A new novel crosslinker with space structure for low-polymer-loading fracturing fluid

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***Abstract*—** *Boron-based crosslinkers are used commonly to increase viscosity and to improve fluid-loss control and proppant transportability of guar and its derivative fluids. Boron crosslinkers are usually preferred because of their ability to reheal after shearing and their favorable environmental properties. In order to reduce both the formation and the proppant-pack damage from polymer residues and to reduce over-all fluid cost, more-efficient crosslinkers capable of crosslinking fluids with reduced polymer loading is of great interest. Previous studies demonstrated that polymer solutions have critical overlap concentration (C*), below which no intermolecular crosslinking leading to increased viscosity can occur. However, recent studies demonstrated that increased crosslinker size or length can lead to the crosslinking of polymer solutions well lower than the C* and can reduce polymer loading without compromising the rheology of the fracturing fluid.*

This paper shows the effect of new crosslinkers with space structure capable of interacting with multiple poly-saccharide strands to form crosslinking networks at lower polymer loadings than conventional guar fluids. The crosslinker is formed by the reaction of boric acid and a Polyamine with six-member ring to improve the spatial structure. The formation procedures of the new crosslinker by Boric and six-member Polyamine is very simple, and the synthetic condition is also very mild. The concentration of guar fluid with this new crosslinkers can be reduced by 30%. In addition, the crosslinker reacted with glucose to improve the control of the fluid-viscosity buildup can make the product fit into broader applications. The time of the fluid-viscosity buildup ranges from 15 to 180s. The pH value is very important to the heat resistance characteristics of the fracturing liquid system, the heat resistance characteristics increase with the increase NaOH loading. The polymer residual of the new fracturing system with new crosslinkers is much lower than that with conventional crosslinkers because of the low polymer loading. The cost of new crosslinkers is low because of the low price of raw material and the simple formation procedure and the mild synthetic condition, which is very important for extensive used in the oil field.

Keywords*— *Cross linker Boric acid, Polyamine space structure.

I. INTRODUCTION

Wells drilled into low-permeability reservoir need to be treated with hydraulic fracturing to increase the conductivity and thereby to obtain the economic production. Hydraulic-fracturing cracks in the zone are created by forcing a fluid at a pressure higher than the parting pressure of the rock. The fractures expanded as the continued injection of fracturing liquid with proppants. When the predetermined amount of liquid is injected into the formation, the pressure in the surface is released, and the fracturing gel will break and retreat from the formation to the surface leaving the proppants in the fractures to inhibit the fractures from closing. The viscosity of the fluid is typically generated by polymers, such as polysaccharides and its derivatives. Hydrated guar and derivatives create linear gels that do not achieve the required viscosity for proppant transport at elevated temperatures [1]. Thus, crosslinkers, such as boron, zirconium or titanium compounds, are used to significantly increase the viscosity of the fluid system. Boron-Based crosslinkers are used to increase viscosity, fluid-loss control and proppant transportability of guar fluid. Boron crosslinkers can reheal after shearing, so they are used very commonly in the oil field. Guar grum contain protein species, insoluble even after the breaking of the fluid that is damaging to the formation, so that less polymer usage will result in less damage to the subsurface formation. More efficient crosslinkers capable of crosslinking fluids with reduced polymer loading have always been of great interest to reduce formation and proppant pack damage from polymer residues, and to reduce overall fluid cost [1].

The lower polymer loadings can be realized by several ways: firstly, the processed enhanced guar can be used to reduce the guar loadings, for example, Dawson et al. [4] developed a new generation of guar that yields high crosslinked fluid viscosity at reduced loadings. Cramer and Woo [5] utilized processed enhanced guar crosslinked with borate at a reduced polymer loading and applied the borate crosslinked PEG for treatment of several wells in the Monument Butte area. Secondly, Dawson et al. [2] and Clark [3] demonstrated that polymer solution have critical overlap concentration, below which no intermolecular crosslinking leading to increased viscosity can occur. However, Sun and Qu [1] demonstrated that increased crosslinker size or length can lead to the crosslinking of polymer solutions well lower than C* and can reduce polymer loading without compromising the rheology of the fracturing liquid, at the same time, they reported the synthesis of polyaminoboronates (PAB), bulky compounds containing multiple boron sites and capable of interacting with multiple polysaccharide strands to form more complex crosslinking networks at lower polymer loadings than conventional guar fluids. The PAB was successfully used in two wells in green River sandstone formations of the Uintah Basin In 2014 [6]; Lu Yongjun et al. [7] formed a new novel crosslinker by sodium borate and salt of organic acid, such as sodium gluconate, sodium lactate; Xue Xiaojia et al. [8] formed a novel crosslinker including borate, NaOH, sodium carbonate, Benzene boron cyclic compound, with the new crosslinker, the guar loading can decrease more than by 25% than conventional fracturing liquid system; Sui Mingwei [9] formed a new crosslinker with raw materials of sisodium tetraborate decahydrate, glucose. The amount of crosslinking agent was used to crosslink 0.2% guar glue solution is 1.2%-1.6%. Temperature tolerance can be as high as 80□. Thirdly, the thermal enhanced agent can also used to decrease the guar loading, for example, Du et al. [10] used organic bases, including triethanolamine, ethanediamine, as the thermal enhanced agent to form a fracturing liquid with low guar loadings.

However, the raw material of novel crosslinker in the literatures of Sun and Qu [1] is very expensive, so the cost down by the low guar loading is offset by the higher cost of the crosslinker. A lower-cost combination of raw materials is sought in order to improve the marketable acceptance of the product. In this work, the tripolycyanamide is used to replace the tetraethylenepentamine (TEPA) as the base scaffold, which has two merits: firstly, tripolycyanamide is much cheaper than TEPA; secondly, the tripolycyanamide has better spatial outstretched capacity than TEPA.

II. EXPERIMENTAL PROCEDURES

Approximately 150ml of alcohol and 100ml of water were added into a 500-cm3, three-necked, round-bottomed flask equipped with a thermometer and a Dean-Stark adaptor equipped with a reflux condenser; 50 g of boric acid was added to the flask and heated for five minutes. And then 50g of tripolycyanamide was added to the flask. The reaction mixture was then heated at 90 □ for 4h. 90g of glucose was added and heated for 1 hour in order to obtain the delay properties. 10g of NaOH is added and stirred until the NaOH dissolved completely. A white liquid was obtained as the final solution.

III. RESULTS AND DISCUSSION

3.1 Pick-up time

The crosslinking performances of two new type crosslinkers are evaluated by the time that fracturing liquid can be picked up by the glass rod. 0.3g hydroxypropyl guar gum was added in 100 ml water, and stirred for 20 min to make sure that the guar gum was swelling sufficiently. And then NaOH solution and crosslinker were weighted into the guar gum solution, respectively. The solution was stirred with the glass rod until the solution can be picked up, the time from the injection of the crosslinker into the solution to the solution can be picked up is the pick-up time. The pick-up time usually depends on the NaOH, the crosslinker, and polymer loadings.

The experimental results were shown in Table 1. The pick-up time of crosslinkers without glucose in 0.3% guar gum, at 10wt% NaOH solution loadings of 0.1-0.6ml, was in the range of 15 to 40 seconds. However, the pick-up time of crosslinkers with glucose in the same condition was in the range of 25 to 150 seconds. The glucose can extend the pick-up time, a logical explanation for this observation is that the reaction between glucose and hydroxides of crosslinker effectively blocks the borate sites of the crosslinker, resulting in improved pick-up closure. It can be seen from table 1 that the NaOH has a higher influence on crosslinker with glucose than that without glucose. The pick-up time decreased with the increase of crosslinker loadings, which is because that higher crosslinker loading will result in more crosslinking points density and then increase the crosslinking rate.

TABLE 1
SUMMARY OF PICK-UP TIME FOR GUAR LINEAR GEL CONTAINING DIFFERENT NAOH AND CROSSLINKER LOADINGS AT ROOM TEMPERATURE

Crosslinker	Guar Loading (g)	NaOH Loading (ml)	Crosslinker Loading (g)	Pick-up Time (s)
Without glucose	0.3	0.1	0.3	15
Without glucose	0.3	0.3	0.3	25
Without glucose	0.3	0.6	0.3	40
Without glucose	0.3	0.3	0.4	32
Without glucose	0.3	0.3	0.5	22
With glucose	0.3	0.1	0.3	48
With glucose	0.3	0.3	0.3	90
With glucose	0.3	0.6	0.3	150
With glucose	0.3	0.3	0.4	76
With glucose	0.3	0.3	0.5	47

3.2 Sand-Carrying Capacity of Crosslinked Fluid

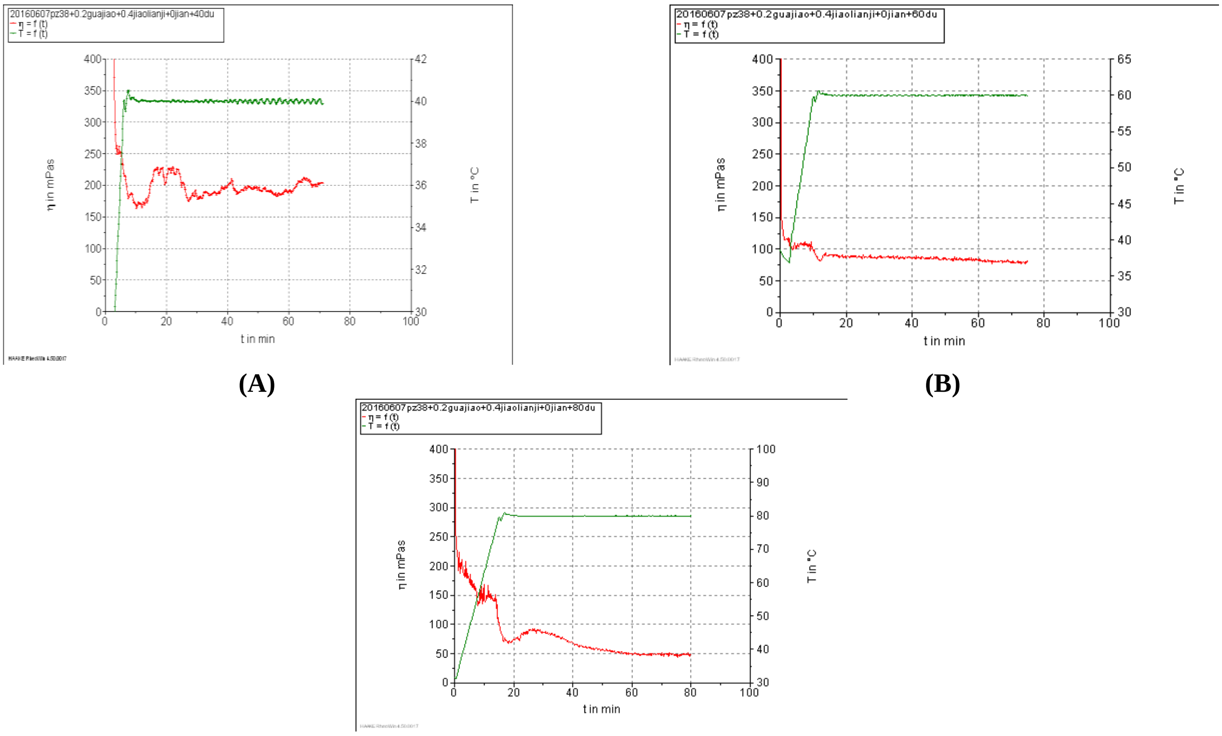
About 90 ml of hydrated guar fluid were mixed with 20 ml of 20/40 sand, buffered and crosslinked with novel crosslinker while stirring. The sand crosslinked fluid suspension was poured into 100 mL graduated cylinders. Picture was taken at 40 min after the sample was placed on the table. Illustrated in fig. 1 is the sand settling test picture for 0.4 wt% borate-crosslinked guar gel contained 20 wt% of 20/40 sand. After 40 min, sand settling level was at 97mL from initial 110ml, which illustrated that the gel has a good sand-carrying capacity.

FIG. 1 SAND SETTLING TEST OF NEW NOVEL BORATE-CROSSLINKED GUAR GEL CONTAINED 20 WT% OF 20/40 SAND AT ROOM TEMPERATURE. A 0.3WT% GUAR LOADING IN FRESH WATER WAS ADDED INTO 0.4ML NaOH (10%) AND CROSSLINKED WITH 0.4 ML NOVEL CROSSLINKER.

3.3 Rheology

The compounds were evaluated as crosslinkers in guar fluids on HAAKE RS6000 rotary rheometer, by placing 50 ml of gel in the Fann 50 cup and positioning the cup on the rheometer. The sample was sheared at a preconditioned and constant shear rate of 170 sec-1 for 65 minutes. The fluid was heated to the experimental temperature at the rate less than 3.2 ^{o}C/min. When the final viscosity of the liquid is larger than 50 mPa·s, the crosslinker is eligible at this temperature and guar loading. The influence of NaOH and guar loading on the thermal endurance was evaluated in the experiments. The rheology profile of the liquid with 0.2wt% and 0.3wt% guar loading are shown in fig.2 to fig.3, respectively, with the same loading of 0.4wt% NaOH solution, 0.4 wt% crosslinker. Illustrated in fig.2 is the rheology profiles of borate-crosslinked gel at the temperature of 40, 60, 80℃, respectively, with 0.2wt% guar loading. It can be seen that the final viscosity of the liquid with new crosslinker is 155 and 78 mPa·s at the temperature of 40 and 60 ℃, respectively, and is larger than 50 mPa·s for 40 min. Illustrated in fig. 3 are the rheology profiles of borate-crosslinked gel at the temperature of 100, 120℃, respectively, with 0.3wt% guar loading. It can be seen that the final viscosity of the liquid with new crosslinker is 100 and 65 mPa·s at the temperature of 100 and 120 ℃, respectively. With the new novel crosslinker, the guar loading can be reduced by 30% than conventiaonal crosslinker, while the cost of crosslinker does not increase.

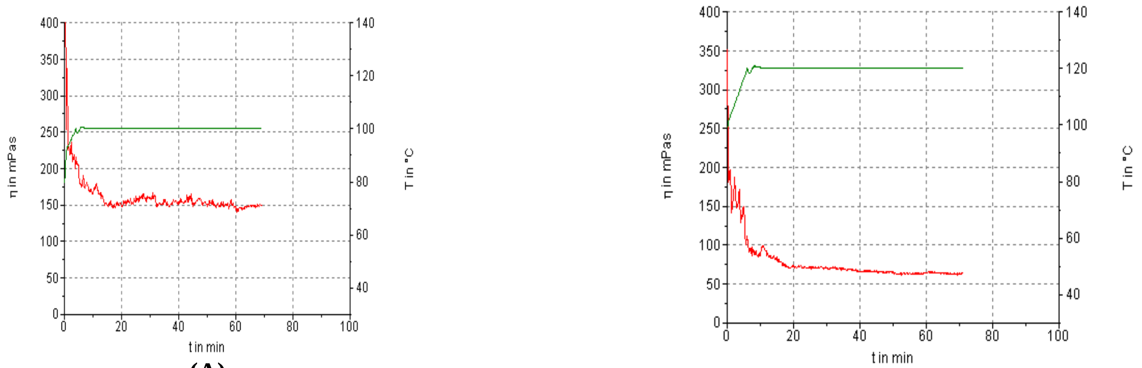
During the gel was injected into the oil reservoir, the gel would go through the pump and the shot hole, the gel will endure intense shear, so the gel need good reheal gel ability to transport proppant after shearing. In this work, the reheal ability of the gen crosslinked with novel crosslinker is measured. The cup is filled with gel and the sample was sheared at 170 sec-1, the rate of temperature increase is controlled in 3.0±0.2□ until the experimental temperature (±0.2□), and keep this temperature in the whole experimental progress. The changed shear rate experiment was started when the temperature kept for 20 minutes. The progress includes two stages, firstly shear rate decrease from 170 sec-1 to 0 sec-1, and then increase from 0 sec-1 to 170 sec-1. Each stage was kept for 15 sec. Illustrated in fig. 3 are the rheology profiles of gel at the temperature of 120□, with 0.4wt% guar loading in fresh water and added into 0.4ml NaOH (10%) and crosslinked with 0.4 ml novel crosslinker. It can be seen from the fig. 4 that the viscosity of the gel can maintain the primary viscosity after the shear rate return to the 170 sec-1, which means the gel crosslinked with new crosslinker has good shear reheal ability.



(A) (B)

(C)

FIG. 2 RHEOLOGY PROFILE OF THREE SAMPLE OF NEW NOVEL BORATE-CROSSLINKED FLUID AT DIFFERENT TEMPERATURE OF 40 □ (a), 60 □ (b) and 80 □ (c), RESPECTIVELY. A 0.2wt% GUAR LOADING IN FRESH WATER WAS ADDED INTO 0.4ML NaOH (10%) AND CROSSLINKED WITH 0.4 ml NOVEL CROSSLINKER.



(A) (B)

FIG. 3 RHEOLOGY PROFILE OF THREE SAMPLE OF NEW NOVEL BORATE-CROSSLINKED FLUID AT DIFFERENT TEMPERATURE OF 100 □ (a), 120 □ (b), RESPECTIVELY. A 0.3wt% GUAR LOADING IN FRESH WATER WAS ADDED INTO 0.4ml NaOH (10%) AND CROSSLINKED WITH 0.4 ml NOVEL CROSSLINKER.

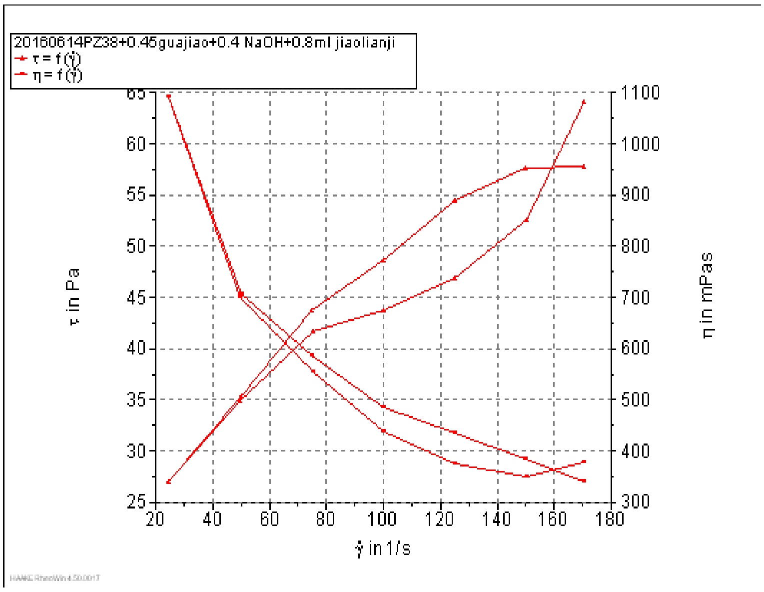


FIG. 4 RHEOLOGY PROFILE OF A SAMPLE WITH CHANGED SHARE RATE FROM 170 sec-1 to 0 sec-1 AND THEN FROM 0 sec-1 to 170 sec-1. A 0.4wt% GUAR LOADING IN FRESH WATER WAS ADDED INTO 0.4ml NaOH (10%) and CROSSLINKED WITH 0.4 ml NOVEL CROSSLINKER.

3.4 Gel breaking and residue of the gel residual

0.3 wt% guar loading in fresh water was stirring for 20 min to make sure that the guar was swelled absolutely, which is called base fluid. While the fluid is stirring, the crosslinker and gel breaker are added into the base fluid until the gel can be picked up and avoid forming bubbles. The fracturing liquid is filled into closed container and putted into the thermostatic waterbath of 60□ for 4 h. After the gel breaks, the viscosity of supernatant liquor is measured. The breaking gel is filtered by the filter paper, and measured the residual of the breaking gel. Fig. 5 shows the sample pictures of fracture liquid after breaking with different ammonium persulphate loading of 0.02 wt%, 0.03wt%, 0.04wt% and 0.05wt%, respectively. It can be seen from fig. 5 that the gel can break at the four breaker loading. The viscosity of supernatant liquor is less than 5 mPa·s. The residual of the gel is 170 mg/L.

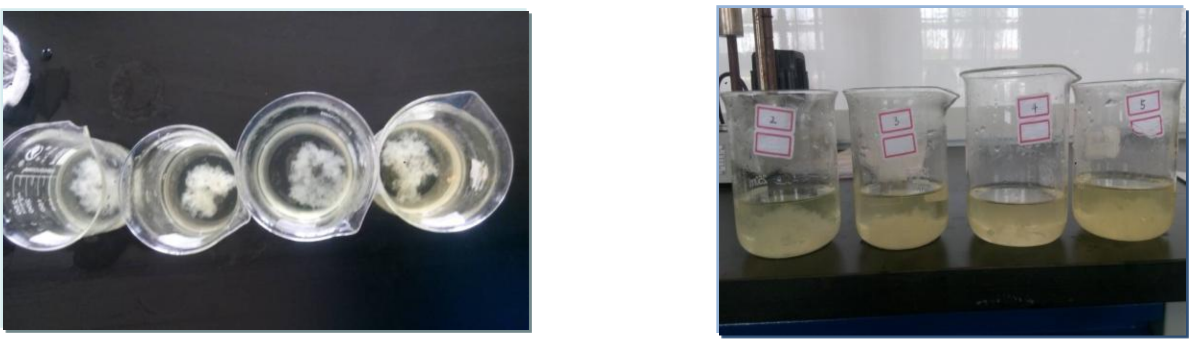


FIG. 5 SAMPLE PICTURES OF FRACTURE LIQUID AFTER BREAKING WITH DIFFERENT AMMONIUM PERSULPHATE LOADING OF 0.02 wt%, 0.03wt%, 0.04wt% and 0.05wt%, RESPECTIVELY.

3.5 Liquid loss

Two pieces of filter paper and the sample were filled into the filter cartridge, respectively. The measure cup was putted into the heating jacket. The filter cartridge was pressured with the initial pressure and heated to the experimental temperature in 30 min. After that, the filter liquor will filter out under the differential pressure of 3.5 MPa. The amount of filter liquor within 36 min is collected and measured. The experiment results is shown in table 2, it can be seen that the filtration property of the new liquid system is very similar to the conventional liquid system, and much lower than the standard value in the criterion. The results indicate the formation of a good filter cake by new crosslinked fluid, minimizing potential fluid loss to the formation.

TABLE 2
EXPERIMENTAL FILTRATION PROPERTY RESULTS OF DIFFERENT FRACTURE LIQUID SYSTEM

	Fracture fluid with new crosslinker (0.28% guar gram)	Conventional fluid system (0.45% guar gram)	Standard value in the criterion
Filtrate loss coefficient, m	0.5×10^{-4}	0.46×10^{-4}	6×10^{-4}
Spurt loss amount, m^3/m^2	0.35×10^{-3}	0.35×10^{-3}	1×10^{-3}
filtration rate, m/min	0.085×10^{-4}	0.076×10^{-4}	1×10^{-4}

3.6 Field Application

The new crosslinker was used in a vertical well in Sulige gas field of Ordos Basin. The geothermal gradient of this well is 3.06□/100m, and the temperature of target stratum is 108□. The formula of the fracturing system is composed of 0.28% Hydroxypropylguar gum, 0.3% antiswelling agent, 0.5% cleanup additive, 1.0% potassium chloride, 0.35% sodium carbonate and water. The dosage of the crosslinker is 0.3% of the fracturing liquid system. The closure stress of stratum is 50 MPa, so the proppant with medium volume density of 1.75g/cm³ is selected, which diameter is between 0.425 mm and 0.85mm.

The well depth of the target stratum is between 3649.3-3652.4m, the operating pressure is 37.7-42.1MPa, the cracking pressure is 39.1MPa, the injection rate of fracture liquid is 3.5-3.9m3/min, the volume of liquid nitrogen is 6 m3, the volume of sand is 15 m3, the largest sand proportion is 18.5%. The total volume of injection liquid is 205 m3. The operation curve is shown in fig 6. With the new novel crosslinker large-scale applications, the dosage of the guar gram decreased from 0.45% to 0.28%, which will protect reservoir and induce huge economic benefit.

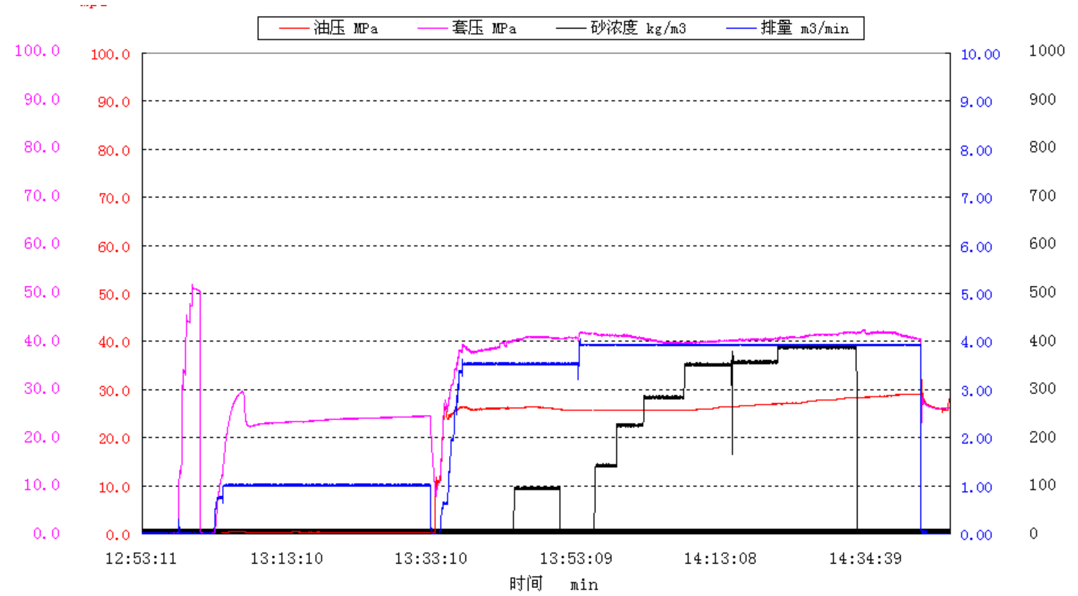


FIG 6 THE OPERATION PRESSURE CURVE IN A VERTICAL WELL IN SULIGE GAS FIELD OF ORDOS BASIN WITH NEW CROSSLINKER FRACTURE FLUID.

IV. CONCLUSION

A new chemistry was developed on the basis of the condensation reaction of boric acid with a polyamine scaffold of tripolycyanamide to yield a polyaminoboronate crosslinker with multiple boron sites. The molecular size of new crosslinker enables crosslinking guar or its derivatives at lower concentration, thus reducing the loading of polymer required. New chemistry was developed in which glucose was incorporated into the crosslinker to delay the crosslink rate at the boronate sites. The NaOH has a great influence on the crosslink rate and thermal endurance, at the same time, the pick-up time increase with the increase of crosslinker loading. With the new chemistry, the fracturing gel can endure 120℃ with 0.3wt%

guar loading, which is lower than conventionla guar loading by 30%. The new novel crosslinker also has good performance of gel breaking, gel residuals and fluid loss.

REFERENCES

[1] Sun, H. and Qu, Q. 2011. High-Efficiency Boron Crosslinkers for Low-Polymer Fracturing Fluids. Paper SPE 140817 presented at the 2011 International Symposium on Oilfield Chemistry, The Woodlands, Texas, 11-13 April. http://dx.doi.org/10.2118/140817-MS.

[2] Dawson, J.C., Le, H.V., and Kesavan, S. 2000. Polymer Expansion for Oil and Gas Recovery. US Patent No. 6,017,855.

[3] Lei, C. and Clark, P.E. 2004. Crosslinking of Guar and Guar Derivatives. Paper SPE 90840 first presented at the 2004 SPE Annual Technical Conference and Exhibition, Houston, Texas, 26_29 September, and peer-approved 31 May 2007. http://dx.doi.org/10.2118/90840-MS.

[4] Dawson,J.C., Cramer,D.C., Le, H.V. (2004) Reduced Polymer Based Fracturing Fluid: Is Less Really More?, paper SPE 90851 presented at the Annual Technical conference and Exhibition held in Houston, Texas, 26-29 September, 2004.

[5] Cramer, D.D., and Woo, G.T. (2004) Development and Implementation of a Low-Polymer-Crosslinked Fracturing Fluid for Low-Temperature Applications, paper SPE 91418 presented at the Eastern Regional Meeting held in Charleston, WV, 15-17 September, 2004.

[6] Magnus Legemah, Frances Debenedicitis, Nigatu Workenh, David Smith, Hoang Le, Hong Sun, Qu Qi, Baker Hughes, Mickey Moulton, 2014. Successful Treatment of a Green River Sandstone Formation Using a Novel Low-Polymer Crosslinked Fluid. SPE 168186.

[7] Lu Yongjun, Wang Liwei, Cheng Xingsheng, Guan Baoshan, Liu Ping, Cui Weixiang, Cui Mingyue, Liu Yuting, Zhai Wen. Crosslinker used in ultra low hydroxypropylguar gum loading fracturing liquid and corresponding fracturing liquid. China Patent No. 102732244 A.

[8] Xue Xiaojia, Mu Lijun, Zhao Zhenfeng, Li Xianwen, Liu Jing, Zhao Wen, Ding Li, Tang Meirong, Lv Haiyan, Lv Baoqiang, Wu Jing, Bi Weiyu, Fan Huabo. High efficiency crosslinker to decrease guar loadings and its preparation method. China Patent NO. 102775979.

[9] Sui Mingwei. Preparation of low-concentration guar gum fracturing fluid crosslinker and study on their laboratory evaluation. 2012, Shanxi University of Science and Technology, Master Thesis.

[10] Du Biao, Yang Haiyan, Zhao Wen, Ding Li, Wan Hua, Yang Jigang, Zhao Yanhong, Lv Junhua, Ye Zhi, Hu Pengfei, Dou Miao, Li Peng, Lv Baoqiang, Guo Jun, An HengWen, Cheng Fang. Ultra-low polymer loading fracturing liquid and its preparation method. China Patent No. 102329602 A.