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a ProMinent Company

Experts in Chem-Feed and Water Treatment

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

Periphyton and fouling conference
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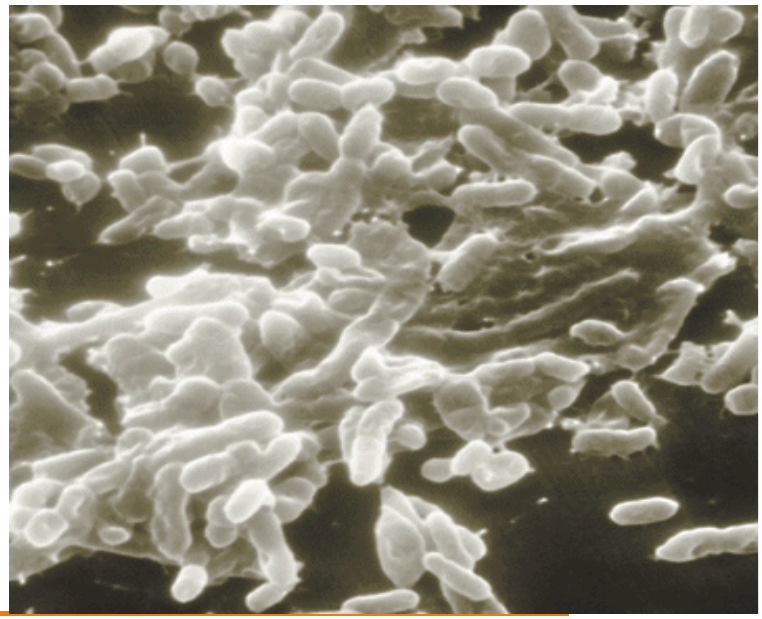
Biofilm - a universal problem

- 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

	chlorine	ClO_2	ozone
disinfection capacity	medium	strong	strongest
Oxidation potential [V]	1,49	0,95	2,07
dependence from pH-value	extreme	none	low
depot effect	hours	days	minutes
disinfection by-products	THM, AOX and other chlorinated organics	chlorite	evt. bromate
resources	Cl_2-gas, hypo-chlorite or electrolysis	HCl & $NaClO_2$	electr. energy, air or oxygen

Comparison of Disinfectants

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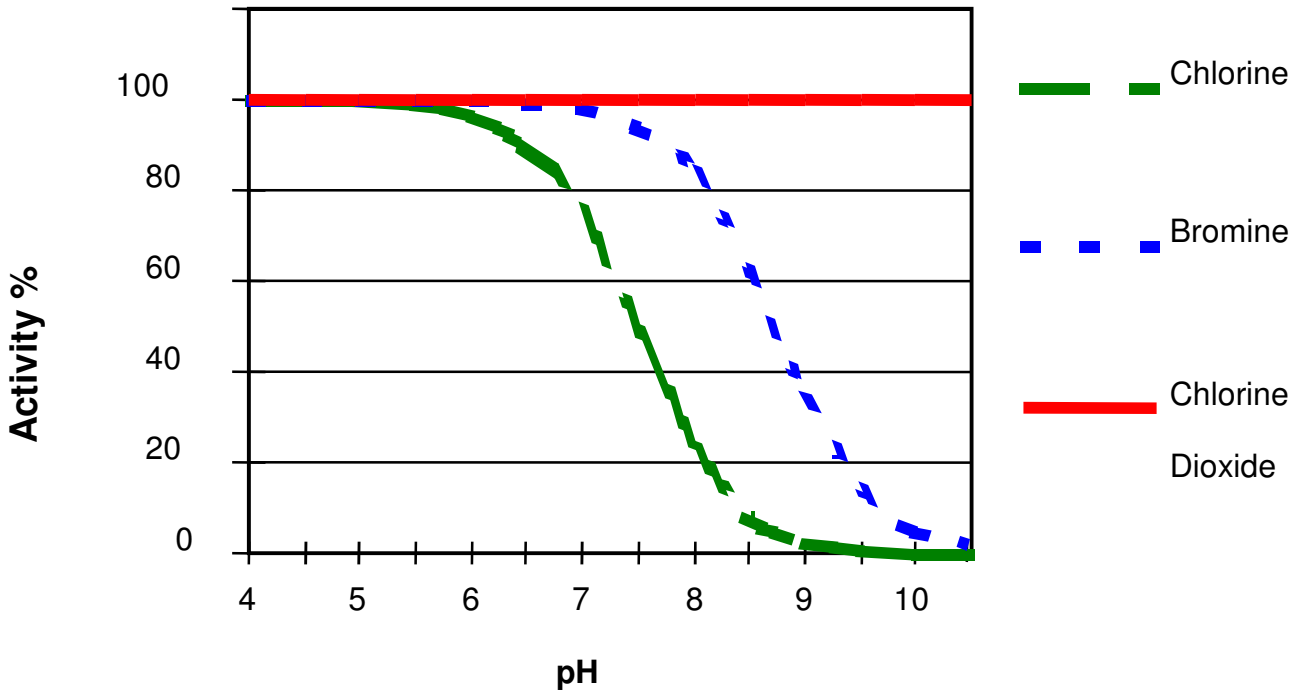
Micro-organism	Reduction Rate	Chlorine	Chlorine Dioxide	Ozone
	(%)	c x t (ppm x min)	c x t (ppm x min)	c x t (ppm x min)
Crypto-sporidium parvum	99.9	1440	> 120	> 5
Giardia lamblia	99.9	104-122	23	1.4
Escherichia Coli	> 99.99	3-4	1.2	0.012 - 0.4

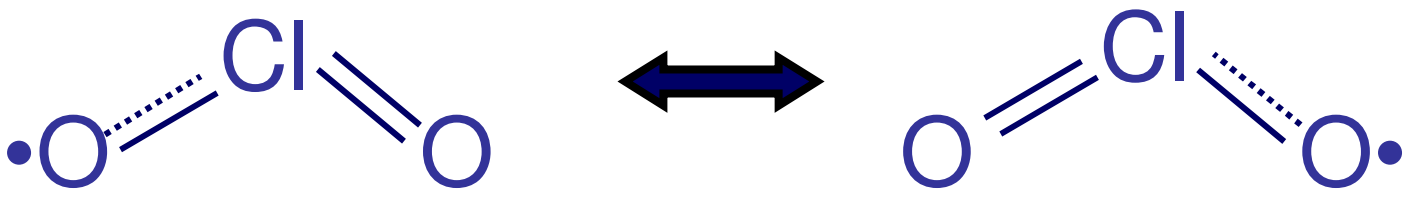
Chlorine based treatment – the best solution??

- Efficiency highly pH-dependent



- AOX formation
- Contribution to inorganic load
- High chlorine/chloride concentrations promote corrosion in metals
- High chlorine level necessary due to bioresitance

Properties of Chlorine Dioxide



- unpaired electron, considered to be a free radical: high reactivity for oxidation and disinfection
  $ClO_2 + e^- \rightarrow ClO_2^-$ (Chlorite) $E^0 = 0.95$ 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 selecitve reactant

Ecological Aspects

- ClO_2 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

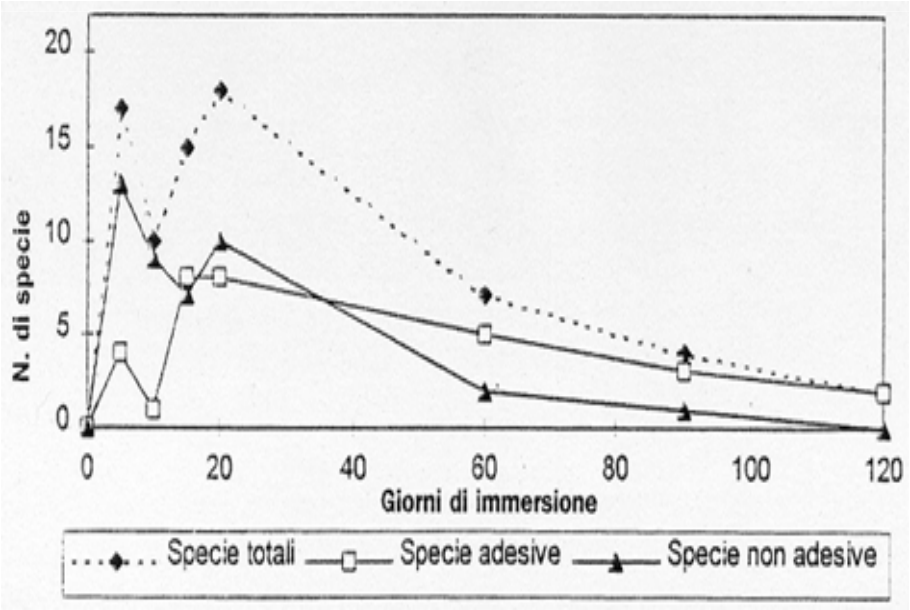
Power Plant ENEL near Rome, Italy

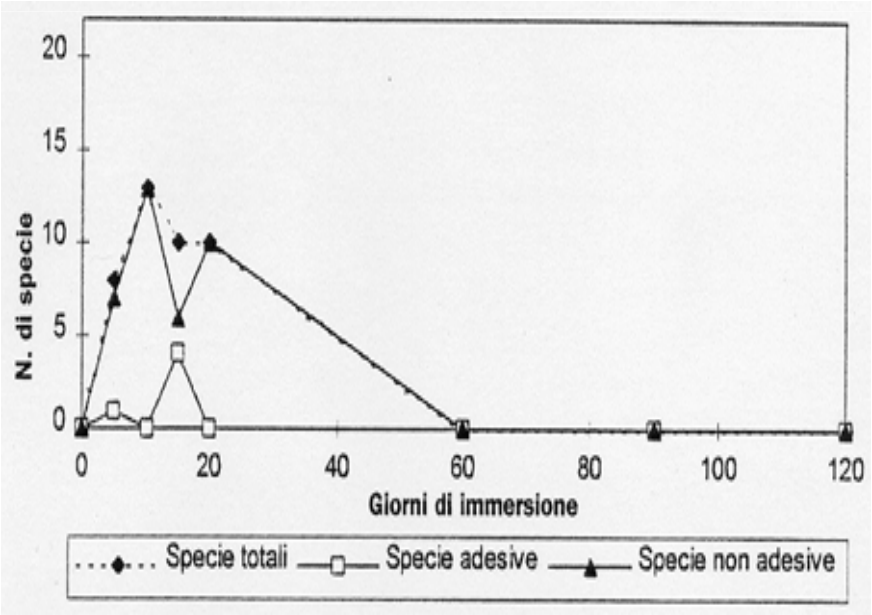
- 432.000 m³/h sea water used for cooling purpose
- temperature 8 – 20 °C
- circulated directly back into the Mediterranean Sea
- anti-fouling treatment with 4 plants BelloZon® à 10 kg/h
- dosage designed: 0.1 ppm
- dosage practised: 0.05 ppm

Results of Project ENEL

- 0,2 ppm Cl_2 dosage
- reduction of biofouling
- residual adhesive species still present

- 0,1 ppm ClO_2 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

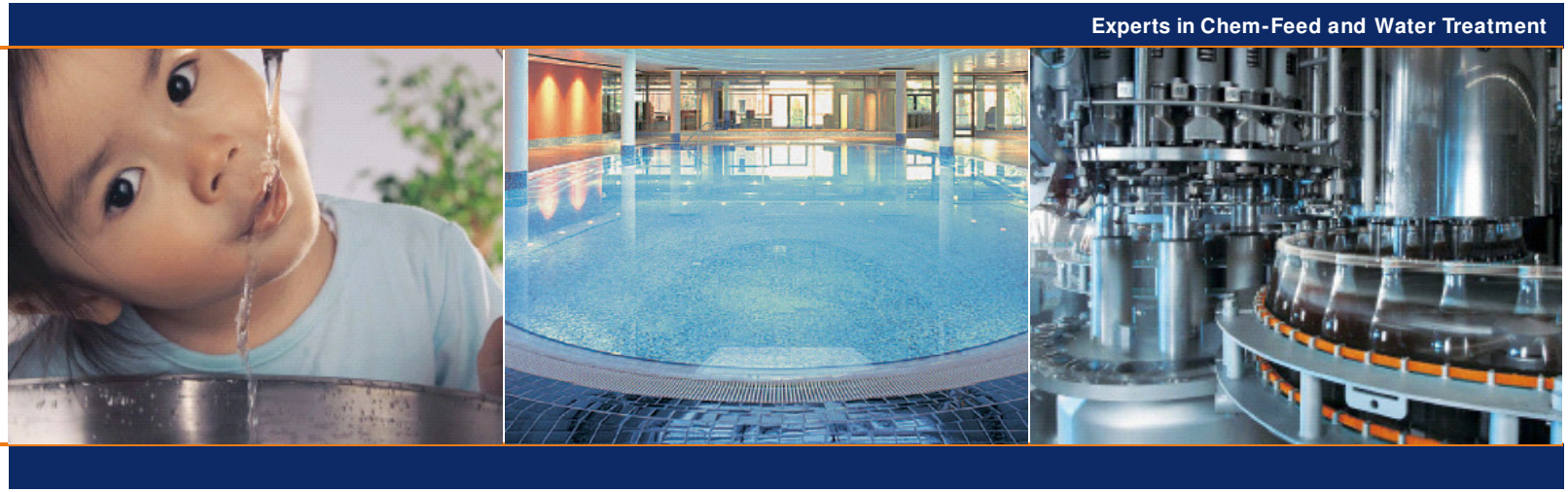
treatment method	**chlorine** up to 0,5 ppm residual	**chlorine dioxide** reduction of chlorine to 0 ppm, dosage of 6 ppm ClO_2 *) up to 0,3 ppm residual			
date in 2003	**02. Okt**	**13. Okt**	**16. Okt**	**20. Okt**	**27. Okt**
bacteria (CFU/ml)	$3,5 \times 10^3$	< 10	< 10	< 10	< 10
fungae (CFU/ml)	$2,3 \times 10^3$	< 10	< 10	< 10	< 10
turbidity (NTU)	5,2	2,7	3	2	2,7
chloride (ppm Cl^-)	150	124,5	107	100	92,8
pH at 25 ºC	6,9	7,2	7,1	7,2	7

***) reduction to 3,5 ppm ClO_2 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?