

Experimental Study on Corrosion Mechanism in Guangli Oilfield

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Abstract

Casing corrosion is serious and the injection efficiency is considerably low due to high injecting water corrosion in Guangli oilfield. Casing corrosion mechanism is retrieved through SEM observation, energy spectrum analysis, XRD analysis spectrum, TGA analysis of corrosion fouling. The results show casing corrosion mechanism varies with depths; casing corrosion is the result of the combined action of carbon dioxide, dissolved oxygen, sulfate-reducing bacteria and high salinity. To extend the life of casing, appropriate casing protection measures should be adopted, which can reduces the cost of production of the oilfield.

Key words: Casing corrosion; Fouling; SEM observation; Casing protection; Dissolved oxygen

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INTRODUCTION

Casing corrosion is a ubiquitous problem in the production progress of water injection, which not only damages the injecting equipments but also block up the suction channel due to the accumulation of corrosion products at the bottom of the hole^[1]. Thus contradiction between layers is obvious, injecting pressure is increased and water absorbing capacity is decreased. The dominant

factors in casing corrosion are dissolved oxygen, carbon dioxide, hydrogen sulfide, SRB, TGB, temperature, pH, velocity of flow, extent of mineralization and routine of injection and so on^[2-3], casing corrosion mechanism varies with depths and blocks. This paper analyses the corrosion conformation, and casing corrosion mechanism is retrieved through SEM observation, Energy spectrum analysis, XRD analysis spectrum, TGA analysis of corrosion fouling, which serves as guidance of casing protection.

1. SITUATION OF CASING CORROSION IN GUANGLI OILFIELD

The most discharge water in Guangli oilfield is recovered after treating in sewage plant. Its oil content is about 35 mg/L, its PH is around 6.5, and it has higher content of hydrogen sulfide, which increases the corrosion rate. Since its development in 1974, the first casing breakdown occurred in 1986, presently, 16% of oil wells and 53.8% of injecting wells are facing casing problem, in addition, 83 wells are abandoned because of casing corrosion. This phenomenon enormously decreases the quantity of wells and their outcome.

The conformation of casing corrosion is shown in Figures 1 to 3. Casing corrosion has the following characteristics: (a) The corrosion fouling in outer layer of the casing wall is easy to fall off, its color is black and the thickness is 2-3 mm, and the inner layer of the casing wall is made up of rust material with different sizes, which indicates acute local corrosion (Figure 1). (b) There is even corrosion fouling covering the inner wall of the casing, its color is tawny and the thickness is 1-2 mm and it is not likely to fall off, the inner wall is characterized by local potholes corrosion (Figure 2). (c) Some of the exterior surface of the casing is eroded by superficial water or even punched (Figure 3) and it can occur in just 8 months since its putting into production, which directly affected the normal operation of the oilfield and its safety.



Figure 1 External Corrosion of Casing



Figure 2 Internal Corrosion of Casing



Figure 3 Casing Corrosion Punching

2. INVERSION OF CASING CORROSION MECHANISM

The wells in Guangli oilfield are about 2,000 m depth and the dominant factor of corrosion varies with depths, so the mechanism of casing corrosion is inevitably different. Corrosion fouling of different depths is analyzed, and the results can serves as guidance of casing protection.

2.1 Casing Corrosion Mechanism of 10 m Depth

The corrosion fouling of surface is collected and analyzed with SEM observation and Energy spectrum analysis and the results are shown in Figure 4 and Table 1.



20 µm Electronic image 1

Figure 4 SEM Picture of Corrosion Fouling of 10 m Depth Table 1

Energy Spectrum Analysis of the Corrosion Fouling of 10 m Depth

Element	Mass ratio (%)	Atom percent (%)
0	40.42	68.74
Cl	7.95	6.10
Fe	51.63	25.15

It can be seen from Figure 4 that corrosion fouling is likely to fall off. SEM observation indicates that the product of corrosion mainly contains 3 elements: O, Fe and Cl. The reason for the casing corrosion of 10m depth is thought to be the electrochemical erosion initiated by Cl⁻, and its mechanism is shown as follows:

First of all, the ionization reaction takes place:

$$H_2O \rightarrow H^+ + OH^-$$
 (1)

And then the Fe^{2+} that dissolved in water combines with the OH⁻, generates ferrous hydroxide.

$$Fe^{2+}+2OH^{-}=Fe(OH)_{2}$$
(2)

When iron is enveloped with hydrogen, its ionization is inhibited like electrodeposit. Since the ferrous hydroxide in the water is alkaline, the surface of the iron is acidic, so its ionization is inhibited.

While if there is oxygen in the water, the hydrogen that envelopes the iron combines with oxygen and then restore water. So the iron is exposed to the water again and its ionization restarts. Meanwhile, part of the dissolved oxygen combines with ferrous hydroxide, generates ferric hydroxide which is unconsolidated and likely to deposit, resulting in the vanishing of alkalinity and the iron is likely to dissolve again.

$$4Fe (OH)_2 + O_2 + 2H_2O = 4Fe (OH)_3$$
 (3)

In addition, when iron contacts with water, a special part contacts with more oxygen while the other is short of oxygen and then a corroding electrode cell is formed. The anoxic part is positive while the oxic part is negative, the reaction is as follows:

The positive side:

$$Fe \rightarrow Fe^{2+}+2e$$
 (4)

The positive side:

$$2H^{+}+1/2O_{2}+2e \rightarrow H_{2}O \tag{5}$$

After this reaction, Reaction (3) will resume and $Fe(OH)_3$ is generated, resulting in deep potholes in some special parts. As time goes on, casing strength decreases sharply and finally even punched.

2.2 Casing Corrosion Mechanism of 100 m Depth

The corrosion fouling of 100 m is analyzed with SEM observation and Energy spectrum analysis and the results are shown in Figure 5 and Table 2.



Figure 5



Table 2Energy Spectrum Analysis of the Corrosion Fouling of100 m Depth

Element	Mass ratio (%)	Atom percent (%)
C	16.11	33.59
0	22.82	35.73
Si	0.56	0.50
Cl	12.05	8.51
Fe	47.32	21.22
Cu	1.15	0.45



Figure 6 XRD Analysis Spectrum of the Corrosion Fouling Picture of 100 m Depth

The results show that the main element in the corrosion fouling is O and C, Fe and Cl followed. XRD analysis spectrum is adopted, and it can be analyzed that the corrosion products are mainly $FeCO_3$, $Fe_2(OH)_3$, $Fe_2O_3 \cdot nH_2O$, which is shown in Figure 6. So we can safely come to the conclusion that the main reason for the casing corrosion of 100 m depth is oxygen corrosion and carbon dioxide corrosion, and the existing of Cl⁻ increases the corrosion.

The mechanism of casing corrosion by CO_2 is as follows^[4-7]:

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{6}$$

 $H_{2}CO_{3} \rightarrow H^{+} + HCO_{3}^{-}$ $HCO_{2}^{-} \rightarrow H^{+} + CO_{2}^{2-}$ (8)

$$CO_3 \rightarrow H + CO_3 \tag{8}$$

 $Fe \rightarrow Fe^{2^{+}} + 2e \qquad (9)$ $2H^{+} + 2e \rightarrow H_{2} \qquad (10)$

$$Fe^{2^{+}}+CO_{3}^{2^{-}}\rightarrow FeCO_{3}$$
(11)

2.3 Casing Corrosion Mechanism of 100 m to 1,000 m Depth

The corrosion fouling of 500 m is collected and analyzed with SEM observation and Energy spectrum analysis and the results are shown in Figure 7 and Table 3.

Table 3Energy Spectrum Analysis of the Corrosion Fouling of500 m Depth

Element	Mass ratio (%)	Atom percent (%)
С	24.38	42.30
0	26.66	34.72
Si	0.58	0.43
S	7.40	4.81
Са	16.73	8.70
Fe	24.26	9.05



Figure 7 SEM Picture of Corrosion Fouling of 500 m Depth

The results show that the main element in the corrosion fouling is C and O, Fe and Ca follow. XRD analysis spectrum is adapted, and it can be analyzed that the corrosion product of 500 m depth are mainly Fe_9S_8 , CaCO₃ and FeCO₃, which is shown in Figure 8.

So we can safely come to the conclusion that the main cause of the casing corrosion of 500 m depth is SRB, the reasons are as follows: (a) The temperature of 100 m to 1,000 m depth is about 30 to 40 Celsius degree, which falls in the limits that fits the build-up and reproduce of SRB; (b) The S elements of the Energy spectrum analysis are not from crude oil; (c) The Fe₉S₈ found in XRD analysis spectrum is one of the classic products of SRB corrosion.

The mechanism of casing corrosion by SRB is as follows^[8]:

The positive side:

$$4Fe \rightarrow 4Fe^{2+} + 8e \tag{12}$$

The negative side:

 $8H^++8e \rightarrow 8H$ (13)

The depolarization in negative side resulting from SRB:

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$$SO_4^{2-}+8H\rightarrow S^{2-}+4H_2O$$
 (14)
Water hydrolysis reaction:

$$\mathrm{H}_{2}\mathrm{O} \rightarrow 8\mathrm{H}^{+} + 8\mathrm{O}\mathrm{H}^{-} \tag{15}$$

Corrosion products:

$$Fe^{2\tau} + S^2 \rightarrow FeS$$
 (16)

$$3Fe^{2+}+6OH^{-}\rightarrow 3Fe(OH)_2$$
 (17)

The net reaction:

$$4Fe + SO_4^{2-} + 4H_20 \rightarrow FeS + 3Fe(OH)_2 + 2OH^2 \quad (18)$$



XRD Analysis Spectrum of the Corrosion Fouling Picture of 500 m Depth

To further verify the conclusion from the SEM observation and XRD analysis spectrum, TGA analysis is practiced on the corrosion fouling of 500 m depth. The temperature is controlled between 20 and 900 Celsius degree, N_2 is chosen as the shielding gas and the heating rate is 20 Celsius degree per minute, as shown in Figure 9.



TGA Analysis of the Corrosion Fouling Picture of 500 m Depth

After analyzing of TGA analysis results, it can be easily seen that there are two temperature weightless intervals: 141.3-240.23 $^{\circ}$ C and 333.24-464.36 $^{\circ}$ C.They respectively correspond to the hydrate decomposition and the decomposition of FeCO₃. Besides, there are some twists and turns in the curve which indicates various compounds in the sample.

From above analysis, the main reasons for casing corrosion come to CO_2 corrosion and SRB corrosion.

2.4 Casing Corrosion Mechanism of 1,000 m to 2,000 m Depth

The corrosion fouling of 1,600 m depth from the ectooecium of oil tube of injecting well A is collected and

analyzed with SEM observation and Energy spectrum analysis and the results are shown in Figure 10 and Table 4. From Table 4 we can see that the main elements in the corrosion fouling are still C, O and Fe. The result of XRD analysis spectrum shows that the corrosion product is mainly (Ca,Mn)CO₃ (Figure 11), it also indicates serious scale deposit in this injecting well. The existence of CO_3^{2-} indicates that CO_2 corrosion is the main reason for the casing corrosion in this layer.



30 μm Electronic image 1

Figure 10 SEM Picture of Corrosion Fouling of 1,500 m Depth Table 4

Energy Spectrum Analysis of the Corrosion Fouling of 1,500 m Depth

Element	Mass ratio (%)	Atom percent (%)
С	16.09	25.26
0	52.75	62.16
Cl	1.19	0.63
Ca	13.81	6.50
Fe	16.16	5.46



XRD Analysis Spectrum of the Corrosion Fouling Picture of 1,500 m Depth

2.5 Casing Corrosion Mechanism of More Than 2,000 m Depth

With the increasing of the well depth, the temperature increase correspondingly, and at the depth of about 2,000 m, the temperature is generally about 50 $^{\circ}$ C to 70 $^{\circ}$ C. The

corrosion fouling of 2,100 m is collected and analyzed with SEM observation and Energy spectrum analysis and the results are shown in Figure 12 and Table 5.



Figure 12 SEM Picture of Corrosion Fouling of 2,100 m Depth Table 5

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Element	Mass ratio (%)	Atom percent(%)
C	42.96	61.49
0	25.80	27.72
S	3.07	1.64
Cl	1.98	0.96
Са	1.02	0.44
Fe	25.18	7.75

The results show that the main elements in the corrosion fouling are orderly C, O, Fe, S and Cl. Of all of them, C and O are much more, which indicates the corrosion product is mainly carbonate. XRD analysis spectrum and TGA analysis are practiced on the corrosion fouling and the results are shown in Figures 13 and 14. The results show that the corrosion product is mainly FeCO₃. It also shows that casing corrosion in this layer is mainly resulting from CO_2 corrosion.



Figure 13 XRD Analysis Spectrum of the Corrosion Fouling Picture of 2,100 m Depth



TGA Analysis the Corrosion Fouling Picture of 2,100 m Depth

CONCLUSION

(a) Casing corrosion is serious in Guangli oilfield, to take relevant measure to retard corrosion and reduce the cost of production, the corrosion conformation is analyzed and casing corrosion mechanism is retrieved through SEM observation, Energy spectrum analysis, XRD analysis spectrum and TGA analysis of corrosion fouling.

(b) Casing corrosion in Guangli oilfield is the result of the combined action of Carbon dioxide, dissolved oxygen, SRB and high salinity, while dissolved oxygen and Carbon dioxide are the main corrosion factors.

(c) Bacteria commonly exist in the rejected sewage and its corrosion can't be ignored, so the water quality in the reinjection progress should be strictly controlled. By the using of electrochemical equipment, water electrochemical reaction can be irritated, helpful strong oxidizing substance can be produced, which can kill the bacteria in the water, turn Fe^{2+} to Fe^{3+} and eliminate S²⁻, with the help of flocculant, the water is purified and the corrosion is inhibited.

REFERENCES

- [1] Smith, L. (1999). Control of corrosion in oil and gas production tubing. *British Corrosion Journal*, *34*(4), 237-253.
- Palacios, C. A., & Hernandez, Y. (1997). Application of simulation of techniques for internal corrosion prediction. Retrived from http://www.nace.org/cstm/Store/Product. aspx?id=1ed82266-e46e-4261-8d60-4f54820c3540
- [3] Albarran, J. L., Martinez, L., & Lopez, H. F. (1999). Effect of heat on the stress corrosion resistance of microalloyed pipeline steel. *Corrosion Science*, 41(6), 1037-1049.
- [4] Zhang, X. Y., Di, C., & Lei, L. C. (2000). *Corrosion and control for dioxide*. Beijing: Chemical Industry Press.
- [5] Kermani, M. B., & Morshed, A. (2003). Carbon dioxide corrosion in oil and gas production-A compendium. *Corrosion*, 59(8), 659.
- [6] Heuer, J. K., & Stubbins, J. F. (1998). Microstructure analysis of coupons exposed to carbon dioxide corrosion in multiphase flow. *Corrosion*, 54(7), 566-575.
- [7] Deberry, D. W. (1998). CO₂ corrosion in oil and gas production. Houston, USA: National Association of Corrosion Engineers.
- [8] Machel, H. G., Krouse, H. R., & Sassen, R. (1995). Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. *Applied Geochemistry*, 10(4), 373-389.