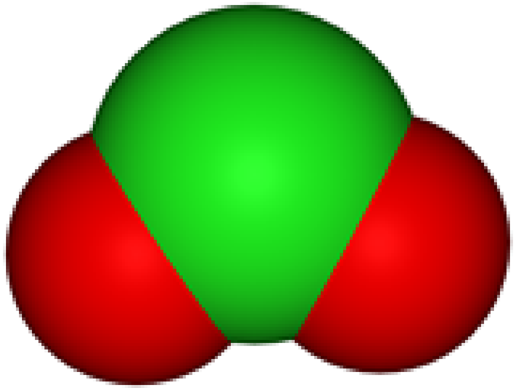


Introduction to Purate Technology & ClO2.

Paul Beattie

February 2016.

Summary

- Chlorine dioxide : What is it?
- Chlorine dioxide advantages vs other biocides
- Chlorine dioxide biofilm removal action
- Chlorine dioxide producing methods: pros and cons
- SVP Purate technology
- Purate: when to consider it
- Purate safety
- Purate examples

Chlorine Dioxide Gas and Disinfectant Characteristics

Greenish-Yellow Color, Similar Smell to Chlorine

Highly Soluble in Water

- Applied as a **dissolved gas** in water
  - Does not hydrolyze like Cl_2 : no loss of effectiveness at higher pHs
  - Kills bacteria, spores, viruses, fungi, algae very fast and no immunity development
  - It can diffuse into biofilms attacking the bacteria generating the biofilm

Reacts by Oxidation (select oxidizer)

- No loss of biocide effectiveness due to byproduct reaction
- No byproduct AOX or THMs

Cannot be compressed or shipped

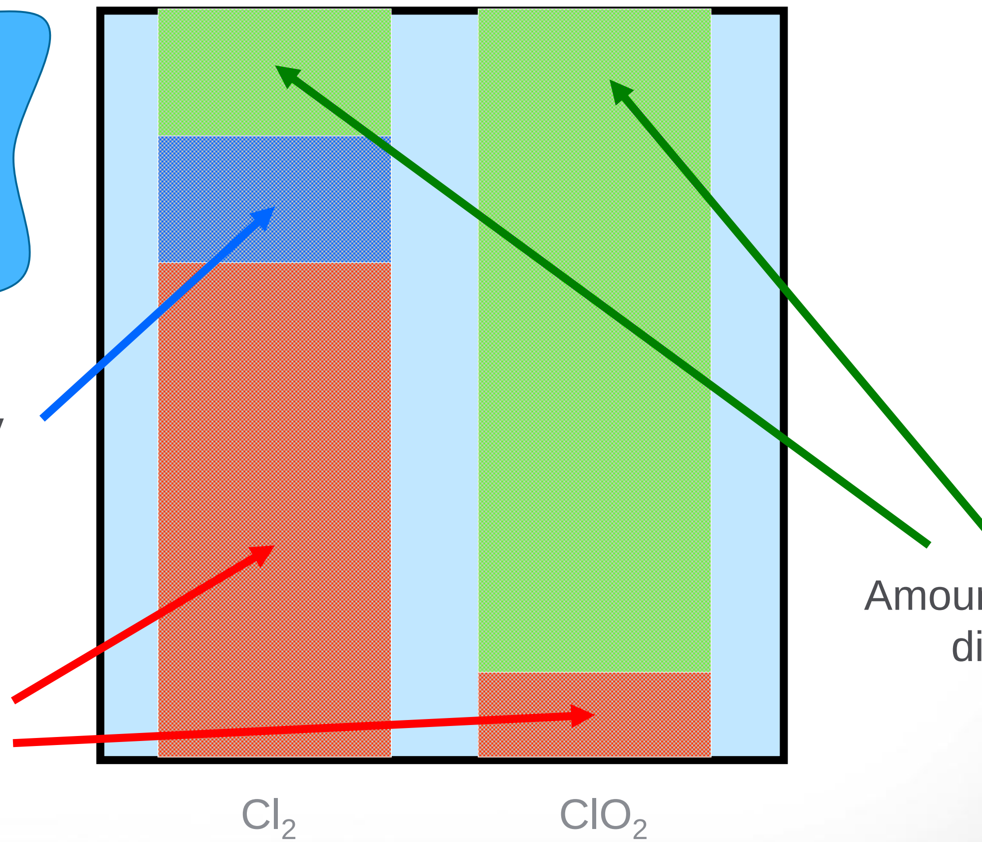
Chlorine Dioxide Advantages over other Biocides.

Advantages of ClO2 over Cl2 / Hypo

- Very fast rate of disinfection
- Excellent control of Bio-films
- Effective at low dosage rate
- Non Reactive with Organics (No THM or HHA, Low TOX, Low stable consumption)
- Non reactive with ammonia (low and stable consumption)
- Slow bacterial recovery after disinfection (Chlorite ion)
- Disinfection less dependent on pH (stability, economy)
- Significantly lower corrosion rate
- Safer handling/storing

Why Use ClO2 - Selectivity

How chemistry impacts dosage requirements



Property	Hypochlorite	Chlorine Dioxide
Active species	HOCl Hypochlorous acid OCl^- Hypochlorite ion	ClO_2 Chlorine Dioxide
Disinfection efficacy with varying pH	Powerful <7.5 Decreasing 7.5 - 8.2 Reduced above 8.2	Powerful 6 - 10
Disinfection by-products of environmental concern	Forms trihalomethanes, adsorbable organic halogens and non purgeable organic halogens	None
pH impact of dosing	Increase Excess caustic in solution (pH 11-12)	Slight decrease Excess acid in solution (pH 1-3)
Reaction with Natural Organic Matter	Rapid Forms chlorinated organic compounds	Intermediate Forms oxidised organic compounds
Reaction with ammonia	Reacts to form chloramines which are poor biocides and highly toxic to aquatic life	No Reaction
Reaction with biofilm	Fair	Excellent
Product Stability	Poor Degrades readily	Good Generated on site

Chlorine Dioxide Oxidation Potential.

Oxidant Species	Oxidation Potential, Eo(V)	Oxidation Capacity
Ozone (O_3)	2.07	2 e^-
Hydrogen peroxide (H_2O_2)	1.76	2 e^-
Permanganate ion (MnO_4^-)	1.68	3 e^-
Hypochlorous acid (HOCl)	1.49	2 e^-
Chlorine (Cl_2)	1.36	2 e^-
Hypobromous acid (HOBr)	1.33	2 e^-
Bromine (Br_2)	1.07	2 e^-
Chlorine dioxide (ClO_2)	0.95	5 e^-
Sodium hypochlorite ion ($NaOCl^-$)	<0.50	2 e^-

Dosages - Best Practice Guidelines for Recirculating Cooling Water.

Continuous residual of 0.10 – 0.50 mg/l

- Based on circulation rate (Calculate to 0.10 – 0.20)
- Monitored by ORP

Intermittent slug doses

- 0.10 – 5.0 mg/l residual
- (Calculate to 2.00 mg/l) Based on system volume
- 4-6 times daily
- Monitored by ORP (e.g. slug from 200 – 600 mV)

Direct replacement (active:active) of existing oxidizer

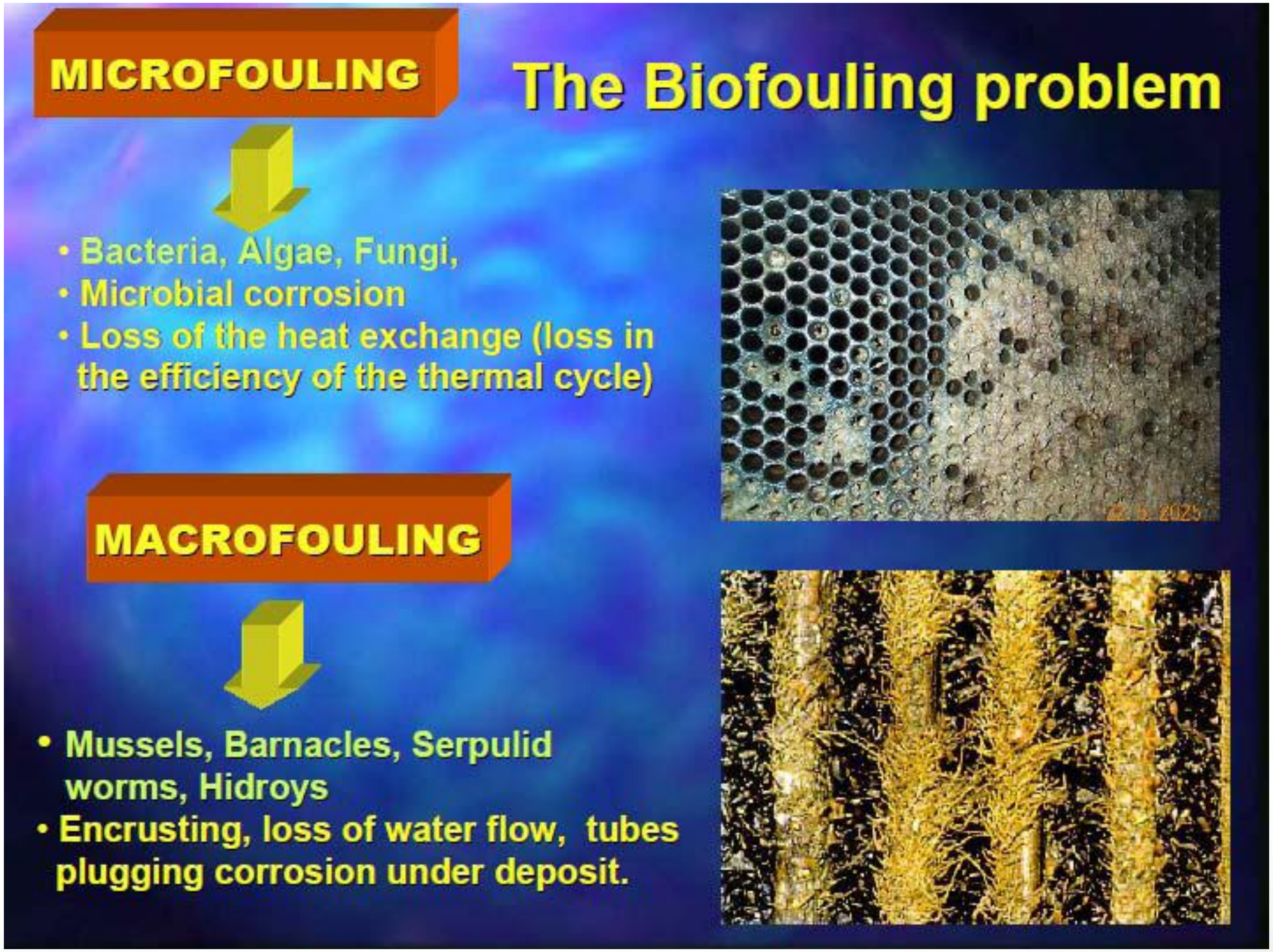
- Low demand systems only
- pH dependent

How does Chlorine Dioxide Work.

ClO2 disinfects via two separate mechanisms. As a permeable gas, it migrates through the cell membrane and reacts selectively with cellular components (amino acids: cystine, tryptophan and tyrosine) and proteins. It also inhibits critical cell physiological functions, including the disruption of protein synthesis via the oxidation of the disulfide bonds in amino acids and alteration of the permeability of the outer cell membrane.

Chlorine Dioxide Biofilm Removal Action.

The Biofouling Problem

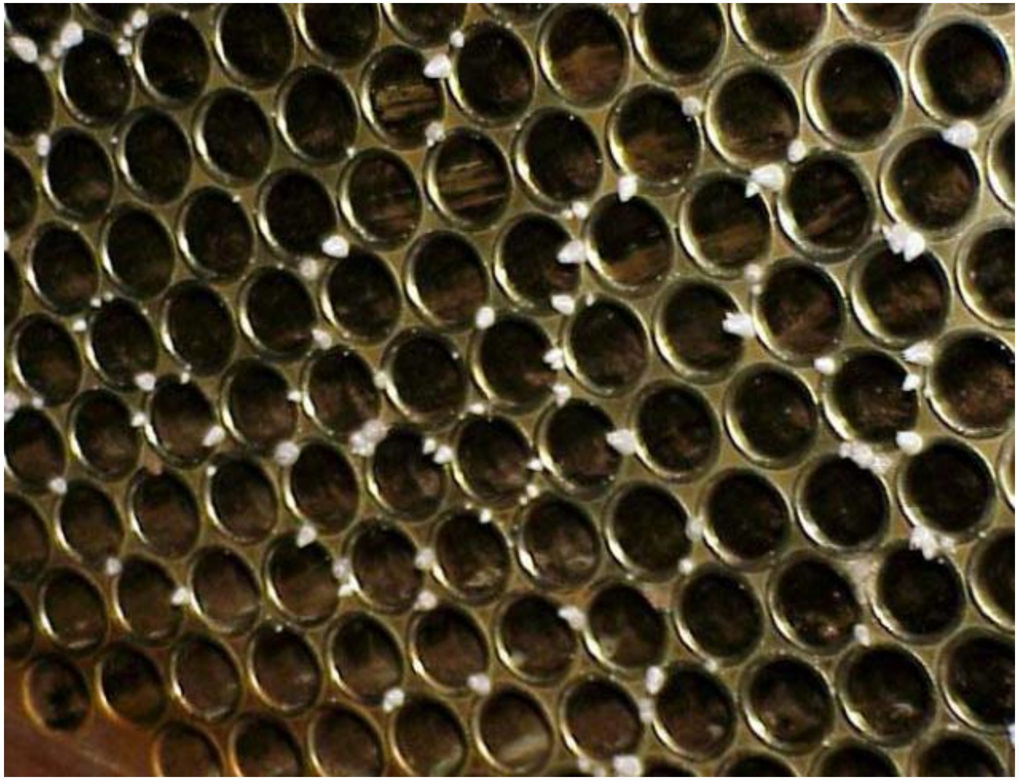


Power Station Treated with Chlorination

Heat exchanger from a power station treated with chlorine

Power Station Treated with Chlorine Dioxide

Heat exchanger from a power station treated with chlorine dioxide



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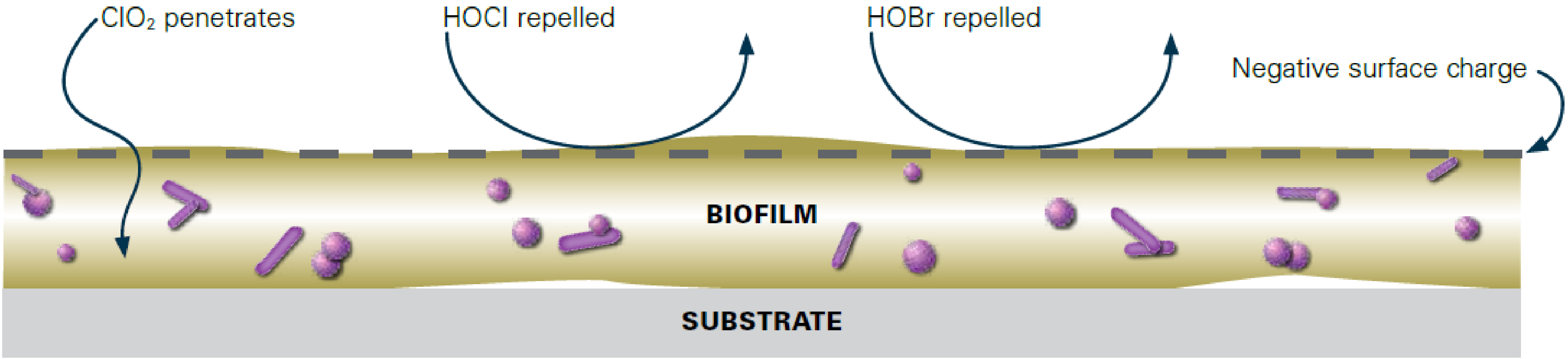
The Menace of Bio-films

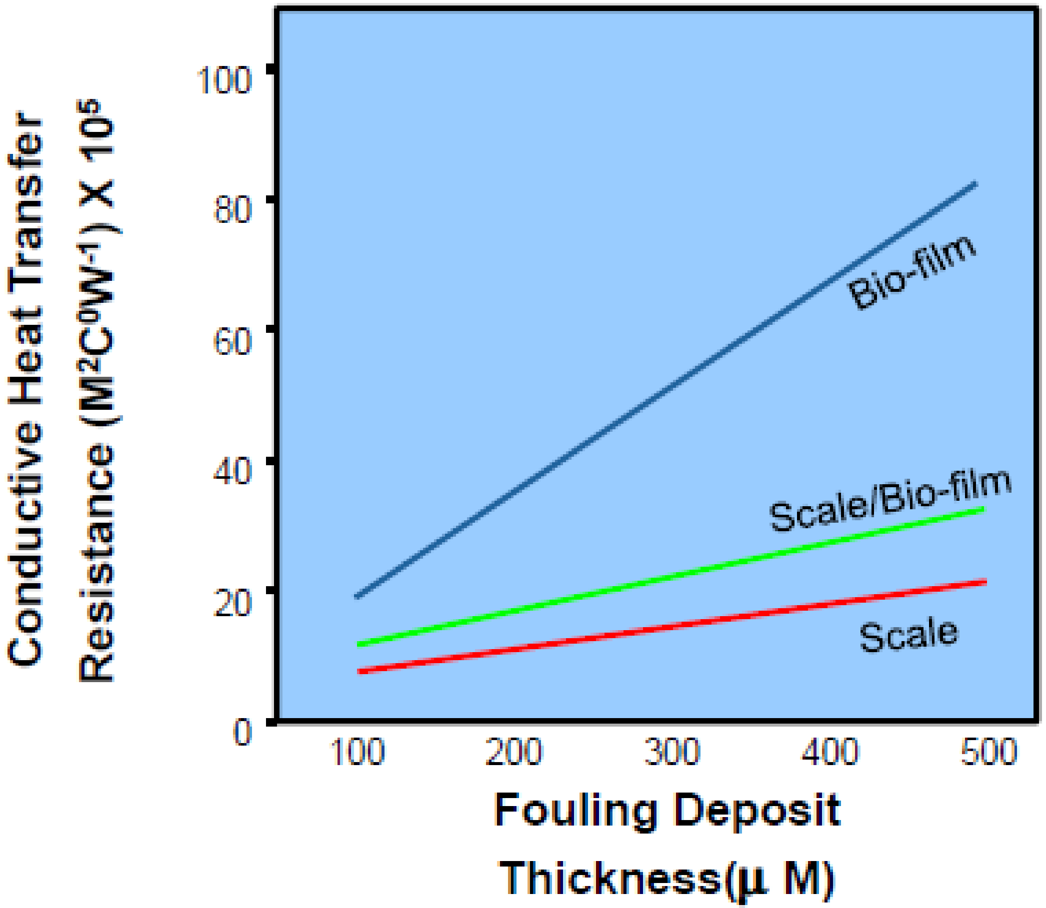
- Reduce heat transfer in heat exchangers
- Home for pathogenes
- Cause micro-biologicly induced corrosion (MIC, pitting)
- Reduce cooling water flow

Because ClO2 is a true dissolved gas in solution, it can rapidly diffuse and penetrate the polysaccharide-based biofilm substrate, killing microbes both throughout and beneath the biofilm

Chlorine Dioxide Kill Mechanism.



Microbiological Growth & Heat Transfer.



Chlorine Dioxide Generating Methods Pros & Cons.

Methods for producing ClO2 – chlorite oxidation

- Chlorine + Chlorite

$$2NaClO_2 + Cl_2 \qquad 2ClO_2 + 2\ NaCl$$

Advantage

- 100% theoretical chemical conversion efficiency
- Relatively low cost especially if Cl2 is locally available

Disadvantage

- Produces THM’s
- Gaseous chlorine is required
- Safety issues for storage. transportation, and handling
- Higher corrosion (in recirculating system)

Methods for producing ClO2 – chlorite oxidation

- ABC method: acid + bleach + chlorite

$$2NaClO_2 + NaOCl + HCl \quad 2ClO_2 + 3NaCl + H_2O$$

Advantages

- 100% theoretical chemical conversion
- Elimination of Cl_2 Gas

Disadvantages

- Bleach degradation (especially in warm climates)
- Three chemical system makes it more difficult to control & optimize
- High vapor pressure of HCl

Methods for producing ClO2 – chlorite oxidation

- Chlorite + acid

$$5NaClO_2 + 4HCl \quad 4ClO_2 + 5\ NaCl + H_2O$$

Advantages

- Elimination of Cl_2 Gas
- Two component system
- Lowest THM formation of the chlorite systems
- Most robust and safe system of the Chlorite processes

Disadvantages

- Max 80 % chemical conversion efficiency
- High vapor pressure of HCl
- Relatively high cost

Methods for producing ClO2 – chlorate reduction

- Purate + acid

$$\underbrace{NaClO_3 + \tfrac{1}{2} H_2O_2}_{\boxed{\text{Purate}^{®}}} + \tfrac{1}{2} H_2SO_4 \rightarrow ClO_2 + \tfrac{1}{2} Na_2SO_4 + \tfrac{1}{2} O_2 + H_2O$$

SVP-Pure® Process

Advantages

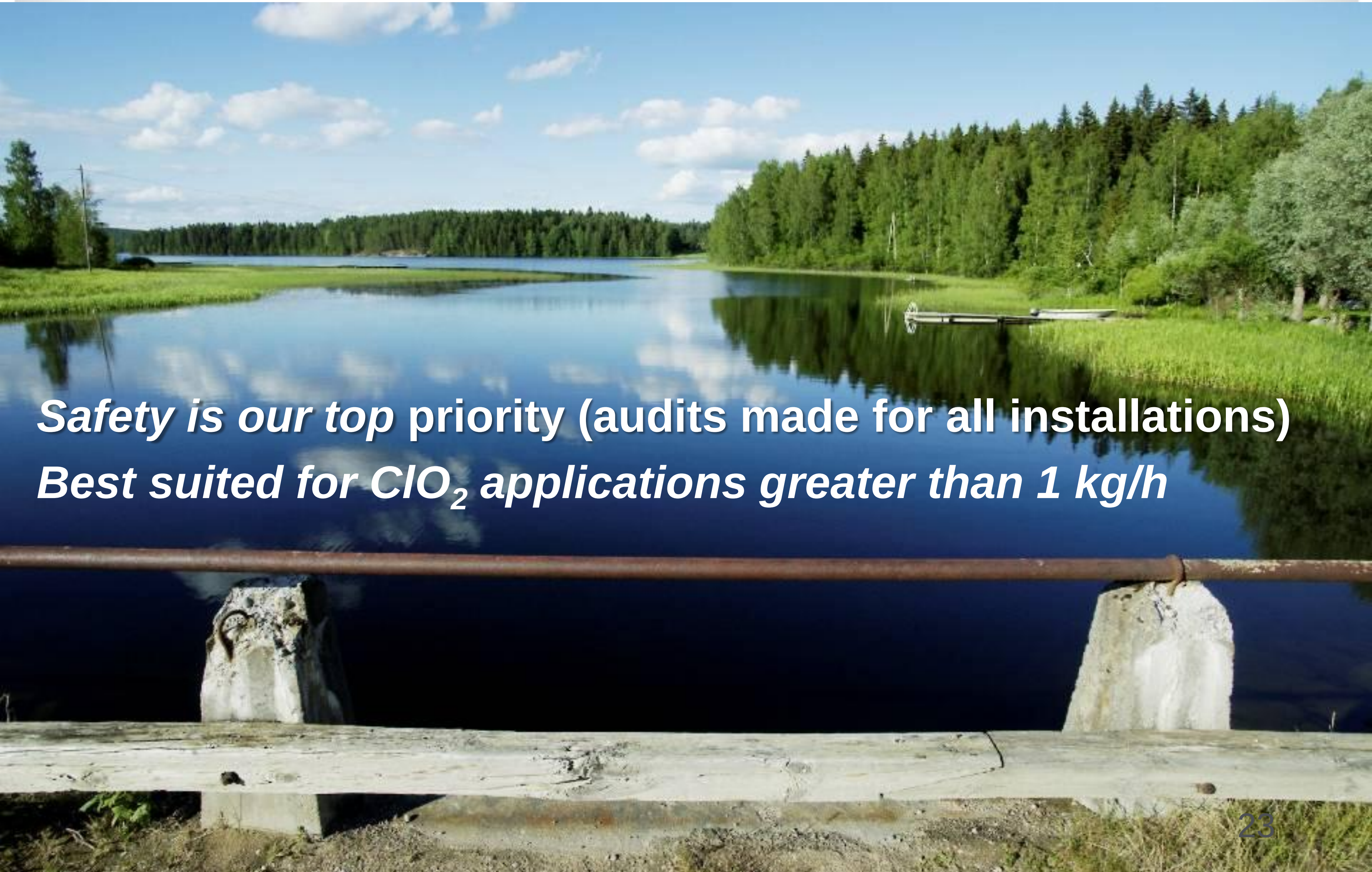
- Efficient – 95% conversion at standard conditions
- No need of Cl_2 Gas
- **No chloride contribution**
- **High precursor concentration minimize storage requirements and freight costs**
- Converts chlorate directly to ClO_2 (not via intermediates as the Chlorite processes)
- Excellent cost structure
- Chlorine Free – no AOX or THM formation
- **Two Chemical Program – reduces truck traffic**
- Patented
- **High quality equipment – safe and reliable**

Chemical feed rates per unit mass of requested ClO_2

Purate ®	78%* H2SO4	93%* H2SO4	98%* H2SO4
4.15	5.16	4.33	4.11

* Only one of the acid choices is needed for SVP-Pure® chemistry. Acid strengths higher than 78% must be diluted down before using.

SP Purate® Technology



Safety is our top **priority (audits made for all installations)**

Best suited for ClO_2 applications greater than 1 kg/h

SVP-Pure ® ClO_2 Generator Model AD DS

SVP-Pure® ClO_2 generator + four-point dosing system

Back pressure control valve

Control Valves

Mag Flow Meter

Water Booster Pump

ClO2 Booster Pump

24

40 Feet ClO_2 Production Container

Maximum safety and ease of operation

Fully Enclosed Container (FEC) Inside View

Purate : - when to consider it

Large cooling systems with problems

- >2000 l/day bleach

Open recirculating cooling systems

- Minimum recirculation rate 7500 m3/h

Electro-Chlorintors high generating and maintenance costs.

Once through Sea Water Cooling Systems:

- Minimum 20 000m3/h

Purate Examples.

Sea Water Cooling System.

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Leading ClO_2 Technology™

The Sea Water Cooling System in the Middle East has a history of bio-fouling leading to poor thermal efficiency and under-deposit corrosion.

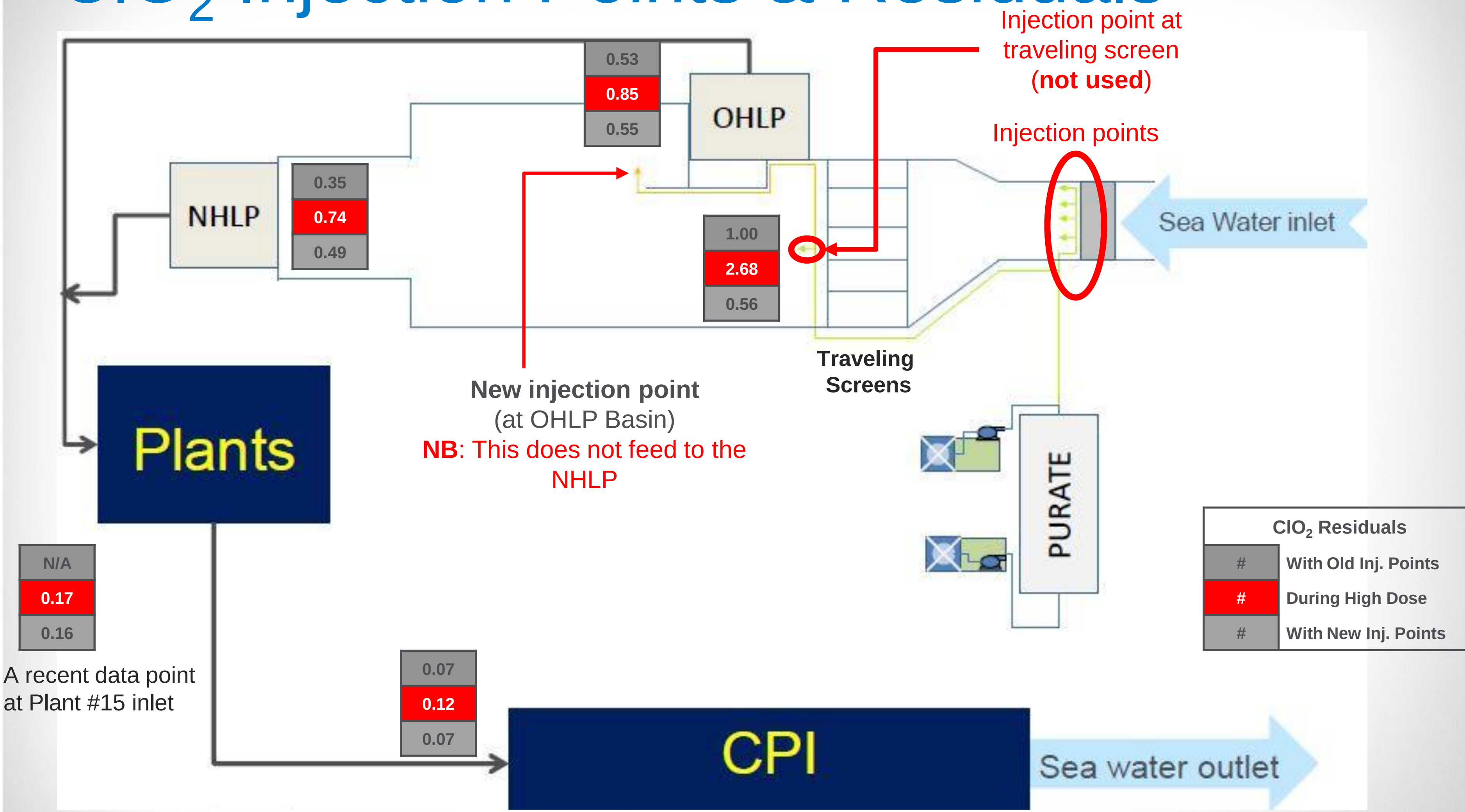
Historical attempts to address this had not been successful due to a variety of factors including efficacy and control problems.

Purate technology has addressed these factors and is providing a significant improvement in microbiological control and thermal efficiency.

The trial has focused on better targeting of the chlorine dioxide to further improve cost-effectiveness as we work towards finalizing the target dosage.

Further improvements to safety and monitoring required.

ClO_2 Injection Points & Residuals



Heat Exchanger Performance

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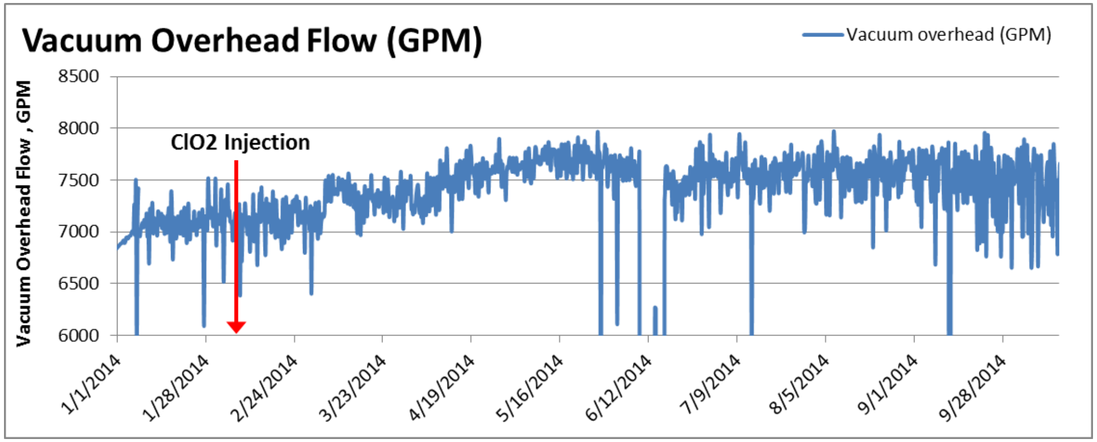
	Total Heat Transfer coefficient (U)	Cleanliness factor (%)	Cooling Water Flow (m^3/h)	Flow Velocity (m/s)	U-normalized by SW flow U/SW Flow	Cleanliness factor normalized Cleanliness factor/SW Flow
Average 2013 (Feb to 14-Oct)	145.9	16.9	400.9	1.6	0.3675	0.0427
Average 2014 (7-Feb to 14-Oct)	176.1	20.5	454.9	1.8	0.3892	0.0452
% Change	20.7	20.7	13.5	13.5	5.92	5.90



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Plant Data.

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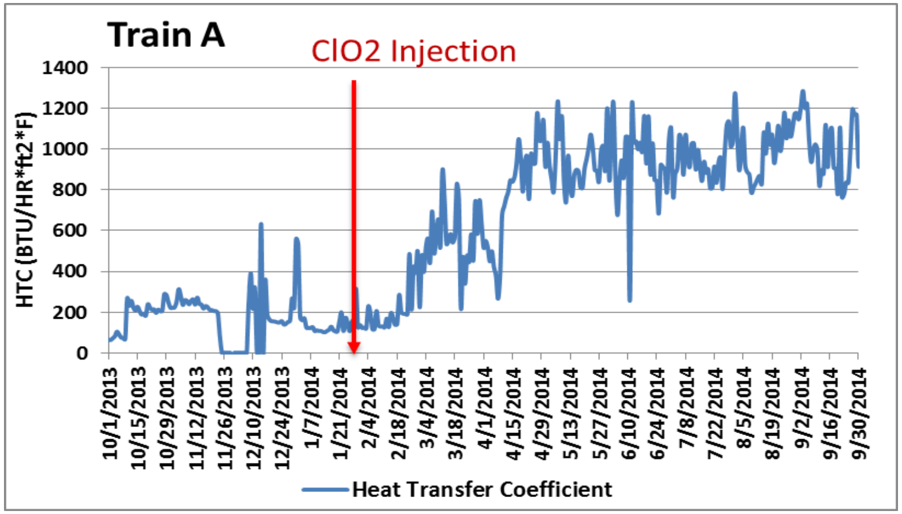

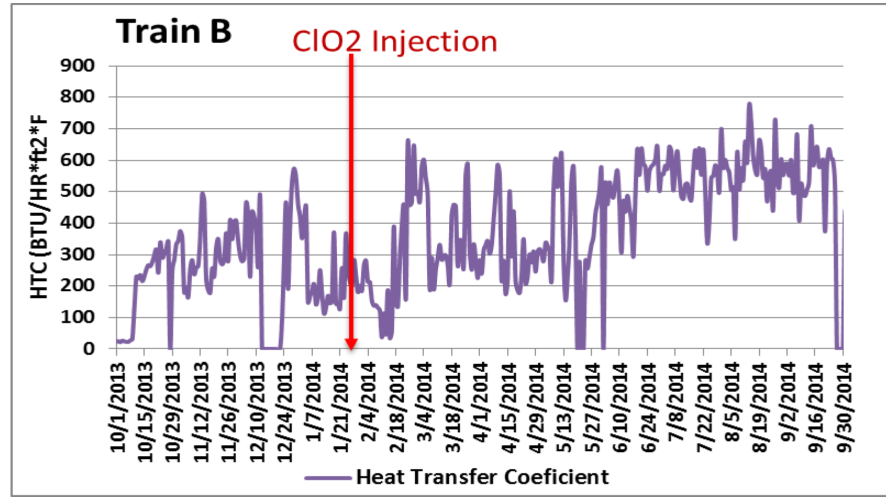

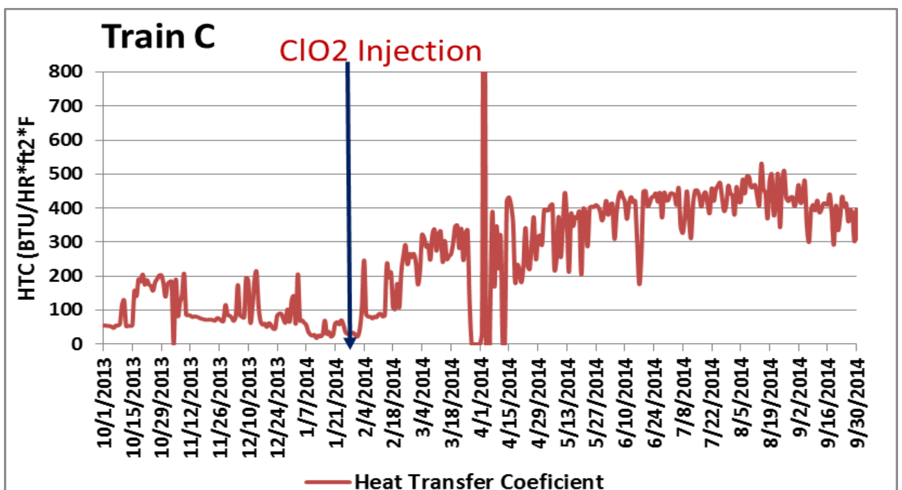

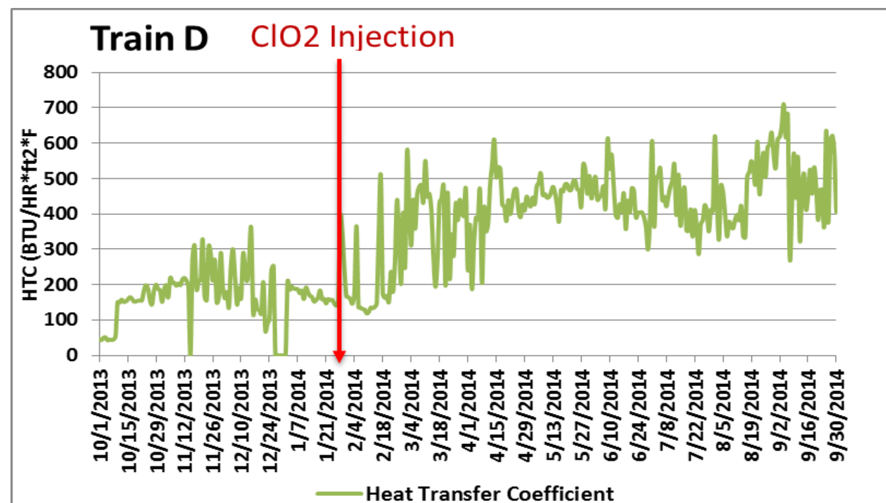

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Visual Inspection

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Before Treatment	After Treatment
	
	

Microbiological Analysis

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Plant 35 – Plate # 4	BEFORE ClO2 INJECTION	AFTER ClO2 INJECTION
Analyte	**Result**	**Result**
AEROBIC BACTERIA		
Total Viable Count @ 35°C	130 000 CFU/gram	9 000 est. CFU/gram
Pigmented Bacteria	1 Type	Not Detected
Total Coliforms	<1 000 CFU/gram	<1 000 CFU/gram
E. coli	<1 000 CFU/gram	<1 000 CFU/gram
Pseudomonas spp @ 35°C	7 000 est. CFU/gram	<1 000 CFU/gram
Spores	3 200 CFU/gram	4 300 CFU/gram
ANAEROBIC BACTERIA		
Sulfate Reducing bacteria	30 000 CFU/gram	300 CFU/gram
FUNGI		
Mold	<100 CFU/gram	<10 CFU/gram
Yeast	<100 CFU/gram	<10 CFU/gram

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Chemical Consumption Results & Target

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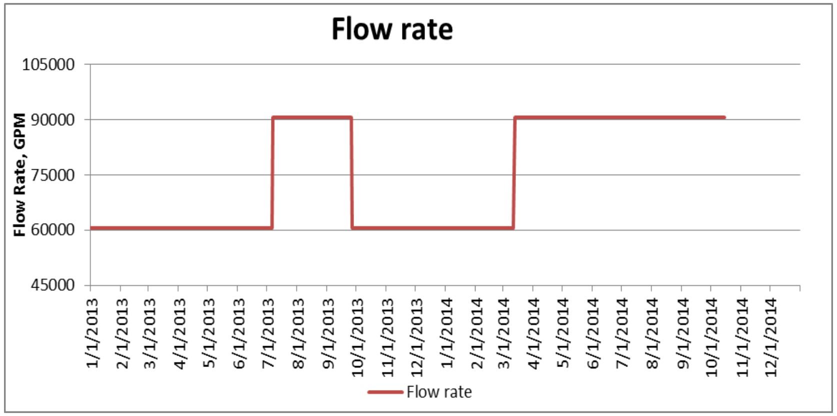

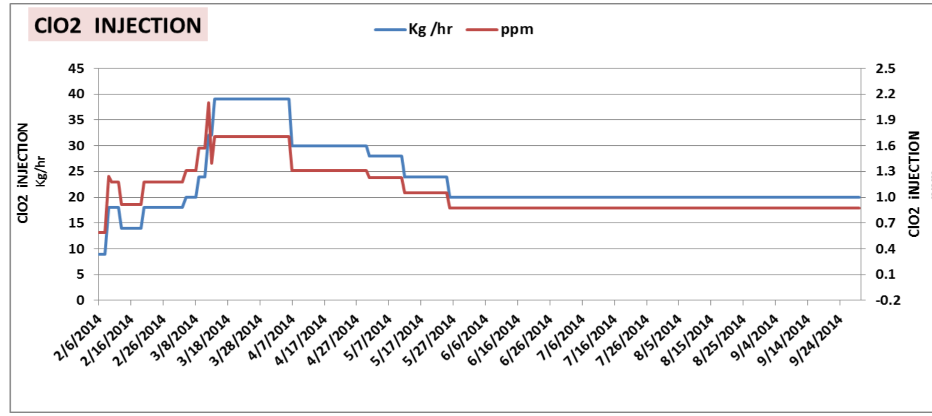

Last Purate Consumption

Months	Feb	Mar	Apr	May	June	July	Aug	Sept	Total
PURATE, Kg	8,562	22,257	19,352	17,845	9,845	11,826	12,611	13,796	116,094

Target Consumption based on current level of monitoring

Purate	Winter		Summer	
	2 Pumps	3 Pumps	2 Pumps	3 Pumps
Taget dosing, ppm	1		1	
Running hours, day	4		6	
Flow Rate, M3/hr	13,581	20,371	13,581	20,371
Consumption, Kg Monthly	7,153	10,730	10,730	16,095

Summary of Improvements

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Aspect	Improvement
Safety	A safer system for employees and environment but more to do
Monitoring & Control	Significant improvements achieved with additional monitoring (ORP) recommended.
Analysis & Visual	Considerable reductions in microbiological activity known to contribute to fouling and under deposition corrosion. Cleaner surfaces.
P15- VDU strainer backwash frequency improvement	330%
P15 –VDU HX Heat Transfer Coefficient	~ 21/6%
P15- VDU Over-Head Production	~ 7%
MED- Heat Transfer Coefficient	~ 70 %

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Mussels: Why ClO2?

Sea water flow, 7 000 -10 000 m^3/h

Problem with biofilm and mussels

Production losses

Annual cleaning costs in **2010: 2400 k€**

High NaOCl dose but little effect
Does not remove the bio-film
AOX and THM problems
Authorities would like them to change disinfection method

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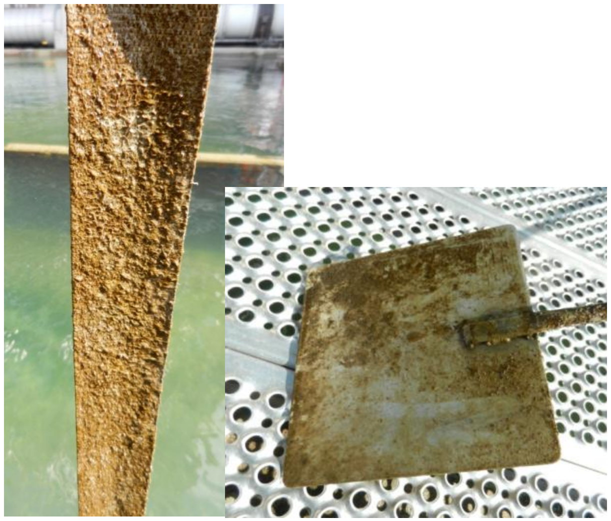
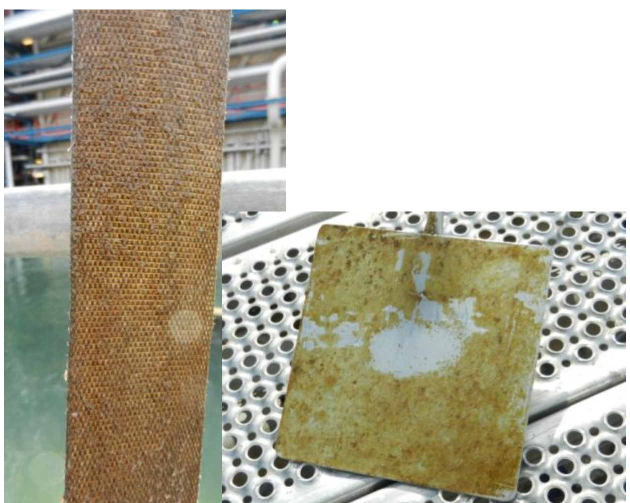
Trial follow up – Mussels and bio-film

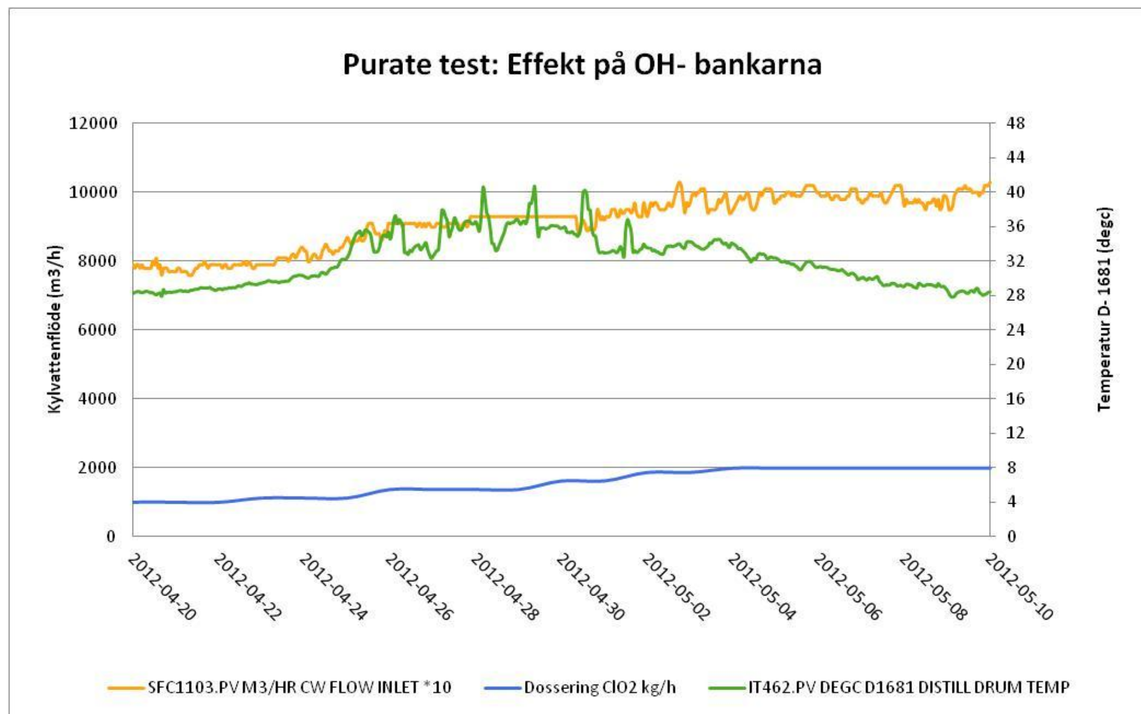
6 weeks after start up



8 weeks after start up



- Continued to dose hypo during the two first weeks of the trial
- Gradually increased the dose to avoid the bio-film to block the heat exchangers
- **Dosing scheme**
    - 0,2 ppm at the beginning / 0,8 ppm during the summer
    - Future expections: 0,2 ppm in winter / 0,5 – 0,6 ppm in summer



K.S.A. Purate Users

- Aramco Ras Tanura
- Saudi Kayan
- Chevron
- Safco (Interested)
- Sharq (Interested)
- Tasnee (Interested)
- Ar Razi (Interested)

Questions?