

Sewage Treatment

Chapter 8

- problem of whether sewage is treated at all – including in Canada – and mixed municipal storm/domestic sewers  
Rhine, Mississippi, Yangtze, Danube ← Sewage, industry recreation, drinking
- primary settling (“advanced primary treatment” by the addition of coagulants – same as in DW treatment)
- secondary treatment: biological treatment using trickling <sup>microorganisms dine on organic matter</sup> sand filters or activated sludge reactors: reduce BOD by means of microbial oxidation (say, a 90% reduction) <sup>enclosed tank (aerated) i.e. no trickle</sup>  
byproduct of secondary treatment is sewage sludge – (“biosolids”!), an excellent source of fertilizer elements N, P, K and of organic matter to amend soil **but** also contains toxic metals, including Cu, Cd, Pb, Hg, Zn, Cr, Ni, mostly because of deposition of industrial liquids into the municipal sewers (+ some oxidn resistant organics, e.g. organo-chlorine compounds.)
- Ontario produces 400,000 t of sludge annually
- alternative to land treatment is incineration or landfilling → leachates
- amount of sludge that can be applied safely depends on soil type: clays bind metal cations. Ontario MOE has **guidelines** for land application, but few analyses are done <sup>→ to the land as fertiliser</sup>
- sludge is **digested** in order to dewater it → solid material **or** is spread directly as “liquid biosolids” → concern about microbial contamination
- possibility of entry of toxicants into human food supply through pathways such as soil → plant → human **or** soil → plant → animal → human

Least many years. Take up space. Work poorly in winter

see top of p237 (text) regarding the safe use of sludge as a fertiliser.

Often, after 2<sup>nd</sup> treatment the sewage is discharged, ... rivers etc, often with aeration (p237).

Section 8.1.3 *not always done... often different kinds of methods* (141) *organics* *BOD reduction* *e.g. heavy metals* *iron removal* *xs inorganic ions*

Focus here on *degradation & ageing of lakes. Classic example - Lake Erie in the 60s (see P. 240) Algae flourish, die. BOD demand increases, less O<sub>2</sub> aquatic life perishes.*

tertiary treatment to remove specific contaminants *for biomass*

phosphorus (eutrophication problem since P is usually the limiting nutrient: ratios of C: N: P for optimal growth 100: 15: 1): see text pp. 238-240 *also agriculture ... phosphate fertilisers*

major source of P in sewage is detergents, levels of which are now limited

P content of detergents is sodium tripolyphosphate (STP) which is used to sequester Ca<sup>2+</sup> (in hard water) *see notes p143*

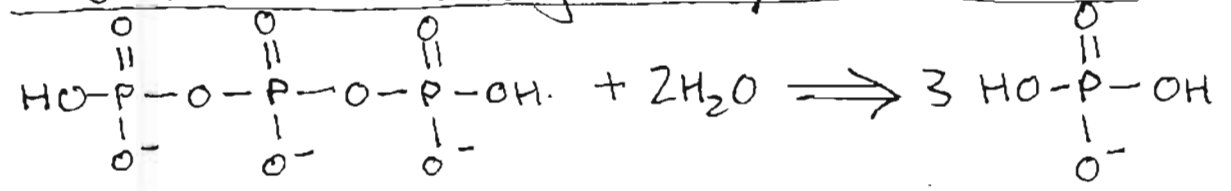
complex chemistry of Ca-PO<sub>4</sub> systems:  $PO_4^{3-}$ ,  $HPO_4^{2-}$ ,  $H_2PO_4^-$

Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is highly insoluble (rock phosphate) and has to be solubilized to be used as a fertilizer (superphosphate) *an aside*

- polyphosphates have the structure -O-(PO<sub>2</sub>-O)<sub>n</sub>-PO<sub>2</sub>-O- and are analogous to ATP. Both linear and cyclic polyphosphates exist *adenosine triphosphate* *high energy species available free energy*
- unlike monophosphate, polyphosphates form soluble complexes with Ca<sup>2+</sup>
- like ATP, polyphosphates hydrolyze to monophosphate; monophosphate is discharged to the environment from sewage plants if untreated

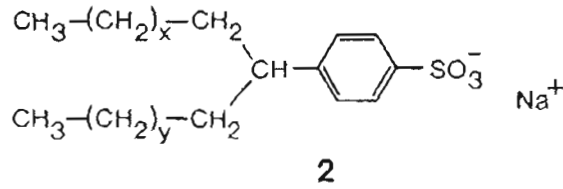
- usual tertiary treatment for PO<sub>4</sub><sup>2-</sup> is precipitation with either Al<sup>3+</sup> or Fe<sup>3+</sup> → AlPO<sub>4</sub> or FePO<sub>4</sub> (insoluble) *More complex than this & need to control pH*
- other tertiary treatments include micro-straining and disinfection with chlorine (now out of favour): see also ammonia removal, later

Biological phosphate removal also used (incorporate into biomass of microorganisms)

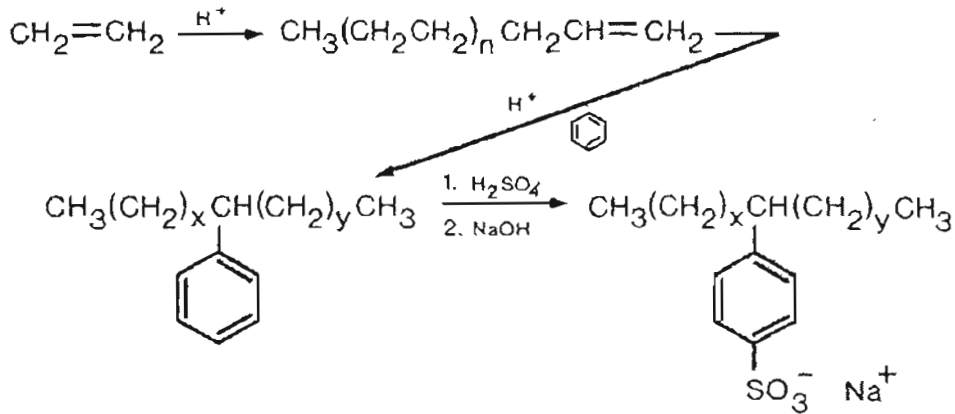




- **linear** alkylbenzenesulfonates are degraded more readily than branched analogs during sewage treatment



- alkylbenzenesulfonates are made by Friedel-Crafts acid-catalysed alkylation of benzene, followed by sulfonation



- Detergent 1 (previous page) made from propene
- **builders** (source of OH<sup>-</sup>) are added to detergents to improve grease-cutting

- RCO<sub>2</sub><sup>-</sup> acts as its own builder i.e. polyphosphate ions
- phosphates have a dual role: builder and Ca sequestration (i.e. scavenge metal ions to allow the surfactants to work efficiently)
- sodium carbonate is a non-phosphate builder, but precipitates Ca
- "industrial" detergents often contain NaOH (pH > 12)

this was the use of phosphates in detergents.

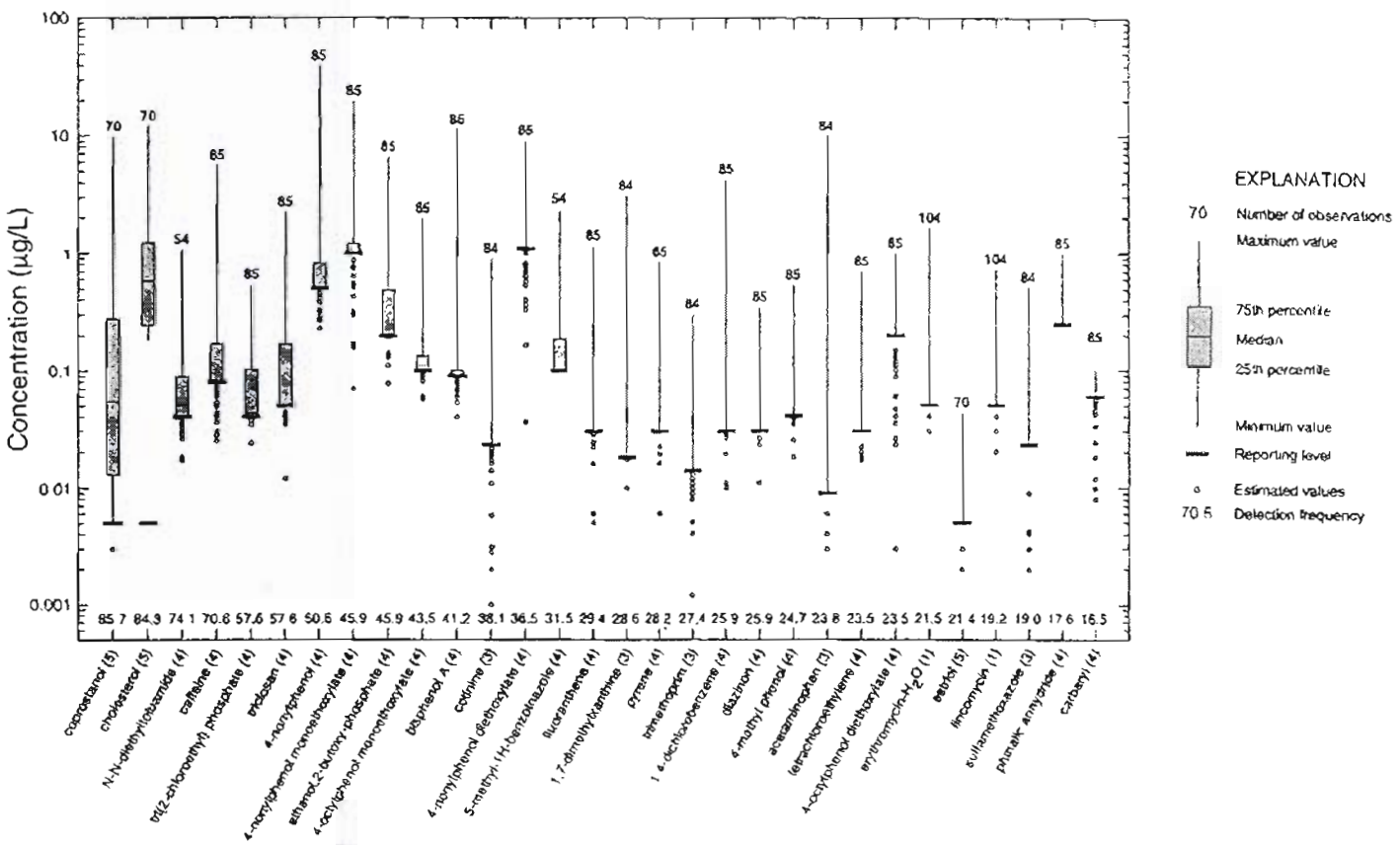
In phosphate-free detergents the phosphates are replaced by either:

- alternative builders like zeolites or aluminosilicates
- and inc. concn of surfactants

(but, some of these materials may be toxic ... deal with in sewage plant)

- emerging concern: pharmaceuticals in treated sewage (*Environ. Sci. Technol.*, 36, 1202, 2002)
  - bigger issue in Europe than North America (population density)
  - compounds detected include antibiotics, prescription and non-prescription drugs, steroids (see later: endocrine disrupters), as well as “wastewater-related” chemicals

– and the metabolites produced by patients.



- data refer to 139 US rivers and streams

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Industrial aqueous wastes - Section 8.2.1.

- biological treatment the best option for organic wastes
- "bioX" reactors = aerobic, analogous to activated sludge reactor for sewage
- major industries: food; pulp and paper; BOD makes these wastes damaging to the environment if untreated. Major goal is BOD reduction
  - huge amounts of "organic" waste
- aerobic process: oxidising microorganisms. Fast. organic matter converted to CO<sub>2</sub> + microbial biomass
  - reduces residence time in reactor (hence smaller facility)
  - The reactor/lagoon is aerated
- anaerobic reactors less common: slower (hence less throughput), "off gases" are <sup>mal</sup>odorous amines and sulfides
  - reductive treatment
- volume of reactor depends on treatment time and volume of waste to treat per unit time

$$V(\text{reactor}) = \text{Flow rate (m}^3 \text{ h}^{-1}) \times \text{Residence time (h)}$$

i.e. resistant to oxidation.

- problems of recalcitrant and toxic compounds
  - { recalcitrant = discharged untreated
  - { toxic = shuts down the reactor (can poison the microorganisms)

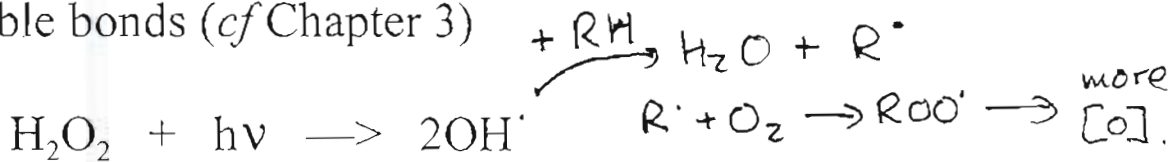
→ One approach to these guys is to concentrate them in an adsorbing agent (e.g. granulated activated carbon (GAC)). High cost method and still need to dispose of the adsorbent.

Section 8.2.2.

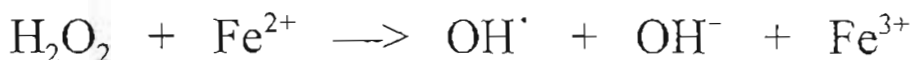
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“Advanced Oxidation Processes” for recalcitrant and toxic wastes: generally involve aqueous hydroxyl radicals

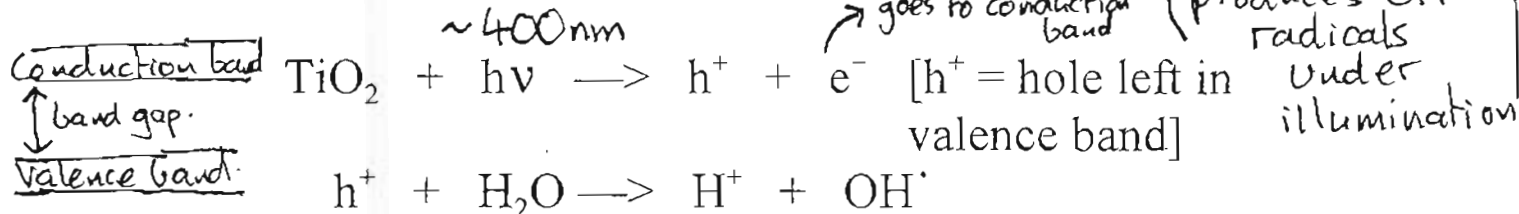
- UV-ozone or UV-hydrogen peroxide: source of  $\text{OH}_{\text{aq}}$  which initiate oxidation by H-abstraction or addition to double bonds (cf Chapter 3)



- “Fenton” chemistry:  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$



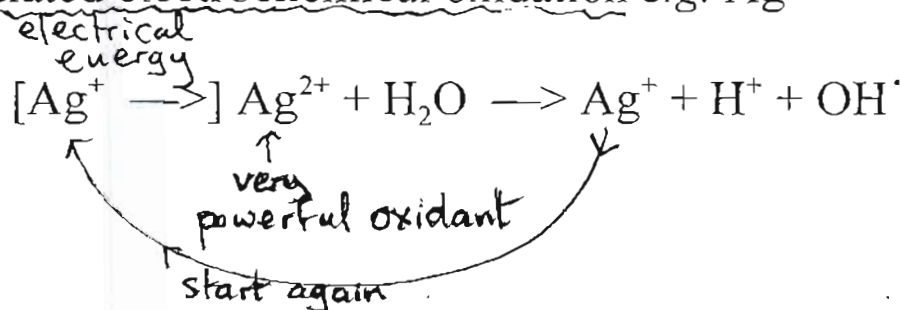
- semiconductor assisted oxidation (much hyped!)



The idea is that sunlight could be used because  $\text{TiO}_2$  absorbs in the UV-A region

- electrochemical oxidation: a “green” approach as only electrons are involved. Problems include the need for a supporting electrolyte; electrodes made of inexpensive materials free from fouling

- mediated electrochemical oxidation e.g.  $\text{Ag}^+$



$\text{OH}^\cdot$  radicals can initiate destruction of organic compounds, inc. PCBs, PAHs and chloroalkanes

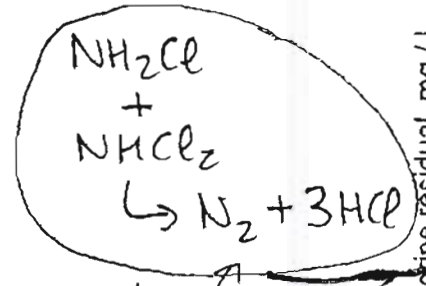
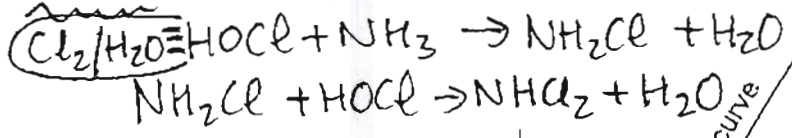
blow air onto aqueous spray. Volatile contaminants transfer, aq → gas

Inorganic aqueous wastes

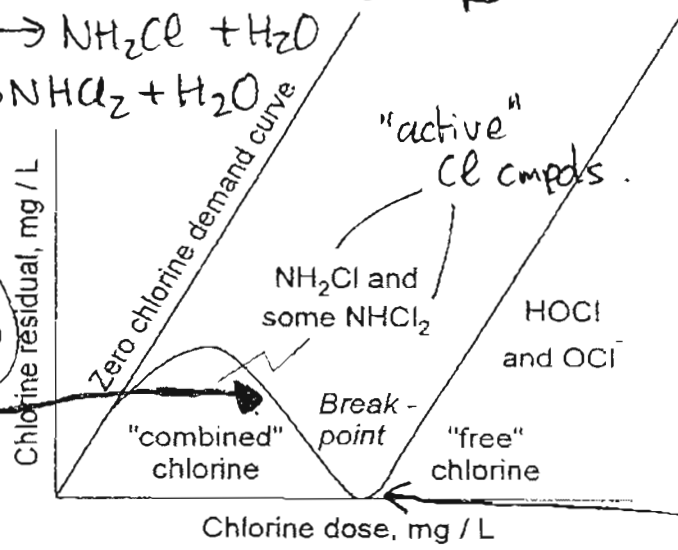
- air stripping (Henry's Law) for ammonia (and also for low molar mass organics): undesirable because it releases material to the atmosphere → e.g. VOCs
  - neutralization (waste acids and bases)
- inexpensive but pollution simply transferred to gas phase.

\* (see bottom)  
NH<sub>3</sub>

breakpoint chlorination of ammonia toxic to aquatic life



this rx. taking place, "active" Cl compounds reacting



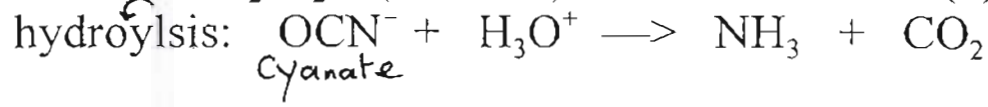
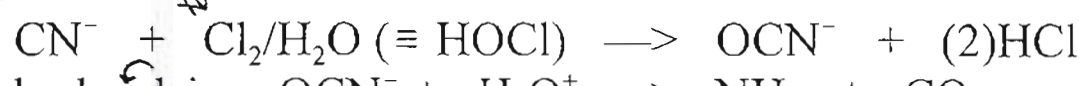
Schematic of the progress of a breakpoint chlorination

better to pass over an [O] catalyst → CO<sub>2</sub>

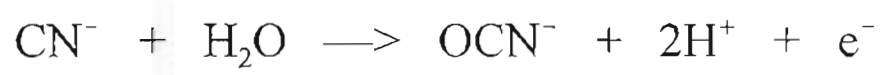


oxidation/hydrolysis of cyanide ion (used in electroplating & metal finishing)

CN<sup>-</sup>



CN<sup>-</sup> can also be oxidized electrolytically



So metals + CN<sup>-</sup> often found together

NH<sub>3</sub>

\* Nitrification also: Microbial oxidation of ammonia ⇒ NO<sub>3</sub><sup>-</sup>

at industrial sites etc.

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## Remediation of contaminated soil Section 8.6

- Organics can be remediated; metals cannot. Bioremediation is the preferred option.
- Most contaminated areas are former industrial sites or dumps; gas stations; wood treatment. Unremediated "brownfields" sites cannot be redeveloped.
- In situ remediation by stimulating microbial growth: <sup>including genetically engineered organisms \* see bottom</sup> limitation of "bugs in a bag"  
→ Land set aside to spread waste, oily stuff. Eventually (years) biological [b] does its thing.
- Land farming: issues of VOC release and accumulation of high molar mass compounds including PAHs
- "Natural bioremediation" = do nothing
- Use of vegetation for in-situ decontamination
  - Phytoremediation: both inorganics and organics: for metals need "hyperaccumulators". Also applicable to aqueous streams: engineered wetlands  
→ high press. jets of H<sub>2</sub>O
  - Soil washing followed by treatment of the fines in a bioreactor: expensive and destroys soil structure; horseradish peroxidase as an enzymatic approach  
→ electrodes placed in soil, melts (~2000°C), vitrifies. Organics are incinerated.
- Incineration and vitrification: "last resort" methods, but guaranteed as permanent solutions
- Costs per site usually tens of million \$\$: US Superfund legislation for "orphaned" sites

\* Such "super organisms" don't always work 'cos the indigenous microbes, knowing their territory, out-compete the foreigners

→ one example of the "ultimate treatment methods"

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Solidification – cement and lime-based technologies (see text p272)

Cement manufacture:  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2$  Typically contains 60-65% CaO, 20-25%  $\text{SiO}_2$  (see text, p. 272)

Making concrete:  $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$

Setting concrete:  $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$   
i.e. hardening (+ interlaced silicate fibres)

Examples:

- setting the finely divided solids from flue gas (coal burning power stations) desulfurization (where  $\text{SO}_2$  escape is minimised) e.g.  $\text{CaSO}_3/\text{CaSO}_4$ .
- radioactive wastes: combination of vitrification and concrete encapsulation: Yucca Mountain, Nevada

For a story on Yucca Mountain in *Chem Eng News* see:

<http://pubs.acs.org/isubscribe/journals/cen/81/i01/html/8101gov1.html>

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Website re-designed and restructured

Traditionally thought of as "pure" water (wells, etc.)

~~WATER~~  
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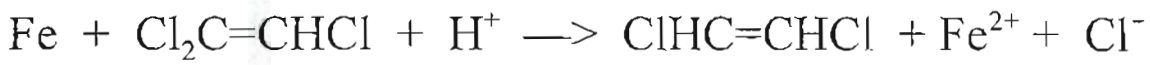
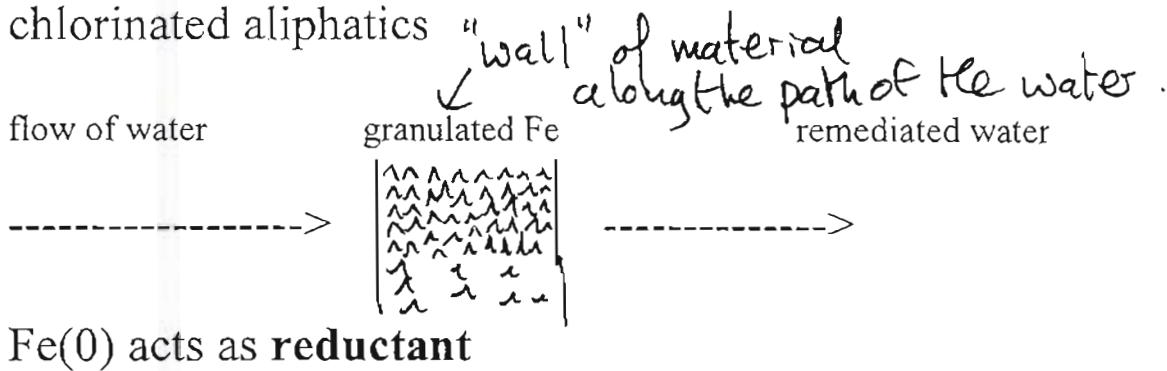
Remediation of ground water (no section in book for this)

- flows often slow:  $m\ yr^{-1}$ ; slowest in clay  
Becoming depleted... susceptible to contamination
- commonest contaminants trichloroethylene (TCE) and tetra/per chloroethylene (PCE). Also nitrate ions,  $NO_3^-$   
(and many other organics) (my notes p 139)  
halogenated/aromatic
- pump-and-treat methods usually unsuccessful, due to DNAPL sources continuing the contamination [DNAPL = dense non aqueous phase liquid]  $\Rightarrow$  oily blobs of polychlorinated solvents + creosote & coal tar.

act as reservoirs of the nasties

treatment usually involves oxidation: peroxide; Fenton's reaction;  $KMnO_4$   
 $H_2O_2/Fe^{2+}$

- in situ permeable reactive barriers (PRBs) involving granulated iron (Gillham, U of Waterloo): useful for chlorinated aliphatics



then  $\rightarrow$  further reduction of dichloroethylene  $\rightarrow C_2H_4 + 3Cl^-$

- Read descriptive material in the text pp. 258-280
  - $\rightarrow$  8.3. Hazardous and toxic wastes
    - 8.3.1 Landfilling (leachate from old sites - also release of  $CH_4$  + other gases)
    - 8.3.2 Love Canal (nr. Niagara Falls, N.Y.); houses built on a dumpsite.
    - 8.3.3 Other dumping procedures.
    - 8.4 Treatment of wastes (recycling, plastics...)
    - 8.5. Ultimate treatment methods for hazardous wastes. (solidification, incineration, cement/lime, plastics & encapsulation, vitrification)
    - 8.6. Soil and site remediation.