SAFETY IN APPLYING BINARY MIXTURES FOR OIL PRODUCTION STIMULATION

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Abstract. The article considers theoretically, on a qualitative level, the rates of filtration and decomposition of ammonium nitrate, depending on the time of heat release and on the rate of nitrate entry into the porous space of the reservoir near the perforations. It is assumed that field tests at different rates of nitrate solution injection into the well will yield quantitative data on filtration, heat transfer and kinetics of heat release in the reservoir. To estimate the temperature increase in the reservoir under the action of the binary mixture reaction (nitrate + oxidant), the temperature was calculated when the nitrate was decomposed in an aqueous solution (300 g of water per 1 kg of nitrate), taking into account the oxidation of a small fraction of oil in the reservoir near the well with oxygen released during the decomposition of nitrate.

Keywords: oil production, binary mixtures, nitrate, explosive safety, skin layer
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Introduction

The binary mixture (BM) is ammonium nitrate (AN) and the initiator of its exothermic decomposition (ID), whose aqueous solutions are pumped into the bottomhole zone of the treated well in order to increase oil recovery by heating and removing the "skin layer" responsible for the shortage from the depths of about half of the explored reserves. Aqueous solutions of AN and ID are pumped into the well through separate channels, and they react in the zone of the productive formation, releasing hot gases whose mass is equal to the mass of the nitrate pumped into the well. Hot gases are released into the reservoir under the pressure created by the reaction. Explosion safety in (Aleksandrov et al., 2016) was achieved by adjusting the reaction process of the BM in the well in order to keep the temperature in the reaction zone below 320 °C. T = 320 °C is the lower limit of temperature, after which an explosion of small portions (1-5 cm^3) of a working solution of ammonium nitrate (AN 67%, water 33%) was recorded on the stand.

Cases of nitrate explosions in operated oil wells in order to stimulate oil production with the help of BM cannot be found in the available literature. To confirm the safety of the AN used to enhance the oil recovery of oil reservoirs, a justification based on the modern theory of explosive processes and on the experiment performed at the stand and/or in the wells is needed. The selection of reagents and the creation of conditions are the basic factors, in which, during the course of the BM reaction, the released heat is mainly absorbed by non-nitrate molecules, as it is during the explosive reaction in the well, with the reservoir rocks and water whose share in the reservoir oil-containing fluid of hard-to-recover reserves is usually close to 0.9; and in non-recoverable reserves the share of water is close to 99.99 (Aleksandrov et al., 2016; Kuznetsov, 2016).

The impact of the BM on the processes in the reservoir depends on the temperature of the medium and on the rate of introduction of reagents into the porous space of the oil reservoir near the perforations. The rates of filtration and nitrate decomposition are theoretically investigated in the present paper, depending on the time of heat release and on the rate of AN entry into the porous space, which is on the average 20-40% of the volume of the reservoir near the perforations. To estimate the increase in temperature in the reservoir under the reaction BM (AN + ID), the temperature at the nitrate decomposition in the aqueous solution (300 g of water per 1 kg of nitrate) was calculated taking into account the oxidation of a small fraction of oil in the reservoir near the well with the oxygen released during the nitrate decomposition.

The article consists of three sections. In the first two sections, the modes of fast and slow injection of BM solutions into the formation near the well are considered. The third section shows the results of calculating the temperature, which is established in a closed volume of the porous space, reservoir filled with an aqueous solution of nitrate, which, as a result of its decomposition and partial (0.01-0.03) oxidation of oil contained in the formation fluid water + oil, warms up the bottomhole zone, contributing to the complete removal of the skin layer that blocks oil access to producing wells

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(Aleksandrov et al., 2016; Aleksandrov, Aleksandrov, Kuznetsov, etc., 2013). It should be noted that in the experiments at the wells only the rapid introduction of reagents into the formation has been studied.

I. Fast input mode of 10-20 tons of BM in the reservoir (within 1 hour)

In this case, according to practice, a comparatively small amount of hot steam or a BM heated with special additives accelerating the decomposition of nitrate in the BM reaction is first introduced into the reservoir. As a result, a relatively thin hot layer is created near the perforations in the reservoir. Then a cold BM is introduced under a pressure of hundreds of atmospheres. The cold BM leaves the perforations in the form of jets and, before it has heated up in a thin hot layer near the perforations, penetrates through it into the cold porous rock, displacing oil and water from the pores in the bottomhole zone.

By the time of injection completion in the bottomhole zone of 2-3 tens of tons of BM into the reservoir, there is a layer of rock of approximately cylindrical shape, filled in the pores with a solution of nitrate. We call it layer 1. For porosity ¼, the volume (V) of this layer is four times larger than the volume (V_p) of the introduced solution of nitrate. The radius of the cylinder (that is, the thickness of layer 1) is expressed by the formula:

$r = (V_p/\pi L)^{1/2}$,

where L is the length of the perforated part of the tube. Hence, at $V_p = 80$ m^3 and L = 4 m, r = 2.52 m. The actual boundary of the layer 1 filled with the BM solution will be blurred according to the filtration law, forming a transient sublayer of thickness ~ 1 m, in which the filling of the pores with the solution of injected reagents changes from ~ 100% to almost zero. According to the experimental data, with a rapid injection of a large portion of the BM aqueous solution (tens of m^3) into the well for an hour to 2 hours, the heat release in the reservoir lasted from day to 4 days (Kuznetsov, 2016), i.e. two orders of magnitude longer than the BM input time.

When an inhomogeneous jet stream passes through a thin layer near the perforations, as experience has shown, small regions with a high temperature remain (Aleksandrov et al., 2016). According to the theory (Kuznetsov, 2016), heat is then transferred to a rock containing a fixed solution when the BM injection to the well is stopped. When it is heated due to the heat of the BM reaction and the oxidation of oil, a heat wave is formed by the liberated oxygen (Kuznetsov, 2016). Let us note that the same state of the reservoir can be obtained by creating a hot layer near the perforations before injecting the entire volume of the cold BM in the reservoir, and after such input.

The heat wave is analogous to the combustion wave. Like laminar combustion, it moves slowly through the substance. To propagate into the detonation wave, the propagation of combustion must be accelerated. For this, combustion must become turbulent. But with the propagation of combustion in the pores, its turbulence is impossible due to friction and, accordingly, small Reynolds numbers (Landau, Lifshitz, 1986). Therefore, the possibility of detonation in the case under consideration should be excluded.

II. The slow input mode (for 10-20 hours) of 20-30 tons of BM aqueous solution into the reservoir. Injection of BM solutions into the porous space of the reservoir

This case has not yet been fully implemented in practice, but its implementation in different versions would be useful for obtaining quantitative experimental data on the kinetics of heat release in the reservoir. When analyzing the motion of the BM and the heat in the reservoir, we use the analogy between the processes when the BM is injected into the well and into the reservoir and when natural gas components are used in the gas burner. Gas leaving the burner in a closed air space without ignition, eventually forms a mixture with air, which can explode, for example, when lighting a match or a spark in an electrical appliance. However, when the burner is running, only the products of gas combustion enter the surrounding space, and the possibility of an explosion is thereby excluded. Similarly, nitrate in the reservoir can not explode if it decomposes in the reservoir near the perforations. This condition can be satisfied if the BM is injected slowly enough. In this case, the proofs of explosion safety given in the first section become superfluous.

The dependence of the nitrate volume (y) the reservoir on time (t) is described by the equation:

$$dy/dt = J - y/\tau, \quad (1)$$

where J is the injection rate of nitrate into the reservoir, and τ is the decomposition time of nitrate upon interaction with the second component of the BM.

The solution of equation (1) is expressed as:

$$y = \exp\left(-\int_0^t dt/\tau\right)\int_0^t \exp\left(\int_0^z dz/\tau\right) J dz. \quad (2)$$

For variables J and τ (depending on time), equation (2) is solved only numerically. If J and τ are constant, then the integrals in (2) are taken and

$$y = J\tau\,[1 - \exp(-t/\tau)]. \quad (3)$$

From here

$$y = J\tau \text{ at } t/\tau >> 1. \quad (4)$$

This intermediate asymptotic with an accuracy of 5% occurs even at $t/\tau = 3$. The amount of decomposed nitrate (Y) in the asymptotic form (4) is:

$$Y = J(t - \tau) \approx Jt >> y. \quad (5)$$

The yield to the intermediate asymptotic (4) is obtained in the approximation of a constant value of τ. But in time (4), according to (5), the large amount of nitrate (in comparison with y) will be decomposed, and a lot of heat will be released, respectively. This will lead to a rise of temperature in the reservoir near the perforations and to a decrease in the time τ by an order of magnitude or more. Accordingly, an intermediate asymptotic with a constant value of τ is not reached and to compute y it is necessary to know the dependence of τ on time and solve equation (1) or integrals in (2) numerically. The function $\tau(t)$ can be found as the solution of the inverse task from the experimental data of the supposed practical implementation of the slow introduction of the BM.

III. Calculation of temperature

To determine the temperature that can be achieved in the reservoir under the action of BM (with ammonium nitrate), we present the temperature calculation for the decomposition of nitrate in an aqueous solution (300 g of water per 1 kg of nitrate) filling the porous rock, and oxidation of oil with oxygen released during the nitrate decomposition in the reaction:

$$NH_4NO_3 \rightarrow N_2 + 2H_2O + 1/2O_2 + Q_1. \quad (I)$$

Q_1 = 2600 kJ/(kg of nitrate) (Andreev, Belyaev, 1960).

In the oxidation of oil in reactions:

$$\mathbf{1/3}C_nH_{2n+2} + 1/2O_2 \rightarrow 1/3(C_{n-1}H_{2n} + CO_2 + H_2O) + Q_2, \quad (II)$$

the heat Q_2 = 2380 kJ/(kg of nitrate) is released. The temperature is calculated for the isochoric process. The energy of the reaction products (I) was calculated in the ideal gas approximation. The energy of translational, rotational, and vibrational degrees of freedom of molecules was taken into account. The desired temperature for the release of heat Q_1+Q_2 is determined by the transcendental equation of energy balance:

$$E_п + E_в + E_к + E_{исп} + E_{1п} = Q_1 + Q_2, \quad (III)$$

where $E_п$, $E_в$, $E_к$, $E_{исп}$ и $E_{1п}$ – are the increments in the energy of translational and rotational motion of molecules, the energy of intramolecular vibrations, the heat of evaporation of water, and the increment in thermal energy of the solid rock, respectively. All these terms, like Q_1+Q_2, are attributed to 1 kg of nitrate. From one mole of nitrate in the reactions (I) and (II), 1 mole of N_2, 8/3 mole of water, and 1/3 mole of CO_2 are formed. In addition, the products will remain from an aqueous solution of nitrate containing 30% by weight of water, and another 1.2 moles of water. Total in products will be 8/3 + 1.2 ≈ 3.9 moles of water. To recalculate from one mole of nitrate to one kilogram, the above amounts of moles are multiplied by 12.5. The characteristic temperatures of intramolecular vibrations of molecules necessary for calculating E_k are: for nitrogen, 3300 K; for water – 5260 K, 5400K, 2295K; for carbon dioxide – 1995 K, 3380 K, 960 K, 960K (Kratkii spravochnik fiziko-khimicheskikh velichin ..., 1957). The heat of evaporation of water at normal temperature (273 K) is 600 kcal/g ≈ 2.51 kJ/g.

It is believed that the pore volume in the rock is four times smaller than the rock volume along with the pores and is three times less than the volume of the porous rock minus the pore volume. The rock density and density of nitrate are taken equal to 1.3 g/cm^3 and 1.735 g/cm^3. The average heat capacity of the rock in the temperature range 273-1273 K is about 1.1 kJ/(kg K) (Kratkii spravochnik fiziko-khimicheskikh velichin ..., 1957; Spravochnik. Fizicheskie velichiny ..., 1991). Equation (III), taking into account the above data, was solved by the iteration method. The temperature increment was found to be 366 K. In this case:

$$T = 366 + T_1, \quad (IV)$$

where T_1 is the initial temperature of the reservoir, depending on the depth of occurrence of the oil-bearing rock. At a depth of 1 km, for example, $T_1 \approx 300$ K. Here it follows from (11): T = 670 K.

After the rock has been heated, the introduction of new portions of the nitrate solution into the reservoir will lead to an additional increase in temperature. The mechanism for raising the temperature is similar to what happens to the temperature of water that filled the glass when a stream of hotter water flows into it, and the excess water pours out.

Conclusions

1. The ratio of the characteristic filtration times of the BM in the porous rock of the reservoir and the heat release during the nitrate decomposition essentially depends on the rate of introduction of the BM into the well.

2. The initiation process of the BM must be controlled so that the exothermic decomposition of the nitrate occurs mainly in the reservoir, and not in the well. The ability to control the reaction process of the BM was thus discovered in the work (Aleksandrov et al., 2016).

3. The use of the BM for the stimulation of oil production is safe at any rate of its introduction into the reservoir, if paragraph 2 is fulfilled.

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