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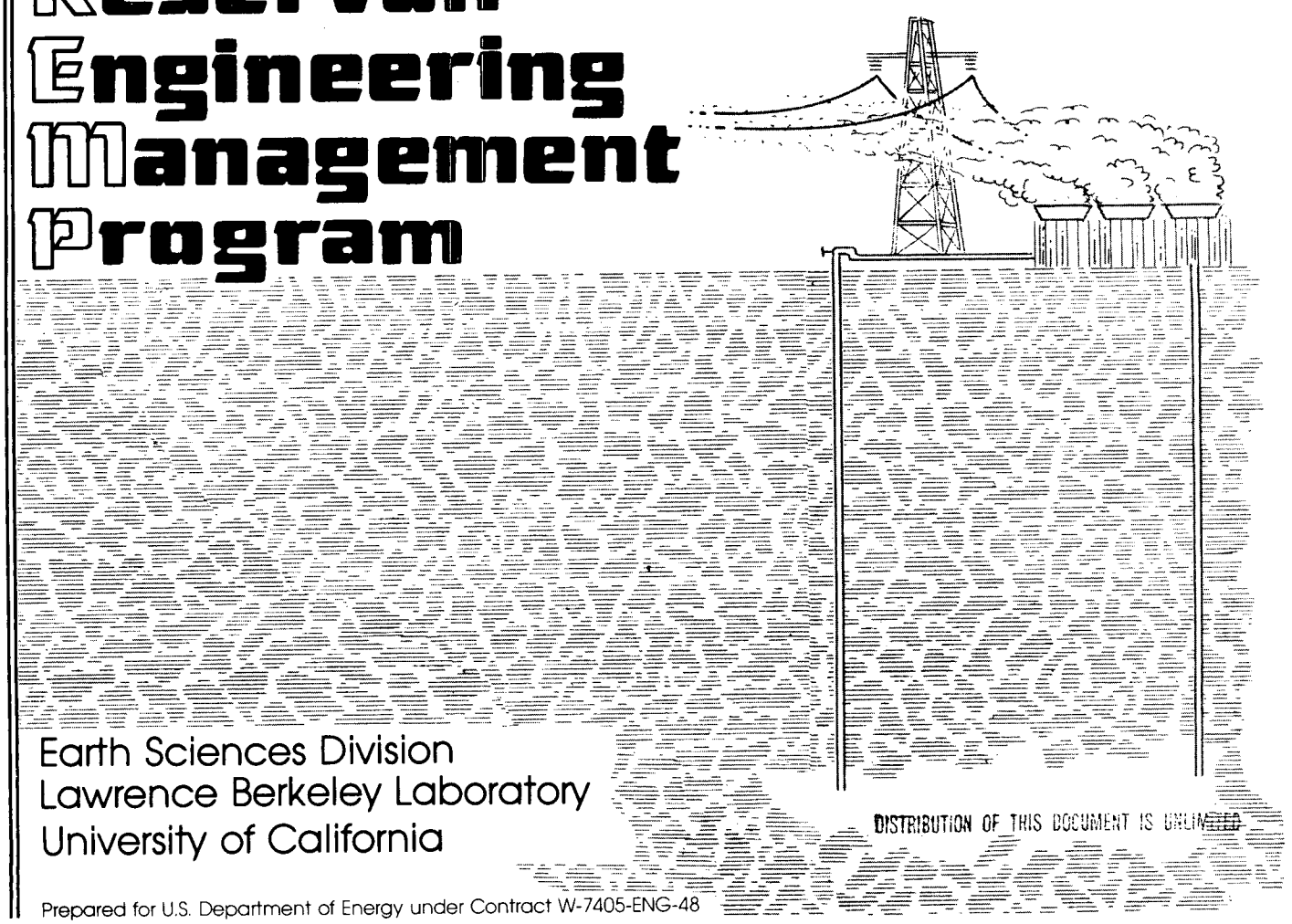
# $CO_2$ and Carbonate Chemistry Applied to Geothermal Engineering

Donald E. Michels
Republic Geothermal, Inc.

January 1981

**Geothermal Reservoir Engineering Management Program**



Earth Sciences Division
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# $CO_2$ AND CARBONATE CHEMISTRY APPLIED TO GEOTHERMAL ENGINEERING

## Guidance for interpreting and using chemical data about geothermal resources

January 1981

By
Donald E. Michels

Submitted to
Lawrence Berkeley Laboratory
under the
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Order No. 4555402

By

Republic Geothermal, Inc.
11823 E. Slauson Avenue
Santa Fe Springs, California 90670

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## SUMMARY

The geothermal resource has several attributes that are outside the scope of older industries and scientific/technical disciplines. Although many chemical approaches give insight about geothermal resources, engineering development of geothermal resources will be better served through a chemical philosophy that focuses squarely on factors that are uniquely geothermal. It is hoped that through this report, those factors and their uniqueness will become better understood and more broadly recognized.

The flashing of steam from geothermal liquids initiates an assortment of chemical reactions. In the resource discovery stage these reactions must be understood in order that geochemists may accurately interpret the analytical data about steam and residual liquid issuing from test wells. In the development stage, characteristics of the pre-flash liquid and its responses at different stages of flashing must be known to the engineers who are making and evaluating alternative designs for wellbores and plants which might use the resource. This report treats both, but aims especially at the engineer's use of data about the resource. The chemistry of high-$HCO_3$ resources is emphasized because they present special complications about data interpretation, development of vapor, and potential for scale deposition.

Solubility of $CO_2$ and its exsolution from liquids is treated according to the unique context presented by geothermal resources. Contrasts between this approach and the treatment of $CO_2$ solubility in physical chemistry and other geochemical contexts are presented. Dimensional units for solubility coefficients different from those of physical chemists are presented to favor engineering applications. The effects of $CO_2$ on wellbore flow, initiation of flashing, and depth of the 2-phase zone are described and illustrated with examples.

A substantial redistribution of dissolved components occurs upon flashing, of which scale deposition is only one aspect. Knowledge about the entire web of chemical reactions is shown to be valuable for interpreting the analytical data obtained from common field samples of vapor and liquid, and specially preserved samples of each. Reconstruction of (characteristics of) the pre-flash fluid is a principal goal of the geochemist. This requires a thorough review of the reaction web, tailored to each field sampling.

The field samples provide (generally) only one circumstance of fluid behavior upon flashing, whereas a range of circumstances can be set up in engineered hardware. The design engineer can manipulate, to a degree, the chemical response of the fluid. More importantly, in many ways he must adapt his equipment to fit the chemical processes in which the fluids participate. To aid the understanding of fluid behavior and the interplay with the design process, specially constructed charts -- chemical maps -- are presented, examples given for their use, and directions given for their construction.

Besides $CO_2(g)$, other gases are present, commonly $N_2$, $CH_4$, and others. These are sometimes as important as $CO_2$ for settling designs of downhole pumps and selecting the depths to which they are set. Because these non-$CO_2$ gases are less soluble than $CO_2$ by factors near 20, their effects on flash initiation (bubble point) are much larger than their compositional proportions.



## ACKNOWLEDGEMENTS

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## I. INTRODUCTION

The design engineer uses a mathematical model of the fluid; the geochemist must build a suitable model based on the chemical data yielded from early testing of wells [reservoirs]. This report aims to present these aspects of carbonate chemistry so that the engineering can be better focused on the design requirements a specific resource presents.

The principles of physical chemistry apply throughout. Yet it is useful to point to the different contexts used by the physical chemists who developed the relevant theory, and the geochemists who apply that theory in sampling and describing a geothermal resource. In the simplest form, the contrast is this: the physical chemist describes a static (or microscopically reversible) system that has a definite temperature, pressure, and composition, whereas the geochemist samples (and the engineer designs for) a PROCESS in which temperature and pressure may change by hundreds of units per minute and components execute a variety of irreversible chemical reactions. Although it is a truism that both SYSTEM and PROCESS must obey the same laws of chemistry, it does not follow that the same mathematical expression of those laws is equally convenient or appropriate for both circumstances.

One approach to this problem of adapting concepts of chemical equilibrium to geothermal processes utilizes high speed computers to calculate a new equilibrium situation for small increments of change. Since circumstances in geothermal exploitation seldom reach chemical equilibrium, a "finite differences" approach becomes useful only in a qualitative way, despite its quantitative heritage and numerical output. Because the outputs are digital, the results do not inspire an intuitive sense for the processes it models, making difficult the task of optimizing tradeoffs in the engineering sense.

With those problems in mind, this report has been aimed also at developing an intuition for the behavior of $CO_2$ and carbonate chemistry. This intuition is to be applied to the context of what may be called geothermal dynamics, emphasizing that PROCESSES, more than chemical SYSTEMS or events, are the objective for understanding.

A modest problem in communication may exist for persons who have become familiar with the terminology and approaches used in water treatment for boiler scale and similar contexts wherein $CaCO_3$ deposits from heated water. Terms like alkalinity, total $CO_2$ and hardness turn out not to be useful in describing geothermally deposited $CaCO_3$ or the waters which carry the components. Additionally, the analytical chemistry of carbonate systems has a traditional jargon that obscures important differences among gaseous $CO_2$, dissolved $CO_2$, $H_2CO_3$, $HCO_3^-$, and $CO_3^=$. Especially tradition does not distinguish between $CO_2$ (aqueous) and $H_2CO_3$ whereas the distinction is mandatory when dealing with deposition processes of geothermal $CaCO_3$ which are only linked to (not caused by) massive losses of $CO_2(aq)$ from a flashing liquid. It is also mandatory when combining the results of several component analyses of flashed liquid and vapor into a "mathematical pre-flash liquid," the most important task of the geothermal chemist.

The principles and techniques given in this report are not appropriate for all geothermal systems or problems of geothermal scale. They apply best to those geothermal resources wherein calcium concentration is subordinate to bicarbonate and wherein pH is controlled by carbonate equilibria. The type example where this approach applies is the East Mesa field of the Imperial Valley, California. Two features of a geothermal resource should be checked before applying concepts of this report to it. The ratio of $Ca/HCO_3$ concentrations in geothermal resources ranges from ca. 0.01 to ca. 300. This report applies best to those in which $Ca/HCO_3$ is smaller than 0.5. Furthermore, the pH's of geothermal liquids may be controlled by carbonate equilibrium or by silica/silicate equilibria, or some other. This report applies fully to those systems wherein pH is controlled by carbonate equilibria.

Happily, the behavior of $CO_2(g)$ and $CO_2(aq)$ in geothermal systems is not so complicated as the $CaCO_3$ scale potential. The description of $CO_2$ behavior given here does apply to all geothermal systems, being even less complicated where bicarbonate is scarce and pH is controlled by equilibria other than carbonate.

$CO_2$ provides an important component to the total vapor pressure of geothermal fluid before steam flashes from it. Accurate interpretation of temperature and pressure surveys of flowing wells cannot be made without considering that. Furthermore, wellbore design for flash-flowing wells and specifications for downhole pumps must allow for this effect of $CO_2$. The pressure component due to $CO_2$ ranges greatly between reservoirs, and somewhat between individual wells within a reservoir. For example, at East Mesa the $CO_2$ pressure is ca. 35± 20 psi, whereas in the Niland field it generally exceeds 300 psi and may exceed 1,000.

The organization of this report begins with the interactions of $CO_2$ and water, leading through the effect of $CO_2$ on solubility of $CaCO_3$. Concepts about the redistribution of components, including scale deposition that occurs upon flashing, is the heart of this report. Following that are steps for making a mathematical reconstruction of the pre-flash liquid, based on post-flash analytical data. This might be viewed as a quantitative inversion of the processes of redistribution involved with flashing.

Two conceptual approaches are used here, one common to geological problems; the other to the physical sciences. The geological view is

basically historical, accepting the data as they appear, then asking the question, "What must have been true in the past in order that the processes have yielded what we now measure?" It is that point of view which yields the mathematically reconstructed pre-flash liquid.

On the other hand, an engineer who draws on the physical science approaches asks the inverse question, "Beginning with the pre-flash liquid, what processes and equipment are needed to efficiently recover the energy while minimizing complications and costs due to other reactions the fluid could participate in?" and "What reactions can be avoided or accommodated by engineering design?"

The difference in these points of view is not trivial, and many people who are very good at one of them are quite uncomfortable with the other. Mainly for this reason it is inefficient to use raw chemical data for post-flash gases and liquids when designing wells, pumps, and power plants. Test conditions are not equivalent to plant conditions; hence, test data are only indirectly relevant. Their maximum utility is gained through the intermediary of the mathematical pre-flash liquid which, also mathematically, is to be used for evaluating alternative engineering designs.

Descriptions of the processes must be communicated, in both qualitative and quantitative modes. A system of charts called chemical maps is presented which allows one to keep track simultaneously of the many variable factors that relate to carbonate equilibria. Additionally, these charts permit the consideration of non-equilibrium processes. Good design of engineered geothermal facilities will depend much on the intuition of the designer, partly because each geothermal field presents distinctive complications for development. The chemical maps are presented as a means for helping develop these necessary intuitions.

Lastly, worked example problems are presented to show application of these concepts to the geothermal context of wellbore flow and optimization of power plant designs.

## II. $CO_2$ IN WATER, SALT SOLUTIONS, AND GEOTHERMAL FLUIDS

### A. Hydration of $CO_2$

Making a clear distinction between the linear structure of $CO_2$ molecules and the trigonal-planar structures of $H_2CO_3$, $HCO_3$, and $CO_3$ (Figure 1) is important for understanding their chemical behavior. Conversion between the linear and trigonal-planar forms obviously involves major structural changes. The linear-to-trigonal conversion is slow compared to most inorganic reactions, including its inverse, the trigonal-to-linear conversion. Hydration of $CO_2$, the linear-to-trigonal conversion, can occur by reaction sequence 1, 2. About 3% of the available $CO_2$ converts via eq (1) per second at 70°F, (Kern, 1960), and is faster at higher temperatures.

$$CO_2 + H_2O \rightarrow H_2CO_3 \text{ (slow)} \quad (1)$$

$$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O \text{ (instantaneous)} \quad (2)$$

Hydration can also occur by reactions 3, 4 (Kern, 1960).

$$CO_2 + OH^- \rightarrow HCO_3^- \text{ (fast)} \quad (3)$$

$$HCO_3^- + OH^- \rightarrow CO_3^= + H_2O \text{ (instantaneous)} \quad (4)$$

The sequence (3 + 4) predominates above pH 10. In neutral and acid solutions, the population of $OH^-$ is too low for reaction 3 to be significant.

The dehydration, or trigonal-to-linear conversion, can occur by (5).

$$H_2CO_3 \rightarrow H_2O + CO_2 \quad (5)$$

Reaction (5) is much more rapid than (1) with the result that the linear form of dissolved $CO_2$ [hereafter called $CO_2(aq)$] is much more abundant in solutions than the trigonal-planar $H_2CO_3$. The ratio, $CO_2$ (aq)/$H_2CO_3$, has a value near 600 at 70°F, as indicated by the ratio of rate constants described by Kern (1960).

The $H_2CO_3$ form is relatively scarce in solutions in all circumstances. Unfortunately, most chemical analyses do not distinguish between $CO_2(aq)$ and $H_2CO_3$. It has become conventional for chemists to report dissolved, linear $CO_2(aq)$ as if it were trigonal-planar $H_2CO_3$. Furthermore, reported dissociation constants for $H_2CO_3$ are smaller than the true dissociation constants, approximately by the factor 600 above, and its counterparts at higher temperatures. This is because the $H^+$ in the measured solutions came from a much smaller (true) population of $H_2CO_3$ than the convention recognizes.

No serious calculational problem develops from this so long as all calculations made concern just the dissolved species, as noted by Garrels and Christ (1965). However, when one considers also the processes of flashing, $CO_2$ exhalation from the liquid, Henry's law solubility/pressure of $CO_2$, and a few reactions of $HCO_3$, the distinction between $CO_2(aq)$ and $H_2CO_3$ becomes important. Only the linear form participates in the sensible pressure of $CO_2$ in the solubility relationship of Henry's law. The trigonal-planar forms have no measurable vapor pressure.

In alkaline solutions, breakup of the trigonal-planar form can occur by reaction (6)

**FIGURE 1**
**STRUCTURAL COMPARISONS**

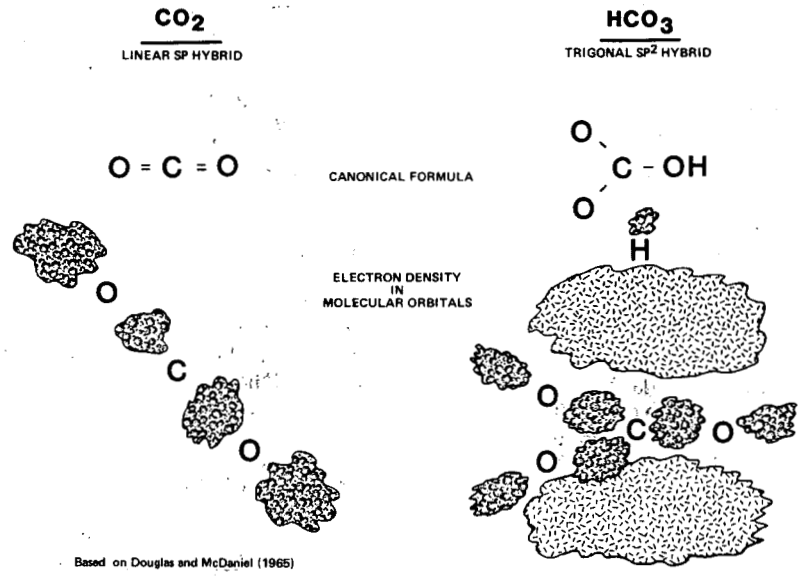



FIGURE 1: Electrons are the glue that holds atomic nuclei into molecular structures. Each nucleus has a definite set of orbitals wherein the electrons can reside. Molecular structures result from the simultaneous accommodation of bonding electrons into the orbitals of two or more nuclei. As a consequence, molecular structures tend to be geometrically simple, fairly symmetrical, and structurally resiliant. Describing the 3-dimensional structures with simple 2-dimensional diagrams can be misleading, as is the canonical formula above. Actually, the H in $HCO_3$ is outside the plane of the $CO_3$, opposite the central C nucleus and not associated with just a single O nucleus. The second H in $H_2CO_3$ is located symmetrically on the opposite side of the $CO_3$ plane beyond the $\pi$-electron cloud. The perspective view of the electron density distribution shows the general locations of the bonding electrons and nuclei in $CO_2$ and $HCO_3$. Conversion of one structure to another requires major alteration of electron arrangements, giving a morphologic sense for the kinetics reviewed by Kern (1960).

$$2HCO_3^- \rightarrow H_2O + CO_2 + CO_3^= \qquad (6)$$

which is mechanically different from the sequence indicated by (7, 8)

$$HCO_3^- \rightarrow OH^- + CO_2 \qquad (7)$$

$$OH^- + HCO_3^- \rightarrow H_2O + CO_3^= \qquad (8)$$

Reaction (6) would be predicted to have second order kinetics which are reported by Shukla and Datar (1972). Sequence (7, 8) would show first order kinetics because (7) is essentially a spontaneous fission.

## B. Henry's Law Solubility of $CO_2$

Geothermal exploitation begins with a static $CO_2$-charged liquid with no vapor phase. The dissolved $CO_2$ contributes to the vapor pressure of the liquid and, upon the flashing of steam, the $CO_2$ pressure and the total pressure are markedly and quickly reduced, as is the temperature. The purpose of this section is to show how the data and models of laboratory investigations on static systems can be applied to the conditions of geothermal developments, including the explosive context of flashing superheated brine.

In this regard it is useful to recognize the different points of view between the physical chemist and the geothermalist. A physical chemist's view of a gas-liquid system commonly focuses on the gas pressure over a static liquid and the amount of gas which enters the liquid phase. Contrastingly, the geothermal system is most often measured after flashing has progressed substantially. The geochemist aims to reconstruct the pre-flash (one-phase liquid) conditions of pressures and $CO_2$ concentrations.

The amount of $CO_2$ which is present in a water solution at equilibrium is remarkably proportional to the partial pressure of the $CO_2$ which contacts the solution. The proportionality is experimentally linear (Ellis and Golding, 1963) when the solubility coefficient is expressed as the ratio of $CO_2$ fugacity (effectively ideal gas pressure) to mole fraction of $CO_2$ in the solution. Those units are awkward for engineering purposes, both because of their unfamiliarity and the extra effort required to find and use fugacity coefficients and total compositions of the fluids. Fortunately, throughout the range of conditions in geothermal developments, simpler, more intuitive units are practical, specifically psia/ppm where the psia refers to the $CO_2$ partial pressure in units of pounds per square inch absolute and the ppm to parts of $CO_2$ by weight per million parts of solution. Uncertainty in calculations due to using these simplified units is small since the fugacity coefficient for $CO_2$ is about 0.98 ± .04 over the exploitable range of geothermal conditions.

Solubility coefficients reported by different workers are out of agreement by a few to several percent, amounts that generally are larger than the differences between pressure and fugacity. Furthermore, in a real geothermal field a range of $CO_2$ contents will be observed across it, perhaps greater than a factor of 2. The engineering design must accommodate this larger range. Thus, the practical context suppresses the significance of malagreement among laboratory data and the inexact parallelism between the units used by the physical chemist and those used here.

Figure 2 shows the $CO_2$ solubilities listed in several references and reduced to the same units. Both pure water and NaCl solutions are involved. The solubility equation (9) applies, in which P represents measurable pressure of $CO_2$, C is concentration of the linear molecules, and the solubility coefficient, h, has the units of psia/ppm.

$$P = Ch \qquad (9)$$

The data of Ellis and Golding (1963) are preferred by me. They are presented alone in Figure 3, as a response surface map in which isopleths of psia/ppm are drawn in a field of temperature and NaCl content. Figure 3 can form one basis for an engineering evaluation of the $CO_2$ in a geothermal fluid.

## C. $CO_2$ in Geothermal Fluids

It is important to carry a concept of $CO_2$ gas pressure inside the liquid phase, especially when no bubbles of $CO_2$-rich vapor are present. Hydrostatic pressures in geothermal liquid reservoirs preclude the presence of any vapor. Yet, this calculable vapor pressure becomes physically expressed when the fluid passes up a wellbore to where flashing begins.

The system pressure at the initial flash point is a sum due to all the volatile components in the liquid. Mainly these are $H_2O$ and $CO_2$. Other materials, especially $N_2$, $CH_4$, and Ar, contribute according to their respective Henry's Law relationships. Each can be considered separately, and the calculated total vapor pressure of the system is the sum of all the separately calculated pressures, plus $H_2O$. $CO_2$ often dominates the suite of volatile gases in terms of amounts present. Often those other gases are ignored. Much care should be exercised when deciding to ignore the non-$CO_2$ gases because most have much higher Henry's Law pressures per ppm. A method of using data for them is presented in a later section. Their Henry's Law pressure coefficients are shown in Figure 4.

**FIGURE 2**
**PRESSURE CONCENTRATION FOR $CO_2$ VS TEMPERATURE AND NaCl CONTENT**

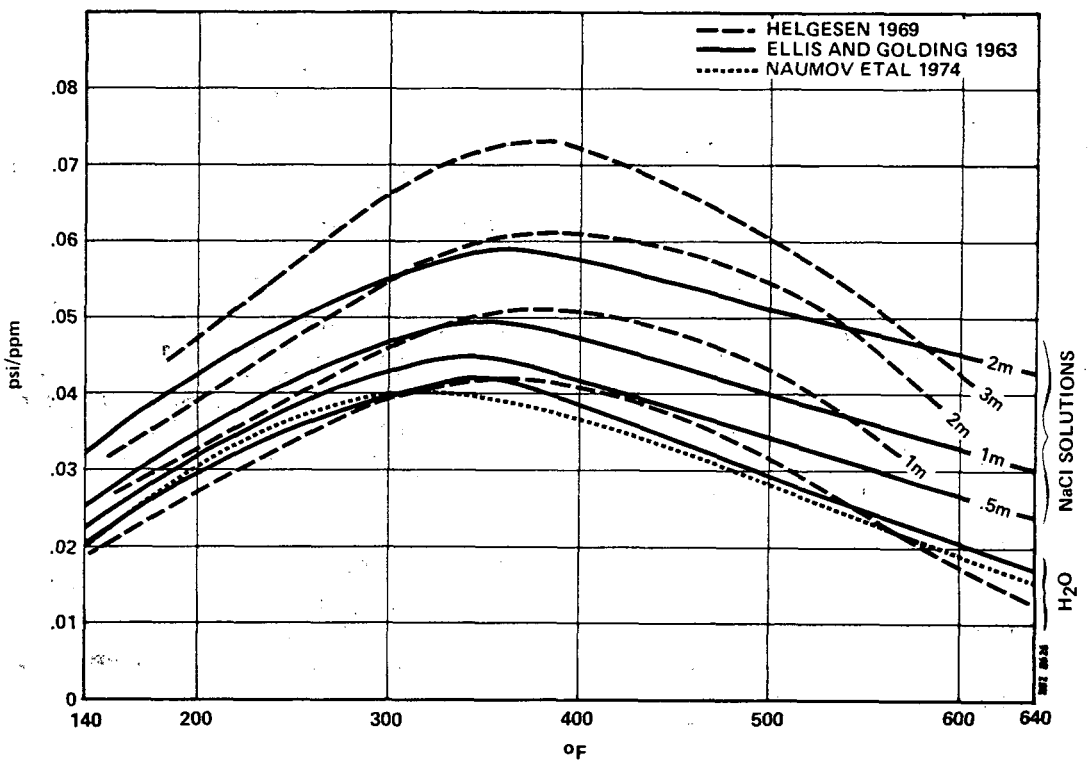


FIGURE 3. RESPONSE SURFACE MAP-
PRESSURE OF $CO_2$ (aq) VS TEMPERATURE AND SALT CONTENT.
UNITS ARE PSI PER 1000 ppm $CO_2$(aq). Based on Ellis and Golding, 1963.

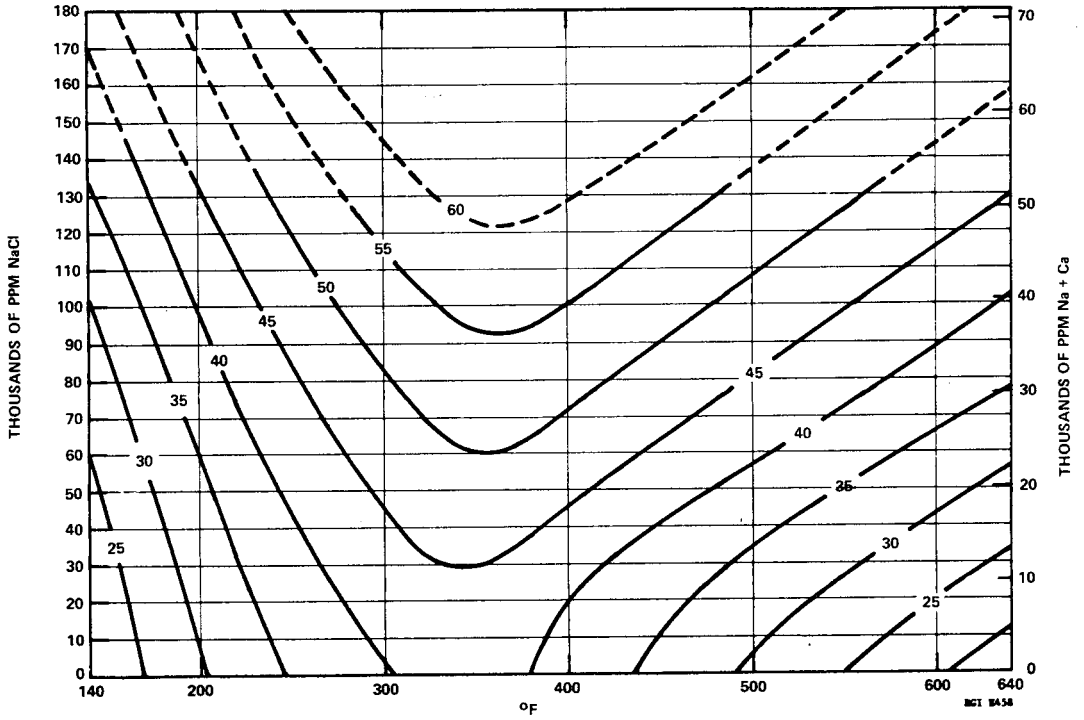
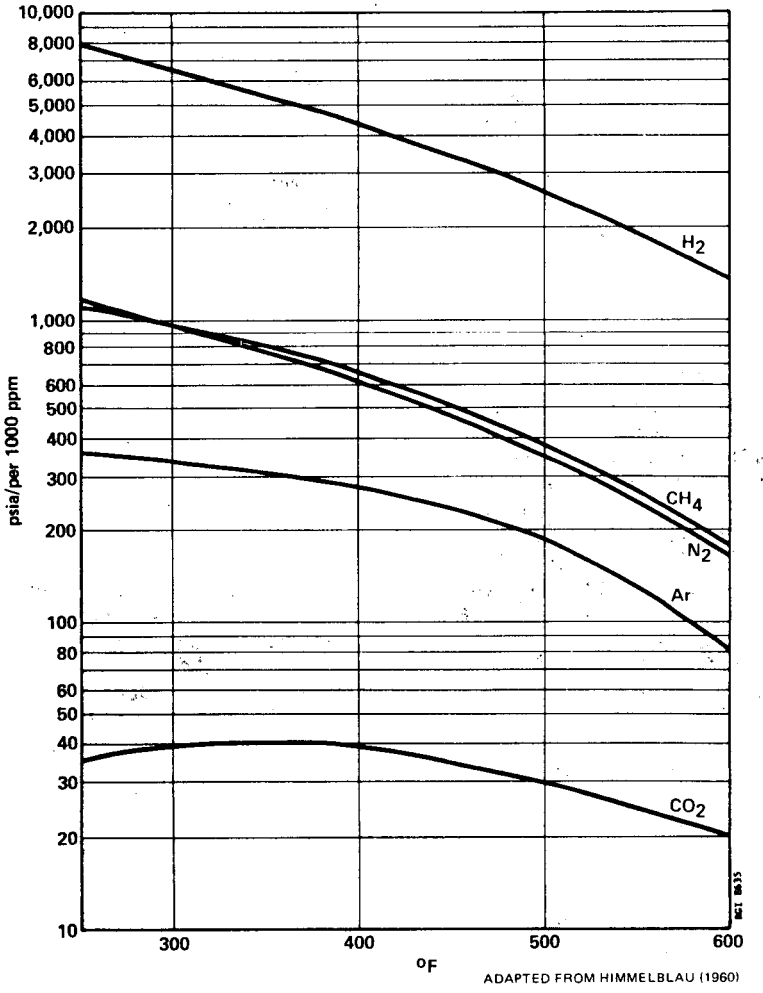


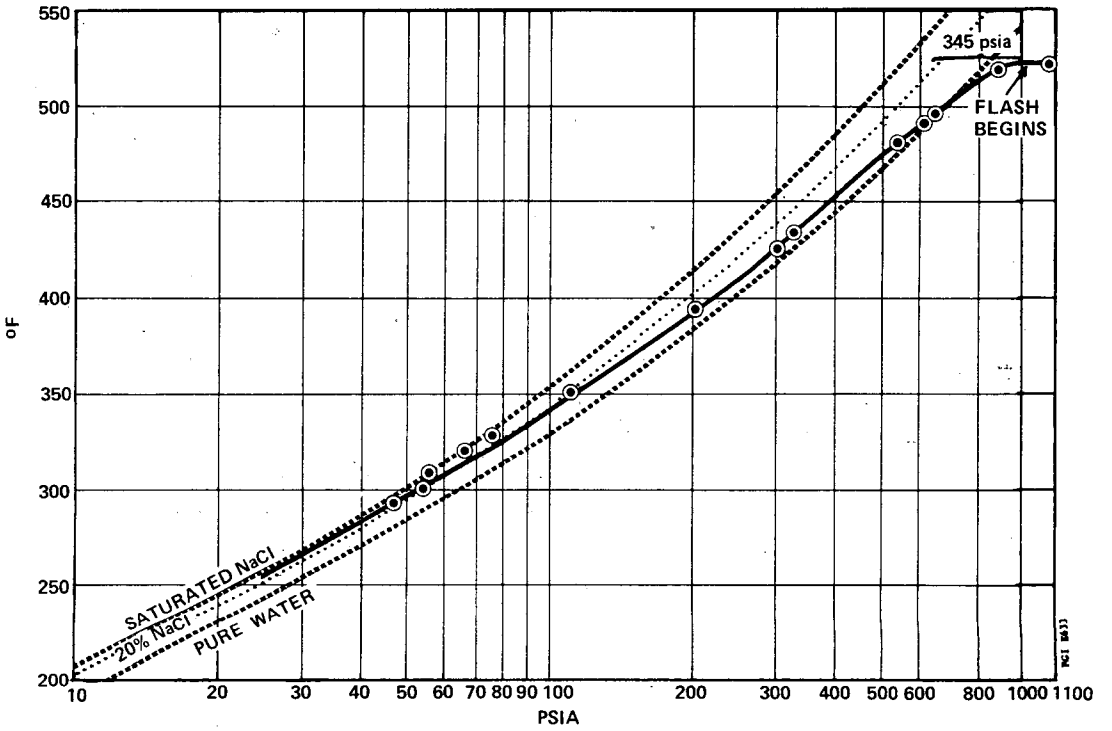

FIGURE 4. HENRY'S LAW PRESSURE COEFFICIENTS




ADAPTED FROM HIMMELBLAU (1960)

FIGURE 5

VAPOR PRESSURE CURVE
NILAND - CLASS WELL




During flashing a vapor phase develops and its composition depends on the composition of the pre-flash liquid. Usually, water vapor is the most abundant component of the gas phase even at low percentages of steam flash. Furthermore, water becomes an increasingly significant component of the vapor as flashing progresses and the total pressure of the system will approach the vapor pressure for water or brine as given in tables.

Figure 5 shows this effect for pressure-temperature measurements in a production system for a well of the Niland KGRA. The pre-flash pressure of $CO_2$ is estimated to be 345 psia, based on the $H_2O$ vapor pressure being initially that of a 22% NaCl solution, an expedient approximation. This figure results from pressure and temperature measurements made at several places in the wellbore and surface equipment during a test flowing of the well. The data show the vapor pressure curve for the flashing liquid. Note that the vapor pressure curves for pure water or for $CO_2$-free salt solutions are not good approximations of the P-T relationships, except at conditions of well-developed flash.

The $CO_2$ pressure in the vapor phase diminishes from its initial value as flashing progresses. Most of the mass of $CO_2$ is exsolved in the first few weight percent of flashing. It becomes increasingly diluted as the volume of the vapor phase is expanded jointly by increments of freshly flashed $H_2O$ and expansion of "old" vapor due to lower pressures.

In the range of conditions relevant to geothermal engineering, the pressures of $H_2O$ and $CO_2$ are additive (Ellis, 1959) without need for adjustments due to details of the physical chemistry. This leads to the rather remarkable chart, Figure 6, in which the $CO_2$ pressure in a developing vapor phase can be expressed as a function of three factors, namely its initial pressure, the present temperature (or $H_2O$ vapor pressure) of the system, and the weight percent of flashing that has developed. The mathematical development is given in section IV D 3.

Comparing Figures 5 and 6 is instructive because they are complementary views of the same phenomenon.

D. Effect of $CO_2$ Pressure on Initiation of 2-Phase Flow

Presence of $CO_2$ causes the transition between 1-phase and 2-phase flow to happen deeper in the wellbore than one would expect by ignoring the $CO_2$. The position of the point of flashing depends also on the density of the liquid which, for approximations, can be taken as 2.5 feet of depth per psia of $CO_2$.

Some geothermal fields have substantial $CO_2$ contents that have large effects on the depth in a wellbore where 2-phase flow begins. Table 1 shows some comparative numbers.

FIGURE 6

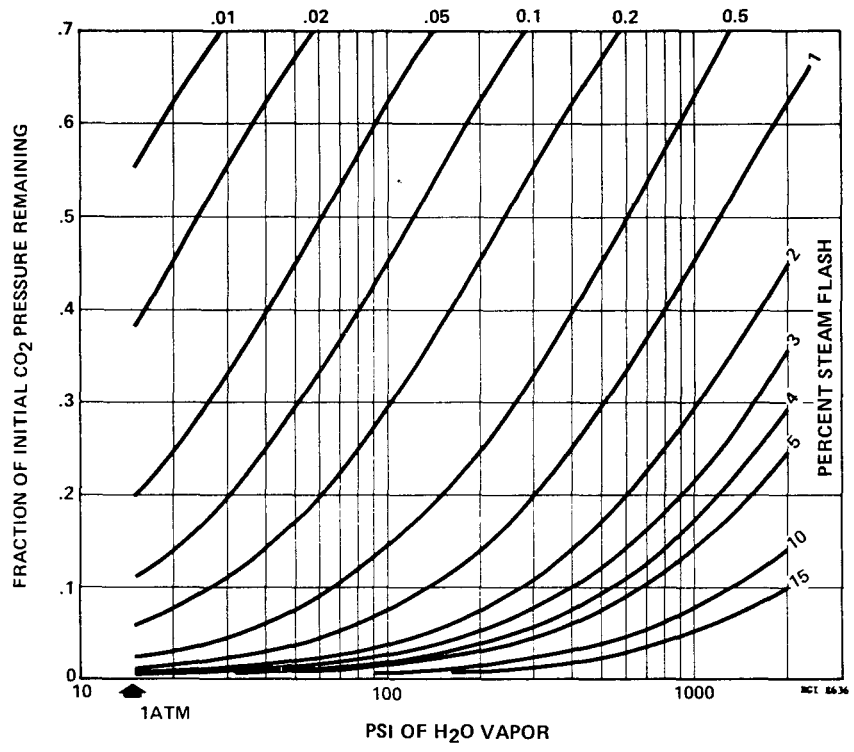



Table 1

$CO_2$ CONTENTS AND PRESSURES IN SELECTED GEOTHERMAL FIELDS

| Field | Pre-flash $CO_2$ ppm | Approx. Temp °F | Pre-flash Salt Content | $CO_2$ psia | Wellbore Effect |
|---|---|---|---|---|---|
| Broadlands | 5,000 | 500 | 4,500 ppm | 120-200 | 300-500' |
| Wairakei | 430 | 500 | 4,300 | 14 | 35' |
| Kizildere | 16,000 | 390 | 4,500 | 640 | 1,600' |
| East Mesa | 400-1,000 | 320-360 | 2,000-6,000 | 16-50 | 40-130' |
| Niland | 6,000-20,000 | 570-640 | 200,000+ | 350-1,400 | 900-3,500' |
| Roosevelt | 4,000-8,000 | 480-500 | 6,500 | 140-300 | 350-750' |

The right-hand column of Table 1 shows the extra length of 2-phase flow that can be called an effect of $CO_2$. This effect can propagate into requirements for larger well casings than a $CO_2$-free situation would require. The engineering selection of casings for geothermal wells depends on the expected/required production of the well. The dynamics of 2-phase flow can limit the output of small-diameter wells and longer runs of 2-phase are more serious. Selecting too small a casing makes a well uneconomic regarding its rate of payout, even if well-located in a productive reservoir.

In some situations geothermal fluid may flash in the rocks before entering the wellbore. The $CO_2$ promotes this effect. Several subsidiary effects derive from this. Whether flashing within the reservoir is advantageous must be decided on a case-by-case basis. Some factors to consider are:

1. Is $CaCO_3$ scale deposition a serious accompaniment to the exsolution of $CO_2$?

2. $CO_2$ content of steam from a matrix-flash context would diminish as the production continued.

3. What are the consequences for wellhead pressures and pressure requirements for hardware in the surface installation?

## E. Effect of $CO_2$ on the Solubility of $CaCO_3$

The practical difference between the viewpoints of the field and the laboratory has a striking significance to this topic. Nearly all published treatments of calcite solubility repeat a 1929 derivation by Frear and Johnston wherein the calcium concentration is found to be proportional to the cube root of the $CO_2(g)$ pressure. Yet, that proportionality seldom occurs in geothermal contexts. Because that purported relationship has become widely published, and because its limited range of applicability is not discussed elsewhere, an elaboration here is worthwhile.

The origin of the cube root proportionality begins with a laboratory context: a system of calcite, water, and $CO_2$ wherein equilibrium is approached through dissolving the calcite. Upon writing the several chemical equations which describe the formation of carbonic acid and the development of a calcium bicarbonate solution, one may note that the solution holds calcium and bicarbonate ions in the molar ratio of 1:2. That proportion allows the substitution of Ca concentration for bicarbonate activities in the mathematical equilibria. Algebra then yields the cube root relationship between $CO_2$ pressure and calcium concentration.

Geothermal solutions are generally far from a 1:2 ratio of $Ca:HCO_3$, hence the algebraic substitution above is seldom appropriate, if ever. Furthermore, for a disturbed geothermal fluid, equilibrium is approached through deposition of $CaCO_3$, which tends to distort the $Ca/HCO_3$ ratio even more.

The true relationship between $CO_2$ pressure and Ca concentration upon flashing depends on the resource. For example, where $HCO_3 >> Ca$, as at East Mesa where (molar) $HCO_3:Ca$ is 35:1, the Ca concentration is proportional to the first power of the $CO_2$ pressure. Contrastingly, in the Salton Sea KGRA where $HCO_3:Ca$ is near 1:450, the calcium concentration is independent of the $CO_2$ pressure.

Large computer models of geothermal chemical equilibria which use the basic equations for carbonate reactions without the cube root simplification would not suffer from the algebraic shortcut described above. However, some smaller privately held calculational models do incorporate the inappropriate cube root relationship. Users should be wary also about forecasts of scale deposition or related calculations.

## F. Example Calculations

### 1. Measurements and Conversions

In a test of a geothermal well, flashing occurred in the wellbore and steam/water separation was made at the surface. Sampling the steam off the separator yielded a $CO_2$ content of 1.2%.

Question: If steam comprised 14% of the produced fluid at the point of sampling, what was the $CO_2$ content before flash in units of ppm?

Answer: Virtually all the available $CO_2$ will follow the steam phase, which comprises only 14/100 of the pre-flash liquid; 1.2% is 12,000 ppm. Pre-flash concentration is:
(12,000)(0.14) = 1,680 ppm.

This value may be used as a first approximation of the pre-flash content of $CO_2(aq)$. It may be necessary to make adjustments for three chemical phenomena described in subsequent sections: breakup of $HCO_3$, deposition of $CaCO_3$, and analytical interference by ammonia. However, these adjustments partly are self-compensating. A first approximation such as this one is not likely to be in error by more than 15% (relative), providing the $CO_2$ analysis and percent flash are accurately stated.

Question: What is the $CO_2$ pressure before flashing if the post-flash total dissolved solids (TDS) in the liquid (mainly NaCl) is 94,000 ppm and a pre-flash temperature of 480°F was measured downhole in 1-phase liquid during the test?

Answer: Find the pre-flash TDS, then use it, T=480° and results from question 1 to enter Figure 3.

Pre-flash TDS is (94,000)(1 - .14) = 80,800 ppm; 8.1%.

In the absense of more detailed information about the fluid's cooling in the wellbore during transit, use the 480° to enter Figure 3 and find 46.2 psi per 1000 ppm $CO_2$;

$CO_2$ partial pressure is
(1680/1000) (46.2) = 77.6 psia.

Question: What is the total vapor pressure of the pre-flash fluid?

Answer: Pure water has a vapor pressure of 566 psia at 480°F. The presence of salt depresses this. Interpolation of tables given in Haas (1976) yields 536 psia for 8.1% NaCl at 480°. $CO_2$ pressure is in addition to this; total vapor pressure is 536 + 78 = 614 psia. [Note: This excludes effects of non-$CO_2$ gases.]

For comparison, note that this vapor pressure is the same as pure water at 489°F or a $CO_2$-free solution of NaCl (8.1%) at 495°F.

# III. REDISTRIBUTIONS OF COMPONENTS UPON THE FLASHING OF STEAM

## A. Processes vs. Events

The concept of flashing steam from geothermal fluid commonly focuses on the change of phase that $H_2O$ undergoes. There are several concomitant processes (not to be considered as events) that occur in the same general interval of time. Each process involves a rate of change, but their starting times, times of peak activity, and endings are not simultaneous. One aim of this section is to present the flashing as a mix of processes that are linked to one another, yet are describable as individual processes.

This point of view is intended to contrast with the more common approach to this topic which considers the processes as events. Processes are treated as events when one compares the final conditions of the system with the initial conditions, irrespective of time, timing, or atomic scale mechanism. Failure of an event to lead to the thermodynamically most stable state then acquires some sense of mystery.

However, when one considers the chemical reactions as processes for which several circumstances and linkages must be favorable, including transport and orientation of ions, it quickly becomes evident that the only

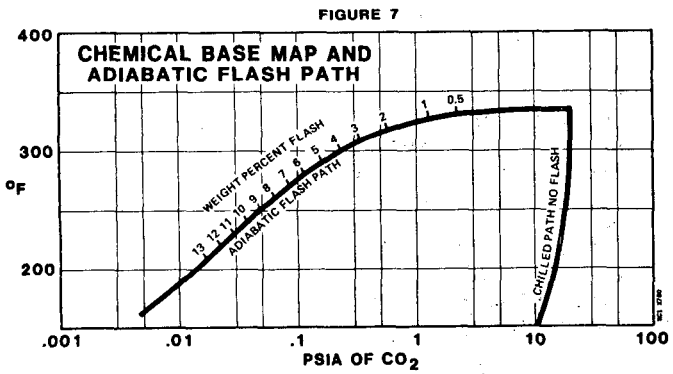
thermodynamic requirement concerns the First Law. There must be a net loss of free energy to drive a reaction, but mechanisms may not operate which would maximize the free energy loss. Other functional mechanisms often do operate to relieve the chemical supersaturations. It may even be possible to identify mechanistic hurdles through chemical inferences. It is hoped that this point of view will remove some of the mystery about why disturbed geochemical systems generally fail to reach equilibrium. It also is hoped that this approach will help lead to an intuitive understanding of the chemical system needed to make engineered solutions to geothermal problems.

B. A Chemical Base Map

The most profound changes in a flashing system involve the temperature and total pressure. Yet, the component of total pressure due to water vapor depends mainly on the temperature and only slightly on the changing salt concentration due to the flashing. Thus, the temperature data alone imply almost all one needs to know about the $H_2O$ component of the system. Furthermore, since the $H_2O$ vapor pressure usually dominates the total pressure, most knowledge about the total pressure is redundant with the temperature; hence, using both is not an efficient description of a flashing system. Thus, the pressure of $H_2O$ will not be used here as a dimension (descriptor) of the system.

This simplification allows the use of the pressure dimension for just the non-$H_2O$ components. The most important of these is $CO_2$ and the axes of the chemical base map are selected as temperature and pressure of $CO_2$ (Figure 7). Important to this concept is the clear specification that the $CO_2$ pressure intended is not a sensible pressure in the vapor phase, but rather the calculable Henry's Law pressure due to the $CO_2$(aq) in the liquid as expressed in eq (9). This

FIGURE 7




specification does two things: (1) it focuses attention on the liquid phase wherein the important chemical reactions occur, some of which lead to scale deposits, and (2) it enables one to consider the liquid phase irrespective of whether a vapor phase is present or whether the liquid and vapor are in equilibrium.

Every geothermal fluid regardless of its condition or history has a temperature and a Henry's Law $CO_2$ pressure that can be identified by coordinates as in Figure 7. A point on the map gives two important descriptors of a system. Moreover, a line on the map represents a unique [chemical] pathway between its two end points. For the case of a flashing geothermal fluid, the starting point in the map can represent the pre-flash condition. A mathematical basis for these maps is elaborated in Section IV.

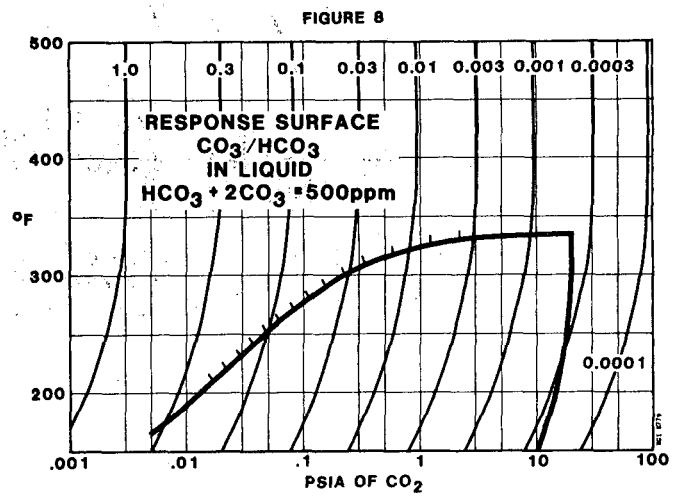
One may calculate a sequence of temperatures and $CO_2$ pressures for a process the system might undergo. The line on the map which connects the calculated points represents the continuous process. Two such lines are presented in Figure 7. One represents an adiabatic flashing (expansion), the other represents chilling without the forming of any vapor. The two lines have a common origin and if additional processes are invoked the extended pathway lines could [be made to] have a common end point. The area bounded by those two lines represents the limits within the map that real, perhaps non-equilibrium, processes can operate. Any line across that space could be taken to represent a process and describe basic facts about it. For example, it could indicate a kind of chemical [map] distance from an equilibrium process.

C. Additional Chemical Maps

Since the resource has a definite composition before flashing (at least within definable limits), information about the components which vary during flashing can be displayed. A preferred format for display uses isopleths of concentration (or activity) for selected components. These can be interpreted in the same way as are elevation contours in a topographic map; in fact, this device is mathematically identical to a topographic map. The surface represented by the isopleths is called a response surface, e.g. Hicks (1964), since its "elevation" reflects what the liquid phase would look like [when chemically equilibrated] at a coordinate location.

Figure 8 is such a map for the $CO_3/HCO_3$ concentration ratio, based on a pre-flash $HCO_3$ content of 500 ppm. In practice, one would construct a new map if a

FIGURE 8



different pre-flash content of $HCO_3$ were considered. For two maps differing modestly in reference to initial $HCO_3$ contents, the trends of the isopleths would be similar. One map may look much like the other except that the isoplethal lines would appear to have been shifted.

A pathway line (for a calculated or suggested process) can be superimposed on the response surface and even indexed for related factors; for example, percent flash, as is done in Figures 7 through 10. A more extensive set of these maps can be built which would involve all the components interesting to the design engineer. With these maps one may readily cross-reference several chemical parameters of the liquid with positions in a hardware diagram, commonly specified there by total pressure alone.

FIGURE 9

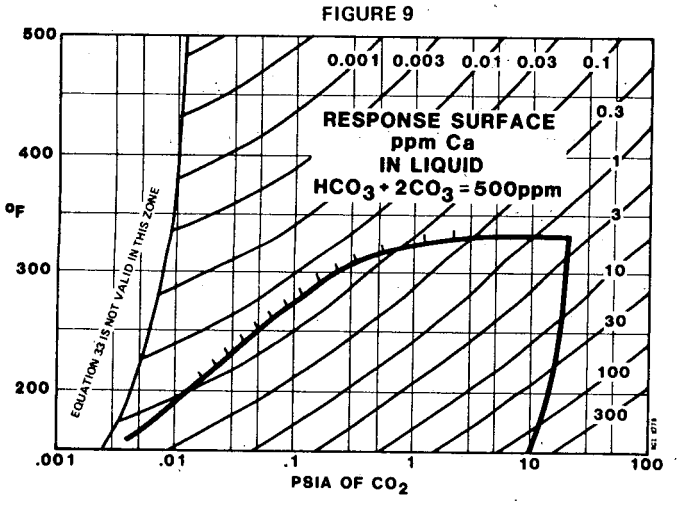
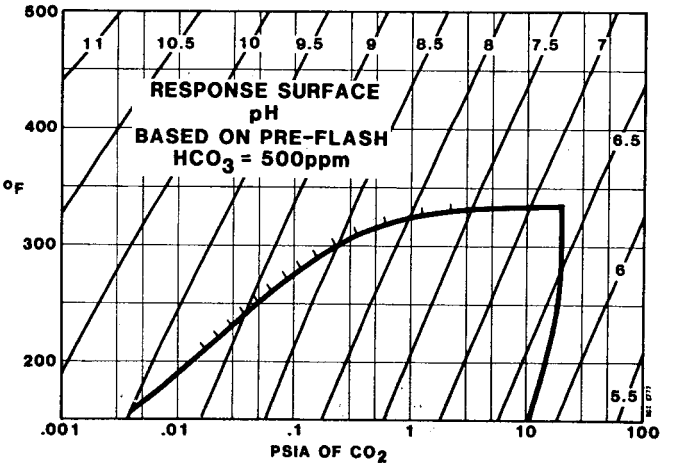



FIGURE 10




Additional maps of this sort that are relevant to carbonate chemistry involve calcium concentration (Figure 9), and pH (Figure 10), as well as $CO_3/HCO_3$ ratio. Those three provide a generally sufficient set, although other maps are possible. For example, the $CO_3$ concentration and $CO_2$(aq) concentration can be represented as maps and such maps could be worthwhile for emphasizing certain aspects of a process.

D. Example Application of a Chemical Map

Figures 8, 9, and 10 comprise a set based on a pre-flash $HCO_3$ concentration of 500 ppm. Each has superimposed on it the equilibrium adiabatic pathway and the chilled (no-flash) pathway.

Considering the deposition of $CaCO_3$, there are two reactions which are especially relevant:

$$2HCO_3^- \rightarrow H_2O + CO_2(g) + CO_3^= \qquad (6)$$

$$Ca^{++} + CO_3^= \rightarrow CaCO_3 \qquad (10)$$

From the maps one may deduce that for the equilibrium adiabatic path, reaction (10) is substantially complete at 4% flash -- the path becomes parallel to the Ca isopleths, hence no new thermodynamic drive for (10) is being generated. By contrast, reaction (6) persists beyond 10 percent flash, which is effectively atmospheric pressure, as evidenced by the pathway lines crossing the $CO_3/HCO_3$ isopleths at substantial angles throughout the process. This outcome is due to the great inequality of the Ca and $HCO_3$ concentrations. Initially they are present in the molar ratio of $Ca:HCO_3 = 1:35$. Conversion of a small percentage of $HCO_3$ to $CO_3$ is profoundly significant to the solubility product constant for calcite (or aragonite) as in (11).

$$K_{sp} = [Ca][CO_3] \sim 10^{-9} \text{ (moles } /\ell)^2 \qquad (11)$$

Because $HCO_3$ is so dominant, development of only a small portion of $CO_3$ causes the available Ca to be consumed early in the $HCO_3$ conversion process.

E. Cause-Effect and Independent Variables

In a mathematical expression variables are described as independent or dependent, but choice about which is which is made for convenience. For chemical systems at equilibrium one can be similarly flexible. However, for a chemical system which is undergoing irreversible reactions, dependence/independence acquires a physical interpretation. In the case of a high-$HCO_3$ brine with Ca concentration small, the Ca would be quickly consumed upon a relatively small change in the $CO_3/HCO_3$ ratio. In this context, the Ca concentration is considered to be a dependent variable.

In a related way, the $CO_3/HCO_3$ is independent of $H_2CO_3$ since in the related equations (12) and (13), the flow of material goes from $HCO_3$ to $CO_3$ without more than a trivial contribution from $H_2CO_3$.

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \qquad (12)$$

$$H = K' \frac{H_2CO_3}{HCO_3} \quad (12a)$$

$$HCO_3^- \rightleftharpoons CO_3^= + H^+ \quad (13)$$

$$H = K'' \frac{HCO_3}{CO_3} \quad (13a)$$

Similarly, pH (=-log[H]) is here a physically dependent variable. Its value may characterize the $CO_3/HCO_3$ ratio as in equation (13a), but it is not proper to consider that the $CO_3/HCO_3$ ratio is "controlled" by pH in this context because $H^+$ always is scarce compared to $HCO_3$ and/or $CO_3$.

Flashing is not reversible, hence the direction of cause and effect for the physical processes should be carefully imitated by the mathematical formulations. Some available computer models, when applied to the flashing process, use pH as an input (independent) variable. The outputs of such models are somewhat unrealistic since major components, especially $CO_3/HCO_3$, are thereby constrained to match somewhat arbitrary choices of what amounts to a pre-selected outcome. This aspect is important to calculational methods applied to the context of flashing geothermal fluid. In the next section a particular effort is aimed at calculating carbonate equilibria without involving pH.

## IV. CHEMICAL MAPS

### A. Theoretical Basis

A general system for making numerical calculations about carbonate equilibria is given by Garrels (1960), and Garrels and Christ (1965). Their approach has been followed by many others, notably Helgesen (1969), Stumm and Morgan 1970, and Holland (1978). In that approach, five chemical reactions are used along with their equilibrium constants. Those five include reactions (12) and (13) in addition to (14), (15), and (16) below.

$$CaCO_3 \rightleftharpoons Ca^{+2} + CO_3^= \quad (14)$$

$$K_{sp} = \frac{[Ca][CO_3]}{[CaCO_3]} \quad (14a)$$

$$CO_2(g) + H_2O \rightleftharpoons H_2CO_3 \quad (15)$$

$$K^\circ = \frac{H_2CO_3}{P_{CO_2}} \quad (15a)$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad (16)$$

$$Kw = \frac{[H][OH]}{[H_2O]} \quad (16a)$$

When calculations are to be made about specific contexts, the five equations with equilibrium constants can be augmented by additional equation(s) for electric charge balance and material balances in the reacting solutions. An entire set of equations is to be solved simultaneously, sometimes after specifying a concentration for one of the components and defining the chemical activities of $CaCO_3$ and $H_2O$ to be unity.

In Garrels' presentation five different cases are examined in which the set of equations is applied to calculating the equilibrium conditions for a collection of materials initially not at equilibrium. Although the basic pattern for solving the equations is similar in the several cases, there are subtle differences in the setup of components which have important effects in the outcome. For example, a simple system of water, calcite, and $CO_2$ comes to a different equilibrium condition depending on whether it is always closed to the atmosphere, open only initially, or open until equilibrium is reached. These subtleties, results, and the concepts behind them deserve close attention by all serious students of carbonate equilibria. It is important to note that none of the cases used as examples by Garrels or his followers apply to the context of flashing geothermal fluids.

### B. Adaptation to a Context of Geothermal Flashing

The most profound differences between a flashing geothermal context and other applications of carbonate equilibria referenced above concern (1) disturbing a system initially at equilibrium and tracking its irreversible processes, (2) the immensely higher $CO_2$ pressures (concentrations) for the pre-flash geothermal case, (3) the large and prompt changes in temperature and pressures, and (4) the non-proportionality of Ca vs $HCO_3$ in the pre-flash and post-flash geothermal fluids compared to traditional examples.

For liquids, like at East Mesa, which are substantially alkaline at all degrees of flash, equation (12) is not relevant to the process. Additionally, equation (15) confounds the dissolution of $CO_2$ gas with the hydration of $CO_2(aq)$. Garrels and his followers have recognized, in footnotes, the confounding that occurs in equation (15) and there is no necessity to account for it in the non-flashing systems they considered. In the development here, equation (15) is dealt with according to the discussion in the first section of this report. Lastly, some way is required to demote the pH from its common use as a master variable and make its calculation subject to the distribution of major components of the system.

### C. Making pH Calculations Dependent on $HCO_3/CO_3$ Ratio

An intermediate objective at this point is to find a calculable expression for $CO_3/HCO_3$, which is done below, in terms

of the pre-flash $HCO_3$ concentration. Smith (1963, p. 249) points out that equation (17) is independent of pH. It can be derived by combining 12a and 13a, wherein $H_2CO_3$ has its conventional meaning and can be replaced by the $CO_2(g)$ pressure and the Henry's Law solubility coefficient.

$$CO_3 = \frac{(HCO_3)^2}{H_2CO_3}\left(\frac{K''}{K'}\right) \qquad (17)$$

$H_2CO_3 = CO_2(aq) = P/44h$ when P = $CO_2$ pressure in psia and h is the Henry's Law solubility coefficient (from Figure 3) in units of psi/1,000 ppm. Thus, equation (17) can be rewritten as (18), $\gamma$'s representing activity coefficients.

$$\frac{CO_3\ (P)}{(HCO_3)^2} = \frac{44hK''}{K'}\left(\gamma^2_{-1}/\gamma_{-2}\right) = Aa \qquad (18)$$

Where (a) represents the activity coefficient term $(\gamma^2_{-1}/\gamma_{-2})$ and terms $CO_3$ and $HCO_3$ refer to concentrations, not activities.
Notably, A in (18) is a function only of temperature.

During flashing, some $HCO_3$ converts to $CO_3$ according to (6) which can be stated algebraically as (19) in which B is the initial concentration of $HCO_3$; the initial concentration of $CO_3^=$ is approximately zero.

$$HCO_3 + 2CO_3 = B = HCO_3(\text{initial}) \qquad (19)$$

Rearranging (19) yields (20) which, when substituted into (18), yields (21)

$$CO_3 = \frac{B-HCO_3}{2} \qquad (20)$$

$$A = P\left[\frac{B-HCO_3}{2(HCO_3)^2}\right]\left(\frac{1}{a}\right) \qquad (21)$$

Rewriting (21) into standard form (22)

$$2Aa(HCO_3)^2 + P(HCO_3) - PB = 0 \qquad (22)$$

yields a solution (23) which is appropriate only with the $(+)\sqrt{\ }$.

$$HCO_3 = \frac{-P + \sqrt{P^2 + 8AaPB}}{4Aa} \qquad (23)$$

Rewriting (18) as (24) and combining with (23) yields (25)

$$\frac{CO_3}{HCO_3} = \frac{AaHCO_3}{P} \qquad (24)$$

$$\frac{CO_3}{HCO_3} = \frac{Aa(-P + \sqrt{P^2 + 8AaPB})}{4AaP} \qquad (25)$$

which reduces to (26), the desired relationship.

$$\frac{CO_3}{HCO_3} = \left(\frac{1}{16} + \frac{AaB}{2P}\right)^{\frac{1}{2}} - \frac{1}{4} = R \qquad (26)$$

R is a ratio of concentrations, not chemical activities. Equation (26) applies to the flashing process during which P represents the Henry's Law $CO_2$ pressure in the residual liquid. Values of A can be calculated for selected temperatures using tables for K' and K", as shown by Helgesen (1969) or Kharaka and Barnes (1973) or others, plus values of h from Figure 3 of this report. Alternatively, A-values may be taken from Figure 11 of this report. Activity coefficients may be calculated by standard methods. They are more readily obtained from Figures 12 and 13 in this report which are based on Debye-Huckle theory and prepared by Cheatham and Lessor (1980).

The format of (26) is compact enough for hand-held programmable calculators and suitable for making chemical maps of which Figure 8 is an example.

Equation (26) does not involve an adjustment for ion pairing of $HCO_3$. In Ca-poor geothermal solutions, this is not serious because $HCO_3$ concentrations are generally much greater than concentrations of all cations except Na; and ion pairs of $NaHCO_3$ are scarce enough to ignore.

Equation (26) is especially significant because it describes the temperature dependence of a major component without reference to pH of the system. Consequently, the pH can be described as a dependent entity by combining equation (13a) with (26) to yield (27).

$$pH = -\log\left[K''\ b\left(\frac{HCO_3}{CO_3}\right)\right] = \log\left[\frac{1}{bK''}\left(\frac{CO_3}{HCO_3}\right)\right]$$

$$= \left\{\log\ \frac{1}{bK''}\left[\left(\frac{1}{16} + \frac{AaB}{2P}\right)^{\frac{1}{2}} - \frac{1}{4}\right]\right\} \qquad (27)$$

Where (b) is the activity coefficient term $(\gamma_{-1}/\gamma_{-2})$.

Maps of pH can be based on (27) of which Figure 10 is one example.

## D. Construction of Specific Maps

Computers can be used to construct maps, but hand methods are also simple in some cases. They have the advantage of giving extra insight into chemical processes for the person who calculates and plots the isopleths. An efficient method of constructing isopleths in a chemical map consists of selecting a value for an isopleth and spotting several coordinate pairs of its position on graph paper, then sketching in the curve. Since most data on equilibrium constants and activity coefficients are listed in tables for selected temperatures, it becomes practical to use those data as part of the input, thereby fixing a set of temperature coordinates. Then, specifying the isopleth value allows one to calculate the pressure coordinate and plot a coordinate position of the

FIGURE 11

A-VALUES FOR EQUATIONS 17 THRU 27
WHEN $CO_2$ PRESSURE IS IN PSIA
B, INITIAL $HCO_3$ CONTENT, IS IN PPM

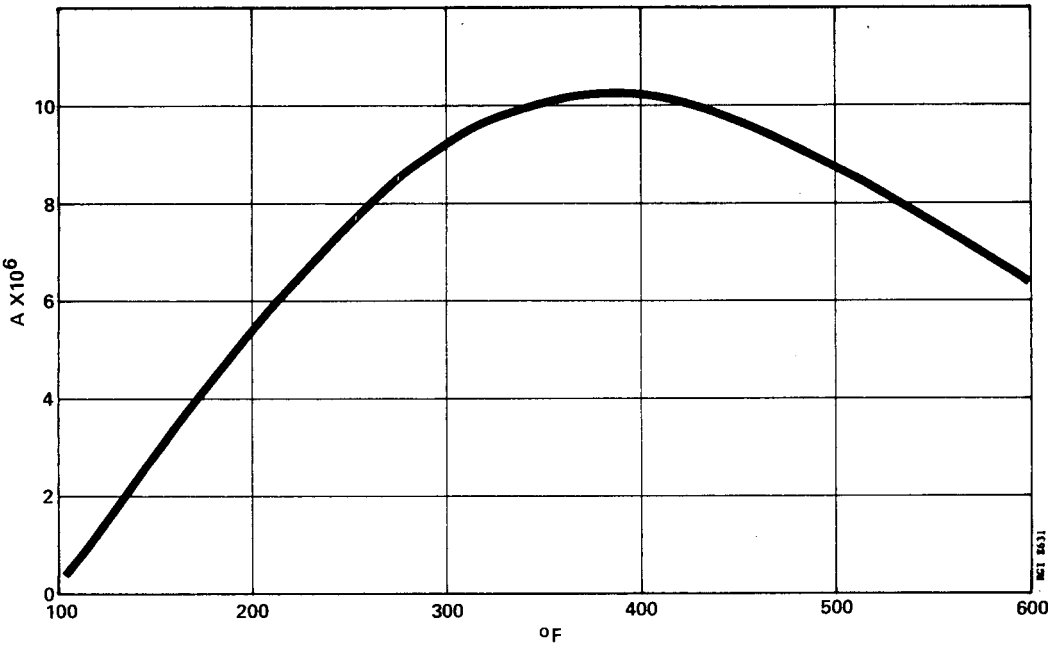
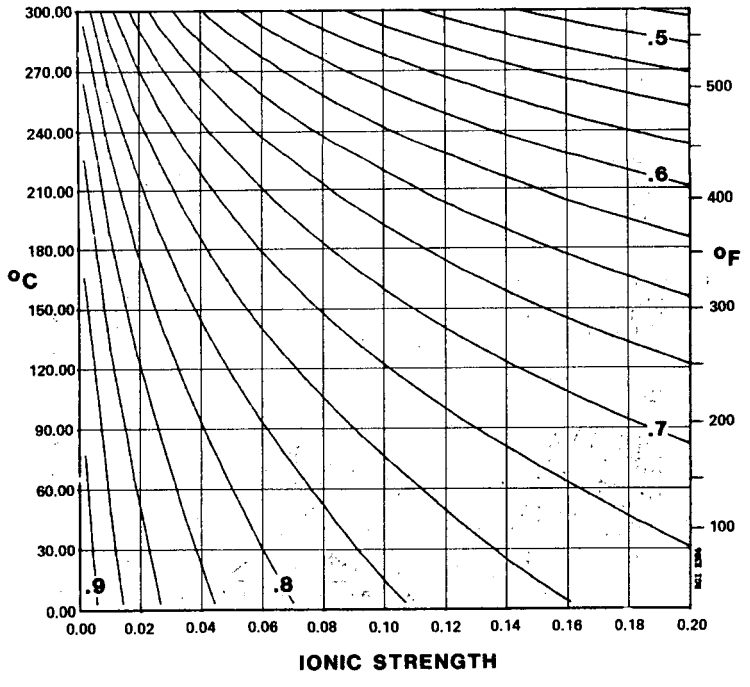



FIGURE 12

**ACTIVITY COEFFICIENT, $\gamma$-1**
**$HCO_3^-$**

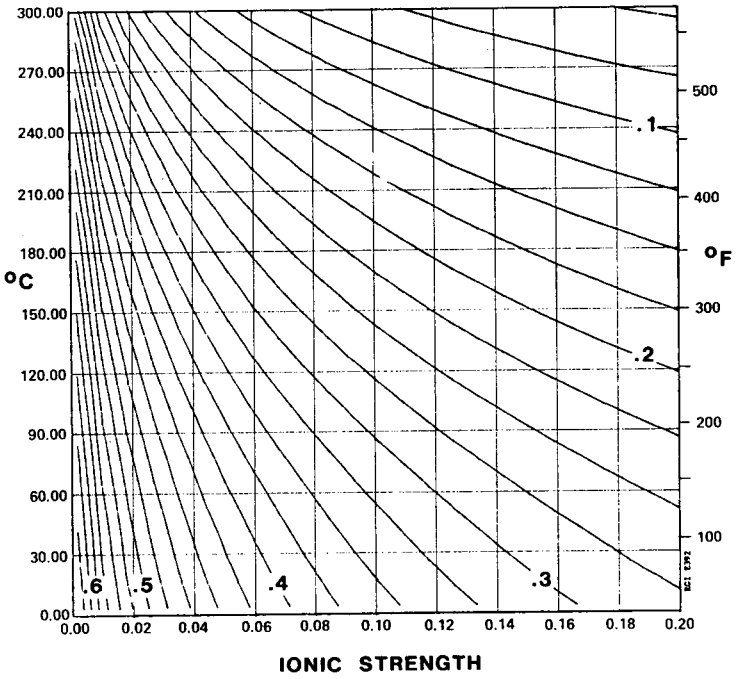



CHEATHAM AND LESSOR, 1980

FIGURE 13

ACTIVITY COEFFCIENT, $\gamma$-2

$CO_3^{=}$

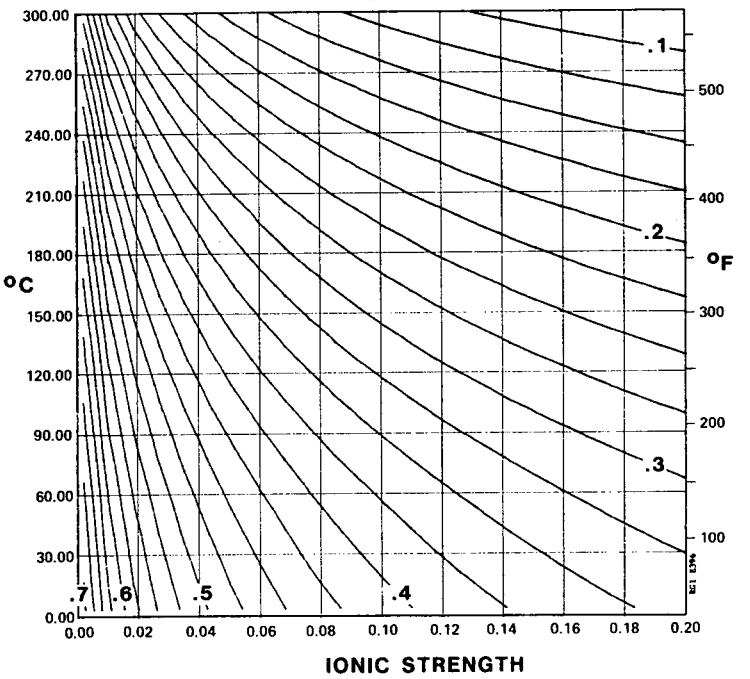



CHEATHAM AND LESSOR, 1980

FIGURE 14

ACTIVITY COEFFICIENT, $\gamma$+2

$Ca^{2+}$




CHEATHAM AND LESSOR, 1980

isopleth with good precision. A convenient working equation for this procedure is made by rewriting equation (26) to (28) in which $R = CO_3/HCO_3$.

$$P = \frac{AaB}{R(2R+1)} \tag{28}$$

1. Map for pH

Equation 13a can be rewritten in terms of R, equation (29), and substituted directly into (28) to make the working equation, (30).

$$R = \frac{K''}{H^+} = \frac{K''}{\exp(-pH)} \tag{29}$$

$$P = \frac{\exp(-2pH)AaB}{bK''[2bK'' + \exp(-pH)]} \tag{30}$$

Alternatively, equation (27) can be rearranged into eq. 30 by noting that $pH = \log \frac{1}{H^+}$.

Equation (30) is the basis for a 6-step map-building process: (1) select a value of B, the initial $HCO_3$ concentration, which will apply over the entire map; (2) select a temperature for which values of K', K", and h are precisely available for calculating A-values or use Figure (11) (an intermediate table is useful); (3) select a pH value for an isopleth and enter into the program for (30) along with A and K" values; (4) calculate a value for P and locate the P-T coordinate on graph paper; (5) choose another value for T (or pH) and iterate, eventually filling the entire area of interest; (6) connect the plotted coordinates with smooth lines and label.

2. Map for Calcium

Constructing a map for Ca can be done analogously to the process described above for pH. The difference is in substituting for the R-value in equation (28). For making the Ca map, use equation (14a) to derive (31) in which (c) represents the product of the activity coefficients for Ca and $CO_3$. Substitute (31) into equation (19) to yield (32); then combine (31) and (32) to form R, yielding equation (33), which then is substituted into the working equation (28), retaining all activity coefficients.

$$CO_3 = \frac{K_{sp}}{Ca\ \gamma_{+2}\ \gamma_{-2}} = \frac{K_{sp}}{Ca(c)} \tag{31}$$

$$HCO_3 = B - \frac{2K_{sp}}{cCa} \tag{32}$$

$$R = \frac{CO_3}{HCO_3} = \frac{K_{sp}}{BcCa-2K_{sp}} \tag{33}$$

Activity coefficients for Ca, $\gamma_{+2}$, and for $CO_3$, $\gamma_{-2}$, can be read from Figures 13 and 14 which are due to Cheatham and Lessor (1980).

The 6-step process described above yields a response surface for calcium, but the labels on the isopleths may be out of calibration with the resource one intends to represent. This is partly because most of Ca present in a $HCO_3$-rich fluid is in the form of the ion pair $CaHCO_3^+$, not $Ca^{2+}$, and Ca in all forms is minor compared to $HCO_3$. Thus, using ($Ca\gamma_{+2}$) in (33) to calculate $CO_3/HCO_3$ involves the same logical error as in using pH to calculate $CO_3/HCO_3$. The damage to the map is not serious since the spacing of the calculated isopleths and their relative values will represent the shape of the response surface. The isopleths could be calibrated by field data obtained to represent Ca at the pre-flash temperature and $CO_2$ pressure, but valid analyses for pre-flash calcium may be difficult to obtain. Special efforts generally are necessary since few wells are flowed in their early testing stages without flashing in the bore. This risks deposition of Ca before the fluid can be sampled.

In the absence of valid calcium analyses with which to calibrate the isopleths, there still is much in the response surface map that applies to engineering problems. For example, the fraction of available Ca deposited at increments during the flashing process can be estimated from an uncalibrated map. One procedure begins with spotting the pre-flash coordinates on the map, then calculating the adiabatic flash path. The apparent value at the pre-flash coordinates represents the liquid with all of the Ca dissolved. That point can be labeled "unity" and the isopleths below it relabeled in the indicated proportions. The differences from unity represent "fraction deposited." An alternative method is used in an example problem in section VI.

3. Overlay of an Adiabatic Flash Path

This overlay requires finding simultaneous values for temperature, percent flash, and pressure of $CO_2$. The following procedure suffices.

Calculate the flash fraction (f) by equation (34) wherein subscript "o" refers to the initial temperature and "i" refers to some lower temperature. Steam tables can be used to find simultaneous values of temperature (T), liquid enthalpy (L), and steam enthalpy (S).

$$f = \frac{L_o - L_i}{S_i - L_i} \tag{34}$$

The partial pressure, P, of $CO_2$ is given accurately enough by the ideal gas equation, PV = ZnRT, in which n and V are defined according to the conditions of flashing and Z has a value near 0.99 for most exploitable geothermal resources. The

volume occupied by $CO_2$ is identically that occupied by the steam and is given by eq (35). $V_s$ is the specific volume listed in steam tables.

$$V = V_s f \tag{35}$$

The value of (n), the number of moles of $CO_2$ initially in the liquid less the number still present, is given by (36).

$$n = \frac{C_o - 1000\ P/h}{44 \times 10^6} \tag{36}$$

$C_o$ is in ppm, P is psia, h is psia per 1,000 ppm, 44 refers to the molecular weight of $CO_2$, and $10^6$ converts ppm to a unit basis. Combining (34), (35), (36), and the gas equation yields (37).

$$P = \frac{(C_o - 1000P/h)\ RTZ}{44 \times 10^6\ V_s f} \tag{37}$$

Equation (37) can be reduced to a working form (38) in which $M = 44 \times 10^6/RZ = 3.866 \times 10^6$ in English units. T is the Rankine temperature (°F + 460).

$$P = \frac{C_o}{MV_s f/T + 1000/h} \tag{38}$$

The vapor pressure of $H_2O$ need not be specified at this point; it is implied in the temperature. The ideal gas equation as used here applies only to the $CO_2$ component.

## V. RECONSTRUCTION OF PRE-FLASH LIQUID CHARACTERISTICS FROM ANALYSIS OF FIELD SAMPLES

The increase in dissolved solids concentrations due to loss of $H_2O$ upon flashing is not fully treated in many reports of geothermal data. For nonvolatile materials, correct adjustment is simple and as accurate as the estimate of the flash fraction.

For volatile components and a few of their associates, a more complicated system of adjustment is appropriate, which is the major subject of this section. Components involved are $CO_2$, non-$CO_2$ noncondensables, $HCO_3$, $CO_3$, Ca, $NH_3/NH_4$, and $H_2S$. The objective is not only to find the pre-flash concentrations, but also to find the components of vapor pressure, the total vapor pressure, and the extent some components are partitioned between the liquid and vapor.

Much of the following is an inversion of some discussion of the preceding sections. The intent is to provide a guide for geochemists who must convert field analytical data into a form usable by design engineers. Some of the data require special sampling methods. In some cases, alternative sampling methods have different analytical interferences and are not straightforwardly comparable. These factors must be recognized when reconstructing the pre-flash liquid composition.

### A. Pre-flash $HCO_3$

The pre-flash $HCO_3$ content is easily and reliably deduced from field samples. It is the master variable to consider when engineering high-$HCO_3$ geothermal resources. A numerical understanding of the fate of $HCO_3$ upon flashing is required for interpreting field data and for making adjustments to $CO_2$ (g) determinations. Eq (6) provides the basic relationship which is expressed algebraically as (39).

$$HCO_3 + 2CO_3 = \text{constant} \tag{39}$$

Deposition of $CaCO_3$ via eq (9) has an effect on (39) that is described by (40).

$$Ca + 2HCO_3 \rightarrow CaCO_3 + H_2O + CO_2 \tag{40}$$

A more general counterpart of (39) can be written as (41), which is expressed in numbers of ions, and accounts for deposition of $CaCO_3$ scale.

$$HCO_3 + 2CO_3 + 2(Ca_i - Ca_r) = \text{constant} \tag{41}$$

Subscripts on Ca refer to initial and residual amounts.

For high-$HCO_3$ resources in which Ca is subordinate to $HCO_3$ the residual amount of Ca after flashing may be smaller than the uncertainty in the analyses for $HCO_3$ or $CO_3$. $Ca_r$ could then be ignored as a practical matter. The constant in eqs (39) and (41) is the $(HCO_3)_i$ present before flashing. Its concentration in ppm units can be based on analysis of $(HCO_3)_a$ in post-flash liquid, as in (42). Subscript (a) refers to the analytically measured concentrations.

$$(HCO_3)_i = \left[(HCO_3)_a + 2(CO_3)_a + \frac{122}{40} Ca_{(s)}\right](1-f) \tag{42}$$

Subscript "s" refers to Ca lost to $CaCO_3$ scale and 122/40 includes a gravimetric conversion factor. $Ca_{(s)}$ is approximately equal to $Ca_{(i)}$.
The chemical symbols in (42) imply ppm units, f is the flash fraction. The numerical values include gravimetric conversion factors and Ca refers to some estimate of how much has been lost to $CaCO_3$, most often approximately its preflash concentration.

Changes in the $CO_3/HCO_3$ ratio of a liquid sample during transport before analysis are irrelevant to the working of eq (42) if they are due either to losses of residual $CO_2$ or to

gain of $CO_2$ from the atmosphere. Both aspects are incorporated by eq (6) which is part of the basis for (42). Thus, use of eq (42) simplifies requirements for sampling and packaging the sample for transport to an analytical laboratory.

B. pH

Field measurements of pH characterize the joint effects of flashing and sampling. Values for pH could be entered into a counterpart of Figure 10 (constructed with an appropriate reference for initial $HCO_3$). It would there serve as an end point for a (map) process described by two joined line segments--one representing the flashing and fluid transport to the point of sampling, the other from the point of sampling to the point of analysis. Such efforts should be saved for advanced stages of resource characterization.

Field measurements of pH have some practical applications, but characterization of a high-$HCO_3$ resource is not among them. Questions about pH in the system during active flashing, are best answered by reference to a well constructed (appropriate pre-flash $HCO_3$ content) counterpart of Figure 10. Significantly, a useful pH is not measurable in the field. This is because pH is dependent on $CO_3/HCO_3$ ratio (eq 29) and the $CO_3/HCO_3$ ratio is jointly dependent on temperature and residual $CO_2(aq)$. It is not possible to transport a sample to a pH meter and make a measurement that corresponds to conditions at the point of sampling. This problem exists also for so-called "inline pH meters" which function on a cooled sidestream of fluid.

In testing a new well, as soon as one establishes that fluid pH is controlled by the $CO_3/HCO_3$ ratio, measurements of field pH can be abandoned without sacrificing useful information. Information about pH during flashing is best obtained from calculations based on measurements of $CO_3$ and $HCO_3$ in residual liquid, augmented by data on $CO_2$ contents.

Measuring pH may have some other utility. For example, during a multiday test of a geothermal well, measurements of pH could show stability of the system (or lack thereof). In an operating plant, pH monitoring could be useful for some control functions.

C. $CO_2$

High-$HCO_3$ resources possess two numerically different $CO_2$ contents of relevance to engineering design. The lower one corresponds to the $CO_2(aq)$ which is responsible for the Henry's Law pressure in the pre-flash liquid. It is to be used when calculating a position of initial flashing in wells flowed without pumping, when designing downhole pumps and when selecting setting depths for pumps.

A somewhat larger amount of $CO_2$ is exsolved upon flashing because some of the non-Henry's Law $HCO_3$ disproportionates according to eq (6). This non-Henry's Law component may amount to 20% of the exsolved $CO_2$ from high-$HCO_3$ resources, ranging toward zero for resources that are low in $HCO_3$ or chemically acidic after flashing. This larger amount must be accommodated in methods for removing $CO_2$ within a flashed steam electric plant either from the condenser or with equipment located upstream of the turbine. Special designs of turbine interiors to accommodate mixtures of steam and $CO_2$ may be considered if $CO_2$ is to exceed 10 to 15% of the throughput mass.

In order to resolve these different engineering contents of $CO_2$, chemical analysis must be made on both the flashed steam and the post-flash liquid. Analysis of pre-flash liquid for total carbon species does not provide data that is directly useful for the $CO_2$ question. However, the results could provide a check on the mass balance implied by analysis of different carbon species in the separated phases.

Besides the breakup of $HCO_3$, other reactions affect the measured amounts of $CO_2$. One is deposition of $CaCO_3$. Additionally, the presence of ammonia in steam affects the apparent $CO_2$ content. All these effects are quantified below, and accommodated into a working equation to convert analytical data to pre-flash concentrations of $CO_2$.

1. Effect of $HCO_3$ Disproportionation

Equation (6) shows that in the disproportionation of $HCO_3$, equal amounts of $CO_2(g)$ and $CO_3$ are produced. When seeking a value such as the pre-flash Henry's Law pressure for $CO_2$, the apparent amount of $CO_2$ in pre-flash liquid, which will be based on steam analysis, should be reduced by an increment equal to the molar amount of $CO_3$ in the residual liquid at the point of steam separation. That value is obtained most accurately by reference to a counterpart of Figure 8 which yields a value for $CO_3/HCO_3$ ratio that can be multiplied by pre-flash $HCO_3$. Before such a figure as 8 is available, the relevant $CO_3$ content may be estimated as the amount determined by analysis of post-flash liquid. Whether this is an over- or underestimate may be decided later when a counterpart Figure 8 is constructed. Whether the mal-estimate is serious can be decided at the same time and should incorporate also a consideration of the $CaCO_3$ deposition described next.

2. Effect of Calcite and Aragonite Deposition

Deposition of $CaCO_3$ robs the liquid of $CO_3$ produced according to eq (6). The chemical system responds by disproportionation of more $HCO_3$. This is because the $CO_3/HCO_3$ ratio depends on temperature as well as on $CO_2$ pressure and even more because (if) $HCO_3$ is a prominent component. In this circumstance, item 1 by itself underestimates the incremental

adjustment of the apparent $CO_2$ content. A correct adjustment requires knowledge of how much Ca was lost to $CaCO_3$. The relevant chemical equation is (40) which shows that each ion of Ca that precipitates as $CaCO_3$ provides one molecule of $CO_2$ that is detectable in the steam. This is in addition to the $CO_2$ increment described in item 1.

3. Effect of Ammonia/Ammonium

Ammonia partly follows the steam during the flashing process and presumably is converted to ammonium bicarbonate in the condensate, according to eq (43).

$$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3 \qquad (43)$$

In this form, the $HCO_3$ does not participate with $CO_2(g)$ that many sampling schemes aim to collect in condensate. Hence, presence of $NH_3$ may cause an underestimate of the $CO_2$ in flashed steam. Eq (43) shows a 1-to-1 proportion between $NH_3$ and uncounted $CO_2$. Analysis of $NH_4$ in condensate enables one to make the correction. Samples for ammonium in condensate should be preserved with a nonvolatile, nonoxidizing acid such as dilute $H_2SO_4$.

Methods which collect a sample of gaseous $CO_2$ over the condensate are subject to this problem. Alternative methods which collect $CO_2$ by reacting the condensate steam with strong base are not affected if subsequent analysis involves boiling the sample in the presence of an acid which effectively displaces all the $CO_2$.

4. Losses of $CO_2$ to Condensate

Collecting only gaseous samples of $CO_2$ (along with other noncondensable gases) risks losing part of the $CO_2$ at the point of sampling because of its solubility in water (condensate). This loss may be serious since below 16°C (61°F) a volume of condensate under a $CO_2$ partial pressure of one atmosphere holds more than an STP volume of $CO_2$. At 0°C the solubility (Bunsen coefficient) is 1.713 STP volumes of $CO_2$ per unit volume of (pure) water per atmosphere of $CO_2$ pressure.

Correcting for this effect requires separate measurements of liquid temperature and liquid volume in addition to some indication that the dissolved $CO_2$ is in chemical equilibrium with the vapor. Several sampling methods reported in the literature are subject to this problem, but it is ignored in descriptions of some of them. Data from such methods should be considered as approximations only, perhaps as lower limits. More authoritative sampling methods may be required to gain data on $CO_2$ for design engineering purposes.

Since the solubility of $CO_2$ in condensate (relatively pure water) is well understood it can be used to advantage as the basis of an analytical method (Michels, 1978). This method is unique in yielding an unbiased measurement for the mole fraction of non-$CO_2$ gases in the noncondensable suite. The utility of this measurement is reviewed in a subsequent section.

5. Adjusting the Apparent $CO_2$ Content of Steam to a Pre-flash Liquid Basis

Beginning with the analytical result for $CO_2$ in steam, a correction for ammonia is made. Then, the content basis is changed from steam to total fluid. Additional adjustments for $HCO_3$ disproportionation and $CaCO_3$ deposition are then made. Eq (44) applies.

$$CO_{2(i)} = \left[CO_{2(a)} + \frac{44}{18} NH_{4(a)}\right] f - \frac{44}{60}\left[(1-f)\, CO_{3(a)} + Ca_{(i)}\right] \qquad (44)$$

All chemical symbols in (44) refer to consistent concentration units, e.g., ppm.

The results from (44) can be used with a factor from Figure 3 to estimate the Henry's Law pressure of the pre-flash liquid as required for models of wellbore flow (position of flash initiation), considerations about cavitation on pump impellers, and setting depth for downhole pumps.

D. Non-$CO_2$ Noncondensables

A host of other gases exist in geothermal fluids, the most common being $N_2$, $H_2$, Ar, $CH_4$, and higher saturated hydrocarbons. In some fields $CO_2$ may be subordinate to those, but generally $CO_2$ comprises 80 to 99+ mole percent of the noncondensable suite. However, the non-$CO_2$ gases have much greater Henry's Law pressures per ppm as shown in Figure 4. Their effects on cavitation and pressure of initial flashing cannot be safely ignored, even if the effects of $CO_2$ are correctly calculated.

Translating the concentrations of non-$CO_2$ gases in steam to a basis of pre-flash liquid requires a kind of data not usually obtained without bias, namely mole percent non-$CO_2$ gases in the noncondensable suite. A few sampling methods yield a sample, collected over condensate, which can be analyzed by gas chromatograph (GC) or mass spectrometer (MS). Most of those methods lose an uncalibrated amount of $CO_2$ to the condensate, yielding an overestimate of the non-$CO_2$ fraction. Use of such biased results, without adjustments, may not cause problems since a conservative

engineering conclusion would be a logical outcome. The effect may be small as well, hence ignoring the bias could be an acceptable alternative--but ignoring the non-$CO_2$ gases altogether is not!

Traditionally, $CO_2$ is reported in units of weight percent in steam, whereas individual non-$CO_2$ species are reported in units of mole percent in the analyzed gas (by GC or MS). If $CO_2$ is listed also then conversion of non-$CO_2$ proportional amounts to a ppm basis works through the $CO_2$. If $CO_2$ is not listed in the mole percent tally, from the GC or MS, then a value for "mole percent of gross non-$CO_2$ gases in the noncondensable suite" must be obtained separately. This latter case applies to sampling methods which collect gases over a NaOH solution which solubilizes the $CO_2$.

A practical calculational method begins with finding a multiplier, F, by eq (45) which operates on the mole percent values to convert them to ppm units, as indicated in eq (46). The principal inputs are apparent weight percent $CO_2$ in steam, mole percent $CO_2$ in noncondensable gas, and flash fraction, f. Do not use results from eq (44) in (45) because the adjustments in (44) are irrelevant to the non-$CO_2$ gases.

$$F = \frac{(wt\%)\ (f)\ 10^4}{44\ (mole\%)} \qquad (45)$$

The ppm concentrations of the other noncondensable gases can be obtained from eq (46) wherein W refers to the molecular weight of a gas species and M to its mole percent in the noncondensable suite

$$ppm = F(W)(M) \qquad (46)$$

Lastly, a table of results, similar to Table 2, should be prepared. Pressure coefficients can be taken from Figure 4.

TABLE 2

VAPOR PRESSURE OF FLUID FROM WELL E.M. 87-6

| Gas | Mole Percent Apparent | Mole Percent $CO_2$-free | ppm pre-flash basis | Pressure Coefficient psia/1000 ppm 335° | Pressure Coefficient psia/1000 ppm 350° | Henry's Law Pressure psia 335° | Henry's Law Pressure psia 350° |
|---|---|---|---|---|---|---|---|
| $CO_2$ | 93.27 | | 923* | 40.8 | 40.8 | 37.7 | 37.7 |
| $N_2$ | | 45.87 | 20.42 | 815 | 760 | 16.6 | 15.5 |
| $CH_4$ | | 51.88 | 13.20 | 875 | 805 | 11.6 | 10.6 |
| Ar | | 1.287 | .82 | 320 | 311 | .3 | .3 |
| | Pressure of NCG | | | | | 66.1 | 64.1 |
| | Pressure of $H_2O$ | | | | | 110.3 | 134.6 |
| | Total Vapor Pressure | | | | | 176.4 | 198.7 |

* Calculated by eq (44)

Table 2 shows that even though $CO_2$ comprises more than 93 percent of a suite of noncondensable gases, it yields less than 60 percent of the total Henry's Law vapor pressure. In geothermal resources where $CO_2$ is less than 90% of the noncondensable suite, the non-$CO_2$ gases will dominate the Henry's Law pressure and dominate also the engineering considerations about the wellbore and pumps that (might) go in it. This contrasts to the surface installation wherein dealing with noncondensables at the condensers, the effects of non-$CO_2$ gases are merely proportional to their relative mole percent there.

E. Calcium

Two approaches are available to the problem of obtaining a pre-flash concentration for calcium: field techniques to obtain a valid sample or calculational methods based on suspected relationships.

1. Field Techniques

For geothermal resources that deposit $CaCO_3$ upon flashing, unflashed samples are hard to get and some methods of getting them are equivocal as regards contamination or retention of calcium or having obtained a sample that represents the resource.

The most reliable sample is obtained from a pumped well when over-pressured unflashed liquid is available at a surface facility in large steady throughput. Equipment to penetrate the flow lines and chill the sample can be easily manipulated. Abundant resource allows through flushing of sampling equipment and repeat samples are obtainable.

These circumstances are uncommon and expensive to set up. When they exist, a heavy sampling program should be implemented. Its objectives should go beyond finding the general concentration of calcium, seeking also patterns in its variations, as they may exist. One should seek information and make interpretations about different Ca outputs from multiple productive zones within the well.

Studies of the variations should be aimed also at finding patterns which can be extrapolated into future production of the well. As a matter of perspective, a well and its patterns of production provide only one sample point for a geothermal field; yet it is the field which must be characterized when designing an electric plant. Patterns of calcium concentrations across the field, as well as across time, are important to questions about scale inhibition, equipment for same, problems of blending fluids, design of mixing equipment, choices of which streams to blend and in what order, and whether some streams are seriously incompatible. To obtain merely the statistical ranges of concentrations of Ca would be an insufficient return from such an opportunity.

Some geothermal wells have a positive wellhead pressure even when the shut-in liquid column in the bore has equilibrated

to the local geothermal gradient. These wells can be flowed slowly so that single-phase geothermal fluid (bottoms-up time in the range of 1 to 2 hours) can be obtained at the wellhead. Temperature will be unrepresentatively low. Samples can be collected in the same way as for a pumped well and absence of flashing would yield a sample with calcium content still intact. However, sample quality could be suspect. For example, if previous flashing flow in the wellbore had deposited $CaCO_3$, an uncertain amount would dissolve in the cooling $CO_2$-charged fluid as it rose in the bore. Such samples clearly would yield a useful upper limit for the Ca content, yet data on variations might be unreliable.

Downhole samplers of several types exist. They may suffer from problems of potential contamination or mechanical malfunction. Also, the representativity of the fluid being sampled may be uncertain. They will not be described here.

2. Calculational Methods

In principle, data on pre-flash $CO_2$, $HCO_3$, temperature, ionic strength, and ion-pair formers for Ca can be obtained from ordinary flashed samples, and the Ca concentration calculated by standard (computer) methods that deal with the requisite number of simultaneous equations involved.

A somewhat simpler method would use a chemical map similar to Figure 9 which was (1) constructed for a similar pre-flash $HCO_3$ content and ionic strength, and (2) calibrated with a firm analysis for Ca. This rather fortunate circumstance can exist during the field development stage. The unknown Ca concentration ($Ca_2$) can be estimated by multiplying the known Ca concentration ($Ca_1$) by a series of ratios, as in eq (47), where

$$Ca_2 = Ca_1 \left[\frac{HCO_{3(1)}}{HCO_{3(2)}}\right] \left[\frac{CO_{2(2)}}{CO_{2(1)}}\right] \left[\frac{\gamma_{Ca_1}}{\gamma_{Ca_2}}\right] \quad (47)$$

the several concentration terms refer to the different wells and the activity terms refer to the appropriate temperatures and ionic strengths. The ratios of activity coefficients et al are likely to be more accurate than either numerator or denominator because they share some biases. Thus, eq (47) can be expected to yield a more accurate result than calculation by theoretical methods.

Simpler still are the several geothermometers that involve calcium. Since pre-flash temperatures are routinely determined, either by downhole probes or measurements of enthalpy at the surface, the geothermometer equations are readily utilized in inverted forms.

The NaKCa geothermometer (Fournier and Truesdell, 1973) can be used in two ways. Inverting the form to yield Ca directly also yields a term for Na to the third power, which makes the calculated Ca concentration sensitive to small errors in Na analysis. Alternatively, one may enter into the Fournier-Truesdell form a series of values for Ca until a satisfactory match for temperature is obtained. This results in a lesser sensitivity to errors in data for Na and K.

Additional geothermometers (in °C units) by Tonani (1980) use Ca with either (but not both) Na or K, as in equations (48) and (49). Results from all three geothermometers can be compared and perhaps pooled, according to one's judgment.

$$T_{CaK} = \frac{1930}{\log \frac{\sqrt{Ca}}{K} - 2.92} - 273 \quad (48)$$

$$T_{CaNa} = \frac{1096.7}{\log \frac{\sqrt{Ca}}{Na} + 2.37} - 273 \quad (49)$$

F. Condensable Gases

Several materials are subject to incomplete separation from the liquid phase upon flashing. Among these are $NH_3/NH_4^+$, $HS^-/H_2S$, and compounds of boron. Environmental issues may require similar information about Hg, As, and others. The extents to which substances become partitioned depend jointly on the specific chemical forms present and on the mechanical/timing aspects of the flashing. In order to reliably characterize their presence in the pre-flash liquid, samples of both steam (condensate) and post-flash liquid are required. Additionally, the samples require special efforts for preserving the components for analysis and for packaging and transport.

Partitioning, as quantified by field samples acquired during early testing stages, may not accurately represent partitioning in a power plant using the same resource. This is because of the different dynamics of flashing that occur in the different configurations of hardware used.

The pre-flash concentration of a partitioned species can be calculated as a weighted average of the concentrations in the separate phases, as in eq (50).

$$C_p = C_s(f) + C_l(1-f) \quad (50)$$

In (50), C stands for concentrations, f for flash fraction, and subscripts p, s, and l refer to pre-flash liquid, steam, and post-flash liquid, respectively.

Some condensable gases, for example, $NH_3$ and $H_2S$, are important to considerations of corrosion and the avoided use of certain susceptible materials, notably copper alloys.

## G. Nonvolatile Materials

The simplest components to deal with are the soluble, nonvolatile materials, including halides, the alkali series, transition elements and others that are inherently stable or can be stabilized against precipitation by acidifying the samples. Other materials, for example, barium and strontium (in low-sulfate resources) and sulfate in low-barium resources present no serious complications in sampling, preservation, and analysis. Minor and trace elements are generally scarce enough that their losses are not analytically serious unless they are carried by a prominent scale former. An example is loss of strontium when aragonite deposition occurs.

Some minor reactions can be expected to yield unforeseen deposits in an operating plant. Identifying these problems before a plant acquires operating experience can be attempted through using computer codes. The best use of such codes depends on accurate characterization of the resource to be modeled, as well as on the structure of the code.

For nonvolatile, nondepositing materials, their concentrations in the pre-flash liquid can be based on analyses of post-flash liquid concentrations, $C_{(p)}$ according to eq (51). Symbolism is the same as for (50); $V_1$ and $V_a$ refer to sample volume and volume of added preservative solutions, if any, as prepared in the field.

$$C_{(p)} = C_1(1-f)\ \frac{V_1 + V_a}{V_1} \qquad (51)$$

## VI. EXAMPLE APPLICATIONS

### A. $CO_2$ Removal and $CaCO_3$ Scale Deposition in a Multi-stage Flash System

Consider a resource as described in Table 3. It represents a fluid saturated in $CaCO_3$ and capable of yielding $CO_2$ from the Henry's Law relationship as well as from the disproportionation of $HCO_3$, eq (6) and deposition of $CaCO_3$, eq (40). It is similar to the resource on which Figures 8, 9 and 10 are based.

TABLE 3

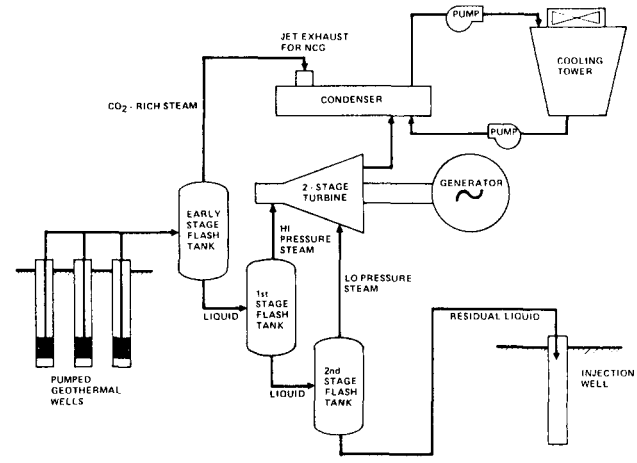
SELECTED CHARACTERISTICS OF AN EXAMPLE PRE-FLASH LIQUID

| | |
|---|---|
| Temp. | 335° |
| $CO_2$ (aq) | 500 ppm |
| $HCO_3$ | 500 ppm |
| Ca | 8 ppm |
| TDS | 2,500 ppm |

A proposed method of exploiting this fluid is diagrammed in Figure 15. A small "early-flash" allows most of the Henry's Law $CO_2$ to be vented with a minor sacrifice of steam; the output might drive a gas ejector system on the condenser. Steam from the first- and second-

FIGURE 15

TWO STAGE FLASH SYSTEM WITH EARLY REMOVAL OF $CO_2$




stage flash will drive the turbine and contains some $CO_2$ which must be ejected from the condensers. The first calculation for examining trade-offs sets the early-flash at 1%, the first-stage flash tank at 65 psig, and the second-stage flash tank at 3 psig.

Question: How much $CO_2$ will be present in the early-flash stream and in the turbine stream?

Answer: Since the early-flash fraction of 1% is arbitrary, it becomes practical to make tables of temperature, $CO_2$ pressure, and other calculated items, as in Table 4. Additionally, graphs of temperature vs each of the calculated items may be made as in Figure 16. Plotting graphs enables one to use the steam tables

TABLE 4

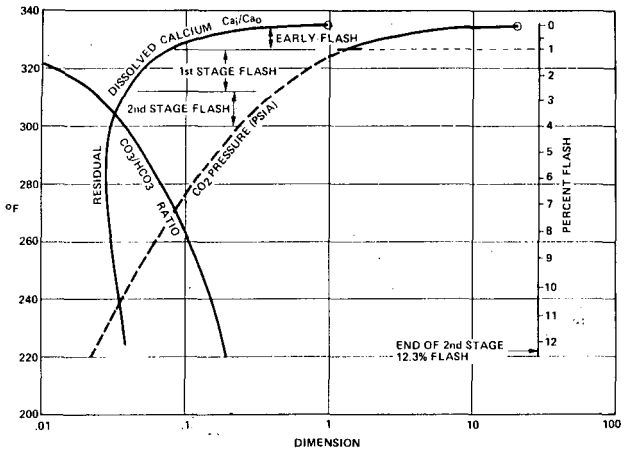
WORKSHEET FOR CONSTRUCTION OF FIGURE 16

| Temp. | f | h | $P_{CO_2}$ | $A \times 10^6$ | $CO_3/HCO_3$ | -log $K_{sp}$ | $Ca_i/Ca_o$ |
|---|---|---|---|---|---|---|---|
| 335 | -0- | 42 | 21 | 9.92 | .00047 | 10.70 | 1.000 |
| 330 | .00588 | 42 | 2.13 | 9.86 | .0046 | 10.65 | .115 |
| 320 | .0174 | 41.5 | .698 | 9.70 | .014 | 10.54 | .0485 |
| 310 | .0288 | 41.0 | .365 | 9.49 | .025 | 10.42 | .036 |
| 300 | .0399 | 40.0 | .231 | 9.29 | .037 | 10.31 | .031 |
| 290 | .0508 | 39.5 | .158 | 9.03 | .052 | 10.20 | .0285 |
| 280 | .0615 | 38.8 | .113 | 8.75 | .068 | 10.09 | .0282 |
| 270 | .0720 | 38.1 | .0835 | 8.43 | .086 | 9.98 | .0287 |
| 260 | .0823 | 37.2 | .0628 | 8.06 | .106 | 9.87 | .030 |
| 250 | .0925 | 36.2 | .0478 | 7.68 | .128 | 9.76 | .032 |
| 240 | .1025 | 35.5 | .0368 | 7.28 | .152 | 9.66 | .034 |
| 230 | .1120 | 34.0 | .0285 | 6.84 | .170 | 9.56 | .038 |

without interpolation. Also, graphs are more useful in iterations of the design. A final optimization would certainly inquire about early flashes different from 1%, and the same graphs can be used.

The relevant equations for generating the tabular data begin with (34) for flash fraction and (38) for $CO_2$ residual pressure; inputs to them can be drawn from steam tables and Figure 3 (or 2). Upon construction of Figure 16, the

FIGURE 16
PROCESSES DURING FLASHING




residual $CO_2$ pressure at 1% flash can be read as 1.24 psia at 326°F. The residual $CO_2$(aq) content is given by P/h = (1,000)(1.24)/42 = 29.5 ppm on a basis of total fluid.

Most of this residual $CO_2$(aq) will be exsolved in the first-stage flash tank, but steam from both flash tanks will be blended before reaching the condenser. The sum of exsolved $CO_2$ from both tanks can be placed on a steam basis by dividing the concentration calculated above by the net flash (.123 - .01 = .113), as in eq. 52.

Residual Henry's Law $CO_2$ =
29.5/.113 = 261 ppm or .026%. (52)

Additional $CO_2$ will arrive at the condenser due to disproportionation of $HCO_3$ which occurs mainly in the second-stage flash tank. The relevant equation is (26) which yields the $CO_3/HCO_3$ ratio. Suitable values for A in (26) can be read from Figure 11 which is based on Kharaka and Barnes (1973). Values for A (taken from Figure 11) and calculated values for $CO_3/HCO_3$ ratio (R) from (eq 26) are listed in Table 6. The R-values are also plotted in Figure 16.

Negligible $CO_3$ is generated in the early-flash step; but in the second-stage flash tank, the value of R rises to 0.185. The concentration of $CO_3$ can be derived from equations (6) and (53), which is a total fluid basis. The amount of non-Henry's Law $CO_2$ yielded (eq 6) is smaller than the $CO_3$ by the gravimetric factor 44/60.

$$CO_2 = \frac{44}{60}\left[\frac{500\ R}{1 + 2\ R}\right] = 45 \text{ ppm} \qquad (53)$$

On a "net steam" basis, the non-Henry's Law $CO_2$ contribution is 398 ppm, about 150% of the residual Henry's Law $CO_2$. Both sources together yield a $CO_2$ concentration in the steam of 660 ppm (0.66%).

Note: The calculation so far has not accounted for $CO_2$ generated by formation of $CaCO_3$ nor that solubilized by ammonia.

Question: How much $CaCO_3$ scale will deposit (in an unprotected system) and where will it be located?

Scale deposition could be estimated by constructing a map for calcium as described in a previous section. An alternative method yields an easily calculated approximation.

Eq (33) can be recast as (33r) and the ratio of current/initial Ca concentrations written as eq (54).

$$Ca = \frac{K_{sp}\ (1-2R)}{BcR} \qquad (33r)$$

$$\frac{Ca_i}{C_o} = \left[\frac{R}{K_{sp}}\right]_o \left[\frac{K_{sp}}{R}\right]_i \qquad (54)$$

The activity coefficients can be ignored because in (54) they occur as a ratio which varies little compared to the ratio of Ca concentrations.

Values of $Ca_i/Ca_o$ were calculated and are listed in Table 6 and plotted in Figure 16. The results suggest the Ca precipitates from the fluid only a little less fully than $CO_2$ is exsolved.

These results assume that "equilibrium" is sustained during flashing, in the sense that $CaCO_3$ deposition keeps pace with the buildup of its supersaturation. Accepting that, one could conclude (Figure 16) that about 93% of the $CaCO_3$ would precipitate in the early-flash equipment and most of the rest in the first-stage separator. This would amount to about 18.6 and 1.4 ppm $CaCO_3$ respectively, in those two places. For a throughput of 10.6 million pounds of total fluid per hour (60 Mwe plant), that would amount to 198 and 15 pounds of $CaCO_3$ per hour respectively.

Consideration of nonequilibrium should be given to the processes described in Figure 16. For example the actual processes for $CO_2$ exsolution and $CaCO_3$ deposition may lie (in the map) somewhat to the right of the equilibrium curves. To the degree one has insight into this issue, a counterpart line for $CO_2$ exsolution could be sketched into the graph. Subsequently, a counterpart of Table 6 could be calculated based on the sketched $CO_2$ estimate. In this way effects in (or demands on) equipment could be considered based on "describable" nonequilibrium responses of the fluids.

The deposition of $CaCO_3$ is concommitant with emission of a third increment of $CO_2$(g) according to eq (40) and (55), bringing the total $CO_2$(g) in the turbine stream to 737 ppm.

$$CO_2\ (calcite) = \left[\frac{8\text{ppm Ca}}{.113}\right]\left[\frac{44}{40}\right] = 78 \text{ ppm} \qquad (55)$$

For a nominal 60 Mwe plant with throughput of 1.2 million pounds of steam per hour, that $CO_2$ content would yield a pumping requirement of

about 9,400 cubic feet per hour. An additional allowance should be engineered for air leakages into the condenser.

B. Setting Depth for a Downhole Pump

The liquid pressure at the impellers of a rotating pump must be great enough to prevent development of vapor bubbles due to Bernoulli effects. A partial criterion for this effect is given by NPSH (net positive suction head), essentially the minimum submergence depth of the pump's intake. The NPSH is a design feature of a pump and it is larger for greater pumping rates. The NPSH of a pump generally is specified on the presumption that the liquid's density and vapor pressure are that of cool water.

Geothermal liquids may be substantially less dense than water and the vapor pressures are large and often augmented by dissolved gases. Additionally, pumping liquid from the deep reservoir causes a fall (drawdown) of the column of static liquid in the annulus of the well which is in connection with the pump's intake. Selecting a setting depth for a geothermal downhole pump must account for all of those effects (NPSH, density, water vapor pressure, dissolved gases, and drawdown). NPSH and density are the least significant. (Nominal values for NPSH are in the range of 15 to 50 feet of water head.) Additionally, selection of a setting depth should anticipate changes in well (reservoir) characteristics over the lifetime of the installation.

FIGURE 17
COMPONENTS OF SETTING DEPTH FOR A DOWNHOLE PUMP

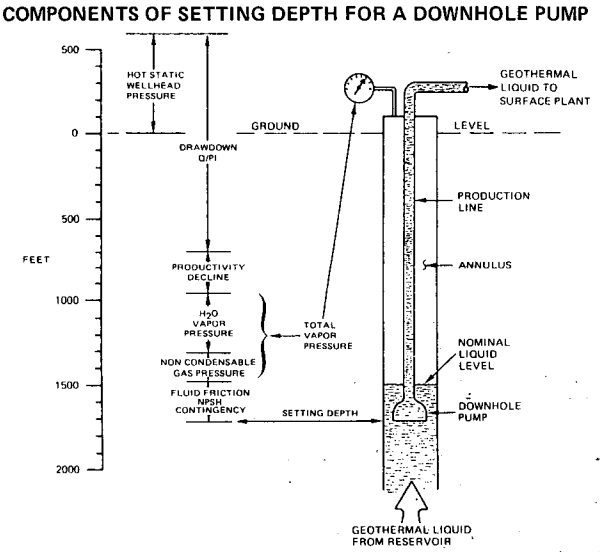



Figure 17 shows the context of this problem for a fluid described by Table 4; the objective being to assure that the submergence depth (D) times the fluid's specific gravity never is less than the NPSH. In a geothermal case, the annulus will be sealed to prevent discharge of water vapor that could come from boiling at the liquid level. Consequently, the pressure in the annulus, measured by a gauge at the wellhead, would indicate substantially the vapor pressure of the superheated liquid (slightly less due to the weight of the vapor column).

The position of the liquid level is due mainly to depression by the vapor pressure and drawdown due to the effect of pumping. The drawdown commonly is expressed as a pressure as in equation (56).

$$\frac{Q}{PI} = \text{Drawdown} \qquad (56)$$

The production rate is Q, and PI (productivity index) is a property of the reservoir which has the units mass/hr per unit of drawdown pressure. Values of PI for commercial wells range upward from X00 lb/hr per psi to X000 lb/hr per psi. Reservoir engineers reference the drawdown to the elevation of the producing zone in the well. Thus, the drawdown referenced to the pump's intake will be larger than given by eq (56) due to the friction (head) losses between production zone and pump intake.

For this example consider the fluid described in Table 2 at a temperature of 350°F, Q = 500,000 lb/hr, and PI = 1,000. Drawdown can be calculated by eq 57.

$$(144\ \text{in}^2/\text{ft}^2)(500\ \text{lb/in}^2)$$
$$(.01799\ \text{ft}^3/\text{lb}) = 1{,}296\ \text{ft} \qquad (57)$$

The third term in parentheses is the specific volume of water at 350°F, given in steam tables.

The several factors which are summed to establish the setting depth can be set out as in Table 5, wherein the entries can be calculated analogously to eq (57).

TABLE 5
COMPONENTS AFFECTING SETTING DEPTH OF A DOWNHOLE PUMP

| | ITEM | PRESSURE | EQUIVALENT DEPTH |
|---|---|---|---|
| 1. | Drawdown | 500 psi | 1,296 ft |
| 2. | Fluid Friction Below Intake | 15 | 39 |
| 3. | $H_2O$ Vapor Pressure | 134.6 | 349 |
| 4. | $CO_2$ Pressure | 37.7 | 98 |
| 5. | Non-$CO_2$ Gas Pressures | 26.4 | 68 |
| 6. | NPSH | | 50 |
| 7. | Hot Static Wellhead Pressure | -230 | -597 |
| | SUBTOTAL | | 1,303 |
| 8. | Forecast Decline in Reservoir Pressure | 100 | 259 |
| 9. | Contingency | | 150 |
| 10. | Recommended Setting Depth | | 1,712 ft |

Item 7: Hot static wellhead pressure is the difference between reservoir pressure and the weight (pressure) of the hot geothermal liquid in the production column beneath the wellhead. A positive wellhead pressure diminishes the requirement for setting depth.

Item 8: Decline in reservoir pressure would come from a reservoir engineering study beyond the scope of this report.

Item 9: Contingency can be based on several factors, among them, uncertainty in any of the values in the table.

Note that values for the Henry's Law pressures of $CO_2$ and non-$CO_2$ gases reflect their buildup over the longer term. As operations continue one should expect the gases to build up because the "static" annulus is in communication with freshly produced liquid. The values in Tables 2 and 5 identify upper limits for the gas pressures that would be approached closely by a long-term operation. The buildup of non-$H_2O$ gases would be manifest as an excess pressure beyond that corresponding to $H_2O$ at the wellhead temperature.

C. Depth of the 2-Phase Zone in a Flowing Well

The concept of flash pressure leads to a simple way of estimating where, in a geothermal bore, the transition will occur between 1-phase and 2-phase flow. It is relevant to point out that the flash pressure is a property of the fluid, not of the wellbore nor of the flow within it. Thus, all the processes involved with mass transfer above the point of initial flashing can be disregarded for fundamental reasons. They are only indirectly related, if at all, to the flash pressure.

One can thus readily recognize that if the wellbore processes are viewed from the well bottom upward rather than from the wellhead downward, the position of the flash point can be identified without regard to events or processes in the 2-phase zone. Thus, it is sufficient to consider the pressure in the reservoir $P_f$, less the drawdown Q/PI, as being due to the vapor pressure at the point of flash ($P_v$), the weight of the 1-phase column ($\rho H$) between the point of flashing and a reference level in the reservoir, and 1-phase flow friction (fH) below the point of flashing, as in eq. (58) and Figure 18:

$$P_f - Q/PI = fH + P_v + \rho H. \qquad (58)$$

In eq (58), Q represents flow rate, PI the productivity index (units of mass per time per unit of drawdown pressure), $\rho$ the fluid density, H the height of the 1-phase column above the reservoir, and f the frictional pressure drop. The depth of the 2-phase zone is simply the difference between the depth of the well, measured from the wellhead, and the 1-phase height, H.

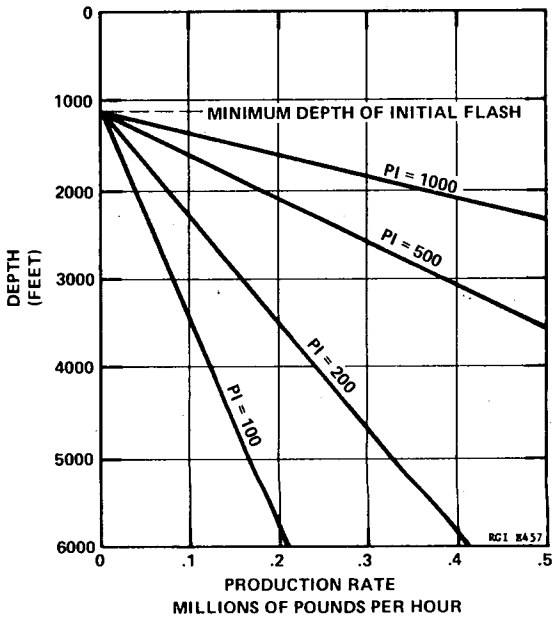
A useful reference height can be obtained from eq (58) by setting Q = 0 in which case also f = 0. It is not intended here to make that context refer to a shut-in condition of the well but rather to a special conceptual condition. Namely, consider the wellbore and the fluid within it to be fully heated, that is, to be at the temperature resulting from a stabilized period of flow. Applying eq (58) to this (fictitious) condition yields a maximum value for H (minimum depth of 2-phase zone), as in eq 59.

$$H_{max} = \frac{P_f - P_v}{\rho} \qquad (59)$$

Figure 18 is a graphical solution to the problem of finding flash depth, as a function of production rate. The value of H for Q = 0 is an important reference. A line drawn from that point describes the desired relationship once a productivity index (PI) is available. Wellbore friction causes only a minor deviation from the slopes of lines in Figure 18 which represent a range of PI values.

FIGURE 18

FLASH DEPTH VS PRODUCTION RATE




FLUID PROPERTIES:

TEMP. 400°F

$CO_2$ CONTENT 0.5%, PRE-FLASH

SALINITY EQUIVALENT TO 15% NaCl

DENSITY 0.98 g/cm$^3$ AT 400°

$P_{H_2O}$ = 223 PSIA

$P_{CO_2}$ = 320 PSIA

RESERVOIR PRESSURE
2600 PSI STATIC
AT 6000 FT.

$$H_{MAX} = \frac{2600-223-320}{(.98)\ (.433)} = 4847$$

DEPTH TO FLASH POINT
AT "ZERO" FLOW RATE
6000-4847 = 1153

For very hot wells or wells with high concentrations of $CO_2$, the value of $P_v$ may be over 1,000 psig. Such wells will have 2-phase zones that are thousands of feet long especially if their productivity indices are small. In one case near the Niland KGRA, the 2-phase zone was found to be more than 5,900 feet long. The vapor pressure at the point of flashing was 1,040 psia, 345 psi above the brine vapor pressure of 695 psi. The hot liquid density was 0.96 g/cm$^3$. The actual depth of flashing was 825 feet deeper than would have been predicted by a model of wellbore flow that ignored the non-condensable component but was otherwise accurate.

The $CO_2$ content of that unflashed liquid was 0.6% by weight, a value intermediate among geothermal resources. Thus, if one ignores the pressures of non-condensable gases, one can expect 1,000-foot sized mismatches between forecast and actual depths to flashing.

## VII. NOTES ON CONTROL OF CARBONATE SCALES

Calcite and aragonite are the most common and may be related as in the equations below.

$$Ca^{+2} + 2HCO_3^- \rightarrow CO_2 + H_2O + CaCO_3 \text{ (calcite)}$$

$$Ca^{+2} + CO_3^= \rightarrow CaCO_3 \text{ (aragonite)}$$

Both minerals may form at the same time in the same fluid stream, but their places of deposition on pipe surfaces are not the same. Aragonite is associated with deposition from more advanced stages of flashing wherein the $CO_3/HCO_3$ ratio has increased and the pH is higher than in early stages (Michels, 1980).

Other carbonate minerals are possible, siderite ($FeCO_3$), rhodochrosite ($MnCO_3$), witherite ($BaCO_3$), strontianite ($SrCO_3$), but these are generally found only as trace materials. Some of the cations can substitute for Ca in the mineral structures; for example Sr or Ba in aragonite and Fe or Mn in calcite. Magnesium generally is too scarce in geothermal fluids to be important in scales. The remainder of this report will deal with only the calcite and aragonite.

Several principles of scale control are possible, but not all are equally practical in the geothermal context. They may be described as:

1. Reducing Ca chemical activity through sequestering Ca(aq) into a soluble complex ion.

2. Reducing availability of $CO_3^=$ by:
   a. adding strong acid to make a conversion to $CO_2$(g)
   b. adding $CO_2$ to the system, converting $CO_3^=$ and $CO_2$ to $HCO_3^-$
   c. inhibiting the conversion of $HCO_3^-$ to $CO_3^=$

3. Interfering with the crystal growth processes at the crystal surface.

4. "Preserving" low pre-flash concentrations of $CO_3^=$.

Methods 1 and 2 operate on materials dissolved in the liquid phase. To be effective they must be applied upstream of the point of flashing and applied in a quantity (concentration) proportional to that of the native component on which they operate. Their initial cost is mainly due to equipment used to inject liquids downhole and perhaps including a long tubing. Because downhole tubing is at a great risk of damage followed by expensive repair and shut-down time, the risk deserves to be computed as a cost also. Chemicals for injection are an operating cost, and the continued operation of the plant thereby depends on continued availability as well as continuous monitoring/maintenance.

Method 2b has the advantage of recycling the $CO_2$ which is produced along with the geothermal fluid, thereby capturing a supply of chemical and eliminating one operational cost (U.S. Patent 3,782,468 Kuwada). Also, the injection of $CO_2$ combined with a high wellhead pressure gives a gas-lift effect that can increase the productivity of the well if injection is sufficiently deep (U.S. Patent 4,189,923 Berg). Both versions of this technique require a subsystem to separate $CO_2$ from the flashing fluid and pump it back downhole. Since $CaCO_3$ will deposit at the point of $CO_2$ separation, the technique amounts to displacing the scale deposits to locations where they are more easily handled, not permanently inhibited. A scale inhibition system at the point of $CO_2$ separation is one option.

Method 3 depends on specially formulated molecules that attach to the surface of $CaCO_3$ crystals and interfere with the mechanisms required for placing additional Ca or $CO_3$ onto the crystal structure. The most successful of these are derivatives of phosphoric acid, known collectively (and colloquially) as phosphonates.

Eventually (in a statistical sense) the phosphonate molecules will detach from the crystal surfaces or be overgrown by $CaCO_3$. When either of those happens, growth continues in an ordinary way.

Fortunately, concentrations of phosphonates can be very small in the fluid in order to sustain a functional population on the crystals. Concentrations of 1 ppm in the liquid are effective under some circumstances (Vetter and Campbell, 1979). This is equivalent to one phosphonate molecule (in the liquid) per 100 Ca ions there. By comparison, Method 1 would require nominally one sequestering molecule per Ca ion in order to be similarly effective.

Equipment for placing crystal growth inhibitors into the pre-flash liquid is superficially the same as for methods 1 and 2 but can be physically smaller due to the lesser volumes of injectate required.

Geothermal (pre-flash) temperatures strain the chemical stability of all the scale inhibitors. One aim of current development is to make functional molecules that have the required thermal stability. The crystal growth inhibitors, e.g., phosphonates, demand a second kind of thermal stability as well, vis. resistance to simple desorption from the crystal surfaces.

Method 4 can be described by reference to the chemical maps. All no-flash processes follow a map line parallel to the one shown in Figures 7 through 10. This approach is chemically effective. Compared to a simple flash system these costs of scale control are partly those of a downhole pumping system plus heat exchanger and working liquid. However, a downhole pump increases output from a well, so the true cost of this scale inhibition method may be difficult to define.

## VIII. CONCLUSIONS

Geothermal fluids are not simply another source of steam or hot water; those who treat them as if they were cause a peril for all the geothermal projects they touch. Bicarbonate-rich geothermal liquids exhibit a multitude of chemical reactions while steam and volatiles are flashing from them. For purposes of geothermal engineering and interpretation of analytical data there are practical reasons to consider those reactions as processes, linked through the nature of the pre-flash liquid and the circumstances which attend the flashing. Cause-effect within this reaction web hinges mainly on interconversions among $CO_2$, $CO_3$, and $HCO_3$ which depend on temperature and the degree to which the vapors are confined as they issue from the liquid during flashing.

In this system, the heavyweights are $CO_2$ and $HCO_3$. Their abundance dominates all the reactions in which they participate. For example, pH is physically dependent on the $CO_3/HCO_3$ ratio; $CaCO_3$ deposition depends on the buildup of $CO_3$ which in turn depends mainly on the pre-flash $HCO_3$ content and residual $CO_2$ pressure, and minorly on the liquid temperature. The exact mathematical dependencies vary among resources accordingly as the ratios of key components vary among them. This cause/effect kind of dependency is physically real because most of the reactions are irreversible.

During flashing, the several processes exhibit definite, yet coordinated patterns of behavior. The starting times, times of peak activity, and ending times for the describable processes are not synchronized. Moreover, the pattern of waxing and waning that occurs with one resource is not the same as for another resource which has different (initial) proportions of reactants. Consequently, astute engineering of geothermal hardware demands that each resource be quantitatively characterized for the details of its chemical behavior. In this way, the energy extraction processes can be optimized for the specific complications the resource presents.

$CO_2$ and carbonate chemistry are only one class of chemical complications presented by geothermal fluids. $CO_2$ pressures, especially when large, force themselves into design criteria for well casings. In exploratory wells, casings must be selected before the well yields fluids which may be analyzed for $CO_2$ content. Casing selection for development wells leans on earlier results from wells already complete, so that the emphasis on $CO_2$ shifts toward finding the patterns of variation across the field and forecasting changes with time. Deposition of $CaCO_3$ scale, how much, and where within the flashing process it will and will not occur can be studied for similarly practical ends.

The best reference condition for correlations and interpretations is the pre-flash liquid--a substance seldom sampled and perhaps impossible to sample with the thoroughness required for the study of patterns mentioned above. However, all characteristics of the pre-flash liquid can be deduced from sampling the steam and residual liquid, working backward upon the chemical processes. This report provides a structural model for those chemical processes.

For a new resource, geochemical engineering aims to give numerical calibrations to all the parts of the model that are relevant to the chemistry of the resource and the set of alternative means for its development.

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