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KINETICS OF GAS GENERATION IN WATER SOLUTION

Abstract

Results of researches of prominent features of rheochemical gas generation process on the basis of test laboratory experiments by in-situ carbon dioxide formation are presented. Results of experimental tests show effect of quantitative parities and physical and chemical characteristics of reacting solutions on the generated volume and pressure dynamics during reaction of gas-yielding and gas forming water solutions.

Carbon dioxide is used as a gas phase at gas-fluid fringe creation in technological process of waterflooding of oil reservoir [1, 2, 6].

Gas-liquid mixture possessing non-equilibrium properties generates additional energy in a deposit or stimulates natural reservoir energy [2, 3]. In situ generation of the gas-liquid medium formation is accompanied by the distortions causing reaction of medium. There is an intensive growth of fluctuation that leads to system's instability [4] in a point of new structure formation. Such fluctuations have mainly internal character induced by process of formation and dissolution of gas embryo. Fluctuations attenuation is a condition providing stability of a system on new level. Such reaction of formation medium on spontaneous, fluctuations is closely connected with a principle of "decrement " when the withdraw of a system from an equilibrium, steady condition is accompanied by the compensating processes aspiring to return it in former position, but at a new thermodynamic level.

In situ generation of carbon dioxide in a stratum is more effective from the standpoint of thermobaric conditions change of a productive stratum, and it naturally influences on instability of filtrational process, changes such parameters as viscous ratio of liquids participating in rheochemical reactions, oil volume factor and a residual oil content, etc. Allocation of embryonic gas bubbles reducing aqueous phase volume of outgassing solution, promotes pressure increase (in the consent with Le-Shatelie-Brown principle) [4, 5]. Consequence of CO_2 interaction with formation fluid will be change of fluid's rheophysical specifications.

With the purpose of research of characteristic properties of rheochemical gas generation process we conducted test laboratory experiments by formation of carbon dioxide in porous medium. Results of the first series of experimental researches show influence of qualitative parities and physical-chemical characteristics of reacting solutions on generated gas volume and pressure dynamics during reaction of gas-yielding and gas-generating solutions [fig.1, 2].

In laboratory experiments water solutions of carbonates salts prepared on distilled fresh water of Shollar type, and also formation water of Binagadi deposit physical and chemical characteristics of which is shown in tables, were used.

Table1.
Physical and chemical characteristics of Shollar fresh water (Azerbaijan)

Ca^{2+},	Mg^{2+},	Fe	Na^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}	$\sum K$	$\mathrm{Si}\,O_3^{2-}$
				$mg.eq/l$				
3,8	2,2	Ca^{2+} + Mg^{2+} 6,0	0,5	0,2	1,9	4,4	6,5	18,2

Table2.
Physical and chemical characteristics of Binagadi's deposit formation water (Azerbaijan) Kalin sunk.

Ca^{2+}	Mg^{2+}	$Na+K$	Cl	SO_4^{2-}	HCO_3+CO_3	$RCOO$	HB_4O_7
				$mg.eq/l$			
15.0	24.6	17.9	771.8	4.2	27.9	9.1	1.4

Comparison of stoichiometric reactions results between the gas-yielding water solutions prepared on distilled fresh water of Shollar type, and also formation water of Binagadi deposit (Azerbaijan) showed that baro- and volumetric characteristics of reaction differ depending on type of the aqueous phase participating in reaction. This difference is expressed, first of all, in rate of pressure change at allocation of carbon dioxide in the researched volume on initial stage of reaction [fig.1].

Solubility of carbon dioxide in water substantially depends on pressure, temperature and a chemical composition of a fluid. According to Setchenov's equation solubility of carbon dioxide from concentration in water of salts is equal to:

$$b_i^* = b_i \cdot 10^{-k_i n},$$

where: b_i is the content of pure water soluable i-th component being in balance with gas; b_i^* – the content of i-th component in saline, being in balance with the same gas; k_i is Setchenov's coefficient describing influence of the given salt on solubility of a gas component i; n is concentration of the water soluble salt.

Hence, in view of cited above, it is natural that solubility allocated in intrastratal reaction process of carbon dioxide in formation water is much less than in fresh water used as a aqueous phase of the gas-yielding agent. Thus, taking into account low solubility of gas, part of CO_2 is in a free phase, and this "surplus" being dissolved in oil, changes parity of viscosities of displacing and displaced fluids and by that can promote to the best sweep of dead areas of the oil-saturated reservoir.

These results are well coordinated with assumptions of authors [6]. Under identical thermodynamic conditions the fast allocation of CO_2 in a zone of contact with formation mineralized water also changes the volumetric charge at fringe flow and leads to essential reorganization of water and oil saturations distribution in displacement zone.

For the description of gas liberation curves it is possible to use exponential functions equivalent to used in relaxation model in the form of linear differential equations of the 1-st order. On the other hand this approach does not allow to take into account all details of the current processes, particularly, in case of high values of a water salinity.

Considering that already formed gas bubbles (C is bubbles concentration) are partly dissolved and also promote to gassing delay, we shall assume that speed of their formation:

$$\nu = \nu_1 - \nu_2 C - \nu_3 C^2; \tag{1}$$

where: ν_1 is speed of gas formation without disturbance;
ν_2 is speed of gas bubbles dissolution;
ν_3 is speed of delay of new gas bubbles formation.

Thus the models describing gas evolution in the form of nonlinear kinetic equations similar to ones given below, are offered:

$$\frac{dC}{dt} = \nu - \alpha C \tag{2}$$

where α is solubility coefficient.

$$\frac{dC}{dt} = \nu_1 - \nu_2 C - \nu_3 C^2 - \alpha C \tag{3}$$

Having accepted that between bubbles concentration and pressure there is a line communication:

$$P = KC$$

K is rate of pressure change;

Then:

$$\frac{dP}{dt} = k\nu_1 - (\alpha + \nu_2) P - \frac{\nu_3}{k} P^2 \tag{4}$$

$\alpha_1 = k\nu_1$ is a parameter influencing on pressure change under gas liberation;

$a_2 = \alpha + \nu_2$ is a parameter taking into account influence of partial dissolution of gas embryo on pressure change;

$a_3 = \dfrac{\nu_3}{k}$ is coefficient taking into account influence of already available gas embryo on pressure change.

Then we shall receive:

$$\frac{dP}{dt} = a_1 - a_2 P - a_3 P^2 \tag{5}$$

For estimation of a_1, a_2, a_3 coefficients we shall use advantage of the method [7] based on the positions of sensitivity theory. In case of presence of coefficients (a_2 and a_3) taking into account, accordingly, partial dissolution of bubbles and influence of already formed gas germs on change of pressure in a gassing zone, the solution of (5) will have the form:

$$P = \frac{1}{2a_3}\left[A\left(1 - \frac{2}{1 + e^{A(t+c)}}\right) - a_2\right], \tag{6}$$

where $A = \sqrt{a_2^2 + 4a_1 a_3}$ – (fig.1 - curves 1, 2).

In the case, when formation water (Binagadi type) is used as aqueous phase of a gas-yielding solution, the coefficient taking into account influence of gas embryos dissolution, as it follows from experiments results, is insignificantly small. Therefore, the equation (5) can be written as:

$$\frac{dp}{dt} = a_1 - a_3 P^2 \tag{7}$$

whose solution can be presented as dependence of P on t:

$$P = \sqrt{\frac{a_1}{a_3} 1 - \frac{2}{1 + e^{2\sqrt{a_1 a_3}(t+C)}}} \tag{8}$$

describing curve 3 (fig. 1.)

At the following stage of the reaction in porous medium (composed of 95 % quartz sand and of 5 % montmorillonite clay) is considered. Here we reveal the effect slightly different from previous test – pressure grows up to some extreme value in initial moment and then decreases. Presence of porous medium in reactionary medium influences on dynamics of pressure change in stoichiometric reactionsprocess. Connection between pressure and gassing is of essentially nonequilibrium character, since a pressure change leads to slow processes of gas liberation in the form of bubbles germs and their dissolution after reaction (fig. 3, curves 1,2). In contrast at the presence of rock in the reactionary medium of a gas-yielding solution, whose water phase is formation water, dynamics of pressure has monotone character (fig. 3, curve 3).

Fig.1. Dynamics of pressure under stoichiometric reactions of gas-yielding and gas-forming solutions.

Fig.2. Dynamics of the generated volume of carbon dioxide under stoichiometric reactions of gas-yielding and gas-forming solutions.

Fig.3. Dynamics of pressure under reaction of gas-yielding and gas-forming solutions in the porous medium (95 % of quartz sand + 5 % of clay).

Pressure reduction on the final stage of gas evolution in systems with porous medium is connected (as authors note [7, 8]) with gas embryos adsorption on surface of particles with the subsequent diffusion of gas molecules inside of rock grains. In this case, expression describing formation and dissolution of gas embryos is [7]:

$$\frac{dP}{dt} = a_1 - a_2 P\left(t\right) - a_3 P^2\left(t - \tau\right),$$

a_2 and a_3 are factors determining of pressure change in view of influence already formed and diffusing gas molecules in rock particles;

- characteristic time of diffusion.

In a case, when reaction of gas evolution proceeds at the presence of porous medium, and aqueous phase of a gas-yielding solution is formation water (such as Binagadi type), the factor taking into account influence of dissolution of gas germs and their diffusion in rock grains, as it follows from the results of experiments, is insignificantly small. Therefore, in this case gasification will proceed similarly to the process without the porous medium and the equation can be written as (7), whose solution can be presented as dependence of P on t (equation (8), describing curve 3 (fig. 3)).

In this expression there is no a member describing diffusion process. The carried out researches permit to conclude that in case of using the gas-yielding water solutions prepared in formation water, fast rate of gas liberation to the third phase during the initial moment of reaction is observed, and absence of diffusion factor leads to achievement of the best result during distribution of water and oil saturations in a drive zone. Intensive gas evolution on the initial stage of reaction slightly slows down flow rate of forward jump of saturation and, hence, reduce rates of water influx in comparison with fresh water. The given conclusion evidently confirms the results of laboratory experiments on oil displacement from porous medium by pseudoboiling gas-fluid system fringe in which formation water is used as a aqueous medium of gas-yielding solution .

Experiments on displacement were carried out on the laboratory model simulating a porous medium of a productive stratum. The filtrational medium represented a model of a stratum with heterogeneous porosity. At the first stage oil displacement was conducted by gas-fluid fringe which aqueous phase was distilled water. In the second series of experiments at identical filtrational characteristics of porous medium oil was displaced by fringe of solution in fresh water, and in the third series - as a displacing fluid was used fringe, in which basis of a gas-yielding solution was formation water. The results of researches shown on fig. 4, represent dependence of oil saturation of medium on volume of the liquid displaced from the porous medium. As we see from the fig.4 character of oil saturation is various under oil displacement by fringes with different physical-chemical structure of aqueous phase. Change is characterized by the fact that under oil displacement by PGS fringe on formation water we observe relatively bigger decrease of oil saturation that testifies to the best oil replacement from the porous medium. In this case, relatively high waterless factor of oil displacement is also observed.

Thus, the results received in laboratory researches can form a basis for the directed regulation of in situ carbon dioxide generation process in technology of displacement by fringe of pseudoboiling gas-fluid system. In zones with a high residual oil saturation the address use of gas-yielding solutions promoting more full clean of residual hydrocarbons is effective.

Fig.4. Dynamics of oil saturation under displacement of oil model by list of reacting solutions.

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