Marine ecological impact analysis of residual chlorine emission from LNG transfer station

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Abstract: During the operation of LNG terminals, sodium hypochlorite was used to prevent Marine organisms from attaching to the equipment, resulting in aquatic life problems caused by residual chlorine discharge. The free residual chlorine in seawater is more toxic to aquatic organisms, and the maximum inhibitory effect on Chlorella growth is shown when the concentration of residual chlorine is 0.20mg/L. Meanwhile, Chlorella growth is greatly affected by residual chlorine, and the recovery time is longer. The concentrations of zooplankton affected by continuous exposure to chlorine were lower than those affected by intermittent exposure. The effect of residual chlorine on shellfish is relatively small. When the residual chlorine concentration is lower than 1mg/L, shellfish can still open their shells to feed, but the feeding speed decreases.

1 Introduction

In our country’s energy structure, the proportion of high-quality energy such as natural gas is accounted for low weight, energy structure is obviously unreasonable. In recent years, natural gas as a new energy is becoming an important part of our energy strategy. Uses in our country all walks of life proportion enhances year by year. Under the guidance of the “energy” strategy, China National Petroleum Corporation, construction of liquids in coastal areas such as Jiangsu, Liaoning, Guangdong and other coastal areas began construction of liquid Chemical natural gas (LNG) receiving station. Aiming to promote the clean energy represented by LNG to a certain extent. Source application, adjust the energy structure, alleviate and improve regional energy consumption pair. Environmental pollution degree, improve the environmental carrying capacity of regional development. However, new ones with chlorine-containing cold drainage were also produced water environmental pollution problem. To remove algae microorganisms attached to the pipeline during the production of the LNG terminal, chlorine gas (Cl2) is added to the circulating water so that the discharged water contains residual chlorine.

Brook et al. made a comparative study of the influence of chloride-containing and chloride-free warm drainage on phytoplankton, and found that chlorine-containing wastewater discharged into the ocean inhibited photosynthesis and respiration of phytoplankton[3][4]. Zeng Jiangning et al. analyzed the effects of residual chlorine on phytoplankton, shellfish and fish, and came to the conclusion that residual chlorine had a relatively obvious effect on Marine fish[6]. Chlorine is a common treatment agent for preventing and controlling fouling organisms in the cooling water of riverside and coastal enterprises. In recent years, the application of chlorine in enterprise cooling water and the research results on the effects of chlorine on phytoplankton, zooplankton, shellfish, fish etc. at home and abroad were summarized, which provided a reference for the formulation of the discharge standard of residual chlorine in cooling water and the rational layout

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of aquaculture. In view of the situation that a large number of coastal power plants are about to be established in China, the deficiencies of the research on residual chlorine in Chinese waters were analyzed. The research direction of the influence of chlorine on Marine life in different aspects is put forward.

2. Morphology and decay of residual chlorine in seawater

The Marine ecosystem is a dynamic system, with many food webs interlocking. Changes in any one population may lead to dramatic changes in other populations. Residual chlorine has strong oxidation, it can not only kill bacteria, but also produce harm to biological organisms, so it will have a certain impact on the ecological environment of the adjacent sea[7]. The residual chlorine in water exists in two forms: free residual chlorine (FRC) and combined residual chlorine (CRC), among which the free residual chlorine is more toxic to aquatic organisms, about 6 times of the combined residual chlorine[8]. The free residual chlorine in seawater is unstable, and the residual chlorine combines with ammonia or organic amine in seawater to produce chloramine. Studies have shown that its half-life in seawater is about one hour.

2.1 Effect of residual chlorine on phytoplankton

The residual chlorine in cold drainage of LNG receiving station is the main factor that damages phytoplankton, but the thermal shock of cold drainage has little effect on phytoplankton. 0.2mg/L of chlorine can directly kill 60 to 80 percent of algae in cooling water. But GLasstone et al. argue that even if 20% of the phytoplankton population were killed, the net effect on the water could be ignored. According to Sarvanane et al., when the effective chlorine concentration of the coastal industrial seawater outlet is controlled within 0.2 ~ 0.5mg/L, the three water samples from the inlet, the cooling pipe and the outlet are cultured in the laboratory, and the initial concentration of diatoms is 413, 352 and 381ind/mL, respectively. It takes 3, 6 and 8 days to reach the same cell density (617×10^4 ~ 813×10^4ind/mL), respectively, indicating that phytoplankton has strong recovery potential, and the damage of residual chlorine to phytoplankton can recover quickly. In addition, chlorine had different effects on phytoplankton under different water quality conditions. When the proportion of total particulate matter and dissolved organic carbon in seawater is higher, the same concentration of chlorine has less effect on phytoplankton, because a large amount of chlorine is mainly consumed by the former.

2.1.1 Inhibitory effect of residual chlorine on algal growth

According to the experimental results of Jin Shi et al., under the condition of 27℃, the maximum inhibition effect of residual chlorine on Chlorella appeared in the 0.20mg /L group for 48h, and its immediate inhibition rate was 25.95%, which was similar to the experimental results of Yang Jia. At low concentration (0.02mg /L), residual chlorine promoted the growth of Chlorella. The experimental results could be explained by the sting effect of poison, that is, low concentration residual chlorine not only did no harm to Chlorella but also stimulated the growth of Chlorella. This boost lasted from the beginning of the trial to the end, and the boost was equivalent. After 48h, the inhibition effect of each residual chlorine concentration on Chlorella was weakened. At 96h, only the 0.20 mg /L high concentration group showed residual chlorine inhibition on Chlorella. The growth value of chlorella in 0.05 mg /L group was close to the growth curve of the control group, indicating that algae could adapt to and recover growth under the condition of low residual chlorine concentration. In this study, the algae growth adaptation period was longer under the influence of high residual chlorine, the growth rate slowed down, and the number of algae cells was significantly reduced compared with the control group. Because the repair time of Chlorella in 0.05mg /L and 0.10mg /L groups was shorter, the Chlorella in 0.20mg /L group entered the rapid growth phase faster than that in 0.20mg /L group. In conclusion, at 27℃, residual chlorine stimulated and promoted the growth of Chlorella at an extremely low concentration (0.02mg /L). Residual chlorine showed the maximum inhibitory effect on Chlorella growth at a concentration of 0.20mg /L, and the maximum inhibitory effect appeared at 48h. The inhibitory effect of high concentration (0.20mg /L) residual chlorine on algae growth was longer than that of 0.05mg /L and 0.10mg /L concentration groups.

2.1.2 Characteristics of relative loss of residual chlorine in algal growth at different concentrations

The growth curves of algae in the experimental group and the control group were respectively compared under various residual chlorine concentrations. The shaded area between the two curves represents the relative amount of algae loss. The growth rate of Chlorella in 0.02mg /L group was faster than that in the control group. This result was due to the rapid growth of Chlorella stimulated by low concentration of residual chlorine. The two curves will continue to grow at their respective rates in the short term and will not intersect. The cumulative loss rate of Chlorella in 0.05mg /L group was the largest at 72h and 96h. At the end of the experiment (96h), the number of Chlorella cells was close to that of the control group. The results indicated that the growth of Chlorella was inhibited by residual chlorine at the initial stage, and with the increase of experimental time, Chlorella gradually recovered its growth ability. The maximum accumulated loss rate of 0.10mg /L in the concentration group occurred at 72h, and the cumulative loss rate decreased to the same level as that at 48h at 96h. The results indicated that Chlorella in 0.10mg /L group was inhibited due to the high residual chlorine concentration at first. With the increase of experimental time, Chlorella gradually recovered its growth ability and then began to accelerate its growth. At the end of the experiment (96h), the cell density of
Chlorella could be greater than that of control group. The cumulative loss rate of the 0.20mg/L group increased with the increase of time, indicating that Chlorella growth was seriously hindered under the influence of high concentration (0.20mg/L) residual chlorine. At the end of the experiment, the two curves were far apart from each other, so it is speculated that if the experiment continues, the two curves may still intersect in a long time, indicating that Chlorella is greatly affected by residual chlorine under high concentration conditions, and it takes a long time to recover its growth.

2.2 Estimation and analysis of phytoplankton growth loss caused by residual chlorine

The relative loss was calculated by the cumulative loss rate of Chlorella and the total biomass of the current year rather than the product of the inhibition rate and the total biomass of the current year. In the 0.05mg /L group, the maximum cumulative loss rate was 8.73%, so the cumulative relative loss amount of phytoplankton affected by residual chlorine was $1.95 \times 10^{12}$ within 72h, and the relative loss amount of phytoplankton caused by residual chlorine discharge was $1.95 \times 10^{15}$ per month (30d). The survey area was located in the Yangtze River estuary. When the runoff from the Yangtze River entered the sea, the restoration time of Chlorella in the 0.05mg /L and 0.10mg /L groups was shorter, and the Chlorella in the 0.20mg /L group entered the rapid growth phase faster than that in the 0.20mg /L group. In conclusion, at 27 ℃, residual chlorine stimulated and promoted the growth of Chlorella at an extremely low concentration (0.02mg /L). Residual chlorine showed the maximum inhibitory effect on Chlorella growth at a concentration of 0.20mg /L, and the maximum inhibitory effect appeared at 48h. The inhibition effect of high concentration (0.20mg /L) residual chlorine on algal growth was longer than that of 0.05 mg /L and 0.10 mg /L concentration groups.

Liu Lanfen et al. pointed out that natural water contains a large number of suspended aquatic organisms, some reducing substances and organic matter, which are easy to consume atomic chlorine decomposed by hypochlorous acid. Moreover, the influence of water temperature, heavy mixing in cooling water discharge and the reduction of pressure will accelerate the decay of residual chlorine. Therefore, as long as environmental protection measures are implemented to control the discharge of high concentration residual chlorine, the effect of residual chlorine on phytoplankton is controllable.

2.3 Effects of residual chlorine on zooplankton

Although zooplankton is an important part of aquatic ecosystem, it can be seen from Table 1 that zooplankton is sensitive to chlorine, and a lower concentration of chlorine can have an obvious effect on zooplankton. The concentrations of zooplankton affected by continuous exposure to chlorine were lower than those affected by intermittent exposure.

Table 1 Effects of residual chlorine on zooplankton

<table>
<thead>
<tr>
<th>Species</th>
<th>Temperature (℃)</th>
<th>Salinity (‰)</th>
<th>Decision</th>
<th>Influence concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mysisops is bahia</td>
<td>25±1</td>
<td>20</td>
<td>96hLC₅₀</td>
<td>0.062</td>
</tr>
<tr>
<td></td>
<td>25±1</td>
<td>20</td>
<td>96hLC₅₀</td>
<td>0.210</td>
</tr>
<tr>
<td></td>
<td>25±1</td>
<td>20</td>
<td>96hLC₅₀</td>
<td>0.073</td>
</tr>
<tr>
<td>Neomysis sp</td>
<td>15</td>
<td>28</td>
<td>LC₅₀</td>
<td>0.267</td>
</tr>
</tbody>
</table>

2.4 Effect of residual chlorine on shellfish

Residual chlorine can reduce the sublethal parameters of shellfish, such as filter feeding rate, foot movement frequency, shell opening and closing frequency, oxygen consumption, bicus secretion, fecal discharge, and so on, so that shellfish lose the ability to adhere. When the residual chlorine concentration was lower than 1mg/L, shellfish could still open the shell for feeding, but the feeding rate decreased. MasiLamoni et al. suggested that the toxic mechanism of residual chlorine on shellfish may be as follows: (1) Chlorine directly harms the gill epithelial cells of shellfish; (2) Oxidation caused by chlorine destroys the respiratory membrane of shellfish, leading to anoxia and asphyxia in the body; (3) Chlorine directly participates in the oxidation of shellfish enzyme system.

2.5 Effects of residual chlorine on fish

Residual chlorine has a damaging effect on gill tissue, causing gill tissue lesions, such as tissue hyperplasia, epithelial tissue detachment, accumulation of large amounts of mucus in the gill, and formation of aneurysms, etc., thus affecting and obstructing the exchange of dissolved oxygen between the gill and the water. Residual chlorine may also penetrate into the blood through the gill tissue, oxidizing the reducing hemoglobin that can carry oxygen in the blood into methemoglobin that cannot carry oxygen, and inhibiting the activity of methemoglobin reducing enzyme, thus reducing the oxygen carrying ability of the blood.

Some fish can produce certain resistance to chlorine through their own regulation, improve their tolerance to chlorine. Lotts et al. believe that 0.04-0.08 mg/L residual chlorine can trigger the adaptation ability of cyprinids to chlorine, but the physiological and biochemical changes in this adaptation process are not clear.

The data show that fish have an obvious avoidance effect on residual chlorine in water. The Environmental Research Center of Virginia and the Institute of Ecology in the United States have conducted a comparative study on the avoidance effect of 10 fish species on fish, and found that the response concentration of residual chlorine avoidance ranges from 0.04 to 0.41mg/L[9].
## 2.6 Experimental results of ecological effects of residual chlorine

According to relevant research results, the toxicity mechanism of residual chlorine to aquatic organisms is mainly to destroy the ability of animals to absorb dissolved oxygen from water, and has obvious damage to the gill organs of fish, while the damage of prawn is relatively small, and it has an inhibitory effect on the development of fertilized eggs of shellfish. The toxicity of residual chlorine to aquatic organisms is related to the form, concentration, stress time and sensitivity of aquatic organisms to residual chlorine.

Generally speaking, the higher the concentration of residual chlorine in water, the greater the toxicity to aquatic organisms, the smaller the individual organisms, and the greater the sensitivity to residual chlorine. The results showed that the safe tolerance limit of residual chlorine to fish was 0.3mg/L, and the toxicity and lethal concentration of residual chlorine to fish and shrimp larvae were shown in Table 2 and Table 3. In addition, 0.5mg/L residual chlorine can cause 50% death of crustaceans, and 0.05mg/L residual chlorine can significantly inhibit the development of shellfish fertilized eggs. Residual chlorine has harmful effects on most entraining organisms, but the effect on phytoplankton is more obvious. 0.1–0.7mg/L residual chlorine can reduce their productivity by 50–90%. When the residual chlorine was 0.25–0.75mg/L, 50% of zooplankton died.

### Table 2

<table>
<thead>
<tr>
<th>Residual chlorine concentration (mg/L)</th>
<th>Oxygen consumption rate (mg/(h·g))</th>
<th>Survival rate (%)</th>
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<tr>
<td>0.00</td>
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<table>
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<tr>
<th>Residual chlorine concentration (mg/L)</th>
<th>Oxygen consumption rate (mg/(h·g))</th>
<th>Survival rate (%)</th>
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<th>Survival rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black snapper larvae</td>
<td></td>
<td></td>
<td>Penaeus prawns</td>
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<td>6.44</td>
<td>0.60</td>
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### References


