Ozone as effective biocide for microbiological and antifouling control water system

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Biofilm - a universal problem

- slimy coatings of microorganism and extracellular compounds in pipelines, tanks and heat exchanger surface
- pathogenic germs (e.g. E. coli or Legionella) are living in biofilms
- biofilm reduces the efficiency of heat exchangers
- biofilm causes corrosion in metal surfaces MIC
- biofilms are extremely resistant against most disinfectants
- chlorine dioxide and ozone are the only suitable disinfectants, able to kill and to remove biofilms in water pipes and tanks
Microbiological control in water systems

- mechanical methods
  - manual cleaning of piping

- chemical methods
  - oxidizing chemicals
    - chlorine, chloramine
    - chlorine dioxide
    - ozone, peroxides and other oxidants
  - organic biocides and other chemicals
## Comparison of chemical disinfectants

<table>
<thead>
<tr>
<th></th>
<th>chlorine</th>
<th>ClO_2</th>
<th>ozone</th>
</tr>
</thead>
<tbody>
<tr>
<td>disinfection capacity</td>
<td>medium</td>
<td>strong</td>
<td>strongest</td>
</tr>
<tr>
<td>Oxidation potential [V]</td>
<td>1.49</td>
<td>0.95</td>
<td>2.07</td>
</tr>
<tr>
<td>dependence from pH-value</td>
<td>extreme</td>
<td>none</td>
<td>low</td>
</tr>
<tr>
<td>depot effect</td>
<td>hours</td>
<td>days</td>
<td>minutes</td>
</tr>
<tr>
<td>disinfection by-products</td>
<td>THM, AOX and other chlorinated organics</td>
<td>chlorite</td>
<td>evt. bromate</td>
</tr>
<tr>
<td>resources</td>
<td>Cl_2-gas, hypo-chlorite or electrolysis</td>
<td>HCl &amp; NaClO_2</td>
<td>electr. energy, air or oxygen</td>
</tr>
</tbody>
</table>

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## Comparison of Disinfectants

<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Reduction Rate</th>
<th>Chlorine (c x t, ppm x min)</th>
<th>Chlorine Dioxide (c x t, ppm x min)</th>
<th>Ozone (c x t, ppm x min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryptosporidium parvum</td>
<td>99.9</td>
<td>1440</td>
<td>&gt; 120</td>
<td>&gt; 5</td>
</tr>
<tr>
<td>Giardia lamblia</td>
<td>99.9</td>
<td>104-122</td>
<td>23</td>
<td>1.4</td>
</tr>
<tr>
<td>Escherichia Coli</td>
<td>&gt; 99.99</td>
<td>3-4</td>
<td>1.2</td>
<td>0.012 - 0.4</td>
</tr>
</tbody>
</table>
Chlorine based treatment – the best solution??

- Efficiency highly pH-dependent

- AOX formation
- Contribution to inorganic load
- High chlorine/chloride concentrations promote corrosion in metals
- High chlorine level necessary due to bioresistance
- Removal of residual chlorine before discharge
Approaches for chemical mollusc control

- to effect mortality of adult mussels
  - high disinfectant‘s concentration are required
  - deposits of dead mussels are still present

- to effect mortality of free swimming veligers
  - high disinfectant‘s concentration are required
  - cleaned piping will be protected against re-infestation

- to effect settling-inactivation of veligers
  - low disinfectant‘s concentration are required
  - cleaned piping will be protected against re-infestation
  - best ecological valuation
Physical Properties Ozone $\text{O}_3$  

- ozone is the strongest oxidant used in water treatment $E^0 = 2.07\, \text{V}$  
- solubility depending on temperature and ozone concentration in the gas phase  
- has to be generated on site due to short half life time  
- reacts without residuals resulting in $\text{O}_2$  
- ozone works without formation of undesired by-products  
  - no formation of THM  
  - no formation of AOX
Hydroelectric Power Plant Itaipu

- bi-national project between Brazil and Paraguay
- 1.350 km² surface reservoir, drainage area of 820,000 km²
- 20 Francis-turbines with following data, each:
  - 715 MW capacity
  - 125 m altitude difference
  - 660 m³/s water flow
Profile of the Dam

- bypass with 2.253 m³/h for use as cooling water
- stainless steel cartridge filter, mesh size 2 mm
- distribution on 11 blocks of heat exchangers
Problems caused by mussel growth

- growth of Limnoperna fortunei (Golden Mussel) on every wetted surface, even at 12.5 bar
  - blocked central filter
  - blocked heat exchangers
- frequently interruptions of the generators to clean filter and heat exchangers
Treatment of One Cooling Circuit with Ozone

Experts in Chem-Feed and Water Treatment

Sample valves for monitoring ozone

Coupon for monitoring corrosion

Bio boxes for monitoring mussel growth

Ozonator OZVa 4

Heat exchanger block

Output ozone

Booster pump

Venturi

Flow meter

4.2 m³/h

Flow meter

34 m³/h

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Determinations of Ozone dose

- ozonation
  - dosage rates: 0.1, 0.2, 0.3, or 0.4 ppm (calculated on 34 m³/h)
- measurement of the ozone
  - ozone detectable directly after the dosing point
  - no ozone detectable at the heat exchangers
- visual check of the heat exchangers after 3 month
- bio boxes
  - microscopic determination of plastic plates to identify dead and living veligers
  - 5 pairs of plates allow 5 tests / period
- corrosion coupon test at the heat exchanger
  - incubation period: 87 days

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Results: Visual Control of the Heat Exchanger

- 3 month after last cleaning without ozonation
- 3 month after last cleaning with ozonation
Results: Bio Boxes

- bio box 1:
  - before ozonation

- bio box 2:
  - after ozonation (0.3 ppm)

![Graph showing the number of veligers before and after ozonation.](image-url)
Results: Corrosion Coupon

- no corrosive effect of the ozonation detectable
- determination of general corrosion following international standard ASTM D2688-94
- incubation period: 87 days
- corrosion rate: 0.3 mpy (mpy = mils per year)
  - 0 to 2 mpy = excellent
  - 3 to 5 mpy = good
  - 6 to 10 mpy = acceptable
  - > 10 mpy = unacceptable
Summary

- low dosage of ozone in natural river water avoids mussel growth in cooling water circuits
- ozonation is a very ecological water treatment
  - no precursor chemicals required (oxygen or ambient air)
  - reaction in the water back to oxygen
- ozonation is a very economical water treatment
Thank you for your attention

Any question?