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Chlorine dioxide as a successful antifoulant treatment in large cooling system-Case history
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ClO2 technologies and service
“UNDERWATER TECH.”
SEAWATER ANTIFOULING TREATMENT

- Power plant
- Petrochemical plant
- Refinery
- Steel mills
- Fertilizer plant
- Thermal and R.O. desalination plant make up
CHLORINE DIOXIDE CHARACTERISTICS

**CHARACTERISTICS**

The biocidal activity is constant over the pH 6 - 9

**SUITABLE FOR:**

- Sea water once-through cooling system (pH 8.5)
- Recirculating cooling water system (pH > 8)
- Fertiliser & ammonia plant cooling system
- Waste water
- Refinery and petrochemical cooling system
- Seawater desalination plant

- No reaction with ammonia and urea
- No reaction with organic matter and oil
CHLORINE DIOXIDE CHARACTERISTICS

**CHARACTERISTICS**

- No formation of halogenated compounds (TTHMs-dangerous for human health)
- Strong biocidal activity against anaerobic bacteria
- Oxidation of sulfide to sulfate (sulfide scavenger)

**SUITABLE FOR:**

- Potable waterworks
- Food and beverage industry
- Waste water treatment plants
- Minimize corrosion
- Minimize bad smell
CHLORINE DIOXIDE

\[ \text{ClO}_2 + \text{e}^- \rightarrow \text{ClO}_2^- \quad (E_o = 0.95 \text{ V}) \]

\[ \text{ClO}_2 + 4 \text{H}^+ + 5 \text{e}^- \rightarrow \text{Cl}^- + 2 \text{H}_2\text{O} \quad (E_o = 1.51 \text{ V}) \]

Chlorine Dioxide is very active against:

- bacteria
- viruses
- algae
- fungi
- macroorganism
CHLORINE SPECIES FORMATION IN WATER ACCORDING TO pH
Cl₂ → pH 8-8.5 → 80% ClO⁻, 20% HOCl → Bacteria wall → NEW GROWING

ClO₂ → 100% ClO₂⁻ → Bacteria wall → NO growing
CHEMICAL FEATURES OF CHLORINE DIOXIDE (ClO₂)

- It is a gas and must be generated on site.
- It is soluble in water.
- It does not undergo hydrolysis at pH of cooling water.
- It is a strong oxidising agent.
The Biofouling problem

**Microfouling**
- Bacteria, Algae, Fungi,
- Microbial corrosion
- Loss of the heat exchange (loss in the efficiency of the thermal cycle)

**Macrofouling**
- Mussels, Barnacles, Serpulid worms, Hidroys
- Encrusting, loss of water flow, tubes plugging corrosion under deposit.
Chlorine dioxide and chlorine comparison against bacteria

- Cl2 demand = 1.7 mg/l
- ClO2 demand = 0.9 mg/l
CHLORINE DIOXIDE AND CHLORINE COMPARISON ON MACROFOULING GROWTH

Dosage mg/l
- Cl2 2.0
- ClO2 0.4

Summer
- Cl2 2.0
- ClO2 0.4

Winter
- Cl2 1.3
- ClO2 0.2
CHLORINE DIOXIDE AND CHLORINE COMPARISON ON THM FORMATION IN SEAWATER HAVING A TOC OF 5 MG/L

From “environmental impact of biocidal antifouling alternative treatments of seawater once through cooling systems” R. Ambrogi ENEL
CHLORINE DIOXIDE ADVANTAGES

- very performant in short time contact system
- reduced corrosion (compared with chlorine)
- very performant at high pH (sea water, all organic and Zn/phosphonate treat.)
- very performant in ammonia contaminated system (fertilizer and ammonia plant)
- It can be applied by a simply chlorine plant modification or possibility no chlorine treatment
- environment friendly disinfection treatment
**CHLORINE DIOXIDE GENERATION**

*ClO₂* can be generated on site by using water solutions of:

*Sodium Chlorite, Hypochlorite and acid*

according to the following reaction:

\[
2\text{NaClO}_2 + \text{NaClO} + 2\text{HCl} \rightarrow 2\text{ClO}_2 + 3\text{NaCl} + \text{H}_2\text{O}
\]

Or by using

*Sodium Chlorite and Chlorine*

according to the following reaction:

\[
2 \text{NaClO}_2 + \text{Cl}_2 \rightarrow 2 \text{ClO}_2 + 2 \text{NaCl}
\]

Or by using

*Sodium Chlorite and Hydrochloric Acid*

according to the following reaction:

\[
5 \text{NaClO}_2 + 4 \text{HCl} \rightarrow 4 \text{ClO}_2 + 5 \text{NaCl} + 2 \text{H}_2\text{O}
\]
NaClO from electrochlorinator

Chlorine dioxide to dosage point

HCl 33%

Sodium chlorite
ClO$_2$ “hypochlorite” generating system

Conversion of hypochlorite from electrochlorinator into Chlorine Dioxide
ClO₂ “under water” generating system

Reaction chamber located into the dilution water line

NaClO₂
H₂O
HCl
Dilution
H₂O

ClO₂
Water solution

Water to be disinfected
Chlorine dioxide reagents storage tanks
Chlorine dioxide reagents pumping station and control monitoring system
Chlorine dioxide “underwater reaction chambers”
Reaction chambers located inside the racket pipe.
Description of the Facility and Cooling Water (PLANT 1)

PLANT: LARGE PETROCHEMICAL

FEEDING: SEAWATER FROM THE INTAKE

SYSTEM: BASIN, SCREEN FILTERS, PUMPING STATION BASINS, COOLING TOWERS BASIN, HEAT EXCHANGERS, RETURN TO THE TOWERS, BLOW DOWN TO THE SEA.

FLOWRATE: RR. 175,000 m3/h (full capacity)

CHLORINE DIOXIDE DOSAGE:
- from March to October 2 shot/day at 0.5 ppm as long as 1.5 hour each shot (TOTAL 3 H/DAY).
- Winter 2 shot/day at 0.5 ppm as long as 1 hour each shot (TOTAL 2 H/DAY).

DOSAGE START UP: February 2009.
Description of the Facility and Cooling Water (PLANT 2)

PLANT: LARGE PETROCHEMICAL

FEEDING: SEAWATER FROM THE INTAKE

SYSTEM: SCREEN FILTERS, PUMPING STATION, PUMPING STATION, HEAT EXCHANGERS, RETURN TO THE SEA.

FLOWRATE: 32,000 m³/h (full capacity)

CHLORINE DIOXIDE DOSAGE:
2 shot/day at 0.3 ppm as long as 1 hour each shot (TOTAL 2 H/DAY).

DOSAGE START UP: February 2009.
Why chlorine dioxide?

Chlorine dioxide was selected, to treat the 2 plants instead of chlorination for safety, environmental and performance reasons.

In fact, chlorine and sodium hypochlorite are responsible of bromate and bromoform formation in seawater which are considered very toxic for aquatic life of the Arabian Gulf.

Chlorine dioxide demonstrated to be very efficient at very low dosage rate, minimizing its residual and the formation of brominated compounds at the discharge point.
EasyaReadox SYSTEM

electrochemical biofilm sensor.
As chlorine dioxide shots increase, the baseline come back to its original value showing no biofilm activity
Constant baseline value indicates that no biofilm activity takes place and the whole system is clean.
Conclusions

We underline the following advantages:

• Chlorine dioxide has allowed to minimize the growing of both micro and macro-fouling inside cooling systems of petrochemical plants at very low dosage rate,

• Monitoring system has demonstrated to be the “Brain” of the treatment programme. It has permitted to inject chlorine dioxide in a proper quantity and in the right moment, saving material and protecting the environment.
Thank you very much for your hospitality and your kind attention

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