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CEE 370 Environmental Engineering Principles

Lecture #35

Hazardous Waste I:

Intro and Treatment

Reading: Mihelcic & Zimmerman, Chapter 10

Reading Reading: Davis & Cornwall, Chapt 9

Reading: Davis & Masten, Chapter 14

Hazardous Wastes

- Definition
- Sources
- Health Effects
- Regulations
- Minimization
- Treatment & Disposal
- Site Remediation

Introduction

- A special class of wastes: special handling and disposal required
- Materials which pose a certain threat to human health and the environment
- byproducts of 20th century industry and technology
- large amounts have been disposed of carelessly
  - Love Canal
  - Times Beach

Haz. Waste Legislation

- Toxic Substances Control Act (TOSCA); 1976
  - toxic effects of new chemicals
  - testing of existing chemicals
  - warning labels to outright bans (e.g., PCBs)
- Resources Conservation and Recovery Act (RCRA); 1976, later reauthorized
  - designation of hazardous wastes
  - requirements for facilities that generate, transport, treat, store or dispose (TSDFs) of HW, "cradle to grave"
    - uniform HW manifest
    - permitting of TSD facilities
  - underground storage tanks

Legislation (cont.)

- Comprehensive Environmental Response, Compensation, and Liabilities Act (CERCLA); 1980
  - "Superfund" to clean up abandoned sites
  - Hazard Ranking System (HRS)
  - National Priority List (NPL)
  - Reauthorized in 1986 (SARA)

Designation of HW under RCRA

- Ignitability
- Corrosivity
  - pH 2 and below; or pH 12.5 and above
  - corrodes steel 0.25 in/y at 55 C
- Reactivity
  - reacts violently with or without water
  - generates toxic gases
- Toxicity
  - Toxicity Characteristic Leaching Potential (TCLP) and toxicity characteristics

See: Mihelcic & Zimmerman, Section 10.2.6

Contaminants

EPA NO.	CONTAMINANT	MAXIMUM CONC., MG/L	EPA NO.	CONTAMINANT	MAXIMUM CONC., MG/L
D004	Arsenic	5.0	D008	Lead	5.0
D005	Barium	100.0	D009	Mercury	0.2
D018	Benzene	0.5	D010	Selenium	1.0
D006	Cadmium	0.1	D011	Silver	5.0
D019	Carbon tetrachlo-ride	0.5	D012	Endrin	0.02
D020	Chlordane	0.03	D013	Lindane	0.4
D021	Chlorobenzene	100.0	D014	Methoxychlor	10.0
D022	Chloroform	6.0	D015	Toxaphene	0.5
D007	Chromium	5.0	D016	2,4-D	10.0
			D017	2,4,5-TP Silvex	1.0

Alternative Definition for HW

HW from Non-specific sources

Hazardous Waste No.	Waste Description	Hazard Code1
F001	Spent halogenated solvents used in degreasing, tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and the chlorinated fluorocarbons; and sludges from the recovery of these solvents in degreasing operations.	T
F006	Wastewater treatment sludges from electroplating operations.	T
F007	Spent plating bath sludges from electroplating operations.	R,T
F010	Quenching bath sludge from oil baths from metal heat treating operations.	R,T

HW from Specific Sources

Hazardous Waste No.	Waste Description	Hazard Code1
Wood Preservation:K001	Bottom sediment sludge from the treatment of wastewaters from wood preserving processes that use creosote and/or pentachlorophenol	T
Inorganic Pigments:K005	Wastewater treatment sludge from the production of chrome green pigments	T
Organic Chemicals:K020	Heavy ends from the distillation of vinyl chloride in vinyl chloride monomer production	T
Pesticides: K032	Wastewater treatment sludge from the production of chlordane	T
Explosives: K044	Wastewater treatment sludges from the processing of explosives	R
Petroleum Refining: K052	Tank bottoms (leaded) from the petroleum refining industry	T
Leather Tanning Finishing: K053	Chrome (blue) trimmings generated by the following subcategories of the leather tanning and finishing industry:	T
Iron and Steel: K060	Ammonia still lime sludge from coking production	T

HW from Discarded Products, etc.

Hazardous Waste No.	Description
P012	Arsenic trioxide
P089	Parathion
P110	Tetraethyl lead
U051	Creosote
U151	Mercury
U226	1,1,1-trichloroethane

RCRA Classifications

- Four Program Areas
  - Hazardous Waste Program
  - Solid Waste Program
  - Underground Storage Tanks (UST) Program
  - Medical Waste Program
- Generators
  - Small Quantity (SQG): 100-1000 Kg
    - 180-270 days storage
  - Large Quantity: >1000 Kg
    - 90 days storage; many obtain TSDF permits for longer times
  - Must initiate a manifest; Special labeling and handling; training required

RCRA (cont.)

- Transporters
  - must have EPA ID number and take responsibility
- Treatment, storage and disposal facilities
  - administrative standards
    - rules on waste analysis, site security, inspections, training emergency preparedness and manifests
  - general standards
    - record keeping, groundwater monitoring, closure, postclosure monitoring & maintenance (30 yrs for landfills), financial considerations
  - permit-specific standards
    - specific to type of facility, e.g., landfills must have double liners and double leachate collection systems

CERCLA

- Also known as Superfund or SARA
- Intended as a solution to those previously contaminated sites with no-one to pay (no PRPs)
- Two levels
  - emergency response
    - immediate threat to human health or environment
  - long term remediation
    - if Hazard Ranking System (HRS) shows a score over 27.5, it is added to the National Priorities List (NPL) for Superfund cleanup
    - 1300 sites on NPL in 1990, more to come

Waste Minimization

- Recycling
  - reuse of a waste product
  - example: electroplating and recovery of heavy metals by ion exchange, reverse osmosis, etc.
- Source Reduction
  - process modification to reduce the use of toxic materials
  - example: electroplating and movement away form cyanide-based processes.

Treatment and Disposal Methods

- Physical and Chemical Treatment
  - Precipitation and Coagulation
  - Filtration
  - Neutralization
  - Oxidation and Reduction
  - Air stripping & extraction
  - Adsorption Processes
- Landfill Disposal
- Incineration
- Chemical Fixation

Precipitation and coagulation

Used mostly to remove metals from wastewater

Many metals become insoluble at pHs from 8 to 10

Addition of lime for raising pH

$$Cu^{+2} + Ca(OH)_2 \rightarrow Cu(OH)_2 \downarrow + Ca^{+2}$$

$$2Cr^{+3} + 3Ca(OH)_2 \rightarrow 2Cr(OH)_3 \downarrow + 3Ca^{+2}$$

Wet Air Oxidation

- Zimmerman process
- oxygen at elevated temperature & pressure
  - 300-3000 psig; 175-325 C
- once started it is usually self-sustaining
- Applicability:
  - wastes that are too wet for incineration and too toxic for biodegradation
- Commercial operations:
  - Zimpro (Rothschild, WI)
  - IT Enviroscience (Knoxville, TN)

Chemical Oxidation: chlorine

Cyanide destruction by chlorine

$$CN^- + OCl^- + H_2O \rightarrow CNCl + 2OH^-$$

Cyanogen chloride

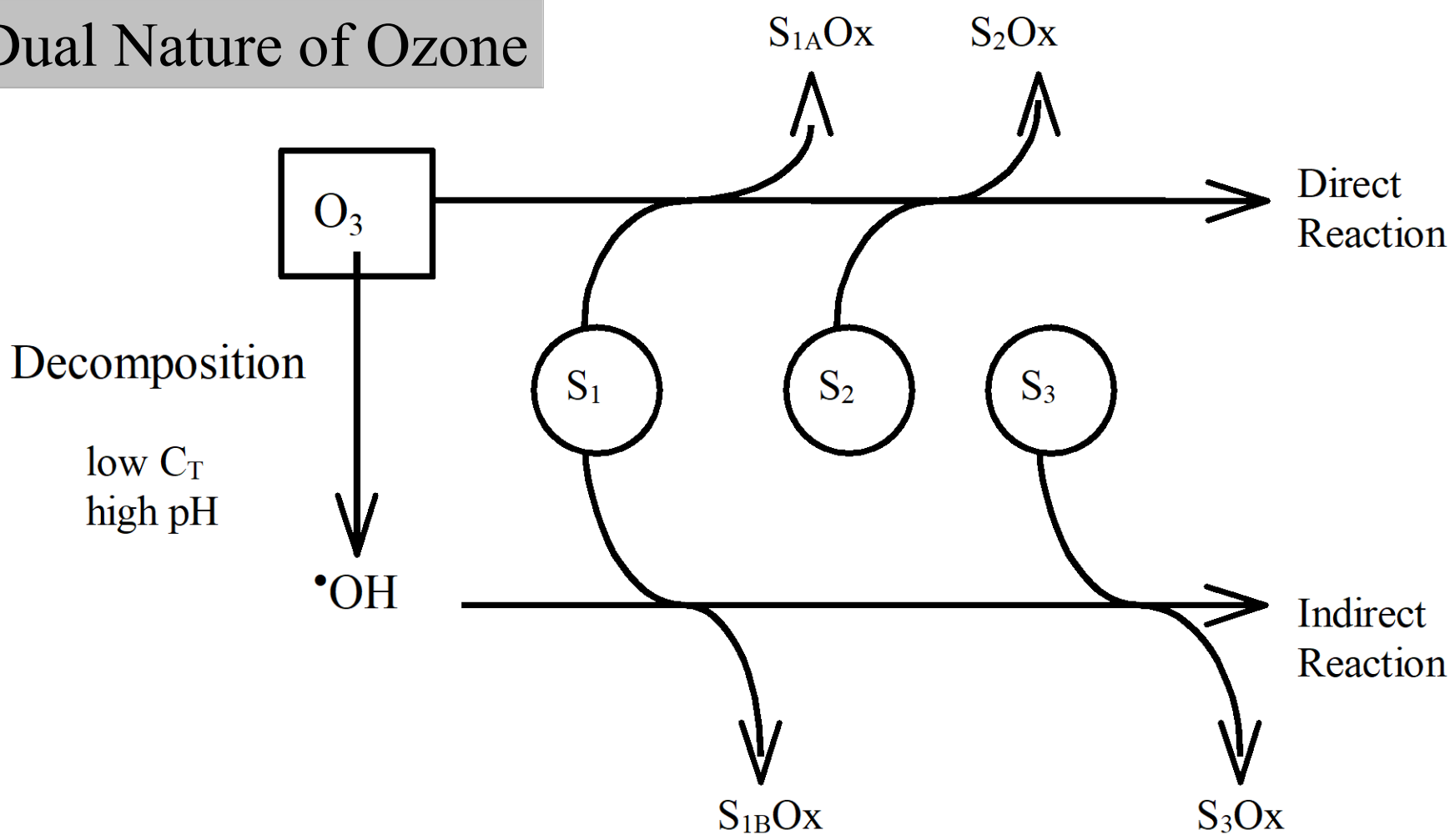
$$CNCl + 2OH^- \rightarrow CNO^- + Cl^- + H_2O$$

$$2CNO^- + 3HOCl + H_2O \rightarrow 2HCO_3^- + N_2 + 3Cl^- + 3H^+$$

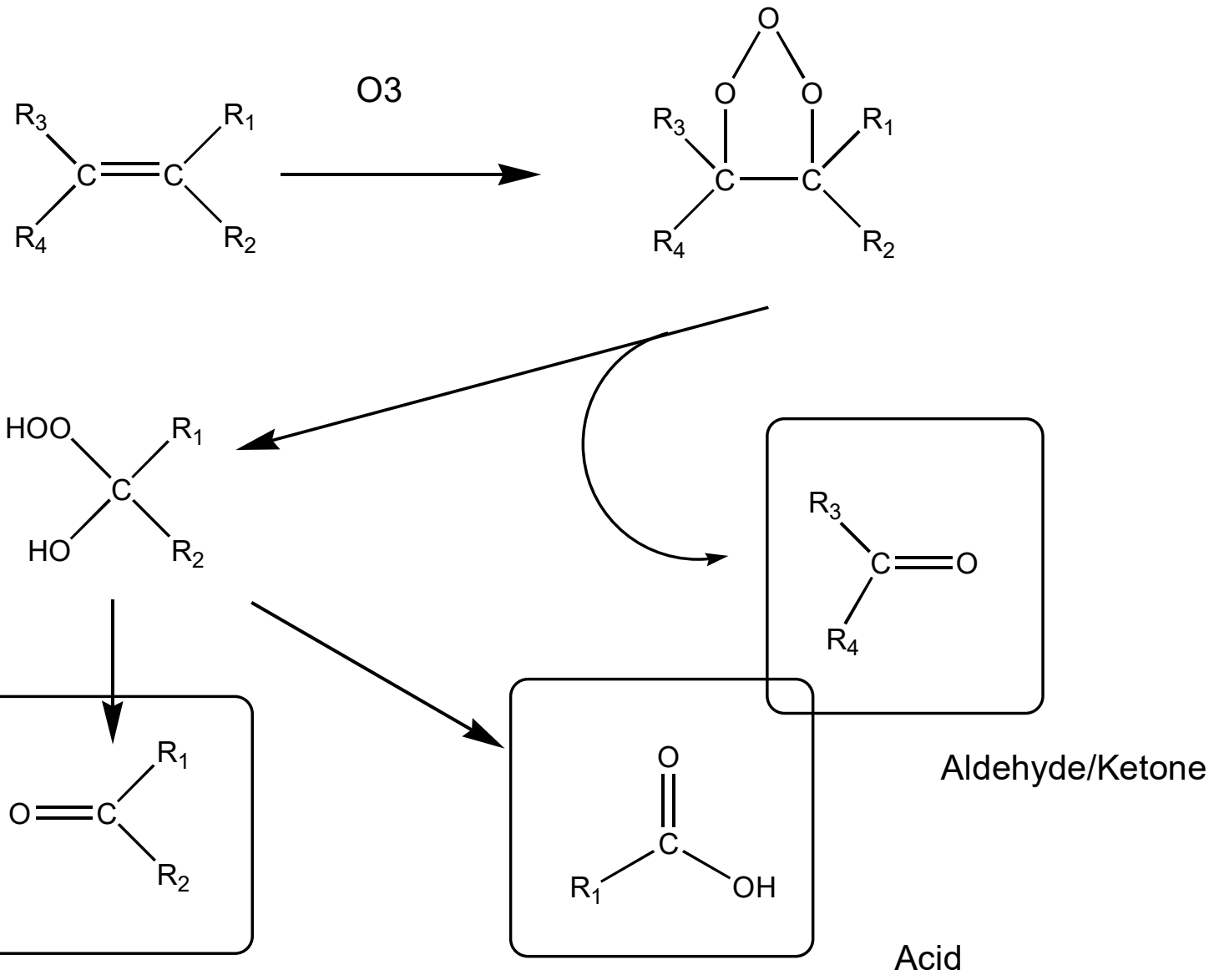
Can achieve up to 99.9% cyanide removal

Chemical Oxidation: Ozone

Dual Nature of Ozone



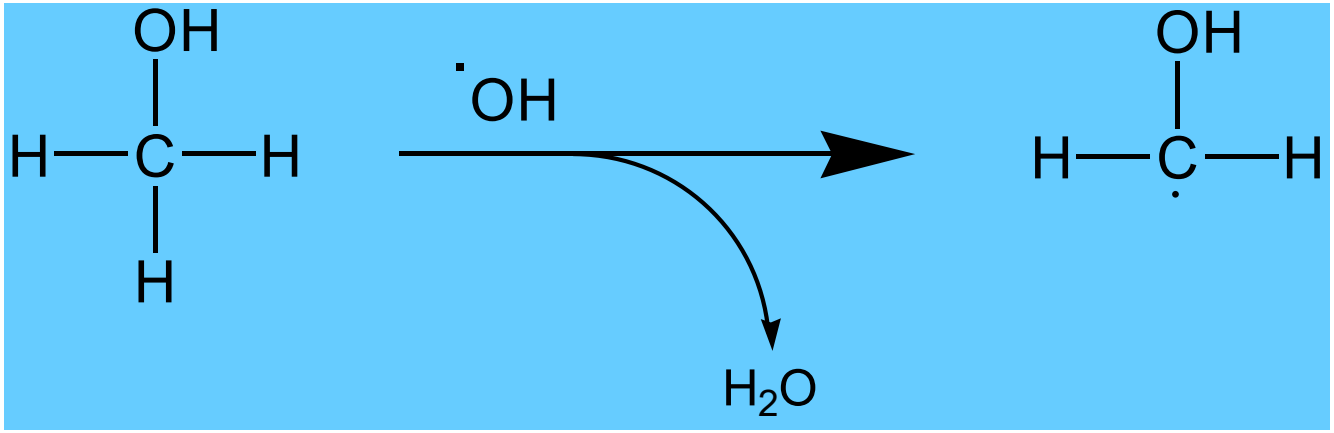
Criegee Ozonolysis Mechanism



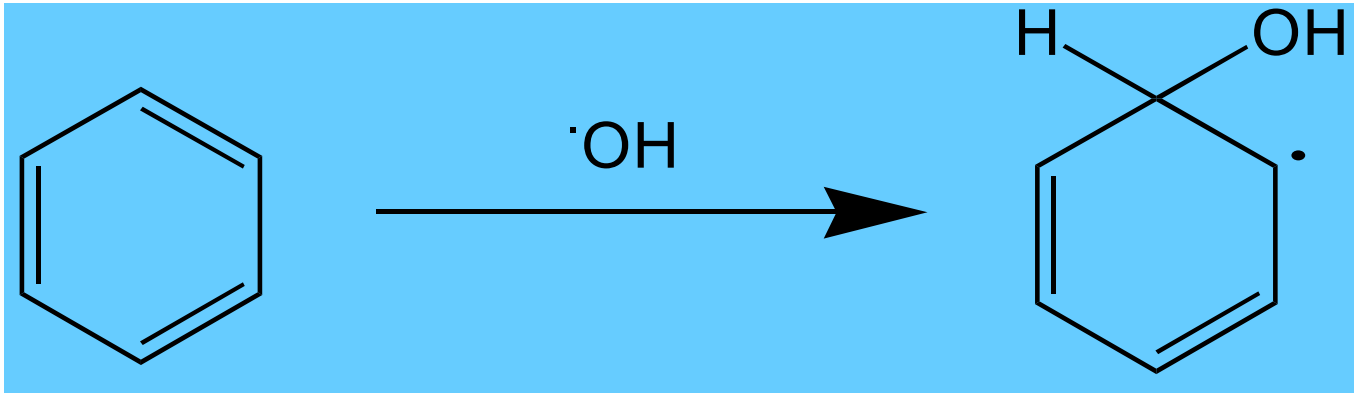
David Reckl

Radical reactions

Hydrogen Abstraction



Addition



Ozone

- Commercial Operations
  - ozone: hydrogen peroxide & UV:
    - removal of 1,1-DCA and 1,1,1-TCA
    - Ultrox; Santa Ana, CA
  - ozone, UV and ultrasound:
    - use ultrasound to first extract organics
    - treatment of PCBs and chlorinated phenols
    - Ozonics: Boca Raton, FL

Landfill Disposal: Landfilling

- best for solids that have little leaching capacity
- organic solvents, dioxins and some other toxics are banned from landfilling
- new landfills must have two liner systems, and two leachate collection systems, as well as a gas collection system
- must be capped
- groundwater must be monitored

Incineration

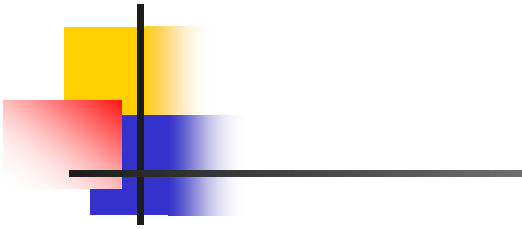
- Preferred option for many HWs
- must have wet air scrubber to remove acids particulates, etc.
- large volume is reduced to:
  - residual ash
  - air-scrubber sludge
- little or no liability
- example: incineration of PCB:

$$C_{12}H_6Cl_4 + 12\tfrac{1}{2}O_2 \rightarrow 12CO_2 + H_2O + 4HCl$$

Chemical Fixation

- Also known as stabilization or solidification
- use of a solidification agent to create a non-leachable solid

Solidification Method	Applicable Wastes
Portland cement	Sludges, contaminated soil, metal salts, low level radioactive waste
Lime or quick lime	Sludges containing metals and oils, contaminated soils, flue gas desulfurization wastes, other inorganic wastes
Thermoplastics	Strong oxidizers, inorganic salts, low molecular weight volatiles, radioactive wastes
Self-cementation	Flue gas desulfurization wastes, other wastes with large proportions of calcium sulfate or calcium sulfite



- To next lecture