The decay kinetics of residual chlorine in cooling seawater simulation experiments

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Received 25 November 2007; accepted 10 October 2008

Abstract
To find out the decay character of residual chlorine (RC) in the sea water, the concentration of RC was analyzed by N, N-diethyl-p-phenylenediamine (DPD) method under different simulation experimental conditions, in which salinity, temperature, and Chemical Oxygen Demand (COD) were selected. The water used in the experiment was the mixture of aging ocean water, coastal water and extracting solution of coastal sediment at appropriate level. Results are shown as follows: (1) Piecewise function can well reflect the decay dynamics of RC in the cooling seawater. Concretely, the decay dynamics of first 1 min is too rapid to ascertain using a specific kinetic function, and that of the time from 1 to 30 min is fit for the first-order kinetic model. (2) The results could be the foundation of the chemical behavior of RC in seawater, and be used as not only the guidance of the coastal power plants production and sea water desalting companies, but also the establishment of the correlative trade standard.

Key words: residual chlorine, cooling seawater, decay rate, kinetic model

1 Introduction

Coastal power plants and seawater desalting companies usually make the use of seawater as the cooling water (Poornima et al., 2006), and chlorine, as an effective biocide with cheap price and handy operation, is widely used to prevent the marine defiling organisms from adhesion to the cooling system (Nebot et al., 2006; Taylor, 2006; Alonier et al., 1999; Fisher et al., 1999; Jenner et al., 1998). Methods, such as directly adding liquid chlorine or sodium hypochlorite, are widely adopted in enterprises’ antisepsicising phase, to deal with the biofouling of the cooling system. With the growing number of coastal power plants, residual chlorine (RC) in the effluent has become a serious problem of the coastal area environment, meanwhile, its influence on the marine ecology is getting more and more attention, either on the individual creature, or the whole aquatic system (Poornima et al., 2006, 2005; Zeng et al., 2005; Liu et al., 2004; Choi et al., 2002).

Investigating the possible influence of RC on marine ecosystem around power plants thorough research is necessary to be done on the chemical behavior of residual chlorine in seawater. Researches on disinfection by adding chlorine in the city freshwater providing system have developed several kinetic models to explain the behavior of chlorine decaying (Boccelli et al., 2003; Clark and Sivaganesan, 2002; Hua et al., 1999; Clark, 1998; USEPA, 1992), however, deep research work was rarely seen on chlorine decaying in sea water yet, especially quantitative analysis (Liu et al., 2004; Shams El Din et al., 2000). Moreover, it was because of the variety of marine characteristics and the natural conditions that the published studies were lack of the integrality and pertinence, to some degree (Dang et al., 2005; Shams El Din et al., 2000; Huang et al., 1998; Wen et al., 1993). To determine the mode and concentration of the chlorine adding in cooling seawater (CSW), judge the effect and radiate range of the RC to marine environment, as well as make the regional RC discharge standard, the chemical behavior of RC is of special importance.

Cases under different conditions of seawater, including the salinity, temperature, chemical oxygen demand (COD), were designed to study the decaying
characteristics of RC.

2 Materials and methods

2.1 Apparatus and reagents

RC concentration was tested by HANNA HI93734 RC detector, using \(\text{N}, \text{N-diethyl}-p\)-phenylenediamine (DPD) method (precision is \(\pm 0.03 \text{ mg/dm}^3\)). The concentration of RC in this study is total residual chlorine (TRC). The water temperature was tested by mercury thermometer (precision is \(\pm 0.1 \text{ C}\)), and the temperature was controlled by electrically-heated thermostatic water bath \((\pm 1 \text{ C})\). The pH of seawater was tested by STATORIUS PB-10 acidity detector (precision is \(\pm 0.01\)). Salinity was tested by MR 220 water quality analyzer \((\pm 0.1)\). Light intensity was tested by TES-1334A photometer. COD was tested by the method of alkalinity potassium permanganate (GB 17378.4–1998).

The research work began in May 2006. The water used in the experiment was the mixture aging ocean water \((S=35.2, \text{ COD is 0.24 mg/dm}^3, \text{ pH}=8.08)\) and coastal water \((S=24.5, \text{ COD is 1.06 mg/dm}^3, \text{ pH}=8.10)\). NaClO solution with more than 5% effective chlorine (the trade name is Antiformin) was diluted to liquor \(C_1\) (the effective chlorine is \(1 \text{ g/dm}^3\)) by distilled water, and then refrigerated in shadow for spare.

Before beginning any sampling, all the containers being used were cleaned to ensure that no chlorine demand was present. The cleaning involved washing them in distilled water, standing them overnight filled with distilled water which was super-chlorinated \((10 \text{ mg/dm}^3)\), flushing them with distilled water and then allowing them to dry (Department of the Environment, 1981). Because of the instability of sodium hypochlorite, the initial adding dose of chlorine \(C_0\) should be ascertained by experiments. To acquire the data of \(C_0\), operations were performed in the following steps: adding 100 ml distilled water without chlorine into 125 ml brown glass bottle, then adding quantitative liquor \(C_1\), and testing the effective chlorine concentration. Such operation was repeated five times to get the mean value of \(C_1\), which was thought of as the appropriate value of \(C_0\).

2.2 Hypothesis of kinetic model

In the research of adding chlorine into seawater, the synthesized reaction equation was founded based on the equivalent compound which was proposed by Hua et al. (1999) as shown in Eq.(1):

\[
[\text{Cl}] + \alpha X \rightarrow \text{products},
\]

where \([\text{Cl}]\) represents the TRC; \(X\) represents all the reactants which react with chlorine; \(\alpha\) is the stoichiometry constant (Dossier-Berne et al., 1997). Moreover, the initial concentration of \(X\) was supposed to far exceed the concentration of TRC greatly (Chambers et al., 1995), and the first-order kinetic equation of TRC decaying velocity was gained as Eq.(2):

\[
C_t = C_0 e^{-k_1 t},
\]

where \(t\) represents the reaction time \((\text{min})\); \(C_t\) the TRC concentration at time \(t\); \(C_0\) the initial concentration of TRC \([\text{i.e., concentration (mg/dm}^3\) of TRC at \(t=0\text{ min}]\); and \(k_1\) the decaying constant of TRC in seawater.

2.3 Methods

To obtain the suitable result adapting to practical production, the initial concentration of adding chlorine was controlled between 2.35 and 2.45 mg/dm\(^3\) (Liu et al., 2004; Saravanan et al., 1998; Rajagopal et al., 1996).

Case 1 (salinity gradient): Liquor \(C_1\) was added into 100 ml seawater at the different salinity levels, which included level 35.2, 28.2, 21.2, 14.1, 7.0 and 0 respectively, the seawater is the mixture of aging ocean water and distilled water with different ratios at room temperature. The concentration of liquor \(C_0\) was set at 2.45 mg/dm\(^3\).

Case 2 (temperature gradient): Eight temperatures were set, 10, 15, 20, 25, 30, 35, 40 and 45\(^\circ\text{C}\). The temperature was controlled by water-bath. Liquor \(C_1\) was added into 100 ml coastal water in the condition of darkness, making \(C_0=2.35 \text{ mg/dm}^3\).

Case 3 (COD gradient): The surface layer sediments of Zhejiang coastal water were added into aging ocean water. The mixture was processed by centrifugation and filtration, afterwards, solution \((C_2)\) with 5.12 mg/dm\(^3\) COD was got for the following use. Oceanic water was comixed with liquor \(C_2\) at a certain ratio to obtain six COD levels of seawater respectively, 5.12, 4.14, 3.07, 2.07, 1.02 and 0.51 mg/dm\(^3\). The salinity of six COD levels of seawater was 33–35, pH 8.08–8.12 and water temperature 25.5\(^\circ\text{C}\). Liquor \(C_1\) was added into the seawater mentioned above in the condition of darkness, making \(C_0=2.45 \text{ mg/dm}^3\).

The concentration variety of TRC with the time change was recorded from experiments of Cases 1–3.
2.4 Data processing

SPSS13.0 software was used in data processing. SigmaPlot 9.0 and SPSS13.0 software were used in plotting.

3 Results

3.1 The effect of salinity on residual chlorine in seawater

Almost no chlorine decaying was discovered in the distilled water, instead, other chlorine decaying processes at different salinity levels were apparently divided into two phases (Fig. 1). Phase 1 is the rapid decay process, lasting 1 min, and mainly supposed to be the rapid reaction between chlorine and the inorganic chlorine-demanded substance in water. Phase 2 is the slow decay process. The first-order kinetic equation, like \( \ln C = \ln C_0 - k_1 t \), under the influence of salinity at Phase 2 is obtained through the regression analysis by testing the results during 1–30 min (Table 1).

![Fig.1. Decay curves of residual chlorine in different salinity.](image)

### Table 1. Residual chlorine decay at different salinity at 1–30 min (\( P < 0.05 \))

<table>
<thead>
<tr>
<th>S (‰)</th>
<th>( k_1/\text{min}^{-1} )</th>
<th>( \ln C = \ln C_0 - k_1 t )</th>
<th>( r^2 )</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.2</td>
<td>0.059 21</td>
<td>( \ln C = 2.020 5 - 0.059 21t )</td>
<td>0.982 8</td>
<td>13</td>
</tr>
<tr>
<td>28.2</td>
<td>0.038 86</td>
<td>( \ln C = 2.308 0 - 0.038 86t )</td>
<td>0.919 3</td>
<td>14</td>
</tr>
<tr>
<td>21.1</td>
<td>0.049 57</td>
<td>( \ln C = 2.175 6 - 0.049 57t )</td>
<td>0.955 9</td>
<td>14</td>
</tr>
<tr>
<td>14.1</td>
<td>0.055 16</td>
<td>( \ln C = 2.036 0 - 0.055 16t )</td>
<td>0.968 2</td>
<td>14</td>
</tr>
<tr>
<td>7.0</td>
<td>0.060 30</td>
<td>( \ln C = 2.452 5 - 0.060 30t )</td>
<td>0.937 2</td>
<td>13</td>
</tr>
</tbody>
</table>

3.2 The effect of temperature on residual chlorine in seawater

TRC decaying increased with the increase of temperature. When the temperature of seawater exceeded 30°C, the initial concentration 2.35 mg/dm\(^3\) of TRC decomposed completely in 30 min (Fig. 2). The decaying of TRC at 1–30 min is also fit for first-order kinetic equation (Table 2).

![Fig.2. Decay curve of residual chlorine at different temperatures.](image)

### Table 2. Residual chlorine decay character at different temperatures at 1–30 min (\( P < 0.05 \))

<table>
<thead>
<tr>
<th>( T/°C )</th>
<th>( \ln C = \ln C_0 - k_1 t )</th>
<th>( k_1/\text{min}^{-1} )</th>
<th>( r^2 )</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>( \ln C = 1.410 9 - 0.345 0t )</td>
<td>0.345 0</td>
<td>0.985 0</td>
<td>14</td>
</tr>
<tr>
<td>15</td>
<td>( \ln C = 1.471 4 - 0.386 9t )</td>
<td>0.386 9</td>
<td>0.992 1</td>
<td>14</td>
</tr>
<tr>
<td>20</td>
<td>( \ln C = 1.359 2 - 0.365 4t )</td>
<td>0.365 4</td>
<td>0.986 0</td>
<td>13</td>
</tr>
<tr>
<td>25</td>
<td>( \ln C = 1.393 1 - 0.401 3t )</td>
<td>0.401 1</td>
<td>0.975 0</td>
<td>14</td>
</tr>
<tr>
<td>30</td>
<td>( \ln C = 1.279 2 - 0.382 4t )</td>
<td>0.382 4</td>
<td>0.975 9</td>
<td>14</td>
</tr>
<tr>
<td>35</td>
<td>( \ln C = 1.118 7 - 0.366 8t )</td>
<td>0.366 8</td>
<td>0.984 9</td>
<td>13</td>
</tr>
<tr>
<td>40</td>
<td>( \ln C = 1.122 2 - 0.390 1t )</td>
<td>0.390 1</td>
<td>0.976 6</td>
<td>9</td>
</tr>
<tr>
<td>45</td>
<td>( \ln C = 1.073 7 - 0.393 0t )</td>
<td>0.393 0</td>
<td>0.945 7</td>
<td>8</td>
</tr>
</tbody>
</table>

3.3 The effect of COD on residual chlorine in seawater

The decaying feature of TRC can also be divided into two sections (Fig. 3). At the second section, TRC and time show good logarithmic correlation (Table 3).
4 Discussion

4.1 Decaying kinetic character

After adding chlorine into sea water, the chlorine decay went through a rapid decay phase (the first phase), which lasted 1 min, and then gradually went into a relatively stable phase (the second phase) (Fig. 4). Moreover, the higher the initial concentration, the faster the rapid decay phase process. For example, when $C_0$ is 5.9 mg/dm$^3$, the decaying dose reaches 2.0 mg/dm$^3$ in the first 1 min.

In the practical production process, CSW added chlorine at intake, then run into environmental water system after 30 min, thus the TRC of incompletely chemical attenuation was diluted mainly by the intensively physical effect. As a result, studying the RC decay in the pipeline is more reasonable because it works with the same dark condition. Then we can describe the TRC in cooling seawater pipeline using first order decaying model.

The results could be easily applied to the practical process. In view of the process controlling, dynamic monitor of TRC should be built in the middle of cooling system. Combined with result estimated from the first-order kinetic model and relative environmental standards of the outflow, the monitoring feedback could be helpful to determine the dose of chlorine adding in the front cooling system. Moreover, the two phases of chlorine decaying in seawater can be united to summarize an empirical statistical relationship like that of freshwater disinfectant (Sohn et al., 2004).

4.2 Impact factors of residual chlorine

4.2.1 Relationship between salinity and residual chlorine

The experiments show that nearly no decaying of TRC is detected at the level of salinity=0 (Fig. 1). Then it is definite that decaying of TRC can be caused by the reaction between chlorine and other materials in water system, instead of its self-decaying. Eppley (1976) used ultraviolet radiation to oxidate the inorganic substances of chlorine-demanding and organics in seawater, and added chloride into seawater. The result shows that TRC did not decay, which indicates the correctness of the deduction mentioned above. TRC decaying in seawater is a complex process composed of a series of chemical processes, including the oxygen-demanding, the halogenation of organic substances, and the decomposing of halides, etc. (Allonier et al., 1999; Abarnou and Miossec, 1992; Doré, 1989). How-

![Fig.3. Residual chlorine decay at different COD.](image)

![Fig.4. Residual chlorine decay profiles for seawater at different initial chlorine dose.](image)

<table>
<thead>
<tr>
<th>COD/mg·dm$^{-3}$</th>
<th>ln$C$=ln$C_0$-k$_1$t</th>
<th>k$_1$/min$^{-1}$</th>
<th>r$^2$</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51</td>
<td>lnC=2.097 8-0.117 3t</td>
<td>0.117 3</td>
<td>0.970 6</td>
<td>14</td>
</tr>
<tr>
<td>1.02</td>
<td>lnC=2.038 7-0.117 3t</td>
<td>0.117 3</td>
<td>0.889 1</td>
<td>14</td>
</tr>
<tr>
<td>2.07</td>
<td>lnC=2.012 5-0.154 2t</td>
<td>0.154 2</td>
<td>0.932 6</td>
<td>14</td>
</tr>
<tr>
<td>3.07</td>
<td>lnC=1.967 5-0.177 7t</td>
<td>0.177 7</td>
<td>0.963 1</td>
<td>14</td>
</tr>
<tr>
<td>4.14</td>
<td>lnC=1.928 0-0.182 8t</td>
<td>0.182 8</td>
<td>0.951 7</td>
<td>14</td>
</tr>
<tr>
<td>5.12</td>
<td>lnC=1.870 4-0.187 7t</td>
<td>0.187 7</td>
<td>0.984 1</td>
<td>14</td>
</tr>
</tbody>
</table>
ever, it is because of the complication of marine system that the composition of the substances reacting with TRC and the reaction mechanism are still unclear. Although the results of the experiments indicate that the reaction between TRC and seawater during 1–30 min conforms to the first-order reaction character, the actual reaction cannot be expressed accurately. So the reaction rate constant $k_1$ is actually the apparent constant.

### 4.2.2 Relationship between temperature and residual chlorine

The higher the water temperature, the faster the TRC decaying, and the more the water chlorine-demanding (Davis and Coughlan, 1983). Powell et al. (2000) and Zhang et al. (1992) reported that the decaying rate constant increased with the increase of temperature by chlorine-adding in natural water system, which conformed to the results of the present work. Poornima et al. (2005) designed a series of experiments around coastal power plant at 28 and 42 $^\circ$C, with the initial concentration of TRC 1, 2 and 3 mg/dm$^3$, respectively. Thirty minutes after adding chlorine into the seawater outside the intake, concentrations of TRC at 28 $^\circ$C were 0–0.02, 0.14–0.20 and 0.90–1.00 mg/dm$^3$ respectively, while the concentrations at 42 $^\circ$C were 0, 0.04–0.06 and 0.50–0.70 mg/dm$^3$ respectively.

The method of chlorine-adding by fixed concentration is difficult to control the biofouling in the cooling system when the seasonal temperature difference is great, such as the Xiangshan Harbor (water temperature varies from 6.7 to 30.6 $^\circ$C). In summer, TRC has already decayed over before the cooling water running out of the cooling system, so that the biofouling at the end part of the cooling system is out of control; while in winter, the concentration of TRC discharged into seawater may exceed the permitted value by the same adding dose. The Chinese coastal line crosses tropical, subtropical and temperate zones, consequently, due to the obviously great temperature difference between the south and north water area, it is unsuitable to take the same dose of chlorine-adding and standard for discharge of chlorine.

### 4.2.3 Relationship between COD and residual chlorine

COD is defined as the quantity of the oxidant consumed by the dissolved and suspended materials (DSMs), which proceeded under the condition of alkalessent heating and oxidation of excessive potassium permanganate. DSMs are reductive materials that can easily react with chlorine, such as Br$^-$, NH$_3^+$, NH$_4^+$, NO$_2^-$, Fe$^{2+}$, and some typical organic substances (Boccelli et al., 2003; Allonier et al., 1999; Huang et al., 1998; Abarnou and Miossec, 1992; Doré, 1989).

Gaining the COD is much easier and cheaper than total organic carbon (TOC), besides, COD shows good correlation with TOC, thus COD usually means the organics quantity of seawater in the environment supervision and survey. Many researchers have already shown that the reaction velocity between organics and chlorine is slower than the one between inorganic substances chlorine-demanding and chlorine (Sohn et al., 2004; Allonier et al., 1999; Clark, 1998). This can be the explanation that the reaction velocity of COD case is slower than other case. It can be deduced that the crucial decaying reaction of residual chlorine is the reaction between chlorine and organic substances in water system. Organic contribution to COD differs from coastal and oceanic water, and the former, remnant baits and plankton detritus have been proved to be the main compositions of COD, which resulted in the increase of resident time of TRC. Obviously, it should be noticed that the negative affects the environment caused by the situation mentioned above.

## 5 Conclusions

The decaying process of TRC in the power plants cooling water system could be divided into two phases in the practical chlorine adding range: (1) 0–1 min, rapid decaying phase, (2) 1–30 min, slow decaying phase. At dark condition, affected by different salinity, temperature and COD, the second stage decaying of TRC in cooling sea water could be described by first-order equation like

$$\ln C = \ln C_0 - k_1 t.$$  

### References


