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Study on Modified Starch Gel Physicochemical Characteristics and Parameters Quantification

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Abstract. Both laboratory and oil field tests have documented that enhanced oil recovery can be obtained by performing positioning blockage technology with the lower cost and the higher strength. Modified starch gel (MSG) is the preferred gel for positioning blockage technology considering its resistance abilities on temperature, salty and shear of the graft copolymerization between starch and allyl monomer. Due to the complexity of the reaction which is fractional and its rate bases on velocity, the physicochemical characteristics of MSG are totally different from conventional gel. Based on published data, graft copolymerization reaction rate equation with velocity and concentration is established and physical process for generated copolymer adsorption is characterized, which agreed with documented experimental facts. The dynamic characteristics of injection pressure are obtained by laboratory displacement experiment, which is designed including the early water driving stage, the middle MSG driving stage and the subsequent water driving stage. The quantitative results of characteristic parameters, such as residual resistance coefficient, maximum adsorption amount and viscosity, are achieved by fitting the injection pressure curve of laboratory displacement experiment using numerical simulation technology by CMG software. The viscosity of gel is about three times higher than that of polymer. MSG system had good gelation property which is helpful to enhance the plugging ability.

1. Introduction

With the continued downturn in oil prices, low cost, small dosage and high strength of positioning blockage technology are gradually favored by the major domestic oil fields. Positioning blockage technology is to make profile control agent slug accurately position to the appropriate location and to make the enhanced oil recovery efficiency of secondary flooding fluid slug to achieve the best [1, 2]. Compared with the common profile control technology, positioning blockage technology has many advantages. Such as bigger sweep efficiency and bigger sweep volume [3], more beneficial to reflect characteristics of different chemicals [4] and so on. MSG could meet the requirements of dosage and strength of profile control agent slug in positioning blockage technology, and obtains obvious effect in the fractured, low permeability reservoir test [5, 6].

MSG is made of acrylamide, modified starch, cross-linking agent and initiator. Starch graft copolymer is formed after gelling. It has wide molecular chains and good thermal stability [7]. MSG is a vinyl unsaturated monomer graft copolymer with polar groups, obtained by graft copolymerization of polymer with vinyl monomer. It has hydrophilic starch backbone and plenty of flexible polyacrylamide branches [8, 9]. Such branches are obtained by chain transfer reaction and initiation of macromolecule active center [10]. SEM pattern and XRD pattern of starch and starch graft copolymer show that starch granules are spherical or ellipsoidal with different sizes and micrometer scale [8]. Gap between granules and granules is larger. But starch graft copolymer after modified does not have these two shapes. It is gel multiple empty agglomeration with many microspores of varying sizes. This difference further confirmed that MSG is obtained by graft copolymerization of starch and monomer.

Laboratory experiment shows that MSG has characteristics of controllable gelling time, strong plugging capability and strong stability. It is suitable for different strongly anisotropism reservoir with fractures and low permeability. Cooperating with combination flooding, foam flooding, gas (CO2) flooding and another flooding, oil recovery enhances more than 30% [11,12]. MSG can effectively block fracture channel, forcing flood water diversion to improve recovery of 35.5% [13,14]. Enhanced oil recovery of the combination flooding, “modified starch gel+ alkaline-surfactant-polymer flooding”, is 45.3% and 34.4% when core permeability is 30×10-3/2000×10-3μm2 and 30×10-3/500×10-3μm2. When reservoir anisotropism is more serious, effect of this combination flooding is better [15]. The combination flooding, “modified starch gel+ foam flooding”, could improve foam cross-flow problem and sweep volume of foam. The final oil recovery of core can reach 63.11% by combination flooding [16]. The combination flooding, “modified starch gel+ ethidene diamine”, could effectively reduce the carbon dioxide emission strength. Oil recovery enhances more than 20% [17].

Physicochemical characteristics of MSG, corresponding mathematical model and residual resistance coefficient of MSG are obtained on the basis of systematic literature research and experimental data. The fitting result of laboratory experiment data verified their correctness and completeness. And it is possible to quantify and finely design the reservoir positioning blockage technology by mathematical model and accurate geological description technology.

2. Physicochemical properties of MSG

2.1. Reaction kinetics

Generally, initiator concentration is thought to be main controlling factor of gelling time for MSG system [5, 18]. However, since high temperature in real oil reservoir, initiator concentration is usually tracer in MSG system (smaller than 0.006mol/L). On low initiator concentration situation, according to the experimental results and the analysis of reaction route, starch graft copolymerization begins with formation of free radicals, terminating in the double-base coupling. It is multi-stage reaction [20]. Apparent rate (RG) equation of graft copolymerization is as follows [21,22].

$$R_G = k^{eq} M^{eq} C_{AM} {C_{St}}^{0.5} {C_{Lin}}^{0.5} \tag{1}$$

Where, k^{eq} is kinetic coefficient of graft copolymerization; M^{eq} is reaction rate correction coefficient by shearing; C_{AM} is acrylamide monomer; C_{St} is modified starch; C_{Lin} is concentration of cross-linking agent.

2.2. Reaction rate correction

Seepage of MSG system can change intermolecular relative position and affect reaction rate of graft copolymerization, although it does not affect occurrence of graft copolymerization. The documents compare static and dynamic gelling capability of MSG system [23,24], which illustrate that flow velocity can enlarge the total gelling time.

As shown in Table 1, total gelling time has positive correlation with flow velocity, while the breakthrough pressure grade has small change.

Tab. 1 Reaction rate, degree and breakthrough pressure grade with different flow velocity

Flow velocity cm/s	Total gelling time h	Amount of gelling %	Breakthrough pressure grade MPa/m
0.0027	22	93	7.0
0.0053	25	91	7.2
0.0080	27	92	6.9
0.0107	27	90	6.9
0.0133	27	91	6.7

To describe the reaction velocity change, a variable M^{eq} is defined as the ratio between dynamic reaction rate under shearing and static reaction rate. Based on the total gelling time in Table 1, Fig. 1 illustrates the change law of reaction rate correction coefficient, M^{eq}, which decreases exponentially with increasing flow velocity. By fitting the change law, the relationship equation is obtained as shown in Eq. 2.

$$M^{eq} = 0.2936v^{-0.134} \tag{2}$$

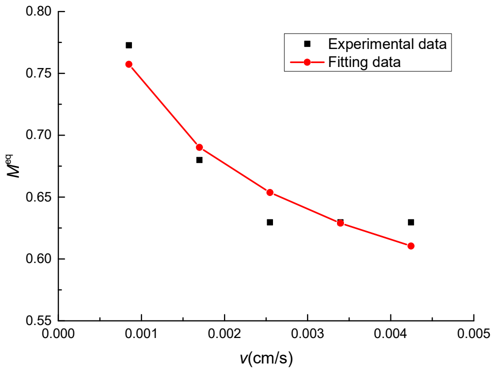

Fig. 1 Relationship between reaction rate and liquid velocity

2.3. Stability after gelling

After gelling, MSG system can form star and comb-shaped polymers, which flexible side chains infiltrate with rigid backbone. This type polymers have a strong resistance to high-temperature, salty, shearing and long-term stability [9,19].

According to experimental results in the Table 2, when injecting 2PV and 9PV water respectively, pressure grade is nearly invariable. This phenomenon indicates that MSG system has strong plugging ability and scour resistance in core simultaneously. Field application also shows useful life of MSG system is larger than one year [7].

Tab. 2 Starch copolymer stability on different permeability

Core number	Water permeability /$10^{-3}\mu m^2$		breakthrough pressure grade	residual resistance coefficient when water flooding is 9PV	plugging rate
	Before plugging	After plugging	MPa/m		%
1	9469	6.6	8.20	1435	99.93
2	823	5.7	7.80	144	99.31
3	199	6.6	7.96	30	96.66

CT scanning results on MSG shows that MSG has excellent gelling ability and can well bond with pore wall surface [25]. And position of copolymer in pore does not change. In order to characterize starch graft copolymer achieving positioning blockage, supposing that copolymer adsorption on solid surface is irreversible. That is, the residual adsorption amount (Ads_r) is equal to maximum adsorption amount(Ads_{max}), as shown in equation 3.

$$Ads_r = Ads_{\max} \tag{3}$$

3. Experimental verification

3.1. Laboratory experiment
The laboratory displacement experiment was carried out using sand packed model to study the MSG blockage effect and quantification of characteristic parameters.

Tab. 3 The parameters of both core and MSG

Core		MSG	
Length / cm	78	Molecular weight / 10^4	2500
Diameter / cm	3.8	Concentration / (mg/L)	2000
Permeability (water test) / $10^{-3}\mu m^2$	58.5	Injection volume / PV	0.3

The experiment steps of laboratory displacement were as follows:
①In the early stage, injected water for 2 hours with the injection speed of 5ml/min.
②In the middle stage, injected MSG of 0.3PV with the injection speed of 3ml/min.
③After the injection of MSG, waited 24 hours to glue.
④In the last stage, injected water of 2PV with the injection speed of 5ml/min.

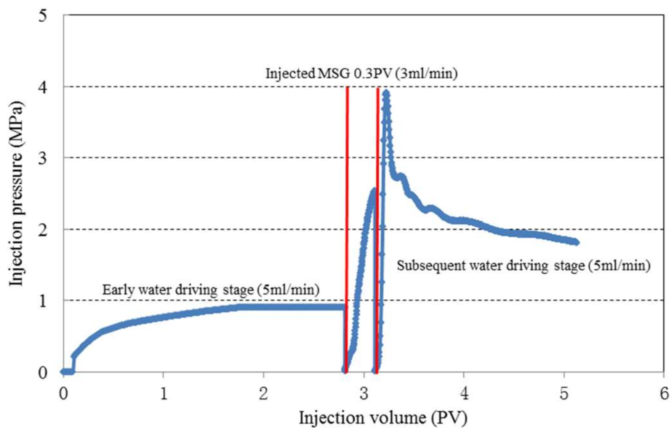

Fig. 2 Results from laboratory experiment

As shown in figure 2, there was a starting pressure (0.21MPa) at the initial water driving stage. The injection pressure began to rise slowly as the water injection increasing after overcoming the starting pressure. When the total volume of water injection reached 1.84PV, the injection pressure reached the maximum value (0.91MPa), and didn't rise with the injecting of water. At the MSG driving stage, the injection pressure rised rapidly as the MSG injection increasing. And the pressure reached 2.53MPa at the end of the MSG driving stage. After waiting for gelling for 24 hours, the injection pressure rised from 0.01MPa to 3.91MPa with only 0.12PV water injection of the subsequent water driving. After that, the injection pressure began to decline until the end of displacement. And the injection pressure reached the minimum value (1.81MPa), which was about twice as many as the maximum value (0.91MPa) at early water driving stage.

The plugging agent front was present migration, deposition and blockage during the MSG system migrating in the core, which leaded to the injection pressure increasing continuously, the rock skeleton continuous destructing and the core permeability improving.

3.2. Numerical simulation

A three-dimensional simulation core model was established by the software of CMG, which had 78 grids in the X direction with the grid length of 1cm, 2 grids both in the Y direction and in the Z direction with the grid length of 2cm. The total number of model grid was 312. The fitting results of the displacement experiment simulation were shown in Fig. 3.

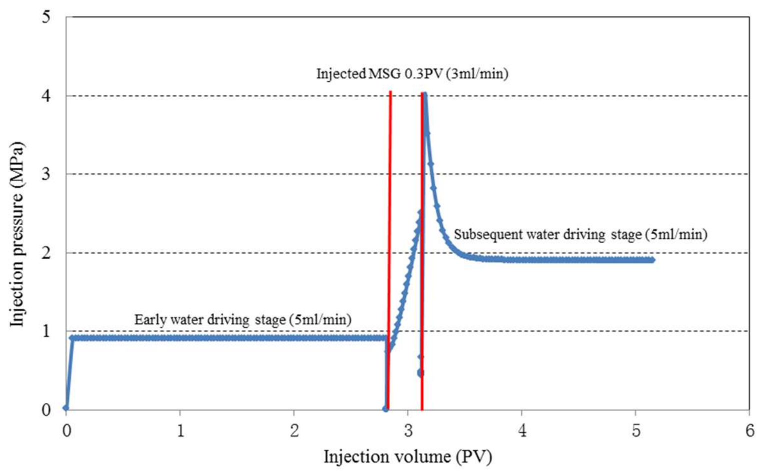

Fig. 3 Results from numerical simulation

The quantitative results of characteristic parameters in the displacement process of MSG system injection were obtained through pressure fitting by CMG. The fitting results were shown in Table 4.

Tab .4 The quantitative results of characteristic parameters

Residual resistance coefficient f	The max. adsorption of MSG system mg/g		The viscosity of MSG system in core mPa•s	
	Polymer	Gel	Polymer	Gel
5	0.118	0.145	130	522

As shown in Table 4, there was not much different from the maximum adsorption of MSG system between polymer and gel. However, the viscosity of gel was significantly higher than that of polymer, which the former was about four times the latter. The results indicated that MSG system had a good gelation property which was helpful to enhance the plugging ability of MSG system.

4. Conclusion

On the basis of laboratory experiment of MSG, reaction rate, dynamic gelling reaction rate and stability after gelling are systematically summarized, and the characteristic equations are established. The quantitative results of characteristic parameters are achieved by fitting the injection pressure curve of laboratory displacement experiment by numerical simulation of CMG software.

(1) The gelatinization principle of MSG is graft copolymerization. Starch graft copolymerization initiated by low concentration of initiator begins with formation of free radicals, terminating in the double-base coupling. It is a multi-stage reaction.

(2) The shear rate affects copolymerization reaction rate of MSG. With increase of flow velocity, correction coefficient of reaction rate decreases exponentially.

(3) MSG has excellent gelling ability and can well bond with pore wall surface, so copolymer produced by MSG has irreversible adsorption on solid surface.

(4) The plugging agent front was present migration, deposition and blockage during the MSG system migrating in cores, which leads to the injection pressure increasing continuously.

(5) The viscosity of gel is about three times higher than that of polymer. MSG system had good gelation property which was helpful to enhance the plugging ability.

Acknowledgments

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References

[1] Zhang Tongkai, Hou Jirui, Zhao Fenglan, et al. Journal of Xi'an Shiyou University (Natural Science Edition), 2011, 26(6): 47-51.
[2] Yin Xiangwen, Xia Lingyan, Liu Chengjie, et al. Special Oil and Gas Reservoirs, 2014, 21(2): 141-143+158.
[3] Jia Xiaofei, Lei Guanglun, Jia Xiaoyu. Special Oil and Gas Reservoirs, 2009, 16(4): 6-12.
[4] You Qing, Yu Haiyang, Wang Yefei, et al. Fault-Block Oil & Gas Field, 2009, 16(4): 68-71.
[5] Yang Limin, Hou Jirui, Song Xinmin. Oil Field Chemistry, 2006, 23(4): 337-340.
[6] Yang Limin, Hou Jirui, Song Xinmin, et al. Petroleum Geology & Oilfield Development in Daqing, 2007, 26(5): 95-97.
[7] Yang Chengwei, Xia Lingyan, Hou Jirui, et al. Petroleum Geology and Engineering, 2012, 26(5): 128-131.
[8] Wang Juan, Wan Tao, Sun Zishun, et al. Guangzhou Chemistry Industry, 2012, 40(8): 70-72.
[9] Wang Ping. New Chemical Materials, 1996, 8: 26-29.
[10] Zhao Yanfeng, Zhou Guochen. Paper Chemicals, 2009, 21(4): 18-21.
[11] Xu Hongming, Hou Jirui, Zhao Fenglan, et al. Oil Field Chemistry, 2013, 30(1): 80-82.
[12] Yuan Guangyu, Hou Jirui, Luo Huan, et al. Drilling & Production Technology, 2013, 36(1): 81-84.
[13] Leng Guangyao, Hou Jirui. Oil Field Chemistry, 2016, 33(4): 629-632.
[14] fractures and heterogeneity[J]. Journal of Petroleum Science and Engineering, 2016, 146, 890-901.
[15] Leng Guangyao, Zhao Fenglan, Hou Jirui, et al. Oil Field Chemistry, 2014, 31(2): 286-289.
[16] Zhao Fenglan, Lv Chunyang, Hou Jirui, et al. Oil Field Chemistry, 2016, 33(3): 425-430.
[17] Zhao F., Hao H., Hou J., et al. CO2 mobility control and sweep efficiency improvement using starch gel or ethylenediamine in ultra-low permeability oil layers with different types of heterogeneity [J]. Journal of Petroleum Science and Engineering, 2015, 133, 52-65.
[18] Li Fenli, Hou Jirui, Liu Yinghui, et al. Petroleum Geology & Oilfield Development in Daqing, 2007, 26(2): 80-82.
[19] Wang Zhonghua. Fault-Block Oil & Gas Field, 2010, 17(2): 239-245.
[20] Gao J P, Tian R C, Yu J G, et al. Graft copolymers of methy methacrylate onto canna starch using manganic pyrophosphate as an initiator [J]. Journal of Applied Polymer Science, 1994, 53(8): 1091-1102.
[21] Zhang Yujun, Chen Jierong, Feng Haiqing. Journal of Henan University of Technology (Natural Science Edition), 2006, 27(2): 5-9.

[22] Wang Baijun. Study on Synthesis and Reaction Kinetics of Starch Graft Copolymer [D]. Nanjing: Nanjing University of Technology, 2003.
[23] Cao Gongze, Hou Jirui, Yue Xiang'an, et al. Petroleum Geology and Recovery Efficiency, 2008, 15(5): 72-74.
[24] Li Hongling, Hou Jirui, Yue Xiang'an, et al. Oil Field Chemistry, 2005, 22(4): 358-361.
[25] Leng Guangyao, Zhao Fenglan, Hou Jirui, et al. Petroleum Geology and Recovery Efficiency, 2015, 22(2): 78-82.