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Study on emergency treatment of minor oil leakage of closed circulation cooling water system

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Abstract. With the increasing shortage of water resources and the requirements of environmental protection, the closed circulation cooling water system will inevitably usher in a larger application space. However, when the leakage of the system, especially minor oil leakage, occurs, which is common and inevitable, the water quality of closed circulation cooling water will be deteriorated, and the cooling efficiency of the system will be affected due to the limited drainage and water refill. In view of such situations, this paper focuses on the slight oil leakage in the closed circulation cooling water system of Shaanxi Natural Gas General Plant, through the analysis of the water quality of the closed circulation cooling water system and the system basket filter intercepts in the case of slight oil leakage, with the experimental device of rotary hanging piece method and the inoculation of fresh intercepts to simulate the field conditions of slight oil leakage, the treatment effects of different treating agents are studied. The results show that: In the case of slight oil leakage in the closed circulation cooling water system, the corrosion of carbon steel and stainless steel increases and the corrosion of carbon steel is more serious than that of stainless steel. The metal material attached to the system is mainly corrosion products, and the bactericidal stripping agent SW-01 has almost no effect on the stripping effect of corrosion products, with excellent bactericidal effect. After 6 days of , 3.0g/L of the corrosion inhibition stripping agent HS-01 was added, the peeling effect of corrosion products was obvious, and the peeling effect of 0.3g/L biological dispersant was improved to a certain extent, but not particularly obvious. The peeling effect of the fixtures could be completed on the 9th day. This treatment method can make the corrosion rate of carbon steel and stainless steel fully meet the requirements of circulating cooling water under the condition of little drainage and large water refill, and the peeling effect of the fixtures is obvious. The effect can meet emergency handling requirements.

Keywords: Closed circulation cooling water; oil leakage; Corrosion inhibition; Stripping.

1. Introduction

With the increasing shortage of water resources and the requirements of environmental protection, the closed circulation cooling water system will inevitably usher in a larger application space [1-4]. However, when the system leaks, especially slight oil leaks, which is common and inevitable [5-8], the metal surface of the heat exchange equipment will be covered by oil film and the thermal conductivity will decrease, which will affect the contact between the water treatment agent and the metal surface to a certain extent. The protective film effect is hindered to give full play to, and the corrosion problem of equipment deteriorates [9,10]. If not treated in time, oil products will also provide nutrient support for the breeding and propagation of microorganisms, promote the large-scale breeding of sulfate-reducing bacteria, and continuously increase the

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turbidity of circulating water, which will have a great negative impact on the operation effect of heat exchange equipment [8,11-12]. Moreover, the cooling efficiency of the system will be seriously affected due to the limited drainage and water refill. However, the existing literature is all about the countermeasures of material leakage in the open circulating cooling water system [13-18], and there are few literatures about this aspect for the closed circulating cooling water system that cannot carry out large drainage and large replenishment. The closed cooling tower of Shannbei Natural Gas General Plant provides circulating cooling water to the water cooler, compressor motor and frequency converter in the process plant area, air compressor in the air nitrogen station, heat medium circulating pump and steam condenser in the heating system, so as to achieve the purpose of cooling the heat exchange medium. There are many internal ports in the system with high leakage risk. After running the system for more than two years, the water quality of the closed circulation cooling water system deteriorates and the water contains oil, and the heat transfer effect is not ideal. It is urgent to study the emergency treatment methods for minor oil leakage in the closed circulation cooling water system under the condition of little drainage and large water replenishment, and to provide reference for the problems existing in similar systems.

2. Material and method

2.1 Reagent and instrument

Petroleum ether, hydrochloric acid, sodium hydroxide, silver nitrate, methyl red, barium chloride, phenolphthalein and methyl orange were all analytically pure. Bactericidal stripping agent SJ-01, corrosion inhibition stripping agent HS-01, biological dispersant SW-02 are all industrial products. D/MAX-2400 model X-Ray Diffraction (XRD), Nissei Corporation, Japan); Quantu 600F Scanning electron microscope (SEM), FEI Corporation, USA.

2.2 Method for analysis of intercepts in closed circulating water basket filter

After drying, the samples were ground fine in a mortar for reserve use. The oil content was determined by extraction with petroleum ether, and the samples were calcined at 550℃ for 2h in Muffle furnace to determine the calcined reduction. The calcined plugging products were dissolved by adding acid to the filtrate to measure the cation content, and the filter slag was used to determine the acid insoluble content. D/MAX-2400 X- ray diffractometer was used to analyze the crystal composition of the dried clog products.

2.3 Emergency treatment of minor oil leakage

According to the method specified in GBT 18175-2014 "Determination of Corrosion Inhibition Performance of Water Treatment Agent Rotary Hanging Piece Method" and combined with the field process parameters, the emergency treatment method for minor oil leakage was studied. The experimental water was taken from the closed cycle cooling water of Shanbei Natural Gas General Plant, nitrogen was used for deaeration for 30min, and the working pressure was 0.6MPa. According to the position of the hanging piece in the simulated pipeline, the linear flow velocity is 1m/s, and the temperature is 38℃. Reaction time of reactor: 72h. Combined with the characteristics of closed circulating water pipe in Northern Shaanxi Natural Gas General Plant, 20# steel, Q345R, S31603 and S22053 were selected, with 3 pieces of each material. The experimental equipment is shown in Figure 1. Before hanging into the reactor, the electronic balance was weighed, the blank experiment was carried out for 3 days, and then the fresh basket filter intercepts from the site were inoculated into the system. The initial number of bacteria and the content of heterotrophic bacteria in the process were measured at different times, and different agents were added for mud stripping, sterilization and corrosion inhibition evaluation experiments, and the surface morphology of the hanging pieces was observed.

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3. Result and discussion

3.1 Water quality of closed circulating cooling water in different periods

Table 1 shows the water quality analysis results of closed circulating water at different periods.

Table 1.Water quality analysis results of closed circulating water at different periods

Item	Demineralized water	Closed circulating water
pH	9.44	8.31
Ca2+(mg/L）	10.02	15.03
Mg2+(mg/L）	Negative	6.08
Turbidity（mg/L）	0.1	4.43
Conductivity（μs/cm）	16.8	84.5
Oil(mg/L）	Negative	2.87
Total hardness（CaCO3）（mg/L）	25.02	62.57
Heterotrophic bacterium（CFU/mL）	0	6.0×102

As can be seen from Table 1, the water quality of closed circulating water deteriorates, resulting in oil pollution and increased bacterial content.

3.2 Analysis of the trapping properties of the closed circulating water basket filter

The intercepts were taken from the closed circulating water basket filter, and the appearance of the intercepts after drying in the basket filter and after being calcined at 550℃ by petroleum ether extraction was shown in Figure 1, the residue after petroleum ether extraction was analyzed by X-ray diffraction, and the analysis results were shown in Figure 2. The physical properties of the intercepts in the basket filter were analyzed in Table 2.

Figure 1 The basket filter intercepts after drying and after oil extraction and 550℃calcination

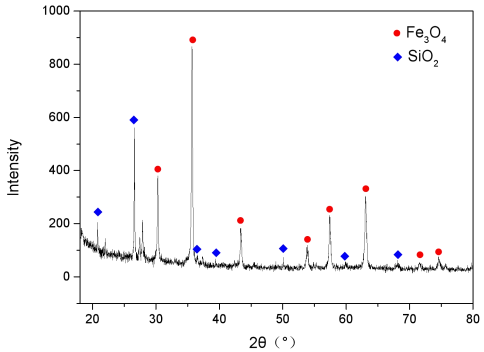

Figure 2 XRD analysis of the closed circulating water plug

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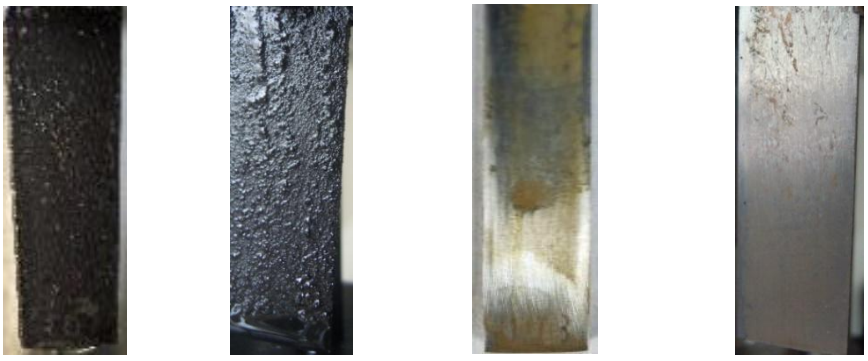
Table 2 Results of the analysis of the physical properties of the basket filter (Dry weight, w/w, %)

Composition	Oil	550℃ burning reduced	Crystalline inorganic (XRD, 100% calculation)		Acid insoluble matter after burning	Acid soluble matter after burning			
			SiO2	Fe3O4		Total	∑Fe	Ca2+	Mg2+
Content	4.37	8.96	23.3	76.7	5.46	81.34	38.01	0.5694	0.2541

Figure 1, figure 2 and Table 2 show that after drying, the intercepts contain 4.37% oil, 8.96% organic matter and 5.46% acid insoluble matter, mainly SiO_2. In the intercepts, the main components of crystalline inorganic matter are Fe_3O_4 and SiO_2, while the amorphous inorganic matter is Fe_2O_3 and $FeCO_3$.

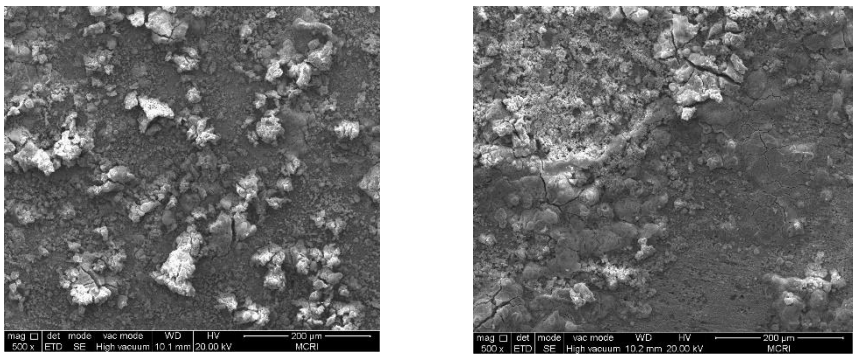
3.3 Study on emergency treatment methods for minor oil leakage

In the case of simulated slight oil leakage, the appearance of hanging pieces of different materials 3 days after inoculation of basket filter intercepts is shown in figure 3. The scanning electron microscope photos of hanging pieces with more surface adhesions are shown in figure 4. the comparison of corrosion rates of different materials at different treatment stages is shown in figure 5.The stripping of adhesion on the surface of 20# steel at different emergency treatment stages is shown in Table 3.



20# Q345R S31603 S22053

Figure 3. Appearance of different materials after inoculation of basket filter intercepts for 3 days



Q345R 20#

Figure 4 SEM photos of Q345R and 20# steel inoculated basket filter after retention

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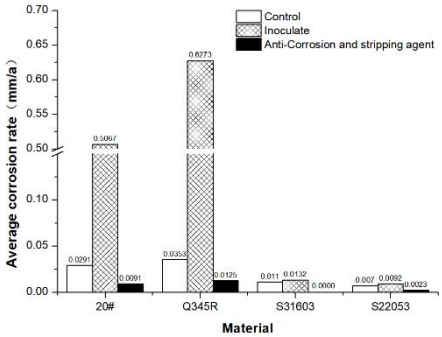
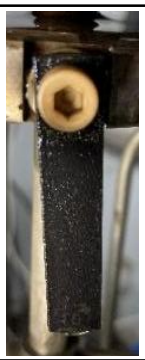
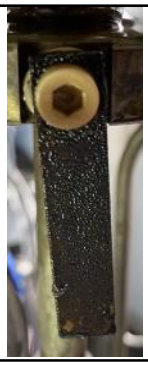


Figure 5 Comparison of corrosion rates of different materials at different treatment stages

Table 3 Comparison of corrosion products and stripping conditions on the surface of 20# steel hanging sheet at different treatment stages and changes in heterotrophic bacteria content

Time	Inoculation					
	Day 3	Day 6	Day 9	Day 12	Day 15	Day 18
Step	SJ-01 300mg/L	HS-01 3.0g/L	Drain 1% water and add the same amount of debrine (HS-01 3.0g/L)	Drain 1% water and add the same amount of debrine (HS-01 3.0g/L, SW-01 0.3g/L)	Drain 1% water and add the same amount of debrine (HS-01 3.0g/L)	Finished
Corrosion products, and stripping conditions						
Heterotrophic bacterium （CFU/mL）	6.0×102	2.0	3.0×101	1.0×101	1.3×102	6.0×102

Note: The area with poor peeling effect at the lower end of the hanging piece 18 days after inoculation is the coded steel mark area of the hanging piece, and the high roughness will affect the peeling effect of the attachment.

As shown in figure 3-5, corrosion rate of 20#, Q345R, S31603 and S22053 increased significantly after inoculation with fresh residues. Corrosion rate of carbon steel was higher than that of stainless steel, and there were a large number of attachments on the surface (FIGURE 4). Combined with the change of corrosion rate and scanning electron microscopy (FIGURE 8), it can be seen that the adhesion on the surface of carbon steel is mainly corrosion products, and the stripping and corrosion inhibition effects are good after the addition of corrosion inhibition stripping agent (Table 3). After 3.0g/L of corrosion inhibition stripping agent HS-01, the stripping effect of corrosion products is obvious 6 days later, and 0.3g/L of biological dispersant continues to be added. The peeling effect was improved to a certain extent but not particularly obvious. The peeling was basically completed on the 9th day, and the corrosion rate of metal materials 20#, Q345R, S31603 and S22053 met the requirements of circulating cooling water.

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4. Conclusion

(1) After drying, the basket filter intercepts contain 4.37% oil, 8.96% organic matter and 5.46% acid insoluble matter, mainly SiO2. In the intercepts, the main components of crystalline inorganic matter are Fe3O4 and SiO2, and the amorphous inorganic matter is Fe2O3 and FeCO3.

(2) The corrosion rate of 20#, Q345R, S31603 and S22053 increased significantly after inoculation of fresh interception. The corrosion rate of carbon steel was higher than that of stainless steel. There were a large number of attachments on the surface, which were mainly corrosion products.

(3) Adding bactericidal peeling agent SJ-01 300mg/L can effectively reduce the content of heterogeneous bacteria in the system without large drainage and water replenishment. The peeling effect was obvious on the 6th day after the addition of corrosion inhibition peeling agent 3.0g/L. The peeling effect of biological dispersant SW-01 0.3g/L was improved to a certain extent, but not particularly obvious. The stripping of the attachments can be completed on the 9th day. The addition of corrosion inhibition stripping agent HS-01 3.0g/L and biological dispersant SW-01 0.3g/L can effectively deal with the adhesion of corrosion products on the metal surface caused by long-term oil leakage and reduce the content of heterotrophic bacteria. The corrosion rate of metal materials meets the standard requirements.

Reference

[1] Wang Xiaomin. Discussion on the design of closed circulation cooling water system [J]. Industrial Water and Wastewater,202,53(04):61-64.

[2] Bo Liu, Yufei Wang, Xiao Feng. Optimization of circulating cooling water systems based on chance constrained programming[J]. Chinese Journal Journal of Chemical Engineering, 201,40(12):167-178.

[3] Sun Xiuhui, Zhang Di, Guan Xiaolong. Design of closed circulation cooling water system of natural gas pipeline compressor station [J]. Oil & Gas Field Surface Engineering,2018,37(06):49-51.

[4] Jiaze Ma, Chen Li, Fuyu Liu. Optimization of circulating cooling water networks considering the constraint of return water temperature [J]. Journal of Cleaner Production,2018,199:916-922.

[5] Lu Wenqiong. Application of solid phase microextraction technology in the detection of hydrocarbon distribution of micro-leakage oil in circulating water system [J]. Petroleum Refining and Chemical Industry, 2005,36 (3) : 51-54.

[6] Yang Zunjian. Study on the hazards of leakage materials in petrochemical plant to circulating water treatment [J]. Chemical Management, 2020 (11) : 67-68.

[7] Yan P. Influence and Countermeasures of material leakage in circulating water system of petrochemical enterprises [J]. China Water Supply and Drainage, 2006 (10) : 90-93.

[8] Huiyun Zhong, Fang Liu, Jinjin Lu. Effect of diesel leakage in circulating cooling water system on preponderant bacteria diversity and bactericidal effect of biocides[J]. Environmental Technology, 2015, 36(9):1147 -- 1159

[9] Chen Hongxia, Wang Yunjuan, Peng Wei. Analysis of influence of light oil leakage on circulating water system and treatment measures [J]. Total Corrosion Control,2017,31(11):1-4.

[10] Huang Kegen. Leakage detection of water cooler and cleaning of circulating water System in Refinery [J]. Corrosion and Protection in Petrochemical Industry,2004(05):42-43+47.

[11] R. Liang, J. Li, M. Liu, Z.Y. Huang. Influence of inhibitors on the adhesion of SRB to the stainless steel in circulating cooling water [J]. Colloids and Surfaces B: Biointerfaces,2018(172):1-9.

[12] Yu Qi, Jin Li, Rui Liang. Chemical additives affect sulfate reducing bacteria biofilm properties adsorbed on stainless steel 316L surface in circulating cooling water system[J]. Front. Environ. Sci. Eng. 2017, 11(2): 14

[13] Yang Yanqiu, Cui Meijuan, Yu Baowei. Analysis and treatment of material leakage in circulating cooling water system [J]. Industrial Water and Wastewater, 2009, 40 (2) : 56-57. (in Chinese)

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[14] Feng Jianqing. Feasibility study on the stable operation of circulating water system with high concentration ratio under leakage background [J]. Environmental Protection of Petrochemical Industry, 2002 (3) : 63-64.

[15] Pan Xinming, Ma Weidong, Shi Ke, et al. Application of highly dispersible pharmaceutical formulation in oil leakage circulating water system [C]//. Proceedings of the Third National Annual Meeting of Water Treatment Chemicals Industry.[Publisher unknown],2007:271-275.

[16] Ye Hongcheng. Water Quality analysis and treatment of Different Materials Leakage in circulating water system of Oil Refinery [J]. Petrochemical Technology,20,27(08):18-19.

[17] Wang Wei, Zhao Xiaolei, Yan Lianhe. Experimental study on the treatment of oil leakage in circulating water by microbial degradation technology [J]. Industrial Water Treatment,2002(12):16-18.

[18] Shixin Zhao, Lida Wang, Wen Sun. Synergistic sterilization effects produced by weak electrolysis process in simulated industrial circulating cooling water[J]. Separation and Purification Technology, 2022, 292:121011.