

A Review of the Literature Pertaining to Passive and Hybrid Treatment Systems for Removal of TDS from Mining Impacted Waters

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ASMR CONFERENCE

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Outline

Motivation

Review of Regulations

Overview of Treatment Methods

Passive Systems

Hybrid Systems

Conclusions



Motivation

More Stringent Discharge Limits

Total Dissolved Solids (TDS), Specific Conductivity (SC)

Need for Cost-Effective and Reliable Technology

Passive, Active, Hybrid

Gap of Knowledge in Terms of TDS Removal

Review of Regulations: Surface Mining Control and Reclamation Act (1977)

Created Office of Surface Mining

Regulates:

- Active Mines
- Abandoned Mines

Key Recommendations:

- Restore to Original Topography
- Isolation of Acid-Forming Materials



Image Source: World Coal

Review of Regulations: Clean Water Act (1972)

Point Source Regulations

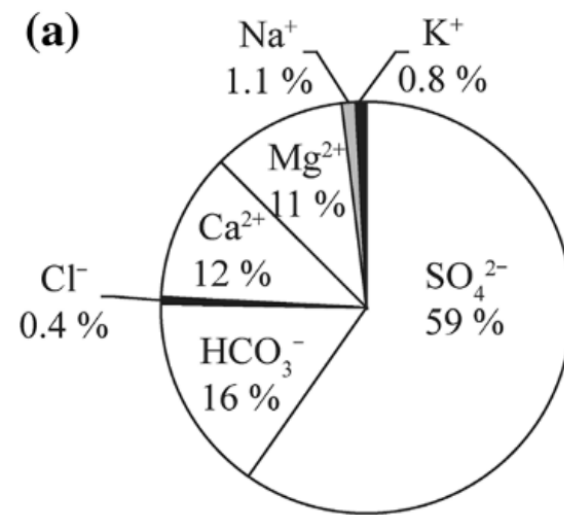
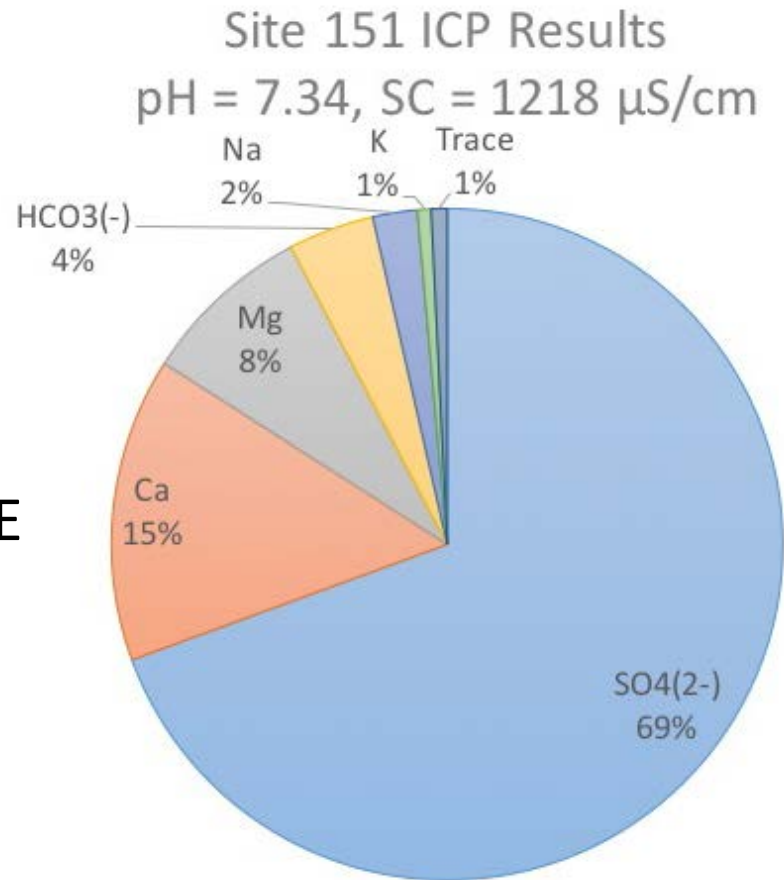
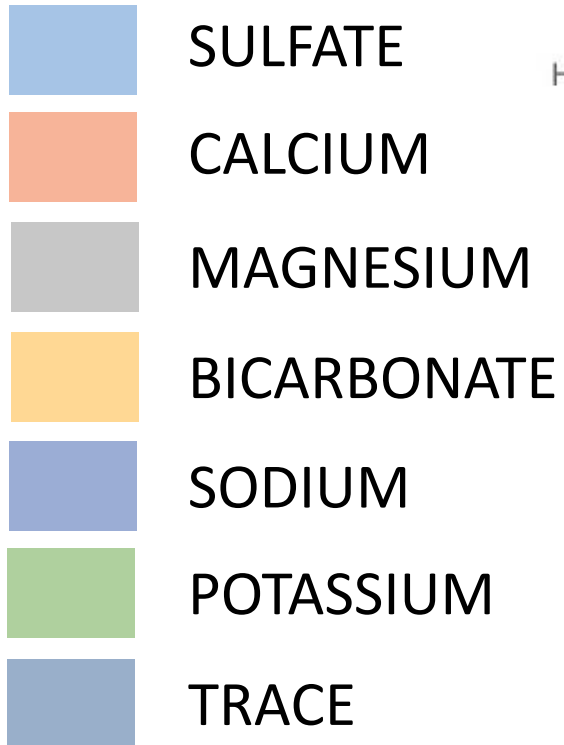
2009-2011

- Attempted to Set Specific Conductivity Standard of 500 $\mu\text{S}/\text{cm}$
- Equivalent to 350 mg/L TDS
- Did Not Pass

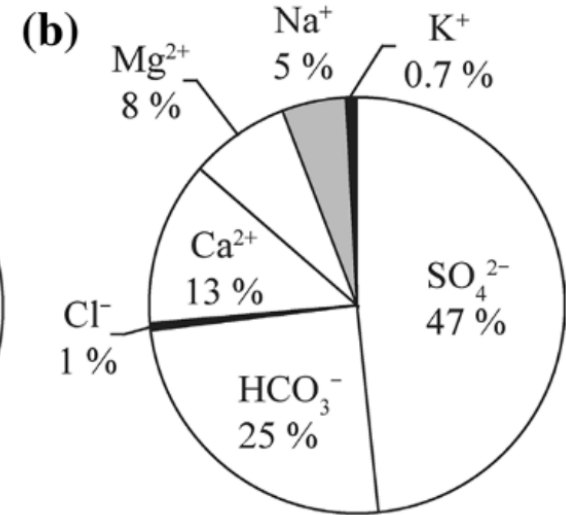


Image Source: Center for Environmental Rights

Total Dissolved Solids (TDS)



Pond et al. 2008

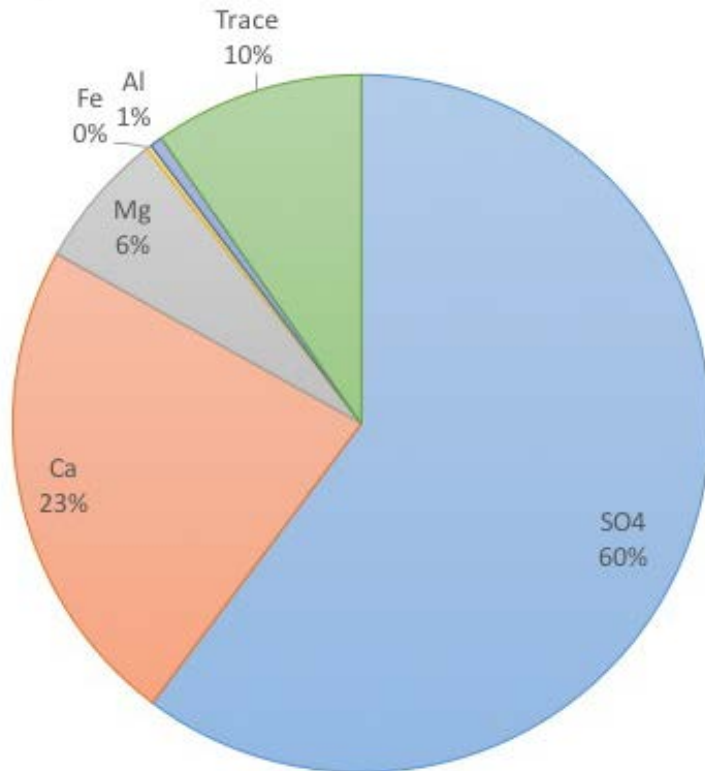


Timpano 2011

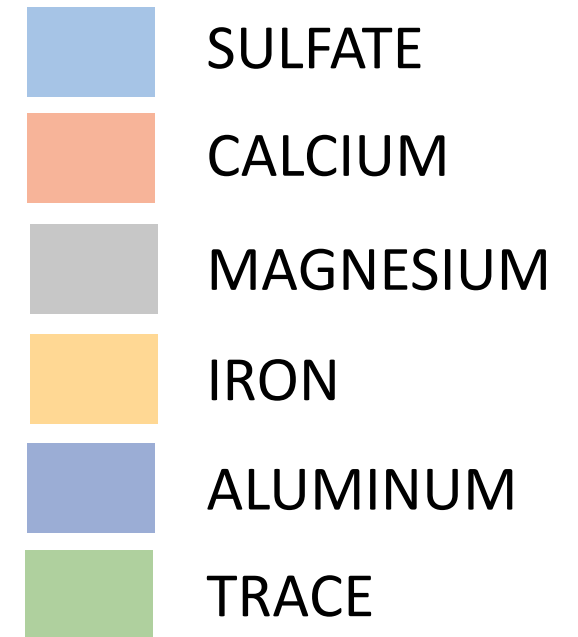
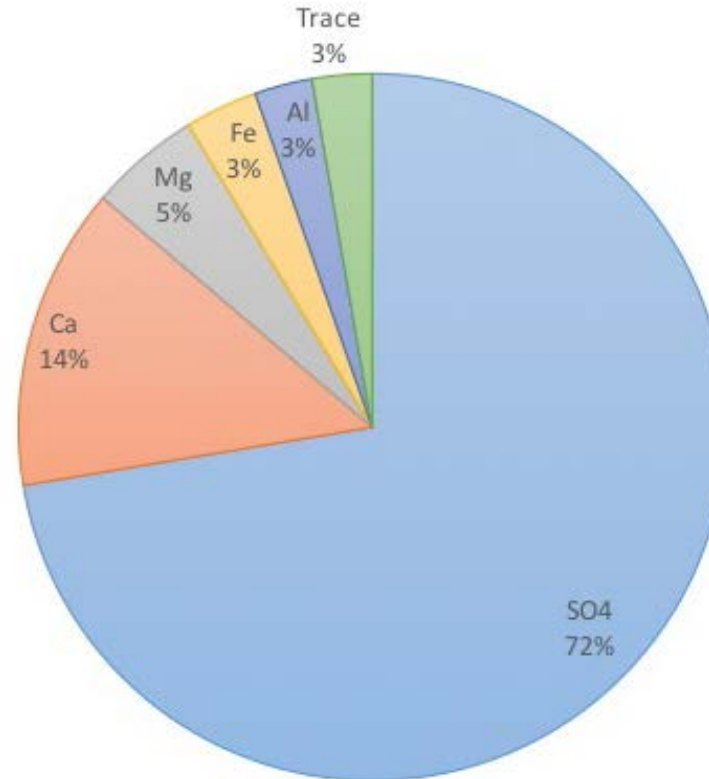
Daniels et al. 2014

Total Dissolved Solids (TDS) - AMD

Moderate AMD Characterization
Adapted from Merovich et al. 2007



Severe AMD Characterization
Adapted from Merovich et al. 2007



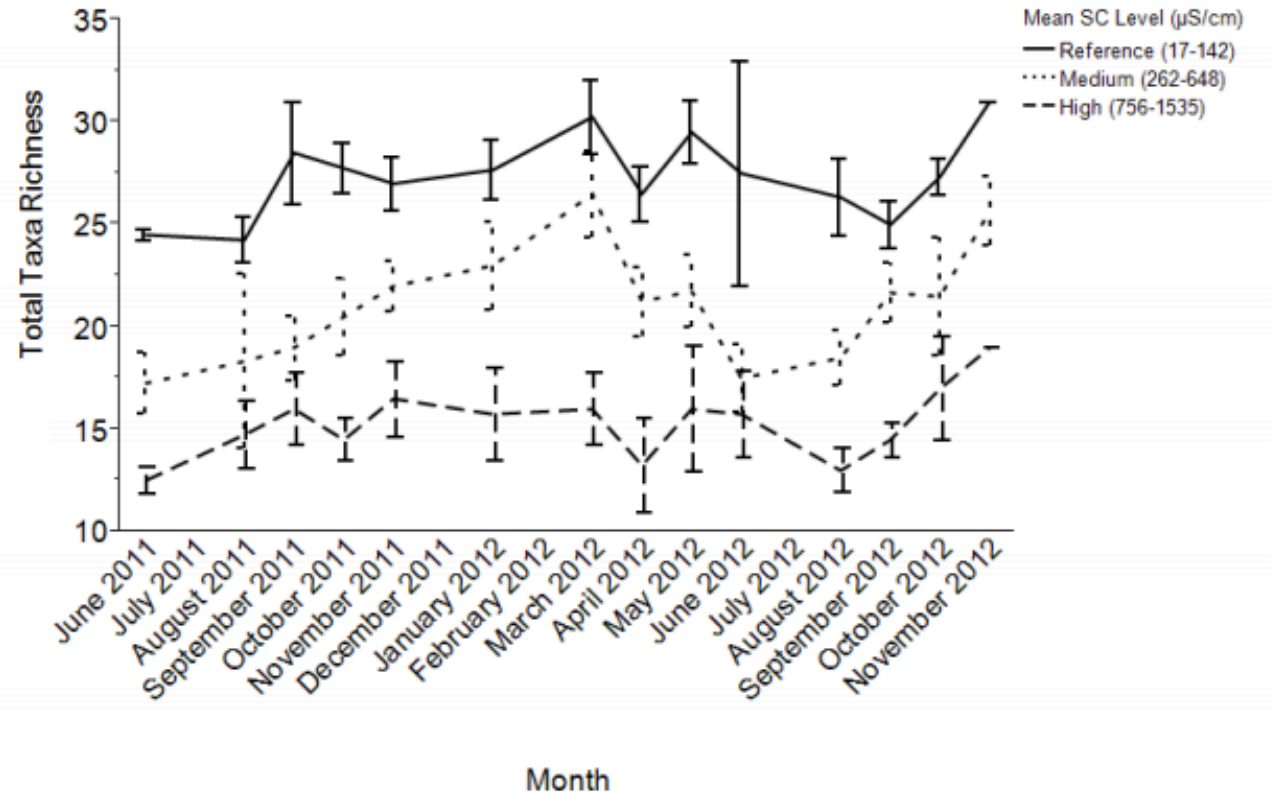
Implications of High TDS on Streams

Stream Impacts

- Salinization
- Aesthetics

Ecological Impacts

- Potential Decrease in Benthic Macroinvertebrates
 - Ephemeroptera, Plecoptera, Trichoptera
 - Pond et al. 2008, Boehme 2013
- Variability



Boehme 2013

Overview of Treatment Methods

Active Systems

- Chemical Addition (Lime, etc.)
- Settling & Sludge Disposal

Passive Systems

Hybrid Systems

- Combination of Active & Passive

Passive Systems

Examples of Passive Systems

Anoxic Limestone Drains (ALDs)

Open Limestone Channels (OLCs)

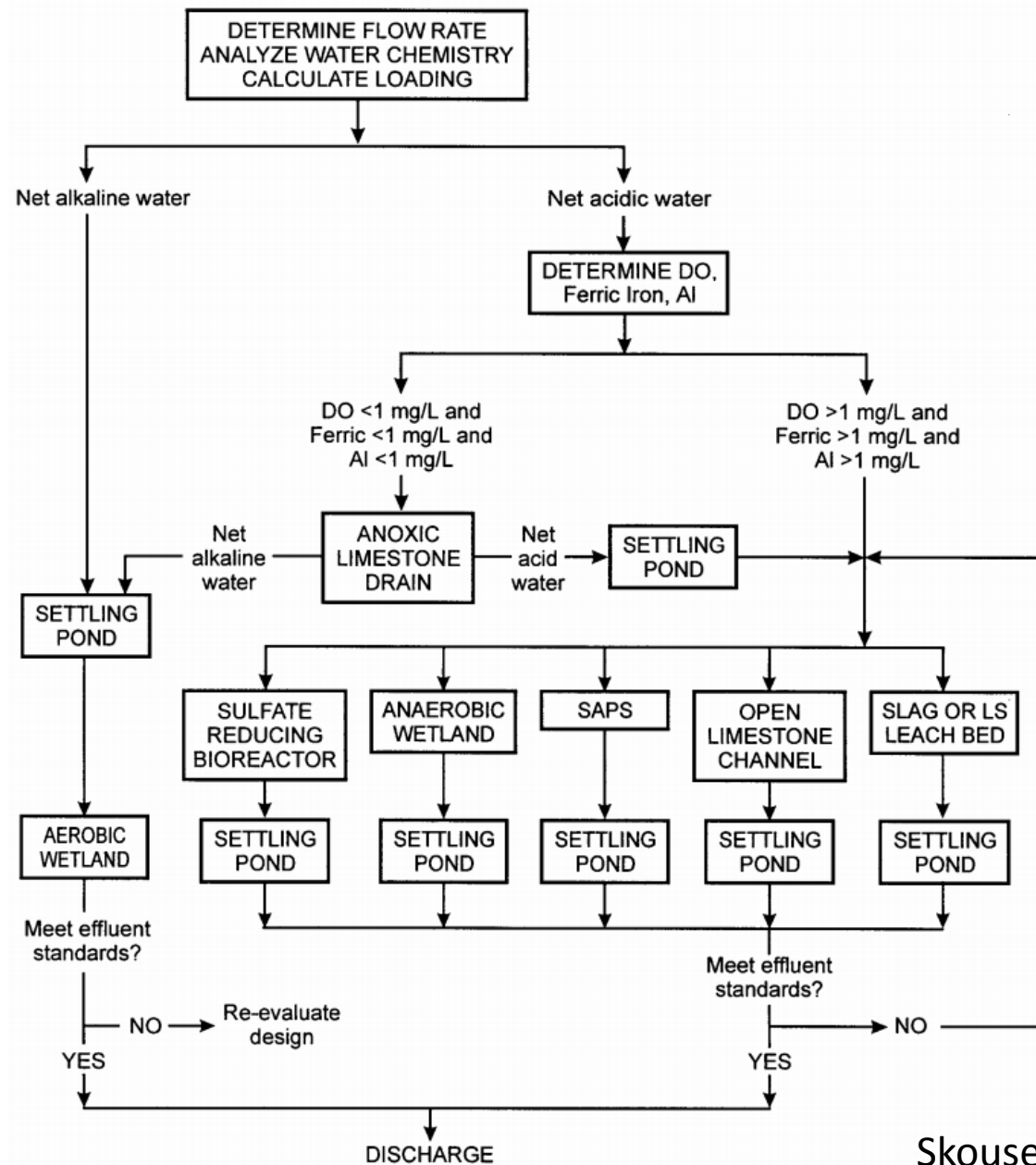
Permeable Reactive Barriers (PRB)

Successive Alkalinity Producing Systems (SAPS)

Constructed Wetlands (Aerobic & Anaerobic)

Sulfate Reducing Bioreactors (SRBs)

Selection of Passive Systems



Skousen and Ziemkiewicz 2005

Anoxic Limestone Drains (ALDs)

Best Suited For:

- Net acidic conditions
- Low DO, Fe^{3+} , Al^{3+}

Issues

- Clogging
- Does NOT Encourage TDS Removal

Best Used for Pretreatment of AMD



Image Source: EPA 2014

Case Study: Watzlaf et al. 2000

Reduced Acidity

Raised Alkalinity

- Increased Ca Concentrations
- Increased pH

Minimal Metal/Ion Removal

- Little to No Sulfate Removal

ALD Survey Data

Parameter	Percent Removal (%)
Acidity	63.6
Alkalinity	- 634
Iron	13.1
Manganese	3.0
Calcium	- 45.4
Sulfate	6.7

Table Adapted from Watzlaf et al. 2000 (Tables 4 & 5)

Open Limestone Channels (OLCs)

Similar to ALDs

Best Suited For:

- Net acidic conditions
- Low DO, Fe^{3+} , Al^{3+}
- Steep Slopes

Issues

- Armoring
- Not a Feasible Standalone



Image Source: USDA

Case Study: Ziemkiewicz et al. 1994

Reduced Acidity

- Increased pH

Alkalinity Trends

- Initially Decreases ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$)

Varying Metal/Ion Removal

- Fe/Mn Most Significant (>20%)
- Sulfate Removal Varied

DOLA OLC Water Quality

Parameter	Percent Removal (%)
Acidity	100
Alkalinity	- 56
Iron	80
Manganese	61
Aluminum	100
Calcium	- 7
Magnesium	2
Sulfate	28

Table Adapted from Ziemkiewicz et al. 1994 (Table 3)

Permeable Reactive Barriers

Various Barriers

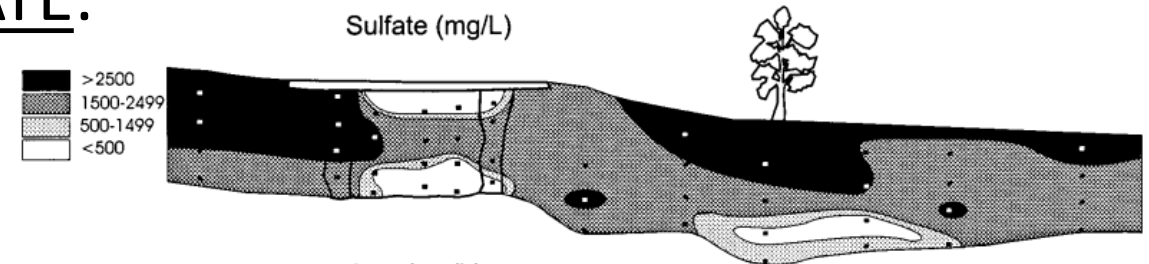
Best Suited For:

- Metal/Anion Removal

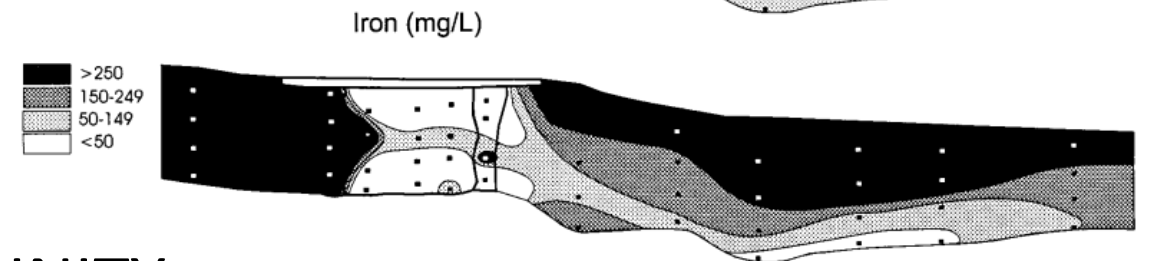
Limitations:

- Optimization Required
- Clogging
- Long-term Performance Unknown

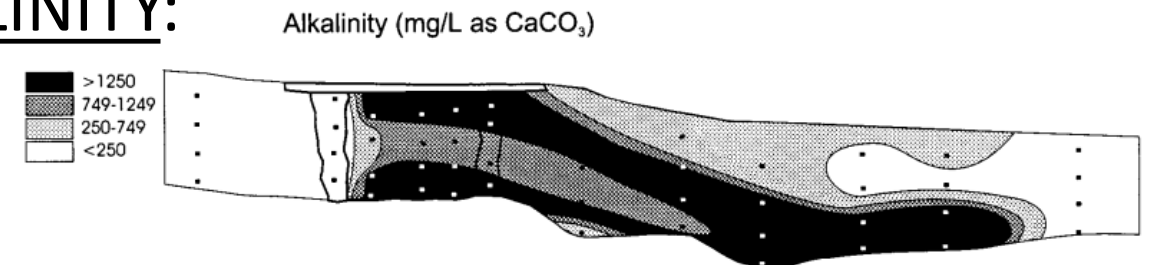
SULFATE:



IRON:



ALKALINITY:



DIRECTION OF FLOW →

Successive Alkalinity Producing Systems or Vertical Flow Systems

Best Suited For:

- Net acidic conditions
- Fe^{2+} , Al^{3+} , Cu Removal

Issues

- Clogging
- Replenishment of Organic Layer
 - Potential for Heavy Maintenance

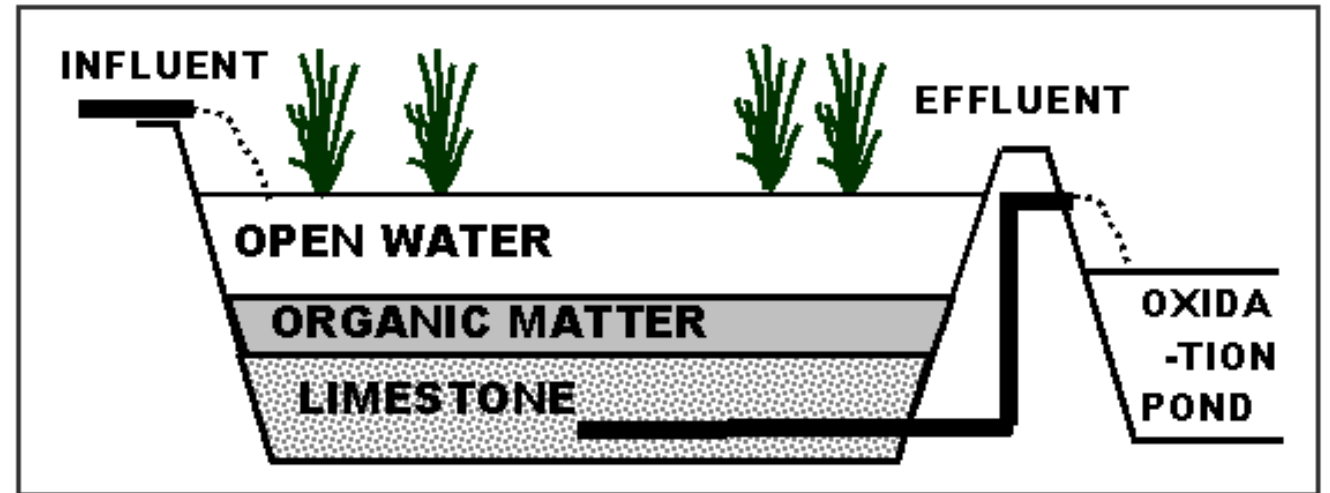


Image Source: VT Powell River Project

Case Study: Kepler and McCleary 1994

	<u>Howe Bridge SAPS</u>		<u>Schnepp Road SAPS</u>	
Parameter	Influent	Effluent	Influent	Effluent
pH	4.7	6.2	6.0	6.6
Acidity (mg/L of CaCO ₃)	321.0	92.6	83.5	5.2
Calcium (mg/L)	182.4	230.2	196.2	221.2
Magnesium (mg/L)	94.8	99.8	N/A	N/A
Sulfate (mg/L)	1,189.0	1,033.0	750.0	717.0
Ferrous Iron (mg/L)	193.0	102.0	1.6	1.0
Ferric Iron (mg/L)	1.6	0.0	19.0	0.1

Table Adapted and Reformatted from Kepler and McCleary 1994 (Tables 3/8)

Constructed Wetlands - Aerobic

Operating Conditions

- Aerobic

Best Suited For:

- Fe/Mn Removal
- Mildly Acidic or Net Alkaline Waters

Limitations

- May Acidify Effluent
- Large Area Required
- Plant Uptake Limited
- Turnover Potential



Image Source: Zipper et al. 2011

Case Study: Hedin et al. 1994

Percent Change (%) of Various Ions at Eight Different Aerobic Wetlands

Site	Ca	Mg	Na	SO ₄
Donegal	-1	-2	0	0
Emlenton	+1	-1	-2	-1
FH	+55	0	+2	-25
Gourley	+3	+3	+6	+3
Latrobe	+14	-2	+8	-20
Piney A	+2	+4	+4	-3
Piney B	0	0	-2	+2
Somerset	+53	0	+15	-16

Table Adapted and Reformatted from Hedin et al. 1994 (Table 10)

Constructed Wetlands - Anaerobic

Operating Conditions

- Anaerobic

Best Suited For:

- Metal Capture & Removal
- Acidic, Neutral, or Alkaline Waters

Limitations:

- Large Land Requirement
- Long HRT
- Odor

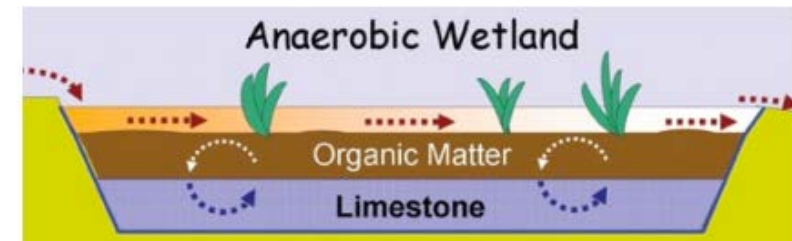
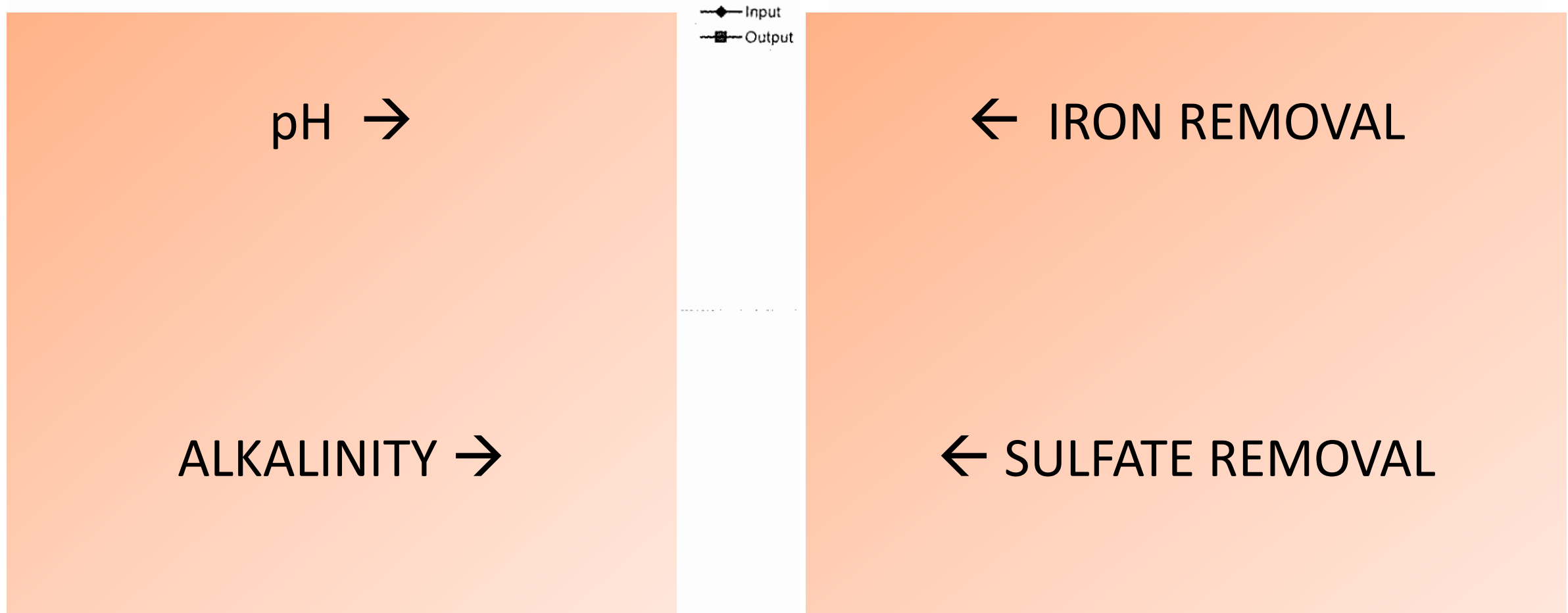


Image Source: Zipper et al. 2011



Image Source: Skousen and Ziemkiewicz 2005

Case Study: Rees and Bowell 1999



Sulfate Reducing Bioreactors

Similar to SAPS

Operating Conditions

- Anaerobic
- Mixture of Organic Substrate & Limestone

Best Suited For:

- Sulfate Removal
- Metal Capture & Removal
- Acidic Waters

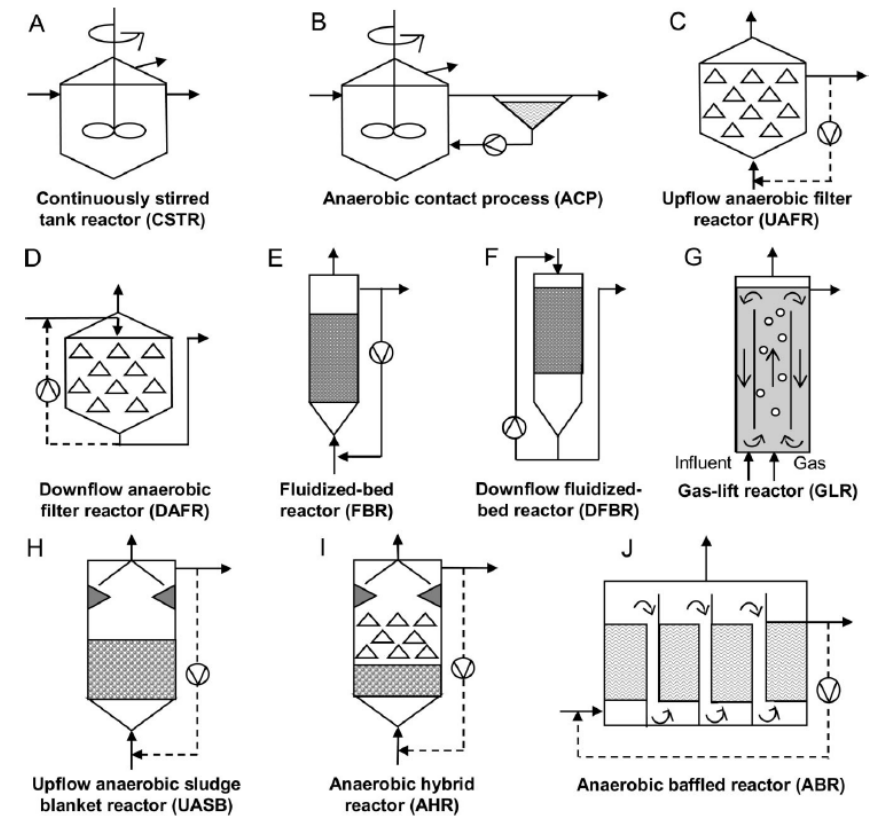


Image Source: Kaksonen and Puhakka 2007

Sulfate Reducing Bioreactors

Advantages

- Able to Handle Varying pH
- Can use Waste Organics
- Resilient
- Able to remove Trace Metals
- Generates Alkalinity
- Low Maintenance

Disadvantages

- Odor
- May Require External Carbon Source (e.g. Ethanol)
- Long Startup Time
- Bed Compaction
- Potential Sludge Production
- Potential Release of Soluble Organics

Case Studies:

Hiibel et al. 2008 & Nancucheo and Johnson 2014

Hiibel et al. 2008

- Increase in pH
- Removals at Two Sites
 - Sulfate: 37/64 %
 - Iron: 18/86 %
 - Aluminum: 46/100 %

Nancucheo and Johnson 2014

- Significant SO_4^{2-} removal could be achieved in very acidic waters

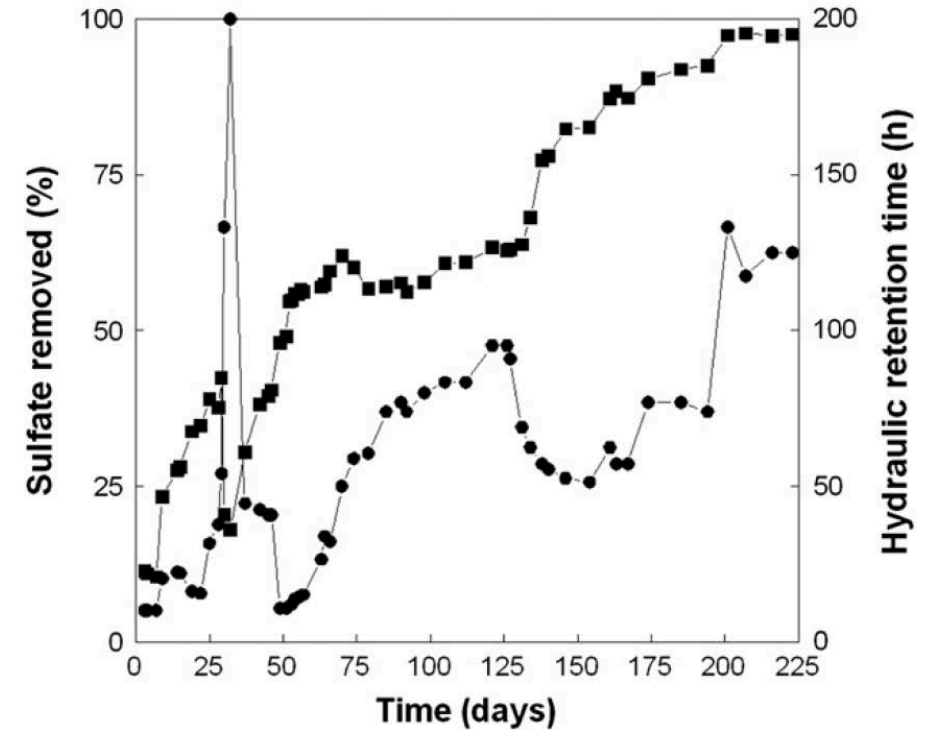


Fig. 1. Relationship between the percentage of sulfate removed (■) from synthetic NGW and hydraulic retention time (●).

Nancucheo and Johnson 2014

Hybrid Systems

Case Study: Semi-Passive BSR System

Configuration

- Settling Pond
- Carbon Addition
- Biological Sulfate Reduction Reactors
- Polishing Pond

Limitations

- Drop in Performance in Winter
- Solids Removal

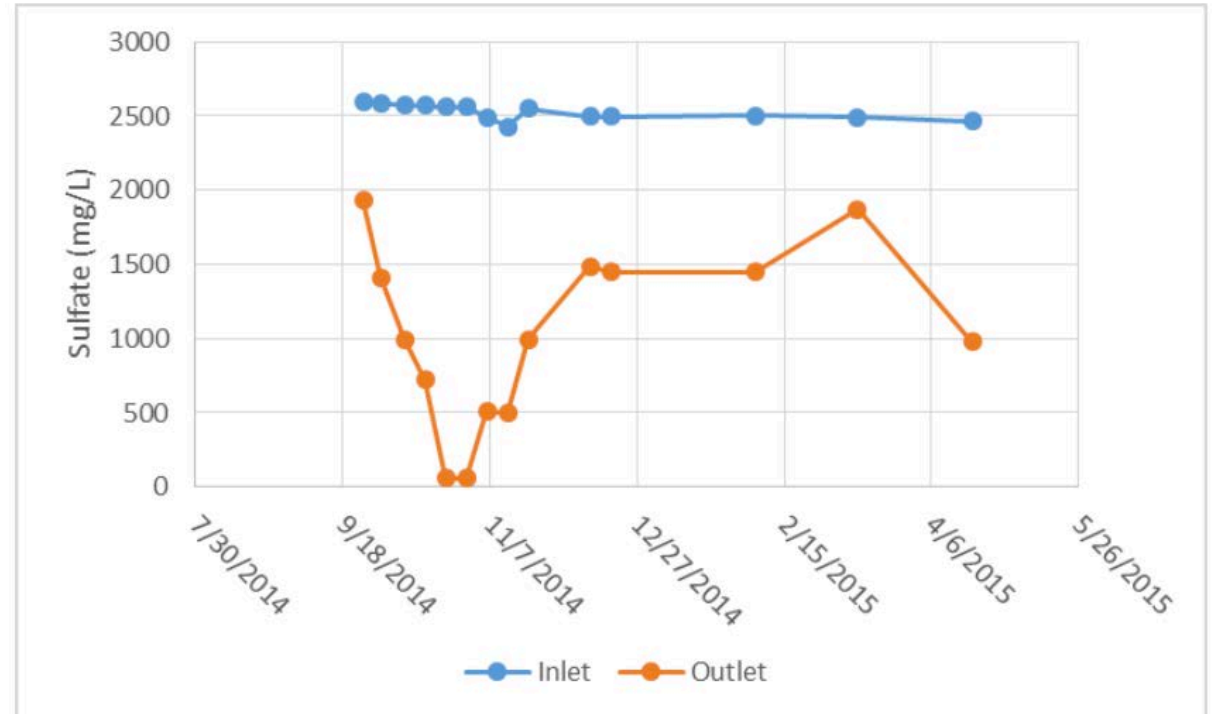


Figure 6. Sulfate Influent and Effluent of SRB Pilot Plant

Walker et al. 2015

Case Study: Sericite & Microalgae System

Configuration:

- Sericite Bead Compartment
- Microalgae Photobioreactor

Sericite Beads

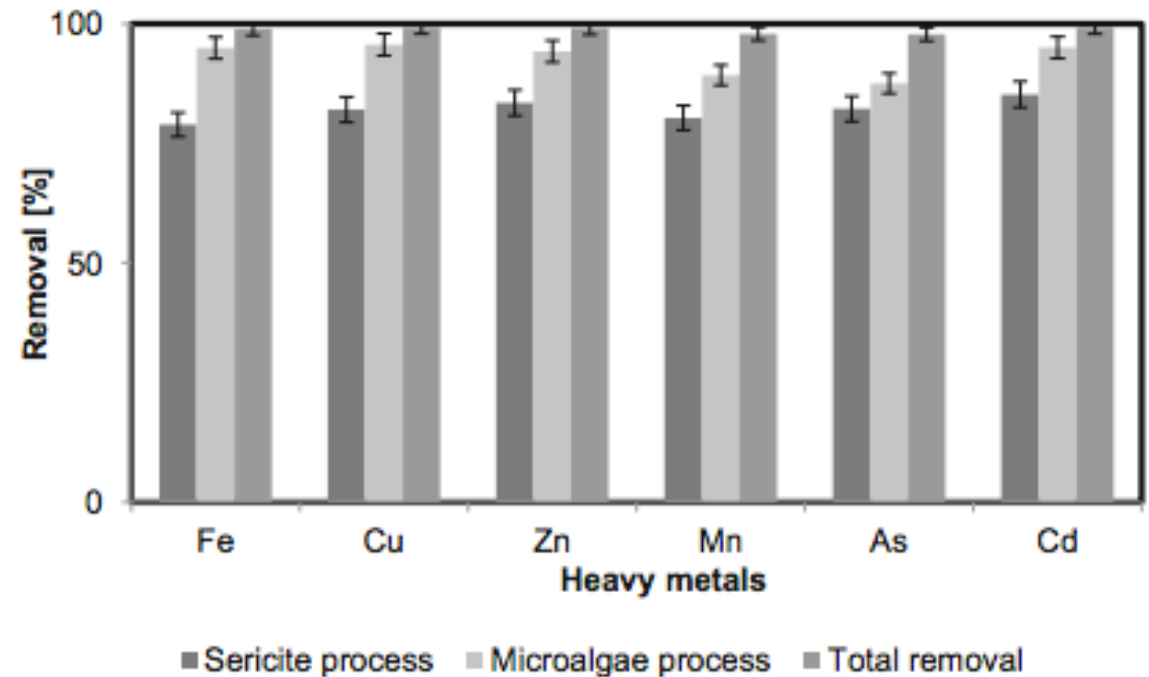
- Neutralization
- Metal Removal

Microalgae Photobioreactor

- Metal Removal

Limitations

- Light Source



Choi 2015

Conclusions

Gap in Knowledge

Sulfate Typically Largest Constituent

Passive Systems Needed

- Combination
- In Conjunction with Active Technologies

Acknowledgements

ARIES



VirginiaTech
Invent the Future

Questions?

AMD Ionic Makeup

	Reference (98)	Soft (32)	Hard (42)	Moderate AMD (32)	Transitional (134)	Severe AMD (37)
pH	6.9 (0.5)	5.0 (0.8)	7.1 (0.5)	6.0 (1.0)	6.8 (0.7)	3.5 (0.7)
Cond	94 (80)	74 (96)	591 (543)	171 (103)	125 (130)	703 (455)
Alk	21.3 (18.8)	2.3 (2.9)	82.4 (102.7)	25.4 (55.9)	22.9 (21.3)	0.5 (1.6)
Al	0.01 (0.01)	0.21 (0.14)	0.04 (0.05)	0.43 (0.97)	0.06 (0.08)	9.72 (9.37)
Ba	0.03 (0.01)	0.03 (0.01)	0.04 (0.01)	0.04 (0.03)	0.04 (0.01)	0.03 (0.01)
Ca	9.8 (9.4)	1.9 (1.3)	58.3 (33.9)	16.9 (12.1)	11.0 (7.6)	51.0 (45.3)
Cd ^a	3.0 (0.3)	3.0 (0.0)	3.2 (8.9)	4.0 (2.2)	3.9 (1.8)	3.5 (1.5)
Cl	1.7 (1.5)	1.5 (2.2)	48.5 (252.3)	3.8 (4.4)	6.4 (7.6)	3.9 (3.1)
Co ^a	1.5 (1.1)	1.9 (1.3)	2.6 (2.2)	19.7 (95.9)	1.6 (3.5)	57.4 (47.8)
Cr ^a	2.2 (1.4)	1.9 (1.1)	2.3 (1.3)	2.2 (1.1)	2.2 (1.2)	4.9 (3.0)
Cu ^a	1.6 (1.5)	2.0 (3.1)	2.2 (3.2)	2.0 (3.1)	1.7 (2.4)	15.9 (13.4)
Fe	0.03 (0.03)	0.09 (0.1)	0.13 (0.33)	0.17 (0.13)	0.14 (0.11)	12.23 (19.91)
Mg	1.7 (1.6)	0.6 (0.4)	15.7 (11.0)	4.7 (3.6)	2.2 (1.2)	18.7 (21.6)
Mn	0.01 (0.01)	0.07 (0.05)	0.35 (0.31)	0.38 (0.37)	0.10 (0.16)	1.85 (2.50)
Na	1.6 (1.7)	0.7 (1.4)	43.6 (124.4)	2.9 (3.4)	4.8 (5.5)	3.9 (2.9)
Ni ^a	2.4 (1.9)	3.1 (1.6)	5.3 (4.8)	18.5 (13.2)	2.4 (1.4)	87.9 (62.9)
Zn ^a	2.9 (3.4)	17.5 (50.2)	5.2 (5.6)	23.3 (27.3)	2.3 (2.0)	173.6 (121.8)
SO ₄	9.6 (11.4)	7.7 (3.4)	198.9 (201.2)	44.5 (47.2)	14.6 (8.0)	266.2 (210.1)
PC 1	-0.87A (0.30)	-0.66A (0.45)	0.40B (0.29)	-0.18C (0.43)	0.94D (0.34)	2.25E (0.60)
PC 2	-0.00A (0.56)	-1.68B (0.51)	1.56C (0.78)	0.25A (0.64)	-0.37D (0.71)	-0.90E (0.39)

^a Units = µg/L.

Merovich et al. 2007

Case Study: Watzlaf et al. 2000

Table 4. Average water quality before and after contact with the anoxic limestone drain.

ALD	Net Acidity, ¹ mg/L as CaCO ₃		Alkalinity, mg/L as CaCO ₃		Calcium, mg/L		pH, s.u.		Sulfate mg/L	
	In	Out	In	Out	In	Out	In	Out	In	Out
Howe Bridge 1	472	352	32.6	155	115	223	5.74	6.30	1319	1314
Howe Bridge 2	411	274	35.3	163	157	209	5.40	6.48	1210	1211
Elklick	52.0	-63.0	33.8	159	258	232	6.06	6.73	334	327
Jennings	280	-33.5	0	139	ND	201	3.23	6.16	633	620
Morrison ²	387	51.4	28.7	278	82.9	208	5.19	6.35	1256	1016
Filson-R ²	100	-139	47.9	299	69.2	180	5.73	6.49	408	438
Filson-L ²	104	-175	47.9	317	77.1	129	5.73	6.60	408	395
Schnepp ³	307	-42.5	0	168	69.2	189	3.28	6.17	980	745
REM-R ³	1148	835	0	54	258	206	4.28	5.45	2825	2394
REM-L ³	ND	259	ND	113	ND	198	ND	6.00	ND	1256

¹ Negative net acidity values indicate net alkalinity.

² "In" concentrations based on water quality of a nearby seep.

³ "In" concentrations based on historical water quality data of the untreated mine drainage prior to construction of the ALD. Numbers are not available for REM-L. ND = Not Determined

Table 5. Additional water quality parameters before and after contact with the anoxic limestone drain.

ALD	Iron, mg/L		Manganese, mg/L		Aluminum, mg/L		Cobalt, mg/L		Nickel, mg/L		Zinc, mg/L	
	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out
Howe Bridge 1	276	275	41.5	41.5	<0.2	<0.2	0.48	0.48	0.51	0.50	0.62	0.55
Howe Bridge 2	250	248	36.6	35.9	<0.2	<0.2	0.39	0.39	0.40	0.40	0.42	0.39
Elklick	59.2	53.3	4.77	4.89	<0.2	<0.2	0.07	0.07	0.10	0.09	0.13	0.08
Jennings	75.6	59.3	8.39	8.33	20.9	1.1	0.13	0.15	0.40	0.40	0.66	0.54
Morrison ¹	207	156	48.7	40.9	0.5	<0.2	0.86	0.75	0.79	0.65	0.95	0.72
Filson-R ¹	59.3	55.5	19.9	19.8	0.4	<0.2	0.23	0.23	0.18	0.18	0.27	0.18
Filson-L ¹	59.3	68.6	19.9	15.9	0.4	<0.2	0.23	0.13	0.18	0.10	0.27	0.17
Schnepp ²	92	61.5	28	26.3	6.7	<0.2	ND	0.27	ND	0.33	ND	0.34
REM-R ²	589	447	136	126	4.5	3.2	ND	1.49	ND	1.54	ND	246
REM-L ²	ND	185	ND	50.8	ND	<0.2	ND	0.60	ND	0.66	ND	0.76

¹ "In" concentrations based on water quality of a nearby seep.

² "In" concentrations based on historical water quality data of the untreated mine drainage prior to construction of the ALD.

ND - Not Determined

Case Study: Ziemkiewicz et al. 1994

Table 3. Water quality from grouted limestone OLCs on Brownton and Dola AML sites in West Virginia

Site	Ft from Top	pH	Acid	Alk	Fe	Mn	Al	Ca	Mg	SO ₄
Brownton										
	0	5.6	10	90	28	3	0	185	67	854
	100	6.0	0	63	27	3	0	187	66	854
	200	6.1	0	60	25	3	0	187	64	827
	400	6.2	0	53	24	3	0	187	64	827
	500	6.3	0	55	22	3	0	208	65	849
% Change			-100	-39	-21	0	0	12	-3	-1
Dola										
	0	6.0	154	101	162	28	3	483	129	2263
	100	6.1	219	28	152	34	2	475	137	2192
	400	6.5	0	81	35	24	0	552	135	2227
	700	6.6	0	231	32	11	0	519	126	1629
% Change			-100	56	-80	-61	-100	7	-2	-28

***Double
Check Units

Case Study: Kepler and McCleary 1994

Table 3. Influent-effluent water quality, Howe Bridge SAPS, January 23, 1992 through July 27, 1993, effluent corrected for dilution-concentration.

Parameter ¹	n	(Influent)			n	(Effluent)		
		Mean	Range			Mean	Range	
pH, s.u.....	6	NA	3.29 -	6.14	6	NA	5.84 -	6.49
Acidity.....	6	321.0	207 -	396	6 ²	92.6	0 -	278.8
Calcium.....	6	182.4	136.0 -	230.8	6	230.2	192.2 -	279.4
Magnesium....	6	94.8	67.1 -	114.6	6	99.8	77.8 -	123.6
Sulfate.....	6	1,189	875 -	1,407	6	1,033	621 -	1,258
Fe ²⁺	6	193.0	149 -	231	6	102.0	47.7 -	159.0
Fe ³⁺	6	1.6	0 -	9.6	6	0	0	

NA Not applicable.

¹ Acidity is presented as mg/L of CaCO₃ equivalent; all other values are in mg/L.

² n = 3 < 10 mg/L readings, calculated as zeroes.

Table 8. Influent-effluent water quality, Schnepf Road SAPS, July 15, 1992 through July 13, 1993, effluent corrected for dilution-concentration.

Parameter ¹	n	(Influent)			n	(Effluent)		
		Mean	Range			Mean	Range	
pH, s.u.....	4	NA	5.86 -	6.20	4	NA	6.29 -	6.88
Acidity.....	4	83.5	69 -	102	4	5.2	0 -	18
Calcium.....	4	196.2	184 -	212	4	221.2	207 -	237
Sulfate.....	4	750	654 -	846	4	717	622 -	810
Fe ²⁺	4	1.6	0.4 -	3.6	4	1.0	0.6 -	1.2
Fe ³⁺	4	19.0	16.5 -	21.2	4	0.1	0 -	0.2
NA, Not applicable								

NA Not applicable.

¹ Acidity is presented as mg/L of CaCO₃ equivalent; all other values are in mg/L.

Case Study: Hedin et al. 1994

Table 10.—Influent and effluent concentrations of Ca, Mg, Na, and sulfate at eight constructed wetlands

	Ca			Mg			Na			SO ₄		
	In, mg·L ⁻¹	Eff, mg·L ⁻¹	Change, %	In, mg·L ⁻¹	Eff, mg·L ⁻¹	Change, %	In, mg·L ⁻¹	Eff, mg·L ⁻¹	Change, %	In, mg·L ⁻¹	Eff, mg·L ⁻¹	Change, %
Donegal	244	241	-1	81	79	-2	6	6	0	729	729	0
Emlenton	429	433	+1	308	306	-1	11	10	-2	2,810	2,770	-1
FH	122	189	+55	51	51	0	5	7	+2	1,125	842	-25
Gourley	117	120	+3	114	117	+3	3	4	+6	1,000	1,030	+3
Latrobe	244	256	+14	127	125	-2	6	11	+8	1,525	1,225	-20
Piney A	416	426	+2	251	262	+4	15	16	+4	2,190	2,120	-3
Piney B	355	354	0	217	216	0	27	27	-2	2,050	2,100	+2
Somerset	307	469	+53	312	312	0	6	7	+15	2,740	2,300	-16

Eff Effluent.

In Influent.

FH Friendship Hill National Historical Site.

Case Study: Hiibel 2008

Table 4. Water chemistry and removal data for the Luttrell and PJK field-scale bioreactors treating AMD.

<i>Luttrell field site</i>	Influent		Effluent		Average removal rate (mg/l/day)	
	Week ^a	Long term ^b	Week ^a	Long term ^b		
Flow (l/d)	30 091	4168	30 091	4168		
pH	5.24	3.64	5.99	6.07		
Temp (°C)	5.6	10.9	5.4	11.4		
			Percent removal			
			Week ^a	Long term ^b	Week ^a	Long term ^b
Sulfate (mg l ⁻¹)	988	3776	73	64	3.0×10^{-2}	2.2×10^0
Fe (mg l ⁻¹)	n.a.	61.59	n.a.	86	n.a.	4.8×10^{-2}
Al (mg l ⁻¹)	n.a.	67.15	n.a.	100	n.a.	6.1×10^{-2}
Zn (mg l ⁻¹)	n.a.	204.53	n.a.	99	n.a.	1.9×10^{-1}
Cu (mg l ⁻¹)	n.a.	15.81	n.a.	100	n.a.	1.4×10^{-2}
Cd (mg l ⁻¹)	n.a.	1.39	n.a.	99	n.a.	1.3×10^{-3}
Mn (mg l ⁻¹)	n.a.	195.40	n.a.	59	n.a.	1.1×10^{-1}
Ni (mg l ⁻¹)	n.a.	0.52	n.a.	0	n.a.	0.0×10^0

<i>PJK field site</i>	Influent		Effluent		Average removal rate (mg/l/day)	
	Week ^a	Long term ^b	Week ^a	Long term ^b		
Flow (L/d)	204 390	116 170	181 498	88 108		
pH	6.35	6.89	6.55	6.69		
Temp (°C)	6.7	10.3	7.8	12.6		
			Percent removal			
			Week ^a	Long term ^b	Week ^a	Long term ^b
Sulfate (mg l ⁻¹)	98.0	87.1	28	37	7.7×10^{-3}	5.5×10^{-1}
Fe (mg l ⁻¹)	0.10	0.23	11	18	3.2×10^{-6}	6.9×10^{-4}
Al (mg l ⁻¹)	0.02	0.07	11	46	6.4×10^{-7}	5.4×10^{-4}
Zn (mg l ⁻¹)	1.95	0.64	41	-11	2.3×10^{-4}	-1.2×10^{-3}
Cu (mg l ⁻¹)	0.03	0.01	70	24	6.0×10^{-6}	4.1×10^{-5}
Cd (mg l ⁻¹)	0.01	0.01	11	24	3.2×10^{-7}	4.1×10^{-5}
Mn (mg l ⁻¹)	4.19	1.51	41	2	5.0×10^{-4}	5.3×10^{-4}
Ni (mg l ⁻¹)	0.01	0.01	11	24	3.2×10^{-7}	4.1×10^{-5}

a. Average values the week prior to sampling.

b. Average lifetime values (2002–2005 for Luttrell, 2003–2005 for PJK).

n.a., data not available.

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Table 3 Heavy metal removal using sericite beads and microalgae hybrid system in the AMD

Heavy metals		Fe	Cu	Zn	Mn	As	Cd
Sericite beads process	Initial concentration (mg/L)	137.48±10.34	22.78±3.26	19.77±2.54	10.35±1.54	0.45±0.02	0.27±0.01
	End concentration (mg/L)	28.99±3.64	4.09±0.45	3.27±0.32	2.04±0.15	0.08±0.001	0.04±0.001
	Removal (%)	78.91±1.04	82.04±1.56	83.46±1.67	80.29±1.34	82.22±1.21	85.19±0.98
Microalgae process	Initial concentration (mg/L)	28.99±3.64	4.09±0.45	3.27±0.32	2.04±0.15	0.08±0.001	0.04±0.001
	End concentration (mg/L)	1.48±0.03	0.18±0.01	0.19±0.01	0.22±0.01	0.01±0.00	0.007±0.00
	Removal (%)	94.89±1.02	95.60±1.05	94.19±1.54	89.22±1.24	87.50±1.12	95.00±1.32
Total removal (%)		98.92±1.34	99.21±1.45	99.04±1.42	97.87±1.37	97.78±1.12	99.26±1.21