COMPATIBILITIES AND INTERACTIONS

SECTION B3
DIFFUSION OF GASES IN FORMATE BRINES

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B3.1 Introduction

Diffusion of reservoir fluids into the wellbore is known to be a serious well control problem with oil-based drilling fluids. In water-based fluids, the diffusion of reservoir gases is known to be much lower.

A study carried out by Technip Offshore Engineering investigates how reservoir gases diffuse through formate brines. The study consists of the following projects:

1) The development of a simple analytical model for gas diffusion coefficient in aqueous and hydrocarbon fluids.
2) Use of this model to predict diffusion coefficients, diffusion fluxes, and accumulated influx of carbon dioxide (CO_2) from the gas cap into a formate packer fluid and the diffusion flux and accumulated influx of methane (CH_4) through filtrate-invaded formation into a wellbore with formate brine density ≈2.0 g/cm^3.

As the work has been extensively reported in three reports (Technip, 2003a; Technip, 2003b; Technip, 2003c) and a paper (Shukla et al.), which are all available from Cabot), full details of the modeling work are not explained here. Some examples of predicted diffusion coefficients, diffusion fluxes, and gas accumulation are reported though. Modeling did not include the reaction of diffused CO_2 with CO_3^{2-}.

B3.2 The diffusion model

A simple and efficient analytical model for the diffusion coefficient has been developed and is valid for diffusion of reservoir gases into formate brines. This model is based on a previous model developed by Shukla et al., itself based on kinetic theory of gases and extended to the variety of cases of gas and liquid systems consisting of hydrocarbons and aqueous fluids. The new work includes an improved diffusion-coefficient model, which means it can be applied to both gas and liquid systems consisting of more general classes of fluids, including hydrocarbons and aqueous fluids under HPHT conditions.

Following Shukla's work, the diffusion coefficient of a solute i in solvent j can be expressed analytically as follows:

$$D_{ij} = F(\psi\, MW_j)^{0.5}\, T/(\eta_m V_i^{\xi}) \qquad (1)$$

where D_{ij} [cm^2/s] is diffusion coefficient of solute i in solvent j, ψ is association parameter, MW_j is molecular weight of solvent j, T is temperature [K], η_m is viscosity [cP] of the mixture, V_i [cm^3/mol] is molar volume of

solute at its boiling point, F is a constant factor, F = 7.4 x 10-8, and ξ is a volume parameter. In previous work ψ = 1, ξ = 0.6, and η_m were represented by the viscosity of the pure solvent. In the improved model, η_m is the mixture's viscosity at the given temperature, pressure, and composition of the mixture constituents, while ψ and ξ depend on fluid system type. In this work, ψ and ξ parameters are optimized by comparing model results with experimental data for a variety of fluids under ambient to high conditions of temperature, pressure and dilute to finite compositions of liquids and gases. The model is currently available in the form of an Excel spreadsheet.

The model has been tested against systems for which experimental data were available in the literature. Results were found to compare well with available experimental data for several binary and multicomponent systems, ranging from ambient to HPHT conditions.

With diffusion coefficients predicted by the above model, standard diffusion equations are applied to predict diffusion fluxes through linear systems, e.g. diffusion of CO_2 from gas cap and into packer fluid, and radial diffusion of gas through invaded filtrate zone and filtercake into the wellbore. In order to determine diffusion fluxes, gas solubility data is required as reported elsewhere in this manual.

B3.3 Diffusion of CH_4 in formate brines

Diffusion and mass influx of gas through the formation and into the wellbore is known to be a serious well control problem when drilling with oil-based mud. Even in overbalanced wells, large amounts of gas influx can be experienced, particularly in horizontal and high-angle wells.

It has been shown that diffusion of CH_4 into the wellbore is dramatically reduced with formates as compared to either water- or oil-based fluids.

B3.3.1 Predicted diffusion coefficients

The above diffusion coefficient model (1) has been used to predict the diffusion coefficient for methane in 2.09 g/cm^3 / 17.44 lb/gal cesium formate brine. Predicted diffusion coefficients as functions of pressure and temperature are shown in Table 1. The fluid viscosity is vital input in this model. It is important to keep in mind that these diffusion coefficients are valid for base brine only. For a formulated drilling fluid containing viscosifiers, diffusion rates are significantly lower.

B3.3.2 Examples of use

Diffusion flux of CH_4 through a mud cake

By using diffusion coefficients and available solubility data (reported elsewhere in the manual), diffusion fluxes for diffusion of methane in 2.09 g/cm³ / 17.44 lb/gal formate brine can be determined and compared with similar data for water- and oil-based filtrates. Comparison of solubility, diffusion coefficients, and diffusion flux for these three systems in 0.5 cm thick mud cake under HPHT conditions (149°C / 300°F and 69 MPa / 10,000 psia) are shown in Table 2. As can be seen, diffusion coefficient for CH_4 in formate brine is predicted to be one and a half times lower than that in oil-based filtrate and four times less than in water-based filtrate. The diffusion flux of CH_4 through formate brine is reduced by a factor of 16 when compared with water, and by a factor of 210 when compared with oil. The reason for larger differences between diffusion fluxes than diffusion coefficients is that fluxes are dependent on CH_4 solubility, which is much lower in formates than in water- and oil-based fluids.

Mass influx of CH_4 into the wellbore

Using the same data, accumulated mass influx of CH_4 gas into a 21.6 cm / 8.5" diameter wellbore for a typical HPHT reservoir (149°C / 300°F and 68.9 MPa / 10,000 psi) with a filtrate-mud invaded zone of 30 cm / 11.8" thick has been determined and compared to that of water. The porous medium is represented by porosity of 20% and tortuosity of 2. Figure 1 shows accumulated mass influx into the wellbore as a function of time for 2.09 g/cm³ / 17.44 lb/gal cesium formate brine compared with water. The huge difference in final accumulated mass influx is caused by a ten-fold difference in solubility of CO_2 in the two. The much lower rate of accumulation in formate brine is caused by a considerably lower diffusion coefficient.

Table 1 Predicted diffusion coefficients for 2.09 g/cm³ / 17.44 lb/gal cesium formate brine at various temperature and pressure conditions.

Fluid	Temperature		Pressure		D_{ij} x 10⁸
	[°C]	[°F]	[MPa]	[psia]	[m²/s]
Cesium formate	37.8	100	13.8	2,000	0.116
			34.5	5,000	0.112
			68.9	10,000	0.108
			110.3	16,000	0.103
	93.3	200	13.8	2,000	0.431
			34.5	5,000	0.398
			68.9	10,000	0.352
			110.3	16,000	0.310
	148.9	300	13.8	2,000	1.267
			34.5	5,000	1.044
			68.9	10,000	0.807
			110.3	16,000	0.634
	176.7	350	13.8	2,000	1.988
			34.5	5,000	1.512
			68.9	10,000	1.081
			110.3	16,000	0.806

Table 2 Comparison of solubilities, diffusion coefficients, and diffusion fluxes for CH_4 in water, oil filtrate, and 2.09 g/cm³ / 17.44 lb/gal cesium formate brine at 149°C / 300°F and 68.9 MPa / 10,000 psi.

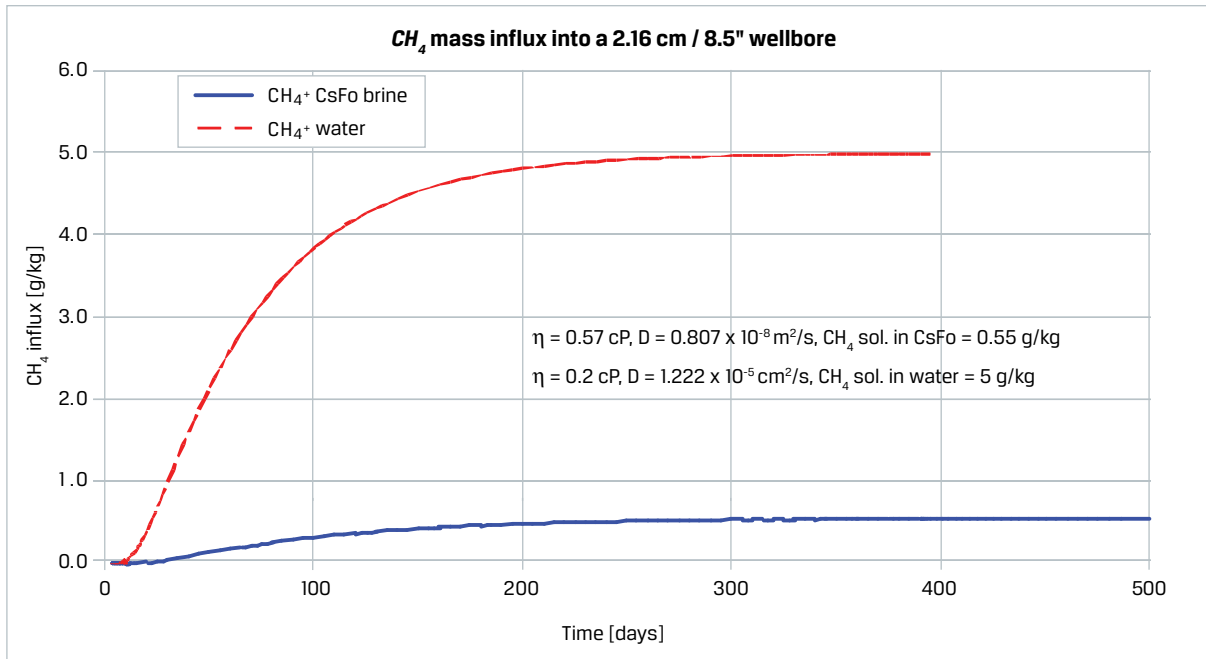| Fluid	Solubility [kg/m³]	Diffusion coefficient [m²/s]	Flux x 106 [kg/m²s]
Water	4.8	2.93	3.98
Oil	164	1.15	53.3
Cesium formate	1.09	0.81	0.25

Figure 1 Accumulated mass influx of CH_4 into a 21.6 cm / 8.5" wellbore. This is based on diffusion through a 30 cm / 11.8" invaded zone at HPHT conditions (149°C / 300°F and 68.9 MPa / 10,000 psi).

B3.4 Diffusion of CO_2 in formate brines

A major requirement for effective use of formate-based drilling, completion, and workover fluids is pH maintenance in the presence of acidic gases, such as CO_2 and H_2S. High pH prevents formation of less thermally stable formic acid and reduces corrosion rates.

The diffusion model can be used to predict diffusion coefficients for CO_2 diffusion into formate brines. These diffusion coefficients, together with solubility data, can be used to predict diffusion fluxes and accumulated mass influx. Useful examples are:
- diffusion of CO_2 in a wellbore (or annulus)
- diffusion of CO_2 through reservoir rock and filtercake into completion fluid

What the model is still missing, however, is the ability to handle the chemical reaction taking place between CO_2 diffusing into formate brine and the carbonate / bicarbonate buffer added to the formate brine.

B3.4.1 Diffusion coefficients

Using the diffusion coefficient model (1), the diffusion coefficient of CO_2 in cesium formate brine was predicted over a range of pressures and temperatures for 80 %wt cesium formate brine. The results are plotted in Figure 2. Compared with diffusion of CO_2 in water, the diffusion coefficient in cesium formate was shown to be about four to five times lower at

atmospheric pressure and 38°C / 100°F (0.6 X 105 vs. 2.6 X 105 cm²/s).

It is important to keep in mind that viscosity is vital input to this model and the predicted diffusion rate is very dependent on viscosity. The viscosity decreases with increasing temperature and decreasing pressure.

B3.4.2 Examples of use

Case 1: Diffusion of CO_2 from a gas cap in packer fluid
As an example, the model has been used to predict the concentration of carbon dioxide in an unbuffered formate packer fluid as a function of temperature and pressure. Solubility of CO_2 in cesium formate brine as a function of temperature and pressure is available (see Section B2 Solubility of Gases in Formate Brines) and has been included. For this example, it is assumed that concentration of CO_2 at the interface to the gas cap, C_0, is constant (= the solubility value of CO_2 in 80% cesium formate brine at the actual temperature and pressure).

Figure 3 shows the concentration profile (C/C_0) inside of cesium formate brine as a function of the distance from the gas cap. The example shown is for conditions of 38°C / 100°F and 68.9 MPa / 10,000 psi. As can be seen, diffusion of CO_2 into the packer fluid is a slow process.
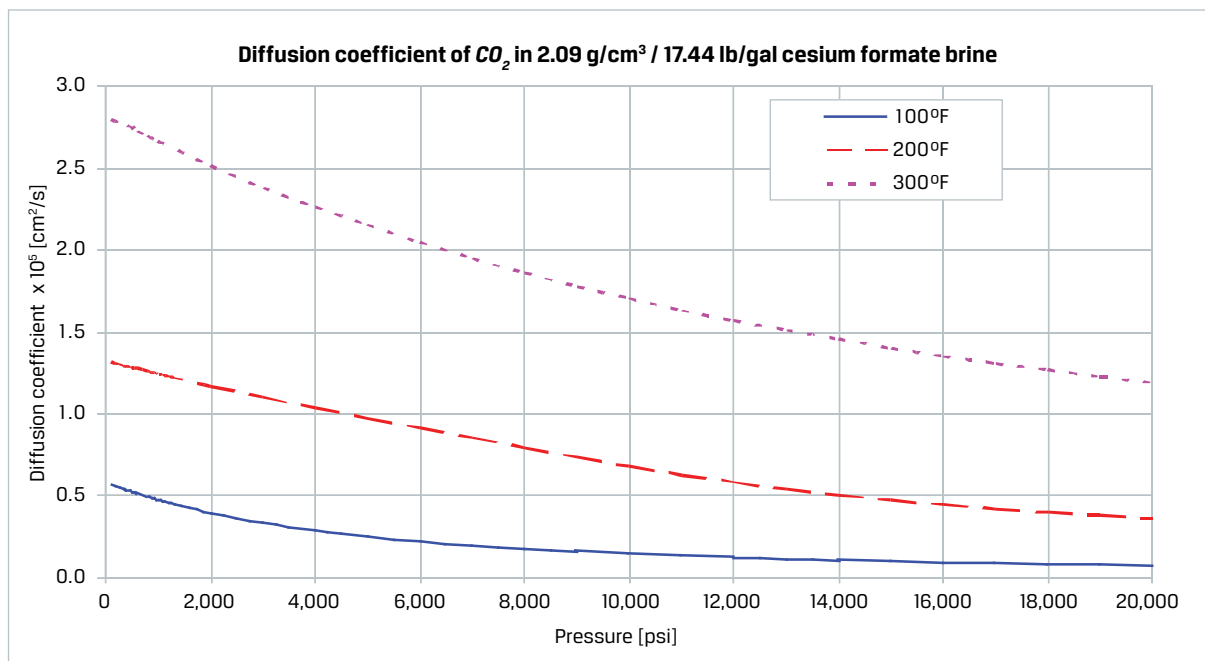
Figure 2 Diffusion coefficient of CO_2 in 2.09 g/cm³ / 17.44 lb/gal cesium formate brine.

Case 2: Mass influx of CO_2 into wellbore

As for CH_4, presence of the porous medium (filtercake + filter-invaded zone) significantly slows down diffusion of CO_2 into the wellbore.

As an example, the predicted gas influx into a 21.6 cm / 8.5" wellbore as a function of time for various lengths of the invaded zone is shown in Figure 4, where properties of the invaded zone are assumed to be ϕ = 0.2 and τ = 1.41.

As for methane, the accumulated mass influx into the wellbore is lower in a zone invaded with formate brine than in a zone invaded with water.

B3.4.3 Effect of pH buffer

Formate brines are used with a carbonate / bicarbonate pH buffer. The capacity of 8 ppb carbonate / bicarbonate buffer is about 3.3 g CO_2 per kg formate brine. Introducing this buffer therefore heavily influences predictions from the model. Until the buffer is overwhelmed, carbonic acid formed when CO_2 dissolves in water is converted to bicarbonate (HCO_3^-), and pH remains high (± 10.2). The fact that the diffusion model doesn't consider absorption of CO_2 by the buffer as it starts diffusing through formate brine makes the predicted diffusion rates too high. It is therefore not recommended to use this model for quantitative prediction of CO_2 diffusion into formate brines without considering the buffer's impact.

References

Technip (2003). "Modeling of CO_2 Diffusion in an HTHP Reservoir into an Unbuffered Cesium Formate Fluid: Diffusion Coefficient Model Development and Verification – Phase 1", Technip report 303718-AVE-RA-0001, May 2003.

Technip (2003). "Modeling of CO_2 Diffusion without Porous Media in an HTHP Reservoir into an Unbuffered Cesium Formate Fluid – Phase 2", Technip report 303718-AVE-RA-0002, August 2003.

Technip (2003). "Modeling of CO_2 Diffusion through Porous Media in an HTHP Reservoir into an Unbuffered Cesium Formate Fluid – Phase 3", Technip report 303718-AVE-RA-0002, November 2003.

Shukla, K., Olsvik, G., Storhaug, J., Magri, N., Benton W., Low, E., Hermansson, L.: "Improved Well Control in HPHT Wells using Formate Fluids", unpublished paper, draft, version 1.
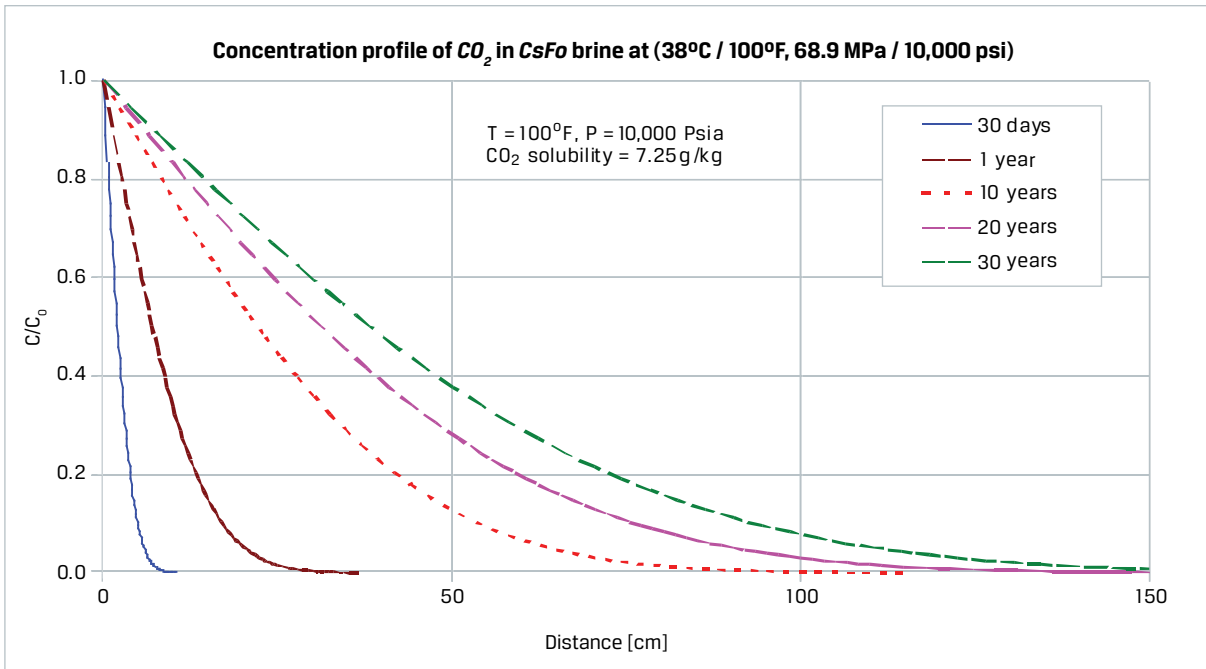
Concentration profile of CO_2 in *CsFo* brine at (38ºC / 100ºF, 68.9 MPa / 10,000 psi)

T = 100°F, P = 10,000 Psia
CO_2 solubility = 7.25 g/kg

Legend:
- 30 days
- 1 year
- 10 years
- 20 years
- 30 years

y-axis: C/C_0

x-axis: Distance [cm]

Figure 3 Concentration profile (C/C_0) in unbuffered cesium formate brine as a function of distance.
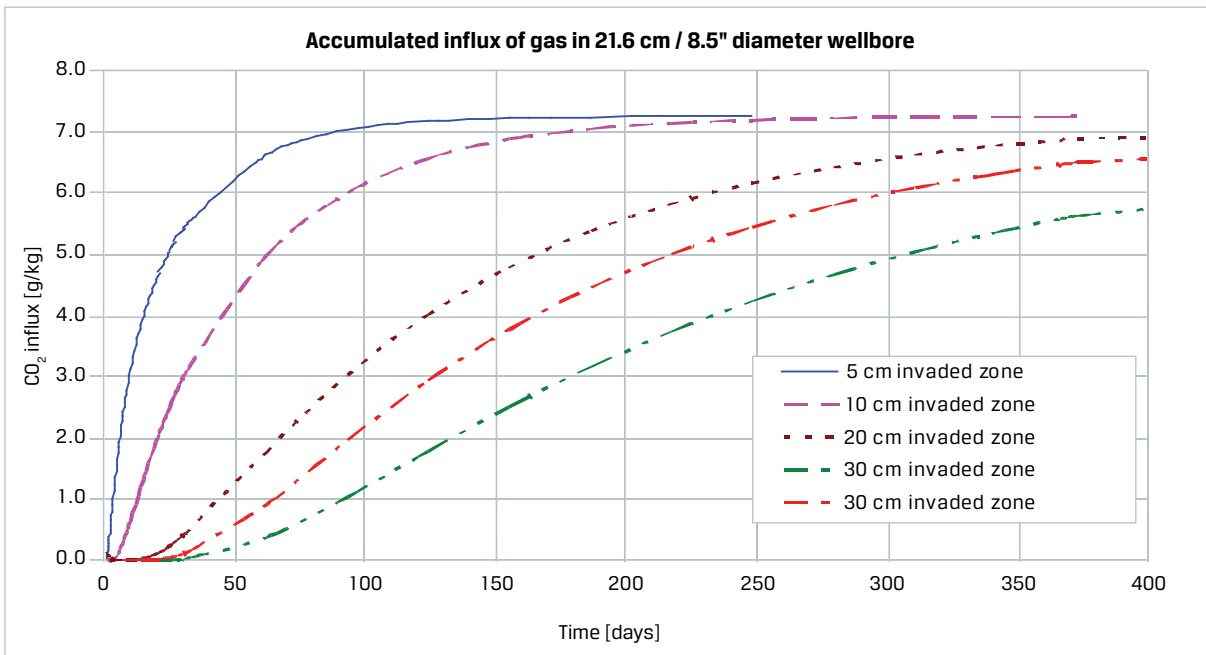Temperature = 38°C / 100°F and pressure = 68.9 MPa / 10,000 psi.

Accumulated influx of gas in 21.6 cm / 8.5" diameter wellbore

Legend:
- 5 cm invaded zone
- 10 cm invaded zone
- 20 cm invaded zone
- 30 cm invaded zone
- 30 cm invaded zone

y-axis: CO_2 influx [g/kg]

x-axis: Time [days]

Figure 4 Accumulated mass influx of CO_2 into a 21.6 cm / 8.5" wellbore. Based on diffusion through a 30 cm / 11.8" invaded zone at HPHT conditions (149°C / 300°F and 68.9 MPa / 10,000 psi). CO_2 solubility = 7.25 h/kg.