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SSSDP FLUID COMPOSITIONS
AT FIRST FLOW TEST OF STATE 2-14

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ABSTRACT

Brine and steam were sampled on December 29 and 30, 1985. A four-step temperature cascade was established in a test section of the flowline. In this way, enthalpy data could be obtained from the chemical data.

Brine compositions, on a basis of total flow, are computed separately for Dec. 29 and 30; total dissolved solids were 25.54+0.23 and 25.47+0.036 weight percent. Carbon dioxide and hydrogen sulfide were 1664+20 and 7.01 ppm, respectively, on Dec. 30. CO₂ and H₂S comprised about 98.5 mole percent of the suite of non-condensable gases. Data on other components are tabulated.

Effective pre-flash enthalpys were 335 and 349 Btu/lb on December 29 and 30, respectively. These correspond to temperatures of 548 and 567°F. The greatest observed steam yield was 18.5 weight percent at 328°F on Dec 30.

INTRODUCTION

The Salton Sea Scientific Drilling Project (SSSDP) well, State 2-14, was test flowed on December 28-30 from the interval 6000-6227 feet. The surface facility consisted mainly of 10-inch diameter flowline. It was equipped with a four step temperature cascade, with access ports for sampling liquids and gases at each step, and terminated with a James tube and a silencer. More than 20 geochemists participated in sampling and/or analysis of the brine, steam, and related materials. This report provides the reference composition of the fluids.

The general layout of the test sections is shown in a companion paper (1) which also describes the chemical method used to determine steam fractions in the temperature cascade.

Four insulated zones in a test section were separated by orifice plates in order to set up a cascade of temperature-pressure conditions. The full flow of the geothermal fluid passed through this test section. Individual steps in the cascade involved increments in steam yields of about 1 to 8 weight percent (total flow basis). This corresponds to about 7 to 70 relative percent on a basis of steam.

One objective of sampling was to follow tracers in the steam and brine phases with enough precision to quantify those steam increments. Key tracers were natural carbon dioxide in the steam and natural chloride in the brine. Another major objective was to characterize the brine composition in terms of major and minor elemental components.

STEAM FRACTIONS AT THE SAMPLING PORTS

For Dec 30, the steam fractions at the sampling ports were determined by a chemical method (1). Results are shown here without further explanation. In addition, that method yielded thermodynamic data for the mixed-salt brines. However, the totally chemical approach could not be used for the Dec 29 situation -- no data were obtained for CO₂ in steam. Instead, the steam fractions for December 29 were computed by combining the measured chloride values with the enthalpy relationships determined in (1). The principle is similar to the description in (2).

Results are shown in Table 1. The numbering of ports is retained from field designation. Port 3 was in the first test spool, Port 6 was in the fourth. Although brine and steam sampling points were physically different on each test spool, they are given the same port numbers.

In addition to the flash fraction results, estimates of the pre-flash brine

enthalpy are obtained. In the case for Dec 29, a preflash chlorinity of 153,688 ppm, obtained in (1) for December 30, is used to derive a pre-flash enthalpy value of 335 Btu/lb. This corresponds to an effective flash temperature of 548°F. This is lower than the estimate of 567°F for Dec 30, but not unreasonable considering that the well was still in the early warming stages on Dec 29.

The flash-temperature relationships for Dec 29 and 30 are given in Figure 1. Enthalpy-temperature-composition relationships found in this work show the mixed-salt hypersaline brines have significantly smaller enthalpies than pure NaCl brines (3) of comparable concentrations and temperatures.

TABLE 1:

STEAM FRACTIONS AT SAMPLING PORTS

Dec 29, enthalpy 335 Btu/lb				
Port	3	4	5	6
°F	431	373	327	309
Flash	.10700	.14621	.17288	.18166
Dec 30, enthalpy 349 Btu/lb				
°F	455	395	346	328
Flash	.10513	.15474	.17781	.18522

BRINE SAMPLING AND PREPARATION

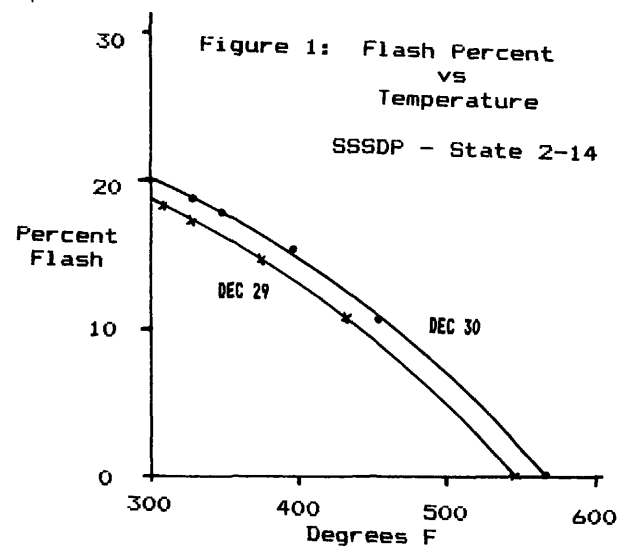
Two kinds of brine samples were taken, one for the chloride tracer and the other for general composition. Both were taken with the same port equipment but differed in sample handling procedures.

Brine sampling equipment is diagrammed in Figure 2. Welded to the 10-inch test spools and fully open to the two-phase flow inside, were downcomers of 4-inch diameter pipe which terminated in a system of access valves. The brine in the downcomer tends to deposit scale, so operating the blowdown valve assures that sampled liquid is relatively fresh.

A 1/4-inch (heavy wall) stainless steel tubing was passed through an access valve to tap the one-phase liquid that collected in the downcomer. The probe was integral with a section of 1/8-inch diameter stainless tubing, shaped into a coil and cooled in a water bath. Ice was used to prevent the cooling water from getting hot, but ice temperatures were avoided. A collection temperature of 100 to 140 F is considered ideal. Flow through the probe system was controlled by a valve on the cool end of the 1/8-inch tubing. Brine exited the probe

system as a jet into the atmosphere. Samples were collected by directing the jet into polyethylene bottles that contained pre-weighed amounts of diluents.

Samples for general composition were collected into 50-ml bottles that contained about 30 g of 0.1N nitric acid. Enough brine was collected to make the acid:brine ratio about 5:2. The brine stream from the valve spigot was caught directly in the sample bottle without pre-measuring the brine. This technique delivers the brine from hot flowline to sample bottle in just the few seconds of travel time through the tubing. The quick dilution and acidification are considered advantageous, especially for silica. Samples of hypersaline brines are stable for many months when collected in this way.



Dilution factors are determined by weighings to the nearest milligram on an analytical balance. They are accurate to better than +0.0001 (relative).

The acidified brine samples were reweighed in the DMA laboratory. Aliquots were taken and diluted further into 20 percent nitric acid. Subsequent analysis was by a commercial laboratory, mainly using inductively coupled plasma (ICP). Chloride was determined (independently from the oceanographic method) by titration, sulfate by turbidimetry, and ammonia by specific ion electrode.

The commercial lab results were based on volumetric standards (ppm = mg/l). These were converted to a weight basis (ppm = mg/kg) through density measurement of the 20 percent nitric acid carrier (1.145 g/ml) and the use of

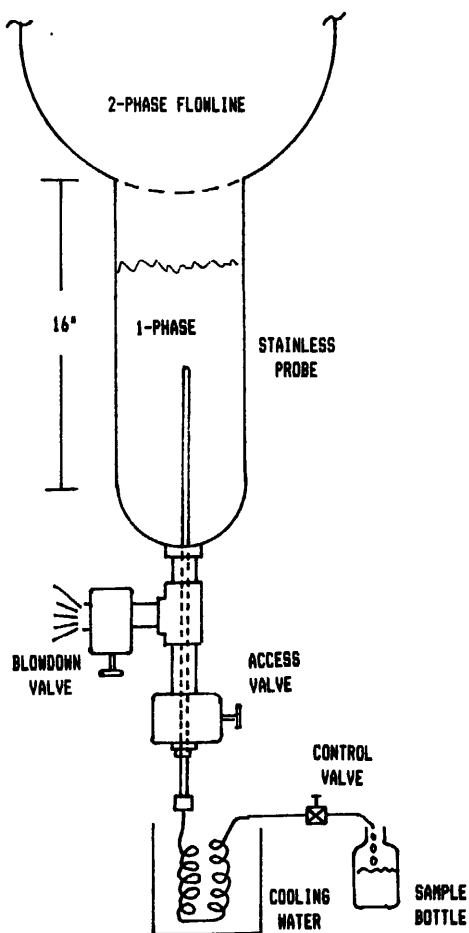


FIGURE 2: BRINE SAMPLING ARRANGEMENT

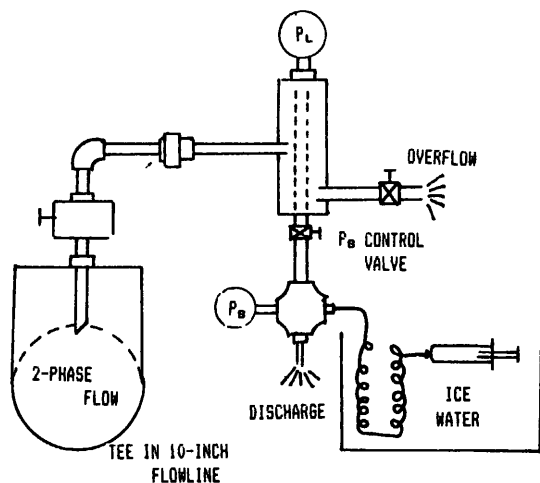


FIGURE 3: STEAM SAMPLING ARRANGEMENT

P_L = Line Pressure (to 450 psig)
 P_s = Syringe Pressure (12 psig)

weighings to determine the other dilution factors. Density of whole brine is near 1.2 g/ml, thus the distinction between mg/l and mg/kg is important. All concentrations referred to in this paper are on weight basis.

Samples for determination of the chloride tracer were collected similarly, except that about 100 g of distilled water was used and brine was collected to bring the mixture into the range of seawater chlorinity. (Chlorinity and chloride content are used synonymously in this report).

The mixture was reweighed and titrated immediately in a field laboratory by an oceanographic method that involved standardization by standard mean ocean water (4). Subsequently, in the home laboratory, (MIT), the titrant was restandardized and other acidified samples were analyzed. The final selected results are believed accurate to about ± 0.002 (relative), for single analyses. Replicate analyses yield proportionally better values.

GAS SAMPLING AND ANALYSIS

Brine-free steam samples were obtained through in-line separator devices built into the test spools. Because brine carryover occurred at some ports, a portable centrifugal separator was attached in series between the in-line separator and the gas sampling equipment. This arrangement (Figure 3) provided high quality steam samples and was used at all steam sampling ports.

Surging of pressure (and temperature) in the two-phase flowline was prominent, but steamside pressure was leveled by manual control of the steamside control valve. In principle, the surging is concomitant with incremental differences in flash fraction and hence composition of steam inside the separator. Cycle frequency in this case was about 4/minute, thus, the collections, which take 3 to 7 minutes, provided considerable averaging about the mid-range conditions.

Sampling and analysis for non-condensable gases in steam was done by a syringe method (5) modified to improve precision. A syringe clamp was used that set the working volume of the syringe to be the same for all samplings. The volume was standardized in the laboratory by weighing and calculating the temperature correction. Condensate was recovered into pre-weighed vials for re-weighing.

The principle of the syringe method (5) for CO₂ assay is to establish the pressure and volume of the gas and condensate at ice temperature. Then the amount of CO₂ in the condensate is given by the Bunsen coefficient (STP ml of gas per ml of liquid at 1 atm. gas pressure) and the gas equation is applied to the gas phase and the Bunsen volume to compute the total amount of CO₂. Calculation requires the absolute pressure of CO₂.

The non-CO₂ gases (nitrogen, methane, hydrogen, etc.) are normally determined with the CO₂ assay as an undifferentiated group. This provides data to compute a molar ratio of CO₂/non-CO₂ gases which in turn permits calculating the CO₂ pressure fractions in the other collections.

An alternative was provided by an independently determined composition of the gas mixture (6). Both compositions were used to compute CO₂ assays and each result was within the error limits of the other. The assay computations based on (6) are preferred and reported here.

Ammonia, present in the steam, is suspected to be dissolved in condensate upon formation of NH₄⁺ and HCO₃⁻ by reaction with CO₂. It involves no significant vapor pressure in the assay and the CO₂ consumed by ammonia is disregarded.

Hydrogen sulfide was determined in the mixture of condensate and NaOH obtained from the collection regarding the other non-CO₂ gases. The mixture is stabilized in the field with zinc acetate solution and analyzed in a lab by iodometry.

TABLE 2:

SUMMARY OF GAS CONTENTS

Port	3	4	5	6
Temp	455	395	346	328
Steam Fraction	.10513	.15474	.17781	.18522
CO ₂ (ppm)				
Steam	15524	10521	9462	8988
Total Flow	1662	1638	1687	1668
H ₂ S (ppm)				
Steam		46.2	38.3	
Total Flow		7.15	6.86	

Averages on a total flow bases:
CO₂ 1664±20; H₂S 7.01

ADJUSTMENTS TO BRINE CONCENTRATIONS

Analysis by ICP in a commercial laboratory provided the basic data for cations. Lab results are adjusted by the dilution factors and carrier densities to yield gross concentrations of field samples. These gross concentrations are susceptible to further adjustments that relate to electrical charge balance.

Chloride accounts for more than 99.9 percent of the negative charge in the brine composition. The precisions and accuracies of the oceanographic chloride values are the best in the entire data set. They are also considered to be unbiased. Thus, rather than simply reporting the size of the charge imbalance between cations and anions, the cation concentrations are adjusted to match the charge of the chloride. These adjusted values are considered to be the best available representation of the brine composition.

The overall bias of the cation analysis is given by summing the cation charges and comparing the result with the chloride. For ten samples, the average bias is +0.0262 of the chloride value and the standard deviation is 0.0106. No samples show a negative bias. Thus, the gross precision of the ICP data is better than the bias and an upward adjustment is warranted.

In making the charge balance, the relative precision of each individual cation was determined from replicate analyses. These relative precision values were multiplied by nominal concentrations of the respective cations to obtain an index. The total balancing charge needed was then assigned to each cation in proportion to its index. In this way, the more abundant components carried most of the charge adjustment and no adjustment of a single cation exceeded its own analytical precision. For example, sodium carried 0.427 of the charge adjustments and five components, Na, K, Ca, Fe, and NH₄⁺, collectively carried more than 0.94 of the adjustment.

FIELD COMPOSITION OF BRINES

The field compositions reported in Table 3 include the charge balancing procedure described above. Dilution factors, described earlier, are also incorporated. Averages are used where replicates were available (Ports 3, 4, and 6 on Dec 30).

There was no sample for Port 6 on Dec 29. The listing in Table 3 is based on the average of the other ports on Dec 29, with conversions made through the flash

fraction values as appropriate.

Sulfate determinations were made on two samples; Dec 30, Ports 3 and 4. Values are 136 and 117 ppm, respectively. Analytical detection limit was about 50 ppm, considering dilutions of the samples.

Silica concentrations show marked reductions through the test system. The implied deposition rate is much greater than indicated by thicknesses of scale deposits. Reasons for the mismatch deserve study.

TABLE 3:
FIELD COMPOSITIONS OF BRINE AT SAMPLE PORTS

DAY	DECEMBER 29				DECEMBER 30			
	1750	1755	1755		1215	1341	1430	1255
PORT	3	4	5	6	3	4	5	6
CODE	B	I	J	CALC	G	C	A	E
FLASH	.10700	.14621	.17288	.18166	.16513	.15474	.17781	.18522
SODIUM	58658	61988	64348	64574	58756	62405	63794	64753
CALCIUM	29939	31435	33331	33052	29428	30995	32614	32967
POTASSIUM	18357	19823	20419	20451	18398	19488	20109	20316
IRON	1682	1834	1906	1892	1697	1774	1857	1897
MANGANESE	1533	1654	1704	1707	1531	1651	1688	1702
ZINC	571	604	626	628	559	603	616	624
SILICA	511	470	342	465	530	466	434	380
STRONTIUM	453	482	499	500	450	480	496	498
AMMONIUM	389	364	383	397	382	413	361	415
BORON	282	304	314	314	281	300	309	311
BARIUM	220	236	251	246	218	224	237	243
LITHIUM	212	226	237	236	211	222	232	235
LEAD	108	114	119	119	105	108	115	122
MAGNESIUM	41	45	43	45	41	40	45	48
OCEAN CL	170980	179160	186890	188589	171720	181800	186900	188600
SUM	283936	298736	311414	313215	284307	300968	309808	313109

TABLE 4:

	ELEMENT/LITHIUM RATIOS				ELEMENT CONCENTRATIONS			
	DEC 29		DEC 30		DEC 29		DEC 30	
	AVG	U.M.	AVG	U.M.	AVG	U.M.	AVG	U.M.
SODIUM	274.15	1.96	277.86	.97	52843	299.11	52661	50.94
CALCIUM	140.31	.90	139.89	.17	27048	277.91	26515	119.20
POTASSIUM	86.82	.62	87.07	.21	16736	231.68	16502	17.82
IRON	8.03	.07	8.03	.02	1548	29.81	1522	7.25
MANGANESE	7.25	.05	7.31	.04	1397	18.55	1385	6.00
ZINC	2.67	.02	2.67	.01	514	3.10	506	1.61
SILICA	1.98	.31	2.05	.14	380	56.07	387	25.90
STRONTIUM	2.12	.01	2.14	.01	409	3.28	405	.79
AMMONIUM	1.69	.10	1.78	.05	325	15.48	336	8.56
BORON	1.33	.01	1.34	0.00	257	3.25	253	.44
BARIUM	1.05	.01	1.02	.01	202	3.62	194	1.49
LITHIUM	1.00		1.00		193	2.44	190	.63
LEAD	.51	0.00	.50	.01	98	.65	95	1.36
MAGNESIUM	.19	.01	.19	0.00	37	1.06	36	1.00
OCEAN CL	795.91	7.43	810.82	2.71	153410	1087	153668	0
SUM					255396	2257	254654	351

PRE-FLASH BRINE COMPOSITION

The pre-flash compositions for the two sampling days are given in the right half of Table 4, in terms of averages and uncertainties of the mean (U.M.). Table 4 is derived from the Table 3 values multiplied by (1-f) and averaged over each days samples. The averages are different by amounts that approach significance in terms of the U.M. values.

An alternative comparison of the brine compositions on the different days can be made through ratios of components. Specifically, lithium determinations are the most reproducible, based on the replicate samples. Thus, the ratio of element concentration to the lithium concentration is a sensitive indicator of variation between samples.

The averages and U.M. values for element/lithium ratios are given in the left half of Table 4. The differences in the U.M. values, vis-s-vis the two sampling days, are relatively less than their concentration counterparts in the other side, as expected.

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REFERENCES

1. Michels, D. E., 1986, A chemical method for measuring steam quality in two-phase flowlines: Geoth. Res. Coun., Transactions, this volume.
2. Ellis, A.J. and W.A.J. Mahon, 1977, Geochemistry and geothermal systems: Academic Press, New York, p. 230.
3. Haas, J.L., 1976, Thermodynamic properties of the coexisting phases and thermochemical properties of the NaCl component in boiling NaCl solutions: U.S. Geol. Surv. Bul. 1421-B Revised, 71 pp.
4. Campbell, Andy, and Chris Measures, 1986, MIT Department of Oceanography, personal communication.
5. Michels, D. E., 1978, CO₂ in geothermal steam - a rapid, precise, and accurate field assay technique: Geoth. Res. Coun. Trans, v. 2, p. 445-8.
6. Alfred Truesdell, 1986, personal communication.