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# Report of the Committee to Review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations


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Lawrence Livermore National Laboratory


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## Section 1
## Introduction

In June of 1987, the Waste Management Project Office (WMPO) of the Department of Energy conducted a special audit of the activities of the Nevada Nuclear Waste Storage Investigation (NNWSI) Project at Livermore. Observation No. 1 of the audit report (WMPO Audit S-87-1) stated that "The rationale for use of Well J-13 water as the basis for the reference criteria for NNWSI Project activity (until water samples from the unsaturated zone are available) is not clear." A brief reply to that observation was given by the NNWSI Project staff, citing discussions of the justification for using J-13 water in the Yucca Mountain Environmental Assessment Report (1), which in turn outlines some of the relevant literature on this point. However, it has been noted that there never has been a comprehensive, well-documented examination of the basis for the use of J-13 water in the nuclear waste storage investigations.

The management of the NNWSI Project at Livermore therefore asked that a committee be formed to review more thoroughly the question of the validity of the use of J-13 water as a reference material. This committee was composed of scientists who had expertise in the requisite technical areas, but who were not involved in the current activities of the NNWSI Project. The committee was also charged with reexamining and recommending, in the light of the assessment of the technical validity of the use of J-13 water, the NNWSI quality-assurance level to which future activities involving J-13 water should be assigned. This document is a report of these findings.

It was apparent to the committee from the outset that the overall question of the rationale for use of J-13 water extends beyond just the Livermore studies, which mostly have dealt with phenomena in the so-called "near-field" region of the repository, which is the region that will be influenced by heat from the radioactive waste. Thus far, the Livermore work has focussed mostly on experimental and computer-modeling studies of rock/water, metal-alloy/water, and waste-form/water interactions. Other investigators, particularly at Los Alamos National Laboratory, have been concerned with the behavior, e. g., transport, of radionuclides in the ground waters outside the immediate Yucca Mountain area of the repository site. Thus the question of the validity of J-13 water as a reference material is a more global one, and should be asked

in terms of the NNWSI program as a whole, and not just with respect to waters in the unsaturated zone as was done by the WMPO audit committee. In this sense, we may have enlarged the scope of the enquiry somewhat, but we believe it has led to a more coherent, if not more satisfying answer.

Water from the J-13 well has been used experimentally in waste storage studies for at least ten years. Beginning in about 1977 (2) at Los Alamos, the ready availability of J-13 water and its known similarity to the other Nevada Test Site ground waters made it a natural choice as a surrogate water for experiments designed to measure phenomena related to the behavior of nuclear waste in that locale. Through subsequent work at Los Alamos, and the Livermore studies beginning in the early 1980s, J-13 water has often been referred to as the "reference water," and its chemical composition (for a particular set of analyses) has been designated as the "reference composition" (see, for example, Reference 3). One aspect of the committee's investigation was to examine the meaning(s) of the term "reference" in this context.

Much of the doubt about the validity of the use of J-13 water derives from several factors: (1) the chemical composition of the water found in the pores and fractures of the unsaturated zone at the repository site at Yucca Mountain is unknown, thus near-field experiments are being conducted without knowledge that J-13 water is a good representative water; (2) the J-13 well is not located precisely at the repository site at Yucca Mountain, and it is not known whether the controls on its water chemistry are the same as those at Yucca Mountain; and (3) for far-field geochemical studies, it is not completely known to what extent J-13 water is typical of waters that radionuclides might encounter in being transported away from the repository. All of these factors are obviously important in developing information to predict the performance and integrity of the repository systems.

Two other criteria are also regarded as important if J-13 water is to be considered as a valid and useful surrogate or reference: (1) the water must be stable in chemical composition over a period of time both before and after sampling from the well, and (2) the water must be readily available in sufficient quantities for all experimenters. The first of these characteristics has not been examined in detail, especially with regard to the sensitivities of the water parameters in the NNWSI experiments, but J-13 water is generally regarded as meeting these criteria.

In our assessment of the rationale for the use of J-13 water in the NNWSI investigations, the committee has divided the overall issue into several individual questions, as follows:

1. Does the J-13 well produce from the Topopah Spring member of the Paintbrush Tuff, which is the same formation in which the repository will be located, thus possibly being chemically similar to the unsaturated-zone water?

2. What is the hydrogeologic source of the water in the J-13 well? If water from the Yucca Mountain repository site flows toward, and eventually into the J-13 production horizon, would it then be a more representative water?

3. Has there been any variation in the chemical composition of J-13 water over a period of time?

4. How does the chemical composition of J-13 water compare to that of other ground waters at Yucca Mountain and vicinity?

5. What can be said about the likelihood of J-13 water resembling the waters of the unsaturated zone at Yucca Mountain?

6. Would Yucca Mountain precipitation that penetrates to the Topopah Spring horizon at the repository site approach a chemical composition like that of J-13 water?

7. How do variations in the composition of a test water (such as J-13) affect the results of various experiments that are conducted in the NNWSI Project? In other words, how sensitive are the phenomena measured to changes in the composition of the water?

Each of these questions in turn are addressed in the following sections of This Report. In each case the answer is not always completely definitive, because certain important information is usually missing or not fully developed. Nevertheless, the detailed discussions of each of these questions collectively provide a reasonable overall conclusion regarding the use of J-13 water. Except for Question 6, which was examined by means of a new computer modeling study, all of the issues were examined on the basis of information gathered from the literature and from persons working in the NNWSI Project. In addition, we have briefly discussed the meaning of the term "reference" as it is applied to the use of J-13 water.

At first glance, it may appear that This Report is rather voluminous in comparison with the apparent simplicity of the question of the validity of J-13 water. However, on the order of 100 publications have appeared which

deal directly or indirectly with the use of J-13 water in the NNWSI Project, and a fairly complex, multidisciplinary array of experimental and theoretical studies have been carried out with the ultimate goal of containing radioactive waste for a long period of time at the proposed repository in Nevada. The importance of the water is that it is involved in the principal mechanisms and is the major route by which the radionuclides could escape from the repository. In This Report we have tried to review each of the issues as concisely as possible, perhaps generating a new perspective in a few places, while highlighting the points that are germane to the rationale for the use of J-13 water in the NNWSI Project.

The committee is especially indebted to a number of individuals for their assistance. Kevin Knauss was responsible for the computer modeling study described in Section 7; he conducted a very informative tour for the committee to Yucca Mountain; and in general, he has furnished much valuable insight for several aspects of this work. We also thank Larry Ramspott, Dave Short, and John Dronkers for outlining many of the technical and Quality Assurance policy issues of the questions that were examined. The NNWSI task leaders and their colleagues also were very helpful in providing information of the effects of the various parameters of J-13 water on the waste-package systems. These include Bill Glassley (Package Environment); W. L. Bourcier, Carol Bruton, Henry Shaw, and Roger Aines (Geochemical Modeling and Release Rate); and Joe Farmer and Dan McCright (Container Design). Rich Van Konynenburg discussed radiation effects. At Los Alamos National Laboratory, Julie Canepa was very helpful in discussing the ongoing work there and in providing some unpublished data.

References.

1. Environmental Assessment Report, "Yucca Mountain Site, Nevada Research and Development Area, Nevada," Vol. II, May, 1986.

2. K. Wolfsberg, et al, "Sorption-Desorption Studies on Tuff. I. Initial Studies with Samples from the J-13 Drill Site, Jackass Flats, Nevada," LANL Report LA-7480-MS, April, 1979.

3. W. R. Daniels, et al, "Summary Report on the Geochemistry of Yucca Mountain and Environs," LANL Report LA-9328-MS, December, 1982.

## Section 2
## Stratigraphic Origin of J-13 Well Water

Introduction. One reason given for the use of J-13 water as a reference is that it produces from the same stratigraphic unit as that of the repository, the Topopah Spring Member of the Paintbrush Tuff. The supposition is that if the rock chemistry in contact with the water is similar, the waters may also be similar.

Examination of the well construction details, however, raises the question of the degree to which the J-13 Well produces from the Topopah Spring Member. The construction of well J-13 includes perforations from a long section below the depth of the Topopah Spring Member, thus potentially allowing flow to enter the well from other formations (the tuffaceous beds of Calico Hills; the Crater Flat Tuff Members, Prow Pass, Bullfrog and Tram; and Tuff of Lithic Ridge).

Figures 2.1, 2.2, and 2.3 provide background into the construction of well J-13. Figures 2.1 and 2.2 are taken from the "Hole History Data" of Fenix and Scisson (1), and Figure 2.3 is from the comprehensive report of Thordarson on the geohydrology of the J-13 well (2). Figure 2.4 is a geologic cross section of the area (3) and shows the relationship of the J-13 well to Yucca Mountain, the location of the proposed repository. The J-13 well has been producing continually ever since completion in early 1963, and an extensive history of its water chemistry is available and is summarized in Section 4 of This Report.

In the configuration of the well, there appears to be some discrepancy as to whether the entire length of 5-1/2-in. liner is slotted, or whether only the interval below 2690 ft is open. The original "Hole History Data" sheet (1) states that the "5-1/2-in." liner was perforated between 1499'-3400' before running", whereas subsequent diagrams show the liner "slotted 2690' to 3312'". The distinction is minor, however, because there is no cement behind the liner, thus providing access to the well to any fluids entering the borehole below about 1550 ft.

**FENIX & SCISSON, INC.**
**HOLE HISTORY DATA**
**NNWSI**

Approved: Work Copy
Date:

| | | |
|---|---|---|
| Hole No.: J-13 Water Well **** | | Type Hole: Water Supply |
| User: | Area: 25 | Contract #: AT (29-2)-1302 |
| Location: NTS | County: Nye | W.O. #: None |

Surface Coordinates: N 749,209.32' E 579,650.59'

| | | |
|---|---|---|
| Ground Elev.: 3317.7'*** | Pad Elev.: | Top Casing Elev.: |
| Bottom Hole Coord: None | @ | Ref: |
| Rig On Location: 09-15-62 | Spudded: 09-19-62 | Completed: 01-08-63 |

Circulating Media: Conventional-mud-air, soap, water-areated mud
Main Rig & Contractor: Rig #22-Western Republic Drlg. Co.
No. Of Compressors & Capacity: N/A

| Bore Hole Record | | | Casing Record | | | | | |
|---|---|---|---|---|---|---|---|---|
| From | To | Size | O.D. | Wt/Ft. | Wall | From | To | $Ft^3$ Cement |
| 0' | 445' | 26" | 18" | NA | | 0' | 444' | 1000 |
| 445' | 1008' | 17-1/2" | | | | | | |
| 1008' | 1331' | 17" | 13-3/8"* | NA | | 0' | 1313' | |
| 1331' | 1556' | 15" | 11-3/4"* | NA | | 1313' | 1546' | 175 |
| 1556' | 1561' | 9-7/8" | | | | | | |
| 1561' | 2020' | 9" | | | | | | |
| 2020' | 3498' | 7-5/8" | 5.5"** | 15.5# | 0.275" | 1484' | 3385' | None |

Total Depth: 3498' Plugs: None
Junk: None
Logging Data: Electric (2), Gamma ray-neutron (1), Sonic (1), Density (1), Acoustic (1), Caliper (1)

**Rigs Used**

| Rig No. | Name | Class | Days Operating | Sec. W/Crew | Sec. W/O Crew | Total Days On Location |
|---|---|---|---|---|---|---|
| #22 | Western Republic Drlg. | | NA | | | 115.33 |

Remarks: * 13-3/8" and 11-3/4" casing are in same string with perforations between 1006' and 1400'.
** 5-1/2" liner was perforated between 1499'-3400' before running.
*** Rotary rig kelly bushing 10' AGL.
**** Hole was formally HTH #6.

SWL at hole completion was 925'.

Prepared By: JEC:llh

Figure 2.1. First page of hole history data for Well J-13 (from Ref. 1).

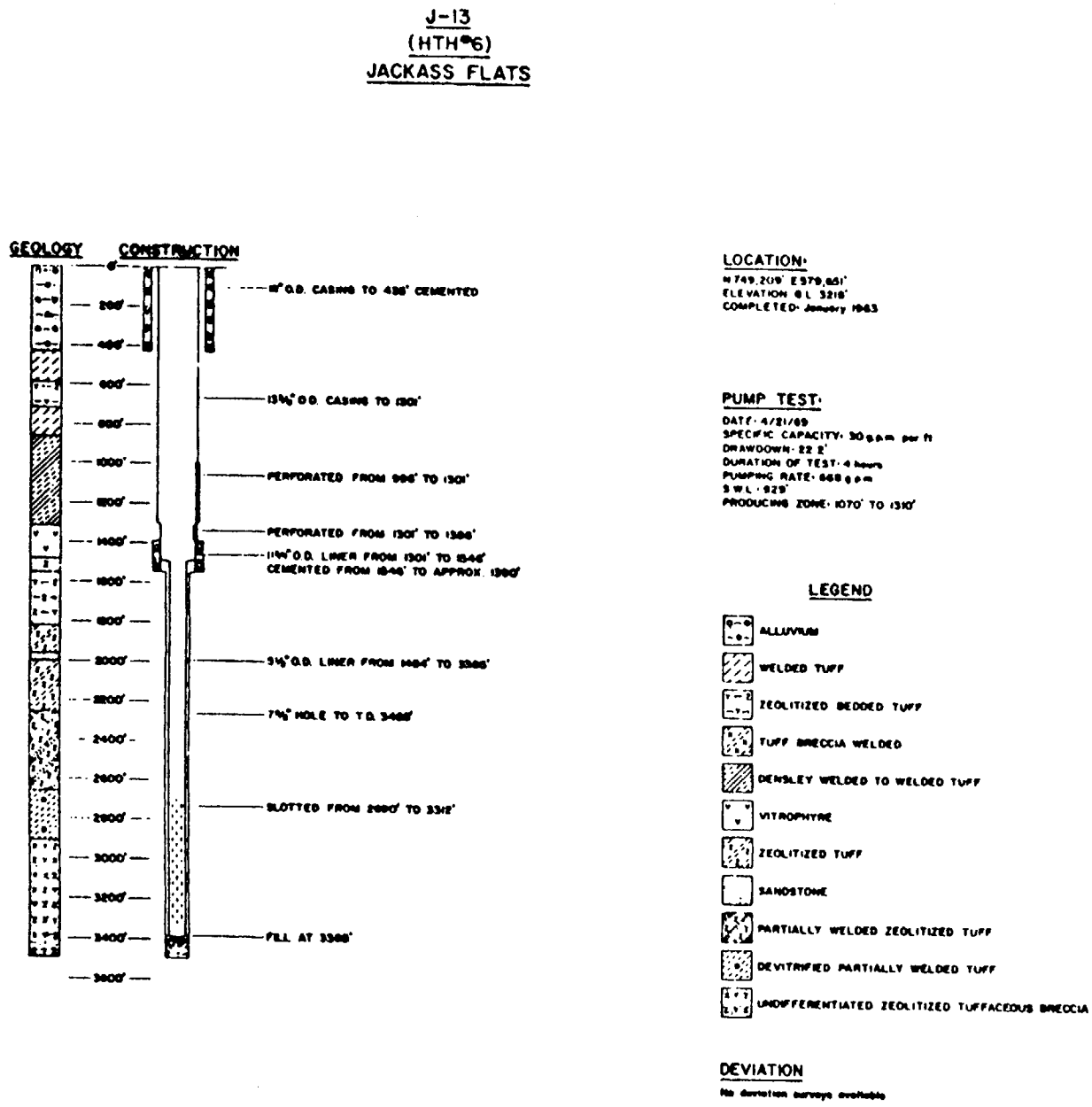



Figure 2.2. Well J-13 construction diagram from Hole History Data, Ref. 1.

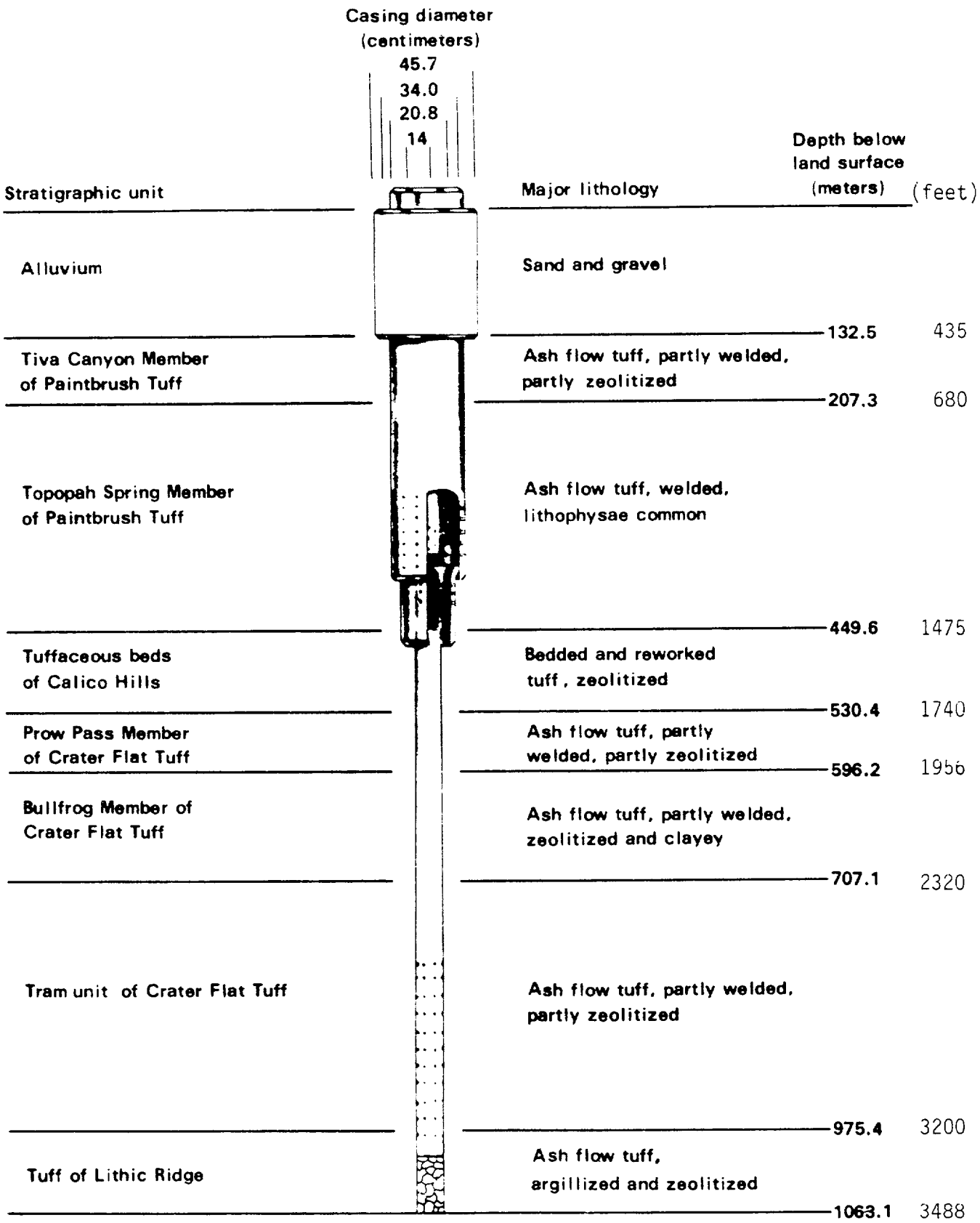



Fig. 2.3. Well J-13 construction diagram and lithologic units penetrated, from Thordarson, Ref. 2.

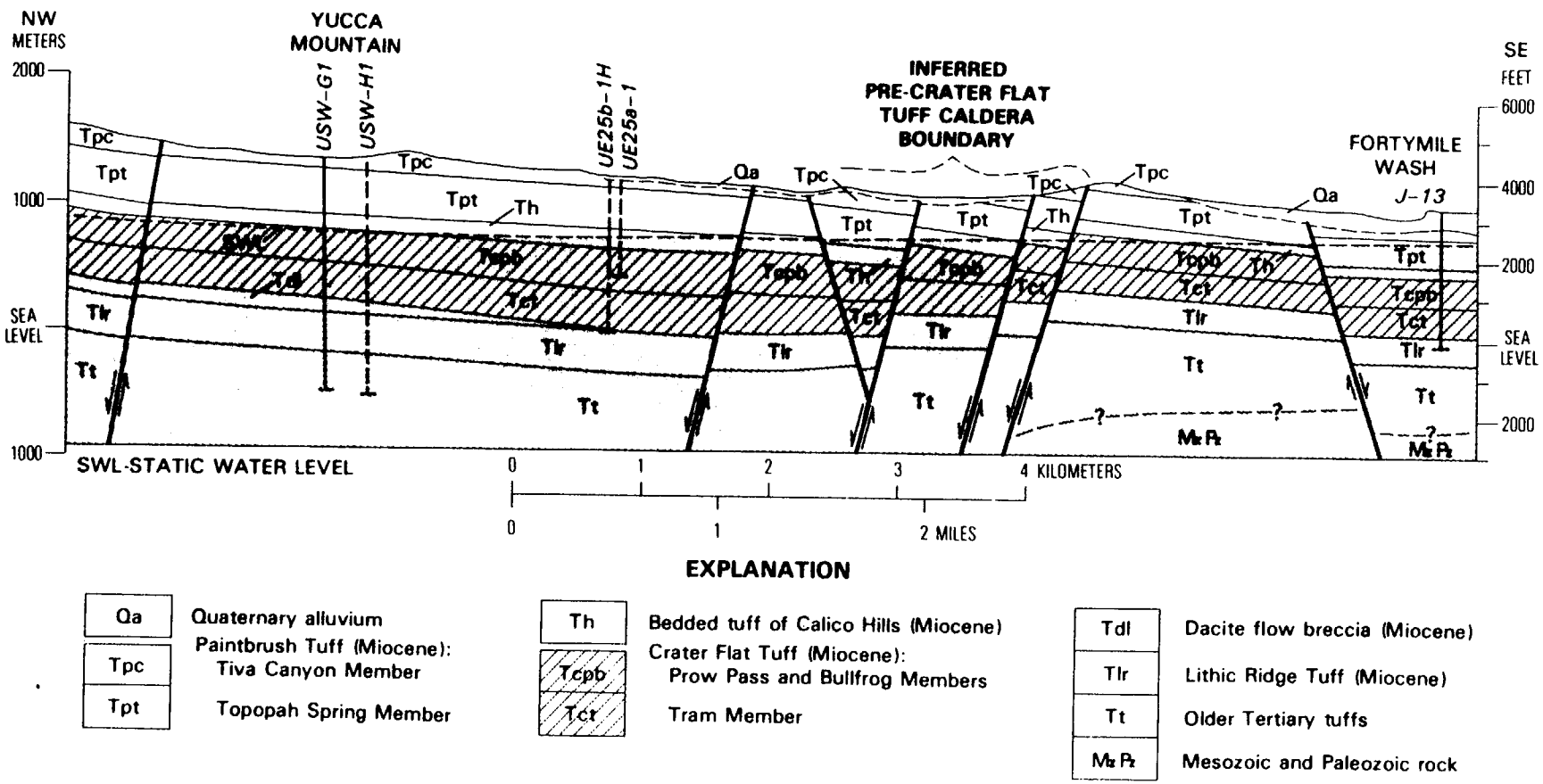



Figure 2.4. Geologic cross section between drill holes USW G-1 and J-13 in the Yucca Mountain area, Nye County, Nevada. Shaded area is below the static water level (from Ref. 3).

Discussion. There are two general arguments in support of J-13 water coming primarily from the Topopah Spring Member. The percentage of extraneous waters that would significantly affect the water chemistry remains undetermined.

1. Hydraulic tests were performed during the drilling and completion of J-13, as described by Thordarson (2). Of the two pumping tests providing useful information, the first tested only the Topopah Spring Member by placement of a bridge plug at about 1480 ft depth (see Figs. 2.3 and 2.4 for the approximate depths of the geologic units). This test was interpreted to indicate a transmissivity of 120 $m^2/d$. A second pump test which appears to have been conducted on the entire well yielded results interpreted as a transmissivity of 140 $m^2/d$. Whether a direct subtraction is proper is moot; however, the clear indication is that a major portion of the flow is likely to come from the upper (Topopah Spring) zone. (A straight subtraction is likely to overstate the percentage of the water which came from the Topopah Spring Member, but would indicate a level of about 86%.)

Additional slug and injection tests of lower zones, performed between straddle packers, did not identify any other zone with hydraulic conductivity as great as that indicated for the Topopah Spring zone. Numerical values of these slug and injection tests are difficult to compare directly with longer-period pumping tests, especially if complicated by a well geometry which includes a long open annular space.

2. Although qualitative, it has been affirmed by parties involved that other wells nearby which have been completed only in the deeper zones were not very productive, when compared to J-13. This would also suggest that most of the production in J-13 came from the Topopah Spring Member.

Some concerns remain.

1. It is not clear how large a contribution of water from other zones would be necessary to cause a significant change in the chemistry of the produced water.

2. The hydraulic-test data do not appear adequate to quantify exactly what percentage of the water produced could come from entries other than the Topopah Spring Member. If such a determination were warranted, a spinner survey would be potentially possible, depending upon the current physical configuration of the well (e.g. electrical wiring within the casing) and tools available for such a configuration.

3. The Pan Geo Atlas and Schlumberger geophysical logs of well J-13 (4,5) run in 1962 indicate a number of low resistivity zones (with other suggestive geophysical signatures), which could potentially contribute water to the well flow. Several of the logs even have original notations such as "aquifer" by the zones 1450 ft to 1850 ft (Tuffaceous beds of Calico Hills and Prow Pass Member of Crater Flat Tuff), and 2315 ft to 2460 ft (Tram unit of Crater Flat Tuff).

Conclusions. It seems quite likely that a major portion of the water produced from J-13 enters from the Topopah Spring Member, but as much as 20% of the flow may come from other pathways to the well. Whether this will materially affect the water chemistry is not clear, partly because the individual water chemistries and mixing percentages are not known independently.

Further investigations, possibly including a spinner survey or sampling of specific zones within J-13 or a newly drilled well, could help resolve these questions, if warranted.

There continues to be a discrepancy regarding the well perforations in the 5-1/2-in liner. Because there is no cement behind the liner, however, this discrepancy is of minor consequence.

References.

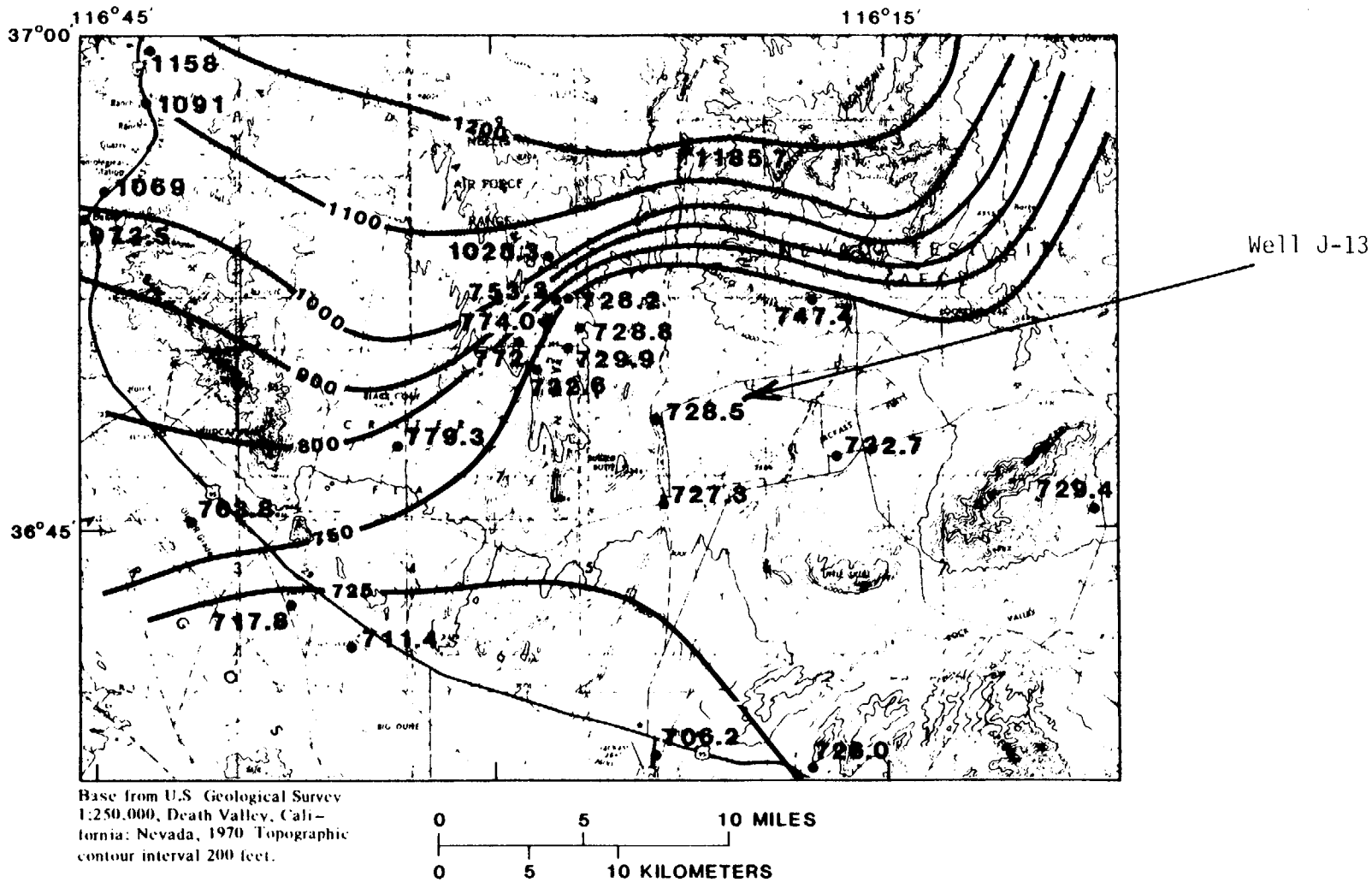
1. Fenix and Scisson, Inc., "Hole History Data, J-13 Water Well," 1963.

2. W. Thordarson, "Geohydrologic Data and Test Results from Well J-13, Nevada Test Site, Nye County, Nevada," USGS Water-Resources Investigations Report 83-4171, 1983.

3. W. J. Carr, F. M. Byers, Jr., and P. P. Orkild, "Stratigraphic and Volcano-Tectonic Relations of Crater Flat Tuff and Some Older Volcanic Units, Nye County, Nevada, USGS Professional Paper 1323, 1986.

4. Pan Geo Atlas Electrical Logs, 1962; Electrical Logs run on 11-Nov-62 and 18-Dec-62: note comments regarding "aquifers" on original Field Print of 11-Nov-62.

5. Schlumberger Electrical Logs, 1962; Induction Log and Laterolog, both run 1-Nov-62: also note Sonic Log run 1-Nov-62 and Formation Density Log run 2 Nov 62.




Base from U.S. Geological Survey 1:250,000, Death Valley, California: Nevada, 1970 Topographic contour interval 200 feet.

**EXPLANATION**

—800— **POTENTIOMETRIC CONTOUR--** Shows altitude of potentiometric surface, 19--. Contour interval, in meters, is variable. Datum is sea level.

•747.4 **TEST HOLE--** Number is measured composite water level, in meters above sea level.

Figure 3.1. Potentiometric surface in vicinity of Yucca Mountain and J-13 well. (from Ref. 4).

## Section 3
## Geographic Source of J-13 Well Water

Introduction. Although not a necessary condition to be a reference water, it is of interest to know whether water from the J-13 well may have come from the proposed repository site. As discussed in the previous section of This Report, most of the production of J-13 appears to be from the Topopah Spring Member of the Paintbrush Tuff, which is the same formation in which the proposed repository will be located. The repository will be located in the unsaturated zone in the Topopah Spring Tuff at Yucca Mountain, while at the J-13 well this formation is below the water table. If water from the Yucca Mountain site flows toward, and eventually into, J-13, that water is perhaps more likely to be representative of Yucca Mountain water.

Discussion. As shown in Figure 2.4 on page 2.5 and Figure 5.1 on page 5.3 of This Report, a prominent feature in the local area is Fortymile Wash located between Yucca Mountain and the J-13 well. This channel is believed to be a factor in the origin of the water in J-13 well. The general flow direction from north to south proposed by Winograd and Thordarson (1) for ground water beneath the Nevada Test Site makes highland areas to the north of Yucca Mountain such as Pahute Mesa potential recharge areas for Yucca Mountain and J-13. However, White (2) and White and Chuma (3) have concluded that ground water from Pahute Mesa flows into Oasis Valley, but that it is not a source for ground water in Fortymile Wash. The relationship between water from Pahute Mesa and Yucca Mountain is thus somewhat uncertain at this time.

Measurements of the potentiometric surface (4) have been used to construct contour maps of the surface in the vicinity of Yucca Mountain (see Figure 3.1). There is a generally very gentle southward gradient through the area of J-13, however data are scarce in the mile or so to the north. Wells G-4 and H-5 have measured heads only 0.5 and 1.5 ft above that at J-13. To the west and north of the repository site and in the upper reaches of Fortymile Wash, gradients steepen sharply. The limited depth data show downward flows within the saturated zone throughout the area.

Fortymile Wash is a well defined, incised channel which remains dry except during flood flow. The intermittent flow, with a deep water table, suggests that flood waters within the Wash provide recharge to the underlying ground

water table. Under present climatic conditions, recharge occurs at Pahute Mesa, at mountain ranges farther north, and perhaps Timber Mountain, either by direct contribution to the water table or by runoff into Fortymile Wash, which infiltrates while flowing southward.

Horizontal flow rates of ground water are slow in the area of J-13 and the repository. Using the conductivity determined in tests of J-13 (3 ft/d), and the gradient of approximately 1 ft/3000 ft, yields approx. 0.001 ft/d, or less than half a foot per year. Flow rates of this magnitude allow considerable time for equilibrium to be established with the local geochemistry, and leave less significance to the route by which water came to the well.

Kerrisk (5) reports isotopic data for wells in the Yucca Mountain and Fortymile Wash area; some of these data are also summarized in Section 5 of this Report. Both percent modern carbon and tritium values suggest that the waters produced from wells along Fortymile Wash are younger than those close to the repository site. This supports the hypothesis that much of the water produced from J-13 (and other wells along the Wash) results from relatively recent water infiltration and movement along the axis of Fortymile Wash.

Conclusions: Water from the Yucca Mountain repository site may flow toward J-13, however it is likely to be only a small component of the inflow to the well. The majority of the J-13 water probably comes from subsurface flow and infiltration along Fortymile Wash.

References.

1. I. J. Winograd and W. Thordarson, "Hydrogeologic and Hydrochemical Framework, South-Central Great Basin, Nevada-California, with Special Reference to the Nevada Test Site, USGS Professional Paper 712-C, 1975.

2. A. F. White, "Geochemistry of Ground Water Associated with Tuffaceous Rocks, Oasis Valley, Nevada, USGS Professional Paper 712-E, 1979.

3. A. F. White and N. J. Chuma, "Isotope and Carbon Models of the Oasis Valley-Fortymile Canyon Ground Water Basin," to be published in Water Resources Research, 1986; cited by Kerrisk, Ref. 5 below.

4. R. K. Waddell, J. H. Robison, and R. K. Blankennagel, "Hydrology of Yucca Mountain and Vicinity, Nevada-California -- Investigative Results through Mid-1983," USGS Water Resources Investigations Report 84-4267, 1984.

5. J. F. Kerrisk, "Ground Water Chemistry at Yucca Mountain, Nevada, and Vicinity," LANL Report LA-10929-MS, February, 1987.

| Date of Sample Collection | Organi-zation | Report Author | Ref. | Concentration, mg/L Na | Si | Ca | K | Mg | pH | Alkalinity, as $HCO_3^-$ | Concentration, mg/L $F^-$ | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-1-1963 | USGS | Claassen | 1,2 | 46 | 26.7 | 14 | 6.6 | 2.4 | 7.0 | 124 | 2.0 | 8.4 | 5.6[a] | 25[a] |
| 5-25-1964 | " | " | " | 48 | 27.1 | 14 | 5.0 | 1.8 | 6.8 | 136 | 2.4 | 7.4 | 4.5[a] | 23[a] |
| 11-1966 | " | " | " | 44 | 28.5 | 13 | 4.8 | 2.1 | 7.6 | 126 | 2.7 | 7.2 | 6.8 | 18 |
| 4-21-1969 | " | " | " | 44 | 26.7 | 14 | 5.4 | 2.5 | 7.3 | 124 | 2.4 | 5.4[a] | 9.0 | 18 |
| 3-26-1971 | " | " | " | 42 | 26.7 | 12 | 5.0 | 2.1 | 7.4 | 124 | 2.4 | 7.1 | 7.2 | 17 |
| 12-1977 | LANL | Wolfsberg | 3 | 47 | - | 13 | 4.7 | 2.0 | 7.3 | 130 | 1.7 | 7.7 | - | 21 |
| 4-1978 | " | " | " | 50 | - | 13 | 4.7 | 2.0 | 7.3 | 130 | 1.7 | 7.5 | - | 20 |
| 1981? | " | " | 4 | 46 | 31 | 12 | 5.5 | 1.7 | | 170[a] | 2.1 | 6.4 | 9.9 | 18 |
| 6-1981 | " | Daniels | 5 | 45 | 30.0 | 11.5 | 5.5 | 1.73 | 6.9 | 143 | 2.1 | 6.4 | 10.1 | 18 |
| 1-1982 | " | " | " | 50 | 37.6[a] | 14 | 5.0 | 2.2 | 8.3 | 127 | 1.8 | 6.3 | 9.1 | 18 |
| 1983? | USGS | Moore | 6 | 44 | 28.5 | 12 | 4.5 | 1.9 | 7.7 | 120 | 2.2 | 8.1 | 8.1 | 17 |
| 1983? | " | " | " | 44 | 26.6 | 12 | 3.7 | 2.0 | 7.6 | 120 | 2.2 | 7.0 | 8.3 | 19 |
| 1984? | LANL | Ogard | 7 | 45 | 30.0 | 11.5 | 5.3 | 1.8 | 6.9 | 143 | 2.1 | 6.4 | 10.1 | 18 |
| 1983-1984 | LLNL | Oversby[b] | 8,9 | 44 | 27.0 | 12.5 | 5.1 | 1.9 | 7.6 | 125[c] | 2.2 | 6.9 | 9.6 | 18.7 |
| 3-6-1984 | " | Harrar | 11 | 45 | 27.2 | 12.5 | 4.8 | 1.9 | - | - | 2.2 | 7.0 | 8.4 | 18.1 |
| 3-1986 | " | " | 12 | 45 | 27.2 | - | - | - | - | - | - | - | - | - |
| 1985? | ANL | Bates | 13 | 47 | 30.9 | 14 | - | 2.1 | - | - | - | - | - | - |
| 1986? | HEDL | Wilson | 14 | 50 | 31.9 | 15.0 | 5.5 | 2.1 | 7.2 | 118 | 2.7 | 7.3 | 8.7 | 18.8 |
| 1987? | LANL | Canepa | 15 | 45 | 30 | 13 | 4.5 | 2.0 | 8.2 | 143 | 2.1 | 7.1 | 8.9 | 18.7 |
| | | Mean, $\hat{\mu}$ | | 45.8 | 28.5 | 13.0 | 5.04 | 2.01 | 7.41 | 128.9 | 2.18 | 7.14 | 8.78 | 18.4 |
| | | s, std. dev. | | 2.29 | 1.85 | 0.99 | 0.61 | 0.21 | 0.44 | 8.6 | 0.29 | 0.61 | 1.03 | 1.03 |
| | | Range | | 8 | 4.4 | 3.5 | 1.9 | 0.8 | 1.5 | 25 | 1.0 | 2.1 | 3.3 | 4 |
| | | n' | | 19 | 16 | 18 | 17 | 18 | 15 | 15 | 17 | 16 | 13 | 15 |
| | | Max, $s_{\hat{\mu}}$ | | 0.53 | 0.46 | 0.23 | 0.15 | 0.049 | 0.11 | 2.2 | 0.070 | 0.15 | 0.29 | 0.27 |

? = Sampling date not reported.
[a]Data rejected in calculation of mean.
[b]Data reported as 12-mo average of analyses.
[c]From Ref. 10.

## Section 4
## Stability of the Chemistry of J-13 Well Water

Introduction. One of the prerequisites of a water for use as a reference standard is stability of chemical composition. In the case of a well water, such as that from the J-13 Well, one important aspect of stability is the reproducibility of the chemical composition of the water, over a period of time, upon repeated sampling from the well. A second factor that is important in the experimental use of the water is stability of composition both before and during storage of the water.

The stability of the chemistry of the water produced by the J-13 Well has not been explicitly addressed in the recent NNWSI literature; however, sample analyses covering an 8-year period after the well was completed in 1963 were compared by Claassen (1) Thordarson (2), and additional data have accumulated subsequently to provide a good view of this issue. Several investigators have also discussed changes in the chemistry of J-13 water that have been observed during storage.

History of Chemical Analyses of J-13 Well Water. Tables 4.1 and 4.2 summarize the readily available information on the chemical analyses of J-13 water, which cover almost a 25-year period. Most of the data are found in published reports, and represent analyses by five different laboratories; the U. S. Geological Survey (USGS), Los Alamos National Laboratory (LANL), Lawrence Livermore National Laboratory (LLNL), Argonne National Laboratory (ANL), and Hanford Engineering Development Laboratory (HEDL).

An attempt was made in compiling these tables to find and cite the original publications in which the data were reported. Several sets of these data reappear frequently in other later publications, sometimes in somewhat puzzling fashion. For example, the 1984 data of Ogard and Kerrisk at Los Alamos (7) are presented in the draft Site Characterization Plan (16), but in Kerrisk's recent publication (17), which is a comprehensive survey of the ground water chemistry at Yucca Mountain, only the USGS data of 1971 (1) are listed. Different laboratories also have different sets of what they consider to be the "reference" composition of J-13 water. Daniels, et al, at Los Alamos (5, p. 21) tabulated a "reference" composition for J-13 water that is neither of the sets mentioned above. At LLNL, Oversby's average composition (8) is cited by Delaney (9), but Glassley (18) lists Ogard and Kerrisk's 1984 data.

Water Sampling and Analysis. There are several complications in using these data to assess the stability of the chemistry of the water, but none appear to invalidate the final conclusions, primarily because a fairly long history is represented. First of all, a deficiency in most of the more recent data is that the exact date of well sampling was not reported, and it is not often clear whether the composition reported represents a single or multiple sampling of the well. There are a number of other factors that contribute to the variability of the data shown in Tables 4.1 and 4.2. These include the interlaboratory differences in sample handling and analysis, and changes in the analytical methods themselves over the years, not all of which are reported in the cited literature.*

For example, in the sample handling, it is not always reported whether or not the water samples are filtered. Filtration, and the specific pore size of the filter, can have a pronounced effect on the apparent minor-constituent concentrations, especially those of the less-soluble metals such as iron, aluminum, and manganese (1); see also Appendix B of Ref. 17. The preferred technique for characterizing a ground water is field filtration followed by acidification to stabilize the metals in solution (19). Variations in this technique are probably the major reason for the extreme variations of the concentrations of the minor constituent metals shown in Table 4.2, although, as Daniels, et al (5) have found, the reproducibility of the analyses of even the same sample of water can be poor for such elements as iron and manganese. The pore size of the filter has no demonstrable effect on the measured concentrations of the major constituents or characteristics of raw J-13 water, but consistency of this technique would be required to accurately trace the history of the minor constituents in the J-13 water.

In the 1960s and early 1970s work, the cations were measured by spectrophotometric and atomic absorption techniques, and the anions by ion-selective electrode and other techniques. At the present time, DC plasma and inductively-coupled plasma emission spectrometry are most often used

*It might be possible to trace these details further by consultation with the principal scientists, but this would require an effort beyond the scope of the present investigation, and the additional information does not appear crucial to our assessment of the stability of J-13 water.

Table 4.2. Reported Concentrations of Minor Constituents in J-13 Well Water.

| Date of Sample Collection | Organi-zation | Report Author | Ref. | Concentration, μg/L | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Li | B | Al | Mn | Fe | Sr | $PO_4^{3-}$ |
| 1-1-1963 | USGS | Claassen | 1,2 | 40 | – | – | 240 | 160 | 100 | 120 |
| 5-25-1964 | " | " | " | – | 140 | 62 | 110 | 40 | – | <10 |
| 11-1966 | " | " | " | 40 | – | – | 30 | <10 | 90 | <10 |
| 4-21-1969 | " | " | " | 40 | 130 | 8 | <10 | <10 | 90 | <10 |
| 3-26-1971 | " | " | " | 40 | – | – | <10 | <10 | 20 | <10 |
| 12-1977 | LANL | Wolfsberg | 3 | 50 | – | – | – | 0.0[a] | 60 | – |
| 4-1978 | " | " | " | 50 | – | – | – | 0.0[a] | 40 | – |
| 1981? | " | " | 4 | – | – | 8 | 12 | 11 | 40 | – |
| 6-1981 | " | Daniels | 5 | 70 | – | 26 | 11 | 44 | 40 | 100[b] |
| 1-1982 | " | " | " | 59 | – | 40 | 14 | 39 | 45 | <100 |
| 1984? | " | Ogard | 7 | 60 | – | 30 | 1 | 40 | – | – |
| 1983-1984 | LLNL | Oversby | 8,9 | 42 | 128 | 12 | – | 6 | 35 | – |
| 3-6-1984 | " | Harrar | 11 | – | 142 | – | – | – | – | <100 |
| 1985? | ANL | Bates | 13 | 49 | 130 | <100 | <5 | <10 | 41 | – |
| 1986? | HEDL | Wilson | 14 | – | <100 | 110 | – | – | – | 2800[b] |
| 1987? | LANL | Canepa | 15 | 40 | – | <100 | – | <10 | 40 | – |
| | | Mean, $\hat{\mu}$ | | 48 | 134 | | | | | |
| | | s, std. dev. | | 10 | 6.5 | | | | | |
| | | Range | | 30 | 14 | | | | | |
| | | n' | | 12 | 5 | | | | | |
| | | Max, $s_{\hat{\mu}}$ | | 2.9 | 2.9 | | | | | |

[a] As reported in Ref. 3

[b] Probably erroneous

Table 4.3. Reproducibility of Analyses of J-13 Water

| Organization & Technique | Ref. | n | Cations Std. deviation, mg/L Na | Si | Ca | K | Mg | Li |
|---|---|---|---|---|---|---|---|---|
| LANL | | | | | | | | |
| DCP-ES | 5 | 6 | 0.57 | 0.90 | 0.075 | 0.29 | 0.019 | 0.007 |
| LLNL | | | | | | | | |
| AAS | 11 | 7-11 | 0.36 | 1.3 | 0.30 | 0.07 | 0.01 | |
| DCP-ES | 12 | 5 | 0.20 | 0.10 | | | | |
| ICP-ES[a] | 11 | 4-21 | 1.02 | 0.64 | 0.36 | 0.07 | 0.03 | |
| ICP-ES[b] | 8 | 6 | 0.41 | 0.10 | 0.09 | 0.37 | 0.007 | |

| | Ref. | n | Anions Std. deviation, mg/L $F^-$ | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ | $HCO_3^-$ | $HCO_3^-$ Technique |
|---|---|---|---|---|---|---|---|---|
| LANL | 5 | 6 | 0.1 | 0.4 | 0.4 | 0.1 | 2 | Titration |
| LLL | 20 | 17 | 0.14 | 0.3 | 0.9 | 0.7 | 7 | $CO_2$ evolution (10) |

[a]Scanning instrument.
[b]Polychromator instrument; Table 1c in Ref. 8.

DCP-ES DC plasma emission spectrometry
ICP-ES Inductively-coupled plasma emission spectrometry
AAS Atomic absorption spectrophotometry

for the metals, while ion chromatography is used for the anions. At least three different methods remain in use for the alkalinity ($HCO_3^-$) measurements (20). An illustration of the differences in the precision of several of these techniques is presented in Table 4.3. These data also reveal differences in two different laboratories using the same nominal technique. In addition to differences in the reproducibility of the measurement technique, there are differences in the biases that each technique may have. This has also been studied in one instance (11,12). All of these factors thus contribute to the fluctuations that are apparent in the values shown in Tables 4.1 and 4.2.

Some of the values listed in Table 4.1 were rejected in the statistical averaging because they are clearly inconsistent with the other results. Such outliers are also usually evident as an inbalance in the anion-cation ion balance. Although not too far out of line, several constituents of the HEDL results (Na, Si, Ca, and $F^-$) are suspect; in this set of data, there is a 16% excess in the cation concentration. In general, the ion balance is an excellent test of the internal consistency of a J-13 water analysis (9)

In Table 4.2, there is so much scatter in the values for Al, Mn, Fe, Sr, and $PO_4^{3-}$ that no averages would be meaningful. Further work needs to be done on the sample handling and measurement techniques in order to obtain definitive values for these constituents.

Statistical Analysis of Data of Tables 1 and 2. With just a few exceptions (5, 8, 10-12), we do not know whether the values listed in the tables are single measurements (which is unlikely), or mean values. If they are means, we do not know, as mentioned above, how many measurements were made on identical or different well samples. It is thus not possible to combine all of these data in an optimal fashion to arrive at an estimate of the overall mean and variance for each constituent. Since full information on each analysis is not readily available, the overall means and standard deviations shown in Tables 4.1 and 4.2 were simply calculated giving equal weight to each individual table entry.

If each measurement were a single determination, these standard deviations would properly measure their dispersion, and if there were no biases, their means would be an accurate measure of the true values of the constituents of J-13 water as it was when the samples were taken. If, however, these means are actually the results of, say, 5 to 10 or more determinations, then our

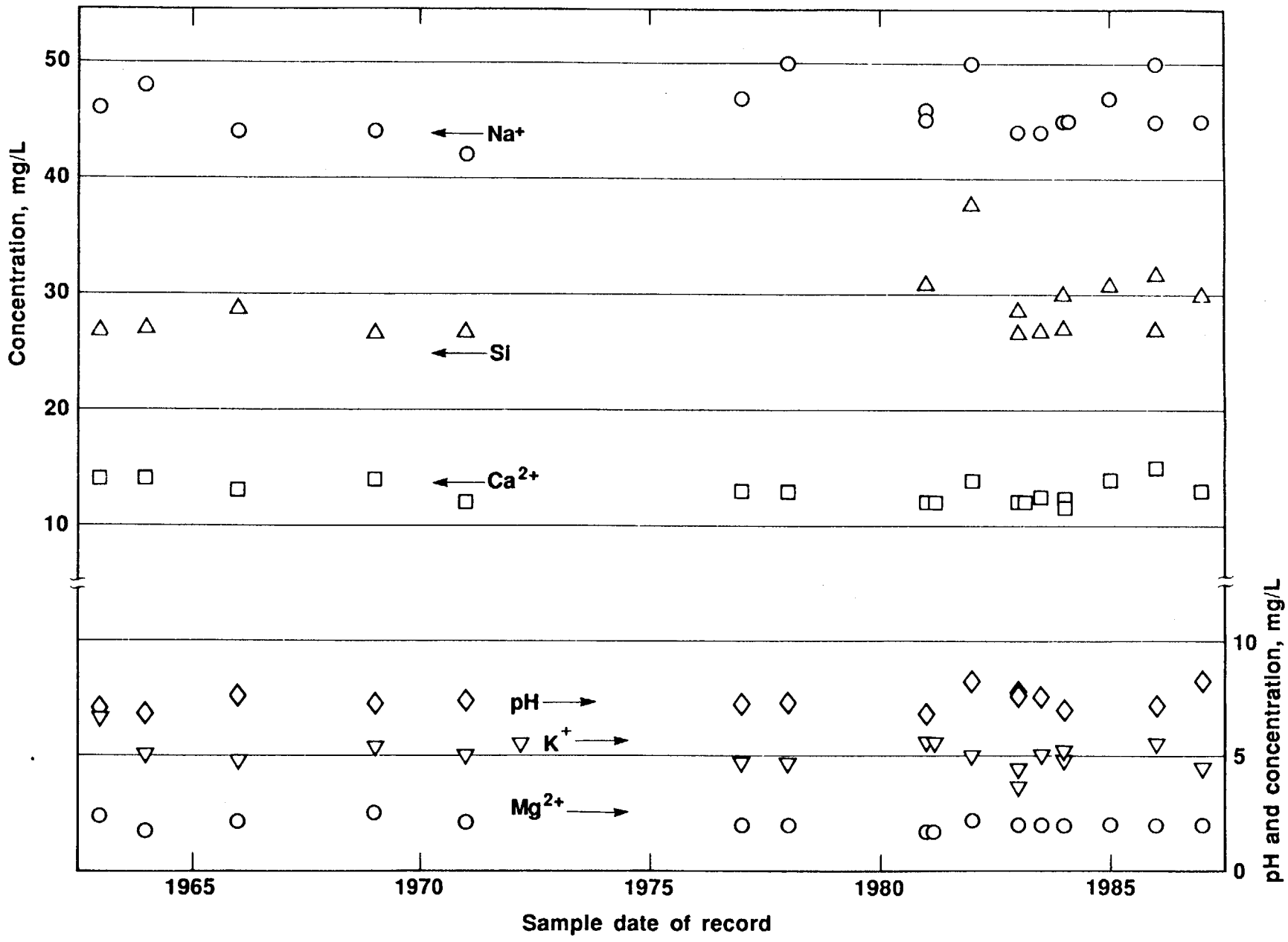



Figure 4.1. Variation of measured concentrations of major constituents of J-13 water.

standard deviation is a distorted measure of the between-sample (between-date) variation, and the information contained within those samples would be lost. Some, and probably most of the reported values are means. The "max s " values shown for Tables 4.1 and 4.2, however, were computed using n = 1 for each sample, thus the values shown are upper limits for estimates of the standard errors of the means. If the within-sample variation were known, these limits might be a little smaller or even much smaller.

In Figure 4.1 the values for the major cations and pH are plotted against the sample date of record. As seen in Table 4.1, the entire body of data really consist of two parts -- a set due to the USGS work of Claassen (1) and Thordarson (2) up to 1971, and a set from all of the laboratories beginning in 1977 after the advent of the NNWSI Project. It can be seen in Figure 4.1 that there appears to be a slight shift upward in the values for sodium and silicon between the early and the later portion of the data, but essentially no change in the other parameters. Examination of the trends in the anions shows that there is an apparent 19% increase in the nitrate, the only one that is statistically significant. The apparent changes in sodium, silicon, and nitrate are very likely due to changes in the accuracy of the analytical techniques used, which, as discussed above, have changed over the years. In general, the newer techniques are more accurate, especially for the anionic constituents. As a result of this examination of the apparent variations in the J-13 water composition, and all of the factors that could contribute to this variation, we conclude that the major cationic and anionic composition of J-13 well water has been stable for a considerable period of time.

Stability of J-13 Water During Storage. Many, if not most of the analyses of J-13 water have been performed on water taken from the well and stored for a period of time. There still remains the question of the extent of changes in the composition of the water after a sample is taken from the well. In general, sampling and then storing a groundwater may result in changes in the water temperature and changes in the content of dissolved gases such as $O_2$ and $CO_2$, which in turn may cause changes in redox potential (Eh), alkalinity, and pH. Equilibria involving the dissolved species may in turn be shifted, and precipitation of insoluble compounds may then result.

Measurements of the minor constituents such as Fe, Al, and Mn, on the other hand, are largely suspect -- the reported values are widely varying and they are known to be greatly influenced by the sample handling techniques. For these minor elements, and probably other trace constituents, no conclusion can reached as to the stability of their concentrations. Also for these elements, because their true values in the wellhead water are not well established, it is not possible to assess any differences that might exist between J-13 water and the repository or other local waters. It would be useful to undertake a water sampling and analysis project, including proper sample handling at the wellhead (19), and a study of the effects of filtration, to measure more accurate concentrations for the minor constituents. This would also result in tighter reference values for the major constituents.

References


1. H. C. Claassen, "Water Quality and Physical Characteristics of Nevada Test Site Water-Supply Wells," USGS Report 474-158, 1973, pp. 30-37.

2. W. Thordarson, "Geohydrologic Data and Results from Well J-13, Nevada Test Site, Nye County, Nevada," USGS Water Resources Investigations Report 83-4171, 1983, pp. 50-55.

3. K. Wolfsberg, et al, "Sorption-Desorption Studies on Tuff. I. Initial Studies with Samples from the J-13 Drill Site, Jackass Flats, Nevada, LANL Report LA-7480-MS, April, 1979, p. 12.

4. K. Wolfsberg, W. R. Daniels, B. R. Erdal, and D. T. Vaniman, "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, April 1 to June 30, 1982," LANL Report LA-9484-PR, October, 1982, p. 8.

5. W. R. Daniels, et al, "Summary Report on the Geochemistry of Yucca Mountain and Environs," LANL Report LA-9328-MS, December, 1982, pp. 21-25.

6. D. E. Moore, C. A. Morrow, and J. D. Byerlee, "Changes in the Permeability and Fluid Chemistry of the Topopah Spring Member of the Paintbrush Tuff (Nevada Test Site) When Held in a Temperature Gradient: Summary of Results," LLNL Report UCRL-15620, June, 1984, p. 4. Note: these authors were at the USGS under contract to LLNL.

7. A. E. Ogard and J. F. Kerrisk, "Groundwater Chemistry Along Flow Paths Between a Proposed Repository Site and the Accessible Environment," LANL Report LA-10188-MS, November, 1984, pp. 8-13..

8. V. M. Oversby, "Reaction of the Topopah Spring Tuff with J-13 Water at 120°C," LLNL Report UCRL-53574, July, 1984, p. 5, Table 1d.

The literature on J-13 well water indicates that it is a fairly stable water after it is pumped from the well. The downhole temperature of the water is 31°C (1,17 ). Measurements of the $O_2$ concentration of fresh samples at the wellhead (5,21,22) yield values of 5.5 to 5.7 mg/L, which is about 90% of air saturation at the well temperature and atmospheric pressure at that elevation (21). At sea level and 25°C, air saturation is 8 mg/L $O_2$. The Eh of the water at the wellhead has been found to be +340 mV vs. SHE (21), which is consistent with the high concentration of dissolved $O_2$. No observations of changes on storage, if any, have been reported. No sulfide or nitrite have ever been detected in raw J-13 water. Thus there is no doubt that J-13 water has the characteristics of an oxygenated water.

The pH of the water is observed to rise by a few tenths after sampling, presumably because of the loss of some dissolved $CO_2$ (5,9). At the J-13 wellhead, pH values of 6.9 (7) and 7.1 (5) have been measured; the laboratory pH is typically 7.4-7.6 (8,9). Measurements of the alkalinity of J-13 water and other Yucca Mountain area waters, at both the wellhead and in the laboratory, have resulted in essentially no difference in this parameter (23). No gross post-sampling precipitation of solids from the water has ever been observed, but the erratic analytical values for iron and manganese leaves open the possibility that these elements may be affected by slight changes in the pH and oxygen levels of the water after wellhead sampling and during storage.

Conclusions and Recommendations. It is concluded that, in spite of the varying conditions of sample handling and analysis over the years, which prevent a rigorous statistical interpretation, the levels of major constituents and principal characteristics of J-13 water have not changed in the 25 years since the well has been used. Parameters of the water in this category are the concentrations of Na, Si, Ca, K, Mg, Li, B, $HCO_3^-$, $F^-$, $Cl^-$, $NO_3^-$, $SO_4^-$, and $O_2$; and the values of Eh and pH. The mean values for these parameters found in Tables 4.1 and 4.2 can taken as reasonable *de facto* reference values, and there is a reasonable assurance that they will not change during future experiments with the water. It is noteworthy that the J-13 well is pumped frequently as a local water at the Nevada Test Site, thus logistically it is ideal as a source of reference experimental water.

9. J. M. Delaney, "Reaction of Topopah Spring Tuff with J-13 Water: A Geochemical Modeling Approach Using the EQ3/6 Reaction Path Code," LLNL Report UCRL-53631, November, 1985, pp. 5-7.

10. Memorandum, K. Knauss to V. M. Oversby, Lawrence Livermore National Laboratory, January 15, 1985.

11. Memorandum, J. E. Harrar to W. E. Glassley, Lawrence Livermore National Laboratory, May 14, 1986.

12. Memorandum, J. E. Harrar and J. F. Carley to V. M. Oversby and W. E. Glassley, Lawrence Livermore National Laboratory, January 16, 1987.

13. J. K. Bates, T. J. Gerding, T. A. Abrajano, Jr., and W. Ebert, "NNWSI Waste Form Testing at Argonne National Laboratory, Semiannual Report, July- December, 1985," LLNL Report UCRL-15801, March, 1986, p. 14.

14. C. N. Wilson, "Results from Cycles 1 and 2 of NNWSI Series 2 Spent Fuel Dissolution Tests," Westinghouse-Hanford Company Report HEDL-TME 85-22, May, 1987, p. B-9.

15. J. M. Canepa, Los Alamos National Laboratory, private communication, April, 1988 (Technical Milestone M316).

16. Site Characterization Plan, Consultation Draft, Volume II, January, 1988, Chapter 4, "Geochemistry," pp. 4-39 to 4-51.

17. J. F. Kerrisk, "Groundwater Chemistry at Yucca Mountain, Nevada, and Vicinity, LANL Report LA-10929-MS, February, 1987, Appendix A.

18. W. E. Glassley, "Reference Waste Package Environment Report," LLNL Report UCRL-53726, October, 1986.

19. H. C. Claassen, "Guidelines and Techniques for Obtaining Water Samples That Accurately Represent the Water Chemistry of an Aquifer," USGS Open-File Report 82-1024, 1982.

20. Memorandum, J. E. Harrar and S. P. Perone to V. M. Oversby and W. E. Glassley, Lawrence Livermore National Laboratory, November 25, 1986.

21. K. Wolfsberg and B. R. Erdal, Compilers, "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, October 1 to December 31, 1980," LANL Report LA-8739-PR, April, 1981, pp. 21-22.

22. I. J. Winograd and F. N. Robertson, Science, 216, 1227 (1982).

23. L. V. Benson, J. H. Robison, R. K. Blankennagel, and A. E. Ogard, "Chemical Composition of Ground Water and the Locations of Permeable Zones in the Yucca Mountain Area, Nevada," USGS Open File Report 83-854, 1983, P. 10.

composition of water in the repository unsaturated zone cannot be given a definitive answer. A discussion of this aspect of the evaluation will be given in Section 6 of this report.

Here we will be concerned primarily with Regions (3) and (4) and the question of whether J-13 water is a representative water for these regions. To the extent that this is true, it also be provides some evidence for the possibility that J-13 water will be representative of the near-field and unsaturated-zone waters as well. In this section, we will first compare the characteristics of J-13 water with waters from wells within the repository exploratory block, then with waters from wells at Yucca Mountain in the immediate vicinity of the exploratory block, and finally with other wells in the general area of Yucca Mountain. The comparisons will be limited to the major parameters and the levels of constituents for which there appears to be accurate data. As noted in Section 4 of this report, the concentrations of some of the trace elements (e. g., Al, Fe, Mn) are not well enough known to use in comparing waters.

A number of wells have been drilled in the Yucca Mountain area, and the locations of those considered in this report are shown in Figure 5.1. Both the U. S. Geological Survey and Los Alamos National Laboratory have been active in measuring the water chemistry of these wells, and some very useful data have been accumulated. Good summaries of these data with discussions are found in the publications of Benson and McKinley (1), Benson, et al (2), Ogard and Kerrisk (3), and Kerrisk (4); and additional details of construction and characteristics of the wells can be found in the geohydrology reports for the individual wells. Other useful summaries have appeared in Guzowski, el al (5) and the draft Site Characterization Plan (6).

Several authors have made detailed comparisons of the waters of Yucca Mountain and vicinity to help explain the origins of the chemical species, the geochemical controls on the compositions, and the hydrology of the area. Many useful graphical correlations among the variables and between the water chemistry and well location have been presented. Particularly noteworthy are the reports of Winograd and Thordarson (7; see also Ref. 5), Benson, et al (2), and Kerrisk (4). The last is a very comprehensive discussion using all of the most recent measurements.

## Section 5

## Comparison of Water Chemistry of J-13 Well with Chemistries of Other Wells in the Yucca Mountain Area

Introduction. One of the requirements of a reference water for use in the nuclear waste storage investigations is that there must be a reasonable probability that the chemical composition of the water will resemble, if not match that of the water that will interact with the waste package and the radionuclides which may migrate away from the waste storage site. The degree of similarity desired will depend on the specific water characteristic (e. g., chloride concentration, pH, etc.) and the phenomenon (e. g., corrosion, metal complexation, sorption, etc.) being considered, but in general there should be a correspondence.

The question of the validity of J-13 water for use as a reference water can be thought of in terms of four regions in the vicinity of the nuclear waste repository:

(1) the "near-field" environment in the unsaturated zone of Yucca Mountain, which comprises the region around the emplaced waste package that is influenced by the heat generated by the radioactive waste,

(2) a region in the unsaturated zone not influenced by the waste-package heat,

(3) a region in the relatively shallow saturated zone where the water composition is governed by the tuffaceous formations underlying Yucca Mountain,and

(4) a second region in the "far-field" environment, in the deeper aquifers in the vicinity of Yucca Mountain, where the composition of the waters is different than in the shallow zones.

In Region (2), and in the absence of heat in Region (1), the only existing water is that found in the pores and fractures of the rock. However, neither pore water nor fracture water from the repository location has yet been available for chemical analysis, thus their chemical compositions are presently unknown. Experiments are being conducted to obtain and analyze representative pore water, and some comparisons using pore and fracture waters from other locations have been made, but as yet, questions relating to the

It is generally concluded that all of the waters of the Yucca Mountain area that are derived from the shallow saturated zones of the tuffaceous aquifers are of the sodium-potassium-bicarbonate type (4,7). Most waters have a pH's in the 7-to-8 range, temperatures between 25 and 40°C, and are nearly saturated in oxygen. Sodium is the primary cation and bicarbonate is the primary anion. Other major cations present are calcium, potassium, and magnesium; and other major anions are sulfate and chloride, with lesser amounts of fluoride and nitrate.

Although it is well established that the Yucca Mountain regional waters collectively are similar, we wish to examine in the present context whether J-13 water is a suitable representative of this class for experimental purposes. The chemical analyses of the waters from the different wells represent variations in the lithology and geohydrology of the regions from which the water was pumped. In some cases the samples of waters analyzed are integral, i.e., from the entire production zones of the wells. In other cases, certain zones were isolated and sampled, and correlations have been made between the type of rock of the zone and the water chemistry. This aspect will be briefly mentioned, but our principal objective here is to select the most relevant data and set up a comparison between J-13 water and the general characteristics represented by groups of wells.

Comparison with Repository-Block Wells. In Table 5.1, the characteristics of J-13 water are compared to the ranges of parameters exhibited by water from wells USW G-4, H-4, and H-5. The values for J-13 water are the mean values derived from the 25-year history of analyses evaluated in Section 4 of this report. Also shown are values of 3X the maximum standard deviation of the means calculated from those data. Two different sets of data (except for the stable isotopes) are given in Table 5.1 for each well -- one from the USGS and one from LANL. The ranges are listed on the basis of the lowest and highest values reported, and then the mean plus-or-minus $3s_{\mu}$ for J-13 is compared to determine whether it falls within the range of the other wells. The ranges would be wider if the uncertainties associated with the other well data were known.

In the isotopic data, which are taken from Benson and McKinley (1), $\delta D$ (del deuterium) and $\delta^{18}O$ are reported in parts per thousand relative to standard mean ocean water, $\delta^{13}C$ is reported in parts per thousand relative

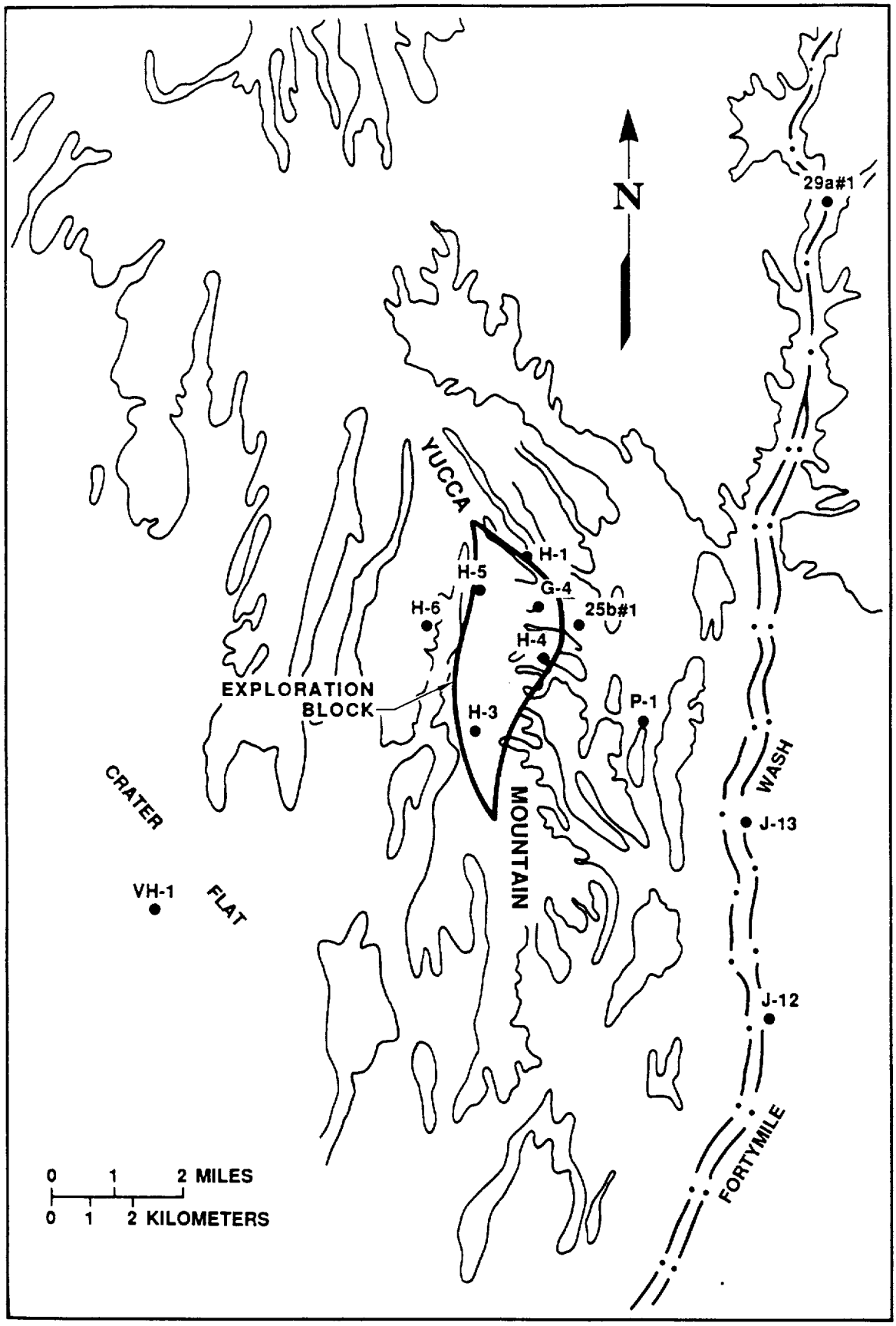



Figure 5.1. Drillhole and well locations in and near the Yucca Mountain exploration block. (Numbers of wells abbreviated for clarity; map adapted from Ogard and Kerrisk, Ref. 3).

to Peedee belemnite, and the $^{14}C$ apparent age is in years before the present. The isotopic data are probably not as relevant as the other water parameters as far as interactions with waste package components are concerned, but are included here because they afford another interesting point of comparison for the hydrogeochemistry and the source waters of J-13.

The data for well USW H-3 are listed separately in Table 5.1 because this well is a special case. Unlike the integral water samples from the other wells (J-13, G-4, H-4, and H-5), the water from H-3 was obtained from a deep, packed-off zone between 822 and 1,220 m (1,3). Its water chemistry is not typical of that of the other Yucca Mountain wells: its pH is two units higher, and it is practically anoxic, with a low Eh. The high alkalinity and sodium are also found only in the water of the other deep well UE-25p#1 to be discussed below. Although the H-3 and UE-25p#1 well waters might not resemble the unsaturated-zone repository water, they are still important to consider because they are certainly typical of other waters that radionuclides might eventually encounter after escaping from the repository.

Comparing J-13 water with the near-repository waters of G-4, H-4, and H-5, it is seen in Table 5.1 that J-13 is outside the ranges for only Na, K, Mg, $\delta D$, and the $^{14}C$ age. The differences for sodium, $\delta D$, and age, however, are not very large. The most significant differences are those of the concentrations of potassium and magnesium, which are much higher in J-13 water. Note that all of these wells are very similar in pH and anion concentration, and all are oxidizing in character.

When three other waters from wells just outside the exploratory block are included in the comparison, as shown in Table 5.2, the range of characteristics is somewhat wider, and both sodium and $\delta D$ now fall within the range. Well UE-25b#1 has higher potassium and magnesium than the group of three in Table 5.1, but still not as high as J-13. The water from J-13 appears to be younger in age than any of the repository-block or near-repository waters on the basis of the $^{14}C$ dating. Tritium concentrations have been measured for some of these waters, but not well enough to verify this finding (1).

Also included in Table 5.2 are the measurements reported for well UE-25p#1 (1,3,8). This well was drilled primarily to obtain information about rocks of Paleozoic age that were presumed to underlie the volcanic tuffs of Tertiary age which have been penetrated by previous wells in the Yucca Mountain

Table 5.1. Comparison of composition of water from J-13 well with compositions of waters of other Yucca Mountain wells in the repository exploratory block.

(Concentrations are in mg/L except as noted; see text for units of isotopic analyses.)

| Parameter | Repository Exploration Block Wells[a] G-4 | | H-4 | | H-5 | | Range | J-13[b] Mean | 3sμ | J-13 within range? | H-3[c] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Na | 57 | 56 | 73 | 84 | 60 | 54 | 54 - 84 | 45.8 | 1.6 | No | 120 | 124 |
| Si | 21.0 | 19.6 | 21.5 | 25.9 | 22.5 | 17.4 | 17.4 - 25.9 | 28.5 | 1.5 | Yes | 20.1 | 16.9 |
| Ca | 13 | 9.2 | 17 | 10.8 | 1.9 | 1.1 | 1.1 - 17 | 13.0 | 0.6 | Yes | 0.8 | 0.8 |
| K | 2.1 | 2.5 | 2.6 | 2.6 | 2.1 | 2.3 | 2.1 - 2.6 | 5.0 | 0.5 | No | 1.1 | 1.5 |
| Mg | 0.2 | 0.15 | 0.29 | 0.19 | 0.01 | 0.03 | 0.01- 0.29 | 2.01 | 0.15 | No | 0.02 | 0.01 |
| Li | 0.067 | 0.08 | 0.130 | 0.16 | 0.062 | 0.04 | 0.04- 0.16 | 0.048 | 0.009 | Yes | 0.22 | 0.22 |
| Field pH | 7.7 | 7.1 | 7.4 | 7.4 | 7.8 | 7.1 | 7.1 - 7.8 | 7.4 | 0.3 | Yes | 9.2 | 9.4 |
| " Eh, mV | - | 402 | - | 216 | - | 353 | 216 - 402 | 340 | - | Yes | - | -143 |
| " $HCO_3^-$ | 139 | - | 173 | - | 126 | - | 126 - 173 | 129 | 7 | Yes | 274 | - |
| " $O_2$ | - | 6.4 | - | 5.8 | - | 6.3 | 5.8 - 6.4 | 5.6 | 0.2[d] | Yes | <0.1 | <0.1 |
| $F^-$ | 2.5 | 2.4 | 4.8 | 4.5 | 1.4 | 1.3 | 1.3 - 4.8 | 2.18 | 0.21 | Yes | 5.5 | 5.4 |
| $Cl^-$ | 5.9 | 5.5 | 6.9 | 6.2 | 6.1 | 5.7 | 5.5 - 6.9 | 7.1 | 0.5 | Yes | 5.5 | 8.3 |
| $NO_3^-$ | - | 5.5 | - | 4.7 | - | 8.6 | 4.7 - 8.6 | 8.8 | 0.9 | Yes | - | 0.2 |
| $SO_4^{2-}$ | 19 | 15.7 | 26 | 23.9 | 16 | 14.6 | 14.6 - 26 | 18.4 | 0.8 | Yes | 31 | 31.2 |
| δD | -103 | - | -104 | - | -102 | - | -102 to -104 | -98 | 2[d] | No | -101 | - |
| $\delta^{18}O$ | -13.8 | - | -14.0 | - | -13.6 | - | -13.6 to -14.0 | -13.0 | 0.3[d] | Yes | -13.9 | - |
| $\delta^{13}C$ | - 9.1 | - | -7.4 | - | -10.3 | - | -7.4 to -10.3 | -7.3 | 0.3[d] | Yes | -4.9 | - |
| $^{14}C$ age, yrs | 12,160 | - | 17,200 | - | 13,700 | - | 12,160 to 17,200 | 9,900 | 100[d] | No | 18,100 | - |

[a]First entry in each column from Benson, et al (2); second entry in each column from Ogard and Kerrisk (3).
[b]J-13 water data from Tables 4.1 and 4.2 of this report; isotopic data from Benson and McKinley (1).
[c]First entry in column from Benson and McKinley (1); second from Ogard and Kerrisk (3).
[d]Estimated uncertainty.

area (8). The so-called Tertiary water was sampled at a depth of 381-1,197 m, and the Paleozoic water at 1,297-1,805 m in a Silurian dolomite formation (8). The source of the water in the LANL work is not clear from the report (3). Even the so-called Tertiary water is, in fact, from deeper zones than most of the other wells, and, like the LANL sample, is probably a mixture of the Tertiary and Paleozoic (4). As can be seen, it is higher in sodium, and significantly higher in calcium, potassium, and magnesium. The concentrations of the latter three elements are much higher in this well water than in J-13 water.

In Table 5.3 are listed the characteristics of the waters from wells in the vicinity of Yucca Mountain (see Figure 5.1), but some distance removed from the repository site. J-13 well itself is in this category. Well J-12 apparently has not been sampled and analyzed since the 1971 work of Claassen (9). Test well UE-29a#2 was drilled to obtain geohydrologic data at a location upgradient from Yucca Mountain in an area where no nearby drill holes exist (10). This well, J-12, and J-13 each sample waters beneath Fortymile Canyon, which is an important feature in the hydrology of the region.

Even though some of the information is missing, it can be seen that the chemical compositions of all of the waters listed in Table 5.3 are quite similar. As would be expected from their location and depths, J-12 and J-13 are very similar in water composition (9), and both wells have the only waters (except for the deep well UE-25p#1) that are high in both potassium and magnesium. The levels of these elements in J-13 water seem to be the only notable characteristic that distinguishes this water from the other waters of the shallow saturated zones. The water from UE-29a#2 (see Table 5.3) is the only one whose estimated $^{14}C$ age is younger than the waters of J-12 and J-13, and it is interesting that all three are the youngest of the overall group. This is believed by Claassen (11) and Kerrisk (4) to be due to higher local recharge of the ground water beneath Fortymile Canyon.

Conclusions. Because almost all of the characteristics of J-13 water fall within the ranges found for the waters of the shallow tuffaceous aquifers in the vicinity of Yucca Mountain, it is concluded that J-13 water is a good representative of this class. Compared to the waters of the saturated zone in and near the repository exploratory block, J-13 water is elevated in potassium and magnesium, but these are not high compared to levels in the waters of the

Table 5.2. Comparison of composition of water from J-13 water with compositions of waters of Yucca Mountain wells near the repository exploratory block.

(Concentrations are in mg/L except as noted; see text for units of isotopic analyses.)

| Parameter | H-1[a] | | H-6[b] | | UE-25b#1[c] | | J-13 mean | J-13 within range? | UE-25p#1 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Tertiary[e] | Paleozoic[e] | Integral?[f] |
| Na | 51 | - | 86 | 74 | 46 | 46 | 45.8 | Yes | 92 | 150 | 171 |
| Si | 22.0 | - | 22.5 | 20.0 | 17.8 | 28.7 | 28.5 | Yes | 22.9 | 19.2 | 30 |
| Ca | 4.5 | - | 4.1 | 5.5 | 17 | 18.4 | 13.0 | Yes | 37 | 100 | 87.8 |
| K | 2.4 | - | 1.3 | 2.1 | 3.5 | 2.5 | 5.0 | No | 5.6 | 12.0 | 13.4 |
| Mg | < 0.1 | - | 0.09 | 0.22 | 0.59 | 0.68 | 2.01 | No | 10 | 39 | 31.9 |
| Li | 0.040 | - | 0.082 | 0.10 | 0.22 | 0.30 | 0.048 | Yes | 0.23 | 0.59 | 0.32 |
| Field pH | 7.7 | - | 8.1 | 7.4 | 7.5 | 7.2 | 7.4 | Yes | 6.8 | 6.6 | 6.7 |
| " Eh, mV | - | - | - | 395 | - | 220 | 340 | Yes | - | - | 360 |
| " $HCO_3^-$ | 115 | - | 182 | - | 139 | - | 129 | Yes | 330 | 710 | - |
| " $O_2$ | - | - | - | 5.6 | - | 1.8 | 5.6 | Yes | - | - | - |
| $F^-$ | 1.2 | - | 4.7 | 4.1 | 1.6 | 1.2 | 2.18 | Yes | 3.4 | 4.7 | 3.5 |
| $Cl^-$ | 5.7 | - | 7.6 | 7.7 | 8.5 | 7.1 | 7.1 | Yes | 13 | 28 | 37 |
| $NO_3^-$ | - | - | - | 5.3 | - | 0.6 | 8.8 | Yes[d] | - | - | < 0.1 |
| $SO_4^{2-}$ | 18 | - | 29 | 27.5 | 22 | 20.6 | 18.4 | Yes | 38 | 160 | 129 |
| $\delta D$ | -101 | - | -106 | - | -101 | - | -98 | Yes | -106 | -106 | - |
| $\delta^{18}O$ | -13.5 | - | -13.8 | - | -13.4 | - | -13.0 | Yes[d] | -13.5 | -13.8 | - |
| $\delta^{13}C$ | -11.4 | - | -7.5 | - | -10.4 | - | -7.3 | Yes | -4.2 | -2.2 | - |
| $^{14}C$ age, yrs | 12,000 | - | 14,600 | - | 14,400 | - | 9,900 | No | 26,900 | 30,300 | - |

[a]Upper zone; from Benson and McKinley (1).
[b]First column, integral sample 10/16/82, from Benson and McKinley (1); second column from Ogard and Kerrisk (3).
[c]First column, integral sample 9/1/81, from Benson and McKinley (1).
[d]Including wells G-4, H-4, and H-5 in the comparison.
[e]Data from Benson and McKinley (1) and Craig and Johnson (8).
[f]Data from [illegible] and Kerrisk (3).

deeper aquifers. In two of the most important characteristics of the water for nuclear waste investigations -- pH and oxygen concentration -- J-13 water is quite similar to the other shallow waters. Provided that the concentrations of potassium, magnesium, and the trace elements which could not be assessed here, do not not significantly influence the phenomena of interest, J-13 water should serve as a good reference water for experimental work on such topics as radionuclide solubility, speciation, sorption, and rates of transport. The similarity of J-13 water to waters of the repository unsaturated zone is still an open question, which is discussed further in Section 5 of This Report. The chemical variations of the shallow, saturated-zone waters in the Yucca Mountain region are not large for ground waters in general. This suggests that the variations to be found within the unsaturated zone would also not be large, and would tend to fall within the bounds observed for the saturated-zone waters.

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Table 5.3. Chemical composition of water from other wells in the Yucca Mountain area.

| | VH-1[a] | UE-29a#2[b] | | J-12[c] | J-13, mean[d] |
|---|---|---|---|---|---|
| Na | 78 | 44 | 51 | 38 | 45.8 |
| Si | 22.9 | 20.6 | 25.8 | 25.3 | 28.5 |
| Ca | 9.9 | 10 | 11.1 | 14 | 13.0 |
| K | 1.8 | 1.3 | 1.2 | 5.1 | 5.0 |
| Mg | 1.5 | 0.3 | 0.34 | 2.1 | 2.01 |
| Li | 0.090 | 0.11 | 0.10 | 0.040 | 0.048 |
| Field pH | 7.5 | 7.0 | 7.0 | 7.1 | 7.4 |
| " Eh, mV | - | - | 305 | - | 340 |
| " $HCO_3^-$ | 162 | 54.9 | - | 119 | 129 |
| " $O_2$ | - | - | 5.7 | - | 5.6 |
| $F^-$ | 2.7 | 0.9 | 0.56 | 2.1 | 2.18 |
| $Cl^-$ | 10 | 8.8 | 8.3 | 7.3 | 7.1 |
| $NO_3^-$ | - | 9.7 | 18.7 | - | 8.8 |
| $SO_4^{2-}$ | 44 | 21 | 22.7 | 22 | 18.4 |
| $\delta D$ | -108 | -93 | - | -98 | -98 |
| $\delta^{18}O$ | -14.2 | -12.8 | - | -12.8 | -13.0 |
| $\delta^{13}C$ | -8.5 | -13.1 | - | -7.9 | -7.3 |
| $^{14}C$ age, yrs. | 17,000 | 4,100 | - | 9,100 | 9,900 |

[a]Data from Benson and McKinley (1), sampled 2/11/81.
[b]First column, from Benson and McKinley (1) and Waddell (10), sampled upper zone, 1/15/82. second column from Ogard and Kerrisk ( ), integral sample.
[c]Data from Claassen (11) et seq (1, 3-6) sampled 3/26/71.
[d]From Table 4.1 of this report.

9. H. C. Claassen, "Water Quality and Physical Characteristics of Nevada Test Site Water-Supply Wells," USGS Report 474-158, 1973.

10. R. K. Waddell, Jr., "Hydrologic and Drill-Hole Data for Test Wells UE-29a#1 and UE-29a#2, Fortymile Canyon, Nevada Test Site," USGS Open-File Report 84-142, 1985.

11. H. C. Claassen, "Sources and Mechanisms of Recharge for Ground Water in the West-Central Amargosa Desert, Nevada, A Geochemical Interpretation," USGS Open-File Report 83-542, 1983.

## Section 6
## Composition of Waters in the Unsaturated Zone

Introduction. Because the Nevada nuclear waste repository will be located above the water table at Yucca Mountain, i. e., in the unsaturated zone, only vadose* water will be present, but it will have a major influence on the behavior and integrity of the waste package system. One of the key pieces of information about the environment of the repository site, therefore, is the chemical composition of the vadose water. There will probably be two types of vadose water: water present in the interstices or pores of the rock, and relatively more mobile water present in the rock fractures.

In the near-field repository environment, which by definition is the zone that will be influenced by heat from the radioactive waste, most of the vadose water is expected to vaporize after initial emplacement of the waste. It is estimated that the rock temperature 1 m from the waste-package borehole would peak at about 190°C at 10-20 years after emplacement (1). Following the high thermal period, as the waste package temperature drops, the near-field rock is expected to rehydrate by capillary action or flow from the surface. The chemical composition of the fluids during these periods are likely to be different from the initial vadose-water composition, and all of these individual compositions, or ranges of compositions, are relevant to the behavior of the waste package. (A more detailed description of the expected near-field environment and a scenario of the various types of interactions between the ground water and the waste package is given in Section 9 of This Report.) The composition of the water in the region of the unsaturated zone that is not influenced by the waste package heat is also of interest, because this water resides in the pathway of potential release of the radionuclides to the surrounding environment.

When samples of rock from the repository site are eventually obtained, and vadose water has been extracted and characterized, it will then be possible to perform waste-package experiments using water that more closely approximates the real environment. However, even then, it is unlikely that a sufficient quantity of representative water will be available for all of the required experiments. In any event, the important question still is whether J-13 water is a valid reference water for tests conducted on the effects of water on

*Vadose is derived from the Latin word vadosus, meaning "shallow."

components of the nuclear waste package. In the future, as more information becomes available, the suitability of J-13 water as a reference water can continue to be evaluated.

At the outset, it must be stated again that the similarity of the chemical composition of J-13 water to that of the vadose waters at the repository site, or even Yucca Mountain, is an open question. Although experiments to extract vadose water from related rocks are ongoing, no definitive chemical analyses have yet been reported in the open literature. However, we believe that it is useful, as others have done, to examine some data that have been obtained in a study at another area of the Nevada Test Site (NTS), Rainier Mesa, where the lithology is similar to that of Yucca Mountain, and where the investigators were able to compare the compositions of several types of indigenous waters with one another and with ground waters at NTS in general. From these comparisons, it is possible to draw some tentative conclusions as to (1) the likelihood of the composition of J-13 water approximating that of the repository site, and (2) some aspects of validity of the use of J-13 water in experiments designed to measure the effects of repository water on the rocks and waste-package components.

Studies of Rainier Mesa Water. Rainier Mesa is located approximately 30 miles northeast of Yucca Mountain, and the rocks comprising this area are primarily Tertiary (Miocene) volcanic tuffs overlaying a Paleozoic basement composed principally of Devonian carbonate. The geology of Rainier Mesa, based on previous work, has been summarized by White, Claassen, and Benson (2). These authors, and earlier Benson alone (3), carried out a detailed study of the geochemistry of the water of the area. Water samples were obtained from the surface, from interstitial pores in core sections by means of centrifugation and squeezing, and from free-flowing fractures. Henne (4) also measured the compositions of surface and fracture water samples, and Clebsch and Barker (5) analyzed samples from tunnels. All of these results have been tabulated, summarized, and discussed recently by Kerrisk (6), particularly with regard to the possible similar controls on ground water chemistry at Yucca Mountain and vicinity.

In the work of White, et al (2), and Benson (3), samples of water were examined from a large number of locations, and attempts were made to correlate the water chemistries with trends in the mineralogy of the core samples. It is beyond the scope of this report to discuss these findings in detail, but in the present context, there were some significant findings. First of all, it was found that the composition of the waters varied considerably even within a given formation. This is illustrated in Figure 6.1, which shows the variation of the concentrations of several of the major species as a function of the depth of the rock sample. As can be seen, there are some clear trends, such as the decreasing concentrations of calcium and magnesium with depth, and the increasing sodium. Most significant are the large differences in concentrations of some species (as much as factor of three) at the same depth. Presumably, these variations are real variations in the local water chemistry, and are not due to the technique of extraction of the water. (These variations are definitely much larger than the analytical uncertainties.)

There is a similar, fairly wide variation in the composition of the individual samples of water taken from the fractures, surface soils, and tunnels (2, 4-6). By means of additional laboratory experiments on the dissolution of well-characterized samples of the Rainier Mesa minerals, some of these differences in water chemistry could be explained by White et al (2). The mineralogy of the rock was found to be extremely important, as even two tuff samples having the same bulk chemistry produced aqueous solutions of different chemistry, because of differing proportions of the vitric and crystalline phases.

Such variations in vadose water chemistry with location are also likely to be encountered at the repository site at Yucca Mountain. The mineralogy is similar, the controls on water chemistry are similar, and the average composition of the waters at Yucca Mountain and Rainier Mesa overlap (6). This last point is illustrated by the data presented in Table 6.1. The mean values are given for the waters of Rainier Mesa, but as noted above, these values alone should be used with caution because of the rather wide ranges involved. The ranges of composition given for the Yucca Mountain well waters

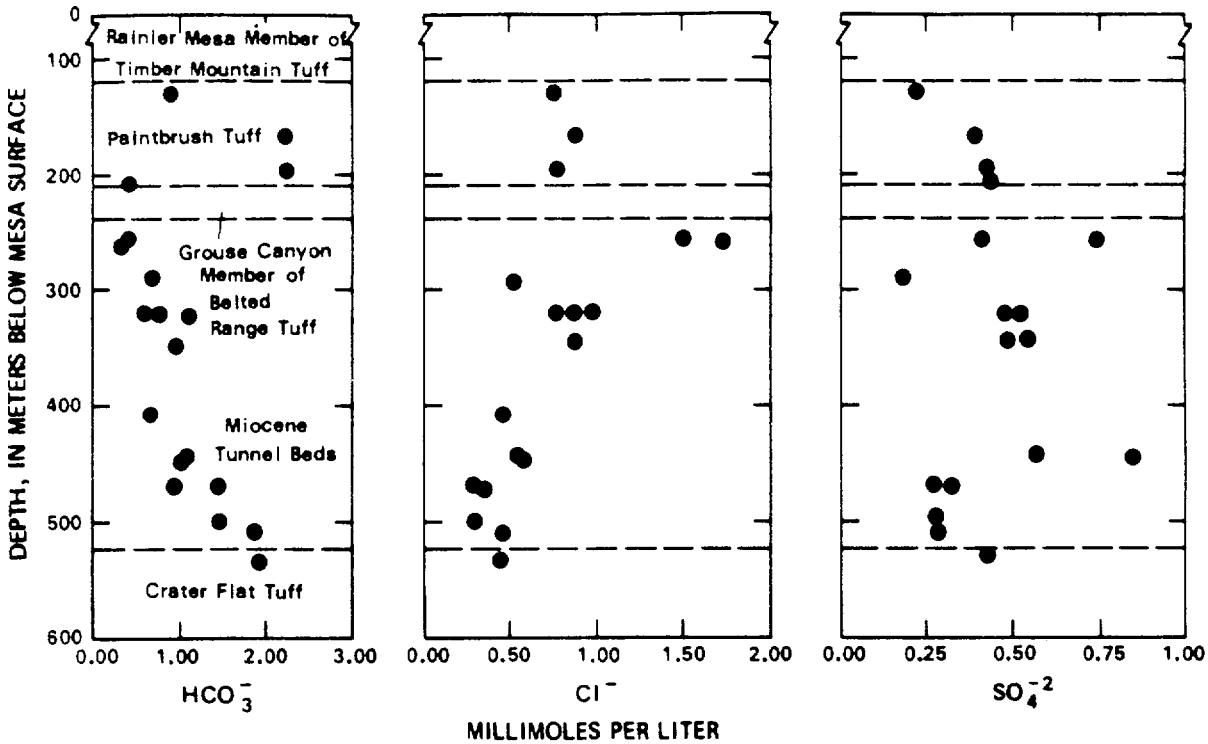


Figure 6.1a Concentrations of anions in interstitial waters as a function of depth.

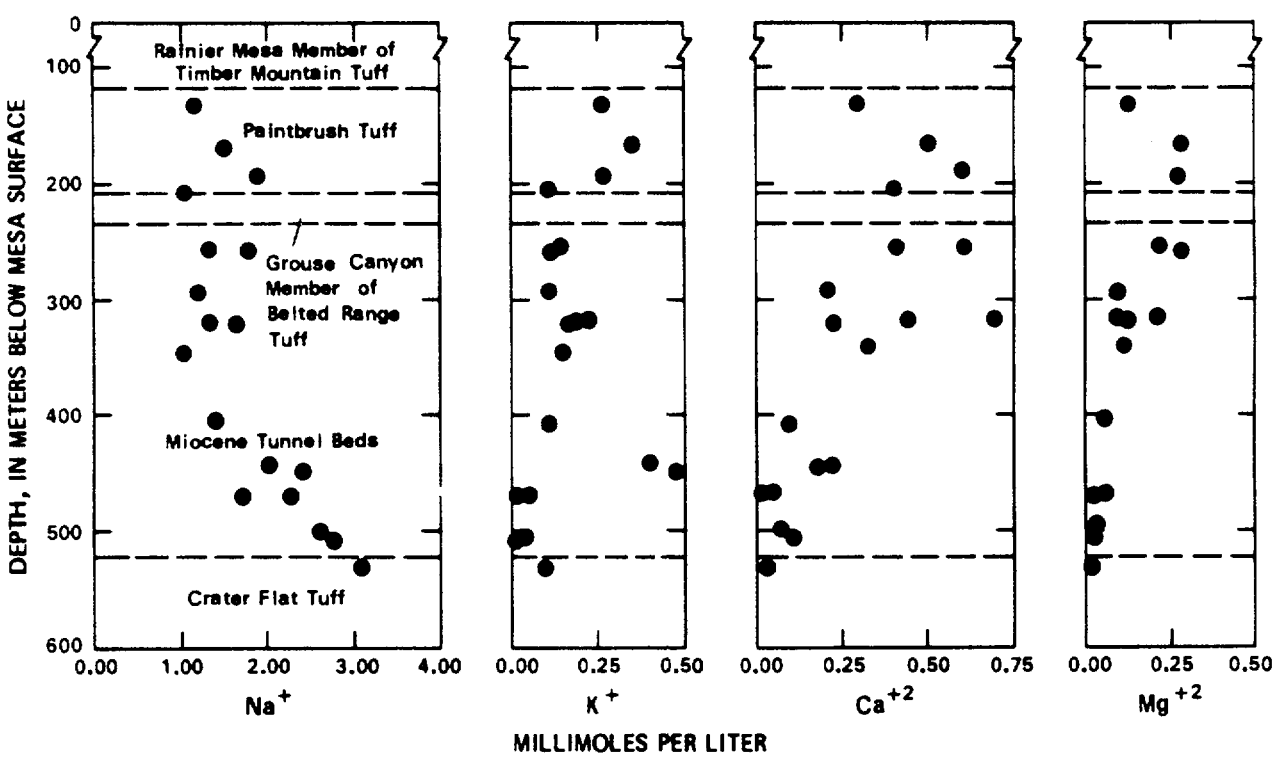


Figure 6.1b Concentrations of cations in interstitial waters as a function of depth (from Ref. 2).

Table 6.1. Comparison of Yucca Mountain and J-13 well waters from the unsaturated zone at Rainier Mesa.
[Concentrations in mg/L; adapted in part from Glassley (1)]

| | Rainier Mesa Waters | | | | |
|---|---|---|---|---|---|
| | Interstitial[a] | Fracture[a] | Tunnel[b] | Yucca Mountain Wells[c] | J-13 Well[d] |
| Na | 40 | 35 | 53 | 54 - 84 | 45.8 |
| Si | 27 | 25 | 21 | 17 - 26 | 28.5 |
| Ca | 10.8 | 8.4 | 3.2 | 1.1 - 17 | 13.0 |
| K | 7.0 | 4.7 | 4.3 | 2.1 - 2.6 | 5.0 |
| Mg | 2.4 | 1.5 | 0.2 | 0.01 - 0.29 | 2.01 |
| pH | 7.8 | 7.5 | 7.0 | 7.1 - 7.8 | 7.4 |
| $HCO_3^-$ | 70 | 98 | 137 | 126 - 173 | 129 |
| $F^-$ | - | 0.25 | 0.20 | 1.3 - 4.8 | 2.18 |
| $Cl^-$ | 27 | 8.5 | 6.4 | 5.5 - 6.9 | 7.1 |
| $NO_3^-$ | - | - | 3.3 | 4.7 - 8.6 | 8.8 |
| $SO_4^{2-}$ | 42 | 15 | 10 | 14.6 - 26 | 18.4 |

[a]From White, Claassen, and Benson (2).
[b]From Henne (4), except $F^-$ and $NO_3^-$ from Clebsch and Barker (5).
[c]Range of wells USW G-4, H-4, and H-5; from Table 5.1 of this report.
[d]Mean value; from Table 4.1 of this report.

are those found for the three existing wells within the repository exploratory block at Yucca Mountain. The chemistry of J-13 well water is also shown for a further comparison.

The general similarities of these waters are apparent, especially in the major parameters such as sodium, silicon, calcium, pH, and alkalinity ($HCO_3^-$). Oxygen concentrations and Eh information are lacking for the Rainier Mesa waters, but are also probably similar, because all of these waters (as well as the repository site water) originate in the zone of aeration. The only significant differences that can be seen in the data of Table 6.1 are: (1) fluoride is lower at Rainier Mesa, but J-13 and the other Yucca Mountain waters are nearly alike, and (2) in the levels of potassium and magnesium, the Rainier Mesa waters more nearly resemble J-13 water than the waters of Yucca Mountain.

Conclusions. Pending the development of further information on the characteristics of the vadose water at the repository site, there are several reasons why J-13 water can be considered a valid reference for experimental purposes. First of all, the pronounced variation of the composition of the vadose waters at Rainier Mesa at specific locations within the same stratigraphic unit suggests that there will also be no single "typical" or unique "reference" value for the waters of Yucca Mountain. Thus a reference experimental water such as J-13 need not match such a composition as exactly as might be supposed. Secondly, all of the comparisons that we and other authors have made among J-13 water, Rainier Mesa waters, and Yucca Mountain waters show that they are generally similar, and the geochemical reasons why they are similar are also fairly well understood.

It will be important in the near future to learn the range of water compositions that exist at the repository site, both in the interstices and the fractures of the rock, so the initial conditions to be encountered by the waste-package system can be bounded. It appears very likely (but by no means a certainty) that most of the characteristics of J-13 water will fall within the range of characteristics of the vadose water that actually exist at the repository site. As mentioned in the introduction, the effects of heat and the reentry of water at the repository after the thermal period will generate new water compositions that will also have to be assessed. To the extent that

there are, and probably will be, differences between J-13 water and the initial or later-time waters, relationships will have to be developed to allow extrapolation of the results from experiments using J-13 water to expected responses in the real environment.

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## Section 7

## Modeling of Composition of Water Resulting from Rain Reacting with Topopah Spring Tuff

(Adapted from a Contribution of Kevin Knauss*)

Introduction. In assessing whether J-13 well water is a valid reference water for the nuclear waste package experiments, another approach to obtaining an early reading on the chemical composition of the vadose water at the repository site is to determine, via computer modeling, the composition of the water that would result from precipitation (rain or snow) interacting with the minerals of the repository rock. Since the lithology of the repository horizon is similar to the lithology of the main production zone of the J-13 (see Section 2 of This Report), it is also of interest to compare the modeling results to the composition of J-13 water. The similarity of these lithologies has been another of the links that has been cited to justify the experimental use of J-13 water.

Accordingly, at the Committee's request a brief simulation was performed using the geochemical modeling code EQ3/6 (1,2), with a typical composition of rainwater (3), and rock compositions from core samples at Yucca Mountain that are believed to be representative of the rock at the repository horizon (4-6). The potential repository horizon is in the lower, densely-welded and devitrified portion of the Topopah Spring member of the Paintbrush tuff (4). Water passing through this formation would contact mineralogy of both the host rock and the coatings of fractures within the host rock; thus these two cases were considered in the simulation.

By necessity, there are a number of simplifications and approximations in the simulation. First, the model cannot reproduce the actual, entire history of the fluid as it contacts all of the rock types in reaching the repository. Secondly, the simulation was performed by letting the reactions proceed until each of the original rock minerals reached equilibrium with the evolved fluid or were entirely consumed. In contrast, in the real environment, none of the reactions will be in equilibrium all of the time. A third limitation is that

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the fate of the chemical species can be modeled accurately only if they are present initially in both the water and the rock minerals. Thus aluminum was arbitrarily included in the water at a low level to follow its interaction with the rock. Other species such as the anions $Cl^-$, $F^-$, $SO_4^{2-}$, and $NO_3^-$ do not influence the simulation, because they are present at only very low concentrations in the real rocks, and thus they are not included in the database mineral formula used by the model. Although not a deficiency of the model, no iron or manganese is present in the simulation, so no redox chemistry is operative. In spite of these qualifications, some interesting results emerge regarding several of the major constituents of the water and rock, which enable us to draw some conclusions about the geochemistry of the J-13 water issue.

Initial Water Conditions. The initial composition of the water was first modeled by means of EQ3, starting with a rainwater composition given by Hem (3). The fluid was assumed to be in equilibrium with $CO_2$ in the atmosphere, the concentration of aluminum was taken to be $8 \times 10^{-6}$ mg/L, and electrical balance was achieved by adjusting the pH. The temperature was assumed to be 25°C to approximate the initial temperature at the repository location. Table 7.1 summarizes the initial composition of the water.

Table 7.1 Initial composition of water in reaction simulations.

| Element/ Species | Concentration, mg/L (ppm) | Species | Concentration, log[activity] |
|---|---|---|---|
| Al | $8 \times 10^{-6}$ | $H^+$ | -5.50 |
| Ca | 0.65 | $CO_2$ in atmos. | -3.50 |
| Mg | 0.14 | | |
| Na | 0.56 | | |
| K | 0.11 | | |
| $SiO_2$ | 0.30 | | |
| $Cl^-$ | 0.57 | | |
| $NO_3^-$ | 0.62 | | |
| $SO_4^-$ | 2.18 | | |

Reaction of Rainwater with Topopah Spring Tuff. In this simulation, the rock was assumed to consist of the major devitrification products (quartz, cristobalite, and sanidine), the phenocrysts (plagioclase and sanidine), and clay (5). For the clay, a database composition equivalent to Mg-beidellite was used (6). The calculation was performed starting with one mole of each mineral and one kg of water. As would be the case with the water in the repository unsaturated zone, this is a fairly high ratio of rock to water, which in general leads to the rock dominating the composition of the water.

The results of the simulation are shown in Figures 7.1 to 7.5. The abscissa of these plots is proportional to the mass of rock dissolved; it can be related to real time if mineral dissolution rate constants are incorporated in the calculation. As shown in Figure 7.5, the equilibrium mineral assemblage consists of quartz, muscovite, smectite, mesolite, paragonite, and albite. Very early in the run, gibbsite is present but disappears; kaolinite comes and goes. Comparison of the composition of the water with the compositions of the waters of the wells at Yucca Mountain and the J-13 well (see Table 5.1 on page 5.5 of This Report) reveals some large differences. The pH of the simulated water rises to >9, whereas the well waters are in the range of 7.1 to 7.4. Sodium and $HCO_3^-$ are also much higher in the simulated water, but silicon is much lower. Potassium rises to about 2.3 mg/L, which is similar to its concentration in the water of wells G-4, H-4, and H-5, and not too far from the 5.0 mg/L in J-13 water, but then it decreases to a low value. It would continue to rise if it were not for the formation of muscovite The concentration of calcium also rises and falls, and is always somewhat lower than the levels in all of the wells except H-5. The early concentrations of magnesium are in the range found in all of the wells except J-13, but then it too decreases.

As discussed in Section 5, the major differences between J-13 water and the Yucca Mountain waters are the higher concentrations of potassium and magnesium in J-13 water (5.0 and 2.0 mg/L, respectively). It is interesting that in the simulation, the concentrations of these elements start to approach these higher values in J-13 water. As noted above, the simulation cannot account for the presence of fluoride, chloride, nitrate, and sulfate in the well waters, because the minerals used in the simulation do not contain these species.

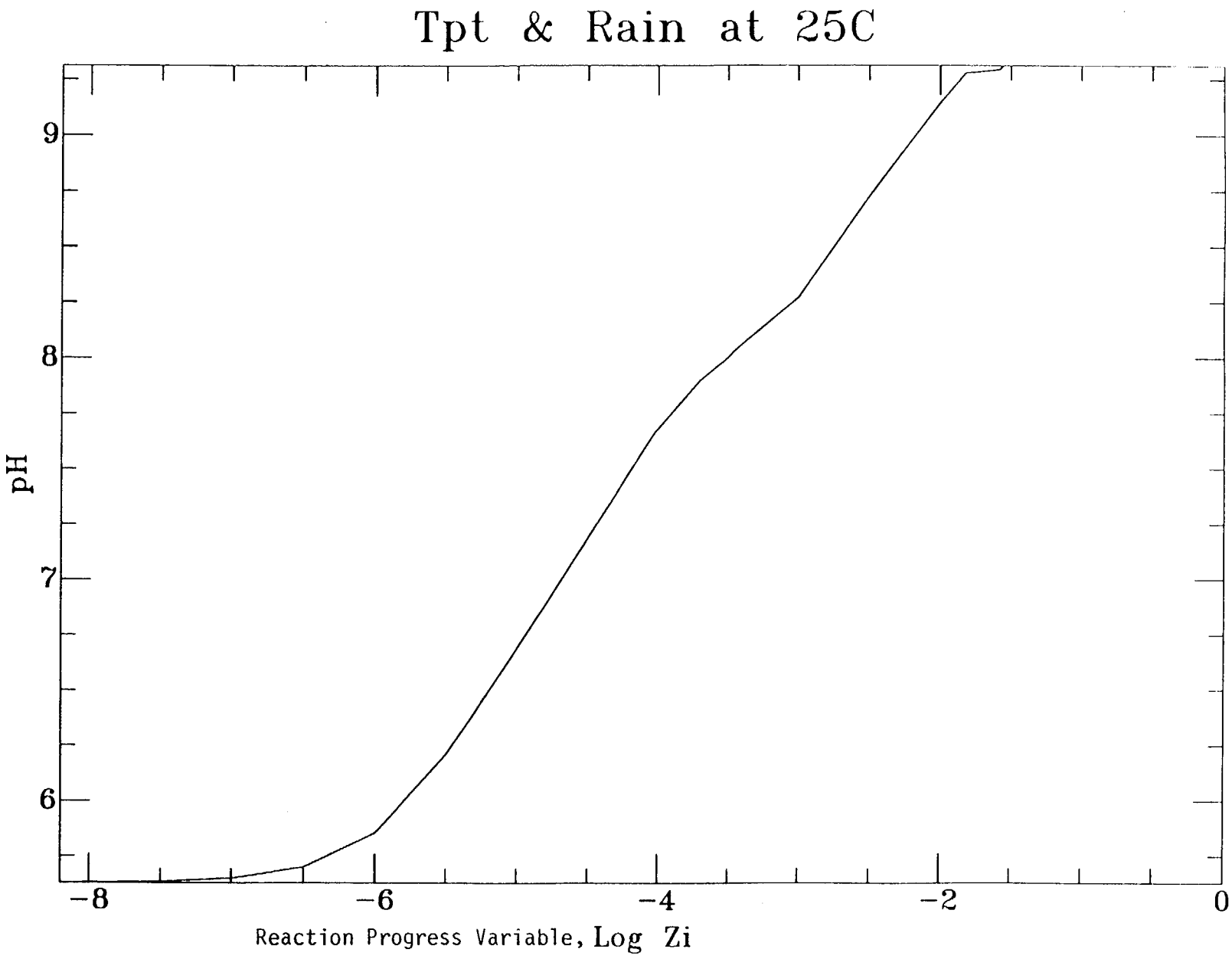


Figure 7.1 pH during reaction of rainwater with Topopah Spring tuff.

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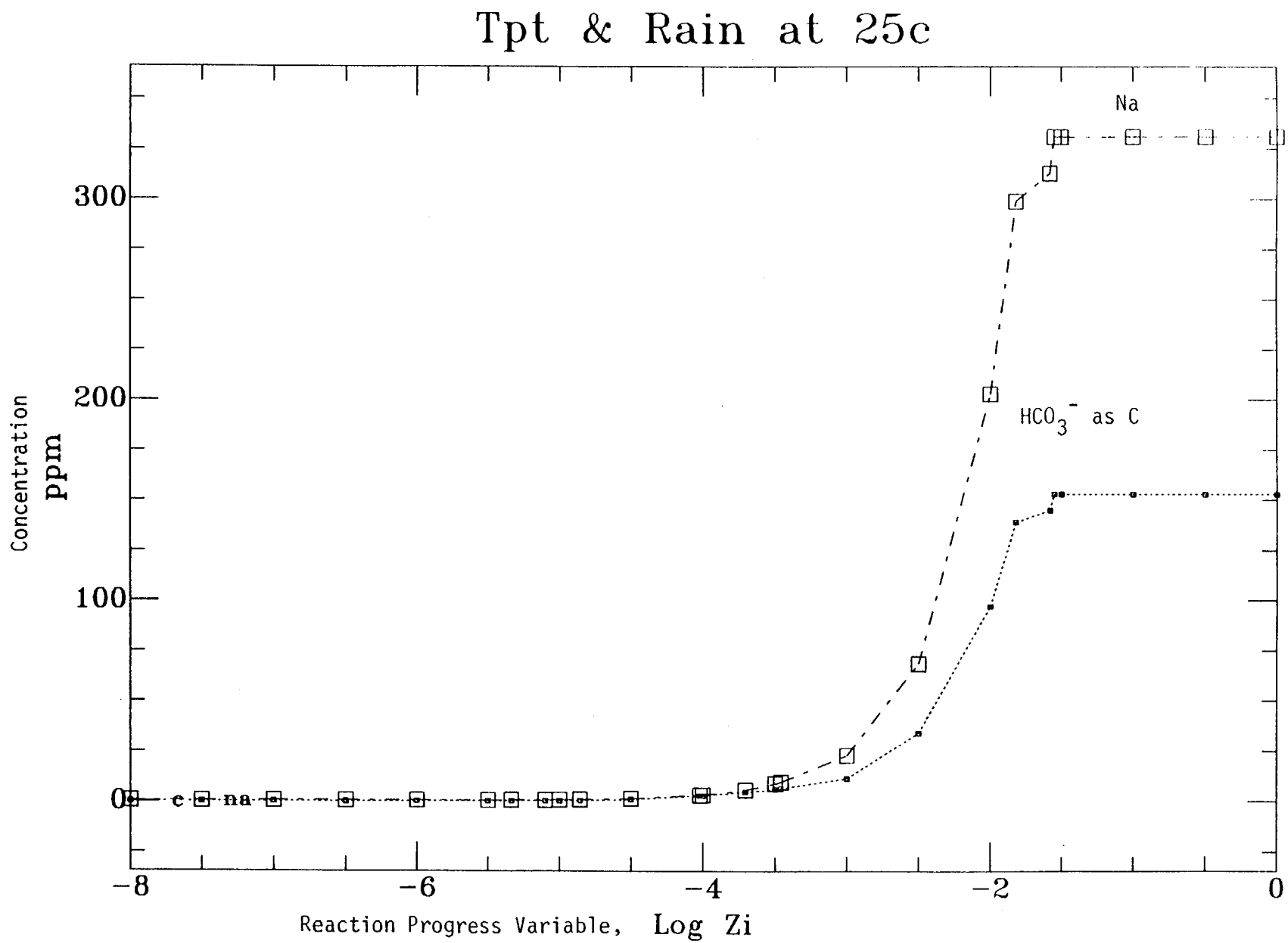


Figure 7.2 Concentrations of sodium and bicarbonate during reaction with Topopah Spring tuff.

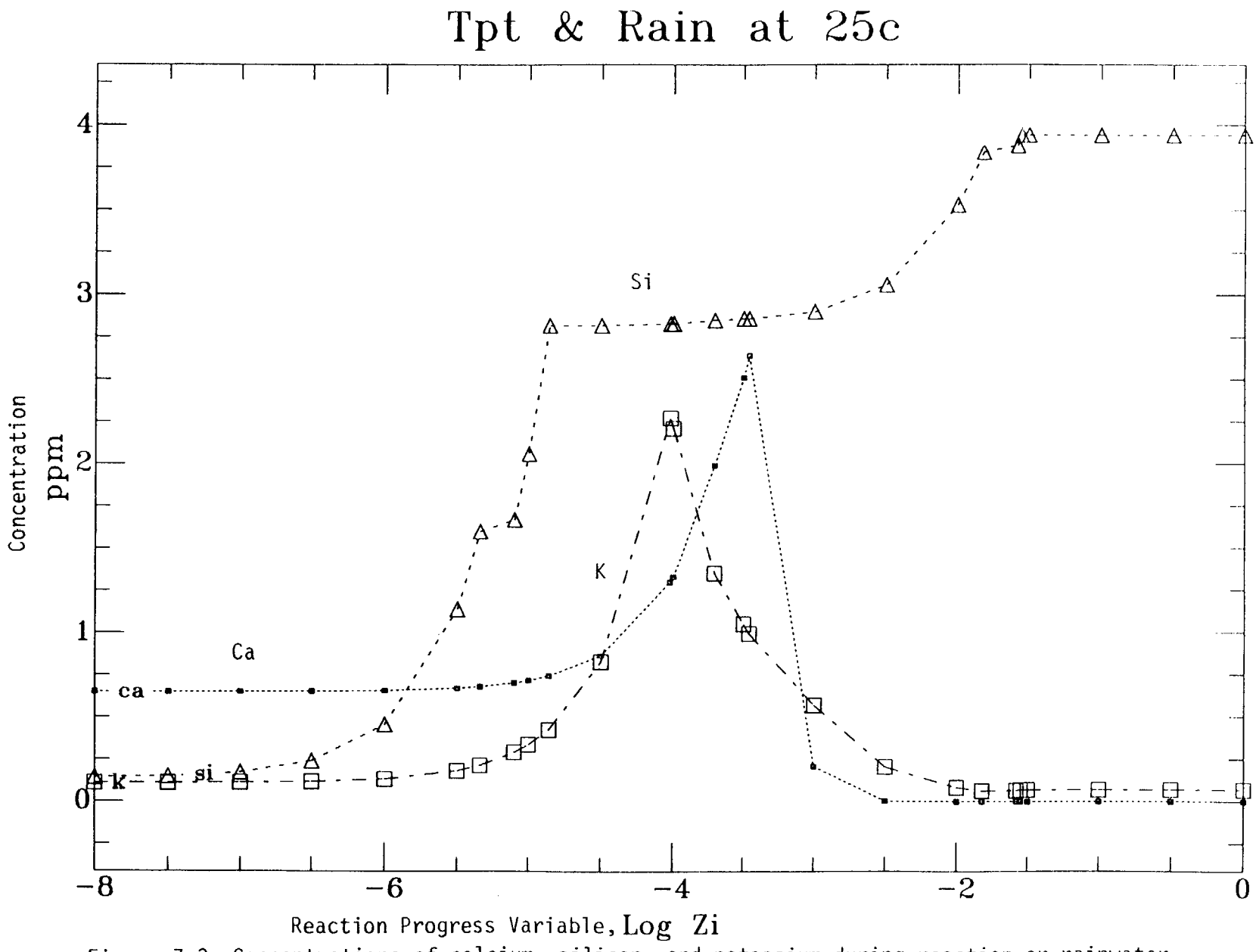


Figure 7.3 Concentrations of calcium, silicon, and potassium during reaction or rainwater with Topopah Spring tuff.

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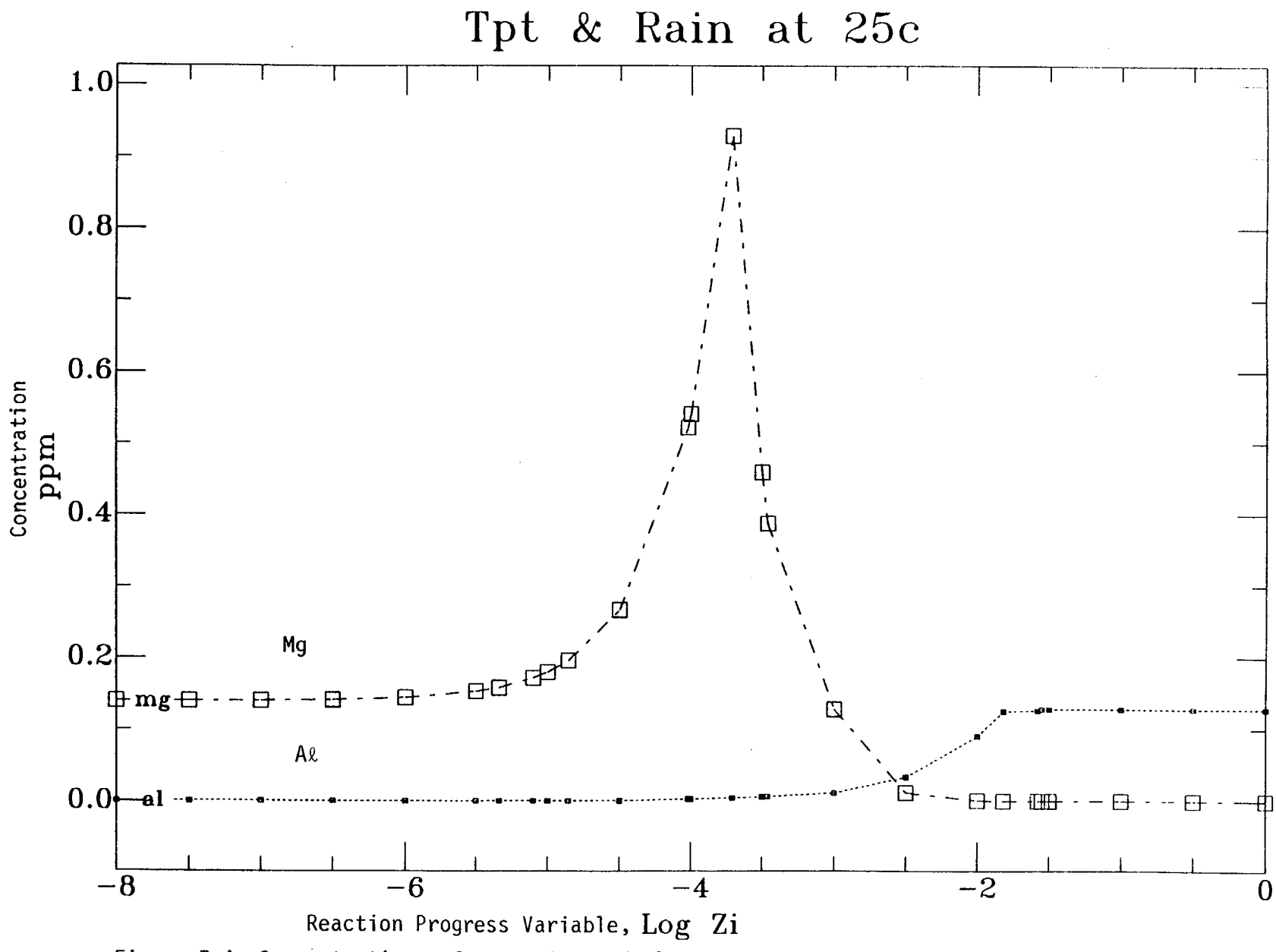


Figure 7.4 Concentrations of magnesium and aluminum during reaction of rainwater with Topopah Spring tuff.

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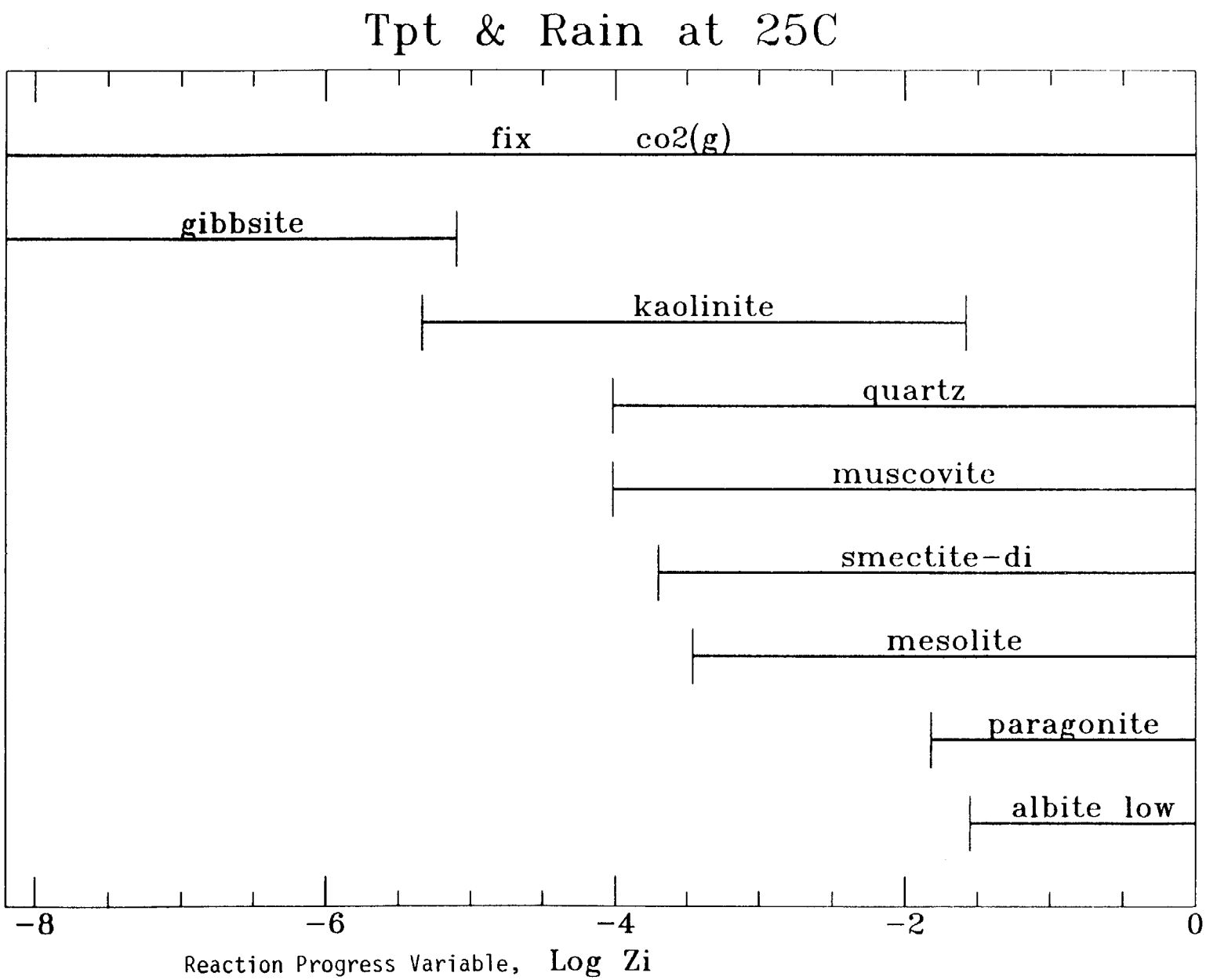


Figure 7.5 Mineral assemblage during reaction of rainwater with Topopah Spring tuff.

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Reaction of Rainwater with Unsaturated-Zone Fractures. In this simulation, the initial mineral assemblage was chosen on the basis of the work of Carlos (5), and consisted of quartz, cristobalite, sanidine, tridymite, and mordenite. In her study, Carlos examined core from above the static water level in well G-4 at Yucca Mountain. At run termination, the mineral assemblage consisted of quartz, muscovite, mesolite, albite, phengite, and microcline. At intermediate values of reaction progress, the minerals gibbsite, kaolinite, smectite, and paragonite appear, but are unstable with respect to the other phases as the reaction progress increases.

Several of the principal features of the water chemistry are similar to those of the simulation with the host rock. The results are shown in Figures 7.6 to 7.10. The pH, and the concentrations of sodium and bicarbonate are again high, and the concentration of silicon, although higher than in the tuff simulation, is still a factor of 4-5 lower than in the waters of J-13 and the Yucca Mountain wells. Potassium peaks at about the same value in both simulations, but for the fractures, it equilibrates at about 1.0 mg/L, compared to about 2.0 and 5.0 for the Yucca Mountain and J-13 wells, respectively. The behavior of calcium is nearly the same in both simulations. The final equilibrium concentration of magnesium is very low in both cases, but the fracture concentration never exceeds 0.14 mg/L, the initial rainwater value. As noted above, these concentrations are not unlike those of the Yucca Mountain wells, which range from 0.01 to 0.29 mg/L, but are unlike the 2.0 mg/L of J-13 water. The final concentration of aluminum in the tuff water (see Figure 7.4) is about 0.13 mg/L and that in the fracture water (see Figure 7.9) is about 0.07 mg/L. Experimental values for aluminum in the well waters are sparse and are erratic because the low solubility of aluminum makes the measurement of this element is quite subject to sample-handling techniques. However, it appears from the data on J-13 water (see Table 4.2 on page 4.3 of This Report) that its concentration of aluminum is about 0.01-0.04 mg/L.

Conclusions. Two principal questions can be asked in the light of this modeling study: (1) what does it mean in terms of the probable composition of the vadose water in the Topopah Spring member at Yucca Mountain? and (2) what does it say about the composition of J-13 water?

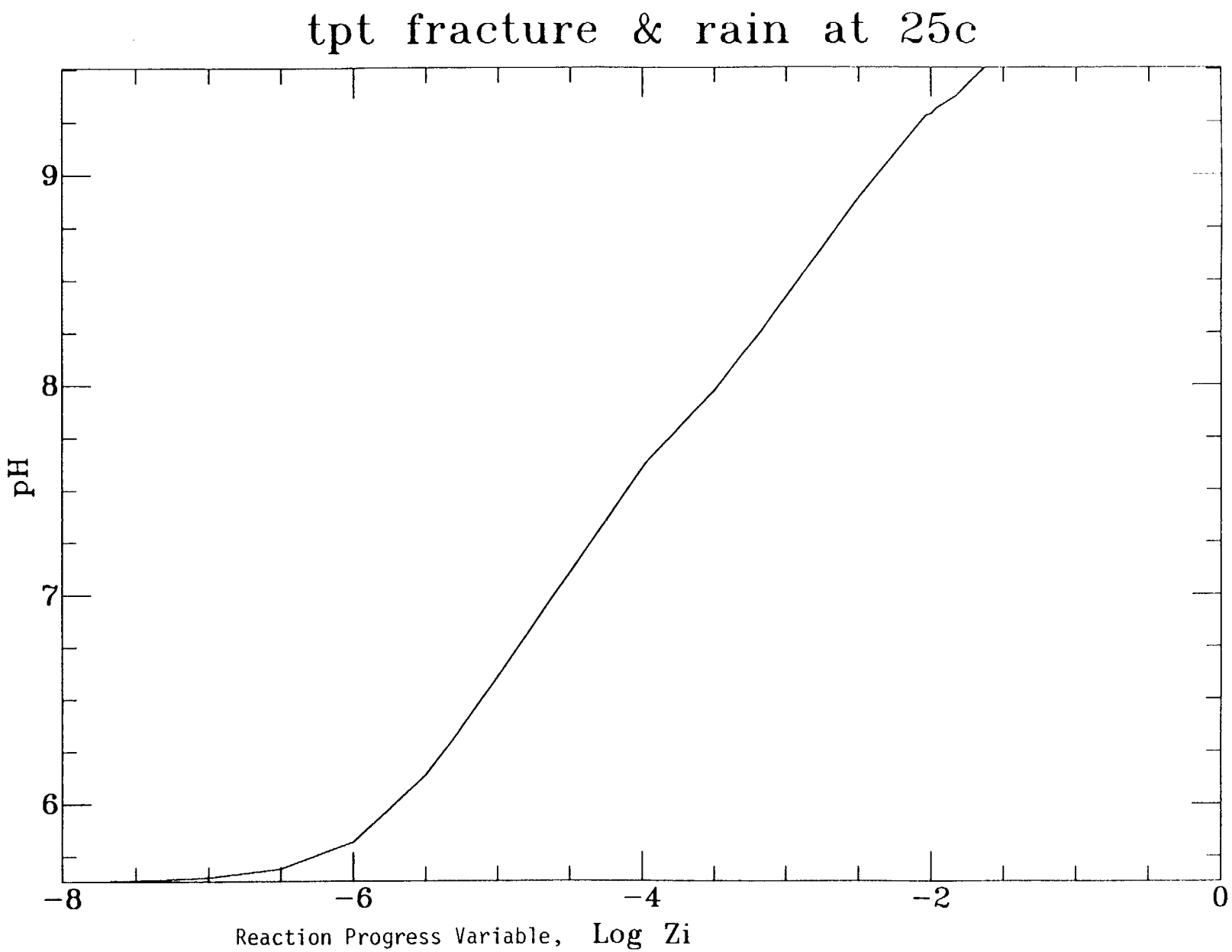


Figure 7.6 pH during reaction of rainwater with fracture minerals

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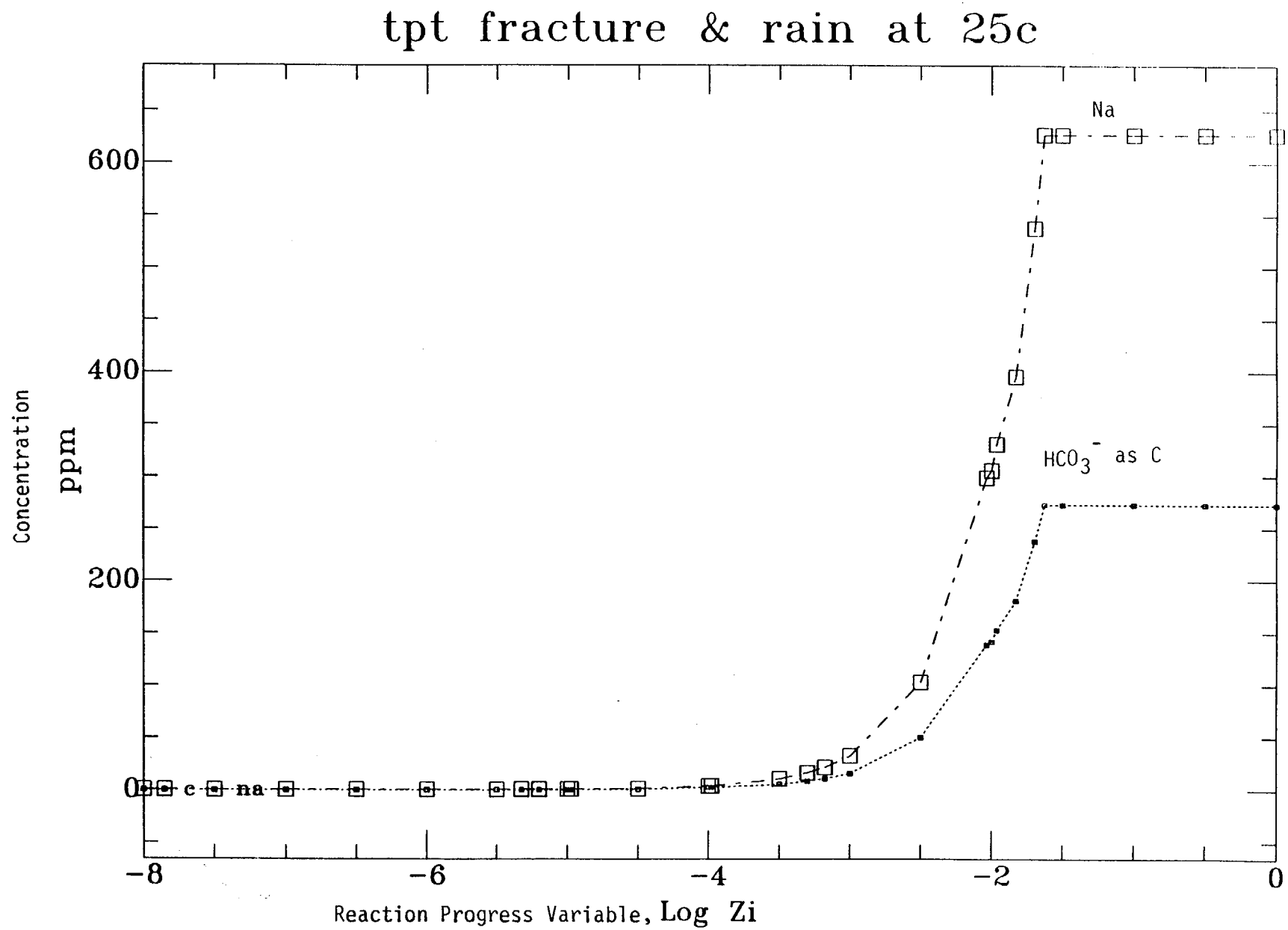


Figure 7.7 Concentrations of sodium and bicarbonate during reaction of rainwater with fracture minerals

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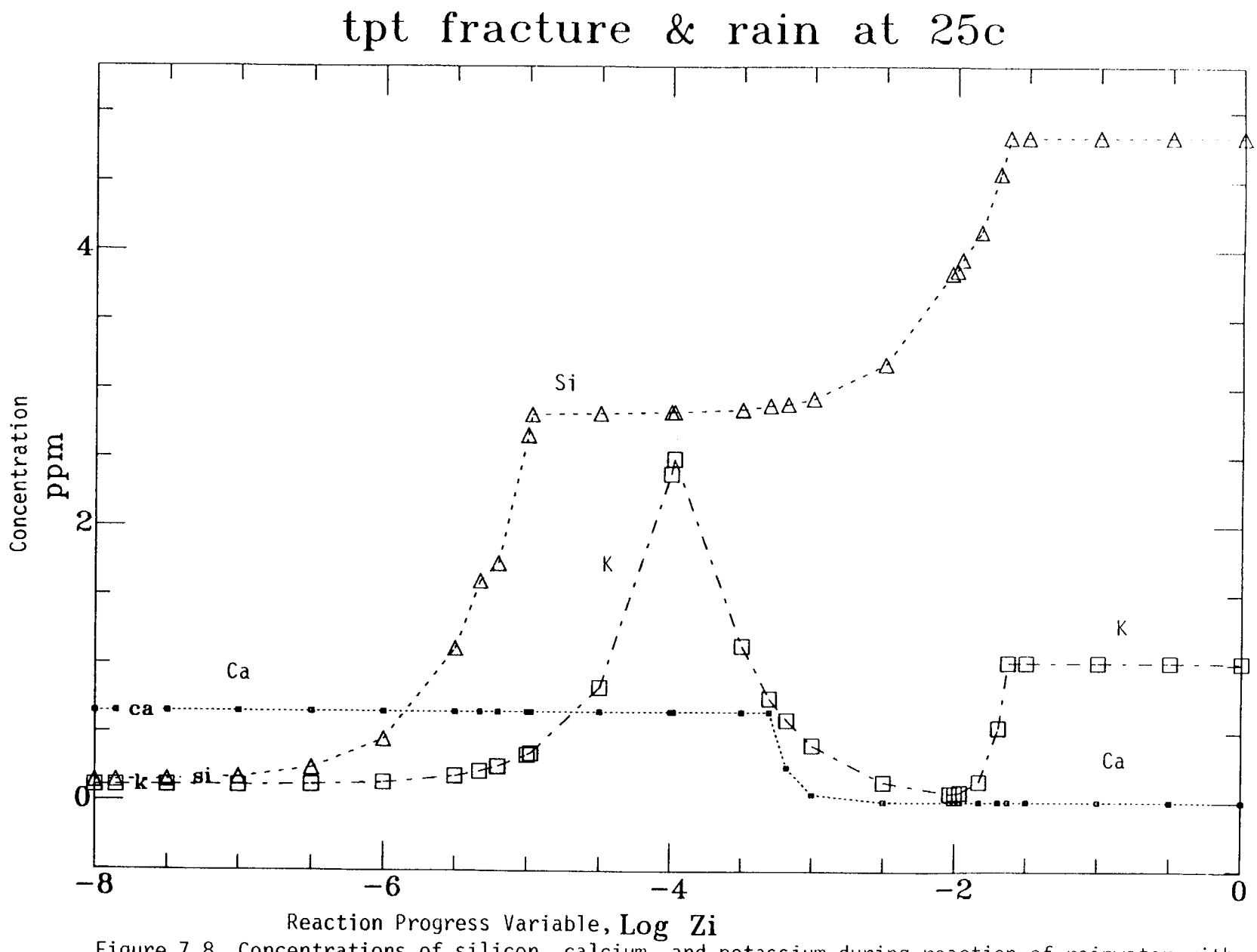


Figure 7.8 Concentrations of silicon, calcium, and potassium during reaction of rainwater with fracture minerals

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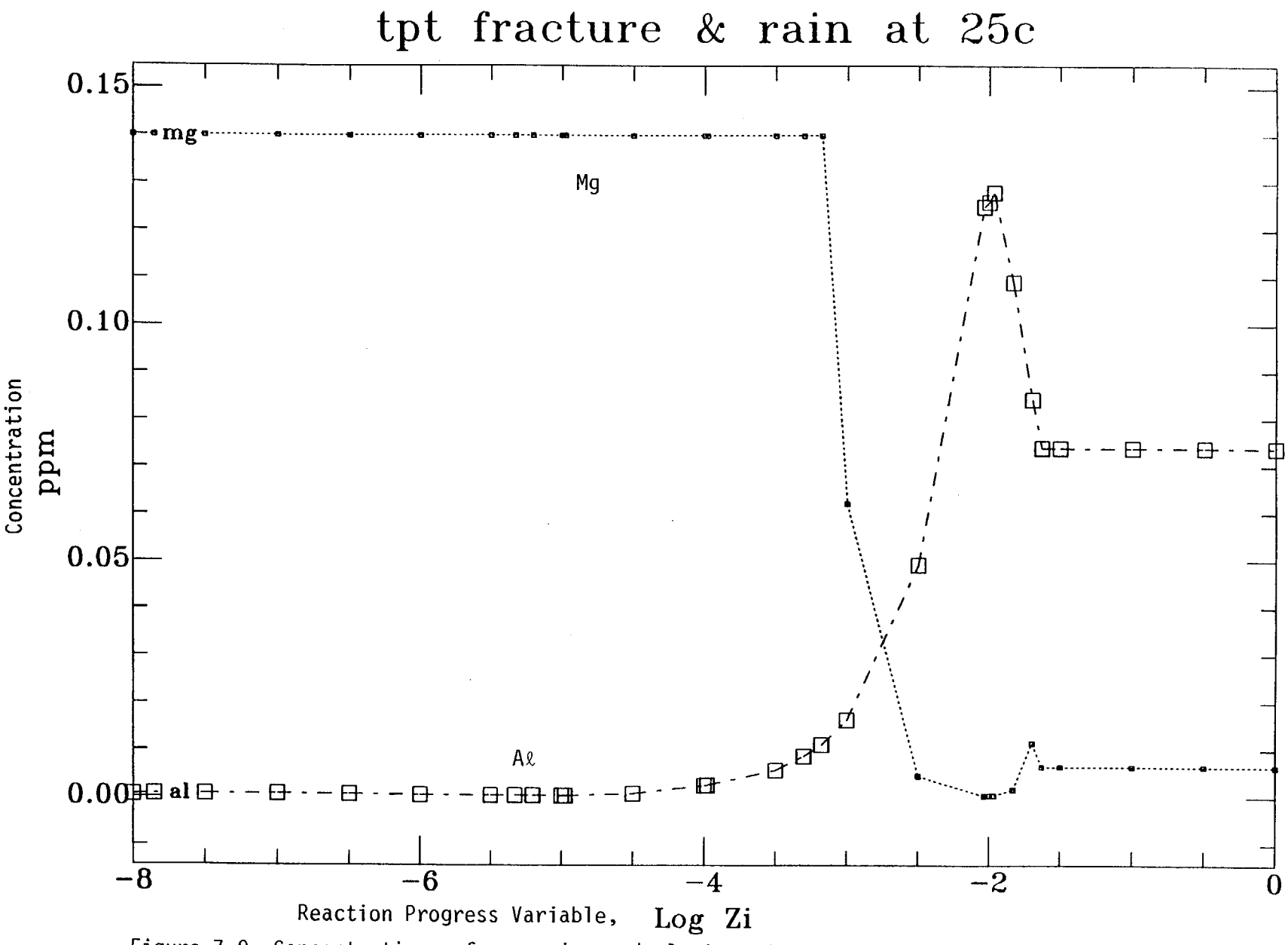


Figure 7.9 Concentrations of magnesium and aluminum during reaction of rainwater with fracture minerals

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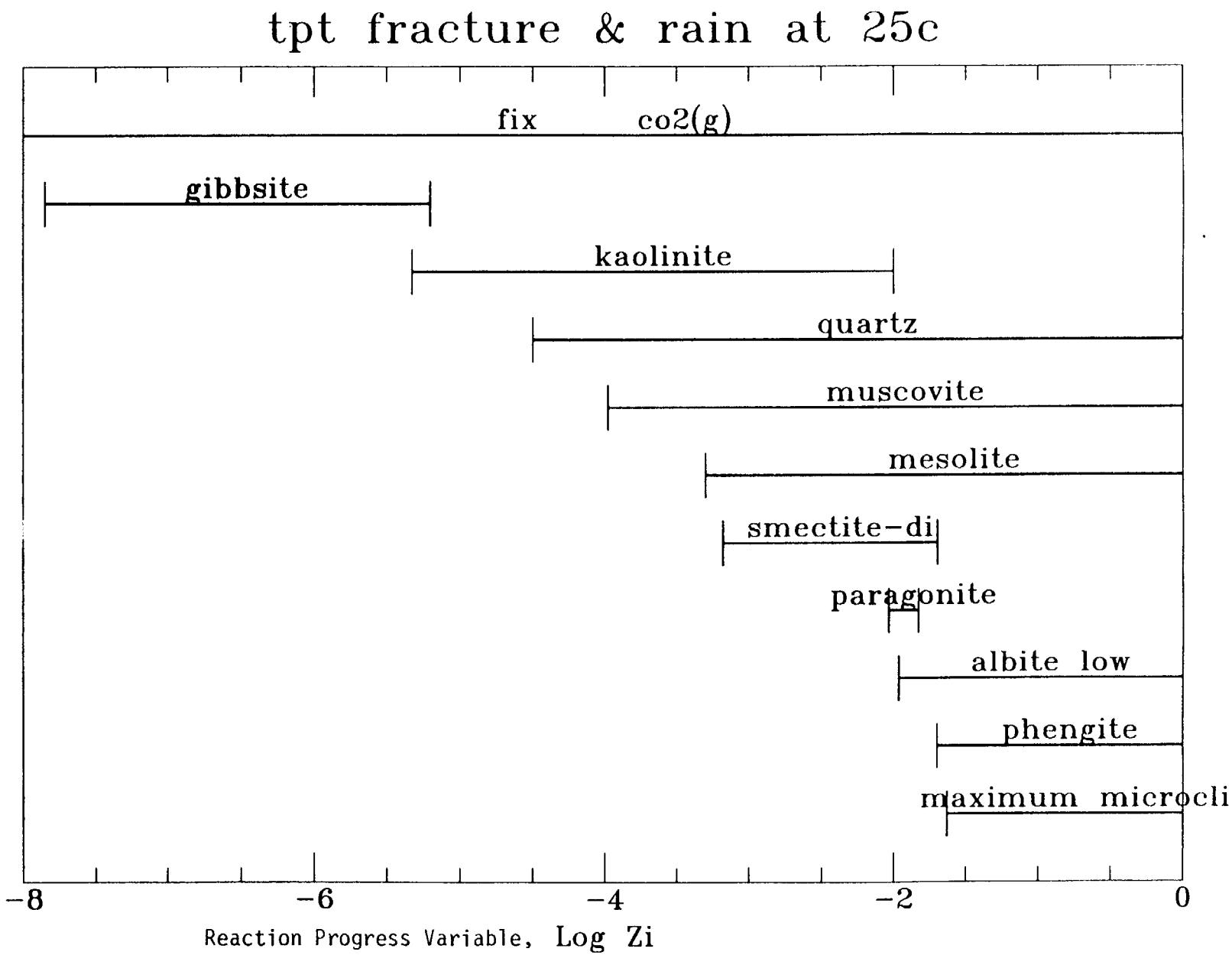


Figure 7.10 Mineral assemblage during reaction of rainwater with fracture minerals

The fact that the ionic strength of the simulated water, principally due to the $NaHCO_3$, is much higher than the waters of either the wells at Yucca Mountain (G-4, H-4, and H-5) or the J-13 well, as well as the significant differences in several of the individual-species concentrations, indicate that none of these well waters are in equilibrium with the surrounding rock. Very little additional information on the actual composition of the vadose water can be inferred from the results, except to lend further weight to the conclusions reached in Sections 5 and 6 that the general type of water is likely to be the same as that found in the local wells.

In the case of J-13 water, it is therefore somewhat irrelevant that its production zone is largely in the Topopah Spring tuff. As discussed in Section 3 of this report, the majority of the water in J-13 well probably comes from subsurface flow from the north and from infiltration along Fortymile Wash. The composition of its water is determined by a kinetic steady state of interactions between rainwater at the infiltration sites and all the rock types it contacts on the way toward the J-13 well. J-13 water is supersaturated (at the downhole temperature of the water, 31°C) with respect to many minerals that are present in the devitrified tuff. Why is equilibrium not achieved? One reason is that precipitation kinetics are generally very slow at this temperature and there may be other forms of kinetic inhibition. J-13 water also contains significant concentrations of species that are virtually absent in Topopah Spring rock. The presence of species such as fluoride at levels of about 2 mg/L in all of the well waters shows clearly that minerals other than those considered have been encountered by the water.

When the repository is actually in operation, the zone close to the waste will be at high temperatures for a considerable period of time (4). Under these conditions, reaction rates will increase, and rock/water systems will approach equilibrium more rapidly than at lower temperatures. This has been illustrated by the results of laboratory experiments and other modeling studies of rock/water interactions (see, for example, Refs. 6-8). These experiments are discussed in more detail in Section 9 of This Report, and Table 9.1 on p. 9.17 shows the changes in water chemistry that result from heating both J-13 water and deionized water under various conditions. In comparing these results with one another and with the rainwater modeling results, one must keep in mind that two important factors will determine both the reaction pathway (sequence of mineral dissolution) and the steady state or final equilibrium state of the rock/water system. These are (1) the

temperature, and (2) whether or not the rock/water system is in equilibrium with the atmosphere (i.e., to what extent it is an open or closed system). Certain mineral/water-species reactions are faster than others, and atmospheric $CO_2$ strongly influences both the pH and the carbonate mineral reactions. However, since we are dealing with a rock-dominated environment and the repository-relevant time periods are long, many initially dilute waters, on being heated, will tend to reach similar compositions.

Thus in the present context, the question of the similarity of the initial composition of J-13 water to that of the repository waters, both at low temperatures compared to the repository, is somewhat diminished in significance. In experiments designed to investigate phenomena under the conditions of the "hot" repository, either J-13 or other dilute synthetic or natural ground waters could be used, depending on the objectives of the experiments.

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## Section 8

## Comments on the Presence of Particulate Matter in J-13 Water

One characteristic of the repository water that has not received a great deal of attention, but which may be important to the containment of the radionuclides is the nature and level of particulate or colloidal matter in the water. Such material may be most significant to the transport of radionuclides, because particulates such as fragments of the rock or natural colloids such as iron hydroxides could selectively sorb waste species and carry them through fractures or other open porosity. Suspended solid matter in the waters might also influence the various interfacial chemical reactions that may occur between the water and the waste-package components. There is a question, therefore, of how this aspect of the experimental testing is being addressed by the use of J-13 water as a reference material.

Because the suspended solids concentrations have not been measured for the well waters of Yucca Mountain (nor for the vadose waters), comparisons with J-13 well water are not yet possible. J-13 water itself, however, has been fairly well characterized, on one occasion, in a series of experiments by Ogard (1). In addition, Daniels, et al (2), and Oversby and Knauss (3) have examined the characteristics of the suspended solids in J-13 water after contacting samples of tuff rock in the laboratory.

Ogard (1) filtered a large quantity of J-13 water in-line at the wellhead by passing the water through 400- and 5-nm filters in series. He found that 99% of the suspended solids were retained by the 400-nm filter, and based on the quantity collected, the calculated concentration was 0.027 mg/L. Chemical analysis of the solids fractions yielded the following:

| | Concentration, wt.% | | | | |
|---|---|---|---|---|---|
| Pore Size | Na | Si | Ca | Al | Fe |
| 400 nm | 0 | 60 | 11 | 4 | 20 |
| 5 nm | 44 | 42 | 8 | 0 | 4 |

The suspended solids level measured for J-13 water is very low, and even so may represent some contamination from the piping, as evidenced by the high concentration of iron in the 400-nm fraction.

If the low solids level of J-13 water is typical of the waters at Yucca Mountain, transport of radionuclides by the particulates may not be very important. Ogard has estimated conservatively for the J-13 water, typical sorption conditions, and in comparison with transport by dissolved species, that the particulates would contribute less than 10% to the total waste element flux (1).

However, as mentioned in Section 4, the actual particulate level, and how samples are filtered can significantly affect the measured concentrations of the trace elements that tend to be insoluble, such as iron, aluminum, and manganese. Thus the interpretation of the results of experiments may be influenced by the presence of suspended colloidal matter and the exact technique of solution filtration. A number of experiments on rock/water interactions have been performed in which the water is mixed with crushed tuff, agitated, heated, and then the mixture filtered and the filtrate analyzed. It has been found at both Los Alamos (2) and Livermore (3) that a 0.05 or 0.10-micron pore-size filter is required to accurately separate the solid and solution phases, especially when the elements iron and aluminum are of interest. Thus attention must be paid to this fact when carefully analyzing the waters, and when these elements are important in the waste storage experimentation.

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3. V. M. Oversby and K. G. Knauss, "Reaction of Bulldog Tuff with J-13 Water at 90°C and 150°C," LLNL Report UCRL-53442, September, 1983, et seq.

## Section 9
## Effects of Variations in Water Chemistry on the Behavior of Components of the Waste Package System

Introduction. An important objective in the design of experiments to test the behavior of candidate waste-package components and measure the transport of radionuclides is an assessment of the sensitivity of the measured characteristics to changes in the composition of the water. For example, in the evaluation of the corrosion resistance of candidate alloys, what is the significance if the concentration of chloride in the repository water varies from 1 to 100 mg/L? Information of this type should be developed in the testing to examine this range of chloride concentrations, or at least enable a prediction about the likely effects, if the concentration is outside the range tested.

Similar considerations exist in the rationale for the use of J-13 well water in the NNWSI experiments. J-13 water has been selected, in part, because it is believed to be representative of actual waters that the waste package components will encounter. If certain characteristics of the actual water are greatly different from those of J-13 water, what difference will it make? The importance of the characteristic will depend on the particular phenomenon being considered, such as rock/water interactions, and how sensitive it is to changes in the characteristic. In previous work, it has been assumed that J-13 water is representative of the waters of the repository and vicinity. However, in the extreme, if the composition of the actual water turns out to be significantly different from that of J-13 water, and further, if a great many phenomena are highly sensitive to the water composition, then J-13 water may not be a valid reference for waste package experiments. By the same token, if a certain characteristic of the actual water is likely to be different from that of J-13 water, but it has virtually no influence on the behavior of the waste package or the release of the radionuclides to the environment, then J-13 water is not diminished in value as a reference material.

In most discussions of the validity issue, as mentioned, the usual question is whether J-13 water is in fact representative of the water that now exists in the unsaturated zone, i. e., the vadose water comprising both interstitial and fracture water. However, an important additional question is

whether J-13 water is a suitable reference water for the conditions that will exist in the repository after the waste is in place. This aspect of the matter has already been examined briefly in connection with the discussion of the unsaturated-zone water in Chapter 6 and the modeling study described in Section 7 of This Report. Because of the heat and radioactivity, these conditions will be considerably different, at least for an initial period of time, from the present undisturbed state. These conditions are especially germane to the rock/water interactions and the metal-barrier evaluation projects, where J-13 water has been used frequently as the experimental water.

In this section, we first summarize, from the reports of Glassley (1) and McCright, et al (2), the environmental conditions that are expected in the near-field and vicinity of the repository. We then attempt to outline the known effects of the various parameters of ground waters in general on the phenomena related to nuclear waste package behavior, with the point of reference being the known ranges of composition of the waters of Yucca Mountain and J-13 well. This is done in four categories, as follows:

1. Metal/water corrosion effects
2. Interactions of water with spent fuel and glass waste forms.
3. Rock/water interactions
4. Transport of radionuclides

Finally, in the context of the sensitivity question, we offer an opinion as to the relevance of the use of J-13 water in the NNWSI experiments.

Although it appears that there has not been a great deal of effort in this direction in previous work, there now seems to be a trend toward greater emphasis in the NNWSI Project on the sensitivity of the various phenomena involving the waste isolation to changes in the environment. Experiments are being conducted to measure these sensitivities, for example, to ascertain the effects of water parameters when they are at the limits of the expected ranges. This information will be invaluable in relating the results obtained in the laboratory to the actual conditions.

Waste Package Environment . The exact configurations of waste package and the details of their emplacement are still under development; however, in

simple concept, the waste will be contained in a metal or ceramic canister which will be placed in a borehole in the tuff. In this context, on the basis of numerous studies, Glassley (1) has presented a detailed description of the chemical and physical environment of the proposed repository, and McCright, et al (2), have summarized the expected conditions as they might affect the containment materials. The essential features are the following.

Depending on the areal density of the waste packages and the type of radioactive waste, for a significant period of time after initial emplacement, the near-field environment will be influenced by heat and radioactivity from the nuclear waste. The heat output will be such that the surfaces of most of the waste packages will remain above the boiling point of water for a major part of the initial 300- to 1000-year containment period.* Investigators estimate that the rock temperature 1 meter from the waste-package borehole would peak at about 190°C at 10 to 20 years after emplacement. The resulting temperature rise would vaporize all of the unconfined pore water in the rock. During the containment period, the immediate package environment will thus consist of moist air and largely dry rock. The corrosion environment experienced by the canister would be somewhat analogous to an atmosphere of steam.

As the temperature of a region of the repository returns to 96°C (the boiling point of water at the repository elevation), the rock is expected to rehydrate, and then liquid water from the surrounding rock could enter and remain in contact with the waste package. However, it is also envisioned that, during the "hot" period, there may also be processes that would lead to contact by waters of higher salt content than the original vadose water (2).

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*This containment period is defined by regulations promulgated by the U. S. Nuclear Regulatory Commission (NRC), which set limits on the release of radionuclides from geologic repositories. NRC regulation 10CFR60 (3) specifies that containment of radionuclides will be "substantially complete" for a period of time yet to be determined, but with a minimum of 300 years and a maximum of 1000 years. Following this containment period, the regulation limits the release of any radionuclide from the engineered barrier system to one part in 100,000 per year of the inventory of that radionuclide present at 1000 years after permanent closure of the repository.

This could come about by at least two mechanisms: (1) a repeated evaporative or refluxing process, and (2) repeated dripping of water from a fracture onto the hot canister surface. These processes would leave behind salt deposits that could become wet or be dissolved by water entering the repository at the later, cooler time.

In addition to the thermal effects, gamma radiation from the waste will interact with the atmosphere and water to produce changes that can affect the integrity of the waste package (1-4). The initial gamma dose rate will be in the $10^4$ rad/hr range for spent fuel and in the range of $10^3$ rad/hr for borosilicate glass. The presence of radiation and radiolysis effects in the moist air environment are not expected to affect the rock itself significantly, but are expected to change the water chemistry, which in turn will affect metal corrosion phenomena (2,4). This is discussed in more detail below. However, because of the relatively rapid decay of the intensity of the radiation field, the gamma dose rate will be at low levels (<100 rad/hr) when liquid water returns to the near-field environment. Thus, except for waste packages placed at the periphery of the repository, which will cool faster, and except as noted above, the waste packages in general will not be exposed simultaneously to liquid water and a high radiation field.

Metal-Barrier Corrosion Phenomena. Two types of alloys have been selected as primary candidates for fabrication of the waste-package container (2): one type is a group of iron-base to nickel-base, austenitic stainless steels (AISI 304L, AISI 316L, and Alloy 825); the other comprises high-purity copper, and the copper-base alloys CDA 613 and CDA 715. Some ceramic materials are also being considered, but these will not be discussed here. As is well known, these two types of alloys, stainless steel and copper-base, each have quite different characteristics in their corrosion behavior in general, and even in the presence of the relatively benign sodium-bicarbonate water expected to be present at Yucca Mountain, it can be predicted that certain characteristics of the water will have different effects on the two classes of materials.

Most of the corrosion phenomena are complicated by the interacting effects of two or more characteristics of, or chemical species in, the water, and the situation is further complicated by radiolysis of the water. Thus the following discussion probably oversimplifies the actual phenomena. It should be recognized, however, that what we are trying to do is present at least a

qualitative picture of the relative importance of the water characteristics in the corrosion effects. To do this, we will briefly examine each of the water parameters in turn, say something about the corrosion sensitivity for the two types of alloys in terms of the possible range of the parameter. We anticipate that the alloy finally chosen for the waste package will be the one that has greatest corrosion resistance and the lowest sensitivity to the range of important parameters affecting corrosion.

After emplacement, the waste-package container materials could undergo any of several modes of degradation. These include atmospheric oxidation, uniform aqueous-phase corrosion, stress-corrosion cracking, and localized forms of corrosion such as crevice and pitting corrosion. Problems specific to welds and alloy phase instability are also considered. In general, it appears that most of the concern with the vulnerability of the container centers on the localized and stress corrosion effects, because the rates of uniform corrosion are expected to be very low (5).

Parameters Affecting Alloy Corrosion. As is true in all aqueous corrosion, the pH of the water is one of its most important parameters. However, all indications are that the pH of the water in the unsaturated zone at Yucca Mountain will be in the range of 6 to 8 (probably the more narrow range of 7 to 8; see Sections 5 and 6 of This Report); and within this range, changes in pH alone probably will not significantly affect the corrosion rates. Also in this pH range, the yields of the primary products of the radiolysis of water are not greatly affected by changes in the pH (6). The only exception to this is in the case of the copper alloys, when ammonia is also present as a result of radiolysis (4) or microbial action (7). In this situation, stress-corrosion cracking of copper is very sensitive to pH on either side of a value of 7.3, because this is the borderline of the stability fields of $Cu_2O$ and $Cu(NH_3)_2^+$ (8).

Probably the most important water parameter of all is the concentration of oxygen, both because of its direct participation in the corrosion reactions (2,5) and its reaction with hydrated electrons in the radiolytic environment to form superoxide ions, $O_2^-$ (4,6), which also promote many corrosion phenomena. On the basis of the measurements of dissolved oxygen in the well waters of Yucca Mountain (see Section 5 of This Report), and the fact that the repository will be located in the relatively shallow unsaturated zone, it is

expected that the corrosion environment will be aerated. When liquid water is present, after the hot thermal period, the concentration of oxygen in the water should be at or near that of air saturation (about 6.0 mg/L). These conditions generally signify a high value for the Eh as well, and can be described qualitatively as oxidizing.

High oxygen and Eh alone might actually be beneficial to the corrosion resistance of the stainless steels, but other species are also present that can react with components of the alloys and change their characteristics. For example, the austenitic stainless steels are subject to stress corrosion cracking (SCC) in aerated water if chloride ions are also present (2,9). At the higher levels of oxygen in the oxidizing environment, the susceptibility to SCC is sensitive to chloride concentration in the low range (1 to 10 mg/L) expected at Yucca Mountain (9). An increase in the chloride concentration via evaporation of the water, and the radiation field are expected to enhance the effects. Chloride ions also play a role in the pitting corrosion of copper-based alloys (5,10).

The concentration of bicarbonate ion in the water is important for a number of reasons. Foremost of these is the pH-buffering action it provides, which counteracts acidic conditions leading to localized forms of corrosion. This will be especially important in the radiation environment, because the radiolysis of the air/water environment is known to produce nitric in the water and a lowering of the pH in unbuffered media (4,11). The water at Yucca Mountain initially will likely have a bicarbonate concentration of at least 100 mg/L, and probably in the 100 to 200 mg/L range (see Sections 5 and 6 of This Report). Modeling studies (such as that described in Section 7 of This Report) and rock/water interaction experiments (12,13) show that the expected reactions of the repository water with the rock at higher temperatures, and with the atmosphere (and $CO_2$; see Ref. 14), should generally be beneficial in maintaining a mildly alkaline pH and the buffer capacity of the water.

The level of bicarbonate ion in water also has a direct effect on the pitting corrosion of copper alloys, and the Yucca Mountain waters (and J-13) are right at the borderline (about 100 mg/L) between susceptibility and non-susceptibility (10). However, the susceptibility and type of pitting that occurs is also a function of the concentrations of other constituents such as oxygen and sulfate ions (10). Higher concentrations of $HCO_3^-$, and higher

ratios of $HCO_3^-/SO_4^{2-}$ such as exist in the Yucca Mountain waters (and J-13 water), are expected to mitigate against localized attack (5). Bicarbonate is also important as an environmental factor affecting the growth of organisms (7).

Fluoride ion can act like chloride in breaking down the passive film on the stainless steels, so perhaps the sum of these two constituents should be considered in assessing the susceptibility to corrosion. However, the solution chemistry of fluoride is quite different from that of chloride. In any case, the Yucca Mountain waters will probably have levels of fluoride in a fairly narrow range (see Sections 5 and 6 of This Report): 0.2 to 5.0 mg/L, and halide effects will be dominated by chloride.

Nitrate ion at the levels expected initially in the Yucca Mountain waters (5 to 10 mg/L) is not of great importance as a direct corrodent; in fact, it can act as an inhibitor for the SCC of stainless steels. Copper-based alloys would more likely to be affected adversely. On the other hand, $NO_3^-$ is one of the scavengers for the hydrated electron in radiolysis chemistry (4), and it will be involved in equilibria, as mentioned above, in the atmospheric generation of $NO_3^-$, $NO_2^-$, and nitrogen oxides (11), which will have an important effect on the corrosion phenomena. The lower nitrogen oxides and ammonia can also be produced by microbial reduction of $NO_3^-$, and as also mentioned above, the presence of ammonia makes copper-based alloys vulnerable to corrosion.

Sulfate has already been mentioned as a factor in the pitting of copper alloys. In addition, it is a nutrient for organisms that reduce it to sulfide and hydrogen (7), and these are species that can have a greater effect on various corrosion phenomena than sulfate itself.

The anions in general are more important in corrosion phenomena than cations or neutral species, especially in dilute waters such as those considered here, but some of the cations and neutrals may also play a minor role. The doubly-charged cations, $Ca^{2+}$ and $Mg^{2+}$, are known to be more aggressive than the singly-charged cations, $Na^+$ and $K^+$, because of hydrolysis effects, but this is probably not relevant to the dilute, buffered solutions with which we are dealing. The concentrations of these cations do not materially affect radiolytic reactions either.

A metal ion that may be important in corrosion, even though present at very low levels, is iron. Ferric iron favors pitting attack of copper-based alloys (2), and can act as an anodic depolarizer in other SCC and pitting reactions of stainless steels. Manganese can act similarly through its redox reactions. The iron and manganese redox reactions can also influence the water chemistry during radiolysis (4), and even at trace levels, catalyze the decomposition of radiolysis products such as hydrogen peroxide. These are species whose concentrations in the Yucca Mountain and J-13 waters have not been well established. Because the environment is aerated, iron would be expected to be present as Fe(III); however, its solubility in the pH 7 water is very low. As discussed in Section 4 of This Report, reported values for iron in the waters are erratic because the measurements are highly dependent on the sample pretreatment techniques. However, the more recent measurements reported by Oversby (15,16), which are probably reliable, suggest that the concentration of dissolved iron is in the range of 0.006 to 0.015 mg/L.

Other trace constituents such as aluminum, strontium, barium, and lithium, which are present at concentrations of the order of 0.01 mg/L, are not expected to be important in the corrosion reactions.

Silicon (at 20 to 30 mg/L) and boron (at about 0.1 mg/L) are present largely as $H_4SiO_4$ and $H_3BO_3$ in the waters of Yucca Mountain and vicinty. They will not have a major, direct effect on the corrosion phenomena, but they might be participants in scale formation, and as weak acids, can have the same beneficial buffering effect as bicarbonate ion in mitigating pH changes. The rock/water interaction studies (1,12,15,16) show that at high temperatures, the concentration of silicon increases dramatically to the point where silica species tend to dominate the water chemistry. At the high temperatures, silicic acid may in fact be a more important buffering agent than carbonic acid. On the other hand, because its pKa s are in the range of 9-10, silicic acid can buffer only against more alkaline conditions than the pH 7-8 tuff waters.

As is apparent from the foregoing discussion, each parameter or constituent of the water must be examined carefully by itself, and in terms of coupled or secondary interactions in the media in order to arrive at a sensitivity for the parameter. However, as a way to qualitatively summarize

these sensitivities we can rank the various constituents of the waters in the following categories of importance in metal corrosion:

<u>Relative Importance of Water Parameters in Metal Corrosion</u>

Very Important: $O_2$, pH, Eh, $HCO_3^-$, $Cl^-$
Less Important: $SO_4^{2-}$, $NO_3^-$, Si, $F^-$, Fe
Very Little Importance: Na, K, Ca, Mg
No Importance: B, Li, Al, Sr, Ba

These rankings are of course based, as a reference point, on the expected values of the parameters in the Yucca Mountain waters, and J-13 water as a representative of those waters. It can be said that if the actual repository water differs significantly in a certain characteristic from that of the reference water, and that characteristic is important, (or if the alloy chosen for the container is different from that discussed here) then the potential corrosion phenomena should be examined very carefully in light of that difference. For example, if the concentration of chloride is higher in the vadose water than expected, or it reaches much higher levels because of evaporation and concentration of the water, that should be taken into account in the laboratory experimentation.

We reiterate that the expected environment that the waste packages will experience initially, namely, that of a dry or wet steam atmosphere, is quite different than the aqueous environment on which the corrosion sensitivities described above are based. The high temperature alone is an important difference, since it can affect the relative rates of many reactions. However, many of the same relationships and general effects still apply even during the "hot" period, and will have a direct bearing on the behavior of the waste package as the environment cools.

For experiments designed to ascertain the corrosion behavior of candidate materials immersed directly in the aqueous environment, J-13 water is a good reference or baseline medium because it is representative of the waters of Yucca Mountain. Other dilute waters (synthetic, spiked J-13, or ground waters) would also be suitable for parameter sensitivity studies. Because bicarbonate ion and pH are very important to all of the corrosion phenomena, especially in the radiation environment, synthetic waters should generally be

prepared to match these characteristics in the natural waters. For atmospheric corrosion tests (i.e., tests in which only a gas phase is in contact with the specimens), bicarbonate and pH are still important, but other constituents in the water that are not involved in equilibria with volatile species are less important.

Parameters Affecting Radionuclide Release from Waste Forms. Two types of nuclear waste forms are planned to be emplaced in the containers of the repository: spent reactor fuel from commercial power plants, and a waste form in which the waste itself is vitrified in borosilicate glass. Glass waste forms containing nuclear waste of two, somewhat different compositions will be produced by the Defense Waste Processing Facility at the Savannah River Plant and by the West Valley (NY) Demonstration Project. Various studies are being performed to determine the behavior of these waste forms when the metal barrier containment is inevitably lost. When containers are breached, the radioactive waste will then be exposed to ambient air and water. Leaching of the waste by water will cause some of the radionuclides to dissolve in the water, thus leading to their transport into the surrounding environment. Containment periods of the order of 10,000 years are considered probable (2,17).

In addition to regulations on the allowable release of radionuclides mandated by the Nuclear Regulatory Commission (see the footnote on p. 9.3), the Environmental Protection Agency has also established limits that are somewhat different (18). Oversby (19,20) and Aines (21) have examined these regulations, the compositions of the various waste forms, the properties of the radionuclides, and the containment scenario, and have identified the isotopes of greatest concern. There are some differences that depend on the particular waste form; but in general, the isotopes of plutonium and americium are most important. Also important are isotopes of uranium and the other actinides (thorium, neptunium, and curium), as well other elements such as nickel, zirconium, technetium, and cesium. Another important radionuclide that may be released is carbon-14 (half-life, 5730 yr) as gaseous $CO_2$ (22,23).

Experimental tests of waste forms and modeling of waste-form behavior have centered on the interactions of water with bare fuel, fuel with cladding, and glass waste forms, to develop information on the chemistry of the leaching

processes, and ultimately provide a source term for the migration of radionuclides from the repository. The nuclear fuel and the glass waste forms themselves represent extremely complex chemical systems. The spent fuel is a uranium oxide matrix containing fission products, clad with Zircaloy (24); glass waste forms loaded with simulated or actual waste are composed of as many as 14 metals as the oxides at concentrations above 0.1% (25).

As one of the earliest activities in the field of nuclear waste isolation, a large amount of work has been done in the leach testing of waste forms, and a considerable body of literature exists on this topic. Recent reviews and an introduction to the state of knowledge in leach testing can be found in the following reports: for spent fuel, the reports of Reimus and Simonson (26) and the NNWSI Plan of Shaw (27); for glass, the report of Mendel (28), the papers of Harker and Flintoff (29) and Abrajano and Bates (30), and the NNWSI Plan of Aines (31). Modeling of the dissolution of spent fuel and glass in J-13 water is the subject of two recent papers (32,33) from the NNWSI Project.

Because waste-form leach testing has been performed in the contexts of many different types of geologic repositories (granite, basalt, salt, and tuff), a variety of solutions have been used as leachants. In the NNWSI Project, the three most common leachants have been deionized water, J-13 water, and J-13 water previously equilibrated with tuff rock. The latter, known as "equilibrated J-13 water," has been used frequently by Bates and coworkers at Argonne National Laboratory. Bates and Gerding (34) give a procedure for the preparation of this water for leach testing; in essence, it is prepared by heating J-13 water with crushed tuff (caliche-free) at 90°C, and then storage at ambient temperature. There are differences in the literature as to the composition of water prepared in this manner (15,30,34-36), which depend in part on the conditions of the heating (type of vessel, open or closed system, state of subdivision of the rock, etc.), but in general, compared to raw J-13 water, "equilibration" at 90°C increases the silica and sodium concentrations by about 5-20%, slightly decreases the $HCO_3^-$, calcium, and magnesium, and has no effect on $Cl^-$, $F^-$, $NO_3^-$, and $SO_4^{2-}$. Bates and coworkers never report values for $HCO_3^-$ or potassium, but Knauss and coworkers' experiments (36,37) suggest little change in either species at 90°C in a closed system. Among the minor

constituents, aluminum increases from a very low concentration to a few tenths of a mg/L.

What effects do the constituents of the water, and in particular, water of Yucca Mountain or J-13 water, have on the leach behavior of the waste forms? In spite of the large amount of work on leaching, the mechanisms and roles of the various water species are not completely understood (20,26,28). In general, it can be said that the total chemistry of the water is important, perhaps to a greater extent than it is in metal/water interactions or transport phenomena. All of the solution components have some effect on the complex processes of dissolution, precipitation, and secondary-compound formation that accompany waste-form dissolution. Also, as is true of all of the near-field interactions, radiolysis effects will be superimposed on the normal chemical reactions. Nevertheless, as would be expected from the relevant chemistry, certain constituents will be somewhat more important than others, and there will be some differences in sensitivity depending on the type of waste form considered.

There have been [illegible]led studies of the effect of pH alone on the dissolution of spent fuels or waste glasses in the narrow region around pH 7, but significant effects are expected if changes in pH are large (26,28). Glass leaching is controlled by surface layers and reactions that are in part pH controlled (31,38). The effect of pH on the release of the actinides is in turn highly dependent on another parameter of the water, namely, its redox character, or Eh (26).

In accordance with expectations, a number of leaching experiments have shown that changes in the pH of the water can apparently have effects on the solubilities of constituents of the waste forms, but it is not always possible to separate the effect of pH from other differences in the solutions. For example, a study of the release of radionuclides from spent fuels by Wilson and Oversby (39) showed that there was a greater release (of U, Pu, Am, Cm, Np, and Tc) into deionized water than J-13 water. Part of the this difference in leach rates may have been due to the fact that, during the experiments, the pH of the deionized water decreased to 5.7-6.4, presumably because of the radiolytic formation of $HNO_3$, while that of the J-13 water rose slightly to 8.2-8.5 (40). J-13 water did not become acid because it is buffered by bicarbonate ion. However, also influencing the results were the formation of

colloidal particles of the relatively insoluble actinide compounds, which were formed during the test, and the presence of bicarbonate, which is a complexant for the actinides, in only the J-13 water. Cesium, whose solubility is not sensitive to pH, leached to about the same extent into both waters.

Computer simulations of the dissolution of spent fuel (32) and waste glasses (33) in J-13 water in closed systems illustrate some of the effects of pH changes in the water during the dissolutions. The radionuclides and other components of the waste forms are found to precipitate as oxides and hydroxides, together with silicates, carbonates, and if phosphorous is present, as phosphates. For example, the solubilities of the important radionuclides, americium and neptunium, appear to depend directly on the solution pH in the region of pH 7 to 8. In contrast, the solubilities of plutonium and thorium remain low even as the solution composition changes.

As already indicated, the concentration of bicarbonate ion in the water is also important, for a number of reasons: as one of the buffers of pH changes resulting from mineral dissolution or radiolysis (4,41), as a complexing agent for the actinides (26), as a participant in the formation of solid phases [although it does not appear as important here as silicate (32,33,38)], and as a species that can exchange $^{14}C$ with gaseous $CO_2$ (22,23).

The two correlated water parameters -- Eh and concentration of oxygen -- are also very important to the behavior of the waste forms. The redox potential of the water has a large effect on the solubility of the multivalent elements, especially the actinides (26,32,33,42), which in general are more soluble in their higher oxidation states. Thus spent fuel, as a matrix of $UO_2$, is more soluble under oxidizing than reducing conditions (26), and the leaching of the actinides (e.g., plutonium and neptunium) from waste glass decreases as the solution Eh decreases (33).

In regard to experiments on leaching that are performed with a water such as J-13, some additional comments can be made. First of all, both the level of oxygen and the Eh should be known initially for whatever water is used. The measured Eh is determined by the response of a noble-metal electrode to the potential-determining species in solution that comprise electrochemically reversible (fast electron exchange) couples, such as $Fe^{3+}/Fe^{2+}$, but not oxygen directly. The concentration of oxygen and history of the raw water, however, do determine whatever redox equilibrium exists. A difficulty in the

accurate measurement of Eh for the very dilute, benign waters of Yucca Mountain and vicinity is that the concentration of potential-determining species is very low. For J-13 water, the most abundant one, iron, is at a level of about 0.01 mg/L (10 ppb) (15,16). Such water has a very low redox buffer capacity, thus it is easily perturbed. In the case of the waste-form dissolution, the Eh (and $O_2$) of the water, after dissolution is well underway, will be determined chiefly by the elements dissolving from the wasteform in the presence of the radiation field, and the initial values will assume less importance. Thus the choice of reference water when Eh is important deserves careful consideration, but the actual initial values of this parameter are probably much less important than the concentration of oxygen, both before, and after leaching begins. If it could be measured, the ferric/ferrous ratio of the ground water would be more useful than the Eh (42).

Among the other constituents of the water, probably the most important is silicon, for several reasons:

1. As mentioned above, silicon, in its various forms such as silicic acid, dominates the chemistry of the water in contact with the tuff during the hot thermal period (12,15,16,36,37).

2. Along with bicarbonate, silicon, as silicic acid, is a pH buffer (43), perhaps the most important one at high temperatures, but only against more alkaline conditions than the pH 7-8 tuff waters.

3. Silica is a major constituent of the waste glasses, and silicates are important alteration phases in both the waste glass and spent fuel dissolution (26,28,31-33). In the case of spent fuel, modeling has shown that the silica in J-13 water, via the formation of uranyl silicate complexes and a precipitate schoepite, will have a controlling effect on the solubility of uranium (32).

Several of the other elements found in J-13 water are important in the leaching of glass waste forms, because they are concentrated in the outer layer of the leached glass and influence the rate of dissolution. These include calcium, strontium, aluminum, and as mentioned above, silicon (44). At low temperatures, the concentrations of strontium and aluminum are initially quite low in the J-13 water, especially in comparison with the levels in the glasses (33). At high temperatures, in the water in contact with the rock, aluminum will be much higher, but calcium (and magnesium) will

be low (12). Silica, sodium, aluminum and calcium also form precipitates that incorporate many of the radionuclides (32,33,44).

Two of the minor anions of the tuff waters, fluoride and sulfate, are of some interest because they can form complexes with the actinides in solution, but at their concentrations in J-13 water, these species are not very important in comparison with bicarbonate, silicate, and in the case of waste glass dissolution, phosphate (33). Phosphorous is present in the waste glass, but only trace levels are present in J-13 water (see Section 4 of this report). Nitrate and chloride, also at low concentrations, appear to have very little effect on waste form dissolution.

Because of the many interacting effects, and the less well developed knowledge of mechanisms, the ranking of the sensitivity of the water constituents in the release of radionuclides for waste forms is not as clear cut as in the case of metal corrosion. Nevertheless, the following seems reasonable:

Relative Importance of Water Parameters in Waste-Form Leaching

Very Important: pH, $O_2$, Eh, $HCO_3^-$, Si

Less Important: Al, Na, Ca, Fe (except as it may determine Eh)

Very Little Importance: Sr, $SO_4^{2-}$, $F^-$, B, K, Mg, $NO_3^-$, $Cl^-$

No Importance: Ba, Li

The radiation field will modify the chemistry of the solution to some extent, as discussed by Van Konynenburg (4), and as outlined above in the context of metal corrosion. The major possible effect again is a pH shift due to the production of $HNO_3$ in the moist air system, but the solution buffered by $HCO_3^-$ should mitigate this. Production of hydrogen peroxide and a raising of the Eh could enhance the dissolution of some of the radionuclides. Scavenging of radicals by $NO_3^-$ and $Cl^-$ (4) to produce more reactive oxidizing species make these anions somewhat more important. However, the effects on waste-form leaching are presently not very well known (4).

Parameters Affecting Rock/Water Interactions. An important part of the NNWSI Project is to characterize the processes that will occur in the repository environment during its perturbation by the heat and radiation from the emplaced waste packages. A major effort has been directed at the

interaction of water with the tuff, and many of these hydrothermal interaction experiments have already been cited in This Report. Of special interest here is the composition of the water resulting from heating in the presence of rock, and in laboratory experiments, the effects of the initial composition of the water on the results. This area of investigation is part of the plan for waste package environment testing described by Glassley (45).

Most of the experiments in the area of rock/water interactions thus far have been performed by Oversby and Knauss and their coworkers (1,15,16,36,37,46), and have been combined with modeling (12) to aid in interpretation and prediction. In addition, many other other experiments have been performed in so-called integrated testing (13,24,34,35,39-41,47), in which water is heated in the presence of rock and radiation, but the objective in these experiments is primarily to measure the release of radionuclides (47). In the basic rock/water interaction studies, the water used has either been that from the J-13 well or deionized water. Most of the samples of Topopah Spring tuff have come from an outcrop at Fran Ridge near Yucca Mountain (46) or from a drillcore from hole USW G-1, at a depth correlated with that of the potential repository at Yucca Mountain (37, and references therein). The G-1 drillhole is located not far from the USW wells H-1 and G-4 near the repository exploration block (see map on p. 5.3 of This Report, and listing of the chemistries of those wells in Section 5).

The water resulting from contact with the repository rock, as modified by heat and radiation, will likely be one of the types of water (others being condensed steam and evaporated water) which in turn will interact with the metal container, the waste forms, and, in the near field, will be the medium by which radionuclides may migrate away from the repository. Thus, as indicated in the foregoing discussions, the expected composition of the water --at temperature -- is of great interest in planning experiments on the waste-package-component/water interactions. Some of the changes in the water have already been mentioned in several places. Table 9.1 is a collection of data that illustrates several principal results from the rock/water interaction studies.

The data in Table 9.1 represent waters obtained by techniques that have some fundamental differences, which are reflected in differences in the concentration values. The composition of the so-called "Equilibrated J-13"

Table 9.1. Reported steady-state compositions of J-13 water after heating with Topopah Spring tuff (concentrations in mg/L).

| Parameter | Raw J-13 25°C | "Equil." J-13 90°C | "Equil." J-13 150°C | J-13 + Core wafer 150°C | Computer simulated J-13 150°C 100 yrs. | D.I. Water + Core wafer 150°C |
|---|---|---|---|---|---|---|
| Na | 45.8 | 40 | 40 | 45.3 | 74.4 | 14.0 |
| Si | 28.5 | 49 | 122 | 119 | 147 | 135 |
| Ca | 13.0 | 8 | 3 | 6.6 | 0.007 | 0.22 |
| K | 5.0 | 9 | 9 | 4.9 | 1.65 | 2.8 |
| Mg | 2.0 | 0.2 | 0.1 | 0.035 | 0.0 | 0.11 |
| Al | $\leq$0.01 | 0.4 | 1 | 0.54 | 23.7 | 1.30 |
| pH, 25°C | 7.4 | 8.5-9 | ~8.7 | 6.8 | 8.4 | 7.4 |
| $HCO_3^-$ | 129 | ~113 | ~100 | 124[a] | 7.4 | 37 |
| $F^-$ | 2.2 | 2 | 2 | 2.1 | see text | <0.1 |
| $Cl^-$ | 7.1 | 7 | 7 | 6.8 | 6.7 | 1.1 |
| $NO_3^-$ | 8.8 | 9 | 9 | 8.4 | 9.1 | 2.0 |
| $SO_4^{2-}$ | 18.4 | 18 | 18 | 17.1 | 17.9 | <0.2 |
| Reference: | This Rept. page 4.2 | 15 | 15 | 37 | 12 | 37 |

[a]Estimated from charge balance

water, the 90°C version of which has been used by Bates and coworkers (30,34,35), is given here from the work of Oversby (15). It is prepared by heating J-13 water with crushed tuff in a sealed Teflon vessel. The data given in Table 9.1 are for time periods of 50 to 72 days. The core wafer data are those of Knauss and coworkers (37), who heated solid wafers of tuff in gold-bag autoclaves for 60 to 70 days. In experiments with the Teflon vessel, $CO_2$ could escape from the solution, but true equilibrium with the atmosphere did not exist (48,49). The gold-bag, on the other hand, is completely impermeable to gases. Thus, with respect to the ambient atmosphere, the gold

bag is a closed system, while the Teflon vessel might be described as an imperfect open system. The open vs. closed system condition has a significant effect on the $CO_2/HCO_3^-/CO_3^{2-}$ equilibria, and hence the chemistry of the rock/water system. A second difference is that the particle size of the solid phase, and the solid-surface-area to solution-volume ratio, can influence the chemical pathway of rock dissolution and alteration because of differences in the rates of dissolution of the individual minerals.

Which set of conditions best matches the repository is speculative, and depends on the scenario envisioned. The natural system could be considered closed at depth, in the interior of the rock. The solid wafer results are probably more definitive in terms of the actual behavior of the rock and water because one variable, particle surface area, has been removed, and most of the repository rock will actually be intact.

Another interesting set of data, shown in Table 9.1 for comparison, is from the simulation of Delaney (12). She modeled the reaction between J-13 water and tuff for a time period of 100 years, at 150°C, and as an open system by fixing the fugacity of $CO_2$. The known rate constants for the dissolution of the various minerals were incorporated in the calculation. In her study she also simulated the closed system results of Knauss, et al, and found good agreement between the calculated and actual compositions of the water.

The differences between the open and closed system water chemistries shown in Table 9.1 can be explained qualitatively, and a complete discussion of the mineral reactions and alterations can be found in the reports cited above. In the core-wafer closed system, there is an initial decrease in calcium in the solution because of the precipitation of calcite, $CaCO_3$, which has a retrograde solubility. At longer times, calcium is controlled by the minerals Ca-smectite and Ca-clinoptilolite (12). In Delaney's open system, the equilibrium with $CO_2$ allows the pH to rise, preventing the precipitation of $CaCO_3$, but then the solution calcium eventually decreases to a very low concentration due to the other minerals. In the Teflon-vessel experiments, the pH also rises due to the escape of $CO_2$, but the solution calcium still decreases because of the precipitation of calcite (15).

Silica, sodium, and aluminum increase significantly in all of the experiments compared to their concentrations in raw J-13 water. Dissolution

of the sanidine component is believed to be responsible for the sodium and aluminum; and first cristobalite, then clinoptilolite, controls the solubility of silica (12,37). Magnesium is always found to decrease to low concentrations. In the core wafer experiment, potassium increased initially, which might correspond to the result of the Teflon-vessel run, but then slowly decreased. Knauss, et al (36) found potassium at 5.5 mg/L after 70 days at $150^{o}$ using crushed tuff. Potassium in the simulation ultimately reached a still lower concentration.

Among the other anions, it is noteworthy that $Cl^-$, $NO_3^-$, and $SO_4^{2-}$ remain unchanged in all of the experiments. The concentration of fluoride did not change in any of the short-term tests at 90°C, but it did rise to 3.9 mg/L at 250°C in the crushed-tuff experiments (36). In the computer simulation, fluoride was reported as 7.6 mg/L (12), but this is apparently a typographical error, because the mineral assemblage did not contain fluoride.*

Knauss and coworkers (37) also examined the effects of heating deionized water with the tuff core wafers, and the composition of the resulting water is shown in the last column of Table 9.1. These data suggest which species in the initial water are most important to consider in experiments of this relatively short duration. Silica rather quickly reaches a concentration not greatly different from that in the other 150°C waters, and the pH stays about the same as the J-13 water experiment. The initial low buffer capacity of the pure water, however, keeps the $HCO_3^-$ lower and changes the dissolution of the K, Na, and Ca-containing minerals so that the concentrations of these elements are lower. As also evidenced by the high concentration of aluminum, the reaction history during this time frame is distinctly different for the two waters. The concentrations of the minor anions also remain low because of their very low concentrations in the rock. As mentioned above, essentially pure water is one of the possible leachants or corrodents, thus it would interesting to model it with tuff in a long-term simulation as was done with J-13 water.

One other interesting aspect of the rock/water interactions emerges in the present context. We noted in Section 5 in the comparison of J-13 water with the other waters of Yucca Mountain and vicinity that the high levels of potassium and magnesium in J-13 water are practically the only features that

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*Personal communication, K. Knauss and J. Delaney, 1988.

distinguish it from the other well waters. The high temperature rock/water studies show that this difference is of little consequence, since potassium and magnesium are lower at elevated temperature anyway. This fact, and the results using deionized water appear to reinforce the validity of using J-13 as an experimental reference water. Morever, if synthetic dilute waters are used to represent vadose or ground water, they should at least contain the expected concentration of bicarbonate and be adjusted to a pH of about 7.5.

In regard to the effects of radiolysis of the water on the dissolution of rock, many of the same re[illegible]s concerning waste-form leaching apply here, except i[illegible] appears that even less is known in detail. It is known that the rock itself is little affected (1), and in general, it appears the overall effect of radiation on the rock/water interactions would not be large. The tuff, through the dissolution of its minerals, should provide an even more effective pH buffer than the bicarbonate water alone (50). One difference between rock dissolution and metal or waste-form reactions is the relative importance of dissolved oxygen, oxidizing conditions, or Eh. These parameters would affect only the minerals containing transition metals, and these are relatively insignificant in the tuff.

Because in rock/water interactions we are dealing experimentally only with a thermally-hot environment, and we are considering only the effect of the initial characteristics of the water to be significant in the use of a water as a reference, the ranking of parameter sensitivity is a little bit different from that of the interactions examined previously. Thus the following ranking seems reasonable:

Relative Importance of Water Parameters in Rock/Water Interactions

Very Important: pH, $HCO_3^-$

Less Important: Na, Ca, Si, K, Al

Very Little Importance: $SO_4^{2-}$, $F^-$, Eh, $O_2$, B, Mg

No Importance: $Cl^-$, $NO_3^-$, Sr, Ba, Li, Fe

Note that silicon and aluminum are ranked lower here, because, starting from different initial values, they should establish steady-state concentrations quickly at the higher temperatures. Also note, however, that if the water and rock are used in integrated testing at low temperatures, or if particular

parameters are more sensitive for the third material in the test, then the criteria and ranking will be different.

Parameters Affecting Radionuclide Migration. The ability of a geological setting to retard the migration of the radionuclide elements into the environment will depend on the properties of the rock, the characteristics of the ground water, and the chemistry of the radionuclides themselves. The rates of migration will be controlled by first of all by the inherent solubility of the elements in the water, by hydrodynamic dispersion, by the processes of sorption and desorption, and by the advection of bulk water through the environment. Certain elements may also form colloids that can be carried by the water, and others may attach themselves to natural colloids. The factors controlling radionuclide migration comprise the fourth general class of experiments in which the chemistry of the water is important, and the chemical phenomena here have much in common with those of waste-form leaching.

The two primary factors in the retardation of radionuclide transport -- solubility and sorption/desorption -- have been the subject of numerous studies in the context of nuclear waste isolation for many years. In the NNWSI Project, the Los Alamos National Laboratory is responsible for characterizing the far-field environment of the Yucca Mountain repository, and has performed a number of investigations of the behavior of the radionuclides in tuff and J-13 water (51). The question of the sensitivities of the phenomena measured to changes in water chemistry cannot be answered definitively in many cases because of the complexity of the effects. Nevertheless, some very useful information along these lines has been developed, and there appears to be a growing emphasis on such sensitivity studies and attempts to bound the phenomena in terms of the anticipated extremes of water composition. LLNL is also planning somewhat similar types measurements to obtain data leading to a source term from the near-field environment (47).

A good indication of how some of the characteristics of the water may control the solubility of the radionuclides is a calculation done using the geochemical modeling code EQ3/6 (52) by Ogard and Kerrisk (see pp. 22-28 in Ref. 43). A condensed version of their results is presented in Table 9.2; the original report should be consulted for a more detailed discussion and

Table 9.2. Calculated solubilities of radionuclide elements in waters of Yucca Mountain and vicinity (from Ogard and Kerrisk, Ref. 43).

| | Well | | |
|---|---|---|---|
| | J-13 | UE-25p#1 Paleozoic | H-3 |
| ph | 7.4 | 6.6 | 9.4 |
| Eh, mV | 340 | 360 | -143 |
| $HCO_3^-$, mg/L | 129 | 710 | 274 |
| Uranium | | | |
| Solid | $UO_2(OH)_2\ H_2O$ | $UO_2CO_3$ | $UO_2$ |
| Primary Species | $(UO_2)_2CO_3(OH)_3^-$ | $UO_2(CO_3)_2^{2-}$ | $UO_2(CO_3)_3^{4-}$ |
| Solubility, mol/L | $3.7 \times 10^{-3}$ | $1.7 \times 10^{-3}$ | $4.1 \times 10^{-8}$ |
| Plutonium | | | |
| Solid | $Pu(OH)_4$ | $Pu(OH)_4$ | $Pu(OH)_4$ |
| Primary Species | $PuO_2^+$ | $Pu(OH)_5^-$ | $Pu(OH)_5^-$ |
| Solubility, mol/L | $1.8 \times 10^{-6}$ | $3.1 \times 10^{-8}$ | $1.3 \times 10^{-5}$ |
| Americium | | | |
| Solid | $Am(OH)CO_3$ | $Am(OH)CO_3$ | $Am(OH)CO_3$ |
| Primary Species | $AmCO_3^+$ | $AmCO_3^+$ | $Am(CO_3)_2^-$ |
| Solubility, mol/L | $9.9 \times 10^{-9}$ | $2.2 \times 10^{-8}$ | $6.9 \times 10^{-10}$ |
| Strontium | | | |
| Solid | $SrCO_3$ | $SrCO_3$ | $SrCO_3$ |
| Primary Species | $Sr^{2+}$ | $Sr^{2+}$ | $Sr^{2+}$ |
| Solubility, mol/L | $8.0 \times 10^{-4}$ | $5.3 \times 10^{-4}$ | $3.3 \times 10^{-6}$ |
| Radium | | | |
| Solid | $RaSO_4$ | $RaSO_4$ | $RaSO_4$ |
| Primary Species | $Ra^{2+}$ | $Ra^{2+}$ | $Ra^{2+}$ |
| Solubility, mol/L | $3.4 \times 10^{-7}$ | $9.3 \times 10^{-8}$ | $2.9 \times 10^{-7}$ |
| Technetium | | | |
| Solid | --- | --- | $Tc_3O_4$ |
| Primary Species | $TcO_4^-$ | $TcO_4^-$ | $TcO_4^-$ |
| Solubility, mol/L | Large | Large | $2.06 \times 10^{-12}$ |

additional information on the the mineralogy and element speciation. This is very illustrative work because it shows the effects of three waters, including J-13, whose chemical compositions are at the extremes expected to be encountered at Yucca Mountain. The chemistries of these waters were summarized and discussed in Section 5 of This Report. Water from well USW UE-25p#1 is from the dolomite aquifer beneath Yucca Mountain, and is very high in bicarbonate. Well USW H-3 is in the exploratory block (see p. 5.3) and this water, which is distinguished by its reducing character, was obtained at depth from a packed-off zone. These three wells actually exhibit a much wider range of pH, Eh, $HCO_3^-$, and concentrations of several other constituents than is expected in the vadose zone at Yucca Mountain (see Section 5). But if radionuclides escape from this zone and enter the deep water tables, they will encounter chemistries similar to those of UE-25p#1 and H-3.

As shown in Table 9.2, the features of the water that most influence solubility are pH and Eh, and species that form complexes with the waste elements such as hydroxyl and carbonate. Note the much higher solubility of uranium and technetium in the oxidizing waters. Ogard and Kerrisk's calculation also predicts fluoride- and sulfate-containing species in some of the waters even though these anions are at low concentrations (2.1-5.4 mg/L for $F^-$ and 18.1-129 mg/L for $SO_4^{2-}$). The chemistries of strontium and radium are simple since they exist in only one oxidation state and form weak complexes. The radionuclide element cesium would be very soluble under all of these conditions.

In Ogard and Kerrisk's simulation, plutonium exists mostly in the +5 and +6 oxidation states in J-13 water, and the +4 state in the water of the other two wells. However, plutonium would probably dissolve initially as Pu(IV); in this oxidation state and at near-neutral pH in the dilute waters, Pu(IV) polymerization and colloid formation are probable (53,54)), and may keep Pu in the +4 state. Such actinide colloidal and particulate matter is common in laboratory waste-form leach tests (40,41), and complicates the interpretation of experimental results.

The large differences in the character of the three waters and in their effects on the solubility of the radionuclides show that, at least for this property, J-13 water would certainly not serve as a good surrogate water for

conditions represented by these other waters. J-13 water is chiefly representative of waters having a pH range of 7.0 to 8.0, together with an aerated, oxidizing redox condition, and a bicarbonate concentration of about 50 to 200 mg/L.

The second important phenomenon that will limit the release of radionuclides from the geologic environment is the tendency of materials in solution (and colloidal suspension) to be retained by the minerals of the rocks through which the water travels. The retention has several underlying mechanisms: specific adsorption of ions and neutral molecules on the mineral surfaces, ion exchange with elements in the minerals, formation of precipitates with constituents of the mineral surface, and particulate filtration. Experiments to determine sorption, and its complement, desorption, provide information to calculate the related parameter, the retardation of radionuclides by rock. Because of the variety and complexity of the mechanisms involved, the nature and constituents of the water will obviously have equally diverse effects on the extent of desorption. In general, in the NNWSI Project, it appears that there is less detailed knowledge of the sensitivities of the water parameters in sorption/desorption than there is in the other phenomena.

Thomas (51) has summarized the results of the sorption studies undertaken at Los Alamos between 1977 and 1985, and has discussed some of the effects of the variables on the sorption behavior of the radionuclides. Most of that work has dealt with the effects of changes in the mineralogy of the tuff and the physical variables on sorption from J-13 water. Work has continued there recently to define more carefully the effects of changes in the composition of the water. Knight and Thomas, in a preliminary, unpublished study (55), have examined the sorption/desorption ratios of the elements Sr, Cs, Ba, Sn, and Eu (as an actinide analog) in the same waters as the solubility study of Ogard and Kerrisk, namely waters from wells J-13, UE-25p#1, and H-3. They also tested waters consisting of J-13 water to which additional amounts of $Na_2SO_4$, $NaHCO_3$, or $CaCl_2$ were added, to measure the effects of the individual constituents and the increased solution ionic strength. Water from well H-3 was presumably used in the aerated, high-Eh state.

Several tentative conclusions were drawn from the results. One was that the initial pH of the waters, in the range of 6.7 to 8.7 for their samples,

was not a significant factor in explaining the sorption differences. This parameter was important in the solubility modeling studies of Ogard and Kerrisk, but the suite of elements was different, and europium may not be an adequate stand-in for the actinides. In the case of colloids, the charge on the particles is very dependent on solution pH. Cesium sorption probably takes place largely by cation exchange, thus higher concentrations of sodium in the water would be expected to decrease the sorption of cesium. This effect was in fact observed, but it was not very large. Depending on the tuff composition, a fivefold increase in sodium in the water decreased the cesium sorption ratio by a factor of 1.5-2.

The same type of trend was followed by strontium and barium, where calcium in the $CaCl_2$-spiked J-13 and UE-25p#1 waters (120 and 88 mg/L, respectively, vs. 13 in J-13 water) provided the competition for ion-exchange sites, but in general, the mineralogical composition of the tuff (especially the presence or absence of zeolites) had a greater effect than the range of water composition. In the sorption results for europium and tin, the effect of the tuff composition again appeared to dominate the water compositional changes. Overall, it was not possible to identify single water constituents that had a dramatic effect on sorption, but it was found that for the elements and ranges of conditions examined, all of the elements were retarded to a significant degree as far as waste isolation is concerned.

It is worth noting that the investigation of Knight and Thomas may be the first example of a laboratory study in which ground waters from Yucca Mountain and vicinity other than J-13 were used.

The knowledge developed thus far on radionuclide migration in tuff and $NaHCO_3$ water does not enable as precise a ranking as given for the other phenomena. In addition, like waste-form leaching, sensitivities are different for different radionuclides and different minerals. For example, Eh is not as important for elements such as strontium and cesium as for the actinides. This also may be an area where more is known about the effects of the rock than the water. Nevertheless, on the basis of solubility information and some knowledge of the types of mechanisms involved, for radionuclide migration, the following ranking can be presented:

Relative Importance of Water Parameters in Radionuclide Migration

Very Important: pH, Eh, $O_2$, $HCO_3^-$

Less Important: Na, Ca, $SO_4^{2-}$, $F^-$, Si, Fe

Very Little Importance: $Cl^-$, K, Mg, B, Al, Sr, Ba, Li, $NO_3^-$

Iron may be more important if it controls the Eh and/or if colloidal, hydrous iron compounds are present to sorb and carry radionuclides. Radionuclide migration and retardation are phenomena of concern in both the near-field and far-field regions. In the near field, as discussed above, both heat and radiolysis of the water will alter the chemistry of the radionuclide migration process.

Conclusions. In surveying the material presented in this section, two water parameters clearly emerge as being important in all of the four major phenomena of nuclear waste isolation. These are the pH and concentration of bicarbonate ion in the water. Two other features, Eh and the concentration of oxygen, are very important in all but the rock/water interactions. These are the parameters that must be most carefully examined in designing experiments, and are the parameters most important in possible variations of the water chemistry at Yucca Mountain. Even though important, the major phenomena appear not to be overly sensitive to changes in the values of these parameters, in the ranges of, say, the following:

| | |
|---|---|
| pH, 7.0 to 8.0 | Eh, 200 to 400 mV |
| $HCO_3^-$, 50 to 200 mg/L | $O_2$, at least 3 mg/L |

The validity of the use of J-13 water for the near-field experiments hinges in part on how representative it is of the real Yucca Mountain waters. The evidence shows (see Section 5) that J-13 water is similar to the other waters, especially in the most important characteristics, thus for many types of experiments there is considerable confidence in J-13 as a reference water.

On the other hand, J-13 water is not necessarily always the best choice of water. It depends on the phenomenon being measured, and the objectives of the experiment. Certain phenomena are uniquely sensitive to certain minor constituents of the water, which tend to vary more on a relative basis. For example, metal corrosion is sensitive to chloride; and to some extent,

waste-form leaching is influenced by the aluminum concentration. The concentration of these in J-13 water may not adequately represent the values in the Yucca Mountain waters. To bound the water conditions, other Yucca Mountain ground waters should be used, as has been done by Los Alamos in their studies of solubility and radionuclide migration. Finally, in experiments involving the hot environment, the importance of the initial composition of the water must be carefully assessed. In these and other experiments, more might be learned by using simpler synthetic waters containing just the constituents known to be important.

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## Section 10

## Comments on the Meaning of the Term "Reference"

In addition to examining the technical basis for the use of J-13 water in the NNWSI experiments, it is useful to comment on what is meant by the term "reference" as a designation for J-13 water or its composition. At first glance, as an experimental material, J-13 water historically does not appear to have been used in the classical sense of a reference material. J. K. Taylor of the National Bureau of Standards has defined a reference material as "a substance for which one or more properties are established sufficiently well to calibrate a chemical analyzer or to validate a measurement process" (1). That meaning is the sense of the term as applied to the certified reference materials that are issued by the NBS and other standards organizations. These would usually be called "reference standards."

In the various NNWSI measurements, J-13 water has usually been used as a material which, it was believed, is a good approximation to the waters that will interact with components of the waste repository system and the radionuclides that may escape from it. In this sense, J-13 is a surrogate water, not a reference water. For example, the significance of many measurements such as the rock/water interactions lies in the changes that the J-13 water undergoes from its initial composition, rather than the absolute value of its initial composition. When accurate measurements of the repository environment become available, the information developed using J-13 water will then have to be translated or extrapolated to the actual repository conditions. J-13 water has never been used explicitly as an analytical calibrating material or reference standard, but the apparent invariance of its composition (as discussed in Section 4) has probably led some workers to use J-13 water as a validating reference material in their measurements.

There is, however, a quasi-official meaning that has been attached to the term "reference material" in nuclear waste materials investigations, which can definitely be applied to J-13 water. The now-defunct Materials Review Board (2) of the U. S. Department of Energy, together with the Materials Characterization Center at Battelle's Pacific Northwest Laboratory has developed and published a series of test methods designed to be used to measure the characteristics of candidate materials related to nuclear waste

storage. Several of these test methods involve the use of solutions prepared to evaluate the chemical durability of waste storage components. A good example is the method designed to test the water leachability of a nuclear waste form, Method MCC-1P (3). In this procedure, specimens are immersed in leachant solutions at various temperatures, and changes in the composition of the solutions and specimens are measured. The following language is taken from the document describing MCC-1P:

> "The MCC-1 Static Leach Test Method is intended principally to distinguish differences in the leaching behavior of candidate waste forms. Data obtained by the test will also become part of a much larger body of data that may be used in repository licensing. The test method is the basis for an initial ranking of the leach resistance of waste forms. Data obtained by the MCC-1 Static Leach Test Method using the reference leachants, the reference temperatures, and the reference time periods given in the test matrices will qualify for entry in the Nuclear Waste Materials Handbook..... When additional leachants, representative of specific repository waters, are used, the rigor with which the data are obtained must be the same as for the three reference leachants."

The various MCC test methods that involve water interactions treat the water or solution as a material of fundamental importance, one which certainly has the status of a baseline or reference material. Although apparently never officially adopted by the nuclear waste storage community, the MCC procedures themselves are analogous to many of the experiments being conducted in the NNWSI Project. Thus semantically, in the manner in which it has been used experimentally, there is considerable justification for calling J-13 water a "reference" water for NNWSI investigations. This is true irrespective of whether the chemistry of J-13 water is representative of the chemistry of the repository water and its environs.

References.

1. J. K. Taylor, Quality Assurance of Chemical Measurements, Lewis Publishers, Chelsea, Michigan, 1987, p. 159.

2. M. J. Steindler and W. B. Seefeldt, "Functions of the Materials Review Board," in Scientific Basis for Nuclear Waste Management, C. M. Jantzen, J. A. Stone, and R. C. Ewing, Eds., Materials Research Society, Pittsburgh, 1984, pp. 717-722.

3. "MCC-1P Static Leach Test Method," in Nuclear Waste Materials Handbook, Pacific Northwest Laboratory, September 30, 1983.

## Section 11

## Summary, Conclusions, and Recommendations

Rationale for Use of J-13 Water in NNWSI Experiments. In each of the sections of This Report, an issue relating to the use of J-13 water has been addressed. The conclusions drawn can be summarized as follows.

A major portion of the water (possibly 80%) produced from the J-13 well comes from the Topopah Spring member of the Paintbrush Tuff, which is the same formation as that at Yucca Mountain proposed for the repository.

However, the major source of the water in the J-13 well is from subsurface flow and infiltration along Fortymile Wash, rather than from Yucca Mountain.

Water from the J-13 well has several general characteristics that are desirable for a baseline or reference experimental water. The J-13 well is flowed frequently, so fresh water is readily available. In terms of its major constituents, the water has been stable in chemical composition for 25 years, and after sampling, it is stable in storage. It is already an aerated, high-Eh water, so precautions need not be taken to maintain this characteristic. The water is very low in suspended solids. On the other hand, the concentrations of several of its minor constituents need to be better established.

The chemical composition of J-13 water is very similar to the compositions of the other wells that produce from the shallow, aerated, saturated zone in and near Yucca Mountain. Only two constituents, potassium and magnesium, differ significantly, but rock/water interaction studies show that these elements would be of little or no consequence in the near-field during the hot thermal period of the nuclear waste.

No direct information is yet available on the composition of the vadose water in the unsaturated zone at Yucca Mountain; however, there are two reasons why J-13 should still be valid as a baseline water for experiments relating to the unsaturated zone. First, there are strong indications that the composition of the vadose water will vary considerably from location to location, even in the same stratigraphic formation; and secondly, there is a high probability that the composition of J-13 water will fall within the bounds of the vadose water compositions at Yucca Mountain.

Modeling of the interaction of rainwater with the Topopah Spring tuff has shown that the J-13 water is not in equilibrium with the Topopah Spring tuff, but the general type of water to be found at Yucca Mountain should be of the

same sodium bicarbonate type found in J-13 and the local wells. It is thus somewhat irrelevant that J-13 produces from the Topopah Spring member, or that there is a connection between it and Yucca Mountain.

Four types of NNWSI experiments were examined with respect to their use of J-13 water: metal corrosion, waste-form leaching, hydrothermal rock/water interactions, and radionuclide migration. In general, the most important parameters of the water in affecting the results of these experiments are pH, concentration of bicarbonate ion, and except for the rock/water interactions, the concentration of oxygen and Eh. These are the chemical parameters in which there is the greatest confidence that J-13 water will be representative of the unsaturated-zone waters of Yucca Mountain.

In the area of nomenclature, J-13 water cannot be considered a "standard reference material," because its composition has not been established by a controlled, interlaboratory comparison analysis. However, in the manner of its use, and in accordance with the usual meaning of the term, we consider it valid to call J-13 water a "reference water," as is done in much of the NNWSI literature.

Conclusions and Recommendations. As outlined above, there is considerable justification for the use of J-13 water as a baseline, or reference water for the NNWSI experiments. However, this water is not necessarily the only or the best choice of water for the NNWSI experiments or modeling. Depending on the objectives of the experiments, other types of waters may be more valuable. For example, for mechanistic studies, single-compound synthetic waters such as a simple $NaHCO_3$ or silicate water, perhaps spiked with another constituent of interest, could be used. Other Yucca Mountain ground waters should also be used to test the effects of extreme values of the constituents. In studies of the hot, near-field environment, deionized water might be used to simulate wet steam or condensate, and concentrated waters could be used for the evaporated water. J-13 water definitely is not representative of the deep, saturated-zone waters, which are anoxic and of much higher ionic strength than those of the shallow zone.

More complicated synthetic waters could be examined by an appropriate multivariate experimental design. In modeling the various phenomena, we recommend that more emphasis be placed on parameter sensitivity analysis,

where this type of testing should be easier to do than laboratory experiments. Data on the effects of heat and radiation on the chemistry may not be available to permit good modeling, but then the experiments should be performed initially with as few other variables as possible, and maximum use should be made of the techniques of experimental design.

In a word, J-13 water should be regarded as "a" reference water, but not "the" reference water. The mere fact that J-13 water is a natural ground water may contribute to a good demonstration and some preliminary knowledge, but contribute very little to the understanding of specific mechanisms. An understanding of the mechanisms of the various phenomena will be essential to the interpolation and extrapolation of results and long-term predictions.

Quality Assurance Level. Given that J-13 water is a suitable reference water for NNWSI studies, the next question is: at what Quality Assurance Level (I, II, or III) are the activities of sampling, transportation, receiving, storing, and subsequent distribution to be conducted? First, as we read the NNWSI QA documentation, the choice in the case of J-13 water is between QA I and QA III, the latter being defined to us as essentially "good scientific practice." Does it automatically follow that, because J-13 water is a reference water, it should be handled at QA I? We believe not, for the near-field studies, for the key reason that it is still not known with absolute certainty that J-13 water is representative of the water in the unsaturated repository horizon. For the far-field region, away from the heat and radiation, and especially in the shallow saturated zone where J-13 water has been convincingly demonstrated to be a representative water, QA I is appropriate.

The situation for the near-field region is quite different. Here, the QA question applies to the studies involving metal corrosion, waste-form leaching, and rock/water interactions. Because of the past, present, and future importance of J-13 water as a baseline or reference water in NNWSI studies, as established in this review, we could easily recommend that it be handled at Quality Assurance Level I. This would not mean that the studies using J-13 water themselves would necessarily be carried out at Level I, but only that the procedures of procurement, transportation, storage, and distribution of J-13 water be at this level. However, it appears to us at this point in time that the only reason for designating J-13 water as QA I

would be to absolutely ensure the eventual legality of repository licensing. Scientific reasons alone are not compelling.

We believe that the fact that J-13 water has heretofore not been handled at Quality Assurance Level I should have no bearing on the validity of past experiments in the NNWSI Project. Previous handling of J-13 water may not have been accompanied by rigorous traceability protocols, but the identity of the material used, via traceability protocols, is really not in doubt. In general, our examination of the extensive literature indicates that most of the experimental results obtained thus far involving J-13 water are adequately defensible on scientific grounds. A chemical analysis of the water used in the experiments is almost always reported, and we have shown that J-13 water has a distinctly characteristic signature.

Regardless of the assignment of QA level, there are certain procedures that could be implemented which would improve the scientific quality of the work with J-13 water. We note that even QA I practices do not guarantee scientific validity. Specifically, we recommend that the usual chemical analysis practice be augmented by (1) a more complete analysis of each batch of J-13 for its trace-level constituents, and (2) a study to establish the limits of variability of the composition of J-13 water for acceptance prior to experimentation. The newer technique of ICP-MS could be used to advantage in the minor constituent analysis. An organized program of comparing analyses of J-13 water among several laboratories would contribute greatly toward establishing a more precise mean composition, at least for the major constituents. This more complete analytical characterization would place the usage of J-13 water on a firmer scientific foundation, and make the QA level of secondary importance.

In summary, we recommend that if the generally accepted techniques of ground-water sampling, storage, and analysis are rigorously employed, along with the above-mentioned studies, and if experiments are always accompanied by a chemical analysis of the water, then QA Level III procedures can be followed with J-13 water. At the present time, there is no scientific justification for a QA level other than III. When a comprehensive chemical analysis of the waters of the repository horizon is available, and if it is confirmed that J-13 is representative of these waters, then the question of the QA level of J-13 water may again arise. The committee is divided on whether QA I or III would then be appropriate.

Appendix 1

Documentation

Submitted to the

J13 Water Committee

(The following is a list of the documents that were given to all of the members of the committee to examine. Additional documents are cited in the References of each section of This Report.)

1. Maps of Yucca Mountain and Repository Area.

2. Sketch of Geologic Cross Section of Repository Area.

3. J-13 Water Chemistry: p. 6 excerpt from J. M. Delaney, "Reaction of Topopah Spring Tuff with J-13 Water: A Geochemical Modeling Approach Using the EQ3/6 Reaction Path Code, LLNL Report UCRL-53631, November, 1985.

4. Excerpt from "Repository Site Data Report for Tuff: Yucca Mountain, Nevada," U.S. Nucl. Reg. Comm. Report NUREG/CR-2937,1983, pp. 58-65.

5. Audit Committee Observation and LLNL Response, including excerpts from Environmental Assessment Report "Yucca Mountain Site, Nevada Research and Development Area, Nevada," Vol. II, 1986.

6. Correspondence between NNWSI management and Chairman and members of J13 Water Committee.

7. Excerpt from Chapter 17 on Reference Materials in J. K. Taylor, Quality Assurance of Chemical Measurements, Lewis Publ., 1987.

8. Excerpt from MCC-1P, "Static Leach Test Method," Nuclear Waste Materials Handbook, 1983.

9. Excerpt from "MCC Guidelines for Accuracy and Precision of Data," Nuclear Waste Materials Handbook, 1984.

10. Excerpt from "NNWSI Project QA Plan," N-QA-040, 1/87

11. Checklist for Assigning Quality Assurance Levels, NWMP Quality Assurance Element Assignment, and Level of Quality Assurance Level Assignment Approval Sheet; excerpts from 033-NWMP-P 20.0, Dec. 24, 1986.

12. Outline of Nevada Nuclear Waste Storage Investigation (NNWSI) Project at Livermore; Organization and Tasks, Dec. 3, 1987.

13. L. V. Benson, "Mass Transport in Vitric Tuffs of Rainier Mesa, Nye County, Nevada," Report No. NVO-1253-10, 1976.

14. L. V. Benson and P. W. McKinley, "Chemical Composition of Ground Water in the Yucca Mountain Area, Nevada, 1971-1984," USGS Open-File Report 85-484, 1985.

15. W. E. Glassley, "Reference Waste Package Environment Report," LLNL Report UCRL-53726.

16. J. F. Kerrisk, "Groundwater Chemistry at Yucca Mountain, Nevada, and Vicinity," LANL Report LA-10929-MS, 1987.

17. "Peer Review," Lawrence Livermore National Laboratory Nuclear Waste Management Program Document No. 033-NWMP-P 2.2, November 19, 1987.

18. Letter from A. E. Ogard & K. Wolfsberg of LANL to David Coles of LLNL, March 26, 1982.

19. Excerpt from K. Wolfsberg, et al, "Sorption-Desorption Studies on Tuff. I. Initial Studies with Samples from the J-13 Drill Site, Jackass Flats, Nevada, LANL Report LA-7480-MS, April, 1979.

20. K. Wolfsberg and B. R. Erdal, Compilers, "Research and Development Related to the Nevada Nuclear Waste Storage Investigations, October 1- December 31, 1980," LANL Report LA-8739-PR, April, 1981.

21. R. Guzowski, et al, "Repository Site Data Report for Tuff: Yucca Mountain, Nevada," USNRC and Sandia Albuquerque Report NUREG/CR-2937, SAND82-2105, October, 1983.

22. W. R. Daniels, et al, "Summary Report on the Geochemistry of Yucca Mountain and Environs," LANL Report LA-9328-MS, December 1982.

23. W. J. Carr, F. M. Byers, Jr., and P. P. Orkild, "Stratigraphic and Volcano-Tectonic Relations of Crater Flat Tuff and Some Older Volcanic Units, Nye County, Nevada," USGS Prof. Paper 1323, 1986.

24. H. C. Claassen, "Sources and Mechanisms of Recharge for Groundwater in the West-Central Amargosa Desert, Nevada -- A Geochemical Interpretation," USGS Open-File Report 83-542, 1983.

25. R. K. Waddell, J. H. Robison, and R. K. Blankennagel, "Hydrology of Yucca Mountain and Vicinity, Nevada-California -- Investigative Results through Mid-1983," USGS Water Resources Investigations Report 84-4267, 1984.

26. A. E. Ogard and J. F. Kerrisk, "Groundwater Chemistry Along Flow Paths Between a Proposed Repository Site and the Accessible Environment," LANL Report LA-10188-MS, November 1984.

27. W. Thordarson, "Geohydrologic Data and Results from Well J-13, Nevada Test Site, Nye County, Nevada," USGS Water Resources Investigations Report 83-4171, 1983. See especially p. 50, the statements that essentially all of the J-13 well water comes from the Topopah Spring Member.

28. D. H. Lobmeyer, "Geohydrology of Rocks Penetrated by Test Well USW G-4, Yucca Mountain, Nye County, Nevada," USGS Water Resources Investigations Report 86-4015, 1986.

29. W. Thordarson, F. E. Rush, and S. J. Waddell, "Geohydrology of Test Well USW H-3, Yucca Mountain, Nye County, Nevada," USGS Water Resources Investigations Report 84-4272, 1985.

30. M. S. Whitfield, Jr., E. P. Esholm, W. Thordarson, and D. M. Schaeffer, "Geohydrology of Rocks Penetrated by Test Well USW H-4, Yucca Mountain, Nye County, Nevada, USGS Water Resources Investigations Report 85-4030, 1985.

31. Fenix & Scisson, Inc., "Hole History Data, NNWSI, J-13 Water Well."

32. Geophysical Logs, Well J-13, from Ray Draper, LLNL NTS.

33. R. A. Zielinski and J. N. Rosholt, "Uranium in Waters and Aquifer Rocks at the Nevada Test Site, Nye County, Nevada," J. Res. U. S. Geol. Survey, 6, 489 (1978). This is the source of the data quoted incorrectly in Reference 21 above.

34. P. Montazar and W. E. Wilson, "Conceptual Hydrologic Model of Flow in the Unsaturated Zone, Yucca Mountain, Nevada," USGS Water Resources Investigations Report 84-4345, 1984.

35. H. C. Claassen, "Water Quality and Physical Characteristics of Nevada Test Site Water-Supply Wells," USGS Report 474-158, 1973.

36. H. R. MacDougall, L. W. Scully, and J. R. Tillerson, Compilers, "Site Characterization Plan Conceptual Design Report," SNL Report SAND84-2641, September 1987, Vol. 6, Drawing Portfolio.

37. Site Characterization Plan, "Consultation Draft," U. S. DOE Report DOE/RW-0160, Vol. II, Chapter 4, January, 1988, pp. 4-39 to 4-52.

38. Site Characterization Plan, "Consultation Draft," U. S. DOE Report DOE/RW-0160, Vol. IV, Chapter 8, January, 1988, pp. 8.3.1.2-101 to 8.3.1.2-106.

39. Site Characterization Plan, "Consultation Draft, U. S. DOE Report DOE/RW-0160, Vol. IV, Chapter 8, January, 1988, pp. 8.3.1.2-109 to 8.3.1.2-122.

40. S. D. Knight and K. W. Thomas, "Sorption of Radionuclides Using Different Groundwater Compositions," Los Alamos National Laboratory NNWSI Project Milestone No. M316, 1988. (This is an unpublished document that should not be cited without permission in the open literature.)

41. K. W. Thomas, "Summary of Sorption Measurements Performed with Yucca Mountain, Nevada, Tuff Samples and Water from Well J-13," LANL Report LA-10960-MS, December, 1987.

42. J. Farmer, Memorandum, May 23, 1988; Response to Committee Memorandum of May 2, 1988 -- Sensitivity Analysis of Metallic Corrosion.

43. W. L. Bourcier and C. J. Bruton, Memorandum, June 22, 1988; Response to Committee Memorandum of May 2, 1988 -- Modeling of Glass and Spent Fuel Dissolution.

44. W. Glassley, Memorandum, July 8, 1988; Response to Committee Memorandum of May 2, 1988 -- Experiments on Rock/Water Interactions and Vadose Water.

45. A. F. White, H. C. Claassen, and L. V. Benson, "The Effect of Dissolution of Volcanic Glass on the Water Chemistry in a Tuffaceous Aquifer, Rainier Mesa, Nevada, USGS Water Supply Paper 1535-Q, 1980.

46. C. J. Bruton and H. F. Shaw, "Geochemical Simulation of Reactions Between Spent Fuel Waste Form and J-13 Water at 25°C and 90°C," LLNL Report UCRL-96703 Preprint, November 1987.

47. C. J. Bruton, "Geochemical Simulation of Dissolution of West Valley and DWPF Glasses in J-13 Water at 90°C," LLNL Report UCRL-96703 Preprint, November, 1987.

48. R. D. McCright, W. G. Halsey, and R. A. Van Konynenburg, "Progress Report on the Results of Testing Advanced Conceptual Design Metal Barrier Materials Under Relevant Environmental Conditions for a Tuff Repository," LLNL Report UCID-21044, December, 1987.

49. K. B. Krauskopf, "Geology of High-Level Nuclear Waste Disposal," in Annual Review of Earth & Planetary Sciences, Vol. 16, G. W. Wetherill, A. L. Albee, and F. G. Stehli, Eds., Annual Reviews, Inc., Palo Alto, 1988.

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51. H. F. Shaw, "Plan for Spent Fuel Waste Form Testing for NNWSI," LLNL Report UCID-21272, November, 1987.

52. W. E. Glassley, "Plan for Waste Package Environment for NNWSI," LLNL Report UCID-21326, February, 1988.

53. V. M. Oversby, "Plan for Integrated Testing for NNWSI Non-EQ3/6 Data Base Portion," LLNL Report UCID-21274, May, 1987.

geothermal energy, including geophysical modeling, reservoir delineation, seismicity, exploration, environmental studies, and regulatory affairs. He is a registered geophysicist in California, and is a member of the American Geophysical Union, the Society of Exploration Geologists, the Geothermal Resources Council, the National Water Well Association, and the Association of Groundwater Geoscientists.

Ellen Raber is presently Group Leader for Applied Technology in the Special Projects Division. She has a B.S. in geology from Lafayette College and an M.S. in geochemistry from the University of Massachusetts. At LLNL she has been a research geochemist and project leader in geothermal energy development, environmental geochemistry in underground coal gasification, radionuclide migration, water treatment and mineral recovery from brines, and has had program management responsibility for the Earth Sciences Department. She is especially interested in the use of hydrogeological, geophysical, and geochemical measurements in field site assessment. She is a member of Sigma Xi, the American Association for the Advancement of Science, the National Water Well Association, and the American Association of Petroleum Geologists.

Appendix 2
Biographical Sketches
of
Committee Members

Jackson E. Harrar is Section Leader for Inorganic Analysis in the Chemistry and Materials Science Department. He has a B.S. in chemistry from Purdue University and a Ph.D. in analytical chemistry from the University of Washington. His research interests are in electroanalytical chemistry, solution chemistry, electrosynthesis, field and laboratory water analysis, chemical instrumentation, geothermal chemistry, and nuclear materials analysis. He was a member of the Materials Review Board of the U. S. Department of Energy from 1980 to 1987, and was the lead chemist of the LLNL geothermal energy program from 1977 to 1981. He is a member of the American Chemical Society, The Electrochemical Society, and Sigma Xi.

James F. Carley is a staff scientist in the Polymers Section of the Chemistry and Materials Science Departemnt. He earned his undergraduate and Ph.D. degrees in chemical engineering at Cornell. Before coming to LLNL, he was a faculty member at the Universities of Colorado and Arizona. He has also held industrial positions at DuPont, Prodex Corporation, where he was technical director, and Celanese Plastics. His interests are in polymer processing, oil-shale research, engineering design with plastics, statistics, quality assurance, and experimental design. He is a registered professional engineer by exam in California and Colorado, and is member of Tau Beta Pi, Sigma Xi, American Institute of Chemical Engineers, and the Society of Plasics Engineers (Fellow).

William F. Isherwood is a member of the Earth Sciences Department and is presently Project Leader for the Livermore Site Ground Water Project. He has an A.B. in mathematics from Princeton, an M.S. in geophysics from the University of Utah, a Ph.D. in geological sciences from the University of Colorado, and an M.B.A. from Golden Gate University. Before joining LLNL he was the senior geophysicist at GeothermEx, Inc., was chief of geothermal evaluation and deputy conservation manager at the U. S. Geological Survey, and was a principal investigator at the Stanford Research Institute. He has directed a variety of activities in the field of geophysics, especially