

# REPUBLIC OF AZERBAIJAN

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## ABSTRACT

of the dissertation for the degree of Doctor of Science

### **DEVELOPMENT OF RHEOKINETIC BASIS FOR APPLICATION OF HETEROGENEOUS FLUIDS IN OIL AND GAS PRODUCTION**

Specialty: 2525.01 – Oil and gas field  
development and operation

Field of science: Technical sciences

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**Baku - 2024**

The work was performed at the «Fluid Mechanics» Department of the Institute of Mathematics and Mechanics of the Ministry of Science and Education of the Azerbaijan Republic.

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## OVERALL RESEARCH CHARACTERISATION

**Relevance and degree of research of the topic** heterogeneous fluids have an extremely important place in oil production and hydrocarbon transport in view of their wide distribution and use, exceptional role in oil production processes and due to their specific physical and chemical properties. Heterogeneous systems include such systems as heterogeneous porous media, oil and natural bitumen, cements and concrete mixtures, clay solutions, and all multiphase types of foams and emulsions that differ so dramatically in chemical and phase compositions, physical properties, and applications. Heterogeneity, i.e., inhomogeneity and dispersion are common for such systems. The role of these factors in manifestation of various properties of the systems and, first of all, their impact on filtration instability becomes more significant with increasing dispersity and corresponding decrease in the pore size of the reservoirs. Another factor is the shear dilution effect and, in the case of filtration, shear thickening, which manifests itself as an anomalous increase in flow resistance in porous media (Marshall R.I., Metzner A.B, Abdo M.K.). The mentioned phenomena noted by the well-known scientists (Andersen S.I., Berland C.R., Dennis Siginer, Everett D.H., George B. Benedek, Hoffmann H., Israelachvili J., Rehage H., Speight J.G., Barenblatt G.I., Mirzajanzadeh A.Kh., Shvetsov I.A., etc.) are explained by viscoelastic effects, relaxation phenomena, coagulation process, especially intensively occurring in lyophobic aggregately unstable disperse systems. When a certain critical concentration of dispersed phase particles is reached, these effects lead to the spontaneous formation of a volumetric spatial structural mesh. The components of such a structural grid are contacts between particles and the particles itself, which together form spatial cells in the entire volume. In this case, the disperse system becomes structured, i.e. it enters a completely new state. Heterogeneous systems considered in fluid flow processes in reservoirs are complex multi-component mixtures containing, as well as oil, inclusions of water, gas, asphalt-resin and paraffin substances, mechanical impurities, etc., the presence of which is conditioned by both production conditions and peculiarities of some types of

pipeline transportation. At the same time, the heterogeneous mixtures flow is accompanied by a number of complicating factors: formation of waves at the interface of flow components, mass exchange processes between the components of the flowing fluids, increased pressure oscillations in the flow, flow locking in the pores, etc., which entails an increase in the non-equilibrium of the system as a whole. A number of works by Ametov I.M., Barenblatt G.I., Bocharov O.B., Yentov V.I., Zheltov Yu, Kosterin A.V., Kuznetsov V.V., Kurbanov A.K., Medvedkov V.I., Mirzajanzade A.Kh., Nigmatulin R.I., Nikolaevsky B.N., Panahov G.M., Suleymanov B.A., Shakhverdiev A.Kh. and others. To solve such problems a lot of algorithms have been previously developed (Tikhonov A.N., Ivanov V.K., Lavrentiev M.M., etc.), which are widely used in the control and management of oil and gas production processes (Seright R.S., McCool C.S., Green D.W., Skauge A., Ametov I.M., Basovich I.V., Bakhtizin R.N., Khasanov M.M., Mamedzade A.M., Mirzadjanzade A.H., Pirmamedov V.G., Sattarov R.M., Panahov G.M., Shakhverdiev A.H., etc.). However, all of them are based on one or another way of taking into account a priori information, which allows narrowing the area in which the solution of the inverse problem is sought. Application of a deterministic approach to the study of the separate behavior of multicomponent mixtures leads to an increase in the number of parameters introduced into the computational models and, consequently, to an increase in the calculation error due to the noise of the initial information (Berland C.R., Everett D.H., Tager A.A., George B. Benedek, Israelachvili J., Andersen S.I., Speight J.G., Rehage H., Hoffmann H., Jalalov G.I., Khuzhayorov B.H.).

The main factors defining the importance of the stated research are the increasing share of hard-to-recover oil reserves in the total volume of produced hydrocarbons, poor implementation of technological innovations, difficult exploitation conditions in environmentally sensitive oil and gas producing regions, and, finally, decreasing oil recovery of oil fields developed using conventional methods. Taking into account the importance of the present study of heterogeneous systems application in the development of oil and gas

fields, in the thesis work the task of research of reokinetik effects in inhomogeneous fluids under complicated field conditions and development of new technologies of gas and gas-liquid impact on reservoir systems as methods of oil recovery enhancement was set.

**Object and subject of research.** The main object of research is rheokinetic effects in heterogeneous fluids and the development of innovative industrial technologies of impact on the oil-saturated reservoir by in-situ generation of carbon dioxide. The subject of research is non-equilibrium anomalies in in-situ gas generation as a method of enhanced oil recovery (EOR), regulating the hydrodynamic flow behavior of heterogeneous fluids during displacement in inhomogeneous porous media and depleted oil-saturated reservoirs.

**Research aims and objectives.**

Development of reokinetik bases of heterogeneous fluids application in oil and gas production processes, its control taking into account complicating factors, finding correspondence of thermodynamic conditions of pore space gas saturation to specific conditions of liquid hydrocarbon deposits location and creation of technologically effective industrial technologies of impact on the reservoir using gas-generating systems.

**Research Methods.**

The scientific work is of theoretical and applied nature. The tasks set in the dissertation were solved by means of laboratory experimental research, mathematical processing of the results and analysis of the data received with the use of software and probabilistic-statistical methods. The developed methods of diagnosing the state of heterogeneous gas-generating systems are tested on model and practical some examples, and confirmed by the developed innovative technologies with proven industrial efficiency.

**The main points to be defended:**

1. Rheological features of heterogeneous hydrocarbon systems and methods of adjustment. Factors of thixotropic flow of fluid with variable component structure and variable external conditions, methods of regulation of non-equilibrium process by gas-generating compositions.

2. Methods of adjusting non-equilibrium properties of complex hydrocarbon fluids. Algorithms for describing kinetics of in-situ gas generation that take into account the effect of dissolution of gas nuclei in reservoir fluid on the intensity of gas release.

3. Reo-kinetic effects in heterogeneous fluids in the process of rheo-gas-chemical generation of carbon dioxide. Methodological bases of a new method of in-situ carbon dioxide CO<sub>2</sub> gas generation aimed at recovery of residual hydrocarbon from heterogeneous oil and gas reservoirs.

4. Technological aspects of residual oil recovery during in-situ generation of carbon dioxide. Methods of optimization of concentrations of foaming agents and inhibiting additives in gas-forming solutions during in-situ generation of blocking barriers in highly permeable zones of porous medium.

5. Technical and technological bases for implementation of rheo-gas-chemical technologies of enhanced and improved oil recovery with proven industrial efficiency in order to produce hard-to-recover oil reserves.

6. Methodological bases for evaluation of technical and technological efficiency of gas impact methods using CO<sub>2</sub> carbon dioxide injection.

### **Scientific novelty of the research.**

1. The effect of oil viscosity fluctuations as a result of dynamic equilibrium in the process of thixotropic structuring of heterogeneous composition has been revealed. Directed control of rheological characteristics of the investigated systems by means of interphase gas generation has been implemented.

2. For the first time there were developed compositions and rheo-gas-chemical method of carbon dioxide generation as a method of hydrodynamic impact on oil-saturated reservoir presented by heterogeneous reservoir structures.

3. The kinetics of gas formation of heterogeneous solutions under various thermodynamic conditions is estimated and the intrapore generation of "wet" carbon dioxide is investigated.

4. A rheo-gas-chemical technology was developed, researched and implemented, including simultaneously with isolation of highly

permeable water inflow zones in response production wells and blocking of highly permeable interval in injection wells in order to stabilize the filtration barrier for injected water and connect immobile oil-saturated reservoirs to the development.

5. An innovative technology for enhanced oil recovery based on in-situ generation of pseudo-boiling gas-liquid composition slug has been created. It is experimentally shown that the process of gas generation due to thermochemical reaction is associated by pressure and temperature growth in the impact zone.

6. For the first time, a method of suffusive cleaning of porous medium by using in-situ generated carbon dioxide CO<sub>2</sub>, which shows properties of supercritical fluid under specific thermobaric conditions, has been developed.

### **Theoretical and applied value of the work.**

1. The results achieved in the dissertation work made it possible to develop methods of control of non-equilibrium properties of heterogeneous gas-liquid compositions taking into account the factors complicating the flow, which have found use in implementing technological processes of oil and gas production and transport of hydrocarbon products.

2. 2. A method of in-situ gas generation and a technique for estimation of gas generation kinetics depending on the concentration of reacting compositions and mineralization of aqueous solutions were developed.

3. 3. A series of technological techniques and technologies, protected by patents for inventions of the Republic of Azerbaijan, Russian Federation, USA, aimed at the use of in-situ generation of carbon dioxide in EOR and IOR processes have been developed.

4. The results of theoretical and experimental studies were used in the implementation of the designed industrial technologies on the fields of Azerbaijan, the Russia Federation, USA, People's Republic of China, Vietnam.

### **Implementation of the research findings.**

1. The complex of theoretical and laboratory studies provided the basis for the implementation of the developed technology in a number of fields in Azerbaijan, Russian Federation, USA, PRC in

2002-2023 in conditions of both continental and offshore oil production.

2. Pilot operations were carried out in the Russian Federation as part of an innovation and investment project at the AB1-3, AB4-5 and BV8 reservoirs of the Samotlor field, at the Novo-Pokurskoye field (reservoirs YV(1) and YV(2)), as well as at the fields of Zhongyuan Oilfield Company, Sinopec (PRC), Petrochina, and CNOOC. Pilot tests of the new technology of carbon dioxide generation were also carried out at the SOCAR oil fields. The total additional oil production at the pilot section of the Bohai Bay field (PRC) for the post-operational period was  $\Delta Q_{\text{н}} \approx 6000$  tones.

3. The results of estimating the technological efficiency of the pilot project implementation at the test site of Vatyeganskoye oilfield for 21 producing wells confirmed the feasibility of the wide use of the developed methods - the incremental oil production was 5759 tons (12.8% of the current oil production increment).

4. Pilot tests were performed on three wells in the Muskogee field area (Oklahoma, USA) - TR-2-15, 3TW-25, TR2 W-11, which showed successful results in increasing incremental oil production from responding production wells.

5. Implementation of suffosion methods of bottom-hole zone cleaning in production wells on the Binagadi Oil Company, Absheron Oil, Karasu Oil fields resulted in a 20-30% increase in the post-operation average daily flow rate.

**Approbation of the work.** The main statements of the work were reported at:

Scientific and Practical Conference “Factor 4”, Baku, 2001; International Scientific Conference ‘Modern Problems of Oil Recovery (“Oil Recovery-2003”’, 19-23 May 2003; “Transport Phenomena in Manufacturing and Materials Processing” Conference, Houston, TX, June 19-23, (2005), (USA); ASME Joint U.S.-European Fluids Engineering Summer Meeting, Miami, FL, July 17-20, 2006; Symposium on “Advances in Materials Processing Science”, ASME International Mechanical Engineering Congress and Exposition, Chicago, IL, November 5-10, 2006; International Conference on Mathematics and Mechanics devoted to the 70-th



Anniversary of corr. member of NASA, prof. Isgenderov B.A., 2006; SPE Production and Operation Symposium, Oklahoma City, OK, March 31 - April 3, 2007; SPE International Symposium on Oilfield Chemistry Proceedings, 28 February – 2 March, 2007, Houston, TX, USA; 6th Symposium on Transport Phenomena in Manufacturing Processes, 5th Joint 2007 ASME/JSME Fluids Engineering Summer Meeting, San Diego, CA, July 30-August 2, 2007; VII Scientific and Practical Conference “Geology and Development of Fields with Hard-to-Recover Reserves”, 25-27 September 2007, Gelendzhik; International Scientific Conference “Geopetrol-2008”, Poland, Krakow. - 2008; International Scientific and Practical Conference “Khazarnftgazayatag-2008”, 2008, Baku; FEDSM2009, ASME 2009 Fluids Engineering Division Summer Meeting, August 2-6, 2009, Vail, Colorado USA; International Scientific and Technical Conference “Geopetrol 2010” “New methods and technologies of oil production”; International Conference “Continuum mechanics and related problems of analysis” dedicated to the 120-th birthday Anniversary of academician N. Muskhelishvili, Georgia, Tbilisi, September 2011; International Scientific Seminar “Non-Newtonian Systems in Oil and Gas Industry”, Ukhta, 15-16 November 2011; International Seminar “Non-Newtonian Systems in Oil and Gas Industry”, dedicated to the memory of the outstanding scientist, Professor, Doctor of Technical Sciences Azat Khalilovich Mirzajanzadeh, Ufa, 22-23 November 2012; International Conference dedicated to the 90th anniversary of the birth of Heydar Aliyev, 2013; Akademik A.X. Mirzəcanzadənin 85-illik yubileyinə həsr olunmuş «Neftqaz sahəsində qeyri-Nyuton sistemlər» mövzusunda Beynəlxalq elmi konfrans, Bakı, 21-22 noyabr, 2013; International Scientific Conference ‘Geopetrol-2014’ (Zakopane, Poland), 2014; ASME/IMECE International Mechanical Engineering Congress & Exposition, Phoenix, Arizona, November 11 – 17, 2016; International conference dedicated to the 90th anniversary of academician Azad Mirzajanzade, Baku, Azerbaijan, December 13-14, 2018; International Scientific and Practical Conference ‘New Ideas in Earth Sciences’, Russia, Moscow, 23 Miklukho-Maklaya St., Russia, 03-05 April 2019; International Conference "Modern

Problems of Mathematics and Mechanics" devoted to the 60th anniversary of the Institute of Mathematics and Mechanics, 23-25 October, 2019, Baku, Azerbaijan; International Conference "Modern Problems of Mathematics and Mechanics" devoted to the 60th anniversary of the Institute of Mathematics and Mechanics, 23-25 October, 2019, Baku, Azerbaijan; International Scientific and Practical Conference 'Innovative Technologies in Oil and Gas Industry. Problems of Sustainable Development of Territories' dedicated to the 10th anniversary of the North Caucasus Federal University, 09-10 December 2021, Stavropol, RF; International Conference on Actual Problems of Applied Mechanics – APAM-2021 Samarkand, Uzbekistan October 27-29, 2021 – «Evaluation and control of gas-dynamic parameters of gas pipelines transporting heterophase mixtures»; International Scientific and Practical Online Conference “Innovative Solutions in Geology and TRIZ Development” Moscow - 16-17 November 2021; First International Bilateral Workshop on Science between Dokuz Eylül University and Azerbaijan National Academy of Sciences; 19 November 2021; International conference dedicated to the 110th anniversary of Academician I.I Ibrahimov, ANAS, Institute of Mathematics and mechanics; International Conference Mathematical Analysis and its Applications in Modern Mathematical Physics, September 23-24, 2022; Samarkand, Uzbekistan / Ministry of Higher and Secondary Special Education of the Republic of Uzbekistan Samarkand State University - Mathematics Institute of The Academy of Science of Uzbekistan; V International Workshop “Thermal Methods for Enhanced Oil Recovery: Laboratory Testing, Simulation and Oilfields Applications” THEOR2022, Baku, Azerbaijan, November 3-5, 2022; International Conference “Modern Problems of Mathematics and Mechanics” dedicated to the 100th anniversary of national leader Heydar Aliyev, Institute of Mathematics and Mechanics, Baku, 26-28 April 2023; Eighth International Scientific Conference “Actual Problems of Applied Mathematics and Information Technologies - Al-Khwarizm 2023” dedicated to the 105th anniversary of the National University of Uzbekistan, 1240th anniversary of Musa al-Khwarizmi. SGU, Samarkand, Uzbekistan,

25-26 September 2023; International Scientific and Practical Seminar “Innovative Technologies of Oil and Gas Production” dedicated to the 95th anniversary of Academician Azad Mirzajanzade, Azerbaijan State University of Oil and Industry (ASUNP), Research Institute “Geotechnological Problems and Chemistry of Oil and Gas”, 29 September 2023.

**Personal contribution of the researcher.** Author was directly involved in the planning of research work presented in the dissertation study, problem formulation, selection of research methods, development of experimental setups, laboratory research and field implementation. He managed the issues of the published scientific papers covering the subject of the dissertation work, justification, creation of the research methodology, scientific literature review, and analysis of the results obtained.

**Author’s publications.** On materials of the dissertation work 82 scientific works, including 49 in scientific journals (31 - abroad), 17 patents for invention and 1 certificate of registration of software product (Azerbaijan Republic, Russian Federation and USA); 15 articles or theses in materials of conferences, forums, sessions (15 - abroad) have been published.

**Name of the organization where the work was completed.**

The dissertation work was conducted at the «Fluid Mechanics» Department of the Institute of Mathematics and Mechanics of the Ministry of Science and Education of the Azerbaijan Republic.

**Structure and scope of the dissertation work.** The total volume of the dissertation work is 339739 symbols, including title page (463), table of contents (3567), introduction (72188 symbols), 6 chapters (chapter 1 - 70097 symbols, chapter 2 - 43063 symbols, chapter 3 - 24189 symbols, chapter 4 - 64588 symbols, chapter 5 - 35823 symbols, chapter 6 - 23765 symbols), which are divided into 30 subchapters, conclusions and recommendations (1996 symbols), list of references and appendices. The volume of the dissertation is 340 pages, includes 122 figures, 52 tables, 204 titles of used literature.

**Acknowledgement.** Author considers it his duty to express deep gratitude to the memory of academician A.H. Mirzajanzade for the knowledge and skills acquired at his scientific school. Author expresses his deep gratitude to the scientific adviser - Corresponding Member of the National Academy of Sciences of Azerbaijan, Doctor of Technical Sciences, Professor Geylani Panahov for fruitful ideas, actual formulation of research problems, organization of industrial tests, valuable advice and constant attention in the process of work on the dissertation. I express my gratitude to the Vice-President of RANS, Doctor of Technical Sciences, Professor Azizaga Shakhverdiev for assistance in the implementation of scientific and applied tasks, organization of applied research and tests. The author expresses sincere gratitude to numerous co-authors for many years of cooperation and support: Sayavur Bakhtiyarov, Ramil Bakhtizin, Arif Mamed-zade, Gadji Melikov, Bagir Suleymanov, Arif Suleymanov, Ilya Mandrik, Renqi Jiang, all colleagues in joint research. I express my gratitude to the staff of the organizations involved in the development and implementation of the thesis. I express my deep gratitude to my colleagues at the of “Fluid Mechanics” Department of the Institute of Mathematics and Mechanics for co-operation and assistance in the research.

## **CONTENT OF RESEARCH WORK**

**The introduction** substantiates the relevance of the conducted research, formulates the purpose and the main defended scientific statements, methods of solving the set tasks, applied value and implementation of the results of the work.

**In the first chapter** of the dissertation work the basic principles, approaches, methods of determining the main factors, physical and chemical effects shown in the flow of investigated compositions and formation fluids are formulated. The necessity of this is explained by the important role that phase inclusions play in the formation of the structure and physical and mechanical properties of heterogeneous systems. Increasing production of paraffinic and high-viscosity oils, as well as increasing production of high-viscosity and fast-flowing petroleum products requires the study of their

rheological characteristics and selection of optimal parameters for displacement of various non-Newtonian systems. At the same time, one of the most important flow problems is the study of heterogeneous behavior of oils determined by the content of paraffin-asphalt-resin components in them. Considering the impact of each of the components, it can be noted that the presence of spatial structure depends mainly on the presence of paraffin fractions in the oil composition. Structural and mechanical properties of oils are determined mainly by the following factors: velocity gradient, temperature of the system, manifestation of thixotropy, etc.

The phenomenon of viscosity anomaly was discovered in the early studies of polymer and petroleum systems. Under viscosity anomaly conditions, steady-state flow behavior is described by the function  $f(\tau, \gamma) = 0$ . Its graphical illustration is called a flow curve. Quite often the experimental data are also presented in the form of dependences  $\eta(\tau)$  or  $\eta(\gamma)$ . Since at the viscosity anomaly  $\gamma$  the viscosity changes more strongly than  $\tau$ , the dependence  $\eta(\gamma)$  is weaker than  $\eta(\tau)$ . These dependencies are an important physical characteristic of non-Newtonian systems. In addition, it is possible to consider viscosity anomaly as a manifestation of linear and nonlinear viscoelasticity. Commonly available method of taking “flow curves” is rotational viscometry, which gives information only on the nature of change of tangential stresses  $\tau$  from viscosity  $\eta_s$  or velocity gradient  $\gamma$  in the usual way  $\eta_s = \tau / \gamma$ , where  $\gamma$  - shear rate. Interpretations of experimental measurements of viscosity  $\eta_s$  as a function of shear stress gradient  $\gamma$  in coordinates  $x = \tau^2$  and  $\gamma = 1 / \eta_s^2$  gives an indication of the nature of elastic properties of the liquids under study. The properties of liquids associated with anomalous dependence of viscosity on  $\tau$  or  $\gamma$  can be classified by the nature of the elastic properties of the system under study. Any fluid will exhibit elastic behavior if the shear stress becomes comparable to its elastic modulus. Conversely, the correction is negligible and deviations from the property are observed, as shown

by the Ree-Eyring<sup>1</sup> equation, any viscoelastic fluid will have an “inelastic region” in which  $\tau^2 \ll 4G^2$  and  $\eta_t \approx \eta_0$ . In this region, the elastic correction is negligible and deviations from the Newtonian flow properties are observed, which can be attributed to the change in  $\eta_t$ . One of the reasons for the display of anomalous viscosity is super micellar structure formation, which has been found in many hydrophobic colloidal solutions. The cause of particle sticking may be due to impaired aggregative stability and coagulation. In nonpolar media, to which hydrocarbon liquids-and, in particular, heterogeneous oils, the bonds between particles arise due to partial recrystallisation or attraction to each other of polar groups of compounds such as resins, naphthenic acids and others. In the thixotropic theory of viscoelasticity, it is assumed that if the elastic energy reaches a certain critical value, the corresponding structural element will collapse, which then ceases to participate in the development of stresses. The process of spontaneous thixotropic bond breaking-rebuilding in a structured system can be described as follows<sup>2</sup>:

$$-\frac{dN_t}{dt} = k_1 N_+^n - k_2 N_-^m \quad ,$$

where  $N_+$  and  $N_-$  - concentration of unbroken and broken bonds;  $k_1$  and  $k_2$  – rate constants of bond destruction and restoration processes;  $n$  and  $m$  – constants, which, by analogy with chemical reactions, determine the reaction order of bond breaking and bond repair processes;  $t$  - time. It is quite natural to assume that the concentration of unbroken bonds determines the remoteness of the system state from the state of ultimate failure, which is characterized by the value of  $\eta_\infty$ . Then,  $N_+ = [\eta(t) - \eta_\infty] / (\eta_0 - \eta_\infty)$  and,

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<sup>1</sup> Taikyue Ree, Henry Eyring; Theory of Non-Newtonian Flow. I. Solid Plastic System. J. Appl. Phys. 1 July 1955; 26 (7): 793–800. <https://doi.org/10.1063/1.1722098>

<sup>2</sup> Larson, Ronald & Wei, Yufei. (2019). A review of thixotropy and its rheological modelling. Journal of Rheology. 63. 477-501. 10.1122/1.5055031.

consequently,  $N_- = [\eta(0) - \eta(t)] / (\eta_0 - \eta_\infty)$ . Under the impact of deformation, the dynamic equilibrium of the processes of destruction and restoration of bonds is shifted, and the degree of destruction of the structure increases. The equation takes the form of the equation when flowing with shear rate:

$$\frac{1}{\eta_0 - \eta_\infty} \left( -\frac{d\eta}{dt} \right) = k_1 \left( \frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} \right)^n \gamma^P - k_2 \left( \frac{\eta_0 - \eta}{\eta_0 - \eta_\infty} \right)^m,$$

$P$  - constant determining the influence of shear rate on the process of structural bond failure in the system. Once steady-state flow is reached, there must be an equilibrium between the processes of destruction and reconnection in the system. This is satisfied by the condition  $(d\eta/dt) = 0$ . Then the viscosity in the steady-state flow regime is determined from equation:

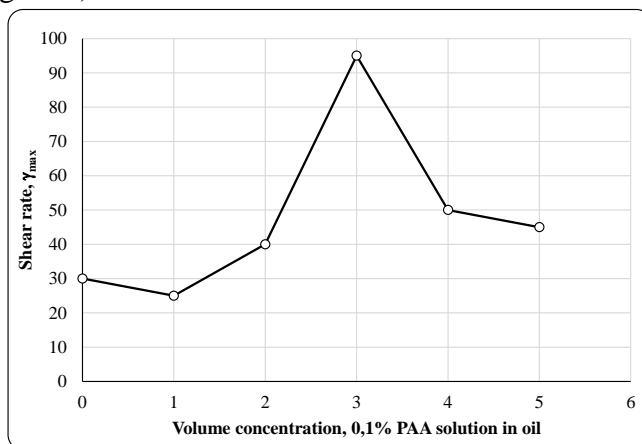
$$k_1 \left( \frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} \right)^n \gamma^P = k_2 \left( \frac{\eta_0 - \eta}{\eta_0 - \eta_\infty} \right)^m.$$

Thus, knowing the constants it is possible to estimate the dependence of effective viscosity on shear rate. The process of destruction and restoration of the internal structure of the system is closely related to viscosity fluctuations and, ultimately, determines the dynamics of thixotropic behavior of compositions. When injecting aqueous polymer solutions in oil reservoir, the conductivity of filtration paths for oil and water is levelled to a great extent, levelling the displacement front by changes in viscous heterogeneity, prolonging the water-free period of well operation, which as a result contributes to the increase in oil recovery<sup>3</sup>. The use of water-soluble

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<sup>3</sup> Castro, Ruben & Maya, Gustavo & Jimenez-Diaz, Robinson & Quintero, Henderson & Díaz-Guardia, Venus-Minerva & Colmenares-Vargas, Kelly-Margarita & Palma-Bustamante, Jorge-Mario & Delgadillo, Claudia & Perez, Romel. (2016). Polymer flooding to improve volumetric sweep efficiency in waterflooding processes. CT y F - Ciencia, Tecnología y Futuro. 6. 71-90. 10.29047/01225383.10.

polymers makes it possible to control the viscous instability at different shear rates of heterogeneous systems. Addition of water-soluble polymer (polyacrylamide) to oil in a certain volume ratio enhances its relaxation properties. It should be noted that when 0.1% aqueous solution of polyacrylamide is added to oil, the manifestation of non-Newtonian viscoelastic thixotropy is observed in the sample. The addition of the polymer to the studied heterogeneous system favours its transition to a strongly relaxing state<sup>4</sup>. Further increase of polyacrylamide concentration in the composition breaks this tendency (figure 1).



**Figure 1. Dependence of oil rheological behavior on the concentration of water-soluble polyacrylamide (PAA)**

This fact may be related to the formation of a persistent emulsion in the oil-polymer composition. The rheological behavior of a series of compositions including oil and  $\text{Na}_2\text{CO}_3$  sodium carbonate additives was also investigated in this work.

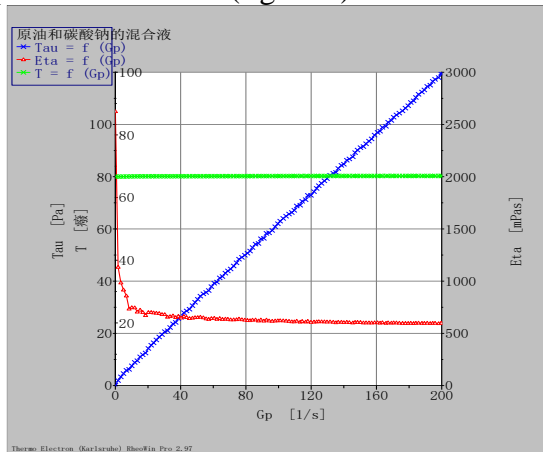
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<sup>4</sup> Abbasov, E.M., Huseynov, V.G., Jafarova, U.F., Nasibova, S.I. In situ gas generation in dispersed systems to control structure formation // Trans. Natl. Acad. Sci. Azerb. Ser. Phys.-Tech. Math. Sci. Mechanics, 2022, 42 (8). - Pp. 3-16.



Research was carried out on a HAAKE Rheostress 600 rheoviscometer, rheological measurements were carried out at adjustable modes of shear rates.

Thermostating was carried out at a temperature of 65°C, the pressure was kept at 2.0 MPa. At certain angular shear rates, the values of tangential shear stress  $\tau$  (Pa) and effective viscosity  $\eta$  (mPa's) were determined.  $\eta_{\phi} = \eta_{\phi}(\dot{\gamma})$  dependences were plotted based on the experimental results (figure 2).



**Figure 2. Rheological curve for the mixture “oil+2% Na<sub>2</sub>CO<sub>3</sub>”**

Analysis of the obtained dependences showed that the rheological behavior of the studied oil samples has a thixotropic character. It should be noted that at additions of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) at a concentration of 2.0 vol. % to the oil sample one can note a poor manifestation of thixotropy in the sample volume. The observed effects can be explained by gas formation at chemical reaction of naphthenic acids contained in oil composition with sodium carbonate additives.

In a number of technological systems exhibiting relaxation properties, non-equilibrium effects characterized by the duration of transient processes are observed. Non-equilibrium properties of such systems can have a significant impact on the hydrodynamic behavior of gas-containing insulating solutions in the ‘well - formation’

system, in this connection the study and evaluation of these properties of such systems is of practical interest.

Applying dilatant properties to the solution at high shear rates, it is possible to achieve a significant increase in hydraulic resistances in the absorbing channels. If absorption occurs in a porous medium, the absorption intensity of a viscoelastic solution can be determined from the following expression:

$$q = \frac{2\pi kh}{\mu} p_0 \frac{2Tx^2}{2T_0x^2 \ln x + T}$$

where  $k$  – permeability of the near-wellbore zone of the absorbing formation;  $h$  – bed thickness;  $\mu$  – solution viscosity;  $T_0$  – abnormal formation pressure;  $T_0=r_c^2/4\alpha$ ;  $r_c$  – borehole radius;  $\alpha$  – reservoir piezoconductivity;  $X = \frac{R(t)}{r_c}$ ;  $R(t)$  – radius of loss zone.

Calculations on this dependence show that the intensity of absorption of viscoelastic solution with  $T=10^3$  s is 3-4 times less than that of viscous fluid into the borehole zone of the absorbing formation ( $x=10\div 100$ ) under other equal conditions.

Naturally, technological processes of reservoir pressure maintenance in an oil-saturated reservoir should be combined with regulation of the hydrodynamic state of the porous medium, providing reduction of filtration resistance and restoration of primary permeability.

The results of the study revealed the effect of activation of systems in a porous medium by means of artificial cavitation and as a result of non-equilibrium filtration in the volume. In contrast to traditional methods of activation of mixtures in porous medium in the mode of flow turbulisation, in the proposed method it is provided by inclusion of gas-generating components in the composition of mixtures, the thermochemical reaction of which in aqueous medium proceeds with intensive gas formation.

As the latter, weak salts of carbonic acid (calcium carbonate  $\text{CaCO}_3$ , sodium hydrogen carbonate  $\text{NaHCO}_3$ , soda ash or sodium carbonate  $\text{Na}_2\text{CO}_3$ ) were used in our studies. Intensive gas formation with the formation of gas bubbles (carbon dioxide) in the mixture

goes in parallel with the process of their collapse, which is followed by local pressure jumps and, as a consequence, the destruction of the oil sheath surface. The manifestation of artificial activation in the process of gas generation is due to the change in the radius of curvature of the surface of homogeneous nuclei of the new phase. At deformation of nuclei the Laplace condition of their stable equilibrium in the pores of the medium is violated, and they pass into the category of critical and supercritical form.

The kinetics of gas phase release and the size of the formed bubbles depend on the specific regularities inherent in this case. The pressure in a growing gas bubble obeys the equation of state:

$$P = \frac{m RT}{M V_2} = \frac{3}{4\pi} \frac{m RT}{M r_2^3}$$

The surface energy force compensates for this pressure, defined by Eq:  $P_\sigma = 2\sigma_{\text{мсз}} / r_2$

In addition, the forces required to overcome the viscous resistance during the expansion of a bubble in a viscous-plastic medium of oil trapped in pores should be taken into account here. This mixture behaves as a Schvedow-Bingham body, and at deformation of oil as an incompressible medium there is only a shift of some layers relative to others, i.e.

$$P_\mu = \sigma_T,$$

where  $P_\mu$  - pressure required to deform the solution around the growing bubble;  $\sigma_T$  is the ultimate shear stress of the solution film. Then, the expansion of the gas bubble in the pinched oil must satisfy the following condition:

$$\sigma_T r_2 + 2\sigma_{\text{мсз}} r_2^2 < \frac{3}{4\pi} \frac{m}{M} RT,$$

where  $m$  – gas weight;  $M$  – gas molecular weight.

Cavitation in jammed oil will occur when a gas bubble expands rapidly. When bubbles remain in a low-pressure zone for a short period of time and mix in deposited oil, as well as immediately after

the fluid moves into a normal or high-pressure region, bubble collapse will occur<sup>5</sup>.

The estimates show that such oil, which has a dimension with surface tension values  $\sigma_T = 10^2$  Pa,  $\sigma_{жсз} \approx 6,4 \cdot 10^{-3}$  Pa, satisfies the condition of expansion of a carbon dioxide bubble with a size  $r_T > 1,7$  mm. Stoichiometric reaction taking place between the gas-forming components of the mixture, in most cases allows to achieve favorable conditions for bubble expansion.

We have performed experiments to determine the effect of hydrogen index on the gas volume generated in the process of rheochemical reaction of gas-generating agents. Studies were carried out at constant thermostating of the system at temperature  $T=293$ K and different volume ratios of gas-emitting and gas-generating agents - aqueous solution of sodium carbonate  $\text{Na}_2\text{CO}_3$  and “sour” water with different values of the hydrogen index.

In the performed experiments the concentration of sodium carbonate in the aqueous solution was 12 %, and the value of the hydrogen index pH varied from 3 to 6.

The results of experiments indicate that the most intensive gas formation in the reactive solutions occurs at the value of  $\text{pH} = 3$ . The volume of generated gas (carbon dioxide) is sufficient for adequate gas saturation and thus activation of jammed oil.

The process was studied through laboratory experiments to evaluate the change in the strength and rheological characteristics of oil during the initialization of the gas generation process. Solution samples were prepared, which were mixing on ordinary fresh water and prepared on water with hydrogen index  $\text{pH}=3$  with inclusion of soda ash in the oil composition.

However, the small size of the pore space impacts the dynamics of the generated gas volume, reducing the process rate. When reducing the influence of porous medium on gas generation in oil, the results of research on the use of a special phase state of

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<sup>5</sup> Шленский О.Ф. Влияние слабых механических воздействий на частоту зародышеобразования и скорость терморазложения конденсированных систем // Химическая физика, т. 17, №7. – 1998. – С. 95-102.

carbon dioxide, called “supercritical”, are of special interest. The research served as a basis for further studies of the gas generation process in reservoir conditions. It is known that when oil interacts with carbon dioxide, its volumetric expansion occurs. This effect, along with changes in the viscosity characteristics of fluids, is one of the main indicators determining the efficiency of carbon dioxide application in the processes of oil production and recovery in the process of waterflooding of reservoirs. The volumetric expansion of oil is a function of pressure, temperature and the amount of dissolved gas. The volumetric expansion of oil under the influence of CO<sub>2</sub> is also affected by the content of light hydrocarbons (C<sub>3</sub> - C<sub>7</sub>). The greater the light hydrocarbon content of oil, the greater its volumetric expansion. As a result, the pore pressure increases, which causes additional displacement of some residual jammed oil to production wells. Volumetric expansion of oil even at partial saturation with CO<sub>2</sub> increases the displacement factor by 6 - 10% due to increased phase permeability for hydrocarbons, and, consequently, the final oil recovery.

Thus, the experiments carried out in the chapter were the basis for setting up and implementing experimental and applied studies of rheological effects during gas generation in porous media and developing methods for the control of field production operations.

**The second chapter** investigates rheokinetic effects in heterogeneous structures for developing control methods for technological processes in oil and gas production.

First of all, the factors causing changes in the fluid behavior in the reservoir are considered. Among the main anthropogenic causes that have a negative impact on the filtration properties of the bottomhole formation at the main technological stages of the well life are:

- solid phase of drilling mud penetration to the formation bottom-hole zone during drilling stage clogging the reservoir pores, significantly reducing the permeability of the medium up to complete cessation of flows from certain intervals of the section;

- penetration of mineral fluids into the porous medium leads to disturbance of the equilibrium state of the rock system, blocking the oil flow paths;

- change of the pore space structure also results from the impact of the drill bit on the borehole walls;

- at the stage of well support, the penetration of cement and cement slurry filtrate into the reservoir has a negative impact on the bottomhole cavity;

- the stage of well completion provides for maintenance of excessive hydrostatic pressure in the well. During perforation, debris from explosive materials invades the formation, resulting in pore plugging, fracture and compaction of the downhole formation zone;

- in the process of well exploitation, during well workover operations accompanied by well killing, complications similar to those manifested at the drilling stage (penetration of solid phase and external fluids to the reservoir) occur.

One of the ways to overcome the arising problems is proposed in the creation of technology of selective impact on wells. Its main purpose is to ensure, under certain boundary conditions, the greatest drainage coverage of multilayer development objects. Relevance of research of technological compositions has emerged in connection with the spread of new technologies based on heterogeneous fluids and carbonated fluids, which have a different mechanism of flow and participation in the processes of isolation of the bottomhole zone of the well. In the world and domestic practice as agents of reservoir pressure maintenance and increase of oil recovery factor, injection of various chemical solutions, including compositions based on water-soluble polymers, is widely used.

Theoretical and applied works in the field of filtration of heterogeneous systems taking into account heterogeneity, carried out by academician Azad Mirzajanzade and his school, provided the basis for the creation of a whole scientific direction in oil and gas production. In the works of the scientific school, as well as the world practice of enhanced oil recovery, physical and chemical methods of oil field development based on oil displacement from the reservoir by water, water-gas mixtures and hydrocarbon solvents, including

hydrocarbon (natural) gas at high pressure and carbon dioxide are widely studied and applied. When oil is displaced from the reservoir by agents mixed with it, the problem of eliminating the interface between oil and the displacing agent is fundamentally solved, capillary forces are levelled, mutual dissolution of oil and injected fluid takes place, and, ultimately, the completeness of its displacement is increased.

Gas methods of reservoir stimulation and enhanced oil recovery methods, in particular, injection of carbon dioxide slugs, are the most effective way to oil recovery, including from depleted reservoirs and reservoirs with hard-to-recover liquid hydrocarbon reserves. In the context of the proposed carbon dioxide use as a method of enhanced oil recovery in the presented work the mechanism of gas generation process in reservoir conditions with formation of pseudo-boiling gas-liquid system used as a rim for oil displacement and increase of reservoir coverage by displacement is considered. At the same time, the most important from the technological point of view is the need to establish the correspondence of thermodynamic conditions of gas saturation of pore space to specific conditions of occurrence of liquid hydrocarbon reservoirs. One of the main factors of impossibility to provide complete displacement of oil by water from reservoirs during waterflooding is the presence of viscosity and density heterogeneity and the problem of miscibility of displaced and displacing fluids, as a result of which a fractal interface is formed.

Oil displacement with miscible agents fundamentally solves the problem of complete elimination of the interface between oil and displacing agent, capillary forces “disappear”, oil dissolves in the injected fluid, resulting in increased recovery. Fluids that mix well with oil include carbon dioxide  $\text{CO}_2$ , which is used as the agent injected into the reservoir to displace hydrocarbons. Dissolving in heavy components of oil, carbon dioxide promotes swelling of hydrocarbons adsorbed on the surface of porous medium, their loosening and detachment from rock grains. Under pressure of about 10 MPa and temperature of 300-310 K, up to 250-300  $\text{m}^3$  of  $\text{CO}_2$  measured under standard conditions can be dissolved in 1  $\text{m}^3$  of oil.

However, the use of traditional methods of CO<sub>2</sub> injection causes noticeable corrosion of production equipment, which reduces its service life and requires special anti-corrosion treatment. At the same time, the disadvantages of traditional gas injection technologies also include: the need to have a gas source in the required volumes; using of high-pressure gas; complication of the well design due to increased requirements to the tightness of the production string; significant capital investments in the implementation of an optimal gas supply system, etc.

One of the most technologically and economically efficient methods of carbon dioxide generation is its formation as a result of chemical reaction between gas-emitting components. In the experimental laboratory studies, the thermobaric conditions of carbon dioxide release during the reaction of calcium carbonate samples of different fractional composition with “acidic” water (pH=3÷5) were evaluated.

We experimentally simulated the chemical reaction conditions between the gas-forming (aqueous hydrochloric acid solution) and carbonate rock samples, followed by the release of carbon dioxide and pressure changes in the system. In the conducted series of experimental studies, the dynamics of pressure and temperature changes of the reacting medium in the process of stoichiometric reaction of hydrochloric acid HCl and calcium carbonate CaCO<sub>3</sub> was studied<sup>6</sup>.

In the following series of laboratory tests comparative dependences of pressure change and volume of released CO<sub>2</sub> gas at reaction of aqueous solutions of sodium carbonate and hydrochloric acid prepared on fresh and formation water of Sianshor field (Azerbaijan) are given.

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<sup>6</sup> Panakhov, G.M., Bakhtiyarov, S.I., Shakhverdiyev, A.Kh., Abbasov, E.M. Oil Recovery by In-Situ Gas Generation: Volume and Pressure Measurements // ASME Joint U.S.-European Fluids Engineering Summer Meeting, Miami, FL, July 17-20, 2006, Paper # FEDSM2006-98359. - pp. 1 - 6.  
<https://doi.org/10.1115/FEDSM2006-98359>



Comparative analysis of indicators confirmed that at identical concentrations and volumes of reacting solutions the intensity of gas formation is higher in solutions prepared on formation water.

Laboratory tests have been conducted to study the effect of water phase salinity and oil component composition on the solubility of generated CO<sub>2</sub> in water. The solubility of carbon dioxide in water depends significantly on pressure, temperature and chemical composition of the fluid.

According to Sechenov's equation, the dependence of carbon dioxide solubility on the salt concentration in water is equal to:  $b_i^* = b_i \cdot 10^{-k_i n}$ , where:  $b_i$  - content of the  $i$ -th component dissolved in pure water that is in equilibrium with the gas;  $b_i^*$  - the content of the  $i$ -th component in the salt solution that is in equilibrium with the same gas;  $k_i$  - Sechenov's coefficient characterizing the influence of the given salt on the solubility of the gas component  $i$ ;  $n$  - concentration of the salt dissolved in water<sup>7</sup>. The degree of carbon dioxide dissolution released during the reaction is much less in formation water than in fresh water, which is the basis of the aqueous phase of the gas-emitting agent. At the same time a part of CO<sub>2</sub> is in the free phase and this "excess", dissolving in the system, changes the properties of fluids. Under constant temperature with increase of oil saturation pressure with carbon dioxide, viscosity decreases the more, the higher the pressures, that with increase of solubility of carbon dioxide in oil.

Under constant pressure, viscosity decreases with increasing temperature as carbon dioxide dissolves in it. The density of a mixture of oil and carbon dioxide can be fairly accurately calculated from the formula:

$$\rho_{cm} = \rho_n + 0,0008C,$$

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<sup>7</sup> Ентов В.М., Зазовский А.Ф. Гидродинамика процессов повышения нефтеотдачи. М.: Недра. – 1989. – 232 с.

where:  $\rho_{cm}$  и  $\rho_n$  – respectively density of mixture and oil in reservoir conditions, g/cm<sup>3</sup>;  $C$  – concentration of carbon dioxide in oil, %.

As part of the performed tests, the conditions of stoichiometric reaction between gas-releasing and gas-forming aqueous solutions in a free container were modelled. In view of the fact that the reaction between the investigated compositions happens according to the scheme of convective diffusion, the system was stirred to ensure complete contact of the reacting compositions. The pressure dynamics during the stoichiometric reaction is shown in Figure 7.

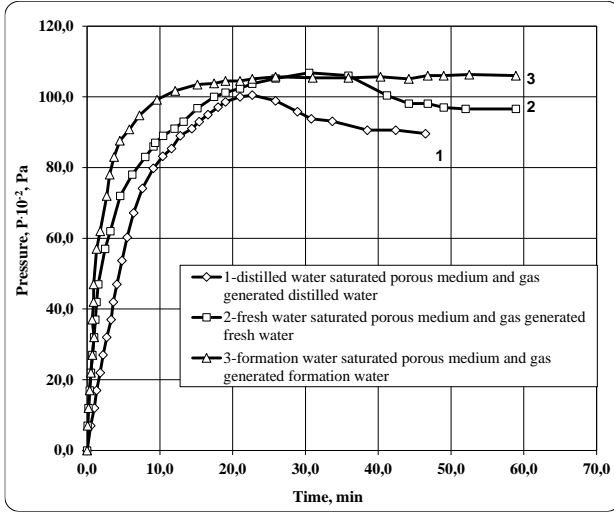
A gas-liquid mixture with non-equilibrium properties also generates additional energy in the reservoir or stimulates reservoir energy. Carbon dioxide generation in the reservoir is more effective in terms of changing the thermobaric conditions of the pay zone, and it naturally affects a number of filtration parameters such as changes in the viscosity ratio of the fluids involved in the rheochemical reaction, oil volume ratio and residual oil saturation, etc.

In the case of stoichiometric reaction in the structure of porous medium (composed of 95% quartz sand and 5% montmorillonite clay), the effect is somewhat different from the character of pressure change in the system observed in previous experiments. In the studies it is found that the pressure at the initial moment increases to some extreme value and then decreases. In the reaction medium, the presence of porous medium affects the dynamics of pressure change during the stoichiometric reaction. In contrast, in case of the availability of rock in the reaction medium of the gas-emitting solution, the aqueous phase of which is formation water, the pressure dynamics has a monotonic character (figure 3, curve 3).

The pressure decrease at the final stage of gas release in systems with porous medium is associated with adsorption of gas bubbles on the surface of particles with subsequent diffusion of gas molecules inside the rock grains.

To describe the gas release curves it is possible to use exponential functions equivalent to the functions used in the relaxation model in the form of linear differential equations of the first order. On the other hand, this approach does not allow to take

into account all details of current processes, in particular, in case of high values of fluid mineralization.



**Figure 3. Pressure dynamics during the reaction of gas-generating and gas-forming solutions in porous medium (95% silica sand + 5% clay)**

Considering that the gas bubbles formed already ( $C$  is the concentration of bubbles) partially dissolve and also contribute to slowing down the gas release, let us assume that the rate of their formation is equal:

$$v = v_1 - v_2 C - v_3 C^2; \quad (1)$$

где:  $v_1$  – the rate of gas formation without disturbance;  $v_2$  - dissolution rate of gas bubbles;  $v_3$  - the rate of slowing down the formation of new gas bubbles.

In this case, we propose models describing gas release in the form of nonlinear kinetic equations such as the one below. Assuming that there is a linear relationship between bubble concentration and pressure:  $P = KC$ ,  $K$  is the rate of change of pressure.

Then the kinetic equation can be written in the form:

$$\frac{dP}{dt} = kv_1 - (\alpha + v_2)P - \frac{v_3}{k}P^2 \quad (2)$$

$a_1 = kv_1$  - parameter affecting the pressure change during gas release;

$a_2 = \alpha + v_2$  - parameter, taking into account the influence of partial dissolution of gas nuclei on the pressure change;

$a_3 = \frac{v_3}{k}$  - coefficient, taking into account the influence of previously formed gas nuclei on the pressure change.

Then, we have:

$$\frac{dP}{dt} = a_1 - a_2P - a_3P^2 \quad (3)$$

To estimate the coefficients  $a_1$ ,  $a_2$ ,  $a_3$ , we will use a technique based on the provisions of the sensitivity theory. In the case of coefficients ( $a_2$  and  $a_3$ ), taking into account, respectively, partial dissolution of bubbles and the influence of the formed gas nuclei on the pressure change in the gas release zone, the solution (3) will have the form:

$$P = \frac{1}{2a_3} \left[ A \left( 1 - \frac{2}{1 + e^{A(t+c)}} \right) - a_2 \right], \quad (4)$$

where  $A = \sqrt{a_2^2 + 4a_1a_3}$  - (Figure 7 – curves 1, 2).

In the case when formation water is used as the aqueous phase of the gas-releasing solution (Binagady oil field), the coefficient that takes into account the effect of dissolution of gas nucleates, as it follows from the experimental results, is negligible. Therefore, equation (3) can be written in the form:

$$\frac{dp}{dt} = a_1 - a_3P^2, \quad (5)$$

the solution of which can be represented as a dependence  $P$  on  $t$ :

$$P = \sqrt{\frac{a_1}{a_3} \left( 1 - \frac{2}{1 + e^{2\sqrt{a_1a_3}(t+C)}} \right)}, \quad (6)$$

describing curve 3 (figure 6).

The pressure decrease at the final stage of gas release in systems with porous medium is associated with adsorption of gas bubbles on the surface of particles with subsequent diffusion of gas molecules inside the rock grains. In this case, the expression describing the formation and dissolution of gas bubbles is possible in the form:

$$\frac{dP}{dt} = a_1 - a_2P(t) - a_3P^2(t - \tau), \quad (7)$$

$a_2$  и  $a_3$  – ratios determining the pressure change taking into account the influence of gas molecules already formed and diffusing into the rock particles;  $\tau$  - is the characteristic diffusion time. In general, the solution of equation (7) is found in the form:

$$t \geq t_0, \quad P(t) = P_0(t), \quad t \in E_{t_0} = (t_0 - \tau, t_0] \quad (8)$$

Let us find a solution satisfying these conditions. Suppose that  $\tau > 0$  - lag constant. On the function segment  $P_0(t)$  function  $a_1 - a_2P(t) - a_3P^2(t - \tau)$  at  $t \geq t_0$  continuous. First, let us consider the solution of the problem (7) - (8) on the segment  $I_1 = [t_0, t_0 + \tau]$ . It's obvious that at  $t_0 \leq t \leq t_0 + \tau$ . As a consequence, for  $t \in I_1$   $(t - \tau) = P_0(t - \tau)$  and the problem under consideration reduces to finding a simple differential equation satisfying the condition:

$$P(t_0) = P_0(t_0) \quad (9)$$

Here, the function  $F(t) = a_1 - a_2P(t) - a_3P_0^2(t - \tau)$  on a segment  $t_0 \leq t \leq t_0 + \tau$  - continuous. Then, from Peano's theorem, there is a solution of functions (7), (9) on the segments  $[t_0, t_0 + \alpha]$ ,  $0 < \alpha \leq \tau$ . Assuming that  $\alpha < \tau$ , a solution is sought to  $I_1$ . Denoting this solution as  $P_1(t)$  and continuing the process:

$$P(t) = \begin{cases} P_0(t), t \in E_{t_0} \\ P_1(t), t \in I_1, \\ P_2(t), t \in I_2 \end{cases}$$

and continuing the process  $P(t)$  is the solution (7) – (8). The solution to the problem is represented as:

$$P(t) = \begin{cases} \sqrt{\frac{a_1}{a_3} \left( 1 - \frac{2}{1 + e^{2\sqrt{a_1 a_3}(t+c)}} \right)} = P_1(t) \\ P_1(t) - \frac{C + a_2 - a_3 e^{C(t-\tau)}}{-2a_3} \end{cases}$$

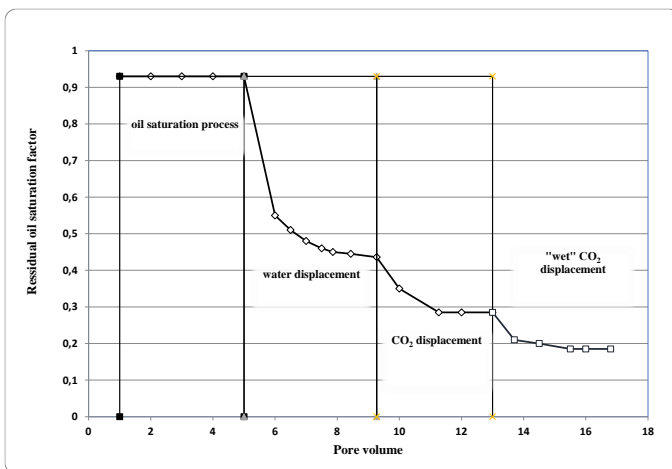
The solution to the problem is represented as:  $P(t) = e^{2t - e^2(t - \tau)}$ .

Performed researches allow to conclude that in case of use of gas-extracting aqueous solutions prepared on formation water, there is a fast rate of gas release into the third phase at the initial moment of reaction, and no diffusion factor leads to achievement of the best result in the distribution of water and oil saturations in the displacement zone<sup>8</sup>.

Mixing CO<sub>2</sub> displacement is particularly favorable in enhanced oil recovery methods, but it should be kept in mind that displacing oil with fluids differing in density ( $\rho$ ) and viscosity ( $\mu$ ) characteristics leads to flow initiation and stratification and unstable finger formation at the displacement front. When CO<sub>2</sub> dissolves in oil, the viscosity of the latter decreases, while its density increases depending on the carbon dioxide concentration. As a consequence, it is to be expected that when CO<sub>2</sub> is injected into a porous medium, the gas is concentrated at an initial point in time in the upper part of the medium and gradually dissolves into the formation oil due to molecular diffusion. To evaluate the efficiency of oil displacement from a porous reservoir by conventional carbon dioxide and CO<sub>2</sub> released in the process of gas formation reaction, laboratory experiments were carried out. In the first series of tests, oil was displaced from the porous medium by water, then, at the second stage, additional displacement by carbon dioxide (CO<sub>2</sub>) was carried out and, subsequently, a rim of “wet” carbon dioxide generated in an “acidic” medium in reaction with limestone fill was injected into the reservoir model. As experiments have shown, the additional displacement by “wet” CO<sub>2</sub> allowed to provide additional washing of hydrocarbons from the areas of porous medium, not covered by displacement by water and “pure” CO<sub>2</sub> (figure 4):

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<sup>8</sup> Panakhov, G.M., Bakhtiyarov, S.I., Shakhverdiev, A.Kh., Abbasov E.M. Kinetics of Gas Generation in Water Solutions // Transactions of AMEA, issue Mathematics and Mechanics series of physical-technical & mathematical sciences, XXIV, Baku, 2006. - pp. 239-246.



**Figure 4. Change in residual oil saturation ratio**

The “acid” medium injected into the reservoir in contact with the gas-forming component intensively generates carbon dioxide, which, mixed with water, forms a stable gas-liquid system. The field implementation of the technology is also of great environmental importance, as it provides for the use of waste from the processing of natural mineral raw materials - a source of air pollution by greenhouse gases.

**In the third chapter** modelling of the method of increasing the efficiency of the oil production process based on the process of in-situ gas generation is carried out. A series of laboratory tests were conducted on core samples simulating conditions of productive reservoirs. The tests were aimed at adapting the developed gas generation technology to the geological and technical-technological conditions of the fields. It was found that there is an optimal inhibitor concentration to ensure the minimum corrosion rate of downhole equipment. The results of observation of the investigated systems with inhibitor additives showed that inhibitors A1, A2 and A3 are sufficiently compatible with field conditions, injection water characteristics and exhibit anti-corrosion activity. In order to effectively implement the design solutions, a set of preliminary analytical and laboratory studies on the selection of gas-generating compositions was developed and carried out. Experiments on

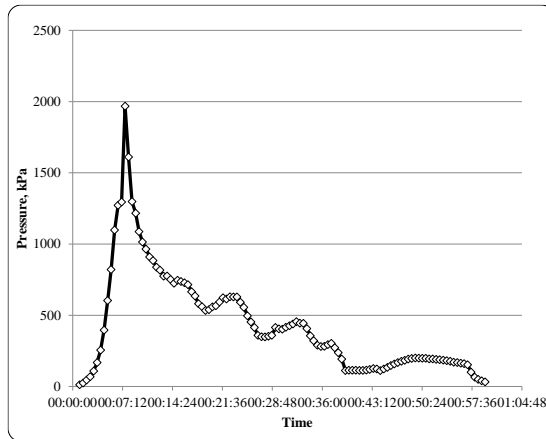
filtration were carried out on the CoreTest Systems FFES 655 filtration unit for physical modelling of the oil reservoir. Filtration of agents and compositions was carried out under conditions corresponding to reservoir conditions through a composite rock sample of cylindrical shape prepared from natural cores of the AV8 formation of the Vatyegan oil field. The results of the experiments confirmed the effective displacement of residual oil by the rim of pseudo-boiling gas-liquid system (PBS) based on the in-situ generation of carbon dioxide. The pressure dynamics during the stoichiometric reaction has a variable character with different periods. According to the results of experiments the effect of heterogeneity of displacement along the core samples strike is observed. The studies also showed that in the conducted experiments the highest efficiency of residual oil displacement is observed in the permeability range of 50-150 mD. In the context of innovative solutions of in-situ formation of gas-liquid CO<sub>2</sub> slug, the work considers the results of theoretical and experimental studies on laboratory adaptation carried out in recent years, as well as the results of industrial implementation of the rheo-gaschemical method for the recovery of residual oil reserves in the fields of the People's Republic of China<sup>9</sup>. Laboratory studies considered oil displacement from a porous medium. Laboratory experiments were staged on artificial core samples modelling real reservoir system conditions. Pressure changes in the porous medium in the process of injection of gas-forming solutions is characterized by periodic oscillations. Summarizing the laboratory experiments, it should be noted that the developed method of in-situ gas generation of carbon dioxide and formation of gas-liquid slug on its basis is effective for displacement of residual oil reserves in oil and gas fields of the People's Republic of China. The presented studies analyze the mechanism of gas generation process in reservoir conditions with formation of pseudo-boiling gas-liquid system, which in turn is used as a rim for oil

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<sup>9</sup> Geylani M. Panahov, Eldar M. Abbasov, Renqi Jiang The novel technology for reservoir stimulation: in situ generation of carbon dioxide for the residual oil recovery // *J Petrol Explor Prod Technol*, Vol. 11, № 4 - pp. 2009 – 2026 (2021). <https://doi.org/10.1007/s13202-021-01121-5>



displacement and increase of reservoir coverage. At the stage of oil displacement with formation water, a fluid flow rate equal to  $Q = 0.017 \text{ cm}^3/\text{sec}$  was maintained. At this stage three pore volumes of water 3PV - 54 ml were injected, the volume of displaced oil was  $V_{\text{oil}} = 8.0 \text{ ml}$ . At the stage of oil pre-displacement by CGS rim the parameters of injection of gas-forming reagent rims were as follows: liquid flow rate  $Q = 0.017 \text{ cm}^3/\text{s}$ , and the volume of displaced oil was  $V_{\text{oil}} = 6 \text{ ml}$ . Pressure change in the porous medium in the process of injection of gas-forming solutions is characterized by periodic oscillations, the dynamics of which is shown in figure 5.



**Figure 5. Pressure dynamics in the process of oil displacement by the CO<sub>2</sub> slug**

The presented studies analyze the mechanism of gas generation process in reservoir conditions with formation of pseudo-boiling gas-liquid system, which in its turn is used as a slug for oil displacement and increasing reservoir coverage. At the same time, the most important from the technological point of view is the necessity to establish the correspondence of thermodynamic conditions of gas saturation of the pore space with the foam system. In the experiments, a self-generating foam system was studied, in which polyacrylamide (PAA) prepared with an aqueous solution of soda ash was used as a foaming agent. The purpose of the laboratory tests was to study the potential application of the developed compositions as an isolation system for blocking highly permeable reservoirs, as well

as in the process of development of production wells at oil, gas and gas condensate fields.

In the course of research laboratory experiments on studying the rheology of compositions of surfactant solutions and polymers were set. Spontaneous gas (bubbles) extraction from such high-viscosity media is quite problematic for polymer liquids with freely suspended gas inclusions. To evaluate the rheological characteristics of such systems, it is necessary to take into account their change in time due to the destruction of the polymer and foam framework.

In order to obtain a stable foam structure, it was proposed to add a chemical reagent - trivalent metal salts - as one of the components of the foam-forming system, which imparts thixotropic properties to the foam. Stability of the gel structure formed in the formation depends not only on the presence of complexing agents, but also on a number of reasons.

The research on studying the rheological properties of gas release systems was based on the choice of polymer type and crosslinking reagents. During the experiments, the fact that the strength characteristics of polymer blocking systems change depending on the reservoir temperature conditions was taken into account. In the work it was established by experimental study that at temperature increase (thermostatisation up to 420 K) there is a decrease in foam system stability, which is explained by the process of coagulation of long polar parts of PAA molecules, as a result of which the solution viscosity decreases and, consequently, the stability of foam systems decreases.

To increase the stability of the generated foam solutions, it was proposed to use additives of chromolignosulfonates stabilizer, which have an effect on the coagulation process of polymer tangles during heat treatment. The results of the conducted experiments have shown that the addition of chromolignosulfonate chemical reagents in the volume of 2.0 - 4.0 vol.% to blocking viscoelastic polymer compositions contributes to achieving the stability of compositions in the temperature range of 273 - 423 K.

We also proposed to use a composite gas-generating system based on polyacrylamide with additives of modified bentonite clay

powder as a blocking high-permeability zones of the exposure interval. A series of laboratory studies were carried out in which the selectivity of the blocking effect of the composite system was evaluated. For this purpose, the conditions of porous medium consisting of two layers of different permeability were modelled on a specially designed filtration unit. The permeability of the first layer was  $0.1 \mu\text{m}^2$ , and that of the second highly permeable interval was  $1.0 \mu\text{m}^2$ . In the first stage, the model was saturated with oil and the filtration resistance of the flow was determined  $R_1 = Q_h/Q_l$ , where  $Q_h$  и  $Q_l$  – respectively, fluid flow rates in high-permeability and low-permeability reservoirs. Then, a gas-forming agent representing 0.25% aqueous solution of polyacrylamide with 12 wt.%  $\text{Na}_2\text{CO}_3$  sodium carbonate and 5 wt.% bentonite clay powder was injected into the model and the filtration flow distribution  $R_2$  was established again. In the next series of experiments, a gas-extracting agent with the addition of bentonite powder at a concentration of 5 wt.% and a gas-forming solution of hydrochloric acid were successively injected into the porous medium, and the distribution of filtration flow was established. At the next stage of experiments, a gas-extracting agent (clay powder concentration was 10 wt%) and hydrochloric acid was injected into the model as an aerator of the polymer-clay system. In order to compare the results of the conducted studies, experiments were carried out in the next series, in which aqueous solutions of polyacrylamide with addition of 12 wt.% sodium carbonate without bentonite clay powder and aqueous hydrochloric acid solution were used as a gas-extracting composition. The total volume of reacting solutions was 0.3 pore volume of the model.

**The fourth chapter of the dissertation work** evaluates and provides justification of the technological basis for the recovery of residual hydrocarbon reserves during in-situ generation of carbon dioxide. Designed rheo-gaschemical technology based on carbon dioxide generation in reservoir conditions, without its injection from surface communications has not only technological, but also significant economic efficiency. In this technology carbon dioxide is generated in reservoir conditions as a result of thermochemical stoichiometric reaction of aqueous solutions of gas-forming and gas-

emitting chemical reagents sequentially injected into the reservoir. Water-soluble sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and hydrochloric acid (HCl) were used as reacting chemical agents in the studies. The concentrations of reactants in aqueous solution and their volumes were estimated based on the amount of carbon dioxide released as a result of stoichiometric reaction. It is known that at full neutralization of 1 ton of sodium carbonate with 0,7 tons of hydrochloric acid in the reaction process under normal conditions  $210 \text{ nm}^3$  of carbon dioxide is emitted. When selecting of regime conditions of chemical compositions injection, the volume of reacting agents at thermodynamic conditions of a formation is estimated depending on temperature and pressure.

It can be expected that in the system containing carbon dioxide, with the change of the above parameters changes the relative permeability for phases, and, consequently, and residual oil saturation. In this kind of systems containing  $\text{CO}_2$ , the analytical form of the relative permeability dependence remains unchanged and only the values of residual and current oil saturation change depending on the concentration of dissolved in the oil hydrocarbon and carbon dioxide gases.

The system generated in the formation has a number of synergetic characteristics that allow achieving positive effects for oil recovery: an additional source of reservoir energy is used; a volumetric effect is shown due to the dissolution of carbon dioxide generated in reservoir conditions, which provides an increase in the oil recovery factor; chemical agents used in the process of gas generation and products of the in-situ reaction have pronounced visco-elastic and electrokinetic properties. Density differences cause gas segregation into the roof of the reservoir; the  $\text{CO}_2$  generated is also the gas phase in the foaming reaction in the reservoir, which blocks highly permeable channels in the reservoir (or bottomhole zone), deflecting the injected water away from the waterflooded areas of the reservoir. Technology also provides for periodic foam generation in remote areas of the reservoir. The process results in:

- extraction of hydrocarbon components from the surface of pore channels under certain thermobaric conditions corresponding to

the 'supercritical state of CO<sub>2</sub>' at the same time the bottomhole zone is cleaned from asphaltene and other contaminating deposits;

- in-situ formation of gas-liquid rims equalizes the injectivity profile, i.e. it ensures that new reservoirs are brought into operation during flooding of the deposit and makes it possible to regulate the flooding process by cyclic formation of gas-liquid slug.

In-situ generated carbon dioxide dissolving in the displaced oil reduces its viscosity, and as a consequence reduces viscous instability during the subsequent injection of water, reduces the surface tension at the interface when displacing oil from the stagnant zones of the formation, eliminates gas breakthroughs to the producing wells, which takes place when injecting large-volume CO<sub>2</sub> slugs in traditional gas injection technologies. The technological character of the technique allows to find optimal conformity of operational parameters depending on the conditions corresponding to the particular implementation sites. Pilot implementation of the technology at the Vatyegan oil field (Russian Federation) was carried out at the geological object formation AB8. The formation (AB8) consists of three independent sandy-clay deposits, indexed as formations AB8-1, AB8-2a and AB8-2b.

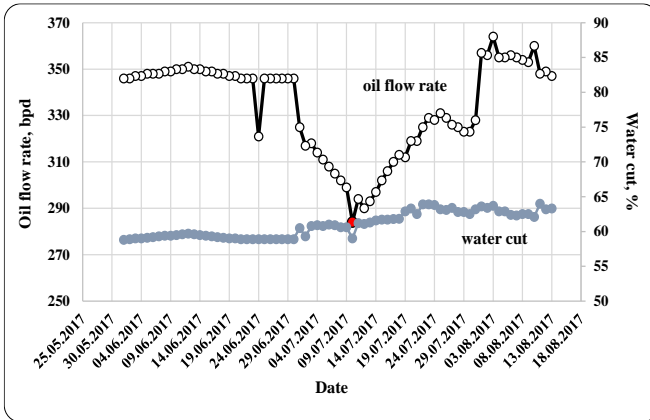
Experimental industrial implementation of the technology of impacting the reservoir with a slug of pseudo-boiling gas-liquid system confirms the technological efficiency of the current oil production increase in the surrounding producing wells within 6-9 months.

The results of calculation of technological efficiency of the project implementation at the pilot area of Vatyegan field for 21 producing wells that reacted to the impact: when calculated for individual production wells of the site, additional oil production totalled 5684 tonnes (12.6% of the increase in current oil production); when calculated for the site as a whole, additional oil production was 5759 tonnes (12.8% increase in current oil production).

As the experience of field operations shows, effective oil recovery under conditions of in-situ generation of gas-liquid rim and blocking of highly permeable intervals is possible with increase of

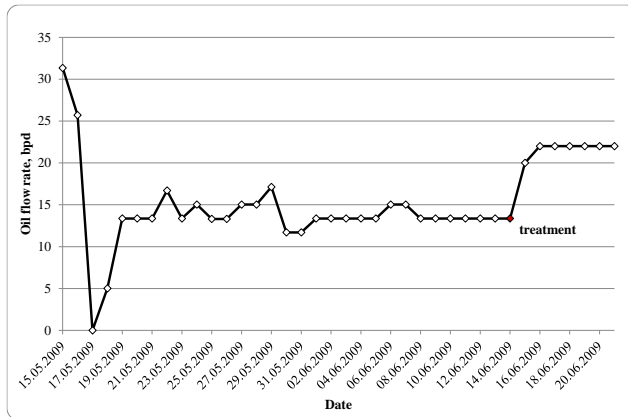
injected water volumes as a necessary condition for increase of formation coverage by displacement and extraction of residual hydrocarbons from stagnant and poorly drained zones. Pilot works on testing technologies for oil recovery from watered reservoirs were carried out at the pilot area of the Novo-Pokurskoye field. At the Novo-Pokurskoye field of NGP-6, 3 well treatments were carried out on injection wells Nos. 1114/7, 1112/7, 64/13 operating in the SW1(2) formation. The first treatment was carried out at well 1114/7 by two cycles of reactive compositions injection, the total injection volume was 120 m<sup>3</sup>. Then well 1112/7 was treated, the operation consisted of 2 cycles, the total injection volume was 130 m<sup>3</sup>. The third treatment was performed on well 64/13, a 2-cycle operation with a total injection volume of 110 m<sup>3</sup>. In the process of wells treatment it was established that injectivity values of wells increased, and the dynamics of injection pressure change was as follows: for well 1114/7 initial pressure was  $R_n=18.5$  MPa, pressure after the first cycle  $R_1=15$  MPa, pressure at the end of injection  $R_k=18$  MPa; for well 1112/7  $R_n=16$  MPa,  $R_1=13$  MPa,  $R_k=15$  MPa; for well 64/13  $R_n=15.5$  MPa,  $R_1=11$  MPa,  $R_k=15$  MPa. As a result of analysis of the development performance of the pilot site of the Novo-Pokurskoye field, 10 wells reacted positively to the impact, and additional oil production during the period of technology implementation was 3,906 tonnes. Pilot implementation of the technology was also realised at the Orenburg oil and gas condensate field. The productive section of the Artinsk deposit is composed of carbonate rocks with relatively low filtration-capacity characteristics. Field testing and implementation of the residual oil recovery method has been widely used on the oil fields of the People's Republic of China. Oil fields lithology is highly variable in porosity and permeability distribution, which generally complicates operating conditions. Some examples are Daqing, ShengLi, Dagang, Zhongyuan fields, where there is a random pattern of distribution of oil "pockets" at different depths. The wide application of CO<sub>2</sub> stimulation technologies is limited by both the shortage of industrial CO<sub>2</sub> reserves and technical constraints to the widespread application of CO<sub>2</sub> EOR technologies. A successful testing of the technological technique was also carried out

at the Penglai oil field site (PengLai, China). The technology was implemented at a group of wells in the offshore Penglai field of the SNOOC Oil Company with the support of the COSL service company at two injection wells (2017 - 2018). Technological operation was carried out by several cycles of injection of gas-forming and gas-releasing chemical compositions at the injection wells located on a stationary offshore platform. Dynamics of the average daily flow rate and water cut in the surrounding wells of the 9-point system of the field section development are shown in figures 6. Field testing of the technology of residual oil recovery from depleted reservoirs at the late stage of reservoir development was carried out at the pilot section of the Maskogee field (Oklahoma, USA). Within the framework of the pilot project for recovery of residual reserves in depleted Oklahoma reservoirs, 3 well operations were carried out. The reservoir is represented by low-permeability reservoirs -  $9\div 15 \cdot 10^{-6} \mu\text{m}^2$ , porosity - 13-17%, reservoir temperature -  $28^\circ\text{C}$ ; reservoir pressure - 5.5 MPa.



**Figure 6. Production and water cut performance of the C36ST1 well before and after the in-situ CO<sub>2</sub> stimulation operation**

According to the results of the stimulation, the average daily oil flow rate of three wells in the wells of the implementation area almost doubled from 13 to 26 barrels per day (figure 7). The results of field operations confirmed the effectiveness of CO<sub>2</sub> stimulation for recovery of oil contained in low permeability reservoirs.

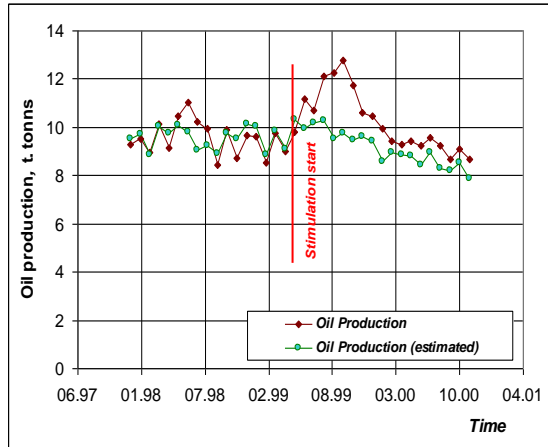


**Figure 7. Oil flow rate dynamics of the pilot well at the Muskogee field**

Implementation of a system technology for in-situ generation of carbon dioxide and isolation of highly conductive channels with blocking compositions has been implemented in the fields of Western Siberia.

Technology of blocking highly permeable intervals of the formation consists of sequential injection of viscoelastic composition (VEC) and OPGS into the bottomhole zone of the formation. Prior to injection of the viscoelastic composition, an aqueous polymer solution is injected into the bottom-hole zone of the formation at a pressure higher than the pressure at which the solution begins to filter into the low-permeability oil-saturated intervals. The wellhead pressure was then relieved and viscoelastic composition (VEC) was injected into the well. Pilot testing of OPGS technology in combination with a blocking composition was carried out at the Samotlor field site. An analysis of the production performance of the responding wells in the reservoir site after the pilot tests showed that most of the wells in the pilot site reacted to the injection of the slug by changing the operating parameters. This was expressed in some cases by a decrease in water cut, in other cases by an increase in oil flow rate. The dynamics of changes in the development indicators of the entire section are shown in figure 8.





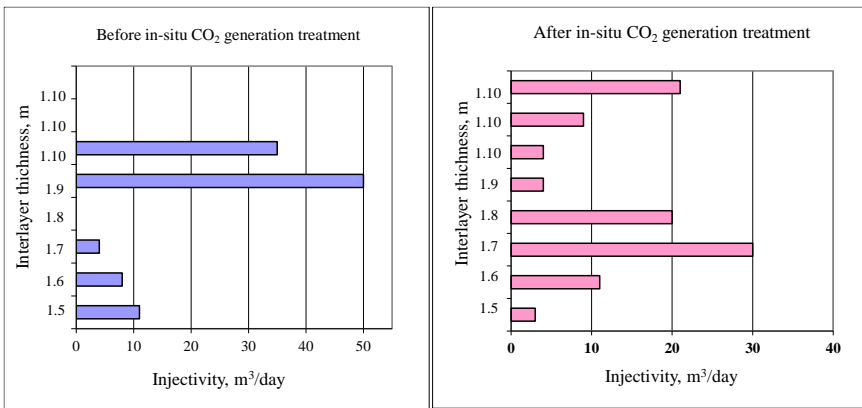
**Figure 8. Trends in changes in oil flow rate**

Later, Tyumen Oil Company widely used the technology of systemic impact on productive formations AB4-5 and BB8 of the Samotlor field. 12 well operations were carried out using the developed method with high technological efficiency.

**The fifth chapter** presents the results of laboratory and field studies on suffusion cleaning of the bottom-hole zone of wells with gas-generating compositions. Geological and technical steps to maintain reservoir pressure must be combined with the treatment of the bottom-hole zone of the formation (BHZ), ensuring cleaning and restoring the primary permeability of the porous medium. It should be noted that the interaction of hydrochloric acid HCl with the rocks composing the bottomhole zone is accompanied by the formation of insoluble sediments in the pores and channels of the reservoir. Field realization of the technology of in-situ gas generation at Zhongyuan field. The productive object is oil-saturated LianHua sediments of the third tier of the Tertiary Sheiji Formation. The depth of the pay zone varies from 1,430 to 1,690 meters. The average thickness of the pay zone is 57.74 meters and the area of the site is 2.39 km<sup>2</sup>. Estimated balance reserves of oil amount to 1653,104 thousand tons. Field operations on formation stimulation by the technology of in-situ gas generation were realized for the first time on four sections of Zhongyuan field covering 25 injection wells. To implement the

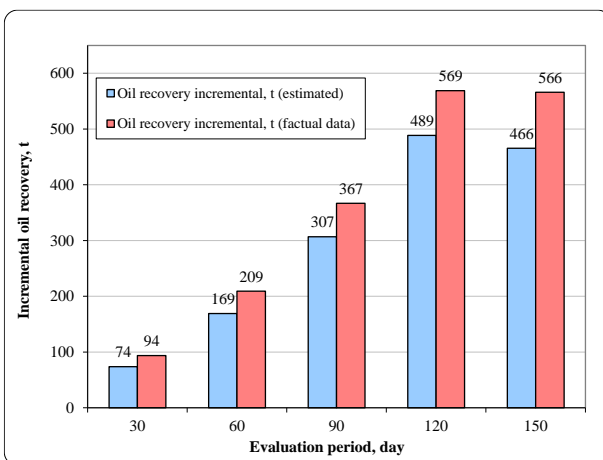
technology in the selected area of the field, the existing waterflood infrastructure was used, which is a significant advantage of the technology that does not require additional costs for additional equipment and communications. The injectivity and injection pressure values determined the change in throughput ( $Q/R_{inj}$ ) of the injection wells before and after the technological operation.

As shown in Table 4, the flow rates of most wells (with the exception of well 316VC) changed significantly after the operation, indicating increased reservoir coverage by the injected system (figure 9).



**Figure 9. Injectivity profile before and after the technological operation**

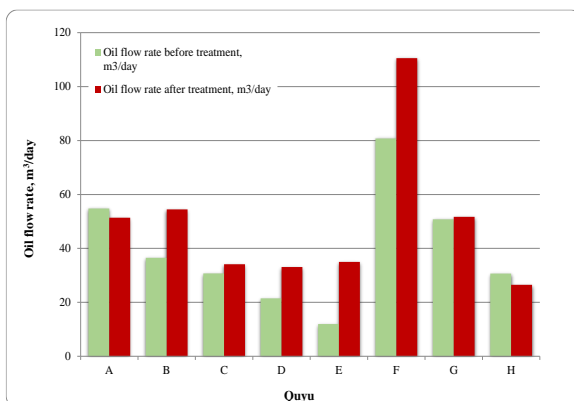
Analysis of the dynamics of the current performance of the injection and production well stock at the pilot section of the Zhongyuan field, as well as the prehistory of the deposit development allows us to conclude that the technology of in-situ carbon dioxide generation has an effective impact and is feasible (figure 10).



**Figure 10. Dynamics of forecast and actual oil production at the Zhongyuan field area**

The technology was also implemented at a group of wells in the offshore Bohai Bay field of CNOOC oil company with technical assistance of the service company COSL at two injection wells (2009 - 2010). Two groups of wells were considered as objects proposed for test operations: the first group is represented by injection well E25 and surrounding production wells E19, E24, E20, E21, F4, F5, G1; the second group is represented by injection well H5 and surrounding production wells F32, F33, H4, H11, H12, H13, H6, G25. E25.

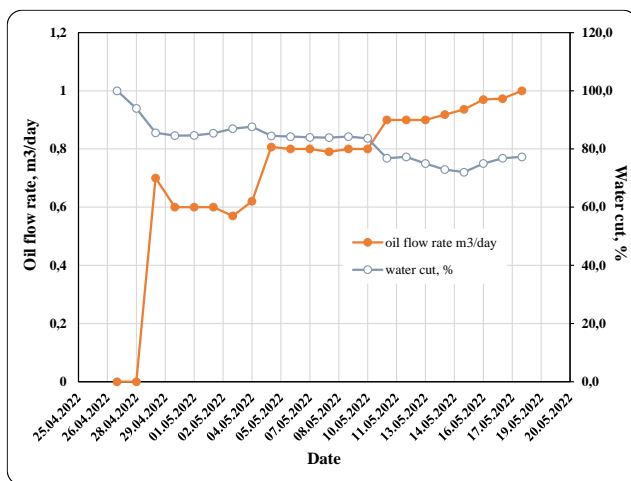
Analysis of water injection pressure dynamics after the technological operation showed that there was a change in injection pressure from 1.4 MPa to 5.7 MPa ( $\Delta P=4.3$  MPa), which indirectly indicates an increase in hydraulic resistance at the injection front and redirection of flow towards low-permeability reservoir channels, previously not covered by displacement. Preliminary results of implementation confirmed that the total incremental oil production for all wells of the H5 section for six months after the event was  $\Delta Q_o \approx 7000,00 \text{ m}^3$ . Dynamics of average daily flow rate and water cut for 8 surrounding wells of the 9-point field development system are shown in figures 11.



**Figure 11. Dynamics of average daily flow rate for 8 surrounding wells of the pilot site**

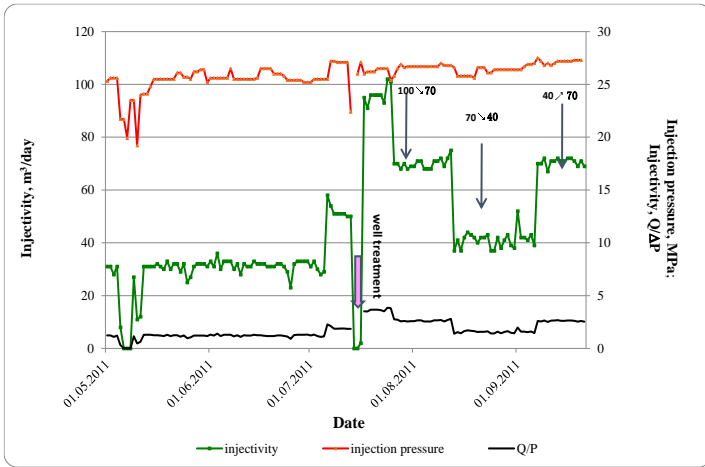
Analysis of the dynamics of indicators of the E25 injection well group of oil production and water cut of the responding wells showed that there is a positive reaction to the impact of gas-liquid slug, which was shown by a change in the average daily oil flow rate and a decrease in the water cut of the produced products for most of the surrounding wells of the test area. Preliminary results of the technological operation confirmed that the total additional oil production for the post-operational period since the event (taking into account the production reduction of three producing wells) was  $\square Q_{H1} = 5893,69$  TOHH.

An innovative technology is proposed to ensure oil production increase in producing wells and cleaning of bottomhole formation zone from colmatants and asphalt-resin-paraffin deposits. The pilot works on oil production improving were carried out at the production wells of “Binagady” field (Azerbaijan). Pre-operational average daily oil flow rate of the studied wells was 0.5 tons/day. Aqueous solutions of chemical agents were injected into the wells, and by adjusting the wellhead settings coverage of the treated bottom-hole zone was achieved. Indicative dynamics of efficiency (cumulative oil production) based on the results of the operation on one well is shown in figure 12.



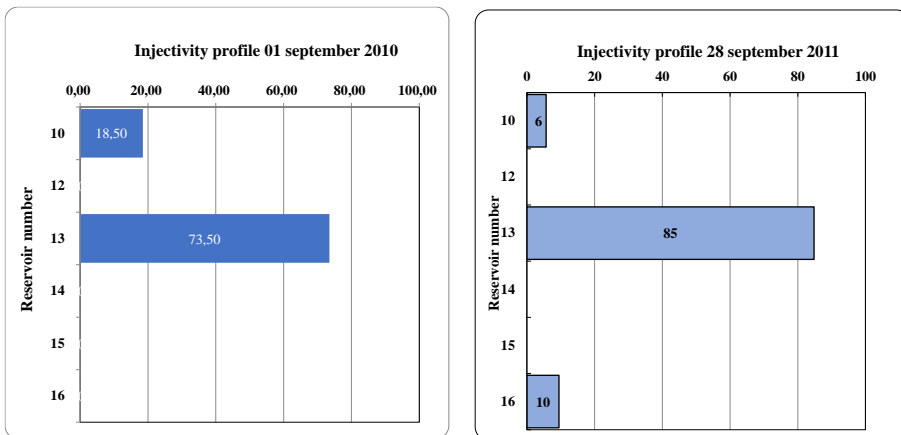
**Figure 12. Dynamics of efficiency of IOR field operation at the well of Binagadi field (Azerbaijan)**

Suffosion cleaning of injection wells with gas-generating compositions at LiuZan fields. Another industrial project of rheo-gaschemical stimulation of the reservoir was implemented in the northern section of LiuZan field. Two injection wells: LB1-19-20-ES33 and LB2-10-ES33 are located in the field area. The main goal of the project of field implementation of the technology in the LiuZan field is to increase injectivity at well LB1-19-20-ES33 while maintaining injection pressure at the pre-operational level, as well as conformance control at well LB2-10-ES33 by reducing injectivity of reservoir 10 and increasing water injection into reservoirs 8 and 9. Monitoring of the post-operational dynamics of injected water flow rate and pressure confirmed the effectiveness of the implemented field treatments (figure 13). At well LB1-19-20-ES33 there was an increase in injectivity of formations 10, 12 and 16 from 30 to 100 m<sup>3</sup>/day, which was subsequently reduced to 70 m<sup>3</sup>/day as part of technological measures at the technology implementation site.



**Figure 13. Key parameters trends of the injection well LB1-19-20-ES33 before and after OPGS treatment operation**

At well LB2-10-ES33 during 3 months after the operation, water injectivity increased at an average of 30 m<sup>3</sup>/day, which compared to the preoperative level was almost 3-fold increase in injection volumes while maintaining the same injection pressure. As part of post-operational studies, injectivity profiles were measured at injection wells LB1-19-20-ES33 and LB2-10-ES33, which confirmed the effectiveness of the measures taken and the achievement of the primary technological goals. At well LB1-19-20-ES33 the injectivity of reservoir 13, as the main productive reservoir of the impact interval, increased by 13.5 % (73.5 to 85 %), at the same time there was a redistribution of injected water flow from reservoirs 10 and 16 (reservoir 10 reduced by 68 %; no injection in reservoir 16, figure 14).



**Figure 14. Results of injectivity profile measurements before and after the operation at well LB1-19-20-ES33**

On the well #LB2-10 the change of injectivity was ensured: in reservoir 10 the injectivity decreased by 23% (from 69.01 to 53%), in reservoir 8 - increased by 5%, and in reservoir 9 - increased by 76% (from 4.51 to 19%). Thus, the planned objectives of the measure were achieved, which ensured injectivity of the reservoir.

**Chapter 6** evaluates the technological and economic aspects of implementing in-situ carbon dioxide generation technology.

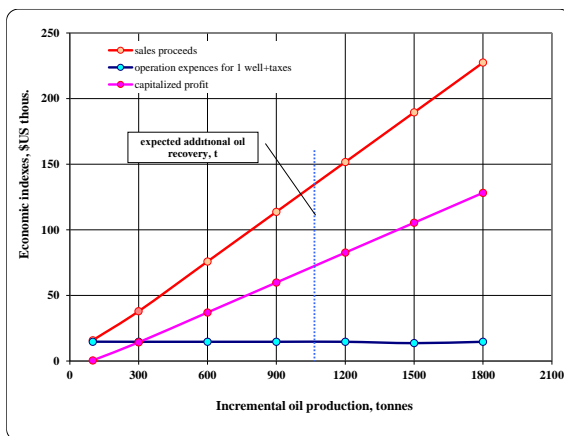
Capturing, transporting and injecting CO<sub>2</sub> carbon dioxide into the formation as a displacing agent in enhanced oil recovery technologies is often considered also as a promising way to cost-effectively prevent CO<sub>2</sub> emissions into the atmosphere. If carbon dioxide capture and transport is handled by an entity other than the oil field operator, one would expect the two entities to have different and possibly competing objectives. Therefore, when considering the correlation between CO<sub>2</sub> sequestration and EOR-CO<sub>2</sub> technologies, it is important to also consider the goals of oil producers.

The comparison shows that, depending on the combination of scenarios considered, the added value of using the CO<sub>2</sub> EOR method instead of chemical stimulation techniques ranges from -€4 to €33 per barrel of oil produced, equivalent to between €4 and €56/t CO<sub>2</sub> of carbon dioxide captured. In most of the cases considered, the EOR-CO<sub>2</sub> technology method will be preferred, but the cost of operations

may vary from case to case. Estimates show that at an oil price less normal production costs of €50/bbl, the cost of oil to be considered in applying carbon dioxide EOR ranges from €8 to €41 per barrel of hydrocarbons produced. The cost that a company is willing to pay to deliver CO<sub>2</sub> to its field varies from -4 to 56 euros/t CO<sub>2</sub> depending on the scenarios considered and can therefore be significantly lower than in cases where chemical EOR is not an alternative method.

Conventional gas stimulation techniques involve injecting several hundred thousand cubic meters to saturate the reservoir with gas or create high-volume carbon dioxide slug.

In spite of small volumes of generated gas and relatively high cost of used chemical reagents, the achieved effect allows estimating the method as technologically and economically profitable. Below is the estimated graph of economic indicators in \$US, i.e. the dependence of costs per 1 well operation, accumulated profit, revenue from oil sales (figure 15). These indicators are based on our obtained effects of achieving additional production in the range of 10-12 % (i.e. additional oil production amounted to 1000 tons per one well operation):



**Figure 15. Economic evaluation of the effectiveness of the developed technology**

The chapter also provides an assessment of technological efficiency of pilot implementation of the technology of in-situ carbon dioxide generation. As it is known, multi-efficiency of the



technology of in-situ CO<sub>2</sub> generation leads to changes in a number of indicators of the filtration process, in particular, the oil displacement coefficient or phase permeability of oil and water<sup>10</sup>. Changes are due to the growth of volumetric coefficient  $V_o$ , which represents the ratio of oil volume in reservoir conditions  $Q_o$  to the volume of oil in standard conditions  $Q_{os}$ . As it is known the change of oil volume (oil swelling) before and after dissolution of carbon dioxide in it is represented as:

$$B_n = \frac{Q_n}{Q_{n.c}}; \quad B_o = \frac{Q_o}{Q_{o.c}}; \quad (10)$$

From the formula (10) determine the volumes of initial  $Q_{io}$  and residual  $Q_{ro}$  oil in standard conditions, respectively:

$$Q_{io} = \frac{Q_i}{B_i}; \quad Q_{ro} = \frac{Q_r}{B_r}; \quad (11)$$

The volumes of initial and residual oil in reservoir conditions are equal:

$$Q_i = \sigma_i \cdot V_{cov}; \quad Q_r = \sigma_r \cdot V_{cov}; \quad (12)$$

where  $\sigma_i$  и  $\sigma_r$  – initial and residual oil saturation, respectively.

Substituting (12) into (11) for standard conditions, we get:

$$Q_{os} = \frac{\sigma_o \cdot V_{cov}}{B_o}; \quad Q_{rs} = \frac{\sigma_r \cdot V_{cov}}{B_r}; \quad (13)$$

Accumulated oil  $Q$  from the seepage-covered volume  $V_{cov}$  for standard conditions is:

$$Q = Q_{is} - Q_r = \frac{\sigma_o \cdot V_{cov}}{B_i} - \frac{\sigma_r \cdot V_{cov}}{B_r} = V_{cov} \cdot \left( \frac{\sigma_i}{B_i} - \frac{\sigma_r}{B_r} \right) \quad (14)$$

Dividing (14) by the total pore volume of the reservoir  $V_o$ , we obtain the oil recovery factor due to OPGS during waterflooding:

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<sup>10</sup> Шахвердиев, А.Х., Мандрик, И.Э., Панахов, Г.М., Бахтияров, С.И., Аббасов, Э.М. Перспективные реогазохимические технологии повышения нефтеотдачи пластов при извлечении остаточных запасов углеводородов // АМЕА-нын Хəбəрлəri, «Yer elmləri» seriyası, № 3, 2007. – S. 38-47.

$$\eta_+ = \frac{V_{cov}}{V_i} \cdot \frac{\left(\frac{\sigma_i - \sigma_r}{B_i - B_r}\right)}{\frac{\sigma_i}{B_i}} = \eta_r \cdot \left(1 - \frac{\sigma_r \cdot B_i}{\sigma_i \cdot B_r}\right) = \eta_r \cdot \eta_{1+}, \quad \eta_r = \frac{V_{cov}}{V_i}; \quad (15)$$

где  $\eta_+$  – oil recovery coefficient by OPGS slug during waterflooding;  $\eta_{1+}$  – coefficient of oil displacement by OPGS slug during waterflooding;  $\eta_{cov}$  – is the oil displacement coverage coefficient of oil displacement by the OPGS rim during waterflooding. When oil is displaced solely by water, the displacement ratio is calculated as:

$$\eta_1 = \frac{\sigma_i - \sigma_r}{\sigma_i} \quad (16)$$

Transforming formula (15) taking into account (16), we obtain:

$$\eta_+ = \eta_r \cdot \left(1 - \frac{\sigma_i - (\sigma_i - \sigma_r)}{\sigma_i} \cdot \frac{B_i}{B_r}\right) = \eta_r \cdot \left(1 - (1 - \eta_1) \cdot \frac{B_i}{B_r}\right) \quad (17)$$

Thus, the oil displacement coefficient with the use of OPGS technology at waterflooding is respectively equal to:

$$\eta_{1+} = \left(1 - (1 - \eta_1) \cdot \frac{B_i}{B_r}\right) \quad (18)$$

In this case the increase in oil displacement ratio will be as follows:

$$\Delta\eta_{1+} = \left(1 - (1 - \eta_1) \cdot \frac{B_i}{B_r}\right) - \eta_1 = (1 - \eta_1) \cdot \left(1 - \frac{B_i}{B_r}\right) \quad (19)$$

$\Delta\eta_{1+}$  - increase in the displacement ratio due to the use of OPGS technology.

Theoretical and laboratory studies, as well as the results of industrial implementation of the method of recovery of residual oil reserves by CO<sub>2</sub>-based gas-liquid rim serve as a sufficiently weighty confirmation of the technological and economic efficiency of the proposed solution. The results of laboratory and applied studies indicate that rheophysical characteristics and volumes of reacting heterogeneous fluids, dynamic conditions of their injection into the formation, along with taking into account the thermodynamic

parameters of the oil deposit, are selected in such a way that the in-place generation of carbon dioxide CO<sub>2</sub> would provide single-phase or non-equilibrium gas phase. The imposition of these technological constraints allows to provide a targeted impact on the oil deposit and the efficiency of recovery of residual oil reserves from poorly drained zones of the reservoir. The experience of laboratory and field studies of the rheo-gaschemical technology at oil fields of the main oil and gas bearing regions of Russia, Azerbaijan, USA and China showed that it has a good enough reproducibility and efficiency in a wide range of geological and physical characteristics of oil deposits, their constituent reservoirs and saturating fluids. The processability of the method makes it possible to find optimal correspondence of operating parameters depending on the conditions corresponding to certain areas of implementation.

## KEY FINDINGS AND RECOMMENDATIONS

1. The effect of oil viscosity fluctuations as a manifestation of dynamic disequilibrium in the process of thixotropic structuring of heterogeneous composition has been revealed. In the course of research, the methods of regulating the process non-equilibrium by viscoelastic and gas-generating compositions have been developed.

2. Compositions and rheogaschemical method of carbon dioxide generation in heterogeneous reservoir conditions have been developed for the first time. The influence of component composition of fluids and concentration of reagents on the character of intra-pore carbon dioxide generation in free volume and in porous medium was evaluated.

3. The kinetics of gas formation of heterogeneous solutions in various conditions with regard to the influence of the nature of dissolution of gas nuclei in formation fluids during rheogaschemical generation of carbon dioxide has been evaluated, and the effect of intrapore generation of “wet” carbon dioxide has been studied.

4. The methodological basis has been developed and the rheogaschemical technology including simultaneous blocking of highly permeable reservoir intervals for the purpose of directed extraction of residual hydrocarbon reserves from immobile oil-saturated reservoirs has been implemented.

5. Optimal concentrations of foaming agents and inhibiting additives in gas-forming solutions were determined, and a number of physical and hydrodynamic effects were obtained, which are manifested in the process of in-situ generation of gas phase in highly permeable zones of porous reservoir.

6. For the first time a method of suffosion cleaning of porous medium by using carbon dioxide  $\text{CO}_2$  generated in formation conditions, which acquires the properties of supercritical fluid under certain thermobaric conditions.

7. Design and engineering solutions for the implementation of rheogaschemical technologies of enhanced oil recovery and oil production intensification with proven industrial efficiency, aimed at the recovery of hard-to-recover oil reserves has been developed.

8. The results of theoretical and experimental studies are used in the implementation of developed industrial technologies in the fields of Azerbaijan, the Russian Federation, the United States, the People's Republic of China, Vietnam in the processes of gas influence on the reservoir and suffosion cleaning of bottom-hole zone of wells.

**The main content of the dissertation is covered in the following publications:**

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#### **Researcher's personal contribution:**

[1, 3, 8, 12, 14, 16, 17, 23, 26, 30, 32, 34, 35, 44, 52 - 54, 56 - 58, 61, 65 - 67, 69, 71 - 73, 76 - 82] involvement in problem statement and summarizing results, [2, 4, 5 - 7, 9 - 11, 13, 15, 18, 19 - 22, 24, 25, 27 - 29, 31, 33, 36 - 43, 45, 51, 55, 59, 60, 62 - 64, 68, 74, 75] participation in research, summarizing, analyzing and field implementation of the results achieved.





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