Factors influencing hydrogen peroxide decomposition dynamics for thermochemical treatment of bottomhole zone

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Abstract
Recently, interest in on-site heat generation has increased due to injection of thermochemical fluids as a complex effect on well productivity. The method of thermochemical treatment with H2O2 while restoring and increasing the filtration characteristics of the bottomhole formation zone is a relatively new and insufficiently studied technology. The article discusses the key factors affecting the exothermic decomposition of this fluid when this fluid is injected into the well. The heat effects, pressure growth and decomposition time of H2O2 were determined depending on the salinity of the water, the composition of terrigenous rock, and various concentrations of H2O2. Physical 1-D modeling of H2O2 injection was carried out on rock models with mobile and stationary oil, which demonstrated a sharp increase in temperature by 100–240 °C caused by the decomposition of H2O2 due to the catalyst and the presence of catalytic active sites in the rock. As a result of this thermochemical treatment, the rock was partially cleaned of immobile oil and heavy sediments. Injection of H2O2 with a catalyst has shown the effectiveness of displacement of mobile oil from the filled sand model. Thus, the results of this study can provide a preliminary assessment of the effectiveness of H2O2 thermochemical treatment in fields operated at a later stage of development.

Keywords Thermochemical treatment · Hydrogen peroxide · Bottomhole zone · Heat effects · Physical 1-D modeling

Introduction
Recent analysis suggests many large global deposits are in the final stages of development. Thus, further development of producing oil deposits in mature fields requires intense processes for increasing recovery and well productivity. This involves the use of complex technologies for purposes such as cleaning the bottomhole formation zone and enhancing oil-saturated zones with deteriorated filtration-volumetric properties.

In wells producing from terrigenous reservoirs, the following types of impact on the bottomhole formation zone are most often used: thermogascochemical, electric heating, warming up with hot water and oil, treatment with solutions of surfactants and solvents, and hydraulic fracturing of the formation (Shah et al. 2010, Al-Bahlani et al. 2011, Hasssan et al. 2019, Shafiai et al. 2020). Chemical methods are used to influence the bottomhole formation zone in carbonate reservoirs, where treatment with an aqueous solution of hydrochloric acid is most often carried out. For the treatment of terrigenous reservoirs with a carbonate content of less than 10%, clay-acid solutions are used, prepared from hydrochloric and hydrofluoric acids (AlMubarak et al. 2015; Dashti et al. 2007). However, the use of acids can lead to severe damage to the formation, which is associated with acid-oil emulsions, or the deposition of asphaltenes in some carbonate reservoirs with low permeability.

In practice, it is well known that the innovative method of thermochemical influence on the formation can help in such cases. This technology involves the injection of solutions, mainly inorganic salts of nitrates, chlorides, and nitrates, in addition to initiators of their decomposition, forming an energy-generating composition (Kuznetsov et al. 2017). Mahmud M. and colleagues are actively
working in this direction, having studied in detail the kinetics and energy analyses of typical chemical compositions (NH₄Cl and NaNO₂) and preliminary evaluation of performance in recovery of heavy oil and gas condensate (Alade et al. 2019; Hassan et al. 2018). The dual salt process is the injection of two chemicals that react together in the downhole environment to generate heat and nitrogen, thereby significantly increasing pressure and temperature. Thermochemical stimulation for stimulation provides a number of advantages over the cyclic steam treatment technology, such as investment of lower capital costs, injection of a smaller volume of injection agent, reduction of well-operation time and reduction of the time to warm up the bottomhole zone to the required temperature.

A review of other chemical agents capable of generating increased energy and gas production during their injection into the formation allows us to consider the class of peroxide compounds for this purpose. Peroxides are characterized by a weak dissociation of the O–O bond (190–210 kJ/mol), which is less than half the strength of the C–C, C–H, and C–O and leads to easy breaking of the O–O bond (Bach et al. 1996). Therefore, a weak acid such as hydrogen peroxide (H₂O₂) can be considered as a suitable injection agent for thermochemical technology the reaction of its exothermic decomposition (∆H_d = −2884.5 kJ/kg), accompanied by a vigorous evolution of oxygen (Eq. 1) (Pedziwiatr et al. 2018, Plaučka et al. 2016). The use of H₂O₂ as an injection agent is attractive from the point of view of the availability of the reagent, as well as its compliance with environmental standards, having non-toxic decomposition products (water and oxygen):

\[ \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + \text{heat} \] (1)

One of the first studies to use H₂O₂ as a thermal enhanced oil recovery method was carried out by Bayless in 1989 (Bayless et al. 1989). This study determined that after H₂O₂ injection into the formation zone, there is a waiting period before the decomposition of H₂O₂, which leads to the release of the required amount of heat to increase the temperature of the formation. The peculiarity of using this reagent is that during its injection, not only a large amount of heat is released, but also active oxygen is released, which contributes to the exothermic process of oil oxidation, which contributes to additional heating of the formation. The decomposition of H₂O₂ has a few controllable parameters, such as temperature, concentration, pH and catalyst type, which according to Bayless make H₂O₂ a particularly useful agent in the production of high viscosity oils.

The possibility of using H₂O₂ solutions as a liquid oxidant in thermochemical methods for extracting high-viscosity oil was also studied by Khlebnikov et al. (2013). Their proposal was to introduce a catalyst (manganese oxide IV, ferrous oxides) in the form of an aqueous suspension to create a catalyst pad at the bottomhole, after which a 10–40 wt.% H₂O₂ solution is injected into the formation. According to their data, if the initial temperature of the injected solution is in the range of 10–20 °C, then as a result of the exothermic reaction, the temperature of the water–gas mixture can reach 86–286 °C when the concentration of hydrogen peroxide changes from 10 to 40 wt.%. They come to the conclusion that the heat released during the autooxidation reaction of residual oil will maintain high water temperatures and compensate for heat losses in the higher and lower horizons, as well as heating the reservoir rock and reservoir fluids.

The data discussed in the works cited above only indirectly answer questions about the possibility of thermochemical treatment of the formation with H₂O₂, without affecting detailed laboratory studies that play a significant role in the operation of this technology. And with the growing interest in using such technology in the field, data on thermodynamic and kinetic behavior are definitely important and are touched upon in the present work.

Successful initiation of thermal treatment with H₂O₂ in the formation zone can be caused by factors such as reaching the self-decomposition temperature (SADT) of H₂O₂, the presence of catalytic impurities (for example, most transition metals) or additional injection of a decomposition initiator (Takagi et al. 1985, Lousada et al. 2012, Xing et al. 2018). Catalysis of peroxide under standard reservoir conditions can take place both in the aqueous phase (homogeneous) and on a solid surface (heterogeneous). Regardless of the initial method of injection into the formation, upon contact with the surface of metal equipment and during filtration through the rock there will be a contribution from heterogeneous catalysis (Pham et al. 2012; Teel et al. 2007). The catalytic decomposition of H₂O₂ on the surface of metals or metal oxides has been investigated in recent years, including Fe, W, Cu, UO₂, ZrO₂, CuO, Cu₃O (Yang et al. 2015, Björkbacka et al. 2015). The kinetics of decomposition of H₂O₂ upon contact with a different type of surface is determined by the first order rate constant, which includes the rate constant of decomposition in the aqueous phase (homogeneous) kₕ and at the wall surface kₜₕ. Lin and colleagues investigated the kinetics of H₂O₂ decomposition on relatively inert materials including Teflon, glass, stainless steel and titanium (Lin et al. 1991). They found that the rate constant for H₂O₂ decomposition in a stainless-steel metal tube (k₁₂5°C = 0.0016 s⁻¹) is approximately 80 times higher than in a tube made of an inert material (k₁₃₂°C = 0.000019 s⁻¹), and the activation energies varied from 68.2 to 106.3 kJ/mol. The observed rate of decomposition of H₂O₂ in volume on a solid
catalytic surface can be determined as follows (Croiset et al. 1997; Liu et al. 2018):

\[ k_{\text{obs}} = k_h + k_{\text{sur}} \left( \frac{S_A}{V} \right) \]  

(2)

where the value \( S_A/V \) is the ratio of the overall surface area of a pure metal or solid catalytic particles to a unit volume of a liquid medium. In general, the catalytic effect of a solid catalyst is associated with the process of charge transfer with the participation of radicals which is determined according to the equation (Hiroki et al. 2005):

\[ \text{H}_2\text{O}_2 \xrightarrow{k_{\text{1, surface}}} \text{I} \xrightarrow{k_{\text{2, surface}}} \text{O}_2 + \text{H}_2\text{O} \]  

(3)

where \( I \)–intermediate compound (for example, \( \text{OH}^- \text{or} \text{O}_2^- \)), obtained as a result of the reaction of \( \text{H}_2\text{O}_2 \) with the solid surface of the catalyst.

The main goal of the study is to understand the ability of \( \text{H}_2\text{O}_2 \) to act as a highly active thermochemical fluid in reservoir conditions. In the results and discussion section, the thermochemical and kinetic aspects of the decomposition of \( \text{H}_2\text{O}_2 \) depending on its different concentration, the influence of terrigenous rock, salt water and metal surface are analyzed, and also physical modeling of \( \text{H}_2\text{O}_2 \) injection into a model containing immobile heavy oil and saturated with oil to evaluate \( \text{H}_2\text{O}_2 \) as a possible bottom hole cleaning agent and its displacement capacity is discussed. Before the discussion, the methodological part of the conducted research is given.

**Materials and methods**

\( \text{H}_2\text{O}_2 \) with a concentration of 37 wt.% (Khimprom Novocheboksarsk, Russia) and sodium permanganate with a concentration of 40 wt.% (Hefei TNJ Chemical Industry, China) were used in this study. Crude oil, formation water and core samples were taken from one of the oil fields in Tatarstan Republic (Russia). Before experiments the provided full-size core from terrigenous reservoir was crushed. Extraction of the crushed core was extracted in a Soxhlet apparatus, the operation lasted a week at the condensation temperature of 30°C. After each step, the waiting time for search of reaction was 30 min. The criterion for finding the reaction was the self-heating of the system by more than 0.02 °C/min. When a reaction was found, the ARC automatically switches to the adiabatic mode and follows the reaction. The closed spherical containers (nickel-molybdenum-chromium heat resistant alloy) with a 7 ml volume were used for the experiments. The volume of the reaction mixture for research was 1 ml. Temperature control is carried out by means of a thermocouple (Control TC), which is directly attached from the outside to the calorimetric cell.

**Experimental procedure**

*Thermal Analysis* An accelerating rate calorimeter ARC 254 manufactured by Netzsch (Germany) was used to study heat effect and kinetics of hydrogen peroxide decomposition. Calibration of a calorimeter is a process of heating an empty cell to the specified temperatures with a step of 50 °C (50, 100, 150…500 °C). Each of the obtained temperatures corresponds to a certain voltage. Calibration of the device is reduced to entering a coefficient and when multiplied by it, the reference temperature values for a given thermocouple are obtained. Experiments were carried out in heat-wait-search (HWS) mode according to our previous works (Zhao et al. 2019, Yuan et al. 2020). The sample was heated with a step of 5 °C. After each step, the waiting time for search of reaction was 30 min. The criterion for finding the reaction was the self-heating of the system by more than 0.02 °C/min. When a reaction was found, the ARC automatically switches to the adiabatic mode and follows the reaction. The closed spherical containers (nickel-molybdenum-chromium heat resistant alloy) with a 7 ml volume were used for the experiments. The volume of the reaction mixture for research was 1 ml. Temperature control is carried out by means of a thermocouple (Control TC), which is directly attached from the outside to the calorimetric cell.

*High-pressure reactor* The study of the dynamics of pressure and temperature growth during the decomposition of \( \text{H}_2\text{O}_2 \) in a liquid state in a closed system was carried out in a sealed cylindrical high-pressure reactor (Fig. 1) made of steel grade AISI 304, equipped with an inlet for a pressure sensor. The experimental cell was filled by 37 ml H2O2 solutions of various concentrations from the total volume of the system in each measurement. For the safety of the process, this cell was in a special protected oven during the experiment.

**Filtration technique** A self-designed experimental set-up for physical modeling of thermochemical methods for IOR studying the thermochemical effect of hydrogen peroxide injection in sand pack model under reservoir conditions (Fig. 2). The operation details of the unit were described in
The injection agent supply system consists of a precision high-pressure plunger pump (1), metering hydraulic fluid at a constant rate to the inlet to the piston containers (2), which are connected to a core holder (4) placed in the high-pressure chamber (3). The fluid collection system consists of a back pressure regulator (8), which maintains the reservoir pressure in the model and the fluid is discharged into the separation burette (9). A nitrogen cylinder is used to create pressure.

Core samples from the studied oilfield were crushed to a fraction of 0.1–1.0 mm. The resulting sample was pressed into a core holder with a diameter of 50 mm and a length of 300 mm. The permeability (K) of the disintegrated rock sample with immobile oil pressed into the core holder was 1056 mD. The permeability (K) of the model sand with mobile oil pressed into the core holder was 1243 mD. Reservoir conditions were created in the pressed-in model before fluid injection, and the initial pressure was 5 MPa. The injection of water and H₂O₂ was carried out at a constant rate of 1 ml/min, and the temperature changes along the entire length of the sand-pack model were measured using 4 thermocouples.

Results and discussion

Decomposition of H₂O₂ on various types of surfaces

For a quantitative interpretation of the processes in which the decomposition of hydrogen peroxide is possible both in the formation zone and during its injection, calorimetric studies were carried out in this work with the determination of thermodynamic parameters. Investigations of the process of decomposition of H₂O₂ in calorimetric experiments can be divided depending on the type of container surface and the effect of various chemical properties of individual substances (Table 2).

Thermal decomposition of H₂O₂ by adiabatic calorimetry

Factors such as concentration, temperature and pressure are important considerations when H₂O₂ is injected into the wellbore. The influence of each factor is an important condition for assessing the total exo-effect, the reaction start time, as well as the process safety associated with these
characteristics. This is due to the possible explosive boiling of an aqueous solution during the decomposition of H₂O₂ (Nikitin et al. 1992). The most serious H₂O₂ accidents are usually associated with one of three types of decomposition processes: organic pollution; inorganic pollution; and decomposition caused by alkali (Hart et al. 2011).

In this work a series of thermochemical studies were conducted to determine the heat power of the decomposition of H₂O₂ by the method of adiabatic calorimetry (ARC) to analyze the criteria selectable when using H₂O₂ as a thermochemical agent in the formation and treatment of the bottomhole zone (West 1963; Duh et al. 1996).

The first thing that was studied at the ARC was the effect of concentration on the exo-effect of the reaction of decomposition of H₂O₂ with formation water involvement (Fig. 3). The ∆T of a dilute H₂O₂ solution from 7 to 30 wt.% (initial form) varies in the range from 9,0 to 78,6 °C and is described by a linear equation (R² = 0.99) depending on the concentration (Table 3). Using this correlation, it is possible to predict the amount of heat released for various concentrations of hydrogen peroxide on a surface of the type B (Table 2). Therefore, the selection of the correct concentration of H₂O₂ and/or addition of an inhibitor can lead to reliable control of the exothermic decomposition reaction of H₂O₂, and therefore a given heat release.

To select an agent for pushing H₂O₂ through tubing into the formation (distilled or formation water), it is necessary to investigate the impact of the water salinity on the time for initiation of H₂O₂ decomposition. It is also important to consider the effect of water salinity on the wellhead equipment and oil-well tubing, that do not have an inert surface and can therefore affect the process of H₂O₂ decomposition. Salt water can damage not only low-alloy steels, but also stainless steel, copper, aluminum, nickel alloys (Fink 1963). The composition of water can affect the decomposition of H₂O₂, since an increase in water salinity can lead to both a zero effect with the content of ferrous sulfate and chloride in formation water, and a possible increase in the reaction rate with the content of sodium and magnesium chlorides.

Experiments utilizing ARC have shown that an increase in the salinity of an H₂O₂ solution upon dilution with water characterized by a high salinity in the range of 250 g/l leads to a reduction in the time for the onset of the decomposition reaction (Fig. 4). While the importance of water salinity on the decomposition of H₂O₂ is recognized, the exact mechanism of the effect of salts in solution in combination with

### Table 2

| Type | Vessel material | Surface activity/composition | Conditions* | Effect |
|------|----------------|-------------------------------|-------------|--------|
| A    | Glass vessel   | Inert/Glass                   | Tres, Pres = 25 °C, 5 MPa | Oil phase composition |
| B    | Hastelloy C-276 (ARC cell) | Active/Ni, Mo, Cr, W | Tres, P = 0.1 MPa (rising); Tres, P = 0.1 MPa; Tres, Pres | Salinity water, solid rock surface |
| C    | Stainless steel (core holder, high-pressure reactor) | Active/Fe, C, Cr, Ni, Mo | Tres; P = 0.1 MPa; Tres, Pres | Salinity water, solid metal surface |

*Tres = 25 °C, Pres = 5 MPa

### Table 3

| H₂O₂ content (wt.%) | ∆T (°C) |
|---------------------|---------|
| 7                   | 9.0     |
| 15                  | 30.8    |
| 20                  | 44.8    |
| 30                  | 78.6    |
the effect of the ARC cell surface (type B) is not known. This study shows that in the region where there is a reduction in the initiation time of the reaction, there is a region of linear dependence, which is proportional to the degree of diluted formation water. With a decrease in the salt solution concentration (> 50%), the effect of H₂O₂ decomposition is less intense and the reaction time increases (Fig. 5).

The bottomhole formation zone contains a large quantity of solid particles (minerals, mixtures of oxides, etc.), which are effective catalysts for the decomposition of H₂O₂. The removal of iron-containing material from the oil-well tubing into the bottomhole zone can provide an environment for the decomposition of H₂O₂. At the same time, the rock can exhibit varying reactivity in relation to H₂O₂, depending on the area and properties of the metal surface. It is known that the coordination between the surface of mixed phases of Fe, Al, and Si oxides (for example, iron-containing aluminosilicate minerals) is more efficient in the decomposition of H₂O₂ than a surface of pure oxides. Thus, to predict the decomposition during injection of H₂O₂ in the bottomhole formation zone, it is necessary to assess the effect of given catalysts within the given reservoir.

In this work, two types of rocks were analyzed in the ARC experiments: non-extracted rock containing immobile oil and fully extracted rock. In a calorimetric cell, mixtures were prepared in two different ratios of 1 g of rock/1 g of H₂O₂ solution, as a model of the behavior of the system, and 5 g of rock/1 g of H₂O₂ solution, as a model of the behavior of the system close to the reservoir. The ratio 1:5 is considered in relation to the porosity of the rock equal to 20%. H₂O₂ solutions with a concentration of 20 wt.% and 30 wt.% were prepared in distilled water to eliminate the contribution of the metal cell wall. H₂O₂ with a concentration of 37 wt.% was not used in this experiment, so as not to create a stronger thermobaric effect in the cell. Figure 6 shows curves of temperature variation with time of decomposition of H₂O₂ of various concentrations under the influence of each of the rocks.

We show that when the ratio of H₂O₂ to the rock is 1:5, there is no rise in temperature due to the low diffusion rate during the propagation of heat through the dense membrane of the rock (Fig. 6, purple curve). This also proves that the rate of H₂O₂ decomposition in porous media depends not only on the surface area of solid catalytically active particles, but also on the pore size in the system. When calculating the parameters of H₂O₂ decomposition on the surface of solid mineral systems, it is desirable to additionally introduce an average pore size parameter, which embraces all the catalytic centers of the rock. When the ratio of H₂O₂ solution to rock is 1:1, an increase in heat release is observed. The ∆T of H₂O₂ diluted with distilled water in the case of a 30% solution of H₂O₂ was 55.0 °C on the oil saturated and 49.7 °C on the extracted rock, in the case of a 20% solution of H₂O₂, 34.2 °C and 27.4 °C, respectively (Table 4). A slightly greater exo-effect on non-extracted rock may indicate the
influence of metal complexes in the composition of immobile oil.

**Decomposition of H$_2$O$_2$ in the oil phase**

When studying the effect of the oil phase on the decomposition of H$_2$O$_2$, an inert surface (type A) was used. For reliable comprehension of phase behavior during the decomposition of H$_2$O$_2$ in the oil phase, the oil-H$_2$O$_2$ solution (in a 1:1 wt. ratio) with a catalyst was used. For this purpose, pure oil and an H$_2$O$_2$ solution were placed in a glass cylinder connected to a gas burette. To accelerate the decomposition of H$_2$O$_2$, an iron oxide-based catalyst was initially added to the solution. The initial temperature of the experiment was 25 °C. As soon as we carried out the catalytic decomposition of H$_2$O$_2$, migration of released oxygen from the aqueous phase to the oil phase was observed, as a result of which oil foamed and caused a gradual increase in the volume of the oil phase (Fig. 7). In this process, there was no gas (oxygen) breakthrough from under the oil cap.

The dynamics of the increase in the volume of oil $\Delta V/V_0$ are shown in Fig. 8. The rate of increase in the volume of the oil phase with a decrease in concentration from H$_2$O$_2$ 37 wt.% solution to 10 wt.% was expected to drop. Liquid oil in the presence of H$_2$O$_2$ does not undergo serious heat treatment and itself is not capable of increasing the exo-effect, as a result of which such a fluid cannot lead to a reduction in the time of H$_2$O$_2$ decomposition in the oil formation.

The experiment carried out indicated that the continuous increase (displacement) of the oil phase caused by the liberated oxygen from the aqueous phase may be a favorable factor for oil displacement in a porous medium.

**Pressure growth dynamics during the decomposition of H$_2$O$_2$**

One of the important factors that should be considered when injecting H$_2$O$_2$ into a well is the pressure increase associated with an increase in the volume of oxygen during the
decomposition of H$_2$O$_2$. If the process is very violent, it can provoke the destruction of underground equipment, so it is desirable that this process has strict control.

Thus, a study was undertaken to evaluate the effects of the catalytic environment, including the combination of metal surface (type C) and water salinity, which collectively affect the decomposition of hydrogen peroxide. A pressure growth analysis was carried out in a sealed system, which allows online recording of the pressure rise. In the experiments, H$_2$O$_2$ solutions were used, diluted with formation and distilled water to concentrations of 15, 20, 30 wt.%. 

A study on a solid metal surface with the participation of formation water showed that the decomposition of hydrogen peroxide proceeds much more intensively than with a liquid that does not contain salt ions. For solutions of lower concentrations of 15–20 wt.%, the pressure rise slowed down and is comparable in time. The rate of pressure increases in the static mode for a H$_2$O$_2$ 30 wt.% solution diluted with formation water reaches 1 MPa/h, for 15 and 20% H$_2$O$_2$ solutions—0.6 MPa/h (Fig. 9). The decomposition time of H$_2$O$_2$ solutions mixed with distilled water of 10–20 wt.% water in the cell is reduced by 60–100 times (Fig. 10). Thus, the experiment carried out showed that injection of H$_2$O$_2$ with a concentration of 15–30 wt.% is possible, however, an increased content of saline medium should be avoided to reduce the catalytic effect of the pumping and compressor equipment. The presence of a spacer fluid can also allow H$_2$O$_2$ injection to be controlled to the required parameters for safe injection, but coiled tubing technology is also recommended. The well must be equipped with blowout preventers to exclude water and gas manifestations during the thermochemical treatment.

**Filtration test of H$_2$O$_2$ injection in a model with different states of oil**

Studies carried out at ARC and in a closed metal cell have shown that the decomposition of H$_2$O$_2$ is capable

![Fig. 9](image_url) Dynamics of pressure growth in a metal cell during the decomposition of H$_2$O$_2$ (formation water participation)

![Fig. 10](image_url) Dynamics of pressure growth in a metal cell during the decomposition of H$_2$O$_2$ (without formation water participation)
of generating different amounts of heat and contributing to a rapid increase in pressure in systems, which depends on the catalytic capacity of the surface, the salinity of the liquid, the mineralogy of the rock and the concentration of hydrogen peroxide itself. Therefore, this fluid can be considered a high-potential energy and gas generating agent for injection into the formation zone. To assess the effect of the decomposition of H$_2$O$_2$ on a real rock in reservoir conditions, two filtration tests were carried out with the injection of H$_2$O$_2$ in a commercial form of 37 wt.% into a disintegrated rock containing immobile heavy oil fractions. To assess the displacement ability of hydrogen peroxide, a filtration test was carried out through the injection of oil-saturated sand in order to determine the cumulative oil recovery. Previously, in both experiments, a 5 wt.% sodium permanganate solution was injected for a sharp initiating effect of the reaction. It can be noted here that, with terrigenous rocks, the initiation of the hydrogen peroxide decomposition reaction occurs regardless of the presence of a catalyst, as noted in Sect. 3.1, but has a delay time.

**Physical bottomhole zone treatment 1-D modeling**

When simulating the effect of H$_2$O$_2$ on crushed rock with immobile oil, the model rock was saturated with a catalyst pressed into the core holder, with H$_2$O$_2$ subsequently injected. In this case, the rock from the terrigenous reservoir was taken in a milled state to assess the greater coverage of catalytic centers in the rock for the decomposition of H$_2$O$_2$ in order to observe the maximum exo-effect. After doing so, the temperature in the model rose from 25 to 240 °C (Fig. 11). The sharp increase in the initiation of H$_2$O$_2$ decomposition is influenced by a combination of factors: the participation of the introduced catalyst, the content of solid metallic material in the rock, and the presence of active metal centers in the composition of the residual oil. After pressing out from the core holder, a change in the oil saturation of the rock is visually observed (Fig. 12). From the first to the last zone of the model, a gradual increase in the immobile part of oil is observed. Removal of immobile oil from this rock in the initial zones leads to its intense discoloration. The organic matter content was determined to be 8.9% before H$_2$O$_2$ was injected into the model. After the experiment in each of the

**Fig. 11** Temperature profile when pumping H$_2$O$_2$ into a crushed rock with immobile oil

**Fig. 12** Rock type before (left) and after (right) pumping H$_2$O$_2$ through a crushed rock with immobile oil
zones, the content of organic matter was: 0.78% (zone 1); 1.4% (zone 2); 3.1% (zone 3); 14.1% (zone 4).

Physical 1-D modeling mobile oil recovery

When simulating H₂O₂ treatment on a model with oil-saturated (mobile oil) sand, the temperature rise above 100 °C was observed on the model of the compressed oil-saturated sand (Fig. 13), after which the oil inflow was observed on the line of the fluid inflow. The most intense oil displacement occurred in the range from 0.5 up to 1.5 pore volume units (Fig. 14). The cumulative oil recovery factor was 61%. In the absence of a solid catalytic surface in the rock and active sites in the residual oil for the decomposition of H₂O₂, the exo-effect is accompanied only by the participation of the catalyst, which becomes sufficient for the advancement of the fluid flow. After processing the H₂O₂ model and stopping the temperature rise, formation water was pumped, but no more oil displacement from the model was observed.

Summary and conclusions

On the example of a terrigenous field (RF), the possibility of using the H₂O₂ injection technology as a method for treating the bottom-hole formation zone has been explored.

- Based on the performed filtration tests of physical 1-D modeling on disintegrated rock with mobile and immobile oil, a sharp increase in temperatures of 100–240 °C was demonstrated, caused by the decomposition of H₂O₂ with a powerful exo-effect, as a result of which either the rock was cleaned from immobile oil, or the displacement of the liquid phase of oil was observed with determination of the recovery factor.
- It was shown that the key factor that contributes to the decomposition of H₂O₂ in the formation zone is the catalytic ability of the mineralogical composition of the terrigenous rock to activate the decomposition of H₂O₂.
- It is also shown in this study that an important factor for assessing the risks when injecting H₂O₂ into a well is the catalytic feature of the metal surface and water salinity, which together affect the decomposition of hydrogen peroxide and lead to a pressure increase.

Based on the data obtained, in the future, attention should be focused on mathematical modeling to justify the conduct of thermochemical treatment on a real reservoir in order to take into account how to increase the productivity of the well, as well as to assess the risks associated primarily with the presence of gaseous oxygen and water vapor, and the resulting increase in pressure.

![Temperature profile after pumping hydrogen peroxide on the oil sand model](image-url)
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Declarations

Conflict of interest  On behalf of all the co-authors, the corresponding author states that there is no conflict of interest.

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