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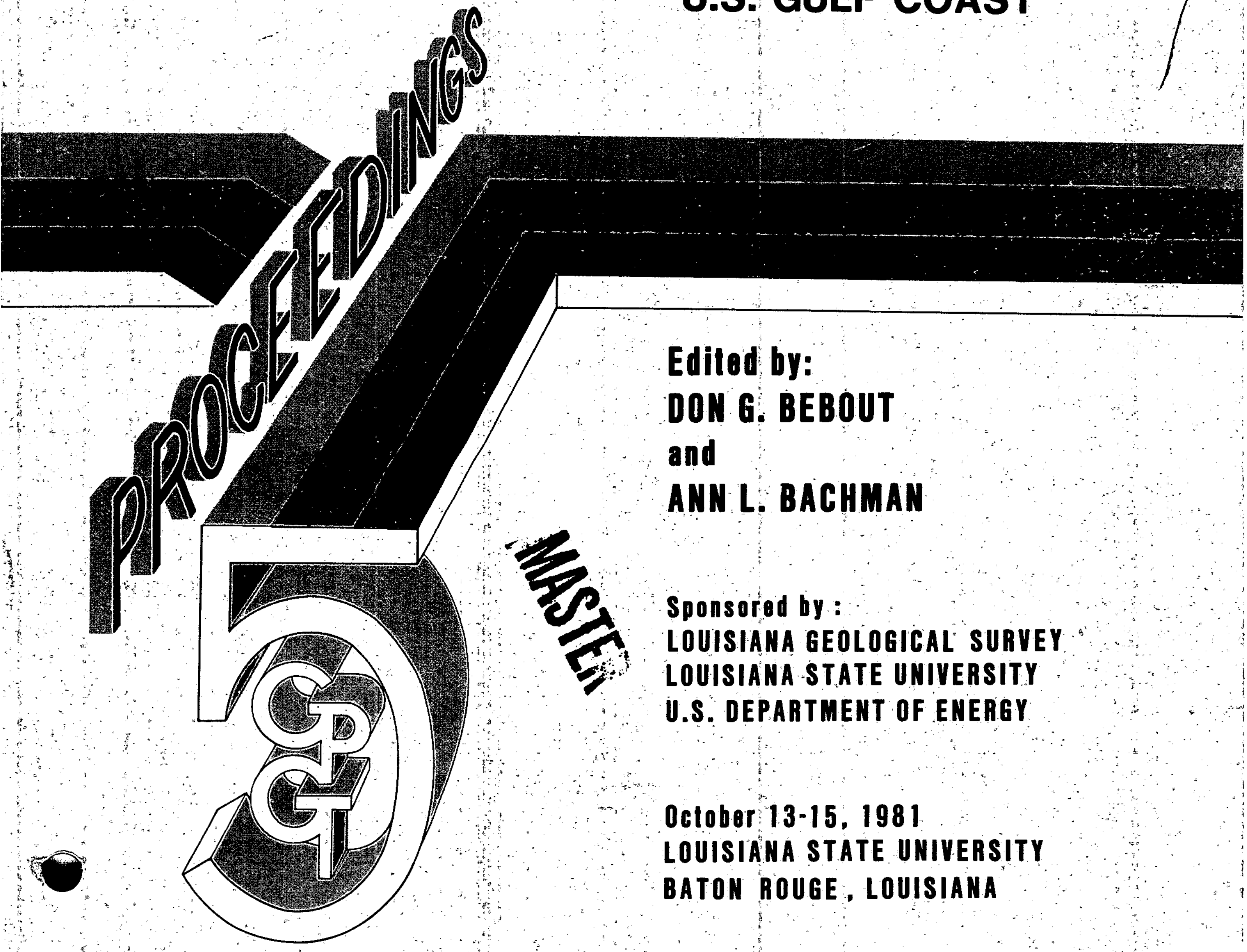

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$CaCO_3$ PRECIPITATION IN HIGH TEMPERATURE AND PRESSURE BRINES IN THE PRESENCE OF SCALE INHIBITORS USING NOVEL SATURATION INDEX CALCULATIONS

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ABSTRACT

A simplified method to calculate $CaCO_3$ saturation is developed using only commonly measured field parameters. The calculated saturation index (SI) and pH values are shown to be accurate at high temperatures and pressures in brines and are compared to less sophisticated and more complex calculations.

The SI is defined as:

$$SI = \log_{10} \frac{iap}{K_{sp}},$$

where iap is the ion activity product of Ca^{2+} and CO_3^{2-} and K_{sp} is the solubility product of calcite. The final form of the SI and pH calculations are derived using conditional equilibrium constants dependent on temperature, pressure, and ionic strength which eliminate the need for activity coefficients. The derived equation for the pH calculation (pH_c) is:

$$pH_c = -(\log \frac{P_T \, X_{CO_2}}{Alk}) + 8.6812 + 4.0539 \times 10^{-3}T + 0.4583 \times 10^{-6}T^2 - 3.0673 \times 10^{-5}P - 0.4772I^{1/2} + 0.1930I,$$

where P_T is total pressure (psi), X_{CO2} is the mole fraction of CO_2 in the gas phase (unitless), Alk is bicarbonate alkalinity (molarity), I is ionic strength (molarity), T is temperature (°F), and P is pressure (psi). The SI equation is presented in forms for calculation with known or derived pH and where the pH of the solution is unknown. The general form of the saturation index equation is:

$$SI = \log \frac{T_{Ca} \, Alk^2}{P_T \, X_{CO2}} + 5.8946 + 15.4880 \times 10^{-3}T - 4.2596 \times 10^{-6}T^2 - 7.4401 \times 10^{-5}P - 2.5261I^{1/2} + 0.9197I.$$

Application of the SI is shown by calculating the scaling tendency of geopressured energy wells of the Gulf Coast region.

The study of calcium carbonate scale inhibition has led to the development of a flow system with high temperature and pressure capability. A high pressure (performance) liquid chromatograph (HPLC) was modified by the addition of a backpressure valve while bypassing the HPLC packed column. Solution mixing and temperature are computer controlled and $CaCO_3$ precipitation is monitored by inline pH measurement. Simulated and real brine samples were used to evaluate scale inhibitors and $CaCO_3$ precipitation was related to the saturation index (SI). The inhibitors evaluated (In, ppm) and the brine SI with respect to $CaCO_3$ were:

Inhibitor	SI	In
Hydroxyethylidenediphosphonic acid (HEDP)	1.87	0.20
Polymaleic acid (PMA)	1.87	0.35
Polyacrylic acid (PAA)	1.87	0.35

INTRODUCTION

Calcium carbonate precipitation has been and continues to be a problem in aqueous systems. Calcium carbonate scale is most prevalent at higher temperatures because $CaCO_3$ solubility decreases with the increasing temperature.

Less sophisticated methods for determining scaling tendency, such as the Langelier and Stiff-Davis Saturation Indices, have built-in constraints when considering closed aqueous systems (Langelier, 1946 and Stiff and Davis, 1952). With both methods, the solution pH must be known to begin the calculations. At high temperatures and pressures, no technique exists for reliable pH measurement. Neither method can account for pressure changes in the system nor the changing solubility of $CO_{2(g)}$ with temperature and pressure. The Stiff and Davis (1952) constant K is not known above 194°F(90°C) (Cowan and Weintritt, 1972). The method presented in this paper follows the Stiff and Davis method very closely at temperatures in range of the Stiff and Davis calculation and at known pH. Table 1 is a comparison of the saturation index (SI) presented here to the Stiff and Davis Index for four oilfield brines (Bradley, 1972). The method will enable calculations of pH, if not known, and considers total pressure as well as varying $CO_{2(g)}$ partial pressures from commonly measured variables in the field, i.e., total calcium, bicarbonate alkalinity, ionic strength, temperature, pressure, and the mole fraction of CO_2 in the gas phase.

Table 1. A comparison of the supersaturation index (SI) to the Stiff and Davis index for four oilfield brines at 122°F and atmospheric pressure (data from Bradley)[2,4]

	Molar					
Field	Ca^{2+}	HCO_3^-	Ionic Strength	pH	Stiff-Davis Index	SI Work
Battle Canyon	8.0×10^{-4}	2.8×10^{-2}	0.15	7.5	0.9	0.70
Luft	1.2×10^{-3}	4.8×10^{-2}	0.11	7.7	1.6	1.38
Mount Hope	1.2×10^{-3}	1.1×10^{-2}	0.15	6.7	-0.4	-0.33
Beaucoup-South	6.0×10^{-3}	2.0×10^{-2}	1.49	6.9	0.2	0.12

More complex computer codes exist for the calculation of $CaCO_3$ scaling tendencies in aqueous systems at high temperatures and pressures, but these are constrained by the need for mainframe computers, complex codes, and large data bases. A sophisticated code, EQUILIB, developed by Shannon et al. (1977) at Battell-Northwest requires computer facilities and does take pressure into account. This offers an opportunity to check the calculations

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presented herein. Shannon et al. (1977) present two examples of results, an unflashed and a flashed brine, in their paper. The results and a comparison to the SI presented in this paper are presented in Table 2 and good agreement with the more complex calculations is demonstrated.

Calculation of the Saturation Index (SI)

The calculaton of the SI in brines poses the problem of changing chemical equilibria in solutions of interest with temperature, pressure, and ionic strength. The changing equilibria in the solutions can be dealt with by allowing the equilibrium constants in the governing chemical equations to vary with the changing conditions of the brines. The equilibrium constants then become conditional constants whose values depend on temperature, pressure, and ionic strength. Since the conditional equilibrium constants are adjusted for ionic strength, there is no need for complex activity coefficient calculations. Compressibility of the fluid due to pressure and thermal expansion due to temperatures were considered and found to be small and to essentially cancel one another.

Table 2 A comparison of the SI to the more complex Shannon et al. code[5]

	Shannon et al.		This Work	
	pH_C^*	SCALING	pH_C^*	SI**
Unflashed Brine	5.31	No	5.26	-1.10
Flashed Brine	7.19	Yes	7.20	+0.31

$^*pH_C$ = calculated pH

** SI positive indicates scaling.

The solubility product (K_{sp}) for calcite is the ion activity product (iap) of the calcium ion concentration times the carbonate, or

$$K_{sp} = (\text{iap}) \; . \; . \; . \; . \; . \; . \; (1)$$

When the K_{sp} is exceeded by the iap of Ca^{2+} and CO_3^{2-}, the solution is supersaturated with respect to calcite and scaling is possible. Scaling may or may not occur for kinetic reasons, but these will not be discussed here.

The ratio of the iap of Ca^{2+} and CO_3^{2-} to the K_{sp} should be an indication of the scaling tendency of aqueous solutions with varying chemistries if the K_{sp} is adjusted for temperature, pressure, and ionic strength. The saturation ratio (SR) is defined as:

$$SR = \frac{\text{iap}}{K_{sp}} \qquad (2)$$

A commonly measured parameter in the field is the alkalinity. In carbonate systems, the alkalinity is often determined by the HCO_3^- concentration in solution (Stumm and Morgan, 1970). This assumption can be verified by lowering the pH, driving off the carbonates as $CO_{2(g)}$ and back-titrating for alkalinity other than HCO_3^- and is a valid assumption in geopressured wells. The CO_3^{2-} can be expressed as a function of the HCO_3^- with the second equilibrium constant of carbonic acid (K_2):

$$K_2 = \frac{(H^+)(CO_3^{2-})}{(HCO_3^-)}, \; . \; . \; . \; . \; (3)$$

or

$$CO_3^{2-} = \frac{(HCO_3^-)K_2}{(H^+)}, \; . \; . \; . \; . \; (4)$$

Substituting Eq. 4 into Eq. 2 and substituting the alkalinity (Alk) for the HCO_3^-, the expression for the SR becomes:

$$SR = \frac{(Ca^{2+})(Alk)\ K_2}{(H^+)\ K_{sp}} \; . \; . \; . \; . (5)$$

If the pH of the solution is known, this expression is adequate for the equilibrium constants are made conditional. However, in most high temperature-pressure solutions the pH is unknown and cannot be practically measured. The pH can be found from the alkalinity and the partial pressure of $CO_{2(g)}$ (P_{CO_2}) by the combination of Henry's law constant (K_H) and the first apparent equilibrium constant (K_1) of carbonic acid. Henry's law constant has the form:

$$K_H = \frac{H_2CO_3^*}{P_{CO_2}}, \; . \; . \; . \; . \; . \; (6)$$

where $H_2CO_3^*$ is the sum of the aqueous CO_2 and the true carbonic acid, H_2CO_3. The first apparent equilibrium constant of carbonic acid is:

$$K_1 = \frac{(H^+)(HCO_3^-)}{H_2CO_3^*} \; . \; . \; . \; . \; (7)$$

Substituting Eq. 6 into Eq. 7 and rearranging, the following is obtained:

$$(H^+) = \frac{P_{CO_2}\ K_1\ K_H}{(HCO_3^-)} \; . \; . \; . \quad (8)$$

Substituting Eq. 8 into Eq. 5, the SR has a usable form in aqueous systems:

$$SR = \frac{T_{Ca}\ Alk^2\ K_2}{P_{CO_2}\ K_1\ K_H\ K_{sp}}, \; . \; . \quad (9)$$

where (Ca^{2+}) has been replaced by total calcium (T_{Ca}). The P_{CO_2} is the mole fraction (X_{CO_2}) of $CO_{2(g)}$ in the gas phase multiplied by the total pressure, P_T:

$$P_{CO_2} = P_T\ X_{CO_2} \; . \; . \; . \; . \quad (10)$$

Substituting this into Eq. 9, the final SR equation is derived:

$$SR = \frac{T_{Ca}\ Alk^2\ K_2}{P_T\ X_{CO_2}\ K_1\ K_H\ K_{sp}}, \; . \; . \quad (11)$$

where T_{Ca} and Alk are in molar units. The SI is defined at this point as follows:

$$SI = \log SR \; . \; . \; . \; . \; . \; . (12)$$

A positive SI defined in this manner indicates a solution capable of precipitating calcite; a negative sign indicates a solution which can dissolve calcite.

The equilibrium constants expressed in Eq. 11 must now be made conditional and equations found to express each in terms of temperature, pressure, and ionic strength. The authors realize more complex functional forms for equations have been suggested for the dependence of equilibrium constants on temperature and ionic strength than those in the following discussion. However, the equations used adequately describe the data, as will be demonstrated in each case, and maintain the desired simplicity.

The form of the polynomial used to describe the dependence of the conditional constants on temerature is:

$$pK_i = a + bT + cT^2, \ . \ . \ . \quad (13)$$

where $pK_i = -\log(K_i)$. The data to describe pK_1 and pK_2 is from Helgeson (1967) which correlates very well with that from Ryzhenko (1963). The temperature dependence of pK_H can be found also from data by Helgeson (1967). The temperature dependence of pK_{sp} is found from data **by** Ellis (1963). The coefficients for Eq. 13 found by non-linear regression are shown in Table 3 where R^2 is the coefficient of determination and temperature is in °F.

The functional form for the pressure dependence of the conditional constants is:

$$pK = b + mP \ . \ . \ . \ . \ . \quad (14)$$

The pressure dependence of pK is found from Read (1975), pK_2 from Disteche and Disteche (1967), and pK_{sp} from MacDonald and North (1974). The coefficients for Eq. 14 found from linear regression are listed in Table 4 in psi units.

Data for the ionic strength dependence of pK_1 and pK_2 are taken from Disteche and Disteche (1967), for pK_{sp} from Hansson (1972). The functional form of the ionic strength dependence equation is taken from Millero (1979):

$$pK = a + bI^{1/2} + cI, \ . \ . \ . \quad (15)$$

where I is the ionic strength in molar units. The coefficients for Eq. 15 found by non-linear regression are shown in Table 5. The ionic strength dependence of pK_H is found empirically as 0.075 times the ionic strength added to pK_H:

$$pK_H = pH_H{}^{I=0} + 0.075I, \ . \ . \ . (16)$$

from data by Ellis and Golding (1963).

Table 3 The coefficients in Eq. 12 for the temperature dependence of the conditional constants.

	a	bx10^3	cx10^{-6}	R^2
pK_1	6.4093	-1.5936	8.5157	0.994352
pK_2	10.6059	-4.9700	13.3080	0.996936
pK_{sp}	7.8192	6.4641	8.5901	0.999508
pK_H	2.2720	5.6475	-8.0574	0.987828

Table 4 The coefficients in Eq. 13 for the pressure dependence of the conditional constants.

	b	mx10^5	r
pK_1	6.00	-3.0673	0.999875
pK_2	9.50	-2.6239	0.999750
pK_{sp}	8.40	-6.9967	0.998534

Table 5 The coefficients in Eq. 14 for the ionic strength dependence of the conditional constants.

	a	b	c	R^2
pK_1	6.3067	-0.4772	0.1180	0.98367
pK_2	10.3383	-1.1660	0.3466	0.99376
pK_{sp}	8.2821	-3.2149	1.0733	0.98322

The terms for the temperature, pressure, and ionic strength dependence of the conditional constants may now be assembled into one equation. The temperature dependence of pK_1 is given by:

$$pK_1^T = 6.4092 - 1,5936 \times 10^{-3}T + 8.5157 \times 10^{-6}T^2, \ . \ . \ . \ . (17)$$

substituting Eq. 17 into the pressure corrected equation yields $pK_1{}^{P,T}$ as a function of pressure and temperature, or:

$$pK_1{}^{P,T} = pK_1^T - 3.0673 \times 10^{-5}P \ . \ . (18)$$

Substituting Eq. 18 into the ionic strength dependence equation yields:

$$pK_1{}^{I,P,T} = pK_1{}^{P,T} - 0.477^{1/2} + 0.1180I \ . \ . \ . \ . \ . \ . \ (19)$$

The final equation for pK_1 is then:

$$pK_1 = 6.4092 - 1.5936 \times 10^{-3}T + 8.5157 \times 10^{-6}T^2 - 3.0673 \times 10^{-5}P - 0.4772I^{1/2} + 0.1180I \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . (20)$$

Similar treatment of the other conditional constants results in the following:

$$pK_2 = 10.6059 - 4.9700 \times 10^{-3}T + 1 \ . \ 090 \times 10^{-6}T^2 - 2.6239 \times 10^{-5}P - 1.1660I^{1/2} + 0.3466I \ . \ (21)$$

$$pK_{sp} = 7.8192 + 6.4641 \times 10^{-3}T + 8.5901 \times 10^{-6}T^2 - 6.9967 \times 10^{-5}P - 3.2149I^{1/2} + 1.0733I.(22)$$

$$pK_H = 2.2720 + 5.6475 \times 10^{-3}T - 8.0574 \times 10^{-6}T^2 + 0.075I \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . (23)$$

Assuming that the dependence equations of one variable (e.g., temperature) are not functions of the oterh two variables (e.g., pressure and ionic strength) is not rigorously correct, but in practice causes little error when calculated values are compared to measured ones.

The pH of the solution of interest may now be found by substituting the total pressure (P_T) and the mole fraction of CO2 in the gas phase (X_{CO2}) for P_{CO2} and Alk for HCO_3^- into Eq. 8:

$$(H^+) = \frac{P_T \, X_{CO2} \, K_1 \, K_H}{Alk} \ . \ . \ . \ . \ . \ . (24)$$

and by substituting the expressions for the conditional constants into Eq. 24:

$$pH_C = -\left(\log \frac{P_T \, X_{CO2}}{Alk}\right) + 8.6812 + 4.0539 \times 10^{-3}T + 0.4583 \times 10^{-6}T^2 - 3.0673 \times 10^{-5}P - 0.4772I^{1/2} + 0.1930I, \ . \ . \ . \ . \ . \ . \ (25)$$

where pressures are in psi, temperatures in °F, ionic strength and concentrations in molar units and pH_C denotes calculated pH. The SI can be determined without initially determining pH by substituting the expressions for conditional constants into Eqs. 11 and 12:

$$SI = \log\frac{T_{Ca}\ Alk^2}{P_T\ X_{CO2}} + 5.8946 + 15.4880 \times 10^{-3}T - 4.2596 \times 10^{-6}T^2 - 7.4401 \times 10^{-5}P - 2.5261I^{1/2} + 0.9197I \ \ldots\ldots (26)$$

If the pH is known or calculated, the expressions for conditional constants can be substituted into Eq. 5, and the resulting equation is:

$$SI = \log(T_{Ca}\ Alk) \pm pH - 2.7867 + 11.4341 \times 10^{-3}T - 4.7179 \times 10^{-6}T^2 - 4.3728 \times 10^{-5}P - 2.0489I^{1/2} + 0.7267I, \ \ldots\ldots (27)$$

where ionic strength and concentrations are in molar units, temperature in °F, and pressure in psi. If total calcium and alkalinity are known in ppm rather than molarity, multiply T_{Ca} by Alk and divide the product (in ppm) by 2.44×10^9 to correct to molarity and substitute the result into the respective equation for (T_{Ca} Alk).

The SI is a measure of the scaling tendency. If the sign of the SI is positive, the solution has a scaling potential; a negative sign indicates the brine will dissolve $CaCO_3$. The calculation does not require separate tables or large computer facilities and relies only on parameters typically measured in the field. Results will be discussed further in the following section.

The calculations as presented do not account for significant flashing of the water. However, by adjusting the T_{Ca} and Alk terms for increased concentration in the aqueous phase due to flashing character. For example, if 20% of the brine has flashed, increase the T_{Ca} and Alk concentrations by 20% as shown in the comparison of the data of shannon et al. in Table 2.

Practical Application of the SI Equation

Geopressured energy wells of the Gulf Coast offer an opportunity to take practical advantage of the SI presented in this paper.

The decrease in pressure from the producing aquifer to the surface causes $CO_{2(g)}$ to evolve out of solution, increasing the pH of the brine and the tendency for $CaCO_3$ precipitation. It is important to note that these pH changes do not affect total alkalinity and any alkalinity measurement taken in the system can be projected to other points in the system as long as no actual scaling takes place. In other words, the evolution of $CO_{2(g)}$ does not change total alkalinity. If the brine is cooled because of calcite being more soluble at lower temperature, the scaling tendency can actually be deminished, but at economic flow rates (estimated at 40,000 B/D [6359 m^3/d]) the temperature with respect to downhole is essentially constant without the addition of cooling equipment or heat exchangers.

Table 6 lists the calculated pH(pH_C), the SR, and SI for the five geopressured wells. Notice *that the SI is within 0.43 of 0.0 (the saturation value)* when the calculations are projected downhole, indicating not all solutions are saturated with respect to calcite downhole. This is in excellent agreement with the predicted values considered errors in chemical analyses, pressure and temperature measurements, ant in the calculations which are all reflected in the final SI calculation.

The SI may now be applied to the surface equipment to determine scaling tendencies throughout the system. Table 7 lists the flow parameters of the Pleasant Bayou No. 2 well. The SI is positive at the tree, but increases dramatically after the choke. Upon completion of the test, scale was found throughout the system and scale inhibitors were used and are planned for future tests at this location.

Table 6 pH_C and SSR downhole for the indicated wells.

INDICATED WELLS

Well Name	pH_c	SR	SI
Wainoco-Girouard	5.08	0.54	-0.27
Pleasant Bayou No. 2	4.30	0.99	-0.01
Riddle-Saldana	5.00	0.77	-0.11
Beulah Simon	4.47	0.38	-0.43
Prairie Canal	4.42	0.38	-0.42
		Average	-0.25 ± 0.24

To prevent calcium carbonate scale formation, *either the thermodynamic driving force must be* delayed by various types of inhibitors (for a literature review of scale prevention (Cowan and Weintritt, 1976). Because of the volume of brine produced per scf (std m^3) of natural gas recovered (~30 scf/bbl (0.85 std m^3), *it is important to minimize* inhibitor dose while maintaining effectiveness.

Table 7. Flow parameters and SI's in the Pleasant Bayou No. 2 well system.

Location	T(°F)	P_T	pHc	SI
Downhole	306	10134	4.30	-0.01
Christmas Tree	283	6127	4.60	0.32
After Choke	283	910	5.58	1.54

To study the problem of calcium carbonate scale inhibition in geopressured energy wells, the parameters of brine flow, temperature, and pressure should be duplicated in the experiment to produce a similar scaling regime. Open beaker experiments were not considered applicable because $CO_{2(g)}$ could not be maintained in solution, temperatures were limited to less than 212°F(100°C), and pressures were limited to atmospheric.

More sophisticated experimental designs than open beakers have been developed to consider the problem of calcium carbonate scale. Vetter (1970) designed a Teflon bomb which contained two sample cells which were combined at high temperature to produce scale. The precipitated scale and the solution were then analyzed to determine the amount of scale formed. This apparatus did not, however, meet the requirements of a flow system nor did it allow for changing pressure regulation. Beasley and McKinney (1973) and Jones (1961) have described procedures to determine scaling tendency and inhibitor effectiveness, but neither could reach temperatures of interest in geopressured well studies. Sone et al. (1964) designed a flow system with temperature and pressure regulation, but were limited to 350°F(176.5°C) and 1000 psi (69 bars). In addition, the scale was detected on a coupon requiring solutions which were unrealistically supersaturated to produce measurable scale in a reasonable time (Cowan and Weintritt, 1976).

An experimental system for scale and corrosion inhibitor testing described below overcomes most of the disadvantages of the above static testing procedures. Temperatures, pressures, flow rates and fluid chemistry typical of geopressured surface equipment have been simulated in this instrument. Results from these laboratory experiments are being used to guide inhibitor applications in the field.

EXPERIMENTAL

The high temperature-pressure flow system has been simulated with a modified high pressure (performance) liquid chromatograph (HPLC). The HPLC used in these experiments was a Spectra-Physics SP 8000. Tubing from three 1 dm^3 storage bottles leads to a proportioning valve which allows for computerized mixing of the solutions in any proportion. The solution then passes through the proportioning valve, continues through two mixers, and finally into the high pressure pump. The pressurized brine then passes through coiled stainless steel tubing in the instrument oven and continues to a water bath followed by a backpressure valve. The solution then passes to an in-line pH electrode before being discharged. To monitor solution optical density an in-line spectrophotometer has been inserted at various times between the backpressure valve and the pH electode. Thirty-five ft (10.67 m) of a 50 ft (15.24 m) length of tubing was coiled in the oven to insure good heat transfer. The water bath was found to be necessary to eliminate temperature effects on the pH electrode. Flow rate, temperature, and pressure are computer controlled by use of the HPLC electronics. Temperature in the oven can be raised to 266°F (130°C) and pressure can be maintained at 8000 psi (552 bars) with slight adjustment of the HPLC circuitry.

The tubing size was chosen to maintain similitude with respect to Euler's number at flow rates practical with the machine (1 to 30 ml/min.)(Daugherty and Franzini, 1977). All experiments were run at 10ml/min flow rate. The tubing used was 50 ft (15.24 m) of either 1/16 in OD x 1/32 in. ID (0.16 cm x 0.08 cm) 304 or 1/16 in. OD x 1/32 in. ID (0.16 cm x 0.08 cm) 316 stainless steel. The residence time of the solution in the tubing from the pump to the pH electrode was calculated to be one minute.

Laboratory solutions were prepared which had the same saturation index (SI) or thermodynamic tendency to precipitate as the field brines. Simulated brine compositions used in the inhibitor evaluation experiments are shown in Table 8. The solution was prepared to be comparable in composition to the Department of Energy Pleasant Bayou No. 2 Design well.

Table 8 Simulated brine compositions used in inhibitor evaluation experiments.

Ca^{2+} = 0.25 M

HCO_3^- = 1.253 x 10^{-3}

$T_{HCO_3^-}$ = 1.340 x 10^{-3}

NaCl = 2.0 M

I = 2.50 M

pH = 7.000

SI @ 77°F(25°C) = 0.10 @ 1000 psi

SI @ 257°F(125°C) = 1.87

The experiments were conducted by flowing 10 ml/min of solution at 77°F (25°C) through the HPLC at 1000 psi (69 bars) to simulate separator pressures. The temperature was then raised through a temperature gradient to 257°F (125°C). The pH of the brine was continually monitored on the chart recorder and the temperature at the initiation of nucleation was noted. The pH decreased upon the initiation of $CaCO_3$ nucleation according to the equation:

$$Ca^{2+} + HCO_3^- = CaCO_3 + H^+$$

The pH of the solution decreased at 223°F(106°C) due to $CaCO_3$ precipitation. The decrease was from 7.00 to 6.08 for a solution with no inhibitor added. Between runs the machine was flushed with 0.5 M HCl solution for approximately one minute, or until the pH had decreased to one or less. The machine was then flushed with the prepared water. At the beginning of the next run, the pH of the effluent was allowed to return to 7.00 before the temperature gradient was begun. Various amounts of inhibitor were then added to the solution to evaluate the effectiveness of each respective inhibitor. The inhibitors evaluated were hydroxethylidenediphosphonic acid (HEDP), polymaleic acid (PMA), and polyacrylic (PAA). The HEDP was a Dequest 2010 inhibitor from Monsanto and the PAA was from Arco, Inc., and the PMA from Ciba-Geigy.

RESULTS

Results of brine pH vs. brine temperature experiments were recorded as the temperature when precipitation was initiated, if it occurred. The results of the technique for HEDP, PMA, and PAA evaluations are shown in Table 9.

Notice that precipitation was totally inhibited at 0.20 ppm HEDP in the brine at 257PF(125°C). The calculated SI at this temperature and pressure in a brine of this composition is 1.87. With no inhibitor the brine will nucleate at 223°F(106°C) and precipitation will continue to 257°F(125°F) where an equilibrium pH of 6.08 is reached. The SI at a temperature of 257°F(125°C) and 1000 psi (69 bars) in this brine is -0.07, or only 0.03 difference from the theoretical value of 0.0, which indicates the calculations are quite close. Note that PMA is less effective than HEDP in inhibiting $CaCO_3$ precipitation in the brine. PAA also does not completely inhibit precipitation until the concentration is 0.35 ppm.

Table 9 The results of experimental technique for three inhibitors.

	SI	Inhibiting Concentrations (ppm)
HEDP	1.87	0.20
PMA	1.87	0.35
PAA	1.87	0.35

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