

## GEOCHEMICAL OVERVIEW OF THE WASTE ISOLATION PILOT PLANT

NEAR CARLSBAD, NEW MEXICO\*

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### Abstract

The Waste Isolation Pilot Plant is a US Department-of-Energy-sponsored repository for the long-term storage of transuranic defense-related nuclear waste, located in the Delaware Basin near Carlsbad, New Mexico. During excavation, numerous large fluid inclusions were collected from highly recrystallized halite at the repository horizon. The inclusion fluid compositions define two distinct populations, based on analyses for Ca, Mg, K, Na, Cl, Br, and SO<sub>4</sub>. Chemical and mineralogical evidence supports our conclusions that the fluid inclusion compositions arise from early diagenetic changes involving alteration of calcium sulfate (gypsum or anhydrite) to polyhalite, and calcium carbonate (calcite or aragonite) to magnesite.

Other brines occurring in the repository (as "weeps" oozing from the walls or collecting in drill holes in the floor) were also analyzed. These fluids were found to differ significantly from the fluid inclusions mainly by depletion of magnesium relative to potassium. The stratigraphic association of these fluids with argillaceous and anhydritic halite suggests an origin in evaporating seawater that was subsequently modified by dewatering of clays and/or gypsum, and selective uptake of magnesium relative to potassium during clay diagenesis. This interpretation is compatible with our observations of a suite of authigenic minerals that includes quartz, magnesite, and magnesium silicates.

### INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) is a Department of Energy-sponsored repository for the long-term storage of transuranic defense-related nuclear waste. The WIPP is located at a depth of 2150 feet below ground surface, in flat-lying bedded halite of the lower Salado Formation (Permian), in the Delaware Basin, southeastern New Mexico. Accessory mineralogy in the halite includes minor amounts of anhydrite, magnesite, polyhalite, and clays. In addition, the salt contains approximately 0.6 percent (by weight) intragranular water in the form of fluid inclusions<sup>1</sup>. In addition, brines occur in macroscopic quantities within the WIPP, as "weeps" or wet places on freshly excavated walls and as puddles on the facility floor or as seepage into drill holes.

Preliminary drilling revealed the presence of large brine reservoirs in the Castile Formation, several hundred feet below the facility horizon<sup>2</sup>; these occurrences prompted a detailed examination of brines observed within WIPP and the adjacent halite in order to elucidate brine source(s), amounts, and rates and directions of possible movement. The analytical data we have collected does not resolve all of the questions regarding the origin and diagenetic history of the brines observed in the WIPP. Our objective is to attempt to shed some light on the possibility of fluid inclusion movement within the waste repository and to provide a historical perspective from which the question of fluid migration in this waste repository can be addressed.

### ANALYTICAL WORK

Initially, core samples were taken from depths ranging from deep in the Castile Formation through

the upper part of the Salado. Halites from these samples were examined for fluid inclusions, and conventional freezing-point-depression measurements were made<sup>3</sup>. No correlation was found between freezing temperatures and depth, although the data suggested a large variability in inclusion fluid composition that is most probably attributable to a range of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup> concentrations.

These fluid inclusions were also analyzed by laser Raman spectroscopy for dissolved sulfate. A K-Ar laser was used to excite the  $\nu_1$  SO<sub>4</sub><sup>2-</sup> band, which was then normalized to the OH<sup>-</sup> band for quantitative measurements<sup>4</sup>. Again, no obvious correlation with depth in the Salado was observed, but sulfate analyses of Castile samples differed significantly from those in the Salado. Also, analyses from the Salado inclusions suggested a correlation with the occurrence of the mineral polyhalite, Ca<sub>2</sub>K<sub>2</sub>Mg(SO<sub>4</sub>)<sub>4</sub>·2H<sub>2</sub>O.

Finally, very large (~10-100  $\mu$  on an edge) fluid inclusions from the WIPP facility horizon were examined by direct extraction of the fluids<sup>5,6</sup>. Analyses were made for Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup> by D.C. argon-plasma emission spectroscopy; SO<sub>4</sub><sup>2-</sup> and Br<sup>-</sup> by ion chromatography; and Cl<sup>-</sup> by titration. The results are generally in good agreement with similar investigations<sup>7</sup> and indicate that the compositions of the observed fluid inclusion populations are strongly influenced by diagenetic processes and authigenic mineral formation.

Other brines observed in the WIPP included the "weeps", or wet places on newly-excavated drifts. A total of 52 holes, each approximately 8 to 10" long and ~3/8" diameter, were drilled and filled with pre-weighed absorbent material. The holes were then

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re-sealed and left for periods of 6 to 8 weeks. Upon retrieval, these sponges were reweighed and the absorbed moisture was then eluted in distilled water and analyzed for Ca, Mg, K, Na, SO<sub>4</sub>, Cl, and Br. These results differed significantly from the inclusion fluids, primarily by having a much higher average K/Mg value.

Finally, waters from holes in the facility floor, walls, and roof were sampled and analyzed as before. As none of these samples were taken with any degree of stratigraphic control, the results are of significance only in that they differed from both the fluid inclusion and weep compositions and that they suggested an as-yet poorly understood correlation with distance from the anhydritic unit (Marker Bed 139) that immediately underlies the facility floor. We present these results as element weight ratios primarily to minimize errors introduced by large and variable dilution factors, and to simplify graphical representation of the data.

#### DISCUSSION

It is apparent that mineralogy, both indigenous and authigenic, plays an important role in determining compositional variations in the brines observed in the WIPP. Details of the geochemical implications of this conclusion are discussed in a separate paper<sup>6</sup> and will only be summarized here. Two cores, one extending fifty feet vertically upward from the facility horizon and the other fifty feet downward, were sampled approximately every other foot and analyzed for mineral constituents<sup>8</sup>. It was found that the WIPP halite, in general, contains mineral impurities of the order of approximately 5 weight percent or less. These impurities consist of quartz, anhydrite, gypsum, magnesite, polyhalite, and clays. The quartz has been examined by scanning electron microscopy and appears to be almost entirely authigenic and probably resulted from free silica liberated by clay mineral alteration. Polyhalite (K<sub>2</sub>MgCa<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>·2H<sub>2</sub>O) appears almost ubiquitously as a secondary mineral and is thought to result from the alteration of either gypsum or anhydrite by reaction with a concentrated brine<sup>9</sup>. Authigenic magnesite (MgCO<sub>3</sub>) also occurs in abundance and also functions as a sink for dissolved Mg<sup>2+</sup>. Detailed clay mineralogy studies are currently in progress<sup>10</sup>; results thus far are entirely consistent with the observed fluid compositions and indicate that the clay compositions are significantly modified by uptake of Mg<sup>2+</sup>. Our observations are also consistent with Bodine's work<sup>11,12</sup> regarding the prevalence of Mg-rich sheet silicate assemblages in Delaware Basin rocks.

The chief programmatic value of our work, to date, is to set forth a methodology whereby specific problems can be addressed, assuming availability of sufficient resources, rather than to provide a body of "facts" able to withstand critical examination from the point of view of site suitability. In particular, our data can be directly applied to questions related to facility hydrology, brine migration, and materials testing/backfill performance<sup>13</sup>.

The geochemical significance of the brine compositions discussed in Stein and Krumhansl<sup>6</sup> bears on a number of questions related to the emplacement of nuclear waste in a halite repository. Briefly, a discussion of the programmatic applications of this brine study is divided into three general areas: hydrology, brine migration, and materials testing. Although some tentative conclusions are advanced

with regard to each topic, it cannot be stressed too strongly that they are based on a very small number of analyses.

In the overall field of nuclear waste management few questions are as important as quantifying the extent to which the groundwaters in a repository communicate with groundwaters in the adjacent units. Although present only in small amounts, groundwater clearly exists at the stratigraphic level of the WIPP repository (at a depth of 2150' in the Permian Salado Formation). Further, the presence of the brine "weeps" indicates that, near an excavation, it is at least locally mobile. Lower down in the stratigraphic section, large brine pockets occur within fractured anhydrites of the Castile Formation<sup>2</sup>, 1981) and apparently are related to zones of intensely deformed halite. Because of the large size of such pockets, it is relevant to inquire whether the Castile brine occurrences are in any way related to the macroscopic brine occurrences observed in the WIPP facility. Therefore it is also a matter of significant interest to compare the chemical compositions of the Castile brines to those obtained from the brines collected from the WIPP facility, within the Salado Formation (as reported here). In fact, the compositional diversity that we describe herein apparently indicates that reservoirs of substantially different compositions located in close proximity to each other (e.g., within tens of feet) have failed to homogenize over periods of time far longer than that required for the isolation of nuclear waste. Nor do any of these compositions bear much resemblance to those found either above or below the Salado, in the Rustler and Castile Formations, respectively. Thus, the geochemistry of the system seems to preclude the existence of an interconnected hydrologic network able to transfer components in solution on any time scale shorter than that required for the low-temperature silicate diagenesis, presumably tens of millions of years.

The matter of brine migration is related to hydrology, but is distinct in that the focus is on the influence of the repository on fluid distribution. Two points may be made regarding this subject. First, prior to this study, it was thought that the weeps represented fluid inclusion mobilization by localized relief of the stress field in the halite adjacent to the open mine workings. Unless future analytical work yields a population of fluid inclusions of substantially different composition from those discussed here, this explanation of the origin of the weeps seems unlikely. Instead, it seems probable that the fluids giving rise to the weeps are intergranular in nature and hence may migrate by mechanisms other than those thought to affect fluid inclusions (or the same mechanisms but to different degrees). Second, this suggests the importance of investigating various migration phenomena. In the ongoing field tests at the WIPP, much effort and expense has been devoted to making large scale measurements of brine migration in salt adjacent to experimental waste canisters. McTigue<sup>14</sup> has developed a predictive model for brine migration for the simulated high-level waste experiments of Molecke<sup>15</sup> based on the porothermoelastic behavior of salt around a heated borehole. Unless it is known what type of fluid is migrating as well as the migration mechanism(s), it seems likely that the results from such experiments may either be uninterpretable, or interpreted incorrectly. Since the fluids are compositionally distinct, though, this matter may be resolved if the salt deposits formed on the heater hole walls are collected and analyzed. Further,

since different fluids may migrate to the heater over time, some thought should be given to the order in which various mineral components appear in these encrustations.

Finally, an examination of brine compositions bears directly on the matter of materials testing in general and backfill performance specifically. Again, interpretation of the results from such testing is predicated on an accurate assessment of the fluid composition in which canister corrosion and alteration of backfill materials may take place. Of practical importance is the degree to which the brine analyses presented here resemble the reference brines formulated for environmental testing pertinent to WIPP. In some respects, the synthetic Brine A<sup>15</sup> appears to be a reasonable match. At elevated temperatures several brine-bentonite interactions can occur, depending on the chemical nature of the brine involved<sup>13</sup>. Brine A in fact contains sufficient magnesium and potassium to test the relative importance and consequences of formation of different clay mineral types. The formation of mixed layer illite-smectite clays consumes K<sup>+</sup> and may degrade performance of backfill material around the waste canisters<sup>13</sup>. Alternatively, trioctahedral magnesium-rich smectite clays effect a drop in magnesium concentration in coexisting fluids and a lowering of the brine pH. The case for the general application of any one standard synthetic brine to radionuclide migration studies is at this writing ambiguous and requires more work.

Other aspects of the bentonite-brine problem relate to low-temperature backfill performance, and are less easily dealt with. The rheological properties of a bentonite backfill depend on the nature of the exchangeable cation on the clay. For example, the exchange of Ca or Mg for Na may significantly alter its swelling and plasticity. With regard to predicting far-field radionuclide migration, it is also necessary to make measurements in fluids that will reasonably approximate the compositions of those actually encountered in the WIPP. As an example, both Brines A and B are much depleted in sulfate relative to those found in the field. Increasing the sulfate concentration from 3.5 to 25 parts per thousand increases the solubility of the actinide americium. This occurs because in the reference brines, sulfate complexes comprise less than 5 % of the americium whereas in the field those complexes would account for about 35 % of the dissolved americium. Of this thirty-five percent, about a third exists as anionic Am(SO<sub>4</sub>)<sup>2-</sup>, which presumably would not sorb nearly as well as the cationic AmCl<sub>2</sub><sup>+</sup> and AmCl<sub>2</sub><sup>2+</sup>, which would predominate in brines A or B.

With regard to the general topic of materials testing, then, the following generalizations can be made as a result of this study. It is probable that a variety of fluids may come in contact with the components under consideration (e.g., backfill, waste, or canister). Whether these variations will influence the course of interactions around a waste canister cannot be reliably determined in advance, otherwise there would be little justification in experimentally evaluating their performance. Consequently, any program in materials testing must employ a wide range of brine compositions rather than one or two reference brines as has been the practice in the past. We note here that the focus of our work, to date, is only the compositions of, and possible consequences related to, Salado brines. The work presented here presupposes an environment that is

completely isolated, e.g., by successful plugging and sealing. However, other scenarios have in fact taken into account influxes of brines from other sources, in much larger amounts and of different compositions than those discussed here.

## CONCLUSIONS

In conclusion, the data we have obtained thus far suggest that the wide variety of fluids found in the WIPP indicates 1) that an interconnected hydrologic system capable of transporting radionuclides away from the repository does not exist; 2) that brine migration studies must consider the mobility of intergranular fluids, in addition to fluid inclusions; and 3) that materials testing programs need to evaluate a wide range of brines rather than the few reference brines currently in use.

Several fundamental conclusions may be drawn from our study of brines in and adjacent to the WIPP repository. These brines are not simple Na-Cl solutions; rather, they are characterized by variable but significant amounts of SO<sub>4</sub><sup>2-</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>. The formation of secondary minerals such as polyhalite and magnesite appear to exert strong control on fluid compositions. Furthermore, fluid inclusion analyses indicate limited vertical movement of fluids and that this movement occurred soon after deposition (e.g., prior to the end of the Paleozoic era). Our observations of the brine chemistry in the WIPP suggest that ours is a valid approach in estimating the extent to which groundwater within the WIPP communicates with fluids in adjacent stratigraphic units. Our analytical results also suggest that alternative mechanisms to fluid inclusion migration must be considered. Finally, our examination of WIPP brines indicates the need to modify fluid compositions currently in use for backfill performance and materials testing.

## REFERENCES

1. U. S. Department of Energy, 1983, Results of site validation experiments. Vol. II of II, Supporting Documents 5 through 14. Technical Support Contract DE-AC04-78AL05346, TME 3177, March 1983.
2. Register, J. K., 1981, Brine pocket occurrences in the Castile Formation, southeastern New Mexico. March 1981. TME 3080 TSC/D'Appolonia Consulting Engineers, Inc. for Sandia National Laboratories. 14 p.
3. Stein, C. L., 1985a, Preliminary report on fluid inclusions from halites in the Castile and lower Salado Formations of the Delaware Basin, southeastern New Mexico. SAND83-0451, Sandia National Laboratories, Albuquerque, NM. 44 p.
4. Tallant, D. R., Higgins, K. L., and Stein, C. L., 1983, Raman microscopy through transparent materials. SAND83-0373, Sandia National Laboratories, Albuquerque, NM.
5. Stein, C. L., and Krumhansl, J. L., 1984, Compositions of brines in halite from the lower Salado Formation, southeastern New Mexico (abst.) In Abstracts with Programs, 97th Annual Meeting, Geological Society of America, vol. 16, no. 6, Sept. 1984, p. 667.
6. Stein, C. L., and Krumhansl, J. L., 1986, An Interpretational Model for the evolution of brines in salt from the lower Salado Formation, southeastern New Mexico (ms submitted to *Geochimica et Cosmochimica Acta*).

7. Holser, W. T., 1963, Chemistry of brine inclusions in Permian salt from Hutchison, Kansas, in Symposium on Salt, J. L. Rau, ed.: Northern Ohio Geological Society, p. 86-103.
8. Stein, C. L., 1985b, Halite mineralogy in the WIPP facility stratigraphic horizon. SAND85-0321, Sandia National Laboratories, Albuquerque, NM. 32 p.
9. Harvie, C. E., Weare, J. H., Hardie, L. A., and Eugster, H. P., 1980, Evaporation of seawater: calculated mineral sequences. Science, v. 208, p. 498-500.
10. Krumhansl, J. L., Sorenson, W. R., and Stein, C. L., 1986, Clay mineral diagenesis and magnesium silicate formation in halite from the WIPP site, southeastern New Mexico (ms in preparation).
11. Bodine, Jr., M. W., 1978, Clay-mineral assemblages from drill core of Ochoan evaporites, Eddy County. New Mexico Bureau of Mines and Mineral Resources, Circ. 159, p. 21-31.
12. Bodine, Jr., M. W., 1983, Trioctahedral clay mineral assemblages in Paleozoic marine evaporite rocks. In Sixth International Symposium on Salt, vol. I, p. 267-284.
13. Krumhansl, J. L., 1984, Observations regarding the stability of bentonite backfill in a high-level waste (HLW) repository in rock salt. SAND83-1293, 86 p.
14. McTigue, D. F., Brine flow to a heated borehole; to C. L. Stein, Aug. 13, 1984. Internal memorandum.
15. Molecke, M. A., 1983, A comparison of brines relevant to nuclear waste experimentation. SAND83-0516, 58 p.