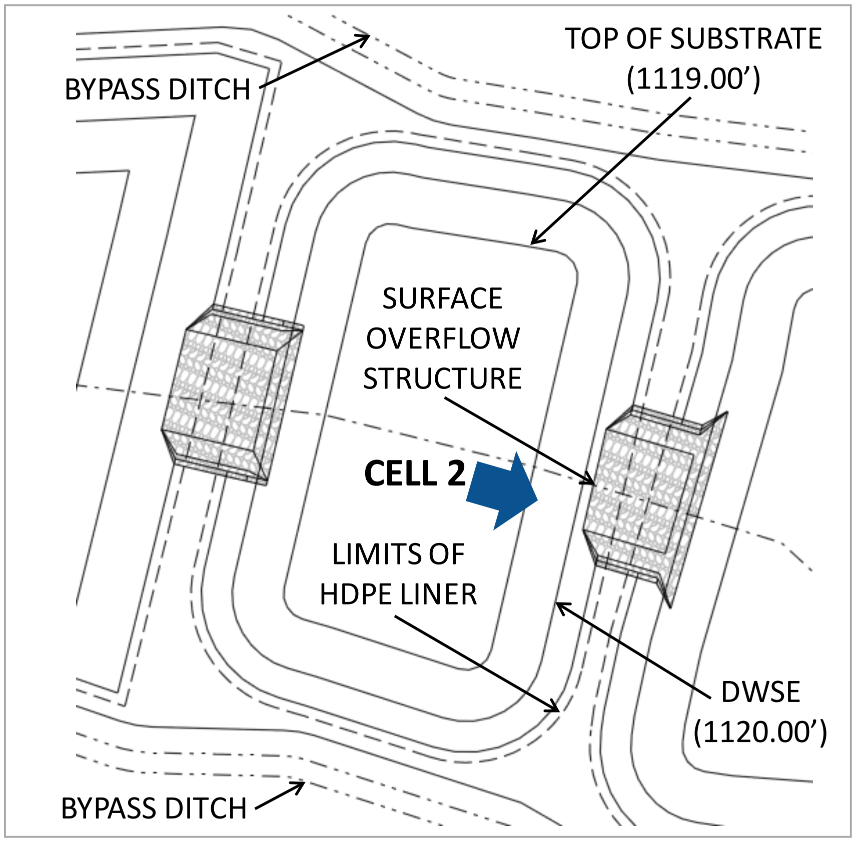
Plan



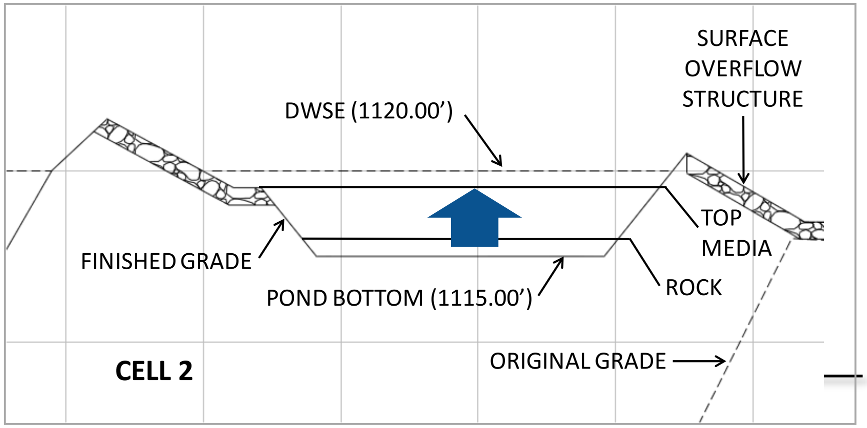
m^2	Type	Media	Plants	Function
526	Downflow biochemical reactor	Mixed organic	None	Selenium reduction

Cell 2: Upflow Anaerobic Wetland

Plan



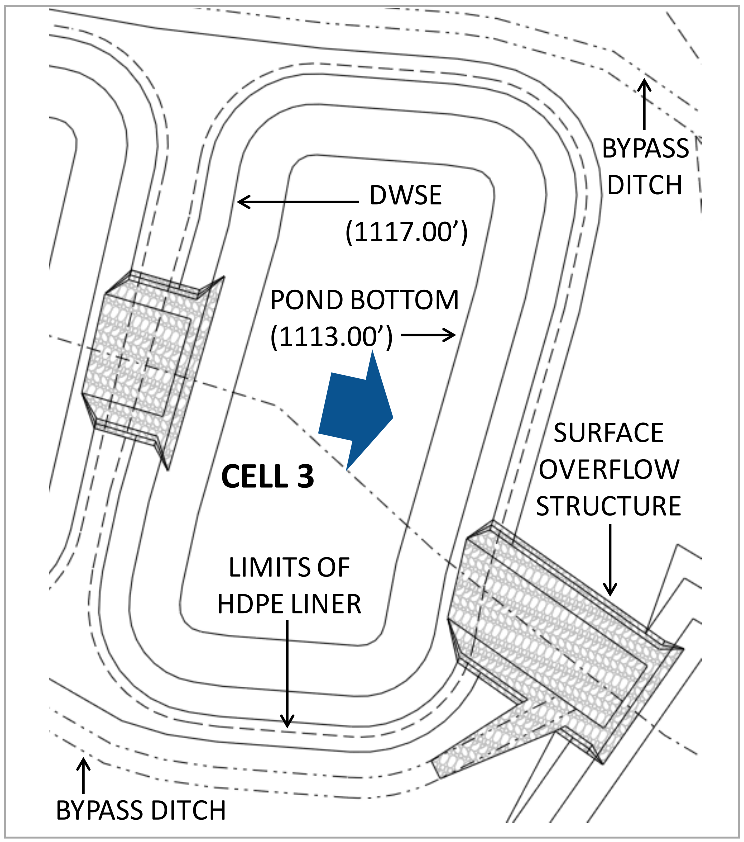
Profile



m^2	Type	Media	Plants	Function
567	Upflow anaerobic	Peat	Sedges, rush	Selenium reduction, Byproduct polishing

Cell 3: Fill-and-Drain Polishing Wetland

Plan



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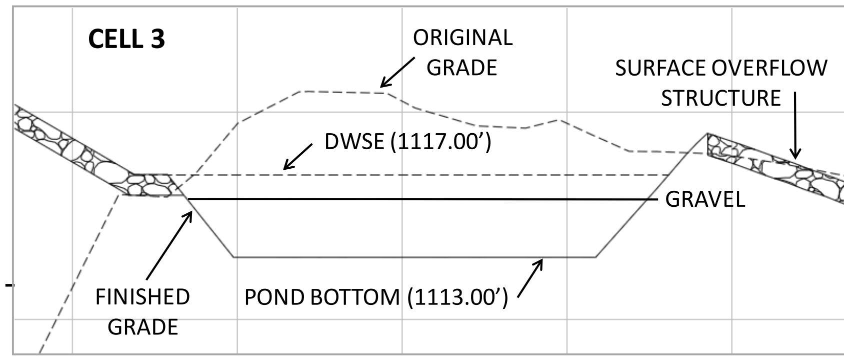
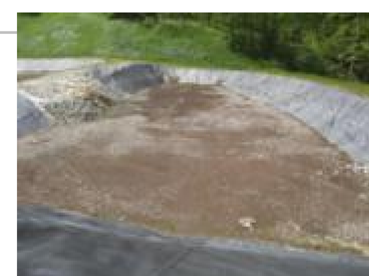
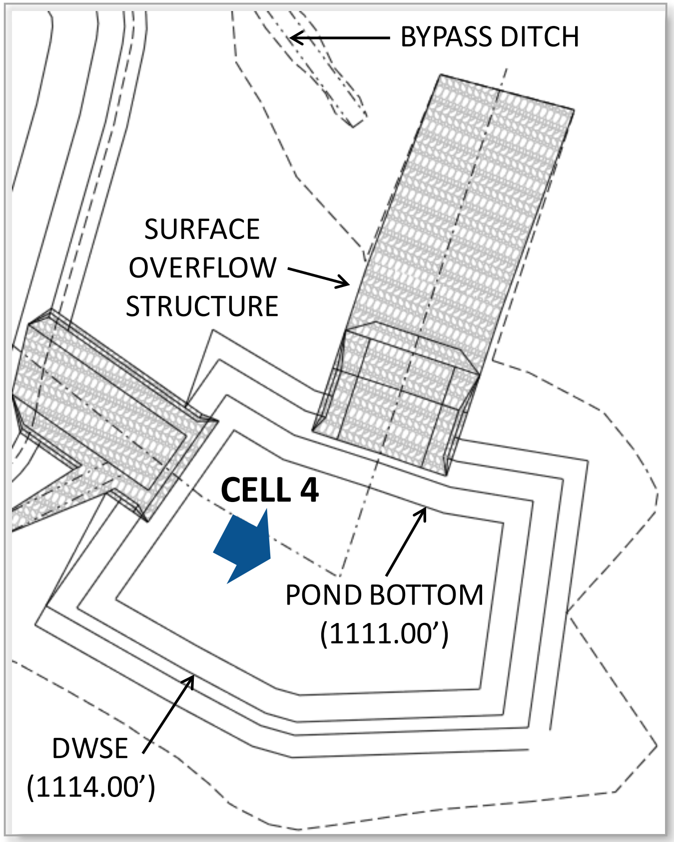


m^2	Type	Media	Plants	Function
648	Subsurface fill and drain	Limestone gravel	Cattails	Byproduct polishing

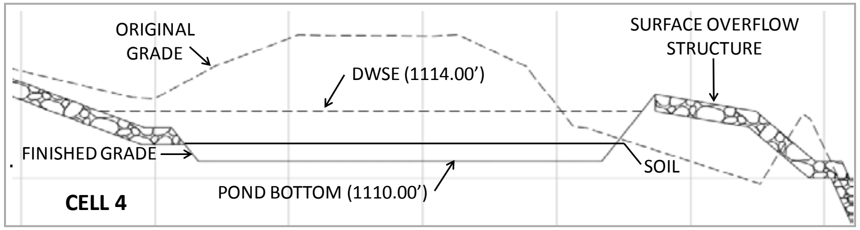


Cell 4: Free Water Surface Polishing Wetland

Plan

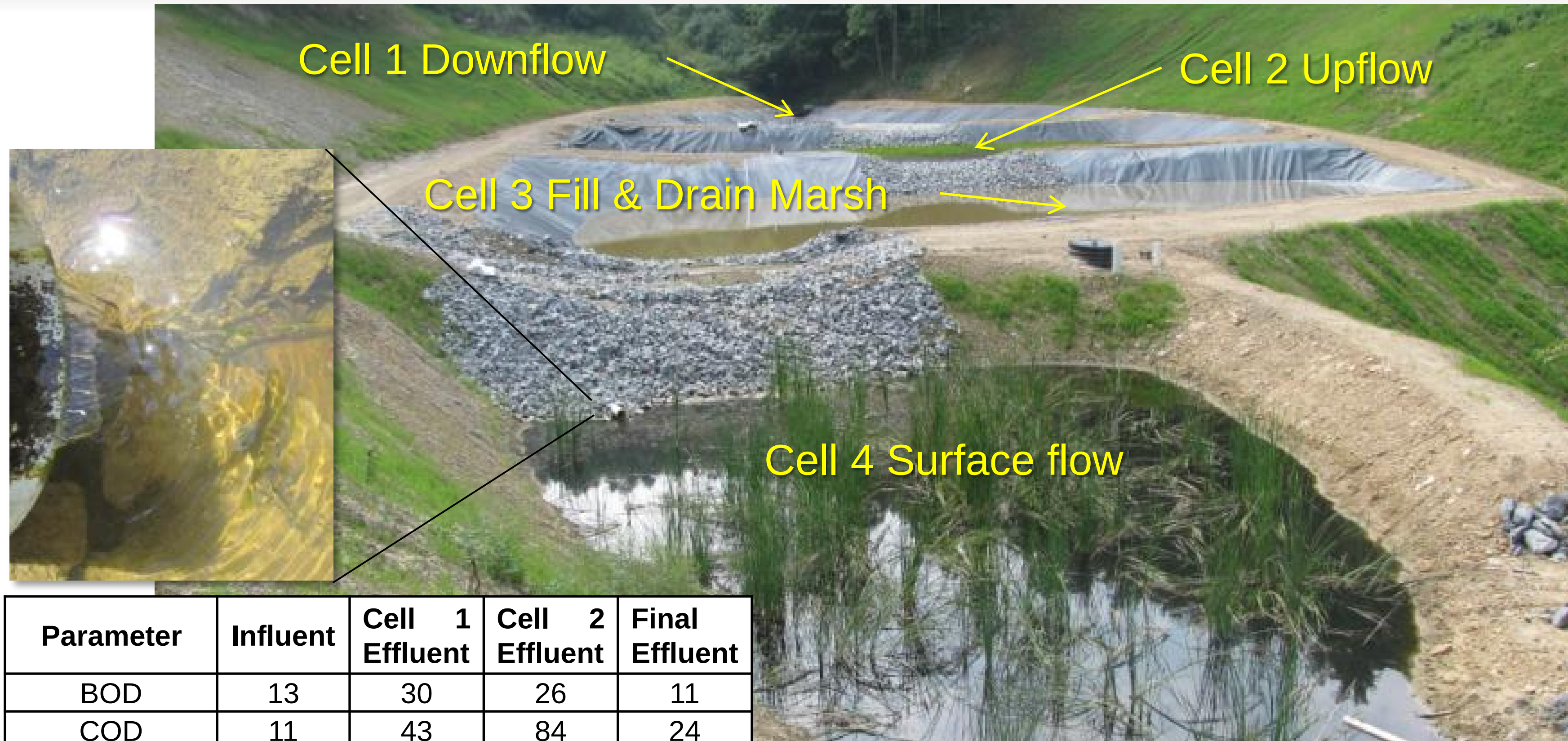


Profile



m^2	Type	Media	Plants	Function
445	Free water surface	Topsoil and ponded water	Cattails	Byproduct polishing

PTS A:
Completed Passive Se Treatment System



Parameter	Influent	Cell 1 Effluent	Cell 2 Effluent	Final Effluent
BOD	13	30	26	11
COD	11	43	84	24
NO_2+NO_3-N	3.6	1.5	2.4	1.2
Total Phosphorus	0.28	0.09	0.13	0.1
All units = mg/L				
[a] Monitoring data from February through July 2012				

Source:
Thomas, R. (2011)

On Balance, Natural Systems Favored (Coal Mine Drainage Example)

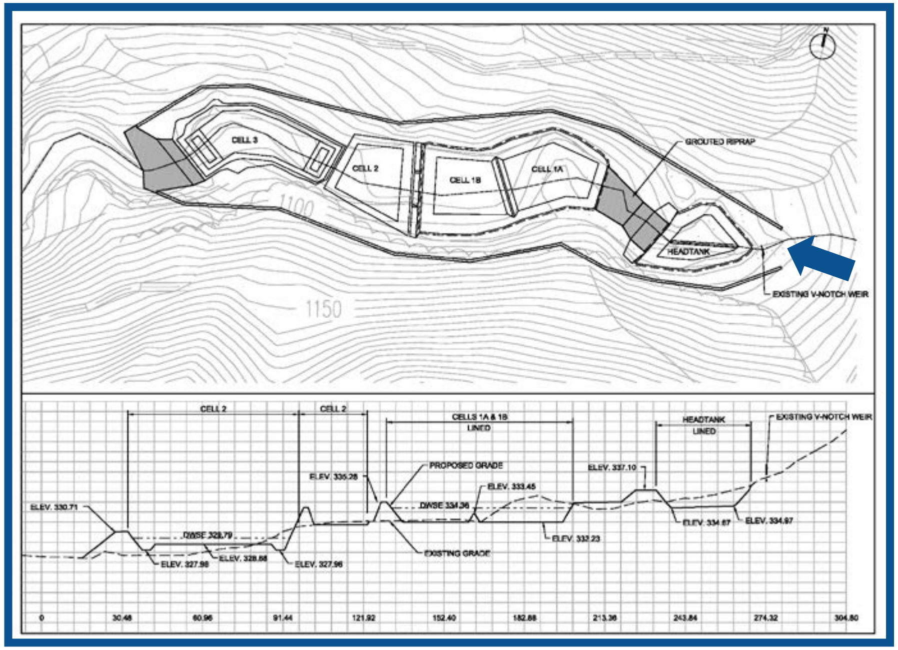
Natural Systems

- BCR+wetland footprint fits (just)
- Construction $762K
- Natural processes
- O&M $15K/yr

Conventional Systems

- Can be made to fit
- Construction $18MM
- Engineered processes
- O&M $500K

PTS B: Higher Flow, Higher Concentration

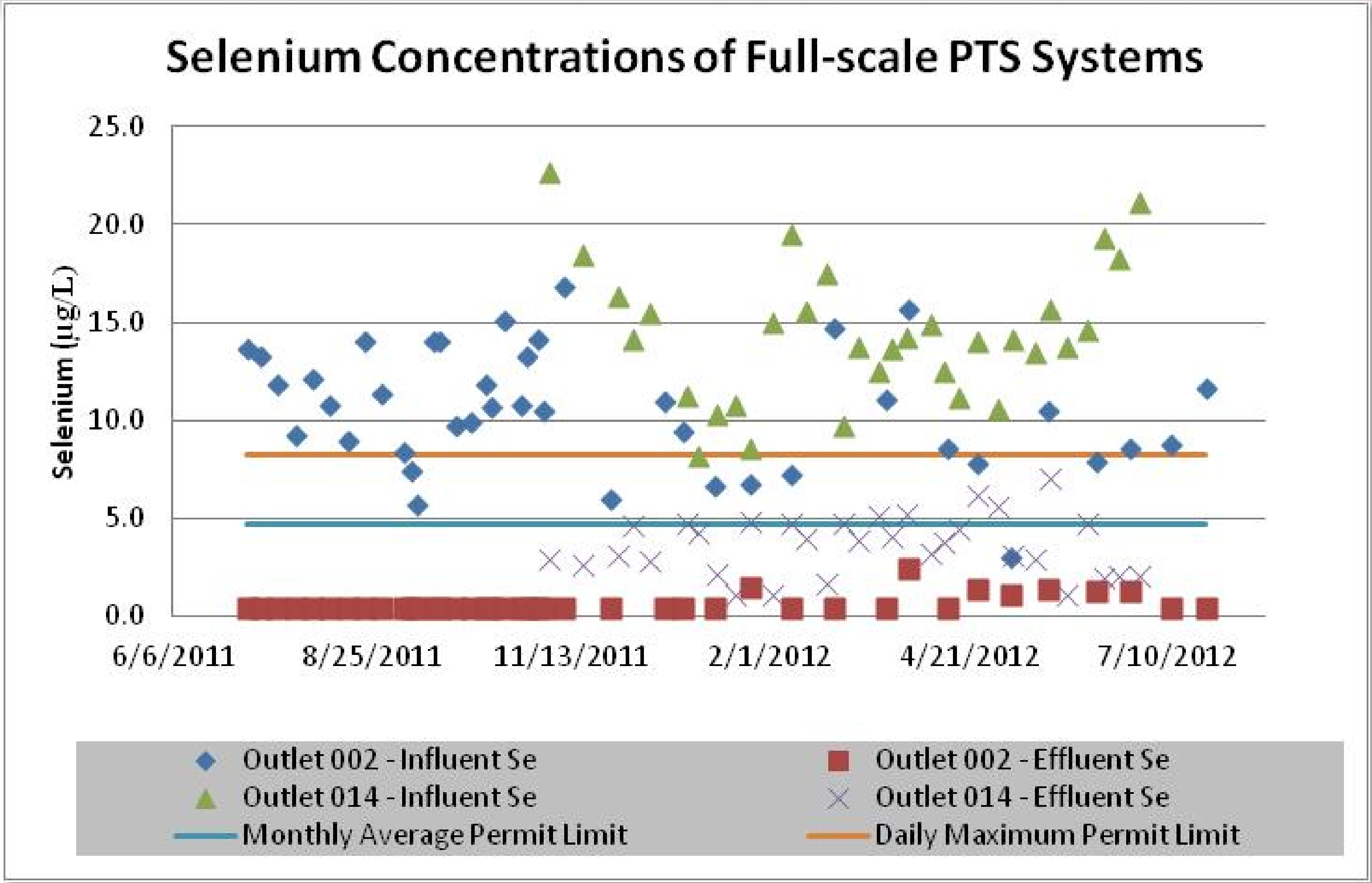


- Five cells-in-series:
  1. 0.12 ac Head tank
  2. 0.48 ac Upflow BCR
  3. 0.30 ac Upflow BCR
  4. 0.23 ac Surface flow marsh
  5. 0.38 ac Sedimentation pond

- ➢230 gpm base flow
- ➢24 µg/L mean Se to <4.7

Source:
CH2MHILL (2011)

Selenium Treatment Performance Achieved WQ Targets



Source:
CH2MHILL (2012)

Case History (2011-2012): Field-Scale Demonstrations for Coal Mine Drainage in WV

Source:
J Bays (2011)

- Three reactors: 35 ft x50 ft
- Duration: 290, 203, 203 days
- Se in: 2-25 µg/L
- Se out: 1-4 µg/L
- Se RR: 0.22 mg/d/ft^3
  - » 7.7 mg/d/m^3
  - » 5-10°C
- Substrate: Haybales, MC
- Results used for full-scale plan:
  - 250,000 ft^3 substrate
  - 800 gpm
  - Se in: 14.88 µg/L
  - Se out: 2.35 µg/L
  - 10 hr HRT

Source:
Meek (2012)

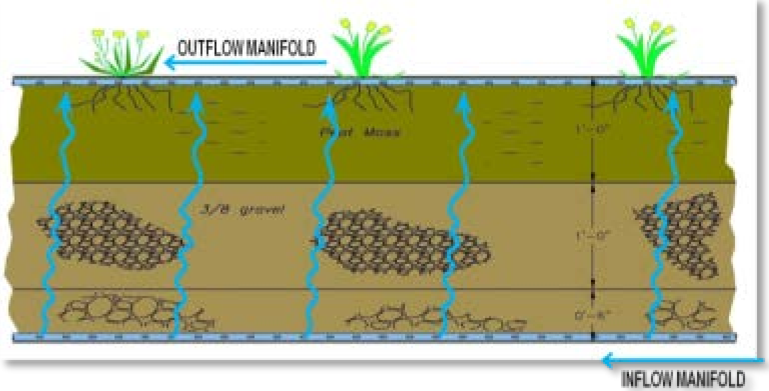
Case History (2008-present)
Cold Climate Coal Mine, Alberta CA

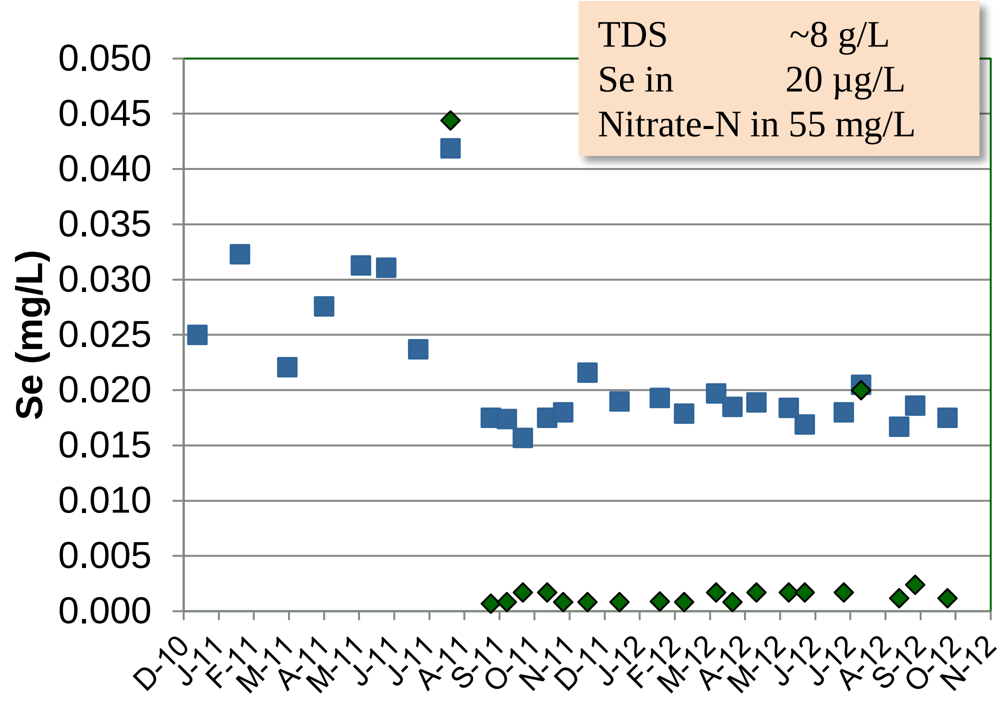
■ Date:	2008-present
■ Type:	Downflow VF
■ Volume:	253 m^3
■ Temp in:	3.2°C avg
■ Se in	195 µg/L
■ Se out:	33 µg/L (3 min)
■ Se CR:	>90%
■ NO3N in:	36 mg/L
■ NO3N RR:	5 $g/d/m^3$
■ Se RR:	17 $mg/d/m^3$
■ HRT:	4-8 days

- Year-round operation, passive

Source: Schipper & Rutkowski. 2012.
www.asmr.org

Case History (2010-present) Continuous Se Removal in Mixed Organic Media for Saline RO Membrane Concentrate





■ Bin 2 Influent (RO Conc.) ◆ Bin 2 Effluent

www.usbr.gov

Sources: CH2MHILL (2012) Image Source: Bays, J. (2012)

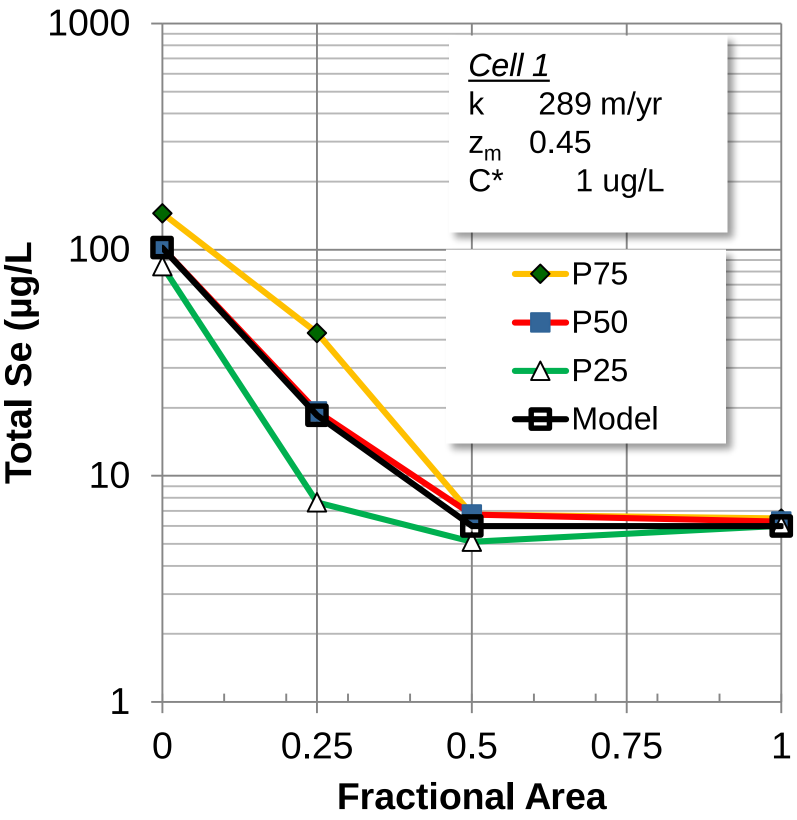
Case History (2012): Treatment of Saline FGD Wastewaters Shows Selenium Removal

Pilot Study

Downflow Bioreactor

TDS	2-10 g/L
Se in	129 – 290 ug/L

Treatment Trend: Se Profile

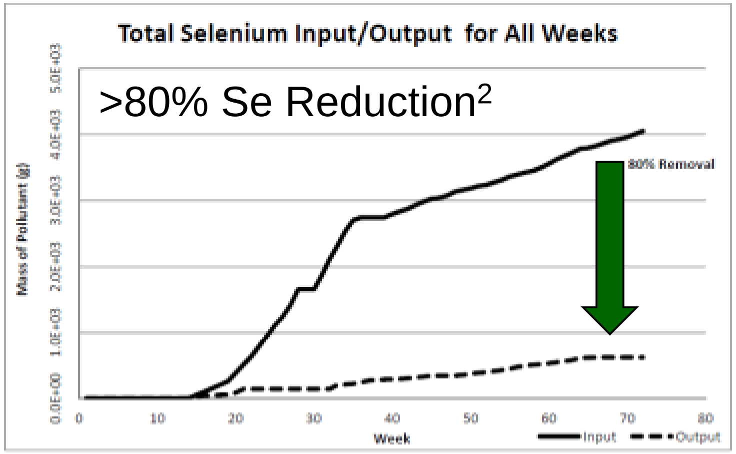


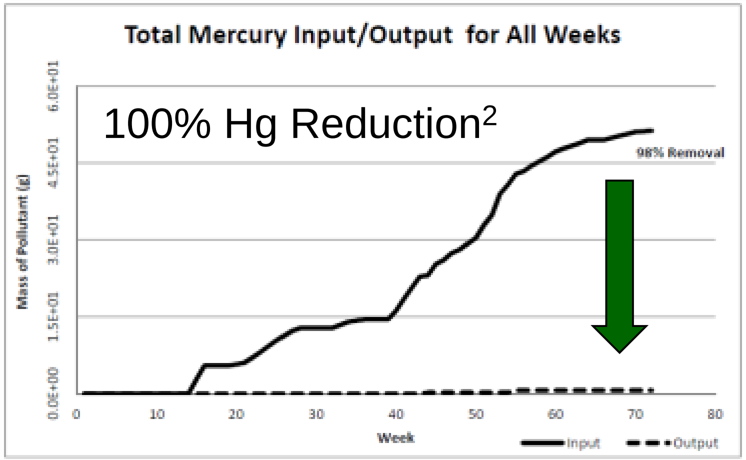
Source:
CH2MHILL (2013)

Case History (2011-2012): Jeffrey Energy Center Pilot Wetland Westar Energy KS

Vertical Flow Cells for Se, Hg Reduction[1]

TDS	~2 g/L
Se in	~70 µg/L
Area	2 ac





Sources:
[1] Morrison ,J. (2012) www.kdheks.com
[2]. Talley, M. (2012).

Passive Treatment of Selenium: BCR Byproducts

- BOD, COD, Low DO, Color, Nitrogen (NH_4^+, NO_3^-/NO_2^-, TKN, etc), Phosphate, and Sulfide
- Recognition of the issue in early studies
- Why byproducts are an issue in Se treatment
- Expectations
  - Initial flush
  - Long-term generation of by products

Functional Role of Aerobic Wetlands in Anaerobic + Aerobic Combination

Surface Flow Wetlands

Functions

- Treat BCR by-products
  - Oxidize BOD, COD
  - Trap particulates
  - Assimilate excess nutrients
  - Odor reduction
  - Reduce color
- Se polishing to trace levels
  - Biological vegetation uptake, transformation and burial
  - Hydrologic attenuation to equalize possible variation in flows and concentrations

Aerobic Polishing Cells (APCs): How Well Do They Work?

Conventional Parameters

Parameter	Removal Efficiency	Limit
BOD	50 – 90%	2 – 10 mg/L
TSS	50 – 90%	2 – 10 mg/L
TN	50 – 90%	1 – 3 mg/L
TP	40 – 90%	< 1 mg/L

Note: Removal efficiencies and effluent concentrations depend on influent concentration and hydraulic loading rate.

Conclusions

- Se control can be critical to agriculture runoff, power generation, and mining industries
- Se control includes active and passive technologies
- Passive treatment:
  - Uses natural processes to reduce and capture Se
  - Requires less operational effort and management
  - Demonstrated as a viable option for Se treatment
- Site-specific applications based on Se concentration, flow rate, topography, and general influent geochemistry
- Early success achieved; optimization ongoing as systems age and performance is evaluated through changing climatic and flow conditions

Acknowledgements

- Thanks to all of our collaborating partners in the West Virginia Coal Mining Industry
- Thanks to supporting engineering and science staff at CH2M HILL

Questions