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Advancements in Iron Terrace Design for Metal Mine Sites

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Outline

- Passive Treatment 101 – “It’s <u>not</u> a constructed wetland”
- Iron Terraces – Mother Nature @Work
- Interesting chemical reactions
- Quick case studies
  - Moran Tunnel, Idaho
  - Western USA
  - Elizabeth Mine, Vermont
- What we do and don’t know…

What Is the Passive Treatment Process?

Passive Treatment of Mining Influenced Water (MIW) involves the:

***S**equential*

***E**cological*

*e**X**traction*

Of metals in a man-made but naturalistic bio-system

P.T. Metal Removal Mechanisms

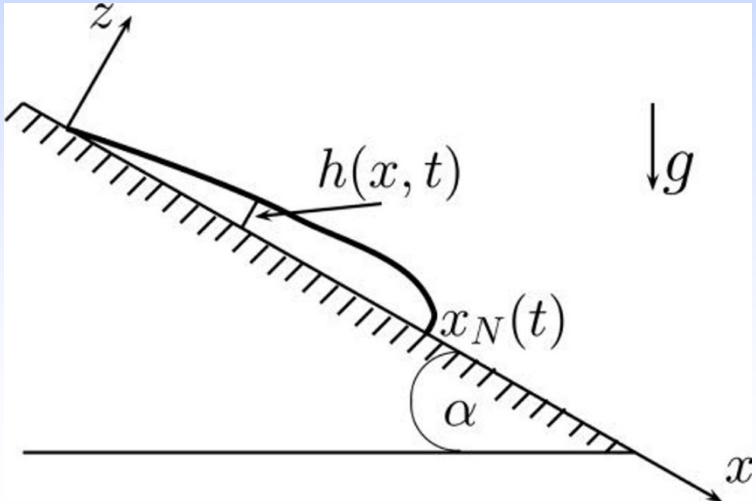
Major

- Sulfide and carbonate precipitation via sulfate reducing bacteria, et al.
- **Hydroxide and oxide precipitation by *thiobacillus ferro-oxidans* bacteria, *et al*.**
- Filtering of suspended materials and precips
- Carbonate dissolution/replacement

Minor

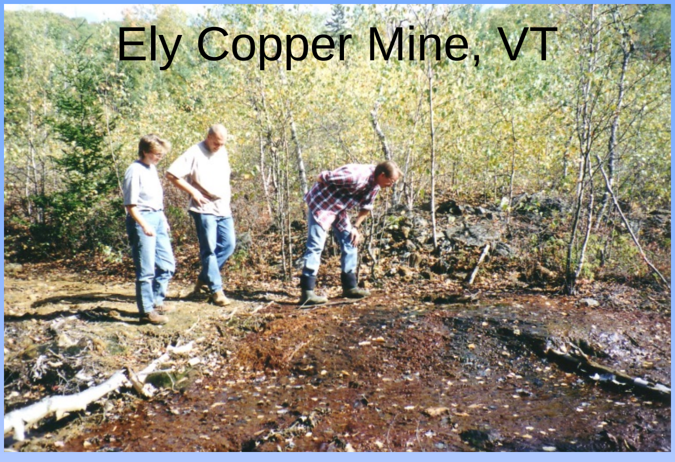
- Metal uptake into live roots, stems and leaves
- Adsorption and exchange with plant, soil and other biological materials

Why Do Terraces Form?



Water flowing on rough inclined planes. A shock-like pattern forms with uniform spacing and constant velocity. Why? Fisher equation?

Iron Terraces – Coast to Coast (USA): Mother Nature at Work



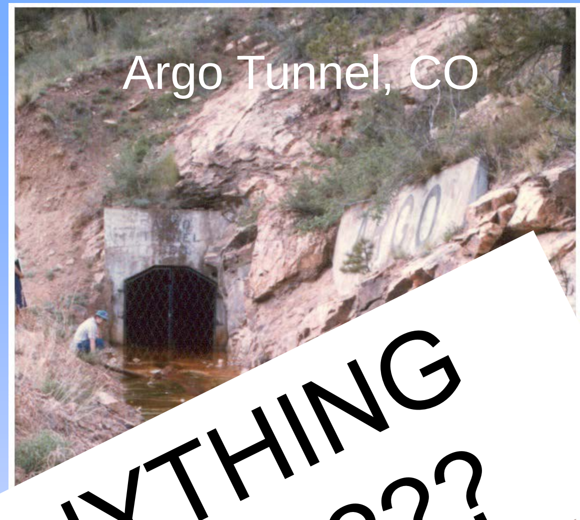
Some ferricrete deposits in the Animas Basin, Colorado are 9,000 years old!

Moran Tunnel Site - November 2013

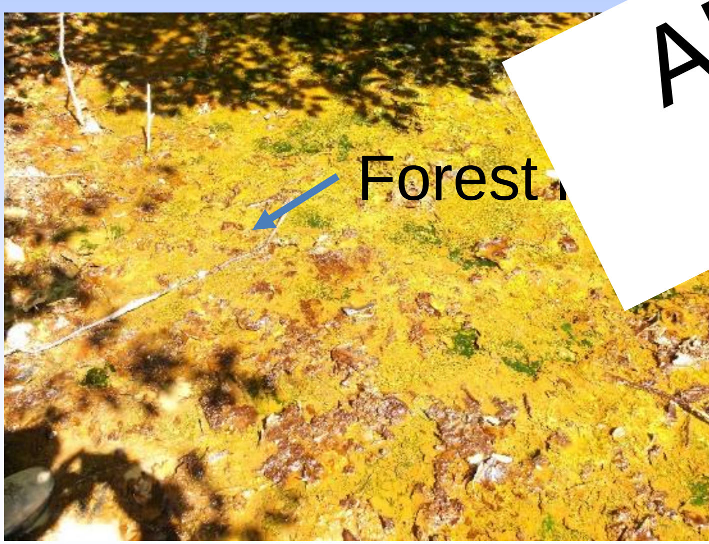
More than a century ago, Louis Pasteur said, "*Chance favors* only *the prepared mind*."

Cyanobacteria/Algae

Fe^{+2}, Forest Litter & Algae, the Common Denominators



ANYTHING ELSE????



Passive Treatment Chemistry 101

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

REDUCING/ ANAEROBIC CONDITIONS

(Sulfate reduction and neutralization by bacteria)

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

(Sulfide precipitation)

OXIDIZING CONDITIONS

$$Fe^{+3} + 3\ H_2O \rightarrow Fe(OH)_3\ (s) + 3\ H^+$$

(Hydroxide precipitation)

ALL CONDITIONS

$$H^+ + CaCO_3 \rightarrow Ca^{+2} + HCO_3^-$$

(Limestone dissolution)

IRON TERRACE REACTIONS?

$$6H^{+} + (C_6H_{10}O_5)n + 3/2\ O_2 \rightarrow 6C + 16\ H_2O + heat$$

(Cellulose Dehydration by Acidity)

$$Fe^{+2} + H^{+} \rightarrow Fe^{+3}$$

(Ferrous iron oxidation)

$$Fe^{+3} + 3\ H_2O \rightarrow Fe(OH)_3\,(s) + 3\ H^{+}$$

(Iron hydrolysis & hydroxide precipitation)

Reactions consume H^{+} & pH rises

Cellulose Dehydration by Acidity

$$6H^{+} + (C_6H_{10}O_5)n + 3/2\ O_2 \Rightarrow 6C + 16\ H_2O + \text{heat}$$

Cyanobacteria/Algae Can Raise pH

PHOTOSYNTHESIS IS AN IMPORTANT PROCESS FOR INCREASING pH

$$6\ HCO_3^-\ (aq) + 6\ H_2O \xrightarrow[\text{chlorophyll}]{\text{sunlight}} C_6H_{12}O_6 + 6\ O_2 + 6\ OH^-$$

glucose

6 H_2CO_3 (aq) – carbonic acid

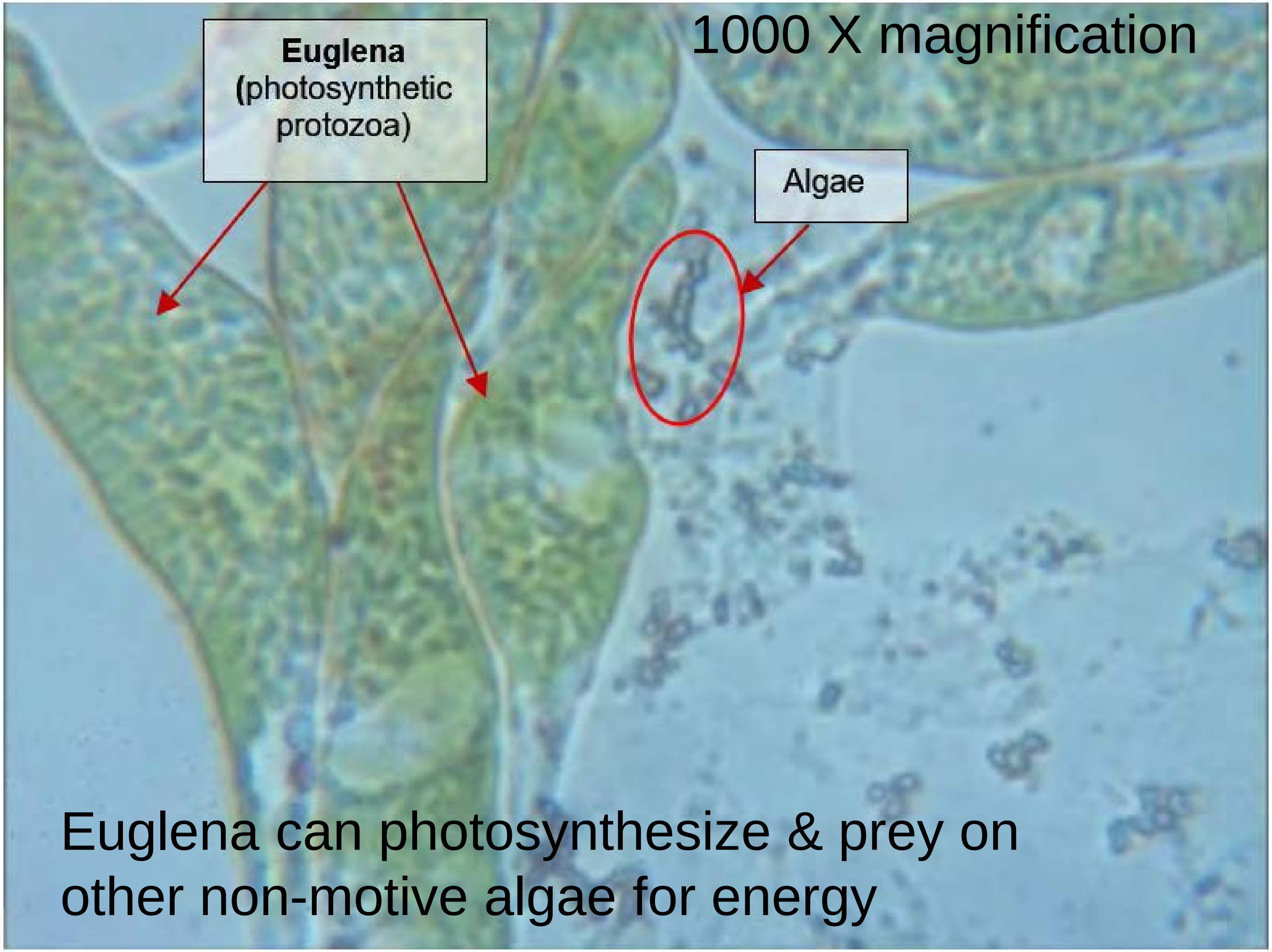
COMPARE WITH

$$6\ CO_2\ (g) + 6\ H_2O \xrightarrow[\text{chlorophyll}]{\text{sunlight}} C_6H_{12}O_6 + 6\ O_2$$

glucose

Ref: T. Wildeman, 2005

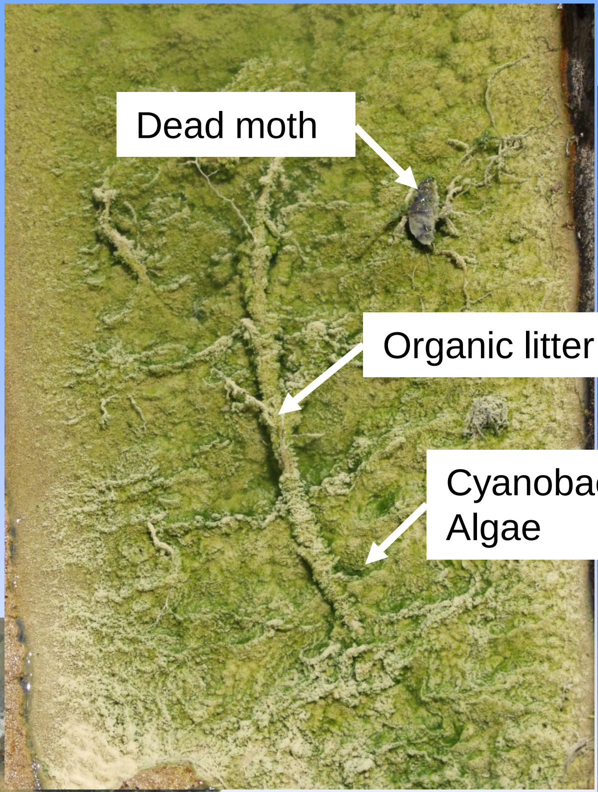
Algae in Portal Biofilm

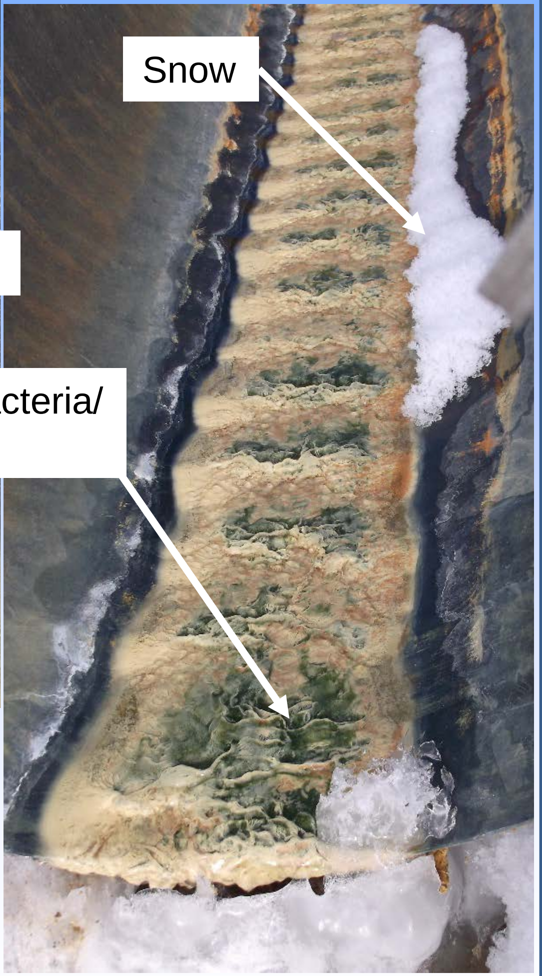


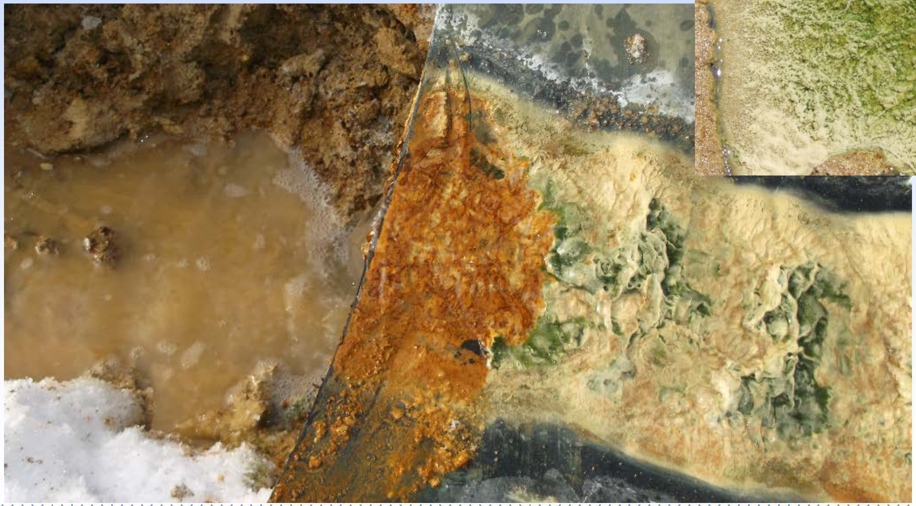
Courtesy Dave Jenkins, ECM

Three Quick Case Studies

Iron & Al Terrace @ Moran Tunnel, ID







pH 3.2
Al 800 mg/L
Fe 1,700 mg/L

Analysis of Existing Precipitates

Sampling Location		**PORTAL**		**CREEK**		**BEAVER POND**	
Parameter	Units	Value	Moles/ Kg	Value	Moles/ Kg	Value	Moles/ Kg
Sulfate	mg/kg	16,000	0.17	15,000	0.16	160,000	1.67
Total Solids	*%*	*36.7*		*22.9*		*27.6*	
Aluminum	**mg/kg**	**5,400**	**0.20**	**2,400**	**0.09**	**4,300**	**0.16**
Calcium	mg/kg	790	0.02	1,500	0.04	58,000	1.45
Copper	mg/kg	300	0.00	280	0.00	1,300	0.02
Iron	**mg/kg**	**140,000**	**2.51**	**190,000**	**3.40**	**3,100**	**0.06**
Lead	mg/kg	3.3	0.000	5.2	0.000	2.9	0.000
Magnesium	mg/kg	440	0.02	610	0.03	13,000	0.53
Manganese	mg/kg	120	0.002	130	0.002	1,600	0.03

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Spec. Gravity Solids 1.7 to 2.3

grams/day/m² Removal Rates in Test Troughs

Constituent	T1	T2	T4
	Solids analytical results		
Sulfate (mg/Kg)	30,000	48,000	49,000
Iron (mg/Kg)	77,000	100,000	100,000
Aluminum (mg/Kg)	6,100	2,500	3,800
Mass of solids recovered (Kg)	5.9	12.7	2.8
Area of media (m^2)	2.8		
Days of testing	56		
	Grams removed per sq meter per day		
Sulfate	1.13	3.89	0.88
Iron	2.90	8.10	1.79
Aluminum	0.23	0.20	0.07
	Organic	**Non-Organic**	**Oxygenated**

Moran Tunnel Fe/Al Terrace Demo (Dec. 2016)

Fe Terrace Pilot (Western USA)

pH 6.1
Alkalinity 200 mg/L as $CaCO_3$
Fe 35 mg/L

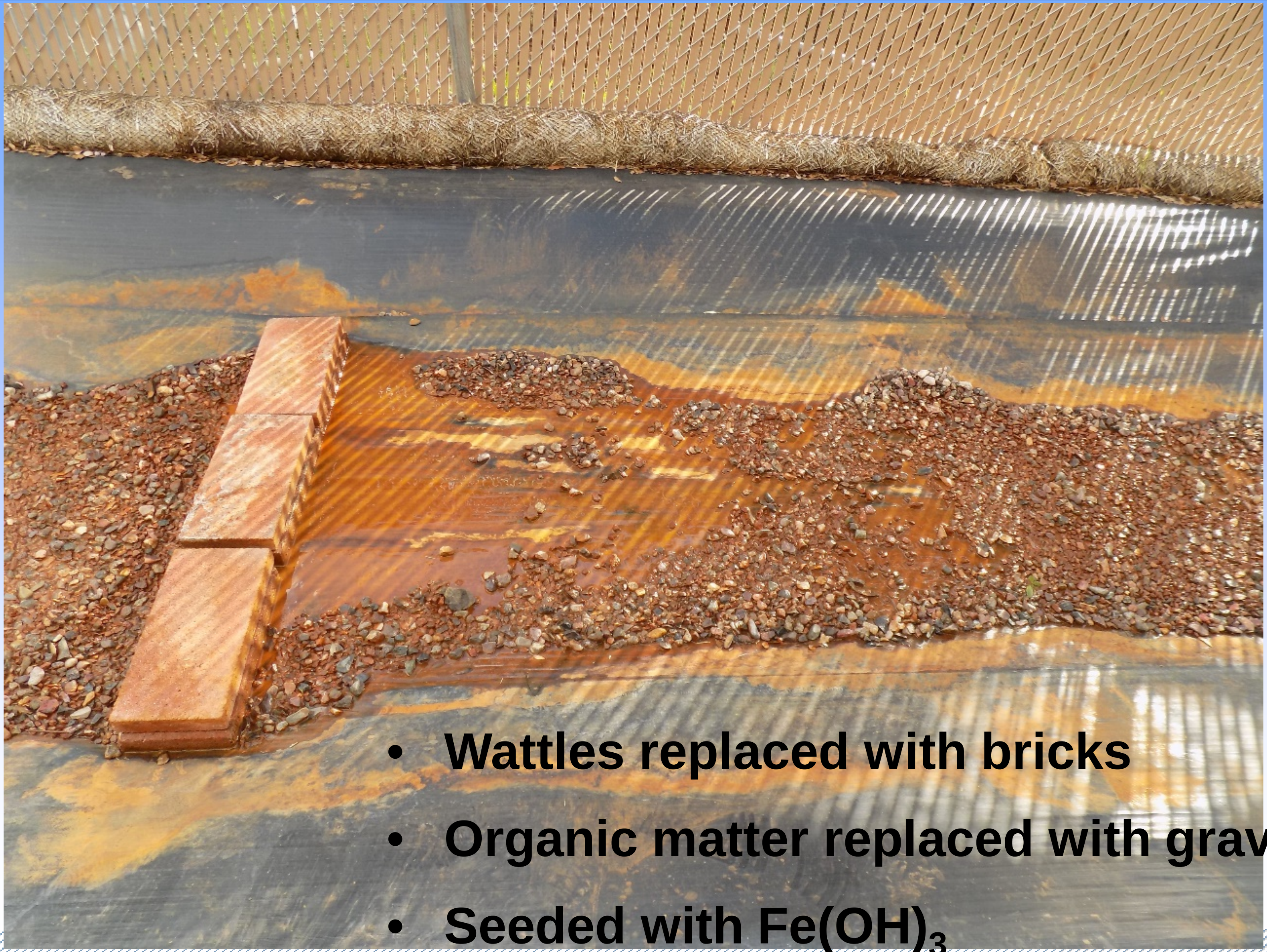
24 weeks of testing
Iron Terrace modified week 15
Flow rate increased in week 18

Initial IT Configuration

- **Permeable HDPE wattles used to encourage terrace formation**
- **Seeded with organic matter**
- **Seeded with $Fe(OH)_2$**

0.4 grams Fe day/m^2
At 250 mL/min

Modified IT Configuration



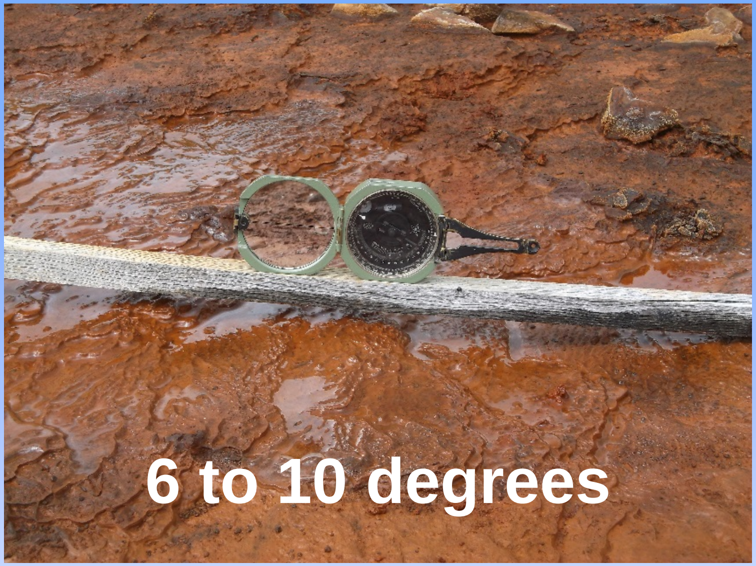
- **Wattles replaced with bricks**
- **Organic matter replaced with gravel**
- **Seeded with $Fe(OH)_3$**

Modified IT Configuration

0.8 grams/day/m^2
At 250 mL/min

3.6 grams/day/m^2
At 1,050 mL/min

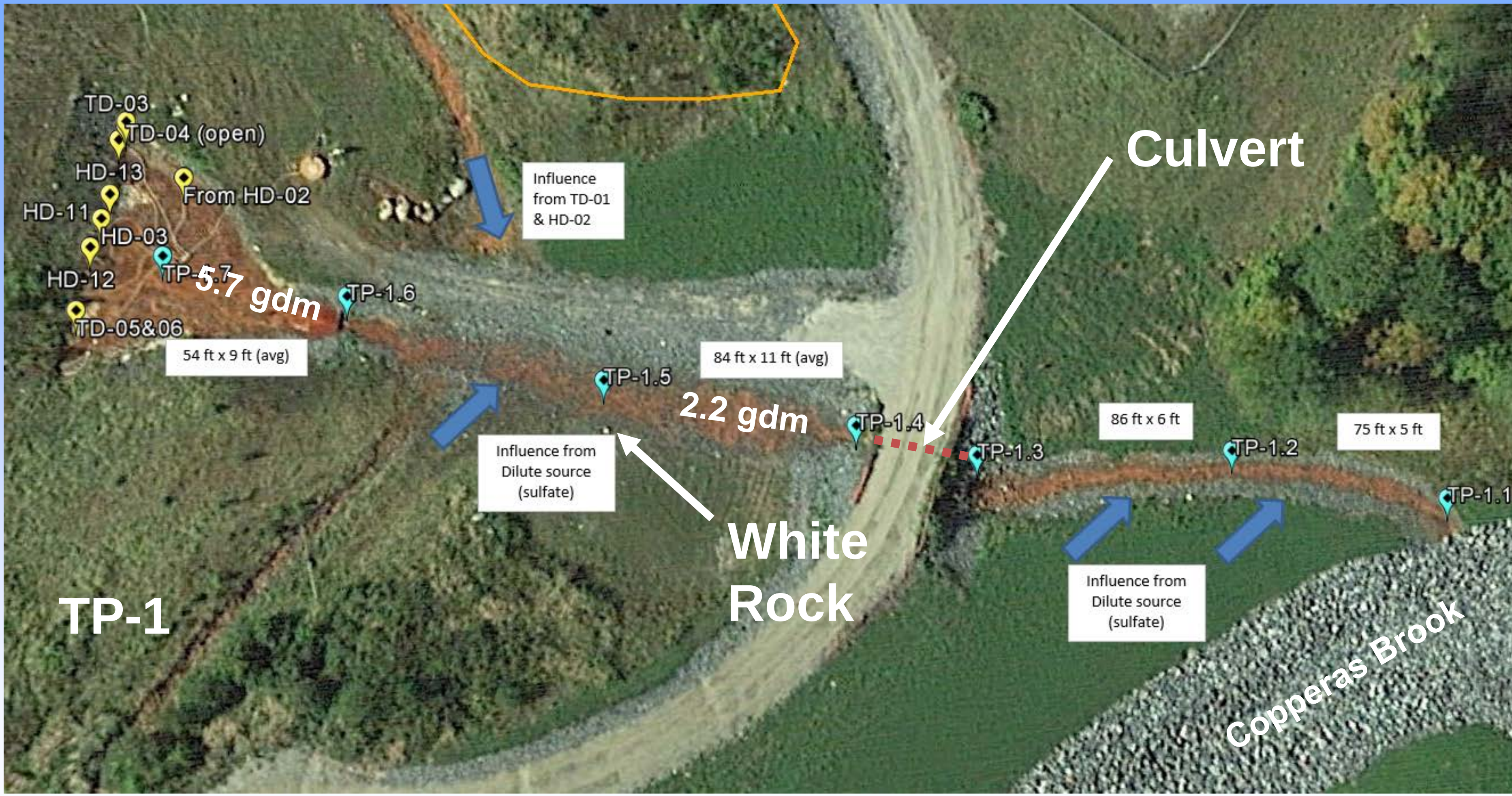
Volunteer Fe Terrace (Elizabeth Mine, VT)



Primary Removal Mechanism Evidence

Primary Removal Mechanism Evidence

Informal Sampling Event 5.24.16



Flow 15 gpm/57L/min **pH varies 3.2 to 7.1 6.0 is "typical"** *Google Earth*

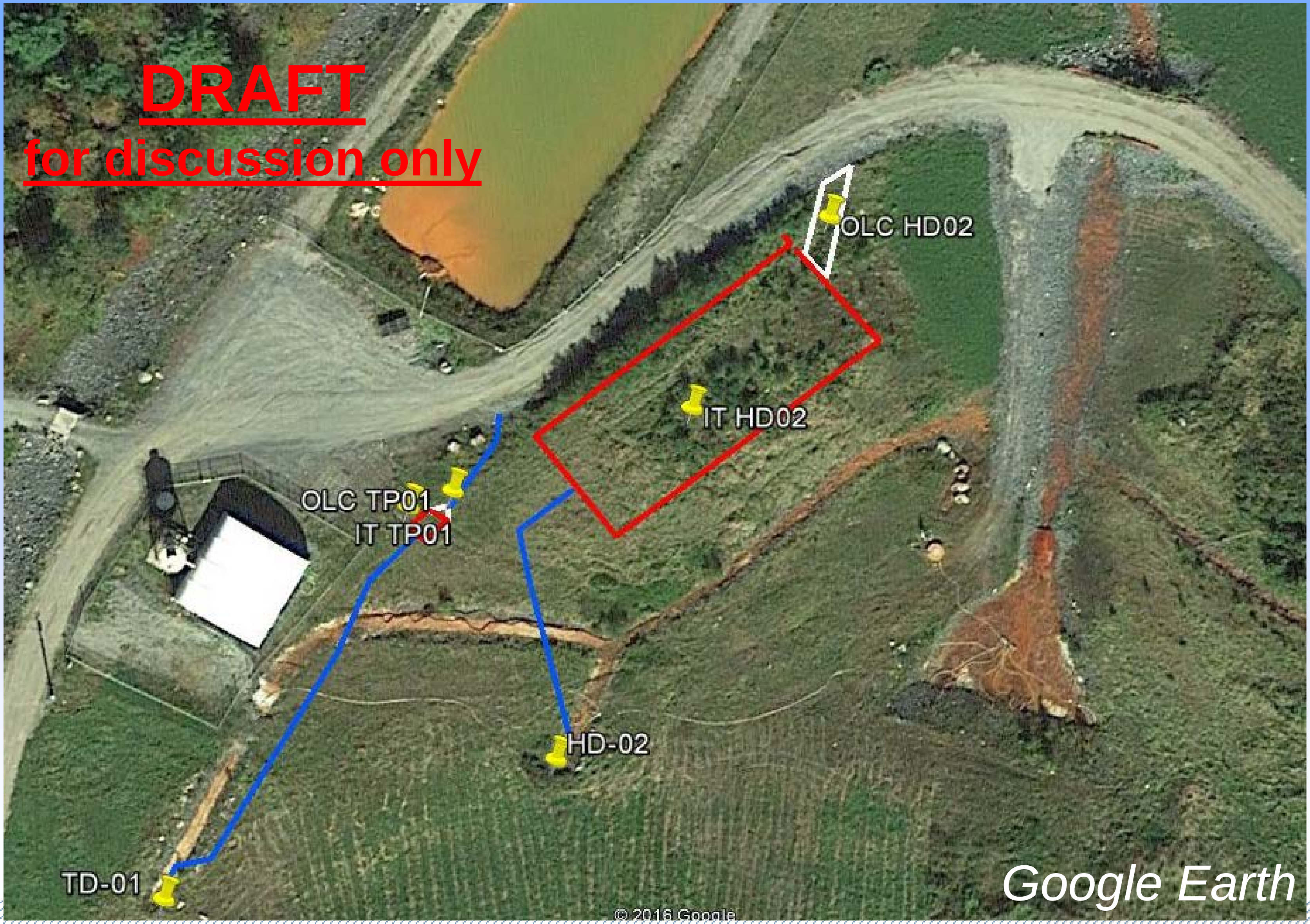
Informal Sampling Event 5.24.16

Filtered samples; analyzed by Colorado School of Mines

	TP-1.7	TP-1.6	TP-1.5	TP-1.4	TP-1.3	TP-1.2	TP-1.1
	Manifold	V-Notch Weir	“White Rock”	Culvert Inlet	Culvert Outlet	Mid-Way	Confluence Copperas Brook
Iron	**265**	**206**	**72**	**53**	**57**	**38**	**23**
Sulfate	3,300	3,200	2,560	2,530	2,520	2,130	1,640
Fe gdm	*5.7*		*2.2*				
Comments	Consistent w/historical data	Groundwater dilution and contributions from other sources		No change in culvert		GW dilution or sulfate mineral deposition?	

Fe varies from 2.4 to 950 mg/L from 14 horizontal drains

Pilot Design Concept



Iron Terrace Design Variables (2017) 1 of 4

Parameter	Comment/Significance
Loading (grams Fe/day/m²) wetted surface	• Primary design (range from 0.5 to 5?) as per W. Burgos (2008) • But may be *higher* as iron removal is a first order kinetic reaction.
Flow velocity	• The faster the better – this may correlate with bed slope (steeper slopes provide faster velocities) • "Movement" in stream or pond facilitates iron oxyhydroxide precipitation (Devin Sapsford, ICARD 2015 paper)
Ferrous iron	• This will consume H^+ when oxidized to ferric (pre-iron hydrolysis reaction)

Iron Terrace Design Variables (2017) 2 of 4

Parameter	Comment/Significance
pH	• The lower the better for organic matter dehydration.
Acidity	• The higher the better (organic matter dehydration kinetics are faster)
ORP	• Must be positive for ferrous to oxidize to ferric
Dissolved oxygen	• Must be 5 ppm or better?
Slope of the wetted surface	• 6% to 10% Optimum? • Steeper may provide faster velocities (better oxygenation and Fe precipitation kinetics?) Eddies???

Iron Terrace Design Variables (2017) 3 of 4

Parameter	Comment/Significance
Presence/absence of algae	• Algae provide polysaccharides for carbon source via photosynthesis & bicarbonate ion for neutralization
Presence/absence of sunshine	• If no sun, ferrous to ferric reaction becomes more important – see pipes at Elizabeth Mine TP-1
Presence/absence of organic matter	• If algae are not present, leaf & forest litter become important source of organic matter; must have healthy tree or shrub canopy nearby. • This could cut off sunshine during growing season but let in sunshine during the winter. • Organic matter may be *counterproductive* for MIW with low acidity as it will lower the ORP and ferrous iron may form.

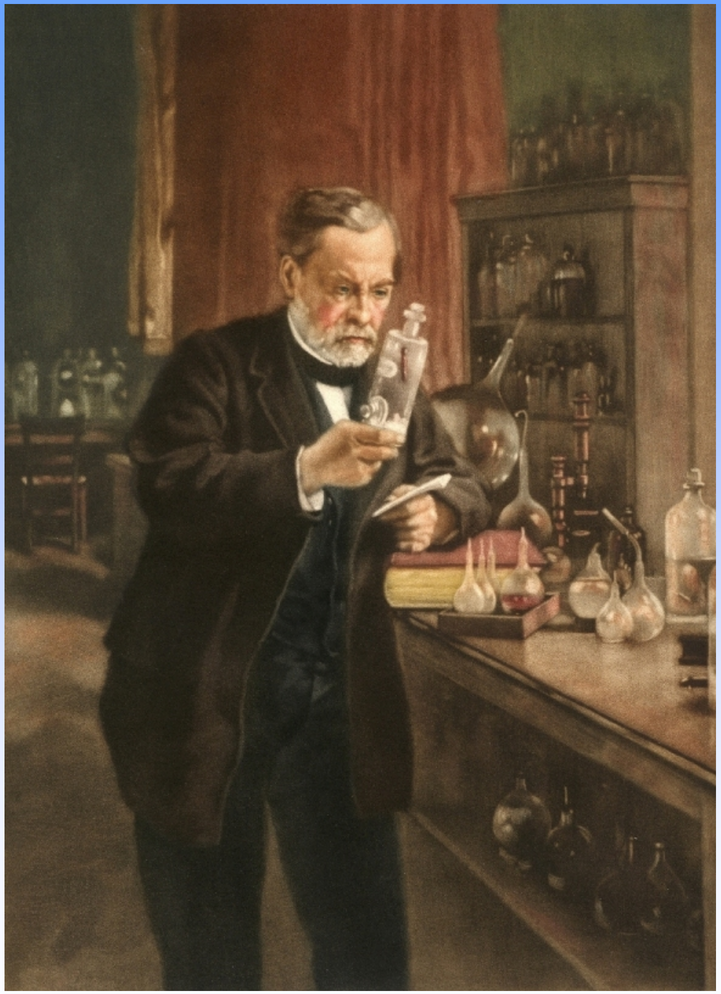
Iron Terrace Design Variables (2017) 4 of 4

Parameter	Comment/Significance
Presence/absence of aluminum	• $Al(OH)_3$ precipitation will compete with iron precipitation in consuming hydrogen ions from organic dehydration or ferrous to ferric reactions. • Al drops out last (Moran tunnel)
Presence/absence of mid-terrace "pooling"	• Semi-stagnant conditions in pools, coupled with organic matter from nearby vegetation, could be counter-productive with regard to iron removal. • If no organic matter influx, pooling is probably OK.
Presence of $Fe(OH)_3$	At startup, having some yellowboy present is recommended as a "seed".

Summary

- Mother Nature has been employing terraces for millennia to remove iron, and calcium carbonate (Yellowstone)
- We probably don't know more than we do know – *"It's complicated"*
- Site-specific bench & pilot tests will be even more important for scale up designs
- A comprehensive "model" for iron terraces may never be feasible but that shouldn't prevent us from using the process

Thank You



In Water Treatment, if you're not part of the **solution**, you're part of the **precipitate**.

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