A NOVEL ENHANCED OIL RECOVERY TECHNOLOGY: IN-SITU CO_2 GENERATION

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ABSTRACT
A new promising enhanced oil recovery technology has developed. The technology involves in-situ generation of carbon dioxide to recover trapped residual oil from reservoirs. This technology has two at least unique features that set it apart from existing technologies. First, CO_2 is injected as part of a dense liquid phase (not simply compressed CO_2). Because the injected fluid is a dense liquid at ambient conditions, there is no need for the expensive compression costs that are associated with convention CO_2 injection processes. The gravity head associated with the fluid column allows CO_2 to be injected in a more cost-effective manner. This proprietary technology allows CO_2 to be released in-situ after injection into the reservoir. A second unique feature of this new technology is that a proprietary surfactant formulation forms foam when the CO_2 is generated in situ. The slim tube and core experimental results demonstrated advantages of the new technology. The technology also was tested in Russian and Chinese oil fields.

INTRODUCTION
Various chemical agents are developed and widely utilized in order to increase the efficiency of the residual oil recovery at the late stages of oil field development via water injection technique. It is well known that a recovery of residual oil from flooded reservoirs is provided via miscible displacement which results in an extremely low inter-phase tension at the contact interfaces. These conditions occur during the displacement of oil by chemical reagents which completely eliminate negative effects of capillary forces during the oil displacement process.

Recently, it was acknowledged that the most promising method to increase the oil recovery efficiency at the various flooding regimes is the injection of CO_2 gas into the productive horizons. A carbon dioxide is characterized by high solvent power, high diffusivity, low viscosity, low surface tension, and adjustable physical properties by pressure and temperature. It is widely and maturely applied to extraction processes due to its non-toxicity, non-residual, and non-combustibility. However, a wide application of this technology is limited due to the high cost of the technique, many technical and technological limitations, difficulties in production and transportation of the large volumes of carbon dioxide. Since the heat transfer coefficients to supercritical CO_2 can significantly reach high value, a special care must be taken under severe whether conditions. The environmental concerns regarding the CO_2 application are baseless because of the following facts. Dissolution of CO_2 in oil is accompanied by mass transfer process: carbon dioxide extracts the light fractions of oil dissolved in a gaseous phase. In process of flow, carbon dioxide is continuously enriched with light hydrocarbons. This leads to increase in concentration of light hydrocarbons, and decrease of pure CO_2 content up to zero. Hence, a gaseous phase enriched by light hydrocarbons effectively displaces oil without any danger to the environment.

The Permian Basin is a good example where water floods were extensively converted to CO_2 floods in order to overcome or change the decline in oil production. After initiating a cost effective CO_2 flood in the 1980s, a 10-15% improvement in oil recovery was observed. One potential concern is the availability of CO_2. Limitations of CO_2 supply are preventing implementation of new CO_2 flooding projects, and tightening the existing ones. An alternative scheme to the traditional methods of oil recovery by injection of carbon dioxide gas is the technology which proposes in-situ CO_2 generation as a result of the thermochemical reaction between water solutions of the gas-forming and gas-yielding chemical agents injected to the productive horizons. This technique excludes CO_2 injection from surface communication systems and does not require expensive delivery equipment. This process allows avoiding many negative consequences of CO_2 injection technology. Based on the in-situ CO_2 generation concept, several new technological schemes were developed in order to provide an integrative effect on the productive horizons.

NEW TECHNOLOGY
A development of new in-situ CO_2 injection technology is based on the decade long theoretical, experimental and

applied researches, which allowed determining the fundamental aspects and the mechanism of CO_2 effect on oil recovery efficiency. The preceding researches and experience in application of carbon dioxide stimulation technologies have shown their high efficiency in oil recovery processes. The advantages of the traditional CO_2 injection technique are:

- Dissolution of CO_2 (~ 5-10 %) in water results in viscosity increase about 20-30 %, and in 200-300% reduction of the mobility factor;
- Dissolution of CO_2 in oil results in viscosity decrease about 150-250 %, and in 10-15 % increase in oil recovery efficiency;
- Dissolution of CO_2 in oil results in reduction of the surface tension between oil and water phases;
- Dissolution of CO_2 in oil results in increase of both oil production and sweep efficiency.

The disadvantages of the existing traditional CO_2 injection technology are:

- CO_2 breakthrough in the production oil wells;
- Small alterations of thermobaric equilibrium conditions (when oil well operation is stopped for certain reasons) result in reducing of CO_2 concentration in oil and consequently, the coagulation and deposition of asphaltenes and resins takes place. Consequently, resinous components of the oil deposit on the rock surfaces. Rigid oil films formed on the rock surfaces cannot be washed out by regular flooding;
- Corrosion of the oil-field equipment;
- Problems related to the transportation of great volumes of carbon dioxide (CO_2);
- Lack of special equipment for safe storage and transportation of CO_2;
- High cost of the technology;
- Insufficient amount of carbon dioxide (CO_2) in many oil fields.

The primary goal of the new technology is a creation such oil field technology, which would keep all positive effects of traditional CO_2 flooding methods, and on the other hand - would prevent the negative consequences faced during the traditional CO_2 injection from the surface. The new technology is based on (i) in-situ CO_2 generation, (ii) excluding the CO_2 injection from the surface, (iii) creation thermo-baric conditions at which CO_2 can be both in a free phase, and in the dissolved state.

We developed a new in-situ CO_2 generation technology and the method of adjusting its supercritical state as a result of reaction between aqueous solutions of the gas-forming and gas-yielding agents under certain thermobaric conditions. The injected gas-forming and gas-yielding solutions are Newtonian fluids and therefore they first penetrate into the high permeable horizons, where the carbon dioxide is generated as a result of the reaction between those two liquids. Generated gas participates in formation of pseudo-boiling gas-liquid system bank (PBGSB) which contains surfactants and water-soluble polymers. The injected liquids will flow into the low permeable horizons due to the temporary blocking of the high-permeable horizons by the generated gas. A water-soluble polymer added to the injected liquids system has two functions. It acts as a foam generating agent when it is necessary to block high-permeable intervals. The injected liquids exhibit viscoelasticity when they penetrate into the low permeable horizons, and therefore the displacement interface flattens. As a result, CO_2 breakthrough into the producing wells is prevented.

On the other hand, micro-bubbles generated due to the exothermal reaction, possess anomalous rheological properties which under equal circumstances allow increasing the sweep efficiency 120-130% and the final oil recovery compared to other traditional oil recovery methods. An anomalous behavior of the generated system is related (1) to the volume fraction of gas bubbles in the mixture generated under the pressures 1.2-2.0 times exceeded a saturation pressure at the same gas contents and the temperatures, and (2) to the supercritical state of the gas under certain thermobaric conditions. An addition of the surfactants promotes hydrophobization of pores during the filtration of the gas-liquid mixture into the horizons in a pre-transitive phase state, and as consequence, an increase its viscoelastic non-equilibrium properties. As a result, the injected liquid system uniformly flows into both high- and low permeable layers, increasing both a sweep efficiency and the oil recovery coefficient. At the same time, a gas-liquid system increases an injectivity factor of the injection wells, because during the filtration of water-gas mixtures in a pre-transitive phase state the flow rate of liquids increases at constant pressure difference, and this increase much higher during the filtration in hydrophobic porous media. Moreover, surfactant additives promote a decrease in corrosion of the oil-field equipment since cationic surfactants are good inhibitors of corrosion and under underground conditions they do not generate deposits. A generated foamy gas-liquid system in high-permeable and washed zones creates a significant additional resistance to the injected water flow. The most portion of carbon dioxide (CO_2) is used for the creation of the barrier from flooded zones. A portion of CO_2 dissolved in oil creates a volumetric effect and sweeps out a residual oil. Carbon dioxide (CO_2) dissolved in water, increases its viscosity, equalizes a displacement front and increases a sweep efficiency.

EXPERIMENTAL RESULTS

The research and development of the bed stimulation technology by the pseudo-boiling gas-liquid system bank (PBGSB) were based on the laboratory test results on in-situ CO_2 generation. The laboratory tests simulated stechiometric reaction conditions in a porous medium. During these model tests the pressure was continuously measured with time. The results of these measurements are presented in Figure 1. First, the generation of the carbon dioxide traces leads to the pressure increase up to the certain level, then the gas bubbles after certain time are dissolved in the liquid system. The variation of the temperature (Figure 2) shows that during the experiments the temperature increases from 293 ^{0}K to 332 ^{0}K. These changes in pressure and temperature are related to the active thermochemical stechiometric reactions.

SUFFOSION IN WELLBORE ZONES OF FORMATION

During the exploitation of oil wells the wellbore zones characteristics deteriorate not only due to the water influx into the productive horizons (mainly, due to the repair operations), but also because of asphaltene-resinous and paraffin depositions, accompanied by the formation of the adsorptive-solvate layers on pore surfaces. This leads to the formation of boundary layers of oil with extremely high viscosity and thickness which dramatically reduces the permeability (especially during high-viscous non-Newtonian oil recovery). In injection wells during water injection permeability decreases due to the gradually clogging of the collector with the oil products and with the micro-particles suspended in the water. In-situ generated carbon dioxide in certain thermobaric conditions possesses strong solvent properties with the high desorption and extraction characteristics. Under the compression and the subsequent heating the density of CO_2 increases almost ten times reaching the density of the liquid, but its viscosity remains close to the gas density. Such gaseous state is called "supercritical fluid state" and this effect is successfully applied in various industrial processes, such as heavy hydrocarbon components extraction from polluted soils, cleaning and synthesis of polymers, etc.

The generated "supercritical CO_2" solution becomes an ideal agent for use in oil recovery process since the thermodynamic mode supported in formation conditions, can be used for the control of dissolving properties of these fluids. The greatest changes of density of "solvent" are reached approximately in a critical point of solvent at which the compressibility of solvent is much higher, and a little changes of the pressure causes a greater changes in the density. The in-situ CO_2-generation method allows providing also conditions for clogging extraction from the porous medium on the basis of the suffusion effects. The well bore zone cleaning by the generated carbon dioxide was simulated in the laboratory tests.

Figure 3 illustrates the results of the non-stationary measurements of the pressure recovery. As seen from the test results, time of the pressure recovery for the polluted model after gas-forming agents treatment changes depending on the pressure level. A relative efficiency of the porous medium cleaning process from resin and asphaltene deposits was estimated by acid treatment and supercritical CO_2 methods. A thermodynamic mode during the experiments was controlled by varying the pressure and by the creation of the conditions to expose the supercritical properties of the carbon dioxide. A comparison showed that the recovery time after the acid treatment is less than that for the polluted porous medium. However, it is much higher than the recovery time after the gas-generated solutions treatment.

A variation of the pressure recovery rate with the pressure level is shown in Figure 4. The point of the inflection on the pressure recovery curve was accepted as a reference point. As shown in this figure, the highest rate of the pressure recovery occurs at the stand-up pressure $P = 8.0$ MPa. Thus, it is obvious that the thermo-baric conditions exposing the supercritical properties are affecting the hydrodynamic characteristics of the porous media.

PSEUDO-BOILING GAS-LIQUID SYSTEM BANK (PBGSB)

Oil displacement technology by carbon dioxide banks is based on the creation of the oil saturated formation CO_2-bank (one or the several, separated by water) which is displaced by pure or carbonized water. In this case carbon dioxide renders favorable effect on oil properties directly at the displacement front of one or several banks. Required amount of carbon dioxide is much less, than that required for continuous displacement. Dissolution of CO_2 in oil is accompanied by mass transfer process, since carbon dioxide extracts the light fractions of oil dissolved in a gaseous phase. In process of flow, carbon dioxide is continuously enriched with light hydrocarbons which concentration increases, and contents of CO_2 decreases up to zero. The formed zone containing light hydrocarbons, effectively displaces the oil. Thus, under certain pressure conditions an oil displacement regime in the reservoir will be established. The pressure required for achievement of CO_2 miscibility with oil much less than the pressure, required for a miscible displacement of oil by natural gas, carbonic oxide or nitrogen. The increase of oil volume under influence of dissolved carbon dioxide, alongside with change of liquids viscosity (reduce of oil viscosity and increase of water viscosity) is considered as one of the major factors defining oil recovery efficiency from flooded layers. With the purpose of displacement front equalization and increase of oil recovery, the pseudo-boiling gas-liquid system bank (PBGSB) technology was offered by IGDFF. The new method possesses essential profitability in comparison with existing traditional technologies of CO_2 injection since carbon dioxide is generated in-situ. Following the conditions of full saturation of carbon dioxide in the created bank are provided with one-phase nature and nonequilibrium system that considerably increases efficiency of an offered method. Unlike existing methods in which supersaturation by carbon dioxide leads to two-phase bunk and consequently to the advancing of the gas breakthrough into the producing wells, and at undersaturation by carbon dioxide, the bank properties practically do not differ from the properties of water. For an estimation of displacement properties of PBGSB, experimental researches have been carried out. The received results have shown, that the application of the offered method allows increasing displacement efficiency in comparison with conventional methods, thus the displacement efficiency increases about 16-18 %. During the application of pseudo-boiling gas-liquid system bank technique it is necessary to inject consistently gas-forming and a gas-yielding agents (Figure 6).

For realization of the newly developed technique at oil field operations the traditional and standard equipment can be used. The volumes and concentration of chemical components to be injected were determined based on the bank volume, underground pressure and temperature, amount of water content, composition and properties of oil. A separator (water) has been injected in the amount of well tube volume in order to avoid the mixing of different chemical reagents. A phase ratio of the in-situ generated gas-liquid system was controlled via the variation of the injection rate and the thermo-baric conditions.

The offered technologies are recommended for application on oil fields with both carbonate and terrigenous reservoirs with both high and low viscous oils at any oil field development stages. The highest efficiency of application of the pseudo-boiling gas-liquid system bank technology will be reached the injection is performed by several times during certain period of time. Thus, the probability of achievement of high sweep efficiency in the reservoir increases.

RESULTS OF INDUSTRIAL APPLICATION OF IN-SITU CO_2 GENERATION

Thermo and rheochemical bed stimulation has been realized in a number of oil-recovery regions of the Russian Federation and China. Essential advantage of the system stimulation is the opportunity of their application in various geology-geophysical conditions of the developed oil fields. First, the pilot project of PBGSB technology has been realized on Samotlor oil field (Russia). Pseudo-boiling gas-liquid system bank was injected into the injection wells in the optimal volumes, both in cycles and alternately. It has generated optimum conditions for complete mixing of injected agents and for dissolving of CO_2 in both reservoir oil and the displacing agent, with formation of the effective bank. A bank generated in the high-permeable and washed out zones creates significant additional resistance to the injected water flow. After injection of the components the well was closed for the reaction, and after 20 hours it was returned to the previous operating regime.

The analysis of producing wells parameters after operation showed that the majority of the wells have reacted on bank injection by changes in the regime parameters. In some cases it was expressed by decreasing of water content, in others cases by increasing the oil production. A variation of the well process parameters is presented in Figures 7 and 8.

The Tyumen Oil Company has widely used PBGSB technology in flooding system on Samotlor oil fields. 121 operations were successfully conducted with the high technological efficiency during 1999-2001. PBGSB technology was also carried out on injection wells of Novo-Pokursky oil field "Slavneft-Megionneftegas" JSC, where the reservoirs are characterized by high level of heterogeneity in permeability and lithology.

Industrial application has been realized on 5 region of Gunyuang Oil Field (China), covering 20 injection and 45 oil producing wells. Estimation of the operations efficiency with comparison of injectivity profile of injection wells has been conducted. In particular, the injectivity profile on a well before and after treatment showed high efficiency of the treatment. As a result, new interlayers were involved into the production and the displacement front was flattened. The results of the treatment operations also showed to the profitable changes of the process parameters: injection pressure was decreased and the injection capacity of the productive reservoir was increased. The changes of process parameters indicates to the realization of the well bore zones cleaning process at the initial stages of the treatment. In injection wells of Gunyuang Oil Field also the tracer injection tests have been carried out. The analysis of the tracer concentration curves demonstrated the inclusion of new oil saturated reservoirs to the oil production process, and the sweep efficiency increase.

The similar results were obtained on oil wells of Novo-Pokursky oil field (Figures 9 and 10). As a result of the technological operation, the injection capacity of the productive reservoirs substantially increased, and the injection pressure decreased, which testified on inclusion new productive reservoirs into the operation.

The effectiveness and technological advantages realized during in-situ CO_2 generation can be shown briefly by the followings:

- a significant additional resistance to the injected water flow due to the generation of a steady foamy barrier in high flooded zones;
- an extraction of hydrocarbon components from a porous medium surface at certain thermobaric conditions of *supercritical* CO_2;
- a sweep efficiency ands recovery factor are increased as a result of the volumetric effect due to the dissolution of in-situ generated carbon dioxide;
- gas accumulation in the cupola of the reservoir due to the differences in the densities.

Thus the technology possesses a number of the following advantages favorably distinguishing it from traditional technologies with use of gas banks:

- The profitability of technology defined by in-situ conditions of CO_2 generation, and creation of the gas-liquid bank;
- The adaptability defined by absence of necessity for search of a source (CO_2 manufacturing plants) and building the gas pipelines;
- An opportunity of carrying out of operations in remote zones and oil recovery regions with severe climatic conditions (Siberia, Alaska, etc.);
- Absence of necessity of build up of additional pipelines and power supply for CO_2 injection from a surface.

COMMERCIALIZATION OF TECHNOLOGY IN UNITED STATES

In order to commercialize this technology in United States the database of leases must be analyzed. It will allow to estimate the effectiveness of in-situ CO_2 generation technology. Figure 11 shows an expected additional oil production and economical indexes of the new technology application in one of US oil fields.

ACKNOWLEDGMENTS

Author would like to acknowledge Dr. Azizaga Kh. Shakhverdiyev (Institute of Geology and Development for Fossil Fuels, Moscow, Russia), Dr. Geilani M. Panakhov and Dr. Eldat M. Abbasov (both from Institute of Mathematics and Mechanics, Azerbaijan Nation al Academy of Sciences, Baku, Azerbaijan) for active participation in development and tests of new technology. I acknowledge Dr. Reid Grigg, Dr. Randy Seright, Mr. Robert Svec and Graduate students Onur Coskun and Amir Gadimipour (all New Mexico Tech, Socorro, NM) for pilot tests and evaluations of new technology for US oilfield conditions. The author gratefully acknowledges the financial support received from National Energy Technology Laboratory, U.S. Department of Energy under the cooperative agreement DE-FC26-05NT15478. Special thanks to Mr. Roy Wales, Mr. Clay Bird and Mr. Howard Kelsey (all: Energy Reclamation, LLC) for invaluable efforts in commercialization of this technology in United States.

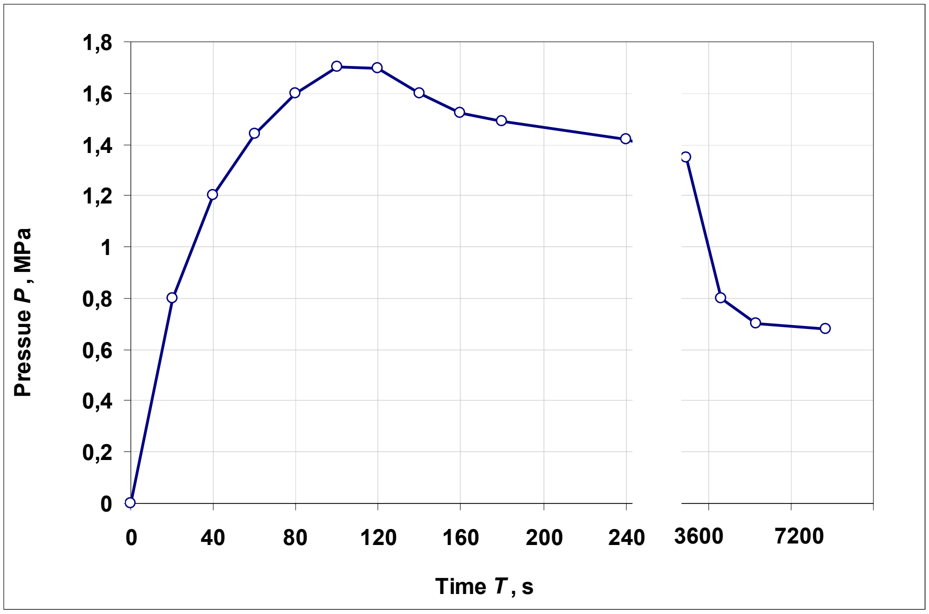

Figure 1- Pressure Changes During Laboratory Tests on CO_2 Generation

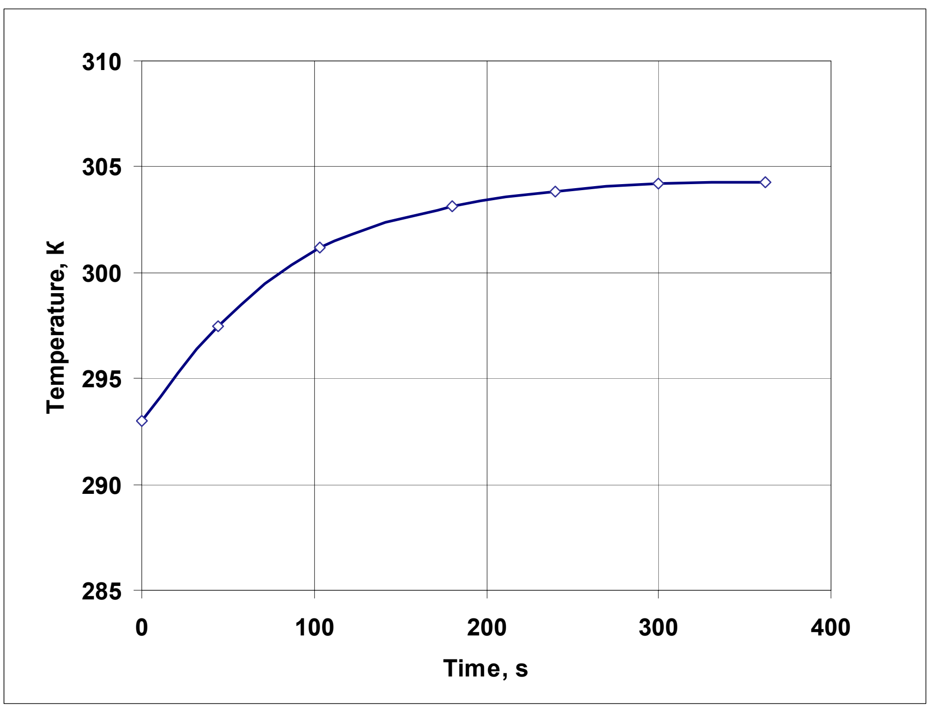

Figure 2 - Temperature Changes in Laboratory Tests on CO_2 Generation

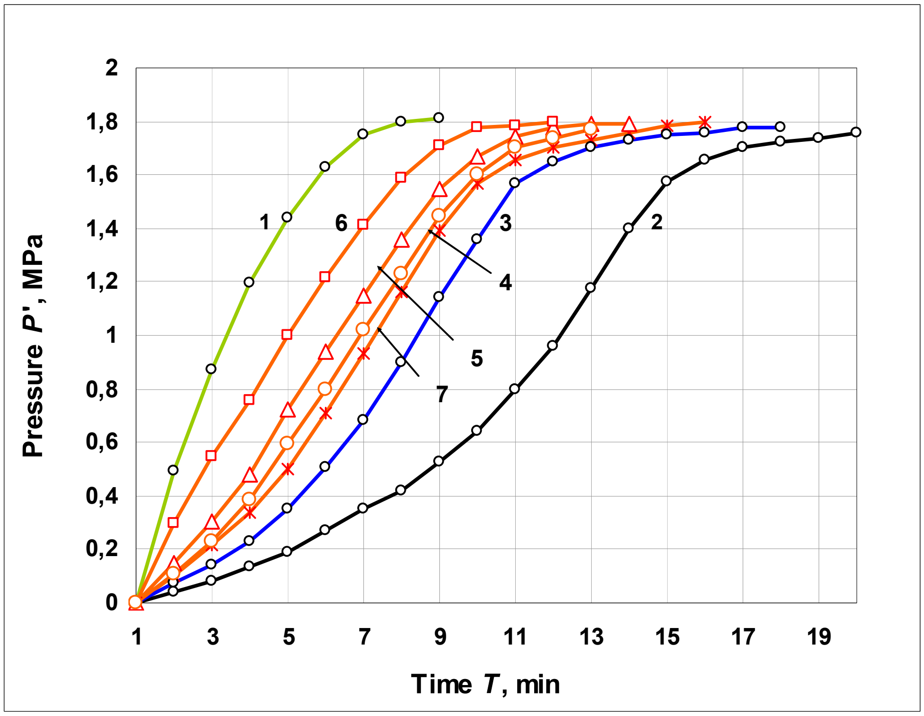

Figure 3 - Experimental pressure recovery curves (*P'* – output pressure change): 1 – pressure recovery curve (PRC) before treatment; 2 – PRC after impurity; 3 – PRC after acid treatment ($P_н$ -10,0 MPa, $P_к$-8,0 MPa); 4 – PRC after CO_2-stimulation at P_1=10,0 MPa; 5 – PRC after CO_2-stimulation at P_1=9,0 MPa; 6 – PRC after CO_2-stimulation at P_1=8,0 MPa; 7 – PRC after CO_2-stimulation at P_1=7,0 MPa

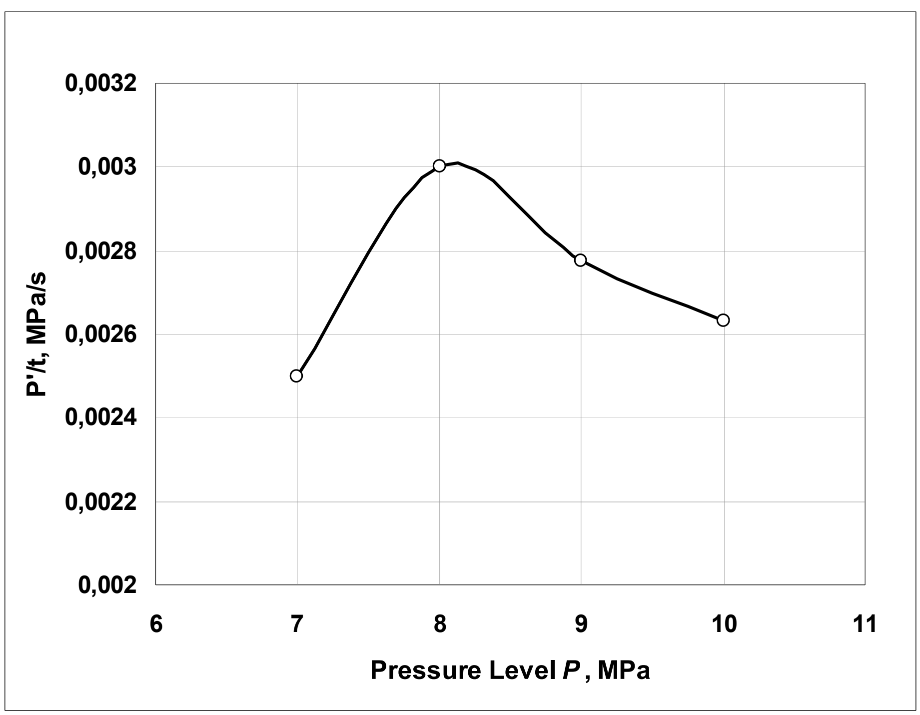

Figure 4 - Pressure Recovery Rate vs. Pressure Level

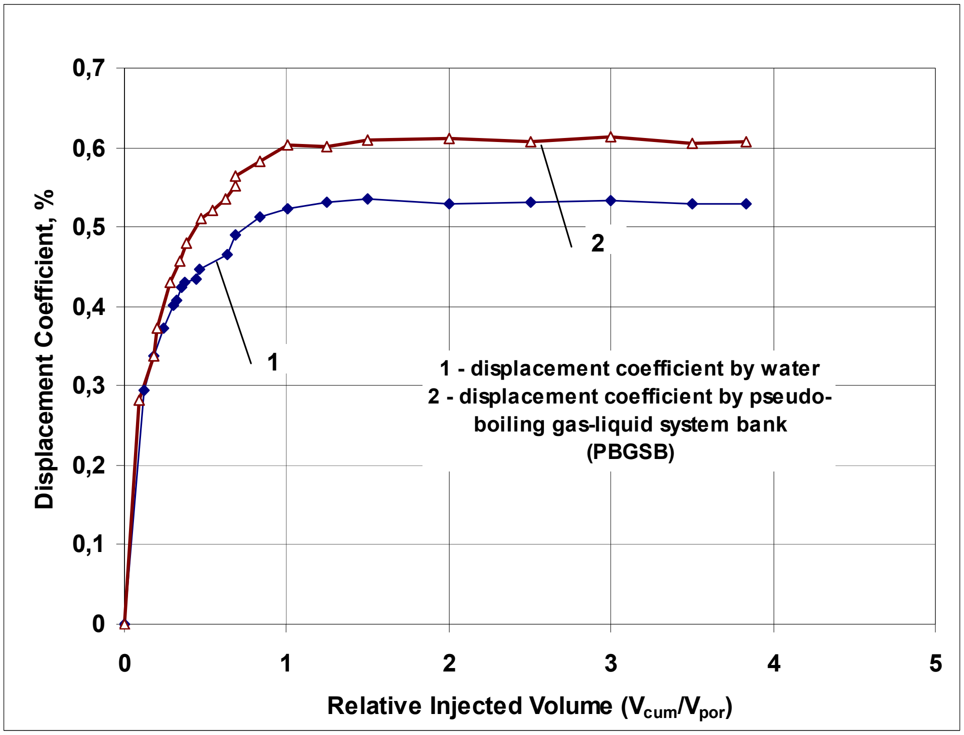

Figure 5 - Displacement Efficiency vs. Related Injection Volume of Water (1) and PBGSB (2)

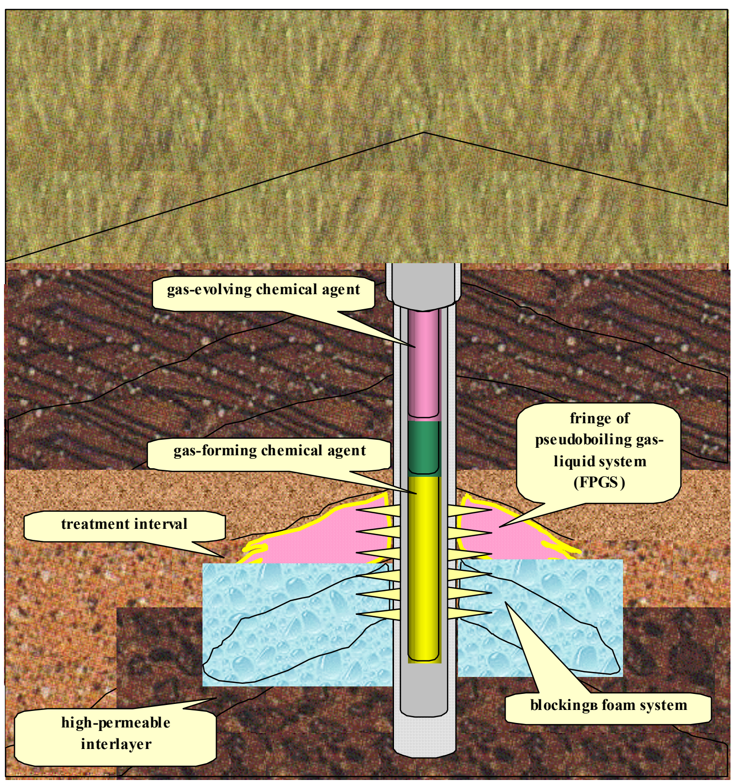

Figure 6 - Sequence of Operations During PBGSB Injection

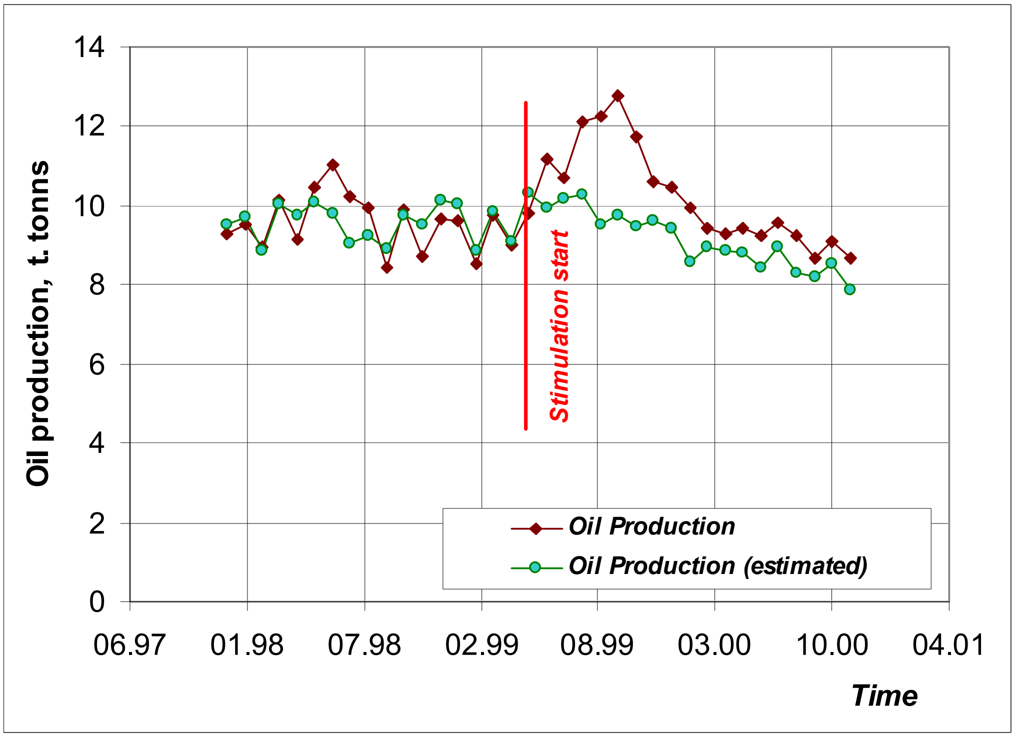

Figure 7 - Oil Production Changes Before and After Treatment

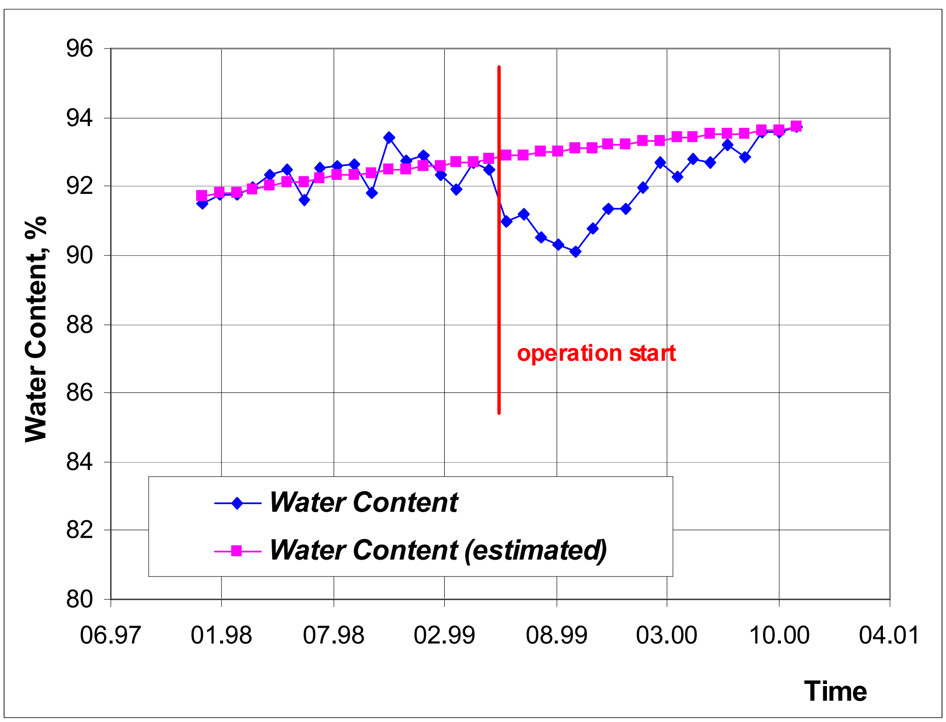

Figure 8 - Water Content Before and After Treatment

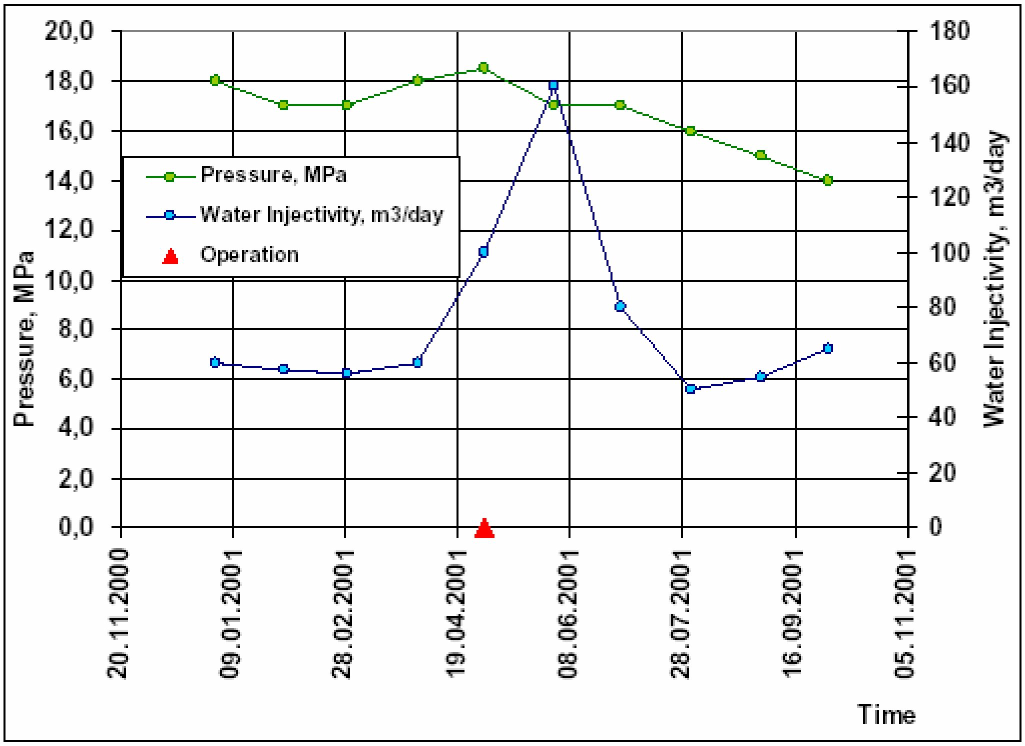

Figure 9 - Variation of Pressure and Water Injectivities with Time

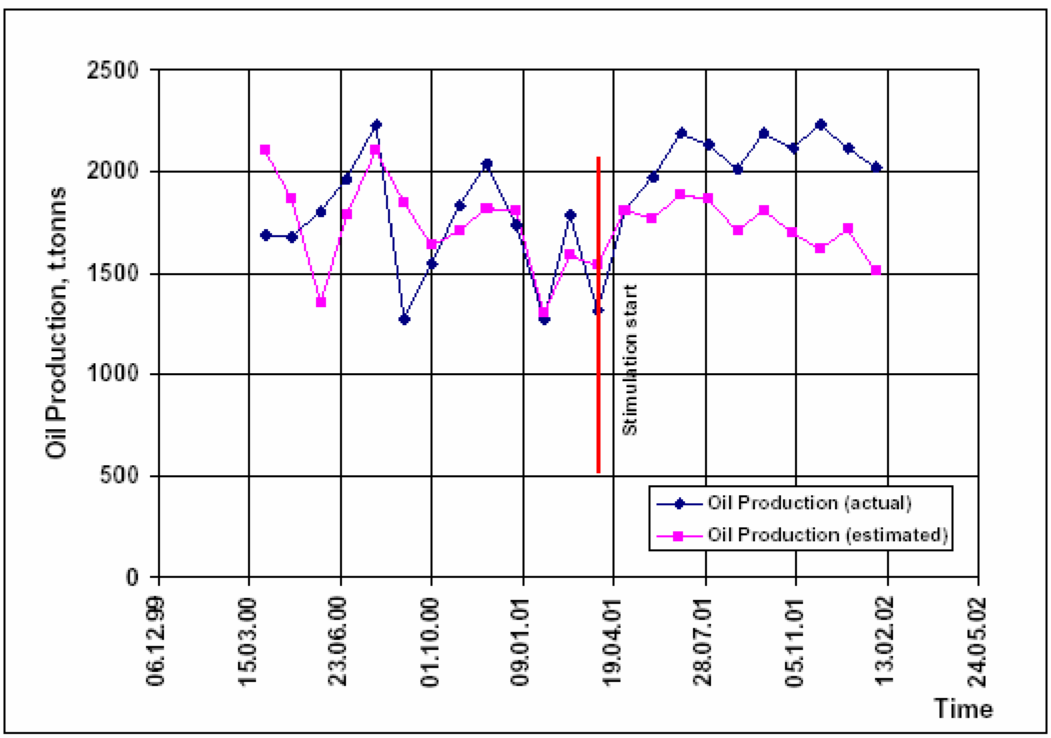

Figure 10 - Variation of Oil Production Rate with Time

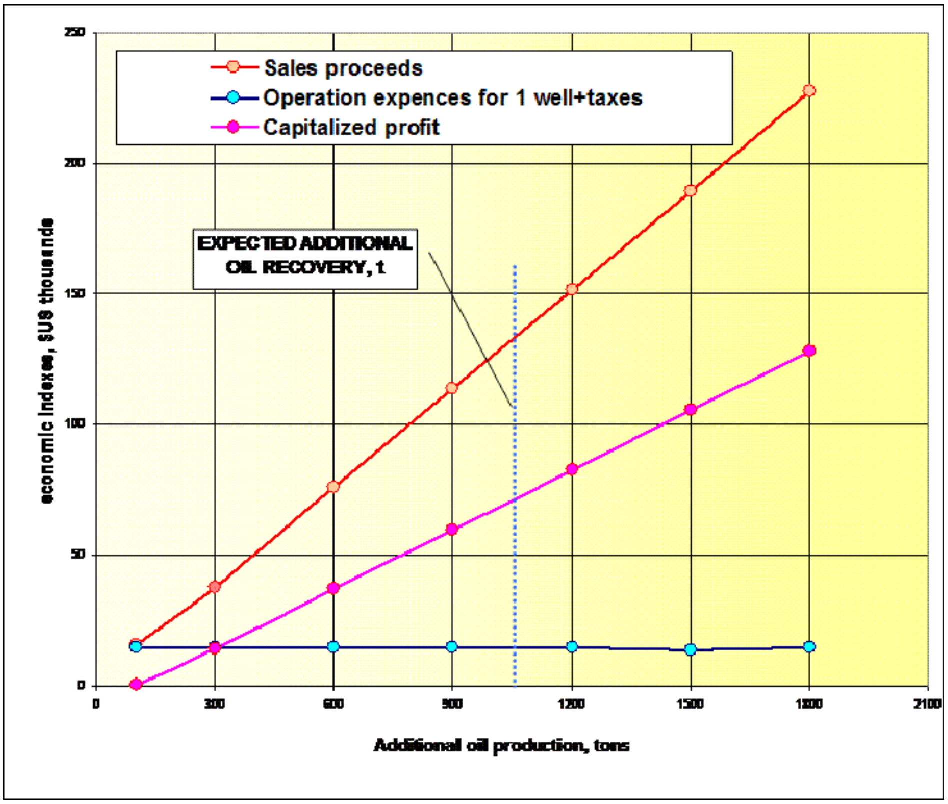

Figure 11 - Expected Additional Oil Production and Economical Indexes of New Technology Application in One of US Oil Fields