Study on Control Methods for Corrosion and Scaling in Alcohol-Containing Wastewater Treatment Systems of Gas Fields

Qishu Zhou [1], Feng Li [2], Bo Gao [2], Hankezi Yisilamujiang [1] and Rongyao Zhang [2]

[1] Institute of Petroleum Engineering, Xi'an Shiyou University, Shaanxi Key Laboratory of Advanced Stimulation Technology for Oil & Gas Reservoirs, Shaanxi Xi'an 710065, China;

[2] The Second Gas Production Plant, Changqing Oil Field, CNPC, Shaanxi Yulin 718500, China

Abstract

To address the blockage issues caused by corrosion and scaling in the alcohol-containing wastewater treatment system of a natural gas processing plant, an efficient solution was proposed through multi-model prediction of scaling tendency, analysis of blockage composition, and optimization experiments of water treatment chemicals. The research results indicated that the produced water was weakly acidic, characterized by high chloride ion concentration and high salinity, with a tendency for CaCO3 and Ba/SrSO4 scaling. The blockage was found to be primarily composed of CaCO3 and iron compounds, mainly caused by scaling and corrosion. Through the screening of corrosion and scale inhibitors, ZQ-1, at a dosage of 100 mg/L, achieved a scale inhibition rate of 93.18% and a corrosion inhibition rate of 96.18%, with no flocculent or precipitate formation observed. The research findings provide a theoretical basis and technical support for controlling corrosion and scaling in high-salinity alcohol-containing wastewater systems.

Keywords

Alcohol-containing wastewater; Corrosion; Scaling; Corrosion and scale inhibitor; Chemical optimization.

1. Introduction

During the extraction of natural gas in northern Shaanxi, large volumes of methanol-containing wastewater with complex properties are generated. This wastewater is treated and subsequently re-injected into the formation as backfill water [1]; the treatment process is illustrated in Fig. 1. Due to its high salinity, acidity, and complex ion composition, the methanol-containing wastewater can cause equipment corrosion, scaling, and blockage, which jeopardise the stable operation of natural gas purification facilities and pose serious threats to production safety. Although existing studies have developed various treatment agents targeting individual corrosion or scaling issues, there is a lack of systematic analysis on the synergistic mechanisms of multiple risks in methanol-containing wastewater. Moreover, conventional agents often prove ineffective in high-salinity environments [2, 3, 4]. This study integrates water quality analysis, scaling prediction, and characterisation of blockages to identify a corrosion and scale inhibitor and verify its applicability in high-salinity methanol-containing wastewater. The aim is to provide an efficient and stable solution for field processes, extending equipment service life and reducing maintenance costs.

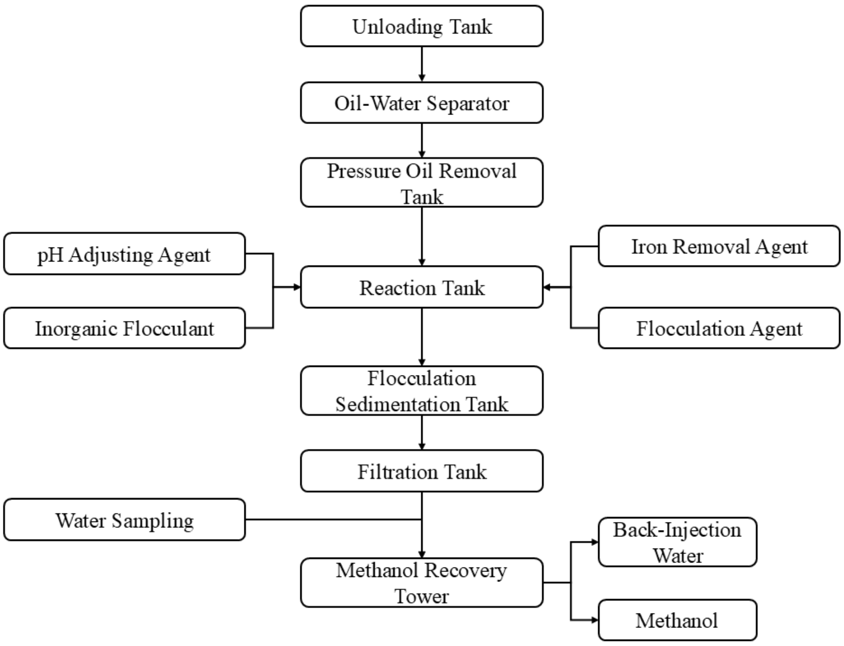

Fig. 1 Process Flow of the Back-Injection Water Treatment System at a Natural Gas Treatment Plant.

2. Experimental Methods

2.1. Water Quality Analysis and Scaling Prediction

In accordance with SY/T 5523-2016 "Analytical Methods for Oilfield Water", methanol-containing wastewater was analysed by titration, and cation content was determined using inductively coupled plasma optical emission spectrometry (ICP). The particle size distribution of suspended solids (SS) was then analysed using a Malvern laser particle size analyser (Model APA2000). With reference to SY/T 0600-2016 "Prediction Methods for Scaling Tendency in Oilfield Water" and SY/T 5329-2022 "Recommended Water Quality Indicators and Analytical Methods for Water Injection in Clastic Rock Reservoirs", scaling tendencies were predicted using models such as the Davis-Stiff saturation index (SI) and the Ryznar stability index (SAI).

2.2. Composition Analysis of Blockage Substances

After pre-treatment of the samples by drying, grinding, and sieving, moisture, oil content, organic matter, and loss on ignition were determined gravimetrically. The mineral composition of the calcined residue was analysed using XRD. Acid-soluble ions were determined by volumetric methods and their contents were calculated. Acidic gases were measured directly, and acid-insoluble substances were analysed by weighing after high-temperature ashing. Barium sulphate was determined via the sodium carbonate fusion method.

2.3. Chemical Optimisation and Performance Evaluation

2.3.1. Determination of Scale Inhibition Rate

With reference to GB/T 16632-2019 "Determination of Scale Inhibition Performance of Water Treatment Agents—Calcium Carbonate Precipitation Method", 250 mL of produced water, a scale inhibitor, and 20 mL of borax buffer solution were added to a 500 mL volumetric flask and made up to volume. No scale inhibitor was added to the blank group. The mixture was heated in a constant temperature water bath at 75 °C ± 1 °C for 5 hours, then filtered immediately while hot using medium-speed quantitative filter paper. 25 mL of the filtrate was taken, and the Ca^{2+} concentration was determined by EDTA titration to calculate the scale inhibition rate.

2.3.2. Determination of Corrosion Inhibition Rate

With reference to SY/T 5273-2014 "Performance Indicators and Evaluation Methods for Corrosion Inhibitors Used in Oilfield Produced Water Treatment", the effect of the corrosion and scale inhibitor on the corrosion current (Icorr) and corrosion potential (Ecorr) of N80 steel at 75 °C was evaluated using potentiodynamic polarization curves, and the corrosion inhibition rate was calculated.

3. Results and Discussion

3.1. Analysis of Water Quality Composition and Scaling Tendency in Methanol-Containing Wastewater

The results of the water quality analysis for the treated methanol-containing wastewater from the natural gas treatment plant are shown in Table 1. As shown in Table 1, the back-injection water from this water treatment system exhibits high salinity, exceeding 40,000 mg/L. The primary cations are Ca^{2+} and Ba^{2+}, the dominant anion is Cl^-, and the water type is $CaCl_2$. The water is acidic and has a high oil content.

Table 1 Water Quality Analysis Results of Methanol-Containing Wastewater

Item	Measurement Result
pH	6.41
$\rho(SS)/(mg\cdot L^{-1})$	630.33
$\rho(Cl^-)/(mg\cdot L^{-1})$	26438.82
$\rho(HCO_3^-)/(mg\cdot L^{-1})$	175.93
$\rho(SO_4^{2-})/(mg\cdot L^{-1})$	65.93
$\rho(Fe^{2+})+\rho(Fe^{3+})/(mg\cdot L^{-1})$	100.10
$\rho(Ca^{2+})/(mg\cdot L^{-1})$	4943.57
$\rho(Mg^{2+})/(mg\cdot L^{-1})$	494.47
$\rho(Ba^{2+})/(mg\cdot L^{-1})$	471.07
$\rho(Sr^{2+})/(mg\cdot L^{-1})$	458.08
$\rho(Na^+)+\rho(K^+)/(mg\cdot L^{-1})$	13710.85
Salinity/$(mg\cdot L^{-1})$	46858.8
Oil Content/$(mg\cdot L^{-1})$	542.28
Water Type	$CaCl_2$

Based on the field water quality, the scaling tendency was predicted at 0.1 MPa and 20 °C; the prediction results are shown in Table 2. Predictions from multiple models indicate that the system is prone to calcium carbonate and barium/strontium sulphate scaling during long-term operation, while the tendency for calcium sulphate scaling is relatively low.

Table 2 Scaling Tendency Prediction of Treated Water

Prediction Method		Parameter	Value	Tendency
Calcium Carbonate	Davis-Stiff Saturation Index	SI	0.4611	Likely
	Ryznar Stability Index	SAI	5.4562	Likely
Calcium Sulphate Scaling		S-c	25.4311	Unlikely
Magnesium Sulphate Scaling		I	13.2260	Likely
Barium Sulphate Scaling		B	0.0007	Likely

3.2. Particle Size Distribution and Analysis of Process Failure Causes

The particle size distribution of the back-injection water was determined using a Malvern laser particle size analyser (Model APA2000); the results are shown in Fig. 2.

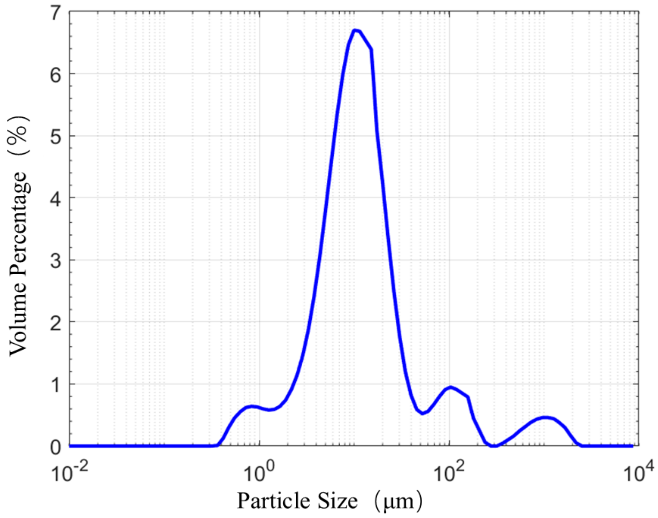

Fig. 2 Particle Size Distribution of Treated Produced Water

The suspended solids (SS) content of the treated water was 630.33 mg/L, far exceeding the conventional standard for back-injection water (typically ≤10–50 mg/L), indicating failure of the pre-treatment system [5]. Analysis of the particle size data revealed that particles in the 0.5–10 μm range—within the colloidal and fine particle fraction—peaked at 6.46%. No particles below 0.3 μm were detected, suggesting insufficient conversion of dissolved pollutants into micro-flocs. The proportion of particles larger than 10 μm decreased sharply. This may be due to insufficient reaction time in the flocculation and sedimentation stage, preventing colloidal particles from being effectively flocculated into settleable particles larger than 50 μm [6]. Alternatively, the filter layer in the filtration tank may have become compacted or experienced channeling, failing to fully retain particles larger than 10 μm. In addition, pH adjustment may not have reached the optimal range for flocculation, leaving the colloidal charge stability unbroken.

3.3. Composition Analysis and Formation Mechanism of Blockage Substances

Table 3 presents the compositional analysis of blockage substances from different sampling points. The blockages from the bag filter, inlet pipeline, and distillation column top were primarily inorganic, with calcium carbonate being the most abundant, followed by iron compounds and sulphates. Acid-soluble substances accounted for over 90% of the content, indicating that the deposition of calcium salts and iron oxides under high-temperature conditions was the main cause of blockage.

Table 3 Chemical Volumetric Analysis Results of Blockage Composition at Different Sampling Points

Composition (mass fraction)（%）		Bag Filter	Inlet Pipeline	Distillation Column Top
Water Content		44.35	2.63	2.67
Oil Content		3.97	5.10	5.59
Loss on Ignition at 550℃		3.00	2.91	3.31
Loss on Ignition at 950℃		34.24	31.48	32.22
Acid-Insoluble Matter		1.74	2.34	0.37
Acid-soluble Matter	Fe3+	3.14	8.03	2.70
	Fe2+	4.08	2.52	5.50
	Ca2+	28.14	27.47	30.25

	Mg2+	0.43	0.56	0.52
	SO42-	0.41	0.46	0.53
Total		98.26	97.66	99.63

3.4. Selection and Performance Evaluation of Corrosion and Scale Inhibitors

3.4.1. Scale Inhibition Performance Evaluation

Figure 3 shows the scale inhibition rates of nine commonly used corrosion and scale inhibitors.

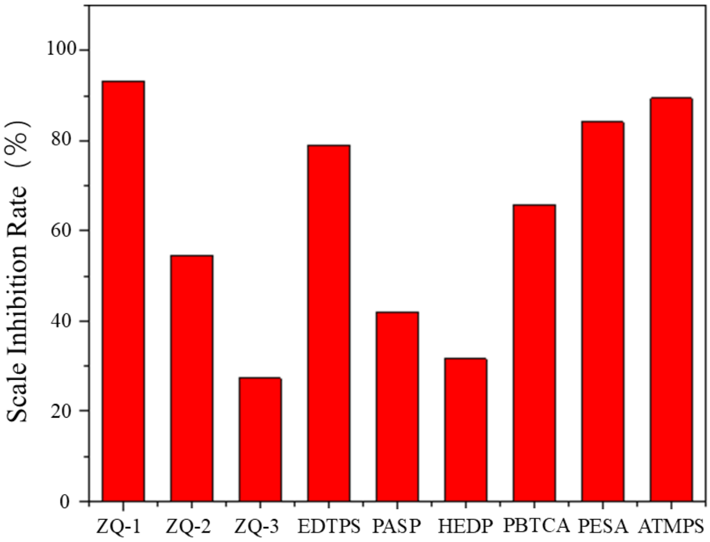

Fig. 3 Evaluation Results of Scale Inhibition Rate of Corrosion and Scale Inhibitors

As illustrated in Fig. 3, inhibitor ZQ-1 from the ZQ series achieved a scale inhibition rate of 95.45% without generating flocs, demonstrating stable performance. Although ATMPA (89.47%) and PESA (84.21%) also exhibited high scale inhibition rates, they produced precipitates, making them unsuitable for high-salinity methanol-containing wastewater systems.

3.4.2. Corrosion Inhibition Performance Evaluation of ZQ-1

The corrosion inhibition performance of ZQ-1 was evaluated; the experimental results are presented in Fig. 4 and Table 4.

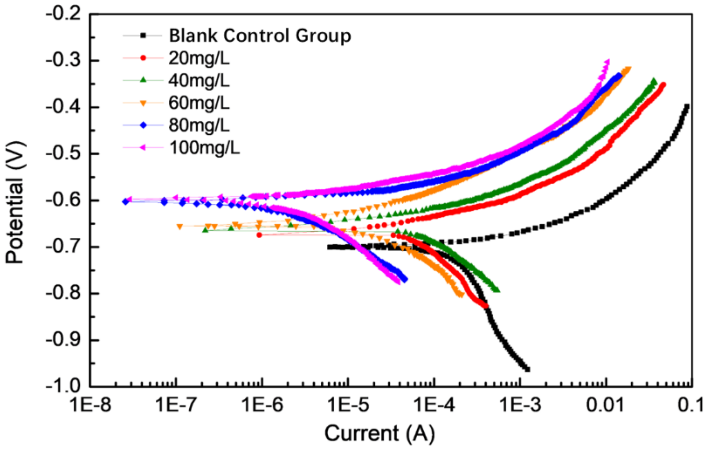

Fig. 4 Polarisation Curves of Different Dosages of ZQ-1 at 75 °C

Table 4 Fitting Results of Polarisation Curves with Different Dosages of ZQ-1 at 75 °C

Dosage(mg/L)	Ecorr(mV)	Icorr(mA·cm-2)	Corrosion Inhibition Rate(%)
0	-698.36	157.23	0
20	-684.64	56.05	64.35
40	-662.87	29.34	81.34
60	-656.62	16.58	89.45
80	-608.37	7.47	95.25
100	-598.29	6.01	96.18

As shown in Fig. 4 and Table 4, as the dosage of ZQ-1 gradually increased, the self-corrosion potential (Ecorr) of the steel shifted in the positive direction, indicating inhibition of the anodic reaction. The corrosion current of the steel decreased significantly. When the dosage of ZQ-1 reached 100 mg/L, the corrosion current reached a minimum of 6.01 mA/cm^2, and the corrosion inhibition rate reached 96.18%.

4. Summary

(1) The methanol-containing produced water is generally weakly acidic. The high Cl^- content may cause pitting corrosion, while the high salinity and significant variations in scaling cation concentrations contribute to a high scaling tendency, potentially leading to carbonate and strontium/barium sulphate scale formation.

(2) The blockage substances are primarily composed of $CaCO_3$ and Fe_3O_4, whose formation is driven by both high-temperature deposition and the adhesion of particles to oil. Fe^{2+} is oxidised to Fe_3O_4 in an aerobic environment, further increasing the hardness and adsorbability of the scale and exacerbating pipeline blockage.

(3) A dual-effect synergy (scale inhibition rate >93%, corrosion inhibition rate >95%) was achieved at a ZQ-1 dosage of 100 mg/L without the formation of flocs, significantly outperforming conventional agents and meeting field requirements.

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