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CARBON DIOXIDE IN GEOTHERMAL FLUIDS

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Abstract

The concentration of carbon dioxide has been measured for the four production wells at the East Mesa Geothermal Test Site. The effect of flashing on the equilibria are discussed. The solubility product constant, K_{sp} , for CaCO_3 is calculated at bottom hole temperatures.

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INTRODUCTION

Carbonic acid and its ions are involved in an extraordinary number of industrial, geological, and biological processes. At a geothermal site, the concentration of CO_2 in the brines is of importance both fundamentally and practically. Such information can contribute to an understanding of the geology of the formation, and from a practical view it can contribute to control of carbonate scale which can be pronounced when these fluids are flashed.

The purpose of the present communication is to report: (1) the concentration of CO_2 in the four production wells at the East Mesa Geothermal Site; (2) the mechanism of $\text{CO}_3^{=}$ formation during flashing; (3) the K_{sp} of CaCO_3 at bottom hole temperatures.

The four wells at East Mesa are:

Well	6-1	6-2	8-1	31-1
Bottom hole Temp °C	200	190	180	160
TDS	26000	5000	1600	2900

RESULTS

Both flashed and unflashed brine was obtained at the wellhead during well flow. Mesa 6-2 had been flowing for several months; Mesa 6-1 had been

flowing for several days at a low flow rate; Mesa 8-1 and Mesa 31-1 were flowed through a 2" line for 24 hours. Unflashed brine was taken through a cooling coil; the temperature of the collected brine was 26°C (79°F) indicating efficient cooling. One sample was taken directly for pH and alkalinity measurements. Another sample was collected in 400 ml of caustic, with brine introduced under the surface of the NaOH solution, to a total of 800 ml of solution for CO₂ concentrations. The cooling coil was then removed, 800 ml of flashed fluid was collected, and 400 ml of this sample was poured into a bottle containing 400 ml of caustic, followed by mixing. The hot solutions were cooled to ambient temperature, and all samples were immediately measured for pH and titrated for alkalinity using the standard P and M end points.

It is customary to represent all aqueous carbon dioxide as H₂CO₃ and to use the dissociation constants of the acid in equilibrium calculations. The equilibria of interest are:

and the sum of (III) and (IV) leads to:

The equilibrium constants are taken from the "Handbook of Physics and

Chemistry". Collection of the brine in caustic will convert all CO_2 and HCO_3^- via equations (III) and (IV). From the alkalinity titrations one can calculate the total CO_2 in solution as well as the pH. The total recovered OH^- obtained from the titration may be compared with the known concentration of the caustic used, and the calculated pH may be compared with the measured pH. Both of these comparisons are a measure of the confidence level of the results obtained. The pH is calculated from equation (I) using the measured $[\text{HCO}_3^-]$ with the carbonic acid concentration

$$(VII) \quad [\text{H}_2\text{CO}_3] = [\text{CO}_2]_{\text{total}} - [\text{HCO}_3^-]$$

This is the value designated as "Free" CO_2 in Table I where the results for unflushed brine are given.

Table I

Well	CO_2 ppm		OH^- % recovery	pH	
	"Free"	Total		meas.	calc.
6-1	>1500	>1700	88	5.63	5.55
6-2	1214	1544	99.7	5.75	5.81
31-1	603	1090	101	6.25	6.27
8-1	282	515	97.0	6.28	6.28

Well 6-1 contained so much CO_2 that it was not possible to absorb all of it in caustic. That is, while no steam was observed, bubbles of gas were seen rising and escaping from the caustic solution. Increasing the depth of the collection solution some 4-5 times did not prevent the escape. Further,

during collection of this "unflashed" brine a precipitate was formed. The precipitate was collected dried and weighed 0.1478 gm. Of this, 0.0046 gm was insoluble in HCL. Therefore, the carbonate portion is 0.1432 gm. Assuming that CaCl_2 was formed during the HCL treatment, the soluble material was dried and weighed 0.1630 gm. The $0.1630/0.1432 = 1.138$, in reasonably good agreement with the ratio of the molecular weights $\text{CaCl}_2/\text{CaCO}_3 = 1.11$. Therefore, it was assumed that the precipitate was CaCO_3 and calculations made on that basis. The total OH^- recovery was 88% indicating that not all of the precipitate was recovered. Therefore, based on this and the observation of escaping CO_2 , only a "greater than" value may be given for well 6-1. For these reasons no attempt was made to collect and analyze flashed 6-1 brine as has been done below for the other three wells.

Flashed Brines

The flashed brines were analyzed in the same manner as the unflashed systems. The total CO_2 in the flashed systems of wells 6-2, 31-1, and 8-1 amounted to 1214, 572, and 343 ppm, respectively. Well 6-2 showed a small amount of CO_3^{--} , and the per cent caustic recovered ranged from 98.4 to 101. Thus, it is tempting to again calculate the pH via equations (I) and (VII). Very poor agreement is obtained. If the measured pH is used and the $[\text{H}_2\text{CO}_3]$ is calculated, the carbonic acid concentrations for the three flashed systems are all near $8 \times 10^{-5}\text{M}$, much smaller than that when equation (VII) is used. This will be commented on below.

The flashed systems reach a pH near 8.3, and any mechanism for flashing must account for the increase of pH and carbonate ion production concomitant with the loss of carbon dioxide during the process. The sudden release of CO_2 (and therefore reduction in H_2CO_3) momentarily leaves the system with a

disproportionately high concentration of HCO_3^- than required by equation (I).

The bicarbonate ion then undergoes hydrolysis and disproportionation reactions

Consideration of these two reactions leads to

$$\text{(X)} \quad [\text{H}_2\text{CO}_3] = [\text{OH}^-] + [\text{CO}_3^{2-}]$$

Using the appropriate equilibria K_1 , K_2 , and K_w yields

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{K_1} = \frac{K_w}{[\text{H}^+]} + \frac{K_2[\text{HCO}_3^-]}{[\text{H}^+]}$$

$$[\text{H}^+]^2 = \frac{K_1 K_w}{[\text{HCO}_3^-]} + K_1 K_2$$

$$\text{(XI)} \quad [\text{H}^+]^2 = \frac{4.45 \times 10^{-21}}{[\text{HCO}_3^-]} + 2.1 \times 10^{-17}$$

Table II lists the pH values calculated along with the measured bicarbonate concentrations and pH.

Table II

Well	HCO_3^- meas.	pH	
		meas.	Eqn (XI)
6-2	$8.54 \times 10^{-3} \text{ M}$	8.35	8.31
31-1	5.8×10^{-3}	8.27	8.30
8-1	1.15×10^{-2}	8.48	8.31

Using the development for equation (XI) the carbonic acid concentrations are calculated to be in the range $6 - 13 \times 10^{-5}$ M, in good agreement with the values near 8×10^{-5} M discussed above. This is a further indication for the correctness of the suggested mechanism for flashing.

The Solubility Product, K_{sp} , for CaCO_3

In the following discussion activities are not considered - the salinities of these wells are relatively low. The solubility product is reported by Homer (1) for temperatures up to 80°C . Using seawater data, Standiford (2) has extended these to 125°C . In Figure 1 these are the solid line and broken line, respectively. The dashed line is a further extrapolation for the following discussion.

In the geothermal aquifer, the equilibria of the solubility product

$$K_{sp} = [\text{Ca}^{++}] [\text{CO}_3^{--}]$$

and equation (II) coexist.

$$K_2 = \frac{[\text{H}^+] [\text{CO}_3^{--}]}{[\text{HCO}_3^-]}$$

A simple manipulation yields

$$[\text{Ca}^{++}] = \frac{K_{sp}}{K_2} \cdot \frac{[\text{H}^+]}{[\text{HCO}_3^-]}$$

The ionization constant K_2 is a function of temperature and has been given by Homer (1) for temperature up to 80°C . These have been extended by Standiford (2) to 125°C using data for seawater. A further extrapolation of these data indicate a variation from 5.3×10^{-11} for the hottest well at East Mesa to a value of 6.2×10^{-11} for the coldest well. Therefore, the ambient value of

5.6×10^{-11} will be used to calculate the Ca^{++} concentrations in each well using the dashed line extrapolation in Figure 1 for K_{sp} and $[\text{H}^+]$ and $[\text{HCO}_3^-]$ as measured in the unflushed brines. Table III compares these calculations with the measured values of $[\text{Ca}^{++}]$. It also lists the K_{sp} calculated using the measured concentrations of Ca^{++} , H^+ , and HCO_3^- .

Table III

Well	Temp °C	Ca^{++}		Ratio ($\frac{\text{meas.}}{\text{calc.}}$)	K_{sp} calc.
		meas.	calc.		
6-1	200	$3.4 \times 10^{-2} \text{ M}$	$3.8 \times 10^{-4} \text{ M}$	90	8.75
6-2	190	4.1×10^{-4}	4.4×10^{-5}	9	9.65
8-1	179	2.12×10^{-4}	5.6×10^{-5}	4	9.82
31-1	163	2.32×10^{-4}	4.1×10^{-5}	6	9.48

Since the calculated values of Ca^{++} are in remarkably good agreement with the measured values using the extrapolated values of K_{sp} , the calculated K_{sp} may be meaningful and indicate a either reversal in the temperature effect on solubility near 180°C or sources of Ca^{++} other than considered. It may be noted that the discrepancies follow the TDS values of the wells, therefore in all probability the K_{sp} are close to the extrapolated values.

References

- (1) Homer, "Industrial Water Treatment Practice", Buttersworth, London 1961.
- (2) Standiford, F. C., "The Carbonate - Bicarbonate - Carbon Dioxide System in Seawater", Distillation Digest, 6, 17(1972).

Figure I. Solubility product constant of calcium carbonate.