Integrated Treatment Options for Meeting Stringent Selenium Regulatory Limits Using Anaerobic Bioreactors

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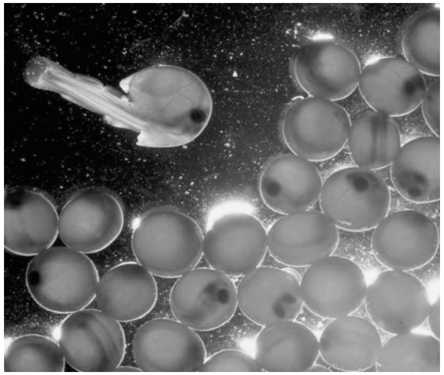
Overview

1) Background
2) Selenium Block Flow Diagram
3) 4 case studies
4) Conclusions

Background – Selenium (Se)



- Naturally occurring non-metal
- Essential for health of humans, other animals, some plants
- In excess and in critical chemical species in diet can cause reproductive failures / abnormalities in egg-laying vertebrates (**fish, birds, amphibians, reptiles**)
- Concentrations increasing globally due to mining, power generation, agriculture and animal husbandry

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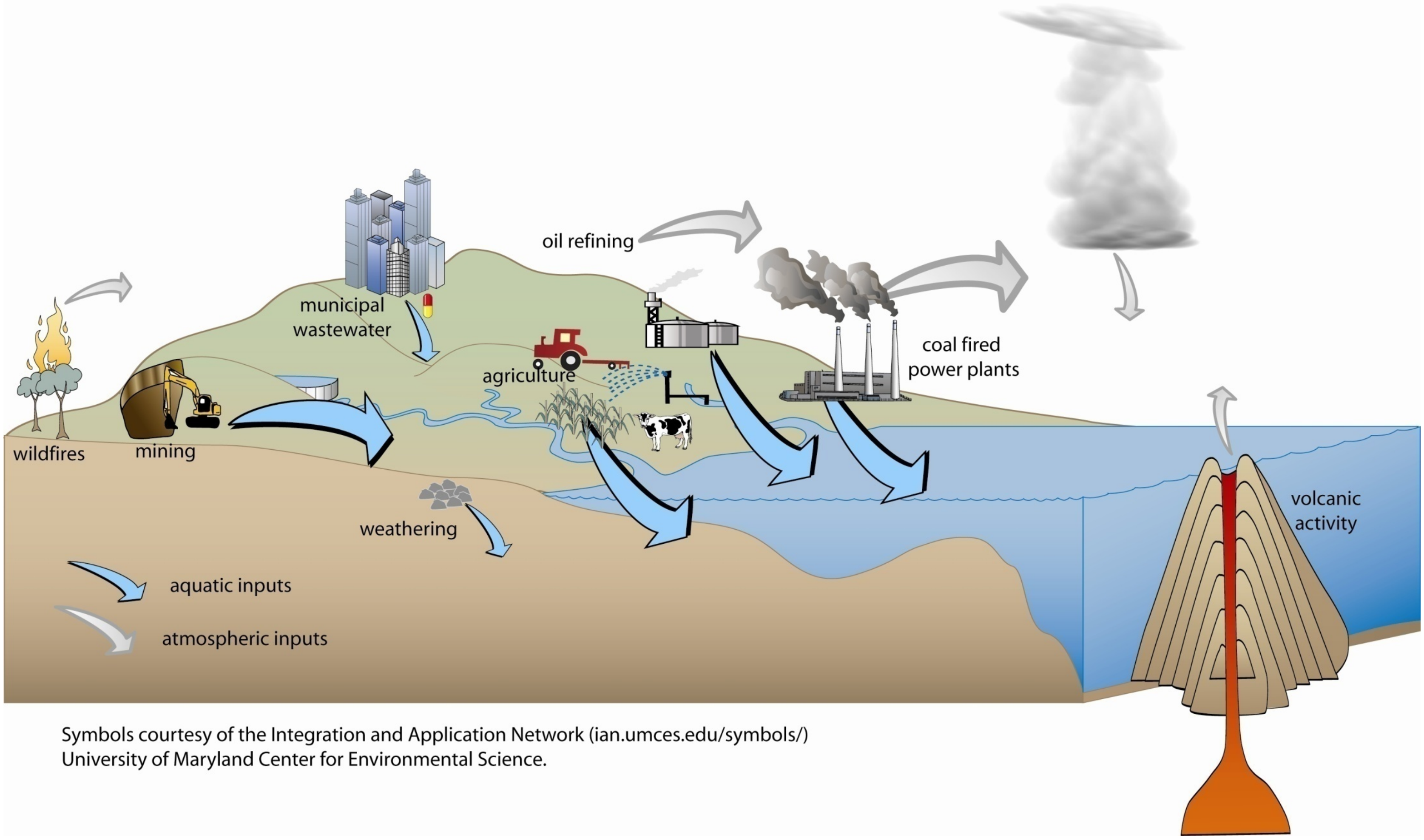
Background: Potential Sources of Selenium



Symbols courtesy of the Integration and Application Network (ian.umces.edu/symbols/)
University of Maryland Center for Environmental Science.

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Background: Chemistry

- 4 oxidation states
  - +6 selenate (SeO_4^{-2})
  - +4 selenite ($HSeO_3^-$ and SeO_3^-)
  - 0 elemental selenium Se_0
  - -2 selenide Se^{-2}

Background: Mine Water Challenges

- **<u>Problem: How to achieve ~5 µg/L end-of-pipe</u>**

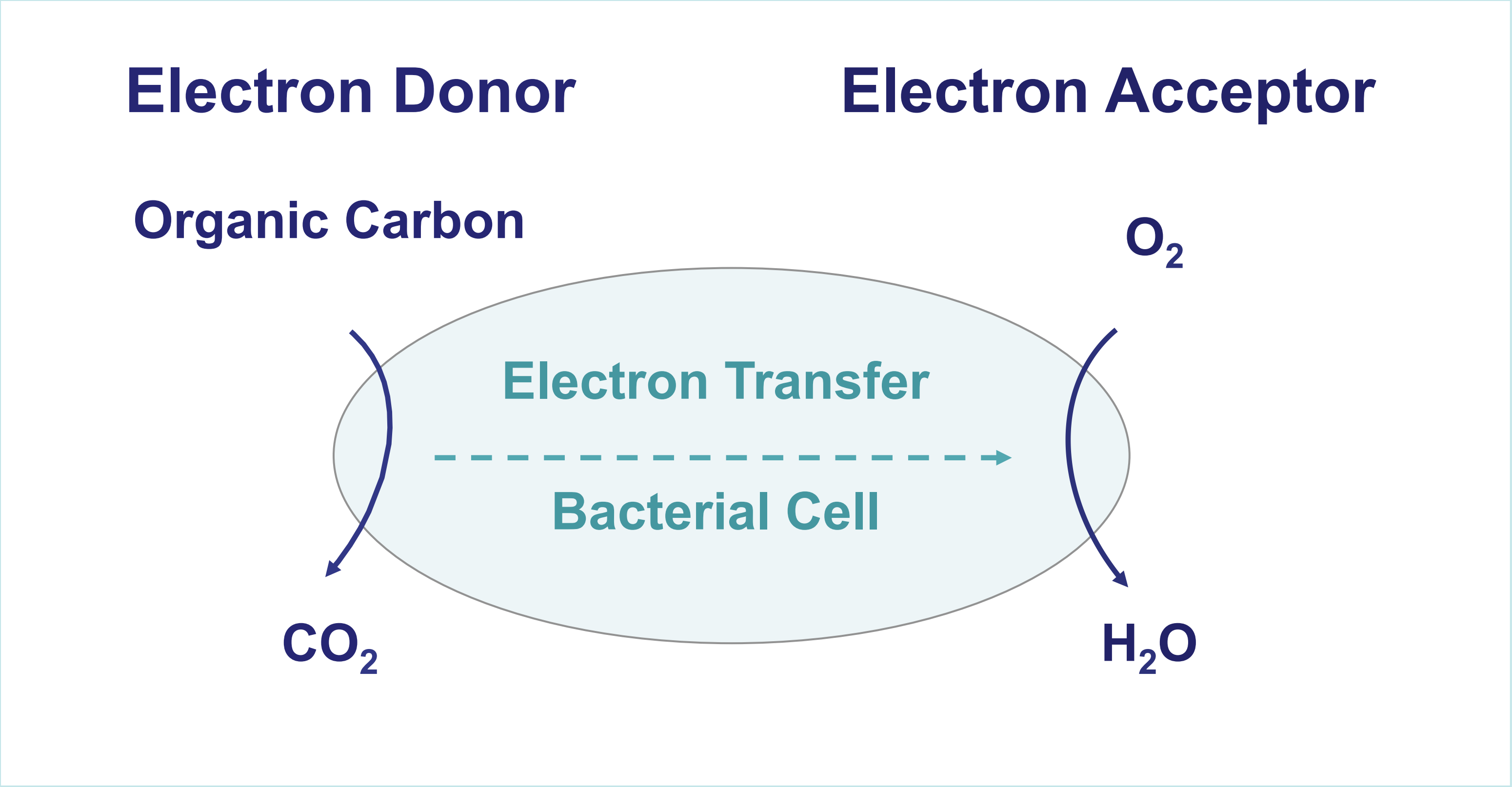
- Challenges
  - Variable water quality
  - Competing electron acceptors
  - High flow, low concentrations

- Few full-scale, proven treatment alternatives to achieve < 5 µg/L
  - RO
  - Biological Treatment

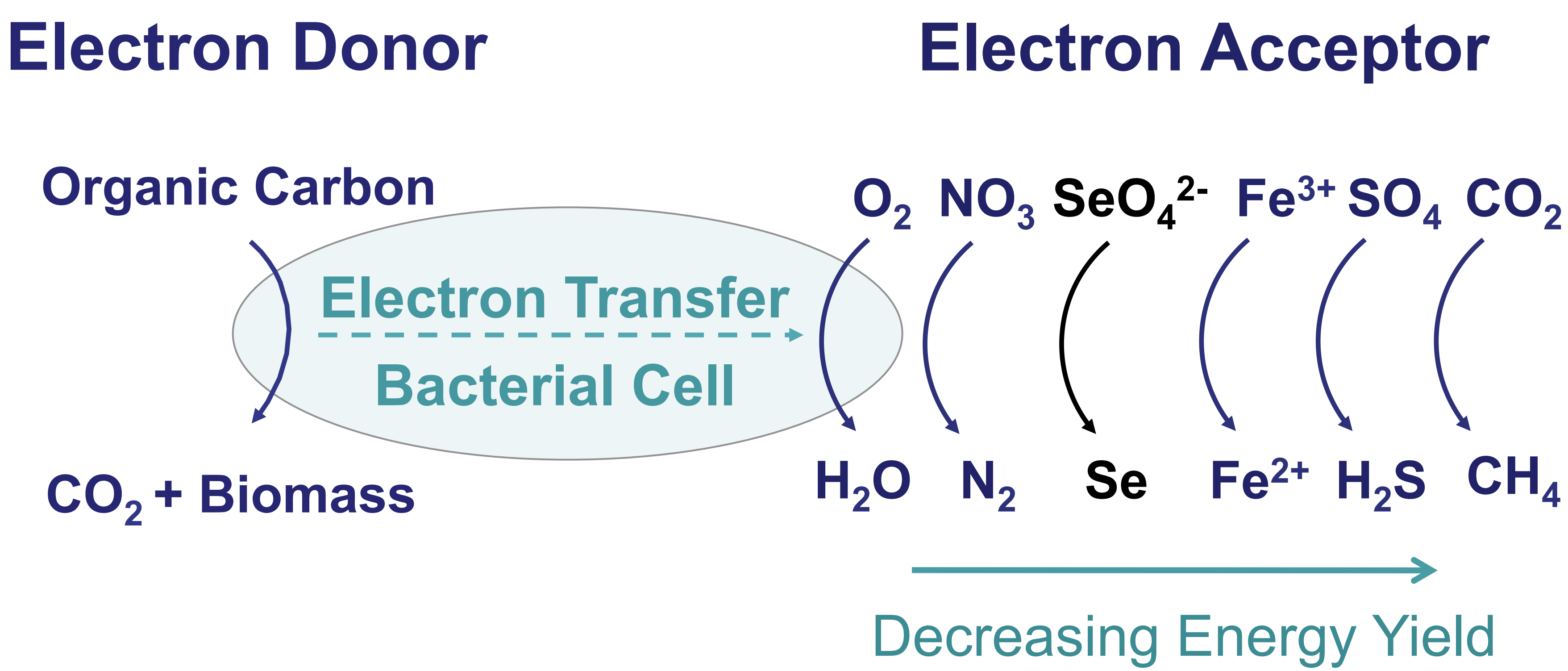
- A single technology is not always sufficient to achieve < 5 µg/L

Treatment Technologies: Biological

- Biological treatment relies on oxidation-reduction reactions



Treatment Technologies: Biological



Treatment Technologies: Biological

- Biological selenium reduction:

$$SeO_4^{2-} + 2CH_2O \rightarrow Se^0 + 2CO_2 + 2H_2O$$

- Elemental selenium retained in bioreactor
- Anaerobic reaction (ORP range from -180 to -350 mv)
- HRTs: minutes to hours to days
- Facultative heterotrophic bacteria (denitrifiers, selenium reducers)
- Includes packed bed reactors, fluidized beds and passive reactors
- Biological treatment capable of 80 to >95% removal
  - When influent > 50 µg/L, additional unit processes may be necessary to reach 5 µg/L.

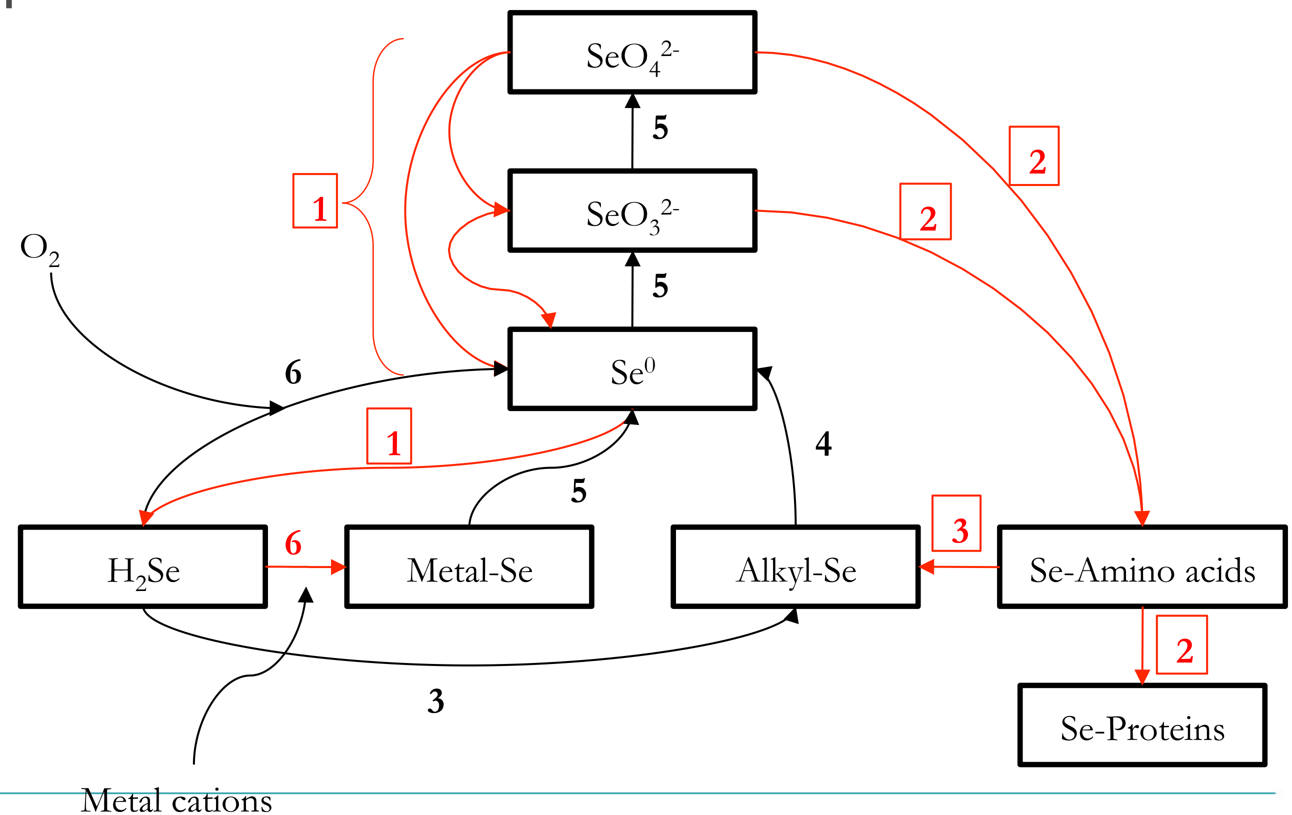
Treatment Technologies: Biological

Residual selenium in bio-effluent –

1) particulate
2) reduced species

Se pathways -

1) Dissimilatory reduction
2) Assimilatory reduction
3) Alkylation
4) Dealkylation
5) Oxidation
6) Bio-induced precipitation



Adapted From Lenz 2008.

Se removal pathways are shown in red.

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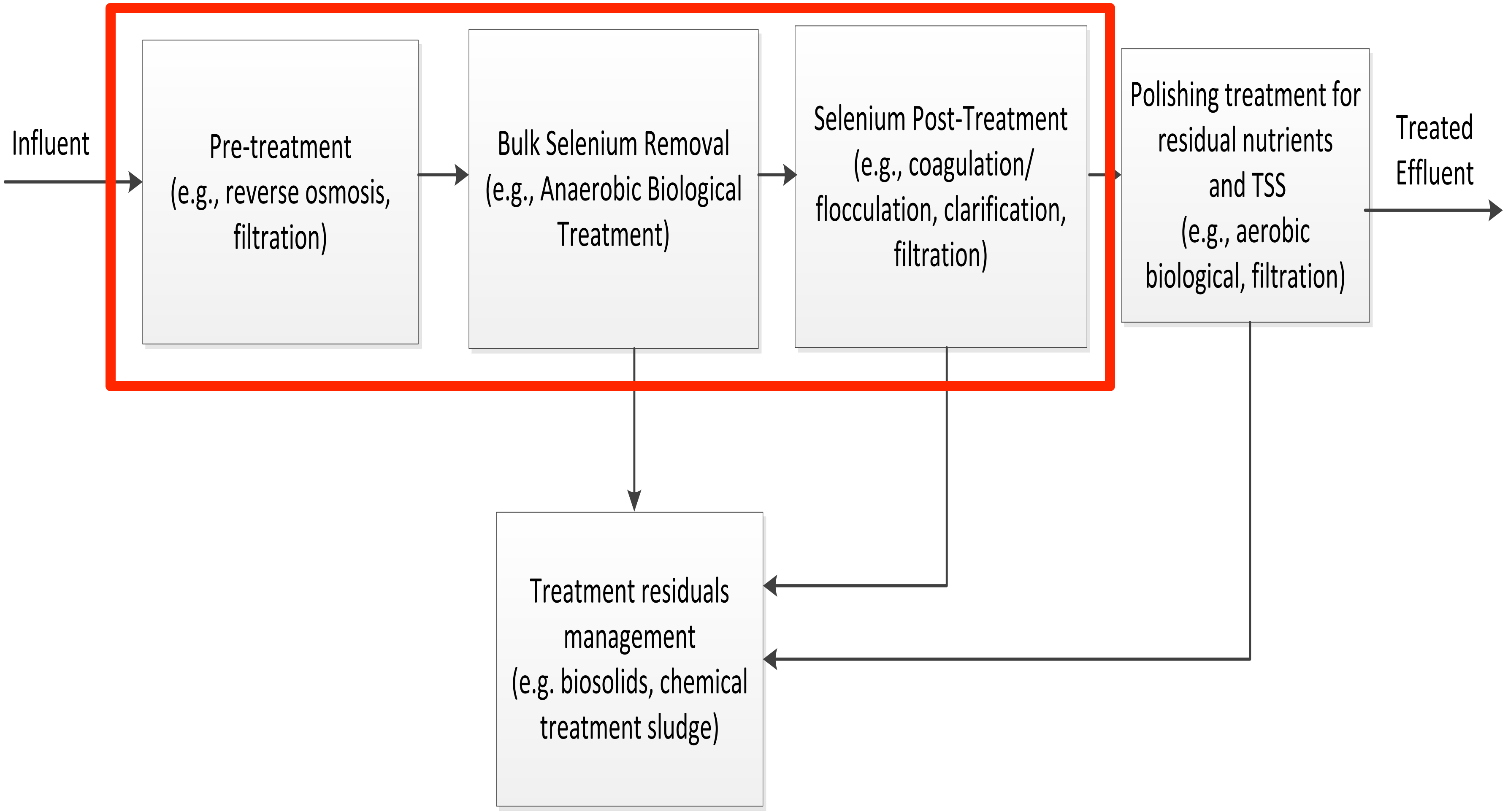
Treatment Technologies: Block Flow



Case Studies

Case Study 1

- Waste rock seepage
- 250 - 700 gpm capacity
- Molasses used as carbon source
- Reverse osmosis system used during high flow – 700 gpm
- Selenium treatment goal of 4.6 µg/L

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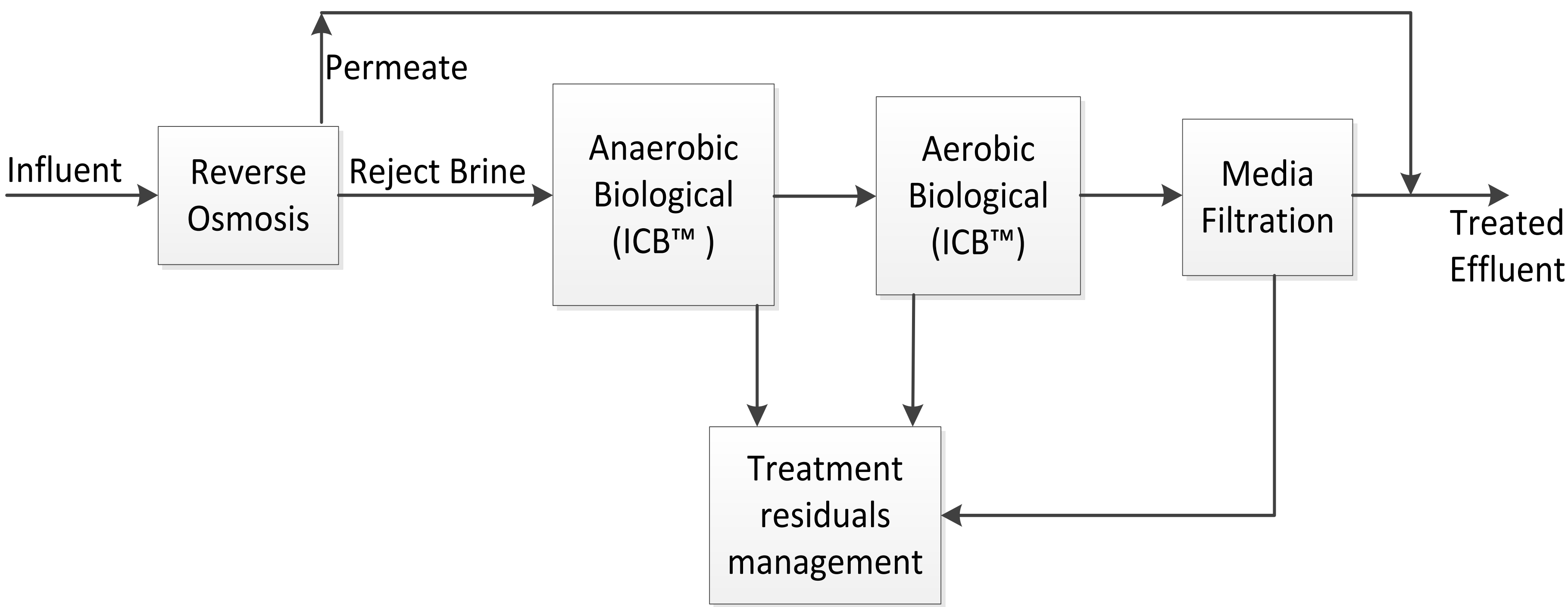
Case Study 1: Block Flow



Case Study 1: Influent Concentrations

Parameter	Low Flow Raw Seepage	High Flow RO Brine
Selenium, µg/l	~30 µg/l	~70 µg/l
Sulfate, mg/l	~6,000 mg/L	~13,500 mg/L

Plant has been in compliance for 6 years.

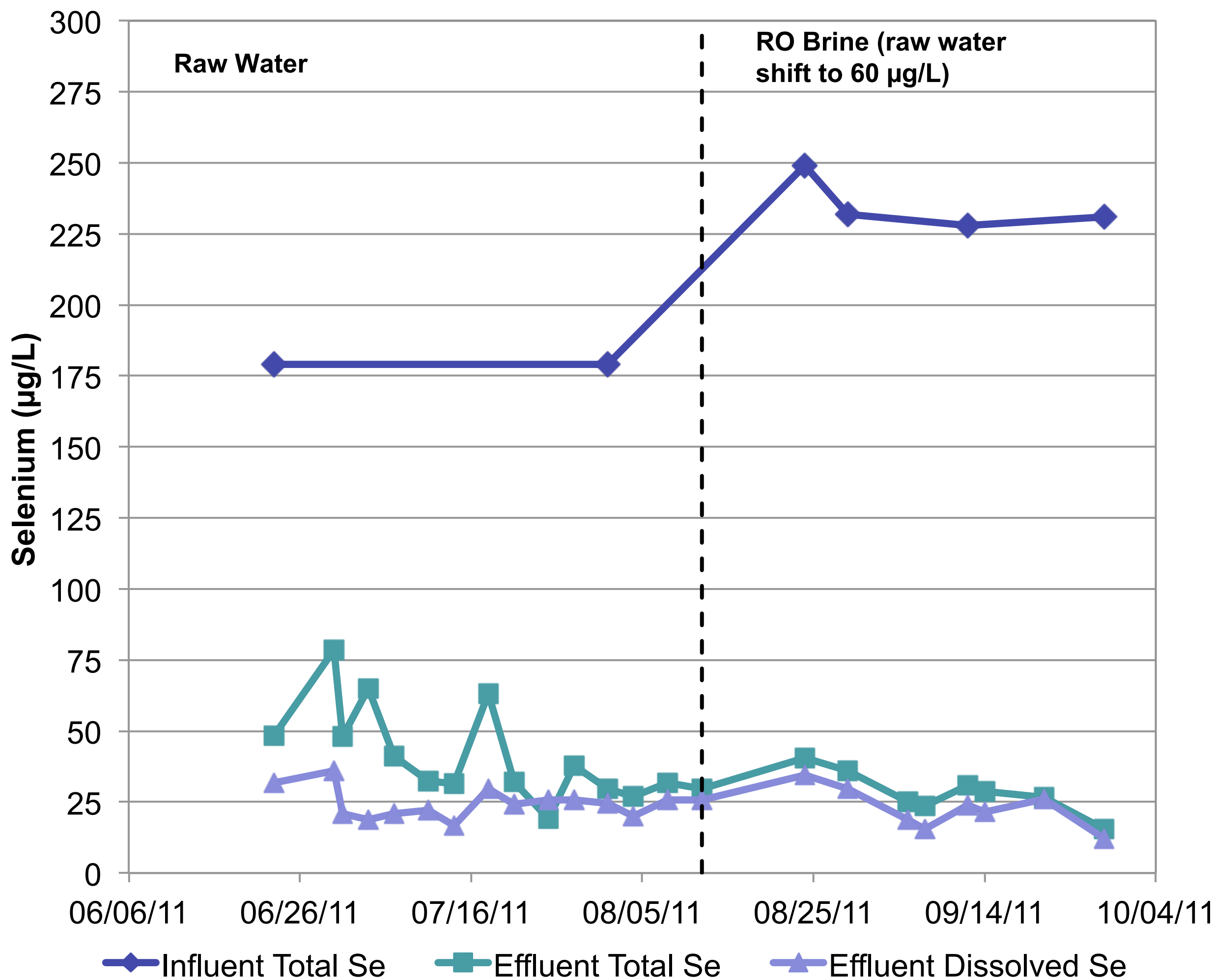
Conclusion: RO + Bio able to achieve 5 µg/L

Case Study 2: Project details

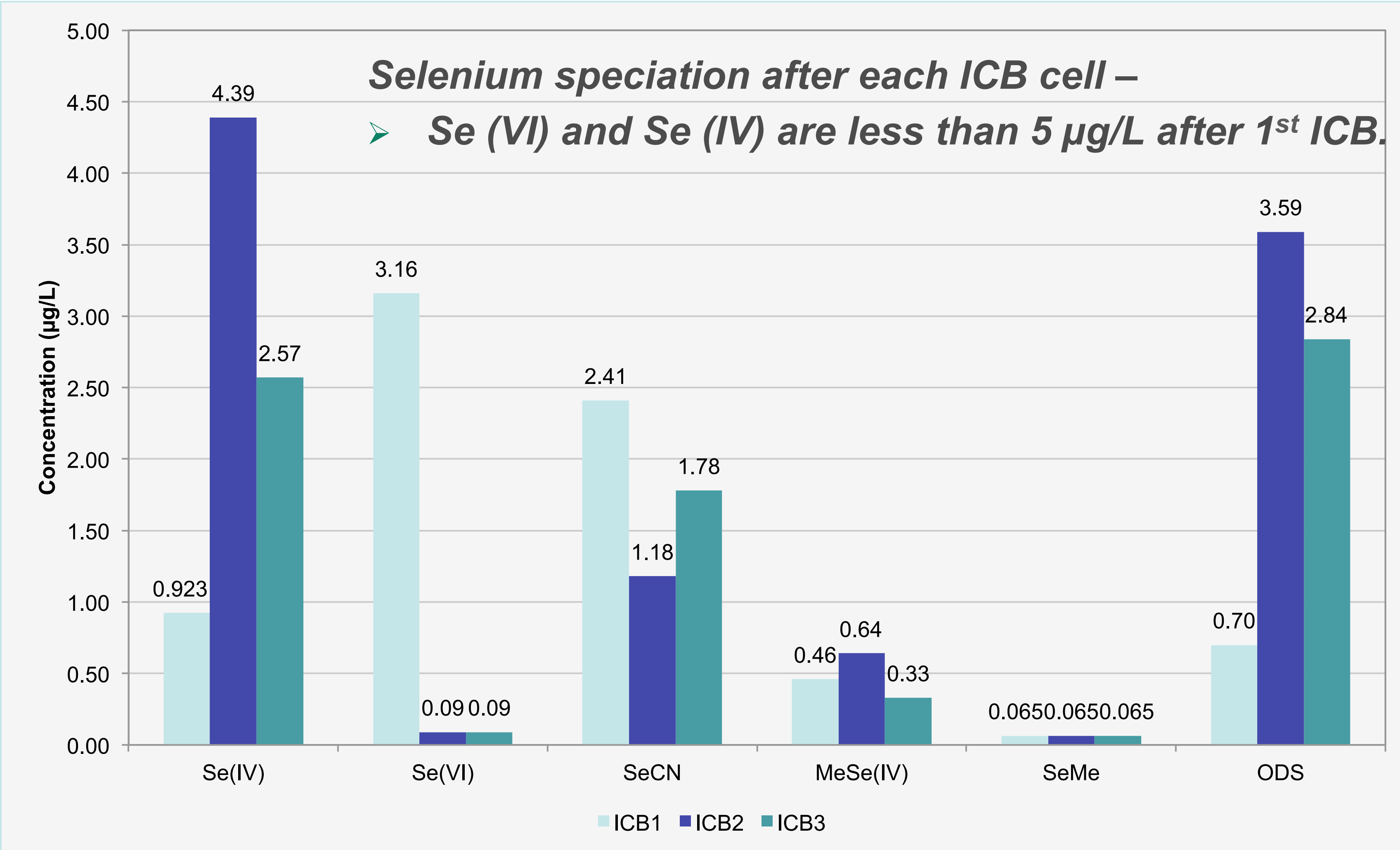
- Coal mine water
- Process Evaluation– RO, Bio, Se post-treatment (Coagulation/ flocculation/filtration)

Case Study 2: Total and Dissolved Se

- Complete nitrate removal achieved (165 mg/L as N)
- Influent Se= 175 - 250
  Effluent Se = 25
- Switch to brine did not raise effluent concentrations
- RO removal was >99%



Case Study 2: Selenium Speciation



Influent Selenium ~ 200 µg/L selenate

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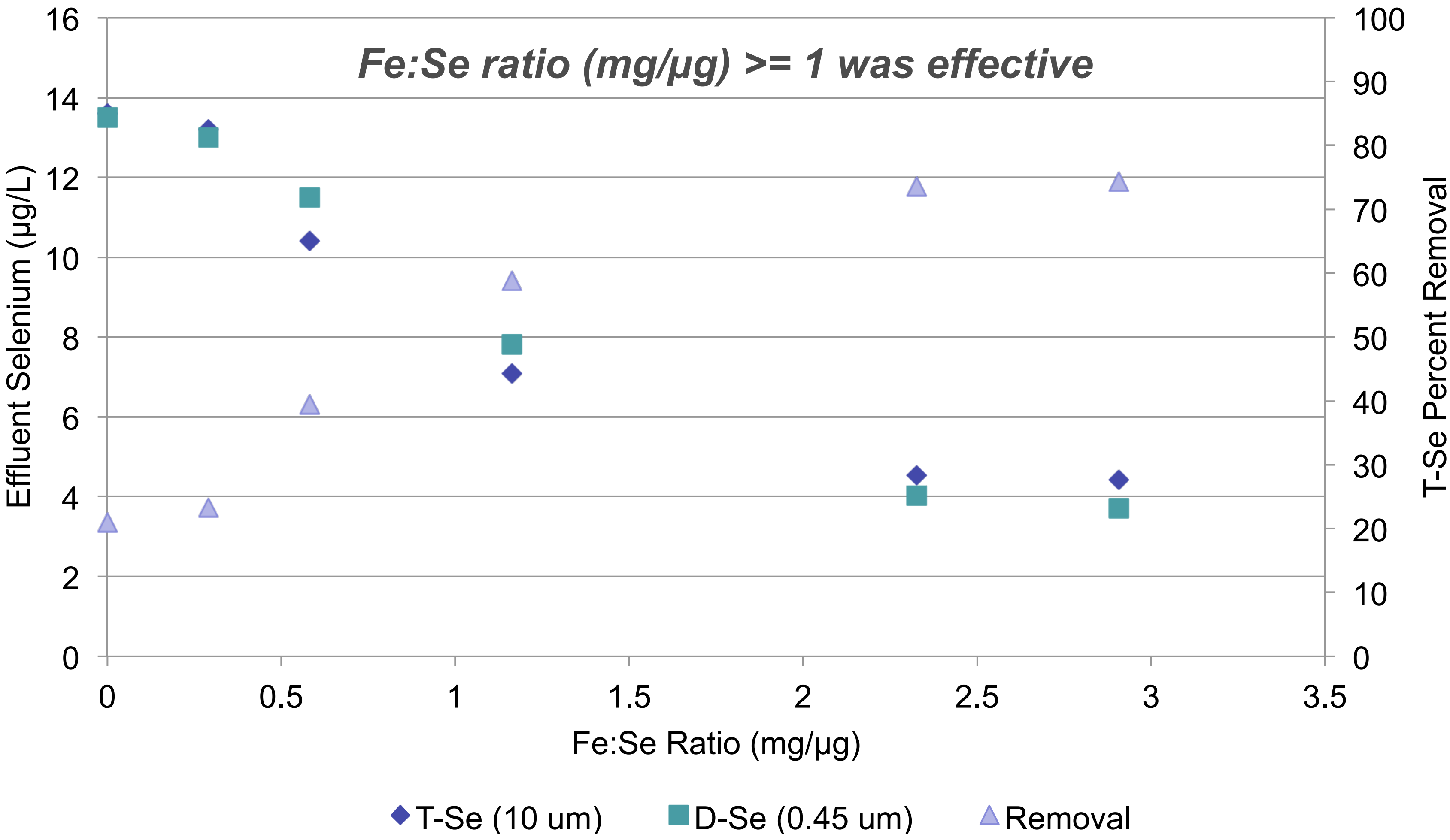
Case Study 2: Coagulation Testing



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Case Study 2: Conclusion

With elevated selenium (175 - 224 µg/L) and nitrate (165 mg/L as N):

- Bio achieved 23 µg/L
- RO + Bio + Se Post-Treatment achieved 5 µg/L

Case Study 3: Project Details

- Location - Sand and gravel pit in Grand Junction, Colorado
- Bench and pilot testing funded by the US Bureau of Reclamation

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Case Study 3: Passive Biological Treatment

- Downward flow vertical biochemical reactor (BCR)
- Solid phase media: 30% sawdust, 30% wood chips, 20% limestone, 10% hay, 10% cow manure
- Design flow rate of between 3 and 15 gpm
- Pilot operated for one year

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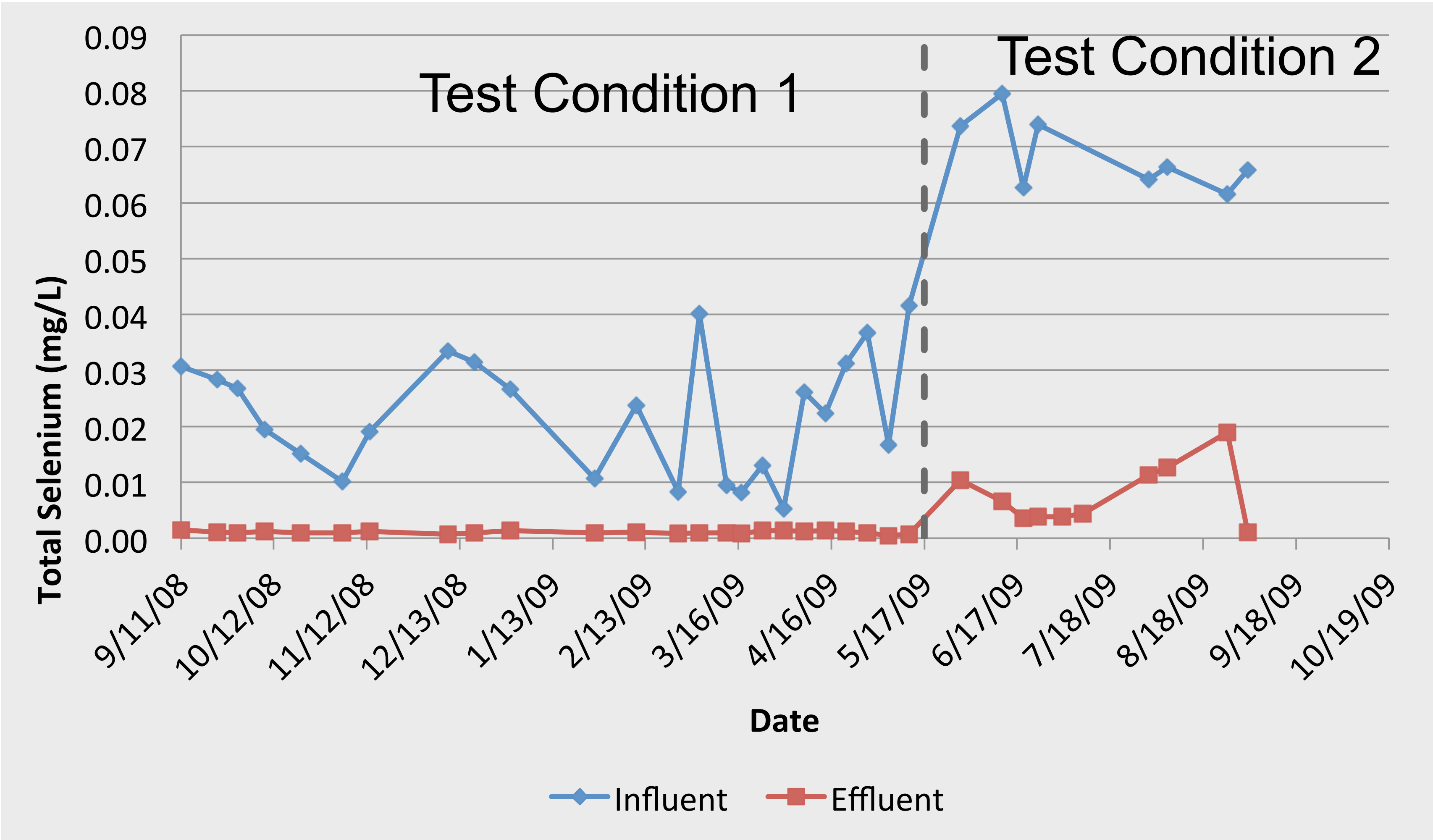
Case Study 3: Results



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Case Study 3: Results

Test Condition 1

Description	Influent Selenium, Total (ug/L)	Biological Effluent Selenium, Total (µg/L)	Biological Treatment, Percent Removal
Average	22.3	1.0	94%
Minimum	5.3	0.5	75%
Maximum	41.6	1.5	98%

Test Condition 2

Description	Influent Selenium, Total (ug/L)	Biological Effluent Selenium, Total (µg/L)	Biological Treatment, Percent Removal
Average	68.5	8.5	87%
Minimum	61.5	1.1	69%
Maximum	79.5	18.9	98%

Case Study 4

- Mine pit dewatering
- Design Build - 400 gpm demonstration plant
- Influent selenium – 30 µg/L
- Treatment goal of 4.6 µg/L
- Side by side biological pilot testing

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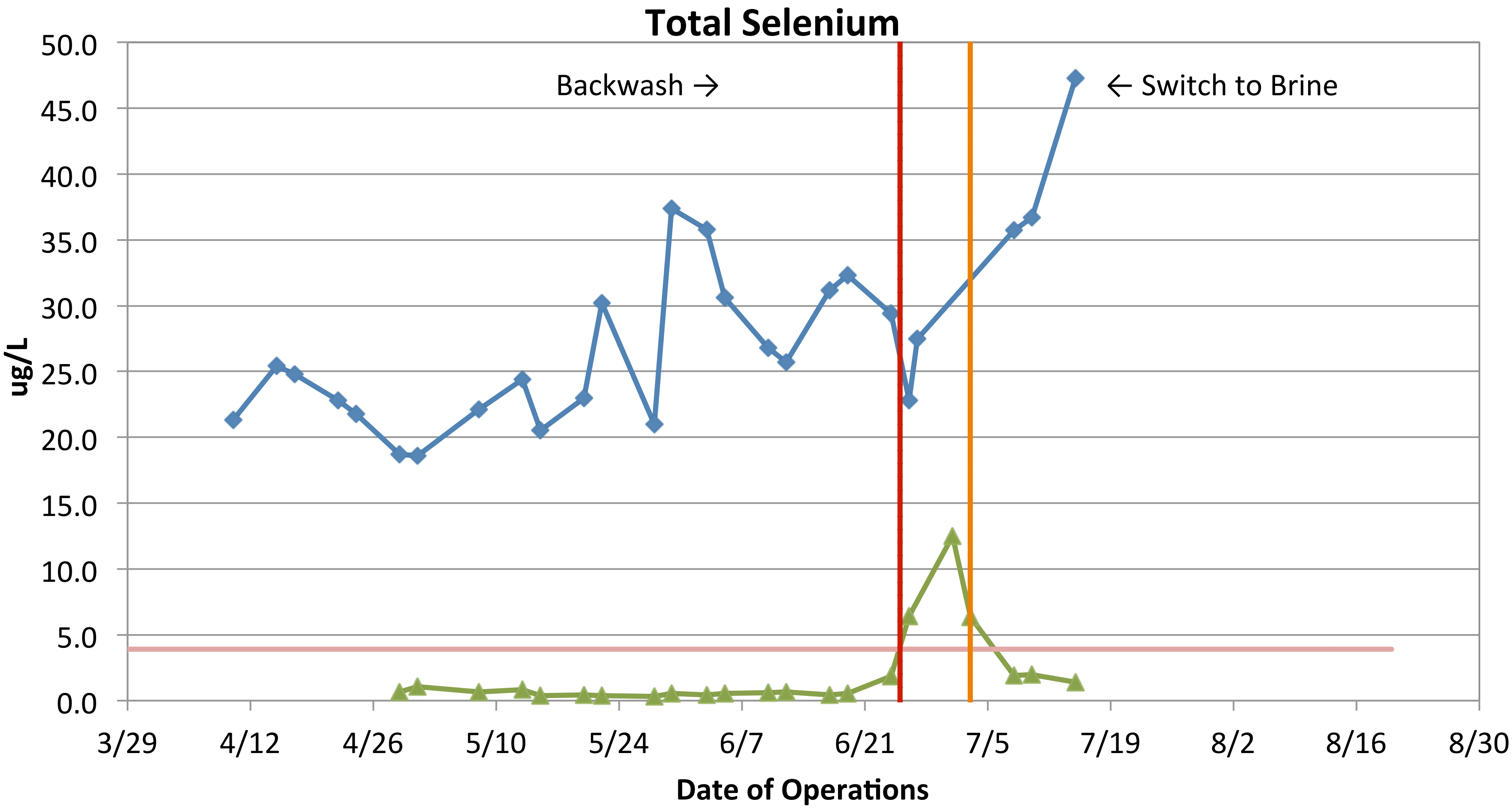
Pilot Selenium Results



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Overall Conclusions

- When Se < 50 µg/L, biological and <u>other technologies</u> can achieve 5 µg/L.
- When Se > 50 µg/L, achieving 5 is a challenge.
  - Bio alone may be insufficient
  - Additional unit processes may be necessary
    - Pre-treatment with RO
    - Selenium post-treatment
- New bio technologies are providing a more competitive market

Questions?

Potential Benefit of RO

Bio Only

Influent	Bio Effluent (90% Removal)
100 ug/L	10 ug/L

RO + Bio

Influent	RO Brine (99% Se rejection rate, 75% recovery rate)	Bio Effluent (95% removal)	Recombined flow (permeate + bio-treated brine)
100 ug/L	400 ug/L	20 ug/L	5 ug/L

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