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# Sanitation & Oxidation

# Sanitation

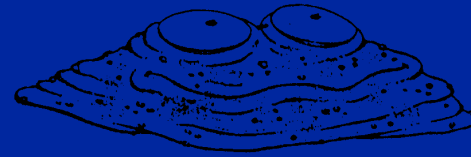
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Process of destroying pathogenic organisms (bacteria, fungi, protozoa, viruses...) harmful to human health in order to control communicable disease

# Oxidation

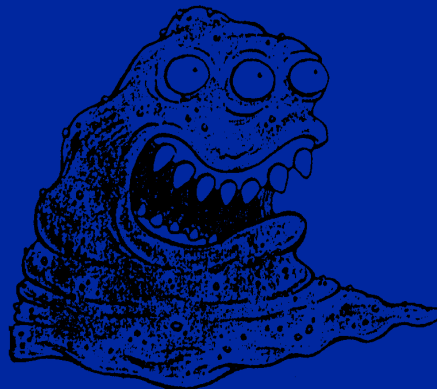
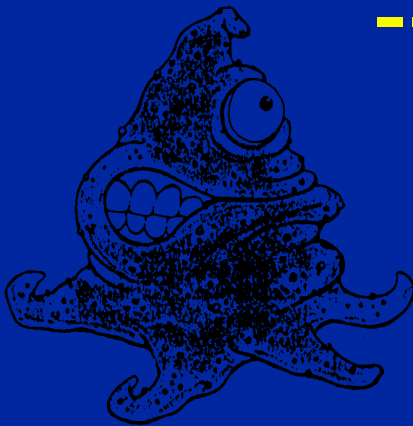
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Process of chemically removing organic debris (perspiration, saliva, urine, body oils & wastes, particulate matter...) from the water



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“You can't clean germs  
-- you have to kill them”



# Bactericides

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- Chlorine
- Bromine
- Potassium Iodide
- Hydrogen Peroxide
- UV Light
- Ozone
- Ionization of Metals
- Chlorine Generators
- Polymeric Biguanide

# Chlorine

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- Elemental gas chlorine
- Sodium hypochlorite
- Calcium hypochlorite
- Lithium hypochlorite
- Sodium dichloro-s-triazinetriene
- Trichloro-s-triazinetriene

# Elemental Gas Chlorine

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- Common name: Gas
- Appearance:
  - Greenish gas
  - Delivered under pressure in 150 pound cylinders or 1 ton steel tanks
- % available chlorine: 100%
- Produced by:
  - Separating salt into its elemental products: chlorine, hydrogen gas and sodium hydroxide
- To raise chlorine level 1 ppm/10,000 g: 1.3 ounces
- pH: 1.0 or less
- Inorganic

# Elemental Gas Chlorine

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- Injection equipment:
  - Chlorinator
  - Scale
  - Booster pump
- Advantages:
  - Inexpensive to purchase
  - 100% chlorine, no additives or inert ingredients
- Disadvantages:
  - Expensive to dispense
  - Extremely dangerous if handled improperly--toxic to humans, animals and plant life
  - Use of chlorine gas for pool water treatment is prohibited in some states
  - Lowers pH significantly



# Elemental Gas Chlorine

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- Special precautions:
  - Stored indoors, at or above ground level, in a separate, well ventilated room
  - Exhaust fan
    - Capable of 60 air exchanges per hour
    - Draws from floor level (heavier than air)
  - Tanks individually chained to the wall in an upright position
  - Audio and visual alarms
  - U.S. Bureau of Mines (USBM) or National Institute for Occupational Safety (NIOSH) approved gas mask and fresh canister (dated), or self contained breathing apparatus (SCBA)
    - Worn while exchanging tanks
    - Stored immediately outside the chlorine room

# Elemental Gas Chlorine

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- Special precautions (continued...):
  - Do not work alone in a gas chlorine room -- use the buddy system
  - Safety training
    - Only individuals trained in proper procedures should be permitted to handle gas chlorine equipment
    - Licensing required in some states
    - Initial training & refresher training every 6 months
  - Ammonium hydroxide (commercial strength ammonia) to test for leaks
  - Keep spare tanks capped
  - Keep the wrench provided on the stem to shut off the valve if leaks develop (turn clockwise to close)

# Elemental Gas Chlorine

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- Special precautions (continued...):
  - Make tank exchanges only when the pool is closed to the public
  - Replace gaskets when changing tanks to help avoid leaks
  - Post all required signage
  - Posted emergency pool evacuation procedures
  - Conduct evacuation drills on a regular basis (move up-wind and to a higher elevation)
  - Keep emergency exit doors unlocked
  - Inject chlorine under vacuum, not under pressure

# Sodium Hypochlorite

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- Common name: Liquid chlorine, bleach
- Appearance:
  - Yellowish-green clear liquid
- % available chlorine: 10 - 15%
- Produced by:
  - Bubbling gas chlorine through a solution of sodium hydroxide
- To raise chlorine level 1 ppm/10,000 g: 1.0 - 1.5 cups
- pH: 13
- Inorganic
- Injection equipment:
  - Chemical metering pump
  - Peristaltic, diaphragm, piston pumps

# Sodium Hypochlorite

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- Advantages:
  - Relatively safe to handle unless splashed or swallowed
  - Nonflammable
- Disadvantages:
  - Storage space: bulky
  - Short half life: Loses its effectiveness rapidly in heat and sunlight
  - Significantly raises pH
    - Approx. 1 quart of muriatic acid is needed to counter the effect of each 1 gallon of sodium hypochlorite used
  - Rapid build-up of TDS
  - Sodium dissolved in the water will eventually give the water a salty taste

# Sodium Hypochlorite

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- Special precautions:
  - Secondary containment required
  - Personal protective gear:
    - Goggles or full face shield
    - Neoprene gloves
    - Splash guard apron
  - Store covered in a dark, cool location
  - Sodium hypochlorite test kit should be used to test product strength

# Calcium Hypochlorite

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- Common name: Cal hypo, HTH
- Appearance:
  - White granule
  - White tablet
- % available chlorine: 65 - 75%
- Produced by:
  - Passing chlorine gas over sodium hydroxide (lime)
- To raise chlorine level 1 ppm/10,000 g: 2 ounces
- pH: 11.8
- Inorganic
- Injection equipment:
  - Made into a liquid then injected using a metering pump
  - Erosion-soaker feeder

# Calcium Hypochlorite

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- Advantages:
  - High percentage of available chlorine
  - Convenient and easy to use in tablet form
- Disadvantages:
  - Flammable and combustible -- unsafe if improperly stored, allowed to get wet or contaminated with a foreign product
  - Raises pH
  - Partially insoluble
    - Often improperly added directly to pool
    - May cloud water, damage pool surfaces or cause chemical burns if added directly to the pool or in too great a quantity in too short a period of time
    - Dispose of residue -- only the dissolved liquid should be pumped into the return lines of the pool
  - May contribute to scale formation and calcification problems



# Calcium Hypochlorite

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- Special precautions:
  - Store in its original container in a cool, dry place
  - Open containers outdoors in a well ventilated location
  - Personal protective gear including respiratory protection should be worn while handling
  - Do not dispose of spilled chemical in the trash or in a dumpster -- fire may result
  - Do not re use storage containers -- rinse, crush and destroy prior to disposal

# Lithium Hypochlorite

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- Common name: Lithium
- Appearance:
  - White powder
- % available chlorine: 35%
- Produced by:
  - Bubbling gas chlorine through lithium, sodium and potassium sulfates, then drying
- To raise chlorine level 1 ppm/10,000 g: 10.5 ounces
- pH: 10.7
- Inorganic
- Injection equipment:
  - Pre dissolve then inject using a chemical metering pump

# Lithium Hypochlorite

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- Advantages:
  - Totally soluble -- no residue
  - Nonflammable, non combustible
  - Dust free
  - Long shelf life
- Disadvantages:
  - High cost
  - Unstable
  - Raises pH
- Special precautions:
  - Do not try to introduce through an erosion feeder -- dissolves much too rapidly

# Sodium Dichloro-s-triazinetriene

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- Common name: Dichlor
- Appearance:
  - White granule
- % available chlorine: 56 or 62%
- Produced by:
  - Adding sodium bicarbonate and cyanuric acid to trichlor
- To raise chlorine level 1 ppm/10,000 g: 2.25 ounces
- pH: 6.9
- Organic (contains cyanuric acid)
- Injection equipment:
  - Dichlor feeder

# Sodium Dichloro-s-triazinetriene

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- Advantages:
  - Stabilized
  - Instantly soluble -- no residue or cloudiness
  - Neutral pH
- Disadvantages:
  - Cyanuric acid build-up
  - Ties up chlorine and reduces ORP -- higher minimum chlorine residuals may be required by code
  - More frequent draining and refilling of pool
- Special precautions:
  - Never place dichlor in a trichlor feeder -- rapid dissolving may result in a pressure build-up and explosion
  - Do not use in indoor pools

# Trichloro-s-triazinetriene

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- Common name: Trichlor
- Appearance:
  - Solid white tablets or sticks
  - Granular form sold as a algaecide
- % available chlorine: 90%
- Produced by:
  - Drying cyanuric acid in the presence of gas chlorine
- To raise chlorine level 1 ppm/10,000 g: 1.5 ounces
- pH: 2.9
- Organic (contains cyanuric acid)
- Injection equipment:
  - Erosion feeder (in-line)

# Trichloro-s-triazinetriene

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- Advantages:
  - Easy to store and use
  - Long shelf life -- can be purchased and delivered in quantity
- Disadvantages:
  - Cyanuric acid build-up
  - Ties up chlorine and reduces ORP -- higher minimum chlorine residuals may be required by code
  - More frequent draining and refilling of pool
  - Significantly lowers pH
    - 4 ounces of sodium carbonate is needed for each 1 pound of trichlor added to the pool

# Trichloro-s-triazinetriene

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- Special precautions:
  - Never place tablets directly in the pool
    - Children may try to eat and be poisoned
    - Tablets will damage the pool surface
  - Do not place trichlor tabs in skimmer baskets
  - Do not use floating trichlor feeders in commercial pools
  - Do not use in indoor pools



# Cyanuric Acid

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- AKA: conditioner, stabilizer
- Added to pool water to prevent loss of chlorine through dissipation when exposed to ultraviolet light
- Should not be used in indoor pools
- Maximum level permitted by most health codes is 100 ppm (EPA limit 100 x safety factor)
- 85% of chlorine retention occurs with a 10 ppm CYA level, and there are diminishing returns after 20 ppm
- As cyanuric acid level increases, ORP decreases

# Cyanuric Acid

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- To stabilize a 60,000 gallon pool to 20 ppm of CYA, use (6.5 oz) per (5 ppm) per (10,000 g)  
 $(6.5) (4) (6) = 156 \text{ ounces} \div 16 = 9.75 \text{ pounds}$
- "Chlorine lock" does not exist
- Flawed 1966 study conducted at the Belmont Plaza Olympic Pool in Long Beach showed exposure to cyanuric acid could cause gallstones and kidney damage
- Use of cyanuric acid or chlorinated isocyanurates is banned in New York State
- To reduce CYA levels: drain, nanofiltration, melamine

# Chlorination

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- $\text{Cl}_2 + \text{H}_2\text{O} = \text{HOCl} + \text{HCl}$
- HOCl is the active sanitizing ingredient
- HOCl then partially dissociates to  $\text{H} + \text{OCl}^-$
- Free chlorine consists of a mixture of HOCl and  $\text{OCl}^-$
- $\text{OCl}^-$  has a tendency to combine with nitrogen and ammoniated impurities in the water
- Proportion of HOCl to  $\text{OCl}^-$  is both pH and temperature dependent

HOCl	Hypochlorous acid
HCl	Hydrochloric acid
H	Hydrogen ion
$\text{OCl}^-$	Hypochlorite ion

# Process of Chlorination

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- Dissipation
- Chlorine demand
- Chlorine residual (TAC)
  - Free available chlorine (FAC)
    - Minimum level may be specified by code
    - Maximum levels are often (improperly) specified by code
    - Set at a level where 750 mV ORP is achieved
  - Combined available chlorine (CAC)
    - AKA: Chloramines, ammoniated chlorine compounds
    - Cause eye and mucous membrane irritation
    - Unpleasant “chlorine” odor
    - Ineffective: 60 - 100 times slower than FAC (too stable)
    - Should not be allowed to exceed 0.2 ppm

# Too Much Chlorine?

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Do high chlorine levels cause bathing suits to disintegrate?

My Frigidaire washing machine holds approximately 10 gallons of water. I normally add 1/4 cup (2 ounces) of 5% available chlorine bleach (Clorox) to the wash to whiten and brighten my clothes. This is the equivalent of adding 1 ounce of 10% available sodium hypochlorite. The dosage required to introduce 1 ppm of 10% sodium hypochlorite to 10,000 gallons of pool water is 12 fluid ounces. Therefore, adding 1 ounce of sodium hypochlorite or the equivalent 2 ounces of Clorox to my wash water would raise the chlorine level to approximately 83 ppm.

$$(12 \text{ oz})(1 \text{ ppm})(10,000 \text{ g}) = (1 \text{ oz})(.083 \text{ ppm})(10,000 \text{ g}) = (1 \text{ oz})(83.3 \text{ ppm})(10 \text{ g})$$

# ORP

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- Oxidation reduction potential
- AKA: Redox
- Maintaining proper sanitizer levels has less to do with the quantity of chemical added to the water (ppm), and more to do with having enough sanitizer in the water to achieve the chemical reaction needed to remove harmful bacteria and waste products
- ORP is a standard method of measuring the chlorine's (or bromine, ozone or other sanitizer-oxidizer's) ability to remove undesirable products from the water
- ORP is a good indicator of bacteriological water quality

# ORP

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- Qualitative rather than quantitative measurement
- Measured in millivolts (mV)
- ORP sensors:
  - Measure conductivity of water
  - Indicate the potential generated for oxidation or work potential
  - Permit constant monitoring of sanitation levels
- ORP takes into consideration all water constituents (chemicals, pH, temperature, oil, grease, dissolved solids, cyanurates, decaying matter, organic bather waste products--sweat, urine, creatinine, nasal discharge, cosmetics, hair products, soaps, deodorants...)

# Chemical Feed Pumps

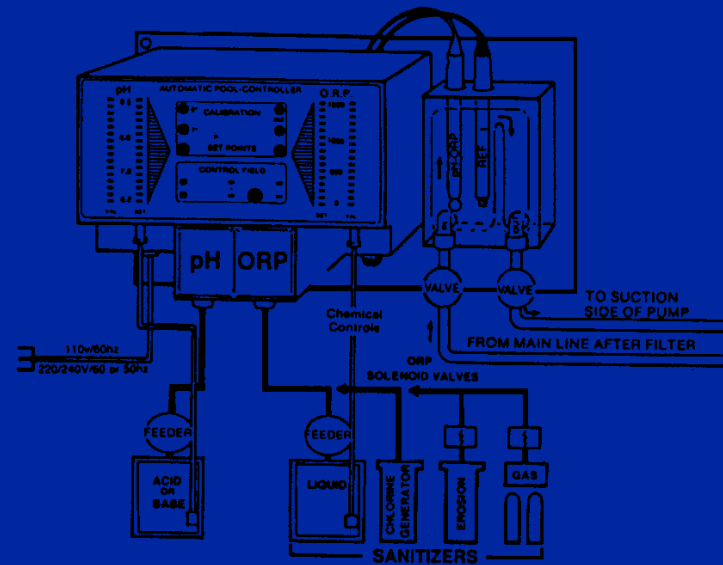
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- Hand feeding of chemicals into commercial pools is not permitted
- Positive displacement pumps
  - Diaphragm
  - Piston
- Peristaltic pumps
- Gas chlorinators
  - Pressure
  - Vacuum
- Erosion feeders
- Erosion-soakers



# ORP

- Chemicals should be introduced in quantities needed to maintain ORP levels at a minimum of:
  - 750 - 900 mV (Commercial pools and spas)
  - 650 mV (Residential pools)



# pH/ORP Controllers

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- Automated controllers should be installed on all commercial spas and pools
- Continuously monitor and regulate pH and ORP levels simultaneously and make chemical adjustments as necessary
- Manually testing FAC and pH levels several times per hour is simply impractical
- Controllers use probes (AKA: sensors, electrodes) to sense the pH and ORP levels in a slip stream of water off the effluent return lines and compare them to a set standard or set-point range

# pH/ORP Controllers

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- If the levels are not within set parameters, the controller sends a signal to the chemical metering pump, erosion feeder or chemical injection system to impart the appropriate chemical to the water
- When the correct level is achieved, the controller signals the chemical injection process to cease imparting chemicals to the water
- Peaks and valleys are avoided
- Prevents periods where the pool is without adequate sanitizers needed to kill harmful pathogens

# pH/ORP Controllers

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- Conversion charts should not be needed to obtain oxidation reduction potential readings from ppm values
- Water temperature should not influence correct chemistry value readout
- Components:
  - Probes
  - Control box
  - LED or digital read-outs for pH and ORP
  - Built-in surge protection
  - Power and feed indicators: automatic, off, proportional, and manual override feed mode options
  - Flow loss warning indicators or alarms
  - Safety: interlock with circulation pump, flow control switch

# pH/ORP Controllers

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- Optional equipment available on some models includes:
  - Automatic probe rinses
  - Data-voice communications
  - Remote and local log-on
  - Data down loading and programming features
- The quoted price should include the cost of:
  - Installation
  - Training the on-site staff
  - Installation and maintenance manuals

# Oxidation

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- Related terms
  - Shock
  - Superchlorination
  - Breakpoint Chlorination
- Purpose:
  - To remove unwanted organic compounds from the water
  - To break apart the the chemical bond that holds chlorine and ammonia together (eliminate chloramines)
- Breakpoint: point at which this chemical bond is broken
- Non chlorine oxidizers

# Breakpoint Chlorination

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- 7.6 molecules of free chlorine are needed to break apart 1 molecule of combined chlorine (use factor of 10 in calculations)
- Several chemical reactions take place and monochloramines, dichloramines and trichloramines form before the breakpoint is achieved
- All or nothing reaction
- If breakpoint is not reached, the problem will be worse (water balloon analogy)
- When chemical bond with ammonia is broken, free chlorine, nitrogen, water and chloride (salt) remain

# Nitrogen Tri-chloride

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- Chloramines:
  - Monochloramine, dichloramine, trichloramine or nitrogen tri-chloride
- Problems:
  - Superchlorination won't go to completion (difficulty reaching breakpoint)
- Possible cause:
  - Process of superchlorination may cause the formation of tri-chloramines in pools with high bather load to water volume ratios & heavy organic loading
- Remedies:
  - Maintain high chlorine levels (>10 ppm) for several days
  - Superchlorinate, de-chlorinate using sodium thiosulfate, and re establish normal FAC levels



# Calculating Breakpoint

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- Find FAC
- Find TAC using a DPD test kit
- Subtract FAC from TAC to find the difference (CAC)
- Multiply CAC by the factor 10 (7.6) to determine the number of ppm of chlorine that must be added to the pool to reach breakpoint
- Determine the number of gallons of pool water to be treated and the % of available chlorine in the product that will be used to superchlorinate the pool
- Calculate the amount of chlorine needed by weight, or refer to a standard chart or a chart provided by the chlorine manufacturer

# Calculating Breakpoint

## Example 1: Chart

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- FAC            1.0
- TAC            2.5
- CAC            1.5
- $1.5 \times 10 = 15$  ppm
- $V = 360,000$  gallons
- 10% sodium hypochlorite
- (1.5 cups) (1 ppm) (10,000 gallons)
- (1.5 cups) (15 ppm) (36) = 810 cups
- $810 \text{ cups} \div 16 = 50.6$  gallons

# Calculating Breakpoint

## Example 2: Calculation

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- $2.5 \text{ ppm (TAC)} - 1.0 \text{ ppm (FAC)} = 1.5 \text{ ppm (CAC)}$
- $1.5 \times 10 = 15 \text{ ppm}$
- $V = 360,000 \text{ gallons} \times 8.33 \text{ (weight of 1 g of water)} = 2,998,800 \text{ pounds of water in a 360,000 gallon pool}$
- $1,000,000 \div 2,998,800 \text{ pounds} = 0.33 \text{ ppm/1 pound}$
- $15 \text{ ppm} \times 0.33 = 4.95 \text{ pounds of available chlorine}$
- $4.95 \div .10 \text{ (10\% sodium hypochlorite)} = 49.5 \text{ pounds is needed to raise the chlorine level 15 ppm}$

# Non Chlorine Shock

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- Potassium peroxymonosulfate
- AKA: monopersulfate, permonosulfate, oxygen shock
- Buffered chemical compound which uses oxygen to prevent organic build-up and destroy ammoniated compounds
- Advantages
  - Oxidizer will destroy organics at a 10:1 ratio (actually 7.6 --same as chlorine)
  - Any amount added to the water will destroy some organics. Reaching breakpoint is not necessary
  - If more than the required dose (1 lb/10,000 g) is added, a residual will remain that will prevent organic compounds and combined chlorine from forming

# Non Chlorine Shock

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- 100% soluble, dissolves quickly
- Does not affect pH
- Will work in poorly ventilated indoor pools, or under pool covers
- Bathers can re enter the pool immediately after its introduction. Good choice for use in warm water pools with high bather load to water volume ratios which require frequent shocking.
- Disadvantages
  - High price
  - Will not kill bacteria or algae
  - High sulfate levels may lead to bather irritation (250 ppm federal EPA limit for potable water)
  - May cause false DPD readings

# Bromine

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- Forms of bromine used in pool water treatment:
  - Elemental bromine (red-brown liquid)
  - Sodium bromide (salt)
  - Bromo-chloro-dimethylhydantoin (tablet)
- Member of the halogen family
- Forms hypobromous acid (HOBr) and hypobromite ions (OBr<sup>-</sup>)
- Bromamines form but are still effective sanitizers
- Bromamines do not give off a “chloramine” odor -- rather a fishlike odor is produced
- 2.25 times the molecular weight of chlorine
- Other uses: Flame retardant in pajamas

# Elemental Bromine

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- Reddish - brown liquid
- Difficult to handle
- 3 times heavier than water
- Toxic, corrosive
  - Contact with skin will cause burns
  - Fumes can damage eyes and mucous membranes
- Use of elemental bromine has been discontinued in the U.S., but it is still used for pool water treatment in Europe

# Sodium Bromide

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- Not EPA approved for use in commercial pools
- 2 part system using:
  - Bromine salt ( $\text{Br}^-$ )
  - Oxidizer that activates the bromine salt to form hypobromous acid ( $\text{HOBr}$ )
    - Chlorine, ozone, potassium peroxymonosulfate
- Most often used to treat residential pools and spas



# Bromo-chloro- dimethylhydantoin (BCDMH)

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- White tablets, 1" or 3"
- 66% bromine, 27% chlorine
- Introduced into the water through an erosion-soaker feeder (brominator)
- pH 4.0
- Tendency to lower total alkalinity. Need 0.6-0.7 lb of sodium bicarbonate per pound of BCDMH used
- 1" tablet weighs 20 grams -- there are 23 tablets to a pound of BCDMH

# Bromine Advantages

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- Less irritating to eyes and mucous membranes
- Very little odor produced
- More active at pH levels typically maintained in pools
  - 94% HOBr is produced at pH 7.5 vs. 47% HOCl
- More stable in heat
  - Chlorine begins to dissipate at 30° F while bromine doesn't dissipate until 105°
- Bromamines form but recombine with hypochlorous acid to regenerate hypobromous acid
- DPD test kits can be used to test for bromine but multiply result by 2.25
  - Br has 2.25 x the molecular weight of Cl

# Bromine Disadvantages

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- Contact dermatitis rash, halogen sensitivity
  - Drs. Steven Kurtin and Alex Fischer's recent medical paper
- Ineffective oxidizer and algaecide
- DMH build-up makes reaching breakpoint very difficult
- Degrades rapidly from UV light exposure & cannot be stabilized
- May turn water a dullish green color
- May impart a light brown-manila color to walls and decks
- Sudsing
- Biofilm growth (orange-yellow),
  - Nematode problem in NY and AK
  - Less effective against *P. aeruginosa*

# Potassium Iodide

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- Member of the halogen family
- Elemental iodine is a purple or blue-black solid crystal at room temperature
- Potassium iodide (KI) is the form of iodine use for pool water treatment
- White crystal
- 70% available iodine by weight
- 4 pounds of crystal potassium iodide is dissolved in 40 gallons of water and pumped into the return line using a chemical metering pump

# Potassium Iodide

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- Used as a sanitizer only -- not effective in oxidizing organic matter
- Chlorine or potassium peroxymonosulfate must also be added to the water to ionize iodide ions to form hypoiodous acid (HOI) and hypoiodite ions
- Free iodine reverts back to iodine ions and can be re ionized with the addition of chlorine
- Usually maintained in the range of 1.0 - 2.0 ppm
- Leuco-crystal test kits are used to measure free iodine in the presence of chlorine, and distinguish between free iodide and iodide ions

# Potassium Iodide

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- Advantages:
  - Not a bleach
  - Swimmer comfort: not a eyes or skin irritant
  - Residue or precipitate is not formed
- Disadvantages:
  - Does not combine with ammonia to form iodamines
  - Very little effect on pH
  - Imparts a dark green tint to water
  - Will discolor some metal hardware in the pool and jewelry worn by bathers
  - Iodine odor if pH drops
  - Not effective as an algaecide

# Hydrogen Peroxide

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- Sanitizer, but primarily used as an oxidizing agent
- Residual usually maintained in the 30 - 40 ppm range
- Colorless liquid
- Often used in combination with ultraviolet light
- Dissipates rapidly from pool water
- Dissolves D.E. -- cannot use hydrogen peroxide in pools with D.E. filters
- Can also be used to:
  - Remove chlorine from water
  - Bleach stained plaster (35 - 50% concentration)
  - Remove phenols from polluted water when mixed with chopped horseradish

# Ultraviolet Light

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- Water flows through clear, quartz glass or Teflon tubes past low pressure mercury vapor lamps or UV fluorescent bulbs housed in a chamber
- Bulbs generate a UV light ray of 254 nanometers
- UV light kills pathogens by destroying nucleic acid in cells
- Disinfectant level is related to light intensity and exposure time
- UV dosage is measured in microwatt seconds per square centimeter (MWS/cm<sup>2</sup>)
- 6,000 - 10,000 MWS/cm<sup>2</sup> are needed to destroy pathogenic organisms



# Ultraviolet Light

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- No residual disinfectant
- UV light does not oxidize water -- often used in combination with hydrogen peroxide
- No change in water color, temperature, taste, pH or chemical composition
- Turbid water will absorb UV light and make UV less effective as a disinfectant
- Lamp life is approximately 8,000 hours of continuous use, so light bulbs need to be replaced about once or twice per year.

# Ozone

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- $O_3$ , activated oxygen, tri-valent oxygen
- Ozone generation methods:
  - Ultraviolet light
  - Corona discharge
  - German DIN Standard ozone systems
- Use in combination with low residual levels of chlorine or bromine

# Ozone History

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- From the Greek word "ozein" meaning "to smell", named by C.F. Schoenbein in 1840
- Ozone was first used for drinking water disinfection in 1893 in Oudshoorn, The Netherlands
- Nice, France began disinfecting its public water supply in 1906 and still does today
- Potsdam, NY was the first U.S. city to treat drinking water with ozone
- Largest ozone generation plant in the world:
  - Los Angeles water filtration plant in Sylmar at the terminus of the L.A. aqueduct system. The plant can treat up to 600 million gallons of water per day.
- Also used to treat air and sewage

# Ozone History

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- Pool disinfection with ozone has been common in Europe since the 1950's
- First pool in the U.S. to use CD ozone:
  - Mohawk Cruiser Swim & Tennis Club, Byram, NJ.
  - System was installed in 1937 and is still in operation
- A swimming pool ozone system was displayed at the 1939-1940 New York World's Fair
- German DIN Standard 19,643 CD Ozone test sites:
  - JCC of Milwaukee, WI -- Peck Aquatic Facility (1987)
  - City of Westminster, CO -- City Park Rec Center (1992)

# Ozone is Effective Against

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- Organic Contaminants
  - Organics such as perspiration, urine, creams, ointments, cosmetics, nasal secretions, and creatinine (chemical normally found in blood and excreted into urine by kidneys) are only slightly reactive with ozone.
  - After being partially oxidized, microflocculation allows their removal by filtration.
- Microbiological Contaminants
  - Disease causing bacteria, viruses (flu, herpes, AIDS), yeasts, amoebae and cysts are all destroyed by ozone, depending on contact time and concentration of ozone in the water.

# Ozone is Effective Against

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- Inorganic Contaminants
  - Ammonia  
(Reactions significant at pH <9.0)
  - Chlorine  
(Keep FAC levels at 0.2 - 0.5, and excess will not be lost)
  - Bromine  
(Ozone will oxidize bromide ion Br<sup>-</sup> into HOBr + OBr<sup>-</sup>)
  - Iron and manganese  
(Will be physically filtered out)
  - Sulfide ions  
(Oxidized to innocuous sulfate form)
  - Monochloramines  
(Constant oxidation of CAC to form chloride and nitrate ions)

# Factors Which Affect Ozone Chemistry

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- Solubility
  - Ozone is only partially soluble in water, while chlorine is totally soluble.
  - The higher the concentration of ozone in the air coming into contact with the water, the more ozone that will dissolve in the water.
  - Therefore the more ozone present in water, the more oxidation and disinfection ozone will do.
- Ozone Decomposition
- pH
  - Between 7.2 - 8.0, both  $O_3$  and very reactive OH (hydroxyl free radicals) will be present to oxidize and sanitize.

# Factors Which Affect Ozone Chemistry

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- Temperature
  - Solubility of ozone decreases as temperature rises, but reaction rate increases.
- Transfer Efficiency
  - Transfer of gaseous ozone into water is usually by Venturi injector.
  - The partial vacuum draws ozone into the Venturi where ozone is transferred into water.
- Concentration of Ozone Generated
  - UV light: 0.1 - 0.001%
  - CD: 1 - 2% by weight  
(greater if pure oxygen is utilized)



# UV Ozone Systems

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- Air is drawn into a chamber and passed near special mercury vapor UV lamps made of quartz glass which produce light of a specific wavelength
- $O_2$  molecules are bombarded with UV rays, break into  $O_1$  and recombine as  $O_3$
- The  $O_3$  is transferred, usually by Venturi action, into the water
- Very low concentrations of ozone are generated
- Not effective in treating heavily used or commercial pool waters

# Corona Discharge (CD) Slip Stream Ozone Systems

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- Preferred method of generating ozone on-site
- Air is oxygen enriched then dried to prevent nitric acid from forming
- Then sent past a di-electric or high voltage electrodes, which give off a bluish glow or “corona discharge”
- $O_2$  is split into individual oxygen atoms which recombine into  $O_3$ .
- Ozone is then injected through a venturi and transferred into a side stream of water drawn off the pool water return line
- Contact chamber
- Degassing units to remove the ozone from the water prior to its entering the swimming pool

# Corona Discharge (CD) Ozone Systems

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- Ozone is injected through a venturi and transferred into either a slip stream of water or directly into the pool water return line
- Contact chamber (2 - 3 minutes, preferably 4 minutes)\*
- Degassing unit to remove ozone from the water prior to its entering the pool \*\*
- The water is filtered, heated and chemically treated immediately prior to the water returning to the pool \*

\* Only on some systems

\*\* Not necessary when used in combination with bromine rather than chlorine

# Corona Discharge (CD) Slip Stream Ozone Systems

- Proper installation of a quality ozone generation system will lead to easier to maintain, less costly, and better smelling, better tasting, and better quality pool water. As a minimum, the ozone system should:
  - Utilize 95% concentrated oxygen
  - Dry the air to prevent nitric acid formation
  - Be capable of discharging 6% ozone by weight under vacuum into a 25% slip-stream
  - Remain in contact with the water in a reaction or contact chamber for at least 4 minutes so that CT values of at least 1.6 are achieved [(C = concentration of ozone in mg/l = 0.4) x (T = time = 4 minutes)]
  - Utilize a ozone destructor of either granulated activated carbon (GAC) or a manganese dioxide catalytic converter, and vent off-gassed air to the outside

# Corona Discharge (CD) Amount of Ozone Needed

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Take into consideration several factors which influence the amount of ozone needed to meet the needs of the facility:

- Facility type and pool location
- Owner's motivation for wanting to install an ozone system
- Pool volume
- Average daily bather load and bather load to water volume ratio
- Temperature at which the water is typically maintained
- Flowrate and turnover time
- Type of filter media, filter area, and filter design flowrate
- Demographic information
- Age of the facility
- Chemical use profile of the pool including chemicals, the chemical feed system and controllers used

# Corona Discharge (CD)

## Goal

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The goal of side stream sizing is to achieve one complete turnover of water in a given period.

- Volume of the pool in gallons is divided by the time factor in minutes in a day, and then by the actual flowrate in gallons per minute.
- Example: 95,000 gallons of water divided by 1,440 minutes in a day divided by a flowrate of 265 gpm (6 hour turnover rate), equals 0.248. Therefore, a minimum 25% side stream is required.
- The side stream is usually sized between 25 and 33 percent, however, if you reduce the side stream, the dose concentration goes up inside the contact chamber.

# Corona Discharge (CD) Sizing Formula

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Ozone generator sizing is based on the formula

- \_\_\_\_ gallons per minute flow rate
- Multiplied by 0.227 grams per gallon conversion factor
- Multiplied by 0.4 milligrams per liter
- Equals \_\_\_\_ grams per hour”.
- May also want to multiply by an assigned motivational factor, temperature factor, location factor, and ozone factor (bather load divided by flowrate).

# Derivation of 0.227 Constant

Derivation of the 0.227 conversion constant for use in calculating ozone generator size is based on:

- Water flow rate in gpm times  $X\mu$  times ppm = grams per hour.
- $X\mu$  equals grams per hour times minutes per gallon.
- $X\mu$  equals 60 minutes per hour times grams per gallon
- 1 ppm is equivalent to 1 milligram per liter which equals 0.00379 grams per gallon.
- Therefore,  $X = 0.00379$  grams per gallon times 60 minutes per hour, or  $X = 0.2271$  grams per gallon.



# Goal of Contact Chamber Sizing

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The goal of contact chamber sizing is:

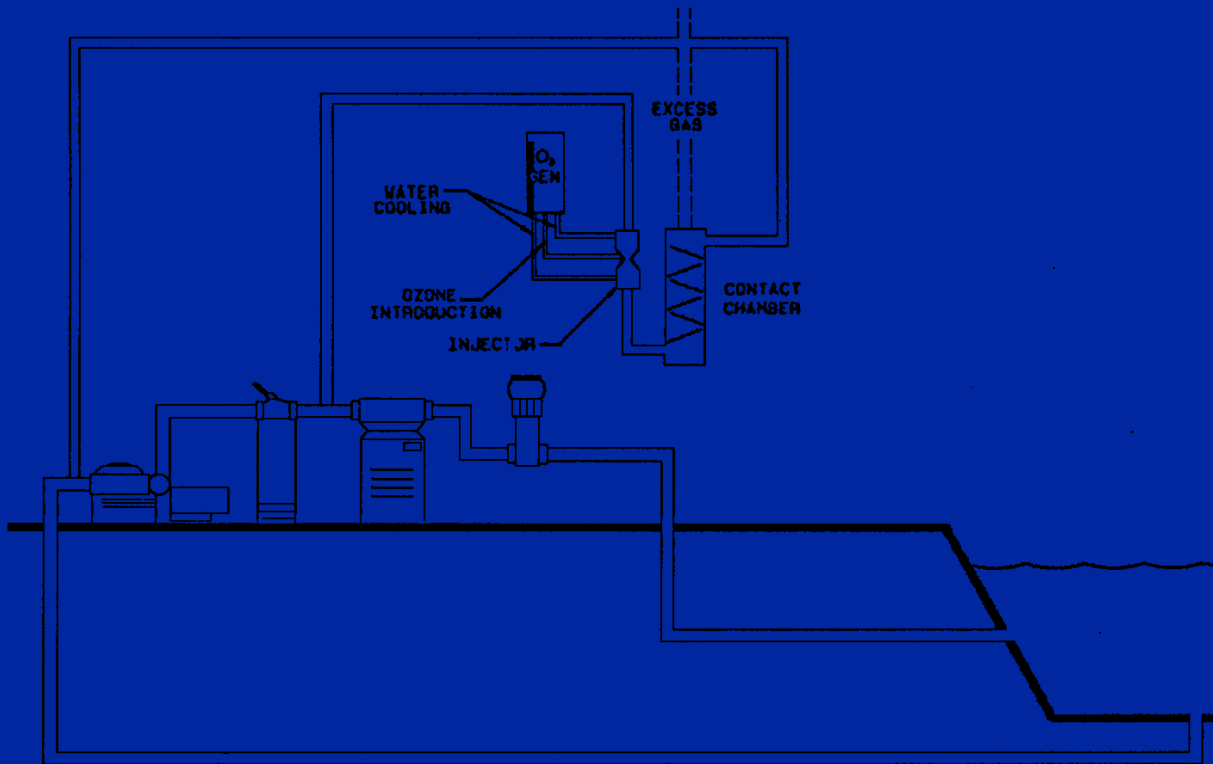
- To achieve enough contact time between the ozone produced and water in the side stream to allow at least 4 minutes of retention of the side stream flow in a contact chamber, tower, or vessel
- An ozone dose of 1.6 ppm in the side stream when ozone is the primary oxidant.
- CT values of at least 1.6 are achieved when the concentration of ozone in milligrams per liter equals 0.4 for a time of 4 minutes.
- Flowrate in gallons per minute is multiplied by 4 minutes to determine the minimum size of the contact vessel in gallons.

# CD Ozone System Includes

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- Generator
  - Size based on grams per hour & pounds per day of O<sub>3</sub> production
- Side stream
  - Sized in gallons per minute and percentage of main flow
- Electrical specifications
- Oxygen feed gas flow
- Cooling water requirements
- Contact tank
- Degassing valve
- Ozone destruct
- Injector
- Booster pump
- Ambient ozone monitors

# Corona Discharge (CD) Ozone Systems - Diagram



# German DIN Standard 19,643

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- "Treatment & Disinfection of Swimming & Bathing Pool Water"
- Deutsch Industrie Normen
- Standard adopted by the European Community
- FINA requires water standards compatible with the 1992 DIN standard during international swimming competition
  - Free chlorine: 0.3 - 0.6 mg/L
  - Combined chlorine: < 0.4 mg/L
  - Total trihalomethanes: 20  $\mu$ g/L

# German DIN Standard Ozone Systems

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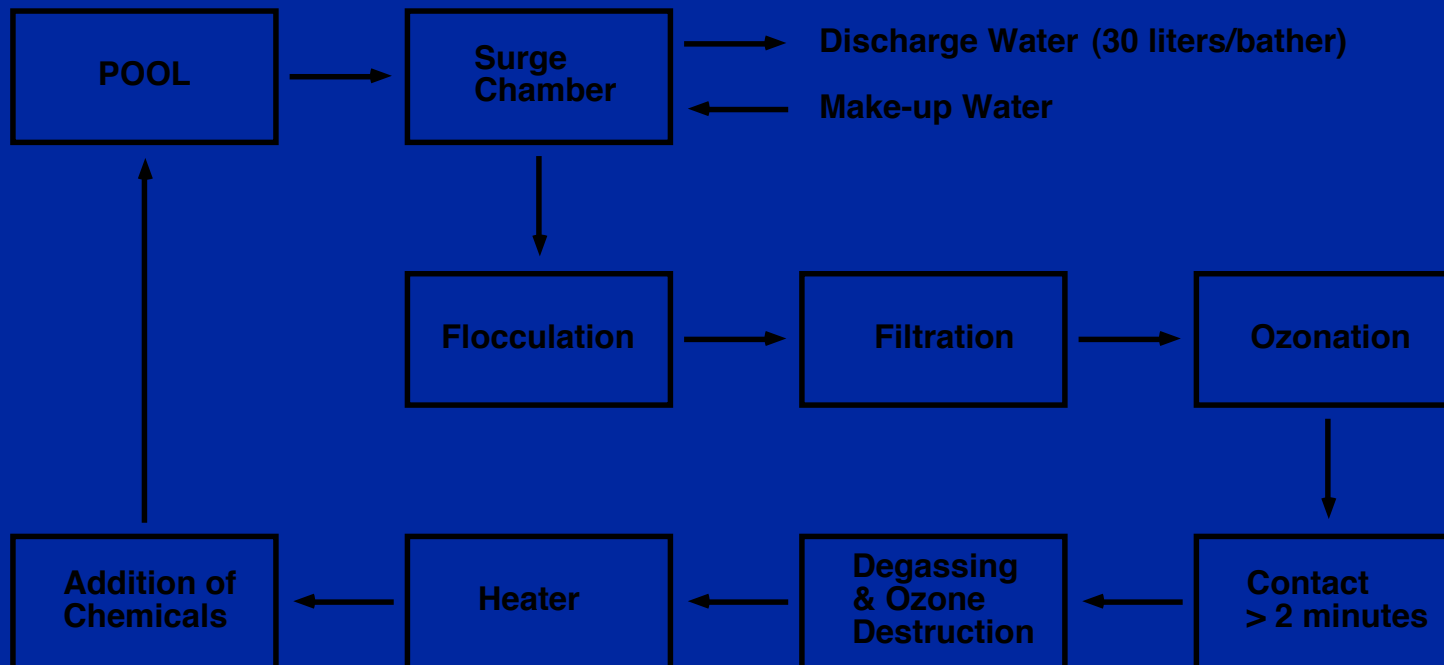
- Water leaves the pool through the main drains and perimeter overflow system
- Water enters the surge chamber (FAC  $\leq$  0.5 ppm, pH 7.2 - 7.8) where up to 20% of water is continuously discharged to waste and an equivalent amount of fresh water is added to the surge chamber (DIN requires 30 L (7.8 gallons)/day/bather)
- Flocculation (aluminum sulfate)
- Sand filtration
- Ozonation (1 - 1.2 mg/L)

# German DIN Standard Ozone Systems

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- Contact time 2 - 3 minutes in a contact chamber (ORP 780 mV)
- Degassed to remove excess ozone
- GAC filtration to destroy any residual ozone or chlorine remaining
- pH adjusted (7.2 - 7.5) with acid or CO<sub>2</sub>
- Free chlorine level brought up to 0.2 - 0.5 (levels higher than 0.5 will be destroyed by GAC filters)
- Water re enters the pool through bottom inlets

# German DIN Standard Ozone Systems - Diagram



# Ozone Benefits

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- Reduced halogen consumption--less halogen needed to maintain ORP and lower required halogen residual required
- Fewer chemicals needed to adjust pH and water balance
- No objectionable odor--ozone smells "like watermelons"
- Ozone bacterial kill rate is faster than chlorine or bromine
  - (Bacterial kill rates in tests:  
Cl<sub>2</sub>: 5 -500 minutes, O<sub>3</sub>: 6 - 60 seconds)



# Ozone Benefits

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- Ozone is better at killing waterborne viruses, spores, and amoebas
- Slower TDS build-up, since ozone does not contribute to TDS build-up. May actually reduce TDS because of coagulating particles. Less frequent draining and refilling pool required.
- Ozone does not dry skin
- Ozone does not bleach hair
- Ozone won't bleach or discolor pool surface
- Less storage and transportation of large quantities of hazardous materials

# Ozone Benefits

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- Ozone is generated on-site as needed
- No foaming--ozone destroys foam causing organic compounds
  - Organics are reduced to nitrates (through oxidation) which can be removed through GAC filtration.
  - Chlorine reacts with organic materials in water and forms carcinogenic substances called trihalomethanes.
  - Ozone will remove THM precursors so THM formation is decreased.
  - (EPA has set THM limit in drinking water at 100 ppb)
- No PCB (polychlorinated biphenyls) formation
- Not carcinogenic

# Ozone Benefits

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- Reduced formation of chloramine compounds
- Need to shock or superchlorinate only infrequently
- Less eye, sinus, mucous membrane and throat irritation from chlorine and chloramines eliminated
- Decreased sensitivity to halogens and resulting rashes
- Cost savings
- Ozone will floc particulate matter increasing filter effectiveness
- Clearer water, due to removal of colloidal particles
- Less bathtub ring formation on pool walls
- Ozone destroys oils and converts them to CO<sub>2</sub>

# Ozone Benefits

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- Ozone helps remove minerals which dull water
- Softer water
- Ozone is not explosive
- Ozone is not flammable
- Safe: Ozone lines are under vacuum. If a leak in an ozone line should occur, air would leak into system rather than ozone leaking into air
- Swimmers can swim faster in an ozonated pool due to decreased friction as a result of more complete oxidation and higher water oxygen levels

# Ozone Disadvantages

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- Natatorium ventilation must be good.
  - Ozone is denser and therefore heavier than air.
  - If ozone off-gasses it will form a gaseous ozone layer directly above the pool surface.
  - Swimmers and staff would breathe the ozone gas which even at low levels would be hazardous to swimmers with respiratory problems.
- Ozone leak and air quality monitoring devices must be installed.
  - PEL (Permissible Exposure Limit) time-weighted exposure limit set by OSHA: 0.1 ppm level in air 6 inches above water surface for a 8-hour work shift in a 40 hour week (100 ppm irritation, 1,000 ppm toxic)

# Ozone Disadvantages

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- Ozone is known to oxidize and corrode copper pipe. Stainless steel or CPVC schedule 80 pipe must be specified for all circulation lines.
- More frequent backwashing of filters will be required, because ozone is better at removing impurities from water.
- Ozone oxidizes dissolved organics to oxygen containing organics (increasing dissolved oxygen content of water) which is ideal for promoting algae growth

# Effects of Overexposure to Ozone

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- 1.5 - 2.0 ppm for as little as 2 hours:
  - Eye irritation
  - Dry throat, nose, mouth
  - Constrictive chest pain
  - Difficulty articulating words and loss of coordination
  - Headache
  - Decreased mental ability
  - Upset stomach, vomiting, loss of appetite
  - Coughing, shortness of breath, decreased vital capacity
- High levels of exposure can cause:
  - Chronic lung impairment
  - Pulmonary edema
- Ozone odor is detectable at 0.1 ppm

# Installation Problems:

## European Ozone Systems in U.S. Pools

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- High cost of installation, equipment, monitoring, and system service by a factory trained technician
- No CD pool ozonator has NSF approval
- Lack of uniform circulation and extensive dead spots in many pools
- European pools that use CD ozone have 2 - 4 hour turnover periods. Faster turnover rates would require re configuring of the hydraulic system and filter up sizing (space restraints, economic feasibility)
- Ozone systems use air dried through desiccant dryers or 99.5% pure industrial oxygen to prevent corrosive nitric acid formation. Air must be taken from a well ventilated pump room.



# Installation Problems:

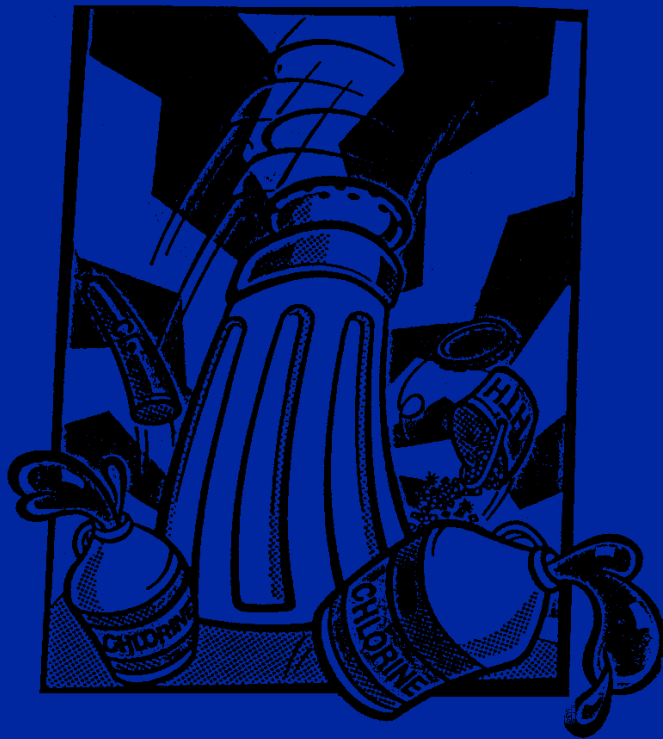
## European Ozone Systems in U.S. Pools

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- German standards require water to enter the pool at the bottom and flow upward to perimeter overflow. Bottom reverse flow inlets must be installed.
- DIN standard requires removal of water (30 L/day/bather or approx. 7.8 gallons per bather) and replacement (water conservation concerns)
- Alum flocculation is not compatible with high rate sand or D.E. filters most common in U.S. pools
- GAC filters need approximately the same amount of media surface area as the primary sand filters. Where would they fit in an already overcrowded pump room?

# Chlorine Generators

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- Electrolytic cells, or chlorine generators, change non iodized salt or low calcium and magnesium salt (salt pellets like those used in water softeners or for making home-made ice cream) into 100% chlorine gas

# Chlorine Generators

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- Two methods: in-line and off-line
- Generate chlorine on-site at the pool
- Electrically separate the chlorine from the by-product sodium hydroxide
- One pound of chlorine can be produced from 1.67 pounds of salt

# Off-Line Chlorine Generators

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- AKA “brine” or “diaphragm” method
- Two chambers separated by a membrane
- Electricity is passed through a salt water anode (positive electrode) chamber to a distilled water (negative electrode) cathode chamber
- The brine solution is split, the chlorine is freed from the salt and bubbles to the top of the chamber
- Current carries the sodium ions through the membrane to the cathode chamber, where it reacts with distilled water to form sodium hydroxide and hydrogen
- The hydrogen gas is vented off into the air
- Chlorine gas made in the process is drawn into the circulation system by Venturi and mixes with pool water

# In-Line Chlorine Generators

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- 200 - 500 pounds of salt for each ten thousand gallons of water is added directly to the pool
- Pool water is circulated through an electrolytic cell consisting of electrically charged layered plates
- Chlorine gas is produced, as are sodium hydroxide and hydrogen gas. All three products are introduced into the pool.
- Excess chlorine gas generated using this method reverts back to salt in the water to be reused
- Most pools in Australia are sanitized using this method

# Chlorine Generator

## Advantages & Disadvantages

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- Advantages:
  - pH is not affected because the sodium hydroxide neutralizes the acidic gas chlorine (in-line)
  - Water treatment costs are low
  - Eliminates the hazards associated with storing and transporting chlorine
- Disadvantages:
  - Chlorine generating equipment must be cleaned and maintained regularly to prevent fouling
  - With the in-line method, pool water has a slightly salty taste
  - TDS levels build rapidly

# Ionization

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- Electrolysis of metals
- Copper only, copper-silver, or iron-zinc systems
- In most ionization systems, a low voltage DC current is passed through a set of copper and silver metallic electrodes set slightly apart from each other in the recirculation lines before the filter
- Atoms on the electrodes become positively charged ions, try to cross the gap between the 2 electrodes, but are carried away by the flow of water
- Some non electric devices are just placed in the hair & lint strainer or in a skimmer basket. Water flowing past the device erodes metals into the water -- the stronger the current, the more metals imparted

# Ionization

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- Copper ions act as an algicide
- Silver imparted to the water acts as a bactericide
- Regardless of claims made by some manufacturers and distributors of ionization systems, ionization systems should be used in combination with low levels of chlorine or bromine
- The systems have bactericidal properties only. No oxidizer is present.



# Ionization Advantages

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- Reduced dependence on the use of halogen chemicals such as chlorine or bromine in treating pool water
- NSF Standard 50 approved systems allow use with chlorine residuals as low as 0.4 ppm (0.8 ppm bromine) \*

\* Health codes may require higher minimum levels

# Ionization Disadvantages

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- If copper levels become excessive
  - Staining and water discoloration may occur
  - Swimmers' hair and finger nails may begin to turn green
- If chlorinated isocyanurates are inadvertently used for shocking the pool water silver ions may precipitate and cause a black stain to form on the walls and equipment
- High total dissolved solids levels may reduce ion formation because the flow of current between electrodes is inhibited
- Water must still be superchlorinated or shocked regularly to oxidize out organic contaminants

# Polymeric Biguanide

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- Blue, chlorine free liquid
- AKA: polyhexametamethylene biguanide, PHMB
- Similar to the anti-microbial scrubs used in hospitals
- Works as a disinfectant by penetrating bacteria cell walls then bursting the cells from within
- Used in conjunction with a clarifier, an algaecide, and a hydrogen peroxide oxidizer
- Maintained at 30 - 50 ppm
- Residual PHMB is measured with a liquid reagent color comparator test kit or with test strips

# Polymeric Biquanide

## Advantages

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- Only non halogen sanitizer approved by EPA
- Does not alter the pH of pool water -- corrosion and calcification do not result from its use
- Does not cause bleaching
- It's stable -- high temperatures and ultraviolet light do not cause it to dissipate into the atmosphere
- Sold under trade names: Baquacil (1977 -1994 patented), Soft Swim
- Bather eye comfort
- No odor

# Polymeric Biguanide Disadvantages

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- Cost of using polymeric biguanide is relatively high when compared to the alternatives
- Not compatible with many products commonly used in pools -- discolored water and severe pool wall staining will occur if it's accidentally used with chlorine
- White water mold, pink slime
- White pool walls may turn a grayish color
- Not CA EPA approved for use in any pools in California, or in commercial pools in many states