RESULTS OF EXPERIMENTAL STUDIES OF INTEGRATED PHYSICO-CHEMICAL IMPACT IN CARBONATE RESERVOIRS

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A b s t r a c t

The article highlights the experimental studies results of carbonate rock dissolution kinetics in order to develop effective methods of slowing down the acid reaction rate in the heterogeneous structures. It was found that the intensity of carbonate reservoirs leaching process with the addition of hydrocarbon solvents such as dioxanes increases due to the acetals transition to the oil phase, dissolution of highly active oil components and more intense penetration of an aqueous solution of hydrochloric acid to the carbonate matrix of the reservoir rock, which intensifies the process of leaching. The technology of complex physico-chemical impact on carbonate reservoirs has been developed. It is shown that the use of a aqueous hydrochloric acid solutions mixture and an organic solvent leads to an increase in the dissolution efficiency to 88% and the reaction rate increases by a factor of 3.5.

Keywords:
Carbonate rock;
Reservoir;
Porous medium;
Heterogeneity;
Leaching kinetics;
Hydrochloric treatment;
Solvent.

Many researches study the process of rock leaching in various acids solutions [1-6]. The main part of these studies was carried out in connection with the technologies development used for acidizing the bottom-hole zones of oil-producing and water-injection wells due to the dissolution channels formation and increasing the permeability of the bottom-hole formation zone. Moreover, the slower the acid solution is neutralized, the more effective the treatment is. That is why, when studying the kinetics of the carbonate rocks dissolution, the goal was to find ways to slow down the acid reaction rate «in order to achieve the goal of pushing the acid to the maximum distance from the wellbore while maintaining a greater proportion of its activity» [6, 7].

This approach is applicable for the technology of forcing an acid solution into a productive reservoir, represented by porous, porous-fractured and fractured-porous types [4]. With a more complex structure of the pore space, characterized by a lenticular structure, such technologies are not efficient and in many cases lead to negative consequences [3, 7]. For such reservoirs, the most effective hydrochloric acid treatment leads to the activation of isolated lenses in the productive formation.

When carrying out hydrochloric acid treatment, the process intensification can be achieved by increasing the rate and dissolution efficiency in the carbonate rock [3].

In the paper [2], as a result of a planned experiment, a regressive equation was obtained for the complete dissolution time in clean carbonate rock

$$Y=4.633-0.644 \cdot X_1-1.14 \cdot X_2+0.506 \cdot X_3-0.535 \cdot X_4-0.411 \cdot X_{42} \quad (1)$$

where Y - time of complete dissolution, minutes;

X_1 - temperature;
X_2 - concentration of hydrochloric acid;
X_3 - fractional composition of the rock;
X_4 - mixing intensity. X values are coded.

In real-life productive formations, a significant factor influencing the kinetic characteristics of oil-saturated carbonate rock leaching is the presence of adsorbed active oil components on its surface which form a boundary layer [9, 10], which seals this surface and reduces the area of phase contact of the acid with the rock. In addition, as follows from [10], there are carbonaceous (similar in composition to coke) components of geological and kinetic origin on the surface of the reservoir pore space, which also impede the access of active acid to the rock.

The above facts lead to the need to set up a series of experimental research works to study the process of natural carbonate reservoir rock leaching

in solutions of hydrochloric acid and methods of its intensification. The presence of a screening film on the rock surface suggests an organic solvent as an intensifying factor. Such a solvent in study [10] is 4,4-dimethyl-1,3 dioxane from the heterocyclic acetals class, which is an intermediate product of isoprene production and it haa a number of positive properties (high solubility of hydrocarbon components, solubility in water, anti-corrosion properties, availability, etc.).

The presence of acetals in water or in aqueous solutions of hydrochloric acid leads, according to [2-4], to their adsorption on an oil film, consisting mainly of heavy asphalt-resinous compounds, what leads to bonds weakening and destruction of the solvation shell covering the asphaltenes. This further causes a focal destruction of the film integrity and an increase in the area of the rock matrix phase contact with the acid solution. Naturally, this process' kinetics depends on the redistribution rate of acetals in the «oil-water» system.

In this regard, experimental work was carried out to study the diffusion process occurring in the «oil - aqueous solutions of acetals» system, depending on the concentration of the solvent in water and the process temperature. To study these processes, one of the well-known methods of mathematical planning of experiments was used - central composite rotatable design of experiments (CCRD) of the second order [10]. As input variables chosen were X_1 - initial concentration of solvent in water, %; X_2 - process temperature, ^{o}C. The output parameter (response function) is Y - the solvent distribution coefficient in the «oil-water» system. Partition coefficient is defined as the ratio of the solvent concentration in oil to the solvent concentration in water after contact with oil. Solvent solutions of a given concentration were prepared and poured into separating funnels containing oil. The amounts of solvent and oil aqueous solutions in all experiments were the same. Then, the contents of the separating funnels were thermostated at a certain temperature for 24 hours. The contact duration choice is justified by the fact that the solvent redistribution process occurs during the first day. The solvent concentration in water before and after contact with oil was determined using the IR spectrometry method, which makes it possible to determine the chemical reagents content in an aqueous solution with high accuracy [10]. The solvent concentration in water before and after contact with oil was used to determine its amount redistributed into oil, and then the distribution coefficient was calculated.

After processing the planned experiment results, the following regression equation was obtained

$$Y=2.365+0.935 \cdot X_2+0.122 \cdot X_{12}+0.164 \cdot X_{22} \qquad (2)$$

It adequately describes the experiment according to Fisher's criterion.

Obtained regression equation analysis allows to draw the following conclusions:

1) the response function has a non-linear character and it can be described as a surface of the second order;

2) the response function is symmetric to the line X_1=0 (the solvent concentration in water is 7.5 %);

3) the process temperature influence on the distribution coefficient is much greater than the initial solvent concentration in water.

With an increase in the initial solvent concentration from 0.1 to 7.5%, a slight decrease in the distribution coefficient occurs over the entire range of the studied temperatures. With a further increase in the solvent concentration to 15%, this coefficient increases. It should be noted that the dependence of the distribution coefficient on the solvent concentration has a parabolic shape with a minimum at 7.5%. A slight decrease in the distribution coefficient at a given solvent concentration is evidently explained by steric factors, which are actively manifested in such a complex system as oil-dioxane-water.

With an increase in the process temperature, a monotonic increase in the distribution coefficient from 1.26 to 4.04 is observed at all investigated solvent concentrations.

Thus, the study of the solvent activity in the oil-water system showed that the distribution coefficient is independent from the initial dioxane concentration and it significantly depends on the process temperature. As the temperature rises, the distribution coefficient increases. So, at 20 °C, the solvent concentration in water after 24 hours is 45% of the initial, and at 80 °C - only 20%, i.e. with an increase in temperature, the amount of solvent in the aqueous phase decreases, and the amount of solvent that has passed into oil increases.

Let investigate the kinetics of non-isothermal carbonate reservoir leaching with a hydrochloric acid solution. The observed significant transition of acetal to the oil phase will contribute to the dissolution of highly active oil components, disruption of the oil film integrity and more intensive penetration of an aqueous solution of hydrochloric acid to the carbonate reservoir rock matrix. A series of experimental works was carried out to study the kinetics of the oil-saturated carbonate rocks leaching under various conditions.

An oil-wet core sample was taken as a skeleton of the carbonate formation. It was disaggregated, a fraction of 2-2.5 mm was taken and placed in oil for 72 hours (the time required for the boundary layer formation) [10]. To obtain a film, the disaggregated sample was transferred from the oil to a desiccator on a filter paper. To avoid oxidation, oil was poured to the bottom of the desiccator in order to drain the oil in an atmosphere saturated with its vapors. The filter paper was changed as it became contaminated. The oil was pulled by capillary absorption and due to gravitational forces until the filter paper became clean after a day's exposure.

A sample of the carbonate rock prepared in this way was placed in a temperature-controlled flask

and the solvents were poured. The leaching process kinetic characteristics were presented in the form of the yield dynamics of carbon dioxide released during the rock dissolution, the volume of which was measured using a gas meter connected through a separator to a reaction flask.

At the first study stage, preliminary experiments were carried out, before which the task was set to assess the addition of a solvent effect on:

1) the rate of hydrochloric acid interaction with oil-saturated rock;

2) the completeness of the rock dissolution;

3) the interaction rate of hydrochloric acid with clean carbonate rock.

The research results show that the solvent additive to the HCL solution gives the following results:

1) the interaction rate with the rock is 3.5 times higher;

2) the carbonate rock dissolution completeness with acid increased from 49.2 to 87.5%.

In addition, experiments have shown that the addition of an organic solvent does not affect the kinetics of the clean carbonate rock (no oil film) dissolution process.

At the next stage, the process of oil-saturated carbonate rock dissolution with 15% hydrochloric acid solution was used varying the temperature. The range of temperature variation 20...80 °C was selected from the technological conditions for the use of hydrochloric acid solutions in oilfield practice (conventional hydrochloric treatments, thermal acid treatments, etc.) [10].

When processing the experimental results, the following solvent kinetic characteristics were analyzed:

1) reaction delay time;

2) the reaction end time;

3) completeness of dissolution;

4) reaction rate.

When the oil-saturated carbonate rock dissolves, the interaction of hydrochloric acid with the carbonate rock matrix does not begin immediately, but after a certain time, which is called the «reaction delay time». This is due to the screening of the carbonate skeleton by the oil film, which, apparently, will be observed in real conditions [4]. With an increase in the process temperature, the reaction delay time decreases and at 75 °C the dissolution process begins almost immediately after the interaction of the hydrochloric acid solution with the oil-saturated carbonate rock. Indeed, as the temperature rises, the oil film viscosity of shielding the surface of the carbonate skeleton decreases, its integrity is violated, and, naturally, its permeability to hydrochloric acid solution increases. Therefore, at elevated temperatures, the hydrochloric acid solution easily penetrates rock skeleton and the reaction begins [8].

The reaction end time was taken as the time corresponding to the flattening of the kinetic curve plotted in the coordinates «volume of carbon dioxide – time». According to the obtained dependences, the dependence of the reaction completion time on temperature has a minimum at a temperature of 61.8 °C, which is explained by the effect of screening the rock surface by the released gas phase. As the temperature rises, the intensity of the release of carbon dioxide increases, and when a certain temperature is reached, the released carbon dioxide makes it difficult for the acid to access the carbonate skeleton, which leads to the reaction time increase. The temperature at which the process of oil-saturated carbonate rocks leaching takes place has a significant effect on the dissolution efficiency and on the reaction rate. The dissolution efficiency increases from 50% at a temperature of 25 °C to 96% at a temperature of 75 °C, and the dissolution rate increases from 0.04 dm^3/s to 0.009 dm^3/s, respectively.

When analyzing the dependences of the delay time and the dissolution efficiency on temperature, a decrease in the influence of the oil film presence on the carbonate rock skeleton on the kinetics of the leaching process is noted. When the process temperature reaches 80 °C, the dissolution efficiency becomes 100%, while the acid solution immediately begins to react with the rock (the reaction delay time is zero). But even at this temperature, oil saturation affects the dissolution process rate, which was shown by further experiments [10, 11]. Obtained dependences of the rates of the carbonate dissolution reaction on temperature under various conditions. Indeed, the rate of carbon dioxide evolution during of oil-saturated carbonate leaching increases with temperature rise, but the dissolution rate of carbonate without an oil film remains always lower in the entire studied temperatures rang. This is explained, in our opinion, by the high viscosity value of the medium into which carbon dioxide is released during the reaction. When «clean» carbonates dissolve, gaseous carbon dioxide is released into an aqueous calcium chloride solution. When dissolving oil-saturated carbonate rock, carbon dioxide is formed in a complex heterogeneous system «aqueous solution of calcium chloride – oil», the viscosity of which is greater than the calcium chloride solution viscosity. Under these conditions, the removal of the evolved carbon dioxide the rate and the inflow of a new acid solution portion is much less than under the dissolution of «clean» carbonate conditions.

The obtained dependence of the dissolution rate of oil-saturated carbonate rock with a mixture of aqueous hydrochloric acid solutions and 4,4-dimethyl-1,3-dioxane indicates that the organic solvent presence in an aqueous hydrochloric acid solution significantly intensifies the leaching of oil-saturated carbonate rock process.

Later, in a more detailed study of the leaching process kinetics of carbonate oil-saturated rock with a composite solvent, the mathematical apparatus of central composite rotatable design of experiments of second-order experiments was used.

The following parameters were selected as input variables: X_1 - concentration of the organic solvent 4,4-dimethyl-1,3-dioxane mixed with 15% aqueous hydrochloric acid solution; X_2 - process temperature. The output parameters (response functions) were Y_1 - end of reaction time; Y_2 and Y_3 - respectively, coefficients C and α in the equation (3) of the process kinetic characteristics:

$$V = C \cdot \tau^{\alpha} \qquad (3)$$

where V - volume of carbon dioxide emitted;

τ - time response;

Y_4 - dissolution efficiency;

Y_5 - the rate of dissolution of the rock.

After processing the results of the planned experiment, the following regressive equations were obtained.

$$Y_1=474-410X_1+974X_2-171X_{12}+140X_{22}+309X_1X_2 \qquad (4)$$

$$Y_2 = 0.23 + 0.41X_1 + 0.22X_{12} \qquad (5)$$

$$Y_3=0.45-0.26X_1+0.08X_2+0.06X_{12}-0.11X_1X_2 \qquad (6)$$

$$Y_4 = 80.79 + 8.08X_1 - 10.90X_{12} \qquad (7)$$

$$Y_5 = 0.02 + 0.02X_1 + 0.01X_{12} \qquad (8)$$

Obtained equations adequately describe the experiment according to Fisher's criterion.

The regression equations analysis allows to draw the following conclusions:

1) all response functions are non-linear;

2) the functions Y_1 and Y_3 are surfaces of the second order, and the form of the functions Y_2, Y_4, Y_5 corresponds to the parabola equation, and depends only on X_1 - the higher the solvent concentration in the mixture, the greater the coefficient C in the natural kinetic characteristic and the dissolution rate;

3) an increase in the solvent concentration in the mixture leads to a reduction and an increase in temperature, on the contrary, to an increase in the reaction end time. Moreover, the temperature influence on Y_1 is significant, the interaction of these two factors also leads to an increase in the values of Y_1;

4) an increase in the solvent concentration leads to a decrease in the coefficient in the natural kinetic characteristic, and an increase in temperature leads to its growth, moreover, the influence of X_1 is more significant than the effect of X_2, and the mutual influence, as a result, is unidirectional with the influence of X_1;

5) the graph of the function Y_4 has a maximum at $X_2 = 0.366$ (9.4% solvent).

Conclusions

1. The process of carbonate oil reservoirs leaching with a hydrochloric acid solution is characterized by low values of the dissolution efficiency due to the presence of a boundary oil layer on the pore space surface.

2. The leaching process intensification is achieved by increasing the temperature and using composite solvents (aqueous solutions mixtures of hydrochloric acid and organic solvent).

3. An increase in the process temperature up to 75 ºC allows to increase the rock dissolution efficiency up to 96%, and the reaction rate - by a factor of 2.65.

4. The use of an aqueous solutions mixture of hydrochloric acid and an organic solvent of 4,4-dimethyl-1,3-dioxane as a solvent leads to an increase in the dissolution efficiency to 88%, and the reaction rate increases by a factor of 3.5.

5. The results obtained were used in the development of a technology for the complex physico-chemical treatment of carbonate reservoirs. It is recommended to use a mixture of a 15% aqueous solution of hydrochloric acid and an organic solvent of 4,4-dimethyl-1,3-dioxane with a concentration of 5-15% (reservoir temperature is less than 35 ºC) or up to 5% (reservoir temperature is more than 35 ºC).

References

1. Andreev, V. E., Blinov, S. A. (1987). Kinetics of the dissolution process of oil-saturated carbonate rocks in a mixture of aqueous solutions of hydrochloric acid and an organic solvent. In: *Problems of Dynamics of Relaxing Media. Ufa.*

2. Ibragimov, G. Z., Khisamutdinov, N. I. (1983). Handbook on the use of chemical reagents in oil production. *Moscow: Nedra.*

3. Chizhov, A. P., Ivanov, D. V., Chibisov, A. V., Andreev, A. E. (2016). Improving the effectiveness of impact on the residual reserves of carbonate reservoirs of the Volga-Urals. In: *Oil and Gas Technologies and New Materials. Problems and Solutions. Ufa: USPTU.*

4. Andreev, V. E., Chibisov, A. V., Chizhov, A. P., et al. (2016). Increasing the efficiency of oil recovery from deposits represented by carbonate reservoirs. *Problems of Collection, Preparation and Transportation of Oil and Oil Products,* 3(105), 43-51.

5. Chibisov, A. V., Chizhov, A. P., Efimov, E. R. (2016). Influence of the features of the geological structure of oil deposits in carbonate reservoirs of the Tournaisian stage on the efficiency of reserves development. In: *International Scientific and Technical Conference «Modern Technologies in Oil and Gas Business - 2016» dedicated to the 60th Anniversary of the Branch.*

6. Chizhov, A. P., Andreev, V. E., Chibisov, A. V., et al. (206). Intensification of inflow from carbonate reservoirs for the conditions of the Volga-Urals. *Problems of Collection, Preparation and Transport Oil and Petroleum Products*, 3(105), 35-42.

7. Kudinov, V. I., Suchkov, B. M. (1996). Stimulation of viscous oil production from carbonate reservoirs. *Samara: Book House.*

8. Loginov, B. G., Malyshev, L. G., Garifullin, Sh. S. (1966). Well acidizing guide. *Moscow: Nedra.*

9. Mamedov, T. M. (1984). Oil production using hydrocarbon solvents. Moscow: Nedra.

10. Surguchev, M. L., Kolganov, V. I., Gavura, A. V., et al. (1987). Oil extraction from carbonate reservoirs. *Moscow: Nedra.*

11. Chizhov, A. P., Chibisov, A. V., Efimov, E. R., Andreev, V. E. (2017). On the issue of complex impact on complexly constructed carbonate development objects. In: VI *International Scientific and Practical Conference «Innovations and High Technology in Education and Economics».*

Результаты экспериментальных исследований комплексного физико-химического воздействия в карбонатных коллекторах

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Реферат

В статье освещаются результаты экспериментальных исследований кинетики растворения карбонатных пород с целью разработки эффективных способов замедления скорости кислотной реакции в гетерогенных структурах. Установлено, что интенсивность процесса выщелачивания карбонатных коллекторов с добавлением углеводородных растворителей, таких как диоксаны, увеличивается из-за перехода ацеталей в нефтяную фазу, растворения высокоактивных компонентов нефти и более интенсивного проникновения водного раствора соляной кислоты в матрицу карбонатной породы, что интенсифицирует процесс выщелачивания. Разработана технология комплексного физико-химического воздействия на карбонатные коллектора. Показано, что использование смеси водных растворов соляной кислоты и органического растворителя приводит к увеличению эффективности растворения до 88%, а скорость реакции увеличивается в 3.5 раза.

Ключевые слова: карбонатная порода; коллектор; пористая среда; неоднородность; кинетика выщелачивания; соляно-кислотная обработка; растворитель.

Karbonatlı kollektorlarda kompleks fiziki-kimyəvi təsirin eksperimental tədqiqatlarının nəticələri

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Xülasə

Məqalədə heterogen strukturlarda turşunun reaksiya sürətinin yavaşladılmasının effektiv üsullarının işlənməsi məqsədilə karbonat süxurlarının həllolma kinetikasının eksperimental tədqiqatlarının nəticələrinə baxılmışdır. Müəyyən olunmuşdur ki, dioksan kimi karbohidrogen həlledicilərinin əlavə edilməsi ilə karbonatlı kollektorların yuyulma prosesinin intensivliyi asetalların neft fazasına keçməsi, neftin yüksək dərəcədə aktiv komponentlərinin həll olması və xlorid turşusunun sulu məhlulunun karbonat süxur matrisinə daha intensiv nüfuz etməsi sayəsində artır. Karbonatlı kollektorlara kompleks fiziki-kimyəvi təsir texnologiyası işlənmişdir. Göstərilmişdir ki, xlorid turşusu və üzvi həlledici sulu məhlullarının qarışığının istifadəsi həllolma effektivliyinin 88% -ə qədər, reaksiya sürətinin isə 3.5 dəfə artmasına səbəb olmuşdur.

Açar sözlər: karbonatlı süxür; kollektor; məsaməli mühit; qeyri-bircinslilik; yuyulma kinetikası; xlorid turşusu ilə işlənmə; həlledici.