ANALYTICAL RESULTS OF TAGGED SYNTHETIC BRINE MIGRATION EXPERIMENTS AT AVERY ISLAND, LOUISIANA

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ABSTRACT

Vapor condensates were collected during experiments attempting to measure brine migration in a thermal gradient in rock salt. From variations in the deuterium concentrations measured in the condensates it is concluded that deuterium from a tagged synthetic brine emplaced in the salt migrated to the heater hole.

INTRODUCTION

Re/Spec Inc. recently conducted a series of in situ brine migration experiments in dome salt at the Avery Island mine, near Lafayette, La. The objective of the experiment was to investigate, under controlled conditions, the movement of synthetic and natural brine fluid inclusions through the salt in a temperature field induced by electric heaters. This paper presents analytical data obtained by U.S. Geological Survey personnel in support of the experiments and some discussion of the results.

EXPERIMENT DESIGN AND PROCEDURE

Three variations of the experiment were conducted at adjacent sites:

(1) AB --natural brine movement at ambient temperature (~75°F),

(2) NB --natural brine movement at elevated temperature,

(3) SB --synthetic brine movement at elevated temperatures.

Sites AB and NB used the brine naturally contained in the Avery Island salt (~0.02 percent) H_2O) (Fairchild and Jenks, 1978) as the migrating fluid. The composition of the synthetic brine, WIPP-A tagged with D_2O which was used in test SB, is given in Table 1.

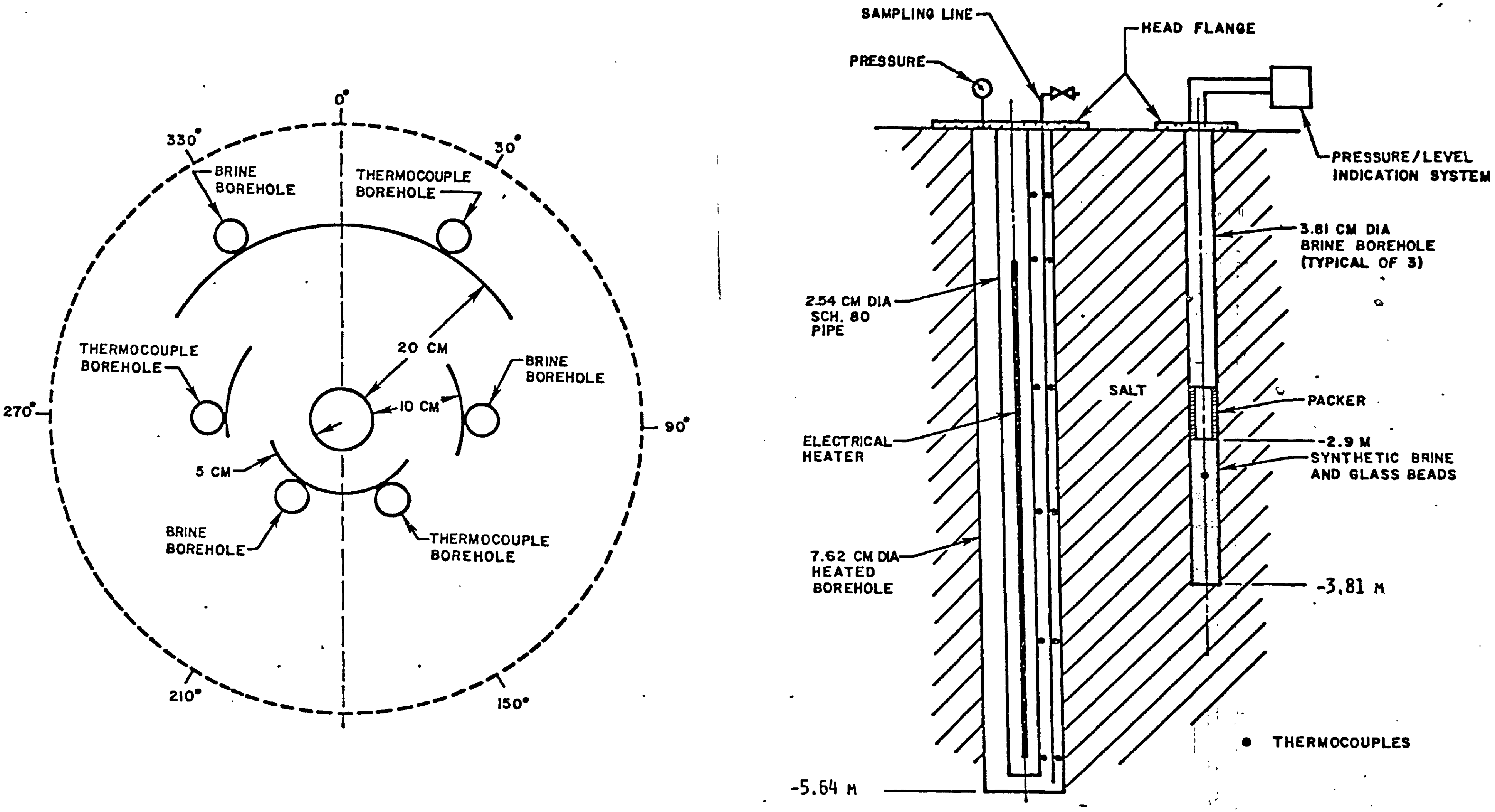
Figure 1 illustrates the borehole configuration for each experiment. All boreholes were checked for microfractures using dry nitrogen; none were found. At site SB one liter of synthetic brine was placed in each brine borehole with glass beads to minimize convection. Then the boreholes were pressurized to 100 psi with nitrogen. At sites AB and NB the empty brine boreholes were pressurized. Details of the borehole configuration, heater emplacement, and temperature monitoring can be found in Krause and Gnirk (1979) and Van Sambeek and Ubbes (1980). A post-test inspection and analysis of the sites will be performed by Re/Spec. Moisture collection rates were reported by Van Sambeek and Ubbes (1980).

Table 1. Synthetic Brine Composition.

Component	g/l	wt. percent
$MgCl_2$	137.08	11.42
$NaCl$	101.55	8.46
KCl	57.20	4.77
$CaCl_2$	1.71	0.14
Na_2SO_4	5.175	0.43
D_2O	25.00	2.08
H_2O	872.345	72.69

Weights are for the anhydrous salts.

Brine density at 20°C = 1.2021 ± 0.0002 g/cm^3



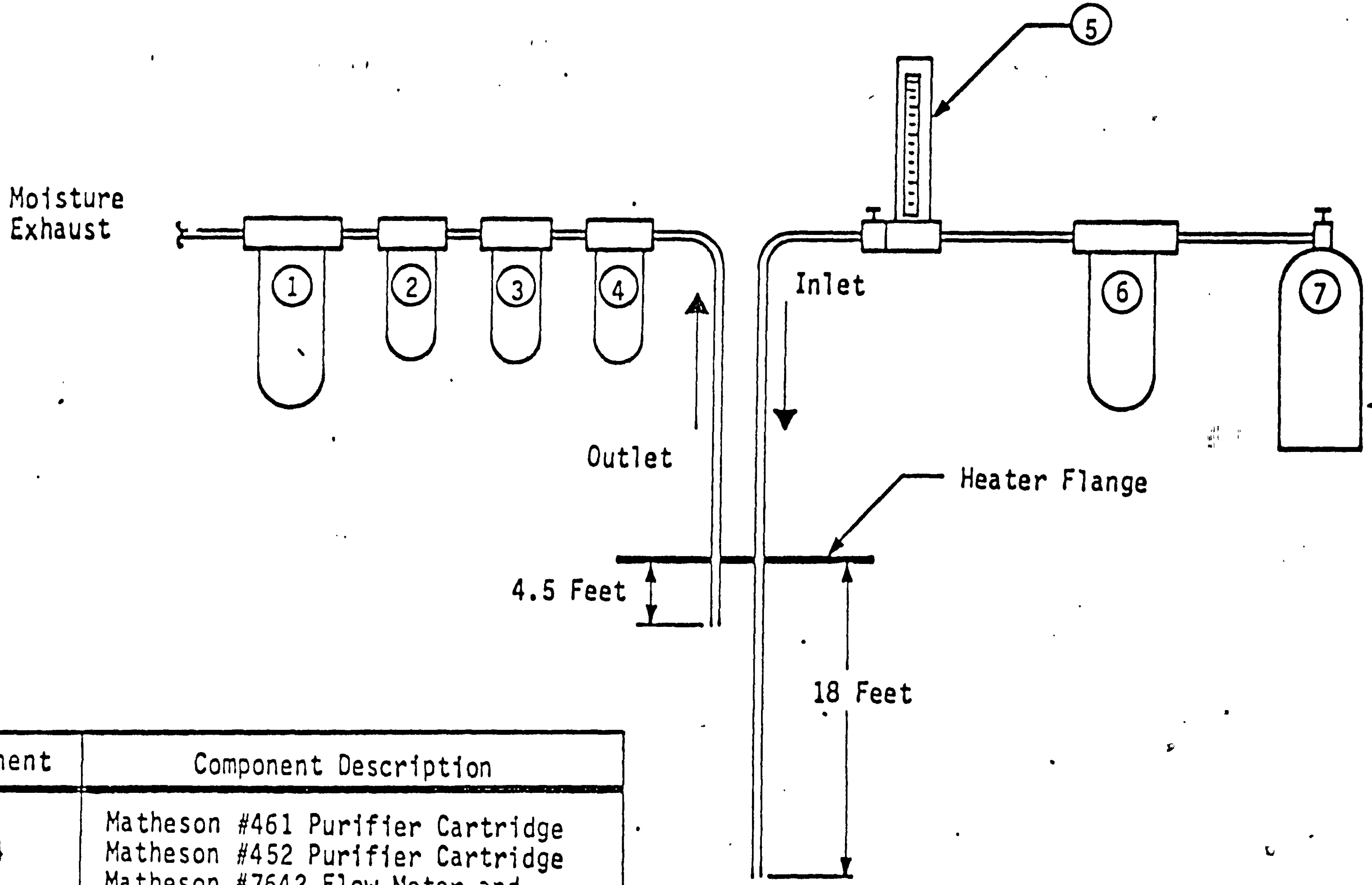
TOP VIEW OF LAYOUT OF BOREHOLES FOR BRINE MOVEMENT EXPERIMENT AT AVERY ISLAND

CROSS-SECTIONAL VIEW SHOWING HEATED BOREHOLE AND BRINE BOREHOLE

Figure 1 (Krause and Gnirk, 1979)

One-kilowatt electric heaters were used at each site to simulate a three-kilowatt waste canister heat load in a larger borehole. At steady state (100 days heating time), the borehole surface temperature reached 52°C and at 30 cm into the salt the temperature reached 41°C. The thermal gradient in the salt ranged from 1.4°C/cm near the heater hole -- salt interface to approximately 0.09°C/cm at 30 cm from the interface.

In order to measure the amount of brine that migrated to the heater hole, each heater hole was equipped with a vapor extraction system (Fig. 2) which operated by flushing dry nitrogen through the heater hole and trapping water evaporated from the brine in Matheson No. 452 purifier cartridges containing a zeolite dessicant (Linde 4A). This method does not measure the amount of brine directly but can be used to estimate the amount of brine in the heater hole (Clynne and others, 1980).



Component	Component Description
1,6	Matheson #461 Purifier Cartridge
2,3,4	Matheson #452 Purifier Cartridge
5	Matheson #7642 Flow Meter and Metering Valve
7	Matheson #8 Pressure Regulator and Dry Nitrogen Supply Bottle

Figure 2
Schematic Diagram of Moisture Collection System for Sites NB and SB -- Brine Migration Experiments. (W.B. Krause, written commication, 1979).

EXTRACTION PROCEDURE

The zeolite dessicant cartridges were removed from the vapor collection system, weighed and individually packaged in airtight plastic bags by Re/Spec personnel. At the time of deuterium analysis each cartridge was removed from its airtight wrapping and opened; the dessicant beads were poured into a noble metal lined autoclave with a noble metal seal. The dessicant beads were exposed to the atmosphere for less than one minute. After placing the autoclave in a furnace, most of the residual air was quickly removed with a vacuum pump. The autoclave was then heated, and the released water vapor successively extracted into an airtight glass syringe at 25°C intervals. The temperature limit of the system is 500°C. Figure 3 schematically illustrates the extraction apparatus.

The method of Bigeleison and others (1952) was used for the deuterium analyses.

The sample notation includes the site designation (SB or NB, no AB samples were analyzed), canister number, and date of removal from the vapor collection system at Avery Island.

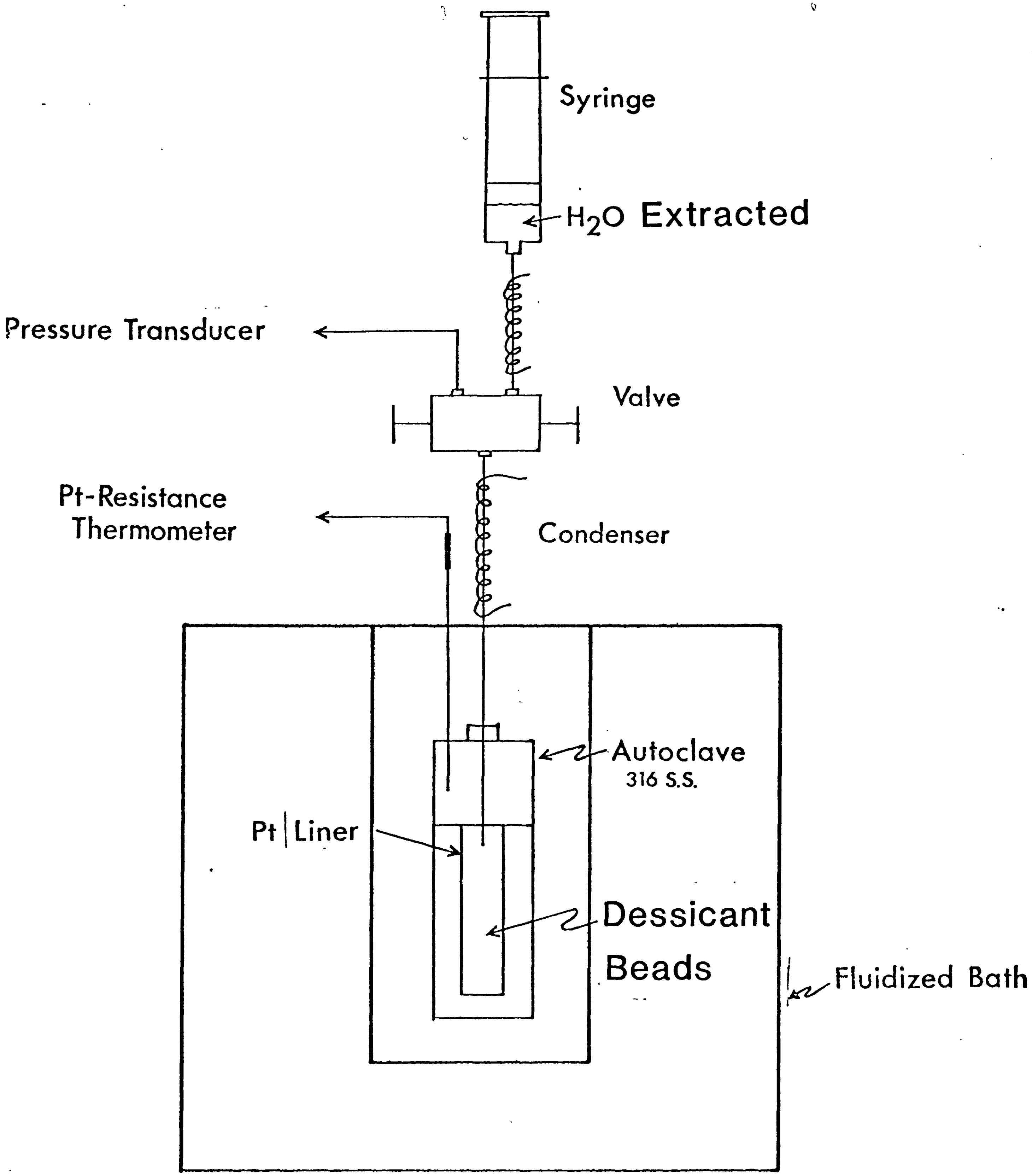


Figure 3 Extraction Apparatus

RESULTS

The results of the deuterium analyses are given in Table 2. Isotopic variations are expressed in delta units (δ), defined as follows. If R is the isotopic ratio (deuterium/hydrogen) in a sample and R* is the ratio in some standard material, then:

$$\delta = [(R/R^*) - 1]1000$$

The δ values are expressed in parts per thousand or per mil (°/°°). The standard for hydrogen in natural waters is standard mean ocean water (SMOW). The concentration of HDO in SMOW, in molecules per 10^6 total water molecules is 316, (Craig, 1961).

The first set of samples was measured by placing each sample directly into the mass spectrometer. Samples SB-1 (5/7/80) and SB-2 (5/7/80) swamped the filament and thus minimum values of δD were obtained. Later analyses of SB-1 (9/4/80) and SB-2 (9/4/80) suggest that the first set of δD values for the SB samples could be low by a factor of up to 50. The second set (SB-1 (9/4/80) and SB-2 (9/4/80)) were diluted 1:1000 with water of known isotopic composition. The precision for SB samples is conservatively estimated as ±100°/°°. The precision of NB samples is ±0.5°/°°.

Table 2. δD values of vapor condensates.

Sample Site	Sample collection Period	δD
NB-0	1/21/80 - 1/29/80	+247.7
NB-1	1/29/80 - 5/7/80	+69.3
NB-2	1/21/80 - 5/7/80	+5.6
NB-3	1/21/80 - 5/7/80	-73.6
SB-1	12/29/79 - 5/7/80	>>2000
SB-2	12/29/79 - 5/7/80	>>2000
SB-3	12/29/79 - 5/7/80	ND
SB-1	5/7/80 - 9/4/80	+47,790
SB-2	5/7/80 - 9/4/80	+21,040
SB-3	5/7/80 - 9/4/80	-160

ND = not determined

DISCUSSION

It is difficult to use the δD data to estimate the precise HDO concentrations in brine arriving at the heater holes because of hydrogen/deuterium fractionation at different times and places as discussed below.

(1) Evaporation of the brine arriving at the heater hole fractionates deuterium. In the Avery Island situation, where vapor is continually removed from the system and the brines are very saline, evaporation initially enriches the residual solution in deuterium. As evaporation proceeds a reversal takes place and the residual solution is depleted in deuterium. The point of reversal is dependent upon evaporation rate, temperature and brine chemistry (Sofer and Gat, 1975).

(2) A second fractionation in the brine arriving at the heater hole involves the crystallization of hydrated minerals. The volumetrically important hydrated minerals crystallizing from NaCl-saturated WIPP-A at 55°C are carnallite ($KMgCl_3 \cdot 6H_2O$) and bischoffite ($MgCl_2 \cdot 6H_2O$) (D'Ans, 1933). There is a deuterium fractionation between water of hydration in minerals and the solution from which they crystallized, and the process is temperature and composition dependent. Although the crystallization of hydrated minerals normally enriches the residual brine in deuterium, minerals that deplete brine deuterium are known. No data exist for the effect of carnallite and bischoffite crystallization on isotopic composition.

(3) There is strong fractionation of H and D between vapor and the zeolite dessicant. Canisters SB-1 (9/4/80), SB-2 (9/4/80), and SB-3 (9/4/80) were on the extraction system at the same time; however, δD SB-1 >> SB-2 >> SB-3. Therefore isotopic values should be weight averaged to get δD values for individual sites and time spans.

(4) At the time of analysis it was assumed that each canister would be isotopically homogenous; for some samples, water was extracted from only one-half the beads. Isotopic homogeneity from top to bottom of each canister is not the case. Therefore, the δD values are not representative of the entire canister. The magnitude of this effect is unknown, and it could be large. Because the beads were removed from the bottom of the canister, the δD values are minimum numbers. Samples SB-1 (5/7/80) and SB-2 (5/7/80) and NB-1 are those for which one-half the beads were used for the extraction. The least precise values were obtained for SB-1 (5/7/80) and SB-2 (5/7/80) so little data is lost. The NB samples contain little deuterium so the value of NB-1 has been only slightly affected by analyzing one-half of the beads.

(5) Approximately 10 percent of the water in the beads is not extracted, even at the 500°C temperature limit of the extraction system. The fractionation produced by this effect is unknown, but it is probably not large because the approximate weight average of NB-1, NB-2, and NB-3 is a value near SMOW and similar to brine from pools near the test site (Clynne and others, in preparation).

The magnitudes of fractionations (4) and (5) could be evaluated by allowing fresh beads to absorb water of known isotopic composition. This has not been done. Fractionations (1) and (2) are relatively unimportant, affecting the δD values by <100°/oo. The effect of fractionation (3) can be mitigated by weight averaging canisters for each site.

The water used to make the synthetic brine was 2.8 percent D_2O or 5.6 percent HDO. Neglecting the D content of the remaining water, this gives 56,000 HDO molecules per 10^6 molecules of water. A weight average of

SB-1 (9/4/80), SB-2 (9/4/80), and SB-3 (9/4/80) gives δD ~32,000 or 100,000 HDO molecules. To account for the observed D_2O content of the vapor collected would require that ~18 percent of the water in the heater hole came from the synthetic brine. This calculation is made tenuous by the fractionation factors previously discussed.

CONCLUSION

Because the NB samples have δD values similar to the Avery Island brine pools and the SB samples are ~32 times as concentrated in HDO, the conclusion that the SB site contains some water from the synthetic brine is inescapable.

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