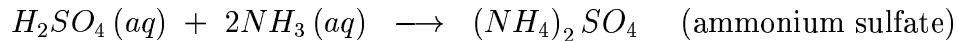


Fate of Acids in Clouds

1. Combination with bases dissolved in clouds: acids neutralized



- Ammonium sulfate falls to earth- a fertilizer

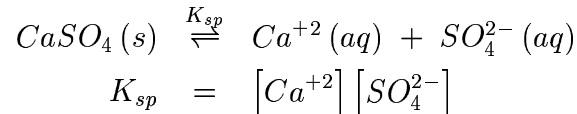
2. Precipitates un-neutralized to earth

(a) Falls into soil

- i. Buffered in soil by carbonates: precipitates formed



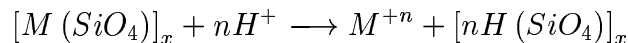
- Solubility product K_{sp} measure solubility of compounds



- Generally, ionic compounds more stable than ions in water: Low K_{sp}
- Introduction of external sources of SO_4^{2-} decreases amount of dissolved $CaSO_4$

- ii. Ion exchange mechanism: clay buffering

- Proton H^+ (a cation) replaces cation M^{+n} in silicates



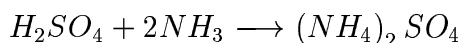
- Order of difficulty to replace: $M = Al^{3+} > H^+ > Ca^{+2} > Mg^{+2} > K^+ > NH_4^+ > Na^+$.
- Order of exchange depends on relative affinity of cations for anionic site
- Method used to deionize water
- Buffering through exchange limited by number of exchangeable sites: cation exchange capacity
- Consequence of buffering: High concentration of cations-hard water
- Hardness: typified by high concentration of Ca^{+2} and Mg^{+2} .
 - Removed by detergents: micelles of detergents float freely
 - Detergent products bind cations through multiple coordinated bonds: “chelating agents”
 - Cations bind micelles together which then precipitate

(b) Rain falls directly into lakes and streams: buffering in river and lake beds

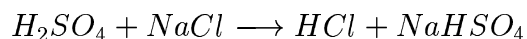
Acid Fogs: pH 2-3

- Unusual cloud chemistry due to fog: coastlines
 - Can lead to very acid water: London fog of January, 1955 caused 4,000 deaths!
1. Fog over ocean in humid air: Largely H_2O condensed on sea-salt ($NaCl$) aerosols
 $NaCl \cdot nH_2O$
 2. Fog moves over land: SO_2 and NO_2 absorbed
 3. Photochemical processes: $O_3/H_2O_2 + \text{fog} \longrightarrow H_2SO_4 + HNO_3$
 4. If fog continues over land, picks up bases like NH_3 (from cows, for example)

- Acid-Base chemistry: acids neutralized to form salts



- Other reactions



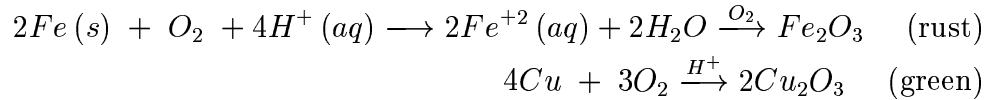
5. Warm air evaporates fog: leave dense haze of salt aerosols which cause respiratory problems.

Effects of Acid Rain

1. Vegetation: SO_2 is toxic to plants
 - Leaves damaged below pH 3.5: Chlorosis-yellowing of leaf
 - Soil chemistry affected: germination of seeds and growth adapted for soils of specific acidity
 - Needles fall from pines: Evident in Sudbury
2. Health issues:
 - SO_2 believed to be carcinogenic
 - Toxic aerosols: acid fogs
3. Structural erosion:
 - Limestone and Marble erosion: $CaCO_3$ -calcium carbonate

- Net reaction: $CaCO_3 + H_2SO_4 \longrightarrow CaSO_4(s) + CO_2 + H_2O$
- Like neutralization of acids with antacid tablets
- Cologne cathedral-covered in gypsum (plaster: $CaSO_4$) due to acid rain
- Athens and Rome cathedrals and statues: pollution leads to acid rain

- Steel/Iron/Copper corrosion



- Aluminum is typically in form with oxide film on surface: already oxidized

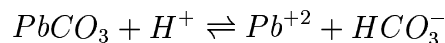
4. Effects on natural waters

(a) Acidifying of lakes and streams

- Impact depends on **buffering** capacity: variable effects like in Algonquin
 - Clay lake/stream beds with silicates buffer well via cation exchange mechanism
 - Chalk and limestone beds buffer well via neutralization reaction: Granite does not: principle being adding crushed limestone to lakes in adirondacks
 - Geology plays a large role: pre-cambrian shield of granite in Northern part of North America
 - Acid eats away small portion of rock
 - Acid snow runoff: rapid drop in pH in spring when snow melts-Also has impact on soil chemistry

(b) Mobilization of toxic metals: Cd^{+2} , Pb^{+2} , Hg^{+2} , Al^{+3}

- Al^{+3} forms aluminum hydroxide $Al(OH)_3$: forms on gills of fish and suffocates them
- Toxic metal anions are more soluble at lower acidities
- Acid frees of toxic metals from bedrock via reactions like



(c) Loss of nutrients

Acid Rain Control

- Key: control emissions of NO_x and SO_2

1. NO_x emissions: catalytic converters on automobiles and factories

2. SO_2 emissions: mainly due to coal burning and steel production

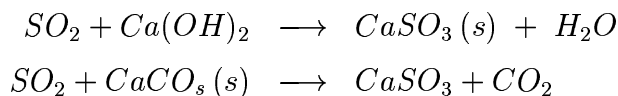
- Strategies:

- (a) Minimize production of SO_2 -low sulfure coal (purified) and cleaner fuels
- (b) Dilute pollutants to minimize local effects-big smoke stacks (400m in Sudbury)
- (c) Convert pollutant into harmless substances

- Coal-burning power plants: Remove iron pyrites FeS_2

- Oil flotation method: crush coal and suspend on mixture of air/oil/water-separation by density
 - * Problem is leaves organically bound sulfur
- Genetically engineered microorganisms that extract sulfur but leave carbon skeleton of coal intact.

- Trapping SO_2 : Flue gas desulfurization

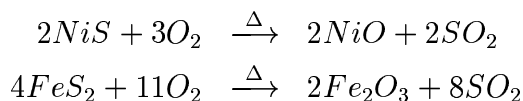


- Expensive to implement due to cost of $Ca(OH)_2$ and $CaCO_3$ in large amounts
- Also expensive to clean gypsum from stacks

- Fluidized bed combustion: coal pulverized and mixed with particles of limestone and burned as coal gas
- Research: UV light chemistry of gases to get sulfate and nitrate salts: sold as fertilizers

3. Metal extraction: Example-Inco Ltd. in Sudbury

- Roasting of ores NiS , FeS_2 , CuS



- Reduction of oxides to extract metals

- In Sudbury, SO_2 collected to make H_2SO_4 for commercial sale: used in fertilizer industry
 - Drawback: costly to trap SO_2

Political Controls

- Difficult due to cost and verifiability
 - Estimated that it would cost 2 – 4\$ billion to cut SO_2 emissions in U.S. by 50%.
Translates to a 20% increase in electricity prices.
- 1990 U.S. Clean Air Act:
 - NO_x emissions cut 15%/year for 6 years
 - 65% reduction in SO_2 emissions: cost offset by low oil prices
- In Mississauga, Lakeview generating station is coal-fired: estimated cost of conversion to natural gas: \$850 million.