Proceedings of the Korean Nuclear Society Autumn Meeting
Seoul, Korea, October 1999

Behavior of Uranium Isotopes in the Ground Water on the Okchun Belt

Myung Ho Lee, Mi Kyung Kim, Hyun Sang Shin, Gun Sik Choi, Kwang Hee Hong,

Yung Hyun Cho, Chang Woo Lee

Korea Atomic Energy Research Institute

ABSTRACT

The ground water samples obtained from the Okchun Belt in Korea were separated into particulate and filtered fraction using filtration techniques with 0.45 μm of membrane filter, and concentrations and activity ratios of uranium isotopes in the fractions were determined by the chemical separation and alpha spectrometric measurements. Most of the uranium isotopes in the ground water was found in the filtered water. Only less than 1 % of total uranium isotopes was detected in the particulate fraction. The concentrations and activity ratios of uranium isotopes in the ground water measured in this study were variable, depending upon its solubility in the ground water as well as the geological characteristics of the aquifer. The concentrations of ^{238}U in the ground water at the hot spring area were found to be about four times higher than those at other sites in the Chungcheng area. The activity ratios of ^{234}U/^{238}U in the ground water at the hot spring water were close to the equilibrium value (1.10 ± 0.07), while in other sites in Chungcheng area, the activity ratios of ^{234}U/^{238}U were variable with the range from 1.20 to 3.58.

1. Introduction

Natural radionuclide existing in the environment is important in the general study of radionuclide migration. Among the natural radionuclides occurred in the environment, uranium isotopes are good tracers to study the behavior of these radionuclides, because natural uranium can be easily detected in nearly all materials from the environment.

Most groundwaters contain a few ppb of dissolved uranium. The uranium concentration in most surface and near surface continental waters is somewhat lower and more variable, ranging from less than 0.1 ppb to more than 1000 ppb [1]. In case of the ground groundwater, uranium concentrations greater than 50 ppb are quite rare, and have generally been found only in aquifers containing uranium mineralization. However, Okchun Metamorphic Belt which is covered with low uranium-bearing black shales [2] has been focused by many environmental researchers in recent years because of significance in environmental geochemistry. Average contents of uranium in the Okchun black shale is about 250 μg/g [2,3]. This value is higher than contents of uranium in any other regions of the Korean Peninsular. The contents of uranium greater than 50 ppb in the ground water have been easily found. Therefore, high uranium concentrations in groundwater may lead to harmful biological effects in humans, if one uses the underground water as a drinking water. Uranium accumulated in humans may have a dual effect due to its chemical and radioactive properties. The chemical toxicity of natural uranium is a major hazard to the kidneys. Radiotoxicity also arises from the irradiation of bone surfaces and red bone marrow by uranium isotopes. Therefore, it is necessary to determine the concentration of uranium isotopes in the groundwater for radiological dose assessment.

During the last few years, a number of studies has been carried out to investigate the anomalous behavior of uranium isotopes in soils [4], surface water [5-8] ground water [9-11], and sediment [12-14], but there is not much [15] information available on the concentration of uranium isotopes in the ground water of the Korean Peninsula. The present work aims to determine the concentrations and the activity ratios of uranium isotopes in the ground water on the Okchun Belt of the Korea. This result may be used as reference data in case of an accident in a radioactive waste repository or in a nuclear plant, and elucidated the migration characteristics of uranium isotopes in the ground water under natural conditions.

2. Materials and methods

Sampling sites were chosen to cover the Chungcheng area. As shown in Fig. 1, the sampling sites are part of the Okchun Metamorphic Belt located in the middle of South Korea. The Okchun Belt consists of the granites, tuff, sandstone, U black shale, phyllite and limestone [2]. The trace elements, such as Cr, Cu, Mo, Ni, Pb, U, V and Zn, are highly enriched in the Okchun uranium-bearing black shale of Cambro-Ordovician age [16]. The detailed geology of these sites are given in the literature [3].

The groundwater samples were taken at 19 sites from the hot spring area and 14 sites from the Chungcheng area in 1998-1999. Samples of about 20 L of groundwater were collected at the sampling sites. Except two sampling sites of H 18 and H 19, most of the groundwater samples are used for drinking water by the local in habitants. The sampling depths were in the range of 70 m ~ 400 m.

The suspended matter was separated by filtration through Nuclepore filters of 0.45 μm pore size. Total carbon contents was measured by Shimadzu TOC Analyzer (Model; TOC-5000 A). The pH (Model; Orion 1260) was measured with a glass electrode. The pH values of the ground water samples were found to be in the range of 5.59 to 7.92.

^{232}U as a yield tracer was added to the filtered water and particulate fraction. 15 liters of filtered water were evaporated to dryness until 100 ml using an evaporating system. The condensed filtered water was transferred into 250 ml beaker and evaporated to dryness. The particulated fraction with the membrane filter was calcined at 550 °C for 24 hours in the furnace. The sample was dissolved with 7.2 M HNO_3. Uranium isotopes were extracted from dissolved sample materials using TBP (tributyl phosphate) in carbon tetrachloride. The radiochemical purification of the U fraction was performed with 8 M hydrochloric acid. Back extraction was done using 1 M HCl. Finally, purified uranium isotopes were electrodeposited from the electroplating solution on a polished stainless steel disc and measured by α-ray spectrometry. Detailed description of the experimental procedure has been well described elsewhere [17].

3. Results and discussion

3.1 Concentration of uranium isotopes

The concentrations and activity ratios of uranium isotopes in the ground water were measured and the results were presented in Table 1 and Table 2. Most of uranium isotopes (> 99 %) in the ground water were found in the filtered water. Only less than 1 % of total uranium isotopes were detected in the particulate fraction. The activity concentrations of ^{238}U in the filtered water were plated as the function of total carbon (organic and inorganic) contents, as shown in Fig. 2. The correlation of the uranium activity concentrations with total carbon contents was found to be significant (r = 0.73). This results suggest that most of uranium isotopes in the ground water exist as a dissolved uranium, forming complexes with carbonate ions and dissolved organic matters including humic substances [18] rather than associated with a solid fraction. The total carbon contents at the hot spring area were ranged from 7.5 to 21.9 ppm, and higher than those at other sites in the Chungcheng area, which showing that high amount of organic and inorganic carbon is dissolved in the groundwater of the hot spring water.

The concentrations of uranium isotopes at the different sampling points were variable, as presented in Table 1 and Table 2. The concentration of uranium isotopes largely depends upon its solubility in the ground water as well as the geological characteristics of the aquifer. Comparing Table 1 with Table 2, the concentrations of ^{238}U in the ground water at the hot spring area were relatively higher than those at other sites in the Chungcheng area. The mean activity concentration of ^{238}U in the filtered water was found to be 730 ± 728 mBq/l with the range from 125 to 3273 mBq/l for the hot spring area and 174 ± 187 mBq/l with the range from 6.75 to 606 for other sites in the Chungcheng area, respectively. The increase in the concentrations of uranium isotopes at the hot springs area could be attributed to a physicochemical reaction between the ground water and the mother rocks such as U black shales and granite. The uranium isotopes in the ground water are mainly from uranium which are leached by the water from U black shales and granite rocks. Owing to a violent material exchange between the subterranean hot waters and the rock stratum, the erosion of the rocks has been greatly increased. Hence, uranium isotopes in U black shales area easily dissolve in the hot spring water and the concentration of uranium isotopes has been increased. A similar behavior has been observed in the Ta-Tun volcanic group area in Taiwan [19].

3.2 Activity ratios of uranium isotopes

Activity ratios of uranium isotopes vary with the source and can be utilized to identify the different sources of release. In general, the activity of ^{238}U is nearly equal to that of ^{234}U in natural conditions, because of radioactive equilibrium. However, some studies showed that the ^{234}U/^{238}U activity ratio in the ground water is not constant value but varies depending on several parameters [20]. The variation in the ^{234}U/^{238}U activity ratio observed in the ground water is controlled by several factors such as redox conditions, the differences in the chemical characteristics of uranium, reactive characteristics of groundwater and rock stratum and residence time of groundwater.

In this study, the activity ratio of ^{234}U/^{238}U in the ground water was not unit, ranging between 1.01 to 3.58, as shown Table 1 and Table 2. The activity ratios of ^{234}U/^{238}U in the filtered water at the hot spring area were close to the constant equilibrium value (1.10 ± 0.07). On the while, the activity ratios of ^{234}U/^{238}U in the filtered water at other sites in the Chungcheng area were variable with the range from 1.20 to 3.58. The ^{234}U/^{238}U activity ratios in the particulate fractions, on the other hand, unsystematically varied and were close to the equilibrium value of unity.

Fig. 3 shows a plot of the ^{234}U/^{238}U activity ratio versus uranium concentration for filtered water. The ^{234}U/^{238}U activity ratios have a tendency to decrease with increasing concentration of uranium. Similar results has been reported elsewhere [18-20]. Osmond *et al.* [20] explained this tendency with redox potentials in the aquifer system : High concentration of uranium and low activity ratio occur in oxidizing zone, and low concentration and high activity ratio occur in reducing zones. The main mechanism which may contribute to this disequilibrium in the ground water includes α-particle recoil ejection of ^{234}Th into a solution, preferential solution of ^{234}U due to radiation damage, and the change of ^{234}U to a more soluble U^{6+} in the associated rocks [20]. Therefore, if residence time of ground water is enough, the accumulation of ^{234}U from α-recoil ^{234}U atoms will be increased. These results on ground water may lead to a way to investigate the movement and history of ground water.

It is interesting to compare the activity ratios of ^{234}U/^{238}U in the ground water of the Chungcheng area including the hot spring area. As shown in Fig. 3, the ^{234}U/^{238}U activity ratios at the hot spring area samples showed lower $^{234}U/^{238}U$ activity ratios than those of other regions in the Okchun Metamorphic Belt, although the concentrations of ^{238}U at the hot spring area were higher than those of other regions. These results may be explained by the reactive characteristics of hot spring water and rock rather than residence time of water based on redox potentials. In the hot spring water, the leaching of uranium is more prevailing than the effects of reducing conditions. That is, due to a violent physicochemical reaction between the hot spring waters and the rock stratum, described above, much of the ^{238}U located in the U black shales is easily dissolved and the superiority of being leached owing to daughter's recoil is reduced. Hence, the activity ratio of $^{234}U/^{238}U$ in the hot spring water is close to that in the rock stratum.

Acknowledgements

This study was carried out under the Nuclear R & D program by Ministry of Science and Technology of Korea.

4. References

1. Scott, R. C., Barker, F. B.: Data on uranium and radium in groundwater in the United State. USGS Paper 426, p. 115.
2. Kim, K. W.: Doctoral thesis, University of London, London 1993.
3. Lee, D. H.: *Geology of Korea,* Kyohark-Sa, Seoul 1987, p. 247.
4. Greeman, D. J., Rose, A. W.: Geophys. Res. Lett. **17**, 833-836 (1990).
5. Vera Tome, F., Martin Sanchez, A., Diaz Bejanaro, J.: J. Radioanal. Nucl. Chem. **126(6)**, 419-427 (1988).
6. Sarin, M. M., Krishnaswami, S, Somayajulu, B. L. K., Moore, W. S.: Geochim. Cosmochim. Acta **54**, 1387-1396 (1990).
7. Rodriguez, M. J., Sanchez, F.: J. Radioanal. Nucl. Chem. **190(1)**, 113-120 (1995).
8. Martinez-Aguirre, A., Garcia-Leon, M., Ivanovich, M.: Nucl. Instrum. Meth. Phys. Res. **339**, 287-293 (1994).

9. Copenhaver, S. A. Krishnaswami, S., Turekian, K. K., Shaw, H.: Geophys. Res. Lett. **19**, 1383-1386 (1992).

10. Suutarinen, R., Blomqvist, R., Halonen, S., Jaakkola, T.: Radiochimica Acta **52/53**, 373-380 (1991).

11. Singh, J., Singh, L., Singh, S.: J. Environ. Radioactivity **26**, 217-222 (1995).

12. Barnes, C. E., Cochran, J. K.: Earth Plant. Sci. Lett. **97**, 94-101 (1990).

13. Varinlioglu, A., Köse, A., Cevik, U., Kopya, A. I., Altunbas, M., Karal, H.: J. Radioanal. Nucl. Chem. **201(1)**, 31-37 (1995).

14. Ibrahiem, N. M., Pimpl, M.: Appl. Radiat. Isot. **45(9)**, 919-921 (1994).

15. Han, J. H., Park, K. H.: Econ. Environ. Geol. **29(5)**, 589-595 (1996).

16. Kim, J. H., J.: Korean Inst. Mining Geol. **22**, 35-63 (1989).

17. Lee, M. H., Choi, G. S., Y. H., Lee, C. W., Jung, S. T.: J. Korean Asso. Radiat. Prot. **24(1)**, 1-7 (1999).

18. Higgo, J. J. W., Kinniburgh, D., Smith, B, Tipping, E.: Radiochimica Acta **61**, 91-103 (1993).

19. Chu, T. C., Wang, J. J.: Appl. Radiat. Isot. **48(8)**, 1149-1155 (1997).

20. Osmond, J. K., Cowart, J. B., Ivanovich, M.: Int. J. Appli. Radiat. Isot. **34**, 283-308 (1983).

Table 1. Concentrations and activity ratios of uranium isotopes in the hot spring water at the Chungcheng area

		Filtered water fraction			
Sampling site	TC(ppm)[#]	^{238}U(mBq/l)	U_{total} (ppb)	^{234}U/^{238}U	^{238}U(mBq/l)
H-1	14.8	674 ± 24.7	54.2 ±	1.02 ± 0.12	0.31 ± 0.02
H-2	16.9	804 ± 32.1	64.7 ±	1.05 ± 0.05	0.51 ± 0.04
H-3	8.8	142 ± 8.83	11.5 ±	1.20 ± 0.13	0.99 ± 0.06
H-4	17.0	722 ± 21.8	58.1 ±	1.03 ± 0.11	0.12 ± 0.03
H-5	9.6	170 ± 16.4	13.7 ±	1.14 ± 0.10	2.94 ± 0.36
H-6	10.3	383 ± 20.9	30.8 ±	1.19 ± 0.14	1.92 ± 0.21
H-7	16.8	693 ± 13.4	55.8 ±	1.05 ± 0.08	0.46 ± 0.03
H-8	17.2	842 ± 35.1	67.7 ±	1.04 ± 0.13	0.19 ± 0.02
H-9	14.6	481 ± 13.7	38.7 ±	1.22 ± 0.13	0.69 ± 0.05
H-10	16.7	553 ± 12.5	44.5 ±	1.13 ± 0.10	0.39 ± 0.04
H-11	16.4	715 ± 34.1	57.5 ±	1.01 ± 0.08	0.17 ± 0.01
H-12	17.5	871 ± 28.7	70.1 ±	1.03 ± 0.10	0.20 ± 0.01
H-13	16.1	628 ± 28.3	50.5 ±	1.06 ± 0.05	0.51 ± 0.06
H-14	14.2	318 ± 19.1	25.6 ±	1.15 ± 0.12	0.27 ± 0.02
H-15	15.6	414 ± 12.1	33.3 ±	1.16 ± 0.14	0.25 ± 0.03
H-16	7.5	125 ± 10.2	10.1 ±	1.19 ± 0.13	0.34 ± 0.03
H-17	11.6	204 ± 18.6	16.4 ±	1.09 ± 0.07	1.24 ± 0.14
H-18	18.2	1861 ± 55.2	149.7 ±	1.01 ± 0.12	0.51 ± 0.03
H-19	21.9	3273 ± 94.3	263.2 ±	1.07 ± 0.09	0.38 ± 0.04
Arithmetic		730 ± 728	58.7 ±	1.10 ± 0.07	0.65 ± 0.71

[#] ; Total carbon content

Table 2. Concentrations and activity ratios of uranium isotopes in the non hot spring water at the Chungcheng area

		Filtered water fraction			
Sampling site	TC(ppm)[#]	^{238}U(mBq/l)	U$_{total}$ (ppb)	^{234}U/^{238}U	^{238}U(mBq/
N-1	5.8	46.0 ±	3.70 ±	2.33 ± 0.18	3.94E-2 ± 1.
N-2	10.2	407 ±	32.7 ±	1.83 ± 0.17	0.11 ± 0.
N-3	8.2	293 ±	23.6 ±	1.75 ± 0.18	0.10 ± 0.
N-4	5.9	364 ±	29.3 ±	1.20 ± 0.11	0.09 ± 0.
N-5	6.8	287 ±	23.1 ±	1.23 ± 0.15	0.10 ± 0.
N-6	5.9	150 ±	12.1 ±	2.20 ± 0.21	0.12 ± 0.
N-7	5.4	134 ±	10.8 ±	3.12 ± 0.24	9.24E-2 ± 1.
N-8	5.6	53.6 ±	4.31 ±	2.69 ± 0.19	7.42E-3 ± 5.
N-9	6.0	10.6 ±	0.85 ±	2.83 ± 0.27	1.08E-2 ± 1.
N-10	5.4	19.9 ±	1.60 ±	2.10 ± 0.26	4.32E-3 ± 6.
N-11	5.6	6.75 ±	0.54 ±	3.58 ± 0.29	1.27E-3 ± 9.
N-12	5.4	17.4 ±	1.40 ±	3.42 ± 0.31	1.59E-3 ± 1.
N-13	9.0	606 ±	48.7 ±	1.52 ± 0.12	9.94E-2 ± 1.
N-14	5.6	38.8 ±	3.12 ±	2.52 ± 0.21	5.74E-2 ± 3.
Arithmetic		174 ± 187	14.0 ±	2.31 ± 0.76	5.96E-2 ± 4.

[#] ; Total carbon content