Effective concentration of the biocide injected for chemical control of biogenic H_2S in producing formations

Jerzy Stopa[1]

Efektívna koncentrácia biocídneho vstrekovania pre chemickú kontrolu biogénneho H_2S v Šaģenĺch loģisk§ch.

When injecting chemicals to a wellbore, their concentration in the reservoir may significantly differ from their concentration in the fluid injected to the formation owing to such processes as dispersion, sorption, chemical reactions, biodegeneration.

When designing the injection of biocides to remove hazardous bacteria, it is necessary to establish their effective concentration in the reservoir and variability in time. This concentration should maintain over some efficient value determined in laboratory condition, for a definite time. A mathematical model of the biocide mass transport in a near-wellbore zone is presented in the paper. The results of calculations of efficient concentrations for two field tests in gas wells are reported.

Key words*: Mathematical model of biocide mass transport*

Introduction

Sulfate Reducing Bacteria (SRB) create a serious problem in some oil fields and natural gas storages. Their metabolic by-product is hydrosulfide, aggressive and synthesizing with iron ions, forming iron sediments (Fe_xS_y). A problem in many reservoirs is that levels of hydrogen sulfide in produced fluids increase. Problems associated with the sour production are well known: the corrosion, excess solids, emulsion and the necessity to remove H_2S from gas prior to sale. In the case of gas storages they may strongly reduce the quality of the stored gas and increase the cost of all production and injection operations. Therefore, an efficient control of sulphur bacteria is one of priorities in the USG management.

In practice, H_2S and the population of SRB are controlled by injecting chemical neutralizers of H_2S and biocides into the reservoir. Depending on their concentration they may act on the bacteria either by killing them or biostatically. Exemplary, recommended concentrations of selected biocides are given in Table 1.

Tab. 1. Exemplary, recommended concentrations of selected biocides.

Biocide	Producer	Time of activity	Concentration
Tolcide® PS, [1]	Rhodia WaterPhosphorus and Performance Derivatives	2 h	80 mg/l (ppm)
Glutaraldehyde, [2]	Union Carbide Corporation	-	9.45 ppm
Ucarcide™ Antimicrobials [3]	Trademark of The Dow Chemical Company	1h, 2h, 4h	100 ppm 50 ppm 25ppm

It follows from literature data on the concentration, application modes and the efficiency that it is vital to determine the efficient concentration of chemicals in the reservoir, which may be considerably different from the concentration in the injected stream. Moreover, in the case of a biofilm the necessary contact time can be considerably elongated, even to some days. A mathematical model of biocide mass transport to the near-wellbore zone is presented along with calculation results of the efficient concentration for two test fields in Poland.

Mathematical model of biocide mass transport to the near-wellbore zone

In literature, the influence of a biocide in static conditions is modelled with the use of an equation of diffusion with an additional element describing the chemical reaction [4]. In dynamic conditions, the biocide mass transport to the near-wellbore zone takes place due to superposition of the above-enumerated processes, and an additionaly convection and dispersion.

When injecting one fluid to the wellbore, the interface $r_f(t)$ separating the injected fluid "1" from the original one „2" disperses with time forming a growing transition zone. This causes a dispersion of biocide in the reservoir, with a possible occurrence of sorption effects or chemical reactions. These

[1] *Jerzy Stopa,* AGH University of Science and Technology,Faculty of Drilling, Oil and Gas,Al. Mickiewicza 30, 30-059 Krakow, Poland, stopa@agh.edu.pl
(Recenzovaná a revidovaná verzia dodaná 6. 10. 2006)

processes dynamically modify the biocide concentration in reservoir conditions as compared with the initial concentration of fluids injected to the wellbore.

Having assumed that the biocide may be adsorbed by the matrix of porous medium, the mass balance must include not only the dissolved biocide mass but also the adsorbed biocide mass. While the dissolved concentration C is measured as a mass of biocide per reservoir fluid volume, the adsorbed concentration C_a is measured as mass of biocide per mass of dry matrix material. The total biocide mass in a unit volume of porous medium is given by:

$$\Delta M = C \cdot \phi + (1-\phi)\rho_r C_a \tag{1}$$

where:

C – dissolved concentration of a biocide, mg/dm^3

C_a – adsorbed concentration, mg/g

ϕ – porosity coefficient

ρ_r – density of rock matrix

Allowing a first order chemical reaction, the rate of decay is proportional to the concentration present:

$$\frac{d(C^* \phi)}{dt} = -\lambda \phi C^* \tag{2}$$

where: C^* – total concentration of the biocide, mg/dm^3

λ - constant,

Assuming the radial symmetry of the flow, the equation of biocide mass balance is:

$$\phi \frac{\partial [C \cdot \phi + (1-\phi)\rho_r C_a]}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}(r \cdot K \cdot \frac{\partial C}{\partial r}) - \frac{1}{r}\frac{\partial}{\partial r}(r \cdot u \cdot C) - \lambda [C \cdot \phi + (1-\phi)\rho_r C_a] + q \tag{3}$$

where:

t – time,

r – distance from the wellbore

u – Darcy velocity,

$K=D_M+\beta \cdot u$ – dispersion coefficient,

D_M, β – diffusion and dispersion coefficients

q – volume source and sinks other than first order reactions; further assumed to be q=0.

To complete equation (3) a further equation for the adsorbed concentration C_a is needed. Having assumed that the adsorbed concentration is always in equilibrium with the dissolved concentration, this means that $C_a=f(C)$, where the function f is called sorption isotherm.

According to the reference [4], in the simplest case f(C) is linear:

$$C_a = \kappa \cdot C \tag{4}$$

where: κ - constant. In this case we obtain the transport equation of biocide in the form:

$$\frac{\partial}{\partial t}[\phi \cdot R \cdot C] = \frac{1}{r}\frac{\partial}{\partial r}(r \cdot K \cdot \frac{\partial C}{\partial r}) - \frac{1}{r}\frac{\partial}{\partial r}(r \cdot u \cdot C) - \lambda \cdot \phi \cdot R \cdot C \tag{5}$$

where:

$$R = 1 + \frac{(1-\phi)}{\phi} \cdot \rho_r \cdot \kappa \tag{6}$$

In the general case, the velocity u depends both on the time and the location. However, the solution of the equation is not known in such a situation. Having assumed that the width of the transition zone is much smaller than the geometrical size of the reservoir, the following can be assumed:

$$u(x,t) = u(r_f(t),t) = \phi \cdot \frac{d\, r_f(t)}{dt} \tag{7}$$

where:

u – Darcy velocity,

$r_f(t)$ – fictitious radius representing location of the transition zone.

The initial and boundary conditions should be formulated for equation (5). Assuming that the time of biocide injection is short, one can assume an instantaneous injection, and the initial condition takes the form:

$$2 \cdot \pi \cdot h \cdot \phi \cdot \int_0^{\infty} C(r,0) \cdot r \cdot dr = M \tag{8}$$

where:

h – effective thickness

M – mass of injected biocide

The boundary conditions can be written in the form:

$$C(\infty, t) = 0\,,\ C(r,t) < \infty \ \ for\ t > 0, \tag{9}$$

It is further assumed that $\phi \cdot R = \mathrm{const}$. With this assumption, equation (5) under conditions (8), (9) can be solved by a method similar to that in [5, 6]. It was shown that the transformation of variables:

$$\xi = r^2 - \left[\frac{r_f(t)}{R}\right]^2,$$

$$\eta = \frac{4}{R \cdot \phi} \cdot \int_0^t K(\tau) \cdot r_f(\tau)^2 \cdot d\tau = \frac{4}{R \cdot \phi} \cdot \left(\int_0^t D_M \cdot r_f(\tau)^2 \cdot d\tau + \int_0^t \beta \cdot |u(\tau)| \cdot r_f(\tau)^2 \cdot d\tau \right) \tag{10}$$

reduces equation (10) to the approximated form:

$$\frac{\partial C}{\partial \eta} = \frac{\partial^2 C}{\partial \xi^2} \tag{11}$$

The approximated equation of abrupt interface $r_f = r_f(t)$ can be found on the basis of a mass balance:

$$\int_0^t Q_z(\tau) d\tau = \pi \cdot r_f(t)^2 \cdot h \cdot \phi \tag{12}$$

where: Q_z - injection rate calculated for reservoir conditions, h – thickness, ϕ – porosity coefficient.

Condition (8) takes the form:

$$\pi \cdot h \cdot \phi \cdot \int_0^{\infty} C(\xi, 0) d\xi = M \tag{13}$$

i.e.,

$$C(\xi, 0) = \frac{M}{\pi \cdot h \cdot \phi} \delta(\xi) \tag{14}$$

where: $\delta(\xi)$ - Dirac's distribution

The solution of the differential equation (11), with boundary conditions (9), (14) is [7]:

$$C = \frac{M}{2\pi h \phi \sqrt{\pi \eta}} \cdot \exp\left(\frac{-\xi^2}{4 \cdot \eta} \right) \tag{15}$$

Results of calculating the biocide concentration in the near-wellbore zone

Using the results of laboratory analyses quoted in [8], the linear isotherms of sorption were fitted, and the approximated value of κ =25.6 dm^3/kg was obtained and λ=0 was assumed for the calculations. The following assumptions were made for the remaining parameters: D_M=1.03 10^{-5} m^2/s , β=6.29 m. The calculations were made for 2 field tests performed in an operation wellbore in an underground gas storage in Poland. The biocide solution was injected with the gas stream, in line with data given in table 2.

The results of calculations in the form of changes of the biocide concentration in near-wellbore zones are presented in Figs 1 and 2.

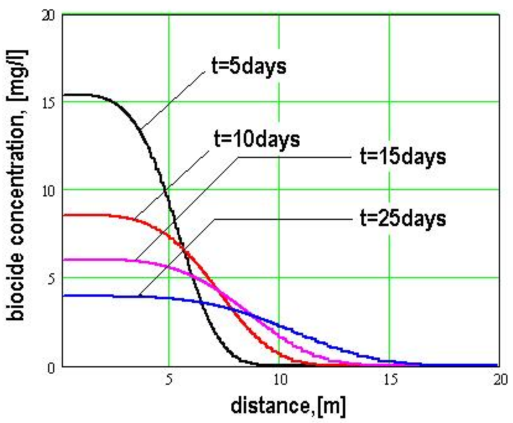

Fig. 1. Distribution of biocide concentration in the reservoir test no.1.

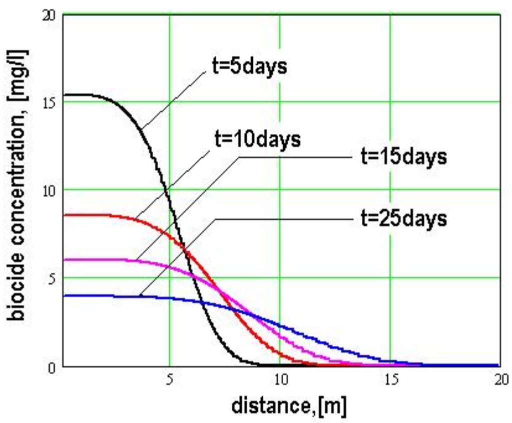

Fig. 2. Distribution of biocide concentration in the reservoir, test no. 2.

Tab. 2. Biocide injection in two field tests.

No. test	Injected solution	Date of injection	Injection rate [m3/d]	Volume of injected solution [m^3]
1	1.0% solution of biocide in a mixture of methanol and water (50%-50%)	2003-08-04	0.3	1.2
2	4.0% solution of biocide in methanol	2005-04-21	576	3.75

Conclusions

The biocide concentration in a reservoir may be determined through the mathematical modeling methods. In the case of an instantaneous injection, the mathematical modeling and the calculation of the biocide concentration were made for two schemes of injection in real field tests carried out in Poland. The laboratory investigations made prior to field tests indicated that the efficient biocide concentration ,needed to control the growth of bacteria responsible for the production of hydrogen sulfide was 100 ppm (ca. 110 mg/dm^3). Assuming that the same concentration should be reached in the reservoir, the following conclusions could be drawn:

- The calculation results show that in the case of test 1 the dosage is too low. The biocide concentration is below the effective value.
- In the case of test 2, sorption causes that the biocide accumulates in the near-wellbore zone to 5-10 m from the wellbore. In this zone, the concentration is sufficient to efficiently control the growth of bacteria.

References

[1] http://www.dow.com/, *Trademark of The Dow Chemical Company brochure, 2004.*

[2] http://www.rhodia-ppd.com/index.asp; "Performance Biocides in Industrial applications"- *brochure Rhodia WaterPhosphorus and Performance Derivatives.*

[3] http://www.unioncarbide.com/; Union Carbide Corporation; "The Right Biocide for Many Environments"- *brochure*

[4] Steward, P., S., Raquepas, J., B.: Implication of reaction-diffusion theory for the disinfection of microbial biofilms by reactive antimicrobial agents, *Chemical Eng. Sc, Vol. 50, No. 19 (1995) 3099-3104*

[5] Stopa, J.: Dispersion Effects Appearing During the Process of Displacing Oil with CO_2. *Zeszyty Naukowe AGH, Drilling Oil Gas, 2, 1986.*

[6] Blicharski, J.: Wpływ parametrów złożowych i technologicznych na skład gazu wydobywanego w procesie wytwarzania podziemnego magazynu gazu, *praca doktorska, WWNiG AGH, Kraków, 2003.*

[7] Carslaw, H., S., Jaeger, J., C.: Conduction of Heat in Solids., *Oxford University Press, London 1959.*

[8] Voulvoulis, N., Scrimshaw, M., D., Lester, J., N.: Partitioning of selected antifouling biocides n the aquatic environment, *Marine Environmental Research 53 (2002) 1–16.*