Article

Study of Chemical Additives for Optimization of Binary Systems Used for Downhole Thermochemical Treatment of Heavy Oil

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Abstract: Currently, most explored oil fields in Russia are at a late stage of development, and in order to maintain high levels of oil production, it is rational to put into operation fields with hard-to-recover reserves. For complicated oil fields, in particular fields with high-viscosity oil, the known traditional methods of development are ineffective. Therefore, the search for new technologies for the development and operation of such fields to significantly increase oil recovery and intensify production is of fundamental importance. One such method of heat treatment of the bottomhole formation zone is the use of heat and gas generating systems on site. In this work, new results were obtained on physical modeling of thermochemical reaction initiation with delayed-action catalyst (2,2-bis(hydroxymethyl)butanoic acid) filtration tests on composite core models of sandstone and carbonate with foam heat generation and initiating additives of binary type. Using hydrodynamic modelling, the results of laboratory studies were reproduced, and the preliminary efficiency of the developed technology for thermochemical treatment of deposits in the Samara region (Russia) was evaluated.

Keywords: exothermic reaction; thermochemical flooding; reaction initiators; heavy oil; binary systems; hydrodynamic modeling; EOR
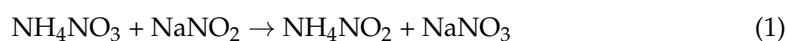
1. Introduction

It is well known that conventional heavy high-viscosity oil has rich reserves in most mature fields and a low recovery efficiency [1]. Initially, oil production is carried out using the natural driving force of the reservoir (primary production), and it is then possible to use other sources of energy in the reservoir (secondary oil recovery/waterflooding). In this regard, in order to increase the oil recovery of the residual oil remaining in mature hydrocarbon reservoirs in the future, tertiary methods need to be used [2–4]. Experience throughout the world has shown that the most common and effective methods for recovering heavy and extra heavy oil are thermal methods [5] and their various modifications [6,7].

In conventional steam-injected production methods, steam is injected from the surface to transfer the thermal energy of the reservoir oil in order to reduce its viscosity and thereby provide the driving force to mobilize the heated oil to the production wells. The main disadvantages of this technology are the high cost of steam production, greenhouse gas emissions, and rapid watering of the reservoir [8,9]. However, a more refined technology

using a heat generation system by injecting thermochemical fluids is also relevant [10,11]. The heat-generating system directs a large amount of heat as a result of its reaction in the reservoir, and this can increase the temperature and the fluidity of the oil in the reservoir, while the reaction products usually have no effect on the field under development [12].

Gas/heat generation technology is a thermochemical method that causes a huge amount of heat and inert gas resulting from the reaction (see Equations (1) and (2) as example) between two inorganic salts—ammonium chloride/nitrate and sodium/potassium nitrite—under the action of special initiating additives, which can be acids, formaldehydes, and others active catalysts that initiate a violent reaction when a certain temperature is reached [13–15]. This method has a universal stimulating effect, helping to clean up heavy oil wells by reducing the viscosity of the oil, and also reducing the hydrostatic pressure in the oil column due to the release of nitrogen gas. Thus, both actions are aimed at ennobling the bottomhole formation zone by improving filtration characteristics as well as removing asphaltene-resin and paraffin deposits from the walls of the well and the wellbore equipment [16].

$$NH_4NO_3 + NaNO_2 \rightarrow NH_4NO_2 + NaNO_3 \tag{1}$$

$$NH_4NO_2 \rightarrow N_2 + 2H_2O + \Delta H \text{ (heat)} \qquad \Delta H = -334 \text{ kJ/mol} \tag{2}$$

Thermochemical treatment can be divided into three main points: (1) the injection of chemicals triggering an exothermic reaction in the reservoir; (2) soaking the well for an estimated period of time; and (3) the production process back to the surface. The importance of using this kind of chemistry in heavy oil production has a particular advantage in deep wells and cold areas, where steam can create problems with wellbore integrity. To increase the efficiency of using thermochemical fluids from various types of reservoirs, various methods and injection regimes have been proposed [17–20].

Since the application of thermochemistry is widespread in petroleum engineering, researchers have studied several sides of the problems with it. Mahmoud [12] used thermochemical treatment to remove a filter cake and to provide experimental evidence in order to clean up the oil and the gas wells after drilling operations. Hassan et al. [21] presented a new technique to remove condensate banking by using thermochemical treatment, and they found that thermochemicals reduce the viscosity of the condensate because of the in situ generation of heat and high-pressure gases. Wang et al. [22] investigated the generation of thermal foam during core flooding by mixing thermochemicals and surfactants. Thermal foams formed as a result of the release of gaseous nitrogen, due to which an increase in oil recovery by 34% in homogeneous rocks and 20% in heterogeneous rocks has been found. Anikin et al. [11] conducted studies on core flooding with hydrogen peroxide solutions, which is an even less common thermochemical agent due to the increased hazards of using it. As a result of the physical modeling with the injection of peroxide composition as well as the achievement of high temperatures caused by the presence of a catalyst and catalytic active centers in the rock, the core model with immobile oil was partially cleaned from heavy deposits due to a powerful thermal front spreading from the first core-cutter zone to the following ones.

This work is also aimed at solving the problem of enhanced oil recovery at large oil fields of the Samara region (the Russian Federation), which have been in industrial development for more than 75 years. Today, in conditions of high depletion of easily recoverable oil reserves, and in order to maintain high levels of oil production in this region, it is rational to commission fields with high-viscosity oil.

Having extensively studied both the features and the possibilities of targeting thermochemical treatment in the literature, we have studied and proposed various compositions capable of causing the generation of heat and gas with a controlled start of the reaction and a significant distribution of the thermal front. The task in this work is to create an effective heat-generating system and application method for the processing of the bottomhole and the remote zone of the productive formation that will have a direct impact on oil-saturated

reservoirs, increase coverage of the productive formation, and thereby connect previously uncovered oil-saturated, low-permeability parts of the reservoir in the development.

2. Materials and Methods

2.1. Materials

The chemicals used in this study included sodium nitrite ($NaNO_2$), potassium nitrite (KNO_2), ammonium chloride (NH_4NO_3), formalin (CH_2O, formaldehyde solution, 37 % wt), and 2,2-bis(hydroxymethyl)butanoic acid ($C_6H_{12}O_4$), and these chemicals were purchased from Sinochem Reagent Co., Ltd. (Beijing, China), whilst hydrogen peroxide (H_2O_2) with a concentration of 37 %wt was purchased from Khimprom (Novocheboksarsk, Russia).

The binary mixture for the experiments was prepared as follows:

1. Ammonium nitrate and sodium nitrite were stirred in fresh water to complete solubility.
2. Potassium nitrite was added to the aqueous solution of the two salts and brought to complete solubility without exposure to elevated temperatures
3. When surfactants were used in the experiments, surfactants of a given concentration were added to the binary mixture solution with stirring until complete dissolution.

Heavy dead crude oil from oil fields in the Samara region (in Russia) was used throughout the experiments. The viscosity of the oil from the Kamenskoye field was 411.3 cP at room temperature, whilst the viscosity of the oil from the Kirgizovskoye field was 451.8 cP at room temperature.

In order to prepare a composite core model used in experiments to determine the effectiveness of heat-generating compositions during filtration studies on a sand reservoir, core samples were taken from well #41 of the Bezvodovsky field from a depth interval of 1497.5–1498.5 m. For filtration studies on carbonate reservoir, core samples were taken from well #251 of the Kirgizovskoye field from a depth interval of 826–827 m.

For filtration experiments, cylindrical-shaped samples were drilled from two wells to make up the composite models.

2.2. Petrophysical Measurement

Routine core analysis was carried out on the prepared samples. Porosity and permeability for each sample were measured (Table 1). The porosity and permeability determination was carried out on a gas permeability and porosity analyser PIK-PP from Geologika (Novosibirsk, Russia). The PIK-PP instrument is designed to determine open gas porosity and permeability in baric conditions using the non-steady-state filtration method.

Table 1. Characteristics of composite core model.

Length, cm	Diameter, cm	Gas Porosity, %	Gas Permeability, mD
Column #1 (sandstone)			
4.85	2.93	24.19	1262.68
5.17	2.92	23.98	1092.54
4.99	2.92	24.15	1016.92
Column #2 (carbonate)			
4.99	2.95	18.81	1562.95
4.86	2.93	16.50	1102.31
5.01	2.95	20.45	749.25

2.3. Gas Chromatography Analysis, Viscosity

A Crystal 5000 chromatograph (Chromatec, Yoshkar-Ola, Russia) was used to determine the composition of the output gases resulting from various chemical reactions occurring during the injection of the binary system and the initiating additive into the cores at reservoir pressure. The gas sample was injected into the gas chromatograph using a

Hamilton (Nevada, USA) gas-tight syringe. The results were processed using Chromatec Analytical 3.1 software.

In order to determine the viscosity of oil at different temperatures, a viscometer SVM-3000 Stabinger (Anton Paar, Graz, Austria) was used.

2.4. Filtration Experiments

Studies to assess the dynamics of decomposition of the heat- and gas-generating system during the flooding of the salt composition and initiating the additives in the oil-saturated pore space were carried out on a filtration unit, described in more detail in [4,11,23,24].

When assembling the model, the core is fixed in the core holder in such a way that there is no possibility of vapor, and liquid overflows through the sealing material between the steel wall of the core holder and the core. The unit uses a flange-type core holder equipped with 3 thermocouples along the entire length of the core model, and it has a core sealing system made of thermally expanded graphite, which provides research up to 400 °C and is pressed between the walls of the core holder. Reservoir pressure was created with nitrogen. The initiator and the foam-salt mixture fluids were fed from separate piston containers into the core holder with needle valves installed at the inlet of the model without allowing mixing. The fluid collection system consisted of a back pressure regulator that maintains reservoir pressure in the model and outputs fluid to a separation burette.

A column with core samples (3×15 cm) with residual water saturation was collected in the core holder of the filtration unit, and thermobaric conditions were created. Displacement of kerosene with oil of at least 3 volumes of voids at a linear velocity of movement of fluids in the sample was carried out. After saturation with oil, the model was aged at reservoir conditions (aging) for 2 days in order to restore the initial wettability. Further, injection of the heat- and gas-generating system was carried out with online temperature and pressure measurements in 3 zones of the core model.

2.5. Hydrodynamic Modeling

CMG's commercial hydrodynamic simulator Stars was used to reproduce the physical modelling results and to find the unknowns. The Stars pseudo-composite simulator allows different amounts of components in the oil, water, gas, and solid phases to be accounted for, thereby enabling the simulation of complex physical processes that occur when different working agents are injected. A key aspect in creating the hydrodynamic model is the development of a kinetic model of the chemical reaction using Arrhenius' law. Based on the results of the laboratory experiments, the parameters of the kinetic model, such as the rate constant of the chemical reaction and the activation energy, were specified. In order to additionally take into account the effect of the dissolution of the solid components on the filtration-volume properties of the rock at increasing temperatures during the injection of the chemical composition that is adsorbed on the surface of the rock, a solid component (ARPD) was taken into account during the dissolution, and the permeability of this was recalculated using the Carmen–Coseny relation.

3. Results and Discussion

One of the most widespread compositions for the thermochemical influence on the bottomhole zone of formation at the moment is a mixture on the basis of salts of ammonium nitrate and sodium nitrite (as in Equation (1)), which is also due to their high availability on an industrial scale in the markets of Eastern Europe. This mixture was field tested at various reservoir types and different thermobaric conditions. One advantages of this composition is the possibility to prepare solutions of high concentration (50–60 %wt) as the reaction leads to a large exo-effect, and it thereby proceeds without the formation of insoluble compounds and the reaction products that cause corrosion of oilfield equipment. However, this composition does not spontaneously start at temperatures below 50 °C, and acid initiation is often used to start the reaction. In this respect, the question of developing

new initiating additives for a heat- and gas-generating effect with a controllable reaction time and controllable parameters is relevant.

The selection of the optimal additive to the mixture of inorganic salts for controlled reaction initiation led to the choice of 2,2-bis(hydroxymethyl)butanoic acid (HMBA), which is a commercially available product, as the initiating additive. At the first stage of the tests, experiments were carried out with initiation with this acid at atmospheric pressure in a free volume. The results of these tests are shown in Table 2, and mass fraction of the mixture of ammonium nitrate and sodium nitrite in the experiments was 60 %wt (NH_4NO_3—32.2 g; $NaNO_2$—27.8 g; H_2O—40 g).

Table 2. Delay time and maximum temperature (T_{max}) during the reaction of ammonium nitrite and sodium nitrite, and the addition of different amounts HMBA at $T_{initial}$ = 25 °C.

#	Concentration of HMBA, %wt	Delay Time, min	T_{max}, °C
1	**0.08**	**72 min**	**>120**
2	0.1	30 min	>100
3	0.2	4 min	>100
4	0.3	3 min	>100
5	0.5	1min	>110

The data obtained in Table 2 show that this mixture does not react at standard atmospheric conditions without the addition of initiating additives. The maximum reaction delay time was obtained with the addition of 0.08 %wt HMBA, and it is more than 1 h. This time may be sufficient to inject the chemical solution in a single stage at an acceptable production well injectivity.

In vertical well treatments with lower injectivity, injection time may be greater than 1 h, and it is therefore worth considering the introduction of an agent into the mixture to delay the reaction in a porous medium. For this purpose, in this work, we tested the addition of ethylene glycol (EG) to an aqueous solution (1:1 water/EG) with HMBA (Figure 1).
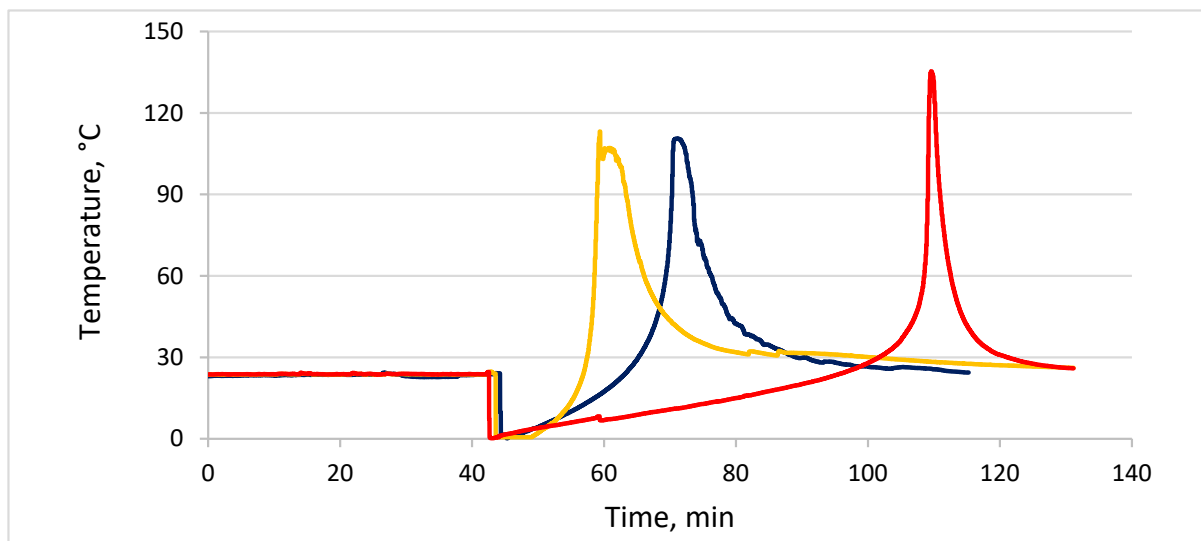

Figure 1. Temperature profiles: (1) HMBA—0.05 %wt/H_2O, yellow curve; (2) HMBA—0.02 %wt/H_2O, blue curve; (3) HMBA—0.05 %wt/H_2O:EG, red curve. Temperature drop (43 min) is connected with endo-effect of salt dissolution in porous medium.

The experiment was conducted in a porous medium (sand/atmospheric conditions). The success of controlled triggering with a long-term delayed reaction using HMBA, though, was different in a filtration experiment with the injection of a mixture of salts and this initiator into a porous medium (sand) under reservoir conditions (P = 5 MPa; T = 25 °C).

The arising effect of delay was observed, but the temperature increase was extremely small (T_{max} = 33 °C), and this excludes such a composition for field tests. As a result, other possible injection methods were tested with the chemical compositions described below.

To increase the overall heat- and gas-generating effect in this work, the concentration of inorganic salts for the chemical composition was increased. The composition, considered above, introduced potassium nitrite, because it has a fairly high solubility in water 300 g/100 mL (25 °C) and allowed us to obtain a chemical composition with a higher salt concentration (72 %wt) without precipitation: ammonium nitrate (35 %wt), sodium nitrite (16 %wt), and potassium nitrite (21 %wt).

The introduction of various surfactants into this composition and their action in the gas-generating effect during the thermal processes has a great prospect, since the formation of a powerful foam flow may allow the coverage of the impact on the treated core section to be increased, redistributing the flows to less permeable areas. However, the success of the heat treatment will then depend on the selection of the best surfactant, which should be resistant to high temperatures. One such reagent is a non-ionic surfactant, such as alkylpolyglycosides of various fractions, and this has the characteristics of both conventional non-ionic and anionic surfactants with high surface activity. We introduced a heat-resistant non-ionogenic surfactant based on C_8–C_{10} alkylpolyglycosides (1 %wt) into a solution of a binary salt system.

The chemical composition with initiation by various organic acids is, for the most part, not so relevant to this technology because the release of nitrogen dioxide formed by the interaction of acid and sodium nitrite necessarily leads to corrosion of the oilfield equipment. In our case, the initiation of the reaction of foam-salt composition at the waterflooding of sandstone core (Table 1) was, in the first case, carried out with formalin solution. The salt-foam composition and formalin were injected at a pressure of 5 MPa at a constant rate of 1.5 mL/min in successive slugs into the core model. Various chemical composition agents were fed from two piston containers into a core holder with needle cocks installed at the model inlet, and this prevented mixing. The temperature profile and parameters during the experiment are shown in Figure 2 and Table 3. As a result of the first flooding of formalin (0.1 PV) and salt mixture (0.8 PV), the maximum exo-effect (115 °C) was observed in the composite core model; at the second injection of slugs formalin (0.1 PV) and salt mixture (0.4 PV), the similar temperature increase could not be reached (and then soaked the system without injection of fluids); and in the gas phase, side reactions in model were not observed, and the nitrogen content was over 99 %mol (Table 4). It is clear that due to the strong foaming and exothermic reaction, the spreading of the heat front occured not only in the first but also in the subsequent core zones, as can be seen in Figure 2.

Table 3. Parameters of the filtration experiment with initiation of a foam-forming composition with formalin solution.

Time, min	PV	ΔP, MPa	Zone 1, °C	Zone 2, °C	Zone 3, °C
9	0.3	0.45	48.6	35.5	27.0
22	0.8	0.19	115.7	71.1	46.5
40	1.1	0.18	92.7	73.8	58.5

During the sequential injection of formalin solution with foam-salt mixture in the pore space, their mixing occurs. The interaction of formaldehyde contained in formalin with ammonium nitrite produces hexamethylentetramine (urotropine) and nitrous acid [20,21] is as follows:
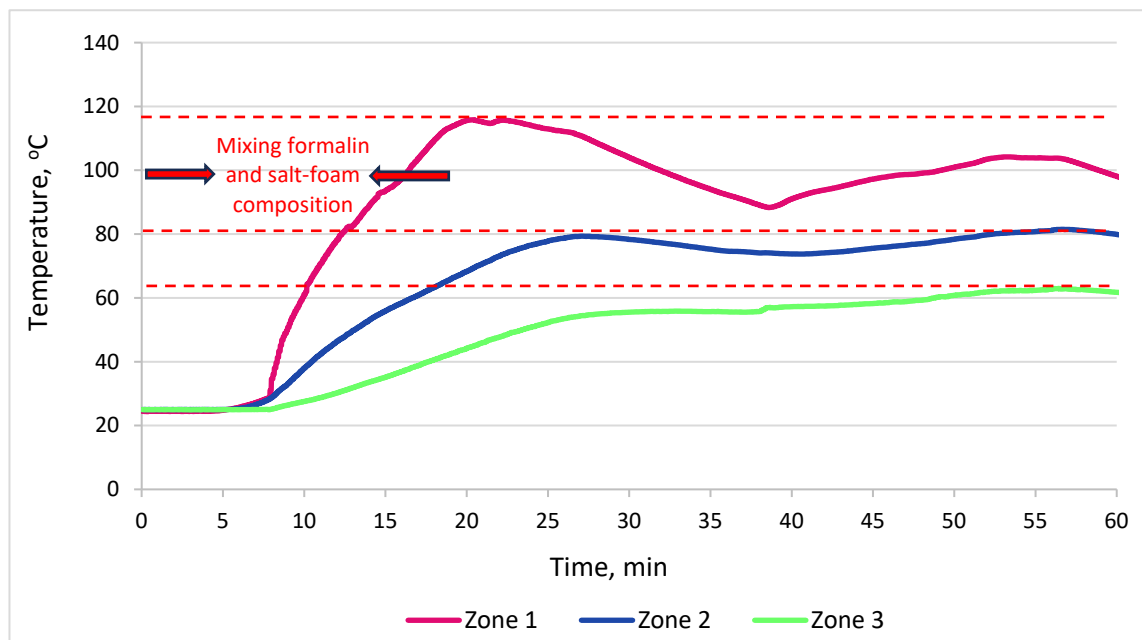
$$4NH_4NO_2 + CH_2O \rightarrow C_6H_{12}N_4 + 6HNO_2 \tag{3}$$
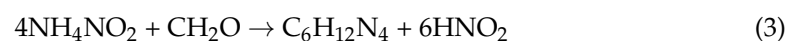
Figure 2. Temperature profile in the experiment with sequential injection of formalin solution and foam-forming salt composition.

Table 4. Component composition of gas at the fluid separation line in experiment.

Component	Concentration, %mol		
	Sampling Time		
	15 min	**25 min**	**45 min**
Carbon dioxide	0.74	0.65	0.53
Nitrogen	99.11	98.73	99.44
Ethane	0.00	0.00	0.00
Methane	0.00	0.32	0.02
Propane	0.13	0.28	0.00
Iso-butane	0.02	0.00	0.00
Butane	0.00	0.02	0.00
Σ	100.00	100.00	100.00

This effect leads to a decrease in the pH of the solution and the initiation of Reaction (1). Increasing the temperature leads to a shift of equilibrium in Reaction (3) to the left with the decomposition of urotropine. The presence of the foam system in the pore space allows directional heat and gas generation, with an effect on the oil-saturated interlayer. When the temperature in the first zones of the core model during flooding and the heat release reaches about 115 °C, the change in the viscosity of the oil used drops by a factor of 57 (Figure 3), however, this does not require a short-term increase in temperature.

To study heat and gas generation in a carbonate reservoir (Kirgizovskoye field), a core column #2 (Table 1) was used saturated with crude oil with a viscosity of 451.8 cP. The concentration of inorganic salts in the core flooding solution was prepared as in the previous experiment, only without the addition of a surfactant. A mixture based on formalin and hydrogen peroxide (37 %wt) in a 1:2 mass ratio was used as an initiating additive.
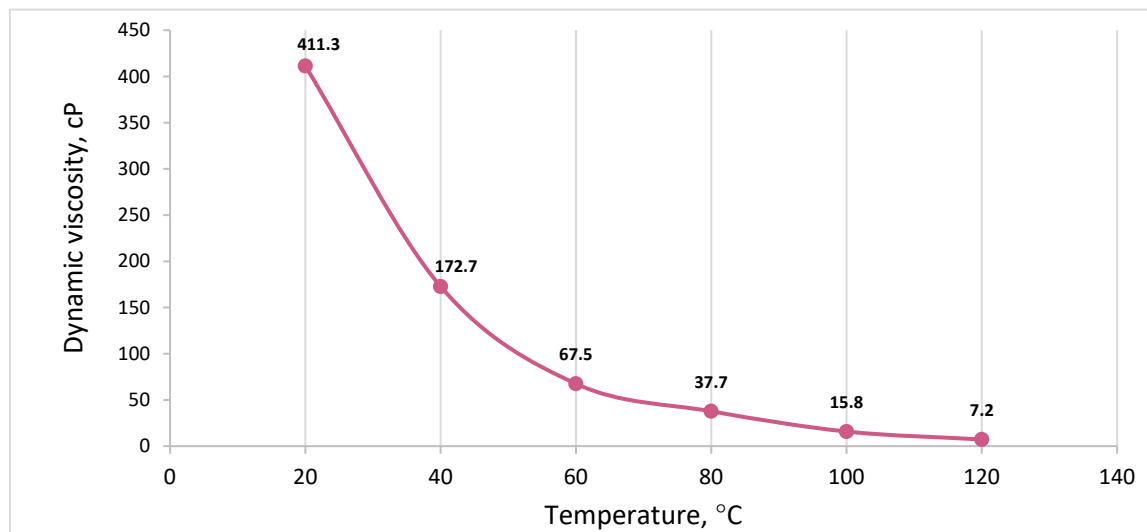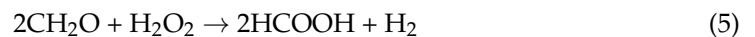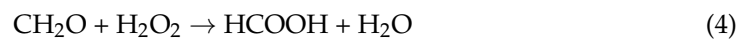
Figure 3. Dynamic viscosity of oil from the Kamenskoye field used in the experiment with foam- and heat-generating composition and formalin, with increasing temperature.

When formalin is mixed with hydrogen peroxide, depending on the reaction conditions, the following oxidative processes occur [25]:

$$CH_2O + H_2O_2 \rightarrow HCOOH + H_2O \tag{4}$$

$$2CH_2O + H_2O_2 \rightarrow 2HCOOH + H_2 \tag{5}$$

$$HCOOH + H_2O_2 \rightarrow 2H_2O + CO_2 \tag{6}$$

When a mixture of formalin with hydrogen peroxide and salt composition is injected sequentially in the pore space of the reservoir, mixing occurs. The formic acid formed by Equation (4) leads to a decrease in the pH of the solution and the initiation of Reaction (1). The rest of the hydrogen peroxide will take part in the oxidation of nitrites, thereby generating additional heat [26,27]. In addition, other side reactions can include the oxidation of oil components as a result of the decomposition of hydrogen peroxide [11], and in some cases, it is possible to react the salt system with organic acids if they are included in heavy and extra heavy oils [28].

The core flooding of the salt composition with initiating additive in this experiment was carried out at a pressure of 8 MPa (reservoir conditions) at a constant rate of 0.5 mL/min. The solutions were supplied from three piston containers to the core holder with needle valves installed at the entrance to the model, which prevented mixing. During the water-flood, 0.1 PV initiating additive and 0.5 PV salt composition were injected three times in succession. The temperature and the pressure drop profile of this experiment as well as the adaptation of the mathematical model are all presented in Figure 4. In contrast to the fast start of the reaction in the case of the foam salt composition when injecting solutions at a high rate into the core sandstone, it was not possible to achieve the same large model heating. However, the distribution of the heat front in porous medium turned out to be more favorable and uniform, not exceeding an injection rate of 0.5 mL/min. After the completion of the filtration experiment, each of the carbonate cores of the composite model were extracted, and oil saturation of each core from the initial one fell by 58% (zone 1), 8% (zone 2), and 3% (zone 3).
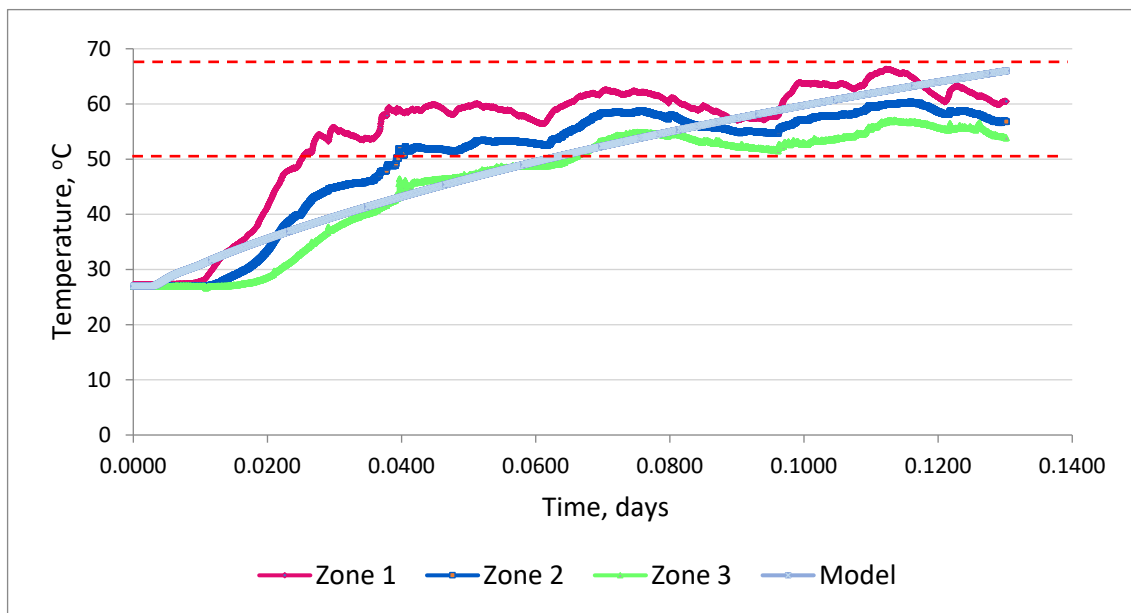
(**a**)
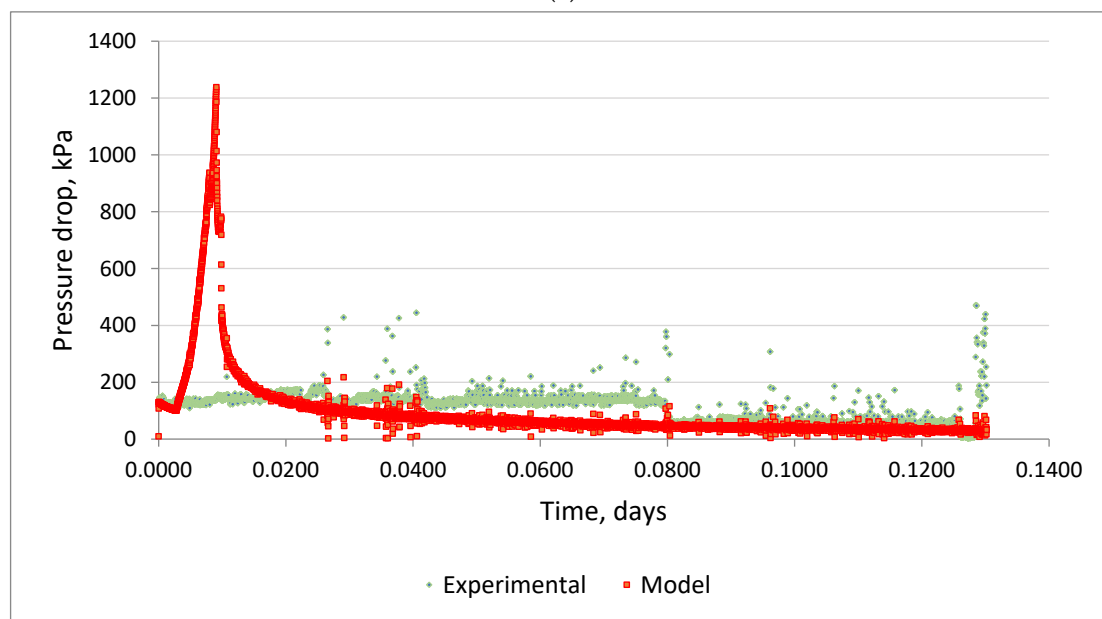
(**b**)

Figure 4. Temperature profile (**a**) and pressure drop (**b**) in the experiment with the sequential injection of formalin/hydrogen peroxide solution and salt composition, and the results of the adaptation mathematical model.

The results of the laboratory experiment were reproduced using a hydrodynamic model. This model was set up for the filtration experiment. During numerical experiments, a four-component model was used. The properties of the components are presented in Table 5.

With the help of the mathematical model, it was possible to clarify the main parameters of the chemical reaction—the frequency factor and the activation energy in the Arrhenius law. The enthalpy of the chemical reaction was calculated analytically by Hess law. The absence of a pressure drop in the core model at the beginning of the experiment can be related to the fact that the injection of the initiating additive at the initial time probably reduced the filtration resistance. The overall temperature trend reproduces the laboratory

data well. Heat losses were not considered in the mathematical model. In the process of adapting the model to the results of the filtration experiment, an activation energy of 22,500 J/mol was selected (Table 6).

Table 5. Properties of components in a mathematical model.

Component	H_2O	NH_4NO_2	Oil	N_2
Molecular weight, g/mol	18.015	64.04	426	28.013
Critical pressure, kPa	21,800	40,530	936	3394
Critical temperature, °C	374	69.85	620.9	−146.95
Density, kg/m^3	1168.43	2390.18	933	0.65

Table 6. Kinetic parameters of the mathematical model.

Parameter	Units of Measure	Value
Reaction frequency factor	day^{-1}	1,995,840
Enthalpy	J/mol	334,000
Activation energy	J/mol	22,500

In order to account for the effect of increased permeability due to the increased temperature and pressure during thermochemical treatment and the subsequent dissolution of heavy components, the hot water dissolution reaction of asphalt-resin-paraffin deposits (ARPD) was incorporated into the hydrodynamic model:

$$H_2O + ARPD \rightarrow \text{Water-based emulsion} \tag{7}$$

The dependence of the reaction rate on temperature in the hydrodynamic model was built so that at the initial reservoir temperature, the reaction rate was close to 0, and at an increased temperature (above 60 °C), due to the exothermic reaction, the reaction rate constant was greater than 0 (0.5 day^{-1}).

Figures 5 and 6 show the results of scaling the technology to one operating well in the Volga-Ural oil and gas province. The model is tuned to historical actual well operation data. Reservoir oil density is 35 °API (heavy). The figures show the results of the prediction of thermochemical technology efficiency. Oil mobility after the injection of the heat-generating system increases fourfold to fivefold on average, and, as a result of the dissolution of the colmatants in the bottomhole zone, the skin factor decreases to an average of "−2".

This paper shows that the injection of an initiating additive based on a mixture of formalin and hydrogen peroxide in a volume of 3 m^3 and the injection of salt composition in a volume of 20 m^3 at well #8 of the Ilmenevskoye field, according to the hydrodynamic modelling results, results in incremental oil production of 716 tons for 1 year.

For field treatment and reagent injection into the bottomhole zone, several steps should be followed. First, preliminarily calculate the maximum allowable pressure on the production string, and, depending on the thickness of the perforated formation, determine the injection volumes of the solutions of the initiator additives and the binary system with or without adding surfactants. It is also necessary to carry out the injection of the proposed fluids in two stages. At the first stage, injection of the initiating additive should be carried out, followed by the injection of buffer liquid, which should be inert with respect to the components of the reacting system, and this should be undertaken after the injection of the main composition. The heat- and gas-generating composition should be forced into the bottomhole zone with a process fluid with a density corresponding to the density of the well-killing fluid, and this should be followed by a process holding time for exo reactions to occur within the intended treatment radius.
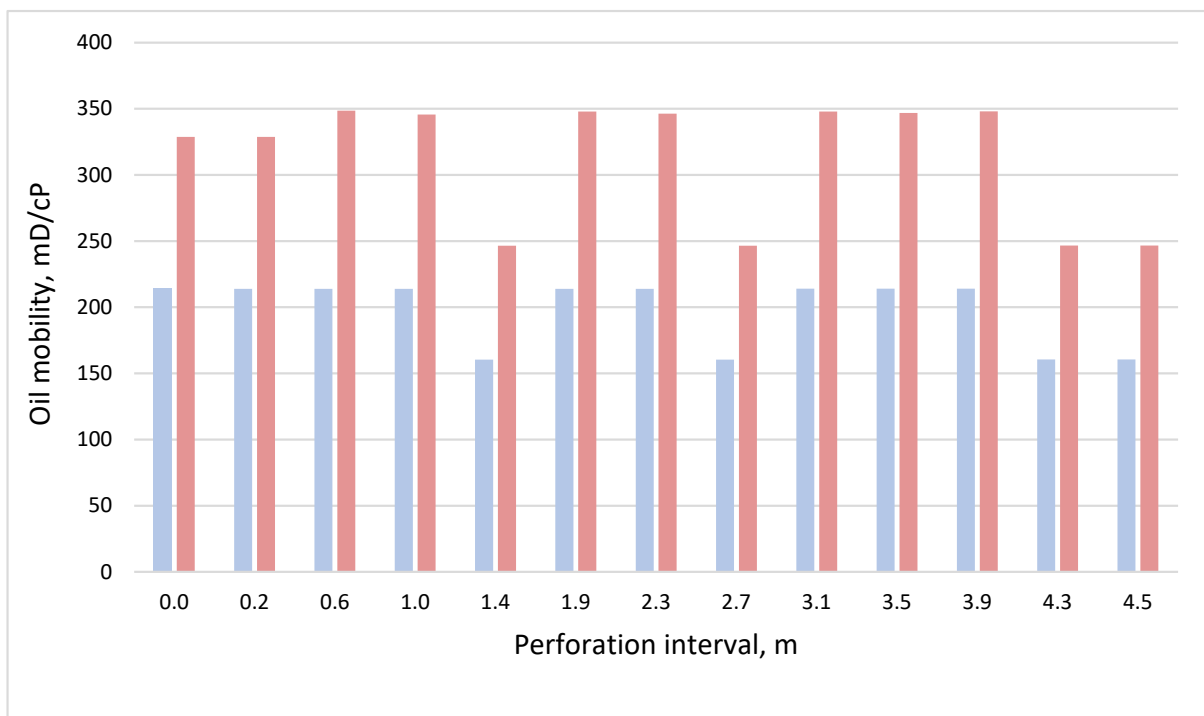
Figure 5. Result of calculating the change in oil mobility before (blue) and after (red) thermochemical treatment on a compositional hydrodynamic model.
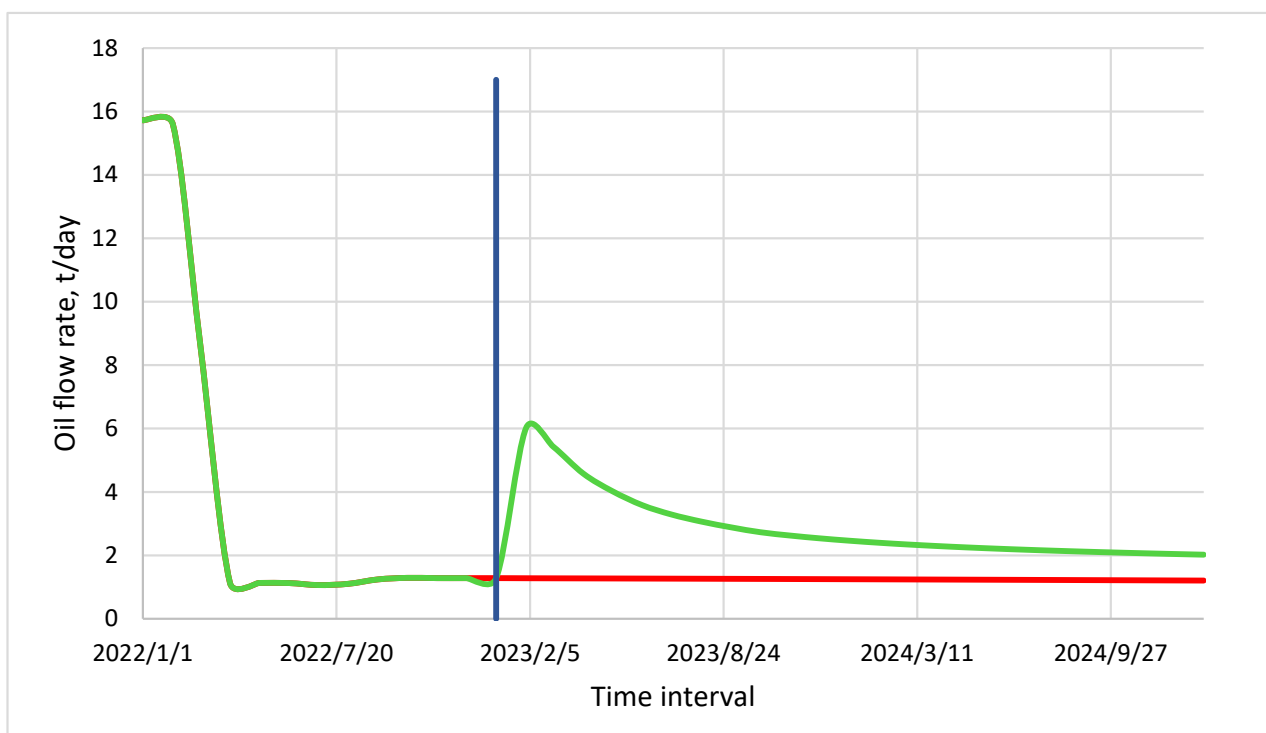

Figure 6. Result of calculating the increase in oil production after thermochemical treatment on a compositional hydrodynamic model: (1) no treatment (red); (2) with treatment (green); (3) start of treatment (blue).

4. Conclusions

The success of bottomhole thermochemical treatment depends on a better understanding of the ability to initiate an in situ heat- and gas-generating system. This study will

help process engineers to design and execute a successful oil flow intensification project in an efficient way. Based on the analysis and the discussion presented in this study, the following conclusions can be drawn:

- We have studied the effect on heat generation of the composition with increasing concentrations of salts in aqueous solution (72 %wt) of a binary mixture that includes ammonium nitrate, sodium nitrite, and potassium nitrite with a chemical initiation additive of delayed action HMBA. It has been shown that the reaction proceeds with a high exo effect in the solution and porous medium, and when EG (1:1 mass ratio H_2O:EG,) is introduced into this mixture, the onset time increases by 1.5 times. However, as shown by the filtration experiment, with a simultaneous injection of this HMBA and binary mixture under reservoir conditions in porous medium, the treatment efficiency is very low.

- We also studied the foam (surfactant—alkylpolyglucosides) salt heat and gas-generating composition with sequential injection into oil-saturated cores at initiation with formaldehyde solution without lowering reaction initiation. However, a powerful reaction allowed the coverage due to foam flow formation and heat and gas spread to increase from the first to the third zone of the composite sandstone core model in the core holder at initial formation conditions of P = 5 MPa and T = 25 °C.

- We have also studied the application as an initiating additive on the basis of the binary mixture of formaldehyde solution and hydrogen peroxide solution in mass ratio 2:1 with sequential injection into carbonate cores under reservoir conditions without the introduction of surfactants into the salt mixture. It has been shown that it is possible to distribute thermal front in porous medium of oil-saturated carbonate cores more favourably and uniformly.

- Calculations were performed using a non-isothermal composite model in order to study the kinetics of chemical reactions and to find the activation energy for calculations on targeted field models to justify pilot tests. As a result of the injection of a chemical additive of a binary type on the basis of hydrogen peroxide and formaldehyde in a volume of 3 m^3 and the salt composition (i.e., the one used in this study) nitrite in a volume of 20 m^3 at well #8 of the Ilmenevskoye field, according to the results of the hydrodynamic modelling, an increase of 716 tons of additional oil production for 1 year was achieved. The results of this prediction demonstrate the efficiency of thermochemical technology. Oil mobility after the injection of the heat-generating system increased fourfold to fivefold on average, and, as a result of the dissolution of the colmatants in the bottomhole zone, the skin factor decreased to an average of "−2".

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