Fate of Acids in Clouds

1. Combination with bases dissolved in clouds: acids neutralized

$$NH_3\,(g) + H_2O \quad \rightleftharpoons \quad NH_3\,(aq)$$
$$H_2SO_4\,(aq) \; + \; 2NH_3\,(aq) \quad \longrightarrow \quad (NH_4)_2\,SO_4 \qquad \text{(ammonium sulfate)}$$

   - 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

$$CaCO_3 + H_2SO_4 \longrightarrow CO_2 + H_2O + CaSO_4\,(aq)$$

      - Solubility product K_{sp} measure solubility of compounds

$$CaSO_4\,(s) \quad \overset{K_{sp}}{\rightleftharpoons} \quad Ca^{+2}\,(aq) \; + \; SO_4^{2-}\,(aq)$$
$$K_{sp} \quad = \quad \left[Ca^{+2}\right]\left[SO_4^{2-}\right]$$

      - 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

$$\left[M\,(SiO_4)\right]_x + nH^+ \longrightarrow M^{+n} + \left[nH\,(SiO_4)\right]_x$$

      - 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 exhangeable 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

    $$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2\, SO_4$$

    - Other reactions

    $$H_2SO_4 + NaCl \longrightarrow HCl + NaHSO_4$$

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

$$2Fe\,(s) \ + \ O_2 \ + 4H^+\,(aq) \longrightarrow 2Fe^{+2}\,(aq) + 2H_2O \xrightarrow{O_2} Fe_2O_3 \quad \text{(rust)}$$
$$4Cu \ + \ 3O_2 \xrightarrow{H^+} 2Cu_2O_3 \quad \text{(green)}$$

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

4. Effects on natural waters

(a) Acidfying 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 behing 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

$$PbCO_3 + H^+ \rightleftharpoons Pb^{+2} + HCO_3^-$$

(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

$$\begin{aligned} SO_2 + Ca(OH)_2 &\longrightarrow CaSO_3\,(s) \ + \ H_2O \\ SO_2 + CaCO_s\,(s) &\longrightarrow CaSO_3 + CO_2 \end{aligned}$$

     - 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

$$\begin{aligned} 2NiS + 3O_2 &\xrightarrow{\Delta} 2NiO + 2SO_2 \\ 4FeS_2 + 11O_2 &\xrightarrow{\Delta} 2Fe_2O_3 + 8SO_2 \end{aligned}$$

   - Reduction of oxides to extract metals

- In Sudbury, SO_2 collected to make H_2SO_4 for commercial sale: used in fertilize 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.