- Pulp and paper waste is primarily lignin.
    - Treated by biological degradation in vigorously aerated lagoons.
    - Alternative treatment involves closed bioreactors (which is less vulnerable to weather variation).
    - Resulting sludge needs to be digested, dewatered, and landfilled.

Low Strength Aqueous Waste

- Oily wastes generated by petroleum refining.
    - Interfere with oxygen transport across surface of water.
    - Broken down by long treatment in aeration lagoons or bioreactors.
    - Mechanical separation is difficult, especially if emulsifiers are present.
    - Water may be removed by evaporation.
    - Oily component may be combusted or ozonized.
- Landfarming is also used.
    - Oily waste is spread out on soil and microbes are allowed to degrade it.
    - Persistent organic compounds accumulate.
    - Volatile organics evaporate.
    - Environmental impact and land costs are issues.
- Treatment with activated charcoal may be considered.

Persistent Organic Pollutants

- Many are toxic.
- Can originate in pesticide manufacture.
- Classified as persistent because they are resistant to oxidation.
    - Do not undergo biological degradation
    - Survive treatment with most chemical oxidants.
    - Can bioaccumulate.
- Therefore waste management strategies are focussed on concentrating these.
    - Activated charcoal is used.
    - Waste stream passes over granulated activated carbon bed.
    - Output of the bed is monitored to determine when breakthrough occurs and bed needs to be replaced.
    - A second bed of activated charcoal is usually in series with monitor of the first bed to ensure that the organic does not get into the environment.
- This treatment merely concentrates the organic, but does not destroy it.
- When breakthrough occurs, the saturated bed is now hazardous solid waste which must be disposed of.
    - Landfilling may not be allowed.
    - Activated charcoal may be incinerated at high temperature to destroy the persistent organic compound.

  - Under properly controlled conditions, the charcoal may be partially burned, which volatilizes the organics which are then subjected to hight temperature combustions. This allows partial recovery of the charcoal for reuse.
- Another approach is chemical treatment of the organics with the intent to degrade them.
  - These methods must be nonselective and work on the entire spectrum of compounds.
- Among the methods considered are:
  - Oxidation with UV and hydrogen peroxide or ozone.
  - Oxidation catalyzed by a semiconductor.
  - Electrochemical oxidation.
  - All of these methods are expensive.

UV assisted oxidation

- Waste stream is aerated and the oxidizing agent (hydrogen peroxide or ozone) is introduced.
- Waste stream is then passed through a quartz tube illuminated by high pressure mercury lamps which are the source of the UV radiation.
- The UV photon promote the formation of OH radicals.

$$\mathrm{H_2O_2(aq) + h\nu \rightarrow 2\ OH(aq)}$$

- These aqueous phase OH radicals initiate degradation of the organic by abstracting H atoms.
- Since the solution is aerated, the adduct with oxygen is readily formed.

$$\mathrm{OH(aq) + RH(aq) \rightarrow H_2O + R\cdot}$$
$$\mathrm{R\cdot + O_2 \rightarrow ROO\cdot \rightarrow \text{further oxidation}}$$

- This method can be used to destroy aromatic N compounds.
- Costs include mercury lamps, the oxidizing agent, and the electrical energy to run the lamps.

Catalytic Oxidation with TiO_2

- OH is produced by irradiation of water containing a suspension of TiO_2 with light of wavelength near 400 nm (i.e. visible).
  - This radiation promotes an electron to the valence band, leaving behind an electron hole at the site of absorption and a free electron.
  - This hole is filled with an electron from a hydroxide ion, producing an OH radical.
  - The free electron is taken up by an electron acceptor (EA) species such as O_2.
  - Competing with these is the recombination of electrons and holes.
  - The reactions of the interest are:

$$\mathrm{h^+ + OH^-(aq) \rightarrow OH\cdot(aq)}$$
$$\mathrm{e^- + EA \rightarrow EA^-}$$

  - OH initiate H abstraction while O_2^- furthers the oxidation.

Electrochemical Oxidation

- Ag(II) is a powerful oxidizing agent.

  - Produces OH.
- The reaction sequences are:

$$Ag^{2+} + NO_3^- \rightarrow Ag^+ + NO_3$$
$$NO_3^- + H_2O \rightarrow NO_3 + H^+ + OH$$
$$Ag^{2+} + H_2O \rightarrow Ag^+ + H^+ + OH$$

- Energy is input to convert Ag^+ to Ag^{2+}.

Air Stripping

- Has the effect of changing water pollution to air pollution.
  - Acceptable for compounds that are naturally oxidized in air.
  - Unacceptable and controversial for compounds that do not break down readily in air.
- Feasible for compounds where equilibrium favours the gas phase.

$$X(aq) \rightleftharpoons X(g)$$

$$K_H' = \frac{1}{K_H} = \frac{X(g)}{X(aq)}$$

  - The larger K_H' is, the more effective air stripping can be.
  - Increasing the temperature increases K_H' (i.e. steam stripping).
  - Steam stripping is convenient to apply to process streams that are already warm.
- Air requires further treatment before being exhausted.
  - Catalytic oxidation
  - Wet air oxidation by heating to temperatures at which complete oxidation can occur.
  - Biofilm treatment.

Inorganic Aqueous Wastes

- Three major classes:
  - Ammonia
  - Cyanide
  - Heavy Metals

Ammonia

- Three methods of addressing NH_3 in aqueous waste.
  - Air stripping
  - Nitrification
  - Breakpoint Chlorination
- Nitrification involves microbial oxidation of ammonia to nitrate.
  - This differs from natural nitrification in soil which gives NO and N_2.
- Breakpoint chlorination involves the oxidation of ammonia by HOCl:

$$2\ NH_3(aq) + 2\ HOCl(aq) \rightarrow N_2(g) + 3\ HCl(aq) + 3\ H_2O(l)$$

  - The oxidation occurs stepwise with intermediate formation of NH_2Cl and $NHCl_2$, which in turn react with each other to form N_2,
$$NH_3(aq) + HOCl(aq) \rightarrow NH_2Cl(aq) + H_2O(l)$$
$$NH_2Cl(aq) + HOCl(aq) \rightarrow NHCl_2(aq) + H_2O(l)$$
$$NH_2Cl(aq) + NHCl_2(aq) \rightarrow N_2(g) + 3\ HCl(aq)$$
- The term “breakpoint” refers to the behaviour of the chlorine residual in the solution as a function of the chlorine dose.
  - Initially the chlorine is taken up as NH_2Cl which is an active form of chlorine.
  - As $NHCl_2$ is formed, it reacts with NH_2Cl to form N_2.
  - Thus the amount of active chlorine drops as NH_2Cl is used up.
  - The point where active chlorine drops to zero is the breakpoint and all NH_3 is converted to N_2.

Cyanide

- Used in a number of industries:
  - mining
  - electroplating
  - metal finishing
- Usually gives rise to aqueous waste contaminated by both cyanide and heavy metal.
- Cyanide is removed by oxidation:
$$CN^-(aq) + HOCl(aq) \rightarrow OCN^-(aq) + HCl(aq)$$
$$CN^-(aq) + Cl_2(aq) + H_2O(aq) \rightarrow OCN^-(aq) + 2\ HCl(aq)$$
- Cyanate (OCN^-) itself hydrolyzes quite easily.
$$CN^-(aq) + H^+(aq) + H_2O(l) \rightarrow NH_3(aq) + CO_2(aq)$$

Heavy Metals

- Generally refers to metal with atomic numbers greater than 26 (Iron).
  - Common usage usually includes vanadium and chromium.
- Many metals with industrial use have been discharged into the environment throughout history.
  - Electroplating can involve copper, chromium, silver, nickel, cadmium.
  - Catalysts include copper, gold, silver, platinum, vanadium, mercury, and nickel.
  - Lead is used in batteries and was formerly used as a gasoline additive.
  - Mercury is used in batteries, switches, and the manufacture of chlorine and sodium hydroxide.
- Metal ions can be precipitated with appropriate anions.
  - Metal sulphides are very insoluble and may be formed by bubbling H_2S through the solution.
$$H_2S(g) + M^{2+}(aq) \rightarrow MS(s) + 2\ H^+$$
  - Precipitation is more efficient at high pH, so lime is used prior to treatment with H_2S.
  - The resulting sludge must be disposed of.

Landfills

- Landfilling refers to dumping on the ground.
- May be secured or unsecured
- May have been regulated or unregulated
- May be done properly or improperly

  - Love Canal (improper landfilling of industrial waste)
  - Times Beach (improper disposal of waste oil)
  - Valley of the Drums (improper disposal of chemicals in unprotected steel drums).
- There is legacy of sites that are unsecured and unengineered.
  - No record of what may have been dumped
  - No means of managing leachate.
- Many sites in North America are “sanitary landfill sites”
  - The focus in on the prevention of disease.
  - Waste is periodically covered with soil to prevent access by rodents.
  - When a site is full, it is covered and planted with vegetation.
  - Meanwhile anaerobic decomposition continues with concomitant settling of the ground and release of gases such as methane which can pose an explosion hazard.

  - These hazards limit subsequent use of the land.
- Per capita waste generation in North America is 1.8 kg per day.
- Historically site selection for landfills and hazardous waste sites has been based on convenience and lack of value of the land for other purposes.
  - This led to wetlands and swamps being used for landfills.
  - In the case of dumping of drums of chemicals, this led to contamination of ground water when the drums corroded.
- Different soils have different properties:
  - Clays are relatively impervious.
  - Sand and gravel are porous.
- Rain and snow seep into landfills and leach soluble material.
  - Depending on the overlying soil structure, the leachate may contaminate ground water and lead to long distance transport of toxins.
- Historically landfills have accepted industrial waste with few (if any) restrictions.
  - Currently landfills are regarded as the least desirable way of dealing with industrial waste.

Secure Landfills

- Carefully planned and operated.
- Sites are selected with a view of protecting aquifers.
  - Bottom liner of impervious clay.

    - Leachate is collected and treated.
    - Surrounding aquifer is monitored.
- Secure operation controls what is dumped at the landfill.
    - Hazardous waste “knowingly” accepted.
    - Fees associated with dumping cover monitoring costs and leachate treatment.
- When landfill is full, it is capped with impervious clay.
    - Minimizes leachate by preventing infiltration by snow and rain.
    - Gaseous anaerobic decay products are collected and vented to prevent cracking of the cap.
    - Methane can be used for cogeneration.
    - Volatilized organics can contribute to air pollution.
- Hazardous waste dumps are further engineered for particular waste.
    - Clay base assessed for transport properties of the specific substances.
    - Monitoring
    - Leachate treatment and collection.
- Historically hazardous waste disposal has been poorly managed or mismanaged.

Love Canal

- Near Niagara Falls, New York.
- Love Canal was initiated in the late 1800’s by William Love to bypass Niagara Falls and generate hydroelectric power.
    - Project went bankrupt leaving a 1.6 km long 15 m wide ditch varying in depth from 3 to 13 m.
- When hydroelectric power did come to the area, industry followed.
    - Hooker Chemical manufactured chlorine and organochlorine compounds.
    - Chlorine is manufactured from NaCl by electrolysis using a flowing mercury cell.
- During World War II, Love Canal began to be used as a chemical dump.
    - 20,000 tonnes of waste accumulated.
    - Love Canal capped with clay.
- Love Canal later developed.
    - Road construction disrupted clay cap.
    - Homes constructed
    - School built on top of canal.
- By the 1970’s problems were evident.
    - Toxic chemicals were found in the schoolyard and in the basements of homes.
    - Residents were evacuated and relocated, and the school closed.
    - Eventually homes were expropriated and site sealed off.
- Lawsuits continue.
- Similar scenarios are being played out across Canada and around the world.

- In Canada, some sites of concern are:
    - Former dump sites developed as residential areas.
    - Sydney Tar Ponds
    - “Valleys of Drums” associated with World War II military installations throughout the north.
    - Former gas station sites.