Geochemical Controls on Limestone Utilization in Abandoned Mine Land Reclamation

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http://anr.ext.wvu.edu/land-reclamation

Project Scope

I. Overview of Acid Mine Drainage (AMD), Remediation Options, and Practices

II. Armoring Process and Associated Concerns

III. Conceptual Model

IV. Experimental Design and Methods

V. Simulation Results and Insights

VI. Critical Research Questions

$$2\,FeS_2(s) + 7\,O_2 + 2\,H_2O \rightarrow 2\,Fe^{2+} + 4\,SO_4^{2-} + 2\,H^+$$

$$2\,Fe^{2+} + 0.5\,O_2 + 2H^+ \rightarrow 2\,Fe^{3+} + H_2O$$

$$FeS_2(s) + 14\,Fe^{3+} + 8\,H_2O \rightarrow 15\,Fe^{2+} + 2\,SO_4^{2-} + 16\,H^+$$

\+ Al, Mn + Trace metals : Zn, Cr, Cu, Ni, Pb

- **Carbonate treatments offer significant neutralization potential :**
- **1 m ^{3} $CaCO_3$ can produce 2.64 X10^4 mg/L alkalinity* !**

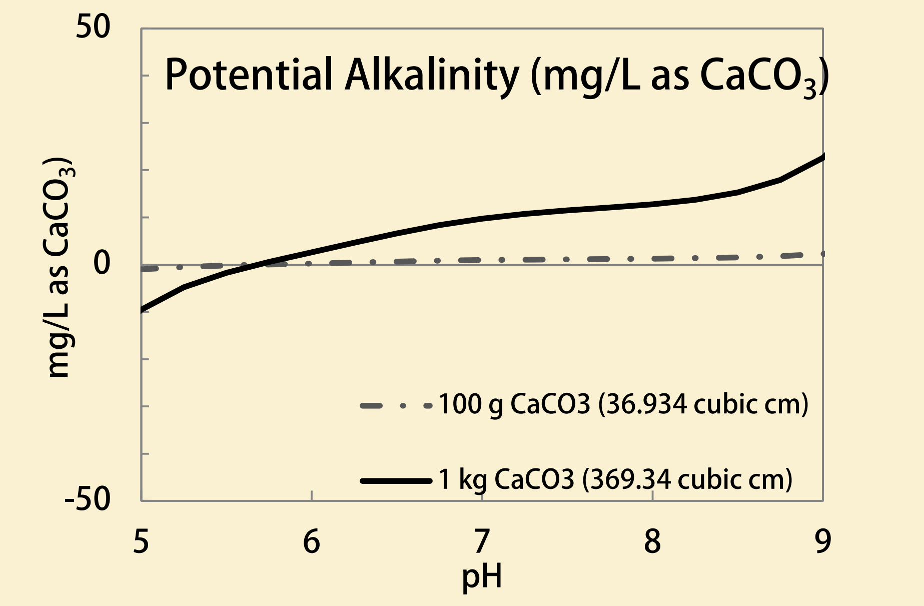
*complete reaction at 25°C, 1 atm, pH 7

www.unitedaggregates.net/knox-county-sand-and-gravel/

$$CaCO_3\,(s) + H^+ \rightarrow Ca^{2+} + HCO_3^-$$

$$CaCO_3\,(s) + H_2CO_3^* \rightarrow Ca^{2+} + 2HCO_3^-$$

$$CaCO_3\,(s) + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^-$$



Limestone-Based Treatments

Open (Oxic) Limestone Drain

Buried (Anoxic) Limestone Drain

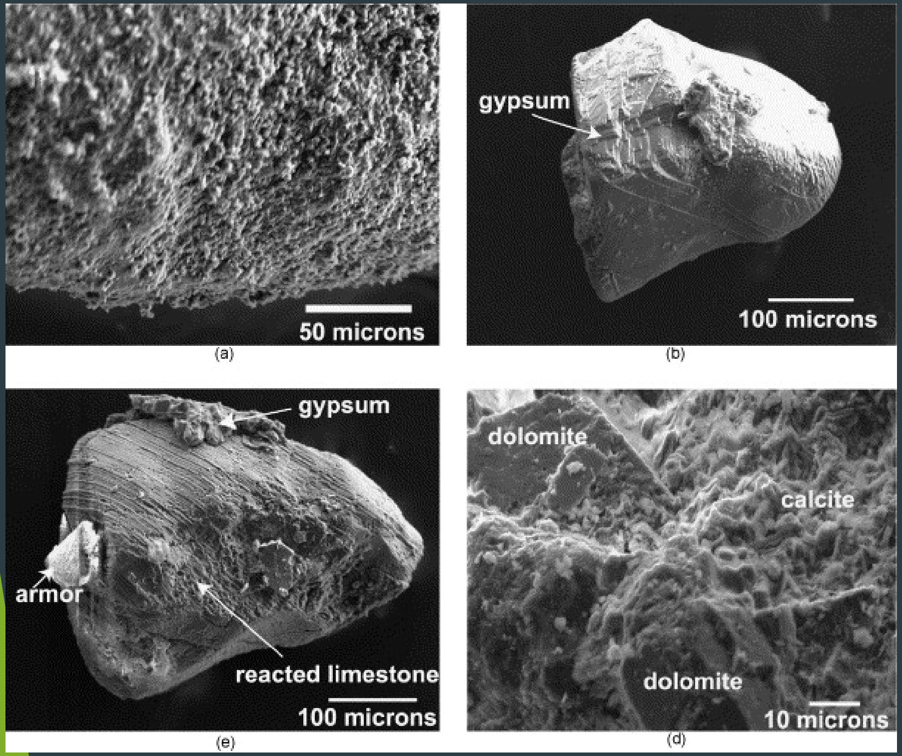
- <u>Natural</u> –no caustic chemical additives (passive system)
- <u>Inexpensive</u>– limestone is readily available, low maintenance
- Multiple well-established options for design and application
- Easy to apply ... ?

- Limestone dissolves in the AMD and adds alkalinity
- However, acidity and alkalinity <u>*co-exist*</u>

  …Some of the produced alkalinity causes metal oxidation and hydrolysis!
- Formation of precipitates limit lifetime of the system

Armored limestone is only ~60% as effective in generating alkalinity as fresh stone

(Pearson and McDonnell, 1975; Ziemkiewicz et al., 1997)



Hammarstrom et al., 2003. Applied Geochemistry, v. 18 (11)

- Coating ("armoring") of grain surfaces
- Pore space plugged

Thus,

- Unreacted limestone is sealed off from acidic solution
- Neutralization process is retarded

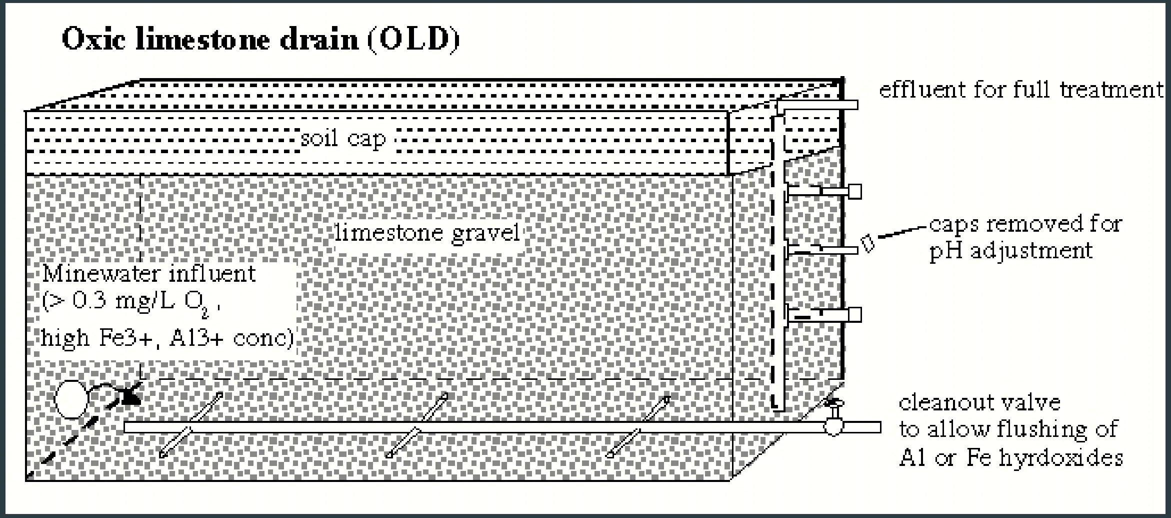
Mineral Name	Reaction
(A) Oxides and Hydroxides	
Iron Oxide	$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+$
Aluminum Oxide	$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3 + 3H^+$
Gibbsite	$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3 + 3H^+$
Goethite	$Fe^{3+} + 2 H_2O \leftrightarrow FeO(OH) + 3H^+$
Lepidocrocite	$Fe^{3+} + 2 H_2O \leftrightarrow FeO(OH) + 3H^+$
Hematite	$2Fe^{3+} + 3 H_2O \leftrightarrow Fe_2O_3 + 6 H^+$
Manganite	$Mn^{2+} + 2 H_2O \leftrightarrow e- + MnOOH + 2 H^+$
Calcite	$CaCO_3$ (s) $+ H^+ \leftrightarrow Ca^{2+} + HCO_3^-$
(B) Sorbates	
Manganese	>(s)FeOH + Mn^{2+} + → >(s)$FeOMn^+$ + H^+ >(w)FeOH + Mn^{2+} + → >(w)$FeOMn^+$ + H^+
Zinc	>(s)FeOH + Zn^{2+} + →>(s) $FeOZn^+$ + H^+ >(w)FeOH + Zn^{2+} + → >(w)$FeOZn^+$ + H^+
Lead	>(s)FeOH + Pb^{2+} + → >(s)$FeOPb^+$ + H^+ >(w)FeOH + Pb^{2+} + → >(w)$FeOPb^+$ + H^+
Copper	>(s)FeOH + Cu^{2+} + → >(s)$FeOCu^+$ + H^+ >(w)FeOH + Cu^{2+} + → >(w)$FeOCu^+$ + H^+

Addressing Details And Mechanics Of Armoring

Literature shows wide range (48-96%) in efficiency

(Ziemkiewicz *et al.*, 1997; Cravotta and Trahan, 1999; Watzlaf *et al., 2000)*

Assume [illegible]% efficiency?

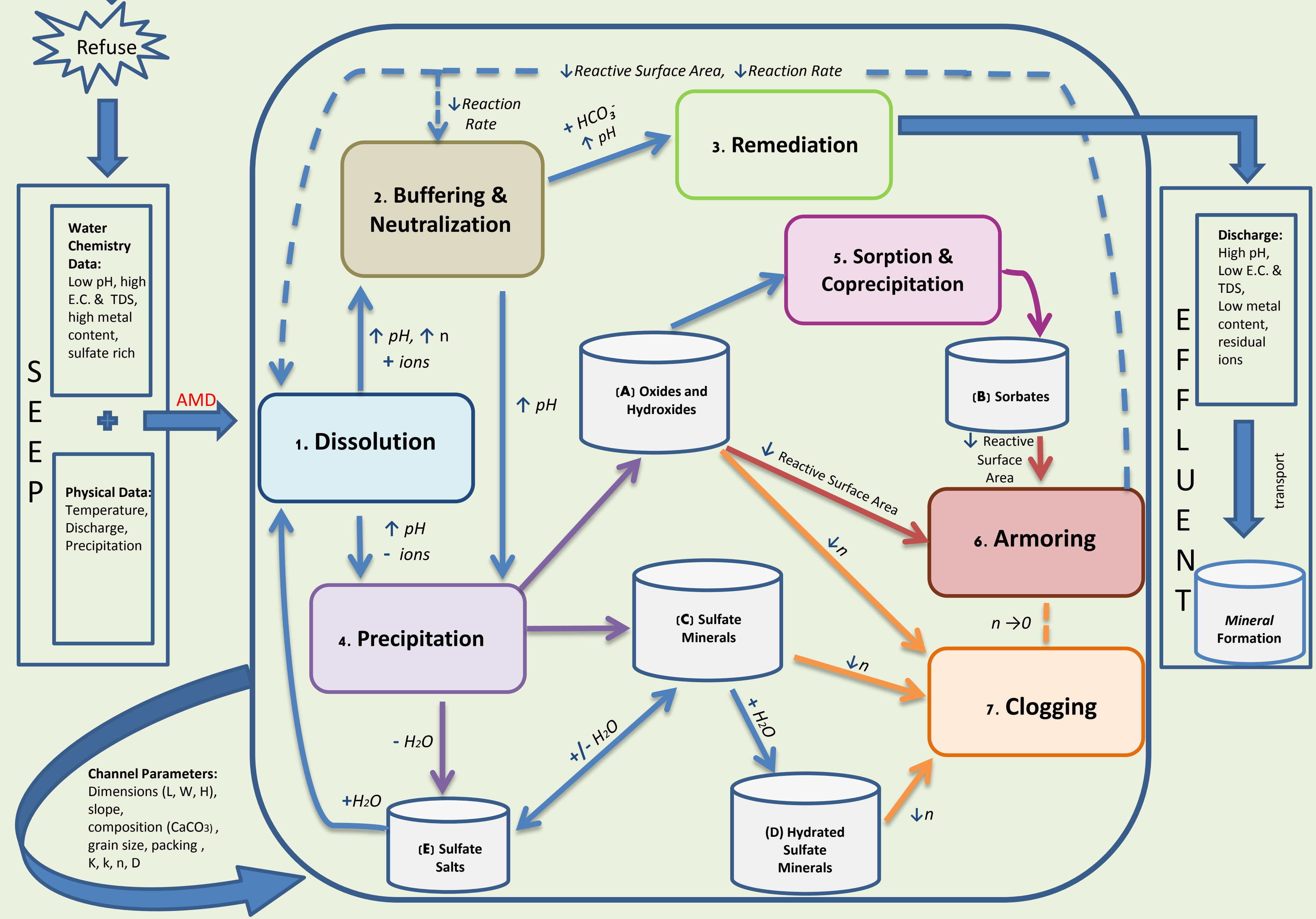


http://www.facstaff.bucknell.edu/kirby/ALDOLD.html

Key Questions:

- Which elementary reactions occur?
- What is their spatial distribution?
- How quickly do reactions proceed?
- How does the system evolve through time?

Acid Mine Drainage (AMD) Treatment in an Oxic Limestone Drain (OLD)



Investigation Methods

Transient numerical modeling provides a quantitative examination of the simultaneously occurring geochemical reactions between limestone drains and AMD.

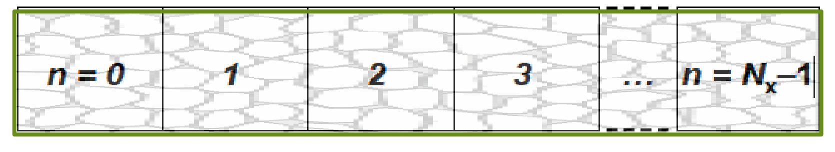
- ➢ "how fast, and to what extent, do elementary and coupled reactions occur over time?"

$$\frac{dC_i}{dt} = \mathrm{D_L} \frac{\partial^2 C_i}{\partial x^2} - v_i \frac{dC_i}{dx} + \sum_{k=1}^{n} R_i$$

Transport
Advection (Darcy's law)
Dispersion (Fick's Law)

Suite of Reactions
Time-dependent Interactions between AMD and rock

- ➢ Develop a model which allows reaction coupling and feedback loops…



Reaction Kinetics

Overall Mineral Reaction Rate:

$$R_i = k \frac{A_0}{V}\left(\frac{m}{m_0}\right)^{\sigma}\left[1-\left(\frac{Q}{K}\right)^{\alpha}\right]^{\beta}$$

specific reaction term
Reaction mechanics, catalysts/inhibitors

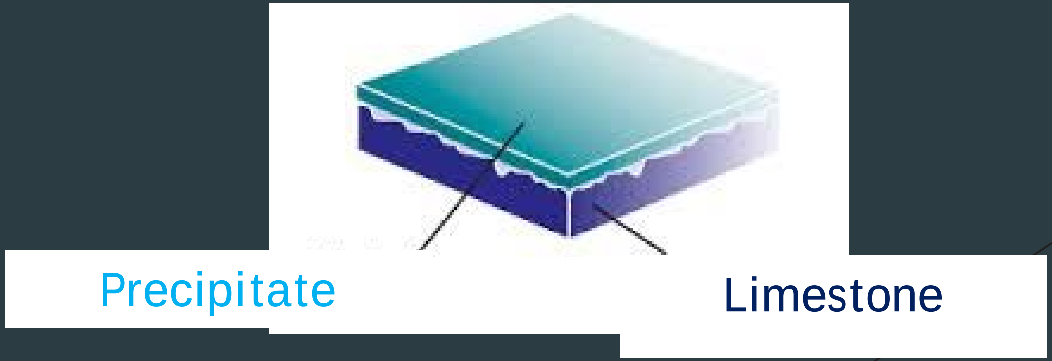
surface area
Grain size and shape

Thermodynamic (Chemical) drive
tendency toward equilibrium with solution

$$k = \left[k_{acid}^{298.15} * \exp\left[\frac{-E_{acid}}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)\right] * a_{H^+}^{\theta} + k_{neut}^{298.15} * \exp\left[\frac{-E_{neut}}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)\right] + k_{base}^{298.15} * \exp\left[\frac{-E_{base}}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)\right] * a_{H^+}^{\vartheta}\right]$$

$$A_0 = GFW \times A_{BET} \times m$$

$$\frac{A_{reactive,t}}{V} = \frac{\left[A_0 - \left(A_{Fe\ oxides,t} + A_{Al\ oxides,t} + A_{Gypsum,t}\right)\right]}{V}$$



Key Minerals and Rates

- $Fe(OH)_3$(a) and $Al(OH)_3$(a): highly soluble → FAST reactions (transport control) → Equilibrium phases
- Limestone, Oxides, Stable Minerals : less soluble → reaction rate is variable (surface control) → Kinetic Phases
- Oxidation : variable rate → pH, biological controls → Kinetics

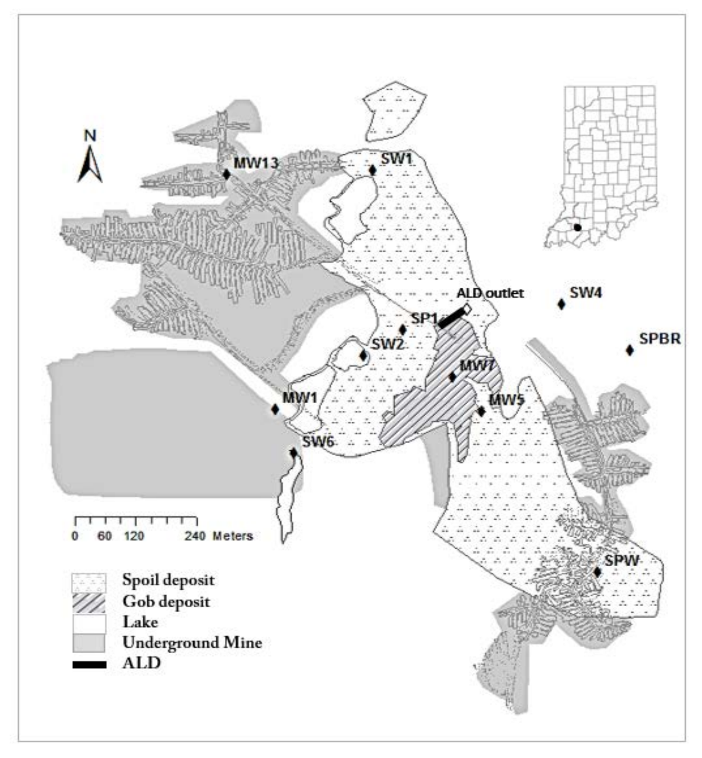
Phase	Specific Reaction Rate Equation (k), at 25°C	Reference
Limestone	$k\left(\frac{mol}{m^2 s}\right) = [10^{-0.3} a(H^+)^{1.0} + 10^{-5.81} + 10^{-3.48} P_{CO_2}{}^{-0.784}]$	Palandri and Kharaka, 2004
Aqueous Iron Oxidation (Abiotic)	$k\left(\frac{mol}{kg \cdot s}\right) = -[2.91^{-9} + 1.33^{-12} a(OH^-)^2 * P_{CO_2}] \times m_{Fe^{+2}}$	Singer and Stumm, 1970
Aqueous Iron Oxidation (Biotic)	$k\left(\frac{mol}{kg \cdot s}\right) = -[1.02^9 * e^{-58.77/RT}][Fe^{+2}][O_2][H^+]C_{bact.}$	Kirby et al., 1999
Goethite	$k\left(\frac{mol}{m^2 s}\right) = 10^{-7.94}$	Palandri and Kharaka, 2004
Gibbsite	$k\left(\frac{mol}{m^2 s}\right) = [10^{-7.65} a(H^+)^{0.5} + 10^{-11.50} + 10^{-16.65} a(H^+)^{-0.784}]$	Palandri and Kharaka, 2004
Alunite	$r_k\left(\frac{mol}{m^2 s}\right) = \begin{vmatrix} 10^{-0.133pH - 10.65} & if\ pH < 5 \\ 10^{0.194pH - 12.53} & if\ pH > 5 \end{vmatrix}$	Miller et al., 2016
Gypsum	$k\left(\frac{mol}{m^2 s}\right) = 10^{-2.79}$	Palandri and Kharaka, 2004

Mineral	GFW (g/mol)	Density (g/cm^3)	Molar Volume (cm^3/mol)	A_{BET} (m^2/g)	Grain Size	A_0/V (cm^2/L)
Limestone	100.09	2.71	36.93	3.45×10^{-5}	6.4 cm	14.02
Goethite	88.85	4.13	21.51	32[a]	0.5 µm[a]	1.1×10^{-5}
Gibbsite	78.00	2.42	32.23	50[b]	0.15µm [c]	1.5×10^{-5}
Gypsum	172.18	2.33	73.90	1.1[d]	20 µm[d]	7.3×10^{-7}

Notes:
GFW = Gram Formula Weight
A_{BET} = Brunauer-Emmett-Teller (BET) Surface Area
A0/V = Mineral surface in contact with solution

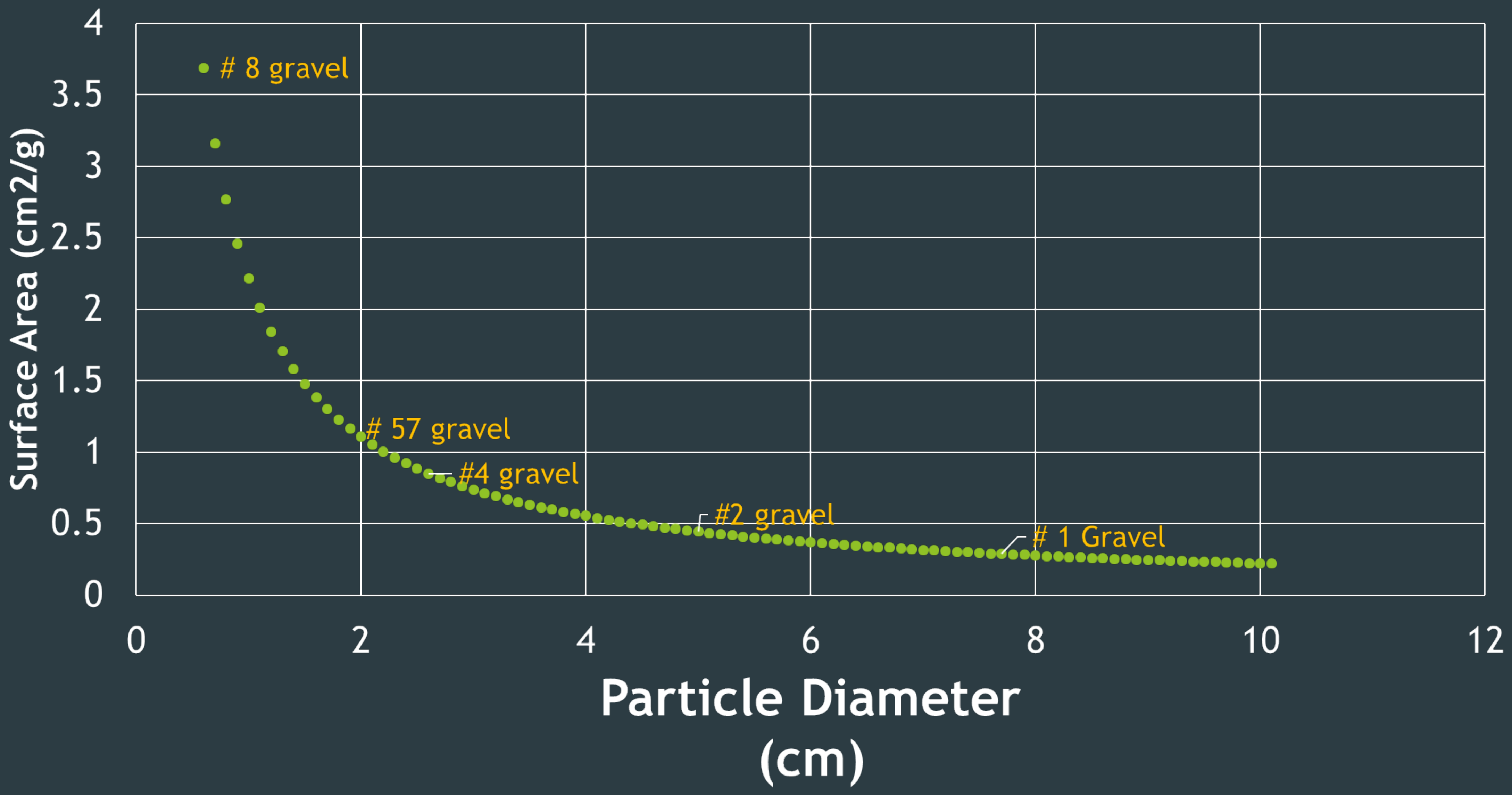
$$\frac{A_{reactive,t}}{V} = \frac{[A_0 - (A_{Fe\ oxides,t} + A_{Al\ oxides,t} + A_{Gypsum,t})]}{V}$$

Midwestern Anoxic Limestone Drain

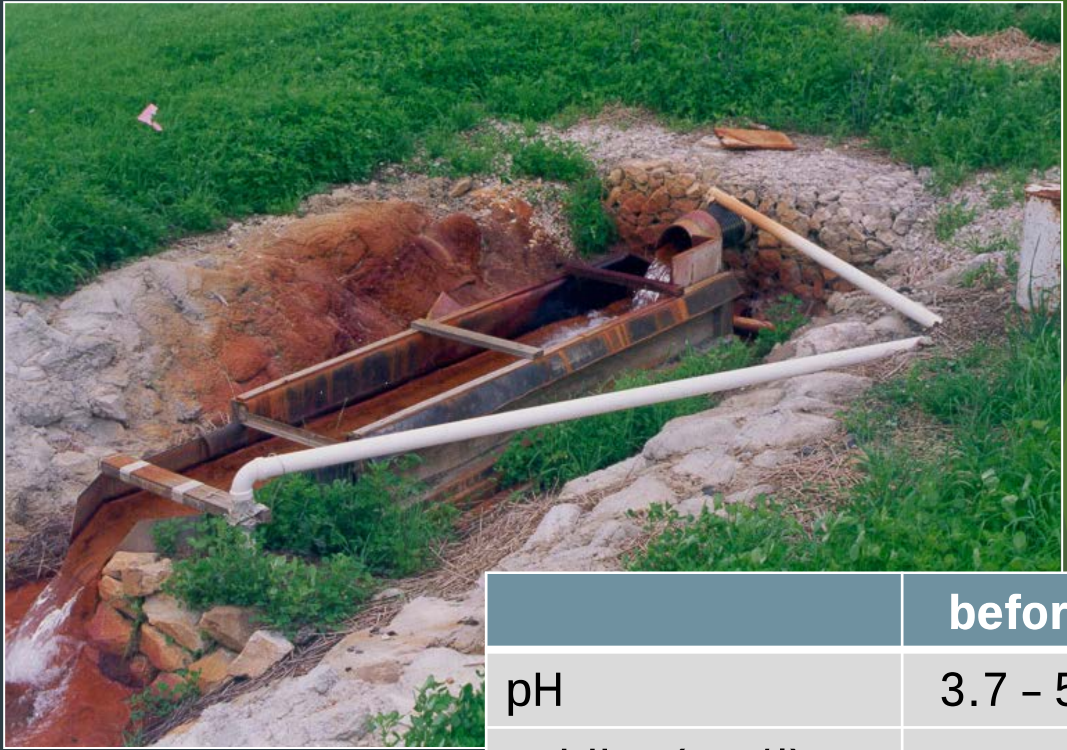


- Surface and underground coal mining operations between 1895 and 1983, leaving coarse-grained refuse piles and fine-grained tailings deposits
- Perennial acidic discharge from a flooded underground mine working
- In 1996, installed a 250 foot ALD followed by a settling pond
- 973.39 m^3 of # 2 grade limestone
- Depth of 5 feet
- Sealed with a low-permeability soil cap and plastic liner
- Discharge through the drain is 54 gpm

Initial Surface Area



Water Quality at the Midwestern AML Site



	before	after
pH	3.7 – 5.1	6.0 – 7.3
Acidity (mg/l)	367	236
Alkalinity (mg/l)	11	267
Iron (mg/l)	76	86
Aluminum	4	<2
Sulfate (mg/l)	1,380	1,463

ALD Model Simulations

Model Design

Mineral Assemblage	Chemical Formula	Initial Volume (%)
Primary		
Limestone Gravel	$CaCO_3$	60
Secondary		
Amorphous Iron Oxide	$Fe(OH)_3(a)$	-
Goethite	FeO(OH)	0.08
Amorphous Aluminum Oxide	$Al(OH)_3(a)$	-
Gibbsite	$Al(OH)_3$	0.07
Gypsum	$CaSO_4 \cdot 2H_2O$	0.16

- 1D model (slice through ALD)
- 5 m cells, containing ultra-pure #2 limestone and negligible oxides
- 40% Porosity
- 15 year simulation at a time step of 5.2 hours
- Amorphous iron and aluminum phases at equilibrium
- Kinetic Abiotic Iron Oxidation and limestone dissolution
- Kinetic reactions for gibbsite, goethite, and gypsum
- Precipitates are 1-3 mm thick (Hammarstrom *et al.*,2003 Ziemkiewicz *et al.*,1994, others)

	Initial pore water	**ALD influent**
Temp	15°C	19°C
pH	6.5	5.1
Eh	227 mV	230 mV
Al	0.6 mg/L	3.5 mg/L
HCO_3^-	535.6 mg/L	16.4 mg/L
Ca	101.8 mg/L	312.5 mg/L
Cl	8.1 mg/L	14.5 mg/L
Fe^{+2}	4.1 mg/L	70.3 mg/L
Fe^{+3}	0.2 mg/L	10.1 mg/L
K	3.3 mg/L	4.9 mg/L
Mg	68.5 mg/L	79.5 mg/L
Mn	0.6 mg/L	5.1 mg/L
Na	15.6 mg/L	15.6 mg/L
SO_4^{-2}	142.2 mg/L	1268.8 mg/L

Boundary Conditions

- Unidirectional Flow at 23 m/day (constant)
- Thickness of precipitates is uniform and constant (non-selective, impermeable armors)
- Influent water a mix of spring, mine and spoil water (17:3:1)
- Cauchy-type flux boundaries (discharge prescribed)
- Diffusion coefficient of 3.0×10^{-10} m^2 s^{-1}
- Newton-Raphson Iteration with convergence tolerance of 10^{-12}

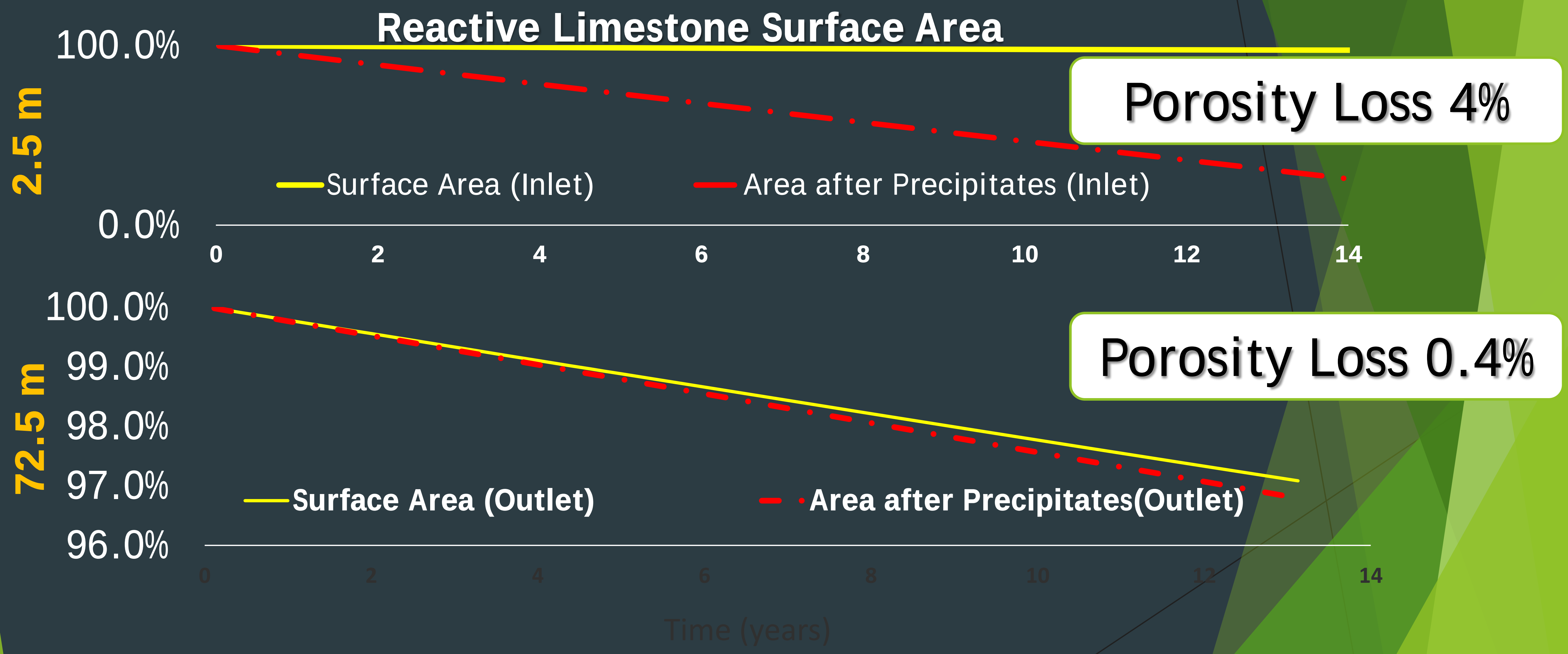
	Actual	Simulated
pH	6.0 – 7.3	6.2
Acidity (mg/l)	236	198
Alkalinity (mg/l)	267	236
Net	31	38
Iron (mg/l)	86	79
Aluminum (mg/l)	1	0
Sulfate (mg/l)	1,463	1390

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x'_i - x_i)^2}$$

$$n = 22$$

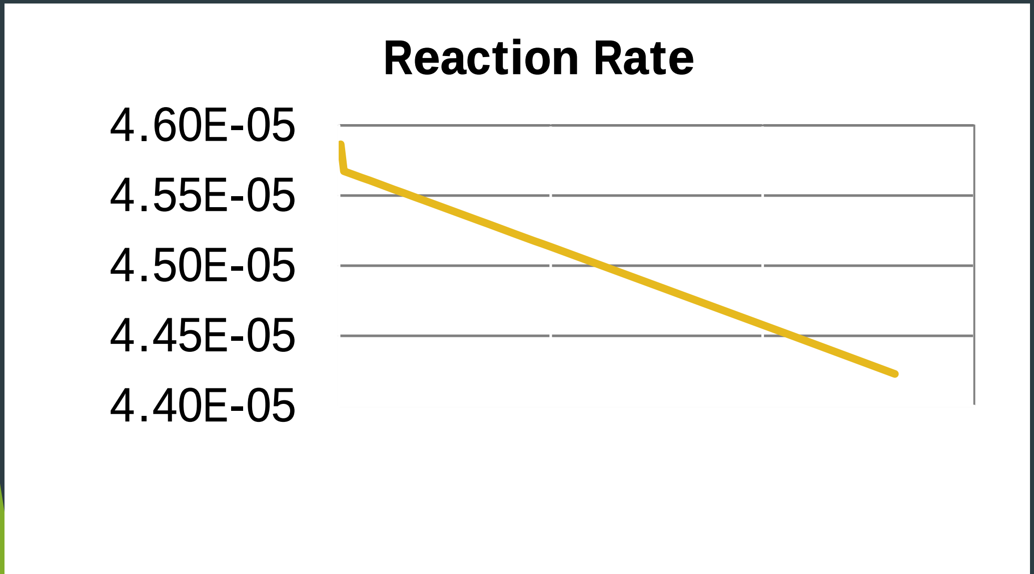
		Midwestern ALD 13-year Performance				Model Deviation	
		Mean	Median	Standard Deviation	Variance	RMSE	NRMSE
Temp.	°C	14.52	14.05	1.13	1.28	4.64	0.32
pH		6.50	6.50	0.23	0.05	0.41	0.06
Eh	V	0.17	0.16	0.03	0.61	0.16	0.98
Net Alkalinity	mg/L $CaCO_3$	41.75	25.00	55.41	3070.59	14.71	0.35
HCO_3^-	mg/L	325.24	330.00	28.39	805.99	61.12	0.19
Total Fe	mg/L	85.20	83.00	11.77	138.60	8.06	0.10
Fe^{+2}	mg/L	82.81	86.00	13.13	172.43	6.18	0.07
Fe^{+3}	mg/L	4.19	1.50	7.60	57.82	8.59	0.25
Al^{+3}	mg/L	1.60	1.90	0.88	0.78	0.47	0.26
Ca^{+2}	mg/L	472.60	470.00	25.30	640.19	51.78	0.11
Cl^-	mg/L	10.33	10.00	4.83	23.36	2.34	0.23
K^+	mg/L	8.42	8.00	3.74	13.96	1.66	0.20
Mg^{+2}	mg/L	97.45	98.00	12.57	157.90	9.46	0.29
Total Mn	mg/L	8.25	8.00	2.20	4.85	2.56	0.31
Na^+	mg/L	16.10	17.00	2.14	4.60	3.97	0.25
SO_4^{-2}	mg/L	1458.19	1481.00	184.84	34165.68	138.68	0.14

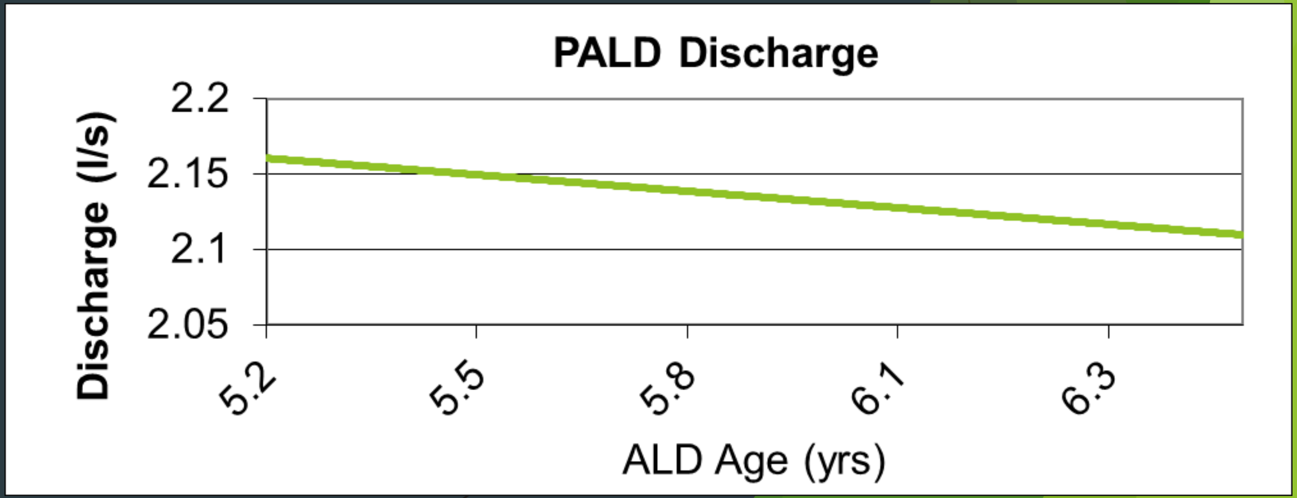
Simulated ALD Precipitates

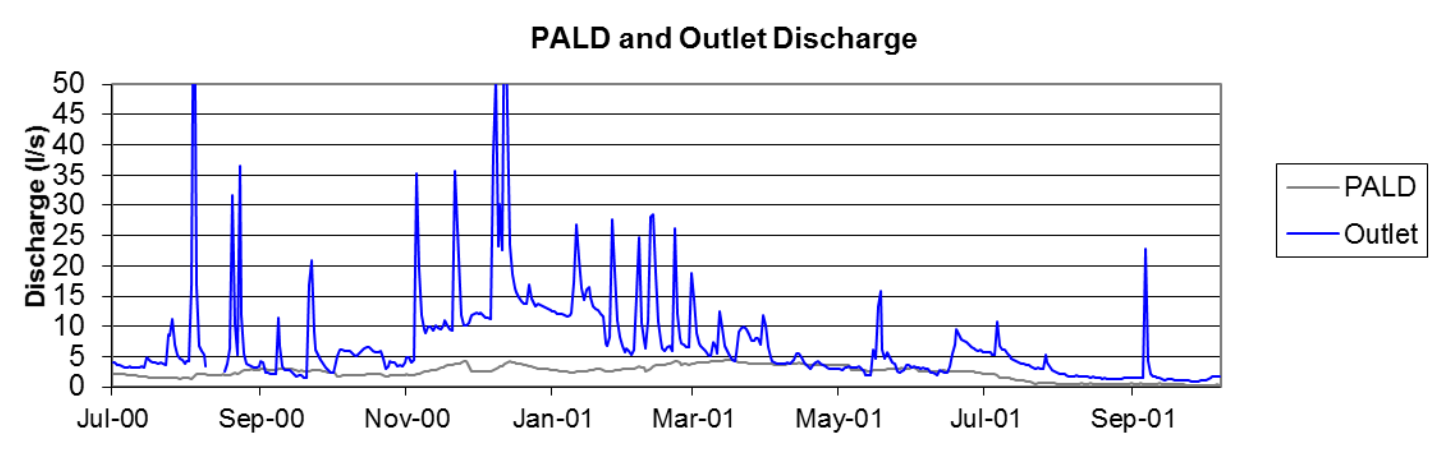


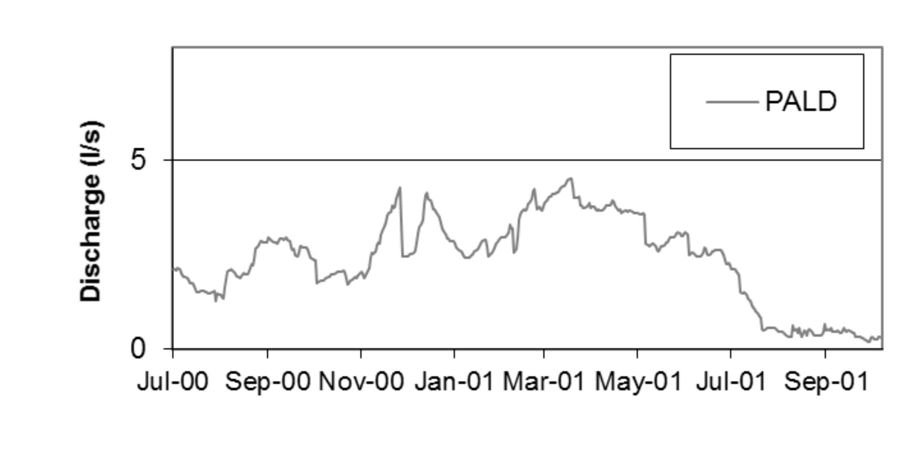
Model Assessment

- Output pH increased to 6- 6.5, Net Alkalinity, Ca^{+2} and HCO_3^- also increased
- Al and Fe decreased consistent with armor precipitation
- Net loss of 10.6 - 1554.6 m^2 surface area in ALD (99 % Al-oxides, 1 % Fe-oxides) with accumulation most pronounced near the inflow
- Limestone dissolution slowed over time, but did not cease
- Porosity loss of 0.41-4.2%
- Errors in Al, Mn, Mg and SO_4^{-2} due to mineral reactions not accounted for in model
- Misfit in Eh and Fe^{+3} attributed to ALD seal conditions and biologic iron oxidation









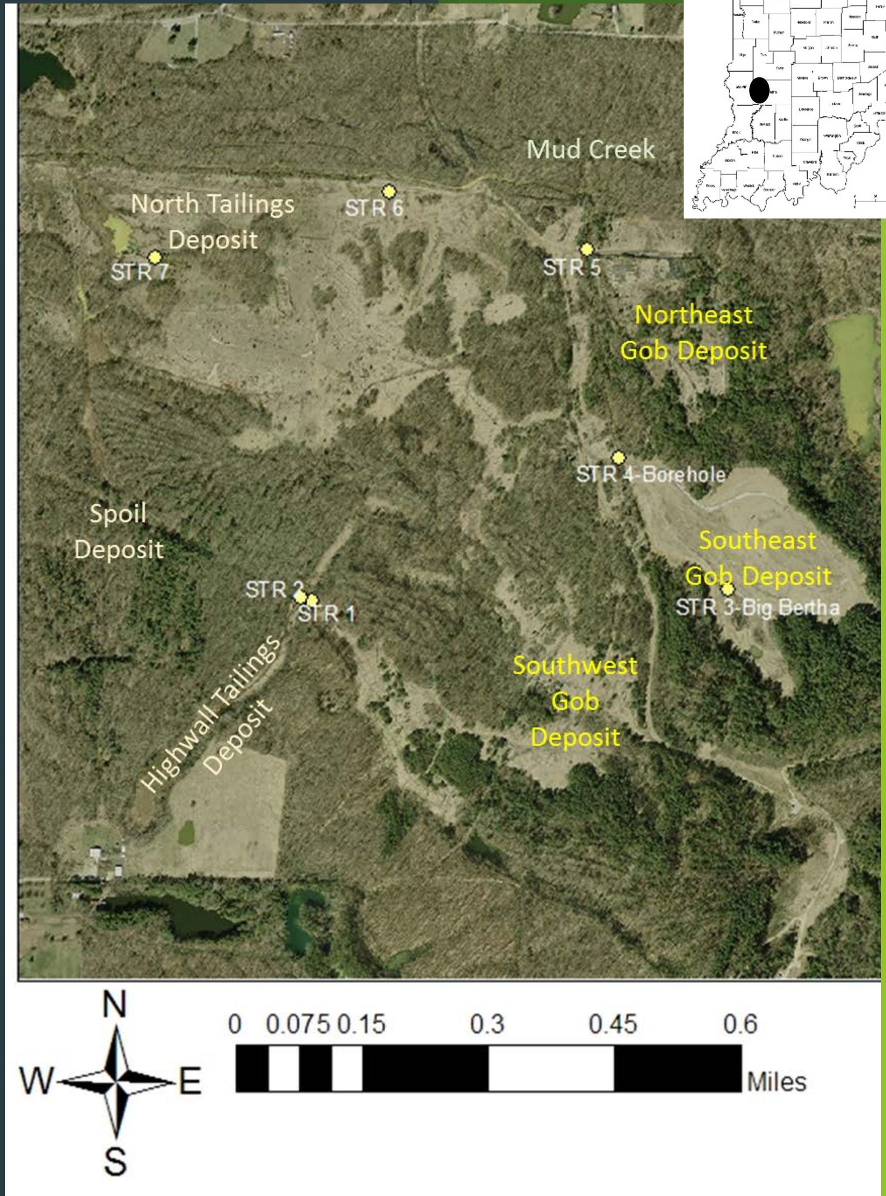
Site	Temp	SpCond	pH	Eh vs SHE	Pot. Acidity	Pot. Alkal.	HCO_3^-	SO_4^{-2}	Ca	Mg	K	Fe(tot)	Fe(II)	Mn(tot)	Al	Na	Cl
		µS/cm		mV	mg/L CaCO3	mg/L CaCO3	mg/L CaCO3	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
MW13	< 60 °F	1022	6.6	236	53	440	536	138	102	70	3	4	4	<1	<1	32	9
MW13	> 60 °F	1086	6.4	216	90	441	536	148	102	66	3	5	5	1	<1	32	8
SP1	> 60 °F	1958	4.4	433	367	11	14	1380	340	75	5	81.5	73	5	4	13	16
MW5	> 60 °F	3555	3.2	523	655	--	--	2695	463	183	5	285	183	18	44	15	12
ALD outlet	< 60 °F	2513	6.5	161	235	265	322	1463	472	101	16	88	84	8	<2	16	11
ALD outlet	> 60 °F	2639	6.6	193	170	278	337	1430	466	90	17	70	63	11	<2	17	8

Flow rate and water chemistry are changing!

Seasonal Variations in Water Quality

Friar Tuck Site

- Former surface and underground mining
- Water Quality Data since 1987
- pH 1 -5, 10-1,000 mg/L of iron, aluminum and sulfate
- Multiple Reclamation Efforts (cap, regrade, CCB, OLD, ponds)
- Inclusion of limestone in new treatment system– *Will it work?*
- *Need to consider the chemistry of discharges present*
  - ✓ Target for modeling Geochemistry!

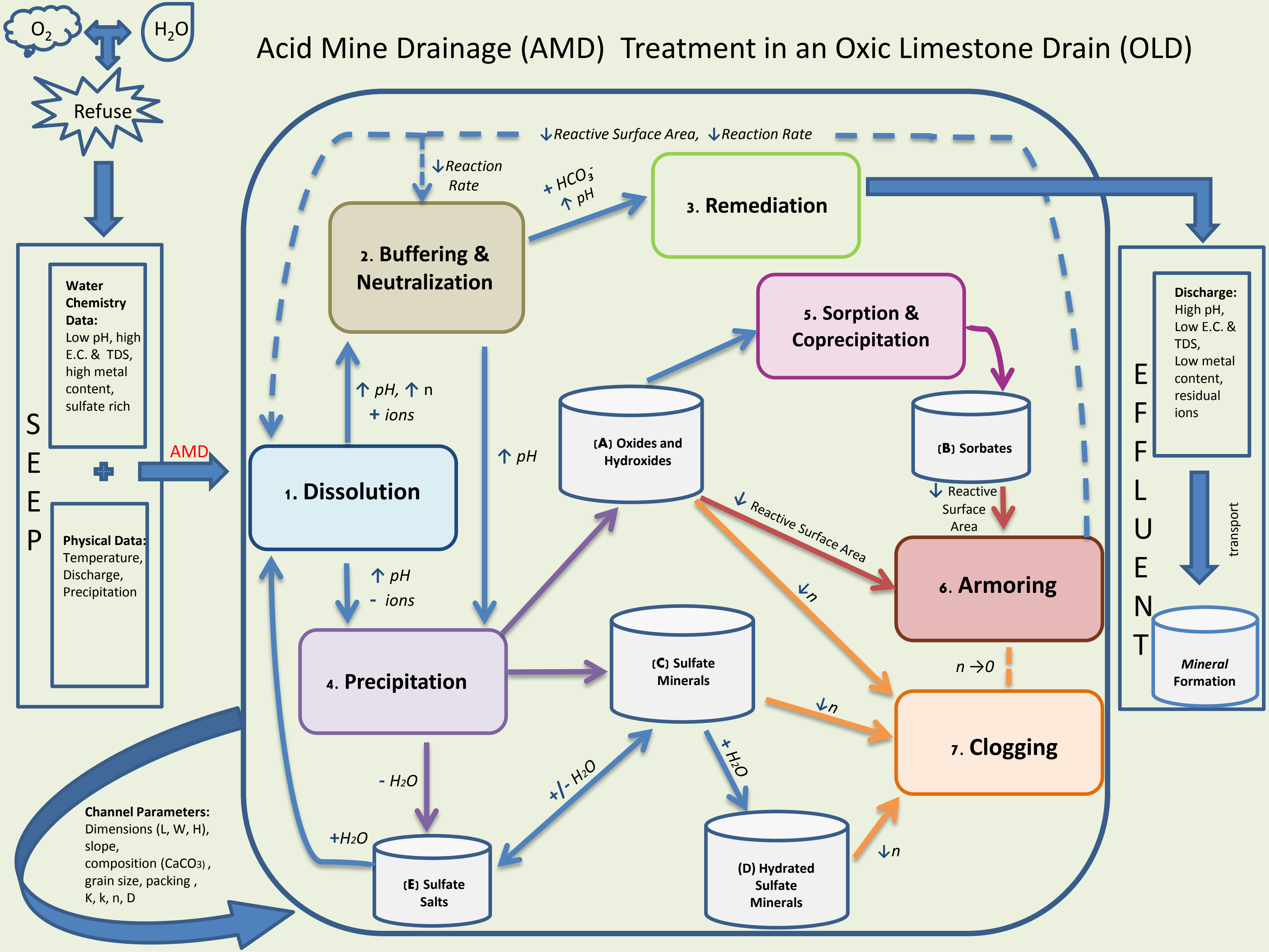


Friar Tuck Site	Period	Temp	SpCond	DO Conc	pH	Eh vs SHE	Pot. Acidity	Alkalinity
		°C	µS/cm	mg/L		mV	mg/L $CaCO_3$	mg/L $CaCO_3$
STR1	March 2015	7.5	4361	4.0	3.8	502		
STR1	June 2015	20.1	3528	4.2	2.8	653		
STR2	March 2015	3.6	3551	3.2	3.0	643		
STR2	June 2015	19.3	2297	2.2	2.9	652	1940	0
STR3	1987-2008 (Oct-Apr avg)	17.2	16075	7.4	2.2	580	24200	0
STR3	1987-2008 (May-Sept avg)	19.6	15223	1.7	2.2	578	22270	0
STR3	1987-2008 T < 60° F	11.4	13684	7.4	2.2	577	20990	0
STR3	1987-2008 T > 60° F	21.5	16782	1.7	2.1	586	24625	0
STR4	March 2015	11.1	3890	4.0	5.6	199		
STR4	June 2015	14.0	3502	1.3	6.0	178	684	219
STR5	March 2015	7.9	4191	11.8	2.6	681		
STR5	June 2015	21.0	4128	4.0	2.8	643	2990	0
STR6	March 2015	5.4	2686	5.7	3.9	530		
STR6	June 2015	21.0	2522	2.7	3.8	532		
STR7	March 2015	11.6	5246	13.8	2.9	622		
STR7	June 2015	23.9	5397	4.4	3.1	567	6150	
Site 120	T < 60° F	7.5	9332	4.2	2.9	585	9800	0
Site 120	T > 60° F	25.0	8774	4.3	2.8	587	9818	0
BB Tributary	T < 60° F	12.6	3795		2.8	583	1785	0
BB Tributary	T > 60° F	16.7	3955	5.1	3.0	607	1048	0

SO_4	Ca	Mg	Fe(tot)	Fe(II)	Mn	Al	Na	K^
mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
354	194	608	404	48	24	15		354
356	166	248	128	37	20	31		356
298	118	290	154	24	20	17		298
351	156	256	158	31	14	23		351
472	1160	4831	4190	259	2546	83	21	472
510	1027	4191	3390	225	2373	65	21	510
466	1097	4356	3533	259	2400	80	14	466
487	1118	4734	719	239	2577	73	26	487
489	147	151	82	2.8	0.1	195		489
550	139	177	157	3.1	0.1	208		550
336	104	102		11	25	41		336
443	151	347	242	25	68	65		443
326	45	95		4	6.1	5.4		326
454	69	194	179	12	190	17		454
390	67	961	434	6.7	116	12		390
491	83	1410	1259	8.3	141	20		491
405	265	3717	3217	110	560			405
439	283	3266	3015	97	547	456		439
520	310	860	350	37	49	44		520
431	257	587	478	24	35	66		431

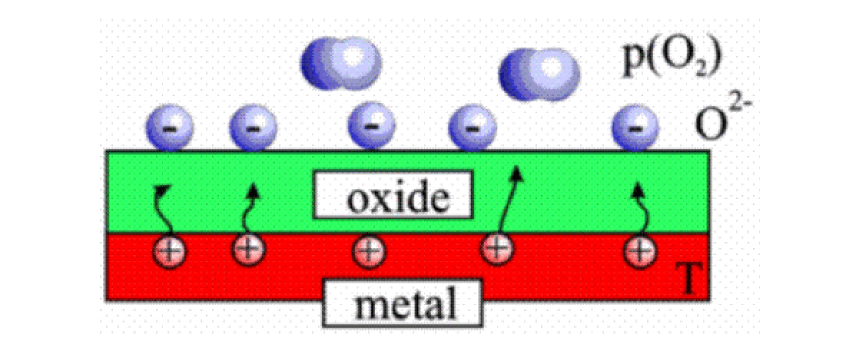
Friar Tuck Site	Period	pH	$Al(OH)_3(a)$	Alunite	Anhydrite	$Fe(OH)_3(a)$	Gibbsite	Goethite	Gypsum	K-Jarosite	Manganite	Melanterite	Pyrolusite
STR1	March 2015	3.75	-5.42		-0.58	1.88	-2.56	7.11	-0.09		-3.75	-9.07	3.95
STR1	June 2015	3.11	-6.76		-0.39	-0.25	-4.03	5.46	-0.03		-3.58	-9.14	2.34
STR2	March 2015	3.48	-6.46		-0.71	1.28	-3.56	6.35	-0.16		-5.05	-9.44	3.25
STR2	June 2015	3.27	-6.46		-0.41	0.25	-3.72	5.93	-0.04		-3.44	-9.02	2.60
STR3	T < 60° F	3.30	-5.05	2.78	-0.28	1.09	-2.23	6.48	0.16	9.16	-3.66	-8.39	3.48
STR3	T > 60° F	2.33	-7.07	-1.16	-0.27	-1.44	-4.34	4.32	0.07	5.26	-4.27	-8.63	1.45
STR4	March 2015	4.51	-5.23		-0.43	2.91	-2.40	8.29	0.03		-2.96	-9.42	4.23
STR4	June 2015	7.12	-0.37		-0.36	5.53	2.43	11.01	0.07		2.69	-11.89	9.47
STR5	March 2015	2.71	-8.27		-0.69	-1.29	-5.41	3.96	-0.20		-6.30	-10.35	1.36
STR5	June 2015	3.29	-5.70		-0.27	0.33	-2.97	6.08	0.07		-3.32	-8.82	2.48
STR6	March 2015	3.99	-5.17		-0.72	2.13	-2.29	7.28	-0.19		-4.50	-9.64	3.52
STR7	June 2015	3.86	-3.27		-0.37	1.64	-0.54	7.38	-0.03		-2.40	-8.88	3.40
STR7	March 2015	3.29	-5.87		-0.50	0.97	-3.05	6.36	-0.05		-5.00	-8.83	2.12
BB Tributary	June 2015	3.56	-4.44		-0.23	1.30	-1.74	7.15	0.08		-2.95	-8.24	2.47
BB Tributary	T < 60° F	3.16	-5.34		-0.42	1.45	-2.48	6.68	0.08		-4.17	-8.63	3.53
Site 120	T > 60° F	3.50	-4.34		-0.26	1.09	-1.65	6.98	0.05		-2.11	-8.04	3.16
Site 120	T < 60° F	3.46	-6.45		-0.44	0.66	-3.65	6.09	0.00		-4.35	-8.94	2.61

Acid Mine Drainage (AMD) Treatment in an Oxic Limestone Drain (OLD)



Key Points

- While limestone will supply alkalinity and raise pH, precipitates accumulate over time and the amount formed depends on water !
- Seasonal fluctuations in discharge include:
  - Eh, total iron, flow rate
- Geochemical models may serve and an important tool in forecasting the extent of armor and how quickly it will form
- Tool to estimate the type and volume of sludge



What's next?

- Shrinking core model
- Diffusion through the armor?
- Additional mineral kinetics
- Sorption of metals (Mn, Cu, Pb and Zn) onto oxide phases

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Thank you!

Questions?