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Title: Application of physical fields and chemical agents in oil production

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ABSTRACT

The dissertation work of MSc entitled “The Application of physical fields and chemical agents in oil production” consists of four chapters and was dedicated to the application of physical fields which increase the efficiency of applied chemical agents in the main processes of oil and gas fields development.

In the first chapter are described main processes having an effect on oil recovery intensity including primary preparation of production fluids (oil, gas, water) under surface conditions that is ultra sound application for increasing the surface active agents influence and intensification of emulsion breakdown using ultrasound waves.

The second chapter has analyzed and studied physically of the magnetic field that increases of influence of the chemical agent for enhance the recovery factor as one of the main and actual production parameter.

In the third chapter there is discussed the scientific analyses of applied agents permeability and conductivity factors and enhancement of their efficiency in the water out reservoirs.

Application and perspective of nanotechnology method as one of modern technology are described in the last chapter.

In the dissertation, were analyzed physical processes, based on application of the physical methods and modern scientific estimation of oil recovery.

References are shown.

Xülasə

“Neftçıxarmada fizikivəkimyəvi sahələrin tətbiqi” mövzusunda magistr dissertasiya işi 4 fəsildən ibarət olub, neft yataqlarının işlənməsində tətbiq edilən kimyəvi reagentlərin effektivliyini artıran fiziki sahələrin tətbiqi məsələlərinə həsr edilmişdir.

Dissertasiya işinin birinci fəslində neftçıxarmanın intensivliyinə təsir edən əsas proseslərdən biri olan neft quyularından çıxarılan flüidlərin (neftin, qazın, suyun) mədən şəraitində ilkin hazırlanması prosesinin, yəni neft-su emulsiyasının parçalanmasının intensivliyinin artırılması üçün tətbiq edilən səthi aktiv reagentlərin təsirinin artırılması üçün ultrasəs dalğalarından istifadə edilməsinin fiziki təsirindən və bu prosesdə yaradılmış ultrasəs dalğaların emulsiyanın parçalanmasının intensivləşdirilməsindən bəhs edilir.

İşin ikinci fəslində neft yataqlarının işlənməsində əsas və aktual parametr olan layın neftvermə əmsalının artırılması üsulunda tətbiq edilən kimyəvi reagentlərin təsirini daha da artırmaq üçün tətbiq edilən maqnit sahəsinin fiziki mahiyyəti öyrənilmiş və maqnit sahələrinin layın neftvermə əmsalına təsirinin mahiyyəti elmi əsaslarla araşdırılmış və təhlil edilmişdir.

Dissertasiyanın üçüncü fəslində sulaşmış neft laylarında fiziki-kimyəvi üsulların neftveriminə təsiri və tətbiq edilmiş reagentlərin effektivliyinin artırılması və reagentlərin təbii parametrləri olan keçiricilik və məsaməlik əmsallarından asılı olaraq neftverməyə təsiri prosesləri öyrənilmiş və onların elmi analizi verilmişdir.

İşin sonuncu – dördüncü fəslində müasir texnologiya olan nanotexnologiyanın neftçıxarmada tətbiqi və bu üsulun perspektivliyi öyrənilmişdir.

Dissertasiya işində təhlil edilən proseslər neftçıxarmada müasir tələblərə elmi yanaşmanın mahiyyətinə uyğun olmaqla fiziki proseslərdən istifadə edilməsinin əhəmiyyəti təhlil edilmişdir.

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INTRODUCTION

Modernization and implementation of new methods in technological processes of oil recovery make possibilities for successful development of oil industry that is strategic element of Azerbaijan economy. Field processing of crude oil and efficiency of enhanced oil recovery(EOR) are current questions among numerous problems of oil production.

Practically, various chemical agents are applied for oil processing and EOR.

Such current questions as physical, ultra sonic and constant magnetic fields are investigated and applied for stimulation of used chemical agents in technological process and decreasing of cost per one ton of oil.

The purpose of work consists of increasing the efficiency of oil preparing processes and oil recovery in order to reduce chemical agent utilization.

Basic objectives of the work:

1. Analysis of ultrasonic and magnetic field impacts on emulsion system during oil preparation and oil recovery process.
2. Studying of the combination of physical fields and chemical agents for these processes.
3. Investigation of thermo-ultrasonic and magnetic actions to these processes.

Solution methods in the given work are decided by the way of authors' literary analysis.

CHAPTER 1. THE ARGUMENTATION OF PRACTIBILITY OF PHYSICAL FIELDS AND CHEMICAL AGENTS APPLICATION FOR STIMULATION THE TECHNOLOGICAL OPERATIONS IN THE PROCESS OF OIL PREPARATION

1.1 The analyses of oil preparation question study state

Many oil fields in Azerbaijan are onshore located and few fields are offshore. Onshore fields have long period of production history with high water cut and viscosity.

Generally oil with high viscosity are non-Newtonian fluids [1].

In such cases, oil field development, preparation and transportation make additional difficulties. Non-homogeneous multiple emulsions are originated from such kind of oil wells.

Complexity and variety of multiple emulsions is predominated by the presence of different heavy hydrocarbons such as resin, asphaltene and paraffin. Also, wide of polymer and surface active agents are used in oil production.

Emulsions are represented as dispersion system as two fluids non-soluble or partially soluble with each other and one of them is dispersed in other as line droplets. Emulsion properties are closer to colloid solutions properties and related to micro heterogeneous systems. And particles are unconscious under microscope vision. During post development period, high water cut producers are characterized by high concentration of contaminations.

High concentration oil contamination makes difficulties during preparation, transportation, storage and refining.

Occurrence of contaminants in effusive oils increases its consistency and requires application of demulsifier.

Emulsion is characterized by high level of consistent dispersion therefore this problem is detail analyzed and it makes possible to choose demulsifier and oil emulsion destruction conditions that increases economic efficiency of the processes of marketable product preparation and transportation to consumer [2].

Available investigations in the area of oil preparation shows that level of emulsion concentration strongly reacts upon emulsion consistency. More concentrated emulsions are less consistent, i.e. which have equal volume of oil and water. Emulsion consistency depends on such factors as physical and chemical properties of oil and water, methods and conditions of oil wells operations. In practice, demulsifiers are selected and applied depending on their character.

Recently, different type of demulsify agents have been made and applied. Development of compound action agents such as oil demulsifier and corrosion protection of equipment is one of these sphere directions.

Domestic and foreign demulsifiers were analysed on oil emulsion of OPGD “Azneft” [3]: proxanole, oxyphos, diproxamin, sulphanoole, proxamin, “XEXST” firm, (ERG), “Neweelks” (Japan), Dissolvan 441, senarol and alkane.

The results of some investigations of chemical demulsification agents are shown in table 1 [4].

The results of chemical agents demulsification properties
Investigations carried out oil OPGD “Azneft”

OGPD	Head grade of water in oil, %	Name of chemical agents	Agent concentration	Heating temperature	Remaining content of water in oil, %
1	2	3	4	5	6
after A.D.Amirov	18,4	Dissolvan 4490	80	342	1,8
			100	342	0,8
	18,4	Progalite	80	342	3,8
			100	342	6,0
	18,4	Separol-25	80	342	6,4
			100	342	5,6
	18,4	Dissolvan- 4411	80	342	1,4
			100	342	0,5
“BibiEybat oil”	12,7	Dissolvan- 4411	50	333	5,3
			100	333	2,1
			150	333	0,9
	12,7	Proxamin 385	50	333	3,9
			100	333	1,8
			150	333	0,9
	12,7	Progalite	50	333	11,2

			100	333	9,1
			150	333	6,3
	12,7	Dissolvant	50	333	11,2
		411	100	333	9,1
			150	333	6,3
	12,7	Separol	50	333	2,8
		3337	100	333	7,9
			150	333	0,9
“Binagadi oil”	10,8	Dissolvant	50	345	0,7
			100	345	0,9
			150	345	0,6

Carried out analyses of agents are indicated that a number of agents do not show a presence of consistent demulsification in the face of positive results of field laboratory tests.

Considering high cost of foreign agents is required to develop the technological methods to stimulate demulsification properties of agents and to improve the process of demulsification in order to preserve its specific rate. It is possible to combine expense of different agents with physical fields.

The laboratory analyses show that there are different technologies those are based on application of physical fields and its combinations can increase an efficiency of technological operations on production, gathering and preparation of well production and improving the reservoir recovery factor.

The analyses carried out in Oil Academy render the direction of quit academician A.Kh.Mirzadzadeh, showed the possibility of unitizing of a number of technological processes in oil production applying physical fields [5,6]. The principals described in this work are based on three “n”: nonlinearity, non uniformity and non homogeneity.

1.2. Sensitivity analyses of ultrasonic machining upon oil preparation process

At present, ultrasonic machining has a wide range of application; a number of fields of modern physics, chemistry industrial technologies are found by ultrasonic.

The first ultrasonic analyses have been carried out last century and were developed as a sphere of technology science for last thirty years. Ultrasonic has an important role in scientific researches of fluids and gases. Ultrasonic is a flexural vibration which exceeds $(1.5\div 2) \times 10^4$ kHz (15-20) kHz.

Depending on wave length and frequency, ultrasonic has a specific feature of analyses, reception, spread and application.

Cavitation is an important effect of ultrasonic field. Cavitation is origin of pulsatory bubbles mass that are fill up by stream, gas or its mixture, at that accelerate different physical and chemical processes [7].

In 1956-1957 ultrasonic generators have been used in Ishinbay oil. The generator action was based on that fluid jet running across the generator. It generates ultrasonic tones to prevent deposition of paraffin inside pipe walls.

The work authors [8] used physical methods for oil dehydration and desalinization.

The basis of the work contain soil demulsification under impulsive electric charges action that originates shockwaves, pressure surge and temperature kick of sharable medium. It is known that surface equipment of oil gathering and storage first take place the delivery fluid, containing paraffin-resin matters, gas, sulfur, waters with dissolved salts besides oil.

Fluid-inflows are usually in emulsified state. Therefore, the crude oil treatment is required before oil transportation.

Ultra sound application in the oil gathering and preparation system can lead to stability augmentation. Example: application of ultra sound for oil demulsification shows a considerable intensification of the processes [9,10].

It should be noted that current technological operations of oil preparation to transportation are inconceivable with-out oil demulsification by chemical agents. At present, various types of demulsifiers are produced by the industry.

According to natural demulsifiers, they are classified on entrance bushing and oil soluble. Oil-soluble demulsifiers and agents of double action feature are widely used.

The efficiency of application: Different types of agents are depending on oil qualitative composition and emulsion water content. An improvement of demulsification processes to rundown unit rate is possible at the cost of combination of different agents with physical fields and its combinations.

The capability of agents stimulation by physical fields allow to attract low efficient and environmentally acceptable agents to the process of demulsification. In order to analyses the effect of ultrasonic waves on the process of demulsification, experimental investigations were carried out in the following mode [4]. Water-soluble emulsions were blended with different additions of agents, checking samples have been tested and prepared solutions are affected by ultrasonic waves. Run time for all analyses was identical. Later on influence of ultrasonic waves upon water oil agent mixture, time of segregation and oil dehydration depth was retested. The results of “Alcan” and “Disolvan” agent effecting on the process of oil demulsification at temperature of 303 K are shown on the figures 1 and 2.

As it is shown from the drawings the efficiency of the process of demulsification with an agent under ultrasonic impact is greater.

It should be noted that activation of agents demulsifier properties by physical field render it possible to eliminate the rate of demulsifiers and use it instead of expensive foreign agents. The possibilities of activation of oil production technology on the base of combined effect of chemical agents necessitate transportation expenses record.

Cutting the cost for oil transmission, associates with decreasing of hydraulic resistance in agent minor additives. Laboratory tests of thermo-ultrasonic treatment on the process of chemical demulsification were carried out [4].

Assigned task have been solved by heating the oil preliminary treated with demulsifier and ultrasonic field effect at the same time.

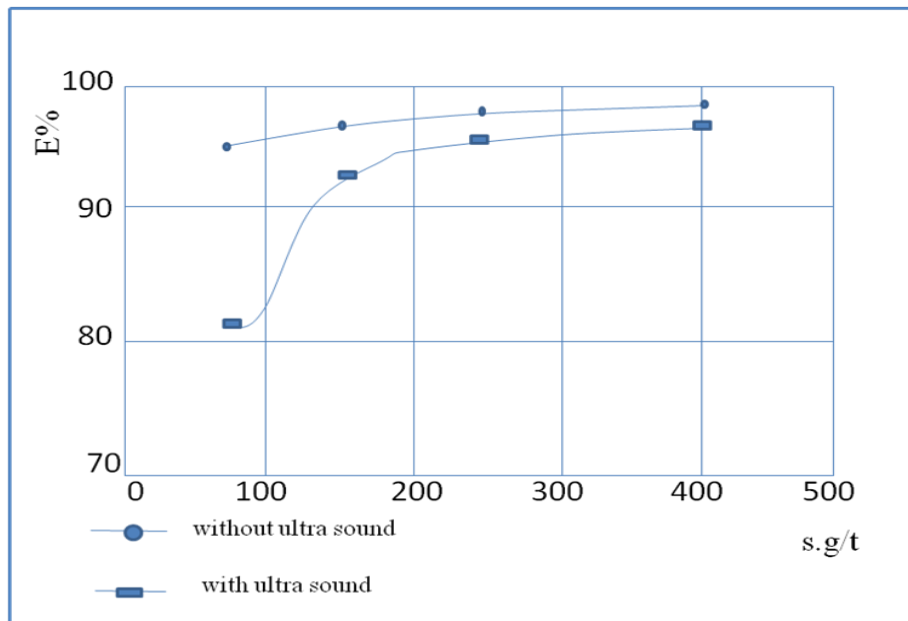


Fig.1. The efficiency of oil demulsification using “Alcane” agent and its combination with acoustic field.

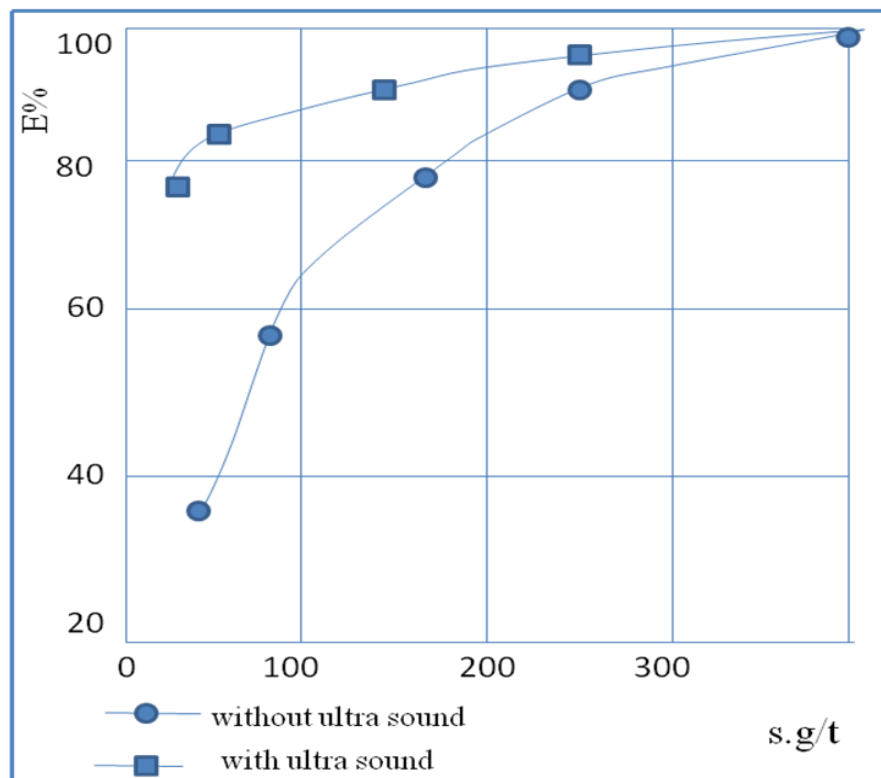


Fig.2 The efficiency of oil demulsification using “Dissolvan” agent and its combination with acoustic field.

The matter of the work is that the efficiency of vibration when heating of emulsion oil preliminary treated by demulsifier is improved.

The methods of emulsion structure destruction using such demulsifiers as “Disolvan”, “Separil”. “Alcan” and their modification are widely used.

Many investigations were carried out for increase demulsification ability of industrial demulsifiers both hydrophilic and hydrophobic emulsions.

For the purpose of demulsifiers flow rate reducing and emulsion destruction speeding process efficiency increase investigation tests of UZDN-1 ultrasonic generator were carried out.

The results of ultrasonic waves influence on emulsion oil are shown in table 2.

As it is shown from the table, the quantity of residual water in emulsion oil in the quantity of 150 and 300 g/t under ultrasonic generator during 60 min. was 0,5 and 5% accordingly. Besides, it was determined by laboratory investigations that water segregation from oil depends on ultrasound effecting time. The effect of oscillation facilitates bringing of agent molecular to phase boundary, releasing and destroying dispersion system structure.

Table 2.

The influence of ultrasonic waves on the process of chemical demulsification.

OGPU	Name of agent	Agent concentration g/t	Temperature	Time of action on US min.	Water quantity %	
					Before demulsification	After demulsification
Absheron oil	Separol,	150	338	60	11	5
	Alcan,	150	338	60	11	0,5
	Disolvan 4411	150	338	60	11	0,5
Salyan oil	Disolvan	250	328	60	58	5,5
Binagady oil	Disolvan	250	303	60	6,0	5,0

Should be noted that native and foreign literature analyses and carried out investigations show that in some cases when ultrasonic treatment of water-hydrocarbonated systems emulsion stability is observed. But stability change and residual water quantity depends on temperature level and time of ultrasonic field influence.

The results of field research of ultrasonic action on the process of chemical demulsification under 313K and different durability of wave of wave influence are shown in table 3.

Table 3.

The action time results of ultrasonic analyses on drip
Oil demulsification under T=313K.

Agent concentration, g/t	Residual water content, ultra sound action time			
	2	10	30	70
C=50	70	69	68	66,7
C=100	64	59,2	56,1	56,2
C=250	54	52	50	48,1

On investigation it was specified that activation of the process of chemical demulsification by ultrasonic effect make a stimulation impact on intensity and quantitative features of the process of chemical demulsification by ultrasonic effect make a stimulation impact on intensity and quantitative features of the process of desalinization and mechanical admixtures disengagement.

1.3. The analyses of thermic and magnetic fields on the process of demulsification.

Impacts of combined thermic and magnetic fields on the efficiency of oil demulsification process have an interest for the practical purposes [11]. For the purpose to analyze this question, authors carried out the investigations of thermic and magnetic fields and their combinations on the process of demulsification.

The dependence of water content from the temperature $B=f(T)$ is shown in the example of Surakhany emulsion oil under chemical agent (figure 3).

Numerous investigations show that temperature factor influence on segregation speed and depth depends on emulsion qualitative content. Further developments of demulsification process carried out at the presence of magnetic fields.

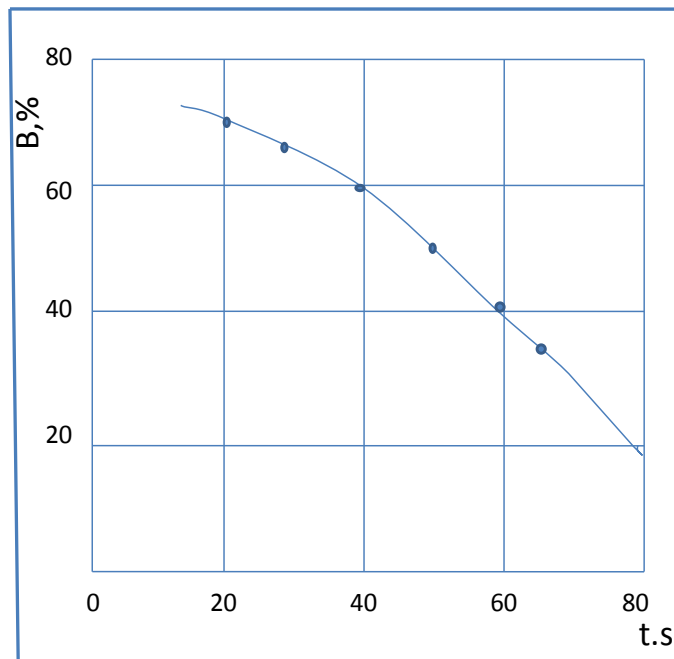


Fig.3. The dependence of water content from Surakhany oil emulsion temperature.

Emulsion systems magnification was made in electromagnetic field. For this purpose a unit has been assembled that allow implementing magnification of flow in unit under different conditions of fluid flow. The analyses show that the efficiency of paraffin emulsion systems magnetic treatment is more essential then applying the emulsions with asphaltene-paraffin agents.

The investigations results analyses show that under one and the same tension of operational force as emulsion watering increase the efficiency of the break process increase.

1.4. The stimulation of agents' properties by physical fields in the process of oil chemical demulsification.

Technological operations from oil preparation to transportation are impossible without the process of oil demulsification by chemical agents. Different organic demulsifiers are industrially produced. They are classified on water and oil soluble according to nature of action. From ecological point of view an application of water soluble demulsifiers is limited because of separated formation water is agent carried, besides the concentration of demulsifier in the water, as a rule, prevails the concentration of the agent in the emulsion volume. Oil soluble demulsifiers and the agents with double nature action are widely used. The efficiency of one or another agent application in many ways is determined by emulsion water content; by emulsion stability depends on oils quality content. Therefore technological order for agent dosage rate in water oil system is not supported and agent rate varies depending on oil quality content and hydrocarbon system components quantity content.

It was considered the possibility of application the agent combination to physical field in order to stimulate the agent demulsification properties agent rate decrease and as a sequence partially return the deficiency of expensive agents imported to the republic.

The possibility of agents' features physical stimulations allows to commend low efficiently and ecologically agents to the process of demulsification. The synergetic approach to solve the problem of oil demulsifications requires to determine the optimal conditions and modes of carried out processes. The magnetic fields of different intensity ultrasonic waves within the range of 15-37 kHz., as vibra fields with different amplitude-frequency response, laser beam of low and average intensity are considered as the physical fields that is used the process of demulsification.

The experimental investigations of magnetic field activation effect of on the process of demulsification were carried out in the following sequence: water oil emulsions were sampled and prepared, then solutions were treated by magnetic fields under flow that is corresponding flow of transition. Treatment time of all analyses was identical. After magnetic treatment of water oil agent mixture, the time of segregation and oil dewatering level were checked again. The investigation results of magnetic fields and "Alcan" agent synergetic action on the process

of oil demulsification from Salyan Oil operation object under the temperature 303K are shown in table 1.

The results of combined demulsification.

Parameters	Magnetic field intensity, e								
	0			760			1240		
	Agent concentration, g/t								
	100	150	250	100	150	250	100	150	250
The quantity of residual water after demulsification	22	14	4	19	12	0,5	14	3	0,2

Analogical tests were carried out of “Mishovdag”, “Bank of Darwin”, “Pirallahy” oil fields, differing by asphaltene-resin and paraffin matters content.

The analyses of chemical agents and magnetic fields synergetic action results shows that the efficiency of such type of action is determined by oil and emulsion initial water content but operations on demulsification should be followed by careful approach to existed conditions of magnetic field intensity rate and agent concentration.

It was determined by tests that there is possibility of ultrasonic application for oil demulsification process stimulation. Activate effect of ultrasonic wave is connected to system dispersion increase and as a sequence, contacting phase area increase.

As surface interface increase under the ultrasonic waves generation conditions, then agents delivering to phase interface boundary line improves, that stimulates the process of demulsification. The efficiency of demulsification process $E = \Delta E / W(\%)$ was estimated by the quantity of removed water $\Delta E = W_0 - W_{ci}$ from initial emulsion with W_0 water content adding the agent and treating it by magnetic field. W_{ci} – residual water content of emulsion with c_i – agent concentration, physically treated.

The results of combined action using different agent and fixed temperature conditions are shown of fig 1 and 2 as $E = f(c)$ dependence.

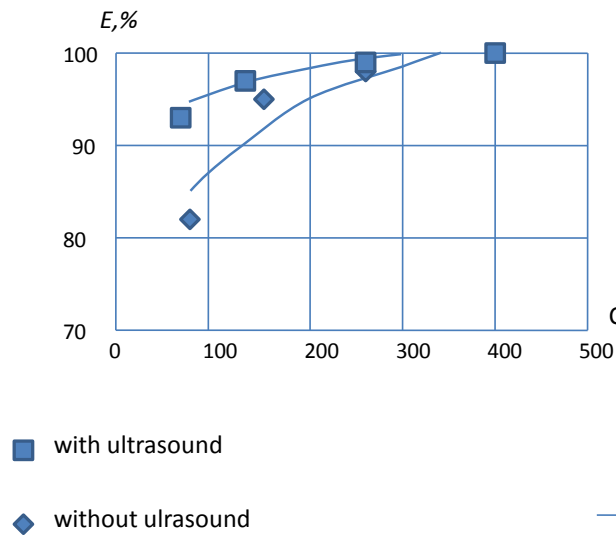


Fig.1 The efficiency of oil demulsification using "Alkan" agent and its combination with acoustic

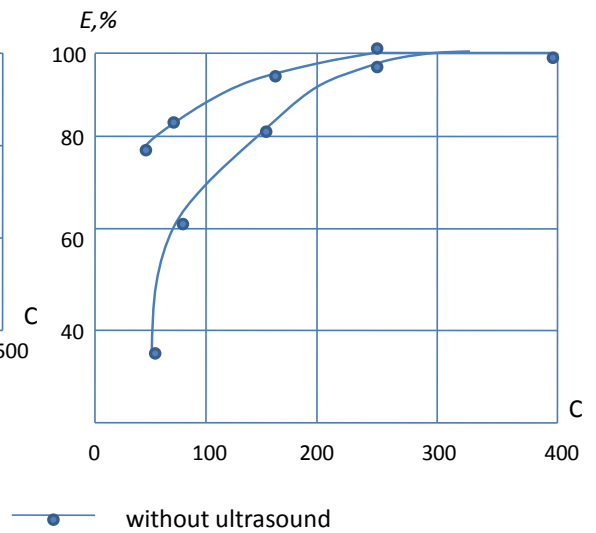


Fig.2 The efficiency of oil demulsification using Dissolvan 4411 agent and its combination with acoustic field.

Fig.1.The efficiency of oil demulsification using "Alkan" agent and its combination with acoustic field.

Fig.2. the efficiency of oil demulsification using "Dissolvan 4411" agent and its combination with acoustic field.

It should be noted that for the mentioned oils there is definite limited concentration or measuring rate where the best results are achieved.

The excess of measure of chemical agents over the essential one has not influence on demulsification parameters but leads only to oil preparation process appreciation.

The results of combined demulsification using "Dissolvan 4411" agent and acoustic field efficiently estimates depending on ultrasound action rate are shown on fig.3. the analyses of these data shows that measures on combined demulsification systems specifications closely picking optimal dosage and action frequency for each specific case.

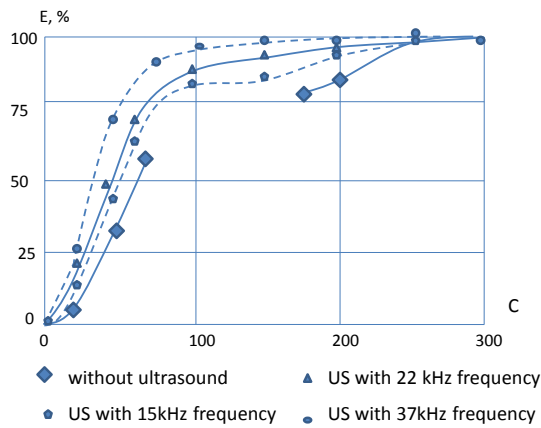


Fig.3 The dependence of combined demulsification efficiency from ultra sound frequency.

The tests carried out using “Separol” agent showed that in $E=f(c)$ dependence there is extremal point, characterizing reasonable concentration of the agent down to the limit. That concentration on “Kursangi” oil field was 300-350g/t. being higher than that rate the reverse effect was observed.

The same qualitative results for dewatering process kinetics were obtained at oils combine demulsification by “Separol” agent and acoustic field. The results of investigations are shown in table 2.

Table 2. Comparative efficiency of the process of demulcification using ultra sound treatment.

“Separol” agent concentration	Demulsification efficiency $E, \%$	
	without ultrasound	with ultrasound
75	30	48
150	54	66
250	76	79
300	80	76
400	80	63
500	61	41

The parameter of φ unit rate, characterizing (c) agent rate per efficient unit of it application (E) was considered in order to feasibility estimation of combined demulsification of “Separol” agent and acoustic field application practicability.

Representative curves $\varphi=f(c)$ for “Separol” agent is shown on fig. 4 As it is shown from figure the minimal agent concentration per efficiency unit decreases after acoustic action.

For the last time laser rays are used in the oil production practice in order to intensify thermo hydrodynamic processes. Laser rays application showed its high exploitability for oil demulsification aims. Here together with frequency-response specification of these rays, the effect of local heat supply is observed. That also promotes demulsification rate decrease.

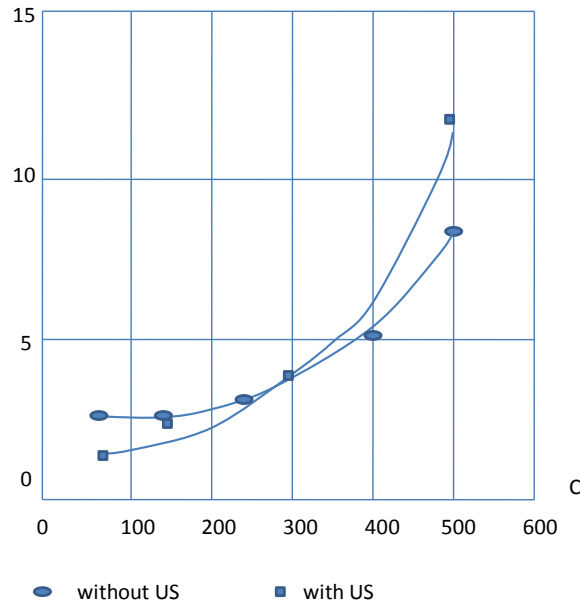


Fig.4. Regulated curve for “Separol” agent

The possibility of oil demulsification process improvement on the base of combination the chemical agents with wave action under vibration condition was studied experimentally. It was determined that following influence parameter-amplitude and vibration frequency has an impact on the process of combined demulsification kinetics. The stimulation of nonequilibrium wave processes within the range of agent low addition and also choose the optimal parameters of combined treatment applying to concrete oils is an important condition for high result achievement . As nonequilibrium level increase that can be estimated by Strukhol parameter [4], the combined demulsification process efficiency increase. Statistic analyses of numerous investigation results showed that impact frequency parameter have more influence with chemical demulsification process kinetics that impact range.

Generalized results of investigations carried out in the range of 20-80 Hz vibration frequency and 1,5-4 mm amplitude, of vibration at 60-18 sec of impact duration is shown on fig.5.

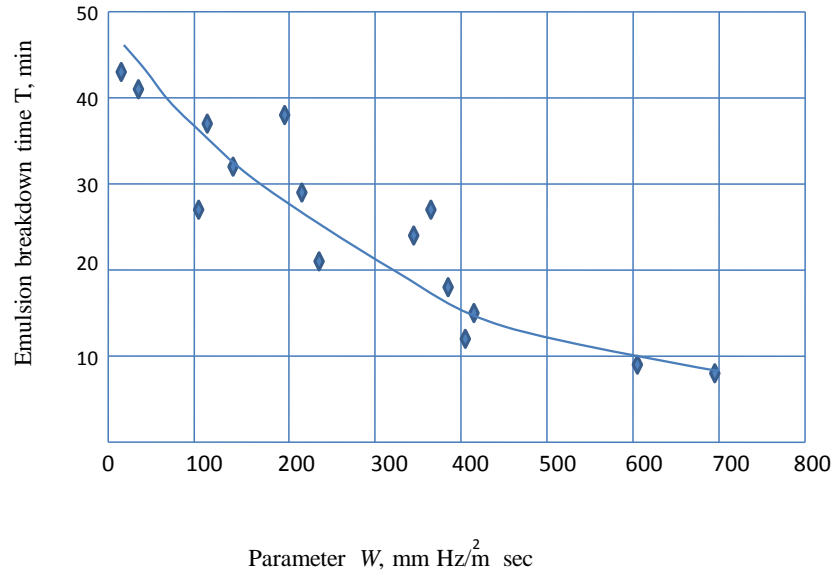


Fig. 5 The dependence of emulsion breakdown time from vibroaction parameter.

Generalized parameter W is characterized the amplitude and frequency of vibroaction per time unit on area unit. The analyses of obtained results shows that it is possible to decrease emulsion breakdown time for several times at the expense of right choice of combined operating conditions.

The results of carried out investigations allow recommending for wide application of combined methods of oil treatment and classified them as resource-saving technologies.

1.5. The ways of light fraction saving for Azerbaijan onshore fields emulsion oil preparation

At present Azerbaijan onshore fields oil demulsification is carried out by thermochemical method applying such industrial agents as dissolvan, separolreanon and their modifications. At that raw emulsion is heated to 50-70 °C. Such temperature increase loads to light fractions evaporation and losses. The investigations to prepare the ways for such losses saving were carried out. The losses at oil demulsifications on OGPD onshore field were determined and results are shown in table 1. It should be noted, that real losses are higher in comparison with mentioned in table. It is explained-that time and parameters of demulsification technology application

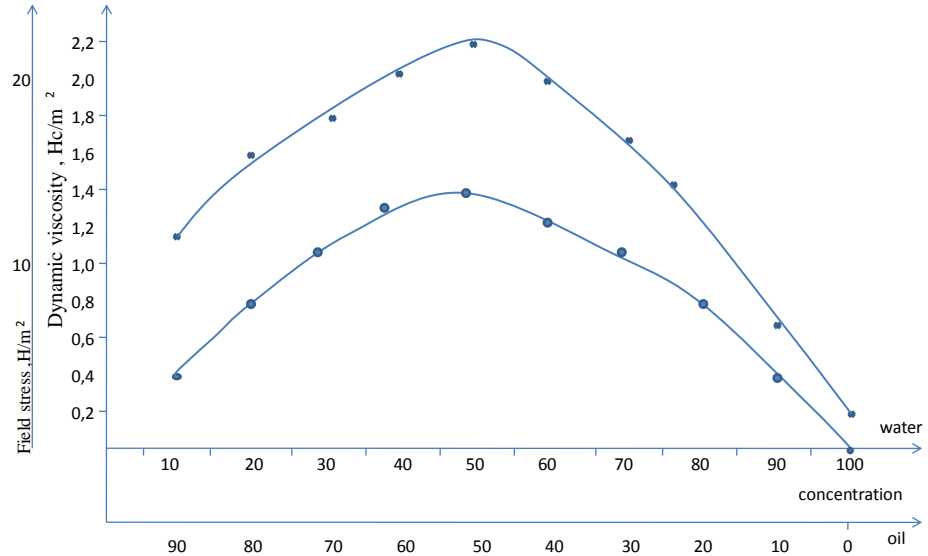
including evaporation surface area and preparation system implementation with necessary isolating equipment have considerable influence upon the losses.

Light fractions savings for different OGPD emulsions are varied in wide limits from fraction to one or higher weight percents (table1). It should be noted that even fraction savings within treated oil surface is essential.

OGPD	Emulsion heating temperature °C	Losses % (weight)
“Balakhanioil”	60	0,05
“Bibiheybatoil”	60	0,08
“Sarakhanyoil”	60	0,07
After A.Amirov	60	0,08
“Binaghadyoil”	60	0,09
After G.Z.Tagiyev	60	0,08
“Shirvanoil”	60	1,28
“Salyanoil”	65	1,28
“Siyazanoil”	60	0,39
“Muradkhanlyoil”	60	3,10
IA on onshore oil and gas production	60	0,57

Real savings are impossible by the way of demulsification process optimization because such demulsifiers are effective only at high temperature. The investigations for technological savings were carried out by the way of finding the agent having high demulsification ability at relatively low temperature (20-25 °C). Microemulsion consisted from hydrocarbon liquid (kerosene, condensate or light crude oil) low mineralized water and produced in lots demulsifiers (separol-3337 or separol 3341) is proposed as such agent. The demulsifier micro emulsion content and its general structural and mechanical properties are shown on the figure. The curve is an indicator of micro emulsion demulsificators preparation practicability. Left part of curve is characterized hydrophobic micro emulsions that should be prepared for demulsification of hydrophobic emulsion oils. Right part of curves (50% and higher of water concentration) is corresponding to micro emulsions, recommended for hydrophobic emulsion oils treatment. At that rheological properties of oil emulsion and micro emulsion should be equal.

The samples of the most natural emulsion that were treated on proposed technology were tested to check up the efficiency of proposed micro emulsion compounds. In all cases analyzed samples were carried to required concentration by micro emulsion demulsifier, i.e. the residual water content in stock oil not exceed 0,5% and in many cases only water traces were revealed. At the same time oil losses were determined.



The dependence of structural and mechanical properties of microemulsion from the concentration of water in oil and oil in water.

Fig1.

Losses data are shown in table 2 , where also oil losses decrease ratio is shown. It was determined that micro emulsion demulsification ability is low depending on temperature and industrial demulsifiers are practically low efficient at temperatures low-than 40-50 ° C. therefore proposed micro emulsion demulsifier is recommended for application only at temperature 20-25°C.

Table 2.

OGPD	Losses % (weight)	Losses decrease ratio
“Balakhanoil”	0,017	2,94
“Bibiheybatoil”	0,026	3,07
“Sarakhanyoil”	0,023	3,04
After A.Amirov	0,026	3,07
“Binaghadyoil”	0,030	3,0
After G.Z.Tagiyev	0,026	3,07
“Shirvanoil”	0,42	3,04
“Salyanoil”	0,37	3,24
“Siyazanoil”	0,13	3,0
“Muradkhanlyoil”	1,02	3,04
IA on onshore oil and gas production	0,19	3,0

Light fraction technological losses decrease when demulsification using micro emulsion demulsificator was determined after the listed method. In this regard losses decrease more than three times was achieved.

After laboratory investigations there was carried out demulsification of emulsion oil on OGPD “Surakhanyoil” using pure Separol 3337 demulsifier at heating temperature to 60°C of crude oil and as microemulsion at heating temperature to 25 °C. at that in first case non-conditioned oil with following indicators: residual bleeding 50%, chloride salt content 350 mg/gm³, mechanical impurities 0,05% was obtained. For the second case the indicators were as following: residual water content 1,0%, chloride salts 143 mg/gm³, mechanical impurities 0,03%. Effectuated calculations confirmed the laboratory analyses. Oil losses decrease ratio in that case was more than 3 times.

CHAPTER 2. APPLICATION OF CHEMICAL AGENTS IN ENHANCING OIL RECOVERY

2.1. Application of chemical agents in oil recovery.

2.1.1. State of the question.

One of the main problems in oil industry is enhancing oil reserve development rate and enhancing oil recovery (oil recovery is a relation of recovered oil quantity (Qg) to recoverable reserves Qr.i.e. $\eta=Qg/Qu$)

The experience of oil field development show that oil recovery is not exceed 40-50% by using existed methods of development under natural conditions.

High-permeability formations with low-viscosity oil are characterized by high oil recovery. Oil composition (asphaltenes, resins, naphthenic acids) has a great effect on oil recovery.

Oil recovery with high water cut is not exceed 30%.One of the main problem of low oil recovery is non-uniformity of formation.

At practice, classic method of water injection (water flooding) is widely used than EOR.

The efficiency of such method depends on quality and quantity of injected water. New methods of oil recovery as injection of thickeners into formation, water solution with surfactants, carbonated water, solvent liquids, enriched gas, dry gas of high pressure, heat water, steam and so on are used to enhance oil recovery and development rate.

For the last years such new methods as magnetic water treatment, microbiological impact, fire flooding is partially used.

To define the efficiency of new methods, it is necessary to reveal the conditions and range of each method application at different stages of development.

Depending on specific conditions, each new method has its own advantages and shortcomings.

Under different conditions, laboratory and field data are not enough to estimate completely the efficiency of new methods.

Specification of natural factors those effects on new methods efficiency are studied at literary sources. As a result of analyses, it was determined that for geological – physical factors the stage of formation depletion, oil specification (density, viscosity) and rock reservoir properties

(porosity, permeability, formation thickness, type of reservoir) have an effect on new methods development.

Oil quality is an essential value for thermal methods application. Therefore, Thermal methods are used for oils having viscosity less than 50 cp, and density 850kg/m^3 . Reservoir properties of productive strata affects on new methods efficiency.

High reservoir properties have necessary impact for doing thermal methods successfully. If the porosity is high, the more oil could be heated and less rock could be heated. Reservoir thickness is important for thermal methods. Geological heterogeneity of reservoir decrease vertical and horizontal sweep efficiency.

The efficiency of EOR methods increases as formation oil saturation increases. There is minimal oil saturation when methods application is economically feasible.

A number of other factors as reservoir condition, current reservoir pressure range, well spacing, applied chemical agents cost and so, on have an effect on oil recovery methods application. Among proposed chemical agents water-soluble surfactants are widely used to enhance oil recovery and oil reservoirs development rate.

Some of these agents even low concentration decrease water surface tension on the border of oil and reservoir surface. The matter is surfactant molecular adsorption on the border of mentioned phases. Surfactant properties are depending on specifications of hydrophilic and hydrophobic groups and their molecular balance.

In oil industry surface active agent is used for modernization of many technological processes as it is very soluble in formation waters of almost all fields of Azerbaijan, because surfactants do not leave sediments in these waters.

2.2. Physical and chemical affecting methods.

The experience of oil fields development shows that residual oil saturation can be decreased by application different methods of oil recovery enhancement only in that case if pressure gradient is enough to overcome capillary forces.

Increase of invading water filtration and viscosity speed increases pressure gradient, but practical decision of this question is one of difficult problem.

There is noted that structure of adsorption layers in the oil-rock-formation water system is one of the main factors complicating water oil drainage.

When oil driving by immiscible water solution run inter phase films could be reduced by chemical agents, injecting surface active agents able to destroy interface links between oil-rock – formation water-injected water.

Surface active agents (surfactants) are the matters able to be absorbed from solution on surface of liquid-liquid, liquid-solid body phase section with appropriate decreasing of surface energy (surface tension) on that surface.

In Azerbaijan surfactants experimental injection was begun in 1964 on Bibi-Eybat field.

For the last time because of cost retention existed surfactants application of fields became unbeneficial from economical point of view. Therefore the application of refinery waste and its compositions with surfactants consider profitable.

2.3. The study of expulsion of oil alkaline waste solution from stratum having difficult recovered oil deposits.

The achievement of maximum oil recovery from developed field, increasing their oil recovery factor is one of the main problems confronting oil men of the Republic.

For increasing oil recovery factor the main rest is done to water flooding method. It is clear that, this method will lose its significance in the nearest ten years.

However, oil recovery factor of flooded reservoirs is defined with its complex row of factors and regarding with the quality of injected water into the bed will be of importance with its oil displacing and oil cleaning properties, which would be improved with way of surface-active agent (SAA) additive to water. Method of SAA use was based on ability, on dissolution of them in water decrease of oil-water interfacial tension, change wet ability in oil-water rock system.

Recently, because of increasing prices of existing SAA, their use in field becomes less effective from economical and ecological point of view.

Connected with this, waste use is considered expedient in highly developed oil chemical industry. Sulfuric, arid waste cleaning of oily distillate neutralized solution of caustic soda is of great importance.

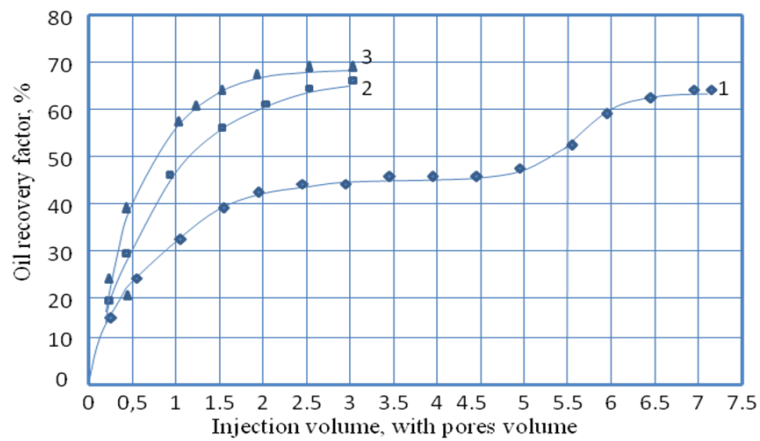


Fig.1 dependence of oil recovery factor from injection volume

1- Bed water injection and water cleaning of remained oil with solution

Researchers studied on waste indicate good oil cleaning and oil displacement ability. Best indexes obtained, on 10% waste solution in formation water (see table) that gives ground to make experiments on oil displacement with given solution. Conformably to the conditions of Kirmaky, formation horizon of Balakhani-Sabuncu-Ramani field.

Table 1

Physico-chemical features of alkaline waste

Concentration	Oil of Kirmany formation			
	Surface tension, mN/m	Density, g/sm ³	Oil cleaning ability, %	pH
0	18,8	1,011	35	6,6
0,1	14,6	1,012	45	7,2
0,3	12,8	1,012	50	7,7
0,5	11,8	1,012	55	8,0
1,0	9,6	1,013	60	8,3
3,0	4,8	1,013	75	8,5
5,0	3,7	1,0135	90	9,2
10,0	1,0	1,014	95	9,9

Experiments made to formation element model with five spot system of well position with oil use and water from given formation. Oil viscosity with addition 10% kerosene is brought to formation significance (30 MPa s), but formation water is alkaline.

the beginning of the process brings to the oil cleaning from bed and connected with water breakthrough to producing wells is delayed.

This, in case of 10% solution waste use in formation water from the beginning of the process the most final oil recovery factor is gained (68,3%). 5% less meaning of oil recovery factor was obtained on oil displacement with formation water next cleaning of oil solution waste. But, injection of 7,2 capacity pores of working agent was need, for cleaning of oil.

It is clear that, such many discharge of working agent from practical point of view it would be inexpedient. If to look through oil recovery factor on single capacity of working agent, oil displacement brings to less oil recovery. In this conditions, in case of solution waste use during whole process and its injection to porous medium on finishing water-free period, final oil recovery factor was differed 68,3% and 65,5%. Great difference was observed in water-free oil recovery in first case water-free oil recovery factor is more than 7,0%.

In fig. 2 oil recovery factor is brought from duration of process. As shown in figure experiment with oil cleaning solution waste-19 hour was given attention.

Experiment on solution waste injection after water break – through and solution use from the beginning of development are completed for 10 -11 hours.

2.4. Microbiological method in oil recovery

It is known from practice, that as far as oil fields development oil production rates decrease owing to geological and energy conditions. Water injection doesn't support total oil recovery from fields and more than half of geological reserves still remain in earth. On fields with high viscous oils their recovery factor increasingly decreases [1].

In this case different methods of bed stimulation, including physical and chemical ones are used to oil recovery enhance.

For the last years along with named microbiological oil recovery method has a wide application. That method attracts by its low capital intensity and high efficiency. Generality is an advantage of microbiological methods. In principle, they substitute at the same time a number a number of known physical and chemical methods of bed stimulation. Injection CO₂ and hydrocarbon gases, acids, polymers, surface-active agents (SAA) and so on. All mentioned composites when microbiological methods of bed stimulation have formed directly in bed and show an active influence on oil displacement.

In world different countries with high developed oil and gas production industry the methods based on injection of organic matters and specially matching microorganisms in productive strata

are developed and successfully tested [16]. AzNIPI Oil jointly with Institute of Microbiological Sciences of Azerbaijan Republic Academy of Sciences arrived out the investigations for development of oil recovery biotechnological enhancement scientific bases relating to Absheron onshore fields [17]. As a nutrient substance there was used a milk whey that provides activation of formation micro flora and oil displacing efficiency increase at the expense of habitability products. Industrial tests of microbiological methods give high results and improve economic coefficients in that branch [18]. However, the mechanism of oil production enhancement under different formation conditions is not studied out and therefore that method requires following research. For the purpose of question study the investigations have been carried out on experimental unit that simulated on oil formation. The model was made in metal column by length of 120 and diameter of 3,8 sm.

Porous medium consisted of 90% of quartz sand and 10% of carbonate rock. Void content in the range of 0,26-0,34 and absolute permeability in the range of 7,2-9,2 mkm^2 was determined after the known fashion in constructed model. Oil and formation water from Fatmai field was used for tests. The model was water saturated, and then water was displaced by live crude. In this regard residual water saturation was 8,4-9,4% of void content and gas saturation was 4,8-6,4%. Oil permeability that ranges from 3,2 to 40 mkm^2 was determined on filtration unit. Primary model of oil formation was constructed like that.

The tests were carried out in two stages. At first stage received medium was displaced by formation water at constant pressure and temperature decrease like 25 °C. Displacement was carried out to full putting a stop to oil show.

The volume of displaced oil and pumped water was gagged in the process of displacement. The results of tests were registered in table 1. Table data show that oil recovery degree ranges from 0,525 to 0,550.

As it is mentioned earlier, after nutritive medium injection microorganisms, reproduced in porous medium, go forward formation depth. For the purpose to study such phenomena and to determine the efficiency of nutritive medium injection on the second stage every model was injected with milk whey (MW) accordingly in 10, 20, 35, 50, 75, 100% quantity. When injection finished column was locked and pressure increase was over watched. For example the pressure change dynamics in model with 50% injection is shown on fig.1.

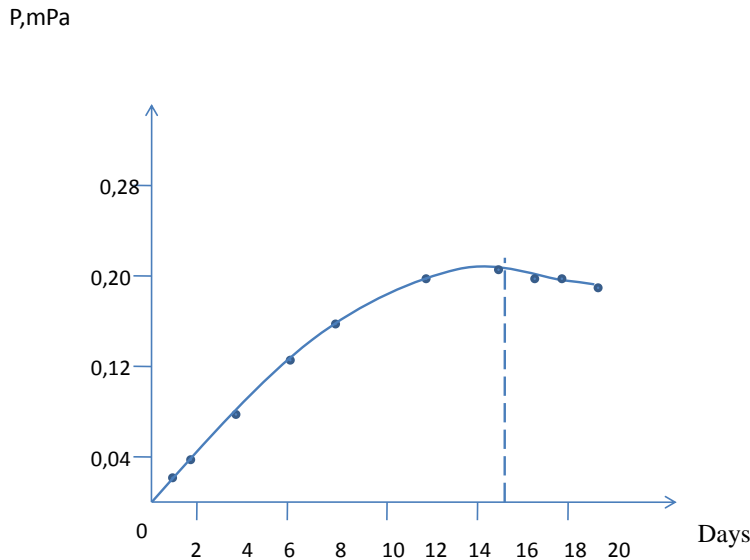


Fig.1 Pressure medium chang after MW injection (50% from void content)

Researches reevaluated that microorganisms occurred in MW medium evolve generous amount of CO_2 , CH_4 and other gases.

A volume of run biogas is 210 ml per 100 ml of MW. Methane CH_4 and carbon dioxide CO_2 , dissolving in oil decrease its viscosity and increase flow ability that fosters additional oil carry-over. Carbon dioxide well dissolving in water increases its viscosity and decreases flow ability. In tests period of pressure rise is 13-15 days. Pressure rise stopping pointed about efficient fermentation completion. When fermentation completed MW was displaced by formation water along porous medium under the same value of pressure and temperature difference. Pumping was continued till oil shows stopping. During the pumping process run exhaust fluid was measured. The results of tests are shown on fig.2 in tab.1.

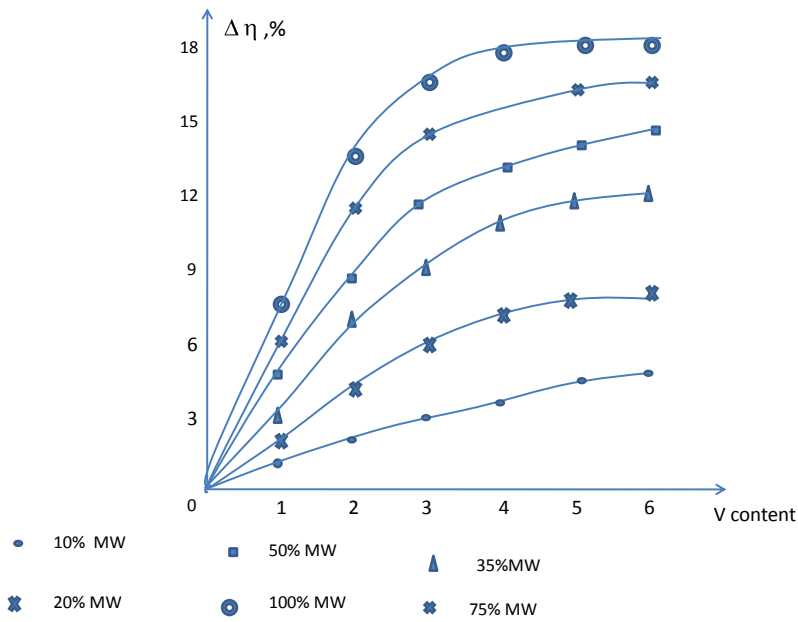


Fig.2. Change of additional oil recovery volume depending on volume of formation water pumping under different values of MW

The diagram of additional recovered oil volume change depending on MW injection was developed to compare obtained results (fig.3). Analyzing a curve, offered on fig.3 we can come to a conclusion that as MW injection volume increases, oil recovery from porous medium enhances. At initial stage of injection oil recovery volume sharply increases then after injection of 50% MW the intensity of oil recovery growth get decrease. Obtained result of analyses renders it possible to propose that microbiological processes include the zones where MW doesn't be injected.

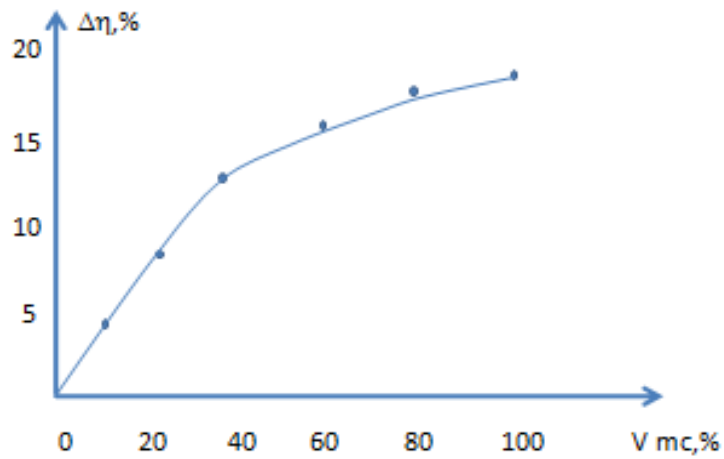


Fig.3 Dependence of additional oil recovery quantity from MW injection volume

As it is shown from results of researches microbiological treatment of formation enhances oil recovery for 19%, where as the most efficient physical and chemical methods increases. To 10-15 % in comparison to oil recovery at usual bleeding. Considering that this method is cost-effective, ecologically clear and easy-to use it can be recommended as one of perspective method in state-of-the-art-technology of oil production enhancement.

Table 1.

Test version	Porosity	Absolute permeability mkm ²	Residual water saturation %	Residual gas saturation %	Before MW injection		Volume of injected MW%	After MW injection		Additionally extracted oil
					Oil satur. %	Oil extract. ratio %		Oil satur. %	Oil extract. ratio %	
1	0,34	9,2	8,4	4,8	40,4	53,6	10	36,9	57,6	4,0
2	0,28	7,4	9,2	6,0	39,2	53,4	20	33,2	60,9	7,5
3	0,32	7,8	9,0	6,2	40,1	52,5	35	31,1	63,2	10,7
4	0,31	9,0	8,9	5,5	39,9	55,0	50	26,7	68,6	14,6
5	0,29	3,1	9,1	6,1	40,3	52,6	75	25,4	70,1	17,5
6	0,26	7,2	9,4	6,4	38,7	53,9	100	23,0	72,6	18,7

Microbiological treatment of formation is based on intensification of formation microflora. To this effect aerated mud of diammonium phosphate is injected, where oil oxidation takes place forming carbonic acid and intermediate products having oil-driving properties.

Microbiological treatment is also based on utilization of special group of bacteria capable to develop under formation conditions and sharply decrease interphaze tension on water-oil border.

The efficiency of microbiological treatment is determined separately for producing wells.

The technology of microbiological has the history, based on more than 50-years experience of research and field tests, carried out in former USSR, USA, Chekhoslovakiya, Poland, Hungary, Romania and other countries. The method is based an injection of microorganisms into depleted reservoirs to increase oil recovery at the expanse of creation of interformation biochemical processes.

Besides chemical and microbiological treatment, plugging and structure compression works upon screen service time. Microbiological treatment is environment contamination both living organisms – production of microbiological industry. Contamination of environment with living organisms and biologically active agents leads to falling ill of man, flora and fauna, because of interaction with living organisms.

Tested areas of microbiological of treatment laid in the base of development of oil recovery efficient technologies on Bashkortostan fields.

For modeling microbiological treatment on 28 producing wells there were revealed 16 different geological and physical and technological factors exercising influence on efficiency of carried out works: additional oil recovery from complex biological treatment (A.Q,t); relative effect (Aq, unit fraction Vq after: effective pay unit (Npl, unit fraction kpch-) summarized exposed effective thickness of pays (hvs.kk%); watering variation coefficient before biotreatment (vff); flow rate variation coefficient before biotreatment (vqi); oil in place reserves determined according Kovalev method (Qbai.t) specific in place reserves per well (AQ/a/, unit fraction).

For the purpose of microbiological treatment on bottom-hole zone, bacterial mass and nutritive slurry is injected into producing well, and then well should be closed for bacterium adaptation to formation conditions.

At the end of 3-6 months well is put into operation. Initial teats, carried out by S.I.Kuznetsov, K.B.Ashirov on sernovodsk and berezovsk fields in 1955, were based on ability of anaerobic microorganisms to destroy oil generating gas. There was revealed some gain of oil field, gas factor and well surface pressure. Light fraction enhancement, specific weight and viscosity decrease, gas factor growth well rate short-term increase was stated in oil content.

Technological effect of complex microbiological treatment is determined by cumulative influence of many different geological-physical and technological parameters, as porosity, oil saturation, formation producing intervals thickness, production rate and watering before treatment, reserves fraction per well and so on. Computer models made using multifactor static analyses are necessary for the given process investigation and adequate chose of indices predicting.

2.5 Magnetic field effect on oil recovery

2.5.1. The analyses of water magnetic treatment action on the process of hydrocarbon fluids displacement.

Recently one of the modern methods for industrial processes intensification – water magnetic treatment (WMT) in water dispersion systems is wide spread. It was determined that there are appeared a number of physical and chemical effects in heterogeneous systems when water magnetic action. These effects are the following: scale formation decrease, formation of water crystals in volume, but not on walls of vascular when water solution vaporition, adsorption properties change, speeding up the process of solids dissolving and so on. It was by tests that MWT has an influence on the process of solid phase welled surface. Some investigators have considered theoretical basics of water oil systems dissolved gas concentration change. It was shown that magnetic treatment of water oil mixture speeds up the process of dewatering, considerably (for 25-45%) increase the separation of water and salt from mixture [19]. Test investigations showed that magnetic field can be successfully used for the number of technological processes of oil recovery and positive results have been obtained for scale control on oil field equipment when oil field operation. In the article it is explained that general conditions of statistical physics and thermodynamics allow proposing that magnetic fields effect on water solutions can not lead to change of thermodynamic properties of pure water. But on the practice there is not pure water but water solution of different salts so observed changes of technological properties of magnetized water solutions are connected to the presence of different salt ions in water. It was determined that cations Ca^{++} , Mg^{++} and onions Cl^- have different effect on water solutions structural change when magnetizing. Compacting effect of cations Ca^{++} and Mg^{++} is predominated ever picking action of anion Cl^- under field intensity to 35 Ka/m.

When magnetic field intensity increases to 40 Ka/m anion Cl^- effect grows and it prevails over compacting effect of cation Ca^{++} . Changing magnetic field intensity to 4000A/m there was analysed the dependence of water quality when magnetic field treatment. It is determined that as magnetic field intensity increases oxygen content, suspended particles, general hardness, PH, temperature and viscosity increases.

The analyses of literature data for water and water systems magnetic treatment allows to propose that magnetic effect can be used as. One of the action factors for water oil displacement processes when oil field operation. The principal possibility of magnetic field action application is revealed from the analyses of recovery coefficient.

2.5.2. Magnetized water injection into the formation.

The field researches show that adsorption and diffusion layers are observed on oil porous medium contact [19].

Physics and chemists have analyzed in details all aspects of that process and the questions of diffusion layer thickness regulation and as sequence hydrocarbon liquid washing off are studied.

Magnetic fields application has old history. Mainly they are applied in medicine, but recently processes, heat technology and oil and gas production processes intensification.

For the first time magnetic fields were analysed by the personnel of Oil and Chemistry institute "Oil fields development and operation" department under the leading of academician A.Kh.Mirzadzadeh. Further magnetic fields were applied for treatment of injected formation water and for oil water separation in water flooded production.

There are shown the results of field research analyses on magnetic fields application in order to enhance oil recovery coefficient.

Literature data analyses shows that magnetic field intensity change can have an influence on potential function in the system of rock adsorption fluid or gas.

There are types of constant magnetic field values are realized in the industry:

- 1) cross flow (upstream)
- 2) longitudinal motion (alongside the fluid stream)
- 3) rotational motion (around fluid stream)

Cross magnetic field the most realized and simple in application.

2.5.3. Field investigations for well-intake capacity enhancement.

The possibility of water magnetic treatment for oil production process intensification was realized on the base of laboratory investigations results.

There was obtained that the most effect of water magnetic treatment is observed when oil displacement from mudded-off formation using constant cross field.

As a matter of that “it was decided to implement magnetic facilities on the fields with mud content in reservoirs.

When field operation one of the difficult problem is that weak-permeable formation poorly take over the water because clay is swell able in water. Firstly the implementation of magnetic treatment of injected water was carried out in the Azerbaijan and Tatarstan.

Chapter 3. Physical and chemical methods of EOR in water out reservoirs

About 30-70% initial oil reserves have not been recovered in water out reservoirs by using usual technology or different improved technologies (cycling, fluid flow direction change, gas-water cycling) or using increased water displacement properties (SAA, Polymers, alkali). Thus, residual oil can be displaced only with working agents that are able to mix with oil and water by having super low interphase tension on contact. Such conditions are observed at oil displacement by carbon dioxide and micellar solution, that completely eliminate negative influence of capillary forces on oil displacement.

Those methods are considered the number of most high potential and perspective, which are able to eliminate residual oil saturation in trapped zone. About 2-5% is recovered by working agent. The main thing of these methods application is provision of oil bed high coverage by efficient displacement agent (carbon dioxide) and micellar solution. For our industry these methods have principal value, because main part of residual oil at known production field remains as water out reservoir. And it will be difficult to recover oil from water out reservoirs than non-water out ones.

3.1. Oil displacement using carbon dioxide.

Alcohols and liquefied carbon dioxide can mix with oil and water. But some alcohols are fixed in water (butyl, propyl alcohols) but others conversely are fixed in oil (ethyl, methyl alcohols). Carbon dioxide is dissolved in water and oil of different content and density. CO₂ analyses have been begun early in 50 years. Carbon dioxide liquates at temperature low than 31.2 °C (fig.62).but because of hydrocarbon content, the temperature, providing the presence of liquid carbon dioxide, increases up to 40 °C. At the temperature of 31 °C carbon dioxide is in gaseous state under any pressure. The pressure 7,2MPa is also critical. At low pressure CO₂ graduates from liquid state to vaporous state (evaporate).

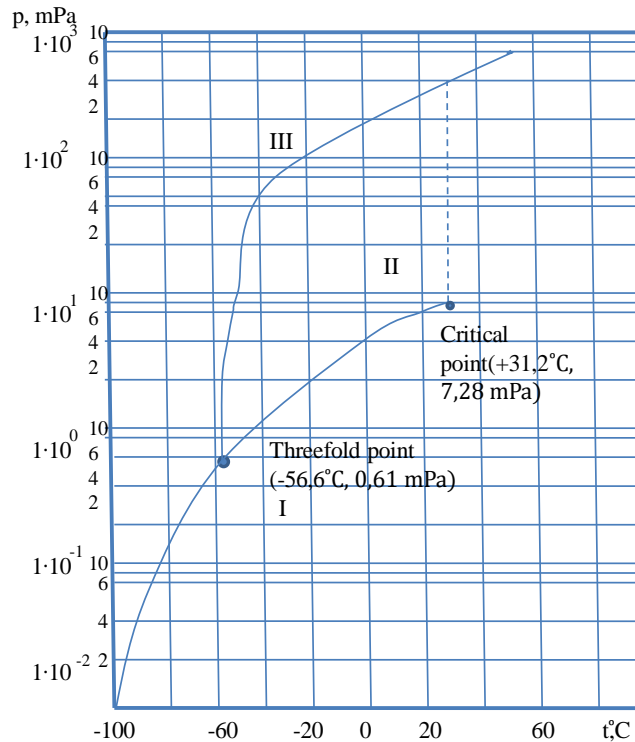


Fig.1. The diagram of carbon dioxide phase state depending on pressure and temperature. Phase: I-gas; II-liquid; III-solid.

The density and viscosity of liquid carbon dioxide changes in the range of 0,5-0,9 t/m³ and 0,05-0,1 mPa·c, gaseous matter-0,08-0,1kg/m³ and 0,02-0,02 MPa under pressure 8-25 mPa and temperature 20-100⁰ C (fig.63).

At high pressures (more than 15 mPa) and low temperature (low than 40⁰ C) of formation, density of liquid and gaseous carbon dioxide is equal (0,6-0,8t/m³). Carbon dioxide dissolves in water rather better than hydrocarbons. Carbon dioxide water solubility increases as pressure increases and decreases as temperature increases.

Carbon dioxide water solubility ranges from 30 to 60 m³/m³ (3-5%) under formation conditions (fig.64). As water mineralization increases carbon dioxide water solubility decreases. When carbon dioxide is solves in water its viscosity increases. Such increasing is not so considerable. But such increase is not so considerable. But stock carbon dioxide content (3-5%) increases its viscosity only for 20-30%, carbonic acid H₂CO₃ solves some types of cement and formation rocks and increases its permeability. According to laboratory data, s permeability of sandstone is increases for 5-15%, and dolomites for b-75%. Shale hydration decreases at the presence of carbon dioxide. Carbon dioxide is solved in oil for 4-10 times better than in water,

therefore it can graduate from water solution in oil. During graduation interphaze tension between then became very low and displacement levels to miscible one.

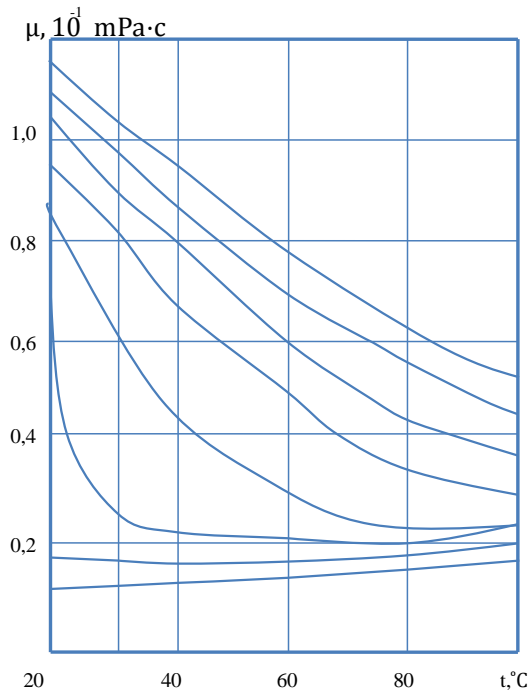


Fig.2. The dependence of carbon dioxide viscosity μ from temperature at different pressures. Pressure, mPa: 1-30, 2-25, 3-20, 4-15, 5-10, 6-7, 7-5, 8-0, 1.

Carbon dioxide water solution promotes disruption and washing out of oil film, covering rocks and decreases water film disruption possibility. Consequently, at low interphaze tension oil drops are floating in pore channels and oil phase permeability increases.

Carbon dioxide is oil solving rather better than methane. CO_2 solubility increases as pressure increases and temperature and oil molecular weight decreases. Methane and nitrogen content decreases CO_2 solubility in oil and increases miscibility pressure. Oils with high content of paraffin hydrocarbons are solving CO_2 better than oils with high content of naphthenic and especially aromatic hydrocarbons.

At pressures higher than total miscibility pressure CO_2 and oil will form one-phase mixture at any content of CO_2 that is unrestricted miscibility.

The pressure of full miscibility for different oils is different and can range from 8 to 30 mPa and more.

For light low-viscosity oil pressure of miscibility is low, for high-viscosity oil is high. At the same time CO_2 and oil miscibility pressure depends on bubble-point pressure. As saturation pressure increases from 5 to 9 mPa, miscibility pressure increases from 8 to 12 mPa. Methane and

nitrogen content in CO₂ increases miscibility pressure. For example, about 10-15% methane and nitrogen content in CO₂ increases miscibility pressure for 50% and more. And conversely high molecular weight ethane and other hydrocarbons addition to carbon dioxide gas decreases miscibility pressure.

The temperature increase from 50 to 100⁰C increases miscibility pressure for 5-6 mPa.

Considering pointed factors action on miscibility pressure CO₂ is partially blended with many oils under real formation pressure. But in formations CO₂ contacting with oil, is often dissolved in oil and at the same time extracts hydrocarbons, enriching by them. It increases CO₂ miscibility and while frontal advance miscibility becomes mixed.

As a result the pressure need for mixed oil displacement by carbon dioxide is considerably low than by hydrocarbon only. So the pressure of 27-30 mPa is required for mixed light oil displacement by hydrocarbon gas, while the pressure of 9-10 mPa is enough for CO₂ displacement.

While CO₂ solving in oil, the viscosity decreases, the density increases, and the volume considerably increases: oil is like to expand.

At high pressure and temperature CO₂ and oil miscibility mechanism is characterized by the process of hydrocarbons evaporation from oil to CO₂, and at low temperature the mechanism corresponds condensation, CO₂ adsorption.

At pressures low than miscibility pressure, CO₂ and oil mixture is divided on composite phases: CO₂ gas with light oil fraction content and oil without light fraction.

Asphaltenes and parafines can precipitate from oil.

Oil density increase not exceeds 10-15% and as a rule composes not more than 2-3% that connects to oil volume considerable extension. When CO₂ dissolving the oil volume increases in 1,5-1,7 time and that contributes to formation oil recovery enhancement when development of low viscous oil fields. The principal factor increasing high viscous oils displacement coefficient is decreasing oil viscosity when CO₂ dissolving in it (fig.6). Oil viscosity decreasing in strong as its initial value is more.

Initial oil viscosity, mPa•c	Oil viscosity at CO ₂ full saturation mPa•c
1000-9000	15-160
100-600	3-15
10-100	1-3
1-9	0,5-0,9

As it is shown, oil viscosity decreases very strong under CO₂ solution action.

I.I.Dunushkin offered empirical formula of calculation the viscosity of oil μ_H , CO₂ saturated with its concentration in C_H oil:

$$\mu_H = A \mu_t^\delta ; A = 0,22 / (0,22 + C_H^2)$$

$$\delta = \frac{0,362}{0,28 + C_H} - 0,295$$

Where A and δ are empiric coefficients;

μ_t - initial oil viscosity, mPa•c

Oil light components transition to carbon dioxide takes place when pressure decrease and immiscibility of oil - CO₂ on sections. At that residual oil is ballasted, its volume and CO₂ solution decreases, and its viscosity and density increases.

Consequently, the mobility of oil, left in the CO₂ displacement front decreases.

The data about Shaim oil properties change when it mixing with different volumes of CO₂ at 18 mPa pressure, 80 °C temperature and following phase separation are shown in tabl.30

At surface T=20 °C and p=0,1mPa. In experiment 1-7 the system CO₂–oil consists of one phase but in test 8-11 divided to two phase – gas and liquid. It is mentioned that as CO₂ part increase light oil fractions decrease after separation and more heavy hydrocarbon fractions moving on carbon dioxide phase and oil volume extension decreases.

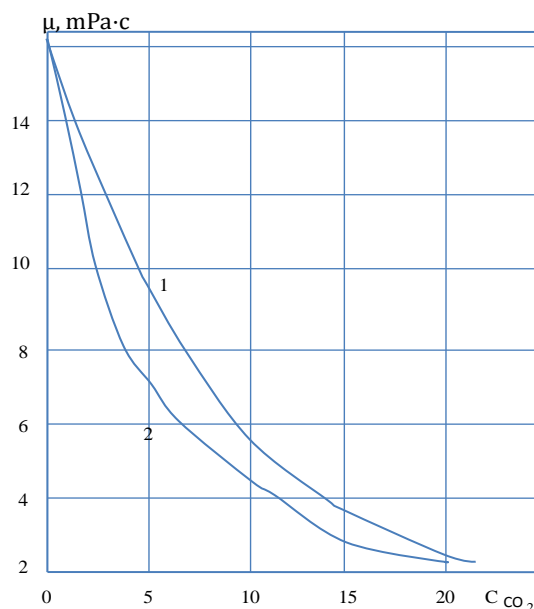


Fig.6 The dependence of oil viscosity μ from CO₂ concentration for oils Arlan and Tuymazin field. Field:1-Arlan; 2-tuymazin.

3.1.1. The mechanism of Oil displacement process

Carbon dioxide will displace oil as usual solvent (mixed displacement) when formation pressure is higher than full miscibility of formation oil with CO₂. Then, three zones are formed in the formation –initial formation oil zone, transition zone (from initial oil properties to injected agent properties) and pure CO₂ is injected in water - flooded pool, then formation water displaced oil wall is formed before CO₂ zone.

The displacement coefficient 1 is achieved in some cases in laboratory conditions when some models of oil displacement by carbon dioxide from homogeneous porous mediums.

But in tests with real oils the coefficient of displacement not exceed 0,94-0,95 % that explains by oil high molecular components settings-out in solid precipitation.

CO₂ is partially dissolved in oil phase, improving its filtration properties and light fractions pass into CO₂ under the formation pressure lower than miscibility pressure.

Fractional separation takes place. Carbon dioxide saturated by light oil fractions, displaces the oil partially CO₂ saturated. Residual oil obtain the properties of heavy residues in the zone washed out by CO₂.

It is determined by laboratory tests that CO₂ better displaces the oil in liquid state than in gaseous one under the temperature near-critical state (31°C) and the pressure near-critical one (7mPa).

At the temperature higher than critical one CO₂ will be in gaseous state under any pressure and displace the oil with all shortcomings, related to agent with low viscosity that is at low coverage of heterogeneous formations by processes. Therefore, it is advisable to inject carbon dioxide in liquid state and choose the objects for application with the temperature slightly modifying from critical one (25-40°C).

The properties of Shaim oil in contacting with carbon dioxide.

Test number	Mass content of CO ₂ in the system %	Formation conditions				Surface conditions				
		Gas phase and mixture fraction	Oil viscosity mPa·s	Oil density kq/m ³	Oil Increment volume	Condensate factor m ³ /m ³	Gas factor m ³ /m ³	Dead oil density kg/m ³	Dead oil viscosity mPa·c	Condensate density kg/m ³
0	0	0	1,7	792	1	-	8	832	4,4	-
1	15,6	0	-	836	1,12	-	84	832	4,4	-
2	34,6	0	-	925	1,31	-	24	882	4,4	-
3	40	0	-	919	1,34	-	0	832	4,4	-
4	41,2	0	-	915	1,48	-	25	832	4,4	-
5	43,5	0	-	893	1,57	-	5	832	4,4	-
6	44,4	0	-	876	1,62	-	32	832	4,4	-
7	45,2	0	0,425	860	1,68	-	0	832	4,4	-
8	50	0,39	0,5	880	1,5	34,1	35	846	14,8	789
9	52	0,42	0,79	900	1,33	31,6	0	848	24,2	796
10	68	0,67	-	930	1,28	27	36	861	26,6	803
11	79,4	0,83	1,63	990	1,04	17,2	0	872	79,2	806
							37			
							5			
							31			
							0			
							26			
							4			
							17			
							0			
							10			
							7			

3.1.2. An influence of bulk effect on oil displacement using carbon dioxide.

Oil volume increase under CO₂ solution condition and liquid viscosity change (oil viscosity) decrease and water viscosity increase) is one of the main factors, determination the efficiency of its application in the processes of oil production and its recovering from water-flooded formations.

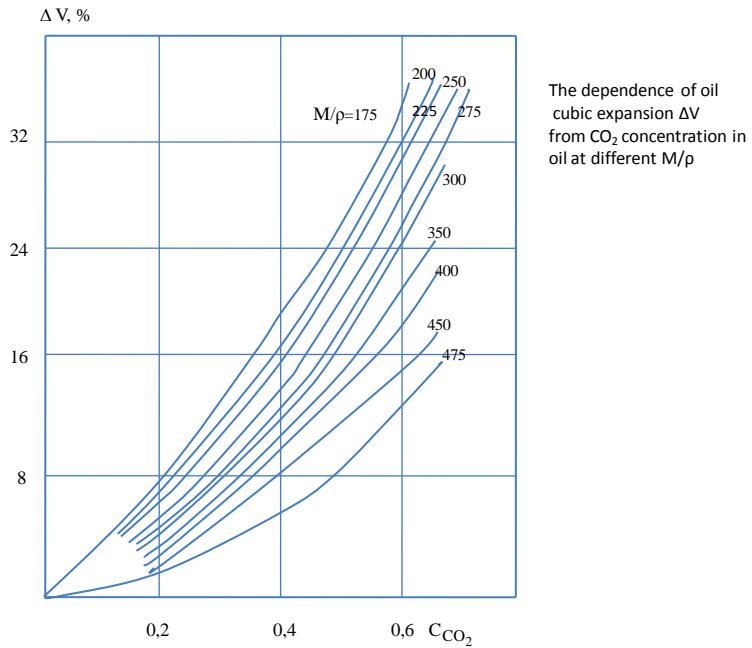
Oil volume extension depends on temperature, pressure and the quantity of dissolved gas. Light hydrocarbons (C₃ – C₇) content also has an influence on oil volume extension. The more light hydrocarbons in oil, the more its volume extension. (fig.68)

Formation oil volume extension causes artificial increase of reservoir pore space oil saturation volume. As a result pore pressure increases and consequently, dead oil residual part is displaced in producing wells. Oil volume extension even by partially CO₂ saturation has increase the displacement coefficient for 6-10% at the expense of oil phase permeability increase and therefore formation final oil recovery. (fig.69,70)

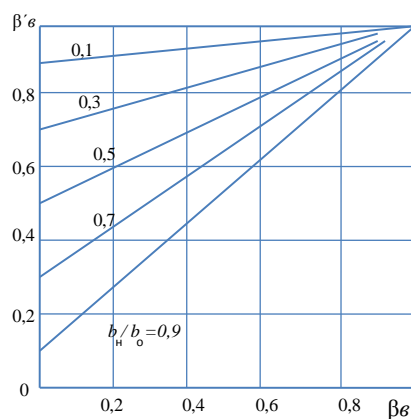
Technologies and systems of development.

Since the pressure determination miscibility, CO₂–oil mixture state and the efficiency of oil displacement, then CO₂ injection pressure and formation pressure maintenance are the main elements of the process technology.

The optimal pressure, when CO₂ the more efficiently displaces the oil, should be determined experimentally in every fixed state under the conditions along to formation i.e. miscibility pressure for formation oils with CO₂ should be carried out in pore medium of actual formation.

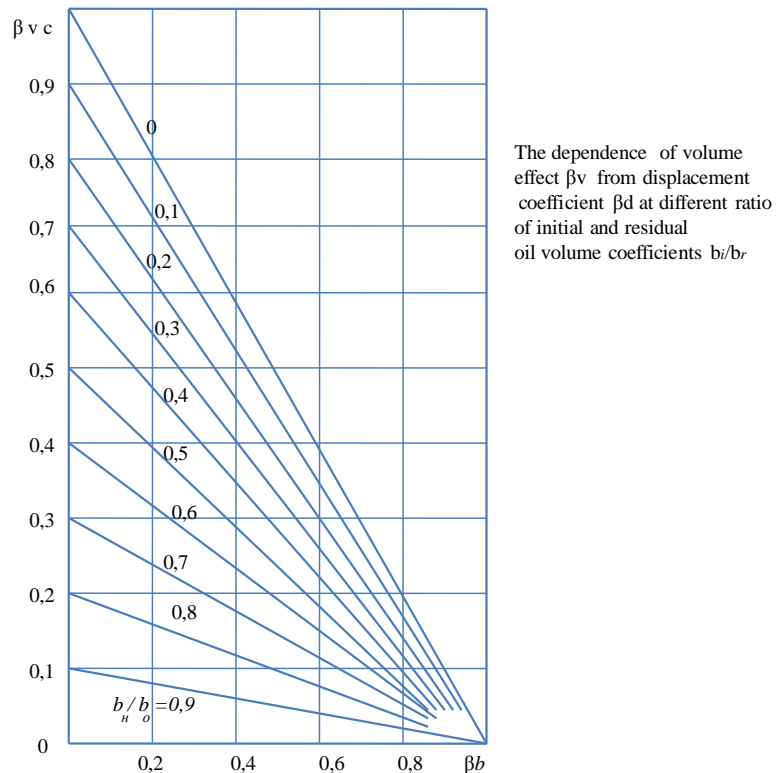


The next important condition of oil displacement technology is purity; the oil miscibility with CO_2 is depended on. Pure CO_2 (99,8-99,9%) has minimal miscibility pressure is better blended with oil and displaces it and when liquidizing it can be injected information by pumps without complications and out gassing. When light hydrocarbons and in active gases large quantity content in CO_2 mixture, its injection is possible only in gaseous state. If CO_2 is injected in formation with methane (natural gas) or nitrogen (waste gas), then miscibility pressure will be very high, and oil displacement efficiency will be decreased. It is explained that methane or nitrogen prohibits from oil miscibility.



The dependence of carbon dioxide oil displacement coefficient β_d from water displacement coefficient β_n at different ratios of volume coefficients of initial and residual oils b_i/b_r .

To displace the oil by CO₂ only, heavy flow of CO₂ is required for oil recovery sensible increase. Because of great difference of CO₂ and oil viscosity and density, there can be quick break through of CO₂ to producing wells on high permeable layers, its gravitational separation and considerably decrease of sweep efficiency in comparison with flooding. Consequently, that effect of CO₂ displacement increase, there can be less loss in oil recovery at the expense of coverage decrease. For the purpose of CO₂ economy, prevention of it is back through producing wells, decrease the gravitational effects and increase the sweeping efficiency, the application of CO₂ is advisably to combine with flooding. Different modifications of this method are applied.



3.1.3. Carbonated waterflooding.

The injection of water fully or partially saturated with CO₂ (3-5%) is the most simple method of CO₂ supply. In formation CO₂ graduates from water to uninvolved oil, changing its volume and filtration properties, viscosity and phase permeability. At that the fronts of CO₂ concentration in water fall behind the front of displacement. The retardation depends on the coefficient of oil-water displacement, the coefficient of CO₂ distribution between oil and water, CO₂ water concentration, pressure and temperature and varies between 2 and 8 time i.e. the distance covered by oil displacement front is more than the distance covered initial CO₂ water concentration in 2-8 times.

This circumstance considerably increases the effect obtaining date, the durability of oil builds development and injected water rate.

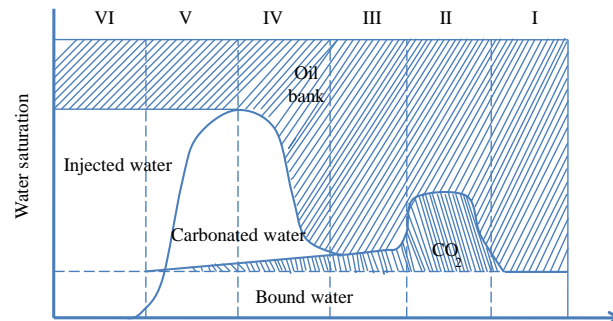


Fig.71 The scheme of oil displacement by gaseous carbon dioxide bank from unwatered formation and distribution of water, oil and CO₂ saturation at partial miscibility

Laboratory tests and numerical calculations shows that the coefficient of carbonated water oil displacement increases only for 10-15% when injection of 5-6 porous volumes in formation. Carbonated water application sweep efficiency is for several times higher, then at a conventional flooding. That is explained by decrease of capillary forces on phase folder, and reduction of contact wetting. Gravitational forces, well net density and development system have the same influence on the process of carbonated water oil displacement as a conventional flooding.

3.1.4. Carbon dioxide bank driving.

The retardation of CO₂ front from oil-water driving front can be avoided (or considerably reduces) by injection of pure CO₂ bank in the formation at the volume of 10-30% from pore volume with further water moving.

The following saturation zones will take place when oil driving from flooding reservoir by CO₂ bank.

Zone 1- one phase oil flow in the presence of retention water.

Zone 3- oil rod motion at the presence of retention water and occluded gas. Here the mass transfer of hydrocarbon between phases takes place, but less than in second zone.

Zone 2- mutual motion of CO₂, oil and water conducted by active mass transfer between these phases.

Zone 4- carbonated water motion at the presence of light fraction deficient and non-mobile oil and restrained CO₂. The mass transfer is extremely limited because the rod of retention water saturated, at the front of CO₂ oil displacement is moving before CO₂ deficient injected water.

Zone 5- injected water motion at the presence of residual oil. CO₂ contained in oil transfers into injected water and its concentration decreases in these zones from maximum rating to zero at the direction opposite to flow direction.

Zone 6- water movement at the presence of residual oil and CO₂ absence.

If the size of CO₂ bank is not large, then the zones second and third are disappeared in the process of time. The water overtakes the CO₂ and oil displacement takes place. Two new zones are appeared between I and IV zones: zone VII where oil water displacement takes place and zone VIII where oil is displaced by carbonated water. CO₂ water saturation takes place in zone IV. As a result CO₂ front retardation from displacement front is always low than when carbonated water injection. Further injected water is CO₂ saturated in the area of occluded gas. Eventually occluded gas is disappeared and only zones VI and V are stay in the formation.

The volume of oil without CO₂ content is considerably low than in zone V. It is important that water carries over CO₂ from the areas where oil is immobile (zones IV and V) to areas not covered CO₂ effect. Therefore in comparison to other solution or hydrocarbons application, even low banks of CO₂ provide noticeable enhanced oil recovery. As the volume of injected CO₂ increases, oil recovery enhances (fig72). As it is shown from the figure the oil displacement coefficient increases as bank size enlarges but at this incremental value decreases.

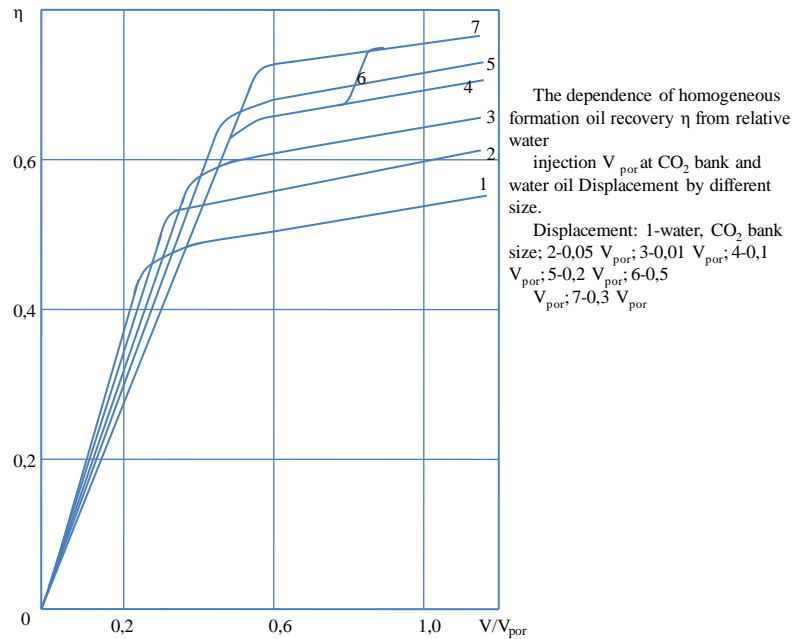


Fig72.

As a result at small banks CO_2 rate per ton of additionally recovered oil is low than at large ones. From the other side as bank enlarges then development time decreases and injected water rate is reduced. Such dependence is observed in heterogeneous formation. In most cases (at low heterogeneity of formation) CO_2 bank optimal volume is limited from 20 to 30% of pores volume.

At oil displacement by CO_2 bank oil recovery is strongly depended from gravitational conditions at large vertical permeability of formation, oil recovery can be for 2-2,5 times low than at zero permeability on formation thickness.

3.1.5. Oil displacement by alternate banks of carbon dioxide and water.

The experimental and analytical investigations show that the higher efficiency of this method can be achieved by injection of CO_2 necessary volume by a few portions, alternately with water or at the same time with water. The efficiency of this process depends on ratio of CO_2 and water portions size. As this ratio decreases then CO_2 feeding movement viscous stability decreases (it more uniformly spreads on surface), CO_2 early breakout possibility decreases and as a result surface efficiency increases. At some ratio of CO_2 and water the surface coefficient can be higher than at usual flooding or when carbonated water injection.

An adverse showing of gravitational instability because of CO₂ and water different densities is possible when gas-water ratio increase. The water will run for down, CO₂ – to upper part of formation. Or under sharp stratified heterogeneity CO₂ will break through high permeable layers to producing wells and water will follow it, providing low sweeping by displacement process. Therefore there is optimal ratio of CO₂ and water volumes, at alternately injection for the most effect achievement, that should be provided by special investigations and calculations based on real conditions of formation heterogeneity, solubility of CO₂ in water and oil. The determination factor when CO₂ and water injection volumes ratio choose is prohibiting of CO₂ breaking to producing wells.

Usually that ratio can change from 0,25 to 1. CO₂ and water portions size can be enough large about 10-20% from pore volume at total miscibility of CO₂ and oil saturation and enough homogeneity of formation.

When low miscibility of CO₂ and water portions should be small at alternately injection as oil viscosity and formation heterogeneity increases then CO₂ and water potions sizes should be decrease. At low viscous oils and weak heterogeneity of heterogeneity it is expedient to apply CO₂ at the beginning of development.

In heterogeneous formations and at high viscous oils it is possible to obtain more higher final oil recovery by using CO₂ at more later stages of development i.e. in flooded formations. Such unexpected effect is explained by different solubility of CO₂ in the oil and water.

3.1.6. Other possibilities of technology increasing displacement of formation.

In some projects it is proposed to inject alternately water and other gas (natural, combustion) after CO₂ and water injection outside of oil displacement by carbonated water and different CO₂ banks.

In this case miscible displacement of unsalable CO₂ takes place, CO₂ formation residual saturation decreases, and as a result its discharge rates are reduced.

Application of water-soluble surfactants, water solutions of sodium silicate forming foam and gel in high permeable layers is possible for decreasing the mobility of free CO₂ in formation at partial miscibility and coverage increase.

The main problem of this are foam stabilization SAA adsorption and gel storing in mineralized medium. Laboratory tests have confirm the practicability of carrying out such measures that increase the miscibility of heterogeneous formation displacement.

In the project of further development of flooded formation B₂ of Radaevsky oil field (oil viscosity 20-22 mPa·s) using CO₂ .all union oil and gas scientific research institute proposed to inject CO₂ alternately with polymer water solution to improve the miscibility and CO₂ distribution by formation volume.

According to estimation, an application of CO₂ and polymers on Radaevsky field can enhance oil recovery from 10% to 13%. Hungarian specialists have realized the following most efficient technology of CO₂ oil displacement from depleted reservoirs.

Carbon dioxide gas is injected to depleted reservoir under low pressure (2mPa) it takes the place of free hydrocarbons. Reservoir pressure increases from 2mPa to initial one (10-13mPa) at the expense of CO₂ injection.

At the presence of free CO₂ in the porous medium the oil is displaced by over saturated carbonated water (28-30m³ of CO₂ per 1m³ of water). Using such technology it was succeed to obtain an oil displacement coefficient in more than 90% of covered part of reservoir at large rate of CO₂(about 0,8 from pore volume) and low rate of water (0,53-0,7 from pore volume). About 70% of injected CO₂ is recovered from reservoir and regeneration it can be used again under corresponding equipment. Such technology is advisable only in those cases when large cheap source of CO₂ is located near the oil field for example natural CO₂ field with high concentration.

Development system.

An application of CO₂ for oil recovery enhancement has not any requirements to the system of development. But it obligatory should be intracontour, five- , three- and one-row or should be applied different modifications of reservoir flooding. Preference should be given to active less-row systems of development. An application of multi-row systems is not advisable because of possible recovery of large volumes of CO₂ by first rows of producing wells. In the case of such systems of application gas water ratio should be eliminated.

Well location is possible at any density of net – to 40-50 ga/well and more. Because CO₂ doesn't degrade the conditions of reservoir drainage.

As it usual flooding, well spacing density should be considered in accordance with reservoir heterogeneity on permeability and discontinuity relying on conditions of larger draining coverage.

When reservoir development where considerable gravitational segregation of water and CO₂ is possible (reservoirs with large thickness and vertical permeability) well spacing density should be increased.

The state, hermeticity, conditions and durability of injected wells operations should be considered when solving the questions of well spacing density. Also it is necessary to drill duplicate wells and take the maximal actions on casing corrosion protection.

Realized projects.

The first field experiment on injection of CO₂ into oil reservoir was carried out on Alexandrov area of Tuymazin field. Testing field involved one injection and two producing wells and had following field geologic property: well line space is 14,2 ga pore volume is 258 800m³, oil saturated thickness is 6,1, porosity is 22%, permeability is 0,6 mkm² reservoir oil viscosity is 15mPa/c, the distance between injection and producing wells is 338 and 263 m accordingly.

About 80 000m³ of water was injected into the injection well before experiment start. On December 1967, in reservoir there was injected CO₂ in the form of carbonated water. Alongside with that process water by the rate of 150-220m³/per day was injected in tubing string in tube space. Mixed injection of CO₂ and water with average rate of 1,4% concentration takes place in bore-hole bottom. Two volume of carbonated water including 4780t of CO₂ (that is about 2% from pore volume) have been injected.

The results of injection well water-intake capacity bear evidence of increase of reservoir coverage by flooding for 30% on thickness.

Injection well water-intake capacity increases for 30-40%. According to BashNIPI oil estimations, about 27,3th.t. of oil was additionally produced at the expense of carbonated water injection. That corresponds to oil recovery enhancement for 15,6% from its initial reserves in comparison to water injection. Additionally about 5,8t of oil was produced per ton of injected CO₂. Such effect is obviously over estimated. In HPR there are fields with considerable volumes content of CO₂. Middle lenticels of Budafa field Upper Lishne section was choose for field experiment carrying out.

The section has the following field-geological characteristic: pore volume is 1 250 000m³, initial geological oil reserves is 713 500t, formation thickness is 4-10m, porosity is 21-22%, permeability is 0,03-0,13mkm² connected water saturation is 30%, the temperature is 68⁰C, pressure is 10,5 mPa, oil viscosity is 1,12mPa•s., gas content is 70m³/m³. About 280 675m³ of oil was recovered at the moment of CO₂ injection, and that was corresponded to 39,3% of oil recovery, including 230 576m³ – at the expense of water injection. Since 1969 CO₂ was injected in order to reconstruct formation pressure after depletion to 12mPa, and then water was injected.

Since September 1970, alternately water and CO₂ injection was carried out in ratio 1:1 and since July 1973 only water water injected. The injection initially was carried out in three wells and since March 1972 – in five wells.

To the end of 1972 about 45 375 100m³ of gas containing 81-83%. Of CO₂ was injected and that compiles about 6% from pore volume. There was recovered about 38 359m³ of oil, that comprises about 5% from balanced reserves of the whole section, about 67 607m³ of water and 22 822 685m³ of gas including 14 017 964m³ of carbon dioxide gas or 31% from injected one.

Using the method of mass balance it was determined that CO₂ exposed reservoir oil recovery increased for 10%. It was mentioned the growth of the coefficient of drain coverage on thickness that at beginning of 1970, middle 1971 and 1972 was 0,58; 0,65; 0,78 accordingly. As it is shown the drain coverage of reservoir is very large. Field development is continued and the further enhancement of reservoir oil recovery is expected.

That experiment on unmissed oil recovery is considered successful.

At the end of 1975 CO₂ injection at Lovasi field was carried out. Here was predicted the enhancement of oil recovery for 10-15%. The largest application of CO₂ for oil recovery is investigated at USA oil fields.

At 50-th and beginning of 60-th years there were carried out some field experiment on carbonated water application.

Injection wells and producing wells rate growth was mentioned. A conclusion about great efficiency of CO₂oil displacement was made on the base of laboratory and theoretical investigations and experimental analyses results. In 60-70 years USA enter upon field experiments of different scale with CO₂ bank. At present 59 experiments by total square of sites more than 40th.ga. and oil recovery more than 1,5bl t/y are carried out. Short information about some large industrial experiments is shown in table 32. In some experiments reservoirs containing high viscous oil were CO₂ injected periodically like huff-and-puff, when after injection of definite volume of CO₂, injection well begun to work as producing one. At this the oil being within these wells branch dissolves the injected CO₂, consequently its viscosity decreases and mobility increases CO₂injection at Kelly Schneider field. Initial geological oil reserves of the field were about 300bln.t. Productive strata is carbonate, permeability is 0,020mkm². Field was revealed in 1948 and to the end 1951 there were drilled 1971 producing wells. To the 1954 the field was developed under the dissolved gas conditions.

In 1953 consolidated company "Sakrok Unit" was formed in order to mutual maintenance of formation pressure by flooding. Host-based system of flooding of 144 wells located along structure crest is active till present. Flooding efficiency is quite satisfied on estimations; it could provide final oil recovery of formation about 50%. Therefore in 1968 consolidated company considering some methods of oil recovery enhancement choose the method of CO₂ injection for industrial implementation. Laboratory test showed that CO₂ can displace 95-97% of oil under

field conditions ($\rho=13,5\text{mPa}$; $T=54^0\text{C}$), but calculations have showed that the bank by size of 20% from pore volume is able to enhance final reservoir oil recovery for 15,8% over flooding.

The project provides CO_2 injection in 202 wells situated on nine pointed pattern on both parties from axle row of water injection wells. There was provided alternate injection of CO_2 and water banks in 2:1 relation, i.e. 6% from CO_2 pore volume and 2,8-3% from water pore volume. Where on formation pressure was less than 10,5mPa where immiscible gas displacement could take place, water was injected to increase the pressure to 15-16mPa that is minimal for miscible displacement relying on laboratory investigations. But at the same time the pressure was less than 10,5mPa in many cells.

CO_2 supply on field was carried out through 400mm pipeline spreading on 350km in the volume $96,5-7) \times 10^6 \text{ m}^3/\text{day}$ from gas fields in Delavor and Valverde basin.

Such volume of CO_2 was enough only to inject in 60-70 injection wells about $80-100^{\text{th}} \text{ m}^3/\text{day}$ of gas or about $200\text{m}^3/\text{day}$ in equivalent of liquid carbon dioxide in every well. There for the field was divided on three section – I, II and III.

Initially CO_2 was injected in the wells of section I. after injection of 6% from pore volume water was injected (3% from pore volume) and CO_2 injection was suffered on the section II and so on. Gasoline plants with the systems of removing CO_2 from hydrocarbon gas were installed on all three sections.

Hot potassium carbonate operating regeneration systems were installed on the I section in the middle of 1973 and on the II section in the end of 1974. On the III section the system is operated on amine.

Total operating capacity of regeneration units is $15 \times 10^6 \text{ m}^3/\text{day}$ i.e. 25% from CO_2 injected volume.

CO_2 injection on the I section was began in January 1972 and in June CO_2 was appeared on producing wells and in November CO_2 production was mention at 100 wells from 236 producing wells of the first section and exceeded the operating capacity of the existing equipment on separation and extraction of CO_2 . Before CO_2 injection oil recovery was $37^{\text{th}} \text{ t/day}$ and in 1973 it increased to $13^{\text{th}} \text{ t/day}$ but was limited and only in the middle of 1973 due to regeneration system it was restored to previous level. CO_2 producing volume had responded to water injection.

During the cycle of water injection CO_2 production was decreased.

In the March of 1974 CO_2 injection was begun on the II section Alternation of water injection with CO_2 injection led to breakthrough of CO_2 to producing wells and flowing loss. As a result of that all producing wells (648) have been changed to mechanical production. In 1977 36 additional injection wells were drilled in those cells where initial injection wells have been

strongly dislocated from the centre. As it was shown from analyses reservoir coverage on area of cells decreased.

In 1973 the volume regenerated gas achieved 0,55-1,1bln. m³/day i.e. about 15-25% from overage level of injection. All this gas was feeder to compressor and was injected in reservoirs. For the period from 1972 to 1977 about 10bcm of CO₂ gas with daily average of 4,5bln m³ was injected into the reservoir on field.

On the I section, firstly developed for CO₂injection, accumulated volume of recycled and injected gas was 15% from the total injected volume. Final volume of recovered CO₂ is estimated as 24% from the total gas injected in fringe and 76% will stay in reservoir.

CO₂ fringe volume was decreased from 20 to 12% from pore volume because additional oil recovery costs decreases to 7-8 times.

Technological and economic efficiency.

The efficiency of CO₂ application for reservoir oil recovery enhancement is expressed in displacement coefficient increase at the expense of oil cubic expansion, its dissolution and miscibility with oil (capillary forces elimination) and oil viscosity decrease.

Within the zone CO₂ passing average residual oil saturation decreases to 1,5-2 times and oil displacement coefficient can achieve about 85-90% i.e. for 15-20% higher than at flooding.

But the efficiency of reservoir oil recovery enhancement is not as high as oil displacement coefficient increase because of working agent reservoir coverage decrease.

Oil viscosity decrease and non-essential water viscosity increase while CO₂solution (for 15-20%) can't balance negative action of gravitational forces and CO₂ high mobility in reservoir if it not solves with oil. Therefore coverage of heterogeneous formation by CO₂ displacement process at incomplete miscibility with water can be less for 5-15% than while flooding not taking care to enlarge coverage.

As a result applying CO₂ reservoir final oil recovery coefficient enhancement can be only 7-12%.

For example, at Kelly Snyder field after CO₂ injection of 8% from reservoir pore volume about 80% of CO₂ and water entered in formation layers, consisting only 20% of reservoir volume, the enter layers occupied 50% from reservoir volume took less than 20% from CO₂ injection volume.

Main task of CO₂ utilization for formation oil recovery enhancement is application of all possible measures and methods of working agent reservoir coverage increase i.e. decrease negative action of gravitational forces and CO₂ mobility. It can be achieved by suitable technology of CO₂ and water injection, formation drilling-in, formation intervals sealing;

bottom-hole equipment, location of wells depending on geological and physical specifications of the fields.

The ratio of injected volume of CO₂ to the additionally recovered oil volume is an important factor of CO₂ efficient utilization. That ratio naturally depends on many factors—oil properties, formation saturation and heterogeneity and largely on technology—bank size.

Bank size can be 10-30% from pore volume. The effect expressing oil recovery enhancement increases as CO₂ bank size growth. But at the same time CO₂ rate per ton of additionally produced oil increases.

On the base of experimental investigations analytical calculations on mathematical models of formation and carried out field test. It is possible to consider that under optimal conditions of CO₂ application its rate per ton of additional oil will be within 800-2000m³ but when utilization and reinjection of CO₂ it will be from 500 to 1300m³ or 1-2,5t/day. Initial oil saturation has an influence on the oil displacement process efficiency.

As oil saturation is large at the moment of CO₂ application, the effect is high because a great part of CO₂ is spend for useful saturation, oil expansion and displacement. The ratio of gas and water volumes has an influence on formation displacement process and CO₂ application efficiency.

Therefore it is very important to determine the optimal sizes of banks and water and gas ratio where alternative injection under geological—physical conditions of the field. It is possible only on the base of mathematical real information about formation construction and saturation state and right economic criteria.

The economic efficiency of CO₂ application for formation oil recovery enhancement is determined considering the rates for oil volume unit at injection well-spring i.e. specific additional oil recovery and oil price.

CO₂ rates can large in wide ranges depending on source of consumption.

Natural CO₂ from reservoirs located near the oil fields will be low-price. Natural CO₂ accumulations are revealed at Semividov field and Astrakhan field. It content about 20-30% non-active components—methane nitrogen and so on.

The most resources of man-made CO₂ are received from electric stations, plants on man-made gas generation from coal, shale and other chemical plants. The plants on man-made hydrocarbon gas generation from coal blows out CO₂ as by-product for 3-4 times more than base product. That gas should be treated, compressed and transported to oil fields. According the estimations of some projects, at haulage to 800km the rate of 1000m³ of CO₂ will be 35-40\$. Even such specific values the method is of industrial interest at modern price for oil.

The method shortcomings, limitations and problems.

The main shortcoming of the method of residual oil recovery using CO₂ consists on decrease the formation displacement coverage in comparison to usual flooding especially at partial miscibility with oil. If it only be possible to provide the CO₂ displacement coverage like when flooding so it will be possible to obtain essential enhancement of formation oil recovery because in the zone oil miscible CO₂ passes there are less residual oil-about 3-5%. As it was mentioned formation coverage can be decreased by different ways-improving the conditions of water and gas banks alternative miscibility, changing its size, selective isolation of definite intervals of formation to straighten CO₂ moving, formation cycling, suitable location of wells and formations drilling-in. the other shortcoming of the method should be considered that under partial miscibility with oil CO₂ extracts light hydrocarbons removes it, heavy fractions of oil are stayed in the formation.

It will be very difficult to further recover because they became less mobile and ball out on pore surface changing medium wet ability.

The presence of CO₂ resources within oil fields or the places accessible for transportation to fields under suitable economic factors is the criteria for reservoir oil recovery enhancement besides the geological and physical criteria. It is considered that CO₂ source removal from field for more than 400-600km, its cost (at the hole of injection well) more than 40-50 rub and low factory price for oil will be serious disturbances for CO₂ application in an industrial scale.

The risk of corrosion of injection and production wells and oil field equipment, the necessity of CO₂ utilization – removing from produced hydrocarbons on surfaces and reinjection in oil formation are the complex problems appeared while CO₂ application for reservoir oil recovery enhancement.

The pure CO₂ (with out moisture) is not dangerous in the case of corrosion. But at alternation it with water in injection well or after mixing in formation and on showings in production wells and on surface it became corrosion active.

Liquid CO₂ transportation, its distribution along the wells requiring special pipes, welding quality and so on is a difficult technical problem.

When using the water in miscible with formation one there are appeared favorable conditions for salting-up in formations, well-bottom holes lifting pipes, surface equipment and so on. This method introduction limiting significant factor large absorption of CO₂ –loses are about 60-75% from total injection volume. They are conditioned by CO₂ retention in on-side open pores and dead zones. All these leads to heavy specific rate of CO₂ per ton of additionally recovered oil.

The method of CO₂ application is the most universal and perspective from all known methods of oil recovery enhancement. According to the mechanism of CO₂ interaction with oil,

water and rocks the method has doubtless advantages in comparison with other methods. An important advantage of the method is the possibility of its application in flooded layers and relatively simple realization.

In force of factors collection the method should be considered as the most priority-oriented method of formation oil recovery enhancement, applied on wide part of oil fields with stable oil recovery enhancement from 5 to 12%. But the method application in the future should be determined by the natural CO₂ resources, because it's difficult to meet the demands. (about 1000-2000m³ per ton of oil production) at the expense of chemical production residuals although that source of CO₂ is cost effective.

The potentialities of formation oil recovery enhancement method according to USA National Oil Council estimations can achieve 40-50% from all reserves additionally recovered by new methods (1,1-5,8bld t) depending on many factors – oil price, minimum rate of profit, natural CO₂ cost, technology efficiency.

Maximal values of additionally recovered reserves and oil production level are determined under extremely favorable conditions –oil price achieves the cost of alternative types of liquid fuel (man-made oil from carbon or shale) high efficient process technology. 10% profit rate CO₂ cost not exceed 35\$ for 1000m³ and so on.

CHAPTER 4. THE NANOTECHNOLOGIES IN OIL PRODUCTION

Introduction

The nanotechnology is one of the high technological branches of modern technique and science that is engaged in investigation of atoms and molecules and creation of wide spectrum of different products.

The specification of nanotechnology consists of that it is not only practical technology of tangible objects application but it is concerned with social world construction that works out the spectrum of its application possibilities. Development of science and technology opens wide possibilities to solve the problems that are insoluble for the human for the last years. At present the nanotechnology is called the third scientific-technological revolution of information technologies. The base of that scientific-technological direction is investigation and application of new nanostructures and constructed products.

Nanotechnology is a new technology of new products obtaining on the base of nanoparticles. Today nanotechnology has the answers on many questions, impulsion the development of human society in metal manufacture, medicine, cybernetics, information technologies and many other branches. [22]

Therefore, nanotechnologies are actual for solving the problems of development and practical application in oil industry.

The author of nanotechnologies practical application in oil production of Azerbaijan was academician Azad Mirzadjanzadeh. [23].

4.1. An application of nanocomposite products for formation system on the last stage of field development.

The scientific investigations, laboratory and field testing works for improvement the technical and technological indices applying nanotechnologies in oil productions have been carried out under the leadership of academician A.Kh.Mirzadjanzadeh. Analyses of carried out works shows that the problems of nanotechnologies application in oil production is multiple-aspect one.

It should be mentioned that beginning since 70-years of the last centre Azerbaijan onshore oil fields are achieved the last stage of development.

At this formation rocks are deformed, consolidated, pores are eliminated, and formation permeability is sharply decreased. Therefore the processes being in formation are weakened and filtration liquid recovery is complicated. Primary and secondary methods of oil objects action are used for intensification of inter formation processes. But it is impossible to achieve balanced state of inter formation system and increase the pressure using existed methods. [22]

For the last 30 years different types of chemical inhibitors were developed and applied in oil and gas industry of Azerbaijan. The inhibitors for formation oil recovery enhancement, gas lift and airlift wells and paraffin deposits control are among them.

In order to improve the inhibitor surface activity at bottom hole action the most noticeable effect was achieved when adding liquid alkaline. At present the inhibitor “Disolvan” was widely used and the positive result was obtained in order to increase the efficiency of applied inhibitors in oil production. New effective nanocomposites on the base of MNP (metal nanoparticles), were developed as a result of test works of State Oil Company of Azerbaijan Republic and Baku State University employees efforts.

The investigations show that new compositions prepared on the base of aluminum nanoparticles and in combine with process water are forming numerous dispersive nanodrops and by that variable rheological properties of liquid. As a result oil and water filtration in oil rocks capillary improves.

Usually, the well operation is carried out in two stages. At the first stage the composition tops up the annular space. At the second stage the composition in combination with formation water is injected in the formation by the way of injection well.

It should be noted that MNP acting on rocks and improving bottom hole rocks filtration increases the coefficient of formation oil recovery and well rate.

According to literature data as a result of nanotechnologies development and application it was succeed to increase oil production for 2-2,5 times, decrease the energy consumption for 15% decrease water quantity for 20% from recovered liquid in low rate and flooded wells of OGPD “Gum adasy”, “Absheronoil”, “Bibieybatoil”, “Surakhanyoil”, “Azneft “IA. Besides applying nanotechnologies in wells operated under complicated conditions salt deposition was decreased for 60%, asphalt-resin-paraffin deposits control was increased for 70% and positive effect in other directions was obtained.

4.2. The analyses of nanoparticles influence on the “clay-rock” system.

The part of offshore fields and near the all onshore fields of Azerbaijan republic are on the post stage of development.

The last stage of oil fields development and operations deals with many problems one of which and the most specified is sanding-up and associated complications.

Currently, offshore oil production wells as “Neft Dashlary “Guneshly” and many onshore oil fields deals with that problem.

In the face of realization of definite and concrete measures on adverse effects and damage infliction prevention that question stay as a factor, decreasing overhaul time of well operation and sharply increasing operation costs. Therefore, the main obligation standing before oil production specialists is deep study of the question, development of new progressive methods for the problem solving, realizing the right approaches.

For the last time an application of nanotechnologies as one of scientific directions of XXI century, obtaining of different liquid systems at the presence of nanoparticles and its utilization in different spheres of oil production were realized at last.

Therefore, the liquids obtaining by physical and chemical methods adding nanoparticles and chemical agent with new nanostructure are widely used in different technological process of drilling and oil production, including oil and gas processing.

The influence of new liquid systems obtained on the base of water soluble polymers adding nanoparticles on the process of sand expansion in pipeline (pseudo liquefaction) was studied in the chapter.

The damages harmed by sand plod in the process of oil production is one of the complications appeared in well bottom hole. Solving this problem is the most actual target, standing before the specialists on oil production.

The influence of nanoparticles on the processes carried out including sand plug parameters was analyzed on the base of comparison of flows under different conditions of sand-liquid mixture movement.

It is known that each oil and gas field has the structure native to it only. The fields being heterogeneous on rock conductivity, concurrently with presence of the sand in rocks differ by the presence of 30% of different clay. It should be noted that in spite of that sand and clay are different on chemical composition in some cases from the point of view of grogs dimensions, the most small fraction fines can be considered the clay. As an example should be shown that application of clay mud in drilling and other processes, the smallest sand particles forms the state of “pseudo liquefaction”.

It is known that clay particles being in rock composition regain in water. As a result pores dimensions decrease and create filtration resistance. Therefore, this phenomena study has a great importance.

Carried out investigations showed that in the process of clay regain in water nanoparticles action has a great influence. [26]

Adding of 0,1% of cuprum nanoparticles in clay regain the process runs down and regain decreases for 20-30%. It should be noted that the quantity of nanosystems during the carried out of test was rather large.

Considering that nanoparticles quantity was decreased to 0,05% and 0,01%. But nanoparticles amount decrease hadn't influence on the final result: expanding percentage ratio stay unchangeable.

One of the main questions is that adding cuprum into the water we can't obtain homogeneous dispersion system. When adding cuprum to water by any method at some time the cuprum separates out and gravitates to the bottom. Besides the cuprum relates to the group of passive element, here the strong difference of elements specific weight is great importance.

Here we can came to conclusion that in order to obtain dispersion mixture when mixing cuprum with water, it is necessary to add come intercellular substance. Undoubtedly, large-size molecular polymers or surface active agent and in some cases both matters can be used. The polymer of carboxyl-methyl cellulose (CMC) that is well soluble in water and widely used in different branches of industry is applied as large size molecular polymer. In [25] there are given large data about investigations of CMC influence on clay swelling in the water solution. The tests were carried out with different marks of cellulose ester of 0,05;0,1;0,25;0,5;0,75;1,0;1,5 and 2% solution analyzing its influence on clay swelling. As a result it was determined that in all cases cellulose ester water solutions considerably decrease clay swelling. At the same time bulking decrease process varies depending on CMC concentration percent. Thus at presence of 0,5 concentration the clay swelling intensity decreases and vice versa when concentration increases the intensity of clay swelling sharply increase. Along with decrease clay swelling cellulose ester water solution promotes swelling average rate decrease and swelling rate time increase. At the same time when concentration increases to 2% these indices are continuously increasing. Noted that clay swelling rate using 0,5% of CMC solution is low in comparison with swelling in water. Obtained results show that clay bulking indices decrease depending of CMC polymerization rate. CMC solution influence on clay swelling can be explained as following: CMC sizes and structures lead to origination of adsorption layer that in his turn blocks the bonding of clay particles. In such state expanding of specific surface is not so much as when

swelling in water considering that the thickness of CMC originated adsorption layer is considerably higher than hydrated layer.

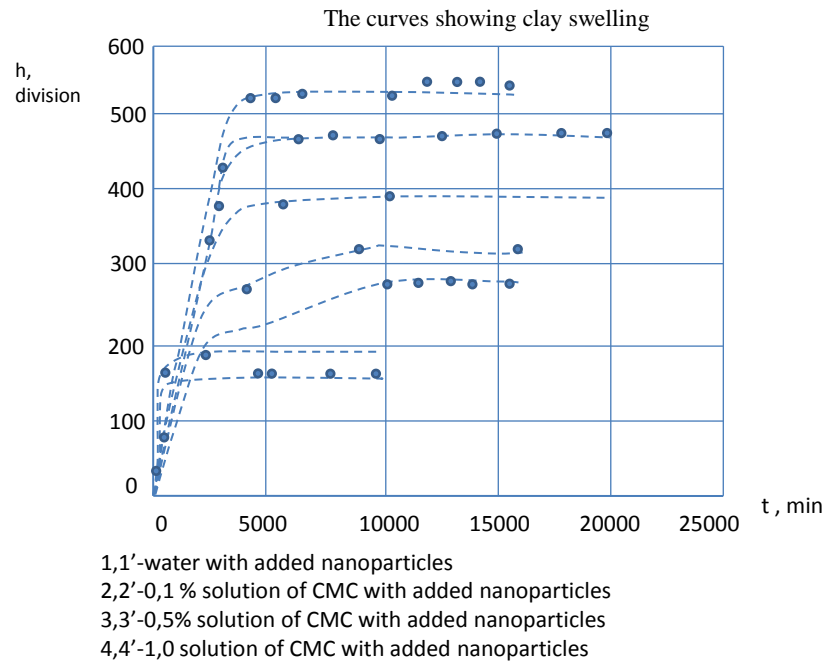


Fig . 4.1.

Therefore fore cited tests were carried out adding definite quantity of nanoparticles into water solution of CMC polymer. First of all 0,1%; 0,5% and 2,0% solutions have been prepared and their influence on clay swelling were analyzed, then 0,01% of cuprum nanoparticles have been added into the solution and nanoliquids on cuprum base were obtained and the influence of three. Component solution on clay swelling was studied. The results of test are shown on fig.4.1. here is clear that both in polymer solution and adding cuprum nanoparticles obtained new system influencing clay swelling clearly point at decrease rate. Therefore it is know from the curves on fig.4.1.that as a result of nano influence clay swelling decreases more than 2 time (curves 2,2-4,4).

4.3. The study of nanoparticles influence on rheological specifications of sand-liquid mixture under dispersion state.

The phenomena of pseudo liquefaction that takes places at the presence of oil, water gas and sand components, entering from reservoir into wellbore is rater complicated process and is possessed of original specifications. The dispersed system formed by sand-water mixture is not very stable, the processes is happened in the system between sand and water particles, their mechanism of movement, hydrodynamic changes happen in pseudo liquefaction layer that are

crude studied. It should be noted that if the analyses of one sizes fines movement in homogeneous fluid flow and development of its mathematical model is simple and easy reached then to prepare an equation of motion lows and express them by one rule for multi component and complex system is very hard task.

Versus to other scopes, the pseudo liquefaction phenomena in oil production is hydrodynamic problem that characterize the behavior of sand-water mixture at different depths of bottom-hole zone under close conditions and therefore that investigation should be carried according the laws of underground hydraulics. Schematically the pseudo liquefaction phenomena its entity and main parameters change depending on flow rate is shown in. [28]

If definite volume of definite height of sand should be set in vertical pipe and that sand bed should be influenced by definite quantity of swelled (liquid or air) agent, so supplied agent will pass thought the sand bed and its position will be stable. When sand bed resistance in swelled agent will be equal to its weight then sand particles begin to move and the bed passes into pseudo liquefaction.

After that supplied flow rate increase will promote the growth of the bed. At the same time the value of its resistance will stay permanent. Further, dynamic level arises at definite meaning of flow rate and at the conformed height.

Generally, pseudo liquefaction bed for some fine material and swelling medium exists within definite rate differences, and if the rate overrun the upper level then sand fines separation and leaving this level takes place.

It is known that in many cases when mixing high molecular polymers with usual Newtonian fluids they obtain new qualitative properties. In this context CMC makes no exception.

CMC water solution acts as non Newtonian fluid considering that the numbers of investigations were carried out in order to obtain homogeneous dispersion liquids adding nano particles in CMC solution. During the experiments on clay swelling study it was revealed that optimal variant of composition for swelling prevention consists of solution containing 1,0% of CMC and 0,01% of nano particles. Considering that the rheological properties of CMC water solution different concentration are studied.

It should be noted that all experiments on rheological parameters study were carried out using capillary viscosimeter. [29] at first stage water rheology was established as standard Newtonian fluid then polymer solutions were prepared adding 0,1; 0,5; 1,0;1,5 and 2,0% of CMC and their rheological parameters have been determined.

Obtained results are shown on the fig.4.2. as it clear from the figure, all the curves cross the coordinate axis under different angles (excluding water because the water is Newtonian liquid

and the right line characterizing it's rheological properties passes through central point of coordinates). That shows their native to viscoplastic properties.

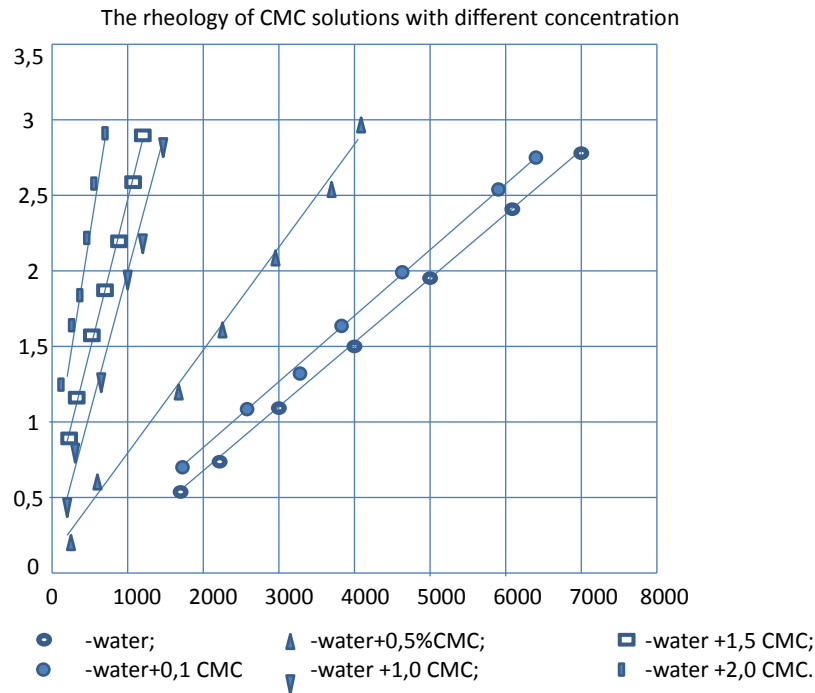


Fig. 4.2.

As it is clear from the fig.4.2., while CMC concentration increases, solution viscosity growths including sliding strain increase that indicates its viscoplastic feature.

Then the tests have been continued adding cuprum nano particles in polymer solutions on the base of “small concentration” effect. Different variations were obtained in order to origin nano liquids of optimal composition, cup run nano particles of 0,054; 0,025; 0,01% were added for each concentration and mixing then by different methods (hydrodynamic, mechanic) their dispersion stability was determined. Therefore, it was established that at concentration of polymer solution low than 1% cuprum particles are precipitated in all cases. The most stable solution is obtained at mixture: water +1%, CMC+0,01%, Cu... if shall increase the CMC concentration to 1,5 and 2% then stability of received liquid will be more.

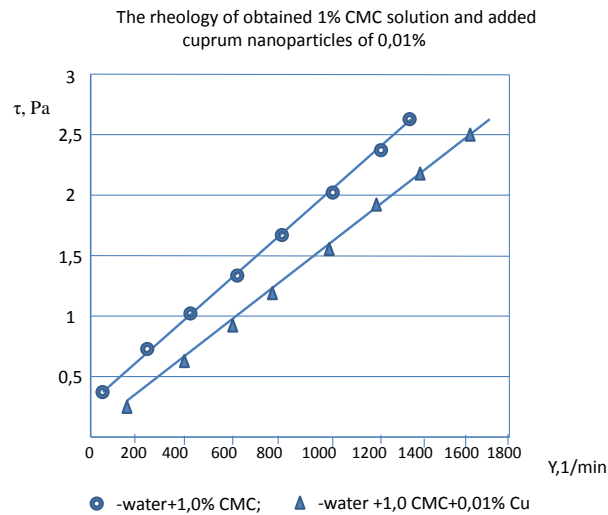


Fig .4.3.

The rheology of obtained liquid (water+1% of CMC+0,01 Cu) is shown on fig. 4.3. Here rheological curve of 1% CMC is shown for comparison. As it is clear from the figure liquid viscosity for two solutions of CMC of equal concentration where nano particles are added is low and sliding stain is comparatively less.

4.4. The study of nanoinfluence on the process of sandy plugs formation.

During the fluid run through the rocks that keep the reservoir slightly stable properties it's skeleton is broken, then sand particles begin to pass to the well bottom.

Gatheredsand particles on the well bottom decrease its capacity level and generally lead to sand plug formation that decrease well operation.[30] The sand plug formation is the most probably at the last stage of field development. Here because of sand plug maintenance shutdown takes place and that is the cause of operation expenses. Therefore, the study of sand plugs formation reason, the analyses of the processes within the plugs formation zone, and these wells operation, development of the efficient method for sand control is the main problem of well operation investigation. Sand plugs and sand accumulations that can take place in several version.

One of the versions is that filter part of old well casing because of long time operation is dotted and destroyed and for this time matter flow regime changes and actually sand entry takes place. Usually in such cases the specially prepared filters are used for operational pipe reconstruction and protective works on well bottom are carried.

For the second case the formation stability is lost and the structure of formation rock components changes deteriorating its reservoir properties that is the cause of sand slug formation.

In third case, for example, wrong action of geotechnological measures can lead to well bottom sand plug formation.

In such cases, if the sand block off the pipe filter part and as a result liquid entry in bottom hole filly stops, such trouble can be eliminated only by well washing-up. If the filter is not fully locking and there is some inflow from the formation then the special matter should be added in annular providing its saving in pseudo liquid faction form or balancing the well operation condition the sand together with liquid should be lifted on the surface.

As it is evident providing normal operation conditions for sandy wells is not so walkover. Therefore, there is a great necessity to develop the methods practically supported and carried out new more efficient scientific-research works.

Obtained results showed that CMC solution places an important role in the process of sand interlayer fluidization. Nano particles addition confers new quality to the process of fluidization. Versus to water CMC solution and especially obtained matter adding nano particles considerably increases pseudo liquefaction height, simultaneously providing their distribution and therefore favorable terms for pseudo liquid faction process at low discharge rate of nano particles. It should be noted that in that passing ability increases because of sand layer expansion and fluid passing through this lightened.

One of the work specifications is that sand out cropping conditions in carried out tests are improved. That provides the effect of sand plug washing by nano fluid. The special attention was paid to fluid rate. In order to avoid any incident after fluid stable flow its average rate was found. As a result of tests, considering obtained information the plot of sand pseudo liquiefacted layer height as a function of fluid discharge rate was made. As it is show from fig.4.4. Proposed liquid mixture (water+0,1% of CMC+0,01% of Cu) is more efficient from the point of pseudolique faction conditions improvement.

The dependence of sand interlayers expansion from liquid discharge rate

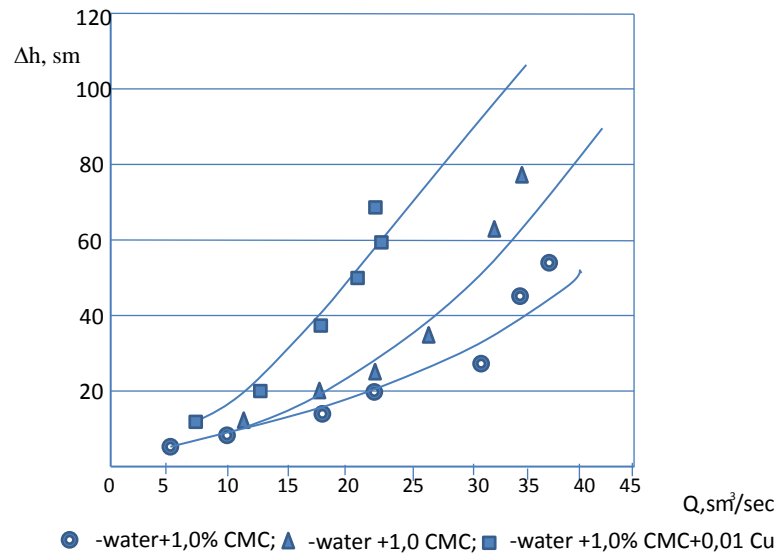


Fig.4.4

The experience shows that proposed nano fluid is able to increase sand layer height expansion for 2 times in relation to water.

Sand layer height increase can be a cause of its porosity and permeability increase and it is more efficient for practice. Thus, it is possible to control the sand producing wells washing out conditions adding nano particles and using nano fluids. In order to study the nano particles influence on the processes of pseudo liquid fraction the number of tests under laboratory conditions have been carried out. The investigations were conducted in two directions: the influence of nano particles on the process of clay swelling; and the influence of nano particles on pseudo liquefaction originated by sand particles. New rheologically more applicable dispersed solution was obtained as a result of mixing nano particles by 80nm sizes and 1,0% solution of CMC polymer. As a result of investigations carried out for clay swelling it was determined that fluid-water mixture with nano particles is more efficient in comparison with other solutions. The investigations connected to pseudo liquefaction showed that obtained liquid on the base of nano particles and under equal conditions considerable improves the state of pseudo liquefaction and under equal indices of sand rate in fluid the height increases for 2 times in average and is a cause of sand inter layer permeability increase and fluid flow enlargement. Based on the results of carried investigations it is possible to propose the idea the sand deposited actual damage on oil fields should be eliminated by application of liquid mixtures consist of nano particles.

CONCLUTIONS

1. The analyses of carried out investigations show that ultrasonic treatment allow reducing 20-30% of agent concentration for oil preparation.

It is determined that the possibility of liquid retention time reducing of combined demulsification with agents under ultrasonic impact for 2 hours.

It is determined that the excess of optimal impact frequency of ultrasonic field lead to decrease oil preparation process efficiency.

It is determined that when combining demulsification with agent and under ultrasonic impact on oil preparation process, light fraction losses decrease for 10-15%.

2. The numbers of agents that are added into injection water in order to originate its intensive movement in porous medium are used for oil recovery. The process of agents' injection magnetic treatment is analyzed in order to increase the injection process efficiency. At that it was determined that magnetic treatment speeds injection movement.

3. The question of physical and chemical agents injection in water out formation was studied. It was determined that adding of polymer components in working fluid decreases the water filtration to well and injection process efficiency.

4. Recently, nanotechnologies are widely used in oil recovery. The objective is adding of working nanoparticles of 9^{-10} nanometers. During nanotechnologies application process, the coefficient of surface tension between formation fluids decreases.

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