

# AMD 101

## Chemistry of Abandoned Mine Drainage

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<http://amrclearinghouse.org>

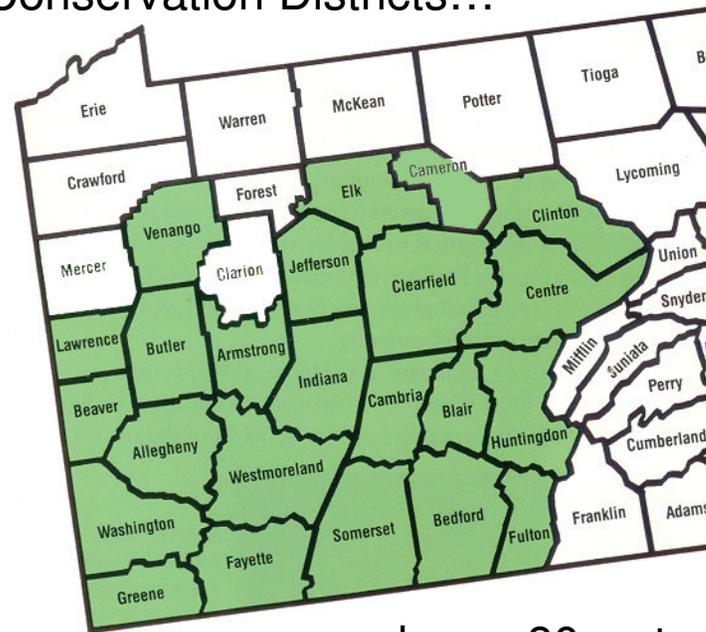
# Western PA Coalition for Abandoned Mine Reclamation



- A helping hand to watershed groups grappling with the legacy of problems from abandoned coal mining.



Serving 23 counties in cooperation with Conservation Districts...



... and over 80 watershed groups in western PA

Funded by  319 NPS Program  
Department of Environmental Protection

# C-SAW

## *Consortium for Scientific Assistance to Watersheds*

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<http://pa.water.usgs.gov/csaw/>

# Setting the Stage

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- About AMD reactions
- Limiting quantities
- Rates of reactions
- Oxygen
- Mining environments

# About AMD reactions

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- The reactions we'll discuss are those that occur both in the mining environment and in treatment systems.
- Some reactions may actually be beneficial, but they play a role in the bigger picture.

# Limiting quantities

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- Keep in mind that chemical reactions can proceed only as long as sufficient amounts of each and every reactant is available.
- If any one reactant becomes exhausted, the reaction shuts down. It doesn't matter if there is plenty of the remaining reactants.
- The reactant in shortest supply limits the extent of the reaction.

# Rates of reactions

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The rate at which a reaction takes place can depend on many factors.

- pH can be a very important factor for some reactions
- The presence of certain bacteria can catalyze some reactions, increasing rates dramatically.
- Some reactions take place almost instantaneously
- Others may take place over days, months, or years.

# Oxygen

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Oxygen can be transported

- as a gas (in air)
- dissolved in water (DO – dissolved oxygen)

# Chemical environments of mines

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Where AMD is most likely to occur

- Deep (Underground) mines
- Surface mining activities
- Waste piles

Tremendous variability in the chemical environments

- Water
- Oxygen
- Pyrite
- Bacteria
- Alkalinity
- Other metal containing minerals

Tremendous variability in makeup of AMD from location to location

# Pyrite Reactions

Net AMD creating reaction

1. Oxidation of pyrite
2. Oxidation of ferrous iron to ferric
3. Hydrolysis of ferric ions
4. Oxidation of pyrite by ferric ions

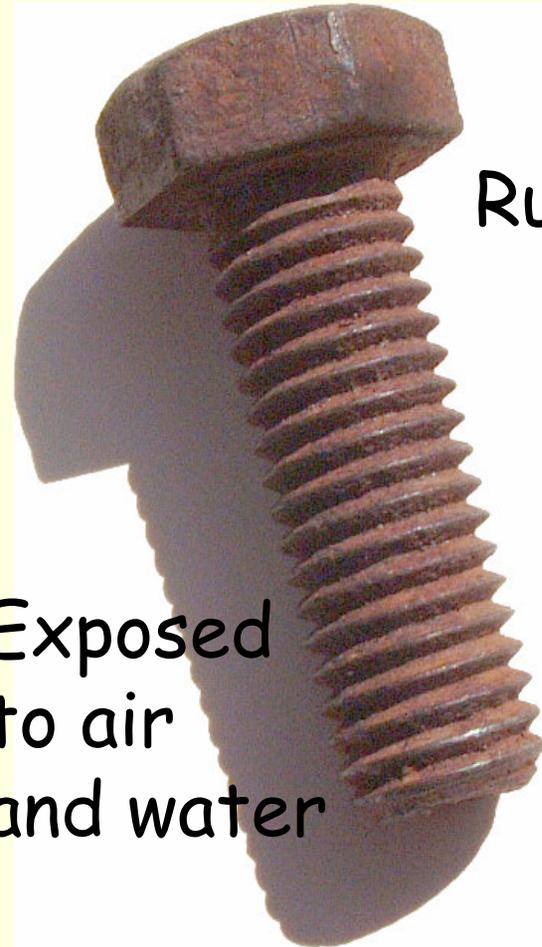
# *Explain the difference*

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No rust

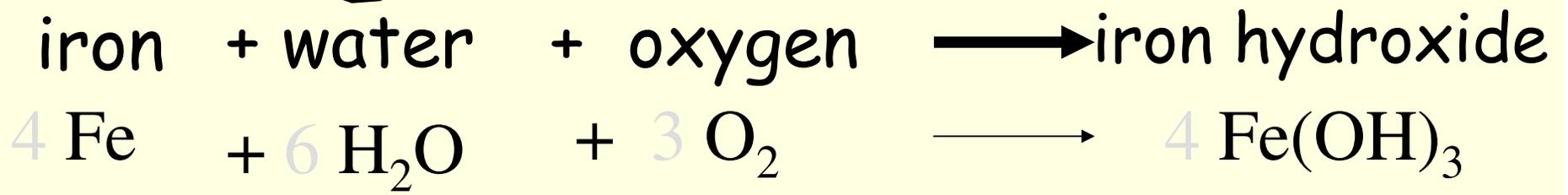
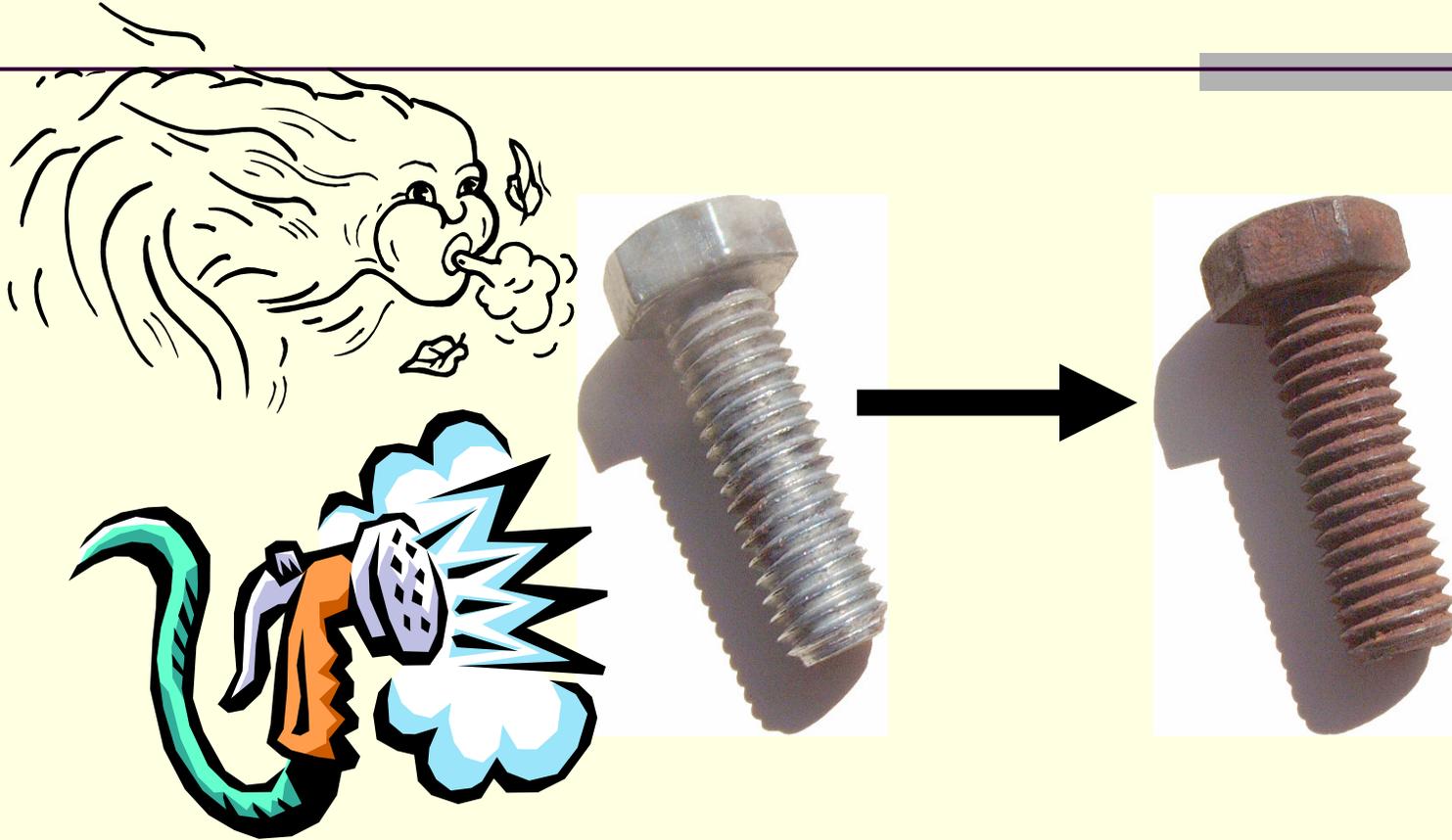
Protected  
from air  
and water



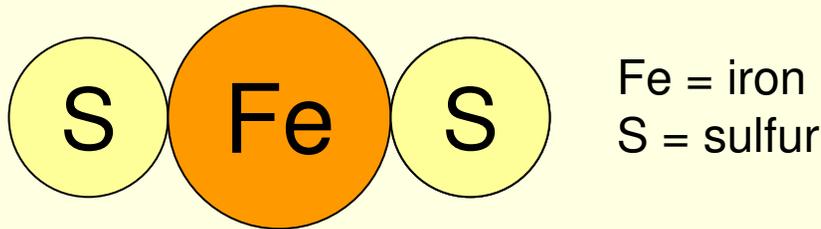
Rusted

Exposed  
to air  
and water

# Rusting - the chemical reaction



# AMD: it starts with Pyrite



Chemical Name: **Iron sulfide**

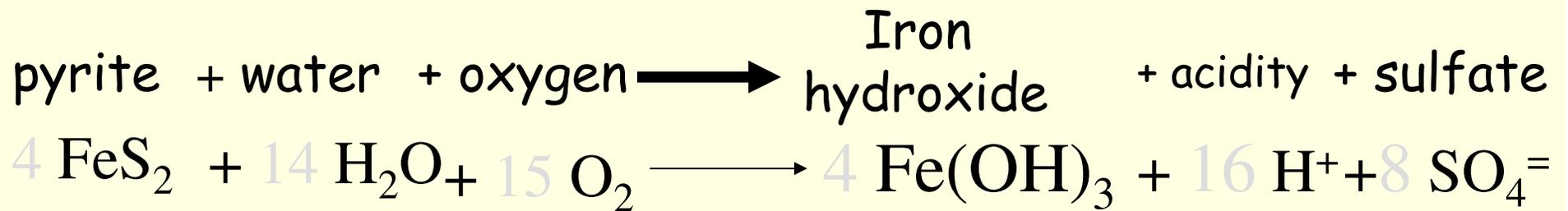
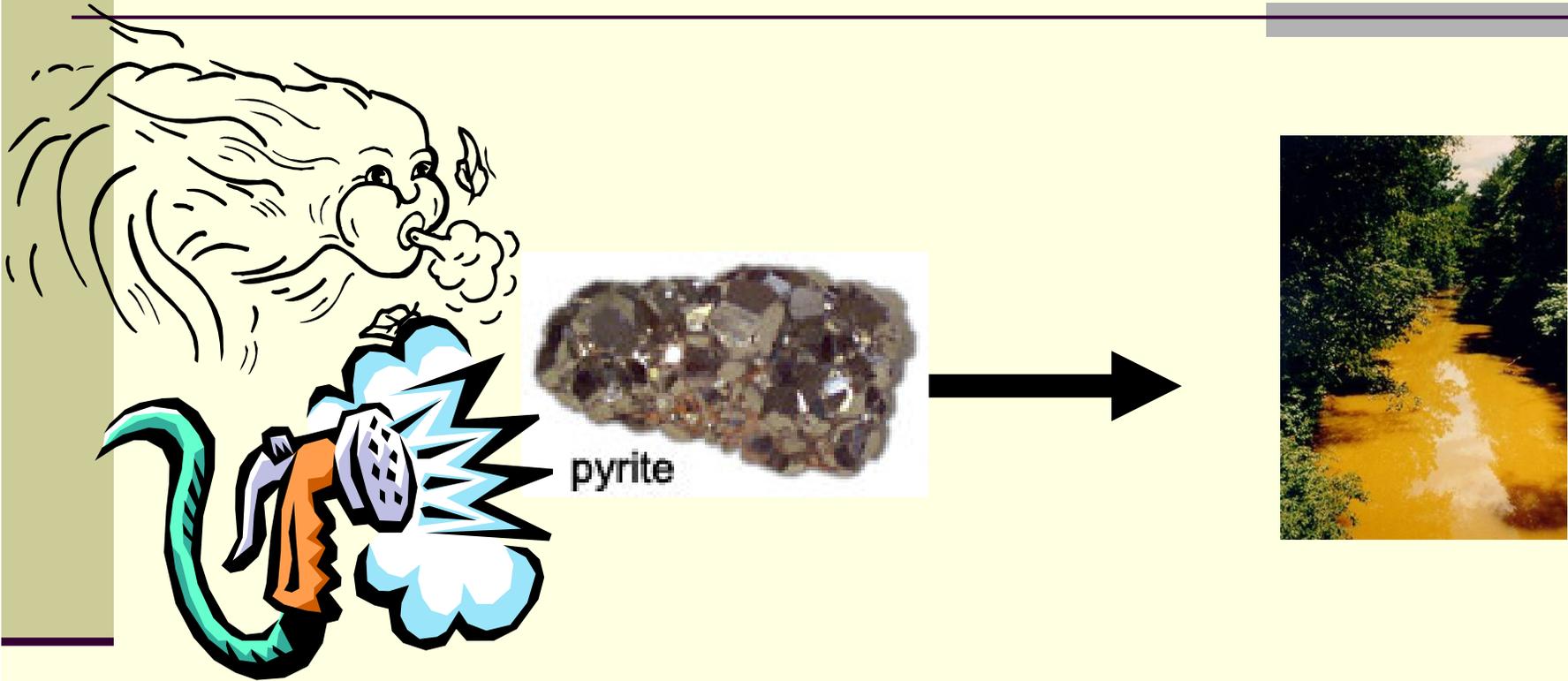
Mineral name: **Iron Pyrite**

Common Name: **Fool's Gold**

Pyrite is a very common mineral almost universally found in and adjacent to coal deposits.

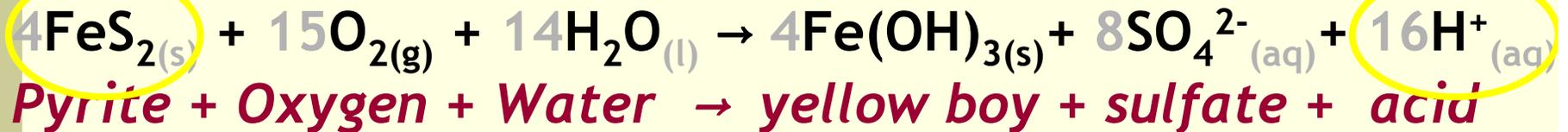
Pyrite is protected from chemical reactions unless disturbed by mining activities.

# Pyrite's chemical reaction



# Net AMD creating reaction

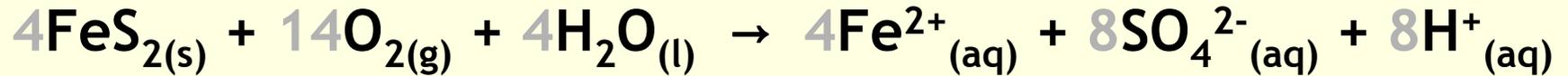
The following reaction is often used to describe the overall formation of AMD



- This is actually a net reaction describing a sequence of 3 separate chemical reactions, which may have been widely separated in time and place.
  - We'll discuss those individual reactions separately.
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- NOTE: For every unit of pyrite that reacts, 4 units of hydrogen ions are produced. (*Prolific acid production!*)

# 1. Oxidation of pyrite

- This is the reaction that sets off the entire AMD process.

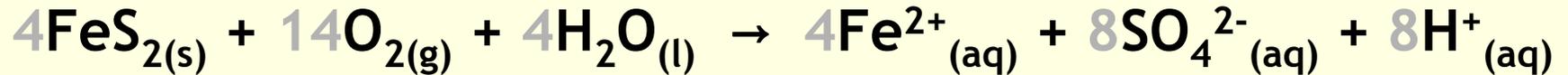


***Pyrite + Oxygen + Water → ferrous ion + sulfate + acid***

- Pyrite ( $\text{FeS}_2$ ) undergoes oxidation, and in the process produces ferrous iron ( $\text{Fe}^{2+}$ ), sulfate ions ( $\text{SO}_4^{2-}$ ), and hydrogen ions ( $\text{H}^+$ ).
  - Pyrite oxidation can be rapid upon exposure to humid air or aerated water.
  - In cases where the available amounts of oxygen or water are low, the oxidation of pyrite can be slow.
  - The bacteria *Thiobacillus ferrooxidans* can greatly speed up this reaction and is thought to be a major culprit in much AMD formation
- Ferrous ions ( $\text{Fe}^{2+}$ ) are colorless when dissolved in water (in aqueous solution)
- All of the original sulfur atoms from pyrite ( $\text{FeS}_2$ ) are converted into sulfate ions ( $\text{SO}_4^{2-}$ ).
  - Sulfate ions ( $\text{SO}_4^{2-}$ ) are also colorless and are not generally considered harmful.
  - The concentration of sulfate [ $\text{SO}_4^{2-}$ ] is a good indicator of the amount of pyrite oxidation that has occurred.

# 1. Oxidation of pyrite (cont)

- This is the reaction that sets off the entire AMD process.

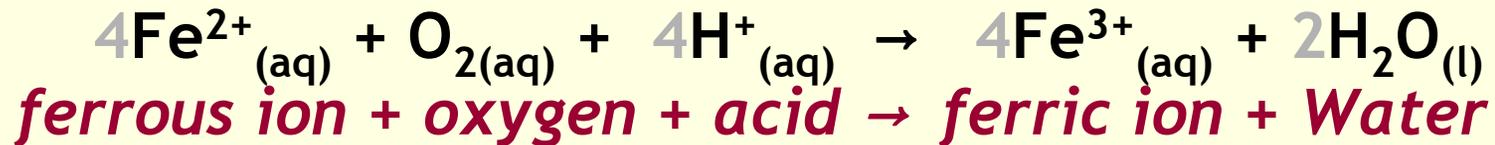


*Pyrite + Oxygen + Water → ferrous ion + sulfate + acid*

- The reaction produces 2 units of acid (hydrogen ions (H<sup>+</sup>)) for every unit of pyrite (FeS<sub>2</sub>) consumed. ( $8\text{H}^+ / 4\text{FeS}_2 = 2$ )
- Often, this is the only reaction that has appreciably occurred for AMD discharges emerging from underground (if underground oxygen (O<sub>2</sub>) is limited)
  - The water is crystal clear, giving an initial appearance that nothing is wrong.
  - Closer examination shows virtually no life in such water, as pH levels are often in the 2-3 range... quite acidic.
  - If this is the state of the water that is captured for treatment, the water will need to be neutralized with alkalinity, and the iron will need to be captured.

## 2. Oxidation of ferrous iron to ferric

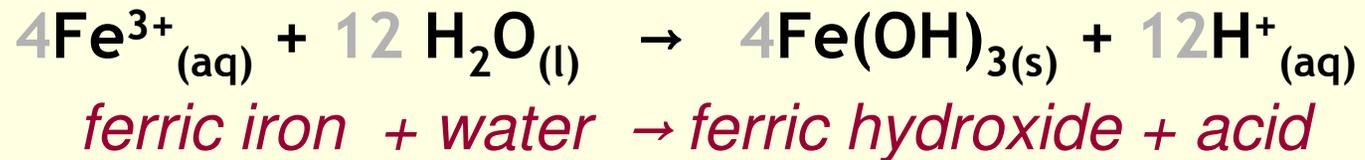
- This reaction oxidizes the ferrous iron ( $\text{Fe}^{2+}$ ) from Reaction 1 in producing ferric iron ( $\text{Fe}^{3+}$ )



- Acidity is actually consumed in this reaction.
- This reaction is often limited by the amount of available dissolved oxygen.
- The rate of reaction is highly dependent on pH. If the pH is less than 3, this reaction is very slow. The higher the pH, the greater the rate.
  - A very acidic discharge meeting up with a stream having alkalinity with higher pH and appreciable dissolved oxygen (DO) will be the scene of this reaction proceeding rapidly.
  - In treating water that has not yet undergone this reaction, alkalinity is typically added (thereby partially neutralizing acid) to increase rate.
- Settling ponds promote this reaction by having large surfaces for exchange of oxygen from the atmosphere.
- Agitation of water in contact with atmosphere will increase DO.
- The bacteria *Thiobacillus ferrooxidans* can also greatly speed up this reaction
- Once this reaction occurs, reaction 3 usually follows in rapid succession.

# 3. Hydrolysis of ferric ions

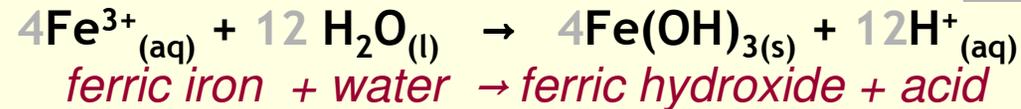
- This reaction typically occurs immediately following Reaction 2 where ferric iron ( $\text{Fe}^{3+}$ ) reacts with water (a hydrolysis reaction) in forming solid ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) and additional acid.



The reaction produces 3 units of acid ( $\text{H}^+$ ) for every unit of ferric ion ( $\text{Fe}^{3+}$ ) consumed. ( $12\text{H}^+ / 4\text{Fe}^{3+}=3$ )

- This can be a very significant source of acidity.
- When metal ions, such as ferric ion ( $\text{Fe}^{3+}$ ), are hydrolyzed, they form hydrogen ions ( $\text{H}^+$ ). Because ferric ions are anticipated to undergo this reaction, ferric ions (as well as other metal ions) are sometimes referred to as mineral acidity. Another common metal ion where this occurs is the aluminum ion ( $\text{Al}^{3+}$ ).

# 3. Hydrolysis of ferric ions (cont)



- Ferric hydroxide ( $\text{Fe}(\text{OH})_3$ )
  - is also called “yellow boy”, a first cousin of rust
  - is an insoluble solid (precipitate) at pH > 3.5
  - is a deep yellow to red-orange in color
  - forms very fine particles which do not easily settle, especially in turbulent water
  - Limits the amount of light penetrating a stream, slowing photosynthesis
  - coats the bottoms of streams with a slippery coating that smothers benthic (bottom dwelling) aquatic life and, interrupting the food chain
  - can be an irritant to fish gills
  - over time reacts to form other rust-like iron oxides.
  - is not toxic in the sense that coming into contact with or ingesting will not generally harm humans
  - can stain skin or clothes
  - will produce visibly orange water and coatings from concentrations as low as 0.5 mg/l
  - is captured (along with other metal hydroxides) in settling ponds.

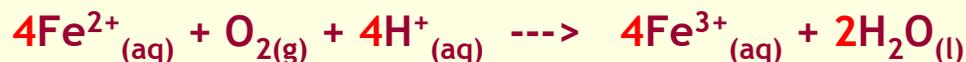
# Review: AMD formation is a 3 step process

- (1) **Pyrite reacts with water and oxygen forming dissolved ferrous iron, acidity and sulfate**



Often, this is the only reaction that has occurred as an AMD discharge emerges from underground (if underground oxygen is limited)

- (2) **Ferrous iron is oxidized to ferric iron**



Constructed sedimentation ponds and aerobic wetlands promote this reaction

- (3) **Ferric iron is hydrolyzed to insoluble iron hydroxide (yellowboy)**



This reaction happens very quickly after (2). Sedimentation ponds & aerobic wetlands provide space for the solid iron hydroxide to be collected.

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- (4) **Net reaction**



## 4. Oxidation of pyrite by ferric ions

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- $\text{FeS}_{2(s)} + 14 \text{Fe}^{3+}_{(aq)} + 8 \text{H}_2\text{O} \rightarrow 15 \text{Fe}^{2+}_{(aq)} + 2 \text{SO}_4^{2-}_{(aq)} + 16 \text{H}^+_{(aq)}$
- *Pyrite + Ferric Iron + Water → Ferrous Iron + Sulfate + Acidity*
- This reaction may act to perpetuate the further formation of AMD along with reaction 1.

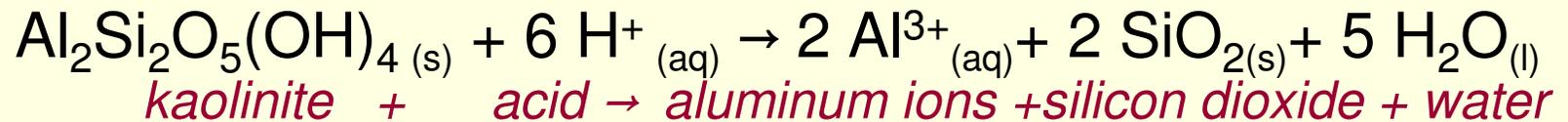
# Aluminum chemistry

1. Dissolution of Aluminum containing minerals
2. Hydrolysis of Aluminum cations

# 1. Dissolution of Aluminum containing minerals

- Aluminum is one of the most common elements in the earth's crust and is a constituent in many minerals.
- Some aluminum containing minerals react readily with acid which liberates dissolved aluminum cations ( $\text{Al}^{+3}$ ).

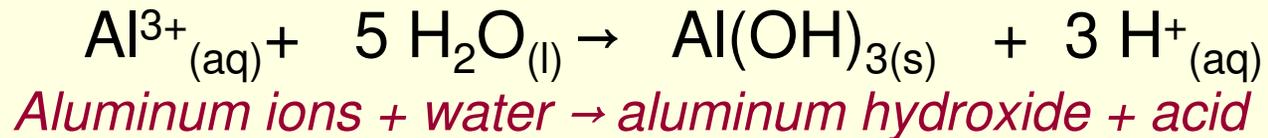
*example*



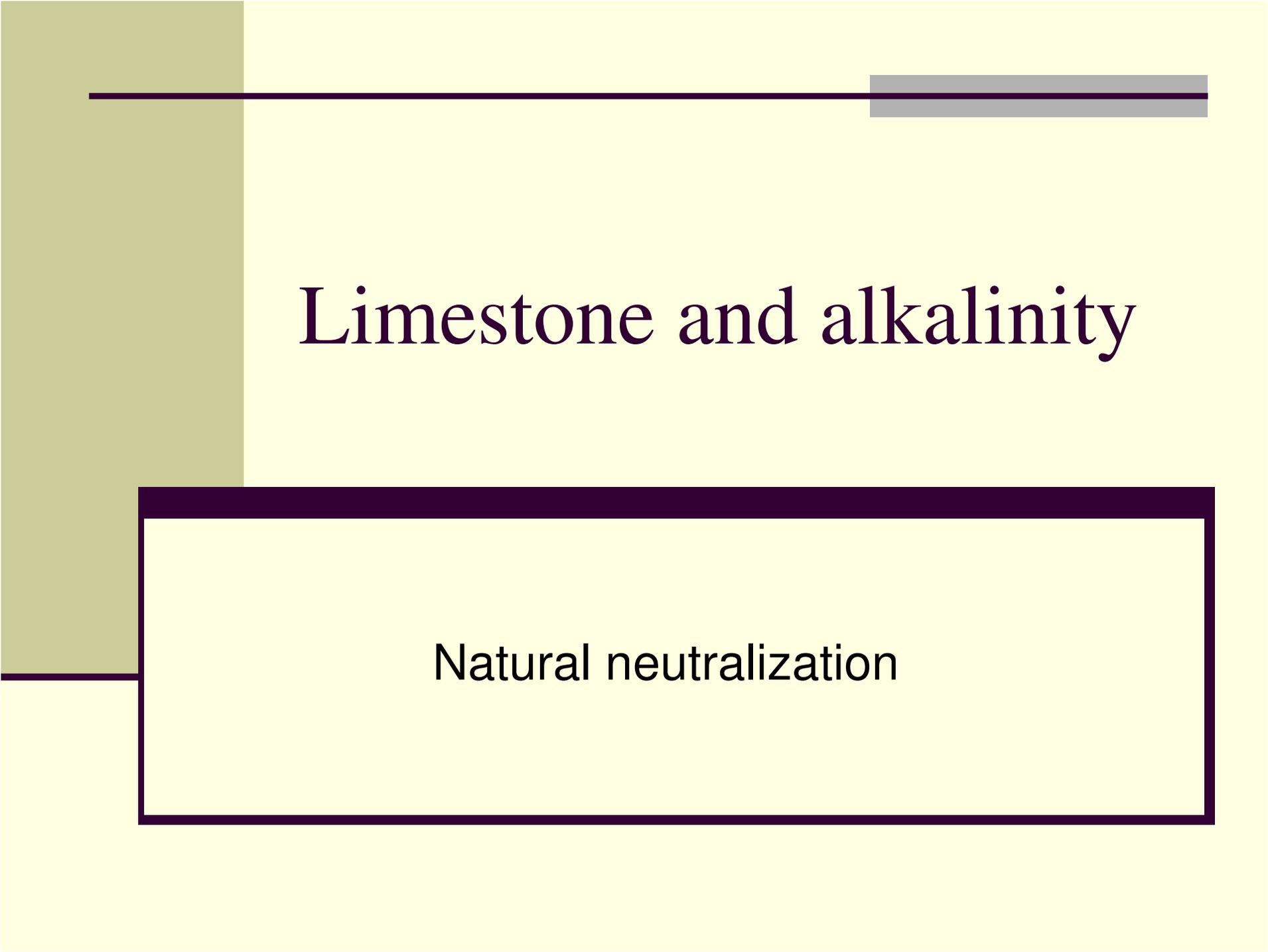
- When acid ( $\text{H}^+$ ) generated from pyrite reactions (or other sources such as acid rain) comes in contact with aluminum containing minerals, reactions similar to the above become possible.
- Dissolved aluminum is acutely toxic to fish and other aquatic life in acid waters.

## 2. Hydrolysis of Aluminum cations

- Aluminum ions ( $\text{Al}^{3+}$ ) remain dissolved in acidic water as long as the pH is less than  $\sim 4.5$
- If pH increases beyond this threshold, a hydrolysis reaction occurs



- The products are aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ), and acid ( $\text{H}^+$ ).
- This is similar to the hydrolysis reaction of ferric ions.
- Aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ) is a white solid.
- If white staining of rocks is seen or a milky appearance of the water present in a stream, chances are good that is aluminum hydroxide.



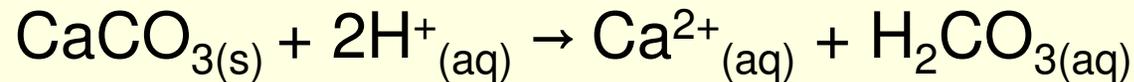
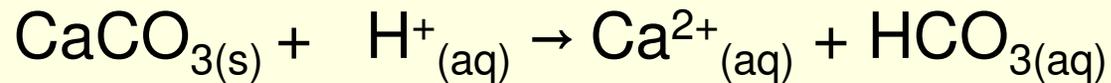
# Limestone and alkalinity

Natural neutralization

# Limestone and alkalinity

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- Limestone is made up primarily of the mineral calcite  $\text{CaCO}_3$  (calcium carbonate)
- It is common to have limestone formations in proximity to coal formations.
- Limestone has alkaline properties – it can directly consume acidity by either of these reactions:

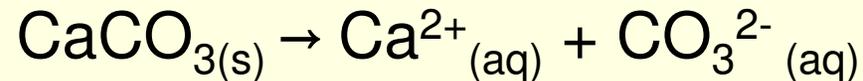
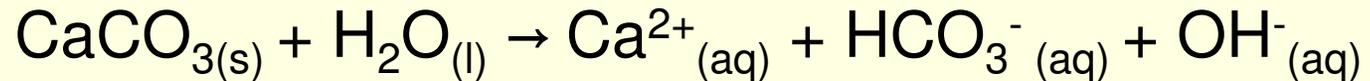


- The presence of limestone can improve the ill effects of AMD by neutralization and by raising the pH of contaminated water.

# Limestone and alkalinity

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- Limestone can also dissolve by the following reactions:

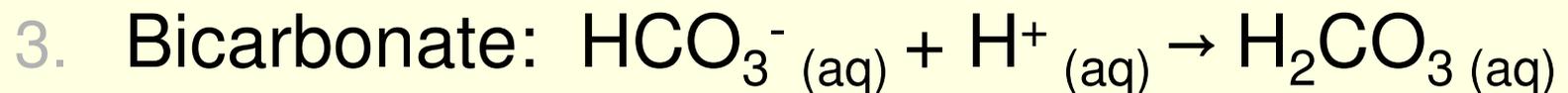
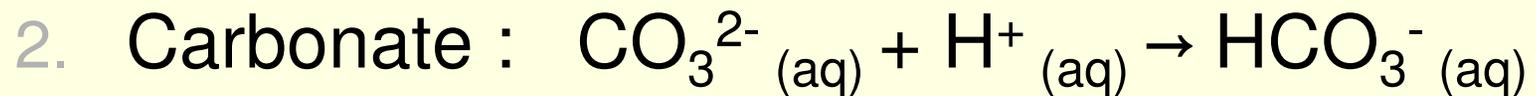
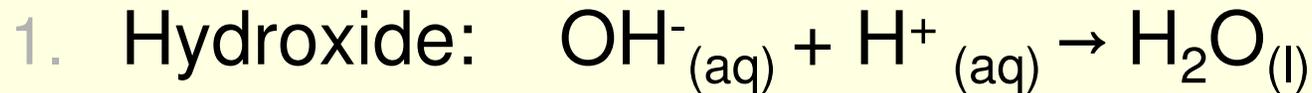


- This can protect a stream by stabilizing the pH close to 6.3 by a set of complex interactions of several related chemical species, collectively known as the carbonate system. *Too complex to discuss here.*
- A stream having appreciable dissolved limestone is called “buffered”... a very good thing... and is more able to withstand assaults by acidic AMD.
- Trout love cold, buffered streams.

# Alkalinity

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In mine water, there is the possibility of having 3 acid consuming species



$$\text{Alkalinity} = [\text{OH}^-] + 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-]$$

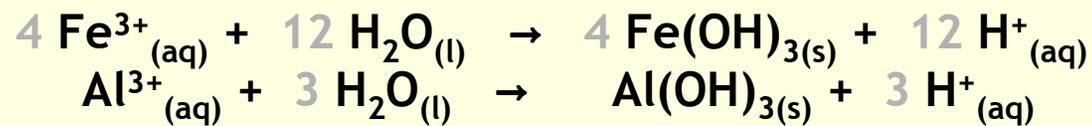
$$\text{Net Alkalinity} = [\text{OH}^-] + 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] - [\text{H}^+]$$

# Quantifying Acidity

Figuring out how much acid is produced  
by all these reactions

# Acidity

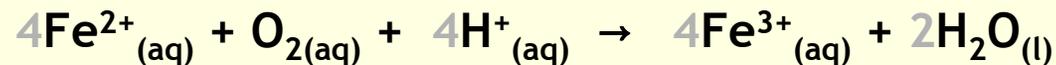
- If you're going to be involved with AMD, one of the measurements that is frequently discussed is acidity. People often have difficulty understanding the term, so here's my explanation.
- Acidity is the ability to consume (neutralize) alkalinity. (and vice versa)
- If we wish to treat AMD, we need to know how much acidity we have in order to figure out how much alkalinity we need to use to neutralize it.
- It might seem that if we know the pH of a sample of mine water (an easy measurement), we can readily figure out its  $[H^+]$  concentration ( $[H^+] = 10^{-\log(pH)}$ ) as the acidity. From that, we should be able to figure out how much alkalinity to add to completely neutralize it. That is true, but only partially.
- Don't forget that there may also be metal ions ( $Fe^{3+}$  and  $Al^{3+}$ ) dissolved in the mine water that can and will undergo hydrolysis as alkalinity is added to raise the pH.



# Acidity (cont)



- The hydrolysis of metal ions always produces additional H<sup>+</sup> ions (mineral acidity) that also need to be neutralized but were not accounted for by the original pH measurement.
- If we also measure the concentrations of the metal ions (Fe<sup>3+</sup> and Al<sup>3+</sup>) we will be able to figure out the H<sup>+</sup> concentrations (3x for Fe<sup>3+</sup>, 3x for Al<sup>3+</sup>) that will come about by metal ion hydrolysis, and include those contributions in the overall acidity.
- There's one other thing we need to consider. Remember that Fe<sup>2+</sup> is converted to Fe<sup>3+</sup> by the following reaction, which consumes one H<sup>+</sup> for every Fe<sup>2+</sup> ion.



- So there will only be 2 net H<sup>+</sup> ions produced (via hydrolysis) for every Fe<sup>2+</sup> ion present.
- The calculation used to figure out the acidity includes terms for the “pH acidity” and the mineral acidities for [Fe<sup>2+</sup>], [Fe<sup>3+</sup>], and [Al<sup>3+</sup>] concentrations.

# Acidity Calculation

- The calculation used to figure out the acidity includes terms for the “pH acidity” and the mineral acidities for  $[Fe^{2+}]$ ,  $[Fe^{3+}]$ , and  $[Al^{3+}]$  concentrations.

**pH and Mineral Acidity as  $CaCO_3 =$**

$$50 \left( \frac{2Mn^{2+}}{54.94} + \frac{2Fe^{2+}}{55.85} + \frac{3Fe^{3+}}{55.85} + \frac{3Al^{3+}}{26.98} + 1000 \times 10^{-pH} \right)$$

**Concentrations of dissolved metals must be in mg/L**

# Characteristics of AMD

Acid mine drainage  
Neutral & alkaline mine drainage

# Variability in AMD from place to place

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- AMD may be either net acidic or net alkaline
- AMD can seriously degrade the aquatic habitat and the quality of water supplies because of toxicity, corrosion, incrustation and other effects from dissolved constituents.
- AMD typically contains elevated concentrations of  $\text{SO}_4^{2-}$ , Fe, Mn, and other ions, but the levels of which are dependent on the local geochemical environment.

# Acid mine drainage

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- mineral acidity exceeds alkalinity
- typically contains elevated concentrations of  $\text{SO}_4^{2-}$ , Fe, Mn, Al and other ions
- may or may not have a low pH (high concentration of  $\text{H}^+$  ions), since the presence of dissolved Fe, Al and Mn can generate hydrogen ions by hydrolysis.
- major source of acidity is oxidation of pyrite ( $\text{FeS}_2$ ) in freshly broken rock that is exposed by mining
- is generally more difficult to treat than alkaline mine drainage

# Alkaline or neutral mine drainage

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- Neutral or alkaline mine drainage has alkalinity that equals or exceeds acidity but can still have elevated concentrations of  $\text{SO}_4^{2-}$ , Fe, Mn and other solutes.
- Dissolution of carbonate minerals produces alkalinity, which promotes the removal of Fe, Al and other metal ions from solution, and neutralizes acidity.
- Neutralization of AMD does not usually affect concentrations of  $\text{SO}_4^{2-}$ .
- Is generally easier to treat than acidic mine drainage