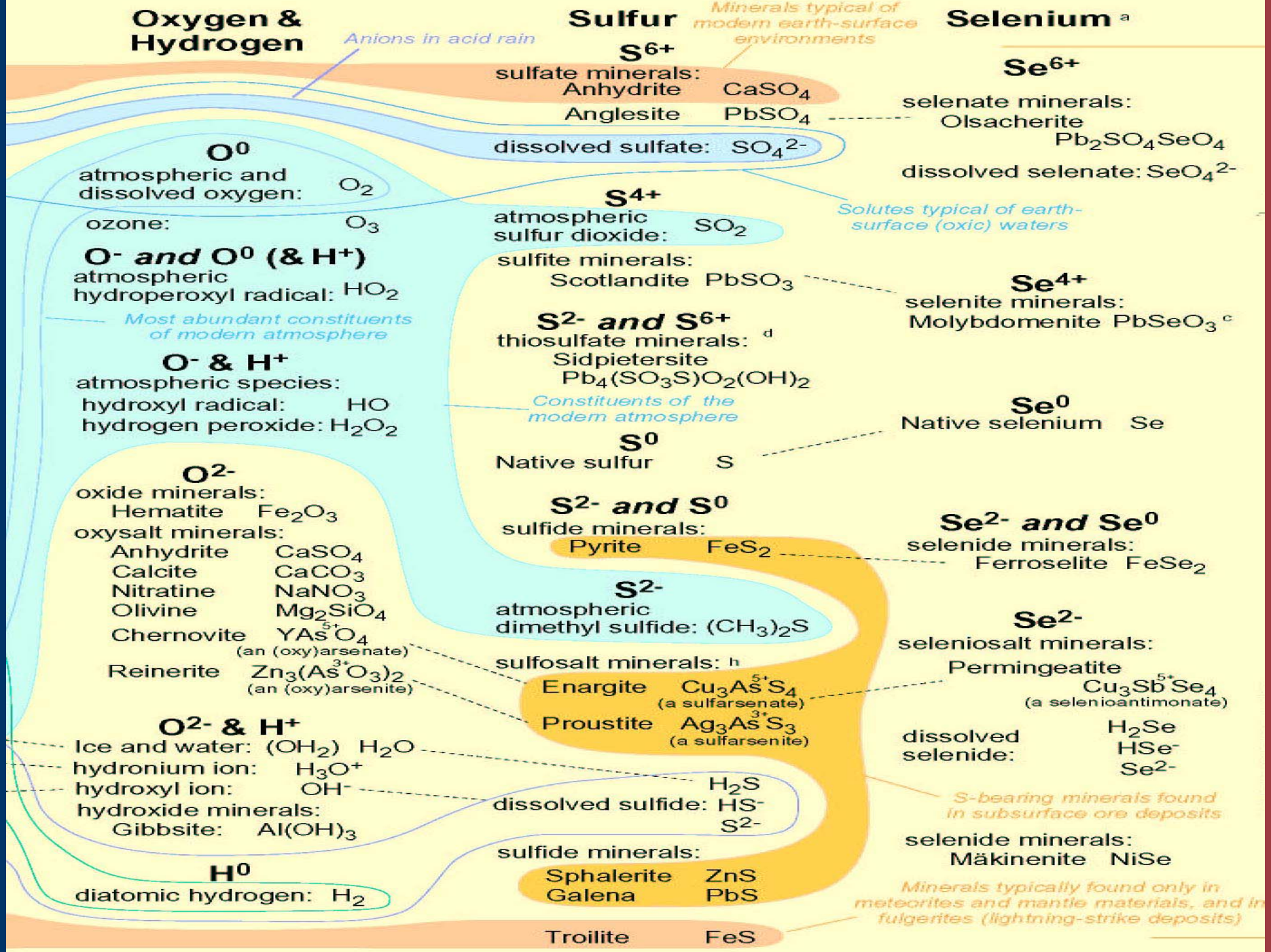
Utilization of High Sulfur Coal for Selenium Removal in Phosphate Mine Waters

prepared by
Sean C. Muller, P.G., **AquAeTer, Inc.**
C. David White, Ph.D., Chemrox Technologies
Harry Bonner, Western SynFuel

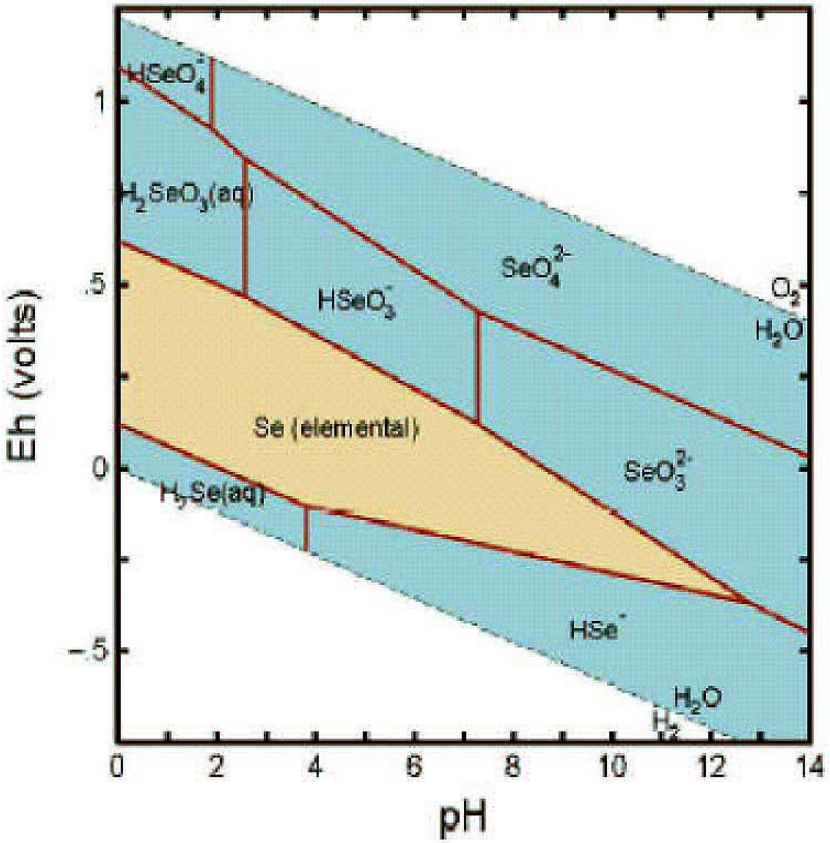
Selenium Species

- Selenide, Se (-II)
- Selenium, Colloidal Se (0)
- Selenite, Se (IV)
- Selenate, Se (VI)
- Diverse organic forms

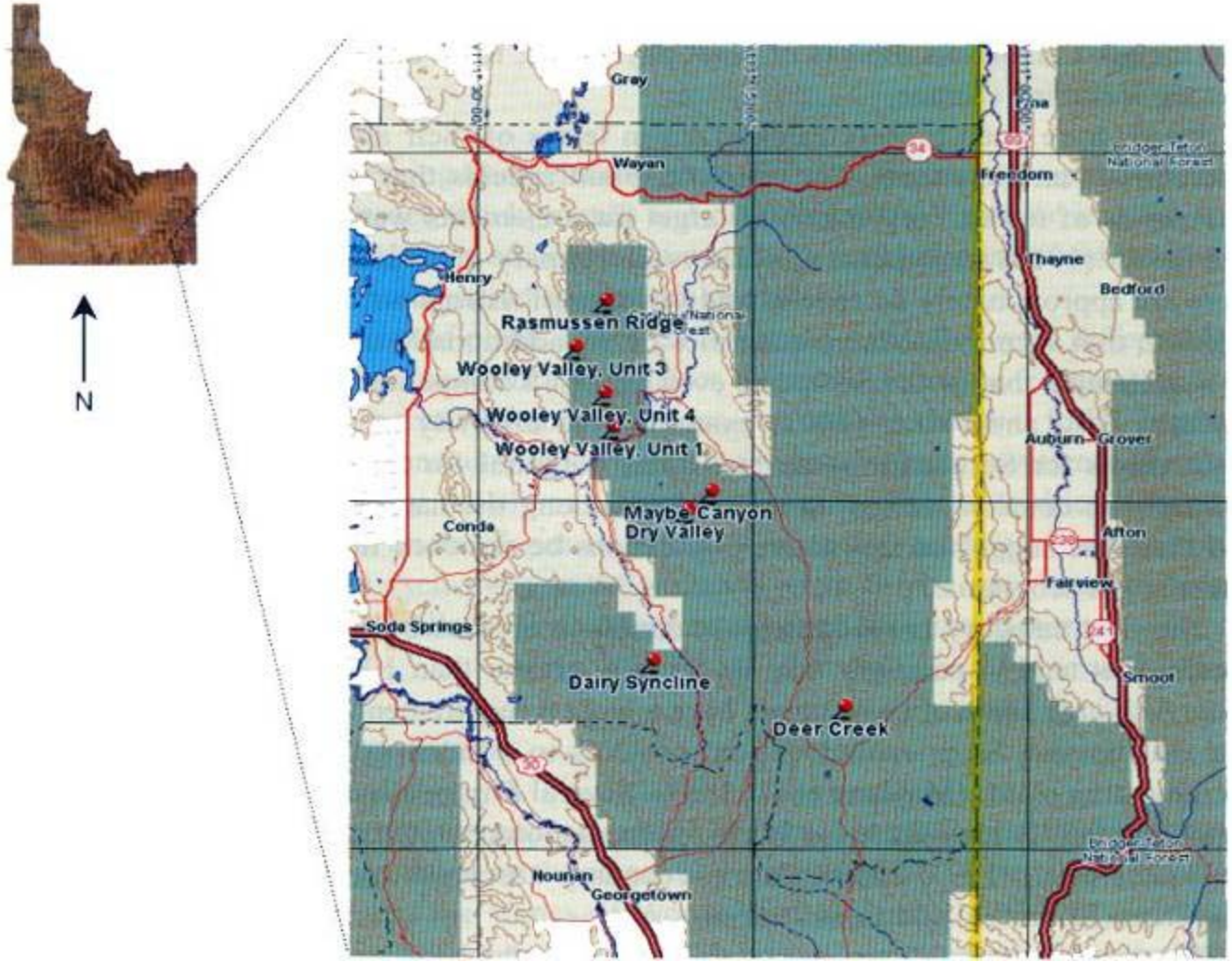
AquAeTer


Oxygen & Hydrogen
Anions in acid rain
Sulfur
Minerals typical of modern earth-surface environments
Selenium a
S6+
sulfate minerals:
Anhydrite CaSO4
Anglesite PbSO4
dissolved sulfate: SO4 2-
Se6+
selenate minerals:
Olsacherite Pb2SO4SeO4
dissolved selenate: SeO4 2-
Solutes typical of earth-surface (oxic) waters
O0
atmospheric and dissolved oxygen: O2
ozone: O3
S4+
atmospheric sulfur dioxide: SO2
sulfite minerals:
Scotlandite PbSO3
Se4+
selenite minerals:
Molybdomenite PbSeO3 c
O- and O0 (& H+)
atmospheric hydroperoxyl radical: HO2
Most abundant constituents of modern atmosphere
S2- and S6+
thiosulfate minerals: d
Sidpietersite Pb4(SO3S)O2(OH)2
O- & H+
atmospheric species:
hydroxyl radical: HO
hydrogen peroxide: H2O2
Constituents of the modern atmosphere
Se0
Native selenium Se
S0
Native sulfur S
O2-
oxide minerals:
Hematite Fe2O3
oxysalt minerals:
Anhydrite CaSO4
Calcite CaCO3
Nitratine NaNO3
Olivine Mg2SiO4
Chernovite YAs5+O4
(an (oxy)arsenate)
Reinerite Zn3(As3+O3)2
(an (oxy)arsenite)
S2- and S0
sulfide minerals:
Pyrite FeS2
Se2- and Se0
selenide minerals:
Ferroselite FeSe2
S2-
atmospheric dimethyl sulfide: (CH3)2S
sulfosalt minerals: h
Enargite Cu3As5+S4
(a sulfarsenate)
Proustite Ag3As3+S3
(a sulfarsenite)
Se2-
seleniosalt minerals:
Permingeatite Cu3Sb5+Se4
(a selenioantimonate)
dissolved selenide: H2Se HSe- Se2-
O2- & H+
Ice and water: (OH2) H2O
hydronium ion: H3O+
hydroxyl ion: OH-
hydroxide minerals:
Gibbsite: Al(OH)3
H2S
dissolved sulfide: HS- S2-
S-bearing minerals found in subsurface ore deposits
selenide minerals:
Mäkinenite NiSe
sulfide minerals:
Sphalerite ZnS
Galena PbS
H0
diatomic hydrogen: H2
Minerals typically found only in meteorites and mantle materials, and in fulgerites (lightning-strike deposits)
Troilite FeS

Selenium Stability Diagram



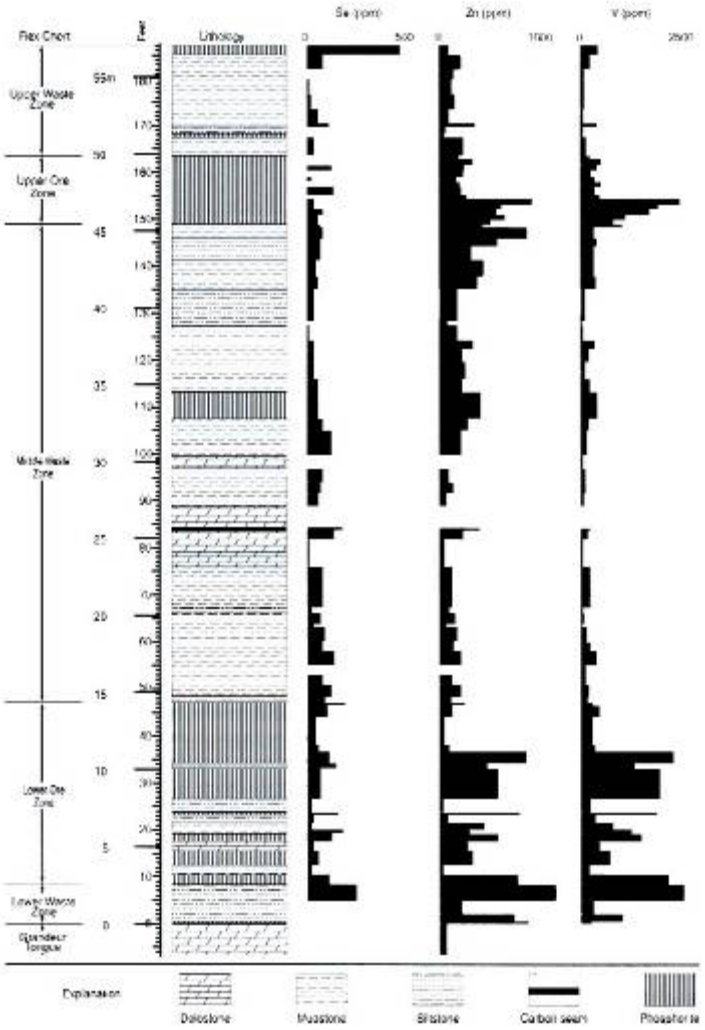
Selenium Occurrence with Phosphate Mining



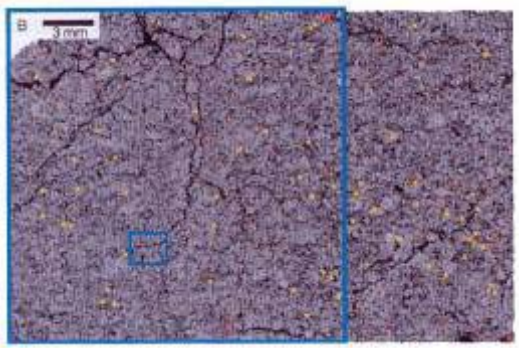
Selenium in Water and Vegetation Has Impacted Certain Grazing Livestock

AquAeTer

Sources for Selenium



- Unoxidized carbonaceous shales
- Select phosphate intervals
- Wasterock
- Surface waters
- Pitwaters



AquAeTer

Selenium Accumulators in SE Idaho

Xylorrhiza glabriuscula
(Woody Aster)

Grindelia squarrosa
(Curleycup Gumweed)

Medicago sativa (Alfalfa)

AquAeTer

Reclamation and Mine Abandonment Issues

- Alfalfa planting on wasterock
- Grazing of livestock
- Exposed pitwater
- Abundant natural selenium accumulators
- Exposed and oxidizing carbonaceous shales
- Controlling water runoff

AquAeTer

Options for the Mining Industry

- Complete backfill and burial of exposed bedrock
- Pitwater control or backfill
- Placement of thick cover over wasterock and tailings
- Control of surface waters
- Control of vegetative growth
- Phytoremediation
- Selenium treatment or removal
- Selenium stabilization

AquAeTer

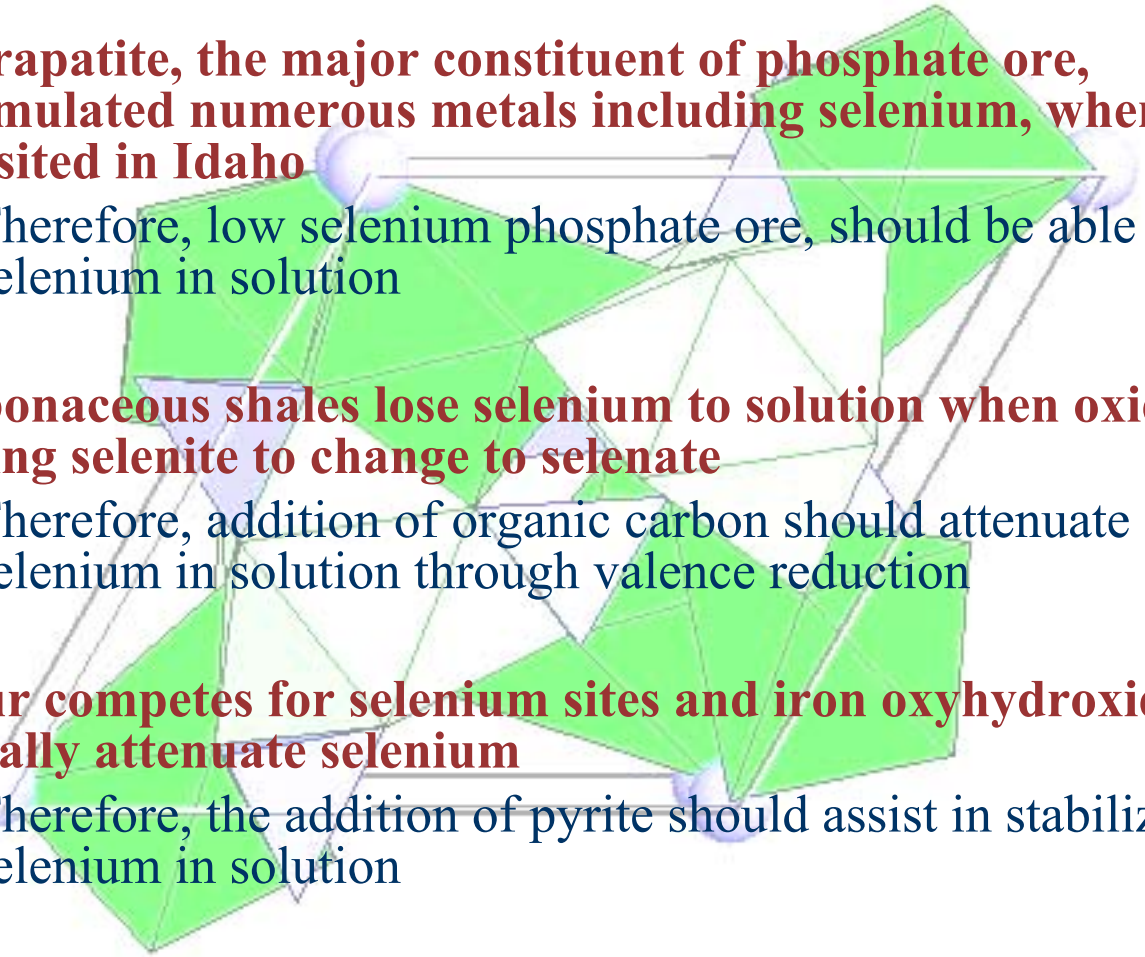
Selenium Stabilization Concepts

- Adsorption by carbon-rich bedrock
- Association with certain phosphate bedrock
- Competition with sulfate
- Iron oxyhydroxides partially adsorb selenium
- Selenite requires reducing conditions
- Concentration in humic wetlands

AquAeTer

Selenium in Pitwater Stabilization Assumptions

- **Fluorapatite, the major constituent of phosphate ore, accumulated numerous metals including selenium, when deposited in Idaho**
  - Therefore, low selenium phosphate ore, should be able to sorb selenium in solution
- **Carbonaceous shales lose selenium to solution when oxidized, causing selenite to change to selenate**
  - Therefore, addition of organic carbon should attenuate selenium in solution through valence reduction
- **Sulfur competes for selenium sites and iron oxyhydroxides partially attenuate selenium**
  - Therefore, the addition of pyrite should assist in stabilizing selenium in solution



AquAeTer

Rationale for Selection of High Sulfur Coal

- Phosphate Waters are Low in Sulfate
- Selenium and Sulfur Compete in Biota Uptake
- High Sulfur Coal is Unacceptable for Combustion
- Separation of Pyritic Fraction of Coal (Syncoal) leaves Zero Waste Product
- Syncoal Byproduct is Good Carbon Source
- Syncoal Byproduct has other Favorable Qualities
  - Hydromorphic
  - Light Weight
  - Lower Air Combustion Temperature

AquAeTer

Pitwater Stabilization Testing Methodology

- Obtain selenium enriched pitwater (re: influent)
- Test influent for a full suite of analytes and parameters
- Prepare a test column using low selenium phosphate
- Prepare a test column using high sulfur coal
- Conduct tests over a 3-week period for selenium plus pH, Eh and EC
- Test effluent for a full suite of analytes and parameters

AquAeTer

Table 1 - Profile II Analytical Results, Influent and Effluent Solutions, Media Attenuation Tests, Coal and Phosphate Media (Substrate)

	Solution Sample		
Analysis, mg/L	Site Solution, Influent	Coal Media, 168 hr. Effluent	Phosphate Media, 168 hr. Effluent
Alkalinity, $CaCO_3$	60	210	70
CO_3, $CaCO_3$	<1.0	<1.0	<1.0
HCO_3	73	250	85
Aluminum	<0.045	<0.045	<0.045
Antimony	<0.0025 SA	0.0035 SA	<0.0025
Arsenic	<0.0050	<0.0050	<0.0050
Barium	0.032	0.059	0.018
Beryllium	<0.0010	<0.0010	<0.0010
Bismuth	<0.10	<0.10	<0.10
Boron	<0.10	1.5	0.17
Cadmium	0.0017	<0.0010	<0.0010
Calcium	81	110	280
Chloride	1.3	2.3	5.7
Chromium	<0.0050	0.0055	<0.0050
Cobalt	<0.010	<0.010	<0.010
Copper	<0.050	<0.050	<0.050
Fluoride	0.91	0.23	3.1
Gallium	<0.10	<0.10	<0.10
Iron	<0.10	<0.010	<0.010
Lead	<0.010	<0.010	<0.050*
Lithium	<0.10	<0.10	<0.10
Magnesium	7.8	63	49
Manganese	0.015	0.20	0.087
Mercury	0.00010	<0.00010	<0.00010
Molybdenum	0.032	0.062	0.13
Nickel	0.018	<0.010	0.12
Nitrate as N	<1.0	<1.0	<1.0
Nitrite as N	<0.010	<0.010	<0.010
pH, stu	6.68	7.90	7.93
Phosphorus	<0.50	<0.50	<0.50
Potassium	0.73	3.5	15
Scandium	<0.10	<0.10	<0.10
Selenium	0.24	<0.0050	0.015
Silver	<0.0050	<0.0050	<0.0050
Sodium	2.8	18	29
Strontium	0.23	1.8	2.8
Sulfate	170	380	900
Thallium	<0.0010	<0.0010	0.0018
Tin	<0.10	<0.10	<0.10
Titanium	<0.10	<0.10	<0.10
Total Dissolved Solids	340	710	1,400
Vanadium	0.051	<0.045	0.034
Zinc	0.016	<0.010	<0.010
Cations, meq/L	4.82	11.6	19.7
Anions, meq/L	4.82	12.1	20.5
Difference, %	<1.0	2.3	2.0

SA = Reported value calculated using the method of standard additions.

* = Detection limit elevated due to matrix interference (run @ 5:1 dilution).

AquAeTer

Column Testing Results

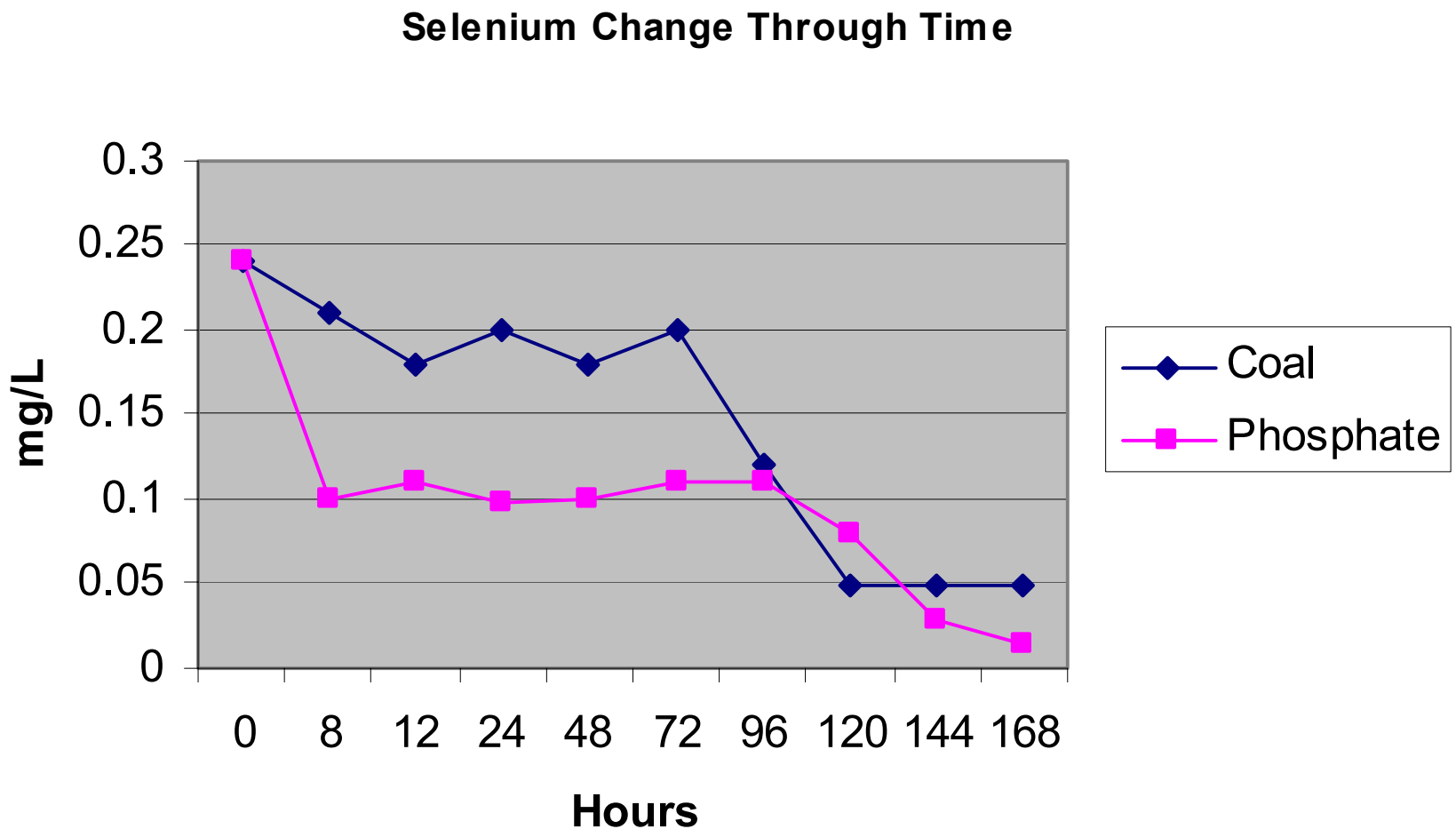
Table 2- Media (Substrate) Attenuation Test Data, Coal Substrate @ P_{80}10 Mesh, Phosphate Substrate @ As Received Size, 6.5 mL/min. Flow

Sample Time, hr	Cumulative Circulation, Liters	Coal Substrate, Effluent Analyses Se, mg/L	pH, s.u.	Eh, mV	EC mS/cm	Phosphate Substrate, Effluent Analyses Se, mg/L	pH, s.u.	Eh, mV	EC mS/cm
0	0 (Influent)	0.24	6.30	220	0.21	0.24	6.30	220	0.21
8	3.120	0.21	6.10	80	0.93	0.10	6.90	150	0.68
12	4.680	0.18	6.20	145	0.71	0.11	7.05	170	1.07
24	9.360	0.20	6.25	155	0.76	0.098	7.15	155	1.17
48	18.720	0.18	6.35	160	0.77	0.10	7.25	150	1.11
72	28.080	0.20	6.40	130	0.82	0.11	7.30	140	1.19
96	37.440	0.12	6.70	120	0.77	0.11	7.35	120	1.20
120	46.800	0.05*	6.75	130	0.80	0.08*	7.40	130	1.22
144	56.160	<0.005	6.90	140	0.79	0.028	7.55	130	1.29
168	65.520	<0.005	7.10	155	0.78	0.015	7.55	150	1.26

Note: The 120 hour effluent samples for both substrates were compromised and results are considered estimates rather than precise analytical results.

AquAeTer

Comparison of Phosphate and Coal Column Tests



AquAeTer

CLIENT:
LOCATION:
PROJECT/FILE:

optimizing environmental resources - water, air, earth

FIGURE 1
Comparison of Phosphate and Coal Column Tests

Additional Data Requirements for Pitwater Stabilization

- Location and mineralogical phase of the selenium on host material
- Potential for solubility or desorption of the selenium species
- Particle surface area considerations for solute reaction
- Volume of solute that can be effected per unit volume of solid
- Potential for agglomeration of the coal and phosphate

AquAeTer

Applicability to Soil or Tailings Substrate

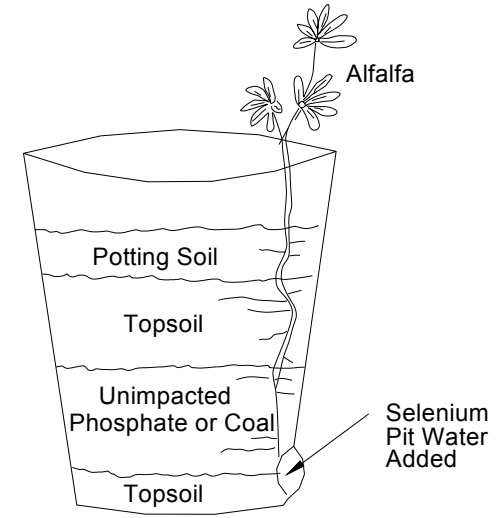
- **Testing has commenced to evaluate potential use of the high-sulfur coal and/or selenium deficient phosphate for soil amendments, selenium enriched soils, or bedrock.**

- **Goal is to determine plant uptake on selenium impacted material including mill tailings**
  - Ancillary goal is to evaluate the material for use as capping material or soil amendment
  - Another goal is to test loaded media (reject tails) for desorption under field conditions

AquAeTer

Procedure for Testing Unimpacted Media

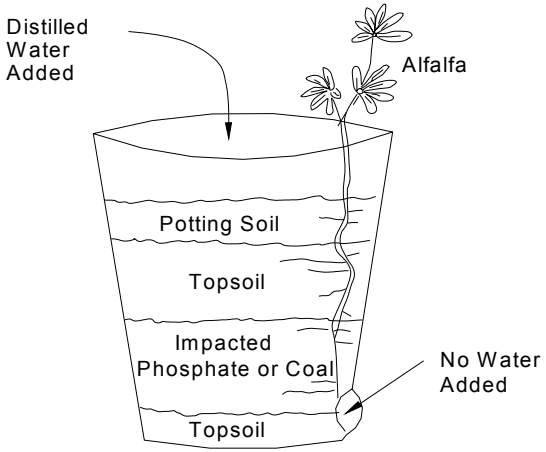
- Placement of unimpacted coal or phosphate (re: media) above selenium water zone
- Topping of unimpacted media with topsoil and then potting soil to encourage plant growth
- Watering below the root zone to mimic the capping of wet selenium-rich soils or tailings
- Planting and harvesting of alfalfa for selenium analysis through time



HEAD REJECT FROM COLUMN TEST

AquAeTer

Procedure for Testing Impacted (loaded) Media



TAILS REJECT FROM COLUMN TEST

- Placement of impacted coal or phosphate (re: media) on unimpacted topsoil
- Topping of impacted media with topsoil and then potting soil to encourage plant growth
- Watering above the root zone to simulate rainfall, run-on, and snow melt
- Planting and harvesting of alfalfa for selenium analysis through time

AquAeTer

Preliminary Growth Results

AquAeTer

Results of Selenium Testing on Vegetation

	Top	Root	n
Phosphate Tail Reject (Impacted)	17.5mm	16.4mm	13
Coal Tail Reject (Impacted)	9.0mm	12.8mm	6
Topsoil Control	8.3mm	8.0mm	4
Phosphate Head Reject (Unimpacted w/ Selenium Water)	21.0mm	13.5mm	2
Coal Head Reject (Unimpacted w/Selenium Water)	20.3mm	29.9mm	7
Topsoil w/ Selenium Water	10.3mm	8.8mm	4

AquAeTer

Planned Tailings Applications

- Placement of unimpacted coal or phosphate (re: media) atop tailings
- Topping of impacted media with topsoil and then potting soil to encourage plant growth
- Watering above the root zone to simulate rainfall, run-on, and snow melt
- Planting and harvesting of alfalfa for selenium analysis through time