

Hydrogen Sulfide in Reservoirs: Chemistry Affecting its Formation, Impacts, Fate, and Management Implications

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Sources of Hydrogen Sulfide, H_2S

- ◆ From where does hydrogen sulfide come?

Sources of Sulfur

- ◆ Sulfur is a ubiquitous element.
- ◆ Various sulfur compounds are present in:
 - The atmosphere
 - Minerals
 - Soils
 - Plant tissue
 - Animal tissue
 - Microbial biomass
 - Sediment
 - Water

General Forms of Sulfur in the Environment

- ◆ Organic sulfur in living plant, animal, and microbial tissue (as essential components of amino acids and proteins)
- ◆ Organic sulfur primarily in soil and sediments as humic material (naturally occurring soil and sediment organic matter)
- ◆ Inorganic sulfur compounds in the atmosphere (sulfur dioxide, SO_2 , and others)
- ◆ Inorganic forms in upland **oxidized** soils and surface waters (sulfate, SO_4^{2-} , is the primary compound). Seawater contains about 885 mg/L (ppm) of sulfate-sulfur and sodium sulfate, NaSO_4^-
- ◆ Inorganic forms in **strongly reduced** sediment and water environments (elemental sulfur, S^0 , and sulfide, S^{2-})

Questions about Sources

- ◆ 1. Is hydrogen sulfide only formed where humans have had an impact on water quality. No.
- ◆ 2. Is hydrogen sulfide more of a problem where humans have had an impact on water quality? Probably

Conditions Required for the Formation of Hydrogen Sulfide

Aerobic and Anaerobic Conditions in Water and Sediment:

This is important to the chemical speciation of elements, affecting which compounds predominate, and thus the solubility, availability, and toxicity of many elements and compounds, **including sulfur** compounds.

Terms and Definitions:

AEROBIC

oxygen present

oxic

oxidized

ANAEROBIC

oxygen absent

anoxic

reduced

(Oxidation- Reduction Conditions, or, Redox Conditions refers to where we are in terms of the **intensity** of aerobic and anaerobic environments)

Range of Oxidized and Reduced Conditions

- ◆ If gaseous oxygen is present in the pore space of a soil, or, if dissolved oxygen is present in surface water or pore water of sediment, then that is all we need to know about the redox chemistry of many important chemical species (nutrients and toxic substances).
- ◆ If gaseous or dissolved oxygen **is not present**, an environment is "anaerobic," or "anoxic," or "reduced." **However**, now the **intensity** of reduction becomes important affecting what chemical species are formed and are stable. There is a wide range in reduction intensity.

Sequence of the Reduction of these Electron Acceptors

Regarding hydrogen sulfide production and stability, the **sequence** or order of reduction of these oxidized species is important.

Reduction Sequence:

First

Oxidized Conditions

O₂ present

O₂ ---→H₂O

Second

Weakly Reducing Conditions

NO₃⁻ → N₂
Mn⁴⁺ → Mn²⁺

Third

Moderately Reducing Conditions

Fe³⁺ → Fe²⁺

Last

Strongly Reducing Conditions

SO₄²⁻ → H₂S
CO₂ → CH₄

Depletion of Oxygen in Flooded Soils, Sediments, and Water:

Depletion of oxygen in bottom waters and sediments requires two processes:

- ◆ 1. The **consumption** of oxygen, and,
- ◆ 2. **Restricting re-supply** of oxygen.

B. Consumption of Oxygen by Microbial Respiration

- ◆ Respiration is a biological process where mostly organic matter serves as a food source, and, as organic matter is oxidized by oxygen, energy is released.
- ◆ Large numbers of microbes in soils, sediments and water also use oxygen in respiration.



Thus oxygen is consumed in surface water, soils, and sediments.

C. Re-supply of Oxygen Consumed by Respiration in Upland Soils (#1)

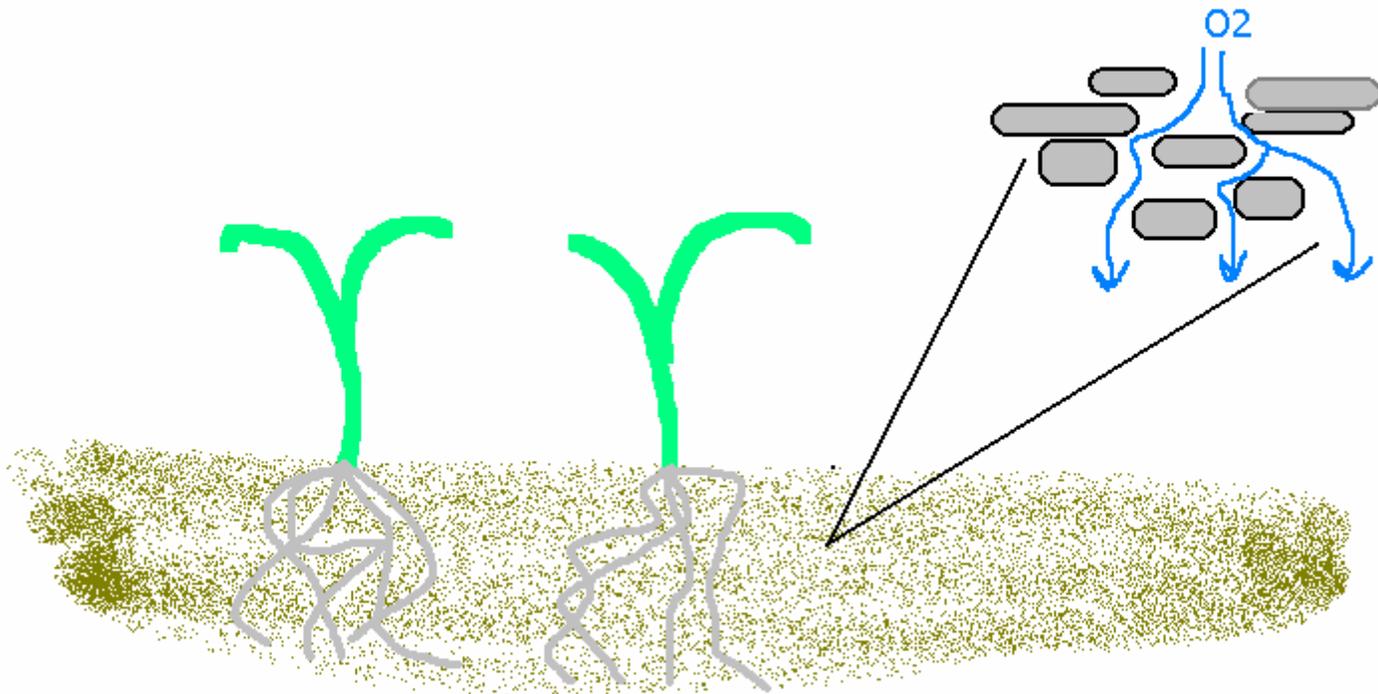
- ◆ The atmosphere is about 21% oxygen, thus there is a plentiful supply.
- ◆ Wind currents mix oxygen in the atmosphere and in the near-ground environment effectively, keeping the concentration uniform.

C. Re-supply of Oxygen Consumed by Respiration in Upland Soils (#2)

- ◆ Oxygen in a gas form (O_2 in the atmosphere) diffuses rapidly. Consider a typical, upland soil that is about 50% interconnected pore space. Gaseous oxygen diffuses rapidly down through the interconnected pore space reaching microbes and plant roots deep in the soil.
- ◆ In summary, there is little limitation in oxygen re-supply in upland, drained soils because diffusion of oxygen through open pore space as a gas is rapid.

Atmosphere, 21% oxygen

Rapid downward diffusion of oxygen through interconnected pore space



D. Re-supply of In Shallow Surface Waters (Streams, Rivers, Bays, Lakes) (#1)

- ◆ In shallow surface waters, dissolved oxygen is usually present from top to bottom in a fairly uniform concentration, such that fish and bacteria can use oxygen for respiration.
- ◆ Stratified lakes and reservoirs are an exception we will cover soon.

D. Re-supply of Oxygen Consumed by Respiration In Shallow Surface Waters (Streams, Rivers, Bays, Lakes)(#2)

- ◆ Dissolved oxygen is usually present in a uniform concentration in shallow water systems because of:
- ◆ rapid transfer of oxygen across the atmosphere – water interface
- ◆ photosynthetic production of oxygen by algae in the water column
- ◆ wind and current mixing of the water column
- ◆ convection (heat currents) mixing of the water column
- ◆ In summary, there is plenty of dissolved oxygen in shallow surface waters

Atmosphere

Oxygen



Oxidized Surface Water

Oxygen concentration uniform because:

- oxygen supply from atmosphere
- oxygen release from algae
- wind mixing
- convection currents

Thin Oxidized Sediment Layer



Thick, Reduced Sediment Layer



E. Limitations in the Re-Supply Rate of Oxygen in Sediments (#1)

- Water saturating sediment pore space is essentially not moving. With no mixing, dissolved oxygen can only move by the slow process of aqueous diffusion.
- ◆ Oxygen dissolved in water diffuses very slowly.
- ◆ Oxygen diffusion in water is about 0.01% as fast as diffusion in air.

E. Limitations in the Re-supply Rate of Oxygen in Sediments (#2)

- ◆ As a consequence, oxygen is used up by respiring microorganisms before it moves very deep, and microbes in most of the sediment must use chemicals other than oxygen for respiration.

E. Limitations in the Re-supply Rate of Oxygen in Sediments (#3)

- ◆ In summary , in hypolimnions (stratified bottom waters) and sediment pore waters, mixing is not occurring and the consumption of oxygen is faster than the re-supply rate resulting in no dissolved oxygen.

F. Substitute Electron Acceptors are Used when Oxygen is Depleted (#1)

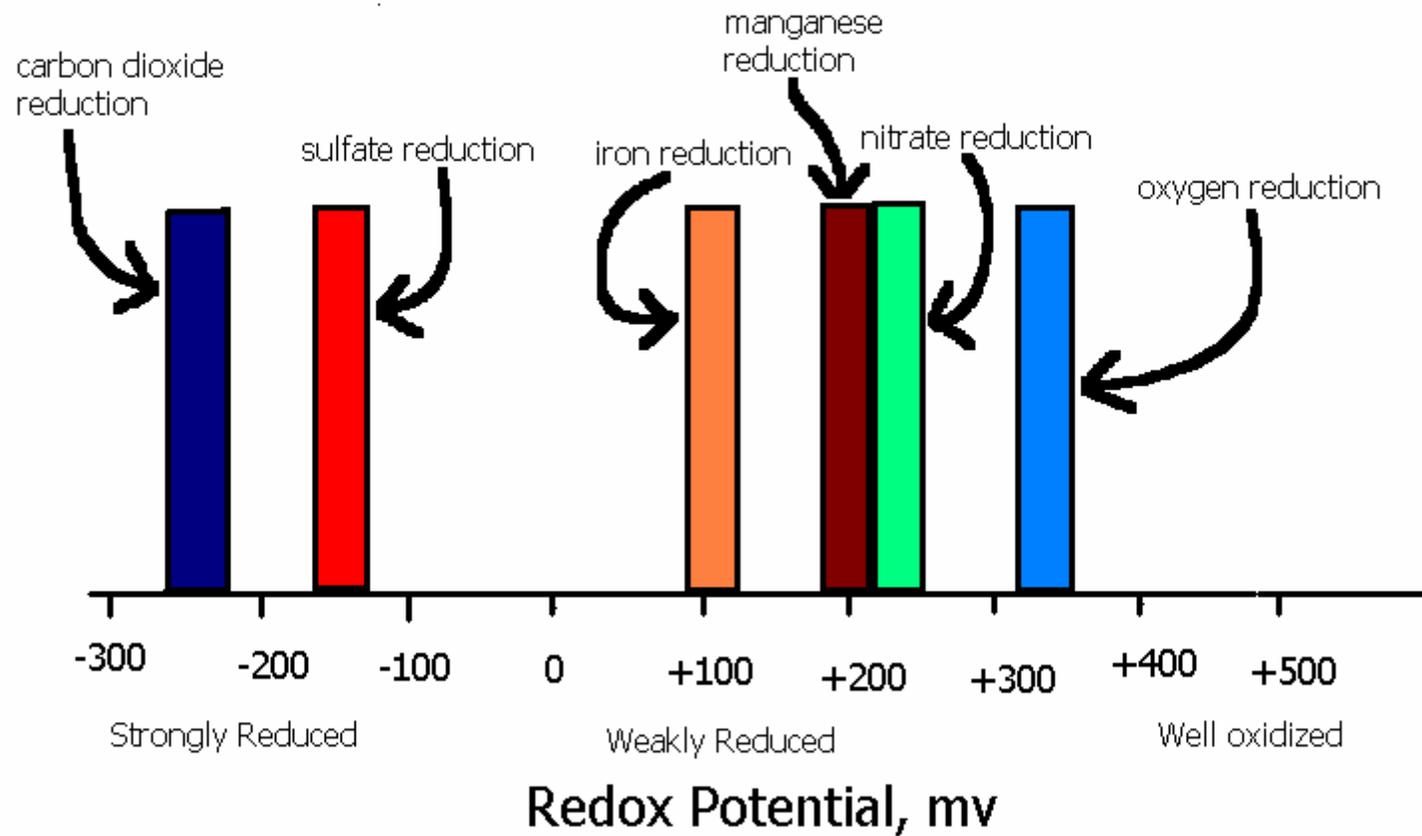
- ◆ Humans, as all higher animals and fish, require O_2 for respiration.
- ◆ Many bacteria living in soils, sediments, and water must also have oxygen for respiration.
- ◆ Some bacteria can use other chemical species in place of O_2 as a terminal electron acceptor.
- ◆ Some bacteria cannot use oxygen in respiration, but must use other chemical species.

F. Substitute Electron Acceptors are Used when Oxygen is Depleted (#2)

- ◆ As long as oxygen is present in soils, water, and sediments, microbes “prefer” using oxygen as the terminal electron acceptor in respiration.
- ◆ When oxygen is used up by microbes faster than it is being replenished, then the microbes have to switch to other chemical species as an electron acceptor in respiration.

Electron Acceptors in Microbial Respiration Other Than Oxygen, and the Chemicals Formed:

Element	Oxidized Form	Properties	Reduced Form	Properties
Oxygen (O ₂)	O ₂	Gas or dissolved gas	H ₂ O	Liquid
Nitrogen (N)	NO ₃ ⁻	Soluble ion	N ₂ , NH ₄ ⁺	Gas, Soluble ion
Manganese (Mn)	MnO ₂ (Mn ⁴⁺)	Insoluble	Mn ²⁺	Soluble ion
Iron (Fe)	Fe ₂ O ₃ (Fe ³⁺)	Insoluble	Fe ²⁺	Slightly soluble ion
Sulfur (S)	SO ₄ ²⁻	Soluble ion	S ²⁻ , HS ⁻ , H ₂ S FeS, FeS ₂	Soluble, Soluble gas insoluble, insoluble
Carbon (C)	CO ₂ , CO ₃ ²⁻ , HCO ₃ ⁻ , or acetate	Gas, Slightly Soluble, Soluble	CH ₄	Gas, not soluble



~~Oxidized and Reduced~~ Conditions in Reservoirs (#1)

Shallow pond or deep lake or reservoir in
the cool seasons:

-During the cool seasons (late fall, winter, and spring), the chemistry and microbiology of the water column is fairly uniform from top to bottom.

~~Oxidized and Reduced~~ Conditions in Reservoirs (#2)

Deep lake or reservoir during the
summer:

- Deep water systems may undergo thermal stratification in the summer, warmer surface waters and cool to cold bottom water. These layers do not mix.

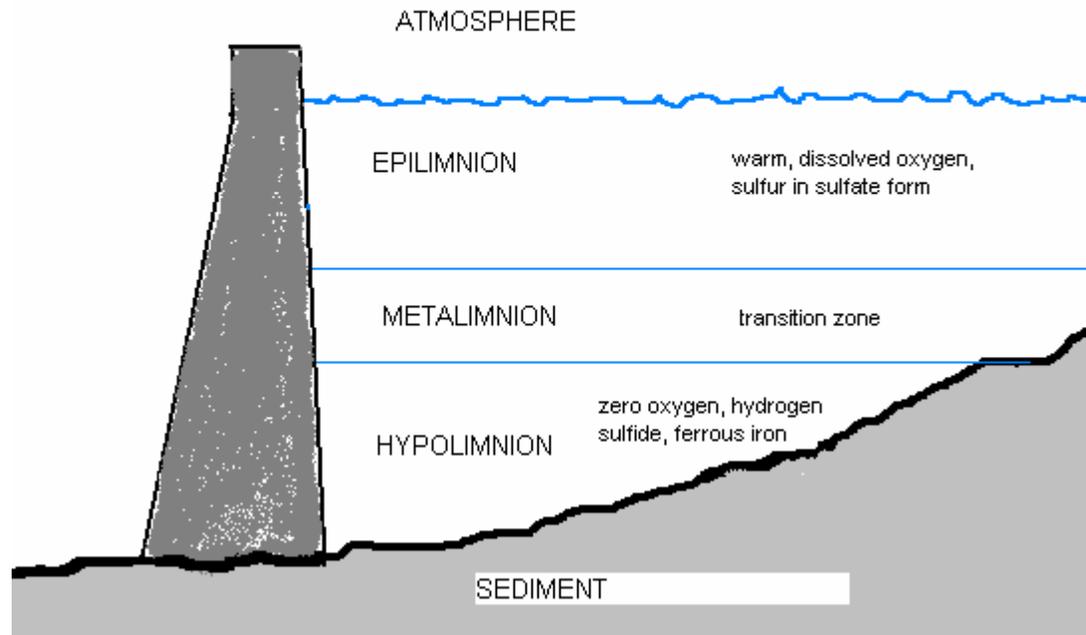
Oxidized and Reduced Conditions in Reservoirs (#3)

- As a consequence, dissolved oxygen levels are adequate for fish and microbial respiration in the surface waters.

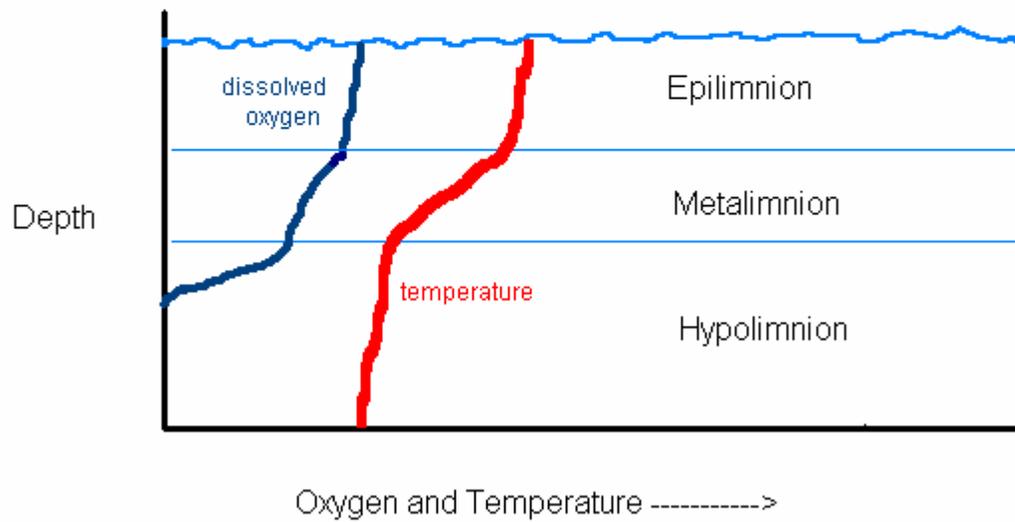
Oxidized and Reduced Conditions in Reservoirs (#4)

- However, microbial respiration causes the bottom water to become anoxic (anaerobic, or reducing).
- Initially, the bottom water is weakly reducing, but, with time becomes more strongly reducing to a point that sulfate is reduced to sulfide.

Stratified Reservoir



Stratified Reservoir, Oxygen and Temperature Profile



Problems With Hydrogen Sulfide (#1a)

- Hydrogen sulfide, H_2S , is a malodorous, toxic, water soluble, acidic gas.
- Hydrogen sulfide can be a nuisance. The human nose is extremely sensitive to its odor:
 - One can often detect H_2S odor working in coastal marshes.
 - Story of graduate student mixing coastal sediment inside a building.



Problems With Hydrogen Sulfide (#1b)



- Reservoir tail-water releases may release hydrogen sulfide to the atmosphere behind a dam.
- Hydrogen sulfide can be released from sewage treatment plants or collection pipe systems.

Problems with Hydrogen Sulfide (#2a)

Hydrogen sulfide can be a problem due to chronic toxicity or its corrosivity:

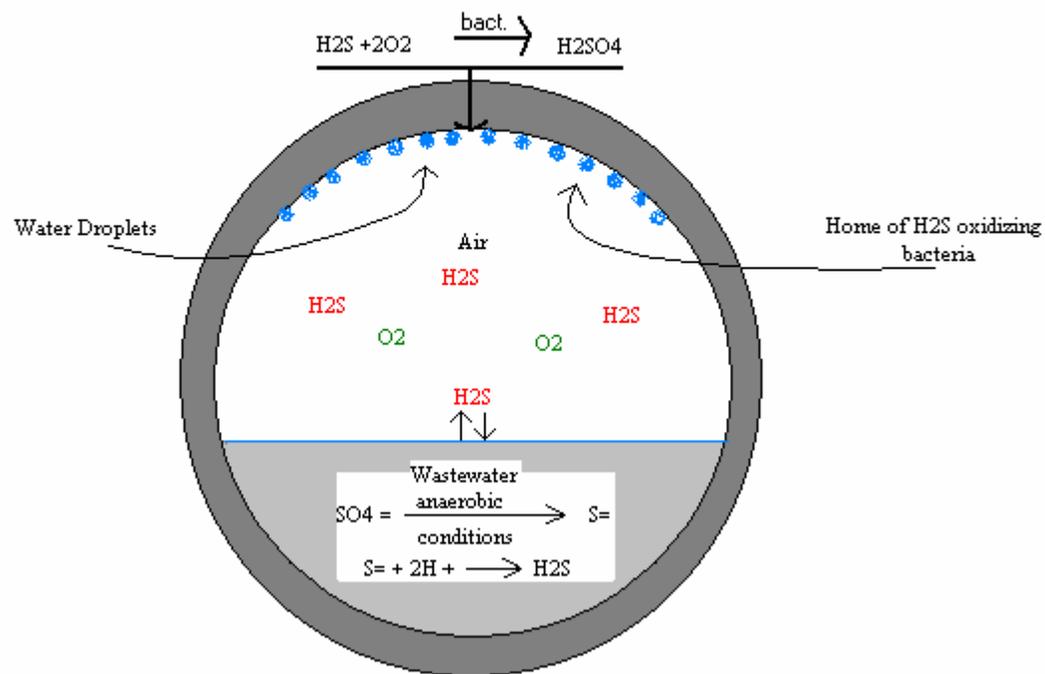
- Under certain conditions, hydrogen sulfide in coastal marsh soils stresses marsh grasses resulting in poor growth, contributing to marsh deterioration (one of may factors contributing to marsh deterioration).
- Hydrogen sulfide can corrode metal pipes and erode concrete structures.





Problems with Hydrogen Sulfide (2b)

- a problem with some reservoir dams and conduits
- a major problem with municipal sewer systems
- buried main sewer lines have collapsed due to steel and concrete pipes being completely eaten away.



Problems with Hydrogen Sulfide (#3a)

Hydrogen sulfide can be deadly:

-example of truck driver dumping industrial waste into a pond

Somewhat diluted NaS + somewhat diluted HCl → Na Cl + H₂S

sodium
sulfide

hydrochloric
acid

sodium
chloride

hydrogen
sulfide

-example of two oil industry workers inspecting large tank in coastal Louisiana

Problems with Hydrogen Sulfide (#3b)

Hydrogen sulfide can be deadly:

--example of a rural East Texas family exposed to hydrogen sulfide released during a problem at a gas well

--recent news story about men working inside a pipeline in a city in Pennsylvania

--Fortunately with hydrogen sulfide in reservoirs and tail-waters, we're usually just dealing with nuisance concentrations that cause odor and corrosion problems.

Odor Thresholds of Selected Substances in Air

(adapted from Olishifski, 1971)

<u>Substance</u>	<u>Description</u>	<u>Concentration</u> (Causes faint odor) -mg/L-
hydrogen sulfide	rotten egg	0.0011
allyl sulfide	garlic odor	0.00005
amyl acetate	banana odor	0.0006
chlorine	irritating odor	0.010
crotyl mercaptan	skunk odor	0.000029
ozone	slightly pungent	0.001

Is it Hydrogen Sulfide (H₂S) that is Causing the Odor Problems? (1)

- ◆ – Probably, but we need to be sure.
- ◆ – There are several reduced sulfur gases that include:
 - ◆ – carbon disulfide, CS₂
 - ◆ – carbonyl sulfide, COS
 - ◆ – methanethiol, CH₃-SH
 - ◆ – dimethyl sulfide, CH₃-S-CH₃
- ◆ – These other reduced sulfur gases do tend to be found in much lower concentrations where people have looked for them, however ...
- ◆ – There are reports from various types of wetlands where some other reduced sulfur gases are released in greater quantities than H₂S.

Is it Hydrogen Sulfide (H_2S) that is Causing the Odor Problems? (2)

- ◆ – Some of these other reduced sulfur gases smell somewhat like H_2S , yet have a much lower odor detection threshold. The odor detection threshold of methanethiol is reported to be 300 times lower concentration than for hydrogen sulfide.
- ◆ – Some of these other reduced sulfur gases form before hydrogen sulfide is produced as a sediment or anoxic water layer is getting more strongly reduced.
- ◆ – Has been reported some are more stable in presence of oxygen and thus may contribute to more water-air fluxes than H_2S .

Chemistry of Hydrogen Sulfide

Requirements for Formation of Hydrogen Sulfide in Lake Sediments and Stratified Lake Bottom Waters:

- Strongly reducing conditions
 - strongly reducing conditions are normal beneath about 1 centimeter in lake sediments.
 - strongly reducing conditions often develop with time (many days to a few weeks) in bottom waters (hypolimnion) of stratified lakes in the summer.
- Dissolved sulfur in the sulfate form (SO_4^{2-}). Normally, there is some dissolved sulfate present.
- Conditions otherwise favorable for bacteria

Microbial Production of Hydrogen Sulfide, H₂S

The following reaction is done by the *Desulfovibrio* bacteria:



S²⁻ is sulfide but it does not stay in this form if pH is less than about 9.5. In water it reacts as follows:



H₂S begins to form just above pH 8.0 and predominates at pH 7.0 and below.

Forms of Sulfide:

◆ a: Soluble or Gaseous:

- H_2S (a soluble gas at near neutral pH levels and below)
- HS^- (a soluble anion at just above neutral pH conditions)
- S^{2-} (a soluble anion at higher than typical pH levels)

b: Insoluble (precipitates):

Insoluble metal sulfide precipitates such as: CuS , ZnS , FeS , CdS , PbS , HgS , and others. They are stable in strongly reducing environments.

Examples of Sulfide and Ferrous Iron Released from Sediments (1)

Net Flux of Various Components from Water Column Above a Sediment Composite Taken from DeGray Reservoir, Arkansas.

Flux for Sediment

<u>Component</u>	<u>Treatment</u>		<u>Transport Between</u>
	-g·m ⁻² ·day ⁻¹ -	- moles-	
dissolved O ₂	- 123.0		water to sediment
total soluble Fe	+ 10.2	0.18M	sediment to water
total soluble Mn	+ 9.5	0.17M	sediment to water
dissolved SO ₄ ²⁻	- 41.0		water to sediment
released S ²⁻	+ 13.7	0.42M	assuming all SO ₄ ²⁻ --> S ²⁻ and S ²⁻ released to water

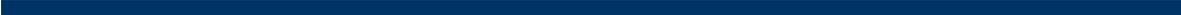
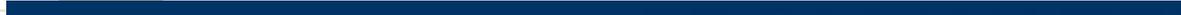
adapted from Gunnison and Brannon, 1981. Tech. Rept. E-81-6, WES, USCOE

Examples of Sulfide and Ferrous Iron Released from Sediments (2)

Reduction and Release of Various Components in Reservoirs and Other Environments

<u>Component</u>	<u>Environment</u>	<u>Rate</u>
		- g·m ⁻² ·day ⁻¹ -
Fe ²⁺ release	anoxic reservoir hypolimnion	0.11 - 0.35
Mn ²⁺ release	anoxic reservoir hypolimnion	0.49 - 0.74
sulfide production	anaerobic sediments	0.40
H ₂ S release	coastal marine sediments	0.22 - 5.2

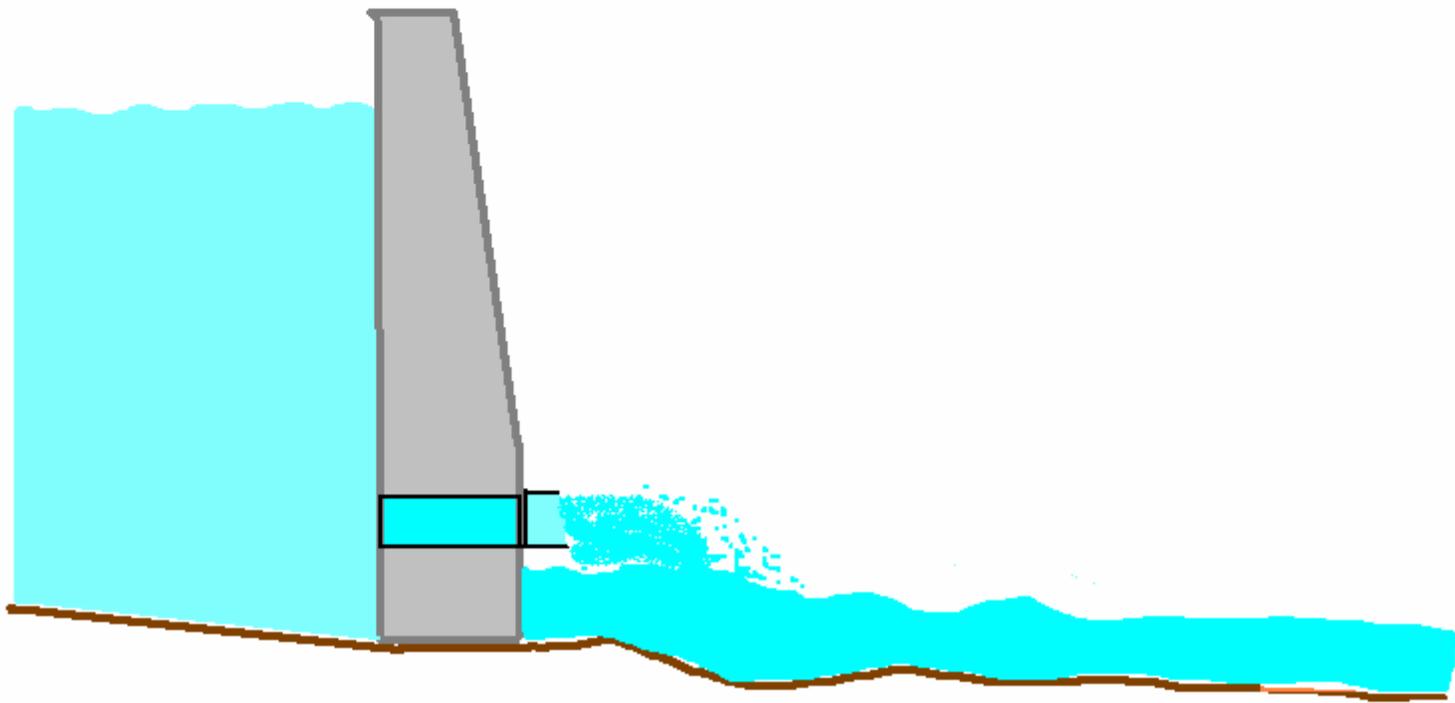
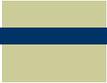
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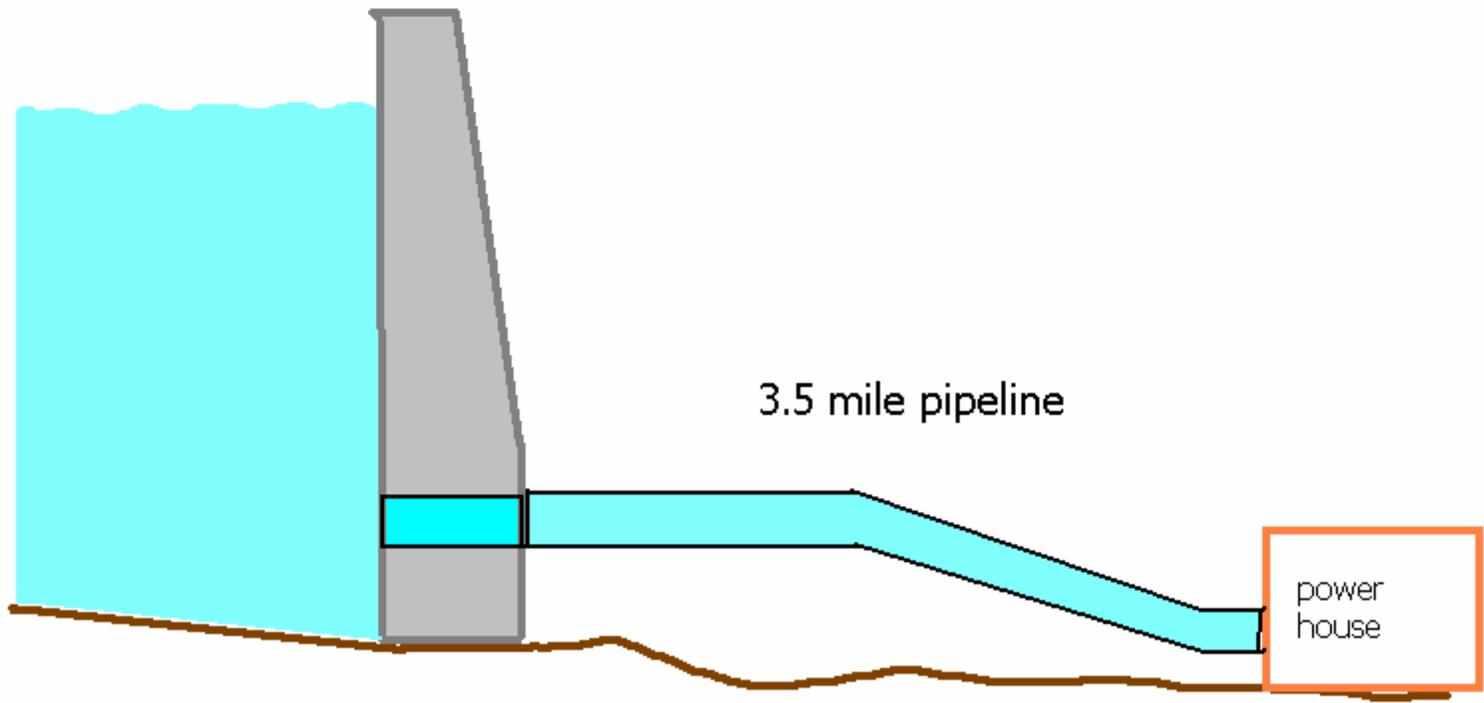


REMOVING HYDROGEN SULFIDE FROM WATER (OR OTHERWISE DEALING WITH THE PROBLEM)

GENERAL COMMENTS

- ◆ Very low concentrations in water contribute to threshold of detection by humans. This water concentration is reported to be between 0.00001 and 0.0001 mg/l (from US EPA. 1974. EPA 625/1-74-005)
- ◆ Feasible removal methods depends on whether we're dealing with wastewater collection and treatment systems, or reservoirs, and, also site specific conditions associated with each.
- ◆ Mention an example with reservoir tailwaters.
- ◆ Most of the experience in dealing with H₂S emissions from reservoirs comes from wastewater treatment systems. Many of these won't work with reservoir problems, but, some are presented here for introducing ideas.







POSSIBLE METHODS

- ◆ Some used, some feasible, some not. Just some brainstorming mixed with some important chemistry considerations
- ◆ Methods for dealing with the problem include possible physical and chemical methods.

PHYSICAL METHODS

- ◆ – Remove the people affected by the H₂S odor.
- ◆ – Purge the H₂S out of the waters in the forebay.
- ◆ – Release epilimnetic waters instead of hypolimnetic waters (no H₂S).
- ◆ – Mix hypolimnetic with epilimnetic waters to reduce the concentration of H₂S if other water quality objectives can be met.

Chemical Removal from Water, Natural Oxidation

- ◆ Oxidation with dissolved oxygen (occurs under natural conditions and as a wastewater treatment):



- ◆ This reaction is usually too slow to treat reservoir tail waters. It has been reported to take as long as 2 days for H_2S to be oxidized if exposed to ambient levels of dissolved oxygen.
- ◆ Thus mixing surface water containing dissolved oxygen with sulfide-containing hypolimnetic waters does not result in sufficiently rapid oxidation of H_2S .

Chemical Removal from Water, Oxidation by Aeration (air injection)

- ◆ Pumping air into hypolimnetic waters in front of dam, a combination of processes may occur
- ◆ As mentioned, oxidation with ambient oxygen levels is slow, how much volume would require pumping air into hypolimnion?
- ◆ Are we trading tailwater releases for H_2S release in the aerated forebay?
- ◆ As mentioned elsewhere, aeration may purge CO_2 quicker than H_2S and shift H_2S to HS^-

Chemical Removal from Water, Oxidation with Chlorine (for wastewater)

- ◆ $\text{H}_2\text{S} + \text{Cl}_2 \rightleftharpoons 2\text{HCl} + \text{S}^0$ (S^0 is elemental sulfur, a solid)
- ◆ This is reported to be a fast reaction in wastewater systems.
- ◆ Sulfate produced if excess chlorine added, however ...
- ◆ The elemental sulfur formed may increase turbidity, depending on levels.
- ◆ Other odorous sulfur compounds have been noted in treated wastewater requiring further treatment steps.
- ◆ May get some other undesirable chemical species produced.
- ◆ May need to deal with residual chlorine
- ◆ Generally not feasible for reservoir tailwaters.

Chemical Removal from Water, Oxidation with Sodium Hypochlorite (for wastewater)

- ◆ Sodium hypochlorite, NaOCl, has shown to be effective for H₂S odor control at municipal waste treatment plants.
- ◆
$$\text{H}_2\text{S} + 4 \text{NaOCl} \text{ -----} > \text{H}_2\text{SO}_4 + 4\text{NaCl}$$
- ◆ Theoretically, about 9 ppm of NaOCl required to oxidize 1 ppm of H₂S, but in practice weight ratios reported effective range from 5:1 to 15:1.
- ◆ Disadvantage of possibly generating chlorinated by-products in water being treated.

Chemical Removal from Water, Oxidation with Hydrogen Peroxide

- ◆ Hydrogen peroxide will oxidize H_2S



- ◆ A 30 minute reaction time may be required
- ◆ Theoretically, 1 ppm of H_2O_2 should oxidize 1 ppm of H_2S , in practice, a vendor says it varies from 1:1 to 5:1, and recent experience with a reservoir indicates a much higher ratio may be needed.
- ◆ Elemental sulfur, S^0 , as colloidal particles may be formed. This may or may not be a problem.
- ◆ Any excess H_2O_2 breaks down into water and oxygen, no problem with residues.

Chemical Removal from Water, Precipitation with Reduced Iron in Particular (2)

- ◆ Why do we find both soluble ferrous iron, Fe^{2+} , and H_2S in hypolimnetic waters?
- ◆ The solubility product constant of the FeS precipitate would indicate we should not find soluble reduced iron and hydrogen sulfide in the hypolimnetic water. The above reaction alone should prevent H_2S from being a problem in many reservoirs.
- ◆ In coastal sediments exposed to high levels of sulfate, H_2S levels are low to moderate.
- ◆ Is the reaction kinetics too slow for compounds present at only a few parts per million?

Chemical Removal from Water, Precipitation with Reduced Iron in Particular (3)

- ◆ Is the reduced iron complexed with soluble organic matter such that it is present as a soluble, neutral species instead of as the reactive cation?
- ◆ (soluble [Fe-organic matter] complex instead of soluble Fe^{2+} ?)
- ◆ If indigenous ferrous iron is ineffective due to its complexation with organic matter, would the addition of inorganic ferrous iron be effective?
- ◆ A small amount of added dissolved oxygen with ferrous iron enhances H_2S removal over just Fe^{2+} additions alone.

Chemical Removal from Water, Precipitation with Reduced Plus Oxidized Iron

- ◆ In wastewater treatment systems, a mixture of ferrous and ferric iron has been found to be more effective than adding either one alone:

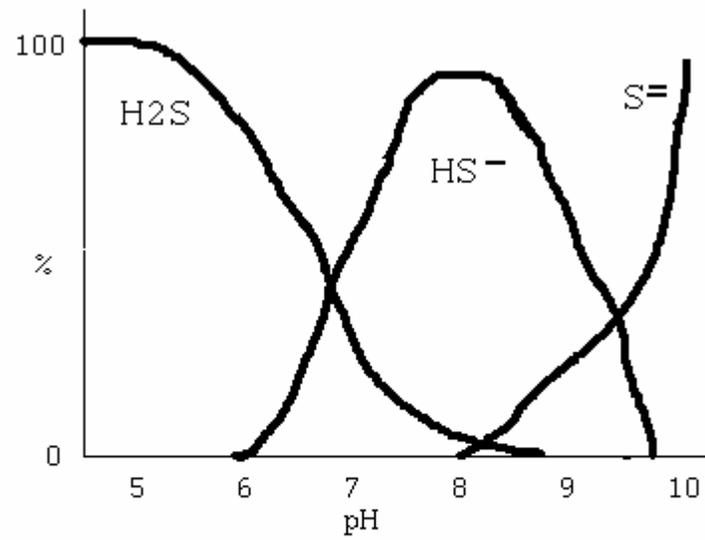


Chemical Removal from Water, pH Adjustment to Convert to Less Volatile Sulfide Species (1)

- H_2S is volatile and can be released as a gas in tailwaters and municipal waste treatment systems. The HS^- form is not volatile and remains in the water where other oxidative processes may remove it with time.
- ◆ Adjusting pH to change the speciation of hydrogen sulfide (H_2S to HS^-).
- ◆
 - Sulfide is 80% H_2S at pH 6.4, but 80% HS^- at pH 7.6.
 - – At municipal waste treatment plants, air stripping alone can remove dissolved CO_2 more rapidly than H_2S . The resulting increase in pH shifts the equilibrium to HS^- , thus some H_2S may be released initially, but some is converted to non-volatile forms.

Chemical Removal from Water, pH Adjustment to Convert to Less Volatile Sulfide Species (2)

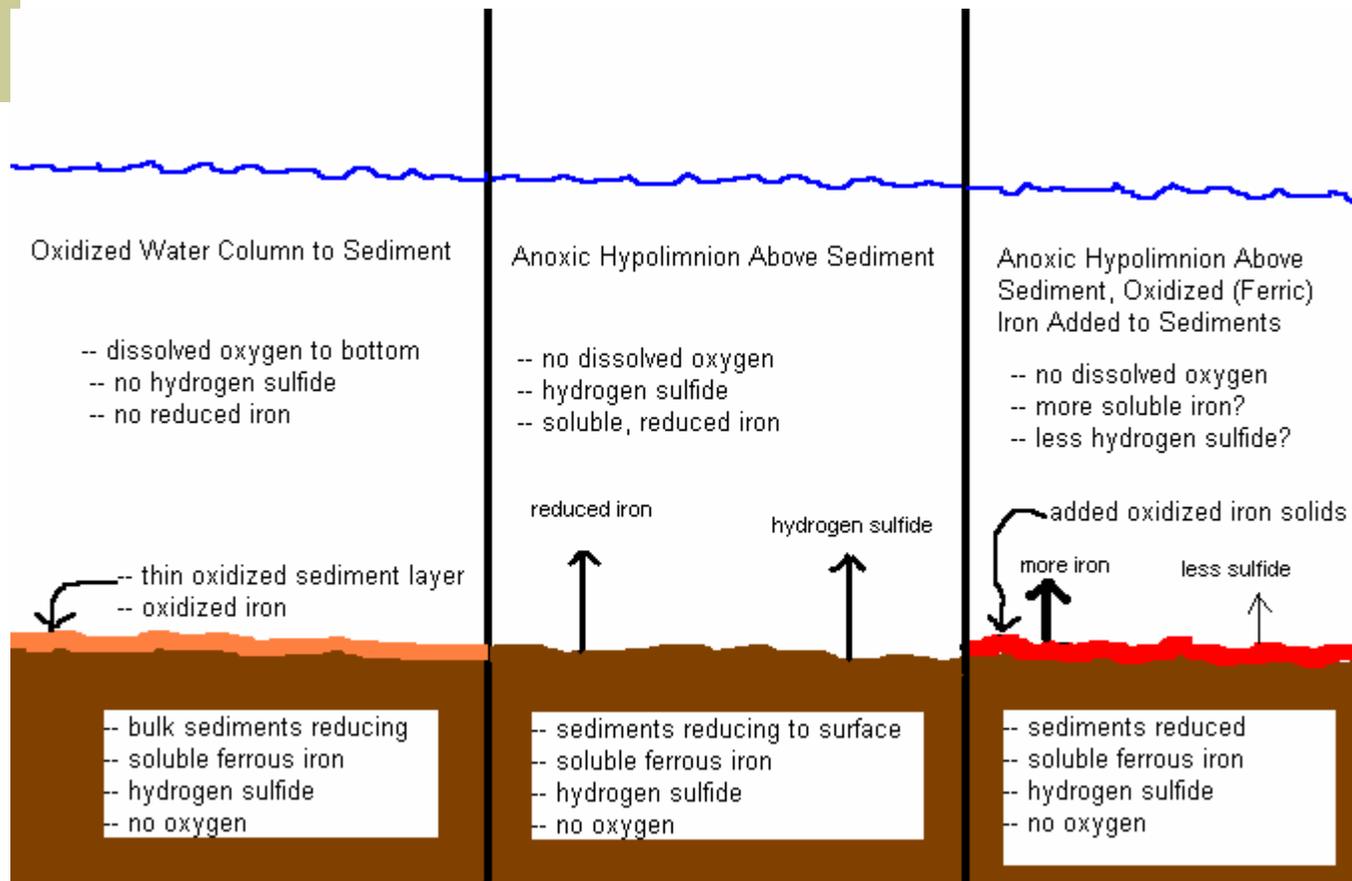
- Increasing pH has been reported to increase the rate of oxidation by some chemical oxidants such as H_2O_2 .
- pH may be adjusted with bulk chemicals such as NaOH or $\text{Ca}(\text{OH})_2$ or others.
- Might be adjusted by passing water over or through coarse limestone filters.
- May be feasible where small pH adjustments will give positive results. (recall the log relationship between pH and the amount of acid or base added).
- Buffering capacity of the hypolimnetic waters must be considered.
- Will other problems arise with pH adjustment?



pH influence on sulfide speciation

Iron addition to Lake Sediments.

- ◆ Adding ferric iron compounds (solids that will sink to the bottom) to a lake may:
 - Increase the amount of soluble ferrous iron that can precipitate sulfide
 - Delay the onset of reducing conditions at the sediment water interface that may delay H_2S formation in the near-surface sediment and reduce the amount of H_2S being transported from sediment porewater to hypolimnetic water by upward diffusion.



A Combination of Treatments may be Useful to Remove H₂S

A number of treatments have shown some useful potential. Individually, no one treatment might be applicable, or effective, or affordable for a site-specific problem.

However, for some site-specific problems, a combination of treatments might be more effective than any single treatment. Consider adding dissolved oxygen, ferrous iron, and adjusting pH for example.