ХОЛОДИЛЬНА ТЕХНІКА ТА ЕНЕРГОТЕХНОЛОГІЇ

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Research of the process of obtaining thermal energy in static conditions of the course of an exothermic chemical reaction

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The generation of thermal energy remains the foundation of the global energy complex, where petroleum plays a pivotal role. For Ukraine, the issue of securing domestic fuel and energy resources is extremely acute, considering that approximately 66% of the 75 million tons of recoverable oil reserves are classified as hard-to-recover. In the late stages of field development, extraction efficiency drops sharply due to a temperature decrease in the near-wellbore zone below the wax appearance point. This triggers crystallization, obstructing pore throat conductivity and necessitating the application of thermal stimulation methods. This study investigates an enhanced oil recovery (EOR) method based on the exothermic reaction between granulated magnesium and hydrochloric acid to generate localized heat. To analyze the kinetics of this process under simulated downhole conditions with pressures up to 40 MPa, a specialized mobile high-pressure autoclave was designed and assembled. The experiments utilized 15% inhibited hydrochloric acid and magnesium granules with a fraction of 0,5-1,25 mm. Experimental data indicate that increased system pressure significantly inhibits the magnesium dissolution rate. This is explained by the reduction in size of the released hydrogen bubbles, which form a stable gaseous barrier on the granule surfaces, restricting reactant diffusion. At a pressure of 10 MPa, the temperature in the reaction zone reaches approximately 130°C within the first 150 seconds. Based on the findings, an empirical equation was derived to accurately describe the relationship between reaction time, amount of reacted material, and pressure. The practical significance of the research is demonstrated through calculated technological parameters for the Lukvynske field, where the proposed method effectively melts paraffin deposits and restores well productivity.

Keywords: *Chemical thermal energy; Exothermic reaction; Granulated magnesium; Hydrochloric acid; Pressure; Temperature.*

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1. Introduction

The economic development of any nation, including Ukraine, is largely dictated by the availability and management of fuel and energy resources. Securing these resources – specifically oil and gas – remains a matter of critical importance. Unfortunately, Ukraine is not fully self-sufficient in terms of domestic oil production, and there is little reason to expect the discovery and development of massive new high-capacity fields in the near future. Currently, Ukraine's recoverable oil reserves stand at approximately 75 million tons, of which roughly 66% are classified as hard-to-recover (Fig. 1).

The current oil recovery factor (ORF) is approximately 30% of the initial oil in place (IOIP), while the recovery factor for dissolved gas stands at 40%.

As natural reserves are gradually depleted, the rational use of energy resources becomes increasingly vital. This necessitates the optimization of existing

field development systems by integrating the theoretical foundations of thermal power engineering, which are rooted in the laws of thermodynamics, heat and mass transfer, and fluid dynamics. Such an approach allows for the study of irreversible thermobaric changes within porous media, providing a framework for improving extraction systems specifically for hard-to-recover oil reserves.

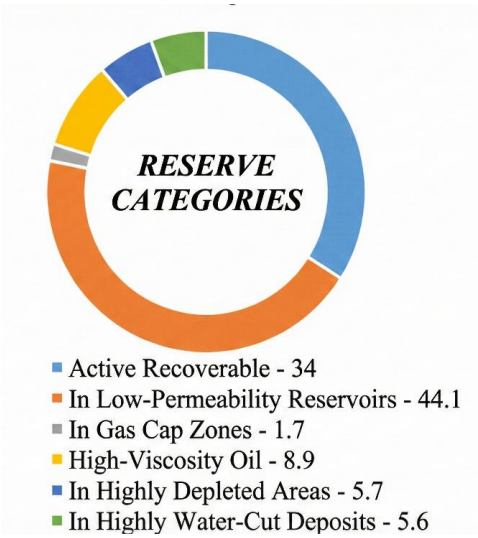

Figure 1 *– Distribution of oil reserves by categories*

2. Literature analysis

Obtaining thermal energy is the primary objective of heat power engineering as a field that integrates energy resources and carriers, production, conversion, transmission, and the utilization of various forms of energy [1, 2, 3, 4]. Currently, over 85% of thermal energy is produced from oil, gas, coal, and uranium, with oil remaining the most widespread and accessible source, accounting for approximately one-third of the global energy supply [5, 6, 7, 8, 9, 10].

Analysis of the development of Ukraine's oil industry indicates that it has passed its peak production period, which is inevitably followed by a decline. The maximum annual oil production (13.3 million tons) was achieved in 1972 [11]. This was ensured by the discovery and accelerated development of fields with relatively significant reserves. After 1972, oil production has been steadily decreasing. In 1976-1982, annual decline rates were 8.5-12%; in 1985-1991, 2.0-2.2%; and after 1992, the decline rates increased to 5-10%. The decrease in production volumes is primarily associated with the intensive depletion of reserves in major fields and their transition, starting from the 1980s, into the late stage of development.

During well operation, especially at the late stage of field development, a temperature drop occurs in the near-wellbore zone of the reservoir down to the paraffin saturation temperature of the oil, caused by adiabatic gas expansion or the Joule-Thomson effect [12].

The radius of the zone of potential paraffin deposits during well operation can reach up to 1.5 m but averages 0.2–0.5 m [13, 14, 15]. This phenomenon is most characteristic of many fields in the Precarpathian region, primarily Bythkiv, Lukvyn, Dovbushanka, Hvizdets, Popeliv, Boryslav, and others [16, 17]. For the same reason, reservoir properties may deteriorate during workover operations and bottomhole zone treatments. Significant cooling of the near-wellbore zone has been noted during the circulation of "cold" process fluids during well repairs and water injection into the reservoir [18, 19, 20].

The consequence of such cooling, or temperature reduction, is the formation and deposition of salt crystals, hydrates, asphaltenes, resins, and paraffins within the pore space and the filter part of the wells. Salt deposition, like hydrate formation, is caused by changes in the thermodynamic conditions of the reservoir system [21, 22]. The primary component of scale is calcium carbonate [23], which most often crystallizes from water due to the release of carbon dioxide as temperature and pressure decrease. The formation of natural gas hydrates occurs in both gas and oil fields [24].

However, the most common phenomenon in oil wells is the precipitation and crystallization of paraffin in the pore space of the reservoir and the wellbore. Research has confirmed that for oils with high paraffin content, the wax appearance temperature (WAT) is usually close to the reservoir temperature [14, 20, 25]. This is also supported by studies of several fields in the Precarpathian region [26].

Under such conditions, a minor change in the thermodynamic state of the reservoir, mainly in the near-wellbore zone, creates favorable conditions for paraffin to precipitate from the oil and transition into a solid phase, which is adsorbed onto the surfaces of pore channels and the near-filter zone [27]. Paraffin precipitates from oil as fine crystals capable of aggregating into dense compounds. This process is accompanied by the manifestation of the visco-plastic properties of the oil, the plugging of part of the pore channels, and, consequently, the deterioration of the reservoir's filtration characteristics.

The degree of interaction between paraffin and the rock depends on the physicochemical properties of the rock and the filtering fluid. The intensity of plugging is also influenced by the permeability of the porous

medium, its structure, the mineralogical composition of the rock, and the component composition of the oil – specifically the presence of asphaltenes, resins, and naphthenic acids. Notably, as the amount of asphaltenes in the oil increases, the number of crystallization centers grows sharply. Consequently, adsorption layers are formed on the surfaces of pore channels, consisting of paraffin along with naphthenic acids, low-molecular-weight resins, and colloidal particles of high-molecular-weight resins and asphaltenes. Asphalt-resinous substances gradually transition into a gel-like state, "cementing" paraffin and mineral particles into a single monolithic layer [28]. Given that the linear dimensions of paraffin crystals are 5-30 μ_m while pore sizes are 10-40 μ_m (and 15-25 μ_m in Precarpathian fields [30]), it can be argued that paraffin deposits predominantly plug the least permeable part of the pore space in the near-wellbore zone, which is most exposed to temperature changes. Thus, in fields with high-paraffin oils where there is a small difference between reservoir temperature and paraffin saturation temperature, slight cooling of the well bottom leads to paraffin precipitation and partial or total plugging of filtration channels, necessitating the use of thermal stimulation methods.

Temperature reduction at the bottomhole occurs both during the completion of productive horizons and during their operation. Studies [28, 29] have shown that when reservoirs are opened with cold drilling mud, especially in winter, paraffin deposits occur in the near-filter part. Analysis of industrial data [13, 20] indicates that as the flow rate of drilling fluid increases during the opening of a productive horizon, the initial productivity index of the well decreases and the cleanup time increases, signifying bottomhole cooling and the creation of conditions for paraffin precipitation in the reservoir, leading to a decrease in initial permeability.

An analysis of oil recovery enhancement methods at the Bytkiv oil field [33] shows that hydrochloric acid treatments and hydraulic fracturing (HF), which involve injecting large volumes of "cold" fluids into the oil-saturated pore space, lead to cooling of the near-wellbore zone, significantly reducing its flow capacity. Research [31] has shown that during hydraulic fracturing, when the fracturing fluid is injected at a temperature lower than the reservoir temperature, cooling occurs at significant distances from the fracture walls, creating conditions for paraffin precipitation and reducing the effectiveness of the HF. Similar results were obtained in studies of temperature changes during acidizing [32] and water shut-off operations.

Well productivity may also decrease due to so-called "pseudo-damage" of the near-wellbore zone. "Pseudo-damage" is caused by the formation of emulsions in the porous medium, the creation of water blocks (especially in gas wells), flow turbulence, and increased oil viscosity. It occurs in both injection and production wells during oil recovery enhancement operations [34, 35, 36].

During thermal treatment of wells with heated fluids to clean tubing and casing of paraffin deposits, the perforation holes in the near-filter part may become plugged with high-molecular-weight paraffins, asphaltenes, and inorganic compounds [37]. Acid treatments can cause reservoir contamination with reaction products, clay particles, colloidal silica, iron compounds, etc. [38, 39]. Thus, the degradation of the reservoir properties of the productive horizon around the wellbore begins from the moment the reservoir is penetrated by drilling and continues throughout the entire operation period. While many causes exist, the most significant ones, especially at the late stage of field development, are those that cause cooling of the reservoir system.

Combating the consequences of cooling is primarily achieved through thermal and thermochemical stimulation [24]. Therefore, thermal power processes play a vital role in increasing the efficiency of oil recovery. The issue of rational use of energy resources through the improvement of existing field development systems, considering the theoretical foundations of thermal power engineering based on the laws of thermodynamics, heat and mass transfer, and fluid dynamics, is becoming extremely urgent. This approach allows for the study of irreversible thermobaric changes in a porous medium and the formulation of directions for improving systems for extracting hard-to-recover oil reserves.

The main thermal power processes occurring in a porous medium are thermal conductivity and convective heat transfer. Thermal conductivity is the process of heat transfer by the structural particles of a substance (molecules, atoms, electrons) that are in chaotic motion and contact with each other. The structural particles of the more heated part of a body, which have higher energy, collide with surrounding particles and transfer part of their energy to them.

This type of heat transfer is observed in any thermally unbalanced bodies or systems of bodies. The mechanism of energy transfer depends on the physical

state of the bodies [40]:

- in metals, heat transfer is carried out through the motion (diffusion) of free electrons; the transfer of heat due to the elastic vibrations of the crystal lattice is considered secondary;
- in liquids and solid dielectrics, heat transfer is carried out through the direct transmission of the thermal motion of molecules and atoms to neighboring particles of the substance;
- in gases, heat transfer by thermal conductivity occurs as a result of energy exchange during the collision of molecules with different speeds of thermal motion (through the diffusion of molecules and atoms).

Thermal conductivity occurs through the solid matrix of the material, through the liquid or gas filling the pores, and at the contact boundaries between the solid phase and the fluid (liquid/gas).

In the porous medium of an oil reservoir, it acts simultaneously across all three phases: through the rock skeleton (as in dielectrics), the oil/water in the pores (as in liquids), and the gas in the pores (via molecular diffusion).

The concept of effective thermal conductivity $\lambda_{еф}$ is frequently used, which accounts for the total heat transfer by both the solid phase and its saturating fluids.

The most common form of heat transfer in a porous medium is convective heat transfer, a process driven by the macroscopic movement of fluid (oil, water, or gas) through a system of interconnected pores [24].

In the context of oil and gas engineering, this process is often referred to as heat transfer during filtration.

The mechanism of thermal convection in a porous medium consists of four components (Fig. 2):

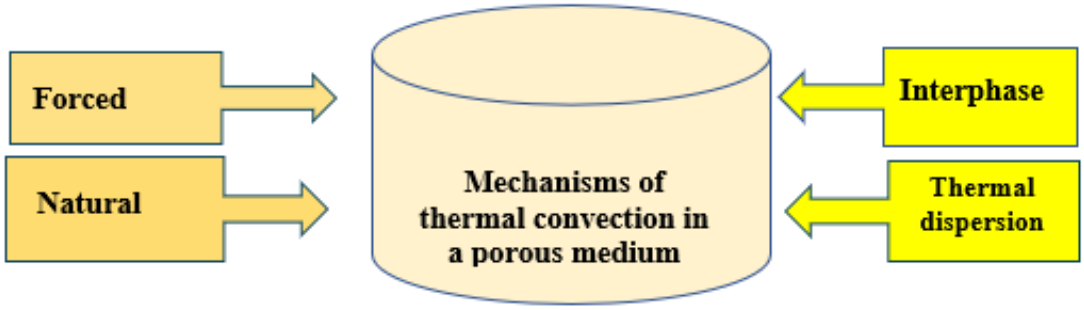

Figure 2 *– Main components of the thermal convection mechanism in a porous medium*

Forced convection occurs due to an external pressure differential, such as when hot steam or water is forcibly injected into the reservoir during the operation of an injection well. This is the primary mechanism in thermal oil recovery methods.

Natural or free convection takes place due to differences in fluid density across various parts of the reservoir, caused by its gravitational and thermal stratification.

Interphase heat transfer is based on the fact that fluid, while moving through the reservoir, constantly exchanges energy with the stationary solid rock skeleton. If the movement velocity is low, the temperatures of the fluid and the rock are considered identical (local thermal equilibrium model). At high velocities, especially near the well bottomhole, a temperature difference arises between the liquid and the rock (thermal non-equilibrium model).

Thermal or convective dispersion manifests when a fluid moves through the interconnected network of pore channels, where it constantly divides and mixes, causing the "blurring" of the thermal front.

The amount of heat transferred by convection depends on the filtration velocity and the thermophysical properties of the fluid:

$$Q_{conv} = \rho_f \cdot c_f \cdot \upsilon \cdot T \qquad (1)$$

where ρ_f – fluid density; c_f – specific heat capacity of the fluid; υ – filtration velocity vector; T – temperature.

Convection is much more efficient than thermal conductivity in terms of the rate of heating a specific section of the reservoir. It is thanks to convection that a thermal front is created, which moves from the injection well to the production well, ensuring oil displacement by hot water or steam and the reduction of oil viscosity.

During filtration convection (convective heat transfer), heat transfer is carried out by a moving fluid (gas

or liquid) filtering through the pores (the phenomenon of heat and mass transfer during filtration).

Intra-pore convective heat transfer is determined by the movement of fluid within individual pores (in the case of larger pore sizes).

All primary types of heat transfer occur within a porous medium, but their intensity and interaction are largely determined by the activity of the thermal action on the reservoir system.

Therefore, the established direction of research is undoubtedly timely and relevant for solving the tasks of providing thermal power engineering with a primary source of thermal energy.

3. Object, subject, and methods of research

One of the most effective methods for maximizing the recovery of residual oil reserves is the application of thermochemical well treatment, generating heat through an exothermic chemical reaction.

These treatments are based on the reaction of granulated magnesium with hydrochloric acid:

$$Mg + 2HCl + nH_2O = MgCl_2 + H_2 + mH_2O \qquad (2)$$

Granulated magnesium (often of the MGP grade – passivated granulated magnesium) consists of a finely dispersed metallic powder or spherical particles of a silver-gray color, containing over 99% pure magnesium (Fig. 3).

Figure 3 *– Granulated magnesium (photo)*

Ukrainian developments became the foundation for the industrial implementation of thermochemical treatment technologies, as it was in Ukraine that the production of granulated magnesium with a fraction of 0.5-1.0 mm was first established. The high efficiency of this technology is confirmed by its international recognition, specifically the launch of two large production facilities in China operating under Ukrainian patents [41, 42]. The practical implementation of the method involves organizing a controlled reaction directly in the well's perforation interval, where the interaction of magnesium granules with a 15% hydrochloric acid solution creates a local source of intensive heat generation to intensify oil production.

The shape of the particles is represented by spherical or ellipsoidal granules, which ensures high flowability. The size of the granules typically ranges from 0.5 to 1.25 mm.

In the oil and gas industry, it is regarded not simply as a substance, but as a "fuel" for initiating the heating of a formation or its specific section. Due to its high chemical activity, it allows for the creation of controlled, sustained heating directly within the zone where the reservoir system is fouled.

The use of magnesium for thermochemical or thermo-acid treatment offers strategic advantages:

- unlike hot water, which loses temperature as it moves down the wellbore, magnesium delivers thermal energy in a "canned" form;
- the temperature of the accompanying fluids in the reaction zone can reach 200-250°C, ensuring the melting of paraffin deposits and their subsequent removal to the surface;
- thermochemical heating ensures the melting of paraffin deposits, transforming them into a liquid phase, which is removed to the surface along with reservoir fluids;
- thermochemical reaction is accompanied by the release of gaseous hydrogen, which penetrates the pore channels, lowering the viscosity of the oil through mutual dissolution and the generated thermal energy;
- the reaction of magnesium granules with acid proceeds intensively until the magnesium is completely dissolved;
- besides the reaction with magnesium, the excess acid reacts directly with the rock, especially those of the carbonate type.

According to eq. (2), the reaction process forms magnesium chloride ($MgCl_2$), which has a sufficiently high solubility in water and is easily carried to the surface along with the oil after the treatment is completed. This guarantees that after the "thermochemical heating," the well will remain "clean."

For such operations, inhibited hydrochloric acid (concentration 12-15%) is typically used to prevent it from "corroding" the metal well pipes during the delivery of the acid to the reaction zone.

In the industry, "technical grade" hydrochloric acid

with a concentration of 33-37% is most commonly used. To bring the acid to a working 15% solution, the concentrated solution must be diluted with water.

The ratio of acid to water is determined by the following dependency:

$$C_1 \cdot V_1 = C_2 \cdot V_2 \qquad (3)$$

where C_1 – initial acid concentration; V_1 – initial volume of concentrated acid; C_2 – required concentration of the solution; V_2 – required volume of the solution.

During the chemical interaction between magnesium and hydrochloric acid, an intensive release of thermal energy occurs, amounting to 458.97 kJ/g-mol or 18.9 MJ per 1 kg of magnesium, providing the specified amount of thermal energy. For such operations, granulated magnesium is used, characterized by a physical density of 1740 kg/m³ and a bulk density of 880 kg/m³.

An important feature of the process is that the released hydrogen remains in a gaseous state; even under extreme conditions of high reservoir pressure and temperature, its solubility in the spent acid solution remains extremely low and does not exceed 18 ml/L. This ensures the effective use of the gas volume to create overpressure and improve the drainage properties of the formation.

There are two main approaches to the practical implementation of this technology, which differ in the sequence of reagent introduction into the reaction zone (Fig. 4).

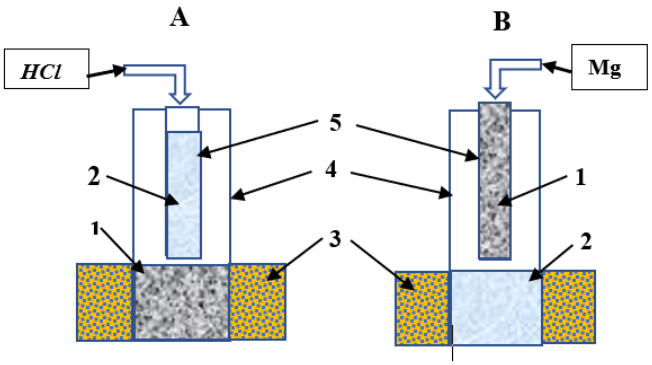

Figure 4 *– Schematic diagrams of thermal energy localization at the well bottomhole: 1 – magnesium granules; 2 – hydrochloric acid solution; 3 – productive formation; 4 – wellbore (production casing); 5 – tubing (production tubing)*

According to Scheme A, the well perforation interval is first filled with granulated magnesium, after which the hydrochloric acid solution is delivered to initiate the thermochemical reaction. Scheme B involves the reverse order: the wellbore itself is prefilled with acid, into which the required amount of magnesium is subsequently washed.

In the final stage, regardless of the chosen option, the spent hot solution is directed under pressure directly into the formation, where the accumulated thermal energy ensures the melting of paraffin plugs and the effective cleaning of the pore space from deposits.

The interaction between hydrochloric acid and magnesium during thermochemical treatments has been covered in works [42, 43, 44], but the authors did not account for the specific characteristics of the reaction under pressures close to wellbore conditions.

Under normal conditions, the interaction of granulated magnesium with hydrochloric acid is accompanied by the active release of hydrogen, which provides natural mixing of the reagents. This promotes the homogenization of the solution concentration and further accelerates the chemical process. However, as the pressure in the system increases, the volume of hydrogen bubbles decreases, which complicates the removal of reaction products from the metal surface. As a result, the interaction mechanism is transformed: the process ceases to be limited by the rate of the chemical reaction itself (kinetic phase) and begins to depend on the rate of mass transfer through the boundary layer (diffusion phase) [45, 46].

In this regard, the development of a suitable device for studying the characteristics of the exothermic reaction under conditions close to reservoir conditions becomes a pressing issue.

To study the specifics of the interaction between granulated magnesium and a hydrochloric acid solution under conditions close to reservoir conditions, a unique mobile autoclave was developed and assembled (Fig. 5).

The key element of the autoclave is a thermally insulated high-pressure chamber, the internal space of which is filled with kerosene, which is chemically neutral to the working system and reagents. Creating and maintaining the required operating pressure with kerosene allows for a detailed analysis of the kinetic parameters of the reaction under significant pressure loads.

Inside the autoclave, there is a glass beaker (2) containing acid, the bottom of which is broken by a brass rod (4) to initiate the reaction, and a porcelain container (3) with the reagent material (granulated magnesium). Sampling of the acid without stopping

the reaction under pressure is carried out using a tube (5), chemically neutral to the reacting substances, into a graduated cylinder (6). Maintaining the specified pressure during the acid solution sampling process is monitored by a master pressure gauge (7) and performed by a manual hydraulic press (8) from a kerosene tank (9). The temperature in the exothermic reaction zone is determined using a thermal sensor (10) with information transmitted to a recording device (11). The acid concentration in the initial solution and the collected samples is determined by the titrimetric method.

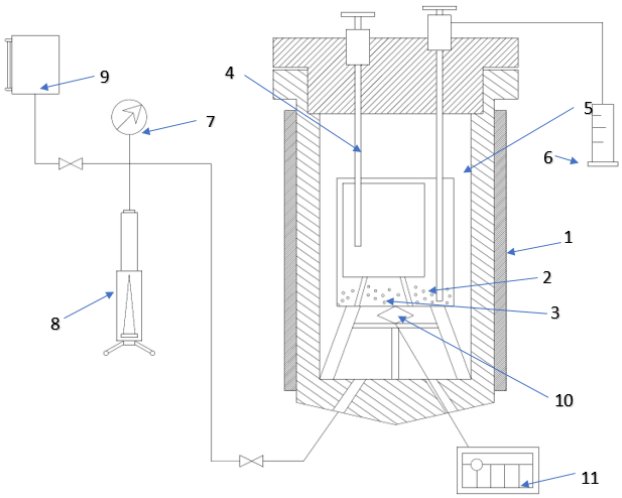

Figure 5 *– Autoclave for studying the kinetics of chemical reactions at pressures up to 40 MPa and temperatures up to 150 °C.*

In the experiments, a constant excess amount of acid (0.22 g-eq) and a constant initial amount of magnesium ($G_2 = 1{,}3 \cdot$g) were used.

The conversion of the amount of acid from g-eq to grams was carried out according to the known dependency [47]:

$$M_{eq} = \frac{M}{n} \qquad (4)$$

where M – molar mass of the substance; n – equivalent number.

According to eq. (4):

$$M_{eq} = \frac{M}{n} = \frac{36,46}{1} = 36,46\frac{g}{eq}$$

where M –molar mass of HCl (36,46 g/mol).

Mass of the pure substance m_{sol}:

$$m_{sol} = eq \cdot M_{eq} = 0,22eq \cdot \frac{36,46}{eq} \text{ or } 8,021\,\text{g} \qquad (5)$$

The mass of a 15% hydrochloric acid (HCl) solution is determined by the following dependency

$$m_p = \frac{m_{sol} \cdot 100\%}{C} = \frac{8,021 \cdot 100\%}{15\%} = 53,47g \qquad (6)$$

In conducting the research, 53.47 g of a 15% HCl solution (excess amount) was adopted for 1.3 g of magnesium.

The calculation of the amount of reacted magnesium (G1) is determined by eq. (6):

$$G_1 = 12,15 \cdot V_1 \cdot (N_0 - N_к) \qquad (7)$$

where G_1 – initial and current acid concentrations, g·eq/l; V_1 – acid volume, l. Initial acid concentration (N_0) in the experiments corresponded to15 %.

4. Results

In laboratory experiments, we have investigated the characteristics of thermal energy generation during the exothermic reaction of granulated magnesium with hydrochloric acid at pressures of 10, 20, and 30 MPa. This pressure range is the most appropriate (characteristic) for the oil fields of Ukraine and is entirely sufficient for obtaining generalized empirical dependencies [49, 50].

In accordance with the formulated conditions, table and Fig. 6 present the statistically processed results of the research on the kinetics of the exothermic dissolution of granulated magnesium in a 15% hydrochloric acid solution at system pressures of 10, 20, and 30 MPa.

Table *– Reaction time and pressure based on amount of reacted magnesium*

Reaction time, h	Amount of reacted magnesium at corresponding pressures, g		
	10 MPa	20 MPa	30 MPa
0,1	0,5	0,1	0,05
0,25	0,6	0,15	0,07
0,5	0,64	0,2	0,1
0,75	0,66	0,23	0,12

1	0,67	0,25	0,135
1,25	0,675	0,27	0,15
1,5	0,68	0,29	0,16
2	0,6802	0,32	0,18
2,5	0,6805	0,35	0,19
3	0,6808	0,37	0,2
3,5	0,681	0,39	0,212
	0,683	0,4	0,22

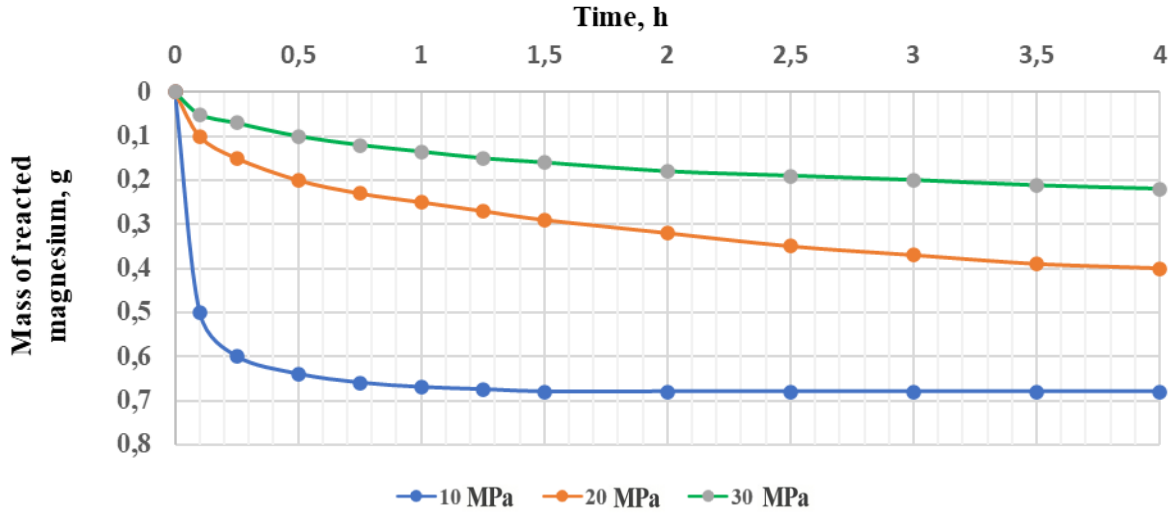

Figure 6 *– Kinetic curves of granulated magnesium dissolution in a 15% hydrochloric acid solution at pressures of 10, 20, and 30 MPa*

Figure 7 presents the results of research on temperature changes in the reaction zone at a pressure of 10 MPa, which is within the operating range of the majority of oil fields in Ukraine that are in the late stage of development [11, 14, 26]

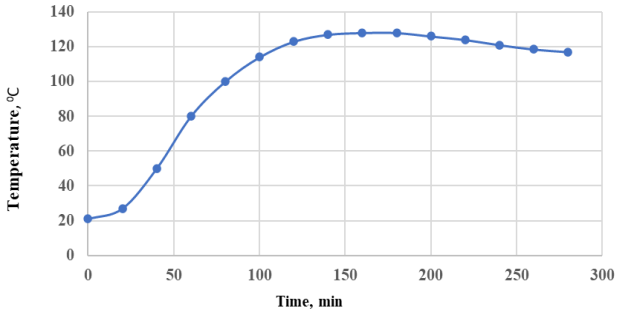

Figure 7 *– Dynamics of temperature change in the reaction zone at a pressure of 10 MPa*

Experimental studies have confirmed that the reaction rate, as well as the intensity of the thermal effect, slow down significantly with increasing pressure in the reaction zone (Figs. 3, 4). Thus, at a pressure of 10 MPa, the temperature reaches approximately 130 °C within the first 150 s, and then monotonically decreases. This is primarily due to the depletion of the active acid concentration and the reduction of the contact area between the reactants.

The mathematical interpretation of the experimental results [48, 49, 50] for system pressures from 0 to 30 MPa is described quite accurately by the empirical equation we obtained:

$$G_1 = G_2 \cdot [1 - \exp \cdot (0,41e^{-0,693P^{0,531}} \cdot \tau^{0,39-0,002P})] \quad (8)$$

where P – pressure in the reaction zone, MPa; τ – time from the start of the reaction, h; G_1, G_2 – amount of reacted magnesium and initial amount before the reaction, g.

Eq. (8) determines the dissolution time of granulated magnesium in a 15% hydrochloric acid solution at system pressures up to 30 MPa:

$$\tau = \left[\frac{\ln\left(1 - \frac{G1}{G2}\right)}{-0,41\exp \cdot (-0,63P^{0,531})} \right]^{\frac{1}{0,39-0,002P}} \quad (9)$$

The interaction of magnesium with hydrochloric acid is a typical example of a heterogeneous process, the intensity of which is determined by the rate of direct and reverse diffusion of reagents and products.

The rate of diffusion processes depends on the concentration gradient, while the kinetics of magnesium dissolution is proportional to the square of the acid concentration at the phase boundary. At a pressure of 10 MPa, approximately 60% of the metal mass dissolves within the first hour (Fig. 3). The decrease in reaction rate with increasing pressure is explained by changes in hydrodynamic conditions; specifically, hydrogen bubbles decrease in size and detach less effectively from the surface of the granules. The formation of such a stable gas shell shields the magnesium, limiting acid access to the metal and increasing the overall duration of the process.

Using the Lukvynske oil field as an example [51, 52], where the reservoir temperature (38 °C) slightly exceeds the paraffin crystallization temperature (35 °C), and its melting occurs only at 55 °C, we have demonstrated the possibility of generating thermal energy in the filter zone, as the most contaminated section of the wellbore.

The calculation of the required amount of heat for the destruction of paraffin deposits and their conversion into a liquid state is carried out on the basis of the classic calorimetric equation:

$$Q_T = \Delta T_1 \sum_{i=1}^{n} \varepsilon_i V_i \qquad (10)$$

where $\Delta T_1 = T_P - T_{por}$ – temperature increment or the difference between the paraffin melting point and the reservoir temperature; ε_i – heat capacity of the reactants; V_i – amount of reagents per linear meter of reservoir thickness or perforation interval.

The required amount of heat, taking into account the volumes of acid and pipes, can be determined by eq. (10):

$$Q = (T_K - T_P) \cdot (\varepsilon_{HCl} \cdot V_{HCl} + \varepsilon_K \cdot V_K) \qquad (11)$$

where T_K – temperature in the reaction zone, °C; T_P – reservoir temperature, °C; ε_{HCl} – specific heat capacity of the hydrochloric acid solution, kcal/kg°C; ε_K – specific heat capacity of the production casing pipes, kcal/kg°C; V_{HCl} – magnesium chloride solution volume, m^3; V_K – volume of the pipe metal within the productive horizon, m^3.

It is known [20, 24] that the amount of heat obtained during the interaction of acid with 1 kg of magnesium Q is 4,520 kcal. Based on this, the implementation of the technological process – for example, according to scheme A (Fig. 1) in a typical well of the Lukvynske field with a production casing diameter of 0.168 m and a perforation interval length of 8 m – requires the use of 86 kg of granulated magnesium (bulk density of magnesium granules is 880 kg/m³), which necessitates determining the optimal amount of reagents involved.

With a specific heat capacity of the hydrochloric acid solution ε_{HCl}, equal to 0,83 kcal/kg°C, for 86 kg of magnesium, the required amount of acid will be:

The ratio of acid to magnesium for the adopted well conditions, by analogy with the experiments (eq. 5), is:

$$m_{HCl} = \frac{m_{Mg} \cdot m_G}{G_2} = \frac{86 \cdot 54,47}{1,3} = 3537 kg \text{ or } 3,5\ \text{m}^3 \qquad (12)$$

where m_G – the amount of acid required to dissolve 1.3 g of magnesium.

In the eq. (11), m_{HCl} and $m_к$ can be calculated using eq. (12):

$$m = V \cdot \rho \qquad (13)$$

The volume of the casing pipes (V_K) in the filter (perforation) interval is determined as:

$$V_K = \left(\frac{\pi d_{outer}^2}{4} - \frac{\pi d_{inner}^2}{4} \right) \cdot h \qquad (14)$$

where d_{inner} and d_{outer} the outer and inner diameter of the production casing, then:

$$V_K = \left(\frac{3,14 \cdot 0,154^2}{4} - \frac{3,14 \cdot 0,146^2}{4} \right) \cdot 8 = 0,022 m^3 \qquad (15)$$

The mass of the pipes m_K is determined by:

$$m_K = V_P \cdot \rho = 0,022 \cdot 7850 = 172,7 kg \qquad (16)$$

The temperature difference between the reaction zone and the reservoir is determined by:

$$\Delta T = \frac{Q \cdot m_{Mg}}{V_{HCl} \cdot \rho_{HCl} \cdot \varepsilon_{HCl} + V_K \cdot \rho_K \cdot \varepsilon_K} \qquad (17)$$

or:

$$\Delta T = \frac{Q \cdot m_{Mg}}{m_{HCl} \cdot \varepsilon_{HCl} + m_K \cdot \varepsilon_K} \qquad (18)$$

It follows that the temperature difference will be:

$$\Delta T = \frac{4520 \cdot 86}{3539 \cdot 0,83 + 172,7 \cdot 0,46} = 128,8\ °C \qquad (19)$$

Based on the temperature difference, it is possible to calculate the required temperature – and, specifically, the amount of heat generated at the bottom of the well – due to the exothermic reaction of magnesium with hydrochloric acid under static reaction conditions:

$$T_r = \Delta T + T_P = 128{,}8 + 35 = 163{,}8\,°C \qquad (20)$$

The presented research results on generating thermal energy at the bottom of the well indicate the feasibility of achieving temperatures significantly higher than the melting point of paraffin.

Thus, applying the principles of thermal engineering to generate heat through an exothermic reaction makes it possible to clear the filtration zone of paraffin deposits and increase the oil productivity of the well.

5. Conclusions

It has been confirmed that fuel and energy resources – the supply of which, particularly oil and gas, remains extremely relevant – are the most widespread in the functioning of thermal power engineering as an industrial sector.

The effectiveness of using an exothermic chemical reaction as a method for generating thermal energy at the bottom of oil wells to increase their productivity has been proven.

It has been shown that the reaction of granulated magnesium with hydrochloric acid allows for the creation of a local thermal energy source at the bottomhole, aimed at clearing paraffin deposits from the filter zone, increasing the flow rate, and improving the recovery of residual, hard-to-extract oil reserves.

A conceptual design for a mobile high-pressure autoclave has been proposed for the rapid study of exothermic reaction kinetics under conditions closely resembling real well environments.

The influence of pressure on the rate of heterogeneous reactions accompanied by the release of a gaseous phase has been experimentally confirmed.

An empirical equation for the kinetics of magnesium dissolution in a hydrochloric acid solution has been obtained in "pressure-reaction time" coordinates.

Technological schemes for implementing the thermal energy generation process under static conditions of an exothermic chemical reaction at the bottomhole have been developed.

The procedure for generating thermal energy at the bottom of a typical well in the Lukvynske oil field has been demonstrated.

The presented research results serve as a significant basis for further studies on the dynamics of exothermic reactions within the oil-saturated pore space.

CRediT author statement

Volodymyr Doroshenko: Investigation, Data Curation, Visualization, Validation Writing – Review & Editing. **Oleksandr Titlov:** Conceptualization, Formal analysis, Project administration, Supervision, Methodology, Writing – Original Draft

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Дослідження процесу отримання теплової енергії в статичних умовах перебігу екзотермічної хімічної реакції

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Генерація теплової енергії залишається основою світового енергетичного комплексу, де нафта відіграє ключову роль. Для України питання забезпечення власних паливно-енергетичних ресурсів є надзвичайно гострим, враховуючи, що приблизно 66 % з 75 мільйонів тонн видобувних запасів нафти класифікуються як важковидобувні. На пізніх стадіях розробки родовища ефективність видобутку різко падає через зниження температури в присвердловій зоні нижче точки появи парафіну. Це провокує кристалізацію, перешкоджаючи провідності порового каналу та зумовлюючи необхідність застосування методів термічної стимуляції. У цьому дослідженні досліджується метод підвищення нафтовіддачі (ПНВ) на основі екзотермічної реакції між гранульованим магнієм та соляною кислотою для генерації локалізованого тепла. Для аналізу кінетики цього процесу в імітованих умовах свердловини з тиском до 40 МПа було спроектовано та зібрано спеціалізований мобільний автоклав високого тиску. В експериментах використовували 15% інгібовану хлоридну кислоту та гранули магнію з фракцією 0,5-1,25 мм. Експериментальні дані свідчать про те, що підвищений тиск у системі значно гальмує швидкість розчинення магнію. Це пояснюється зменшенням розміру бульбашок водню, що вивільняються, які утворюють стабільний газовий бар'єр на поверхні гранул, обмежуючи дифузію реагентів. При тиску 10 МПа температура в зоні реакції досягає приблизно 130°C протягом перших 150 секунд. На основі отриманих результатів було виведено емпіричне рівняння, яке точно описує зв'язок між часом реакції, кількістю прореагованої речовини та тиском. Практичне значення дослідження демонструється за допомогою розрахункових технологічних параметрів для Луквинського родовища, де запропонований метод ефективно плавить парафінові відкладення та відновлює продуктивність свердловин.

Ключові слова: *Хімічна теплова енергія; Екзотермічна реакція; Гранульований магній; Хлоридна кислота; Тиск; Температура*