GET IN the OZONE

The Chemistry of Ozone Disinfection in Wastewater

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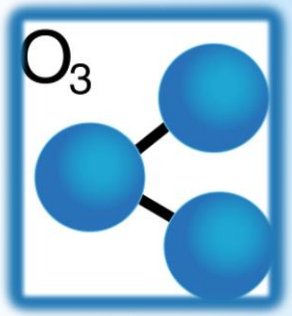
CH2M HILL

Birth of a Molecule

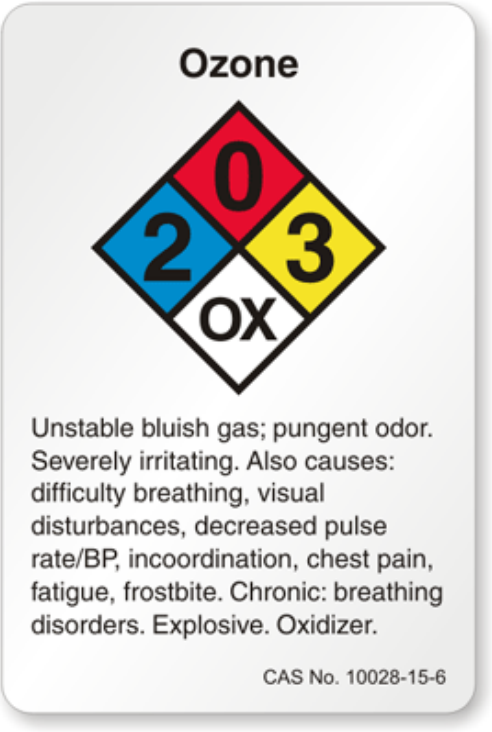


- Dr. Matinus van Marum

  the “odor of electrical matter” was first observed in 1785 during electrical experiments

- Christian Friedrich Schönbein

  discovery in 1840 - Ozone from the Greek word “ozein” – to smell



Ozone Disinfection

- De Méritens

  1886 wastewater disinfectant

- Dr. Fröhlich

  1891 full scale disinfection by Siemens and Halske at Martinikenfeld, near Berlin

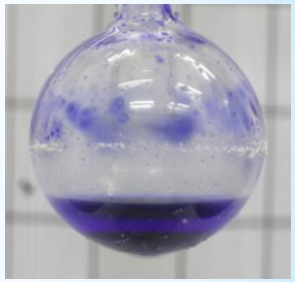
Ozone

Appearance

gas – pale blue

liquid – dark blue (-112°C)

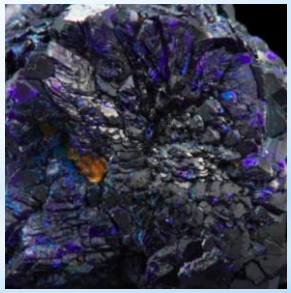
solid – violet black



Odor

pungent smell similar to bleach

detectable at 10 ppm

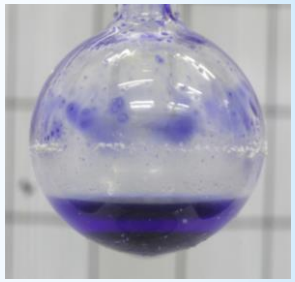


Chemistry

Ozone

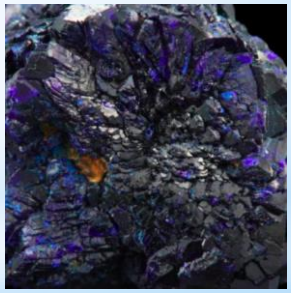
Volatile

- detonates when *warmed* to -111°C
- explosive above 240g/m^3



Oxidizer

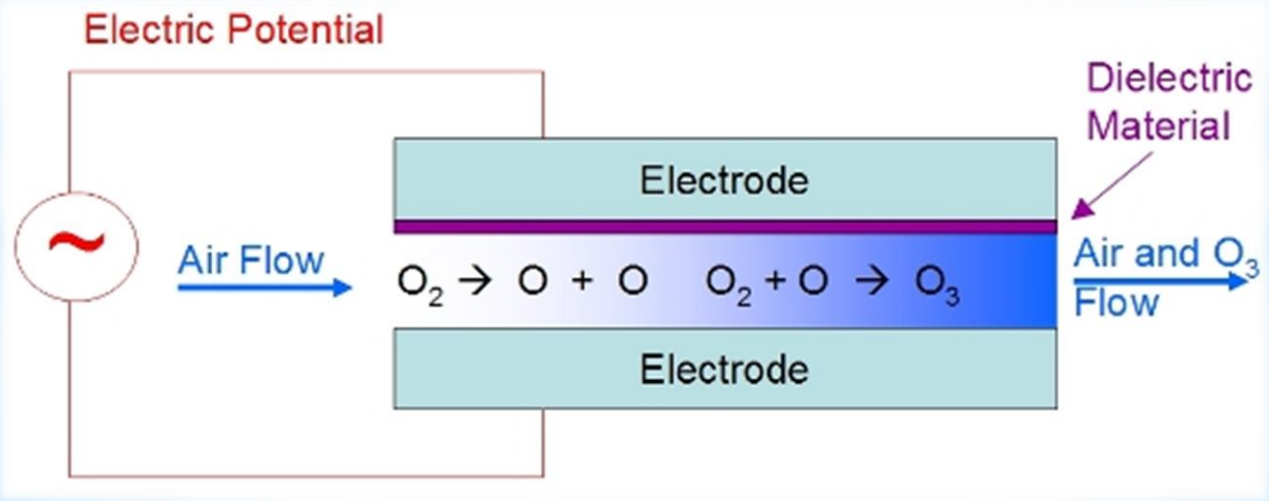
- causes cellular damage to tissues



Chemistry

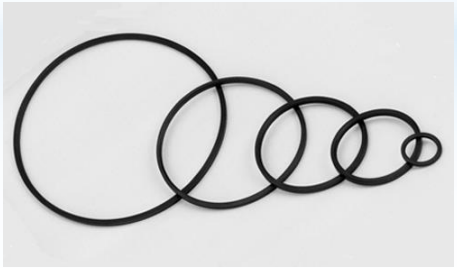
Ozone Generation

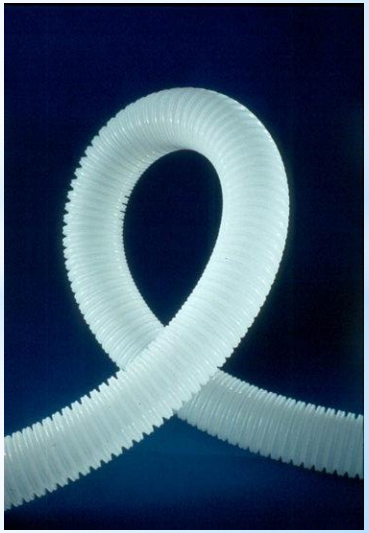
- Oxygen (O_2) molecules are dissociated by an energy source into oxygen atoms which collide with another oxygen molecule to form ozone (O_3)
- Impose a high voltage current (6 to 20 kilovolts) across a dielectric discharge gap that contains an oxygen-bearing gas
- Generated on-site because it is unstable



Ozone Disinfection

- Least used method in the US
- Able to achieve higher levels of disinfection than UV or chlorine with a shorter contact time
- Utilizes specialized equipment and training
- Requires resistant materials due to corrosive nature



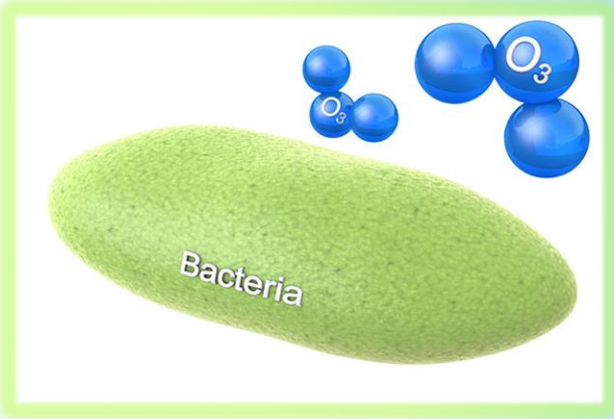


Ozone Disinfection

- Higher capital and maintenance costs, but rapidly becoming a more affordable option
  - Smaller storage and contact requirements
  - No transportation of hazardous materials
  - Chlorine = \$0.028/m^3, with de-chlorination = \$0.0427/m^3
  - Ozone disinfection = \$0.043/m^3

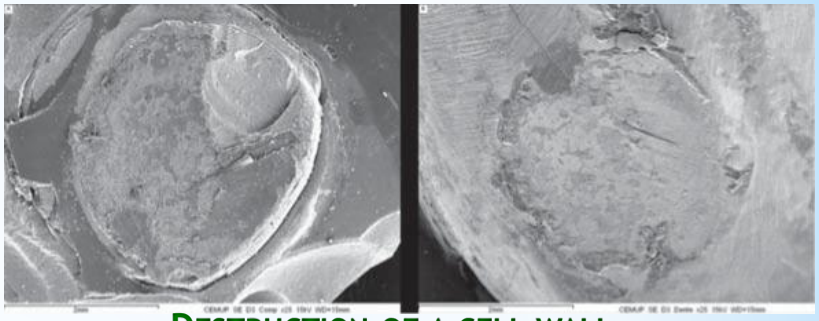
Ozone Disinfection

- Application of ozone in water treatment was performed in 1893 in Holland. Since that time, its use has spread in Europe and the US
- Due to its strong oxidizing properties, ozone is currently known as one of the most efficient and fastest microbicides
- Breaks the cell membrane resulting in 99% removal of bacteria and viruses
- In 1998 USEPA and the Safe Drinking Water Act of 1991 confirm that ozone is effective in removing hazardous pathogens and chlorine resistant Cryptosporidium from water

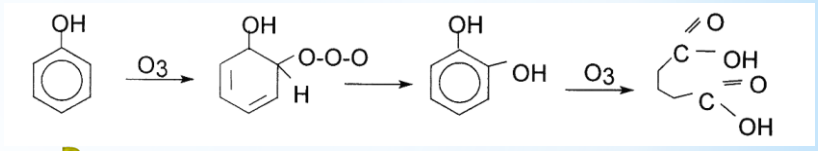


Mechanisms of Disinfection

- Oxidation of the cell wall
- Reactions with (·OH) radical by-products
- Damage to cell components: enzymes, proteins, DNA, RNA
- Breakage of C-N bonds leads to depolymerization
- Oxidizes glycoproteins, glycolipids, certain amino acids, and sulfhydryl groups of enzymes

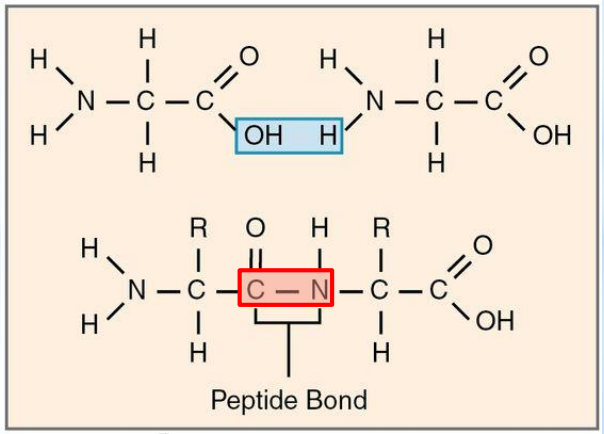


DESTRUCTION OF A CELL WALL



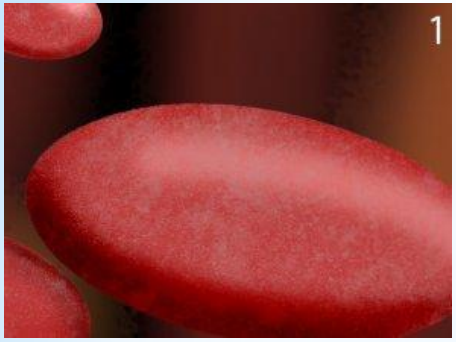
PHENOL – METABOLIC PRODUCT FOUND IN URINE

GLYCINE AMINO ACIDS

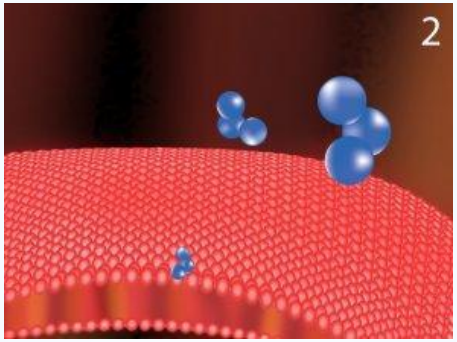


DEPOLYMERIZATION

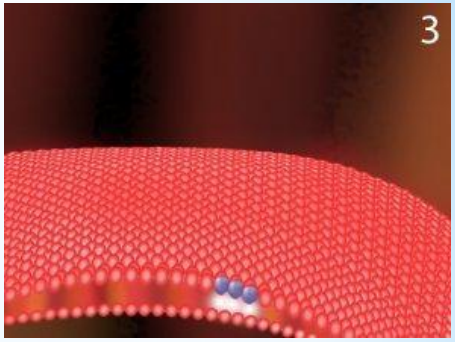
Death of a Cell(s) …man



HEALTHY CELL

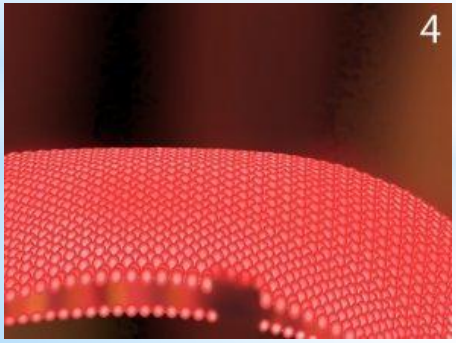


OZONE COMES IN CONTACT WITH CELL WALL

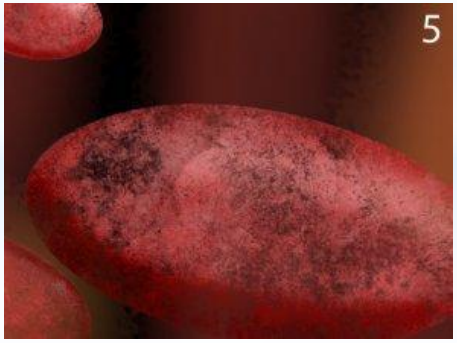


A REACTION CALLED AND OXIDATIVE BURST OCCURS

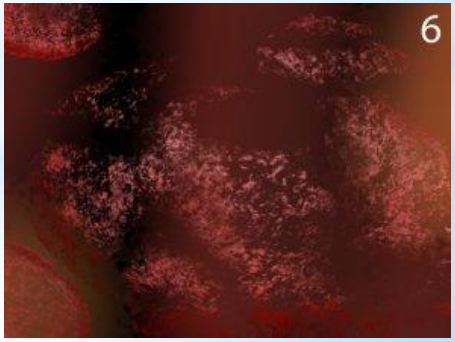
…CREATING A HOLE IN THE CELL WALL



THE CELL WALL LOSES ITS SHAPE AS MORE HOLES ARE CREATED



1000'S OF COLLISIONS IN SECONDS AND THE CELL DIES



Electron microscope image at 15,000x Air Liquide America Corp, Chicago Research Center, James T.C. Yuan, PhD, 2000.

Destruction of cell walls:

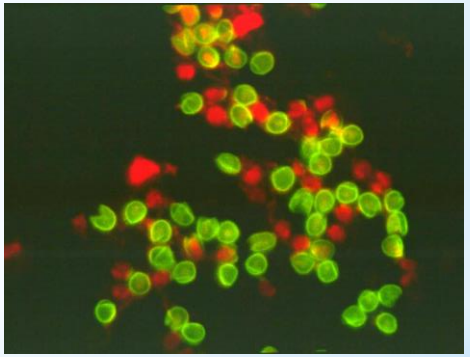
- Osmotic bursting
- Continues to oxidize enzymes, DNA, RNA

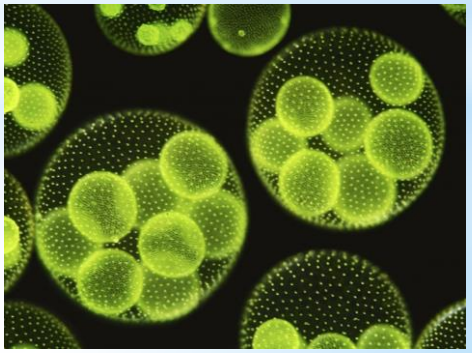
Mechanisms of Disinfection

- Viruses: Ozone oxidizes the proteins of their envelope and modifies the three-dimensional structure. When this occurs, the virus cannot anchor itself onto the host cell

- Spores: Ozone at concentrations slightly higher than the ones used for the rest of bacteria can overcome spore resistance

- Algae: Ozone causes algae to emerge to the surface and oxidizes the metabolic derivatives of the algae, eliminating undesirable tastes and odors



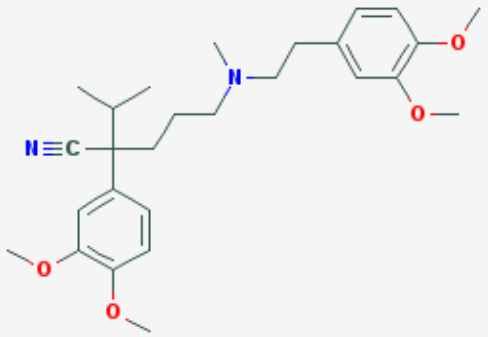


Removal of Pharmaceuticals

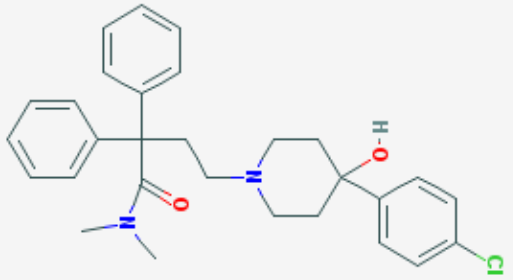
- Ozone is a strong oxidant which attacks electron rich structures in molecules, such as double bonds
- Removes up to 99%
- Paired with H_2O_2 reduces treatment time and reaction tank volume required due to formation of hydroxyl radicals and secondary oxidants

High Ozone Reactivity

- Electron rich methoxy groups, benzene rings and tertiary amines all provide ozone reactive sites
  - Verapamil, a calcium channel blocker
    - 4 methoxy groups
  - Loperamide, antidiarrheal
    - Amine group and 2 benzene rings



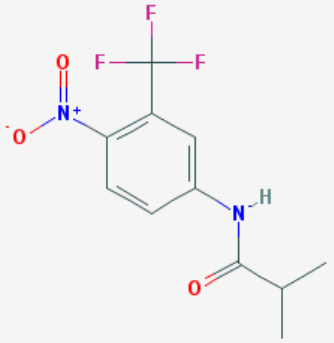
Verapamil



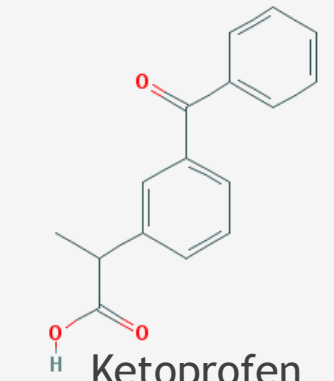
Loperamide

Low Ozone Reactivity

- Electron withdrawing groups result in low ozone reactivity
  - Flutamide, anti-androgen
    - Trifluoromethyl (-CF3) and nitro (-NO2)
  - Ketoprofen, anti-inflammitory
    - Carbonyl group
- Higher dosage will force degradation
  - via secondary oxidation of O_3 into the hydroxyl radical ·OH
    - very reactive with most organic molecules



Flutamide



Ketoprofen

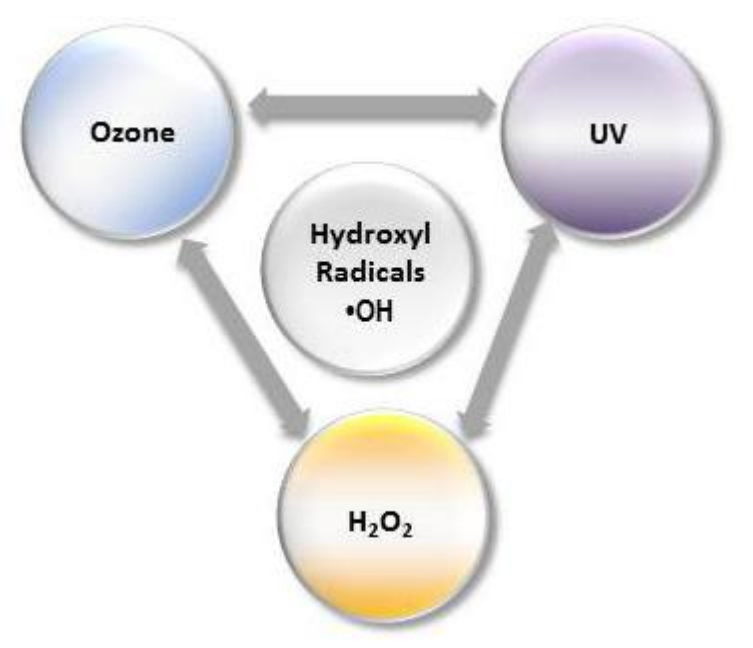
Advanced Oxidation Process (AOP)

- Ozone combined with:
  - Hydrogen Peroxide

    H_2O_2 decomposes in the presence of O_3 into Hydroxyl Radicals – highly reactive free radicals
  - Ultraviolet

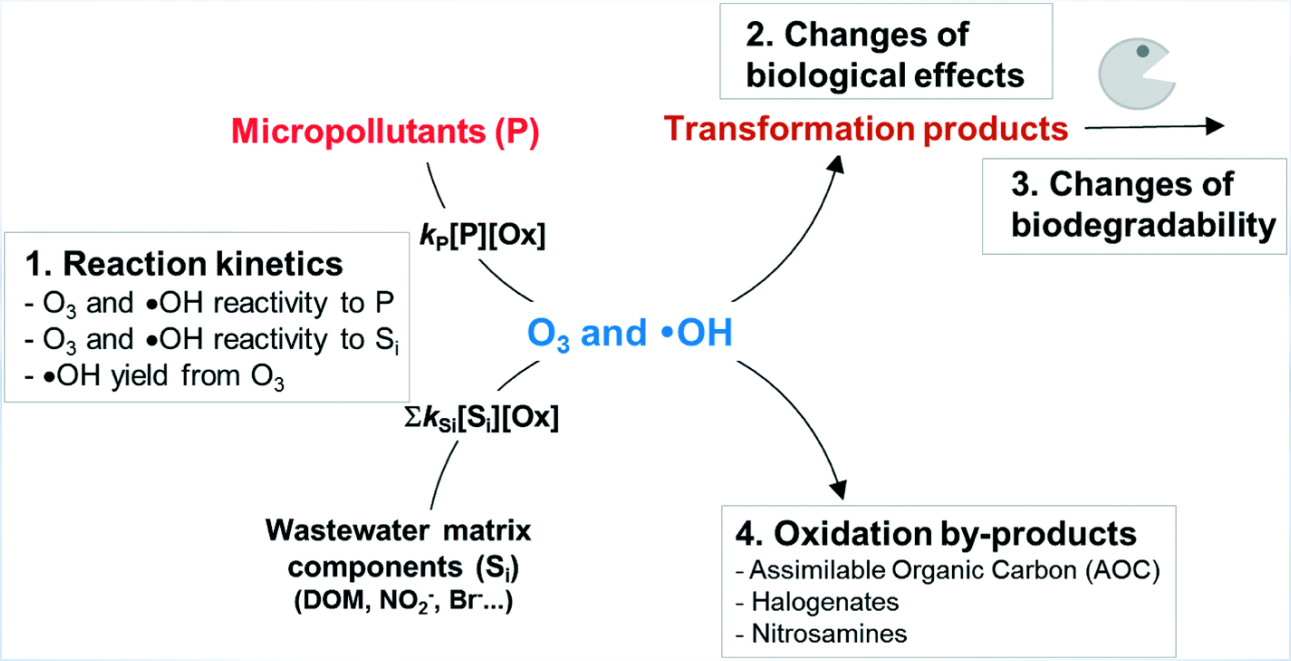
    UV provides energy to break chemical bonds, leaving fragments that are more susceptible to oxidation. Converts H_2O_2 to hydroxyl radicals. Converts O_3 to O_2
  - High pH

    Catalyzes the formation of H_2O_2



Challenges

- Pharmaceuticals are partly degraded into transformation by-products
  - N-oxide by-products of unknown toxicity
  - May exhibit lower *or* higher toxicity than the parent compound
  - May be more easily degraded biologically
  - Polishing step may reduce possible toxicity



Challenges

- High levels of organic carbon compete with the oxidation mechanism
- Treatment design and cost depend upon organic carbon loading
  - BOD, COD, TOC, Suspended Solids
  - OC can fluctuate significantly and unpredictably

Suspended Solids

Biochemical Oxygen Demand

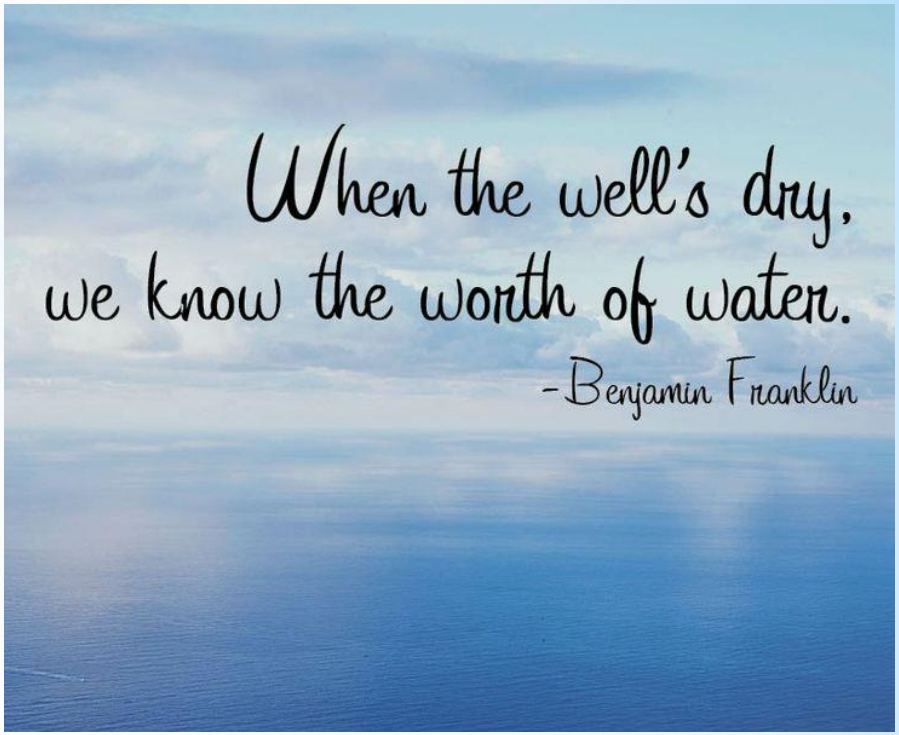
Chemical Oxygen Demand

Total Organic Carbon

Additional Opportunities with Ozone

- Color
- Deodorization
- Decolorization
- Filamentous bacteria
- Surfactants - elimination of foaming problems
- Sludge: Ozonation of sludge - solid waste is transformed into treatable liquid waste
  - Bacterial cell wall is attacked and cellular contents are released (COD)
  - The COD is returned to the basin to be consumed by the bacteria
  - Sludge volume is reduced as much as 40% to 45%

Questions



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