PIMS

Apatite II Treatment of Metal-Contaminated Water

(Pb, Zn, Cd, Cu, Al, SO_4, NO_3, TNT, perchlorate and others)

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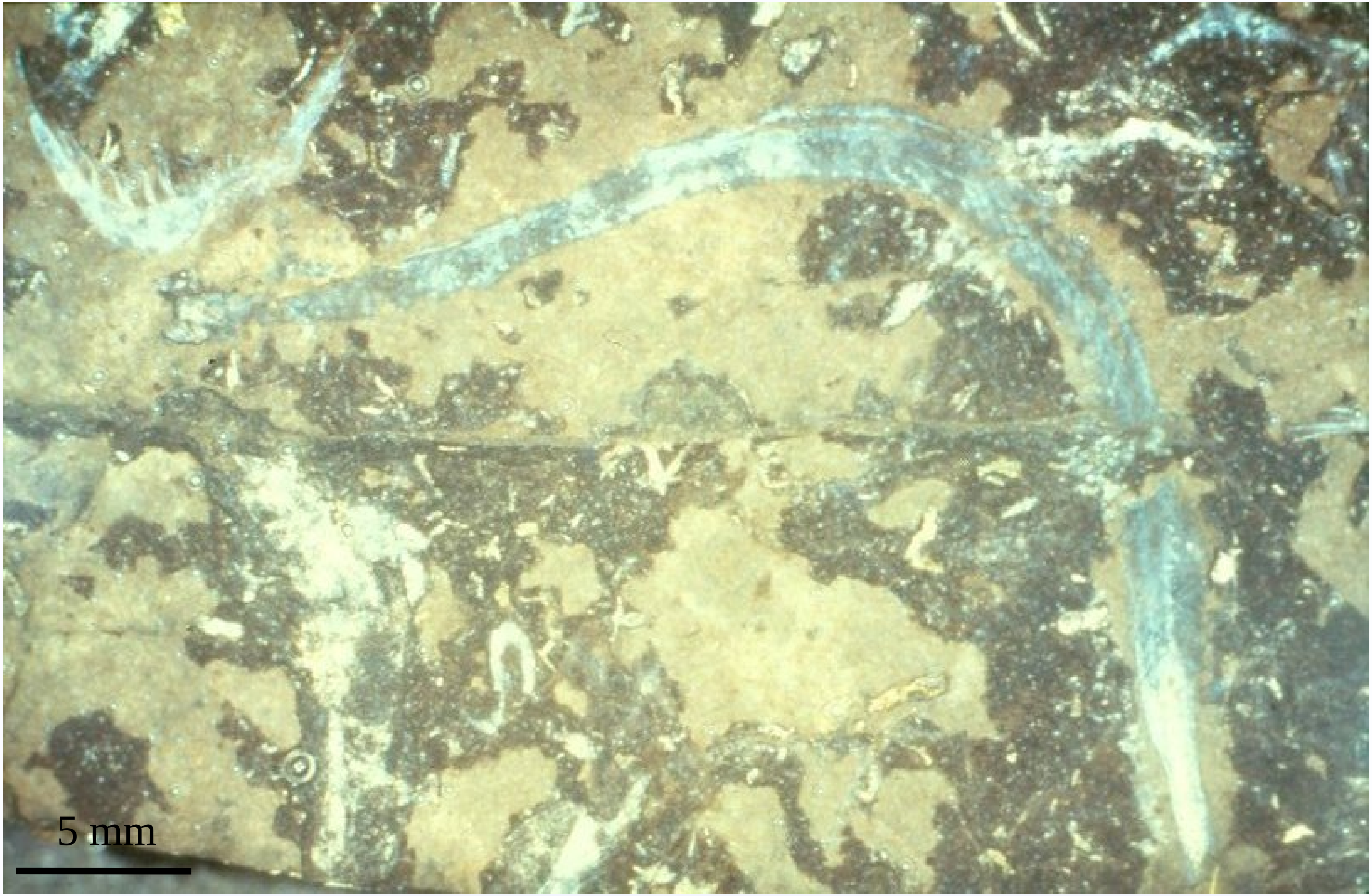
PIMS: Phosphate-Induced Metal Stabilization Technology Description

Take a reactive form of the phosphate mineral group, apatite, and place it in contact with metal-contaminated water, e.g., groundwater, waste streams, soil leachates. Most metals in solution will be immobilized on the apatite mineral by precipitation (U, Pb, Pu, lanthanides), co-precipitation (transition metals) or by surface sorption (most metals).

The apatite can be containerized or free-standing in a trench or culvert as a permeable reactive barrier (PRB).



This work began with Dr. Judith Wright's dissertation work on Conodonts, the first organism to have apatite "teeth" (550 - 180 m.y.)

The Apatite Mineral Group

$$Ca_{10}(PO_4)_6(OH)_2$$

- Ca_{10} → Pb, U, Zn, Cd, Th, Cr, Co, Na, Ni, Sr, Rb, Zr, Cs, REE, Au, Ba, Ir, Hg, Se, As, Ta, Fe, and others
- $(PO_4)_6$ → CO_3, SO_4, SiO_4, XO_y
- $(OH)_2$ → F, Cl, Br, CO_3, X

Apatites compared to soluble phosphates

- **Other phosphate phases are too soluble**
  - Are not persistent in the subsurface, e.g., phosphate fertilizers and phosphoric acid
  - Require large excesses of PO_4^{-3} and metal concentrations in solution and may produce microbial blooms
- **Process requires nucleation sites**
  - Surfaces of the apatite mineral structure provide nucleating sites for precipitation of metal-apatite mineral species thus overcoming large activation energies
- **Apatites are stable in the subsurface**
  - Over geological time - millions of years
  - Persist in the face of subsurface processes and diagenesis
  - Do not induce microbial blooms
- **Apatites are also good non-specific surface sorbers**

Apatite-Pyromorphite-Phosphate Mineral Solubility Constants

$Pb_5(PO_4)_3(OH,Cl,F)$	$\log K_{sp} \ll -76.5$
$Ca(UO_2)_2\,(PO_4)_2 \bullet 10H_2O$	$\log K_{sp} \sim -49.0$
UO_2HPO_4	$\log K_{sp} \sim -10.7$
$Zn_3(PO_4)_2$	$\log K_{sp} \sim -35.3$
$Cd_3(PO_4)_2$	$\log K_{sp} \sim -32.6$
$Am(PO_4)$	$\log K_{sp} \sim -24.8$
$Pu(PO_4)$	$\log K_{sp} \sim -24.4$
$Sr_5(PO_4)_3(OH)$	$\log K_{sp} \sim -51.3$

Other Common Mineral Solubility Constants

Salt (NaCl)	$\log K_{sp} \sim 0.0$
Quartz (SiO_2)	$\log K_{sp} \sim -4.0$

The search for the best apatite to remediate metals included:

- North Carolina phosphorite rock
- Florida phosphorite rock
- Permian Phosphoria Formation phosphorite rock
- Durango apatite (igneous)
- Cow bone
- Bone char
- Cannery waste
- Reagent grade tricalcium phosphate
- Synthetic apatites
- Apatite II

What is Apatite II?

Made from processed fish bones, the nominal composition of Apatite II is:

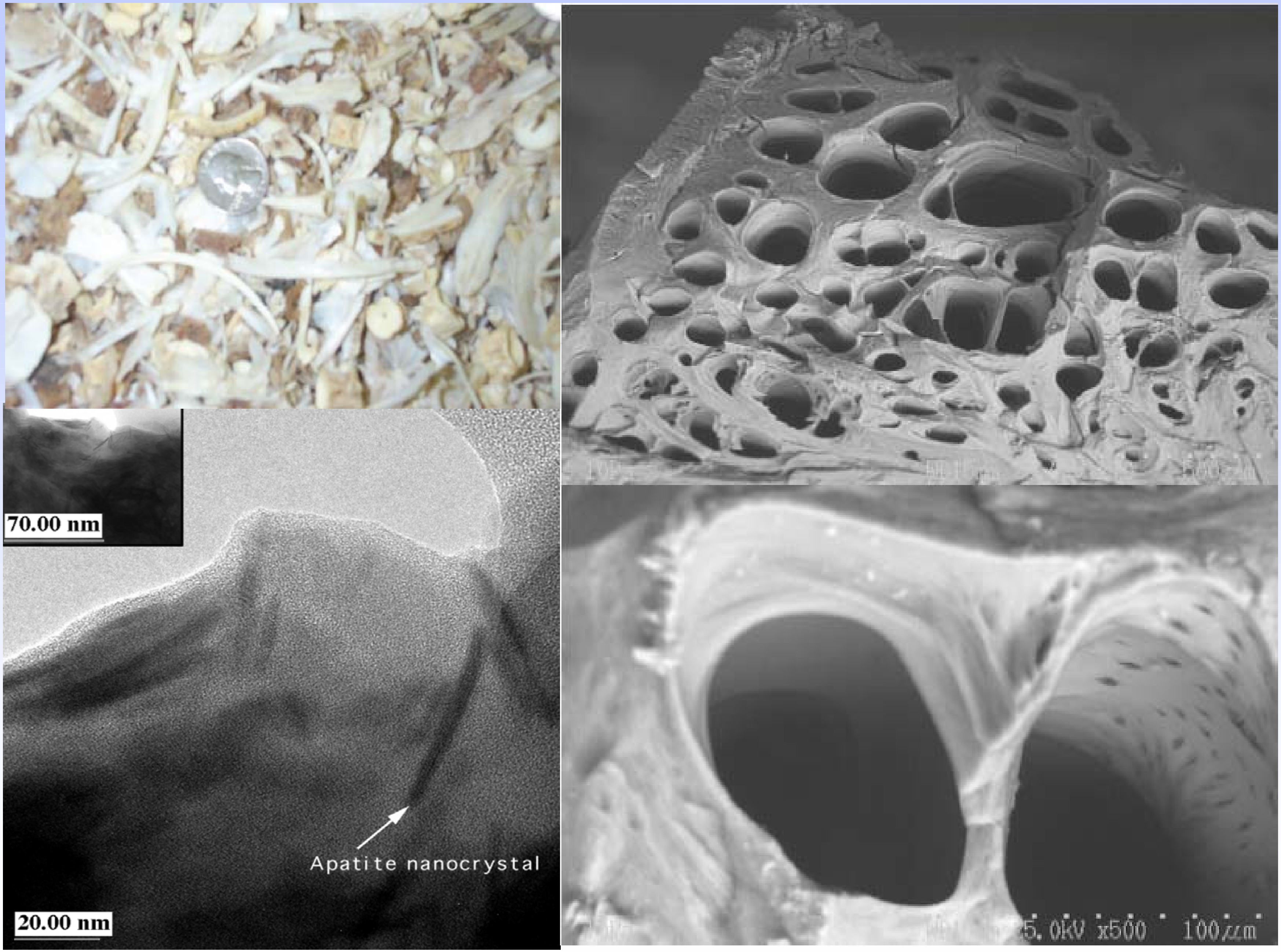
$$Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2$$

where $x < 1$.

Apatite II compared to other apatites

- **Most apatites are less effective**
  - recrystallized - less reactive
  - fully fluorinated - less reactive
  - little microporosity - less reactive
  - no carbonate - less reactive
  - high existing metal content
- **Apatite II is the best**
  - fully carbonated - most reactive
  - no fluorine and low trace metal content
  - microporous - most reactive
  - amorphous with random nanocrystals
  - inexpensive and abundant
- **Apatite II can sequester over 20% of its weight in metals, particularly Pb, U and Pu**

Structure and Chemistry of Apatite II both play critical role unique structure at all scales (cm/mm/μm/nm)



Apatite II works by four general non-mutually-exclusive processes, depending upon the metal, the concentration of the metal and the aqueous chemistry of the system

- **Heterogeneous nucleation--supplying a small amount of PO_4 to solution to exceed the solubility limits of most metal apatites**
- **At low pH, buffers acidity to pH 6.5 to 7 causing precipitation of many metal phases**
- **Chemi-adsorption--uncompensated PO_4 and OH^- groups on the surface induce metal sorption, particularly transition metals**
- **Biological stimulation-- P and bioavailable organics can stimulate microbial community activity in many chemical systems, e.g, high SO_4 or NO_3**

How PIMS using Apatite II stabilizes Pb, Mn, U and Pu

The process consists of two steps:

1) a dissolution reaction

Apatite II provides phosphate to solution…

Apatite II

$$Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2 + 14H^+ \rightarrow (10-x)Ca^{2+} + xNa^+ + (6-x)[H_2(PO_4)]^- + xH_2CO_3 + 2H_2O$$

2) a precipitation reaction on the Apatite II seed crystal

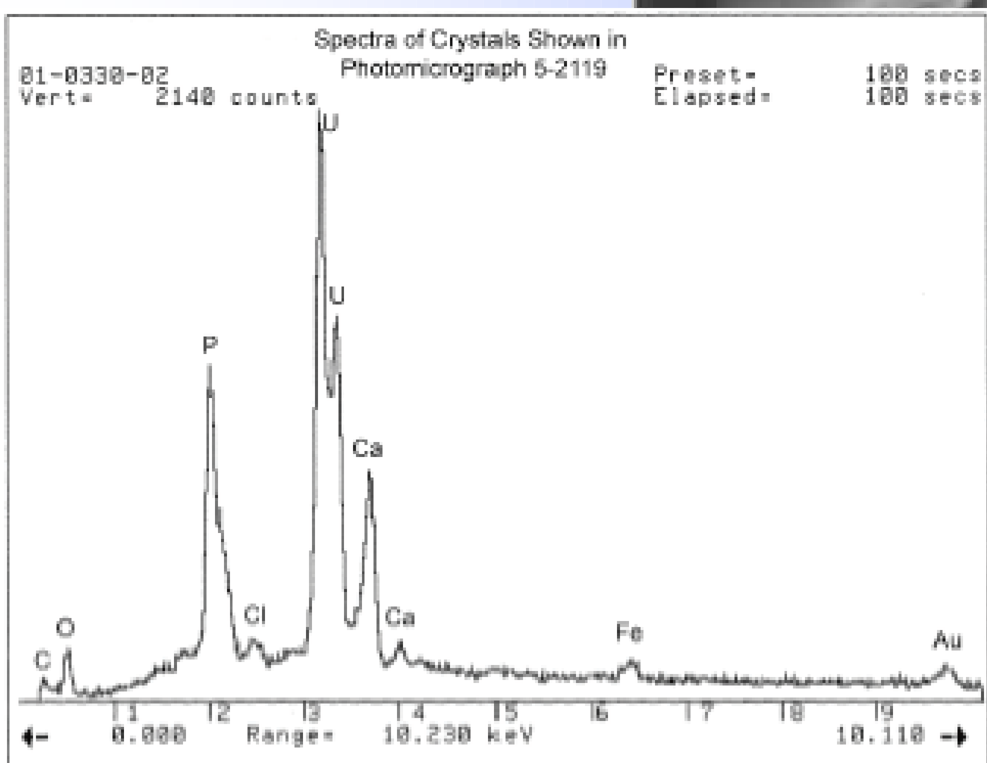
…causing pyromorphite, to precipitate on Apatite II surfaces.

$$10Pb^{2+} + 6H_2(PO_4)^- + 10H_2O \rightarrow Pb_{10}(PO_4)_6(OH)_2 + 12H^+$$

pyromorphite (Pb-apatite)

Similar reactions occur for U, Mn and Pu

SEM-EDS photomicrograph of a uranium-rich precipitate on Apatite II from Oak Ridge Y-12 site.



The plate-like structure and spectra of autunite.

For systems having sulfate, nitrate, perchlorate or other electron acceptors, biological stimulation by Apatite II can dominate:

1) Apatite II provides an optimal amount of phosphate, carbon and other essential nutrients continuously to solution for microbial sulfate reduction

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

2) Sphalerite (and other metal sulfides) precipitate on Apatite II surfaces rapidly

$$Zn^{2+} + HS^- \rightarrow ZnS + H^+$$

The CH_2O represents the organic carbon from the Apatite II that serves as both electron donor and carbon source for the sulfate reducers

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

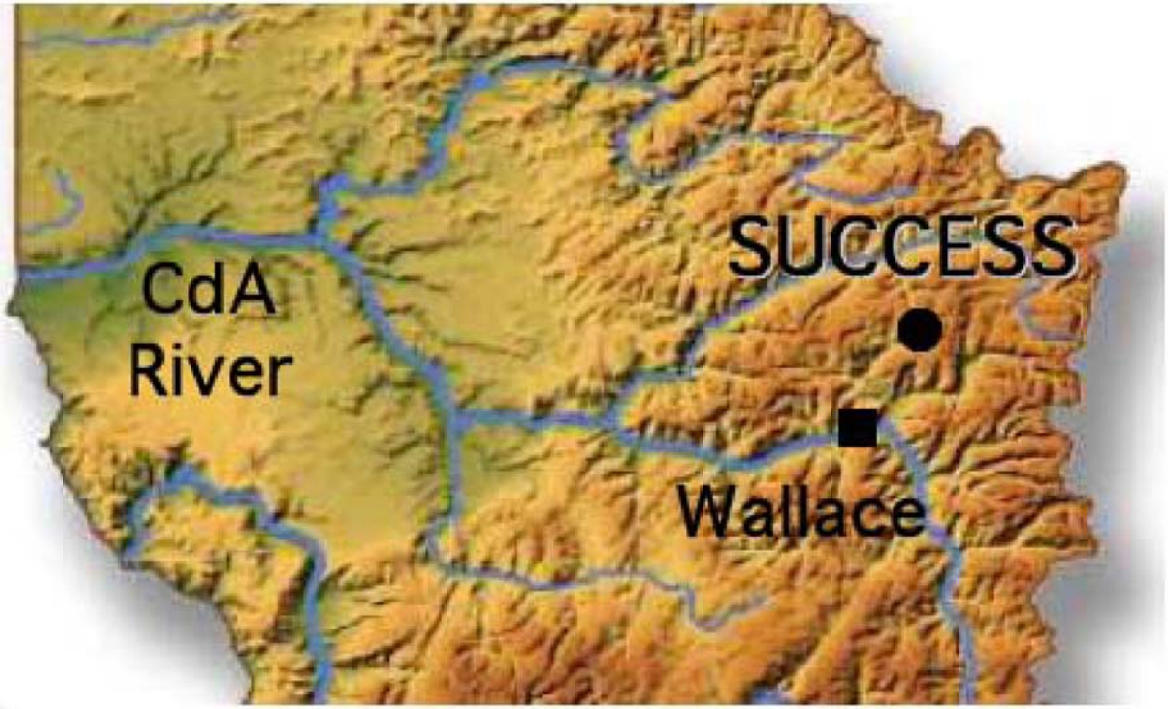
Two Types of Field Applications to water:

Treatment Tank - U, Cd, Zn, Cu, Tc, PCBs in Kentucky

Permeable Reactive Barriers - Pb, Cd, Zn in Idaho

This technology can also be directly applied to contaminated soils and waste by simple mixing.

nmsu



PRB Case Histories

The Success Mine and Mill Site, and the Nevada Stewart Mine Adit, both in Idaho

Environmental degradation through Pb particulate and vapor deposition in Smelterville, Idaho

Inside the smelter at Smelterville

Success Mine and Mill Site

Operated from 1886 to 1956 in Northern Idaho

Over 500,000 ton tailings pile adjacent to the east fork of Ninemile Creek.

Soils: Pb, Zn, Cu and Cd at levels of 1000-4000 mg/kg

Groundwaters and surface seeps (mg/L or ppm)

250 ppm Zn	10 ppm Pb
1 ppm Cd	20 ppm Cu

Based on the feasibility studies of treating soils and groundwater, Idaho DEQ decided to put in a permeable reactive barrier of Apatite II between the Success Mine tailings and Nine Mile Creek

Success Mine tailings pile with Ninemile Creek in foreground. Apatite II PRB is off to the right between pile and creek

Cd, Pb and Zn Levels in groundwater between the tailings and EFNC

Dissolved Analyte	*Concentration Range (ppb)*	*Drinking Water* Criteria (ppb)*	*Aquatic Criteria†(ppb)*
cadmium	**8 - 1,250**	**5**	**1**
lead	**70 – 1,440**	**15**	**2.5**
zinc	**4,850 – 177,000**	**5,000**	**100**

Federal Maximum Contaminant Level (MCL) for protection of drinking water.

†State chronic criteria for the protection of fresh water aquatic life.

PRB Construction

- 445-meter long pressure grouted containment wall installed down to bedrock along edge of creek.
- 4.2-meter high, 4.6-meter wide, 15.4-meter long PRB vault made of Type V Portland cement was constructed to receive seep and alluvial groundwater flow. Vault is baffled to insure even, saturated flow. Discharge from vault occurs onto a rock apron before entering the creek. Plumbed and valved to allow sampling and replacement of reactive media.
- Construction completed January 2001.
- 100 tons of Apatite II was used at a cost of $350/ton
- PRB is performing better than anticipated

Construction of PRB vault between East Fork of Ninemile Creek and the Tailings Pile.

Installation of the Apatite II in the baffles of the PRB vault.

Completed PRB vault at Success Mine. Flow is from bottom of photo to top and into Ninemile Creek behind.

Dissolved Metal Concentrations Entering and Exiting the Apatite II Permeable Reactive Barrier at Success Mine

	Entering Barrier (µg/L;ppb)				Exiting Barrier (µg/L;ppb)			
Date	pH	Cd	Pb	Zn	pH	Cd	Pb	Zn
1/01	---	---	---	---	7.0	< 2	< 5	14
3/01	4.5	333	1,230	44,700	6.0	< 2	< 5	27
10/01	5.0	437	1,110	71,300	6.5	< 2	< 5	74
1/02	5.0	779	1,210	116,000	6.5	< 2	< 5	66
6/02	4.8	726	1,450	57,230	6.9	< 2	< 5	243
8/02	4.2	430	1,185	64,600	7.1	< 2	< 5	83
10/02	4.5	430	1,185	68,350	6.5	< 2	< 5	69
11/02	4.5	430	1,185	65,600	6.5	< 2	< 5	39
12/02	4.5	430	1,185	83,950	6.5	< 2	< 5	91
2/03	4.5	664	983	101,000	6.8	< 2	< 5	46
3/03	4.5	650	1,190	48,700	6.6	< 1	< 1	55
5/03	4.5	477	869	71,300	6.8	< 2	< 2	20
7/03	4.5	749	1,350	146,900	6.8	< 2	< 5	59
10/03	4.6	587	1,330	86,800	7.0	< 2	< 5	< 5
3/04	5.2	404	497	64,500	6.9	< 2	< 5	95
6/04	4.9	436	658	68,000	6.9	< 2	< 5	34

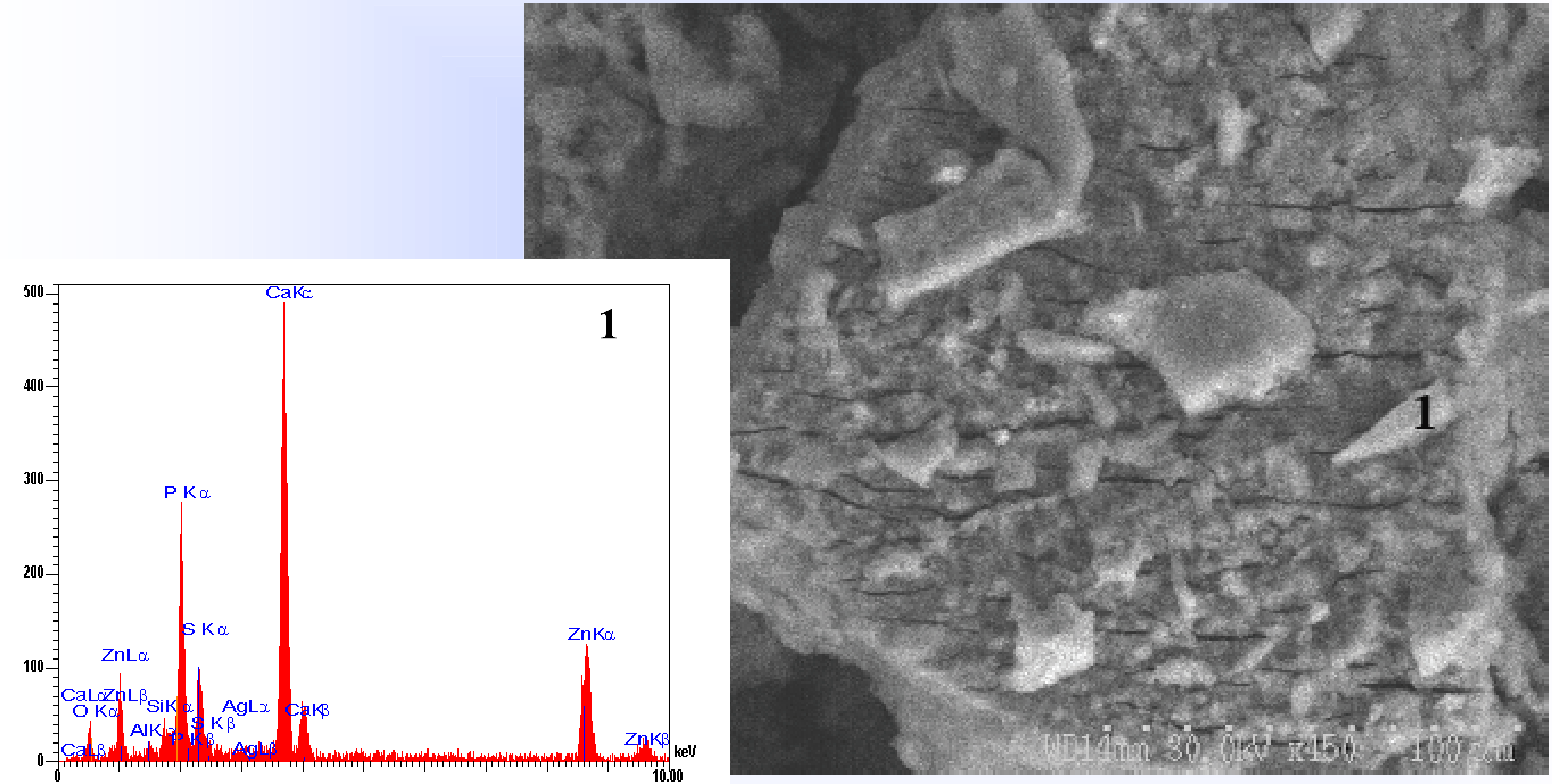
Aqueous Chemistry of Groundwater Entering and Exiting the Apatite II PRB in August 2002

Species	Entering Barrier (mg/L;ppm)	Exiting Barrier (mg/L;ppm)
pH	4.18	7.13
Hardness	78.8	125
Alkalinity ($CaCO_3$)	0	243
TDS	344.9	466.9
Cond. (µS/cm)	421	556
Ag	<0.0002	<0.0002
Al	3.16	0.020
As	0.0007	0.0004
B	0.008	0.012
Ba	0.028	0.001
Be	<0.001	<0.001
Br	<0.02	<0.02
Ca	26.0	44.5
Cd	0.42	<0.001
Cl	0.45	1.05
ClO_3	<0.02	<0.02
Co	0.0069	<0.001
CO_3	<0.5	<0.5
Cr	<0.001	<0.001
Cs	<0.001	0.001
Cu	0.23	0.0014
F	0.24	<0.02
Fe	0.05	0.11
HCO_3	<0.001	297

Species	Entering Barrier (mg/L;ppm)	Exiting Barrier (mg/L;ppm)
Hg	<0.00005	0.0005
K	1.27	1.54
Li	0.006	0.005
Mg	3.27	3.39
Mn	0.94	0.0022
Mo	<0.001	<0.001
Na	3.54	5.06
NH_4	<0.02	43.1
Ni	0.015	0.0021
NO_2	<0.02	<0.02
NO_3	0.58	<0.02
Pb	1.16	0.0007
PO_4	<0.05	49.1
Rb	0.002	0.002
Sb	<0.001	<0.001
Se	<0.001	<0.001
Si	10.6	10.1
SiO_2	22.7	21.6
Sn	<0.001	<0.001
SO_4	216	<0.05
Sr	0.37	0.38
Th	<0.001	<0.001
Ti	0.006	0.036
Tl	<0.001	<0.001
V	<0.001	<0.001
Zn	64.5	0.086

MINTEQ A2 modeling gives saturation indices that exceed 1 for:

- sphalerite, ZnS
- pyromorphite, $Pb_5(PO_4)_3(OH,Cl,F)$
- chlorapatite, $Ca_5(PO_4)_3Cl$



Photomicrograph of Apatite II from the first chamber showing biologically-mediated formation of micron-sized ZnS (sphalerite) crystals forming on surface of the Apatite II within the PRB.

Opening of the Success Mine PRB July 1, 2003

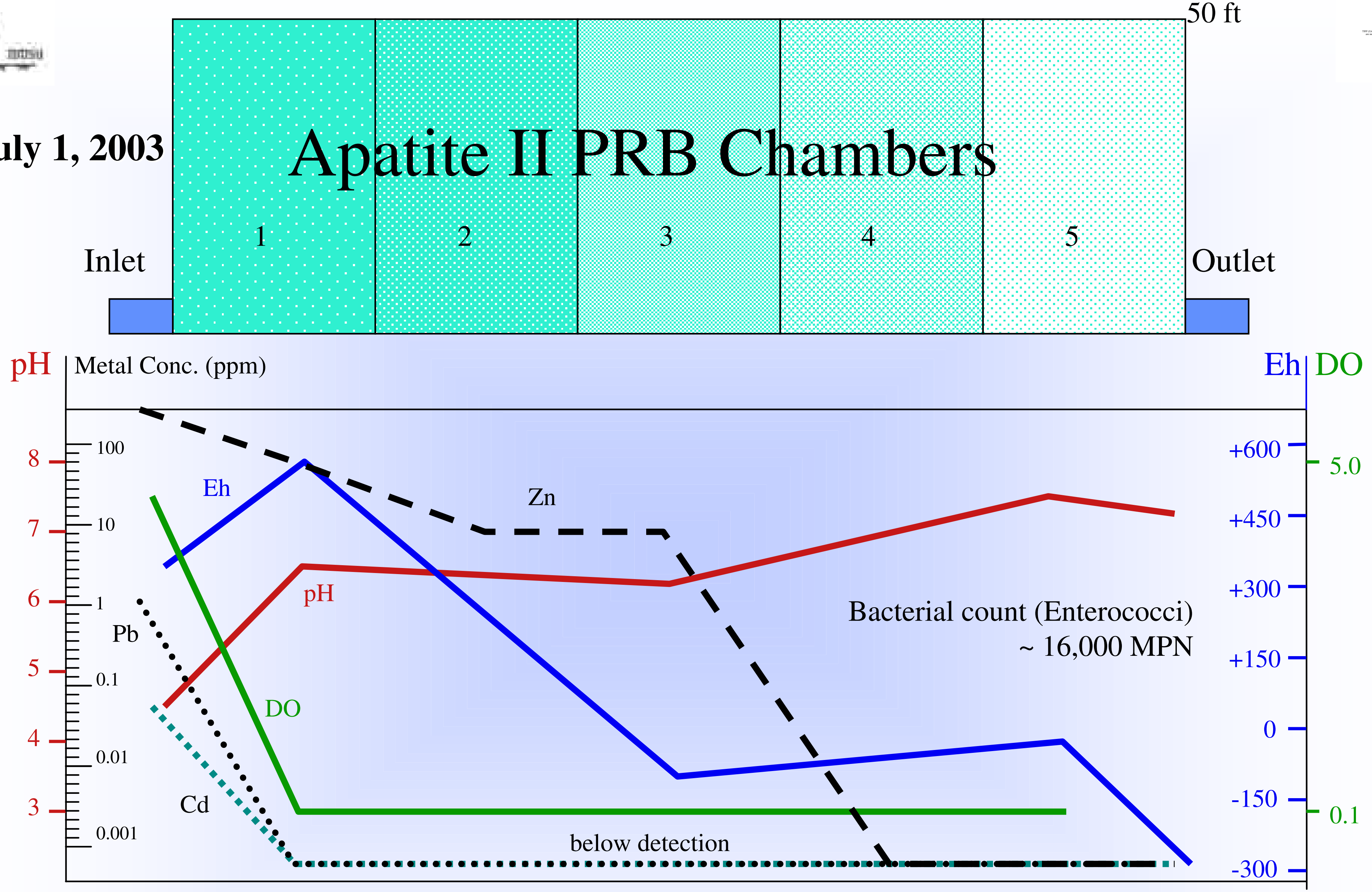
QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

First Chamber of the West Cell

Note ZnS precipitation on almost all surfaces: restricted to the first chamber.

July 1, 2003

Apatite II PRB Chambers



Inlet [sulfate] = 216 ppm
[nitrate] = 0.58 ppm
[phosphorous] = 0.04 ppm
Bacterial count < 1 MPN

Outlet [sulfate] < 0.05 ppm
[nitrate] < 0.02 ppm
[phosphorous] ~ 9-10 ppm
Bacterial count < 1MPN

Fifth Chamber of the East Cell - essentially unreacted

Based on periodic daily metal-loading averages from the Idaho State DEQ, the Apatite II PRB at Success Mine has sequestered

> 10,000 lbs of Zn
> 100 lbs of Cd,
> 150 lbs of Pb and

over the 3.5 years since it was emplaced.

Field investigations indicate less than 40% of the Apatite II is spent.

Nevada Stewart Mine Adit Apatite II PRB (Zn-contaminated outflow)

animal toxicity studies: ***Ceriodaphnia dubia*****, a freshwater invertebrate**

by the Idaho DEQ ***Pimephales promelas*****, the fathead minnow**

Untreated outflow:

No Observed Acute Effect Level (NOAEL)

= 1.6% for *C. dubia* (completely lethal)

= 12.5% for *P. promelas* (highly lethal)

Fifty-percent Lethal Concentration (LC_{50})

= 2.2% for *C. dubia*

= 26.4% for *P. promelas*

after Apatite II PRB:

No Observed Acute Effect Level (NOAEL)

= 100% for *C. dubia* (completely non-lethal)

= 100% for *P. promelas* (completely non- lethal)

Fifty-percent Lethal Concentration (LC_{50})

= 95% for *C. dubia* (completely lethal)

= 100% for *P. promelas* (highly lethal)

no different than the control samples.