2-бөлім Механика

Раздел 2 Механика

Section 2 Mechanics

УДК 53.04

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Modeling of bacterium influence on methane concentration in underground storage of hydrogen

The problem of underground hydrogen gas mixture storage is that unlike natural gas, hydrogen gas mixture undergoes chemical changes in underground storage and thus the concentration of hydrogen and carbon dioxide is reduced, and the concentration of methane increases. It has been found that these changes occur because of the activity of methanogenic bacteria populations inhabiting in a reservoir. This chemical activity, which caused by the bacterial activity, as well as gas and water flow in the reservoir causes the phenomenon of self-organization such as the occurrence of autowave spatial structures, the dynamics of which is characterized by a multiplicity of different scenarios, including the occurrence of chaos and the jump from one scenario to another. In this paper we developed a qualitative theory of self-organization scenarios in the underground hydrogen storage depending on the external and internal parameters. Development of the theory and computer models of transport in underground hydrogen storage will be based on the relating of models of multiphase composite flows in porous media with model of dynamics of bacterial populations which will be based on mechanism of chemotaxis (internal chemical mechanism by which bacteria are able to detect the presence of nutrients in the distance and move in that direction).

Key words: Porous media, Hydrogen, Bacteria, Neuston, Chemotaxis.Population dynamics, Oscillations.

Толеуханов А., Панфилов М., Калтаев А.

Моделирование воздействия бактерий на концентрацию метана при подземном хранении водорода

Проблема подземного хранения газовой смеси водорода состоит в том, что в отличие от природного газа, водородная газовая смесь претерпевает химические изменения в процессе хранения, тем самым концентрация водорода и углекислого газа понижается, а концентрация метана растет. Было установлено, что эти изменения происходят из-за активности популяции метаногенных бактерий, обитающих в пласте. Эта химическая активность, вызываемая деятельностью бактерий, а также течение газа и воды в пласте вызывает явление самоорганизации такое, как появление автоволновых пространственных структур, динамика которых характеризуется множеством различных сценариев, в том числе возникновение хаоса и переход с одного сценария на другой. В настоящем работе предлагается разработать качественную теорию сценариев самоорганизации в подземных хранилищах водорода в зависимости от внешних и внутренних параметров. Разработка теории и компьютерных моделей переноса в подземном хранилище водорода будет строиться на базе связки теории многофазных композиционных течений в пористых средах с моделью динамики популяций бактерий, которая будет основана на механизме хемотаксиса (внутренний химический механизм, благодаря которому бактерии обладают способностью детектировать наличие питательных веществ на расстоянии и двигаться в этом направлении).

Ключевые слова: Пористая среда, водород, бактерия, нейстон, хемотаксис, динамика популяций, осцилляция.

Толеуханов А., Панфилов М., Калтаев А.

Жерастында сутегін сақтаған кезде метанның концентрациясына бактериялардың әсерін модельдеу

Жерасты сутегін сақтау тәртібі жерасты табиғи газ және көмікрышыл газын сақтауға қарағанда түпкілікті өзгешелігі анықталған, себебі қоймада сутегі қоспасының химиялық өзгерісі байқалған. Осының әсерінен сутегі мен көмірқышқыл газының концентрациясы азайған ал метанның концентрациясы өскен. Ол өзгеріс пластағы сутегі протондарын энергия көзі ретінде жұтаттын бактериялардың әсерінен болған. Сонымен сутектің жерасты қоймасы, өзі сақтап тұрған газдың құрамын өзгертіп тұратын табиғи химиялық реактор ретінде болады екен. Газ құрауыштарының бактериялар арқылы сіңірілуі, өз кезегінде бактериялардың популяциясының қарқынды өсуіне және химиялық белсенділікке алып келеді. Бұл бактериялардың қызметінен және пласттағы газ бен судың ағысы нәтижесінде пайда болған химиялық белсенділік өзін өзі ұйымдастырудың динамикасы әртүрлі сценарийлермен сипатталатын, соның ішінде хаостың пайда болуы мен бір сценарийден екіншіге өтуі авто толқындардың кеңістіктік құрылымының пайда болуы болып табылады. Осы қарастырылып отырған жұмыста сутегін сақтаудың сыртқы және ішкі параметрлеріне тәуелді сапалы автотолқынды теориясы мен өзін өзі ұйымдастыруды құруды қарастырамыз.Жер асты қоймасындағы сутек тасымалының компьютерлік және теориялық моделдерінің құрылуы кеуекті ортадағы көпфазалы композиция ағысының теориясы негізінде болады. Бұл моделдердің негізгі қиындығы бактериялар популяциясының динамика моделімен байланысты болуы. Біздің әдісіміз бұл процессті хемотаксис (ішкі химиялық механизм, соның әсерінен бактериялар қоректенетін заттарды қашықтықтан анықтайды және сол бағытта қозғала алады) механизмі көмегімен сипаттау негізінде құрылған.

Түйін сөздер: Кеуек орта, сутегі, бактерия, нейстон, хемотаксис, популяция динамикасы, осцилляция.

Introduction

Increasing energy demand and anthropogenic greenhouse-gas emissions pose serious challenges for national and international energy economies. Low emissions and the increasing efficiency of fuel cells make the case for the use of hydrogen (H_2) as the fuel of the future [1]-[2]. At best, H2 is generated, e.g. through electrolysis, from renewable energy sources. In such a scheme, storing H_2 comes down to storing electricity. However, it may also be produced from fossil fuels, making it easier to contain emissions at the power plants while distributing clean energy in form of H_2, e.g. for transportation.

Today underground hydrogen storage (UHS) in aquifers and depleted gas reservoirs is considered as one of the main ways of storing large amounts of energy[3]-[4]. During the last decade it has been found that the behavior of UHS is radically different from the underground storage of natural gas and carbon dioxide, primarily by the fact that in the storage occur chemical changes of hydrogen mixture by present of bacteria in the formations, which absorbs protons of hydrogen, as the energy source. There are several underground hydrogen storages in the UK, USA, Russia, Germany, Czech Republic, Argentine and France. The unusual behavior of hydrogen gas mixture in underground storage has been observed in Lobodice storage of Czech Republic and Baynes of France. By analysis of the gas samples which were taken from the reservoir, it was found that the composition of stored gas has undergone significant changes.

The explanation for these changes lies in the chemical reaction between hydrogen and carbon dioxide, which produce methane and water. In the reservoir conditions it can occur only in the presence of methanogenic bacteria, populations of which have been detected in the derived rock samples[5]-[8]. Thus, the underground storage of hydrogen behaves like a natural chemical reactor, which eventually significantly changes the composition of stored gas. Absorption of the gas components by bacteria leads to intensive growth of the population and increase chemical activity. This chemical activity, which caused by the bacterial activity, as well as gas and water flow in the reservoir causes the phenomenon of self-organization such as the occurrence of autowave spatial structures, the dynamics of which is characterized by a multiplicity of different scenarios, including the occurrence of chaos and bifurcations – the jump from one scenario to another. Thus, the new industrial technology - underground storage of electricity in the form of hydrogen - leads to an entirely new scientific issues lying at the intersection of several basic sciences: from hydrodynamics and nonlinear physics to chemistry and microbiology.

The following chemical reaction between injected H_2 and CO_2 occurs in reservoir:

$$CO_2 + 4H_2 = CH_4 + 2H_2O, \ or \ CO + 3H_2 = CH_4 + H_2O \tag{1}$$

In the present paper we continue to develop the qualitative theory of self-organization in underground hydrogen storage, published first in [9]-[11], for more complicated processes that include two-phase flow and the mechanism of chemotaxis, which is one of the main types of bacterial movement. The analysis is based on the coupled model of two-phase compositional flow and the model of population dynamics.

Complete Model of the Process. Model of population dynamics

Let us consider an aquifer which contains an initial population of bacteria, as well as water and gas. Now, mixture of gas in injected where it represents the mixture of H_2 and CO_2 with large domination of hydrogen. Consequently, methanogenic bacteria move to the direction of gas-water contact scince feel nutriments contained in the mixture.

The two-phase system in porous medium represents a fine dispersed alternation of gas bubbles or channels with water channels of droplets. At the macrsocale such a system is considered as two interpenetrating continua coexisting at each space point. The water-gas interfaces which are observed on the pore scale disappear in macroscopic description. At any point two phases are identified by saturation of water S.

Both phases can consist of several chemical components:$(1) = H_2, (2) = CO_2, (3) = H_2O, (4) = CH_4$. The gas phase essentially consists of H_2 and CO_2, while liquid consists mainly of H_2O with low concentration of CO_2,H_2 and CH_4 (the injected gas contains low concentration of CO_2, and hydrogen is low soluble in water). This determines the specific situation when bacteria live in water but the major part of nutriments is concentrated in gas phase.

We consider two kinds of bacteria:

- bacteria present in water: they can be plankton or biofilms attached to pore walls wetted by water;
- the neuston: a biofilm situated just at the interface between water and gas.

Bacteria living in water consume dissolved H_2 and CO_2. Bacteria from neuston consume H_2 and CO_2 directly from the gas phase. On the macroscopic scale (Darcy's scale) both phases contain both kinds of bacteria which can be found at any spatial points. Despite the fact that CO_2 in highly soluble in water, it is low present in the injected gas, while hydrogen is very low soluble in water. Therefore, we should consider the concentrations of both these components in water are of the same order.

In gas we have an abundant resource of H_2 and a sufficiently low resource of CO_2. Then the eating rate of bacteria in neuston is controlled only by the concentration of CO_2. Bacterial population can grow due to replication of species and can decay due to natural or forced death. As usually, we assume that the population grow rate is proportional to the eating rate.

Bacteria also can move. We distinguish three types of their motion:

- they can move chaotically similar to brownian motion (bacterial diffusion);
- they can move due to chemotaxis;
- bacteria living in water can be transported by water flow (single-phase bacterial advection);
- bacteria living in neuston can be transported simultaneously with the movement of the water-gas interface (two-phase bacterial advection)

We assume that bacteria in neuston are not transported by chemotaxis but can diffuse. We keep diffusion as it is the mechanism which stabilizes the mathematical properties of the solution, which is considered in the paper [11].

The disappearance of gas-water interfaces in macroscopic equations imposes some difficulties in describing the neuston which represents a pore-scale object. This means that the movement of neuston in macroscopic equations can be obtained by homogenization of its pore-scale motion.

Balance equations

Let $n_w(x,t)$ and $n_{ns}(x,t)$ be the number of bacteria per unit volume of porous space in water and in neuston respectively. Taking into account all assumptions formulated above, we can formulate the following equations of population dynamics:

$$\begin{aligned}&\tfrac{\partial n_{ns}(1-S)}{\partial t} = \eta_{ns}(1-S)\Phi_{ns}(c_g^{(2)}, n_{ns}) - (1-S)\Psi_{ns}(c_g^{(2)}, n_{ns})\\ &-\langle U_{ns} gradn_{ns}\rangle + div(D_b(1-S)gradn_{ns}) + q_{wn};\end{aligned} \tag{2}$$

$$\begin{aligned}&\tfrac{\partial n_w S}{\partial t} = \eta_w S\Phi_w(c_w^{(1)}, c_w^{(2)}, n_w) - S\Psi_w(c_w^{(1)}, c_w^{(2)}, n_w) - U_w gradn_w\\ &+div(D_b S gradn_w) - div(D_{ch}(C^{(1)})Sn_w gradC^{(1)}) - q_w;\end{aligned} \tag{3}$$

where subscripts w and ns refer to water and neuston respectively; S is the water saturation; Φ and Ψ are the rate of eating and death of the overall population, their dimension is $mol/(s \cdot m^3)$; η is the rendering coefficient (the coefficient of proportionality between the eating rate and growth rate), its dimension is $1/mol$; q_{wn} is the rate of bacteria transition from water to neuston; D_b is the coefficient of bacterium diffusion in bulk water; U_{ns} is the velocity of movement of gas-liquid interface; U_w is the water flow velocity; $c_i^{(k)}$ is the mole fraction of chemical component k in phase i; $C^{(k)}$ is the total mole fraction of chemical component k in both phases.

Term $\langle U_{ns} gradn_{ns}\rangle$ represent the advective movement of neuston homogenized over an elementary representative volume of porous medium. As mentioned above, the neuston represents a pore-scale object, so the velocity U_{ns} is a pore-scale variable.

The relation between $c_i^{(k)}$ and $C^{(k)}$ is as follows:

$$C^{(k)} = \frac{\rho_w c_w^{(k)} S + \rho_g c_g^{(k)} (1-S)}{\rho_w S + \rho_g (1-S)} \tag{4}$$

where ρ_i is the molar density of phase i (mol/m^3).

Functions Φ_{ns} and Φ_w have the meaning of the number of moles of nutriments consumed by all bacteria during $1s$ in a volume unite. The ratios Φ/n and Ψ/n are the individual rates of eating and decay per one bacterium. The rendering coefficient η determines at what degree the colony growth rate is different from the eating rate. In particular, if $\eta < 1$ then growing is slower than eating.

In general case the individual eating rate Φ/n depends on the size of the population and on the amount of nutriment. These two effects considered in paper [11] in more detail is provided below:

$\Phi_{ns} = \frac{1}{t_{e,ns}} \frac{n_{ns} c_g^{(2)}}{(1+a_{ns} c_g^{(2)})}$, $\Phi_w = \frac{1}{t_{e,w}} \frac{n_w^2}{(1+n_w^2/n_{wn}^2)} \frac{c_w^{(1)} c_w^{(2)}}{(1+a_{w1} c_w^{(1)})(1+a_{w2} c_w^{(2)})}$,
$\Psi_{ns} = \frac{n_{ns}}{t_d}$, $\Psi_w = \frac{n_w}{t_d}$. where $t_{e,ns}$ and $t_{e,w}$ are characteristic time of eating at vanishing resource; t_d is the time of decay; a_{ns}, a_{w1}, a_{w2} are three additional empirical coefficients.

Reduced equation of population dynamics

Two equations (2),(3) with respect to n_{ns} and n_w may be reformulated with respect to the total number of bacteria $n = n_{ns}(1-S) + n_w S$ and the ratio $\theta = n_w S/n$. Respectively $n_{ns}(1-S)/n = 1-\theta$. Equation for n has the following form:

$$\begin{aligned}\frac{\partial n}{\partial t} &= \frac{\eta_{ns} c_g^{(2)} (1-\theta) n}{t_{e,ns}(1+a_{ns} c_g^{(2)})} + \frac{\eta_w c_w^{(1)} c_w^{(2)} \theta^2 S n^2}{t_{e,w}(S^2+\frac{\theta^2 n^2}{n_{wn}^2})(1+a_{w1} c_w^{(1)})(1+a_{w2} c_w^{(2)})} - \frac{n}{t_d} \\ &+ \langle U_{ns} grad \frac{(1-\theta)n}{(1-S)} \rangle + div(D_b(1-S) grad \frac{(1-\theta)n}{(1-S)}) - U_w grad \frac{\theta n}{S} \\ &+ div(D_b S grad \frac{\theta n}{S}) - div(D_{ch}(C^{(1)}) \theta n grad C^{(1)})\end{aligned} \tag{5}$$

It can be simplified.

First of all, it is possible to neglect the neuston advection in the first approximation. Indeed, the flow of water and gas does not mean that the interface between them moves. A movement of the interface means, on the maroscale, that the local saturation changes. Therefore the term $\langle U_{ns} grad ... \rangle$ is proportional to $\frac{\partial S}{\partial t}$. For slow variation of saturation in time, this term can be neglected.

The second approximation takes into account the fact that concentrations of CO_2 and H_2 in water are low. This means that terms $a_{w1} c_w^{(1)}, a_{w2} c_w^{(2)}$ and $a_{ns} c_g^{(2)}$ are low with respect to 0.

The third simplification consists of assuming that the value of n_{wn} which corresponds to the state of satiety is high, then the value $\frac{n}{n_{wm}} \to 0$.

The fourth approximation can consist of assuming that the ratio θ is close to water saturation S. This means that the fraction of the number of bacteria in neuston is of the same order as gas saturation, and the fraction of bacterial number in water is of the same order as water saturation. Then we can use only one equation for n to describe population dynamics. It takes the following form:

$$\begin{array}{l} \frac{\partial n}{\partial t} = \eta_{ns}(1-S)\frac{c_g^{(2)}n}{t_{e,ns}} + \eta_w S\frac{c_w^{(1)}c_w^{(2)}n^2}{t_{e,w}} - \frac{n}{t_d} \\ -U_w gradn + div(D_b gradn) - div(D_{ch}(C^{(1)})SngradC^{(1)}) \end{array} \tag{6}$$

where $D_{ch}(C^{(1)}) = D_{ch}^{max}e^{-\lambda_{ch}C^{(1)}}$ is the decreasing function, n is bacteria number.

Reactive transport of chemical components

For reactive multi-component transport, the main problem is the coupling between components through the reactive term. Indeed the reaction kinetics depends on the concentrations of several components, which makes necessary to consider large system of coupled transport equations. For the case of an irreversible reaction, the situation is simplified because the reaction kinetics depends only on reagents and does not depend on the reaction products. Then it is sufficient to formulate the transport equations only for hydrogen and CO_2.

The reaction rate is totally controlled by bacteria and, thus, is equal to the rate of bacterial eating $\Phi_w S + \Phi_{ns}(1-S)$. According to the formula of the chemical reaction (1), one mole of consumed nutriment contains $1/5$ of CO_2 and $4/5$ of H_2. As the result, the model of CO_2 and H_2 transport has the following form: $k = 1, 2$

$$\begin{array}{l} \phi\frac{\partial}{\partial t}(\rho_g c_g^{(k)}(1-S) + \rho_w c_w^{(k)}S) + div(\rho_g c_g^{(k)}V_g^{(k)} + \rho_w c_w^{(k)}V_w^{(k)}) = \\ \frac{1}{\Omega}G^{inj}c^{(k),inj} - \frac{\phi\gamma^{(k)}(1-S)c_g^{(2)}n}{t_{e,ns}} - \frac{\phi\gamma^{(k)}c_w^{(1)}c_w^{(2)}Sn^2}{t_{e,w}} \\ +div(\rho_g D_g^{(k)}\phi(1-S)gradc_g^{(k)} + \rho_w D_w^{(k)}\phi S gradc_w^{(k)}) \end{array} \tag{7}$$

For the total fluid:

$$\phi\frac{\partial}{\partial t}(\rho_g(1-S) + \rho_w S) + div(\rho_g V_g + \rho_w V_w) = \frac{1}{\Omega}G^{inj} \tag{8}$$

where

$V_g = -\lambda_g(gradP_g - \rho_g^m g)$, $V_w = -\lambda_w(gradP_w - \rho_w^m g)$, $\lambda_i = \frac{Kk_i(S)}{\mu_i}$;

$V_i^{(k)} = V_i + V_{iD}^{(k)} = -\frac{\phi D_i^{(k)}S_i}{c_i^{(k)}}$, $i = g, w$;

$P_w = P_g - P_c(S)$;

Dissolution:

$$c_g^{(3)} = 1 - c_g^{(1)} - c_g^{(2)}; \tag{9}$$

$$c_w^{(k)} = H^k(P_w)c_g^{(k)}, k = 1, 2, 3; \tag{10}$$

where S is the water saturation; P is the pressure; ρ is the molar density; μ is the dynamic viscosity; K is the absolute permeability; ϕ is the porosity; $k_{g,w}(S)$ is the relative permeability; G^{inj} is the molar rate of gas injection (mol/s), Ω is the total volume of the reservoir, $c^{(k),inj}$ is the injection concentration of component k in the injected gas (constant value);$\gamma^{(k)} = \left\{ \begin{array}{l} 4/5, k=1 \\ 1/5, k=2 \end{array} \right.$. $C^{(k)}$ is the total mole fraction of chemical component k in both phases.

Analytical and Numerical results Asymptotic model for low gas saturation

Let's consider asymptotic model for low gas saturation. In this case the neuston is very modest and bacteria living in water dominate far from the interface. Consequently, the chemotaxis which determines the neuston formation should be taken into account. Since the reaction kinetics depends on concentrations of both CO_2 and H_2, the model of the process resulting from (6) and (7) consists of three equations in this case:

$$\left\{ \begin{array}{l} \frac{\partial c_1}{\partial t} = q_1 - \alpha_1 c_1 c_2 n^2 + D_w^{(1)} \Delta c_1 \\ \frac{\partial c_2}{\partial t} = q_2 - \alpha_2 c_1 c_2 n^2 + D_w^{(2)} \Delta c_2 \\ \frac{\partial n}{\partial t} = -\beta n + \alpha_3 c_1 c_2 n^2 + D_b \Delta n - D_{ch}^{max} \nabla (exp(-\lambda_{ch} c_1) n \nabla c_1) \end{array} \right. \tag{11}$$

where
$c_k = c_g^k$, $q_k = \frac{G^{inj} c^{(k),inj}}{\Omega \phi \rho_w H^{(k)} S}$, $\alpha_1 = \frac{4H^{(2)}}{5t_{e,w}\rho_w}$, $\alpha_2 = \frac{4H^{(1)}}{5t_{e,w}\rho_w}$, $\alpha_3 = \frac{\eta_w H^{(1)} H^{(2)} S}{t_{e,w}}$, $\beta = \frac{1}{t_d}$
Moreover, when the concentration of one of the components is very low, we obtain the model which may be analyzed without simplifications. Let us assume that water can contain very low concentration of hydrogen, that is $c_1 << c_2$. Then concentration c_2 may be considered as variable with small change. From (11) the following expression is obtained:

$$\left\{ \begin{array}{l} \frac{\partial c_1}{\partial t} = q_1 - \alpha_1 c_1 n^2 + D_w^{(1)} \Delta c_1 \\ \frac{\partial n}{\partial t} = -\beta n + \alpha_3 c_1 n^2 + D_b \Delta n - D_{ch}^{max} \nabla (exp(-\lambda_{ch} c_1) n \nabla c_1) \end{array} \right. \tag{12}$$

which is the Turing model [12], if chemotaxis term is neglected.

Analytical study: Limit Stationary Spatial Waves

The resulting model (12) has a limit cycle in time, if diffusion term and chemotaxis are neglected. In the paper [10],[13]-[14] there is a criterion for the existence of a limit cycle for the case $\alpha_1 = \alpha_3 = \beta = 1$:

$$0.90032 < q_1 < 1.0 \tag{13}$$

Stationary solutions of the system (12) represent the second kind of limit behavior at ($t \to \infty$). In the 1D case the system of equations correspond to the model:

$$\left\{ \begin{array}{l} D_w^{(1)} \frac{\partial^2 c_1}{\partial x^2} = \alpha_1 c_1 n^2 - q_1 \\ D_b \frac{\partial^2 n}{\partial x^2} - D_{ch}^{max} \frac{d}{dx} (exp(-\lambda_{ch} c_1) n \frac{d}{dx} c_1) = \beta n - \alpha_3 c_1 n^2 \end{array} \right. \tag{14}$$

The simplest non-trivial stationary solution corresponds to the limit case: $D_{b=0}$,$D_{ch}^{max} = 0$

$$\begin{cases} D_w^{(1)} \frac{\partial^2 c_1}{\partial x^2} = \alpha_1 c_1 n^2 - q_1 \\ 0 = \beta n - \alpha_3 c_1 n^2 \end{cases} \tag{15}$$

System (15) requires two boundary conditions:

$$c_1 \mid_{x=0} = c^0, \frac{dc_1}{dx} \mid_{x=0} = 0 \tag{16}$$

Then the system (15) may be reduced to one ordinary differential equation of the second order:

$$\frac{d^2 c_1}{dx^2} = f(c_1), f(c_1) = \frac{\alpha_1 \beta^2}{\alpha_3^2 D_w^{(1)} c_1} - \frac{q_1}{D_w^{(1)}} \tag{17}$$

Equation (17) may be reduced to a non-linear autonomous dynamic system:

$$\begin{cases} \frac{\partial c_1}{\partial x} = U \\ \frac{\partial U}{\partial x} = f(c_1) \end{cases} \tag{18}$$

We have obtained the non-linear autonomous second-order system which can be analysed using the traditional methods of the theory of non-linear dynamics. The Jacobi matrix of the system is:

$$J = \begin{pmatrix} -1 & 1 \\ -\frac{\alpha_3^2 q_1^2}{\alpha_1 D_w^{(1)} \beta^2} & -1 \end{pmatrix} \tag{19}$$

One stationary point exists: $U_s = 0$, $c_s = \frac{\alpha_1 \beta^2}{\alpha_3^2 q_1}$. Then we calculate eigenvalues $\nu_{1,2}$ of matrix J at the stationary point U_s, c_s:

$$det(J - \nu I) = \begin{vmatrix} -\nu & 1 \\ -\frac{\alpha_3^2 q_1^2}{\alpha_1 D_w^{(1)} \beta^2} & -\nu \end{vmatrix} = 0$$

The eigenvalues are:

$$\nu_{1,2} = \pm \frac{\alpha_3 q_1}{\sqrt{\alpha_1 D_w^{(1)} \beta}} i \tag{20}$$

Thus, point $p(U_s, c_s)$ is the center if the expression $\frac{\alpha_3 q_1}{\sqrt{\alpha_1 D_w^{(1)} \beta}} > 0$ is positive, which is the condition of existence of periodic solutions of system (15).The phase portrait of (15) calculated for $\alpha_1 = \alpha_3 = 1$, $D_w^{(1)} = 1$ and $q_1 = 0.95$ is shown in Fig.1. The corresponding periodic oscillations of H_2 concentration are shown in Fig.2 for the case of the boundary condition:

$$c_1 \mid_{x=0}= 0.1, \frac{dc_1}{dx} \mid_{x=0}= 0 \tag{21}$$

Numerical study

Then we analyze the problem (12) of gas injection in two-dimensional case with constant initial conditions and Neumann boundary conditions which correspond to impermeable boundaries:

$$n|_{t=0} = 1, c_1 \mid_{t=0}= 1, \frac{dc_1}{d\nu} \mid_{\partial\Omega}= 0, \frac{dn}{d\nu} \mid_{\partial\Omega}= 0 \tag{22}$$

The initial values are located within the zone of attraction of the limit cycle, so that the solution of this problem is space-invariant and oscillating in time. The flow rate q_1 in equation (12) represents the hydrogen injection into the reservoir.

This space-invariant solution was perturbed in the form of an instantaneous non-zero concentration gradient applied to the small vicinity of the origin. The evolution of the perturbation is shown in Fig. 3- Fig. 4. And, Table 1 shows the data used in the calculations.

Таблица 1: Calculated data.

Computational grid	32×32
Time step	0.006104
q_1 (perturbation)	$0.95 + 0.01$
q_1	0.95
$D_w^{(1)}$	0.01
D_{ch}^{max}	0.001
α_1	1
α_3	1
β	1
λ_{ch}	1

After perturbation, the irregular waves traveling throughout the overall domain were observed. Their evolution was very fast establishing to the structure presented by regular periodic waves invariable in time. The Fig. 3 and 4 represents the results of numerical calculation of the evolution of the hydrogen concentration, changes in the number of bacteria at $t = 40..1000$ with diffusion as well as taking into account chemotaxis which was used the calculated data from Table 1. This means sufficiently regular ring waves are developed with excess and deficiency of hydrogen and bacteria in the space, which alternate with each other. In areas with high bacteria concentrations where the reaction (1) is rapid, alternation

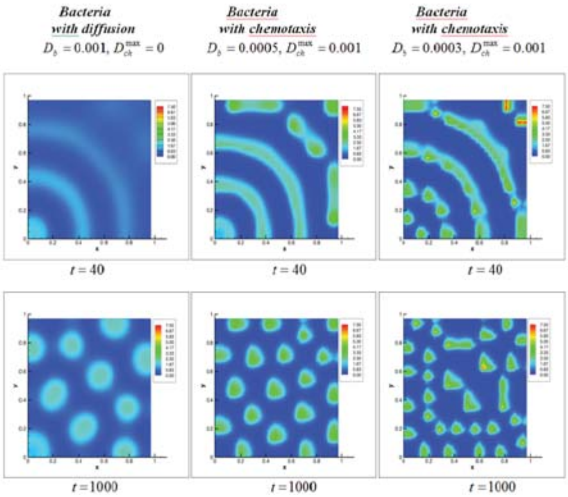

Figure 1-Evolution of auto-waves of bacterial population with diffusion and chemotaxis at $t = 40..1000$

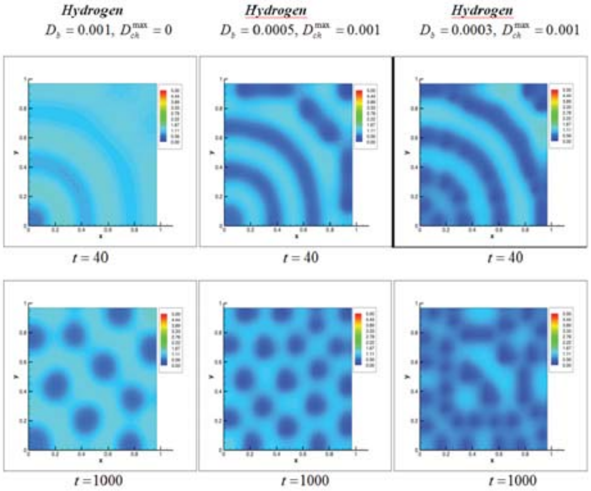

Figure 2-Hydrogen concentrations at $t = 40..1000$

with the ring excess and deficiency of bacteria appear, whereby the methanogenic bacteria generates methane.

In case of taking into account the chemotaxis of bacteria, the bacteria forms neuston formation. In this work an attempt has been carried out to qualitatively analyze the impact of methanogenic bacteria on the dynamics of the formation of methane in underground hydrogen storage. Occurrence of undamped oscillations during the time which tends asymptotically to periodic waves, means that the system undergoes self-organization of new structures in the form of methane. It should be noted that, not only in the case of consideration of diffusion but also chemotaxis damping oscillations were observed in space.In the limit of computational time steady-state spatial pattern of frozen waves is observed. Following results in Fig. 2 and Fig. 4 predicts the effect of a natural in situ separation of hydrogen gases, which was observed in practice.

Conclusion

In papers [7] and [8] it was proved that an underground storage of hydrogen can function as a natural chemical reactor producing methane from hydrogen and carbon dioxide. The reaction between H_2 and CO_2 (1) is catalyzed by methanogenic bacteria and happens in the form of the metabolism process.

In paper [10] the first mathematical model of the process was developed. It was based on single-phase flow model coupled with population dynamics equation. The bacterial population was considered in the average and various forms of its existence were reflected in nonlinear kinetics of population growth.

In paper [11] we developed the two-phase flow model coupled with the dynamics of two bacterial populations. One of them represents bacteria living in water, while the second one is the neuston - a thin biofilm situated at the interfaces between water and gas. We also developed the mathematical model of chemotaxis in two-phase fluid, which is the main mechanism of neuston formation: bacteria living in water feel the presence of nutriments concentrated in the injected gas and move to the direction of the interfaces water-gas without crossing them. We have shown that the chemotaxis law should satisfy some specific conditions to ensure the neuston formation. In particular, the bacteria diffusion is shown to be a regularizing mechanism which ensures mathematically the existence of regular solutions.

In this paper, we used above mentioned mathematical model from [11], analystically and numerically studied the equations of mathematical model for the case of low gas saturation, and compared the results.

In case of low gas saturation, asymptotic model (12) related to hydrogen and population of bacteria, taking into account $D_b = 0$ and $D_{ch}^{max} = 0$ when $t \to \infty$, was analytically studied. This model leads to non-linear autonomous dynamic system which depends on space coordinates, that is, (18). When the model in (18) which is second-order system was studied using traditional methods of the theory of non-linear dynamics, stationary point of that system was found and its type found out to be center (Fig. 1). It means that the considered system has a periodic solution, that is, the hydrogen is periodically distributed over the space which can be noticed from Fig. 2. This periodic distribution phenomenon is also detected, when model (12) is solved by taking into account the bacteria diffusion and chemotaxis.The results provided in Fig. 4 is obtained by perturbation theory. Moreover, the steady-state distribution of the hydrogen concentration over the space is achieved when time is at least $t = 1000$. After $t = 1000$ the periodic distribution is frozen, which means, now, it does not depend on time. The obtained results describe natural gas in situ separation in the underground hydrogen storage.

The results in Fig. 3 compare two cases: a) the model takes into account the diffusion of bacteria b) the model takes into account chemotaxis of bacteria. It is noticed that in case of chemotaxis, amount of bacteria was higher concentrated in the places where hydrogen concentration is high compared to the case when the model uses diffusion of bacteria. This physically means that more the bacteria is concentrated faster the chemical reaction (1). As a result of this phenomena, the methane gas is generated in underground hydrogen storage.

In a word, the results provided above show the natural in situ separation of hydrogen mixture and the generation of methane gas during the underground hydrogen storage.

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