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EOR Pilot Tests With Modified Enzyme in China

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Abstract
Micro and macro evaluations were conducted to understand modified enzyme EOR mechanisms using various fluids. Huff n puff tests and flooding tests were carried out with variable modified enzymes concentrations in several reservoirs. Resulted production performances were considerably improved. At reservoir temperature 50-80°C, lab experiment indicated that the modified enzyme solution was adaptable to both light and heavy oil and was not sensitive to minerals water with bivalent cation (1000mg/l) and high salinity (10%) . The enzyme working performances were further enhanced with microorganism occurrence in the solution. Micro modeling experiment revealed that spontaneous emulsification and solubilization could take place between the modified enzyme and crude with emulsion particle 2-6μm in diameter, which is produced through striping as a result of solubilization. Core desorption and flooding experiments presented that desorbed crude volume and displacement efficiency were related to modified enzyme concentrations which usually ranged 5 to 10％with the optimum being 8％. In optimal conditions, recovery can be averagely increased by 16.9%. Experiments also proved that the modified enzyme and crude oil could form emulsion but the emulsion was not stable. One specific pilot test with modified enzyme had achieved additional oil production 22,869 bbl.

Introduction
With time in oil development, some oil components precipitate and composites of organic and inorganic scales deposit. Formation fine grains migrate and clay swells. These are barriers to fluid flow and productivity, causing much oil unrecoverable underground. Modified enzymes were applied to improve biological activity of normal enzymes and protection of pay through opening pore paths and thus to introduce, stimulate and merge remaining oil into flows. Huff and puff tests and flooding tests have been implemented in Dagang, shengli, Daqing and others both in China and abroad all show improved performance [1-6, 10-11]. Yet it is not quite clear why and to what extent it works. So a collection of experiments were performed on modified enzyme EOR mechanism evaluation. A field test was made and is presented here.

Enzyme Working Mechanism
The environment-friendly enzyme agent is a water soluble product which can strongly release oil from reservoir grain surface. It can alter pay rock from oil-wet to water-wet, reducing interfacial tension of grains and oil flow resistance through pores.

Enzyme works in three stages. First it makes attachment, subsequently takes biochemical reactions and creates enzyme/oil complex, Fig.1. Then, the complex decomposes themselves into induced-fits and particles. The induce fits would continuously decompose and release enzyme until oil and enzyme are separate and consequently enzyme is restored.

Different from its chemical and bacterial counterparts, the above process is biological. It doesn't change any oil property or produce any derivatives. Instead, the process restores the environment-friendly enzyme to its original state after working. Theoretically, the enzyme will never be consumed out. In fact, its effectiveness and activity will degrade after processes. But that is solved by added sacrificial agents.

Enzyme Modification
Enzyme SL is a product of gene, cell and enzyme engineering techniques. To produce it, the bacteria that can separate oil from sands are selected and DNA is extracted. The selected bacteria were put into a nutrition solution and cultivated with high protein. Then the bacteria are removed of all of its activity to be a non-active catalyst. The enzyme resolves in water, not in oil, and can split hydrocarbons from rock grains.

To reduce cost, it is necessary to make modifications for less cost. The enzyme is combined with chemical surfactants to achieve synergy that is almost equivalent to the American enzyme efficacy. In a pay zone, the surfactants will make absorption on and effect on rocks, fluids and oil. Some surfactants act as sacrificial agents to ensure minimum even zero decrease of the original enzyme concentration and its activity.

Lab Experiments

Experiment Condition: In lab experiment, the SL-modified environment-friendly enzyme was granted with 100% concentration. Also involved was the produced crude and water from a Well Ban 64-30, Dagang Oilfield. Experiment temperature was between 50 and 80°C.

Experiment Method: In experiment, oil-bearing sand packages were placed in solutions of the modified enzyme and produced water. The packages had been prepared through mixing dehydrated crude with the washed and dried reservoir sands at a ratio of 1 to 4. Every package had been covered and banded by six layers of absorbent gauzes. At experiment temperature, the enzyme solution concentration changes and oil production were measured each day. After the optimal modified enzyme concentration range was determined, salts like sodium chloride, calcium chloride and magnesium chloride in variable concentrations were added to confirm modified enzyme adaptability to salts. Oil from different blocks was used in the packages to experiment if the modified enzyme is suitable to the oil. Disinfected and infected produced water was separately used in modified enzyme solution to figure out the performances with and without indigenous bacteria. Several natural cores were saturated with water, and then flooded with water to irreducible water saturation. The cores without flooding and those with 90% water-cut after flooding were separately put into the modified enzyme solution to see its capability and timing of desorbing oil. In another experiment, natural cores were flooded with the modified enzyme solution at various concentrations. A transparent micro-model was constructed for research of the micro-displacement mechanism.

Experiment Results

The optimal modified enzyme concentration experiment: On the second day at the package was placed in solution, the modified enzyme solution turned cloudy and oil came out of the package. Cloudiness increased as concentration rose. From the third day on, more and more oil particles were released out of the 8% modified enzyme solution. The longer the time, the quantity of oil release the more. On the forth day, the completely dispersed oil was blending with water while another solution of 20% modified enzyme turned yellow. On the seventh day, oil particles in the 8% modified enzyme solution merged and the dispersion process terminated. Oil appeared separated from solution and floating on the surface. The 20% modified enzyme solution showed better emulsification than the 8% one. From the ninth day on, performances deteriorated and oil and the solution separated into two phases. It was thus concluded that the optimal modified enzyme concentration is 8%, Fig.2.

Emulsification improves with increasing concentration of modified enzyme and the optimal ranges 5 to 10% and the best is 8%. The best performance for 8% concentration was observed on the 4^{th} day and deteriorated on the 7^{th} day. The oil dispersing process lasted only 3 days, preferential for produced fluids treatment on the ground.

Modified enzyme adaptability to oils: the adaptability was studied using oil samples from Well Zao 41 in the Zaoyuan block, Well Kong 1017-7 in the Kongdian block, Well Jia 31-51 in the Wangguantun block and Well Ban 64-30 in the Banqiao block. The packages were separately experimented with the 8% modified enzyme solution. Results showed little difference. All samples were emulsified to some extent, particularly on the 6^{th} day. But on the 7^{th} day, emulsification seemed dim and oil trended to split from solution. Performance improvement recovered on the 9^{th} day. Two days later, oil separated from solution. It was inferred that oil dispersal with the modified enzyme repeated and was related to its own dynamics. In fact, during the process in reservoir, this happens again and again, Table 1.

It is therefore concluded that production performance with the modified enzyme is not associated with oil properties.

The adaptability to salts and salinity: Usually, surfactants are poorly adaptive to water of great salinity or high content of metallic divalent cations, such as magnesium and calcium[8], which always is the case of most formation waters.

The adaptability to brine water: In experiment for adaptation to salinity, sodium chloride was mixed in the 8% modified enzyme solution. For improved performance, measurement pointed to 0.5-10% NaCl and the optimal 0.5-1%, Fig.3.

The adaptability to calcium: In experiment for adaptation to Ca^{2+}, $CaCl_2$ was added into the 8% modified enzyme solution. Data preferred $CaCl_2$ at 0.05-1.0 g/L and the optimal ranged 0.05 to 0.4 g/L for better performance. The upper limit is 1.0 g/L. The range is just the situation of most reservoir waters.

The adaptability to magnesium: In experiment for Mg^{2+}, $MgCl_2$ was employed in the 8% modified enzyme solution. It was observed that $MgCl_2$ at 0.05-0.4g/L and the optimum below 0.2g/L would improve performance. Experiments showed that Mg^{2+} makes more impact on performance than Ca^{2+}. This is consistent with the reference.

Synergy with indigenous bacteria: Mutual effect of modified enzymes and indigenous bacteria was concerned. Normally, metabolic products of bacteria include surfactants, which contribute to performance improvement too. Cultivation took 7 days. In the first 3 days, both infected and disinfected solutions performed closely. On the 4^{th} day, the infected one measured better performance. It justified that bacteria in solution are working together modified enzyme to degraded and emulsify the oil, Table 2.

The temperature adaptability: Reservoir temperature was another factor, most of enzyme will lost its performance at high temperature. Banqiao oil and 8% modified enzyme solution were involved. In one experiment, temperature was below 90°C and pressure was normal. In another, it was 100 °C at 5 MPa. The previous resulted in better performance, indicating the preferential temperature range 30-60°C (Table 4).The second experiment led to carbohydrate coking and lost its action.

Core Desorption Experiment: In Core Desorption experiment, the natural cores were short and had small PV for core holder. Desorption rates varied with oil in the experiment on cores without water flooding in 8% modified enzyme solution. The highest rate was 46.4% for oil from Well Guan 69-8 and followed 33.3% for the Banqiao block oil. In experiment with cores that had been flooded to 90% water-cut, only 0.05 ml oil was produced, negligible amount. It was probably attributed to high water-cut causing the decrease of modified enzyme concentration to beyond the optimal range. So dilution should be taken into account in field test.

The modified enzyme flooding:

Experiment Condition and material: In experiment of oil displacement with modified enzyme, natural cores were taken from Well Xi 42-7-1 of the Gangxi block and Well Ban 834 of the Banqiao block, both in Dagang Oilfield. A HTHP mobile device was utilized at 65°C. Water flooding rate was kept constant at 1m/d. In the horizontal direction, the 150 mm-diameter natural cores were drilled to obtain 25mm-diameter samples which were later treated with solution of absolute ethanol and toluene to extract oil and then dried by oven. Core permeability and porosity were measured. Next, the samples were contained in a closed vessel and evacuated for 3 hours, after which they were saturated with formation water through a 1.2μm filter film for pore volume records.

The experiment method: Held in a holder, a water-saturated core was displaced with oil to irreducible water. The core aged at experiment temperature for 7 days, then flooded with injection water until outlet 90% water-cut was metered. In the whole process oil production was measured for efficiency evaluation. Subsequently, the core was injected with 1.0 PV modified enzyme solution of various concentrations and maintained the inlet and outlet closed at experiment temperature for 12 hr. Water flooding was restored until water-cut exceeded 98% (with total 5PV injection volume). For comparison, 1 PV of water was injected under the same conditions in another experiment.

The experiment Results: As shown in Table 5, enhanced oil recovery rates depend on cores and modified enzyme concentrations. Application of 3%, 6% and 10% modified enzyme improved the recovery by 12.4%-16.3%, 13.9%-20% and 15.7-21.1%, respectively. It was noted that when modified enzyme solution was raised from 3% to 6%, recovery rate was increased by 1.5-3.7%. When modified enzyme concentration was lifted from 6% to 10%, the recovery was only increased by 1.1-2.2%. So, the previous concentration rise (from 3% to 6%) would yield a recovery rate that is 0.4-1.5% higher than the other rise (from 6% to 10%). The optimal concentration would be 6% in EOR.

Micro Simulation Experiment: The methods are described in Reference [9]. A micro-model was evacuated of saturation water and then displaced with oil to 80% oil saturation. Next, oil was flooded by water to 70% water cut and further by 0.5 PV 8% modified enzyme solution. The model stayed at experiment temperature for 2days and measurements were made. It was found out that modified enzyme moved forward along pore margins and converted oil-wet sections into water-wet, which accounted for disbonding (Fig.5). After modified enzyme contacted oil, oil evolved its color, along time, from dark to light and formed emulsified particles in 2-6μm diameter on pore surface (Fig.6). This process was spontaneous and stable, leading to additional solubilization.

In the experiment, oil mobility increased and oil was first mobilized in areas where emulsification was strong (Fig.7). Locally mobilized oil was globally pushed forward. As a result of emulsification, local flowing resistance was increased and consequently micro sweep areas were expanded.

Field Test

Huff and Puff Test

***Dagang modified enzyme huff and puff test*:** The test was carried out on a Well Ban 62-30 of the Banqiao block. The 3.2m-thick pay zone, 1882.4 to 1885.8m deep, is a Sha 3 member of the Dongying group. Permeability is 916 md and porosity averages 32.3%. Reservoir temperature is 78°C. Crude oil contains 10.47% wax. Formation water salinity is 6534 mg/L. The well was put on line in Apr. 2001. Before treatment, it was producing 135.9bbl fluids daily, including 23.4bbl oil. As formation pressure declined and bottom-hole pressure/temperature changed, part of the producing zone was plugged by crude components like wax and colloid and asphaltene and thus inflow was insufficient. In Aug.21, 2005, a huff and puff test was performed with 8% modified enzyme solution. The well was injected first with 62.9 bbl pre-pad, then with 125.8 bbl solution of 8% modified enzyme solution and at last with 106.9 bbl after-pad. After shut in for 4 days, this well resumed production. During treatment period, offset producers and injectors continued normal operation.

Production performance summarized in Fig.8 presents that produced water dropped from 85% to 54%. Before treatment, oil production was 29.2 bbl/d for 30 days. In comparison, post-test output climbed to 77.6 bbl/d, an increase of 41.6 bbl/d. On the production curve, improved performance seems to last for 60 days, corresponding to 2409 bbl incremental oil recovery. This could be explained through unplugging. Clogged by organic materials, poorly permeable layers allowed no oil flow. The primary paths had to be permeable layers where more water flowed through. After injected modified enzyme solution unplugged low-permeability layers, oil flow paths were opened and water flow was reduced. With time, organic material might clog low-permeability layers again and oil output decreased and water-cut increased once more. Therefore periodic treatment was required.

Baise oilfield modified enzyme huff and puff test was aimed to deal with the thin, heterogeneous multi-layered reservoirs at 33-43°C. The pay zones, 900-1100m deep, are continental deposition. Although block area is small, structure is complex. Pay porosity ranges 15 to 20% and permeability is 30 to 300 md. The reservoir is moderately or a little strongly sensitive to water, flow rate and salt and is weakly sensitive to acid. On the ground average crude density is 30^{o}API while underground oil viscosity is 1.1-5mPa·s (at 50°C) with a maximum of 19.07mPa·s (at 5O°C). The pour point is measured at 32-35°C, wax content 12-26.5% and colloid content 17-31.5%. Main production problems include sanding-out, serious emulsifying and waxing.

From 2004 to Jan. 2005, 14 treatments were made on 13 wells in the oilfield. Responses were observed in 12 treatments with accumulative oil production increase 1975.4 bbl. The Well Lei 2-4 was outstanding, which raised fluid rate from 4.8t/d to 62.8 bbl/d and oil rate from 4.4 bbl/d to 12.4 bbl/d, Fig.9. The well produced 496.4 bbl additional oil. Treatment operation turned out to be simple and economic. But it was proposed that modified enzyme stimulation was not applicable to wells of low formation-energy or water-cut below 50%. It is mostly suitable for producers at 50-90% water-cut.

Modified Enzyme Flooding Test

Dagang test was conducted on the Gangxi 41-22 block located in the Beidagang structure, Huanghua Depression. The main target is the upper Tertiary layer, Nm□5, 990-115m deep. Oil-bearing area is 2.24km^2 and OIP is 2.23 million tons. The reservoir is a meander deposition with large lateral variation.

Pay porosity and permeability are 38％and 943md, respectively. Oil saturation is 50%, temperature is 55°C, and pay pressure is 9.8MPa. Reservoir oil viscosity is 14.40mPa·s, pour point is -7°Cand wax content is 2.2%. Formation water is $NaHCO_3$ type and salinity is 4226mg/L.

The block started development in 2002. By end of May 2006, 17 producers had been producing 32.6 bbl/d at water-cut rate 51.4%. Total oil recovery was 2.44 percent of OOIP. There were three water injectors with injection rate of 641.6 bbl/d and cumulative injection 79883 bbl. The underground voidage was estimated to be 454767 bbl.

A Xi 39-20 well group was chosen for flooding pilot test, Table 6 and Fig.10. In the well group, oil-bearing area is 0.15 km^2, net pay 7.8m average and OOIP about 0.21 million tons. The pilot covered one injector and six producers. Data from benefiting producers indicated only one pay zone available that was totally producing 140.9 bbl/d oil at water cut 62.4% average before test.

Core experiments in the above sections are suggesting 6% modified enzyme for field test application.

The modified enzyme volume required for field test was predicted through concentration-PV. On basis of reservoir characteristics knowledge, modified enzyme concentration in plug PV was designed to be 35mg/L·PV and injection amount would be 73 bbl. The injection was made in two plugs. In the first plug, half volume at 4% modified enzyme concentration was injected and in the second plug, another half at 6% concentration was injected. This field test was executed during Aug.23 to 30, 2006.

Among the six beneficial wells, four were responding with remarkably increased oil rate and decreased water-cut. Xi 40-20 (Fig.11) was a best demonstration, in which well the oil production went up from 14.6 bbl/d to 36.5 bbl/d and this performance was quite lasting. From all the wells, additional oil rate was47.4 bbl/d while water production was cut from 78.9% to 64.2%. By Jan. 2007, the stimulation operation led to 7902 bbl more oil recovered. The improved performance was expected for 8 months during which the predicted additional oil volume would be 19053 bbl.

Another field test was conducted in July 2005, on Chang 31 block, Daqing oilfield. Both oil and fluid production was reported significantly improved, but no detail was available.

Conclusion

1. It is feasible to modify enzyme in chemical means.
2. Modified enzyme is adaptive to various types of formation water and oil, and can disperse oil in reservoir below 90° C.
3. When bacteria exist, participation of surfactants in the process helps modified enzyme improve effectiveness.
4. Micro-model simulation and core experiments are evaluated to confirm the mechanism of modified enzyme unplugging and enhancing recovery rate.
5. It is recommended to implement modified enzyme huff and puff stimulation periodically.
6. Modified enzyme concentration requirements for EOR depend on reservoir property.

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References

1. Sun Ying-li, Nie Shu-lan. "New Usage of Enzyme in Oil and Gan Production" World Petroleum Industry. Vol.7(5)pp45-47
2. Wang Qing, Zhao Ming-Chen *et al.* "Use of Enzyme Preparate Greengyme for Removing Inorganic-Organic Precipitate From Sanding Heavy Crude Oil well". Oilfield Chemistry. Vol.19(1).pp24-26
3. Deng Zheng-xian,Liang Yuan-an et al. "Broken down Technology Application of Applo Enzyme in Baise Oilfield". NANFANG OIL AND GAS.Vol.19(1) pp 67—70
4. Wang Yuan, Li Zhao-min et al. "Experimental Research on the Changing Wettability of Rock Surface Using Biological Enzyme". PETROLEUM GEOLOGY AND RECOVERY EFFICIENCY VOL.12 (1)PP71-72
5. KONG Jin，LI Hai-Bao et al. "Enzyme Base Reservoir Blockage Removing Agent SUN and Its Uses in Shengli Offshore Oil Fiel" Oilfield Chemistry. Vol.22(1).pp23-24
6. SPE50621-MS **New Applications for Enzymes in Oil and Gas Production** Harris, R.E., McKay, I.D., Cleansorb Ltd.
7. Wei Shu-zhong. Biological Chemistry. China Light Industry Press. January, 1996. pp130-146
8. Qing-xian Feng, Guo-qing Tang and Chun-yuan Yang. "Experimental Study for Using Petroleum Solvent to Enhance Oil Recovery in Zaoyuan Oilfield" FAULT-BLOCK OIL AND GAS OILFIELD.Vol.6(4)pp51-56
9. Qing-xian Feng, Jia-xi Zhou *et al*. Study on EOR Mechanisms by Microbial Flooding**.**, SPE79176 Research Centre of Dagang Oilfield Company, PetroChina
10. SPE52818-MS Single Step Enzyme Treatment Enhances Production Capacity on Horizontal Wells. Frederick O. Stanley, Phil Rae, BJ Services Company; Juan C. Troncoso, YPF - Maxus Southeast Sumatra LLC
11. SPE97427-MS Wellbore Cleanup by Water Jetting and Enzyme Treatments in MRC Wells: Case Histories. M.B. Al-Otaibi, SPE, H.A. Nasr-El-Din, SPE, Saudi Aramco, and Y.M. Altameimi, SPE, BJ Services Co.
12. Al-Otaibi M B, et al. "Chemical Treatment to Enhance Productivity of Horizontal and Multilateral Wells: Lab Study and Case Histories. SPE89467.

Table 1 Emulsification of Modified Enzyme

Well Code	Zao 41	Guan69-8	Zhuang16-12	Kong1017-7	Jia K31-51	Ban 64-30
Oil Property	Middle-Heavy	High Wax	Low Pour Point	High Gum	High Viscosity	Light
Emulsification,%	90.1	99.5	93.6	91.8	94.4	100

Table 2 Emulsification of Modified Enzyme measured with Oil in Bacteria Presence

Time, d	1	2	3	4	5	6	7
Emulsification,%	5	7.5	35	60	90	95	96

Table 3 Core Data in Desorption Experiment

Core Source	Length	Section Area	Core Size	Pore Volume	Porosity	Oil Source
	cm	cm^2	ml	ml	%	
Ban 5-1	3.58	4.906	17.6	3.25	18.5	Ban64-30
Guan 78-26	3.97	4.985	19.8	4	20.2	Guan69－8

Table 4 Data from Desorption Experiment

Measurement	No Enzyme	8% Modified Enzyme		8% Modified Enzyme		Oil Source
	Water-Cut, 0%	Water-Cut0 %	Desorption Ratio, %	Water-Cut 90%	Desorption Ratio,%	
Oil Output, ml	0.2	0.3	33.3	0.05	0.1	Ban64-30
	0.75	1.4	46.4	0.05	0.1	Guan69-8

Table 5 Data from Modified Enzyme Flooding Experiment

Concentration	3%		6%		10%	
Block Code	Xi42-1	Ban834-1	Xi42-2	Ban834-2	Xi42-3	Ban834-3
Core Code	X30-2	B115-1	X30-1	B115-2	X30-3	B115-3
Porosity，%	21.5	19.3	21.6	19.4	21.5	20.0
Permeability，mD	417.0	81.4	381.0	92.1	278.0	90.2
Pore Volume ,cm3	6.9	4.4	6.8	5.0	6.6	6.2
S_{wi}，%	28.2	23.1	27.6	21.0	23.9	25.0
Recovery by Water Flooding，%	55.9	51.2	57.9	56.9	53.8	47.0
EOR Rate，%	16.3	12.4	20.0	13.9	21.1	16.1

Table 6 Data of Benefiting Wells

No.	Well Code	Net Pay	Po	Permeability	Oil Rate	Water Cut	Cumulative Production
		m	%	μm^2	t	%	10^4t
1	Gang186	5	31.9	3.528	0.78	77.96	0.2744
2	Xi37-23	4.2			6.68	46.17	0.5258
3	Xi38-18	4.1			3.92	64.47	0.1129
4	Xi38-22	3.2	37.7	19.077	4.6	62.17	0.298
5	Xi40-20	3	36.65	17.634	3.38	68.75	0.3692
6	Xi41-22	3	27.93	0.551	2.85	77.4	0.9150
Totally		19.5			22.21	62.4	2.4953

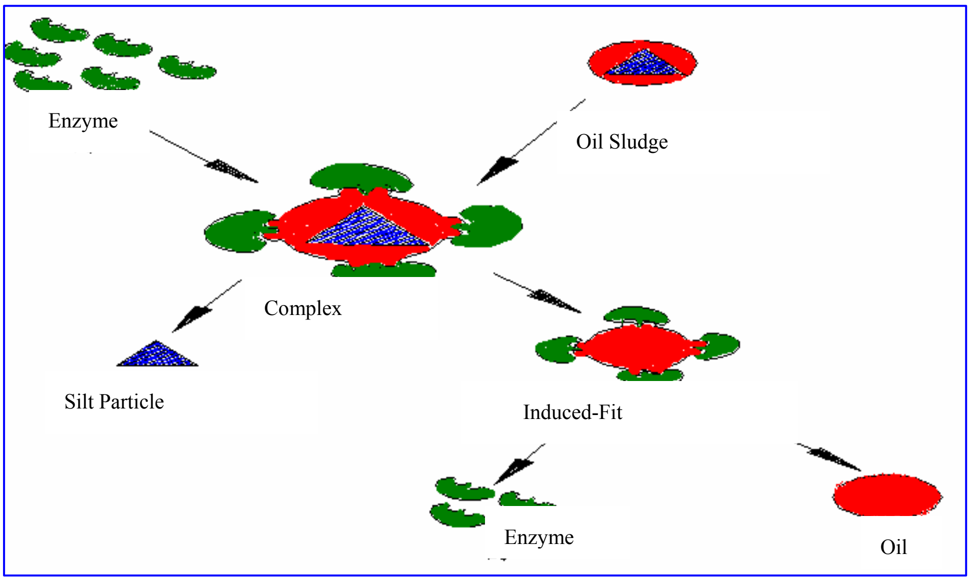

Fig. 1: Schematic of induced-fit of modified enzyme and crude oil.

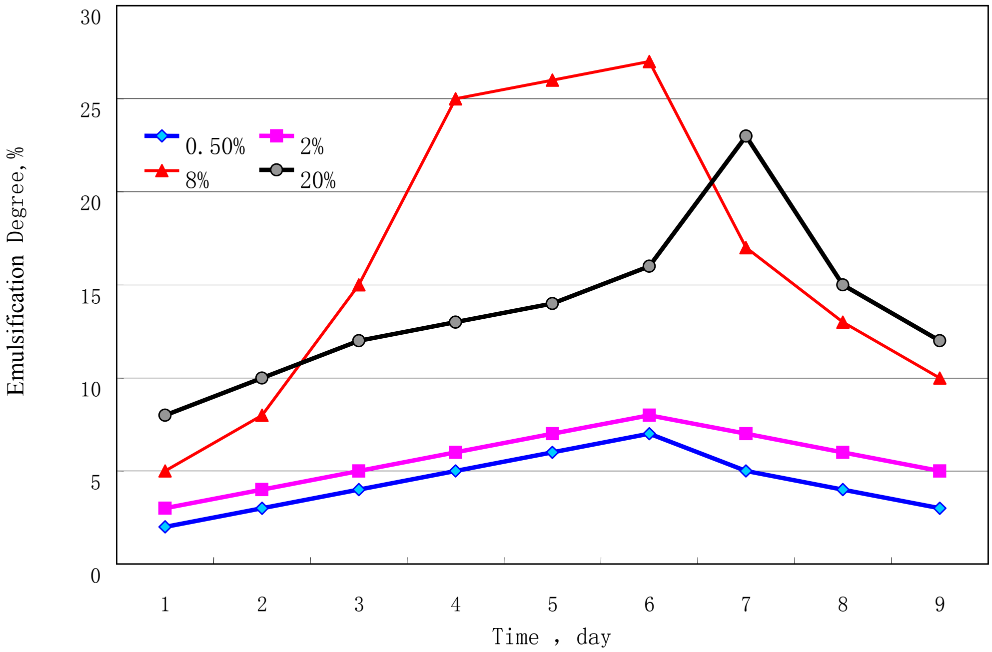

Fig. 2: Tests for the optimal Modified Enzyme Concentrations.

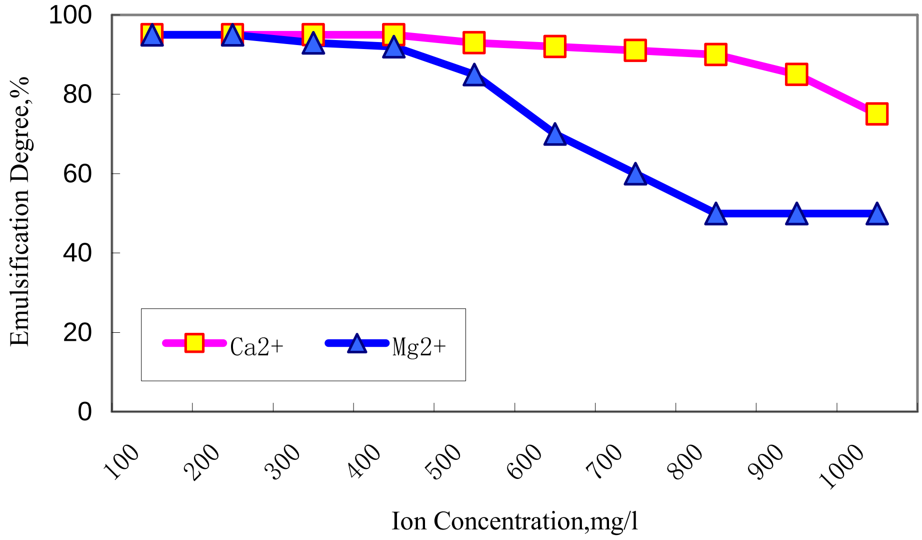

Fig. 3: Concentrations of Ca2+ and Mg2+ impacting emulsification with modified enzyme.

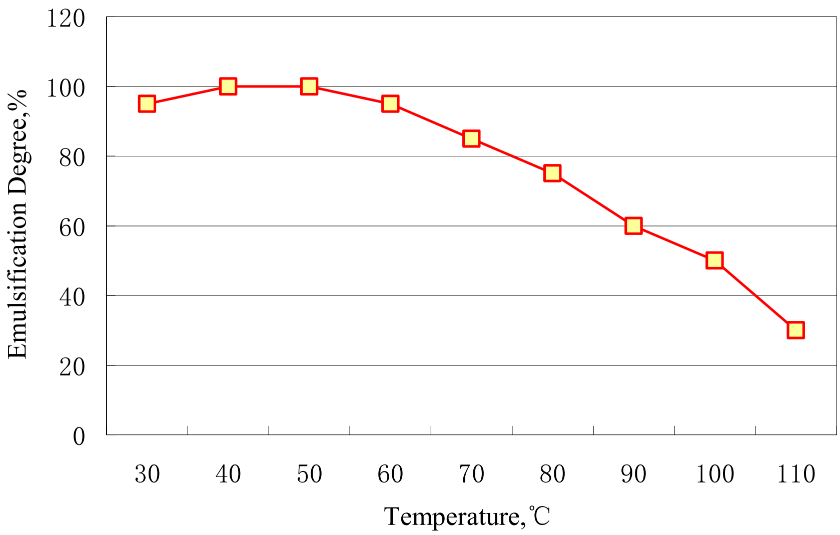

Fig. 4: Impact of temperature on emulsification with modified enzyme.

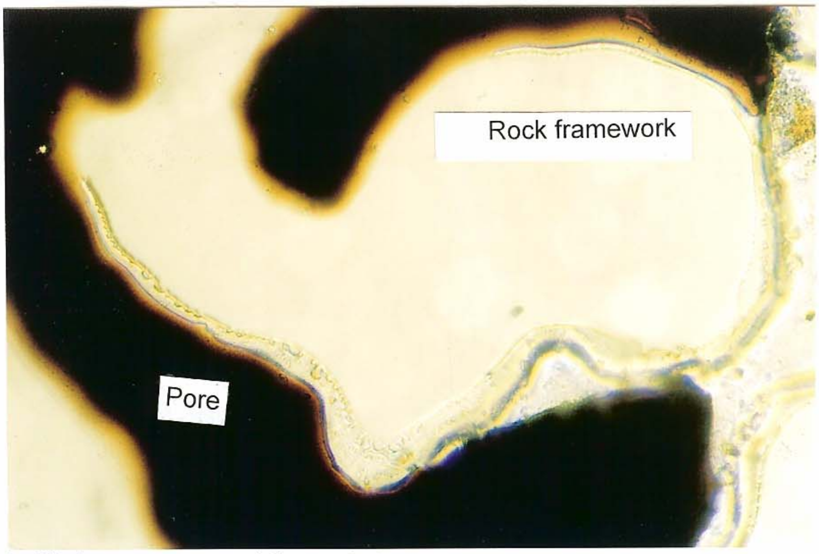

Fig.5 Modified enzyme moved forward along pore margins and converted oil-wet sections into water-wet

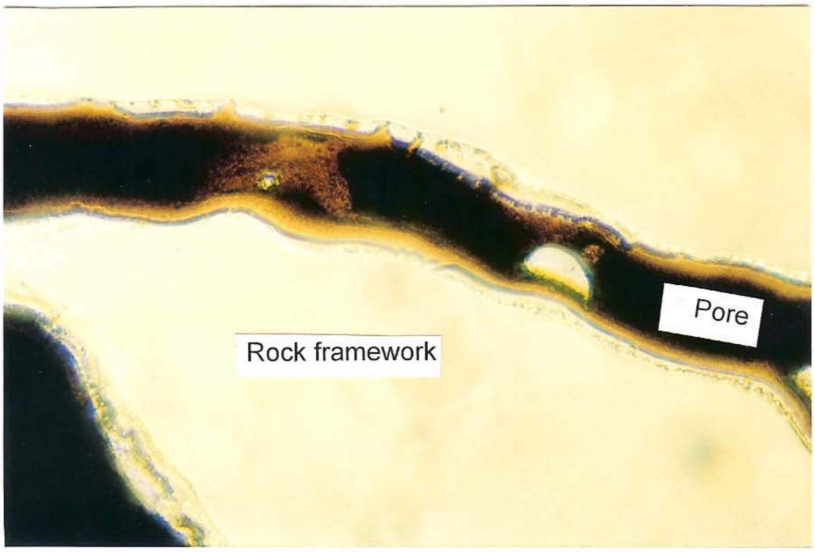

Fig.6 Oil was formed emulsified particles in 2-6μm diameter on pore surface

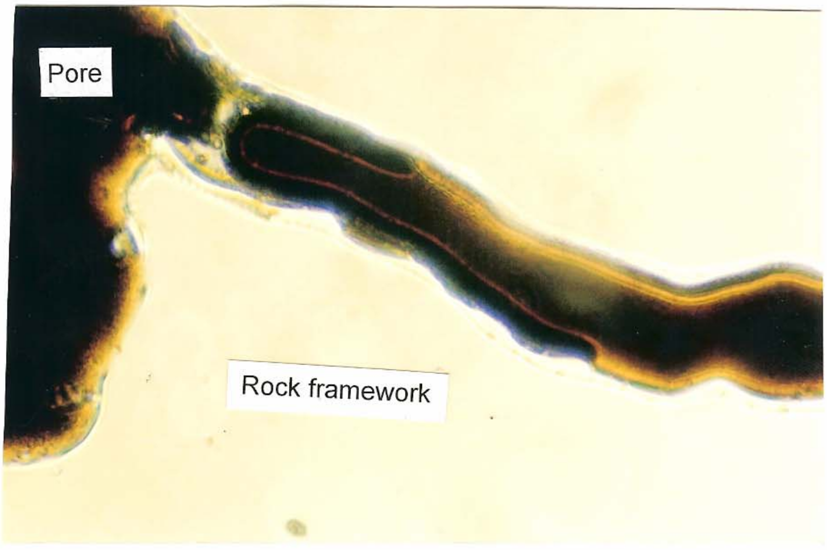

Fig.7 Oil mobility increased by emulsification and first mobilized in the pores

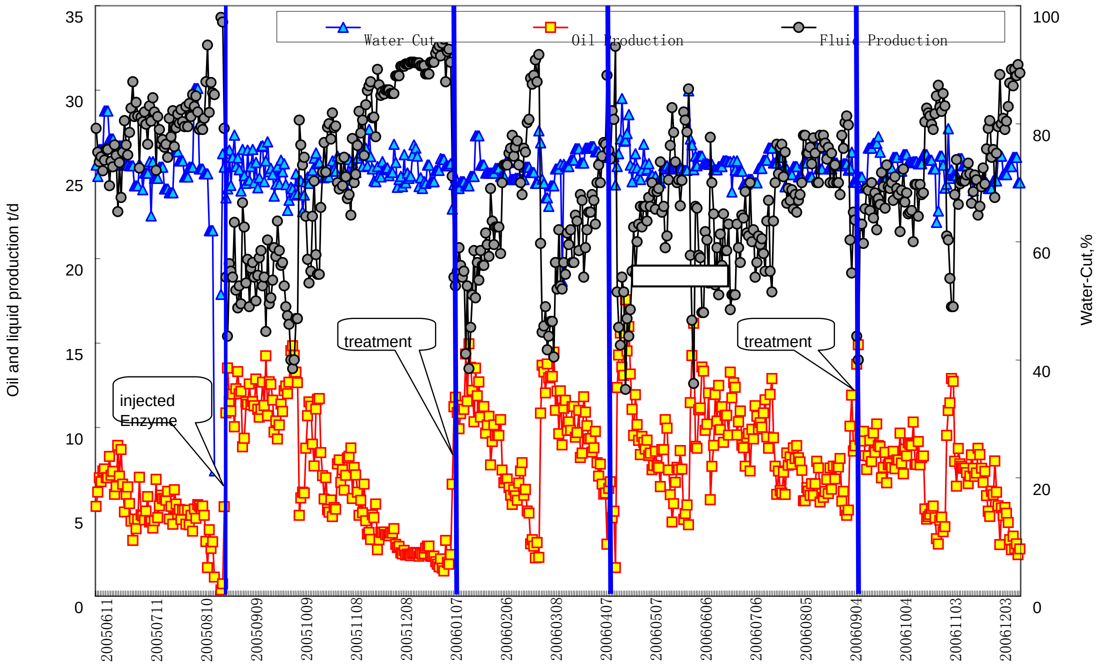

Fig.8: Performance Curves for the Ban 62-30 well, Dagang oilfield, China.

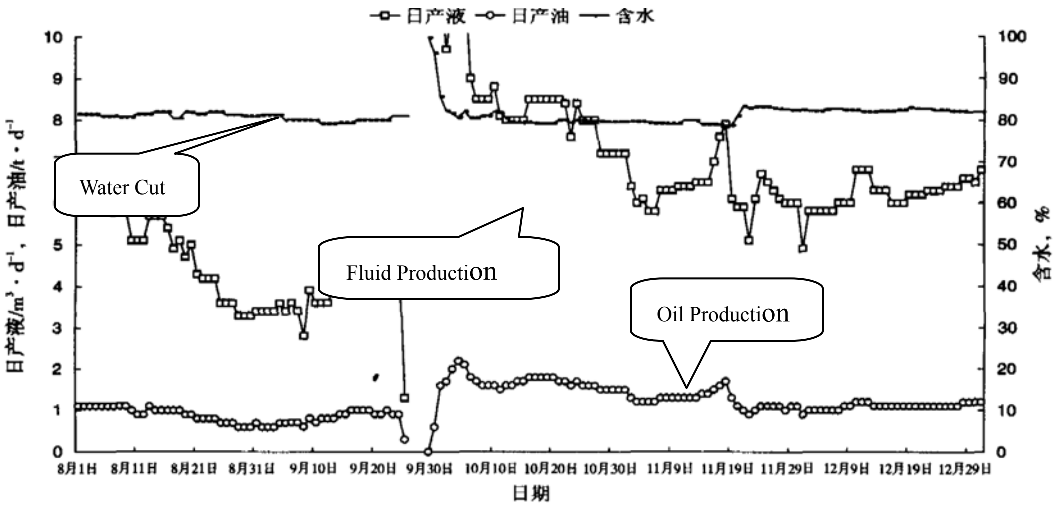

Fig.9: Performance Curves for the Lei 2-4 well, Baise oilfield, China.

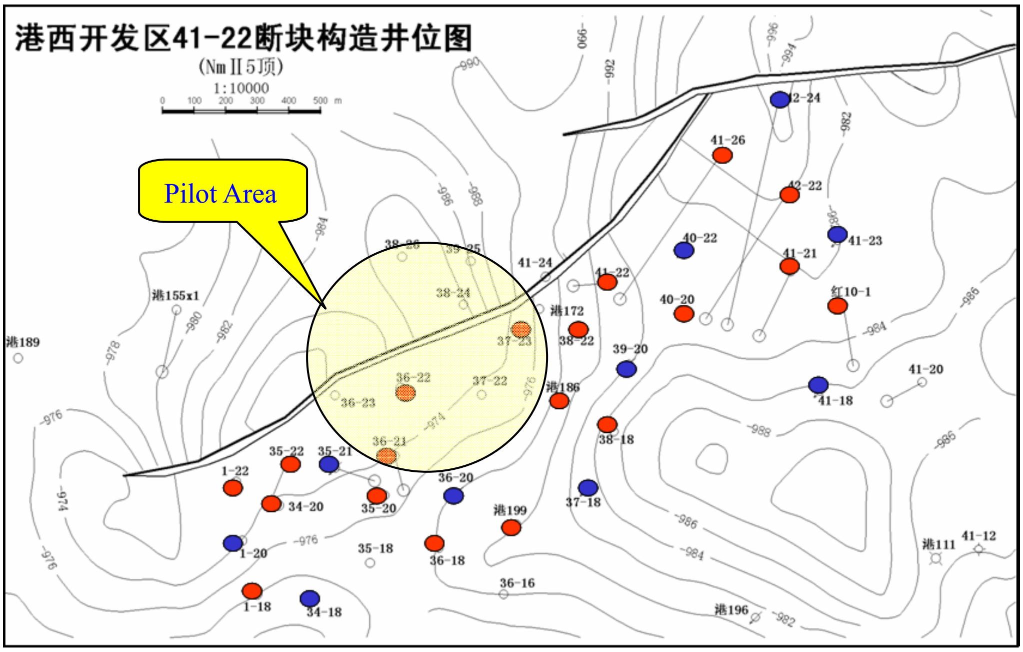

Fig.10: Wells in the modified-enzyme flooding test.

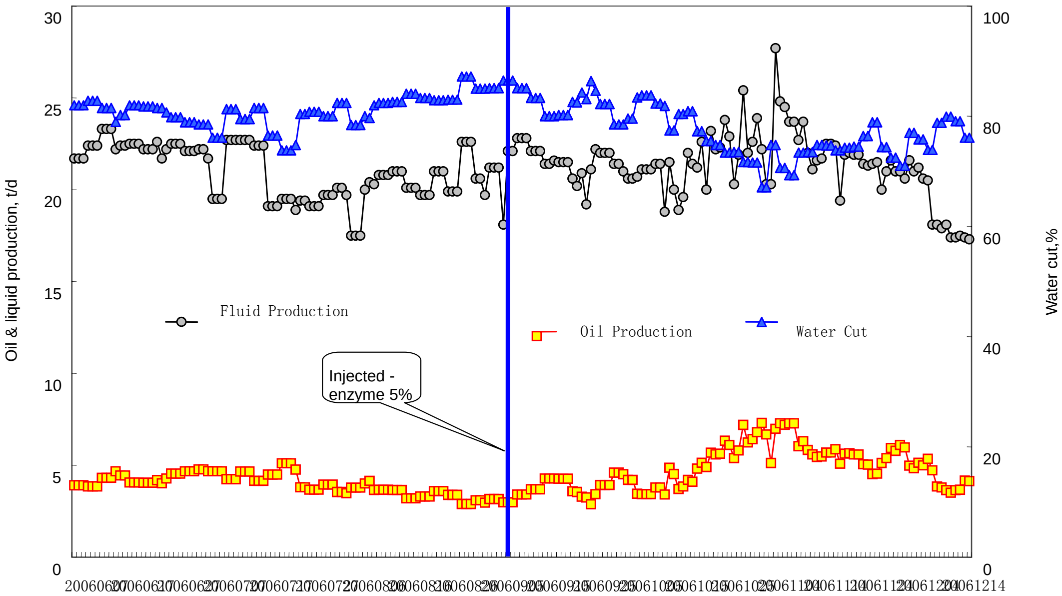

Fig.11: Performance curves for the Xi40-20 well, Dagang oilfield, China