MICROBIAL SELENIUM AND ARSENIC REDUCTION: AN OVERVIEW

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MODIFIED / ACTIVATED CARBON TECHNOLOGY CENTER

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BACKGROUND

- This presentation focuses on selenium and arsenic and encompasses general principals important for metal and inorganic biotreatment
- General principals can be applied to ex situ (bioreactors) or in situ biotreatment of a wide variety of waters
- Generally microbes degrade or transform a contaminant for several reasons
  - As an energy source or key element C:N:P:S source
  - As a detoxification mechanism
  - Because it closely resembles another ion
  - A combination of the above reasons

OCCURRANCE

- Selenium and Arsenic are two of the more common inorganic contaminants throughout the world
  - Occur in wastewaters from petroleum refining, agricultural practices, coal fired power generation, mining activities, and in drinking waters from ‘natural’ sources

- The established MCL is 50 ppb for selenium and arsenic in drinking water
  - Selenium has an MCL goal of 20 ppb and many sites require 2 ppb
  - Arsenic MCL values drop to 10 ppb in 2006

- Selenate and arsenate are the most common forms in oxygenated waters

SELENIUM AND ARSENIC CHEMISTRY

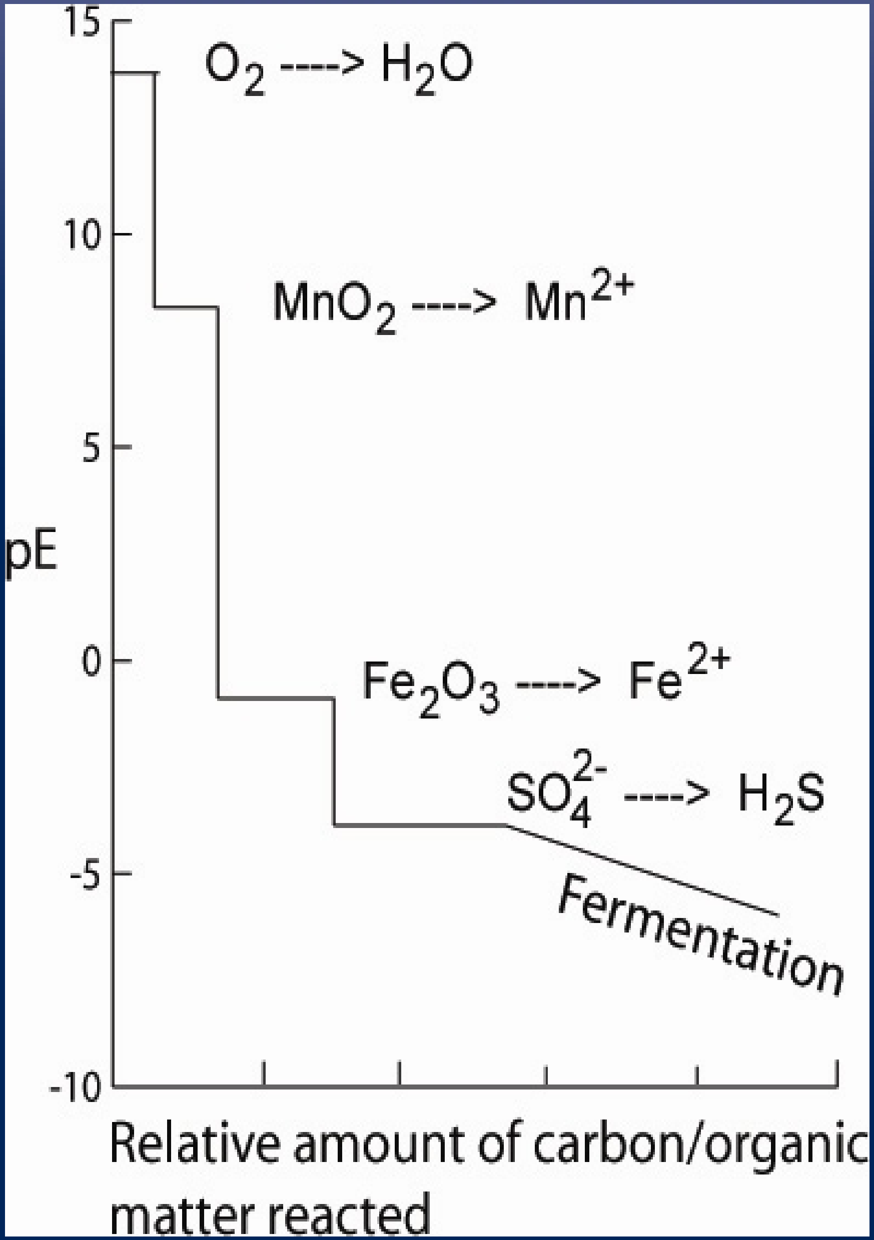
The chemical characteristics of selenium and arsenic are dominated by the fact that they readily change oxidation states or chemical form through chemical or biological reactions that are common in the environment

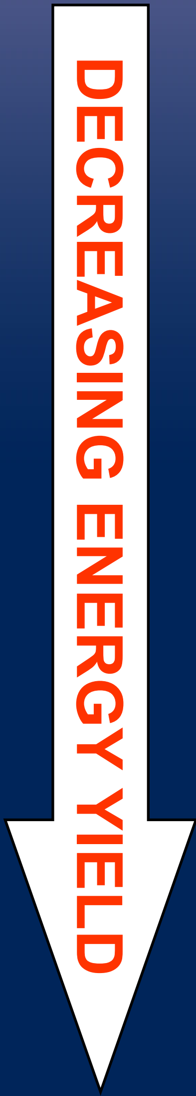
Therefore, rather than solubility equilibrium controlling their mobility, it is usually controlled by redox conditions, pH, biological activity, and adsorption / desorption reactions

Biotreatment transforms soluble selenate and selenite to less soluble elemental selenium and soluble arsenate and arsenite to less soluble arsenic sulfides

REDOX

Sequential utilization of electron acceptors maintains the redox potential at specific intervals until that acceptor is used up





BIOTREATMENT OF SELENIUM AND ARSENIC

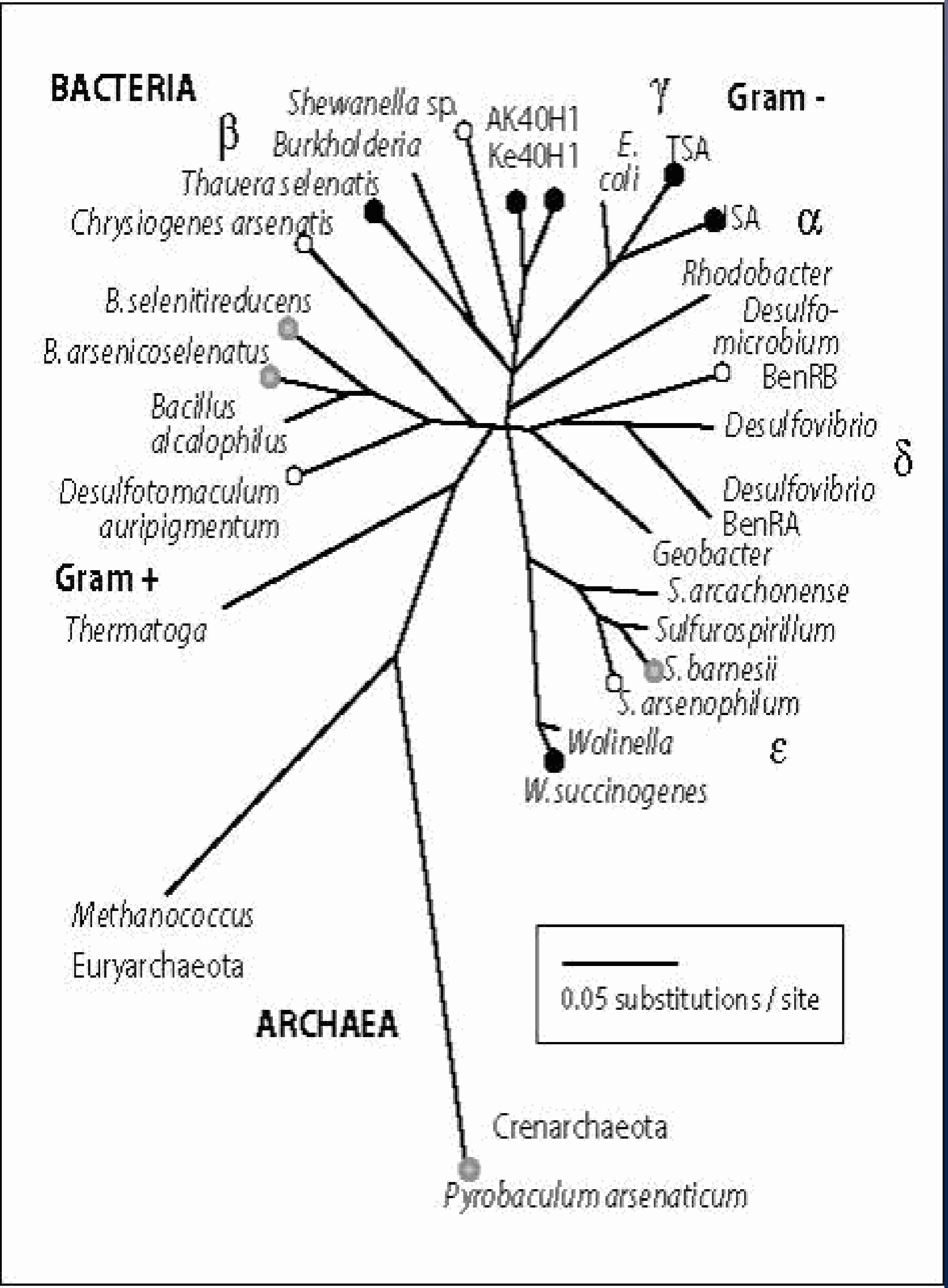
- Biological metal and inorganic transformation/removal methods, in general, produce 1,000's to 10,000 times less sludge than conventional chemical precipitation technologies

- Under conditions found in most environments, natural degradation and transformation processes are usually slow

WHY? @ ~10^6 MICROBES / gm – measurable transformations take weeks to months

@ ~10^9 MICROBES / gm – measurable transformations take hours to days

- An understanding of the microbes involved, site characteristics, and water chemistry is needed to optimize biotreatment kinetics



BACTERIA

Pseudomonas, Alcaligenes, Bacillus, Vibrio, Aeromonas, Arthobacter, Escherichia, Desulfovibrio, Micrococcus, Shewanella

ALGAE

Chorella, Tolypella, Chlamydomonas

FUNGI

Aspergillus, Fusarium, Candida

Aerobes – with O_2
Anaerobes – without O_2
Facultative – with and without O_2

BIOTREATMENT APPROACH

- Site evaluation - understand site chemistry and environmental parameter interactions

- Conduct biotreatability testing in site waters to determine the microorganisms needed for optimal performance under site conditions
  - Microbially mediated reduction of selenate and arsenate occurs relatively rapidly (time scale of hours) in solution under near optimal conditions

- Design / Engineer a biotreatment system to provide desired contaminant removals and conduct on-site pilot-scale testing

SITE EVALUATION

Temperature - 6° to 8° C
300 gal/min
pH - 3.5 to 4.0
NO_3-N – 270 mg/L
Sulfate – 9,800 mg/L
Selenium – 1.0 mg/L
Cyanide – 0.6 mg/L
Aluminum – 31 mg/L
Mg – 70 mg/L

- Seasonal or year round treatment
  - Volume to be treated & treatment system size
- Current and seasonal water chemistry
  - pH, redox (ORP), temperature, suspended solids, conductivity, etc.
  - Contaminants
  - Co-contaminants
- Expected changes in water chemistry

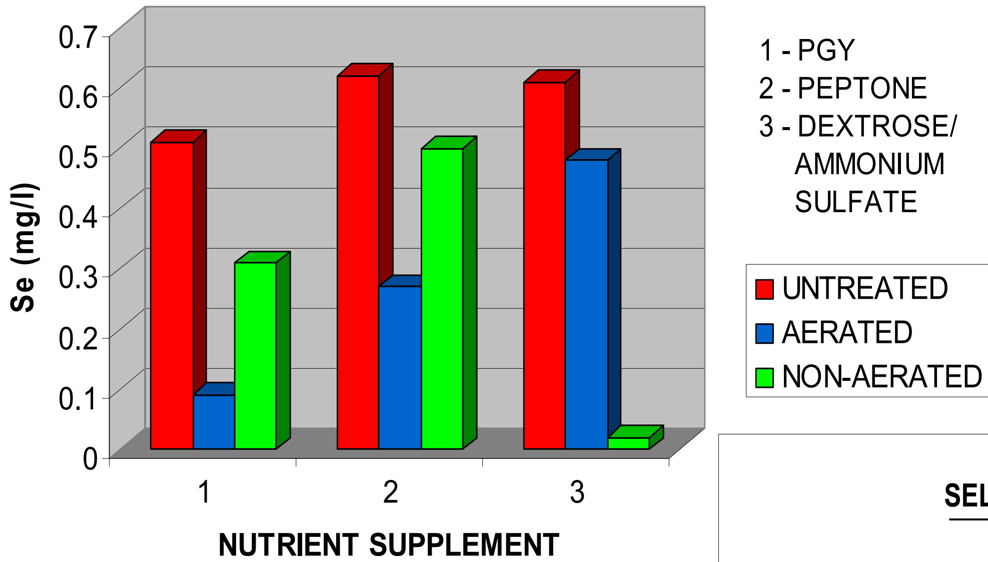
BIOTREATMENT APPLICATION

Whenever bioremediation is applied, a question arises as what bioremediation approach to use.

- Biostimulation - addition of nutrients that stimulate most or many of the site indigenous microbes
- Selective Biostimulation - isolation of key microbes, production of these microbes followed by their reintroduction into the treatment system
- Bioaugmentation - introduction of characterized microbes known to transform the contaminant(s) at high rates
- Bioaugmentation/Selective Biostimulation - a combination of techniques that lead to a population of both new and indigenous microbes

MICROBIAL EVALUATION

NUTRIENT/AERATION SCREEN



Nutrients with lower carbon content cause more moles of amendment to be consumed

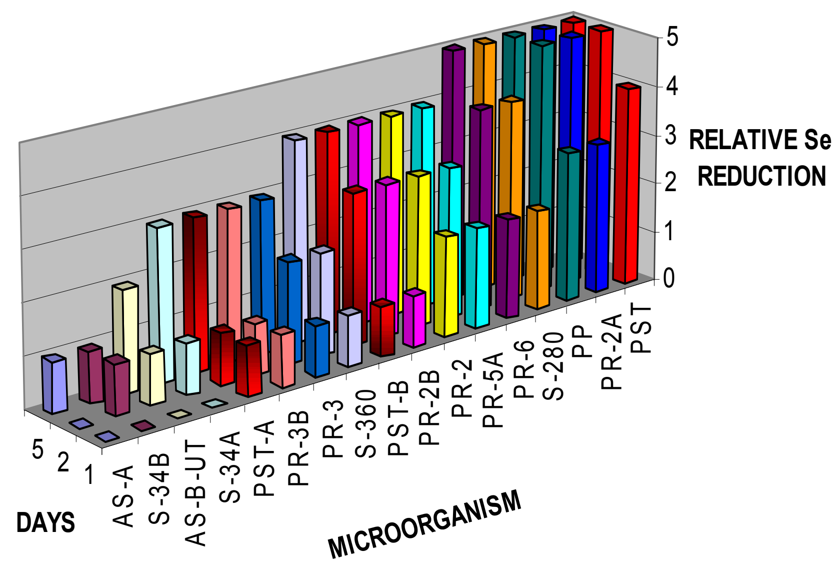
Need balanced C:N:P:S : trace elements : vitamins

Nutrients are key in determining the microbial population(s) established

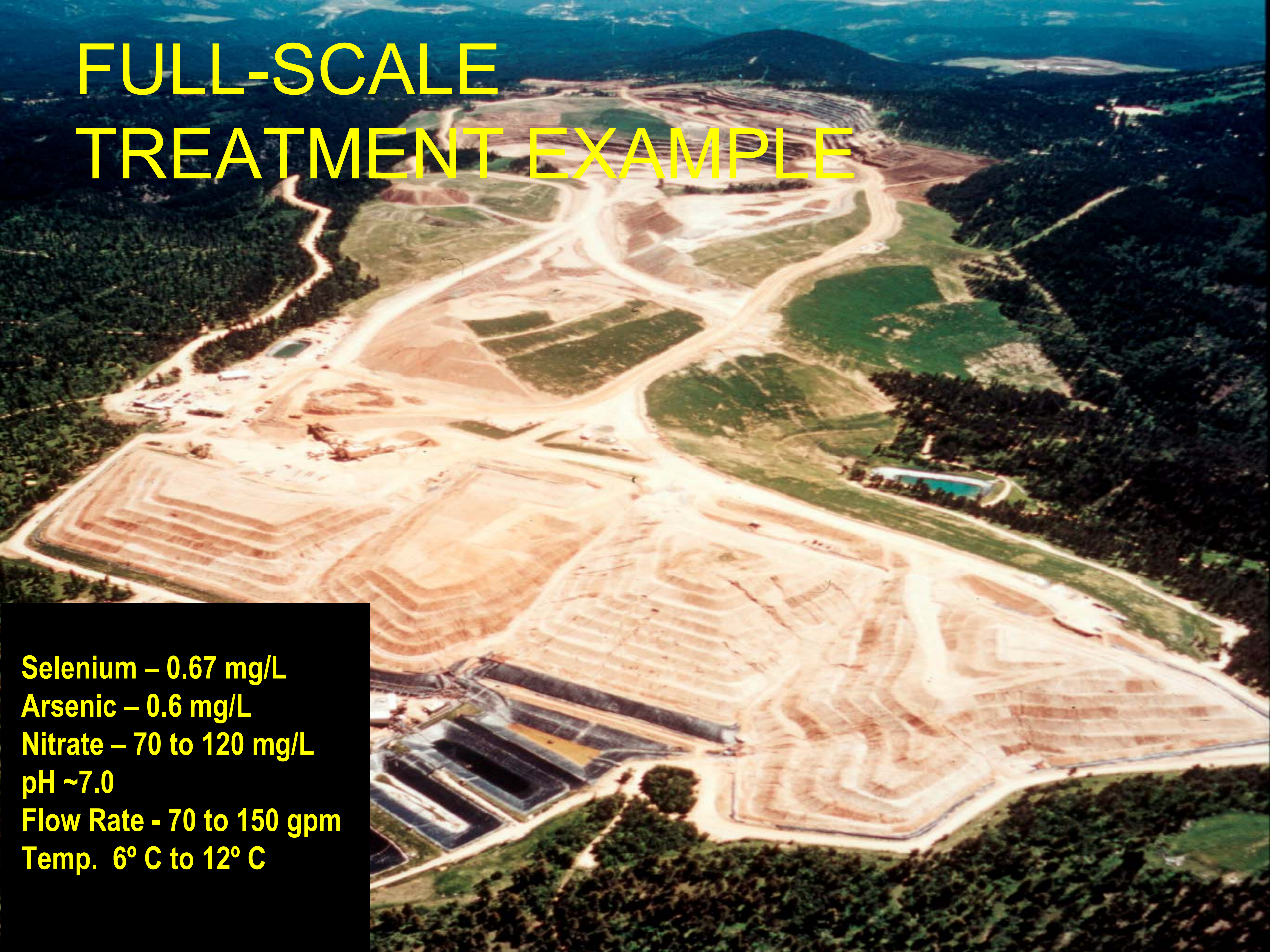
POPULATION PROFILE

DGGE ANALYSIS

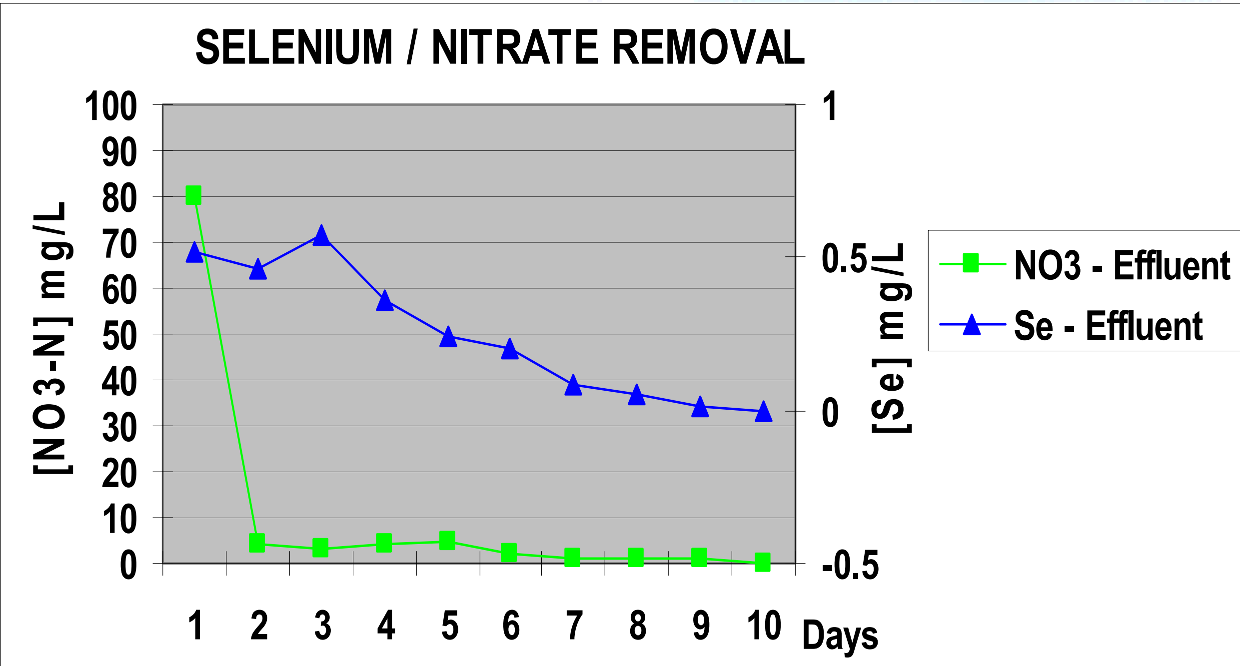
SELENIUM REDUCTION SCREEN

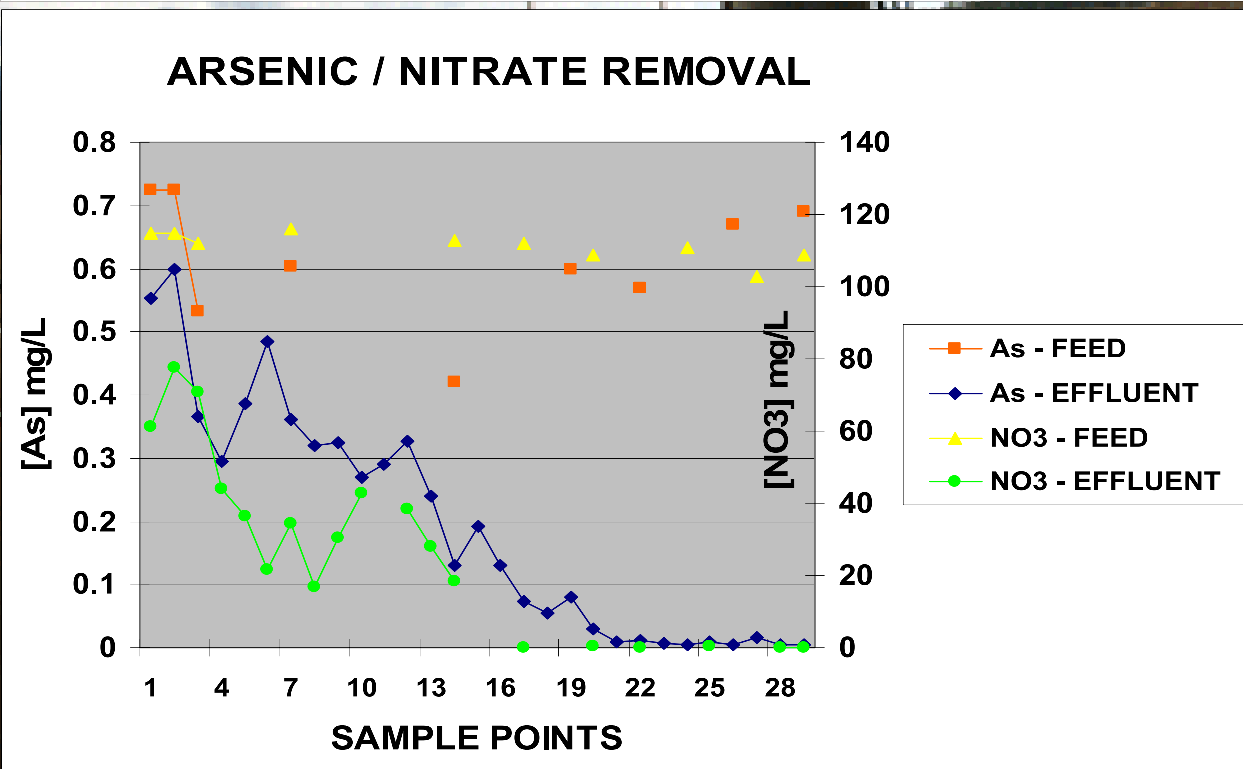


FULL-SCALE TREATMENT EXAMPLE

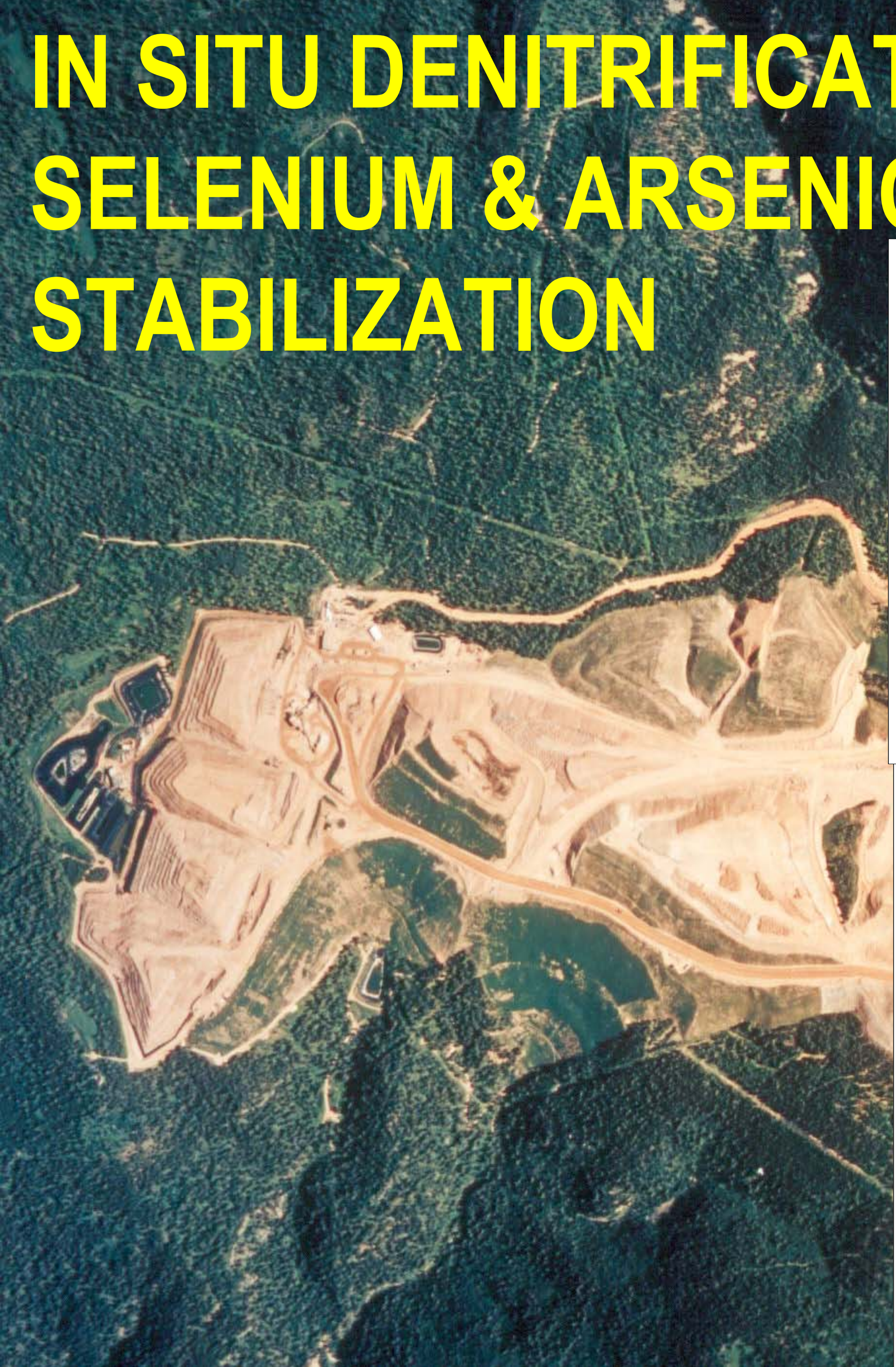


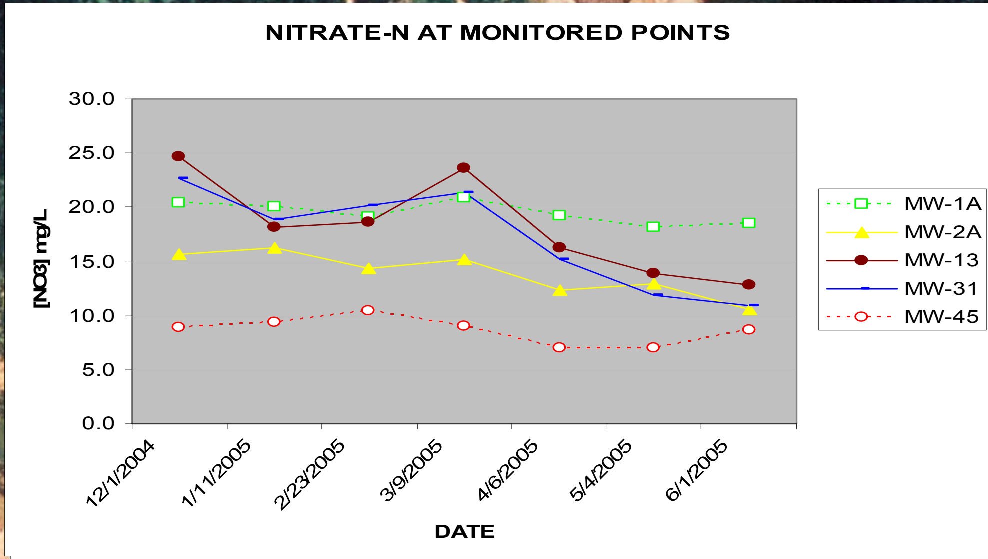
Selenium – 0.67 mg/L
Arsenic – 0.6 mg/L
Nitrate – 70 to 120 mg/L
pH ~7.0
Flow Rate - 70 to 150 gpm
Temp. 6º C to 12º C

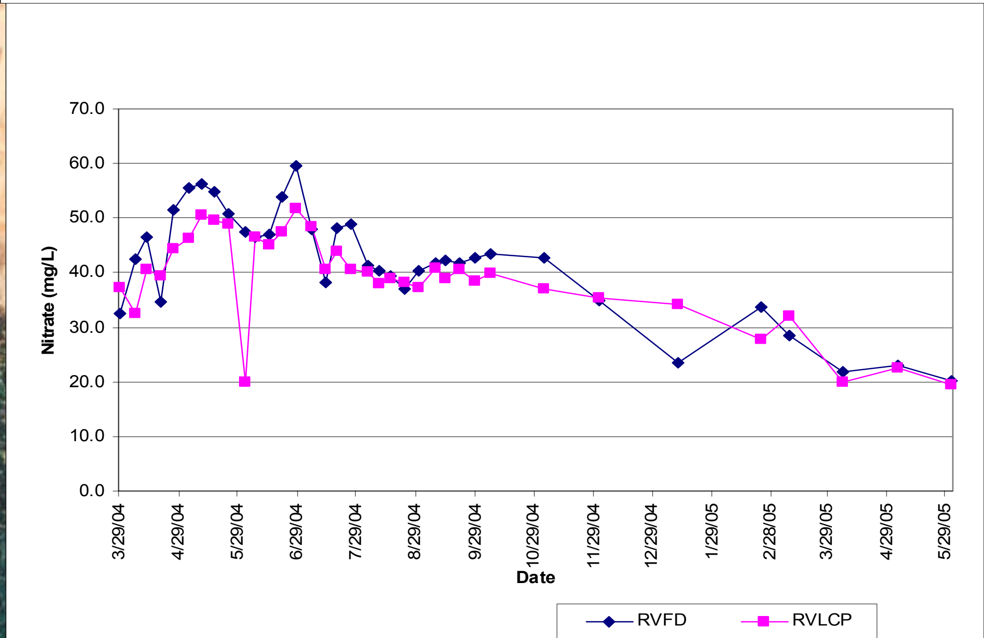

SELENIUM / NITRATE REMOVAL
[NO3-N] mg/L
[Se] mg/L
100
90
80
70
60
50
40
30
20
10
0
1
0.5
0
-0.5
1 2 3 4 5 6 7 8 9 10
Days
NO3 - Effluent
Se - Effluent


ARSENIC / NITRATE REMOVAL
[As] mg/L
[NO3] mg/L
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
140
120
100
80
60
40
20
0
1 4 7 10 13 16 19 22 25 28
SAMPLE POINTS
As - FEED
As - EFFLUENT
NO3 - FEED
NO3 - EFFLUENT

IN SITU DENITRIFICATION SELENIUM & ARSENIC STABILIZATION







MICROBES

- If you do not put them in the treatment system they will not come unless you establish the right environment and provide the appropriate nutrients
  - If you put them in a system and do not maintain the right environment they will leave
  - If it is too crowded when they get there they often will not stay

- Too little of the right nutrient and they will die or not grow and will not be effective for your biotreatment

- Too much nutrient and they will degrade the easiest to use nutrient, not be effective for your biotreatment, and produce more sludge
  - Almost always requires more than stoichiometric amounts of nutrients – C:N:P:S
  - Nutrients are required for energy, growth, reproduction, contaminant degradation / transformation, and to adjust the redox environment

BIOTREATMENT

- When properly configured, biotreatment can remove selenium and arsenic to below detection (multiple treatment system types)

- Biotreatment systems can remove multiple contaminants

- Bioprocesses are currently being used at full-scale for selenium and arsenic and other metal and inorganic removal

- Biotreatment is not a solution for every site, but can be a valuable treatment tool and can be combined with other treatments

NEW WATER BIOTREATMENT APPROACHES

BIOLOGICAL MATERIALS

HAVE A NATURAL ABILITY FOR ADSORBING TOXIC METALS FROM WATER!

Metals adsorbed by biological materials include: arsenic, cadmium, lead, mercury, copper, iron and zinc.

Algae

Moss

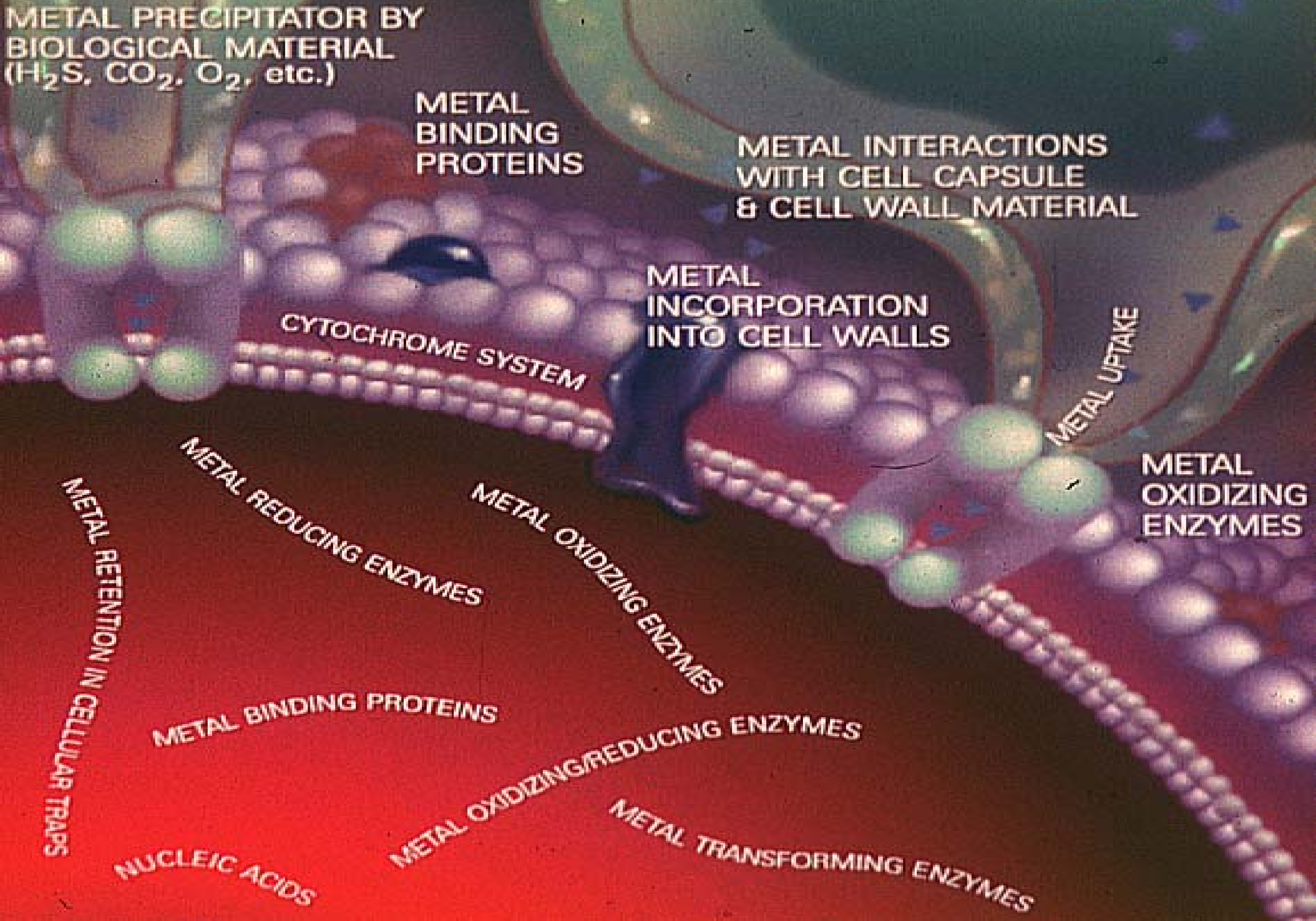
Fungi

Grasses & Shrubs

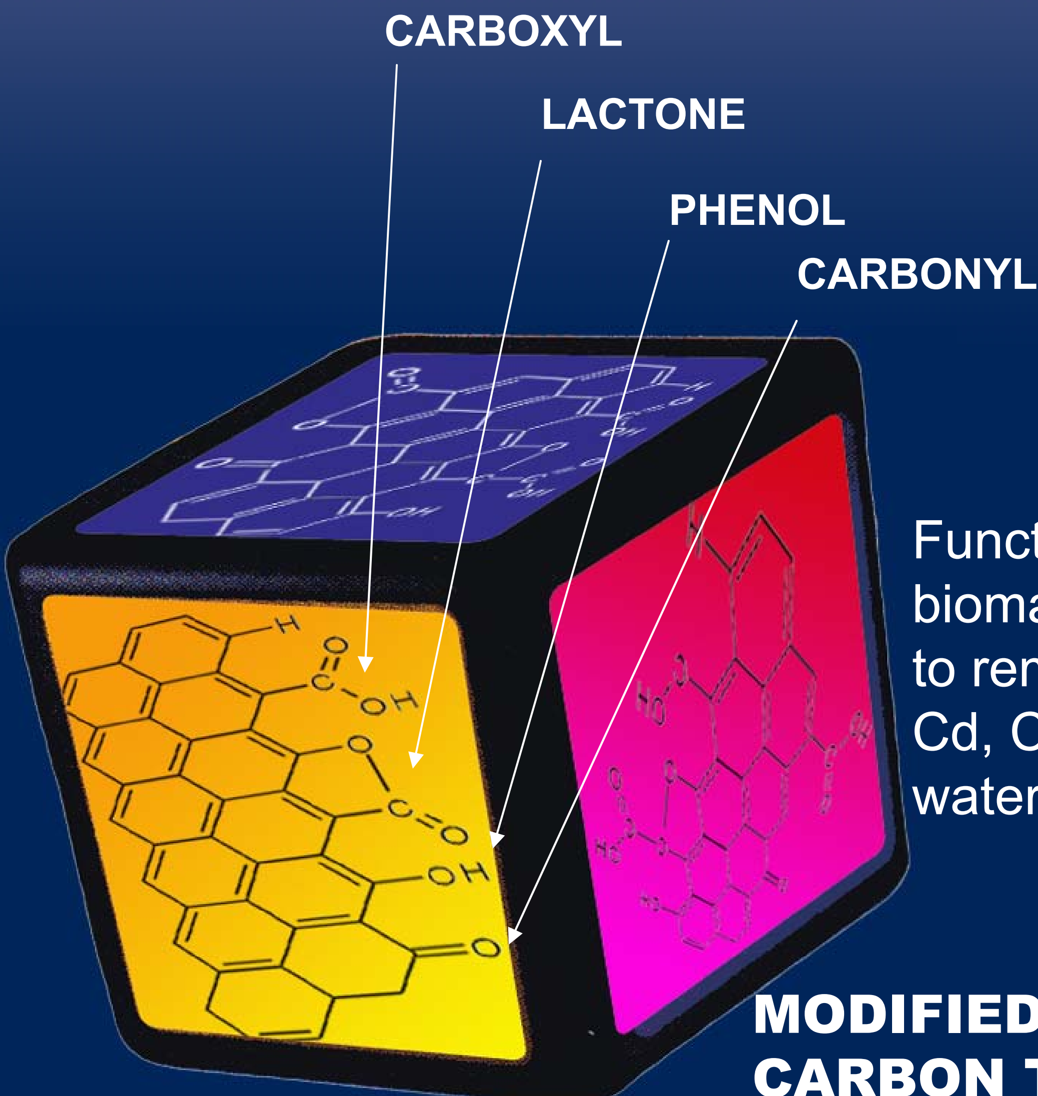
Bacteria

In general, these materials will adsorb metals in a pH range of 3-8 and work well in dilute waste systems.

NON-LIVING COMPONENTS



NEW BIOTREATMENTS



Functional groups found on and in biomaterials have been immobilized to remove metals such as As, Se, Cd, Cr, Hg, Cu, Te, Zn, Ni, etc. from waters

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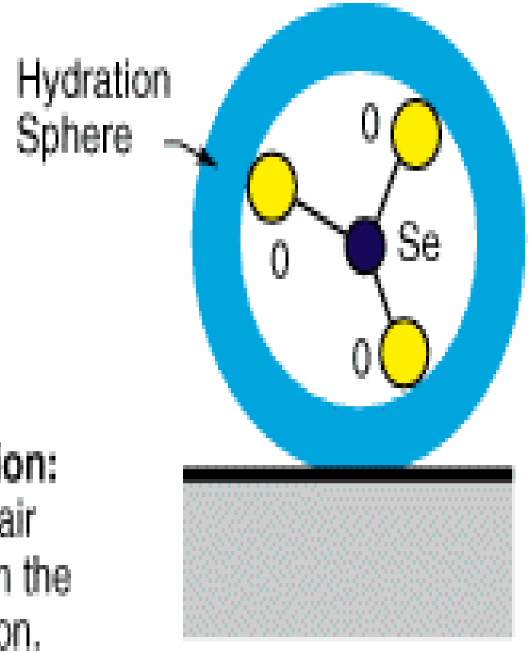
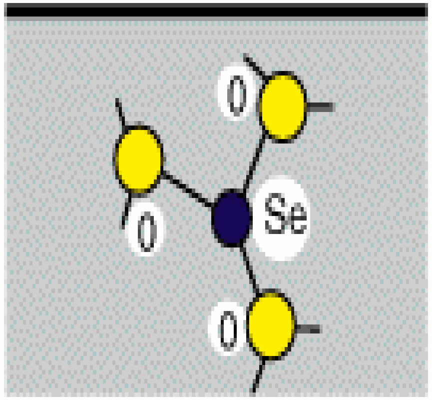
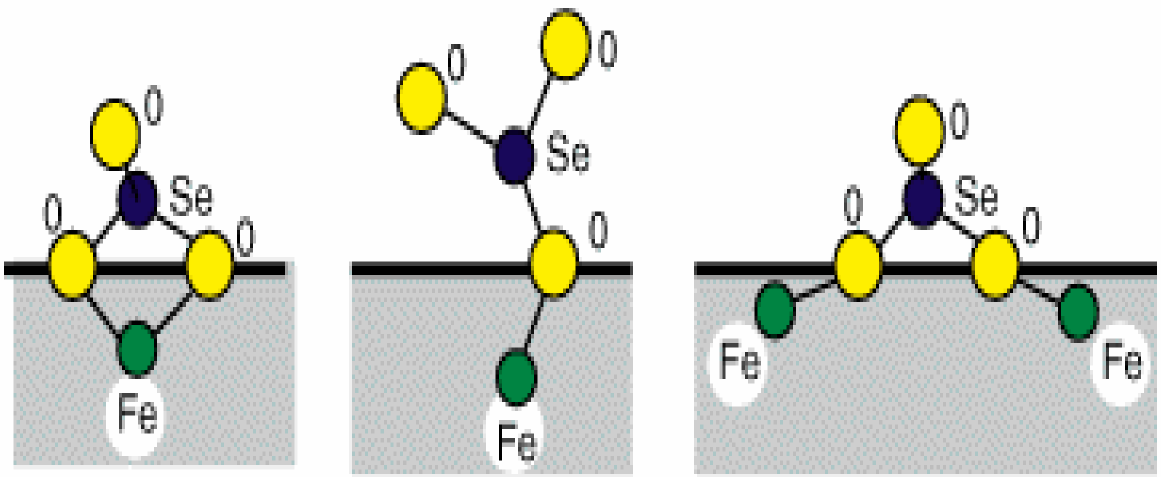


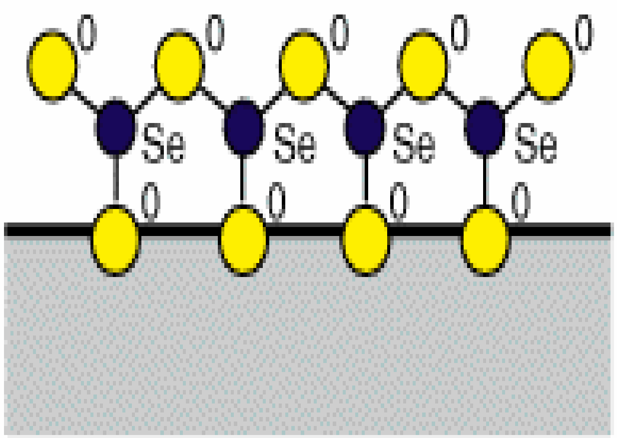
Outer sphere adsorption:
Selenite forms an ion-pair adsorption complex with the surface. Weak interaction.



Absorption:
Selenite is incorporated into the matrix phase. Strong interaction.

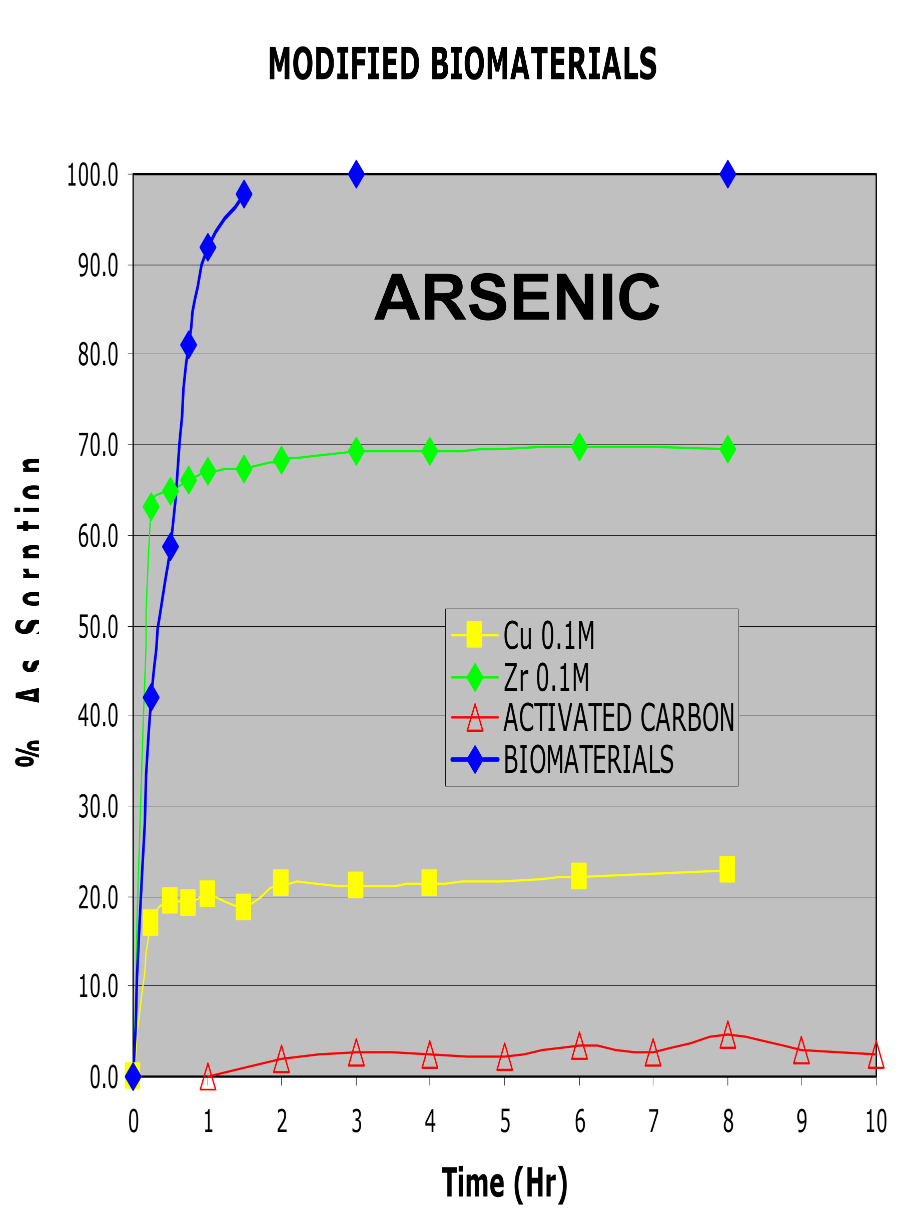


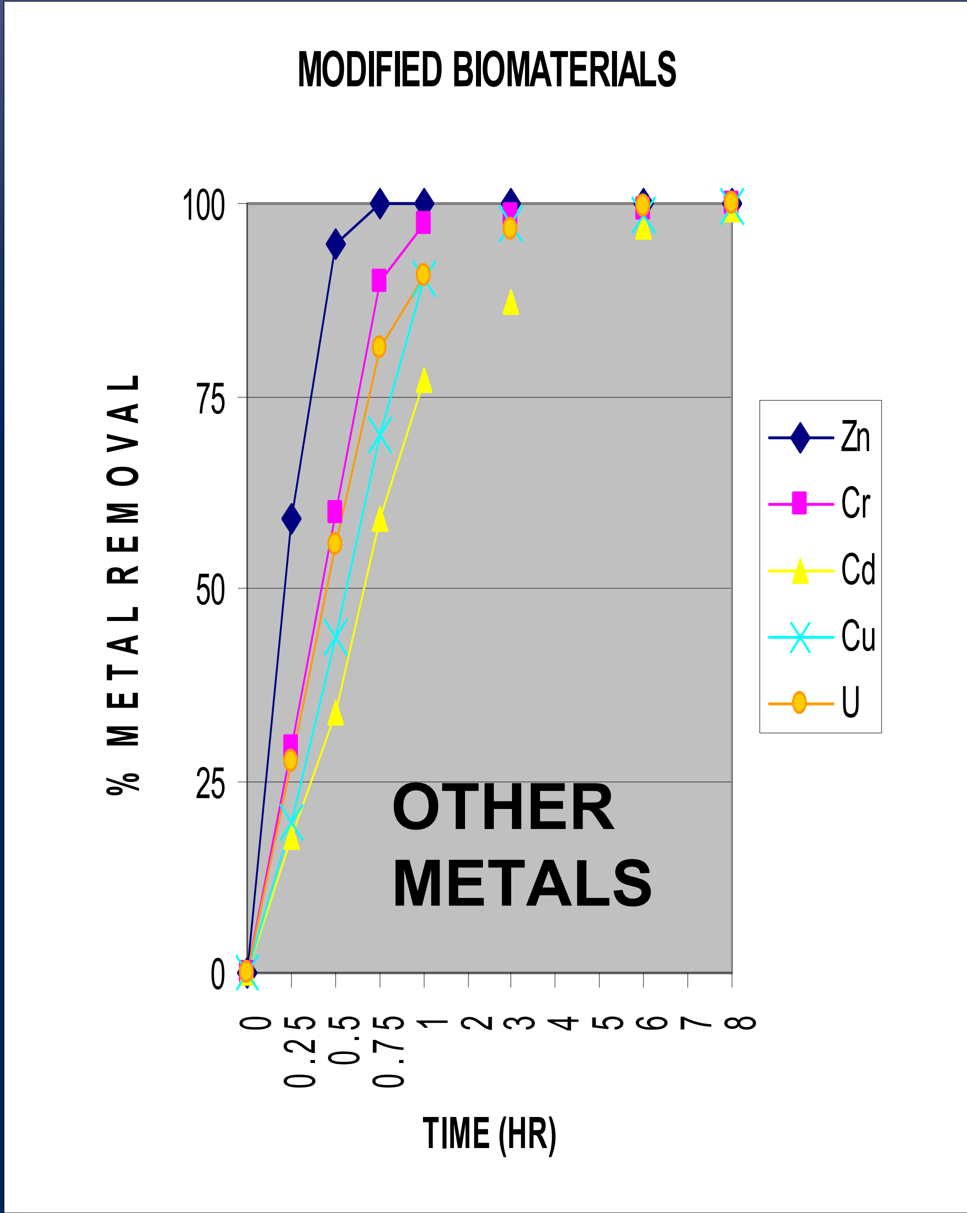
Inner sphere adsorption:
Oxygen atoms of the selenite anion are replaced by those at the surface. Strong interaction.



Suface precipitate:
Adsorbed selenite occurs in "Islands"
Strong interaction.

PRELIMINARY STUDIES





SUMMARY

- Live microbial biotreatments can be effective for treatment of selenium and arsenic and other inorganics if properly applied
  - Treatment costs range from $0.10 to $1.50 / 1,000 gal for nutrients
- New technologies using immobilized biomaterials hold considerable promise for treatment of various metals and inorganics including selenium and arsenic
  - Treatments costs are expected to be below $0.10 / 1,000 gal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