

Study on CO₂ corrosion behavior and protection technology of gas storage injection production well casing

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Abstract. Wen 23 depleted gas reservoir gas storage is the largest underground gas storage in central and eastern China. It shoulders the important tasks of peak shaving, emergency gas supply and smooth operation of pipelines in the natural gas market in central and eastern China. During the construction period of the gas reservoir, a series of anti-corrosion measures, such as high-efficiency annular anti-corrosion protective fluid, have been designed, taking all kinds of corrosion risks of injection and production well casing into full consideration, and the anti-corrosion effect is remarkable. However, after the phase I project was constructed and put into operation, it was found that some injection and production wells had obvious leakage of annulus protection fluid. Based on the identification results of "three aspects and eleven leakage paths", it is believed that the leakage of tubing threads and packers is the main leakage path of annulus protection fluid. The natural gas produced by the original component detection of the gas reservoir contains a small amount of CO₂, which may cause corrosion perforation to the downhole casing under certain circumstances. Through the corrosion perforation experiment on P110 steel selected for injection production well casing, combined with electrochemical test and surface analysis and other corrosion characterization methods, the anti-corrosion coating design for Wen 23 gas storage is completed. The research results show that the corrosion inhibition efficiency of the new salt resistant anti-corrosion coating is more than 80%, the electrochemical slow-release efficiency is more than 85%, and the anti-corrosion effect is outstanding. It can provide a strong technical guarantee for the safe, stable and stable operation of the injection production well of the gas storage.

Keywords: Gas storage, CO₂ corrosion, High salinity, Corrosion inhibitor.

1. Introduction

Wen 23 gas storage, as the key construction object of the 13th five year plan, shoulders the important task of seasonal peak shaving in Beijing, Shanghai, Tianjin, Hebei and other large areas of central and eastern China. It is the largest underground gas storage in central and eastern China. It is mainly reconstructed from the exhausted main block of Wen 23 gas field. The formation temperature is 115~130°C, and the formation water salinity is $23.98\sim30.12\times10^4$ mg/L^[1-2], which is a high-temperature environment with ultra-high salinity. Unlike gas field development, during the operation of the gas storage, the injection and production wells will be in the environment of "strong injection and strong production", high-speed scouring and alternating stress for a long time. The safety and reliability of the wellhead equipment of the injection and production wells and the casings and tools in all layers of the underground will directly affect the normal operation of the gas storage.

During the construction of the gas storage, the conventional electromagnetic flaw detection logging technology diagnosis results of some casings of old gas production wells show that some casings of gas production wells in this block have corrosion, perforation, deformation, leakage and fracture to varying degrees; Among them, 25 wells were corroded, 10 wells were seriously corroded and perforated, and corrosion and perforation accounted for more than 50% of casing damage in old wells^[3-4].

2. CORROSION ANALYSIS

2.1. Corrosion risk judgment

During the construction period of Wen 23 gas storage phase I project, 66 injection and production wells were newly drilled and 11 production wells were used for the old wells. In the initial stage of design, it is considered that the self-produced gas of Wen 23 gas field does not contain H_2S , and only the gas transmission component of Xinjiang coal to gas contains H_2S in the surrounding gas transmission pipeline, and the content is less than $6mg/m^3$. The H_2S partial pressure is only $0.00015MPa$ ^[5-6] converted by the maximum upper limit pressure of $38.6MPa$, so H_2S gas corrosion is not considered. In the self-produced gas components of Wen 23 gas field, the CO_2 content is $0.33-2.47\%$, and the CO_2 partial pressure at the maximum operating pressure is $0.127-0.953MPa$. Referring to API SPEC 6A standard, if there is condensate water in the natural gas produced by injection production, an acidic environment may be generated, resulting in moderate to severe corrosion of the reservoir casing^[7-9]. Based on the above analysis, this paper mainly considers the influence of acidic CO_2 environment and high salinity formation water conditions on the production string.

Table 1. Judgment standard for CO_2 corrosion in API SPEC 6A

Fluid	CO_2 partial pressure(MPa)	Relative corrosivity
General fluid	<0.05	Nothing
	0.05-0.21	Light
	>0.21	Medium-Serious
Acid environment	0.05-0.21	Light
	>0.21	Medium-Serious

In the dynamic monitoring data analysis of the completed second gas production cycle of Wen 23 gas storage, it is shown that the cumulative liquid production of the whole gas production cycle is $918.67m^3$, and the average gas-liquid ratio is $123.38 \times 10^4 m^3/m^3$, produced water $621m^3$, mineralization $292mg/L$, comprehensive judgment: currently produced water is condensate water; Analysis of gas components during gas production shows that CO_2 content is $0.467-0.738\%$; To sum up, the casing of injection and production wells in Wen 23 gas storage currently has a certain degree of CO_2 corrosion risk, and it is urgent to carry out risk point identification and corrosion countermeasure research.

Table 2. Natural GAS analysis results

Horizon	Relative density	C_1 %	C_2 %	C_3 %	C_4 %	C_5 %	CO_2 %	N_2 %
S_4^{1-2}	0.5715-0.5878	93.80-97.13	1.56-3.34	<0.35	0.11-0.33	<0.04	0.33-0.75	0.08-0.64
S_4^{3-4}	0.5715-0.6813	89.28-92.41	1.13-7.26	0.19-0.38	0.09-0.38	<0.20	0.58-1.19	0.46-1.44
S_4^{5-8}	0.5748-0.6037	91.00-96.71	1.57-6.41	0.21-1.81	<0.67	<0.55	0.31-1.51	0.31-1.42

2.2. Corrosion behavior identification

Based on the recognition of corrosion risk, the casing of gas storage injection and production wells may be corroded in CO_2 acid environment at present. In general, the corrosion areas that should be paid attention to during the operation of gas reservoir type gas storage include wellhead, production tree, production casing, oil casing annulus, etc. The EE grade carbon steel gas injection wellhead and production tree used before the injection and production well of Wen 23 gas storage have strong

corrosion resistance and low corrosion risk; Secondly, in the design of the gas reservoir, P110-13Cr steel casing is selected as the main gas producing interval to avoid CO₂ acid corrosion. Through the corrosion test, the corrosion sample of P110-13Cr steel immersed in CO₂ for 7 days has clear scratches and honeycomb corrosion pits, but there is no large area of local corrosion. According to the measurement, the corrosion rate is 0.0734mm·a⁻¹, so no anti-corrosion measures are required.

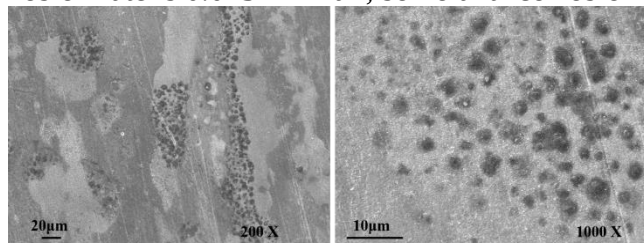


Figure 1. SEM image of P110-13Cr sample steel surface

Because the gas storage is under the condition of "strong injection and strong production" for a long time, the medium has a strong scouring effect on the pipe string, which will enhance the CO₂ corrosion to a certain extent; In addition, the formation water of the gas storage is highly mineralized, and there may be Cl⁻ corrosion to a certain extent. Therefore, during the construction period of the gas storage, the possible dissolved salt corrosion, dissolved oxygen corrosion and microbial corrosion are comprehensively considered, and the annulus protection fluid is added to protect the oil jacket annulus above the packer. The HK-CYY corrosion inhibitor added to the annulus protection fluid currently selected is mainly composed of adsorption film corrosion inhibitor, which has good corrosion inhibition effect and thermal stability. Combined with the indoor evaluation results, the corrosion rate will be lower than the engineering standard of 0.076mm/a⁻¹, and the corrosion risk is low. That is, if there is no leakage of annular protective fluid in the annular space, there is no annular space corrosion.

Table 3. Indoor evaluation of corrosion inhibition test(P110,90°C)

Annulus protection fluid	Quality of test piece before corrosion (g)	Quality of test piece after corrosion (g)	Test piece area (cm ²)	Corrosion rate (mm/a)	Thermal stability/°C
HK-CYY	10.9061	10.9039	13.648	0.0058	≥110
HK-CYY	11.0107	11.0076	13.704	0.0081	≥110

During the actual injection production operation, it was found that the leakage of annulus protection fluid in 6 wells was large. The annulus liquid level of most wells was below -1000m, and the annulus liquid level of some wells exceeded -1700m. Through the leakage analysis of the production string in three aspects, it is considered that the leakage points may exist in 11 potential leakage paths, such as the contact surface between the tubing hanger and the tubing cross, the connection between the tubing hanger and the tubing thread, and the connection between the tubing thread. It is considered that the leakage possibility at the tubing thread and the packer is greater.

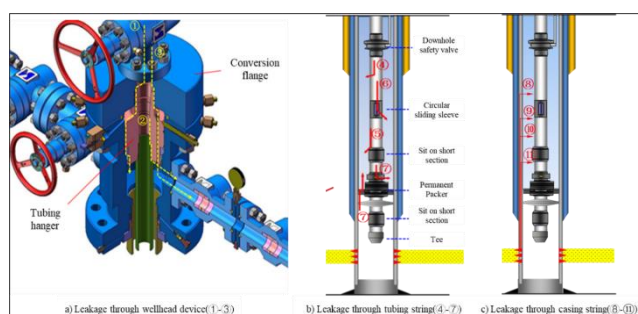


Figure 2. Three aspects and eleven potential ways of leakage identification

Due to leakage of annulus protection fluid in some wells of Wen 23 gas storage, the original combination of annulus protection fluid +HK-CYY corrosion inhibitor failed in some pipe sections, which may lead to corrosion. To sum up, the main potential corrosion hazards of Wen 23 gas storage come from the acidic environment formed by CO₂ and condensate water in the reservoir; The wellhead and gas production tree are made of EE grade acid corrosion resistant carbon steel and P110-13Cr steel for production interval casing to avoid casing corrosion. Under normal conditions, due to the protection of annulus protection fluid +HK-CYY corrosion inhibitor system, the corrosion possibility of other well sections is also extremely low; However, the leakage of annulus protection fluid will weaken the corrosion protection ability of casing. Therefore, the possible corrosion location of Wen 23 gas storage only exists in the P110 Oil Casing Well section where the annulus protection fluid leaks.

3. Simulation experiment method

P110 steel is used in the oil casing well section where the annulus protection fluid of Wen 23 gas reservoir leaks. Based on the common corrosion inhibition method of CO₂/Cl⁻ in oil and gas fields, imidazoline inhibitor is injected for corrosion inhibition. Through preliminary experiments, it is found that the traditional imidazoline inhibitor is difficult to be applied to the site due to the high salinity of Wen 23 gas reservoir^[9-10]. Through preliminary screening, 2-mercaptopyrimidine is selected as the inhibitor for testing.

3.1. Experimental materials and corrosion solution

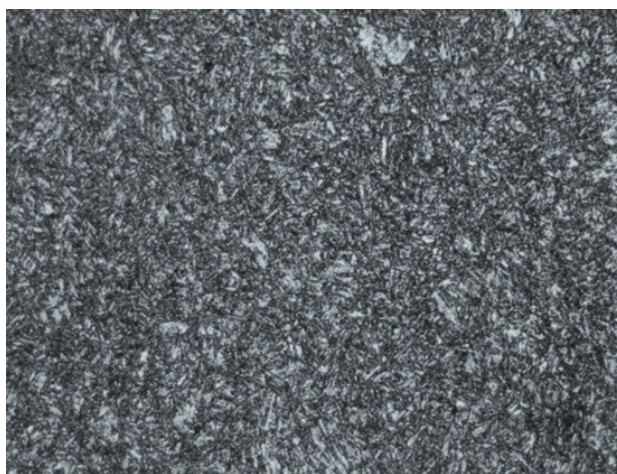


Figure 3. Metallographic structure photo of P110 steel

The materials used in the simulation experiment are taken from P110 Oil jacket in service at the gas storage site. Its components are shown in Table 4 and its metallographic structure is shown in Fig.3. The corrosion medium is simulated formation water solution, and the specific composition is: 35.324 g/L NaCl, 2.471 g/L Na₂SO₄, 18.324 g/L MgCl₂·6H₂O, 2.451 g/L CaCl₂, 1.284 g/L NaHCO₃, 3.512 g/L KCl, and the CO₂ partial pressure is controlled to 0.1 MPa.

Table 4. P110 steel composition table (wt.%)

C	Si	Mn	P	S	Cr	Ni	Cu	Mo	Fe
0.244	0.209	0.457	0.005	0.001	0.500	0.030	0.088	0.744	Balance

3.2. Weight loss experiment and surface analysis

Process P110 sample steel from field casing to 30×10×3mm, and drill a small hole with a diameter of 3mm above the sample for weightlessness suspension. Before the test, mark the samples and test their weight m₀ one by one with a high-precision electronic balance. The test pieces are fixed in the high-temperature autoclave with bolts. The total pressure is controlled at 30MPa, the carbon dioxide

partial pressure is 0.1MPa, and the temperature is 120°C. After 7 days, take out the sample and wash it with the film removal solution. The film removal solution is prepared with reference to 10g of hexamethyltetramine, 100mL of concentrated hydrochloric acid and 900mL of pure water[11].

After drying, use the same electronic balance to measure the weight one by one, and the weight is m_1 . The corrosion rate can be calculated by formula (1)[12]:

$$CR = \frac{87600 \times (m_0 - m_1)}{S \cdot \rho \cdot t} \quad (1)$$

3.3. Electrochemical test

The sample is processed into a cylindrical shape with a diameter of 10mm and a height of 10mm. After removing the oil with acetone, the sample is scrubbed with absolute ethanol. After being dried with nitrogen, the copper wire and the round side are welded firmly with solder, and the conductivity is tested with a multimeter. The other round surface is fixed in the mold, filled with epoxy resin for sealing, and taken out after the epoxy resin solidifies two days later. Use 400#, 800#, 1200# metallographic sandpaper to polish the mirror surface step by step, and soak it in absolute ethanol for use. The electrochemical test uses a three electrode system, saturated calomel electrode as the reference electrode, platinum electrode as the auxiliary electrode, and the working electrode is the P110 electrode processed above. The exposed leakage area is 0.785 cm². After the open circuit potential is stabilized, start to test the impedance spectrum and polarization curve. The frequency of the impedance spectrum is 0.1~105Hz, and the amplitude is 5mV. The initial and end potentials of the polarization curves were $\pm 0.3V$, and the scanning rate was 1mV/s. Considering that mineralization has a major influence on the adsorption of corrosion inhibitors, considering the experimental conditions, the electrochemical test is carried out at normal temperature and pressure, and the solution composition is consistent with the weight loss experiment.

4. Analysis of experimental results

4.1. Weight loss test results and surface morphology

After immersing P110 sample in simulated real working conditions for 7 days, take out the sample to obtain weight loss data and observe its micro morphology. The weight loss results are shown in Fig.4, and the micro surface morphology is shown in Fig.5.

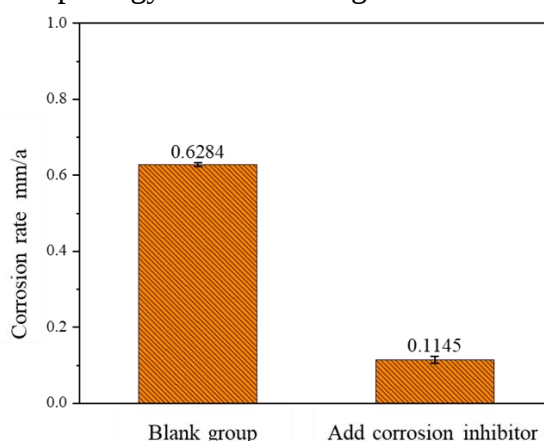


Figure 4. Weight loss test results

As shown in Fig.5, under the condition that no corrosion inhibitor is added, serious local corrosion occurs in the sample, and corrosion pits of different sizes appear. After adding 50mg/L 2-mercaptopyrimidine, it can be clearly seen that the corrosion situation has been greatly improved. The weight loss experimental data (Fig.5) showed that the corrosion rate was 0.6284mm/a in the samples without the inhibitor, and 0.1145mm/a after the inhibitor was added, with a slow-release efficiency of 81.78%. According to the weight loss experiment and surface morphology analysis (Fig.5), the

addition of dimercaptopyrimidine can effectively inhibit the corrosion of P110 metal in the high salinity /CO₂ environment.

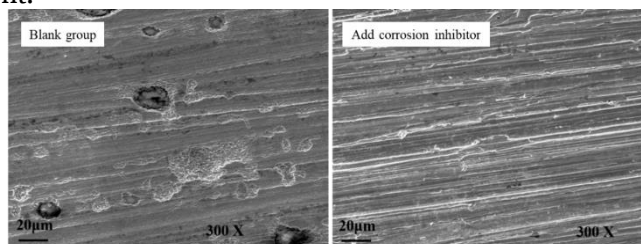


Figure 5. SEM image of P110 sample steel surface

4.2. Electrochemistry

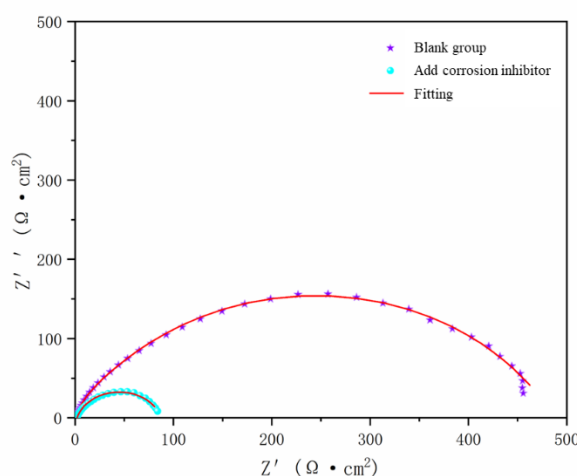


Figure 6. Impedance spectrum

The AC impedance spectrum measured in the simulated formation water solution and after adding corrosion inhibitor is shown in Fig.6. It can be seen from the figure that the resistance arc increases significantly after the inhibitor is added, which indicates that the inhibitor has obvious corrosion inhibition effect in this system^[13-14]. The data after fitting is shown in Table 5, and the equivalent fitting circuit diagram is shown in Fig.7. Where R_s is the solution resistance, R_{ct} is the charge transfer resistance, R_f is the film resistance, and CPE is the long phase angle element.

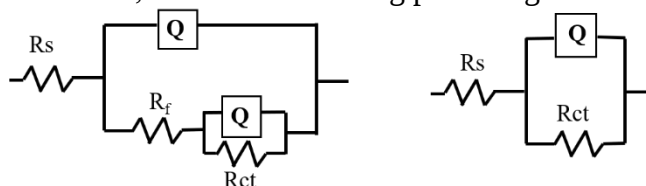


Figure 7. Equivalent circuit diagram

Table 5. AC impedance spectrum fitting results

Group	$R_{ct}/(\Omega \cdot \text{cm}^2)$	Y_0^1	n_1	$R_f/(\Omega \cdot \text{cm}^2)$
Blank group	85.64	5.628×10^{-4}	0.83	/
Add corrosion inhibitor	72.5	1.036×10^{-4}	0.96	413.1

Tafel extrapolation method is used to fit the measured polarization curve (Fig.8) to form the fitting data shown in Table 5. In combination with the data in Fig.8 and Table 5, after adding the inhibitor, the self-corrosion potential moves to the positive direction, which indicates from the thermodynamics that after adding the inhibitor, the metal is less likely to be corroded compared with the blank group^[15-16]. By comparing the corrosion current density, it can be found that the difference between the corrosion current density of the blank group and the corrosion current density after adding the

inhibitor is more than 10 times, which can directly explain that the corrosion is more serious in the blank group electrochemically^[17]. With the addition of corrosion inhibitor, the corrosion rate decreased from $1.3525\text{mm}\cdot\text{a}^{-1}$ to $0.2021\text{mm}\cdot\text{a}^{-1}$, and the corrosion inhibition efficiency was 85.06%. The measured polarization curve data has a high correspondence with the data obtained from the above weight loss experiment, but there is a large error in the corrosion rate, because the electrochemical test is a transient test based on the current corrosion state, while the weight loss experiment is a period of uniform corrosion, and the difference between the two is a normal phenomenon^[18-20].

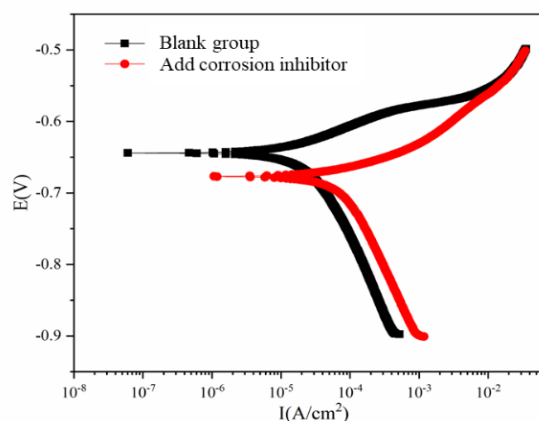


Figure 8. Polarization curve

Table 6. Polarization curve fitting data

Group	ba/(mV·decade ⁻¹)	bc/(mV·decade ⁻¹)	I/(A·cm ⁻²)	E ₀ /V	Corrosion rate(mm·a ⁻¹)	η _p /%
Blank group	64.753	291.99	1.1528×10^{-4}	-0.6771	1.3525	0
Add corrosion inhibitor	41.256	164.57	1.7228×10^{-5}	-0.6441	0.2021	85.06

5. Conclusions

1) As the gas reservoir in Wen 23 gas storage contains CO₂, high salinity formation water and condensate water, there is a risk of CO₂ and Cl⁻ Corrosion in the case of leakage of casing annulus protection fluid. Through experimental simulation, it is found that the corrosion rate of P110 steel in the simulated environment can reach $0.6284\text{mm}\cdot\text{a}^{-1}$, and the potential corrosion harm can not be ignored.

2) During the construction period of Wen 23 gas storage, the anti-corrosion fluid system of annulus protection fluid + HK-CYY corrosion inhibitor was designed according to the anti-corrosion requirements of casing. High specification materials were also selected for key nodes of injection production wells, with good anti-corrosion effect.

3) Loose sealing of casing thread and packer is the main cause of annulus protection fluid leakage. And the leakage of annulus protection fluid will inevitably form an acid corrosion environment in the oil jacket annulus.

4) By simulating the actual working conditions in the laboratory, using 2-mercaptopyrimidine, which is more salt resistant, as an inhibitor can significantly inhibit the corrosion of P110 steel, and the inhibition efficiency can reach 81.78%.

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