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Gel Breaking Affecting Factors Analysis on Polymer Bio-degradation

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Abstract: Recent years have witnessed a renewed interest in the development of coalbed methane (CBM) reservoirs. However, horizontal drilling in unconsolidated and soft coal seam for CBM drainage and exploitation often results in wellbore instability. This paper proposed degradable drilling fluid in CBM horizontal drilling which not only can maintain wellbore stability, but also minimize formation damages caused by drilling fluid. Its factors of gel breaking ratio were systematically studied from the aspects as substrate concentration, pH, temperature, enzyme concentration and reaction time. We found that in a condition when enzyme concentration is abundant, increasing of substrate concentration would result in higher gel breaking ratio. Furthermore, nearly neutral pH (pH≈7), moderate temperature (40˚C ~60˚C), enzyme with higher concentration and longer action time (more than 3 hours) could enhance gel breaking ratio.

Introduction

Recent years have witnessed a renewed interest in the development of coalbed methane (CBM) reservoirs. It had been estimated that 11.7% of total U.S. natural gas resources came from CBM [1]. In China, CBM output has increased to 1.5 billion m^3 at the end of 2010. Drilled wells have been mounted up by 1000 in the past two years. We also notice that drilling horizontal and multilateral wells is gaining popularity in many different coalbed reservoirs [2]. Horizontal and multilateral drilling in unconsolidated or soft coal seam often results in wellbore instability due to coal and gas bursting, soft coal seam, low mechanical strength of coal, etc. When pure water or air were used as drilling fluid, downhole problems such as collapse, pipe-sticking or spit-out often happened and led to low efficiency of CBM exploitation. It becomes one of the rigorous challenges of CBM industrialization in China [3-5]. And the technologies needed to stabilize the wellbore are among the most urgent problems that require being resolved [6].

To overcome the impediment of borehole stability in unconsolidated and soft coal seam, polymers such as starch, cellulose, guar or xanthan are often used in drilling fluid. The starch, cellulose and guar provide viscosity for borehole maintaining, friction reduction and lubrication while xanthan polymer enhances cutting transport capabilities. However, drilling fluids in coal reservoirs should not only be designed to alleviate any previous drilling problems but it also should minimize formation damage [7-8]. Past approaches to minimizing the damage has been the application of acids or strong oxidative breakers systems such as ammonium persulfate. For their non-specificity, they are often only marginally successful, particularly when applied in extended length intervals. The main deficiency of acids and oxidizers is that they are non-specific reactive species which react with anything encountered and is oxidizable including tubular goods, hydrocarbons, and some formation components [9]. Tjon-Joe-Pin et al. [10] introduced technology

utilizing polymer-linkage specific enzymes complexes to hydrolyze polymers to non-damaging fragments. Such applications have been coupled with a follow-up treatment involving an acid wash to remove acid-soluble bridging agents [9]. Cai et al. [11-12] developed biodegradable drilling fluid in coalbed methane horizontal drilling which not only can maintain wellbore stability during the drilling phase, but also at the same time minimize formation damage caused by drilling fluid. Polymers in biodegradable drilling fluid can be destroyed by enzyme breakers in case drilling work is completed. This paper systematically evaluated its factors of gel breaking efficiency from the aspects as substrate concentration, pH, temperature, enzyme concentration and reaction time.

Material and Methods

Materials and instruments used. Materials involved in this section contain degradable polymers such as CMC and guar gum and corresponding enzymes such as enzyme SE-2 and enzyme SE-4. In our previous tests, enzyme SE-2 could only degrade CMC while showed poor degradation performance in degrading guar gum. Enzyme SE-2 could degrade guar gum and CMC quickly.

CMC used was bought from Renqiu Yanxing Chemical Co, Ltd which located in Hebei, China and guar gum was offered by Jingkun Oilfield Chemistry Technology Development Company which located in Jiangsu, China. This company also provided enzyme SE-4 (black liquid) used in these tests. SE-4 was enzyme complexes containing mannosidase, melibiase, endoglucanase and exoglucanase. It showed excellent performance in degrading polymers like guar gum and CMC in our former lab tests. Enzyme SE-2 was offered by Longhua biotechnology Co, LTD, a local manufacturer in Wuhan, China. It was cheap and widely used in the feeding industry and was complexes made of protease, xylanase, amylase, glucanase and cellulose. Ammonium chloride (NH_4Cl) buffer solution was used to adjust the pH of polymer solutions (the same as follows). Table 1 shows the constitution of enzyme SE-2.

Table 1 Constitution of enzyme SE-2

Name	protease	xylanase	amylase	glucanase	cellulose
Activity, u/g	≥15000	≥20000	≥15000	≥8000	≥6000

Instruments used were high speed mixer which was used to mix polymer solutions, ZNN six-speed rotational viscosimeter which was used to measure rheological parameters of fluids and water-bath which was used to offer desired temperature needed.

Experimental methods used. Employing the appraisal method of viscosity reduction and apparent viscosity (AV) as the main evaluating parameter, we analyzed affecting factors of polymer degradation such as substrate concentration, pH, temperature, enzyme concentration and action time. A substrate means a molecule upon which an enzyme acts to yield a product. The objective of these tests is to find the best degradation condition to achieve high degradation efficiency.

In the "substrate concentration" test, the concentration of enzymes was kept constant while polymer (CMC and guar gum) solutions with varied concentrations were heated to 50℃ in a water-bath and lasted for 5 hours. Here enzyme SE-4's concentration was set constant as 0.0125% and enzyme SE-2's concentration was 0.125%. Polymer solutions' apparent viscosities were tested when they were cooled to room temperature (10℃, the same as follows). In other tests, similar methods were employed. Table 2 presents parameter settings of these series tests. Symbols ① to ⑤ refer to substrate concentration test, pH test, temperature test, enzyme concentration test and reaction time test separately.

Then the apparent viscosity and the gel breaking ratio (GBR) could be calculated according to following equations, as in (1) and (2).

$$AV=0.5\times\theta_{600}, \text{ mPa·s} \quad (1)$$

Here, θ_{600} is referring to the dial reading with the viscometer operating at 600 revolutions per minute (rpm).

$$GBR= (AV_0-AV_1) \times 100 / AV_0, \% \quad (2)$$

Here AV_0 and AV_1 are referring separately to AV at the beginning and AV at the end of the test. If AV_1 is as low as 0, it means that guar has been degraded totally by enzyme (GBR=100%).

Test results were graphically shown in figures from Fig. 1 to Fig. 5.

Table 2 Parameters settings of affecting factors analysis of polymer degradation

	①		②		③		④		⑤	
	CMC	Guar	CMC	Guar	CMC	Guar	CMC	Guar	CMC	Guar
Substrate/ wt%*	0.2~1.0		1.0	1.0	1.0	0.6	0.3	1.0	0.3	1
pH	7		5~9		7		7		7	
Temp/℃	50		50		10~90		50		50	
Enzyme/wt %*	0.125	0.0125	0.125	0.0125	0.125	0.0125	0.0625~0.5	0.0125~0.0625	0.125	0.0125
Time/h	5		5		5		5		1~5	

*: wt% refers to weight percent.

Results and discussions

Substrate concentration tests. From Fig. 1, we can see that increasing of substrate concentration results in the continuous increase of gel breaking ratio (GBR) when enzyme was abundant in each enzymatic reaction. However, the ascending rate was more and more gently. This could be explained as follows. With the increase of substrate concentration, polymer solution's viscosity also went up which reduces the molecular diffusion of reactant and reaction rate. In each enzymatic reaction, substrate (S) incorporates firstly with active site of enzyme (E) and forms unstable intermediate (ES) which can further decompose into product (ES_{l+n}). Emergence of inactive intermediate depresses the activity of enzyme.

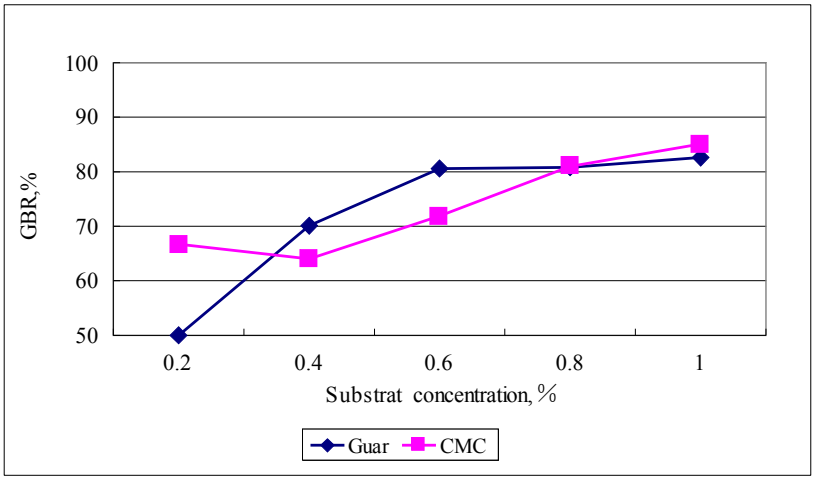


Fig. 1. Affecting patterns of substrate concentration on gel breaking ratio

PH tests. From Fig. 2, it can be deduced that when pH of polymer solution was close to 7, enzyme had the higher activity and better gel breaking efficiency on polymers. This means enzyme complexes used had the highest activity in neutral environment.

Temperature tests. In Fig. 3, we can see that in the temperature range of 40℃ to 60℃, enzymes had higher gel breaking ratio on varied polymers due to their better activity in this range. Take

examples of Si'he mining area and Panzhuang mining area in Shanxi, China, temperature of coal bed methane (CBM) reservoir mainly varies between 20℃ to 30℃. Methods of increasing the temperature of CBM reservoir such as injecting hot nitrogen (N_2) and carbon dioxide (CO_2) can be employed to enhance the gel breaking efficiency of polymers.

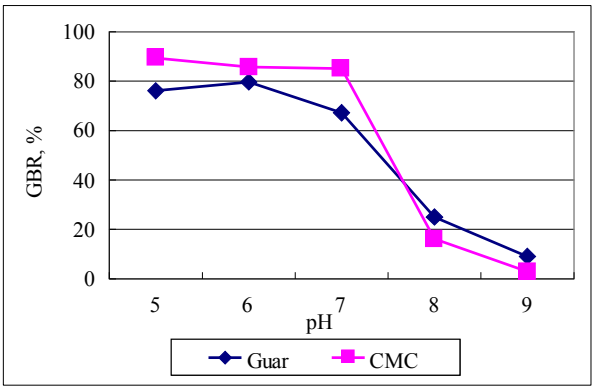


Fig. 2. Affecting patterns of pH on gel breaking ratio of polymer.

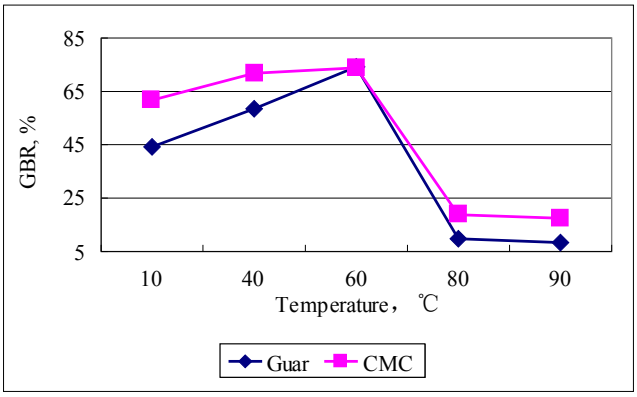
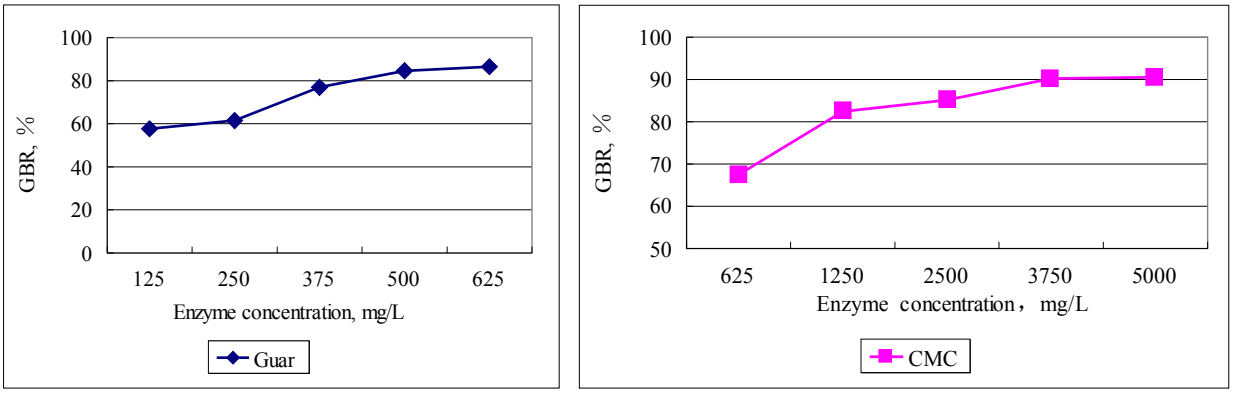


Fig. 3. Affecting patterns of temperature on gel breaking ratio of polymers.

Enzyme concentration tests. From Fig. 4, it can be deduced that an increase of enzyme concentration ensured single polymer molecular had more chances to combine with enzyme molecular thus increased gel breaking efficiency.



(a)Guar (b) CMC

Fig. 4. Affecting patterns of enzyme concentration on guar gum's and CMC's gel breaking ratio.

Reaction time tests. Fig. 5 presents affecting pattern of reaction time on the gel breaking efficiency of polymers. It indicated that prolonged reaction time especially when reaction time was over 3 hours, ensured more enzymatic reaction to occur resulting in higher gel breaking efficiency of polymers.

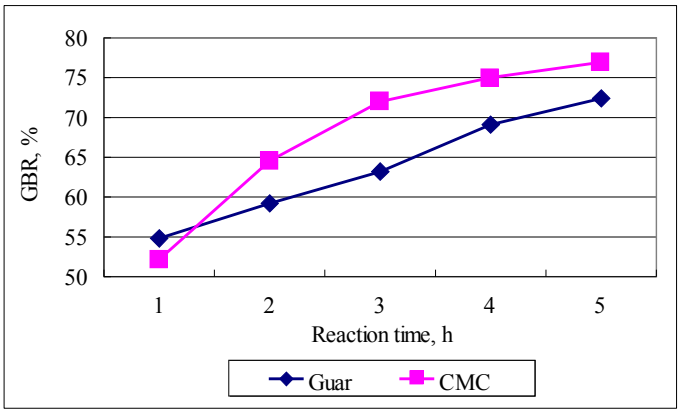


Fig. 5. Affecting patterns of reaction time on gel breaking ratio of polymers.

Summary

Conclusions can be derived from the research above.

(1) In a condition when the enzyme concentration is abundant, increase of substrate concentration could lead to higher gel breaking efficiency while increasing amplitude was less and less.

(2) Nearly neutral pH (pH≈7), moderate temperature (40˚C to 60˚C), enzyme with higher concentration and longer action time (more than 3 hours) could also enhance gel breaking efficiency.

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