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Effects of combined calcium hypochlorite and chlorine dioxide on drinking water quality in Qatar and disinfection by-products formation

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ABSTRACT

Chlorite, chlorate, bromate and trihalo methanes (THMs) are included in WHO guidelines for drinking water quality. This study examined dosing different chlorine concentrations as calcium hypochlorite ($Ca(ClO)_2$) to water containing chlorine dioxide to evaluate the control of water quality in storage and the distribution system in Qatar with emphasis on chlorite, chlorate, bromate, pH and other parameters. Seven water samples were collected from the Ras Laffan-Q Power desalination plant outlet in amber bottles having a chlorine dioxide concentration of 0.3 mg/L in 1 liter. The bottles were spiked with $Ca(ClO)_2$ in sequence to give concentration of 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 mg/L as free chlorine. The mixtures were stored for 7 days at 25°C in the dark then heated to 45°C for two days more, and analyzed daily for physical and chemical parameters. A total of 312 sub-samples were analyzed for chlorite, chlorate, bromate, bromide, chloride, nitrate, nitrite, sulfate, THMs, temperature, pH, electrical conductivity, and chlorine and chlorine dioxide residuals. Chlorite concentration reductions were observed from the first day forward as 59, 65, 68, 94, 100, and 100%, and 17.4, 22.1, 39.2, 63.9, 66.0, 68.9% (from 0.157 to 0.049 mg/L) respectively based on observed means for seven days the commensurate respective chlorate concentrations increases were 196, 344, 516, 602, 703, 787% (from 0.035 to 0.313 mg/L) based on observed mean values for seven days. These data were statistically analyzed by multivariate regression. There were no significant changes in THMs concentrations and the reductions in chlorite and increases in chlorate concentration are chlorine dosage dependent. No bromate formation was observed. Chlorine dioxide levels decrease as the free chlorine residual levels increased. This study demonstrates that hypochlorite/chlorine dioxide can be used as an operational tool to control the chlorite levels, and slow the disappearance of the chlorine dioxide over time during distribution, that is usually faster than chlorine disappearance. The original chlorine dioxide dosage will determine the ultimate chlorate concentration.

Keywords: Disinfection by-products (DBPs); Bromate; Chlorite; Chlorine dioxide

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1. Introduction

As per USEPA's general statement, combining disinfectants is done to overcome the disadvantages of the individual disinfectant [1]. Multiple disinfectants have been used with increasing frequency in recent years to meet the varied requirements for inactivation of microbials and reduction in DBPs. Chlorite, chlorate, bromate and trihalo methanes (THMs) are included in WHO guidelines for drinking water quality [2]. Chlorine dioxide (ClO_2) has been examined as a possible alternative for traditional chemical disinfection

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with chlorine. Since Qatar has decided to change over from chlorine to chlorine dioxide the output of the study will be significant in terms of maintaining a disinfectant residual in the distribution system, simultaneously with controlling the water quality.

Natural organic matter (NOM), a precursor of most disinfection by-products (DBPs), is known to react with chlorine to form THMs and haloactetic acids (HAAs) [2]. This is a minor issue for desalinated water due to the very low level of total organic carbon (TOC). But the opposite is true for inorganic disinfection by-products. For example the bromate formation is predictable if the chlorinated water contains bromide. The formation of organohalogens e.g., (THMs and HAAs) with ClO_2 is typically much lower when compared to the use of free chlorine (HOCl) [3,4]. This is primarily attributed to the difference in oxidation reaction mechanisms, where ClO_2 reacts via free radical electrophilic abstraction versus oxidative substitution and addition for HOCl [5]. Many factors are involved to protect the community from risks, including waterborne disease, workplace accidents and the release of disinfectant chemicals, consequently balancing these factors is still challenging for many utilities. The following factors are crucial for drinking water.

1.1. Water distribution

In storage and distribution, drinking water must be kept safe from microbial contamination. Frequently, slippery films of bacteria, known as biofilms, develop on the inside walls of pipes and storage containers. Among disinfection techniques, chlorination is unique in that a pre-determined chlorine concentration may be designed to remain in treated water as a measure of protection against harmful microbes encountered after leaving the treatment facility. Maintaining an active residual is difficult if chlorine dioxide alone is used. In the event of a significant intrusion of pathogens resulting, for example, from a broken water main, the level of the average “chlorine residual” will be insufficient to disinfect contaminated water. In such cases, while monitoring of chlorine levels the sudden drop in the chlorine residual provides the critical indication to water system operators that there is a source of contamination in the system [6].

1.2. Water chemistry

As they consider alternative disinfectants, drinking water utilities must account for several scientific facts. First, not all source water is of the same quality or chemistry, and second, not all disinfectants are equal. Taken together, these facts mean that certain disinfectants may be better suited to certain waters than alternative chemicals would be, in terms of reliably producing safe, treated drinking water. For example, gaseous chlorine is exceptionally effective against most bacteria and viruses and is very good at oxidizing many chemical contaminants that may be present in source water. The most common liquid form of chlorine, sodium hypochlorite, is just as effective as gaseous chlorine against most organisms but can be less effective against some others (such as giardia), depending on site specific water chemistry and pH, unless other changes are made in the water treatment process. Sodium hypochlorite requires proper storing and rapid especially in hot areas to reduce spontaneous degradation and conversion to chlorate and perchlorate. It also adds sodium to the water and increases total dissolved solids, which can be a problem in some waters. Likewise, in waters containing bromide, ozone leads to the formation of bromate, a regulated contaminant. Chloramines are widely used as a secondary disinfectant to provide a residual disinfectant to reduce regrowth in the distribution system, as required by law, but they are very weak disinfectants and not as effective as other forms of chlorine against pathogenic microorganisms, such as viruses, parasites, and bacterial spores. Ultraviolet light inactivates some organisms but at water treatment doses it does not treat many chemical contaminants that are effectively oxidized by chlorine. Membranes are good at removing many organisms and contaminants from water but are generally the highest cost alternative and provide no residual disinfection. They also reduce the volume of water that can be delivered by “rejecting” some of the water being treated; this can be a significant issue in areas of water scarcity. Another aspect of this decision concerns disinfection by products. All disinfectants create a complex family of by product compounds, some of which are of human health concern and are regulated by USEPA and in WHO Guidelines. For example, both gaseous chlorine and sodium hypochlorite react with organic material in water to form chlorinated organic compounds. The use of chlorine dioxide can lead to formation of chlorite, chlorate (regulated contaminants) and chloride (for which there is a secondary standard). Ozone forms a different family of by products, some of which are of regulatory concern. Sodium hypochlorite degrades under warm storage conditions into chlorite, chlorate, and perchlorate. While utilities take great care and can control such by products to a degree, they cannot eliminate them entirely [7].

Chlorine dioxide at treatment plants, acts as an oxidant but not a halogenating agent. After application, chlorite is the dominant species in drinking water through one electron transfer during oxidation/reduction.

$$ClO_{2(aq)} + 1e = ClO_2^- \ (E_o = 0.954V) \tag{1}$$

Chlorine dioxide for drinking water treatment can be generated by several on-site methods including the reaction of sodium chlorite with gaseous chlorine, hypochlorous acid, or hydrochloric acid through the following reactions (Eq. (2a)–(2c)) (USEPA 815-R-99-014 1999) [8].

$$2NaClO_2 + Cl_2\,(g) \rightarrow = 2ClO_2\,(g) + 2NaCl \tag{2a}$$

$$2NaClO_2 + HOCl \rightarrow 2ClO_2\,(g) + NaCl + NaOH \tag{2b}$$

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2\,(g) + 5NaCl + 2H_2O \tag{2c}$$

(used in Qatar)

Chlorine dioxide produces chlorite and chlorate, in the distribution system; however, chlorine as calcium hypochlorite can produce bromate and chlorate in desalinated water. We are obviously aiming that, combining calcium hypochlorite and chlorine dioxide can overcome the disadvantages of both compare to when used individually.

The oxidation of aqueous chlorite (the major by product of chlorine dioxide) by chlorine or hypochlorous acid gives chlorine dioxide or chlorate. Chlorine (in acid solution) is present as dissolved molecular gas. The stoichiometries of the two reactions are [9]:

$$Cl_2\,(g) + 2ClO_2^- = 2ClO_2 + 2Cl^- \quad (3)$$

and

$$Cl_2(g) + 2ClO_2^- + H_2O = ClO_3^- + 2Cl^- + 2H^+ \quad (4)$$

In solution near neutral pH, where chlorine is present largely as hypochlorous acid, the stoichiometries are:

$$HOCl + 2ClO_2^- = 2ClO_2 + Cl^- + OH^- \quad (5)$$

and

$$HOCl + 2ClO_2^- + OH^- = 2ClO_3^- + Cl^- + H_2O \quad (6)$$

In alkaline solution, chlorine is present as hypochlorite ion, the reaction is very slow and the only product formed is chlorate ion:

$$OCl^- + ClO_2^- = ClO_3^- + Cl^- \quad (7)$$

1.3. Objectives of this study

The aim of this study is to evaluate the use of mixed chlorine/chlorine dioxide oxidants and their effect in the quality of distributed drinking water from Qatar desalination plants compared to the use of either chlorine or chlorine dioxide alone. In particular, this is an issue when storing drinking water post treatment as would occur with the mega reservoirs project in Qatar which has been design to increase the water storage capacity up to seven days. It is also intended to evaluate disinfection by-products (DBPs) formation, including bromate, chlorite, chlorate, and THMs.

2. Materials and methods

2.1. Site study

The area under study is located in Doha, Qatar. The produced water was taken from the outlet of the desalination plant - Ras Laffan-Q Power, plant that uses the multi stage flash (MSF) desalination.

2.2. Sample preparation and collection

All glassware was washed and cleaned in a glass washer, and then transferred to a drier at 110°C. Two control samples were examined in this study in order to monitor the contribution from chlorine dioxide (S1) and calcium hypochlorite (S8) while mixing.

Bulk samples were collected from the desalination plant as per description in Tables 1 and 2.

Table 1
Bulk source water (after treatment) sample

NO	Water samples
S1	Water source (treated with chlorine dioxide 0.3 mg/L)
S2	Water source spiked with 0.2 mg/L chlorine
S3	Water source spiked with 0.4 mg/L chlorine
S4	Water source spiked with 0.6 mg/L chlorine
S5	Water source spiked with 0.8 mg/L chlorine
S6	Water source spiked with 1. 0 mg/L chlorine
S7	Water source spiked with 1.2 mg/L chlorine
S8	Q. Power - Desalinated water spiked with 1.0 mg free chlorine

Table 2
Source raw water analysis at site

No	Water quality parameter	Results
1	pH @ 25°C	7.81
2	Electrical conductivity 25°C	169
3	Temperature	36°C
4	ClO_2	0.30 mg/l
5	Chlorite	180 µg/l
6	TOC	<0.5
7	Turbidity	<0.5

The seven water bulk samples were collected from Q power as actual water quality samples used to feed the distribution system in Qatar. Seven 1 L water samples were collected from the Ras Laffan-Q Power desalination plant outlet in amber bottles having a chlorine dioxide concentration of 0.3 mg/L. The calcium hypochlorite solution was prepared by dissolving 0.220 g (70%) in 1000 mL deionized water to prepare 220 mg/L. The bottles (1000 mL) were spiked with $Ca(ClO)_2$ (1.3, 2.6, 3.9 5.2, 6.5 and 7.8 mL) before sample collection in sequence to give concentrations of 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 mg/L as free chlorine (HOCl). The mixtures were rapidly cooled to 4°C and transferred to the laboratory and stored for 7 d at 25°C in the dark are then heated to 45°C for two days more. The mixtures were analyzed daily for physical and chemical parameters. A total of 312 sub-samples (39 samples/d) were analyzed for chlorite, chlorate, bromate, bromide, chloride, nitrate, nitrite, sulfate, THMs, temperature, pH, electrical conductivity, chlorine and chlorine dioxide residuals. Water quality parameters (temperature, pH, electrical conductivity, chlorine dioxide and residual chlorine) were measured during the process of sampling using Orion pH [10], and conductivity meter Model 1230 [11], chlorine and chlorine dioxide were measured by Chlordiox plus (US- EPA approved) [12], which is based on electrochemical determination (amperometric). The THMs, water samples were collected in a headspace-free 40 mL glass bottle with a screw cap of Teflon (PTFE) faced silicon septum and analyzed directly by Agilent GC-MS according EPA Method 524.2: Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry [13]. Inorganic disinfection by products and inorganic ions water samples were collected in 100 mL high density polyethylene beakers and sparged with nitrogen for 5 min and then measured by Metrohm Ion Chromatography Model 885 Professional, with chemical suppressor. They included fluoride, chlorite, bromate, chloride, nitrite, chlorate, bromide, nitrate and sulfate according to US EPA 300.1 A and B [14] per the following instrument configurations

Column: 6.1006.630 Metrosep A Supp 7 – 250
Eluent: 3.6 mmol/L sodium carbonate
Suppressor: sequential suppression: MSM (50 mmol/L H_2SO_4), MCS
Flow: 0.8 mL/min temp.: 45°C
Injection volume: 250 µL

3. Results and discussion

Table 3 summarizes the rapid changes in water quality after dosing different amounts of $Ca(ClO)_2$. The results also show the direct effect of disinfectant dosing in chlorite and chlorate formation within 24 h and the level of chlorine and chlorine dioxide residuals.

3.1. Physical and chemical parameters

Temperature and pH are critical factors for water quality due to their impacts on many reactions, including disinfectant decay and disinfection by-product formation. Chlorine dioxide will rapidly vaporize (purge) from the water due to its low boiling point (11°C) and low solubility. The mixtures were kept in a dark area and in brown bottles to protect chlorine dioxide and chlorite from photo oxidization by sunlight, as well as to maximize the contact time between calcium hypochlorite and chlorine dioxide in order to demonstrate a clearly worst case scenario for the mixture in ideal conditions. Therefore, during our study, the water temperature has been controlled @ 25°C ± 2.

Monitoring pH tracked the trend of pH in different dossing of calcium hypochlorite, as well as to assess the equilibrium of hypochlorous acid and hypochlorite ion in the final water quality [15].

$$HClO \leftrightarrow ClO^- + H^+ \tag{8}$$

No significant change was observed in pH values between the mixtures; pH values ranged between 7.6 and 7.9 (average 7.8). The chlorite concentration reduction was obviously detected from first day of the mixture while calcium hypochlorite dosing increased from 0.2–1.2 mg/l. However, chlorine dioxide residual decay was recorded by the control water sample (S1), (Table 3 and Fig. 1).

To a significant degree, chlorine dioxide is dissolved in water as a gas, so it will readily purge out to the air. In Qatar desalinated water has very low organic carbon content so there is little for chlorine dioxide to react with, so it is quite stable under those conditions. Chlorine dioxide will eventually form chlorite, while about 10% will form chlorate [16]. In both cases in Qatar due to high water temperatures more decay will be expected as well as unpleasant odder if the chlorine dioxide level is high. On the other hand, chlorine reacts with water to produce HCl and HClO in equilibrium with the chlorine. They are much more soluble in water; the temperature effect would be less, but still existing. Chlorine is also more chemically reactive and indiscriminate than chlorine dioxide so more would be consumed by reaction with whatever organic carbon is present. In addition to the odor of chlorine dioxide which is acrid and unpleasant, it

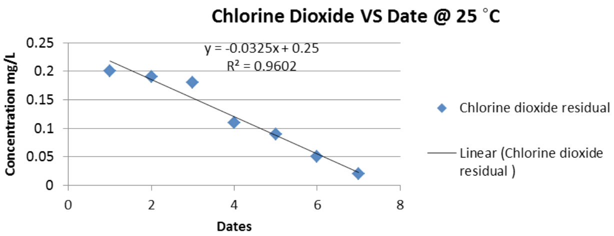

Fig. 1. Linear relationship of chlorine dioxide decay vs time @ 25°C.

Table 3
The measurement results for the first day (after 24 h of mixing)

	@25°C		Dose (mg/L)		Residual (mg/L)		Residual (µg/L)		Anion (µg/L)		
First day	pH	EC* µS/cm	ClO_2	HOCl*	ClO_2	HOCl	Chlorite	Chlorate	Bromate	Chloride	Bromide
S1	7.60	164.60	0.30	0.00	0.20	<0.02	288.30	34.20	ND	12605.00	64.20
S2	7.70	165.00	0.30	0.20	0.18	0.04	118.30	84.00	ND	15034.20	43.70
S3	7.90	164.40	0.30	0.40	0.13	0.37	102.20	108.00	ND	24343.10	58.20
S4	8.00	165.30	0.30	0.60	0.09	0.31	91.50	147.50	ND	27856.20	31.00
S5	8.10	176.00	0.30	0.80	0.07	0.67	16.60	190.00	ND	18126.70	30.00
S6	8.00	165.00	0.30	1.00	0.06	0.82	ND	195.40	ND	17921.10	32.50
S7	7.90	166.80	0.30	1.20	<0.02	0.92	ND	230.00	ND	17541.70	19.40
S8	8.40	45.20	0.0	1.00	<0.02	1.03	ND	64.00	ND	21704.50	51.30

*EC; Electrical conductivity ND; not detected (MDL in µg/l, for 1- bromate < 2.0, 2- chlorite < 1.0)
*HOCl; free chlorine

also has the ability to react with some chemicals in the gas phase to create other unpleasant odors [17].

Many in Qatar use rooftop storage tanks. There was a reduction of THM levels observed overtime for seven days; this is not directly linked with calcium hypochlorite. THMs were approximately 40 µg/l in the outlet water (chlorine dioxide only-control sample S1), then levels dropped to 10 µg/l (75%) in 4 d and dropped a gain to 3.2 after 7 d (Fig. 2). This indicates that storage of water for more than three days can cause a significant decrease on THMs levels and enhance water quality. This result agrees with low levels of TOC in desalinated water, because there is no sign of THMs formation after calcium hypochlorite dosed as per previous study statement if water contains high level of TOC [18]. In the level of 0.3 mg/L of chlorine dioxide at entry of the distribution system in Qatar will maintaining the disinfection byproduct level, chlorite and chlorate as well as reducing the evaporation rate of chlorine dioxide to air due to high temperature. But, as the same time the distribution system will be at risk because of low residual at remote area in term of biofilm formation.

Chlorite and chlorate are main disinfection by-products of chlorine dioxide; chlorite and chlorate levels are always are proportional to chlorine dioxide concentration in water. The result of mixing shows significant reduction of chlorite while free chlorine concentrations increased. Chlorite concentration reductions were observed from the first day forward (Fig. 3) as 59, 65, 68, 94, 100, and 100%, and 17.4, 22.1, 39.2, 63.9, 66.0, 68.9 % (from 0.157 to 0.049 mg/L) respectively based on observed means for seven days the commensurate respective chlorate concentrations increases were 196, 344, 516, 602, 703, 787 % (from 0.035 to 0.313 mg/l) based on observed mean values for seven days. The average chlorate contributed by chlorine dioxide was only 10% (average 35 µg/l) and by calcium hypochlorite in the mixture as a second source of chlorate was calculated (65 µg/l) from control samples S8. A significant negative correlation was recorded between free chlorine and chlorite; these agreed with previous studies and demonstrate the oxidation of chlorite by free chlorine.

The oxidation of chlorite by chlorine:

$$HOCl + ClO_2^- + OH^- \rightarrow ClO_3^- + Cl^- + H_2O \tag{9}$$

and

$$HOCl + 2ClO_2^- \rightarrow 2ClO_2 + Cl^- + OH^- \tag{10}$$

In the first reaction 1 mole of chlorite reacts with 1 mole of free chlorine to produce one mole of chlorate. This not desired because chlorate is also potentially harmful to human health from excessive exposures. In the second reaction 1 mole of free chlorine reacts with 2 moles of chlorite to produce 2 moles of chlorine dioxide. Under the conditions of this study the more likely end product was chlorate rather than chlorine dioxide, moreover a major reduction of chlorine dioxide (50%) started in the level of 0.6 mg/L of calcium hypochlorite. At low doses of calcium hypochlorite (0.2–0.4 mg/L) the reaction produces chlorine dioxide; the undesirable chlorite is converted to chlorine dioxide and provides more disinfection power in the mixture [19].

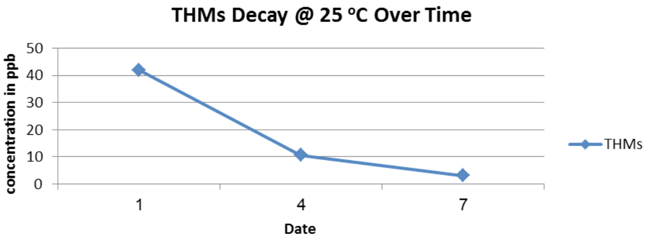

Fig. 2. THMs decay over time @ 25°C by chlorine dioxide.

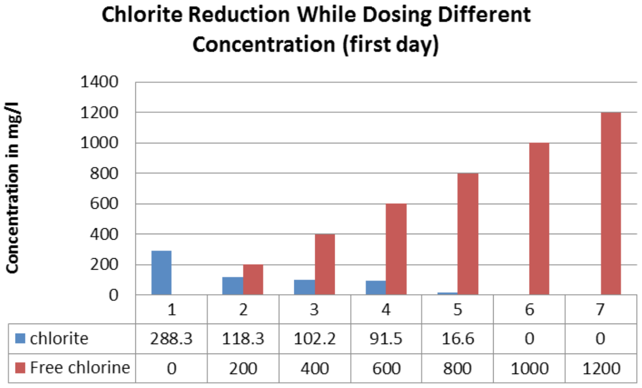

Fig. 3. The influence of different dosage of free chlorine on chlorite reduction over time for one day.

These data were statistically analyzed by multivariate regression and correlation. Figs. 4 and 5 show the impact of different dosages of free chlorine on chlorite and chlorate reduction over times for seven days.

There is no bromate formation takes place even in high dosage of calcium hypochlorite and the presence of bromide ions (average 60 µg/l), this may be connected to pH and temperature effect.

The decay of chlorine dioxide with time under the experimental condition of 25°C showed that the decay was linear. This indicates that temperature effect should be considering the time of year (winter and summer). A linear trend line with R2 (coefficient of determination) of 0.96 shows a linear relationship for chlorine dioxide decay. The equation $Y = -0.00325 + 0.25$ can be used to calculate the decay rate.

The chlorite reduction with time under the experimental condition of 25°C and the influence of free chlorine shows that the reduction was linear. A linear trend line with R2 (coefficient of determination) of 0.93 demonstrates the liner relationship of chlorite reduction. The equation $Y = -19.31 + 172$ can be used to calculate the reduction rate of chlorite by free chlorine.

The chlorate formation with time under the experimental condition of 25°C and the influence of free chlorine shows that the formation was linear. A linear trend line with R2 (coefficient of determination) of 0.97 demonstrates the linear relationship of chlorate formation. The equation $Y = 54.75 + 16.3$ can be used to calculate the formation rate of chlorate by free chlorine.

From the above the following equation can be used to calculate the chlorite reduction and chlorate formation while dosing $Ca(ClO)_2$

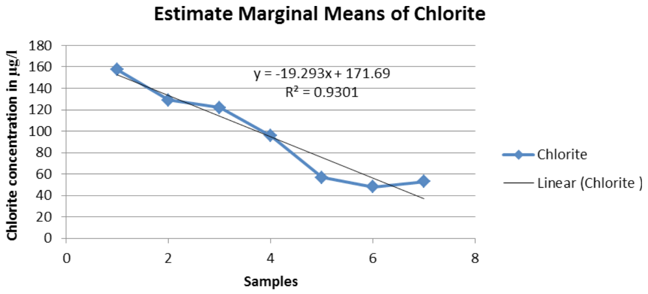

Fig. 4. Impact of different dosage of free chlorine on chlorite reduction over times for seven days.

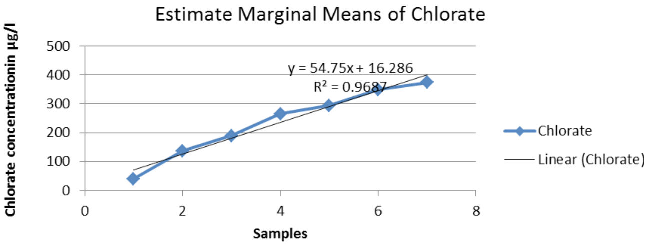

Fig. 5. Impact of different dosages of free chlorine on chlorate formation over time for seven days.

For chlorite:

In the equation Y = 172 – 19.31; 19.31 µg/l indicates the intercept of the trend line at the y axis and 19.3 µg/day (per specific dosing of $Ca(ClO)_2$) indicates the decay rate for the zero order reaction. Based on this interpretation the decay at 25°C can be represented via the following equation:

$$C_t = C_0 - 19.3 \times t \ @\ 25°C$$

C_t = Concentration of chlorite at time t, µg/l; C_0 = Initial concentration of chlorite, µg/l; t = time, d.

For chlorate:

In the equation Y = 54.75 + 16.3; 54.75 µg/l indicates the intercept of the trend line at y axis, and 54.75 µg/d (per specific dosing of $Ca(ClO)_2$) indicates the formation rate for the zero order reaction. Based on this interpretation the formation at 25°C can be represented via the following equation:

$$C_t = C_0 + 54.75 \times t \ @\ 25°C$$

4. Conclusion

- There are several conclusions that can be derived from this study:
- No bromate formation was observed even in the presence of bromide.
- The reductions in chlorite and increases in chlorate concentration are chlorine dosage dependent.
- The chlorate produced in consistently about 10% of chlorine dioxide at the desalinated water outlet.
- Chlorine dioxide levels decrease as the free chlorine residual levels increased.
- There were no significant changes in THMs concentrations due to the mixing, nonetheless the maximum THMs reduction was recorded over storage time for 3 d.

This study demonstrates that hypochlorite/chlorine can be used as an operational tool to control chlorite levels, and slow the disappearance of the chlorine dioxide over time during distribution, that is usually faster than chlorine disappearance. The original chlorine dioxide dosage will determine the ultimate chlorate concentration.

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To Qatar General Electricity and Water Corporation (Kahramaa)

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