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USE OF CALCITE AS A CO_2 GEOBAROMETER FOR ESTIMATION OF RESERVOIR PRESSURES IN THERMALLY ASSISTED OIL RECOVERY*

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ABSTRACT

Two observations form the basis for a calcite-based CO_2 reservoir geobarometer: 1) Unconsolidated sand or sandstone reservoirs often produce abnormal amounts of CO_2 from the breakdown of carbonate minerals during thermally enhanced oil recovery. 2) Calcite is one of the most reactive minerals in these reservoirs; if present, it will be close to equilibrium with the produced fluids. The CO_2 geobarometer is based on the equilibrium reaction calcite + $2H^+ = Ca^{2+} + H_2O + CO_2$. Fluid pressure in the reservoir may be estimated using the CO_2 geobarometer if the reservoir temperature and the chemistry of the reservoir fluids are known. Reservoir temperature can be estimated by silica geothermometry. This temperature estimate is combined with the fluid chemistry and measurements of the relative masses of produced water, oil and gas from production wells and entered into the geochemical code SOLMINEQ.88 to calculate the reservoir pressure. Use of the calcite geobarometer is illustrated by calculating reservoir pressure trends with time during steam stimulation and steam-drive recovery.

Keywords: geobarometer, calcite, CO_2, reservoir, steam-assisted recovery.

SOMMAIRE

Le géobaromètre fondé sur la calcite, utilisé pour évaluer la pression du CO_2 dans un réservoir, repose sur deux observations: 1) Le sable non consolidé ou les réservoirs situés dans les grès produisent assez couramment des proportions anomales de CO_2 par déstabilisation des carbonates pendant la récupération thermiquement assistée du pétrole. 2) La calcite est un des minéraux les plus réactifs dans ces réservoirs. Elle est toujours près de l'équilibre en présence des fluides produits. Le géobaromètre est fondé sur l'équilibre calcite + $2H^+ = Ca^{2+} + H_2O + CO_2$. Il peut servir à estimer la pression de la phase fluide dans un réservoir si la température et la composition de ce fluide sont connus. La température du réservoir peut être évaluée à partir du géothermomètre fondé sur la silice. A la lumière de ce paramètre, de la composition du fluide, et des masses relatives mesurées de l'eau, de pétrole, et de gaz émanant des puits en production, il est possible de calculer l'état de la pression du réservoir au moyen du logiciel à caractère géochimique SOLMINEQ.88. Nous illustrons l'utilisation de ce géobaromètre en calculant la variation de la pression du réservoir avec le temps au cours d'une stimulation avec la vapeur et d'une récupération assistée par la pression de la vapeur.

(Traduit par la Rédaction)

Mots-clés: géobaromètre, calcite, CO_2, réservoir, récupération assistée par la vapeur.

INTRODUCTION

In slow-flowing geothermal systems, the proportion of CO_2 is known to be controlled by mineral equilibria (Giggenbach 1980, 1981, Arnórsson 1985, 1986, Arnórsson & Gunnlaugsson 1985) by reactions of the form: plagioclase + CO_2 = clay + calcite. If flow rates increase in a reservoir as a result of an increase in permeability or drive pressure or if mixing of fluids occurs, disequilibrium may prevail; then only the more rapidly reacting mineral phases such as calcite will approach equilibrium with the fluids. Reactions involving other minerals, such as the above reaction, will be out of equilibrium and cannot be used as a CO_2 geobarometer. Then CO_2 geobarometers must be based on reactions of the form: calcite + $2H^+ = Ca^{2+} + H_2O + CO_2$.

Most production wells in steam-assisted thermal recovery of oil also produce gas, a significant amount of which is CO_2. Until recently, most of the CO_2 produced during this process was considered to originate either from aquathermolysis (Hyne *et al.* 1984, Hyne 1986) or to have already been present in the reservoir. Many of these reservoirs contain carbonate minerals, which react rapidly (Gunter & Bird 1988, Talman *et al.* 1990) with reservoir fluids compared to silicate minerals at the elevated temperatures imposed by contact with steam. Cathles *et al.* (1987) and Hutcheon *et al.* (1990) make use of the ^{13}C isotope signature of

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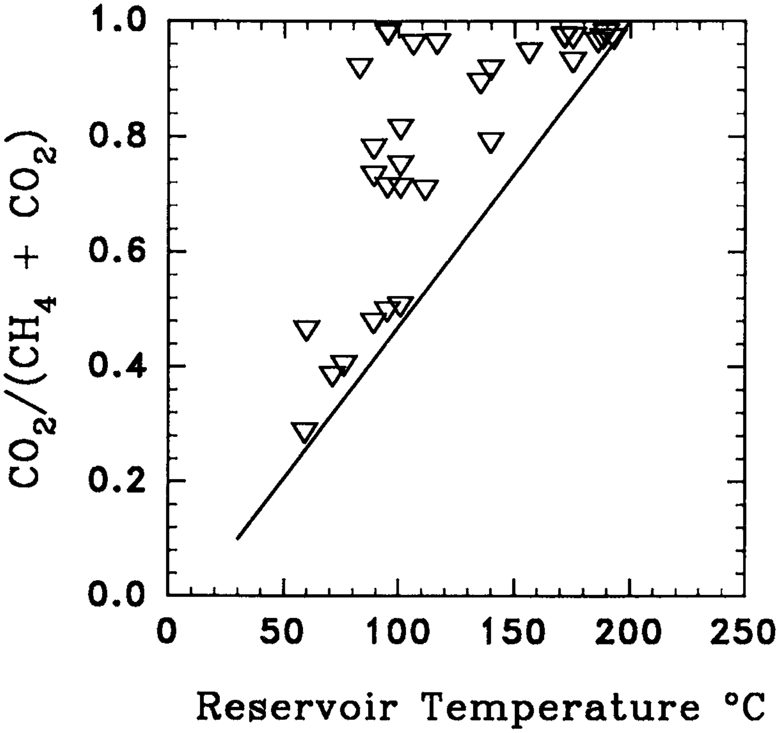

FIG. 1. Reservoir temperature versus mole fraction CO_2 in the reservoir gas. Note that there is a critical maximum mole fraction of CH_4 (indicated by solid line), which decreases with increasing temperature. CO_2, CH_4 and water vapor represent more than 98% of the gas fraction.

calcite to argue that the majority of CO_2 produced in steam flooding originates from the breakdown of carbonate minerals. A consequence of this breakdown is that CH_4, which is a dominant gaseous component of many oil reservoirs, decreases with respect to CO_2 as the temperature of the reservoir increases (Fig. 1). Most reservoirs containing carbonate minerals become gas-saturated during the heating of the reservoir and accompanying breakdown of the carbonate minerals. At high temperatures, the CO_2 component typically is greater than 90% for steam-heated reservoirs containing calcite (Fig. 1). The CO_2 released dissolves in the water and oil, and also forms a separate vapor phase that can enhance oil recovery through a solution-drive mechanism. If equilibrium has been established between the fluids and carbonate minerals in the reservoir, and if this condition can be quantitatively described, the reservoir pressure can be estimated. Chemical data on the water and gas produced, the tubular and annulus flow from the production well and the reservoir temperature are needed for the calculation. In this paper, such a method is outlined to determine trends in reservoir pressures during thermally enhanced oil recovery (EOR).

DATA COLLECTION

The fluids at the production well are produced in two streams (Fig. 2). Each well consists of two concentric pipes. The inner pipe is called the tubing string and typically contains a sucker rod pump. The larger-diameter outer pipe is called the annulus. The gas separates from the liquids as the reservoir fluids enter the well through the perforations located above the bottom of the production well. During production, noncondensible gases (normally CO_2 and CH_4) and steam propagate naturally upward through the annulus; liquid water and oil either flow or are pumped downward from the perforations, upward through the pump and the tubing string to the surface. The hot liquids from the tubing string are sampled on the surface at wellhead temperature and pressure; several pore volumes of fluid are made to flow through a stainless steel sampling cylinder, which allows all the drop in pressure to take place across the

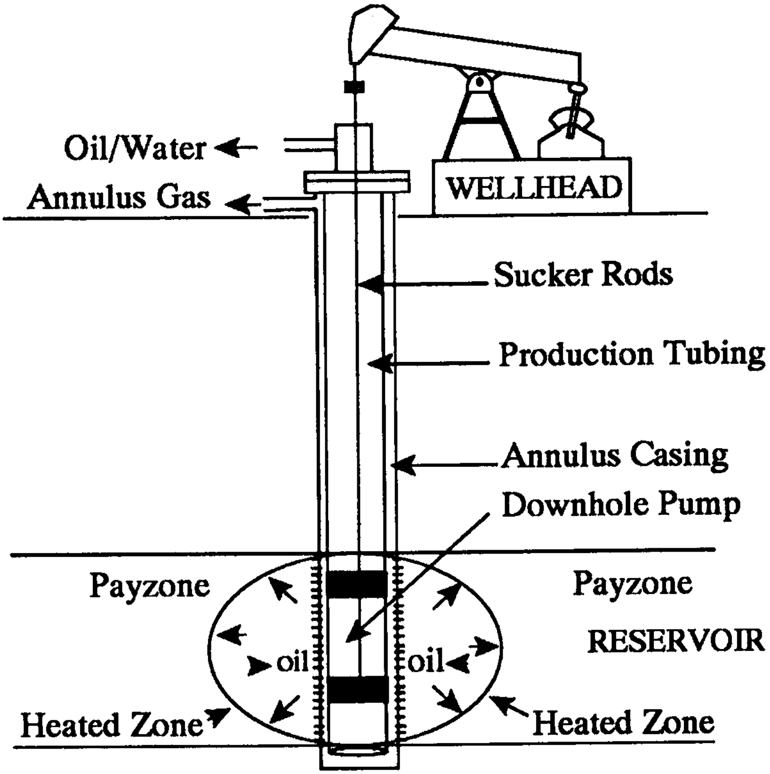

FIG. 2. Wellhead cross-section showing annulus and tubing for a cyclic steam well in production mode. Annulus casing is perforated (indicated by stacked dashes) in payzone to allow oil to flow into the well. The distance from the reservoir to the wellhead for the samples discussed here ranges from 0.2 to 0.5 km.

regulating valve at the downstream end of the cylinder. The noncondensible gases are sampled from the annulus through a train containing a condensing coil, a coalescing filter and aluminum sampling cylinder or Teflon sampling bag. The liquid flow in the tubing is split into an oil and water component; their ratio is normally measured by the oil company by periodically diverting the flow to a test separator. The gas flow in the annulus is measured by inserting an orifice plate and differential pressure cell in the annulus line at the wellhead. Samples collected are separated and treated in the field; unstable chemical components are analyzed or preserved for analysis in the main laboratories (Lico *et al.* 1982, Hull *et al.* 1984, Gunter & Bird 1989).

METHOD OF CALCULATION

It is necessary to numerically recombine the fluids produced from the annulus and tubing string to simulate the equilibrium conditions in the reservoir in order to solve for calcite saturation. A critical measurement in the chemical analysis of the quenched water produced from the tubing string is the pH at which the TIC (total inorganic carbon) or alkalinity is measured. The alkalinity titration is done in the field as soon as the sample has cooled, whereas the TIC analysis is done up to several days later at our permanent laboratory site. The alkalinity titration must be carried out to include the effect of organic acids (Carothers & Kharaka 1978, Willey *et al.* 1975). The lab pH taken at the time of the TIC measurement is usually higher than the field pH taken at the start of the alkalinity titration (Fig. 3). This difference in pH is attributed to escape of CO_2. Our standard procedure to correct for the lost CO_2 is to use the geochemical computer code SOLMINEQ.88 (Kharaka *et al.* 1988) to numerically titrate in enough CO_2 to reduce the lab pH to the field pH. Then the complete results of the chemical analysis are used in SOLMINEQ.88 to calculate alkalinity. The calculated alkalinity is compared to the measured

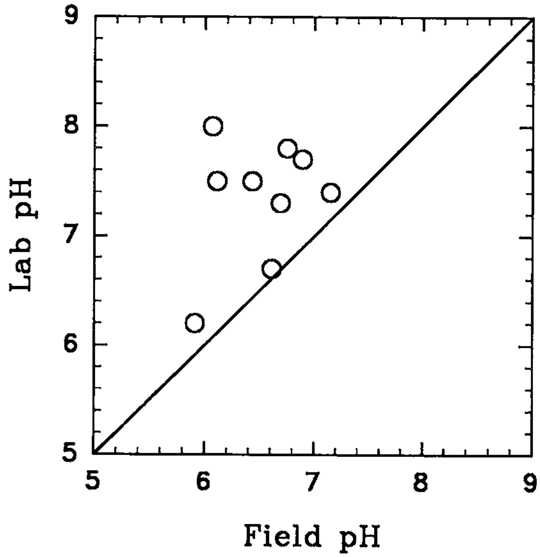

FIG. 3. Comparison of field pH and lab pH for wellhead samples of hot water produced from a steam-drive reservoir. Circles would fall on 45° line for exact agreement. Symbol size exceeds measurement error.

alkalinity. This and charge balance are used as a measure of the correctness of the chemical analysis, a procedure advocated by Merino (1979). The corrected value for TIC is an estimate of the TIC in the tubing string at the wellhead. Since there are gradients in temperature and pressure between the sandface and the wellhead, some CO_2 has been lost from the water as it travels up the tubing string to the surface. This amount cannot be corrected for easily, but can be ignored as long as the mass of CO_2 produced up the annulus is significantly larger. Generally this is true for gas-saturated reservoirs.

Calcite is assumed to be present and in equilibrium with the fluids in the reservoir. The fluid sampled at the wellhead of the production well reflects that equilibrium. Precipitation of any scale minerals in the wellbore is assumed not to occur or is small relative to the total mass of fluid. Reservoir conditions are simulated by recombining the annulus CO_2 with the tubular water using the temperature of the reservoir calculated from calibrated geothermometers (Kharaka & Mariner 1988). These calculations are done stepwise using SOLMINEQ.88 (Perkins & Gunter 1989, Perkins *et al.* 1990) in the following manner. The Saturation Index (SI is the logarithm of the ratio of the activity product or reaction quotient, Q, to the equilibrium constant, K) of calcite is determined at the reservoir temperature using the reservoir temperature and the tubing-string-produced water analysis. The SI will be positive owing to loss of CO_2 up the annulus. The methane and carbon dioxide produced from the annulus are soluble in both the oil and the water in the reservoir. Using the Henry Law constants for these gases (and any other gases such as H_2S that may be present in significant quantities) in water and oil, and the relative masses of produced water, oil and noncondensible gases, the annulus gases are numerically titrated back into the water and oil until the SI of calcite is equal to zero. $P(H_2O)$ is fixed during titration and is equal to the water vapor pressure at saturation at the reservoir temperature. $P(CO_2)$ and $P(CH_4)$ increase as the titration progresses. The calculated reservoir pressure is equal to the sum of $P(CO_2) + P(CH_4) + P(H_2O)$ at a calcite SI of zero. If other gas components, such as H_2S, are important, they would have to be included in the pressure equation.

As a very rough rule of thumb for reservoirs less than 500 meters deep, the SI of calcite changes approximately 0.1 SI units for every 5 bars change in CO_2 pressure at a fixed temperature. The calculation is very sensitive to errors in measurement of the quench pH and in estimates of reservoir temperature. An error of one half of a pH unit or 25°C shifts the calculated SI by approximately 0.6.

EFFECT OF GAS SATURATION ON THE GEOBAROMETER

Two cases are distinguished in the calculation of reservoir pressure: 1) gas-saturated (*i.e.*, a free gas phase exists), and 2) gas-undersaturated (*i.e.*, no gas phase exists). Existence of a free gas phase under reservoir conditions is illustrated by the solid line in Figure 4 for a two-component gas phase, CO_2 and H_2O, for the following composition of water produced from a steamed reservoir; reservoir temperature: 140°C, field pH: 6.97, lab pH: 7.50, (the following concentrations, derived from a chemical analysis, are in ppm) Na 4600, K 120, Ca 130, Mg 76, Fe 1.0, Sr 4.6, Ba 2.1, Cl 7090, Br 86, SO_4 58, TIC 340, SiO_2 220, B 100, NH_3 160, and alkalinity (as ppm HCO_3) 1570. The SI – Reservoir Pressure curve has a steep slope, which decreases toward lower values of SI. If the system passes from gas-saturated at the wellhead to gas-undersaturated in the reservoir, the SI – Reservoir Pressure curve falls on the gas-saturated curve at higher values of SI and abruptly changes to a slope close to zero when the free-standing gas phase disappears at lower values of SI (Fig. 4, dotted line). At this point, all of the available CO_2 has been dissolved in the water and oil. The composition of the water does not change with further increase in pressure. Only as long as a gas phase exists will the SI remain very sensitive to pressure. Consequently, the geobarometer becomes insensi-

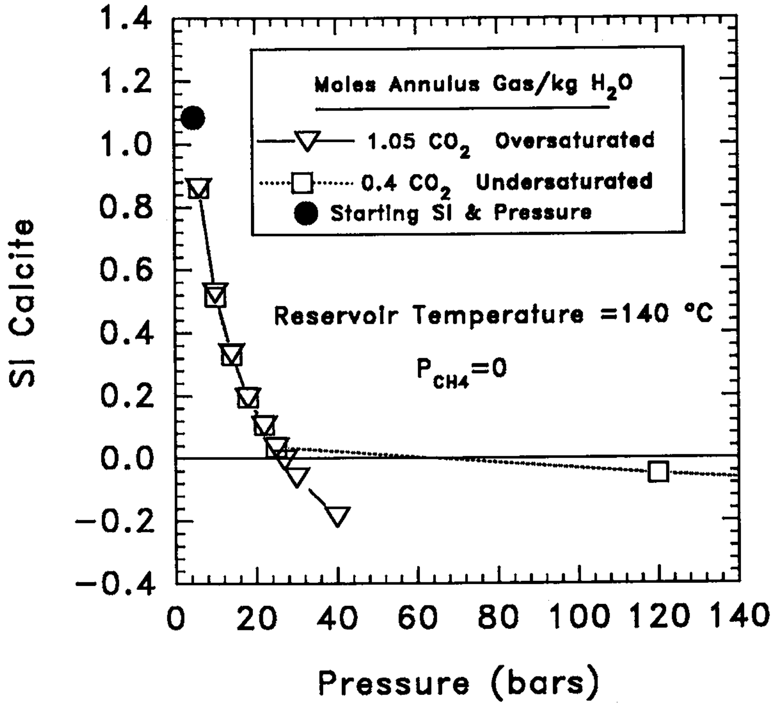

FIG. 4. SI - reservoir pressure plot that compares the gas-saturated case (solid line) to gas-undersaturated case (dotted line) for a pure CO_2 gas source. Note that pressure effect on the SI is much smaller for the undersaturated case.

tive for the undersaturated case and is inappropriate for use. Since the calculation always starts with excess gas (*i.e.*, the saturated state), a minimum reservoir pressure can always be estimated. It is the pressure obtained by extrapolating the gas-saturated portion of the SI - Reservoir Pressure curve to an SI of zero.

EFFECT OF GAS COMPOSITION ON THE GEOBAROMETER

The SI of calcite is not sensitive to $P(CH_4)$, as aqueous CH_4 is inert and does not affect the pH. The only effect of CH_4 is to increase the total fluid pressure. For a given composition of water, reservoir pressure and temperature, the value of the SI depends only on the ratio of CO_2 to CH_4 in the gas phase, and is independent of the absolute number of moles of gas present. Consequently, a SI - Reservoir Pressure plot can be contoured for mole fraction CO_2 (solid sloping lines) in the gas phase and $P(CO_2)$ (horizontal dotted lines), as done in Figure 5a for each unique composition of water. In these plots, lines of constant SI or zero slope are lines of constant $P(CO_2)$. The $P(CO_2)$ isobars are intersected by the steeply sloping CO_2-CH_4 contours. These contours evolve from the case of lowest pressure (*i.e.*, pure CO_2) to successively higher pressures as the mole fraction of CH_4 increases. If a composition of the gas phase is not available, the calculation can be made with the assumption that no CH_4 is present; a minimum reservoir pressure thus will be estimated. CH_4 is less soluble than CO_2 in the aqueous phase, but approaches the solubility of CO_2 in bitumen at higher temperatures (Fig. 6). Consequently, for equivalent amounts of CO_2 and CH_4 in the gas phase, less CH_4 will dissolve in the liquids, and the mole fraction of CO_2 in the gas phase will decrease as the numerical titration of gas proceeds to higher pressures. Hence on Figure 5a, the gas-titration curves for a changing mole fraction of CO_2 will have shallower slopes than the illustrated contours of constant mole fraction of CO_2. The pressure of CH_4 can be estimated in Figure 5a from the distance in bars along the constant $P(CO_2)$ isobar to the desired constant mole fraction of CO_2. The effect of CH_4 content in the gas phase on the estimate of SI is less than one might expect; a difference in SI of approximately 0.3 is calculated in going from

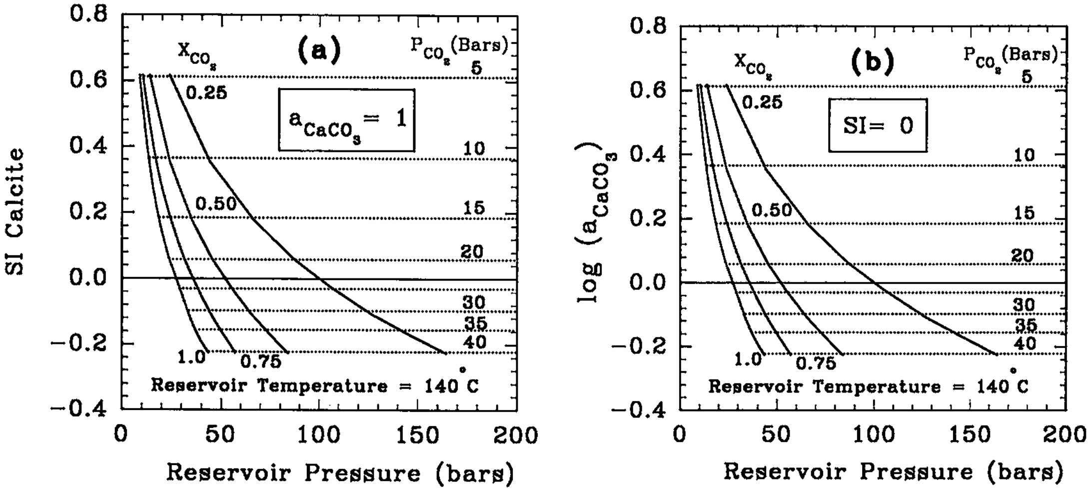

FIG. 5. a) SI – reservoir pressure plot contoured for P(CO_2) and *X*(CO_2) in the gas phase for a gas-saturated reservoir. b) *a*(Calcite) – Reservoir Pressure plot contoured for P(CO_2) and *X*(CO_2) in the gas phase for a gas-saturated reservoir.

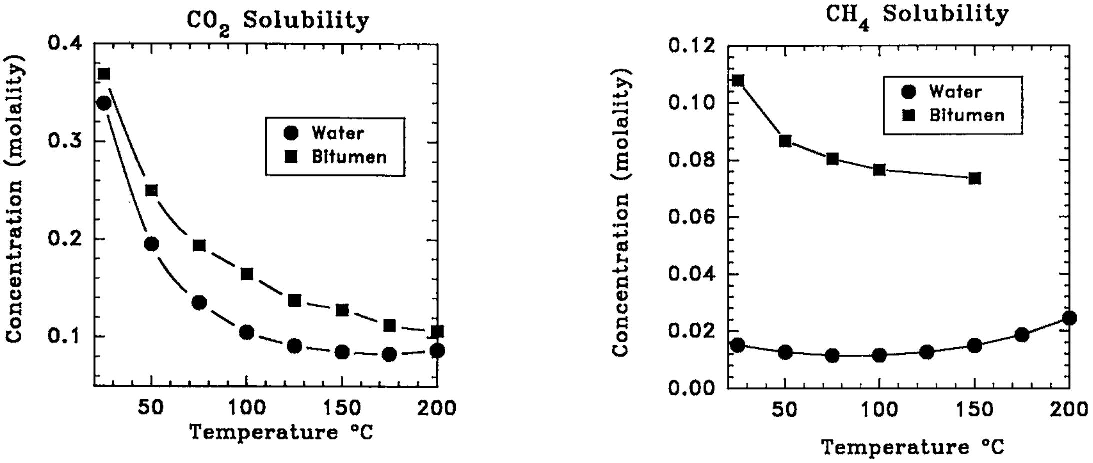

FIG. 6. Solubility of CH_4 and CO_2 in water and oil for a gas pressure of 10 bars.

zero CH_4 to equal molar amounts of CH_4 and CO_2. This change corresponds to a doubling of reservoir pressure. Oil acts as an additional sink for the gases. The presence of oil has no effect on the titration curve if the amount of CH_4 is very small (or nil), and a substantial excess of gas exists.

The calculations are more complex if H_2S is present. H_2S is very soluble in water and dissociates readily in basic solutions releasing protons, affecting the carbonate equilibria. However, geochemical codes such as SOLMINEQ.88 can model the combined effects of H_2S, CH_4 and CO_2 on the calcite geobarometer. The procedure for inclusion of H_2S is exactly the same as for CO_2 and CH_4.

EFFECT OF CALCITE COMPOSITION ON THE GEOBAROMETER

A change in the composition of the calcite (*e.g.*, Fe, Mg, Mn and Sr can replace Ca) controlling the fluid equilibrium also will affect the calculated reservoir-pressure. The effect of solid solution is easy to correct for, as can be seen from the expression for SI for the reaction Calcite + $2H^+$ = Ca^{2+} + H_2O + CO_2:

$$SI = \log(Q/K)$$
$$= \log a(Ca^{2+}) + \log a(H_2O) + \log P(CO_2) - \log a(Calcite) + 2pH - \log(K)$$

The line for SI equals zero is equivalent to an *a*(Calcite) of 1.0 [*i.e.*, log*a*(Calcite) = 0] on Figure 5a; if *a*(Calcite) equals 0.8, [*i.e.*, log*a*(Calcite) = -0.1], the SI of zero condition shifts to SI = -0.1 on Figure 5a. Consequently, the activity of the $CaCO_3$ component in the carbonate solid-solution [*i.e.*, *a*(Calcite)] can be substituted directly for SI on the SI - Reservoir Plot. Figure 5b, an *a*(Calcite) - Reservoir Pressure plot, is a duplicate of Figure 5a, except that the ordinate has been replaced by log*a*(Calcite), and SI is a constant equal to zero.

ASSUMPTION OF EQUILIBRIUM WITH CALCITE

A packet of fluid has a residence time of days to months in the reservoir, but only minutes to hours in the wellbore during production. The wellbore is a severe environment, going from reservoir conditions to surface conditions over several hundred meters. Rapid drops in pressure can cause boiling off of CO_2 and (potentially) precipitation of calcite, which is partially offset by the increased solubility of calcite at lower temperature. Modification of the fluid by formation of a calcite scale in the wellbore will lead to incorrect assumptions about the compositions of the reservoir fluid based on the chemical composition of the fluids collected at the wellhead. The experience gained, after several years of recovery from an oil reservoir, should be used to identify wells that are active scalers. In the absence of such historical data, simple calculations can be made to estimate a well's scaling potential, and to find out whether formation of a small amount of scale will alter the chemistry of the production water enough to affect the geobarometry calculation. For example, 100 grams of calcite scale will form per day if the dissolved calcium drops 1 ppm between the wellhead and the reservoir in a typical well with a production rate of 50 cubic meters per day. This would amount to 36 kg of calcite scale forming in a year, which normally would certainly restrict if not halt production. Such wells should be avoided when sampling for the purpose of calcite geobarometry.

Equilibrium may not be established between the carbonate and silicate minerals in the reservoir. Gunter & Bird (1988) have shown that production of large amounts of inorganic CO_2 requires the reaction of silicate with carbonate minerals. The silicate minerals supply the acid necessary to break down the carbonate minerals and release the CO_2. Furthermore, the rapid dissolution of calcite relative to the silicates at elevated temperatures and its reaction with the silicate phases commonly prevent the silicate phases from saturating the fluid until the production of CO_2 has slowed down. If the appropriate silicate mineralogy to provide a source of acid does not exist, then production of inorganic CO_2 will be small. In this case, organic CO_2 formed by aquathermolysis may dominate. The source of the CO_2 is not critical to the calculation, but regardless of source, the CO_2 must establish equilibrium with calcite in the reservoir if the calcite geobarometer is to be applied. A residence time of days for the fluid in the reservoir normally is a sufficiently long period for equilibrium to be attained with calcite.

RESERVOIR TEMPERATURES

Extrapolation of wellhead temperatures to reservoir temperatures by an account of heat losses and boiling in the wellbore has not been successful, owing to the presence of large gradients in temperature. Temperatures measured at the sandface by thermocouples are much closer to reservoir temperatures but are usually not available. Silica geothermometers have been used extensively to estimate temperatures of geothermal reservoirs (Fournier 1981, 1985). Application to thermally stimulated oil reservoirs has shown that the dissolved silica in the produced water increases with wellhead temperature and is generally close to being in equilibrium with one of the silica polymorphs at temperatures above 100°C. In Figure 7, the fluids produced from ten different wells on steam drive in a single oil reservoir were sampled on the same day, and their wellhead temperatures and geothermometer temperatures plotted. The reservoir temperatures (predicted by the silica geothermometer) are approximately 80°C higher than the wellhead temperatures (measured with a thermocouple). Seyer & Langdon (1990) compared the predictions of geothermometers to directly measured bottomhole temperatures and found that silica geothermometers gave the best estimates under stable conditions of production, generally being within 20°C of the measured temperature of the reservoir.

The correct form of the silica geothermometer must be used for each reservoir if reasonable estimates of temperature are required. Figure 8 shows the large errors involved if the quartz form of the silica geothermometer is used where the concentration of dissolved silica in the reservoir is controlled by a more soluble polymorph of silica. For example, the use of quartz solubility to calculate reservoir temperature will result in an

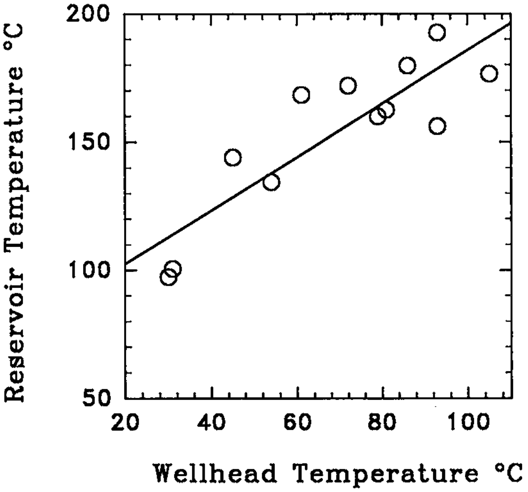

FIG. 7. Reservoir temperature predicted from the silica geothermometer compared to wellhead temperature measured by thermocouple. Solid line drawn through data indicates an approximate temperature shift of +80°C between the surface wellhead and the reservoir.

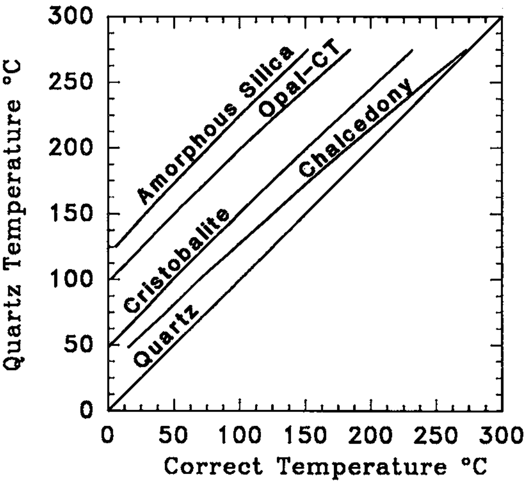

FIG. 8. Silica geothermometers (after Fournier 1981); predicted temperature compared to quartz-based temperature. Quartz-based temperature is based on a match of the temperature of quartz saturation to the measured dissolved silica produced from a reservoir and is only correct if quartz controls the concentration of dissolved silica in the reservoir.

estimate that is approximately 125°C too high if amorphous silica is the solid phase controlling the levels of dissolved silica in the reservoir fluids. The temperature trends can still be predicted correctly using the wrong polymorph because the solubility of all the silica polymorphs increases with temperature.

The silica geothermometers used for the two reservoirs discussed later were calibrated over a range of temperatures in a series of dissolution experiments in an autoclave using the reservoir sands and appropriate simulated formation-fluids. These results were extrapolated back to the water/rock ratios in the reservoirs to estimate minimum residence times of the fluid required to achieve equilibrium with respect to silica. At temperatures greater than 100°C, a minimum residence time of 1 day is necessary to reach a steady-state concentration of silica close to equilibrium for the two reservoirs investigated. Residence time of the fluid in steam-based enhanced oil recovery (EOR) is normally one to two orders of magnitude greater, a condition necessary to use the silica geothermometers successfully.

TRENDS IN RESERVOIR TEMPERATURE AND PRESSURE IN EOR

Steam-assisted thermal recovery is a common technique used to recover viscous oil from heavy oil and tar sand reservoirs throughout the world. The steam heats the oil and lowers its viscosity *in situ* so that it can flow from the reservoir to the surface. Process conditions range from 13 MPa and 330°C to surface temperatures and pressures. In highly viscous oils, the first phase of reservoir exploitation is to establish a communication path between the injection and production well. This is normally done by injecting steam and producing from the same well after a suitable soaking period; this is a process called steam stimulation, or huf'n'puf, or cyclic steam. Once the steam chests of two huf'n'puf wells intersect, a communication path is established. When this occurs, the process is changed to steam drive by placing one well on continuous production and the other on continuous injection. The steam not only acts as the heat source but also pushes the oil to the production well.

The success of a thermal EOR (enhanced oil recovery) operation depends on minimization of the amount of steam injected per unit of oil recovered and maximization of contact of steam with the oil in the reservoir. The latter is determined by a prior knowledge of the distribution of the oil in the reservoir and by actively monitoring the distribution of heat in the reservoir. Heat distribution is determined by observation wells, geophysical and geochemical monitoring. Geophysical methods include ground leveling, 3-D seismic and temperature profiling of wells, whereas geochemical methods include tracers and geothermometers

(Gunter *et al.* 1989). Geothermometers and geobarometers are the cheapest tools to implement in such a surveillance program. Geobarometers, to our knowledge, have not been developed for or applied to EOR previously.

Monitoring of temperature and pressure trends in the reservoir can be used to detect changes in the position of the steam front relative to the wells being monitored. The observed patterns are different for steam drive and for cyclic steam wells. Typically in a steam drive, the temperature and pressure vary slowly with time (a variation of approximately 12°C and 10 bars over a six-month monitoring period is typical: Fig. 9a) and show no regular trends unless injection and production are controlled by operator intervention in adjacent injection or production wells. In cyclic steam (Fig. 9b), there are well-defined patterns in temperature and pressure. When the well goes into production, the temperature and pressure steadily drop. The temperature at the sandface measured by a downhole thermocouple during production usually starts out above the reservoir temperature (as predicted by the silica geothermometer) and then drops below it as the well moves further into the production cycle (Gunter & Bird 1989). Near the end of the cycle, the temperature and pressure in the reservoir remain relatively constant. In some cases, the temperature remains constant, but the pressure increases. This pattern can usually be attributed to an adjacent well being placed on steam injection, with the accompanying pressure increase being transmitted to nearby production wells. With continued injection, some of the injected water would arrive at the production wells, and a corresponding increase in temperature would be seen. When injection is stopped and the injection well is turned around to production, the nearby wells that are already on production will experience pressure and temperature decreases. In the example of cyclic steam shown in Figure 9b, where four samples were taken over a period of four months from a production well, this process is seen. When the first sample was taken, the reservoir temperature and pressure were 181°C and 11 bars. The pressure increased to 28 bars, but the temperature dropped 4°C when injection was started in a nearby well; this was followed by a temperature increase of 5°C and a further pressure increase of 26 bars to 54 bars when some of the injected fluid reached the production well. When the injection well was turned off, the production well saw a drop in pressure and temperature to 28 bars and 178°C, as illustrated in Figure 9b. In the absence of other active injectors, this production well should revert to a normal cooling trend in the future. Such information can be combined with geochemical tracers to help assess reservoir sweep during thermally enhanced oil recovery.

CONCLUSIONS

The application of the calcite geobarometer to estimate reservoir pressures relies heavily on the establishment of equilibrium between the reservoir fluid, calcite and the mineral used as a geothermometer, and the lack of modifications in the composition of the reservoir fluid before sampling.

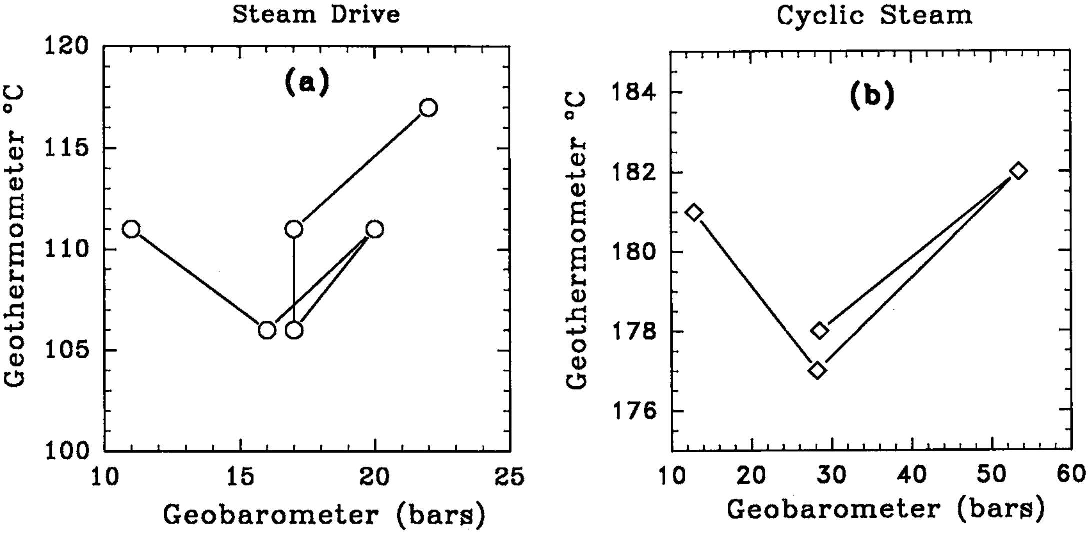

FIG. 9. Plot of reservoir temperature *versus* reservoir pressure for a) a steam-drive production well over a six-month period and b) a cyclic steam well on production (lines joining points indicate relative time of sampling). Temperatures were estimated from a silica geothermometer, and pressures, from the calcite geobarometer.

Geothermometry is suspect below 100°C owing to kinetics, and other more direct methods should be used where available. Experiments are useful to test the calibration of a specific geothermometer. Generally, geothermometers will predict the correct trends in temperature even if the absolute temperatures are in error; then they can be used to predict pressure trends through the calcite geobarometer. The slower reaction-kinetics among silicates at lower temperatures also may allow biogenically formed CO_2 or that formed from reduction of sulfate by CH_4 to be more important than CO_2 generated from decomposition of carbonate minerals. We must emphasize that the source of the CO_2 is irrelevant as long as the CO_2 formed establishes an equilibrium with calcite. The EOR examples discussed previously were from shallow reservoirs, less than 0.5 km deep; times for ascension of the fluid from the reservoir to the surface for deeper or more slowly flowing wells may allow the fluid composition to be altered significantly. Care must be taken to assess the importance of these changes, and to evaluate whether a reconstruction of the fluid composition as it exited the reservoir is possible. In the example discussed in this paper, separate gas streams and liquid streams were available for analysis; if the gas and liquid are contained in a single stream, some means must be found to take a representative sample so that the relative masses of gas and liquid can be determined. If it is known that the reservoir is gas-saturated, this restriction can be relaxed somewhat depending on the relative mass of the free gas phase.

If these conditions are met, trends in reservoir pressure and temperature can be monitored during thermally enhanced oil recovery by estimation of reservoir pressures and temperatures for gas-saturated reservoirs by a combination of the calcite geobarometer (calcite must be present in the reservoir), a detailed chemical analysis of the produced water from the reservoir, and a silica geothermometer to estimate reservoir temperature. In cases where complete data are not available for such an analysis, some limits may be calculated. In reservoirs that do not contain calcite, a minimum reservoir pressure may be estimated by assuming calcite equilibrium. The presence or absence of a separate gas phase in calcite-containing reservoirs can be determined, if one assumes calcite equilibrium at the reservoir temperature, from a knowledge of the composition of the water produced from the reservoir, the composition of the annulus gas and the ratio of annulus gas produced relative to produced liquids. If a separate gas phase is present in calcite-containing reservoirs, and the reservoir pressure and the chemistry of the produced water are known, the composition of the gas can be determined by assuming calcite equilibrium at the reservoir temperature.

Other applications need testing. Different carbonate minerals (*e.g.*, siderite, dolomite, ankerite or any combination thereof) may control the CO_2 equilibria in other reservoirs. The equilibrium relationships may be calculated if data are available or established by experiment. In sour gas reservoirs, H_2S dominates the gas fraction, but these reservoirs also are a target for use of the carbonate geobarometer. More general applications of carbonate geobarometers throughout geothermal or sedimentary basins may be possible. The calcite geobarometer has been shown to be useful here for thermal EOR; potentially it may have a much broader value in helping to define physical conditions within the earth's crust.

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