

## REUSE OF PRETREATED COAL GASIFICATION WASTEWATER AS COOLING TOWER MAKEUP

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### GOALS AND OBJECTIVES

Coal gasification wastewater, containing various high concentrated organic and inorganic contaminants, reuse and recycling is practiced in coal gasification plant for two primary purposes: to reduce wastewater discharge amount and to protect environment. Cooling systems are major consumers in many coal gasification plants. Therefore, reuse of pretreated coal gasification wastewater as cooling tower makeup may bring considerable saving in fresh water consumption and protection of environment.

It is possible to find a feasible approach for the reuse of coal gasification wastewater with large amount discharge and various high concentrated pollutants. Some tests of pretreated wastewater for industrial cooling have been reported [1, 2, 3]. However, the reuse of the wastewater as cooling tower makeup presents both operating and environmental problems, especially in severe biological fouling and organic emissions.

The principal goals of the research project are to develop an advanced process for the treatment and reuse of gasification wastewater. Another object is to test alternative treatment method that may be necessary for

execution of gasification wastewater zero discharge.

#### WASTEWATER PRODUCTION AND PRETREATMENT

Wastewater tested in this study was the effluent from Lurgi fixed-bed gasification and coal cooking plant. Raw gasification wastewater pretreatment process for removing tar, phenolic compounds and ammonia was performed by a pilot facility<sup>(4)</sup>. Flotation cell is used to remove residual suspended tars. Phenols and ammonia in the wastewater are reduced by an improved solvent extraction system with steam stripping<sup>(5)</sup>. In the process, di-isopropyl ether is used as the solvent. 98% (fixed-bed gasification) and 95% (coal coking) phenol removal efficiency and less than 100 mg/l phenol in effluent are obtained at a wastewater-to-solvent ratio of about 10:1. After extraction, the wastewater is directly pumped to steam stripping column. By separating distillate, 98% recovery efficiency of ammonia and 99% recovery efficiency of the solvent dissolved in the wastewater are obtained.

The next step of the pretreatment involves biological oxidation and dualmedia filtration to remove organic contaminants and suspended solids.

Table 1 and 2 show the average composition of the fixed-bed gasification and coal coking wastewater before and after each of these pretreatment respectively. As shown in table 1 and 2, after these pretreatment, the wastewater characterization doesn't meet the national discharge criteria. As shown in the table, it can be reused as makeup in an evaporative cooling tower.

**TABLE 1 AVERAGE WASTEWATER CHARACTERISTICS FOLLOWING EACH PRETREATMENT STEP ( FIX-BED GASIFICATION )**

Constituent*	Raw Wastewater	Solvent Extraction Effluent	Steam Stripping Effluent	Activated Sludge and Filtration Effluent
COD	38500	20600	2900	670
BOD <sub>5</sub>	15600	--	1518	40
Phenol	2450	48	36	0.42
Ammonia	1300	1250	210	163
Sulfide	48	38.4	18.4	14.4
Cyanide	3.5	0.27	0.04	0.013
pH	9.77	9.18	8.7	7.6
Oil	8326	273	40	23
Fatty acid	85	43.7	1.5	0.067

\* All concentrations in mg/l except pH

**TABLE 2 AVERAGE WASTEWATER CHARACTERISTICS FOLLOWING EACH PRETREATMENT STEP ( COAL COKING )**

Constituent*	Raw Wastewater	Solvent Extraction Effluent	Steam Stripping Effluent	Activated Sludge and Filtration Effluent
COD	25000	13500	2783	510
BOD <sub>5</sub>	2970	--	1025	36
Phenol	1285	70	45	0.51
Ammonia	1520	1515	190	185
Sulfide	23	14.6	4.87	4.4
Cyanide	9.86	9.36	9.6	6.48
pH	9.08	9.10	8.4	7.18
Oil	300	170	110	74.7
Fatty acid	81.6	38.9	0.24	0.11

\* All concentrations in mg/l except pH

## COOLING TOWER EXPERIMENTAL PROCEDURES

Two series (phase 1 and 2) were conducted by using fixed-bed wastewater showing in Table 1. A series ( phase 3 ) was conducted by using coal coking wastewater showing in Table 2. The most significant difference between phase 2, 3 and phase 1 was biocide addition which was used to control biological fouling. Another difference between phase 2, 3 and phase 1 was filtration which was used to reduce Suspended Solid in the cooling water. A schematic of the test cooling tower system is presented in Figure 1. The cooling tower design parameters are as the following liquid-to-gas ratio 1:830  $m^3/m^3$ , flow per unit area of packing surfac: 11.8  $m^3/m^2$ . The design cooling range of 10 °C to 15 °C and 10 cycles of concentration were maintained in each of the three tests. A 300 l/h cooling water circulation rate, a 6l/h pretreated wastewater makeup rate, and a blowdown rate of approximately 10% of the makeup were kept in order to maintain 10 cycle operation. In addition to hydraulic control, during day-to-day operation of both segments of all phase tests, the cycles of concentration were monitored using the concentration of sodium ions. All three tests were run for 350 hours.

As shown in Figure 1, the blowdown water was pumped into an evaporator, in which the water was further concentrated by 10 times and condensate was return to the basin. Therefore only approximately 1 % of the wakeup was discharged. Cooling water in the tower basin is pumped through a test heat exchanger wich can be used for measuring the steel corrosion both of carbon and stainless steel and monitoring fouling and heat transfer performance. The test heat exchanger was equipped with carbon steel tube, and operated with tube-side fluid velocity of 1.0 m/sec. The shell side was heated by steam.

During phase 2 and 3 the biocid (  $ClO_2$  ) and bypass filtration were added. The biocid was added every six hours with dosage of 20 mg/l (calculated on total cooling water volum). The flow rate of bypass filtration was 8 l/h.

## COOLING TOWER TEST RESULTS

Characterization of Water. The average makeup and cooling water analysis results for all phase 1, 2 and 3 are presented in Table 3. The most significant difference between phase 1 and phase 2, 3 was the concentration of

suspended solids. TSS of phase 2, 3 was significantly reduced 1/2 comparing with phase 1. This is likely due to the biocide addition which led to reduced bacterial population. In phase 1, without biocide, the counts of total bacteria in the cooling water was  $8.2 \times 10^7$  /ml. In both Phase 2 and 3, used  $\text{ClO}_2$  as biocid, the counts was less  $1.5 \times 10^4$  /ml. It appears that  $\text{ClO}_2$  is a effective biocide for cooling tower operating with pretreated coal gasification wastewater as makeup.

TABLE 3 ANALYSIS RESULTS OF WATER FROM THE TESTS

Constituent*	Fixed-bed gasification				Coal cooking	
	Phase 1		Phase 2		Phase 3	
	Makeup	CW	Makeup	CW	Makeup	CW
COD	897	3787	889	4828	510	4211
BOD <sub>5</sub>	40	88.4	38	249	38	250
Phenol	0.4	1.2	0.42	1.8	0.51	1.7
Ammonia	155	1020	155	1015	185	400
Alkalinity	175	825	195	445	115	325
Calcium	4.16	24.3	19.5	90	12	62.5
Sodium	57.1	588	81.8	583	42.8	423
Magnesium	4.19	8.35	2.58	22.2	3.51	31.8
TSS	48	1840	40	540	110	780
TVSS	0.52	0.53	0.53	0.25	0.52	0.54
TDS	830	5158	916	8718	1448	11942
TVDS	538	3842	548	4242	960	7588
pH	7.1	8.82	7.6	8.7	7.78	8.9
Conductivity	0.0132	0.0878	0.013	0.074	0.034	0.138

\* All concentrations in mg/l, conductivity in ms  
**System Fouling.** Figure 2 illustrates the rates of fouling and heat transfer coefficient loss in carbon steel tubes observed in all three test phases. All tests showed that the heat transfer coefficient loss was zero after 200 hours. Figure 2 showed the HTC during first 200 hours for each test. As shown in Figure 2 both the rate of fouling and heat transfer coefficient loss in phase 1 were greater than that in phase 2 and 3. It is indicated that the use of  $\text{ClO}_2$  as biocide tested in phase 2 and 3 was beneficial for the reduction of biofouling, because the use of biocide ( $\text{ClO}_2$ ) can control the extent of biological deposition that happened in phase 1. Calculating on the basis of the Kern-Seaton Model<sup>(6)</sup>, the limit of fouling thermal resistance for phase 2 and 3 tests was  $3.324 \times 10^{-4}$  and  $5.86 \times 10^{-4}$  m<sup>2</sup> · h · °C /Kcal respectively. The relationship between fouling thermal resistance (R) and time (t) is as following:

For the pretreated fixed-bed gasification wastewater

$$R = 3.324 \times 10^{-4} (1 - e^{-0.0086t}) \text{ m}^2 \cdot \text{h} \cdot \text{C} / \text{kcal}$$

For the pretreated coal coking wastewater

$$R = 5.86 \times 10^{-4} (1 - e^{-0.0078t}) \text{ m}^2 \cdot \text{h} \cdot \text{C} / \text{kcal}$$

**Corrosion.** Corrosion rates in the cooling tower system were determined using weight loss coupons. Table 4 presents a summary of the corrosion rate during the all three bases tests. As showing in Table 4, the highest corrosion rate always occurred at heat exchanger outline where the temperature of cooling water was the highest. The corrosion rates for carbon steel varied from 0.0036-0.037 mm/y for the various locations, and for stainless steel varied from 0.0002-0.0014 mm/y.

TABLE 4 CORROSION RATES DURING THE TESTS (mm/y)

Metallurgy	Location	Phase 1	Phase 2	Phase 3
Carbon steell	Basin	0.0036	0.0086	0.0078
Carbon steell	HE inlet	0.0184	0.0144	0.0039
Carbon steell	HE outlet	0.0385	0.0182	0.0280
1Cr18Ni8Ti SS	Basin	0.0019	0.0014	0.0014
1Cr18Ni8Ti SS	HE inlet	0.0005	0.0002	0.0010
1Cr18Ni8Ti SS	HE outlet	0.0024	0.0014	0.0014

Based on measuring corrosion rates from each of these tests, corrosion wasn't a significant problem for reusing pretreated gasification wastewater as makeup. These low corrosion rates indicated that the pretreated wastewater from fixed-bed gasification or coking were suitable for makeup to a cooling tower without the addition of corrosion inhibitors. This is likely due to that some organic materials (phenols and cynide et al.) in the wastewater act as inhibitors.

## CONCLUSIONS

Several conclusions can be drawn from the data collected during the three Phases of cooling tower reuse testing with pretreated Lurgi fixed-bed gasification and coal coking wastewater. Use of these wastewater as direct makeup to a cooling tower resulted in a high level of biological activity, which influenced the fouling and heat transfer performance of the equipment in test process. The steel corrosion both carbon and stainless steel in these operations were not high which would be acceptable in a commercial use.

The Phase 2 and 3 indicated that reuse pretreated gasification wastewater was suitable for makeup to a cooling

tower with the biocide ( $\text{ClO}_2$ ) addition. The limit of fouling thermal resistance of the Lurgi fixed-bed gasification and coal coking wastewater was  $3.24 \times 10^{-4}$  and  $5.86 \times 10^{-4} \text{m}^2 \cdot \text{h} \cdot ^\circ\text{C} / \text{kcal}$  respectively; the highest carbon steel corrosion was 0.0182 and 0.028 mm/y respectively and the highest stainless steel corrosion were 0.0014mm/y for both. All those results well meet the national criteria of China. These results have led us to conclude that Lurgi fixed-bed gasification and coking wastewater, after removal tar, extraction phenol, stripping ammonia, biological oxidation and dualmedia filtration treatment, will make a suitable cooling tower makeup at ten cycles of concentration with the addition of biocide ( $\text{ClO}_2$ ) and without the addition of corrosion inhibitors. The study also showed that the reuse of this streams were beneficial both for water resource saving and reducing environmental pollution due to the reduction of wastewater discharge.

#### REFERENCES

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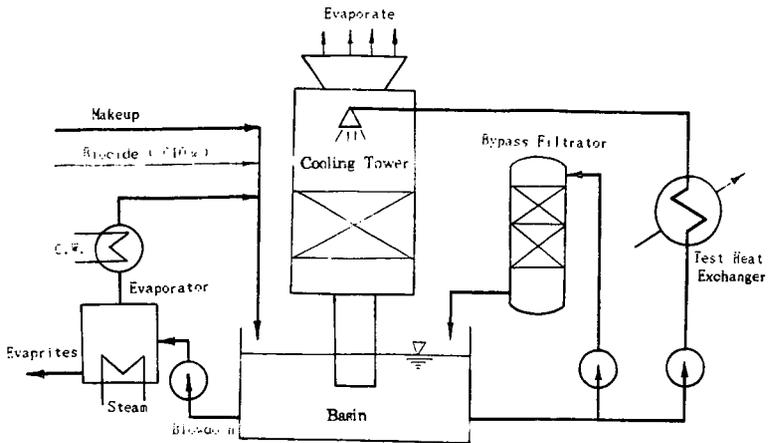


Figure 1 — Schematic of the Test Cooling Tower System

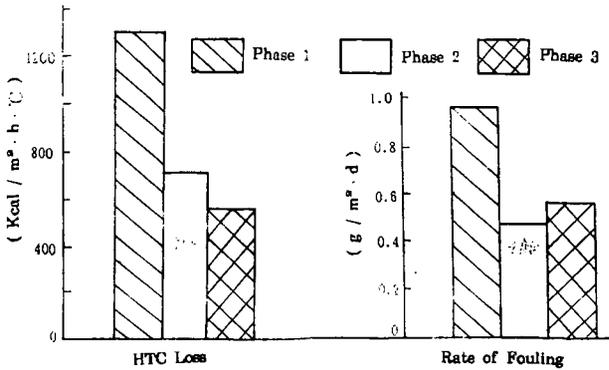


Figure 2 — Results of Average Fouling and Heat Transfer Coefficient Loss in Carbon Steel Tube