Study on Autogenous Heat Technology of Offshore Oilfield: Experiment Research, Process Design, and Application

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1. Introduction

Autogenic heat technology originated from an invention patent of the Shell Company. The principle of heat generation is mixing 2-3 kinds of inorganic saline solution, with catalysis; the exothermic chemical reaction occurs to produce inert gases and generate a large amount of heat [1]. In theory, the complete reaction of a 1 m³ 5 mol/L heat generation system can release $1 \times 10^6$ kilojoules of heat. The thermochemical reaction formula is

$$A + B \xrightarrow{\text{cat.}} C + D [2H_2O + Q]$$  (1)

The autogenic heat system releases a large amount of heat after reacting in the reservoir, which can increase the reservoir temperature and reduce the viscosity of crude oil. At the same time, increasing the oil fluidity of reservoirs by chemical viscosity reduction and the reaction products have no effect on the formation [2]. Autogenic heat technology is mainly used in high viscosity and high pour point reservoirs. According to the existing offshore process conditions, it is an attempt to develop offshore heavy oil by using autogenic heat chemical synergistic technology with less investment and quick response.

Heavy oil thermochemical synergistic technology is relatively mature in onshore oilfields [3, 4], but compared with an onshore oilfield, an offshore oilfield has its particularity, so it is necessary to carry out thermochemical synergistic technology research according to the characteristics of the offshore oilfield [5].
2. Study on Autogenic Heat System

2.1. Optimization of Autogenic Heat System.

There are mainly two kinds of commonly used autogenic heat systems.

System 1:
\[ \text{NO}_2^- + \text{NH}_4^+ \xrightarrow{\text{cat.}} \text{N}_2 + 2\text{H}_2\text{O} + 332.58 \text{ kJ/mol} \]  

System 2:
\[ \text{NaNO}_2 + \frac{1}{2}\text{CO(NH}_2)_2 + \text{HCl} \xrightarrow{\text{cat.}} \text{NaCl} + \text{N}_2 + \frac{1}{2}\text{CO}_2 + \frac{3}{2}\text{H}_2\text{O} + 213 \text{ kJ/mol} \]

According to Figures 1 and 2, both systems can increase the temperature of the wellbore or formation [6]. Under the same peak temperature difference, the concentration of system 1 is obviously lower than that of system 2; system 1 can obtain higher heating temperature with lower system concentration [6]. During the experiment, a large amount of gas was produced in both systems, and the colorless and odorless gas N\textsubscript{2} was produced in system 1. At the same time, system 2 produces a lot of brown-red toxic gases [7], which are by-products of the experimental reaction, NO and NO\textsubscript{2}. Therefore, system 1 was selected for further experiments.

2.2. Study on the Performance of Autogenic Heat System.

The reaction of NO\textsubscript{2} and NH\textsubscript{4}\textsuperscript{+} ions at low temperature follows the general law of chemical reaction. The reaction rate equation is as follows:
\[ \frac{dC_{\text{NO}_2^-}}{dt} = K C_{\text{NO}_2^-}^{a} \cdot C_{\text{NH}_4^+}^{b} \]
In the formula, $K$ is a constant of reaction rate, and it is a function of temperature. Usually, the $K$ value will increase by $2\sim 4$ times when the temperature increases by 10°C, and $\frac{dC_{NO_2^-}}{dt}$ is the rate of change of instantaneous $NO_2^-$ concentration with time. $C_{NO_2^-}$ and $C_{NH_4^+}$ are the instantaneous concentrations of $NO_2^-$ and $NH_4^+$, respectively, and $\alpha$ and $\beta$ are the characteristic constants of the equation [8].

It can be seen from the above equation that the higher the temperature, the greater the initial concentration of reactants and the faster the reaction rate. In order to minimize the heat loss and make full use of the heat released by the reaction to heat the reservoir, it is necessary to establish a method to control the heating rate. According to the chemical reaction mechanism, for an exothermic chemical reaction, when the concentration of the reactant is given, the

| Concentration (mol/L) | Peak temperature (°C) | Temperature range (°C) | Experiment conditions |
|-----------------------|-----------------------|------------------------|----------------------|
| 0.5                   | 63                    | 4                      | 100 mL 1.0 mol/L NaNO$_2$ solution+100 mL 1.0 mol/L NH$_4$Cl solution |
| 1.0                   | 79                    | 19                     | 100 mL 2.0 mol/L NaNO$_2$ solution+100 mL 2.0 mol/L NH$_4$Cl solution |
| 1.5                   | 127                   | 67                     | 100 mL 3.0 mol/L NaNO$_2$ solution+100 mL 3.0 mol/L NH$_4$Cl solution |
| 2.0                   | 142                   | 82                     | 100 mL 4.0 mol/L NaNO$_2$ solution+100 mL 4.0 mol/L NH$_4$Cl solution |
| 2.5                   | 157                   | 97                     | 100 mL 5.0 mol/L NaNO$_2$ solution+100 mL 5.0 mol/L NH$_4$Cl solution |
| 3.0                   | 178                   | 118                    | 100 mL 6.0 mol/L NaNO$_2$ solution+100 mL 6.0 mol/L NH$_4$Cl solution |

Note: catalyst concentration: 0.3%; base brine: 60°C.
heat released is a certain amount; only the reaction speed is variable. The factors that affect the reaction rate are temperature, pressure, and the type and concentration of catalyst. From the relationship between the saturated vapor pressure of water and temperature, we can know that the saturated vapor pressure of water is 0.1175 MPa at 119°C, and the pressure in formation is far greater than the saturated vapor pressure of water at this temperature. Therefore, it is not necessary to study the effect of pressure on the heating rate. The main research objects are temperature and the type and concentration of catalyst.

2.2.1. Calorific Value of Autogenic Heat System under Ideal Conditions. It can be seen from formula (4) that after mixing different concentrations of the NaNO₂ aqueous solution with different concentrations of the NH₄Cl aqueous solution, a large amount of heat can be generated, which greatly increases the temperature of basic brine. Table 1 shows the heat release calculated according to the data of standard molar enthalpy of formation in formula (4).

From the above table, it can be seen that the mixture of 0.5 m³ of the NaNO₂ aqueous solution whose concentration is 3.0 mol/L with 0.5 m³ of NH₄Cl aqueous solution whose concentration is 3.0 mol/L can theoretically produce 498.8 MJ of heat, 33.6 m³ (0.1 MPa, 25°C) of nitrogen, and 1.5 mol/L of NaCl aqueous solution (which is harmless to most oil and gas reservoirs) and can also make it possible for the temperature of base brine to increase by 119°C.

Table 3: Experimental data of gas production rate of autogenic heat system.

| Concentration (mol/L) | Quantity of gas (N mL) | Experiment conditions |
|-----------------------|------------------------|-----------------------|
| 0.5                   | 1545                   | 100 mL 1.0 mol/L NaNO₂ solution+100 mL 1.0 mol/L NH₄Cl solution |
| 1.0                   | 3495                   | 100 mL 2.0 mol/L NaNO₂ solution+100 mL 2.0 mol/L NH₄Cl solution |
| 1.5                   | 5850                   | 100 mL 3.0 mol/L NaNO₂ solution+100 mL 3.0 mol/L NH₄Cl solution |
| 2.0                   | 8155                   | 100 mL 4.0 mol/L NaNO₂ solution+100 mL 4.0 mol/L NH₄Cl solution |
| 2.5                   | 10192                  | 100 mL 5.0 mol/L NaNO₂ solution+100 mL 5.0 mol/L NH₄Cl solution |
| 3.0                   | 12500                  | 100 mL 6.0 mol/L NaNO₂ solution+100 mL 6.0 mol/L NH₄Cl solution |

Note: catalyst concentration: 0.3%; base brine: 60°C.

2.2.2. Calorific Value of Autogenic Heating System under Laboratory Condition. Different concentrations of heating agent solution were added to the high temperature and high pressure reactor, and the vessel was sealed immediately to observe the temperature change in the reactor. According to the experimental results in Table 2 and Figure 3, it is found that (1) under the same heating agent concentration and base brine temperature, the higher the concentration
of the heating agent, the more heat generated, and the larger the heating range of the system. However, when the concentration of the heating agent is lower than 1.0 mol/L, the reaction speed is lower, and the reaction time is prolonged, resulting in the increase of heat loss in the experimental process. (2) Due to the limitation of the solubility of inorganic salts, when the concentration of the heating agent exceeds 2.5 mol/L, it is difficult to prepare the heating system and to dissolve other additives in the system. Therefore, it is suggested that the concentration of the heating agent should be controlled in the range of 1.0 mol/L-2.5 mol/L.

2.2.3. Gas Production Rate of Autogenic Heat System under Laboratory Conditions. Figure 4 shows the experimental process of the autogenous heating system for gas generation. The gas volume obtained by the reaction is collected by the drainage method. The total amount of gas collected is recorded after the experiment is completed. The gas yield of the system under formation or wellbore conditions is controlled and mastered by changing the concentration of the heat generating agent. Table 3 and Figure 5 show the relationship between the concentration of the heat generating agent and the amount of gas generated.

2.2.4. The Control of Thermal Peak of Autogenic Heat System. Taking the same initial temperature, let two kinds of heat-generating agents react exothermically under an apparent adiabatic condition. By changing the type and concentration of the heat-generating agent, the temperature rise rate can be controlled, and the thermal peak can be reduced or eliminated. Table 4 and Table 5 show the relationship between the concentration of the heat generating agent and the temperature rise rate.
Figure 6: The effect of catalyst concentration on heat generation rate of system.

Figure 7: The effect of catalyst types on heat generation rate and thermal peak.

Table 6: The effect of ambient temperature on heat generation rate and thermal peak.

| Ambient temperature: 60°C | Ambient temperature: 75°C | Ambient temperature: 85°C |
|--------------------------|---------------------------|---------------------------|
| Time (min) | Temperature (°C) | Time (min) | Temperature (°C) | Time (min) | Temperature (°C) |
| 0 | 25 (indoor) | 0 | 25 (indoor) | 0 | 25 (indoor) |
| 1 | — | 1 | — | 1 | — |
| 2 | 23 | 2 | 32 | 2 | 42 |
| 3 | 26 | 3 | 41 | 3 | 63 |
| 4 | 37 | 4 | 57 | 4 | 80 |
| 5 | 43 | 5 | 78 | 5 | 86 |
| 6 | 52 | 6 | 85 | 6 | 94 |
| 7 | 64 | 7 | 83 | 7 | 92 |
| 8 | 72 | 8 | — | 8 | — |
| 9 | 78 | 9 | — | 9 | — |
| 10 | 75 | 10 | — | 10 | — |
| 11 | — | 11 | — | 11 | — |

Concentration of system: 100 mL 2.0 mol/L NaNO₂ solution + 100 mL 2.0 mol/L NH₄Cl solution catalyst: 1.0% HCl.
amount of the catalyst, we can understand the relationship between the amount of catalyst and the reaction speed.

Tables 4 and 5 and Figures 6 and 7 show the same catalyst concentration and base brine temperature.

(1) The thermochemical reaction of sodium nitrite and ammonium chloride can hardly be observed at room temperature without adding acid, and only when the solution is heated to more than 60°C can the reaction occur, and the reaction rate is very slow.

(2) The thermochemical reaction rate of sodium nitrite and ammonium chloride can be increased by either liquid acid or solid acid and strong acid or weak acid.

(3) The catalytic intensity of acid to the reaction between sodium nitrite and ammonium chloride is related to strength of the acid. The higher the catalyst concentration and strength, the greater the rate of thermochemical reaction. It can be seen from the experimental results that the catalytic strength of phosphoric acid is almost the same as that of hydrochloric acid and nitric acid. This is because phosphoric acid is a polybasic acid; when the temperature rises, its dissociation constant increases, providing more H⁺ ions for the reaction.

(4) The higher the catalyst concentration and strength, the shorter the peak time of the system, but the peak temperature is not affected by the catalyst concentration.

When the catalyst concentration is high (the concentration limits of different catalysts are different), the pyrogenic reaction will be accompanied by brown gas, mainly nitric oxide and nitrogen dioxide (toxic). Therefore, when using the pyrogenic system, the concentration of acidic catalyst should be controlled to reduce the production of toxic products.

(5) The addition of a very small amount of acid can greatly increase the rate of thermochemical reaction, indicating that the thermochemical reaction of sodium nitrite and ammonium chloride in acid solution is a typical acid-catalyzed reaction.

(6) When the concentration and type of catalyst change, the peak position of the pyrogenic system will change.

(7) Catalyst MX reacted smoothly and slowly released H⁺, and no brown by-product gases such as NO and NO₂ were produced during the experiment.

2.2.5. The Effect of Ambient Temperature on Autogenic Heat System. The relationship between ambient temperature and reaction rate can be understood by changing the ambient temperature of the heating system under the condition of same heating agent concentration, the same catalyst type and concentration, and the apparent adiabatic. The result shows that the higher the ambient temperature is, the faster the heat generation rate of chemical reaction is. Table 6 and Figure 8 show the influence of ambient temperature on heat generation rate and heat peak.

2.3. Evaluation of Application Effect of Autogenic Thermochemical Synergistic System

2.3.1. The Viscosity-Reducing Property of Autogenic Thermochemical Synergistic System. A certain amount of simulated crude oil from an oil field is placed in a beaker, and the autogenous heat system components are added to the beaker in turn to make it react fully in the beaker, and the temperature changes are recorded. The viscosities of the system of the "thermal peak" and at the end of the reaction are measured by parallel experiments. According to
Table 7 and Figure 9, the experimental results show that the heat generated during the reaction can effectively reduce the viscosity of heavy oil. And the viscosity of heavy oil can be reduced from 2984 mPa·s to 121 mPa·s when the reaction reaches the peak. The temperature of the mixture can be maintained above 60°C for more than 30 minutes during the reaction process, and the obvious viscosity reduction effect can also be maintained at the end of the reaction.

2.3.2. The Dissolving Paraffin Performance of Autogenic Thermochemical Synergistic System. A certain amount of solid paraffin was placed in a beaker, and those components of the system were added to the beaker in turn to make it react fully in the beaker. The residual solid paraffin content was measured at the end of the reaction, and the reaction time was recorded. It can be seen from the experimental results in Table 8 that the autogenic thermochemical system has a good dissolution effect on the fixed paraffin. With the increase of the concentration of the heating agent, the amount of dissolving solid paraffin increases, and the time of dissolving solid paraffin is shorter.

2.3.3. The Cleaning Organic Fouling Performance of Autogenic Thermochemical Synergistic System. A certain amount of rock particles adhering to heavy oil and organic matter were placed in a beaker, and then, those components of the system were added to the beaker in turn to make it react fully in the beaker. At the end of the reaction, the amount of residual organic matter was measured, and the cleaning capacity of the 100°C distilled water was compared with that of the system. It can be seen from the experimental results in Table 9 that the autothermal system has a good cleaning effect on heavy oil and organic matter, compared with 100°C distilled water, and the autothermal system has a better cleaning organic fouling performance.

The SARA of heavy oil is as follows: saturated hydrocarbon 41.04%, aromatic hydrocarbon 26.24%, resin 14.13%, and asphaltene 18.59%. And the calculation method of the cleaning effect is as follows: reduced weight after cleaning/total weight before cleaning.

2.3.4. The Plugging Removal Performance of Autogenic Thermochemical Synergistic System. The test core is the Minghua formation oil sands in the Bohai oilfield (core pipe: 25 mm * 100 mm). Core basic parameters are permeability 3130 md, porosity 28%, and oil saturation 71.5%, consistent with reservoir parameters.

Crude oil is an oil sample from a well in the Bohai oilfield (degassing viscosity at 50°C 1931 mPa·s).

The system formulation is as follows:

(i) Base solution: 2%KCl solution
(ii) Acid system: 10% HCl+6% HBF₄
(iii) Autogenic heating composite system: 2.0 mol/L NaNO₂+2.0 mol/L NH₄Cl and acid system is alternately injected by 3 slugs

According to Table 10 and Figure 10, the experimental results show that the core permeability is significantly increased than the benchmark permeability, the permeability is increased by more than 2.0 times, and the increase range of core permeability is large, which indicates that the plugging removal effect of the self-heating system combined with the HBF₄ system can relieve the pollution of the Bohai heavy oil wells.

3. Field Test

There are 4 wells of two oil fields that have employed the thermochemical synergistic technology of heavy oil.

3.1. Chemical Deicing and Plugging Removal of a Well. In February 2011, the low temperature caused tube freezing from the Christmas tree to the sea level, and the length is
about 14 m, which seriously affected the static pressure test and subsequent daily production of the well P2.

### 3.1.1. Process Plan

(1) **Dosage of System.** The amount of autogenous heating system prepared and the number of solutions currently prepared are shown in Table 11.

(2) **Slug Design.** According to the current situation of the well, the process design is shown in Table 12.

(3) **Process Program.**

1. Close the main valve, open the paraffin removal valve after emptying, pour 2 L of the pour point reducer into the tubing, then close the paraffin removal valve to open the main valve
2. Close the main valve, open the paraffin removal valve after emptying, pour 5 L of NaNO₂+NH₄Cl supersaturated solution into the tubing, then close the paraffin removal valve to open the main valve
3. Close the main valve to open the paraffin removal valve, pour 0.5 L of the catalyst solution into the tubing, close the paraffin removal valve to open the main valve, shut down the main valve after the liquid flows into the wellbore, and let the solution of the autogenous heat system in the wellbore react for a certain time to release more heat
4. Cycle above until removal of ice blockage in tubing

### 3.1.2. Effect Analysis

(1) Take deicing and plugging removal operations in this well, from March 10 to March 16, during which the actual operation lasted for four days, and the ice column in the plugged tubing was removed for nearly 14 m
Table 12: Design of deicing and plugging removal.

| Slug   | Name                          | Dosage (L) | Effect                                                                 |
|--------|-------------------------------|------------|------------------------------------------------------------------------|
| First  | Pour point reducer solution   | 2          | Reduce the solidification point of solution in wellbore               |
| Second | NH₄Cl+NaNO₂ supersaturated solution | 5          | The autothermic main agent was added to the solution in the wellbore and dissolved |
| Third  | Catalyst solution of autothermal reaction | 0.5        | Accelerate the self-heating reaction to release heat quickly to melt the ice |

Table 13: Scale design of injection solution.

| Liquid name            | Liquid level | m³ | Liquid level | bbls | Note                                           |
|------------------------|--------------|----|--------------|------|------------------------------------------------|
| Prepad                 | 10.0         | 62.9 | Prepare one for each 30 m³ acid tank                               |
| Treating fluid         | 20.0         | 125.8| Prepare one for each 30 m³ acid tank                               |
| Afterpad               | 10.0         | 62.9 | Simultaneous prepare with the prepad                               |
| Autogenic hydrothermal | 30.0         | 188.7| Prepare one for each 30 m³ acid tank                               |
| Spacer fluid           | 12.0         | 75.5 | Prepare one for each 30 m³ acid tank                               |
| Displacement fluid     | 32.0         | 201.3| Prepare one for each 30 m³ acid tank                               |
| Total fluid volume     | 114          | 717.0|                                                         |

Table 14: Program of plugging removal and draining in well A23.

| Stage | Frequency (Hz) | Running time (hr) | Estimated drain speed (m³/hr) | Discharge fluid volume every stage (m³) | Estimated cumulative liquid discharge (m³) |
|-------|----------------|-------------------|------------------------------|----------------------------------------|------------------------------------------|
| 1     | 35             | 4                 | 5-7                          | 20                                     | 20                                       |
| 2     | 40             | 6                 | 5-7                          | 30                                     | 50                                       |
| 3     | 45             | 8                 | 5-7                          | 40                                     | 90                                       |
| 4     | Power frequency | 5-7               |                              |                                        | >220                                     |

Note: the estimated discharge velocity is calculated according to the rated displacement of the pump.

Figure 11: Production curve of well.
(2) According to the location of the ice column in the well, adjust the operational scheme of the reagent to meet the needs of the field. It shows that the heat generating position and time of the solution can be controlled.

3.2. Field Test of Plugging Removal in Well A23 by Autogenous Heat. The A23 well is located at the high part of the reservoir at the top formation. It initially produces the main oil layer of formation. The vertical depth of the perforated interval is 1645.6 m-1659.3 m and the vertical thickness of the oil layer is 13.7 m.

The well carried out second plugging removal operations on April 15 to 16, 2010, and the effect of plugging removal was very good. But a month later, the liquid production began to decrease. The output of the well was low in October 2010, and the reservoir near the wellbore was damaged.

3.2.1. Plugging Removal Process Design

(1) injection mode: oil ring annulus reverse extrusion, alternate injection

(2) Construction discharge: 3.0-5.5 bpm, which can be adjusted according to spot pressure

(3) Construction pressure: <12 MPa (1740 psi)

The fracture pressure gradient is calculated according to 0.017 MPa/m, and the formation fracture pressure is 28.1 MPa. The annular friction is 1 MPa/1000 m, and the maximum injection pressure at the wellhead is 12.45 MPa.

Table 13 shows how many the injection solutions are needed, and Table 14 estimates how the plugging removal and draining in a well will perform.

3.2.2. Effect Tracking. Figure 11 shows the production curve. As of July 1, 2012, the liquid production of the well increased from 85.8 m³/d to 275.3 m³/d, and the liquid production increased by 3.2 times. Oil production increased from 4.285 m³/d to 16.9 m³/d to 27.8 m³/d, and cumulative oil increment is increased by 3.2 times. Oil production increased from 4.285 m³/d to 16.9 m³/d to 27.8 m³/d, and cumulative oil increment is increased by 3.2 times.

4. Conclusions

(1) The autogenous heating system was optimized, which could produce high heat at low concentration and was nontoxic

(2) By controlling the type and concentration of the catalyst, the time to reach the thermal peak of the autogenic heating system can be controlled

(3) When the concentration of autogenous heating agent is 1.5 mol/L, the temperature rise is 67°C, which meets the performance requirements of more than 50°C

(4) The autogenic thermochemical synergistic system can effectively reduce the viscosity of heavy oil, dissolve solid paraffin and clean organic fouling, and effectively improve reservoir permeability and increase crude oil production.

Data Availability

Data availability is on request.

Conflicts of Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work; there is no professional or other personal interest of any nature or kind in any product, service, and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, “Study on Autogenous Heat Technology of Offshore Oilfield: Experiment Research, Process Design, and Application.”

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