AN ASSESSMENT METHOD FOR ENVIRONMENTAL IMPACTS OF THE RESIDUE CHLORINE IN THE COOLING WATER EFFLUENT OF THERMAL (NUCLEAR) POWER PLANTS

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Abstract: For the vast cooling water flow of thermal (nuclear) power plants and the large amount of the Chlorine adding to prevent biofouling in the cooling water systems, the residue Chlorine is a severe threat to the water environment. How to properly estimate the impacting range and extent is an outstanding problem in the EIA field of thermal power plants. Based on former researches and EIA works, the authors present several case studies trying to answer the questions arising in different construction stages and different Chlorine adding methods, and make a comprehensive summary and discussion of the applicability of different methods, which include the in-situ monitoring and experimental method, the numerical method, and so on.

Key word: Residue Chlorine，Water environment，Field observational method, Field experimental method，Numerical method，Attenuation regularity，Convection and diffusion

1. INTRODUCTION

To maximally alleviate biofouling phenomenon in the cooling water system of thermal (nuclear) power plants, Chlorine adding method is widely used in most countries for its simplicity and convenience. In China it is the most widely used method in thermal (nuclear) power plants.

For those once-through cooling thermal (nuclear) power plants which use the Chlorine adding method for anti-biofouling purpose, a large quantity of warm water is discharged into the water body, and the residue Chlorine (RC) would also be carried into the water body. For the sake of the RC poisoning effect toward the aquatics and the potential accumulating effect toward the riparian ecosystem and even the human beings, along with the vast cooling water flow and the large amount of RC added, RC may make a severe threaten to the water environment, the RC impact upon the water environment is always an important question in the environmental impact assessment (EIA) of thermal power plants. In USA, the Chlorine criteria is set in two categories: in fresh water, CMC is $19 \mu g/L$, CCC is $11 \mu g/L$, while in salt water, the criteria are lowered to be $13 \mu g/L$ and $7.5 \mu g/L$ separately. The effluent RC concentration requirements by EPA are less than average 0.2 ppm for any 24 hours period and not exceed 0.5 ppm maximum level in 24 hours. In China the cooling water of power plants was once excluded from the sewage water and there is no such Chlorine water quality requirement yet, but in 2002 the cooling water effluent was regarded as sewage water in an explanatory reply letter of SEPA. So the RC adverse impact will unavoidably draw much more public attention. With the unsteady nature of residue Chlorine and the varied water flow

conditions, how to properly estimate the RC impacting range and extent remains an outstanding question. Based upon former research and EIA works, this article presents several case studies of different construction stages and different Chlorine adding methods, the experimental results and the range and the extent of the RC impacts are also illustrated. Furthermore, this article gives a summary about the different methods and tries to give an instructional advice to the question.

2. IN-SITU RC MONITORING METHOD

This method applies to the operating thermal power plants. Under the normal working condition, water samples are gathered from the receiving water body and analyzed in-situ to get the quantitative RC distribution in the water body near the discharge opening. To get an accurate result, attentions should be paid: 1) A reasonable sampling plan should be worked out by carefully studying the discharging and receiving water body conditions. 2) The analysis should be carried out as soon as possible. For the quick variation of RC concentration in the water, this method can give a direct measurement to the RC and thus gain a highest precision result. The shortage is the much higher cost and labor needed.

Case study: In-situ RC monitoring to the nearby water body of Daya Bay Nuclear Power Station.

The Daya Bay Nuclear Power Plant lies in the north coast of the Dashiao Bay in Shenzhen, Guangdong Province. The plant has an installed capacity of $2 \times 1000MW$, and uses the sea water direct flow cooling process with an cooling water flow of $108m^3/s$. The Chlorine adding process is as follows: NaClO was got by electrolyzing the sea water pumped and put in the cooling water at the intake. The adding amount varies in summer and winter, and the average concentration is 1.0 mg/L. The concentration in the warm effluent is 0.1−0.15 mg/L.

Sampling sites and frequency

The warm effluent is drained via an open channel into the sea. Sampling sites were determined regarding the tidal direction and the RC potential impacting range. Totally 18 sites were determined and were divided into 2 groups. The first group has 7 sites marked A−G along the open channel direction at intervals of 50m, with 3 sites before outlet terminal and 4 sites in the sea. The second group consisted of 2 sections including 10 sites and 1 site located at the bay mouth of Dashiao Bay and the sites were marked 1−11 respectively. They are shown in Fig. 1.

Sampling were carried out every season for a year and the bottom and surface water is sampled for each site.
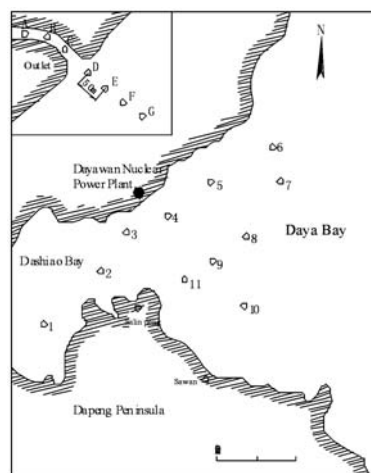

Fig. 1 the RC sampling sites distribution at the Dashiao Bay

Analytical method

The water samples were analyzed by DPD spectrophotometer method to get the total concentration and the different state concentration of the RC in the water. The RC includes the free state RC and the compounding state RC, the chloramines, which is formed by the reaction of Chlorine with the ammonia or the amino compound in the seawater. Iodine ion is added to catalyze the color development reaction of the chloramines with the DPD reagent, by controlling the adding amount and sequence of the iodine ion, three compounding states and the free state of the RC are measured separately.

Results and discussion

In-site monitoring results showed that the RC concentration has an average value of 0.01−0.02mg/L and a slightly seasonal variance with a lower concentration in summer and higher concentration in winter. The result is partly due to the higher temperature in the summer promoting the RC degradation. In planar distribution, the high value part lies in the drainage channel, and experiences a successive decrease along the discharge direction, the values at site A, B, C are 0.20, 0.17,and 0.13mg/L, while the concentration at the site D, E, F, G are 0.08,0.06,0.04,0.03 mg/L. Among the second group, the 4# site has a concentration of 0.03−0.04mg/L, the concentration at the sites near the northern coast are 0.02−0.03 mg/L, while the sites far from the coast have a concentration lower than 0.01mg/L. The RC concentration has an even vertical distribution, the bottom and the surface water does not have an obvious variance.

3. IN-SITU RC DEGRADATION EXPERIMENTAL METHOD

This method applies to the operating thermal power plant that adopted the regular interval adding method. Sampling can be done in-situ from the warm effluent during the Chlorine adding period to get the time taken for degradation to a relatively safe concentration. Compared with the length of no adding period, one can assess the impacting extent of the RC upon the impacted water body. This method has considered the influence of shining, water temperature, water quality and the partial dilution, but not considering the diffusion and dilution effect of the receiving water body, so the result is a conservative result. This method is rather simple and easy to carry out and has a high in-situ precision.

Case study: In-situ RC degradation experiment for the cooling water effluent of the Huaneng Shanghai Shidongkou Power Plant.

The plant is a coal-fired power plant having an installed capacity of $2 \times 600MW$ and a once-through cooling water flow of 38.24m^3/s. The cooling water is drawn from the tidal research of Yangtze river. Chlorine is added once a day at the amount of 286 kg in an hour; the RC concentration at the outlet is 0.25mg/L.

Experimental method

Sampling was carried out in-situ in the adding Chlorine period; the RC concentration, water temperature and pH were measured to get the concentration variation and the degradation velocity of the RC.

For the RC unstableness in the water, especially that containing organic compounds or reducing organic compounds, o-Tolidine spectrophotometric method was chosen to make a quick and easy done measurement. This method applies to measure the TRC (total residue Chlorine) and the free state Chlorine, with a minimum-detecting limit of 0.01mg/L. The RC can react with the o-Tolidine in the acid solution with a pH value of lower than 1.8 to form yellow quinonoid compound, this method can use the RC standard solution made up by the Potassium Dichromate - Potassium Chromate solution to carry out the spectrophotometric analysis.

Experimental result and analysis

In-situ experimental result is shown in Fig. 2.
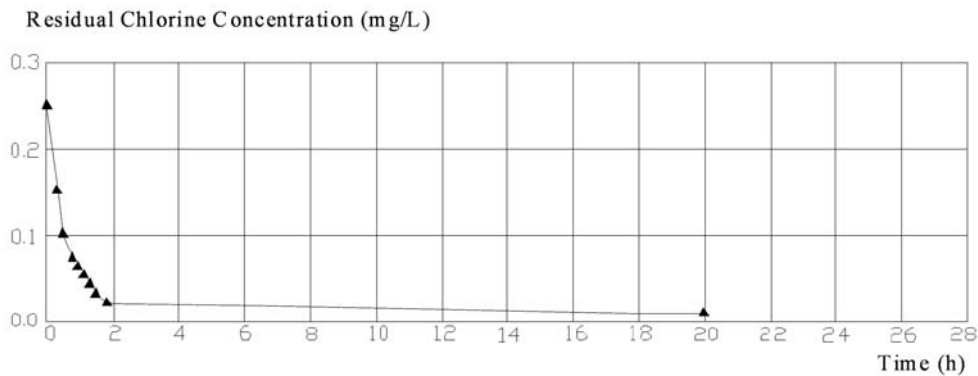
Residual Chlorine Concentration (mg/L)

Fig. 2 the RC degradation curve

The in-situ experimental results show that after a degradation time of as long as 9 hours, the RC concentration in the effluent can be degraded to the concentration safe for riparian organisms under the similar Chlorine adding condition as the Huaneng Shanghai Shidongkou Power Plant.

4. NUMERICAL SIMULATION OF THE FIRST-ORDER RC DEGRADATION REACTION DYNAMICS

This method originates from the research of Y. S. Lin etc. in 1983, and can be applied for not only the calculation of the RC impacts of the operating plant but also the impact forecasting and assessment of the power plants to be constructed.

4.1 The analysis of the dynamic characteristic of the degradation of the hypochlorus acid

After RC has entered into the receiving water body along with the warm effluent, the concentration distribution is determined by the convection, diffusion and dilution characteristic of the water body and RC chemical degradation.

Kim etc. has studied the degradation velocity of the monochloramine and found that the degradation velocity is the function of the concentration of the monochloramine, pH and water temperature. Also the expression of the function is conferred. The degradation velocity of monochloramine forms a first-order reaction relationship between the concentration of monochloramine:

$$r = -K_1 C [H^+]^n \tag{1}$$

Where, r is the velocity of NH_2Cl at unit durance and unit volume; C is the concentration of NH_2Cl; K_1 is the velocity constant; n is the reaction order. For an enclosed system, when pH is constant, exist the following formulas:

$$\frac{dC}{dt} = -KC \tag{2}$$

$$\ln \frac{C}{C_o} = -Kt \tag{3}$$

Where, $K = k_1 [H^+]^n$ is a constant; C_0 is the initial concentration of NH_2Cl.

Use the deionic water to carry out the degradation experiments at different concentration, temperature, pH, and sunlight, the following regularities are conferred:

1) When pH=7.4, the degradation reactions at fixed temperature and the ultraviolet ray irradiation follow the first-order reaction and has the same velocity constant, Fig. 3.
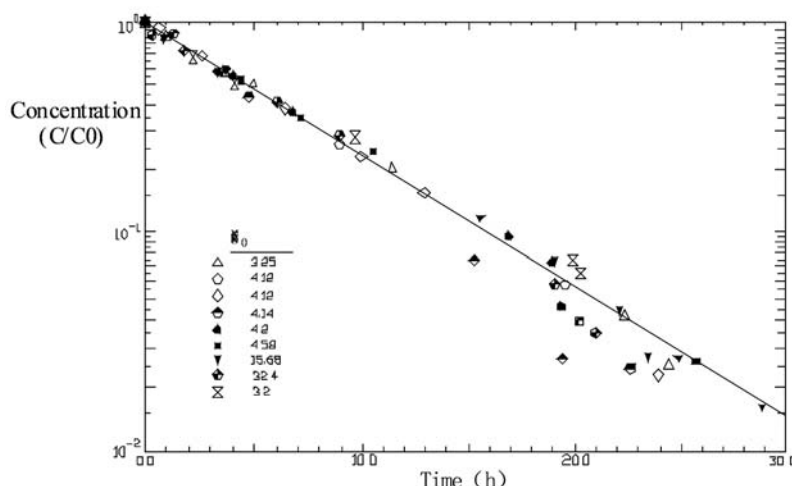
Fig. 3 the concentration attenuation of NH$_2$Cl in sunlight.

2) When pH=7.4, at the temperature variance range of 3−39.5℃, the degrading velocity constant K_{d1} is:

$$K_{d1} = 2428\exp[-5622/RT] \tag{4}$$

Where, R is the atmopheric constant; T is the temperature.

3) When pH is at 7.4−10.0 and the other condition remains unchanged, the degrading velocity constant K_{d2} is:

$$K_{d2} = 0.42[\text{H}^+]^{0.0636} \tag{5}$$

Combining the equation (4) and (5), the expression of degrading velocity constant K_{d2} that consider the pH and T is:

$$K_{d2}(\text{T,pH}) = 7180\exp(-5622/RT)[\text{H}^+]^{0.0636} \tag{6}$$

Equation (6) can apply to the situation that pH is 7.4−10.0, temperature is 3−39.5℃, and has a tolerance of 10% compared with the actual measurement value.

While in the river water the degrading velocity constant is also a first-order reaction on the whole. In order to correct the influence of the sunlight, a correcting coefficient Φ is introduced:

$$K_\gamma = \phi 7180\exp(-5622/RT)[\text{H}^+]^{0.0636} \tag{7}$$

Kr is the first-order velocity constant in the river water, Φ is 0.03 in the darkness and 0.491 in the sunlight.

From the upper analysis, one can confer that the most important factor is the illumination condition among all the impacting factors.

4.2 The numerical model of the RC distribution

The two dimensional transportation equation of the monochlomarine is:

$$-u\frac{dC}{dt} + E_x\frac{d^2C}{dx^2} + E_y\frac{d^2C}{dy^2} - KC = 0 \tag{8}$$

Where x is the longitudinal distance from the outlet, y is the transverse distance from the outlet; E_x, E_y is the diffusion coefficient in x, y direction respectively. At $x=0$, the concentration distribution in y direction is:

$$C = \frac{G}{\pi\sqrt{E_xE_y}}\sum\{(\frac{\pi}{2B})^{1/2}\exp[-B+\frac{ux}{2E_x}]\}$$

Where w is the river width; G is the material releasing velocity per unit length:

$$B = [\sqrt{ux^2 + (y - 2nw)^2 E_x / E_y} \bullet \sqrt{1 + 4KE_x / u^2}] / 2E_x$$

4.3 Case study

The interested power plant draws a flow of 900Cfs of the Tennas river water as the cooling water and discharges into the river. The receiving river segment is 450ft in width and 25ft in depth. The average flow is 4000Cfs. Use the equation (6) and (8) to forecast the NH_2Cl degrading velocity in darkness and sunlight. The related parameters are set as follows: pH=7.4; T=20℃;

$$E_x = A_x \frac{n}{1.49} g^{1/2} uH^{5/6}$$

$$E_y = A_y \frac{n}{1.49} g^{1/2} uH^{5/6}$$

Where A_x, A_y is position specific constant in x and y direction respectively, and is to be A_x=200, A_y=0.5; n is the roughness coefficient of the river bottom; g is the gravity acceleration velocity; H is the river water depth.

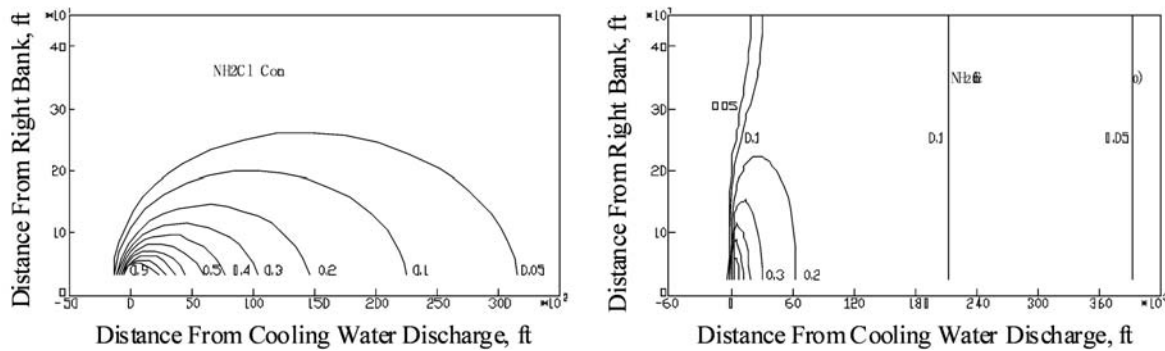The C/C_0 distribution in the river of NH_2Cl is shown in the Fig. 4.

Fig. 4 The NH_2Cl concentration distribution under the condition of darkness and sunlight

The calculation neglected the background Chlorine demand of the receiving water body, and didnot consider the vertical difference and water temperature variance in the bottom and surface.

The calculation result shows:

1) NH_2Cl degrading reaction complies with the first-order reaction regularity, and is influenced by the sunlight, water temperature and pH condition. The combination of the degrading velocity constant with the river pollutant transportation equation can make a forecasting of the NH_2Cl distribution in the river.

2) The degradation and diffusion are the main factors among those having influence upon the distribution, while the convection influence is rather small.

3) Under the sunlight condition, the maximum impacting range of that the concentration degrades to 5% of the initial RC concentration can reach the 56% of the river width, while in the darkness, the concentration degraded to 10% of the initial concentration can reach the opposite bank of the river. From these facts, one can see the illumination condition is obvious. So this result is consistent with the result of the reference article, which is a case study of a power plant located in the south bank of the Yantze River.

5. TWO-DIMENSIONAL CONVECTION-DIFFUSION NUMERICAL MODEL FORECASTING METHOD

In the project preliminary research period, for the uncertainties about the final decision and the limited data precision, it's necessary to get the rough estimation of the impacting range

and extent of the RC. The two-dimensional convection-diffusion numerical model mainly considers the influence of the convection, diffusion and the dilution effect of the receiving water body, and can harmoniously meet the estimation precision need in the project preliminary research.

5.1 TWO-DIMENSIONAL CONVECTION-DIFFUSION BASIC EQUATION GROUP

Continuum equation: $\dfrac{\partial \varsigma}{\partial t} + \dfrac{\partial (Hu)}{\partial x} + \dfrac{\partial (Hv)}{\partial y} = 0$

Momentum equation:

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} = -g\frac{\partial \varsigma}{\partial x} + fv - \frac{g}{C_f^2}\sqrt{\frac{u^2+v^2}{H}}u + \frac{\tau_{sx}}{\rho H} + \varepsilon\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right)$$

$$\frac{\partial v}{\partial t} + u\frac{\partial v}{\partial x} + v\frac{\partial u}{\partial y} = -g\frac{\partial \varsigma}{\partial y} - fu - \frac{g}{C_f^2}\sqrt{\frac{u^2+v^2}{H}}v + \frac{\tau_{sy}}{\rho H} + \varepsilon\left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2}\right)$$

Concentration equation: $\dfrac{\partial c}{\partial t} + u\dfrac{\partial c}{\partial x} + v\dfrac{\partial c}{\partial y} = \dfrac{1}{H}\dfrac{\partial}{\partial x}\left(HE_x\dfrac{\partial c}{\partial x}\right) + \dfrac{1}{H}\dfrac{\partial}{\partial y}\left(HE_y\dfrac{\partial c}{\partial y}\right) - Kc$

Where t is the time; c is the RC concentration; ξ is the tidal level; H is the actual water depth; u is the vertically average velocity in x direction; v is the vertically average velocity in y direction; f is the coriolis force coefficient; g is the gravity acceleration; C_f is the Chezy's coefficient; ρ is the environmental water density; τ_{sx}, τ_{sy} is the water surface wind stress in x and y direction respectively; ε is the turbulent viscosity coefficient; E_x, E_y is the RC concentration diffusion coefficient in x, y direction; K is the RC degrading coefficient.

5.1.1 Case study

The EIA research about RC impact upon the water body in the 2nd stage construction of the Huaneng Dalian Power Plant.

The plant lies in the monk island in the north of the Dalian Bay of the Liaodong Peninsula, and the 1st stage has an installed capacity of 2×350MW, the 2nd stage will install another 2×350MW capacity. The cooling water is pumped from the Dalian Bay. When the 2nd stage finishes, the cooling water flow can amount to be 42.5m^3/s. The continuous Chlorine adding method with the subsidiary impulse Chlorine adding method is adopted with the adding concentration being 1.0mg/L. The discharging concentration is 0.15mg/L; the effluent concentration during the impulse adding period is 0.45mg/L.

5.1.2 Parameterization

The turbulent viscosity coefficient ε =10.0m^2/s; the roughness coefficient n =0.025; the concentration diffusion coefficient E_x= E_y = 20.0m^2/s. The RC's degrading coefficient K is chosen on the assumption that the RC concentration complies with the regularity $C=C_0e^{-Kt}$, where C_0 is the initial concentration, $K=\ln2/t_{1/2}$, $t_{1/2}$ is the time taken to degrade to be the 50% initial concentration. $t_{1/2}$ is set to be 3600s by the analysis of the experimental result.

5.1.3 Forecasting result

The calculation result is shown in Table 1 and Fig. 5.

Table 1 the RC impacting range of the 2nd stage of the Dalian Power Plant (km)

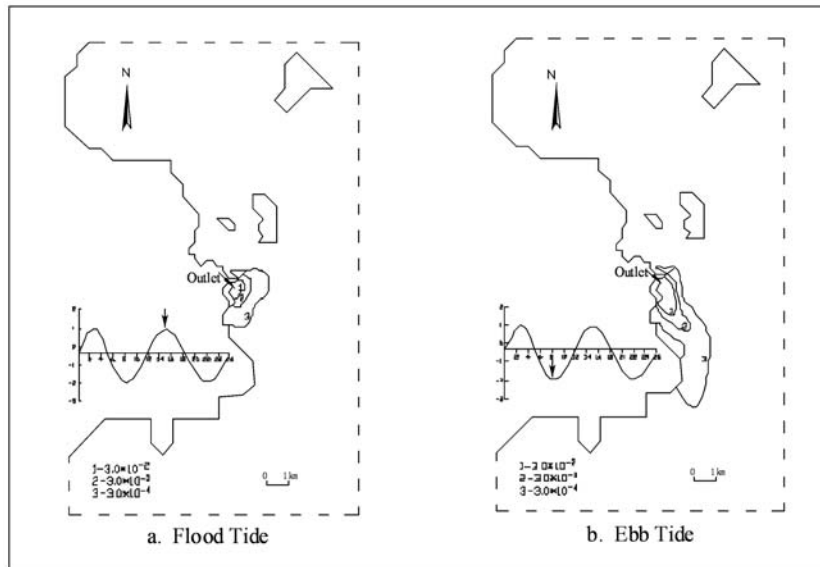| Concentration(mg/L) \ Tide	0.05	0.02	0.01	0.001
flood tide	0.058	0.193	0.349	0.489
ebb tide	0.033	0.194	0.388	0.764
Average	0.039	0.194	0.374	0.616

Fig. 5 The RC concentration distribution during the flooding and ebbing tide

6. CONCLUSION

How to get the range and the extent of the RC impact upon the water environment and make a quantitative analysis for the impact remains an outstanding question in the EIA field of thermal (nuclear) power plants. Based on the former research work and EIA work, this article makes a summary of the different methods and corresponding case studies, and discusses the applicability of those methods including in-situ monitoring, in-situ experiment, numerical method and the integration of the numerical and experimental methods. Based on the results of the presented case studies, the range and extent of the RC impacts by different Chlorine adding patterns are also discussed. Finally the authors develops the principal of method choosing based on the different construction stages of thermal (nuclear) power plants, it can be expected to efficiently serve as a powerful tool for the EIA and post-assessment of the thermal (nuclear) power plants.

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