Sulfur and Sulfate

Dr. Kozet YAPSAKLI

WHAT is sulfur?

Atomic number: 16.

Symbol: S

Native form: is a yellow crystalline (crystal like) solid.

In nature: it can be found as the pure element, and as sulfide and sulfate minerals.

commercial uses: fertilizers, gunpowder, matches, insecticides, fungicides, vitamins, proteins and hormones.

It is critical in the environment, climate and the health of ecosystems.

It’s the tenth most abundant element in the universe

Importance

* Drinking water
  * cathartic effect when present in excessive amounts
  * EPA secondary standard: should be < 250 mg/L
* Public and industrial water supplies:
  * Have the tendency to form scaling in boilers and heat exchangers
* Sewer systems
  * odor
  * crown corrosion

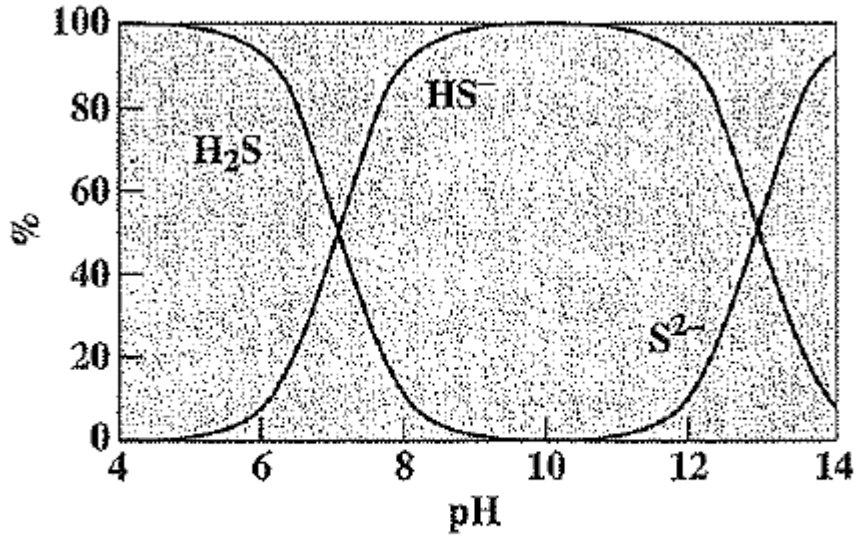


Figure 29.2
Effect of pH on relative distribution of sulfide species in water.

SULFATE (continue)

* If pH > 8 HS^- and S^{-2} [(H_2S) is small] → no odor problem

* If pH < 8 equilibrium shift right → @pH 7 80% H_2S

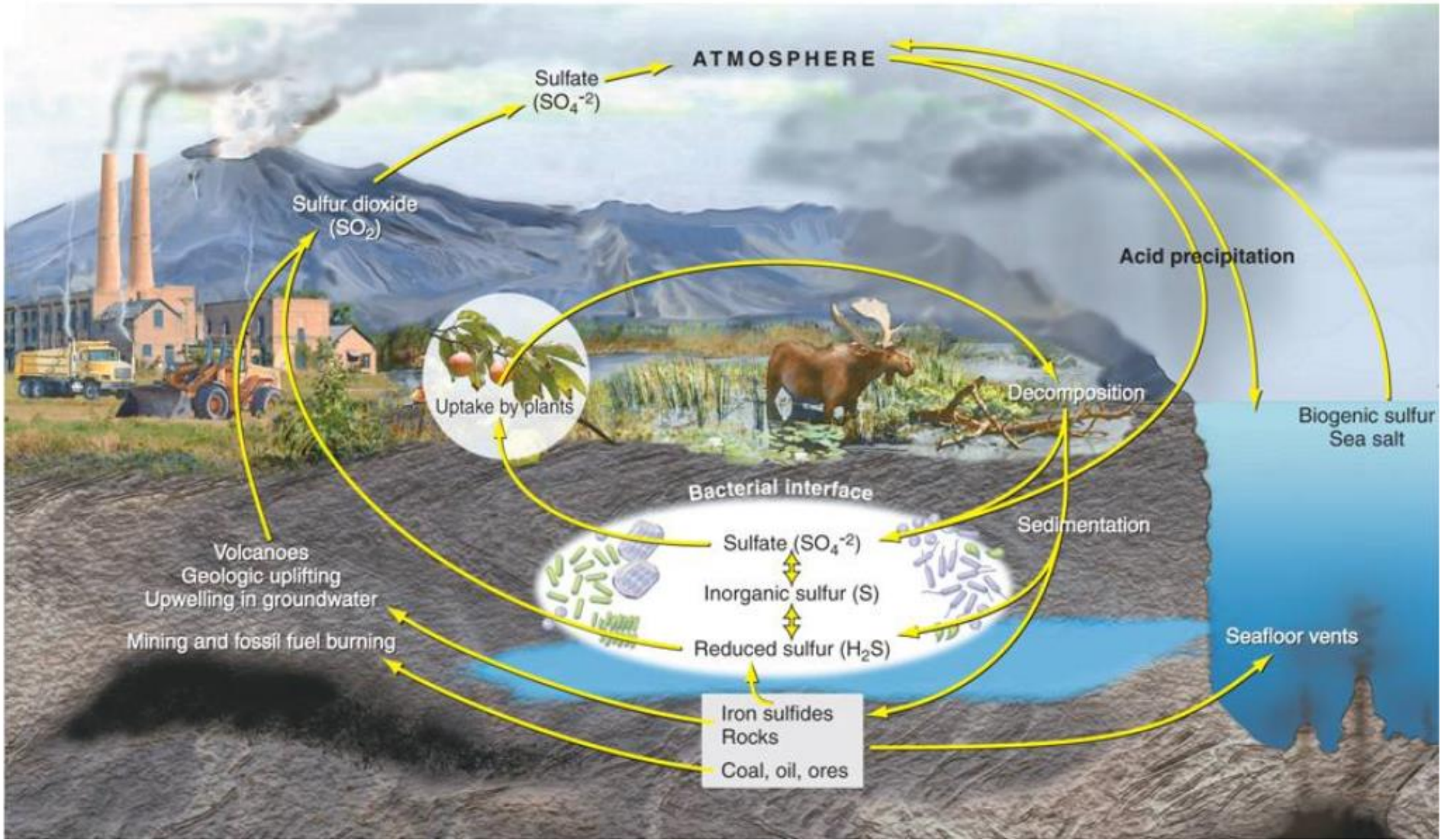
* If concentration > 20 ppm toxic

Concentration Levels & Effects

The following table below lists the health effects of exposure to H_2S.

Concentration	Health Effects
10 ppm	Beginning eye irritation
50-100 ppm	Slight respiratory tract irritation after 1 hour exposure.
100 ppm	Coughing, eye irritation, loss of sense of smell after 2-15 minutes. Altered respiration, pain in the eyes, and drowsiness after 15-30 minutes followed by throat irritation after 1 hour. Several hours exposure results in gradual increase in severity of these symptoms and death may occur within the next 48 hours
200-300 ppm	Severe respiratory tract irritation after 1 hour of exposure. Possible pulmonary edema (fluid in the lungs).
500-700 ppm	Loss of consciousness and possibly death in 30 minutes to 1 hour.
700-1,000 ppm	Rapid unconsciousness, loss of respiration, and death after 1-3 minutes.
1,000-2,000ppm	Unconsciousness at once, loss of respiration and death in a few minutes. Death may occur even if individual is removed to fresh air at once.

Sulfur Cycle



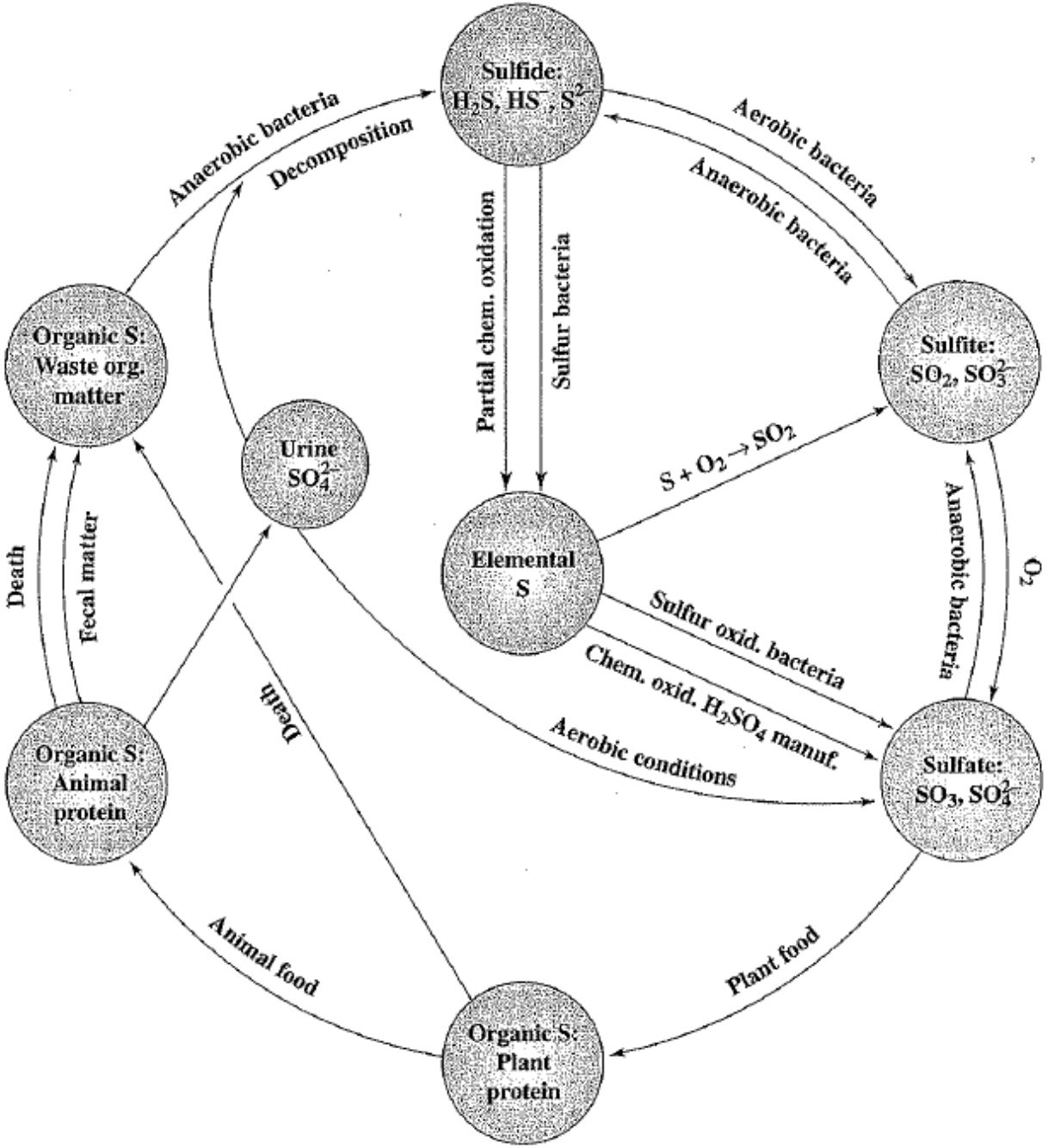


Figure 29.1
The sulfur cycle.

Effect of acid rain on a forest, Jizera Mountains, Czech Republic

Sewer Corrosion

* High temperature, long detention times→sulfate cause crown corrosion in concrete sewers
* H_2S responsible (indirectly) for crown corrosion
* H_2S is weaker than carbonic acid→ little effect on good concrete

Crown Sewer Corrosion

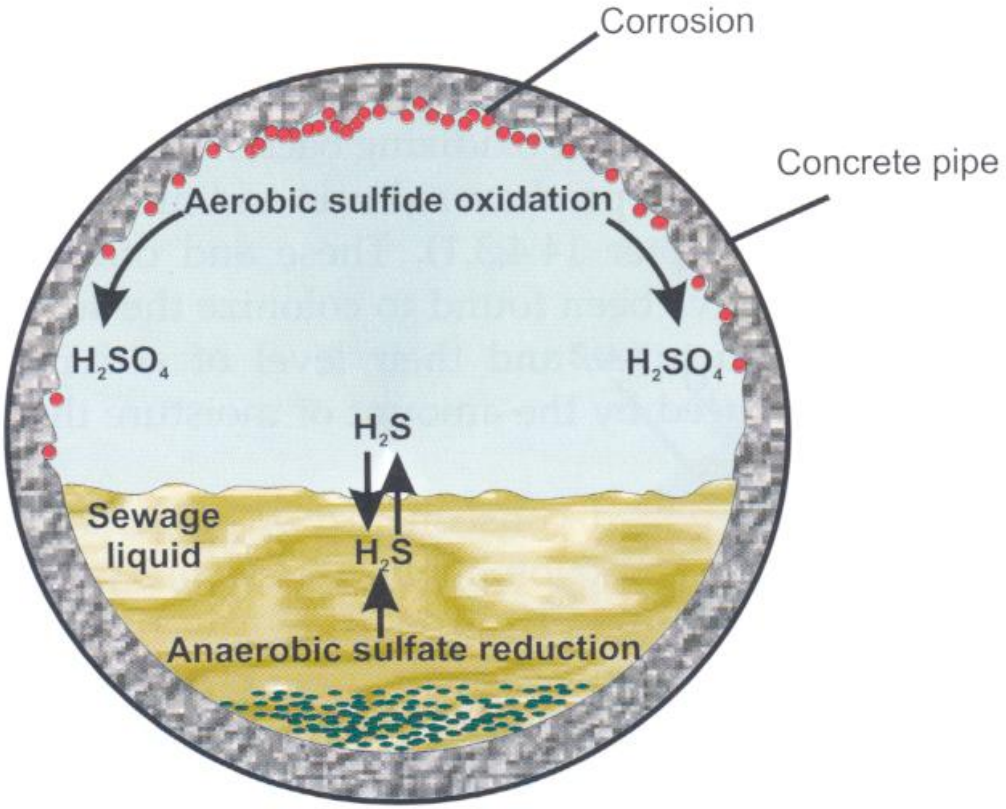


FIGURE 15.3 Cross section showing microbial involvement in the corrosion of a concrete sewer pipe. (Adapted from Sydney *et al.*, 1996.)

$$SO_4^{2-} + \text{organic matter} \xrightarrow[\text{bacteria}]{\text{anaerobic}} S^{2-} + H_2O + CO_2 \qquad (29.1)$$

$$S^{2-} + H^+ \rightleftharpoons HS^- \qquad (29.2)$$

$$HS^- + H^+ \rightleftharpoons H_2S \qquad (29.3)$$

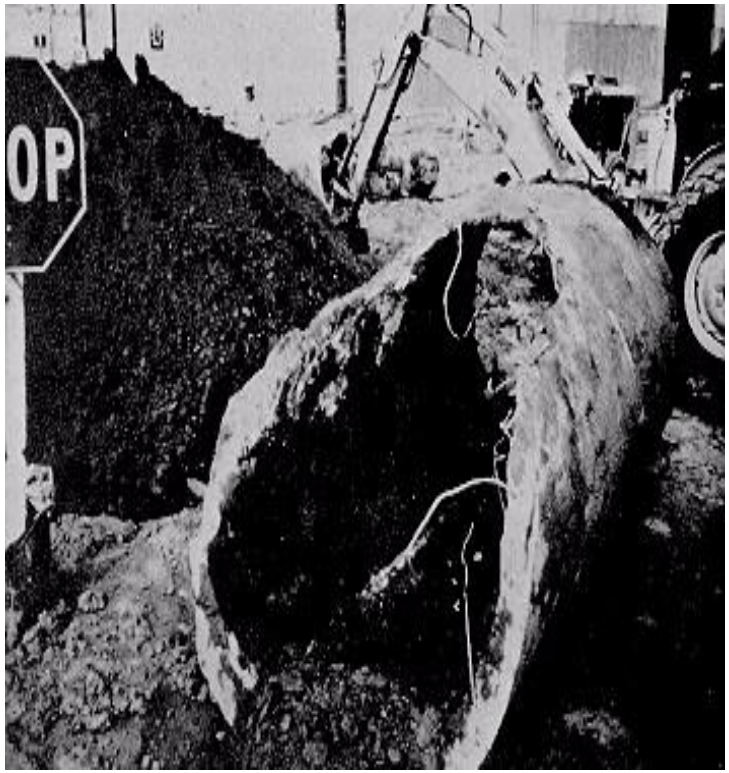
Summary by Example: Pipe Corrosion

* organics in sewage are used as energy source to convert SO_4 to $S^=$ by sulfate reducers (chemoorganoheterotrophs)
* $S^=$ in equilibrium with dissolved H_2S
* Dissolved H_2S in equilibrium with gaseous H_2S

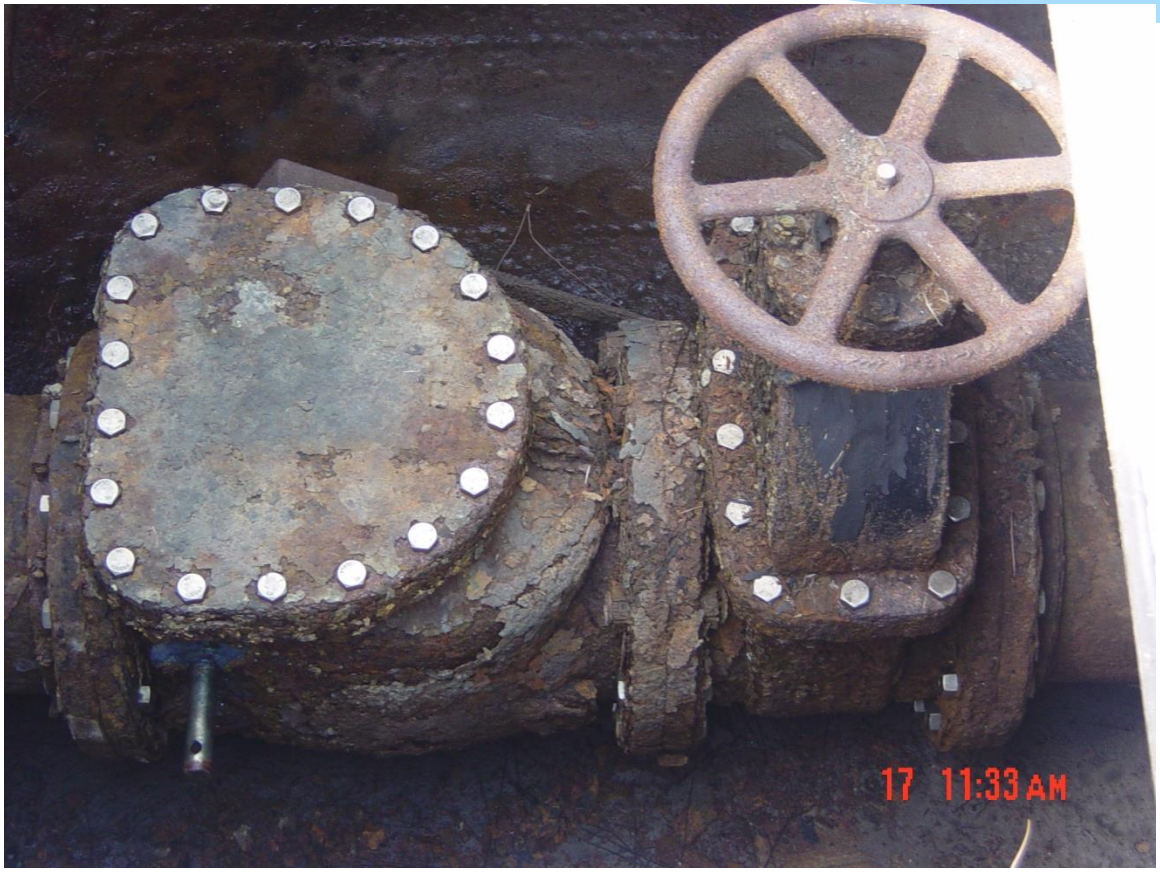
Example Continued

* Gaseous H_2S dissolves into condensate at crown of sewer pipe and is used as energy source by sulfide oxidizers (chemolithoautotrophs)
* As H_2S metabolized, acid is produced which dissolves concrete crown causing pipe to collapse
* Well ventilation→ no problem

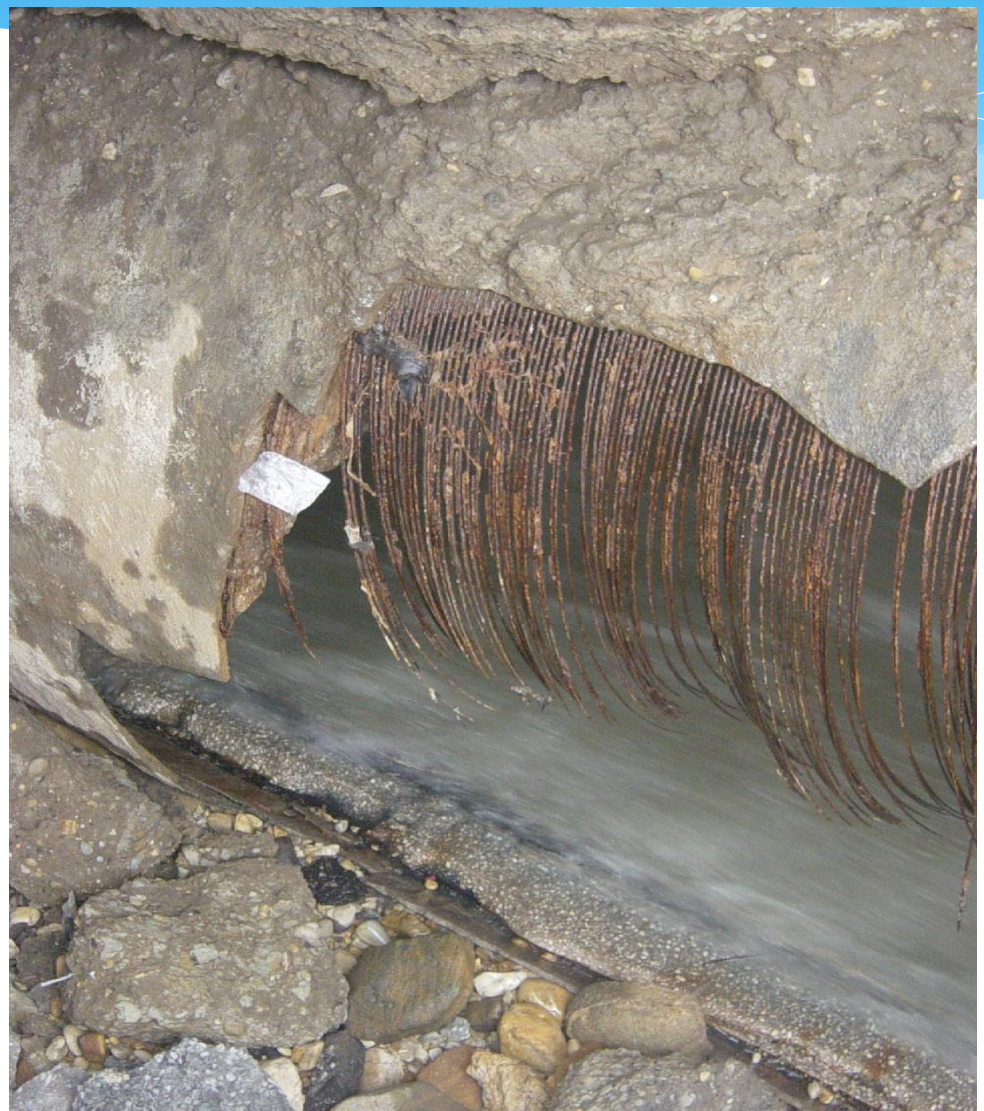
Crown Corrosion



Hydrogen sulfide corrodes cast iron pipe, valves and fittings:



Hydrogen Sulfide corrodes cast concrete sewer mains:



Hydrogen sulfide corrodes manhole and wet well structures:

Methods of Analysis

* Ion chromatograph
* Formation of insoluable $BaSO_4$
* According to the quantity of $BaSO_4$ formation
  * Gravimetric → precipitate is weighed
  * Turbidimetric
  * Methylthymol blue method

Methods of Analysis (continue)

* **Gravimetric :** > 10 mg/L
* $Ba^{+2} + SO_4^{-2} \rightarrow BaSO_4$
* Add $BaCl_2$ in slight access

* Acidify w/HCl → eliminate $BaCO_3$ ppt
* Keep near boiling point

Methods of Analysis (continue)

* Excess $BaCl_2$ → common ion effect
* Formed $BaSO_4$ → colloidal form can not be removed by filter
* Digestion @ temperature near boiling point → crystalline forms
* Filter the crystals with special filter

Methods of Analysis (continue)

* **Turbidimetric method :**
  * Colloidal formation is enhanced in the presence acidic buffer solution
  * (Magnesium chloride, potassium nitrate, sodium acetate, acetic acid)
  * Calibration curve

Methods of Analysis (continue)

* **Automated Methylthymol Blue**
  * Continuous flow analytical instrument
  * $BaCl_2$ added @low pH→ $BaSO_4$
  * pH adjusted to 10
  * Methylthymol blue added

Methods of Analysis (continue)

* Combines with excess Barium → blue chelate

* Umcomplexed methylthymol blue remaining → grey color (automatically measured)