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Study on the Killing Effect of Sodium Hypochlorite and Benzalkonium Bromide and the Compatibility of Them with the Scale and Corrosion Inhibitor

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Abstract. The killing effect of sodium hypochlorite and benzalkonium bromide and the compatibility of them with the scale and corrosion inhibitor in the seawater is studied in the paper. The research result shows that sodium hypochlorite and benzalkonium bromide have good killing effect, sodium hypochlorite or benzalkonium bromide is not only compatible with a scale inhibitor, also compatible with a corrosion inhibitor formulation.

Introduction

One of the most effective and common method to control microorganism growth in the cooling water system is to add killing agent into the cooling water.

From the investigated market situation, there are many kinds of biocides, most of them are used in the freshwater cooling system, and fewer is aiming at the complex seawater cooling system. Because there are many types of marine organisms in seawater, the higher requirement for the biocide performance is put forward. With the improvement of environmental protection consciousness, the traditional efficient biocide is gradually restricted to be used. In order to balance the environmental protection, economic benefits and the killing effect, the killing method to combine the traditional biocide chlorine with the non oxidizing biocide, such as to combine sodium hypochlorite with quaternary ammonium salt, is chosen. [1-13]

Test Methods

The Test Method for Killing

Take 5 reagent bottles of 1000 mL, 800mL seawater sample and sodium hypochlorite or benzalkonium bromide with different dosage are added in each bottle, and bottles are placed in the water of the constant temperature water-bath at 45℃. After biocide is added in the seawater, sampling analysis of residual chlorine and bacteria is immediately done, and it is done again after 2h.After 24h, sampling analysis of residual chlorine and bacteria should be done and a certain amount of biocide is added in each bottle to make the biocide concentration double, then sampling analysis of residual chlorine and bacteria is done. After 48h, sampling analysis of residual chlorine and bacteria should be done.

The Scale Inhibition Effect Test Method of The Scale Inhibitor

Add the scale inhibitor and biocide with a certain concentration in a certain seawater, and the seawater is condensed to specific multiple. When the seawater is condensed, to observe by macroscope that there is or not water scale formed, water quality is determined to estimate scaling trend of the water sample and compare the scale inhibition effect change of the scale inhibitor before and after the biocide added.

The Inhibition Effect Test Method of the Corrosion Inhibitor

Add the corrosion inhibitor and biocide with a certain concentration in a certain seawater. When the specimens of carbon steel Q235 are hung in the seawater, to observe by macroscope that the surface of the specimens changes or not. Determine the surface area and the mass of the specimens before and after test, and calculate the corrosion speed and the inhibition efficiency, and compare the inhibition effect change of the corrosion inhibitor before and after the biocide added.

The Water Quality of the Test Seawater

The test seawater is from Zhuhai cross drain, provided by Guangdong Power Grid Electric Power Science & Research Institute. The conventional water quality analysis result of the seawater is shown in table 1.

Table 1. The conventional water quality analysis result of the seawater

No.	Analysis item	Unit	Result	No.	Analysis item	Unit	Result
1	Total solid	mg/L	23210.00	17	Mg^{2+}	mg/L	750.39
2	Dissolved solid	mg/L	22400.00	18	NH_4^+	mg/L	< 0.10
3	Suspended solid	mg/L	810.00	19	F^-	mg/L	< 0.10
4	Total hardness	mmol/L	40.60	20	Cl^-	mg/L	11525.82
5	Carbonate hardness	mmol/L	2.20	21	NO_2^-	mg/L	< 0.10
6	Non-carbonate hardness	mmol/L	38.40	22	NO_3^-	mg/L	6.10
7	Total alkalinity	mmol/L	2.20	23	SO_4^{2-}	mg/L	1694.38
8	Phenolphthalein alkalinity	mmol/L	0.00	24	PO_4^{3-}	mg/L	< 0.10
9	Free carbon dioxide	mg/L	12.76	25	HCO_3^-	mg/L	134.38
10	All silicon	mg/L	2.55	26	CO_3^{2-}	mg/L	0.00
11	Activated silica	mg/L	2.49	27	OH^-	mg/L	0.00
12	Non-activated silica	mg/L	0.06	28	pH(25^0C)	/	7.44
13	Chemical oxygen demand(COD_{Mn})	mg/L	11.78	29	Total iron	mg/L	0.12
14	K^+	mg/L	203.57	30	Turbidity	NTU	1.56
15	Na^+	mg/L	6882.43	31	Electrical conductivity	ms/cm	32.40
16	Ca^{2+}	mg/L	218.07				

The Killing Effect of Sodium Hypochlorite and Benzalkonium Bromide

The killing effect of sodium hypochlorite or benzalkonium bromide with different dosage is shown in table 2, and the killing effect of sodium hypochlorite with 8mg/L or benzalkonium bromide with 5mg/L is shown in table 3.

Table 2. The killing effect of sodium hypochlorite or benzalkonium bromide with different dosage

Biocide	Concentration (mg/L)	Time (h)	Residual chlorine(mg/L)	Bacterium number /mL
Seawater (blank)	/	/	/	1.8×10^6
NaClO	4	0	0.8342	1.8×10^6
		2	/	3×10^5
		24	0	/
		24(biocide is added again)	0.8342	1.0×10^6
		48	0	/
NaClO	8	0	2.5025	1.8×10^6
		2	/	2×10^5
		24	0	/
		24(biocide is added again)	3.7537	8×10^5
		48	0	/
Benzalkonium bromide	1.25	0	/	1.8×10^6
		2	/	4×10^5
		24	/	/
		24(biocide is added again)	/	4×10^5
		48	/	/
	2.5	0	/	1.8×10^6
		2	/	2×10^5
		24	/	/
		24(biocide is added again)	/	2×10^5
		48	/	/

Table 3. The killing effect of sodium hypochlorite with 8mg/L or benzalkonium bromide with 5mg/L added in the seawater for 2h

Water sample	Bacterium number /mL	
Seawater (blank)	1.5×10^6	1.7×10^6
Seawater +NaClO (8mg/L)	4×10^5	4×10^5
Seawater + benzalkonium bromide (5mg/L)	2×10^5	2×10^5

As shown in table 2 and table 3, the killing effect of sodium hypochlorite with 4mg/L or 8mg/L and benzalkonium bromide with 1.25mg/L, 2.5 mg/L and 5mg/L added in the seawater for 2h is good.

The Compatibility of Sodium Hypochlorite and Benzalkonium Bromide with the Scale Inhibitor

Because there are the scale inhibitor (6.25mg/L PESA +6.25mg/L HPMA) and 50mg/L 5% benzalkonium bromide (amount to 5mg/L benzalkonium bromide) included in the corrosion inhibitor formulation, when the scale inhibiting effect of the corrosion inhibitor formulation in the seawater is tested, the compatibility of benzalkonium bromide with the scale inhibitor is tested. The scale inhibiting effect of the corrosion inhibitor formulation with 8mg/L NaClO added in the seawater is tested. All the test results are shown in table 4.

As shown in table 4, the scale inhibiting effect of the scale inhibitor (6.25mg/L PESA +6.25mg/L HPMA) in the seawater is not effected by sodium hypochlorite or benzalkonium bromide, namely sodium hypochlorite or benzalkonium bromide are compatible with the scale inhibitor (6.25mg/L PESA +6.25mg/L HPMA).

Table 4. The scale inhibition effect of the corrosion inhibitor formulation with scale inhibitor (PESA6.25mg/L+HPMA6.25mg/L) in the seawater when sodium hypochlorite or benzalkonium bromide is added

Test medium	Concentration multiple					ΔA	Test phenome-non
	Expres-sed by volume	Expressed by calcium hardness	Expressed by total hardness	Expre -ssed by Cl^-	Express-ed by alkalinity		
Seawater (blank)	2.48	2.52	2.43	2.52	1.63	0.89	Seawater cloudy and white scale formed
Seawater + scale inhibitor (PESA6.25mg/L+HP MA 6.25mg/L)	2.5	2.42	2.50	2.48	2.43	0.05	Seawater transpare-nt
Seawater + the corrosion inhibitor formulation with scale inhibitor (6.25mg/L PESA+6.25mg/L HPMA）and 2.5 mg/L benzalko- nium bromide	2.31	2.52	2.43	2.52	3.05	-0.54	Seawater transparent
Seawater + the corrosion inhibitor formulation with scale inhibitor (6.25mg/L PESA +6.25mg/L HPMA）and 2.5mg/L benzalkoni- um bromide + 8mg/L NaClO	2.31	2.34	2.23	2.28	2.27	0.01	Seawater transpare -nt with few scum and adherentcrysta lline grain

(Notes: ΔA is the difference between concentration multiple expressed by Cl^- and expressed by alkalinity)

The Compatibility of Sodium Hypochlorite and Benzalkonium Bromide with the Corrosion Inhibitor

Because there is 50mg/L 5% benzalkonium bromide (amount to 5mg/L benzalkonium bromide) included in the corrosion inhibitor formulation, benzalkonium bromide is not only biocide but also corrosion inhibitor component, namely the biocide benzalkonium bromide is compatible with the corrosion inhibitor formulation. In order to research further the compatibility of sodium hypochlorite and benzalkonium bromide with the corrosion inhibitor, the inhibition effect to carbon steel of the corrosion inhibitor formulation with NaClO or benzalkonium bromide added in the seawater is tested, and the test result is shown in table 5.

As shown in table 5, when the biocide sodium hypochlorite or benzalkonium bromide is added in the seawater, the inhibition effect of the corrosion inhibitor formulation to Q235 carbon steel in the seawater isn't affected by them, namely the biocide sodium hypochlorite or benzalkonium bromide is compatible with the corrosion inhibitor formulation.

Table 5. The inhibition effect of the corrosion inhibitor formulation to Q235 carbon steel in the seawater when sodium hypochlorite or benzalkonium bromide is added (50℃, 72h)

Test medium	No.	S (cm^2)	m_1(g)	m_2(g)	Δm (mg)	V^- ($g/m^2.h$)	V_h (mm/a)
Seawater concentrated 2 times + the corrosion inhibitor formulation	#6	25.589	11.6725	11.6601	12.4	0.0673	0.0746
	#7	26.319	13.6820	13.6699	12.1	0.0639	0.0708
Seawater concentrated 2 times + the corrosion inhibitor formulation +8mg/L NaClO	#8	26.286	14.2819	14.2699	12.0	0.0634	0.0703
	#9	26.019	14.5669	14.5546	12.3	0.0657	0.0728
Seawater concentrated 2 times + the corrosion inhibitor formulation +100mg/L 5% benzalkonium bromide	#14	26.748	14.6745	14.6624	12.1	0.0628	0.0697
	#16	26.815	15.6198	15.6073	12.5	0.0647	0.0718

(Notes: No.-Specimen number, S-surface area, m_1-the mass of the specimen before it is immersed in the test medium, m_2-the mass of the specimen after it is taken out from the immersed test medium and cleaned by acid, $\Delta m = m_2 - m_1$, V^- - corrosion rate expressed by mass change, V_h - corrosion rate expressed by variation in thickness)

Conclusions

Sodium hypochlorite and benzalkonium bromide have good killing effect. Sodium hypochlorite or benzalkonium bromide is not only compatible with a scale inhibitor, also compatible with a corrosion inhibitor formulation.

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