EOR Pilot Tests With Modified Enzyme—Dagang Oilfield, China

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Summary

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

Introduction

With time in oil development, some oil components precipitate and composites of organic and inorganic scales are deposited. Formation fine grains migrate and clay swells. These are barriers to fluid flow and productivity, causing much underground oil to be unrecoverable. Modified enzymes were applied to improve biological activity of normal enzymes and to protect pay by opening pore paths and, thus, to introduce, stimulate, and merge remaining oil into flows. Huff'n'puff and flooding tests that have been implemented in Dagang, Shengli, Daqing, and others both in China and elsewhere all show improved performance (Ying-li and Shu-lan 2000; Wang et al. 2002; Deng et al. 2006; Wang et al. 2005; Kong et al. 2005; Harris and McKay 1998; Stanley et al. 1999; Al-Otaibi et al. 2005). It is not quite clear why and to what extent it works, so a collection of experiments were performed to evaluate the modified-enzyme EOR mechanism. A field test was made and is presented here.

At the end of last century, Apollo Separation Technology Company began to successfully use enzyme for huff'n'puff operation in producers to overcome pore plugs from organic material deposition. This was introduced to China early this century.

In March 2004, such an agent was applied on Well Yong 8-52 in Shengli oil field, Shangdong, China. Improved production was sustained for 180 days with 10,961 bbl of additional oil. Similar performance was observed in Baise oil field, Guangxi, China, and in other fields. With development for 2 years in China, more than 100 wells saw enzyme application and success ratio greater than 88%. Enzyme-flooding tests in Daqing even recorded more than 1:3 in investment-to-output value.

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Enzyme Mechanism

The environment-friendly enzyme agent is a water-soluble product that 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.

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

Different from its chemical and bacterial counterparts, the process described in the preceding paragraph is biological. It does not 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 SunLight (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 deoxyribonucleic acid (DNA) is extracted. The selected bacteria are put into a nutrition solution and cultivated with high protein. Then the bacteria have all of their activity removed and become nonactive catalysts. The enzyme dissolves in water, not in oil, and can split hydrocarbons from rock grains.

Modified enzyme can alter rock-surface wettability and prevent crude molecules from bonding onto rock surface and, thus, from mutual absorbing of oil and shale.

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 affect 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.

Laboratory Experiments

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

Experiment Method. In the 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 1:4. 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 such as sodium chloride, calcium chloride, and magnesium chloride were added in variable concentrations to confirm modified enzyme adaptability to salts. Oil from different blocks was used in the packages to determine whether the modified enzyme is suitable to the oil. Disinfected and infected produced water was used separately in the modified enzyme

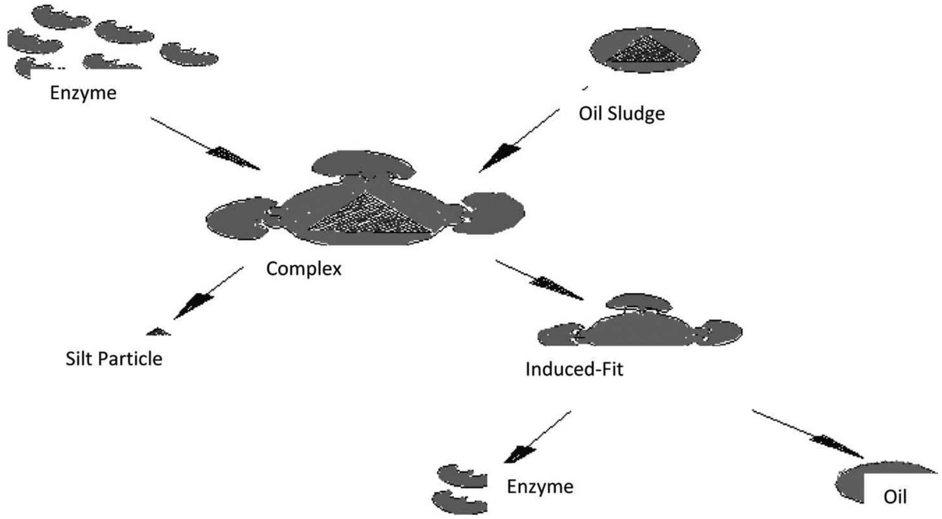

Fig. 1—Schematic of induced-fit of modified enzyme and crude oil.

solution to determine 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 put separately into the modified-enzyme solution to see its capability and the time required to desorb oil. In another experiment, natural cores were flooded with the modified-enzyme solution at various concentrations. A transparent micromodel was constructed to investigate the microdisplacement mechanism.

Experiment Results

The Optimal Modified-Enzyme-Concentration Experiment. On the second day that the package was in the 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 more oil was released. On the fourth 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 floated on the surface. The 20% modified-enzyme solution showed better emulsification than the 8% one. From the ninth day on, performances deteriorated; oil and the solution separated into two phases. It was thus concluded that the optimal-modified enzyme concentration is 8% (see **Fig. 2**).

Emulsification improves with increasing concentration of modified enzyme, and the optimal range is from 5 to 10%, the best being 8%. The best performance for 8% concentration was observed on the fourth day and deteriorated on the seventh 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 investigated with the 8% modified-enzyme solution. Results showed little difference. All samples were emulsified to some extent, particularly on the sixth day. But on the seventh day, emulsification seemed dim and oil trended to

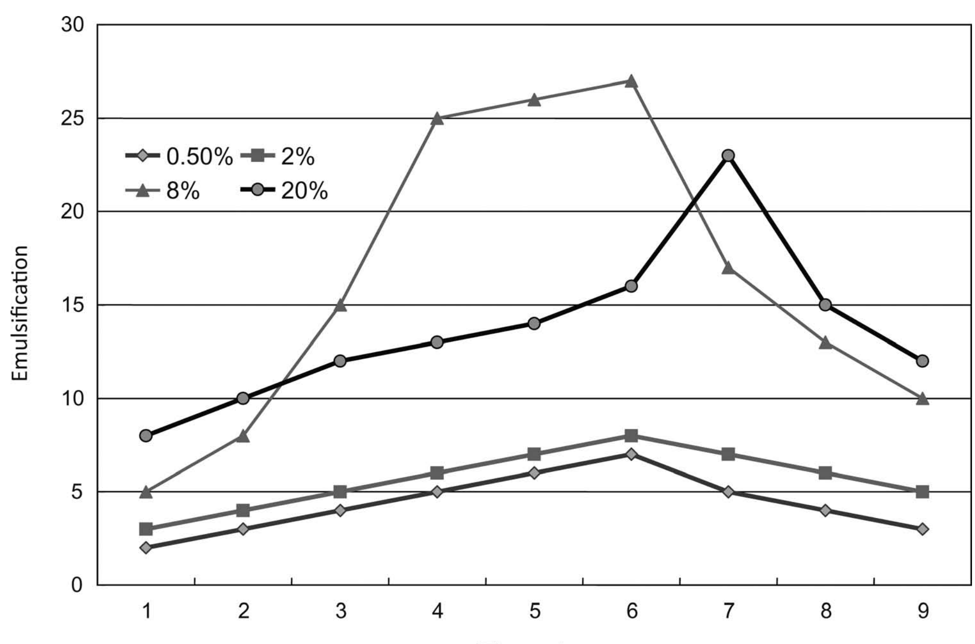

Fig. 2—Tests for the optimal modified-enzyme concentrations.

TABLE 1—EMULSIFICATION OF MODIFIED ENZYME						
Well Code	Zao 41	Guan 69-8	Zhuang 16-12	Kong 1017-7	Jia K31-51	Ban 64-30
Oil Property (°API)	20	26	22	12	16	44
Emulsification (%)	90.1	99.5	93.6	91.8	94.4	100

split from solution. Performance improvement recovered on the ninth 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 the reservoirs, this happens repeatedly (see **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 water with a high content of metallic divalent cations—such as magnesium and calcium—which is the case for most formation waters (Feng et al. 1999).

The Adaptability To Brine Water. In the 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%, (see **Fig. 3** and **Table 2).**

The Adaptability To Calcium. In the 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 the 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 findings in Feng et al. (1999).

Synergy With Indigenous Bacteria. The mutual effect of modified enzymes and indigenous bacteria was considered. 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 fourth day, the infected solution measured better performance. It justified that the bacteria in the solution are working together with the modified enzyme to degrade and emulsify the oil, see **Table 3.**

The Temperature Adaptability. Reservoir temperature was another factor because most of the enzyme will lose 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 former resulted in better performance, indicating the preferential temperature range of 30–60°C **(Fig. 4).** The latter experiment led to hydrocarbon coking and lost its action.

Core-Desorption Experiment. In the core-desorption experiment, the natural cores were short and had small pore volume (PV) for the core holder. Desorption rates varied with oil in the experiment on cores without waterflooding in 8% modified-enzyme solution. The highest rate was 46.4% for oil from Well Guan 69-8, followed by 33.3% for the Banqiao-block oil **(Tables 4 and 5).** In the experiment with cores that had been flooded to 90% watercut, only 0.05 mL oil was produced, a negligible amount. It was probably attributed to high water cut causing the decrease of modified-enzyme concentration to go beyond the optimal range. Dilution, therefore, should be taken into account in field testing.

Modified-Enzyme Flooding. ***Experiment Condition and Material.*** In oil-displacement experiments using 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 oil field. A high-pressure/high-temperature (HT/HP) mobile device was used at 65°C. The waterflooding rate was kept constant at 1 m/d. In the horizontal direction, the 150-mm-diameter natural cores were drilled to obtain 25mm-diameter samples that were later treated with solution of absolute ethanol and toluene to extract oil and then were 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 1.2-μm filter film for pore-volume records.

The Experiment Method. Clamped in a holder, a water-saturated core was displaced with oil to irreducible water saturation. The core was aged at experiment temperature for 7 days, then

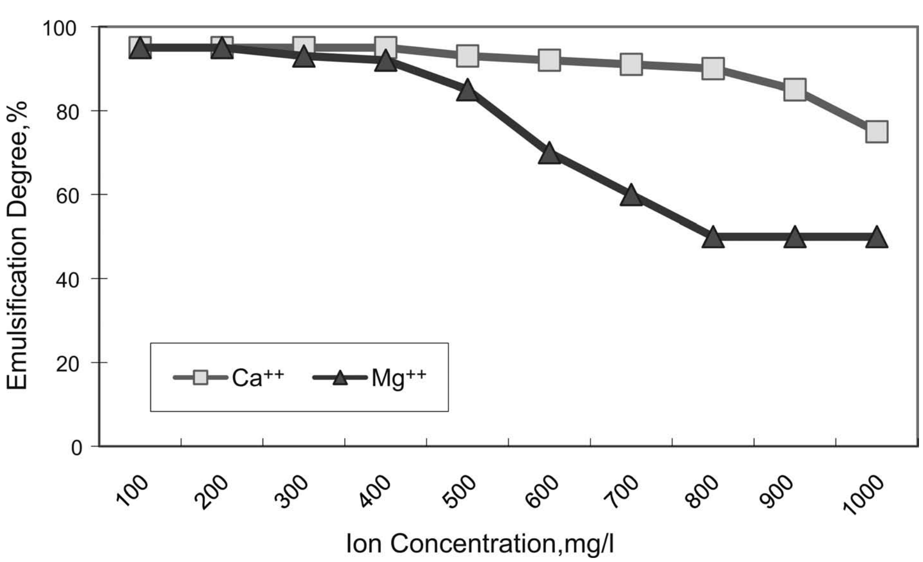

Fig. 3—Concentrations of Ca^{++} and Mg^{++} impacting emulsification with modified enzyme.

TABLE 2—EMULSIFICATION OF MODIFIED ENZYME MEASURED WITH NaCl							
Concentration of NaCl (mg/L)	5000	10 000	20 000	30 000	50 000	80 000	100 000
Emulsification (%)	98	95	90	88	85	80	80

TABLE 3—EMULSIFICATION OF MODIFIED ENZYME MEASURED WITH OIL IN PRESENCE OF BACTERIA							
Time (days)	1	2	3	4	5	6	7
Emulsification (%)	5	7.5	35	60	90	95	96

it flooded with injection water until outlet water cut was measured to be 90%. In the whole process, oil production was measured for efficiency evaluation. Subsequently, the core was injected with 1.0 PV modified-enzyme solution at various concentrations, and the inlet and outlet were maintained closed at experiment temperature for 12 hours. Waterflooding was restored until water cut exceeded 98% (with a total 5 PV injection). For comparison, 1 PV of water was injected under the same conditions in another experiment.

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

Microsimulation Experiment. The methods are described in Feng et al. (2002). A micromodel 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 2 days, and measurements were made. It was found out that modified enzyme moved forward along pore margins and converted oil-wet sections into water-wet sections, which accounted for disbonding **(Fig. 5).** After modified enzyme contacted oil, oil evolved its color from dark to light with time and formed emulsified particles in the 2-to-6-μm-diameter range 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, microsweep areas were expanded.

Field Test

Huff'n'Puff Test. ***Dagang Modified-Enzyme Huff'n'Puff Test.*** The test was carried out on Well Ban 62-30 of the Banqiao Block. The 3.2-m-thick pay zone, 1882.4 to 1885.8 m deep, is a Sha 3 member of the Dongying group. Permeability is 916 md and average porosity is 32.3%. Reservoir temperature is 78°C. Crude oil contains 10.47%, wax and its gravity is 40°API. Formation-water salinity is 6534 mg/L. The well was put on line in April 2001. Before treatment, it was producing 135.9 B/D fluids, including 23.4 bbl of oil. As formation pressure declined and bottomhole pressure/temperature changed, part of the producing zone was plugged by crude components such as wax, colloids, and asphaltene, and thus, inflow was insufficient. On 21 August 2005, a huff'n'puff test was performed with 8% modified-enzyme solution. The well was injected first with 62.9 bbl ahead of the fluid, then with 125.8 bbl solution of 8% modified enzyme solution, and, at last, with 106.9 bbl ahead of the fluid. After shut-in for 4 days, this well resumed production. During the treatment period, offset producers and injectors continued normal operation.

Production performance, as summarized in **Fig. 8,** indicates that produced water dropped from 85 to 54%. Before treatment, oil production was 29.2 B/D for 30 days. In comparison, post-test output climbed to 77.6 B/D, an increase of 41.6 B/D. On the production curve, improved performance seems to last for 60 days, corresponding to 2,409-bbl incremental oil recovery. This could be explained through unplugging. Clogged by organic materials, low-permeability layers allowed no oil flow. The primary paths

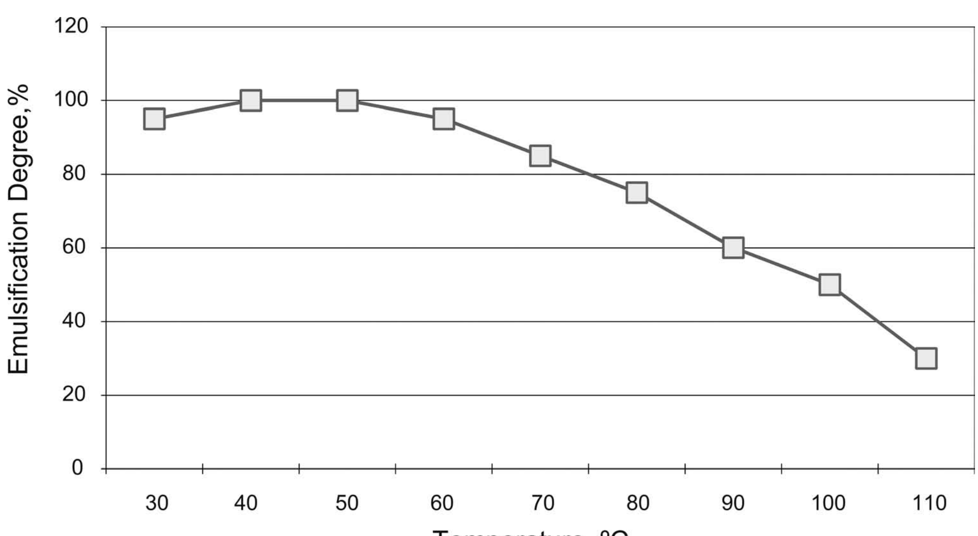

Fig. 4—Impact of temperature on emulsification with modified enzyme.

TABLE 4—CORE DATA IN DESORPTION EXPERIMENT						
Core Source	Length (cm)	Section Area (cm^2)	Core Size (mL)	Pore Volume (mL)	Porosity (%)	Oil Source
Ban 5-1	3.58	4.906	17.6	3.25	18.5	Ban 64-30
Guan 78-26	3.97	4.985	19.8	4	20.2	Guan 69-8

TABLE 5—DATA FROM DESORPTION EXPERIMENT						
	No Enzyme	8% Modified Enzyme		8% Modified Enzyme		
Measurement	Water Cut 0%	Water Cut 0%	Desorption Ratio (%)	Water Cut 90%	Desorption Ratio (%)	Oil Source
Oil Output (ml)	0.2	0.3	33.3	0.05	0.1	Ban 64-30
	0.75	1.4	46.4	0.05	0.1	Guan 69-8

TABLE 6—DATA FROM MODIFIE D-ENZYME-FLOODING EXPERIMENT						
Concentration	3%		6%		10%	
Block code	Xi 42-1	Ban 834-1	Xi 42-2	Ban 834-2	Xi 42-3	Ban 834-3
Core code	X 30-2	B 115-1	X 30-1	B 115-2	X 30-3	B 115-3
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 (cm^3)	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/enzyme flooding (%)	39.6	38.8	37.9	43.0	32.7	30.9
Recovery by final waterflooding (%)	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

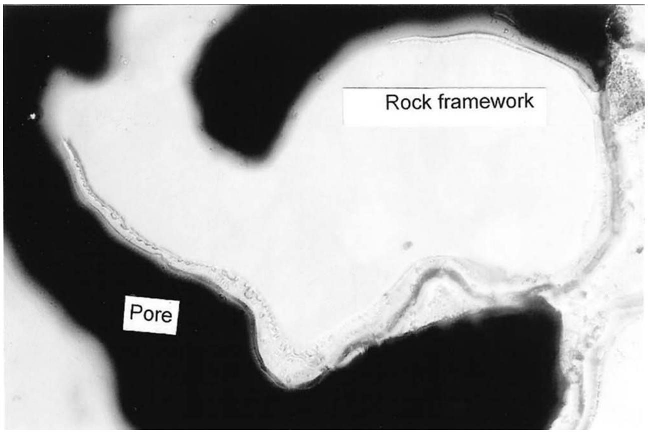

Fig. 5—Modified enzyme moved forward along pore margins, converting oil-wet sections into water-wet ones.

were highly permeable layers that allowed both water and oil to flow through. After the injected modified-enzyme solution unplugged the low-permeability layers, oil-flow paths were opened and water flow was reduced. With time, organic material may clog low-permeability layers again, and oil output will decrease and water cut will increase once more. Therefore, periodic treatment is required.

Baise-Oilfield Modified-Enzyme Huff'n'Puff Test. The test was performed to deal with the thin, heterogeneous multilayered reservoirs at 33–43°C. The pay zones, 900 to 1100 m deep, are continental deposition. Although the block area is small, the structure is complex. Pay porosity ranges from 15 to 20%, and permeability is 30 to 300 md. The reservoir varies from moderate to slight sensitivity to water, flow rate, and salt and is weakly sensitive to acid. At surface conditions, average crude density is 30°API, while underground oil viscosity is 1.1 to 5 mPa·s (at 50°C) with a maximum of 19.07 mPa·s (at 50°C). The pour point is measured at 32–35°C, wax content 12 to 26.5% and colloid content is 17 to 31.5%. Main

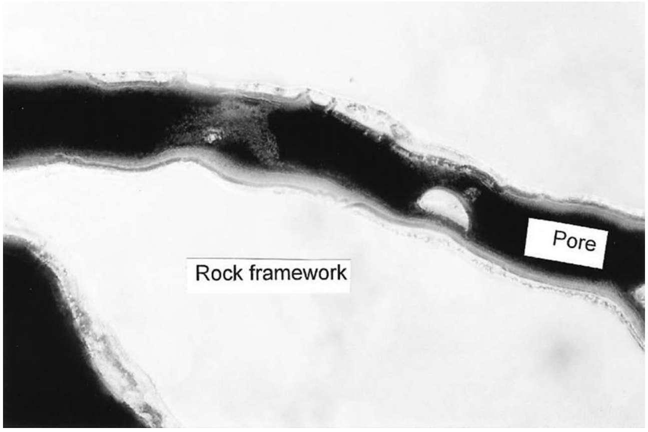

Fig. 6—Oil formed emulsified particles of 2–6-m diameter on the pore surface.

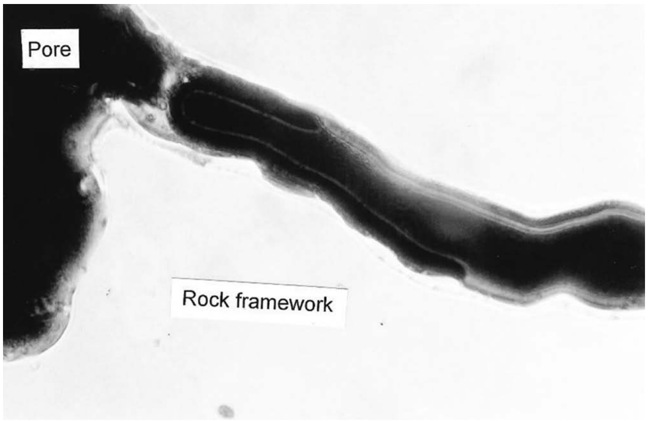

Fig. 7—Oil mobility increased emulsification and first mobilized in the pores.

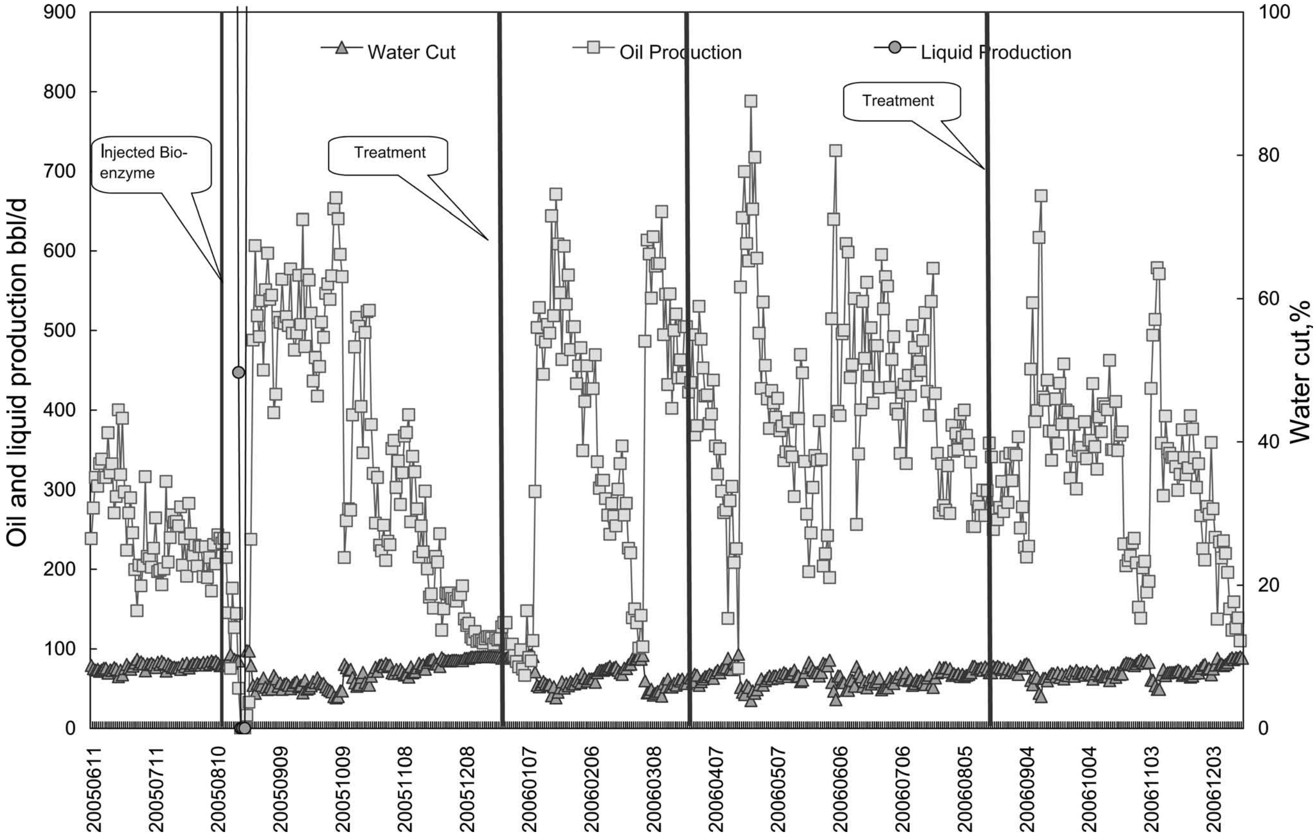

Fig. 8—Performance curves for the Ban 62-30 well, Dagang oil field, China.

production problems include sanding out, serious emulsifying, and waxing.

From 2004 to January 2005, 14 treatments were made on 13 wells in the oil field. Responses were observed in 12 treatments with cumulative-oil-production increase of 1,975.4 bbl. Well Lei 2-4 was outstanding—the fluid rate rose from 32.1 to 62.8 B/D and oil rate from 4.4 to 12.4 B/D (see **Fig. 9**). The well produced 496.4 bbl of additional oil. The 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

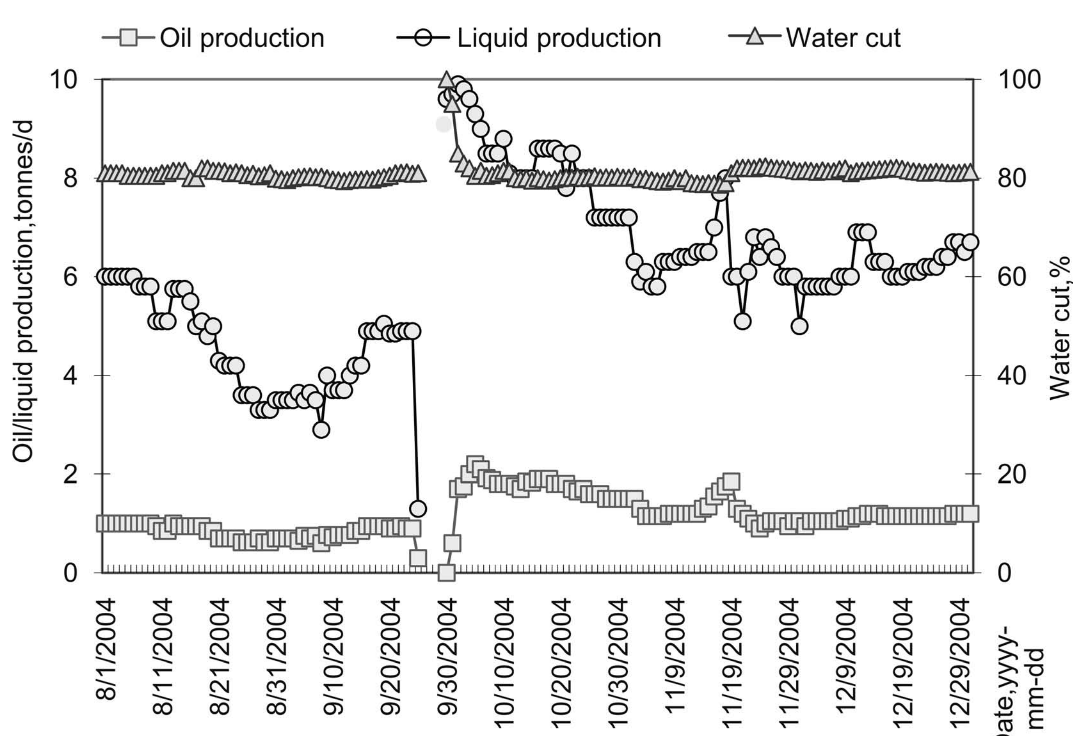

Fig. 9—Performance curves for the Lei 2-4 well, Baise oil field, China.

TABLE 7—DATA OF RECIPIENT WELLS							
No.	Well Code	Net Pay (m)	Porosity (%)	Permeability (μm^2)	Oil Rate (*t*)	Water Cut (%)	Cumulative Production (10^4 tonnes)
1	Gang 186	5	31.9	3.528	0.78	77.96	0.2744
2	Xi 37-23	4.2	–	–	6.68	46.17	0.5258
3	Xi 38-18	4.1	–	–	3.92	64.47	0.1129
4	Xi 38-22	3.2	37.7	19.077	4.6	62.17	0.298
5	Xi 40-20	3	36.65	17.634	3.38	68.75	0.3692
6	Xi 41-22	3	27.93	0.551	2.85	77.4	0.9150
Total		19.5	–	–	22.21	62.4	2.4953

energy or with water cut below 50%. It is most suitable for producers at 50–90% water cut.

Modified-Enzyme Flooding Test

The 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, Minghuazhen Group 5, at a depth of 990 to 1150 m. The oil-bearing area is 2.24 km^2, and original oil in place (OOIP) is 14.94 million bbl. The reservoir is a meander deposition with large lateral variation. Pay porosity and permeability are 3% and 943 md, respectively. Oil saturation is 50%, temperature is 55°C, and pay pressure is 9.8MPa. Reservoir-oil viscosity is 14.40 mPa·s, pour point is −7°C, and wax content is 2.2%. The type of formation water is dicarbonate, with a salinity of 4226 mg/L (ion content).

The block started development in 2002. By end of May 2006, 17 producers had been producing 32.6 B/D at a water cut of 51.4%. Total oil recovery was 2.44% OOIP. There were three water injectors, with an injection rate of 641.6 B/D and cumulative injection of 79,883 bbl. The underground voidage was estimated to be 454,767 bbl.

A Xi 39-20 well group was chosen for flooding pilot test, (**Table 7** and **Fig. 10**). In the well group, oil-bearing area is 0.15 km^2, average net pay is 7.8 m, and OOIP is approximately 1.41 million bbl. The pilot covered one injector and six producers. Data from benefiting producers indicated only one pay zone available that was totally producing 140.9 B/B oil at an average water cut of 62.4% before the test.

Core experiments in the Modified Enzyme Flooding section suggest using 6% modified enzyme for field-test application.

The modified-enzyme volume required for the field test was predicted through PV concentration. On the basis of knowledge of reservoir characteristics, modified-enzyme concentration in plug PV was designed to be (35 mg/L)/PV and the 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 volume at 6% concentration was injected. This field test was executed during 23 to 30 August 2006.

Among the six recipient wells, four responded with remarkably increased oil rate and decreased water cut. Xi 40-20 (**Fig. 11**) was the most responsive well, with oil production rising from 14.6 to 36.5 B/D, and this performance was long lasting. From all the wells, the additional oil rate was 47.4 B/D, while water production was cut from 78.9 to 64.2%. By January 2007, the stimulation operation led to 7,902 bbl more oil recovered. The improved performance was expected to last 8 months, during which the predicted additional oil volume would be 19,053 bbl.

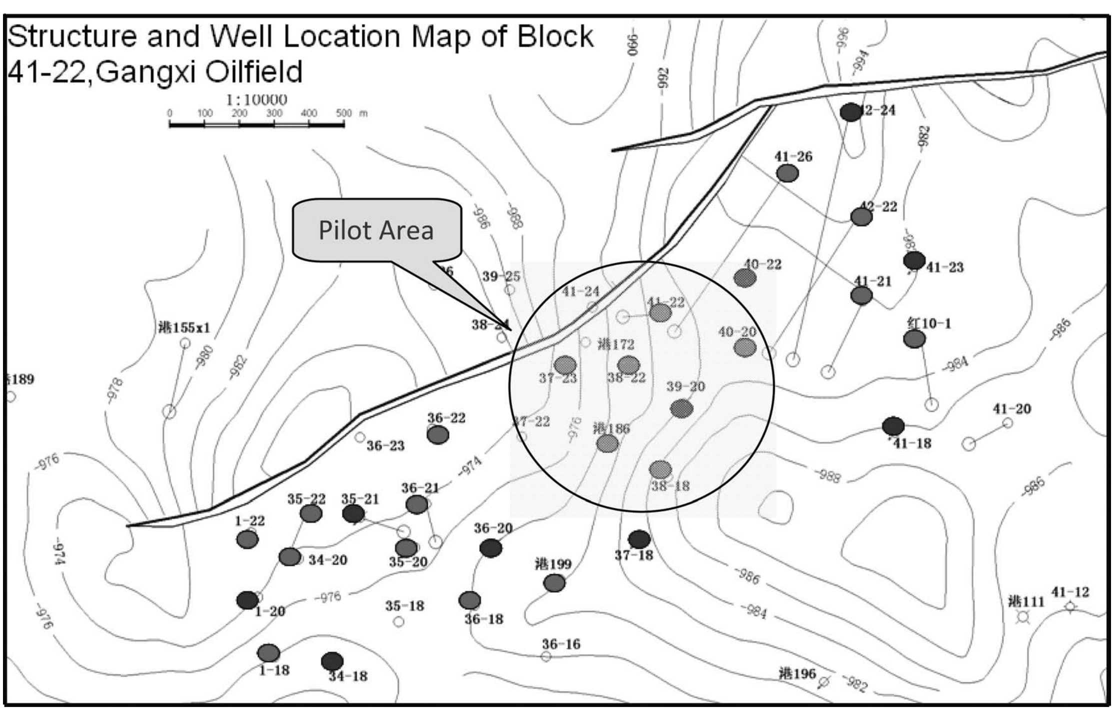

Fig. 10—Wells in the modified-enzyme flooding test.

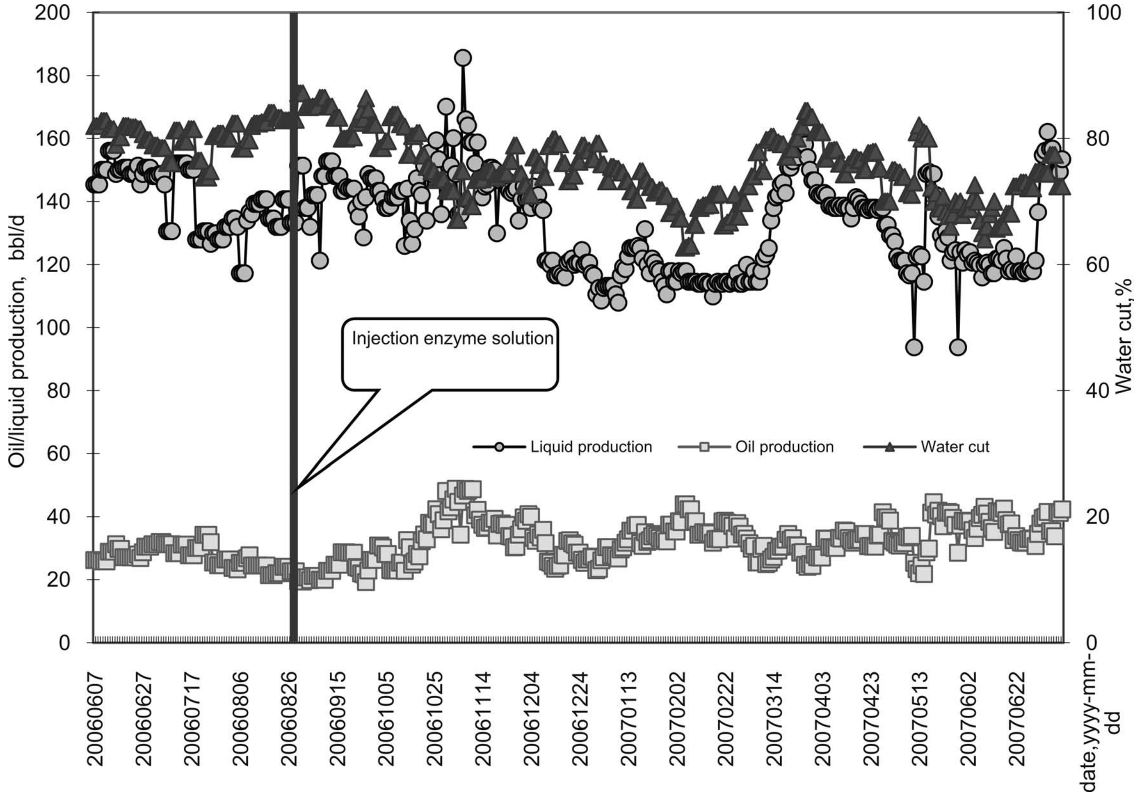

Fig. 11—Performance curves for the Xi 40-20 well, Dagang oil field, China.

Another field test was conducted in July 2005, on Chang 31 Block, Daqing oil field. Both oil and fluid production were reported to be significantly improved, but no details were available.

Conclusions

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

Nomenclature

S_{wi} = irreducible water saturation

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SI Metric Conversion Factors

°API	141.5(131.5 + °API)	= g/cm^3
bbl	1.589 873	E–01 = m^3
°F	(°F − 32)/1.8	= °C

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