SANDIA REPORT

SAND83—0144 • Unlimited Release • UC—70
Printed February 1984

Uranium-Isotope Disequilibrium in Brine Reservoirs of the Castile Formation, Northern Delaware Basin, Southeastern New Mexico
I: Principles and Methods

Steven J. Lambert, Joel A. Carter

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550
for the United States Department of Energy
under Contract DE-AC04-76DP00789

SF2900Q(8-81)

SAND83-0144
Unlimited Release
Printed February 1984

Distribution
Category UC-70

Uranium-Isotope Disequilibrium in Brine Reservoirs of the Castile Formation, Northern Delaware Basin, Southeastern New Mexico I: Principles and Methods

Steven J. Lambert
Earth Sciences Division 6331
Sandia National Laboratories
Albuquerque, NM 87185

Joel A. Carter
Oak Ridge National Laboratories
Oak Ridge, TN 37830

Abstract

We evaluated uranium isotope activity ratios with respect to models for the origin of the brines in two brine reservoirs in the Castile Formation (ERDA No. 6 and WIPP No. 12). In Castile anhydrite, a completely closed water system that was continuously leaching Th-recoil-produced ^{234}U from freshly exposed surfaces of fractured host rock would give rise to uranium 234/238 isotope activity ratio (α) values significantly higher than observed values. Therefore, the brine occurrences are not the result of continuous deformation. Similarly, a model assuming movement of intergranular Permian seawater into fractures was found inconsistent with observed uranium isotope systematics. The observed α-values (95% confidence limits) of ERDA No. 6 (1.34 to 1.58) and WIPP No. 12 (1.74 to 2.54), used in conjunction with an inferred initial α_0 higher than observed values, allows calculation of reasonable finite minimum ages, involving no preferential leaching of ^{234}U in the host rock. If the brine occurrences are inferred to have been connected at one time with a more extensive nearby hydrologic system, the Capitan limestone (α_0 = 5.1), calculated minimum ages of isolation from that system are 700 000 to 880 000 yr for ERDA No. 6 and 360 000 to 610 000 yr for WIPP No. 12. These ranges in ages are the 95% confidence limits based on experimental determinations of α-values. The ages thus derived may reflect an episode of structural deformation in the Pleistocene that allowed water to enter the resulting fractures.

Contents

Figures

Uranium-Isotope Disequilibrium in Brine Reservoirs of the Castile Formation, Northern Delaware Basin, Southeastern New Mexico
I: Principles and Methods

Introduction

Previous Work

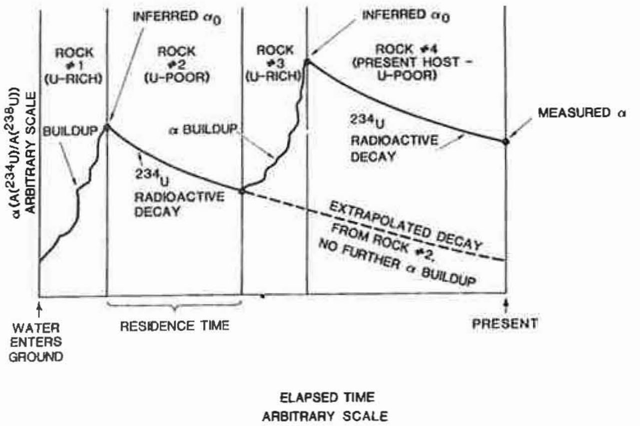
The natural deviation of the $^{234}U/^{238}U$ specific activity ratio from its secular equilibrium value of unity provides a basis for tracing the flow of subsurface groundwater (Kronfeld et al, 1979). In addition, since the ratio (hereafter "α") in groundwater approaches unity by radioactive decay at a predictable rate (^{234}U decays much faster than ^{238}U), the decay of α along inferred flow paths was used by Barr et al (1979) to establish limits to the isolation time of a particular groundwater reservoir in the Castile Formation in the Delaware Basin of southeastern New Mexico. Detailed systematics of the uranium-decay series in nature were reviewed by Osmond and Cowart (1976).

Application of uranium isotope disequilibrium to determining the "age" of groundwaters has been concerned largely with buildup of α in a closed system. For example, knowledge of the amount of leachable uranium in a rock, together with inferences about porosity and leaching behavior in a system of rock plus water, can lead to calculations of the time the system has been closed (Andrews and Kay, 1982). In some groundwater systems, evidence of the ultimate source of the water molecules may no longer be preserved in the geologic record; thus the ultimate origin may be indeterminate. In other systems, the issue of interest is not the age when water was isolated from the atmosphere (for which the cosmic ray methods such as carbon-14 and chlorine-36 may apply), but the age of mutual isolation of various bodies of groundwater. If the occurrence of groundwater is by inference genetically related to a specific geologic event such as the creation of fracture porosity, the age of interest is either that of cutoff of the groundwater body from its source, or the time at which fresh rock surfaces ceased to be locally generated to allow preferential leaching of ^{234}U. These and other points were discussed by Barr et al (1979).

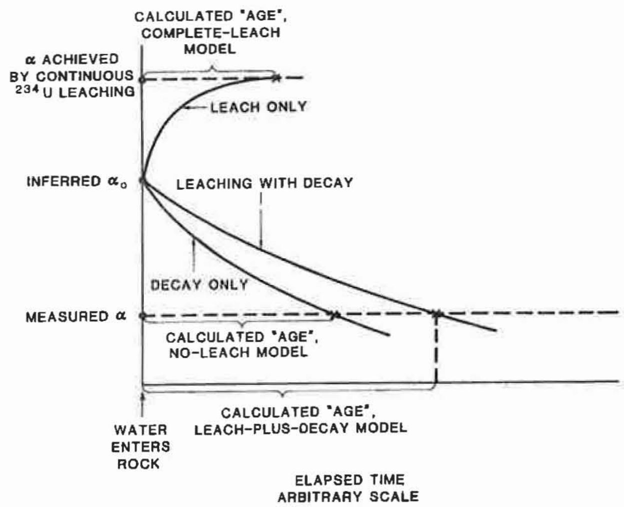
The work of Barr et al (1979) was concerned with an occurrence of groundwater of unusual solute and isotopic composition that was encountered in anhydrites of the Castile Formation (Ochoan, Permian) during exploratory drilling for the Waste Isolation Pilot Plant (WIPP). The WIPP is a subsurface facility for disposal of transuranic radioactive waste from the defense sector. In November 1981, a similar brine occurrence was encountered during deepening of WIPP No. 12, ~4 mi south-southwest of ERDA No. 6. This report evaluates various evolutionary paths for the uranium isotope systematics of the Castile brine reservoirs at boreholes ERDA No. 6 and WIPP No. 12. The report is based on the additional sampling of ERDA No. 6 since the work of Barr et al (1979) and on sampling from WIPP No. 12.

Basis for Age Calculations

The uranium-isotope disequilibrium method (the U method) of determining the residence time of old groundwaters depends on the systematic preferential buildup of ^{234}U with respect to ^{238}U in one part of the groundwater system, and on the radioactive decay of ^{234}U (faster than that of ^{238}U) in another part of the system. Several examples of deviation of the $^{234}U/^{238}U$ specific activity ratio (α) from unity provide a basis for tracing groundwater flow paths (Kronfeld et al,



1A. Buildup of the $^{234}U/^{238}U$ specific activity ratio (α) occurs in reducing zones of rocks relatively rich in uranium (No. 1, No. 3), the ratio radioactively decaying in uranium-poor rocks (No. 2, No. 4). Extrapolated decay of the ratio from rock No. 2 would result in an observed α lower than if no buildup occurred in rock No. 3.



1B. While continuous preferential leaching of ^{234}U causes the α to rise rapidly toward an asymptotic limit (upper curve), if decay is the dominant process, then a younger age is calculated by using no leaching (lower curve) than would result from using a finite, yet-unknown, leach rate along with decay rate (middle curve).

Figure 1. Hypothetical Schematic Evolutionary Paths of Uranium Isotopes in Groundwater.

Rock No. 2 is assumed to contain virtually no uranium. During the residence time of water in rock No. 2, the ^{234}U decays much faster than the ^{238}U, decreasing the α in the water. Since rock No. 2 contains no uranium, there is no compensating tendency for α to increase. The water may then enter another U-rich body of rock (rock No. 3 in Figure 1A), again allowing α to increase, followed by α-decay in a U-poor rock (rock No. 4 in Figure 1A) and so on. The situation in rock No. 4 illustrates the no-leaching model of Barr et al (1979), with an inferred α_0, as the water enters rock No. 4 and decays with no further increase in α caused by leaching. In any rock, including the observable host rock, the leaching model may partly apply if the competing processes of preferential leaching of ^{234}U to increase α and of radioactive decay to decrease α are occurring simultaneously.

Figure 1A also shows the variations in calculated age that can arise from the choice of various α_0 values, and illustrates several concepts of "age." If groundwater could be collected at the contact between rock No. 1 and rock No. 2 and if its measured α is inferred as α_0, a similar measurement of α in water at the interface between rock No. 2 and rock No. 3 could be used with the inferred α_0 to calculate residence time of groundwater in rock No. 2, assuming water is moving from rock No. 1 toward rock No. 3. If the no-leaching model is used, the resultant residence time in rock No. 2 will be an underestimate, or minimum age. This is because preferential leaching of any available ^{234}U from the rock counteracts radioactive decay and tends to raise the α-value above the value obtainable by decay alone. For example, if the inferred α_0 from the contact between rock No. 1 and rock No. 2 is allowed to decrease by radioactive decay (the water somehow bypassing the buildup episode in U-rich rock No. 3), the extrapolation of the trend to the present time (represented by the dashed line) would result in an observed α significantly lower (and a significantly different calculated age) than the solid line resulting from both α increase in rock No. 3 and α decrease in rock No. 4. Additional ^{234}U leaching "resets the clock," raising the α above the trajectory of α versus time that would result from decay alone. The rate of α-buildup in many geological systems may be difficult to assess.

As a special and more detailed case of Figure 1A, consider Figure 1B, which shows the possible changes in α experienced by a groundwater within a single host-rock type. With an inferred value of α_0, it has been shown above that complete and continuous leaching of ^{234}U from host rock results in a fairly rapidly increasing α-value in groundwater; α asymptotically approaches an upper limit governed largely by the concentration of the leachable uranium in the host rock (the upper curve in Figure 1B). With no additional leaching of ^{234}U from the host rock once the water has established residence, the lower curve is the

Discussion

Analytical Results

Uranium data are presented in Table 1. The α for ERDA No. 6 is between 1.34 and 1.58 at the 95% confidence level (3 replicates); for WIPP No. 12, it is between 1.74 and 2.54 (8 replicates). These confidence limits will be used in calculations of age. The "total flow" column in Table 1 represents a relative degree of contaminant purging and of steady-state abatement of chemical reaction between effluent and apparatus in the hole.

Transients in Flow Testing

The total U content of the WIPP No. 12 effluent varied with time during flow testing. In the first brief flow test in December 1981, the total U was 15×10^{-12} g/g. In May 1982 (Figure 2), after 35 h of flow the total U was 12×10^{-12} g/g; 40 h later the total U had stabilized to between 8×10^{-12} and 10×10^{-12} g/g.

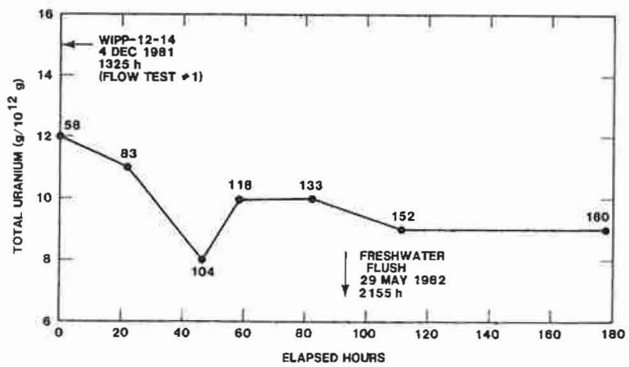


Figure 2. Variations of Total U in WIPP No. 12 Effluent as a Function of Time Elapsed Since Collection of Sample WIPP-12-58. (Numbers along the line are individual sample numbers.)

Variations in the α-value (Figure 3) are more important than variations in total U concentration, since α-values are the basis for age calculations. Water from the first flow test (a single sample) had an α of 2.8. In the first 80 h after initial purging during the second flow test, the α had stabilized to between 1.9 and 2.1. On May 29, 1982, the wellhead apparatus was flushed with fresh water to remove encrustations of salt. Whereas this contamination had little effect on total U (Figure 2), the effect was apparently profound in α (Figure 3). Perhaps the flush water had a similar U content to that of effluent, but its α may have been significantly different. In any case, there is no a priori reason to eliminate WIPP-12-152 from further consideration since no profound transient fluctation was observed in the solutes (Popielak et al, 1983). The effect of retention of this data point is to widen the confidence limits of the age calculation for WIPP No. 12.

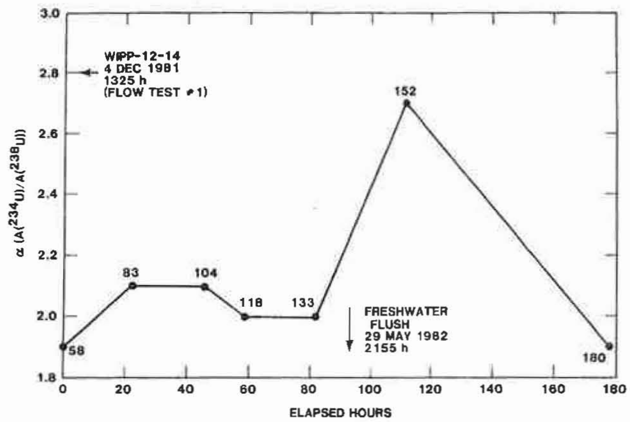


Figure 3. Variations of $^{234}U/^{238}U$ Specific Activity Ratio (α) in WIPP No. 12 Effluent as a Function of Elasped Time. (Note the apparent effect of isotopic contamination by the fresh-water flush.)

Models for Ages

Observe that in Figure 1 it is possible to calculate a negative age according to the no-leaching model, if the inferred α_0 and the observed α are taken to represent the initial and final states of the system, respectively. The apparent negative age arises if the α_0 is less than the observed α, since the no-leaching model calculation ignores any increase in α once the α_0 is established. An age could apparently be calculated based on α-buildup in a closed, stagnant system of groundwater in contact with host rock. Andrews and Kay (1982) calculated α as a function of time for water containing 40 parts in 10^{12} total U in a closed system with 2 parts in 10^6 by weight total U in a coexisting oolitic limestone. These calculations show that, beginning with an α_0 of 1, a closed system of age 5000 yr is required for the α to build up to 1.5 and ~20 000 yr for the α to build up to 2.3. Andrews and Kay (1982) concluded that simple leaching of ^{234}U from the Inferior Oolite probably did not occur because the groundwater found there was a mixture of inflowing groundwater and porewater that had not derived ^{234}U from the ooliths.

Using the same method and the value for U content of anhydrite in the ERDA No. 6 reservoir (2 parts the Capitan limestone at one of its known active recharge points, the Pecos River near Carlsbad. Moving eastward in the Capitan, the water gathered uranium and leaching recoil-generated ^{234}U from the rock. The most abundant known occurrences of uranium in the Capitan are associated with sandstone dikes described by Hayes (1964). A uraninite-bearing silt derived from such a dike covers much of the floor of the New Mexico Room of Carlsbad Caverns and has a total U content of 6.6×10^{-6} g/g and an α of 1.17. Water in a pool developed in the floor has a total U content of 1.1×10^{-9} g/g and an α of 2.9. Water in cavern pools is continuously lost by seepage, and this α-value developed in the water during the geologically short lifetime of the pool. Thus, α-buildup in waters of the Capitan is both documented and rapid. During a tectonic disturbance or gravity-induced deformation that caused fracturing of Castile anhydrite (Borns et al, 1983), water migrated out of the Capitan basinward into the adjacent Castile. The α-value then began to decrease by decay, like the process shown in Figure 1.

In analogy with Figure 1, the contact between rock No. 2 and rock No. 3 is taken to be recharge into the Capitan from meteoric water (total U $= 0.01 \times 10^{-9}$ g/g, $\alpha = 1.74$ for Carlsbad rainwater). As water moved through the Capitan (rock No. 3) in the vicinity of Carlsbad, it sporadically encountered uranium-rich rock and achieved an α of 5.14, the highest observed α-value in the Capitan (Barr et al, 1979). There was subsequent α decrease by radioactive decay in relatively inactive parts of the Capitan, such as at the Hackberry ($\alpha = 1.81$) and Middleton ($\alpha = 1.22$) wells. Observe that the variation in α-values at several localities in the Capitan are not consistent with continuous connected flow. Given a reasonably fast transit time for water in active parts of the Capitan (Hiss, 1976) and, if it is inferred that for a period of time the fractured Castile was connected with the Capitan hydrologic system, this model allows reasonable calculations of the age of the end of the fracturing episode and hence the age of fluid entrapment within the Castile anhydrites. Figure 6 is a family of curves generated by the no-leaching model, taking into account the confidence limits of the analytical data.

For any inferred $\alpha_0 > \alpha$, it is possible to calculate a minimum age of isolation from the Capitan for ERDA No. 6 and WIPP No. 12 brines in their fractures. For WIPP No. 12, the resultant age range (assuming $\alpha_0 = 5.14$) is 360 000 to 610 000 yr, and for ERDA No. 6 is 700 000 to 880 000 yr. The latter is in close agreement with the previous work of Barr et al (1979) for the system in ERDA No. 6.

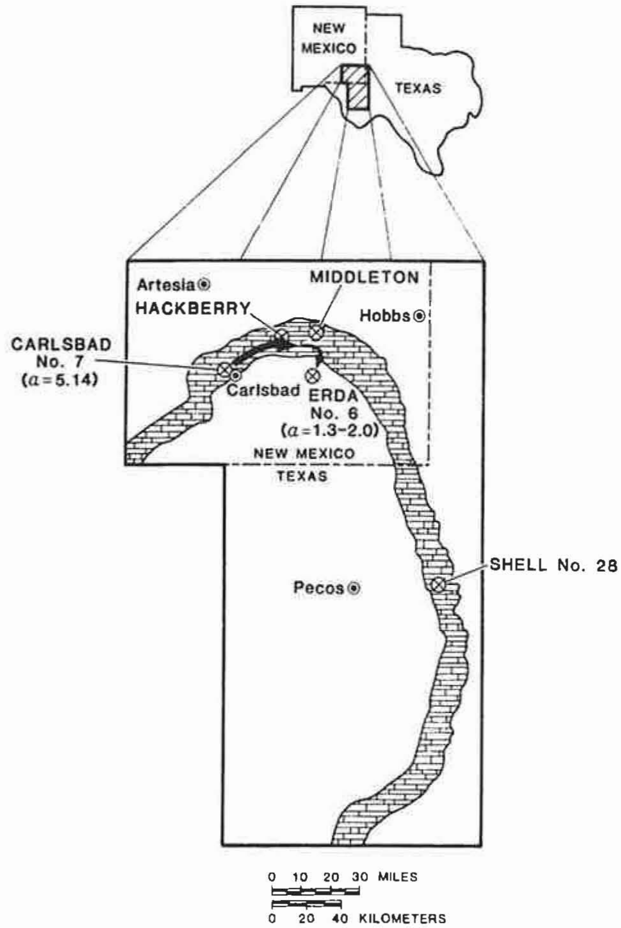


Figure 5. Illustration of Hypothetical Origin of Brine Reservoir by Entrapment of Old Groundwater. (Brine reservoir is inferred to be originally connected with the Capitan hydrologic system (brick pattern), subsequently isolated.)

Bibliography

Andrews, J. N., and R. L. F. Kay (1982), "$^{234}U/^{238}U$ Activity Ratios of Dissolved Uranium in Groundwaters From a Jurassic Limestone Aquifer in England," *Earth and Planetary Science Letters, 57:139-151.*

Barr, G. E., S. J. Lambert, and J. A. Carter (1979), "Uranium Isotope Disequilibrium in Groundwaters of Southeastern New Mexico and Implications Regarding Age-Dating of Waters," *Proceedings of the International Symposium on Isotope Hydrology,* 1978, V 2: International Atomic Energy Agency, STI/PUB/493, pp 645-660.

Borns, D. J., L. J. Barrows, D. W. Powers, and R. P. Snyder (1983), *Deformation of Evaporites Near the Waste Isolation Pilot Plant (WIPP) Site,* SAND82-1069 (Albuquerque, NM: Sandia National Laboratories, 1983).

Carter, J. A., R. L. Walker, D. H. Smith, and W. A. Christie (1980), "Isotope Dilution Resin Bead Mass Spectrometry - An Ultratrace Technique for Measuring Nuclides in Three-Mile Island Water," *International J of Environmental Analytical Chemistry,* V 8, pp 241-248.

Fleischer, R. L. (1982), "Alpha-Recoil Damage and Solution Effects in Minerals: Uranium Isotopic Disequilibrium and Radon Release," *Geochimica et Cosmochimica Acta,* V 46, pp 2191-2202.

Hayes, P. T. (1964), "Geology of the Guadalupe Mountains, New Mexico: United States Geological Survey," *Professional Paper 446,* 69 pp.

Hiss, W. L. (1975), "Stratigraphy and Ground-Water Hydrology of the Capitan Aquifer, Southeastern New Mexico and Western Texas." Unpublished Ph.D. Thesis, University of Colorado, Boulder, 501 pp.

Kigoshi, Kunihiko (1971), "Alpha-Recoil Thorium-234: Dissolution Into Water and the Uranium-234/ Uranium-238 Disequilibrium in Nature," *Science,* V 173, pp 47-48.

Kronfeld, J., E. Gradsztajn, and A. Yaniv (1979), "A Flow Pattern Deduced From Uranium Disequilibrium Studies for the Cenomanian Carbonate Aquifer of the Beersheva Region, Israel." *Journal of Hydrology,* V 44, pp 305-310.

Lambert, S. J. (1978), "Geochemistry of Delaware Basin Ground Waters," in *Geology and Mineral Deposits of Ochoan Rocks in Delaware Basin and Adjacent Areas: New Mexico Bureau of Mines and Mineral Resources,* Circular 159, pp 33-38.

Lambert, S. J. (1983), *Dissolution of Evaporites in and Around the Delaware Basin, Southeastern New Mexico and West Texas,* SAND82-0461 (Albuquerque, NM: Sandia National Laboratories, 1983).

Osmond, J. K., and J. B. Cowart (1976), "The Theory and Uses of Natural Uranium Isotopic Variations in Hydrology," *Atomic Energy Review,* V 14, pp 621-679.

Popielak, R. S., R. L. Beauheim, S. R. Black, W. E. Coons, C. T. Ellingson, and R. L. Olsen (1983), "Brine Reservoirs in the Castile Formation, Southeastern New Mexico," United States Department of Energy Report TME 3153, 191 p.

Thompson, G. M., D. N. Lumsden, R. L. Walker, and J. A. Carter (1975), "Uranium Series Dating of Stalagmites From Blanchard Springs Caverns, U.S.A.," *Geochimica et Cosmochimica Acta,* V 39, pp 1211-1218.

Urey, H. C. (1947), "The Thermodynamic Properties of Isotopic Substances," *Journal of the Chemical Society,* pp 562-581.

Walker, R. L., R. E. Eby, C. A. Pritchard, and J. A. Carter (1974), "Simultaneous Plutonium and Uranium Isotopic Analysis From a Single Resin Bead - A Simplified Chemical Technique for Assaying Spent Reactor Fuels," *Analytical Letters,* V 7, pp 365-574.

DISTRIBUTION (Cont):

J. T. Holloway
Senior Staff Officer
2101 Constitution Avenue, NW
Washington, DC 20418

Atomic Museum, Kirtland East AFB
WIPP Public Reading Room
Attn: G. Schreiner
Albuquerque, NM 87185

Carlsbad Municipal Library
WIPP Public Reading Room
Attn: L. Hubbard, Head Librarian
101 S. Halagueno St
Carlsbad, NM 88220

Thomas Brannigan Library
Attn: D. Dresp, Head Librarian
106 W. Hadley St
Las Cruces, NM 88001

Roswell Public Library
Attn: N. Langston
301 N. Pennsylvania Avenue
Roswell, NM 88201

Hobbs Public Library
Attn: M. Lewis, Librarian
509 N. Ship St
Hobbs, NM 88248

State of New Mexico (2)
Environmental Evaluation Group
Attn: R. H. Neill, Director
320 Marcy Street
PO Box 968
Santa Fe, NM 87503

NM Department of Energy & Minerals (2)
Attn: P. Biderman, Secretary
K. LaPlante, Librarian
PO Box 2770
Santa Fe, NM 87501

Mining & Minerals Division
Attn: E. Kelley, Director
525 Camino de los Marquez
Santa Fe, NM 87501

New Mexico State Library
Attn: I. Vollenhofer
PO Box 1629
Santa Fe, NM 87503

New Mexico Tech
Martin Speer Memorial Library
Campus Street
Socorro, NM 87801

University of New Mexico
Reference Department
Zimmerman Library
Attn: Z. Vivian
Albuquerque, NM 87131

USGS, Water Resources Division (2)
Attn: J. W. Mercer
505 Marquette, NW
Western Bank Bldg, #720
Albuquerque, NM 87102

USGS, Special Projects Branch (2)
Federal Center, Bldg 25
Attn: R. P. Snyder
Denver, CO 80225

New Mexico Bureau of Mines (2)
and Mineral Resources
Attn: F. E. Kottlowski, Director
Socorro, NM 87801

Klaus Kuhn
Gesellschaft fuer Strahlen-und
Umweltforschung MBH Muenchen
Institut fuer Tieflagerung
Berliner Strasse 2
3392 Clausthal-Zellerfeld
FEDERAL REPUBLIC OF GERMANY

Klaus Eckart Maass
Hahn-Meitner-Institut fuer Kernforschung
Glienicker Strasse 100
1000 Berlin 39
FEDERAL REPUBLIC OF GERMANY