Chemical Oxidation and Reduction

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What is *oxidation*?

- Simply put: The adding of an oxygen atom
- You are changing the composition of a molecule in order to change how it behaves

CHEMICAL OXIDATION

The use of oxidizing agents without the need of microorganisms for the reactions to proceed

oxidizing agents : O_3, H_2O_2, Cl_2 or HOCl or O_2 etc

catalysts : pH , transition metals, light , ..etc

Oxidizers

- Fluorine (F^-)
- Hydroxyl Radical (OH^o)
- Ozone (O_3)
- Chlorine (Cl^-)
- Bromine (Br^-)
- Hydrogen Peroxide (H_2O_2)

Types of oxidation Processes

1. **Conventional oxidation processes**

   - Use common oxidizing agents such as ozone, chlorine without production of highly reactive species

2. **Oxidation processes carried out at high temperature/ high pressure**

   - Produce highly reactive species, hydroxyl radicals (HO·)

3. Advanced oxidation processes (AOPs)

- Produce highly reactive species, hydroxyl radicals (HO ·) using oxidizing agents and catalysts

Oxidation rate observed

$$HO\cdot > O_3 > H_2O_2 > HOCl > ClO_2 > KMnO_4 > Cl_2 > O_2$$

Oxidizers

- These oxidizers do not contribute to TDS
  - Hydroxyl Radical (OH^o)
  - Ozone (O_3)
  - Hydrogen Peroxide (H_2O_2)
  - UV light

Common Oxidation Agents Used in Wastewater Treatment

The following strong oxidants find application in waste treatment:

- Sodium hypochlorite .... $NaClO$
- Calcium hypochlorite .... $Ca(ClO)_2$
- Chlorine .... Cl_2
- Potassium permanganate .... $KMnO_4$
- Hydrogen peroxide .... H_2O_2
- Ozone... O_3
- Oxygen... O_2

Common Reduction Agents Used in Wastewater Treatment

The following strong reducing agents find application in waste treatment:

- Sulfur dioxide .... SO_2
- Sodium bisulfite .... $NaHSO_3$
- Ferrous sulfate .... $FeSO_4$

Chlorine as an Oxidation Agent

- Chlorine gas dissolves in water where it hydrolyzes according to the reaction:

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^-$$

- Hypochlorous acid is a weak acid which dissociates forming:

$$HOCl \leftrightarrow H^+ + OCl^-$$

- The equilibrium equations are:

Sodium Hypochlorite and Calcium Hypochlorite as Oxidation Agents

- Sodium hypochlorite and calcium hypochlorite also hydrolyze when placed in solution:

$$NaOCl \leftrightarrow Na^{+} + OCl^{-}$$

$$Ca(OCl)_2 \leftrightarrow Ca^{++} + 2\ OCl^{-}$$

$$H^{+} + OCl^{-} \leftrightarrow HOCl$$

partially reforming the undissociated acid.

- The sum of the (OCl^{-}) and (HOCl) concentration is called the *free available chlorine*.
- The distribution of the ionic species in equilibrium is a strong function of pH

Ozone as an Oxidizing Agent

- Ozone is a gas at normal pressure and temperature. Its solubility in water is a function of its partial pressure and temperature
- Ozone is generated by high voltage discharge in air or oxygen
- Ozone is unstable and tends to react to form:

$$O_3 + H^+ + e^- \rightarrow O_2 + H_2O$$

- Ozone is a very strong oxidizing agent
- Ozone is very effective as a decoloration agent and as a oxidant of organic material

Hydrogen Peroxide as an Oxidizing Agent

- Hydrogen peroxide (H_2O_2) is a colorless water (30 - 70 % solution) which in the presence of a catalyst (such as iron) reacts to form:

$$H_2O_2 + 2\ H^+ + 2\ e^- \leftrightarrow 2\ H_2O$$

- Hydrogen peroxide is a strong oxidant typically used in the treatment of cyanides and wastewaters containing organic materials

Oxygen as Oxidizing Agent in Wet Oxidation

- Wet oxidation is a process in which oxygen dissolved in the wastewater under pressure is used as an oxidizing agent at high temperature and pressure
- Typical temperatures and pressures are 150 - 325 °C and 2000 to 20,000 kPa (gauge pressure), respectively
- The process is extremely effective in oxidizing organic materials, organic sulfur, cyanides, pesticides, and other toxic compounds with removal efficiencies of the order or 99+%

Typical Applications of Redox Reactions to Wastewater Pollutants

- Inorganic Pollutants
  - heavy metals
  - cyanides
  - Sulfides
- Organic Pollutants
  - phenol and chlorophenols
  - pesticides
  - ammonia nitrogen and amines
  - sulfur-containing organic compounds (e.g., mercaptans)

Cyanide Removal from Wastewaters

- Cyanide (CN^-) is a common pollutant found in many industrial applications, especially metal plating
- Because of its extreme toxicity even at low concentrations cyanides must be removed prior to wastewater discharge
- Chemical treatment of cyanide typically involves its oxidation with a strong oxidizing agent to cyanate (CNO^-), followed by the oxidation of the cyanate to carbon dioxide, nitrogen, water and NaCl

Oxidation Reactions for the Conversion of Cyanide to Cyanate

Oxidizing Agent	Reaction
Sodium hypochlorite	$2\ NaCN + 5\ NaOCl + H_20 \rightarrow N_2 + 2\ NaHCO_3 + 5\ NaCl$
Calcium hypochlorite	$4\ NaCN + 5Ca(OCl)_2 + 2\ H_20 \rightarrow 2N_2 + 2\ Ca(HCO_3)_2 + 3\ CaCl_2 + 4\ NaCl$
Chlorine	$2\ NaCN + 5\ Cl_2 + 12\ NaOH \rightarrow N_2 + 2\ Na_2CO_3 + 10\ NaCl + 6\ H_20$

Oxidation Reactions for the Conversion of Cyanide to Cyanate

Oxidizing Agent	Reaction
Potassium permanganate	$NaCN + 2\ KMnO_4 + 2\ KOH \rightarrow 2\ K_2MnO_4 + NaCNO + H_20$
Hydrogen peroxide	$NaCN + H_2O_2 \rightarrow NaCNO + H_2O$
Ozone	$NaCN + O_3 + H_20 \rightarrow NaCNO + O_2$

Mineralization of Cyanide with Chlorine or Hypochlorite

Mineralization (i.e., conversion to CO_2, H_2O and N_2) is carried out sequentially in two steps. Reaction time = 10 - 30 min.

- Step 1: Cyanide conversion to cyanate (pH = 9 -11)

$$NaCN + 2\ NaOH + Cl_2 \rightarrow NaCNO + 2\ NaCl + H_2O$$

using chlorine, or

$$NaCN + NaOCl \rightarrow NaCNO + NaCl$$

using hypochlorite

- Step 2: Cyanate mineralization with Cl_2 (pH = 8.5)

$$2\ NaCNO + 4\ NaOH + 3\ Cl_2 \rightarrow N_2 + CO_2 + 6\ NaCl + H_2O$$

Removal of Iron and Manganese from Wastewater

- Soluble ferrous (Fe^{2+}) and manganous (Mn^{2+}) ions are removed by precipitation as $Fe(OH)_3$ and MnO_2, respectively via oxidation
- The reaction rate is a function of pH, alkalinity, and impurities that can act as catalyst
- As oxidation agents oxygen (O_2), chlorine (Cl_2), or permanganate (MnO_4^-)are typically used

Oxidation Reactions Involved in the Removal of Iron and Manganese

- With oxygen (pH = 7 for Fe; pH = 10 for Mn; 10 - 20 min):

$$2\ Fe^{2+} + 1/2\ O_2 + 5\ H_20 = 2\ Fe(OH)_3\downarrow + 4\ H^+$$

$$Mn^{2+} + 1/2\ O_2 + H_20 = MnO_2\downarrow + 2\ H^+$$

- With Cl_2 (fast reaction):

$$Fe^{2+} + 1/2\ Cl_2 + 3H_20 = Fe(OH)_3\downarrow + Cl^- + 3\ H^+$$

$$Mn^{2+} + Cl_2 + 2\ H_20 = MnO_2 + 2\ Cl^- + 4\ H^+$$

- With $KMnO_4$ (pH = 6 - 9; very fast reaction):

$$3\ Fe^{2+} + MnO_4^- + 7\ H_20 = 3\ Fe(OH)_3\downarrow + MnO_2\downarrow + 5\ H^+$$

$$3\ Mn^{2+} + MnO_4^- + 2\ H_20 = 5\ MnO_2\downarrow + 4\ H^+$$

Removal of Residual Nitrogen (as Ammonia) via Chlorination

Ammonia nitrogen can be chemically removed via reaction with chlorine according to the reaction:

$$2\ NH_3 + 3\ HOCl \rightarrow N_2\ 3\ H_2O + 3\ HCl$$

The reaction pH is typically in the range 6 - 7

Oxidation of Organic Material in Wastewater

- The BOD or COD of wastewater can be chemically reduced using oxidation agents such as Cl2 or ozone. The typical dosage to be used for chemical oxidation of organic material is:

		Dosage (lb/lb removed)	
Chemical	Use	Range	Typical
Chlorine	BOD_5	0.5 - 2.5	1.75
	Reduction	1.0 - 3.0	2.0
Ozone	COD	2 - 4	3.0
	Reduction	3.0 - 8.0	6.0

After Metcalf and Eddy, *Wastewater Engineering*, 1991, p. 755

Chemical Oxidation Treatment Technologies

Pall Life Sciences, Inc.
Treatment Options Considered

- ***Ex situ* treatment**
  - **OH radical based treatment**
    - **ozone/hydrogen peroxide**
    - **UV/hydrogen peroxide**
- ***In situ* treatment**
  - **Ozone treatment**
    - **ozone-rich water injection**
    - **ozone sparging**
  - **OH radical based treatment**
    - **ozone sparging with hydrogen peroxide injection**
    - **hydrogen peroxide/$FeSO_4$ injection (Fenton's reagent)**
    - **hydrogen peroxide injection (Fenton's reagent)**

OH radical Based Treatment

Ozone/H_2O_2, UV/ H_2O_2 and Fenton's Reagent

- **Advantages**
  - **1,4-Dioxane is reactive with $^{\cdot}OH$**
  - **Shown to be effective (especially first two)**
- **Disadvantages**
  - **Carbonate and bicarbonate compete for $^{\cdot}OH$**

OH radical Based Treatment

Relative Reactivities

- **Alkalinity ≈ 300 mg/L as $CaCO_3$**
  - **Bicarbonate ≈ 5.95 x 10^{-3} M**
  - **Carbonate ≈ 0.05 x 10^{-3} M**
- **Dioxane = 100 to 600 ppb ≈ 4.38 x 10^{-6} M**
- **OH radical rate constants**
  - **Bicarbonate ≈ 2 x 10^{7} $M^{-1}\cdot s^{-1}$**
  - **Carbonate ≈ 3 x 10^{8} $M^{-1}\cdot s^{-1}$**
  - **Dioxane ≈ 6 x 10^{9} $M^{-1}\cdot s^{-1}$**

OH radical Based Treatment

Relative Reactivities

$$\frac{-d[^{\cdot}OH]}{dt} = (k_{CO_3^{2-}}[CO_3^{2-}] + k_{HCO_3^-}[HCO_3^-] + k_D[D] + k_{H_2O_2}[H_2O_2])[^{\cdot}OH]$$

where D= 1,4-dioxane

- **First order rate constants**

  $k_{Bicarbonate} = (2 \times 10^7\ M^{-1}\cdot s^{-1})(5.95 \times 10^{-3}\ M) = 1.19 \times 10^5\ sec^{-1}$

  $k_{Carbonate} = (3 \times 10^8\ M^{-1}\cdot s^{-1})(0.05 \times 10^{-3}\ M) = 1.5 \times 10^4\ sec^{-1}$

  $k_{Dioxane} = (6 \times 10^9\ M^{-1}\cdot s^{-1})(4.38 \times 10^{-6}\ M) = 2.6 \times 10^4\ sec^{-1}$

Assumes concentrations of species are constant.

OH radical Based Treatment

Ozone/H_2O_2, UV/ H_2O_2 and Fenton's Reagent

- **Advantages**
  - 1,4-Dioxane is reactive with $^{\cdot}OH$
  - Shown to be effective (especially first two)
- **Disadvantages**
  - Carbonate and bicarbonate compete for $^{\cdot}OH$
  - Byproducts formation

OH radical Based Treatment

Degradation Products

- **1,2-ethanediol monoformate ester: O=CH-O-CH_2CH_2OH**
- **1,2-ethanediol diformate ester: O=CH-O-CH_2CH_2O-CH=O**
- **Methoxyacetic acid: CH_3OCH_2COOH**
- **Glycolic acid: $HOCH_2COOH$**
- **Glyoxal: OHCCHO**
- **Glyoxylic acid: OHCCOOH**
- **Oxalic acid: HOOCCOOH**
- **Formaldehyde: HCHO**
- **Formic acid: HCOOH**

No mention of rates!

$^{\cdot}$OH from UV/H_2O_2 (Stefan and Bolton, 1998)

OH radical Based Treatment

Ozone/H_2O_2, UV/ H_2O_2 and Fenton's Reagent

- **Advantages**
  - 1,4-Dioxane is reactive with $^{\cdot}OH$
  - Shown to be effective (especially first two)
- **Disadvantages**
  - Carbonate and bicarbonate compete for $^{\cdot}OH$
  - Byproducts formation
  - Costs
  - Safety

Fenton's Reagent

- Fenton's Reagent : catayzed hydrogen peroxide.
- Catalyzer is a transition metal (usually Fe^{2+}).
- Goal is to produce •OH; a strong, non-specific, oxidizing agent.
- Catalyzer can be added in solution or can be an mineral present in the soil

Fenton's Reagent

Advantages:

- Un-reacted H_2O_2 degrades to oxygen.
- Reaction times with most organics and OH radicals are fast.

Disadvantages:

- Large amounts of reagents needed
- Many side reactions due non-specific nature of $^{\cdot}OH$

Ozone

- **Considerations**
  - **Strong, selective oxidant**
    - **Reaction of 1,4-dioxane with molecular ozone is slow**
  - **Kinetics**
    - **$k_{dioxane}$ = 0.32 $M^{-1}s^{-1}$**
    - **typical aqueous ozone concentration = 2 mg/L**
    - **Assuming, ozone concentration is constant at 2 mg/L; half life of dioxane is 14.4 hrs**

Ozone

- **Considerations**
  - **Degrades to form OH radicals**
    - **powerful, nonselective oxidant**
    - **reaction of 1,4-dioxane with OH radicals is rapid**
  - **Byproduct formation?**
  - **Costs**
  - **Safety**

Work Plans and recent Report focus on in-situ remediation treatment

In-situ Chemical Oxidation Treatment (ISCO)

Goal is to convert contaminants into less hazardous compounds and ultimately CO_2. However, it is unlikely that mineralization will be achieved with a single oxidant at cost-efficient doses and times.

- Used with a wide range of contaminants.
- Efficacy depends on the reactivity of the oxidant and the target chemical and the ability to deliver the oxidant to the contaminated area.
- Most common oxidants: $KMnO_4$, H_2O_2 (as Fenton's Reagent), and O_3.
- Sometimes combined with biological treatment.

Alternatives Considered

- **Fenton's reagent**
  - **hydrogen peroxide/$FeSO_4$ injection**
  - **hydrogen peroxide injection**

Fenton’s Reagent

Advantages:

- Used in soil in saturated and unsaturated zones.
- Capital costs for treatment are low.
- Operating costs are moderate.
- Believed to enhance bioremediation of some chemicals, by increasing dissolved oxygen.

Fenton's Reagent

Disadvantages:

- Large amounts of reagents needed
- Lack of monitoring or site characterization may result in adverse effects.
- Lack of catalyzer or inefficiency of catalyzer to be recycled affects the system
- Concentrations as low as 11% can cause ground water to boil.

Fenton's Reagent

Safety Issues:

- Hydrogen peroxide is highly reactive.
- Reactions are exothermic and significant increases in temperature may occur.
- Rapid evolution of oxygen, steam and carbon dioxide can occur.
- Allowances should be made to ensure adequate venting of these gases.
- If possible, the H_2O_2 should be added stepwise or in a slow, controlled continuous fashion.

Selected H_2O_2 Field Testing

- **Applied's Vadozone**
  - ***In situ*** **chemical oxidation technology (patents pending) is designed to deliver hydrogen peroxide (H_2O_2) into a contaminated water via nested injection points.**
  - **Hydrogen peroxide injection rates are tightly controlled to eliminate the potential for significant temperature increases in the subsurface. A Soil Vapor Extraction (SVE) system is also frequently employed in the area of injection to remove accumulated gasses.**

Selected H_2O_2 Field Testing

- **Printing Facility, North Carolina**
  - **A Fenton's reagent ISCO pilot study was completed in Spring 2003 to address 1-4 dioxane in saprolitic soils and groundwater at an active printing facility. GCI was able to deliver reagents and establish an effective radius of influence from each of the injectors. Based on analytical data collected 45-days post-injection, 1-4 dioxane had been reduced by 98% in the treatment zone with similar reductions found downgradient to the treatment area.**

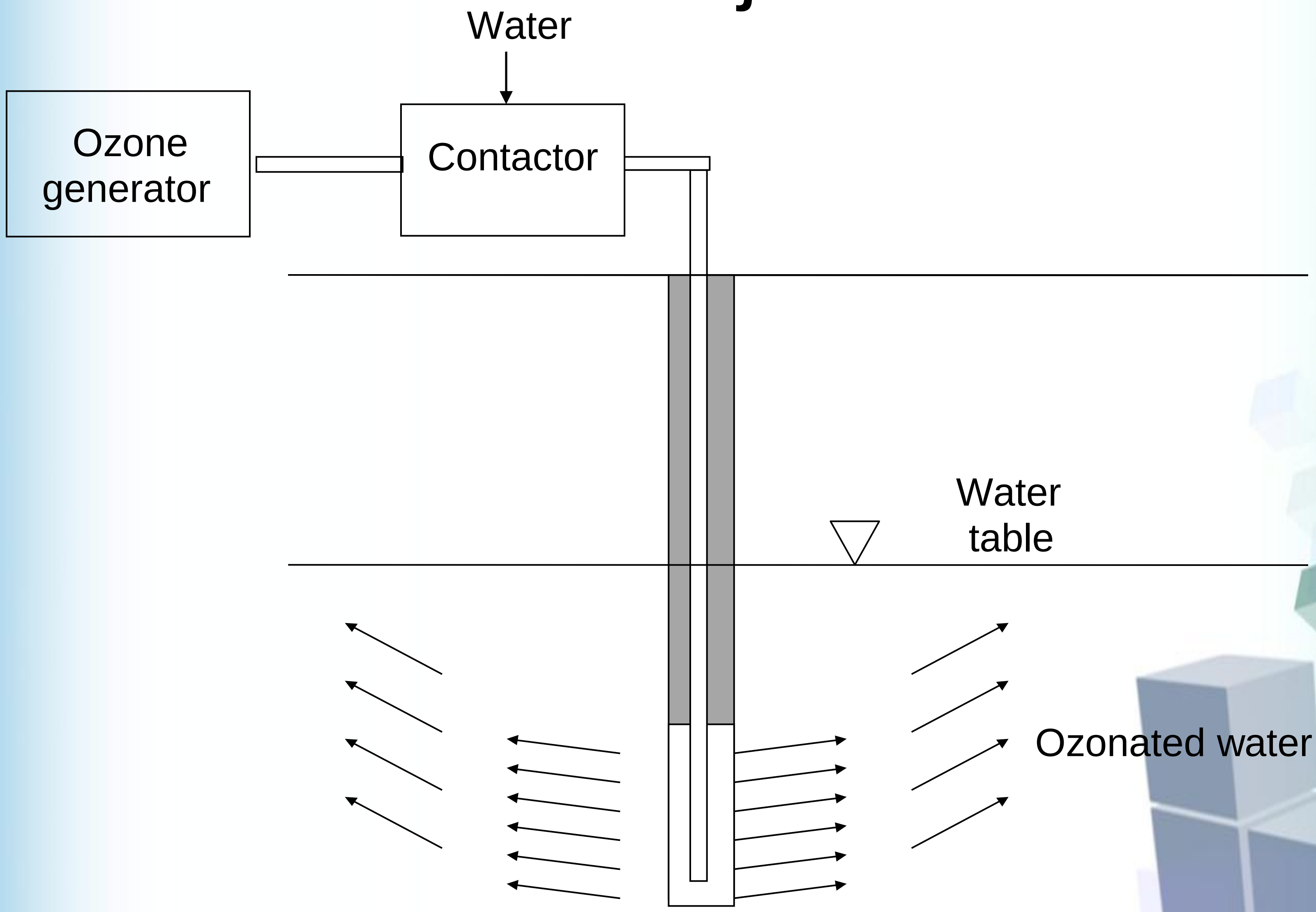
Alternatives Considered

- **Ozone processes**
  - **Injecting ozone-rich water into aquifer**
  - **Ozone sparging**
  - **Ozone sparging with hydrogen peroxide injection**

Considerations in Using *In-Situ* Ozonation

- **Considerations**
  - **Soil organic matter and moisture content consume ozone**
  - **Rates of reaction of ozone vs. OH radical**
  - **High bicarbonate concentrations will favor molecular ozone reactions**
  - **Groundwater has high bromide concentration, bromide reacts with ozone to produce bromate, which is regulated at 10 ppb under the Safe Drinking Water Act**
  - **Ozone by-products from 1.4-dioxane**
  - **Biodegradability of ozone by-products**
  - **Effect of ozone on the natural soil microbial community**

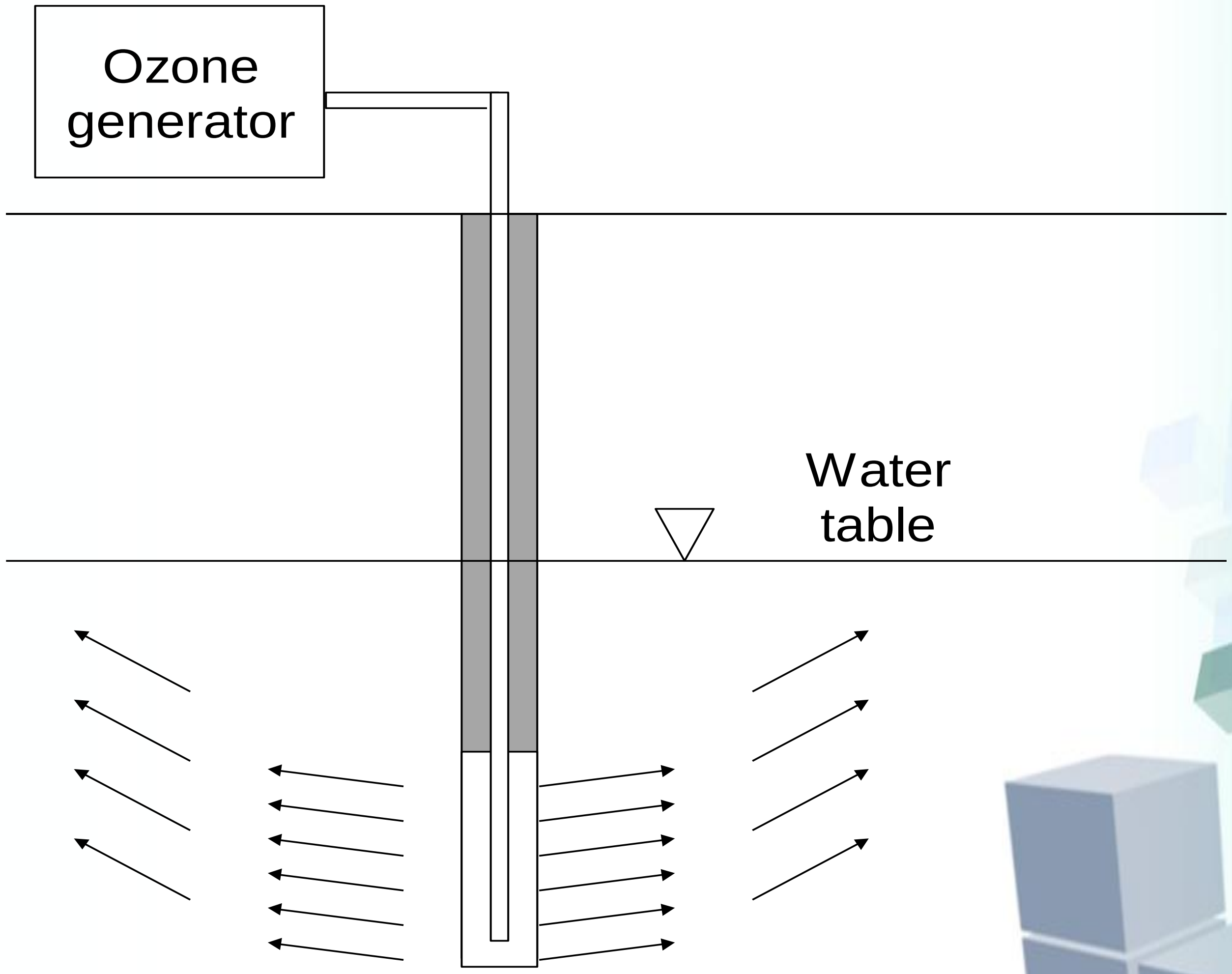
In-situ Ozonated Water Injection



In-situ Ozonated Water Injection

- **Special Considerations**
  - **Same as those for ozone based processes**
  - **Ozone decomposition in water within contactor**
  - **Dilution of water in aquifer**
  - **Ozone destruct unit required on contactor for off-gas treatment**

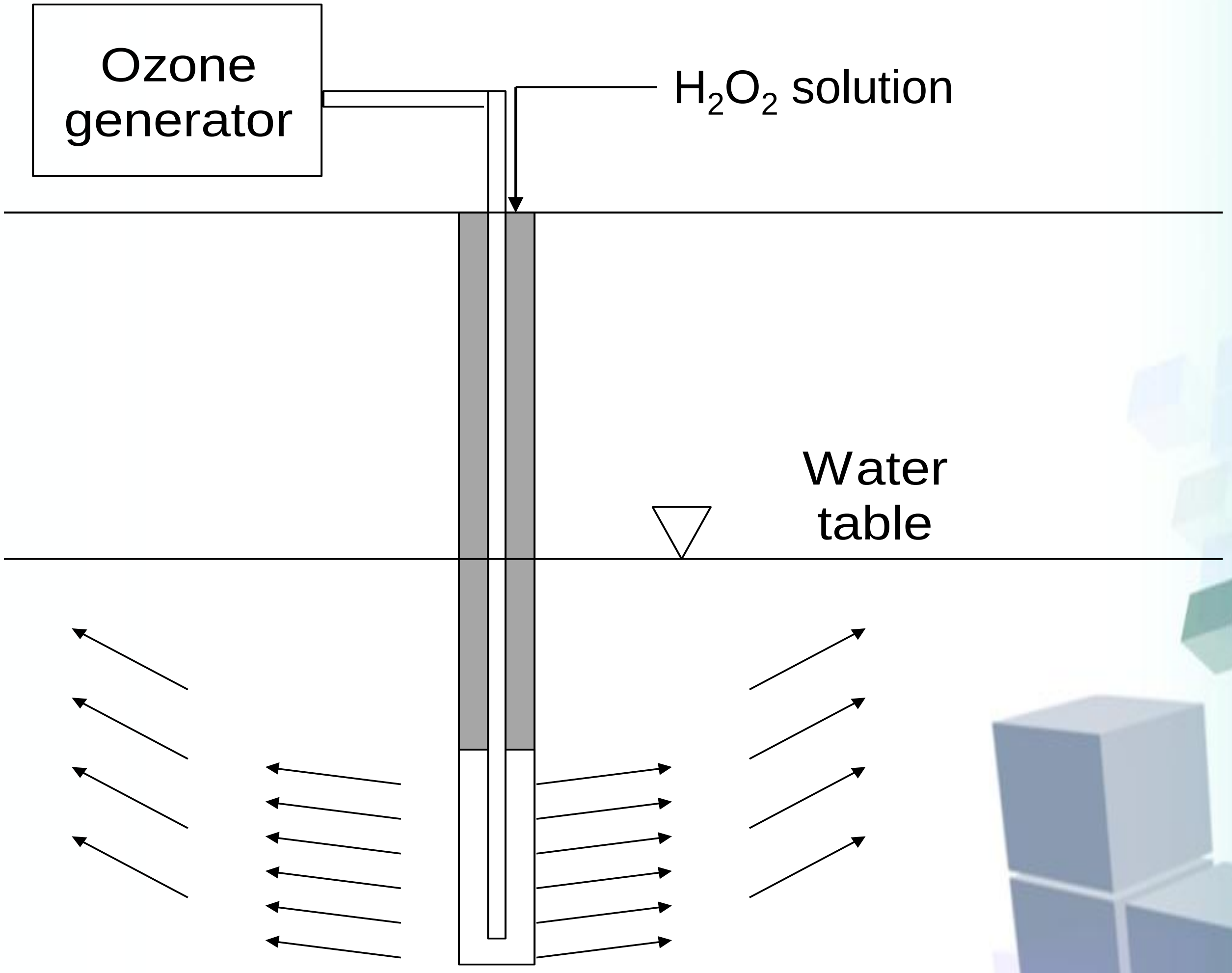
In-situ Ozone Sparging



In-situ Ozone Sparging

- **Special Considerations**
  - **Same as those for ozone based processes**
  - **Gas transfer into groundwater**
  - **Radius of influence**
  - **Contact of contaminants in groundwater with ozone**

In-situ Ozone Sparging with H_2O_2



In-situ Ozone Sparging with H_2O_2

- **Special Considerations**
  - **Same as those of OH radical based processes**
  - **Gas transfer into groundwater**
  - **Liquid transfer through different well?**
  - **Radius of influence**
  - **Contact of contaminants in groundwater with short-lived OH radicals**

Recommendations

- **Address the following issues**
  - **Dilution vs. oxidation**
  - **Rates of oxidation**
  - **Determination of radius of influence**
  - **Formation of oxidation byproducts**
  - **Gas production**
  - **Potential for exothermic reactions**
  - **Need for off-gas ozone destruction**
  - **With in situ ozone/H_2O_2, injection of liquid and gas**

Source:

Chemical Oxidation Treatment Technologies

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