SPE 112355

New Agent for Formation-Damage Mitigation in Heavy-Oil Reservoir: Mechanism and Application

Y. Wang and A. Kantzas, SPE, University of Calgary; B. Li and Z. Li, China University of Petroleum (East China); and Q. Wang and M. Zhao, Dongxin Oil Company, Shengli Oil Branch, SINOPEC, P.R.China

This paper was prepared for presentation at the 2008 SPE International Symposium and Exhibition on Formation Damage Control held in Lafayette, Louisiana, U.S.A., 13–15 February 2008.

Abstract

Migration of formation fines has been shown to cause production decline in many wells, especially for sand production wells in heavy oil reservoir. Filter cakes in wire wrapped liner, which were formed by the attachment of viscous crude oil blended with formation fines, may block the flow paths of viscous oil. The solution to this problem is appropriate treatment to mitigate this type of formation damage.

In this paper the performance at laboratory-scale of a new type of agent for formation damage mitigation is presented and some guidelines for its application including the injected pore volume and injection concentration are provided.

The mechanism for damage mitigation with this type of agent in heavy oil reservoir was introduced in detail, it mainly include that this type of agent can reduce interfacial tension between crude oil and water and change the wettability of rock surface, which may lead to the breakaway of resins and asphaltenes attached to the rock surface.

By simulation experiments and core flood tests the effectiveness of this type of agent to mitigate the damage in heavy oil reservoir was identified. Simulation experiment results show that, damage mitigation in cores with the permeability higher than 1μm^2, is more effective than those with the permeability lower than 1μm^2, and core flood experiment results also indicate that this type of agent with the concentration of higher than 5% can remarkably increase recovery factor for cores with the permeability higher than 1μm^2. Finally some results on the behaviour of its application in heavy oil reservoir are presented.

Introduction

At present, treatment of oil and gas wells with chemicals and biological enzymes are widely practiced to stimulate the production rate of the wells (Harold, 2003, McRae, 2004, M.A. Siddiqui, 2003, M.B. Al-Otaibi, 2004), principally through the removal of production related damages or by increasing the permeability or conductivity of the rock matrix with natural or induced fracture. Also some chemical agents produced by enzymes in oil or gas well can increase water injection, and control water cut (e.g., water shut-off and profile adjustment) as well as sands. Biological enzyme, a new type and efficient plug-removal agent, shows good application results in such countries as Venezuela and Indonesia, etc. Also very good results have been obtained in wells in China (Qin, 2002).

The enzyme used in this research possesses following superiorities (Qin, 2002, RadEx Technology):

- Made from DNA microbes, chosing DNA nutrition as a protein base and biological liquid enzyme as non living catalyst which facilitates the entire biological reactions.
- Changing rock wettability, where oil is trapped among the clusters of rocks and initially difficult to extract, could be produced.
- Neither affected by pH and salinity of the formation fluid, nor affected by reservoir temperature and pressure.
- When it is applied into formation, it would not changing porosity and permeability of rocks.
- Environmental friendly, pH 5-7, non pathogenic, dissolves in water, doesn't dissolves in oil.

The production process of the biological enzyme includes that: Choosing and fostering the micro-organism that can make the oil and sand separated totally at first, and then drawing its DNA, fostering the high protein nourishing liquid, then making the protein link with DNA of the edible oil micro-organism (oil-eating microbe), and at last getting rid of the biological activation of all micro-organism, making the non-active catalyst that has ability to separate oil from sand surface.

For sand production well in heavy reservoir, part of fine sands can still be produced with oil after the operation of sand prevention. Filter cakes in wire wrapped liner, formed by the attachment of viscous crude oil blended with fine sands, may block the flow paths of crude oil. As a result, daily production capacity of oil well will decline; sometimes the filter cakes may lead to stop production, which is the most difficult problem in heavy oil reservoir production unresolved.

After biological enzyme solution extracts crude oil from sand surface, where the enzyme molecule affixes to, enzyme can make oil and sand flow separately, prevent from formation of mud cakes, and so improve the mobility of crude heavy oil. In this paper, according to the geological condition of Y8 reservoir of Shengli Oil Field, the mechanism for plug removal with biological enzyme in heavy oil reservoir was studied in detail. Research results will provide guiding principles for field application of biological enzyme.

Reservoir Characterization

Y8 reservoir, with the area of 1.3 square kilometre, whose original oil in place (OOIP) was estimated to be 89 million barrels, has argillaceous cement fine sandstones, and is a blocklike heavy oil reservoir (Qin, 2002). The main features of Y8 fault block reservoir are its high content of sulfur, high percentage of resin, and high oil viscosity. The formation has constant pressure system and a bit higher temperature system, namely, its temperature varies between 71 and 86 degrees Celsius, its pressure ranges between 17 MPa and 20MPa. The formation has the maximal permeability of 31μm^2, which results in high mobility, oil viscosity at surface condition is between 880 and 4800 mPa.s. Its density at surface condition is between 0.929 and 0.962 g/cm3. **Table.1** shows features of crude oil in Y8 reservoir.

Experiments and results

Test of Interfacial Tension (IFT)

Interfacial tension between crude oil and biological enzyme solution was measured by Type 12 interfacial tensiometer, namely KRUSS made in GmbH Inc, Hamburg, Germany. **Tabel.2** and **Fig.1** shows the results of interfacial tension test. IFT between crude oil and biological enzyme solution deceases with the increasing of concentration of biological enzyme solution, IFT reaches its lowest value when concentration of biological enzyme solution varies between 6% and 8%, then it increases with the increasing of concentration of biological enzyme solution.

Test of Changing Wettability of Rock Surface

Wettability is defined as “the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids” (Craig, 1971). When the fluids are water and oil, the wettability is the tendency for the rock to preferentially imbibe oil, water, or both. The wettability of a rock is important because it controls the location, flow, and distribution of fluids within reservoir rocks (Anderson, 1986A). Generally the following criteria are used to decide the wettability of rock.

(1) Contact Angle

The contact angle, θ, is used as a measure of the wettability of a solid surface by a fluid in contact with another immiscible fluid.

The contact angle is defined as:

$\theta = 0°$: the fluid is spreading on the solid surface (perfectly wetted),

$\theta < 90^o$: the solid is generally wetted by the fluid and the fluid is called a wetting phase.

$\theta > 90^o$: the solid is generally not wetted by the fluid and the fluid is called a non-wetting phase.

The capillary pressure characteristics of a given reservoir will impact the choice of recovery method(s) and displacement mechanisms. For instance, the displacement of oil by water in a water-wet reservoir requires a totally different process compared to the displacement of oil by water in an oil-wet reservoir. According to Laplace's equation of capillarity, the capillary pressure can be calculated by

$$p_c = \frac{2\sigma_{wo}\cos\theta}{r} \qquad \text{Equation (1)}$$

(2) Work of adhesion

Solid surfaces are present in porous media, along with fluid phases, and solid fluid interfaces contribute to fluid flow behavior and fluid distribution. Considering a drop of oil on a solid surface, the mechanical equilibrium force balance between oil, water and solid surface yields Young's equation of capillarity, using the solid surface as a convenient plane of reference.

$$\sigma_{ro} = \sigma_{rw} + \sigma_{ow}\cos\theta \qquad \text{Equation (2)}$$

Work of adhesion is the work done on the system to make the wetting liquid detached from solid surface.Work of adhesion for water phase is in the form of

$$W_w = \sigma_{ro} + \sigma_{ow} - \sigma_{rw} \qquad \text{Equation (3)}$$

inserting it into Young's equation of capillarity yields

$$W_w = \sigma_{ow}(1+\cos\theta) \qquad \text{Equation (4)}$$

For oil phase, the contact angle is $180^0 - \theta$, so work of adhesion for oil phase

$$W_o = \sigma_{ow}\left(1+\cos\left(180^0 - \theta\right)\right) \qquad \text{Equation (5)}$$

namely

$$W_o = \sigma_{ow}(1-\cos\theta) \qquad \text{Equation (6)}$$

Therefore work of adhesion for water increases with the decreasing of contact angle, while work of adhesion for oil increases with the increasing of contact angle. So it's easy to enhance oil recovery for reservoir with increasing of water wetting ability because oil film on rock surface is easy to be detached by injected water.

Several methods have been presented in the literature for determining the wettability of a rock. The three most common quantitative methods are contact angle measurements, the Amott method, and the USBM method (Anderson, 1986B). In this paper Contact angle measurements was selected to determining the wettability of the rock, because the magnitude of the contact angle gives a direct indication of the wettability of the rock. Contact angle measurements involve a water drop coming in contact with a rock surface and surrounded by oil. Oil and water are allowed to come to equilibrium and the contact angle between the water drop and the rock surface is measured.

Experiment results (See **Fig.2**) show that: (1) Biological enzyme can change the wettability for sandstone slice from weakly oil-wet to strongly water-wet in a short time, increase relative permeability to oil phase, decrease the relative permeability to water phase, so reduce water cut of produced liquid; Whereas biological enzyme slowly changes the wettability for limestone slice (See **Tabel.3**). (2) For water-wet reservoir, when oil phase is displaced by water phase (imbibition process), biological

enzyme can increase driving force, while for oil-wet reservoir, biological enzyme can decrease resistance force (drainage process), which will result in remarkably increasing of actuation, aggregation and movement of residual oil in porous media (See **Tabel.4**). (3) Biological enzyme can decrease work of adhesion for oil phase, and make easy strip off the residual oil on the surface of rock, so improve oil recovery (See **Tabel.5**).

Core Flood Experiments

Core samples for core flood experiments were man-made cemented rock samples, basic properties of core samples are shown in **Tabel.6**. The medium for experiments include the oil with relative density of 0.90148, viscosity of 70.96mPa.s (measuring at the temperature of 50^0C), and formation water with total salinity of 2817mg / L. Core flood experiments were carried out at the temperature of 75^0C and pressure of atmospherical pressure (Shen, 1995, Qin, 2002).

The experimental procedures include (1) Vacuum a core and saturate the core with formation water, then measure permeability to water phase. (2)Put the core in core holder and put it in thermostatic oven (set its temperature 75^0C), then flood the core with oil until no more water is produced. Calculate the initial water saturation, initial oil saturation, and permeability to oil phase. (3)Displace the core with injection water until 98% water cut of produced liquid; calculate the recovery factor (RF1). (4) Inject biological enzyme solution with the injected volume of 0.3 pore volume. (5) Displace again the core with water until 98% water cut of produced liquid; calculate the recovery factor (RF2).

Core flood experiment result with No.1 and No.2 core samples, whose permeabilities are less than $1\mu m^2$, shows that recovery factor didn't improve with the concentration of 1‰ and 5‰ biological enzyme solution (See **Fig.3**). In order to reduce experiment error, core flood with the concentration of 2% biological enzyme solution (i.e. No.3 core sample) was carried out (See **Fig.4**); recovery factor didn't show remarkable increment. Finally water displacement result with the concentration of 5% biological enzyme solution demonstrated that high recovery factor increment can be achieved (See **Fig.5**).

Simulation Experiments of Plug Removal

In this experiment three methods were researched to make simulation of block: (1) Agglomeration method, which is a method to simulate the deposition of resin and asphaltene in core sample at the reservoir condition. (2) Lowering temperature method, which is a way to lower the temperature in order to accelerate the deposition of resin and asphaltene. (3) Dispersion method, which is a means to increase the concentration of resin and asphaltene in core sample in order to accelerate the deposition of resin and asphaltene. Experiment results show that, on one hand it's difficult for agglomeration method to deposit large amount of resin and asphaltene in core samples in a short period, on the other hand it's hard to acquire resin and asphaltene samples added to core flooding. So lowering temperature method is feasible to be chosen to do simulation experiment (Wu, 2000).

The oil used is crude oil from Y8 reservoir; the experiment was carried out with the temperature of 80^0C. Inlet and outlet pressures and volumetric flow rates are recorded at different time, Darcy's law can be used to decide core permeability at different states (i.e., before block, after block and after plug removal), and one can evaluate efficiency of biological enzyme with the changing of permeability. The experimental procedures include (1) Using steady-state method to measure initial core permeability to brine water (K_0). (2) Using lowering temperature method to block the core. (3) Measuring the core permeability to brine water (K_1) before plug removal. (4) Inject 2 pore volumes of biological enzyme to the core sample; allow the core and biological enzyme solution to interact for 24 hours in order to remove the plug in the core. (5) Measuring

the core permeability to brine water (K_2) after plug removal.

According to results, by defining the following parameters one can evaluate the efficiency of biological enzyme for plug removal.

1) Reduce rate of permeability *RRP1*: *RRP1 = K1 / K0×100%*
2) Extent of damage *ED*: *ED= (K0- K1)/K0×100%*
3) Reset rate of permeability *RRP2*: *RRP2 = K2 / K0×100%*
4) Extent of plug removal *EPR*: *EPR = (K2 – K1) / K0 ×100%=RRP2-RRP1*

From the simulation experiment results (See **Tabel.7** and **Fig.6**), combining with IFT test result (see **Fig.1**) and core flooding experiment results (See **Fig.5**), one can determine the optimum condition for field application of biological enzyme.

Simulation experiment test results show that, plug removal in cores with the permeability higher than 1μm2, are more effective than those with the permeability lower than 1μm2. The reason is that, for the cores with the permeability lower than 1μm2, organic matter stripped by biological enzyme will congregate together to block pore throat, this is termed as Jamin effect, which will decrease relative permeability to oil phase. While for the cores with the permeability higher than 1μm2, organic matter stripped by biological enzyme can flow easily, so such cores have plug removed efficiently.

Field Applications

According to experiment results, biological enzyme was applied to plug removal in Y8 fault block reservoir in Shengli Oil field, SINOPEC. According the geological condition and predicated incremental oil rate, one can decide the injected pore volume of biological enzyme solution, for vertical well the injected pore volume varies between 0.3 m^3 and 0.5 m^3 per meter layer, while for horizontal well the injected pore volume is from 10 percent to 20 percent of that for vertical well. **Tabel.8** shows the main results of field application. Application results demonstrate that it's efficient for biological enzyme to remove plug, which is caused by deposition of resin and asphaltene, in heavy oil reservoir, at the same time daily oil production rate can be improved remarkably.

Conclusions

The principles for plug removal with biological enzyme solution in heavy oil reservoir include biological enzyme can both reduce IFT between oil and water and change the wettability of rock surface : (1) Biological enzyme can change the wettability for sandstone slice from weakly oil-wet to strongly water-wet in a short time. (2) When oil phase is displaced by water phase, biological enzyme can increase displacing force for water-wet reservoir (imbibition process), while for oil-wet reservoir, biological enzyme can decrease resistance (drainage process). (3) Biological enzyme can decrease work to adhesion for oil phase.

Core flood experiments show that biological enzyme with the concentration of higher than 5% can remarkably increase recovery factor for cores with the permeability higher than 1μm^2.

Simulation experiments of plug removal with biological enzyme for cores with the permeability higher than 1μm^2, is more effective than those with the permeability lower than 1μm^2.

Combining IFT test with core flood experiments and simulation experiments of plug removal, one can determine the optimum condition for field application of biological enzyme.

Nomenclature

C = concentration of biological enzyme solution (dimensionless, by volume)

θ = contact angle (degree)

p_c = capillary pressure (Pa)

K_1 = permeability of core after blocking (μm^2)

W_o = work of adhesion for oil phase (mN/m)

K_0 = initial permeability of core (μm^2)

K_2 = permeability of core after antiblocking (μm^2)

W_w = work of adhesion for water phase (mN/m)

σ_{wo} = interfacial tension between oil and water (mN/m)

r = radius of capillary tube (m)

Acknowledgements

The authors would like to thank Y.Guo for the time he committed to helping with the simulation of these experiments. His advice and support made this portion of the paper possible. We also acknowledge Dongxin Oil Company, Shengli oil field, SINOPEC for its permission to publish this paper.

References

1. Anderson, William G. [A], Wettability Literature Survey – Part 1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability, *JPT, October 1986, pg 1125 – 1144.*
2. Anderson, William G. [B], Wettability Literature Survey – Part 2 Wettability Measurement, *JPT, November 1986, pg 1246 – 1262.*
3. Craig, F.F., The Reservoir Engineering Aspects of Waterflooding; *monograph series (1971), SPE,* Richardson, TX.
4. Harold D. Brannon, Robert M., Paul S.Carmon et al, Enzyme Breaker Technologies: A Decade of Improved Well Simulation; *SPE 84213, SPE Annual Conference and Exhibition held in Denver, U.S.A, 5-8 October 2003.*
5. J.A McRae, S.M. Heath, C.Strachan et al, Development of an Enzyme Activated, Low Temperature, Scale Inhibitor Precipitation Squeeze System; *SPE 87441, the 6th international Symposium on Oilfield Scale held in Aberdeen, UK, 26-27 May 2004.*
6. M.A. Siddiqui, H.A. Nasr-EI-Din, Saudi Aramco, Evaluation Of Special Enzymes As A Means To Remove Formation Damage Induced By Drill-In Fluids In Horiztonal Das Well In Tight Reservoir; *SPE 81445, SPE 13th Middle East Oil Show And Conference held in Bahrain 5-8 April 2003.*
7. M.B. Al-Otaibi, H.A. Nasr-El-Din, and M.A. Siddiqui, Saudi AramcoChemical Treatments to Enhance Productivity of Horizontal and Multilateral Wells: Lab Studies and Case Histories; *SPE89467, 2004 SPE/DOE Fourteenth Symposium on Improved Oil Recovery held in Tulsa, Oklahoma, U.S.A., 17-21 April 2004.*
8. Pingping Shen, Experimental Technology of Petrophysics*; Oil Industry Press, P.102-104, 1995.*

9. Qin Wang, Mincheng Zhao, Honxia Meng, Use of Enzyme Preparate Greengyme for Removing Inorganic-Organic Precipitate From Sanding Heavy Crude Oil Well; *Oilchemistry, Vol.19, No.1, P. 24-26, February,2002.*
10. RadEx Technology, http://www.radex.no/, Apollo Greenzyme - a Unique Technology to Improve Oil Recovery.
11. Zenggui Wu, Bingshan Ju, Zhi'an Luan, A systematic study of the formation damage caused by asphaltene deposition in Chengbei oil field; *Petroleum Exploration and Development, Vol.27, No.5, P. 98-101, October,2000.*

SI Metric Conversion Factors

D × 9.869 233 E – 01 = μm^2
$g/cm^3 \times 1.0$* E – 03 = kg/m^3
md × 9.869 233 E – 04 = μm^2
mN/m×1.0* E – 03 = N/m
mPa.s × 1.0* E – 03 = Pa.s

* Conversion factor is exact

Acronyms and Abbreviaions

ED = extent of damage (dimensionless)
EPR = extent of plug removal (dimensionless)
IFT = interfacial tension
RF1 = recovery factor for first flooding (dimensionless)
RF2 = recovery factor for second flooding (dimensionless)
RRP1 = reduce rate of permeability (dimensionless)
RRP2 = reset rate of permeability (dimensionless)

Table.1: Main features of crude oil in Y8 reservoir

Fromation	Density g/cm^3	Viscosity mPa.s	Freezing Point ℃	Wax%	Sulfur%	Asphalt%	Resin%
S_2^5	0.9300	1130	21	3.85	1.511	1.741	35.63
S_2^6	0.9302	1642	19	4.89	1.824	0.915	36.75
S_2^7	0.9392	4735	15	3.79	1.881	0.255	38.31

Table.2: Interfacial tension between oil and biological enzyme solution

No	concentration	IFT (mN/m)
1	0	19.36
2	2%	2.39
3	4%	1.49
4	5%	0.01
4	6%	0.10
5	8%	0.11
6	10%	3.95

Table.3: Effect of biological enzyme on rock surface wettability

Slice type	Time (minute)	0	5	300	1800	Reduce rate
Sandstone	θ (degree)	94.35	8.89	2.62	0	100%
Limestone		133.64	132.49	124.77	115.76	13.38%

Table.4: Effect of biological enzyme on capillary pressure according to Equation (1)

Initial state		Final State (after 30 hours)	
θ (^{0})	$P_c(P_a)$ $\times 10^4$	θ (^{0})	$P_c(P_a)$ $\times 10^4$
133.64	-2.67	115.76	-0.01
94.35	-0.29	0	0.2

Note: "-" means resistance force, "+" means driving force

Table.5: Effect of biological enzyme on work of adhesion according to Equation (6)

Initial state		Final State (after 30 hours)	
θ (°)	W_o (mN/m)	θ (°)	W_o (mN/m)
133.64	32.72	115.76	0.14
94.35	20.83	0	0

Table.6: Basic properties of core samples used in core flood experiments

No	Diameter (cm)	Length (cm)	Porosity (%)	Permeability (md)	Concentration
1	2.490	6.570	15.7	189.6	5‰
2	2.536	7.456	14.2	123.2	1‰
3	3.0	17.0	36.0	850	2%
4	3.0	17.0	38.6	1030	5%

Table.7: Results of simulated plug removal with biological enzyme

No	K_0(D)	K_1(D)	K_2(D)	C	RRP1	ED	RRP2	EPR
1	0.360	0.0697	0.0382	10%	19.36%	80.64%	10.61%	-8.75%
2	0.474	0.0656	0.0398	10%	13.84%	86.16%	8.40%	-5.44%
3	0.907	0.0034	0.0134	10%	0.37%	99.63%	1.47%	1.10%
4	1.370	0.0138	0.355	10%	1.01%	98.99%	25.91%	24.90%
5	1.635	0.0312	0.194	10%	1.91%	98.09%	11.87%	9.96%
6	2.307	0.950	1.701	8%	41.18%	58.82%	73.73%	32.55%
7	2.503	0.860	1.388	2%	34.36%	65.64%	55.45%	21.09%
8	2.872	0.921	1.714	10%	32.07%	67.93%	59.68%	27.61%
9	2.912	0.930	1.657	13%	31.93%	68.06%	56.93%	25.00%
10	2.958	1.394	2.234	6%	47.13%	52.87%	75.52%	28.39%
11	3.100	1.101	1.786	14%	35.51%	64.48%	57.63%	22.12%
12	3.224	1.608	2.380	4%	49.88%	50.12%	73.82%	23.94%

Table.8: Results of well treatments of Y8 reservoir

Well	Daily Production rate before plug removal			Daily Production rate after plug removal		
	Liquid (m^3)	Oil (m^3)	Water cut	Liquid (m^3)	Oil (m^3)	Water cut
Y8 - 52	0	0	30 ~ 50%	22	21.1	2%
Y8 - 44	0	0	0	3.4	3	12%
Y8X4	0	0	0	8.7	7.6	13%
Y8 - 33	36.6	17.9	51%	48.0	30.7	36%
Y8 - 42	32.5	12.3	63%	53.2	22.5	57.7%
Y8 - 22	8.4	6.7	20%	9.3	7.2	22%

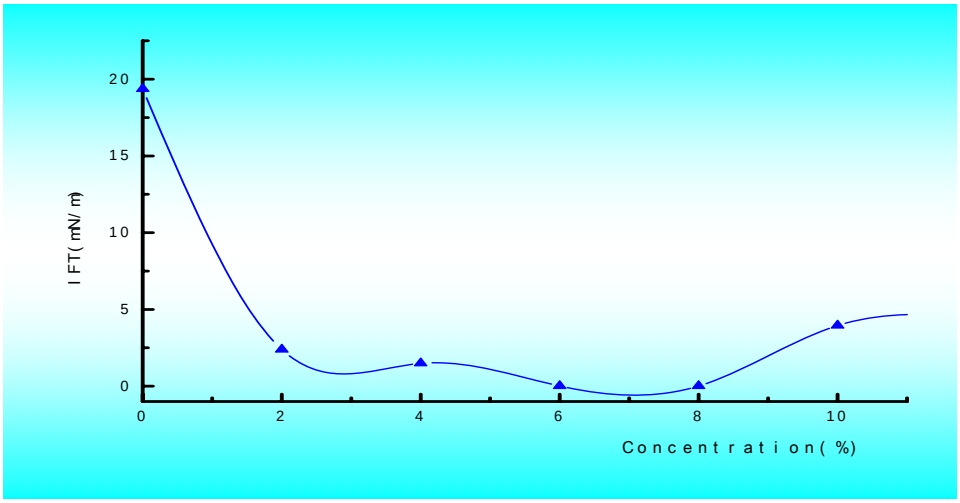
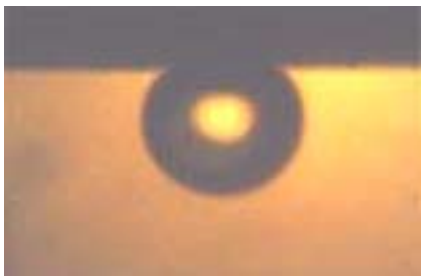
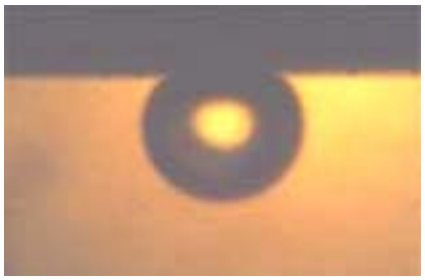


Fig.1 Relationship between concentration of biological enzyme and IFT



Limestone (initial): θ =133.64°

Sandstone (initial): θ =94.35°

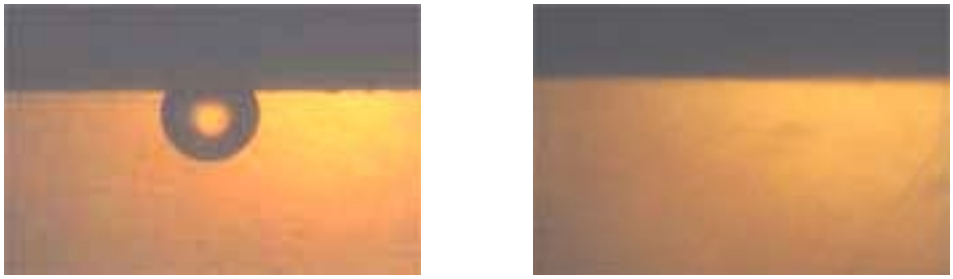


Limestone (5minutes): θ =132.49°

Sandstone (5minutes): θ =8.89°

Limestone (5hours): θ =124.77°

Sandstone (5hours): θ =2.62°



Limestone (30hours): θ =115.76° Sandstone (30hours): θ =0°

Fig.2: Wettability changes with time for limestone and sandstone

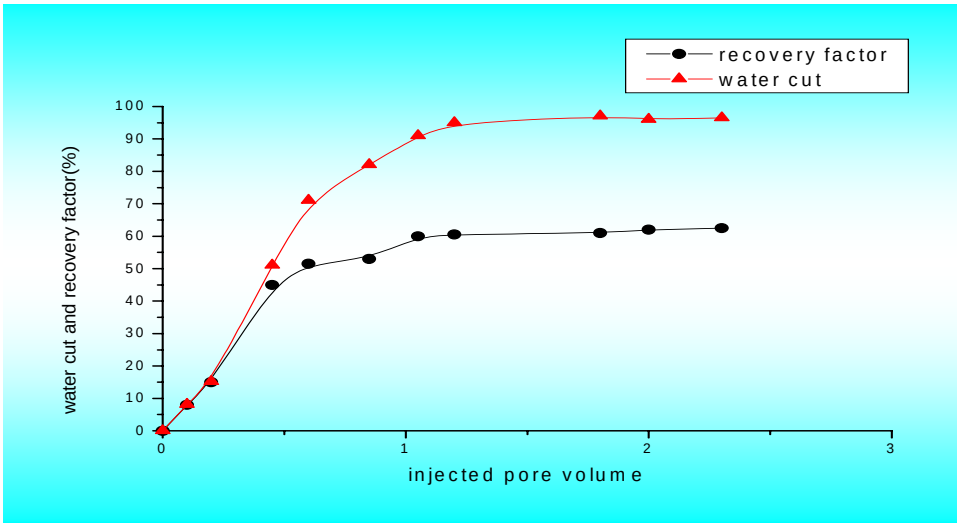


Fig.3: Recovery factor and water cut of No.1 core sample flooding with biological enzyme concentration of 5‰

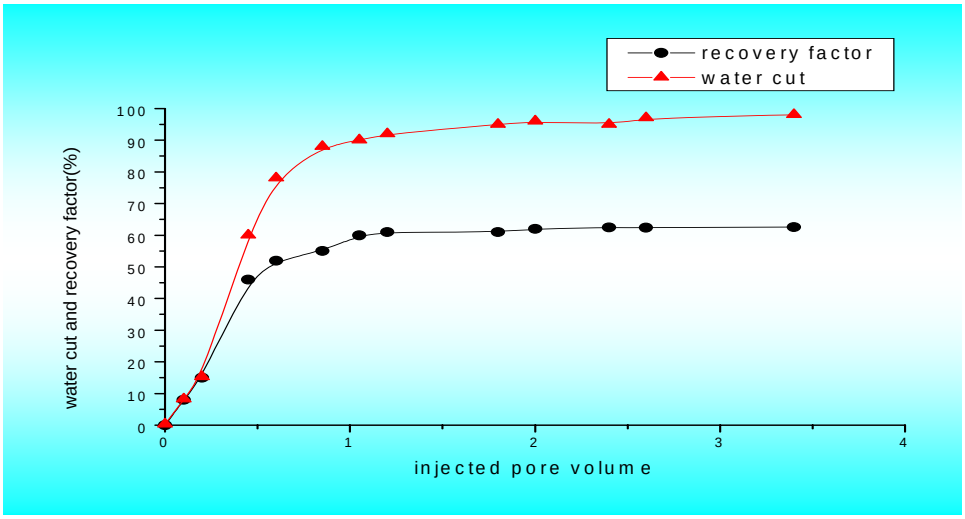


Fig.4: Recovery factor and water cut of No.2 core sample flooding with biological enzyme concentration of 2%

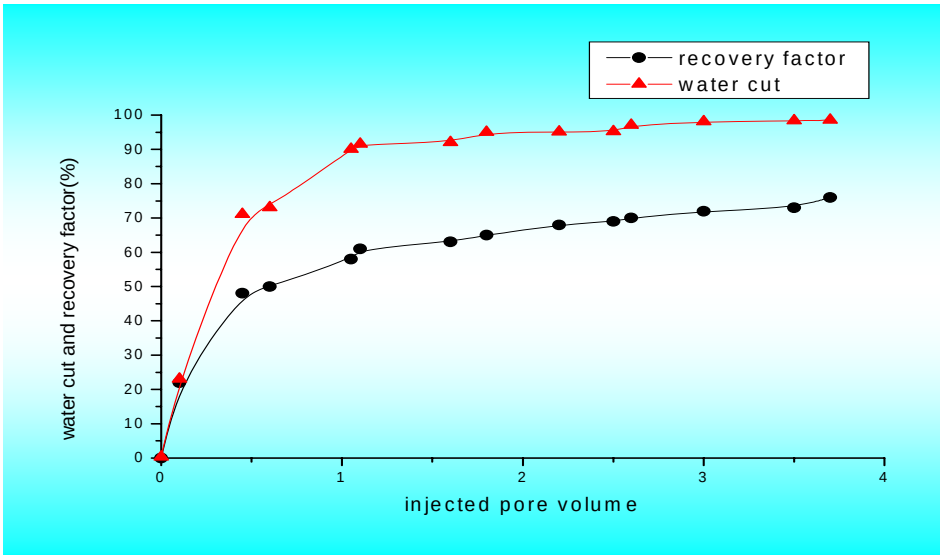


Fig.5: Recovery factor and water of No.3 core sample flooding with biological enzyme concentration of 5%

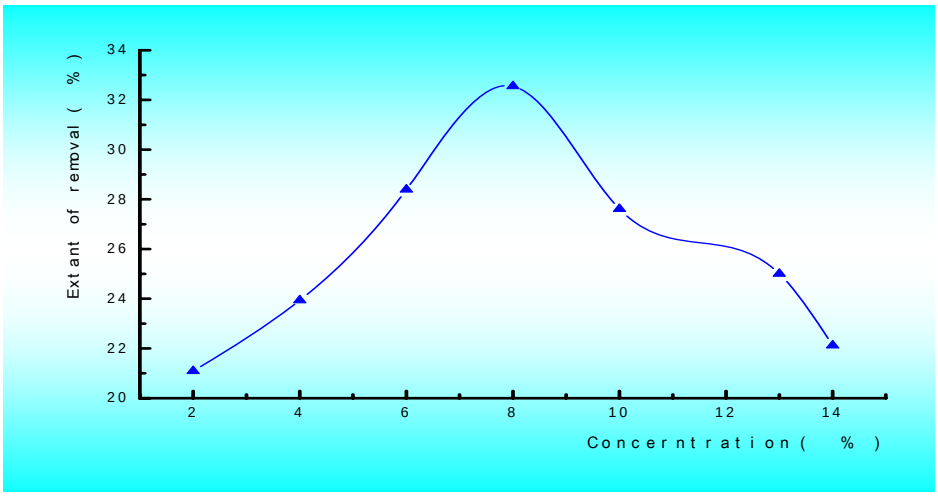


Fig.6: Relationship between concentration of biological enzyme and extent of plug removal (EPR)