Sulfate Reducing Bioreactor Engineering Principles

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Passive Treatment System Design Components

Biological Components

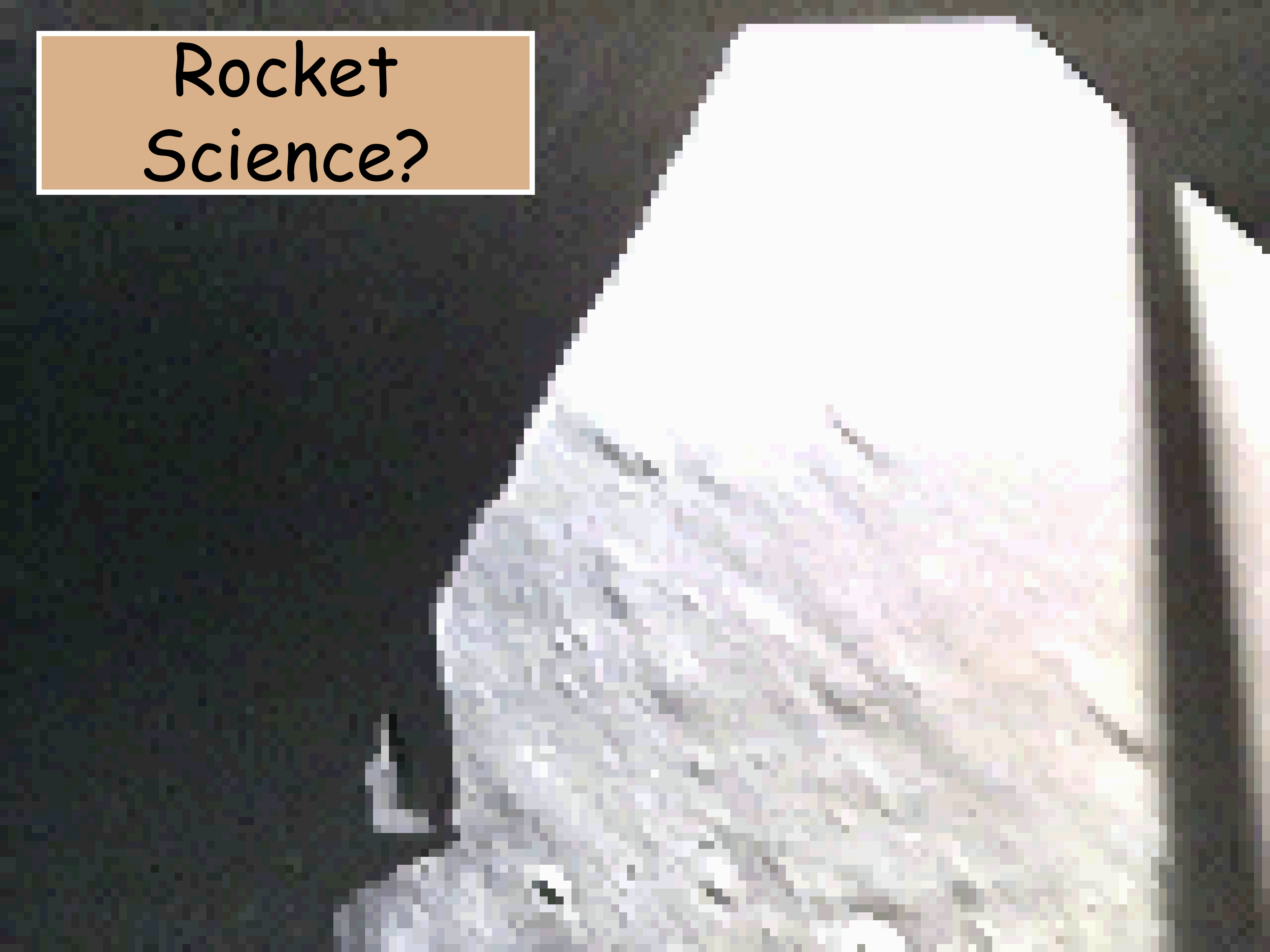
- Anaerobic SRBR's
- Aerobic Cells or Rock Filters
- Successive Alkalinity Producing Systems (SAPS)

Limestone Components

- Limestone Sand
- Anoxic Limestone Drains (ALD's)
- Alkaline Ponds
- Open Limestone Channels

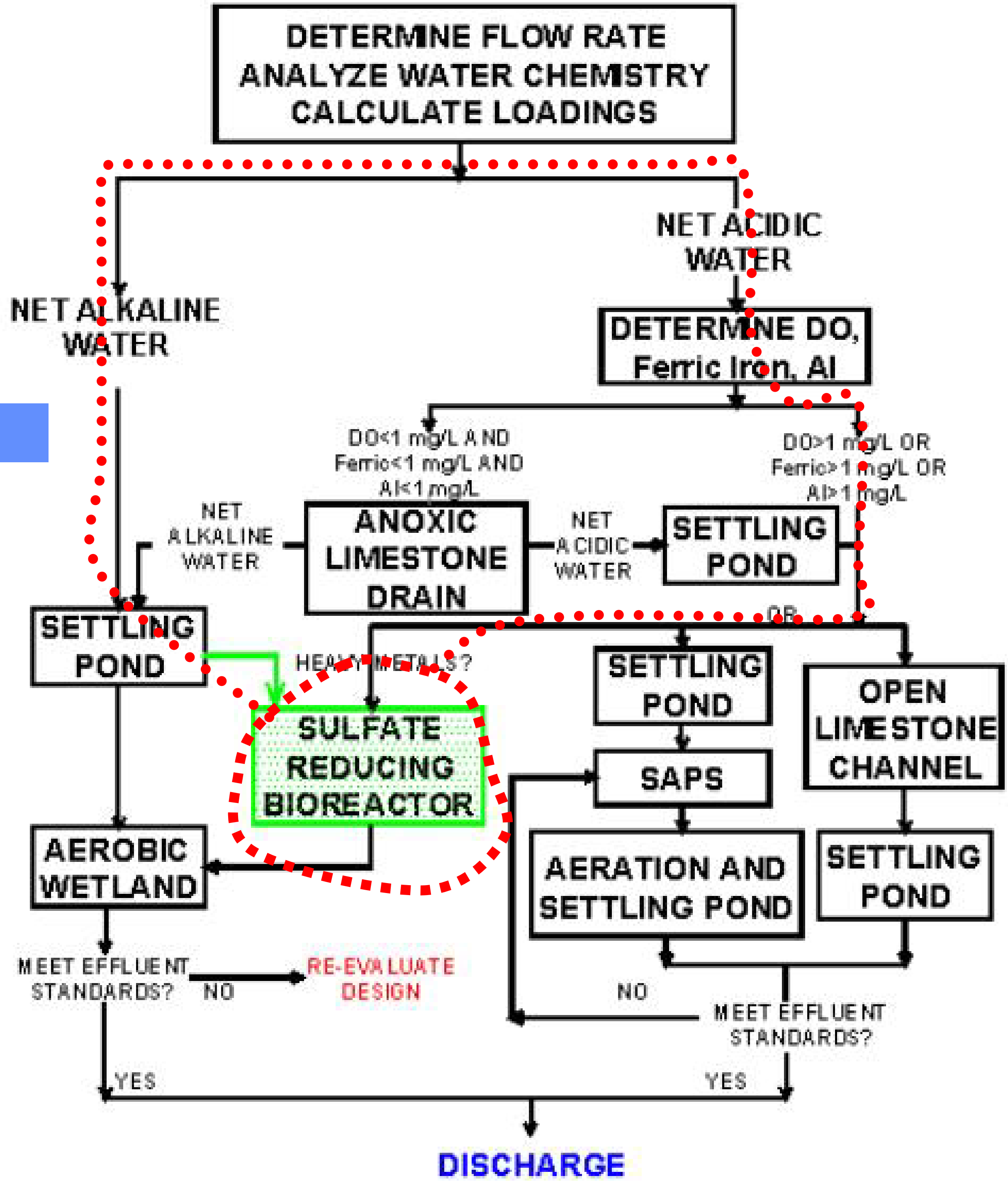
Settling Ponds & Flow Equalization Ponds, Fluid Conveyances (Pipes & Channels)

Rocket Science?

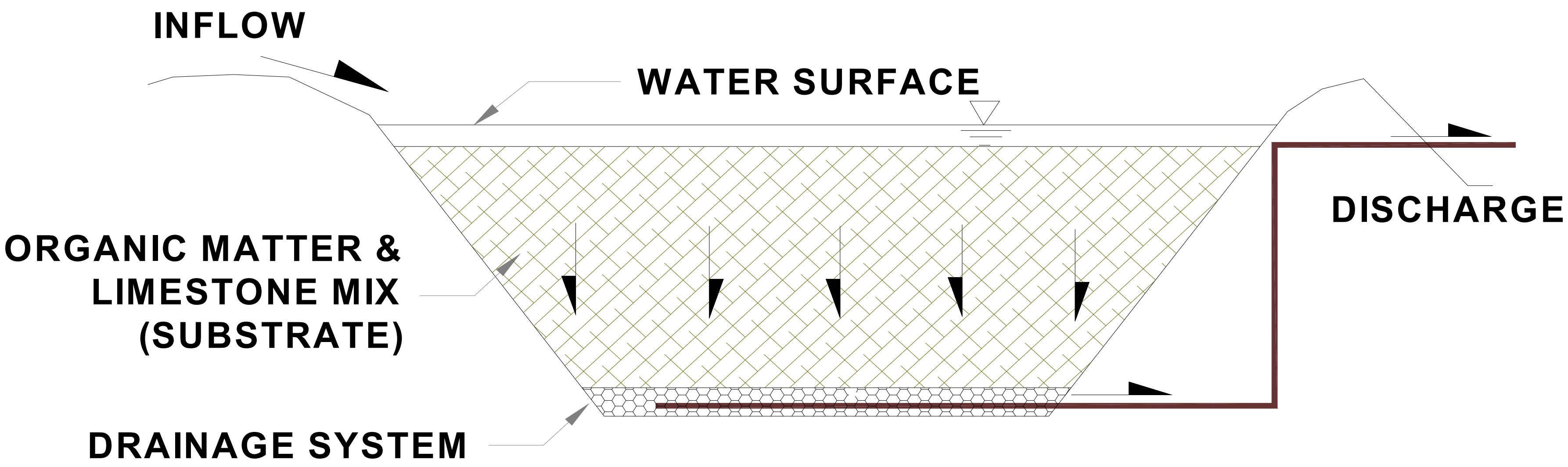


Design Flowchart

SRBR Design



Sulfate Reducing Bacteria Cell Schematic Cross Section



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Anaerobic SRBR's

AKA Vertical Flow Reactors

Aluminum and heavy metal removal, pH adjustment, alkalinity addition

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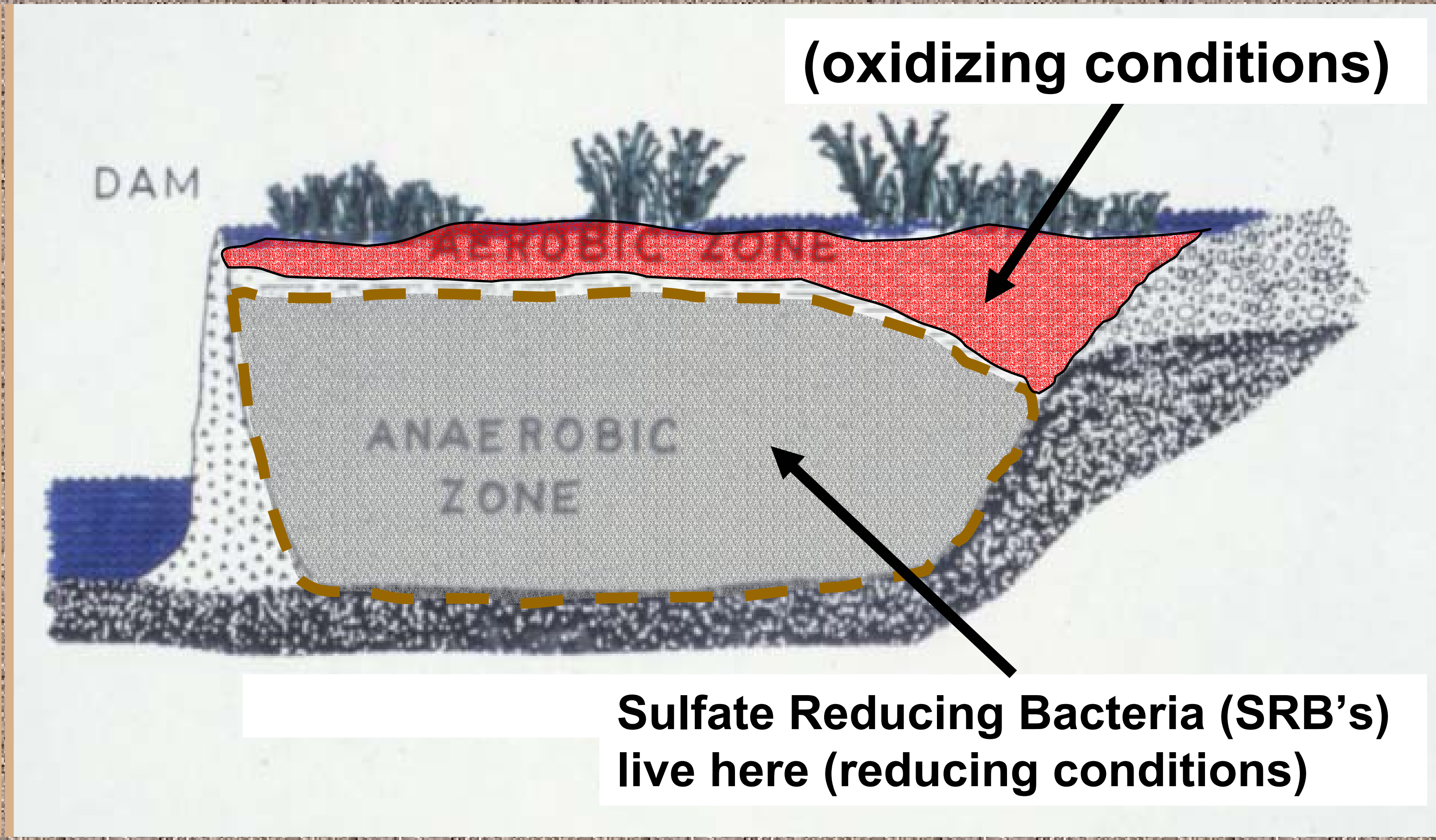
Typical Wetland Ecosystem



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Oxidation and Reduction Processes in Competition

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SRBR Chemistry 101

$$SO_4^{-2} + 2\ CH_2O \rightarrow H_2S + 2HCO_3^-$$

(Sulfate reduction and neutralization by bacteria)

$$Fe^{+2} + H_2S \rightarrow FeS_2$$

(Sulfide precipitation)

$$Fe^{+3} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+$$

(Iron hydrolysis)

$$H^+ + CaCO_3 \rightarrow Ca^{+2} + HCO_3^-$$

(Limestone dissolution)

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SRBR Chemistry 102
Aluminum Precipitation Reactions

$Al^{3+} + 3H_2O \Rightarrow Al(OH)_3$ (Gibbsite) $+ 3H^+$

(problematic due to sludge buildup)

$3Al^{3+} + K^+ + 6H_2O + 2SO_4^{2-} \Rightarrow KAl_3(OH)_6(SO_4)_2$ (Alunite) $+ 6H^+$

$2Al^{3+} + 12H_2O + 3Ca^{2+} \Rightarrow Ca_3Al_2H_{12}O_{12}$ (Katoite) $+ 12H^+$

$2Al^{3+} + H_2O + 2H_4SiO_4(aq) \Rightarrow Al_2Si_2O_5(OH)_4$ (Kaolinite) $+ 6H^+$

There are at least another 123 possible reactions.

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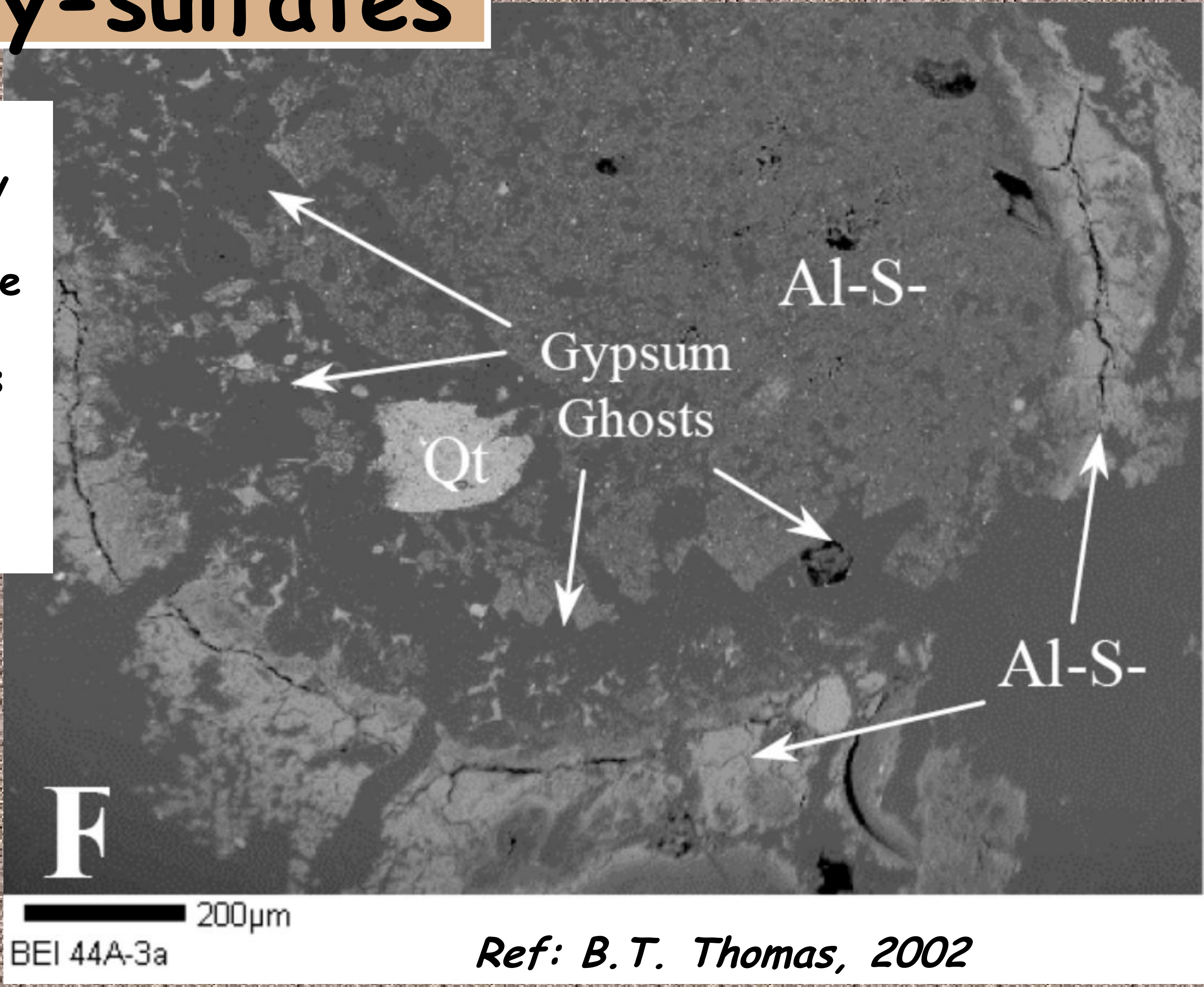
Aluminum Hydroxy-sulfates

Limestone ghost outlined and partially filled by aluminum hydroxy-sulfate. The former presence of blocky gypsum grains is preserved by the later aluminum hydroxy-sulfate.



Ref: B.T. Thomas, 2002

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SRBR Chemistry 103
Selenium Removal Reactions

Reduction / Precipitation

Se^{6+} and Fe^{2+} => Se^{4+} and Fe^{3+} (or other reductant)

$3Se^{4+}$ + $2Fe(OH)_2$ + $8H_20$ + $1/2O_2$ => $Fe_2(SeO_3)_3$• $4H_20$ + $12H^+$
(amorphous ferric selenite)

Se^{6+} + bacteria (*P. stutzeri*) + nutrients => Se (elemental selenium) This process may be restricted to Se concentrations greater than about 10 ppb due to bacterial "starvation".

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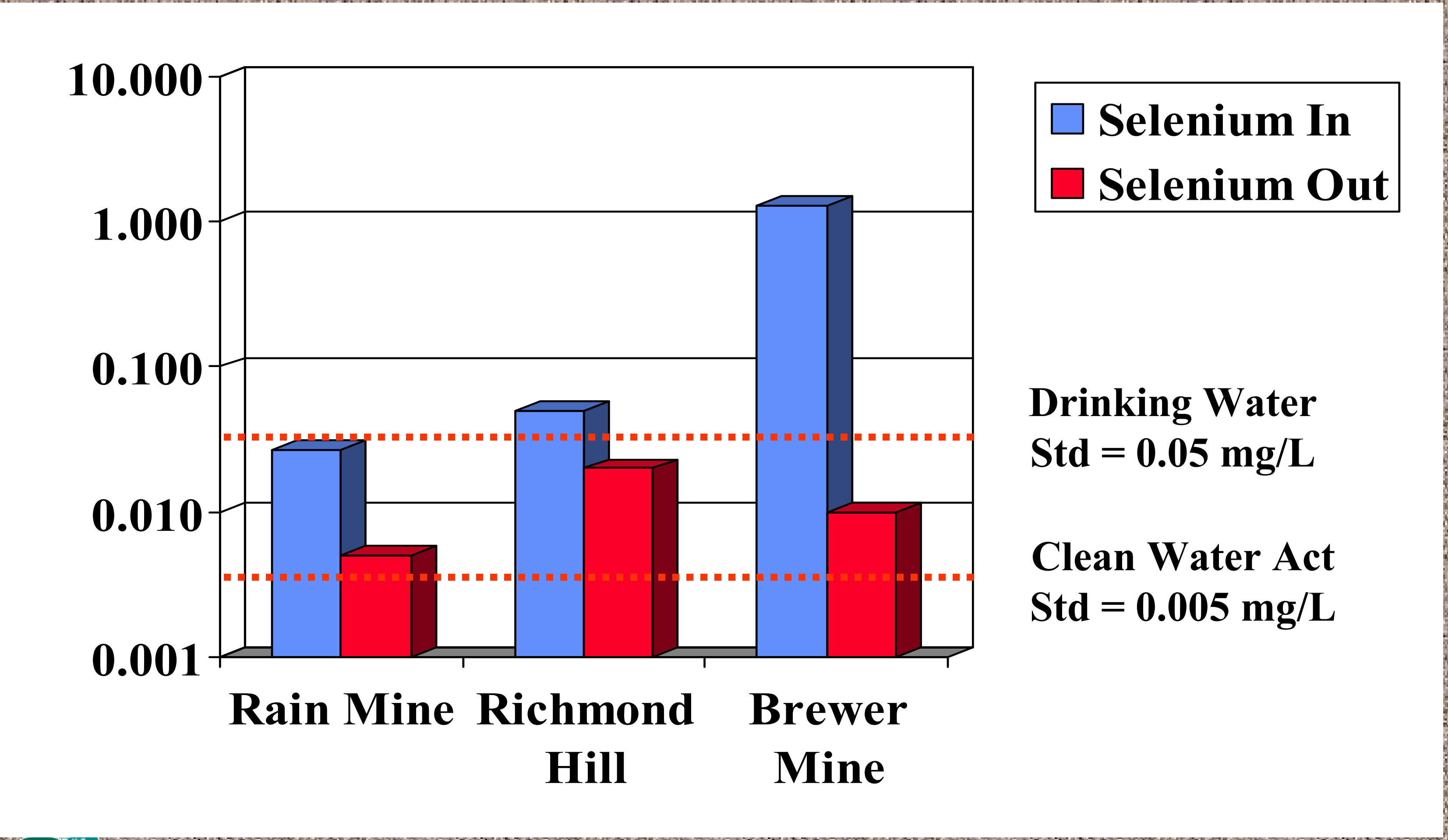
Secondary Selenium Passive Treatment



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SRBR Chemistry 104
Arsenic Removal

Removal as a sulfide either as

ORPIMENT (As_2S_3),

or *REALGAR* (AsS)

or *ARSENOPYRITE* (FeAsS)

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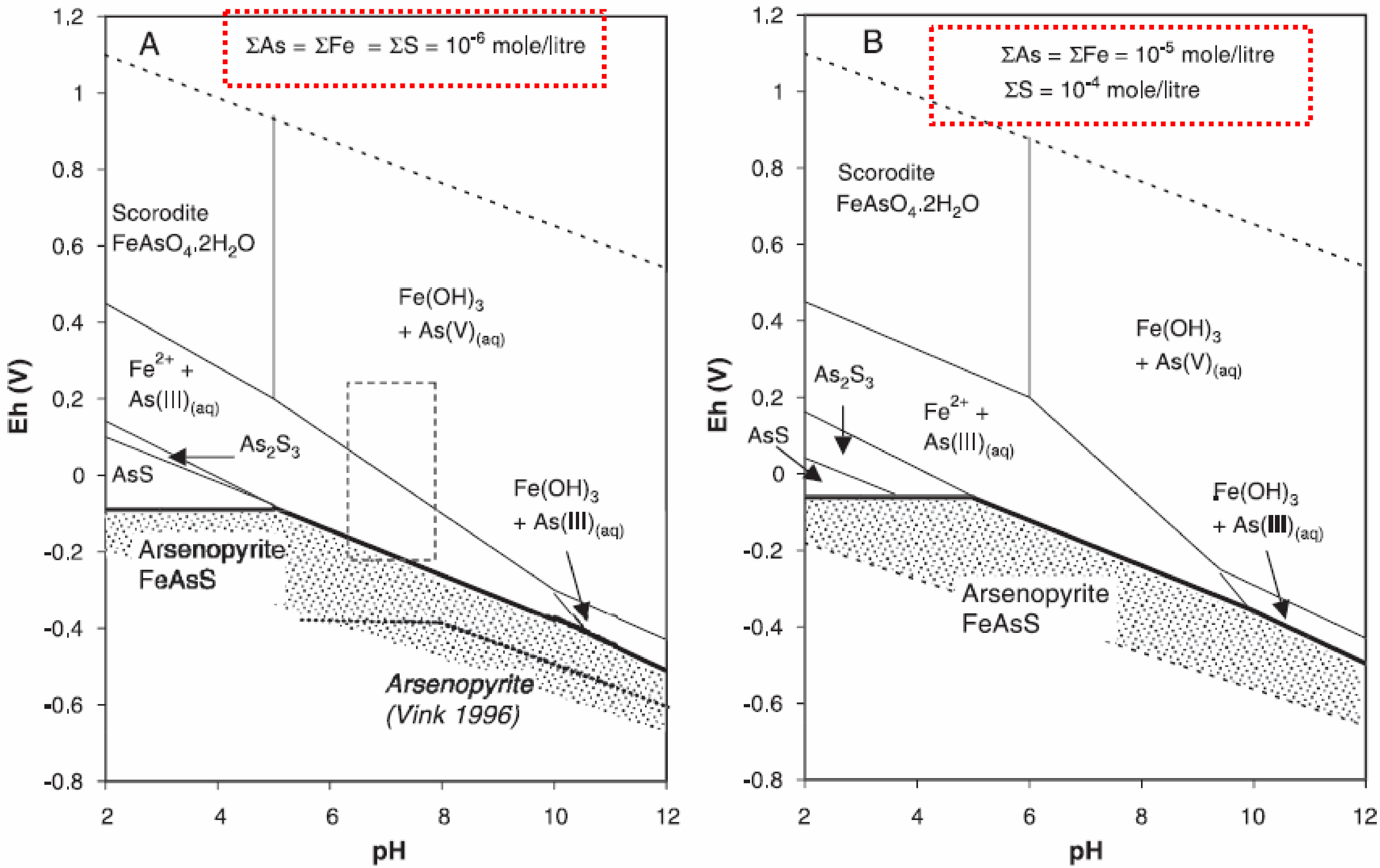
pH-Eh Diagrams Arsenic



(A) Diagram calculated for dissolved As, Fe, and S of 10^{-6} mol/l.
(B) Diagram calculated for dissolved As and Fe of 10^{-5} mol/l and S of 10^{-4} mol/l.

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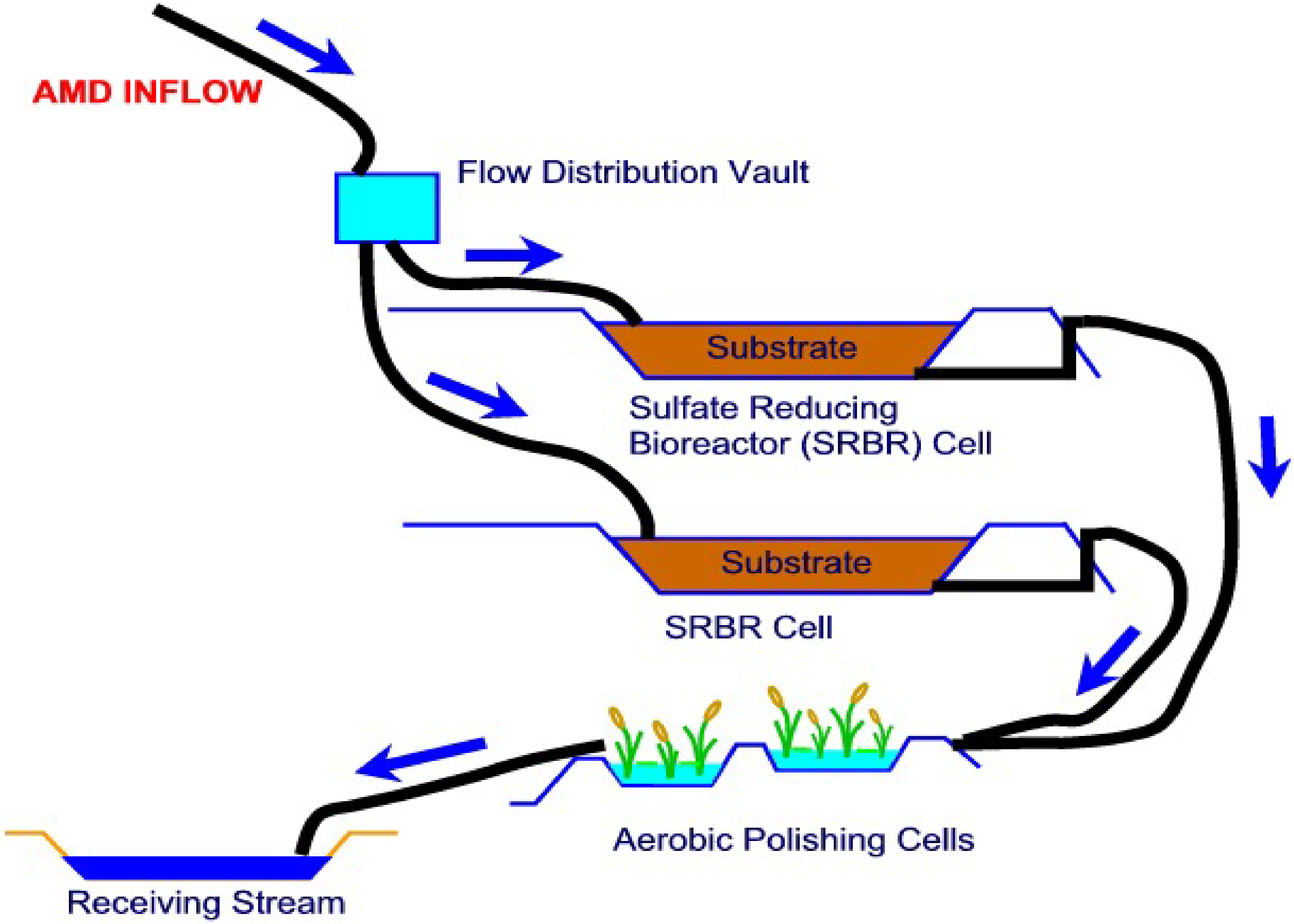

Typical SRBR System Layout

Passive Treatment System Containment Structures

- Natural soil-lined excavation
- Geomembrane-lined excavation
- Structural concrete (OK for pilot systems)
- Pre-fabricated metal/fiberglass tanks (OK for pilot systems)
- Other (rock excavations -underground?)

SRBR Design Parameters

NO COOKBOOK (YET)

- ARD Geochemistry (cell sequencing & cell type)
- Metal Loading = (concentration X flow rate)
- Surface Area is a function of loading
- Cell Depth is a function of loading

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Metal Loading

Metal Loading = (concentration X flow rate)

20 mg Fe/Liter x **8 gal/min** x 3.785 L/gal x 1 gram/1000 mg x 1,440 min/day =

872 grams Fe per day = 15.6 moles/day

1 mole of Fe weighs 55.85 grams
one mole of sulfate (96 grams) is consumed for every mole of iron

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- **Darcy's Law** is satisfied, slight ponding on the surface of SRBR cells (to discourage emergent plants and distribute flow evenly)
- **Area Loading Factor/Flux** may vary with pH or mineral acidity; USBM recommended 50 grams acidity/day/m^2 as a starting point ***(may not be conservative enough)***
- Rule of Thumb: **Precipitated Metal Mass Loading** - 0.3 moles of metal per cubic meter of cell volume per day (function of substrate "roughage" characteristics)
- **Sulfate Reducing Stoichiometry** - carbon/organic and alkalinity content of substrate mass are most likely limiting factors on substrate longevity

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Design Methods I – SRBR Cells

- **Precipitated Metal Volumetric Loading** - filling of substrate void spaces with precipitates (not limiting)
- **Self-Sustaining Capability** - dying plants replenish substrate to provide void spaces and more organic material
- **Water Balance** - evapotranspiration effects
- **Surface and Ground Water Hydrology** – protect system from the design storm and consider local ground water conditions

Design Methods II – SRBR Cells

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DARCY'S LAW
$Q = k \times i \times A$

Where:

Q is flow, cubic centimeters/second
k is permeability of material,
centimeters per second
i is the hydraulic gradient, unitless, but it is also the pressure loss, dH, over the depth of the substrate material, L;

$$\text{i.e.,} = \frac{dH\ (cm)}{L\ (cm)} = i$$

A is the cross sectional area of the SRBR perpendicular to the flow path

FLUX = Q/A = FLOW/AREA (velocity)

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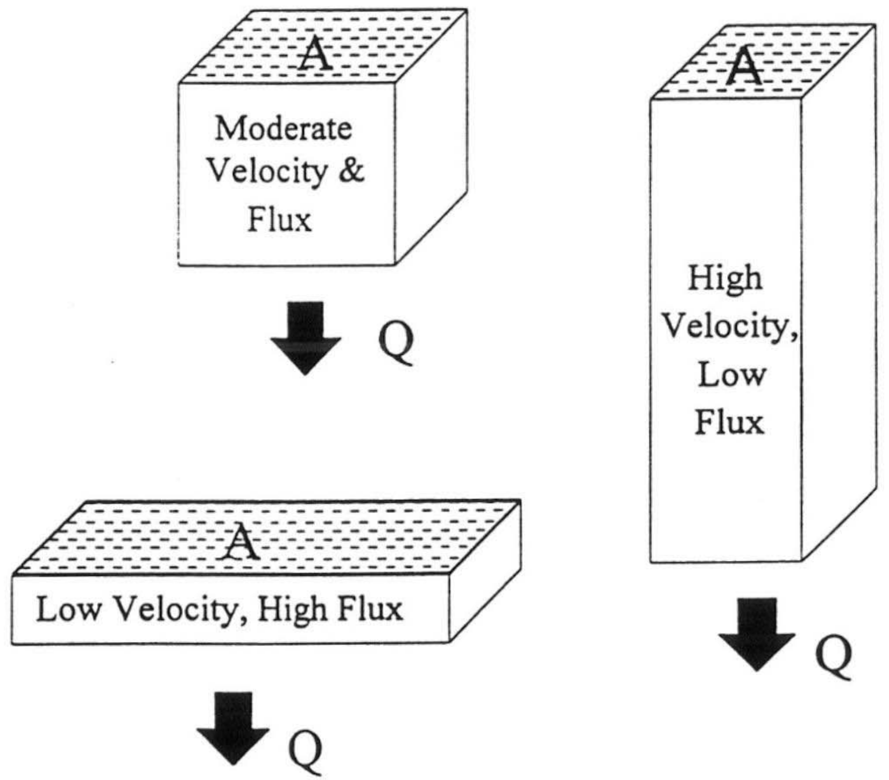
Area Loading Factor/ Flux What does it mean?

$$\frac{1}{\text{DARCY FLUX}} = \frac{\text{Area}}{\text{Flow}} \approx \text{0.25 to 500 sq m per Liter/min}$$

Area Loading Factor

The higher the acidity, the higher the flux value/area loading factor



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SRBR Cell Design Parameters I

- 0.3 moles of sulfate reduction per cubic meter per day (volumetric load)
- Organic Substrate that's permeable
- Organic Substrate with alk. source
- 10 to over 2000 ft^2/gpm (function of AMD mineral acidity)**

** *The better the water, the smaller the footprint*

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Substrate Selection Chemical Characteristics

- Net Alkaline (this can be added limestone)
- SRBR Anaerobic Microbe Suite Source
- Low in Nitrogen
- Sulfate Reduction Potential is greater than the Anaerobic Fermentation Potential
- Check Methanogenesis Potential

$$2\ CH_2O \dashrightarrow CH_4 + CO_2$$

- Electrical conductivity of substrate is roughly equal to the conductivity of AMD
- (New) measurement of Ethanol Soluble and Non-Soluble fractions targeting Cellulose/Cellobiose
- Variety of organic types to assist in startup but sustain long-term performance

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Organic Substrate Degradation

- Wood chips
- Sawdust
- Rice hulls
- Yard waste
- Mushroom compost
- Animal manure
- Hay and straw (spoiled)
- Nut shells
- Cardboard
- Soy bean hulls
- Waste alcohols including antifreeze
- Waste dairy products
- Sugar cane processing residue (Bagasse)
- Rice straw
- Cotton waste

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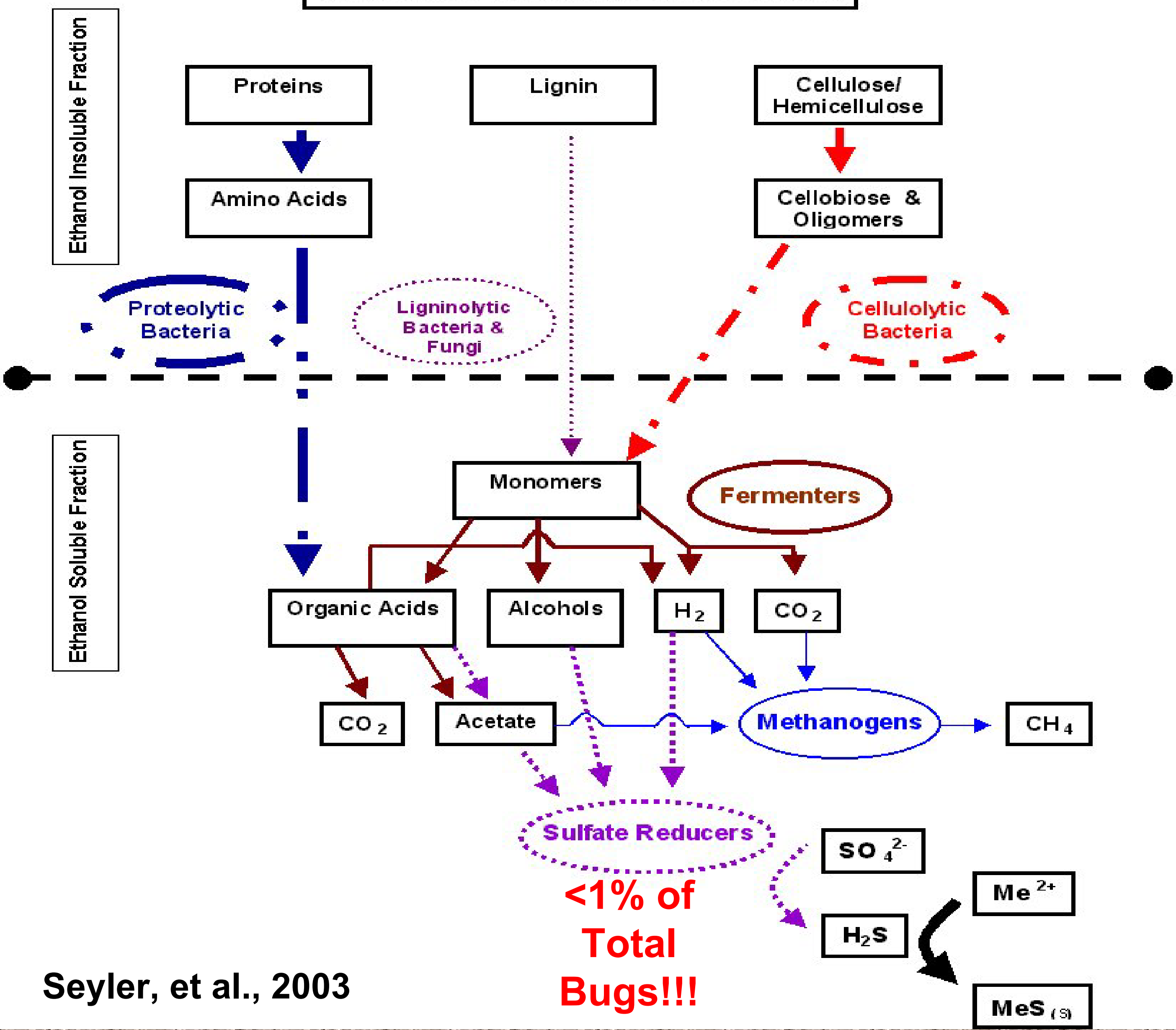
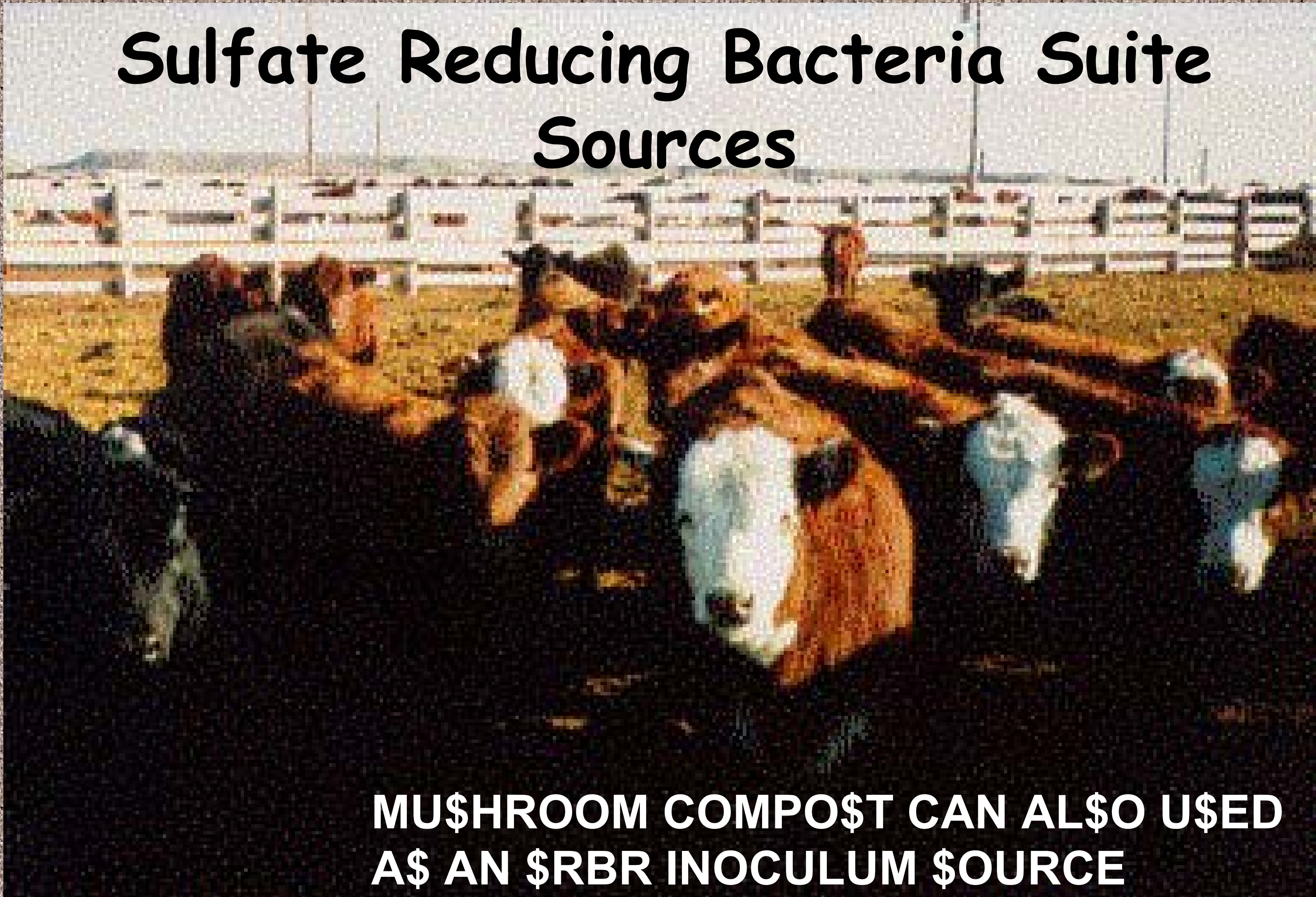
Conceptual Microbial Process Model



<1% of Total Bugs!!!

Seyler, et al., 2003

Sulfate Reducing Bacteria Suite Sources



MU$HROOM COMPO$T CAN AL$O U$ED A$ AN $RBR INOCULUM $OURCE

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Inorganic Material Sources

- Limestone
- Dolomitic Limestone?
- Cement Kiln Dust or Clinker
- Zero Valent Iron (ZVI)
- Steel Slag
- Other alkalinity generating wastes
- Inert drainage rock

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Substrate Physical Parameters

- Saturated Hydraulic Conductivity (permeability) – tough to measure with bacterial activity
- Material Classification (size distribution & carbon content)
- Moisture-density/compaction relationships (can you drive equipment on it?)
- Porosity/void ratio (needed to estimate retention times)
- Specific gravity of solids (est. mass depletion rates)
- "Shrinkage" factors (what happens when two dissimilar solids are mixed?)
- Bulk Density of mix (how much volume and/or tonnage is needed to build the cell?)

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Passive Treatment
Staged Design Phases

- Lab (proof of principle) tests
- Bench tests
- Pilot tests
- Limited full scale (modules)
- Full scale implementation

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Passive Treatment
Lab - Proof of Principle Tests

Buckeye Landfill, OH
POP Test Bottles

Brewer Gold Mine, SC
POP Test Bottles

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Passive Treatment Bench Scale Tests

Weekly sampling schedule is typical

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Bench SRB Biopsy

Bench Test Biopsy

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SRBR Pilot Scale Cells


Wyoming


Missouri

Peru


Pennsylvania

Operation and Maintenance Considerations I

Stresses On Organic Substrate:

- Precipitation of metals in void spaces *(this is somewhat counter-balanced by substrate dissolution)*
- Consumption of organic matter/carbon
- Consumption of alkalinity (especially with aluminum in AMD)
- Loss of permeability from compaction, settlement or humification

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Operation and Maintenance Considerations II

System Stresses:

- Sub-freezing conditions
- Precipitate plugging valves and pipes
- Burrowing animals
- Storm event damage and drought (bypass extraordinary high flows and mix with net alkaline SRBR effluent)

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Operation and Maintenance Considerations III

How do you measure SRBR performance?

- pH (if low, it had better go up and if neutral, it shouldn't change)
- Conductivity (minor increase expected after break-in)
- Calcium ***in*** vs Calcium ***out*** (limestone depletion)
- Sulfate ***in*** vs Sulfate ***out*** (estimate organic depletion)
- Oxidation Reduction Potential (less than -100 millivolts in effluent indicative of reducing conditions)
- Manganese unchanged
- 99%$^{+}$ removal of all metals
- Alkalinity increase to about 300 mg/L
- After break in period, if Mn increases or effluent metals are greater than influent metals, SRBR is likely overloaded.

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Major Overhaul & Maintenance Considerations in Design

- Removal of existing substrate materials Removal of some aspects of cell plumbing/water distribution system
- Protection of liners
- Substrate processing for metal removal?
- New substrate purchase & installation
- Replanting vegetation (aerobic polishing)
- Temporary treatment of effluent during overhaul (parallel systems or holding pond)

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Why Don't SRBR/Passive Systems Always Work As Designed?

- No design "Just build a swamp here, fill that pond over there with manure and call it good."
- Poor design Undersized for load, applying wrong geochemical approach, phased design lacking, complex geochemistry, startup and operational procedures.
- Not enough maintenance (<u>low</u> maintenance does not mean "NO" maintenance).
- Last minute changes to construction specs can affect system performance - experience helps.

SRBR Design Parameters

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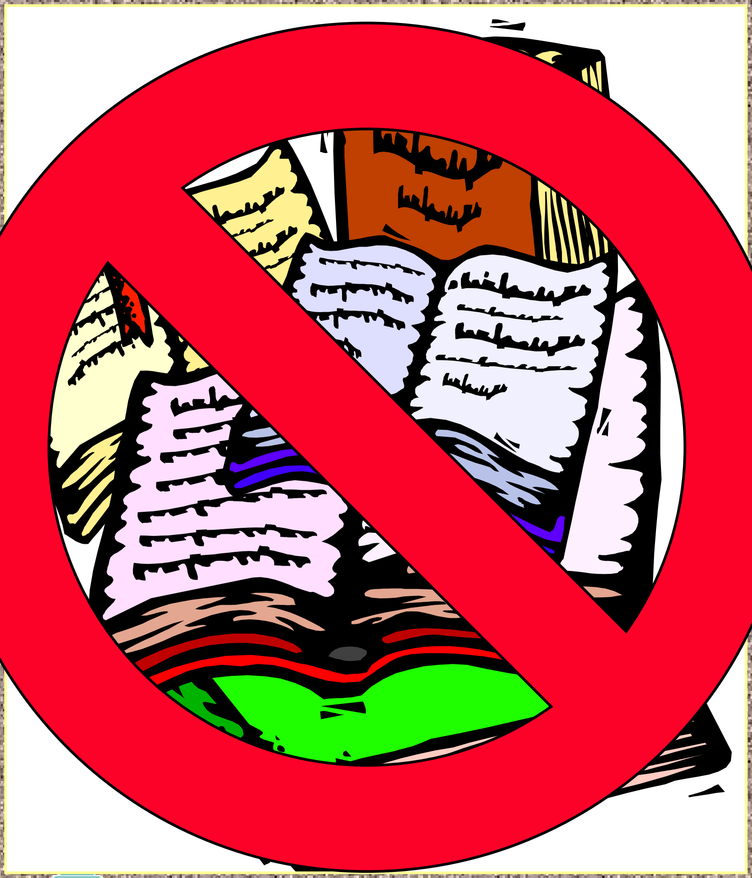

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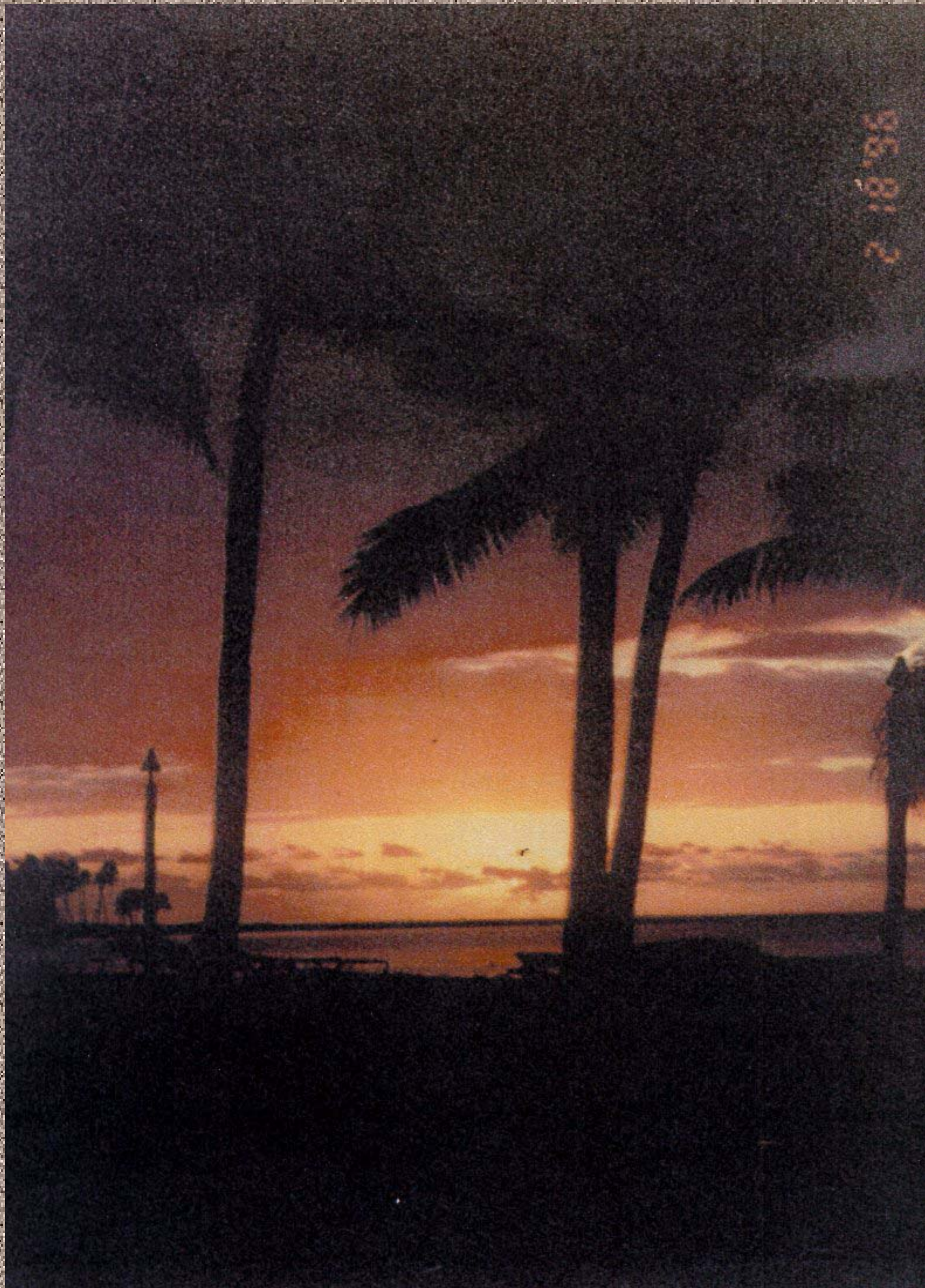

In Water Treatment, If You're Not Part of the Solution, You're Part of the Precipitate.

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