Corrosion Behavior under Black Deposit on Low Cr Bearing Steels in NaCl Completion Fluid

Hideki TAKABE,¹⁾ Masakatsu UEDA²⁾ and Shinji FUJIMOTO³⁾

1) Corporate Research & Development Laboratories, Sumitomo Metal Industries, Ltd., 1-8 Fuso-cho, Amagasaki 660-0891 Japan.

2) Sumitomo Metal Industries, Ltd., 1850 Minato, Wakayama 640-8555 Japan.

3) Division of Material and Manufacturing Science, Graduated School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871 Japan.

(Received on April 7, 2008; accepted on September 8, 2008)

3 % Cr steel has been developed as a tubing material for CO₂ oil well considering CO₂ corrosion resistance. However, an oil leakage problem occurred 6 months after the start of oil production in a CO₂ oil well which was completed by tubing of 3 % Cr steel. 3 % Cr steel was exposed to an alkaline NaCl completion fluid environment before exposed to the oil production environment. Corrosion under the black deposit, which developed locally on 3 % Cr steel in the NaCl completion fluid, was identified to be a cause of oil leakage. The conditions of the black deposit formation on 1 % Cr and 3 % Cr steels were investigated by immersion test in a simulated NaCl completion fluid varying dissolved oxygen (DO) concentration, pH and temperature. 1 % Cr steel is a representative Cr bearing steel and used as a comparable material. If the fluid was alkaline and DO concentration was above 77 ppb, the black deposit formed locally on 1 % Cr and 3 % Cr steels. Localized corrosion was observed just under the black deposit. If the DO concentration was equal to or less than 33 ppb, the black deposit did not form. Corrosion behavior of the specimens with the black deposit was also investigated in a simulated oil production environment. It is concluded that corrosion progress under the black deposit on 3 % Cr steel in the production environment resulted in the oil leakage 6 months after the start of production. The black deposit was identified as Fe₃O₄ mainly by X-ray diffraction analysis. In order to prevent oil leakage on 3 % Cr steels in the oil production environment, it is necessary to control the DO concentration in the alkaline NaCl completion fluid to or below 33 ppb that prevents formation of the black deposit.

KEY WORDS: Cr bearing steel; 3 % Cr steel; 1 % Cr steel; NaCl; completion fluid; Fe₃O₄; corrosion.

1. Introduction

CO₂ corrosion is one of the serious problems in the oil and gas industries. Therefore, 3 % Cr steel has been developed as a tubing material with approximately 4 times longer lifetime than carbon steels in the CO₂ environments¹⁻⁴⁾ and was employed as the tubing material for two CO₂ oil wells in Statfjord field at the North sea. However, oil leakage occurred for the one well due to localized corrosion at a seal portion of threaded joint 6 months after the start of oil production. For the other well, no leakage occurred and oil production has been continued. The difference between the two wells was the exposure time to alkaline NaCl completion fluid. There are two stages for oil well construction. The first is a drilling stage where a borehole is drilled and steel tubings and casings are installed. The second is a completion stage where a completion fluid, which is high-density mixed brine solution, is poured into the inside of the tubing and the annular space between tubing and casing to keep oil from invading and to clean the inside of the tubing which is dirtied by mud during drilling. The tubings are normally exposed to the completion fluid for 7 to 10 d. In the case of the well of oil leakage, the tub-

ing of 3 % Cr steel was exposed to NaCl completion fluid for about 30 d. In the case of the well without oil leakage, the exposure period was 10 d. The completion fluid used for the both wells was a mixture of high-density NaCl brine, biocide and oxygen scavenger. The previous investigation using 3 % Cr steel indicated that a black deposit was formed locally on 3 % Cr steel in the NaCl completion fluid with pH more than 11.⁵⁾ Under the black deposit formed on 3 % Cr steel, localized corrosion progressed extremely which might extend as leakage. However, it was not clear the relationship among DO concentration, pH and temperature for the formation of the black deposit. Moreover, it was not clear the corrosion mechanism under the black deposit and the process to reach the leakage not immediately after the production start-up but 6 months after.

In this study, immersion tests of 3 % Cr steel were carried out in NaCl solution varying DO concentration, pH and temperature to investigate the NaCl completion fluid conditions under which the black deposit formed locally. Electrochemical tests were also conducted to examine corrosion behavior of the steels in NaCl completion fluids. In addition, immersion test in a simulated oil production environment was carried out using crevice specimens in order to

investigate corrosion progress under the black deposit. 1% Cr steel was also used as comparable material. Based on the test results, the corrosion mechanism under the black deposit and elimination method for the black deposit are proposed.

2. Test Procedures

2.1. Materials and Test Specimens

The materials examined were 1% Cr and 3% Cr steels. 1% Cr steel is a representative oil country tubular goods (OCTG) and used as a comparable material. The chemical compositions of the test materials are shown in **Table 1**.

The materials were cut from pipes that were hot rolled, quenched and tempered in a mill. The yield strengths ranged between 550 to 654 MPa.

Coupon specimens and crevice test specimens were used for corrosion tests in simulated NaCl completion fluids and oil production environments. The size of coupon specimen was 30 mm width×40 mm length×3 mm thickness. The crevice test specimen set was a couple of the larger coupon of 30 mm width×30 mm length×3 mm thickness, and the smaller coupon of 15 mm width×30 mm length×3 mm thickness with holes of 5 mm diameter for fastening together using a bolt and nuts. Electrochemical tests for 1% Cr and 3% Cr steels were also conducted to measure corrosion potential and anodic polarization curve. The specimen size for the electrochemical test was 15 mm width×15 mm length×2 mm thickness. The side and back of the specimen were covered with silicon gel and the exposed tested area was approximately 1 cm². All the test specimens were polished with the silicon carbide #600, and then degreased and rinsed with dichloromethane and methanol.

2.2. Corrosion Test

2.2.1. Corrosion Tests in Simulated NaCl Completion Fluid Environments

Crevice test specimens were immersed in the different simulated NaCl completion fluid by using glass vessel.

The NaCl completion fluid used for the well of oil leakage consisted of 1.03 specific gravity (SG) NaCl (3.75 wt% NaCl), biocide and oxygen scavenger, and its pH was adjusted at approximately more than 11 by sodium hydroxide, as shown in **Table 2**.

However, in this study, 1.03 SG NaCl solution was used as test solution to simplify experiment. **Table 3** shows the test conditions. In order to investigate the condition of black deposit formation, DO concentration and pH in the 1.03 SG NaCl solution were changed. The NaCl solutions with different DO concentration and pH are referred as simulated NaCl completion fluids in this paper.

The following methods were used for changing DO concentration: (a) deaerated test solution with N₂ purging, (b) deaerated test solution by adding oxygen scavenger and (c) aerated test solution.

The following methods were applied for changing pH in test solution: (a) No adjusted (pH=5.5 to 6.5), (b) Adjusted at around 4 by HCl and (c) Adjusted at around 12 by NaOH. The crevice specimens were placed in the glass vessel, and the simulated NaCl completion fluid was poured into the vessel and heated up to test temperature if neces-

Table 1. Chemical composition (mass%) of materials.

Steel	C	Si	Mn	Cr	Mo
1%Cr	0.26	0.25	0.84	1.12	0.32
	0.26	0.26	0.80	0.96	0.09
3%Cr	0.17	0.24	0.40	3.22	0.01

Table 2. Completion fluid.

	Chemical
Brine	1.03SG NaCl
Biocide	0.5ml/l Glutaraldehyde
Oxygen scavenger	0.5ml/l NaHSO ₃
Sodium hydroxide	Adjusted at pH more than 11

SG=specific gravity

Table 3. Test conditions of simulated completion fluid environments.

Test solution	Deaeration	pH (aiming value)	Temperature (°C)	Exposure duration (hr.)
1.03SG NaCl	No	4 (adjusted by HCl)	25, 50, 70, 90	120
	No	No control (5.5 to 6.5)	25, 50, 70, 90	120
	No	12 (adjusted by NaOH)	25, 50, 70, 90	120
	Yes (purging with N ₂ gas)	No control (5.5 to 6.5)	90	720
	Yes (purging with N ₂ gas)	12 (adjusted by NaOH)	90	720
	Yes (adding OS ^{*1})	12 (adjusted by NaOH)	90	120

*1: OS(oxygen scavenger) = 0.5ml/l NaHSO₃

sary. The specific solution volume (solution volume divided by specimen surface area) was more than 20 mL/cm².

After testing, specimens were taken out and corrosion products were removed from crevice test specimens. Test specimens were immersed in 10 wt% ammonium citrate dibasic solution. Then, corrosion products were removed by a nonwoven abrasive sheet. After removing corrosion products, corrosion rate was calculated and localized corrosion was evaluated by visual observation. In this paper, all corrosion rates were calculated by dividing weight loss by the all surface area of specimen and test duration.

The corrosion products were analyzed using X-ray diffraction for the black deposit.

In order to measure the pH under the black deposit, the corrosion products were partially scraped using knife blade to expose their cross section. pH at the corner of the cross section and the revealed substrate steel was measured using micro pH probe as the pH at the interface between corrosion products and steel. Coupon test specimens were also immersed in the simulated NaCl completion fluid with DO concentration of 25 ppb to investigate corrosion products and secondary ion mass spectroscopy (SIMS) analysis was carried out on tested coupon specimen without removing corrosion products for studying Cr enrichment in the corrosion products.

2.2.2. Corrosion Tests in Simulated Oil Production Environment

As shown in **Table 4**, an immersion test was carried out using an autoclave in a simulated oil production environment of 0.3 MPa CO₂ at 90°C. The test solution had the same chemicals as the production fluid in the well of oil

Table 4. Test condition of a simulated oil production environment.

Test solution	T(°C)	Gas/Partial pressure (MPa)	Calculated pH	Duration (hr.)
Na ⁺ =8640mg/l K ⁺ =190mg/l Ca ²⁺ =300mg/l Mg ²⁺ =70mg/l Ba ²⁺ =60mg/l Sr ²⁺ =50mg/l Cl ⁻ =14300mg/l HCO ₃ ⁻ =1100mg/l CH ₃ COOH=397mg/l	90	CO ₂ /0.3	5.7	720

Fig. 1. Crevice test specimens used in this study. (a) Smaller specimen, (b) larger specimen.

leakage. The calculated pH of the test solution is 5.7 at the test condition. In order to investigate the corrosion behavior under black deposit on 1% Cr and 3% Cr steels in the oil production environment, crevice specimens with a black deposit between the smaller and the larger test coupons were used as shown in **Fig. 1**. Coupon test specimens were also used to examine the corrosion behavior without black deposit. The black deposit used in this study was made by a 5 d-immersion of 3% Cr steel in the aerated 1.03 SG NaCl solution of pH 12 at 90°C. The test solution was fully deaerated by purging with N₂ gas for 20 h in order to make DO concentration in the test solution be equal to or less than 10 ppb. Then, the deaerated test solution was transferred to the autoclave under vacuum.

Corrosion rate and localized corrosion were evaluated by the same manner as corrosion tests in the simulated NaCl completion fluid environments.

2.2.3. Electrochemical Test

The corrosion potentials of 1% Cr and 3% Cr steels were measured for 1 h in aerated and deaerated 1.03 SG NaCl solutions with pH of 12.0 at 90°C.

As explained later, black deposit developed on 1% Cr and 3% Cr steels in the aerated alkaline NaCl solution with pH of 10 to 12. The pH was 3.6 to 5.4 at the interface between metal surface and black deposit. Therefore, in the aerated NaCl solutions with different pH of 12.0 and 4.6 that was intermediate value of pH at the interface between metal surface and black deposit, the anodic polarization curves of 1% Cr and 3% Cr steels were measured at 90°C after 1 h exposure in the solutions with sweep speed of 20 mV/min to examine each corrosion behavior under alkaline NaCl completion fluid and under black deposit envi-

Fig. 2. The relationship among localized corrosion under black deposit, dissolved oxygen and pH in NaCl solution at 90°C. **Fig. 3.** The appearance of tested specimen (aerated 1.03 SG NaCl, pH=12.0, 90°C, 5 d). (a) Before descaling, (b) after descaling.

ronments.

An Ag/AgCl/saturated KCl electrode was used as the reference electrode, and platinum was used as the counter electrode.

3. Results and Discussion

3.1. Corrosion Tests in Simulated NaCl Completion Fluid Environments

3.1.1. The Effect of DO Concentration and pH

Figure 2 demonstrates the form of corrosion under black deposit in NaCl solutions for various pH and DO concentration at 90°C. DO concentration and pH were measured at room temperature. In the NaCl solutions with pH more than 10 and DO concentration equal to or more than 77 ppb, black deposit developed locally on 1% Cr and 3% Cr steels. Namely, the local black deposit develops in the alkaline environment with high DO concentration. **Figure 3** shows the appearance of tested crevice specimens of 3% Cr steel. The black deposit was not observed at the crevice portion but on the larger coupon around the smaller coupon fasten to the larger coupon. The black deposit was also observed on the smaller coupon around the PTFE (polytetrafluoroethylene) washer. Moreover, it was also observed that localized corrosion occurred under the black deposit. However, the surface without the black deposit remained metallic luster. When DO concentration was 33 ppb or less, specimens remained metallic luster and did not suffer from any localized corrosion regardless of pH in the range between 5 and 12. When pH was less than 7, all specimen surfaces were covered with corrosion products and specimen suf-

Fig. 4. The relationship between corrosion rate and dissolved oxygen in 1.03 SG NaCl solution at 90°C.

Fig. 5. SIMS analysis results on film formed on 3% Cr steel in 1.03 SG NaCl with pH of 11.2 at 90°C (DO=25 ppb).

ferred general corrosion with corrosion rate from approximately 0.1 to 0.25 mm/year in the aerated test solutions. The corrosion rates of general corrosion did not depend on pH.

Figure 4 describes the corrosion rate in NaCl solutions with pH above 10 as a function of DO concentration at 90°C. Corrosion rates of 1% Cr and 3% Cr steels increased with increasing DO concentration. This increase in corrosion rate is due to the progress in the localized corrosion under the black deposit, because corrosion was observed only under black deposit. **Figure 5** shows the SIMS depth profile of the surface film formed on the coupon specimen of 3% Cr steel, which exhibits the metallic luster, in deaerated NaCl solution with 25 ppb DO at 90°C. Cr, Fe and O were detected from the surface until approximately 0.15 μm in depth (9.4 min). At the peak of Cr located at approximately 0.06 μm (4 min), the Cr and Fe contents in metals included in film were approximately 20 and 80 at%, respectively. From these results, the reason of the remaining metallic luster on 1% Cr and 3% Cr steel in NaCl solutions with low DO concentration (33 ppb or less) is considered to be the formation of Cr enriched iron oxide film which acts as protective film. **Figure 6** shows X-ray diffraction pattern of the black deposit which developed on 3% Cr steel in NaCl solution at 90°C. Strong and weak peaks that were identified to be Fe_3O_4 and $\beta\text{-FeOOH}$, respectively, were observed. The pH under the black deposit developed on 3% Cr and 1% Cr steels in NaCl solution at 90°C was from 3.6 to 5.4 and lower than that in bulk NaCl solution as shown in

Fig. 6. X-ray diffraction analysis result of black deposit on 3% Cr steel (1.03 SG NaCl, pH=11.7, 90°C, 5 d).

Table 5. pH measurement results on black deposit formed on steel at 90°C.

Steel	pH under black deposit	pH in bulk solution	Solution	
			Chemical	DO(ppb)
1%Cr	3.6 to 4.5	10.2	1.03SG NaCl+NaOH	77
3%Cr	4.5 to 5.4			
1%Cr	4.9	12.0	1.03SG NaCl+NaOH	7740
3%Cr	5.2			

Table 5. This lowering of pH is considered to be an increment in H^+ ion due to Fe_3O_4 and FeOOH formation reactions, as discussed later.

3.1.2. The Effect of Temperature

The condition for formation of the black deposit was examined in aerated NaCl solution by varying temperature and pH. The results were shown in **Fig. 7**. When pH was approximately 12, the black deposit was observed on 1% Cr and 3% Cr steels at temperatures between 25 and 90°C. However, the black deposit was not observed at pH of 4 and 6. Hence, the Cr enriched oxide film formed on 1% Cr and 3% Cr steels is considered to become unstable locally in aerated alkaline completion fluid at temperatures above 25°C. The average corrosion rates of crevice specimens of 1% Cr and 3% Cr steels, which are obtained by weight loss after immersion test, in NaCl solutions with pH of approximately 4 and 12 are shown in **Figs. 8(a)** and **8(b)** as a function of temperature. The average corrosion rate in NaCl solution with pH of approximately 12 did not depend on temperature at between 25 and 90°C.

Figure 8 also shows that corrosion rate in NaCl solution with pH of approximately 4 was almost same as that in NaCl solution with pH of approximately 12, except for data of 1% Cr steel at 25°C. However, corrosion morphology was different with pH. The corrosion morphology was general corrosion at pH of approximately 4 and localized corrosion under black deposit at pH of approximately 12.

3.2. Corrosion Tests in Simulated Oil Production Environment

The results of immersion test in the simulated oil production environment are shown in **Table 6**. All coupon specimens, on which the black deposit was not put before testing, did not suffer from localized corrosion but general corrosion, and no black deposit developed on the specimens. The general corrosion was attributed to CO_2 corrosion. The corrosion rate was from 0.8 mm/year to 1.6 mm/year and

Fig. 7. The relationship among localized corrosion under black deposit, temperature and pH in aerated 1.03 SG NaCl solution. (a) 1% Cr steel, (b) 3% Cr steel.

Fig. 8. The relationship between average value of corrosion rate and temperature in aerated 1.03 SG NaCl solutions (pH=11.7-12.0). (a) 1% Cr, (b) 3% Cr.

Table 6. Test results in a simulated oil production environment.

Steel	Crevice with black deposit			Coupon w/o black deposit	
	Corrosion rate(mm/y) L ⁻¹	LC ³ under S ⁻¹	BD ⁴	Corrosion rate (mm/y)	LC under BD
1%Cr	1.547	1.025	Yes	1.625	No
	1.524	0.990	Yes	-	-
3%Cr	0.837	0.584	Yes	0.838	No
	0.818	0.575	Yes	-	-

*1: L= Large specimen(30mm W x 30mm L x 3mm t)

*2: S= Small specimen(15mm W x 30mm L x 3mm t)

*3: LC=localized corrosion, *4: BD= black deposit

was higher than that in the simulated alkaline NaCl completion fluid environments.

On the other hand, all the crevice specimens with the black deposit being loaded before testing, the slight corrosion proceeded under the black deposit as shown in Fig. 9. As described above, the black deposit was identified to be mainly Fe_3O_4 . Many authors reported that in a reduction atmosphere with low oxygen concentration, anodic reaction on carbon steel will be accelerated due to cathodic reduction of Fe_3O_4 on the steel.⁶⁻⁹⁾ The corrosion progress under the black deposit observed in this corrosion test might be due to reduction of Fe_3O_4 , because the DO concentration in this test was very low (10 ppb or less).

The reason of the oil leakage in the filed occurred 6 months after the start of production is considered to be the continuous active dissolution of the steel under the black deposit which is maintained by the CO_2 corrosion and ca-

thodic reduction of Fe_3O_4 . Therefore it is important to keep the DO concentration in alkaline NaCl completion fluids low below 33 ppb to prevent developing of black deposit that could accelerate the localized corrosion in oil production environments.

3.3. Electrochemical Test

Table 7 shows the corrosion potentials of tested materials in the 1.03 SG NaCl solution with pH of 12. The corrosion potential of each material in the aerated solution tends to be more noble than that in the deaerated solution. Figures 10(a) and 10(b) show the anodic polarization curves in aerated NaCl solutions at 90°C with pH of 12.0 and 4.6, respectively. In the solution with pH of 12.0, the current density of 3% Cr and 1% Cr steels was stable in the potential range between -520 and -460 mV (SSE), and between -550 and -500 mV (SSE), respectively. In these potential ranges, Cr enriched iron oxide film would be formed on 3% Cr and 1% Cr steels. Above these potentials, current density increased as potential became noble and the black deposit was observed clearly on each material above approximately -400 mV (SSE). Therefore, black deposit could develop on the 3% Cr and 1% Cr steels where Cr enriched iron oxide film is broken for some reason. In the solution with pH of 4.6 which is simulated test solution under the black deposit, the current density of 3% Cr and 1% Cr steels monotonously increased as potential became noble. This means that Cr enriched iron oxide film would not be

Fig. 9. The appearance of tested specimen with black deposit (after descaling) Upper half surface: no black deposit, Lower half surface: black deposit was put. (a) 1% Cr, (b) 3% Cr.

Fig. 10. Anodic polarization curve in aerated 1.03 SG NaCl solution at 90°C. (a) pH=12.0, (b) pH=4.6.

Table 7. Corrosion potential in 1.03 SG NaCl solution at 90°C.

Water property	Corrosion potential(mV)	
	3%Cr	1%Cr
pH=12.0, Aerated	-552(SSE ^{*1})	-682(SSE)
pH=12.0, Deaerated	-575(SSE)	-769(SSE)

*1: SSE=saturated silver silver chloride electrode

formed and corrosion progresses in acidity solution such as the solution under the black deposit.

3.4. Corrosion Mechanism under the Black Deposit

This study revealed that the localized black deposit would develop on 1% Cr and 3% Cr steels in alkaline NaCl completion fluid with high DO concentration. On the other hand, the black deposit did not develop in the oil production environment in which DO concentration is low and H^+ ion concentration is slightly lower than neutral. Under the black deposit, localized corrosion was accelerated in both NaCl completion fluid and oil production environments. Since the corrosion behaviors of 1% Cr and 3% Cr steels were almost same, the corrosion acceleration process under the black deposit on 3% Cr steel is described in the following:

- 1st Step: Black Deposit Formation in Alkaline NaCl Completion Fluid Environment

In Fig. 11, the potential-pH diagram of Cr-H₂O system (red dotted line) at 100°C is superimposed on that of Fe-H₂O system (solid line). In this figure, ion species concentration is 10^{-3} mol/L. A closed circle mark indicates corrosion potential measured in the electrochemical test of 3% Cr steels in the aerated NaCl solution with pH of 12.0 at 90°C. Since the corrosion potential was in the stable region of Cr₂O₃ and Fe₂O₃ and Cr, Fe and O were confirmed by

①: $2CrOH^{2+} + H_2O = Cr_2O_3 + 4H^+$, ②: $2Cr^{2+} + 3H_2O = Cr_2O_3 + 6H^+ + 2e^-$, ③: $2Cr + 3H_2O = Cr_2O_3 + 6H^+ + 6e^-$, ④: $2CrO_2^- + 2H^+ = Cr_2O_3 + H_2O$, ⑤: $Cr_2O_3 + 5H_2O = 2CrO_4^{2-} + 10H^+ + 6e^-$, ⑥: $Cr_2O_3 + 5H_2O = 2HCrO_4^- + 8H^+ + 6e^-$

Fig. 11. Potential-pH diagram of Fe-H₂O system at 100°C. ●: Corrosion potential of 3% Cr in aerated NaCl with pH of 12, ○: expected point of black deposit initiation, △: expected point under black deposit condition, ion species = 10^{-3} mol/L.

SIMS analysis, Cr enriched iron oxide film would form at the corrosion potential of 3% Cr steel in the alkaline NaCl completion fluid environment. The black deposit of Fe₃O₄ is considered to develop where Cr enriched iron oxide film is broken. Since the corrosion potential is considered to be a mixed electrode potential between cathodic reaction of O₂ consumption reaction, and anodic reactions such as Fe₃O₄ formation reaction and Cr enriched iron oxide film formation reaction, the potential at the surface of 3% Cr steel could be less noble than the corrosion potential. In addition, the black deposit formed in immersion test was not indenti-

Fig. 12. Potential-pH diagram of Fe-H₂O system at 100°C concerning stable ion species.

fied as Fe₂O₃ but Fe₃O₄ mainly by X-ray analysis.

Therefore, at the site of oxide breakdown, potential would become less noble closely to the equilibrium potential between Fe and Fe₃O₄, as indicated in an open circle mark in Fig. 11. As a result, Fe₃O₄ could develop as the black deposit.

Moreover, the black deposit was observed in the NaCl test solutions of pH from 10 to 12 with DO concentration equal to or more than 77 ppb and HFeO₂⁻ is the stable ion species in the pH range between 10 and 12 according to the potential-pH diagram for stable ion species concerning Fe-H₂O system at 100°C, as shown in Fig. 12.

Therefore, the corrosion reaction with Fe₃O₄ formation is described as follows:

Cathodic reaction (consumption of DO at the exposed steel surface)

Anodic reaction

If the concentration of HFeO₂⁻ ion is increased, Fe₃O₄ would be formed by the reaction (3).

From reactions (2) and (3), Fe₃O₄ formation reaction is described as follows:

• 2nd Step: Corrosion Growth under the Black Deposit in Alkaline NaCl Completion Fluid Environment

The black deposit of Fe₃O₄ grows up to certain amount, then H⁺ ion generated by reaction (4) would be accumulated under the black deposit. Consequently, pH of the solution could be lowered under the black deposit, as shown in Table 5. Corrosion under the black deposit could be progressed during the lowering of pH. The lowering of pH is considered to continue to the stable region of Fe²⁺ ion as shown in open triangle mark in Fig. 11, because the measured pH under the black deposit was from 3.6 to 5.4.

According to the potential-pH diagram shown in Fig. 12, the stable ion species vary with pH. Therefore, anodic reactions of Fe dissolution reaction during the lowering of pH are described as follows:

If the concentration of HFeO₂⁻, FeOH⁺ and Fe²⁺ ions increase, Fe₃O₄ would be formed by oxidation reaction of aqueous ions including ferrous ion such as reactions (3) and (4).

On the other hand, possible cathodic reactions are reductions of DO, Fe₃O₄ and of H⁺ ion.

DO reduction (1) in this step occurs at the outside of black deposit because DO under the black deposit would be almost consumed in the step 1.

H⁺ reduction (8) would occur under the black deposit when H⁺ ion increases (low pH). Taking account of corrosion under the black deposit, possible anodic reactions are Fe₃O₄ formation (4) and Fe dissolution reaction (6). If Fe²⁺ ion increases by reaction (6), Fe₃O₄ reduction (7) would hardly occur.

From reactions of Fe₃O₄ formation (4) and H⁺ reduction (8), corrosion reaction under the black deposit is described as the following reaction (9). In reactions of (9) and (6), H⁺ does not form under the black deposit. Therefore, after the consumption of H⁺ under the black deposit, cathodic reaction would be only DO reduction (1) at outside the black deposit.

• 3rd Step: Corrosion Growth under the Black Deposit in the Oil Production Environment

In this step, corrosion progressed gradually under the black deposit by the CO₂ corrosion and reduction of Fe₃O₄ (7) in production fluid environment with low DO concentration.

The oil leakage occurred 6 months after the start of production on 3% Cr steel is attributed to corrosion progress which started under the black deposit in the alkaline NaCl completion fluid and then continued in production fluid. Since the corrosion rate in the simulated oil production environment was higher than that in the simulated alkaline NaCl completion fluid environments, corrosion progress under the black deposit in the oil production environment would be faster than that in the alkaline NaCl completion fluid environments. The black deposit might accelerate the corrosion as oxidant. Since the black deposit developed on 1% Cr steel in the alkaline NaCl solutions, same leakage could occur on 1% Cr steel. Therefore, it is important to

keep DO concentration in alkaline NaCl completion fluid low (33 ppb or below) for elimination of the black deposit.

4. Conclusion

(1) In the completion fluid of NaCl whose pH is from 5 to 12, if the dissolved oxygen concentration is below 33 ppb, Cr enriched iron oxide film on 1% Cr and 3% Cr steels will be stable and act as corrosion protective film.

(2) In the alkaline NaCl completion fluid whose pH is from 10 to 12, if the dissolved oxygen concentration is above 77 ppb, local black deposit of Fe_3O_4 develops on 1% Cr and 3% Cr steels.

(3) Corrosion progresses under the black deposit in both NaCl completion fluid and oil production environments. The corrosion progress could cause oil leakage after oil production.

(4) In order to prevent oil leakage problem on the low Cr tubing exposed in alkaline NaCl completion fluid, it is necessary to eliminate the black deposit formation in the

completion fluid and it is important to control the dissolved oxygen in the completion fluid to or below 33 ppb.

REFERENCES

- 1) P. I. Nice, H. Takabe and M. Ueda: Proc. Int. Conf. of Corrosion 2000, NACE, Texas, (2000), paper No. 00154.
- 2) H. Takabe and M. Ueda: Proc. Int. Conf. of Corrosion 2001, NACE, Texas, (2001), paper No. 01066.
- 3) H. Takabe and M. Ueda: Proc. Int. Conf. of Corrosion 2002, NACE, Texas, (2002), paper No. 02041.
- 4) H. Takabe and M. Ueda: *Zairyo-to-Kankyo*, **56** (2007), 514.
- 5) P. I. Nice, A. M. Buene, H. Takabe: Proc. Int. Conf. of Corrosion 2006, NACE, Texas, (2006), paper No. 06134.
- 6) H. Watanabe, A. Nishikata and T. Tsuru: Proc. 46th Jpn. Conf. of Material and Environments, JSCE, Tokyo, (1999), 261.
- 7) A. Araoka, H. Watanabe, A. Nishikata and T. Tsuru: Proc. 2000 Fall Meeting of Electrochemical Society of Japan, (2000), 191.
- 8) T. Tsushima, N. Hara and K. Sugimoto: *Zairyo-to-Kankyo*, **52** (2003), 545.
- 9) Y. Kojima and S. Tsujikawa: Proc. 44th Jpn. Conf. of Material and Environments, JSCE, Tokyo, (1997), 421.