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A CHEMICAL METHOD FOR MEASURING STEAM QUALITY IN TWO-PHASE FLOWLINES

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ABSTRACT

Brine-free steam and steam-free brine were obtained from a flowline in which a temperature (pressure) cascade was set up in a series of four pipe spools separated by orifice plates. The full flow of the well was carried in this test section, but the temperature, pressure, and steam fractions were different in successive spools. The test section was insulated except at the sample point take-offs. By using natural carbon dioxide as a tracer in the steam and chloride as a tracer in the brine, the steam fraction in each sampling spool was determined entirely from the data on concentrations.

The required efforts for sampling, analysis, and computation were considerable, but the results were remarkably precise. As a bonus, some data on heat capacity was extracted that relate to the thermodynamic differences between pure NaCl and mixed-salt brines. Notably, the heat capacity of the mixed-salt hypersaline brine is less than for pure NaCl brines of comparable concentrations.

INTRODUCTION

For the Salton Sea Scientific Drilling Project (SSSDP) well, State 2-14, 9-5/8 inch casing was installed to 6000 feet on December 14, 1985. Drilling continued to 6227 feet, from where, on Dec. 22, it was decided to perform a flow test. Flow began on the evening of Dec. 28, with fluid sampling by more than 20 geochemists on Dec. 29-30. This report describes one element of the sampling/analysis effort -- determining the extent of steam development from the brine at each of four sampling ports on Dec. 30.

Brine sampling that involves two-phase flow must be supported by measurements of steam fractions. However, the Bechtel-DOE design for the

surface facility denied full-flow steam separators, and with them, the traditional mechanical rate measurements of steam and brine. Although a James tube was to be used to characterize the fluid, its potential success was limited because there are no adequate correlations for the hypersaline brines. Also, the Salton Sea brines are prone to severe scaling and salt deposition that could foul the James tube apparatus, as well as atmospheric sampling methods.

Accordingly, a method was used that involved a series of pipe spools as a test section for the full flow of the well. The system is diagrammed in Figure 1. Flowline and test spools were made of 10-inch diameter line pipe. Test spools were ten feet long. Flow rate during sampling was about 200,000 pounds per hour, total flow, and all of it was passing through the test section during sampling. The spools were separated by orifice plates so that a temperature (pressure) cascade was set up in them. Sample points were less than three feet above the downstream orifice plates. In-line separator devices were provided for the extraction of brine-free steam and vapor-free brine. They differed from the description in (1) by having separate entry to the brine phase at a 6-o'clock position. Additionally, a portable Webre separator was used on the steam side to assure separation from brine. The brine and steam were sampled for chloride and carbon dioxide, respectively, which served as natural tracers. Their apparent concentrations were different in successive spools in proportion to the increments of new steam.

Concentrations of Cl in brine and CO₂ in steam were determined using special techniques to obtain especially high precision and accuracy. Those concentrations were then used in a novel computational method which yields the weight fractions of steam in the two-phase conditions within each pipe spool of the series. Presenting that procedure is one objective of this report.

MICHELS

Part of the principle of this method was shown in (2) and (3), but they differed by (i) using only two steps in the T-P cascade, and (ii) using temperature-enthalpy (T-H) relationships to compute the increment of steam flash between sample points.

For the Salton Sea brines, T-H relationships are not sufficiently known for that approach to succeed. Observing the incremental chloride concentrations for two steps in a cascade (three sample points) is somewhat equivalent to learning the T-H relationship. In this case, four test spools provided redundancy, to assure that at least three sample points could be observed that had a reasonably large separation of temperature. In this case, all four worked, and the redundancy provided statistical weight.

SAMPLING AND ANALYSIS

Stainless steel probes were inserted through valves of the in-line separators to tap zones of single-phase liquid. Sampling procedures and other analytical results are described elsewhere in his volume (4). Probes were integral with cooling coils and brine exited to the atmosphere without additional flashing. The exiting streams were caught in pre-weighed amounts of distilled water so that dilution brought the chloride concentration into the range of seawater. The exact dilution was determined by reweighing the mixture.

Field analysis for chloride was made by titration involving an oceanographic technique standardized with standard mean ocean water (SMOW). Field results were later verified in the lab by re-standardization of the titrant and additional analysis of brine samples that were preserved with acid. Accuracy of this method is about ±0.22% relative error for single measurements.

CO₂ assays in the vapor phase were made by the syringe method (5) modified to yield higher precision. Specifically, collections of gas and condensate were made into a fixed working volume of the syringe which was calibrated in the lab by weighing. Condensate collected in the syringe was transferred to tared bottles for weighing. Precision of these CO₂ assays is about ±1.2% relative error for single determinations, based on precisions of weighing and volume measurement. Results of the sampling and analysis are given in Table 1.

Table 1: CO₂ in Steam and Cl in Brine (measured ppm by weight)

Spool #	1	2	3	4
Conc. CO ₂	15524	10521	9432	8988
Cl	171720	181800	186900	188600

COMPUTATIONAL PATHWAY

The values in Table 1 refer to brines at unselected conditions of steam release. A principal objective is to express the Cl and CO₂ concentrations relative to a practical reference -- specifically the brine in its pre-flash condition. The concentration data in Table 1 are sufficient for this task. The conversion is easier to describe when the inverses of weight fractions are used, namely, 1,000,000/ppm.

The inverse (I) of a tracer weight fraction represents the amount of solution that accompanies a unit amount of the tracer. Inverse weight fractions for chloride in brine and CO₂ in steam are shown in Table 2 for the series of four sampling spools.

Successive decreases in the chloride inverses for the series represent the relative weights of water lost as steam between the sample points. Concomitantly, the CO₂ inverses in steam increase through the series of sample points, due to identically the same steam that affected the brine samples. Since the calculation of steam fractions from data of this kind appears not to have been reported earlier, it will be given here in detail.

Converting inverse concentrations, as sampled, to steam fractions on a basis of pre-flash brine, is a five-step process.

1. Compute steam fractions based on an intermediate brine (partly flashed) using the brine tracer.
2. Determine proportionalities between the steam fractions in step 1 and the incremental inverses for CO₂ in steam.
3. Use the results of step 2 to determine the steam fraction in the first spool on a basis of intermediate brine.
4. Convert all steam increments from Step 3 to a basis of pre-flash brine.
5. Sum the incremental steam fractions through the series of spools.

The steps are described in detail in the following paragraphs and the numerical values are given in Table 2.

For step 1, let subscript i, j represent sampling ports, with i being upstream (hotter). Then, the steam fraction $(S_{1,j})_1$ is the weight fraction of new steam released between ports i and j on the basis of i -Port brine, Equation 1.

$$(S_{1,j})_1 = (I_1 - I_j) / I_1 \quad (1)$$

For Step 2, let $IC_{1,j}$ represent the concentration inverses for carbon dioxide at the successive sampling ports. There is a $(IC_j - IC_1)$ for every $(I_1 - I_j) / (I_1)$. Each combination provides a separate estimate of the proportionality, K , in Equation (2). Three estimates are available when i refers to spool 1, and j refers successively to spools 2, 3, and 4.

$$K = [(I_1 - I_j) / (I_1)] / (IC_j - IC_1) \quad (2)$$

For Step 3, let subscript o refer to the pre-flash brine. Since there is no steam phase at that condition, IC_o is non-existent. Thus, steam fraction at the first spool is merely the proportionality established in Step 2 applied to IC_1 at the first spool. Equation 3 applies separately to each of the i, j pairs of spools. These could be averaged, or alternatively, the averaging could be done at Step 2.

$$(S_{o1})_1 = [IC_1] (S_{1,j})_1 / (IC_j - IC_1) \quad (3)$$

In Step 4, the steam fraction given by (3) is converted to a basis of pre-flash brine, $(S_{o1})_o$, by Equations 4a and 4b.

$$(S_{o1})_o = (S_{o1})_1 / [1 + (S_{o1})_1] \quad (4a)$$

The flash fractions for intermediate steps, computed from (1), are likewise convertible to a basis of pre-flash brine using the proportionality of (4a) in Equation 4b.

$$(S_{1,j})_o = (S_{1,j})_1 [(S_{o1})_o / (S_{o1})_1] \quad (4b)$$

Step 5 is the simple accumulation of incremental steam fractions (f) from the series of sampling ports, using a basis of pre-flash brine, as in Equation (5). Values for $(S_{o,j})_o$ represent the flash fractions (f_1) in the spools.

$$f_1 = (S_{o,j})_o = (S_{o1})_o + (S_{1,j})_o \quad (5)$$

The procedure above presumes that all the CO_2 tracer is in the vapor phase when actually from 0.2 to 1.8 percent was

still in the brine. This effect can be accommodated by iteration. The first set of flash fractions (f) computed from Eq. 5 can be used in Equation 6 to compute c_1 , the fraction of the total amount of CO_2 which is in the vapor phase.

$$c_1 = 1 / [RT_1(1-f_1) / f_1 V_e h_1 + 1] \quad (6)$$

V_e represents the specific volume of steam and h the Henry's law solubility coefficient for CO_2 at appropriate temperature and salt contents. The CO_2 solubilities used here were based on extrapolations from data given in (6) without allowance for non-sodium cations in brine.

In Equation 7, C_{M1} represents the measured concentrations of CO_2 and C_{T1} represents the concentrations that would have been observed if all the CO_2 were in the vapor phase. Values for C_{T1} are used in subsequent cycles of the iteration.

$$C_{T1} = C_{M1} / c_1 \quad (7)$$

Pre-flash concentrations of CO_2 , (C_P), are given by $C_{M1}(f_1) / c_1 = C_P$; each spool provides an independent estimate. Pre-flash chloride is given by $Cl_1(1-f_1)$, but all estimates are identical, they are not independent.

RESULTS

The values for each step of the above procedure are shown line by line in Table 2.

Table 2:
Computation of Steam Fractions

Spool	1	2	3	4	Eq.
Temp	455	395	346	328	
CO_2 MEAS	15524	10521	9462	8988	
Cl MEAS	171720	181800	186900	188600	
c_1	.98171	.99409	.99733	.99802	(6)
C_{T1}	15813	10584	9487	9006	
Inverses					
CO_2	63.239	94.486	105.40	111.04	
Cl	5.8234	5.5006	5.3505	5.3022	
$(S_{1,j})_1$.05545	.08122	.08950	(1)
$IC_j - IC_1$		31.247	42.165	47.801	
K		.001774	.001926	.001872	(2)
$(S_{o1})_1$.11221	.12181	.11841	(3)
$(S_{o1})_o$.10513*	.04962	.07268	.08009	(4)
$(S_{o,j})_{o=f}$.10513	.15474	.17781	.18522	(5)
Preflash Concentrations					
CO_2	1662.4	1637.7	1689.6	1668.1	
Cl	153668	153668	153668	153668	

* Average based on 3 estimates of $(S_{o1})_1$

The uncertainties in the computed steam fractions can be estimated from variations in the sampling results and other factors that are involved in error propagation. For $S_{01}=f$, these amount to about 2.2% relative error. Uncertainty in $(1-f)$ is less, between 0.24 and 0.42% relative error. This would be equivalent to about 400 to 600 ppm chloride, slightly more than the analytical uncertainty mentioned earlier. The computed CO_2 concentrations (1664±20 ppm) show a dispersion of about ±1.2% relative error, which is just what was expected, based on propagation of errors from sampling, etc., mentioned in the section on sampling.

ENTHALPY-TEMPERATURE RELATIONSHIPS

Having the data from three or four test spools permits extending results to the heat content of brine and steam. These data can be used to compute other important quantities, such as the effective preflash temperature and the enthalpy at other places in the wellbore.

The computational approach described next uses equations relating temperature and salt content to enthalpy of brine and enthalpy of steam-over-brine.

Equations for brine enthalpy, HB, and for heat of vaporization, HV, are given by Equations 8 and 9, which are based on (7). Units are Btu/lb of brine (Eq. 8) or per pound of steam (Eq. 9). Temperature is Fahrenheit, N represents weight percent NaCl in a simple brine, n is the multiplier that relates a mixed brine of N weight percent TDS and a simple brine with the same N-value. For solutions of pure NaCl, $n=1$.

$$HB = 0.36(T)^{1.14}[\exp_{10}(-.006Nn)] \quad (8)$$

$$HV = 1134 - (.7969)(T) + 2.482(Nn) \quad (9)$$

The enthalpy of total fluid, HF, is given by Equation (10).

$$HF = HB + (S_{01})_0 HV \quad (10)$$

It is asserted here that the mixed-salt geothermal brine properties follow equations essentially similar to those for pure NaCl, except for the values of coefficients for terms involving salt concentration. That is, any mixed-salt brine of a given gross concentration (based on TDS or chlorinity) has the enthalpy relationships of a specific NaCl brine, but with a somewhat different numerical concentration. For practical engineering purposes, the two concentrations are related by a simple multiplier, (n). Part of the task in the subsequent section is to deduce a

numerical value for (n) that applies to the mixed-salt geothermal brine.

Temperatures in the spools were determined by a platinum resistance thermometer. The probe was immersed in thermal wells, near the sample points, that had been filled with silicone oil. Using those measured temperatures in Equations 8-10 yields estimates of HF for each sampling port. The objective is to find a value for (n) which yields the minimum variance among the four estimates of (HF) that were associated with the sampling. Results are given in Table 3.

Table 3: Enthalpies of total Fluid

Spool	1	2	3	4
Temp °F	455	395	346	328
HF	346.7	352.6	348.6	347.0

$$\text{average HF} = 348.7 \text{ Btu/lb} \\ n = 1.37$$

the Mixed-Salt Effect

The n-value of 1.37 minimizes the sum of the squares of differences among estimates of HF that can be computed for Table 3. In computing HF from eq. 10, the mathematical effect of n is of opposite sign for the brine and vapor phases, but the effect on the brine is quantitatively dominant. This is because numerically, an increment of n has a larger effect on a unit weight of brine than on the heat of vaporization of steam. Also, in this system there is much more brine than steam.

The fact that n is larger than unity shows that the mixed-salt condition causes a more intense modification of the enthalpy of water substance than does pure NaCl. In terms of molecular and ionic processes, it appears that the non-sodium ions of the mixed-salt brine coordinate more strongly with the water molecules than sodium ions would have.

For expediency, the salt effect on thermodynamics of water is sometimes disregarded. Equations 8 and 9, which contain factors nN, may be used to show the error involved. The concept of different effects due to non-sodium cations is not new, but the factor (n) provides a concise way to describe it.

Since chloride is nearly the sole anion (>99% of the (-) charge), it is reasonable to view the mixed-salt brines as NaCl brines that have evolved through considerable sodium exchange (depletion) in water-rock reactions (8). Compared to a pure NaCl brine, the Na of these brines has been depleted by about 46 percent. This amount of substitution is

associated with the change of n from 1.00 to 1.37. Calcium is the most abundant non-sodium cation in these brines, followed by potassium, iron, and manganese (4).

Effective Pre-Flash Temperature

The preflash enthalpy of the previous section can be used in Eq. (8) to compute an apparent flash temperature. The result is 568°F. One would expect this computed temperature to be less than the measured temperature by several degrees due to heat losses from the wellbore, etc., which tax the evolution of steam prior to sampling. A flash temperature of 575°F was measured in the wellbore by Kuster tools at the end of the sampling period at a depth of 4500 feet. This difference of 7 degrees is relatively small compared to other experience. It corresponds to a heat loss of 5.2 Btu/lb of fluid or a heat loss rate of only about 230 Btu/hr per linear foot of wellbore. The actual heat losses were likely two to three times as great, thus alleging a discrepancy between the measured and computed flash temperatures. Whether it is in the measurement or in Equations 8 or 9 cannot be resolved with currently available data.

COMMENTS

In principle, other tracers besides chloride or CO_2 could be used. The practical requirements are that analysis be accurate in the range of concentrations involved. Using multiple tracers in single samples of brine and/or steam is feasible. Overall success of the

computation method is sensitive to the accurate functioning of all measurements. Loss of one data point effectively foregoes correlating with the remaining data points.

In application, sampling eight ports, four each of brine and steam, is an arduous and demanding task. Particularly, the CO_2 measurements are made in triplicate at each port and additional gas collections are needed to identify the non- CO_2 components of the gases before the computations shown in this report can begin. Overall, sampling, sample preparation, and analysis required 6 to 8 man-hours of time by two teams to deliver one set of steam fraction results. In principle, the effort could be reduced since the mathematical work can be completed with data from just three sample ports. However, that approach would not provide any redundancy for judging errors or other issues. Salton Sea wells provide a natural laboratory thermodynamics of mixed-salt brines.

ACKNOWLEDGEMENTS

I am grateful to Andy Campbell and Chris Measures of the MIT Department of Oceanography for the chloride analyses, to Al Truesdell for providing a portable cyclone separator, to Wilfred Elders for his confidence and motivation at all times, and to Bechtel Int and U.S. DOE for their reluctance to provide a steam separator, which precipitated the need for this approach. The work was performed through the University of California, Riverside, with support by NSF Grant EAR 8303557.

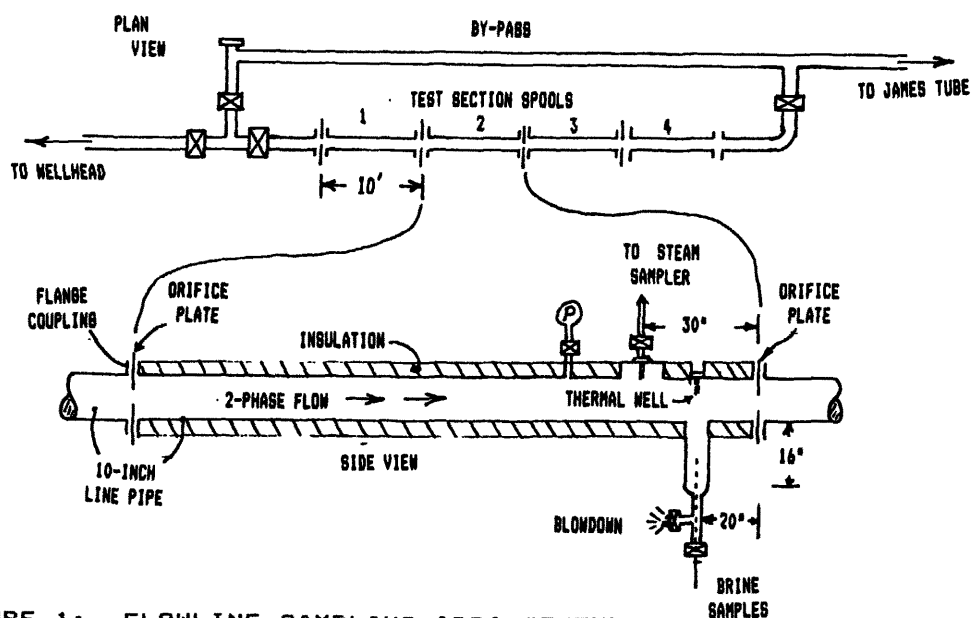


FIGURE 1: FLOWLINE SAMPLING ARRANGEMENT (DIAGRAMMATIC)

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