Saline Water Conversion Corporation Kingdom of Saudi Arabia



## Evaluation of Chlorine Dioxide (ClO<sub>2</sub>) Generation System for Disinfection in RO Product Water at SWCC Jubail Plant

**Desalination Technologies Research Institute** 



## Investigators

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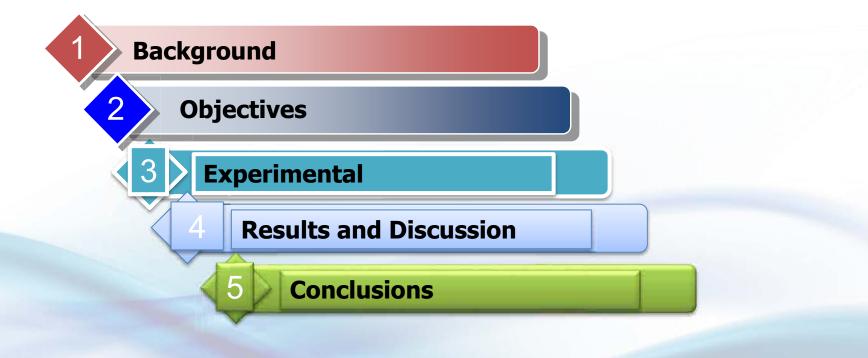
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## CONTENTS





Recent studies have shown the formation of bromate in desalination-derived drinking water, especially when the desalinated water is treated with sodium hypochlorite solution produced by electrolyzing seawater.

*Environmental Health Criteria 216, WHO (2000),* Disinfectants and Disinfection By- products, *ISBN 9241572167, 30-31.* <u>http://www.who.int/ipcs/publications/ehc/ehc\_216/en/</u>



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Bromate formation in chlorinated water under special conditions has been explained by the following reaction.

Chlorine gas hydrolyses in water almost completely to form hypochlorous acid (HOCI):

$$\begin{array}{cccc} Cl_2 + H_2O & \longrightarrow & HOCI + H^+ + CI^- & (1) \\ HOCI & \longrightarrow & H^+ + OCI^- & (2) \end{array}$$

The hypoclorous acid reacts in waters containing bromide ion to produce hypobromous acid HOCl +  $Br^{-} \longrightarrow HOBr + Cl^{-}$  (3) OCl<sup>-</sup> +  $Br^{-} \longrightarrow OBr^{-} + Cl^{-}$  (4)



This reaction of hypobromous acid formation is irreversible. The presence of bromide in hypochlorite solutions can ultimately lead to the formation of bromate  $(BrO_3^{-})$ . Hypobromous acid is a weak acid  $(pk_a = 8.7)$ ; like hypochlorite, hypobromite is metastable. In alkaline solution, it decomposes to give bromate and bromide.

(5)

 $3OBr^{-} \longrightarrow BrO_{3}^{-} + 2Br^{-}$ 

1. Macalady, D. L.; Carpenter, J. H.; Moore, C. A. (1977), Sunlight induced bromate formation in chlorinated seawater. Science, 195(4284), 1335-1337.

2. Kumar, K.; Margerum, D. W., (1987), Kinetics and Mechanism of general – acid- assisted oxidation of bromide by hypochporite and hypochlorous acid. Inorg. Chem., 26(16), 2706-2711.

3. Margerum, D.W.; Huff Hartz, K.E., Role of halogen (I) Cation Transfer Mechnisms in water chlorination in the presence of bromide ion. J. Environ. Monit., 2002, 4, 20-26.

4. Beckwith, R. C.; Margerum, D. W., (1997), Kinetics of hypobromous acid disproportionation. Inorg. Chem., 36, 3754-3760.

5. Chao Liu, Urs von Gunten, and Jean-Philippe Croué, (2012), Environ. Sci. Technol., 46, 11054-11061.





In view of the above observations of enhanced bromate formation in water distribution systems containing bromide disinfected by chlorination under alkaline conditions, there appeared a need to choose an alternative to chlorine in curtailing the bromate formation.





If any disinfectant is to replace free chlorine as the most commonly used disinfectant, several criteria must be met, as follows:

- 1. It must be easily generated and be in wide use
- 2. It must be a good biocide.
- 3. It must provide an easily measured residual.
- 4. It must not produce or reduce undesirable byproducts than does free chlorine, and
- 5. It must be cost effective.



## Chlorine dioxide

Based on a review of the literature chlorine dioxide was found to be the best alternative for the following:

- 1. It does not react with bromide to form hypobromites which could contribute to the formation of organo bromine compounds and bromate.
- 2. It is not a chlorinating agent and does not form halogenated organic compounds (i.e., THMs).
- 3. It is efficient over a wide pH range (5.0 to 9.5).
- 4. Very active against bacteria, viruses, algae, fungi and microorganisms.
- 5. Environmentally friendly.
- Eva Agus, Nikolay V., David L. Sedlak, (2009), Disinfection byproducts and their potential impacts on the quality of water produced by desalination systems: A Literature Review, Desalination 237, p. 214-237.
- Chao Liu, Urs von Gunten, and Jean-Philippe Croué, (2012), Environ. Sci. Technol., 46, 11054-11061.



Chlorine dioxide exists almost entirely as monomeric free radicals. Concentrated chlorine dioxide vapour is potentially explosive, and attempts to compress and store this gas, either alone or in combination with other gases, have been commercially unsuccessful. Because of this, chlorine dioxide, like ozone, must be manufactured at the point of use.



### Table 4-1. Commercial Chlorine Dioxide Generators

GENE RATOR TYPE	MAIN REACTIONS Reactants, byproducts, key reactions, and chemistry notes	SPECIAL ATTRIBUTES
ACID-CHLORITE:	4HCI + 5NaClO2 → 4ClO 2000 + ClO3*	Chemical feed pump interlocks required.
(Direct Acid System)	<ul> <li>Low pH</li> </ul>	Production limit ~ 25-30 lb.day.
	<ul> <li>CIOs<sup>-</sup> possible</li> </ul>	Maximum yield at ~80% efficiency.
	<ul> <li>Slow reaction rates</li> </ul>	
AQUEOUS CHLORINE-	Cl₂ + H₂O → [HOCI / HCI]	Excess Cl₂ or acid to neutralize NaOH.
CHLORITE:		Production rates limited to ~ 1000 lb/day.
(Cl <sub>2</sub> gas ejectors with chemical	[HOCI#ICI] + NaCIO₂ →	High conversion but yield only 80-92 %
pumps for liquids or booster pump for ejector water).	CIO 2000 + H/OCI" + Na OH + CIO3"	More corrosive effluent due to lowpH (~2.8-3.5)
hands on allower annul?	<ul> <li>Low pH</li> </ul>	Three chemical systems pump HCI,
	<ul> <li>CIOs<sup>-</sup> possible</li> </ul>	hypochlorite, chlorite, and dilution water to reaction chamber.
	<ul> <li>Relatively slow reaction rates</li> </ul>	reaction champer.
RECYCLED AQUEOUS CHLORINE OR "FRENCH	2HOCI+2NaClO₂→2ClO₂+Cl₂+ 2NaOH	Concentration of ~3 g/L required for maximum efficiency.
LOOP		Production rate limited to ~ 1000 lb/da y.
(Saturated Cl: solution via a recycling loop prior to mixing with chlorite solution .)	<ul> <li>Excess G<sub>2</sub> or HG needed due to NaOH formed.</li> </ul>	Yield of 92-98% with ~10% excess Cl <sub>2</sub> reported. Highly corrosive to pumps; draw-down calibration needed. Maturation tank required after mixing.
GASEOUS CHLORINE-	Cl₂ (g) + Na ClO ₂(w) → ClO ₂(w)	Production rates 5-120,000 lb/da y.
CHLORITE	<ul> <li>Neutral pH</li> </ul>	Ejector-based, with no pumps. Motive water is
(Gaseous Cla and 25% solution	<ul> <li>Rapid reaction</li> </ul>	dilution water. Near neutral pH effluent. No
of sodium chlorite ; pulled by ejector into the reaction column.)	<ul> <li>Potential scaling in reactor under vacuum due to hardness of feedstock.</li> </ul>	excess Cl <sub>2</sub> . Turndown rated at 5-10X with yield of 95-99%. Less than 2% excess Cl <sub>2</sub> . Highly calibrated flow meters with min. line pressure ~ 40 psig needed.
GASEOUS CHLORINE-	Cl₂ (g) + Na ClO ₂(g) → ClO ₂(g) + NaCl	$G_2$ gas diluted with $N_2$ or filtered air to produce
SOLIDS CHLORITE MATRIX	<ul> <li>Rapid reaction rate</li> </ul>	~8% gaseous CIO: stream. Infinite turndown is possible with >99% yield. Maximum rate to
(Humidified Cl, gas is pulled or pumped through a stable matrix containing solid sodium chlorite.)	<ul> <li>Newtechnology</li> </ul>	~1200 lb.klay per column; ganged to >10,000 lb.klay.
ELECTROCHEMICAL	NaClO <sub>2000</sub> → ClO <sub>2000</sub> + e <sup>-</sup>	Counter-current chilled water stream accepts
(Continuous generation of CIO) from 25% chlorite solution recycled through electrolyte cell)	<ul> <li>Newtechnology</li> </ul>	gaseous CIO <sub>2</sub> from production cell after it diffuses across the gas permeable membrane. Small one-pass system requires precise flowfor power requirements (Coulombs law).
ACID/PEROXIDE/CHLORIDE	2NaClO3 + H2O2 + H2SO4 → 2ClO2 +	Uses concentrated HxOx and HxSO 4.
	02 + NaSO4 + H20	Downscaled version; Foam binding; Low pH.

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## **OBJECTIVES**

- To evaluate the performance of ClO<sub>2</sub> generating system (Scotmas-UK represented by SENDAB, KSA) in RO product water of SWCC plant.
- To Study the purity and efficiency of ClO<sub>2</sub> product and the percentage yield.
- Optimization of the required Chlorine Dioxide dosage to disinfect the RO product water.
- To study the DBPs formation with the use of ClO<sub>2</sub> generating system..





### Pretreatment of RO plant

The existing pretreatment comprised rapid mix/coagulation using ferric chloride (40%), flocculation, sedimentation and dual granular media (sand and anthracite) filtration.

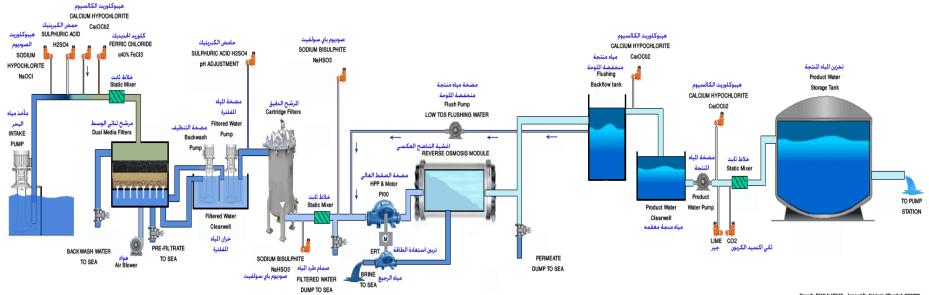
Coagulant was dosed at 2.0 to 3.5 ppm (mg/L) and pH was adjusted to 6.8 by adding sulphuric acid (98%).

Chlorine was dosed from the electro chlorinators of intake and the residual chlorine was kept in the range of 0.3 - 1.5 ppm. However, to compensate for deficiencies & shutdowns at intake chlorination, separate chlorination lines from calcium hypochlorite dosing system of RO plant have been provided. These dosing lines are located in the dosing pit upstream of dual media filters



المؤسسة العامية لتحلية المياه المالحية SALINE WATER CONVERSION CORPORATION

### عملية قلية مياه البحر بالتناضح العكسى SEA WATER REVERSE OSMOSIS PROCESS



Drawn By: ESAM ALAITHAN Approved By: Abdulaziz AlPugaibah 19/03/2013

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SCOTMAS Bravo MX chlorine dioxide generating system was installed on the agreed location. Both reagents [sodium chlorite (31%) and hydrochloric acid (32%)] are reacted within a submerged is chamber that installed within a bypass line of the water to be treated.



5NaClO<sub>2</sub> + 4HCl

 $4ClO_2 + 5NaCl + 2H_2O$ 





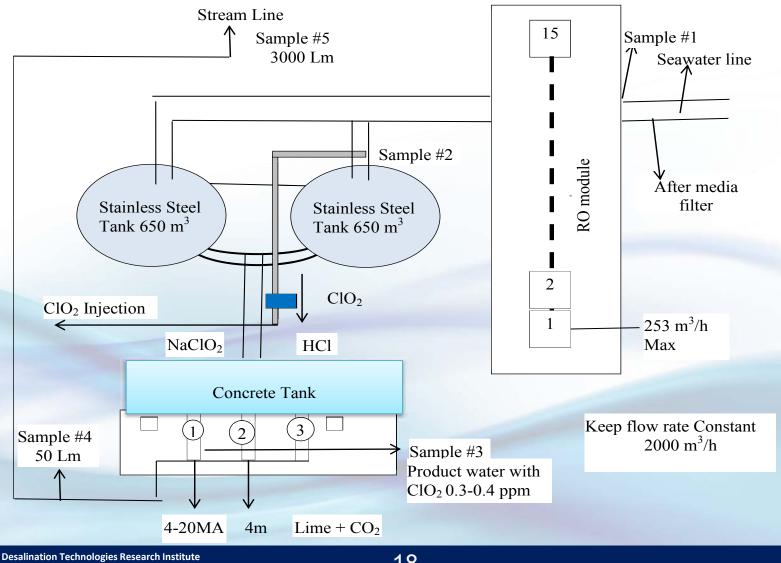
Dosing of  $ClO_2$  with the flow of water was controlled by online analyzer and directly recorded on the screen by the operator. The sensors used are ion-specific amperometric 2-electrode systems, protected by a membrane, for accurate measurement of both chlorine dioxide and chlorite, and minimum detection limit is 0.05ppm.



Agreed sample points are five as given below:

- Sample #1 : Intake seawater.
  Sample #2 : After RO (Before ClO<sub>2</sub> dosing)
  Sample # 3: 10 m after dosing of ClO<sub>2</sub> (before CO<sub>2</sub> & lime dosing)
  Sample # 4 : 50 m after RO (after CO<sub>2</sub> & lime dosing)
- Sample # 5: 3000 3500 m after dosing of  $ClO_2$ .







Samples were collected for analysis to check the agreed parameters as follows:

Residual ClO<sub>2</sub>, chlorate, chlorite, residual chlorine, bromate, organics, THMs, and biological analysis.

Additional parameters; residual sodium bisulfite (SBS), residual free chlorine and pH at agreed locations.





Trihalomethanes (THMs) Analysis by GC/MS

All samples were analyzed According to the Standard Methods based on the described procedures in APHA Standard Methods (APHA, 2003).

Bromate and Chlorate Analysis by Ion Chromatography Bromate and chlorate in water was measured by ion chromatography using suppress conductivity detection according to U.S. EPA Method 300.1 B.

\* Chlorine dioxide and Chlorite Analysis

Residual Chlorine dioxide and Chlorite levels were measured by means of an online amperometric probe.



## **ANALYTICAL TECHNIQUES**

Chlorine dioxide and chlorite concentrations were also measured by manual grab sampling and analysis as part of normal on site test procedures using DPD or a Palintest ChlordioX Plus portable monitoring instrument calibrated for chlorine dioxide.







## \*Biological Analysis

Water samples were withdrawn from the sampling points employing aseptic techniques and analyzed using "APHA Method 9215: Standard Methods for the Examination of Water Wastewater"





Table shows Results from sampling point # representative of permeate. Bromate, chlorite and chlorate were found to he negligible or nil for the whole evaluation period. Though some amount of THMs, predominantly bromoform (~40 ppb) was detected, the total THMs values (<1) were well below the regulated values (WHO=1).

5. No.	Sample Date	Sample Point	Chlorine Dioxide Residual Palintest	Chlorite (ClO <sub>2</sub> <sup>-</sup> ) Palintest		Organics	Bromoform	THMs (total)	pH
			1	2	3	4	5	6	7
	Uo	oM	mg/1	mg/1	μg/1	μg/1	μg/1		
1	21/4/16	2	0.01	0.02	NA"	NA	NA	NA	NA
2	23/4/16	2	0.01	0.02	NA	NA	NA	NA	NA
3	24/4/16	2	0.01	0.01	NA	NA	NA	NA	NA
4	25/4/16	2	0.01	0.01	<2	ND <sup>+</sup>	36	0.36	NA
5	26/4/16	2	0.01	0.01	<2	ND	34	0.34	NA
6	27/4/16	2	0.01	0.01	<2	ND	37	0.37	NA
7	28/4/16	2	0.01	0.01	<2	ND	34	0.34	5.45
8	30/4/16	2	0.01	0.01	NA	NA	NA	NA	NA
9	1/5/16	2	0.01	0.01	<2	ND	38	0.38	5.65
10	2/5/16	2	0.01	0.01	<2	ND	37	0.37	5.1
11	3/5/16	2	0.01	0.01	<_	ND	37	0.37	5.41
12	4/5/16	2	0.01	0.03	<2	ND	35	0.35	5.3
13	5/5/16	2	0.01	0.01	<2	ND	33	0.33	5.2
14	7/5/16	2	0.03	0.01	NA	NA	NA	NA	NA
15	8/5/16	2	0.01	0.01	<2	ND	39	0.39	5.33
16	9/5/16	2	0.01	0.01	<2	ND	40	0.4	4.9
17	10/5/16	2	0.01	0.01	<2	ND	29	0.29	5.3
18	11/5/16	2	0.01	0.01	<2	ND	27	0.27	5.29
19	12/5/16	2	0.01	0.01	<2	ND	30	0.3	5.3
20	14/5/16	2	0.01	0.01	NA	NA	NA	NA	NA
21	15/5/16	2	0.01	0.01	<2	ND	30	0.3	5.34
22	17/5/16	2	0.01	0.01	<2	ND	31	0.31	5.41
23	22/5/16	2	0.01	0.01	<2	ND	33	0.33	5.34
24	25/5/16	2	0.02	0.01	<2	ND	32	0.32	NA
25	1.001			0.01	374	27.4			
25	1/6/16	2	0.01	0.01	NA	NA ND	NA 32	NA 0.32	NA 5.28
26	7/6/16	2	0.01	0.01	<2 <2	ND	32	0.32	5.28
27	8/6/16 16/6/16	2	0.01	0.01	<2	ND	27	0.33	5.28 NA
28 29	20/6/16	2	0.01	NA	<2	ND	30	0.2/	5.65
		2	0.01	NA	<2	ND	34	0.34	5.39
30	22/6/16 27/6/16	2	0.01	NA	<2	ND	34	0.34	5.39
31 32	29/6/16		0.01	NA		ND	29	0.33	5.20
32	29/0/10	2	0.01	INA	<2	ND	29	0.29	5.5
33	4/7/16	2	0.01	NA	<2	ND	27	0.27	5.33
34	6/7/16	2	0.01	NA	NA	NA	NA	NA	5.33
35	11/7/16	2	0.01	NA	<2	ND	29	0.29	5.35
36	13/7/16	2	0.01	NA	<2	ND	27	0.27	5.46
37	18/7/16	2	0.01	NA	NA	NA	NA	NA	5.29
38	20/7/16	2	0.01	NA	NA	NA	NA	NA	5.21





### Tuning of the ClO<sub>2</sub> generating system

- Generally, to produce ClO<sub>2</sub> using acidchlorite generation technologies a 1:1 volumetric ratio between sodium chlorite solution and acid solution precursors will be utilized
- Through intensive research and development, it was found that this excess of acid generally dosed is unnecessary and tuning can be carried out during commissioning and the initial operation of these systems to optimize ClO<sub>2</sub> generation.
- Tuning the generator, hydrochloric acid was dosed at approximately 30 -38% less compared to the sodium chlorite dose rate with the conversion efficiency within the range of 84% to 96%,

	Dose	Rate (Lhr <sup>-1</sup> )	
Date	31 % Sodium Chlorite	32% Hydrochloric acid	Volumetric Ratio
25/4/16	3.24	2.25	0.69
27/4/16	3	2.13	0.71
05/5/16	2.77	1.93	0.70
08/5/16	2.63	1.83	0.70
09/5/16	2.38	1.65	0.69
21/5/16	2	1.34	0.67
22/5/16	1.9	1.27	0.67
23/5/16	1.8	1.2	0.67

			Equivalent Concentrations		
	Date	31 % Sodium Chlorite (Lhr <sup>-1</sup> )	Theoretical	Actual	Conversion Efficiency (%)
C	01/5/16	3	0.44	0.32	72.13
C	02/5/16	2.92	0.43	0.39	92.33
C	03/5/16	2.92	0.43	0.39	90.94
C	04/5/16	2.92	0.43	0.38	89.98
C	05/5/16	2.77	0.40	0.38	94.55
C	07/5/16	2.77	0.40	0.31	75.59
C	08/5/16	2.63	0.38	0.29	76.14
C	09/5/16	2.38	0.35	0.33	96.37
1	10/5/16	2.38	0.35	0.30	85.27
1	1/5/16	2.38	0.35	0.29	84.49
1	12/5/16	2.38	0.35	0.27	78.17
1	14/5/16	2.38	0.35	0.23	66.69

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## **Optimization of ClO<sub>2</sub> Dose Rate**

The dosing control for chlorine dioxide was monitored at sample point # 3. A dosage of  $ClO_2$  with a residual in the range of 0.3 to 0.4ppm was controlled as per the requirement for initial disinfection.

A dose rate in the range of 0.18 - 0.20 ppm of residual  $ClO_2$  was found to be optimum dose rate and the test was continued with this rate and monitoring the microbiological analysis the performance was evaluated.

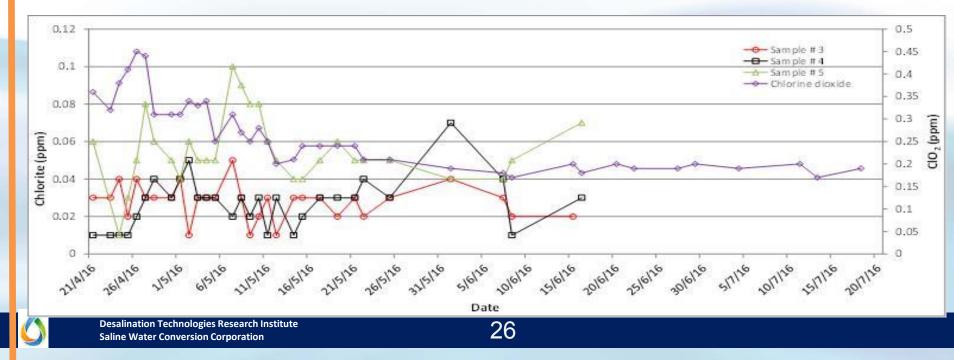
Sample	Sample	Chlorine Dioxide	Chlorine Dioxide	Chlorite	Chlorite	Chlorate	Bromate		Bromo	THMs	Biological	
Date	Point	Residual Palintest	Residual Online	(ClO <sub>2</sub> <sup>-</sup> ) Palintest	(ClO <sub>2</sub> -) Online	(ClO <sub>3</sub> -)	(BrO <sub>3</sub> <sup>-</sup> )	Organics	form	(total)	Analysis	рН
		1	2	3	4	5	6	7	8	9	10	11
	UoM	mg/l	mg/l	mg/l	mg/l	mg/l	μg/l	μg/l	μg/l			
21/4/16	3	0.36	NA	0.03	0.03	NA	<2	ND	NA	NA	Negative	NA
23/4/16	3	0.32	0.34	0.03	0.03	NA	<2	ND	NA	NA	Negative	NA
24/4/16	3	0.38	0.33	0.04	0.03	NA	<2	ND	NA	NA	Negative	NA
25/4/16	3	0.41	0.34	0.02	0.02	NA	<2	ND	38	0.38	Negative	NA
26/4/16	3	0.45	0.33	0.04	0.03	NA	<2	ND	35	0.35	Negative	NA
27/4/16	3	0.44	0.39	0.03	0.03	NA	<2	ND	37	0.37	Negative	NA
28/4/16	3	0.31	0.29	0.03	0.03	NA	<2	ND	35	0.35	Negative	8.55
30/4/16	3	0.31	0.32	0.03	0.03	NA	<2	ND	NA	NA	Negative	NA
										-		
1/5/16	3	0.31	0.3	0.04	0.03	NA	<2	ND	40	0.4	Negative	7.48
2/5/16	3	0.34	0.32	0.01	0.03	NA	<2	ND	38	0.38	Negative	8
3/5/16	3	0.33	0.31	0.03	0.03	0.07	<2	ND	38	0.38	Negative	8
4/5/16	3	0.34	0.33	0.03	0.03	0.05	<2	ND	35	0.35	Negative	7.9
5/5/16	3	0.25	0.3	0.03	0.04	0.07	<2	ND	33	0.33	Negative	NA
7/5/16	3	0.31	0.32	0.05	0.04	NA	<2	ND	NA	NA	Negative	NA
8/5/16	3	0.27	0.31	0.03	0.07	0.05	<2	ND	39	0.39	Negative	7.8
9/5/16	3	0.25	0.3	0.01	0.07	0.08	<2	ND	40	0.4	Negative	NA
10/5/16	3	0.28	0.29	0.02	0.04	0.05	<2	ND	32	0.32	Negative	8.5
11/5/16	3	0.25	0.26	0.03	0.05	0.06	<2	ND	27	0.27	Negative	7.55
12/5/16	3	0.2	0.23	0.01	0.05	0.03	<2	ND	32	0.32	Negative	7.22
14/5/16	3	0.21	0.22	0.03	0.04	0.02	<2	ND	NA	NA	Negative	NA
15/5/16	3	0.24	0.22	0.03	0.04	NA	<2	ND	32	0.32	Negative	7.2
16/5/16	3	NA	NA	NA	NA	NA	NA	ND	NA	NA	Negative	NA
17/5/16	3	0.24	0.22	0.03	0.04	0.01	<2	ND	33	0.33	Negative	NA
19/5/16	3	0.24	0.2	0.02	0.05	NA	<2	ND	NA	NA	Negative	NA
21/5/16	3	0.24	0.2	0.03	0.05	NA	<2	ND	NA	NA	Negative	NA
22/5/16	3	0.21	0.18	0.02	0.05	0.01	<2	ND	35	0.35	Negative	7.82
25/5/16	3	0.21	0.21	0.03	0.05	0.01	<2	ND	34	0.34	Negative	NA
1/6/10	2	0.19	0.2	0.04	0.05	0.01	<2	ND	34	0.34	Negative	NIA
1/6/16 7/6/16	3		0.2	0.04	0.05	0.01	<2	ND ND	34	0.34	Negative	<u>NA</u> 7.5
8/6/16		0.18	0.16	0.03	0.07	0.01	<2	ND ND	27	0.33	Negative	
8/6/16	3	0.17	0.17	0.02	0.07	0.05	<2	ND ND	30	0.27	Negative Negative	NA 8.53
20/6/16	3	0.2	0.21	0.02 NA	0.06	0.02	<2	ND	34	0.30	Negative	<u>8.55</u> 5.53
20/6/16	3	0.18	0.19	NA NA	0.07	0.01	<2	ND ND	34	0.34	Negative	5.36
27/6/16	3	0.2	0.19	NA	0.07	0.01	<2	ND	33	0.33	Negative	5.25
29/6/16	3	0.19	0.2	NA	0.08	0.01	<2	ND	27	0.31	Negative	5.25
29/0/10	3	0.19	0.21	INA	0.08	0.01	~2	IND	- 21	0.27	riegative	5.47
4/7/16	3	0.2	0.15	NA	0.08	0.01	<2	ND	25	0.25	Negative	5.31
11/7/16	3	0.19	0.13	NA	0.08	0.01	<2	ND	23	0.23	Negative	5.3
13/7/16	3	0.19	0.15	NA	0.08	NA	<2	ND	NA	NA	Negative	5.34
18/7/16	3	0.2	0.13	NA	0.08	NA	<2	ND	NA	NA	Negative	5.31
20/7/16	3	0.17	0.19	NA	0.07	NA	<2	ND	NA	NA	Negative	5.20
20/7/10	5	0.19	0.2	11/1	0.09	11/4	~2	ND	INA	INA	Regative	5.20





## Disinfection By-products (Chlorite)

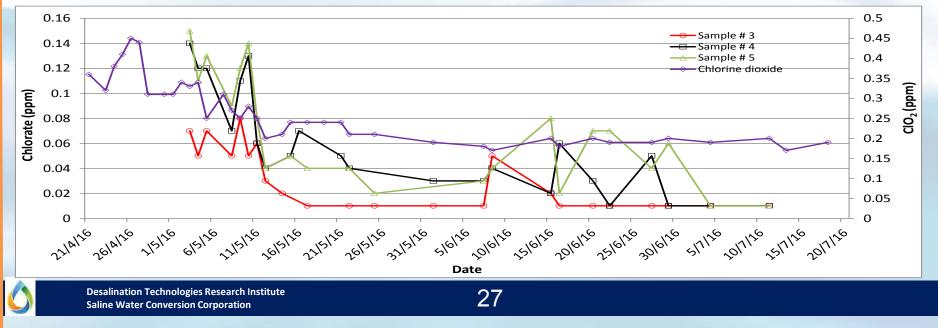
The concentration of the chlorite for all the sampling points was found to be well below the regulation value (0.7 ppm, WHO), moreover, the values were very low (0.01 - 0.04 ppm) except for the sampling point # 5 the values were a little higher (0.04 - 0.1 ppm), which is known to occur due to disproportionation of chlorine dioxide upon increasing pH. However, it was interesting to note that there was no significant effect on the formation of chlorite with adjustment of the ClO<sub>2</sub> dose.





## Chlorate

The concentration of the chlorate for all the sampling points # 3, 4 and 5 during the optimization and for the duration of test with the optimized dose rate was found to be well below the regulation value (0.7 ppm, WHO). Initially at a higher dose rate of  $ClO_2$ , Chlorate concentrations were found to be a little higher (0.05 – 0.14 ppm). But as the dose rate of  $ClO_2$  were reduced and at the optimum dose rate of 0.19 ppm  $ClO_2$ , the chlorate values for sampling point # 4 and # 5 were reduced and found to be in the range of 0.02 - 0.06 ppm whereas for sampling point # 3 the values were almost consistent at 0.01ppm.





### Bromate

Bromate concentration determined were found to be <2 ppb for all the sampling point indicating negligible o no bromate formation with ClO<sub>2</sub> treatmen during the whole tria period. Bromate concentrations for eacl sample poin throughout the trial

	Sample Date	Sample Point	Chlorine Dioxide Residual Palintest	Chlorine Dioxide Residual Online	Chlorite (ClO <sub>2</sub> <sup>-</sup> ) Palintest	Chlorite (ClO <sub>2</sub> <sup>-</sup> ) Online	Chlorate (ClO <sub>3</sub> -)	Bromate (BrO <sub>3</sub> -)	Organics	Bromo form	THMs (total)	Biological Analysis	рН
			1	2	3	4	5	6	7	8	9	10	11
		UoM	mg/l	mg/l	mg/l	mg/l	mg/l	μg/l	μg/l	μg/l			
	21/4/16	3	0.36	NA	0.03	0.03	NA	<2	ND	NA	NA	Negative	NA
IS	23/4/16	3	0.32	0.34	0.03	0.03	NA	<2	ND	NA	NA	Negative	NA
	24/4/16	3	0.38	0.33	0.04	0.03	NA	<2	ND	NA	NA	Negative	NA
	25/4/16	3	0.41	0.34	0.02	0.02	NA	<2	ND	38	0.38	Negative	NA
d	26/4/16	3	0.45	0.33	0.04	0.03	NA	<2	ND	35	0.35	Negative	NA
Ч	27/4/16	3	0.44	0.39	0.03	0.03	NA	<2	ND	37	0.37	Negative	NA
	28/4/16	3	0.31	0.29	0.03	0.03	NA	<2	ND	35	0.35	Negative	8.55
e	30/4/16	3	0.31	0.32	0.03	0.03	NA	<2	ND	NA	NA	Negative	NA
	1/5/16	3	0.31	0.3	0.04	0.03	NA	<2	ND	40	0.4	Negative	7.48
-c	2/5/16	3	0.34	0.32	0.01	0.03	NA	<2	ND	38	0.38	Negative	8
IS I	3/5/16	3	0.33	0.31	0.03	0.03	0.07	<2	ND	38	0.38	Negative	8
	4/5/16	3	0.34	0.33	0.03	0.03	0.05	<2	ND	35	0.35	Negative	7.9
	5/5/16	3	0.25	0.3	0.03	0.04	0.07	<2	ND	33	0.33	Negative	NA
)r	7/5/16	3	0.31	0.32	0.05	0.04	NA	<2	ND	NA	NA	Negative	NA
	8/5/16	3	0.27	0.31	0.03	0.07	0.05	<2	ND	39	0.39	Negative	7.8
	9/5/16	3	0.25	0.3	0.01	0.07	0.08	<2	ND	40	0.4	Negative	NA
n	10/5/16	3	0.28	0.29	0.02	0.04	0.05	<2	ND	32	0.32	Negative	8.5
	11/5/16	3	0.25	0.26	0.03	0.05	0.06	<2	ND	27	0.27	Negative	7.55
	12/5/16	3	0.2	0.23	0.01	0.05	0.03	<2	ND	32	0.32	Negative	7.22
nt	14/5/16	3	0.21	0.22	0.03	0.04	0.02	<2	ND	NA	NA	Negative	NA
IL	15/5/16	3	0.24	0.22	0.03	0.04	NA	<2	ND	32	0.32	Negative	7.2
	16/5/16	3	NA	NA	NA	NA	NA	NA	ND	NA	NA	Negative	NA
~	17/5/16	3	0.24	0.22	0.03	0.04	0.01	<2	ND	33	0.33	Negative	NA
al	19/5/16	3	0.24	0.2	0.02	0.05	NA	<2	ND	NA	NA	Negative	NA
	21/5/16	3	0.24	0.2	0.03	0.05	NA	<2	ND	NA	NA	Negative	NA
	22/5/16	3	0.21	0.18	0.02	0.05	0.01	<2	ND	35	0.35	Negative	7.82
<b>e</b>	25/5/16	3	0.21	0.21	0.03	0.05	0.01	<2	ND	34	0.34	Negative	NA
							-						
	1/6/16	3	0.19	0.2	0.04	0.05	0.01	<2	ND	34	0.34	Negative	NA
h	7/6/16	3	0.18	0.16	0.03	0.07	0.01	<2	ND	33	0.33	Negative	7.5
	8/6/16	3	0.17	0.17	0.02	0.07	0.05	<2	ND	27	0.27	Negative	NA
	16/6/16	3	0.2	0.21	0.02	0.06	0.02	<2	ND	30	0.30	Negative	8.53
+	20/6/16	3	0.18	0.19	NA	0.07	0.01	<2	ND	34	0.34	Negative	5.53
It	22/6/16	3	0.2	0.19	NA	0.07	0.01	<2	ND	33	0.33	Negative	5.36
	27/6/16	3	0.19	0.2	NA	0.08	0.01	<2	ND	31	0.31	Negative	5.25
	29/6/16	3	0.19	0.21	NA	0.08	0.01	<2	ND	27	0.27	Negative	5.27
_	4/7/16	2	0.2	0.15	NIA	0.00	0.01	-2	ND	25	0.25	Mantin	5.21
	4/7/16	3	0.2	0.15	NA	0.08	0.01	<2	ND	25	0.25	Negative	5.31
	11/7/16	3	0.19	0.2	NA	0.08	0.01	<2	ND	28	0.28	Negative	5.3
-	13/7/16	3	0.2	0.15	NA	0.08	NA	<2	ND	NA	NA	Negative	5.34
	18/7/16	3	0.17	0.19	NA	0.07	NA	<2	ND	NA	NA	Negative	5.31
	20/7/16	3	0.19	0.2	NA	0.09	NA	<2	ND	NA	NA	Negative	5.20

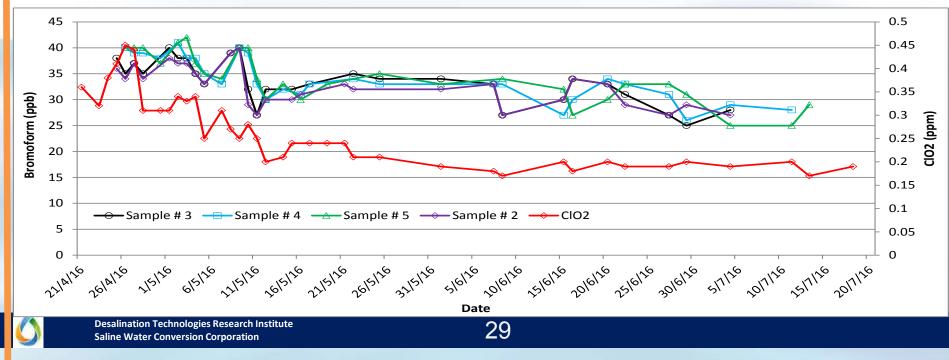


28



## Trihalomethanes (THMs)

Negligible or very small amount of THMs were detected, bromoform (~40 ppb) being the predominant. It should be noted here that the THMs values are the carryover from the chlorination of sea water and intermittent chlorine dose before the membranes and that the values were consistent as found in the sampling point # 2. This indicated that  $ClO_2$  had no effect on the THMs formation. TTHMs were also found to be in good control for all the sampling points (<1) and well below the WHO regulated values of 1.





➤A dose rate in the range of 0.18 – 0.20 ppm as residual ClO<sub>2</sub> was found to be optimum dose rate on the performance of disinfection observed from the microbiological analysis.

Biological analyses showed total Coliforms & E.Coli in all the sampling points was negative indicating ClO<sub>2</sub> to be very efficient in killing the bacteria and therefore a suitable alternative to chlorination.

Residual ClO<sub>2</sub> at the sampling point # 4 and # 5 were found to be in the range of 0.1–0.16 ppm.





Disinfection byproducts chlorite and chlorate formed at the ClO<sub>2</sub> control point (sampling point # 3) were found to be in the range of 0.01 – 0.04 ppm which are well below the WHO regulation values of 0.7 ppm.

The combined ClO<sub>2</sub>, chlorite and chlorate concentrations did not exceed the maximum limit of 1mgL<sup>-1</sup> currently recommended by USEPA.



- Show the second termined were found to be <2 ppb for all the sampling points indicating negligible or no bromate formation with ClO<sub>2</sub> treatment.
- Negligible or very small amounts of THMs were detected throughout the trial even through adjusting ClO<sub>2</sub> dose. Bromoform (~40 ppb) being the predominant THM detected, was found to be carryover from the chlorination of sea-water and intermittent chlorine dose due to its presence before the RO membranes with no significant change after ClO<sub>2</sub> injection. TTHMs were found to be well below the WHO regulated values of  $\leq 1$  throughout the whole of the trial.

The consistent values of disinfection by-products (TTHMS) recorded, resulting from the chlorination of sea-water before and after treatment with  $ClO_2$  has proven that these results could be avoided by use of the SENDAB (SCOTMAS-UK)  $ClO_2$  generating system.



The authors would like to thank Mr. Ghazzay Auwayidh Alhajji Almutairi, Lab. Supdt., Hosam Mustafa Abdulmuhsin Alsanea, RO Operation Division Chief and Mr. Abdulaziz R A AlRugaibah, Technical Support Department Manager, Jubail plant, for their cooperation and support.





Desalination Technologies Research Institute Saline Water Conversion Corporation



### **ClO**<sub>2</sub> Generator Standards

## EN 12671:2009



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Date 11<sup>th</sup> November 2011

Dear Mr Callachan

### APPROVAL GIVEN UNDER REGULATION 31(4)(a) OF THE WATER SUPPLY (WATER QUALITY) REGULATIONS 2000 No. 3184 & THE WATER SUPPLY (WATER QUALITY) REGULATIONS 2001 (WALES) No.3911

We are pleased to enclose the "Product Approval Confirmation" for your product for use in England and Wales. The Drinking Water Inspectorate advises both the Secretary of State for Environment, Food and Rural Affairs (DEFRA), and the National Assembly of Wales (collectively referred to as "the Authorities") on the approval of products used in the provision of public water supplies.

Desalination Technologies Research Institute Saline Water Conversion Corporation