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Influence of Sodium Ferrocyanide as an Alternative Inhibitor of Sodium Chloride Crystallization in Tight Sandstone Gas Wells

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In the process of producing gas reservoir, after the high salt formation water flows into the wellbore, the salt dissolved in the formation water will gradually separate out to form salt plugging due to the sharp decrease of temperature and pressure, resulting in the decrease of gas volume in gas wells. Chemical desalination is one of the important means to solve the problem of salt plugging. Sodium ferrocyanide was selected as an alternative inhibitor. Firstly, static technological parameters, such as inhibitor concentration, temperature, and service period were optimized, and the effect of pressure drop, temperature and flow rate on inhibitor performance was discussed. Then, the field application of the inhibitor in the blocked Daji 1 - 7 gas well was demonstrated. Results showed that the addition of sodium ferrocyanide significantly increased the chlorine ion concentration of formation water from 80.6 g/L to 144.1 g/L, which indicated that sodium chloride recrystallization was inhibited. Scanning Electron Microscopy (SEM) results revealed that the addition of the inhibitor induced the doping of several prismatic crystals into numerous dense small cubic crystals. The size of the cubic crystals reduced to 39 μm. The length of prismatic crystals in the presence of the inhibitor was only 200 μm and was less than that of crystals in the absence of the inhibitor.

1. Introduction

Tight sandstone gas reservoirs are unconventional gas reservoirs. They have recently received increased attention given that they are potential sources of massive amounts of gas. However, salt plugging cannot be ignored during the exploitation of tight sandstone gas reservoirs. Salt from sandstone can dissolve in formation water and induce saturation. Salts that are originally dissolved in the formation water would begin to nucleate and form salt crystals when highly saline formation water enters the wellbore along with gas given that sodium chloride solubility decreases with the reduction in temperature and pressure from the wellbore to the ground pipeline; the formation of salt crystal results in the blockage of gas wells and ground pipelines, and the production of gas well decreases greatly in a short time, which seriously restricts the development of gas field (Wang et al., 2018).

Some well-known gas fields provide many effective measures to prevent salt plugging, such as Wen 23 gas field in China adopts high-pressure gas reinjection method and double-line water injection method to treat salt-forming gas wells (Yang et al., 2014), Salt plugging is treated by chemical salt prevention in Hubuzhai gas field (Liu et al., 2010). Chemical desalting with inhibitors is the most efficient and long-term method for preventing salt plugging. Inhibitor screening is the key to chemical desalting. The mechanism of action of inhibitors is generally by changing the surface properties of crystals, leading to changes in nucleation and growth of crystals, changing the shape of crystals and their aggregation/dispersion behavior (Bracciale et al., 2020). According to research, potassium ferrocyanide (Cui et al., 2016) and sodium ferrocyanide (Lubelli et al., 2010) have a good inhibitory effect on salt crystallization. The addition of sodium ferrocyanide will inhibit the formation of crystal nuclei and change the morphology of salt crystals (Liu et al., 2015). And surfactants (Qazi et al., 2017), sodium

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polyacrylates (Logutenko et al., 2018), tartrate family members (Tian et al., 2016) are widely used in the gas field or industrial circulating water systems.
However, the behaviors of inhibitors in gas wells have been rarely systematically studied. In this work, sodium ferrocyanide was applied as an inhibitor in the severely salt-plugged Daji 1 - 7 gas well in Northern China. The concentration, temperature, and service period of the inhibitor were optimized, and the effect of flowrate and pressure drop on the behavior of sodium chloride recrystallization was investigated, and the inhibitor was also satisfactorily applied in the field in the Daji 1 - 7 gas well.

2. Experimental Section

2.1 Analysis of formation water and crystals from the Daji 1 - 7 gas well

Metal cations in formation water from the Daji 1 - 7 gas well in Northern China were tested by using an atomic absorption spectrophotometer (AAS, AA-6880, Shimadzu, Japan). The chloride ion concentration of the formation water was measured through ion chromatography (Integrion, ThermoFisher, USA).The crystal structures of solid samples were analyzed through X-ray powder diffraction (XRD) with CuKα radiation (λ = 0.1541 nm) in the 2θ range from 10 ° to 80 ° at a rate of 10 °/min (XRD-6100, Shimadzu, Japan).

2.2 Optimization of inhibitor parameters in static indoor experiments

A total of 200 mL of saturated sodium chloride–water solution was prepared at 70 °C by using formation water from the Daji 1 - 7 gas well. The solution was divided into four portions and transferred into four beakers. The solution was mixed with a certain concentration of sodium ferrocyanide (0.1 %, 0.3 %, 0.5 %, or 0.7 %) and maintained at a specific temperature (3 °C, 20 °C, or 50 °C) for a certain service time (12 h, 24 h, or 72 h). The concentrations of chloride ions in the solutions and the structure of sodium chloride crystals in the presence or absence of the inhibitor were determined through ion chromatography and scanning electron microscopy (SEM, MAIA3LMH, TESCAN, Czech).

2.3 Experiment under simulated field conditions and filed test

The simulation ranges of flowrate and pressure drop were determined in accordance with the site condition of the Daji 1 - 7 well bore. The effect of flow rate on sodium chloride recrystallization was tested by using a gas-liquid two-phase flow device equipped with a condenser circulation system. Saturated sodium chloride-water solution was prepared at 70 °C as the liquid phase and added into the bottom of the gas-liquid two-phase flow device. Nitrogen was applied as the gas phase, which was dispersed by sand cores in the bottom of the device and allowed to flow into the device from the bottom. Saturated sodium chloride water solution at 70 °C was dispersed and gradually cooled from the bottom to the top of the device. The gas-liquid two-phase flow system was maintained at 5 °C. The flow rate of the gas phase was adjusted by using a gas gauge. The chloride ion concentration of the liquid phase was analyzed after a specific duration of circulation. The effect of pressure drop on sodium chloride recrystallization was simulated by adjusting the rotation speed and vacuum degree of the rotary evaporator. The morphology and particle size of sodium chloride crystals were analyzed through SEM. The field test of inhibitor performance was carried out in the blocked Daji 1 - 7 gas well.

3. Results And Discussion

3.1 Analytical results for the formation water and crystals from the Daji 1 - 7 gas well

Table 1 lists the AAS results for metal cations in the formation water from the Daji 1 - 7 gas well. In addition to Na^+, other metal cations, such as Mg^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Ca^{2+}, and K^{2+}, were present at non-negligible amounts.

Table 1: AAS results for metal cations in the formation water from the Daji 1-7gas well

Elements	Na^+	Mg^{2+}	Cu^{2+}	Fe^{2+}	Mn^{2+}	Ca^{2+}	K^{2+}
Daji 1-7 [10^{-6} g/mL]	59,710	74,820	5	646	32	71,558	1,572

The XRD patterns of the three crystals from different salt plugging locations are presented in Figure 1. PDF#05-0628 and PDF# 25-1035 show that the diffraction peaks of cubic sodium chloride planes (111), (200), (220), (222), and (420) were located at 2θ = 27.3 °, 31.7 °, 45.4 °, 56.5 °, and 75.3 °. The diffraction peaks of triclinic CaCl2(H2O)4 at 2θ = 19.3 °, 29.2 °, 33 °, 34.3 °, and 37.7 ° were ascribed to (1 - 11), (1 - 21), (0 - 13), (- 212), and (013) planes. The characteristic diffraction peaks of crystals from ignited and burned pipe walls included the peaks of sodium chloride and hydrated calcium chloride, whereas the diffraction peaks of the solid sample from the pipeline mainly comprised peaks of pure sodium chloride.

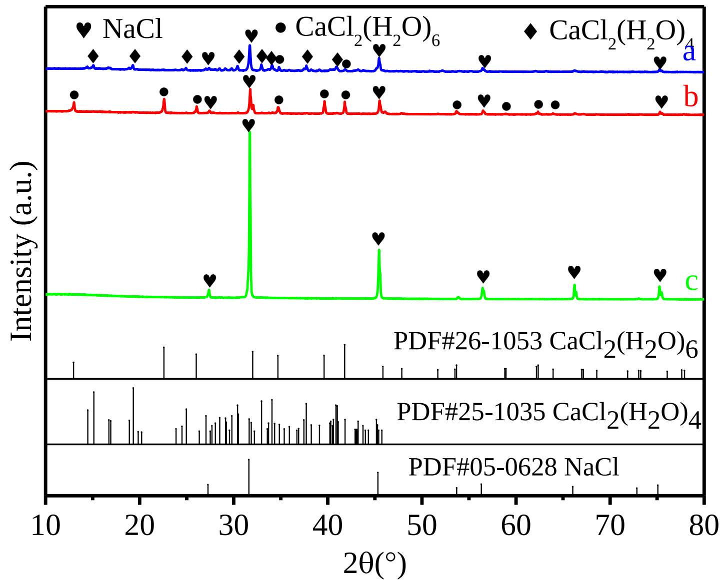


Figure 1: XRD patterns of three solid crystals from different salt plugging locations in the Daji 1 - 7 gas well (a and b from ignited and burned pipe walls, c from the pipeline)

3.2 Optimization of technological inhibitor parameters in the static indoor experiment

Table 2: Chloride ion concentration with the change of inhibitor concentration, service time, and formation water temperature

Inhibitor	Technological parameters	Cl^-(g/L)
	0	80.6
	0.1 %	41.2
Concentration	0.3 %	144.1
	0.5 %	103.3
	0.7 %	90.17
	12 h	53.3
Service time	24 h	144.1
	72 h	104.4
	3 °C	52.5
Temperature	20 °C	144.1
	50 °C	125.7

The variations in chloride ion concentration with inhibitor concentration, service time, and formation water temperature are listed in Table 2. The highest chloride ion concentration was observed at 24 h and 20 °C in the presence of 0.3 % sodium ferrocyanide. This result indicates that the inhibitor demonstrated the best inhibiting efficiency under these conditions.

3.3 Effect of pressure drop and flowrate

Inhibitor efficiency with the change in pressure drop and flowrate was simulated to verify the feasibility of the onsite application of the inhibitor. Figure 2 shows the effect of different flowrates on chloride ion concentration. The increase in chloride ion concentration in the presence of the inhibitor at all tested flow rates indicates that sodium chloride recrystallization was well suppressed even if the temperature of the formation water sharply decreased from 60 °C to 5 °C. Chloride ion concentration tended to decrease with the increase in flow rate in the presence or absence of an inhibitor likely because crystals would be washed away before growing under high flow rate. The persistence of crystals under low flow rates would result in chloride ion enrichment. In addition, the progressive increase in the gap between chloride ion concentration in the presence or absence of an inhibitor shows that inhibitor efficiency can be further enhanced under high flow rates.

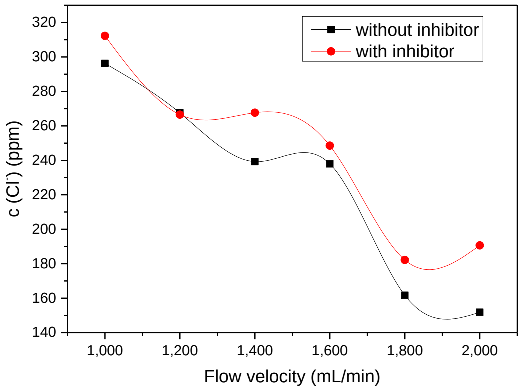


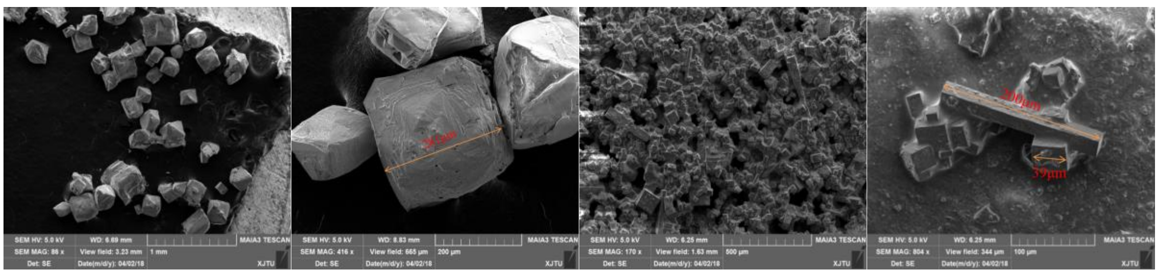
Figure 2: Effect of flow rate on chloride ion concentration in the presence or absence of an inhibitor

Table 3: Effect of pressure drop on sodium chloride recrystallization

T (°C)of the water sample	ΔP (kPa)	Recrystallization time (min) or grain size (nm)	
		With inhibitor	Without inhibitor
Daji 1-7 (10^{-6} g/mL)	59,710	74,820	5
60	2.375	30	40
65	3.128	25	27
70	3.897	17	25
75	4.820	13	20
80	5.922	10	18
Formation water from the Daji 1 - 7 gas well	/	1,311	2,780
Deionized water	/	832	1,480

The effect of pressure drop on chloride ion concentration in the presence or absence of an inhibitor is listed in Table 3. A sharp pressure drop was beneficial for the vaporization of pure water and further promoted the recrystallization of sodium chloride. Although the addition of the inhibitor can accelerate recrystallization under the same pressure drop, the crystals changed from dense cubic crystal to loose dendritic or long strip crystals and the crystal size obviously decreased. The inhibitor likely did not interfere with nucleation rate but instead reduced crystal growth kinetics. The crystals in formation water from the Daji 1 - 7 gas well were larger than those in deionized water because the existence of excessive impurities or metal ions increased crystal size.

3.4 Influence of the inhibitor on sodium chloride recrystallization



a b c d

Figure 3: Recrystallization of sodium chloride in the absence or presence of an inhibitor (a: Low magnification without inhibitors, b: High magnification electron microscopy without inhibitors, c: Low magnification with inhibitors, d: high magnification with inhibitors)

Sodium chloride crystals that formed in the presence or absence of sodium ferrocyanide were observed by SEM to confirm the influence of the inhibitor on crystal morphology (Figure 3). Dense cubic sodium chloride crystals with an individual grain size of approximately 281 μm formed in the absence of the inhibitor (Figure 3a and 3b). The addition of sodium ferrocyanide modified the recrystallization form of sodium chloride (Figure 3c and 3d). Numerous small dense cubic crystals and several prismatic crystals could be observed. The size of the cubic crystals decreased to 39 μm. The length of prismatic crystals was only 200 μm. These results show that the addition of sodium ferrocyanide indeed reduced the crystal size, inhibited the crystal growth, and promoted the preferential growth of specific crystal faces. Earlier findings by Lubelli B et al. demonstrated that the presence of sodium ferrocyanide facilitates the generation of elongated prismatic crystals.Combining SEM results with the experimental data of pressure drop on sodium chloride recrystallization revealed that sodium ferrocyanide inhibits sodium chloride nucleation and forms a supersaturated solution after dissolution, promoted the change of crystal form.

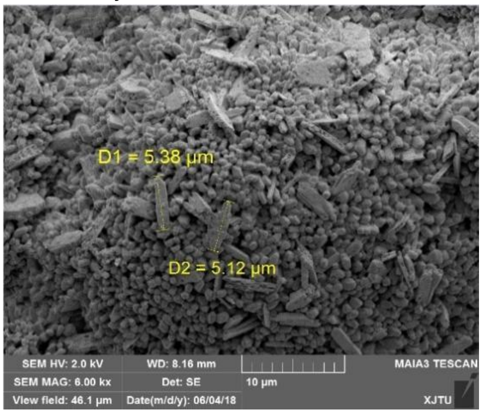
3.5 Field application results

In the field test, water output, tubing and casing pressure returned to normal after the batch addition of the inhibitor into the blocked Daji 1 - 7 gas well for 1 month. This result indicates that sodium ferrocyanide exhibited the good inhibitor performance. Discharge water at different stages was collected and their chloride ion concentration were analyzed and listed in Table 4. At the beginning of discharge, the concentration of chloride ion in the water is low, which implies that most of sodium chloride remained crystallized. The stabilization of chloride ion concentration with the increase of water flow indicates that the inhibitor has begun to take effect. Specifically, crystals had begun to redissolve and chloride ion concentration had begun to increase to saturation.

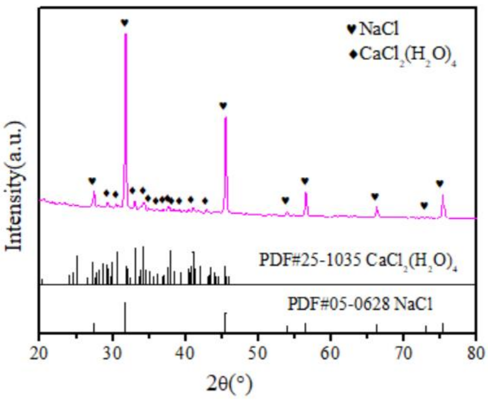
Table 4: Chloride ion concentrations in different water samples and discharge water flow from field application at different stages

Stages	Discharge water flow (m^3)	Chloride ion concentration (g/L)
Beginning of discharge	3.8	119.1
Before mass discharge	8.3	196.4
Middle period of discharge	22.5	183.9
Before ignition	/	183.8
After ignition	67.5	189.4
Late period of discharge	75.8	181.5

The XRD patterns and SEM results of salt deposits from the discharge water are shown in Figure 4. The XRD patterns confirm that the crystals were primarily composed of sodium chloride with some hydrate calcium chloride. Seen from SEM results, the decrease of crystal size and long strips of crystals with the length of 5 μm could be obviously found. Which further provides the addition of inhibitor changed the morphologies of sodium chloride crystals.



(a) SEM images



(b) XRD patterns

Figure 4: Salt deposited in formation water

4. Conclusions

The best salt crystallization inhibitor, sodium ferrocyanide, was screened through experiments, and the optimal technological parameters for the application of sodium ferrocyanide were determined. The results showed that its addition changed the morphological structure of the growth of sodium chloride crystals, and significantly inhibited the recrystallization process of sodium chloride in the formation water of Daji 1 - 7 gas well. The field application effect of sodium ferrocyanide is good, which can effectively solve the problem of salt plugging of the ground pipeline of Daji 1 - 7 gas well. However, it should be noted that only the salt crystallization inhibitors that perform well on the market are tested and studied experimentally. With the development of the times and the deepening of research, it is believed that more inhibitors with excellent performance will be researched and developed. There is still tremendous room for research and optimization of the method of adding inhibitors to solve the problem of salt plugging in gas wells.

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