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Abstract

Ruthenium-106 has been observed to migrate at the same velocity as ^{3}H in ground water from the site of an underground nuclear explosion to a pumped satellite well. This finding contradicts laboratory sorption studies using material from this site that indicate that ^{106}Ru should migrate at a much slower rate than ^{3}H. These field measurements raise doubts about the wisdom of relying on simple laboratory sorption measurements to predict field radionuclide migration. Field tests are needed for verification for nuclides that can exhibit complex solution chemistries(1).

Introduction

In order to assess the potential for ground-water migration of radioactivity deposited in aquifers by underground nuclear tests, a program was begun by the Department of Energy's Nevada Operations Office (NV) to study the interaction of nuclear explosion debris and ground water. This program can also shed light on what might happen in a flooded nuclear waste repository. Participants in this program are the University of Nevada's Desert Research Institute, the U. S. Geological Survey, the Los Alamos Scientific Laboratory (LASL), and the Lawrence Livermore National Laboratory (LLNL)(2). Results of the laboratory studies and a review of the migration of radionuclides in ground water have previously been published (3-5). We report here the results of field studies which show a significant discrepancy between migration rates found in the laboratory and those measured in the field.

The nuclides we measured were produced in the Cambric test, which was detonated in NTS tuffaceous alluvium on May 14, 1965, with a yield of 0.75 kt. At the Frenchman Flat explosion site the static water level was 220 m below the land surface. The explosion point was 294 m deep. Figure 1 is a cross section of the experiment site. In order to determine the concentration of radioactivity in the ground water at the explosion site, water was sampled from a well that intersected the explosion cavity (6). The only radionuclides measured at levels above MPC(7) were ^{3}H and ^{90}Sr, even though the water had been in direct contact with nuclear debris for more than 15 years. The concentration of ^{106}Ru was 120 pCi/liter.

During April 1974 a satellite well was drilled 91 m south of the explosion point coordinates to enable the study of migration rates of the radionuclides present in the cavity water. A pump was placed in the well at the same depth as the explosion point. Pumping induced an artificial ground water gradient between the explosion point and the well. If one assumes that ^{3}H is not retarded, the relative movement of observed radionuclides can be compared to ^{3}H movement, and an *in situ* retardation factor can be determined.

No radioactivity was observed in the satellite well until ^{3}H was detected after 1.44 X 10^{6} m^{3} of water had been pumped (8,9). With further pumping, the ^{3}H concentration continues to increase in the satellite well and has decreased fifty-fold in the cavity well after more than two years of pumping(8).

Measurement Program

After establishing that cavity water had been drawn to the satellite well, we wondered whether it would be possible to measure other radionuclides besides ^{3}H. From calculations based on the known relative concentrations of radionuclides, dilution factors, and the "volume pumped curve" of Hoffman (8), we concluded that the activities of the radionuclides would be below the limits of analytical detection. The calculated activity of ^{106}Ru was 0.02 pCi/liter.

To solve this problem we collected 200-liter water samples, and evaporated them in the laboratory. The resultant salts (approximately 150 g) were counted on an ultra-low background Ge(Li) Compton suppressed gamma-ray spectrometer (10,11). This special counting equipment was necessary because the activity level for these samples was very low. Normal counting equipment would have been unable to detect the low levels of ^{106}Ru observed. In order to attain even greater sensitivity, a field distillation apparatus was designed and built to evaporate up to 1000 liters of water at the well-head. To date, three samples ranging from 700 to 860 liters of water have been field-evaporated successfully and the resultant salts gamma-counted in the laboratory.

For all samples nearly the same levels of the natural radioactive species ^{40}K, ^{235}U, and ^{238}U were observed (Table 1). Ruthenium-106 was also observed in all samples. The level of ^{106}Ru activity tends to increase with time, although counting-statistics errors are generally large. The $^{106}Ru/^{3}H$ ratios were the same for all water samples. This similarity indicates that ^{3}H and ^{106}Ru are traveling together from the explosion site to the satellite well.

Discussion

Sample contamination is always a threat in low-level studies. Laboratory contamination at LLNL was ruled out by an LLNL analysis of two unidentified specimens prepared from 200-liter samples that had been collected by LASL. One sample when counted yielded ^{106}Ru results within the counting error compared with one of our samples. The other showed no ^{106}Ru but similar levels of ^{40}K, ^{235}U, and ^{238}U. The latter sample turned out to be a blank from an NTS well located 2.25 km from the satellite well. This well pumps water from the same aquifier at a depth of 230 m.

We regard field contamination as unlikely because the ^{106}Ru content approximated the predicted value (12), no other explosion-related radionuclides were observed, the $^{106}Ru/^{3}H$ ratios of the samples were similar to the values in the cavity well (Table 2), and the blank specimen furnished by LASL contained no detectable ^{106}Ru. The ratio of ^{106}Ru to ^{3}H should remain constant from the cavity well to the satellite well if ^{3}H and ^{106}Ru migrated together. Table 2 is a listing of the $^{106}Ru/^{3}H$ ratios for the cavity well and the six samples from the satellite well. The values agree well, leading to the conclusion that the ^{106}Ru present in the source water was migrating with ^{3}H.

Table 2 also gives the value for the $^{106}Ru/^{3}H$ ratio that was calculated for the amount produced during the nuclear explosion. The calculated value is about a factor of 100 higher than that observed in the original source ground water and the satellite-well ground water. Since ^{3}H exchanges rapidly with the hydrogen in water, most of the ^{3}H produced in the explosion is probably in the ground water. However, since ^{106}Ru can become immobilized in the melt glass (4) or be unavailable due to sorption or precipitation, only about 1% of the total produced became a mobile species in the ground water. We also analyzed a 400-liter sample from the cavity well four years after the pumping was begun in the satellite well. While 120 pCi/liter of ^{106}Ru was observed in water from the cavity well before pumping began at the satellite well, in the much larger sample taken four years later no ^{106}Ru was observed above the detection limit of 0.01 pCi/liter for that sample. 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.

Having concluded that our field observation was valid, we then considered its relationship to previous data, both field and laboratory. Many reports (3, 5, 13, 14) show ruthenium to have K_d values ranging from 10 to 8000, which should cause it to migrate at a significantly slower rate than ^{3}H. We note here that a K_d of zero defines a nonsorbed species; any K_d greater than 1 would result in retardation sufficient to eliminate the ruthenium from our samples. We conclude that all indications from laboratory studies were that we should not have detected ruthenium in the water.

Very little data for ruthenium geochemistry exist, and only a few field investigations on the migration of ruthenium have been reported. Ames and Rai (14) report that ruthenium is considered to exist only as complex ions in solution. Based on simplified Eh (redox potential)-pH diagrams for the range of Eh and pH values expected for ground waters, Brookins (15, 16) indicates that three species could exist, depending on Eh conditions and assuming that certain anions were present. For reducing conditions, $\overset{+4}{RuS_2}$ is a potential stable phase. For more oxidizing conditions, $\overset{+4}{RuO_2}$ is a potential stable phase. At still stronger oxidizing conditions, a stability field exists for the complex ion $\overset{+6}{RuO_4^{2-}}$. Ames and Rai also point out that the most stable aqueous ions in an oxidizing soil environment would be $\overset{+7}{RuO_4^{-}}$ and $\overset{+6}{RuO_4^{2-}}$. Since little thermodynamic data exist for ruthenium, these chemical species are speculative but they do point out some possible species as well as demonstrate the confused state of understanding of aqueous ruthenium geochemistry.

The laboratory experiments discussed by Ames and Rai are varied and confusing. Values for K_d on Hanford soil ranged from 40 to 752 within the range for ground-water pH [7-9] values. Depending on the solution variables, they state that ruthenium can simultaneously exist as a colloid, cationic form, and anionic form.

A few other field observations of ruthenium migration have been made, mostly from leaking storage tanks or waste pits near the ground surface. In most of the cases discussed by Ames and Rai, ruthenium showed significant mobility and in one case was observed to migrate with tritium and technetium (17). Gancarz et al. (18) have inferred limited ruthenium migration at the OKLO uranium deposit in Gabon, Africa. A review by Onishi et al. (19) concluded that ruthenium migration in the field has been well-documented, while on the other hand laboratory tracer experiments have shown high K_d values for ruthenium. These authors concluded that anionic forms of ruthenium are generally nonsorptive, that nitrate complexing accounted for the migration from nitrate-rich waste tanks, and that accurate thermodynamic data for ruthenium complexes did not exist. Knowledge of ruthenium speciation is necessary before its behavior can be understood.

The character of ground water in the tuffaceous alluvial aquifer of Frenchman Flat has been well-documented by chemical analysis from several wells near the Cambric site (4, 5, 6, 20). The ground-water composition of the satellite well is considered here as a typical Frenchman Flat ground water, although some variability exists in the composition of the other nearby well samples, which are as much as 6.6 km apart. An understanding of the oxidation-reduction (redox) conditions is critical to interpreting radionuclide behavior in ground water. Knowledge of valence distribution is required for predicting chemical speciation of elements in aqueous systems, and this speciation information provides insight to the mechanisms that caused the observed behavior of the radionuclide in the 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 (21) have shown that many deep aquifers have nearly saturated contents of dissolved oxygen (DO). Because he has studied the NTS ground water also and observed nearly saturated levels of DO there, we conclude that the ground water in this study is oxidizing. Wolfsberg (5) measured the platinum electrode Eh at the satellite well and observed mildly oxidizing conditions (+330 mV). Based on the DO content in these waters and the Eh-pH diagrams for ruthenium (15, 16), we would expect some migration of ruthenium at the Cambric site, probably as RuO_4^{2-}.

Laboratory K_d measurements (both sorption and desorption) were done on samples of tuffaceous alluvium from the cavity well using satellite water. A range of K_d values for ruthenium of 976 to 3390 was reported (5). These laboratory measurements were designed to be specifically relevant to the Cambric study; they were done on the same medium with the Cambric ground water. The conclusions, based solely on the laboratory work, are contrary to observations in the field. The laboratory "batch" K_d methodology employed in the Cambric study (5) is similar to that currently utilized as a primary K_d data-gathering source for use in assessing the quality of various geologic media for nuclear waste disposal repositories (13, 22, 23). This technique is attractive because it is inexpensive, simple to carry out, and allows for high sample throughput. These features are important to the task of screening many different candidate media. However, the present observation of ^{106}Ru migration raises the question of whether this type of laboratory evaluation of radionuclide sorption behavior can be extrapolated to the actual repository conditions, at least for nuclides with complex solution chemistry.

The fact that ^{106}Ru has been confirmed to migrate with ^{3}H in a tuffaceous alluval aquifer at the NTS does not indicate a hazard from potential ground-water migration from nuclear tests to off-site wells or springs. First, the ^{106}Ru initial concentration in the chimney itself is well below MPC for drinking water (6). Second, the ^{106}Ru half-life is so short (1.01 years) that it would never reach distant wells before it had completely decayed away. Only 1% of the total ^{106}Ru was mobile and it was not replenished after the pumping swept the initial amount from the cavity region.

The significance of this work, rather, is the disagreement between complementary laboratory and field studies. Careful, relevant laboratory sorption measurements predicted essentially no ground-water migration of ^{106}Ru. Under field conditions ^{106}Ru was observed to migrate with essentially no retardation relative to ^{3}H. While these field observations provide insufficient data for invalidating "batch" K_d measurements, they do demonstrate that the batch K_d values must be used with caution and verified with <u>in situ</u> radionuclide migration studies. Certainly there is a need for additional work to interpret and understand the field observations. In particular, an understanding of chemical speciation of multi-valence elements like ruthenium (e.g., Tc and actinides) is needed in order to grasp their behavior in a ground-water environment. For predominantly low-valence elements (e.g., Sr and Cs), the batch K_d measurements may be quite adequate.

Table 1. Radioactivity (pCi/liter)[*] observed in salts from evaporated[+] large volume water samples from satellite well, Cambric Site, NTS.

Radionuclides	Sample/(sample volume in parenthesis)						
	Blank[±]	11/29/78[±]	2/7/79	3/14/79	8/29/79	4/17/80[#]	7/23/80
	(200-l)	(200-l)	(200-l)	(200-l)	(710-l)	(740-l)	(860-l)
^{40}K	8.6 ± 2%	10. ± 2%	7.2 ± 3%	7.7 ± 2%	10. ± 2%	12. ± 1%	8.6 ± 1%
^{106}Ru	≤0.02	0.04 ± 45%	0.04 ± 40%	0.04 ± 30%	0.07 ± 7%	0.08 ± 45%	0.08 ± 21%
^{235}U	0.07 ± 6%	0.09 ± 6%	0.05 ± 7%	0.08 ± 5%	0.04 ± 4%	0.12 ± 7%	0.09 ± 2%
^{238}U	1.9 ± 5%	2.5 ± 5%	1.0 ± 35%	1.6 ± 26%	0.90 ± 6%	3.0 ± 16%	2.2 ± 4%

[*] Data recomputed to 15 years after original shot time so that all values are closer to current observed levels in water. Errors are 1σ counting statistics only.

[+] We have been collecting various 200-l samples from the satellite well since April 1977. Some have not been evaporated, and a few others were contaminated.

[±] These samples were supplied by LASL. The blank was taken from NTS well 5B which is located 2.25 km south of the Cambric site. It was unknown to us at the time of the analysis that this was a blank sample. It is the water supply well for Mercury, NV, but from the same aquifer as the satellite well.

[#] This sample was counted on a Ge(Li) gamma-ray spectrometer different from that used to count the other samples. Since that spectrometer had a higher background, the ^{106}Ru was more difficult to observe. This is shown by the high counting statistics error for ^{106}Ru as well as for both ^{235}U and ^{238}U.

Table 2. $^{106}\text{Ru}/^{3}\text{H}$ activity ratios[+] from various Cambric water samples.

Original source[*]	Cavity samples[±]		Satellite well samples					
	Zone II	Zone III	11/29/78	2/7/79	3/14/79	8/29/79	4/17/80	7/23/80
4×10^{-6}	5×10^{-8}, 3×10^{-8}	2×10^{-8}	5×10^{-8}	4×10^{-8}	4×10^{-8}	4×10^{-8}	3×10^{-8}	3×10^{-8}

[+] Because ^{3}H and ^{106}Ru decay with different half-lives, all these ratios were calculated for 15 years after the detonation.

[*] This is the ratio calculated for the total ^{3}H and ^{106}Ru produced by the explosion. If all of the produced activity were soluble in the ground water, then the pumped water should have an identical ratio. Since the calculated source ratio is approximately a factor of 10^{2} higher, less than 1% of ^{106}Ru produced is in the ground water.

[±] Reference 6.

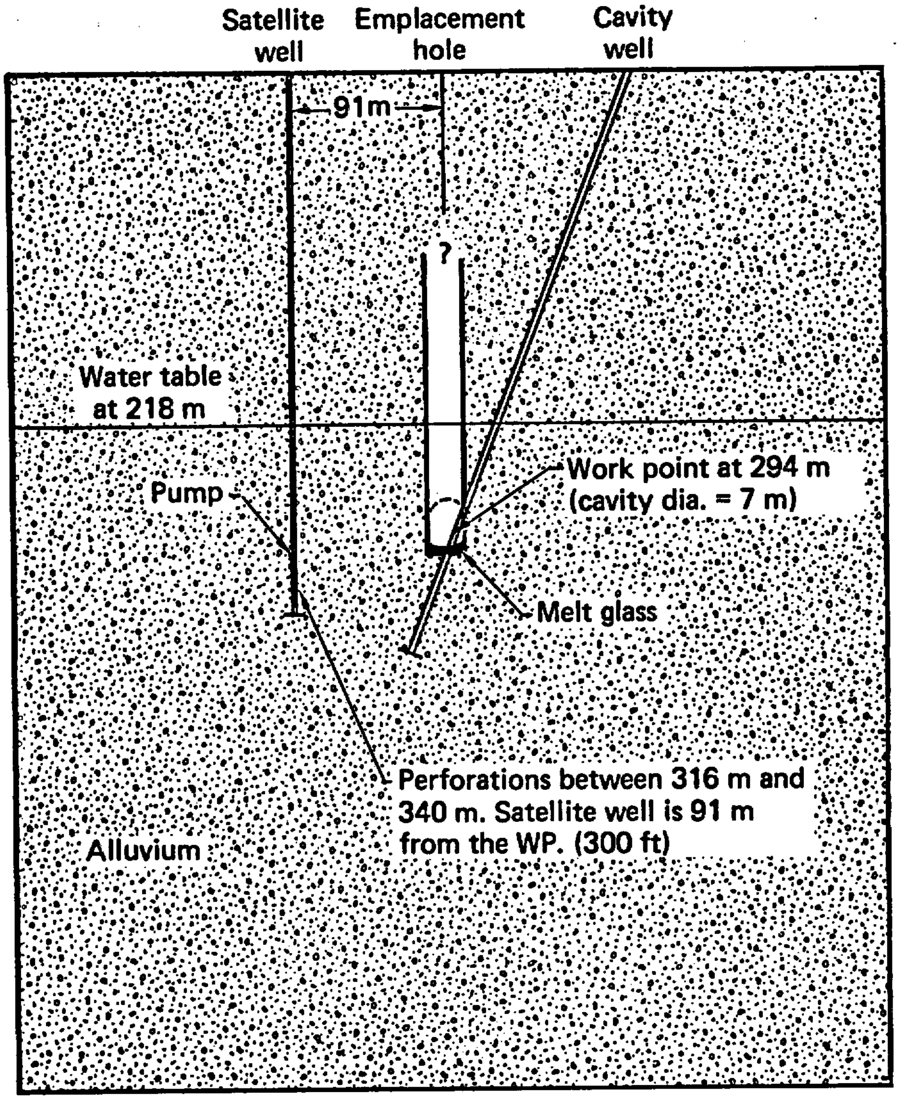

Fig. 1. Cross section of Cambric Experiment Site.

References and Notes

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