A Kinetic Model of CO_2 Generation and Mineral and Isotopic Alteration During Steamflooding

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Summary. CO_2 is commonly produced during steamflooding. In higher-temperature steamfloods the amount of CO_2 produced is such that the only viable source is carbonate minerals. We show by reference to CO_2 concentrations in natural geothermal systems that in most common rocks and sediments, CO_2 is generated naturally under hydrothermal (~572°F) conditions by the dissolution of carbonate minerals. CO_2 solubility is a strong positive function of temperature and, at 572°F, is more than sufficient to account for high CO_2 concentrations like those encountered at Chevron's Buena Vista (BV) Hills steamflood pilot test. A linear kinetic model is developed to describe chemical equilibration and CO_2 generation in the hot parts of the reservoir. The model also describes CO_2 removal through carbonate precipitation in the cooler parts of the rock formation where the fluid moves ahead of the thermal front. Changes in carbon isotope concentration are included in the model. The small difference between the ^{13}C in the produced gas and the source carbonates at BV Hills suggests that little CO_2 is precipitated as carbonate within that reservoir, a prediction that can be tested by poststeamflood coring.

Introduction

The steamflooding process for oil recovery often produces large quantities of CO_2. Over 1 year at Chevron's BV Hills, CA, steamflood pilot project, for example, 80×10^6 scf of CO_2 was produced at an average ratio of 31 scf of CO_2/bbl steam injected [cold water equivalent (CWE)]. At Texaco's steamflood in the San Ardo Field,[1] gas that was 80% CO_2 was produced at the rate of 3.5×10^6 scf/D (35 scf/bbl steam injected). CO_2 production during steamflooding was also documented at the Lacq Supérieur field in southwestern France.[2] CO_2 production appears to occur in all steamfloods, with greater quantities occurring in higher-temperature steamfloods.

CO_2 production is important because it can accelerate corrosion and because in-situ generation and precipitation of CO_2 can affect mass-balance and pressure calculations in reservoir engineering models of the steamflood process. To the best of our knowledge, there has been no previous attempt to account for quantitatively or to explain the CO_2 produced during steamflooding with an integrated physical/chemical kinetic model.

The purpose of this paper is to present a model of CO_2 production during steamflooding that identifies the principal variables controlling the amount of CO_2 produced and that provides insight into the consequences of the CO_2 production for reservoir simulation of the steamflooding process.

BV Hills Steamflood

From May 1985 through May 1986, 65 acres of the 120-ft-thick oil-bearing Pliocene Wilhelm formation at BV Hills was subjected to steam injection. Steam (80 wt%) and hot water (20 wt%) entered the Wilhelm at about 2,500-ft depth and 572°F under a driving pressure of 1,700 psi. Injection into 12 wells was steady over the year at about 7,000 B/D (CWE). Water, oil, and gas were produced from 20 production wells, drawn down to atmospheric pressure. The wells were arranged in five-spot patterns with about 340 ft between injection and producing wells. At the start of the test, the reservoir pressure in the test area had been reduced by previous oil production to about 130 psi. Reservoir temperature was about 113°F. At the end of the first year, the temperatures in the producing wells had risen to 140 to 180°F.

In the first year about 2.5 million bbl of steam (CWE) was injected and about 1 million bbl of water and 105 million scf of gas were produced. Gas production began a few months after the start of the test and then increased linearly to about 700,000 scf/D by the end of 1 year. Initially, most of this gas was methane (and higher hydrocarbons), but, during the year, CO_2 in the gas steadily increased until it was about 90 mol% at the end of the year. On average for the year, the gas produced ran about 75 mol% CO_2.

Several lines of evidence indicated that the produced CO_2 derived from the breakdown of inorganic carbonate in the Wilhelm formation. First, this was the only source of carbon large enough. The water injected contained ~133 ppm HCO_3, but this accounts for only 0.9% of the 80 million scf (~100 million g mol) of CO_2 produced in the first year. Formation water could have contributed at most 5%, and organic acids in all the Wilhelm formation oil in the test site could have contributed at most 16%. The amount of CO_2 that could have been produced from organic sources is actually much less than this. Because of channeling, only a fraction of the Wilhelm formation in the test area is believed to have been heated sufficiently to cause the breakdown of organic acids to CO_2.

On the other hand, the Wilhelm formation contains a few wt% calcite and 4 to 21 wt% dolomite. One wt% carbonate in a 6-ft sand layer within the 65-acre test area could generate 92 million mol of CO_2.

The isotopic composition of the Wilhelm carbonate is unusually heavy [15 to 28‰ vs. PDB (*Belemnitella americana* from the Cretaceous Peedee formation, SC) as shown in **Table 1**]. The isotopic composition of the produced CO_2 matches this unusual composition almost exactly (19 to 26‰ vs. PDB, as shown in **Fig. 1**). CO_2 generation from CH_4 is unlikely because of the very slow kinetics of the reaction and the lack of an obvious oxidant. In any case, CO_2 generation from CH_4 at 392 to 572°F would have the wrong isotopic composition (−5‰) if the source CH_4 had the isotopic composition of the CH_4 produced (Fig. 1).[3] Field and chemical evidence thus strongly suggests that the CO_2 produced at BV Hills came from carbonate breakdown.

The question that must be addressed is how this breakdown is achieved during steamflooding. Further questions of interest are how much CO_2 is precipitated ahead of the thermal front and what do the chemical changes in the reservoir imply for the evolution of the steamdrive and the physical properties of the rock formation?

CO_2 Generation in Natural Geothermal Systems

A clue to the processes that may be involved is provided by data from natural geothermal systems. Waters in natural geothermal systems contain large amounts of CO_2. As shown in **Fig. 2**, the CO_2 content of unboiled geothermal waters is relatively independent of the mineralogy of the host formation and increases strongly with temperature.

Several authors[4-8] have analyzed the reactions that control the concentration of CO_2 and other elements in geothermal solutions. They have shown that under geothermal conditions most solution species, including CO_2, are in equilibrium with such common rock minerals as quartz, calcite, feldspar, and clay. Aluminosilicates buffer pH between 5 and 7, depending on solution salinity. Our

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TABLE 1—CARBON ISOTOPIC COMPOSITION OF DOLOMITES FROM THE WILHELM FORMATION

Depth (ft)	$\delta^{13}C$‰ vs. PDB
2,472	22.95
2,476	28.01
2,503.5	15.29
2,532	22.78
2,546.0	24.05
2,552.5	19.32

interpretation is that alteration of minerals such as kaolinite or feldspar to montmorillonite or other clays provides the H^+ required to dissolve carbonate phases in the rock; carbonate is dissolved and clay produced until the concentration of CO_2 in solution reaches saturation with respect to carbonate reactions and therefore is no longer consumed by them. Laboratory experiments confirm this process.[9-11] Steamflooding experiments produce CO_2, and clay formation always accompanies carbonate destruction.[12-22] The porosity of samples generally increases as the result of CO_2 production, but the permeability decreases because of grain coating by low-density smectite honeycombs. Mercury injection tests together with permeability measurements suggest that small pore throats are reduced in size, while the pores themselves are enlarged.[23]

For quantification of CO_2 production, we find the geothermal literature most useful. Giggenbach[7] made a thorough analysis of rock-buffered CO_2 concentration in geothermal systems. He developed a simple formula to describe the partial pressure of CO_2 (given below as Eq. 1) and converted it to give the concentration of CO_2 (Eq. 4) with Drummond's[24] expression of Henry's law constant (Eq. 2).

$$\log p_{CO_2}=15.26-7{,}850/T. \quad (1)$$

$$\log K_H=8.769-0.00745T-1517.7/T. \quad (2)$$

$$p_{CO_2}=K_H C_{H_2CO_3}. \quad (3)$$

$$\log C_{H_2CO_3}=6.491-6332.3/T+0.00745T. \quad (4)$$

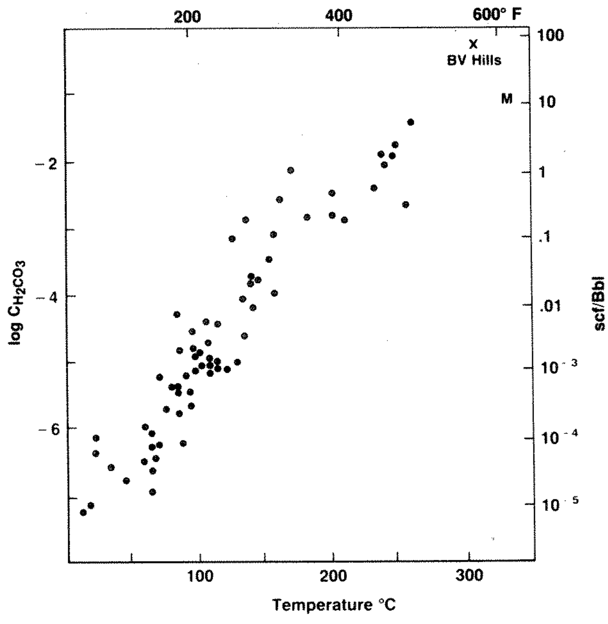

Fig. 2—The molal concentration of CO_2 dissolved in natural geothermal waters (from Arnorsson[4] and Henley[5]).

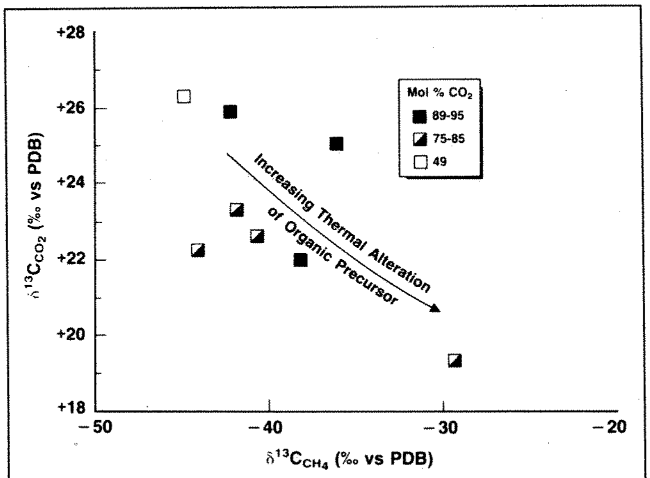

Fig. 1—Carbon isotopic composition of CO_2 and CH_4 produced in the BV Hills test. All samples were collected from different wells 11 months after the start of the test. The $\delta^{13}C_{CH_4}$ spread probably results from the increasing thermal maturity of the organic matter from which it is derived. If so, this suggests that the $\delta^{13}C_{CO_2}$ may have been decreasing over the course of the field test (arrow).

For completeness, we add a simple expression for the partial pressure of steam as a function of temperature.[25]

$$\log p_s=0.085-0.794(T/100)+2.203(T/100)^2$$
$$-1.976(T/100)^3+1.503(T/100)^4. \quad (5)$$

Eqs. 1 through 5 provide the basis for a model of CO_2 generation during steamflooding.

Conceptual Model for CO_2 Generation During Steamflooding

Fig. 3 illustrates what happens when the rock formation is heated by injected steam. With the assumption that the steamflooded formation contains the common minerals (such as quartz, feldspar, and carbonate) necessary for the CO_2 rock buffer shown in Fig. 2 and that the 572°F solutions equilibrate quickly with these minerals, CO_2 concentration will increase to about 0.51 mol CO_2/kg solution, as can be seen by Fig. 2 or by evaluation of Eq. 4.

Eqs. 3 and 5 show that if water/rock equilibrium had been closely approached, a CO_2-steam phase would have been maintained at BV Hills. Eq. 3 shows that the partial pressure of CO_2 above a 572°F solution containing 0.51 mol CO_2/kg is 37 bars. The partial pressure of steam at 572°F, as indicated by Eq. 5, is 86 bars. Hence, the sum of the partial pressure is 123 bars, which exceeds the 1,700-psi steam injection pressure. As CO_2 builds up in the injected water, the partial pressure of CO_2 will help preserve (or generate if necessary) a separate gas phase. Loss of CO_2 will main-

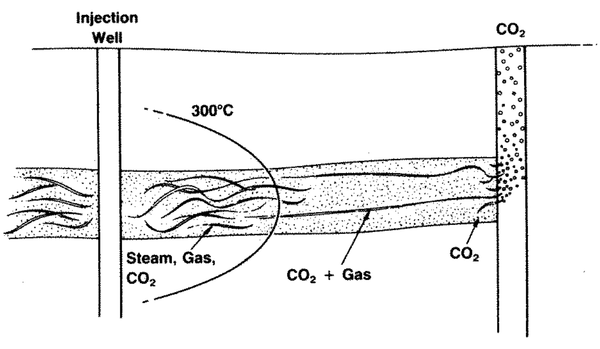

Fig. 3—Conceptual model of CO_2 generation during steamflooding. CO_2 is generated behind the thermal front and partially precipitated as calcite while passing through the front.

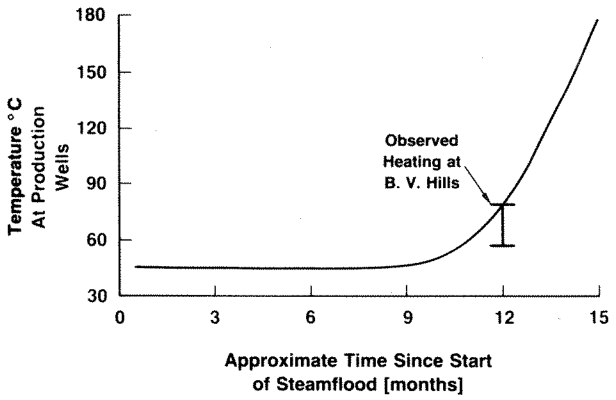

Fig. 4—Temperature response at production wells predicted by our model compared with the heating observed after the first year of the BV Hills test.

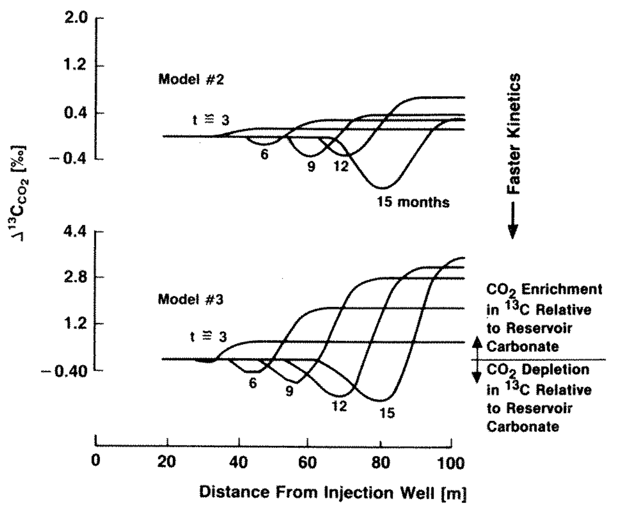

Fig. 5—Dissolution and precipitation of carbonate as a function of time (and advance of the thermal front).

tain the CO_2 concentration in the water phase below the concentration that could be maintained by mineral equilibria. The high-temperature part of the steamflood in cases like BV Hills will thus steadily generate CO_2, as shown in Fig. 3. The CO_2 may largely reprecipitate as calcite or some other carbonate as the fluid moves through the thermal front. Some gaseous CO_2 may reach the production wells. At the lower pressures near the production well, CO_2 may again exsolve as a separate gas phase.

Process Model for CO_2 Generation During Steamflooding Including Carbon Isotopic Effects

The conceptual model can be converted to a quantitative kinetic model that predicts the amount and isotopic composition of CO_2 generated during steamflooding. The quantitative model combines a physical description of the movement of the thermal front of a steamflood with a chemical kinetic model that calculates the rate of CO_2 generation and precipitation, including the respective isotopic compositions, from first-order rate constants. The rate constants appropriate for steamflooding are determined by comparing model predictions for a range of kinetic parameters to the results of the steamflood at BV Hills.

Major Assumptions. The model makes a number of simplifying assumptions.

1. The model does not incorporate pressure transients.

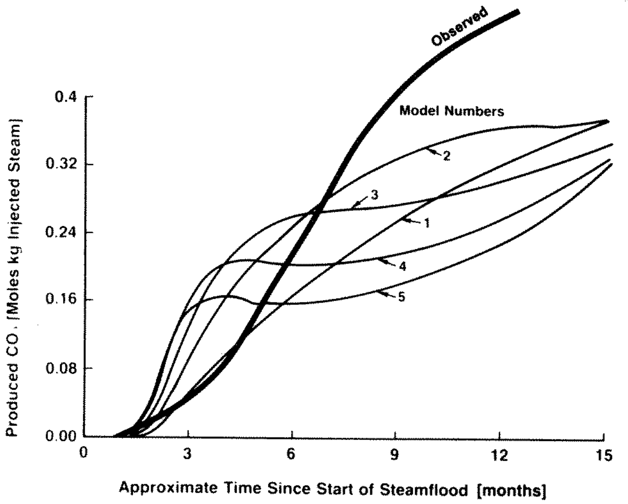

Fig. 6—Profiles from injection into production wells showing the isotopic signature of CO_2 gas (or H_2CO_3) relative to the isotopic signature of the carbonate from which the gas was derived.

2. Changes in fluid chemistry are assumed to be immediately transmitted throughout the reservoir. There is no delay, as would be physically required, to allow the fluid chemically altered in one part of the reservoir time to migrate to other areas.
3. The model considers the gas phase to move with the liquid phase and, in fact, to be just an extra store of CO_2.
4. The fractionation between carbon isotopes in CO_2 and calcite was assumed to be that of Mook *et al.*[28] Some literature suggests a smaller isotopic difference between CO_2 and calcite.[3,26] A smaller fractionation factor would reduce the calculated isotopic shifts caused by calcite precipitation, and reduce the usefulness of carbon isotopes in monitoring processes that occur during steamflooding.

These assumptions are believed not to affect the conclusions drawn.

Thermal Model. A 1D radial heat-balance model is used to describe the movement of the thermal front from the injection to production wells in a typical five-spot at BV Hills. The formation between the injection and production wells is divided into concentric shells of equal volume. Each shell is treated as an isothermal stirred tank and heat balance is required as volumes of water are progressively moved into each shell from the shell nearer the injection well.

The distance to the outer diameter of successive shells is

$$s_\alpha = d\sqrt{\alpha/n_t}\ . \qquad (6)$$

It can be shown by Laplace transformation that for constant-temperature fluid injection, the temperature profile is a simple function of the number of thermal parcels, n, injected, where a thermal parcel is defined as

$$n = n_f(c_{vw}/c_{vr}). \qquad (7)$$

The temperature at the midpoint of each shell is given in terms of the temperature at the midpoint of the preceding shell by the following formula:

$$T_{\alpha+1}(n) = T_\alpha(n) - (T_0 n^\alpha e^{-n}/\alpha!), \qquad (8)$$

where T_0 = injection temperature.

To account approximately for the conductive heat losses from areas of concentrated flow within the Wilhelm, the heat capacity of the sand unit was doubled. With this modification, the increase in temperature in production wells is similar to the range observed for the injection rates used (**Fig. 4**). The radial model properly accounts for the geometrically dictated decrease in fluid velocity at greater distances from the injection well; however, it does not account for fluid acceleration near the production wells.

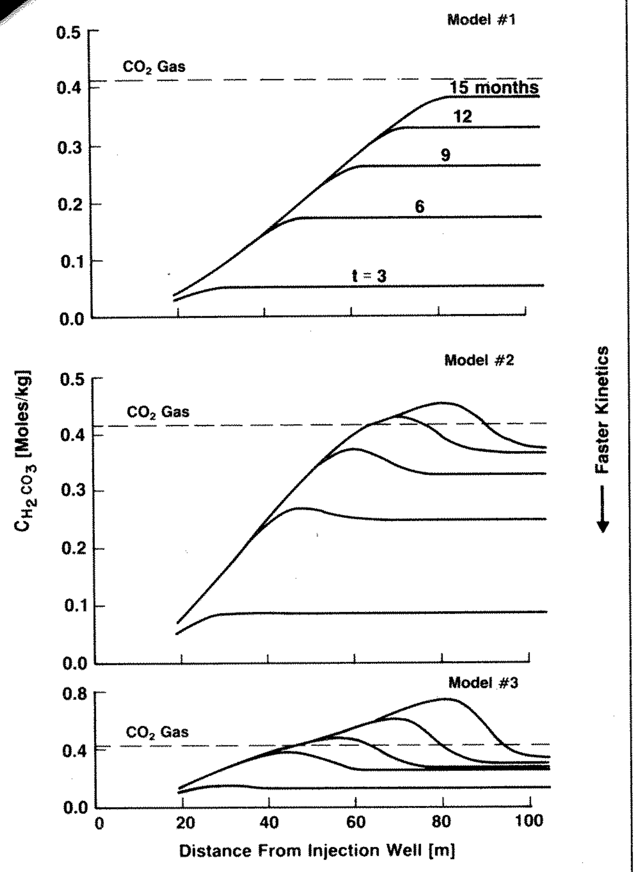

Fig. 7—Production of CO_2 by the various models in Table 2.

CO_2 Kinetic Model. The rate of the carbonate dissolution process in the hot parts of the system near the injection well is assumed to be proportional to the degree of undersaturation of the liquid with respect to CO_2 (linear, first-order kinetics). The term "process" is used to emphasize that the silicate reactions buffering the pH are probably the slowest, and therefore the rate-controlling, reactions. Acid dissolution of carbonates is a relatively fast reaction.[27]

As fluid proceeds toward the production wells and temperature drops, the water phase becomes oversaturated in CO_2. In these areas, CO_2 will precipitate as calcite. Any CO_2 in the gas phase will contribute CO_2 to the liquid phase and prolong calcite precipitation.

The CO_2 concentration in solution is calculated with the following first-order kinetic expression:

$$\rho\phi\partial C/\partial t = fk_o\rho e^{-E/RT}[C_{eq}(T)-C]\equiv j_c. \quad\text{. . . . . (9)}$$

Here, f, the fractional rate of precipitation, has a value of 1.0 for $C\leq C_{eq}$, but may have values different from 1.0 for $C>C_{eq}$. If $\partial t'$ is defined at $\partial t/\phi$, and $\Delta t'$ is defined as the time required to inject a fluid volume equal to the volume of one of the concentric shells, e.g.:

$$\Delta t' = \pi R_0^2 h/n_t i, \quad\text{. . . . . (10)}$$

then Eq. 9 can be integrated over any shell to give a propagator solution to the CO_2 profile in terms of the incremental input of a volume of water equal to the volume of a shell:

$$C(s_{\alpha+1}) = C_{eq}(T)+[C(s_\alpha)-C_{eq}(T)]\exp(-fk_o\Delta t' e^{-E/RT}), \quad\text{. . (11)}$$

where T is the temperature in kelvin.

In this expression, $C_{eq}(T)$ is the smaller of the saturated value given by Eq. 4 and the maximum concentration allowed by the reservoir pressure p_{max} given by Eq. 12:

$$C_{eq}(T)=[p_{max}-p_s(T)]/K_H(T). \quad\text{. . . . . (12)}$$

TABLE 2—INPUT PARAMETERS FOR THE KINETIC MODEL DESCRIBED IN THE TEXT (Figs. 5 through 9)*

Model	Pre-exponential Kinetic Term, k_o (seconds^{-1})	Fractional Rate of Calcite Reprecipitation, f
1	0.025	0
2	0.050	0.5
3	0.1	1
4	0.2	1
5	0.3	1

*k_o and f are defined in Eq. 9.

$p_s(T)$ and $K_H(T)$ are given by Eqs. 5 and 2, respectively.

Isotopic Model. Isotopic alteration occurs as carbonates are dissolved or precipitated. When carbonate is dissolved, no isotopic shift takes place. The CO_2 entering the solution has the isotopic composition of the carbonate that is dissolved. When the fluid precipitates calcite, however, the calcite precipitated is in isotopic equilibrium with the solution. The "fractionation factor" that describes the difference between the isotopic composition of dissolved CO_2 and calcite is assumed to be the same as that between CO_2 and HCO_3^-, which has been measured[28,29] and is represented in the following expression:

$$\Delta^{13}C_{soln\text{-}solid}\cong\Delta^{13}C_{CO_2-HCO_3^-}=23.89-9483/T. \quad\text{. . . . . (13)}$$

Because the fractionation is positive at temperatures above about 248°F, calcite precipitation will leave the residual CO_2 isotopically enriched in ^{13}C. Precipitation of CO_2 as calcite at temperatures above ~248°F therefore could help account for the large positive signature of the residual CO_2 produced in the BV Hills test. The model remembers the amounts and isotope composition of precipitated calcite and takes this into account when this calcite is subsequently redissolved by the advancing thermal front. Redissolution of ^{13}C-depleted calcite produces the ^{13}C-depleted CO_2 shown in **Fig. 5**.

The mass-balance equation for the change in ^{13}C concentration in solution for constant $\rho\phi$ can be written

$$\rho\phi\partial^{13}C/\partial t = j_c[(^{13}C/C)_{solid}-(^{13}C/C)], \quad\text{. . . . . (14)}$$

where j_c is given by Eq. 9. The definition of $\delta^{13}C$ can be used to convert the ratios in Eq. 14 to the more standard $\delta^{13}C$ notation. For example, $\partial^{13}C$ is by definition equal to $[(^{13}C/C)/R_{std}-1]\times 1{,}000$, so $^{13}C/C=(\delta^{13}C/1000+1)R_{std}$, where R_{std} is the isotopic ratio of the PDB standard (a constant). Substitution of this expression into Eq. 14, together with substitution from Eq. 9 and utilization of the definition of $\Delta t'$, gives

$$\Delta\delta^{13}C=\Delta t' fk_o e^{-E/RT}[(C_{eq}/C)-1](\delta^{13}C_{solid}-\delta^{13}C). \quad\text{. . (15)}$$

We have made the approximation that the quantities on the right side of Eq. 15 are constant over $\Delta t'$. Eq. 15 is a propagator solution to the isotopic profile because $\Delta\delta^{13}C$ can be thought of as the change in $\delta^{13}C$ across the shell:

$$\Delta\delta^{13}C=\delta^{13}C(s_{\alpha+1})-\delta^{13}C(s_\alpha). \quad\text{. . . . . (16)}$$

When carbonate is being dissolved (i.e., $C_{eq}/C<1$), $\delta^{13}C_{solid}$ is the isotopic composition of the carbonate. When calcite is being precipitated (i.e., $C_{eq}/C>1$), $\delta^{13}C_{solid}=\delta^{13}C-\Delta^{13}C_{soln/solid}$.

The isotopic composition and quantity of the calcite precipitated is recorded so that when calcite is subsequently dissolved, as a result of thermal front movement, the proper isotopic composition of the solid is known. The amount of calcite dissolved is also accounted for; the isotopic composition of the carbonates in the original rock formation is used when the precipitated carbonate is all redissolved. The moles of CO_2 per gram of solution generated or precipitated as a result of the injection of a shell fluid volume can be converted to weight percent calcite dissolved or precipitated by multiplying ΔC by

$$(\rho M_{CaCO_3}/\rho_r)\times 10^2\cong 5{,}000, \quad\text{. . . . . (17)}$$

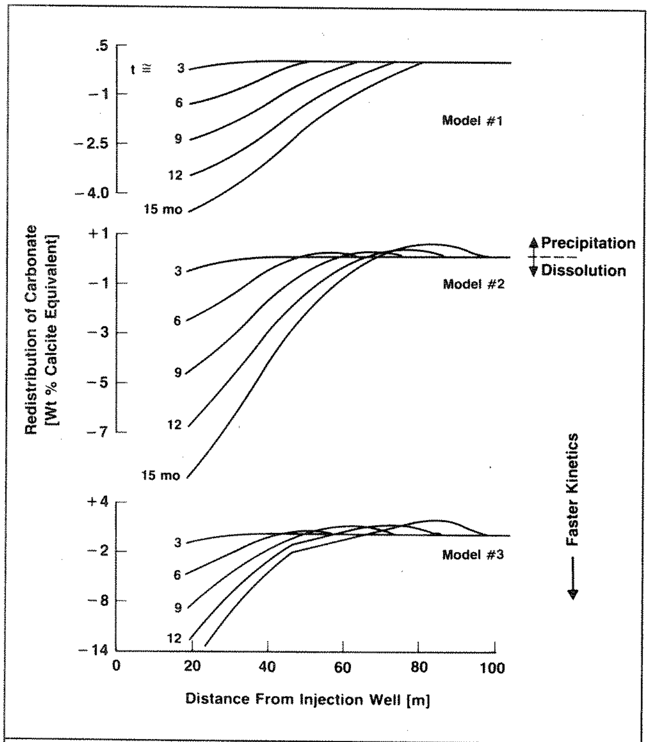

Fig. 8—Concentration of dissolved CO_2 in the pore fluids at various times after the start of steam injection.

where M_{CaCO_3} is the gram molecular weight of calcite.

The isotopic model does not take into account the effects of calcite precipitation during dolomite dissolution because the carbon isotopic fractionation between calcite and dolomite is very small at $T>392$°F. Dolomite is $<1\%$ heavier than calcite[30]; therefore, only a slight shift in the fluid CO_2 to heavier $\delta^{13}C$ values is anticipated. Core experiments confirm this expectation.[12]

Model Results

The results, for a model with 30 equal-volume shells, a spacing of 340 ft between injection and production wells, and 572°F fluid injection (all appropriate for the BV Hills test) are shown beginning with **Fig. 6**. At the flow rates at BV Hills, a fluid volume equal to one model shell volume takes about ½ month to inject (13.8 days).

Calculations were made for the different kinetic parameters shown in **Table 2**. The rate of carbonate dissolution and calcite precipitation generally increased from Model 1 to 5.

Fig. 6 shows that CO_2 produced in the faster kinetic models (Models 3 through 5) rises steeply and then plateaus or even drops, and only rises again as the thermal front breaks through into the production wells. This behavior reflects the increased calcite precipitation that occurs as the thermal front moves away from the injection well and the fluid velocity through it decreases. The pre-exponential kinetic term and fractional rate of calcite precipitation were adjusted in the models so that the CO_2 content of the produced water was on average about 0.2 molal.

A plateau or drop in CO_2 production was not observed. Thus, from here on, we show Model 3 as the sole example of the faster kinetic models.

Fig. 7 shows calculated profiles of the CO_2 between injection and production wells in a BV Hills five-spot at approximately 3-month intervals since the start of production. The CO_2 concentration at which CO_2 will exsolve as a separate gas phase at 572°F and 115 bars total pressure is shown as a dashed line on each diagram.

Fig. 8 shows the weight percent carbonate dissolved and precipitated between injection and production wells. At the faster dissolution rates, more carbonate is dissolved near the injection well than was originally in the host formation. The models assume that an excess of carbonate is always present. Calcite depletions exceeding the amount of calcite originally present should be interpreted as indicating complete carbonate removal.

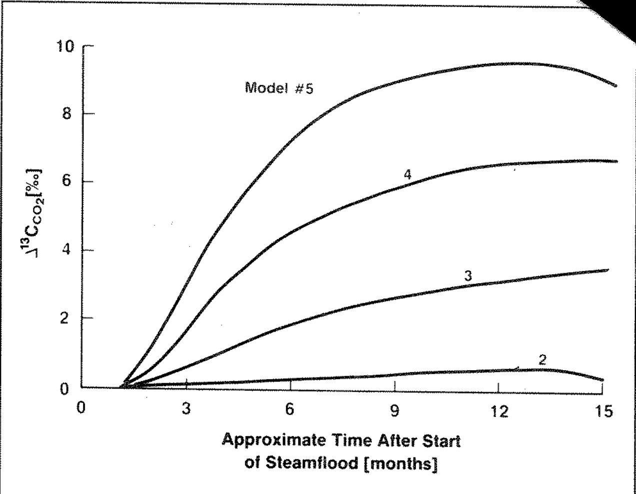

Fig. 9—Increase in ^{13}C in produced CO_2 relative to the ^{13}C in the carbonate from which the CO_2 was derived as a function of time. Similarity of ^{13}C in reservoir carbonate and produced CO_2 suggests Model 2 is most appropriate.

Fig. 5 shows the shift in $\delta^{13}C_{CO_2}$ relative to the $\delta^{13}C$ of the reservoir carbonate ($\Delta^{13}C_{CO_2}$). Of course, no change in the $\delta^{13}C_{CO_2}$ occurs if no calcite is precipitated (Model 1). The shift in $\delta^{13}C_{CO_2}$ becomes progressively larger as the fraction of CO_2 precipitated in the reservoir increases (faster kinetic models).

Fig. 9 shows the isotopic shift, $\Delta^{13}C$, of the produced CO_2 relative to reservoir carbonate as a function of time. The slower kinetic models with little carbonate reprecipitation require the initial reservoir carbonate to have a $\delta^{13}C>20\%$. The fastest kinetic model (Model 5) has sufficient CO_2 precipitation that source carbonates with $\delta^{13}C<11\%$ could generate the isotopically heavy CO_2 produced in the BV Hills test. The slow (Model 2) and fastest (Model 5) kinetic models show a drop in $\delta^{13}C_{CO_2}$ after about 1 year, in agreement with the drop implied in Fig. 1.

Because the rock carbonates in the Wilhelm formation appear to be uniformly isotopically heavy, the large isotopic shift that could be provided by extensive carbonate dissolution and precipitation is not needed. The isotopic results thus confirm the conclusion based on the shape of the CO_2 production curve that carbonate dissolution and precipitation kinetics are relatively slow (Model 1 or 2 favored). For the slow kinetic models, minimal CO_2 exists as a separate gas phase within the BV Hills reservoir. All considered, a model with some carbonate precipitation and some CO_2 generation as a separate gas phase (perhaps intermediate between Models 1 and 2) probably best describes the generation of CO_2 at BV Hills.

Model Predictions

A model between Models 1 and 2 makes a large number of predictions that could be tested by poststeamflood coring, laboratory experiments, or the proper observations during steamflooding.

1. About 4 to 7 wt% carbonate is dissolved near the injection wells.
2. Up to about ½ wt% calcite is precipitated ahead of the greatest advance of the 572°F isotherm in any five-spot.
3. Precipitated calcite should be isotopically zoned with the calcite last precipitated containing less ^{13}C than that first precipitated (up to 7‰). The first precipitated calcite should have an isotopic composition about the same as the host carbonate (~20%).
4. Dissolution of carbonates should be accompanied by both dissolution and precipitation of silicate phases because paired aluminosilicate reactions are required to produce the acid that dissolves the carbonates and CO_2.
5. The pH in the hot parts of the steamflood should be near the rock-buffered value of 6.5.

6. Synthetic laboratory cores with carbonate (other than perhaps siderite) but no aluminosilicate phases should not generate CO_2 if saturated with water and heated to 572°F. If appropriate aluminosilicates are added, CO_2 should be generated.

Implications

CO_2 production during steamflooding has many interesting implications for secondary oil recovery. Furthermore, it should be possible to control the rate of CO_2 generation and its effects in a number of ways by engineering design. For example, the temperature and fluid injection rate affect the CO_2 generation rate. Faster or lower temperature injection would not permit the buildup of H_2CO_3 to the concentrations that allow a separate gas phase to be generated. In this case, the CO_2 gas generation will be "turned off." Conversely, slow injection will "turn up" the CO_2 generator.

Significant CO_2 concentrations in the liquid phase can alter the pressure conditions of a steamflooded reservoir. For example, a liquid with 0.41 mol CO_2 (the concentration of CO_2 attainable at 1,700 psi near the injection wells at BV Hills) generates 40 bars pressure at 356°F. The movement of water with 0.41 mol dissolved CO_2 to lower-pressure and -temperature portions of the reservoir thus could have significantly increased the 9-bar initial reservoir pressure at BV Hills. Exsolution of CO_2 near production wells will lower the relative permeability to water near these wells while opening a particularly permeable pathway for escape of gaseous CO_2 from the reservoir.

Substantial movement of CO_2 within the reservoir could facilitate the transport of distilled hydrocarbons. Lowering CO_2 concentration could cause distillate condensation before reaching the producing well. If the condensation and attendant mineralogic reactions are volume filling, as would be anticipated from reactions complementary to the porosity-producing CO_2-generation reactions, the trapped distillates might be difficult to flush out.

Review

An overall model of the process that generates CO_2 during steamflooding has been developed. The model considers the radial movement of the thermal front away from an injection well and accounts for broadening of the front and the drop in fluid velocity at increasing distances from the injection well. CO_2 generation occurs as the hot water chemically equilibrates with common minerals in the host formation. Support for this concept is provided by the chemistry of geothermal systems and by previous laboratory experiments. The rate of equilibration (and CO_2 generation) is described by a first-order kinetic model of the reaction between hot water and rock minerals. Carbon isotopic shifts are included because they potentially reflect the amount of CO_2 produced and precipitated within the reservoir.

The model is used to evaluate the BV Hills steamflood. It is shown that, although a range of kinetic models could account for the amount and isotopic composition of CO_2 produced at BV Hills, the observed accelerating production of CO_2 favors the slower kinetic models. Relatively little carbonate probably is precipitated within the reservoir at BV Hills. The similarity in carbon isotopic composition between the produced CO_2 and the dolomites in the steamflooded Wilhelm formation support this conclusion.

Perhaps the most important aspects of the model and its application to BV Hills are the phenomena and their interdependencies that are identified. CO_2 generation (relative to the CWE of steam injected) during steamflooding should be favored by higher temperatures of injected steam, lower initial reservoir pressures, and slower injection rates over larger formation intervals (i.e., slower steam and hot-water movement through the reservoir). CO_2 generation can significantly alter the pressure evolution of a steamflooded reservoir. Calcite precipitation could affect reservoir permeabilities and trap hydrocarbon distillates within the reservoir. The model can be tested by analyzing field cores and by selective laboratory experiments. Historical isotopic gas compositions (unavailable at BV Hills) reflect the amount of calcite precipitation and should be collected in future tests. The model could be usefully extended to include carbon isotopes in organic gases. We hope the simple model presented may afford a basis for further investigation of the phenomena that occur during steamflooding.

Nomenclature

c_{vw} = heat capacity=1, cal/(cm^3·°C)
c_{vr} = heat capacity of rock=1, cal/(cm^3·°C)
^{13}C = moles of ^{13}C/g of solution
$^{13}C_{solid}$ = moles of ^{13}C/g of solid
C = moles of CO_2/g of solution
C_{eq} = equilibrium concentration of CO_2 in Eq. 4, mol/g solution
$C_{H_2CO_3}$ = molal concentration of H_2CO_3
d = distance from injection to production well in five-spot (340 ft×30.48 cm/ft), cm
$\delta^{13}C$ = carbon isotopic signature of solution relative to the PDB standard (19 to 25‰), ‰
$\delta^{13}C_{solid}$ = carbon isotopic signature of carbonate relative to PDB standard (15 to 25‰), ‰
$^{13}C_{soln/solid}$ = equilibrium carbon isotopic fractionation between solution and solid (Eq. 13)
E = activation energy for dissolution of carbonate and precipitation of calcite=15,000, cal/mol
f = rate of calcite precipitation/rate of dissolution (Eq. 9)
h = injection interval (6 ft×30.48 cm/ft), cm
i = injection rate per well, CWE=1226, cm^3/s
j_c = flux of j carbon from formation to solution (Eq. 9)
k_o = kinetic pre-exponential term, first-order rate constant times surface area/unit volume of reacting mineral (Eq. 9), seconds^{-1}
K_H = Henry's law constant relating concentration of CO_2 in solution and partial pressure of CO_2 in vapor phase in equilibrium with that solution (Eq. 2)
M_{CaCO_3} = gram molecular weight of calcite
n = number of thermal parcels (Eq. 7)
n_f = number of fluid parcels injected where volume of one fluid parcel equals volume of a shell ($\pi R_0^2 h/n_t Q$)
n_t = total number of equal-volume concentric shells between injection and production wells=30
p_{max} = maximum allowed reservoir injection pressure (15 bars), bars
p_s = partial pressure of steam (Eq. 5), bars
R = gas constant=2 cal/(mol-K)
R_{std} = isotope ratio of PDB standard
s_α = distance to outer boundary of αth equal-volume shell (Eq. 6)
$\Delta t'$ = time required to inject a volume of CWE equal to volume of shell (Eq. 10)
T = temperature, K
ρ = water density=1.0, g/cm^3
ρ_r = rock density=2.7, g/cm^3
ϕ = total reservoir porosity=0.2

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SI Metric Conversion Factors

acres	×	4.046 873	E±	=	ha
bars	×	1.0*	E+05	=	Pa
bbl	×	1.589 873	E−01	=	m^3
ft	×	3.048*	E−01	=	m
ft^3	×	2.831 685	E−02	=	m^3
°F		(°F−32)/1.8		=	°C
°F		(°F+459.67)/1.8		=	K
g mol	×	1.0*	E−03	=	kmol
lbm	×	4.535 924	E−01	=	kg
psi	×	6.894 757	E+00	=	kPa
scf/bbl	×	1.801 175	E−01	=	std m^3/m^3

*Conversion factor is exact.

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