DIFFERENCES IN THE BEHAVIOR OF ^{233}PA, ^{237}NP AND ^{239}PU IN BENTONITE CONTAMINATED BY SULFATE-REDUCING BACTERIA

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ABSTRACT

The behaviors of ^{233}Pa, ^{237}Np and ^{239}Pu in high level radioactive wastes from nuclear fuel reprocessing were investigated by a laboratory experiment. Radioactive wastes are glassified and disposed of in geological repositories encased in bentonite as an additional artificial barrier to protect the environment. There is, however, the possibility that some anaerobic bacteria, especially sulfate-reducing bacteria, may flourish within the bentonite during the long disposal period (more than a century). The effects of sulfate-reducing bacteria on the behavior of the radionuclides within bentonite were investigated using the distribution coefficient (Kd) of ^{233}Pa, ^{237}Np and ^{239}Pu. The Kd was obtained with a 0.22 m membrane filter separating radionuclide contents in solid and liquid phases. The anaerobic bacteria, including sulfate-reducing bacteria, used for this investigation originated from the anaerobic treatment of pulp and paper waste and operated for more than one year at Eh around -85 mV. The bentonite used for this study was produced in Japan.

The active anaerobic bacteria clearly accumulates considerable amounts of ^{233}Pa and ^{239}Pu by producing high Kd values of nearly 100,000, while Kds of ^{233}Pa and ^{239}Pu for the sterilized anaerobic bacteria were less than 10,000. In other words, live anaerobic bacteria can hold considerably higher amounts of the radionuclides compared to dead bacteria. Furthermore, high Kd values were obtained for anaerobic bacteria at pH 5-9. In contrast, Kd values for the radionuclide ^{237}Np were not influenced by the anaerobic bacteria but were controlled by chemical environmental conditions such as like pH.

Another comparison was conducted for the radionuclides for mixtures of non-sterilized bacteria with bentonite.

INTRODUCTION

Japanese high level radioactive wastes produced by commercial nuclear power plants will be disposed of in geologic repositories using bentonite as an artificial barrier. These repositories will be secured for a period of more than 10,000 years. During this period, groundwater will penetrate

the artificial bentonite barrier and anaerobic bacteria can grow within the barrier, interacting with long half-life radionuclides such as, ^{231}Pa, ^{237}Np and ^{239}Pu.

Here, we report preliminary experimental results of important radionuclides, ^{233}Pa, ^{237}Np and ^{239}Pu, interacting with bentonite, which would be used as an artificial barrier at disposal sites. Living (non-sterilized) bacteria absorbed and/or adsorbed a considerable amount of ^{233}Pa and ^{239}Pu in the optimum range of pH, compared to sterilized bacteria. The mixture of living bacteria and bentonite reacted more than the mixture of dead bacteria. In contrast, Kd value for the radionuclide ^{237}Np was not influenced by the anaerobic bacteria but was controlled by chemical environmental conditions such as pH.

In this investigation, we explored the possibility that bentonite would be contaminated by anaerobic bacteria, especially sulfate-reducing bacteria, which may flourish at disposal sites and play an important role in the behavior of ^{231}Pa, ^{237}Np and ^{239}Pu at these sites in the future. Furthermore, aspects on the effects of bacteria concerning the movement of radionuclides in the geologic environment will be explored using the experimental results. Some of our experimental results regarding ^{239}Pu were already published elsewhere (Kudo et al., 1997).

EXPERIMENT

The bentonite used in the experiments originated in a Japanese mine and no treatment was conducted before usage, even though the bentonite was used as a diluted solution with distilled deionized water at a concentration of 0.1%. There was some quartz in the bentonite, which was not suspended in the diluted stock solution. To produce a homogeneous bentonite solution, the solution was shaken before use. X-ray diffraction analysis, x-ray photo spectroscopy analysis and energy dispersion x-ray analysis indicated that the main components of the bentonite were quartz and montmorillonite, and minor components included as beidellite.

Anaerobic bacteria, including sulfate-reducing bacteria, were originally used for the treatment of pulp and paper wastewater in granule form. The gases produced during the treatment included H_2S, CH_4, CO_2 and H_2. The granules were dissolved and diluted in distilled deionized waster after expelling the dissolved oxygen. The concentration of the anaerobic bacteria was adjusted to 0.1% (dry weight). An autoclave was used for sterilization to produce dead anaerobic bacteria.

To obtain the distribution coefficients (Kd) for ^{233}Pa, ^{237}Np and $^{23}9Pu$, membrane filters with a pore size of 0.20 m were used to separate the radionuclides into solid and liquid phases. The filtration of bacteria, bentonite and the mixture of both solutions were conducted by applying positive pressure for quick separation. After filtration, the walls of filtration glassware and the membrane filters were washed with a strong acid solution of HNO3 to obtain more reasonable distribution coefficients.

The analyses of ^{233}Pa and ^{237}Np were conducted using their gamma energies (92.29 keV and 311.90 keV, respectively) while ^{239}Pu was examined after long chemical extraction, concentration, purification, and electro-plating to a polished stainless disk, according to an analytical method combining the methods used in the USA, Germany and Japan (Harley, J.H., 1972, Japanese Science and Technology Agency, 1978, Schttelkopf, H., 1981) and used in our previous investigations (Mahara, Y. and Miyahara, S., 1984, Mahara, Y. et al., 1988, Kauri, T. et al., 1991, Kudo, A., et al., 1991, Kudo, A., et al., 1991, Kudo, A., et al.,1993, Kudo, A., et al., 1995, Kudo, A. et al. 1995.) The electro-plated plutonium samples were analyzed by alpha spectrometry. The certified internal standard, ^{236}Pu, was used to adjust the chemical separation process, and the standard was purchased from Harwell, United Kingdom.

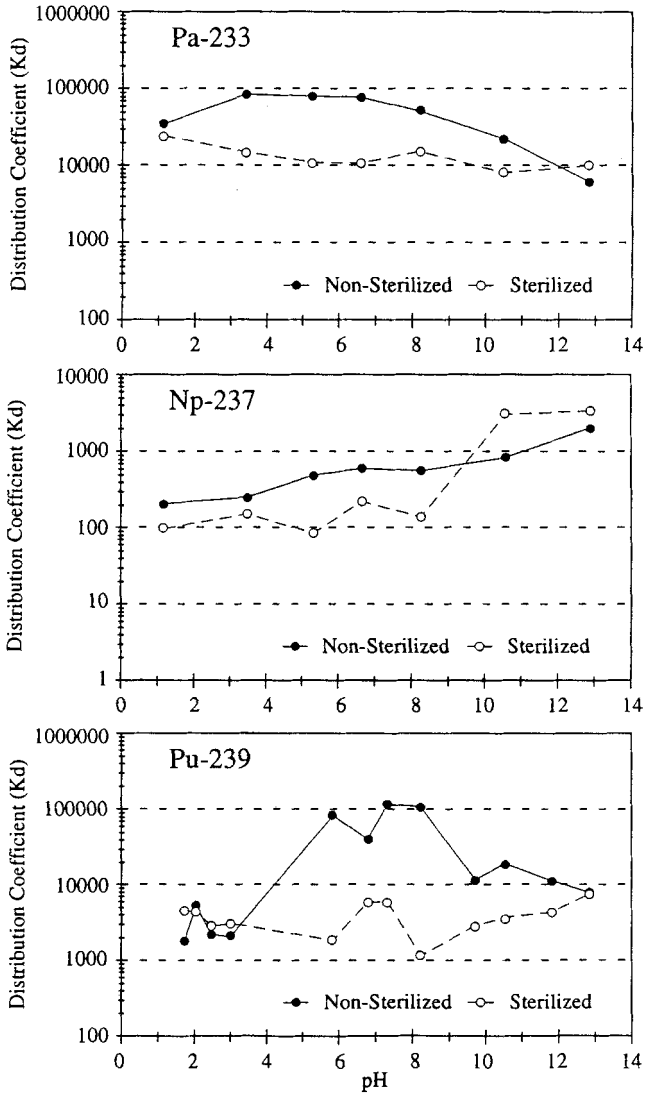

Figure 1 Distribution Coefficient of ^{233}Pa, ^{237}Np and ^{239}Pu interacting with non-sterilized and sterilized anaerobic bacteria.

RESULTS

The living anaerobic bacteria play an important role in the behavior of ^{233}Pa, ^{237}Np and ^{239}Pu within the geological disposal sites, which use bentonite as the artificial barrier. The radionuclides interact with non-sterilized and sterilized anaerobic bacteria over a pH range from 1.74 to 8.25. Figure 1 shows the distribution coefficients, Kd, of three radionuclides, ^{233}Pa, ^{237}Np and ^{239}Pu. There were a considerable differences in Kds of these radionuclides, the difference was especially marked between two groups, ^{233}Pa and ^{239}Pu, and ^{237}Np.

In an extremely hash environment, however, such as strong acidic conditions (below pH 3.01), there were no significant difference in the distribution coefficients of ^{233}Pa, ^{237}Np and ^{239}Pu between non-sterilized and sterilized anaerobic bacteria, ranging from 2,500 to 3,500 for 233a, from 180 to

190 for ^{237}Np and 804 to 5,266 for ^{239}Pu, Figure 1. Although the coefficients stayed within a similar range of a few thousand for sterilized bacteria, the coefficient for non-sterilized bacteria jumped to 90,000 for 233Pa and 110,000 for ^{239}Pu at pH 8.25. On the other hand, ^{237}Np behaved completely differently from ^{233}Pa and ^{239}Pu. It seemed that the influence of anaerobic bacteria was limited for ^{237}Np.

Apparently, there were some unknown reactions which could increase Kd values for the living bacteria, while there were no changes for the autoclaved bacteria, Figure 1. Further investigations are warranted to determine the cause of these interesting phenomena as well as to investigate the distribution of ^{233}Pa, ^{237}Np and ^{239}Pu over a wide range of pH, temperature and other environmental conditions.

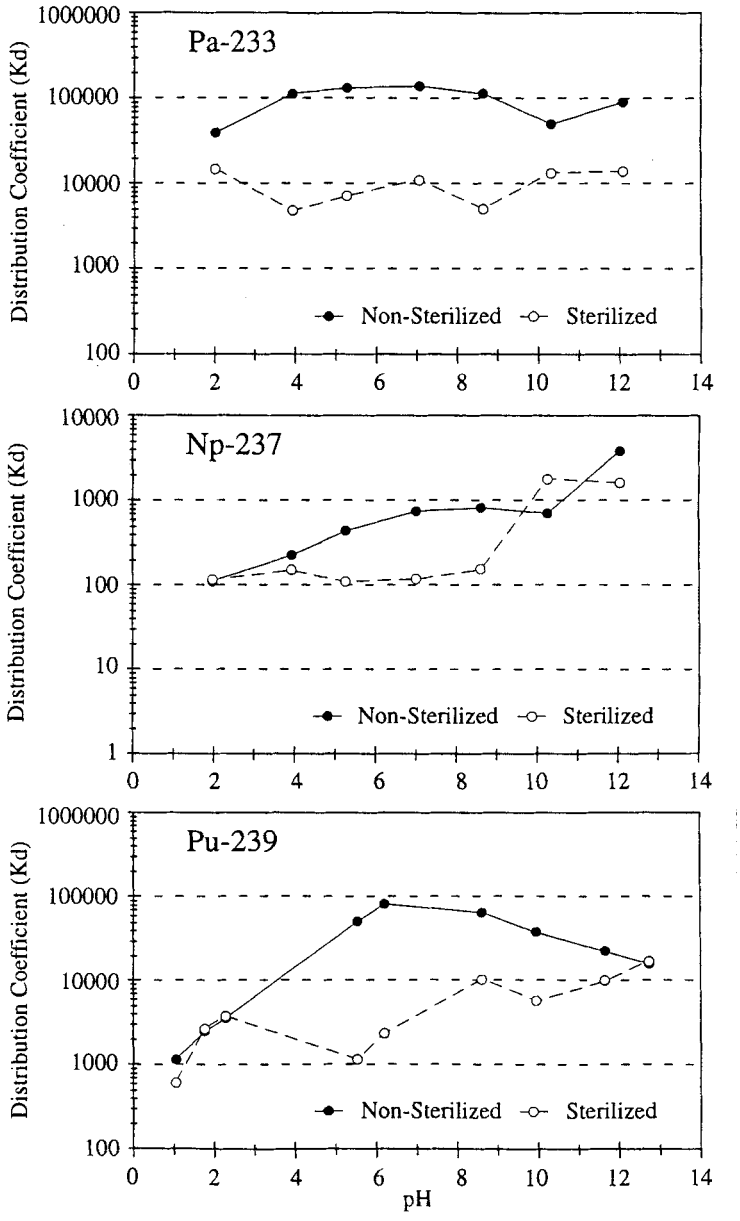

Figure 2. Distribution coefficients of ^{233}Pa, ^{237}Np and ^{239}Pu interacting with non-sterilized and sterilized of anaerobic bacteria and bentonite.

The effects of living (non-sterilized) anaerobic bacteria on the distribution coefficients of ^{233}Pa, ^{237}Np and ^{239}Pu were further examined in mixtures of anaerobic bacteria and bentonite, Figure 2. Again, there were a considerable differences in Kd values of these radionuclides; the difference was especially marked between two groups, ^{233}Pa and ^{239}Pu, and ^{237}Np. For the mixed solution, the distribution coefficients of ^{233}Pa and ^{239}Pu remained under a few thousand for both the non-sterilized and the sterilized solutions in a strong acidic environment, Figure 2.

When the surrounding environment became more closer to the optimum conditions such as at pH 6.5, the distribution coefficient jumped again to more than 100,000 for ^{233}Pa and more than 90,000 for ^{239}Pu for the non-sterilized mixture, while that for the sterilized mixture remained less than

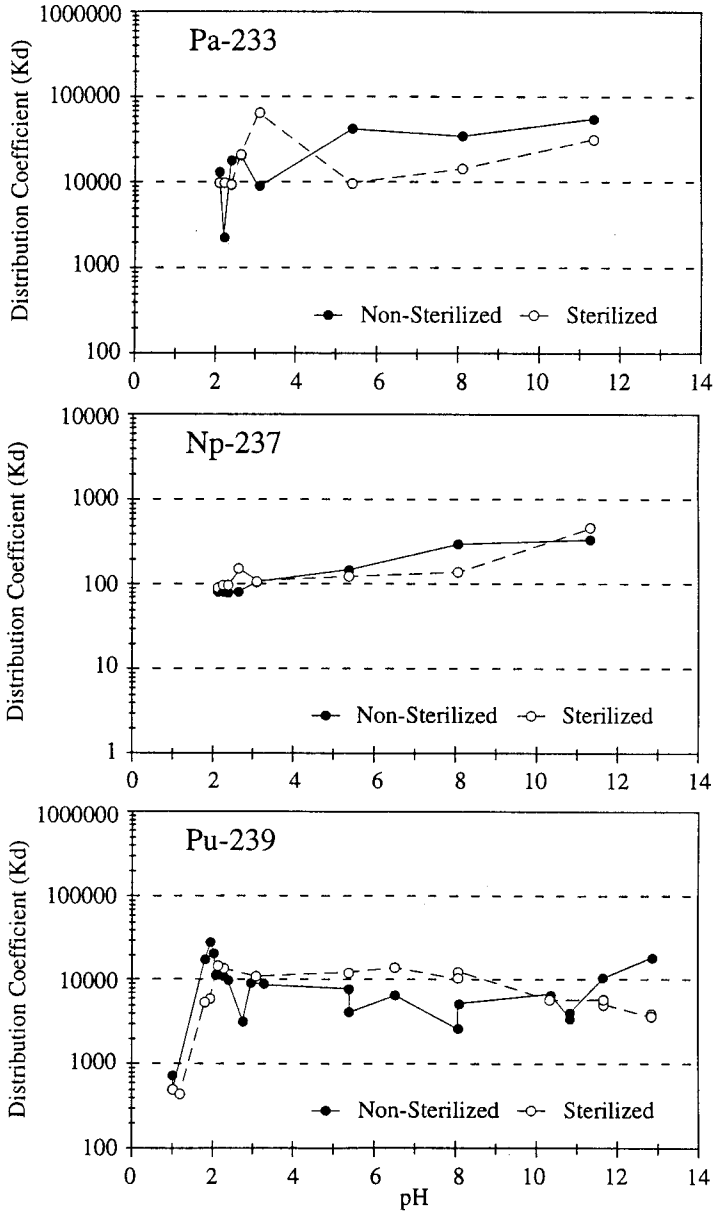

Figure 3. Distribution Coefficient of ^{239}Pu interacting with non-sterilized and sterilized bentonite.

10,000 in this pH range. For both radionuclides, the distribution coefficients for the non-sterilized mixture increased by over 35-fold relative to those of the sterilized mixture in a comfortable environment. When the environment became extremely alkaline, the distribution coefficients for both non-sterilized and sterilized mixtures reached similar values. This is further evidence that there is a definite biological contribution to the distribution coefficients of ^{233}Pa and ^{239}Pu.

The effects of sterilization (autoclaving) of the bentonite on the distribution coefficients of ^{233}Pa, ^{237}Np and ^{239}Pu were examined with changes in pH. The distribution coefficients of all radionuclides investigated for both non-sterilized and sterilized bentonite were similar and constant except at a low pH of 1.02. The values showed a narrow range for most of the pH range, Figure 3. In other words, the differences in the distribution coefficients of ^{233}Pa, ^{237}Np and ^{239}Pu obtained for non-sterilized and sterilized anaerobic bacteria were not caused by sterilization of the bentonite but by whether the anaerobic bacteria were living or dead.

Almost all types of bacteria will be carried to man-made geologic disposal sites. Over a century or more, these sites will be ideal places to flourish for some types of bacteria. The effects of bacteria should be investigated further to establish safe geologic disposal sites for high level radioactive wastes (Stroes-Gascoyne, S. and West, J. M. 1995, Francis, 1994).

CONCLUSIONS

Based on the preliminary experimental results reported in this paper, the following conclusions were obtained. Living bacteria played considerable roles interacting with ^{233}Pa, ^{237}Np and ^{239}Pu. The effects, however, were not the same and were separated into two groups; ^{233}Pa and ^{239}Pu, and ^{237}Np. The distribution coefficient (Kd) values for the living anaerobic bacteria reached more than 100,000 between neutral pH values of 6.83 and 8.25, while those for sterilized bacteria were less than 10,000, Figure 1. The Kd for ^{237}Np was low and the microbial effects were not significant.

For the mixtures of bacteria and bentonite, the Kd values of ^{233}Pa and ^{239}Pu showed similar values to those of living sulfate-reducing bacteria and the Kds for ^{237}Np were not high for mixtures with living bacteria. The interactions of ^{233}Pa, ^{237}Np and ^{239}Pu with bentonite were not affected by sterilization. The other important biological effects such as the production of organic materials and gases when bacteria decompose were not investigated in this report.

ACKNOWLEDGEMENTS

A part of this investigation was financially supported by the Ministry of Education of Japan (Monbusho), Ministry of Foreign Affairs (JSTF) of Canada.

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