Chlorine dioxide as effective biocide for microbiological and antifouling control water system

Periphyton and fouling conference
St. Petersburg, 22.october 2008

Wolfgang Matheis
ProMinent ProMaqua GmbH
Maaßstraße 32/1, D-69123 Heidelberg
Tel. +49 (6221) 6489-0, Fax. +49 (6221) 6489-400
w.matheis@promaqua.com www.promaqua.com
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>ClO₂</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>Cl₂-gas, hypo-chlorite or electrolysis</td>
<td>HCl &amp; NaClO₂</td>
<td>electr. energy, air or oxygen</td>
</tr>
</tbody>
</table>
## Comparison of Disinfectants

<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Reduction Rate (%)</th>
<th>Chlorine $c \times t$ (ppm x min)</th>
<th>Chlorine Dioxide $c \times t$ (ppm x min)</th>
<th>Ozone $c \times t$ (ppm x min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crypto-sporidium 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>

Product Management, W. Matheis 20.10.2008
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
Properties of Chlorine Dioxide

- unpaired electron, considered to be a free radical: high reactivity for oxidation and disinfection
  \[ \text{ClO}_2^- + e^- \rightarrow \text{ClO}_2^- \text{ (Chlorite)} \quad E^0 = 0.95 \text{ V} \]

- soluble in water as a gas
  - reactivity independent of pH
  - able to penetrate cellular membranes
  - able to kill and remove biofilm

- high depot action due to low rate of self-decomposition in water and selective reactant
Ecological Aspects

- ClO₂ reacts only as an oxidant
  - no formation of THM (trihalomethanes)
  - no formation of chlorophenols
  - no formation of AOX (adsorbable organic halides)
  - no reaction with ammonium

- 75 ppm chlorite is non-toxic to Rainbow trout larvae

- 0.3 ppm chlorine dioxide influences growth parameters of Rainbow trout larvae after 20 days exposition

- 0.1 ppm chlorine dioxide: only little influence on planctonic organism such as foraminifera and diatom algae

Product Management, W. Matheis 20.10.2008
Power Plant ENEL near Rome, Italy

- 432,000 m³/h sea water used for cooling purpose
- temperature 8 – 20 °C
- circulated directly back into the Mediterranean Sea
- anti-fouling treatment with 4 plants BelloZon® à 10 kg/h
- dosage designed: 0.1 ppm
- dosage practised: 0.05 ppm
Results of Project ENEL

- 0.2 ppm Cl₂ dosage
- reduction of biofouling
- residual adhesive species still present

- 0.1 ppm ClO₂ dosage
- removal of biofouling
- no adhesive species present after 20 days

numbers of different bacterial species after 0 – 120 days of treatment
Project RECAP, Brazil

- treatment of extremely polluted water of river Tamaduatei
  - classified as „class 5“ (domestic and industrial waste water)
  - pre-treatment for use as cooling water, industrial process water and drinking water after reverse osmosis
- former problems:
  - formation of by-product such as chloramines and trihalomethanes
  - low efficiency of disinfection
  - corrosion problems in cooling systems
  - accidents with chlorine gas
- solution:
  - substitution of chlorine gas by chlorine dioxide
Results of Project RECAP

- 3-log reduction of biofouling
- reduction of turbidity
- reduction of corrosion

<table>
<thead>
<tr>
<th>treatment method</th>
<th>chlorine up to 0,5 ppm residual</th>
<th>chlorine dioxide reduction of chlorine to 0 ppm, dosage of 6 ppm ClO₂ *) up to 0,3 ppm residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>bacteria (CFU/ml)</td>
<td>3,5 x 10³ &lt; 10 &lt; 10 &lt; 10 &lt; 10</td>
<td></td>
</tr>
<tr>
<td>fungae (CFU/ml)</td>
<td>2,3 x 10³ &lt; 10 &lt; 10 &lt; 10 &lt; 10</td>
<td></td>
</tr>
<tr>
<td>turbidity (NTU)</td>
<td>5,2 2,7 3 2 2,7</td>
<td></td>
</tr>
<tr>
<td>chloride (ppm Cl⁻)</td>
<td>150 124,5 107 100 92,8</td>
<td></td>
</tr>
<tr>
<td>pH at 25 °C</td>
<td>6,9 7,2 7,1 7,2 7</td>
<td></td>
</tr>
</tbody>
</table>

*) reduction to 3,5 ppm ClO₂ after one month without result‘s impairment
Summary

- chlorine dioxide is a better biocide against industrial biofouling than chlorine
  - better biocide performance
  - better environmental performance

- design of systems against industrial biofouling
  - treatment’s aim has to be defined
    - disinfection to yield organism-free systems
    - treatment to effect organism’s settling-inactivation
  - lowest possible concentration of chlorine dioxide has to be determined by tests

- chlorine dioxide is a very economical water treatment
Thank you for your attention

Any question?