



Mathematical Characterization of Inorganic Salt Precipitation From the Reaction of CO₂ With Formation Brine and Its Application

Zhou Yuan*, Xinwei Liao, Kuaile Zhang, Xiaoliang Zhao, Hongyang Chu and Jiandong Zou

School of Petroleum Engineering, China University of Petroleum, Beijing, China

OPEN ACCESS

Edited by:

Wei Yu,
The University of Texas at Austin,
United States

Reviewed by:

Hongbing Xie,
Beijing Karst Technology Co., Ltd.,
China

Mauricio Xavier Fiallos Torres,
The University of Texas at Austin,
United States

*Correspondence:

Zhou Yuan
yuanz1987@163.com

Specialty section:

This article was submitted to
Advanced Fossil Fuel Technologies,
a section of the journal
Frontiers in Energy Research

Received: 13 April 2020

Accepted: 10 June 2020

Published: 14 July 2020

Citation:

Yuan Z, Liao X, Zhang K, Zhao X,
Chu H and Zou J (2020) Mathematical
Characterization of Inorganic Salt
Precipitation From the Reaction
of CO₂ With Formation Brine and Its
Application. *Front. Energy Res.* 8:141.
doi: 10.3389/fenrg.2020.00141

In the process of CO₂ enhanced oil recovery (CO₂-EOR), CO₂ interacts with formation brine containing high concentrations of scale-forming ions to produce inorganic salt precipitation, which blocks the rock pore throats, changes the characteristics of the reservoir, and thereby reduces the oil recovery rate. In this study, a series of experiments on the static reaction of CO₂-formation brine was conducted. The amounts of precipitation formed from the interaction of CO₂-formation brine under various conditions were tested. Using the PHREEQC software, the mathematical characterization formulas between the precipitation amount and various environmental factors (e.g., temperature, pressure difference, scale-forming ion concentration, and pH) were established. On this basis, a numerical simulation model of CO₂ flooding in a typical area of oil field C was established. The distribution of inorganic salt precipitation during continuous gas flooding was predicted, and the effect of inorganic salt precipitation on oil field recovery was analyzed.

Keywords: CO₂-formation brine, inorganic salt precipitation, mathematical characterization formula, numerical simulation, CO₂-EOR

INTRODUCTION

As indicated by relevant studies on CO₂ flooding for enhanced oil recovery (EOR), the injected CO₂ is involved in strong chemical reactions with the formation brine, and the generated precipitates block the rock pore throats and reduce the porosity and the permeability of the reservoir. This leads to significant changes in the physical properties of the formation rocks (Fischer et al., 2010; Zhao et al., 2010; Liu et al., 2012; Yu et al., 2012; Alam et al., 2014; Lu et al., 2016) and thereby lowers the oil recovery rate.

The laboratory experiment is the most commonly used method to investigate the CO₂-brine interaction. The research results by Wigand et al. (2008), Ketzer et al. (2009), Fischer et al. (2010), and Wandrey et al. (2011) are the most representative. Studies have shown that the reaction between CO₂ and formation brine is reversible, the equilibrium of which is affected by temperature, pressure, and the mineralization degree of the formation brine. Inorganic carbonate precipitates are formed in the case of over-equilibrium.

Upon dissolving in the formation brine, most CO₂ still exist in the form of free molecules, while only a small fraction of CO₂ combines with the formation brine to form carbonic acid (H₂CO₃).

Due to the dissociation of H₂CO₃, bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions are further generated, which then interact with scale-forming ions in the formation brine to produce inorganic carbonate precipitation (e.g., CaCO₃ and MgCO₃).

Sbai (2011) described the kinetic mechanism of solid particle suspension in porous media and suggested that these particles may cause clogging of the pores. Shiraki and Dunn (2000), Assayag et al. (2009), Bacci et al. (2010), and Luquot et al. (2012) conducted a series of CO₂ core displacement experiments under reservoir conditions. The experiments indicated that when CO₂ is injected into geological reservoirs, it reacts with the formation brine to form carbonates, and the precipitation of carbonates significantly affects the porosity and the permeability of the formation rocks.

Employing numerical simulation technology, Zeidouni (2009) simulated the carbonate precipitation phenomenon during the CO₂ flooding process and evaluated the impact of salt precipitation on oil field development. Yang et al. (2010) and Delshad et al. (2010) also conducted corresponding studies to simulate CO₂ distribution during the CO₂-EOR process.

At present, most studies are qualitative research studies that have not quantified the influencing factors of the precipitation amount. Based on previous research results, in this paper, the influences of various environmental factors (e.g., pressure difference, temperature, and scale-forming ion concentration) on precipitation formation from the reaction of CO₂ and brine were investigated quantitatively. Meanwhile, using the PHREEQC software, the effect of pH values was also simulated, and the corresponding exponential mathematical characterization formula was established *via* mathematical regression. On this basis, the Eclipse E300 module was used with the mathematical characterization formula to correct mathematical model parameters, optimize reservoir engineering parameters, simulate the distribution pattern of inorganic salt precipitation generated during the CO₂-EOR process in a block of oil field C, and determine the effect of precipitation on the oil field's ultimate recovery rate.

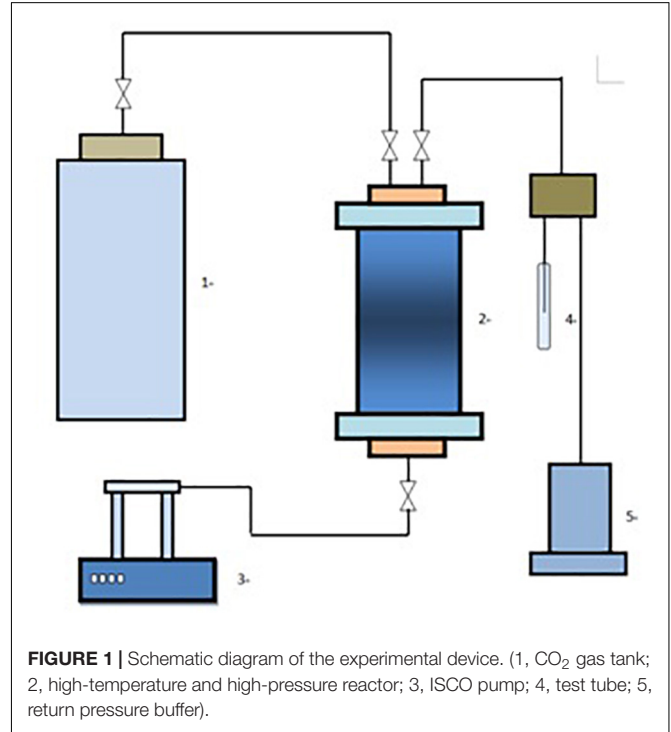
DETERMINATION OF PRECIPITATION AMOUNT AFTER THE INTERACTION OF CO₂ AND FORMATION BRINE

Experimental Method and Procedure

In this experiment, formation water, taken from three wells in a block of oil field C (the water properties are shown in **Table 1**), was used as the medium. Afterward, CO₂ was injected into a high-temperature and high-pressure reaction device (**Figure 1**) filled with 100 ml formation water until saturation was reached. Using the ISCO pump to raise the pressure of the device to the target pressure (8–16 MPa), it was put into the thermostat, and the pressure and the temperature (20–80°C) were kept stable and left to stand for 6 days. Subsequently, the pressure was released to atmospheric pressure and the system was left still for 1 day, followed by the determination of ion concentrations, precipitation composition, and precipitation amount.

TABLE 1 | The scale-forming ion analysis of the formation of brine sample.

Sample	Ca (mg/L)	Mg (mg/L)	Ba (mg/L)	Sr (mg/L)
1	2,012	198	0.006	19.4
2	5,145	209	0.057	25.4
3	10,590	222	0.028	18.8



The scale-forming ions in the formation brine sample were mainly Ca²⁺, Mg²⁺, Ba²⁺, and Sr²⁺. Among them, Ca²⁺ was the main component, taking up 95% of the total scale-forming ions, followed by Mg²⁺. The concentrations of Ba²⁺ and Sr²⁺ were very low.

Experimental Results

According to the principle of orthogonal experiment design, three brine samples with varied properties were employed for static experiments under different temperature (20, 30, 50, and 80°C) and pressure difference (8, 10, 12, and 16 MPa) conditions.

The concentrations of Ca²⁺ in the initial formation brine and the liquid samples taken out of the system each time were determined by inductively coupled plasma emission spectrometry. By subtracting the Ca²⁺ concentration in the initial formation brine from the Ca²⁺ concentration of each liquid sample, the variation of the Ca²⁺ concentration under different temperature and pressure conditions was obtained, which was then used to calculate the mass of CaCO₃ precipitation based on the molecular weight of the precipitate.

Since the experimental pressure was too high to measure the pH value of the solution, the PHREEQC software was applied to fit the experimental and the simulation results of the precipitation amount under different pH conditions to obtain a complete set of

data. The experimental and the simulation results are shown in Table 2.

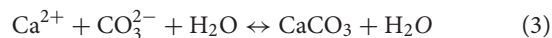
In order to confirm the presence of inorganic carbonate, the precipitates produced in the experiment were processed and tested for elemental composition (Figure 2). The main elements in the precipitates were C, O, and Ca and a small amount of Mg. The main inorganic salt precipitate produced by the reaction was CaCO₃, with the rest being CaCl₂ and MgCl₂. The ratio of the three precipitates (CaCO₃:CaCl₂:MgCl₂) was 10:0.25:1. The specific concentrations are shown in Table 3.

PRECIPITATION FACTOR ANALYSIS AND MATHEMATICAL CHARACTERIZATION METHOD OF CO₂-FORMATION BRINE INTERACTION

Analysis of Mechanism and Influencing Factors of Precipitation Formation From CO₂-Formation Brine Interaction

Reaction Mechanism

The precipitation formation from CO₂-formation brine interaction can be described by the following chemical reactions:



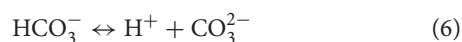
The precipitation and the dissolution of inorganic salts is a chemical equilibrium process. According to the chemical equations, the reversible reactions are affected by the concentrations of HCO₃⁻, CO₃²⁻, Ca²⁺, and H⁺ in the solution.

Therefore, the conversion form of the CO₂-brine system must be clarified first.

Gaseous CO₂ dissolves in brine and forms H₂CO₃:



H₂CO₃ then further ionizes:



Based on Eqs (4–6), the following equations can be obtained:

$$K_{\text{CO}_2} = \frac{[\text{H}_2\text{CO}_3]}{P_{\text{CO}_2}} \quad (7)$$

$$K_1 = \frac{[\text{H}^+] + [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad (8)$$

$$K_2 = \frac{[\text{H}^+] + [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

TABLE 2 | The experimental and the simulation results of the precipitation amount.

Sample	Temperature (°C)	Pressure difference (MPa)	pH value	Precipitation capacity (mg/L)
1	20	8	5.5	90
	20	10		130
	20	12		100
	20	16		150
	30	16		120
	50	16		50
	80	16		20
	80	16		20
2	20	8	6.2	160
	20	12		180
	20	16		200
	20	18		240
	30	16		130
	50	16		70
	80	16		10
	80	16		10
3	20	8	7	140
	20	10		220
	20	12		220
	20	16		270
	30	16		230
	50	16		110
	80	16		30
	80	16		30
1	20	8	7	170
	20	10		200
	20	12		170
	20	16		240
	30	16		190
	50	16		100
	80	16		50
	80	16		50
2	20	8	7	310
	20	12		330
	20	16		390
	20	18		510
	30	16		220
	50	16		150
	80	16		70
	80	16		70
3	20	8	7	300
	20	10		470
	20	12		480
	20	16		570
	30	16		480
	50	16		240
	80	16		80
	80	16		80
1	20	8	7	210
	20	10		260
	20	12		220
	20	16		300
	30	16		230
	50	16		110
	80	16		60
	80	16		60
2	20	8	7	370
	20	12		410

(Continued)

TABLE 2 | Continued

Sample	Temperature (°C)	Pressure difference (MPa)	pH value	Precipitation capacity (mg/L)
3	20	16		490
	20	18		650
	30	16		280
	50	16		190
	80	16		40
	20	8		410
	20	10		720
	20	12		790
	20	16		920
	30	16		750
	50	16		370
	80	16		190

K_{CO_2} is the equilibrium constant for the dissolution of CO₂, while K_1 and K_2 are the equilibrium constants for H₂CO₃ dissociation and HCO₃⁻ dissociation, respectively. The values in the square brackets represent the activity of each ion.

Under ambient temperature conditions, only H₂CO₃ exists in acidic (pH < 4.5) brine, while CO₃²⁻ mainly exists in an alkaline (8.34 < pH < 12) environment. As for neutral, weakly acidic, and weakly alkaline brine, the main species is HCO₃⁻, without the presence of CO₃²⁻. Moreover, this phenomenon is very weakly affected by temperature or fluid pressure (Zai-Hua and Dreybrodt, 2005).

The pH value of the formation brine used in this study is 6.2 at normal temperature and pressure. Thus, the ionization of Eq. 6 would not proceed. Therefore, it can be determined that the precipitation mechanism of the CO₂-formation brine interaction is as described by reactions (1) and (2).

It is generally considered that as long as the ion product of CaCO₃ is greater than its solubility product, CaCO₃ will precipitate. However, in actuality, CaCO₃ will only precipitate

TABLE 3 | Elemental composition of the precipitates generated from CO₂-formation brine interaction.

Element	Concentration (m)	Unit
C	10.08	wt. %
O	44.87	wt. %
Mg	1.91	wt. %
Cl	7.56	wt. %
Ca	34.57	wt. %
Total	100.00	wt. %

and deposit when the supersaturated state is exceeded. This is because CaCO₃ is a slightly soluble inorganic salt, and in its saturated solution, the supersaturation is often significantly greater than the solubility, causing the crystal nuclei to cease growing after nucleation. Therefore, only extremely high ion concentrations in the solution enable the growth and the precipitation of crystal nuclei.

Analysis of Influencing Factors

Influence of temperature

Figure 3 shows that temperature has a significant impact on the production of precipitation; the higher the temperature, the less precipitation there is. Moreover, the amount of precipitation is more sensitive to temperature when the scale ion content is high.

The phenomenon is evidently closely related to the solubility of the CO₂-formation brine system (i.e., temperature has a significant influence on H₂CO₃ formation from the dissolution of CO₂ in brine).

With a constant P_{CO_2} , K_{CO_2} is inversely proportional to temperature. This is because temperature is inversely proportional to CO₂ solubility in brine, and the activity of H₂CO₃ decreases when temperature increases, leading to a lower HCO₃⁻ concentration from its dissociation. Even if the chemical reaction rate increases upon temperature elevation (Shukla et al., 2010), the total amount of CaCO₃ precipitates will still decrease.

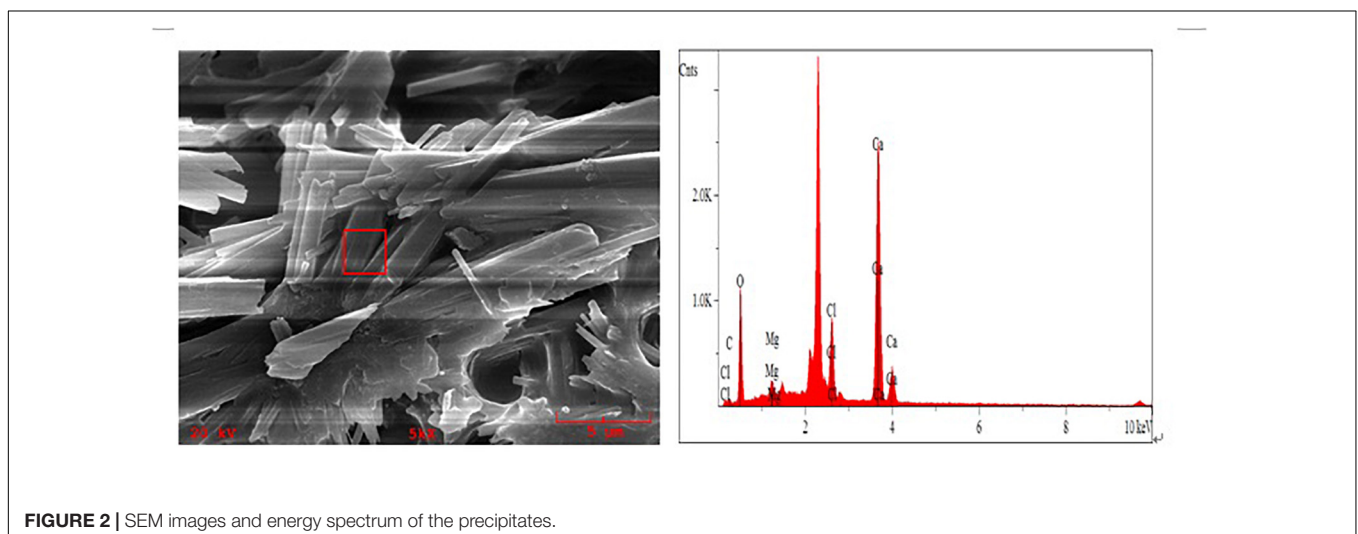


FIGURE 2 | SEM images and energy spectrum of the precipitates.

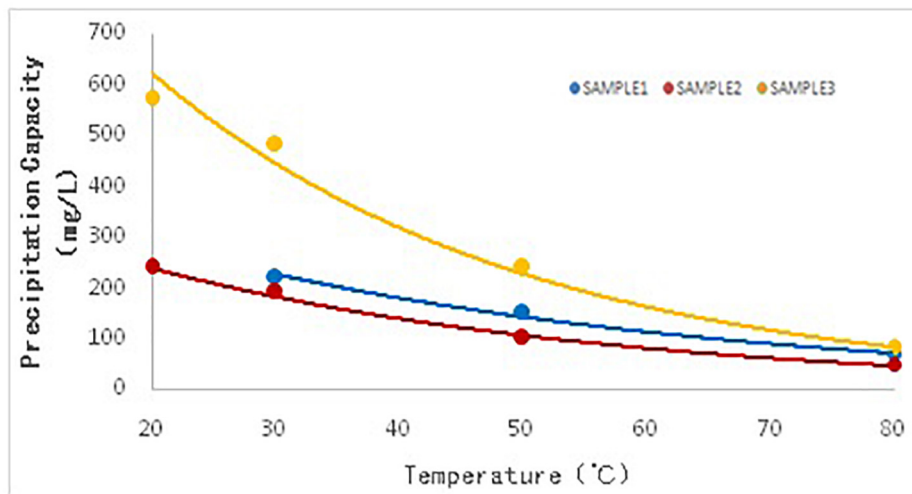


FIGURE 3 | The relationship between temperature and the precipitation capacity of inorganic salt.

Influence of pressure difference

A pressure increase does not lead to precipitation; conversely, precipitates appear upon lowering the pressure. This is because a higher pressure means a higher P_{CO_2} , under a constant temperature. The activity of H_2CO_3 in the CO_2 -formation brine system improves with a higher P_{CO_2} , which indirectly results in a higher activity of H^+ and thus increased acidity of the solution. Moreover, the solubility product of $CaCO_3$ is proportional to P_{CO_2} . Thereby, even if the amount of $CaCO_3$ produced increases, it will only reach a saturated stable state without precipitation.

When the pressure starts to decrease, P_{CO_2} decreases, implying a lower solubility product of $CaCO_3$. Thus, $CaCO_3$ crystals grow and precipitate out of the solution.

Influence of scale-forming ion concentration

From **Figure 5**, we can see that the greater the scale ion content, the more sediment will be formed.

This is caused by the oversaturation of $CaCO_3$. The $CaCO_3$ saturation formula is:

$$S_C = \frac{[Ca^{2+}][CO_3^{2-}]}{K_c} \quad (9)$$

where S_C is the saturation degree of $CaCO_3$, K_c is the activity product of $CaCO_3$, and the values inside the square brackets represent the activity of each ion.

The increased concentration of scale-forming ions implies a higher concentration of free Ca^{2+} ions, and the solution is highly supersaturated in terms of Ca^{2+} , which results in higher nucleation and growth rate of $CaCO_3$ (Al Nasser and Al Salhi, 2014). According to formula (10), S_C increases, promoting the generation and the precipitation of $CaCO_3$. The activity of H^+ decreases rapidly with the increase of Ca^{2+} concentration, which is also very beneficial to the formation of $CaCO_3$.

It needs to be noted that in "Practical Aspects of CO_2 Flooding," Perry and Charles (2002) pointed out that the salinity of the brine also affects the solubility of CO_2 ; specifically, the

higher the salinity, the lower the solubility. However, in the current experiment, CO_2 dissolves in brine to form H_2CO_3 , which then dissociates to generate HCO_3^- . The HCO_3^- ions then react with the large amount of Ca^{2+} in the solution to form $CaCO_3$, which in turn causes more CO_2 to dissolve in brine and promotes the formation of more $CaCO_3$. The $CaCO_3$ generated will then precipitate after supersaturation is reached.

Influence of pH

Glenn and Reginald (2003) believes that the dissolution of CO_2 in formation brine from the formation fluids lowers the pH value of the formation brine and that $CaCO_3$, a weak acid salt, is greatly affected by the pH value, which is the main controlling factor of generation from H_2CO_3 dissociation. A higher pH value leads to increased HCO_3^- concentration and enhanced HCO_3^- activity and thereby an increase in the amount of $CaCO_3$.

Mathematical Characterization Method of Precipitation Amount From CO_2 -Formation Brine Interaction

According to **Figures 4–6**, the inorganic salt precipitation amount has an exponential relationship with temperature, pressure difference, and scale-forming ion concentration. The following mathematical formulas can be used:

$$y = ae^{bx} \quad (11)$$

Take the logarithm of both sides of (Eq. 11):

$$\lg y = \lg a + bx \quad (12)$$

Assign Y as $\lg y$:

$$Y = \lg a + bx \quad (13)$$

Equation 13 is a linear equation where Y changes linearly with X , and the data in **Table 3** were substituted into Eq. 13 for linear regression. Each X value has a corresponding actual value Y_1 and predicted value Y_2 . In order to minimize the square of the difference between the two values, set:

$$Q(a, b) = \sum_{i=1}^n (Y_i - (aX_i + b))^2 \quad (14)$$

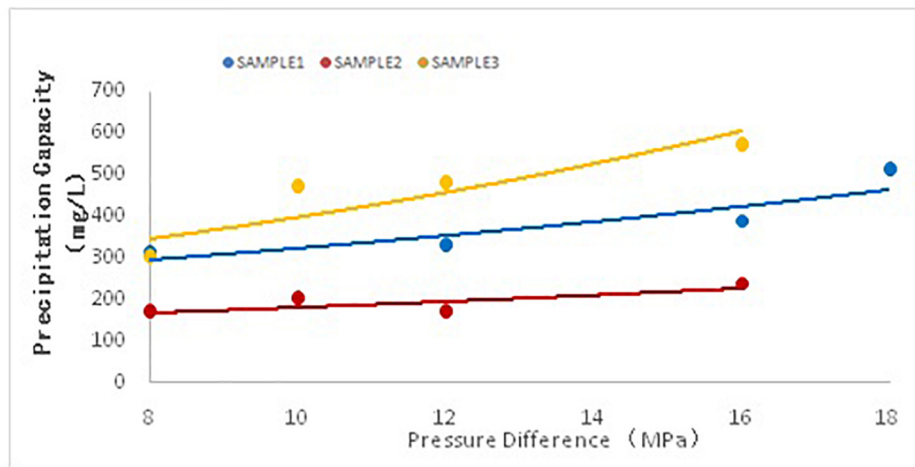


FIGURE 4 | The relationship between pressure difference and precipitation capacity.

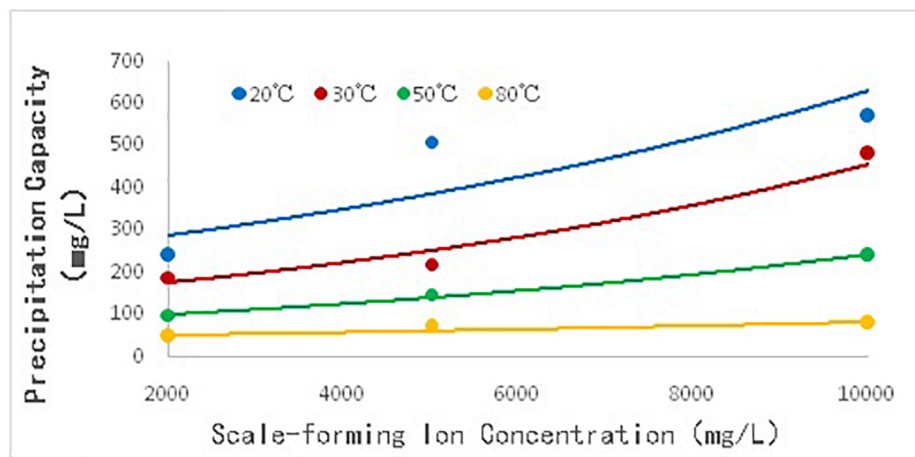


FIGURE 5 | The relationship between scale-forming ion content and precipitation capacity.

TABLE 4 | Regression parameters.

	Coefficients	Standard error	t statistic	P-value	Lower 95%	Upper 95%
Intercept	0.836256	0.380804	2.196027	0.032174	0.073709	1.598803
Scale-forming ion content	9.7E-05	9.58E-06	10.12754	2.36E-14	7.79E-05	0.000116
Temperature	-0.03435	0.001776	-19.3443	1.01E-26	-0.03791	-0.03079
Pressure Difference	0.062037	0.01211	5.122985	3.72E-06	0.037788	0.086286
pH value	0.667493	0.054766	12.18805	1.64E-17	0.557825	0.77716

Expand the brackets and take the average value:

$$Q(a, b) = n\bar{Y}^2 - 2an\bar{X}\bar{Y} - 2bn\bar{Y} + a^2n\bar{X}^2 + 2abn\bar{X} + nb^2 \quad (15)$$

By solving the partial derivatives of Q toward a and b, respectively, and assigning 0 to the partial derivatives, the solution formulas of a and b were obtained:

$$\begin{aligned} a &= \frac{\bar{X}\bar{Y} - \bar{X}\bar{Y}}{(\bar{X})^2 - \bar{X}^2} \\ b &= \bar{Y} - a\bar{X} \end{aligned} \quad (16)$$

As suggested by **Table 4**, the standard error is very small, indicating a high parameter accuracy. The corresponding P-value is less than 0.05–0.0001, and the confidence of the model is as high as 95–99.99%.

Therefore, the quantitative characterization equation of inorganic salt precipitation can be obtained:

$$y = 2.30771e^{(0.0000097M - 0.03435T + 0.062037\Delta P + 0.667439pH)} \quad (10)$$

TABLE 5 | Model parameters.

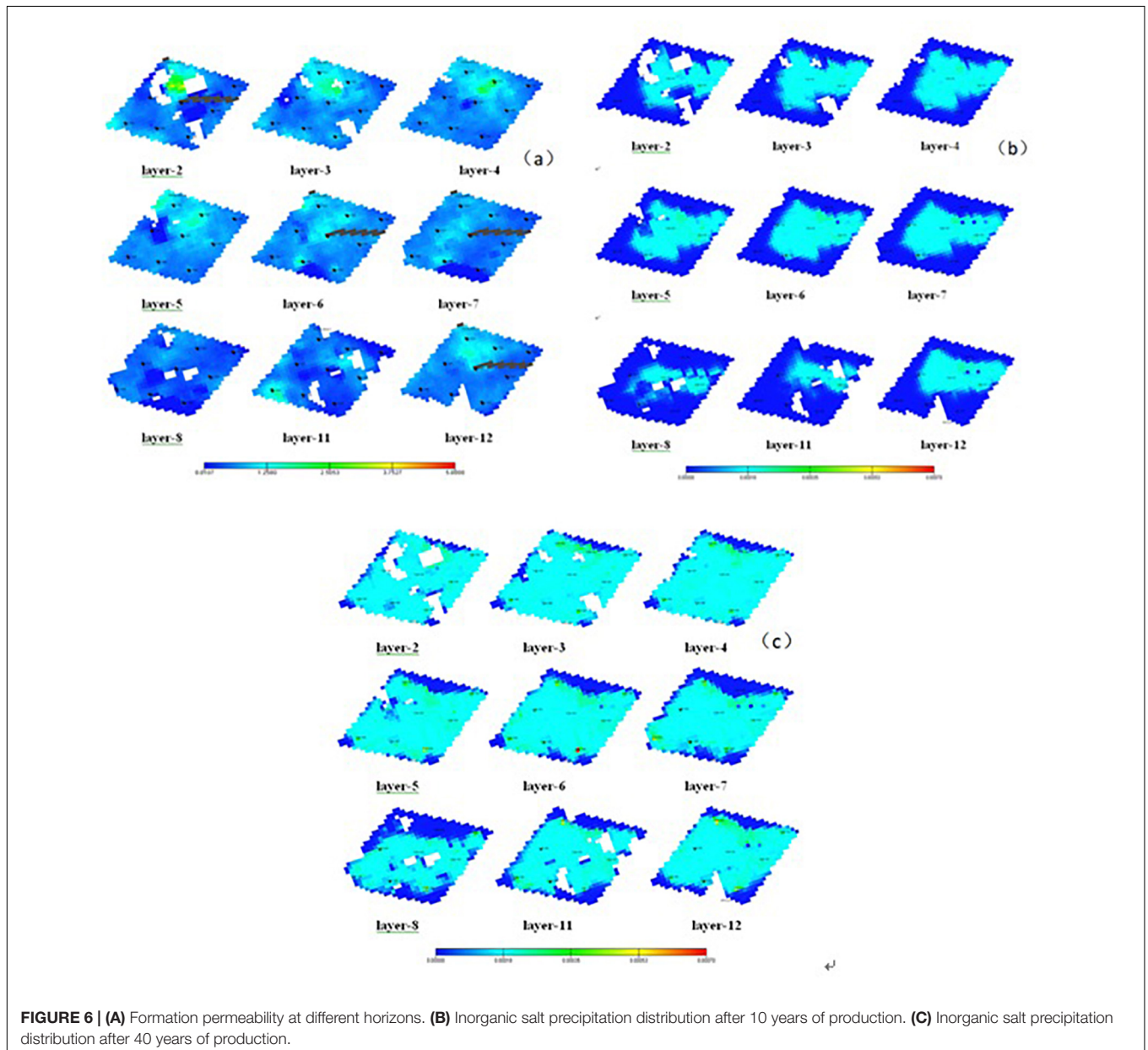
Parameter	Value	Parameter	Value
Crude oil viscosity (mPa·s)	1.81	Reservoir temperature (°C)	80
Permeability ($\times 10^{-3} \mu\text{m}^2$)	0.2	Rock density (kg/m ³)	2,500
Porosity (%)	10	Dissolved gas–oil ratio (m ³ /m ³)	43
Initial brine saturation	53%	Initial oil saturation	0.6
Reactant H ₂ O coefficient	1,280	Chemical reaction rate constant	5×10^{-6}

where y is the precipitation amount (mg), T is the temperature (°C), ΔP is the pressure difference (MPa), M is the concentration of scale-forming ions (mg/L), and pH is the pH value of the solution.

ANALYSIS OF INFLUENCE OF PRECIPITATION FROM CO₂-FORMATION BRINE INTERACTION ON OIL FIELD DEVELOPMENT

Establishment of Reservoir Numerical Model Considering Inorganic Salt Precipitation

The reservoir in a block of oil field C has an average porosity of 10.01% and a permeability of 0.3 mD. It is classified as an ultra-low permeability reservoir with an extremely low asphaltene concentration. The formation brine contains a high concentration of calcium ions (12,150 mg/L). The burial depth of



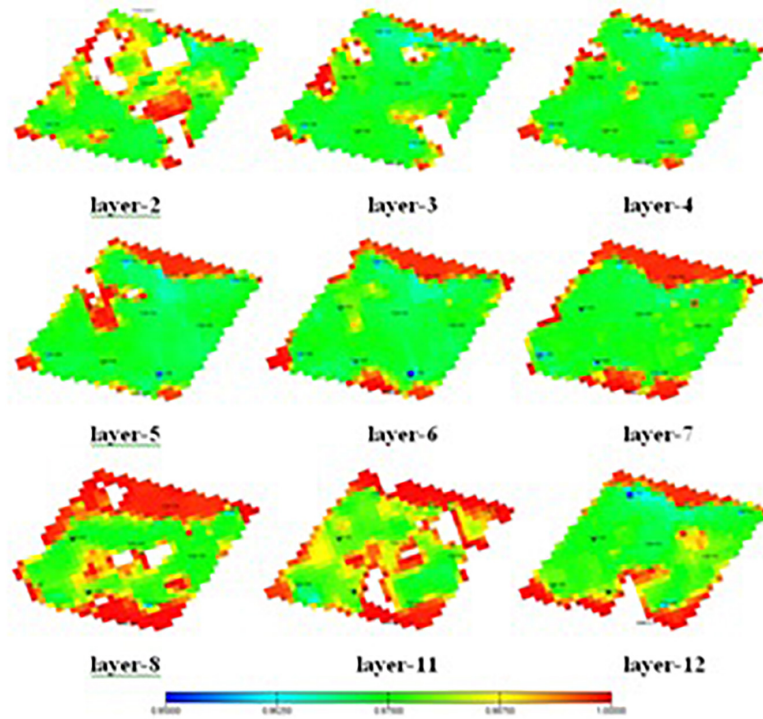


FIGURE 7 | Coefficient of fluidity change at the 40th year of the CO₂ enhanced oil recovery.

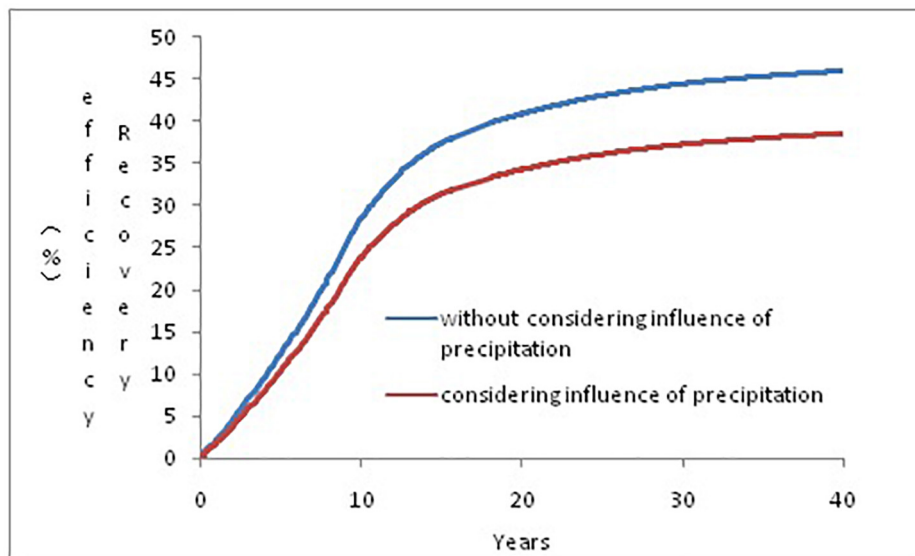


FIGURE 8 | Recovery rate at the 40th year with and without considering the influence of precipitation.

the reservoir is 2,700–2,900 m, with the formation temperature and pressure being 80°C and 21 MPa, respectively. Meanwhile, the comprehensive brine cut is 53%. The research block is a rhombic anti-nine-point well pattern with a water drive recovery

factor of 35.4%, and there is a high permeability zone connecting the injection and the production well inside the well pattern.

First, a suspended precipitation module was established, which simulated the precipitation formation with the production

well. Thereby, the precipitation amount generated by the CO₂-brine interaction could be directly output through the software. Then, the precipitation amount was fitted using Eq. 17 to obtain the key parameter: the reactant H₂O coefficient and the chemical reaction rate constant. On this basis, an adsorbed precipitation module was established for simulating the precipitation effect.

The CaCO₃ precipitation reaction is determined by the chemical reaction equation and the reaction rate. The chemical reaction equation is realized by adjusting the chemical reaction coefficient of the reactant and the product, and the specific process is as follows.

Chemical reaction equation:

$$\sum (S_{Rri} \cdot C_i) \rightarrow \sum (S_{Pri} \cdot C_i) \quad (11)$$

S_{Rri} : reaction coefficient of reactant C_i

S_{Pri} : reaction coefficient of product C_i

Reaction rate:

$$R_r = V_b \cdot A_r \cdot \exp(-E_r/(RT)) \cdot \prod_{c_{ri}}^{n_{ri}} \quad (12)$$

V_b : rock pore volume

A_r : reaction rate constant

E_r : reaction energy

R : gas constant

T : temperature

n_{ri} : component index

Suppose the initial solid saturation is 0 and the final output solid saturation is the resulting precipitation saturation, the effect of solid deposition on fluidity is obtained. Changes in fluidity can also reflect changes in permeability.

$$M_p^c = x_p^c \Delta k_s \Delta k_{rp} (S_p) \Delta \frac{b_p}{\mu_p} \quad (13)$$

x_p^c : molar fraction of components

k_s : fluidity multiplier in the presence of solids

k_{rp} : relative permeability of phase p

S_p : saturation of phase p

b_p : molar density of phase p

μ_p : viscosity of phase p

k_s : reduced mobility caused by solid adsorption blocking pore throat

The model parameters are shown in Table 5.

Evaluation of the Influence of Inorganic Salt Precipitation on Development

By simulating the production situation after 10 and 40 years, the inorganic salt precipitation distribution and its influence on the reservoir were obtained, as shown in Figure 6.

Figure 6 displays the precipitation distribution in the reservoir after production. Upon CO₂ injection, precipitation first occurs near the high-permeability zone. After 10 years of production, precipitates are gradually formed in the area, with relatively high permeability. In the 40th year, the precipitates are widely distributed in a large area in the research block

and reach a maximum value at the production well and its surrounding area. This precipitation trend is because CO₂ is first injected along the high-permeability zone where the fluid pressure is relatively high and the CO₂ solubility is large in brine. Then, the soluble bicarbonate [Ca(HCO₃)₂] is formed rapidly from the reaction of CO₂ and scale-forming ions in the formation brine. In the presence of a pressure difference in the formation, the reaction equilibrium shifts toward the direction of precipitation, thereby generating calcium carbonate precipitates. The pressure difference at the production well and its surrounding area is the largest, which explains the highest precipitation amount.

Figure 7 shows the distribution of fluidity change in the reservoir at the 40th year of CO₂-EOR. The fluidity of the study block decreases generally. This is because, during gas flooding, the pressure in the formation decreases gradually, resulting in the gradual generation of precipitation, which blocks the pore throats and reduces the fluidity.

Figure 8 illustrates the recovery rate change during the CO₂-EOR process with and without considering precipitation. As suggested by the figure, precipitation already has a great impact from the early stage of oil field development, which is mainly due to the rapid reaction of CO₂-brine. As the development continues, more and more precipitates are generated, blocking the pore throats and reducing the recovery rate. The recovery rate excluding the influence of precipitation was 46%, and it dropped by 7 to 39% when the influence of precipitation was considered.

CONCLUSION

- (1) In this paper, based on the static CO₂-brine immersion experiment, the reaction laws of the CO₂-formation brine system under various pressure difference, temperature, and scale-forming ion concentration conditions were studied. A greater pressure difference led to a larger amount of precipitation, while a higher temperature favored a smaller precipitation amount. Meanwhile, under constant pressure and temperature, greater concentrations of scale-forming ions in the formation brine led to the formation of larger amounts of precipitation.
- (2) Quantitative research was conducted on the precipitation amount, and the corresponding exponential mathematical characterization formula was obtained.
- (3) According to the numerical model, upon CO₂ injection, precipitation first occurs near the injection well. As CO₂ continues to migrate to the production well, the corresponding area has the highest precipitation amount.
- (4) By employing the modified numerical model, the oil recovery in a block of oil field C was predicted. The recovery rate considering precipitation was 39%, while that excluding the influence of precipitation was 46%, with the difference being 7%. The poor development of the oil field considering precipitation is due to the universal deposition of the precipitates generated from the CO₂-formation brine interaction in the reservoir.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

REFERENCES

- Al Nasser, W. N., and Al Salhi, F. H. (2014). Kinetics determination of calcium carbonate precipitation behavior by inline techniques. *Powder Technol.* 270, 548–560. doi: 10.1016/j.powtec.2014.05.025
- Alam, M., Hjuler, M., Christensen, H., and Fabricius, I. (2014). Petrophysical and rock-mechanics of CO₂ injection for enhanced oil recovery: experimental study on chalk from South Arne field. *North Sea. Pet. Sci. Eng.* 122, 468–487. doi: 10.1016/j.petrol.2014.08.008
- Assayag, N., Matter, J., Ader, M., Goldberg, D., and Agrinier, P. (2009). Water-rock interactions during a CO₂ injection field-test: Implications on host rock dissolution and alteration effects. *Chem. Geol.* 265, 227–235. doi: 10.1016/j.chemgeo.2009.02.007
- Bacci, G., Korre, A., and Durucan, S. (2010). An experimental and numerical investigation into the impact of dissolution/precipitation mechanisms on CO₂ injectivity in the wellbore and far field regions. *Int. J. Greenh. Gas Control* 5, 579–588. doi: 10.1016/j.ijggc.2010.05.007
- Delshad, M., Wheeler, M. F., and Kong, X. (2010). *A Critical Assessment of CO₂ Injection Strategies in Saline Aquifers*. Tulsa: Society of Petroleum Engineers.
- Fischer, S., Liebscher, A., Wandrey, M., and The CO₂ Sink Group, (2010). CO₂-brine-rock interaction -First results of long-term exposure experiments at in situ P-T conditions of the Ketzin CO₂ reservoir. *Chem. Erde* 70, 155–164. doi: 10.1016/j.chemer.2010.06.001
- Glenn, T. H., and Reginald, T. (2003). The experimental determination of solubilities. *Chem. Int.* 25, 30–33.
- Ketzer, J. M., Iglesias, R., Einloft, S., Dullius, J., Ligabue, R., and Lima, V. (2009). Water-rock-CO₂ interactions in saline aquifers aimed for carbon dioxide storage: experimental and numerical modeling studies of the Rio Bonito Formation (Permian), southern Brazil. *Appl. Geochem.* 24, 760–767. doi: 10.1016/j.apgeochem.2009.01.001
- Liu, F., Lu, P., Griffith, C., Hedges, S. W., Soong, Y., Hellevang, H., et al. (2012). CO₂-brine-cap rock interaction: reactivity experiments on Eau Claire shale and a review of relevant literature. *Int. J. Greenh. Gas Control* 7, 153–167. doi: 10.1016/j.ijggc.2012.01.012
- Lu, J., Nicot, J.-P., Mickler, P. J., Ribeiro, L. H., and Darvari, R. (2016). Alteration of Bakken reservoir rock during CO₂-based fracturing—an autoclave reaction experiment. *Unconv. Oil Gas Resour.* 14, 72–85. doi: 10.1016/j.juogr.2016.03.002
- Luquot, L., Andreani, M., Gouze, P., and Camps, P. (2012). CO₂ percolation experiment through chlorite/zeolite-rich sandstone (Pretty Hill Formation–Otway Basin–Australia). *Chem. Geol.* 294–295, 75–88. doi: 10.1016/j.chemgeo.2011.11.018
- Perry, J., and Charles, F. (2002). *Practical Aspects of CO₂ Flooding*. Tulsa: Society of Petroleum Engineers.
- Sbai, M. A. (2011). Numerical modeling of formation damage by two-phase particulate transport processes during CO₂ injection in deep heterogeneous porous media. *Adv. Water Resour.* 34, 62–82. doi: 10.1016/j.advwatres.2010.09.009
- Shiraki, R., and Dunn, T. L. (2000). Experimental study on water-rock interactions during CO₂ flooding in the Tensleep Formation, Wyoming, USA. *Appl. Geochem.* 15, 265–279. doi: 10.1016/s0883-2927(99)00048-7
- Shukla, R., Ranjith, P., Haque, A., and Choi, X. (2010). A review of studies on CO₂ sequestration and caprock integrity, 2010. *Fuel* 89, 2651–2664. doi: 10.1016/j.fuel.2010.05.012
- Wandrey, M., Fischera, S., Zemke, K., Liebscher, A., Scherfb, A. K., Hillebrandb, A. V., et al. (2011). Monitoring petrophysical, mineralogical, geochemical and microbiological effects of CO₂ exposure—Results of long-term experiments under in situ conditions. *Energy Procedia* 4, 3644–3650. doi: 10.1016/j.egypro.2011.02.295
- Wigand, M., Carey, J. W., Schütt, H., Spangenberg, E., and Erzinger, J. (2008). Geochemical effects of CO₂ sequestration in sandstones under simulated in situ conditions of deep saline aquifers. *Appl. Geochem.* 23, 2735–2745. doi: 10.1016/j.apgeochem.2008.06.006
- Yang, F., Bai, B. J., Tang, D. Z., Shari, D. N., and David, W. (2010). Characteristics of CO₂ sequestration in saline aquifers. *Pet. Sci.* 7, 83–92.
- Yu, Z. C., Liu, L., Yang, S. Y., Li, S., and Yang, Y. Z. (2012). An experimental study of CO₂-brine-rock interaction at in situ pressure-temperature reservoir conditions. *Chem. Geol.* 326–327, 88–101. doi: 10.1016/j.chemgeo.2012.07.030
- Zai-Hua, L., and Dreybrodt, W. (2005). Equilibrium chemistry of the CaCO₃-CO₂-H₂O system and discussions. *Carsol. Sin.* 24, 1–14.
- Zeidouni, M. (2009). Analytical solution to evaluate salt precipitation during CO₂ injection in saline aquifers. *Energy Procedia* 1, 1775–1782. doi: 10.1016/j.egypro.2009.01.232
- Zhao, R. B., Sun, H. T., Wu, Y. S., Zhao, C. F., and Xue, X. A. (2010). Influence of CO₂ corrosion on rock structure and its mechanical characteristics. *Sci. China Tech. Sci.* 53, 822–828.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Copyright © 2020 Yuan, Liao, Zhang, Zhao, Chu and Zou. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.