

**4TH INTERNATIONAL CONFERENCE ON ACID ROCK
DRAINAGE**

**TREATMENT OF ACID MINE DRAINAGE
PART I**

**JUNE 1, 1997
VANCOUVER, BC
08:30-12:00**

**Authors: Jim Gusek
Tom Wildeman**

PASSIVE TREATMENT OF MINE WATERS

- I. CHEMICAL PRINCIPLES - TOM WILDEMAN**

- II. DESIGN PRINCIPLES - JIM GUSEK**

- III. LABORATORY (PROOF-OF-PRINCIPLE)
STUDIES - TOM WILDEMAN**

- IV. BENCH SCALE PROJECTS - JIM GUSEK**

- V. PILOT SCALE PROJECTS - TOM WILDEMAN**

- VI. FULL-SCALE PROJECTS - JIM GUSEK**

**Jim Gusek & Tom Wildeman, Knight Piesold, LLC,
1050 17th Street, Suite 500, Denver, CO 80265-0500.
Phone 303-6298788. FAX 303-6298789**

COURSE STRUCTURE

- A. TRY TO EMPHASIZE COLD WEATHER SITUATIONS**
- B. TRY TO EMPHASIZE METAL-MINING OPERATIONS**
- C. USE AS MANY EXAMPLES AS POSSIBLE.**
- D. IN THE SPECTRUM OF COURSE DESIGN**

**LESS MATERIAL,
MORE INTERACTIVE
PROBLEM SOLVING**

**MORE INFORMATION
TRANSFER, LESS
WORKSHOP ACTIVITIES**

**THIS COURSE LEANS TOWARDS INFORMATION
TRANSFER.**

- E. NOT USING THE HANDBOOK BECAUSE FOCUS OF
THE COURSE IS NOT JUST ON WETLANDS.**

WARNINGS

- 1. THE GEOTECHNICAL DESIGN PRINCIPLES ARE
ESTABLISHED BUT IN SOME CASES, APPLYING
THESE PRINCIPLES TO ACTUAL SITUATIONS HAS
NOT BEEN DONE.**
- 2. DESIGN & CONSTRUCTION OF TREATMENT
SYSTEMS IS A DEVELOPING TECHNOLOGY, NOT
EVERYTHING THAT IS SAID WILL STAND THE TEST
OF TIME.**
- 3. THE INSTRUCTORS WILL TAKE THE CONCEPTS TO
THE EDGE OF DEVELOPMENT & TRY TO LEAVE YOU
WITH METHODS TO APPLY THE TECHNOLOGY TO
YOUR SITUATION.**

RESOURCE LIST

Wildeman, T.R. J.J. Gusek, A. Miller, and J. Fricke, 1997. Metals, sulfur, and carbon balance in a pilot reactor treating lead in water. In: Proceedings of the 4th In Situ and On-Site Bioremediation Symposium, Vol. 3, pp 401-406, Battelle Press, Columbus, OH.

Wildeman, T., and D. Updegraff, 1997, Passive bioremediation of metals and inorganic contaminants. In: Perspectives in Environmental Chemistry, D.L. Macalady, Ed. Oxford University Press, New York.

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Gusek, J.J., and T.R. Wildeman, 1996, New developments in passive treatment of acid rock drainage, Technical Solutions for Pollution Prevention in the Mining and Mineral Processing Industries, Engineering Foundation Conference, January, 1995, Palm Coast, FL.

Gusek, J.J., 1995, Passive-treatment of acid rock drainage: What is the potential bottom line? Mining Engineering, vol. 47, pp. 250-253.

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T. R. Wildeman, Gusek, J. J., East, D. R., and A. de Villiers, 1995, Design of a tailing lining and cover to mitigate potential acid rock drainage: A geochemical engineering project. In: Proceedings of the 12th annual meeting of ASSMR, G. E. Schuman and G. F. Vance Eds., ASSMR, Princeton WV, pp. 681-687.

T. R. Wildeman, L. H. Filipek, and J. Gusek. 1994. Proof-of-Principle Studies for Passive Treatment of Acid Rock Drainage and Mill Tailing solutions from a Gold Operation in Nevada. In Proceedings of the International Land Reclamation and Mine Drainage Conference, Vol. 2, pp. 387-394. U.S. Bureau of Mines Special Publication SP 06B-94.

Wildeman, T. R., J. Cevaal, K. Whiting, J. J. Gusek, and J. Scheuring. 1994. "Laboratory and Pilot-Scale Studies on the Treatment of Acid Rock Drainage at a Closed Gold-Mining Operation in California." In Proceedings of the International Land Reclamation and Mine Drainage Conference, Vol. 2, pp. 379-386. U.S. Bureau of Mines Special Publication SP 06B-94.

D. R. East, L. H. Filipek, A. de Villiers, and T. R. Wildeman, Design of a tailing facility to mitigate potential acid rock drainage. In: *Hydrometallurgy 94*, Chapman and Hall, London, pp. 961-969, 1994.

Wildeman, T. R., Updegraff, D. M., Reynolds, J. S., and J. L. Bolis. Passive Bioremediation from Water Using Reactors or Constructed Wetlands. In: *Emerging Technology for Bioremediation of Metals*, J. L. Means and R. E. Hinchey, eds. Lewis Publishers, Ann Arbor, MI, pp. 13-25, 1994.

Wildeman, T. R., et. al. Passive Treatment Methods for Manganese: Preliminary Results from Two Pilot Sites. Proceedings of the 1993 National Meeting of the American Society of Surface Mining and Reclamation, ASSMR, Princeton, WV, 1993, pp 665-677.

Bolis, J. L., Wildeman, T. R., and H. E. Dawson. Hydraulic Conductivity of Substrates used for Passive Acid Mine Drainage Treatment. Proceedings of the 1992 National Meeting of the American Society of Surface Mining and Reclamation, American Soc. Surf. Mining and Reclam., Princeton, WV, 1992, pp 79-89.

Duggan, L.A., Wildeman, T. R., and D. M. Updegraff. The Aerobic Removal of Manganese from Mine Drainage by an Algal Mixture Containing *Cladophora*. Proceedings of the 1992 National Meeting of the American Society of Surface Mining and Reclamation, American Soc. Surf. Mining and Reclam., Princeton, WV, 1992, pp 241-248.

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Wetland Design for Mining Operations

Thomas Wildeman, Gregory Brodie, James Gusek

This volume, originally published in March 1992, combines the results of two projects which use constructed wetlands for the treatment of mine drainage.

The Colorado School of Mines have developed subsurface wetland systems that emphasize anaerobic processes for the treatment of drainage from metal mines. The Tennessee Valley Authority have successfully developed surface style wetlands that emphasize aerobic removal processes. The volume is divided into four sections:

- Section 1: Anaerobic constructed wetlands handbook. Final Report EPA-ETP Big Five Wetland Project. Edited by Thomas Wildeman
- Section 2: Aerobic Constructed Wetlands Handbook. Staged, Aerobic, Wetlands-Based Acid Drainage Treatment Systems: Design, Construction, and Operation. Written by Gregory A. Brodie
- Section 3: Supplementary Papers for the Aerobic Constructed Wetlands Handbook
- Section 4: Supplementary Papers for the Anaerobic Constructed Wetlands Handbook and Recent Papers on New Wetland Concepts

The concepts, procedures, and methods introduced in this volume may or may not be suitable to a specific site. Wetlands for the control of metal mine drainage is a new technology, developments are occurring rapidly. It is anticipated that this volume will be updated as the results of continuing research becomes available to the industry.

1993; Soft cover, 8.5 x 11; 408 pages. BiTech. ISBN 0-92109-27-9. \$88.00 CDN/\$80.00 US

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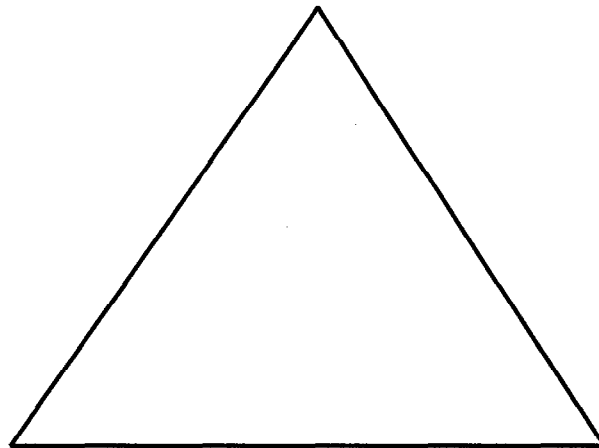
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THE TRIANGLE OF FRUSTRATION IN ENVIRONMENTAL TREATMENT

MONEY



LAND AVAILABILITY

TIME

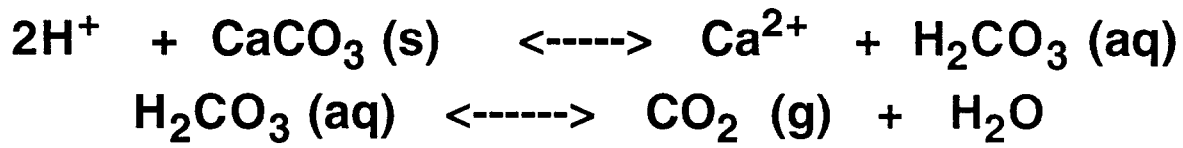
TYPICAL MINE WATERS -- ABOVE pH = 5.5 -- (CONC. IN mg / L)

SPECIES	#1	#2	#3	#4	#5	#6	STDS
pH	6.0	5.7	5.9	5.9	5.5	6.5	6-9
Al			21		0.2		---
Mn		8	20		20	2	0.05
Fe	1.4	12	580	0.5	40	110	0.05
Co	1.2			0.3			---
Ni	18		0.10	1.4			---
Cu	0.6		0.03	7	1		1.0
Zn	0.4		0.24	1	10		5.0
As			0.01	3			0.05
Se				1			0.01
Cd				0.01			0.01
Pb			0.02		0.07		0.05
SO₄	1300		750		900	1150	---

ALKALINITY GENERATION: STEP ONE

CaCO₃ NEUTRALIZATION OF ACID DRAINAGE

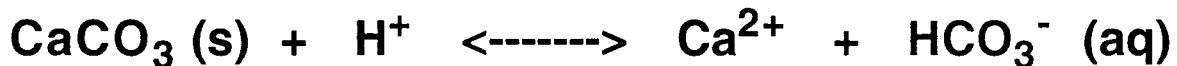
BELOW pH 6.3:



ABOVE pH 6.3:



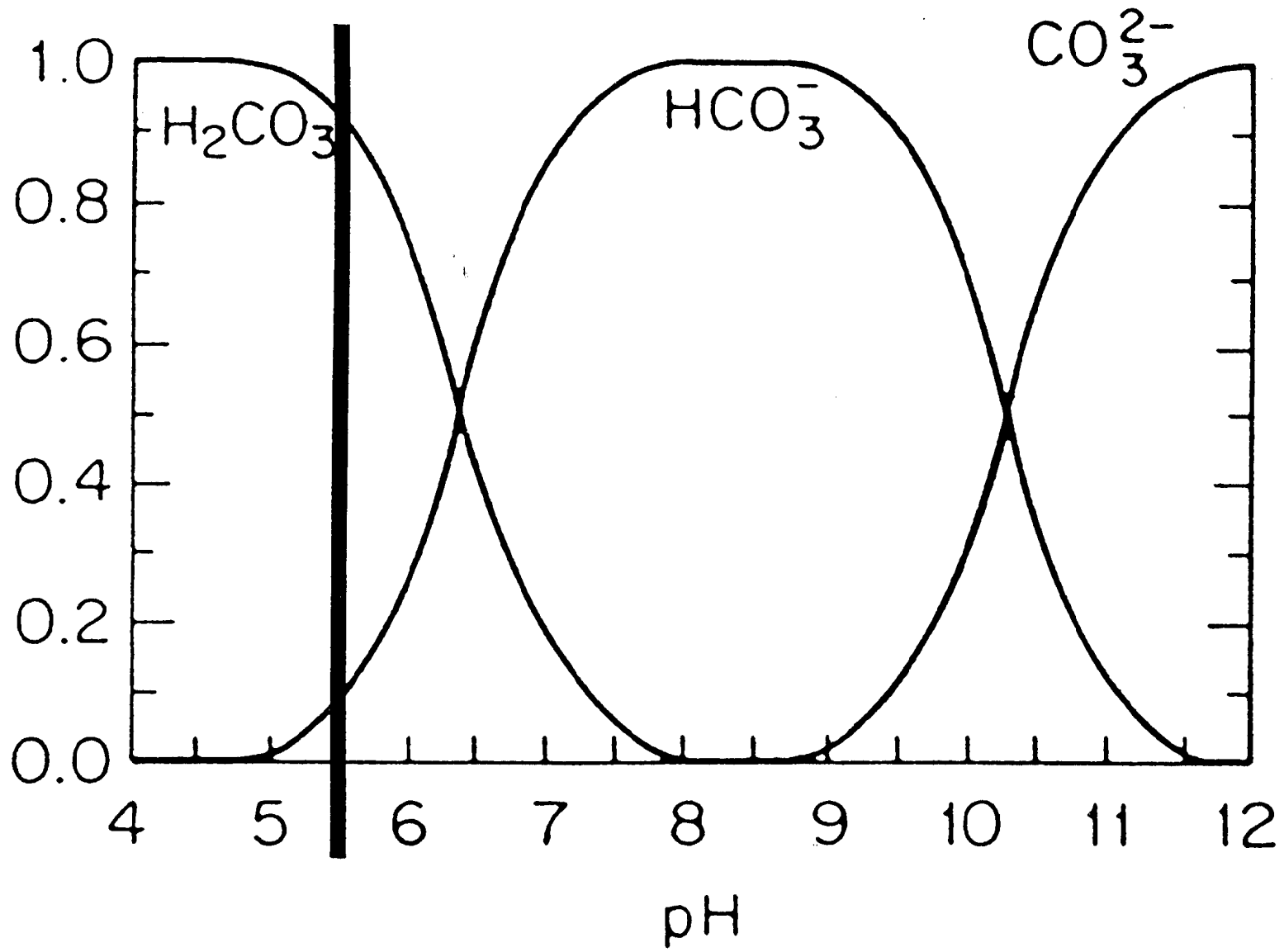
THEN NEUTRALIZATION IS:



SUMMARY

1. RAISING THE pH TO >6.0 IS ESSENTIAL TO STABILIZING MINE DRAINAGE.
2. AT THIS pH, Fe³⁺ & Al³⁺ WILL DEFINITELY HYDROLYZE TO CREATE MINERAL ACIDITY.
3. THE OXIDATION OF Fe²⁺ IS RAPID ENOUGH TO GENERATE MINERAL ACIDITY.
4. THE RATE OF OXIDATION OF Mn²⁺ IS SLOW & ITS CONTRIBUTION TO ACIDITY IS LESS WORRISOME.

Fraction as designated species



ALKALINITY GENERATION: STEP TWO

- 1. REMOVAL OF Mn BY FORMATION OF MnO_2 IS BEST ACHIEVED WHEN THE pH IS >8.0 .**
- 2. AEROBIC REMOVAL OF Zn, Cu, & Cd IS BEST ACHIEVED WHEN THE pH IS >8.0 .**

SOURCE OF ALKALINITY

- 1. HCO_3^- WILL RAISE THE pH TO ABOVE 8. HOWEVER, THE RATE OF DISSOLUTION OF LIMESTONE IS VERY SLOW ABOVE pH =6.**
- 2. REQUIRE A DIFFERENT SOURCE OF HCO_3^- OR PERHAPS A SOURCE OF OH^- .**
- 3. IN ACTIVE TREATMENT, JUST ADD MORE LIME. IN PASSIVE TREATMENT, THIS NEEDS TO BE GENERATED NATURALLY.**

FURTHER ISSUES

- 1. IF THE pH IS TOO HIGH ABOVE 8, OTHER SPECIES SUCH AS As, U, & AI MAY BE RELEASED INTO THE WATER.**

**HALF-LIVES FOR OXYGENATION OF Fe(II) & Mn(II) SPECIES
(OM=) MEANS BOUND TO A METAL OXIDE SURFACE**

		Fe (II) SPECIES	APPROX. pH	Mn (II) SPECIES	APPROX. pH
HALF LIFE	100 y	Fe^{2+}	~ 3	Mn^{2+}	~ 3
	1 y			MnOH^+	~ 7
	1 d			Mn(OM=)_2	~ 7
	1 h	Fe(OM=)_2	~ 7	Mn(OH)_2	> 8
	1 min	FeOH^+	~ 7		
	1 s				
	1 ms	Fe(OH)_2	~ 8		

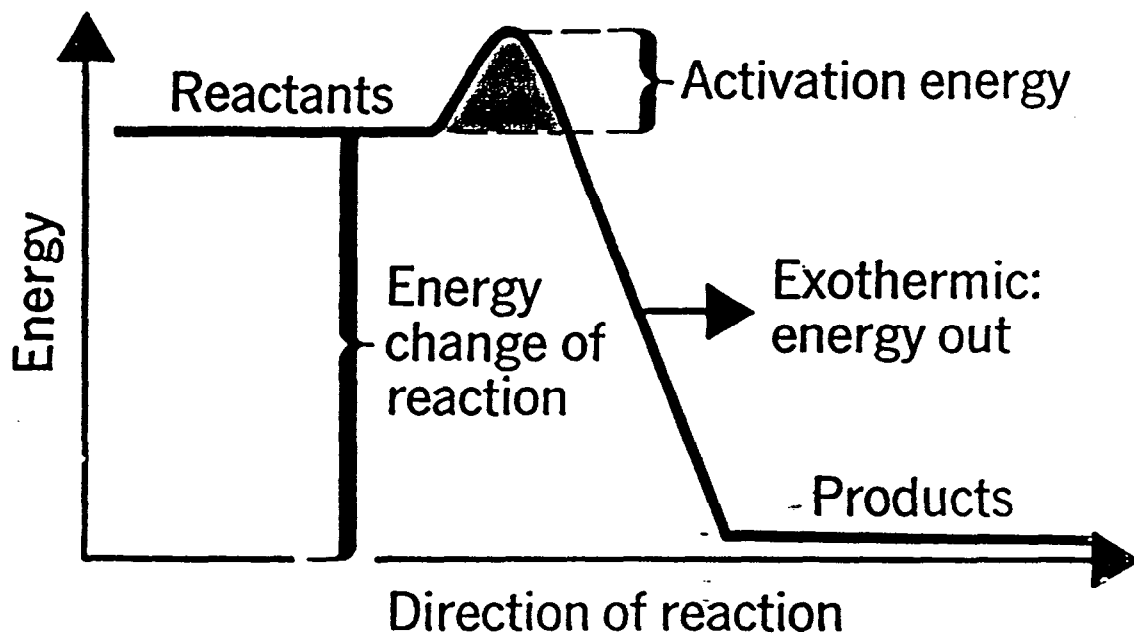
From Wehrli & Stumm (1989)

**METALS REMOVAL THROUGH
PASSIVE MICROBIAL MEDIATION**

HOW CONSTRUCTED WETLANDS WORK

**THOMAS WILDEMAN & DAVID UPDEGRAFF
DEPT. CHEMISTRY & GEOCHEMISTRY
COLORADO SCHOOL OF MINES**

GEOMICROBIOLOGY 101



AQUATIC ENVIRONMENT
NATURALLY OCCURRING COMPOUNDS
ENERGY RELEASED CHEMICALLY
SLOW REACTION

RESULT IS BACTERIAL MEDIATION

TWO OBJECTIVES

1) RAISE pH

2) REMOVE METALS AS:

- A) SULFIDES: CuS , PbS , ZnS , CdS , FeS
- B) HYDROXIDES: $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, MnO_2
- C) CARBONATES: FeCO_3 , MnCO_3 , ZnCO_3

USE BACTERIA FOUND IN TYPICAL AQUATIC ENVIRONMENTS BECAUSE

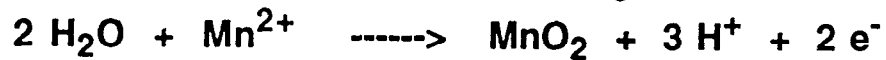
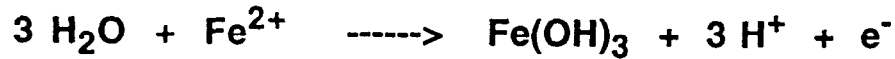
- 1) REQUIRE THE PRODUCTS OF BACTERIAL ACTIVITY MORE THAN ENZYMATIC USE OF THE METALS.
- 2) A CONSORTIUM OF BACTERIA RATHER THAN A SINGLE SPECIES ARE GENERATING THE PRODUCTS.

**IN AQUATIC ENVIRONMENTS
MICROBIAL ACTIVITY
CENTERS ON
OXIDATION - REDUCTION CHEMISTRY**

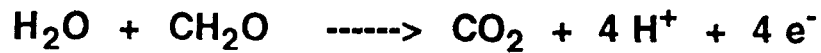
**COMPOUNDS DONATING ELECTRONS: OXIDIZED
COMPOUNDS ACCEPTING ELECTRONS: REDUCED**

ELECTRON DONORS

METAL OXIDATION

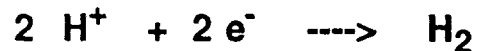
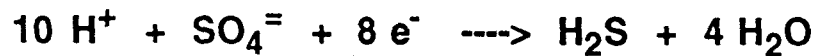
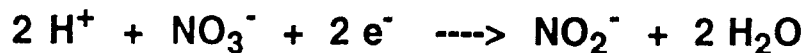


ORGANIC DECAY



REACTIONS RELEASE H⁺

ELECTRON ACCEPTORS



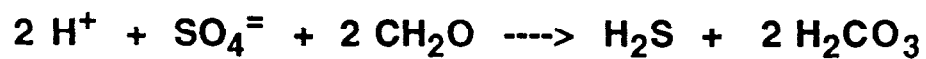
REACTIONS CONSUME H⁺

3 POSSIBILITIES FOR TOTAL REACTION

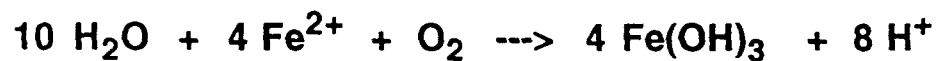
BALANCE H⁺'S

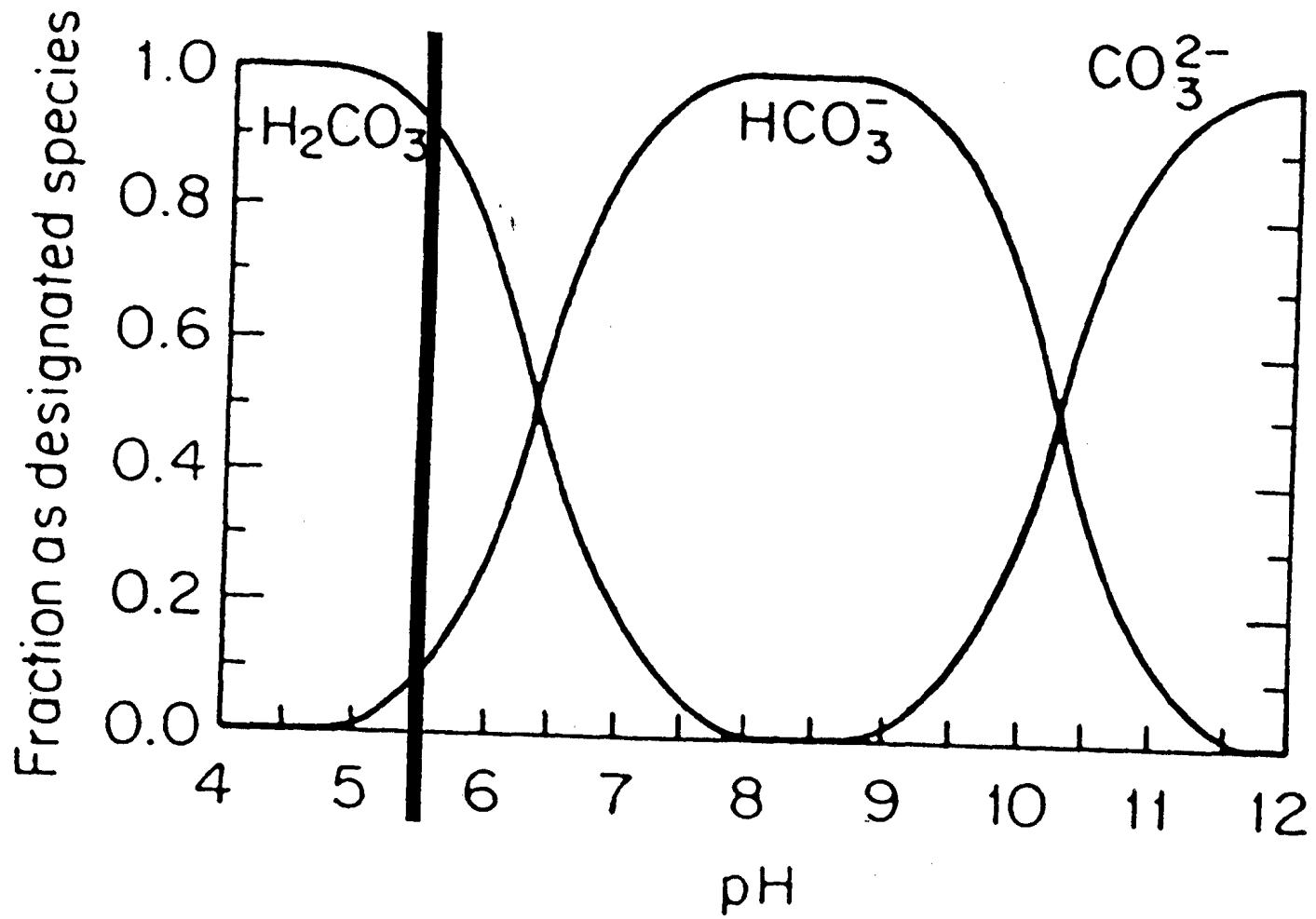


CONSUME H⁺'S



GENERATE H⁺'S





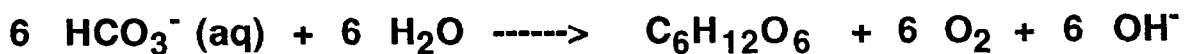
GUIDELINES: AEROBIC MICROBIAL SYSTEMS

AEROBIC SYSTEMS FUNCTION BEST
WHEN WATER pH > 5.5.

1) HCO_3^- (AS MEASURED BY ALKALINITY)
SHOULD BE PRESENT IN THE WATER.

2) IF: $\text{Fe}^{2+} \text{ -----> Fe(OH)}_3$
OR: $\text{Mn}^{2+} \text{ -----> MnO}_2$
pH WILL BE LOWERED ESPECIALLY IN
WATERS WHERE pH < 5.5.

3) PHOTOSYNTHESIS IS AN IMPORTANT
PROCESS FOR INCREASING THE pH.

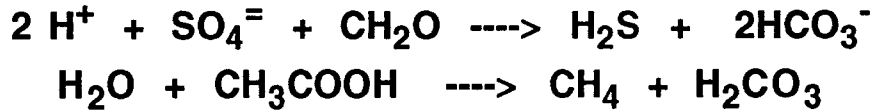


COMPARE WITH

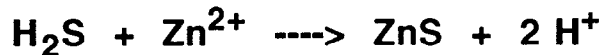


GUIDELINES: ANAEROBIC MICROBIAL SYSTEMS

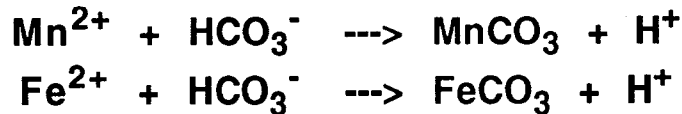
- 1) USE MICROBES TO TRANSFORM STRONG ACIDS INTO WEAK ACIDS.



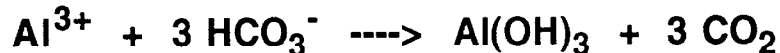
- 2) USE HYDROGEN SULFIDE TO PRECIPITATE METAL SULFIDES.



- 3) USE BICARBONATE TO PRECIPITATE METAL CARBONATES.



- 4) USE HIGHER pH TO PRECIPITATE METAL HYDROXIDES



SUMMARY

- A) THE SULFATE-REDUCING CONSORTIUM WORKS WELL AT RAISING pH & CAUSING METAL PRECIPITATION.
- B) TO BE EFFECTIVE, THE pH RAISING REACTIONS HAVE TO DOMINATE OVER THE METAL PRECIPITATION REACTIONS.

MICROBIAL SYSTEM COMPARISON

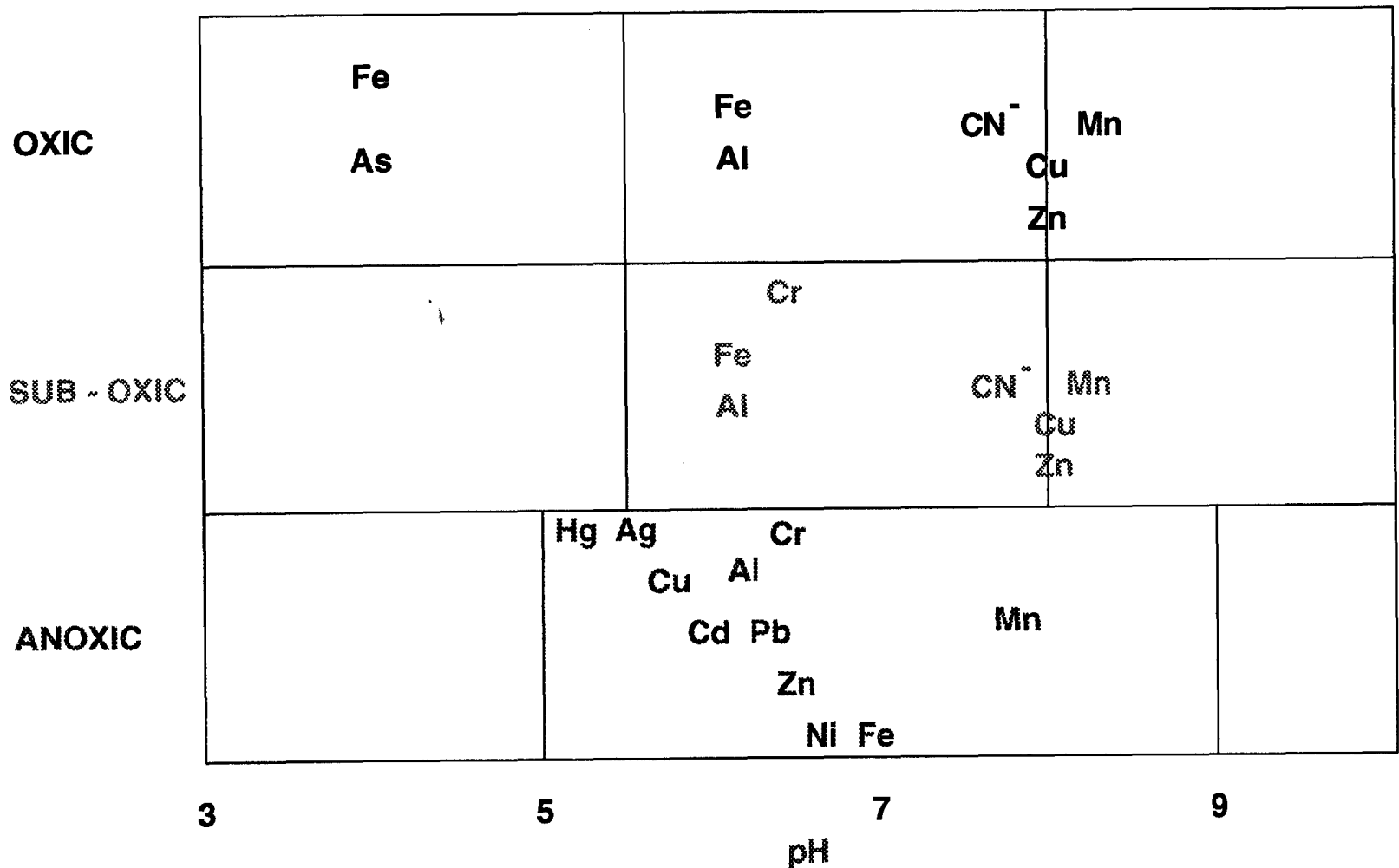
AEROBIC

1. EMPHASIZE OXIDATION
2. SURFACE FLOW OF WATER
3. OXIDE PRECIPITATES
4. PROCESSES CAN LOWER pH
5. OPERATE BEST AT pH > 5.5
6. MIGHT FREEZE IN THE WINTER
7. REMOVES Fe QUITE WELL

ANAEROBIC

1. EMPHASIZE REDUCTION
2. SUBSURFACE FLOW OF WATER
3. SULFIDE PRECIPITATES
4. PROCESSES CAN RAISE pH
5. CAN BE EFFECTIVE AT pH ~ 2.5
6. CAN OPERATE THROUGH THE WINTER
7. REMOVES OTHER HEAVY METALS QUITE WELL.

REMOVAL OF INORGANICS IN THE AQUATIC ENVIRONMENT



UNKNOWN: As, Se, U

APPLICATION OF CRITERIA IS A CONTINUUM

ACTIVE <-----> **PASSIVE**

pH
< 2.5 <-----> > 6.0

CONDUCTIVITY
> 4000 <-----> < 1000

ACIDITY <-----> **ALKALINITY**
> 700 <-----> > 50

Fe + Al
> 250 mg / L <-----> < 25 mg / L

REGULATORY LIMITS FOR WATERS
(as interpreted by T. R. Wildeman)

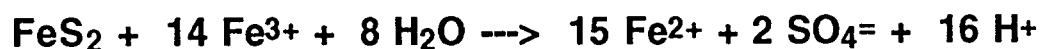
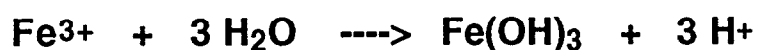
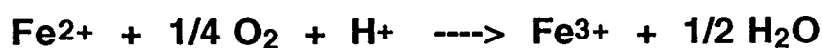
SPECIES	UNITS	DRINKING WATER		MINING NEVADA	CLEAR CK. CO AQUATIC
		PRIMARY	SECONDARY		
pH	S. U.	---	6.5 - 8.5	6.5 - 8.5	6.5 - 9.0
Al	mg / L	---	0.05-0.2	0.05	0.75
Fe	mg / L	---	0.3	0.3-0.6	0.3 (DISS.)
Mn	mg / L	---	0.05	0.1	0.05 (DISS.)
Zn	mg / L	---	5	5	0.012 (DISS.)
Cu	mg / L	---	1.0	1.0	0.009 (DISS.)
Pb	μg / L	50	---	0.5	0.03 (TOTAL)
As	μg / L	50	---	0.5	0.05 (TOTAL)
TDS	mg / L	---	500	500-1000	400
SO ₄ ⁼	mg / L	---	250	250-1000	250

BEST AVAILABLE TECHNOLOGIES ESTIMATES
(GUESSES FROM PRESENT EXAMPLES BY T. R. WILDEMAN)

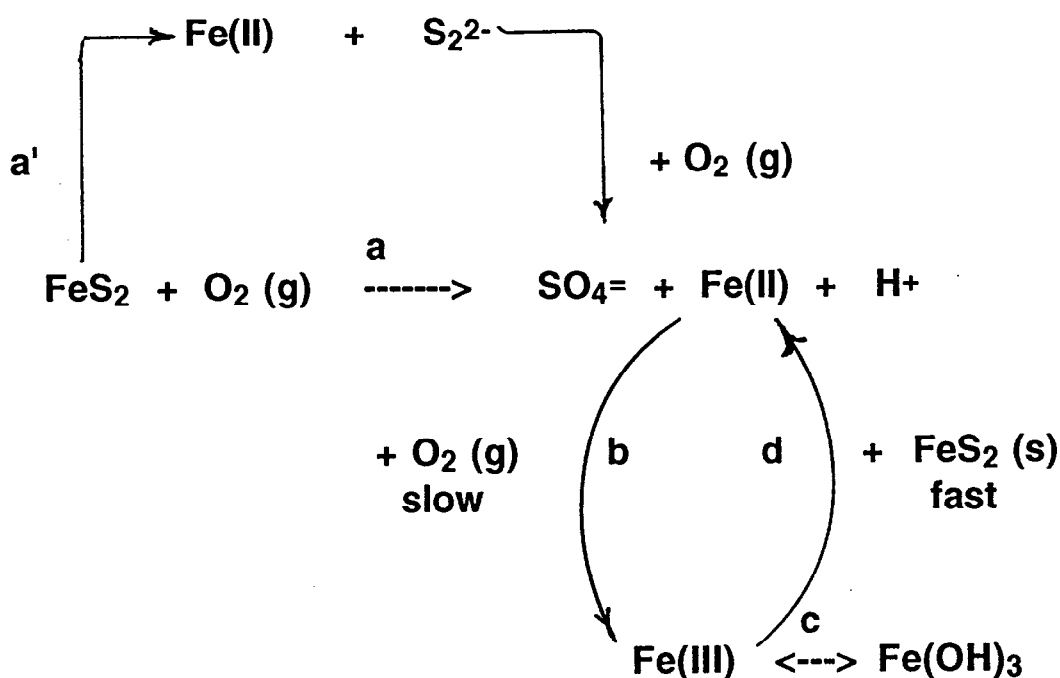
SPECIES	UNITS	REALISTIC	THEORY	METHOD
pH	S. U.	6.5-8.5	---	AEROBIC WETLAND
Al	mg / L	0.1	<0.05	AEROBIC WETLAND ANAEROBIC SYSTEM
Fe	mg / L	<0.3	---	AEROBIC WETLAND
Mn	mg / L	0.1	<0.05	ALGAL POND AEROBIC WETLAND
Zn	mg / L	0.5	<0.03	ANAEROBIC SYSTEM
Cu	mg / L	<0.01	<0.001	ANAEROBIC SYSTEM
Pb	µg / L	<0.02	---	ANAEROBIC SYSTEM
As	µg / L	<0.05	---	ALGAL POND AEROBIC WETLAND
SO ₄ ⁼	mg / L	<250	---	ANAEROBIC SYSTEM

FROM STUMM AND MORGAN, 1981

THE STOICHIOMETRY FOR THE DISSOLUTION OF PYRITE IS:



THE ACCEPTED REACTION PATH FOR THE DISSOLUTION OF PYRITE IS:



DETERMINING ACID PRODUCTION POTENTIAL *APP*

CLOSEST ACTUAL SITUATION



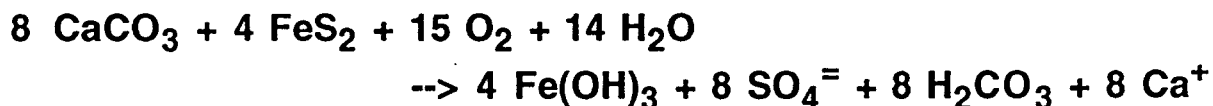
DETERMINE PYRITE TO FIND ACID PRODUCED

CONSERVATIVE SITUATION



DETERMINE ALL FORMS OF REDUCED SULFIDE TO FIND ACID
PRODUCED. DO NOT INCLUDE SULFATE

STOICHIOMETRY



$$1 \text{ gm S} \times \frac{1 \text{ mole S}}{32.08 \text{ gm S}} \times \frac{8 \text{ mole CaCO}_3}{8 \text{ mole S}} \times \frac{100.09 \text{ gm CaCO}_3}{1 \text{ mole CaCO}_3} \\ = 3.125 \text{ g CaCO}_3$$

ANALYTICAL REPORT

REPORTED AS TONS CaCO_3 NEEDED PER 1000 TON OF ROCK

$$\% S \times 1 \text{ TON S} / 100 \text{ TON ROCK} \times 10 \times 3.125 = \text{APP}$$

OR

$$\% S \times 31.25 = \text{APP} = \text{TON } \text{CaCO}_3 / 1000 \text{ TON OF ROCK}$$

**ACID NEUTRALIZATION POTENTIAL (ANP)
OR
NEUTRALIZATION POTENTIAL (NP)**

I. DETERMINATION METHOD DICTATES RESULTS

- A. DIGEST IN EXCESS HCl.
- B. TITRATE EXCESS WITH NaOH TO pH = 7.



II. WHAT IS INCLUDED IN ANP

- A. ALL CARBONATES BECAUSE H_2CO_3 GAS IS FORMED.
- B. OTHER MINERALS ARE PROBABLY NOT ACCOUNTED CONSIDER $\text{Al}(\text{OH})_3$ AS AN EXAMPLE.



MOST OTHER MINERALS WOULD CONSUME SAME AMOUNT OF HCl AND NaOH, ESPECIALLY BECAUSE NaOH TITRATION IS CONDUCTED TO PH OF 7.

**ACID NEUTRALIZATION POTENTIAL (ANP)
OR
NEUTRALIZATION POTENTIAL (NP)**

ANALYTICAL REPORT

REPORT AS TONS CaCO₃ PROVIDED PER 1000 TON OF ROCK

$$\frac{\text{MOLE HCL}}{\text{gm ROCK}} \times \frac{1 \text{ MOLE CaCO}_3}{2 \text{ MOLE HCL}} \times 100.09 \text{ gm CaCO}_3 = \text{gm CaCO}_3 / \text{gm ROCK}$$

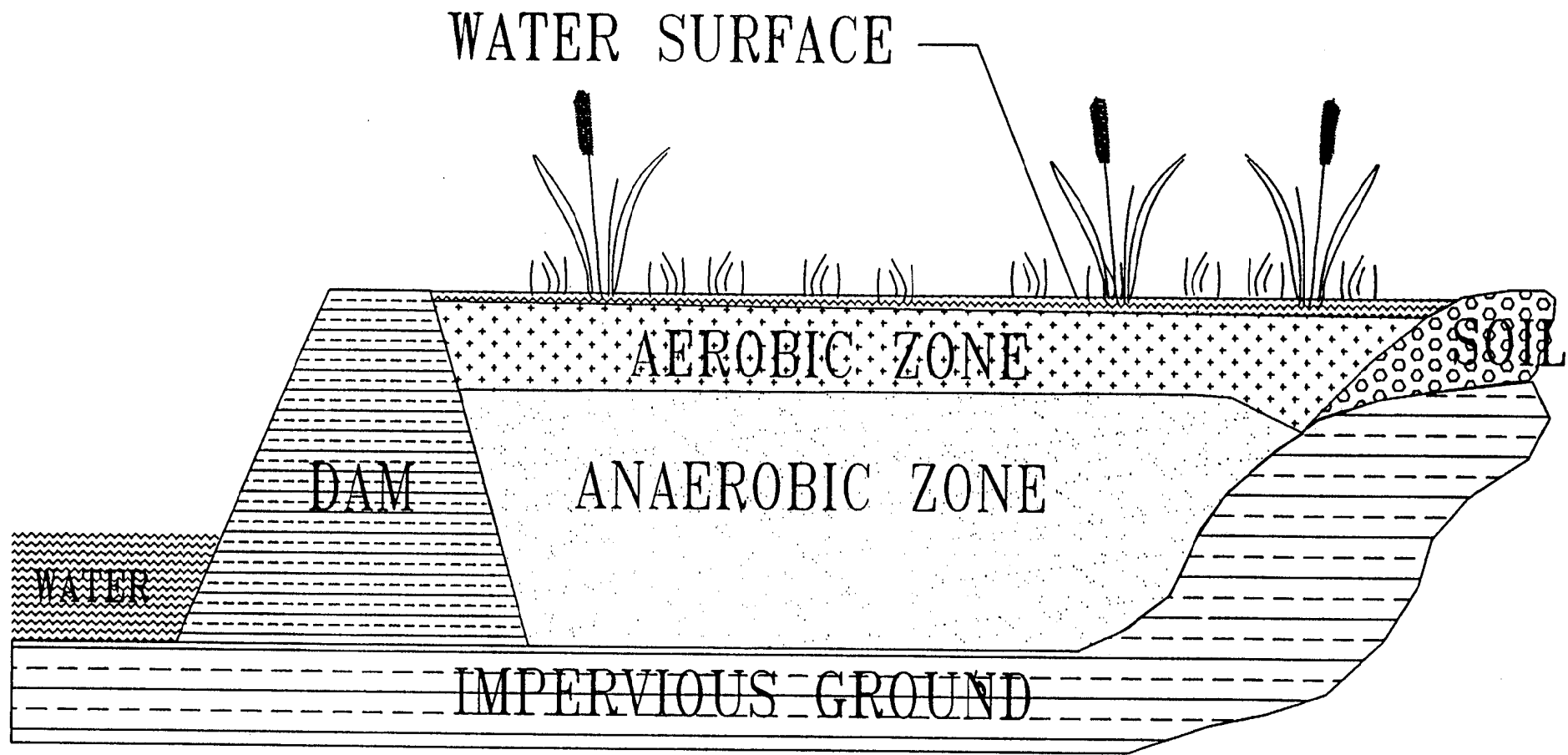
$$\frac{\text{gm CaCO}_3}{\text{gm ROCK}} \times 1000 = \text{TON CaCO}_3 / 1000 \text{ TON OF ROCK}$$

SUMMARY EQUATION

$$\frac{\text{MOLE HCL}}{\text{gm ROCK}} \times 50.0 \times 1000 = \text{TON CaCO}_3 / 1000 \text{ TON OF ROCK}$$

CAUTION

**COULD CONSUME MORE NaOH THAN HCl & HAVE
A NEGATIVE ANP**



TYPICAL WETLAND ECOSYSTEM

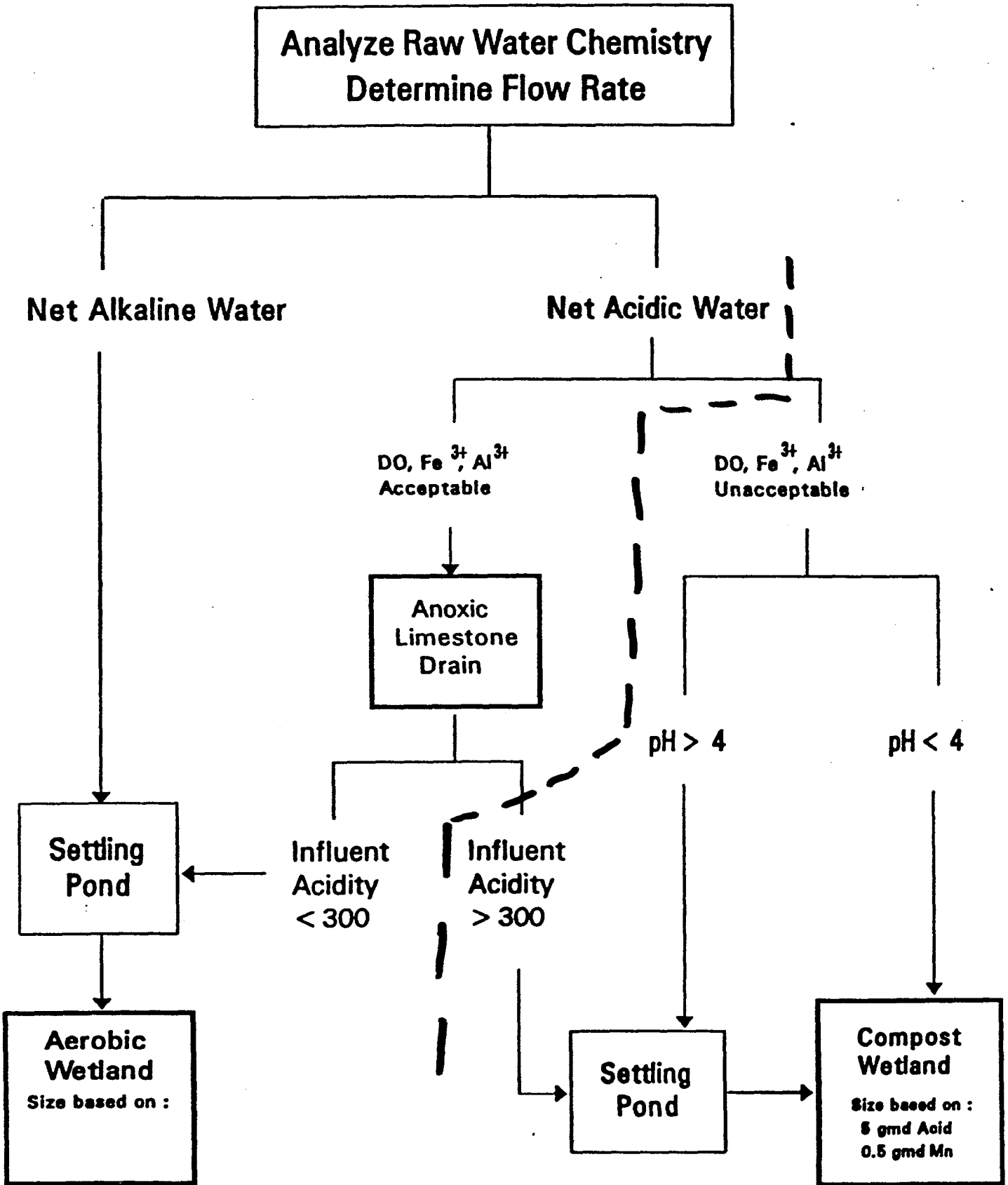


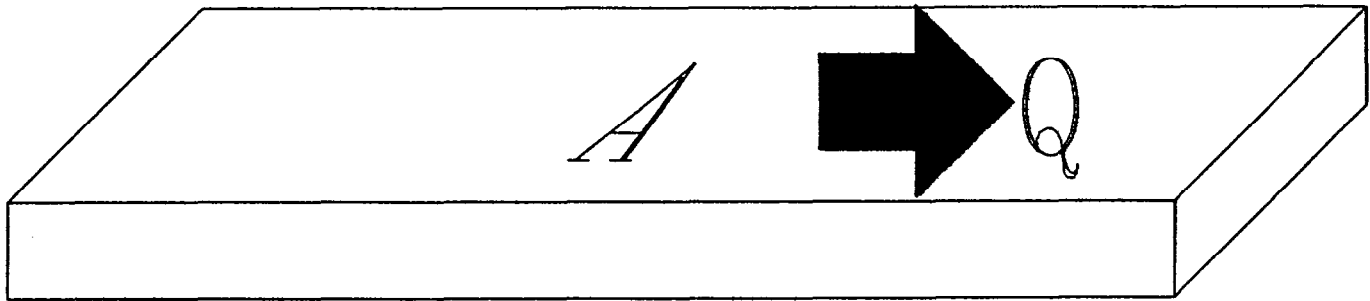
FIGURE 1. Flowchart for designing and sizing passive mine drainage treatment systems.

PASSIVE TREATMENT CELL COMPARISON

AEROBIC	ANAEROBIC
1. Emphasize Oxidation	1. Emphasize Reduction
2. Surface Flow of water	2. Subsurface Flow of water
3. Oxide Precipitates	3. Sulfide Precipitates
4. Processes Lower pH	4. Processes Can Raise pH and even generate excess alkalinity
5. Operate Best at pH>5.5	5. Can Be Effective at influent pH 2.5
6. Might Freeze in Winter	6. Can Operate Through the Winter
7. Remove Fe, Mn and As Quite Well	7. Removes Fe and Other Heavy Metals Quite Well
	8. Can Remove Dissolved Oxygen Upstream of an Anoxic Limestone Drain

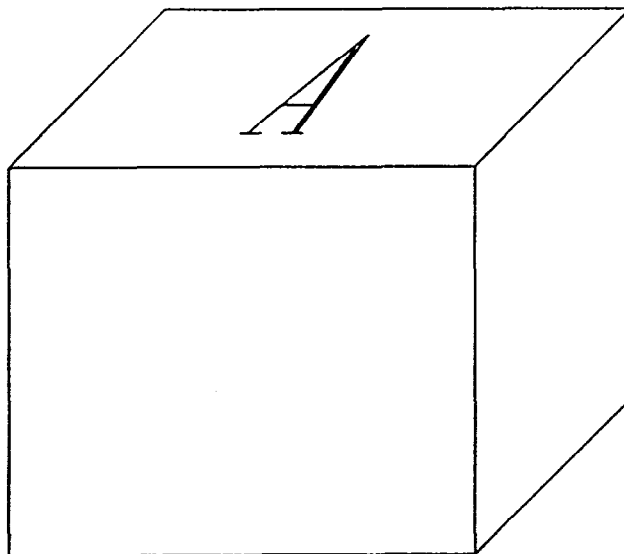
WETLAND CONFIGURATIONS

AEROBIC



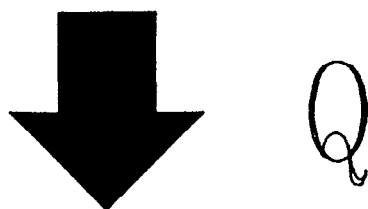
FLOW ACROSS THE SURFACE,
AREA (A) IS SURFACE AREA (PARALLEL TO FLOW)
CONFIGURATION MAXIMIZES OXYGEN CONTACT

ANAEROBIC



GRAVITY FLOW,
AREA (A) IS
PERPENDICULAR
TO FLOW
DIRECTION

CONFIGURATION
MINIMIZES
OXYGEN CONTACT



PHASED DESIGN OF PASSIVE TREATMENT SYSTEMS

- **Laboratory Studies (Proof of Principle)**
- **Bench-Scale Tests (Kinetic in Field or Lab
- trash can sized reactors)**
- **Pilot-Scale Systems (5 gpm typical flow)**
- **Full-Scale Systems (use pilot as module?)**

PASSIVE TREATMENT SYSTEM **DESIGN COMPONENTS**

- **AEROBIC CELLS**
- **ANOXIC LIMESTONE DRAINS**
- **LIMESTONE CHANNELS**
- **ANOXIC PONDS**
- **ANAEROBIC CELLS**
- **ANOXIC ALKALINITY GENERATORS**
- **FLUID COLLECTION & DIVERSION**
- **FLUID DISTRIBUTION and INSTRUMENTATION**

MORE PASSIVE TREATMENT **DESIGN COMPONENTS**

- **SAPS**
**(Successive Alkalinity
Producing Systems)**

- **“ALUMINATORS”**
**(Flushable aluminum-stripping
pre-treatment cells for Anoxic
Limestone Drains)**

AEROBIC

PASSIVE TREATMENT SYSTEM

DESIGN CRITERIA SUMMARY

**All components are designed based on
influent water chemistry**

- **AEROBIC CELLS** - vary the surface area for removal of Fe, Al, Mn, As, CN, Hg and to raise pH; from 2 to 11 grams Fe removed per day per m² of area.
- **ANOXIC LIMESTONE DRAINS (ALD)** - vary retention time (about 24 hrs) and grain size to add alkalinity to ARD prior to aerobic cells; this buffers against iron hydrolysis reactions.
- **ANOXIC PONDS** - (used upstream of ALD's) vary volume to decrease dissolved oxygen, to reduce Fe(III) to Fe(II) and to remove Al.
- **FLUID COLLECTION/DIVERSION** - try to minimize oxygen contact for ALD; maximize oxygen contact for aerobic cells
- **FLUID DISTRIBUTION and INSTRUMENTATION** - should be simple to operate, durable and inexpensive.

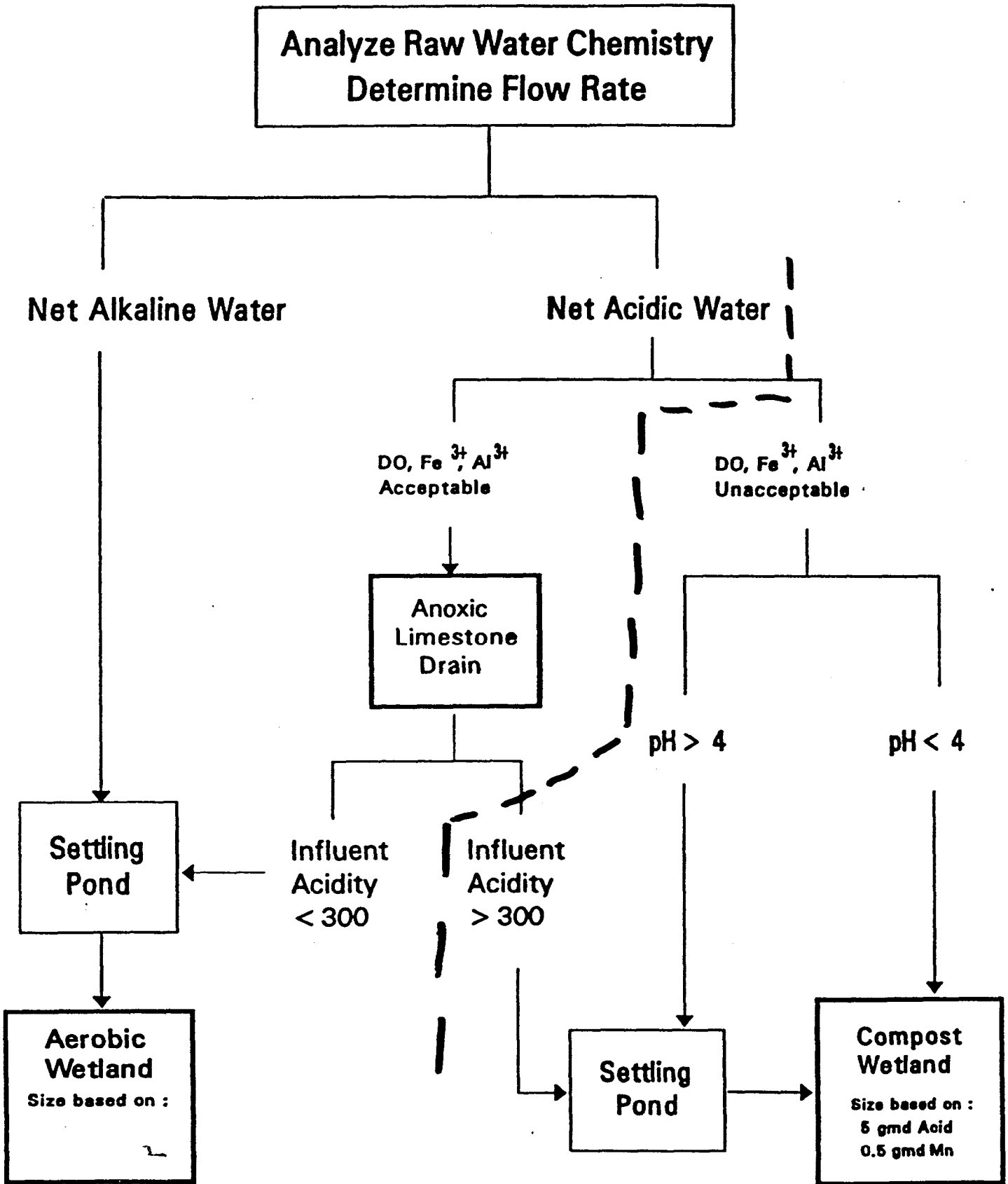


FIGURE 1. Flowchart for designing and sizing passive

ANAEROBIC
PASSIVE TREATMENT SYSTEM
DESIGN CRITERIA SUMMARY

**All components are designed based on
influent water chemistry**

- **ANAEROBIC CELLS** - vary volume and surface area to remove Fe, Cu, Pb, Zn, Hg, Cd, Al, SO₄, and to raise pH;
 - design for 0.3 moles of metal/m³ of wetland volume,
 - 20 m² area per L/sec. of flow (varies w/pH or acidity).

- **ANOXIC ALKALINITY GENERATORS** - vary volume and surface area to generate alkalinity when Anoxic Limestone Drain is inappropriate.

- **FLUID COLLECTION/DIVERSION** - try to minimize oxygenation of inflow stream.

- **FLUID DISTRIBUTION and INSTRUMENTATION** - should be simple to operate, durable and inexpensive.

AREA LOADING FACTOR vs pH
ANAEROBIC WETLAND CELLS DESIGNED BY KNIGHT PIESOLD, 1987-1997

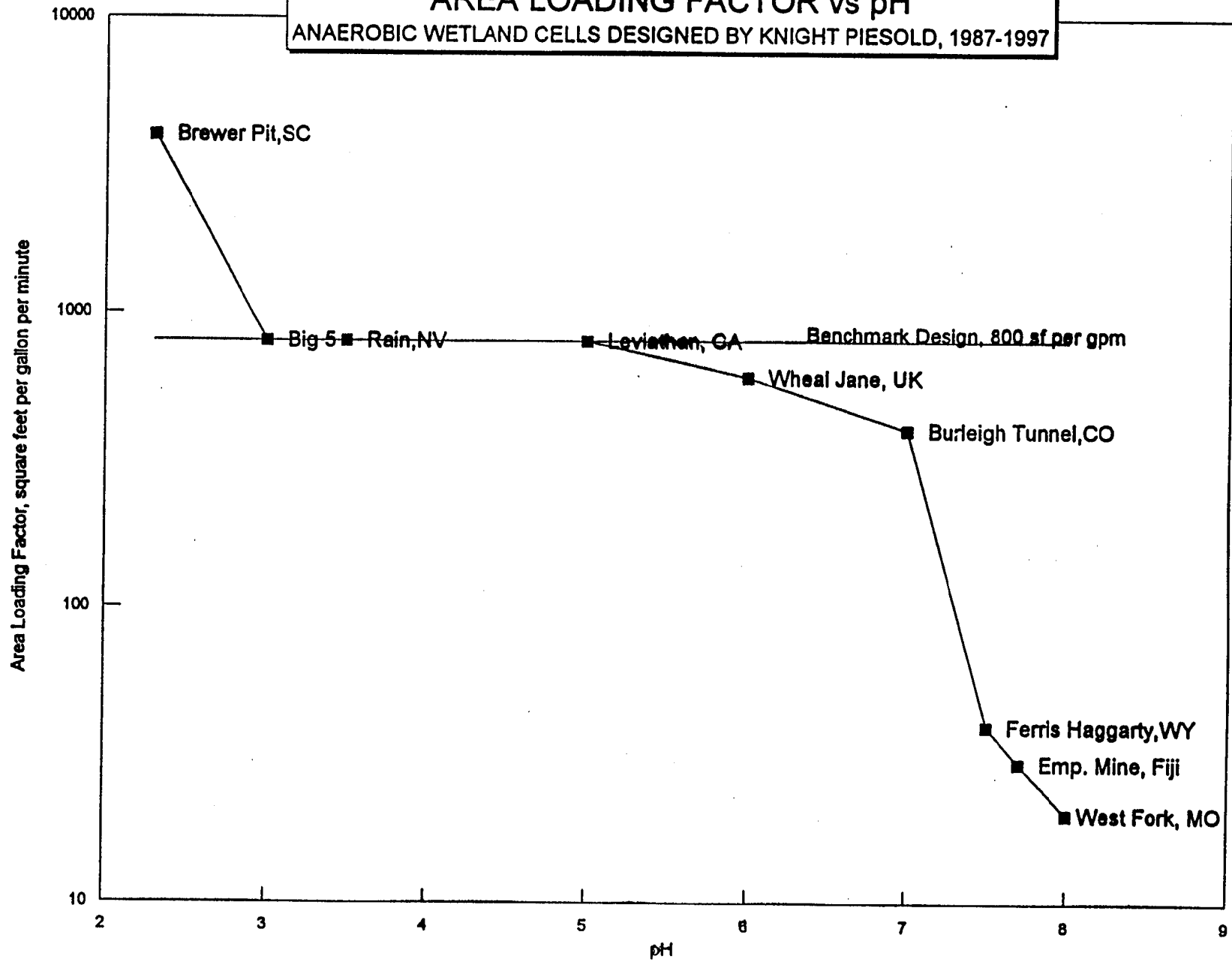


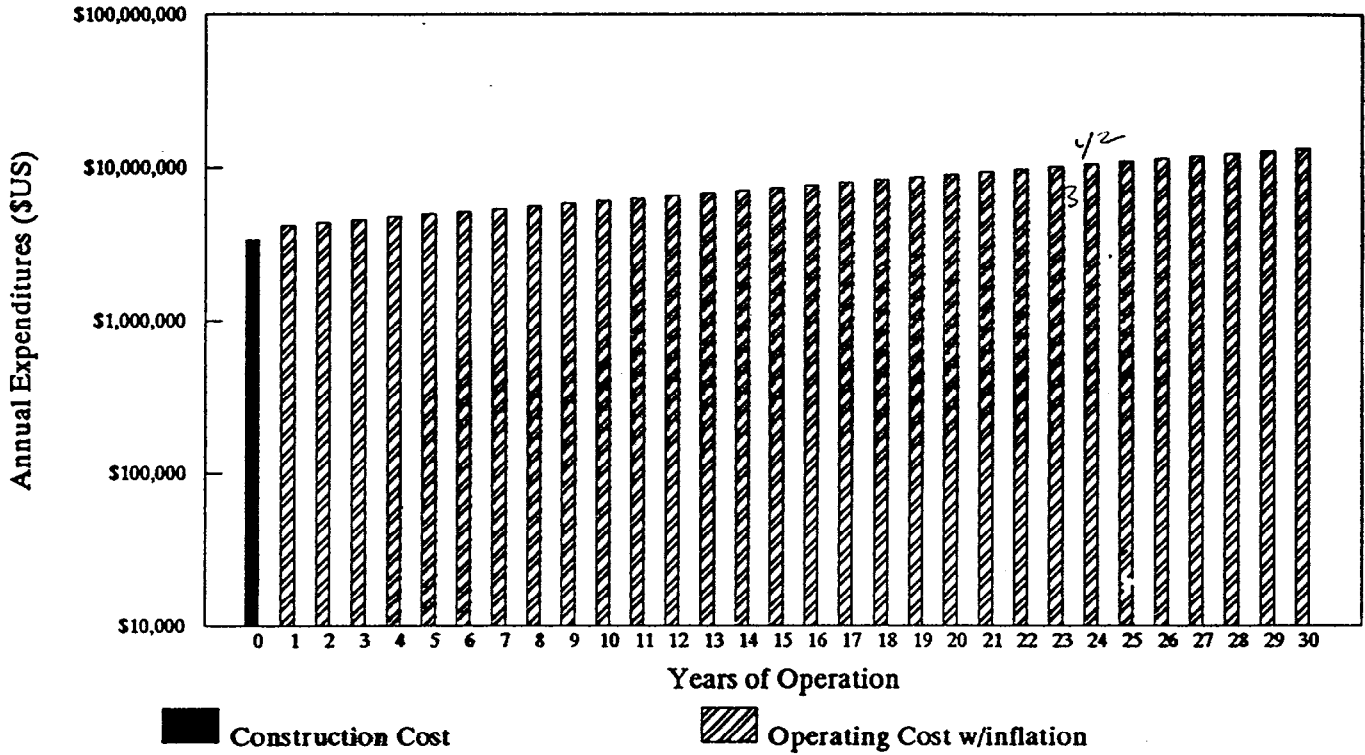
TABLE 1
Passive Treatment Experience
Knight Piésold and Co., Denver, Colorado USA

Project	pH	Other Parameters total mg/L	Flow, L/min	Typical Treatment Results total mg/L	Comments/ System Configuration
Asarco West Fork Unit, Missouri	7.9	Pb - 0.4 to 0.6 Zn - 0.18	8, 85 & 4,540 1200 gpm	Effluent pH 7.0 Pb - <0.02 Zn - <0.008 Sulfate reduction @ 2 to 3 moles per cubic meter per day in the summer.	One anaerobic cell (bench/pilot scales @ 8 & 85 L/m) Full scale, 1,200 gpm system : - settling basin - 2 anaerobic cells - rock filter wetland - aeration basin
Leviathan Mine, California	4.7	Fe- 310 Al - 48 As - 0.4 Ni - 1.8	3.8 19gpm	Effluent pH 6.5 Non-detect Al, As, Ni Fe, 90% removal	3 cells: ALD, aerobic & anaerobic
Gold Mine Tailing Seeps, Nevada	6 to 8	WAD CN - 31 As - .12 Hg - 0.0008 Cu - 1.8 Zn - 1.0 Fe - 0.05	38 10 gpm	Effluent pH 6 - 9 WAD CN - 1.2 - 6.7 Fe - 0.03 As - 0.054 Hg - <0.0002 Cu - 0.63 Zn - 0.08	14 chambered aerobic system with algae
Gold Mine ARD, Nevada	3.2	Fe - 216 As - 2.7 Cu - 7.4 Mn - 7.1 Se - 0.3 Zn - 1.8	23 6 gpm	Effluent pH 6.5-7.1 Fe - 0.9 As - .032 Cu - <0.05 Mn - 2.9 Se - .005 Zn - <0.05	3 cells: aerobic pond, anaerobic, rock filter with algae
Brewer Gold Mine, S. Carolina Pit Cell	2.3	Fe - 735 Cu - 76 Al - 113	4 1 gpm	Effluent pH 6.0 Fe - 215 (as Fe ²⁺) Cu - 15.9 Al - 30	One anaerobic cell, substrate of limestone, turkey litter wood chips and cow manure
Brewer Gold Mine, S. Carolina Heap Leach Pad Cell	2.0 to 4.7	Fe - 25 to 3900 Cu - 2 to 103 Al - 220	6.8 175 gpm	Effluent pH 6.5 Fe - 44 Cu - 0.25 Al - 12.4	One anaerobic cell, substrate of limestone, turkey litter wood chips and cow manure
Burleigh Tunnel, Colorado	6.8	Fe - 5 Zn - 50	76 20 gpm	Upflow; Zn < 1.0 last 7 month avg 0.35 mg/L No Ceriodaphnia mortality Downflow Zn 10 mg/L	Two anaerobic cells, 38 l/min each; one upflow, one downflow
Emporer Gold Mine, Fiji; CN Tailings Decant Solution	7.9	Mn - 6.6, Cu - 0.6 As - 0.3, Ni - 0.4	0.2 B	Mn - 9, Cu - <0.01, As - 0.1, Ni - 0.09	7 bench scale anaerobic cells w/various substrate recipes, downflow
Ferris Haggarty Copper Mine, Sierra Madre Mts., WY	7.1	Cu - 4.5	.08 B	Effluent pH 7.1 Cu - 0.05 Temp 10C to 0.5C; 0.15 moles sulfate reduction per cubic meter per day.	Five anaerobic bench cells Full scale system may be placed in underground mine

B = Bench

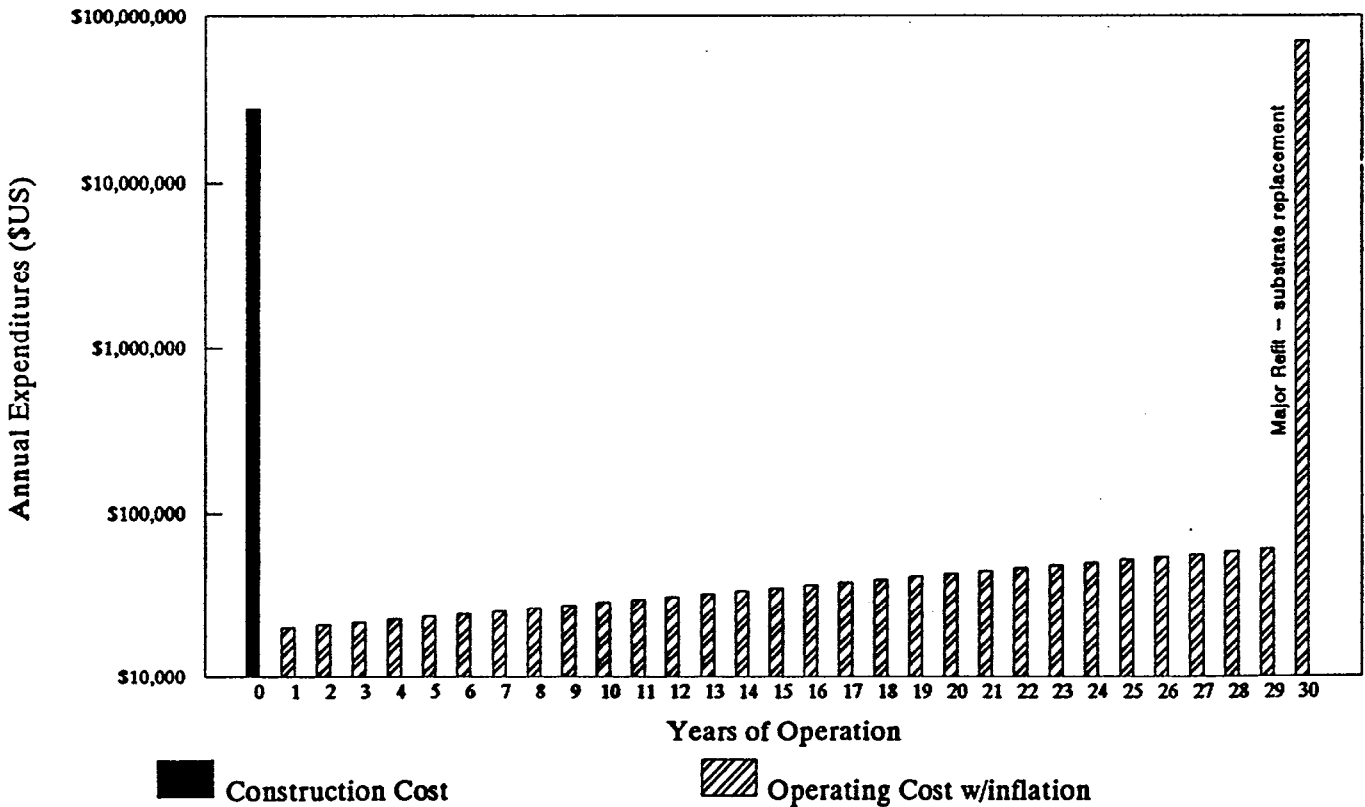
Lime Precipitation Cost–Time Line

ARD 1,453 GPM; pH 2.3; 1,000 mg/L metals; 4% annual inflation



Anaerobic Passive Treatment Cost–Time Line

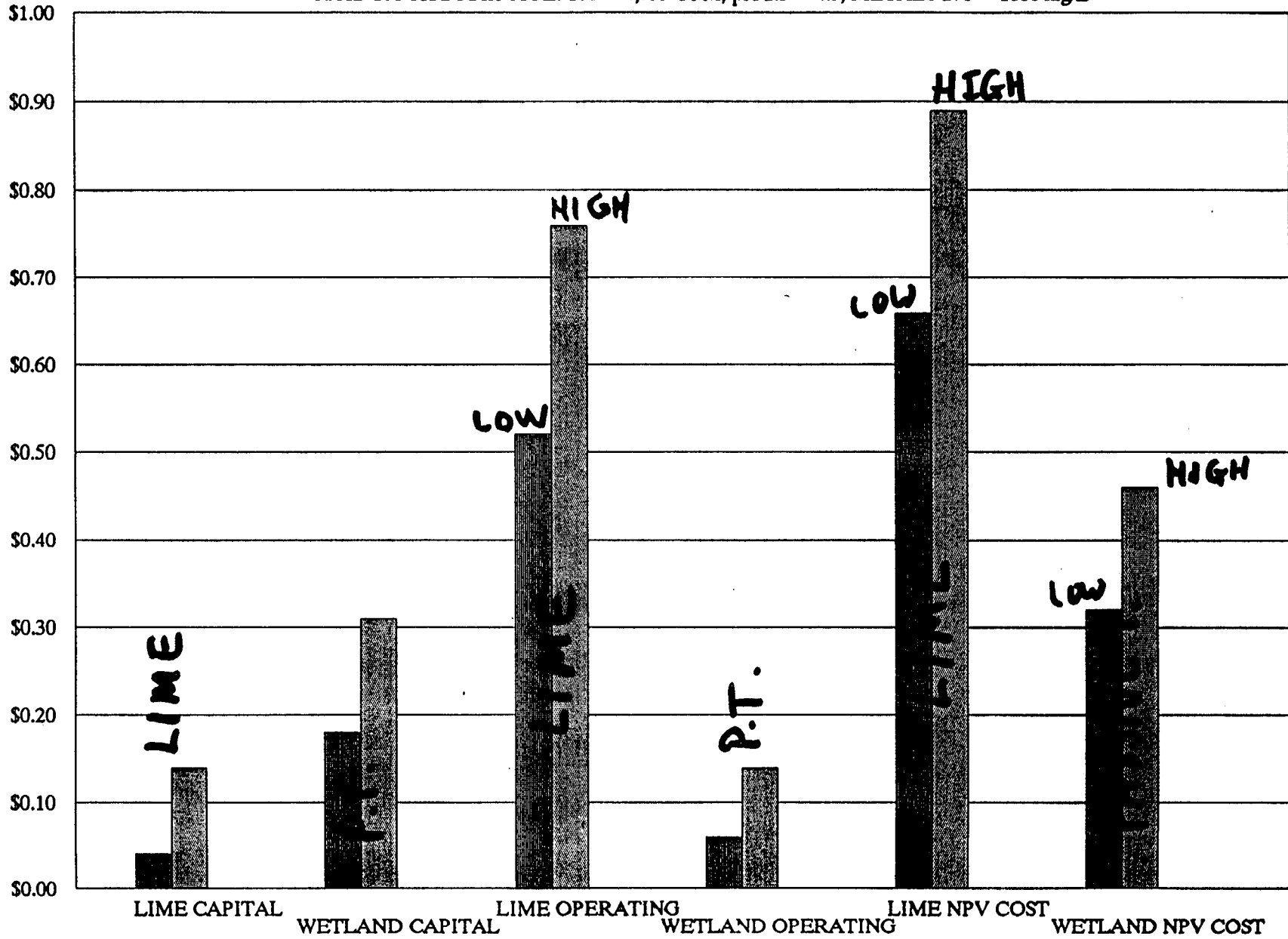
ARD 1,453 GPM; pH 2.3; 1,000 mg/L metals; 4% annual inflation



COST COMPARISON, ACTIVE VS PASSIVE TREATMENT

ACID ROCK DRAINAGE: 100 - 4,755 GPM; pH 2.3 - 4.5; METALS 270 - 1000 mg/L

COST PER KG METAL REMOVED



HIGH AND LOW RANGE OF CAPITAL, OPERATING & NPV COSTS

PASSIVE TREATMENT CONSIDERATIONS

ADVANTAGES

- Lower NPV cost
- No moving parts
- Simple to operate
- Resilient to quality variations
- Mimics Mother Nature
- Blends into landscape
- Potential wildlife habitat
- Long-term (not permanent) solution
- Non-hazardous waste (typical)
- Regulatory acceptance
- Potential future metals resource

DISADVANTAGES

- High front-end cost
- Nurturing needed at startup
- Perceived to be unproven technology
- Evaporation losses may increase
- Can be subject to weather
- Needs lots of land
- Food chain impacts of metals
- Typically not a walk-away solution
- Potentially hazardous waste substrates
- Uncertainty on longevity

**STAGED DESIGN
OF
PASSIVE REACTOR SYSTEMS**

LABORATORY STUDIES

BENCH-SCALE STUDIES

PILOT-SCALE SYSTEMS

FULL-SCALE SYSTEMS

LABORATORY STUDIES

PURPOSES ARE TO:

- 1. MEASURE RATE OF MICROBIAL ACTIVITY**
- 2. MEASURE METALS REMOVAL TENDENCY**
- 3. TEST LOCAL SUBSTRATE MATERIALS FOR EFFECTIVENESS**
- 4. "PROOF-OF-PRINCIPLE" THAT PASSIVE TREATMENT IS POSSIBLE**
- 5. FIND A LOCAL SOURCE OF APPROPRIATE BACTERIA**

CULTURE BOTTLE TESTS

20 -- 100 g SUBSTRATE

60 -- 100 mL CONTAMINANT WATER

MONITOR FOR 10 -- 100 DAYS

EXAMPLES OF SUBSTRATE MATERIALS

I. ANIMAL WASTES

- A. COW & HORSE MANURE**
- B. TURKEY LITTER**
- C. LLAMA DUNG**

II. OTHER ORGANIC MATERIALS

- A. HAY**
- B. ALFALFA**
- C. PEAT**
- D. FRESH SOFT WOOD SAWDUST**
- D. AGED SOFT WOOD SAWDUST**
- E. AGED HARD WOOD SAWDUST**
- F. NEWSPRINT**
- G. YARD WASTES**
- H. CHOLLA SKELETONS**
- I. GRASS CLIPPINGS**
- J. MUSHROOM COMPOST**

III. INORGANIC MATERIALS

- A. POTTING SOIL**
- B. LIMESTONE**
- C. LAKE BOTTOM SEDIMENT**
- D. ALLUVIAL SEDIMENTS**
- E. BASALT GRAVEL**
- F. MINE TAILINGS**

IV. INOCULUM

- A. FRESH COW & HORSE MANURE**
- B. ALGAE**
- C. WETLAND BOTTOM SEDIMENTS**

LABORATORY STUDIES DONE TO DATE

- 1. REYNOLDS: SULFIDE PRODUCTION RATES. PAPER INCLUDED.**
- 2. BUCKEYE LANDFILL SUPERFUND SITE "PROOF-OF-PRINCIPLE" STUDY.**
- 3. DUGGAN: Mn TREATMENT STUDIES - AEROBIC AND ANAEROBIC. PAPER INCLUDED.**
- 4. REED: MARSHALL NO. 5 TUNNEL.**
- 5. CHANG & PLUMMER: SUBSTRATE OPTIMIZATION.**
- 6. GREY EAGLE: SUBSTRATE SELECTION & OPTIMIZATION**
- 7. SIX STUDIES DONE FOR PRIVATE CLIENTS.**

DISCUSS TODAY

**TREATMENT OF GREY EAGLE MINE DRAINAGE BY ANAEROBIC
SULFATE REDUCTION**

GREY EAGLE EXPERIMENTAL PROTOCOL

**Base substrate: 1/3 planter mix, 1/3 manure,
1/3 limestone chips.**

**Base mix: 30 grams of substrate, 90 grams of mine drainage.
for the anaerobic cultures, add a minor amount of
distilled and sterilized water to fill to the top of the bottle.**

CULTURE BOTTLES

- 1 Base substrate with base drainage - substrate mix.**

- 10 Base substrate with mix of 10 g substrate to 100 mL drainage.**

- 11 Base substrate with mix of 25 g substrate to 100 mL drainage.**

- 12 Base substrate with mix of 60 g substrate to 60 mL drainage.**

- 20 1/3 limestone, 1/3 sawdust, 1/3 manure with base drainage - substrate mix.**

- 21 1/3 limestone, 1/3 sawdust, 1/3 planter mix with base drainage - substrate mix.**

- 22 1/3 planter mix, 1/3 sawdust, 1/3 manure mix with base drainage - substrate mix.**

**pH & Eh OF CULTURE BOTTLES AT END
OF EXPERIMENT (28 DAYS)**

CULTURE BOTTLE	pH	Eh
1	6.5	-10
10	6.2	190
11	6.7	-100
12	6.9	-75
20	6.1	-15
21	4.7	345
22	5.9	-10

**CONCENTRATION IN mg/L in ORIGINAL WATER (OW),
AND FINAL SUPERNATENTS.**

EFFLUENT LIMITS (EF) ARE ALSO GIVEN

Sample	Cd	Cu	Fe	Mn	Ni	Zn	SO₄=
OW	0.088	140	290	28	0.95	40	1500
1	<0.005	0.025	0.31	0.63	0.05	0.021	173
10	<0.005	0.94	40	7.6	0.10	2.3	1630
11	<0.005	2.7	25	6.4	0.07	0.83	744
12	<0.005	0.13	2.5	0.99	0.04	0.17	274
20	0.005	4.9	13	3.0	0.07	2.7	1190
21	0.006	0.77	39	7.4	0.12	4.3	591
22	0.010	3.6	10	2.8	0.06	2.4	1020
EF	0.01	1.0	0.3	---	0.7	0.02	---

ROUND ONE EXPERIMENTS

1. TRIED LOCAL SOIL AND SAWDUST. TOO ACIDIC.
2. BEST MIX WAS COMPOSTED MANURE, LIMESTONE,
AND POTTING SOIL IN EQUAL AMOUNTS BY WEIGHT.

**GREY EAGLE
SUBSTRATE BOTTLES
ROUND TWO**

BOTTLE	SUBSTRATE	AMOUNT
1	MANURE	60 G
2	LAKE BOTTOM SEDIMENT	60
3	1/3 LIMESTONE, 1/3 MANURE, 1/3 LAKE SEDIMENT	30
4	1/3 LIMESTONE, 1/3 MANURE, 1/3 LAKE SEDIMENT	60
5	1/2 MANURE, 1/2 LIMESTONE	30
6	1/2 LAKE SEDMNT, 1/2 LIMSTNE	30
7	1/4 LIMESTONE, 1/4 MANURE 1/4 LAKE SDMNT, 1/4 CORN	30
11	1/3 LIMESTONE, 1/3 MANURE, 1/3 LAKE SEDIMENT INOCULATED W. SULFATE REDUCERS	30
12	1/4 LIMESTONE, 1/4 MANURE 1/4 LAKE SDMNT, 1/4 CORN INOCULATED W. SULFATE REDUCERS	30
13	1/3 LIMSTN, 1/3 LAKE SEDIMENT 1/3 HAY, INOCULATED W. MANURE	30

SUBSTRATE DESIGN

ROUND TWO EXPERIMENTS

- 1. MANURE WAS VERY FRESH AND DIDN'T CONTAIN A HIGH ACTIVITY OF SULFATE REDUCERS.**
- 2. LAKE BOTTOM SEDIMENT CONTAINED NO SULFATE REDUCERS. IT WAS QUITE ORGANIC & HAS A LOW HYDRAULIC CONDUCTIVITY.**
- 3. CONCLUSIONS FOR PASSIVE SYSTEM:**
 - A. NEED AN INOCULUM OF SULFATE REDUCING BACTERIA (DIRTY BARNYARD MANURE).**
 - B. LAKE BOTTOM SEDIMENT IS PRIMARILY A FILLER TO MAINTAIN HYDRAULIC CONDUCTIVITY.**
 - C. LIMESTONE DOES SOME CONTROL OF pH.**

FINAL SUBSTRATE ASSESSMENT

- 1. HANDLING THE MANURE WAS TRICKY BECAUSE IT WAS DELIVERED WET & LOST THE MAJORITY OF ITS MASS UPON DRYING. JIM GUSEK'S ANALYSIS WAS QUITE IMPORTANT.**
- 2. ONCE THE SUBSTRATE WAS MIXED, IT WAS EASY TO HANDLE AND LOAD INTO THE SYSTEM.**

TWO IMPORTANT DEVELOPMENTS IN DESIGN, CONSTRUCTION, AND OPERATION OF THE PILOT SYSTEM

- 1. THE IDEA OF A VOLUME BASED LOADING FACTOR
BASED ON THE AMOUNT OF SULFIDE GENERATED
WAS USED TO SET THE FLOW.**
- 2. THE SUBSTRATE WAS DESIGNED BY APPLYING
MICROBIOLOGIC PRINCIPLES AND "READILY
AVAILABLE" LOCAL MATERIALS WERE USED.**

VOLUME BASED LOADING FACTOR

- 1. 300 nanomole / cm³ / day OF SULFIDE GENERATION. VOLUME IS THE TOTAL VOLUME AND NEGLECTS PORE SPACE AND MOISTURE CONTENT.**
- 2. FOR MINE DRAINAGE WATER, CONCENTRATION OF HEAVY METALS IS APPROXIMATELY 800 mg / L AT AN ATOMIC WEIGHT OF ABOUT 55 grams / mole.**
- 3. PASSIVE SYSTEM SIZE IS 9 ft X 6 ft X 36 ft. THIS IS 1944 ft³ OR 55.0 m³.**

**MOLES S= GENERATED PER DAY IS 16.5.
MOLES OF HEAVY METALS REMOVED PER DAY IS 16.5.
LITERS / MIN OF FLOW IS 0.79
GALLONS PER MIN OF FLOW IS 0.21**

**THE CALCULATION IS A CONSERVATIVE ESTIMATE
BECAUSE
OF THE CONCENTRATION OF HEAVY METALS USED,
AND THE ATOMIC WEIGHT USED.**

**USUALLY THE SULFIDE GENERATION IS CALCULATED ON
THE MASS OF DRY SUBSTRATE. WE ASSUMED THAT THE
DENSITY OF DRY SUBSTRATE WAS 1.0 g / cm³**

**COMPARISON OF WHOLE WATER SAMPLES
AVERAGE CONC. IN mg / L**

	ORIGINAL WATER	PASSIVE SYSTEM	30 g SUBSTRATE 90 g WATER	60 g SUBSTRATE 60 g WATER	EFFLUENT LIMITS
Cd	0.12	<0.0005	<0.005	<0.005	0.01
Cu	130	0.42	0.025	0.13	1.0
Ni	1.0	0.049	0.05	0.04	0.7
Fe	320	14	0.31	2.5	0.3
Mn	31	17	0.63	0.99	---
Zn	42	0.07	0.021	0.17	0.02
SO₄⁼	2900	2200	170	270	---

**FERRIS-HAGGARTY/OSCEOLA
TUNNEL DRAINAGE STUDY**

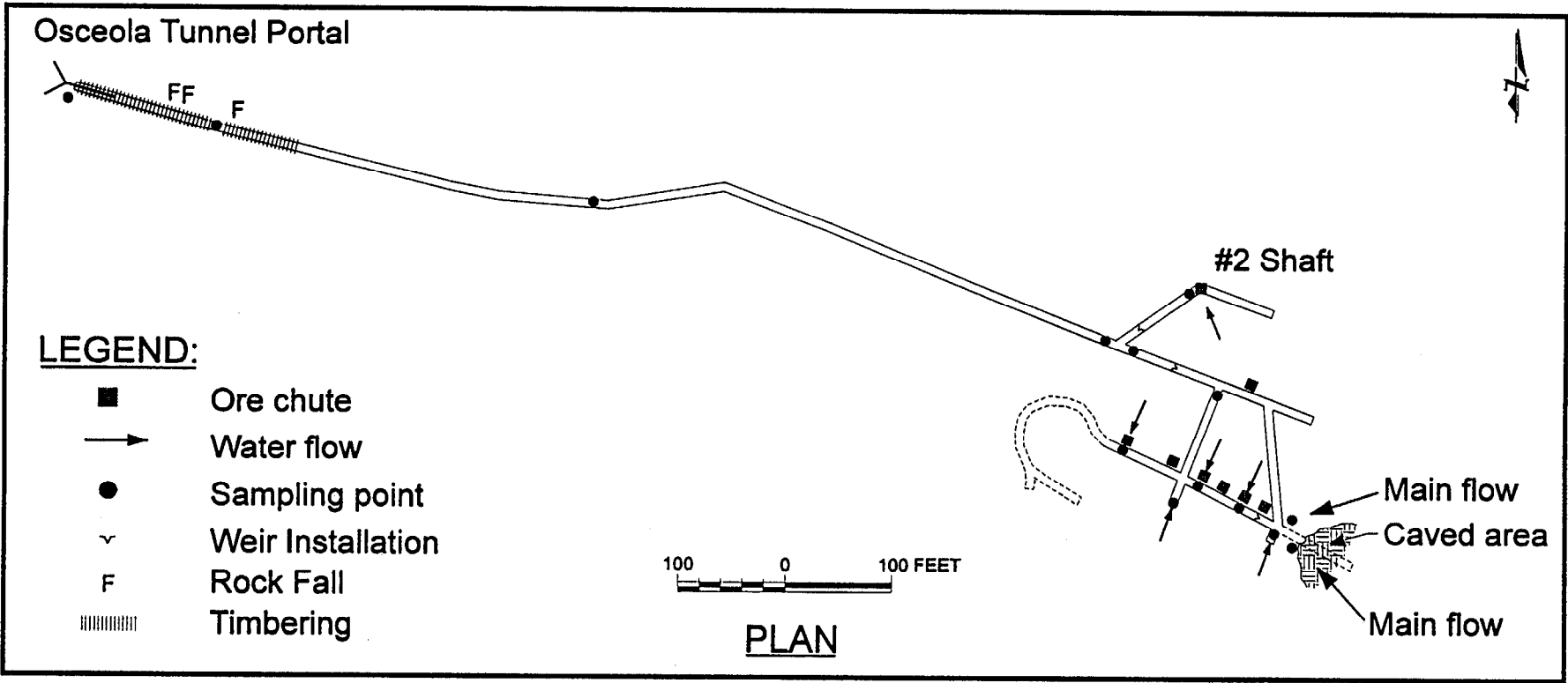
**WYOMING AML PROJECT
4C-II**

SITE LOCATION

- **Sierra Madre Mountains**
- **25 Miles West of Encampment**
- **185 Miles Northwest of Denver**



TUNNEL LAYOUT AND SAMPLING STATIONS

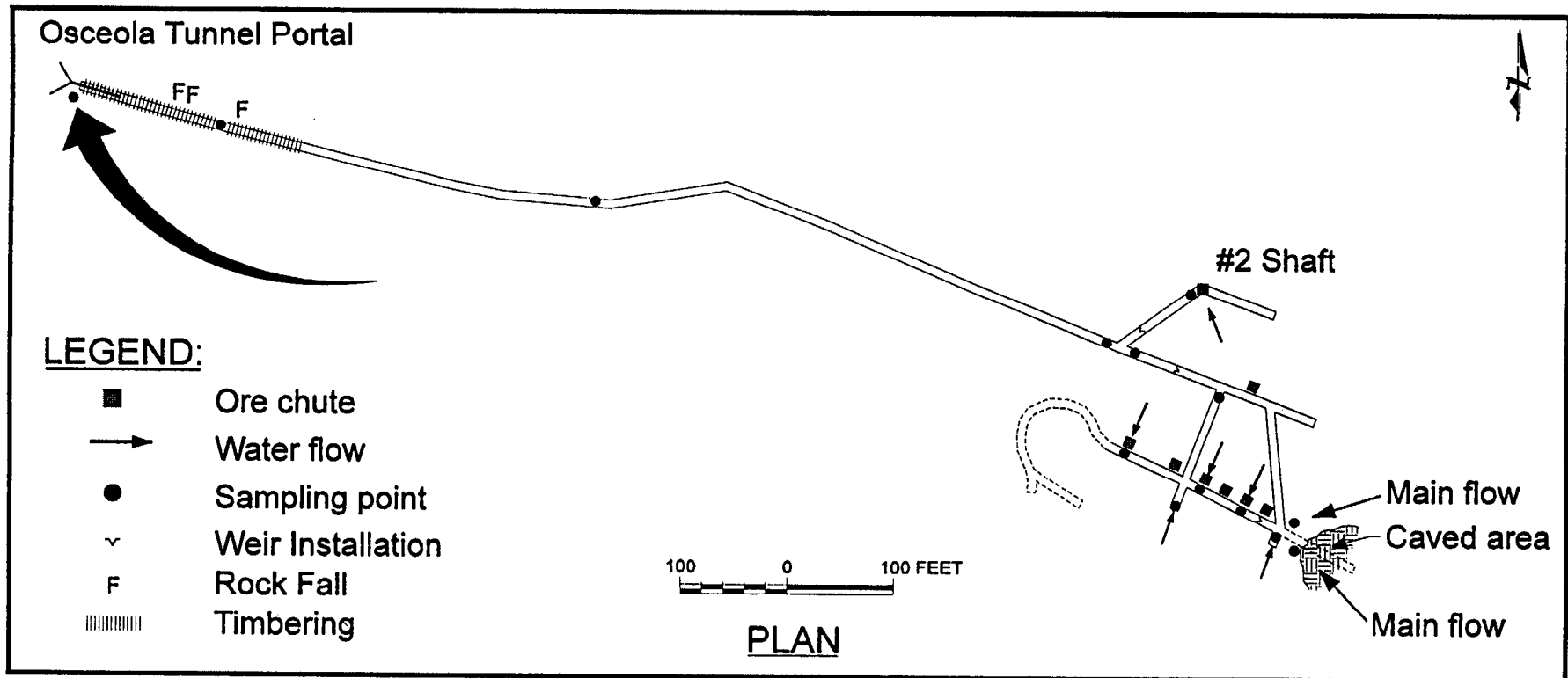


OBSERVATIONS DURING LOW FLOW CONDITIONS

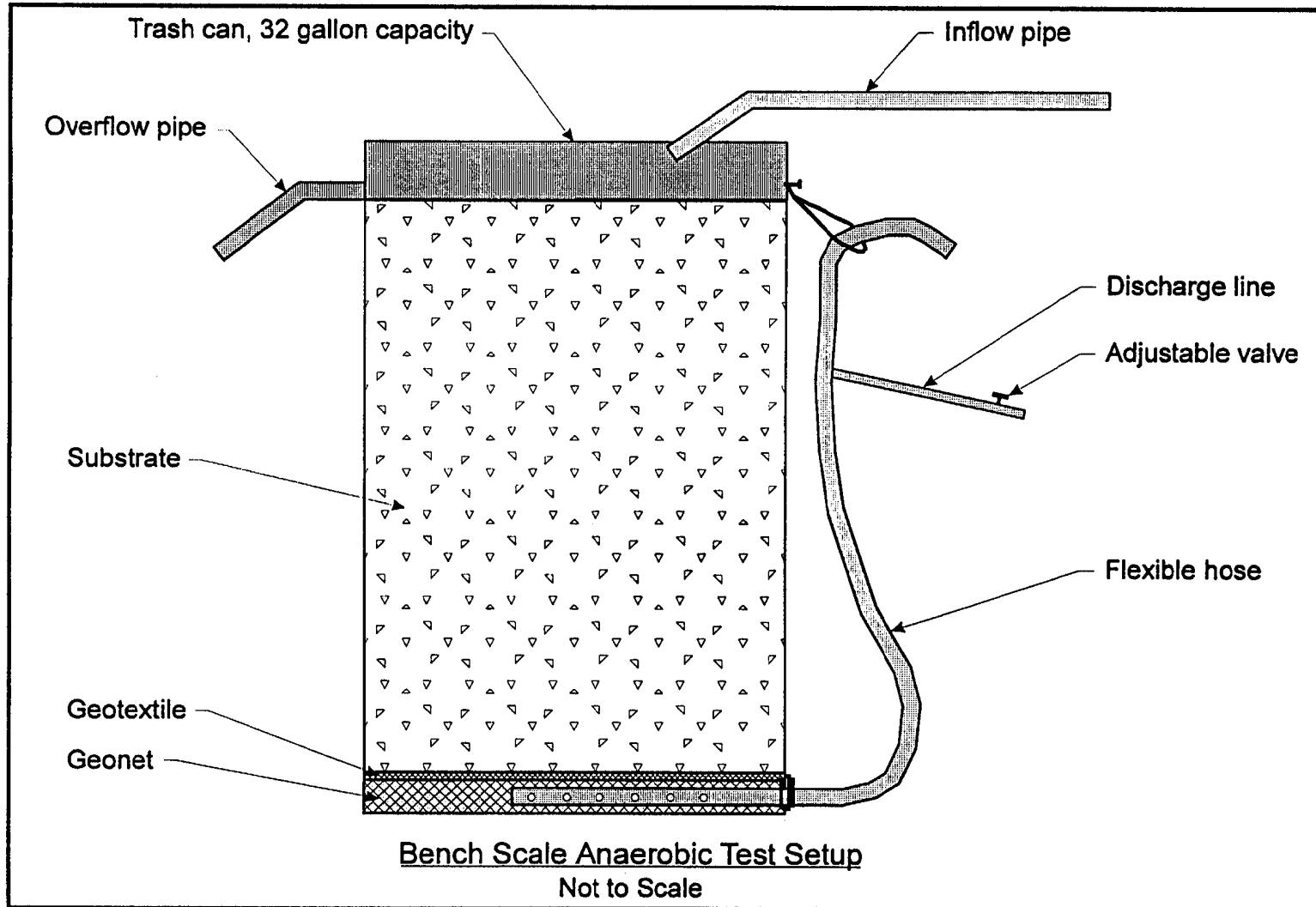
- **Several Different Flow Sources**
- **Main Flow Source is Winze Area**
- **92% of Copper Loading from:**
 - #4 Chute (43%)
 - Winze (38%)
 - #2 Shaft (11%)
- **Slimes May Act as Source/Sink**

- pH 6.50
- Cu 3.73 mg/L
- Flow 30 gpm

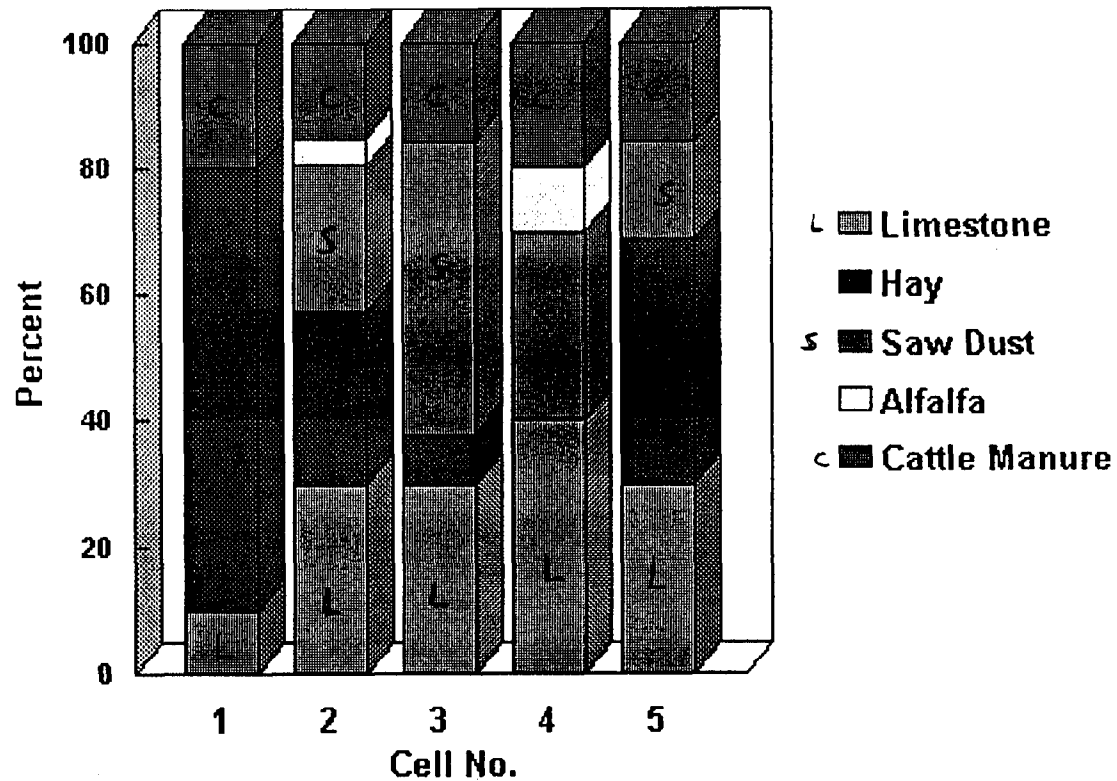
- Cu Loading 1.34 lb/day
- Conductivity 102 umhos/cm



TRASH CAN DESIGN



TRASH CAN SUBSTRATE RECIPES



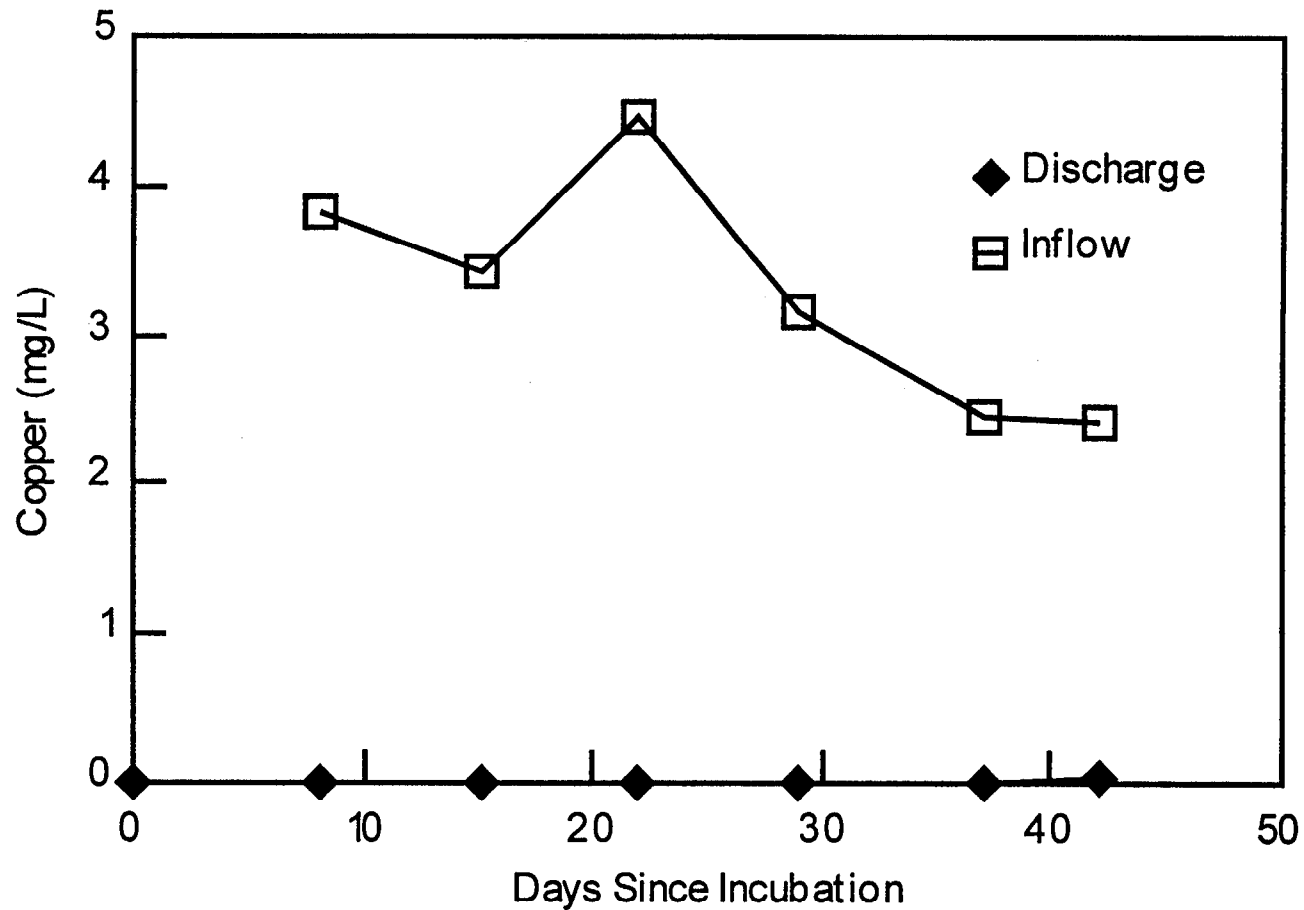
TRASH CAN SUBSTRATE RECIPIES

	Limestone		Native Hay		Aged Saw Dust		Alfalfa		Cattle Manure	
	Lbs	%	Lbs	%	Lbs	%	Lbs	%	Lbs	%
Trash Can #1	2.42	10.0	16.95	70.0	--	--	--	--	4.84	20.0
Trash Can #2	13.23	30.0	12	27.2	10.3	23.4	1.71	3.9	6.85	15.5
Trash Can #3	25.76	30.0	6.7	7.8	40	46.6	--	--	13.4	15.6
Trash Can #4	40	40.0	--	--	30	30.0	10	10.0	20	20.0
Trash Can #5	12.5	30.0	16.15	38.8	6.5	15.6	--	--	6.5	15.6

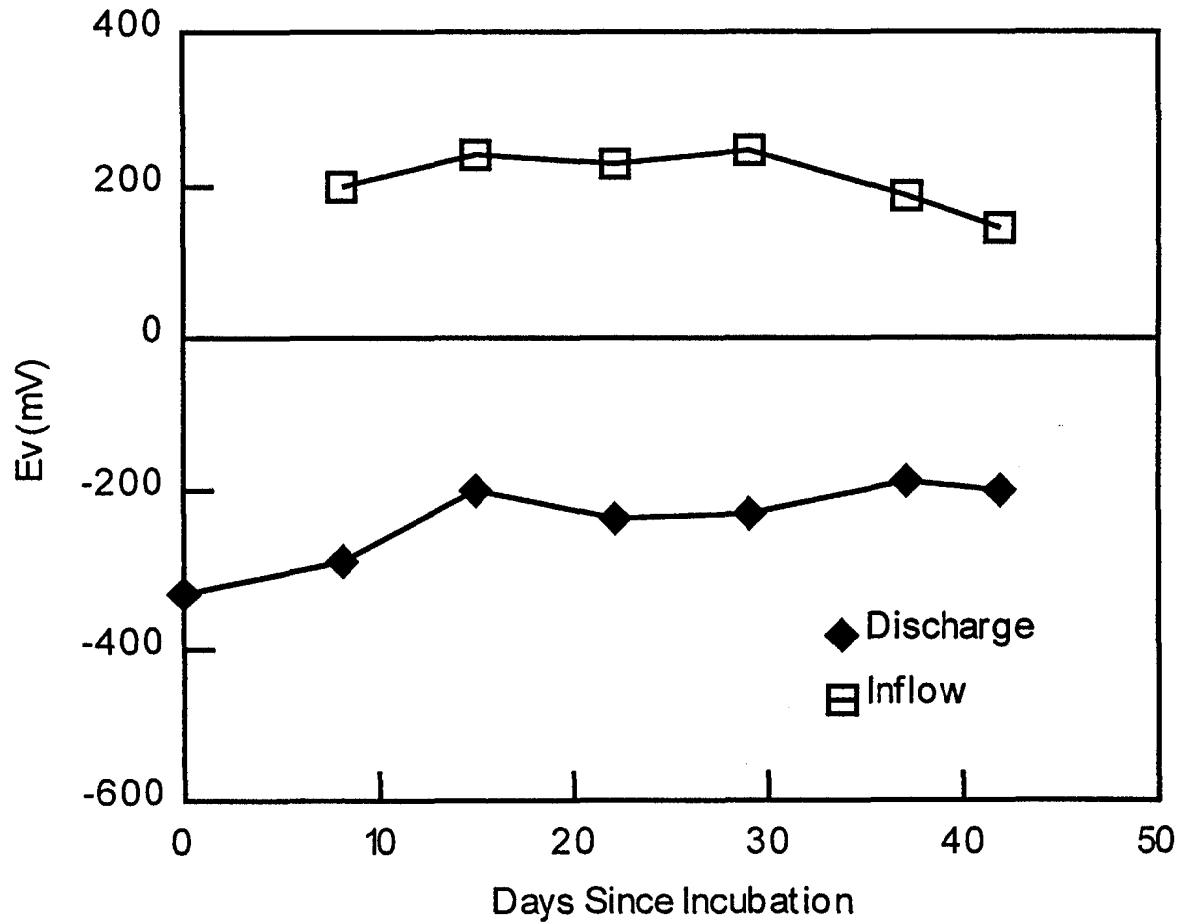
Note: 0.6 pound gypsum board also added to each trash can.

Knight Piésold LLC

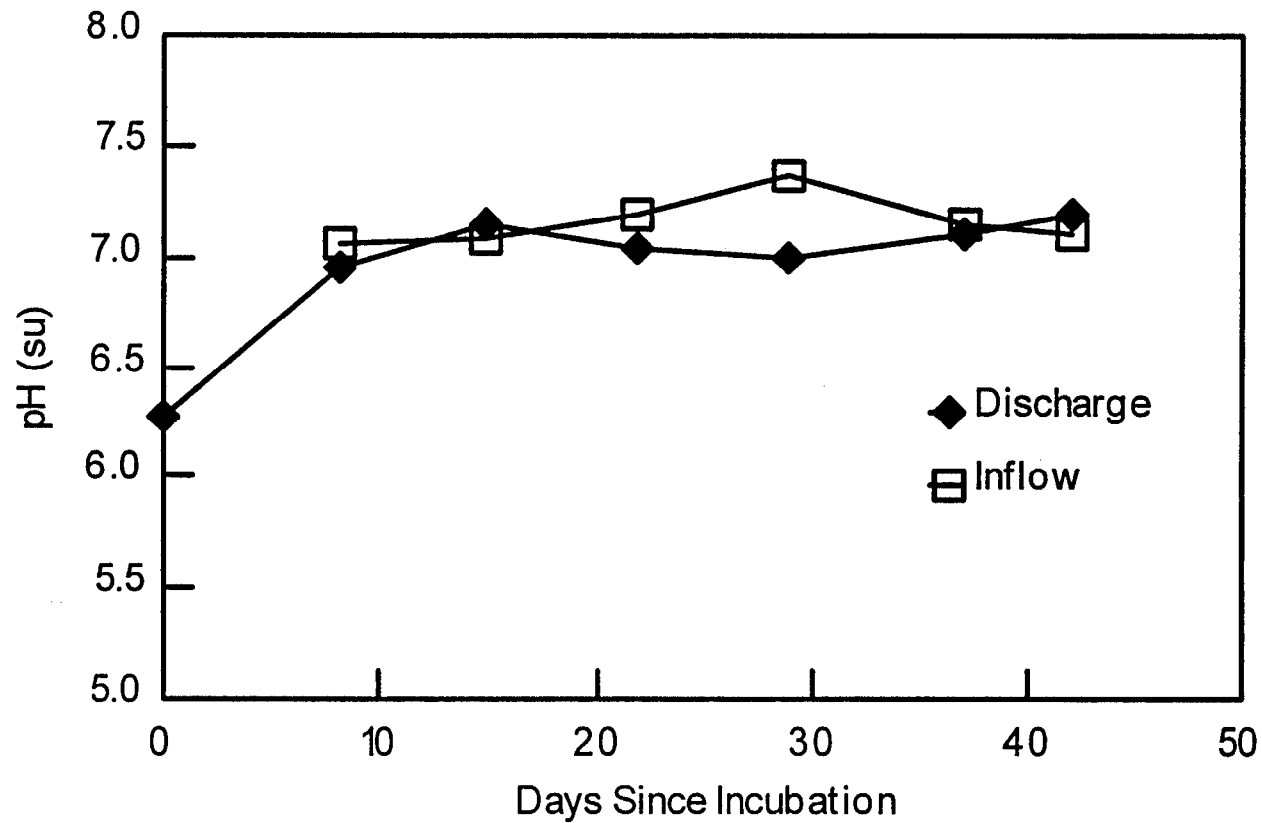
COPPER CONCENTRATION OF TRASH CAN NO.3



Ev OF TRASH CAN NO.3

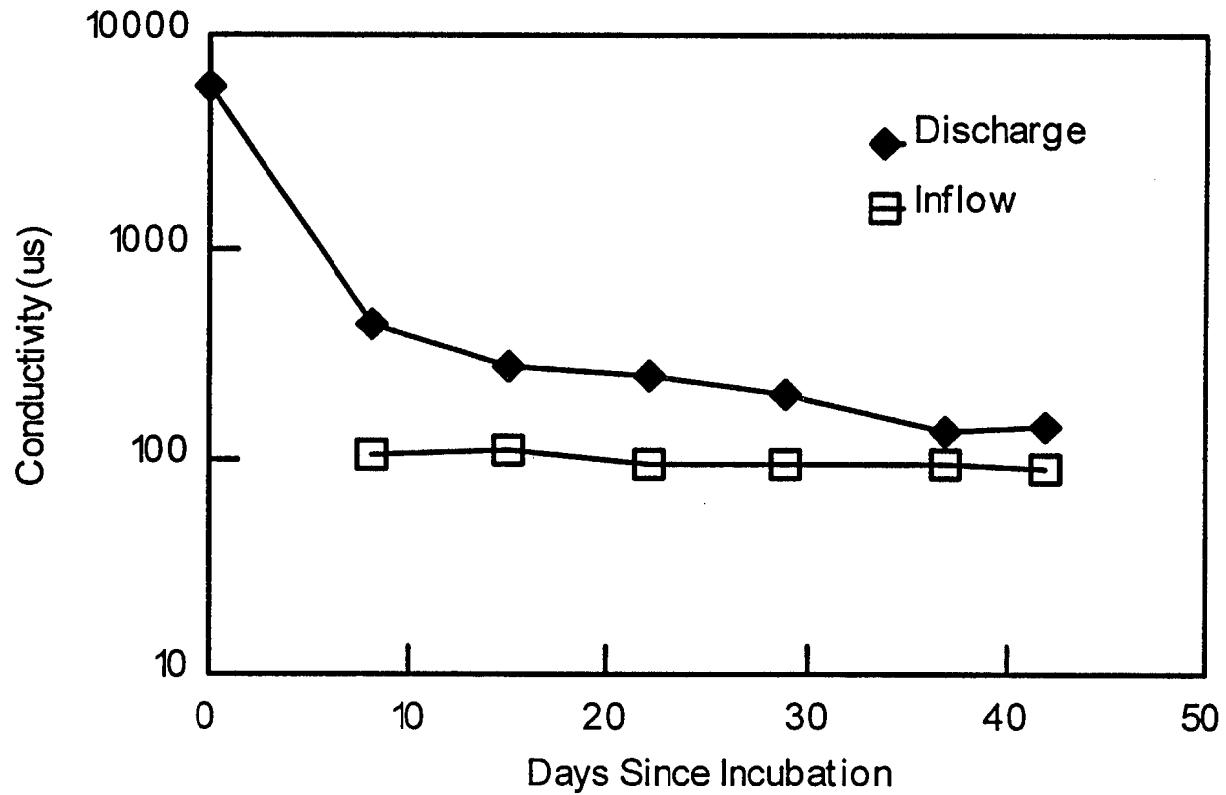


pH OF TRASH CAN # 3



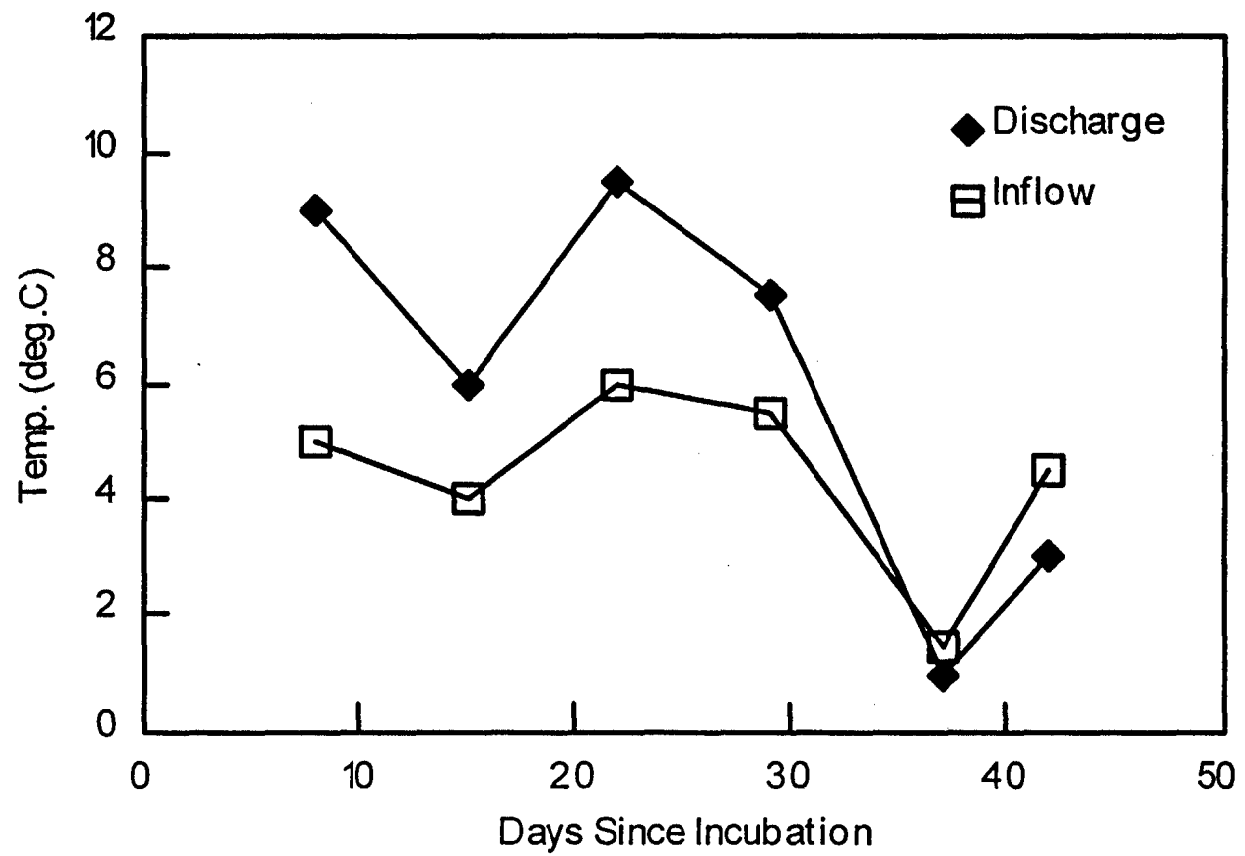
Knight Piésold LLC

CONDUCTIVITY OF TRASH CAN #3



Knight Piésold LLC

TEMPERATURE OF TRASH CAN #3



Knight Piésold LLC

**STAGED DESIGN
OF
PASSIVE REACTOR SYSTEMS**

LABORATORY STUDIES

BENCH-SCALE STUDIES

PILOT-SCALE SYSTEMS

FULL-SCALE SYSTEMS

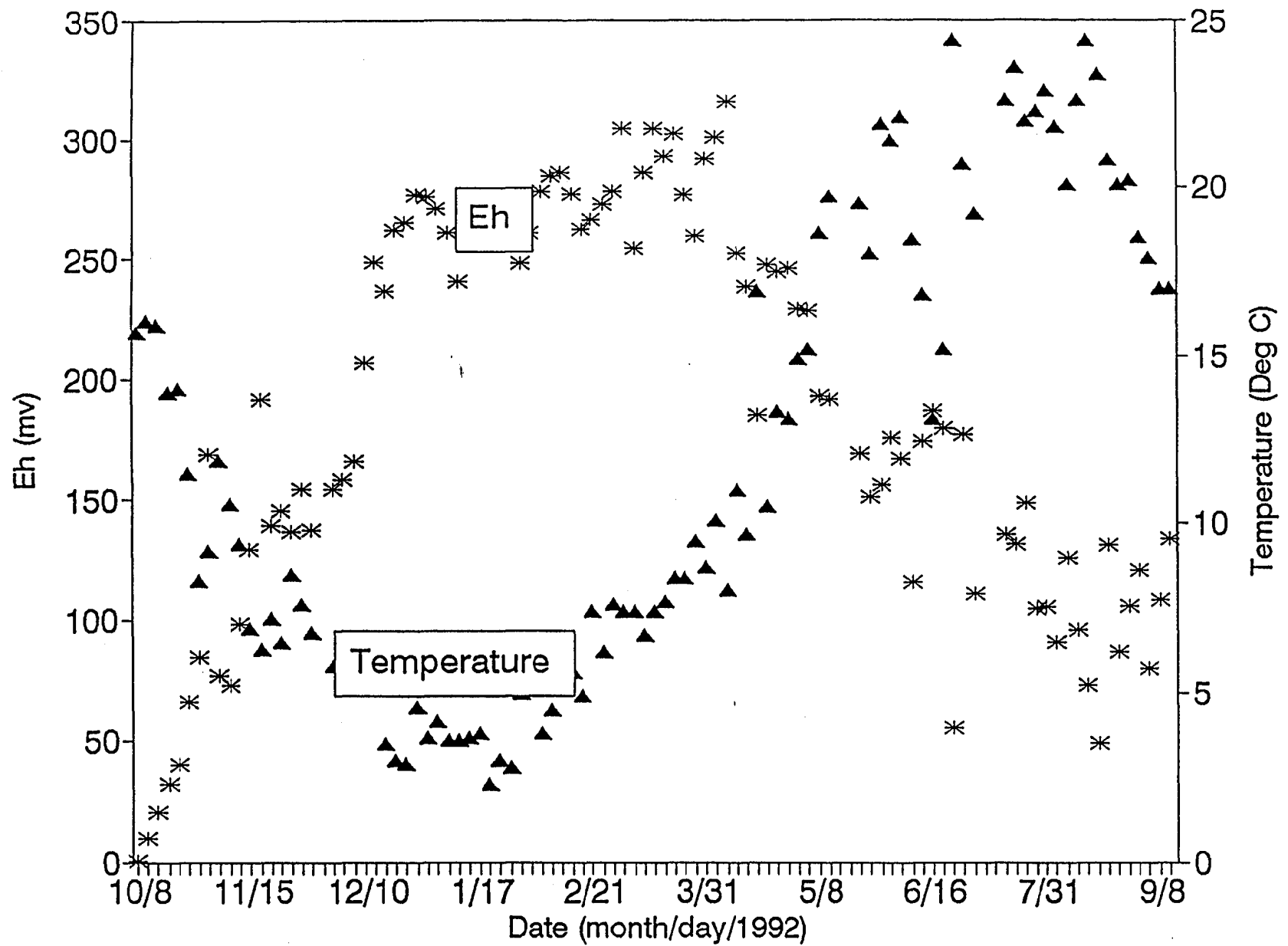
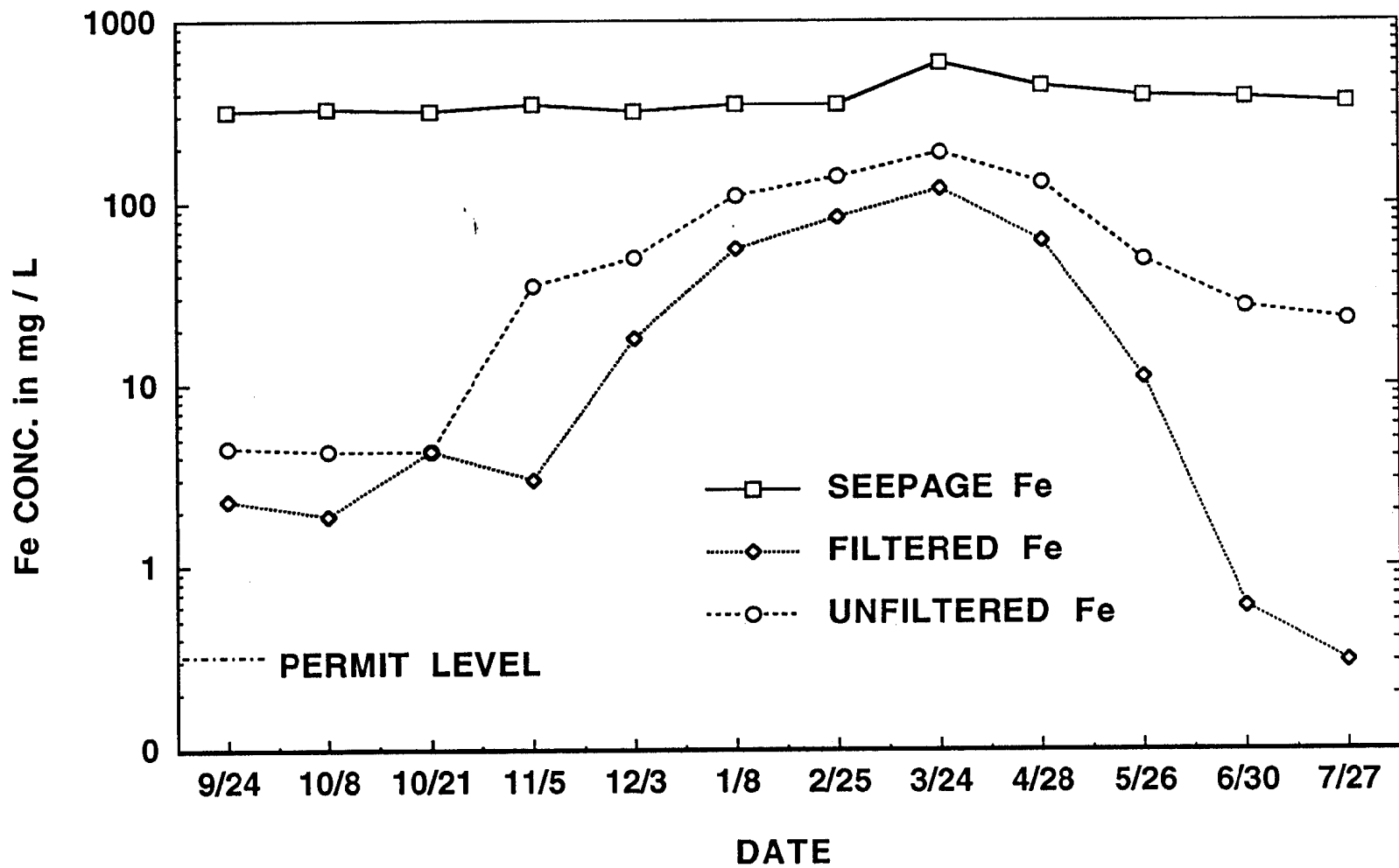


Figure No. 3 Variation of oxidation-reduction potential (Eh) with ambient temperature

GREY EAGLE Fe



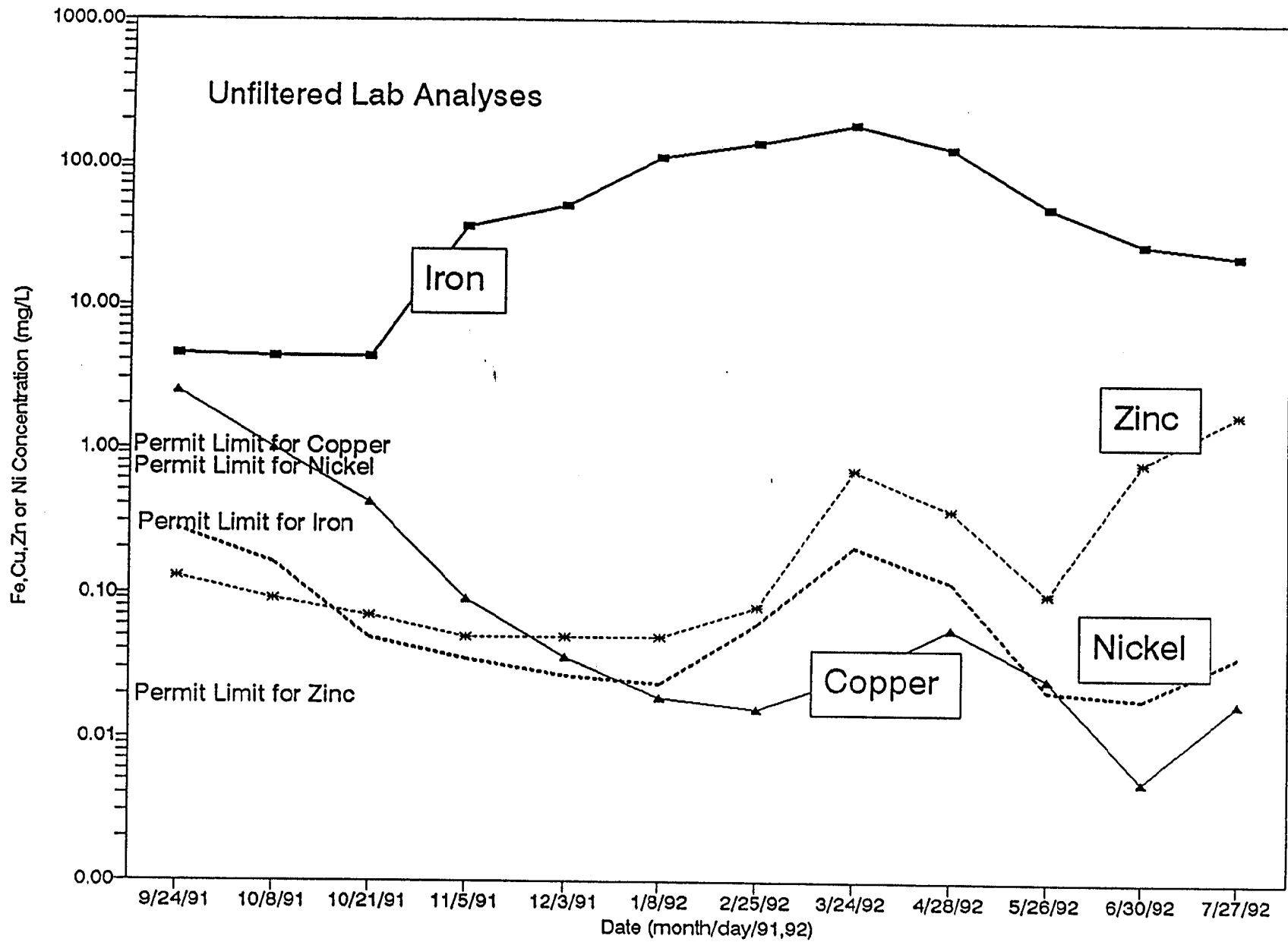


Figure No. 1 Effluent metal concentrations

***METALS, SULFUR, & CARBON BALANCE
IN A PILOT REACTOR
TREATING LEAD IN WATER***

**TOM WILDEMAN & JIM GUSEK
KNIGHT PIESOLD, LLC, DENVER**

**AARON MILLER
ASARCO INC., ANNAPOLIS, MO**

**JIM FRICKE
ADVANCED GEOSERVICES CORP.,
SANDY, UTAH**

SITE BACKGROUND

**SITE
ASARCO OWNED LEAD MINE.**

**LOCATION
NEW LEAD BELT, CENTRAL MISSOURI.**

AQUEOUS SYSTEM

- **SUMP WATER COMING OFF THE FACE OF THE MINE LOCATED APPROXIMATELY 1000 FEET BELOW THE GROUND SURFACE.**
- **PARENT MATERIAL IS CARBONATE SEDIMENTARY ROCK (LIMESTONE), ORE IS GALENA.**
- **WATER IS PUMPED TO THE SURFACE, FLOWS THROUGH A SERIES OF PONDS AND EXITS THE MINE PROPERTY.**

MEASURED COMPONENT CONCENTRATIONS

CONSTITUENT	CONCENTRATION (mg/L)
ALKALINITY	156 (as CaCO ₃)
Ca	51
Mg	31
Na	25
K	6.3
SO ₄ ⁻²	63
Cl	10
NO ₃ ⁻	6
Cu	0.019
Zn	0.21
Pb	0.13
Mn	0.011
Cd	0.002
As	0.023
pH	7.9

PROBLEM

CONTAMINANT OF CONCERN

LEAD, Pb = 0.13 mg/l

IS KNOWN AS A POSSIBLE CARCINOGEN

MCL = 0.05 mg/l (as of 1980)

IN THIS SITUATION 0.029 mg/l IS REGULATORY LIMIT

**ALL OTHER CHEMICAL CONSTITUENTS ARE ACCEPTABLE
FOR RELEASE TO SURFACE WATERS.**

INVERSE MODELING

DEFINITION

- **PROCESS OF RECONSTRUCTING THE ENVIRONMENTAL CONDITIONS WHICH CAUSE OBSERVED AQUEOUS CONCENTRATIONS.**

INCLUDES

- **DETERMINING EQUILIBRIUM CONDITIONS.**
- **DETERMINING THE SPECIES THAT MAY BE CONTROLLING THE CHEMISTRY OF THE SYSTEM.**

TO FIND EQUILIBRIUM CONDITIONS, INPUT CONCENTRATIONS SHOULD EQUAL OUTPUT CONCENTRATIONS.

MASS DISTRIBUTION OF DISSOLVED LEAD

SPECIES	PERCENT %
PbCl^+	0.01
$\text{Pb}(\text{CO}_3)_2^{-2}$	1.24
PbOH^+	2.52
$\text{Pb}(\text{OH})_2$ (aq)	0.07
PbSO_4 (aq)	0.29
PbCO_3 (aq)	92.45
PbHCO_3^+	1.22
Pb^{+2}	2.19

IMPLICATION

ALMOST ALL DISSOLVED LEAD EXISTS IN COMPLEXES.

INVERSE MODELLING CONCLUSIONS

- 1. OXIDIZED GALENA ORE**
- 2. DISSOLVED CARBONATE MINERALS CONTAINING Pb^{+2} AS A TRACE ELEMENT CONTROL Pb DISSOLUTION.**

THIS COULD BE POSSIBLE IN A KARST TERRAIN WHERE METEORIC WATERS COULD BE CONNECTED TO THE DEEP ORE SYSTEM.

- 3. DISSOLVED LEAD IS IN EXCESSIVE CONCENTRATIONS BECAUSE OF STRONG TENDENCY OF LEAD TO FORM COMPLEXES IN SOLUTION.**

FORWARD MODELING

DEFINITION

- **PROCESS OF STARTING THE SYSTEM AT AN INITIAL EQUILIBRIUM AND ADDING CONSTITUENTS OR CHANGING AMBIENT PHYSICAL CHARACTERISTICS AND ALLOWING THE SYSTEM TO REACH A NEW EQUILIBRIUM STATE.**

SPECIAL CONSIDERATIONS

- **USED TO PREDICT RESULTS OF TREATMENT METHODS FOR REMOVAL OF SPECIFIC CONSTITUENTS.**
- **USED MINTEQAQ BECAUSE IT IS BETTER DESIGNED TO ADD OR SUBTRACT CONSTITUENTS IN INCREMENTS.**

RESULTS

FOR BOTH CO_3^{-2} AND OH^-

- 1. TOTAL DISSOLVED Pb REMAINED UNCHANGED.**
- 2. PbCO_3 (s) or Pb(OH)_2 (s) NEVER REACHED SATURATION.**
- 3. FORMS OF Pb IN SOLUTION DID NOT CHANGE SIGNIFICANTLY.**

IMPLICATIONS

- 1. THE SYSTEM IS TOO STRONGLY BUFFERED BY DISSOLVED AND SOLID CARBONATE.**
- 2. ANY ADDITIONS OF CO_3^{-2} AND OH^- WERE CONSUMED BY OTHER CONSTITUENTS.**

CONCLUSIONS

REMOVAL OF Pb AS A PRECIPITATE IN AN OXIDIZED SYSTEM IS DIFFICULT.

LABORATORY STUDIES

- 1. TESTED LOCAL ORGANIC MATERIALS TO DETERMINE THE ABILITY FOR SULFATE REDUCTION.**
- 2. ALSO TRIED LOCAL ALGAL MATERIAL TO SEE IF AEROBIC REMOVAL WAS POSSIBLE.**

LABORATORY STUDY RESULTS

- 1. LEAD WAS REMOVED IN ANAEROBIC TESTS, PROBABLY THROUGH SULFATE REDUCTION.**
- 2. LEAD WAS ALSO REMOVED IN AEROBIC TESTS, PROBABLY THROUGH ADSORPTION ONTO METAL OXIDES.**

DECISION

MAKE AN ANAEROBIC PILOT CELL

CELL SPECIFICATIONS

CELL SIZE

53 m³ IN VOLUME, SUBSTRATE 1.5 m DEEP

SUBSTRATE COMPOSITION

**HARDWOOD SAWDUST, MANURE, HAY
DOLOMITIC TAILINGS, CARBONATE MINE WASTE
INOCULUM 1:1 SAWDUST & MANURE
FROM ANOTHER REACTOR.**

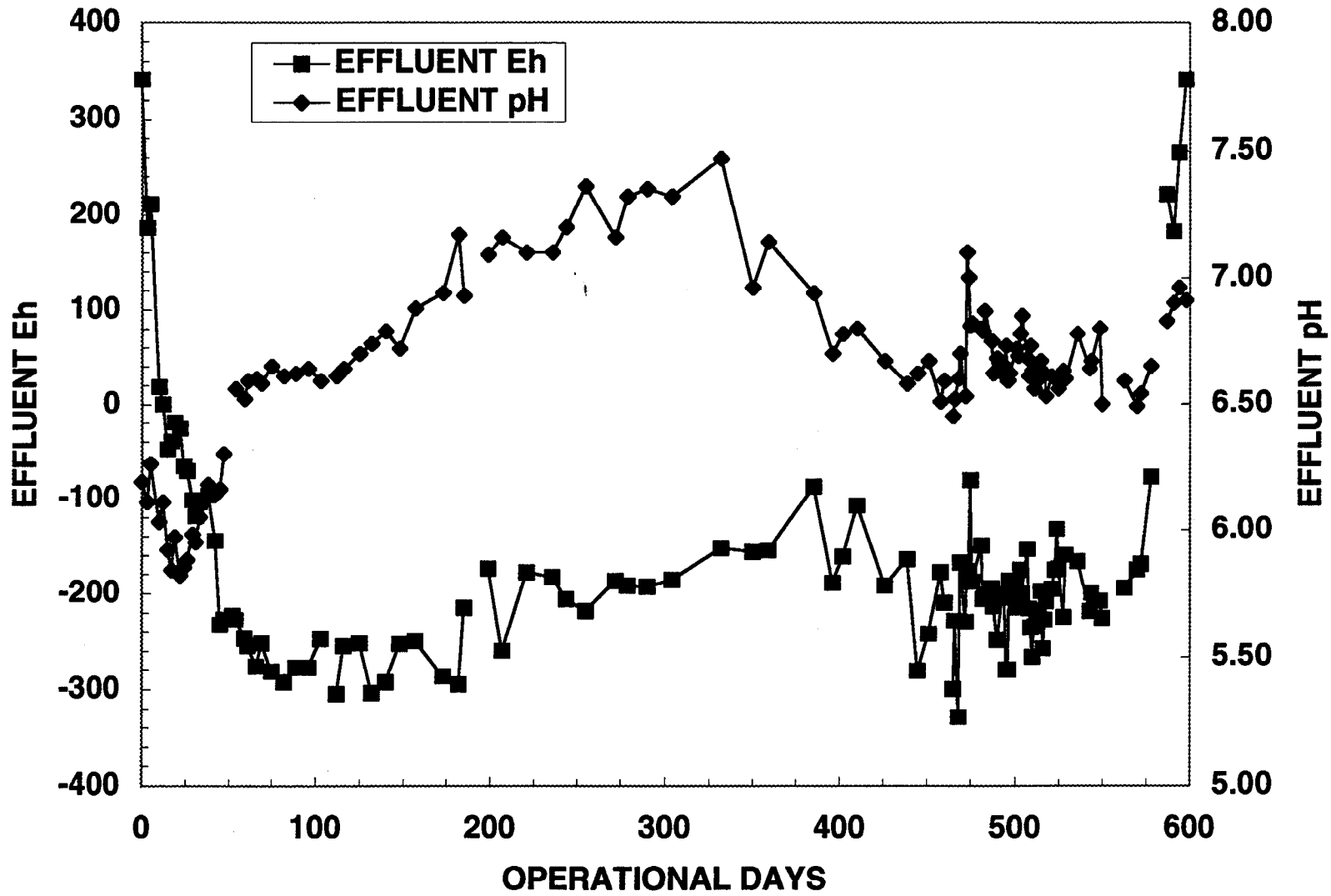
OPERATION

**DOWNFLOW CONFIGURATION FOR 600 DAYS
DESIGN FLOW RATE: 77 L / min
FLOWS REACHED 185 L / min**

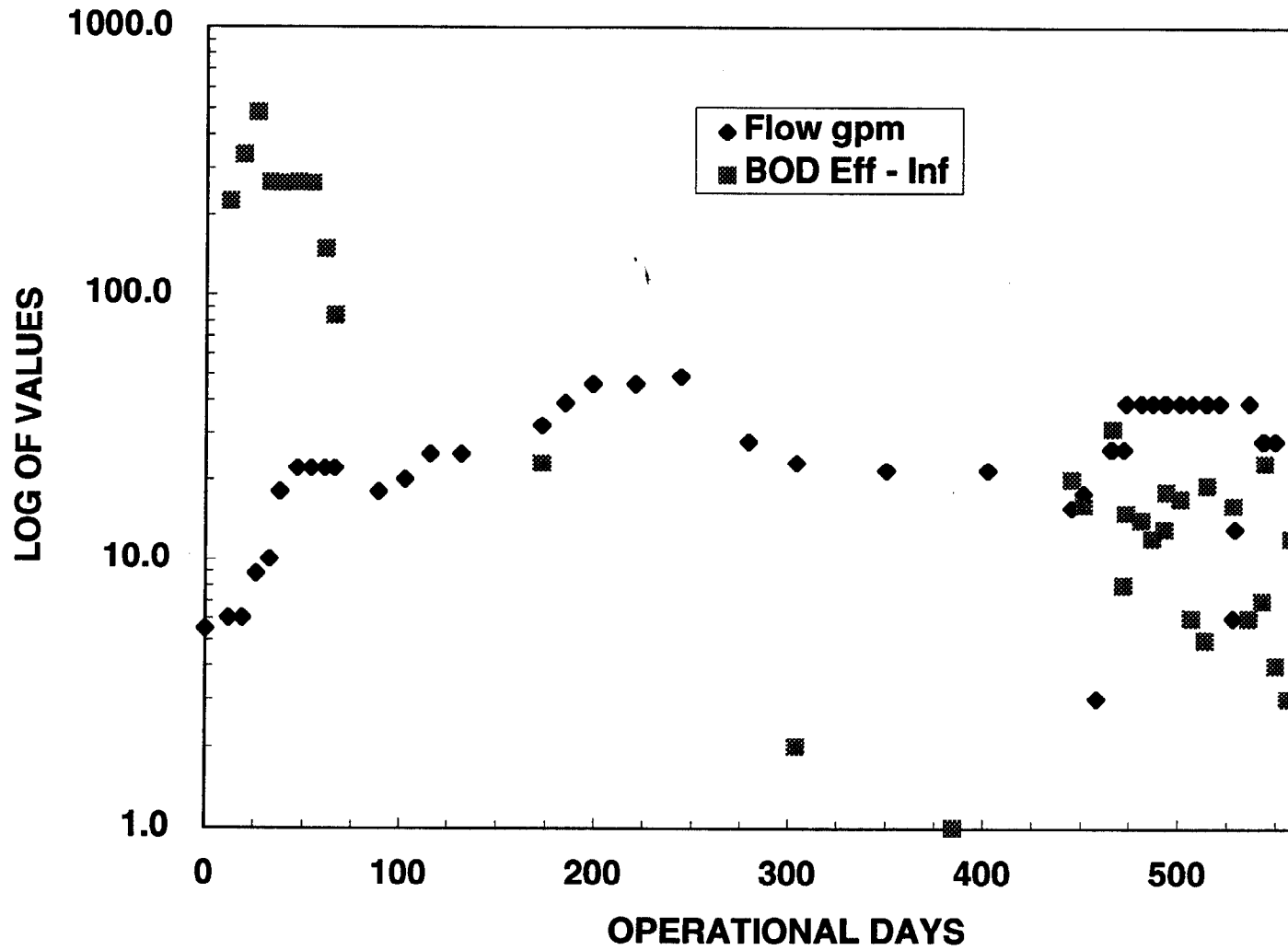
RESULTS

- 1. DURING OPERATION, Pb and Zn WERE ALWAYS REMOVED TO BELOW DETECTION LIMITS OF 0.02 & 0.008 mg / L RESPECTIVELY.**
- 2. FULL SCALE SYSTEM HAS BEEN BUILT TO TREAT 1500 gpm OF MINE WATER.**

pH & Eh IN THE ASARCO PILOT CELL EFFLUENT



FLOW & BIOLOGICAL OXYGEN DEMAND IN THE ASARCO PILOT CELL



FLOW AND BOD (ORGANIC CONTENT) OBSERVATIONS

- 1. INCREASES IN FLOW WERE USED TO CONTROL THE GENERATION OF SULFIDE.**
- 2. FOR BOD (ORGANIC CONTENT) IN THE EFFLUENT:**
 - a) LARGE CONCENTRATIONS AT START UP AS LABILE ORGANICS ARE LEACHED FROM THE SUBSTRATE.**
 - b) DEFINITE INCREASE IN THE SUMMER.**

BOD IMPLICATIONS

- 1. BOD IN THE EFFLUENT REPRESENTS ORGANIC MATERIAL THAT IS LOST FUEL FOR SULFATE REDUCTION.**
- 2. LOST ORGANIC MATERIAL DECREASES THE LIFE OF THE BIOREACTOR. ESTIMATES SUGGEST THAT AT START UP SUBSTRATE WOULD BE USED UP IN 10 YEARS. WHEN BOD DROPPED TO ZERO THE ORGANIC SUBSTRATE WOULD LAST FOR 100 YEARS.**
- 3. TO REALLY TEST A PILOT CELL THE SYSTEM HAS TO BE RUN FOR AT LEAST ONE YEAR.**

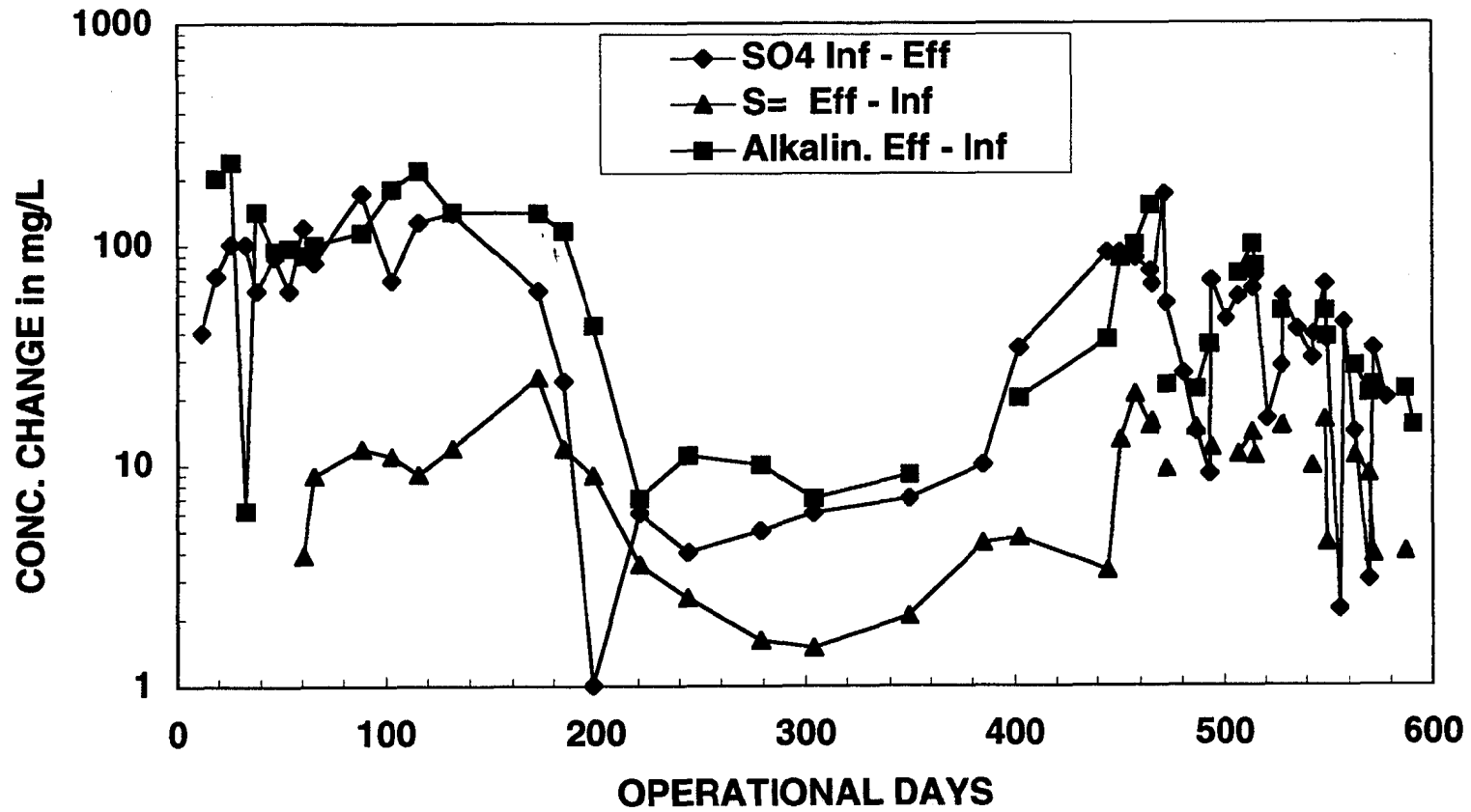
PILOT CELL PROVIDES THE OPPORTUNITY TO FOLLOW SULFATE REDUCTION REACTION



CAN FOLLOW REACTION BY

- 1. REDUCTION OF SULFATE IN WATER
(SO₄²⁻ MAY BE LEACHED FROM THE SUBSTRATE)**
- 2. INCREASE IN ALKALINITY IN WATER
(ALKALINITY MAY BE USED TO NEUTRALIZE WATER
OR TO PRECIPITATE METALS)**
- 3. INCREASE IN SULFIDE IN WATER
(SULFIDE MAY BE USED TO PRECIPITATE METALS
OR MAY RELEASE AS H₂S)**

CHANGES IN SULFATE, ALKALINITY, AND SULFIDE IN THE ASARCO PILOT CELL WATER



SULFIDE PRODUCTION RATE

USUAL METHOD

$$\frac{(\text{SULFATE IN} - \text{SULFATE OUT}) \text{ mmol / L} \times \text{FLOW L / min} \times 1.44}{\text{SUBSTRATE VOLUME m}^3}$$

$$= \text{MOLE SULFIDE PRODUCED / m}^3 \text{ DAY}$$

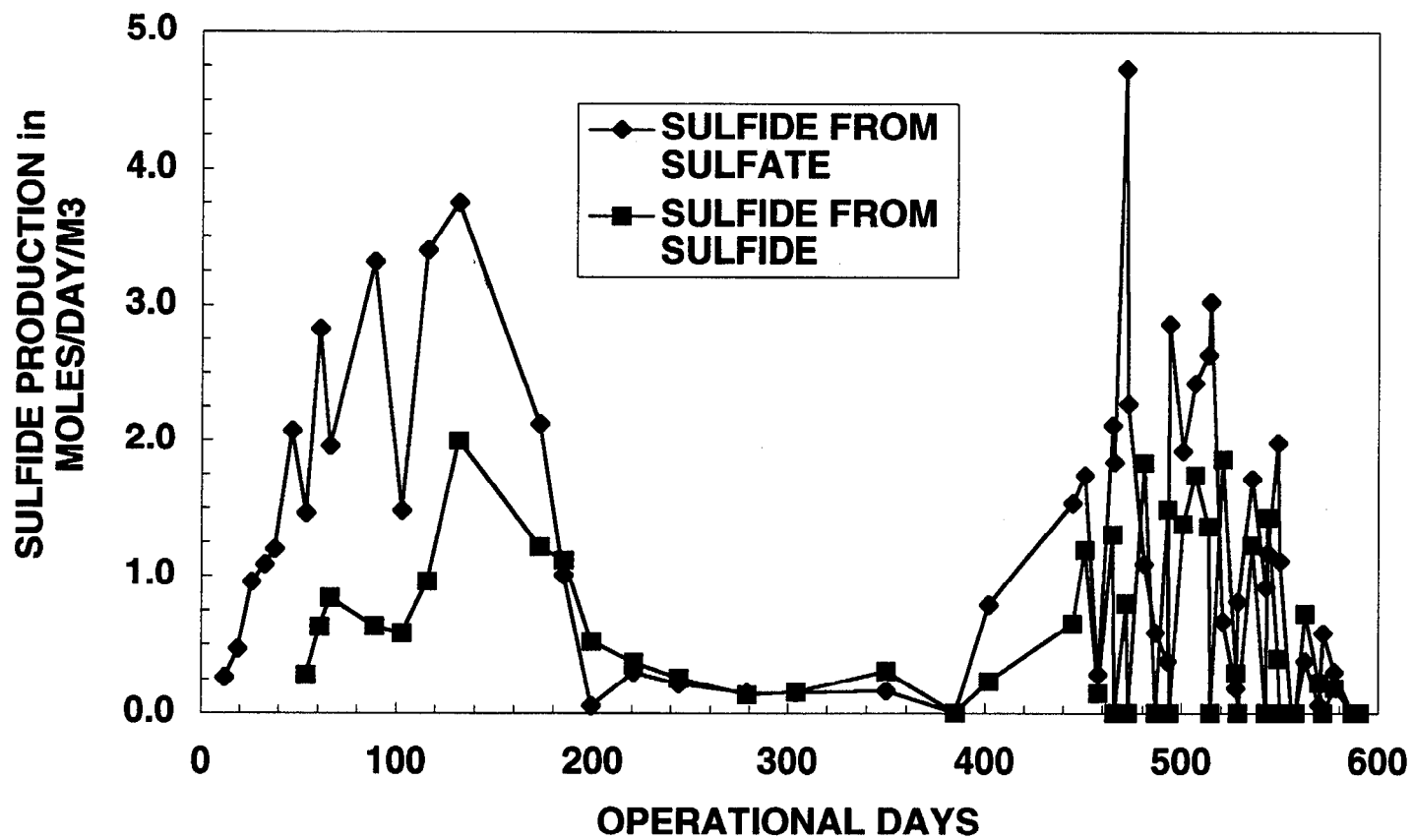
**THE VALUE IS THE BASIC SIZING PARAMETER FOR A
SULFATE REDUCING BIOREACTOR**

FOR ASARCO PILOT CELL WATER

- 1. pH = 8.0 & Fe & Al ARE ABSENT; NO ALKALINITY SHOULD BE USED TO NEUTRALIZE WATER.**
- 2. HEAVY METALS ARE IN LOW CONCENTRATION; LITTLE SULFIDE USED FOR PRECIPITATION.**
- 3. AFTER ~ 100 DAYS SULFATE NO LONGER LEACHED.**

CONSEQUENTLY, THIS PILOT CELL OFFERS THE BEST OPPORTUNITY TO FOLLOW THE SULFATE REDUCTION REACTION.

**SULFIDE GENERATION CALCULATED FROM
SULFATE REDUCED AND SULFIDE PRODUCED**



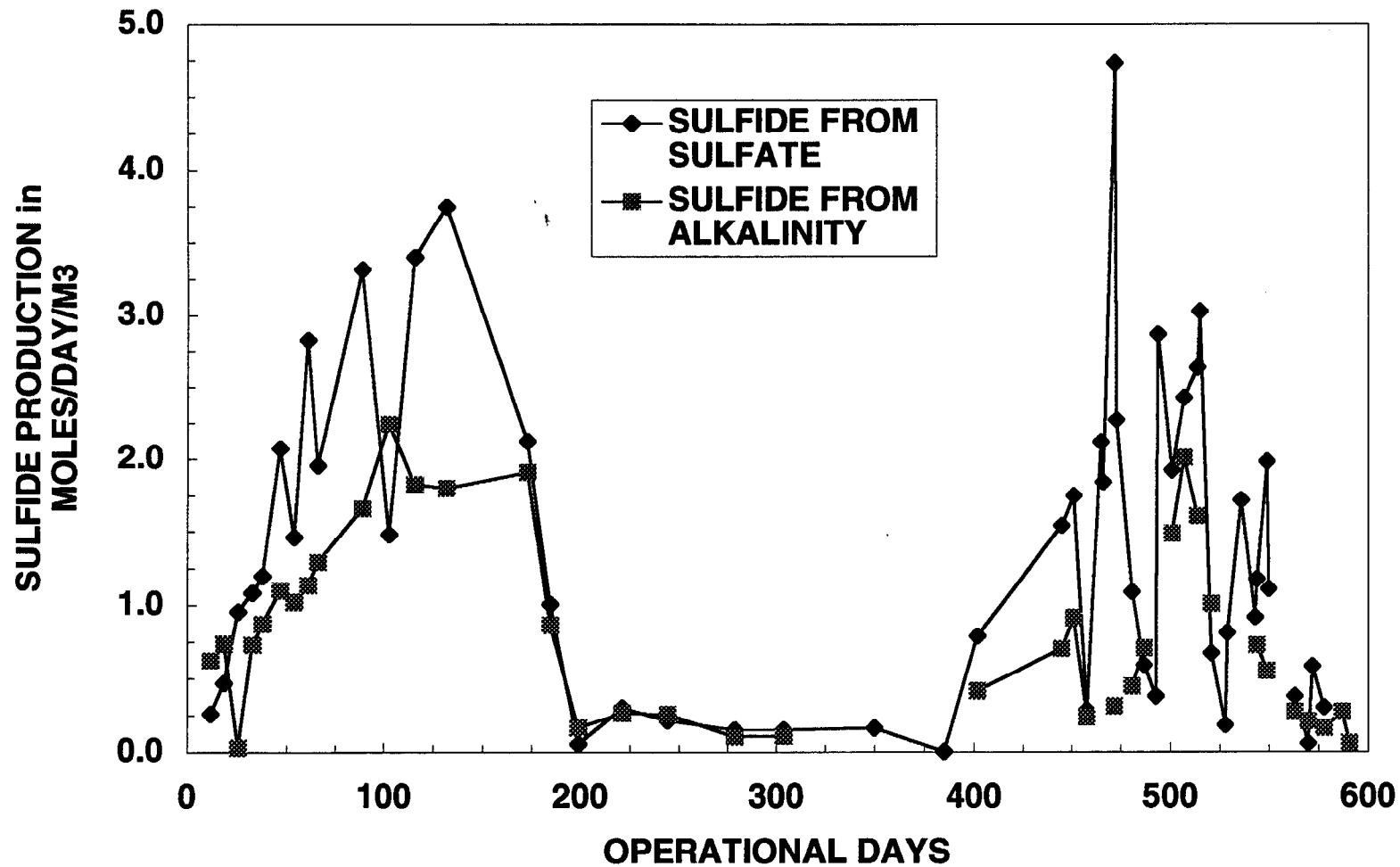
SULFIDE GENERATION CONCLUSIONS

- 1. DURING BOTH SUMMERS, PRODUCTION OF SULFIDE REACHED:**
 - a) 2 mole S^{2-} / m³ day, BASED ON SULFIDE.**
 - b) 4 mole S^{2-} / m³ day, BASED ON SULFATE.**
- 2. THE USUAL RULE OF THUMB IS:**
 - a) 0.15 mole S^{2-} / m³ day, BASED ON SULFATE FOR MINE WATER WITH pH < 3.**
 - b) 0.30 mole S^{2-} / m³ day, BASED ON SULFATE FOR MINE WATER WITH pH > 5.**

OUR OPINION

- 1. NO SECRET MATERIALS IN THE SUBSTRATE.**
- 2. THE ALKALINITY & pH OF THE MINE WATER ARE PERFECT FOR SULFATE REDUCTION.**

SULFIDE GENERATION CALCULATED FROM SULFATE REDUCED AND FROM ALKALINITY GENERATED



SULFIDE GENERATION CONCLUSIONS II

- 1. DURING THE WINTER, PRODUCTION OF SULFIDE FELL TO:**
 - a) 0.20 to 0.5 mole S^{2-} / m³ day, BASED ON SULFIDE.**
 - b) SAME VALUES, BASED ON SULFATE.**
- 2. THE USUAL RULE OF THUMB IS:**
 - a) 0.15 mole S^{2-} / m³ day, BASED ON SULFATE FOR MINE WATER WITH pH < 3.**
 - b) 0.30 mole S^{2-} / m³ day, BASED ON SULFATE FOR MINE WATER WITH pH > 5.**

OUR OPINION

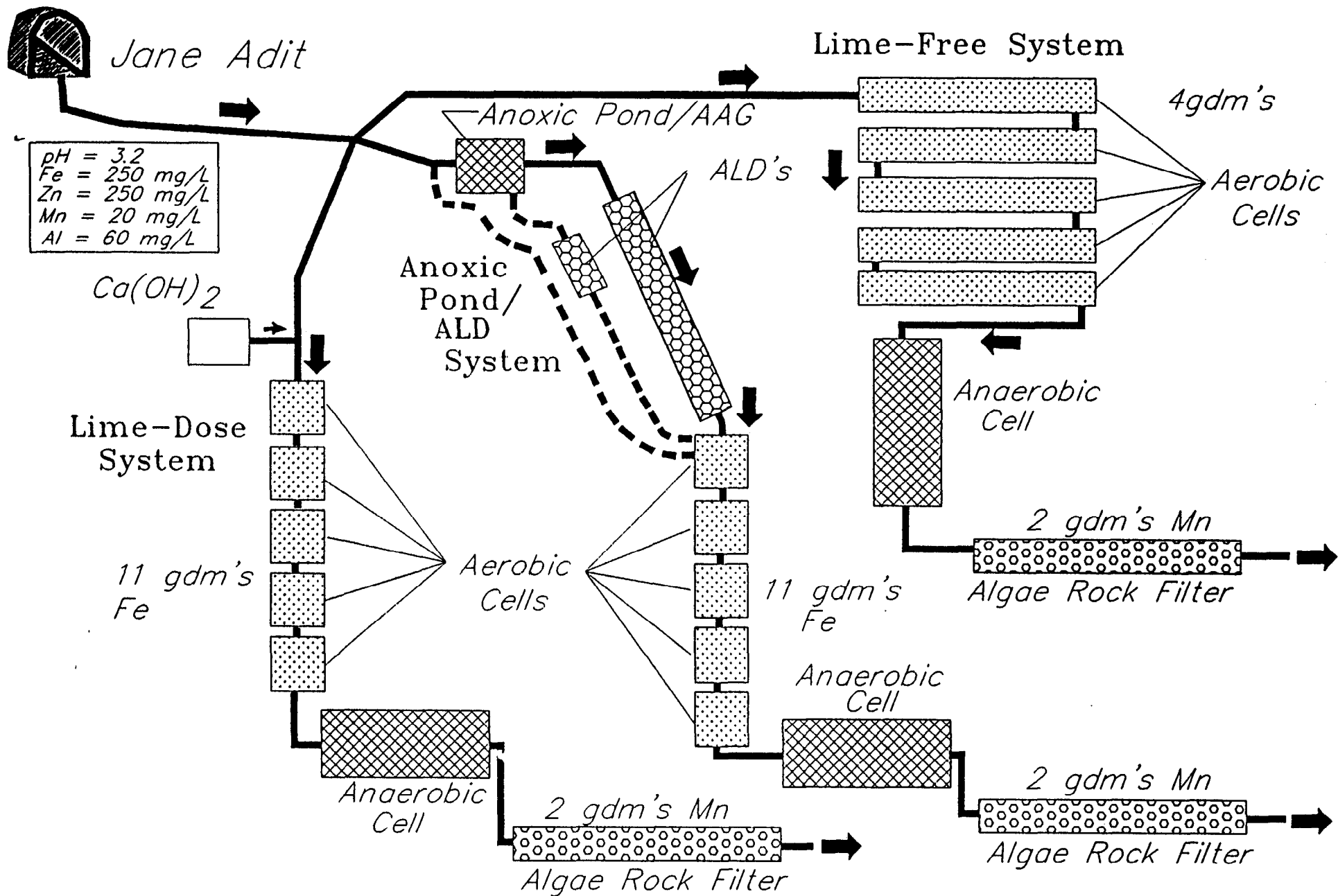
- 1. LABILE ORGANICS RAN OUT AT DAY 200.**
- 2. THE WATER IS HELD IN A SETTLING POND BEFORE THE PILOT CELL. THE INFLUENT TEMPERATURE FELL FROM 26 ° C IN THE SUMMER TO 6 ° C IN THE WINTER.**

SULFIDE GENERATION CONCLUSIONS III

- 1. SULFIDE PRODUCED BASED ON SULFATE REDUCTION IS GENERALLY THE HIGHEST.**
- 2. SULFIDE IS LOWER BECAUSE IT IS EASILY LOST.**
- 3. ALKALINITY COULD BE LOWER BECAUSE IT IS CONSUMED BY ORGANIC ACIDS.**

FULL-SCALE SYSTEM FEATURES

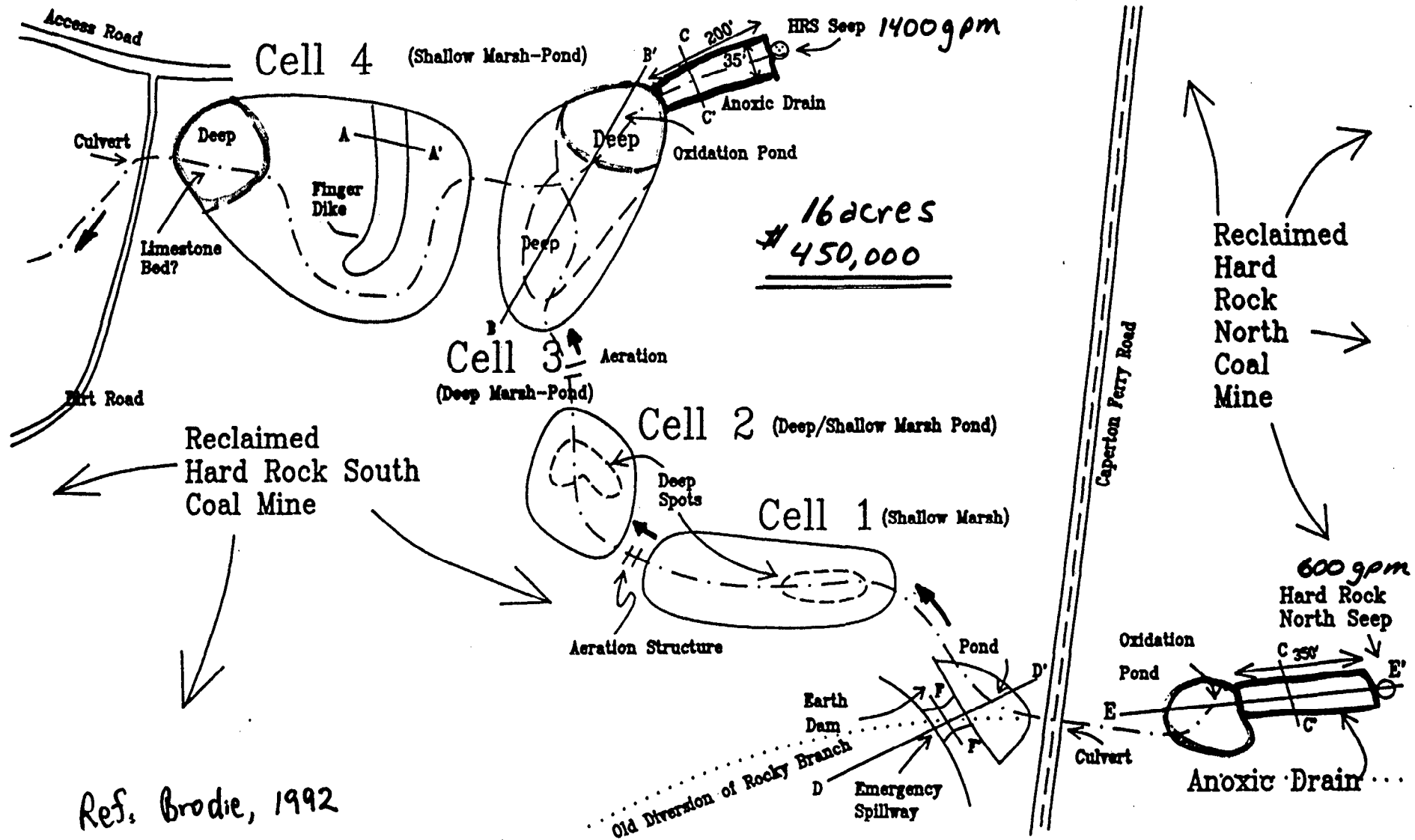
- 1. A FLOW OF 1500 gpm.**
- 2. TWO PARALLEL CELLS WERE BUILT SO ONE COULD BE TURNED OFF DURING THE SUMMER.**
- 3. MULTIPLE INLET SYSTEMS WERE BUILT TO TRY TO USE ONLY A PORTION OF THE CELL WHEN SULFIDE PRODUCTION IS HIGH.**
- 4. A ROCK-FILTER POLISHING CELL WAS BUILT TO REDUCE EXCESS SULFIDE & BOD.**



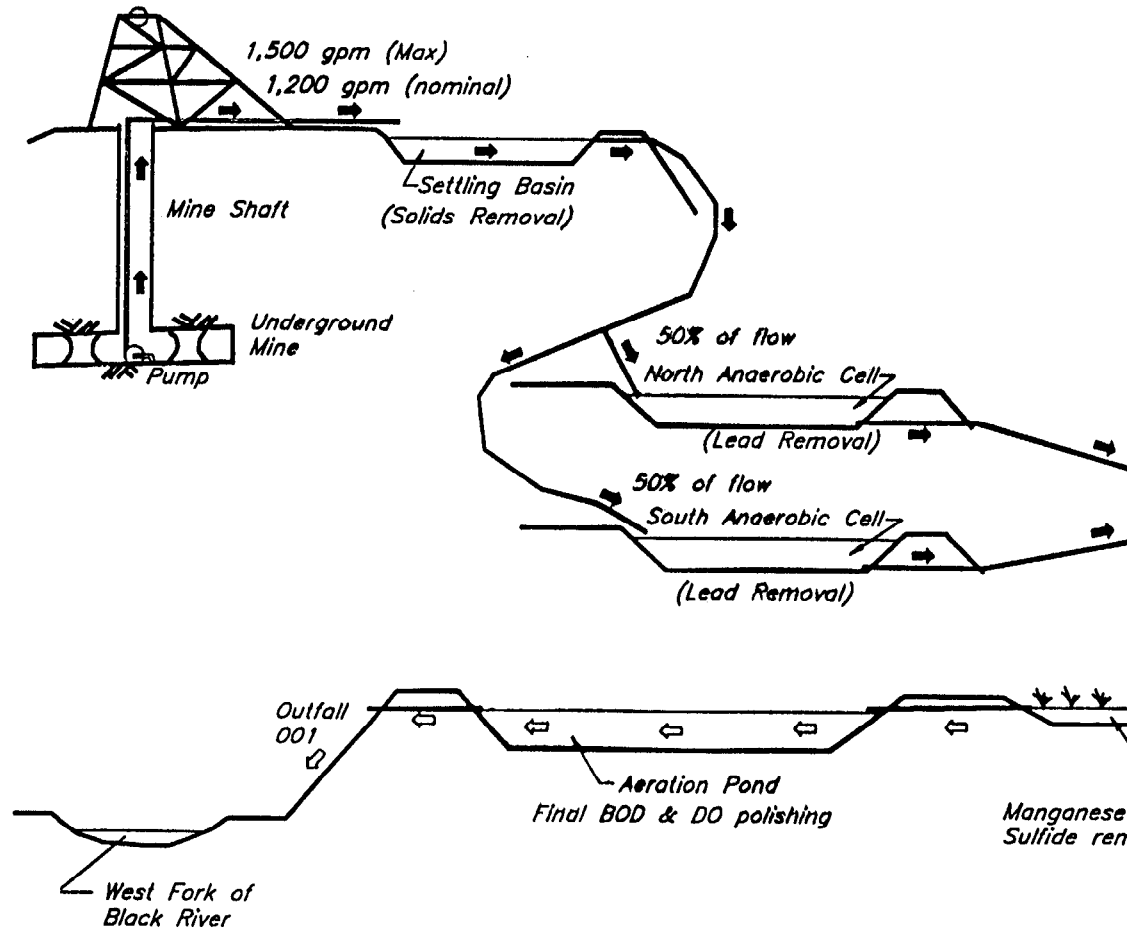
WHEAL JANE MINE, CORNWALL, UK
 PILOT SCALE PASSIVE TREATMENT SYSTEMS

pH Fe Mn Alk Acid.
 1400gpm 5.5 40 17 40 -
 600gpm 5.5 40 11 - 200

CONCEPTUAL DESIGN
 Hard Rock Constructed Wetlands
 Fabius Coal Mines, Jackson Co., AL



Full Scale System La



Part II

ACID MINE WATER TREATMENT

Authors:

R. Knapp, Dave Orava - SENES

Grant Feasby, Geneviève Béchard, Janice Zinck, CANMET

TOPICS:

- Sources / Treatment Concerns
- Fundamentals of Metal Precipitation
- Reagents
- Coagulation / Flocculation / Settling
- Process Alternatives
- Sludge Production / Characteristics
- Costing
- Non-Metallic Contaminants
- The HDS, Advanced Processes
- Issues, Emerging Technologies

SOURCES / CONTAMINANTS IN MINE WATER

	Acidity	Metals	CN	T S S	Nutrients			Organics		Thiosalts
					NH ₃	NO ₃	PO ₄	O & G	Other	
Underground Mine	P	P	▣	P	P	P	▣	S	▣	▣
Open Pit Mine	P	P	▣	P	S	S	▣	S	▣	▣
Site Runoff	S	S	S	P	▣	▣	▣	S	S	▣
Stockpiles	P	P	S	P	P	P	▣	▣	▣	▣
Waste Rock	P	P	▣	▣	▣	▣	▣	▣	▣	
Tailings	P	P	P	P	S*	S*	S	▣	S	P
Sewage	▣	▣	▣	P	P	P	P	▣	P	▣

P	-	Primary Potential Source
S	-	Secondary Potential Source
▣	-	Likely Not a Significant Contaminant

FUNDAMENTALS OF METAL PRECIPITATION

→ Reagents

→ Precipitation Reactions

→ Reactor Design

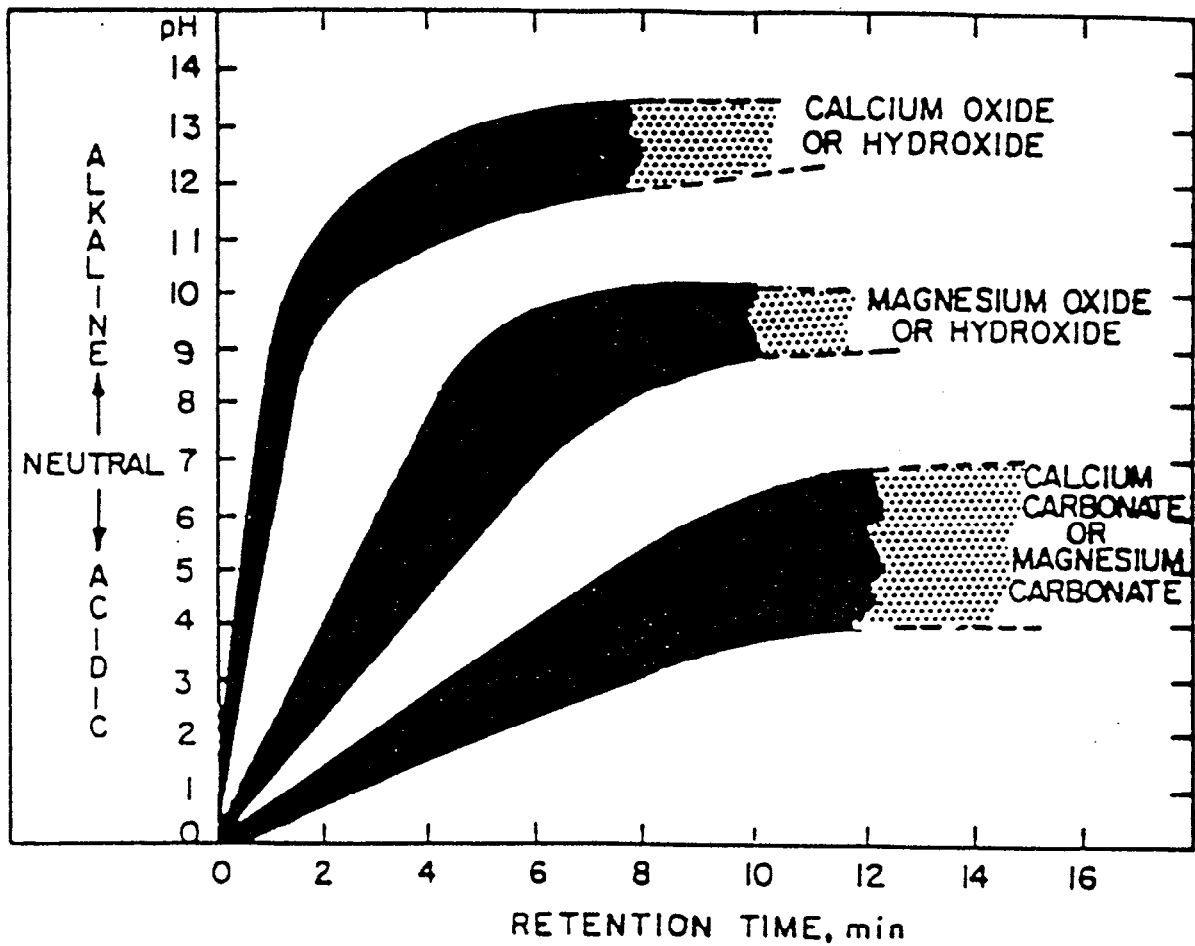
→ Staged Precipitation

NEUTRALIZING REAGENTS

	Relative Effectiveness	Relative Cost
CaO	1.00	1.0
Ca(OH) ₂	1.33	1.6
CaCO ₃	1.79	0.3
Na OH	1.43	8.8
Na ₂ CO ₃	1.89	3.8
Mg O	0.72	3.4

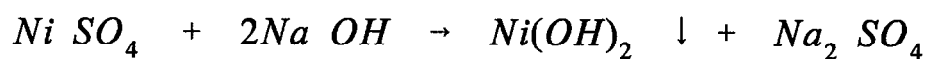
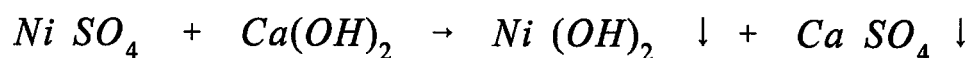
FIGURE 2.2

GENERALIZED REACTION RATES
FOR CALCIUM AND MAGNESIUM HYDROXIDES
AND FOR CORRESPONDING LIMESTONES

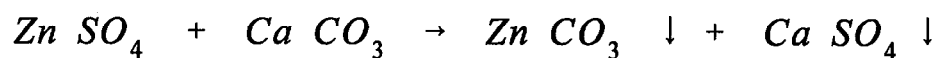


Precipitation Reactions

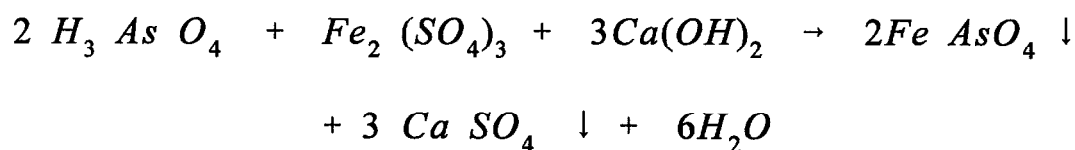
Hydroxides



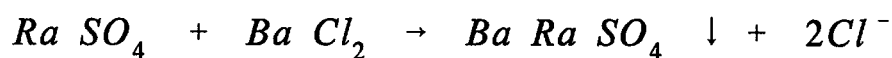
Carbonates



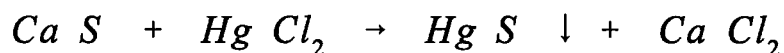
Iron Reactions



Co-precipitation



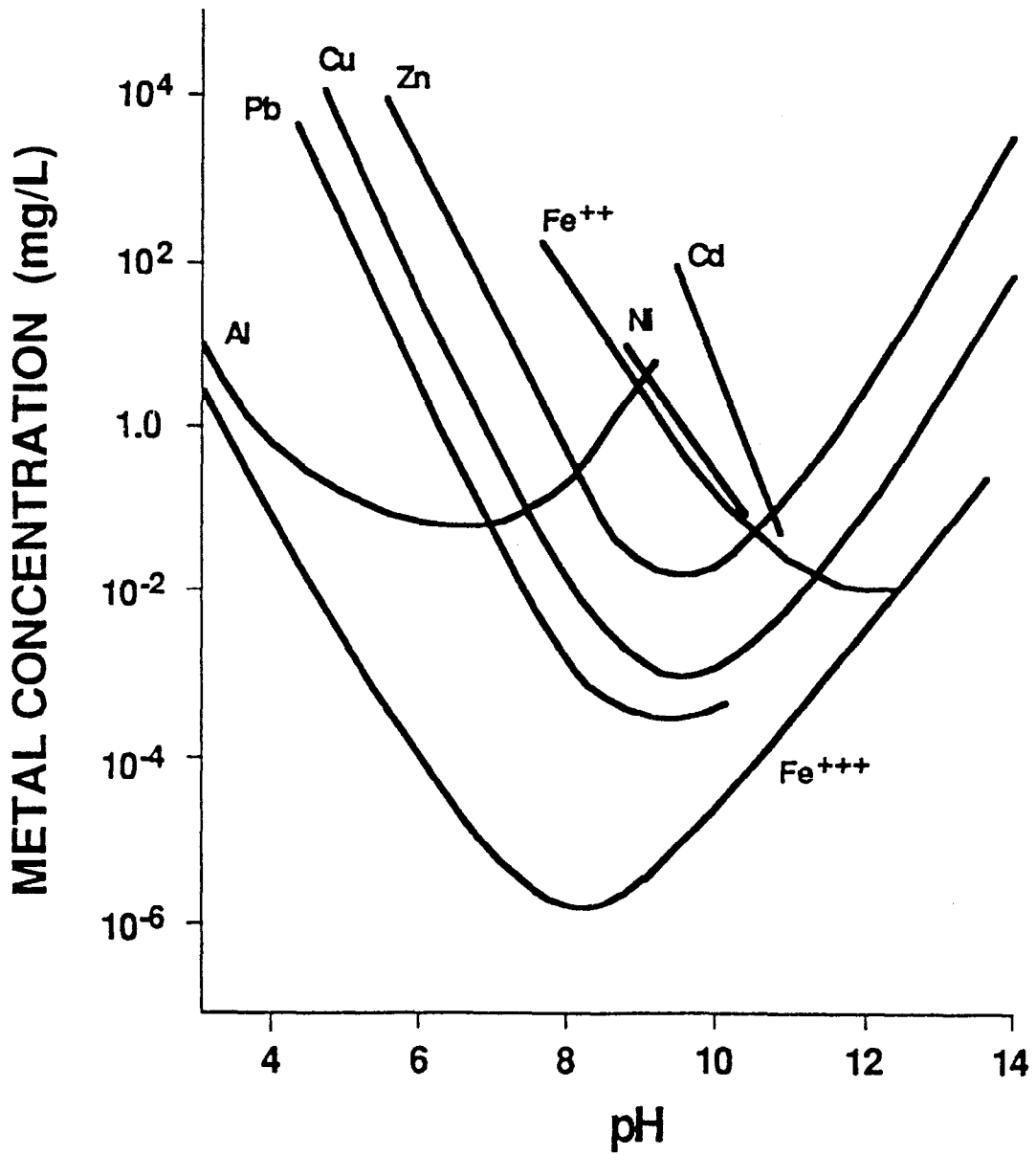
Sulphide Precipitation



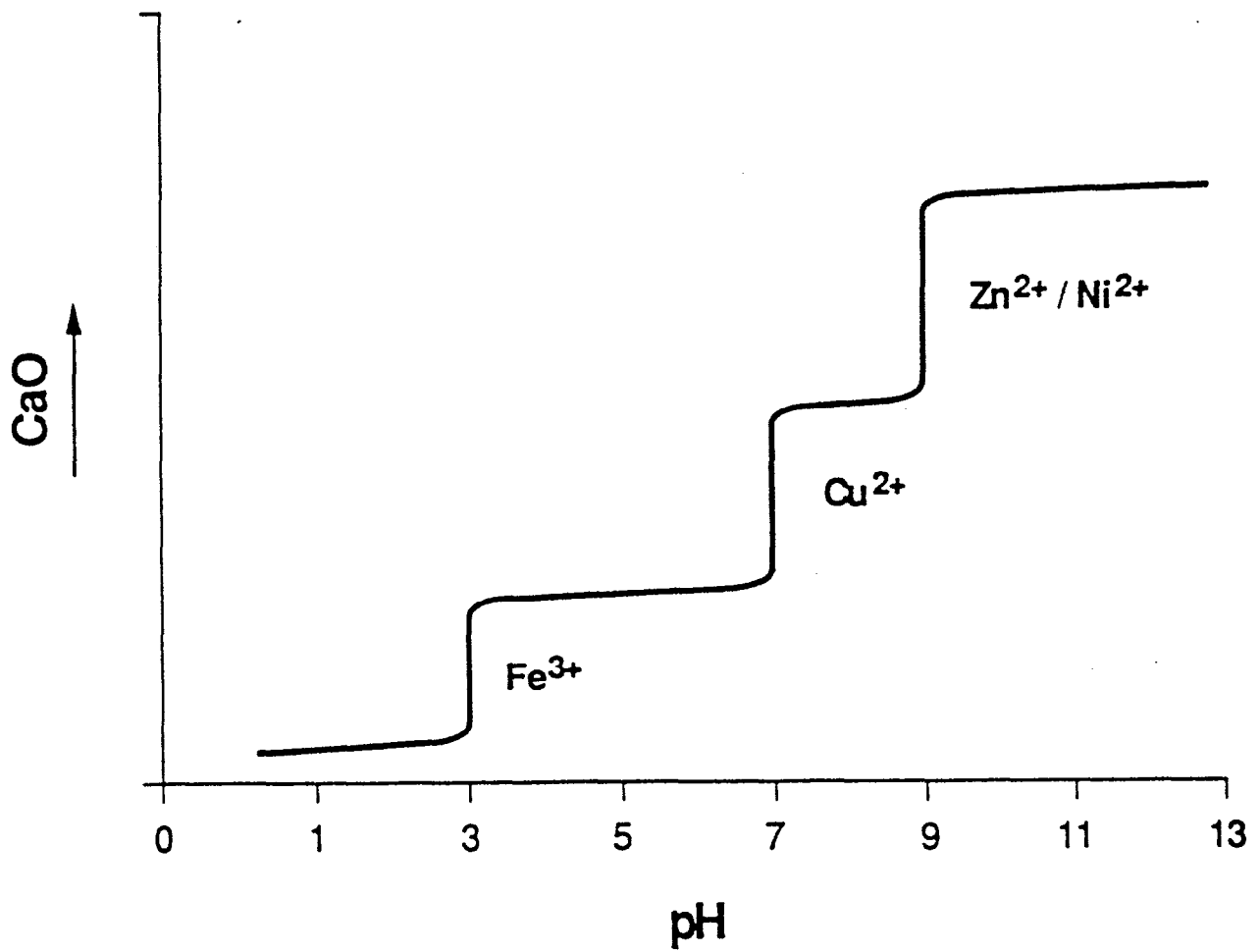
Reactor Design

- Dependent on Flow Variability (peak rate)
- Highly Dependent on Reaction Rate
- Highly Dependent on Reagent/Function
 - pH adjustment - 5-10 min
 - metal precipitation - “ “
 - Arsenic precipitation - 20-40 min
 - Radium precipitation - 10-30 min
 - Suspended solids - variable

Metal Solubilities



MULTIPLE STAGE PRECIPITATION - TITRATION CURVE



Single and Multiple Stage Precipitation

Single Stage - Simple Hydroxide Precipitation

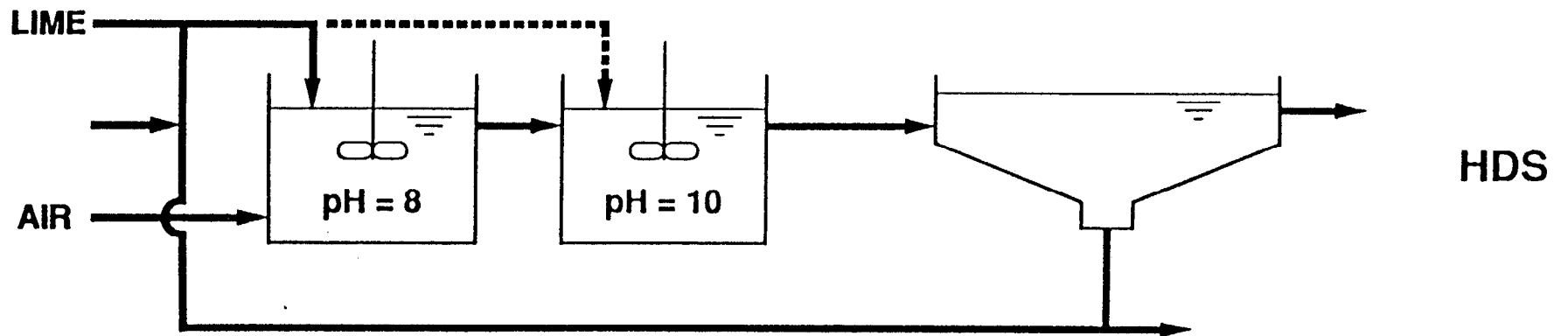
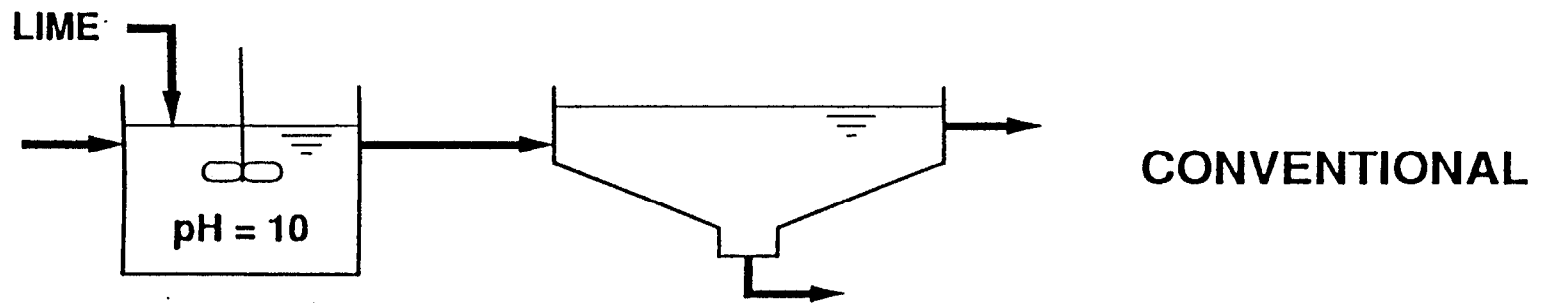
Multiple with Dual Stage Solids Separation
(e.g. Mo + Metals- eg Zn, Ni)

Multiple - Dual Reagent Addition
(e.g. Arsenic + Metals)

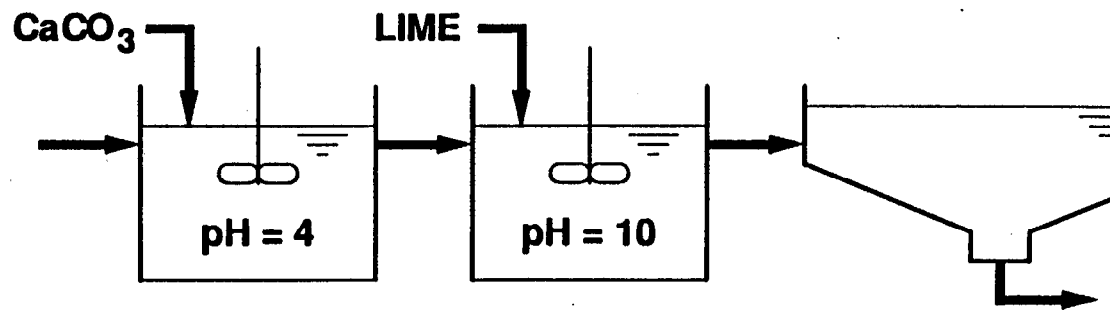
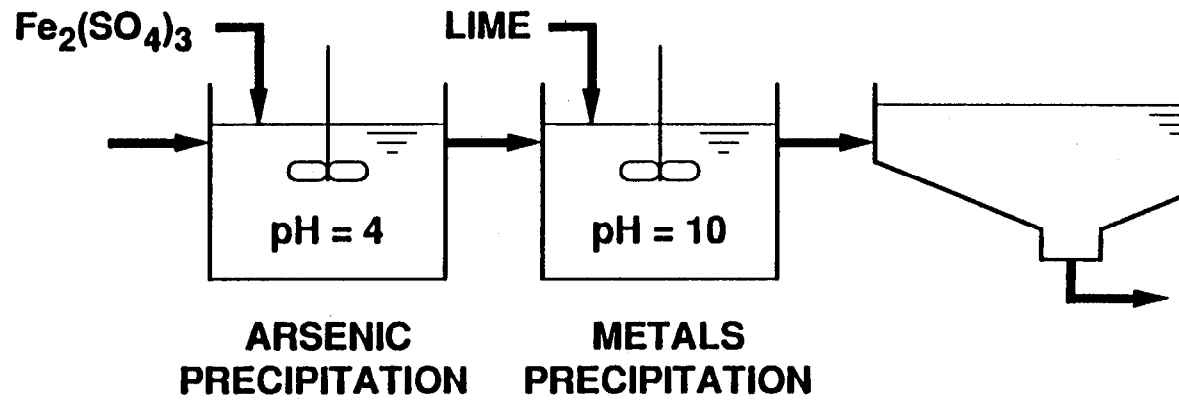
Multiple - Multiple Reagents
(e.g. Ra, As, Metals)

See Figures

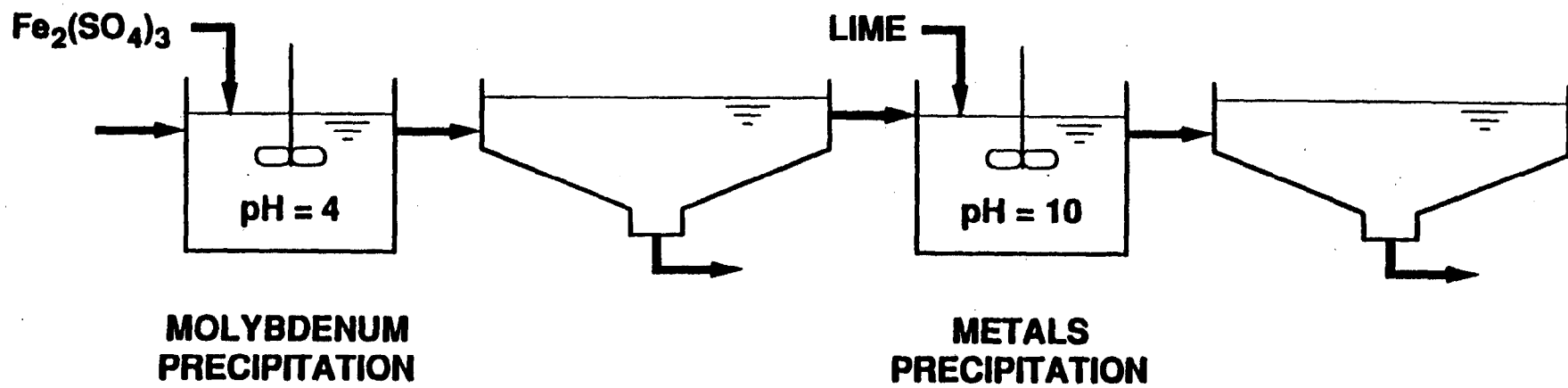
SINGLE - STAGE PRECIPITATION WITH Zn, Ni, Fe²⁺ / Fe³⁺



MULTIPLE REAGENTS



MULTIPLE REAGENTS / MULTIPLE SOLIDS / LIQUID SEPARATION



Typical Reagent Demands

→ Acidity Removal - metals precipitation

Final pH related - 1.15 to 1.3 times
theoretical demand

→ Arsenic Precipitation

- 2 to 6 times theoretical demand
- As/Fe ratio, pH important

→ Co-precipitation/Adsorption

- highly solution dependent
- removal generally a function of
addition rate

COAGULATION / FLOCCULATION

Processes to optimize settling of colloidal solids

Coagulation

- process of particle aggregation

Flocculation

- formation of particle / polymer flocs

Colloids

- finely charged particles dispersed in water (typically $< 100 \mu\text{m}$)
- clays, hydrous metal oxides
- charge affected by pH, ionic strength
- may be formed by any particle with low solubility in water
- metallic oxides typically positive

DESTABILIZATION OF COLLOIDS

There are 4 primary methods to destabilize

- 1) Compression of the Diffuse Layer
 - increased salinity / attraction of counter ions
 - allows particles to come closer / collide
- 2) Adsorption / Charge Neutralization
 - adsorption by polymer / salt
 - neutralization of charge allows flocculation
- 3) Enmeshment
 - use of coagulant to trap colloid
 - e.g. Fe Cl_3 , $\text{Al}_2 (\text{SO}_4)_3$
 - also includes adsorption / particle bridging
- 4) Adsorption / Interparticle Bridging
 - use of a polymer
 - polymer forms bridges to flocculate particles

Summary - More an Art than Science

MOST COMMON REAGENTS

- Metallic Salts (Fe^{3+} , Al^{3+})

- Organic Polymers
 - Nonionic
 - Anionic
 - Cationic

- Silicates

- Starches

- pH Adjustment

- Typically screen reagents through jar tests

Sedimentation

Class 1 - Clarification

- settling of dilute suspension with little tendency to flocculate

Class 2 - Clarification

- settling of a dilute suspension of flocculent particles

Class 3 - Zone Settling

Class 4 - Compression

See Figures

IDEAL, DISCRETE PARTICLE ———
 HINDERED, ZONE - - - - -
 FLOCCULENT ······
 MIXTURE, FLOCCULENT AND HINDERED SETTLING - · - · -

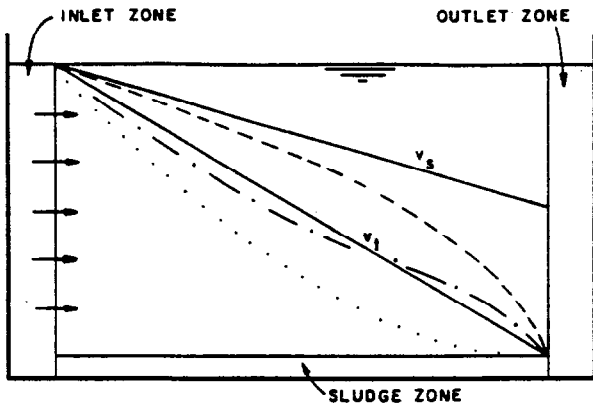
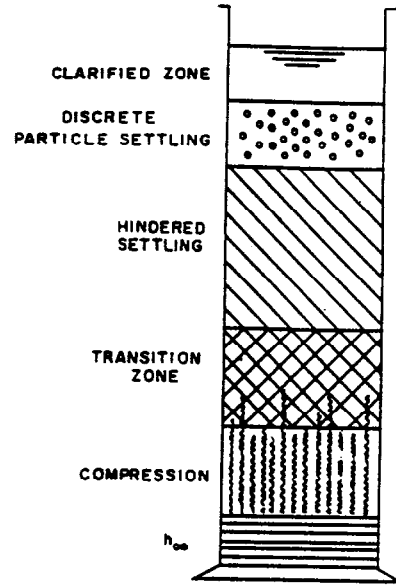
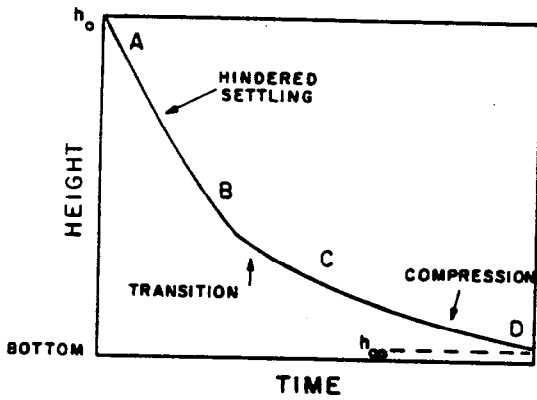


Figure 3-4 Discrete particle settling.



Zone sedimentation.



Height of interface in zone settling.

FROM WEBER (1972)

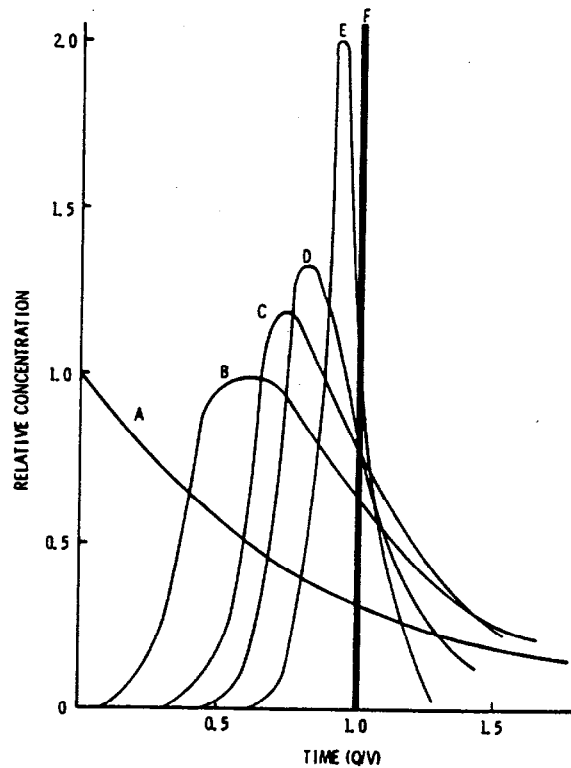


Figure 3-12 Typical dispersion curves.

Settling / Residence Requirements

- Wastewater / Process Specific (Test Data)

- Typical Design Loadings
 - Overflow rate: 500 - 2,000 USGPD/ft² (Thickener)

 - Residence - 12 hours in Thickener

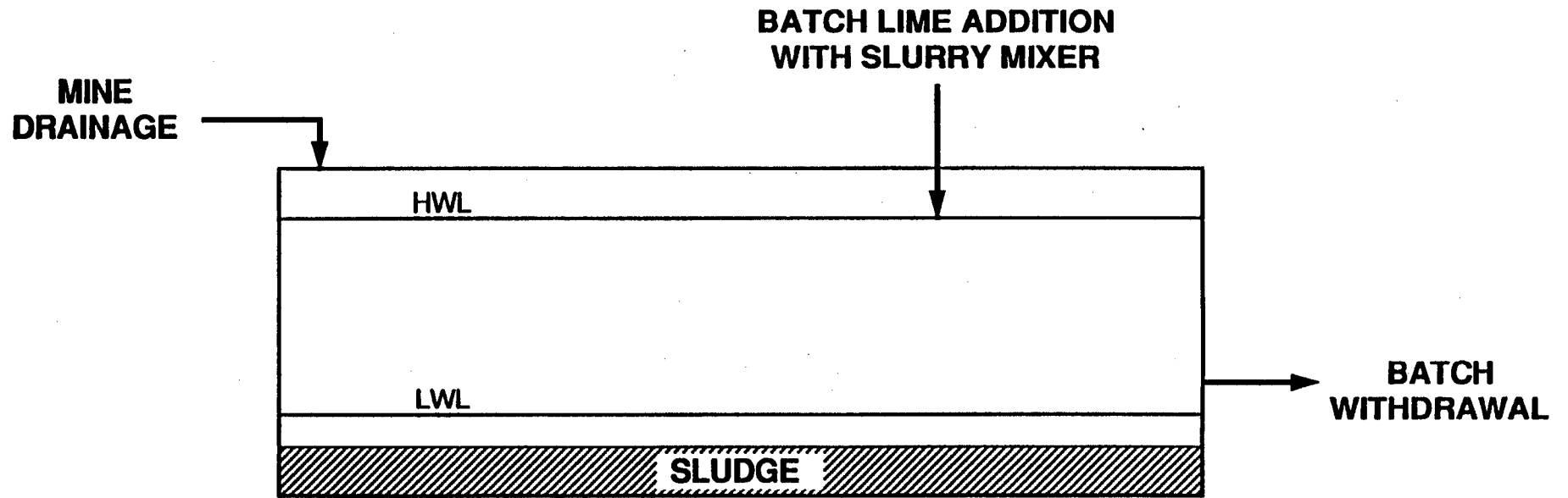
 - Natural Pond / Lagoon: 5 - 10 days

 - Engineered Pond / Lagoon: 2 - 5 days

LIME TREATMENT OPTIONS

- Batch
- Conventional Lagoons / Clarifier
- High Density Sludge (HDS)
- Advanced HDS
- New Techniques

BATCH TREATMENT



Liming/Settling Pond

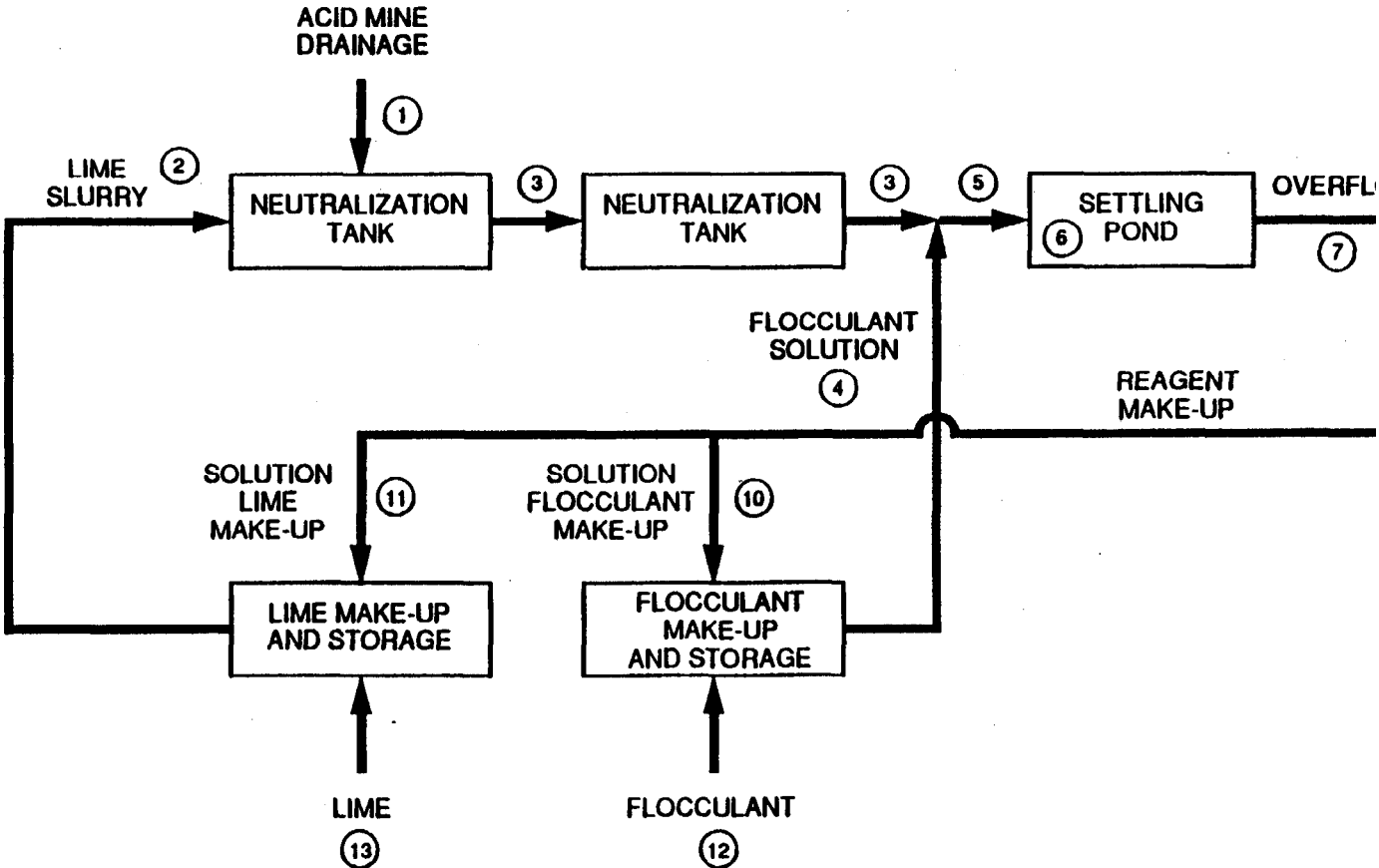
ADVANTAGES

- low capital cost
- easy maintenance and operation

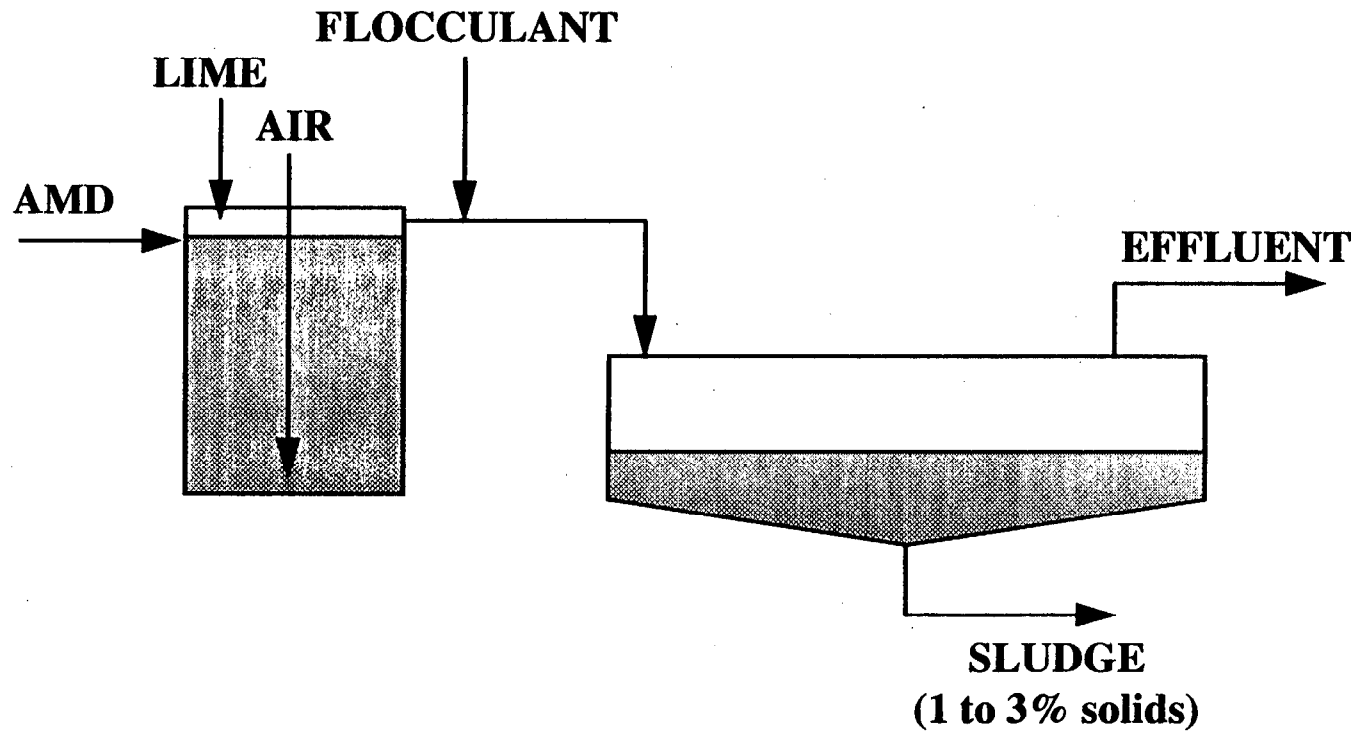
DISADVANTAGES

- low efficiency, very little control
- need to remove sludge periodically
- no aeration - unstable sludge

CASE 1: BA



Conventional Treatment



Conventional Treatment

ADVANTAGES

- relatively low capital cost
- easy maintenance and operation
- good control, high efficiency

DISADVANTAGES

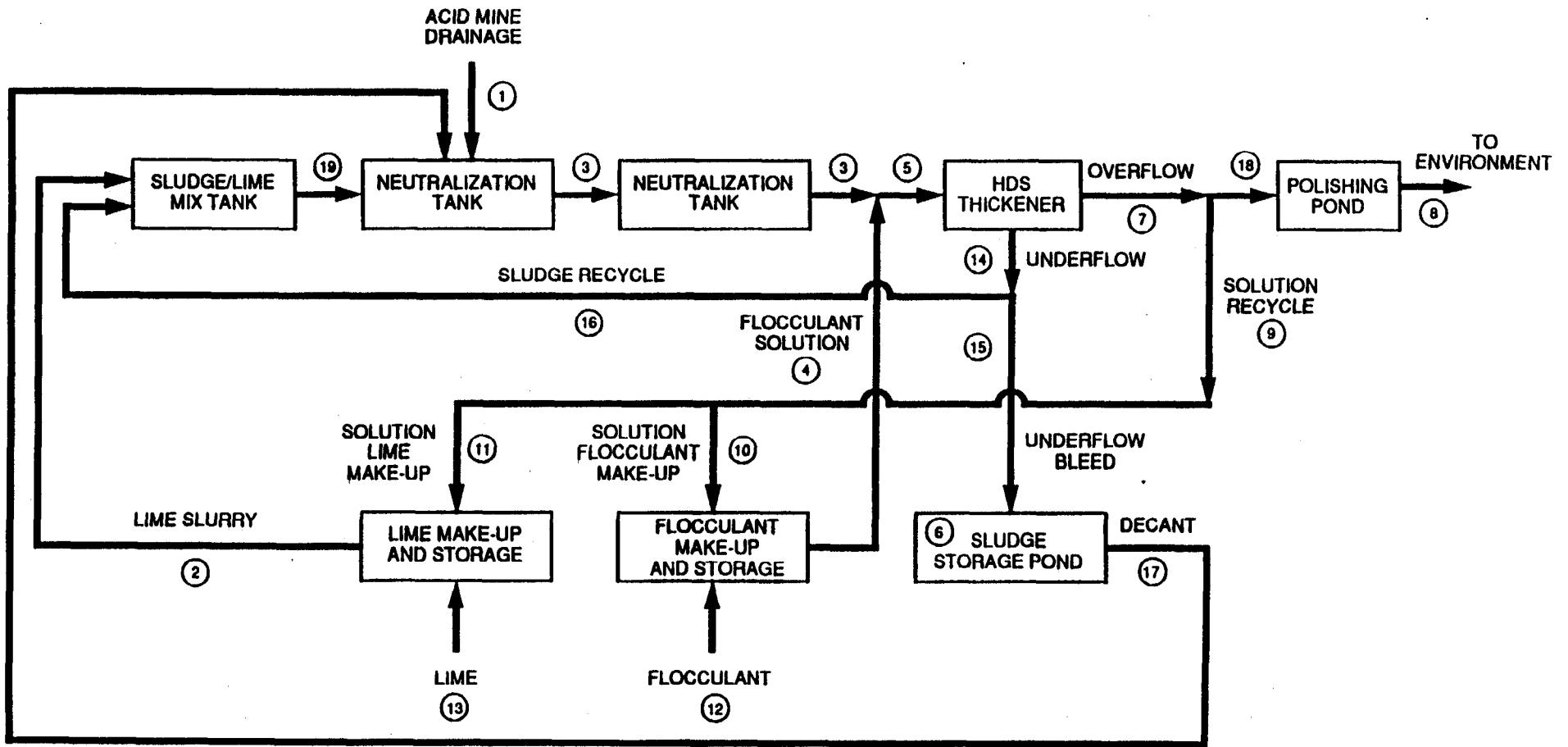
- low density sludge

EXAMPLE

- most old treatment plants

FIGURE 2.10

CASE 2: CURRENT ADVANCED TECHNOLOGY



High Density Sludge Proc

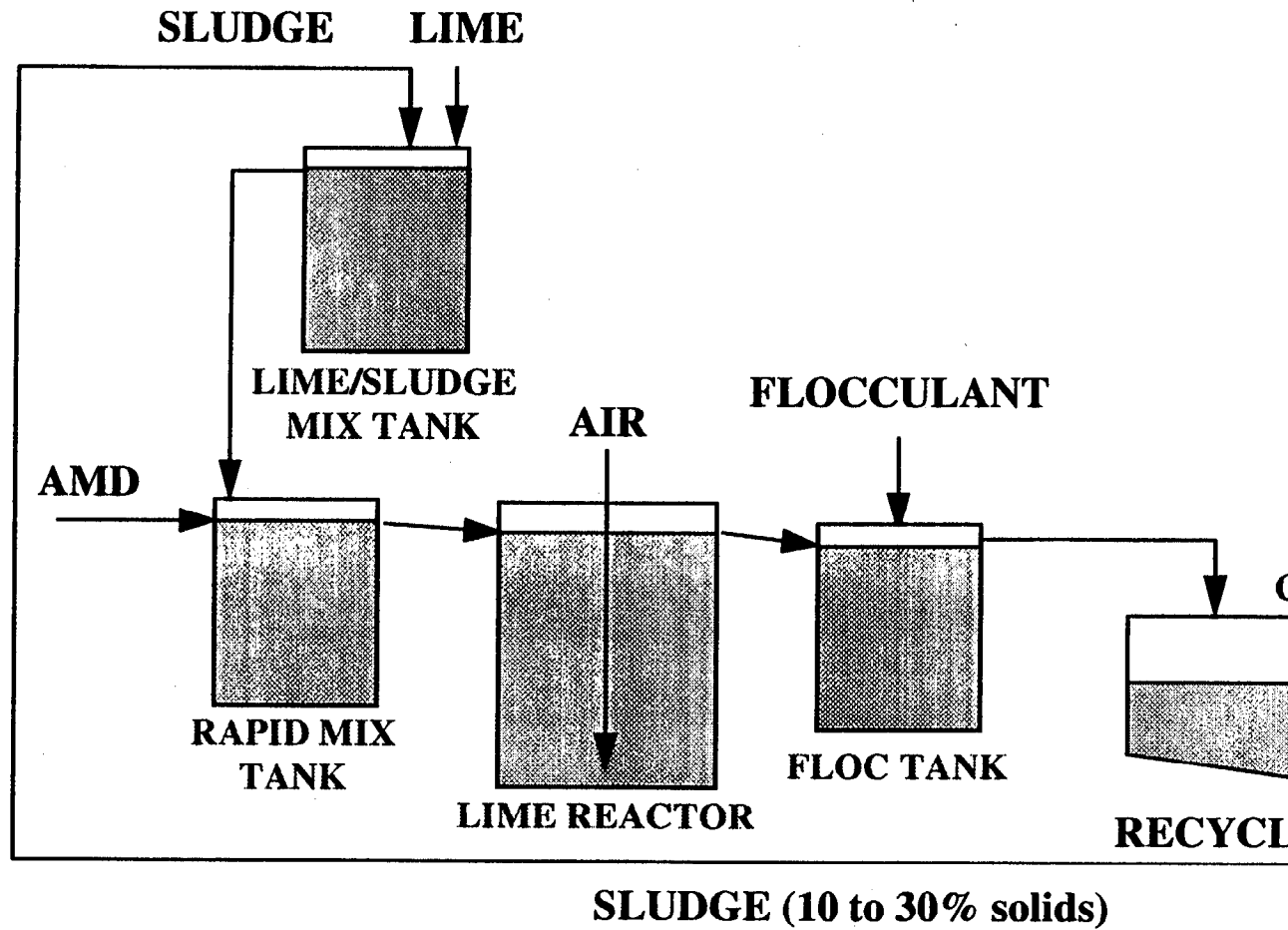
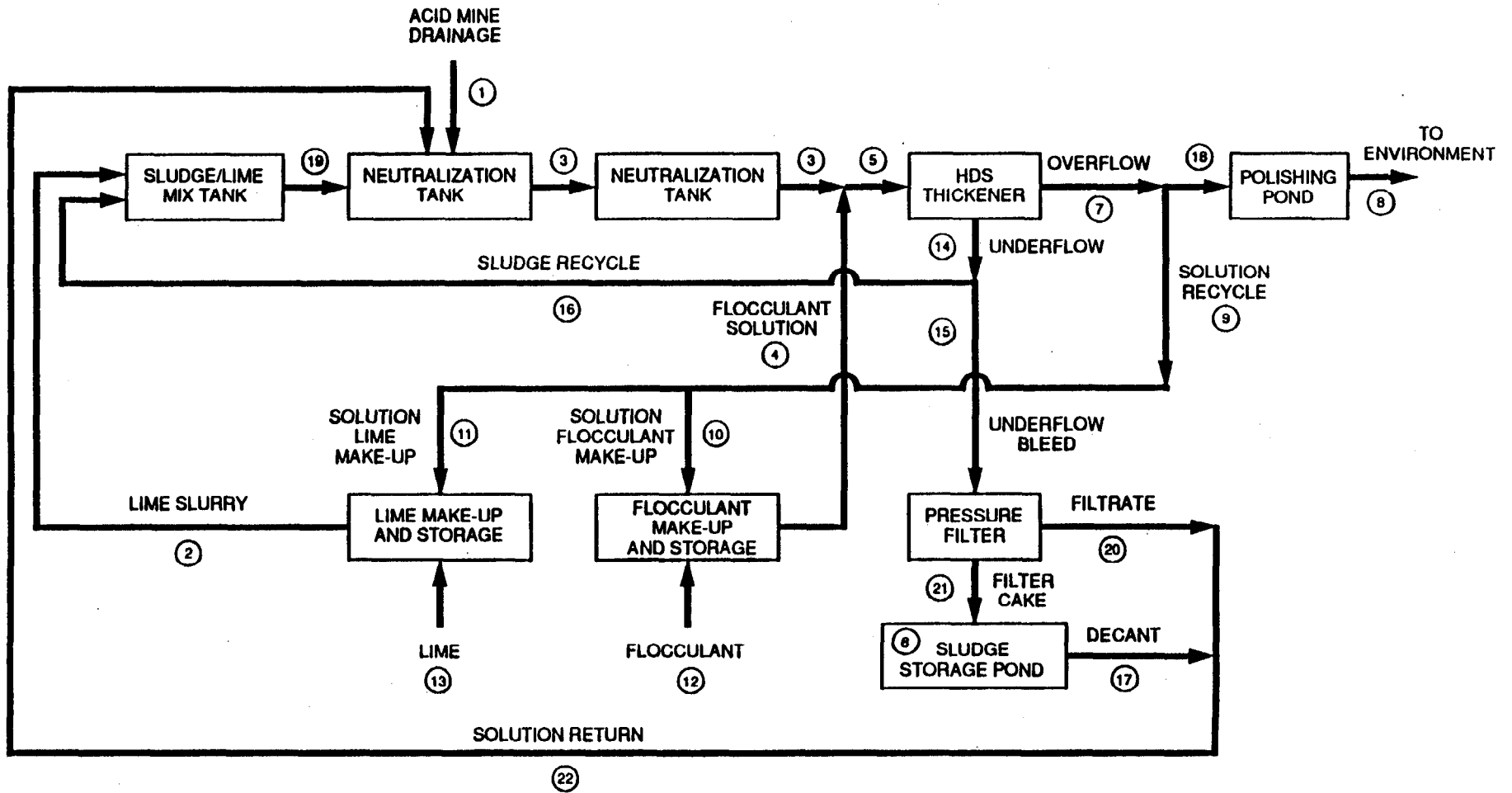


FIGURE 2.11

CASE 3: ENHANCED HIGH DENSITY SLUDGE TREATMENT



High Density Sludge Process

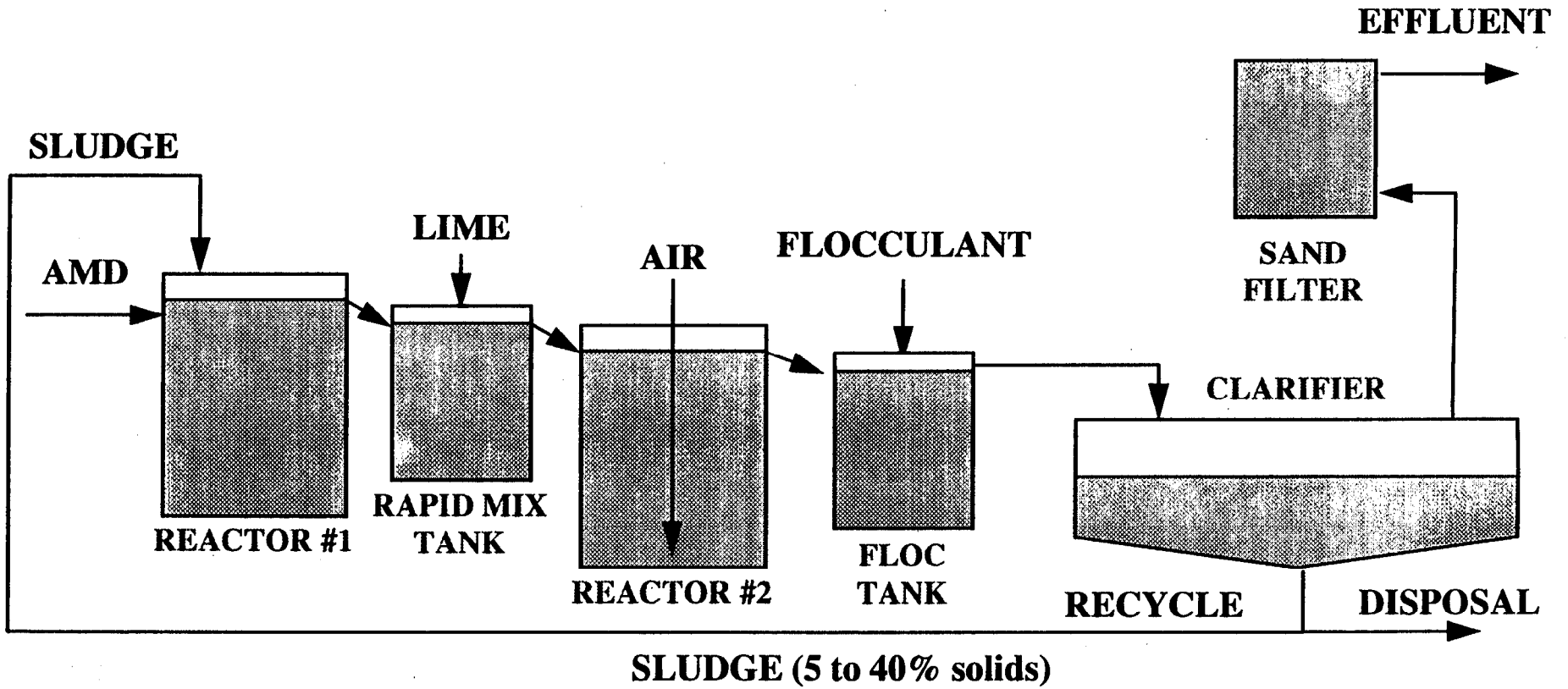
ADVANTAGES

- high sludge density
- good control, high efficiency

DISADVANTAGES

- high capital cost
- high sludge viscosity
- possible scaling problems with lime/sludge mixing

Geco Process



Geco Process

ADVANTAGES

- possibility of high sludge density and low viscosity
- high efficiency
- flexibility

DISADVANTAGES

- high capital cost
- new process
- solid/liquid separation unsure

EXAMPLE

- Geco

Common Problems at Water Treatment Plants

- Raw water variability
- Density gauges on sludge
- Sludge viscosity
- Lime system
- Plugged-up lines
- Others

ALTERNATIVE PROCESSES

Metals Recovery

- Cementation - Cu
- Ion Exchange - metals
- Solvent Extraction - metals
- Carbon Adsorption - organics
- Reverse Osmosis - \$\$, TDS, SS limits
- Sulphide Precipitation - chemical, biological
- Biological Treatment

BIOLOGICAL TREATMENT / SULPHATE REDUCTION

Potential Application to Mine Waters

Key Limitations

- supply of organics
- temperature - low reaction rates, flow
- process control - hydrology

Key Reactions

$$\text{Costs} \sim f(\text{Volume}, [\text{SO}_4], [\text{M}^{x+}], \text{Reagent}, \text{Other})$$

Result - reduced SO_4^- levels and low metal solubility,
residual alkalinity

ESTIMATING CAPITAL COSTS OF TREATMENT FACILITIES

- *"Treatment Facilities"* include the physical treatment plant including equipment, and the building.
- Capital costs can be estimated for the 3 types of treatment facilities using the costing models.
- Cost models use two basic pieces of information:
 - average hourly flowrate of AMD to be treated; and
 - the net acidity of the water to be treated.
- Capital (and operating) costs are a function of several factors including:
 - (1) treatment rate
 - (2) loading
 - (3) sludge disposal method
 - (4) water collection and pumping requirements
 - (5) other site-specific requirements such as effluent objective

ESTIMATING CAPITAL + TREATMENT COSTS

$$\text{Costs} \sim f(\text{Volume}, [\text{SO}_4], [\text{M}^{x+}], \text{Reagent}, \text{Other Site-Specific Conditions})$$

TYPE OF PLANT	→	Conventional
	→	High Density
	→	Enhanced High Density
VOLUME	→	55 m ³ /hr
	→	190 m ³ /hr
	→	820 m ³ /hr
ACIDITY	→	50 mg/L
	→	500 mg/L
	→	5,000 mg/L

MODELLED CAPITAL AND TREATMENT COSTS HIGH DENSITY SLUDGE TREATMENT FACILITY (TREATMENT PLANT COSTS ONLY)

Parameter	Average Flow Rate	Influent Acidity (mg/L)		
		50	500	5,000
Capital Cost	55 m ³ /hr	\$1,300,000	\$1,500,000	\$1,800,000
	190 m ³ /hr	\$1,800,000	\$2,000,000	\$2,400,000
	820 m ³ /hr	\$3,900,000	\$4,200,000	\$5,100,000
Operating Cost	55 m ³ /hr	\$0.39/m ³	\$0.52/m ³	\$1.10/m ³
	190 m ³ /hr	\$0.16/m ³	\$0.27/m ³	\$0.72/m ³
	820 m ³ /hr	\$0.09/m ³	\$0.14/m ³	\$0.60/m ³

See Figure

FIGURE 6.1

FLOW RATE VS. CAPITAL COST
FOR CONVENTIONAL TREATMENT

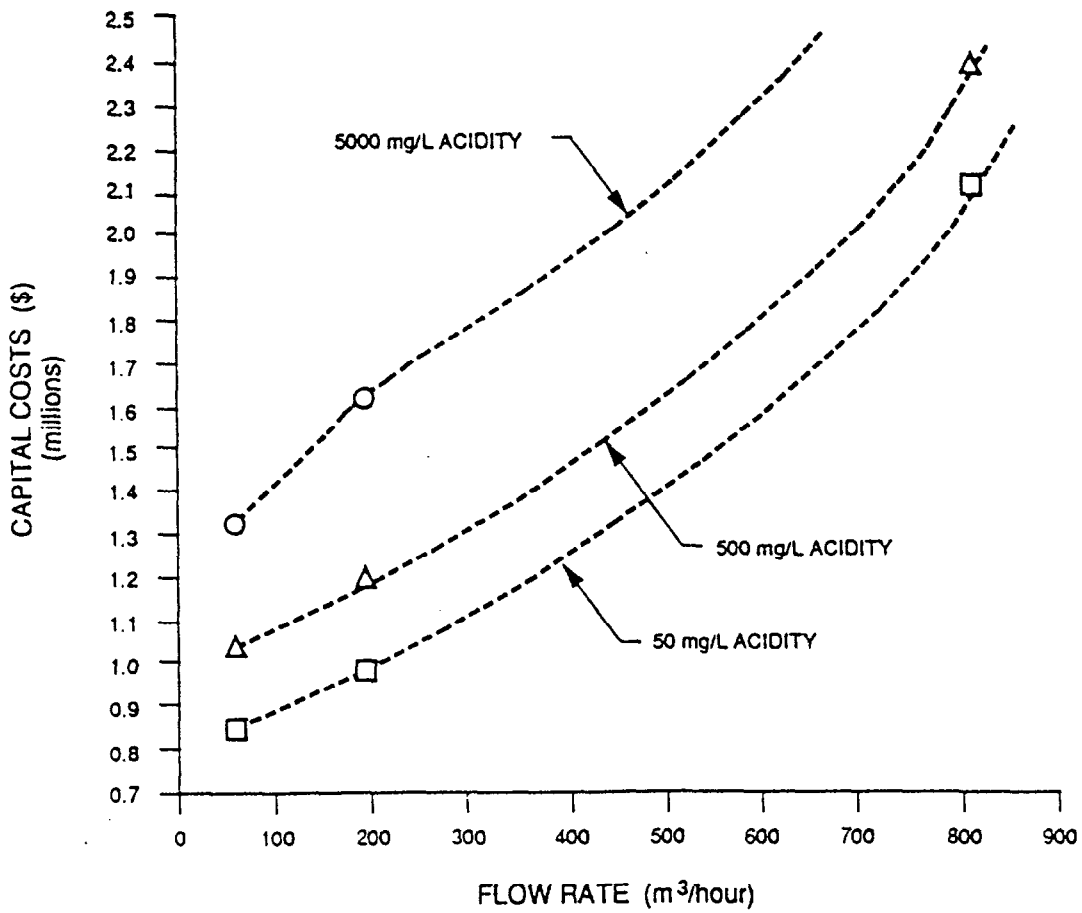


FIGURE 6.3

FLOW RATE VS. CAPITAL COST
FOR ENHANCED HDS TREATMENT

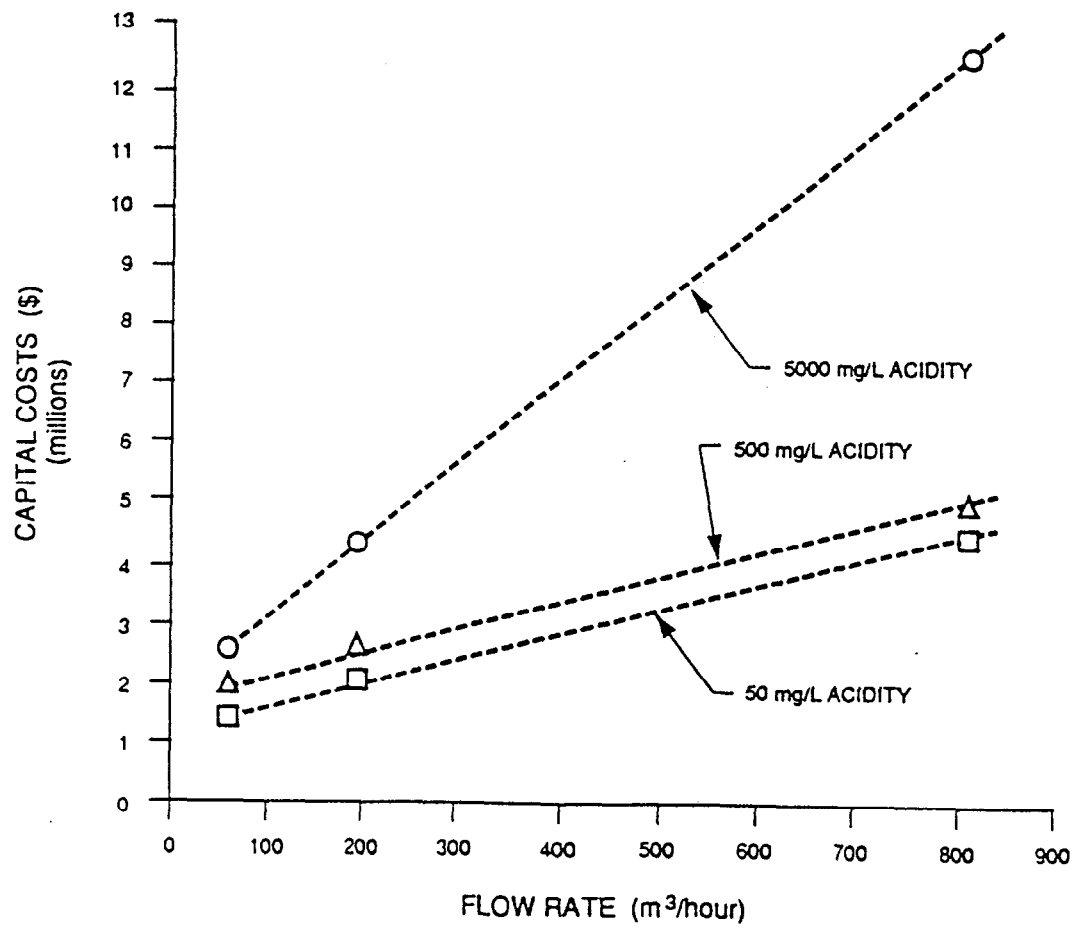
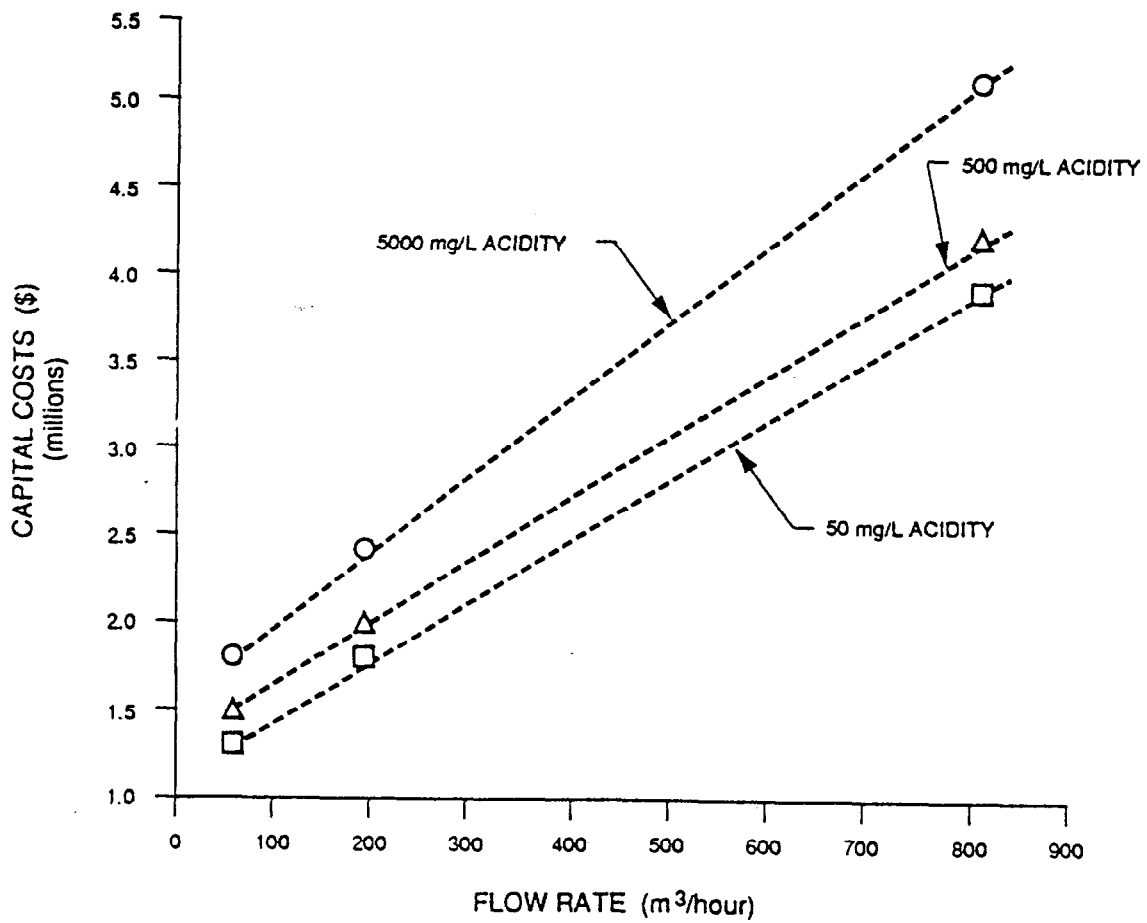


FIGURE 6.2

FLOW RATE VS. CAPITAL COST
FOR HDS TREATMENT



ILLUSTRATIVE CAPITAL COST ESTIMATE HIGH DENSITY SLUDGE TYPE PLANT (190 m³/hr, 500 mg/L)

Item	Cost
NEUTRALIZATION CIRCUIT (Feed pumps, sludge/lime mix tank, rapid mix tank, lime reactor tank, HDS thickener, floc tank, underflow pumps, and recycle water pumps)	\$ 293,800
LIME CIRCUIT (Bin, discharge lime conveyor, pneumatic loading system, lime slaker or make-up tank, and distribution pumps)	\$ 86,200
FLOCCULANT CIRCUIT (Flocculant make-up unit, storage tank with agitator, and distribution pumps)	\$ 35,600
SERVICES (Compressors/Blowers)	\$ 138,400
Total Equipment	\$ 554,000
Equipment Installation @ 10%	\$ 55,400
Process Piping @ 30%	\$ 166,200
Electrical @ 20%	\$ 110,800
Instrumentation @ 16%	\$ 88,600
Building @ 37% (thickener located outside)	\$ 205,000
Polishing Pond Allowance	\$ 43,000
TOTAL DIRECT COST	\$1,223,000
Spare Parts @ 2%	\$ 24,500
Construction Overheads @ 13%	\$ 1,590,00
Engineering, Procurement + Management @ 15%	\$ 183,500
TOTAL INDIRECT COST	\$ 367,000
TOTAL DIRECT AND INDIRECT COST	\$1,590,000
Contingency @ 25%	\$ 397,500
TOTAL CAPITAL COST	\$1,987,500
Say	<u>\$2,000,000</u>

MAJOR CAPITAL COST COMPONENTS OF A TREATMENT SYSTEM

Component	Capital Cost
Lime Treatment Plant	\$2,000,000 (in this example)
Site Infrastructure (Roads, Powerline, Camp, ...)	Additional
Water Management System (Collection, Peak Flow Control, Pump System)	Additional
Sludge Disposal (Cost to Construct Basin)	Additional
Other Site-Specific Requirements (i.e. effluent criteria, special requirement to handle peak flows through plant, etc.)	Additional
TOTAL CAPITAL COST	"Sum of All Costs"

ESTIMATING TREATMENT COST

- The "*Treatment Cost*" is essentially the cost to run the treatment plant and includes the cost of lime, flocculant, labour, maintenance, electrical power, and indirect costs:
 - Sludge disposal costs may add considerably to the treatment cost

- Treatment costs can be estimated for the 3 types of facilities using the costing model.

- Estimated annual treatment cost for this example \$450,000/year.

- Not included: security, remote power costs, recapitalization

**ILLUSTRATIVE OPERATING COST ESTIMATE
HIGH DENSITY SLUDGE TYPE PLANT
(190 m³/hr, 500 mg/L acidity)
(700 IGPM, 1150 USGPM)**

Item	Cost/Yr	%
Lime	\$152,800	41%
Flocculant	\$ 22,700	6%
Operating Labour	\$ 22,500	6%
Maintenance (Labour + Supplies)	\$ 69,600	19%
Electrical Power	\$105,500	28%
TOTAL DIRECT COST	\$373,100	<u>100%</u>
Indirect Costs @ 10%	\$ 37,300	
Contingency @ 10%	\$ 37,300	
TOTAL OPERATING COST	\$444,700	
Say	\$450,000	

(\$330,000 US)

MAJOR OPERATING COST COMPONENTS OF TYPICAL TREATMENT SYSTEM

Component	Operating Cost
Plant Operation	\$450,000/yr (in this example)
Cost to Operate and Maintain Infrastructure	Additional
Cost to Operate and Maintain the Water Management System	Additional
Cost to Dispose of Sludge	Additional
Other Site-Specific Requirements Including Environmental Program	Additional
TOTAL OPERATING COST	"Sum of All Costs"

LONG TERM TREATMENT COST

(190 m³/hr, 500 mg/L, 100 years)

	Conventional	HDS Type	Enhanced HDS Type
NPV Plant Cost	\$ 1,400,000	\$ 1,900,000	\$ 2,800,000
NPV Treatment Costs	\$21,800,000	\$24,650,000	\$32,230,000
NPV Total Cost	\$23,200,000	\$26,550,000	\$35,030,000
Relative Comparison	1.00	1.14	1.51

SLUDGE PRODUCTION

(190 m³/hr, 500 mg/L)

Item	Conventional Treatment	HDS Type Treatment	Enhanced HDS Type Treatment
% Solids	5	25	40
Sludge Volume Over 100 Years	12 x 10 ⁶ m ³	2.1 x 10 ⁶ m ³	1.2 x 10 ⁶ m ³

SLUDGE DISPOSAL COST

SLUDGE DISPOSAL IN AN OPEN PIT (At \$1/m³ to MANAGE SYSTEM)

Item	Conventional Treatment	HDS Type Treatment	Enhanced HDS Type Treatment
Annual sludge disposal cost	\$120,000/yr	\$20,500/yr	\$11,600/yr
NPV for 100 yrs of sludge disposal costs	\$3,790,000	\$648,000	\$367,000

SLUDGE DISPOSAL IN AN ENGINEERED BASIN (At \$4/m³, INCLUDES BASIN CONSTRUCTION COSTS)

Item	Conventional Treatment	HDS Type Treatment	Enhanced HDS Type Treatment
Annual sludge disposal cost	\$480,000/yr	\$82,000/yr	\$46,400/yr
NPV for 100 years of sludge disposal costs	\$15,170,000	\$2,590,000	\$1,470,000

TOTAL TREATMENT AND DISPOSAL COST

(190 m³/hr, 500 mg/L, 100 years)

Item	Conventional Treatment	HDS Type Process	Enhanced HDS Type Process
Capital Cost of Treatment Facility (A)	\$ 1,400,000	\$ 1,900,000	\$ 2,800,000
Net Present Value of Treatment Costs (B) ⁽¹⁾	\$21,800,000	\$24,650,000	\$32,230,000
Net Present Value of Pit Disposal (C) ⁽¹⁾	\$ 3,790,000	\$ 648,000	\$ 367,000
Net Present Value of Sludge Disposal in Engineered Impoundment (D) ⁽¹⁾	\$15,170,000	\$ 2,590,000	\$ 1,470,000
Total NPV Pit Disposal (A+B+C)	\$26,990,000	\$27,198,000	\$35,397,000
Total NPV Impoundment Disposal (A+B+D)	\$38,370,000	\$29,140,000	\$36,500,000

COMPARISON OF COSTS (PERCENT OF TOTAL COST)

	Batch Plant	Conventional Plant	HDS Plant	Enhanced HDS
CASE 1				
Capital	<1	4	8	9
Operating NPV	55	66	86	87
Sludge Disposal NPV	45	30	6	4
Total Cost (10 ⁶ \$)	24.6	36.9	30.4	34.0
CASE 2A (IMPOUNDMENT)				
Capital	-	4	7	8
Operating NPV	-	57	85	88
Sludge Disposal NPV	-	39	8	4
Total Cost (10 ⁶ \$)	-	38.4	29.1	36.5
CASE 2B (PIT DISPOSAL)				
Capital	-	5	7	8
Operating NPV	-	81	91	91
Sludge Disposal NPV	-	14	2	1
Total Cost (10 ⁶ \$)	-	27.0	27.2	35.4
CASE 3				
Capital	-	5	9	11
Operating NPV	-	81	88	88
Sludge Disposal NPV	-	14	3	1
Total Cost (10 ⁶ \$)	-	48.3	47.6	61.4
CASE 4				
Capital	-	3	6	11
Operating NPV	-	61	86	85
Sludge Disposal NPV	-	36	8	4
Total Cost (10 ⁶ \$)	-	129.3	97.0	133.2

- Notes:**
- Capital costs based upon model results.
 - Operating costs calculated - NPV discount rate 3%, 100 years.
 - Sludge disposal costs assume \$4/m³ for engineered storage except option 2b which assumes sludge disposal in a pit at \$1/m³.
 - Sludge disposal NPV discount rate 3%, 100 years.

SLUDGE PRODUCTION

- Issues - Volume
- Chemical Stability
- Disposal Cost

Sludge Volume

→ Can be a Major Problem

- i) Sludge volume can exceed original waste volume; and
- ii) 1 m³ acid water can produce almost 1 m³ sludge.

VOLUME OF SLUDGE FROM

Tailings at 10% Pyrite (FeS_2)

→ Density = 1.5 t/m^3

→ 1 m^3 Tailings Contains

- 0.07 t Fe → 0.14 t Fe(OH)_3

- 0.08 t S → $0.43 \text{ t CaSO}_4 \cdot 2\text{H}_2\text{O}$

= $0.57 \text{ t Precipitates/m}^3$ Tailings Oxidized

Volume = 19 m^3 Sludge @ 3% Solids

5 m^3 Sludge @ 10% Solids

1.3 m^3 Sludge @ 30% Solids

VOLUME OF SLUDGE FROM SOLUTION

Acidity - 25,000 mg/L

SO₄ - 25,000 mg/L

Fe²⁺ - 7,500 mg/L

Sludge Production from Lime Addition

5 kg Inerts (Unreacted CaCO₃, silica)

14 kg Fe(OH)₃

40 kg CaSO₄·2H₂O
59 kg/m³

~ 6% Solids With no Settling

~ 12% Solids With Settling

FACTORS AFFECTING SLUDGE STABILITY

- Excess Buffering Capacity
- Iron Content/State
- Precipitation Agent
- Gypsum Content
- Degree of Crystallinity
- Redox Potential

Table 1: General Site Information MEND SURVEY

Site Code	Location	Operation	Local Geology	Facilities Present	Production Status
D-1	Ontario	Base Metal Ni, Cu		Smelter	Mining ceased 1991 Milling ceased 1988
Q-2	Manitoba	Base Metal Cu, Zn		Concentrator, zinc refinery, copper smelter	Producing
M-3	Ontario	Base Metal Cu, Ni, Co, Pt		Smelter, mill 2@130' dia. reactor clarifiers	Producing
R-4	Québec	Base Metal Cu		Lime neutralization plant	Closed 1962
F-5	NB	Coal	Plateau, lithology is green/grey; fine to coarse	Neutralization facility, sludge storage ponds	Closed 1986
S-6	Ontario	Base Metal Cu, Zn	Flat, underlined by clays	Smelter, refinery, purification leach plant, cell house	Producing
J-7	Québec	Gold	On the Cadillac fault	Mineral treatment	Producing
W-8	NB	Base Metal	Massive sulphide ore body	Underground mine/mill complex	Producing
N-9	Ontario	Uranium	Cdn. Shield, natural bedrock basins	Flooded tailings basin, 2 settling ponds	Closed 1990
B-10	Ontario	Base Metal Cu, Ni		Mill, smelter	Producing
T-11	Ontario	Uranium	Cdn. Shield, exposed bedrock	Elevated tailings, effluent treatment plant, sludge settling	Closed 1968

Table 2: Acid Mine Drainage Characterization - MEND SURVEY 1996

Site Code	Source	Chemical Composition (mg/L)															
		Al	As	Cd	Cr	Cu	Fe _e	Hg	Mg	Mn	Ni	Pb	Ra ₂₂₆	U	Zn	SO ₄ ⁻²	pH
D-1	Tailings					5	<10				<10						2.5
Q-2	Tailings, process waters, residue pond decant			< 0.01		0.1-0.05	0.05-0.5			0.01-0.7	<0.01	<0.04			0.5-3		7-10.8
M-3	Tailings area and smelter	2.55	<0.0131	0.0021	0.0112	0.721	36.3			0.938	11.4	<0.03			0.16	1524	5.93
R-4	Tailings			0.016		1.0	75			4.0		<0.05			5.3	950	2.88
F-5	Tailings, sandstone overburden	126					40									1850	2.8-3.5
S-6	Tailings		0.09-<0.05	200-800		2-0.01	1-20	0.001			0.01-0.05	0.02			0.5-120	1200-2000	3.5-7.5
J-7	Waste rock						774									4516	
W-8	Tailings, waste rock, roadway, process waters					5	150					3			100	3500	4.5
N-9 ²	Beached uranium tailings					1.6	6.0			1.6	0.07	0.08	16 Bq/L	0.3	0.5	1580	4.5
B-10 ³	Tailings area and smelter																
T-11	Tailings, elevated uranium					0.05	487			2.8	0.07	<.1		0.05-2	0.57		3.8

Table 3: Treatment Processes - MEND Survery 1996

Site Code	Effluents Treated	Reagents	Flocculant	Process	Flowrate (m ³ /min)	Difficulties	Comments
D-1	AMD/smelter process water	Ca(OH) ₂	None	Lime / air	27.3 (max)	Inefficient treatment process (54-85%)	Precipitation cells; 4.5 kg Ca(OH) ₂ /min
Q-2	Tailings/process water	Lime	On occasion	Settling with finishing pond		Seasonal influences; process upsets	
M-3	AMD, watershed, process waters	Slaked lime	Percol 338	Lime/air	76	Very large watershed	
R-4	AMD	Hydrated lime	Percol 90L	HDS/lime/flocculant/air	6		
F-5	AMD	Slaked lime	None	Lime precipitation	11		By placing sludge on the waste rock, the acidity dropped over a # of yrs.
S-6	Tailings/process water	Slaked lime	None	Lime precipitation	6.94	Seasonal variability	Zn values change with mill values
J-7	Tailings/process water	Slaked lime	Percol 338	HDS/lime/air	19		
W-8	AMD	Slaked lime	Percol 727	HDS/lime/air	60	Difficulties with Zn removal	
N-9	AMD and mine effluents	Slaked lime	None	Lime precipitation	7.8	Short circuiting in settling ponds	
B-10	AMD, watershed	Slaked lime	Percol 338	Lime precipitation	8	Slag dump water is higher in iron	Shut plant off in summer
T-11	AMD	Lime slurry	None	Lime precipitation	4	Short circuit from inlet to outlet	

Table 4: Sludge Management Practices - MEND Survey 199

Site Code	Sludge Production (m ³)		Disposal Scenario	Pond History	Difficulties
	Annual	Total			
D-1	4,100	70,000	Settling pond	17 years sludge accumulation	Very little densification with aging
Q-2	40,000	800,000	Free settling	20 years sludge accumulation, pH final discharge at 10	
M-3	2,000,000	10-15 M	Co-disposal with tailings		
R-4	2,500				Principal drainage ditch
F-5	30,000	300,000	10 active sludge ponds, 3-6 ponds dredged every year	Last dredged in 1995	Cost of dredging; can't keep sludge on surface of waste rock
S-6	3,500,000 - 4,000,000		Sludge impounded in tailings volume reduced by freeze/ thaw	25 years sludge accumulation; divided into 2 ponds in 1992	Low sludge density and poor effluent quality
J-7	70,000	350,000	Sludge pond, moving to co-disposal in 1997	5 years sludge accumulation	
W-8	40,000		Co-deposit with mill tailings		Periodic turbidity
N-9			Sludge to ponds	Pond #1 full, overflow to pond #2	Short circuiting in settling pond
B-10			Sludge to ponds with sulphide thickener overflows	Sludge deposited in pond with thickener overflows; dredged 2-3 years, sludge is stockpiled	
T-11			Located in permanent location in bottom of lake	26 years sludge accumulation	Short circuit in winter from inlet to outlet

Table 6: Physical Characteristics, pH and E_h of Sludge Samples

Site Code	Sample	Physical Characteristics							pH	E _h (mV)
		Colour	Percent Solids (wt. %)	Particle size (μm, 50%)	Particle size (μm, ma)	Particle size (μm, mn)	Bulk density (g/cm ³)	Dry sludge density ² (g/cm ³)		
D-1	fresh	grey-brown	3.7	5.74	5.35	3.21	1.05	2.48	9.45	161
	aged	grey-brown	7.2	7.96	24.01	3.96	1.09	2.39	9.51	315
Q-2	aged	grey-brown	2.14	6.78	3.95	0.930	1.05	3.10	11.41	239
	aged	green-brown	9.6	11.86	16.73	5.19	1.11	2.54	9.66	175
M-3	fresh	grey-brown	6.9	25.2	32.56	19.63	1.08	2.20	9.42	232
R-4	fresh	red-brown	18.0	3.96	5.36	2.83	1.15	1.87	8.90	112
	aged	red-brown	24.8	5.27	6.46	3.44	1.21	1.85	8.32	262
F-5	fresh	grey-brown	3.7	42.45	59.23	10.30	1.06	2.44	9.62	300
	aged	dark brown	12.5	13.62	21.2	30.10	1.12	1.89	8.20	296
S-6	fresh	grey-brown	3.4	6.67	4.14	7.63	1.08	3.24	10.85	239
	aged	brown	4.1	21.06	39.39	11.63	1.05	2.76	10.56	201
J-7	fresh	red-brown	26.3	4.18	17.88	2.85	1.19	1.83	9.22	121
	aged	red-brown	32.8	10.22	15.53	7.46	1.37	2.27	9.22	92
W-8 ¹	fresh	dark brown	32.2	4.09	4.19	2.85	1.26	1.85	10.04	166
	aged	dark brown	10.4	21.25	20.16	7.46	1.10	2.03	10.66	60
N-9	aged	grey	7.6	23.76	40.42	9.59	1.09	2.16	9.36	212
B-10	fresh	grey-brown	3.9	16.11	23.54	11.93	1.06	3.04	10.54	252
T-11	fresh	dark green	2.4	20.72	53.26	8.55	1.05	3.34	9.34	58

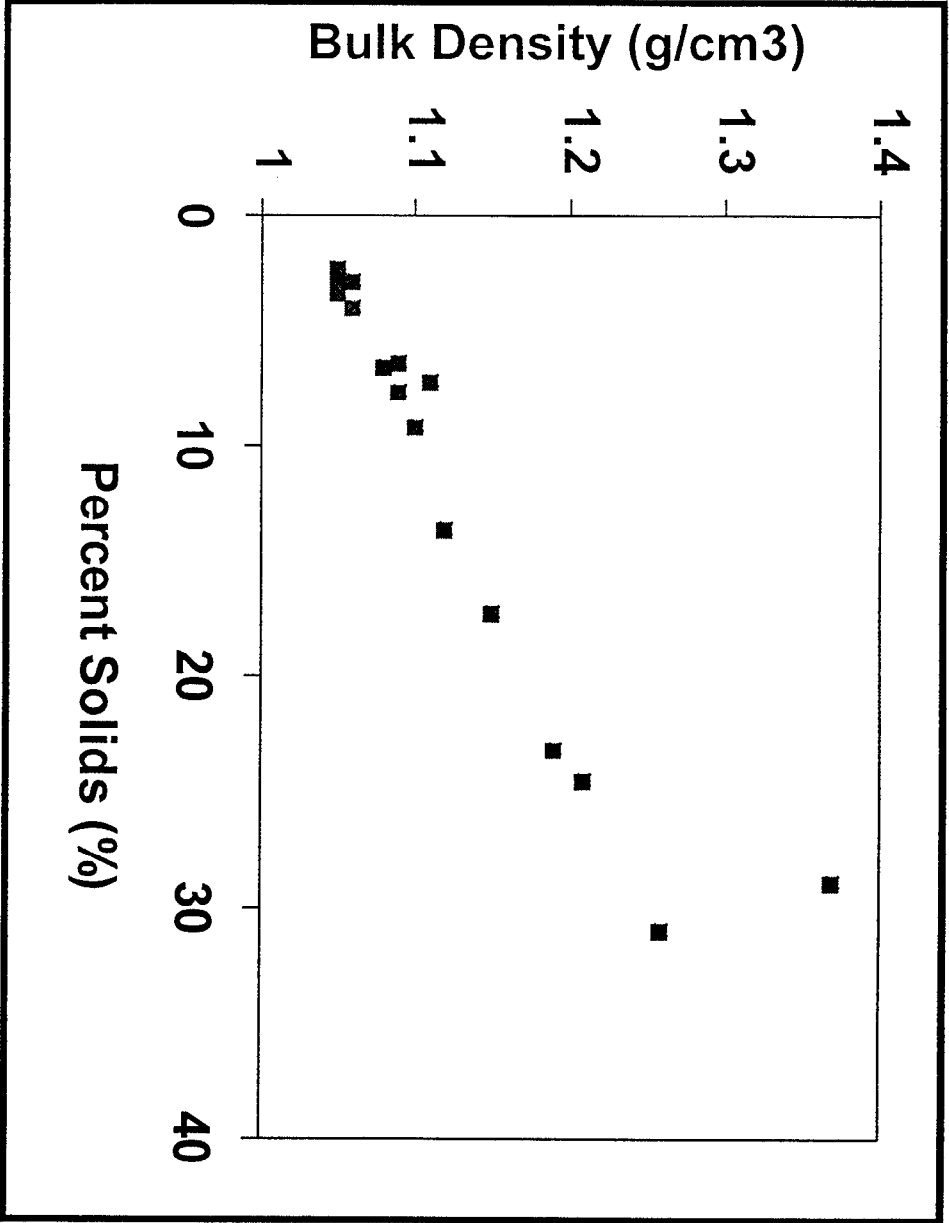


Table 8A: Chemical Composition

Site Code	Sample	Chemical Composition (%)												
		Al	Ag ¹	As	Ba	B	C	Cd	Ca	Cr	Cu	CO ₂	Fe _t	Hg
D-1	fresh	0.1		<0.0016	0.012	0.0051	7.11	0.0002	26.6	<0.054	0.05	25.9	4.8	<0.0008
	aged	0.5	1.5	0.0023	0.005	<0.002	6.57	0.0009	22.9	<0.054	0.021	23.4	7.1	<0.0008
Q-2	fresh	1.0	10.40	0.011	0.004	0.009		0.059	6.9	<0.060	0.041	6.45	2.9	0.00011
	aged	1.8	6.6	0.0978	0.05	<0.002	3.29	0.0825	9.6	<0.054	0.25	11.6	12.3	<0.0008
M-3	fresh	1.5	19.5	0.0105	0.014	<0.002	1.97	0.0094	6.0	<0.054	0.27	6.45	14.7	<0.0008
R-4	fresh	2.8	1.0	<0.0016	0.020	<0.002	1.75	0.0029	8.3	<0.054	0.33	5.22	10.8	<0.0008
	aged	3.3	1.2	0.0025	0.005	0.0017	2.42	0.0025	7.4	<0.054	0.27	8.20	26.1	<0.0008
F-5	fresh	7.7	1.1	0.0018	0.005	0.29	1.34	0.0004	14.0	<0.052	0.0029	4.80	1.5	<0.0008
	aged	11.2	1.2	0.0020	0.005	0.16	0.98	0.0005	9.9	<0.052	0.010	3.41	6.2	<0.0008
S-6	fresh	1.3	7.3	0.0056	0.010	<0.002	4.57	0.0674	17.2	<0.052	0.15	16.1	2.3	<0.0008
	aged	0.6		0.0051	0.011	<0.002	2.40	0.1390	10.0	<0.054	0.20	8.66	3.0	<0.0008
J-7	fresh	4.3	4.7	<0.0016	0.005	0.0066	0.54	0.0002	13.0	<0.055	0.077	1.87	12.8	<0.0008
	aged	3.4	0.9	<0.0016	0.003	0.0049	0.30	0.0001	14.2	<0.055	0.054	0.95	13.4	<0.0008
W-8 ²	fresh	3.9	13.7	0.0248	0.014	0.0041	0.55	0.0137	3.8	<0.054	0.12	1.76	15.0	<0.0008
	aged	1.8	15.2	0.0487	0.022	<0.002	1.36	0.0057	11.6	<0.054	0.05	4.76	10.9	<0.0008
N-9	aged	4.9	1.1	0.0021	7.8	0.22	1.86	0.0014	5.0	<0.055	0.029	5.44	7.7	<0.0008
B-10	fresh	3.6	4.1	<0.0016	0.005	<0.002	2.52	0.0058	4.6	<0.054	1.48	7.73	22.2	<0.0008
T-11	fresh	0.6	1.8	<0.0016	0.011	<0.002	1.35	<0.0001	10.2	<0.055	0.001	4.80	28.1	<0.0008

¹ ppm ² Fresh sludge was produced with HDS process; aged sludge was produced from basic lime treatment process.

Table 8B: Chemical Composition, Cont.

Site Code	Sample	Chemical Composition (%)												
		Mg	Mn	Na	Ni	Pb	Se	Si	S	U	Zn	SO ₄	NNP	AP
D-1	fresh	5.8	-	0.17	0.26	<0.43	<0.0009	1.1	1.43	-	0.067	3.70	NA	6
	aged	6.3	-	0.07	1.06	<0.43	<0.0009	2.0	1.10	-	0.021	3.60	725	-
Q-2	fresh	18.1	-	0.24	0.005	<0.20	-	2.8	1.75	-	7.5	3.01	796	25
	aged	7.9	-	0.21	<0.11	<0.43	0.0296	5.2	3.18	-	5.9	3.22	359	66
M-3	fresh	7.3	-	0.21	4.19	<0.43	0.0148	4.5	3.00	-	0.98	5.95	293	32
R-4	fresh	5.5	-	0.04	-	<0.43	<0.0009	7.2	1.85	-	1.4	5.20	315	4
	aged	2.6	-	0.06	<0.11	<0.43	<0.0009	4.4	1.34	-	1.1	3.77	207	3
F-5	fresh	6.0	3.6	0.11	0.059	<0.43	<0.0009	1.7	7.46	-	0.14	18.80	335	38
	aged	1.2	2.1	0.07	0.059	<0.43	<0.0009	2.7	7.24	-	0.15	18.98	94	25
S-6	fresh	5.7	-	0.31	0.13	<0.42	0.0159	4.8	2.92	-	8.5	6.90	452	19
	aged	7.8	-	0.21	0.20	<0.43	0.0169	2.3	4.58	-	14.4	11.29	497	26
J-7	fresh	2.2	0.47	0.03	<0.03	<0.44	<0.0009	1.2	9.97	-	0.0031	26.71	84	34
	aged	1.7	0.24	0.03	<0.03	<0.44	<0.0009	0.8	11.3	-	0.019	30.71	74	34
W-8 ¹	fresh	3.13	-	0.08	<0.11	<0.43	<0.0009	1.28	4.14	-	14.2	11.80	135	7
	aged	6.3	-	0.28	<0.11	<0.43	<0.0009	2.0	5.75	-	4.6	14.2	346	32
N-9	aged	3.8	1.1	0.15	<0.11	<0.45	0.0039	3.0	5.34	0.605	0.270	11.2	154	50
B-10	fresh	7.4	-	0.24	<0.11	<0.43	<0.0009	4.9	1.77	-	0.17	4.55	345	8
T-11	fresh	2.6	0.21	0.03	<0.11	<0.45	<0.0009	1.2	6.56	0.011	0.029	18.61	167	11

¹ Fresh sludge was produced with HDS process and aged sludge was produced from basic lime treatment process.
 NNP = Net Neutralization Potential (tonnes CaCO₃ equiv. / 1000 tonnes sludge); AP = Acid Potential (tonnes CaCO₃ equiv. / 1000 tonnes sludge); LOM = Loss of Moisture; LOI = Loss on Ignition

Table 9: Mineralogical Analysis (not in decreasing abundance)

Site Code	Sample	Mineralogy
D-1	fresh	Calcite (CaCO ₃), amorphous phase (Ca,Mg,Fe,Si,C,S,O, trace Mn,Al)
	aged	Calcite (CaCO ₃), trace Quartz (SiO ₂), Gypsum (CaSO ₄ ·2H ₂ O), Fe oxide, K-Al, Fe-Mg-Ca, Fe-Mg silicates amorphous phase (Ca,Mg,Fe,Si,C,S,O, trace Mn, Al)
Q-2	aged	Calcite (CaCO ₃), Quartz (SiO ₂), Clinocllore ((Mg,Fe) ₅ Al(Si ₃ ,Al)O ₁₀ (OH) ₈), Pyrite (FeS ₂), Talc (Mg ₃ Si ₄ O ₁₀ (OH) ₂ , Ankerite (CaFe(CO ₃) ₂), amorphous phase (Ca,Fe,Mg,CO ₃ , Si,SO ₄ ,Zn,Na,Cl)
M-3	fresh	Calcite (CaCO ₃), Quartz (SiO ₂), amorphous phase (Fe,Mg,O,C,Si,Na,Ca,Zn,S,Ni,Al,Mn,Cl), (Mg,Fe,Ca)CO ₃ , Fe oxide, Pyrite (FeS ₂), ZrSiO ₄
R-4	fresh	Calcite (CaCO ₃), amorphous phase (Mg,Al,Si,Fe,S,Ca,Zn,Mn), Mg-Al-Fe silicates, Quartz (SiO ₂), Fe oxide, minor Gypsum (CaSO ₄ ·2H ₂ O)
	aged	Calcite (CaCO ₃), Quartz (SiO ₂), amorphous phase (Fe,Mg,Al,Si,Ca,S,O,Zn,Mn), Fe-Ca-Mg-Al silicates, Na-Fe-Mg-Al silicates
F-5	fresh	Bassanite (CaSO ₄ ·0.5H ₂ O), Gypsum (CaSO ₄ ·2H ₂ O), Calcite(CaCO ₃), amorphous phase (Al,O, Fe,Ca,SO ₄ ,Cu,Si,Mg,Mn,Na)
	aged	Gypsum (CaSO ₄ ·2H ₂ O), Calcite (CaCO ₃), Quartz (SiO ₂), amorphous phase (Al,O, Fe,Ca,S,Cu,Si,Mg,Mn,Na), Fe oxide, Mn-Al oxide, K-Al silicates
S-6	fresh	Gypsum (CaSO ₄ ·2H ₂ O), Calcite (CaCO ₃), amorphous phase (Mg,C,O,Na,Ca,S,Zn,Si,Mn,Fe), silicates, Pyrite (FeS ₂), Chalcopyrite (CuFeS ₂), (Ca,Zn,Mg)CO ₃
	aged	Calcite (CaCO ₃), Gypsum (CaSO ₄ ·2H ₂ O), Clinocllore ((Mg,Fe) ₅ Al(Si ₃ ,Al)O ₁₀ (OH) ₈), Muscovite (KAl ₂ (AlSi ₃)O ₁₀ (OH) ₂ , amorphous phase (Mg,C,O,Zn,S,Si,Ca,Na, tr. Mn,Fe)
J-7	fresh	Gypsum (CaSO ₄ ·2H ₂ O), amorphous phase (Fe,Ca,Al,Mg,,S,O,Si,Mn,Zn)
	aged	Gypsum (CaSO ₄ ·2H ₂ O), amorphous phase (Fe,Ca,S,O,Al,Mg,Si,P,Mn,Zn), trace Fe oxide, Quartz, silicates
W-8	fresh	Calcite (CaCO ₃), Bassanite (CaSO ₄ ·0.5H ₂ O), Ettringite (Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O), Gypsum (CaSO ₄ ·2H ₂ O), amorphous phase (Fe,Zn,Mn,Ca,O,Na,Mg,Al,Si), trace Quartz (SiO ₂)
	aged	Gypsum (CaSO ₄ ·2H ₂ O), Bassanite (CaSO ₄ ·½H ₂ O), Ettringite (Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O), trace Calcite (CaCO ₃), amorphous phase (Fe,Ca,S,O,Zn,Al,Mg,Si,Mn,Na), trace Pyrite (FeS ₂), trace Sphalerite (ZnS), trace Quartz (SiO ₂), trace Fe oxide
N-9	aged	Barite (BaSO ₄), Calcite (CaCO ₃), amorphous phase (Mg,Al,Si,Fe,Ba,Ca,S,C,O,Mn,Zn,Na), (Ce,La,Ca,Ba) carbonate
B-10	fresh	Calcite (CaCO ₃), Quartz (SiO ₂), Albite (NaAlSi ₃ O ₈), amorphous phase (Fe,Mg,Al,Si,O,C,S,Na,Ni,Cu), Pyrite (FeS ₂), Fe oxide
T-11	fresh	Gypsum (CaSO ₄ ·2H ₂ O), Calcite (CaCO ₃), amorphous phase (Fe,Ca,Mg,S,O,C,Si,Al,Mn), Fe oxide, Quartz (SiO ₂),

Table 10: Main Phases Identified by X-Ray Diffraction for Thermal Analysis

Site Code	Sample	XRD Before Heating ¹	XRD After Heating in Air
D-1	fresh	CaCO ₃	Ca ₂ Fe ₂ O ₅ , MgO, Ca(OH) ₂ , CaSO ₄ , CaO, trace SiO ₂ , possible (Fe,Mg)SiO ₃
	aged	CaCO ₃ , trace SiO ₂ , CaSO ₄ •2H ₂ O	Ca ₂ Fe ₂ O ₅ , U*, MgO, Ca(OH) ₂ , CaO, CaSO ₄ , trace SiO ₂
Q-2	aged	CaCO ₃ , SiO ₂ , FeS ₂ , P*, C*, possible Mg(OH) ₂	Fe ₃ O ₄ , Ca ₂ MgSi ₂ O ₇ , CaSO ₄ , CaMgSiO ₄
M-3	fresh	CaCO ₃ , SiO ₂ , CaSO ₄ •2H ₂ O	Fe ₂ O ₃ , CaSO ₄ , CaMgSiO ₄
R-4	fresh	CaCO ₃	Fe ₂ O ₃ , possible Ca ₂ MgSi ₂ O ₇
	aged	CaCO ₃ , SiO ₂	Fe ₃ O ₄ , possible MnFe ₂ O ₄ , Ca ₂ MgSi ₂ O ₇
F-5	fresh	CaSO ₄ •0.5H ₂ O, CaSO ₄ •H ₂ O, CaCO ₃	CaSO ₄ , Ca ₄ Al ₆ O ₁₂ SO ₄ , Mg(Al,Fe) ₂ O ₄
	aged	CaSO ₄ •2H ₂ O, trace SiO ₂ , CaCO ₃	CaSO ₄
S-6	fresh	CaCO ₃ , SiO ₂ , CaSO ₄ •2H ₂ O	MgO, CaSO ₄ , SiO ₂
	aged	CaCO ₃ , SiO ₂ , CaSO ₄ •2H ₂ O	CaSO ₄ , Fe ₂ O ₃ , MgO, ZnO
J-7	fresh	CaSO ₄ •2H ₂ O	CaSO ₄
	aged	CaSO ₄ •2H ₂ O	CaSO ₄
W-8	fresh	Amorphous	Fe ₂ O ₃ , CaSO ₄
	aged	CaCO ₃ , CaSO ₄ •0.5H ₂ O, P*, E*, SiO ₂	Fe ₂ O ₃ , CaSO ₄ , MgO, SiO ₂
B-10	aged	CaCO ₃ , SiO ₂ , NaAlSi ₃ O ₈	(Mg,Fe)(Cr,Al) ₂ O ₄ , Ca ₂ MgSi ₂ O ₇ , CaMgSiO ₄

¹ All the starting materials contained an amorphous phase.

C* = Clinocllore (Mg,Fe)₆(Si,Al)₄O₁₀(OH)₈ (chlorite mineral)

E* = Ettringite Ca₆Al₂(SO₄)₃(OH)₁₂•26H₂O (sulphate mineral)

P* = Pyroaurite Mg₆Fe₂CO₃(OH)₁₆•4H₂O (carbonate mineral)

U* = Unidentified phase

Table 11: TG% Weight Losses in Air

Site Code	Sample	% Weight Loss 25-200°C (hydrates)	% Weight Loss 200-500°C (hydroxides, possible trace carbonates)	% Weight Loss 500-800°C (carbonates)	% Weight Loss 800-1185°C (sulphates, silicates..)
D-1	fresh	4.47	7.02	27.57	0.38
	aged	5.99	7.49	23.73	0.18
Q-2	aged	6.36	7.09	9.72	3.26
M-3	fresh	12.92	9.78	5.52	4.29
R-4	fresh	11.45	12.01	3.35	3.62
	aged	12.8	8.36	5.38	2.0
F-5	fresh	11.79	11.08	5.91	1.16
	aged	15.71	10.91	2.74	4.47
S-6	fresh	5.82	5.97	16.14	0.41
	aged	10.5	9.1	8.45	1.47
J-7	fresh	17.11	6.48	1.06	4.28
	aged	16.66	5.37	0.52	4.54
W-8	fresh	13.24	9.11	1.16	5.96
	aged	14.87	9.28	4.03	1.07
B-10	aged	9.46	10.58	7.06	2.95

Table 12: Estimated Composition of AMD Sludges Based on Thermal Analysis and XRD

Site Code	Sample	Estimated composition based on thermal analysis and XRD
D-1	fresh	CaCO ₃ , Ca(OH) ₂ , Mg(OH) ₂ , CaSO ₄ •?H ₂ O, iron oxide, SiO ₂
	aged	CaCO ₃ , Ca(OH) ₂ , Mg(OH) ₂ , CaSO ₄ •?H ₂ O, iron oxide, SiO ₂
Q-2	aged	CaCO ₃ , carbonate mineral, chlorite mineral, CaSO ₄ •?H ₂ O, SiO ₂ , iron oxide, Ca(OH) ₂ , Mg(OH) ₂ , Zn phase (oxide?), possible FeS ₂ , trace Cl ⁻
M-3	fresh	CaCO ₃ , carbonaceous material, Ca(OH) ₂ , Mg(OH) ₂ , CaSO ₄ •2H ₂ O, iron oxide, SiO ₂ , trace NH ₄ ⁺ , Cl ⁻
R-4	fresh	CaCO ₃ , carbonaceous material, Ca(OH) ₂ , Mg(OH) ₂ , CaSO ₄ •?H ₂ O, iron oxide, SiO ₂ , trace NH ₄ ⁺ , Cl ⁻ , F ⁻
	aged	CaCO ₃ , carbonaceous material, Ca(OH) ₂ , Mg(OH) ₂ , CaSO ₄ •?H ₂ O, iron oxide, SiO ₂ , trace NH ₄ ⁺ , Cl ⁻ , F ⁻
F-5	fresh	CaSO ₄ •0.5H ₂ O, CaSO ₄ •2H ₂ O, Ca(OH) ₂ , Mg(OH) ₂ , CaCO ₃ , iron oxide, possible alumina hydrate, trace Cl ⁻ , F ⁻
	aged	CaSO ₄ •2H ₂ O, possible alumina hydrate, Mg(OH) ₂ , trace SiO ₂ , CaCO ₃ , trace Cl ⁻ , F ⁻
S-6	fresh	CaCO ₃ , CaSO ₄ •2H ₂ O, Ca(OH) ₂ , Mg(OH) ₂ , SiO ₂ , iron phase, trace Cl ⁻
	aged	CaCO ₃ , CaSO ₄ •2H ₂ O, Ca(OH) ₂ , Mg(OH) ₂ , iron phase, SiO ₂ , zinc phase (oxide), trace Cl ⁻
J-7	fresh	CaSO ₄ •2H ₂ O, iron phase, Mg(OH) ₂ , trace CaCO ₃ , SiO ₂ , Cl ⁻ , F ⁻
	aged	CaSO ₄ •2H ₂ O, iron phase, Mg(OH) ₂ , trace SiO ₂ , Cl ⁻ , F ⁻
W-8	fresh	CaSO ₄ •?H ₂ O, Ca(OH) ₂ , Mg(OH) ₂ , iron phase, SiO ₂ , zinc phase (oxide?), trace SiO ₂ , Cl ⁻
	aged	CaCO ₃ , CaSO ₄ •0.5H ₂ O, Mg(OH) ₂ , carbonate mineral, sulphate mineral, SiO ₂ , iron oxide, trace Cl ⁻
B-10	fresh	CaCO ₃ , carbonaceous material, Ca(OH) ₂ , Mg(OH) ₂ , CaSO ₄ •?H ₂ O, iron oxide, SiO ₂ , trace NH ₄ ⁺ , Cl ⁻

Table 13: Estimated Composition of AMD Sludges based on Chemical Analyses, Mineralogy and Thermal Analysis

Site Code	Sample	Sludge Composition
D-1	fresh	amorphous phase (Ca,Mg,Fe,Si,C,S,O, trace Mn,Al), CaCO ₃ , Ca(OH) ₂ , Mg(OH) ₂ , CaSO ₄ ·?H ₂ O, Fe oxide, SiO ₂
	aged	amorphous phase (Ca,Mg,Fe,Si,C,S,O, trace Mn, Al), CaCO ₃ , trace SiO ₂ , CaSO ₄ ·2H ₂ O, Fe oxide, K-Al, Fe-Mg-Ca, Fe-Mg silicates, Ca(OH) ₂ , Mg(OH) ₂ , Fe oxide
Q-2	aged	amorphous phase (Ca,Fe,Mg,CO ₃ , Si,SO ₄ ,Zn,Na,Cl), CaCO ₃ , SiO ₂ , (Mg,Fe) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈ , FeS ₂ , Mg ₃ Si ₄ O ₁₀ (OH) ₂ , CaFe(CO ₃) ₂ , Ca(OH) ₂ , Mg(OH) ₂ , Fe oxide, Zn phase (oxide?), trace Cl ⁻
M-3	fresh	amorphous phase (Fe,Mg,O,C,Si,Na,Ca,Zn,S,Ni,Al,Mn,Cl), CaCO ₃ , SiO ₂ , Ca(OH) ₂ , Mg(OH) ₂ , CaSO ₄ ·?H ₂ O, (Mg,Fe,Ca)CO ₃ , Fe oxide, FeS ₂ , ZrSiO ₄ , trace Cl ⁻ , NH ⁺
R-4	fresh	amorphous phase (Mg,Al,Si,Fe,S,Ca,Zn,Mn), CaCO ₃ , Mg-Al-Fe silicates, Ca(OH) ₂ , Mg(OH) ₂ , SiO ₂ , Fe oxide, carbonaceous material, minor CaSO ₄ ·2H ₂ O, trace Cl ⁻ , NH ⁺ , F ⁻
	aged	amorphous phase (Fe,Mg,Al,Si,Ca,S,O,Zn,Mn), CaCO ₃ , SiO ₂ , Fe-Ca-Mg-Al silicates, Na-Fe-Mg-Al silicates, Fe oxide, Ca(OH) ₂ , Mg(OH) ₂ , carbonaceous material, minor CaSO ₄ ·2H ₂ O, trace Cl ⁻ , NH ⁺ , F ⁻
F-5	fresh	amorphous phase (Al,O, Fe,Ca,SO ₄ ,Cu,Si,Mg,Mn,Na), CaSO ₄ ·0.5H ₂ O, CaSO ₄ ·2H ₂ O, CaCO ₃ , Ca(OH) ₂ , Mg(OH) ₂ , possible alumina hydrate, Fe oxide, trace Cl ⁻ , F ⁻
	aged	amorphous phase (Al,O, Fe,Ca,SO ₄ ,Cu,Si,Mg,Mn,Na), CaSO ₄ ·2H ₂ O, CaCO ₃ , SiO ₂ , possible alumina hydrate, Mg(OH) ₂ , Fe oxide, Mn-Al oxide, K-Al silicates, trace Cl ⁻ , F ⁻
S-6	fresh	amorphous phase (Mg,C,O,Na,Ca,S,Zn,Si,Mn,Fe), CaSO ₄ ·2H ₂ O, CaCO ₃ , Ca(OH) ₂ , Mg(OH) ₂ , SiO ₂ , silicates, FeS ₂ , CuFeS ₂ , (Ca,Zn,Mg)CO ₃ , trace Cl ⁻
	aged	amorphous phase (Mg,C,O,Zn,S,Si,Ca,Na, tr. Mn,Fe), CaCO ₃ , CaSO ₄ ·2H ₂ O, (Mg,Fe) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈ , Ca(OH) ₂ , Mg(OH) ₂ , SiO ₂ , KAl ₂ (AlSi ₃)O ₁₀ (OH) ₂ , Fe phase, Zn phase (oxide?), trace Cl ⁻
J-7	fresh	amorphous phase (Fe,Ca,Al,Mg,SO ₄ ,Si,Mn,Zn), CaSO ₄ ·2H ₂ O, Mg(OH) ₂ , trace CaCO ₃ , SiO ₂ , trace Cl ⁻ , F ⁻
	aged	amorphous phase (Fe,Ca,S,O,Al,Mg,Si,P,Mn,Zn), CaSO ₄ ·2H ₂ O, Mg(OH) ₂ , trace Fe oxide, SiO ₂ , silicates, trace Cl ⁻ , F ⁻
W-8	fresh	amorphous phase (Fe,Zn,Mn,Ca,O,Na,Mg,Al,Si), CaCO ₃ , CaSO ₄ ·0.5H ₂ O, Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O, CaSO ₄ ·2H ₂ O, Fe oxide, Zn phase (oxide?), Ca(OH) ₂ , Mg(OH) ₂ , trace SiO ₂ , Cl ⁻
	aged	amorphous phase (Fe,Ca,S,O,Zn,Al,Mg,Si,Mn,Na), CaSO ₄ ·2H ₂ O, CaSO ₄ ·½H ₂ O, Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O, Mg(OH) ₂ , carbonate material, sulphate material, trace CaCO ₃ , FeS ₂ , ZnS, SiO ₂ , Fe oxide
N-9	aged	amorphous phase (Mg,Al,Si,Fe,Ba,Ca,S,C,O,Mn,Zn,Na), BaSO ₄ , CaCO ₃ , (Ce,La,Ca,Ba) carbonates
B-10	fresh	amorphous phase (Fe,Mg,Al,Si,O,C,S,Na,Ni,Cu), CaCO ₃ , SiO ₂ , NaAlSi ₃ O ₈ , FeS ₂ , Fe oxide, Ca(OH) ₂ , Mg(OH) ₂ , SiO ₂ , Fe oxide, carbonaceous material
T-11	fresh	amorphous phase (Fe,Ca,Mg,S,O,C,Si,Al,Mn), CaSO ₄ ·2H ₂ O, CaCO ₃ , Fe oxide, SiO ₂

Table 14: Sludge Leaching Characteristics, Ontario Leachate Extraction Procedure

Site Code	Sample	Leachate Composition ($\mu\text{g/L}$)												
		Ag	As	Ba	B ¹	Cd	Cr	Cu	Fe, ¹	Hg	Ni	Pb	Se	Zn ¹
D-1	fresh	<2	<5	9.4	124.2	<1	<7	<13	<40	<4	4.9	<2	<24	<50
	aged	<2	<5	38.8	397.6	<1	<7	73.3	<40	<4	769.3	<2	<24	<50
Q-2	fresh	<4	<5	109.0	120	35.7	<24	<196	<40	–	<91	<0.7	144.8	0.16
	aged	<6	<6	104.3	149.8	43.0	<34	<235	<40	<27	8.0	<10	153.2	140
M-3	fresh	<6	<6	86.8	293.7	<4	<34	<235	<40	<27	942.6	<10	<97	<60
R-4	fresh	<6	<6	30.0	68.1	<4	<34	<235	<40	<27	32.8	<10	<97	330
	aged	<6	<6	22.4	<62	<4	<34	<235	<40	<27	11.8	<10	<97	160
F-5	fresh	<6	<6	23.1	<77	<3	<8	<28	<40	<40	<6	<5	<35	<60
	aged	<6	<6	65.5	<77	<3	<8	<28	<40	<40	413.0	<5	<35	300
S-6	fresh	<4	<6	60.2	79	47.8	<24	<196	<50	<30	<112	<1	132.4	480
	aged	<2	<5	29.4	150.0	3.7	<7	<13	<40	<4	8.2	<2	186.3	<50
J-7	fresh	<2	<5	219.2	927.1	<1	<7	<13	<40	<4	25.2	<2	<24	<50
	aged	<2	<5	53.3	278.6	<1	<17	<12	<40	<4	60.1	<2	<24	<50
W-8	fresh	25.7	<6	117.7	228	375.5	<24	<196	<40	<40	<91	<5	<35	27,200
	aged	<6	<6	64.9	<77	<3	<8	<28	<40	<40	24.9	<5	<35	80
N-9 ²	aged	<6	<6	49.0	1719.4	3.2	<24	<196	<40	<40	391.7	<5	<35	270
B-10	fresh	<6	<6	40.8	<62	<4	<34	<235	<40	<27	<7	<10	<97	<60
T-11 ³	fresh	<6	<6	16.4	124.5	<3	<8	<28	<40	<40	<6	<5	<35	<60
Most Stringent Cdn. Regulated Limit⁴		5,000	5,000	100,000	500,000	500	5,000	10,000	1x10 ⁶	100	5,000	5,000	1,000	10,000

¹ Since analytical results were originally in mg/L, trailing zeros may not be significant. ² U = 5,015 $\mu\text{g/L}$ ³ U < 11 $\mu\text{g/L}$ ⁴ See Table 16 (U limit is 2,000 $\mu\text{g/L}$)

Table 15: Sludge Leaching Characteristics, Modified Leachate Extraction Procedure

Site Code	Sample	Leachate Composition ($\mu\text{g/L}$)												
		Ag	As	Ba	B ¹	Cd	Cr	Cu	Fe ₁ ¹	Hg	Ni	Pb	Se	Zn ¹
D-1	fresh	<2	<5	9.8	131.8	<1	<7	<13	<40	<4	5.2	<2	<24	<50
	aged	<2	<5	16.9	74.2	<1	<7	28.3	<40	<4	26.5	<2	<24	<50
Q-2	fresh	<4	<5	48.4	200	<0.7	<24	<196	<40	-	<91	1.0	141.4	40
	aged	<6	<6	48.8	95.0	4.4	<34	<235	<40	<27	<7	<10	115.7	<60
M-3	fresh	<6	<6	38.3	111.6	<4	<34	<235	<40	<27	187.0	<10	<97	<60
R-4	fresh	<6	<6	<5	<62	<4	<34	<235	<40	<27	<7	<10	<97	<60
	aged	<6	<6	<5	<62	<4	<34	<235	<40	<27	<7	<10	<97	<60
F-5	fresh	<6	<6	23.5	<77	<3	<8	<28	<40	<40	<6	<5	<35	<60
	aged	<6	<6	13.8	<77	<3	<8	<28	<40	<40	<6	<5	<35	<60
S-6	fresh	<3	<3	23.1	<49	9.7	<9	<94	<40	<30	19.9	<9	89.8	5200
	aged	<2	<5	28.2	147.8	3.5	<7	<13	<40	<4	7.2	<2	177.5	<50
J-7	fresh	<2	<5	47.9	317.8	<1	<7	<13	<40	<4	4.6	<2	<24	<50
	aged	<2	<5	7.3	66.1	<1	<7	<13	<40	<4	5.3	<2	<24	<50
W-8	fresh	<6	<6	32.3	<77	<3	<8	<28	<40	<40	<6	<5	<35	<60
	aged	<6	<6	24.4	<77	<3	<8	<28	<40	<40	24.8	<5	<35	<60
N-9 ²	aged	<6	<6	24.9	762.4	<3	<8	<28	<40	<40	<24.2	<5	<35	<60
B-10	fresh	<6	<6	40.7	<62	<4	<34	<235	<40	<27	<7	<10	<97	<60
T-11 ³	fresh	<6	<6	16.3	117.0	<3	<8	<28	<40	<40	<6	<5	<35	<60
Most Stringent Cdn. Regulated Limit⁴		5,000	5,000	100,000	500,000	500	5,000	10,000	1x10 ⁶	100	5,000	5,000	1,000	10,000

¹ Since analytical results were originally in mg/L, trailing zeros may not be significant. ² U = 405 $\mu\text{g/L}$ ³ U = 11 $\mu\text{g/L}$ ⁴ See Table 16 (U limit is 2,000 $\mu\text{g/L}$)

BM-1	1%	Settling ponds.
BM-1	1%	No clarifier, disposal to tailings basin.
BM-2	3%	Conventional clarifier, no sludge recycle.
BM-6	2%	Reactor clarifier, no sludge recycle.
PM-2	15-20%	Reactor clarifier, no sludge recycle.
BM-7	1%	Clarifier, no sludge recycle.
BM-5	2%	Reactor clarifier, sludge recycle.
BM-4	10-15%	Reactor clarifier, sludge recycle.
BM-3	7-10%	Sludge recycle operation.
BM-8	5%	No clarifier.
BM-9	20-30%	High density sludge operation.
PM-1	2-5%	Settling ponds.
PM-3	2-5%	Reactor clarifier, no sludge recycle.
BM-11	5-10%	Sludge lagoon.
BM-10	5-8%	Sludge pond.

Notes: BM - Base Metal Industry Facility
PM - Precious Metal Industry Facility

**Table 3.4
SLUDGE LEACHATE ANALYSIS***

	Leaching** Procedure	Initial pH	Final pH	As (mg/L)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Ni (mg/L)	Pb (mg/L)	Sb (mg/L)	Zn (mg/L)
BASE METAL SLUDGE												
BM-1	L1	4.00	8.96	-	0	-	0	0	0	0	-	0
	L2	2.50	6.70	-	0.1	-	0	0.3	0	0	-	16.0
	L3	4.00	4.00	-	0.1	-	0.3	0.5	0.2	0	-	95.0
	L4	2.30	2.30	-	0.1	-	0.4	45.0	0.3	0	-	120.0
	L5		4.66	-	0.1	-	0.3	2.0	0	0	-	90.0
	L6		9.83	-	0	-	0	0	0	0	-	0
BM-2	L1	4.00	9.86	0.006	0	-	0.3	0	0	0	-	0
	L2	2.50	8.90	-	0.2	-	0.3	0	0	0	-	0
	L3	3.90	3.90	-	63.0	-	0.3	1.0	0.5	6.7	-	220.0
	L4	2.67	2.67	2.7	63.0	-	0.4	4.1	0.6	4.2	-	225.0
	L5		5.47	0.57	59.0	-	0.2	0.3	0.5	12.0	-	208.0
	L6		10.39	-	0.1	-	0	0	0	0	-	0
BM-3	L1	4.00	8.30	-	0.1	-	0	0	0	0	-	1.3
	L2	2.50	6.96	-	0.7	-	0	0	0	0	-	7.5
	L3	4.05	4.05	-	3.2	-	21.0	1.0	0.3	1.5	-	1900.0
	L4	2.56	2.56	-	3.2	-	21.0	6.4	0.3	2.0	-	1900.0
	L5		5.52	-	2.7	-	18.0	0.3	0.4	2.0	-	1900.0
	L6		8.77	-	<0.1	-	0	0	0.2	0	-	2.7
BM-4	L1	4.00	9.39	-	0	0	0	0	0	0	-	0
	L2	2.50	8.72	-	0	0	0.1	0	0	0	-	0
	L3	4.10	4.10	-	2.1	0	12.0	3.5	0.8	0	-	970.0
	L4	2.59	2.59	-	2.2	0	13.0	22.0	1.0	0.5	-	970.0
	L5	4.50	6.25	-	0.4	0	2.0	0	0.7	0	-	680.0
	L6		9.85	-	0	-	0	0	0	0	-	1.5
BM-5	L1	4.00	9.32	-	0	-	0	0	0	0	-	0
	L2	2.50	8.87	-	0	-	0	0	0	0	-	0
	L3	4.00	4.21	-	0.4	-	2.0	3.0	0.8	0	-	310.0
	L4	2.50	2.58	-	0.4	-	3.0	25.0	0.9	0.5	-	375.0
	L5	4.50	5.30	-	0.4	-	1.0	1.0	0.7	0	-	400.0
	L6		8.47	-	0	-	0	0	0	0	-	0.8
BM-6	L1	4.00	8.20	-	0	-	0	0	0	0	-	0
	L2	2.50	5.62	-	0.1	-	0.7	2.0	0	0	-	13.0
	L3	4.00	4.13	-	0.1	-	0.3	2.5	0	0	-	34.0
	L4	2.50	2.40	-	0.1	-	0.3	87.0	0.3	0	-	30.0
	L5	4.50	4.60	-	0.1	-	0.3	1.0	0.2	0	-	21.0
	L6		7.88	-	0	-	0	0	0	0	-	0

	Leaching Procedure	Initial pH	Final pH	As (mg/L)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Ni (mg/L)	Pb (mg/L)	Sb (mg/L)	Zn (mg/L)
BASE METAL SLUDGE LEACHATES, CONT'D												
BM-7	L1	4.00	8.66	-	0	-	0	0.5	1.2	0	-	0
	L2	2.50	6.78	-	0	-	0	0.5	9.5	0	-	0
	L3	4.00	4.24	-	0	-	0.8	0.3	28.3	0	-	0.6
	L4	2.50	2.40	-	0	-	1.1	42.0	33.0	0	-	0.6
	L5	4.50	4.64	-	0	-	1.0	1.0	27.5	0	-	1.1
	L6		8.91	-	0	-	0	0.5	1.0	0	-	0
BM-8	L1	4.00	8.98	-	0	-	0.3	0	0	0	-	0.9
	L2	2.50	3.16	-	0	-	0.7	6.1	0	0	-	5.9
	L3	4.00	4.03	-	0	-	0.3	3.1	0	0	-	5.7
	L4	2.50	2.67	-	0	-	0.5	22.0	0.3	0.1	-	6.1
	L5	4.50	4.61	-	0	-	0.5	2.0	0.2	0.2	-	6.5
	L6		9.05	-	0	-	0	0	0	0	-	0.1
BM-9	L1	4.00	9.10	-	-	0	0	0	0	0	-	0.1
	L2	2.50	8.87	-	-	0	0	0	0	0	-	0.1
	L3	4.00	4.34	-	1.5	-	11.0	0	2.3	1.0	-	365.0
	L4	2.50	2.72	-	1.8	-	66.0	125.0	2.5	5.0	-	420.0
	L5	4.50	7.87	-	0	-	0	0	0	1.0	-	0.1
	L6		9.23	-	0	-	0	0	0	0	-	0.1
BM-9-0	L1	4.00	8.27	-	0	-	0	0	0	0	-	0.1
	L2	2.50	8.17	-	0	-	0	0	0	0.3	-	0.1
	L3	4.00	4.27	-	1.2	-	0.8	0.5	4.5	1.0	-	850.0
	L4	2.50	3.29	-	2.3	-	7.5	6.0	5.5	4.0	-	1265.0
	L5	4.50	7.40	-	0	-	9	0	9	0.7	-	0.2
	L6		9.17	-	0	-	0	0	0	0	-	0.1
BM-10	L1	4.00	9.28	-	0	-	0	0.5	0	0	-	0
	L2	2.50	9.10	-	0	-	0	0.5	0	0	-	0.1
	L3	4.00	4.10	-	0.4	-	18.6	1.0	1.0	0.3	-	232.0
	L4	2.50	2.54	-	0.5	-	49.0	770.0	1.3	0.8	-	266.0
	L5	4.50	7.17	-	0	-	0	0.5	0.2	0.4	-	1.4
	L6		9.17	-	0	-	0	0	0	0	-	0
BM-10-0	L1	4.00	9.14	-	0	-	0	0.5	0	0	-	0
	L2	2.50	8.88	-	0	-	0	0.5	0	0	-	0.1
	L3	4.00	4.22	-	0.3	-	6.6	2.0	0.7	0	-	170.0
	L4	2.50	2.73	-	0.8	-	58.0	220.0	0.8	0.4	-	330.0
	L5	4.50	7.90	-	0	-	0	0	0.2	0.4	-	0.1
	L6		9.03	-	0	-	0	0	0	0	-	0
BM-11	L1	4.00	11.07	-	0	-	0	0	0	0	-	0.3
	L2	2.50	11.07	-	0	-	0	0	0	0	-	0.2
	L3	4.00	4.15	-	18.0	-	55.0	1.0	1.3	0	-	5120.0
	L4	2.50	2.56	-	21.0	-	93.0	690.0	1.5	1.9	-	5380.0
	L5	4.50	10.49	-	0	-	0	0.5	0.3	0.4	-	0.1
	L6		11.16	-	0	-	0	0	0	0	-	0
PRECIOUS METAL SLUDGE LEACHATE												

	Leaching Procedure	Initial pH	Final pH	As (mg/L)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Ni (mg/L)	Pb (mg/L)	Sb (mg/L)	Zn (mg/L)
PM-1	L1	4.00	10.67	-	0	-	0.2	1.5	0	0	-	0.1
	L2	2.50	10.06	-	Tr	-	0.2	0.5	0	0	-	0
	L3	4.00	4.21	-	0.1	-	11.0	0	1.3	0	-	7.6
	L4	2.50	2.62	-	0.1	-	13.0	67.0	1.5	0	-	8.1
	L5	4.50	4.72	-	0.1	-	11.0	14.0	1.0	0	-	7.5
	L6		9.30	-	0	-	0	0	0	0	-	0
PM-2	L1	4.00	9.40	-		-	1.7	8.6	0.5	0	1.1	0.1
	L2	2.50	7.98	-	0	0	0.4	1.5	0.5	0	-	0
	L3	4.00	4.13	-	0	-	40.0	0.3	18.3	0	-	2.0
	L4	2.50	2.56	-	-	-	55.0	94.0	21.1	0	0.014	2.4
	L5	4.50	7.32	-	0	0	39.0	0.5	13.6	0	0.11	2.3
	L6			-	0	0	0.2	1.0	0	0	-	0
PM-3	L1	4.00	7.30	0.012	0	-	0	0	0	0	-	0
	L2	2.50	3.40	-	0	-	4.4	1.0	0	0	-	1.6
	L3	4.0	4.02	-	0	-	3.4	0	0	0	-	1.5
	L4	2.50	2.57	0.118	0	-	4.7	55.0	0	0	-	1.6
	L5	4.50	4.57	0.014	0	-	3.2	0	0.2	0.3	-	1.4
	L6		7.50	-	0	-	0	0	0	0	-	0

Note:

- (-) not determined
- (o) below detection limit

Leaching Procedure

- L1 - 1/10 dilution of sludge in H₂SO₄ solution at initial pH 4
- L2 - 1/10 dilution of sludge in H₂SO₄ solution at initial pH 2.5
- L3 - 1/10 dilution of sludge in H₂SO₄ solution maintained at pH 4
- L4 - 1/10 dilution of sludge in H₂SO₄ solution maintained at pH 2.5
- L5 - 1/10 dilution of sludge in acetic acid and sodium acetate solution at initial pH 4.5
- L6 - 1/10 dilution of sludge in distilled water

Source: Gionet et al. 1987.

Table 3.3 (a)

SLUDGE PHYSICAL PROPERTIES ANALYSIS

	Total Solids %	Suspended Solids %	pH	Density g/mL	Sulphate wt%
BASE METAL SLUDGE					
BM-1	2.08	1.37	9.56	1.005	0.86
BM-2	3.63	3.22	10.30	1.010	0.05
BM-3	7.64	7.60	8.46	1.048	2.84
BM-4	20.55	-	9.38	1.135	0.45
BM-5	3.93	2.88	9.35	1.013	0.11
BM-6	1.87	1.22	8.22	1.003	0.43
BM-7	0.59	0.55	8.80	1.003	0.12
BM-8	0.35	0.16	9.84	1.000	0.12
BM-9 Fresh	20.60	-	9.43	1.132	1.87
BM-9 Aged	79.00	-	8.59	2.200	9.72
BM-10 Fresh	15.40	-	9.42	1.060	1.17
BM-10 Aged	25.90	-	9.16	1.170	2.83
BM-11	48.7	-	10.97	1.220	3.60
PRECIOUS METAL SLUDGE					
PM-1	2.81	2.23	10.68	1.008	1.00
PM-2	2.31	2.02	9.40	1.003	0.15
PM-3	2.01	0.76	7.47	1.004	0.15

Source: Gionet et al. 1987.

Table 3.3 (b)

SLUDGE METALS ANALYSES

	WEIGHT (%) (based on dry weight)													
	Al	As	B	Ca	Cd	Cu	Fe	Mg	Mn	Na	Ni	Pb	Sb	Zn
BASE METAL SLUDGE														
BM-1	1.9	-	6.5	1.8	-	-	3.7	2.5	2.1	-	-	-	-	6.3
BM-2	0.63	1.2	2.2	1.1	2.4	-	1.2	5.6	0.7	1.8	-	2.0	-	7.0
BM-3	-	-	1.1	0.8	-	-	-	-	-	-	-	-	-	27.4
BM-4	-	-	-	34.4	-	-	0.6	1.2	-	-	-	-	-	5.2
BM-5	-	-	0.63	16.0	-	-	0.7	3.1	-	3.3	-	-	-	1.4
BM-6	-	-	-	8.2	-	-	29.4	2.1	-	-	-	-	-	2.6
BM-7	-	-	6.6	16.5	-	-	10.1	4.5	0.5	-	6.3	-	-	-
BM-8	-	-	-	14.7	-	-	6.6	4.4	-	-	-	-	-	1.6
BM-9 Fresh	1.0	-	-	2.5	-	-	25.3	7.3	1.5	-	-	-	-	2.4
BM-9 Aged	1.9	-	-	8.1	-	2.5	25.0	3.1	1.8	-	-	0.66	-	2.5
BM-10 Fresh	3.0	-	-	3.9	-	-	19.3	5.1	0.5	-	-	-	-	1.4
BM-10 Aged	2.0	-	-	5.8	-	-	20.5	4.2	-	-	-	-	-	0.9
BM-11	1.2	-	-	8.2	-	-	2.0	1.0	-	-	-	-	-	14.3
PRECIOUS METAL SLUDGE														
PM-1	2.4	-	2.1	20.8	-	-	2.7	1.6	-	-	-	-	-	-
PM-2	7.3	-	-	26.5	-	6.5	38.4	1.2	-	-	1.7	-	5.4	-
PM-3	-	1.5	-	13.6	-	-	16.9	-	-	6.5	-	-	-	-

Source: Gionet et al. 1987.

What have we learned from all these sampling and measurements?

- There's a large variability in sludge, including some with high metal values
- Sludge density and chemical stability increases with sludge aging
- Sludge volume/density remains a serious issue even after aging over several freeze-thaw cycles.
- NP/NNP and metal content are good indicators of stability
- AMD treatment sludges would not generally be classified as hazardous wastes based on current leaching protocols and regulated contaminant limits.
- Mineralogical data suggest long term aging (thousands of years) could transform the sludge into a stable carbonate rock with a minor iron oxide component.

Therefore:

The principle issue for lime treatment sludges is disposal volume and density.

No surprises

DISPOSAL PRACTICE IN CANADA

Tailings Ponds - 40%

Sludge Ponds - 20%

Recycle - 5%

Landfill - 25%

Open Pit - 10%

Sludge Densities

	<u>% Solids</u>
● Low density in ponds	1 to 15
● Simple clarifier	1 to 15
● Sludge lagoon	10 to 25
- freezing	Up to 40%
● HDS - thickener	20 to 40
- after storage	up to 50%
● See examples	

Treatment Processes

- **Basic:** slaked lime added directly to stream (1-5% solids)
- **Conventional:** mechanically or air agitated reactors (3-10% solids)
- **HDS:** sludge recycling with lime, aeration, S/L separation with thickener (10-30% solids)
- **Staged Neutralization:** chemical crystallization technology to control the level of supersaturation in the solution (45%+ solids)

CANMET - Mining and Mineral Sciences

Optimum Sludge Density

- increasing sludge density, reduces sludge volume and disposal costs
- maximum sludge density
 - viscosity ("pumpability")
 - solids loading
 - technological limits
- impact of post treatment practices on densification

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METALS, SULFUR, AND CARBON BALANCE IN A PILOT REACTOR TREATING LEAD IN WATER

Thomas Wildeman (Colorado School of Mines and Knight Piesold, LLC, Denver, Colorado)

James J. Gusek (Knight Piesold, LLC, Denver, Colorado)

Aaron Miller (ASARCO Inc. Annapolis, Missouri)

James Fricke (Advanced Geoservices Corp., Sandy, Utah)

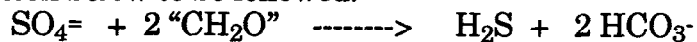
ABSTRACT: Water from an underground lead mine has pH of 8.0 with 0.4 to 0.6 mg /L of Pb and 0.18 mg/L of Zn. A pilot scale reactor using sulfate-reducing bacteria was built to remove lead to below the environmental limit of 0.030 mg/L. The system utilized 53 m³ of a mixture of sawdust, manure, hay, dolomitic tailings, and coarse mine waste. Throughout the two-year operation, the system has treated from 8 to 185 L/min of water, and lead and zinc have been reduced to below detection limits of 0.02 and 0.008 mg/L, respectively. Because pH of the water was neutral and the loading of heavy metals was low, the sulfate reduction reaction could be followed. Sulfide and alkalinity in the water increased as SO₄⁼ in the water decreased. During the summer, sulfide production reached 2 moles S⁼ produced/m³/day. In the winter, sulfide production dropped to more typical design values of 0.3 moles S⁼ produced/m³/day. This change in production of sulfide is partially attributed to the change in temperature of the water flowing through the pilot cell.

INTRODUCTION

Because of the formation of soluble neutral complexes, lead solubility in neutral to alkaline waters is often above the drinking water standard of 0.050 mg/L. In addition, normal methods of removing metals from water such as the addition of hydroxide or carbonate only make lead more soluble in slightly alkaline waters (McMillan, et al. 1994). Modelling studies suggest that one method to overcome this problem is by the addition of S⁼, which causes the precipitation of a highly insoluble sulfide. From the viewpoint of passive bioremediation, generation of sulfide through the activity of sulfate-reducing bacteria has been used in the removal of metals from water (Wildeman, et al., 1994). In most instances this type of treatment technology has been used on acidic coal- and metals-mining drainages (Wildeman, et al., 1993, 1995). However, in this study, the objective was the removal of lead from a slightly alkaline water generated from the dewatering of an underground lead mine that is hosted in a dolomitic country rock.

The site of the mine is the New Lead Belt in Missouri. The treatment objective is to reduce the lead concentration to below the water quality standard of 0.030 mg/L and insure that other contaminants are not added to the water during the treatment. Because the water was buffered by the carbonate host rock, the pH ranged from 7.9 to 8.2. The concentration of dissolved lead ranged from 0.07 to 0.12 mg/L while total lead ranged from 0.4 to 0.7 mg/L. Besides lead, the concentration of dissolved zinc and manganese ranged from 0.1 to 0.7 and 0.01 to 0.5 mg/L respectively.

This paper reports on the successful operation of a pilot cell that tested the feasibility of removal of lead through the precipitation of lead sulfide generated by sulfate reduction. In the treatment of acid mine drainage, the objective is to generate as much sulfide as possible for metals removal (Wildeman, et al. 1993, 1994). However, in this case because the water is neutral and the concentration of metal contaminants is only slightly above the environmental limits, the objective turned out to be to generate just enough sulfide to precipitate the lead and zinc. Because of the chemistry of the water and the desire of ASARCO Inc. to completely understand the chemistry involved in this passive treatment technology, chemical constituents in the water beyond the contaminant concentrations were analyzed throughout the course of the operation of the pilot cell. In particular, SO_4^{2-} , S^{2-} , alkalinity and organic content in the form of biological oxygen demand were determined on a regular basis. This enabled a more thorough analysis of the sulfate reduction equation written below to be followed.



In this reaction, "CH₂O" is used to represent organic matter.

EXPERIMENTAL DETAILS

The pilot cell was approximately 1.5 meters deep and had a working volume of 53 cubic meters. Based on laboratory studies of possible substrate materials, a mixture of sawdust, manure, hay, dolomitic tailings, and coarse mine waste was used. This mixture was inoculated with a 1:1 mixture of cow manure and saw dust that was used in a bench-scale sulfate-reducing reactor. The bench-scale system removed 0.08 mole of Pb and Cu/m³/day. Using this removal rate, the design flow rate in the pilot cell was set at 77 L/min. The pilot cell was started on March 11, 1994 and operated for over 600 days.

During the operation period, the cell was visited at least twice a month and field measurements were taken. Twice a month for the first six months and then monthly there afterwards, water samples were taken. All handling, preservation, and storage protocols were followed. Analysis of water constituents were performed by the environmental labs of ASARCO Inc.

RESULTS AND DISCUSSION

During the operation of the pilot system, lead and zinc were consistently removed to below detection limits of 0.02 and 0.008 mg/L, respectively. Concentrations of the constituents that are the reactants and products of the sulfate reduction reaction reveal interesting trends. In Figure 1, is shown the change in concentration between the influent and effluent water for sulfate, S^{2-} , and alkalinity. Sulfate and S^{2-} concentrations are in units of mg/L and alkalinity is in units of mg CaCO₃/L. Figure 2 plots the S^{2-} generated within the pilot cell in units of moles of S^{2-} /m³ of substrate/day. The moles of S^{2-} generated were determined by two methods: From the reduction in the concentration of SO_4^{2-} in the effluent compared to the influent, and from the concentration of S^{2-} in the effluent. To make this calculation, it is necessary to know the volume of substrate in the pilot cell and the flow of water through the cell. In both figures, the number of days of operation is plotted on the x axis. The first summer is from day 100 to 200, winter is from day 260 to 360, the second summer is from day 460 to 560.

CHANGES IN SULFATE, ALKALINITY, AND SULFIDE IN THE ASARCO PILOT CELL WATER

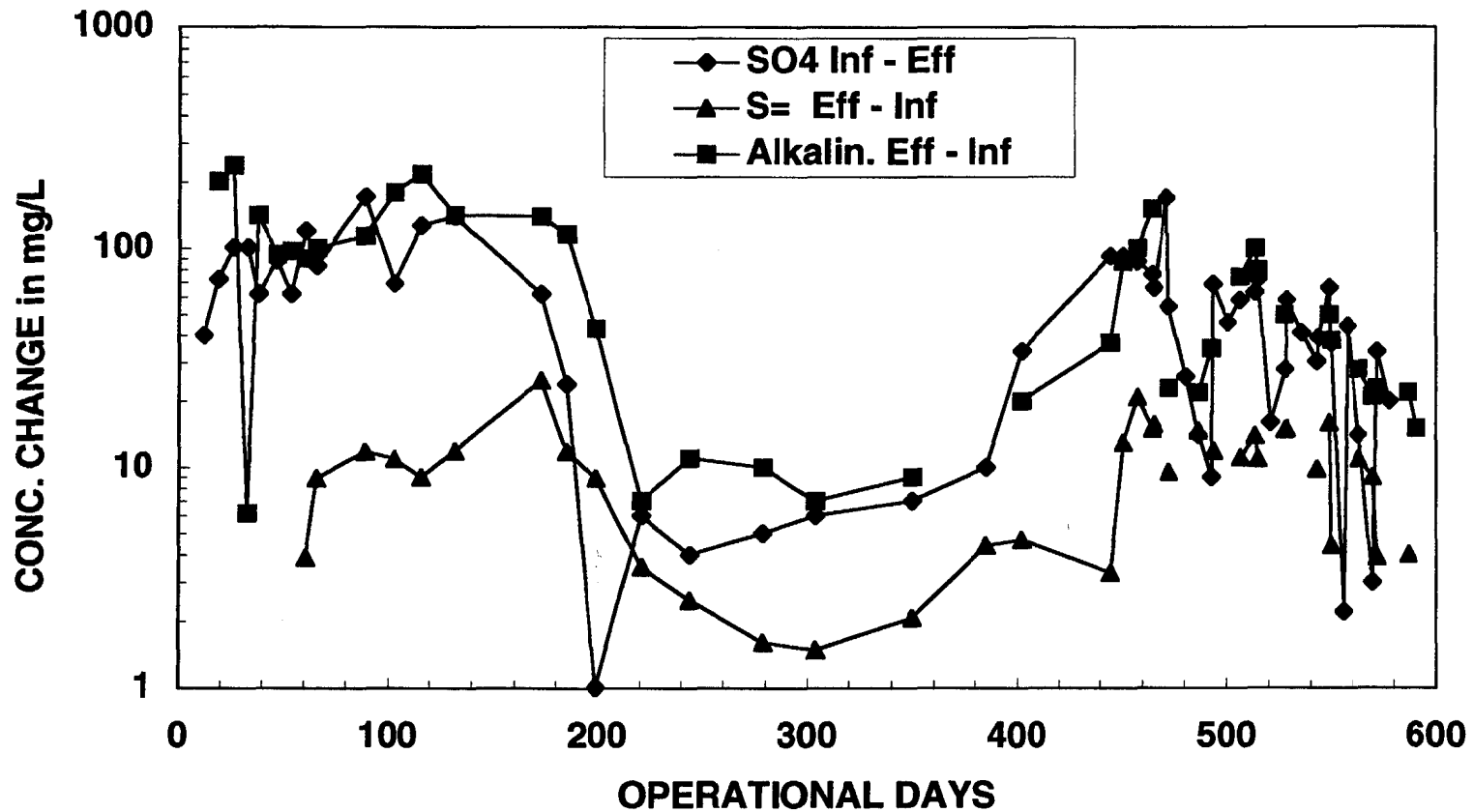


FIGURE 1. The change in concentration between influent and effluent waters in the ASARCO Inc. pilot cell. All concentrations are in mg/L.

**SULFIDE GENERATION CALCULATED FROM
SULFATE REDUCED AND SULFIDE PRODUCED**

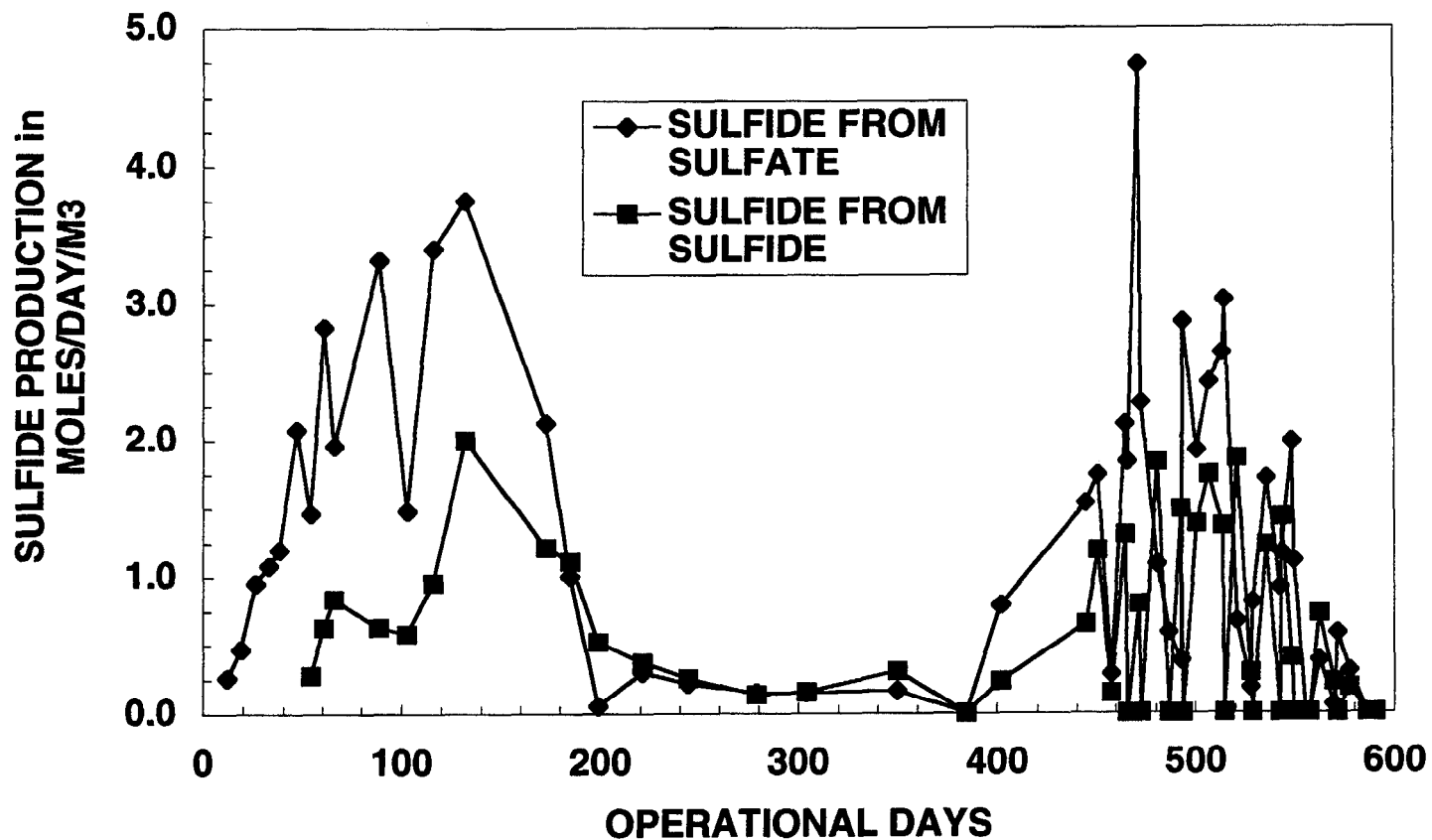


FIGURE 2. Estimates of the amount of sulfide produced in the ASARCO Inc. pilot cell. One estimate is from the change in sulfate concentration between influent and effluent; the other estimate is from the concentration of S⁼ in the effluent. Sulfide production is in moles S⁼/m³/day.

Examination of Figure 1 shows that, in a broad fashion, the reduction of SO_4^{2-} in the water correlates with an increase in alkalinity and S^{2-} . This is what would be expected by the sulfate reduction reaction. On a mole basis, 96 mg/l of SO_4^{2-} reduced would generate 200 mg CaCO_3/L of alkalinity and 32 mg/L of S^{2-} . Taking this into account, if the reduction of SO_4^{2-} in the water is due only to sulfate reducing bacteria, then one would expect the alkalinity and S^{2-} produced to be higher than what is shown in Figure 1. It would be most surprising if the changes in concentration of all three constituents were caused solely by the sulfate reduction reaction.

With respect to alkalinity, the pH of the water drops from an average of 8.0 to values between 6.5 to 7.0 in the summer and 7.0 to 7.4 in the winter. Although unraveling carbonate chemistry in water is complex, it appears that some of the alkalinity produced may be used to neutralize acids produced in the pilot cell. Because this pH drop is seasonal, it may be caused by other biologic reactions that are accelerated in the summer. With respect to S^{2-} , because the concentrations of heavy metals in the mine water are low, little S^{2-} is lost through the precipitation of sulfides. However, because sampling and preservation for S^{2-} is complex, low concentration values are not surprising.

In Figure 2, based on the previous discussion, S^{2-} generation calculated by sulfate reduction can be considered to be an upper estimate while sulfide generation calculated from S^{2-} concentration in the water is a lower estimate. In previous projects, 0.3 moles of S^{2-} produced/ m^3/day calculated from sulfate reduction has been used as the design rule of thumb. In this system, values of sulfide generation of 3 to 4 moles of $\text{S}^{2-}/\text{m}^3/\text{day}$ were achieved. Even if the more conservative estimates based on S^{2-} in the water are used, the summer production values often reached 2 moles produced/ m^3/day . Such high levels of sulfide production in a passive system were surprising.

Because sulfide in the water is not desirable, the flow of water through the system was increased to 185 L/min, more than double the design value. This dropped the concentration of S^{2-} in the water but it did not decrease the generation of S^{2-} within the substrate. In the first summer, some of the highest values of S^{2-} production were achieved at the highest flow rates.

The first reason why the rate of sulfide production might be quite high is because, in this system, slightly alkaline water is being treated. A common sulfide production value used is 0.3 moles of $\text{S}^{2-}/\text{m}^3/\text{day}$ (Wildeman, et al., 1993, 1994). However, this value was generated through experiences in the treatment of acidic waters whose pH ranged from below 3 to about 4. In this study, the pH of the water averages 8.0 which is within 6 to 9, the optimum pH range for sulfate reduction.

In the first summer there were large quantities of mobile organic material readily available for the sulfate-reducing bacteria. This was monitored through the measurement of the biologic oxygen demand that was between 200 and 400 mg/L in the first 60 days of operation and averaged 50 mg/l during the summer months. It was assumed that this low molecular weight organic material was fueling the metabolism of the sulfate-reducing bacteria. This hypothesis seemed to be confirmed by the fact that on about the 200th day of operation, the BOD fell to around 1 mg/L and sulfide production dropped to below 0.5 moles of $\text{S}^{2-}/\text{m}^3/\text{day}$. However, during the second summer, the rates of production again rose to 2 moles of $\text{S}^{2-}/\text{m}^3/\text{day}$.

Because the rate of production of sulfide shows a seasonal trend, an alternative explanation for the changes is the temperature of the pilot system. To reduce suspended solids, the water from the mine enters a settling pond and the water for the pilot cell is taken from this pond. Because of this, the temperature of the influent ranges from 6 °C in the winter to 26 °C in the summer. The temperature of the effluent is always within 1 °C of the temperature of the influent. The temperature dependence on the rate of sulfate reduction in bioreactors has been noted before (Wildeman et al., 1995). The interesting result in this study is that rates of sulfide production appear to be able to reach values of 2 moles of S⁼/m³/day when the reactor temperatures reach 25 °C. Such large variations in the rate of S⁼ production are an important factor to consider in the design of sulfate-reducing wetlands and bioreactors.

CONCLUSIONS

The results of this pilot-scale project on the treatment of lead in water through sulfate reduction has produced the following conclusions:

- Consistent treatment of lead and zinc in circum-neutral water to below environmental limits is possible.
- The sulfate-reduction reaction can be followed by the changes in sulfate, alkalinity, or S⁼ in the water.
- Sulfate reduction appears to be quite dependent on the temperature of the reactor. The production range appears to be from below 0.3 moles of S⁼/m³/day when the temperature is below 10 °C to above 2 moles of S⁼/m³/day when the temperature is above 25 °C.

Based on the results of the pilot-scale study, a full-scale system capable of treating 1,500 gpm has been built and is in its first year of operation.

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CHAPTER **20****Passive Bioremediation
of Metals and
Inorganic Contaminants**

THOMAS WILDEMAN AND DAVID UPDEGRAFF

ABSTRACT. There has recently been considerable interest in the use of constructed wetlands and/or passive bioreactors to remove metal contaminants from water, especially acid-mine drainage. This chapter considers some chemical, geochemical, and engineering design features which govern the effectiveness of constructed wetlands. The discussion focuses on a particular attempt to design a passive bioreactor to treat acid-mine drainage, while introducing general principals and chemical interactions which govern the operation of such systems. Aerobic bioreactor systems operate best when the pH of the influent stream is greater than 5.5 and are most effective at the removal of Fe and Mn as $\text{Fe}(\text{OH})_3$ and MnO_2 precipitates. In anaerobic systems, consortia of sulfate-reducing microorganisms are used to increase the pH of the influent stream and precipitate metals as sulfides.

Constructed wetlands/bioreactors are capable of treating waters with a pH as low as 3 and heavy-metal concentrations in excess of 1000 mg/L. Microbially mediated precipitations dominate the metal-removal processes. This fact facilitates process-level research through a staged design process that is quite similar to the design of other bioremediation systems. The result is that constructed wetlands are viewed as passive bioreactors as opposed to natural ecosystems, which greatly facilitates research and innovation in the bioremediation of metal/inorganic-contaminated waters.

INTRODUCTION

From our childhood, many of us can remember stepping in the wrong place in a swamp and finding ourselves knee deep in muck. We were immediately repulsed by the foul nature of that environment. Ecologists have long understood that soils in wetlands are often foul because they naturally accumulate and treat contaminants. The methods by which a wetland treats contaminants include:

1. Filtering of suspended and colloidal material from the water
2. Uptake of contaminants into the roots and leaves of live plants
3. Adsorption or exchange of contaminants onto inorganic soil constituents, organic solids, dead plant material, or algal material

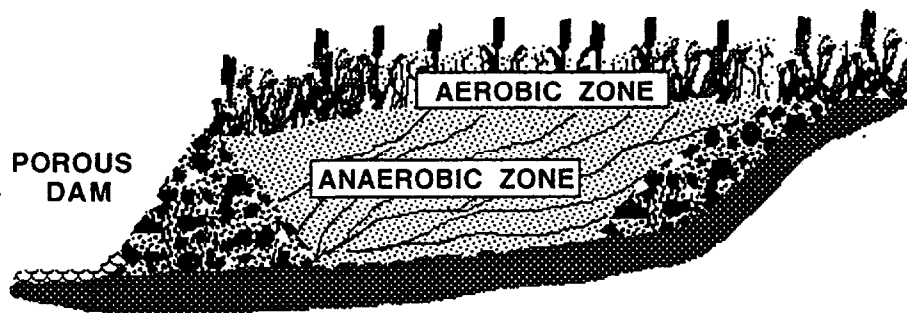
474 INTRODUCTION

4. Neutralization and precipitation of contaminants through the generation of HCO_3^- , H_2S , and NH_3 by bacterial decay of organic matter
5. Destruction or precipitation of contaminants catalyzed by the activity of aerobic or anaerobic bacteria

In the last decade, engineers began to use wetlands for the removal of contaminants from water (Hammer, 1989; Reed et al., 1988). In some instances, natural wetlands were used. However, a natural system will accommodate all the above removal processes and probably will not operate to maximize a desired process. If a wetland is constructed (e.g., Figure 20.1), it can be designed to maximize a specific process suitable for the removal of certain contaminants from water. Engineering as well as ecological reasons lead to the choice of constructing a wetland for contaminant removal rather than using an existing natural ecosystem.

Because of the remote location of many mines and constant flow of effluent, constructed wetlands have particular appeal in treating acid-mine drainage (AMD) (Klusman and Machemer, 1991). Early wetland designs treating coal mine drainage generally included peat or compost substrate, cattails, and limestone gravel within a surface flow system (Brodie, 1991; Brodie et al., 1989a,b, 1991; Eger and Lapakko, 1989; Hiel and Kerins, 1988; Stark et al., 1988). Recently, microbial SO_4^{2-} reduction in wetlands has been used to treat acid-mine drainage from coal mines in the eastern United States (Hammack and Hedin, 1989; Hammack and Edenborn, 1991; Hedin et al., 1988, 1989). In the western United States, metal-mine drainages commonly have low pH and high heavy metal concentrations (Wildeman et al., 1974). One of the first wetlands to be built in Colorado to treat water from such a metal mine was the Big Five pilot wetland in Idaho Springs. The wetland was designed to passively remove heavy metals from metal mine waters and raise the pH (Howard et al., 1989; Wildeman et al., 1993a). The mine drainage flowing from the Big Five Tunnel was chosen for study due to its low pH (3.0), high metal concentrations, moderate flow rate, and accessibility.

It was during the Big Five Project that it was realized that in the anaerobic zone, metals treatment is dominated by bacterial activity. Particularly important for metals precipitation is the sulfate-reducing bacterial (SRB) consortium (Machemer et al., 1993;



TYPICAL CONSTRUCTED WETLAND

Figure 20.1. Cross-sectional view of a wetland where inflow water can flow down through the substrate instead of across the surface.

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Reynolds et al., 1991). In this type of treatment, macroscopic plants become less important (Wildeman et al., 1993b), and the constructed system resembles a flow-through bioreactor (Wildeman et al., 1993a). This bioreactor concept has also been extended to aerobic treatment through the use of algae. In this case, photosynthesis by algae adds oxygen and alkalinity to the water, providing two important reactants for oxidation and hydrolysis reactions (Duggan et al., 1992). It is the purpose of this review to develop and present examples of the biogeochemical principles and engineering methods underlying aerobic and anaerobic passive treatment.

MICROBIAL GUIDELINES FOR METALS REMEDIATION

With an expenditure of energy, metals have been extracted from ores found at the surface or near surface of the earth. Unlike organic compounds, metals generally cannot be degraded to gaseous products or otherwise destroyed. However, just as organic compounds can be mineralized to CO_2 and H_2O , metal contaminants can be mineralized back to the compounds found in ore deposits. Because these inorganic minerals generally represent chemical forms that persisted over geologic time, it is probable that they represent a very stable chemical form for the metal in geologic environments (Wildeman and Laudon, 1989). Consequently, the objective of metals treatment is often to return mobile contaminants to their stable, immobile mineral forms. Many of these minerals, such as FeS_2 and MnO_2 , are formed from water solution in a sedimentary environment, and the reactions are catalyzed by bacteria. Thus, the bioremediation of metal contaminants involves optimizing what has been naturally occurring throughout geologic time.

When treating to remove metal contaminants in water, the objectives usually require adjusting the pH to about 7 and removal of the metals as sulfide, hydroxide, or carbonate precipitates. These objectives generate one of the primary guidelines for metals bioremediation. Because S^{2-} , CO_3^{2-} , and OH^- are common products of bacterial activity, enzymatic uptake of the metal into bacteria is not necessary for remediation. In nature, S^{2-} , CO_3^{2-} , and OH^- are usually generated by a consortium of bacterial species that are working to break down complex organic material. This situation generates a second important guideline for metals bioremediation. This is that inocula of natural bacterial consortia rather than a special, single species are best for effective metals remediation. For the bioremediation of metals, these two guidelines can be combined into the one design criterion of choosing bacterial consortia that are found in typical aquatic environments. This area of study is often called microbial ecology.

Treatment by Traditional Microbial Methods

For this example, consider the reduction of chromate to Cr(III) and its subsequent precipitation as an hydroxide. A traditional treatment study would be initiated by sampling chromium-contaminated site materials. These materials probably contain microbial consortia that include chromate-reducing bacteria. Various colony types from these materials would be transferred to fresh media containing chromate in order to isolate

organisms that reduce chromate. Standard bacteriological procedures involving cultural, morphological, and biochemical tests would be employed to identify the isolates. Such a study has already been accomplished by Komori's group (Komori et al., 1990; Wang et al., 1989). Next, the chromate-reducing bacterial species would be utilized to explore the effects of experimental variables such as:

1. Added inorganic nutrients
2. Competing electron acceptors (including sulfate, nitrate, ferric iron, and Mn (II))
3. Use of different electron donors in the form of various organic compounds
4. Amendment with cellulose and inexpensive plant materials such as hay and alfalfa
5. Supplementation with accessory growth factors including amino acids and vitamins

In addition, using the isolated bacteria, laboratory studies would be designed and accomplished to determine the effect of pH, ionic strength, temperature, and chromate concentration on the rate of reduction of chromate in both contaminated site materials and synthetic culture media. Some cultures would be grown in sealed serum bottles plugged with butyl rubber stoppers, so that the effect of different gaseous atmospheres, including air, nitrogen, hydrogen, and carbon dioxide, could be evaluated. Consideration would be given to the development of biomarkers, such as gene probes, for the principal organisms so that the specific isolates could be readily identified. Analyses would be carried out on contaminated site materials to detect other organic and inorganic co-contaminants, as well as their fate during the chromate reduction process.

Finally after all of the these studies were completed, including adaptation mechanisms (if any) of the isolated organisms, the design of a practical treatment system would be considered. Then, the design would be constructed and operated on a bench- and then pilot-scale level.

Treatment Approach Using Microbial Ecology

The traditional approach emphasizes isolating specific bacterial species and studying how to optimize its removal capabilities. In the microbial ecology approach, emphasis is less on specific species and more on the consortium of bacteria in an aquatic environment that might render inorganic contaminants immobile. As stated above, for most metals, the stable mineral (and presumably thermodynamic) forms are sulfides, hydroxides, or carbonates, which can, under the right conditions, be made to form as precipitates in the bioreactor. The reactants needed to form these precipitates often come from the products of microbial activity, and enzymatic uptake of the metal may not be necessary.

The example of chromate removal can also be discussed from this microbial ecology perspective. In addition to being effective in a natural environment, any chromate-reducing bacterial species isolated by traditional methods would have to be able to survive within a consortium of bacteria indigenous to a specific environment. Also, that specific species will probably have to depend on the consortium to supply the simple organic compounds that it best uses for electron donors (Wildeman and Updegraff, 1994). In this scenario, it is often difficult to determine whether chromate is reduced

by direct microbial activity or whether other readily available reduced constituents such as Fe(II), Mn(II), S(-II), or reactive organic compounds would abiotically reduce Cr(VI). If an aquatic environment is designed to ensure that it remains suboxic and neutral, then Cr may be reduced and removed even if the specific chromate-reducing bacteria are not present.

For this method, soils and scums from different aquatic environments (including a chromate-contaminated site) would be collected. The samples would be exposed to chromate-contaminated waters, and removal progress would be monitored over the course of a month. The tests would be run under aerobic and anaerobic conditions and in sunlight and darkness to see how the microbial systems respond to general external conditions. Systems and conditions that show removal promise would be examined further to determine the nature of removal and possible nutrients, electron donors, and electron acceptors that enhance removal. With this information, a practical treatment system is designed and tested on a bench- and pilot-scale level.

In the end, the treatment system design could be the same regardless of the approach. Using the microbial ecology approach may lead to a more rapid decision on the proper design and a more robust treatment system. This is because removal might not depend upon the activity of one bacterial species.

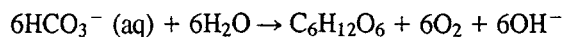
This microbial ecology approach can, of course, be used to design treatment systems for other contaminants. Several of these will be described in later sections of this review. First, however, a review of important microbially mediated reactions will be presented as an aid to understanding these examples (Wildeman and Updegraff, 1994).

APPLICATION OF MICROBIAL ECOLOGY TO WETLANDS AND BIOREACTORS

Microbial processes in aerobic environments are very different from those in anaerobic environments. Aerobic conditions are effective in removing metals whose oxides, hydroxides, or carbonates are relatively insoluble. These include Fe(III) and Mn(IV). Anaerobic processes, including sulfate reduction, are effective in removing metals that form insoluble sulfides. These include Cu, Zn, Cd, Pb, Ag, and Fe(II). Both aerobic and anaerobic processes can neutralize acids (increasing the pH) and add alkalinity to water in the form of HCO_3^- . Consequently, in either environment it is possible to remove Al and Cr(III) as hydroxides, or Zn and Cu as carbonates.

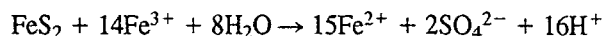
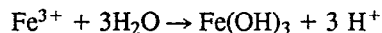
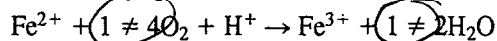
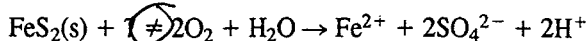
Aerobic Processes

The most important aerobic biological processes in wetlands are iron oxidation and photosynthesis. Both are autotrophic processes in which carbon dioxide is the source of carbon for the organisms concerned. Photosynthesis, carried out by blue-green bacteria, algae, and plants, consumes carbonic acid and bicarbonate and produces hydroxyl ions:



In this case, plants and aquatic organisms are making organic matter by taking up dissolved bicarbonate to produce dissolved oxygen and hydroxide ions (Wetzel, 1983).

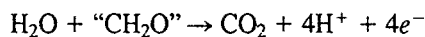
The oxidation of iron pyrite by aerobic autotrophic bacteria of the genus *Thiobacillus* is the cause of acid-mine drainage, as summarized by the following reactions from Stumm and Morgan (1981):



Note that H^+ is produced by the oxidation of bisulfide and by the precipitation of $\text{Fe}(\text{OH})_3$. Manganese oxidation and precipitation also releases H^+ :



Finally, oxidation of organic matter, a half-reaction used by the majority of heterotrophic bacteria, produces H^+ :

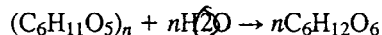


Here, "CH₂O" represents organic matter such as cellulose and other carbohydrates. The reduction potential for the above reaction is lower than that for the formation of H₂ (Stumm and Morgan, 1981). Consequently, organic matter in aquatic environments acts as a strong reducing agent.

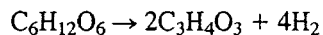
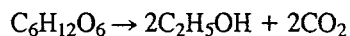
Anaerobic Processes

Under anaerobic conditions in wetlands, five general types of microbial processes are of importance:

1. Hydrolysis of biopolymers by extracellular bacterial enzymes. An example is the hydrolysis of cellulose, the most abundant organic material in plants, to glucose:

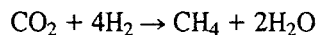


2. Fermentation. Examples are the formation of ethanol and pyruvic acid:

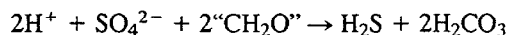


Note that hydrogen is produced in the second reaction. It is a common product of fermentation.

3. Methanogenesis:

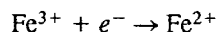


4. Sulfate reduction:



Note that organic matter is used as the reducing agent.

5. Iron reduction:



Again, organic matter could be used as the reducing agent.

Fermentation often produces organic acids, decreasing pH, while sulfate reduction consumes H^+ and increases pH. Methanogenesis also consumes hydrogen ions. Proton-reducing bacteria, which are symbionts with methanogenic bacteria, convert H^+ to H_2 , and this is used by the methanogenic bacteria to reduce CO_2 to CH_4 . In our anaerobic wetland environments, sulfate reduction and methanogenesis proceed together. Because Postgate (1979) reports that the activity of sulfate-reducing bacteria (SRB) is severely limited below pH 5, organic materials in a constructed wetland environment must be chosen so that fermentation does not dominate over sulfate reduction.

Overall Guidelines

Although still not completely understood, the principles outlined above appear to be the predominant removal mechanisms in the treatment of mine drainage and other metal-contaminated waters by constructed wetlands (Hammer, 1989; Wildeman et al., 1993a). In the early 1980s, aerobic removal processes were emphasized and the precipitation of $Fe(OH)_3$ was an important objective (Hammer, 1989; Brodie, 1991). Because precipitation of $Fe(OH)_3$ produces H^+ ions, iron was removed but the pH of the effluent often was around 3. Brodie (1991) has had success with metals treatment using aerobic constructed wetlands as long as the pH of the influent was above 5.5 and carried some alkalinity in the form of dissolved bicarbonate. Around 1987, groups from the U.S. Bureau of Mines (Hedin et al., 1989) and the Colorado School of Mines (Wildeman and Laudon, 1989; Wildeman et al., 1993a) began to investigate the role of anaerobic processes, particularly sulfate reduction, in treating acid-mine drainage.

The microbial guidelines presented above have resulted from these early studies. Application of these guidelines to aerobic wetlands leads to the following four guiding principles for success:

1. Aerobic removal processes are successful when the pH of the effluent water is above 5.5 and dissolved bicarbonate is present.
2. Any practice, such as use of anoxic limestone drains (Brodie et al., 1991), that will raise the pH and add alkalinity should be used.
3. Precipitation of iron and manganese oxyhydroxides is a primary removal process, and other metal contaminants are removed by adsorption onto these precipitates or by precipitating as carbonates.
4. Plants are essential to success because photosynthesis is a primary process for raising pH, adding oxygen to the water, and supplying organic nutrients.

The role of photosynthesis was discussed in the section entitled "Aerobic Processes." At about pH 5.5, significant amounts of bicarbonate can be present in aqueous solution (Stumm and Morgan, 1981), and photosynthesis can occur through uptake of bicarbonate from the water in preference to the uptake of CO_2 from the air. This appears to be why aerobic constructed wetlands require plants and are effective at adding alkalinity when the pH is above 5.5.

Application of the guidelines to anaerobic removal processes is much more direct, because plants can be absent and the system is dominated by microbial processes. The following four practices lead to success:

1. Wetland substrates are formulated so that organic material necessary for metabolism is in high abundance and the wetland soil can provide acid buffering capacity at a pH above 7.
2. Microbial processes that transform strong acids such as H_2SO_4 into weak acids such as H_2S should be promoted.
3. The products of these reactions are used to precipitate metal contaminants as sulfides (CuS , ZnS , PbS , CdS), hydroxides ($Al(OH)_3$, $Cr(OH)_3$), and carbonates ($MnCO_3$).
4. To remain effective, the reactions that consume H^+ must predominate over the reactions that produce H^+ .

In a natural wetland, most water courses across the surface and the anaerobic subsurface remains somewhat isolated. For best application of these guidelines, design of the wetland has to ensure that water goes through the substrate. Hence, the system can look like a plug-flow bioreactor. These passive anaerobic systems have been successful at raising the pH of metal mine drainages from below 3 to above 6 and significantly reducing metal concentrations (Wildeman et al., 1993a). The design of metal-remediation systems using these principles will be the focus of the rest of this chapter.

STAGED DESIGN OF METAL-TREATMENT SYSTEMS

In our studies on treatment of metal-mine drainage by constructed wetlands (Wildeman et al., 1993a), when it was determined that precipitation of metals by sulfide generated from SRB is an important process, it was realized that establishing and maintaining the proper microbial environment in the substrate is the key to success for removal (Wildeman and Updegraff, 1994). If this is the case, then construction of large pilot cells is not necessary to optimize the anaerobic bacterial processes needed for removal (Reynolds et al., 1991).

Consequently, study of wetland processes and design of optimum systems can proceed from laboratory experiments, to bench-scale studies, and then to the design and construction of actual cells. We call this "staged design of wetland systems." Although staged design is best carried out on anaerobic substrates, it has also been used with success on design of aerobic systems. Algal photosynthesizers are excellent generators of oxygen and alkalinity in water, and they can be readily used in laboratory and bench-scale studies of aerobic treatment (Duggan et al., 1992).

Example Laboratory Studies

In early laboratory studies, culture bottle experiments were used for studies on how to establish tests to determine the production of sulfide by bacteria and also to determine what substrate will provide the best initial conditions for growth of SRB

(Reynolds et al., 1991). Recently, laboratory studies have concentrated on the practical aspects of wetland design. In particular, great emphasis is placed on testing local organic and soil materials to determine what mix provides the best environment for sustained SRB activity. Also, a number of studies have been conducted to "prove-in-principle" that treatment of metals and inorganics is possible and to provide an indication of what reduction in concentration is possible. Examples of these studies are described below. Other examples are described in the literature (Wildeman et al., 1994a,b).

Measurement of sulfate reduction activity

In an extensive laboratory study, a series of culture bottles was sealed and incubated at 18°C to determine the activity of SRB and whether metal removal in the laboratory was comparable to that in a demonstration anaerobic reactor (Reynolds et al., 1991). For the laboratory study, 20 g of substrate and 70 mL of mine drainage, whose chemistry is shown in Table 20.1, were sealed into 120-mL serum bottles. The substrate came from an active anaerobic cell from the Big Five Pilot Wetlands in Idaho Springs, Colorado (Wildeman et al., 1993a). On the day of collection, the mine drainage and the effluent from Cell B-Upflow had the chemistry shown in Table 20.1. The results for the metals removal on the first day and after 35 days are also shown in Table 20.1. T20.1

In the baseline bottles, measured 1 day after adding the mine drainage, the pH was significantly higher and metal concentrations were significantly lower than in the mine drainage. As stated in the wetlands guidelines, substrates are formulated to immediately raise the mine drainage pH to neutral conditions. Several processes could have contributed to the immediate removal of metals, including precipitation due to the increase in pH and adsorption onto organic materials (Machemer and Wildeman, 1992). Over the course of 35 days, the pH continued to rise until it was the same as in the effluent from the anaerobic reactor. The concentration of sulfate gradually decreased until, by day 35, sulfate concentration was lower than that in the reactor effluent. At 25 days, the concentration of sulfate matched that in the reactor effluent. Based on this observation, laboratory-scale tests are conducted for at least 4 weeks to simulate conditions in the field. For Fe, the majority was removed by the first day. We believe this is caused by organic adsorption (Machemer and Wildeman, 1992). Then, the Fe concentration continues to decrease until, by day 35, it is at the concentration of the cell

TABLE 20.1
Comparison of pH, Sulfate, and Metal Concentrations in Mine Drainage,
Wetland Output, and Serum Bottles^a

Sample	pH	SO ₄ ²⁻ (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)
Mine drainage	3.0	1720	0.57	39	31	8.6
Reactor effluent	6.7	1460	<0.05	0.64	15.8	0.07
Serum bottles (one-day baseline) ^b	6.1	1680	<0.05	10.5	15.5	0.04
Serum bottles (35 days) ^c	6.7	1240	<0.05	4.51	10.6	0.16

^aAdapted from Reynolds et al. (1991).

^bValues for these samples are the average of four replicates.

^cValues for these samples are the average of three replicates.

effluent. The differences in how SO_4^{2-} and Fe change indicate that more than one process is operating in the treatment of the mine drainage.

Because the serum bottles were sealed, all volatile products were retained. In particular, all retained sulfide species could be titrated and the amount of production gives an estimate of the activity of sulfate reduction. Figure 20.2 shows how that rate of sulfate reduction changes with time. For the first 40 days, this rate was 1.2 $\mu\text{mol sulfide/g substrate/day}$ (Reynolds et al., 1991), and then after 40 days the rate dropped to 0.75 $\mu\text{mol/g/day}$. In design calculations for bench- and pilot-scale reactors, a sulfide production rate of 300 nmol/g/day is used.

Poisoned control bottles were prepared by adding sodium azide until the final concentration of azide was 0.5%. Acid volatile sulfides in these bottles were determined at three times during the course of the experiment, and the results are shown in Figure 20.2. The rate of sulfate reduction in these bottles is negligible compared to those bottles that were not poisoned. This adds to the evidence that bacterial sulfate reduction is indeed responsible for the decrease in sulfate and sulfide precipitation for removal of metals from the mine drainage (Machemer et al., 1993).

Anaerobic removal of cyanide

A certain company was interested in whether cyanide concentrations typical of milling-waste effluents could be treated in an anaerobic reactor or whether the cyanide would kill the SRB (Filas and Wildeman, 1992). The composition of the spent tailings solution is shown in Table 20.3. It contains appreciable free cyanide and also bound CN^- , most likely in the form of Fe and Cu complexes.

To typical culture bottles were added various amounts of substrate, milling efflu-

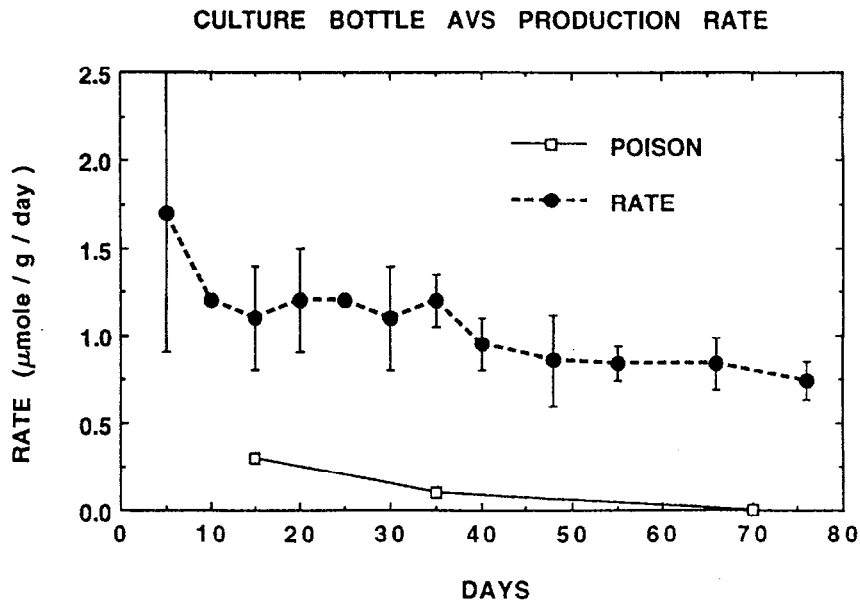


Figure 20.2. Rate of sulfide production in serum bottles and poisoned controls. Error bars represent one standard deviation. Data points without error bars are the average of two samples.

TABLE 20.2
Protocol for the Cyanide Microbiology Experiments Incubated at 27°C

Culture No.	O ₂	Nutrients			Bacterial Inoculation (amt in mL)	Tailings (amt in mL)
		Compost (gm)	Lactate (g/mL)	Sulfate (g/mL)		
5	No	10	None	None	10	140
7	Yes	10	None	None	10	140
8	Yes	10	None	None	10	140
11	Yes	10	6.8	None	10	135
12	Yes	10	6.8	None	10	135
13	No	10	6.8	2.1	None	140
17	No	10	None	None	10	135
18	No	30	None	None	10	125
19	Yes	20	6.8	None	10	125

ent, and inoculum. The laboratory protocol is summarized in Table 20.2. For those bottles containing 10 g of substrate, it was hypothesized that this was a minimal amount of soil necessary to provide organic nutrients for the SRB. To test this, extra amounts of lactate and sulfate were added to some bottles. Also there was concern that the concentration of cyanide would be toxic to the bacteria, so, for three hours, oxygen was bubbled through a subsample of the milling effluent to oxidize cyanide and lower the pH. A group of culture bottles was also prepared using this oxygenated milling effluent (labeled "yes" in the O₂ column of Table 20.2). The bottles were incubated for 50 days and then the solutions in the bottles were analyzed. The analytical results are shown in Table 20.3.

From the results in Table 20.3, it can be seen that cyanide decreased in all the bottles. A decrease in the concentration of sulfate is a good measure of the activity of SRB. In most bottles there was little or no decrease. However, in bottle 11 there was appreciable decrease in the sulfate concentration caused by the activity of SRB. In this bottle there was also a great decrease in total cyanide. It appears that, given the proper conditions, cyanide degradation as well as sulfate reduction can occur in the anaero-

TABLE 20.3
Results of Analyses of the Solutions from Cultures That Showed Decreased Concentrations of Cyanide^a

Culture No.	Fe	Cu	Sulfate	Total Cyanide	Free Cyanide	pH
Original Solution	470	78	298	330	24	9.0
5	85	98	310	57	60	8.9
7	150	90	320	56	49	8.8
8	8.2	9	570	56	54	8.1
11	21	10.4	<5	2.3	<5	7.3
12	5.4	6.0	460	2.2	<5	7.3
13	65	142	4470	120	72	8.4
17	120	38	360	56	27	8.6
18	60	87	320	2.0	<5	8.4
19	23	58	790	57	42	7.0

^aAll concentrations are in milligrams per liter.

bic zone of a wetland substrate. The cyanide disappearance could have occurred by a number of processes, including:

- (i) Volatilization of cyanide by lowering the solution pH
- (ii) Metabolic use of the cyanide by microbes
- (iii) Nonmetabolic degradation of cyanide to cyanate

It is probable that all three are occurring since the inoculum is a consortium of bacteria (Reynolds et al., 1991) and the substrate is complex organic material (Wildeman et al., 1993a). In any event, the laboratory experiment proved in principle that cyanide disappearance, sulfate reduction, and heavy-metal removal are all simultaneously possible in the anaerobic zone of a constructed wetland.

Aerobic removal of manganese

Manganese, a common contaminant in mine drainages, is difficult to remove from solution due to the high pH required to form insoluble manganese(II) hydroxides, carbonates, and sulfides (Stumm and Morgan, 1981; Watzlaf and Casson, 1990). In addition, although MnO_2 should form at a pH as low as 4, the kinetics of oxidation of Mn(II) to Mn(IV) are slow at a pH below 8 (Stumm and Morgan, 1981; Wehrli and Stumm, 1989). As can be seen in Table 20.1 for the Big Five system, even though the pH of the effluent has risen to above 6.7, manganese is still only reduced by about 50%. Thus, a polishing stage system utilizing an alternate microbial process seemed necessary to remove high concentrations of manganese.

A laboratory study that utilized the principles of microbial ecology was conducted to determine an optimum system that would remove manganese from waters where the pH is above 6. Having some alkalinity in the water allowed aerobic experiments to be conducted. A mixture of water, soil, and scum was taken from various ecosystems listed in Table 20.4, including a mining environment where MnO_2 was forming. Ap-

20.4

TABLE 20.4
Individual Inocula Used for Manganese Removal Studies

Ecosystem Sample and Ecosystem	pH	Mn Concentration (mg/L)	
		Initial	Final
Algae growing in acid-mine drainage	3	220	310
Brown precipitate in effluent pipe at Big Five wetland	3	220	392
Black mud in effluent of a wastewater treatment plant	8	190	147
Black manganese oxide (?) solid in acid mine drainage stream	6.5	200	109
Pond scum from freshwater stream	7.5	190	<0.3

proximately 75 mL of each sample was mixed with a Big Five mine drainage adjusted to pH = 7 (Table 20.1) in Erlenmeyer flasks exposed to the atmosphere. To the flasks were added 10 mL of a Mn(II) solution sufficiently concentrated to increase the concentration in the flasks to approximately 200 mg Mn/L. The flasks were incubated in sunlight at laboratory temperatures for 40 days.

The removal results are quite dramatic. Only the pond scum system containing green and blue-green algae (predominantly *Cladophora*) was able to reduce manganese below 100 mg/L, and dissolved Mn was undetectable in this flask. Later studies have shown that the dissolved oxygen and hydroxide ions produced from photosynthesis by the algae are responsible for catalyzing Mn oxidation and precipitation of MnO_2 . Adsorption and metabolic uptake of Mn by the algae are minor removal processes (Dugan and Wildeman, 1996). The study confirms the importance of photosynthesis in aerobic wetland systems and establishes the use of algae and soil bacteria for use in laboratory studies of aerobic wetland processes.

Example Bench-Scale Studies

Anaerobic removal of heavy metals

For anaerobic bench-scale studies, plastic garbage cans were used to conduct experiments to provide answers necessary for the design of a subsurface cell (Bolis et al., 1991). Typical design parameters include the optimum loading factor, substrate, cell configuration, and the hydraulic conductivity of the substrate. A recent study used Big Five mine drainage to determine whether an anaerobic system could raise the pH to above 7 where it was found that $MnCO_3$ would precipitate (Bolis et al., 1991, 1992).

Four reactors using two types of substrate were used. Two reactors contained an organic substrate composed of 75% composted cow manure and 25% planter soil by volume. This mix had been found to be effective in a previous bench-scale reactor study (Bolis et al., 1991). To this was added about 10% by weight of inoculum from currently active anaerobic cells at the Big Five pilot wetland. The second set of reactors contained a primarily inorganic substrate composed of approximately 77% by volume limestone rock, 14% alfalfa, and 9% of the same inoculum used in the first reactors. For both sets of reactors, one was soaked with mine drainage for one week prior to operation and the other was left dry. The flow rate was maintained at approximately 10 mL/min. This value was determined by using the value of 0.3 mol of sulfide generated per cubic meter of substrate per day, evaluating the concentration of heavy metals in the Big Five drainage (Table 20.1), and limiting the flow such that the amount of heavy metals flowing through the system did not exceed the amount of sulfide generated by the substrate (Machemer et al., 1993; Reynolds et al., 1991; Wildeman et al., 1993a). The reactors were run from July through November.

Figure 20.3 shows the pH and the concentration ratios of SO_4^{2-} , Fe, and Mn in the reactor effluent to that in the original mine drainage. For the manure reactors, pH behaved as expected, maintaining a value above 7 for most of the experiment but dropping toward the end when the ambient temperature dropped significantly. For the limestone reactors, the pH remained below 6 for over 30 days. During this time, the reactors were emitting nasty smells indicative of low-molecular-weight organic acids. Apparently, the soaked alfalfa was undergoing anaerobic fermentation. Analysis of the sulfate concentration ratios gives a good measure of how strongly sulfate reduction

F20.3

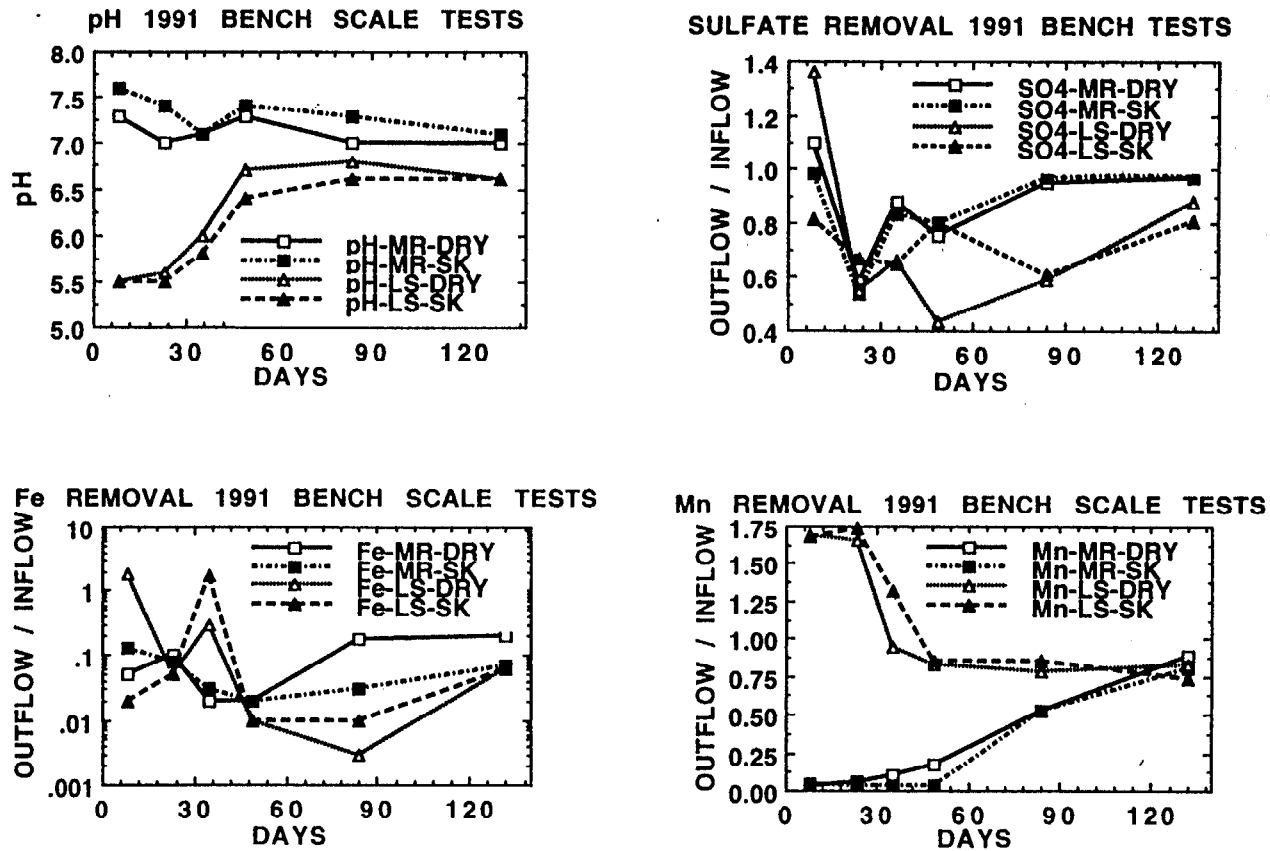


Figure 20.3. pH, sulfate removal, iron removal, and manganese removal versus time for the anaerobic bench-scale study. Removal is the ratio of concentration in reactor outflow over concentration in the mine drainage.

outflow over

was occurring. For all systems in the first month, sulfate was significantly reduced. This is because the low-molecular-weight organic acids that are the primary nutrients for SRB are readily available. For the manure in the later stages of the experiment, sulfate reduction is much less apparent. We assume this is because all the readily available nutrients for the SRBs have been used up and further nutrients are produced by the breakdown of complex organic material. For the alfalfa, sulfate reduction is still active in the later stages. Perhaps this implies that breakdown of organic material is more facile in the alfalfa system.

Copper and zinc were completely removed throughout the entire course of the study. The removal patterns for Fe and Mn are more instructive in terms of the processes occurring in the reactors. For the manure reactors, Fe removal was excellent in the first half of the experiment. Figure 20.3 shows Fe concentration ratios on a log scale so the smaller and larger ratios can be more easily compared. In these systems, iron precipitates as FeS (Machemer et al., 1993), which is somewhat soluble. Consequently, as sulfate reduction decreases, the concentration of Fe in the effluent increases. For the limestone reactors in the early stages of the experiment, Fe is released, probably being dissolved from the limestone. In the later stages of the experiment, the limestone-alfalfa reactors are more efficient at retaining Fe than the manure systems. This is attributed to better sulfate reduction. For Mn, good removal only occurs when the pH is above 7. This is attributed to the formation of $MnCO_3$. Because it appears that continuous maintenance of reactor pH above 7 is difficult, we consider that consistent anaerobic removal of Mn is speculative.

Aerobic removal of manganese

The manganese removal results using algae were encouraging enough that bench-scale studies were conducted (Duggan et al., 1992). In this case, the reservoirs were constructed from small plastic wading pools, approximately 1.1 m in diameter. Each of the two pools initially contained 97 L of effluent from the Big Five Wetland and 5 L of scum comprised primarily of *Cladophora* from a local pond. The Big Five cell effluent used here contained approximately 32 mg/L of manganese and had a pH of 5.8. The only difference between the two reservoirs was that one reservoir also contained 12 kg of limestone. This reservoir is referred to as "reservoir LS," and the reservoir that did not contain limestone is denoted "reservoir NoLS." The reservoirs were placed outside to have full exposure to the environment.

The four-month duration of the experiment was from August to December, during which the reservoirs were exposed to a wide range of weather conditions. The reservoirs were static for the first two months of the experiment, with water being added occasionally to account for water loss due to evaporation. The weather was typically warm and sunny during this portion of the experiment. A flow system was installed during the last two months of the experiment to determine approximate loading and removal rates. This was accomplished using a peristaltic pump to monitor flow from a feed tank into the reservoirs, along with an outlet tube 7 cm above the bottom of each pool. The weather during this portion of the experiment was typically cold and snowy, and the reservoirs froze several times. A high-concentration manganese solution was twice added to the reservoirs during the study period, once during the static portion and once during the flow portion of the experiment. The purpose of these additions was to study the effect of high Mn concentrations on the effectiveness of the

algae in Mn removal. This 100-mg/L manganese solution was prepared using manganese sulfate and deionized water.

For reservoir LS, the concentration of manganese and the pH over the static portion of the study is shown in Figure 20.4. As for the anaerobic system, there is a strong correlation between pH and Mn removal. In this case it is for a different reason. Algal photosynthesis raises the pH to values where oxidation of Mn(II) is rapid (Wehrl and Stumm, 1989) and provides the dissolved oxygen for the oxidation. Addition of

F20.4

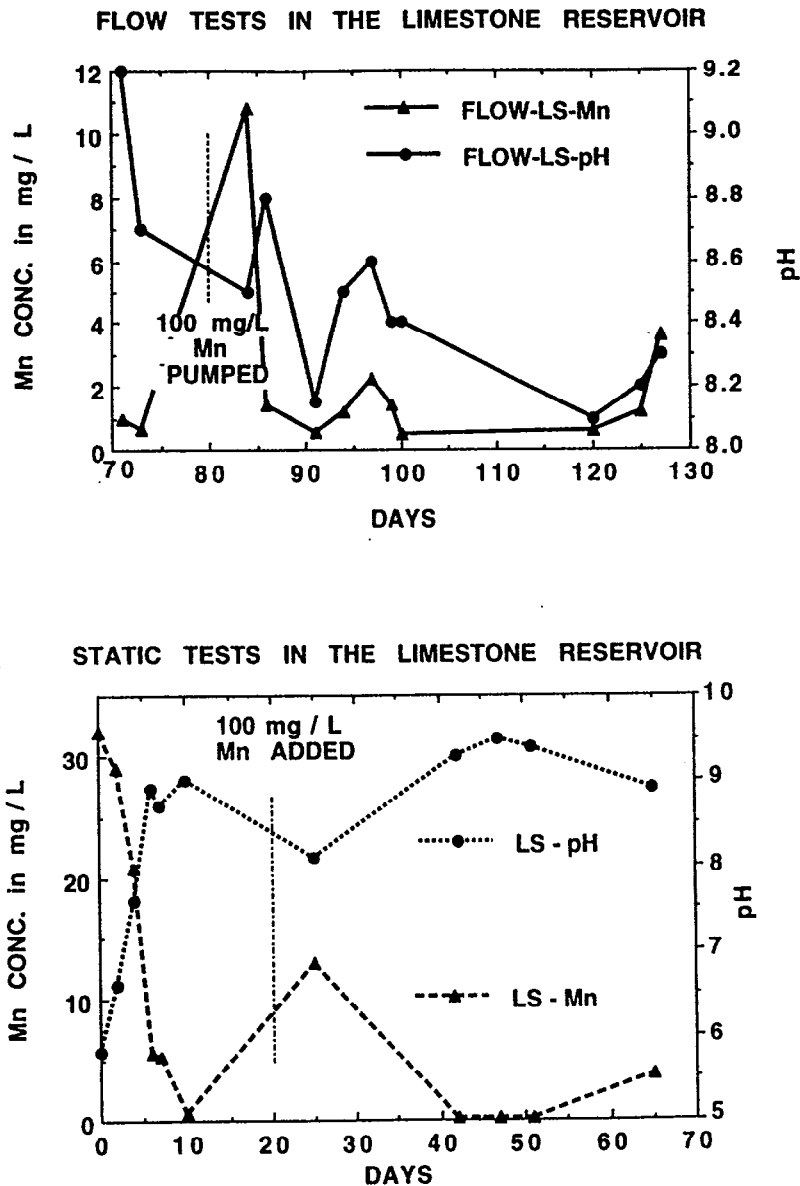


Figure 20.4. Manganese and pH results of the aerobic, static and flow bench-scale study for the limestone reservoir (LS).

the limestone improves removal. This is not due to limestone dissolution because, at the near-neutral pHs in the reservoirs, dissolution is slow. It is more likely that the rock provides surfaces for adsorption of manganese oxides and these sites provide autocatalysis for further Mn oxidation (Stumm and Morgan, 1981). The 40 L of 100-mg/L manganese solution had a pH of 4.9. Its addition put dual stresses of lower pH as well as high Mn concentrations on the system. Recovery of the system occurred within a few days.

During the static portion of the experiment, the algal biomass had grown extensively and appeared healthy, and black precipitates could be seen in the algal mat. Therefore, a flow system was designed to simulate a possible pilot scale wetland and determine the efficiency of the reservoirs at different flow rates. The pump system was installed in mid-October with flow rates varying between 3 and 5 mL/min. During the course of the experiment, the Big Five cell effluent in the feed tank was replaced with the same 100 mg/L manganese solution as was used in the static experiment and was pumped into the reservoirs for 5 days.

Outflow manganese concentrations and pH for the LS reservoir during the flow portion of the study are shown in Figure 20.4. Removal in the NoLS reservoir was less efficient (Duggan et al., 1992). Both systems recovered from the addition of the 100-mg/L Mn solution. This tolerance to high manganese concentrations is important because Mn concentrations as low as 10–20 mM have been shown to greatly inhibit manganese oxidizing microbes (Nealson et al., 1988).

The severe weather conditions present during much of the pump flow study had a visible effect on the health of the biomass. During the static experiment, the thick algal mat was bright green and floated on the surface due to the large number of oxygen gas bubbles produced during photosynthesis. Throughout the pump flow experiment, the algae lost much of its bright green color and most of the algae sank below the water surface. Gas bubbles were still observed during the sunlight hours; this indicated that photosynthesis was occurring, but to a much lesser extent than during the warmer, sunnier months. At the completion of the experiment in mid-December, the reservoirs had frozen several times and the algal biomass did not appear very healthy. The fact that the reservoirs performed so well even under these adverse conditions implies that other removal processes besides photosynthesis are operating. Analyses of the resulting solids points to adsorption of Mn on the limestone as the next most important process (Duggan and Wildeman, 1996). The results from the bench-scale studies have been used to construct a pilot-scale algal pond that has shown to be very successful removal (Wildeman et al., 1993c).

for manganese

Example Pilot-Scale Studies

Big five pilot wetlands

Pilot systems are built to test out new processes with the anticipation that configurations may change if the first designs prove unsatisfactory. The Big Five pilot wetland was an excellent example of this purpose (Wildeman et al., 1993a). The initial cell configuration was primarily a surface flow system. The final configuration that produced the best results was a reactor bed configuration. In between these two configurations, a horizontal plug-flow system was tried and found to be inadequate. Two identical reactor beds were built: one to run upflow, and the other downflow (Machemer

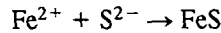
and Wildeman, 1992; Machemer et al., 1993; Wildeman et al., 1993a). The cells were filled with mushroom compost to approximately 3 m × 3 m × 1 m deep. The system was started in September 1989. For the first six months, the flow through the system was 3–4 L/min. After that, a flow was maintained at 1 L/min for the rest of the two-year operation.

20.5

The two-year removal results for the upflow cell are shown in Figure 20.5. The results for the first six months were poor, and this is shown by the erratic pattern in Figure 20.5. After that, complete removal of Cu and almost complete removal of Zn is maintained. Removal of Fe and reduction of Mn and SO₄²⁻ vary with the seasons. At about six months, conditions had been established which eventually led to the understanding necessary to establish the principles given in the section entitled "Overall Guidelines" for the operation of an anaerobic reactor.

A key factor for reactors that depend upon sulfate reduction is the maintenance of an optimum microenvironment for sulfate-reducers. Besides adequate sulfate concentrations, the most important environmental conditions are reducing conditions and a pH of around 7 (Postgate, 1979). Because the wetland cell is receiving mine drainage of pH below 3 and Eh of above 700 mV (Wildeman et al., 1993a), the water can easily overwhelm the microenvironment established by the anaerobic bacteria. This leads to the limiting reactant concept for determining how much water can be treated, and it is our primary guide for loading anaerobic reactors.

Consider the following precipitation reaction, where the sulfide is generated within the reactor substrate and the Fe is delivered to the system by the mine drainage:



At high flow rates of mine drainage through the substrate, sulfide will be the limiting reactant, the microbial environment will be under stress to produce more sulfide, the

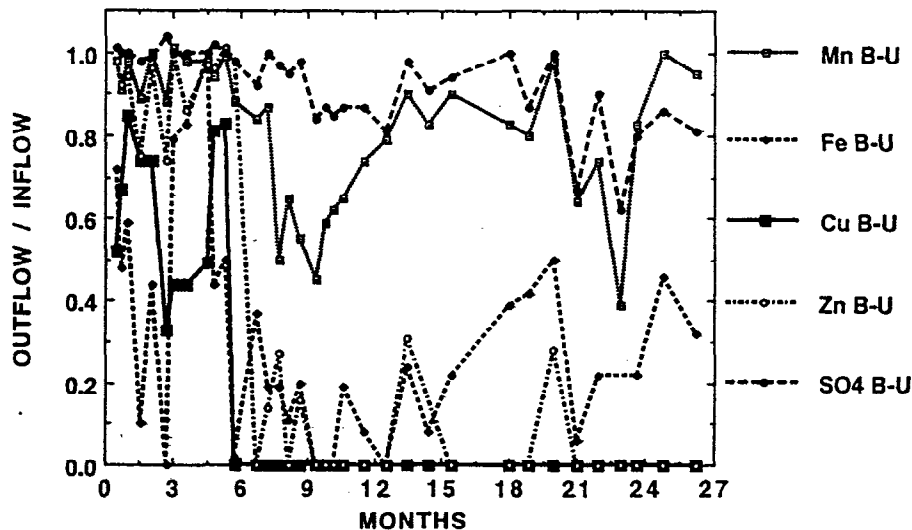


Figure 20.5. Removal (ratio of concentration in reactor outflow over concentration in the mine drainage) over two years for cell B upflow at the Big Five pilot wetland. The system was started in September 1989.

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pH of the microbial environment will drop, and removal will be inconsistent. At low flow rates of mine drainage through the substrate, iron will be the limiting reactant, the excess sulfide will ensure a reducing environment and a pH near 7, the microbial population will remain healthy, and removal of the metal contaminants will be consistent and complete. Using this idea, loading factors should be set such that the heavy-metal contaminants are always the limiting reactants. The goal then is to determine how much sulfide a colony of sulfate-reducing bacteria can produce per cubic centimeter of substrate per day. As previously described, the measurement of sulfate reduction activity is critical to this estimation process.

The results shown in Figure 20.2 show that between 750 and 1200 nmol of sulfide were generated per gram of substrate per day. Other studies (Hammack and Hedin, 1989; Hedin et al., 1989; Dvorak et al., 1991) suggest that a reasonable figure for sulfide generation in a wetland is 300 nmol of sulfide per cubic centimeter of substrate per day. This number, the volume of the wetland cell, and the metals concentrations in the mine drainage are used to set the flow of mine drainage through the wetland cell. This is how the flow of 1 L/min was determined for the flow through Cell B-Up-flow. In Figure 20.5, the results of applying this limiting reactant guideline are obvious.

PROSPECTS FOR THE FUTURE

Rather than providing the usual summary, it may be more useful to speculate on the future of research designed to improve the performance and prospects for constructed wetland treatment systems. The first issue is how to get off the applied research and development track and into the study of fundamentals. Most of the results described above were from applied projects. Any fundamental questions had to be addressed as side projects. It appears that the treatment systems are working even though there are numerous aquatic chemistry and geomicrobiology questions that have been left unanswered. Because the aquatic chemistry and microbiology have been readily transferable, that has sufficed. However, to develop greater loading capacities and tolerances for contaminants, scientific investigations are imperative. Two questions are most pressing:

1. Within each removal process, there is a rate-limiting step that controls how fast treatment can be accomplished. For the removal processes that have been developed, determining this rate-limiting step more specifically would greatly help in devising design modifications that would speed the treatment processes. Because the kinetics involve abiotic and biotic components, investigations are necessarily interdisciplinary.
2. Most of the precipitates formed are amorphous solids (Machemer et al., 1993; Wildeman et al., 1993a), which makes them almost impossible to completely characterize scientifically. This characteristic also makes the precipitates quite reactive, which is generally detrimental from a technical design point of view. Research into how to form crystalline precipitates and into the nature of the precipitates formed is therefore an important research need. For example, amorphous FeS rather than pyrite is formed in anaerobic reactors (Machemer et al.,

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1993). The questions as to why FeS forms and whether pyrite will eventually form are both technically important and scientifically intriguing.

To this point in time, only metals with a comparatively simple aqueous chemistry have been treated. Contaminants with more complex aqueous chemistries may prove to be more challenging. Two important and currently interesting examples are As and Se. The multiple oxidation states exhibited by both of these elements makes the questions associated with the design of a system that provides long-term removal quite complex.

Besides the consideration of metal or metalloid removal, wetlands have also been used to a limited extent to remove organic contaminants from wastewater flows (Hammer, 1989). Since it is almost certain that this type of treatment will be increasingly important in the future, increased efforts to understand organic removal processes in wetlands is important. There are two general types of questions important in consideration of organic processes in wetlands:

1. If there are spills of organics into natural wetlands, what stresses will be put on the ecosystem and what can be done to ensure that the organics will be immobilized and/or destroyed?
2. What are the possibilities for using constructed wetlands to treat various types of organic contaminants and mixed wastes?

Research directed toward answering these questions is virtually nonexistent at the present time, and, therefore these questions represent fertile areas for future research considerations.

The topic of this review has been *passive* treatment of metals using bioreactors. Such systems are designed and constructed with great margins of safety so that maintenance can be kept to a minimum. Nevertheless, the same principles can be applied to an active system that is designed to provide optimum treatment at the price of greater maintenance and control. If active treatment systems for metals removal are investigated, then the questions posed above concerning determination of the rate-limiting step and how it can be accelerated become quite important.

Research in this field has been rewarding because of the close link between scientific principles and their application. In addition, the area is highly interdisciplinary and progress critically depends on cooperative problem solving. It is certain that this field will grow, and it is hoped that 10 years from now the ideas developed in this review will be appear to be rudimentary.

ACKNOWLEDGMENTS

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SOLUBILITY OF Fe (III) AND Al IN AMD BY MODELLING AND EXPERIMENT¹

by

Kevin G. Mitchell², Thomas R. Wildeman³

Abstract: Studies of Fe(III) and Al species in acid mine drainage (AMD) alone and in contact with limestone were conducted by MINTEQA2 modelling and by experiments. The objectives of these studies were to: 1) determine at what pH Fe(III) and Al would be in solution in AMD such that the water would be harmful to an anoxic limestone drain (ALD), and 2) evaluate the theoretical limits to the amount of alkalinity that could be generated by an ALD. Using Fe(OH)₃ as the primary species and the standard values for MINTEQA2, Fe(III) precipitates at pH 2.90 when the concentration is over 453 mg/L. Al precipitates at a pH of 4.00 when the concentration is over 108 mg/L. Experiments found that over 90 % of Fe(III) and 45 % of Al were precipitated at these pH's. Experimental verification of Fe(III) concentrations of pH's from 2.90 to 4.0 found that modelling agreed with experiment when ferrihydrite is the primary solid and the log K_{sp} (solubility product) is -38.9. For Al, gibbsite would be the primary solid and log K_{sp} is -34.1. For AMD in contact with CaCO₃ when CO₂ is conserved, final alkalinity is higher when mineral acidity is higher even though pH of the final solution is lower. This modelling result was confirmed by experiment. Higher mineral acidity causes generation of more CO₂ that reacts with CaCO₃ to generate more dissolved HCO₃⁻.

Additional Key Words: Anoxic Limestone Drain, Mineral Acidity, Alkalinity

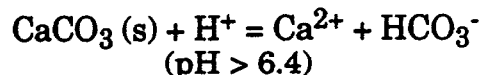
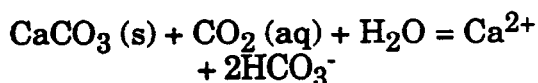
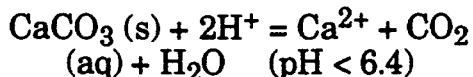
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²Radian Corporation, 1093 Commerce Park Dr., Suite 100, Oak Ridge, TN, 615-483-9870.

³Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401, 303-273-3642.

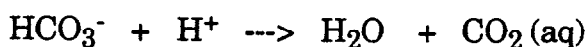
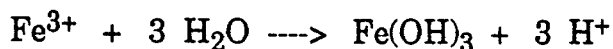
Introduction

Anoxic Limestone Drains (ALD) are an important component in the arsenal of methods that can be used to passively treat acid mine drainage (AMD) (Brodie, et al., 1991; Nairn, Hedin, and Watzlaf, 1991). The function of an ALD is to add alkalinity to the water through the dissolution of calcium carbonate. The chemical reactions that govern this dissolution are:

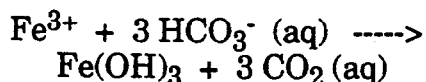


Alkalinity is produced in the form of HCO₃⁻. Below a pH of 6.4, aqueous CO₂ is the primary carbonate species, while above pH of 6.4 HCO₃⁻ becomes the primary species. An oxidation pond is placed after the ALD to oxidize Fe(II) to Fe(III) and use the alkalinity generated to buffer the H⁺ acidity generated

during Fe(OH)₃ precipitation. The step-wise reactions are:



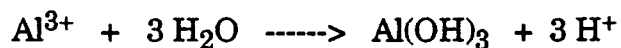
This gives an overall net reaction of:



In this paper, Fe(II), Fe(III), and Al(III) are used to designate all dissolved species of the metal. For example, Fe(III) could include dissolved Fe³⁺, Fe(OH)²⁺, and Fe(OH)₂⁺.

Early in the development of ALD's it was found that dissolved Fe(III) and Al(III) impaired the function of an ALD by armoring the limestone with hydroxide precipitates. This restricted the dissolution of limestone (Brodie, et al., 1991). In addition, buildup of hydroxide precipitates caused ALD's to plug (Watzlaf et al. 1994). Brodie and others (1991) suggested 10 mg/L of Al(III) and 1.0 mg/L of Fe(III) as the maximum amount of Al and Fe in the AMD flowing into an ALD. Hedin and Nairn (1992) advised that if the concentration of Al(III) and Fe(III) exceeded 1.0 mg/L that performance could be compromised. In the latest USBM guidelines on passive treatment, Hedin, Nairn, and Kleinmann (1994) placed the maximum concentrations of Al(III) and Fe(III) that could be tolerated within an ALD at 1.0 mg/L.

Both Al(III) and Fe(III) cause this armoring because they will react with water even in fairly acidic solution to form hydroxides. The reaction for Al is:



For Fe(III), hydrolysis occurs at pH's between 2.75 and 3.25; for Al(III), at pH's between 4.0 and 4.5.

Because the concentrations of

Al(III) and Fe(III) are so critical to determining whether an ALD can be used for treatment, the first objective of this study was to determine what concentrations of these metals were predicted by an equilibrium modelling program such as MINTEQA2 (Felmy, Girvin, and Jenne 1983, Allison, et al., 1991). The second objective was to determine whether the concentrations predicted by MINTEQA2 modelling were confirmed by Fe(III) and Al(III) solutions in the laboratory.

In addition to determining Al and Fe concentrations in AMD, another objective was to determine the maximum amount of alkalinity that can be generated by an ALD. Hedin, Watzlaf, and Nairn (1994) noted significant differences between the alkalinity in two ALD systems that received water of very similar quality. Also, Watzlaf and Hedin (1993) had developed a method for predicting the alkalinity that could be generated in an ALD using cubitainers. The same methods of modelling confirmed by laboratory experiments were used to determine the pH and alkalinity that could be theoretically generated when limestone was brought into contact with various acidic solutions containing Al(III) and Fe(III).

This paper reports on the results of modelling and laboratory studies that were performed on Al(III) and Fe(III) solutions and these solutions in contact with CaCO₃.

Experimental Methods

For the MINTEQA2 modelling exercises, the equilibrium pH was set at various acidic values, Al(III) or Fe(III) was added at various concentrations at the set pH to determine the minimum concentration that must be present for precipitates to form. Sulfate was used to balance charges, and no other ions were entered. For Fe, ferrihydrite (Fe(OH)₃) with log K_{sp} (solubility product) of -37.1 (with

respect to Fe^{3+}) was entered as the possible solid. For Al, crystalline gibbsite ($\text{Al}(\text{OH})_3$) with log Ksp of -33.2 (with respect to Al^{3+}) was entered as the possible solid. In separate runs, amorphous $\text{Al}(\text{OH})_3$ with log Ksp of -31.6 was entered as the possible solid.

For modelling the interaction of CaCO_3 with acidic solutions, CaCO_3 was set as an infinite solid and the above hydroxide precipitates were set as possible solids. Initial pH and Fe(III) or Al(III) concentrations were set, and the system was allowed to come to a new equilibrium. In the calculation, CO_2 partial pressure was allowed to exceed the atmospheric value of $10^{-3.5}$. This is the case in actual ALD's where attempts are made to retain the CO_2 that is generated (Brodie, et al., 1991; Hedin, Watzlaf, and Nairn, 1994). In all cases, 100 % of the Al and Fe precipitated as hydroxides. At the new equilibrium pH, the alkalinity was calculated from the concentration of dissolved HCO_3^- .

In the laboratory experiments where the precipitation curves for Al(III) and Fe(III) were determined, solution concentrations from 1 to 1000 mg/L of the cation were used. Ferric ammonium sulfate and hydrated aluminum sulfates were used to make the stock solutions. The pH of the solution was set using NaOH and H_2SO_4 . Aliquots of the solution were taken at 24, 72, and 96 hours and the pH of the solution was readjusted to the initial value after the first two aliquots were taken. The aliquots were filtered through 0.45 micrometer filters. Fe concentration was determined by flame atomic absorption and aluminum was determined colorimetrically using aluminon reagent.

In the limestone experiments, 3.8 liter collapsible, low-density polyethylene cubitainers were used in a configuration similar to that of Watzlaf and Hedin (1993). A quantity of 4.0 kg of washed limestone of

greater than 90 % CaCO_3 in quality, of 0.3 to 1.0 cm in diameter was added to the cubitainer. Approximately 2 liters of Al(III) and Fe(III) solutions, whose pH's had been set, were added until the cubitainer overflowed and no air was present. At times of 3, 6, 12, 24, and 48 hours, aliquots of 20 mL were removed by squeezing the cubitainer. For each aliquot, alkalinity and pH were measured, then the sample was filtered and acidified and Fe and Al concentrations were determined.

Further details on the modelling and laboratory studies can be found in Mitchell (1994).

Results of the Precipitation and Limestone Equilibration Studies

The modelling results compared with the laboratory-determined, saturation concentrations of Fe(III) and Al(III) are shown in Figures 1 and 2 respectively. The modelling runs for iron were quite surprising because, out to a pH of 4.0, Fe(III) was still in solution at concentrations above 1.0 mg/L. Based on field experiences in Colorado, the rule of thumb we use is that Fe(III) should not be in solution beyond a pH of 3. The rule of thumb was confirmed in the laboratory studies. In experiments where the pH was set to approximately 3.5, the Fe(III) concentrations averaged 0.10 mg/L. In experiments where the pH ranged from 2.99 to 3.01 the concentration of Fe(III) ranged from 1.3 to 4.2 mg/L. The difference between the experimental and modelling results is probably due to the inclusion of Fe(III) complexes, such as $\text{Fe}(\text{OH})_2^+$, in the model.

For aluminum, the experimental results generally followed the modelling concentrations when Al(III) is in equilibrium with crystalline gibbsite. In experiments where the pH was set to approximately 4.0, the Al concentrations ranged from 19 to 46 mg/L. In experiments

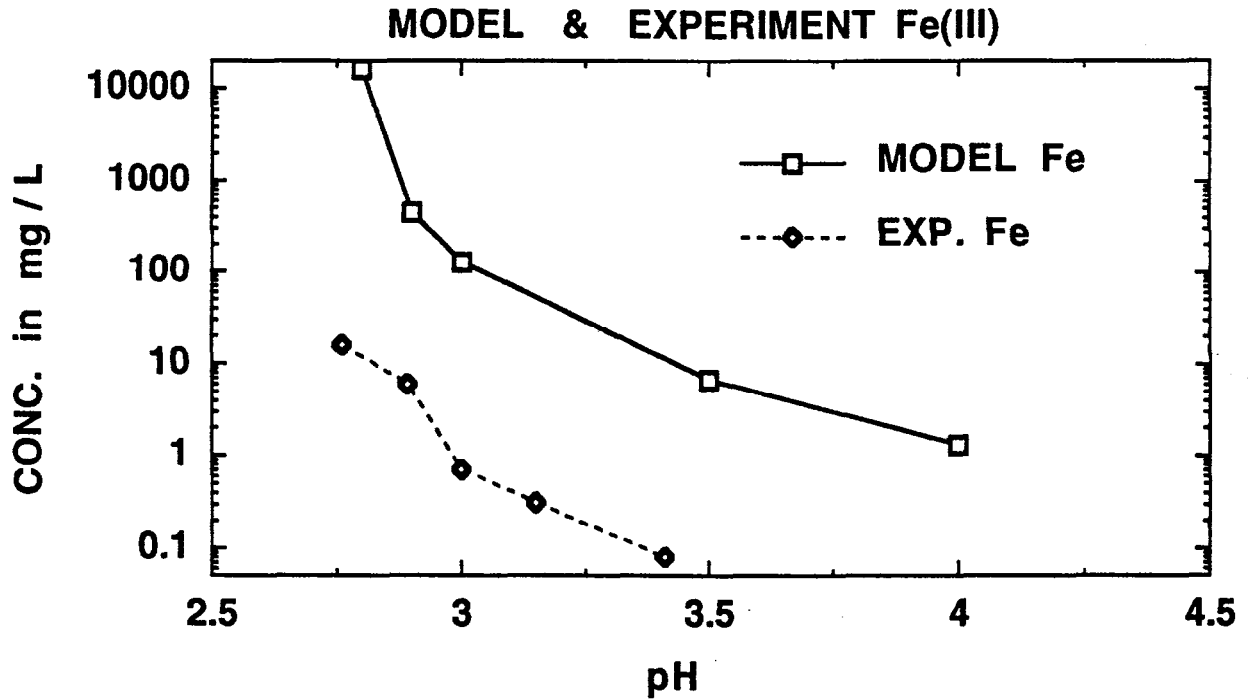


Figure 1. Model and experiment concentrations of Fe(III) in equilibrium with ferric solids at acidic pH values.

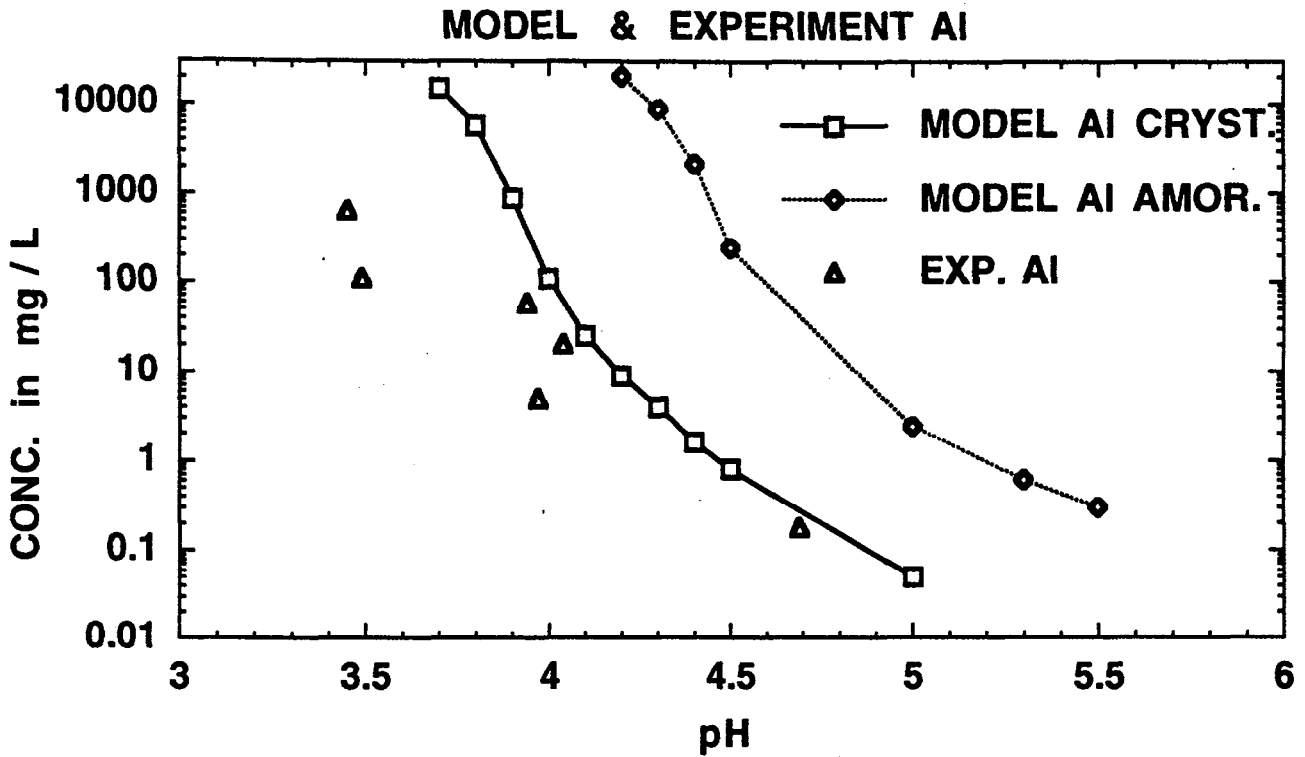


Figure 2. Model and experiment concentrations of Al(III) in equilibrium with aluminum solids at acidic pH.

Table 1. Modelling and laboratory results of limestone equilibrated with solutions of Fe(III) and Al(III) at various pH values. Alkalinity is in units of mg CaCO₃ / L. Laboratory results were after 48 hours of reaction.

Initial pH	Initial Fe(III)	Initial Al	Modelling Results			Laboratory Results	
			Final pH	Final Alkalinity	Log P (CO ₂)	Final pH	Final Alkalinity
2.9	50.0	0.0	7.16	152	-1.94	7.5	131
2.9	50.0	0.0	7.16	152	-1.94	7.5	132
2.9	100	0.0	6.87	213	-1.48	7.35	160
2.9	0.0	0.0	7.84	58	-4.41	7.55	87
4.0	0.0	50	6.93	190	-1.58	7.30	173
4.0	0.0	100	6.57	270	-1.07	7.30	173
3.5	1.0	100	6.57	277	-2.56	7.04	187
3.5	5.0	400	6.02	500	-1.78	6.66	280
3.5	5.0	400	6.02	500	-1.78	6.57	288

where the pH was set to approximately 4.7, the concentration of Al ranged from 0.12 to 0.27 mg/L.

In Table 1, the modelling and laboratory results of limestone equilibrated with waters containing various concentrations of Al(III), Fe (III), and H⁺ are presented. In Figure 3, the experiment and model pH's are compared. In Figure 4, the experiment and model alkalinities are compared.

The modelling results show that when CO₂ gas is conserved, it indeed does exceed the atmospheric value of 10^{-3.5}. In turn, this does indeed increase the alkalinity. For the laboratory samples, except for the acid solution with no Fe(III) and Al(III), the final alkalinity is lower and the pH higher than the model predictions. In Table 1, the final experimental values of the alkalinity taken after 48 hours are given. In systems with high mineral acidity, the excess CO₂ gas far exceeds the atmospheric value. In experiments with 100 and 400 mg /L of Al(III) where there was excess CO₂, the alkalinity peaked at between 12 and 24 hours and then consistently decreased. The maximum values for these experiments are also

plotted in Figure 4.

Discussion

For the precipitation experiments, additional modelling was performed to test the possibility that phases other than ferrihydrite and gibbsite were controlling the Fe(III) and Al(III) concentrations. For Fe, maghemite (Fe₂O₃) gave the best fit. However, this is an unrealistic phase to form in a near surface environment. Use of lepidocrocite (FeOOH) caused the precipitation of too much iron, and use of hydrogen jarosite (HFe(SO₄)₂(OH)₆) caused too much Fe(III) precipitation at low pH's and not enough at high pH's. For Al, diaspore (AlOOH) and jurbanite (AlSO₄) caused the precipitation of too much aluminum. When boehmite (AlOOH) and basaluminite (Al₄(OH)₁₀SO₄) were tried, not enough aluminum precipitated. In the study of Butte, Montana Berkeley Pit water, Davis and Ashenberg (1989) also found that the AMD was supersaturated with respect to jurbanite. Apparently, precipitation of jurbanite is kinetically hindered.

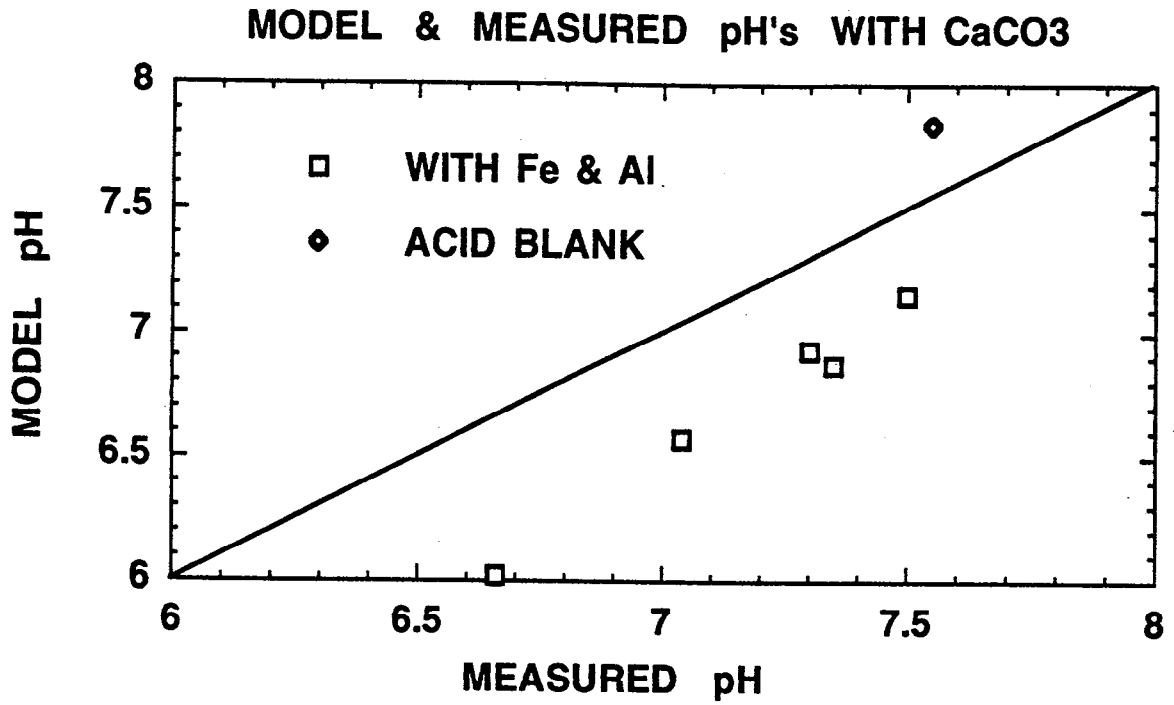
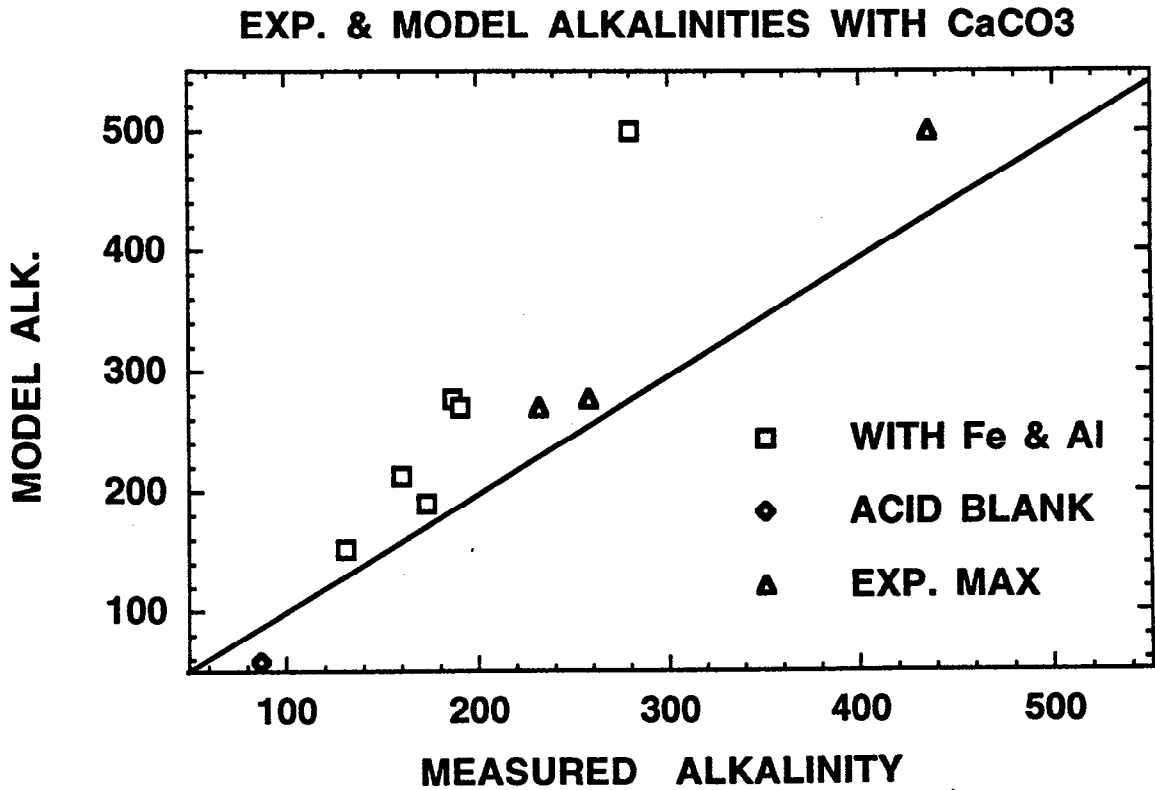


Figure 3. Model and experiment pH values from the reaction of acidic solutions of Fe(III) and Al(III) equilibrated with CaCO₃. In the modelling and experiments, the CO₂ generated was retained.



and Al(III) equilibrated with CaCO₃. In the modelling and experiments, the CO₂ generated was retained. The experimental maxima occurred between 12 and 24 hours. The final values were after 48 hours.

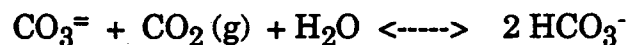
Another possibility for resolving the laboratory results with MINTEQA2 modelling is to determine the solubility product of $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ based on the laboratory results and use this value in the model. For the 15 Fe precipitation experiments, the average solubility product on a log basis is -38.9 ± 0.3 . For the 10 Al precipitation experiments the average solubility product on a log basis is -34.1 ± 0.5 .

Literature values for the log Ksp for ferrihydrite range from -36 to -39 (Chapman, Jones, and Jung 1983). MINTEQA2 allows a range for ferrihydrite log Ksp of -37.00 to -40.44, and uses a default value of -37.1 if nothing is specified. Chapman, Jones, and Jung (1983) studied the processes controlling metal ion concentrations in AMD and determined that ferrihydrite was the most reasonable precipitate and a log Ksp of -39 produced the most consistent results. Based on the results from this and other studies, using ferrihydrite with a log Ksp of -39 as a possible solid phase is the most reasonable procedure for modelling the concentration of Fe(III) in AMD.

Literature values for the log Ksp for $\text{Al}(\text{OH})_3$ range from -31.6 to -36.3 (Chapman, Jones, and Jung 1983). MINTEQA2 has maximum and minimum values for log Ksp of -32.56 to -33.51 for gibbsite, and uses a default value of -33.23 if nothing is specified. Chapman, Jones, and Jung (1983) determined that amorphous $\text{Al}(\text{OH})_3$ was controlling the aluminum concentration, and a log Ksp of -31.6 produced the most consistent results. The value of log Ksp of -34.1 determined in this study is outside the values used in MINTEQA2 and in the Chapman, Jones, and Jung (1983) study. However it is within the range of literature values. Based on the results from this and other studies, using gibbsite as a possible solid phase is the most reasonable procedure for modelling the concentration of Al(III) in

AMD. However, using the default value of log Ksp of -33.23 will produce an upper bound on aluminum concentration and a value of -34.1 will produce a lower bound.

The modelling and laboratory studies of the equilibration of acidic Fe(III) and Al(III) solutions with CaCO_3 do not completely parallel the reaction of AMD in an actual ALD. This is because Fe(III) and Al(III) hopefully are not present when AMD courses through an ALD, and consequently, precipitation of hydroxides is avoided. In these studies, complete precipitation of Fe(III) and Al(III) occurred. Nevertheless, certain aspects of this study apply to any time AMD reacts with limestone including the reaction of AMD in an ALD. In particular, the property of alkalinity increasing and pH decreasing with increasing mineral acidity applies whenever AMD reacts with limestone. This somewhat counter-intuitive property can be understood by considering the following equilibrium reaction:



The reactant CO_2 gas is generated from the reaction of AMD with CaCO_3 according to the first reaction in the **Introduction** and is retained in the system rather than being released. The reactant CO_3^{2-} comes from calcite dissolution. The greater the mineral acidity, the more CO_2 is generated to react with the calcite, and the more bicarbonate alkalinity is produced. If the water is allowed to degas and CO_2 escapes, this shifts the above reaction to the left and alkalinity is reduced. However, when the reaction shifts to the left, more CO_3^{2-} is produced and the pH increases.

With respect to the reaction of AMD with an ALD, the amount of alkalinity generated depends on the pH of the water entering the ALD. If the CO_2 is retained, the lower the pH, the greater the amount of alkalinity that theoretically can be generated. Greater alkalinity does not

necessarily mean a higher pH. In addition, if the CO_2 is retained and reaches pressures greater than the atmospheric pressure of $10^{-3.5}$, then this CO_2 has the possibility of degassing from the water when the AMD breaches the surface after coursing through the ALD. In such a situation, the pH would rise, but there would be less alkalinity available for precipitation of $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$.

Conclusions

Modelling and laboratory experiments studying the chemistry of acidic solutions of $\text{Al}(\text{III})$ and $\text{Fe}(\text{III})$ alone and in contact with CaCO_3 has lead to the following observations:

- The precipitation curve for $\text{Fe}(\text{OH})_3$ occurs at about a pH of 3 so that by a pH of 3.5, the concentration of $\text{Fe}(\text{III})$ is down to 0.1 mg/l. For Al, the precipitation curve for $\text{Al}(\text{OH})_3$ occurs above a pH of 4 and at a pH of 4.7, the concentration is approximately 0.20 mg/L.

- For modelling $\text{Fe}(\text{III})$ chemistry in AMD, ferrihydrite with a log Ksp of -39 is the best choice for a possible phase. For modelling $\text{Al}(\text{III})$ chemistry in AMD, gibbsite is the best choice for a possible phase. The value of log Ksp to use is a bit more uncertain. This study suggests a value of -34.1.

- In the reaction of AMD with CaCO_3 , if the CO_2 is retained, the higher the mineral acidity, the higher the possible alkalinity that can be generated, and the lower will be the pH at equilibrium.

- If, when AMD reacts with an ALD, the CO_2 is retained and reaches pressures far above the atmospheric value of $10^{-3.5}$, the CO_2 can dissolve from the AMD and be lost to the atmosphere when it breaches the surface. If this occurs, the pH will rise and alkalinity will be lost.

From a practical viewpoint, aluminum is not always analyzed in AMD. Consequently, its presence in water may be overlooked in assessing the appropriateness of an ALD. In a 1995 survey of AMD from metal mines in Colorado, a significant number of the waters that had pH below 4 had concentrations of Al above 1 mg/L. In the opinion of the authors, a maximum concentration of Al of 1 mg/L is presently a conservative guideline based on the fact that people are unsure of how much dissolved aluminum will plug an ALD.

The other important feature that this study reveals is how important initial acidity of the water and retention of CO_2 are to the final alkalinity of the AMD. Loss of CO_2 or precipitation of iron within the ALD could account for the alkalinity differences that Hedin, Watzlaf, and Nairn (1994) found in their study. The high alkalinity values shown in Table 1 and in Figure 4, generated when all the $\text{Fe}(\text{III})$ and $\text{Al}(\text{III})$ were allowed to hydrolyze should be carefully considered. This was caused by the generation of more CO_2 which reacted with the calcite. In an actual ALD, no precipitation can occur because it would eventually plug the structure. In Table 1, the alkalinity values for the system where no $\text{Fe}(\text{III})$ and $\text{Al}(\text{III})$ are present may be closer to what should be expected in the field. In-field alkalinity values of 300 mg/L of CaCO_3 may look very desirable. However, such high values may only be an indication that $\text{Fe}(\text{III})$ or $\text{Al}(\text{III})$ are precipitating in the ALD.

Acknowledgement

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NEW DEVELOPMENTS IN PASSIVE TREATMENT OF ACID ROCK DRAINAGE

**James J. Gusek, P.E.
Knight Piésold & Co.
1050 Seventeenth St., Suite 500
Denver, CO 80265-0500**

**Thomas R. Wildeman, Professor
Department of Chemistry and Geochemistry
Colorado School of Mines
Golden, CO**

ABSTRACT

Passive treatment systems for mitigating acid rock drainage are being tested at several active and inactive mine sites with positive and sometimes surprising results. The sites encompass a variety of climatic conditions, indigenous vegetation and acid generating components. As part of long term closure planning, pilot scale passive treatment systems were developed to demonstrate the system performance for use in final closure plans. This paper presents discussions of design criteria, construction and operation and evaluates performance of systems relative to their ability to meet long term waste treatment goals.

INTRODUCTION AND BACKGROUND

Nature has been passively removing dissolved metals from surface and ground water for eons; evidence includes pyrite occurrences in coal beds and bog iron ore (limonite) deposits. For more than a decade, wetlands and bogs have been recognized as nature's method of improving water quality. Contaminant reductions can occur through the precipitation of hydroxides, precipitation of sulfides and pH adjustments. Local conditions, oxidation state, and water and soil chemistries dictate whether these natural reactions will occur under oxidizing (aerobic) or reducing (anaerobic) conditions. Man-made or constructed wetlands employ the same principles as do natural wetlands, but are designed to optimize the processes occurring naturally in a wetland ecosystem.

Water adversely impacted by mining can be acidic and contain significant amounts of dissolved metals. For discussion purposes, the term *acid rock drainage* (ARD) will be used throughout the paper to denote problematic occurrences of mine water even though dissolved metals may be the only issue in a given situation.

In the early 1980's, researchers in America documented improvements in quality as ARD flowed through passive treatment systems. The US Bureau of Mines (USBM), Tennessee Valley Authority (TVA), and academics (Colorado School of Mines [CSM] and others) thought that a "plant ecosystem" was needed for passive treatment to work. Pilot scale systems were built, but confusing successes and failures resulted.

In the interval from 1985 to 1988, Greg Brodie of TVA and Bob Kleinmann of the USBM began to take influent water chemistry into account in the design of aerobic type systems for coal mine ARD. In 1987, CSM, Knight Piésold and Co. and the US EPA developed a pilot system for metal mine ARD at the Big Five Tunnel in Colorado. At the Big Five, anaerobic processes were found to be important in metals removal and ecosystems were not needed; the cells worked fine without plants.

Since 1988, there have been rapid advancements in understanding how passive treatment systems work. Defining "large scale" as over 1,000 gallons per minute (63 liters/sec) of flow, the first large scale aerobic system was built in 1992 by TVA. Pending permitting, the first large scale anaerobic system will be built by Asarco, Incorporated in 1995 for its West Fork underground lead mine in Missouri. The methodology holds promise over chemical neutralization because large volumes of sludge are not generated; metals may be precipitated as oxides or sulfides in cell substrates. The key goal of passive treatment systems is the long term immobilization of metals in the substrate materials.

Metals Removal Mechanisms in Passive Treatment Systems

Several physical, chemical and biological mechanisms are known to occur within passive treatment systems to reduce the metal concentrations and neutralize acidity of the incoming flow streams. Notable mechanisms include:

- Hydroxide precipitation catalyzed by bacteria in aerobic zones;
- Sulfide and carbonate precipitation catalyzed by bacteria in anaerobic zones;
- Filtering of suspended material;
- Metal uptake into live roots and leaves;

- Ammonia-generated neutralization and precipitation; and
- Adsorption and exchange with plant, soil and other biological materials.

Remarkably, some studies have shown that plant uptake does not contribute significantly to water quality improvements in passive treatment systems⁽¹⁾. However, plants can replenish systems with organic material and add aesthetic appeal. In aerobic systems, plant-assisted reactions appear to aid overall metal-removal performance, perhaps by increasing oxygen and hydroxide concentrations in the surrounding water through photosynthesis-related reactions and respiration in the plant root zone.

Research has shown that microbial processes are a dominant removal mechanism in passive treatment systems⁽¹⁾. One anonymous researcher considered a passive treatment system as a "bioreactor with a green toupee", referring to the substrate where most of the bioreactions occur and the collection of plants that grow on top of the treatment cells.

Passive Treatment System Comparison

Selection of the correct passive treatment system is dictated by the chemistry of the water to be remediated. Whether a treatment system is anaerobic, aerobic, or both depends on the local situation. A side-by-side comparison summary of the two passive treatment methods follows.

Aerobic Systems

Emphasize oxidation reactions
 Surface flow of water
 Oxide precipitates
 Processes can lower pH
 Operate best at pH > 5.5
 Might freeze in winter
 Remove iron quite well
 Can remove manganese, selenium, arsenic & WAD cyanide

Anaerobic Systems

Emphasize reduction
 Subsurface water flow
 Sulfide Precipitates
 Processes can raise pH
 Can work at pH ≤ 2.5
 Operates in winter
 Remove other heavy metals quite well

Typical Conditions for Using Aerobic Systems

For slightly acidic ARD (pH greater than 5.5) without excessive dissolved iron concentrations, hydroxide precipitation catalyzed by bacteria may be utilized as the dominant removal mechanism. Aerobic systems are similar to "natural" wetlands in that they typically have shallow depths. For the same level of treatment capacity, aerobic systems typically

require larger areas than anaerobic systems. This can be an important design consideration if land availability is an operational constraint. Aerobic systems have been used to treat coal mine drainages at 17 of TVA's mine and coal washing plant sites in Alabama and Tennessee⁽¹⁾. When the pH of the drainage is greater than 5 and iron is less than 50 mg/L, effluent quality consistently meets off-site discharge criteria.

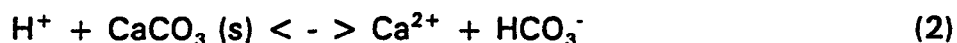
The hydrolysis of iron and other metals is an important chemical principal that underlies the application of aerobic systems. The pH of 5 and 50 mg/L iron concentration criteria presented in the previous paragraph are driven by the iron hydrolysis reaction:



As iron is hydrolyzed, hydrogen ions (H^+) are produced and the pH drops accordingly. Thus, a water sample with a starting pH of 5 and more than 50 mg/L dissolved iron could have a final pH of 2 or 3 after most of the iron is hydrolyzed. This is because of the increased concentration of hydrogen ions that the hydrolysis reaction produces.

Because hydrolysis is the primary aerobic removal process, when the pH is below 3 and iron is above 200 mg/L, remediation using aerobic wetlands is far less efficient. Often alkalinity can be added to provide buffering capacity by pre-treating discharges with an "anoxic limestone drain" (ALD) prior to treatment in an aerobic passive treatment system. ALD's are only effective if the iron is present as iron (II); iron (III) hydroxide precipitation causes armoring on the limestone.

Alkalinity may be added in an ALD environment in accordance with the following reaction:



If oxygen invades an anoxic limestone drain, the limestone may armor with hydroxide precipitate. Furthermore, less alkalinity may result if CO_2 gas is allowed to escape:

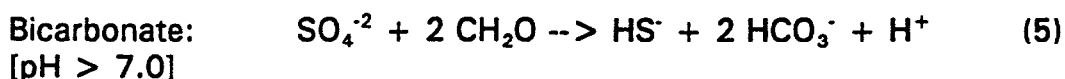
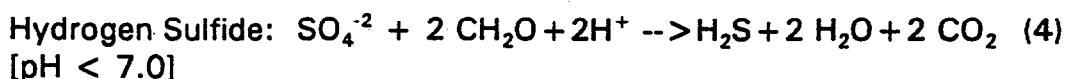


Typical Conditions for Using Anaerobic Systems

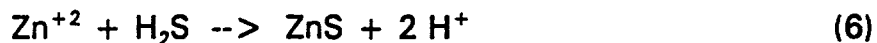
For very acidic waters (pH less than 5.5), sulfide precipitation assisted by sulfate-reducing bacteria (SRB) thriving in anaerobic zones in the wetland substrate has been demonstrated to be the most significant metal removal mechanism. The SRB reactions involve the generation of:

- hydrogen sulfide gas, which combines with dissolved metals to precipitate sulfides and
- bicarbonate, which has been shown to raise the pH of the effluent.

The SRB, which appear to function best above pH 5.0, are believed to produce hydrogen sulfide gas (H_2S) and bicarbonate (HCO_3^-) in accordance with the following reactions:



The hydrogen sulfide gas, bubbling up through the wetland substrate, precipitates metals as sulfides, essentially reversing the reactions that occurred to produce ARD. For example, the following reaction occurs for dissolved zinc, forming amorphous zinc sulfide (ZnS):



The key conditions for SRB health are a pH of 5.0 (maintained by the SRB itself through the bicarbonate reaction), the presence of a source of sulfate (typically from the ARD), and organic matter (CH_2O , from the substrate). Anaerobic wetlands and bioreactors have been successful at substantially reducing metal concentrations and favorably adjusting pH of metal mine drainages.

DESIGN CONSIDERATIONS

System Components

A complete understanding of all the processes at work in passive treatment systems is lacking. In particular, the influences of ARD water quality on passive treatment design is an area worthy of additional research. Currently, the design of passive treatment systems is essentially governed by the chemistry of the water to be treated. Thus,

ARD characterization is usually the first step in any ARD remediation project. The selection process for specific cell types is summarized in Figure 1, which depicts a "decision tree" type of selection procedure. Figure 1 was developed based on work by the USBM for ARD containing iron and manganese. The process becomes more complicated if other heavy metals such as aluminum, copper, lead, zinc, arsenic and mercury are present.

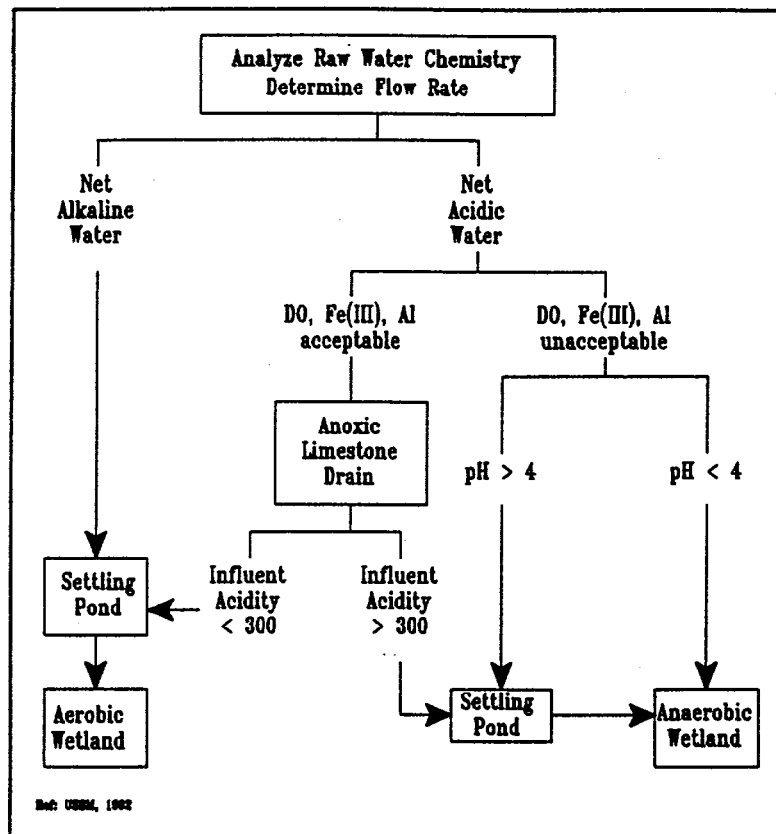


Figure 1
Flowchart for Designing Passive Treatment Systems
(Iron Removal Only)

Typically, the design engineer has the following components from which to select in a passive treatment scheme:

- Aerobic Cells (includes rock filters/algae cells)
- Anoxic Limestone Drains (ALD's)
- Anoxic Ponds
- Anaerobic Cells
- Anoxic Alkalinity Generators (AAG's)

Fluid collection/diversion, fluid distribution and system instrumentation must also be integrated into the passive treatment scheme. Fluid collection, if properly designed, can enhance treatment cell performance. For example, if fluids can be collected prior to oxygen contact, they can be more amenable to ALD treatment. If not, they may need to be passed through an anoxic pond first (see discussion below).

The design of individual components is usually driven by the product of dissolved metals in solution and the volumetric inflow rate, typically called "metal loading". Key design criteria for the primary passive treatment system components follow.

Aerobic Cells - the surface area is varied for removal of Fe, Al, Mn, As, CN, Hg and to raise pH; from 2 to 11 grams of Fe loading can be removed per day per m² of area.

ALD's - retention time (about 48 hours) and size are varied based on design life; an ALD can add alkalinity to ARD prior to aerobic cells to buffer against iron hydrolysis reactions. Ultimate sizing is based on laboratory and field studies.

Anoxic Ponds - (used upstream of ALD's) volume is varied with the goal of decreasing dissolved oxygen and/or reducing Fe (III) to Fe (II) and/or removing Al. Ultimate sizing is based on laboratory and field studies.

Anaerobic Cells - cell volume and surface area are varied for removal of Fe, Cu, Pb, Zn, Hg, Cd, Al, SO₄, and to raise pH; cells are designed for 0.3 moles of metal loading per m³ per day of wetland volume (volumetric loading factor) and 20 m² of area per liter/second of flow (800 sq. ft./gpm) [area-loading factor].

AAG's - cell volume and surface area are varied to generate alkalinity when an ALD is not feasible. Ultimate sizing is similar to Anaerobic Cells but is based on laboratory and field studies.

WORKING SYSTEM EXAMPLES

Knight Piésold and Co. has been involved with over a dozen ARD and mine water remediation projects, some of which have resulted in the construction of pilot scale systems. Asarco's West Fork project is likely to culminate in the construction of a large scale system in 1995. Table 1 is a summary list of selected projects that shows typical influent water quality data, the relative treatment capacity (@pilot scale size), preliminary treatment results and the general types of cells used. Results from these sites are discussed below.

Leviathan Mine, California

ARD flow is collected from a french drain pipe beneath a concrete flume. Total flow is about 189 L/min (50 gpm); the pilot system treats from 1.7 to 3.8 L/min. The site initially had three cell types: an ALD, a three-compartment aerobic cell, and an anaerobic filled with horse manure. All cells are lined with geosynthetic materials.

Results: The system was commissioned in early May, 1993. Typical results show 90% removal of iron, 99% removal of arsenic, 99% removal of nickel, 100% removal of aluminum, pH of effluent 6.5 to 7.2. Just after startup, the anaerobic cell effluent had about 800 to 1000 mg/L of excess alkalinity, capable of neutralizing more ARD if mixed with other flows (which it did after it joined a bypassed flow). The ALD was modified into an AAG due to plugging of the original installation with aluminum precipitates. The AAG effluent combines with raw feed water in the first aerobic cell.

Gold Mine, Nevada

This gold mine approaching closure has two sites, an ARD and cyanide tailing seepage. The ARD site has three cells: 1) an aerobic pond (for arsenic/selenium removal), 2) an anaerobic cell (for iron, copper, and zinc removal); and an aerobic rock filter (for manganese removal). The design flow is 23 L/min; all cells are lined with geosynthetics. The anaerobic cell was filled with composted cow manure and sandy soil and inoculated with fresh manure from a county fair. The rock filter cell was inoculated with algae harvested from a small seepage collection pond on the mine property.

The tailing site has an aerobic system with algae and river rock; it is divided into 14 compartments. Design retention time is 7 days at 38 L/m. The system has an 80 mil HDPE geomembrane liner.

Results: System was commissioned in late November, 1993. Preliminary results on Table 1 show significant reductions in metals in both cells treating ARD and the tailing aerobic system shows reductions in WAD cyanide from 31 ppm down to 4 ppm.

Brewer Gold Mine, South Carolina

This open pit gold mine approaching closure has two ARD sites: a flooded open pit and a spent heap leach pad. Two anaerobic pilot cells were built. The cells were filled with a mixture of composted turkey

droppings, sawdust, phosphate rock reject and cow manure inoculum. The cells treat 3.8 and 2.9 L/min. (pit and pad flows, respectively).

Results: The system was commissioned in early September, 1993. Typical results for both cells show 99% removal of copper, 67% removal of iron, 71 to 88% removal of aluminum, pH of effluents 5.5 to 6.5. Both cell effluents have had about 300 to 600 mg/liter of excess alkalinity, capable of neutralizing more ARD if mixed with other flows. Vegetation on the pad cell was suspected of inducing aerobic conditions; eliminating the vegetation appeared to help cell performance; addition of hay to the surface of the pit cell appeared to assist performance.

Burleigh Tunnel, Silver Plume, Colorado

This high elevation metal mine has neutral pH discharge with 40 mg/L zinc and some iron. The passive treatment scheme includes two anaerobic cells, one upflow, one downflow. The cells were filled with commercially available composted manure product and hay. Aerobic iron precipitation within the tunnel was observed early in the project but it may not continue after a cave-in disrupted the natural air flow. The design flow is 76 L/min., 38 L/min. in each cell. Both cells were lined with geosynthetics.

Results: The system was commissioned in December, 1993. The system had 98% zinc removal at startup; and January, 1994 data showed 88% zinc removal in the dead of winter. Flows appear unimpeded by winter weather; however, the upflow cell effluent froze over during a two day flow interruption.

Asarco, Incorporated West Fork Unit, Missouri

This operating underground lead mine has a neutral pH discharge with 0.4 mg/L lead and 0.18 mg/L zinc. A bench scale anaerobic cell was filled with 50% cow manure and 50% saw dust and was operated at 4 L/min. until December, 1993 and 8 L/min. until February, 1994. The cell was constructed of a 1.3 meter high, 2.7 meter diameter plastic tank. The bench scale contents were used as inoculum in a pilot scale system commissioned in February, 1994. The pilot scale cell utilizes about 53 cubic meters of a mixture of sawdust, manure, hay, dolomitic tailings and coarse mine waste. The pilot cell has treated up to 185 liters per minute (49 gpm).

Results: The bench system removed lead to below detection limits. Geochemistry suggests that sulfate reduction, not organic complexation was the removal mechanism. As shown on Table 1, the pilot scale

system is also removing lead and zinc to below detection limits. Detailed results will be discussed in subsequent paragraphs. A large scale system to treat 8,200 m³ per day (1,500 gpm) is planned to be built at this site in early 1995.

RECENT DEVELOPMENTS

It is not practical to present detailed performance data from all the working system examples; each situation is itself worthy of a separate technical paper. Rather, pertinent observations and performance theories will be presented with the caveat that subsequent data may not necessarily follow expected trends or theories proposed herein. Key "developments" associated with each of the previously introduced working systems follow.

Leviathan Mine

This appears to be the first installation that combined an anoxic limestone drain, aerobic cells and an anaerobic cell at a single site. While the performance of the ALD was compromised by aluminum, the anaerobic cell's production of excess alkalinity introduced the concept of using an anaerobic cell as an anoxic alkalinity generator (AAG). The system also appeared to function during extremely cold weather which contradicted anaerobic cell performance data in a Canadian system⁽²⁾. It is worth noting that the anaerobic cell at Leviathan was primarily filled with horse manure, a readily available source of organic carbon used in sulfate reduction.

Gold Mine, Nevada

The anaerobic cell at this high altitude site froze before it could be fully commissioned. Cell performance after the spring thaw suggests that the winter hiatus did not affect cell performance. Substrate permeability problems suggest that upflow systems may be applicable in some situations. Tailing basin cyanide removal by algae in aerobic cells was unaffected by winter weather but operational constraints forced a brief winter shutdown. Algae productivity may have been temporarily enhanced with minor nutrient additions.

Brewer Gold Mine, South Carolina

Two nearly identical anaerobic cells on the same site performed differently. The elimination of plants on top of one cell (receiving leach pad water) resulted in re-establishment of anaerobic conditions. Plant roots were found nearly 600 mm below the cell surface and were

suspected of injecting excess oxygen into the cell substrate, thereby hindering the anaerobic SRB performance.

The effects of heavy rainfall on anaerobic systems was observed. After a significant rainfall, operating personnel typically discontinued feeding ARD until the water level in the cell dropped. This action allowed plug flow of sulfate-deficient rain water through the cell whose retention time was about 2 weeks. The lack of sulfate in the slug of rainwater passing through the cell appeared to hinder the viability of the SRB which often needed several weeks after the rainfall event to recover. Cell operational protocol was changed to allow increased combined ARD/rainwater flow through the cell to bleed off excess ponded surface water. This change appears to have helped.

In the other cell, poor performance was enhanced (about double, up to the expected 0.3 moles/m³/day) through the addition of a top dressing of alfalfa hay and neutralizing phosphate reject rock (mostly limestone). The enhancement, if short lived, could suggest that "passive" bioreactors could become "semi-active" systems if easily digestible SRB nutrients such as hay or manure are utilized instead of higher "roughage" SRB nutrients such as waste wood products/ sawdust.

Not surprisingly, both cells system removed trace amounts of dissolved uranium and (somewhat unexpectedly) Ra₂₂₆ in the ARD. In addition, uranium, known to occur in the phosphate reject rock (that was a cell substrate component), was not mobilized.

Burleigh Tunnel

The area-loading factor for an anaerobic system was suspected of being a function of pH or mineral acidity. Since the discharge was circum-neutral, the area loading factor was halved (more flow per unit surface area) in bench scale studies. Positive confirmatory results showed that at neutral pH, an area-loading factor less than the benchmark value could be successfully used; this advance was incorporated into the pilot scale design.

The flow at this site has little sulfate (about 40 mg/L). However, the SRB appear to be healthy enough to remove zinc to below aquatic standards. Undiluted cell effluent has no toxicity to Ceriodaphnia, a benchmark dissolved metal toxicity test.

Asarco Incorporated West Fork Unit, Missouri

Due to Asarco's progressive research attitude, the volume of test data available for analysis from this site is more extensive than all the other sites described in this paper combined. Developments from this project follow.

Figure 2 shows the response of the West Fork Unit biocell to doubling of design flow from 25 gpm (95 L/min) to 49 gpm. These data show that at a circum-neutral pH, the area loading factor can be decreased to less than 20 square feet of cell surface area per gpm without a decrease in performance. Previous data (from the Burleigh Tunnel) showed that a value of 400 square feet per gpm was feasible. Note that sulfide production decreased with decreasing area loading factor, but this may have been attributed to other operational factors. Remarkably, the metals loading increased without corresponding increases in metal concentration in the effluent; the cell continued to remove lead and zinc to below detection limits of 0.02 and 0.008 mg/L, respectively. This is thought to be due to the fact that sulfide production still outpaced metal loading on a mole for mole basis.

Another revelation from West Fork Unit data (see Figure 2) was that sulfide production could occur at circum-neutral pH at rates an order of magnitude higher than typical design values of 0.3 moles per cubic meter per day. However, these high rates may be short-lived due to the depletion of readily-digestible SRB nutrients. This theory may be supported by the observation that the sulfide production rates decreased in parallel with decreases in biological oxygen demand values in the cell effluent and appear to be independent of flow rate as shown on Figure 3. These data are consistent with US Bureau of Mines data for "Biogenic Hydrogen Sulfide" active treatment systems for metals removal⁽³⁾.

Wildeman, et al⁽¹⁾ theorized from sulfate reducing stoichiometry that carbon depletion would be the most likely factor limiting the operational longevity of an anaerobic substrate. Simultaneous alkalinity and sulfate reduction values were used to independently estimate carbon consumption rates (and cell lifespan) in West Fork Unit substrate. Figure 4 reveals a steady increase in projected cell longevity (about 80 years) consistent with early estimates by Wildeman, et al.

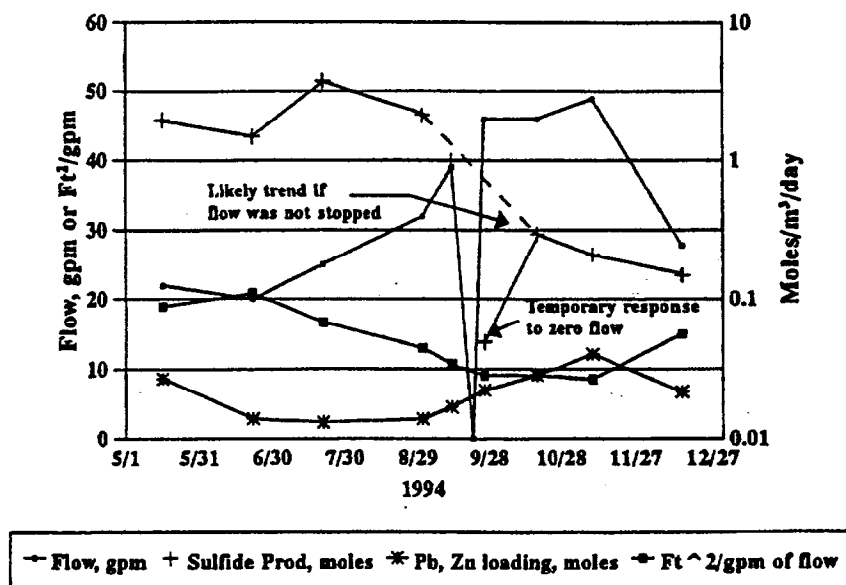


Figure 2
West Fork Passive Treatment System
Sulfate Reduction vs. Flow Rate and Time

SUMMARY

The collective observations from the passive treatment systems described above are summarized below.

- The production of sulfide and alkalinity from anaerobic cells appears to be a function of the "digestibility" of the cell substrate by SRB (the better the digestibility, the higher rates of sulfate reduction/sulfide production and alkalinity generation will be).
- If West Fork carbon consumption rates stabilize at current values (assuming wood waste derived SRB nutrients), anaerobic cell life on the order of a century might be possible at this site.
- As the ARD acidity decreases (combined effects of pH and mineral acidity), the area loading factor for anaerobic cell design can be lowered.
- The design value of 0.3 moles of sulfide production per cubic meter per day might be valid within a wide pH range once easily digestible SRB nutrients are depleted.

- The effects of rainfall on metal loading for a given cell are likely to be hydrologic only. However, covering of anaerobic cells to shed rainfall should be considered.

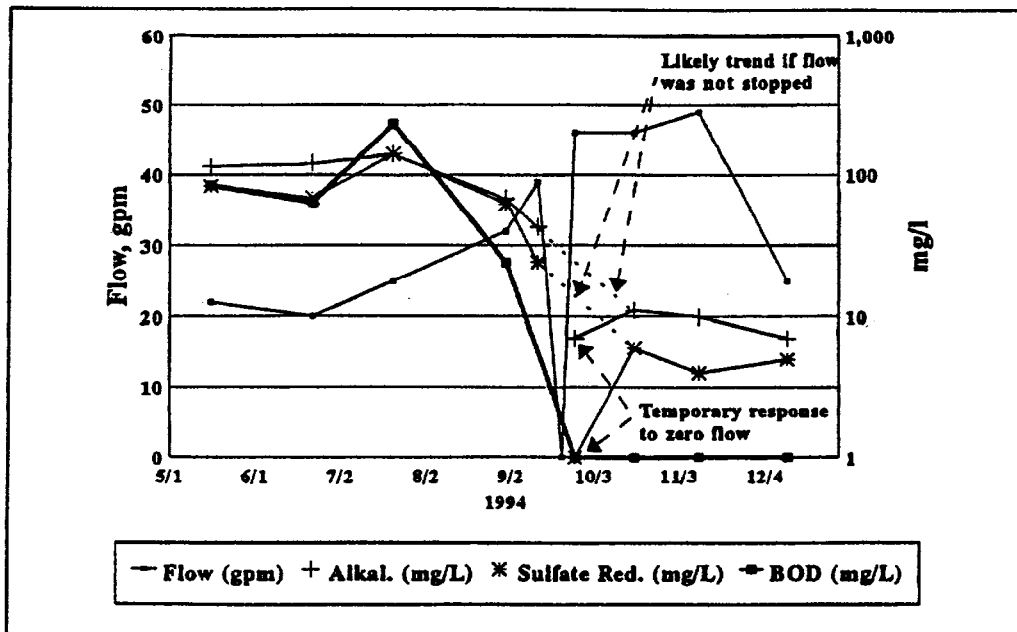


Figure 3
Alkalinity Production and Sulfate Reduction vs Flow Rate and Biological Oxygen Demand

- The propagation of plants on the surface of anaerobic cells, especially shallow ones, should be discouraged. This can be accomplished with excessive ponding depths that discourage emergent vegetation or with covers.

In conclusion, the passive treatment of ARD holds much promise, especially for the chronic, low flows or loadings associated with mine and mill site drainages that nag the closure and reclamation processes. Hurdles remain in completely understanding and designing for the biochemical and geochemical reactions that occur in passive treatment systems. However, the performance data available from five sites considered in this paper appears to be consistent among the group and with the results of previous work.

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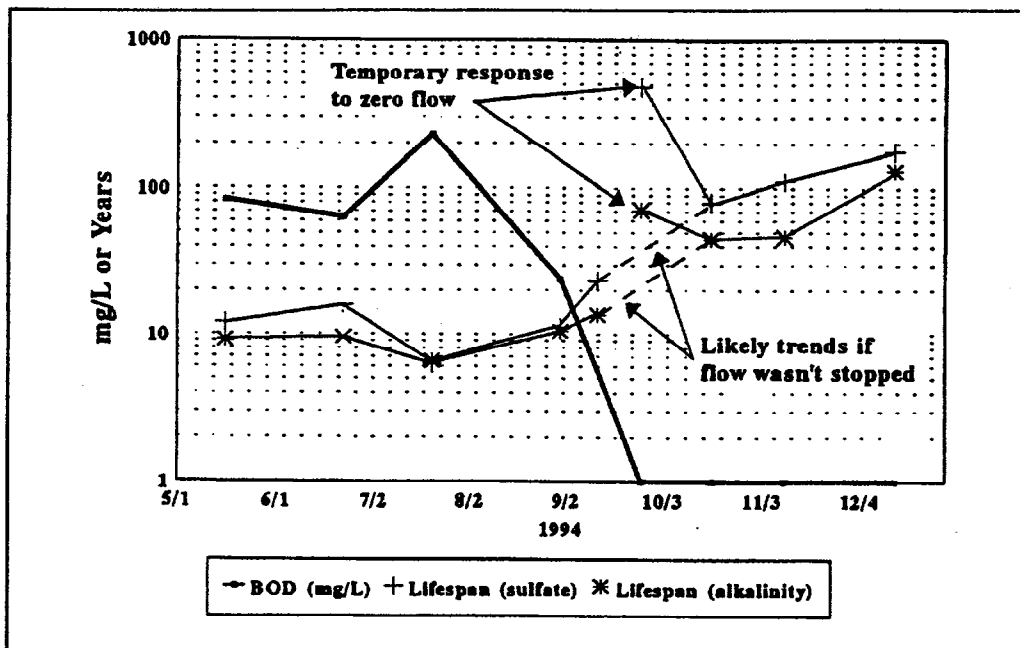


Figure 4
West Fork Passive Treatment System
Cell Life, Biological Oxygen Demand vs Time

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TABLE 1
Pilot Scale Passive Treatment Experience
Knight Piésold and Co., Denver, Colorado USA

Project	pH	Total Fe mg/L	Other Parameters total mg/L	Flow, L/min	Typical Treatment Results total mg/L	Comments/ System Configuration
Leviathan Mine, California	4.7	310	Al - 48 As - 0.4 Ni - 1.8	3.8	Effluent pH 6.5 Non-detect Al, As, Ni Fe, 90% removal	3 cells: ALD, aerobic & anaerobic
Gold Mine Tailing Seeps, Nevada	6 to 8	0.05	WAD CN - 31 As - .12 Hg - 0.0008 Cu - 1.8 Zn - 1.0	38	Effluent pH 6 - 9 WAD CN - 1.2 - 6.7 Fe - 0.03 As - 0.054 Hg - <0.0002 Cu - 0.63 Zn - 0.08	14 chambered aerobic system with algae
Gold Mine ARD, Nevada	3.2	216	As - 2.7 Cu - 7.4 Mn - 7.1 Se - 0.3 Zn - 1.8	23	Effluent pH 6.5-7.1 Fe - 0.9 As - .032 Cu - <0.05 Mn - 2.9 Se - .005 Zn - <0.05	3 cells: aerobic pond, anaerobic, rock filter with algae
Brewer Gold Mine, S. Carolina Pit Cell	2.3	735	Cu - 76 Al - 113	4	Effluent pH 5.54 Fe - 215 (as Fe ⁺²) Cu - 15.9 Al - 30	One anaerobic cell, substrate of limestone, turkey litter wood chips and cow manure
Brewer Gold Mine, S. Carolina Heap Leach Pad Cell	2.4 to 4.7	25 to 380	Cu - 2 to 30 Al - 31	6.8	Effluent pH 6.2 Fe - 44 Cu - 0.25 Al - 12.4	One anaerobic cell, substrate of limestone, turkey litter wood chips and cow manure
Burleigh Tunnel, Colorado	6.8	5	Zn - 50	76	Upflow Zn < 1.0 last 7 month avg 0.35 mg/L No Ceriodaphnia mortality Downflow Zn 10 mg/L	Two anaerobic cells, 38 l/min each; one upflow, one downflow
Asarco West Fork Unit, Missouri	7.9	0	Pb - 0.4 to 0.6 Zn - 0.18	8 & 85	Effluent pH 7.0 Pb - <0.02 Zn - <0.008 Sulfate reduction @ 2 to 3 moles per cubic meter per day.	One anaerobic cell (bench/pilot scales) Full scale, 1,500 gpm system design completed: - settling basin - anaerobic cell - rock filter - aeration basin

Passive-treatment of acid rock drainage: What is the potential bottom line?

James J. Gusek

Passive-treatment systems that mitigate acid-rock drainage (ARD) from coal mines have operating since the mid-1980s. Large systems at metal mines are being contemplated. A 95-L/sec (1500-gpm) capacity system is planned this year at an underground lead mine in Missouri.

Mine, process and environmental managers need to understand how and why passive-treatment systems work. They must understand what operational limitations to expect, as well as the economics of construction and operation compared to the alternatives, like lime precipitation.

Wetlands have been recognized as nature's method of improving water quality. Contaminant reductions can occur through the precipitation of metal hydroxides, sulfides and carbonates and pH adjustments. Local conditions, oxidation state and water and soil chemistries dictate whether these natural reactions will occur under oxidizing (aerobic) or reducing (anaerobic) conditions.

A typical man-made passive-treatment-system can mimic a natural wetland by employing the same geochemical principles. Passive-treatment systems, however, are engineered to optimize the biogeochemical processes occurring in a natural wetland ecosystem. The passive-treatment methodology holds promise over chemical neutralization because large volumes of sludge are not generated. Metals may be precipitated as oxides, sulfides or carbonates in the passive-treatment system substrate. The key goal of a passive-treatment system is the long-term immobilization of metals in the substrate materials.



The pilot-scale passive-treatment system at the Wheal Jane Mine in Cornwall, England is designed to treat 42 L/sec (665 gpm) of ARD (pH 3.0, 250 mg/L iron, 250 mg/L zinc).

Water adversely impacted by mining can be acidic and contain significant amounts of dissolved metals. For discussion purposes, ARD will be used to denote problematic occurrences of mine water even though dissolved metals may be the only issue in a given situation.

The interest in remediation of ARD is high. At the 1994 International Land Reclamation and Mine Drainage Conference and the Third International Conference on the Abatement of Acidic Drainage joint meeting held in Pittsburgh, PA, 12 sessions and 69 papers dealt exclusively with the ARD problem.

While research results are encouraging, a mine manager's perspective is typically driven by the bottom line. "How much will it cost?" and "How long can it last?" are crucial questions in evaluating new technology. Until recently, the answers to these questions were speculative. This situation has abated somewhat with the experience of a large, passive-treatment system treating 126 L/sec (2000 gpm) of coal-mine drainage at Tennessee Valley Authority's (TVA) Fabius Mine in Alabama. A leading base metal producer also plans to develop a passive-treatment system to treat 95 L/sec (1500

gpm) an underground lead mine in Missouri.

The TVA passive-treatment system replaced a lime-treatment plant. The passive-treatment system reportedly is discharging compliant effluent. A pilot-scale system for pH neutral drainage at the underground mine has met discharge quality criteria consistently after completing its four-month break-in period.

The passive-treatment technique may not be applicable in all mine-drainage situations. However, the economics of implementation

will be considered for sites where the present state of passive-treatment-system technology reasonably applies. These costs are compared here with lime precipitation, the conventional ARD treatment approach.

Metals removal in passive-treatment systems

Several physical, chemical and biological mechanisms occur in passive-treatment systems to reduce the metal concentrations and neutralize acidity of the incoming flow streams. Notable mechanisms include:

- Hydroxide precipitation catalyzed by bacteria in aerobic zones.
- Sulfide and carbonate precipitation catalyzed by bacteria in anaerobic zones.
- Filtering suspended material.
- Metal uptake into live roots and leaves.
- Ammonia-generated neutralization and precipitation.
- Adsorption and exchange with plant, soil and other biological materials.

Some studies have shown that plant uptake does not contribute significantly to water-quality improvements in wetlands. However, plants can replenish

James J. Gusek, member SME, is a senior engineer with Knight-Piésold and Co., 1050 17th St., Suite 500, Denver, CO 80265-0550.

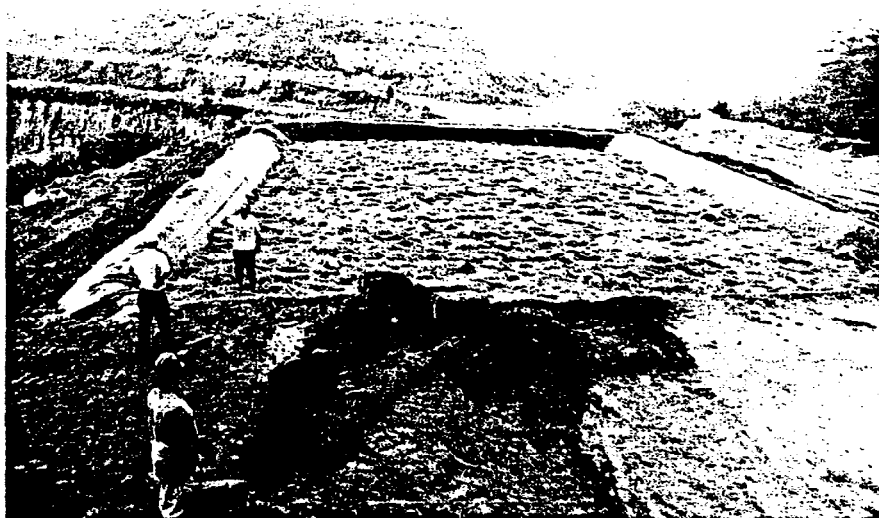
the wetland with organic material and add aesthetic appeal. In aerobic wetlands, plant-assisted reactions appear to aid the metal-removal performance of the system. This might be done by increasing oxygen and hydroxide concentrations in the surrounding water through photosynthesis and respiration-related reactions in the plant root zone. Other studies have shown that some plants, particularly some forms of algae, can bioaccumulate metals.

Wetland system comparison.

Selecting the correct passive-treatment system design layout is governed by the water's chemistry. Whether a passive-treatment system relies on anaerobic reactions, aerobic reactions or both depends on the local situation. The two systems are compared in Table 1. More detailed discussions of passive-treatment system chemistry, design and performance are found in the literature (Wildeman, Brodie and Gusek, 1993; Gusek and Wildeman, 1995 and the International Land Reclamation and Mine Drainage and the Third International Conference on the Abatement of Acid Mine Drainage).

In sizing a passive-treatment system, design engineers have five components from which to select. Designing individual components is driven by the product of dissolved metals in solution and the volumetric inflow rate, or "metal loading." Key design criteria for the primary passive-treatment system components follow. The aerobic cell is appropriate for removing iron, aluminum, manganese, arsenic, cyanide and mercury. It also helps raise pH. And from 2 to 11 g/day/m² of iron can be removed from the cell surface area.

Anoxic limestone drain (ALD) is a bed of crushed limestone that adds alkalinity to ARD. It buffers against pH drops that result from iron precipitation reactions. Retention time is usually about 48 hours. The ultimate size is based on design life, limestone purity and carbonate consumption rate. The



The pilot-scale anaerobic passive-treatment system at the Brewer gold mine in South Carolina treats 2.9 L/sec (46 gpm) of ARD from a flooded pit.

presence of certain amounts of dissolved oxygen, iron (III) and aluminum in the ARD can be fatal to an ALD's long-term performance.

Anoxic ponds are used upstream of an ALD to strip dissolved oxygen and/or reduce iron (III) to iron (II) and/or remove aluminum. Ultimate sizing is based on laboratory and field studies. The cell's concept is similar to the anaerobic cell.

Anaerobic cells are ideal for removing iron, copper, lead, zinc, mercury, cadmium, aluminum, uranium and sulfate, and to raise pH. These cells are designed for 0.3 mole of metal loading per m³ of cell volume (volumetric loading factor) and 20 m² of surface area per L/sec of flow (area-loading factor). Cells are typically filled with organic substrate and inoculated with cattle manure, an easily obtainable source of sulfate-reducing bacteria.

An anoxic alkalinity generator is a special-purpose anaerobic cell that generates excess alkalinity when an ALD is not feasible. Its design is similar to an anaerobic cell.

System longevity and the fate of immobilized metals

Wildeman et al. (1993) speculated that the operable lifespan of anaerobic cells would be limited by initial organic carbon content. They also thought that lifespans on the order of decades were possible. Recent data support earlier cell-longevity estimates (Gusek and Wildeman, 1995). Carbon consumption rates at a pilot-scale, passive-treatment system in Missouri suggest a lifespan approaching 100 years if anaerobic bacterial nutrients are selected based on slow release characteristics. When organic nutrients are exhausted, the depleted metal, sulfide-rich substrate would be replaced with fresh material. The cost of procuring and placing the substrate makes up about half the capital cost of an anaerobic cell.

Theoretically, the heavy-metal sulfides immobilized in an anaerobic cell could be recovered by adapting roasting (to oxidize the sulfides) or vat- and heap-leaching techniques. Flotation concentration might also be considered. If metals recovery is not practical, the depleted substrates could be disposed of in a landfill.

Waste characterization testing would determine whether the material would be classified as hazardous. In today's regulatory climate, it may be more economical to recover the metals solely to render the bulk of the depleted substrate nonhazardous, thus reducing landfill disposal costs. Logically, if metals mobility is suggested from results of standard hazardous material tests like Toxicity Characteristic Leaching Procedure (TCLP, EPA method 1311),

Table 1 — Summary of two passive treatment methods

Aerobic systems	Anaerobic systems
Oxidizing reactions are emphasized.	Reducing reactions are emphasized.
Water flows across the cell surface where treatment occurs.	Water flows through the cell subsurface where treatment occurs.
Metals are removed as oxides.	Metals are removed as sulfides and carbonates.
Biogeochemical processes may lower pH.	Biogeochemical processes can raise pH.
Systems operate best at influent pH greater than 5.5.	Can work at influent pH of less than 2.5.
Cells may freeze in the winter.	Cells can function in subfreezing climates.
Systems can remove iron quite well.	Systems can remove iron and other heavy metals like copper, lead, zinc, cadmium and nickel.
Manganese, selenium, arsenic and WAD cyanide can be removed.	Systems can remove uranium and radium 226.

modified/enhanced TCLP lixivants could be used for metals separation.

Energy for aerobic systems is provided by sunlight. This type of system should last indefinitely. But it may require periodic excavation of accumulated hydroxide or oxide precipitates. Since these are not low-density gypsiferous precipitates, densities approaching natural limonite crusts might be expected. Systems could be designed for cleanout once a decade. However, according to TVA, only one of the 17 passive-treatment systems built since the mid-1980s to treat coal mine ARD has required excavation. And the others do not appear to require any such maintenance in the near future.

Economic analysis

ARD baseline chemistry. Table 2 presents the chemical characteristics, flow rates and lime consumption rates of three Canadian metal mine ARD sites (based on actual case histories), as well as three hypothetical coal mine sites that were used in the economic analysis.

The Canadian sites were assumed to require anaerobic passive-treatment systems. Aerobic passive-treatment systems with ALDs were designed for the hypothetical coal mine sites.

As seen on Table 2, flow rates vary from 6.2 to 300 L/sec (100 to 4755 gpm). Iron concentration varies from 250 to 800 mg/L, while pH varies from

Capital costs of lime-precipitation treatment plants were found to be a function of ARD design flow rate. Similarly, operating costs of these same plants were found to be a function of lime dosage.

2.3 to 4.5. Copper concentration varies from 0 to 120 mg/L. Zinc concentration varies from 0 to 80 mg/L. Manganese varies from 0 to 20 mg/L. Lead concentration varies from 0 to 5 mg/L.

These parameter ranges have been successfully treated by passive-treatment technology on a pilot- or full-scale basis. Lime dosages for the three Canadian sites vary from 1000 to 5600 mg/L CaO.

Economic assumptions. The passive-treatment system economic analysis presented here relies heavily on cost-estimating spreadsheet modules developed for aerobic and anaerobic cells. These modules are based on recent construction experience and

standardized passive-treatment system design criteria for relatively "simple" ARD chemistry. (Aluminum and iron [III] are absent so anoxic ponds and anoxic alkalinity generators are not required for aerobic systems.) Iron (III) occurrence in an anaerobic passive-treatment system is inconsequential. All three aerobic passive-treatment system situations assumed that an ALD is feasible.

Anaerobic passive-treatment system conceptual designs for cost estimation were based on published metal-loading parameters for documented lime precipitation systems at three Canadian locations (Steffen Robertson and Kirsten, 1989). Two out of the three systems use the high-density sludge treatment technique. In this technique, a portion of the gypsiferous iron hydroxide sludge is recycled to aid in particulate settling. Lime treatment costs, capital and operating were originally reported in 1989 Canadian dollars. These values were updated to 1995 US dollars for the analysis. For the present value analyses, an 8% discount rate was used. Capital and operating costs were assumed to inflate at 4% annually.

Space limitations prohibit presenting all unit costs used in the cost-estimating modules. Unit cost values for excavation, geomembrane or clay cell liners and other construction costs were identical for both passive-treatment system cell types. For the anaerobic cells, organic substrate typifies more than 50% of the cell capital cost. The anaerobic substrate was conservatively estimated to cost \$32.70/m³ (\$25/cu yd). Use of sawdust or manure from local sources can further lower unit costs.

Capital costs of lime-precipitation treatment plants were found to be a function of ARD design flow rate (Steffen Robertson and Kirsten, 1989). Similarly, operating costs of these same plants were found to be a function of

Table 2 — Comparison of site ARD chemistries

Parameter	Site 1	Site 2	Site 3	Gallen	Sullivan	Equity
Flow rate L/sec	6.3	31.5	63.0	30.5	300	91.7
pH	4.0	4.0	4.0	3.5	4.5	2.3
Iron, mg/L	250	250	250	500	250	800
Copper, mg/L	0	0	0	10	0.15	120
Zinc, mg/L	0	0	0	40	22	80
Manganese, mg/L	20	20	20	0	0	0
Lead, mg/L	0	0	0	2.6	5	0
Total metals	270	270	270	553	277	1000
Lime dose, mg/L CaO	1209	1209	1209	1850	1000	5600
Tons metal/a	54	268	537	532	2624	2894

Table 3 — Economic comparison of passive treatment systems with lime precipitation

Case	Flow, L/sec	Passive treatment systems				Lime-dosing system			
		Raw capital cost	Amortized annual operating cost	Net present value cost	Net present value cost/kg	Raw capital cost	Amortized annual operating	Net present value cost	Net present value cost/kg
Aerobic passive treatment system with ALD									
Site 1	6.3	\$310,000	\$40,000	\$743,000	\$0.46	\$286,000	\$68,500	\$1,120,000	\$0.70
Site 2	31.5	\$1,460,000	\$120,000	\$2,692,000	\$0.33	\$1,510,000	\$342,500	\$5,684,000	\$0.71
Site 3	63.0	\$2,880,000	\$220,000	\$5,111,000	\$0.32	\$2,300,000	\$685,000	\$10,690,000	\$0.66
Anaerobic passive treatment system									
Gallen	30.5	\$5,208,000	\$140,000	\$6,400,000	\$0.40	\$1,465,000	\$1,030,000	\$14,200,000	\$0.89
Sullivan	300	\$25,670,000	\$560,000	\$30,030,000	\$0.38	\$30,102,000	\$3,342,000	\$69,600,000	\$0.88
Equity	91.7	\$26,626,000	\$610,000	\$31,678,000	\$0.37	\$3,373,000	\$5,280,000	\$69,200,000	\$0.80

flow will also depend on other parameters included in the program. In this study, what flows from the pile is the acid rock drainage.

Table 1. Parameters capable of adjustment in the HELP Model

Parameters That Can be Set by Choosing a Default Site
<ul style="list-style-type: none">· Yearly precipitation· Growing season· Evaporative zone depth· Maximum leaf index data· Mean solar insolation in langleys· Mean monthly temperature
Parameters Set by Each Situation
<ul style="list-style-type: none">· Area of the waste rock pile· Number of soil (rock) layers and thickness of each layer· Soil conservation System (SCS) curve number for the uppermost soil layer<ul style="list-style-type: none">· Type of layers (vertical percolation, lateral drainage, or barrier soil)· Soil porosity - the ratio of the volume of voids to total volume occupied by the soil· Soil field capacity - the ratio of volume of water that a soil retains after a prolonged period of gravity drainage to total volume occupied by a soil.· Soil wilting point - the ratio of volume of water that a soil retains after plants can no longer extract water (thus the plants remain wilted) to total volume occupied by a soil.· Saturated hydraulic conductivity (cm/sec) - the rate at which water moves through soil in response to gravitational forces.<ul style="list-style-type: none">· The slope of the bottom of drainage layers (in percent)· Maximum horizontal drainage distance (in feet)

Modelling the Minnesota Waste Rock Pile

The waste rock pile is sited in northern Minnesota and the climate conditions for St. Cloud Minnesota were chosen. The pile has no topsoil layer. As shown in the diagram of the waste rock pile in figure 1, three layers were chosen:

1. A 380 cm (150 inch) waste rock layer, which is set as a vertical percolation layer. The hydraulic conductivity is 10 cm/s, porosity is 0.4, field capacity is 0.2, and wilting point is 0.1.
2. A 18 cm (7 inch) waste rock layer with the same properties as Layer 1 except that it is set as a lateral drainage layer. To do this, the layer was set upon a 5 ° slope. The actual pile slope is 1.4 °.
3. A 4.5 m (15 foot) native ground layer that was set to be a barrier soil layer. The hydraulic conductivity is 2×10^{-6} cm/sec, porosity is 0.4, field capacity is 0.31, and wilting point is 0.21. The actual piles are underlain by Hypalon® liners.

Layers 2 and 3 serve to cause the drainage to flow from the pile. The actual dimensions of 4.0 m (157 inches) by 13.7 m by 26.0 m (45 ft x 85 ft) for the pile and mass of 1100 metric tons were provided by Lapakko (1994). For the modelling calculations, the SCS runoff curve is set at 85.00, evaporation zone is 20.3 cm (8.00 inches), the total area of cover is 370 m² (4000 ft²).

Using these parameters in the HELP model produced a flow from the pile is 112 m³ / yr (3970 ft³ / yr) or 3.6×10^{-3} L / sec. The average sulfate release is 2.1 to 10.5 millimole SO₄²⁻ / metric ton / day or 2.6 to 13 x 10⁻⁶ kg SO₄²⁻ / sec. Division of the sulfate release by the flow gives a concentration of sulfate in the drainage of between 720 and 3600 mg / L.

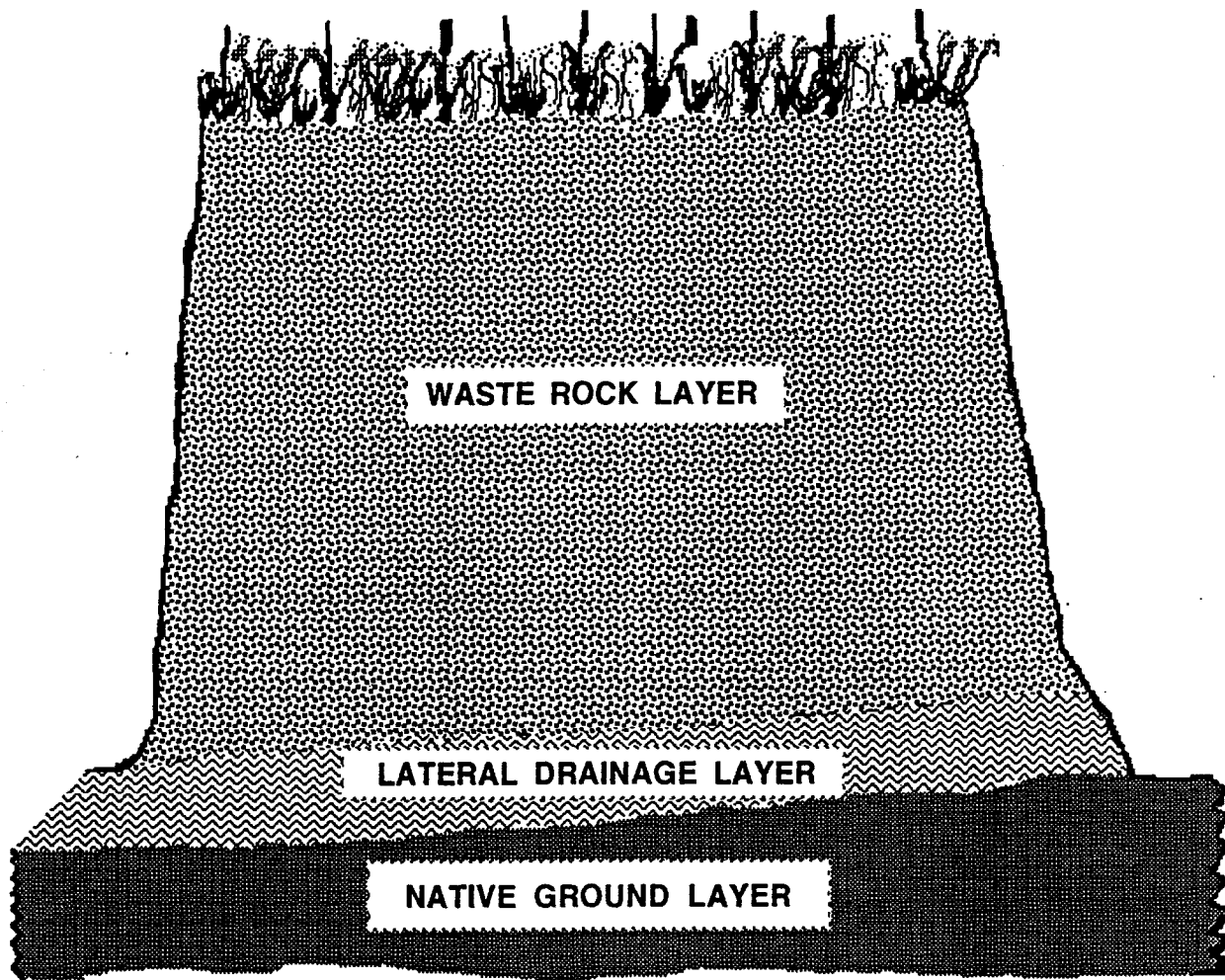


Figure 1. A schematic diagram of the northeastern Minnesota waste rock pile showing the layers used in the HELP model.

Lapakko (1994) reports a flow from the piles of between 0.27 and 0.38 L / mt of rock / day. Converting 112 m³ / yr (3970 ft³ / yr) to this scale gives a value of 0.28 L / mt of rock / day. Because the annual flow rate from the HELP model reasonably approximates the actual annual flow, the sulfate concentration values of between 720 and 3600 mg / L correlate well with the concentrations of 680 - 3800 mg / L over 1989 - 91 from the FL1 waste rock pile (Lapakko, 1994). These concentrations are at least a factor of 2 higher than the sulfate concentration values that Lapakko (1988) reported on humidity cell tests on similar waste rock samples. In more recent laboratory studies, Lapakko and Antonson (1993) found that laboratory release rates of sulfate were 3 to 10 times higher than the field release rates. Lapakko (1994) hypothesized a number of reasons for the differences between laboratory and field release rates, however there is not enough information to suggest a primary cause for the difference.

Effect of HELP Model Variables on Flow

Sensitivity of the flow rate of 112 m³ / yr (3970 ft³ / yr) to changes in many of the parameters shown in Table 1 were slight. Adding a top layer of plant growth medium of 5 inches thickness to act as a vertical percolation layer with a conductivity of 6 x 10⁻⁴ cm / sec had no effect on the amount of flow. Doubling the thickness of this layer also had no effect. Changing the slope of the lateral drainage layer did not affect the flow. Changing the field capacities, wilting point, and thicknesses of the other drainage layers likewise had little effect on the flow. Of course, changing the surface area of the pile while maintaining the same

volume, will change the amount of flow. This is the reason why the model has to be calibrated using an actual situation.

The one parameter that did appreciably change the flow is the amount of precipitation that falls upon the pile and this is a function of climate. This can be tested in the HELP model by "moving" the pile to different sites. To test the effect of climate, all the variables that were not default variables dependent upon the site were kept constant and the HELP model was run in a variety of cities to test the effect of climate. In this exercise, the SCS runoff curve of 85.00 was kept constant but the evaporative zone depth changed with the climate of the site. The predicted drainage flow in cubic feet per year and the ranges and average concentration of sulfate at different cities is given in Table 2. Cities in Table 2 are chosen because they:

1. Provide a diversity of climates,
2. Are near areas of coal or metals mining,
3. Have default historical precipitation data in HELP
4. Have default temperature and solar radiation in HELP.

The sulfate concentration values are comparable to some situations found in metal mining areas. Wildeman, Filipek, and Gusek (1994) report on an acid rock drainage from near Ely, NV. The water had a pH = 2.5 and a sulfate concentration of 3370 mg / L. This is within the range for the Ely site. Wildeman et al. (1994) also report on drainage from a closed gold mine in northern California near Sacramento. It had an average pH of 3.8 and an average sulfate concentration of 2800 mg / L. On the other hand, sulfate concentrations can be quite a bit higher than the Table 2 ranges. In eastern U.S., Gusek, Gormley, and Scheetz (1994) report on the acid rock drainage chemistry from a gold mine near Jefferson, South Carolina that is undergoing closure. The climate is similar to that in Knoxville, TN. For waters that range from pH 2.3 to 2.5, the sulfate concentrations range from 2500 to 3300 mg/L. On the highest side in western US, Alpers and Nordstrom (1991) report that the drainage from the Richmond portal at Iron Mountain, CA near Sacramento has a pH of 0.5 and sulfate concentration of 120,000 mg / L. All the sites mentioned are areas where the oxidation of sulfidic minerals is vigorous enough to lower the pH of the drainage to values below 5, the situation that prevails for the Minnesota waste rock piles (Lapakko, 1994).

Table 2. Yearly flow and ranges and averages of sulfate concentrations from the northeastern Minnesota waste rock pile placed in different sites in the United States.

Geographic Site	Yearly drainage ft ³ / year	Sulfate Conc. Range mg / L	Average Sulfate Conc. mg / L
St. Cloud, MN	3970	720 - 3600	2200
Cheyenne, WY	1470	1940 - 9600	5800
Des Moines, IA	5400	530 - 2600	1600
East St. Louis, IL	6200	460 - 2300	1370
Ely, NV	980	2900 - 14,400	8700
Great Falls, MT	2700	1010 - 5300	3200
Knoxville, TN	8800	330 - 1610	970
Miami, FL	7570	380 - 1860	1120
New Orleans, LA	12,430	230 - 1130	680
Phoenix, AZ	1259	2300 - 11,200	6800
Pittsburgh, PA	6500	440 - 2200	1300
Providence, RI	9430	300 - 1500	900
Sacramento, CA	3000	940 - 4700	2800
San Diego, CA	2365	1200 - 6000	3600
Seattle, WA	7900	360 - 1800	1080

Effect of Other Oxidation Rates on Sulfate Concentrations

Attempts were made to use the published oxidation rate of Bennett and others (1994) of 10^{-8} kg O₂ / m³ of waste rock / sec. In this case, the rate of oxidation is based on oxygen consumption and the amount of sulfate generated is assumed to be based on the pyrite oxidation reaction. Also in this case, oxidation on a volume basis has to be transformed to a mass basis by assuming that the in-place density of rock in the pile is 1.4 gm / cm³. Using these values for a waste rock pile of 1100 mt, gives a sulfate generation rate of 14×10^{-6} kg SO₄²⁻ / sec. This rate would give sulfate concentrations at the high end of the ranges shown in Table 2. In their study, Bennett and others (1994) found that an intrinsic oxidation rate of 10^{-8} kg O₂ / m³ of waste rock / sec was high and made the suggestion that only 14 % of the pile would contribute to the pollution load and the remaining 86 % would contribute little. Considering the high concentration of sulfate that this oxidation rate produces, this suggestion appears reasonable.

Conclusions

In this study, our expectations were to be within the range of sulfate concentrations usually associated with waste rock drainages. In this respect, we met with some success. To the extent that this approach is reasonable, it implies that in considering the causes of waste rock drainage, the primary factors are the amount of water flowing through the pile and the access of oxygen to the inside of the pile. Factors such as mineralogy, the abundance of sulfur, and the flow of water through the pile have a secondary impact. In considering the pyrite oxidation reaction, there are three reactants: pyrite, oxygen, and water. In most instances, oxygen is the limiting reactant and controls the kinetics of the reaction.

With respect to treatment activities, design of the waste rock pile to only minimize flow through the interior will decrease the flow but not decrease the loading. Consequently, the flow will be lower, and the sulfate concentration correspondingly higher. To decrease loading, oxygen access to the interior must be reduced. Gibson, Pantelis, and Bennett (1994) and Hammack and Watzlaf (1990) both suggest that until the atmospheric oxygen concentration falls below 1 %, the rate of oxidation is constant. Elimination of oxygen in the interior of the pile can be accomplished by sealing off the pile or by reacting the oxygen with some other material. If a top-cover is added to the pile that not only eliminates water but also cuts oxygen delivery to the interior of the pile, then addition of a cover may help to eliminate acidic drainage. James Gusek (personal communication) has long advocated the addition of organic material to the top-cover of a waste rock pile. If such a layer consumed the oxygen through oxidation of the organic material then this would be an example of having the oxygen react with another material. Both the addition of a cover to retain water and block oxygen diffusion and the addition of organic material to consume the remaining oxygen have been included in the design of a cover for the closure of a tailings pile in a mountainous region in western United States. This cover is described by Wildeman and others (1994) in another article in this proceedings.

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DESIGN OF A TAILING LINER AND COVER TO MITIGATE POTENTIAL ACID ROCK DRAINAGE: A GEOCHEMICAL ENGINEERING PROJECT¹

Thomas Wildeman², James J. Gusek³, Donald R. East³, and Adriaan de Villiers³

Abstract: In design for closure of a mining facility, both the physical and chemical factors that lead to the desired result should be taken into account. In mining operations, this usually entails flow of water through rocks, soils, or tailing material and chemical reactions of these solid materials with the water. Design and problem solving associated with water - rock - soil interactions can be considered geochemical engineering. These principles were applied to the recent design of a tailing facility to be placed in a mountainous region of western United States where there is an excess of net precipitation. Because the tailing material gave all indications that it would be acid producing, the design issue was to build the facility and reclamation cap to eliminate oxidation and thereby mitigate potential acid production by sulfide minerals. It was assumed that some small amount of underdrainage would occur and the liner design emphasized complete collection of this water and discharge through the foot of the dam into a monitoring sump. Special considerations in the design of the geomembrane liner included providing a cushion for construction equipment, and protection from damage by freezing and UV radiation. Because the underdrain water may require some treatment, special provisions were made to separate the water flowing across the tailing system from that flowing from the underdrain. Operation and closure of the facility is based on subaqueous deposition and storage. The reclamation cap design maintains saturated tailing without a permanent lake. Rather, a permanent water table is maintained near surface and above the tailing, within the multi-layered reclamation cap. To affect surface runoff, a mild sloping final surface was designed with a wetland along the center of the facility for flow control. The water level would be maintained above an organic rich soil layer that would facilitate removal of all dissolved oxygen. Careful control of the hydraulic conductivity of the soil layers in the reclamation cap will help to maintain greater flow of direct precipitation and run-on from an adjacent hillside across the cap instead of vertical flow through the tailings. What little water that does reach the tailings will geochemically interact with the reclamation cap soils such that all oxygen is removed. Acid production from the tailings would thus be minimized.

Additional Key Words: tailing closure, subaqueous closure, sulfidic ores

Geochemical Engineering

To understand geochemical engineering, it is useful to establish the distinction between science and engineering. A simplified explanation based on what people do is that scientists ask and answer questions and engineers solve problems or design products, structures, processes, or systems. In this context, geochemical engineering applies chemistry to design and problem solving situations related to earth structures or processes involving earth structures. Based on this definition, geochemical engineering is obviously related to geological engineering, mineral process engineering, environmental engineering, and mining engineering.

Because of this relationship with so many other fields, the idea of using geochemical engineering in this paper is not a promotion for a new field, but more a call for people in existing fields of engineering to expand their knowledge base for design and problem solving. Besides dealing with earth structures, there do appear to be other elements essential to this area of engineering. First, water is present and usually flowing through or around the structure. Second, chemistry is involved in the extraction, treatment, or passivation of some natural resource that is in contact with the water.

Besides these essential elements, there are other aspects of this field that often describe the problem or design issue. Because earth structures are involved, there are often inherent co-dependencies and ambiguities in the project that have to be considered. This ambiguity is particularly true when the project involves the design of some process. In other areas of process engineering, complete control of the situation is assumed to be an essential to design. Also, geochemically

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²Thomas R. Wildeman, Professor, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO, 80401 (303) 273-3642

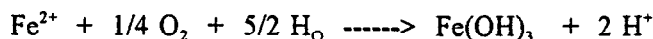
³Donald R. East, Principal, James Gusek, Senior Engineer, Adriaan de Villiers, Senior Engineer, Knight Piesold & Co., Denver, Co (303) 629-8788

The authors realize that the approach applied in this paper is overly simplistic. Basing water chemistry only on an average groundwater flow and a single sulfate generation rate ignores many of the specific physical and chemical influences in waste rock piles. However, this approach can be applied quickly and inexpensively to obtain a "first cut" estimate of waste rock drainage quality. Furthermore, this approach may reveal the relative importance of specific physical and chemical processes on drainage quality, and thereby identify directions for future work.

The modelling concentrates on sulfate generation because it is a primary product in the first step of pyrite oxidation, which is the primary cause of acid mine drainage.



In addition, until the concentration of calcium is high enough for gypsum precipitation, sulfate will generally not be precipitated or adsorbed. Consequently, its concentration in the water is the best indication of the level of pyrite oxidation. Finally, knowing the sulfate concentration provides a good estimate of the total acidity generated through pyrite oxidation even though the water may have been subsequently neutralized. Two moles of hydrogen ions and one mole of Fe^{2+} are released for every two moles of sulfate released. Eventually, the Fe^{2+} will oxidize and precipitate.



This produces two more moles of hydrogen ions so that one mole of sulfate released from pyrite is associated with two moles of eventual acidity. The combination of these three facts makes knowing the amount of sulfate generated as an excellent way to measure the general chemical nature of an acid rock drainage.

From a regulatory point of view, a reasonably reliable prediction of the amount of acidity in the drainage from a waste rock pile would be a useful tool in designing a plan for operation and closure of a mine. How the chemistry of mine drainage is affected by changes in climate, particularly the amount of precipitation, is also an interesting question. Finally, if sulfate is one of the constituents measured in a humidity cell test, then an average sulfate generation rate can be determined from that test (Lapakko, 1988, 1994). Linking that laboratory sulfate generation rate with a physical flow model can give predictions on the chemistry of the drainage from a planned waste rock pile. When this is done, the question will be just how well do those predictions estimate the actual chemistry of the water.

Sulfate generation rates have been published by a few research groups who have extensively studied specific waste rock piles. Since 1978, Lapakko (1994) has been studying waste rock piles in northern Minnesota. Based on field data, he has estimated that the sulfate release rate in these piles is between 2.1 and 10.5 millimol SO_4^- / metric ton / day. Bennett and others (1994) studied a waste rock dump in Australia and found the intrinsic oxidation rate to be about 10^{-8} kg O_2 / m^3 of waste rock / sec. However the values of sulfate generated did not correlate with the oxidation rate. They estimated 14 % of the dump would contribute pollution loads at this rate of oxidation and the remaining 86 % would contribute little to the total pollution load. Gibson, Pantelis, and Ritchie (1994) have used the Australian oxidation rate data to estimate the evolution of drainage chemistry from a pyritic waste rock dump. In their study, they suggest that the oxidation rate is independent of oxygen and sulfur concentrations as long as neither is zero. For microbiologically controlled oxidation, the result that pyrite oxidation is independent of oxygen, when the amount of oxygen in the atmosphere is above 1 %, has been verified in the laboratory by Hammack and Watzlaf (1990). If the oxidation rate is somewhat independent of oxygen and sulfur concentrations, then the generation of acid mine drainage would be somewhat independent of these variables.

Another parameter that is important to the outflow of drainage is transport of the water through the waste rock pile. Snyder and Caruccio (1988) and Wildeman (1991) have found evidence that suggests that, in the field, the release of acid rock drainage is kinetically controlled. It appears that the pyrite weathering

products are retained in microfaults above the water table where the oxidation reaction is most favored. Then, this water is released from the faults when recharge of the ground water in the waste rock pile occurs. If the pile is large enough to maintain somewhat constant outflow, then the chemistry of the acid rock drainage will not change substantially with the seasons or precipitation events (Wildeman, 1991). If this evidence is correct, then the flow of recharge water to reaction sites is limited. In this study, it is also assumed that there is no production or consumption of sulfate during flow to the outlet.

If the above assumptions concerning the generation and release of sulfate are plausible, then linking a physical flow model with a gross oxidation rate should give a reasonable estimate of the amount of pollution. The HELP model used on landfills has been extensively applied to the flow of water through such situations (Schroeder, et al., 1992a, 1992b). The objective of our study has been to estimate flow from the waste rock pile using the HELP model. With this flow value and the sulfate generation rate, the concentration of sulfate in mg/L can be determined. Two additional assumptions made in the calculation are:

1. The concentration of calcium in the drainage is low enough that gypsum solubility does not control the concentration of sulfate.
2. From a chemical viewpoint, the pile is homogeneous and oxidation is equally likely at any place in the pile.

Correlation of this concentration with values from waste rock drainages provides the following insights:

1. If the modelled concentration values are far different from reported values, then generation of acid rock drainage may be much more complex. Further physical and chemical studies will be necessary to understand the process.
2. There may be certain parameters in the HELP model that drastically affect the amount of water flowing from the pile. Can these parameters be used to control the generation of acid mine drainage?
3. The HELP model can be adjusted for different climates and geographies. How does this affect the quality of drainage flowing from the waste rock pile?

The present study focuses on sulfate concentrations in drainage from test piles of Duluth Complex rock in northeastern Minnesota. The sulfate in drainage from these piles is primarily the result of pyrrhotite oxidation (Lapakko, 1994). The annual drainage volume predicted by the HELP model agrees well with reported values (Lapakko, 1994). Given this agreement, HELP model parameters were varied to investigate the influence of these variations on flow and, consequently, predicted sulfate concentrations in the drainage. Finally, the effect of climatic setting on sulfate concentrations was investigated.

HELP Model Considerations

The HELP model is an appropriate simulation for waste rock embankments because it accounts for the hydraulic characteristics of placed materials within unique layers based on physical properties such as permeability, soil moisture capacities, and drainage layer configurations. The model allows the pile to contain up to twelve different layers of materials each with its own characteristics. It also allows the user to select the location of the site, the only restriction being that must be located in the United States for the user to take advantage of the data base that comes with the program. From the data base in HELP, comes the precipitation, growing season, evaporative zone, and maximum leaf index data characteristic for that specific area. The data base includes major cities from all 50 states, however, modifications are possible for remote locations or another site around the world. Table 1 presents the HELP parameters that can be fixed by default and those that must be selected.

Once these data have been entered, the program uses this information to provide the amount of water in cubic feet per year that will percolate through the pile. The amount of percolation will primarily depend on the number of layers, the hydraulic conductivity of these layers, and the amount of rainfall. In addition,

flow will also depend on other parameters included in the program. In this study, what flows from the pile is the acid rock drainage.

Table 1. Parameters capable of adjustment in the HELP Model

<p style="text-align: center;">Parameters That Can be Set by Choosing a Default Site</p> <ul style="list-style-type: none">· Yearly precipitation· Growing season· Evaporative zone depth· Maximum leaf index data· Mean solar insolation in langleys· Mean monthly temperature
<p style="text-align: center;">Parameters Set by Each Situation</p> <ul style="list-style-type: none">· Area of the waste rock pile· Number of soil (rock) layers and thickness of each layer· Soil conservation System (SCS) curve number for the uppermost soil layer<ul style="list-style-type: none">· Type of layers (vertical percolation, lateral drainage, or barrier soil)· Soil porosity - the ratio of the volume of voids to total volume occupied by the soil· Soil field capacity - the ratio of volume of water that a soil retains after a prolonged period of gravity drainage to total volume occupied by a soil.· Soil wilting point - the ratio of volume of water that a soil retains after plants can no longer extract water (thus the plants remain wilted) to total volume occupied by a soil.· Saturated hydraulic conductivity (cm/sec) - the rate at which water moves through soil in response to gravitational forces.<ul style="list-style-type: none">· The slope of the bottom of drainage layers (in percent)· Maximum horizontal drainage distance (in feet)

Modelling the Minnesota Waste Rock Pile

The waste rock pile is sited in northern Minnesota and the climate conditions for St. Cloud Minnesota were chosen. The pile has no topsoil layer. As shown in the diagram of the waste rock pile in figure 1, three layers were chosen:

1. A 380 cm (150 inch) waste rock layer, which is set as a vertical percolation layer. The hydraulic conductivity is 10 cm/s, porosity is 0.4, field capacity is 0.2, and wilting point is 0.1.
2. A 18 cm (7 inch) waste rock layer with the same properties as Layer 1 except that it is set as a lateral drainage layer. To do this, the layer was set upon a 5 ° slope. The actual pile slope is 1.4 °.
3. A 4.5 m (15 foot) native ground layer that was set to be a barrier soil layer. The hydraulic conductivity is 2×10^{-6} cm/sec, porosity is 0.4, field capacity is 0.31, and wilting point is 0.21. The actual piles are underlain by Hypalon® liners.

Layers 2 and 3 serve to cause the drainage to flow from the pile. The actual dimensions of 4.0 m (157 inches) by 13.7 m by 26.0 m (45 ft x 85 ft) for the pile and mass of 1100 metric tons were provided by Lapakko (1994). For the modelling calculations, the SCS runoff curve is set at 85.00, evaporation zone is 20.3 cm (8.00 inches), the total area of cover is 370 m² (4000 ft²).

Using these parameters in the HELP model produced a flow from the pile is 112 m³ / yr (3970 ft³ / yr) or 3.6×10^{-3} L / sec. The average sulfate release is 2.1 to 10.5 millimole SO₄⁻ / metric ton / day or 2.6 to 13×10^{-6} kg SO₄⁻ / sec. Division of the sulfate release by the flow gives a concentration of sulfate in the drainage of between 720 and 3600 mg / L.

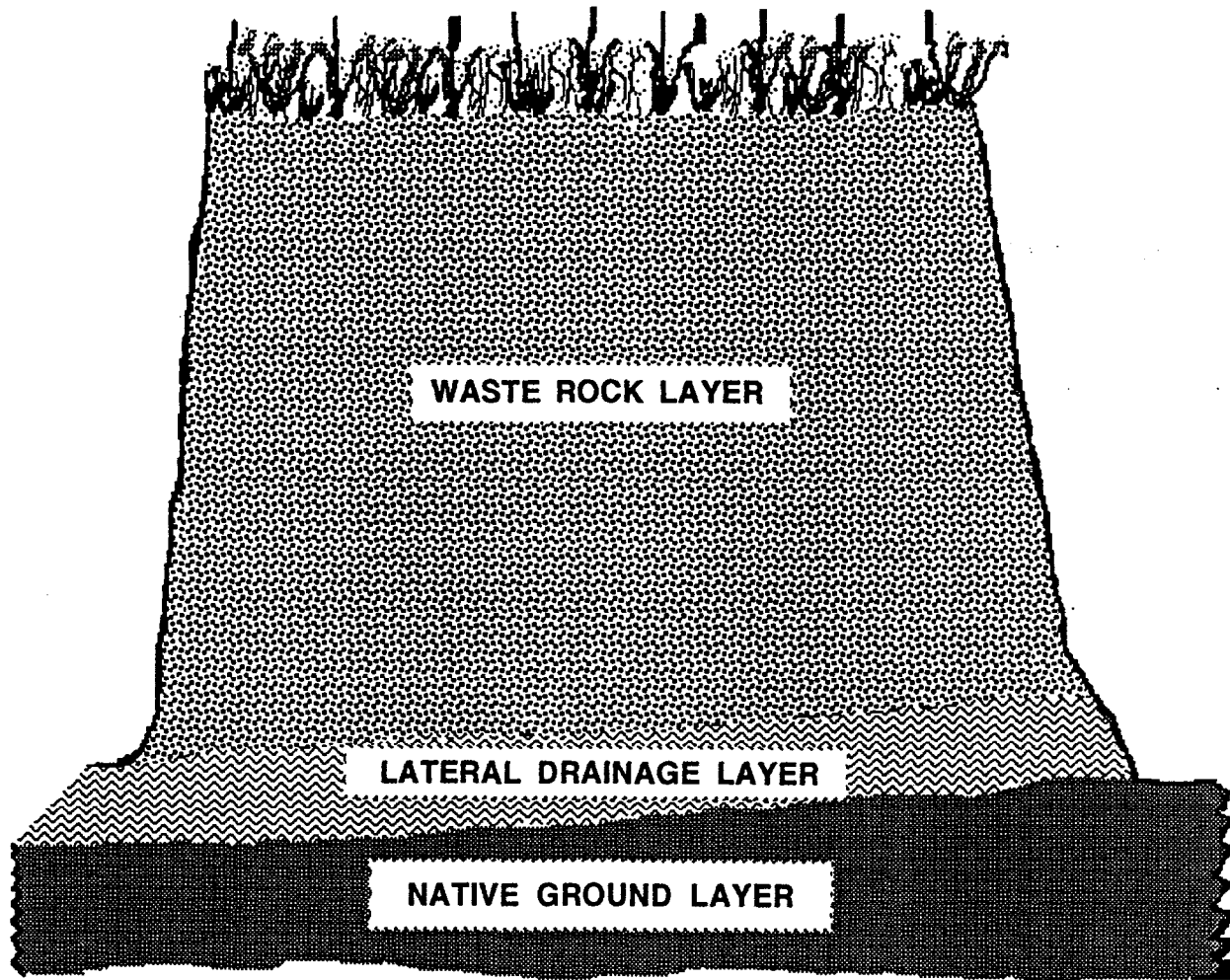


Figure 1. A schematic diagram of the northeastern Minnesota waste rock pile showing the layers used in the HELP model.

Lapakko (1994) reports a flow from the piles of between 0.27 and 0.38 L / mt of rock / day. Converting 112 m³ / yr (3970 ft³ / yr) to this scale gives a value of 0.28 L / mt of rock / day. Because the annual flow rate from the HELP model reasonably approximates the actual annual flow, the sulfate concentration values of between 720 and 3600 mg / L correlate well with the concentrations of 680 - 3800 mg / L over 1989 - 91 from the FL1 waste rock pile (Lapakko, 1994). These concentrations are at least a factor of 2 higher than the sulfate concentration values that Lapakko (1988) reported on humidity cell tests on similar waste rock samples. In more recent laboratory studies, Lapakko and Antonson (1993) found that laboratory release rates of sulfate were 3 to 10 times higher than the field release rates. Lapakko (1994) hypothesized a number of reasons for the differences between laboratory and field release rates, however there is not enough information to suggest a primary cause for the difference.

Effect of HELP Model Variables on Flow

Sensitivity of the flow rate of 112 m³ / yr (3970 ft³ / yr) to changes in many of the parameters shown in Table 1 were slight. Adding a top layer of plant growth medium of 5 inches thickness to act as a vertical percolation layer with a conductivity of 6 x 10⁻⁴ cm / sec had no effect on the amount of flow. Doubling the thickness of this layer also had no effect. Changing the slope of the lateral drainage layer did not affect the flow. Changing the field capacities, wilting point, and thicknesses of the other drainage layers likewise had little effect on the flow. Of course, changing the surface area of the pile while maintaining the same

volume, will change the amount of flow. This is the reason why the model has to be calibrated using an actual situation.

The one parameter that did appreciably change the flow is the amount of precipitation that falls upon the pile and this is a function of climate. This can be tested in the HELP model by "moving" the pile to different sites. To test the effect of climate, all the variables that were not default variables dependent upon the site were kept constant and the HELP model was run in a variety of cities to test the effect of climate. In this exercise, the SCS runoff curve of 85.00 was kept constant but the evaporative zone depth changed with the climate of the site. The predicted drainage flow in cubic feet per year and the ranges and average concentration of sulfate at different cities is given in Table 2. Cities in Table 2 are chosen because they:

1. Provide a diversity of climates,
2. Are near areas of coal or metals mining,
3. Have default historical precipitation data in HELP
4. Have default temperature and solar radiation in HELP.

The sulfate concentration values are comparable to some situations found in metal mining areas. Wildeman, Filipek, and Gusek (1994) report on an acid rock drainage from near Ely, NV. The water had a pH = 2.5 and a sulfate concentration of 3370 mg / L. This is within the range for the Ely site. Wildeman et al. (1994) also report on drainage from a closed gold mine in northern California near Sacramento. It had an average pH of 3.8 and an average sulfate concentration of 2800 mg / L. On the other hand, sulfate concentrations can be quite a bit higher than the Table 2 ranges. In eastern U.S., Gusek, Gormley, and Scheetz (1994) report on the acid rock drainage chemistry from a gold mine near Jefferson, South Carolina that is undergoing closure. The climate is similar to that in Knoxville, TN. For waters that range from pH 2.3 to 2.5, the sulfate concentrations range from 2500 to 3300 mg/L. On the highest side in western US, Alpers and Nordstrom (1991) report that the drainage from the Richmond portal at Iron Mountain, CA near Sacramento has a pH of 0.5 and sulfate concentration of 120,000 mg / L. All the sites mentioned are areas where the oxidation of sulfidic minerals is vigorous enough to lower the pH of the drainage to values below 5, the situation that prevails for the Minnesota waste rock piles (Lapakko, 1994).

Table 2. Yearly flow and ranges and averages of sulfate concentrations from the northeastern Minnesota waste rock pile placed in different sites in the United States.

Geographic Site	Yearly drainage ft ³ / year	Sulfate Conc. Range mg / L	Average Sulfate Conc. mg / L
St. Cloud, MN	3970	720 - 3600	2200
Cheyenne, WY	1470	1940 - 9600	5800
Des Moines, IA	5400	530 - 2600	1600
East St. Louis, IL	6200	460 - 2300	1370
Ely, NV	980	2900 - 14,400	8700
Great Falls, MT	2700	1010 - 5300	3200
Knoxville, TN	8800	330 - 1610	970
Miami, FL	7570	380 - 1860	1120
New Orleans, LA	12,430	230 - 1130	680
Phoenix, AZ	1259	2300 - 11,200	6800
Pittsburgh, PA	6500	440 - 2200	1300
Providence, RI	9430	300 - 1500	900
Sacramento, CA	3000	940 - 4700	2800
San Diego, CA	2365	1200 - 6000	3600
Seattle, WA	7900	360 - 1800	1080

Effect of Other Oxidation Rates on Sulfate Concentrations

Attempts were made to use the published oxidation rate of Bennett and others (1994) of 10^{-8} kg O₂ / m³ of waste rock / sec. In this case, the rate of oxidation is based on oxygen consumption and the amount of sulfate generated is assumed to be based on the pyrite oxidation reaction. Also in this case, oxidation on a volume basis has to be transformed to a mass basis by assuming that the in-place density of rock in the pile is 1.4 gm / cm³. Using these values for a waste rock pile of 1100 mt, gives a sulfate generation rate of 14×10^{-6} kg SO₄²⁻ / sec. This rate would give sulfate concentrations at the high end of the ranges shown in Table 2. In their study, Bennett and others (1994) found that an intrinsic oxidation rate of 10^{-8} kg O₂ / m³ of waste rock / sec was high and made the suggestion that only 14 % of the pile would contribute to the pollution load and the remaining 86 % would contribute little. Considering the high concentration of sulfate that this oxidation rate produces, this suggestion appears reasonable.

Conclusions

In this study, our expectations were to be within the range of sulfate concentrations usually associated with waste rock drainages. In this respect, we met with some success. To the extent that this approach is reasonable, it implies that in considering the causes of waste rock drainage, the primary factors are the amount of water flowing through the pile and the access of oxygen to the inside of the pile. Factors such as mineralogy, the abundance of sulfur, and the flow of water through the pile have a secondary impact. In considering the pyrite oxidation reaction, there are three reactants: pyrite, oxygen, and water. In most instances, oxygen is the limiting reactant and controls the kinetics of the reaction.

With respect to treatment activities, design of the waste rock pile to only minimize flow through the interior will decrease the flow but not decrease the loading. Consequently, the flow will be lower, and the sulfate concentration correspondingly higher. To decrease loading, oxygen access to the interior must be reduced. Gibson, Pantelis, and Bennett (1994) and Hammack and Watzlaf (1990) both suggest that until the atmospheric oxygen concentration falls below 1 %, the rate of oxidation is constant. Elimination of oxygen in the interior of the pile can be accomplished by sealing off the pile or by reacting the oxygen with some other material. If a top-cover is added to the pile that not only eliminates water but also cuts oxygen delivery to the interior of the pile, then addition of a cover may help to eliminate acidic drainage. James Gusek (personal communication) has long advocated the addition of organic material to the top-cover of a waste rock pile. If such a layer consumed the oxygen through oxidation of the organic material then this would be an example of having the oxygen react with another material. Both the addition of a cover to retain water and block oxygen diffusion and the addition of organic material to consume the remaining oxygen have been included in the design of a cover for the closure of a tailings pile in a mountainous region in western United States. This cover is described by Wildeman and others (1994) in another article in this proceedings.

Acknowledgement

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PROOF-OF-PRINCIPLE STUDIES FOR PASSIVE TREATMENT OF ACID ROCK DRAINAGE AND MILL TAILING SOLUTIONS FROM A GOLD OPERATION IN NEVADA¹

Thomas R. Wildeman^{2,3}, Lorraine H. Filipek^{2,4}, and James Gusek⁴

Abstract: Laboratory investigations were conducted to determine "in principle" whether passive treatment is a reasonable option for two water types produced by a surface gold operation in Nevada. One water was acid rock drainage (ARD) containing elevated arsenic and selenium. Arsenic was reduced first by allowing Fe(OH)₃ to form and then adsorbing anionic arsenic onto the positively charged precipitate. Then, all heavy metals, arsenic, and selenium were removed to within drinking water standards in bottle studies that promoted sulfate reduction at room temperature for 5 weeks. The second water type was underdrainage and seepage from a mill tailing pond containing elevated cyanide, nitrate, ammonia, copper, mercury, and selenium. The pH of the solutions was about 8, and the tailing underdrain solution contained greater concentrations of contaminants than the seepage. Both anaerobic and aerobic static tests were conducted at room temperature for 5 weeks. The aerobic tests were successful in reducing cyanide, ammonia, nitrate, copper, mercury, and selenium. Arsenic was reduced if soil as well as algae was present. In the anaerobic tests, cyanide, nitrate, copper, mercury, and selenium were reduced, whereas ammonia and arsenic were either unaffected or increased. The results of the laboratory tests were used to design a settling pond-anaerobic-aerobic passive system for the acid rock drainage and an aerobic passive system for the underdrainage and seepage. The pilot-scale ARD system and the aerobic algal pond for the tailing water were recently constructed to confirm the laboratory results.

Additional Key Words: Heavy metals, arsenic, selenium, cyanide, nitrate, ammonia, passive treatment, constructed wetlands

Introduction

Passive treatment methods that rely on aerobic reactions have been used to treat acid rock drainages (ARD) from coal mines. When the water has an initial pH greater than 5.5 and also has net alkalinity, aerobic constructed wetlands that precipitate iron hydroxides can be effective (Wildeman, Brodie, and Gusek 1993). Some ARD, especially that associated with metal mines, has a lower pH and higher concentrations of iron and other heavy metals. This type of water requires anaerobic passive treatment (Hedin and Nairn 1990). The anaerobic systems rely on bacterially mediated precipitation of metal sulfides.

Currently, little information exists on the ability of passive systems to treat (1) ARD that contains arsenic and/or selenium in concentrations above the Federal drinking water standards or (2) alkaline pH drainage containing low levels of cyanide. Both of these water types have been associated with gold mining operations in the arid regions of the Western United States. High arsenic and selenium concentrations in water are common in arid regions because these elements are more soluble in the natural alkaline and saline waters associated with this type of environment (Jacobs 1989). Additionally, alteration of rocks associated with gold mineralization often produces elevated concentrations of arsenic in ground water. Cyanide and alkaline waters are the products of mineral processing methods that are used to extract gold from ore (van Zyl 1984).

This study presents the results of two laboratory investigations conducted to determine "in principle" whether passive treatment is a reasonable option for these two water types. Both water types were collected from a surface gold mine operation in Nevada where closure is being considered within the decade. The laboratory investigations were the first stage in the investigation of passive systems suitable for closure.

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²Knight Piesold and Co., 1600 Stout St. Suite 800, Denver CO 80202, (303) 629-8788.

³Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401, (303) 273-3642 FAX (303) 273-3629, Geochemistry Program Paper No. 003.

⁴Now at the U. S. Geological Survey, M.S. 972, Box 25046, Denver, CO 80225, (303) 236-7726.

Table 1. Substrates and waters used for the laboratory study.

Substrates used for waste rock drainage		Substrates used for tailings drainage	
Code	Composition	Code	Composition
MLI-B	3/4 M, 1/4 L, 10 g I-B	SI-T	1/2 S, 1/2 I-T
SMLI-B	1/2 S, 1/3 M, 1/6 L	SMI-T	1/2 S, 5/12 M, 1/12 I-T
L	100% L	I-T	100% I-T
H-M	100% H-M	A	100% A
H-J	100% H-J		C-M
100%	C-M	AS	1/3 A, 2/3 S

SUBSTRATE KEY

Substrate Code	Inoculum Code
M = Manure	I-B = Inoculum from Big Five Wetland
I = Limestone	H-M = Horse Manure
S = Mine site soil	H-J = Horse juice
A = Algal solution from seepage pond	C-M = Cow manure
	I-T = Anaerobic slime from seepage pond

WATER KEY

Waste Rock-Drainage		Tailings Water	
Code	Description	Code	Description
#1	Drainage from old waste rock dump issuing from Pipe 1, pH = 2.7	CP	Water from seepage pond taken from the pump outlet to insure a mixture of all sources
#2	Drainage from toe of waste rock pile issuing from Pipe 2, pH = 4.1	U	Water from tailings underdrain collected at the inlet pump into the storage pond
#3	Drainage from new waste rock pile issuing from Pipe 3, pH = 4.7	MX	A mix of 100 volumes of underdrain water to 15 volumes of seepage pond water to simulate water stored in the lined pond
1-2-3	A mix of waters from pipes 1, 2 and 3 in a ratio of 3-1: 3-2: 1-1 to simulate fresh pond water		

In the first case, water tested is ARD from a waste rock pile that contains water with concentrations of iron, arsenic, and selenium as high as 600, 10, and 1 mg/L, respectively. This drainage is presently being collected in a lined settling pond and is subsequently pumped to an alkaline milling process circuit. The drainage is intercepted and transported to the settling pond in three pipes, in volume ratios of three parts pipe 1, three parts pipe 2, and one part pipe 3. The ARD from pipe 1 had the lowest pH and a distinctive red color that was suspended $\text{Fe}(\text{OH})_3$ that settled out upon aging for approximately 16 h.

The other water type is underdrainage and seepage from a drained mill tailing facility receiving cyanide effluents. The underdrainage contains concentrations of cyanide, nitrate, ammonia, mercury, arsenic, and selenium in excess of Federal drinking water standards. The seepage has lower concentrations of cyanide, associated nitrogen compounds, and metals than the underdrainage, which suggests that it has undergone some treatment by natural processes. The underdrainage and seepage are currently collected in ponds and reused in the gold extraction process.

The primary goals of the "proof-of-principle" experiments were (1) to determine the best types of microbial ecosystems to remove As and Se in both acidic and alkaline waters and (2) to determine whether aerobic, anaerobic, or a combination of processes is the most effective passive treatment method for the tailing drainages. Secondary objectives were to (1) determine local sources of sulfate-reducing bacteria (SRB) and bacteria and/or algae capable of

Table 2. Waste rock drainage test bottles - all bottles are anaerobic.

Bottle ¹	Substrate code	Substrate amount, g	Water Code	Water amount, mL	Inoculum	Inoculum amount, g
1	MLI-B	60	#1	60	I-B	10
2(1)	MLI-B	60	#1	60	I-B	10
3	MLI-B	40	#1	80	I-B	10
4	SMLI-B	60	#1	60	I-B	10
5	SMLI-B	40	#1	80	I-B	10
6	H-M	50	#1	60	H-M	50
7	H-J	60	#1	60	H-J	60
8	C-M	60	#1	60	C-M	60
9	L	30	#1	100	None used	NAP ²
10	None used	NAP ²	#1	100	None used	NAP
11	MLI-B	40	#3	80	I-B	10
12	SMLI-B	60	#3	60	I-B	10
13	SMLI-B	40	#3	80	I-B	10
14(13)	SMLI-B	40	#3	80	I-B	10
15	None used	NAP	#3	100	None used	NAP
16	L	30	#3	100	None used	NAP
17	MLI-B	40	1-2-3	80	I-B	10
18(17)	MLI-B	40	1-2-3	80	I-B	10
19	SMLI-B	60	1-2-3	60	I-B	10
20	SMLI-B	40	1-2-3	80	I-B	10
21	H-M	50	1-2-3	60	H-M	50
22	H-J	60	1-2-3	60	H-J	60
23	C-M	60	1-2-3	60	C-M	60
24	None used	NAP	1-2-3	100	None used	NAP

¹Bottle Numbers in parentheses designate duplicates.

²NAP means not applicable

degrading cyanide and associated nitrogen species and (2) develop a mix of organic and inorganic materials (labeled "substrates") that would promote the appropriate microbial activity. The anaerobic tests were patterned after those performed by Reynolds et al. (1991), and the aerobic tests were patterned after those of Duggan et al. (1992).

Collection of Materials

Waste rock ARD and tailing drainages, materials for substrates, and inoculum candidates were collected in May 1992. Individual samples of ARD were collected from each of the three pipes draining into the settling pond. Because any future passive treatment system would treat the settling pond water, a 3-3-1 by volume composite of the ARD waters from the three pipes was made (labeled "1-2-3") and used in some of the bottle tests. Tailing underdrain water and seepage from the tailing dam were also sampled individually. Currently, the ratio of tailing underdrain water to seepage is about 100 to 15. One closure option is to treat this mixed water. Accordingly, a mix of 100 volumes of underdrain water to 15 volumes of seepage water was made (MX) and used in some of the bottle tests.

Table 1 provides a key to the various substrate and inoculum materials that were gathered. Inocula for SRB were collected at a cattle feedlot. Typically, the best sources for SRB bacteria are fresh, wet manure and the mucky places in a feedlot or farm. On this feedlot, all the manure was quite dry. The only mucky place was the area around the watering trough for the horses. In table 1, this muck is labeled "horse juice."

The tailing seepage pond contained abundant floating algae and a blackish anaerobic slime in the sediments. These materials were collected to serve as aerobic and anaerobic inocula, respectively, for the tailing drainage tests because they were expected to contain microbes already acclimated to cyanide and metals (Duggan, et al. 1992, Wildeman, et al. 1993). For most of the other bottles in the anaerobic study, SRB inoculum from the Big Five Pilot Wetlands (Wildeman, Brodie, and Gusek 1993) was used.

Table 3. Tailing water test bottles.

Bottle ¹	Substrate code	Substrate amount	Water code	Water amount, mL	Inoculum	Inoculum amount	Aerobic
25	SI-T	60 g	CP	60	I-T	30 g	No
26	SMI-T	50 g	CP	80	I-T	5 g	No
27(26)	SMI-T	50 g	CP	80	I-T	5 g	No
28	None used	NAP ²	CP	100	None used	NAP	No
29	I-T	30 g	CP	100	I-T	30 g	No
30	SI-T	60 g	U	60	I-T	30 g	No
31(30)	SI-T	60 g	U	60	I-T	30 g	No
32	SMI-T	50 g	U	80	I-T	5 g	No
33	None used	NAP	U	100	None used	NAP	NAP
34	I-T	30 g	U	100	I-T	30 g	No
35	SI-T	60 g	MX	60	I-T	30 g	No
36	SMI-T	50 g	MX	80	I-T	5 g	No
37	None used	NAP	MX	100	None used	NAP	NAP
38	A	30 mL	CP	100	A	30 mL	Yes
39	AS	30 g	CP	100	A	15 mL	Yes
40	None used	NAP	CP	100	None used	NAP	NAP
41	A	30 mL	U	100	A	30 mL	Yes
42(41)	A	30 mL	U	100	A	30 mL	Yes
43	AS	30 g	U	100	A	15 mL	Yes
44	None used	NAP	U	100	None used	NAP	NAP
45	A	30 mL	MX	100	A	30 mL	Yes
46	AS	30 g	MX	100	A	15 mL	Yes
47	AS	30 g	MX	100	A	15 mL	Yes
48	None used	NAP	MX	100	None used	NAP	NAP

¹Bottle numbers in parentheses designate duplicates.

²NAP means not applicable

In both anaerobic and aerobic laboratory studies, a source of neutral to alkaline soil or limestone is needed to help raise pH, control hydraulic permeability, and serve as adsorption sites for bacteria and contaminants (Bolis et al. 1992, Duggan et al. 1992). Alkaline soil from the mine site and limestone from the nearest quarry were collected to serve these functions.

Experimental Design

The collected waters and materials were shipped overnight to the Colorado School of Mines, and the experiments were set up the following day. Splits of the water samples were sent to Core Laboratories for chemical analysis. Materials larger than 10 mesh were removed from the substrate candidates, and mixes of the material were made in the combinations given in table 1. The codes for the substrates and waters are given in table 1.

The anaerobic tests were conducted in 150 mL screwcap culture bottles. A small amount of head space was left in the bottles to accommodate gases evolved during the experiment because this minimizes solution loss. The bottles were incubated for 5 weeks in boxes at ambient temperatures in the laboratory. The aerobic tests were conducted in 500-mL wide-mouthed erlenmeyer flasks that are covered with 250-mL beakers to allow gas exchange. The bottles were incubated for 5 weeks on a sunny window ledge at ambient temperatures in the laboratory. The protocol for the ARD experiments is given in table 2. The protocol for the tailing drainage experiments is given in table 3.

All bottles except 9 and 16 were unsealed to allow access to the solutions during the test period. Color, odor, pH, and Eh were recorded for each bottle once per week. Bottles 9 and 16 were sealed to ensure that atmospheric oxygen did not invade the systems and cause armoring of the limestone. Spot colorimetric tests on a few drops of solution were conducted using HACH kit reagents. The spot tests were conducted once during the course of the experiment for Fe and Cu on both water types, and twice during the experiment for cyanide on the tailing drainage. At the end of the experiments, quantitative determinations were made on representative bottles.

Table 4. Chemistry of waste rock drainages and test bottles after 5 weeks of incubation. All concentrations are in mg/L for unfiltered (total) water.

Bottle	Original	1	2	3	10	Original	20	24	Water Stds
Water	Pipe 1	Pipe 1	Pipe 1	Pipe 1	Pipe 1	1+2+3	1+2+3	1+2+3	NAP ¹
Substrate	NAP	MLI-B	MLI-B	MLI-B	None	NAP	SMLI-B	None	NAP
Sulfate	3370	5360	5130	4350	3850	2160	2350	2070	NAP
Arsenic	12	0.4	0.4	0.4	3	2.7	0.3	0.3	0.05
Cadmium	0.17	0.003	<0.003	<0.003	0.06	0.066	<0.003	0.04	0.01
Chromium	0.50	<0.05	<0.05	<0.05	0.5	0.20	<0.05	0.20	0.05
Copper	18	0.7	1.1	0.55	32	7.4	0.3	15	1.0
Iron	620	4.8	3.6	4.3	422	200	2.8	131	0.3
Manganese	12	1.7	1.4	1.8	11	6.7	5.2	6.4	0.05
Selenium	1.0	<0.01	<0.01	<0.01	<0.01	0.3	<0.01	0.01	0.01
Zinc	2.9	0.2	0.15	0.05	5.4	1.8	<0.05	3.0	5.0
pH	2.5	7.6	7.5	7.4	2.1	2.4	7.1	1.9	6-9

¹NAP means not applicable

Results and Discussion

Anaerobic ARD Experiments

All bottles that tested whether the local cow manure, horse manure, or "horse juice" materials (not shown) were suitable SRB inocula, had Eh values below -100 mV, black solids, and strong hydrogen sulfide odors, indicating that all three materials were good sources of SRB inoculum. The final pH of ARD test bottles that used soil from the site was somewhat lower than that of bottles with undiluted manure, but still above pH 7. In addition, the Eh in bottles with soil tended to decrease over time in a manner that was similar to that in bottles that did not contain soil. These results indicate that the soil can be used to provide hydraulic control within the substrate in the anaerobic passive treatment system.

Initial values for pipe 1 and the expected holding pond water and results for regulated constituents after 5 weeks of incubation are given in table 4 for selected tests. In all cases the analyses were performed on whole, unfiltered waters. Bottles 1 and 2 are duplicates and provide intra-experimental variability. Bottles 10 and 24, which are controls of pipe 1 and 1-2-3 water, respectively, were analyzed to determine whether 5 weeks of iron hydroxide settling causes significant decreases in the concentration of other metals. Bottle 20 simulates the expected holding pond (1-2-3) water to be treated with a mixture of sand, manure, and limestone, the probable substrate of choice.

The results indicated that the pH is raised from around 2 to above 7 and concentrations of cadmium, chromium, selenium, and zinc are reduced to within drinking water standards in all analyzed bottles. Iron and arsenic were reduced by over 95 %, but were not brought to within drinking water standards. Manganese was reduced by 50 to 80 %. Typically, manganese is the most difficult element to remove from ARD (Duggan et al. 1992). These results suggest that the anaerobic system will produce significant reduction of contaminants. However, to meet water quality standards, an aerobic polishing stage may be necessary after the anaerobic treatment.

Analysis of the aged water from pipe 1 (bottle 10) and the 1-2-3 mix (bottle 24), when compared with the original waters, shows that the concentration of Fe is reduced by 30 %. Also, the pH of these waters dropped upon storage, suggesting that Fe(III) hydrolyzed and precipitated from solution. Concomitantly, arsenic in aged pipe 1 water was reduced from 12 to 3 mg/L and in the simulated holding pond water from 2.7 to 0.2 mg/L. In addition, selenium was reduced to less than 0.01 mg/L in both waters. These elements occur in the water as the oxyanions arsenate and selenate. At the low pH of the ARD, the ferric hydroxide precipitate has a high positive surface charge and readily adsorbs the arsenate and selenate anions. Removal of selenium to below drinking water standards and the significant reduction in arsenic makes containment of the ARD in a holding pond a reasonable first step in passive water treatment.

Table 5. Chemistry of tailing waters and test bottles after five weeks of incubation. All concentrations are in mg/L for unfiltered (total) water.

Bottle	Original	30	31	32	41	43	Original	26	39	46	Water Stds.
Water	Under-drain	Under-drain	Under-drain	Under-drain	Under-drain	Under-drain	Seep	Seep	Seep	MX	NAP ¹
Aerobic Substrate	NAP	No	No	No	Yes	Yes	NAP	No	Yes	Yes	NAP
Cyanide-Total	NAP	SI-T	SI-T	SMI-T	A	AS	NAP	SMI-T	AS	AS	NAP
Cyanide, WAD	<4.0	<0.2	<0.2	<0.2	<0.2	<0.2	0.10	<0.2	<0.2	<0.2	0.2
Ammonia (as N)	4	<0.2	<0.2	<0.2	<0.2	<0.2	0.06	<0.2	<0.2	<0.2	0.2
Ammonia (as N)	14	16	11	0.44	0.27	0.08	2.1	8.6	0.19	0.20	-
Nitrate and Nitrite (as N)	19	1.0	1.1	1.9	0.31	0.73	8.3	2.2	0.31	0.60	-
Sulfate	400	15	16	66	478	430	390	210	391	450	250
Thiocyanate	14	<2.5	<2.5	4.9	0.4	<0.25	<0.1	4.4	<0.25	<0.25	-
Arsenic	0.09	0.17	0.15	0.17	0.11	<0.05	<0.05	-	-	<0.05	0.05
Copper	3.3	<0.05	<0.05	0.30	<0.05	<0.05	0.06	-	-	<0.05	1.0
Iron	0.05	1.8	2.5	1.2	<0.1	<0.1	<0.03	-	-	<0.1	0.3
Mercury	0.27	<0.002	<0.002	<0.002	<0.002	<0.002	0.004	<0.002	<0.002	<0.002	0.002
Manganese	0.47	7.6	2.0	2.2	2.15	0.15	1.6	1.35	0.45	0.75	0.05
Selenium	0.2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.1	<0.01	<0.01	<0.01	0.01
pH	8.0	6.6	6.5	6.5	7.5	7.0	7.3	7.1	7.5	7.5	6-9

¹NAP means not applicable.

Tailing Drainage Experiments

Cyanide, related nitrogen species, and other regulated constituents are present in the underdrain in higher concentrations than in the seepage. Thus, the tailing drainage experiments concentrated on this water and the MX water. The results showed that cyanide was destroyed to below 0.2 mg/L in all bottles within 4 weeks. These results indicate that either an anaerobic or aerobic system will destroy cyanide and confirm previous results on anaerobic tests reported by Filas and Wildeman (1992).

Bottles 30, 31, and 32 tested the various anaerobic substrates, and bottles 41 and 43 tested aerobic substrates with underdrainage water. Bottles 26 and 39 tested anaerobic and aerobic substrates, respectively, with the tailing seepage (CP). Bottles 43 and 46 tested the same substrates with the underdrainage water and the mix of seepage pond and underdrainage water (MX). The results for constituents of interest are presented in table 5. For comparison, the analytical results for the original waters and solution mixes are given. In all cases the analyses were performed on whole, unfiltered waters.

Anaerobic Experiments. The black sludge sampled from the seepage pond proved to be an excellent source of SRB for anaerobic passive treatment of tailing drainages. After 1 week, some of the anaerobic bottles that contained the tailing sludge inoculum had negative Eh's and smelled of hydrogen sulfide. The concentration of sulfate was also reduced, confirming that bacterial sulfate reduction was operating. At the cyanide concentrations in these waters, the SRB were not killed. From the results of experiments that studied a tailings solution containing much higher concentrations of total cyanide, Filas and Wildeman (1992) suggested that, below a cyanide concentration of about 10 mg/L, sulfate reduction was possible. Only a small supply of this black, pond sludge exists. If a large anaerobic system were built using this inoculum, the material would have to be mixed with other sources and incubated for a period of time to produce an adequate supply.

The results for nitrogen species were mixed. As discussed previously, cyanide was removed. Thiocyanate was also removed. The ammonia concentration remained high, which was expected in an anaerobic treatment system. The nitrate plus nitrite concentrations were significantly reduced. They were probably converted to nitrogen gas because the concentration of ammonia was not appreciably changed.

Copper, mercury, and selenium were reduced to below drinking water standards. Iron, manganese, and arsenic, which had not been completely removed in the anaerobic ARD tests, were also not reduced to below drinking water standards in the tailing drainages. In fact, these elements were at higher concentrations in the final solutions than in the original underdrain water. It appears that the anaerobic conditions caused dissolution of these elements from the soil, manure, and/or inoculum that were used in the substrate mixes. Apparently, an equilibrium between solid phases and the solutions has been established in these bottles.

These anaerobic test results indicate that an anaerobic passive system will not remove all the contaminants to Federal water quality standards.

Aerobic Experiments. Both the algae alone and the soil-algae mix reduced ammonia, nitrate plus nitrite, and thiocyanate to concentrations that were below the results for the anaerobic experiments. The qualitative tests conducted during the experiment indicated that the concentration of cyanide decreased faster in the bottles with soil and algae (AS) than in the bottles with algae alone (A). At the end of the experiment, the Eh's in those bottles containing only algae (41, 42, 45) had fallen significantly below those of the other aerobic bottles. This decrease in Eh may be the result of death and decay of the algae and suggests that, if an algal pond were not designed properly, the water in the pond could turn anoxic. This phenomenon exists in the current seepage pond at the site, where buried dead algae provided the anaerobic inoculum.

The results of the qualitative tests suggested that the soil-algae mixture functioned better than the algae alone. As reported in table 5, the concentrations of constituents confirm this result. The soil-algae mixture reduced all contaminants except manganese in the underdrain water and in the underdrain-seepage mixture to below drinking water standard concentrations. As seen from bottle 41, algae alone did not reduce arsenic concentrations. Based on the laboratory studies, an algal system containing soil would be the best passive system for removal of all the constituents in the tailing water.

Design Conclusions

For ARD waters containing high concentrations of arsenic and/or selenium, anaerobic passive treatment is possible "in-principle". A holding pond prior to the anaerobic cell would remove substantial quantities of both anions before the water entered the sulfate-reducing treatment system. The anaerobic cell may not remove all constituents to drinking water quality standards. If necessary, an aerobic polishing system can be installed after the sulfate-reducing system to remove these contaminants.

For tailing waters that contain moderate concentrations of cyanide and other metals, the laboratory studies suggest that the best passive system would be an algal pond containing sandy soil. This system removes iron, manganese, and arsenic, as well as all cyanide and its degradation products. Also, such an aerobic system would appear to be a good candidate for the polishing of iron, manganese, and arsenic from the waters exiting the sulfate-reducing anaerobic cell. A possible design for such a system is given by Wildeman et al. (1993).

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LABORATORY AND PILOT-SCALE STUDIES ON THE TREATMENT OF ACID ROCK DRAINAGE AT A CLOSED GOLD-MINING OPERATION IN CALIFORNIA¹

Thomas Wildeman^{2,3} John Cevaal⁴, Kent Whiting⁴, James Gusek³,
and Joseph Scheuering⁵

Abstract: Acid rock drainage from a closed gold-mining operation in northern California was studied first in the laboratory and then on the pilot scale to determine the technical feasibility of passive treatment. The drainage has a pH of 3.8, and concentrations of Cu, Fe, Mn, Ni, and Zn of 140, 190, 28, 0.93, and 40 mg/L respectively. The laboratory studies concentrated on the question of whether local organic and soil materials could be used to support sulfate reduction in a passive treatment system. Samples were incubated at laboratory temperatures for a period of 4 weeks. Soil and wood processing wastes from the immediate vicinity proved to be too acidic to maintain a large population of sulfate reducers. The most reasonable material for sulfate reduction was a mixture of equal amounts by weight of cow manure, planter mix soil, and limestone chips. The final solutions had pH's of 6.5 to 6.9, and average Cu, Fe, Mn, Ni, and Zn concentrations of 0.02, 1, 5, 0.05, and 0.1 mg/L, respectively. Based on the laboratory results, a pilot system was constructed that consisted of a lined steel container filled with a substrate volume that measured 2 by 3 by 12 m. The substrate mixture was the same as used in the laboratory tests. Raw manure from a dairy farm was mixed into the substrate for the sulfate-reducing bacterial (SRB) inoculum. Loading of the system was based on the estimate that 0.3 mol sulfide per cubic meter of substrate per day would be generated, and the inflow of heavy metals should not exceed the sulfide generated. Using these principles, the flow was set at approximately 800 mL/min. Over the course of 9 months, the pilot system achieved removal of Cu and Ni below the effluent standards of 1.0 and 0.7 mg/L. Dissolved Zn concentrations in the effluent averaged approximately 0.1 mg/L, compared with an effluent standard of 0.02 mg/L. Dissolved Fe concentrations in the effluent varied with the seasons, reaching a minimum of 1 mg/L in the summer and rising to a maximum of 120 mg/L in the winter. There is a significant increase in concentrations of Fe in unfiltered waters. This implies that, in a full-scale system, a settling-polishing pond will be needed.

Additional Key Words: Constructed wetland, heavy metals treatment, sulfate reduction, pilot scale reactors

Introduction

In 1989, the use of anaerobic, subsurface wetlands that emphasize sulfate-reduction was in the developmental stage. In eastern United States, systems using mushroom compost that treated coal mine drainage were being studied by scientists at the U. S. Bureau of Mines (Hedin et al. 1988 and 1989, McIntire and Edenborn 1990). In the West, research at the Colorado School of Mines (CSM) was concentrating on the removal of contaminants from metal-mine drainages by sulfate reduction, also using mushroom compost as the substrate (Machemer and Wildeman 1992, Machemer et al. 1993, Wildeman et al. 1993). In 1990, two breakthroughs on wetlands treatment significantly advanced research at CSM: (1) The determination that the primary anaerobic removal process is sulfate reduction and sulfide precipitation mediated by microbes (Reynolds et al. 1991). (2) The loading of a sulfate-reducing system can be determined by the rule of thumb that the level of microbial sulfate reduction should always exceed the amount of sulfide precipitation (Machemer et al. 1993, Wildeman et al. 1993).

These two findings allowed development of anaerobic wetland systems by a staged design process similar to other mineral processing schemes. In particular, because microbial processes dominated, laboratory studies to determine suitable substrates and sulfate-reducing inocula can be conducted with a reasonable degree of certainty. Also, these laboratory studies could be conducted to determine if "in principle" a treatment technique can be effective. Then, because effective treatment relies upon a balance between sulfate reduction and metal sulfide precipitation, bench- and pilot-scale experiments can determine the proper loading factors and how a treatment system can be adapted to on-site conditions.

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²Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401, (303) 273-3642, Geochemistry Program Paper No. 004.

³Knight Piesold & Co., 1600 Stout Street, Suite 800, Denver, CO 80202, (303) 629-8788

⁴Camp Dresser & McKee, 1331 17th Street, Suite 1200, Denver, CO 80202, (303) 298-1311

⁵Noranda Minerals Corp., 2501 Catlin, Suite 201, Missoula, MT 59801, (406) 721-9704

This paper reports on the first pilot-scale passive treatment system that was constructed using these concepts. The site was the Grey Eagle gold mine in northern California, where it is necessary to treat a continuous flow of seepage from a tailings impoundment. The seepage also contains acid rock drainage from historic mining. The composition of the commingled waste water stream is given in table 3. The mine site is owned by Noranda Grey Eagle Mines Inc. which funded the development project.

Laboratory Study

The laboratory study concentrated on microbiology and had the following objectives: (1) To identify a suitable substrate of soil and organic material that would be readily available at the mine site. (2) To measure the removal of the contaminants from the discharge water by analyzing the changes in the substrate-water system with time. (3) To determine a local source of SRB that can be used as the inoculum for the pilot cell.

Local soils and wood wastes were collected from the vicinity of the mine, and were mixed with water in a 1:1 by volume ratio. These paste samples were analyzed for pH, Eh, and electrical conductivity. These general tests indicated that the most easily available materials were unsuitable, primarily because the paste pH's were less than 5. At this low pH, sulfate reduction is severely inhibited (Postgate 1979). To meet objective 2 and determine what types of materials could be considered for objective 1, a protocol for microbiological tests was devised as shown in table 1. It was assumed that limestone, cow manure, and organic soil could be found close to the mine site, so this was established as the base substrate. Other substrates used at the Big Five pilot system in Idaho Springs, CO (Wildeman et al. 1993) were used to give a more complete test of objective 2. To test objective 3, various materials were used without a sulfate-reducing bacterial inoculum being added.

Two features of this type of laboratory study help with the success of the final treatment design. First, qualitative observations and indicative measurements are just as important as analytical measurements. Consequently, during the 4-week study, pH, Eh, color, and odor within the bottles were measured. Second, because the analytical tests are simple, a large number of combinations of organic material, soil, and other amendments can be investigated. At the end of the experiment, selected bottles were sent for analysis in which filtered samples of the supernatant water were analyzed for a suite of metals.

Table 1. Experimental protocol for the laboratory tests on the mine drainage.

Bottle No.	Culture Bottle Composition
	Base substrate: 1/3 planter soil mix, 1/3 manure, 1/3 limestone chips.
	Base mix: 30 g of substrate, 90 g of mine drainage. For the anaerobic cultures, add a minor amount of distilled and sterilized water to fill to the top of the bottle. For the aerobic cultures, no extra water is added and the bottle is left 3/4 full. Record the extra water added.
1 - 6	Base substrate with base drainage-substrate mix.
7 - 9	Big Five Cell E substrate with base drainage -substrate mix.
10	Base substrate with mix of 10 g substrate to 100 mL drainage.
11	Base substrate with mix of 25 g substrate to 100 mL drainage.
12	Base substrate with mix of 60 g substrate to 60 mL drainage.
13	Cow manure with base drainage-substrate mix.
14	Sheep manure with base drainage-substrate mix.
15	Planter mix with base drainage-substrate mix.
16	Limestone chips with base drainage-substrate mix.
17	1/4 planter mix, 3/4 manure with base drainage-substrate mix.
18	1/2 limestone chips, 1/2 manure with base drainage-substrate mix.
19	1/2 planter mix, 1/2 manure with base drainage-substrate mix.
20	1/3 limestone, 1/3 sawdust, 1/3 manure with base drainage-substrate mix.
21	1/3 limestone, 1/3 sawdust, 1/3 planter mix with base drainage-substrate mix.
22	1/3 planter mix, 1/3 sawdust, 1/3 manure mix with base drainage - substrate mix.
23	Original Big Five mushroom compost with base drainage-substrate mix.
24-35	Bottles 1 - 5, 8, 17, 19, 20, 21, 22 and 23 run under aerobic conditions.
36	Base drainage-substrate mix with 10 g of Big Five Cell E substrate added.

Table 2. For the test bottles in table 1, visual observations, pH, electrochemical measurements of hydrogen sulfide, and colorimetric measurements of dissolved copper.

Bottle	Color ¹	pH	H ₂ S ²	Copper ²
1	B	6.5	+	±
2	B	6.7	+	±
3	B	6.7	+	0
4	B	6.7	+	0
5	B	6.7	+	0
6	S	6.8	+	0
7	SS	5.8	+	+
8	SS	5.7	+	NA
9	SS	5.6	0	NA
10	A	6.2	0	NA
11	B	6.7	+	NA
12	B	6.9	+	NA
13	B	6.8	+	NA
14	S	7.1	0	NA
15	A	6.5	0	NA
16	A	6.1	0	0
17	B	7.0	+	NA
18	B	6.9	+	NA
19	B	6.9	+	NA
20	A	6.1	0	NA
21	A	4.7	0	NA
22	S	5.9	0	NA
23	S	6.3	0	NA
24	SS	7.0	0	NA
25	SS	6.9	0	NA
26	SS	6.9	0	NA
27	SS	6.9	0	NA
28	SS	6.8	0	NA
29	SS	4.0	0	NA
30	B	7.0	0	NA
31	B	7.8	0	NA
32	S	7.4	0	NA
33	A	3.9	0	NA
34	A	6.8	0	NA
35	A	6.2	0	NA
36	B	6.9	+	NA

¹B = Bottle black throughout; SS = all of sediment blackened; S = part of sediment blackened; A = no blackening, water is clear or pale brown.

²For the hydrogen sulfide and copper tests, qualitative estimates were made and ++ = strongly positive, + = positive, ± = uncertain, and 0 = not detected, and NA = not analyzed.

Table 2 gives the 2-week results of indicative observations on the bottles. Already strong indications of what substrates would successfully promote the growth of sulfate-reducing bacteria are seen. For example, in bottles 17 and 19, which had appreciable manure in the substrate, the bottles had blackened and H₂S was present. Bottles 30 and 31 had the same substrate mixes as bottles 17 and 19, but the caps had been loosened in an attempt to keep the bottles aerobic. However, sulfate reducing bacterial activity was so strong that these bottles had also turned black. Bottle 21 with no manure had a low pH and no blackening.

The results of analyses on selected bottles are shown in table 3. Although this is a static experiment, the concentrations of contaminants give some indication of what to expect in a flowing system. First, concentrations of sulfate show that vigorous sulfate reduction occurred in bottles (1, 9, 10, 11, 12, 36) that contained organic material other than mushroom compost. Next, in the bottles that contained varying amounts of the base substrate of 1/3

Table 3. Contaminant concentrations in mg/L in the original drainage water (OW), the final supernatant waters in the test bottles, and the regulatory effluent limit (EF).

Bottle or Sample	Cd	Cu	Fe	Mn	Ni	Zn	SO ₄ ⁼
OW	0.088	140	290	28	0.95	40	1,500
1	<0.005	0.025	0.31	0.63	0.05	0.021	173
9	<0.005	<0.005	54	12	0.02	0.077	997
10	<0.005	0.94	40	7.6	0.10	2.3	1,630
11	<0.005	2.7	25	6.4	0.07	0.83	744
12	<0.005	0.13	2.5	0.99	0.04	0.17	274
21	0.006	0.77	39	7.4	0.12	4.3	591
36	<0.005	0.027	0.09	2.1	0.02	0.10	250
EF	0.01	1.0	0.3	None	0.7	0.02	None

planter mix, 1/3 manure, and 1/3 limestone (1, 10, 11, 12), it appears that a ratio of 10 g of substrate to 100 mL of mine drainage lacks sufficient organic material to effect vigorous sulfate reduction. Finally, it appeared that reaching the effluent limits for Cd, Cu, and Ni would be possible, but achieving the regulatory limits for Fe and Zn would be more problematic.

Treatment Decisions

The results of the laboratory study were encouraging enough that it was decided to forego bench-scale experiments and immediately design and construct a small pilot cell. However, there were still some questions to be answered on the selection of the substrate materials. In particular, the first set of local materials were not suitable for an anaerobic treatment system, and it was necessary to make another search for materials that gave good results in laboratory studies. In addition, the inocula of SRB came from Colorado sources and sources from northern California had to be located. Consequently, while the physical design of the pilot-scale reactor was being developed another round of laboratory tests were performed to find suitable organic materials and sulfate-reducing inocula. Because the base substrate mix of manure, limestone, and planter's soil mix was effective in promoting the activity of SRB and removing contaminants, the search for local materials centered upon these materials. They were found, but had to be transported extensive distances.

The manure came from a dairy farm and appeared to be processed so that it contained primarily hay with very little soil. It tested positive as an inoculum for sulfate reducing bacteria; however, the growth of bacteria was slow. In the final designation of the substrate for the pilot reactor, it was decided to use the processed manure for the substrate formulation, but to include 10% of raw, unprocessed manure as the bacterial inoculum.

Pilot-Plant Study

Design of the Treatment Module

The passive treatment system module (PTSM) consisted of influent piping, substrate, and effluent piping installed in a welded steel tank. The rectangular tank was 10.9 m long, 2.7 m wide, and 2.7 m high and open at the top. The interior of the tank was covered with a bituminous polymer coating to protect the steel. The bottom of the tank was covered with a 15-cm layer of 1-cm diameter clean gravel. A network of 5-cm diameter perforated PVC piping was constructed on the gravel layer. An additional 7 cm of gravel was placed on the exposed gravel and pipes. The top of the gravel was covered with needle-punched polyester geotextile fabric.

The substrate consisted of equal masses of processed manure, 1-cm diameter limestone, and dark fine-grained soil. The three components were blended and added to the PTSM in such a way that the substrate was not allowed to fall more than 1 m to minimize compaction. For inoculum, a portion of the substrate was blended with the raw manure and placed in the PTSM at the 1/3 and 2/3 level. A distribution network of perforated 5-cm-diameter PVC piping similar in configuration to the effluent piping was installed on top of the substrate. Water passes downward through the 2-m-thick substrate and is collected in the effluent piping located at the base of the tank. Flow through the system is controlled hydraulically by the elevation of the effluent pipe relative to the level of water within the module.

Table 4 Sulfide generation in mol/L for the passive treatment system module based on sulfate reduction. For comparison, the metals removal in mol/L is also shown.

Date	Sulfate (mg/L)		Sulfide (Molar) Produced	Metals (Mn+Fe+Ni+Cu+Zn+Cd), (Molar)		
	In	Out		In	Out	Removed
9/24/91	2,900	1,100	0.0188	0.0083	0.0002	0.0081
10/8/91	2,600	2,600	0.0000	0.0091	0.0001	0.0090
10/21/91	3,000	2,200	0.0083	0.0083	0.0005	0.0079
11/5/91	2,700	2,300	0.0042	0.0087	0.0006	0.0081
12/3/91	2,600	2,200	0.0042	0.0087	0.0008	0.0070
1/8/92	2,600	2,100	0.0052	0.0084	0.0015	0.0069
2/25/92	2,700	2,100	0.0063	0.0090	0.0019	0.0071
3/24/92	3,200	2,600	0.0063	0.0137	0.0027	0.0109
4/28/92	3,000	2,300	0.0073	0.0109	0.0015	0.0093
5/26/92	3,000	2,200	0.0083	0.0106	0.0005	0.0101
6/30/92	2,900	2,400	0.0052	0.0102	0.0004	0.0098

Operation

The loading of the PTSM was based on the limiting reactant concept for loading of a sulfate-reducing reactor (Machemer et al. 1993, Wildeman et al. 1993). The premise is that the rate of generation of sulfide by the bacteria must meet or exceed the rate of flow of heavy metals (Mn + Fe + Cu + Zn) into the reactor. Based on previous studies (Reynolds et al. 1991, Wildeman, et al. 1993), the rate of sulfide generation was estimated to be 0.3 mol of S²⁻ per m³ per day. The metals concentration in the influent totals ~ 800 mg/L. Therefore, using an average molecular weight of 55 g/mol for the metals in the drainage, this results in a metals influent concentration of 0.014 mol/L. Given the volume of the PTSM as 55 m³, the total sulfide produced per day is 16.5 mol. Therefore, the flow was set so at 800 mL/min that the metals input would not exceed 16.5 moles/d.

To start the test, impoundment seepage was added until the substrate was thoroughly soaked and water breached the surface. Then, the system was left to incubate for 2 weeks. The sulfate in the seepage and the easily extracted organic compounds from the manure serve as excellent nutrients for the SRB. After 2 weeks, it was assumed that the system was an active bioreactor. The initial flow was set at 800 mL/min, and the PTSM was continuously operated for 22 months from October 1991 through July 1993. During this time the physical operation of the PTSM was free of problems.

For the first 10 month period, the analytical results on total constituents in the effluent are given in figure 1. In figure 2, the total concentrations of Fe in the influent and effluent as well as the dissolved Fe concentration in the effluent are shown. For the other constituents, except for excursions in Cu at the beginning of the study and Zn at the end of the period, the concentrations of dissolved constituents were only slightly less than the concentrations of total constituents. During this time, the composition of the influent water was essentially the same as that given in table 3, except in March when annual recharge of the aquifer increased concentrations of contaminants in the drainage by 10% to 70%. This increase can be seen for Fe in figure 2. In table 4, the analytical results of sulfate concentrations in the influent and effluent are presented. The molarity of heavy metals in the influent and effluent are also shown so that the balance between sulfide produced and metals removed can be compared.

At the mine site, Eh, pH, and temperature measurements were performed twice a week as part of the on-site maintenance program. The PTSM tank was built of steel and was above ground. In addition, the tank was not insulated. As a consequence, it responded quite well to changes in temperature as the seasons changed. Figure 3 gives the on-site values of Eh and temperature over the course of the 10 month study. Twice during the study, the temperature of the substrate at various depths and locations was determined. In both instances, the temperature range in the PTSM was less than 3° C with respect to both depth and lateral position.

Analysis of Operation

For the first 6 weeks of operation, removal results were excellent and followed the results achieved in the laboratory study. However, beginning in November, iron removal began to decrease in two respects. In the effluent,

a large difference between total and dissolved iron was observed, and the concentration of Fe increased in both the dissolved and total fractions. This increase could not be attributed to a change in the concentration of Fe in the mine drainage, which was approximately constant until March.

At least two properties of the PTSM operation can account for the change in dissolved Fe concentration. First, as has been shown in Colorado studies of sulfate-reducing reactors (Machemer and Wildeman 1992), in the first 6 weeks, two factors operate to promote metals removal. First, metals are readily removed by adsorption onto sites in the organic substrate. However, after 6 weeks, most of the sites are filled and this method of removal is no longer available; therefore, metal removal decreases. Also during the first 6 weeks, small molecular weight organic compounds are readily available to the SRB. This availability of nutrients causes large bacterial activities in the initial stages of operation. As seen in table 4, other than the anomalous value on October 8, the largest sulfate reduction values occur in the first 4 weeks of operation.

Startup in September, just as temperatures in the tank started falling, can also account for the increase in Fe concentration. SRB activity is known to decrease with temperature decreases, and Kuyucak et al. (1991) found the most drastic decrease when the temperature fell below 10° C. In the PTSM, the temperature fell below 10° C on about November 15 and did not rise above 10° C until about April 15. Fe concentrations would be most affected by a reduction in SRB activity because FeS is the form of iron sulfide formed and it is the most soluble of the acid-volatile sulfides (Machemer et al. 1993, Wildeman et al. 1993).

The reason for the increase in total Fe concentration is not known because material suspended in the effluent was not analyzed. If the increase was from geochemical conditions in the effluent, two reasons could best explain the increase. First, there was a high concentration of suspended organic material in the effluent, especially at the beginning of operation. Cu is strongly adsorbed onto organic material (Machemer and Wildeman 1992), and the large discrepancy between total and dissolved copper in the beginning of operation could be accounted for by suspended organic material. However, during the first month of operation, there is little difference between total and dissolved iron. Thus it appears that adsorption onto suspended organic material may not be the only reason for the increase in total Fe.

The other strong possibility for this difference is the presence of suspended ferric hydroxide in the water. Between pH 6 and 7, which are the operating pH's of the PTSM, ferric hydroxide would be stable at Eh's above 200 mV (Wildeman et al. 1993). The values of Eh in the effluent in figure 3 show that 200 mV was exceeded on about December 15. Consequently, this might account for the large difference between dissolved and total iron during the winter. However, when the Eh of the effluent falls below 200 mV on about May 1, there is still a difference between total and dissolved iron. This behavior suggests that the difference between total and dissolved iron is due to one or a combination of the following causes: (1) The difference is not caused by just one chemical constituent in the effluent water, (2) the difference may be caused by some physical condition in the PTSM that allows suspended Fe to remain in the effluent, or (3) the difference is caused by Fe precipitates still forming after the water has left the PTSM.

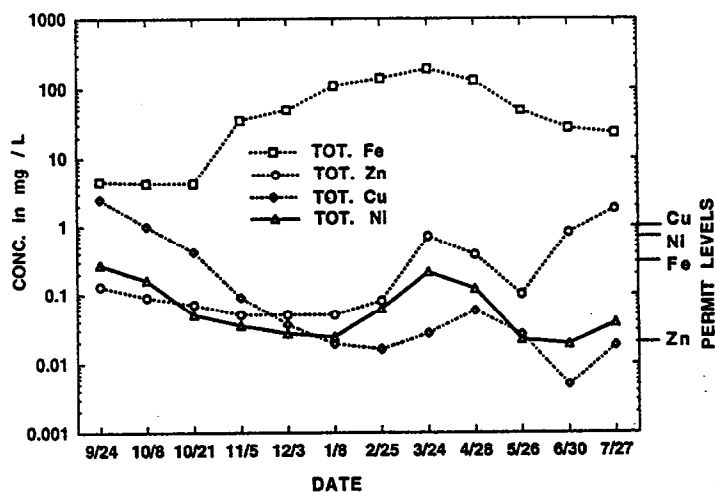


Figure 1. Unfiltered effluent metal concentrations in mg/L.

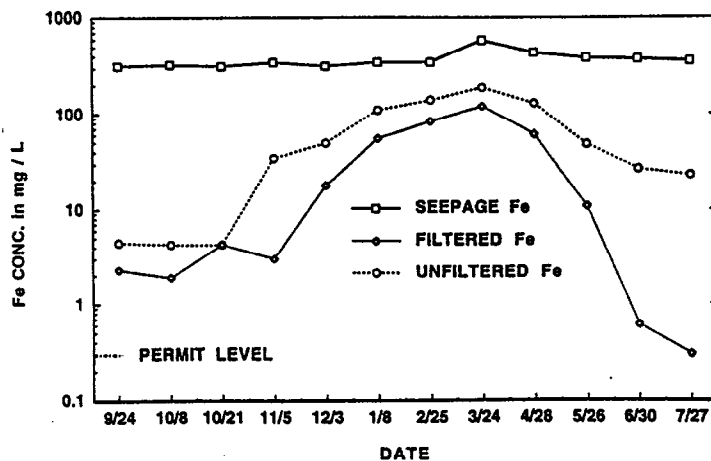


Figure 2. Influent (seepage) and filtered and unfiltered Fe concentrations in mg/L in the PTSM.

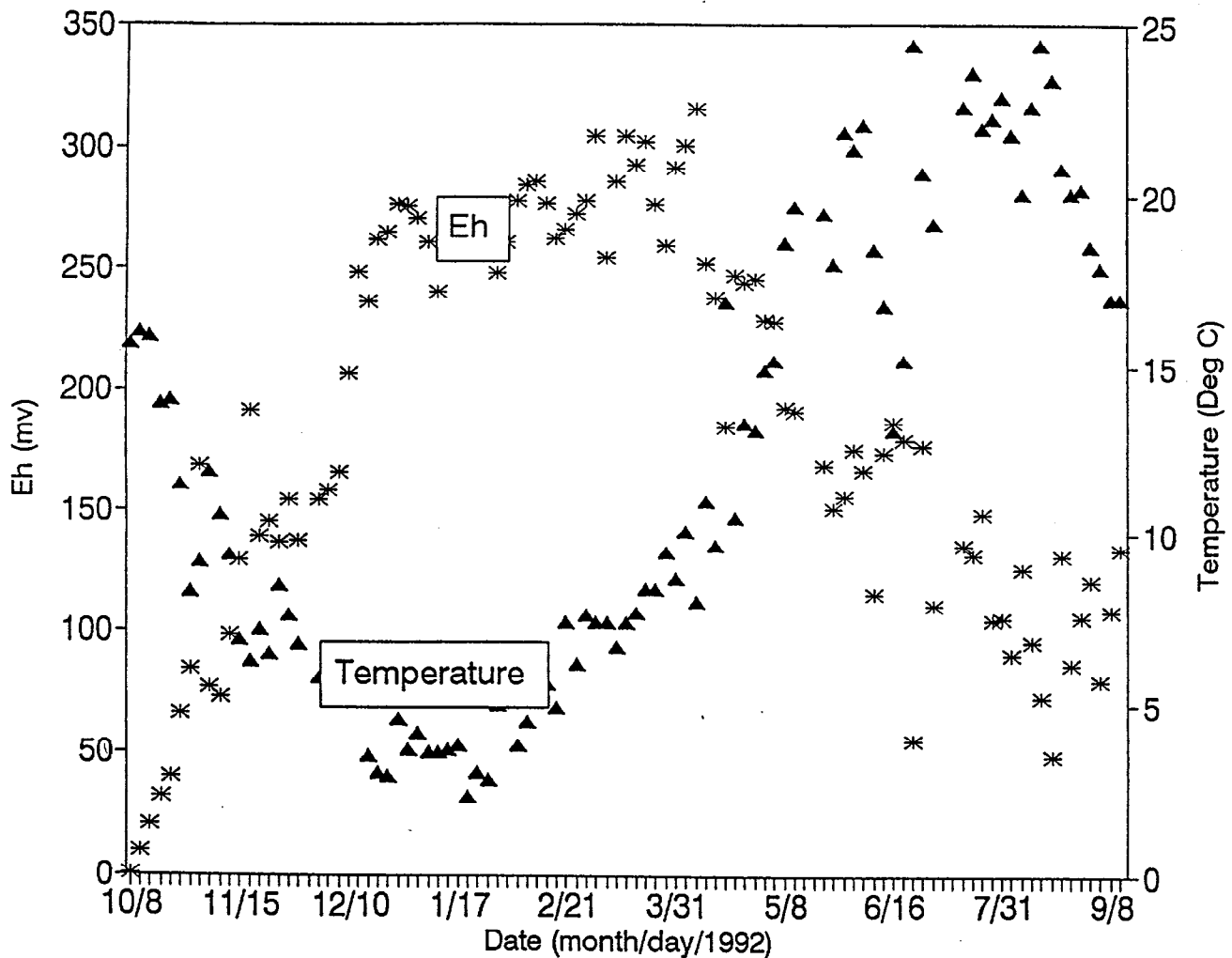


Figure 3. Variation of oxidation-reduction potential (Eh) with PTSM temperature in 1991 and 1992.

The frequent monitoring of the temperature and Eh along with the Fe and sulfate concentration values gives some insight into the activity changes of SRB with temperature. For the PTSM, Eh increased as temperature decreased with little time lag during the fall. The highest Eh occurred in mid December at the lowest temperature. However, the Eh remained high until the end of March, whereas the temperature started rising at about the end of January. In table 4, examination of the sulfide produced implies that the decrease in the rate of sulfate reduction correlates well with decrease in temperature and increase in Eh. However, the peak in the Fe concentration was at about the time when the system is impacted by the increase in metals in the influent. During the time of reduced SRB activity, Ni, Cu, and Zn were consistently removed, quite likely because they form less soluble sulfides. Apparently, the capacity to remove metals continued even though sulfate reduction is diminished.

Conclusions

From this study, a number of conclusions can be made concerning the theoretical and practical development of anaerobic wetlands and reactors to treat mine drainage. The limiting reactant concept of balancing sulfide production with metal inflow appears to control the operation of the PTSM. In addition, when there is not enough sulfide generated, the concentration changes in the effluent can be predicted. Also, there appears to be some excess capacity in the reactor, so that if SRB activity is diminished or Eh increases, removal of Ni, Cu, and Zn will continue, but Fe removal may decrease. From the point of view of substrate development, other organic materials will work as well as mushroom compost as long as they contain a good source of SRB, contain a good supply of organic nutrients, and provide a near-neutral pH environment for bacterial growth. Finally, the expected relation between temperature, SRB activity, Eh, and contaminant removal has been established in the field.

On a practical basis, this study has shown that for anaerobic systems, a well-designed laboratory program will give an excellent indication of how effective removal will be. Also, laboratory experiments will provide the information needed to select the proper substrate materials and inocula. The information provided by these laboratory studies is adequate; thus for typical acid mine drainages, bench-scale studies are not necessary. From an operational viewpoint, nothing unusual occurred during the operation of the PTSM, and typical mine personnel were able to monitor and operate the system.

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Design of a tailing facility to mitigate potential acid rock drainage

D. R. East

Knight Piésold and Co., Denver, Colorado, U.S.A.

L. H. Filipek

Knight Piésold and Co., Denver, Colorado, U.S.A.

Adriaan de Villiers

Knight Piésold and Co., Denver, Colorado, U.S.A.

T. R. Wildeman

Colorado School of Mines, Golden, Colorado, U.S.A.

Abstract

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Keywords: Acid rock drainage, anaerobic conditions, reclamation, subaqueous, sulphidic ore, tailing disposal facility.

1 Introduction

The long-term storage of potentially acid-producing mine and mill waste is becoming an increasingly important aspect of mining reclamation. One such project, in a mountainous region of the western USA where an excess of net precipitation occurs, is being designed for total submergence of the mill tailings both during operation and at reclamation. This paper describes the engineering and geochemical considerations of the reclamation cap design and the long-term mitigation of the area for use as a wetland.

The tailings will be stored in a side valley impoundment with diversion of the existing creek designed to remain the low point of the valley reclamation. The tailing impoundment basin is being designed with a low-permeability soil/geomembrane composite liner system and a managed peripheral spigot tailing discharge system which will form the final shape of the surface in order to provide permanent surface drainage consistent with the concept of totally submerged tailings.

The reclamation cap will comprise a 1.2-meter-thick layer of non-acid-generating crushed rock placed onto a geofabric filter layer which will be the separation layer between the tailings and the caprock. The lower 300 to 600 mm of the caprock will be a selected low-permeability zone with the upper portion consisting of an open-graded high-permeability rock designed to take all precipitation and flow-on from the surrounding hillside. Phreatic levels within the reclamation cap will be controlled by a constant elevation spillway from the synthetically-lined impoundment. The caprock will be covered by about 600 mm of growth medium consisting of highly-organic surface soil removed from the site prior to excavation of the tailing impoundment

8 Conclusions

To achieve zero discharge attention has firstly to be paid to the climate at the mine site. As a first benchmark the P/Eo ratio gives a useful indication as to whether advantageous circumstances exist. Even if unfavourable much can be done to enable outflows to the environment to be minimised, these are :-

- Collect all potentially polluted drainage from rock dumps and other areas and dispose of it in the tailings dam, this is easier if it is located downstream.
- Reduce the requirement for the importation of water for processing purposes by recycling as much water as possible from the tailings dam or water storage dam.
- Where the P/Eo ratio exceeds unity, i.e. rainfall exceeds evaporation, maximise the area of tailings beach and pond to enhance evaporation and adopt frequent rotational deposition techniques.
- If appropriate, collect and return all tailings dam underseepage to the tailings pond. This can be achieved by pumping from sumps and/or from interception wells sited at convenient low points in the groundwater phreatic surface.
- In cases where zero discharge is unlikely to be achieved, as indicated by the P/Eo ratio being significantly in excess of unity, divert as much clean water as economically possible around pollution causing sites.
- If surplus water is inevitable and it cannot be discharged directly, make provision to treat the water by chemical or biological processes before discharging to the environment.

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basin. This material should consume oxygen in the surface water and "condition" the drainage entering the soil, rock, and low-permeability layers to keep the tailing material isolated from oxidizing reactions.

2 Geologic and Geomicrobiological Review

Closure of a mining facility necessitates leaving solid materials in an environment in which they are stable on a long-term basis. If the minerals in the ore deposit are sulfides, then that environment should be anoxic (devoid of oxygen).[1] [2] [3] From a geologic perspective, the occurrences of metals in anaerobic sedimentary deposits such as coals or lignites, should determine the more thermodynamically stable forms of metals deposited under these conditions.[1,2,3,4] In these sediments, the stable iron minerals are pyrite or siderite, the stable manganese material is usually rhodochrosite, and base metals such as Co, Ni, Cu, Zn, As, Cd, Ag, Se, Hg and Pb exist as sulfides.[1] [2] [4] [5] Also, the same mineral association of sulfides and carbonates is seen in anoxic sedimentary ore deposits such as black shales.[1]

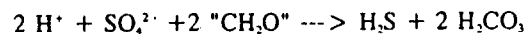
In investigations of recent depositional environments, marine sediments deposited in deep stagnant waters such as fjords or enclosed seas also exhibit the same mineral association as in coals and sedimentary ore deposits.[6] [7] [8] [9] In fresh water environments, anoxic conditions can be established; however the mix of minerals can be quite different because the availability of nutrients, particularly sulfate and nitrate, is often limited.[10] [11]

Application of these principles to the closure of a sulfide ore deposit leads to two conclusions:

1. If a sulfide deposit is to be closed, it best be left in a state where anoxic conditions can be maintained. This usually means storage in a stagnant water environment.
2. If a system is to be maintained undisturbed in an anoxic state, the reactants to produce sulfides and carbonates need to be readily available.

The above questions of stability do not include the issue of reaction rates, whether the constituents in the water and sediments will react rapidly enough to consume all the oxygen. This question of kinetics is controlled by the microbes that inhabit the aquatic environment. Generally, these microorganisms survive in nature by catalyzing chemical reactions that release energy to the organism.[12] [13] [14] In an aquatic environment, the progression to thermodynamic stability is almost always speeded up by microbial activity.[12] [14] [15]

In most instances, reactions include organic material, and the microbes are designated as being heterotrophic. An important example of this process is the reaction upon which the sulfate-reducing microbial consortia survive:[13]



Here, "CH₂O" represents organic matter and the sulfate is dissolved in the water. Sulfate serves as the electron acceptor. This is an anoxic system where microbes are present; that the reaction provides two products in an anaerobic environment; H₂S and hydrogen ions.

To promote sulfate-reducing microbial activity, the reactants in the above reaction. Mine water and sulfate.[16] In most mineralized areas, water is available.[17] Organic-rich sediments provide nutrients. In the review of sedimentary systems, there is always an excess of organic debris.[1] [4] Establishing the proper geomicrobiological environment for organic material.

3 Geotechnical Considerations

In the closure of a tailings deposit, dry cover is used to isolate the sulfidic materials from the atmosphere. For dry cover use, the tailings are used in arid climates where water is scarce.

In most of the geological situations where water is present in the atmosphere, it is water that is the isolating factor. [2] [14] [15] [19] show that water has two

1. The diffusion of oxygen through water
2. Constituents in the water can react with

For these two properties to be most effective, the sedimentary material should not be exposed to intermittent periods of time.

In underwater disposal of tailings, most problems have been by accidental or unregulated disposal. Fresh and salt water lakes have included fresh and salt water lakes. A most of these disposal situations have been by accumulation and there may be considerable release in five years, these disposals have been intentionally sponsored by the Mine Environmental Neutralization Program. Included in these studies have been chemically treated sediments in the lakes. The four lakes that have been studied have the same characteristics. The tailings are all contained and there has been minimal release and sometimes the tailings. Natural production of organic

tailings and generate an anaerobic ecosystem. All the principles reviewed above have been verified in the analysis of the waters and sediment cores from the four lakes extensively studied in the MEND projects.[22] It is important to note that these were situations where tailings were disposed of in natural settings. Little was done to design and engineer the disposal.

There are potential problems with the deposition of tailings into bodies of water. Although molecular diffusion of oxygen may be minimal, convective diffusion caused by the lake overturning in fall can deliver oxygen to the water-sediment boundary.[14] [15] [19] This would certainly mix oxic and anoxic waters. What is needed is consistently stagnant water that will maintain its anoxic character. In addition, wind action on a large water body may also cause convective diffusion of oxygen to the water-sediment boundary. Also, in shallow lakes, wind action may cause agitation of the sediments so that sealing the surface and maintaining isolation of the tailings cannot occur.[15] [19]

What is necessary for underwater disposal of tailings is to maximize the positive aspects of the concept and minimize the potential problems by design. Maximizing the pros and minimizing the cons has been successfully applied to the design and construction of wetlands.[23]

In recent years, the principles of aquatic chemistry and geochemistry have been used in mine closure for the treatment of acid mine drainage (AMD) by use of wetlands. In the case of AMD treatment, wetlands have been constructed so that either aerobic or anaerobic conditions are created that maximize the appropriate treatment reactions.[10] [23] [24] [25] [26] In addition, it is important to control the hydraulics of the water to be treated to ensure that maximum treatment is effected. Use of constructed wetlands is an excellent example of combining geochemical and engineering principles in the design and construction of an effective treatment system.[23] Designs are made so that in one wetland cell a certain process (such as alkalinity generation) is brought to completion before the water enters the next cell where another process (such as aerobic removal of iron) is effected.[23] Natural wetlands are not used because they provide a balance of all processes rather than maximizing one. In anaerobic wetland cells, the reactions controlled by sulfate-reducing bacteria are emphasized.[24] [25] [26] Bench- and pilot-scale systems built to optimize the flow of AMD through a submerged substrate, which has been designed to promote the activity of the sulfate reducers and provide some neutralizing capacity, have successfully treated severely contaminated waters.[23] [24] [26] It has been verified that the metals are removed as sulfides and carbonates. In many of these situations, the flow of the AMD has been down through the substrate and the water covering the substrate has only been a few centimeters in depth.[10] [23] [26]

If success is possible in a natural system where geomicrobiological as well as physical processes are competing against one another, then it should be possible to achieve the same success by designing an underwater tailing disposal site. In this case, design and construction principles would try to maximize anaerobic conditions. To this end the following guidelines would be followed:

1. The tailings would be from sulfidic ores so that the closure objective is to minimize diagenetic reactions that might release contaminants, and maximize the stability of minerals that were formed under anoxic conditions.
2. The setting would be in an area where there was a net accumulation of moisture so that a water cover would be assured even in times of drought.
3. The amount of exposed water would be minimized so that release of contaminants to the environment by that route would be small. Also, this would eliminate problems with overturn, wind and hydraulic head associated with large areas and depths of free water. This would imply that the anaerobic environment would be created in the substrate of a wetland rather than in the sediment below a lake.
4. Any flow of air and water through the tailings would be minimal so that the amount of oxygen that possibly enters the system is minimal.
5. Provisions would be made to capture any water flowing through the tailings. This suggests that the flow through the buried tailings would be downward to ensure that any contaminants in the water flow away from the surface ecosystem.
6. A continuously submerged cover would be constructed in such a way that dissolved oxygen and other oxidizing agents in the water such as Fe(III) and nitrate would be completely consumed before the water reaches the tailings.
7. To effect criteria 4. and 5., the cover soil would have a low hydraulic conductivity, but be slightly higher than the hydraulic conductivity of the tailings. To effect criterion 6., the cover would have sufficient organic material in the soil to insure continuous activity of anaerobic bacteria.

4 Design

Subaqueous tailing deposition in an engineered impoundment at a site where an excess of net precipitation occurs offers a logical opportunity for long-term, "walk away" mitigation of potential acid-producing tailings. To illustrate such a design, the following case is examined:

- ▶ A precious metal mine with pyrite in the ore body.
- ▶ A net annual surplus in precipitation at the site.
- ▶ Precious metals recovery by pyrite flotation.
- ▶ A side-valley impoundment in the valley adjacent to the process facilities is selected as the most appropriate tailing disposal facility.

The potential for long-term acidic drainage from the tailings is an obvious concern to the mining company, state and federal agencies, and the general public. In response to these concerns, a fully-lined impoundment is designed analogous to a liquid containment structure.

The mineral extraction process requires that the process water be maintained at a pH above 10. The make-up water requirements, allowance for design storm containment and operational fluctuations in the supernatant water level, result in an average operational design depth for the supernatant water of no less than 1 meter (3 feet), even during a 100-year drought. Therefore, during the operating life of the

mine, an alkaline water cover can be maintained over the tailings in the impoundment, thus preventing oxygen diffusion and providing neutralization for any acid formation.

Settlement tests on tailing samples demonstrated that the tailings settle and consolidate rapidly even under submerged conditions. Consolidated densities were demonstrated on the order of 16 kN/m³ within one to two years. Therefore, conditions suitable for the support of reclamation activities on the tailings are anticipated.

The objectives of the reclamation cap design are fulfilled by the following components:

- ▶ A layer of organic material overlying the tailings
- ▶ A filter fabric overlying the organic layer (340 grams/m² geotextile)
- ▶ A low permeability caprock layer overlying the filter fabric
- ▶ A relatively coarser-grained caprock layer overlying the lower caprock layer
- ▶ A filter fabric overlying the caprock
- ▶ Organic-rich soils overlying the upper filter fabric
- ▶ A vegetative cover established in the organic-rich soils
- ▶ A surface water diversion channel terminating at a spillway

The purpose of each of the components of the reclamation cap as shown in Figure 1 are further explained below.

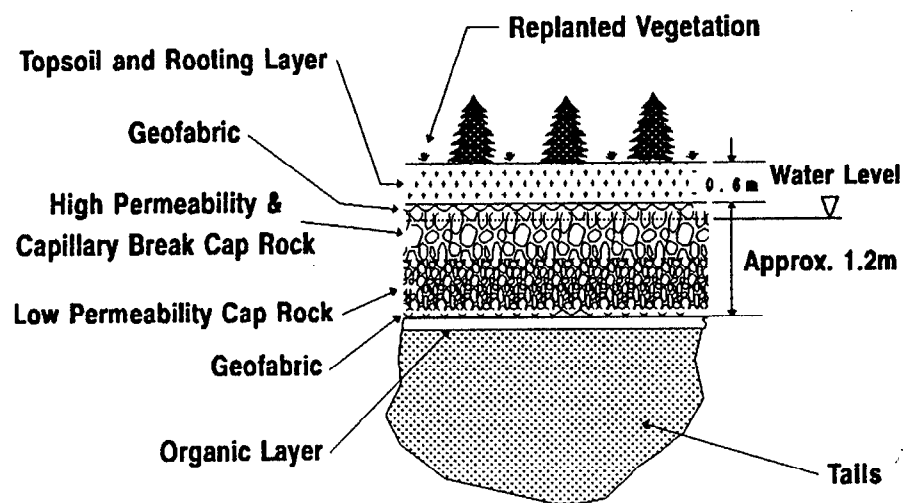


FIGURE 1

From the top down: surface water run-on and direct precipitation onto the impoundment will replenish the water cover which will be maintained within the caprock region. Such water will reach the caprock by filtering through the revegetated soil cover or more directly, at the surface diversion channel with its invert within the

upper caprock region. The vegetation will have a dual effect, i.e. providing nutrients for the promotion of anaerobic bacterial activity as well as the provision of erosion resistance. Aesthetic appeal is also achieved.

The spillway at the end of the diversion channel is designed to provide level control of the water within the caprock and within the impoundment. The filter fabric is designed to prevent migration of fine material from the soil cover to the caprock. The upper caprock region (coarse material) is provided to act as a capillary break to water within the lower (finer) caprock, and to maximize circulation of direct precipitation and run-on to the facility from adjacent areas.

The lower caprock region has as its main function the maintenance of stagnant water over the tailings. This is achieved by selecting material for the lower caprock to provide hydraulic conductivity of one or two orders lower than the overlying, coarser caprock.

The filter fabric underlying the caprock confines the organic material layer and also serves as a construction base for the caprock. Light construction equipment will be able to spread materials over the filter fabric, with limited penetration of the caprock into the tailings.

Finally, the organic layer is provided as an oxygen consumer to assure anoxic conditions at the tailings/cap interface. It may be noted that even without the organic layer, research has indicated that anoxic conditions may be expected at the top of the tailings. [20] [21] [22]

The tailings themselves should also be considered as integral to the reclamation cap design. As a silty, consolidated material, the hydraulic conductivity is expected to be very low.

4 Conclusion

In conclusion, appropriate wetlands technology and research under the MEND program prove the effectiveness of a water cover to mitigate acid production from sulfidic tailings. A man-made subaqueous disposal facility offers the opportunity to maximize and control those positive aspects for acid generation mitigation which researchers have found in tailings disposed of in natural aqueous environments. A mine site where an excess of net precipitation occurs may be an ideal environment for application of subaqueous tailing disposal technology.

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EMERGING TECHNOLOGY
FOR BIOREMEDIATION
OF METALS



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PASSIVE BIOREMEDIATION OF METALS FROM WATER USING REACTORS OR CONSTRUCTED WETLANDS

*T. R. Wildeman, D. M. Updegraff,
J. S. Reynolds, and J. L. Bolis*

ABSTRACT

Guidelines for microbial treatment of metal contaminants come from principles developed in aquatic geomicrobiology. Most treatment is controlled by microbial processes, so laboratory- and bench-scale testing, typical of other process design, can be utilized. One laboratory study confirmed that incubation for 4 weeks produced treatment results comparable to those from demonstration wetlands. The same study found that the rate of sulfide production in an anaerobic system started at 1.2 and decreased to 0.75 micromole of S^{2-} /gm of substrate/day. Bench-scale studies were used to determine the loading capacity of the bioreactor, soil permeability for anaerobic reactors, and design suitability. For anaerobic reactors, loading is based on the concept that there should always be excess sulfide compared to heavy metals. In one anaerobic study that used a severely contaminated drainage, pH was increased from 2.5 to 7.5. Metal concentration changes in mg/L were as follows: Zn (150 to 0.2), Cu (55 to <0.05), Fe (700 to 1), and Mn (80 to 1). The concepts have been tested on anaerobic, pilot-scale passive reactors. The pH was increased from 3.0 to 6.5 and metal concentrations decreased to a lesser degree.

MICROBIAL GUIDELINES FOR METALS REMEDIATION

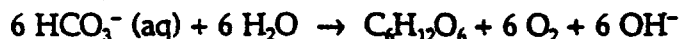
With an expenditure of energy, all metals have been extracted from ores found at the surface or near surface of the earth. Unlike organic

compounds, metals cannot be destroyed. Because minerals form over geologic time, thermodynamics dictates that they represent the most stable chemical form for that metal. Consequently, the objective of metals treatment is to return contaminants to their natural mineral forms. Many of these minerals, such as FeS_2 and MnO_2 , are formed from water in a sedimentary environment. Many of these chemical reactions that occur in an aquatic environment are catalyzed by bacteria. The bioremediation of metal contaminants involves optimizing what has been naturally occurring throughout geologic time.

When remediating metal contaminants in water, the objectives usually require adjusting the pH to about 7 and removing the metals as sulfide, hydroxide, or carbonate precipitates. These objectives generate one of the primary guidelines for metals bioremediation. Because S^- , CO_3^- , and OH^- are common products of bacterial activity, enzymatic uptake of metals into bacteria is not necessary for remediation. Consequently, a more general approach to microbiology is used in passive treatment of metal contamination.

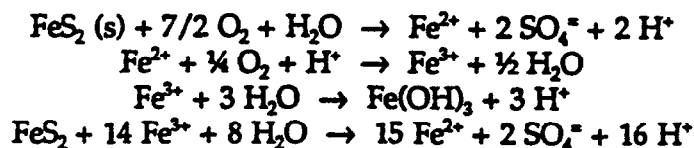
Microbial processes in aerobic environments are very different from those in anaerobic environments. Aerobic conditions are effective in removing metals whose oxides are relatively insoluble. These include Fe(III) , and Mn(IV) . Anaerobic processes, including sulfate reduction, are effective in removing metals that form insoluble sulfides. These include Cu , Zn , Cd , Pb , Ag , and Fe(II) . Both aerobic and anaerobic processes can neutralize acids, increasing the pH, and add alkalinity to water in the form of HCO_3^- . Consequently, in either environment, it is possible to remove Al and Cr(III) as hydroxides, or Zn and Cu as carbonates.

The most important aerobic biological processes in wetlands are iron oxidation and photosynthesis. Both are autotrophic processes in which carbon dioxide is the source of carbon for the organisms concerned. Photosynthesis, carried out by blue-green bacteria, algae, and plants, consumes carbonic acid and bicarbonate and produces hydroxyl ions:



In this case aquatic organisms are making organic matter by taking up dissolved bicarbonate to produce dissolved oxygen and hydroxide ions (Wetzel 1983).

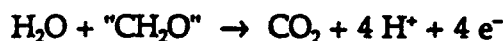
The oxidation of iron pyrite by aerobic autotrophic bacteria of the genus *Thiobacillus* is the cause of acid mine drainage, as summarized by the following reactions from Stumm and Morgan (1981):



Note that H^+ is produced by the oxidation of bisulfide and by the precipitation of $\text{Fe}(\text{OH})_3$. Manganese oxidation and precipitation also releases H^+ :



Finally, oxidation of organic matter produces H^+ :



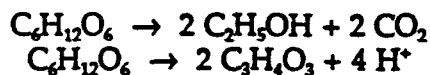
Here, "CH₂O" represents organic matter such as cellulose and other carbohydrates.

Under anaerobic conditions in wetlands, five general types of microbial processes are of importance:

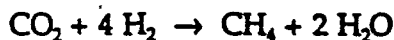
1. Hydrolysis of biopolymers by extracellular bacterial enzymes. An example is the hydrolysis of cellulose, the most abundant organic material in plants, to glucose:



2. Fermentation; examples are the formation of ethanol and pyruvic acid:



3. Methanogenesis:



4. Sulfate reduction:



5. Iron reduction:



Fermentation often produces acids, decreasing pH, while sulfate reduction consumes H^+ and increases pH. Methanogenesis consumes hydrogen ions also. Proton-reducing bacteria, which are symbionts with methanogenic bacteria, convert H^+ to H_2 , and this is used by the methanogenic bacteria to reduce CO_2 to CH_4 . In our anaerobic wetland environments, sulfate reduction and methanogenesis proceed together. Because Postgate (1979) reports that the activity of sulfate-reducing bacteria is severely limited below pH 5, organic materials in a constructed wetland environment have to be chosen so that fermentation does not dominate over sulfate reduction.

MICROBIOLOGICAL GUIDELINES APPLIED TO CONSTRUCTED WETLANDS

Although still not completely understood, the principles outlined above appear to be the predominant removal mechanisms in the treatment of mine drainage and other metal-contaminated waters by constructed wetlands (Hammer 1989, Wildeman et al. 1992). In the early 1980s, aerobic removal processes were emphasized and the precipitation of $Fe(OH)_3$ was an important objective. Because precipitation of $Fe(OH)_3$ produces H^+ ions, iron was removed but the pH of the effluent often was around 3. Brodie (1991) has had success with metals treatment using aerobic constructed wetlands as long as the pH of the influent was above 5.5 and carried some alkalinity in the form of dissolved bicarbonate. Around 1987, groups from the U.S. Bureau of Mines (Hedin et al. 1989) and the Colorado School of Mines (Wildeman & Laudon 1989, Wildeman et al. 1992) began to investigate the role of anaerobic processes, particularly sulfate reduction, in treating acid mine drainage.

The microbial guidelines presented above have been the result of these early studies. Application of these guidelines to aerobic wetlands leads to the following four practices for success:

1. Aerobic removal processes are successful when the pH of the effluent water is above 5.5 and dissolved bicarbonate is present.
2. Any processes, such as anoxic limestone drains (Brodie et al. 1991), that will raise the pH and add alkalinity should be used.
3. Precipitation of iron and manganese oxyhydroxides is a primary removal process and other metal contaminants are removed by adsorption onto these precipitates or by precipitating as carbonates.

4. Plants are essential to success because photosynthesis is a primary process for raising pH, adding oxygen to the water, and supplying organic nutrients.

The role of photosynthesis can be best understood by considering the reaction given in the previous section. At about pH 5.5, significant amounts of bicarbonate can be retained in water (Stumm & Morgan 1981), and this appears to be why such wetlands are effective when the pH is above this value.

Application of the guidelines to anaerobic removal processes is much more direct, because plants are absent and the system is dominated by microbial processes. The following four practices lead to success:

1. Wetland substrates are formulated so that organic material necessary for metabolism is in high abundance and the soil can provide acid buffering capacity at a pH above 7.
2. Microbial processes that transform strong acids such as H_2SO_4 into weak acids such as H_2S are promoted.
3. The products of these reactions are used to precipitate metal contaminants as sulfides (CuS , ZnS , PbS , CdS), hydroxides ($Al(OH)_3$, $Cr(OH)_3$), and carbonates ($MnCO_3$).
4. To remain effective, the reactions that consume H^+ have to predominate over the reactions that produce H^+ .

Using these guidelines results in the construction of systems that work more like passive bioreactors than wetlands (Wildeman 1992). However, they have been successful at raising the pH of metal mine drainages from below 3 to above 6 and have reduced metals concentrations (in mg/L) the following amounts: Fe, 30 to <1; Cu, 1 to <0.03; and Zn, 9 to <0.03. How anaerobic remediation systems are designed will be the focus of the rest of this paper.

STAGED DESIGN OF ANAEROBIC REACTOR SYSTEMS

In our studies on treatment of metal mine drainage by constructed wetlands (Wildeman et al. 1992), when it was determined that precipitation of metals by sulfide generated from sulfate-reducing bacteria is the important process, it was realized that establishing and maintaining the proper environment in the substrate is the key to success for removal.

This means that processes operating on the surface of the wetland may be neglected for design of anaerobic treatment systems. If this is the case, then construction of large pilot cells is not necessary to determine if a wetland that emphasizes anaerobic processes for removal will work.

Consequently, study of wetland processes and design of optimum systems can proceed from laboratory experiments, to bench-scale studies, and then to the design and construction of actual cells. We call this "staged design of wetland systems." Although staged design is best carried out on anaerobic substrates, it has also been used with success on design of aerobic systems. Algal photosynthesizers are excellent generators of oxygen and alkalinity in water, and they can be readily used in laboratory and bench-scale studies of aerobic treatment (Duggan et al. 1992). In actual wetland systems, the growth of glue-green bacteria, algae, and plants on the surface of the system may be important because they increase pH and produce organic matter essential for the growth of sulfate reducers and other heterotrophic bacteria in the subsurface.

Laboratory Studies. In early laboratory studies, culture bottle experiments were used for studies on how to establish tests to determine the production of sulfide by bacteria, and of what substrate will provide the best initial conditions for growth of sulfate-reducing bacteria (Reynolds et al. 1991). In particular, great emphasis is placed on testing local organic and soil materials to determine what mix provides the best environment for sustained sulfate-reducing bacterial activity. Recently, laboratory studies have concentrated on the practical aspects of wetland design. One industrial concern was interested in whether cyanide concentrations typical of milling-waste effluents would kill sulfate-reducing bacteria (Filas & Wildeman 1992). Culture bottle tests showed that sulfate reduction was retarded until the concentration of total cyanide was below 10 mg/L. Another industrial concern wanted to determine whether Cu concentrations above 100 mg/L would kill or retard sulfate-reducing bacteria. Culture bottle tests conducted over the course of 1 month showed that sulfate reduction was still vigorous at Cu concentrations above 100 mg/L.

In the most extensive laboratory study run, a series of culture bottles was sealed and incubated at 18°C to determine the activity of sulfate-reducing bacteria and whether the metals removal in the laboratory was comparable to that in a demonstration anaerobic reactor (Reynolds et al. 1991). For the laboratory study, 20 g of substrate and 70 mL of mine drainage, whose chemistry is shown in Table 1, were sealed into 120-mL serum bottles. The substrate came from an active anaerobic cell from the Big Five Pilot Wetlands in Idaho Springs, Colorado (Wildeman et al. 1992). The rate of sulfate reduction was measured at intervals by two

TABLE 1. Comparison of pH, sulfate, and metal concentrations in mine drainage, wetland output, and serum bottles adapted from Reynolds et al. 1991.

Sample	pH	SO ₄ ²⁻ (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)
Mine Drainage	3.0	1720	0.57	39	31	8.6
Reactor Effluent	6.7	1460	<0.05	0.64	15.8	0.07
Serum Bottles						
1 day (baseline) ^(a)	6.1	1680	<0.05	10.5	15.5	0.04
5 days ^(a)	6.2	1660	<0.05	7.3	10.8	0.53
10 days ^(b)	6.3	1610	<0.05	4.7	9.8	0.27
15 days ^(b)	6.3	1530	<0.05	8.8	15.3	0.13
20 days ^(b)	6.4	1410	<0.05	8.1	12.0	0.37
25 days ^(b)	6.4	1470	<0.05	6.9	11.3	0.22
30 days ^(b)	6.4	1350	<0.05	4.9	9.7	0.21
35 days ^(b)	6.7	1240	<0.05	4.51	10.6	0.16

(a) Values for these samples are the average of 4 replicates.

(b) Values for these samples are the average of 3 replicates.

different methods, one using ³⁴SO₄²⁻ and one not requiring a radioactive tracer. On the day of collection, the effluent from the reactor had the chemistry shown in Table 1. The results for the metals removal are shown in Table 1.

In the baseline bottles, measured 1 day after adding the mine drainage, the pH was significantly higher and metals concentrations were significantly lower than in the mine drainage. As stated in the wetlands guidelines, substrates are formulated to immediately raise the mine drainage pH to neutral conditions. Several processes could have contributed to the immediate removal of metals, including precipitation due to the increase in pH and adsorption onto organic materials. Over the course of 35 days, the pH continues to rise until it is the same as in the effluent from the anaerobic reactor. The concentration of sulfate gradually decreases and sulfide increases until, by day 35, sulfate is below that in the reactor effluent. At 25 days the concentration of sulfate matches that in the reactor effluent. Based on this observation, laboratory-scale tests are conducted for at least 4 weeks to simulate conditions in the field. After 35 days, the pH of the laboratory solutions was the same as for the effluent, and metals removal was comparable. The laboratory studies mimic what is occurring in the demonstration reactor.

Because the serum bottles were sealed, all volatile products were retained. In particular, all retained sulfide species could be titrated and the amount of production gives an estimate of the activity of sulfate reduction. This rate for the first 40 days was 1.2 μM of sulfide/g of substrate/day (Reynolds et al. 1991). From 40 to 80 days, the rate averaged 0.75 $\mu\text{M}/\text{g}/\text{d}$. In design calculations for bench- and pilot-scale reactors, a sulfide production rate of 300 $\text{nM}/\text{g}/\text{d}$ is used.

Bench-Scale Reactors. For bench-scale studies, plastic garbage cans are used to conduct experiments to provide answers necessary to the design of a subsurface cell (Bolis et al. 1991). Typical design parameters to be determined include the optimum loading factor, substrate, cell configuration, and the permeability of the substrate. In a bench-scale study recently completed, garbage cans filled with substrate were used to determine whether using the sulfide generation figure of 300 nM sulfide/ cm^3 substrate/day could be used to set the conditions for treating severely contaminated drainage that flows from the Quartz Hill Tunnel in Central City, Colorado. Contaminant concentrations for this drainage are shown in Table 2. Using the practice guideline described above that the amount of sulfide produced should always be in excess of the amount of heavy metals to be precipitated, with the amount of substrate contained in the garbage can, flow could not exceed 1 mL/m to ensure that produced sulfide would always be in excess.

Contaminant concentrations from the outputs of three different bench-scale cells are shown in Table 2. For Cell A, the mine drainage was passed through the cell with no delay. For Cell B, the substrate was soaked with city water for 1 week before mine drainage started passing through the cell. For Cell C, the substrate was inoculated with an active culture of sulfate-reducing bacteria and soaked with city water for 1 week before mine drainage started passing through the cell. Preparations on Cells B and C were done to ensure that there would be a healthy population of sulfate-reducing bacteria before mine drainage flowed through the substrate. All cells were run in a downflow mode of the mine drainage flow through the substrate. In all three cells removal of Cu, Zn, Fe, and even Mn is greater than 99%. The pH increases from about 2.5 to above 7. These results were maintained consistently for more than 10 weeks of operation.

The substrate used was a mix of $\frac{3}{4}$ composted cow manure and $\frac{1}{4}$ planting soil. The results from Cells A and B show that the cow manure has an indigenous population of sulfate-reducing bacteria that are capable of utilizing the organic material in the manure. Inoculation with an active culture of bacteria is not necessary in this case. Also, because the results

TABLE 2. Constituent concentrations in mg/L in the Quartz Hill Tunnel mine drainage and in effluents from the bench-scale tests.

Sample	Days Operated	Mn	Fe	Cu	Zn	SO ₄	pH
		Concentration in mg/L					
Mine Drainage	24	80.0	630.0	48.0	133.0	4240	2.4
Cell A	24	0.94	1.6	0.06	0.27	450	7.4
Cell B	24	0.91	1.9	<0.05	0.17	770	7.5
Cell C	24	0.99	1.0	<0.05	0.16	412	7.4
Mine Drainage	43	80.0	640.0	50.0	135.0	4300	2.5
Cell A	43	0.97	0.87	<0.05	0.18	1080	7.2
Cell B	43	0.64	0.96	<0.05	0.24	660	7.4
Cell C	43	1.6	0.46	<0.05	0.14	1180	7.2
Mine Drainage	71	70.0	820.0	70.0	101.0	NA	2.6
Cell A	71	0.48	0.40	<0.05	0.21	NA	8.0
Cell B	71	1.6	0.40	<0.05	0.25	NA	7.9

from Cell A are comparable to those of Cells B and C, the population of sulfate reducers can withstand immediate exposure to severe mine drainage and still produce sufficient quantities of sulfide. The key to good initial activity is to ensure that the flow of mine drainage is low enough that its low pH does not disturb the microenvironment established by the bacteria.

Another feature of the results shown in Table 2 is that Mn is removed in all three cells. Typically, Mn is the most difficult contaminant in mine drainage to remove (Brodie 1991, Duggan et al. 1992, Hedin et al. 1989, Wildeman et al. 1992). It is usually presumed that removal of Mn has to be achieved by raising the pH to above 7, and then introducing the effluent into an aerobic wetland cell so that Mn will be oxidized to MnO₂. Removal in an anaerobic cell must be as Mn(II). Analyses of possible species at a pH above 7 suggest that removal could be as MnS or MnCO₃.

Mn does not adsorb onto the organic material as readily as Fe and Cu (Machemer & Wildeman 1992). In this case, it is hypothesized that MnCO₃ is the precipitate because it is more insoluble than the sulfide. In either case, a key to Mn removal in an anaerobic cell appears to be the ability to raise the pH of the effluent above 7. If raising the pH to above 7 can be consistently achieved, then all the contaminants in mine drainage can be removed in one anaerobic cell.

Pilot-Scale Systems. Successful completion of bench-scale tests support a decision to proceed with pilot-scale testing. Bench-scale tests provide relevant results under field climatic and hydrologic conditions. If possible, the pilot cell is a module large enough that expansion to full-scale treatment involves adding more reactor cells. The objective is to collect data on the performance of a reactor module under actual site conditions.

The constructed wetland at the Big Five Tunnel in Idaho Springs, Colorado, is a good example of a pilot-scale facility that has been operated and performance monitored for more than 2 years (Wildeman et al. 1992). This system is an anaerobic wetland for treating acid mine drainage of the chemistry shown in Table 1. From 1987 to 1991, a number of cells have been built and tested. However the cell that was designed using the guidelines presented in this paper was Cell E.

Removal efficiencies for Cell E over a 27-month period are shown in Figure 1. Removal is determined by dividing the wetland effluent by the mine drainage influent concentrations. If removal is complete, the ratio will be close to zero. Examination of Figure 1 shows consistent and complete removal of Cu and Zn. Cell E was started in September 1989, so months 4 through 8 and 16 through 20 would be the winter. Removal of Fe changes with the seasons; it is good in the summer and poor in the

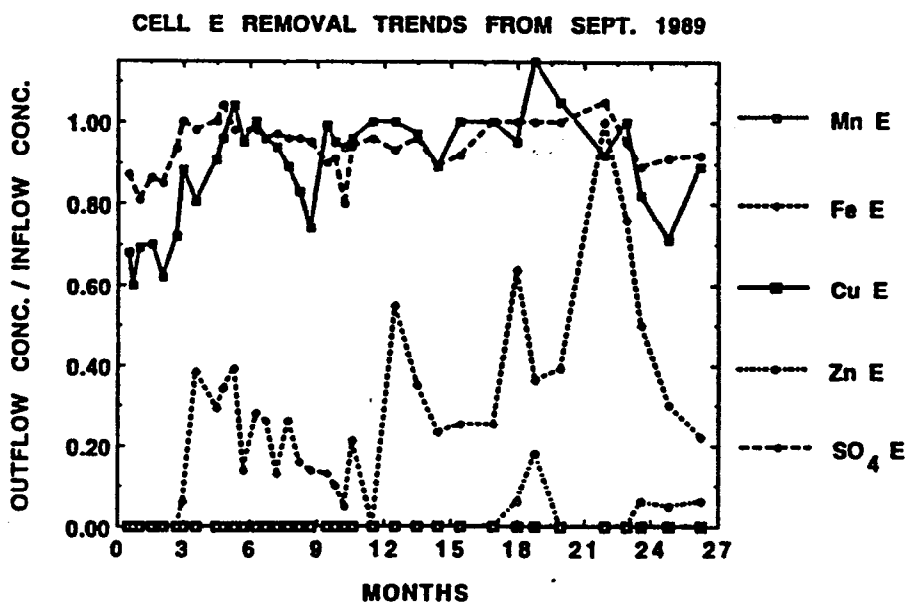


FIGURE 1. Cell E pilot-scale test results. Vertical axis is effluent over mine drainage concentration. The cell was started in September 1989.

winter. Because FeS is more soluble than CuS or ZnS, this winter increase is probably due to the reduction in activity of sulfate-reducing bacteria with decrease in temperature (Postgate 1979). Reduction of bacterial activity appears to be confirmed by the fact that there is a smaller decrease in sulfate concentration in the winter. Because Mn is the most soluble sulfide (Stumm & Morgan 1981), its removal is inconsistent. Note that the results from the pilot cell confirm the laboratory study results given in Table 1.

With the pilot-scale results, actual on-site removal can be assessed and the design criteria for full-scale treatment determined. With this record of treatment, a reasonable case can be presented on how well constructed wetlands and passive treatment reactors will operate in full-scale treatment of contaminated waters.

SUMMARY

Bioremediation of metals can be carried through a staged design process that is comparable to what is used in the bioremediation of fossil fuels (Atlas 1991). Indeed, this is the same approach that is used in mineral processing, and so mine and mill operators readily adapt to the objectives of the treatment. In this paper, passive treatment has been emphasized because it is a cost-effective method for treating effluent from abandoned mines and mills. In passive treatment, maintenance and operations costs are traded for land. All the guidelines given above also could be applied to active systems. In this case, operation and maintenance costs would increase. However, an active system should be able to maintain the activity of bacteria at optimum levels. In active treatment, maintenance and treatment costs would be offset by increased efficiency of treatment.

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PASSIVE TREATMENT METHODS FOR MANGANESE: PRELIMINARY RESULTS FROM TWO PILOT SITES

by

Thomas Wildeman^a, Laura Duggan^a, Peter Phillips^b, Susana Rodriguez-Eaton^b,
Rachael Simms^b, Judith Bender^b, Nick Taylor^c, Cynthia Britt^c, Doreen Mehs^d,
Jay Forse^d, Paul Krabacher^e, and James Herron^e

Abstract In 1991, laboratory and bench-scale studies on the removal of manganese from mine drainage were performed at the Colorado School of Mines. Based on these studies, two experimental systems were built to determine removal efficiency in the field. This paper presents details on the design and construction of the two systems and preliminary results on how well the systems are performing.

A cyanobacteria-algal mat pond, pilot system was built at the Fabius Coal Mines, in Jackson, Co., Alabama by the Tennessee Valley Authority and is being sampled and monitored by faculty from Clark Atlanta University in Atlanta. The water to be treated is effluent from the oxidation and settling pond that is part of the Hard Rock Constructed Wetlands. The algal pond is considered as secondary treatment after the water has traversed the anoxic limestone drain and the settling pond. Consequently, the influent is at a pH above 6, has about 1-4 mg/L of Fe and 3-7 mg/L of Mn. Through photosynthesis, the cyanobacteria and algae add dissolved oxygen to the water and raise the pH above 7. Preliminary results show that removal is complete when flow and loading are respectively set at an average of 3.3 L/min and 2.5 grams of manganese removed per square meter per day in the cyanobacteria-algal mat pond.

Drainage from the Boston Mine, just west of Durango, Colorado, averages in concentrations in mg/L of 16-25 for Mn, 200-500 for Fe, and 9-11 for Zn; pH is 2.4. For a water with this chemistry, an anaerobic system is necessary to raise the pH and reduce metals by sulfate reduction. Also, because winters are severe, a system in which the water travels through the substrate has a better possibility of working year round. For this system, the removal question is whether the pH can be raised from below 3 to above 7 on a consistent basis. If this is achieved, then Mn will be removed as $MnCO_3$. Sampling and monitoring is being done by faculty and students at Fort Lewis College in Durango.

Additional Key Words: manganese removal, constructed wetland, algal pond, pilot-scale reactors, sulfate-reduction

- a. Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO, 80401.
- b. Research Center for Science and Technology, Clark Atlanta Univ. Atlanta, GA 30314.
- c. Tennessee Valley Authority, Knoxville, TN
- d. Chemistry Dept., Fort Lewis College, Durango, CO 81301
- e. Colorado Mined Land Reclamation Division, Denver, CO 80203

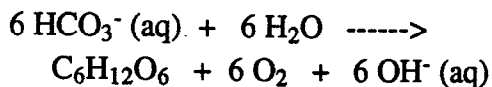
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Introduction

Manganese, a common contaminant in most mine drainages (Wildeman 1991), is difficult to remove from solution because of the high pH required to form insoluble manganese oxides, carbonates, or sulfides (Watzlaf and Casson 1990). In an aerobic environment, MnO_2 should precipitate at a pH above 4 (Stumm and Morgan 1981). However, below a pH of 8, the kinetics of precipitation are quite slow (Wehrli and Stumm, 1989). In an anaerobic environment, $MnCO_3$ is the predominant stable solid. However, in a wetland environment, its solubility product is not exceeded until the pH is above 7 (Wildeman, Brodie, and Gusek 1992).

Aerobic Reactor Experiments

In 1991, laboratory and bench-scale studies were conducted to determine the most effective method of passive treatment of manganese (Duggan, et al. 1992). These studies concluded that if the water contained some alkalinity and the pH was above 5, then the most effective treatment was through the use of an algal mixture containing *Cladophora*. Photosynthesis by the algae appears to be behind this removal. The mechanism can be best understood by considering the following simple reaction for photosynthesis:



In this reaction, the bicarbonate is coming from the water rather than the air. The products raise the pH and add oxygen to the water (Wetzel 1983). In bench-scale studies, the *Cladophora* raised the pH to above 8 and removed manganese to below the Federal limit of 2.0 mg/L (U.S. Code of Federal Regulations 1985 a & b). Of the two bench-scale reservoirs tested, the one with limestone added to the algal pond was more effective than the pond with algae alone. For the limestone reservoir, the manganese removal rate averaged 0.19 gm of manganese/meter²/day (gmd); for the reservoir without limestone, manganese removal averaged 0.15 gmd.

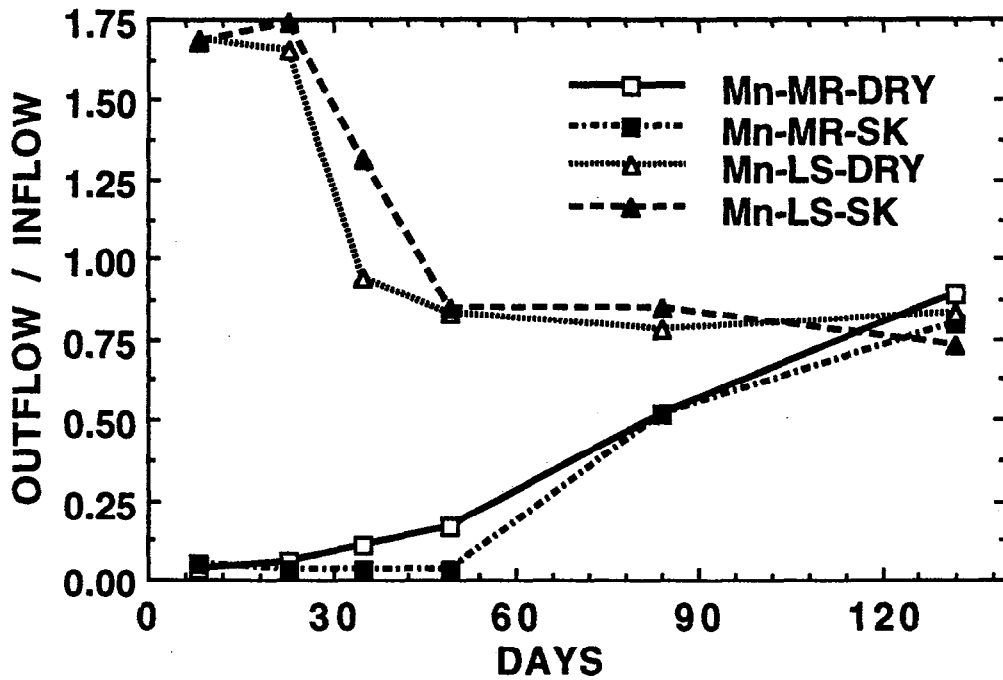
Anaerobic Reactor Experiments

The algal pond system would be most effective as a secondary treatment cell after the pH of the acid drainage had been raised to above 5.5. Also it would operate best in a mild climate where the pond would remain open all winter. Many drainages have a pH of 3 or below (Wildeman 1991) and occur in harsh climates. A passive treatment process capable of removing manganese would be helpful. Consequently, bench-scale studies on anaerobic treatment of an acid drainage below pH 3 were also conducted in 1991 (Bolis, et al. 1992). The objective of these studies was to see if it is possible to consistently keep the effluent from a sulfate-reducing reactor at a pH above 7. If this is possible, then manganese would be removed by precipitation of $MnCO_3$.

Big Five Tunnel acid mine drainage was used for the studies. The water has a pH of 2.8 to 3.0 and concentration of metals in mg/L as follows: Fe-50, Mn-35, Zn-10, and Cu-1. Four reactors with two different substrates were used. One substrate was primarily organic and composed of 70 % cow manure, 20 % planter soil and 10 % inoculum by volume; the other substrate was primarily inorganic and composed of 77 % limestone rock, 14 % alfalfa, and 9 % inoculum by volume. For each substrate, one reactor was soaked with mine drainage for one week prior to operation, another reactor was left dry. The experiment began in July, 1991 and continued through November, 1991. The flow rate was maintained at approximately 10 mL/min; and it was assumed that the activity of sulfide generation was 300 nanomole/cm³/day. At this rate of flow and activity of sulfide generation, the amount of sulfide generated in the substrate should always exceed the amount of iron carried in from the mine drainage (Wildeman, Brodie, and Gusek 1992).

Figure 1 shows the trends in pH and removal of manganese within the four reactors. Manganese removal is measured by effluent outflow over mine drainage inflow. In the initial period of the study, the manure substrate (noted as MR on the figures) performed well. The pH of the effluent was maintained above 7 and manganese was removed to below 2 mg/L.

Mn REMOVAL 1991 BENCH SCALE TESTS



pH 1991 BENCH SCALE TESTS

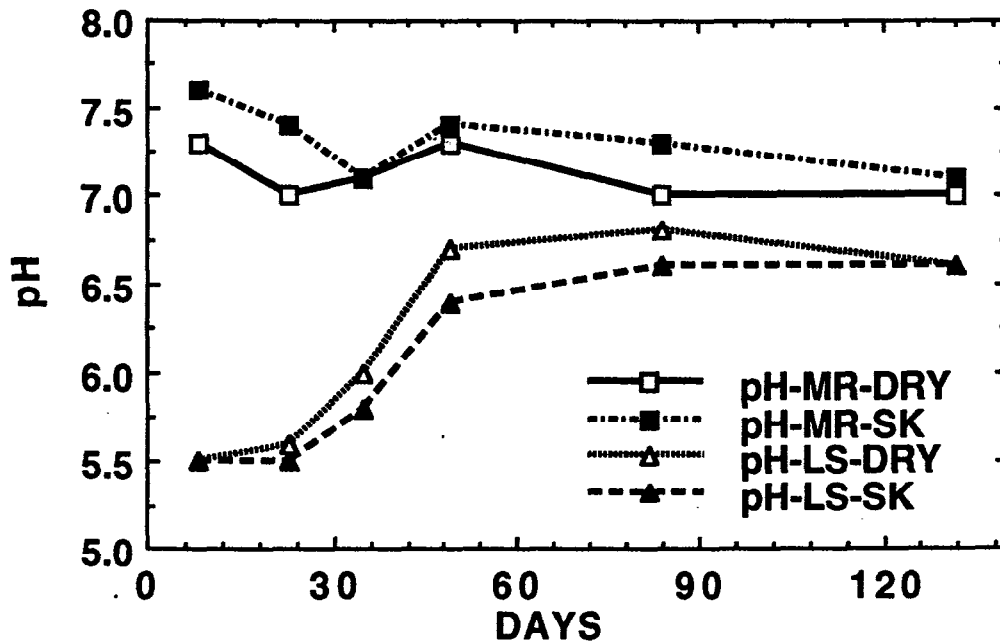


Figure 1. Trends in pH and manganese removal in anaerobic bench-scale reactors. In the figure, Outflow is effluent from the reactor, Inflow is Big Five mine drainage, MR is the manure reactor, LS is the limestone-alfalfa reactor, SK means soaked with mine drainage for one week, and DRY means no soaking was done.

in the soaked manure reactor. However, at the end of the experiment, removal of manganese was poor. This poor removal is attributed to lower activity of the sulfate-reducing bacteria caused by exhaustion of readily available organic nutrients and colder weather.

For the limestone-alfalfa reactors, results were almost opposite to the manure systems. In the initial period, the pH of the systems remained below 6 and manganese was released from the limestone causing the ratio of outflow over inflow to be above 1.0. This low initial pH is attributed to the alfalfa fermenting and releasing low molecular weight organic acids. In the later period of the experiment, sulfate reduction predominates over fermentation, the pH rises, and a minor amount of manganese is removed.

At times, using anaerobic reactors, manganese removal can be excellent. However, removal results are too uncertain to consider an anaerobic treatment system to be the sole method of treatment of manganese in a mine drainage with a pH less than 3. In a severely impacted drainage, a secondary treatment module would have to be added to the end of a sulfate-reduction system to insure that manganese will be removed down to concentrations below 2 mg/L.

Based on these bench-scale studies, two pilot reactors were built during the summer of 1992 to remove excessive concentrations of manganese in water draining from two abandoned coal mines. At the Fabius Coal Mines in Jackson Co., Alabama, the Tennessee Valley Authority built a cyanobacteria-algal mat pond demonstration site. The introduction of the cyanobacteria and green algae and monitoring and sampling is being performed by faculty and students from Clark Atlanta University in Atlanta. At the Boston Mine, in the Perin Peak Wildlife Refuge, four miles west of Durango, Colorado, an anaerobic, sulfate-reducing system was built by the Colorado Mined Land Reclamation Division. Because the pH of the drainage averages 2.4, it is not expected that manganese will be removed in the anaerobic reactor. Consequently, the effluent from the anaerobic cell flows into a rock drain. It is anticipated that the majority of the manganese removal will occur in this drain.

The remainder of this paper describes the design, construction, and initial operation of the two systems.

Aerobic Algal Pond

Design and Construction

The site selected for the cyanobacteria-algal mat pond was at the end of the oxidation pond at the Hard Rock Wetland on the Fabius Property. The drainage has passed through an anoxic limestone drain and the oxidation pond (Brodie et al. 1992a). The two wetland components remove a majority of the iron, and water leaving the oxidation pond has a pH of about 7 and concentrations of Mn and Fe of about 9 and 10 mg/L, respectively. From previous experiences, flow control into a pilot cell is much easier if the flow is at least 1 l/min. Using the loading capacity determined in the bench-scale studies of 0.2 g Mn/m²/day, a pilot pond receiving 1 L/min would be 108 m² (1160 ft²). The bench-scale studies were performed under severe weather conditions, and it was assumed that removal rate could be increased in a mild climate. Consequently, it was decided to make the pilot pond area to be 46 m² (500 ft²) and initial influent flow to be 1 L/min.

The group at Clark Atlanta University have a special research interest in the treatment of waters using cyanobacteria mats (Bender et al. 1991). The primary pond at Fabius was established with a cyanobacteria-algae mat. In addition, two control ponds were included in the study. A plan view of the demonstration site is shown in Figure 2. Water from the oxidation pond (OX) enters a trickling filter pond (TF) that removes some suspended Fe(OH)₃ (Brodie et al. 1992b), and then leaves from one pipe to feed all three ponds with similar water. Each pond was constructed with an uneven rock bottom surface consisting of four-foot wide rock baffles separated by one-foot wide troughs. Over the troughs, the depth of the water averages about 30 cm; over the baffles the water depth is 0 - 5 cm. In Figure 2, a cross section through the length of the pond shows the distribution of baffles and troughs. Two ponds, including the one where

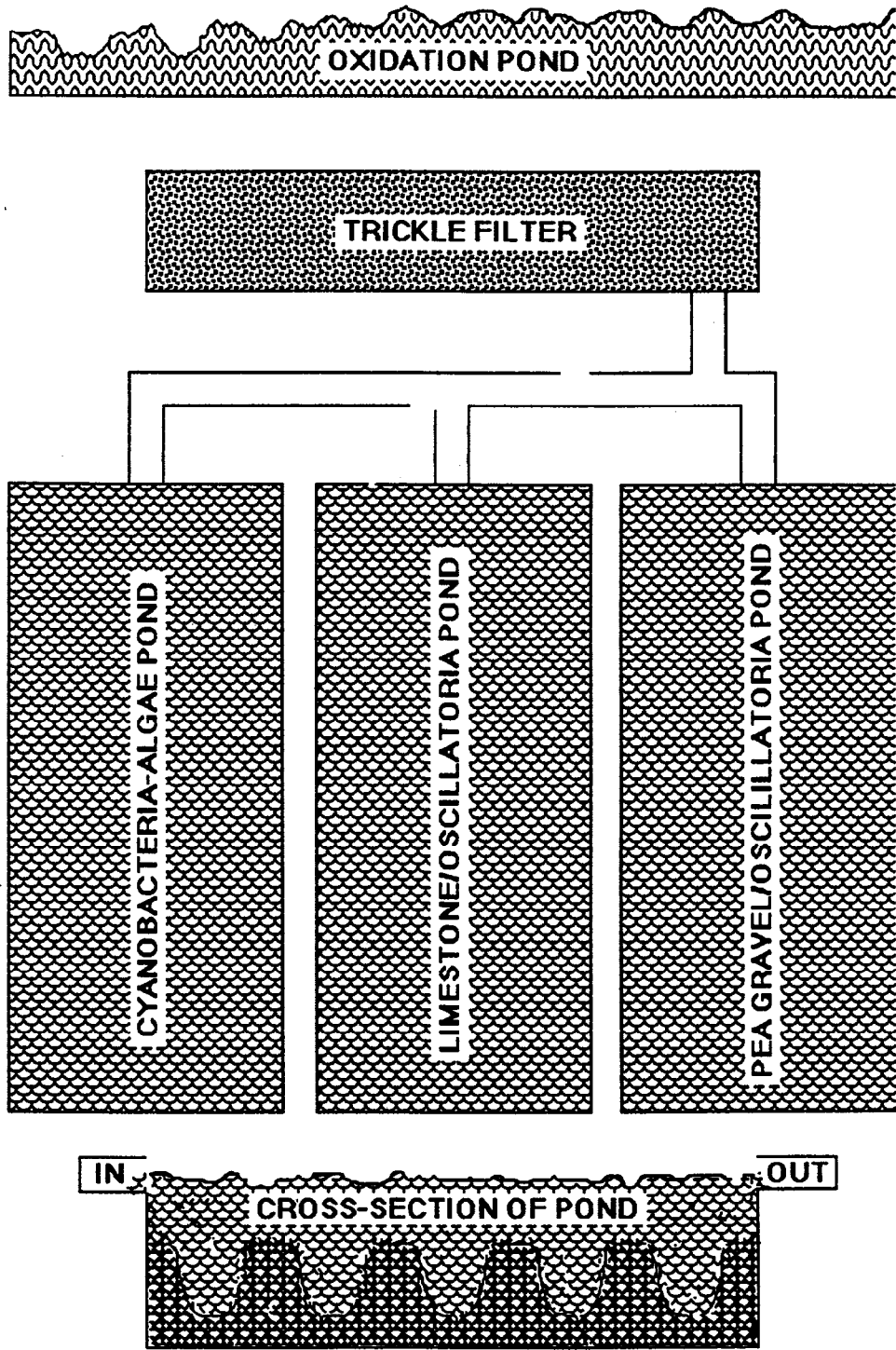


Figure 2. Plan view of the Cyanobacteria-Algal Mat Pond Pilot System at the Hard Rock Wetland, Alabama. Also included is a cross-section view through the length of one of the algal ponds.

the cyanobacteria were established, contained 2.5 cm of the high-calcium limestone rock that has been used for other Fabius projects (Brodie et al. 1992b). The third pond contained 1 cm pea gravel. This was done to study whether rock type would affect Mn removal.

Construction of the ponds involved preparing a slightly sloping pad of one foot in depth, lining the pad with 10 mil black polyethylene, and carefully placing the rock on the pad in the baffle and trough pattern. Water is gravity fed from the trickling filter to the ponds. Flow is controlled with valves. Construction occurred in May of 1992 and establishment of the cyanobacteria-algal mat occurred in June.

Because $\text{Fe}(\text{OH})_3$ buildup rapidly obstructs the flow, significant changes in flow occur over the course of a day. Consequently, daily adjustments of flow are required. This daily change causes problems in determining flow for loading calculations. Beginning in early October, the target flow was chosen as 5 L/min. The clogging problems made this a difficult target to achieve. For calculations, it was decided to average all the flows over the operation period from October through January and use this average as the representative flow. The calculated average is 3.3 L/min.

Start-up and Operation

Each pond has developed a slightly different ecosystem, and so will be discussed separately. The cyanobacteria-algae mat pond (CGM) is an entire ecosystem containing several bacteria species, but dominated by cyanobacteria in a multilayered mat structure. Details of mat preparation are contained in Bender et al. 1991. Microbial strains, including *Oscillatoria* spp., green filamentous algae and *Chromatium* spp. were harvested from the Hard Rock site in February, 1992. These were developed into silage-microbe mats in the laboratory. When there was no flow through the system, these mats, along with silage, were broadcast over the pond in three applications over a four-week period. Within two months, a heavy mat, resembling an old rug pad, was floating through the entire pond just below the surface of the water. the

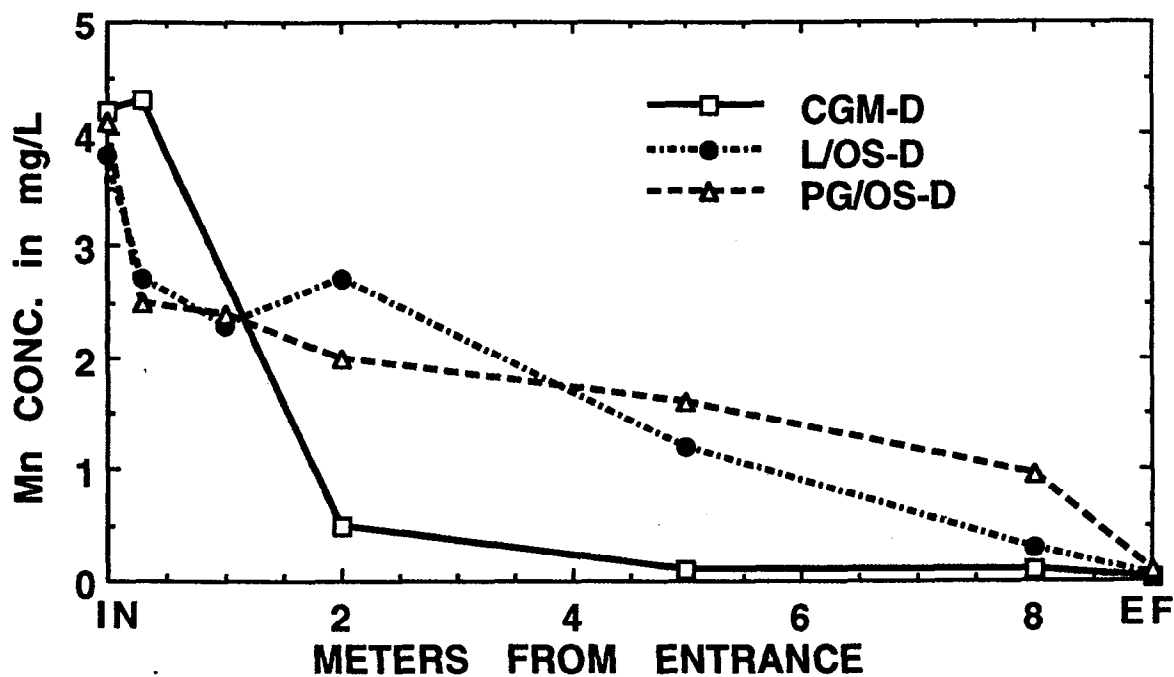
limestone rock became covered with a thick growth of cyanobacteria. Water flows between the floating mat and the cyanobacteria-covered limestone.

It was intended that the other limestone pond remain free of algae and act as a control. However, cyanobacteria from the CGM pond apparently spread into this pond. Also green algae, *Oscillatoria* spp., spread across 10 % of the pond surface. This is now designated as the Limestone/*Oscillatoria* (L/Os) Pond. Similarly, it was intended to keep the pond with the pea gravel bottom free of algae so that it could serve as a control on how rock composition affected manganese removal. However, cyanobacteria have spread into this pond, though not as much as in the (L/Os) pond. This is now designated as the Pea Gravel/*Oscillatoria* (PG/Os) Pond. Flow of 1 L/min through the ponds was initiated in July, 1992 and all three removed Mn to below 2 mg/L.

Because there were no treatment differences within the ponds, flow was increased to 2 L/min on August 26, 1992. Mn was still removed to below 2 mg/L in all three ponds. On October 6, 1992 flow was increased to 5 L/min. However, because of $\text{Fe}(\text{OH})_3$ buildup, the average flow through the three ponds is 3.3 L/min. This is equivalent to a loading capacity of about 1.0 g Mn/m²/day. On October 13 and 14, sampling along the length of the ponds was done during the day and again at night when photosynthesis is not occurring. The water samples were filtered through a 0.45 μm filter, and acidified with nitric acid. The metals were analyzed by flame atomic absorption spectrophotometry. The night and day water chemistry in pond CGM is shown in Table 1. Figure 3 shows the night and day manganese concentrations in all three ponds.

The cyanobacteria in the CGM pond are quite effective at maintaining the high Eh, high dissolved O₂, and high pH conditions that are necessary for the precipitation of MnO₂. Both iron and manganese are removed to concentrations an order of magnitude below the effluent limits. In the other ponds, Figure 3 shows that Mn is also removed to below the

DAYTIME Mn CONC. IN ALGAL PONDS



NIGHTTIME Mn CONC. IN ALGAL PONDS

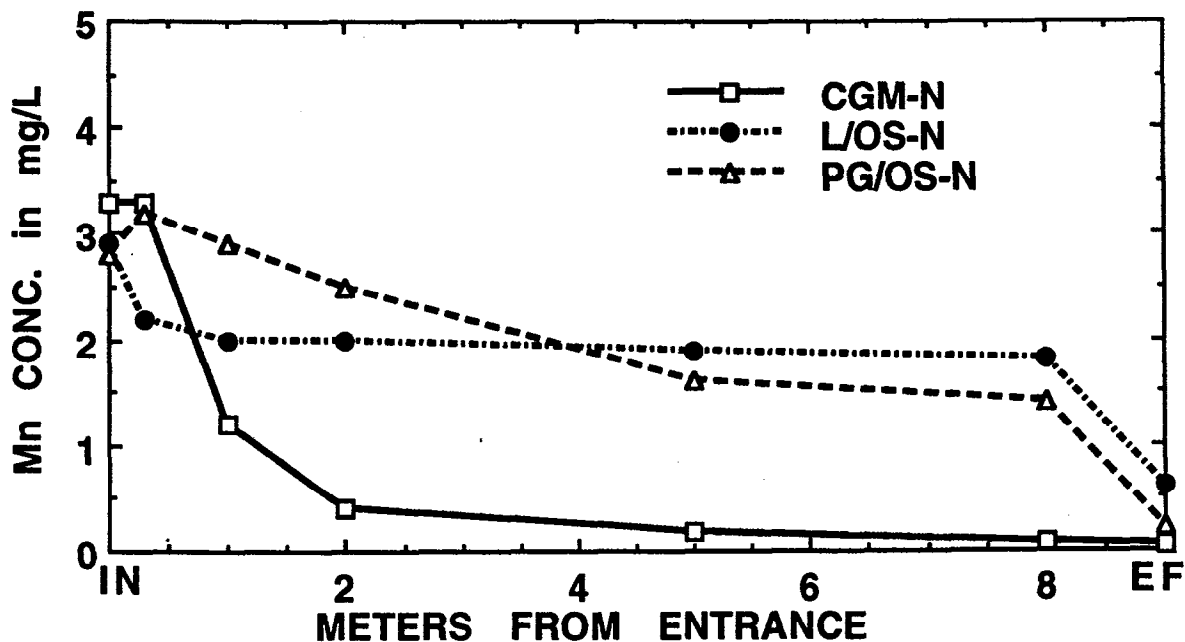


Figure 3. Daytime and nighttime manganese removal in the algal ponds. CGM is the cyanobacteria-algae mat pond, L/OS is the Limestone/Oscillatoria pond, and PG/OS is the Pea Gravel/ Oscillatoria pond.

Table 1. Chemistry of the influents, pond samples, and effluents for the cyanobacteria-algae pond (CGM) at the Hard Rock Wetland at the Fabius Coal Mine. OX is the oxidation pond effluent; TF is the trickling filter effluent; IN is at the CGM pond entrance; and numbers correspond to the distance in meters from the pond entrance. The samples were taken on October 13 and 14, 1993. Each result is a single determination. Average flow rate is 3.3 L/min.

Sample Location	Diss. O ₂ mg/L	pH	Eh mV.	Conductivity μ Siemens/cm	Total Metal Conc. (mg/L)	
					Mn	Fe
DAYTIME SAMPLES						
OX	5.7	6.6	430	703	9.7	11.9
CGM-IN	6.1	6.6	470	689	4.5	16.3
CGM-0.3	4.9	6.7	400	708	4.3	3.2
CGM-1.0	8.0	6.8	440	702		1.9
CGM-2.0	7.2	6.9	470	725	0.5	1.1
CGM-5.0	10.5	7.2	430	778	0.1	0.6
CGM-8.0	16.0	7.7	440	775	0.1	0.4
NIGHTTIME SAMPLES						
OX	7.2	7.0	410	694	9.8	4.7
TF	8.0	7.0	410	698	9.9	10.2
CGM-IN	6.0	6.9	430	649	3.6	
CGM-0.3	6.0	6.8	460	680	3.4	1.0
CGM-1.0	4.5	6.9	460	685	1.2	0.5
CGM-2.0	4.0	7.2	460	681	0.4	0.2
CGM-5.0	3.0	7.2	450	740	0.2	0.2
CGM-8.0	2.0	7.2	450	715	0.08	0.03

Table 2. Water quality parameters of the Boston Mine seeps.

Date	12-6-91	3-13-92	5-11-92
Flow (L/m)	40	20	~80
pH	2.5	2.4	2.3
Mn mg/L	25	20	18
Fe mg/L	290	130	480
Zn mg/L	11	8.2	10.5
Cu mg/L	0.52	0.3	0.8

Table 3. Preliminary water quality parameters at the Boston Mine Wetland.

Date	9-26-92		10-10-92		10-24-92		11-7-92	
	Drainage	Effluent	Drainage	Effluent	Drainage	Effluent	Drainage	Effluent
pH	2.8	3.8	2.6	3.7	2.6	3.2	2.9	3.6
Eh (mV)	720	580	720	540	720	590	730	600
Cond. ^a	8500	12200	10830	12000	9860	9240	8000	10200

a. Conductivity units are in μ Siemens/cm.

effluent limit of 2 mg/L. However, treatment of Mn, especially at night, is not as efficient as in the CGM pond. In the CGM pond, it is seen that the concentration of Mn is appreciably below 2 mg/L after the water has traveled only 2 meters from the pond entrance. Using a Mn concentration of 9 mg/L, an average flow of 3.3 L/min, and an area of 11 m² (corresponding to a pond 2 m instead of 10 m in length), gives a loading capacity of 3.9 gmd for Mn removal in the CGM Pond. This type of calculation has been done for all October-January data for the CGM Pond and the resulted in an average loading capacity of 2.5 gmd for Mn for the CGM Pond during this period.

At night, respiration by the algae will reverse the photosynthesis reaction and begin to use oxygen and lower the pH. This could retard manganese removal. The decrease in oxygen is seen in Table 1 where nighttime dissolved oxygen concentrations drop off at the end of the pond. However, the nighttime decrease in pH is minimal. It may be that other processes operating in the CGM Pond moderate the effect of nighttime respiration. In addition, the biomass in the CGM Pond is substantially larger. This organic material could remove Mn by processes other than oxidation and precipitation. These other processes could significantly contribute to removal during the night.

Other Considerations

All pilot projects produce unexpected results; and this cyanobacteria-algal mat pond is no exception. When the cyanobacteria mat was being established, the ponds were colonized by insect larvae that grazed on the algae. The preference of the grazers was for *Oscillatoria* spp. and not filamentous green algae. The presence of the green algae appeared to protect the cyanobacterial component of the mat. Because the other two ponds were dominated by *Oscillatoria* spp., the effect of the larvae was much more severe.

In this study, as in the Big Five Pilot study, controlling water flows of 4 L/min or less is difficult (Wildeman, Brodie and Gusek 1992). In mine drainage situations, the

suspended solids are dominated by Fe(OH)₃; these rapidly clog any flow control valve. Because the algal-pond influent is coming from an oxidation pond whose function is to create Fe(OH)₃ precipitate, the problem is exacerbated. The current solution is to continue aeration, remove as much precipitate as possible in the trickling filter, and adjust the flow into the ponds every day. However, this solution is far from acceptable.

Anaerobic Reactor

Design and Construction

Although the Boston Mine is underground, flow from the adit is minimal. Coal was mined from rooms that were near, but down-dip, from the adit. Consequently, the drainage is from hillside seeps near the location of these rooms. Depending on the precipitation, drainage is from 8 to 80 L/min. However, the chemistry of the water is always quite severe. Water chemistry and flow at three different sampling times is shown in Table 2. The mine and drainage are on the Perin Peak Wildlife Refuge that was established as an elk winter-grazing area. Because the site is remote and access is limited, a passive system was the only reasonable treatment solution. The Colorado Division of Wildlife was interested in treating the water primarily because the drainage sometimes reaches a cold-water fisheries stream. High concentrations of zinc severely impact the mortality of trout. Low pH and high concentrations of Fe dictate that a sulfate-reducing treatment system is the most reasonable treatment method (Wildeman, Brodie, and Gusek 1992). The chemistry of the water presents a severe challenge for any treatment system.

Using a flow of 20 L/min and concentrations of Fe and Zn of 200 and 10 mg/L, 108 moles per day of heavy metals would enter the treatment system. Using a sulfide production rate of 300 nanomole/cm³/day, 360 m³ of substrate would be required to precipitate the heavy metals as sulfides. The design calculations do not include manganese because it is assumed that it will be precipitated as a carbonate if the pH can be maintained above 7. A flat area just below

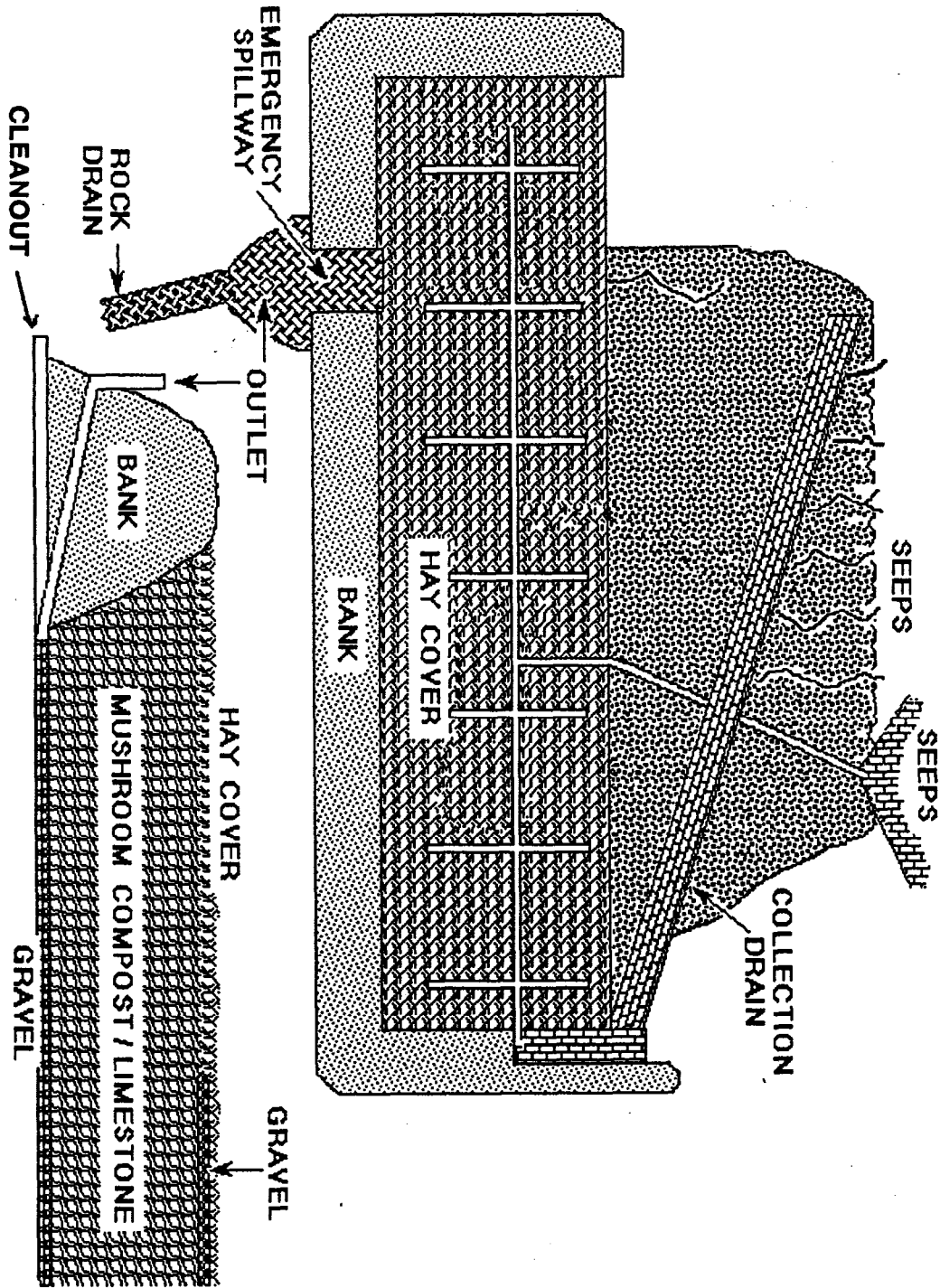


Figure 4. A plan view of the Boston Mine Wetland, including a cross-section view through the width of the anaerobic reactor.

the seeps of 45 m (140 ft) by 10 m (33 ft) was used to construct an anaerobic reactor that was 1.1 m (3.5 ft) deep. This amounts to about 500 m³ (580 y³). A plan view of the treatment system is shown in Figure 4.

The most reliable local source of substrate was mushroom compost composed of white wheat straw, cotton seed meal, poultry waste, and lime. It had been aged for several years and had a soil pH of 7.5. As a neutralizing supplement, limestone fines were mixed with the compost in a volume ratio of 80 % compost and 20 % limestone. The aged compost did not produce a strong activity of sulfate-reducing bacteria and so 10 % of the compost was fresh from the farm and served as the bacterial source.

Because the local soil had a high abundance of clay, the liner for the reactor was made of local compacted soil. The stability of the slope that contained the seeps was a major concern. Consequently, special collection trenches were built on the slope just under the seeps and the side of the wetland closest to the seep slope was covered with gravel in case slumping occurred. The collection trenches are connected to an inflow gallery made of perforated plastic pipe that extends the length of the system. A 10 centimeter-thick gravel layer with perforated pipes was installed beneath the substrate to promote drainage through the bottom of the reactor cell. Effluent flows from the bottom of the reactor and flow is controlled by adjusting the height of the outflow pipe. TYPAR^R landscape fabric was used in two areas to keep fine materials from clogging the system. On top, fabric was placed between the gravel and substrate to keep the silt washed from the hillside from clogging the substrate pores. On the bottom, fabric was placed between the substrate and gravel to keep limestone and other substrate fines from clogging the effluent plumbing. Continuous flow through the substrate helps to insure that the system will operate during the winter. To further insulate the reactor, a 20 cm layer of hay was placed on top of the reactor.

It was assumed that the anaerobic reactor would raise the pH to around 6 and remove all the Zn and Cu, and 90 % of the Fe. Minimal

removal of manganese was expected. To remove manganese and polish the anoxic waters, a gravel lined spillway trench was installed below the reactor to direct the water to the existing gully. The trench is 154 m long, 1.3 m wide, and is filled with 15 cm of 5 cm gravel. Besides polishing the water, it is hoped that algae and bacteria in the trench will promote the oxidation of Fe and Mn.

Start-up and Operation

Construction of the reactor began on August 1, 1992 and was completed on September 12, 1992. It was anticipated that, at a flow of 40 L/min into the reactor, the system would be filled in one week and another week would be used to allow the sulfate reducers to incubate. However, after six weeks, flow from the standpipe was not continuous. Water was to the top of the pipe and at times had flowed from the pipe. However, water had also flowed over the emergency spillway. Water samples were taken from a clean-out plug that drained the bottom of the reactor. The chemistry of these samples and influent waters is given in Table 3.

If sulfate reduction were vigorously occurring, the effluent pH would be about 6 and Eh about 100 mV. It appears that initiation of sulfate reduction using this highly acidic water is taking longer than two weeks. Heavy snowfalls started in mid-November and so the status of treatment may not be completely known until next March.

Other Considerations

Operation of an anaerobic reactor depends strongly on the ability of the contaminated water to uniformly flow through the substrate. To effect this, the system should be adequately lined and the hydraulic conductivity of the proposed substrate should be known (Wildeman, Brodie, and Gusek 1992). In the construction of this reactor, the hydraulic conductivity of the substrate was never determined because it was assumed that the flow through the system would be so low that there would be the necessary water head between the top of the reactor and the top of the standpipe. Also, a conventional liner was not used because it was assumed that local clays

would act as a seal. At this time, it is uncertain if not attending to these two parameters is causing the difficulty with discontinuous flow through the reactor. Having continuous flow through the reactor during the winter is important to ensuring that the system does not freeze. The seep water rarely falls below 10 °C, and the thermal energy that it brings in keeps the bioreactor operating during the winter.

High calcium limestone (minimum 90 % CaCO₃) was used in both the bench-scale anaerobic reactors and in the wetland. In both cases, it alone is not sufficient to bring the pH of the water up to 6 even when all the iron in the drainage is as Fe(II). It appears that limestone dissolution slows down as the pH rises such that it acts as an almost neutral component of the substrate when the pH reaches 5.

Summary

Currently, it appears that, for the cyanobacteria-algal mat pond system, manganese removal can be quite promising. At the high flow rates, removal capacity to below a Mn concentration of 2 mg/L is 2.5 gmd of Mn. In their guidelines, the U.S. Bureau of Mines currently uses a value of 0.5 gmd of Mn (Hedin and Nairn 1992). If the level of removal capacity can be maintained during the winter, the role of cyanobacteria-algal mat ponds for passive manganese removal will be assured.

Another feature of the aerobic study is that algae can be used to simulate the photosynthetic reactions taking place on the surface of a wetland ecosystem. Because the algal experiments can be readily carried out in the laboratory, a scheme now exists to perform staged design of aerobic wetlands in the same way staged design of anaerobic wetlands is carried out (Wildeman, Brodie and Gusek 1992). It is no longer necessary to build a large demonstration system to find out "In-Principle" whether contaminant removal using wetlands is feasible.

With respect to the Boston Mine Wetland, operation is still in the beginning phases.

Important milestones in the operation will include:

- Having water flow through the reactor in the manner in which it was designed.
- Having the system operate throughout this winter and not freeze.
- Having signs of vigorous sulfate reduction in the system appear next spring.

Considering the severe contamination of the water, continuous success at treatment would provide some confidence that the design methods for sulfate-reducing wetland systems are beginning to be understood.

Both systems have not been operating long enough to determine how much continuous maintenance has to be performed. In particular, the issues of whether the cyanobacteria-algal mat ponds need clean-out of precipitate and organic debris and whether the plumbing and substrate in the anaerobic cell will rapidly clog are important to long term operation.

Acknowledgements

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HYDRAULIC CONDUCTIVITY OF SUBSTRATES USED FOR PASSIVE ACID MINE DRAINAGE TREATMENT¹

by

Judith L. Bolis, Thomas R. Wildeman and Helen E. Dawson²

Abstract. In anaerobic wetland systems that emphasize flow of acid mine drainage through the substrate, the hydraulic conductivity of the substrate material is an important variable. This paper describes results of hydraulic conductivity measurements obtained from two sets of bench scale experiments conducted in 1990 and 1991 with substrate-filled reactors that were used to treat acid mine drainage in the Clear Creek-Central City Superfund site. In 1990, the reactors were filled with an organic substrate of manure and planter soil and were subjected to three initial substrate conditions: 1) dry, 2) soaked with water for one week, and 3) inoculated and soaked with water for one week. Flow rate measurements indicated that the hydraulic conductivity of the initially dry substrate remained consistent over time, while the hydraulic conductivity of the soaked substrates increased over time. In 1991, a primarily inorganic substrate of limestone and alfalfa was tested in addition to the previously described organic substrate. Initial substrate conditions for both substrate types were 1) dry and inoculated and 2) inoculated and soaked for one week with mine drainage. Results indicate that in both the limestone and manure reactors which started with dry substrate, the hydraulic conductivity fluctuated considerably. The values for the initially dry limestone ranged from 2.1×10^{-3} - 1.3×10^{-2} cm/sec while the initially dry manure ranged from 9.9×10^{-5} - 7.1×10^{-3} cm/sec. The hydraulic conductivity was more consistent in the soaked reactors ranging from 1.3×10^{-3} - 8.8×10^{-3} cm/sec in the soaked limestone and from 3.4×10^{-4} to 6.9×10^{-3} cm/sec in the soaked manure. These results indicate that presoaking the substrate for wetlands treatment of acid mine drainage can assist in providing a more stable hydraulic conductivity and, therefore, a more consistent flow rate.

Key words: hydraulic conductivity, acid mine drainage, bench scale reactor, permeameter

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²Judith L. Bolis is a graduate student and Helen E. Dawson is an assistant professor in the Department of Environmental Sciences and Engineering, and Thomas R. Wildeman is Professor of Chemistry and Geochemistry in the Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401.

Introduction

Anaerobic treatment of acid mine drainage has been found to successfully remove metals and raise pH through the bacterial reduction of sulfate to sulfides (Howard et al. 1989). This treatment method requires designing a substrate that will facilitate subsurface flow as well as optimize conditions for bacterial reduction. Typically, the effectiveness of constructed wetlands for treating acid mine drainage or other wastewater depends on the hydraulic conductivity of the substrate. Low hydraulic conductivity, caused by a build up of bacterial growth and sediment fines, may cause

short circuiting of a treatment system (Lemke 1989, Cooper 1989, Watson et al. 1989, Staubitz 1989, Trautman 1989). Specifically, in the treatment of acid mine drainage in constructed wetlands, a decrease in the hydraulic conductivity of a substrate may result in surface flow (Steiner 1989) and, thus, affect the removal efficiency of an anaerobic treatment system that depends on subsurface flow (Machemer et al. 1990). Table 1 lists the hydraulic conductivities reported in the literature for various materials that have been used in the wetlands treatment of acid mine drainage and other wastewater.

Hydraulic conductivities measured in bench scale permeameters have been found to be predictive of the hydraulic conductivities in pilot scale wetlands (Lemke 1989). Lemke measured the hydraulic conductivities of fresh and used organic substrates composed of varying ratios of mushroom compost, peat and wood shavings and determined values ranging from 3.0×10^{-4} cm/sec to 6.7×10^{-7} cm/sec. Bench scale experiments used to simulate the removal of metals from acid mine drainage (Bolis et al. 1991) suggested that hydraulic conductivity is a function of the initial condition of the substrate, i.e., dry versus soaked.

This paper compares the results of hydraulic conductivity measurements obtained in previous bench scale experiments (Bolis et al. 1991) to the results obtained from additional experiments designed to more definitively determine the influence of initial condition and time on hydraulic conductivity. The first set of experiments were conducted in 1990 with acid mine drainage from the Quartz Hill and National Tunnel sites in the Central City/Blackhawk mining district as described by Bolis et al. (1991). The second set of experiments were conducted in 1991 with acid mine drainage from the Big Five Tunnel in Idaho Springs, CO. In the latter experiments, both inorganic and organic substrates were tested in the lab and in the field. The results of the hydraulic conductivity measurements are evaluated with regards to the type of substrate and initial condition of the substrate.

Materials and Methods

1990 Experiments

Substrate hydraulic conductivity was initially evaluated using the National Tunnel and Quartz Hill mine drainage reactors. The reactors were

constructed of 32 gallon plastic garbage cans fitted with PVC pipe and designed to operate without valve control in a downflow configuration (Bolis et al. 1991).

The substrate was a mixture of cow manure and top soil in a 3:1 ratio. Three initial substrate conditions were tested for both drainages. Prior to flowing mine drainage through the system, one reactor was dry, a second reactor was soaked with water for one week, and a third was inoculated and soaked with water for one week. The inoculum was a mixture of substrate from the Big Five wetland that contained sulfate reducing bacteria (Batal 1989).

Experimentation began in June 1990 and continued until November 1990. The reactors were operated in a downflow configuration with a constant head reservoir of water on top of the substrate. Flow rates were maintained at 10 ml/min for the National Tunnel drainage and 1 ml/min for the Quartz Hill drainage by adjusting the height with the effluent pipe. An upflow configuration was also evaluated later in the experimentation on both drainages.

1991 Experiments

The Big Five Tunnel acid mine drainage was used for more extensive evaluation of the hydraulic conductivity of substrates. This drainage is characterized with a pH of approximately 3.0 and metals concentrations of 50 mg/L Fe, 35 mg/L Mn, 10 mg/L Zn, and 1 mg/L Cu (Wildeman and Laudon 1989).

The four reactors used in this study were similar to those used in the previous study. Each reactor had a constant head reservoir of water on top of the substrate. Flow rates were maintained at approximately 10 mL/min adjusted by raising or lowering the effluent level.

Two types of substrate were tested in the reactors: an organic and inorganic substrate. Two of the reactors contained the organic substrate tested in 1990 composed of 75% cow manure and 25% planter soil by volume (Bolis et al. 1991). The pH of this substrate was approximately 8.7. The total amount of substrate used in each reactor was 225 lb, of which 25 lb was inoculum. The inoculum consisted of substrate from currently active cells at the Big Five pilot wetland. One of the reactors was soaked for 1 week with mine drainage prior to operation, the other was left dry.

The second set of reactors contained a primarily inorganic substrate composed of

Table 1. Hydraulic conductivity of substrates used in wetlands treatment of wastewater.

MATERIAL	HYDRAULIC CONDUCTIVITY		USE	REFERENCE
	Reported Values	Equivalent in cm/sec		
Mushroom compost (unused) lab downflow bench-downflow pilot-downflow lab-upflow bench-upflow pilot-upflow	3.50 x 10 ⁻³ cm/s 3.14 x 10 ⁻³ cm/s 2.96 x 10 ⁻⁴ cm/s 6.65 x 10 ⁻² cm/s 1.44 x 10 ⁻² cm/s 1.38 x 10 ⁻² cm/s	3.50 x 10 ⁻³ 3.14 x 10 ⁻³ 2.96 x 10 ⁻⁴ 6.65 x 10 ⁻² 1.44 x 10 ⁻² 1.38 x 10 ⁻²	acid mine drainage	Lemke 1989
Old Natural Reed Beds recommended United Kingdom design values gravel pulverized fuel ash quarry rejects pea gravel	5 x 10 ⁻⁶ m/s 3 x 10 ⁻³ m/s 1 x 10 ⁻³ m/s 8 x 10 ⁻⁵ m/s 1 x 10 ⁻³ m/s 8 x 10 ⁻¹ m/s	5 x 10 ⁻⁴ 3 x 10 ⁻¹ 1 x 10 ⁻¹ 8 x 10 ⁻³ 1 x 10 ⁻¹ 8 x 10 ¹	general wastewater treatment	Referenced in Cooper and Hobson 1989
soil beds (in Europe) gravel beds (in Europe) suggested range	2.6 m/d 30 m/d 30 - 864 m/d	3 x 10 ⁻³ 3.4 x 10 ⁻² 3.4 x 10 ⁻² - 1 x 10 ¹	general wastewater treatment	Referenced in Watson et al. 1989
reed bed media range: clays coarse gravel soil beds	1 x 10 ⁻⁷ m/s 1 x 10 ⁻¹ m/s < 3 x 10 ⁻⁵ m/s	1 x 10 ⁻⁵ 1 x 10 ¹ 3 x 10 ⁻⁹	reed bed treatment	Referenced in Hobson 1989
homogeneous mixture (lab test) sorted substrate (lab test)	80 m/d 1600 m/d	9 x 10 ⁻² 1.8 x 10 ¹	landfill leachate treatment	Staubitz et al. 1989

approximately 77% limestone rock, 14% alfalfa, and 9% inoculum by volume. These reactors contained a total of 260 lb of substrate composed of approximately 198 lb limestone, 37 lb alfalfa, and 25 lb inoculum. The limestone rock ranged in size from 1/8 inch to 1/2 inch. Again, the inoculum was obtained from cells at the Big Five wetland. As with the manure substrate reactors, one of the reactors was soaked with mine drainage for one week prior to operation and the other was left dry.

This experiment began in July 1991 and continued through November 1991. The flow rate through the reactors was maintained at approximately 10 mL/min. The optimum flow rates were determined from evaluation of metal removal rates in bench scale experiments and the Big Five pilot treatment system (Bolis et al. 1991, Wildeman et al. 1990).

For both the 1990 and 1991 sets of experiments, the flow rates were measured and adjusted regularly. The difference in height between the standing water on top of the substrate

and the outlet was measured, as well as the height of the substrate in the reactor in order to assess whether compaction of the substrate occurred during the course of the experiments. Field measurements of pH, Eh, conductivity, and temperature were made on a regular basis. Water sampling and constituent analyses followed procedures established for the Big Five constructed wetland.

1991 Lab Experiments

Hydraulic conductivities of the manure and limestone substrates were also measured in the lab, using both the constant head and a falling head techniques described in Fetter (1988) and EPA Method 9100 (1986). The permeameter used was 45 cm high and 7 cm in diameter. A third substrate, a mixture of manure and hay in a 3:1 ratio was also tested in the lab. This substrate has been utilized by others to evaluate wetlands treatment of acid mine drainage (Euler et al. 1991).

Calculation of Hydraulic Conductivity

Hydraulic conductivity of each reactor substrate was determined from Darcy's Law (Fetter 1988, U.S. EPA 1986). Flow through saturated media is governed by Darcy's Law, as follows:

$$Q = K A \frac{dh}{dl} \quad (1)$$

where Q = volumetric flow rate, (ml/min)
 K = hydraulic conductivity, (cm/sec)
 A = cross sectional area, (cm²)
 $\frac{dh}{dl}$ = hydraulic gradient, (cm/cm)

For a constant head system, hydraulic conductivity can be calculated by rearranging equation (1):

$$K = \frac{Q dl}{A dh} \quad (2)$$

For a falling head system, hydraulic conductivity is calculated as:

$$K = \frac{L}{t} \ln (h_0/h_2) \quad (3)$$

where L = length of system, (cm)
 t = time for water to flow from h_0 to h_2 , (sec)
 h_0 = initial water height, (cm)
 h_2 = final water height, (cm)

Equation (2) was used to calculate the hydraulic conductivity of the bench scale reactors, and both equations (2) and (3) were used to estimate hydraulic conductivity of the lab experiments.

The mean hydraulic conductivities obtained from the reactors and lab experiments were compared using t tests performed at the 0.05 level of significance.

Results

1990 Bench Scale Results

Hydraulic conductivity measurements are plotted versus time for the National and Quartz Hill Tunnels reactor experiments as shown in Figures 1a and 1b. Both figures present the results from three simultaneously operated reactors that were subjected to varying initial

substrate conditions.

Initially, the hydraulic conductivity of the soaked National reactors was less than 5.0×10^{-5} cm/sec for the first 42 days and then increased to stabilize at approximately 5.0×10^{-3} cm/sec by day 126. Overall, the dry National reactor shows minor changes in hydraulic conductivity and the soaked downflow reactors shows an increase in hydraulic conductivity over time. The hydraulic conductivity of the initially dry reactor (measured only in the first 60 days) stabilized quickly, averaging approximately 8.0×10^{-3} cm/sec. Statistical analysis indicated no significant difference in hydraulic conductivity between the soaked reactors.

Hydraulic conductivity measurements for the Quartz Hill reactors are shown in Figure 1b. In the initially dry reactors, the hydraulic conductivity varied from 6.0×10^{-4} cm/sec to 2.0×10^{-3} cm/sec in the first 40 days. Hydraulic conductivity of the soaked reactors was initially lower than that observed in the dry reactor for the first 50 days, ranging from 1.0×10^{-4} cm/sec to 5.0×10^{-4} cm/sec. Statistical analysis showed no significant difference exists between the soaked and inoculated and soaked substrates during this time period. However, the difference between the average hydraulic conductivity in these reactors and the dry reactor is significant. The hydraulic conductivity in the soaked reactors increased to at least 3.0×10^{-3} cm/sec by day 123.

The behavior of the soaked Quartz Hill reactors is similar to that of the soaked reactors of the National Tunnel; hydraulic conductivity in both sets of reactors increased by nearly 1 order of magnitude during the experiment (starting at less than 1.0×10^{-4} cm/sec and increasing to approximately 5.0×10^{-3} cm/sec by day 132).

An upflow soaked and inoculated reactor was started in place of the dry downflow reactor. Hydraulic conductivity measurements began on days 98 and 89 for National and Quartz Hill, respectively. As shown by the National soaked downflow data, hydraulic conductivity increases over time nearly one order of magnitude. The hydraulic conductivity of the soaked and inoculated upflow reactor (days 98 - 126) is higher than the soaked and inoculated downflow reactor (days 14 - 28). Statistical analysis verified no significant difference between the two configurations.

However, for Quartz Hill, under the same initial substrate conditions, the upflow reactor (days 89 - 123) had lower hydraulic conductivity

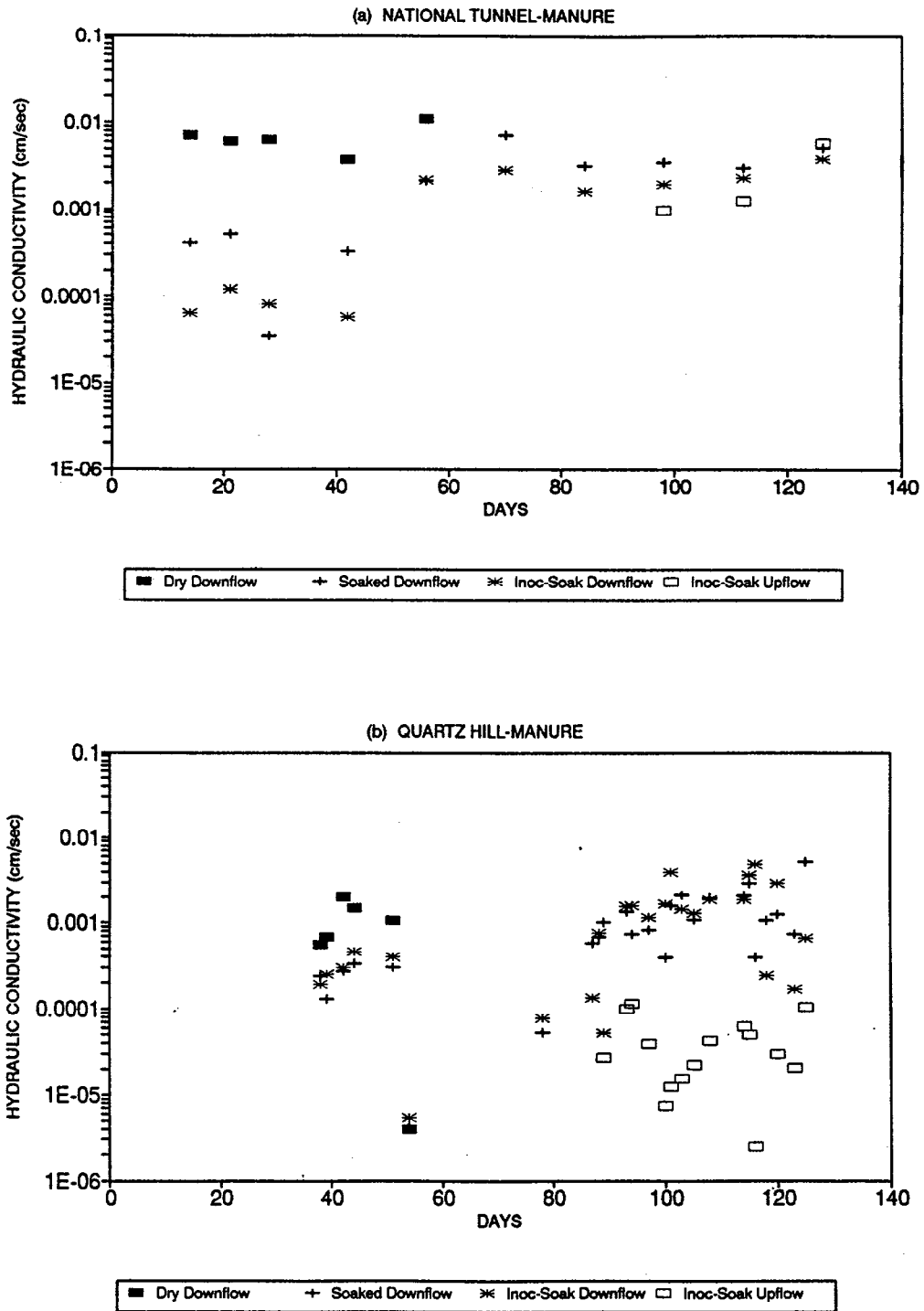


Figure 1. Hydraulic conductivity for the National Tunnel drainage reactors (a) and Quartz Hill drainage reactors (b) with a manure-planter soil substrate operated under three initial substrate conditions in a downflow configuration and one substrate condition in an upflow configuration.

values then the downflow reactor (days 38 - 54). Statistical indicates a significant difference between the hydraulic conductivity values of the two configurations.

The ~~o~~ verify ^{the} difference in hydraulic conductivity between the dry and soaked reactors, and the observed increase in hydraulic conductivity with time for the soaked substrates, field experiments were performed in 1991 to determine whether 1990 results could be duplicated. Also, laboratory permeameter experiments were conducted to determine how well the values corresponded to the field results.

1991 Bench Scale Results

Figure 2a plots the hydraulic conductivity versus time for the inorganic limestone reactors over 132 days of experimentation. The measured hydraulic conductivities for both the initial dry and initially soaked reactors ranged between 1.0×10^{-3} cm/sec and 1.2×10^{-2} cm/sec. Statistical analysis indicates no significant difference in hydraulic conductivity between the dry and soaked limestone between days 5 through 49, but a difference between days 54 through 132 and 5 through 132. The average hydraulic conductivity for the reactors in days 5 through 49 was 5.4×10^{-3} cm/sec, and 4.98×10^{-3} cm/sec and 2.17×10^{-3} cm/sec for the dry and soaked reactors after days 54.

Substrate samples were taken from both the initially dry and soaked limestone reactors after day 132. Limestone rock sizes of the initially dry reactor ranged from 1/8 inch to 1/2 inch and the initially soaked reactor ranged from 1/16 inch to 1/4 inch. The initially dry reactor substrate compacted approximately 6 cm while the soaked reactor substrate compacted approximately 3 cm.

Hydraulic conductivity of the organic manure reactors versus time is plotted in Figure 2b over 132 days of experimentation. The dry reactor fluctuated between 1.0×10^{-4} cm/sec and 6.0×10^{-3} cm/sec during the first 80 days of experimentation. During the last 50 days the hydraulic conductivity fluctuated between 9.0×10^{-4} cm/sec and 7.0×10^{-3} cm/sec. Hydraulic conductivity of the soaked manure reactor ranged between 4.0×10^{-4} to 1.0×10^{-3} cm/sec for the first 80 days of experimentation, then increased gradually to 6.9×10^{-3} cm/sec. Statistics verify a difference in hydraulic conductivity between dry and soaked substrate from days 5 through 49 and days 54 through 132, but show no difference overall between days 5 through 132.

Substrate samples taken at the end of the experiment from the organic substrate reactors indicate sizes ranging from fines to 1/8 inch. Compaction measurements indicate that throughout the 132 days of experimentation the substrate compacted approximately 1 cm to 2 cm.

1991 Lab Results

The hydraulic conductivity values for constant head and falling head lab experiments for three substrates are shown in Table 2. For comparison, Table 2 also contains the hydraulic conductivity for all field experiments. Lab 1990 and field 1990 represent the Quartz Hill and the National Tunnel experiments, respectively. Lab 1991 represents the permeameter experiments that included both constant head and falling head.

The 1991 lab tests hydraulic conductivity values ranged from 2.0×10^{-3} cm/sec to 7.3×10^{-2} cm/sec. The values shown represent an average of at least three tests. Note that the table shows the range of hydraulic conductivity for each substrate analyzed.

Discussion

Field Experiments

Figures 1a and 1b show the initially dry substrate has a higher hydraulic conductivity than the soaked substrate. Hydraulic conductivities of the substrates that had been soaked, including the inoculated reactors, increased after about 40 days to values approximately equal to that of the dry substrate.

In the 1991 experiments, the dry limestone hydraulic conductivities remained fairly consistent over time as shown in Figure 2a. Soaked limestone showed a slightly downward trend over time but remains within the same order of magnitude of hydraulic conductivity as the soaked substrate.

The manure used in the 1991 experiments, as shown in Figure 2b, was the same substrate as the 1990 experiment. The hydraulic conductivity of the dry substrate is higher than the soaked substrate but the values for the soaked gradually increase to the same level. This behavior is similar to that observed in 1990.

Studies report that bacterial growth can block the pore spaces in a wetland system e.g., bacterial growth in a wetland system used to treat landfill leachate decreased the hydraulic conductivity by

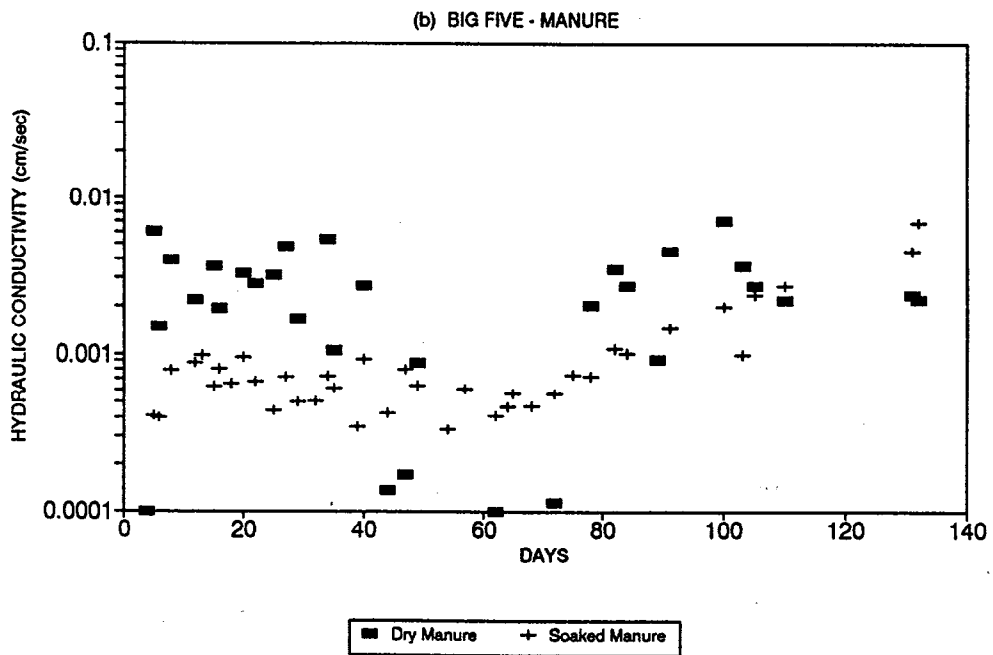
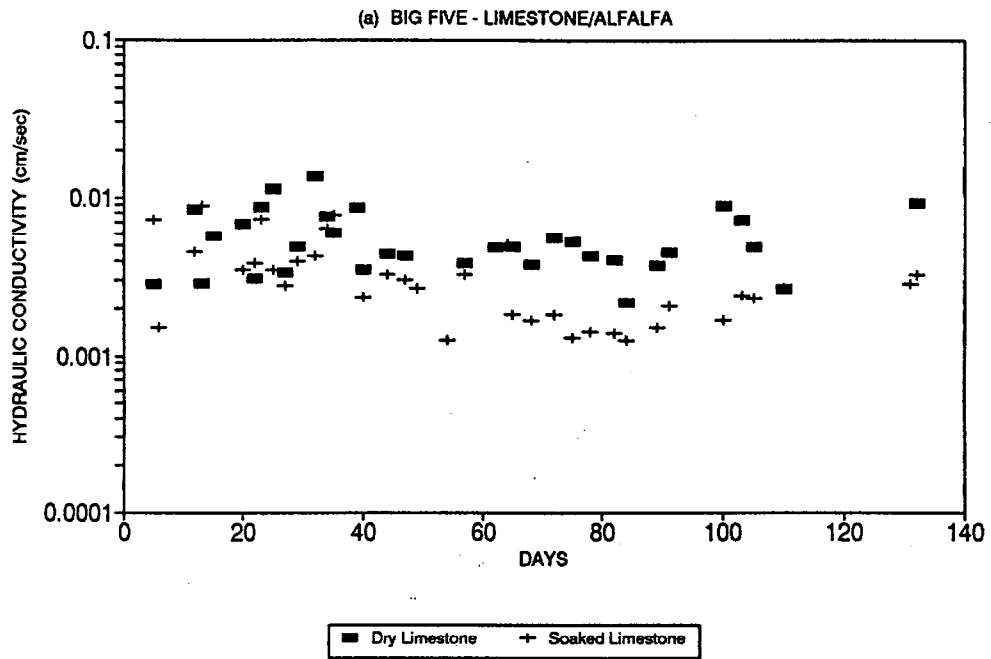


Figure 2. Hydraulic conductivity for the Big Five Tunnel drainage reactors with a limestone-alfalfa substrate (a) and a manure-plant soil substrate (b) operated under two initial substrate conditions in a downflow configuration.

Table 2. Hydraulic conductivity for various substrates, cm/sec.

TEST	TYPE	SUBSTRATE CONDITION	SUBSTRATE		
			Manure	Limestone -Alfalfa	Manure-Hay
LAB 1990 ^a	Constant Head	D	$4.0 \times 10^{-6} - 2.0 \times 10^{-3}$	NE	NE
		S	$4.4 \times 10^{-6} - 2.9 \times 10^{-3}$	NE	NE
		IS	$5.6 \times 10^{-6} - 4.9 \times 10^{-3}$	NE	NE
		ISU	$2.5 \times 10^{-6} - 1.2 \times 10^{-4}$	NE	NE
FIELD 1990 ^b	Constant Head	D	$3.7 \times 10^{-3} - 1.1 \times 10^{-2}$	NE	NE
		S	$3.5 \times 10^{-5} - 7.2 \times 10^{-3}$	NE	NE
		IS	$5.8 \times 10^{-5} - 3.8 \times 10^{-3}$	NA	NE
		ISU	$9.7 \times 10^{-4} - 5.9 \times 10^{-3}$	NE	NE
LAB 1991 ^c	Constant Head	D	4.0×10^{-2}	... ^e	7.3×10^{-2}
		S	... ^e	... ^e	NE
	Falling Head	D	2.1×10^{-2}	2.0×10^{-3}	2.7×10^{-2}
		S	3.0×10^{-3}	... ^e	NE
FIELD 1991 ^d	Constant Head	DI	$9.9 \times 10^{-5} - 7.1 \times 10^{-3}$	$2.1 \times 10^{-3} - 1.3 \times 10^{-2}$	NE
		IS	$3.4 \times 10^{-4} - 6.9 \times 10^{-3}$	$1.3 \times 10^{-3} - 8.8 \times 10^{-3}$	NE

- ^a LAB 1990 = Quartz Hill bench scale lab experiments.
- ^b FIELD 1990 = National Tunnel bench scale field experiments.
- ^c LAB 1991 = lab permeameter testing of substrates.
- ^d FIELD 1991 = Big Five bench scale field experiments.
- ^e No conductivity values could be obtained in the lab.

- NE Not evaluated as part of this experiment.
- D Substrate initially dry, downflow configuration.
- S Substrate initially soaked, downflow configuration.
- IS Substrate initially inoculated, downflow configuration.
- ISU Substrate initially inoculated and soaked, upflow configuration.
- DI Inoculated dry substrate.

50% after 2 weeks (Staubitz et al. 1989). The soaked and inoculated substrate in Figure 1 had anaerobic conditions for 1 week that would allow for a microbial population to become established and thus, lower conductivity. This is also shown in Figure 2b with the soaked manure system. The alfalfa in the limestone substrate also promoted growth of bacteria and may be cause of the minor decrease in hydraulic conductivity of the soaked

substrate through time.

Bacterial activity cannot explain all the observed trends in the hydraulic conductivity. The components of the substrate matrix also affect the hydraulic conductivity, specifically the grain size, pore space and permeability. Another explanation for the trends seen in the manure-soil substrate is that organic material swells when it is soaked and this causes the pore space to decrease. This

would explain why the soaked substrate has a low initial hydraulic conductivity. However, it does not explain why the hydraulic conductivity increases with time. The hydraulic conductivity of the soaked substrate may increase with time as the fines and loosely attached bacteria are worked out. Also, initial low hydraulic conductivity may be due to a buildup of anaerobic slimes that are clogging the substrate (Watson 1989). As the reactors operate, the slime buildup may be slowly removed, therefore causing the increase in hydraulic conductivity.

Significant fluctuations in the hydraulic conductivity of the dry substrates occurred in the first 40 days of experimentation for both years. This variation may be due to variations in the bacterial population as it becomes established. Additionally, entrapped air, and gases such as CO₂ and CH₄ are generated within the substrate, and may clog pore spaces. Because of the wide variation in hydraulic conductivity, the dry reactors were more difficult to maintain at a constant flow in the 1990 and 1991 field experiments.

The soaked manure substrate yielded the most consistent and easily controlled hydraulic conductivities. A consistent hydraulic conductivity is preferred in subsurface treatment systems, particularly in systems with limited area and volume, as it facilitates attachment of microorganisms to the substrate matrix (Steiner and Freeman, 1989).

Lab Experiments

The 1991 lab experiments show hydraulic conductivities for the inorganic substrate that are comparable to the field results. However, the manure substrate, both soaked and dry, have higher conductivities than their field counterparts. For the lab tests the substrate was soaked overnight. This probably is long enough to cause swelling of the organic material, but it is not a long enough inoculation time for the bacteria. Also, the hydraulic conductivity differences could be due to differences in packing and possible sorting of the substrate constituents.

Comparison to Other Conductivity Studies

The hydraulic conductivity values of substrate or materials used in wetlands wastewater treatment systems shown in Table 1 range from 10 cm/sec to 1×10^5 cm/sec, depending on the substrates. The reported values of this research

range from 1.0×10^{-4} cm/sec to 3.0×10^{-5} cm/sec for field experiments only. These values are on the lower end of the range of values in Table 1.

Lemke (1989) evaluated the hydraulic conductivity of mushroom compost used in the treatment of mine drainage; downflow hydraulic conductivity values ranged from 2.96×10^{-4} cm/sec to 3.5×10^{-3} cm/sec. The 1990 and 1991 bench scale data encompass this range. Lemke reported upflow hydraulic conductivity values ranging 1.38×10^{-2} cm/sec to 6.65×10^{-2} cm/sec. The 1990 upflow hydraulic conductivity ranges from 2.5×10^{-6} cm/sec to 5.9×10^{-3} cm/sec.

Most of the other reported hydraulic conductivity values in the table were determined using soils and gravel. The hydraulic conductivity of the soils average 3.0×10^{-3} cm/sec and the gravels range from 1×10^1 cm/sec to 3.4×10^{-3} cm/sec. The pulverized fuel ash (burnt coal waste), used by Copper and Hobson (1989), had a lower hydraulic conductivity than any other substrates listed and exhibited surface flow. The old natural reed beds were reported to have hydraulic conductivity values of 5.0×10^{-4} cm/sec, one of the lower values listed in the table. This value suggests that the hydraulic conductivity may decrease over long periods of time.

Finally, lab tests of a homogenous mixture and a sorted substrate show hydraulic conductivity values higher than the other reported values (Staubitz et al. 1989). This is consistent with the 1991 lab tests that were approximately one order of magnitude higher than those values measured in the field experiments.

Summary

Hydraulic conductivity experiments performed on substrates used in subsurface wetlands have generated the following conclusions:

- For both inorganic and organic substrates, the hydraulic conductivity of initially dry substrate fluctuates and is inconsistent, making it difficult to control the flow of mine drainage through the system. These variable values make it difficult to estimate hydraulic conductivity for a dry substrate.
- For primarily organic substrates such as manure-soil, that are soaked prior to applying mine drainage, hydraulic conductivity ranges between 3.3×10^{-4} to 9.8×10^{-4} cm/sec in the first 50 to 90 days and then gradually increase to approximately an order of magnitude greater, ranging from 1.0×10^{-3} to 6.9×10^{-3} cm/sec.
- For primarily inorganic substrates such as

the limestone-alfalfa mixture tested, hydraulic conductivity remains fairly constant over time, averaging approximately 1.23×10^{-3} cm/sec to 8.8×10^{-3} cm/sec.

• Overall, laboratory and field bench scale studies yield hydraulic conductivities ranging from 2×10^{-6} cm/sec to 1.0×10^{-2} cm/sec for the organic manure substrate. Hydraulic conductivities range from 1.3×10^{-3} to 1.3×10^{-2} cm/sec for the inorganic limestone substrate.

• A method for estimating the expected range of hydraulic conductivity for a candidate substrate is to perform a constant and/or falling head permeameter measurements on dry substrates and on substrates that have been soaked for one week. The permeameter should be at least 2 liters in volume so that a representative sample of heterogeneous material can be tested. For a highly organic substrate, hydraulic conductivities obtained in the laboratory may be higher than the values determined in the field.

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THE AEROBIC REMOVAL OF MANGANESE FROM MINE DRAINAGE BY AN ALGAL MIXTURE CONTAINING *CLADOPHORA*¹

by

Laura A. Duggan, Thomas R. Wildeman, and David M. Updegraff²

Abstract. Manganese is a contaminant common to most metal and coal mine drainages. Mn (II) is difficult to remove from solution without chemical treatment due to the high pH required to form insoluble manganese oxides or carbonates. Laboratory studies have indicated that an algal mixture, primarily comprised of *Cladophora* (a green alga), is effective in removing the manganese from solution and substantially raising the pH of the mine drainage through photosynthesis. Two reservoirs were constructed for a bench scale study to examine the effects of algae containing *Cladophora* on mine drainage that had passed through a constructed wetland treatment, but still contained 32 mg/L of manganese. The reservoirs were run statically for two months and then as a flow system for two months. Each reservoir initially contained 97 L of wetland effluent (pH = 5.8), 5 L of pond scum containing *Cladophora*, and one reservoir also contained 12 kg of limestone. The reservoir containing limestone reduced the manganese to concentrations of less than 0.3 mg/L and performed slightly better than the reservoir without limestone, which reduced the manganese to concentrations below 3 mg/L. The *Cladophora* grew extensively and was resistant to high manganese levels often toxic to microbes. Microscopic and phase studies have suggested that the *Cladophora* removed the manganese from solution by forming manganese oxide crusts in the algal mat. These results indicate that an algal mixture containing *Cladophora* may be used as a second stage process to remove manganese and raise the pH of water that has passed through a constructed wetland treatment. In addition, an algal pool appears to be a good candidate for a bench scale aerobic wetland.

Key Words: manganese removal, wetland, algae

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²Laura A. Duggan is a graduate student and Drs. Thomas R. Wildeman and David M. Updegraff are professors in the Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401.

Introduction

The use of microorganisms for the removal of heavy metals from acid mine drainage has become an important alternative to chemical treatment. Constructed wetlands have been proven to substantially increase the pH of the mine drainage and remove many of the heavy metals by precipitating insoluble metal complexes and precipitates (Brodie et al. 1989 and Wildeman and Laudon 1989). Manganese, a common contaminant in most acid mine drainages, is difficult to remove from solution

due to the high pH required to form insoluble manganese oxides, carbonates, or sulfides (Watzlaf and Casson 1990).

The Big Five Wetland in Idaho Springs, Colorado was constructed as a pilot scale anaerobic system emphasizing the microbial reduction of sulfate to sulfide and subsequent precipitation of insoluble metal sulfides (Howard et al. 1989). The pH of the mine drainage was raised from below 3 to above 6 and over 90% of the Fe, Cu, and Zn were removed (Machemer et al. 1990). However, manganese was not removed from the mine drainage due to the inability of manganese to form stable sulfide precipitates under most wetland conditions. Thus, a polishing stage treatment utilizing an alternate microbial process seemed necessary to remove the high levels of manganese.

A laboratory investigation was conducted to study the microbial oxidation of manganese as a possible removal method. Several different types of bacteria and algae were collected from local eutrophic ponds and mine drainage areas and tested with respect to manganese removal from neutralized mine drainage. A sample of pond scum (primarily green and blue-green algae) was found to substantially increase the pH of the mine drainage and remove the manganese from solution to concentrations below the detection limit (< 0.3 mg/L).

Further laboratory studies were conducted with pond scum collected from different local sources. Those samples which were the most effective in removing the manganese and further raising the pH of the mine drainage that had previously passed through the Big Five Wetland, were samples which contained *Cladophora*, a filamentous green alga, along with much lesser amounts of other green and blue-green algae. It appears that the manganese is removed from the water by the precipitation of manganese oxides on the algal cells. The metal precipitation is believed to be at least partially due to the increase in pH and production of oxygen during photosynthesis, as the precipitation of manganese oxides usually requires a pH between 8 and 9 (Stumm and Morgan 1981). Previous laboratory studies also found a large diurnal pH change associated with photosynthesis due to the uptake and release of carbon dioxide (Stumm and Morgan 1981 and Fuller et al. 1988).

Bench scale studies are helpful to test the

effectiveness of the laboratory results and to determine their potential for larger scale studies. Anaerobic bench scale permeameters have been shown to closely model the Big Five Wetland (Bolis et al. 1991). To further examine the manganese removal process and to evaluate the potential of an aerobic pilot scale wetland, two bench scale aerobic reservoirs were constructed. The objectives of this study also included determining a manganese removal rate and testing the resistance of the *Cladophora* to high manganese concentrations and severe weather conditions.

Materials & Methods

The reservoirs were constructed from small plastic swimming pools, approximately 1.1 m in diameter. Each of the two pools initially contained 97 L of effluent from the Big Five Wetland and 5 L of pond scum comprised primarily of *Cladophora* from a local pond. The Big Five effluent contained approximately 32 mg/L of manganese and had a pH of 5.8. The only difference between the two reservoirs was that one reservoir also contained 12 kg of limestone (limestone pieces were approximately 1 cm). This reservoir will be referred to as "reservoir LS", and the reservoir which did not contain limestone will be denoted "reservoir NoLS". The reservoirs were placed outside to have full exposure to the environment.

This experiment was run for approximately four months, from August to December, incorporating a wide range of weather conditions. The reservoirs were static for the first two months of the experiment, with water being added occasionally to account for water loss due to evaporation. The weather was typically warm and sunny during this portion of the experiment. A flow system was installed during the last two months of the experiment to determine approximate loading and removal rates. This was accomplished using a peristaltic pump to monitor flow from a feed tank into the reservoirs, and an outlet tube 7 cm above the bottom of each pool. The diameter of the pools was 1 m at the height of the outlet. The outflows were collected in plastic containers which were connected to the reservoirs by plastic tubing. The weather during this portion of the experiment was typically cold and snowy, and the reservoirs froze several times. The samples were filtered

and acidified after collection and then analyzed for manganese by flame atomic adsorption.

The pH of the waters were measured frequently, as the formation of manganese oxides is highly pH dependent. During the static portion of the experiment, the pH was taken at different areas in each reservoir to account for differences due to the amount of biomass present and because the amount of sunlight received at each location may affect the amount of photosynthesis. The pH values cited below are geometric averages of the several measurements. Each sample collected was a composite sample containing water from different areas within the reservoir. During the portion of the experiment when the pump was monitoring the water flow, the pH's and samples were taken from the water collected in the outflow containers.

Once during the static portion and once during the pump portion of the experiment, a high concentration manganese solution was added to the reservoirs to examine the effectiveness of the algae in removing high manganese concentrations. This 100 mg/L manganese solution was prepared using manganese sulfate and deionized water.

Results

Static Reservoirs

The initial pH of the water in each reservoir was 5.8 and contained 32 mg/L of manganese. During the first week of the experiment, the pH of each reservoir gradually rose with the pH of reservoir LS usually slightly higher than the pH of reservoir NoLS. On the sixth day of the experiment at 7:10 PM, the pH of reservoir NoLS was up to 8.6 and contained 14 mg/L of manganese, and reservoir LS had a pH of 8.8 and contained only 5.4 mg/L of manganese. However, no diurnal pH fluctuation with photosynthesis was observed up to this point. On the tenth day of the experiment, pH cycling and almost complete manganese removal were observed. On this day, the pH rose 0.3 pH units in each pool between 7:00 AM and 3:00 PM, and reservoir NoLS contained 2.5 mg/L manganese and reservoir LS only 0.5 mg/L. After the tenth day much of the water had evaporated from the reservoirs and most of the manganese had been removed. Therefore, on Day 11 at 1:30PM, 20 L of additional mine

drainage effluent from the Big Five Wetland were added (pH = 6.0). This addition lowered the pH to 7.2 and 7.5 for reservoir NoLS and reservoir LS, respectively. However, on Day 12 at 3:15 PM, the pH's were back up to 8.2 and 8.5 of reservoir NoLS and reservoir LS, respectively. For the rest of the static portion of the experiment, Big Five mine drainage effluent was continuously added about twice a week and the reservoir pH's usually recovered within a day or two of the effluent addition.

On Day 20, 40 L of 100 mg/L manganese solution having a pH of 4.9 was added to each reservoir to study the tolerance and removal efficiency of the algae to high manganese concentrations. Before this addition, the water level in the reservoirs was very low (approximately 40 to 50 L). On Day 25 at 9:30 AM, reservoir NoLS had a pH of 7.6 and contained 51 mg/L of manganese, and reservoir LS had a pH of 8.1 and contained 13 mg/L of manganese. By Day 42 at 9:30 AM, reservoir NoLS had a pH of 8.8 and contained 9.7 mg/L of manganese, and reservoir LS had a pH of 9.3 and contained less than 0.3 mg/L of manganese. Thus, both reservoirs appeared to be removing the manganese from a medium pH, high manganese solution.

During the static portion of the experiment, the algal biomass had grown extensively, appeared healthy, and black precipitates could be seen in the algal mat. Therefore, a flow system was designed to simulate a possible pilot scale wetland and determine the efficiency of the reservoirs at different flow rates.

Pump Flow Reservoirs

The pump system was installed in mid-October, on Day 65, with an initial mine drainage effluent flow rate of 3.1 ml/min into each reservoir. The mine drainage effluent had a pH of 6.3 and contained approximately 23 mg/L of manganese. It took several days for the water levels in the pools to reach the outlet. The results are given in Table 1 and outflow manganese concentrations shown in Figure 1. It took a few days longer for the water to reach the outlet in reservoir NoLS, which didn't contain limestone, so the sample on Day 71 was collected from the pool rather than the collection container. No sample was collected for reservoir NoLS on Day 73. On Day 79, the mine drainage effluent in the feed tank was

Table 1. Results of the Pump Flow Experiment

RESERVOIR NoLS				RESERVOIR LS		
DAY #	FLOW (ml/min)	pH	Mn (mg/L)	FLOW (ml/min)	pH	Mn (mg/L)
71	2.1	9.1	3.2	2.5	9.2	1.0
73	3.9	9.3	-----	3.9	8.7	0.7
84	2.1	8.5	32.1	2.4	8.5	14.0
86	-----	8.5	25.3	-----	8.8	1.4
91	3.0	8.1	13.0	1.5	8.2	0.6
94	4.5	8.2	10.1	4.5	8.5	1.2
97	4.0	8.6	4.8	4.5	8.6	2.2
99	-----	8.5	3.2	-----	8.4	1.4
100	-----	8.3	2.3	-----	8.4	0.5
103	3.7	8.5	2.3	3.9	-----	1.0
120	3.1	8.1	3.8	1.8	8.1	0.6
125	3.0	8.2	5.0	3.8	8.2	0.3
127	3.0	8.2	7.2	3.7	8.3	0.7

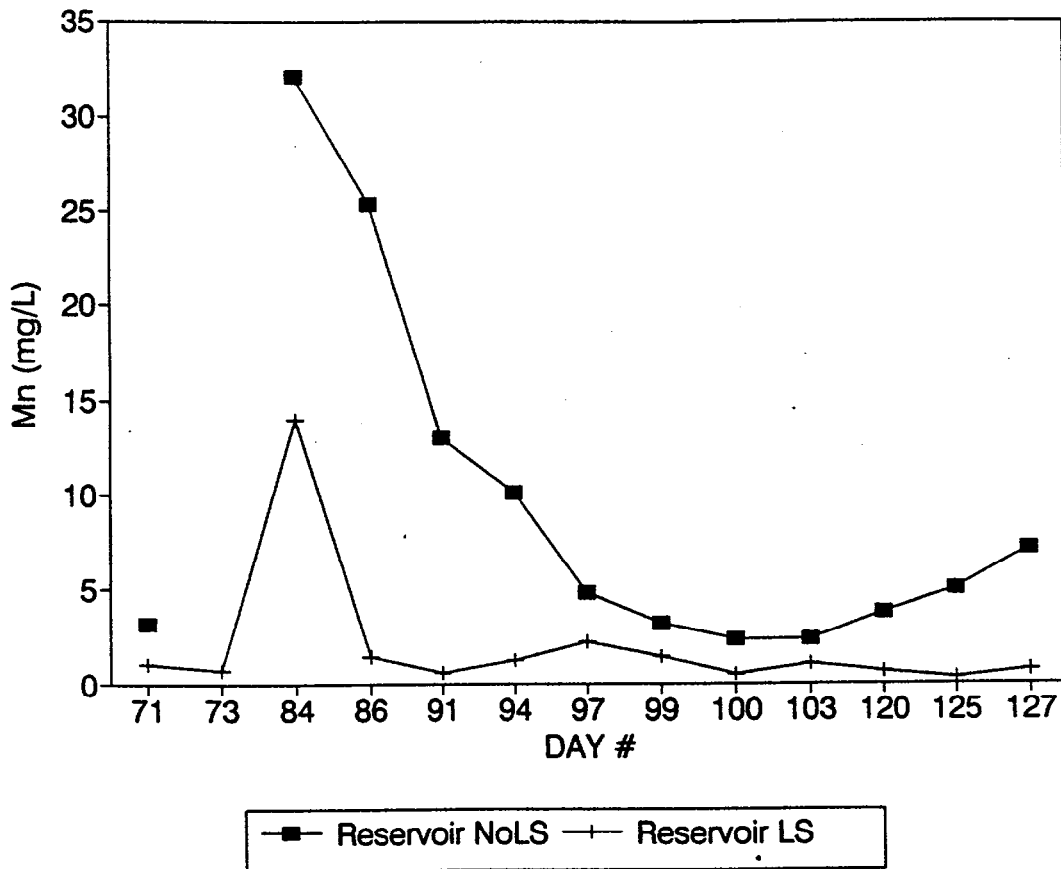


Figure 1. Effluent manganese concentrations for the pump flow experiment.

replaced with the same 100 mg/L manganese solution as was used in the static experiment. This solution was pumped at 5 ml/min until Day 80, when the flow was adjusted to 3 ml/min because the water and algae in the reservoirs were frozen solid except for a small area around the inlet. On Day 84 samples were collected and the remaining 20 L of manganese solution were mixed with 20 L of Big Five mine drainage effluent.

Manganese removal (Table 1) can be used to calculate area adjusted removal rates (Hedin 1990). The units for this rate are grams of manganese removed / day / square meter, which is abbreviated gdm. Figure 2 shows the removal rates which were determined from the following calculation (Hedin 1990):

$$\text{Mn (gdm)} =$$

$$\frac{1.44 * \text{Flow (L/min)} * [\text{Mn in} - \text{Mn out}] \text{ (mg/L)}}{\text{Area (m}^2\text{)}}$$

A value of 29.3 mg/L was used for Mn inflow, which was the average (standard deviation = 3.7 mg/L) manganese concentration of the Big Five Wetland effluent over three of the months this experiment was conducted.

Discussion

The photosynthetic process involves the uptake of carbon dioxide and release of oxygen. A pH greater than 5.5 is required to maintain a supply of carbon dioxide, in the form of bicarbonate, in the water. Since most aerobic wetland treatments involve photosynthesis, this may account for why aerobic wetlands are more effective above pH 5.5 (Brodie et al. 1991). Carbon dioxide is an acid, and therefore its uptake during photosynthesis results in a pH increase. Respiration, the reverse of photosynthesis,

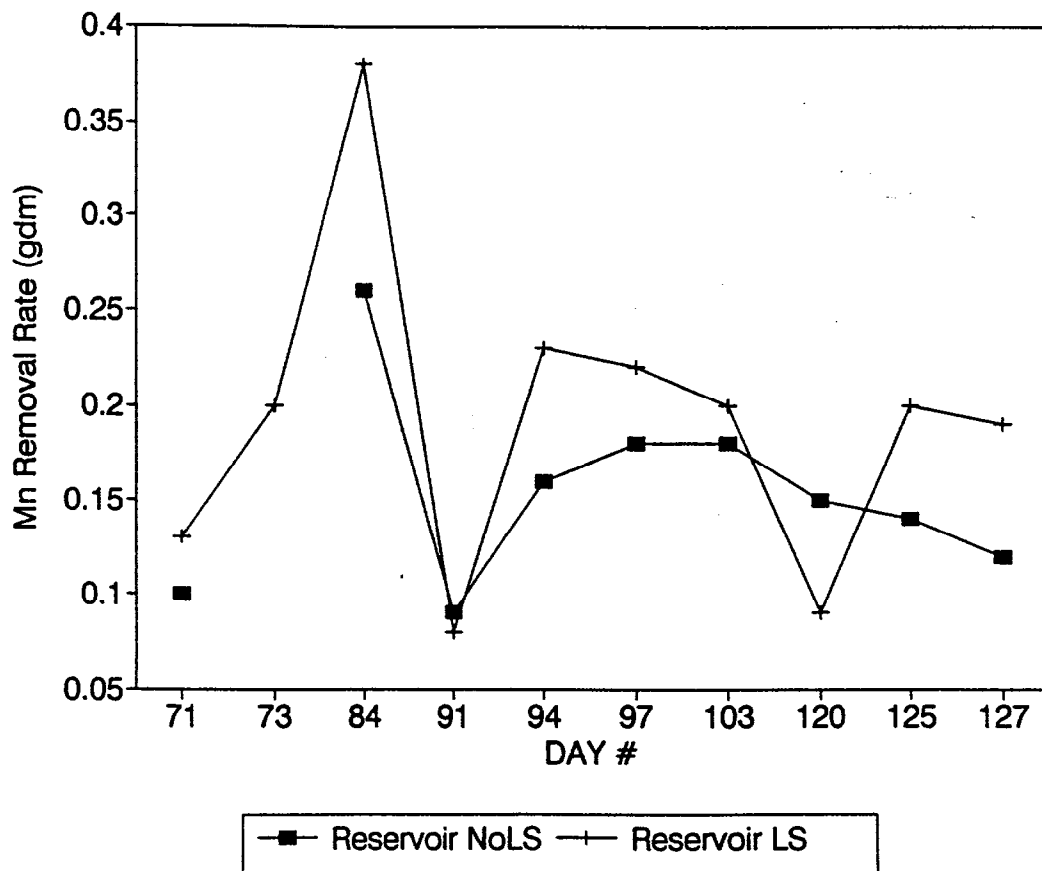


Figure 2. Area adjusted removal rates for the pump flow experiment.

occurs at night and involves the uptake of oxygen and release of carbon dioxide resulting in a lower pH. This uptake and release of carbon dioxide is the cause of the diurnal pH fluctuations observed in the laboratory and reservoir experiments.

The formation of manganese oxides, specifically MnO_2 , is a desirable manganese removal method due to the extreme insolubility and large sorption capacities of manganese oxides. The reaction appears to be autocatalytic, which greatly increases the manganese removal rate from solution once some MnO_2 or Mn_3O_4 is formed (Stumm and Morgan 1981). The formation of rhodochrosite, $MnCO_3$, is also a possible manganese precipitate that could form as it is slightly less soluble than calcite.

The success of the previous laboratory studies and the static portion of this bench scale study indicated that algae containing *Cladophora* is effective in removing manganese from the effluent under warm, sunny, static conditions. However, a large scale wetland treatment system is more dynamic and subject to more environmental stresses. Thus, the pump flow portion of this experiment is probably a more accurate indicator of the potential for *Cladophora* to be used in a larger scale wetland treatment.

Figure 1 shows the outflow manganese concentrations for reservoirs NoLS and LS. Considering that the inflow manganese concentration was 100 mg/L from Day 79 through Day 84 and varied between 28 and 65 mg/L during the rest of the experiment, both reservoirs showed excellent removal, often reducing the effluent to below 5 mg/L manganese. Reservoir LS consistently performed better than reservoir NoLS, with 85% of the samples below 2.0 mg/L manganese, the Federal monthly-average effluent limitation for coal mines (U.S. Code of Federal Regulations 1985 a & b). However, a pH difference in the two reservoirs could not account for the better performance of reservoir LS since the pH's of the two reservoirs during this portion of the experiment were very similar.

Both reservoirs recovered from the addition of the 100 mg/L (58 μM) manganese solution and continued to remove the manganese from the effluent added during the rest of the

experiment. This tolerance to high manganese concentrations is important because manganese concentrations as low as 10-20 μM have been shown to greatly inhibit manganese oxidizing microbes (Nealson et al. 1988). Reservoir LS once again showed more efficient manganese removal than reservoir NoLS. It is also important to note that the reservoirs were almost frozen solid during most of the time the 100 mg/L manganese solution was being added.

The severe weather conditions present during much of the pump flow experiment had a visible effect on the health of the biomass. During the static experiment the thick algal mat was bright green and floated on the surface due to the large number of oxygen gas bubbles produced during photosynthesis. Throughout the pump flow experiment, the algae lost much of its bright green color and most of the algae sank below the water surface. Gas bubbles were still observed during the sunlight hours indicating that photosynthesis was occurring, but to a much lesser extent than during the warmer, sunnier months. At the completion of the experiment in mid-December, the reservoirs had frozen several times and the algal biomass did not appear very healthy. The fact that the reservoirs performed so well even under these adverse conditions is important, though a pilot scale system may be more efficient in a warmer climate.

Figure 2 shows the calculated area adjusted removal rates for both reservoirs. Reservoir LS had a slightly higher average removal rate of 0.19 gdm than did reservoir NoLS of 0.15 gdm. Both reservoirs showed a much higher manganese removal rate on Day 84 when the 100 mg/L manganese solution was being fed. However, the outflow manganese concentrations for both reservoirs were not below the 2.0 mg/L Federal limit (32.1 mg/L for reservoir NoLS and 14.0 mg/L for reservoir LS). Excluding the removal rates for Day 84, the average removal rates decrease to 0.14 gdm for reservoir NoLS and 0.17 gdm for reservoir LS.

There appears to be several processes that are occurring in the reservoirs to remove the manganese from solution. Low magnification microscopy indicates that black precipitates appear to be forming as crusts on the filamentous algae. SEM and XRF analysis suggest that the crusts contain calcium-

manganese oxides which were determined to be amorphous by XRD analysis. The photosynthetic pH increase and production of oxygen would most likely be an important factor in the formation of these manganese oxides. However, it has also been shown that nonliving algae has a high affinity for metal adsorption, indicating a surface adsorption phenomena may be occurring in addition to the formation of oxides (Darnall et al. 1989 and Jeffers et al. 1989). Thus, manganese biosorption by nonliving algae may have been an important manganese removal mechanism during the cold weather when some of the algae may have died. Though further studies need to be performed, it appears that the primary manganese removal processes are adsorption to algal cell walls, auto-oxidation due to photosynthesis, and adsorption to manganese oxides that have formed.

Summary

Both reservoirs were successful in raising the pH and removing the manganese down to below 5 mg/L during most of the experiment. Reservoir LS was more efficient in manganese removal during both the static and flow portions of the experiment, often removing the manganese to concentrations below detection limit. Photosynthesis appears to be an important process contributing to the manganese removal due to its ability to increase pH. Though manganese is required by photosynthetic organisms in the process of oxygen evolution, only trace amounts are usually needed and high manganese concentrations are often toxic to microbes (Nealson et al. 1988). Thus, *Cladophora's* tolerance to high manganese concentrations distinguishes it from many manganese oxidizing microbes. The manganese removal method appears to be the formation of manganese oxide crusts on the filamentous algae. An aerobic wetland treatment utilizing *Cladophora* and limestone would have an estimated manganese removal rate of 0.17 gdm under adverse conditions, and possibly higher under warmer sunnier conditions.

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DRAINAGE FROM COAL MINES: CHEMISTRY AND ENVIRONMENTAL PROBLEMS

Thomas Wildeman
Department of Chemistry and Geochemistry
Colorado School of Mines
Golden, CO 80401

ABSTRACT

Much of the research on coal-mine drainage chemistry was conducted a decade ago, and now increased environmental awareness has brought about renewed interest in the findings. Consideration of the trace minerals and elements in coal points to the possible generation of acidic waters upon weathering, especially when pyrite is present. When pyrite weathers, it produces H^+ and Fe^{3+} which catalyze the incongruent weathering of other carbonates and sulfides. In this weathering mechanism, catalysis by bacteria is important. Of the environmental problems in coal mine drainage, the mineral acidity of the water is the most serious. This is caused not only by the H^+ , but also by Mn^{4+} , Fe^{3+} , and Al^{3+} that are found or generated within the drainage. Case studies in Kentucky, Pennsylvania, Illinois, and Colorado show that the abundance and form of pyrite in the deposit and in the overburden determines the level of acidity and the concentration of heavy metal pollutants in the drainage. Recent trends in environmental enforcement that emphasize integrated stream water standards and biotoxicity assays point to the possibility that the concentrations of heavy metals in coal mine drainages may cause environmental concern.

INTRODUCTION

Acid mine waters are not new. Their production was noted in Roman times, and their possible toxicity was reported by Agricola in *De Re Metallica* (D.K. Nordstrom, personal communication, 1989). Research on the refinement of the causes for acid mine drainage production also is not new. Most of the important ideas on the mechanism of production were generated in the 1960s and 1970s. The primary reactants are pyrite (FeS_2), water, and ultimately oxygen; and important catalysts are bacteria, particularly *Thiobacillus ferrooxidans*. Because many of the ideas on the cause of acid mine drainage were established about a decade ago, they can be found in texts and monographs that often are easier to locate than the primary literature sources. This review will draw extensively on these secondary sources so that the reader can more readily augment this paper. For each section, the useful monographs will be cited.

To define the subject, Table 1 shows the concentrations of constituents that are routinely determined in coal mine drainages, the constituents in a comparable metal mine drainage, the abundance ranges of these elements in coals, and the maximum allowable contaminant levels for public drinking water. The references to the data are noted at the bottom of Table 1. For the coal information, the monographs by Bouska (1983) and Valkovic (1983) are useful. Manahan (1984) gives a good explanation of the environmental effects of each constituent.

Coal Mine Drainage						
Substance	United States	Illinois	Kentucky	Big Five Tunnel	Drinking Water Standards	Coal
Al	—	37	—	18	—	14000
Fe	0.6 - 220	57	50 - 500	50	0.3	16000
Mn	0.3 - 12	6.4	—	32	0.05	100
Cu	0.01 - 0.17	—	—	1.6	1.0	19
Zn	0.03 - 2.2	—	—	10	5.0	39
Cd	0.01 - 0.10	—	—	0.03	0.01	1.3
Pb	0.01 - 0.40	—	—	0.01	0.05	16
As	0.002 - 0.20	—	—	0.02	0.05	15
pH	3.2 - 7.9	3.0	1.8 - 3.5	2.6	6.5 - 8.5	—
SO ₄ ²⁻	—	1300	500 - 12000	2100	250	—
Ref.	1	2	3	4	5	6

1. The 10-90% concentration range of 23 acid drainages from coal mines throughout the United States taken from the EPA effluent limitations document (U.S. Environmental Protection Agency, 1982).
2. Median of 110 drainages from coal refuse disposal sites in Southern Illinois as compiled by Proudman et al. (1982).
3. Regional estimates from Caruccio (1979).
4. A typical metal mine drainage from the Front Range Mineral Belt of Colorado collected by Wildeman and Laudon (1989).
5. Compiled from U.S. Government Printing Office (1988). For mine drainages, effluent limits in milligrams/Liter are: Fe, 7.0 daily maximum, and 3.5 monthly average; Mn, 4.0 daily maximum, and 2.0 monthly average; pH between 6.0 and 9.0 at all times. For the other substances in the table, there are no written restrictions (U.S. Environmental Protection Agency, 1982).
6. Average of U.S. coal compiled by Valkovic (1983).

Table 1. Concentrations of environmentally important constituents in acid mine drainages and in coal. For waters, the concentrations are in milligrams/Liter; for coal, in parts per million.

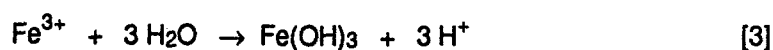
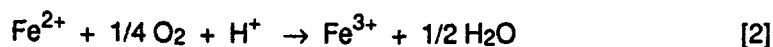
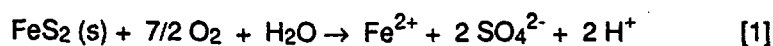
For the coal mine drainages in the Illinois and Kentucky coal regions, the concentrations of the major contaminants are quite similar, and these compare well with the values for the whole U.S. In the U.S. Environmental Protection Agency (EPA) document on effluent limitations for coal mining (U.S. Environmental Protection Agency, 1982), tests were reported on that were done to determine whether drainages from Western U.S. coal mines and Eastern U.S. anthracite mines should be separate categories. No case could be made for subcategories. The Big Five Tunnel (Wildeman and Laudon, 1989) is a metal-mine drainage, and the concentration of most of the constituents fall well within the ranges for U.S. coal-mine drainages. There appears to be reasonable cause to group all acid mine drainages together rather than split the waters into a number of categories. If this is done, then differences from the usual chemistry can be more successfully investigated. Prodan et al. (1982) give means, standard deviations, minimum values, and maximum values for 110 effluents from abandoned coal-refuse sites in Illinois, and the numbers give a good indication of how far waters vary from the median values and from the ranges reported in Table 1.

For the metal and coal mine drainages, the concentrations of iron (Fe), manganese (Mn), aluminum (Al), and sulfate (SO₄²⁻) are in the same range. For a coal seam, the possibility of large abundances of copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), and arsenic (As) exists. However, other than the U.S. Environmental Protection Agency (1982) document, data on concentrations of these constituents in effluents are difficult to find. These heavy metals do exist in metal-mine drainages and are well documented (Wildeman, 1983;

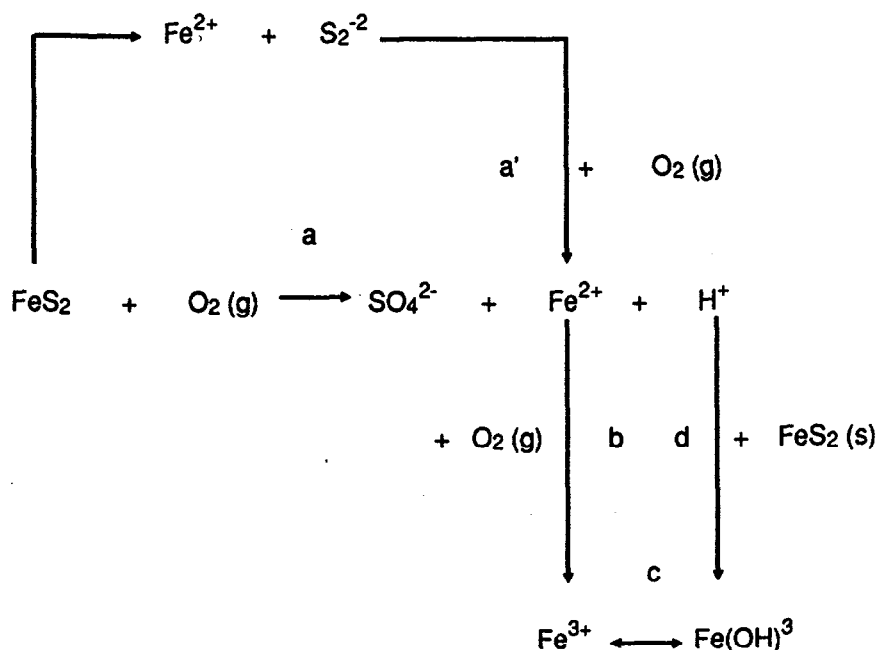
Wildeman et al., 1974; Wildeman and Laudon, 1989). In this section, the geochemistry of the weathering of pyrite will be developed and this will be related to the weathering reactions of the minerals responsible for the other contaminants in mine drainage. The chemistry of mine drainages from the Central City mining district in Colorado will be used as an example of how the weathering reactions are interrelated. Finally, the role of hydrology in the production of acid mine drainage will be reviewed.

Pyrite Oxidation

In coal mining situations, pyrite is the mineral that is responsible for acid drainage problems. This same mineral is also the cause of the problems in metal mining situations. Understanding how pyrite weathers is essential to understanding the causes of the problem and the relationships between coal- and metal-mining pollution problems. Stumm and Morgan (1981) review the chemistry of pyrite weathering and the following description is summarized from their text. The overall stoichiometric reactions are as follows:



The accepted reaction path for the dissolution of pyrite is:



Key features of the stoichiometry and reaction path are as follows:

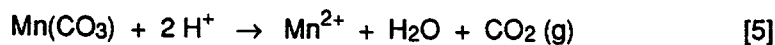
- 1) Weathering is by oxidation. Because pyrite formation only occurs in a reducing environment, oxygen gas from outside the deposit is the ultimate oxidant.
- 2) Hydrogen ions (H^+) are produced by the oxidation. For every mole of pyrite oxidized, two moles of H^+ are produced by the oxidation to sulfate (reaction 1), and two moles of H^+ are produced upon the precipitation of ferric hydroxide (reactions 2 and 3).
- 3) Because ferric hydroxide is so insoluble, pyrite oxidation is among the most acid producing of all weathering reactions.
- 4) The slow step in the reaction path is oxidation in solution of Fe^{2+} to Fe^{3+} . Sulfur (S) oxidation is relatively rapid.
- 5) Once the weathering has produced Fe^{3+} , this species can rapidly oxidize pyrite as shown in reaction 4 and step d of the reaction path. Therefore, Fe^{3+} cannot persist in the presence of pyritic minerals.
- 6) Steps a and d can be separated in time and space to enable the production of acid drainage from different environments.

Microorganisms can significantly catalyze the rate of steps a, b, and d in the mechanism. The monograph by Erlich (1981) is a good review of how weathering reactions can be mediated by bacteria. *Thiobacillus ferrooxidans* can accelerate the rate of steps b and d by orders of magnitude. *Thiobacillus thiooxidans* can catalyze step a. Bacteria are necessary to increase the rate of pyrite weathering to the point that pollution problems will occur (Taylor et al., 1984; van Everdingen and Krouse, 1988).

Recent studies on the stable isotope geochemistry of the sulfate in acid mine drainage have added some refinements to the pyrite weathering mechanism (Taylor et al., 1984; van Everdingen and Krouse, 1988). Reaction 4 is found to be a major cause of sulfide oxidation, and this reaction does not directly use molecular oxygen. Therefore, flooding mine workings to eliminate air-pyrite contact may not necessarily stop pyrite weathering. Weathering could continue by bacterial mediation of reactions 1 and 2 in the unsaturated zone in the soil and then by reaction 4 in the flooded workings. In addition, where pyrrhotite is present along with pyrite, production of acid drainage apparently is more widespread (M. Kalin, personal communication, 1988).

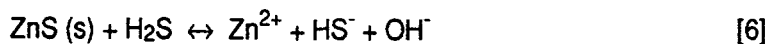
Incongruent Weathering

The concept of congruent and incongruent reactions is important to pyrite weathering and to reactions that form other constituents in acid mine drainage (Garrels and McKenzie, 1971). To demonstrate incongruence, consider manganese in coal which exists as rhodochrosite ($Mn(CO_3)$) (Valkovic, 1983). Below $pH = 4$, the $Mn(CO_3)$ will react accordingly:

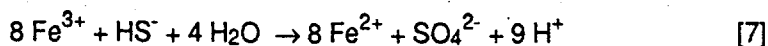


CO_2 gas can escape because it is slightly soluble in water, and if this occurs, $MnCO_3$ cannot be reprecipitated in an acidic solution. This is an example of incongruent weathering. Some other reaction or severe altering of solution conditions is necessary to cause reprecipitation of the reaction products. Reaction 5 is the basis for how Mn exists in coal mine drainages as Mn^{2+} . Reactions 1-4 show that Fe^{3+} and SO_4^{2-} in mine drainage cannot be changed back to pyrite through the reversal of a simple reaction.

Other sulfide minerals can weather by congruent reactions. A possible reaction for the weathering of sphalerite (ZnS) is



However, if ferric ion is present, it can oxidize the bisulfide ion in the same way as in the dissolution of pyrite:



In contact with an acid mine drainage solution, ZnS also will be weathered in a manner that cannot be reversed easily.

Tables 1 and 2 list the chemistry of some acid mine drainages. Iron, Mn, and SO_4^{2-} dominate the constituents in coal mine drainages; reactions 1-5 explain their presence. In drainages from metal and coal mines, Cu, Zn, Cd, Pb, and As often are present in amounts detrimental to the environment. Reaction 6 explains the presence in solution of these base metal cations. The presence of Al in mine drainages is explained best by acidic solutions causing the dissolution of clays (Wildeman, 1983). Groundwater hydrology, fluctuations in rainfall, and the manner of ore deposition also can affect mine drainage chemistry (Wildeman, 1981). The model for the chemistry of the Argo Tunnel is an example of what these other factors can do (Wildeman, 1983). However, reactions 1-7 are basic to the system and the other factors cause secondary changes in the rate and extent of these reactions.

Mineral Acidity

Of all the environmental problems related to mine drainage, the low pH is the most troublesome. Not only do the pHs of the drainages shown in Table 1 fall far out of bounds from the drinking water standards, but increasing the pH to within the drinking water standards also is necessary for long-term removal of all the

Mine Drainages			
Constituent	Central Zone	Intermediate Zone	Peripheral Zone
Al	25 - 100	n.d.	n.d.
Fe	200 - 700	2 - 170	0.5 - 4
Mn	90 - 120	20 - 40	1.0 - 5.0
Cu	6 - 60	0.1 - 5	< 0.01 - 0.11
Zn	60 - 400	7 - 100	0.3 - 8.0
Cd	0.2 - 2.9	< 0.01 - 0.20	< 0.01 - 0.04
Pb	0.1 - 0.5	< 0.01 - 0.20	< 0.01 - 0.06
As	0.2 - 2.7	< 0.001 - 0.01	< 0.001
SO_4^{2-}	2300 - 4000	900 - 1300	240 - 800
pH	2.1 - 2.7	4.0 - 6.0	5.4 - 6.9

Table 2. Dissolved constituents in mine drainages of the Central City mining district from Wildeman (1981) and Wildeman et al. (1974). All concentrations are in milligrams/Liter except pH; n.d. means not detected.

other pollutants. Consequently, most every pollutant removal method relies on raising the pH (Wildeman and Laudon, 1989; Klusman and Machemer, this volume). In addition, for acid-base stability of most natural water, buffering by the carbonic acid-bicarbonate-carbonate system is the most likely method (Stumm and Morgan, 1981). This begins to occur at a pH of between 5 and 6. Any effluent that is released into natural surface waters should be at a pH above 6 to insure that it will not harm the existing ecosystem.

However, the low pH is not caused just by the presence of H^+ ions. Examination of reaction 3 shows that Fe^{3+} hydrolyzes forming $Fe(OH)_3$ precipitate and H^+ . Fe^{3+} should be considered an acid the same as H^+ . Al^{3+} and Mn^{4+} also will strongly hydrolyze, thereby forming H^+ . Because the pH of an acid drainage depends on all these chemical factors, the term "mineral acidity" or just "acidity" is given to the situation. Acidity is defined operationally by how the analysis is conducted (American Public Health Association, 1988). In the analysis, hydrogen peroxide is added, the solution is boiled, and then titrated with standard sodium hydroxide to a pH of 8.2. If the water contains appreciable concentrations of Fe, Mn, and Al, the solubility products of these metal hydroxides will determine which constituents will hydrolyze by a pH of 8.2 and contribute to the acidity.

Using solubility product data from Lindsay (1979), Al^{3+} , Fe^{3+} , and Mn^{4+} will completely hydrolyze by this pH of 8.2, but Fe^{2+} and Mn^{2+} at the concentrations encountered in mine drainages still will be in solution. However, Fe^{2+} can oxidize according to reaction 2 and Mn^{2+} can do likewise. These constituents should be considered potential contributors to the acidity. Because the acidity analysis calls for addition of hydrogen peroxide and boiling, it is certain that Fe^{2+} and Mn^{2+} are oxidized to some extent and counted in the measure of mineral acidity.

Step b in the reaction path shows that the oxidation of Fe^{2+} to Fe^{3+} is slow, and experience with the treatment of mine drainages shows the oxidation of Mn^{2+} to be even slower (Watzlaf, 1988; Klusman and Machemer, this volume). This slow oxidation implies a long-term release of mineral acidity which can cause the reversal of some treatment methods that rely on hydroxide precipitation (Watzlaf, 1988). Slow oxidation also is responsible for the persistence of mine drainage conditions long after the water has breached the surface. For example, the red and roily nature of surface waters associated with mining is caused by the slow oxidation of Fe^{2+} and its subsequent precipitation as $Fe(OH)_3$.

CASE STUDIES OF MINE DRAINAGE PROBLEMS

In analyzing studies of acid mine drainage, there is one common cause: the presence of pyrite. The studies investigate how the availability of the other reactants, such as water or oxygen, affect the water quality (Prodan et al., 1982; Wildeman, 1981), how the nature of the pyrite might affect the water quality (Caruccio, 1979; Caruccio et al., 1977; Wildeman, 1983), and how the nature of the overburden might be used to predict the occurrence of acid drainage problems (Caruccio, 1979; Erickson and Hedin, 1988; Hedin and Erickson, 1988).

Coal Mine Drainage Studies

In Illinois, Prodan et al. (1982) studied runoff water quality from 110 coal refuse disposal sites. As seen in Table 1, these waters are typical of coal mine drainage problems. Two sites were reclaimed by recontouring the waste piles, adding limestone and lime to the surface of recontoured piles, and adding a 30-cm (12-in.) thick topping of natural soil material. It was hoped that these steps would reduce the water and oxygen contact with the pyrite and that the alkaline materials would neutralize any acid which was produced previously. At one site, there was success; however at the other, water quality turned progressively poorer after initial good conditions. The turn to poorer quality was attributed to the inability of reclamation to keep the necessary

reactants of oxygen and water away from the pyrite. In particular, it was suggested that the stored potential of Fe^{3+} salts in the pile kept the weathering of pyrite continuing through reaction 4.

In the 1960s, various people were investigating why some beds in the Appalachian coal field had acid drainage problems and others did not. The accumulated hypotheses then were put to test in Eastern Kentucky by Caruccio (Caruccio et al., 1977; Caruccio, 1979). A major cause for the production of acid waters was suggested to be the type of pyrite in the deposit and not the amount, and the type of pyrite could be related to the depositional environment (paleoenvironment). In particular, coals deposited in marine or brackish-water environments contained appreciable amounts of framboidal pyrite and this form was highly reactive to oxidative weathering. Tests of the hypothesis did indeed show that some coal seams that contained framboidal pyrite did produce highly acidic water; however, others did not. There were some seams that contained framboidal pyrite and whose drainages contained appreciable sulfate, and yet, the drainages were not acidic. The presence of sulfate in the water showed that, indeed, the pyrite was reacting. Further studies revealed that some paleoenvironments also generated calcareous material in the surrounding sediments in amounts sufficient to neutralize the acidity produced.

These findings led to a model for the prediction of the chemistry of water draining from a coal seam, with the model being subdivided into four hydrogeochemical environments. The four environments roughly can be divided into the matrix shown in Figure 1. In the matrix, the amount of pyrite refers to reactive, framboidal pyrite and not coarse-grained, stable mineral, and "carbonate" refers to reactive minerals that will produce alkalinity in the water. If the environment generated a situation where the two constituents in the matrix have opposite abundances, then the water chemistry is quite predictable. When the abundances of the pyrite and

POSSIBLE ENVIRONMENTS

PYRITE

C A R B O N A T E	pH = 3 - 4 SO ₄ ⁻ HIGH HCO ₃ ⁻ LOW	?	L O W
	?	pH = 7 - 8 SO ₄ ⁻ LOW HCO ₃ ⁻ HIGH	H I G H
	HIGH	LOW	

Figure 1. A matrix adapted from Caruccio (1979) showing how abundances of calcareous materials as carbonates and framboidal pyrite in the overburden can affect mine drainage chemistry.

carbonate are both high or low, then results are uncertain. One key factor in uncertain environments is the placement of the calcareous material above and hydrologically antecedent to the acid-producing strata. This situation typically will produce a neutral water with high sulfate concentrations. Application of the model to prediction of coal mine drainage problems requires a study of the paleoenvironments in a coal field, a petrographic analysis of the forms of pyrite in a coal seam, analysis of the chemistry of regional groundwaters to determine the pH, sulfate concentration, and alkalinity, and analysis of the strata over the coal seam for carbonate and pyrite.

Overburden Analysis

The Carruccio study (Carruccio et al., 1977; Carruccio, 1979) and others related to it no doubt influenced the requirement that potentially acid-producing strata be identified and assessed as part of the mine permitting process. This has led to a number of studies on how the composition of the overburden is related to acid production and what analyses of the overburden best predict acid drainage potential (diPreto and Rauch, 1988; Erickson and Hedin, 1988; Hedin and Erickson, 1988). diPreto and Rauch (1988) found that the alkalinity of the overburden as determined by net neutralization potential is the best predictor of acid drainage. Total S content bears little relation to mine drainage quality. However, the ratio of net neutralization to total S content is significantly related to net alkalinity of a mine drainage. Erickson and Hedin (1988) studied how the acid-base account method for overburden analysis works at 32 sites where prediction is difficult. This would correspond to the questionable areas in the Figure 1 matrix. They were able to draw boundaries for prediction but were not capable of making quantitative predictions for these doubtful sites. One of the primary problems they encountered was the heterogeneity of the overburden and the variability of spoils seeps. Methods for aggregating the data were devised to minimize these problems.

In an attempt to find better methods of prediction, Hedin and Erickson (1988) used a laboratory simulation of the weathering process to assess acid production potential. The level of sulfate in the drainage was strongly correlated to the sulfate produced by weathering and this was strongly correlated to the amount of total S in the overburden samples. However, there was still no strong correlation between any of the parameters measured in the weathering tests and the alkalinity of the mine drainage. Presently, limits can be placed on when coal-mine drainage problems will occur, but good predictive tools in questionable situations still are not available.

Heavy-Metal Studies

The levels of heavy metals in coal mine drainages are little reported, and these metals may prove to be causing problems when bioassay techniques are used for environmental assessment (Horning and Weber, 1985; Peltier and Weber, 1985). The effluent guideline study by the U.S. Environmental Protection Agency (1982) did report concentration ranges of heavy metals in coal mine drainages and these are given in Table 1. Note that the concentrations of Cd, As, and Pb can range above drinking water standards. Table 1 also shows that the average abundances of Cd, As, and Pb in coal are at levels appreciably above average crustal abundances (Krauskopf, 1979). How do these heavy metals originate in coal mine drainages, and is there a problem with concentrations in effluents being higher than drinking water standards?

The studies by Wildeman and co-workers (Wildeman, 1981, 1983; Wildeman et al., 1974) on the Central City mining district in Colorado give some perspective on how pyrite affects the concentrations of trace heavy metals in mine drainages. This is a typical example of a zoned hydrothermal deposit of gold and base metals (Sims et al., 1963). The distribution of minerals from the high-temperature Central Zone to the lower-temperature Peripheral Zone is shown in Figure 2. The chemistry of drainages emanating from mines in the various zones is summarized in Table 2. The striking feature about the chemistry of these waters is that Cd, Zn, and Pb are in lowest concentration in the Peripheral Zone even though the ore minerals for these metals are in

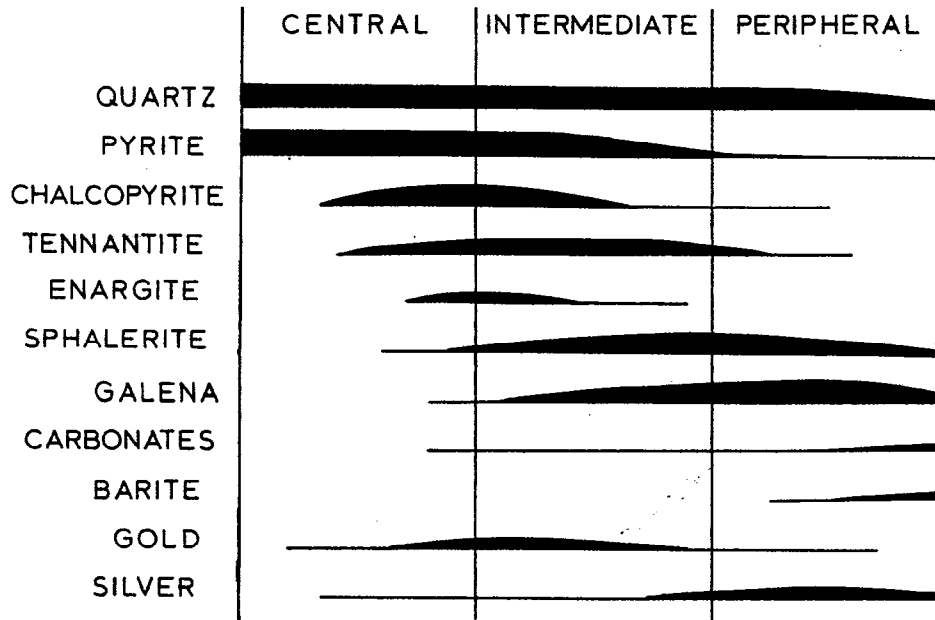


Figure 2. Zonal distribution of vein-forming minerals in the Central City mining district taken from Sims et al. (1963).

highest abundance in that zone. The concentration of all the contaminant metals in the drainages correlates with the abundance of pyrite in the ore. Fe^{3+} and H^+ in the groundwater catalyze the dissolution of the other sulfides to such an extent that they become important constituents in the drainage from a metal mine even though the base metals may be in low abundance in the deposit.

When coal deposits are considered, all the heavy metals listed in Table 1 are associated with the pyrite and other sulfide minerals in coal and its associated overburden (Bouska, 1981; Valkovic, 1983). Consequently, when the pyrite weathers, the products of that weathering are highly likely to release trace heavy metals from the coal. Beyond the U.S. Environmental Protection Agency (1982) study, it is difficult to find information on concentrations of heavy metals in coal drainages. However, Watzlaf (1988) gives some insight into why this is the case. In the treatment of acid drainages, Mn is the most difficult metal to remove. As shown in Table 1, investigations by the U.S. Environmental Protection Agency (1982) did find significant concentrations of heavy metals in untreated coal mine drainages. However, it was found that if Mn was reduced to 2 mg/L in the effluent, the heavy metals also were reduced to acceptable levels. Therefore, limitations on these metals were not promulgated, and the limitation on Mn of 2 mg/L was established. Watzlaf (1988) has determined that this guideline is reasonable. However, the sludge produced is quite unstable and subject to resolubilization.

HYDROLOGY RELATED TO ACID MINE DRAINAGE

Although the presence of pyrite is definitely the key factor that determines mine drainage quality issuing from underground adits, there have been some studies that show how groundwater hydrology is involved. In a long-term study of the Argo Tunnel drainage in Idaho Springs, Colorado, Wildeman (1983) found that the chemistry of the water varied little with the seasons and precipitation events. To explain the findings he used

DIFFUSE	CONDUIT
1. No response to climatological change.	1. Responds to climatological changes.
2. Little fluctuation in flow.	2. Obvious fluctuations in flow.
3. No suspended solids in the water.	3. Carries suspended solids at times of high runoff.
4. Water temperature may not change throughout the year.	4. Water temperature changes with the seasons.
5. Parameters indicative of concentration, such as conductivity ($\mu\text{mho/cm}$) and hardness, do not change with the climate.	5. Parameters indicative of concentration, such as conductivity ($\mu\text{mho/cm}$) and hardness, show obvious changes with storms and runoff.
6. Specific concentrations of ions show little change with the climate.	6. Specific concentrations of ions show obvious changes with storms and runoff.
7. Residence time of months for the water in the aquifer.	7. Residence time of days for the water in the aquifer.

Table 3. Differences between diffuse and conduit aquifers (from Wildeman, 1983).

aquifer models developed to explain the chemistry of carbonate springs in Pennsylvania (Jacobsen and Langmuir, 1974; Shuster and White, 1971). Two simple models for groundwater systems are generated: the conduit flow system and the diffuse flow system. These two models can be treated as the end members of all recharge systems. The properties that distinguish the two systems are given in Table 3. In both aquifers, recharge is from the surface, through the soil vadose zone, and down to the groundwater table (Wildeman, 1983). The Argo Tunnel drainage is an example of a primarily diffuse aquifer.

A surprising characteristic of a diffuse aquifer is that when annual recharge occurs in spring and the flow of water does rise slightly, some constituents in the water will increase in concentration. Wildeman (1983) found that all the metals associated with pyrite dissolution increased in concentration during the spring recharge. He suggested that pyrite weathering is a slower reaction and that if the weathering products are retained in microfaults in the vadose zone above the water table, then the reaction is most favored. This water then is released from the faults during spring recharge.

Many of the adits in Colorado that Wildeman studied are regional systems that serve to lower the groundwater and expose deeper deposits. Some adits in the Eastern U.S. are of this type, but the greater concern is with overburden exposed during strip mining and with coal refuse piles. Caruccio and coworkers have done extensive research related to this problem (Caruccio, 1979; Caruccio et al., 1977; Snyder and Caruccio, 1988).

During studies on how overburden was related to acid mine drainage, Caruccio (1979) noted that the weathering reactions that produced acidity appeared to be much slower than those that produced alkalinity. Because of the slow rate, this suggests that pyrite oxidation is kinetically controlled, whereas because of the faster rate, carbonate dissolution apparently is controlled through equilibrium processes. He suggested that situations that produced frequent flushing intervals of the overburden should reduce acid mine drainage.

Recently, Snyder and Caruccio (1988) tested a comparable hypothesis on two surface coal mine backfills. Through careful monitoring of the water budget, they were able to separate the shallow subsurface flow that is associated with rapid recharge from the slow, deep groundwater recharge. They found that the base flow associated with deep groundwater carries the acidity. This water is associated with the spring recharge which sustains the acid mine seeps for the rest of the water year. The results of the hydrology studies in Colorado and the Eastern U.S. correlate quite well.

MEASURES FOR UNDERSTANDING AND CONTROLLING PROBLEMS

Handling the environmental aspects of a coal mining operation can be just as costly as the actual coal extraction. Furthermore, abatement of the problem is far more troublesome than planning to avoid the problem. Consequently, prior analysis and a complete environmental design are essential to a successful operation. Within this prior analysis should be the following:

- 1) A study conducted of the physical groundwater hydrology of the region that estimates how the region accepts rapid changes due to precipitation events, where the water table is located, and how base flow below the water table is recharged.
- 2) A study conducted of the chemical hydrology that includes a complete chemical analysis of the surface waters, springs and seeps, and groundwaters. This survey definitely should include analyses of acidity, alkalinity, Fe, Mn, sulfate, and bicarbonate. For some constituents, samples should be collected and analyzed monthly so that recharge characteristics of aquifers can be assessed.
- 3) A study conducted of the overburden that includes the identification and estimate of the abundances of minerals. Measures of the net neutralization potential and the maximum potential acidity should be made (diPreoro and Rauch, 1988; Erickson and Hedin, 1988). If overburden analysis and the chemistry of seeps and springs point to the questionable areas in the Figure 1 matrix, laboratory simulations of weathering should be attempted. A thorough environmental plan dealing with questionable overburden is necessary.
- 4) A study conducted of the coal seam to determine the paleoenvironment and the form of pyrite present. Other minor minerals in the coal also should be determined.
- 5) A survey conducted of the regional coal mining operations. This survey should include their analysis of the overburden, paleoenvironment, forms of pyrite, chemical characteristics of seeps and springs, and environmental plans.

If acid mine drainage problems already exist, abatement is likely to require a continuous treatment process. Any measures that can be taken to reduce the volume of water requiring treatment should be taken. In this case, assessment of whether the drainage is a diffuse or conduit aquifer is useful. Surface water infiltration into conduit aquifers should be eliminated. Reducing recharge into groundwater base flow also should be attempted. After the water flowing through the deposits or spoils has been reduced as much as possible, then soil covers and alkaline amendments can be used. If drainage flow has been reduced to less than 0.1 m³/min. (3.5 ft³/min.) and is not subject to large fluctuations in chemistry or discharge rate, then treatment methods using wetlands (Klusman and Machemer, this volume; Wildeman and Laudon, 1989) have a much better chance of success.

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