

Experimental research on a new encapsulated heat-generating hydraulic fracturing fluid system *

WU Jinqiao (吴金桥)^{1**}, ZHANG Ningsheng (张宁生)², WU Xinmin (吴新民)²,
and LIU Xiaojuan (刘晓娟)²

¹ School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China

² School of Petroleum Engineering, Xi'an Shiyou University, Xi'an 710065, China

Abstract During fracturing treatment for low-temperature, shallow and high freezing point oil reservoirs, the first-line problems are to overcome uncompleted breakdown, uncompleted cleanup of fracturing fluids and cold damages to the formations by injecting cold fluid. To avoid those problems, it is suggested to adopt a new encapsulated heat-generating hydraulic fracturing fluid system as described in this paper.

Firstly, two kinds of chemical heat-generating systems were studied and the $\text{NH}_4\text{Cl-NaNO}_2$ system was selected. According to the reaction characteristics of the system, oxalic acid was chosen as a catalyst of reaction and encapsulated using ethyl cellulose and paraffin as coating materials by the phase separation method. Compatibility of $\text{NH}_4\text{Cl-NaNO}_2$ -encapsulated oxalic acid with hydroxypropyl-guar fracturing fluid was also discussed in the paper. The results showed that the hydraulic fracturing fluid containing encapsulated heat-generating agents have a good stability and compatibility. When the fracturing fluid contains $2.0 \text{ mol} \cdot \text{L}^{-1} \text{NH}_4\text{Cl-NaNO}_2$, 0.93% encapsulated oxalic acid and 0.08% ammonium persulfate, the peak temperature can reach 78.0°C and the viscosity of residual liquid is $3.12 \text{ mPa} \cdot \text{s}$ after 4 hours.

Key words hydraulic fracturing fluid; encapsulated; chemical heat-generating agent; compatibility; gel breaking

1 Introduction

Fracturing plays an important role in increasing the production and injection and enhancing the final recovery of oil and gas. At present, the use of a hydroxypropyl guar gum, borate-crosslinked, hydraulic fracturing fluid system has become extremely popular in the oilfield-service industry. But at low-temperature (e. g. at about 50°C or lower) conditions, conventional oxidizing breakers, such as persulfates, are not effective unless used in large concentrations or used with catalysts for a complete break (Bi Hua and Peng Gelin, 1998; Powell et al., 1999; Ren Zuowei et al., 2001). And for a reservoir with a high wax content and high freezing point crude oil, the equilibrium of crude oil can be disrupted within the formation by injecting cold fluids such as those used in fracturing. If the crude oil around near the fracture faces is cooled to its cloud point, its viscosity will increase, even paraffin will be precipitated and may be deposited in the formation pores, partially blocking or plugging the fluid

flow channels, thus restricting the flow (Sutton and Roberts, 1974; Liu Shuzhi et al., 2003; Peng Xuan et al., 2003). There are many low-temperature, high wax-content, high freezing-point oil reservoirs in China, such as the Liaohe Oilfield, the Daqing Oilfield, the Shengli Oilfield, the Dagang Oilfield, the Changqing Oilfield, etc. When conventional hydraulic fracturing fluids (e. g. hydroxypropyl guar gum, borate-crosslinked, hydraulic fracturing fluid) are used in those oil reservoirs, the damage may manifest itself in production decrease, slow cleanup of wells after fracturing, or failure to attain predicted production increases. So, how to solve the problem of conventional fracturing fluid break at low temperature and cold damage to the oil reservoirs with high wax-content and high freezing-point crude oil, is the key to increase fracturing effect in those reservoirs.

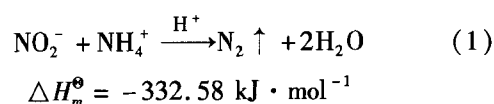
According to the success cases of blocking removal in high wax-content oil wells by the thermo-chemical method, Liu Shuzhi et al. (2003) put forward and studied the *in-situ* heat-fracturing technique. The *in-situ* heat fracturing fluid is based on conventional water-based fracturing fluid, with some NaNO_2 , NH_4Cl and HCl added in the base fluid. When the additives are mixed and react, much heat will be generated. During fracturing treatment, NaNO_2 and NH_4Cl are dissolved

respectively into two shares of base fluids, and then the two shares are injected together and mixed in wellbore and the chemical reaction takes place. Because the mixed fluids begin to generate heat promptly in the wellbore, it should be considered that increasing temperature of fluids would influence the rheological properties of fracturing fluid during *in-situ* heat fracturing. If heat-generating reaction in the fracturing fluid system is not well controlled, it is extremely possible to cause proppant-carrying capacity to be reduced, even fracturing failure. To avoid those problems, it is suggested to adopt a new encapsulated heat-generating hydraulic fracturing fluid (EHFF) system the authors studied. In the system, the catalyst of heat-generating reaction is encapsulated with water-resistant coating by encapsulation technology, and the heat-generating agents, NaNO_2 and NH_4Cl , are dissolved together into one share of conventional hydraulic fracturing fluid. While fracturing, encapsulated catalysts that are distributed evenly into work fluid together with proppants are injected into fractures around the bottom hole. Then, the majority of encapsulated catalysts are broken by closure stress of fractures and lead to the release of H^+ . So chemical reaction begins rapidly and the temperature of fluid increases. Consequently, the fluid breaks down fast, the damage of blocking can be removed, and the cold damage of injected fluid to reservoirs can also be prevented.

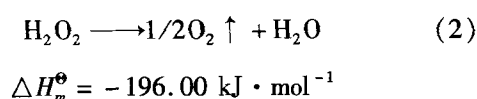
2 Selection of the heat-generating reaction system

As to this subject, it is the primary task to select a kind of heat-generating reaction system that has high heat-generating efficiency but does little damage to reservoirs. At present, there are two kinds of heat-generating systems commonly used in the production of oil and gas.

(1) The nitrite-ammonium salt system (Collesi et al., 1987; Cheng Yunfu and Li Yanmei, 1997; Zhang Junchuang et al., 1999). The reaction is given as follows:



(2) The hydrogen peroxide system (Bayless, 1998, 2000). The reaction is presented as follows:



Following laboratory testing, the $\text{NaNO}_2\text{-NH}_4\text{Cl}$ system can reach 95.8°C , the peak of temperature, in 10 minutes with 25% $\text{NaNO}_2\text{-NH}_4\text{Cl}$, while the H_2O_2 system can reach about 91.0°C in 25 minutes with the same concentrations. Although the systems both have a good heat-generating efficiency, the effects of heat-generating agents on fracturing fluid should be taken into consideration. For the $\text{NaNO}_2\text{-NH}_4\text{Cl}$ system, the NaNO_2 and NH_4Cl aqueous solutions are closely neutral, which have little effect on fracturing fluid. But H_2O_2 can break down fracturing fluid because of its strong oxidation capability. So, the $\text{NaNO}_2\text{-NH}_4\text{Cl}$ system is selected as the heat-generating system.

According to theoretical studies and laboratory investigations, the reaction kinetics equation of the $\text{NaNO}_2\text{-NH}_4\text{Cl}$ system is presented as follows (Wu Anmin and Chen Maotao, 1995):

$$\frac{dC}{dt} = -1.267 \times 10^7 C_H^{1.173} C_r^{1.88} e^{-5630/T} \quad (3)$$

where $\frac{dC}{dt}$ is the consumption rate of reactant (NaNO_2 or NH_4Cl), $\text{mol} \cdot \text{L}^{-1} \cdot \text{min}^{-1}$; C is the concentration of reactant in the system, $\text{mol} \cdot \text{L}^{-1}$; C_H is the concentration of H^+ (catalyst of reaction), $\text{mol} \cdot \text{L}^{-1}$; C_r is the concentration of initialization reactant, $\text{mol} \cdot \text{L}^{-1}$; T is the temperature of system, K. It is obvious that the heat-generating rate can be regulated in terms of the concentrations of H^+ in the system. Therefore, the three solid acids, boric acid, oxalic acid and citric acid, were chosen to investigate their effects on the heat-generating rate of the $\text{NaNO}_2\text{-NH}_4\text{Cl}$ system according to the reaction characteristics and subsequent encapsulated requirement. Finally, oxalic acid was chosen as the catalyst of the heat-generating system.

3 Preparation and properties of encapsulated oxalic acid

3.1 Preparation of encapsulated oxalic acid

Encapsulated oxalic acid was prepared by the organic-phase separation method. According to the matching of the supplies, ethyl cellulose, polyethylene glycol, oxalic acid particles and cyclohexane were added in a suitable vessel. Then it was heated to 81°C by continuing stirring until ethyl cellulose dissolved completely. After stirring for 30 minutes at 81°C , the whole solution cooled to room temperature without stopping stirring. The intermediate products were recovered by filtering, and washed in cyclohexane for three times

and dried at room temperature. And then, a certain amount of paraffin (Range of melting points: 58 – 60°C) was added in a vessel filled up with water, and was heated till it was melted. The intermediate products were added in and stirred for 10 minutes, and cooled to room temperature by continuing stirring. Eventually, the encapsulated oxalic acid was recovered by filtering, and dried at room temperature.

3.2 Properties of encapsulated oxalic acid

The evaluation of the properties of encapsulated oxalic acid includes three aspects: release rate, effective content and encapsulation efficiency. They are determined by measuring changes in electrical conductivity of the water as the oxalic acid is released. Firstly, a standard curve of conductivity on the known concentrations of oxalic acid solution was obtained under certain temperature. Then, the oxalic acid concentrations of the unknown solution could be determined by interpolating the standard curve with the conductivity of the solution. Release rate of the encapsulated oxalic acid is represented by its half-life ($\tau_{0.5}$). The calculation formulas for effective content and encapsulation efficiency are given below:

$$\omega\% = \frac{w_2}{w_1} \times 100\% \quad (4)$$

$$\eta\% = \frac{w_2}{w_2 + w_3} \times 100\% \quad (5)$$

where ω is the effective content of capsule, %; η is the encapsulation efficiency, %; w_1 is the total mass of capsules, g; w_2 is the mass of oxalic acid encapsulated, g; w_3 is the mass of oxalic acid unencapsulated, g.

Oxalic acid capsules encapsulated by ethyl cellulose (Intermediate products) were prepared respectively according to different ratios of core to shell (oxalic acid:ethyl cellulose, ratio of mass) that are 10:0.5, 10:1.0, 10:1.5, 10:2.0 and 10:2.5, and the serial numbers of the products are EC05, EC10, EC15, EC20 and EC25.

Table 1. Properties of oxalic acid capsules encapsulated by ethyl cellulose

Serial number	ω (%)	η (%)	$\tau_{0.5}$ (min)
EC05	90.2	92.8	17
EC10	87.1	94.5	21
EC15	82.6	96.8	26
EC20	78.6	97.1	35
EC25	73.9	97.9	36

With decreasing ratio of core to shell, the effective content of capsule (ω) is reduced thereupon, but the encapsulation efficiency (η) and half-life ($\tau_{0.5}$)

tend to increase (Table 1). By considering the three factors synthetically, oxalic acid capsules encapsulated by ethyl cellulose that the serial number is EC20 were chosen as the intermediate products for next tests.

To increase the half-life of capsules, it needs to be encapsulated by the second layer. Taking EC20 as the core material and paraffin as the second coating material, at the ratios of core to shell of 5:0.5, 5:1.0, 5:1.5 and 5:2.0, double-layer encapsulated oxalic acid was prepared and the serial numbers of the products are ED05, ED10, ED15 and ED20.

Compared with the data in Table 1, the effective contents of oxalic acid capsules are small, but the half-life is long (Table 2). By considering synthetically, ED15 of the encapsulated oxalic acid is regarded as the final product.

Table 2. Properties of the encapsulated oxalic acid

Serial number	ω (%)	η (%)	$\tau_{0.5}$ (min)
ED05	68.9	94.9	42
ED10	66.8	96.8	58
ED15	62.7	97.2	78
ED20	57.1	98.3	175

4 Compatibility of NaNO₂, NH₄Cl and encapsulated oxalic acid with hydraulic fracturing fluid

According to the authors, the heat-generating agents (NaNO₂ and NH₄Cl) should be dissolved into fracturing fluid, and encapsulated oxalic acid as the reaction catalyst was also compounded with the fluid. For this reason, heat-generating agent and encapsulated oxalic acid effects on the rheology and proppant-carrying capacity of fracturing fluid should be taken into consideration.

4.1 Anti-shear property of the new EFFF system

In the experiment described as follows, the compounding of fracturing fluid is: 0.6 wt% hydroxypropyl guar, 0.7 wt% borax, 0.08 wt% ammonium persulfate, 100:5 the ratio of cross linkage. And the concentrations of heat-generating agents (NaNO₂ and NH₄Cl) are 1.5, 1.75 and 2.0 mol · L⁻¹.

Firstly, the influence on the viscosity of fracturing base fluid of NaNO₂ and NH₄Cl dissolved was investigated. The initial viscosity of fracturing base fluid is 81.0 mPa · s. And with increasing concentrations of NaNO₂ and NH₄Cl added in the fracturing base fluid, the viscosity of the base fluid decreases gradually.

In addition, the compatibility of coating materials with fracturing fluid also has been investigated. The

experimental results show that coating materials, ethyl cellulose and paraffin have little influence on the anti-shear property of fracturing fluid.

The preparing procedure of the new EHFF system is described as follows:

(1) Dissolving NaNO_2 , NH_4Cl , ammonium persulfate and hydroxypropyl guar into water to prepare fracturing base fluid.

(2) Regulating the pH of fracturing base fluid to the range of 7.5 – 8.0, adding encapsulated oxalic acid and stirring.

(3) Adding borax crosslinker to form a system according to the volume ratio of fracturing base fluid to crosslinker, 100:5, at the stirring speed of 6000 rpm. Thus, the EHFF system is prepared.

And then, the anti-shear property of the fracturing fluid is determined by means of a Haake rehometer.

Compared with conventional hydraulic fracturing fluid, the viscosity of EHFF drops to some extent. But the EHFF system has a good stability and anti-shear property. Compounding with $2.0 \text{ mol} \cdot \text{L}^{-1}$ NaNO_2 and NH_4Cl , its final viscosity is kept at about $300 \text{ mPa} \cdot \text{s}$ when it is sheared at the rate of 170 s^{-1} in 2 hours, which ensures the fracturing fluid system with a good proppant-carrying capacity during fracturing treatment (Fig. 1).

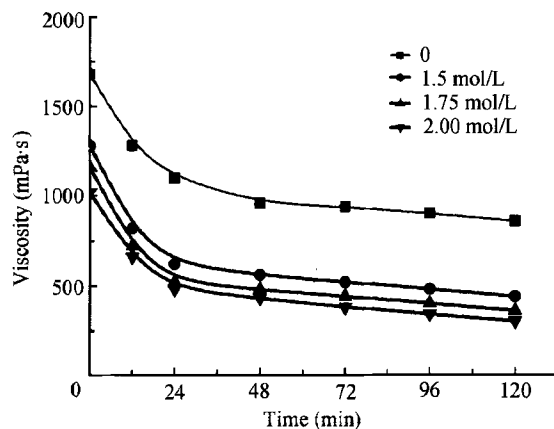


Fig. 1. Effect of heat-generating agents on the anti-shear property of EHFF.

4.2 Heat-generating property of the EHFF system

When the EHFF was prepared, almost no change was noticed in its temperature for a long time. The reason may be that the release rate of oxalic acid capsules is much slower in gluey fracturing fluid than in water solution. The heat-generating reaction goes so slowly that the heat generated almost equals to dissipated heat. So, no change occurred in temperature of the fracturing fluid on the whole.

As we know, the fractures produce enormous pressure while closing in reservoirs. So the experiment to simulate the crash of encapsulated oxalic acid was done in a compactor under a certain pressure. The rate of pressing release of encapsulated oxalic acid is calculated by the following formula:

$$R = \frac{\eta_2}{\eta_1} \times 100\% \quad (6)$$

where R is the rate of pressing release, %; η_1 is the oxalic acid effective content of capsule, %; η_2 is the oxalic acid content of capsule by pressing. The rate of pressing release of encapsulated oxalic acid is 89.61%.

By adding 0.93% encapsulated oxalic acid that was triturated into heat-generating fracturing fluid, the heat-generating property of the EHFF system was determined in an assembly calorimeter.

From the data of Table 3, we can see that the higher the concentrations of heat-generating agents, the higher the peak temperature of the system will be. When the concentrations of NaNO_2 and NH_4Cl are $2.00 \text{ mol} \cdot \text{L}^{-1}$, the peak temperature will be 78°C in 50 minutes. As compared with the results from heat-generating experiments for water, the heat-generating rate and the peak temperature in fracturing fluid show an obvious decrease.

Table 3. Heat-generating property of the EHFF

$\text{NH}_4\text{Cl} + \text{NaNO}_2$ ($\text{mol} \cdot \text{L}^{-1}$)	Peak temperature ($^\circ\text{C}$)	Time duration (min)
1.50	65	75
1.75	71	60
2.00	78	50

4.3 Gel-breaking property of the EHFF

$2.00 \text{ mol} \cdot \text{L}^{-1}$ NaNO_2 and NH_4Cl , 0.93% oxalic acid capsules triturated and ammonium persulfate were mixed with the fracturing fluid, and its gel-breaking property was determined in a closed container. The initial temperature is 30°C and test time is 4 hours. The results are listed in Table 4.

Table 4. Gel-breaking property of the EHFF

Viscosity of residual liquid ($\text{mPa} \cdot \text{s}$)	Concentration of breaker (wt%)			
	0.02	0.04	0.06	0.08
2 h	24.34	14.62	8.90	6.44
4 h	16.86	9.23	6.81	3.12

The results show that the EHFF has a good gel-breaking property. At a concentration of ammonium persulfate of 0.08 wt%, the viscosity of residual liquid is 3.12 mPa · s after 4 hours.

5 Conclusions

(1) Two kinds of chemical heat-generating systems were studied and the NH_4Cl - NaNO_2 system was selected. According to reaction characteristics of the system, oxalic acid was chosen as the catalyst of reaction.

(2) Ethylcellulose-paraffin double-layer encapsulated oxalic acid was prepared by the phase separation method. Ethyl cellulose was used as coating material of the first layer, the mass ratio of core to shell (oxalic acid:ethyl cellulose) was 10:2.0; paraffin was used as coating material of the second layer, the mass ratio of core to shell (the intermediate products:paraffin) was 5:1.5.

(3) Compounding with encapsulated oxalic acid, gel-breaker and $2.0 \text{ mol} \cdot \text{L}^{-1}$ heat-generating agents, the final viscosity of the EHFF was kept at about 300 mPa · s when it was sheared at the rate of 170 s^{-1} in 2 hours. The results show that the EHFF system has a good stability and compatibility. When the EHFF system contains $2.0 \text{ mol} \cdot \text{L}^{-1}$ NH_4Cl - NaNO_2 , 0.93% encapsulated oxalic acid and 0.08% ammonium persulfate, the peak temperature can reach 78.0°C and the residual liquid viscosity is 3.12 mPa · s after 4 hours.

References

- Bayless J. H. (1998) Hydrogen peroxide: A new thermal stimulation technique [J]. *World Oil*. **219**, 29–31.
- Bayless J. H. (2000) Hydrogen peroxide applications for the oil industry [J]. *World Oil*. **221**, 50–53.
- Bi Hua and Peng Gelin (1998) Characteristics of telemagmatic metamorphism of the Ceshui Formation coal in Lianyuan Coal Basin [J]. *Chinese Journal of Geochemistry*. **17**, 379–384.
- Cheng Yunfu and Li Yanmei (1997) Preparation and field uses of heat-generating hydro-fracturing fluids [J]. *Oilfield Chemistry*. **14**, 24–27 (in Chinese with English abstract).
- Collesi J. B., Scott T. A., and McSpadden H. W. (1987) Surface equipment cleanup utilizing *in-situ* heat. In *The Proceedings of the SPE Production Operations Symposium* [C]. pp. 305–311. SPE Inc.
- Liu Shuzhi, Sun Aiyin, and Liu Fujian (2003) Optimization methods of concentration of heat generation agents in *in-situ* heat fracturing treatment [J]. *Oil Drilling & Production Technology*. **25**, 45–48 (in Chinese with English abstract).
- Peng Xuan, Liu Shuzhi, and Cai Changyu (2003) Calculation model for wellbore temperature profiles in high freezing-point oil reservoirs with *in-situ* heat fracturing treatment [J]. *Acta Petrolei Sinica*. **24**, 69–76 (in Chinese with English abstract).
- Powell R. J., McCabe M. A., Slabaugh B. F., and Terracina J. M. (1999) Applications of a new, efficient hydraulic fracturing fluid system [J]. *SPE Prod. & Facilities*. **14**, 139–143.
- Ren Zuowei, Gu Lianxing, Wu Changzhi, and Zhao Ming (2001) Subvolcanic emplacement of the Oulituozi trachyte porphyry in the Liaohhe Basin and its significance to hydrocarbon reservoirs [J]. *Chinese Journal of Geochemistry*. **20**, 258–260.
- Sutton G. D. and Roberts L. D. (1974) Paraffin precipitation during fracture stimulation. In *The Proceedings of the SPE-AIME Rocky Mountain Regional Meeting* [C]. pp. 997–1004. SPE Inc.
- Wu Anmin and Chen Maotao (1995) Study on the reaction kinetics of NaNO_2 with NH_4Cl and its applications in oilfields [J]. *Oil Drilling & Production Technology*. **17**, 60–64 (in Chinese with English abstract).
- Zhang Junchuang, Wang Dezhi, and Ma Qingzhuang (1999) Applied research on oil recovery technique by thermochemistry [J]. *Petroleum Geology and Recovery Efficiency*. **6**, 62–66 (in Chinese with English abstract).