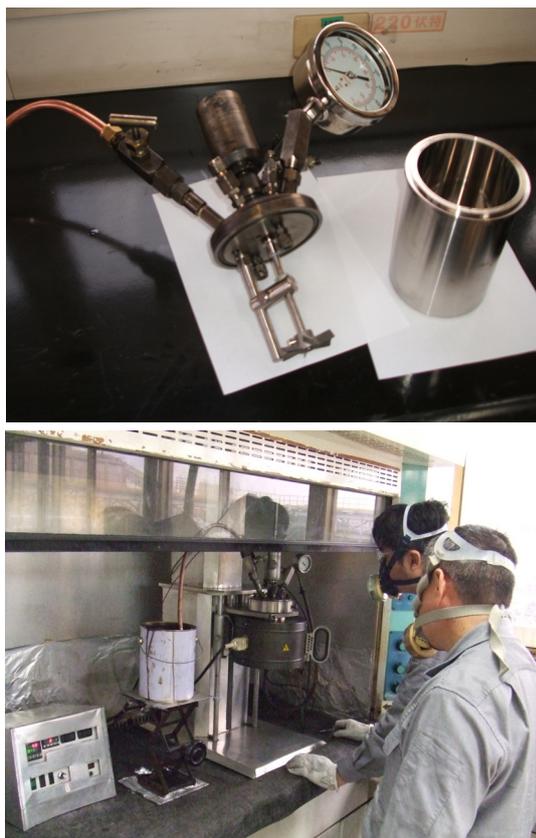




between process parameters and the corrosion rate; (3) Analyses of the CLO quality were conducted to identify possible corrosive compounds; and (4) A suitable corrosion inhibitor was developed to be added to the CLO process to prevent CLO corrosion.

### 2.1 Corrosion test

The appearance of the Parr vessel and the experimental system are shown in Fig.2.



**Fig.2.** Photographs of the Parr vessel and the experimental system.

The test vessel was a custom-designed device fabricated from Hastelloy C-276; it had a measured volume of 1 L, and was equipped with internal thermocouples and a propeller agitator to fully mix samples. A horizontal rod was delicately inserted between the agitator shaft and the thermocouple cell to take advantage of the free movement of the rod support for holding the corrosion coupons used to determine the corrosion resistance of the material.

To perform a test, the test vessel was tightly closed, and maintained at a temperature of 200~350°C; then a mixing speed of 250 rpm was applied, and the system was run continuously for 24 h for 7 days.

The testing procedure was as follows: (1) Approximately 660 g of CLO and four digits of the weight demand of corrosion inhibitors were mixed; then a corrosion coupon, which had previously been cleansed with toluene and blown with nitrogen gas, was installed; (2) A scale was used to obtain the length and width of the coupon and calculate the area of the coupon sheet, and the coupon was precisely weighed; (3) The test vessel was tightly sealed by purging with nitrogen two to three times, while the pressure change was observed to confirm that the device did not leak; (4) After validating the previous steps, the vessel was heated and the mixture was agitated for 7 days; (5) During the experimental period, the temperature and test status was recorded every 2 h; (6) When the test was complete, the corrosion coupon was removed from the vessel after cooling down to approximately 120°C, and was reweighed accurately, as described in step 2 (another option was applying wet chemical absorption methods to capture gas vapor from the vessel, then the absorbed liquid was analyzed by an IC instrument); and (7) Finally, the corrosion rate of the coupon was calculated according to the following formula:

Corrosion rate (mpy; milligrams per year) = (weight loss of coupon, g) / (coupon area, cm<sup>2</sup>) / 7.8 (density of coupon material, such as carbon steel) × 52 (weeks/year) / 2.54 (cm/ inch) × 1000 (unit conversion factor).

### 2.2 Other monitoring items

(1) Analysis of the CLO quality: The working standard methods and practices used are listed in Table 1.

**Table 1** Methods for CLO quality analysis

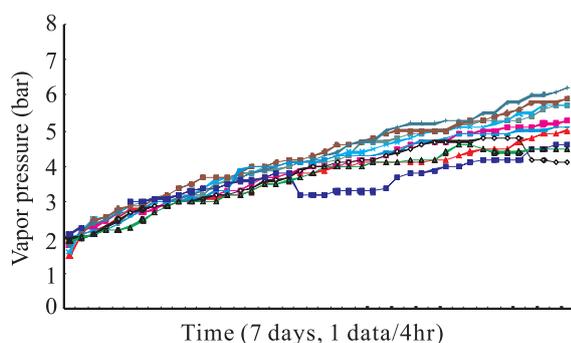
Item	Standard method
Total sulfur content	ASTM D5453
Chloride	JIS K 2425
Water content	ASTM E 203
Sulfide (S <sup>2-</sup> )	CSCC D3-S-781
Total acid number (TAN)	ASTM D664
GC analysis	CSCC D3-S-721

(2) Corrosion rate of on-site coupons used in the CLO process: Eight sets of coupons fabricated from carbon steel were installed around the CLO path. The coupons were coded Nos. 1~8, and were located at the positions corresponding to the bottom of the C121~C123 distillation columns, R121-outlet, R123-inlet, F121-inlet, F121-outlet and P125-outlet (see Fig.1). These coupons were evaluated once every 40 to 45 days to determine the corrosion rate of the CLO process.

### 3. RESULTS AND DISCUSSION

#### 3.1 Corrosion test of CLO

Variations in the gas pressure recorded in the CLO corrosion test (Fig.3) indicated increasing corrosion with time. This trend reflected a chemical reaction state where the stable phase equilibrium could not be achieved. According to thermodynamics theory, the pressure of the gas phase in a closed system eventually reaches a stable equilibrium (i.e., constant pressure) after several minutes or hours, which was confirmed in our previous experiments. By contrast, the vapor pressure of the Parr vessel used for the CLO test was unstable, suggesting that cracking substances were produced continuously in the CLO solution, resulting in an increase in the gas pressure. This indicated that corrosion reactions occurred in the liquid phase of the CLO mixture, causing an unbalanced phase equilibrium state.



**Fig.3.** Variations of the vapor pressure of different CLO samples with time in the Parr experiments.

To verify this conjecture, CLO was used in a similar experiment performed at Company M in the United States. In this experiment, the CLO was heated statically for more than 10 days, and the results are shown in Table 2. It was clear that the CLO decomposed to form a diluted liquid containing small molecules. A 9.8 wt% proportion of CLO changed

qualitatively into low molecular weight chemicals, which likely activated corrosion reactions. Thus, severe corrosion phenomena were easily observed at the CSCC plant after the CLO process had been operating for a long time.

#### 3.2 Behavior of CLO corrosion

##### 3.2.1 Investigation of the relationship with corrosion

This section elucidates the relationships between the process parameters and the corrosion rate, including the operating variables of the CLO distillation towers, the temperature of the furnace, and the flow of the feeding oil. All the parameters were obtained from the DCS information in the plant during the period between January 1, 2007 and July 31, 2009, and the correlated results are shown in Figs.4 to 8. Compared with the trend lines of the process parameters, the variations in the corrosion rate exhibited a substantial positive relationship with the surface temperature of the F121 furnace, and uncertain relationships with the other parameters. These correlations indicated that the high temperature of the CLO process was the major factor influencing the corrosion rate at the CSCC plant; thus, the higher temperatures resulted in higher corrosion rates. Furthermore, the corrosion rate increased with a rise in plant productivity, because an increasing amount of high-temperature CLO was required to provide the thermal energy for plant operation. This proved that CLO continuously cracks at high temperature and reacts with iron; therefore, these factors should be carefully monitored.

##### 3.2.2 CLO analyses

The CLO was analyzed to identify the possible ingredients responsible for corrosion; the results are shown in Table 3. The CLO did not contain naphthenic acid, a major corrosion-promoting compound, which is generally present in the petrochemical industry<sup>(5)</sup>. Therefore, plant corrosion caused by naphthenic acid can be discarded in this case. Other possible corrosive species present in the CLO are discussed as follows:

**Table 2** Properties of CLO analyzed by M Corp. in USA

	Normal	Warning	Low action	Action	Measured value
Kinematic viscosity at 100°F cst	--	--	--	--	10.87
Total acid number, mg KOH/g	0.0-0.3	0.3-0.7	<0	>0.7	0.04
Water content, ppm	0-360	360-700	--	>700	272
Insoluble solids, mg/100 mL	0-125	125-400	--	>400	19.40
Low boilers, wt%	--	--	--	>5	9.80
High boilers plus unaccountable, wt%	--	--	--	>10	1.90

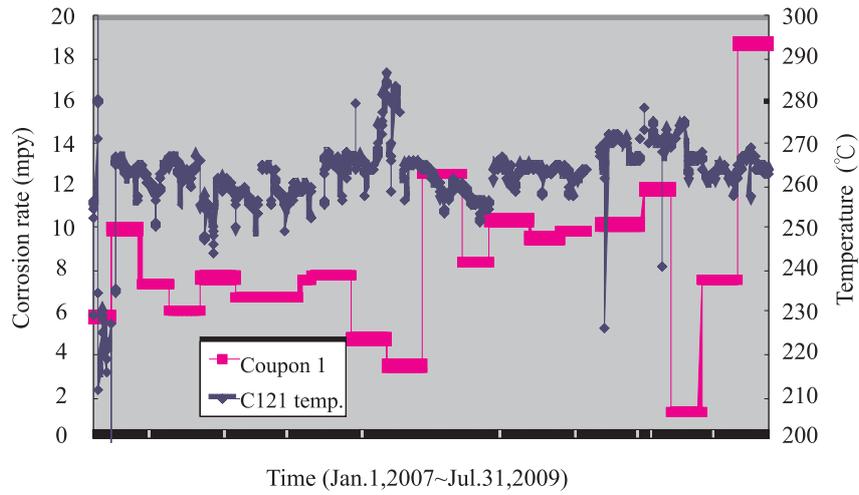


Fig.4. Relationship between corrosion rate and bottom temperature in the C121 distillation tower.

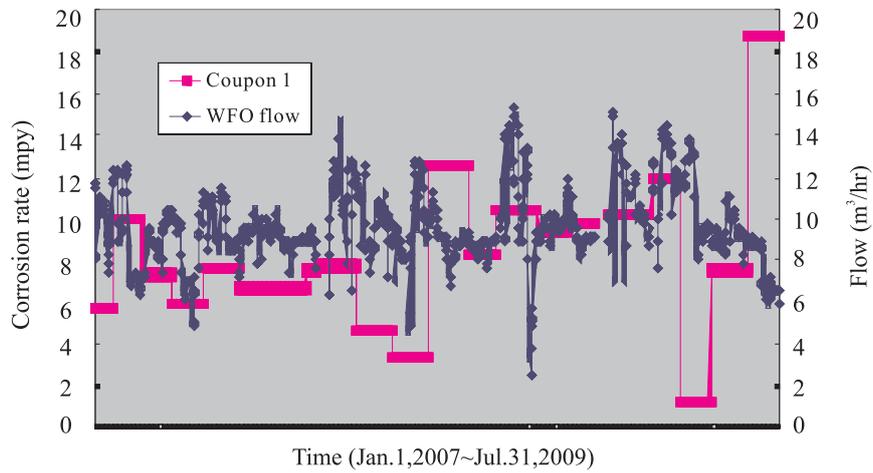


Fig.5. Relationship between corrosion rate and flow of WFO oil.

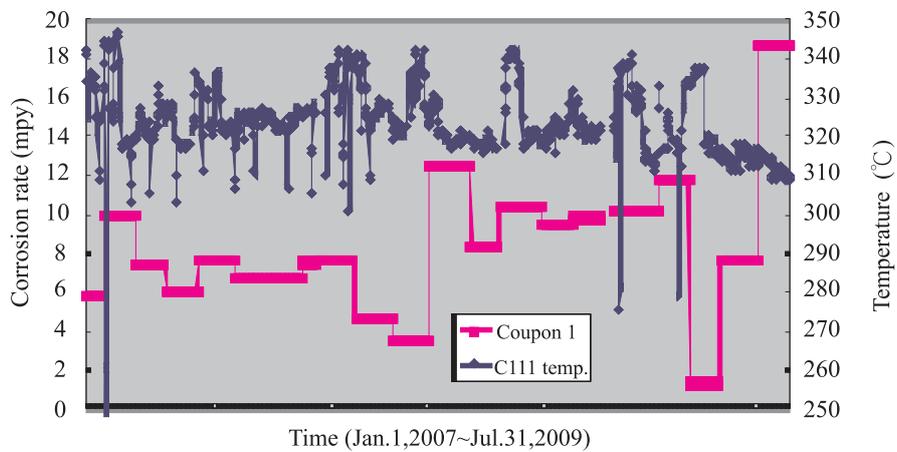


Fig.6. Relationship between corrosion rate and overhead temperature in the C111 distillation tower.

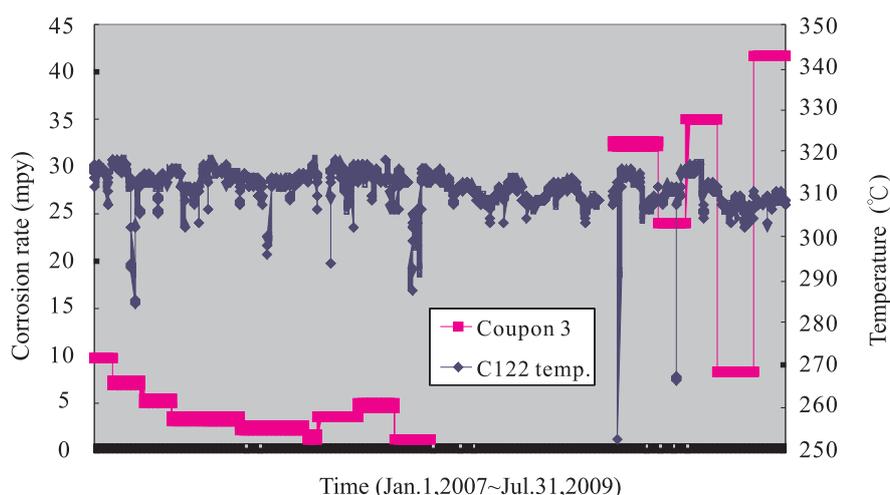


Fig.7. Relationship between corrosion rate and bottom temperature in the C122 distillation tower.

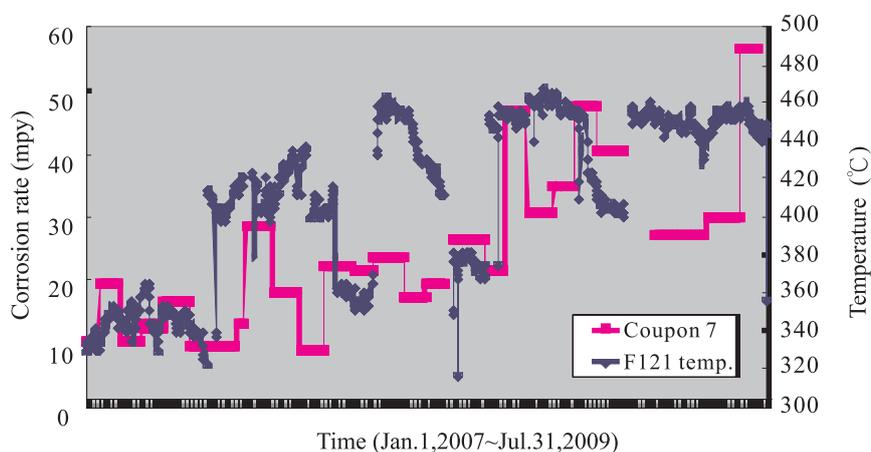


Fig.8. Relationship between corrosion rate and skin temperature in the F121 furnace.

Table 3 CLO quality results obtained in this study

Sample	CLO-1 (70~85 mpy)	CLO-2 (< 20 mpy)
Total sulfur content	0.41~0.42 wt%	0.40 wt%
Sulfide (S <sup>2-</sup> )	200~700 ppm	510 ppm
Total acid number (TAN)	0.04 mg KOH/g	0.03~0.04 mg KOH/g
Water content	400 ppm	471 ppm
Chloride	< 5 ppm	1.15 ppm
Naphthenic acid	N.D. (Not detectable)	N.D.

- (1) The water content of the CLO was approximately 400 ppm, a low level according to the specifications of commercial heating oil. Because it was lower than the standard content of 700 ppm for heating oil,<sup>(6)</sup> the water content exerted negligible effects on the corrosion.
- (2) The chloride content of the CLO was less than

5 ppm; therefore, the effect of chloride on corrosion can also be discounted.

- (3) It is established that the sulfur content of heating oil is close to zero; therefore, the corrosive effects of sulfurous substances on plant operation are not considered in the manufacturing industry. However, the results listed in Table 3 revealed that the total

sulfur content of the CLO was 0.40~0.42 wt%, and that the S<sup>2-</sup> content was within the range of 200~700 ppm. Although S<sup>2-</sup> (which is unstable in solution) is difficult to quantify accurately, this result indicated that a mixture of organic and inorganic sulfur compounds were present in the CLO; therefore, identifying the sulfur species that might affect the corrosion rate during the entire plant operation time would be desirable.

- (4) The total acid number (TAN) of the CLO was low at less than 0.05 mg KOH/g, and it was also far lower than the general warning value (0.5 mg KOH/g) used in the oil industry. Therefore, TAN exerted a negligible effect on corrosion in the CLO process.
- (5) Another crucial item concerning the quality of heating oil is the insoluble content remaining after CLO is immersed in acetone and the solution is filtered. When heating poor quality oil, this value exceeds 400 mg/100 mL. The insoluble content of the CLO was nearly 0.03 mg/100 mL, which indicated the presence of only a few miscellaneous particles within the CLO mixture, suggesting that this factor exerted a negligible effect on corrosion.

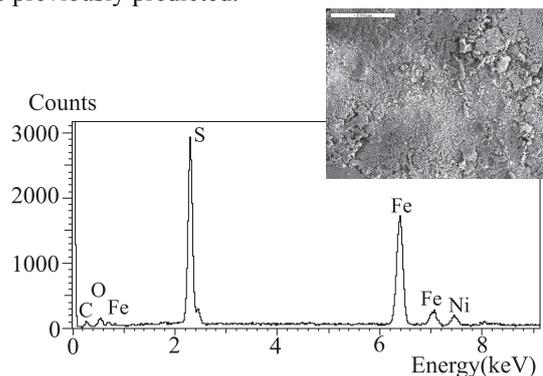
Based on these results, it was clear that the CLO constituents—excluding the high content of sulfur—were close to the composition specifications of commercial heating oil. By simply comparing the CLO samples listed in Table 3, no outstanding correlation between the quality of constituents and the corrosion rate was observed. Therefore, the corrosion was likely caused by certain key sulfur components that react at high temperatures in the CLO solution. By analyzing the CLO mixtures using GC, CLO was observed to contain a high sulfur content of 0.4 wt% or higher; however, most of the sulfur compounds present were stable, and only 0.01 to 0.02 wt% of the organic sulfur species represented active compounds that might easily produce corrosion at high temperatures. The amount of active ingredients increased gradually with higher temperatures and longer operation times, and most of them chemically converted into H<sub>2</sub>S, which quickly reacts with iron to produce corrosion. This assertion can reasonably explain the rising pressure trend observed in the Parr test (Fig.3) and the changes in the

purity of the CLO indicated in Table 2.

### 3.3 Mechanism of CLO corrosion

#### 3.3.1 Identification of corrosion products<sup>(6)</sup>

Corrosion products present in the support ring of the C122 distillation tower were sampled and analyzed using electron microscopy (SEM) combined with energy dispersive spectroscopy (EDS), and the results are shown in Fig.9. The main corrosion product was identified as FeS, which resulted from sulfur corrosion as previously predicted.



**Fig.9.** Compositions of the adhesive residue for C122 support ring analyzed by EM/EDS.

#### 3.3.2 Possible mechanisms of CLO corrosion

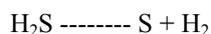
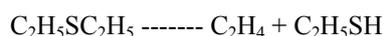
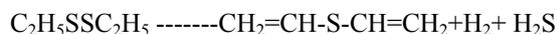
The literatures<sup>(7-10)</sup> concerning the possible mechanisms of sulfur corrosion clearly indicate that when the operation temperature is above 250°C, certain organic sulfur substances may decompose into chemically active sulfurs, namely hydrogen sulfide (H<sub>2</sub>S), sulfur, and mercaptan. All these compounds react with iron, and the reaction is known as sulfur corrosion. By contrast, non-active sulfurs include sulfide ether, disulfide, and cyclic sulfur. Nevertheless, nonreactive sulfurs heated at high temperatures between 200 and 400°C transform into active sulfurs. The most critical substances producing sulfur corrosion are mainly derived from either H<sub>2</sub>S or sulfur, and the reaction thermodynamics<sup>(9)</sup> are described in Table 4. Because the free energy of sulfur reactions is negative, and they are spontaneous reactions, it is difficult to prevent sulfur corrosion.

**Table 4** Free energy changes for the main chemical reactions involved in sulfur corrosion

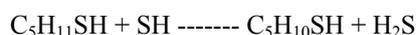
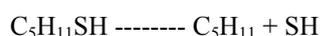
Chemical reactions	$\Delta G^*$ 25°C/kJ·mol <sup>-1</sup>	$\Delta G^*$ 350°C/kJ·mol <sup>-1</sup>	$\Delta G^*$ 600°C/kJ·mol <sup>-1</sup>
$S + Fe \xrightarrow{(350-400^\circ C)} FeS$	-97.17	-94.41	-92.43
$H_2S + Fe \xrightarrow{(>200^\circ C)} FeS + H_2$	-64.56	-40.37	-23.75
$H_2S \xrightarrow{(340-400^\circ C)} S + H_2$	33.02	-6.73	-17.74

The possible chemical mechanisms responsible for sulfur corrosion are as follows<sup>(7)</sup>:

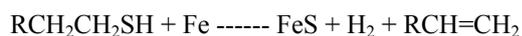
- (1) Thermal decomposition of non-active sulfur substances into active sulfurs



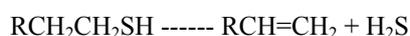
- (2) Decomposition of thiosulfides into H<sub>2</sub>S and free-radical sulfur substances through metal catalyzing



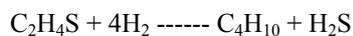
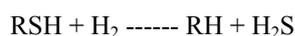
- (3) Reaction of thiosulfide with iron at high temperatures



H<sub>2</sub>S is produced after thermal decomposition, and then reacts with iron.



- (4) Other reactions (e.g., hydrogenation)



According to these corrosion mechanisms, it is difficult to prevent the conversion of the organic sulfur species that are present in CLO into active sulfurs (such as H<sub>2</sub>S). Therefore, with an increase in production capacity at the CSCC plant, involving a substantial temperature rise, the CLO process displayed an increasing tendency to corrode. Although only a little H<sub>2</sub>S(S<sup>-2</sup>) was observed in the CLO at high temperatures, the amount of total sulfur substances was approximately 0.4 wt%. Thus, certain sulfur species were unavoidably converted into active sulfurs, and corrosive sulfur reactions occurred spontaneously<sup>(9)</sup>. Nevertheless, the identity of the organic sulfur

components present in the CLO mixture that are most easily decomposed at high temperatures is unknown<sup>(7-10)</sup>, because CLO contains thousands of aromatic chemicals and most of them cannot be identified in detail.

### 3.4 Prevention of CLO corrosion

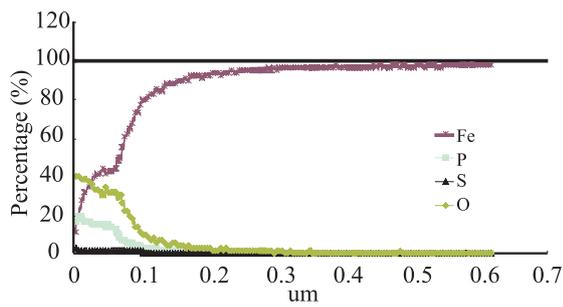
#### 3.4.1 Corrosion inhibitor<sup>(6)</sup>

In this study, an effective corrosion inhibitor was successfully added to the CLO process. The main principle behind corrosion inhibitor agents is to form a strong adhesive film on the surface of pipelines and equipment. This protective film cannot be wiped away with or without solvent, and therefore it can achieve complete protection and avoid the contact of active sulfur species, such as H<sub>2</sub>S and sulfur, with the iron in pipes and equipment. Accordingly, sulfur corrosion can be prevented effectively. The hard protective film differs from the loose FeS structure generated in the corrosion process, and therefore it can withstand the strength of fluid flow or mechanical forces without peeling.

The formulations and dosing conditions of the corrosion inhibitor were developed at the laboratory of China Steel. After adding the optimized dose of the corrosion inhibitor into the CLO solution, where a coupon specimen had been inserted, a protective film (see Fig.10) formed on the surface of the coupon. This film was analyzed using a glow discharge spectrometer (GDS), and the results are shown in Fig.11. The film was thicker than 0.2 μm, and was composed of iron phosphate. The optimal dosing conditions were as follows: minimum operating temperature of 250°C (200°C, invalid); minimum dosage of 2,000 ppm (500 ppm, invalid); initial dosing for over 2 days (1 day, invalid); and a required dose of more than 150 ppm (50 ppm, invalid) to maintain the protective film.



**Fig.10.** The carbon steel specimens: original (left), and, with a full protective film (right).



**Fig.11.** GDS chromatogram of the anti-corrosion film.

### 3.4.2 Applications

The corrosion inhibitor has been applied to the CLO process at the CSCC plant since November 15, 2011, and the results are shown in Table 5. The corrosion rate of the eight sets of coupons located in the CLO path decreased notably from 81 to 10 mpy or less, and an auxiliary online corrosion inductor also exhibited a similar downward trend regarding corrosion. Nevertheless, the corrosion rates of Coupons 4, 5, 7 increased substantially after December 29, 2011, with the corrosion rate at the F121-outlet (Coupon 7) being

particularly high (up to 91 mpy). This suggests that the corrosion inhibitor could not reach the end positions of the CLO process where these three coupons were located; therefore, a new dosing point for Coupon 7 was established at the entrance of the F121 furnace on February 25, 2012. After rearranging the layout of the dosing points in the CLO process, the corrosion rate of the whole plant was effectively reduced. During a dosing period of more than half a year, the overall corrosion rate of the coupons was below 2 mpy, showing an excellent condition. Nevertheless, a slightly increasing corrosion trend was observed in August 2012 because the plant was shut down and the corrosion inhibitor was re-dosed. Furthermore, all the factory hardware, such as distillation towers, pipelines, and pumps, were examined, and the results showed that the anti-corrosion film completely covered the surface of the equipment (Fig.12).

After the corrosion inhibitor was successfully added to the CLO process, there have been no further corrosion problems at the CSCC plant, saving at least NT\$60 million per year, and representing a 140~170% increase in the production yield.

**Table 5** Corrosion rates of coupons measured at various positions of the CLO process

Date (year)/mpy	Coupon 1 C121-bottom	Coupon 2 R121-outlet	Coupon 3 C122-bottom	Coupon 4 C123-bottom	Coupon 5 R123-inlet	Coupon 6 F121-inlet	Coupon 7 F121-outlet	Coupon 8 P125-outlet
9/26 (2011)	8.31	32.23	21.83	22.81	40.52	24.60	28.13	31.79
10/29	4.69	29.82	9.91	15.49	27.12	18.60	81.26	20.72
11/15 Start dosing	5.36	15.73	2.61	2.83	7.97	7.59	1.86	8.31
12/29	3.49	0	2.19	18.31	38.96	12.45	91.43	10.75
2/24 (2012)	5.62	0	1.81	8.78	18.60	0.11	30.59	14.04
4/26	2.30	0	1.42	11.36	23.81	0	0	0
6/14	1.51	0	0	0	0	0	0	0
8/30 Re-dosing	3.79	1.61	0	14.48	7.70	0.83	6.61	2.12
10/5	3.21	0.28	0.63	2.95	0	0	0	0.03
11/2	4.51	0.19	2.10	0	0	0	0	0.95
1/9 (2013)	3.20	1.43	0.16	0.80	0	0.46	0	0.97
3/7	--	0	2.31	0.45	0	0.02	0	0.03



**Fig.12.** Photographs of the anti-corrosion film formed on the surface of a coupon.

#### 4. CONCLUSION

This study aimed to resolve corrosion problems in the CLO process, and the conclusions are summarized as follows.

- (1) Analysis of the detailed composition of the CLO concerning the total acid value, water content, chloride, and naphthenic acid, showed that the quality of the CLO was superior to that of commercial heating oil. Despite this, the CLO contained approximately 0.4 wt% of organic sulfur components, whereas heating oil had almost no sulfur.
- (2) The results of CLO corrosion experiments, conducted at M Corporation or obtained from Parr tests, confirmed that the organic sulfur substances present in the CLO decomposed into small species at high temperatures, and soon afterward reacted with iron. The possible mechanisms of these chemical reactions were presented.
- (3) A suitable corrosion inhibitor was developed and used in the CLO process to form a strong protective film on the surface of the carbon steel, and the optimal operating and dosing conditions were as follows: minimum operating temperature of 250°C, minimum initial dose of 2000 ppm, and minimum subsequent dose of 150 ppm. This procedure makes it possible to avoid the contact between the surface of equipment and the active sulfurs in the CLO, thereby preventing corrosion.
- (4) A corrosion inhibitor has been added to the CLO process since November 15, 2011, and the results indicated that the corrosion rates of all the coupons located in the CLO path decreased from 90 to 10 mpy or less. At present, the corrosion rates of most of the coupons are near 0 mpy, representing an excellent corrosion level in the oil industry.

- (5) After adding the corrosion inhibitor to the CLO process for over one year, CSCC no longer experiences corrosion problems and the production yield has increased 40~70%, reducing corrosion losses by at least NT\$ 60 million per year.

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