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ON THE NECESSITY OF A COMPREHENSIVE STUDY OF THE THERMAL EFFECT OF THE «MAGNESIUM + HYDROCHLORIC ACID» REACTION WHEN SELECTING A COMPOSITION FOR HEAT TREATMENT (USING THE EXAMPLE OF THE «WHITE TIGER» OILFIELD)

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A B S T R A C T

In this paper, the authors conducted a study devoted to determining the most optimal compositions for the implementation of measures to increase well productivity in the conditions of active development of the White Tiger field. The results of basic experiments in the field of selection of reagents for heat treatment of the bottomhole zone of wells, together with a comprehensive analysis of the geological conditions of the studied object, show that in order to restore and multiply the permeability of formations, it is necessary to use such compositions, the mechanism of interaction of which is based on the dissolution of asphalt-tar deposits and substances with a large molecular weight. In this regard, a number of theoretical calculations have been carried out for the «magnesium + hydrochloric acid» reaction in four variants with the gradual introduction of compositions of different chemical composition and origin. At each stage, the reaction temperature was determined using both the main and alternative methods in order to increase the representativeness of the results. Taking into account the imposed restriction on the deviation of the determined temperature from the bottom hole, the composition of the agent that can be recommended for the treatment of productive layers of the White Tiger deposit has been previously successfully determined. It is concluded that it is necessary to study the replication of its application at analog facilities in order to improve the technical and economic performance of oil and gas production departments.

Keywords: bottom-hole formation zone; thermal effect; reservoir temperature; reaction products; oil field development; well productivity improvement.

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It is known that the impact on the bottom-hole zone (BHZ) of the reservoir allows to intensify the process of oil recovery, reduce the cost of oil production and, in general, increase the return on assets of oil and gas companies [1–4]. The presence of a significant number of methods of exposure to BHZ is explained by the variety of deposits in terms of geological, physical and physico-chemical properties of the layers and the fluids saturating them [5-7]. At the same time, it is important to choose the most effective method and determine the technological parameters of the impact that would most reduce the negative impact of natural factors on the oil production process [8-14]. One of the most effective methods of influencing the bottomhole zone is the method based on the use of hydrochloric acid [15-19]. However, as practice shows, the success rate of this method of exposure rarely exceeds fifty percent [20-23]. Justification of the impact parameters based on generalization of well operation experience allows increasing the success rate to 70-80% [24-28]. At the same time, as a rule, the influence of parameters reflecting the features of the geological structure [29-33] and properties of reservoir fluids [34-35], as well as technological parameters of wells and deposits [36] on success and efficiency indicators is studied.

One of the key features of the development of deposits with high viscosity oils or oils with a high paraffin saturation temperature is the possibility of deposition of paraffin-resinous components in the pore space of the bottomhole zone as a result of violation of the thermodynamic equilibrium of the reservoir system. To restore or increase the productivity of wells in the White Tiger field, the method of in-situ thermochemical treatment using an exothermic reaction of interaction of granular or powdered magnesium with acid solutions directly in the bottomhole zone of the formation is widely used [37]. The treatment of wells using the method of thermochemical exposure leads to an increase in their productivity with long-term preservation of the effect. An important aspect of the implementation of effective measures

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is the reasonable selection of compositions that must meet a number of criteria. In the conditions of the development of the White Tiger deposit, the downhole temperature is a key factor influencing the use of a particular composition to increase productivity. Consider a closed system in which a reaction occurs:

$$aA+bB=cC+dD \quad (1)$$

where A, B – reagents; C, D – reaction products; a, b, c, d – stoichiometric coefficients.

The reaction equation between magnesium and hydrochloric acid has the form:

$$2HCl_{(g)}+MgCl_{(ss)}=MgCl_{2(ss)}+H_{2(g)}+Q \quad (2)$$

In equation (2), the components HCl, $MgCl_2$, H_2 and are gases, a Mg – a solid substance. To determine the thermal effect of reaction (2), assume that the reaction takes place under standard conditions. The physico-chemical parameters of the reaction are shown in tables 1, 2.

Substituting into formula 2, we get the value ΔH^0_{298} = =-457.2 kJ/mol. Due to the fact that the reaction occurs at a constant volume, the thermal effect of the reaction when taking into account the sum of moles of the gas starting reagents -1 will be equal to Q_v=-454.723 kJ.

For further calculations, we will calculate the mass unit of magnesium. Obviously, the thermal effect of the reaction is the amount of heat released, i.e., when converted to 1 g of magnesium, we have the amount of heat released equal to 18.946 kJ/g. Consider the transition from isobaric mole heat capacity under standard conditions (C^0_p) for isochoric mole heat capacity under standard conditions (C^0_v) . For a liquid or solid, the difference between (C^0_p) and (C^0_v) insignificant, at the same time, relative to gases, it is possible to imagine:

$$C^0_v = C^0_p - R \quad (3)$$

where R – the ideal gas constant, R=8.314 $J \cdot K^{-1}$.

By analogy with (3), we obtain the values C^0_v for hydrochloric acid and hydrogen, equal 0.791365 and 14.23483 accordingly. In order to reduce the error of the results obtained in determining the most optimal composition of the composition for processing the bottom-hole zone of the formation in the conditions of the development of the White Tiger deposit, we will consider four scenarios for the injection of substances:

- the first case: when 15% concentrations of hydrochloric acid solution (HCl) an active reaction with magnesium is observed (Mg);
- the second case: excess 15% concentration HCl compared to the total flow rate of the liquid during processing;
- the third case: excess 15% concentration HCl and the presence of carrier water for magnesium suspension;
- the fourth case is similar to the third case, except for the addition of a buffer solution at the final stage.

For the first case, let’s assume full interaction Mg with a solution HCl 15%. The total amount of heat that is generated under these initial conditions is 41145718.224 kJ. The mass of hydrochloric acid reacting will be slightly more than 3 g. When she interacts with 24 g magnesium is formed by 95 g salts $MgCl_2$ and 2 g hydrogen gas, i.e. 1 g magnesium reacts with 3.04167 g hydrochloric acid. The amount of heat coming from the starting materials is determined by the formula 4:

$$Q_v = m \cdot C^0_v \cdot 298 \quad (4)$$

Temperature of the mass after the reaction will be 545.437 °K. Here is an alternative way to calculate the desired indicator. Suppose that after the reaction, all the initial components are in standard conditions at a temperature of 298 °K., in which the amount of heat released will be 18946000 KJ. After the interaction, the temperature of the mass of products increases by ΔT from the original value. According to formula 5, the temperature increase will be 524.3 K excluding the initial temperature and 549.3 K provided that the studied compounds are found under standard conditions:

$$\Delta T = \frac{Q_p}{\sum m_i \cdot (C^0_v)_i} \quad (5)$$

The error in this case is no more than 5%, which is an acceptable value for empirical research. In the second case, the change in temperature and the amount of heat in excess conditions is analyzed 15% concentrations HCl compared to its complete dissolution in reaction with magnesium. The initial data and calculation results are presented in table 3.

Table 1
Results of the reaction between magnesium and hydrochloric acid

Standard heat of formation, kJ/mol	Elements				
	Magnesium	Hydrochloric acid	Water	Magnesium chloride	Hydrogen
	0	-92.31	-285.84	-641.82	0

Table 2
Consumption of heat carried away with reaction products (with full interaction HCl 15% with Mg)

Products obtained after the reaction	Mass of the products received, kg	Isochoric molar heat capacity under standard conditions, kJ/kg	Required amount of heat to raise the temperature of the obtained products by 1 degree,kJ/°K
Water	16999.9	4.18263	71104.706
Magnesium chloride	3958.3	0.794729	3145.776
Hydrogen	83.3	14.234830	1185.761
The sum of the required amount of heat for the reaction $(\sum m_i \cdot (C^0_v)_i)$			75436.243

Calculation of the amount of heat carried away with the reaction products - heat consumption is presented in table 4. The temperature of the mass after the reaction, calculated according to formula 5, will be calculated according to the basic and alternative options 513.881 °K and 517.5 °K accordingly. The margin of error is less than 1%. The third case is almost similar to the second, except for the addition of carrier water to the magnesium suspension. The water for the preparation of the carrier solution is calculated in the ratio of 140-150 kg of magnesium per 1 cubic meter of water. The algorithm for calculating the temperature according to the main (459.9 °K) and alternative (462.5 °K) the options are similar to the previous ones. The calculation error is less than 1%.

In the fourth variant, an excess of 15% concentration is used HCl compared with its full use in reaction with magnesium and the presence of a carrier solution and a buffer solution of water in the compositions. The optimal amount of buffer solution between the layers is 0.8 m^3. For a sample consisting of 3 layers, the amount of buffer solution is assumed to be equal to 2.4-2.6 m^3 taking into account the error. In addition, a solvent is additionally introduced into the composition to affect the chemical composition and structure of asphaltenes in a volume approximately equal to 2-4 m^3. In the practice of developing deposits, the geological structure of which is similar to the parameters of the deposits of the studied object, the experience of using large-volume injections of diesel fuel as a solvent agent is known. Its injection into the well is carried out after the reaction, on the basis of which a decrease in temperature due to interaction with octane compounds does not contribute to the colmation of highly permeable areas. Table 5 reflect the results of laboratory tests.

Table 3

The main indicators of magnesium interaction at different volumes of 15% hydrochloric acid

Initial compositions		Mass of reagents,kg	Isochoric molar heat capacity under standard conditions,kJ/kg	Amount of heat coming from the starting materials, kJ
Magnesium		1000	0.983898	293201.604
Sufficient volume of 15% hydrochloric acid	HCl	3041.7	0.791365	717314.286
	H_2O	16999.99	4.182630	21189202.334
Excess of 15% hydrochloric acid	HCl	456.260	0.791365	107598.322
	H_2O	2549.990	4.182630	3178368.073
Heat of reaction (Q_p)				18946000.0
Amount of heat				44431684.619

Table 4

Results of calculations of parameters when mixing excess 15% HCl and water in the composition of the carrier solution

Products obtained after the reaction		Weight of the received products, kg	Isochoric molar heat capacity under standard conditions,kJ/kg	Required amount of heat to raise the temperature of the obtained products by 1 degree $(m_i \cdot (C_v^0)_i)$, kJ/°K
Water		16999.999	4.18263	71104.706
Magnesium chloride		3958.3	0.794729	3145.776
Hydrogen		83.3	14.234830	1185.761
Excess 15% HCl	HCl	456.26	0.791365	361.068
	H_2O	2549.99	4.182630	10665.665
Water for preparation of the carrier solution		6896.550	4.182630	10665.665
Sum of the required amount of heat for the reaction $(\sum m_i \cdot (C_v^0)_i)$				115308.693

Table 5

Results of parameter calculations with full use of the initial reaction compositions

Source materials		Mass of reagents,kg	Isochoric molar heat capacity under standard conditions, kJ/kg	Amount of heat coming from the starting materials, kJ
Magnesium		1000	0.983898	293201.604
Hydrochloric acid, enough for the reaction	HCl	3041.7	0.791365	717314.286
	H_2O	16999.99	4.182630	21189202.333
Excess 15 %	HCl	456.260	0.791365	107598.322
	H_2O	2549.990	4.182630	3178368.073
Water in the composition of the carrier solution		6896.550	4.182630	8596023.644
Buffer solution 4 m^3		4000.0	2.0	2384000.0
Heat of reaction (Q_p)				18946000.0
Amount of heat				55411708.263

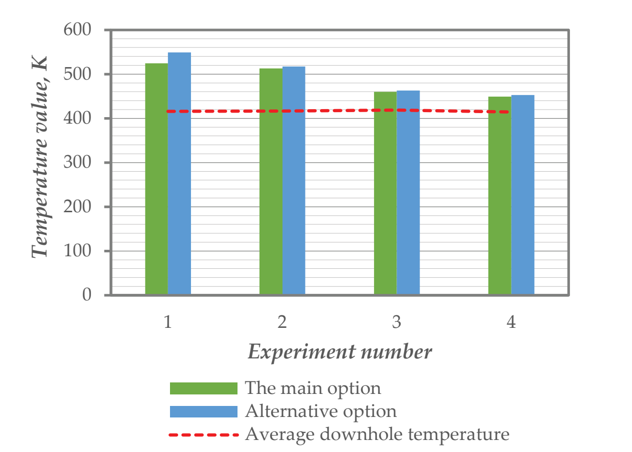

Fig. The dynamics of temperature changes depending on the experiment number and the average value of the bottom-hole temperature

The calculation error for the two options is less than 2%. Based on the results of the study, it should be noted that when magnesium interacts with water, a hydrolysis reaction occurs to produce magnesium hydroxide, which is significantly influenced by temperature. Achieving conditioned temperature values by creating certain conditions during a thermochemical reaction (low pumping speed of an acid solution, excessive volume of magnesium), magnesia cement can form, as a result of which it is possible to «bake» granulated magnesium and magnesium hydroxide powder. This will lead to complete clogging of the pore space and cracks of the bottomhole zone with a multiple decrease in the filtration-capacitance properties of productive formations.

Due to the high chemical activity of hot acid in relation to magnesium and the lack of effective inhibitors that are sufficiently active at high temperatures, thermochemical effects in order to intensify oil production must be carried out at the White Tiger field, subject to a reaction temperature of no more than 30-40 °K from the bottom-hole temperature. The figure shows a histogram of the temperature distribution depending on four different options.

The temperature determined in the fourth version of the study using the main components of the reaction and the buffer solution is higher than the temperature of the deposit at 36 °K, therefore, this composition can be recommended for use for thermochemical treatment of wells at the White Tiger field.

Conclusion

1. The need for a multiple increase in well productivity and the selection of residual oil reserves by economically cost-effective technologies determines the relevance of applied research aimed at empirically determining various parameters and taking them into account when planning real events.
2. The heat obtained as a result of the reaction of magnesium with hydrochloric acid affects the solvent (oil or diesel fuel), on the basis of which rapid dewaxing occurs, and an excessive amount of acid dissolves sediments on the surface of channels in the productive reservoir with additional heat release. This leads to an increase in the filtration and capacitance properties of the productive ones and an increase in the velocity of fluid movement in the borehole formation system.
3. The presented algorithm for calculating the thermal effect of the reaction «magnesium + hydrochloric acid» can be used for various reaction reagents.
4. The use of a composition based on excess 15% concentrations , the carrier water for magnesium suspension and buffer solution is recommended for the implementation of heat treatments at the White Tiger deposit and at facilities with similar geological and physical characteristics, in particular, with high bottom-hole temperature.

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