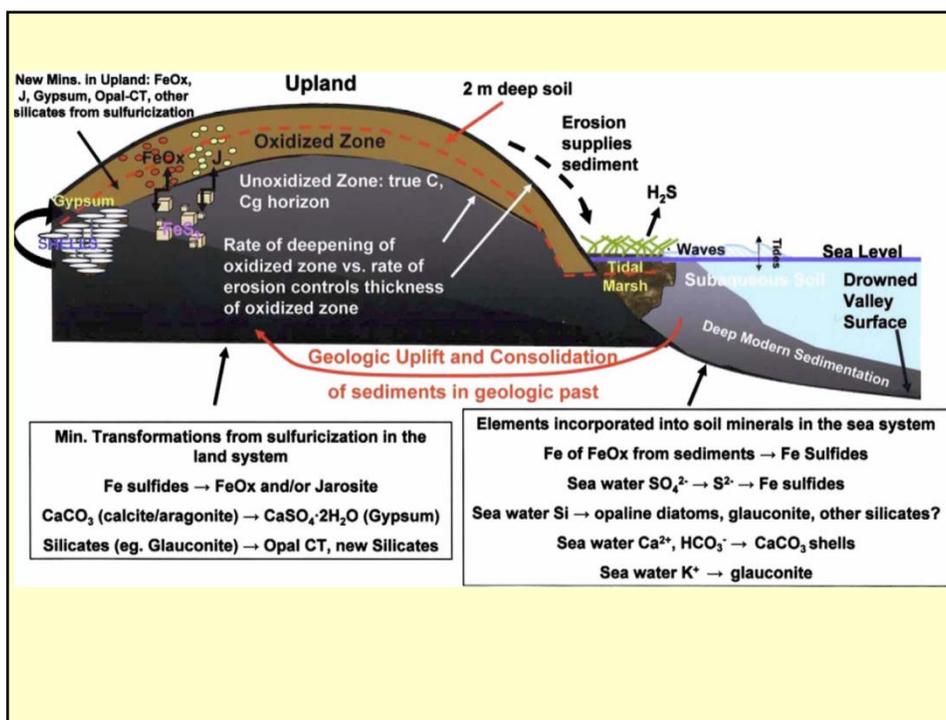


Sulfuricization: What happens when *sulfidic materials* are abruptly exposed to oxidizing conditions?

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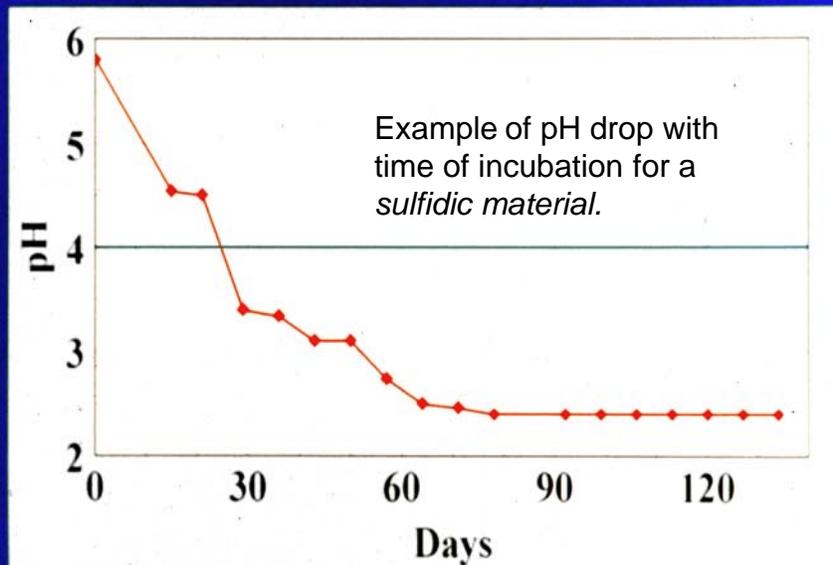
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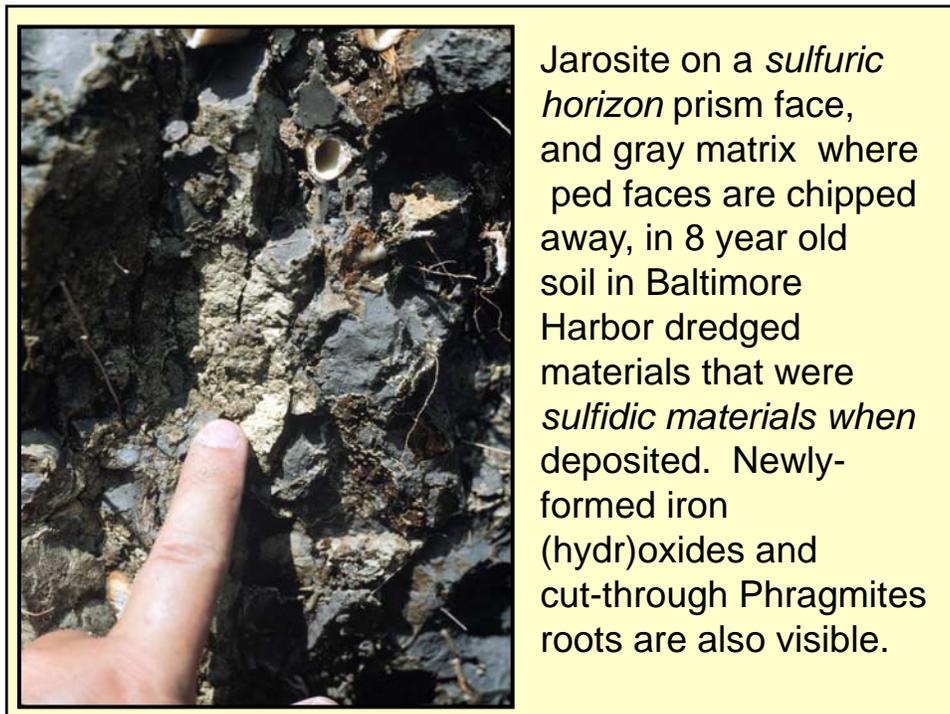
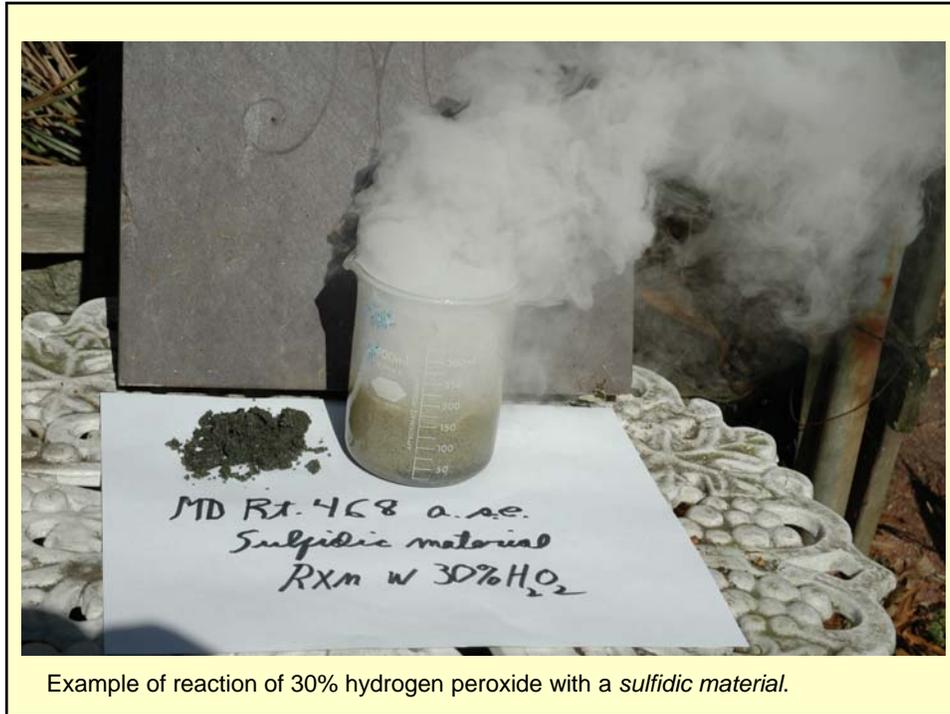


Active Acid Sulfate Soils

- Form where sulfide minerals (most typically iron sulfides and the mineral pyrite) have oxidized in near surface horizons and produced enough sulfuric acid, with insufficient neutralization, to have made the field pH drop to ultra low levels, such that a *sulfuric horizon* as defined by *Soil Taxonomy* is recognized. These soils have also been called raw acid sulfate soils.

Incubation Of Landfill Cover Material From The Fresh Kills Landfill



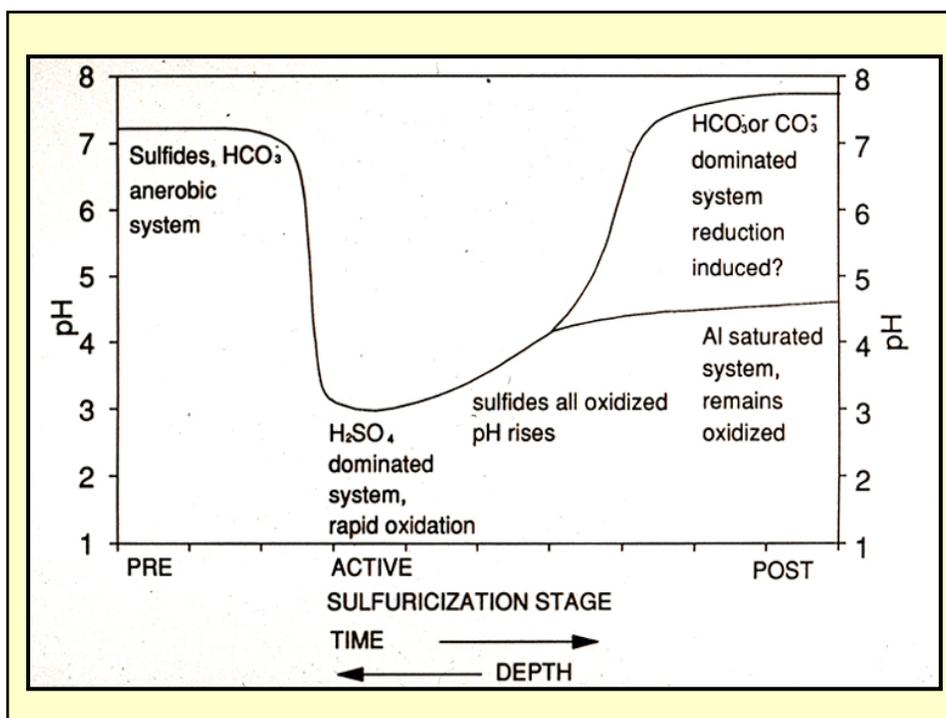


Sulfuricization Defined

- Sulfuricization is the overall process by which sulfide-bearing soil materials are oxidized (and hydrolyzed), minerals are weathered by the sulfuric acid produced, and new minerals are formed from the dissolution products.

Sulfuricization Stages

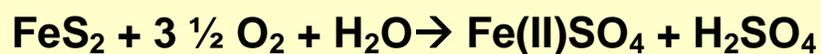
- Stage 1 -- Pre-Sulfuricization.
- Stage 2 – Actively sulfuricizing.
- Stage 3 – Post-sulfuricization
- Can be thought of as a time sequence on an original sulfide-bearing soil material.
- Can also be thought of as a depth sequence – Stage 1 at bottom of column, Stage 2 at top of stage 1, stage 3 as post-active acid sulfate soil at surface of an old stable landscape.



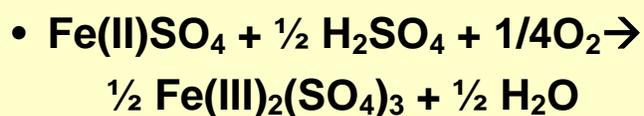
OXIDATION REACTIONS

- When iron sulfide-bearing soil materials are exposed to aerobic conditions the sulfides oxidize to make sulfuric acid.
- Sulfuric acid is also produced upon the hydrolysis of the iron of iron sulfides after the iron is oxidized.
- Some of the main oxidation and hydrolysis reactions are summarized in the following slides.

Oxidation of sulfide of iron disulfide,
e.g. pyrite, by oxygen to form
ferrous sulfate and sulfuric acid

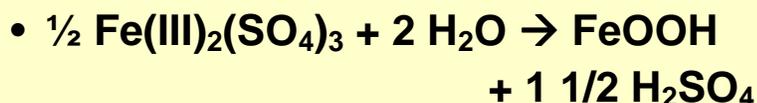


Oxidation of ferrous sulfate
to ferric sulfate



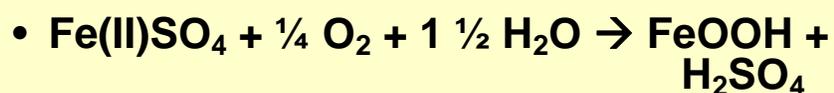
**Note that sulfuric acid, H_2SO_4 , is
consumed in the reaction and that the
oxidant is oxygen (as gas or a
dissolved gas).**

Hydrolysis of ferric sulfate to form an iron oxyhydroxide (e.g. goethite).



Here one and a half moles of sulfuric acid are formed. The iron oxyhydroxide that forms could show up under field conditions as the red gunk in acid mine drainage (AMD) or in acid rock drainage (ARD).

Overall oxidation and hydrolysis of ferrous sulfate.



- This reaction is the combination of the previous two reactions. It shows that the combined oxidation and hydrolysis of 1 mole of ferrous sulfate produces one mole of FeOOH (e.g. the mineral goethite) and one mole of sulfuric acid.

Overall oxidation and hydrolysis of S and Fe of pyrite (or marcasite)

- $\text{FeS}_2 + 3 \frac{3}{4} \text{O}_2 + 2 \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{FeOOH} + 2\text{H}_2\text{SO}_4$
- With complete overall reaction, each mole of pyrite produces 2 moles of sulfuric acid, or we can say that each mole of sulfur makes one mole of sulfuric acid. If one knows the S content of a soil material and assumes it is all in the form of pyrite, one can calculate the quantity of sulfuric acid that can be produced if the reaction goes to completion.

The oxidation of S of pyrite by ferric iron (Fe^{3+}) in solution

- $\text{FeS}_2 + 14\text{Fe (III)} + 8 \text{H}_2\text{O} \rightarrow 15 \text{Fe(II)} + 2\text{SO}_4^{2-} + 16\text{H}^+$
- Under strongly acidic conditions, ferric iron is a rapid and efficient oxidizer of the sulfide of pyrite. It is produced by microbial oxidation of ferrous iron using oxygen by *Thiobacillus ferrooxidans* and other iron oxidizing bacteria, which greatly speed up the rate of the reaction.

A reaction to show the formation of jarosite from ferrous sulfate

- $3 \text{Fe(II)SO}_4 + \frac{3}{4} \text{O}_2 + 4 \frac{1}{2} \text{H}_2\text{O} + \text{K}^+ \rightarrow \text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ (jarosite) + $\text{H}_2\text{SO}_4 + \text{H}^+$
- If assumed that H^+ from right side of equation is consumed by reacting with a silicate mineral (e.g. glauconite) to release the K^+ to form the jarosite, only 1/3 the amount of acid is produced per mole of ferrous sulfate as when the product is FeOOH .

Acid neutralization and other reactions

- Under field conditions these reactions take place simultaneously with the oxidation and hydrolysis reactions shown in the previous slides.

Reaction of sulfuric acid with calcium carbonate

- $\text{H}_2\text{SO}_4 + \text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CO}_2$
- The calcium sulfate formed is the mineral gypsum.
- From this reaction and by knowing the atomic weight of S is 32 and the molecular weight of CaCO_3 is 100, one can calculate that roughly three times the weight of CaCO_3 is needed to neutralize the acidity of a given weight of S as sulfuric acid.

Quantities in Practical Terms based on the sulfuric acid/calcium carbonate reaction

- 1% S in a soil material would represent 10 tons of sulfur for an acre furrow slice weighing 1000 tons.
- If the S was present as pyrite, FeS_2 , and it all oxidized and hydrolyzed according to the overall oxidation and hydrolysis reaction shown previously, this would make 30.625 tons of sulfuric acid.
- 31.25 tons of calcium carbonate would theoretically neutralize this quantity of acid.

Reaction of H^+ to release Al^{3+} from silicate minerals

- The hydrogen ion, H^+ , readily reacts with aluminosilicate (e.g. clay) minerals to release Al^{3+} (presumably 3 H^+ to release each Al^{3+}). The Al^{3+} under strongly acidic conditions, as in active acid sulfate soils, is toxic to plants; when in waters of AMD or ARD, also to fish etc.
- Silica can also be released into solution as silicic acid, H_4SiO_4 , and can go to form new silicate minerals, especially when the pH of percolating waters is raised, e.g. by encounter a calcareous horizon/layer.

Production of acid-forming sulfate salts during sulfuricization

- **Ferrous and ferric sulfates are water soluble. If soil solutions in which they are dissolved dry, these salts can come out of solution as bitter tasting salt minerals such as rozenite, $Fe(SO_4) \cdot 4H_2O$ or melanterite, $Fe(SO_4) \cdot 7H_2O$ in the case of ferrous sulfate.**
- **Reaction with silicates can release Al to form Al sulfates or mixed Fe Al sulfates or hydroxysulfates such as the halotrychite, $Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$, found at the surface of active acid sulfate soils at the new Stafford County, VA Airport in 2001.**

Salts accumulate at surface of active acid sulfate soils during dry periods.

- The flushing of Fe and Al sulfate salts into waterways followed by the oxidation and hydrolysis of the dissolved Fe and hydrolysis of the Al in the water produces AMD and ARD – very acid waters in streams with stream beds coated with iron (hydr)oxide precipitates – very poor for fish and other aquatic organisms. This can result in “dead” streams.
- This is commonly regarded as the most severe environmental problem associated with active acid sulfate soils.

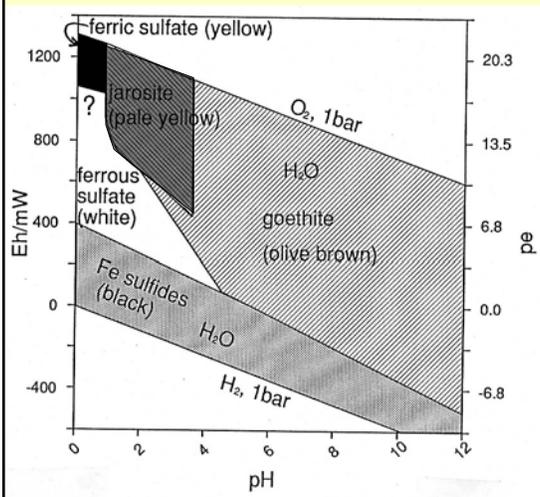


Blisters of acid-forming Fe and Al sulfate salts at the surface of an active acid sulfate soil in Guiné Bissau, West Africa, during climatic dry season.



Dead Stream, Quantico Creek, downstream of old pyrite mine in Prince William Forest Park, VA, seen in 1980. An example of severe AMD.

S-Fe-Water Eh/pH Stability Diagram



- Strength of oxidizing conditions increase upward in diagram – units designated in millivolts for Eh or as pe for electron activity – strength of reducing conditions increases downwards.
- pH increases to right, more acid to the left.

In summary

- We have considered what acid sulfate soils are and the different varieties of them – potential, active and post-active.
- We also considered oxidized vs. unoxidized zones of soil-geologic columns.
- We also considered *sulfidic materials* and the *sulfuric horizon* – taxonomically defined terms that are characteristic of potential and active acid sulfate soils, respectively, and how they form.

Summary Continued

- Iron sulfide minerals, especially pyrite, form in tidal marsh soils and in estuarine and marine sediments by reactions in which S of sulfate (from sea water) and Fe of Fe(hydr)oxides in sediments are chemically reduced by microbes, that oxidize organic matter under anaerobic conditions, and then combine by precipitation to form iron sulfides in an overall process called sulfidization.

Summary continued – last slide

- Upon exposure to aerobic conditions, Fe sulfides oxidize and the oxidized Fe is hydrolyzed to produce sulfuric acid and Fe (hydr)oxides and other minerals under low pH, such as jarosite, during an overall process called sulfuricization.
- Given sufficient time (commonly some decades) all the sulfides can be oxidized away in surficial horizons and the soil can become a post-active acid sulfate soil.
- The amount of lime to neutralize the acid produced can be estimated from the S content of soil materials based on chemical reactions.