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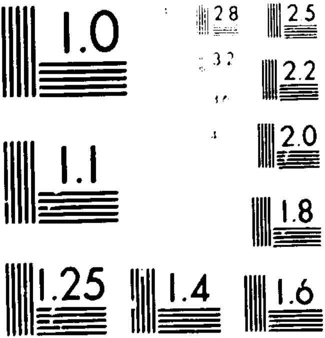
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TREATMENT OF RECIRCULATION COOLING WATER IN A NITROGENOUS FERTILIZER PLANT*

by

Feng Hua-you**

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** Engineer, Cangzhou Chemical Fertilizer Plant, Hebei Province, People's Republic of China

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ABSTRACT

This article presents the chemical treatment of recirculation cooling water in Cangzhou Chemical Fertilizer Plant at the first three stages after it was put into operation in October, 1976. At the initial stage of operation, the production was fluctuated due to the improper treatment of water. Now the production of nitrogenous fertilizer will be never in danger of the quality of recirculation cooling water because the appropriate chemical treatment formulation has been selected according to the water quality of the plant, the control of microbes and management of field operation enhanced and the shell side of carbon steel water coolers protected with a corrosion-resistant paint.

It is important for a nitrogenous fertilizer plant to have a normal operation of recirculation cooling water system. A proper treatment of recirculation cooling water will obtain a normal operation, otherwise the production will be impared. Our plant (including ammonia unit and urea unit) was actually put into operation in 1976. At the initial stage, due to the negligence and improper treatment of the recirculation cooling water, the following consequences were brought about:

1. The heat transfer coefficient was reduced due to the corrosion and fouling in some water coolers. Sometimes the temperature of process gas was occasionally higher than that of design specification.

2. Leakage was found in some water coolers, with a service time less than one year due to comparatively high corrosion rate of water coolers. Therefore, the replacement period of water coolers was shorter than the normal period required.

3. The ammonia unit had to be shut down three times during the period from October 1976 to May 1977 due to the leakage of water coolers and the elimination of leakage or replacement of water coolers. In

result, the continuous long-term operation could not be realized. During this period the maximum operation days was only 128 days, thus resulting in low output and high energy consumption.

For this reason we enhanced the work for treatment of recirculation water and made the improvements on the following points, thus fundamently solving the above problems and getting rid of a "water" threat against the ammonia and urea production.

1. Selection of the chemical treatment formulations appropriate to the water quality:

The make-up water in our plant contains very low content of calcium and higher corrosive ions like chlorine ions (see Table 1). Therefore, the water appears relatively strong corrosion. In order to avoid corroding the stainless steel water coolers in the urea unit by chlorine ions, the chlorine ions should be kept less than 275 ppm, with only 2.1 concentration times. The calcium content is still very low with the above concentration times. At the initial stage of production we used the formulation of phosphate with no zinc added, resulting in comparatively severe corrosion. In order to improve the formulation, we carried out many experiments, first with the testing plates in the cylinder (see Table 2) and then with the dynamic simulation device (heat exchange tubes). In the result of several experiments we gained the experience that the experimental conditions should simulate the field conditions as much as possible (see Table 3). The experiment proved that we had got a better formulation results than the previous ones after we used higher dosage of inhibitor and added low dosage of zinc ions, with the operation conducted still under alkaline conditions. Therefore, we selected the compound formulation of polyphosphate with the zinc added in the recirculation water.

Table 1. WATER QUALITY ANALYSIS OF MAKE-up WATER AND RECIRCULATION COOLING WATER

Analyzed Items	Make-up Water	R.C.Water
$Na^{+} + K^{+}$ ppm	251.0	530.0
Ca^{++} ppm	10.0	20.8
Mg^{++} ppm	8.0	16.8
HCO_3^{-} ppm	345.0	70 - 80
$SO_4^{=}$ ppm	120.0	630 - 700
Cl^{-} ppm	126.7	266.1
$CO_3^{=}$ ppm	7.5	1 - 10
$Fe^{++} + Fe^{+++}$ ppm	0.2-0.3	0.5-0.7
SiO_2 ppm	12.0	25.20
PH ppm	8.3-8.5	2.5-8.2
Turbidity ppm	1.2-2	< 10
Total dissolved solid ppm	850-900	1550-1650
Electrical conductivity 15°C μs/cm	0.1×10^4	0.185×10^4
Concentration times	1	2.1
40°C RYznar index	6.54-6.34	8.04-7.34
80°C RYznar index	5.34-5.24	4.82-4.12

Tab.2. Test Data of Corrosion Specimens

Treating formulations	Composition of formulation					Corrosion rate MPY
	Comp. A ppm	Comp. B ppm	Zn^{++} ppm	Ca^{++} ppm	PH	
Blank	/	/	/	50	7.5 - 8.2	50
Phosphate	5.5	8	/	50	8.0 ± 0.2	15
(Phosphate + zinc) I	20	8	2.2	50	8.0 ± 0.2	0.73
(Phosphate + zinc) II	10	4	2	50	8.0 ± 0.2	0.69
Phosphate + zinc + calcium	10	4	2	75 (make-up 25)	8.0 ± 0.2	0.54

Notes:

Comp. A -- sodium hexametaphosphate

Comp. B is made up of PC, HEDP & MBT.

Zn^{++} as Zn

Ca^{++} as $CaCO_3$

Table 3. EXPERIMENT DATA OF DYNAMIC SIMULATION

Treating formulations	A.C.R. MPY			P.C.D. mm		Fouling factors $m^2 hr.c/kcal$	Appearance
	32°C	44°C	85°C	32°C	44°C		
Blank	12.75	19.29	114.44	/	/	5.05×10^{-4}	red brown scale max. thickness 2.5mm
Phosphate formulation	5.23	8.83	11.75	/	/	0.62×10^{-4}	black red rusty wart
(Phosphate + zinc) I	3.07	2.72	1.75	0.186	0.258	0.2×10^{-4}	brown rusty spots
(Phosphate + zinc) II	2.05	1.77	0.99	0.104	0.08	0.27×10^{-4}	yellow brown rusty spcts
Phosphate + zinc + calcium	2.20	0.97	0.68	0.088	0	0.8×10^{-4}	yellow brown rusty spots

Note: The composition of treating formulations is same as that of Table 2.

2. Strict monitoring and control of microbes:

Negligence is not allowed to the microbes in the recirculation water. The microbes will cause a lot of mud in the recirculation water system, resulting in reduction of the heat transfer coefficient of water coolers and even blockage of the coolers. Furthermore, the microbes will cause the corrosion and holes underneath the scales. The fungi will also erode the wood and damage the wood structure of cooling water towers by erosion. Therefore, the efficiency of chemical treatment will be probably reduced by the microbes. The microbes will also possibly cause the failure of treating formulations even though the formulations which are scaling-and erosion-resistant conform to the actual conditions.

In order to observe and control the activities of microbes, the regulations of monitoring microbes were first established. We not only frequently counted the number of living bacteria (heterotrophic bacteria) by means of flat dish, but also made a monthly general investigation of ferribacteria, sulphate-reducing bacteria, nitrobacteria group, fungi and algae. Besides, we also frequently analyzed the items of NH_4^+, NO_2^- and COD, which could indirectly indicate the growth of microbes.

In nitrogenous fertilizer plants, the recirculation cooling water are contaminated usually by the following three sources:

1) <u>Contamination of water source:</u>

There were less microbes when the underground water (tube well water) was used in our plant. However, when the surface water (river water) was used, there were more bacteria found. Sometimes the algae and mud were also found.

2) <u>Contamination of air in cooling water towers:</u>

For example, a lot of fungi were existing not only in the air, but also easily increased in water in spring and autumn.

3) <u>Contamination of working medium:</u>

It is known that ammonia is easily leaked in any of nitrogenous fertilizer plants. Sometimes the ammoni- leaking into the environment will be brought into the cooling water towers by air or it will directly leak into the system through the water coolers, thus promoting the growth of nitrobacteria group in the water and forming nitrous radical. Of course, in this case the efficiency of killing bacteria with chlorine will be reduced. It was found that when the water cooler (124-C) leaked, the microbes grew vigorously in the recirculation water, thus deteriorating the water quality.

The growth of microbes was related not only to the above factors of contamination, but also to the atmospheric temperature. The microbes were vigorously increased in summer. The hydrolysate (phosphorous), which was produced after polyphosphate chemical treatment, was the nutrient for the microbes. It also promoted the growth of microbes.

In the result of monitoring and general investigation, we made great efforts to have the number of living bacteria (heterotrophic bacteria) controlled and kept below $1 - 5 \times 10^5$/ml, iron bacteria < 100/ml, sulphate-reducting bacteria < 50/ml and fungi < 10/ml.

The chlorine was simply used for killing bacteria previously. The chlorine was introduced into the recirculation water system once per shift. Now the non-oxidation type germicides are used in conjunction with chlorine, mainly chlorine. If necessary, some non-oxidation type germicides may be used alternatively. The chlorophenol germicide was sprayed over the wood structure of cooling water towers during the yearly major overhaul, thus obtaining a better result than the previous one. The experimental data of non-oxidation type germicides adopted are tubulated in Tab. 4.

Table 4. The Experiment

Results / Germicides	Sample location	Dosage ppm	Ph	Surplus Cl ppm	Blank living bacteria /ml.	Change of 1 hr.
Chloro-phenol	Recycled water	100	7.8/8.2	0	3.5×10^6	2.35×10^6
Allicin	"	"	8.2	0.2	2.25×10^6	2.12×10^6
Qaternary amine salt A	"	"	7.8/8.2	0	1.84×10^5	2.43×10^3
Disulfocyno-methane	"	25	7.8/8.2	0.2	4.5×10^4	3.5×10^2
Quaternary amine salt B	"	25	7.8/8.2	0.2	4.5×10^4	5.0×10^2

Data of Germicides

total of heterotrophic bacteria living bacteria number/ml.			Change of rate of bacteria killed %				Max. value of B. killed and appearing time	
4 hr.	12 hr.	24 hr.	1 hr.	4 hr.	12 hr.	24 hr.	Time	Rate of B. killed %
1.05×10^6	0.7×10^6	3.0×10^6	32.9	70	75	19.5	9th hr.	84
1.75×10^6	0.75×10^6	2.0×10^6	4.6	22.3	66.3	11.1	12th hr.	66.3
3.1×10^3	6.8×10^3	5.6×10^4	98.8	98.4	96.2	69.5	1st hr.	98.8
4.0×10^2	3.0×10^2	3.5×10^2	99.2	99.1	99.3	99.2	10th hr.	99.4
8.0×10^2	9.5×10^2	8.6×10^2	98.9	98.2	97.9	98.1	14th hr.	99.5

Note:
B is bacteria.

3. Corrosion-resistant paint of c.s. water coolers:

The chemical treatment employed could not make the flow rate of water through the shell side of c.s. water coolers lower than 0.5m/sec. Most of the water coolers replaced due to leakage in our plant were constructed with c.s. shell side. For this reason, we had some shell sides of c.s. water coolers coated with the corrosion-resistant paint CH784, which was developed in our plant, and the main composition of which is epoxy amino resin. The chemical and physical properties of the corrosion-resistant coating are shown in Table 5 and Table 6. After application of the above corrosion-resistant paint, the life of water coolers has been prolonged and the scales are not easily formed, thus improving the heat transfer coefficient.

4. Enhancement of field operation management:

The field operation management was enhanced after determination of the formulations for chemical treatment and of the proposals for microbes control. The operation against process parameters is not permissible. Efforts were made to have the process parameters qualified to the maximum. It is very important to have the PH of recirculation water stabilized. The said ph was ranged from 7.8 to 8.2 by using automatic controls. It is also critical to introduce chlorine to kill bacteria. Qualification is accepted if the remained chlorine reaches a range from 0.4 to 0.8 ppm. Dosage should be performed continuously so as to avoid occationally high or low content of dose in recirculation water. The strict field management is also an essential phase for improvement of water quality, otherwise the satisfactory efficiency of chemical treatment can not be obtained. We mounted the monitoring plates and installed the heat exchangers at the appropriate localities of recycled water network. The monthly monitoring records should be collected for statistics and the conditions of treatment needs to be studied. Meanwhile, attention should be paid to observation and recording of the working conditions of water coolers during the yearly major overhaul, to the determination of corrosion and analysis of scales as well as to the photos taken for file. By doing this we shall be able to frequently get the information on recirculation water treatment. If necessary, the proposals for treatment may be readjusted.

Since the above four points were adopted, great improvement of the recirculation water treatment has been made. The different results obtained at several stages are shown in Table 7, Fig. 1 and Fig. 2.

Table 5. Physical and mechanical properties of the coating*

Items	Test methods & conditions	Unit	CH 784 paint
adhesive force	circling	grade	1
shock resistance	impact tester	kg/cm^2	50
elasticity	fleximeter	mm	1
hardness	pendulum-rod durometer		> 0.85
water absorption	soaking in ion-free water for 24 hrs.	%	0.34
heat** resistance	200°C, 240 hrs.		no cracks
heat resistance under humid conditions	dry 47°C, humidity 96%, 1442 hrs.		1
*** temperature variation	-180 ~ + 200°C 8 cycles		no cracks
heat cond. coefficient		kcal/hr. m.°C.	0.42

Notes:

* -- The above tests were carried out in accordance with the Standards published by the Ministry of Chemical Industry of the People's Republic of China.

** -- Film thickness 40 μm

*** -- Film thickness 150-200 μm

Tab. 6. Corrosion-resistant properties of coating*

Temp. °C	Medium	Results
95 ± 2	30% HCL, H_2SO_4, HAC, H_3PO_4, KOH, NaOH 20% NH_4OH ph of recirculation water: 8.2	No changes could be found in 224 hrs. with a 4-times magnifier.
room temp.	30% H_2SO_4, HCL	No changes within 21 months
	30% NaOH, KOH H_3PO_4, HAC	No changes within 24 months
	10% HCL, H_2SO_4, NaOH, kerosene, xylene	No changes within 24 months

Note:

* -- testing steel rod Ø15 x 150mm,
two layers of primer plus three layers of finish with a film thickness of 150-200 μm.

Table 7. Comparison between the treatment formulation and efficiency

Date	Treatment formulations	Operation conditions of plant	Working conditions of main water coolers
Oct. 1976- June 1978	phosphate, chlorine used for killing bacteria.	The ammonia unit was shut down 3 times due to the leakage found in the water coolers. The max. duration of operation lasted for 128 days.	Severe leakage was found in 115-c, 116-c and 124-c with a service time less than 1 year. 116-c was discarded with a wervice time less than 1 year.
July 1978- Feb. 1980	(phosphate + zinc compound formulation)I, chlorine used for killing bacteria, non-oxidation type germicides alternatively used.	The problem of circulation water did not cause shutdown.	Normal operation of 115-c, 116-c and 124c, no leakage
March 1980- Dec. 1980	(phosphate + zinc compound formulation)II, chlorine used for killing bacteria, non-oxidation type germicides alternatively used.	- ditto -	- ditto -

Notes: 115-C is methonator outlet gas cooler.

116-c is the intermediate-stage cooler of syn gas compressor.

124-c is the circulating stage cooler of syn gas compressor.

(to be continued)

Date	Conditions of water quality, corrosion and fouling	Corrosion rate (MPY)	
		max. month	average
Oct. 1976- June 1978	Water quality: black and bad smell; A lot of fouling was found in the water coolers with severe corrosion.	21.8	17.44
July 1978- Feb. 1980	The problem of corrosion and fouling was turned better.		4.66
March 1980- Dec. 1980	slight corrosion and less fouling.	< 5	3.91

(to be continued)

Depth of local concave spot due to corrosion (MPY)
78.7

Date	Conditions of control of microbes		
	max. number of living bacteria	average number of living bacteria	application conditions of germicides
Oct. 1976- June 1978	5.26×10^6/ml.	4.62×10^5/ml.	daily consumption of chlorine: 500kg, remained chlorine: 0.1 ppm.
July 1978- Feb. 1980	1×10^6/ml.	2.38×10^5/ml.	daily consumption of chlorine: 200kg, remained chlorine: 0.4 - 0.8 ppm, The non-oxidation type germicides have been used for 36 times.
March 1980- Dec. 1980	7.96×10^4/ml.	2.07×10^4/ml.	The non- oxidation type germicides have been reduced for five times, and the microbes were controlled normally.

Conclusion:

It is importent to guarentee the normal operation of a nitrogenous fertilizer plant with an efficient chemical treatment of recirculation cooling water. Attention should be paid to the following improvements on recirculation water system:

1) Microbes should be strictly monitored and controlled.

2) The appropriate formulations of chemical treatment should be selected for different water quality.

3) Corrosion-resistant paint should be applied for the shell side of c.s. water coolers.

4) Strict management is required for the field operation.

Water passes through the shell side

Water passes through the tube side

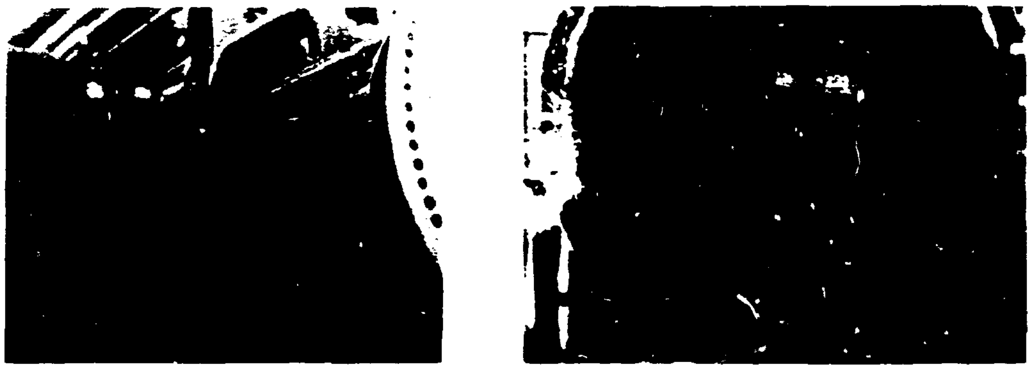

Fig. 1 Corrosion and fouling conditions were found during the period from Oct. 1976 to May 1978

Water passes through the shell side

Water passes through the tube side

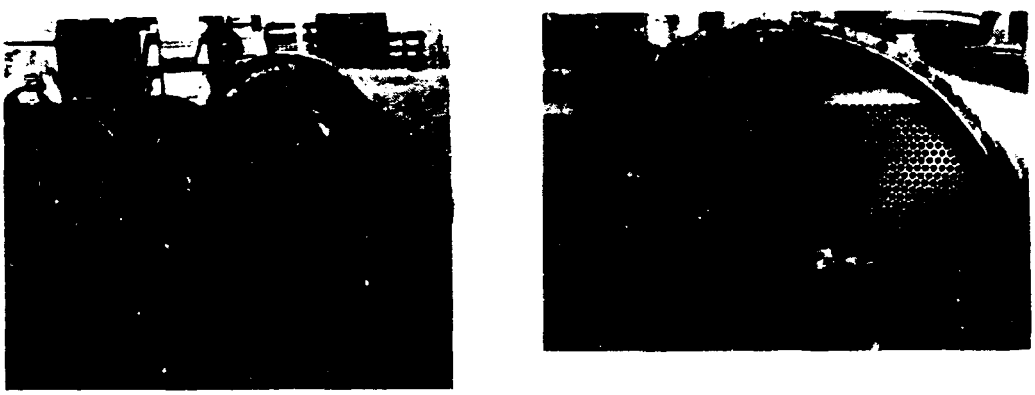

Fig. 2. Corrosion and fouling conditions were found during the period from Oct. 1976 to May 1978