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MEMORANDUM

DATE: August 1, 1985  
FOR: Linda Kovach  
WMGT NRC DC  
FROM: Paul T. Prestholt, Sr. OR-NNWSI  
SUBJECT: Attached Documents:

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For your information enclosed are:

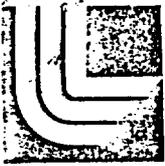
1. Letter, LLNL to Don Alexander dated 7-3-85
2. Paper entitled "Migration of Ruthenium-106 in a Nevada Test Site Aquifer: Discrepancy Betewwn Field and Labroatory Results.

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# Lawrence Livermore National Laboratory

NWM:LR 85-223

July 3, 1985

Don Alexander (RW-24)  
Geosciences and Technology Division  
Office of Geologic Repositories  
U.S. Department of Energy  
Forrestal Bldg.  
Washington, DC 20545

Dear Don:

I am enclosing a copy of a report, "Application of the Ruthenium and Technetium Thermodynamic Data Bases Used in the EQ3/6 Geochemical Codes", UCRL-53594, April 1985, by Dana Isherwood. We have discussed this report earlier and it has now been published. This report was supported by the Weapons Program, but is applicable to nuclear waste disposal. It follows and builds on three related reports, also enclosed:

- "Migration of Ruthenium-106 in a Nevada Test Site Aquifer: Discrepancy Between Field and Laboratory Results", Science, 5 March 1982, Vol. 215, pp. 1235-1237, by Coles and Ramspott.
- "Chemistry and Thermodynamics of Ruthenium and Some of its Inorganic Compounds and Aqueous Species", Chemical Reviews, Vol. 85, No. 1, February, 1985, by Joe Rard.
- "Critical Review of the Chemistry and Thermodynamics of Technetium and Some of its Inorganic Compounds and Aqueous Species", Lawrence Livermore National Laboratory Report UCRL-53440, September 15, 1983, by Joe Rard.

After observing the unexpected migration of ruthenium (the Science report), we documented the ruthenium and technetium data bases (the Rard reports) and applied EQ3NR to explain the migration (the Isherwood report). The purpose of this letter is to tell you some highlights of the Isherwood report and to propose a DOE/NRC Technical meeting on EQ3/6.

The Isherwood report is significant to the OCRWM Program for several reasons. As you know, the Coles and Ramspott Science article in 1982 brought into serious question Kd information for multivalent elements that was gained from sorption studies on ground-up rock samples. (As an aside, it is interesting to me that four years after our results were widely available to the technical community, "peanut butter jar" Kd experiments are still fairly common.) The present report calculates the solubility (and aqueous species) for Ru and Tc for the water at the Cambric site. It shows that the calculated solubility limit for ruthenium (as the aqueous species  $\text{RuO}_4^-$ ) when constrained by  $\text{RuO}_2$  is approximately equal to the concentration of ruthenium found in the ground water in the Cambric cavity ( $2.1 \times 10^{-11}$  vs  $4.5 \times 10^{-11} \text{M}$ ). Thus, we now have a theoretical and calculational basis for why the Ru existed in solution in the cavity and migrated to the observation well.

The Isherwood report also presents information leading to some understanding of why the laboratory results would have predicted "sorption". For example, changes in concentration of ruthenium in solution markedly affect the Eh-pH stability fields of the dominant aqueous ions. In Fig. 2 of UCRL 53594 at  $[\Sigma\text{Ru}] = 10^{-6} \text{M}$ ,  $\text{Ru}_4(\text{OH})_{12}^{4+}$  is broadly distributed throughout the oxidizing part of the Eh-pH diagram at pH from 3 to 13. However, at  $[\Sigma\text{Ru}] = 10^{-11} \text{M}$ , the field has shrunk significantly, and at  $[\Sigma\text{Ru}] = 10^{-15} \text{M}$ , it has disappeared. Alternatively, one can see in Fig. 2, 3 and 5 that only slight changes in Eh or pH near  $10^{-11} \text{M}$  (the observed concentration in the Cambric cavity) are required to move from  $\text{RuO}_4^-$  to a stability field for a species that would not be mobile.  $\text{RuO}_2$  is a solid phase. The positively charged species such as  $\text{Ru}_4(\text{OH})_{12}^{4+}$ ,  $\text{Ru}(\text{OH})_2^{2+}$ , or  $\text{Ru}(\text{OH})_2^+$  should readily sorb onto the solids in laboratory experiments. Having once sorbed, thereby reducing the concentration in solution and shifting the stability fields, then dissolution may be thermodynamically unfavorable. Clearly, experimental conditions that are only slightly different from the in situ values could have a significant effect on Ru concentrations measured in the laboratory and used to calculate Kd.

In addition to explaining why we observed the Ru migration previously documented, one can predict from the information in this report that Tc should have been in the cavity and migrated. Therefore, we are developing

sensitive techniques to check archival samples, realizing that concentrations may still be below our detection limits. Should we find Tc, we will have predicted its presence theoretically before measuring it.

Another significant aspect of this report is that it resolves the differences between reported laboratory measurements and previous calculations for the solubility of Tc in equilibrium with basalt in a reducing environment. The present calculations using the metastable oxide,  $TcO_2 \cdot 2H_2O$ , as the solubility constraint give a value of  $3 \times 10^{-8} M$  vs results in the  $10^{-12}$  to  $10^{-16} M$  range from previous calculations that apparently used  $TcO_2 (c)$  as the solubility constraint. By including  $TcO (OH)_2^0$  in the data base, we obtained calculated values much closer to the experimental results.

The recent lists of DOE/NRC workshops have a number of generic workshops. I propose a generic workshop for EQ3/6 for several reasons. First, it truly is a generic subject. Although most of the present funding comes through the NNWSI, ONWI has supported EQ3/6 for years, and BWIP has contacted us about "joining the team" with a low level of funding in FY86. Second, it crosses WBS. NNWSI funds it in Site, ONWI in Waste Package, and the applications are carried out in Systems, Site, and Waste Package. Finally, it seems to escape an audience. It drops off the end of the agenda for geochemistry workshops and also for Waste Package. Yet we anticipate a significant licensing role and would benefit from early input.

Although we are all busy and need no additional work, from a management viewpoint a workshop on EQ3/6 would be beneficial. You appear to be the right person to contact with this suggestion.



Lawrence Ramspott, Project Leader  
Waste Management Projects

cc w/enclosures:

J. Rotert, DOE/NV  
T. Steinborn, ONWI

see JK

## **Migration of Ruthenium-106 in a Nevada Test Site Aquifer: Discrepancy Between Field and Laboratory Results**

David G. Coles and Lawrence D. Ramspott

## Migration of Ruthenium-106 in a Nevada Test Site Aquifer: Discrepancy Between Field and Laboratory Results

**Abstract.** *Ruthenium-106 has been observed to migrate in ground water at about the same velocity as tritium from the site of an underground nuclear explosion to a pumped satellite well 91 meters distant. This finding contradicts the prediction, based on laboratory batch sorption measurements, that ruthenium-106 should migrate at a much lower rate than tritium. To predict migration of radionuclides in ground water, more relevant laboratory measurements are required.*

To assess the potential for migration of radionuclides deposited in aquifers at the Nevada Test Site by underground nuclear explosions, a program was begun in 1973 by the Department of Energy's Nevada Operations Office to study the interaction of nuclear explosion debris and ground water (1). Results from this program also elucidate what might happen in a flooded nuclear waste repository. We measured the migration rate of ruthenium-106 in the field and found a significant discrepancy between our results and the rate calculated from laboratory batch sorption measurements.

The radionuclides we measured were produced in the Cambic nuclear test in May 1965. The device was detonated at a depth of 294 m in tuffaceous alluvium. To determine the concentration of radioactivity in ground water in direct contact with nuclear explosion debris, water was sampled from a well that intersected the explosion cavity (Fig. 1). Tritium and strontium-90 were the only radionuclides whose concentrations were above the maximum permitted for unrestricted public use of drinking water, even though

the water had been in direct contact with nuclear debris for 10 years (2).

During April 1974 a satellite well was drilled 91 m south of the explosion point to study migration rates of the radionuclides in the cavity water. Pumping from the satellite well induced a gradient between the explosion point and the well. No radioactivity was observed in the satellite well until  $1.44 \times 10^6$  m<sup>3</sup> of water had been pumped over a period of more than 2 years (3). With further pumping, the <sup>3</sup>H concentration continued to increase in the satellite well and decreased 50-fold in the cavity well (3).

After establishing that cavity water had been drawn to the satellite well, we attempted to measure radionuclides other than <sup>3</sup>H. From calculations based on the known relative concentrations of radionuclides and the dilution factor measured for <sup>3</sup>H, we concluded that the activities of other explosion-produced radionuclides would be below the limits of analytical detection in standard water samples, even without sorption.

To solve this problem, we collected 200-liter water samples and evaporated

them in the laboratory. The radioactivity of the resultant salts, whose mass was about 150 g per sample, was measured with an ultralow-background Ge(Li) Compton suppressed gamma-ray spectrometer (4). To attain even greater sensitivity, a field distillation apparatus was designed and built to evaporate up to 1000 liters of water at the wellhead. To date, three samples from 700 to 860 liters have been evaporated in the field and the resultant salts measured for radioactivity.

Nearly the same levels of the natural radioactive species <sup>40</sup>K, <sup>235</sup>U, and <sup>238</sup>U were observed in all samples (Table 1). Ruthenium-106 was also observed in all samples. The <sup>106</sup>Ru activity tended to increase with time, although the errors due to counting statistics were generally large. The <sup>106</sup>Ru/<sup>3</sup>H ratios were nearly the same for all water samples from both wells. This suggests that <sup>3</sup>H and <sup>106</sup>Ru traveled at the same rate from the explosion site to the satellite well.

Contamination was ruled out at our laboratory by an analysis of two unidentified specimens prepared from 200-liter samples that had been collected by Los Alamos National Laboratory. One sample had a <sup>106</sup>Ru content comparable to that of one of our samples. The other showed no <sup>106</sup>Ru but had similar levels of <sup>40</sup>K, <sup>235</sup>U, and <sup>238</sup>U. This sample turned out to be a blank from a Nevada Test Site well which is located 2.25 km from the satellite well and pumps water from the same aquifer at a depth of 230 m. We regard field contamination as unlikely because the <sup>106</sup>Ru content approximated the predicted value (5), no other explosion-related radionuclides were observed, and the <sup>106</sup>Ru/<sup>3</sup>H ratios of the samples were similar to the values for the cavity well.

The calculated <sup>106</sup>Ru/<sup>3</sup>H ratio for the amounts produced by the nuclear explosion is about 100 times higher than that observed in water samples from the cavi-

Table 1. Radioactivity in salts from evaporated large-volume water samples from the satellite well at the Cambic site. Data were recomputed to 15 years after the 1965 explosion so that they are closer to current radioactivity levels. For each value (picocuries per liter), the stated error (in parentheses, expressed as a percent) is based only on the counting statistics. We have been collecting 200-liter samples from the satellite well since April 1977. Some have not been evaporated, and a few (not reported) were contaminated.

Radio-nuclide	Date of sample and volume (liters)						
	Blank* (200)	11/29/78* (200)	2/7/79 (200)	3/14/79 (200)	8/29/79 (710)	4/17/80† (740)	7/23/80 (860)
<sup>40</sup> K	8.6 (2)	10 (2)	7.2 (3)	7.7 (2)	10 (2)	12 (1)	8.6 (1)
<sup>106</sup> Ru	≤ 0.02	0.04 (45)	0.04 (40)	0.04 (30)	0.07 (7)	0.08 (45)	0.08 (21)
<sup>235</sup> U	0.07 (6)	0.09 (6)	0.05 (7)	0.08 (5)	0.04 (4)	0.12 (7)	0.09 (2)
<sup>238</sup> U	1.9 (5)	2.5 (5)	1.0 (35)	1.6 (26)	0.90 (6)	3.0 (16)	2.2 (4)

\*Supplied by Los Alamos National Laboratory. The blank was taken from Nevada Test Site well 5B, located 2.25 km south of the Cambic site. At the time of the analysis we did not know that this was a blank sample. Well 5B is the water supply well for Mercury, Nevada, but draws from the same aquifer as the satellite well. †This sample was tested with a Ge(Li) gamma-ray spectrometer different from that used for the other samples. Since this spectrometer had a higher background, the <sup>106</sup>Ru was more difficult to detect. This is shown by the high counting statistics errors for <sup>106</sup>Ru, <sup>235</sup>U, and <sup>238</sup>U.

ty well or the satellite well. Since  $^3\text{H}$  exchanges rapidly with the hydrogen in water, most of the  $^3\text{H}$  produced in the explosion is probably in the ground water. However, since  $^{106}\text{Ru}$  can become immobilized in the melt glass (1) or be unavailable due to sorption or precipitation, only about 1 percent of the total produced became a mobile species in the ground water.

Some 120 pCi of  $^{106}\text{Ru}$  per liter had been found in the cavity well water before pumping began at the satellite well, but after 4 years of pumping a 400-liter sample from the cavity well contained no  $^{106}\text{Ru}$  above the detection limit (0.01 pCi/liter). This indicates that the mobile species was swept from the cavity and not replenished by leaching of melt glass or by reversible reaction from a sorbed or precipitated form.

Ruthenium is reported to have equilibrium sorption coefficient ( $K_d$ ) values in ground water ranging from 10 to 8000 (1, 6-8), based on batch sorption techniques. Even a  $K_d$  as low as 10 for this rock results in a retardation factor of 64. That is, the nuclide would move at a rate 1/64 that of the water and by July 1980 would have moved only 2.7 m. However, the lowest  $K_d$  for  $^{106}\text{Ru}$  measured (with rock and water from this site) is 976 (6), which would result in only 3 cm of movement. Only nuclides with a  $K_d \leq 0.3$  would have migrated the 91 m to the satellite well by July 1980.

The laboratory batch sorption method gives only the average  $K_d$  for all chemical forms of a radionuclide. The large range in reported  $K_d$  values for  $^{106}\text{Ru}$  could result from a differing proportion of chemical forms in each experiment. These forms could have a wide variation in individual sorption properties, including one or more with an effective  $K_d$  of zero.

Ames and Rai (8) report that ruthenium exists in solution only as complex ions. On the basis of simplified  $Eh$  (oxidation-reduction potential-pH) diagrams for the range of  $Eh$  and pH values expected for ground water, Brookins (9) indicated that three forms could exist, depending on  $Eh$  conditions and the presence of certain anions. For reducing conditions, solid  $\text{RuS}_2$  is a potential stable phase. For more oxidizing conditions, solid  $\text{RuO}_2$  is a potential stable phase. At still stronger oxidizing conditions, a stability field exists for the complex ion  $\text{RuO}_4^{2-}$ .

Laboratory batch sorption experiments on Hanford, Washington, soil produced  $K_d$  values from 40 to 752 within the pH range of 7 to 9 expected for ground water (8). In contrast, field ob-

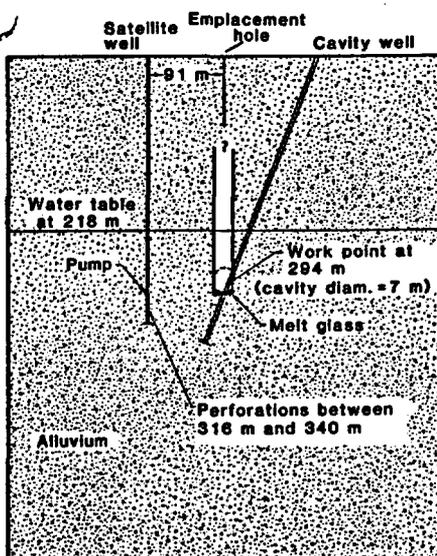


Fig. 1. Cross section of the Cambric experiment site.

servations near leaking storage tanks or waste pits showed significant mobility for ruthenium, and in one case ruthenium migrated with tritium and technetium (10). A review by Onishi *et al.* (11) concluded that ruthenium migration in the field has been well documented; on the other hand, laboratory tracer experiments have shown high  $K_d$  values for ruthenium.

The ground-water chemistry of the tuffaceous alluvium aquifer of Frenchman Flat is documented from several wells near the Cambric site (2, 6, 12). The composition of the satellite well is typical of Frenchman Flat ground water. It has often been assumed that deep aquifers (> 250 m) are reducing since they are isolated from the atmosphere. However, recent studies by Winograd (13) showed that many deep aquifers, including Nevada Test Site ground water, are nearly saturated with dissolved oxygen. Wolfsberg (6) measured the  $Eh$  with a platinum electrode at the satellite well and observed mildly oxidizing conditions (+330 mV). Considering the dissolved oxygen content in these waters and the  $Eh$ -pH diagrams for ruthenium (9), we would expect some migration of ruthenium, probably as  $\text{RuO}_4^{2-}$ .

The fact that  $^{106}\text{Ru}$  migrated at rates similar to those of  $^3\text{H}$  in a tuffaceous alluvium aquifer at the Nevada Test Site does not indicate a hazard from potential ground water migration from nuclear tests to off-site wells or springs. First, the initial concentration of  $^{106}\text{Ru}$  in the chimney itself is well below the maximum permissible concentration for drinking water (2). Second, the half-life of  $^{106}\text{Ru}$  is so short (1.01 years) that the radionuclide would never reach distant

we before it had completely decayed. Third, only  $^{106}\text{Ru}$  has been observed to migrate.

The field observations reported here do not invalidate all batch sorption measurements, but  $K_d$  values thus obtained should be used with caution and verified with field radionuclide migration studies or more relevant laboratory studies. For elements that usually have a single valence (such as strontium and cesium), the batch  $K_d$  values appear to have relevance if sorption isotherms are determined. For multivalent elements, flow system methods rather than batch methods may be required to provide data relevant to field conditions. In addition, an understanding of the chemical speciation of multivalent elements like ruthenium, technetium, and selected actinides is needed in order to predict their behavior in a ground-water environment.

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#### References and Notes

- Participants in this program are the University of Nevada's Desert Research Institute, the U.S. Geological Survey, the Los Alamos National Laboratory, and the Lawrence Livermore National Laboratory. For a review, see I. Y. Borg, R. Stone, H. B. Levy, L. D. Ramsdott, "Information pertinent to the migration of radionuclides in ground water at the Nevada Test Site" (UCRL-52078, Lawrence Livermore Laboratory, Livermore, Calif., 1976), parts 1 and 2.
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12. H. C. Claasse. "Water quality and physical characteristics of Nevada Test Site water: Supply wells" (USGS-474-158. U.S. Geological Survey, Denver, 1973).
13. I. J. Winograd, private communication.
14. This study was performed under the auspices of the Department of Energy by the Lawrence Livermore National Laboratory under contract W-7405-ENG-48. We thank the following colleagues for reviewing the manuscript and making valuable suggestions: E. Douthett, W. Dan-

iels, W. Wilson, H. C. Claasse, I. Winograd, D. Brookins, J. Serne, D. Jander, G. Birchard, R. Ide, D. Isherwood, P. Wolery, R. Schock, and J. Tewhey. J. Schweiger, F. Bazan, and J. Rego provided field sampling support. J. Bazan and L. Gazlay measured the samples for radioactivity.

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