

Study on Prediction Model of Calcium Carbonate Scaling Based on Three-phase Equilibrium

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Abstract

Aiming at the problem of difficult scaling and high risk in experimental determination under high-temperature and high-pressure conditions, a prediction model of calcium carbonate scaling under high-temperature and high-pressure was established. The model starts from chemical equilibrium conditions, based on the carbonate gas-liquid-solid three-phase equilibrium conditions, considering the interaction between carbon dioxide concentration and various ions, using the solubility product rule to establish, using the Pitzer model to solve the compound activity coefficient, and calculating the parameters such as equilibrium constant and gas activity in the solution through the experimental regression model. The model can accurately predict the solubility of calcium carbonate in different aqueous solutions, which the error in pure water and barium chloride solution is within 5%, and the error considering the influence of carbon dioxide partial pressure is 14%. Using the model can accurately predict the scaling situation of the system under high temperature and high pressure, and has theoretical guiding significance for the implementation of downhole scale prevention process.

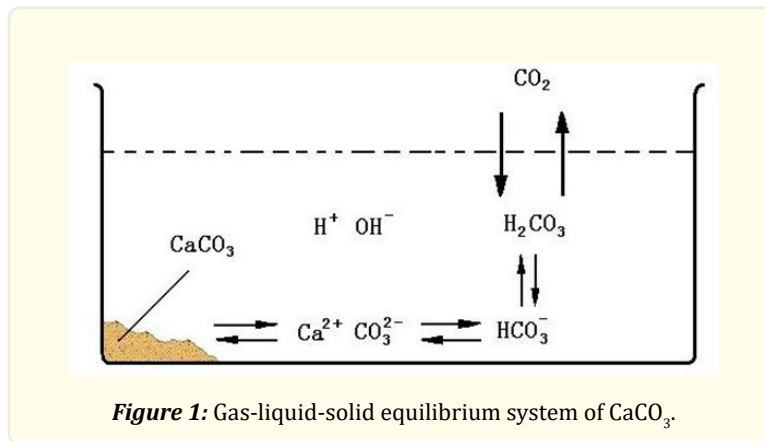
Keywords: High-temperature and high-pressure; Scale formation; The prediction model

Introduction

Scaling is common in oil and gas well wellbores, separators, sewage treatment pipelines, gathering pipelines and other locations, which causes blockage of oil well production systems, reduced production, and frequent operations. It can cause sucker rods to break off, and even oil wells to be scrapped, seriously affecting the normal production of oil and gas fields. Some scaling has problems such as gas partial pressure and interaction between ions, which makes the on-site scaling situation turn very complicated. In addition, the scaling mechanism and scaling law under high-temperature and high-pressure are unknown, and the requirements for experimental equipment are extremely high, which cannot meet the experimental conditions. Aiming at under the condition of high-temperature and high-pressure, the experimental determination of scaling is difficult, the risk is high, and the accuracy of scaling prediction model is low. In this paper, considering the partial pressure of carbon dioxide and the interaction between ions, a calcium carbonate scaling prediction model based on three-phase equilibrium is established and verified by examples.

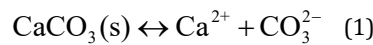
Carbonate scaling prediction model

Carbonate scale, especially CaCO_3 scale, is a common inorganic salt scale in the process of oil and gas exploitation. The formation fluid migrates from the downhole to the surface, the pressure drops significantly, and the CO_2 in the water escapes, which makes the gas-liquid-solid balance go in the direction conducive to the formation of CaCO_3 , resulting in the formation of calcium carbonate precipitation. The solid-liquid-gas three-phase equilibrium principle of $\text{CaCO}_3\text{-H}_2\text{O-CO}_2$ system is shown in figure1:



The actual $\text{CaCO}_3\text{-H}_2\text{O-CO}_2$ equilibrium process involves many reaction equilibria.

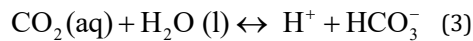
Decomposition of calcium carbonate molecules in solution,



At equilibrium,

$$K_{\text{sp}}^{\text{CaCO}_3} = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}}{a_{\text{CaCO}_3}} = a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}} \quad (2)$$

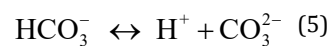
First Decomposition of Carbonic Acid,



At equilibrium,

$$K_1^{\text{H}_2\text{CO}_3} = \frac{a_{\text{H}^+} \cdot a_{\text{HCO}_3^-}}{a_{\text{H}_2\text{CO}_3}} = \frac{a_{\text{H}^+} \cdot a_{\text{HCO}_3^-}}{a_{\text{H}_2\text{O}} \cdot a_{\text{CO}_2, \text{aq}}} = \frac{a_{\text{H}^+} \cdot a_{\text{HCO}_3^-}}{a_{\text{CO}_2, \text{aq}}} \quad (4)$$

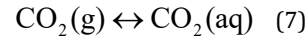
Ionization of bicarbonate radical,



At equilibrium,

$$K_2^{\text{HCO}_3^-} = \frac{a_{\text{H}^+} \cdot a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}} \quad (6)$$

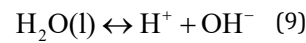
Dissolution of carbon dioxide molecules,



At equilibrium,

$$K_{\text{H}}^{\text{CO}_2} = \frac{a_{\text{CO}_2, \text{aq}}}{f_{\text{CO}_2, \text{gas}}} = \frac{a_{\text{CO}_2, \text{aq}}}{y_{\text{CO}_2} \cdot P \cdot \phi_{\text{CO}_2}} \quad (8)$$

Ionization of water molecules themselves,



At equilibrium,

$$K_{\text{w}} = \frac{a_{\text{H}^+} \cdot a_{\text{OH}^-}}{a_{\text{H}_2\text{O}, \text{l}}} = a_{\text{H}^+} \cdot a_{\text{OH}^-} \quad (10)$$

Total alkalinity of mixed aqueous solution,

$$m_{\text{T}} = 2m_{\text{CO}_3^{2-}} + m_{\text{HCO}_3^-} + m_{\text{OH}^-} - m_{\text{H}^+} \quad (11)$$

Simultaneous (2), (4), (6), (8), (10), (11) equations:

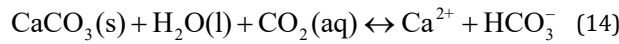
$$\begin{aligned} S_{\text{Ca}^{2+}} &= m_{\text{Ca}^{2+}} = 2m_{\text{CO}_3^{2-}} + m_{\text{HCO}_3^-} + m_{\text{OH}^-} - m_{\text{H}^+} \\ &= \frac{2K_{\text{sp}}^{\text{CaCO}_3}}{a_{\text{Ca}^{2+}} \cdot \gamma_{\text{CO}_3^{2-}}} + \left(\frac{K_1 \cdot K_{\text{sp}}^{\text{CaCO}_3} \cdot a_{\text{CO}_2, \text{aq}}}{K_2 \cdot a_{\text{Ca}^{2+}} \cdot \gamma_{\text{HCO}_3^-}^2} \right)^{1/2} + \\ &\quad \frac{K_{\text{w}}}{\gamma_{\text{OH}^-}} \left(\frac{K_1 \cdot K_2 \cdot a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_2, \text{aq}}}{K_{\text{sp}}^{\text{CaCO}_3}} \right)^{-1/2} - \\ &\quad \left(\frac{K_1 \cdot K_2 \cdot a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_2, \text{aq}}}{K_{\text{sp}}^{\text{CaCO}_3} \cdot (\gamma_{\text{H}^+})^2} \right)^{1/2} \end{aligned} \quad (12)$$

The solubility of calcium carbonate can be obtained by using the above equation, so as to predict its scaling. For other carbonates (such as magnesium carbonate), Eq. (12) is also applicable.

Amount of sedimentation,

$$S_{\text{p}} = m_{\text{Ca}^{2+}} - S_{\text{Ca}^{2+}} \quad (13)$$

The universal expression of dissolution and precipitation equilibrium of calcium carbonate in aqueous solution,



When the system reaches equilibrium,

$$K_{\text{sp}} = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{HCO}_3^-}^2}{a_{\text{CaCO}_3} \cdot a_{\text{H}_2\text{O}} \cdot a_{\text{CO}_2, \text{aq}}} = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{HCO}_3^-}^2}{a_{\text{CO}_2, \text{aq}}} \quad (15)$$

The definition formula of carbonate saturation index,

$$\text{SI} \equiv \ln \left\{ \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{HCO}_3^-}^2}{a_{\text{CO}_2, \text{aq}}} \cdot \frac{K_2^{\text{HCO}_3^-}}{K_{\text{sp}} \cdot K_1^{\text{H}_2\text{CO}_3}} \right\} \quad (16)$$

Activity of carbon dioxide in aqueous solution,

$$a_{\text{CO}_2, \text{aq}} = P_{\text{CO}_2} \cdot \phi_{\text{gas}}^{\text{CO}_2} \cdot K_{\text{H}}^{\text{CO}_2} \quad (17)$$

Substitute Eq. (17) into (16),

$$\text{SI} = \ln \left\{ \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{HCO}_3^-}^2}{P_{\text{CO}_2} \cdot \phi_{\text{gas}}^{\text{CO}_2} \cdot K_{\text{sp}} \cdot K_1^{\text{H}_2\text{CO}_3} \cdot K_{\text{H}}^{\text{CO}_2}} \cdot \frac{K_2^{\text{HCO}_3^-}}{K_1^{\text{H}_2\text{CO}_3}} \right\} \quad (18)$$

Where:

$a_{\text{Ca}^{2+}}$ - the activity of calcium ion, mol/kg;

$a_{\text{HCO}_3^-}$ - the activity of bicarbonate radical, mol/kg;

$a_{\text{CO}_2, \text{aq}}$ - the activity of carbon dioxide in aqueous solution, mol/kg;

K_{sp} - the solubility product constant of calcium carbonate, dimensionless;

$K_2^{\text{HCO}_3^-}$ - the solubility product constant of bicarbonate radical, dimensionless;

$K_1^{\text{H}_2\text{CO}_3}$ - the solubility product constant of carbonic acid, dimensionless;

P_{CO_2} - the carbon dioxide partial pressure, bar;

$\phi_{\text{gas}}^{\text{CO}_2}$ - the fugacity coefficient of carbon dioxide in gas phase, dimensionless;

$K_{\text{H}}^{\text{CO}_2}$ - Henry 's constant of carbon dioxide, dimensionless.

Eq. (18) can be used to determine the scale formation state of carbonate. Determination of scaling state. When $\text{SI} = 0$, the solution is saturated without scaling; when $\text{SI} > 0$, the solution is supersaturated with scaling; when $\text{SI} < 0$, the solution is not saturated without scaling.

Solution of Model Parameters

Solution of equilibrium constant K_{sp} of calcium carbonate

According to the previous chemical potential equation, the solubility product of calcium carbonate is solved.

$$K_{sp}^{CaCO_3} = \frac{a_{Ca^{2+}} \cdot a_{CO_3^{2-}}}{a_{CaCO_3}} = \exp\left(-\frac{\mu_{CO_3^{2-}}^* + \mu_{Ca^{2+}}^* - \mu_{CaCO_3}^*}{RT}\right) \quad (19)$$

Where:

$\mu_{CO_3^{2-}}^*$ - the standard chemical potential of carbonate ions in solution, kJ/mol;

$\mu_{Ca^{2+}}^*$ - the standard chemical potential of divalent calcium ions in solution, kJ/mol;

$\mu_{CaCO_3}^*$ - the standard chemical potential of calcium carbonate, kJ/mol.

Chemical formula	Chemical potential (μ_i^*/RT)	Chemical formula	Chemical potential (μ_i^*/RT)
H ₂ O	-95.6635	Mg(OH) ₂	-335.4
Na ⁺	-105.651	CaCO ₃	-455.6
K ⁺	-113.957	CaCl ₂ ·4H ₂ O	-698.7
CO ₃ ²⁻	-212.944	NaHCO ₃	-343.33
Ca ²⁺	-223.3	MgSO ₄ ·7H ₂ O	-1157.83
Mg ²⁺	-183.468	CaSO ₄ ·2H ₂ O	-725.56
H ⁺	0	NaCl	-154.99
Cl ⁻	-52.955	MgSO ₄ ·6H ₂ O	-1061.6
SO ₄ ²⁻	-300.386	KHCO ₃	-350.06
HSO ₄ ⁻	-304.942	MgSO ₄ ·H ₂ O	-579.8
OH ⁻	-63.435	MgCO ₃	-414.45
HCO ₃ ⁻	-236.751	Na ₂ SO ₄ ·10H ₂ O	-1471.15
CaCO ₃ ⁰	-443.5	Na ₂ CO ₃ ·10H ₂ O	-1382.78
MgCO ₃ ⁰	-403.155	MgCO ₃ ·3H ₂ O	-695.3
CO ₂ ⁰	-155.68	Ca(OH) ₂	-362.12
CO ₂ (gas)	-159.092	K ₂ CO ₃ ·3/2H ₂ O	-577.37
CaSO ₄	-533.73	Na ₂ CO ₃ ·7H ₂ O	-1094.95
CaCO ₃	-455.17	KCl	-164.84
K ₂ SO ₄	-532.39	Na ₂ SO ₄	-512.35
MgCl ₂ ·6H ₂ O	-853.1	Na ₂ CO ₃ ·H ₂ O	-518.8

Table 1: Chemical potential of each substance in aqueous solution.

Solution of ionization equilibrium constants K_1 and K_2 of carbonic acid and bicarbonate radical

The equilibrium constant of carbonic acid and bicarbonate was calculated by the empirical equation of experimental regression of Zhen-hao Duan [1-5] et al. (2008). The model is correlated to temperature and pressure, and the calculation results are high accurate.

$$\begin{aligned} \ln K = & a_1 + a_2 T + a_3 T^{-1} + a_4 T^{-2} + a_5 \ln T + \\ & (a_6 T^{-1} + a_7 T^{-2} + a_8 T^{-1} \ln T)(P - P_s) + \\ & (a_9 T^{-1} + a_{10} T^{-2} + a_{11} T^{-1} \ln T)(P - P_s)^2 \end{aligned} \quad (20)$$

Where:

P - pressure, bar;

T - temperature, K;

P_s - pressure, when $T < 373.15\text{K}$, $P_s = 1\text{bar}$; when $T \geq 373.15\text{K}$, P_s use the saturated vapor pressure of water, bar.

Parameter	$\ln K_1$	$\ln K_2$	Parameter	$\ln K_1$	$\ln K_2$
a_1	233.5159304	-151.1815202	a_7	2131.318848	1389.015354
a_2	0	-0.088695577	a_8	6.714256299	4.419625804
a_3	-11974.38348	-1362.259146	a_9	0.008393915	0.003219994
a_4	0	0	a_{10}	-0.40154414	-0.164447126
a_5	-36.50633536	27.79798156	a_{11}	-0.001240187	-0.000473667
a_6	-45.08004597	-29.51448102			

Table 2: Correlation coefficients of equilibrium constants.

Calculation of CO_2 activity in aqueous solution [6-10]

Dissolution equilibrium of carbon dioxide in aqueous solution, it can be described by its chemical potential (respectively for $\mu_{\text{CO}_2}^v$, $\mu_{\text{CO}_2}^l$) in liquid and gas phase.

Chemical potential of carbon dioxide in gas phase,

$$\begin{aligned} \mu_{\text{CO}_2}^v(T, P, y) &= \mu_{\text{CO}_2}^{v(0)}(T) + RT \ln f_{\text{CO}_2}(T, P, y) \\ &= \mu_{\text{CO}_2}^{v(0)}(T) + RT \ln y_{\text{CO}_2} P + RT \ln \phi_{\text{CO}_2}(T, P, y) \end{aligned} \quad (21)$$

Chemical potential of carbon dioxide in liquid phase,

$$\begin{aligned} \mu_{\text{CO}_2}^l(T, P, m) &= \mu_{\text{CO}_2}^{l(0)}(T, P) + RT \ln a_{\text{CO}_2}(T, P, m) \\ &= \mu_{\text{CO}_2}^{l(0)}(T, P) + RT \ln m_{\text{CO}_2} + RT \ln \gamma_{\text{CO}_2}(T, P, m) \end{aligned} \quad (22)$$

At equilibrium,

$$\mu_{\text{CO}_2}^v = \mu_{\text{CO}_2}^l \quad (23)$$

The definition of carbon dioxide activity in solution,

$$a_{\text{CO}_2}^{\text{aq}}(T, P, m) = m_{\text{CO}_2}^{\text{aq}} \cdot \gamma_{\text{CO}_2}(T, P, m) \quad (24)$$

Where:

$m_{\text{CO}_2}^{\text{aq}}$ - the mass molar concentration of CO_2 in liquid phase, mol/kg;

γ_{CO_2} - the activity coefficient of CO_2 in liquid phase, dimensionless.

(1) At equilibrium, the *-chemical potential of carbon dioxide in the two phases is equal. The concentration [11] of carbon dioxide in the actual solution.

$$\begin{aligned} \ln m_{\text{CO}_2}^{\text{aq}} = \ln y_{\text{CO}_2} \cdot \varphi_{\text{CO}_2} \cdot P - \mu_{\text{CO}_2}^{l(0)} / RT - \\ 2\lambda_{\text{CO}_2-\text{Na}} \cdot (m_{\text{Na}} + m_{\text{K}} + 2m_{\text{Ca}} + 2m_{\text{Mg}}) - \\ \xi_{\text{CO}_2-\text{Na}-\text{Cl}} \cdot m_{\text{Cl}} \cdot (m_{\text{Na}} + m_{\text{K}} + m_{\text{Ca}} + m_{\text{Mg}}) + 0.07m_{\text{SO}_4} \end{aligned} \quad (25)$$

The partial pressure $y_{\text{CO}_2} \cdot P$ of carbon dioxide in the gas phase can be expressed as,

$$y_{\text{CO}_2} \cdot P = P - P_{\text{H}_2\text{O}} \quad (26)$$

Solution of water vapor partial pressure $P_{\text{H}_2\text{O}}$,

$$P_{\text{H}_2\text{O}} = (P_c T / T_c) \left[1 + c_1 (-t)^{1.9} + c_2 t + c_3 t^2 + c_4 t^3 + c_5 t^5 \right] \quad (27)$$

Where:

R - the universal gas constant, the value is $0.08314467 \text{ bar} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$;

P_c - the critical pressure of water, bar;

V_c - the molar volume of water under the critical temperature and pressure, L/mol;

T_c - the critical temperature of water, K.

Parameter	c_1	c_2	c_3	c_4	c_5
Numerical value	-38.64084	5.894842	59.876516	26.654627	10.637097

Table 3: Coefficients involved in the calculation.

Fugacity coefficient of carbon dioxide in gas phase $\varphi_{\text{CO}_2}(T, P, y)$,

$$\begin{aligned} \varphi_{\text{CO}_2} = c_1 + \left[c_2 + c_3 T + c_4 / T + c_5 / (T - 150) \right] P + \\ \left[c_6 + c_7 T + c_8 / T \right] P^2 + \left[c_9 + c_{10} T + c_{11} / T \right] \ln P + \\ \left[c_{12} + c_{13} T \right] / P + c_{14} / T + c_{15} T^2 \end{aligned} \quad (28)$$

Where:

φ_{CO_2} - the fugacity coefficient of carbon dioxide, dimensionless;

P - the total pressure of system, bar;

V - the molar volume of system, L/mol;

T - the temperature of system, K.

Parameters	Temperature and pressure range					
	1	2	3	4	5	6
c_1	1.0	-7.1734882 $\times 10^{-1}$	-6.5129019 $\times 10^{-2}$	5.0383896	-16.063152	-1.5693490 $\times 10^{-1}$
c_2	4.7586835 $\times 10^{-3}$	1.5985379 $\times 10^{-4}$	-2.1429977 $\times 10^{-4}$	-4.4257744 $\times 10^{-3}$	-2.7057990 $\times 10^{-3}$	4.4621407 $\times 10^{-4}$
c_3	-3.3569963 $\times 10^{-6}$	-4.9286471 $\times 10^{-7}$	-1.1444930 $\times 10^{-6}$	0.0	0.0	-9.1080591 $\times 10^{-7}$
c_4	0.0	0.0	0.0	1.9572733	1.4119239 $\times 10^{-1}$	0.0
c_5	-1.3179396	0.0	0.0	0.0	0.0	0.0
c_6	-3.8389101 $\times 10^{-6}$	-2.7855285 $\times 10^{-7}$	-1.1558081 $\times 10^{-7}$	2.4223436 $\times 10^{-6}$	8.1132965 $\times 10^{-7}$	1.0647399 $\times 10^{-7}$
c_7	0.0	1.1877015 $\times 10^{-9}$	1.1952370 $\times 10^{-9}$	0.0	0.0	2.4273357 $\times 10^{-10}$
c_8	2.2815104 $\times 10^{-3}$	0.0	0.0	-9.3796135 $\times 10^{-4}$	-1.1453082 $\times 10^{-4}$	0.0
c_9	0.0	0.0	0.0	-1.5026030	2.3895671	3.5874255 $\times 10^{-1}$
c_{10}	0.0	0.0	0.0	3.0272240 $\times 10^{-3}$	5.0527457 $\times 10^{-4}$	6.3319710 $\times 10^{-5}$
c_{11}	0.0	0.0	0.0	-31.377342	-17.763460	-249.89661
c_{12}	--	-96.539512	-221.34306	-12.847063	985.92232	0.0
c_{13}	--	4.4774938 $\times 10^{-1}$	0.0	0.0	0.0	0.0
c_{14}	--	101.81078	71.820393	0.0	0.0	888.768
c_{15}	--	5.3783879 $\times 10^{-6}$	6.6089246 $\times 10^{-6}$	-1.5056648 $\times 10^{-5}$	-5.4965256 $\times 10^{-7}$	-6.6348003 $\times 10^{-7}$

Table 4: Fugacity coefficient calculation involves parameters.

Standard chemical potential of CO_2 in liquid phase $\mu_{\text{CO}_2}^{(0)}(T, P)$,

$$\frac{\mu_{\text{CO}_2}^{(0)}}{RT} = b_1 + b_2 T + b_3 / T + b_4 T^2 + b_5 / (630 - T) + b_6 P + b_7 P \ln T + b_8 P / T + b_9 P / (630 - T) + b_{10} P^2 / (630 - T)^2 + b_{11} T \ln P \quad (29)$$

(2) Activity coefficient of CO_2 in liquid phase γ_{CO_2} ,

$$\ln \gamma_{\text{CO}_2} = \sum_c 2\lambda_{\text{CO}_2-c} \cdot m_c + \sum_a 2\lambda_{\text{CO}_2-a} \cdot m_a + \sum_c \sum_a \xi_{\text{CO}_2-a-c} \cdot m_c \cdot m_a \quad (30)$$

Where:

λ_{CO_2-c} , λ_{CO_2-a} - they are the interaction coefficients of CO_2 with positive and negative ions in solution respectively, dimensionless;

ξ_{CO_2-a-c} - the interaction coefficient of CO_2 - positive ions- negative ions in solution, dimensionless;

m_c - the concentration of positive ions in the solution, mol/kg;

m_a - the concentration of negative ions in the solution, mol/kg.

Parameters	$\mu_{\text{CO}_2}^{(0)} / RT$	$\lambda_{\text{CO}_2-\text{Na}}$	$\xi_{\text{CO}_2-\text{Na}-\text{Cl}}$
b1	28.9447706	-0.411370585	3.36389723
b2	-0.035458177	6.07632013	-1.9829898
b3	-4770.67077	97.5347708	--
b4	1.02782768	--	--
b5	33.8126098	--	--
b6	9.0403714	--	--
b7	-1.14934031	--	--
b8	-0.307405726	-0.023762247	2.1222083
b9	-0.090730149	0.017065624	-5.24873303
b10	9.32713393	--	--
b11	--	1.41335834	--

Table 5: Parameters involved in the calculation.

Calculation of equilibrium constant K_w in aqueous solution [12]

$$\log K_w = A + B/T + C/T^2 + D/T^3 + (E + F/T + G/T^2) \log \rho_w \quad (31)$$

$$\rho_w = \frac{((((At + B)t + C)t + D)t + E)t + F}{1 + Gt} \quad (32)$$

The density of water ρ_w in formula (31) is calculated by formula (32).

Parameters	A	B	C	D	E	F	G
Numerical value	-4.098	-3245.2	2.2362×10^5	-3.984×10^7	13.957	-1262.3	8.5641×10^5

Table 6: Calculation parameters of water equilibrium constant.

Prediction calculation of deposition amount at equilibrium

$$S_p = \left\{ m_{\text{Ca}^{2+}} + m_{\text{CO}_3^{2-}} - \left[\left(m_{\text{Ca}^{2+}} + m_{\text{CO}_3^{2-}} \right)^2 + 4K_{sp} \right]^{1/2} \right\} / 2 \quad (33)$$

Where:

S_p - the deposition amount of CaCO_3 at equilibrium, mol/kg;

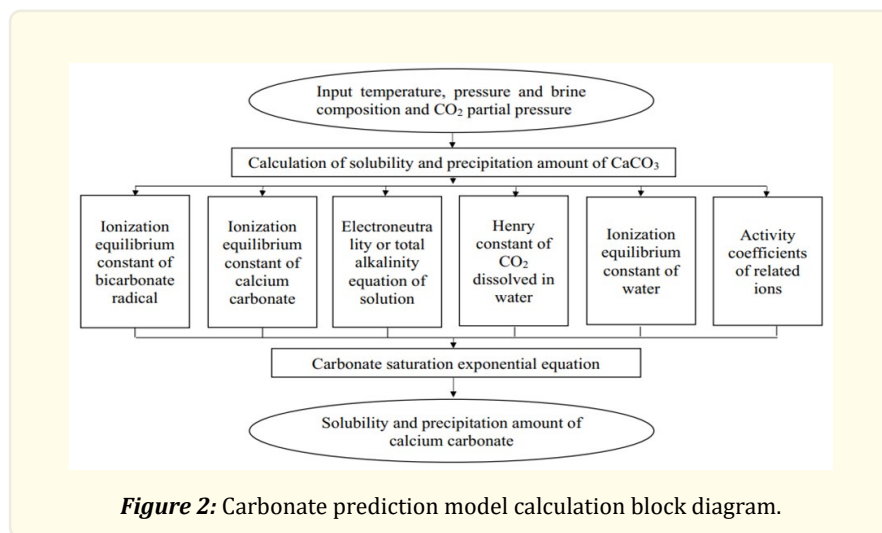
$m_{\text{Ca}^{2+}}$ - the initial mass molar concentration of Ca^{2+} ions, mol/kg;

$m_{\text{CO}_3^{2-}}$ - the initial mass molar concentration of CO_3^{2-} ions, mol/kg;

K_{sp} - the concentration product constant of CaCO_3 , dimensionless.

Model solving block diagram

The program calculation block diagram of carbonate scale is as follows:



Model verification

Scale solubility verification

Use the solubility of calcium carbonate scale was calculated by the prediction model, and the calculated results were compared with the experimental values. The relevant data are shown in Tables 7-9 and Figs 3-5.

From Table 7-9 and Figure 3-5: The solubility of calcium carbonate in water calculated by the model is basically consistent with the experimental data, and the calculation results are slightly larger. The solubility of calcium carbonate in BaCl_2 solution calculated by the model is smaller at first and then larger at 40 MPa, and larger at first and then smaller at 100 MPa, but it is overall close to the experimental value. The influence of carbon dioxide partial pressure on calcium carbonate calculated by the model has a large deviation, but the data trends are basically the same. It fully shows that the model has high calculation accuracy and has certain practicability.

Formation water scaling verification

The scaling prediction model is used to predict the scaling amount of field formation water under experimental conditions. The predicted values are compared with the experimental values, and the predicted data are shown in table 10 and figure 6.

Temperature (°C)	Solubility(mg/L)						
	20MPa			80MPa			
	Experimental values	Calculated values	Deviation (%)	Experimental values	Calculated values	Deviation (%)	
20	13.33	14.01	-1.78	18	18.32	-5.10	
50	14.66	15	-2.48	18.96	19.43	-2.32	
70	15.41	15.82	-1.07	19.62	19.83	-2.66	
90	15.89	16.13	-1.98	20.23	20.63	-1.51	
120	14.38	14.88	-1.86	19.35	19.71	-3.48	
150	16.13	16.22	2.60	21.57	21.01	-0.56	
Average deviations			1.96	Average deviations			2.61

Table 7: Solubility of CaCO₃ in pure aqueous solution.

Temperature (°C)	Solubility(mg/L)						
	40MPa			100MPa			
	Experimental values	Calculated values	Deviation (%)	Experimental values	Calculated values	Deviation (%)	
70	17.86	17.62	1.34	22.67	23.21	2.38	
90	18.11	18.01	0.55	23.44	23.62	0.77	
120	17.37	17.66	-1.67	22.43	22.12	1.38	
150	18.43	18.67	-1.30	24.55	24.03	2.12	
Average deviations			1.22	Average deviations			1.66

Table 8: Solubility of CaCO₃ in BaCl₂ aqueous solution.

Temperature (°C)	Solubility(mg/L)						
	0.1MPa			2MPa			
	Experimental values	Calculated values	Deviation (%)	Experimental values	Calculated values	Deviation (%)	
70	892.41	980.11	-9.83	6789.52	7000.31	-3.10	
90	478.75	555.36	-16.00	3127.66	3780.01	-20.86	
120	296.65	340.1	-14.65	1917.48	2200.36	-14.75	
150	161.19	131.25	18.57	1461.07	1203.36	17.64	
Average deviations			14.76	Average deviations			14.1

Table 9: Effect of CO₂ partial pressure on CaCO₃ solubility.

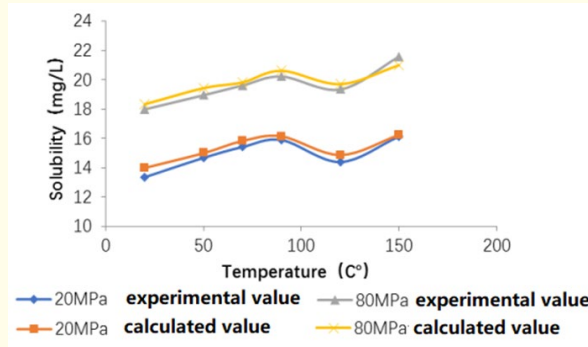


Figure 3: Comparison curve of solubility of CaCO₃ in aqueous solution between experimental value and predicted value.

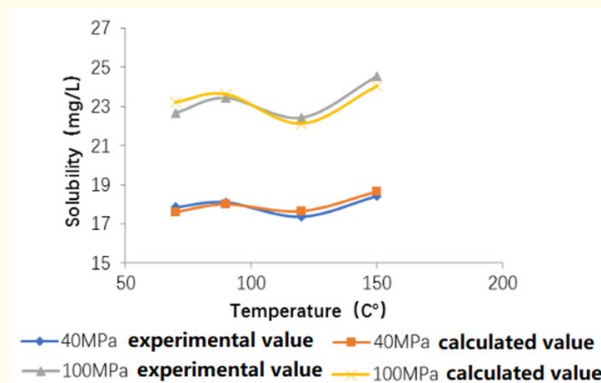


Figure 4: Comparison curve of solubility of CaCO₃ in BaCl₂ aqueous solution experimental value and predicted value.

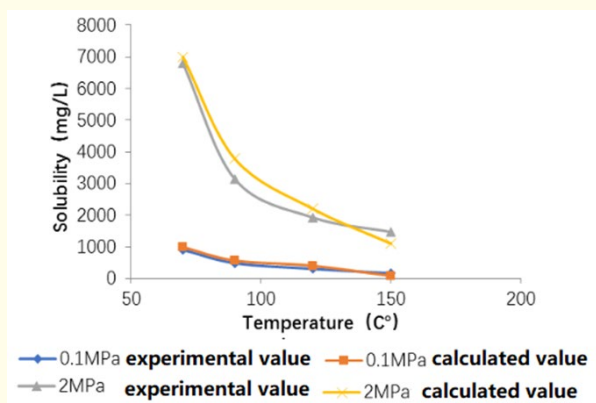


Figure 5: Effect of CO₂ partial pressure on CaCO₃ solubility.

Pressure (MPa)	Scale amount of CaCO ₃ at different temperatures (mg/L)				
	80	100	120	150	170
100	7.25	16.32	22.01	32.63	31.75

Table 10: Prediction value of CaCO₃ scaling amount in formation water.

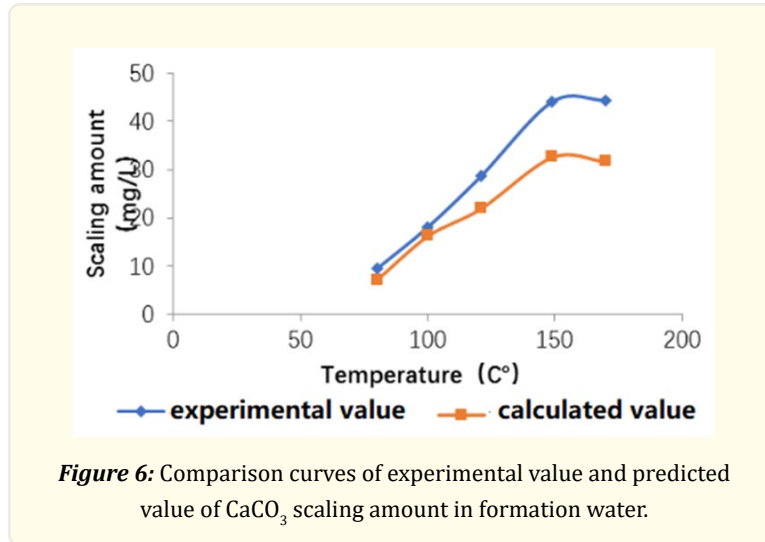


Figure 6: Comparison curves of experimental value and predicted value of CaCO₃ scaling amount in formation water.

From Table 10 and Figure 6 show that: When the current formation pressure is 100 MPa and the temperature is higher than 80°C, CaCO₃ scale will be formed in the field gas well. The amount of CaCO₃ scaling increases with the decrease of pressure and the increase of temperature. When it reaches about 150 °C, it tends to be stable, and the amount of calcium carbonate scale reaches equilibrium and has a downward trend, indicating that the stable existence of calcium carbonate scale is not used under high temperature and high pressure.

Conclusion

Starting from the chemical equilibrium conditions, the influence of pressure on scaling is fully considered, and the interaction between carbon dioxide concentration and ions is considered, the prediction model of carbonate gas-liquid-solid three-phase equilibrium is established. Through the model calculation, we can see that the solubility of calcium carbonate in water calculated by the model is basically consistent with the experimental data. The solubility of calcium carbonate in barium chloride solution calculated by the model was compared with the experimental value. The solubility of calcium carbonate in barium chloride solution first smaller and then larger increased at 40 MPa, and first larger and then smaller at 100 MPa. The error in pure water and barium chloride solution is within 5%, and the error considering the influence of carbon dioxide partial pressure is 14%. The influence of carbon dioxide partial pressure on calcium carbonate calculated by the model has a large deviation, but the data trend is basically the same, which fully shows that the model has high calculation accuracy and certain practicability, and can better predict calcium carbonate scaling.

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