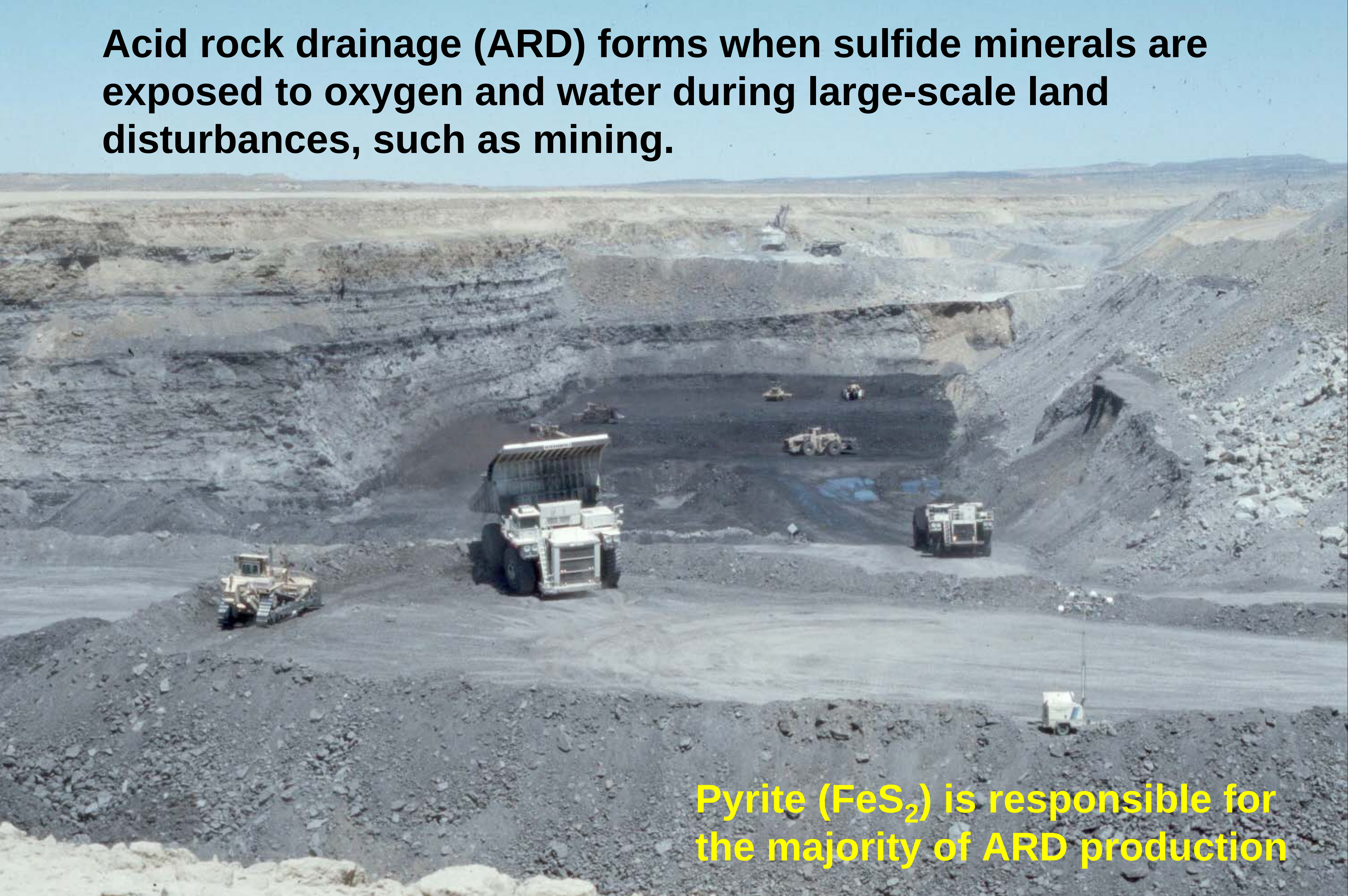
CH2MHILL

Low Maintenance Passive Treatment Systems for Mining Site Contaminants

Robert C. Thomas, Ph.D



Acid rock drainage (ARD) forms when sulfide minerals are exposed to oxygen and water during large-scale land disturbances, such as mining.

Pyrite (FeS_2) is responsible for the majority of ARD production

Oxidation of Pyrite

$FeS_2 + 3.75\ O_2 + 3.5\ H_2O \Leftrightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 4\ H^+$

STEPS:

(1) $FeS_2 + 3.5\ O_2 + H_2O \Leftrightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$

(2) $Fe^{2+} + 0.25\ O_2 + 2.5\ H_2O \Leftrightarrow Fe(OH)_{3\ (s)} + 2\ H^+$

Products Released: Fe^{2+}, Fe^{3+}, SO_4^{2-}, H^+

Remediation of ARD Requires Neutralization of Acidity

Two major sources of acidity in ARD

- **proton acidity (pH)**
- **mineral acidity associated with dissolved metals**

Ferric iron soluble at pH < 3.0

Ferrous iron soluble at pH < 3.0 in presence of O_2, but soluble up to pH 6 in absence of O_2

Therefore, it is possible to have anaerobic ARD with pH 6 (little proton acidity), but significant dissolved ferrous iron (mineral acidity)

In presence of O_2, < 1 mg·L^{-1} iron is soluble at pH > 6.0.

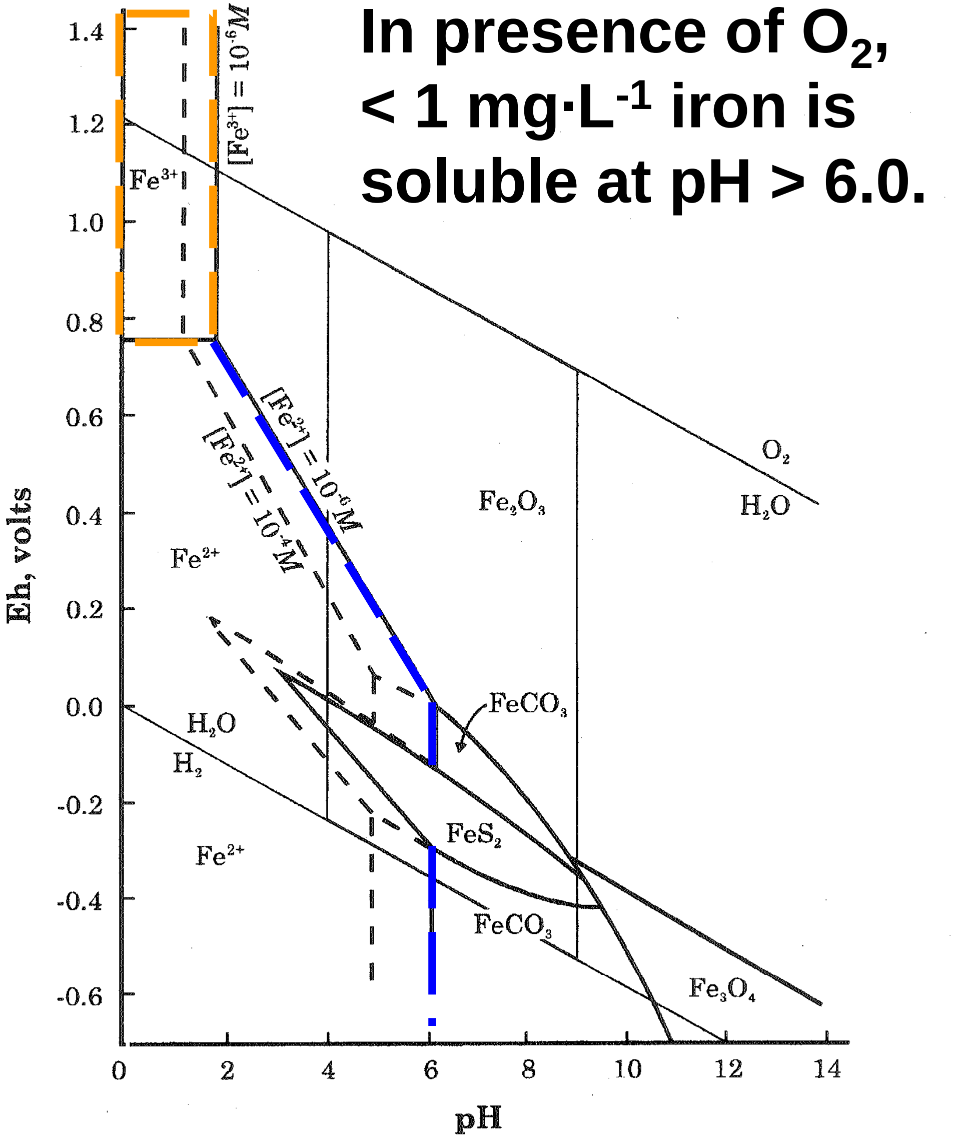
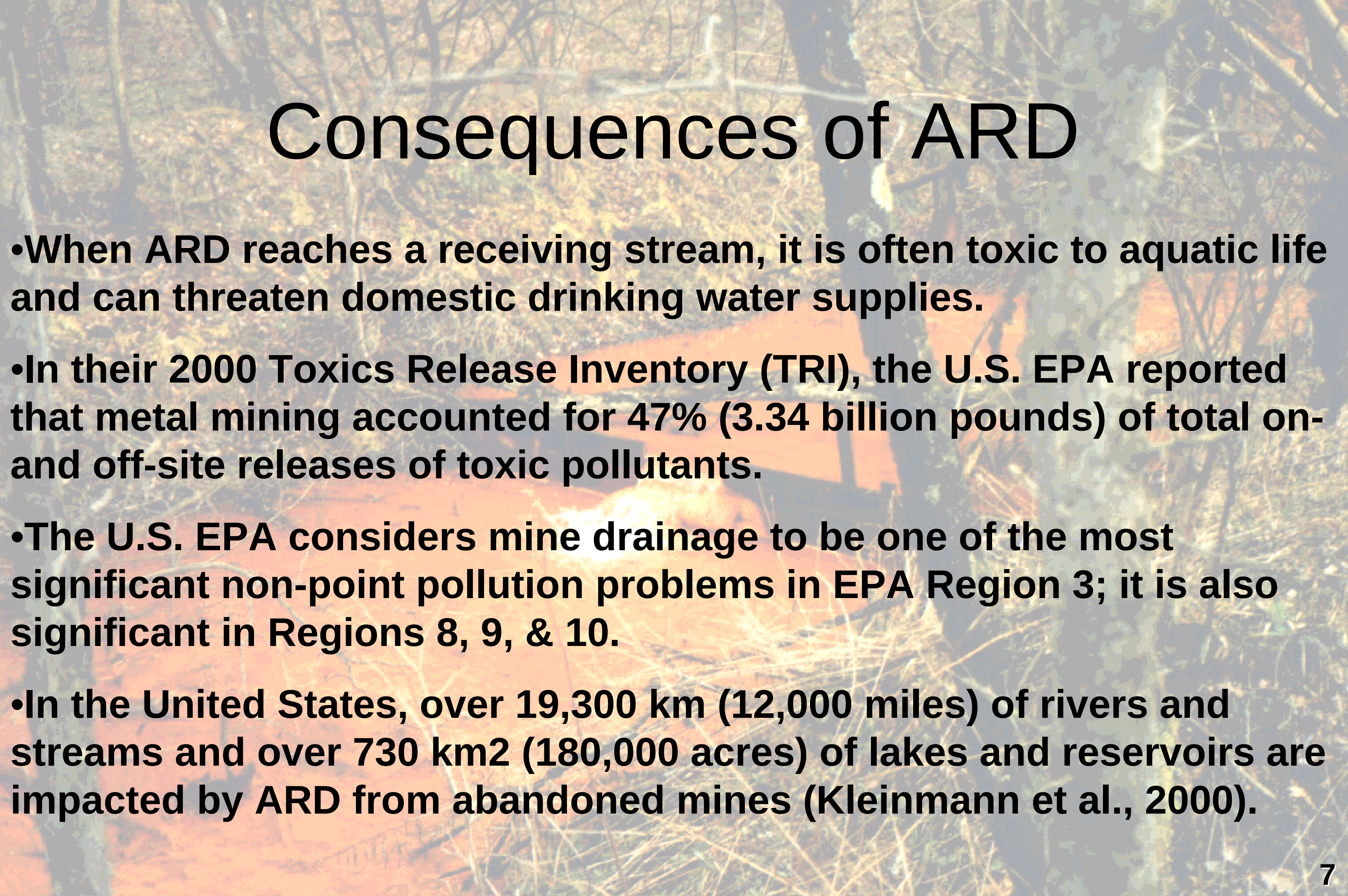
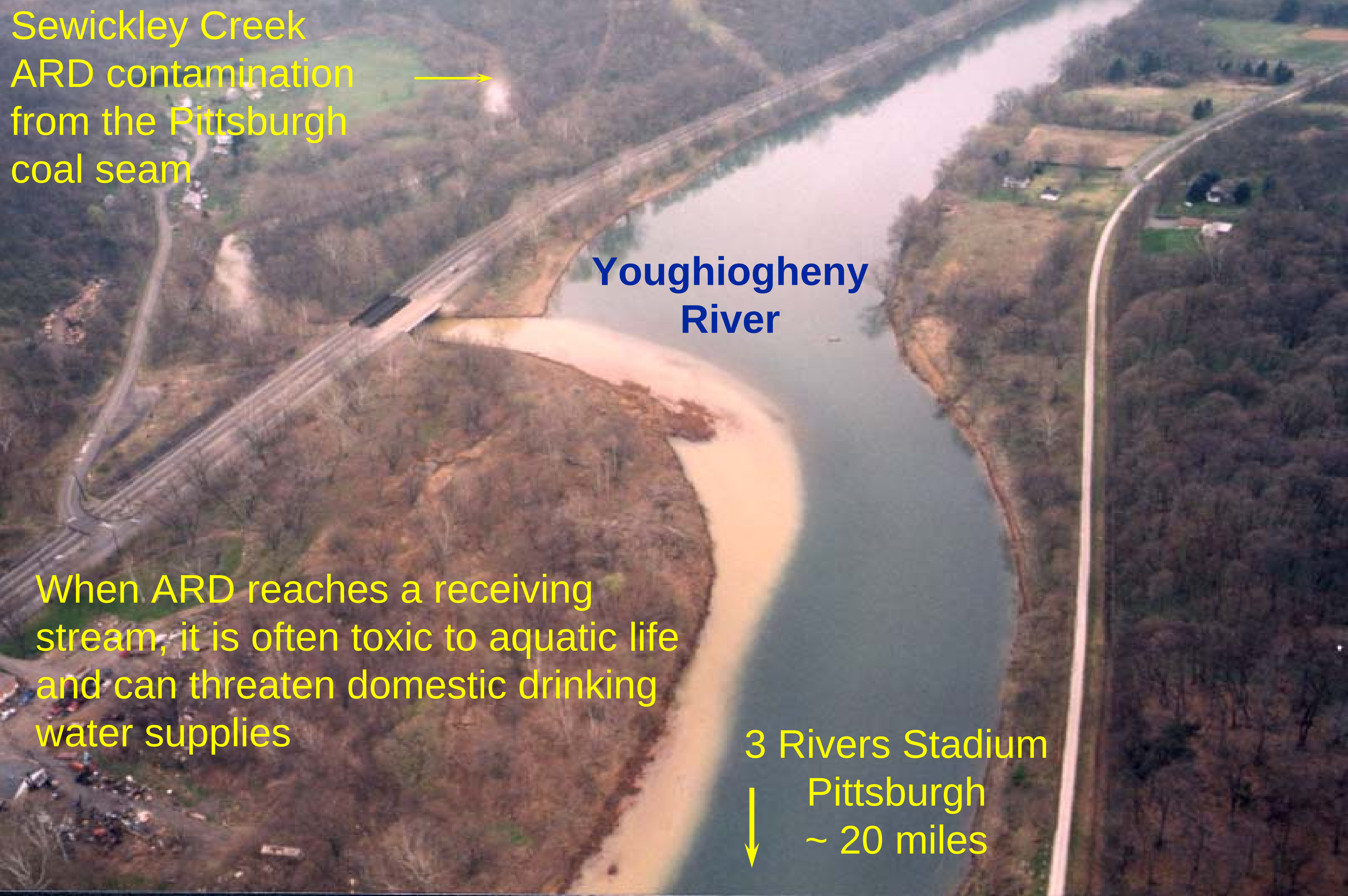


Figure 8.5. Eh-pH diagram showing the stability fields of common iron minerals. Total activity of dissolved carbonate 1*M*, of dissolved sulfur 10^{-6}*M*. Solid boundaries represent 10^{-6}*M* iron; dashed lines 10^{-4}*M*.

Consequences of ARD



- When ARD reaches a receiving stream, it is often toxic to aquatic life and can threaten domestic drinking water supplies.
- In their 2000 Toxics Release Inventory (TRI), the U.S. EPA reported that metal mining accounted for 47% (3.34 billion pounds) of total on- and off-site releases of toxic pollutants.
- The U.S. EPA considers mine drainage to be one of the most significant non-point pollution problems in EPA Region 3; it is also significant in Regions 8, 9, & 10.
- In the United States, over 19,300 km (12,000 miles) of rivers and streams and over 730 km2 (180,000 acres) of lakes and reservoirs are impacted by ARD from abandoned mines (Kleinmann et al., 2000).



When ARD reaches a receiving stream, it is often toxic to aquatic life and can threaten domestic drinking water supplies

Active Treatment

- It is not unusual for water treatment costs to exceed $10,000 per year at sites that are otherwise successfully reclaimed
- The United States coal industry spends over $1 million per day on active treatment of ARD

Passive Treatment

- Any zero or low maintenance ARD treatment method that does not require continual chemical addition and monitoring.
- Advantages of Passive Treatment Systems:
  - ➢Controls ARD at substantially lower operating costs,
  - ➢Environmentally safe, and
  - ➢Can be installed in remote locations.
- Passive treatment is also a viable option during mine closure and should be considered during the earliest stages of mine development.

The concentration of metal contaminants associated with ARD are generally very low in natural waters because chemical and biological processes cause their precipitation in surface water environments.

The same chemical and biological processes remove metal contaminants from ARD, but the metal loadings are often so high that the deleterious effects of these elements persist long enough to result in pollution of receiving waters.

Passive treatment systems function by retaining ARD long enough to decrease contaminant concentrations to acceptable levels.

Efficient passive treatment systems create conditions that promote the processes that most rapidly remove target contaminants. Thus design of passive treatment systems must be based on a solid understanding of ARD chemistry and how different passive technologies affect this chemistry.

Potential Metal Removal Mechanisms

- Cation Exchange
- Binding to Organic Matter
- Precipitation
  - Metal Oxidation and Hydrolysis
  - Sulfide
  - Carbonate
- Coprecipitation / Adsorption

History of Passive Treatment Systems

Passive treatment of ARD can be traced to two independent research projects indicating natural wetlands were ameliorating ARD without incurring any obvious ecological damage.

Powelson Wildlife Area in Ohio	**Tub Run Bog**
Wright State University	West Virginia University
Huntsman et al. 1978	Wieder and Lang, 1982

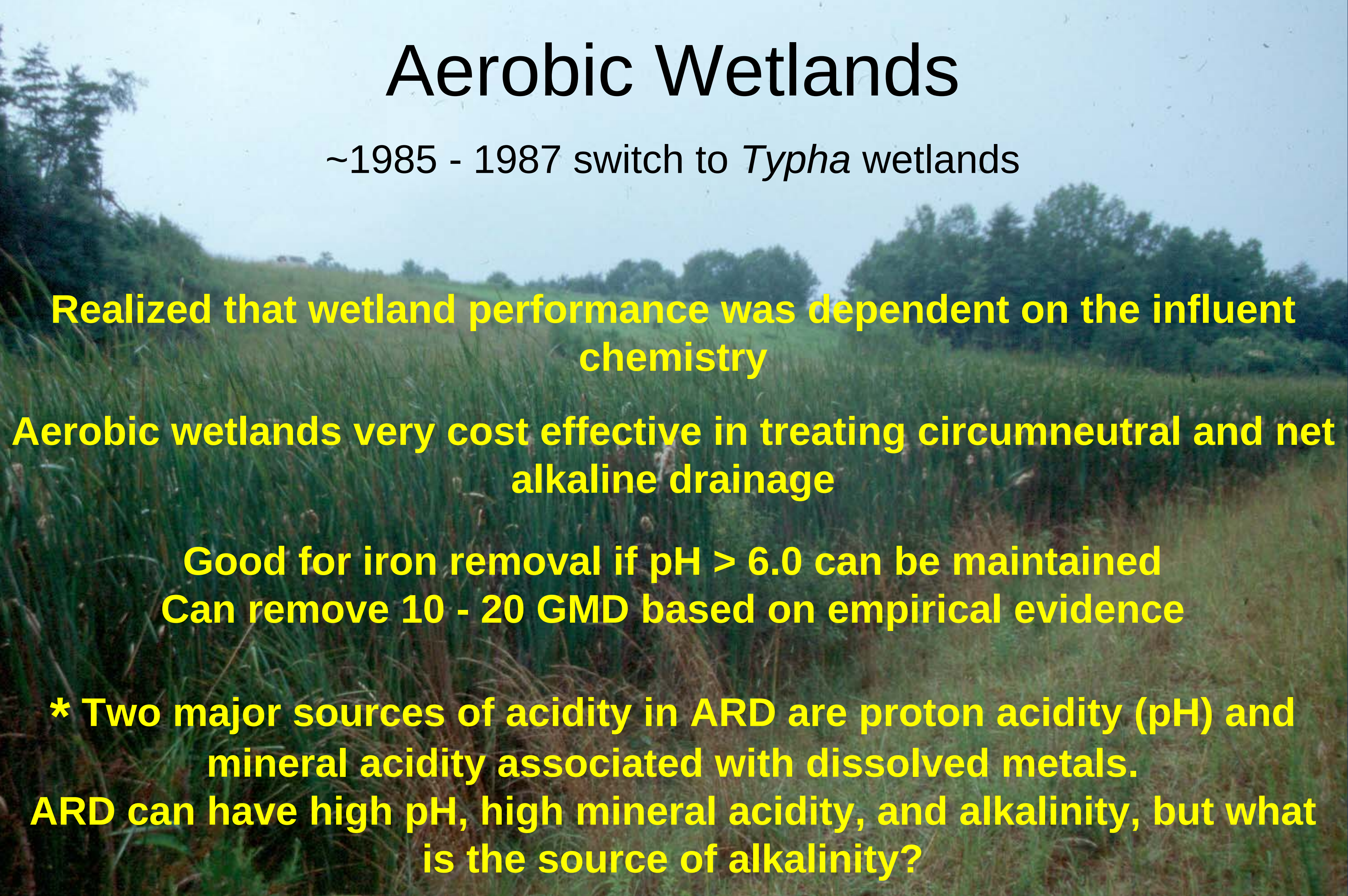
Both *Sphagnum*-dominated wetlands

1982 - 1985 experimental *Sphagnum* wetlands
USBM, Wright State, WVU, Penn. State

Sphagnum not readily available, difficult to transplant, toxic accumulation of metals

Aerobic Wetlands

~1985 - 1987 switch to *Typha* wetlands



Realized that wetland performance was dependent on the influent chemistry

Aerobic wetlands very cost effective in treating circumneutral and net alkaline drainage

Good for iron removal if pH > 6.0 can be maintained
Can remove 10 - 20 GMD based on empirical evidence

*** Two major sources of acidity in ARD are proton acidity (pH) and mineral acidity associated with dissolved metals.**
ARD can have high pH, high mineral acidity, and alkalinity, but what is the source of alkalinity?

Natural Acid Neutralization

Upon migration away from site of oxidation, ARD (i.e., Fe^{2+}, Fe^{3+}, SO_4^{2-}, H^+) reacts with aquifer material which may:

- **Increase pH**
- **Remove O_2**
- **Generate alkalinity**
- **Remove ferric iron**

Net Alkaline Drainage

- pH > 4.5
- Alkalinity > acidity
- Remediation through oxidation
- Metal hydrolysis buffered by alkalinity

Net Acidic ARD

- pH 2.0 - 6.5
- Acidity > alkalinity
- Requires neutralizing agent for effective remediation
- Metal hydrolysis produces acidic water

Higher Fe^{3+} = Lower pH

Hydrolysis Reaction

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

CH2MHILL

Passive Treatments Are Specific To ARD Chemistry

Net Alkaline Drainage

Aerobic wetland

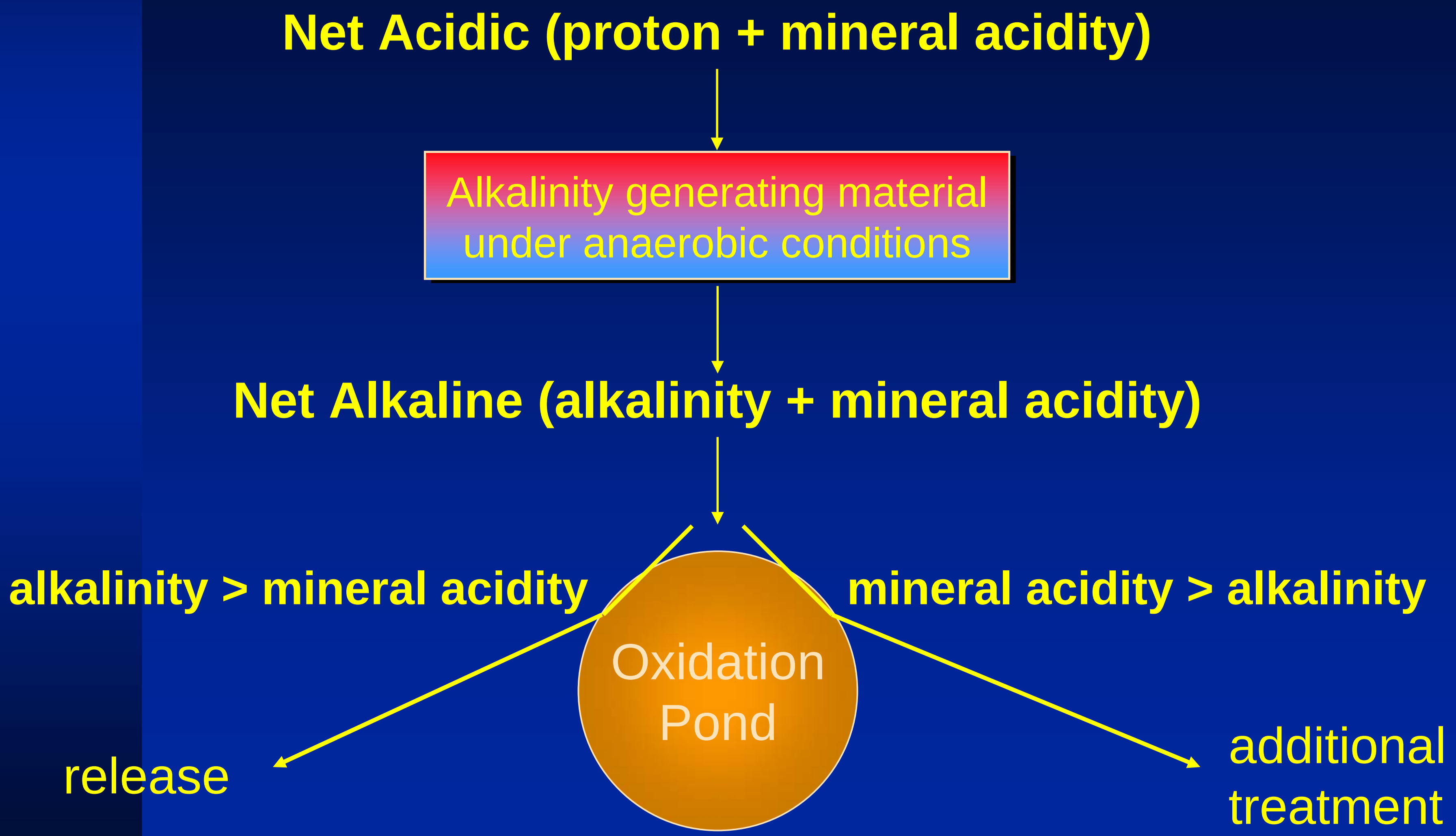
Net Acidic ARD

Alkalinity Generator

+

Aerobic wetland

Designs are conceptually simplistic



Net Acidic (proton + mineral acidity)

Alkalinity generating material under anaerobic conditions

Net Alkaline (alkalinity + mineral acidity)

alkalinity > mineral acidity

mineral acidity > alkalinity

Oxidation Pond

release

additional treatment

Calcitic limestone ($CaCO_3$) is by far the most common alkalinity-generating material used in passive treatment

Limitations of Limestone Dissolution (Armoring)

In presence of O_2, Fe^{2+} oxidation and Fe^{3+} hydrolysis occurs rapidly at limestone surface where pH is near-neutral

Armoring precipitates typically observed:

- **Hydrous ferric iron compounds**
- **Calcium sulfate**
- **Hydrous aluminum compounds**

For past 30 yrs, direct contact only with ARD containing < 1 mg/L:

- **Ferric iron, aluminum, and/or oxygen**

Traditional Division of Net Acidic ARD

- Net acidic, <1 $mg \cdot L^{-1}$ Fe^{3+}, Al^{3+}, and/or O_2

  Direct treatment with limestone

- Net acidic, >1 $mg \cdot L^{-1}$ Fe^{3+}, Al^{3+}, and/or O_2

  Pretreatment before limestone

Direct treatment with limestone

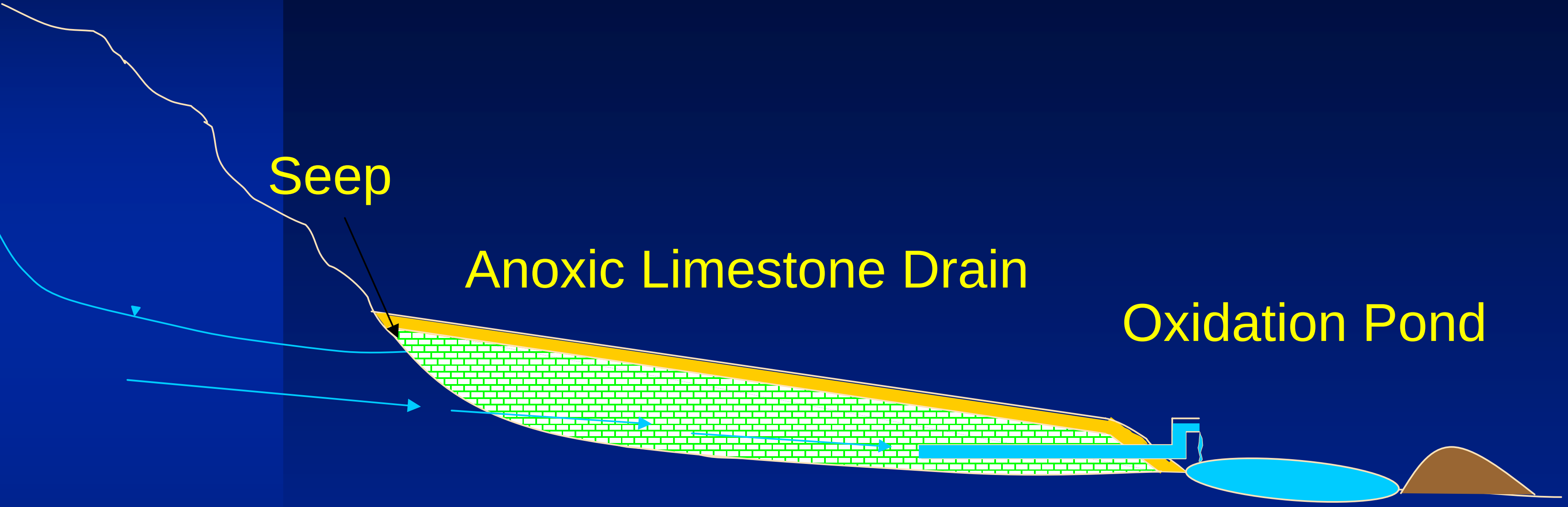
Influent ARD has pH > 5,
ferrous iron-dominated
low O_2

Turner and McCoy (1990) first described the use of buried beds of limestone to treat ARD under anoxic conditions

CH2MHILL

Anoxic Limestone Drain (ALD)

1990 - present



ALDs function by adding bicarbonate alkalinity through limestone dissolution under condition where armoring cannot occur. Anoxia limits the oxidation and hydrolysis of metals (e.g., Fe^{2+}), allowing them to pass through ALDs unchanged. The neutralization of mineral acidity, is achieved downstream in an aerobic wetland system through *ex situ* mineral precipitation buffered by alkalinity generated in the ALD

CH2MHILL

Proton Acidity

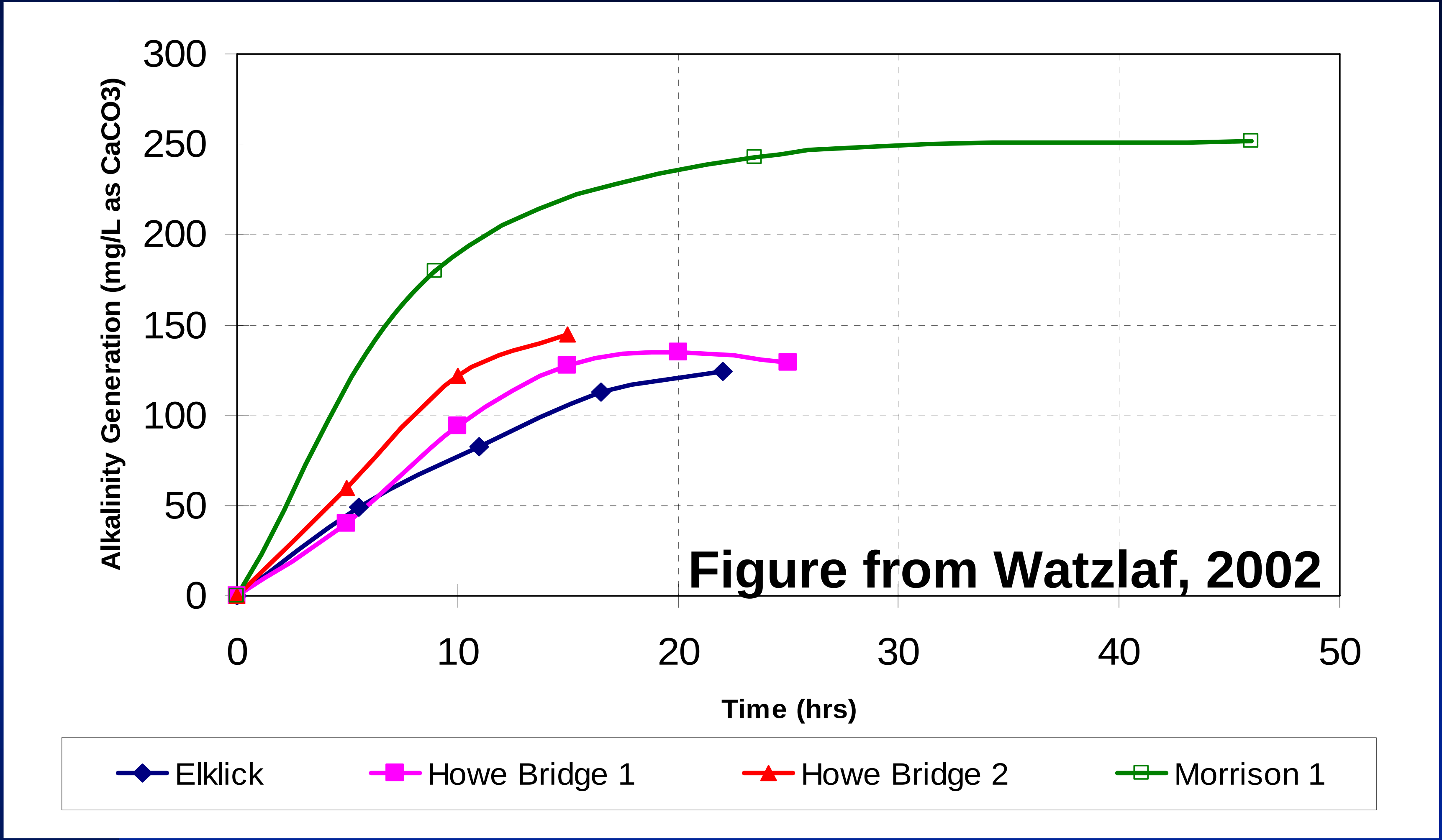
pH	Acidity Equivalents (mgáL^{-1} as $CaCO_3$)
6.0	0.05
5.0	0.5
4.0	5
3.5	16
3.0	50
2.5	158
2.0	500

ALD

$$10^{-pH} \cdot 50{,}045$$

Because mineral acidity is allowed to pass through an ALD, <1 mg·L^{-1} of the total influent acidity is neutralized *in situ*.

Alkalinity Generation in ALDs



With >15 hours residence time in the drain, can generate between 150 - 350 mg/L alkalinity as $CaCO_3$

CH2MHILL

Complete acid neutralization can be achieved only if mineral acidity is < 150 - 350 mg/L as $CaCO_3$,

Traditional Division of Net Acidic ARD

- Net acidic, <1 $mg \cdot L^{-1}$ Fe^{3+}, Al^{3+}, and/or O_2

Anoxic Limestone Drain

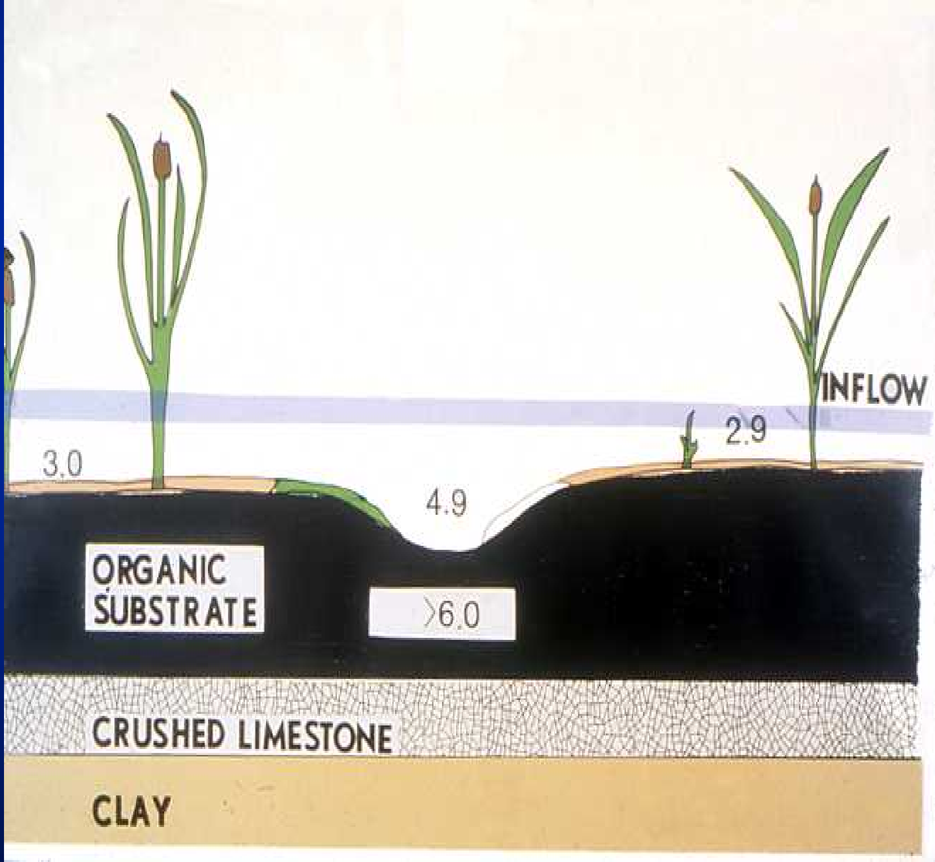
- Net acidic, >1 $mg \cdot L^{-1}$ Fe^{3+}, Al^{3+}, and/or O_2

??????

Compost Wetlands

Treatment of net acidic ARD

~1988 - 1994



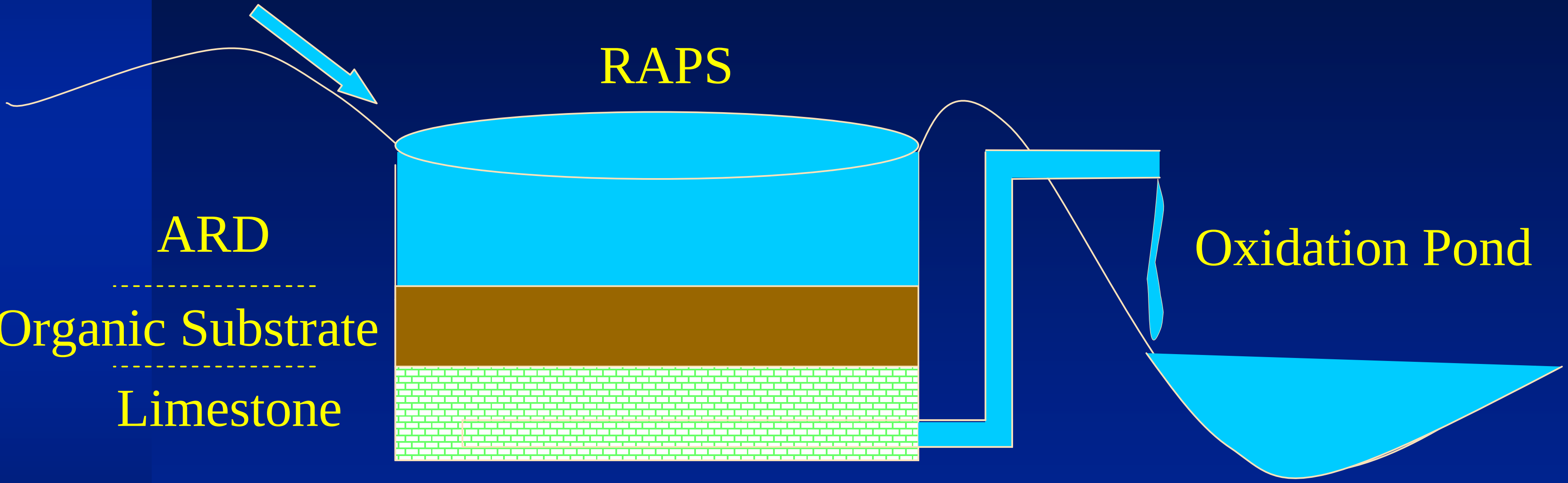
Relies on diffusion to deliver alkalinity to surface ARD

CH2MHILL

Vertical Flow Wetland (VFW) Designs

- Reducing and Alkalinity Producing System (RAPS) or Successive APS (SAPS)
- Limestone Buffered Organic Substrate VFW (LBOS-VFW)
- Sulfate Reducing Bioreactors (SRBR)

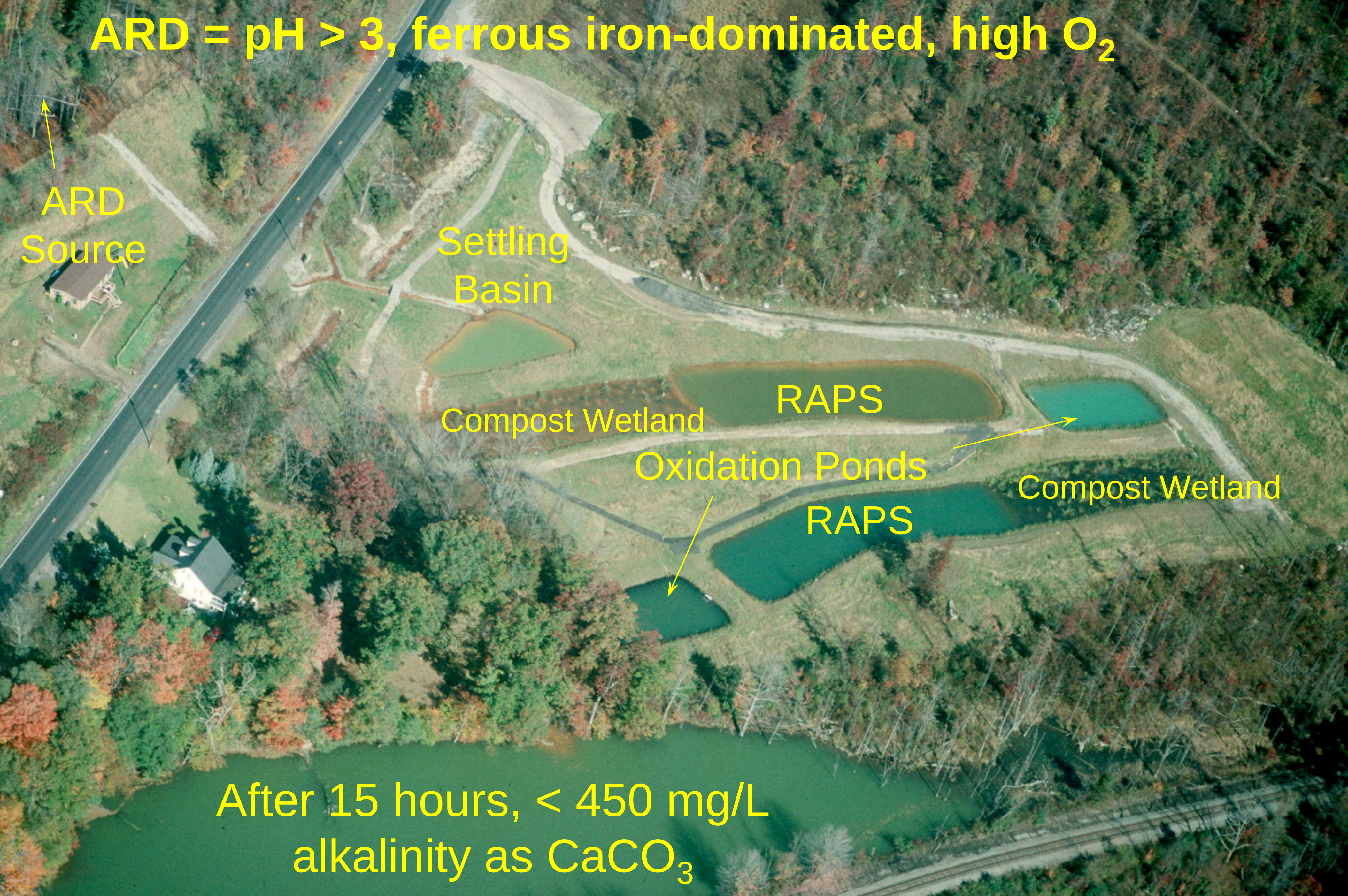
Reducing and Alkalinity-Producing Systems (RAPS)



In theory, the high BOD and low redox of the organic substrate removes DOX and promotes the reduction of Fe^{3+} to Fe^{2+} before ARD reaches the limestone drain. RAPS are not designed for metal retention; metal removal is dependent on *ex situ* mineral precipitation in an aerobic wetland (Kepler and McCleary, 1994)

CH2MHILL

ARD = pH > 3, ferrous iron-dominated, high O_2



After 15 hours, < 450 mg/L alkalinity as $CaCO_3$

Proton Acidity

pH	Acidity Equivalents (mgáL^{-1} as $CaCO_3$)
6.0	0.05
5.0	0.5
4.0	5
3.5	16
3.0	50
2.5	158
2.0	500

ALD

RAPS

$$10^{-pH} \cdot 50{,}045$$

Mineral acidity typically accounts for greater than 85% of the total acidity in ARD with pH > 3.0

Three Common Types of Net Acidic ARD

- **pH > 6, ferrous iron-dominated, low O_2** ALD
- **pH > 3, ferrous iron-dominated, high O_2** RAPS
- **pH < 3, ferric iron-dominated, oxygenated** LBOS

For low pH, ferric iron ARD

ALDs are limited by the presence of both ferric iron and oxygen

RAPS are limited because the low pH is prohibitive to robust anaerobic respiration (mainly iron reduction) and the very high ferric iron content would be too great for the capacity of the system

Limestone Buffered Organic Substrate VFW (LBOS-VFW)

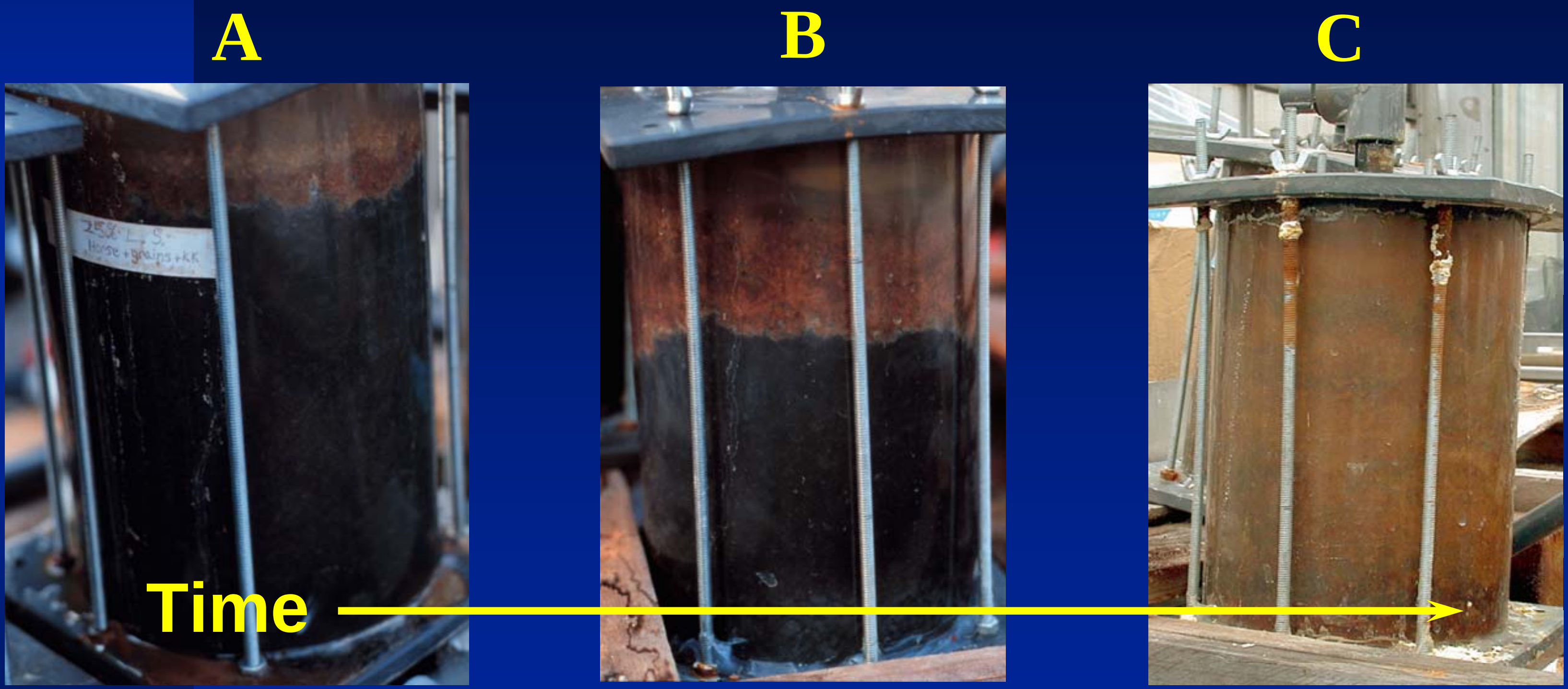
Instead of constructing a VFW with a compost layer overlying a coarse grained limestone drain (i.e., RAPS), LBOS-VFW are constructed with fine-grained limestone mixed in the compost layer

The LBOS-VFW effectively treats low pH (<3), ferric iron-dominated ARD by coupling rapid limestone dissolution to hydrolysis and precipitation of Fe^{3+} & Al^{3+}. This sets up a reaction boundary that "burns" vertically through the substrate until all mineral acidity has been neutralized or all of the substrate neutralization potential has been consumed.

$$Fe^{3+} + 3\ H_2O \Leftrightarrow Fe(OH)_{3\ (s)} + 3\ H^+$$

$$CaCO_3 + 2\ H^+ \Leftrightarrow Ca^{2+} + H_2CO_3^{\ *}$$

Both ALD and RAPS are limited in the amount of acidity they can neutralize, because 1) influent proton acidity is low, 2) they allow mineral acidity to pass, and 3) limestone dissolution is largely driven by pCO_2.



Limestone dissolution in LBOS-VFW is driven by proton attack, so loading rate is more physically limited than chemically limited

CH2MHILL

Sulfate Reducing Bioreactors (SRBRs)

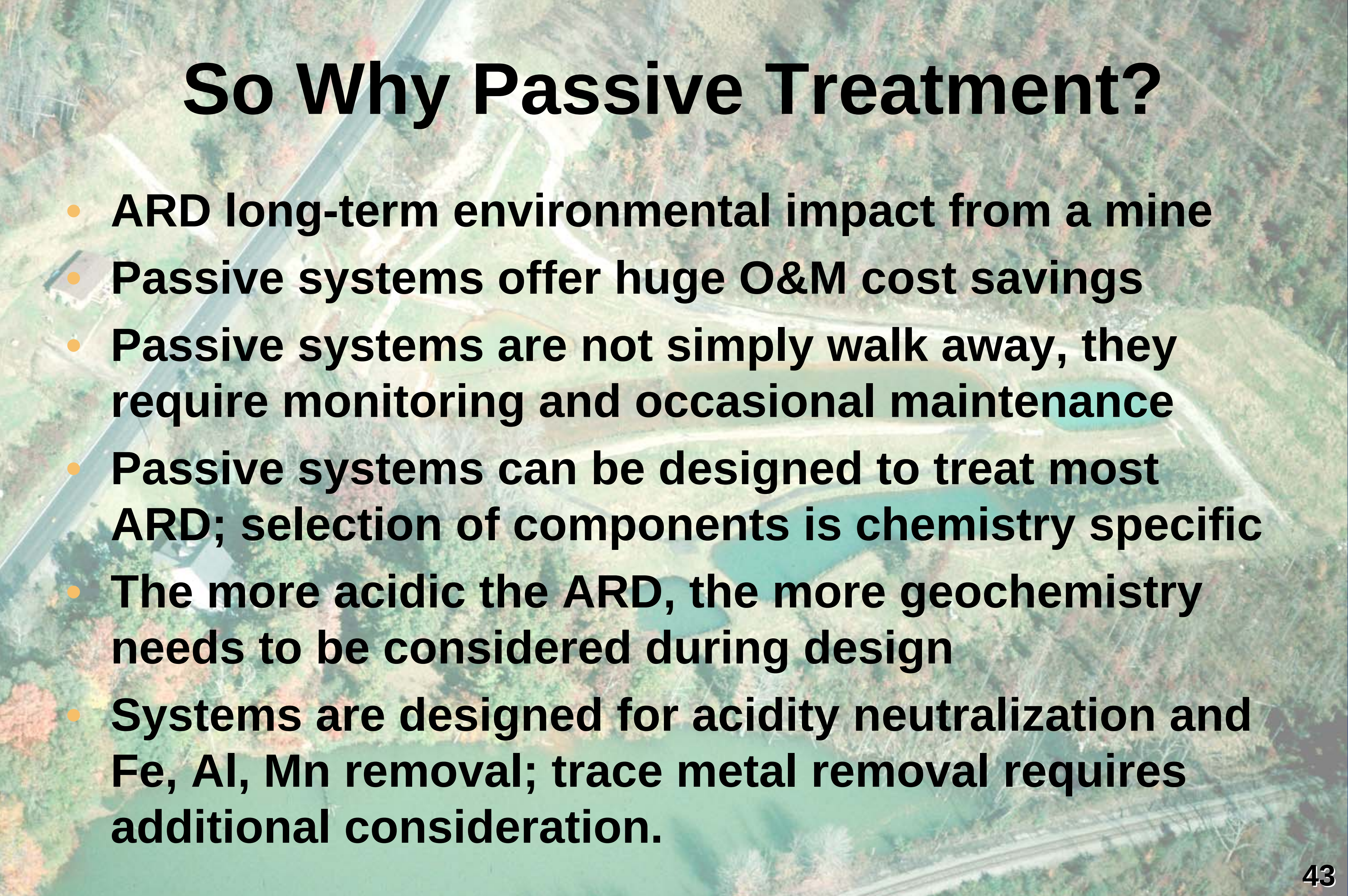
- VFWs designed for metal removal through biogenic sulfide precipitation
- Alkalinity is generated through the biological oxidation of organic matter as opposed to limestone dissolution
- Due to SRB pH sensitivity most are designed with limestone as a buffering agent (similar to LBOS)
- Semi-passive systems have been designed with carbon amendments (e.g., methanol)
- Effective means of trace metal removal

Horizontal Flow Limestone Beds (HFLBs)

- Shallow, open channels or beds (3’ – 4’ deep) filled with limestone and designed such that the water level is generally 6” – 1’ below the top of the limestone.
- Designed for Mn removal, which requires oxidizing, well-aerated water, as well as prior removal of essentially all dissolved Fe and Al (i.e., < 2 mg/L), and pH above about 6.5.
- Limestone surfaces greatly enhance the precipitation of Mn, because of elevated pH at the surface and large surface area.

Summary of Passive Treatment Units

- **Aerobic Ponds & Wetlands** – including settling basins, oxidation ponds; mainly used for oxidation, hydrolysis, and precipitation reactions and as biofilters or final polishing units.
- **Compost Wetlands** – also known as “anaerobic” wetlands contain limestone and composted organic matter in a vegetated (cattails) substrate. Most flow is surficial. Obsolete units that rely on sulfate reduction and limestone dissolution.
- **ALD** – used to treat anaerobic, ferrous iron-dominated ARD, always followed by an oxidation pond
- **RAPS** – VFW subunit used to treat aerobic, ferrous iron-dominated ARD, always followed by an oxidation pond
- **LBOS-VFW** – preferred treatment unit for ferric iron-dominated ARD
- **SRBRs** – VFW subunit relies on metal sulfide precipitation and biologic oxidation of organic matter; most effective when used to remove trace metals
- **HFLBs** – used as a polishing unit to remove manganese



So Why Passive Treatment?

- ARD long-term environmental impact from a mine
- Passive systems offer huge O&M cost savings
- Passive systems are not simply walk away, they require monitoring and occasional maintenance
- Passive systems can be designed to treat most ARD; selection of components is chemistry specific
- The more acidic the ARD, the more geochemistry needs to be considered during design
- Systems are designed for acidity neutralization and Fe, Al, Mn removal; trace metal removal requires additional consideration.

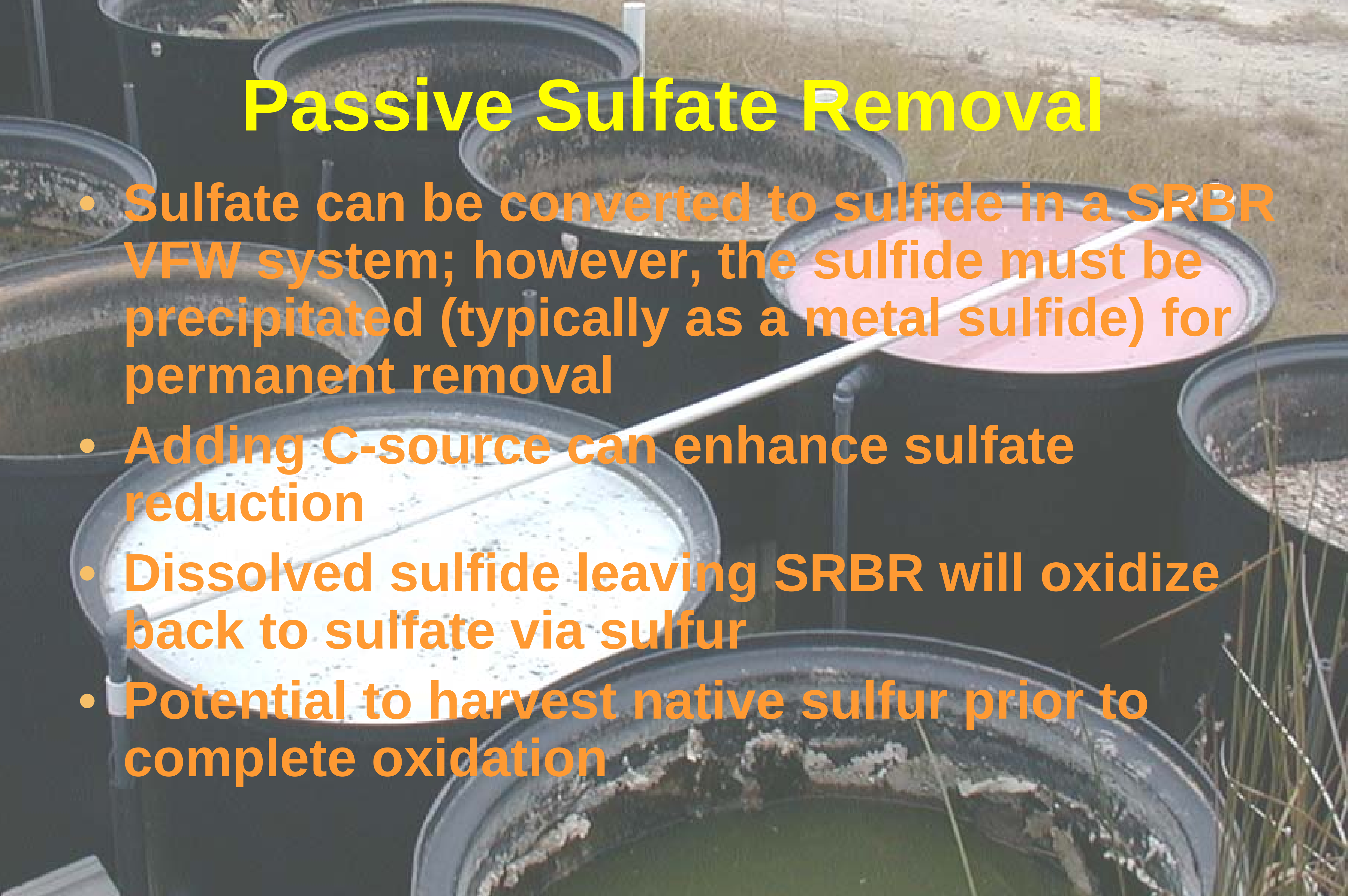
Questions / Further Discussion

bt.thomas@ch2m.com

Design Consideration - Loading

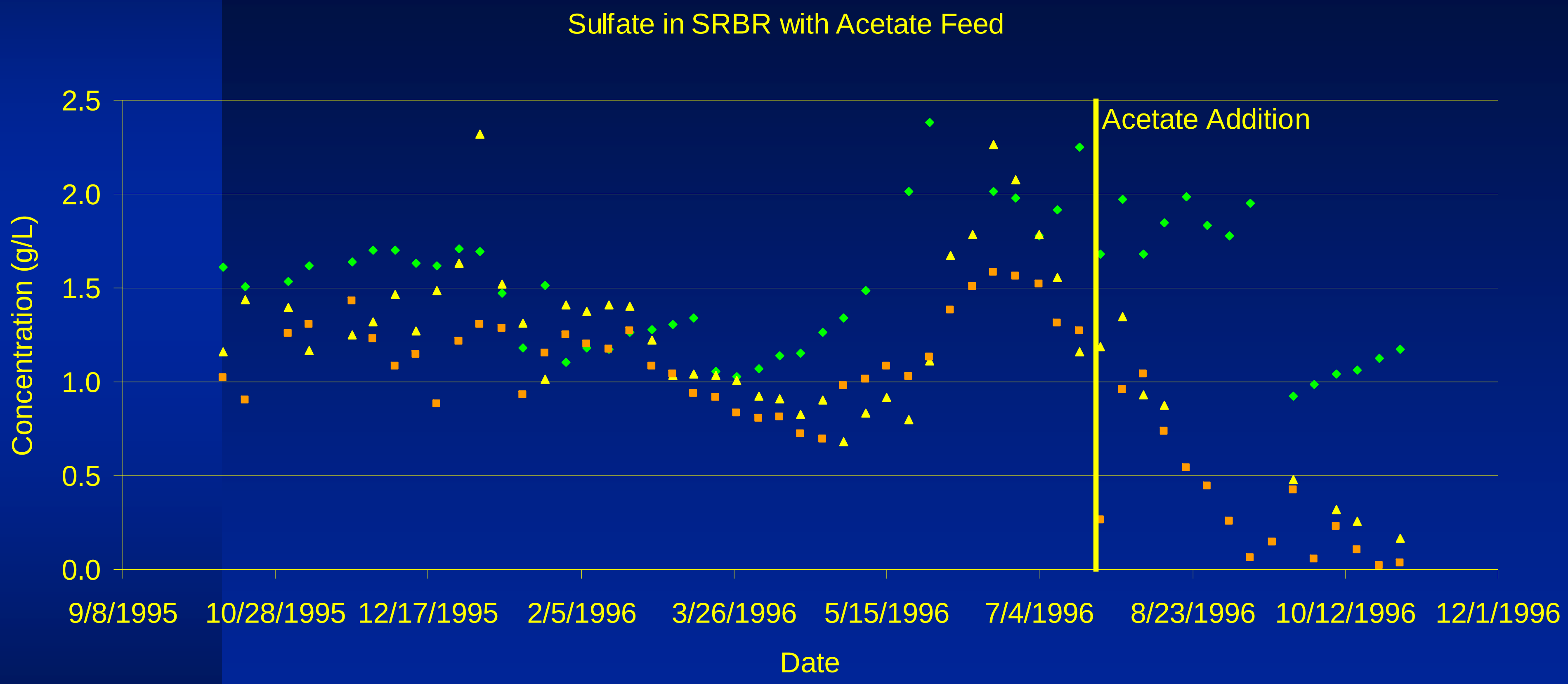
Load (g/day) = Flow (L/min) x Concentration (mg/L) x 1.44 (g min/mg day)

- **Aerobic Ponds**: 20 g*$d^{-1}m^{-2}$ for Fe & 1.0 g*$d^{-1}m^{-2}$ for Mn
- **ALD**: 15 hrs contact time, over 20 year life need 26 tons of limestone for each gal*min^{-1} flow; assume 90% $CaCO_3$ and 49% porosity. Max 300 mg/L alkalinity.
- **RAPS**: 30 – 50 g*$d^{-1}m^{-2}$ of acidity, though 15 hrs of limestone contact time recommended.
- **SRBR**: 0.3 moles sulfide generated * m^{-3} of substrate * day^{-1}.
- **HFLB**: 2.5 g*$d^{-1}m^{-2}$ for Mn



Passive Sulfate Removal

- Sulfate can be converted to sulfide in a SRBR VFW system; however, the sulfide must be precipitated (typically as a metal sulfide) for permanent removal
- Adding C-source can enhance sulfate reduction
- Dissolved sulfide leaving SRBR will oxidize back to sulfate via sulfur
- Potential to harvest native sulfur prior to complete oxidation


Sulfate in SRBR with Acetate Feed
Acetate Addition
Concentration (g/L)
2.5
2.0
1.5
1.0
0.5
0.0
9/8/1995
10/28/1995
12/17/1995
2/5/1996
3/26/1996
5/15/1996
7/4/1996
8/23/1996
10/12/1996
12/1/1996
Date

CH2MHILL

Passive Systems for ARD at CH2M HILL

- **Gossan Lead Pyrite Mine, Galax, VA**
  - Management of one of the oldest VFW (SAPS)
- **Burlington Mine, Colorado**
  - Conceptual stage, initial treatability completed
- **Canyon Creek, Idaho**
  - Pilot Study for US EPA, Region 10
- **Mayer Ranch, Oklahoma**
  - Field scale research wetland being built for Univ. of Oklahoma
- **Empire Mine, California**
  - proposal to treat low concentration of Fe, As, & Mn