Code for calculating wave technology of thermal-gas-chemical formation treatment for oil recovery enhancement

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Abstract. Transition to the development of hard-to-recover hydrocarbons, including in regions the far north, is fraught with difficulties in using classical technologies development. This is due to the low porosity and permeability of the reservoirs, high viscosity of the formation fluid and the manifestation of abnormal (non-Newton) properties of hydrocarbon fluids. In this regard, for more than ten years, pilot field research (FPI) in terms of the selection and optimization of technologies for collectors of complex structures. Since 2011, at the departments of the underground hydromechanics of Gubkin Russian State University of Oil and Gas (NRU) and gas wave dynamics of the Lomonosov Moscow State University, research is underway on the use of thermogas-chemical method with an injection of a binary mixture to stimulate the inflow. Since 2011, several settlement codes of different levels were created, which allowed carrying out support (pilot) in various fields. Based software products managed to evaluate the characteristics in the chemical reaction zone decomposition of the working chemical composition, evaluate safe regimes, excluding damage to the wellbore and assess the prolongation of the effect. Published more than 20 works (including patents) with the participation of the authors. Since 2019 the mathematical model is significantly complicated: the multiphase and non-isothermality of the process, non-uniformity of the flow. Currently established generalizing code, in the mathematical model of which is additionally taken into account different compressibility of phases and rheological properties of fluids, which allows more fine-tune the computational code for the type of a specific field, taking into account its geological features and damage to the bottomhole zone in the previous stages of development.

1. Introduction
To select the most effective technology for the new fields’ development and oil recovery enhancement at the fields in the late stage of development, a deep analysis of the effectiveness of the chosen technology is necessary. In the conditions of transition to the development of high-viscosity oil reserves from low-permeable reservoirs, including the complicated Arctic conditions of continental and offshore fields, the approach combining thermal and chemical methods (TCM) is considered as the most effective. Traditional thermal technologies, as a rule, are based on the application of downhole heaters of various types or injection of heated filtrates (liquid/steam) into the reservoir. But both methods, due to the high degree of energy absorption by the porous mineral matrix, allow to increase the temperature only in a narrow near well-bore area. The application of thermal impact along with multiple hydraulic fracturing (fracking) partially improves the performance, especially for horizontal wells, but the duration of a significant increase in oil production is low and requires a cyclic

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repetition of hydraulic fracturing operations with coolant injection. Methods of heat generation set-up directly in the reservoir can be considered more economically and energetically justified. As a rule, the varieties of technologies of intra-layer combustion (oxidation) are considered, however, such technological modes, firstly, lead to the burning of part of the reservoir hydrocarbons, and secondly, are poorly controlled. Technologies of chemical exposure with injection of chemically active compounds directly into the reservoir are mainly limited to the use of surfactants and acidic compositions. The varieties of these operations are limited by the type of collector (terrigenous or carbonate) and reduce the filtration resistance directly only in the injection zone. Therefore, the search for technologies that allow to warm up the well drainage zone and get a prolonged effect is an urgent task.

In this regard, many petroleum companies are interested in development of complex formations’ treatment methods, combining chemical and thermal treatment with possible controlled and safe thermal process directly in the formation which has specified characteristics of increasing pressures and temperatures. The idea of pumping of mixtures into the reservoir in order to set up an exothermic chemical reaction in the bottom-hole zone was proposed more than twenty years ago, but this technology has been modified and updated recently and has been in the stage of extensive pilot tests in recent years [1, 2, 3]. Currently, the technology has successfully shown its effectiveness in many fields [4].

The essence of the technological scheme is the injection of an aqueous binary mixture (BM) of ammonium nitrate (NH₄NO₃) and sodium nitrite (NaNO₂), into the reservoir, the presence of which allows to complete the decomposition of saltpeter in full, with the sequential supply of specified volumes of displacement fluids to organize an exothermic decomposition reaction at a safe distance from the wellbore [5, 6]. The controllability of the process is ensured by changing the concentration of BM and the sequential supply of the calculated volumes of activators/retarders of the reaction of displacement liquids, acid compositions [2]. Mathematical modeling makes it possible to predict the distance of the reaction zone from the wellbore, the level of pressures and temperatures, and the prolongation of reactions even before conducting pilot tests [7]. In addition, the effectiveness of the pilot tests significantly depends on the state of the reservoir (water content, gas saturation, damage, the composition of the mineral matrix and other factors), so the analysis of the results after the pilot tests is also a necessary stage of supporting the field experiment.

2. Scope of the developed program
Since 2011, the authors of this paper, in cooperation with Lomonosov Moscow State University and Tyumen State University, have created several calculation codes of various levels, which have been successfully used to analyze the technology [7, 8, 9]. In the past two years, the depth case study of the mathematical model has increased significantly. In particular, the complex hydropercolation model created [10] made it possible to track the change in the microstructure of the porous matrix under the influence of chemically active substances. Currently, the approach has been refined considering the possibility of a gas-liquid emulsification, the appearance of which was observed in practice due to the release of reaction gases during the decomposition of BM. To consider this phenomenon, the analysis of the influence of phase mobility changes is required as well as an analysis of the influence of hot gases allocation which are released during the decomposition reaction from the point of view of heat exchange with a fluid-saturated porous medium. The success of the pilots with the injection of BM can be explained with these two factors and the prolongation of the effect at some fields that significantly exceed the duration of the fracture treatment effect. Considering the gas phase as a component of the liquid phase and its precipitation into a separate phase, as well as the emulsification and a change in the nature of the filtration process, the mathematical model required an update and expanding the capabilities of the calculation code. This paper presents the results of calculations of the BM decomposition reaction considering the nonequilibrium of the thermal reactions in the bottom hole zone and the energy accumulation by the mineral matrix.
The modified calculation code is based on the model of interpenetrating continuums [11] in the application to the so-called inertia-free flows, which includes phase masses conservation differential laws, generalized filtration laws and equations of internal energy of phases. In the extension of the model [7] the compressibility of all phases (oil and aqueous solution, gaseous reaction products and elastic skeleton) is considered, for which two-parameter equations of state for pressure and internal energy for each of the phases are applied [12, 13, 14]. In addition, the feature of filtration in porous media (especially in low-permeable rocks) is the non-Newtonian properties demonstration even of those filtrates which are characterized by the linear nature of the dependence of viscous stresses on the shearing rate recorded on a rotary viscometer. While moving in a porous medium, a necessary condition for the beginning of movement is that the pressure gradient reaches a certain limit value [15]. This is especially important while moving gas-liquid systems, when it is also necessary to reach the limit value for bypassed oil reduction [16]. Therefore, when calculating the decomposition of BM from the release of gaseous nitrogen, it is necessary to use filtration equations with a limiting gradient. Thus, the generalized system of equations for describing the problem of decomposition of BM in the formation exists as follows:

\[
\frac{\partial \rho_i}{\partial t} + \text{div}(\rho_i \vec{v}_i) = \sum_j j_{ji}, \tag{1}
\]

\[
\frac{\partial (\rho_i)_{(k)}}{\partial t} + \text{div}(\rho_i \vec{v}_i) = \sum_j j_{ji(k)}, \tag{2}
\]

\[
\begin{cases}
\rho_i^{(n)} = -\frac{k_i^{(n)}}{\mu} (\delta^{(j)} - \frac{\delta^{(g)}}{\text{grad} p}) \frac{\partial p}{\partial x^{(i)}}, & \text{if } |\text{grad } p| > G_i^{(g)} n_i n_i, \text{ for } i=1,2,3 \\
w_i^{(n)} = 0, & \text{if } |\text{grad } p| \leq G_i^{(g)} n_i n_i,
\end{cases}
\]

\[
\begin{pmatrix}
\sum_k \frac{\partial \rho_i^{(k)}}{\partial t} + \text{div}(\rho_i \vec{v}_i U_i) = \sum_k \frac{\alpha_i \rho_i^{(k)}}{\rho_i^{(k)}} \frac{\partial \rho_i^{(k)}}{\partial t} - \sum_k (\text{div}(\lambda_i \text{grad } T_i) - Q_4 + Q), \\
\frac{\partial}{\partial t} \left( (1 - m) \rho_4^{(4)} U_4 \right) = \text{div}(\lambda_4 \text{grad } T_4) + Q_4
\end{pmatrix}
\]

where \(i\)-phase number (1-BM aqueous solution, 2-oil, 3-gas, 4-matrix; \(\rho_i = \alpha_i \rho_i^0\) - medium (shown) density phase, which is defined with true density phase \(\rho_i^0\) and its volume fraction \(\alpha_i\), considering the porosity \(m\) and pore saturation with three mobile phases \(S_i\) (water, oil and gas considering that BM and reaction salts are completely soluble): \(\rho_1 = \alpha_1 \rho_1^0 = m S_1 \rho_1^0\), \(\rho_2 = \alpha_2 \rho_2^0 = m S_2 \rho_2^0\), \(\rho_3 = \alpha_3 \rho_3^0 = m S_3 \rho_3^0\), \(\rho_4 = \alpha_4 \rho_4^0 = (1 - m) \rho_4^0\), \(\sum \alpha_i = 1\).

In (1) and (2) \(j_{ji}\) - the intensity of mass exchange between \(j\) and \(i\) phases (in this case, only the values \(j_{13} = -j_{31}\), will be non-zero and which determine the intensity of the release/absorption of the reaction gas) and are related to the intensity of the mass change of each of the components \(j_{ji(k)}\) (in total, the mass flows must be balanced, since the sum of the continuity equations of the components within the phases will give the equation for the entire phase). Only an aqueous solution is considered as multicomponent \(-\), it is "pure" water and BM before the reaction, and as the reaction proceeds, the components of the reaction products are added, followed by the release of free gas: \(\rho_{1(k)} = \rho_1 c_1(k) = m S_1 \rho_1^0 c_1(k)\) - average (reduced) density of k-component in i-phase \(c_1(k) = \rho_{1(k)}/\rho_1\) - mass concentration of k-component in aqueous solution \((k=1-<\text{pure}\text{> water, 2-BM, 3- reaction salts, 4- dissolved gas})\). For the water phase at all \(\sum_k c_1(k) = 1\), \(\sum_k \rho_{1(k)} = \rho_1\). Equations (1) reflect the change in the specific mass of the phases. Equations (2) the change in the component composition of the water phase is described. The convective terms in equations (1) and (2) are written in terms of the true phase motion velocities \(\vec{v}_i\), related to the filtration rates of mobile phases (1-water, 2-oil, 3-gas):
\[ \bar{w}_i = \bar{w}_i' = S_i m \bar{v}_i'. \] In the model, the diffusion velocities of the components inside the phases are neglected. The pressures in the filtering phases are considered the same (p_1 = p_2 = p_3 = p).

Equations (3) define generalized laws of joint phase filtration in the general case of filtration motion in an anisotropic porous medium characterized by phase permeability tensors \( k_{i}^{(n)} \) considering the limit gradient tensors \( G_i^{(l)} \), which could vary for each phase [17]. When considering media when the absolute permeabilities differ in the lateral and perpendicular planes, it is possible to describe the motion of the symmetry in the lateral area and then the tensors \( k_{i}^{(n)} \) and \( G_i^{(l)} \) will have only a pair of non-zero components, which are determined from experiments on core samples. If the processes are considered in a stationary filtration mode, then equations (3) degenerate into linear generalized multiphase filtration equations with different absolute permeability coefficients in the corresponding direction, considering the relative phase permeabilities.

The last block of differential equations (4) is written as the sum of the equations of the internal energies of the mobile phases (the sum of the equations of the internal energies of water, oil and gas), considering the condition of thermodynamic equilibrium in a mixture of mobile phases \( (T_1 = T_2 = T_3 = T) \) and considering the exothermic reaction heat release and the exchange of heat with a porous medium characterized by temperature \( T \). The system is supplemented with two-parameter equations of state for the pressure and internal energy of the phases [12-14] (in a simplified formulation, it can be assumed that water, oil and the skeleton are incompressible, and the internal energies of these phases are determined only by the thermal component \( c_v i T \).

Chemical reactions and changes in the component composition are considered by changing the volume concentrations of the phases by introducing into the right part of the phase mass conservation equations terms that set the intensity of reactions (determined by semi-empirical formulas while adapting the model to the results of laboratory experiments [6]) and mass equations for mass concentrations of phases. Considering the accordance with the pilot tests protocol, the BM components are injected through separate channels and mixed directly at the bottom, as well as the application of special reaction retarders [2] so it could be assumed that that the reaction begins immediately when the BM solution enters the reservoir with the reaction acceleration over time:

\[ J_{13} = -f(c) e^{t-t_0} \]  

The empirical function of the intensity of the BM mass change per unit volume of a saturated porous medium \( f(c) \) in accordance with the experiment depends on the concentration of BM in an aqueous solution \( c \) and the catalytic activity of the reaction activator and the activator used. As the experiment [6] showed, the induction time \( \Delta t \) is from 15 to 40 minutes from the beginning of the reaction to its explosive acceleration according to the exponential law.

During the decomposition of BM, the reaction products are water-soluble sodium salt, free water, nitrogen gases, and a heat of 300 kJ/mol is released, which is reflected in (5):

\[ \text{NH}_4\text{NO}_3 + \text{NaNO}_2 \rightarrow \text{N}_2 + \text{NaNO}_3 + 2 \text{H}_2\text{O} + 300 \text{ kJ/mol} \]  

During the reaction, nitrogen is released into the water, and remains dissolved in water until the maximum nitrogen concentration is reached. As known, nitrogen is poorly soluble both in water and in oil: laboratory studies of nitrogen pumping through an oil-saturated core show that it does not mix with oil [18]. This fact is applied to practice [19], since nitrogen does not worsen the oil relative permeability (unlike air relative permeability), it is allowed to effectively displace "whole" oil, reduces the saturation pressure of oil, so it helps to increase the efficiency of the displacement process. Therefore, assuming while calculating, that the initial stage of nitrogen release will be its concentration is low, it is represented as a component of an aqueous solution and is described by a separate equation for the mass concentration, and with an increase in the mass concentration of nitrogen above a certain limit value, nitrogen is released as a free gas (at normal temperature, the maximum mass concentration is about 0.035 and decreases with increasing temperature). It is also assumed with calculation, that the characteristic time of complete nitrogen release is about two
minutes after the beginning of the reaction. In addition, the presence of a solubility hysteresis is considered: if the proportion of nitrogen in the mixture falls below the limit level, then it is considered as completely dissolved in water in a characteristic time of about 20 minutes. Also, for the heat exchange of hot reaction products and the soil, the induction temperature relaxation time (establishment of the equilibrium temperature of the skeleton-filtrate) is assumed as of about three minutes. Therefore, for the intensity of heat exchange with the skeleton, the formula will be similar to (3).

Systems of type (1) for a multiphase mixture, as a rule, are hyperbolic, and the Cauchy problem is correct, in the case when not all velocities coincide. An explicit, implicit or semi-implicit numerical scheme can be used to solve the initial boundary value problem. In this case, the last scheme is selected, when the pressures and velocities on the new time layer are selected from the same layer, and for the remaining values from the previous time layer.

For a two-dimensional flow, the system of equations is solved by the iterative method. Fig.1 shows the diagram of the calculated area: an extended horizontal well of radius \( r_c \), the length of the horizontal section is much greater than the thickness of the reservoir \( h \) and the drainage radius \( R_K \) \(( L >> h, R_K \)) and it is covered with an uneven grid thickening in the direction of the well, as shown in Fig.1 (the axis of the well is perpendicular to the plane of the figure). On the upper quarter of the calculated area, the non-flow condition is realized, the vertical and horizontal boundaries are the axes of symmetry, on the remote boundary indicated by the drainage radius, it is assumed that the stationary state with the initial reservoir parameters is fulfilled.

![Figure 1. The diagram of the calculated area and grid](image-url)

3. Calculation results
The calculation model of the development of the process of changing pressures and temperatures around a horizontal well drilled into a layer 1 meter thick, isolated from other interlayers (for example, a clay impermeable layer) was carried out. The considered layer is characterized by different values of permeability in the lateral plane (here the horizontal axis) and vertical permeability significantly lower than the lateral \( k_y \ll k_x \) (calculations were carried out for \( k_x =35\div50 \text{ mD} \) \( k_y =0.05\div0.5\text{mD} \)) with a slight change in porosity \( m=0.2 \) (the numerical code allows us to steadily calculate the process for any type of collector anisotropy). It was assumed that the reservoir was initially filled with oil and water with an initial water saturation of 10% at reservoir pressure values \( P= 123 \text{ bar} \) and temperature \( T= 320 \text{ K} \). Further, in accordance with the pilot tests protocol [2,4] approximately 10,000 seconds (i.e. more than 3 hours) at an excess pressure of 13 bar, water with 50% ammonium nitrate and a reaction activator was pumped into the reservoir, then pure (displacement) water was pumped for another 3000
seconds. According to the technological scheme, the BM components are pumped through separate channels and mixing occurs directly at the bottom with pumping into the formation, due to which the BM decomposition reaction occurs already in the formation. The application of a reaction activator allows to control the process of reaction development, so from the moment the BM is injected into the reservoir, a chemical reaction begins with a relaxation time (the time of the complete end of the reaction) as of 1 hour. The completion of the process is controlled by the completion of the release of reaction gases. The calculation of the redistribution of all parameters in the two-dimensional region was carried out) 0.5 m × 5 m (a quarter of the drainage area) for the control period of the pilot tests (about 13000sec≈3.6 hours). In the field experiment, pressure and temperature taken at this time interval from sensors located near the bottom hole zone.

The following values of physical quantities are used for the calculation.

![Figure 2](image)

**Figure 2.** Dependence of temperature depending on the distance from the center of the well at the moment of time 50 min.

Fig. 2 shows the temperature profiles in the reservoir after the completion of the BM decomposition reaction without taking into account the convective heat transfer beyond the reaction zone, the size of which is determined by the volume of injection of an aqueous solution of a binary mixture/ These results represent a model calculation of the temperature field around the well under the assumption that the reaction begins instantly when the active solution components are supplied to the bottomhole zone of the well. Injection of the BM solution components through separate channels and mixing of the components directly in the formation with the development of the reaction even before the injection of the displacement fluid: the reaction is completed in about 50 minutes, which corresponds to physical experiments, and the temperature reaches 390°C directly at the well. The maximum temperatures develop on the horizontal plane, (the plane of the axis of the horizontal well). The effect is minimal on the plane perpendicular to the borehole axis, which is associated with cooling due to the rocks surrounding the saturated formation. In practice, in order to reduce the heat load on the well, the binary mixture is fed in portions with clean water rims.

4. **Conclusions**

The paper demonstrates that the modification of the mathematical models previously used by the authors makes it possible to consider in more detail the processes occurring in the reaction zone, taking into account the presence of gas in a free form and the formation of a gas-liquid emulsion, which significantly changes the nature of the influence of the decomposition products of the active component and leads in practice to a change not only in the temperature field in the drainage zone of
the well, but also changes the nature of oil mobility, due to the improvement of the displacement characteristics by a water-gas emulsion, including due to an increase in pressure during the release of reaction gases with pressure gradients exceeding the limit values for the shear of oil "pillars". These two circumstances (thermal and hydrodynamic) explain the success of the binary mixture injection method for various fields in the period of active development or the stage of oil production decline, and may be promising in terms of their application in the regions of the Far North, where thermal technologies are preferred.

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