On stability boundary of the flow of an acid solution through a chemically active porous medium

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Abstract. It is known that during the flow, if the displacing fluid can chemically react with the components of porous medium and with the release of a gas phase, then such a flow regime can be unstable. During this process, pressure fluctuations can be observed, and the displacing fluid will move in “waves”. In the course of our research, a simple mathematical model was proposed that provides a qualitative explanation of the reasons for the emergence of such a phenomenon; laboratory modeling was carried out, and the criterion of the “waves” formation was found, depending on the concentration of chemically active components. The proposed model can predict the emergence of the wave instabilities in a laboratory experiment, which will allow to carry out a future experiment on a larger scale.

1. Introduction

Among the methods of increasing hydrocarbon production, one of the most perspective one is the method of acidizing the well \[1, 2, 3\], which involves pumping acid solutions into the bottom-hole zone to dissolve part of the rock and increase the oil mobility. This chemically reacting flow can proceed with various instabilities, which can affect the flow parameters. Such flows generate interest from both experimental and theoretical points of view, while combustion processes are of the greatest interest \[4, 5\], although unstable filtration flows are also very common \[6, 7, 8\].

The focus of our research is the isothermal flow of an acid solution through a porous medium saturated with a highly viscous fluid and containing a component, chemically reacting with the acid accompanied by gas release. It was found that in this case a self-oscillatory flow regime can be observed, when the pore pressure in the reaction area and the flow rate are changed with a certain period, and the gas is released in waves called “secondary waves” \[9\]. Recently this instability was observed in the numerical simulation of Konyukhov and Zavialov \[10\].

At the moment, there is no clear understanding of exactly which parameters lead to the formation of “secondary waves”. The article of Zavialov \[9\] demonstrated that in the experiment pressure gradient was not the main factor leading to their appearance. The aim of this work was to study the phenomenon of “acid waves” depending on the concentration of the reducing agent in the porous medium and the oxidizing agent in the displacing liquid.
2. Experimental results

For the laboratory study of the phenomenon, a flat transparent cell with internal dimensions (height, width, distance between side plates) 350x160x15 mm was constructed (Figure 1). The space between the plates of the cell was filled with a porous medium. The lower part of the cell was closed with a mesh that allows the acid solution to pass through and does not allow the porous medium to fall out of the cell. At the top there are two holes; through one of which liquid was injected, and through the other excess fluids were removed to maintain a constant pressure gradient in the cell. 15 pressure sensors with a pitch of 20 mm are mounted in one plate of the cell along the vertical. Fluids were pumped at a flow rate of 70 ml/min.

![Figure 1](image1.png)

Figure 1. The experimental facility scheme. 1 is the pump, 2 is the cell, 3 are pressure sensors, 4 is the system for constant pressure maintain. Dark blue colour is for acid solution, grey is for mineral oil and blue is for gas phase.

Glass beads mixed with sodium bicarbonate were used as a model of the chemically active porous medium, and a solution of citric acid modelled the oxidizing agent. The porous medium in the cell was saturated with a highly viscous liquid, which is mineral oil. For the flow visualization the acid solution was mixed with ink.

The experiment proceeded as follows. Initially, the cell was filled with a porous medium with a certain mass concentration of sodium bicarbonate. Then, with the pump, the porous medium was saturated with the mineral oil, after which the injection of the acid solution with a given mass concentration began. The solution flowed from top to bottom through the porous medium displacing mineral oil in the cell. The gas that was released during the chemical reaction between the sodium bicarbonate in the porous medium and the acid in the solution also moved in the direction of the solution flow. During the process, readings were taken from pressure sensors. Photo and video recording of the displacement process was performed. The course of the experiment is described in more detail in the work of Zavialov [11].

At certain concentrations of the reaction components, the released gas flowed not in a continuous manner, but in portions at approximately equal time intervals, in the form of waves. The frames of this flow pattern are shown in Figure 2. In each image, arrows indicate a contrast boundary extending in the direction of the acid solution flow (“secondary wave”). Waves appeared at almost equal time intervals and moved noticeably faster than other reaction products. The presence of a periodic process is
confirmed by the measured pressure in the cell (Figure 3). Pressure fluctuations appeared at the same time instants as the fronts of secondary waves.

Figure 2. Photographs of the cell taken during two experiments. The time shift between neighbouring photos is 2 seconds. Acid solution (blue or black because it is coloured with ink) flow vertically downward. The light areas at the bottom of the photo are areas where acid solution has not yet reached and where the porous medium is saturated only with mineral oil.

Figure 3. Readings from pressure sensors during the experiment. The first sensor is at the top of the cell; others are along the vertical with the interval 20 mm. The recording started from the beginning of oil pumping into the cell.
Experiments were carried out with different concentrations of acid in solution and sodium bicarbonate in porous medium. The results obtained are shown in the form of a parametric graph in Figure 4. It can be seen that the area of parameters at which “secondary waves” are observed can be separated by a curve similar to a hyperbola. This curve has a shape that matches with the theoretically predicted one below.

Figure 4. Points corresponding to the experiments performed and experimental curve dividing two flow regimes.

3. Influence of reagent concentrations on the stability of the reaction front

Let us estimate the influence of the reagent concentrations on the formation of self-oscillations. We will consider a simple model in which flow is isothermal, incompressible, and two-phase. The latter assumption means that we neglect the migration of particles of the solid phase, and we also assume that the oil is displaced from the cell by the reaction products at the initial stage of the process, so that the mobility of the remaining oil does not significantly affect the flow of the fluids. The chemical reaction in this process can be described with following equation: $A + B \rightarrow G + C$, where $A$ – acid, $B$ – chemically active component of the skeleton (sodium bicarbonate), $G$ – carbon dioxide, whose solubility is neglected, $C$ – other reaction products. We believe that the flow of fluids obeys Darcy's law, and the rate of a heterogeneous chemical reaction is proportional to the acid concentration, saturation, and effective contact area between acid and sodium bicarbonate. In our approximate model, we assume that the effective contact area is determined by the initial content (volume fraction) $m$ of the solid chemically-active reagent per unit volume of the porous medium and remains constant during the reaction. The one-dimensional case is schematically represented in Fig. 5.

Figure 5. The one-dimensional scheme of the cell. Acid solution flows from left to right, $x_f$ is the reaction zone.

The law of conservation of the mass of the oxidizer in integral form is
\[
\frac{d}{dt} \int_0^L (\varphi Sc) dx + \int_0^L \frac{\partial}{\partial x} (W_A c) dx = -\int_0^L \frac{r}{\rho_A} dx \tag{1}
\]

where \( \varphi \) is porosity of the medium, \( S \) is oxidizer solution saturation, \( c \) is mole fraction of oxidizing agent in the acid solution, \( W_A \) is oxidizer volumetric flow rate, \( r \) is chemical reaction rate, \( \xi_A \) is stoichiometric coefficient of the oxidizing agent in the reaction equation, \( \rho_A \) is molar density of acid solution.

Assuming the reaction region to be rather narrow (in the experiment, the area of gas evolution in the cell was no more than 1 cm in width), we can split the integrals on the left in (1) into integrals within the limits from 0 to \( x_f \) and from \( x_f \) to \( L \) where \( x_f \) is the coordinate of the reaction area. After integrating, we obtain for the rate of change in the amount of oxidant in the reaction zone:

\[
\frac{dn_A}{dt} = (W_A - V_f \varphi_1) c_0 - \xi_A R, \tag{2}
\]

where \( n_A \) is integral amount of acid in the reaction zone per unit cross-sectional area and divided by solution density, \( V_f = dx_f/dt \) is reaction front speed, \( \varphi_1 \) is medium porosity where \( x < x_f \), \( c_0 \) is molar fraction of oxidizing agent in the acid solution before the reaction zone, \( R \) is integral chemical reaction rate.

\( W_A \) can be found with the Darcy law:

\[
W_A = \frac{k_1}{\mu_A} \frac{p_1 - p_f}{x_f} \tag{3}
\]

where \( k_1 \) is absolute permeability of the medium in front of the reaction zone, \( \mu_A \) is oxidizer solution viscosity, \( p_1 \) is cell inlet pressure, \( p_f \) is reaction front pressure.

To find \( p_f \), let’s write down the balance between the components entering \( W_{in} \) and leaving \( W_{out} \) the cell:

\[
W_{out} - W_{in} = \left( -\frac{p_A \xi_A}{\rho_A} - \frac{p_B \xi_B}{\rho_B} + \frac{p_C \xi_C}{\rho_C} + \frac{p_G \xi_G}{\rho_G} \right) R, \tag{4}
\]

where the difference between the incoming (\( W_{in} \equiv W_{out} \)) and outgoing flows is written on the left, and on the right is the generation of the components at the reaction front.

Darcy’s law for the flow leaving the cell under the assumption that the relative phase permeabilities of water and gas beyond the reaction region have a quadratic dependence on gas saturation \( S_G \):

\[
W_{out} = \left( S_G^2 \frac{k_2}{\mu_G} + (1-S_G)^2 \frac{k_2}{\mu_L} \right) \frac{p_f - p_2}{L-x_f}, \tag{5}
\]

where \( k_2 \) is absolute permeability of the medium to after the reaction zone, \( \mu_G \) and \( \mu_L \) are gas and liquid viscosities, \( p_2 \) is cell outlet pressure.

Let’s substitute (5) into (4), express \( p_f \) and substitute this expression in (3). So we obtain for the input flow:

\[
W_A = W(x_f) - N(x_f) R \tag{6}
\]

where the following notations are introduced:

\[
W(x_f) = \frac{k_1 \Delta p}{\mu_A x_f} \left( S_G^2 \frac{k}{\mu_G} + (1-S_G)^2 \frac{k}{\mu_L} \right) \frac{x_f}{L-x_f} + 1
\]

\[
N(x_f) = \left( S_G^2 \frac{k}{\mu_G} + (1-S_G)^2 \frac{k}{\mu_L} \right) \frac{x_f}{L-x_f} + 1
\]
\[ N(x_f) = \frac{-\rho_A \xi_A - \rho_A \xi_B + \rho_A \xi_C + \rho_A \xi_G}{\rho_A \rho_B \rho_C \rho_G} \left( S_G \frac{k}{\mu_G} + (1-S_G) \frac{k}{\mu_L} \right) \frac{x_f}{L-x_f} + 1 \]

\[ \Delta p = p_1 - p_2, \quad \bar{\mu}_G = \frac{\mu_G}{\mu_A}, \quad \bar{\mu}_L = \frac{\mu_L}{\mu_A}, \quad k = \frac{k_2}{k_1} \]

Finally, equation (2) takes the form:

\[
\frac{dn_A}{dt} = W(x)c_0 - \left( \xi_A + \left( N(x) + \frac{\xi_B}{m} \phi_1 \right) c_0 \right) R(t)
\]

where the speed of the reaction front is determined by the rate of consumption of the reducing agent:

\[ V_f = \xi_B \frac{m}{m_c}, \quad \xi_B = \frac{\rho_A}{\rho_B} \xi_B \text{ and } \xi_B \text{ is corresponding stoichiometric factor, } m \text{ is saturation (volume fraction) of the porous medium with the reducing agent.} \]

In the works of Zavialov and Konuykhov [9, 10] it was demonstrated that one of the reasons for the occurrence of self-oscillations is the presence of a reaction delay, i.e. the rate of a chemical reaction at a given time is determined by the concentrations of reducing agent and oxidizing agent at the time moment preceding this one for the time \( \tau_D \). Let us also assume that the reaction rate is proportional to the amount of reacting oxidant. In the paper of De Oliveira [12], which studies the effect of acid on the skeleton, the rate of the chemical reaction is proportional to the average concentration of the acid. The same dependencies are valid for the integral reaction rate and concentration. Then we get:

\[ R(t) = \lambda n_A(t-\tau_D), \quad \lambda = \frac{m^n}{\tau_{react}} \]

\[ \tau_{react} \text{ and } \tau \text{ are the parameters depending on the conditions of the chemical reaction.} \]

Substituting (8) into (7):

\[
\frac{dn_A}{dt} = \alpha(x) - \beta(x)n_A(t-\tau_D),
\]

where the following notations are used

\[ \alpha(x) = W(x)c_0, \]

\[ \beta(x) = \frac{m^n}{\tau_{react}} \left( \xi_A + \left( N(x) + \frac{\xi_B}{m} \phi_1 \right) c_0 \right). \]

\[ n_A(t) = 0, \quad 0 \leq t \leq \tau_D \quad \text{the initial state.} \]

Studying the differential-difference equation (9) for stability gives the following instability condition:

\[ \beta(x)\tau_D > \frac{\pi}{2} \]

Since \( \beta(x) \) is a monotonically decreasing function, the condition for the occurrence of instability when the reaction front periodically moves from the input to the output boundary of the cell has the form

\[ \beta(0)\tau_D > \frac{\pi}{2}. \]

The term \( \xi_B\phi_1c_0 \) is small in comparison with the others and has little effect on the stability mode. So, considering \( \frac{\rho_A}{\rho_G} \gg \frac{\rho_A}{\rho_C} \xi_C, \frac{\rho_A}{\rho_B} \xi_B, \frac{\rho_A}{\rho_A} \xi_A \) we obtain an approximate condition for the transition to the unstable regime:
According to (11), the theoretical function describing the boundary between stable and unstable regimes has the following form $c_0 m^{n}$. Based on the experimental results, we determine the coefficients in (11) $n \approx 0.48$, $\tau_{\text{react}}/\tau_D \approx 80$. It follows from Ошибка! Источник ссылки не найден. that such a theoretical approach is capable of predicting the occurrence of "secondary waves".

4. Conclusion

- On the parametric diagram of reagent concentrations, there is a boundary dividing the parameters at which the considered reacting flow (the flow of an acid solution through a skeleton containing a chemically active component) is stable and the parameters at which self-oscillations arise.
- A simple theoretical model is qualitatively capable of predicting the onset of unstable displacement, and it is the presence of a delay in the gas phase evolution reaction that is the key to the onset of instability.

The results obtained can be helpful in studying acidizing of a well when the composition of the solution is being selected in which the concentrations of the solvent components are very important. Since pressure fluctuations can affect the pumping system and cause difficulties in controlling the reaction front, the concentration of the solvent components should be determined depending on the concentrations of reactive components of the rock.

References

[1] Aljawad M. S. et al. Integration of field, laboratory, and modeling aspects of acid fracturing: A comprehensive review //Journal of Petroleum Science and Engineering. – 2019. – V. 181. – P. 106158. https://doi.org/10.1016/j.petrol.2019.06.022

[2] Mahmoodi A., Javadi A., Sola B. S. Porous media acidizing simulation: New two-phase two-scale continuum modeling approach //Journal of Petroleum Science and Engineering. – 2018. – V. 166. – P. 679-692. https://doi.org/10.1016/j.petrol.2018.03.072

[3] Leong V. H., Mahmud H. B. A preliminary screening and characterization of suitable acids for sandstone matrix acidizing technique: a comprehensive review //Journal of Petroleum Exploration and Production Technology. – 2019. – V. 9. – N. 1. – P. 753-778.

[4] Bityurin V.A., Velikodnyi V.Yu., Tolkunov B.N., Bykov A.A., Dyrenkov A.V., Popov V.V. Experimental study of the ignition of liquid hydrocarbon fuels and stabilization of their combustion by an arc discharge //Plasma physics reports. 2012. V. 38. N. 13. P. 1073-1077.

[5] Krikunova A. I. Effects of Gravity on Plane-Symmetric Rod-Stabilized Flame Stabilization //High Temperature. – 2019. – P. 1-8.

[6] Jurak M. et al. Nonisothermal immiscible compressible thermodynamically consistent two-phase flow in porous media //Comptes Rendus Mecanique. – 2019. – V. 347. – N. 12. – P. 920-929.

[7] Rana C., De Wit A. Reaction-driven oscillating viscous fingering //Chaos: An Interdisciplinary Journal of Nonlinear Science. – 2019. – T. 29. – N. 4. – P. 043115.

[8] Nevezhitskiy Y. Development of Models for Filtration Simulation in Nonlinear Media //SPE Annual Technical Conference and Exhibition. –Society of Petroleum Engineers, 2018.

[9] Zavialov I.N., Konyukhov A.V., Plavnik R.A., Plyashkov E.V. Laboratory study of oscillatory multiphase flow in porous medium with chemically active skeleton //Physica Scripta. – 2019. https://dx.doi.org/10.1088/1402-4896/aafdf5c

[10] Konyukhov A.V., Zavialov I.N. Numerical investigation of oscillatory multiphase flow in porous medium with chemically active skeleton //Journal of Physics: Conference Series. IOP Publishing. – 2016. – T. 774. – N.1. – P. 012059.

[11] Zavialov I., Varov A., Salikhov R., Antsiferov E., Konyukhov A. Laboratory modeling of flow with gas-producing reaction in porous media //Journal of Porous Media. – 2018. – V. 21. – N.
10. – P. 887-893. https://www.doi.org/10.1615/JPorMedia.2018018942

[12] De Oliveira T.J.L., De Melo A.R., Oliveira J.A.A., Pereira A.Z. Numerical Simulation of the Acidizing Process and PVBT Extraction Methodology Including Porosity/Permeability and Mineralogy Heterogeneity //SPE International Symposium and Exhibition on Formation Damage Control. – Society of Petroleum Engineers. 2012.