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Comparison between OCl^--Injection and In Situ Electrochlorination in the Formation of Chlorate and Perchlorate in Seawater

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Abstract: To prevent biofouling from occurring in the cooling systems of coastal power plants, chlorine is often added to the cooling water. In this study, we have evaluated the fate of the total residual oxidants and the formation of inorganic chlorination byproducts including ClO_3^- and ClO_4^- during in situ electrochlorination with seawater. Then, the results were compared with those during direct OCl^--injection to seawater. The in situ electrochlorination method based on Ti/RuO_2 electrodes produced much less ClO_3^-, while a similar level of total residual oxidants could be achieved with a reaction time of 5 min. Moreover, no ClO_4^- was observed, while the direct OCl^--injection system could still result in the production of ClO_4^-. The less or no production of ClO_3^- or ClO_4^- by the electrochlorination of seawater was mainly attributed to two reasons. First, during the electrolysis, the less amount of OCl^- is available for ClO_3^- formation. Secondly, the formation of ClO_3^- or ClO_4^- is affected by the electrode material. In other words, if the electrode material is carefully chosen, the production of harmful reaction byproducts can be prevented or minimized. In short, based on the results from our study, electrochlorination technology proves to be a marine environmentally friendly method for controlling biofouling in the pipes of the cooling system in a coastal power plant.

Keywords: seawater chlorination; electrolysis; chlorate; perchlorate; inorganic chlorination byproducts

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1. Introduction

Inland thermoelectric power plants withdraw natural surface water, underground water, and reclaimed water for their cooling systems [1]. About 10% of global freshwater withdrawal is used by power plants [2]. Therefore, many power plants are built near coastal areas since they can use seawater as a coolant [3]. However, these plants frequently encounter the problem of biofouling or biofilm formation in their inlet pipes and cooling systems. Biofouling is defined as the attachment of micro-/macroorganisms to the inner surface of pipes and the subsequent growth of the organisms. It is caused by a variety of organisms ranging from microorganisms (bacteria, algae) to macroorganisms (mussels, barnacles, etc.), depending on the conditions such as flow regimes of seawater in pipe, the presence of substrate(s), and so on. Biofouling is a huge concern as it blocks seawater flow, which results in the reduced efficiency of heat exchangers, increased loads on pumps, and eventually the failure of power generation [4]. Among all the methods used to control biofouling, chlorination remains the most popular and preferred, because of its proven effectiveness and relatively low cost [5].

Chlorine not only exerts toxic effects on adult organisms but also inhibits the growth of larvae and their attachment to the substratum [6,7]. There are various methods to make chlorine in water, such as (i) dissolution of chlorine gas; (ii) addition of hypochlorite; and (iii) electrolysis of electrolytes containing salt or seawater (i.e., electrochlorination) [8].

Recently, electrochlorination has been applied for biofouling control. Electrochlorination enables the production of sodium hypochlorite, which is produced through the application of electric potential differences between electrodes with NaCl as an electrolyte [9]. Particularly, under direct current (DC) voltage, negatively charged ions such as chloride, hydroxyl, and oxygen ions donate electrons at the anode to form chlorine gas, oxygen gas, hypochlorite ion, hypochlorous acid, and hydrochloric acid. On the other hand, positively charged ions such as hydrogen, sodium, magnesium, calcium, and potassium ions gain electrons at the cathode to form hydrogen gas and hydroxide (reaction 1–7) [10–13].

Anode

$$2\,Cl^- \leftrightarrow Cl_2 + 2\,e^-\ (E_o = 1.36\ V) \tag{1}$$

Bulk solution

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \tag{2}$$

$$HOCl \leftrightarrow OCl^- + H^+\ (pK_a = 7.5\ \text{at}\ 25\ ^\circ C) \tag{3}$$

$$HOCl + H^+ + e^- \leftrightarrow 1/2\ Cl_2 + H_2O\ (E_o = 1.63\ V) \tag{4}$$

$$NaCl + H_2O \rightarrow NaOCl + H_2 \tag{5}$$

Cathode

$$O_2 + 2\,e^- + 2\,H^+ \rightarrow H_2O_2\ (E_o = 0.68\ V) \tag{6}$$

$$2\,H_2O + 2\,e^- \rightarrow 2\,OH^- + H_2 \tag{7}$$

Currently, the ex situ electrolytic production of hypochlorite, which is subsequently injected into pipes, is commonly carried out in practice. Compared with ex situ electrochlorination, in situ electrochlorination in seawater has a few advantages. This does not require supply of NaCl since it uses Na^+ and Cl^- in seawater as electrolytes. In addition, it does not require any space for hypochlorite generation and storage. Therefore, in situ electrochlorination should be more economical than ex situ.

Generally, the residual chlorine concentration of water flowing through the pipe of a cooling system is maintained at 0.2 mg/L or higher to control biofouling [14–16]. In practice, chlorine is added in the inlet of the cooling system and the chlorine concentration at the inlet is varied depending on its level at the outlet [17]. In fact, a large amount of seawater is withdrawn for the cooling system in a power generation system (e.g., 95–230 m^3/MWh for the once-through cooling system of a nuclear power plant [15,18]). So, an enormous amount of chlorine should be applied in the inlet.

Chlorine exerts a biocidal action on microorganisms in water by oxidizing enzymes responsible for microbial growth. However, chlorine also reacts with other constituents in water to generate unwanted organic and inorganic chlorination byproducts (CBPs); in seawater, for example, trihalomethane, haloacetic acids, chloramines, bromate, chlorite, chlorate, and perchlorate are produced [17]. Due to their persistency in the environment and potential negative impacts on aquatic lives, ClO_3^- and ClO_4^- have been of special public interest. In humans, ClO_3^- causes hematological imbalance by decreasing erythrocyte count and hemoglobin. ClO_4^- also interferes with iodine uptake to cause thyroid malfunctions [19]. According to a report from WHO, ClO_3^- may also cause renal tumors [20].

In this study, we have evaluated the fate of the total residual oxidant (TRO) and formation of inorganic CBPs including ClO_3^- and ClO_4^- during in situ electrochlorination with seawater using Ti/RuO_2 electrodes. Then, the results were compared with those during direct OCl^--injection to seawater.

The specific goals of this study were to: (1) monitor TRO fate when electrochlorination or direct OCl^--injection was applied for seawater; (2) compare the amounts of ClO_3^- and ClO_4^- formed during electrochlorination or direct OCl^--injection. We believe that the findings presented in the manuscript will contribute to our understanding of the potential environmental risk associated with ClO_3^- and ClO_4^- formed during in situ electrochlorination of seawater, which is used for the cooling system of a power plant.

2. Materials and Methods

2.1. Materials

Seawater samples were collected from the west coast (Yeonggwang, Korea, 35°23′27″ N, 126°24′25″ E) of the Korean peninsula and the east coast (Uljin, Korea, 37°01′53″ N, 129°24′54″ E) (Figure S1). Once the water samples were collected, they were filtered using GF/C (Whatman, Chalfont, UK) and stored at 4 °C. The water quality of the collected seawater samples is summarized in Table 1.

Table 1. Sampled seawater quality on west and east coast.

Parameter	West Seawater (WS)	East Seawater (ES)
pH	8.3	8.0
Conductivity(ms/cm)	44.37	44.67
Salinity (PSU)	28.66	28.88
TOC (mg/L)	2.2	1.9
TN (mg/L)	1.3	0.5
TP (mg/L)	0.1	0.1

NaOCl (Duksan Chemical, Daejeon, Korea) stock solution of 120,000 mg/L was used for the direct chlorine injection study. For electrochlorination, an anode and a cathode made of Ti and RuO_2, respectively, (0.1 m × 0.18 m, Samsung DSA, Seoul, Korea) were used.

2.2. Experimental Procedure

Chlorination experiments were performed in a 500-mL Pyrex batch reactor, and the temperature of the reactor was set to 20.0 ± 0.5 °C using a temperature-controlled bath (C-331, Sibata, Tokyo, Japan) (Figure 1a,b). The OCl^- solution of desirable concentration was prepared by diluting the NaOCl stock solution (12%) with deionized (DI) water. Then, the OCl^- solution was directly injected to the reactor in the beginning of each experiment.

Electrolysis experiments were performed in a 2-L lab-scale semi-batch reactor. The two electrodes (i.e., Ti and RuO_2) were placed vertically, with a distance of 2.5 cm between each other, in the reactor. A DC power supply (SM Techno, Daejeon, Korea) was used to provide electricity for the electrodes; four different current densities were applied (i.e., 2.2, 9.4, 16.6, and 27.7 mA/cm^2 (Figure 1c). Prior to executing electrolysis, electrodes were washed with DI water to desorb any materials remaining on their surface. During the experiment, the solution in the reactor was rapidly mixed by a magnetic stirrer, and aliquots were withdrawn from the reactor at predetermined times to measure TRO, and inorganic byproducts (i.e., ClO_3^- and ClO_4^-). To measure byproducts, excessive sodium thiosulfate ($Na_2S_2O_3$) was added as a quenching agent to prevent further oxidation of the byproducts by the oxidant.

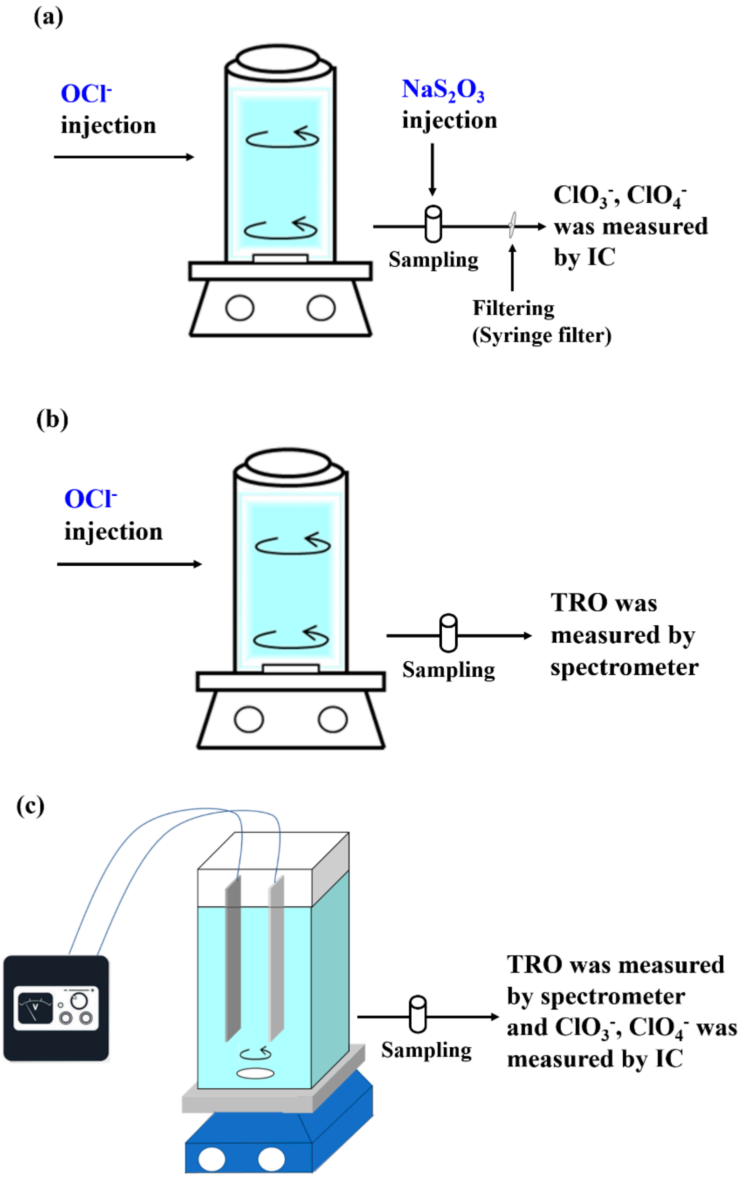

Figure 1. Schematic diagram for (**a**) measurement of inorganic CBPs and (**b**) of residual TRO measure, and (**c**) electrolysis experimental setup.

2.3. Analysis Methods

For quantitative analysis of TRO, EPA method 330.5 (Spectrophotometric, DPD) was used using spectrophotometer (Qvis 5000, C-mac, Daejeon, Korea) [21]. The quantification range of chlorine was 0.02–4.00 mg/L. TRO was measured at a predetermined time interval after an oxidation was initiated.

Concentration of ClO_3^- and ClO_4^- were measured using ion chromatography (883 Basic IC plus, Metrohm, Herisau, Switzerland). The eluent for ClO_3^- consisted of 3.6 mM sodium carbonate (Na_2CO_3) and was delivered at a flow rate of 0.8 mL/min. The eluent for ClO_4^- consisted of a mixture of 10.0 mM Na_2CO_3 and 45% acetonitrile was delivered at a flow rate of 0.6 mL/min. The separation column was IC 82524A, 4.0 mm × 250 mm (Shodex, Tokyo, Japan). The pH was measured using a pH meter (Mettler-Toledo, Greifensee, Switzerland). Conductivity was measured using a multifunction meter (CX-401 waterproof, Elmetron, Zabrze, Poland). TOC wes measured using a TOC analyzer (TOC−VCPH/CPN, Shimazu Co., Kyoto, Japan).

3. Results and Discussion

3.1. Total Residual Oxidant in Direct OCl^--Injection and Electrolysis

3.1.1. Direct OCl^--Injection

Effects of the initial OCl^- concentration on TRO in the direct injection of OCl^- to seawater were investigated. The direct OCl^--injection experiments were carried with WS and ES by varying OCl^- concentrations (0.5, 0.7, 1, 10, 50, and 150 mg/L as Cl_2) and their results are presented in Figure 2. Irrespective of the initial OCl^- concentrations, the TRO concentration dropped rapidly in the beginning and was stabilized within 1 min for both ES and WS (Figure 2a,b). Chlorine demand of both WS and ES increased with the increase of the OCl^- dose. While the chlorine demand of WS increased by 26-fold, that of ES increased by only 12-fold, as the OCl^- dose increased from 0.5 to 150 mg/L. When the OCl^- dose of ≥10 mg/L was applied, WS showed a significantly higher chlorine demand compared to that of ES (Figure 2c). These phenomena might be explained by the characteristics of the seawater used in this study, such as organics or nitrogen contents [22]. In other words, once chlorine is added to seawater, reactions between chlorine and chlorine-demanding substances such as Br^-, NH_4^+, NO_2^-, Fe^{2+}, and residual organics occur rapidly [14,23,24]. Nonetheless, the chlorine demand became obvious when the dose was high. In the case where 150 mg/L OCl^- was injected to WS, the chlorine demand reached 13.0 mg/L (Figure 2c). On the other hand, the chlorine demand reached 0.2 mg/L when 0.5 mg/L OCl^- was injected. Similar results have been reported by others, e.g., Zeng et al. [25], Venkatnarayanan et al. [26], and Saidan et al. [27].

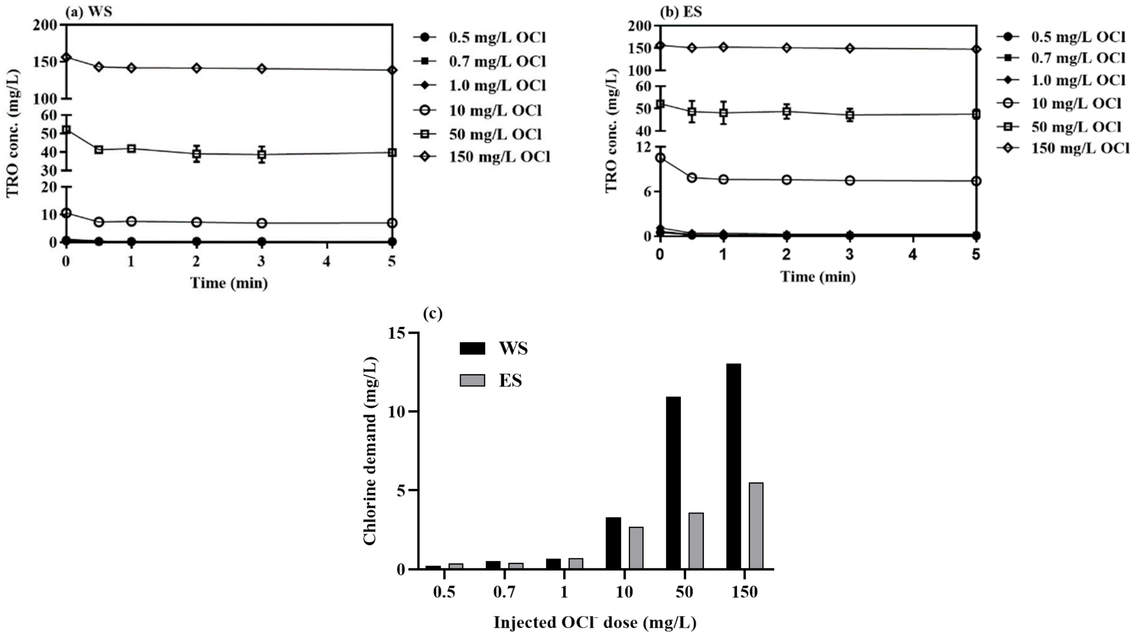

Figure 2. Effect of initial OCl^- concentration on formation of TRO in (**a**) WS and (**b**) ES, and (**c**) comparison of chlorine demands between WS and ES (volume: 0.4 L; temperature: 20 ± 1 °C; salinity: 28.9 PSU for WS and 28.7 PSU for ES; pH: 8.3 for WS and 8.0 for ES).

3.1.2. Effects of Current Density during Electrolysis

Effects of the current density (2.2, 9.4, 16.6, and 27.7 mA/cm^2) on TRO during the in situ electro-chlorination of seawater were investigated. For both WS and ES, the TRO concentration increased as the applied current density and time increased (Figure 3). No significant difference in the TRO concentration was observed between WS and ES, probably because the salinities of WS and ES were almost the same. More than 230 mg/L of TRO could be produced via the in situ electrochlorination of seawater within 5 min under the current density of 27.7 mA/cm^2: 240 mg/L for

WS and 235 mg/L for ES. In other words, at the current density, TRO of 16.8-18 mg Cl_2/cm^2/min can be produced. If an electrode with a width of 0.5 m is installed along the inner surface of a pipe with a radius of 1 m, the surface area of the electrode will be 3.1 m^2 and produce TRO at 520–557 g Cl_2/min. Considering the flow pattern developing along the inner surface of the pipe for a cooling system, the amount of TRO generated by seawater electrolysis will be enough to provide a desirable TRO concentration (e.g., >0.5 mg Cl_2/L) for the cooling water flowing the pipe (confirmed by a simulation; data not shown).

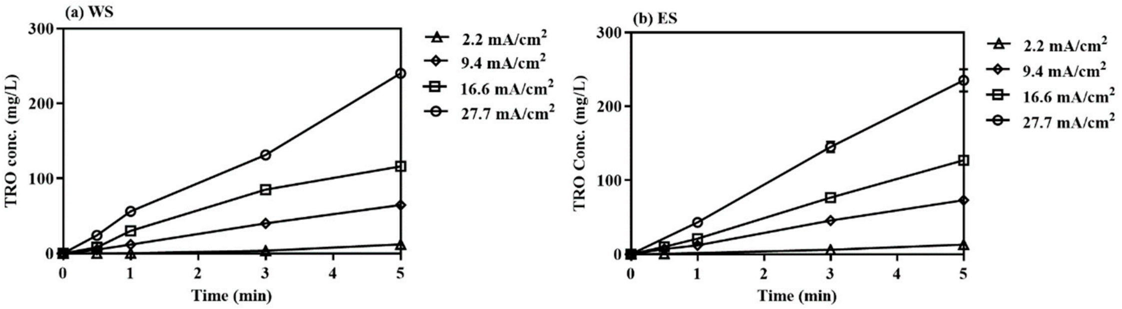

Figure 3. Effect of current density on formation of TRO (**a**) WS, (**b**) ES (volume: 2 L; temperature: 20 ± 1 °C; salinity: 28.9 PSU for WS and 28.7 PSU for ES; pH: 8.3 for WS and 8.0 for ES; electrode area: 0.018 m^2).

3.2. Formation of ClO_3^- and ClO_4^- in Electrolysis and Direct OCl^--Injection

The kinds and concentrations of CBPs depend on several factors, such as oxidant contact time, organic and inorganic contents, reaction temperature, and solution pH [17,28–32]. If chlorine is added to seawater via direct OCl^--injection or the electrochemical process, chlorite, chlorate, or perchlorate can be generated through the following reactions (Equations (8)–(20) in Table 2) (Figure 4) [11,13,33–36].

Table 2. Formation of ClO_3^- and ClO_4^- during chlorination.

Equation	Equivalent	Equations No.
$6\,OCl^- + 3\,H_2O \rightarrow 2\,ClO_3^- + 4\,Cl^- + 6\,H^+ + 3/2\,O_2 + 6\,e^-$	0.46 V	(8)
$6\,HOCl + 3\,H_2O \rightarrow 2\,ClO_3^- + 4\,Cl^- + 12\,H^+ + 3/2\,O_2 + 6\,e^-$	0.46 V	(9)
$Cl^- + 3\,H_2O \rightarrow ClO_3^- + 6\,H^+ + 6\,e^-$	−1.45 V	(10)
$Cl^- + 2\,OH^- \rightarrow OCl^- + H_2O + 2\,e^-$	−0.94 V	(11)
$Cl^- + 4\,OH^- \rightarrow ClO_2^- + H_2O + 4\,e^-$	−0.76 V	(12)
$OCl^- + 2\,OH^- \rightarrow ClO_2^- + H_2O + 2\,e^-$	−0.59 V	(13)
$ClO_2^- + 2\,OH^- \rightarrow ClO_3^- + H_2O + 2\,e^-$	−0.35 V	(14)
$ClO_2^- + OCl^- \rightarrow Cl^- + ClO_3^-$		(15)
$ClO_2^- + HOCl \rightarrow ClO_3^- + H^+ + Cl^-$		(16)
$HClO_2 + H_2O \rightarrow ClO_3^- + 3\,H^+ + 2\,e^-$		(17)
$ClO_3^- + H_2O \rightarrow ClO_4^- + 2\,H^+ + 2e^-$	0.95 V	(18)
$2\,ClO_3^- + 2\,Cl^- + 4\,H^+ \rightarrow Cl_2 + 2\,ClO_2 + 2\,H_2O$		(19)
$ClO_3^- + Cl^- + 2\,H^+ \rightarrow HClO_2 + HOCl$		(20)

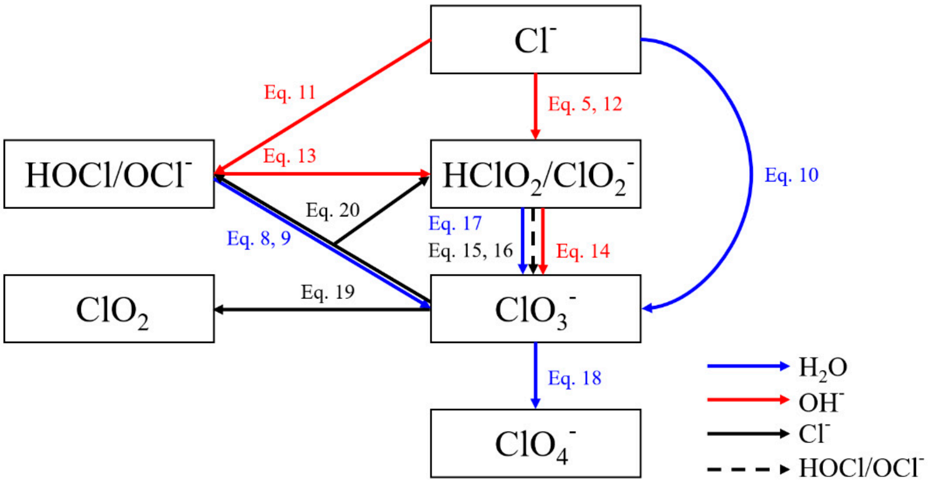

Figure 4. Proposed pathways of ClO_3^- and ClO_4^- formation during seawater chlorination.

3.2.1. Direct OCl^--Injection

The formation of ClO_3^- and ClO_4^- when OCl^- was directly added to seawater was evaluated by varying OCl^- concentration (0.5, 0.7, 10, 50, and 150 mg/L). Figure 5 shows the pattern of ClO_3^- formation during the chlorination of WS and ES as a function of contact time. ClO_3^- was not detected when the OCl^- amount added to the seawater samples was low (i.e., 0.5 mg/L). On the other hand, 816 µg/L and 808 µg/L of ClO_3^- could be observed for WS and ES, respectively when the amount of OCl^- added to the seawater was 150 mg/L. This result could be explained by Equations (8)–(17). ClO_3^- can be formed via either direct or indirect reactions: via either (1) the reaction between OCl^-/HOCl and H_2O to form ClO_3^- or (2) the reaction of added OCl^-/HOCl with Cl^- in seawater to form OCl^-, ClO_2^-, and then to form ClO_3^-. Regardless of the amount of OCl^- added to the water samples, the ClO_3^- formation occurred within the reaction time of 1 min. Then, the ClO_3^- concentration slightly decreased by 8–17% due to Equations (18)–(20).

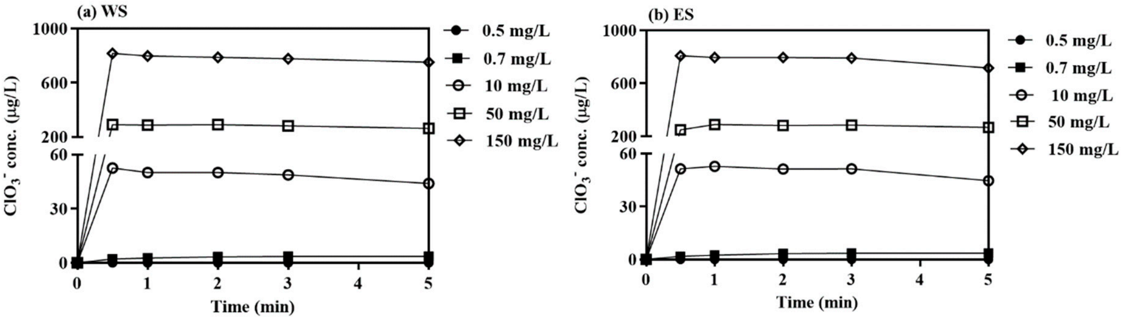

Figure 5. Effect of OCl^- dose on ClO_3^- formation during chlorination of (**a**) WS and (**b**) ES (volume: 0.4 L; temperature: 20 ± 1 °C; salinity: 28.9 PSU for WS and 28.7 PSU for ES; pH: 8.3 for WS and 8.0 for ES).

In the case where ClO_3^- is present at a high level, ClO_4^- can be formed through the reaction of ClO_3^- with H_2O (Equation (18)). Figure 6 shows the time profiles of ClO_4^- formation during the chlorination of WS and ES as a function of contact time. ClO_4^- was not detected from the samples when the OCl^- concentration was $\leq$ 10 mg/L. No significant difference was observed in the formation of ClO_4^- between WS and ES. When the seawater samples were added with 50 and 150 mg/L OCl^-, however, ClO_4^- of 0.36 and 3.44 µg/L, respectively could be observed. These results indicated that at a low concentration OCl^- might not generate ClO_4^- in seawater.

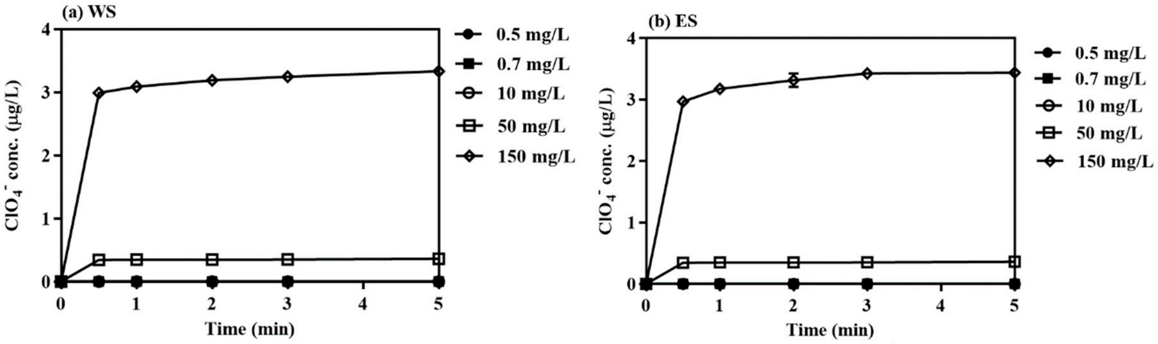

Figure 6. Effect of OCl^- concentration on formation of ClO_4^- (**a**) WS, (**b**) ES (volume: 0.4 L; temperature: 20 ± 1 °C; salinity: 28.9 PSU for WS and 28.7 PSU for ES; pH: 8.3 for WS and 8.0 for ES).

3.2.2. Electrochlorination

Electrochlorination was performed for both WS and ES with different current densities i.e., 2.2, 9.4, 16.6, and 27.7 mA/cm^2) and the formation of ClO_3^- and ClO_4^- was studied. The ClO_3^- concentration increased from 0.60 to 4.75 µg/L for WS and from 0.17 to 4.59 µg/L for ES, as the current density was raised from 2.2 to 27.7 mA/cm^2 (Figure 7). The amount of ClO_3^- formed in ES increased with the increase of the current density. However, in the case of WS, ClO_3^- increase was noted only at a current density of >16.6 mA/cm^2 (Figure 7). Nonetheless, it seems that the amount of ClO_3^- formed during the electrochlorination of seawater depends on both the applied current density and the surface characteristics of electrodes used in the electrolysis. Jung et al. [37] observed 637 µg/L ClO_3^- formed during their electrochlorination of seawater from the east coast using Pt/Ti electrodes with 55 mA/cm^2 of current density. Our Ti/RuO_2-based electrolysis system might produce less ClO_3^- than the Pt/Ti-based one.

Interestingly, in our electrochlorination study with WS or ES, ClO_4^- was not detected even at a current density of 27.7 mA/cm^2. In fact, other researchers could observe ClO_4^- only when higher current densities were applied for their electrochlorination. In their electrochlorination study with seawater samples from the east coast of Korea, Oh et al. [38] could generate 27 µg/L of ClO_4^- with a current density of 110 mA/cm^2; in their experiment, they used Pt/Ti electrodes. From the results of our study and others, it can be concluded that the formation of inorganic CBPs such as ClO_3^- and ClO_4^- is very dependent on the surface characteristics of electrodes or electrode-surface-specific reactions. When electrode material has a lower potential for oxygen evolution, the electrode easily produces oxygen, which reacts with bromine and chloride to form BrO_3^- and ClO_3^- formation [37].

Nonetheless, the amount of ClO_3^- produced from the electrochlorination of seawater was about 170 times lower than that from the direct OCl^--injection. This phenomenon could be explained by the difference in the amount of OCl^- used for the ClO_3^- formation between the direct OCl^--injection system and the electrochlorination of seawater. If a large amount of OCl^- is added to seawater at once, the bromine ions in seawater will rapidly react with OCl^-/HOCl to form OBr^-/HOBr (reactions 1–5 in the Supplementary Materials). However, some of the OCl^- still might be able to participate in reactions that form ClO_3^-. In the case of electrochlorination, OCl^- is gradually produced on the electrode surface. In this case, OCl^- generated on the electrode surface might preferentially react with Br^- and form OBr^-/HOBr. Comparing to the direct OCl^--injection system, thus, a relatively smaller amount of OCl^- will be available for the ClO_3^- formation during seawater electrolysis.

In short, unlike conventional chlorination, electrochlorination produces much less or no inorganic chlorination byproducts, which makes it an environmentally friendly and sustainable technology.

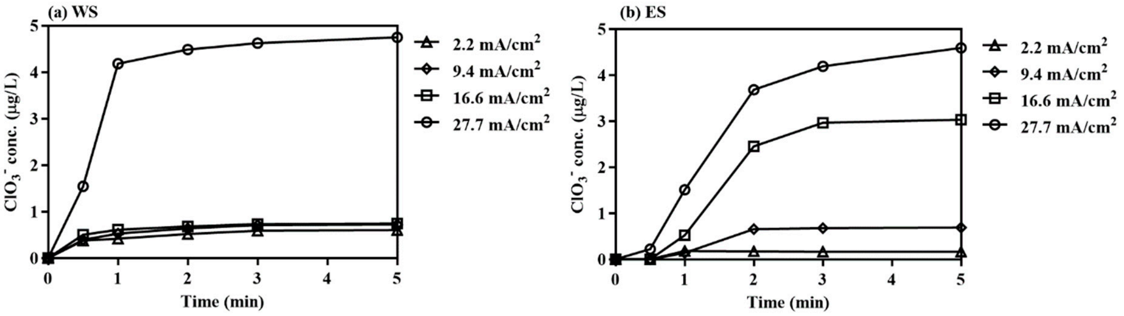

Figure 7. Effect of current density on ClO_3^- formation during electrochlorination of (**a**) WS and (**b**) ES (volume: 2 L, temperature: 20 ± 1 °C; salinity: 28.9 PSU for WS and 28.7 PSU for ES; pH: 8.3 for WS and 8.0 for ES).

4. Conclusions

In this study, we have evaluated the in situ electrochlorination of seawater, which is used as a coolant for coastal power plants in terms of TRO production and formation of inorganic chlorination byproducts such as ClO_3^- and ClO_4^-. Compared to the practice of directly adding OCl^- to cooling seawater, the in situ electrochlorination method based on Ti/RuO_2 electrodes produced much less ClO_3^-, while a similar level of TRO could be achieved with a high TRO production rate of 16.8–18 mg $Cl_2/cm^2/min$. Moreover, ClO_4^- was not observed during electrochlorination, while the direct OCl^--injection system could still result in the production of ClO_4^-. The lower or no production of ClO_3^- or ClO_4^- by the electrochlorination of seawater was mainly attributed to two reasons. First, less OCl^- is available for ClO_3^- formation because the OCl^- supply is limited by the electrode surface area and reaction time. Secondly, the formation of ClO_3^- or ClO_4^- is affected by the electrode material. In other words, if the electrode material is carefully chosen, the production of harmful reaction byproducts can be prevented or minimized.

Based on the results of our study, in situ electrochlorination technology proves to be a marine environmentally friendly and sustainable method for controlling biofouling in the pipes of a cooling system in a coastal power plant. Therefore, this technology should be preferentially considered as an option for antifouling of the cooling system for a thermoelectric power plant.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/9/2/229/s1.

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Conflicts of Interest: The authors declare no conflict of interest.

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