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Study on carbon dioxide thermodynamic behavior for the purpose of shale rock fracturing

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Abstract. The possibility of using CO_2 to fracturing a shale rock has been presented in the paper. The described innovative method which allows for the efficient extraction of shale gas and carbon dioxide storage in a shale rock was developed in Department of Mechanics and Applied Computer Science at the Military University of Technology, Warsaw, Poland. Firstly, the method was verified on the base of analytical and experimental research. In the next stage of the method verification carbon dioxide thermodynamic behavior was studied. The growth in pressure of drop of CO_2 heated in a closed volume was numerically tested. The research confirmed the efficiency of the use of carbon dioxide as a medium for fracturing of rocks. The usage of liquid CO_2 can be alternative for hydraulic fracturing and is safe for the environment.

Key words: carbon dioxide, shale gas, storage system, thermodynamics, FEM.

1. Introduction

According to the most general selection criteria of natural gas, it can be distinguished as a constituent of conventional and unconventional deposits. Exploitation of the first kind of deposits does not cause problems, and a recovery process has been known since 19th century. The situation is different in the case of beds in which gas is dispersed in small pores in the rock [1].

Unconventional gas is more difficult and that makes it less economical to operate. In Poland the so called shale gas is the best known, but also other unconventional deposits types can be distinguished. Besides shale gas tight gas, coal bed methane, deep gas and gas hydrates are also present (Fig. 1). They are mainly differentiated because of a place of extraction (shale rocks, isolated pores of rock, coal deposits) [1].

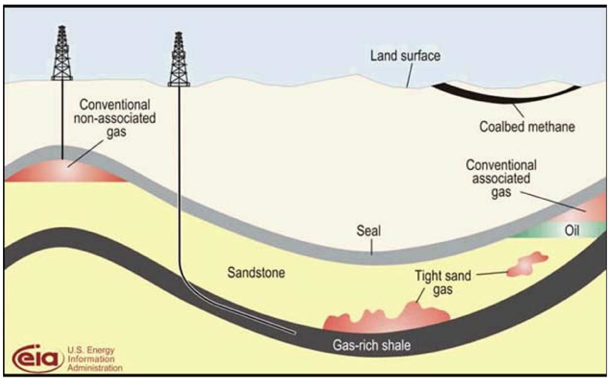

Fig. 1. Types of natural gas deposits after Ref. 1

Natural gas was created over million years from the rotting organic matter – different kinds of plants, plankton and animals covered with a thick layer of organic sediments. After a long heating with the Earth's internal heat, heavy and light fractions of petroleum and natural gas started to precipitate from the compost. Gas was migrating to the surface until it met a trap in the form of porous rocks, also isolated from the top by impermeable rocks [1, 2]. These traps can be assumed as large tanks, from which conventional gas can be recovered with no major problems through the vertical wells.

Shale gas is located in rocks, in which it was originally developed. Having a small permeability, the rocks preserved gas inside not letting him to raise the upper layers of the soil (Fig. 2).

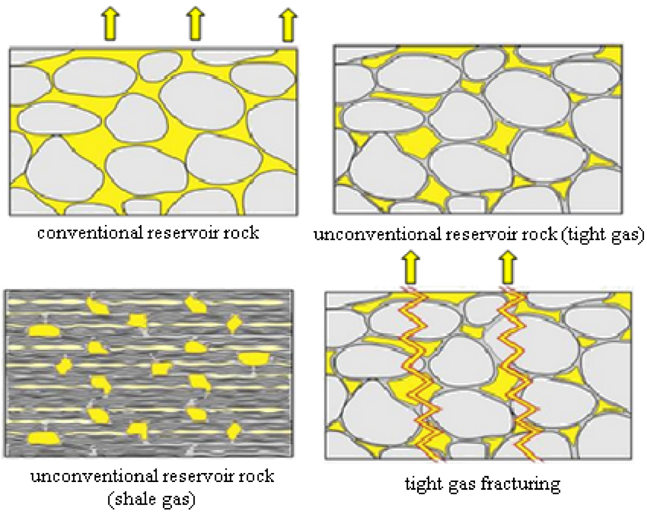

Fig. 2. Natural gas deposits Ref. 1

Similar to a conventional hydrocarbon system, unconventional gas reservoirs are characterized by complex geological and petrophysical systems as well as heterogeneities – at all scales. However, unconventional gas reservoirs typically have

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a very fine grain rock texture, exhibit gas storage and flow characteristics which are uniquely tied to the nano-scale pore throat and pore size distribution and possess the common organic and clay content that serve as gas sorption sites. The gas-shale reservoir pore structures are defined in terms of nanometers to micrometers, whereas most tight gas reservoirs are described at a micrometer or larger scale. Both gas shale and tight gas systems have free gas stored within the pores of the rock matrix. Gas-shale differs in possessing the characteristic of gas adsorption on surface areas associated with an organic content and clay [3].

Bustin et al. [4] states that the relative importance of adsorbed versus free gas varies as a function of the amount of organic matter present, pore size distribution, mineralogy, digenesis, rock texture and reservoir pressure and temperature.

The study on the carbon dioxide thermodynamic behaviour carried out with the use of the finite element method is presented in the paper. The aim of the research is to check if the subcritical CO_2 drop injected on the hot rock surface can explode.

2. Research background

The first attempts to exploit shales was taken in 1821, but due to the low yield of this type of production, they were soon stopped.The change was brought by the development of drilling technology and the usage of vertical drillings instead of horizontal ones coupled with the cracks network methods development. Commonly used method of fracturing is a hydraulic fracturing. This method consists of injecting into the borehole a large amount water with the granules (sand) and chemicals admixture at a pressure of about 60MPa to crack rocks and to release the gas trapped. The admixture of sand is to prevent closing slots after the pressure reduction. The described fracturing method causes many objections. Firstly, it can cause groundwater contamination by chemical substances used in the fracturing process. Secondly, the procedure needs to use a large amounts of water. Consumption and contamination of such significant quantities of water may arise objections. A part of water volume returns to the surface, however, it is additionally contaminated with heavy metals and requires utilization. The described disadvantages of the method caused seeking for another fracturing medium, such as an inert gas easily condensable and widely available in the environment. One of such gases is CO_2. A process of injection of CO_2 cannot only enable rocks fracturing, but also its geological storage. The last argument is particularly important in the context of CO_2 emission limits introduced by the European Union, which are associated with severe financial penalties. These are the arguments for considering CO_2 as a medium in rock fracturing [5].

Shale is characterized by its dual porosity: it contains both primary (micro pores and meso pores) and secondary (macro pores and natural fractures) porosity systems. The primary porosity system contains the vast majority of the gas-in-place, while the secondary porosity system provides the conduit for mass transfer to the wellbore. Primary porosity gas storage is dominated by adsorption. Primary porosity is relatively impermeable due to its small pore size. Mass transfer for each gas molecular species is dominated by diffusion that is driven by the concentration gradient. A flow through the secondary porosity system is dominated by the Darcy flow that relates a flow rate to the permeability and pressure gradient – see Fig. 3 [3].

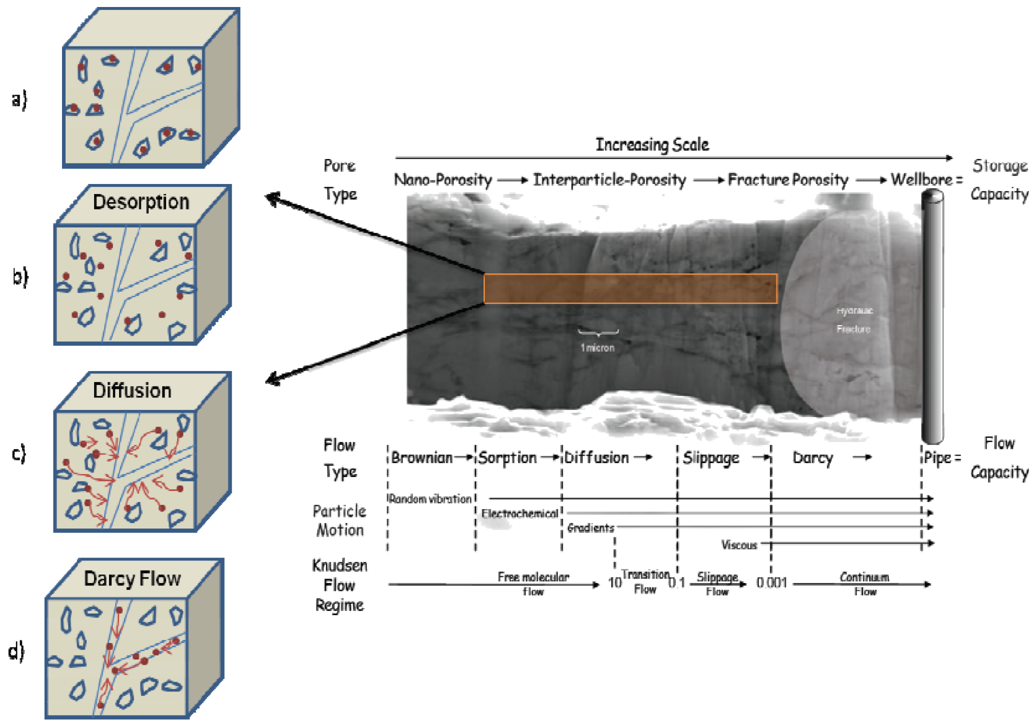

Fig. 3. Flow types and behaviour in shale reservoirs Ref. 3

When the pressure of a natural fracture system in shale drops below the critical desorption pressure, methane starts to desorb from the primary porosity and is released into the secondary porosity system near the natural fractures, and then is reduced. This reduction creates a concentration gradient that results in mass transfer by diffusion through the micro and meso porosity. The adsorbed gas continues to be released as the pressure is reduced [3].

On the base of those mechanisms the analyses of the new innovative method of gas shale fracturing and gas recovery coupled with carbon dioxide storage have been developed in the Department of Mechanics and Applied Computer Science of the Military University of Technology.

The presented method of gas shale fracturing and gas recovery coupled with carbon dioxide storage was submitted by Military University as the patent no P.398228.

The method of the shale gas recovery coupled with CO_2 sequestration from the horizontal small-diameter wellbores made in a single vertical wellbore has been the subject of the proposed innovation.

The steps of the proposed method are presented below:

1. Firstly the horizontal wellbores have to be specially prepared in the shale gas deposit situated between solid rock beds (Fig. 4a). The existing horizontal wellbores can be also used.
2. Then the horizontal small-diameter wellbores are made circumferentially in a single vertical wellbore at a few depths (Fig. 4b).
3. The shale rock in the deepest wellbore can be initially perforated with the use of e.g. quasi-cumulative explosives. The upper not perforated horizontal wellbores are closed with the use of pins or valves. The elastic or half-elastic isolated or pre-cooled pipelines are installed in the open horizontal wellbores (Fig. 4c).
4. Then liquid cooled CO_2 is injected into the shale gas reservoir with the use of a cryogenic pump. During the injection the pipelines are progressively pull out from the horizontal wellbores for the precise filling of fractures. The CO_2 injection process is finished after total pipeline pulling out (Fig. 4d). The CO_2 injection process needs a continuous control of the temperature and pressure in the wellbore.
5. The open wellbores are closed with pins or valves controlled from a surface. The thermodynamic process of heating cooled liquid CO_2 in the reservoir is started. The process adsorption of CO_2 and desorption of CH_4 can last about 2 weeks (Fig. 4e). The temperature and pressure in the reservoir are controlled with the special set of sensors.
6. The upper not perforated horizontal wellbores are opened. The recovery of the shale gas can be carried out intrinsically (Fig. 4f). The whole process can be repeated for upper wellbores.

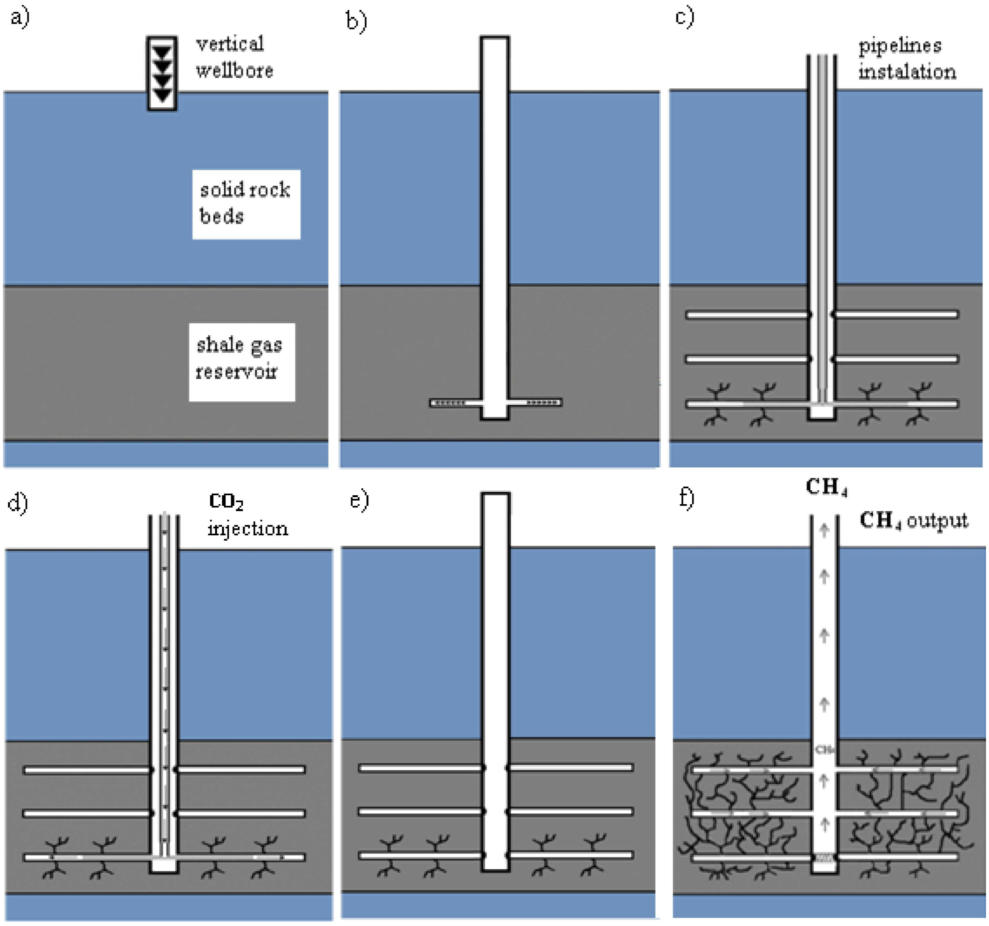

Fig. 4. Scheme of method of gas shale fracturing and gas recovery coupled with carbon dioxide storage

3. Experimental and analytical verification of the method

The method was verified on the base of analytical and experimental research. Assessment of the possibility of using CO_2 to gas fracturing performed on the base of CO_2 thermodynamic behavior chart (Fig. 5).

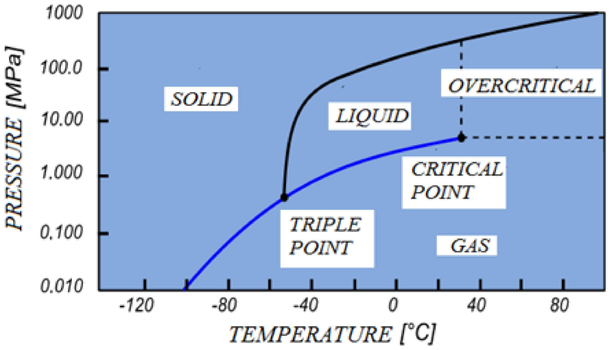

Fig. 5. CO_2 thermodynamic behavior chart

The value of a shale gas tensile strength can be found in the literature [6]. It varies between 3 and 18 MPa (depending on the shale deposit location) under the standard pressure. So, if the pressure of CO_2 after heating in the deposit reaches that value, the method will be assumed to be correct.

The analytical calculations for thermodynamic behavior of isochoric heating of CO_2 from the temperature value of $-40°$ (2 MPa) to 120°C (a temperature in the shale reservoir) and from 20°C (7 MPa) to 120°C.

The calculations were carried out with the use of REFPROP (Reference Properties) computer code developed by the National Institute of Science and Technology (NIST). The code calculates the thermodynamic and transport properties of industry fluids and their mixtures with special consideration of cooling agents and hydrocarbons.

The Span-Wagner equation of state was applied for the CO_2 thermodynamic behavior description. The equation is an empirical representation of the fundamental equation of Helmholtz energy. Usually the dimensionless function of Helmholtz energy $\phi = a/(RT)$ dividend of an ideal gas part ϕ^0 and residual part ϕ^r [7] is used:

$$\varphi(\tau, \delta) = \varphi^0(\tau, \delta) + \varphi^\tau(\tau, \delta), \tag{1}$$

where τ– inverse of reduced temperature $\tau = T_c/T$, δ – reduced density $\delta = \rho/\rho_c$, $T_c$and ρ_c – temperature and density at critical point.

The calculations were performed for two states of liquid CO_2: $(-40^{|circ}$C, 2 MPa) and (20°C, 7 MPa). The analytical calculations results were presented in Fig. 6. On the base of those results it can be concluded that the final value of heated CO_2 exceeded the value of the shale rock tensile strength (212 MPa for the starting point -40°C, 2 MPa and 58 MPa for the starting point 20°C, 7 MPa) and can cause its damage. In both cases the minimum pressure required for the cracking of the rock was achieved.

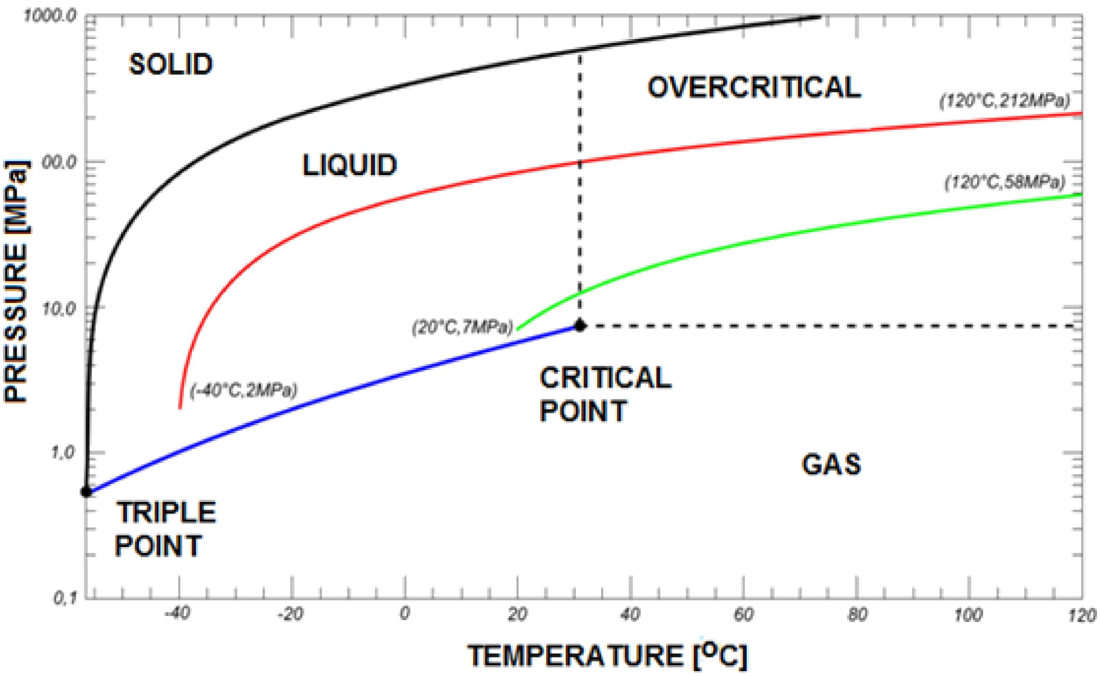

Fig. 6. Isochoric process of heated CO_2

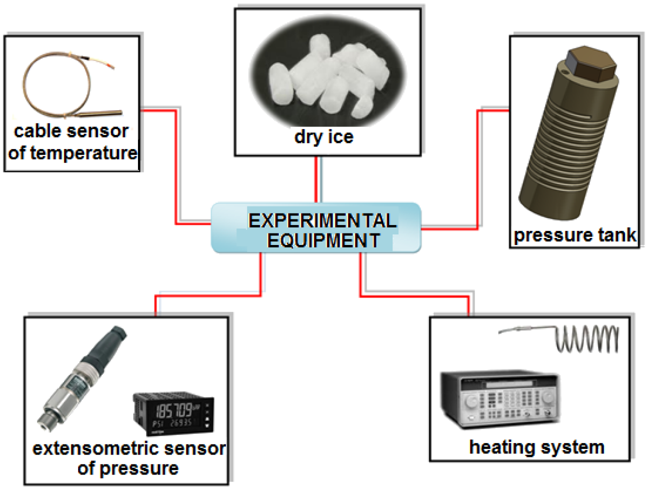

Fig. 7. Research equipment for CO_2 thermodynamic behavior testing

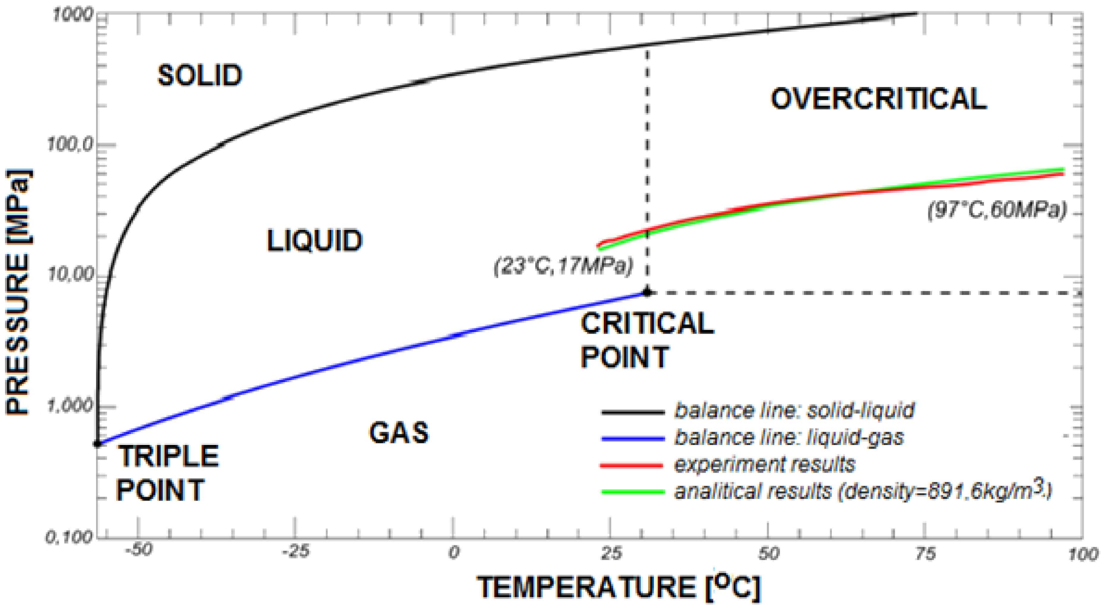

Fig. 8. Comparison of analytical and experimental tests of CO_2 heating

For the purpose of an analytical tests verification the experimental test of the isochoric CO_2 heating process was carried out. The CO_2 was used in the form of a solid dry ice. It was heated in the closed pressure tank from the temperature of 23°C to 97°C. The temperature was measured with the use of a cable sensor and pressure was measured with the use of an extensometric sensor. The research equipment is presented in Fig. 7.

The comparison of both analytical and experimental tests is shown in Fig. 8. The results showed good compatibility that proved the correctness of an analytical method.

4. Numerical study of drop of CO_2 heated in a closed volume growth pressure

The next stage of the analysis of carbon dioxide thermodynamic behavior was to study a growth in pressure of a drop of CO_2 heated in a closed volume.

An analysis was performed with the use of coupled LS-Dyna and REFPROP computer codes. With the use of LS-Dyna the CO_2 temperature vs. time changes were calculated and with the use of REFPROP the nonlinear thermal properties (thermal conductivity and heat capacity) as a function of temperature as well as changes of pressure vs. time on the basis of temperature changes vs. time were calculated.

It was assumed that the drop of carbon dioxide is locked in the closed heating capsule and in the initial phase of an analysis the pressure in the capsule provides a CO_2 liquid state.

In accordance to the symmetry of the researched phenomenon 1/8 model was built (Fig. 9). Dimensions of the model were as follows: 0.75 mm × 0.75 mm × 0.75 mm when the radius of the drop of carbon dioxide was 0.5 mm. On the external surface of a model adiabatic conditions were assumed. The initial temperature of the drop of carbon dioxide was

253K at the density of 1032 kg/m^3. However, the temperature of the capsule, which was used to heat the CO_2 was 373 K and was constant. The analysis was of the nonlinear, thermal type.

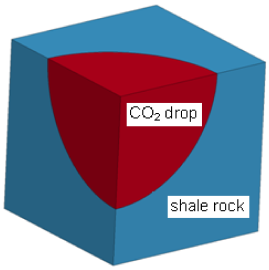

Fig. 9. FE model geometry

The model was developed with the use of 11000 hex finite elements. The description of finite elements is as follows:

- hex elements,
- fully integrated elements,
- every element has eight nodes or 8 points of integration,
- every node has three degrees of freedom [8].

The thermal isotropic material model was used for simulating CO_2 (T01) and shale rock (T02). Physical properties of the materials used to build the model are presented in Table 1 [9].

Table 1
Physical properties of materials Ref. 9

Material	Density [kg/m^3]	Heat capacity [J/kgK]	Thermal conductivity [W/mK]
Shale rock	1500	1200	0.26
Carbon dioxide	1032	See Fig. 10	See Fig. 11

Conduction of heat in an orthotropic solid in LS-Dyna is calculated as follows:

- the differential equations of conduction of heat in a three-dimensional continuum is given by

$$\rho\, c_p \frac{\partial \theta}{\partial t} = (k_{ij}\,\theta_{,j})_{,i} + Q, \tag{2}$$

- subject to the boundary conditions

$$\begin{aligned} \theta &= \theta_s \quad \text{on} \quad \Gamma_1, \\ k_{ij}\,\theta_{,j}\,n_i + \beta\theta &= \gamma \quad \text{on} \quad \Gamma_2 \end{aligned} \tag{3}$$

- and initial conditions at t_0:

$$\theta_\Gamma = \theta_0(x_i) \quad \text{at} \quad t = t_0 \tag{4}$$

where
$\theta = \theta(x_i, t)$ – temperature,
$x_i = x_i(t)$ – coordinates as a function of time,
$\rho = \rho(x_i)$ – density,
$c_p = c_p(x_i, \theta)$ – specific heat,
$k_{ij} = k_{ij}(x_i, \theta)$ – thermal conductivity,
$Q = Q(x_i, \theta)$ – internal heat generation rate per unit volume Ω,
θ_Γ – prescribed temperature on Γ_1,
n_i – normal vector Γ_2.

Equations (2)–(4) represent the strong form of a boundary value problem to be solved for the temperature field within the solid [8].

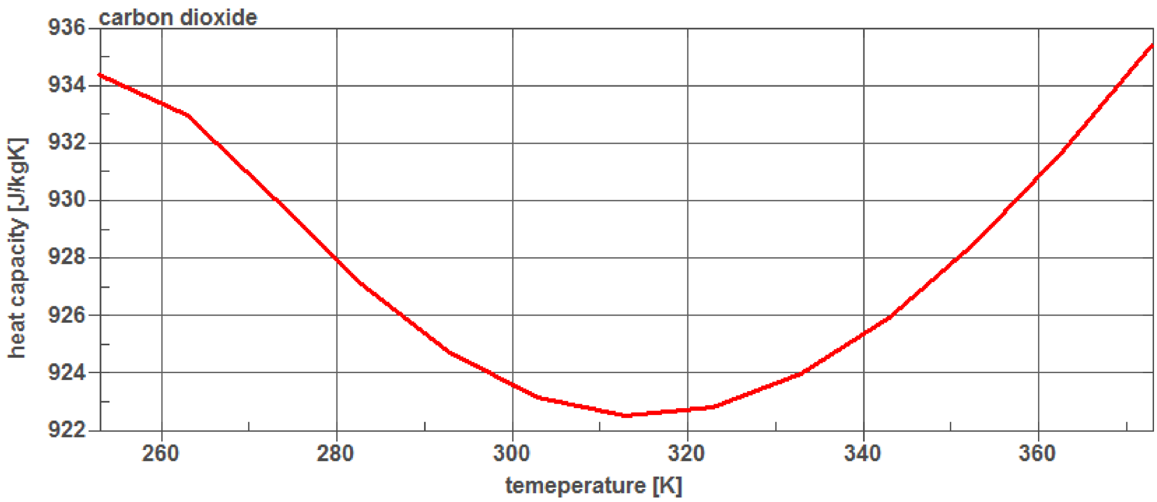

Fig. 10. Heat capacity vs. temperature chart

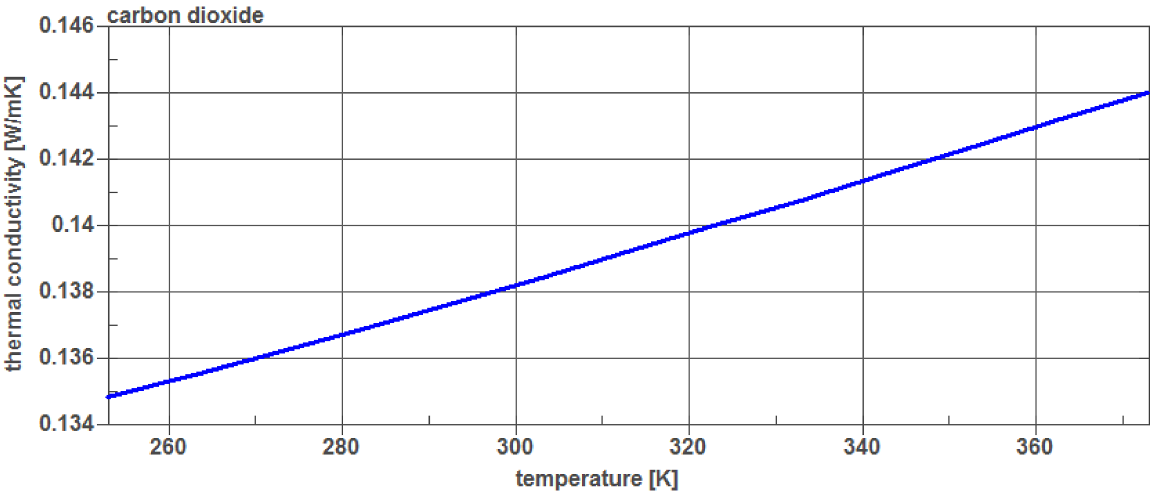

Fig. 11. Thermal conductivity vs. temperature chart

a)

b)

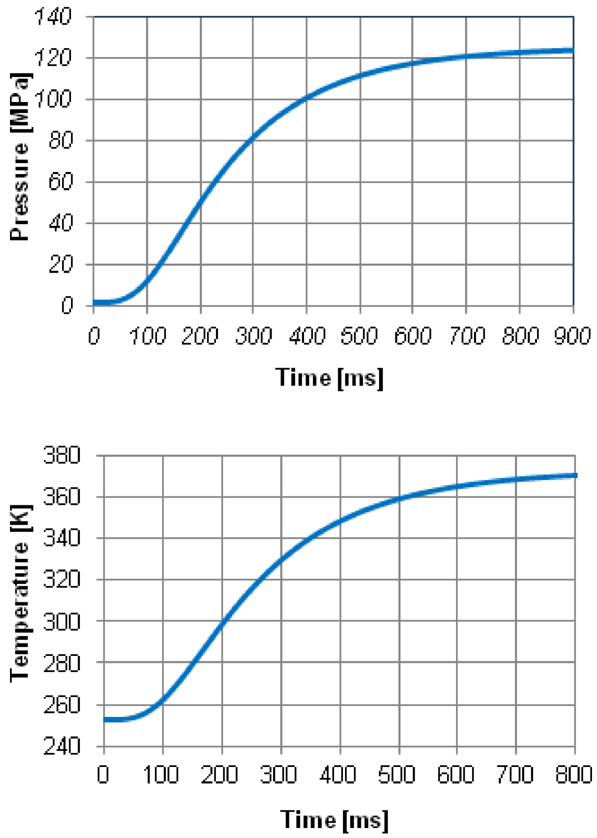

Fig. 12. Drop of CO_2 heating: a) pressure vs. time chart b) temperature vs. time chart

On the basis of nonlinear thermal analysis curves (Figs. 10–11) were determined, which represent thermal properties of liquid carbon dioxide that was transformed isochorically (volume = constants) from the temperature of 253 K to 373 K. They were calculated in REFPROP computer code. In this case the program uses a thermal conductivity of the Vesovic pure liquid model and the Span-Wagner equation of state [7]. The calculation results were implemented in LS-Dyna for modeling CO_2 thermal behavior.

The changes in pressure and temperature versus time achieved with the use of LS Dyna code are shown in Figs. 12a) and b), respectively.

The results presented in the charts Fig. 12a) and b) show that both pressure and temperature of carbon dioxide increases with time. The increase in pressure and temperature is not rapid. The achievement of maximum pressure after the period of 0.9 s allows to conclude that the transformation is not explosive.

5. Conclusions

The paper describes the innovative method which allows for the efficient extraction of shale gas and a carbon dioxide storage shale rock. The method was verified on the base of analytical and laboratory experimental research.

The presented research results showed the possibility of the liquid CO_2 use for shale fracturing and for damage of rocks at a large depth.

The analyses showed that the usage of liquid CO_2 of initial parameters of (20°C,7 MPa), that are close to the thermodynamic state in commonly used carbon dioxide tanks, allows to reach the fracturing pressure of shale rocks.

The usage of liquid CO_2 can be an alternative for hydraulic fracturing that currently uses water and chemicals. The proposed method can be utilized for greenhouse gas storage after the shale gas deposit exploitation by closing the wellbore. It is an ecologically desirable effect.

Moreover, on the base of the analysis of numerical research it can be concluded that the use of carbon dioxide to the crushing of rocks is a safe option. It is proved with a study of growth in pressure of CO_2 drop heated in a closed volume, which showed that the increase in pressure is not rapid, so the process is not explosive. Finally, it can be concluded that the proposed method of shale gas recovery is safe, it will not cause local earthquakes or bounces.

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