MASTER

CHEMICAL REACTIONS IN THE BEDROCK-GROUNDWATER SYSTEM OF IMPORTANCE FOR THE SORPTION OF ACTINIDES

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INTRODUCTION

Most suggested alternatives for deep underground disposal of high-level radioactive wastes rely upon several independent barriers like resistant canister materials, waste forms of low solubility in groundwaters and the use of back-fill material of low permeability and with nuclide retaining capacity. These barriers would retard the eventual release of radionuclides from the repository into the groundwater/bedrock system. The final and the only non-engineered barrier would be the host-rock itself. It would be desirable if the rock alone would be able to retain the long-lived radionuclides coming from the waste for long enough times to allow decay to harmless activity levels before they might reach the biosphere.

The biological hazards from high-level reprocessing waste as well as from unprocessed spent uranium fuel are dominated by the actinides and their daughter products (americium, plutonium, neptunium, thorium, radium) from about three hundred years after discharge from the reactor up to millions of years. In order to allow predictions of the migration of the actinides in the ground, the chemical behavior of these elements in groundwater under environmental conditions and their interactions with geologic media must be studied in detail. Under the anoxic conditions to be expected in a deep underground repository in igneous rock,¹ the

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actinides would be expected to exist predominantly in the tri- and tetravalent states.² The aqueous chemistry of the actinides in these valence states and at environmental pH-levels is largely dominated by hydrolysis reactions.² In oxic systems like surface waters, the penta- and hexavalent states would predominate (for uranium, neptunium, and possibly also plutonium). For these higher valence states, considering AnO_2^+ and AnO_2^{2+} species, the aqueous chemistry would be entirely different at environmental pH levels, with a much lower degree of hydrolysis and higher overall solubility.^{2,3} In this paper, studies of the sorption of americium (trivalent) and neptunium (pentavalent under oxic conditions) on some major rock-forming minerals of igneous rocks and accessory minerals are reported.

MINERALS AND GROUNDWATER IN IGNEOUS ROCKS

The igneous rocks, which are usually classified according to mineralogic composition, grain size and origin, are composed of a small number of major rock-forming minerals. The main constituents of silica-rich rock types like granite are quartz, feldspars, micas and amphiboles, while silica-poor rocks like basalt are dominated by feldspars, pyroxenes and olivine. Moreover, there are some common accessory minerals which would be of importance in a natural system, either for controlling the redox potential or as sources of complexing anions, such as pyrites, apatite, and marble. The minerals and the composition of the two granites employed in these studies have been reported previously.^{4,5}

Based on prevailing mineral/groundwater equilibria and available groundwater analysis data,^{1,5} an artificial groundwater was prepared for use in these studies whose composition has been reported previously.⁴ The composition of this water was not significantly altered by contact with the minerals for several months, except for quartz (giving an increased concentration of total SiO_2 by a factor of 4-5) and hornblende (giving an increased concentration of Ca by a factor of 3).

EXPERIMENTAL

The sorption of americium and neptunium was measured as a function of pH for the minerals and rocks using a batch technique described in detail previously.⁴ All minerals were obtained from Ward's Natural Science Establishment and the rocks from Pacific Northwest Laboratory.⁶ The purity of the minerals was checked by X-ray diffractometry only. Existing impurities were reasonably low (within 5 percent).

The autoradiographic technique employed in these studies used a Polaroid 545 film holder and Polaroid type 57 film. The granite

slabs were mounted in a light-tight box and then covered with a ZnS coated mylar scintillator. This assemblage was placed in direct contact with the Polaroid film by a lever actuated from outside the light-tight box.

RESULTS AND DISCUSSION

The sorption in terms of distribution coefficients (K_d ; moles/kg solid per moles/m³ water) for americium and neptunium is given in Figures 1 and 2 for the various minerals.

Fig. 1. Distribution coefficients vs pH for ²⁴¹Am on selected minerals.

Fig. 2. Distribution coefficients vs pH for ²³⁵Np on selected minerals.

For americium, similar sorption isotherms were obtained for all the minerals studied. The distribution coefficients increase from low values at pH 4 to their maximum values at pH 6.5-8 and then tend to level out or slightly decrease at higher pH. Among the common minerals of igneous rocks, the order of increasing sorption is quartz, the feldspars with augite and olivine, kaolinite and biotite. Hornblende deviates from the general behavior of the other minerals, probably due to the presence of calcite as an impurity, which strongly buffers pH to 7-8.5. The difference between the low-sorbing quartz and the high-sorbing biotite is, however, only about one order of magnitude in terms of distribution coefficients. The cation exchange capacities of the minerals seem to be correlated to their specific surfaces, although there is no quantitative correlation with the distribution coefficients. In most of the systems, however, higher distribution coefficients were obtained for minerals with high surface area of cation exchange capacity. Sorption studies in 4 M NaCl show no significant salt dependence on the sorption in the pH range 4-9 with the exception of biotite and kaolinite.⁴ This result excludes ion exchange as the predominant sorption mechanism. In the case of biotite and

kaolinite the salt dependence only appears at pH below 5. Hydrolysis of americium in aqueous solution would be noticeable above pH 5 (ca. 1% hydrolyzed at pH 5, 50% at pH 6.5 and more than 99% at pH $\geq$ 8) considering the hydrolysis behavior of a typical trivalent actinide.² Thus, the hydrolysis in the aqueous phase seems to be one parameter that can account for the shape of the K_d vs pH-curves. It should be pointed out that the concentration level (2×10^{-9} M) is below the expected total solubility in the pH range that was studied;^{2,3} therefore these sorption reactions cannot be considered as precipitation phenomena.

Also for neptunium, similar sorption isotherms were obtained for the various minerals, with low distribution coefficients at pH below 7-7.5 and then a sharp increase with increasing pH. The order of increasing sorption seems to be the same as for americium, and with a difference between quartz and biotite about one order of magnitude for the distribution coefficients. Sorption studies in 4 M NaCl indicate a slight salt dependence that for most of the minerals is opposite to what would be expected for an ion exchange process, since slightly higher distribution coefficients were obtained in 4 M NaCl than in the groundwater.⁷ This may, however, be due to the presence of carbonate in the groundwater, leading to the formation of anionic carbonate complexes. (For biotite and kaolinite, lower distribution coefficients were obtained in 4 M NaCl than in groundwater.) The hydrolysis of pentavalent neptunium in aqueous solutions would be noticeable at pH above 7 (ca. 1% hydrolyzed at pH 7, 50% at pH 8.5 and more than 99% at pH $\geq$ 10).² Thus, just for americium, there seems to be a relationship between sorption and hydrolysis in the aqueous phase. It can be concluded that the pH of the aqueous phase seems to be one of the most important parameters that determines the sorption on a solid surface.

The sorption on the two granite types is given in Figure 3. The sorption isotherms fall within the expected range covered by the curves for the individual minerals indicated by dashed lines. The distribution coefficients of the rocks are, however, not equal to the weighted average values of the distribution coefficients of the individual discrete minerals of the rock. The only apparent difference in composition between the Climax Stock and Westerly granites that could explain the differences in observed distribution coefficients is the higher biotite concentration in the Climax stock granite.⁵ Probably different degrees of weathering and decomposition would largely influence specific surface area and sorption characteristics. An error due to fractioning of the rock minerals in the crushing/sieving process cannot be excluded. Regardless of these uncertainties, a fair prediction of the distribution coefficient for the rock at a certain pH using data for the individual minerals seems to be feasible. Since the sorption values on the various minerals are similar, an estimated value for rock would always be within a factor of three from the correct value.

Such an estimate would be fully adequate for the use in a migration or safety analysis and may not be worse than many values based on single measurements reported in the literature.

A second mechanism of sorption that has been observed for both Am and pentavalent Np is one involving minerals that contain strong complexing anions. Figure 4 gives sorption of Am on four such minerals. It can be seen in the case of apatite, marble, and dolomite that the sorption is quite strong and pH independent in contrast to the quartz sorption. That strong sorption is most likely due to surface complex formation reaction with PO_4^{3-} and CO_3^{2-} groups. A similar behavior toward Np has been observed for apatite but not for the carbonate containing minerals. This type of sorption reaction could have strong implications for waste isolation since apatite is fairly commonly dispersed in igneous systems and the carbonate minerals are quite common in various sedimentary rock formations.

Fig. 3. Distribution coefficients for ^{241}Am and ^{235}Np vs pH on granites.

Fig. 4. Distribution coefficients for ^{241}Am on accessory minerals vs pH.

A third and final mechanism of sorption involving pentavalent Np reduction by Fe(II)-containing minerals is illustrated in Figure 5. The sorption in these experiments was conducted on Climax stock granite slabs. The slab picture in Figure 5 shows pyrite grains as white, quartz as light gray, the feldspars as dark gray, and biotite as black. It can be seen that on the granite with oxidized surface the sorption is not specific for any mineral. In contrast, the sorption on a fresh surface in air exhibits strong correlation to the Fe(II)-containing minerals (pyrite and biotite). This sorption reaction is enhanced further by purging the solution with nitrogen to get rid of excess oxygen. This reduction of Np by Fe(II)-containing minerals will be of great significance in evaluating migration of radioactive waste through geologic media, not only for Np but Tc, Pu, and U.

CLIMAX STOCK GRANITE

Np IN NITROGEN

Np IN AIR

Np ON OXIDIZED SURFACE

Fig. 5. Autoradiograph of ^{237}Np on Climax stock granite.

CONCLUSIONS

There appears, based on data presented in this paper, that there are three major mechanisms operating to immobilize actinides that might leach out of a nuclear waste repository. The first mechanism appears to involve sorption that correlates with hydrolysis or carbonate complex formation reactions. These reactions have their strongest sorption for Am in the pH range 7-9 and for Np 8-10. These are both reasonable pH's one could expect in a deep geologic repository. The second mechanism seems to involve complex formation on the surface of certain minerals that contain such anions as phosphate and carbonate. Energetically, this reaction appears to be stronger than the first surface sorption reaction and is very pH independent. The third and last mechanism involves reduction of Np by Fe(II)-containing minerals. This is possibly the most important of the sorption mechanisms for nuclear waste isolation since the higher valent actinides tend to be the most mobile. This could mean that NpO_2^+ , UO_2^{2+} , TcO_4^- , and PuO_2^{2+} could be reduced to their less mobile NpO_2 , UO_2 , TcO_2 , and PuO_2 states, respectively.

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