

General model of the carbonate acidizing process with different injection rate

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ABSTRACT

The process of dolomite rock acidizing is considered. Theoretical analysis considers three regimes of the chemical reaction: face and uniform dissolution and wormhole formation. The general model integrates two analytical solutions of the face and uniform dissolution and semi empirical model of wormhole formation. The analytical solutions consider in the paper, appropriate data on semi empirical approach was extracted from Fredd and Fogler investigations. These solutions had been transferred to the dependence of skin factor from the specific acid injection rate, slug volume and acid concentration. The approximation of the dependence involves two Gauss functions and matches to the appropriate asymptotes (low and high injection rates) and describes the wormhole local minimum in the vicinity of critical injection rate. The proposed approximation dependence may be used in different codes for a reservoir acid treatment process. It could be the basis of the process optimization procedure with maximum productivity increase criteria and determination of optimal impact parameters such as acid slug volume and concentration, injection rate and etc.

KEYWORDS

dolomite • hydrochloric acid • face and uniform dissolution • wormhole formation • reservoir acidizing analytical solution

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Introduction

The practice of acid stimulation of productivity in carbonate reservoirs began with the Schlumberger brothers and has a long history [1,2]. The permeability increase of the near wellbore zone and reduction of the skin factor are the main purpose of the stimulation.

At the end of the last century, Fredd and Fogler [3] established that the ratio of the reaction rate and the average mass velocity of acid flow determines the reaction type of an aqueous acid solution with a carbonate matrix. At low velocities, the type of reaction is "face dissolution" with cavern formation at the inlet surface of a well. At high velocities, the acid flows through almost all pore channels, dissolving their walls, increasing the size, and thus increasing the porosity and permeability. This type is often named "uniform dissolution". When the ratio of the reaction rate and acid injection is about one, a dominant channel is formed in the pore space, into which almost all the acid rushes. This leads to the formation of a channel with a diameter of about 1–5 mm, which is called a "wormhole" and the reaction type is named wormhole formation. The authors of the paper [4] considered new regime which they call channeling.



Considering the ratio of permeability in the treated area and in the rest part of a reservoir, then for the first and third reaction types it is several orders of magnitude, for the uniform dissolution it does not exceed several units. The depth of acid penetration to a reservoir at the same volumes of injection is maximum for the uniform dissolution and minimum for the face dissolution type. A general model for predicting these effects or a general approach integrated all described reaction types is needed to predict, optimize the process of acid stimulation of carbonate reservoirs and analyze the technological and economic effect.

The paper proposes the integration of analytical solutions for face and uniform dissolution [5] and the application of semi-empirical models for the analysis of the wormhole formation [6–9]. These solutions are the framework of computational algorithm for the prediction of the volume and concentration of the injected acid slug influence on the well skin factor after stimulation. Of course, there are some physical phenomenon that additionally affect skin factor. For example, permeability modification under pore pressure variation that considered in [10]. The algorithm bases on available experimental data [7,11,12] and the type of acid [3,13].

Solution of the face dissolution problem

The investigation begins with the consideration of the face dissolution problem on the simple example of vertical well stimulation with the open hole completion. Let's the reservoir is represented by dolomites and the chemical reaction with hydrochloric acid is described by the following equation: $4\text{HCl} + \text{CaMg}(\text{CO}_3)_2 = \text{CaCl}_2 + \text{MgCl}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O}$.

Note that the problem of face dissolution refers to the case when the reaction rate significantly prevails acid flow velocity [14]. Let's proceed to formalization of the presented problem. The flow pattern during injection of acid solution into a carbonate formation depends on the well completion method, but is reduced to two types: radial and linear [15]. Here, the "exotic" spherical flow is not considered, and the flow near a horizontal well with strong formation anisotropy is reduced to the radial type by introducing new coordinates that take into account the reservoir anisotropy. Such simplification is valid for small volumes of acid injection, when its penetration into the bottomhole zone is limited by meter or less. The problem of an aqueous acid solution flow in the bottomhole zone of a well with residual (immobile) oil will be considered as single-phase two-component (1 – carrying water with reaction products, 2 – hydrochloric acid) flux. Note that radial or quasi-radial flows are observed near vertical, inclined and horizontal wells, and linear flow is observed near stimulation fractures.

Next, the radial flow pattern will be the focus of consideration; the solution for the linear flow pattern is sought similarly. The equations of the mass conservation of the acid and the aqueous solution with the reaction products in a polar coordinate system are as follows:

$$\begin{cases} \frac{\partial(c\phi\rho_w h(1-S_{or}))}{\partial t} + 2 \frac{\partial(vrc\phi\rho_w h(1-S_{or}))}{\partial r^2} = -Jh, \\ \frac{\partial((1-c)\phi\rho_w h(1-S_{or}))}{\partial t} + 2 \frac{\partial(vr(1-c)\phi\rho_w h(1-S_{or}))}{\partial r^2} = \kappa_w Jh, \\ \frac{\partial((1-\phi)\rho_R h)}{\partial t} = -\kappa_R Jh. \end{cases} \quad (1)$$

Here c , $(1-c)$ are acid mass concentration and aqua phase (water + reaction products); $\emptyset$, h are porosity and specific reservoir thickness; ρ_w , ρ_R are densities of aqua phase and matrix; v is mass averaged flow rate of aqua phase; S_{or} is residual oil saturation; J , $\kappa_w = 1.26$, $\kappa_R = 2.26$ are chemical reaction rate of acid with matrix, mass ratio of reaction products and acid consumption, mass ratio of reacting dolomite and acid.

For the face dissolution problem, the reaction rate J tends to infinity and the reaction itself occurs in a narrow region called reaction front. The movement speed of the reaction front (complete consumption of the injected acid) is determined by the conditions on the acid concentration shock from zero to the initial concentration in the injected solution. Let's transform the mass balance equations (1) to the conservative form:

$$\begin{cases} \frac{\partial}{\partial t} \left(c\emptyset\rho_w h(1-S_{or}) - (1-\emptyset) \frac{\rho_R h}{\kappa_R} \right) + 2 \frac{\partial(vrc\emptyset\rho_w h(1-S_{or}))}{\partial r^2} = 0, \\ \frac{\partial}{\partial t} \left((1-c)\emptyset\rho_w h(1-S_{or}) + (1-\emptyset) \frac{\kappa_w \rho_R h}{\kappa_R} \right) + 2 \frac{\partial(vr(1-c)\emptyset\rho_w h(1-S_{or}))}{\partial r^2} = 0. \end{cases} \quad (2)$$

The mass balance of the chemical reaction reduces to the equation:

$$-J + \kappa_w J - \kappa_R J = 0 \text{ or } \kappa_w - \kappa_R = 1. \quad (3)$$

The divergent or conservative form of the equations gives the possibility to define the algebraic conservation equations at the reaction front [16]:

$$\begin{cases} D \left[c\emptyset\rho_w h(1-S_{or}) - (1-\emptyset) \frac{\rho_R h}{\kappa_R} \right] - 2[v(1-S_{or})r_f c\emptyset\rho_w h] = 0, \\ D \left[(1-c)\emptyset\rho_w h(1-S_{or}) + (1-\emptyset) \frac{\kappa_w \rho_R h}{\kappa_R} \right] - 2[v(1-S_{or})r_f (1-c)\emptyset\rho_w h] = 0, \\ D = \frac{dr_f^2}{dt}, \end{cases} \quad (4)$$

where D is reaction front velocity, r_f is reaction front coordinate, square brackets denote the difference of function's values before and after the reaction front. The boundary conditions of the considered problem determine the solution of these algebraic differences. These conditions define the acid injection concentration c_0 and entire matrix dissolution $\emptyset = 1$ on the inlet and the absence of the acid before the reaction front $c = 0$ and initial value of porosity $\emptyset = \emptyset_0$. Accordantly the balance of values before and after the reaction takes the form:

$$\begin{aligned} r \leq r_f: \quad c^+ &= c_0, \quad \emptyset = 1, \quad Q^+ = Q_0 = 2\pi h(1-S_{or})v^+ r_f, \\ r > r_f: \quad c^- &= 0, \quad \emptyset^- = \emptyset_0, \quad Q^- = Q = 2\pi h(1-S_{or})v^- r_f \emptyset_0. \end{aligned} \quad (5)$$

Here Q_0 is the flow rate of the injected acid solution into the reservoir, and Q is the flow rate of the aqueous phase with the reaction products before the reaction front to be determined. By substituting these values into the algebraic conservation equations at the reaction front (4), all unknown parameters can be determined:

$$\begin{aligned} D &= \frac{Q_0}{\pi h} \frac{1}{(1-S_{or}) + \frac{(1-\emptyset_0)\rho_R}{c_0 \kappa_R \rho_w}}, \\ Q &= Q_0 \left\{ 1 - (1-\emptyset_0) \frac{(1-S_{or}) - \frac{\rho_R}{\rho_w}}{(1-S_{or}) + \frac{(1-\emptyset_0)\rho_R}{c_0 \kappa_R \rho_w}} \right\}, \\ r_f &= \sqrt{Dt + r_w^2}. \end{aligned} \quad (6)$$

For slug volume V with acid concentration c_0 the skin factor after acidizing process could be determined by the formula connecting the skin factor S_f with the effective well radius r_f :

$$S_f = -\ln\left(\frac{r_f}{r_w}\right), \quad r_f = \sqrt{\frac{1}{\pi h} \frac{V}{(1-S_{or}) + \frac{(1-\emptyset_0)\rho_R}{c_0 \kappa_R \rho_w}} + r_w^2}. \quad (7)$$

Unified dissolution problem

Another ultimate case is the unified dissolution when the acid flow rate is much higher than reaction rate. In this case filling of porous matrix is not practically accompanied by chemical reaction and dissolution of carbonate rock begins after saturation of pore space by acid. At this assumption, acid penetrates to the radius r_* of the near wellbore zone:

$$r_* = \sqrt{\frac{V}{\pi h \phi_o (1 - S_{or})}} + r_w^2. \quad (8)$$

Thus, the reaction proceeds without convection and is determined by the equations in the saturated area:

$$\begin{cases} \frac{d(c\phi\rho_w(1-S_{or}))}{dt} = -J, \\ \frac{d((1-c)\phi\rho_w(1-S_{or}))}{dt} = \kappa_w J, \\ \frac{d((1-\phi)\rho_R)}{dt} = -\kappa_R J. \end{cases} \quad (9)$$

Note that J is the volumetric reaction rate with SI dimension $\text{kg} / (\text{m}^3\text{s})$, i.e. takes place in a unit volume of the porous medium. In experimental studies, the reaction rate is determined by volumetric method (by measurement of carbon dioxide release) [17] or on a rotating disk installation [2,18,19]. In the first case, the dimension of reaction rate coincides with J , but the method works in the region of relatively low pressures (up to 70 atm). In the second method, the surface reaction rate j with the dimension $\text{kg}/(\text{m}^2\text{s})$ is determined. To use it in the model, one should multiply j by the specific surface of the reservoir matrix A_s . The specific surface of the porous matrix is determined by the generalized Kozeny-Karman formula [20]:

$$A_s = \frac{B\sqrt{\phi_o(1-\phi_o)}}{\sqrt{k_o}}(1 - S_{or}). \quad (10)$$

Here k_o is matrix permeability, B is the empirical parameter, which value according Kotyachov [21] investigations varies in the interval $1 - 3.5 \cdot 10^5$ for practical calculations ($[k_o] = \mu\text{m}^2$, $[\phi_o] = \text{shares of units}$). For certainty the value $B = 2.5 \cdot 10^5$ was used in further calculations. Note that there are some new investigations connecting specific surface with porosity and permeability [22] during acidizing process.

The rate of surface or heterogeneous reaction is written as $j = Zc^n\rho_w$, where Z is the kinetic reaction constant depending on thermodynamic conditions; n is the reaction order. In the general case of heterogeneous reactions order may be a fractional value (these parameters are determined in an experimental installation with a rotating disk). Reactions of zero and first orders are usually considered [17,23].

$$J = ZA_s c^n \rho_w. \quad (11)$$

First, let's transform the system (6), considering the densities independent of time and neglecting the change in water saturation due to the chemical reaction:

$$\begin{cases} c \frac{d\phi}{dt} + \frac{dc}{dt} \phi = -\frac{J}{\rho_w(1-S_{or})}, \\ (1-c) \frac{d\phi}{dt} - \frac{dc}{dt} \phi = \frac{\kappa_w J}{\rho_w(1-S_{or})}, \\ \frac{d\phi}{dt} = \frac{\kappa_R J}{\rho_R}. \end{cases} \quad (12)$$

For the zero reaction order the solution of the system under initial conditions $t = 0$, $c = c_0$, $\emptyset = \emptyset_0$ allows to obtain full time of the acid consumption, as well as the matrix porosity after consumption:

$$t_l = \tau \frac{c_0}{c_0 + c_*}, \quad \emptyset_l = \emptyset_0 \left(1 + \frac{c_0}{c_*}\right), \quad c_* = \frac{\rho_R}{\kappa_R \rho_w (1 - S_{or})}, \quad \tau = \frac{\emptyset_l \rho_R}{c_* \kappa_R Z S_s}. \quad (13)$$

For the first order of reaction rate, the solution procedure is more complex but it is obvious that the value of final reservoir porosity is the same as for zero reaction order. However, the formation of the final porosity occurs only asymptotically in time.

The dynamics of acid consumption for both orders of reaction rates are presented as follows equations:

$$\begin{aligned} \text{for the zero order } \ln \frac{\left(1 - \left(\frac{c_0}{c_*} + 1\right)^{-1}\right)}{\left(1 - \left(\frac{c}{c_*} + 1\right)^{-1}\right)} + \left(\left(\frac{c_0}{c_*} + 1\right)^{-1} - \left(\frac{c}{c_*} + 1\right)^{-1}\right) &= \frac{t}{\tau}, \\ \text{for the first order } \ln \frac{(1 - x_0)}{(1 - x)} + (x_0 - x) &= \frac{t}{\tau}, \quad x = \frac{\emptyset}{\emptyset_l}, \quad x_0 = \frac{\emptyset_0}{\emptyset_l}. \end{aligned} \quad (14)$$

The obtained dependencies of acid concentration from time are illustrated on Fig. 1.

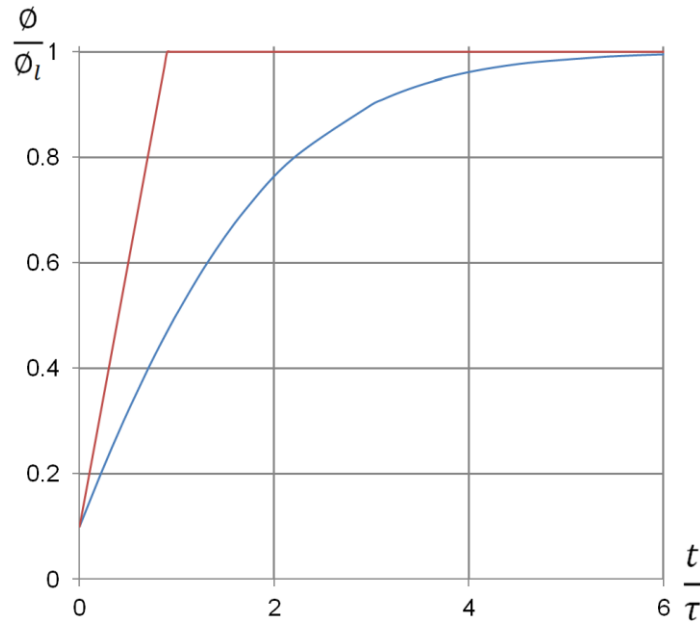


Fig. 1. Dependence of rock porosity from time during acidizing process for the zero and the first reaction order

The final time of acid consumption plays a significant role in the process technology because it defines the delay time for the reaction after acid injection. As for zero reaction order it is determined analytically, for the first order it can be only estimated, for example from Fig. 1 as $t_l \cong 2\tau$.

According to the Kozeni-Karman theory, for each rock of the same type, there is an unambiguous relationship between rock porosity and permeability [20]. Labrid's experiments [2] showed that a similar relationship could be used to relate rock porosity and permeability in the carbonate acidizing process:

$$\frac{k}{k_o} = K \left(\frac{\emptyset}{\emptyset_o}\right)^6. \quad (15)$$

The Hawkins formula [20] could be used for a skin factor determination. For this purpose, Eq. (15) should be applied for calculation of rock permeability determination at the value of final porosity after acidizing process. This procedure gives:

$$S_u = \left(\frac{k_o}{k} - 1 \right) \ln \left(\frac{r_*}{r_w} \right). \quad (16)$$

Application of semi empirical model for calculation of wormhole formation

Semi empirical approach to wormhole formation bases of the results of the experiments of acid injection to a small cylindrical carbonate rock core [6,24,25]. It was found that under critical flow rate per unit surface q_{cr} the volume of acid until breakthrough takes the minimum value. This value is usually transferred to the dimensionless view by division on the core pore volume and is labeled as PV_{cr} . The dependence of PV_b on the specific value of flow rate q [12,26] with definitions of critical values is illustrated on the Fig. 2. The critical values are considered as the conditions of wormhole formation.

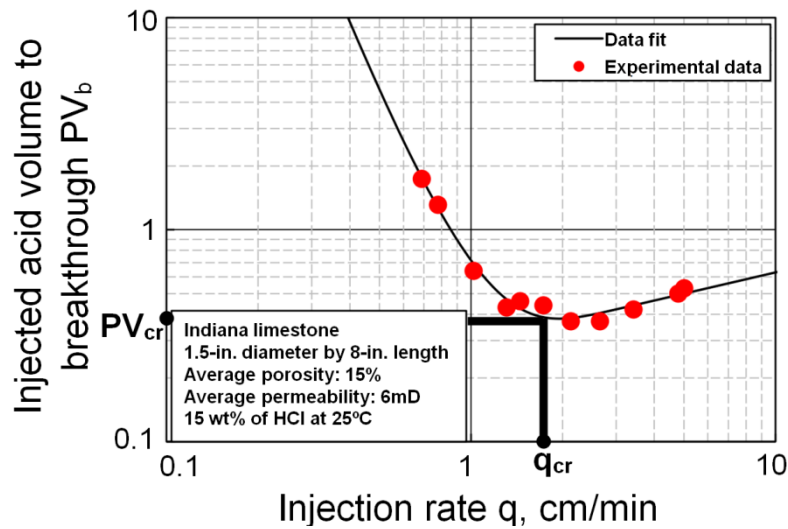


Fig. 2. The dependence of injected acid volume to breakthrough PV_b from the injection rate with determination of the critical values [12]

The determination of the wormhole's length in practice bases on the proposition of its formation similarity in experiments and in near wellbore area [2,23]:

$$l_{wh} = \frac{q_{cr} t}{PV_{cr} S \phi} = \frac{V}{PV_{cr} 2\pi h r_w \phi}, \quad (17)$$

where l_{wh} is the effective wormhole length. The real wormhole length differs from the effective value because of its fractal nature [8,23]. Daccord [23,26,27] connected the fractal structure of wormholes with the definition of effective length by the similar formula (17):

$$l_{wh} = \left(\frac{V l^{d_f-1}}{PV_{cr} 2\pi h r_w \phi} \right)^{\frac{1}{d_f}}, \quad (18)$$

where d_f is the fractal dimension ($1.5 < d_f < 1.7$), f is the parameter of wormholes, defined from experiments. Application of Hawkins formula defines the expression of skin factor after acidizing of carbonate at critical injection rate:

$$S_{wh} = \left(\frac{k_o}{k} - 1 \right) \ln \left(\frac{l_{wh} + r_w}{r_w} \right), \quad (19)$$

where the l_{wh} is extracted from Eq. (18).

The permeability of stimulated by wormholes zone is significantly higher than untreated reservoir. Daccord [28], Huzin [29] considered experimental data and proposed to neglect the ratio k_o / k thus simplified the skin determination:

$$S_{wh} = -\ln\left(\frac{l_{wh}+r_w}{r_w}\right). \quad (20)$$

General model formulation

The obtained solutions define the values of skin factors for all types of reactions. For example, consider the reservoir with typical characteristics: effective formation thickness $h = 20$ m, porosity $\phi_o = 0.12$, reaction ratio $\kappa_w = 1.26$, residual oil saturation $S_{or} = 0.3$, Labrid's coefficient $K = 1.7$, well radius $r_w = 0.1$ m, initial acid concentration $c_o = 0.15$, densities of rock and solution $\rho_R = 2804$ kg/m³, $\rho_w = 1057$ kg/m³, injected slug volume $V = 60$ m³, wormhole formation critical values $q_{cr} = 1.4$ cm/min, $PV_{cr} = 12.4$. Substituting these data to Eqs. (7), (16), (20) the following values of skin factors can be obtained:

$$S_f = -2.27, \quad S_{wh} = -3.4, \quad S_u = -1.98. \quad (21)$$

If the wormhole formation regime is extracted from the analysis of the dependence of skin factor from flow rate the transformation between of face and unified dissolution should be connected by monotonous function. As an example, this function may be approximated by Gauss formula with the height of the curve's peak $|S_f - S_u|$ and half width corresponding by kinetic regime q_{ki} [30]:

$$S_{uf} = S_u + (S_f - S_u) \exp\left(-\frac{q^2}{q_{ki}^2}\right). \quad (22)$$

Here q_{ki} is the boundary rate of kinetic regime. This function has the appropriate asymptotes $q_{cr} \rightarrow 0, q_{cr} \rightarrow \infty$. At low flow rate, it gives the independent from rate skin factor. At high flow rates, the dependence tends to the value S_u with weak dependence

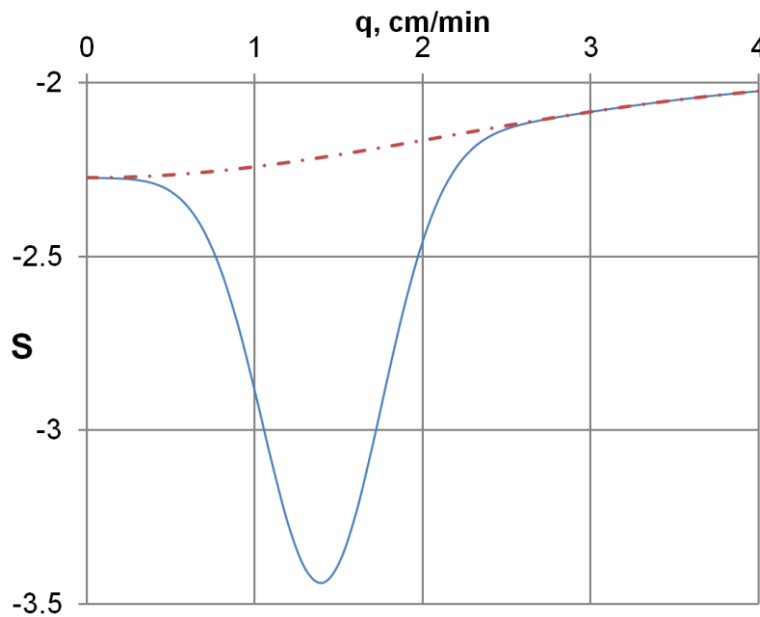


Fig. 3. The supportive (22) (dashed dotted line) and the general (23) (solid line) models of the dependence of skin factor and specific acid injection rate with correct asymptotes and local wormhole minimum close to the experimental data

from rate. The difference ($S_f - S_u$) may be positive or negative and depends on reservoir parameters.

The wormhole formation regime is manifested in the relatively narrow interval of flow rate [7,31] and may be implanted by another Gauss function:

$$S_g = S_{uf} - (S_f - S_{wh}) \exp\left(-\frac{(q - q_{cr})^2}{\Delta q^2}\right), \quad (23)$$

where Δq is the half width of the specific flow rate of wormhole formation regime. Figure 3 also illustrates the general approximation (23) of the model of reservoir acid treatment. The function on Fig. 3 corresponds to the model reservoir data Eq. (21).

The proposed approximation formula may be used in different codes for a reservoir acid treatment process. It could be the basis of the process optimization procedure with maximum productivity increase criteria and determination of optimal impact parameters such as acid slug volume and concentration, injection rate and etc.

Note that the general model involves the main technological parameters: injection rate, slug volume and acid concentration through Eqs. (7), (8), (14), (18). For instance, the influence of the volume of injected acid slug on skin factor is shown in Fig. 4. From the obtained solutions, critical rate does not depend from the slug volume and skin factor is proportional to $-\ln(V^{df} - 1)$, which illustrates Fig. 4. On the other hand, the critical rate depends on concentration and acid concentration growth shifts the graph to the left this feature is shown in Fig. 5.

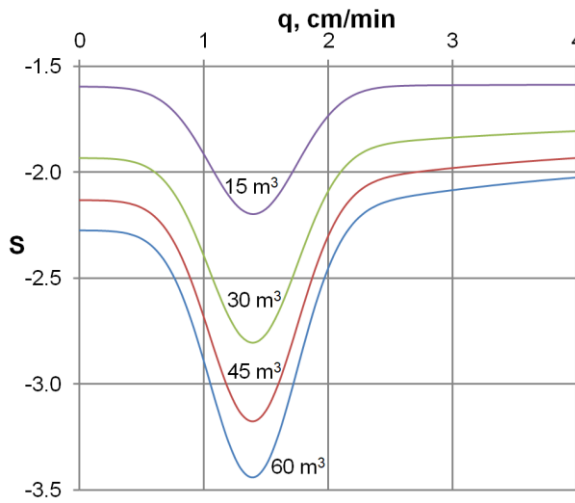


Fig. 4. Calculations of the influence of acid slug volume on the skin factor behavior. Volume values are indicated on graphs

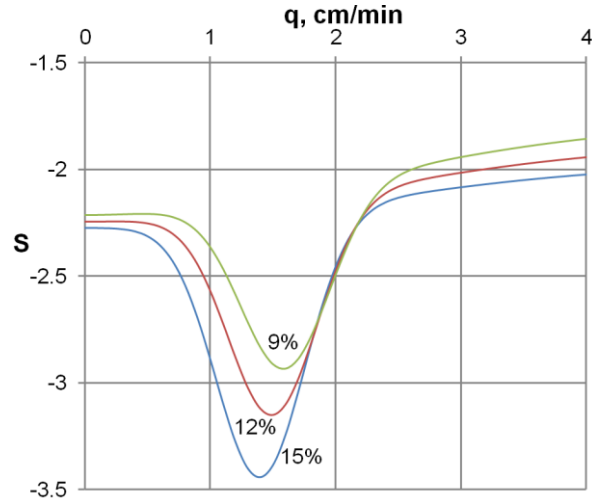


Fig. 5. Skin factor dependence from acid concentration. Concentration values are indicated on graphs

Conclusions

The solutions of the problems of face and unified dissolution of carbonate reservoir due to the injection of acid were obtained. For the wormhole formation process the corrected Gong's model was used. All solutions were transferred to dependence of skin factor from process parameters.

The general model integrates the obtained solutions and Gong model for the prediction of skin factor dependence from injection rate, acid concentration and slug volume for the whole intervals of parameters variation. The model illustrated on the

example of stimulation of vertical well but can be easily transferred to the other types of well completion and acids.

The developed model matches to the appropriate asymptotes ($q_{cr} \rightarrow 0$, $q_{cr} \rightarrow \infty$) and describes the wormhole local minimum in the vicinity of critical injection rate.

Note that since there is no analytical solution (1) for arbitrary speed, a dependency (22) should be obtained from numerical solution [32]. The development of wormhole formation theory will give the framework of approximation (23) improvement.

CRediT authorship contribution statement

Rodion M. Ganopolskij  : writing – section Unified dissolution problem, all calculations; **Konstantin M. Fedorov**  : writing – the general idea of the investigation, original draft; **Alexey E. Folomeev**   : writing – section Solution of the face dissolution problem, review & editing.

Conflict of interest

The authors declare that they have no conflict of interest.

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