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Measurement of Water Lost From Heated Geologic Salt

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MEASUREMENT OF WATER LOST FROM HEATED GEOLOGIC SALT

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ABSTRACT

This report describes three methods used to measure the rate at which water is lost from heated geologic salt. The three methods were employed in each of a series of "proof" tests which were performed to evaluate instrumentation designed to measure the water-loss rate. We found that the water lost from heated, 1-kg salt specimens which were measured according to these three methods was consistent to within an average 9 percent.

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MEASUREMENT OF WATER LOST FROM HEATED GEOLOGIC SALT

Introduction

Sandia Laboratories is researching the basic properties of geologic salt to aid in the design of the Waste Isolation Pilot Plant (WIPP) facility. The water content of geologic salt is essential in understanding the processes by which water may be transported in the region surrounding a heat-producing waste canister placed in geologic salt. The experiment which is described here was designed to measure water lost from samples of geologic salt.

This report describes three methods used to measure the rate at which water is lost or evolved from heated geologic salt. The three methods were employed in each of three "proof" tests which were performed to evaluate instrumentation designed to measure the water-loss rate. The three methods used to determine the amount of water loss are:

1. Measurement of the specimen's mass loss upon being heated.
2. Measurement of the mass increase of a desiccant material that has been placed in the gas-flow stream which had passed over the heated salt.
3. Integration of the time rate of water introduced into the gas-flow stream which had been passed over the heated salt. Water introduced into the gas-flow stream was measured using commercially available dew point hygrometers, absolute pressure gauges, and mass flow rate gauges.

Procedure

Each salt specimen, which weighed approximately 1 kg, was a 5.0-cm-high cylinder with a diameter of 10.8 cm. The cylinders were machined from separate 1-m-long cubic salt blocks supplied by the Mississippi Chemical Company from their mine located about 29 km east of Carlsbad, New Mexico. The salt blocks were removed from ore zone 7, approximately 210 m below the surface in the McNutt Potash Zone of the Salado Formation. The major mineralogical constituents of the rock salt are approximately as follows: 88 percent halite, 5 percent kainite, 4 percent polyhalite, and 3 percent sylvite. Since, between the time they were mined and prior to being heated, the specimens were exposed for up to one year to a laboratory air environment, their water content and permeability may differ from that of in situ salt.

Each specimen was weighed and placed into a gas-tight, stainless steel enclosure with a diameter of 15 cm and a height of 18 cm. The sample was heated using electrical heater tape wrapped around the circumference of the enclosure. Thermal insulation (fiberglass mat, vermiculite, and transite) was placed over the heater tape and surrounded all surfaces of the enclosure. A section view of the sample-heating enclosure is shown in Figure 1. The temperature of the heated salt specimen was measured using a thermocouple in contact with the specimen's top surface. Each specimen was heated sequentially at the three input power levels (0, 67, and 116 W) of the heater tape. For each heater power level, both the time required for the specimen to reach its maximum temperature and the specimen's maximum temperature were affected by the thermal insulation and by the ambient temperature (20° to 30°C). The duration of each run was about 80 hours. The water that evolved from the heated salt was picked up by passing a pure (99.998 percent by weight) dry nitrogen gas stream continuously through the enclosure containing the salt. The gas stream's flow rate, about 400 standard cubic centimeters per minute (SCCM), and the salt specimen's maximum water-loss rate precluded saturation of the flow gas with respect to water. The gas stream's water vapor content, mass flow rate, temperature, and absolute pressure were measured using the

instruments shown schematically in Figure 2. The experimental parameters for each specimen are shown in Table 1.

Figure 1. Assembly: Heated Salt Specimen Apparatus

Figure 2. Flow Gas Water Analysis Instrumentation

TABLE 1
Experimental Parameters for Heated
Salt Specimens

	Salt Specimen Number		
	1	2	3
Maximum Temperature at 67 W Heater Power (°C)	112 + 5	123 + 5	170 + 5
Maximum Temperature at 116 W Heater Power (°C)	168 + 5	188 + 5	256 + 5
Total Test Time (min)	3095	5515	5763
Initial Mass(g)	1007.15	1005.95	987.50

First Water-Loss Measurement Method

In the first method used to measure the specimen's water content, we measured the mass of the salt specimen before and after heating, and the specimen's mass loss upon heating was assumed to be due to the loss of water. This mass loss is really an upper bound to the water lost during heating since other volatiles such as carbon dioxide may be lost from the heated salt in addition to water. No estimate of the error in the specimen's mass loss due to such processes is included. The absolute accuracy of the measurement of the mass of each specimen was estimated as +0.02 g. The specimen did not lose more than 0.03 g in the form of salt fines or flakes when it was removed from the enclosure for weighing. After being cooled to room temperature, the specimens were weighed within ten minutes of their removal from the enclosure; some weight gain due to the absorption of water from the air may have occurred although no estimate of the mass error caused by this effect is included. The estimated total error in each specimen's mass loss measurement is +0.06 g -0.03 g.

Second Water-Loss Measurement Method

In the second method used to measure the specimen's water content, we measured the mass increase of three molecular sieve desiccant cartridges which were placed in the gas-flow stream downstream from the salt

specimen. Each cartridge contained the water-specific molecular sieve, Linde-4A (Matheson model 452), and each cartridge's water absorption capacity was 6 g. Each cartridge was weighed prior to the placement of the salt specimen into the heating enclosure; they were then weighed again following the heating of the salt specimen and the subsequent cooling of the heating enclosure to room temperature. The total of the mass increases of the desiccant cartridges was a measure of the water lost by the salt specimen. An error in this quantity arises because the water vapor in the gas-flow stream is incompletely absorbed by a single desiccant cartridge. We minimized this error by flowing nitrogen through the cartridges in series, and then by adding to their descending sequence of mass gains an additional mass gain which would have occurred if an infinite series array of desiccant cartridges had been used. Water desorption by the enclosure and subsequent absorption by the cartridges may be a source of error. Finally, the dry nitrogen flow gas is not necessarily in equilibrium with the enclosure at the beginning of the measurement; this may be a source of systematic error. An estimated error of 0.05 g was assigned to each water absorption measurement.

Third Water-Loss Measurement Method

In the third method used to measure the specimen's water content, we calculated the rate at which water was introduced into the nitrogen gas-flow stream from the measured parameters of the flow gas; this was integrated over time to give the total amount of water lost by the salt. The rate at which water was introduced into the gas-flow stream was determined by measuring the gas stream's absolute humidity, absolute pressure, absolute temperature, and mass flow rate. The dew point of the flow gas was measured using four dew point hygrometers: two chilled mirror-type hygrometers and two activated aluminum oxide sensor-type hygrometers. An equilibrium dew point of less than -80°C characterized the dry nitrogen source gas. The increase in the dew point of the flow gas was due to its absorption of water from the salt sample as well as from the gas-flow hardware. By running a "blank," we estimated the amount of water desorbed from the system. This process opens the enclosure to air, reseals the enclosure with no salt sample inside, and then heats the enclosure to drive off the absorbed water.

The gas-flow system absolute pressure was measured using Celeco differential pressure transducers which were calibrated against certified Wallace and Tiernan Bourdon tube pressure gauges. Nitrogen mass flow rates were measured using Metheson linear mass flow transducers which had been calibrated for air, but which were corrected to indicate nitrogen mass flow. The absolute temperature of the gas-flow stream was measured using copper-constantan thermocouples and Doric-brand signal conditioning and thermocouple readouts.

The rate at which water is introduced into the gas-flow stream is given by

$$W_f = \frac{P(H_2O)}{P_T} \cdot FR \cdot 7.64 \times 10^{-4},$$

where W_f is the flow rate of water from the salt into the gas stream ($g \cdot min^{-1}$), $P(H_2O)$ is the net partial pressure of water in the gas-flow stream due to the salt (Torr), i.e., the difference between the measured water partial pressure and the partial pressure of water due to background sources. P_T is the absolute pressure of the gas-flow stream (Torr). FR is the nitrogen gas-flow rate (SCCM). The partial pressure of the water vapor in the gas stream is calculated from the measured dew point temperature using the Goff-Gratch expression.¹ Volatile compounds (other than water) which condense on the chilled mirrors of the dew-point gauges were a source of systematic error in the measurement of the gas flow's dew point. We reduced the effects of this phenomenon by using an in-line activated charcoal filter, cleaning and baking the gas-flow hardware, and frequently cleaning the dew point gauge mirrors. A systematic error is introduced in the determination of the water evolved from the heated salt due to an estimated error in the measured dew point: $\pm 2^\circ C \pm 1^\circ C$. The error in the measured dew points corresponds to an error in the measured partial pressures of about ± 10 , ± 5 percent. Estimated errors in the measured flow-gas parameters are:

- Flow rate, ± 2 percent.

- Background correction, ± 2 percent of average gas-flow rate.
- Interpolation of dew point data during periods when gauge readouts were not recorded, ± 5 percent.

The estimated total error in the water lost from the salt, which has been determined by this method, is ± 8 percent.

Test Results

Table 2 summarizes the results of the three water-loss analyses. A typical water-loss rate curve (i.e., the data for sample 2) is shown in Figure 3. The characteristics of this water-loss rate curve that are common to all three samples are:

- The monotonically declining rate after the sample is placed in the enclosure at room temperature.
- The rate increase following an increase in the heater power with the attainment of a maximum followed by a slow, monotonic decrease.

TABLE 2
Results for Heated Salt Specimens

Mass Change (g)	Salt Specimen Number		
	1	2	3
Mass loss upon heating	1.26 + 0.06 - 0.03	0.98 + 0.06 - 0.03	1.47 + 0.06 - 0.03
Time integral of net water-loss rate	1.38 $\pm$ 0.11	0.96 $\pm$ 0.08	1.85 $\pm$ 0.15
Mass gain of desiccant cartridges	1.14 $\pm$ 0.05	0.98 $\pm$ 0.05	1.32 $\pm$ 0.05
Average $\pm$ rms	1.26 $\pm$ 0.12	0.97 $\pm$ 0.01	1.55 $\pm$ 0.27
Mass loss predicted from heating curve for 20-g samples and scaled to specimen mass	0.79 $\pm$ 0.11	0.76 $\pm$ 0.12	1.07 $\pm$ 0.17
Mass loss in postheating pulse (200-min interval), percent of total	N/A	0.097 9.0	0.112 5.5

Figure 3. Representative Water-Loss Rate of Heated Salt Specimen

The third specimen lost more water than the first two because it was raised to a higher maximum temperature and because it dried for a shorter time (only two weeks) prior to heating. Finally, two of the specimens showed an abrupt increase in water loss rate upon removal of heater power. (This may also have occurred during the first specimen's run, but the dew point gauges were not monitored after the power was turned off.) The water released during this sudden outflow is 5 to 10 percent of the total water released by the salt. The increase in the mass loss rate which occurs after the heater power is changed is substantially higher during the postheating water loss "pulse" than it is following the two heater

power increases. For the second specimen, the relative maxima, along with the times of occurrence, are as follows:

Water mass loss rates: $1.6 \times 10^{-4} \text{ g} \cdot \text{min}^{-1}$ at 1445 min
 $2.6 \times 10^{-3} \text{ g} \cdot \text{min}^{-1}$ at 2825 min
 $5.24 \times 10^{-3} \text{ g} \cdot \text{min}^{-1}$ at 4185 min

Water mass loss rate change rates: $2.1 \times 10^{-6} \text{ g} \cdot \text{min}^{-2}$ at 1225 min
 $6.7 \times 10^{-5} \text{ g} \cdot \text{min}^{-2}$ at 2768 min
 $3.2 \times 10^{-4} \text{ g} \cdot \text{min}^{-2}$ at 4180 min

Table 2 includes the three values for each heated specimen's water loss. In general, the values obtained by integrating the water-loss rate data are greater than salt specimen mass losses, which, in turn, are greater than desiccant cartridge mass gains. Water lost from heated, 1-kg salt specimens which have been measured three different ways are consistent to within an average of 9 percent. Additionally, these data are in good agreement (50 percent) with mass loss measurements of small samples (20 g) of similar material which were scaled to the specimen weight.*

The rapid loss of water from the salt specimens following the heater power turnoff is similar to phenomena observed during measurements made in heated geologic salt during project Salt Vault.² A probable cause for the sudden release of water from the salt specimen following the power turnoff is the opening of cracks or joints in the salt due to the tensile stress caused by the cooling of the salt's surface material. Brine or water vapor contained within such a stressed region is released through material of an effectively and suddenly larger permeability.

*A summary of these measurements appears in Appendix 1.

Summary

Taken together, the three methods of measuring the water lost from the heated geologic salt are adequate for determining the water loss to within 10 percent. The use of desiccant cannisters to measure water is easy and inexpensive, but it yields values of water lost which average about 8 percent too low. Integrating the net water loss rate is complex, expensive, and subject to water sensor degradation, but it is the only way to measure time-dependent water loss. Measuring the mass lost by the salt sample is convenient only if an appropriate balance is available. This method will not be practical for bench scale (several tons) salt samples.

References

1. Robert J. List, ed., Smithsonian Meteorological Tables, 6th rev. ed. (Washington, D. C.: Smithsonian Institution, 1951), p. 350.
2. R. L. Bradshaw, et al, Project Salt Vault: A Demonstration of the Disposal of High-Activity Solidified Wastes in Underground Salt Mines, ORNL-4555 (Oak Ridge, Tenn.: Oak Ridge National Laboratory, 1971).

APPENDIX A

MASS LOSS UPON HEATING OF GEOLOGIC SALT

Introduction

This is a brief description of the mass loss measurements made on geologic salt which are referred to in the main body of this report. We undertook these measurements in order to establish baseline data for mass losses upon heating of large specimens of geologic salt. Mass loss data were needed in the design of other heated salt experiments. At one time we thought that the use of large samples (20 g) and, consequently, conventional analytical balances, as well as the capability of measuring several samples at one time, appeared attractive.

Method

We took salt specimens from geologic salt similar to that used in the heated salt experiment described in this report. The experiment's samples consisted of shards chipped, using a hammer and chisel, from a 0.3-m long, cubic salt block. Each of the 10 samples contained from 3 to 16 pieces whose mass totaled nearly 20 g. Each sample was placed in a covered glass vial and weighed at room temperature. The vials were uncovered, and the samples were placed in a desiccator containing desiccant and heated from one to 5 days at each of an ascending sequence of temperatures from 75° to 325°C. After heating the samples at the selected temperature for several days, we removed them from the oven, recovered them to prevent absorption of moisture, cooled them to room temperature, and reweighed them. The specimens then were uncovered and reheated at the next higher temperature. In this fashion, measurements of weight loss continued until one sample decrepitated.

Results

In general, each sample decreased in mass after being heated at each of the elevated temperatures. Considerable sample variability was observed; "wet" samples consistently lost greater mass fractions at each temperature than "dry" samples. The results are summarized in Figure A-1. The errors which are attached to each datum are the standard errors for the ten samples. Comparison with the results of Boultinghouse and Sallach* suggests that the mass loss curve which agrees with these data is most nearly that of type "A", characterized by mass losses less than 0.5 percent.

Figure A-1. Mass Loss of Heated Salt, 20 Gram Samples

*K. D. Boultinghouse and R. A. Sallach, "Thermogravimetric Analysis of ERDA #9 Core Samples," Memorandum to D. W. Powers, January 20, 1977.

Summary

These samples displayed average mass losses of less than 0.1 percent after we heated them up to 250°C. With the onset of decrepitation, an increase in the average mass loss to 0.26 percent was observed after heating the samples to 325°C.

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