

Article

Effects of Groundwater Humic Substances on Sorption of Np(V) on Sandy materials

S. Nagao^{1*}, Y. Sakamoto², R. R. Rao³ and N. Fujitake⁴

¹ Faculty of Environmental Earth Science, Hokkaido University, N10W5, Kita-ku, Sapporo 060-0810, Japan

² Tokai Research and Development Center, Japan Atomic Energy Agency, 2-4, Shirakata Shirane, Tokai, Ibaraki 319-1195, Japan

³ Chalk River Laboratories, Atomic Energy of Canada Limited, Chalk River, Ontario K0J1J0, Canada

⁴ Faculty of Agriculture, Kobe University, 1-1 Rokkodai, Nada-ku, Kobe 657-8501, Japan

Abstract

Sorption behavior of Np(V) onto sandy materials (sand, tuffaceous sand and sandy rock) was studied in the absence and presence of humic substances (HS) using a batch method at pH 5–6 and ionic strength of 0.01 M. Aquatic HS were isolated from lake water, shallow fresh groundwater, and deep saline groundwater using the XAD extraction method. The effects of shallow groundwater HS on the Np(V) sorption depend on the mineralogical components of sandy materials. The distribution coefficient (K_d) of Np(V) increased in the presence of HS. The K_d values were in the order of sand < tuffaceous sand < sandy rock samples. The Np(V) sorption in the presence of HS with different origin for the sandy rock sample was divided into two groups. The K_d values were positively correlated with aliphatic carbon contents of the lake and the shallow groundwater HS, except for the deep saline groundwater HS. These results indicate that the characteristics of sandy materials and groundwater HS are important factors determining the Np(V) sorption because of the presence of Np(V)-bound HS.

Keywords: Sorption/ Neptunium/ Groundwater humic substances/ Sand/ Tuffaceous sand

Introduction

Neptunium in the form of ²³⁷Np(V) is an important component of long-term radioactive waste because of its long half-life (half-life, $T_{1/2}=2.14 \times 10^6$ yr) and the potential hazard it poses to humans. An understanding of Np(V) sorption behavior is necessary to describe the transport of Np(V) in a groundwater system quantitatively.

Results of recent studies have underscored the important role of soluble and colloidal humic substances (HS), which are polyelectrolytic organic acids present in groundwater at concentrations of 0.1–100 mg/l (Thurman, 1985; Nagao, 1995), in the migration behavior of actinides in underground environments (Choppin, 1992; Kim and Buckau, 1993; Moulin and Moulin, 1995). In the presence of HS, sorption of Np(V) onto soil, sediment, and granite

has been reported by several researchers (e.g., Bigoglio et al., 1989; Righetto et al., 1991; Sakamoto et al., 1995). Most sorption experiments have used commercially available humic acid (HA) and HA extracted from soil and sediment. The study on the influence of groundwater HS on actinides sorption is limited because of difficulties of isolation and purification of HS from a large volume of groundwater. The macromolecular structure and chemical properties of groundwater HS differ from those of soil and sedimentary HS (Thurman, 1985; Malcolm, 1990; Nagao, 1995). The sizes and shapes of HS present in various environments are related to the sorption and migration of actinides in the underground layer (Sakamoto et al., 1995, 2000; Labonne-Wall et al., 1997; Nagao et al., 1998). For those reasons, describing the geochemical behavior of Np(V) is important for understanding the sorption behavior of Np(V) in the

* Corresponding author, Present address: LLRL, KU-INET, Kanazawa University, Wake, Nami, Ishikawa 923-1224, Japan.

presence of groundwater HS.

The purpose of this study is to examine effects of aquatic HS on the Np(V) sorption using four kinds of HS isolated from groundwater by sand, peat, and alternating layers of sand and shale. Sorption experiments for Np(V) in the presence of aquatic HS onto sand, tuffaceous sand, and sandy rock were carried out using a batch method in a medium of 0.01 M NaClO₄ solution at pH 5–6. The above-ground water HS and IHSS reference HS were used for comparing their effects on the sorption of Np(V).

Experimental

Geologic materials

Three kinds of sandy materials were used for Np(V) sorption experiments. Sand was collected from a surface layer at the Glass Block (BG) site at Chalk River Laboratories (CRL) of the Atomic Energy of Canada Limited (AECL). The mean particle size was 0.167 mm. Tuffaceous sand and sandy rock were collected respectively at Shimokita and Mutsu in Aomori Prefecture, Japan. The sand and tuffaceous sand samples were air-dried and then homogenized. The sandy rock was crushed and sieved to a particle size of less than 0.5 mm.

Mineral compositions of the sandy materials were measured using X-ray diffraction method. The main mineral components of sand and tuffaceous sand are quartz and feldspar, which together constituted almost 75% of the sand (Killey et al., 1994) and 70% of the tuffaceous sand (Nagao and Senoo, 1995). The sandy rock has low quartz and feldspar contents of up to 27%, but high contents (34%) of halloysite. Halloysite, allophane, and iron oxides are present in the tuffaceous sand (Nagao and Senoo, 1995) and sandy rock (Rao et al., unpublished data). Major chemical components of these sandy materials were

measured using ICP-AES after digestion using HCl-HF-HClO₄; the results were: tuffaceous sand – SiO₂ 77.6%, Al₂O₃ 11.3%, Fe₂O₃ 1.85%; sandy rock – SiO₂ 49.26%, Al₂O₃ 20.9%, Fe₂O₃ 9.65%; no data for sand.

Preparation of groundwater humic substances

Groundwater humic substances (HS) were taken from three area: GB site, Tokachi area and Mobara area. The GB site is in the lower Perch Lake Basin at Chalk River, 200 km northwest of Ottawa, Ontario in Canada. Tokachigawa hot spring *Tokachi*, a vegetable moor hot spring, is located in the southeastern part of Hokkaido, Japan. Mobara area is located in south Kanto, Japan and is the sedimentary basin of the Boso Peninsula. The Mobara groundwater is saline and its chemical composition resembles that of present seawater (Kamei, 1997). The pH, major cation and anion, and dissolved organic carbon (DOC) concentration in the groundwaters are presented in Table 1. Detailed chemical properties of the groundwaters and features of these locations are reported by Jackson and Inch (1980), Killey et al. (1994), Kamei (1997), and Kamei et al. (2000).

In all, 20,000 l of groundwater were collected from a sand layer at the GB site in the CRL. The GB HS was initially concentrated from the groundwater using a nanofiltration system. The nanofiltration retentate solution was loaded onto a column packed with an Amberlite XAD-7 resin (Roham and Hasas) after adjusting the pH to 1.5. Following elution from the XAD-7 column with 0.1M NaOH solution, the solution was passed through a cation exchange resin (AG MP-50; Bio-Rad Laboratories Inc.) to desalinate the elute and to convert the HS to protonated forms. The HS was then freeze-dried. A major part of the groundwater GB HS consists mainly of FA, based on the molecular size distribution, ¹³C-NMR spectra

Table 1. Sampled groundwaters and a lake water, sampling depth, sediment types, basic physicochemical parameters and dissolved organic carbon (DOC) concentration.

Site	Sampling* depth (m)	Lithology	pH	Na ⁺	K ⁺ (mg/l)	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	DOC
Glass Block site	2.8–3.6	Sand	6.7	4.8	2.6	25	11	5.6	15.7	----	2.4
Tokachi**	ca.30	Peat	8.0	462	8.4	10	1.3	551	----	334	81
Mobara	792–1202	Sand, Shale	7.9	10700	3020	229	315	18800	22	903	56
Nordic***	0	----	4.0–4.9	----	----	----	----	----	----	----	10–25

*Sampling depth intervals from the ground surface.

**Hokkaido Institute of Public Health (1997).

***IHSS website.

(Nagao and Sakamoto, 2001), and three-dimensional fluorescence spectra (Nagao et al., unpublished data).

The Tokachi and Mobarra HS were also isolated and purified using a similar procedure with DAX-8 resin from 200 l and 600 l of groundwater, respectively. The sorbed fraction was recovered by back elution with 0.1M NaOH. Acidification of the extract to pH2 led to the precipitation of HA. The purification of HA and FA was carried out by the method of Thurman and Malcolm (1981). The ratio of fulvic to humic acids was 10 for the Tokachi and two for the Mobarra. A reference HS, Nordic fulvic acid (FA), was purchased from the International Humic Substances Society (IHSS). Isolation and purification of the FA were carried out using the XAD extraction method of Thurman and Malcolm (1981).

Characterization of humic substances

The amounts of carbon, nitrogen and hydrogen were measured with a CHN analyzer (Model 2400; PerkinElmer Inc.). The total ash content was determined using the combustion method. The O content was calculated by subtracting the C, H, N, and ash contents from the total weight.

Solution ^{13}C -NMR spectra from the GB HS, Mobarra FA, Tokachi FA, and Tokachi HA were recorded at 62.896 MHz using a spectrometer (DPX250; Bruker Ltd.) by inverse gated decoupling with a 45° pulse (Fujitake and Kawahigashi, 1999). The relative content of each carbon species was calculated based on the percentage of four regions for saturated aliphatic C (10–60 ppm), carbohydrate C (60–110 ppm), aromatic C (110–165 ppm), and carboxyl C (165–220 ppm) to the whole area of ^{13}C NMR spectra. However, the range of chemical shifts for aliphatic and carbohydrate C of the Tokachi FA and HA was modified because of the spectral features as follows: aliphatic C at 10–48 ppm, and carbohydrate C at 48–105 ppm.

The molecular size distribution of HS was measured using ultrafiltration method. The sample solution was ultrafiltered sequentially using simple ultrafiltration filters (Millipore Ultrafree CL filters) having nominal cut-off molecular weight of 100 k Dalton (Da), 30 kDa (polyethersulfone membrane filters), 10 kDa and 5 kDa (regenerated cellulose membrane filters). The concentrations of HS in each size fraction were determined using a UV-VIS spectrophotometer (U-3300; Hitachi Ltd.) at 280 nm.

Sorption experiments

Sorption experiments for Np(V) onto the sandy materials were carried out in 0.01 M NaClO_4 solutions at HS concentrations of 0, 1, 5, 10, 20, 50, 100 and 154 mg/l. The 0.8 g of sandy material was mixed with the HS solution (8 ml) in a polycarbonate centrifuge tube with a screw cap. The solution with the sandy material was agitated gently on a reciprocal shaker for 7 days at 60 rpm after addition of ^{237}Np tracer. The initial concentration of Np(V) was 9.7×10^{-6} M. The liquid phase was separated by centrifugation and filtration with 450 nm filters (Millipore Corp.). All sorption experiments were performed in duplicate or triplicate. The radioactive concentration of ^{237}Np was counted using a liquid scintillation counter (Tri-Carb 2550, Packard Ltd.). We measured the solution pH using a pH meter (F-21; Horiba Ltd.): the final pH of the solutions was pH 5–6. The distribution coefficient (K_d) is defined as the ratio of the concentration of Np retained using the sandy materials at the end of sandy material/solution contact period to the concentration of Np remaining in solution as follows:

$$K_d = ((C_o - C_e)/C_e)V/W$$

C_o : initial concentration of ^{237}Np in the solution (Bq/ml)

C_e : concentration of ^{237}Np in the solution after the sorption experiment (Bq/ml)

V : volume of solution (ml)

W : weight of sandy material (g).

The sorption of HS was also studied using the same procedure with the exception of a solid to solution ratio of 1:10. The ratio was changed to 1:2 because of the low sorption of HS on sandy materials. The HS concentration in the solution after the contact period of seven days was measured using the UV-VIS spectrophotometer at 280 nm.

Results

Characteristics of groundwater humic substances

The elemental composition of the HS is presented in Table 2. The atomic ratio of H/C is 0.9–1.3 within river and groundwater HS (Malcolm, 1990; Artinger et al., 2000). The C/N ratio is 23 for the Mobarra FA, 33–39 for the Tokachi HA and FA, and 84–90 for the GB HS and Nordic FA. The atomic ratios of H/C and O/C are lower in HA than FA. Other studies have reported these features (Nagao, 1995; Artinger et al., 2000).

Table 2. Major elemental compositions of humic substances (HS) used in this study.

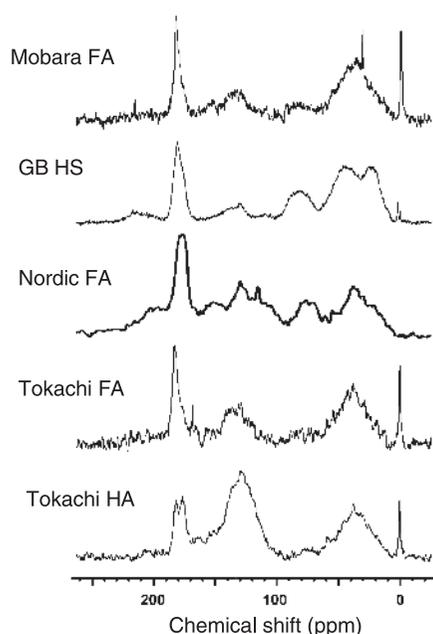
Sample	C	H	N	O	S	Ash (%)
	(ash-free basis%)					
Groundwater HS						
GB HS	53.1	5.66	0.74	39.8	0.19	1.1
Mobara FA	50.8	4.67	2.48	42.3	---	1.1
Tokachi FA	52.4	5.60	1.57	40.4	---	5.0
Tokachi HA	59.6	4.48	2.13	33.8	---	0.8
IHSS reference HS						
Nordic FA*	52.3	3.98	0.68	45.1	0.46	0.5

*IHSS web site.

Table 3. Composition of carbon species estimated from ^{13}C NMR spectra in lake (Nordic FA) and groundwater humic substances (HS).

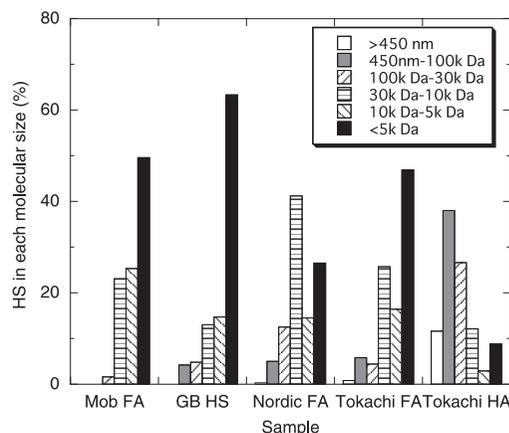
Sample	Aliphatic	Carbohydrate	Aromatic	Carboxylic	Carbonyl (%)
Groundwater HS					
GB HS	49	17	11	18	5
Mobara FA	38	19	22	18	3
Tokachi FA	29	20	28	21	3
Tokachi HA	21	11	52	15	2
IHSS reference HS					
Nordic FA*	18	19	31	24	10

*Thorn et al. (1989).

**Fig. 1.** Solution ^{13}C NMR spectra of HS isolated from a lake water, shallow fresh groundwaters, and a deep saline groundwater. The ^{13}C NMR spectrum of Nordic FA is taken from Thorn et al. (1989).

The ^{13}C NMR spectra of the HS are shown in Fig. 1 and the carbon species distribution is presented in Table 3. Two broad peaks of aliphatic carbon at 10–48 ppm were detected for GB HS. The carbohydrate carbon at 48–105 ppm and/or 60–100 ppm is clearly detected as a broad peak for the GB HS, Mobara FA, Tokachi FA and Nordic FA. The content of aromatic carbon is 11–28% for groundwater FAs, 31% for the Nordic FA, and 52% for the Tokachi HA. The aromatic carbon of groundwater FA is lower than that of the groundwater from the Gorleben FAs (23–41%) (Kim et al., 1990) and the Fuhrberg FAs (33–35%) (Albert et al., 1992) with higher DOC concentration of groundwater in Germany. The COOH content estimated from ^{13}C NMR spectra is 7.5–8.0 meq/g for the Tokachi HA, GB HS, and Mobara FA, and 9.2–10.5 meq/g for the Tokachi FA and Nordic FA.

The molecular size distribution of the HS is depicted in Fig. 2. The dominant size of Tokachi HA is 450 nm – 100 kDa. The FAs have dominant size fractions with 30–10 kDa for the Nordic FA and less than 5 kDa for the GB HS, Mobara FA, and Tokachi FA. These results show that the various groundwater HS used in this study have different structural features.

**Fig. 2.** Molecular size distribution of a lake fulvic acid (Nordic FA), shallow fresh groundwater HS (BG HS), Tokachi FA and HA) and a deep saline groundwater FA (Mobara FA).

Effects of groundwater humic substances on Np(V) sorption for sandy materials

Sorption of Np(V)

Sorption behavior of Np(V) as a function of HS concentration is shown in Fig. 3. The groundwater HS from the GB site was used in this experiment. The increase in solution pH with HS concentration was ca. 0.4. The degree of Np(V) sorption is in the order of sand < tuffaceous sand < sandy rock in the absence of HS. As portrayed in Fig. 3, the Np(V) sorption for tuffaceous sands and sandy rock is enhanced in the presence of HS at pH 5–6. The ΔKd value is 0.8 ml/g for tuffaceous sand and 2.0 ml/g for the sandy rock at the HS concentration of 154 mg/l (Table 4). The increased percentage is 80% for the tuffaceous sand and 69% for the sandy rock.

On the other hand, the Kd of Np(V) decreases at the sand-GB HS experimental system (Fig. 3). The Kd at the HS concentration of 1–10 mg/l, which is typical concentration range, is lower than that for concentrations of HS greater than 50 mg/l. The Kd values of Np(V) are not shown in Fig. 3, but they are 0.6 ± 0.4 ml/g, 0.4 ± 0.2 ml/g and 0.2 ± 0.2 ml/g, respec-

Table 4. Kd of Np(V) onto sand, tuffaceous sand, and sandy rock samples in the absence and presence of a shallow groundwater HS from the GB site in the AECL.

Sandy materials	pH	Kd of Np(V) (ml/g)		ΔKd (ml/g)
		HS 0 mg/l	HS 154 mg/l	
Sand	5.4–5.8	0.8 ± 0.3 (4)	0.4 ± 0.1 (2)	-0.4
Tuffaceous sand	6.0–6.3	1.0 ± 0.09 (2)	1.8 ± 0.1 (2)	0.8
Sandy rock	5.9	2.9 ± 0.1 (2)	4.9 ± 0.02 (2)	2.0

The Kd values indicate average and standard error. The numbers in parentheses show the numbers of replicate experiments.

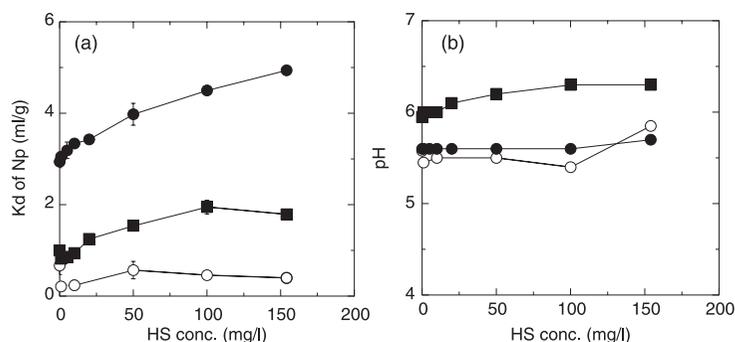


Fig. 3. Distribution coefficient (Kd) of Np(V) for the sand (\circ), tuffaceous sand (\blacksquare), and sandy rock (\bullet) as a function of humic substances (HS) concentration in a 0.01 M NaClO_4 solution (a) and its solution pH (b). The groundwater HS from the sand layer (GB) was used in sorption experiments.

tively, at HS concentrations of 200 mg/l, 300 mg/l and 400 mg/l. The effects of HS on the Np(V) sorption for the sand are small for the HS concentration range of 1–300 mg/l.

Sorption of humic substances

For GB HS-sandy materials, the amounts of the sorbed HS to total concentration mutually differ (Fig. 4). The sorption of HS follows the sequence sand < tuffaceous sand \leq sandy rock. The sorbed HS increases with increasing HS concentration. The rate of increase differs from the sand and the tuffaceous and sandy rock systems. The minerals with pH-dependent charge such as halloysite, allophone, and iron oxides are present for the tuffaceous sand and sandy rock samples, but are not found for the sand (Killey et al., 1994; Nagao and Senoo, 1995). These results indicate that the sorption of HS depends on the mineralogical components of sandy materials.

Np(V) sorption in the presence of humic substances with different origin

Figure 5 shows sorption behavior of Np(V) in the presence of four groundwater HS and a Nordic FA on the sandy rock. The variations in solution pH were ca. 0.1 for each experimental system. The Kd value in the presence of HS from the lake and the shallow fresh groundwaters (Nordic FA, GB HS, Tokachi FA and HA) increases with increasing HS concentration. The percentage of increased Kd (ΔKd) at the HS concentration of 100 mg/l was 20% for the Nordic FA and 30–40% for the shallow groundwater

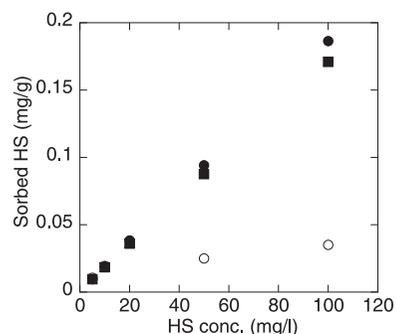


Fig. 4. Sorption of groundwater HS (GB HS) on sand (\circ), tuffaceous sand (\blacksquare), and sandy rock (\bullet) as a function of HS concentration in a 0.01 M NaClO_4 solution. The solution pH was 4.9–5.8.

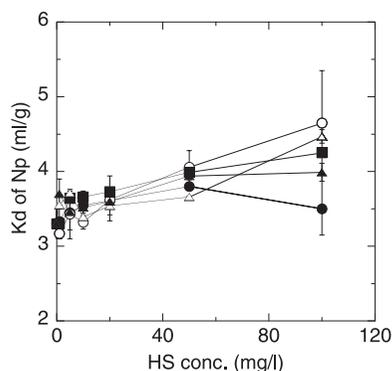


Fig. 5. K_d of Np(V) in the presence of lake and groundwater HS for the sandy rock sample as a function of the HS concentration in a 0.01 M NaClO₄ solution at pH 5.3–6.5. The symbols indicate the following: Mobara FA (●), GB HS (○), Nordic FA (▲), Tokachi FA (△), and Tokachi HA (■).

HS (Table 5). On the other hand, the K_d value of Np(V) in the presence of Mobara FA from the deep saline groundwater HS exhibits an almost constant value at these concentration ranges. The Np(V) sorption on sandy rock varies according to the concentration and characteristics of HS.

Discussion

Effects of sandy materials on Np(V) sorption in the presence of humic substances

The extent of Np(V) reportedly depends on the mineralogical composition of rocks and solution characteristics such as pH and ligands (Righetto et al., 1991; Ticknor, 1993; Tochiyama et al., 1995). In this study, the variations in solution pH at the sorption experiments were negligible: they were less than 0.4 at each sorption experimental system and the variation range of pH 5–6 (Fig. 3). The differences in mineralogical composition were found for the sand, tuffaceous sand, and sandy rock using X-ray diffraction method.

We compared the sorption behavior of Np(V) and HS described above to that of the HS concentration of 5 mg/l to elucidate the influence of HS on Np(V) sorption by sandy materials. The result is shown in Fig. 6. The K_d of Np(V) increases with increasing amounts of sorbed HS for the tuffaceous sand and sandy rock. On the other hand, no relation pertains between the sorption of Np(V) and the HS for the

Table 5. K_d of Np(V) for sandy rock in the presence of humic substances (HS).

Type of HS	pH	K_d of Np(V) (ml/g)*		ΔK_d (ml/g)**
		HS 10 mg/l	HS 100 mg/l	
Mobara FA	5.5	3.6±0.2	3.5±0.05	0.2
GB HS	5.6	3.3±0.09	4.7±0.01	1.4
Nordic FA	5.0	3.5±0.08	4.0±0.1	0.7
Tokachi FA	5.1	3.4±0.01	4.5±0.09	1.2
Tokachi HA	5.1	3.7±0.08	4.3±1.1	1.0

The K_d of Np(V) in the absence of HS was 3.3±0.2 (10).

*The K_d indicates mean and ± standard error.

** ΔK_d was calculated by subtracting K_d value in the absence of HS from that at the HS concentration of 100 mg/l.

sand experimental system. Righetto et al. (1991) reported that zeta potential of alumina surface at pH 5–7 decreased with increasing HA concentration in solution because of the sorption of HA. The presence of HA resulted in greater Np(V) sorption. Similar enhancement of Np(V) sorption was observed at the Np(V)-HA-kaolinite system (Niitsu et al., 1997) and the Np(V)-HA-iron oxides system at pH 5–7 (Jain et al., 2007). Therefore, interaction of Np(V) with the solid phase, tuffaceous sand and sandy rock like that depicted in Fig. 3, might be enhanced by a greater surface content of HS because these sandy materials contain minerals with pH-dependent charge such as iron oxides, halloysite, and allophane. The sand has low sorption capacity for HS so that the enhancement of Np(V) sorption is unclear. The increases in Np(V) sorption might be controlled by the presence of groundwater HS and mineral composition of the sandy materials.

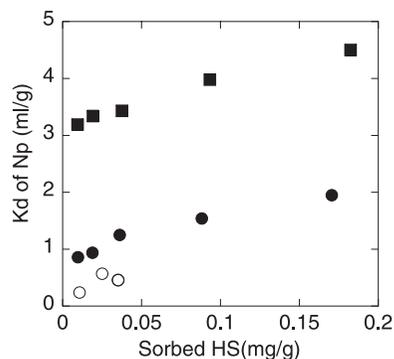


Fig. 6. Relation between K_d of Np(V) and the amounts of GB HS sorbed by sand (○), tuffaceous sand (●), and sandy rock (■).

Effects of characteristics of humic substances on the Np(V) sorption

The sorption behaviors of Np(V) in the presence of HS with various origins by sandy rock differ for groundwater and lake water HS (Fig. 5). The ΔKd values are 0.2–1.4 ml/g (Table 5). Davis and Gloor (1981) reported that HA with different molecular sizes influenced its sorption ability onto different types of soil. High molecular size fraction of HA had greater sorption ability in comparison with the lower molecular size fraction (Tanaka et al., 1997, 2002). As presented in Fig. 2, the dominant molecular size fraction of HS is 100–30 kDa for the Tokachi HA (38%), 30–10 kDa for the Nordic FA (41%), and less than 5 kDa for the groundwater FA (47–63%). Sakamoto et al. (2000) have shown that Np(V) in the presence of Aldrich HA from a commercial reagent was 52% less than 5 kDa and 20% in the size fraction of 30–10 kDa at pH 5 and the HA concentration of 20 mg/l, though Np(V) in the absence and presence of GB HS was less than 5 kDa. Humic substances have polyelectrolytic and size-selective complexation properties for actinides and lanthanides (Monsallier and Choppin, 2003; Nagao et al., 2003, 2007). The structural features of HS might therefore be related to the sorption of Np(V) bound HS on the sandy materials and complexation properties with Np(V).

To elucidate the sorption properties of Np(V) in the presence of HS, we examined the relationship between the ΔKd values of Np(V) and the structural features of HS because the macromolecular structures and chemical properties of HS used in this study different from each other, as described above. Figure 7 shows the ΔKd of Np(V) for the sandy rock sample versus the contents of carboxylic functional groups, aliphatic and aromatic carbon of HS. As pre-

sented in Fig. 7, the ΔKd values have no correlation with the carboxylic contents and the percentage of aromatic carbon and ΔKd of Np(V) except for the Mobara FA. On the other hand, it appears to be a good positive correlation ($r=0.90$) between the aliphatic carbon content and the increased Kd of Np(V), except for the Mobara. These results indicate that the deep saline groundwater HS (Mobara FA) has different sorption properties of Np(V) bound to HS from those of freshwater HS.

Aquatic humic substances are heterogeneous mixtures of organic compounds and their properties vary with environmental conditions (Thurman, 1985; Hessen and Travik, 1998). The decrease in the saturated aliphatic carbon contents directly reflects the increase of the aromatic carbon contents for aquatic FA (Malcolm, 1990; Hessen and Travik, 1998) and soil HA (Swift et al., 1982; Fujitake and Kawahigashi, 1999). With decreasing molecular size of soil and Aldrich HA, aliphatic carbon content decreases whereas aromatic carbon and carboxyl content increases (Swift et al., 1982; Fujitake and Kawahigashi, 1999; Shin et al., 1999). The aquatic FA used in this study has a positive correlation between aliphatic carbon content and percentage of molecular size less than 5kDa except for the Tokachi HA. Therefore, the macromolecular structure of fresh lake and shallow groundwater HS is related to the enhancement of Np(V) sorption for sandy rock. Sorption of HS on the surface engenders fractionation of HS. Selected molecules with aliphatic carbon rich, as a result of Np(V) binding with the HS fraction, might be sorbed on the sandy rock. Consequently, the characteristics of aquatic HS are factors controlling the sorption of Np(V) for the sandy materials.

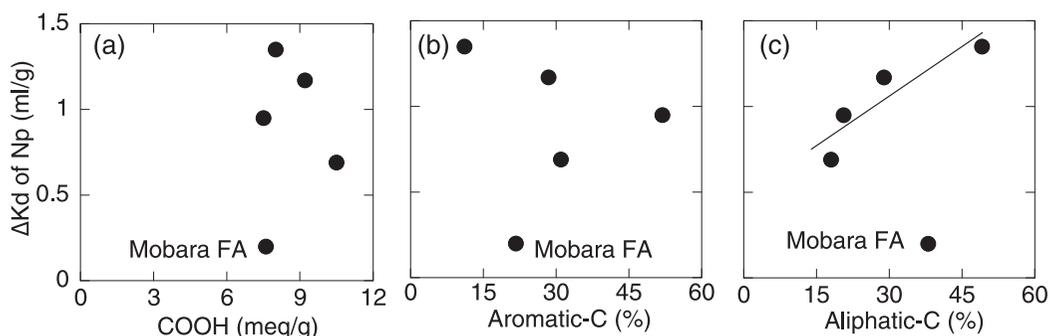


Fig. 7. Increased Kd (ΔKd) of Np(V) for the sandy rock sample at the HS concentrations of 0–100 ml/g versus the contents of carboxylic groups (a), aromatic carbon (b) and aliphatic carbon (c) of HS.

Conclusions

The effects of groundwater humic substances (HS) on sorption of Np(V) for sand, tuffaceous sand, and sandy rock were investigated using a batch method. Three shallow fresh groundwater HS (GB HS, Tokachi FA and Tokachi HA) and one deep saline groundwater HS (Mobara FA) were used together with an IHSS reference HS (lake water FA). Sorption experiments were carried out at pH 5–6, ionic strength of 0.01 M, and the HS concentration range of 0–154 mg/l. Sorption of Np(V) in the presence of GB HS showed two patterns as a function of the HS concentration. Increasing concentrations of the groundwater HS in the solution increased Np(V) sorption for the tuffaceous sand and sandy rock materials. The degree of increase in distribution coefficient (K_d) of Np(V) was as high as 70–80%. Sorption of Np(V) in the presence of GB HS onto sand appeared to show only a small variation. The effects of shallow fresh groundwater HS on the Np(V) sorption depend on the mineralogy of sandy materials such as iron oxides and/or clay minerals.

Characteristics of Np(V) sorption onto the sandy rock were studied in the absence and presence of four HS from groundwater together with the IHSS reference HS using the batch method. The K_d of Np(V) for sandy rock increased with increasing concentrations of three shallow groundwater and reference HS samples, but was constant in the presence of the deep saline groundwater HS. These results indicate that the HS in surface and shallow groundwater might affect sorption of Np(V) on sandy materials at HS concentrations greater than 20 mg/l. The extent of increase in the Np(V) sorption depends on the macromolecular structure of HS in groundwater with different environmental conditions. Therefore, the characteristics of sandy materials and groundwater HS are important factors controlling Np(V) sorption for sandy materials in the presence of HS at pH 5–6.

Acknowledgements.

The authors thank Mr. J. L. Young of AECL for preparation of GB groundwater humic substances and Dr. Y. Nakaguchi of Kinki University for isolation of humic substances from the Tokachi and Mobara groundwater. This work was performed as part of a joint research between JAERI (present: Japan Atomic Energy Agency (JAEA)) and AECL, and as

part of Interorganization Atomic Energy Research Program.

References

- Alberts, J. J., Filip, Z. and Hertkorn, N. (1992) Fulvic and humic acids isolated from groundwater: compositional characteristics and cation binding. *J. Contam. Hydrol.*, **11**, 317-330.
- Artinger, R., Bukau, G., Geyer, S., Fritz, P., Wolf, M. and Kim, J. I. (2000) Characterization of groundwater humic substances: influence of sedimentary organic carbon. *Appl. Geochem.*, **15**, 97-116.
- Bidoglio, G., De Plano, A. and Righetto, L. (1989) Interactions and transport of plutonium-humic acid particles in groundwater environments. *Mat. Res. Soc. Symp. Proc.*, **127**, 823-830.
- Choppin, G. (1992) The role of natural organics in radionuclides migration in natural aquifer systems. *Radiochim. Acta*, **58/59**, 113-120.
- Davis, J. M. and Gloor, R. (1981) Adsorption of dissolved organics in lake water by aluminum oxide. Effects of molecular weight. *Environ. Sci. Technol.*, **15**, 1223-1229.
- Fujitake, N. and Kawahigashi, M. (1999) ^{13}C NMR spectra and elemental composition of fractions with different particle sizes from an Andosol humic acid. *Soil Sci. Plant. Nutr.*, **45**, 359-366.
- Hessen, D. O. and Travik, L. J. (1998) *Aquatic Humic Substances –Ecology and Biogeochemistry–*. Springer, Berlin, p.346.
- Hokkaido Institute of Public Health (1997) Report for analytical data for Tokachigawa hot spring.
- International Humic Substances Society: Chemical Properties of IHSS samples. <http://www.ihss.gatech.edu/chemistry.html>
- Jackson, R. E. and Inch, K. J. (1980) *Hydrogeochemical processes affecting the migration of radionuclides in a fluvial sand aquifer at the Chalk River Nuclear Laboratories*. NHRI Paper No. 7, Science Series No. 104, Nat. Hydro. Res. Int. Inland Wat., Directorate.
- Jain, A., Rawat, N., Kumar, S., Tomar, B. S., Manchanda, V. K. and Ramanathan, S. (2007) Effect of humic acid on sorption of neptunium on hematite colloids. *Radiochim. Acta*, **95**, 501-506.
- Kamei, G. (1997) The source and behavior of iodine dissolving in groundwater in the Mobara gas field. *Shigen Chishitru*, **51**, 145-151 (Japanese with English abstract).
- Kamei, G., Yusa, Y. and Arai, T. (2000) A natural analogue of nuclear waste glass in compacted bentonite. *Appl. Geochem.*, **15**, 141-145.
- Killey, R. W. D., Klukas, M., Sakamoto, Y., Munch, J. H., Young, J. L., Welch, S. J., Risto, B. A., Eyvindson, S. and Moltyaner, G. L. (1994) *The CRNL glass block experiment: radionuclide release and transport during the past thirty years*. p.174, AECL Report RC-1513, AECL.
- Kim, J. I., Buckau, G., Li, G. H., Duschner, H. and Psarros, N. (1990) Characterization of humic and fulvic acids from Gorleben groundwater. *Fresenius J. Anal. Chem.*, **338**, 245-252.

- Kim, J. I. and Buckau, G. (1993) Effects of humic substances on the migration of radionuclides: complexation of actinides with humic substances in natural aquifer systems. In: *Migration of Radionuclides in the Geosphere*. pp.17-24, CEC Report EUR 14690EN.
- Labonne-Wall, N., Moulin, V. and Vilarem, J.-P. (1997) Retention properties of humic substances onto amorphous silica: consequences for the sorption cations. *Radiochim. Acta*, **79**, 37-49.
- Malcolm, R. L. (1990) Variations between humic substances isolated from soils, stream waters, and groundwaters as revealed by ^{13}C -NMR spectroscopy. In: *Humic Substances in Soil and Crop Sciences: Selected Readings* (P. MacCarthy, C. E. Clapp, R. L. Malcolm, P. R. Bloom, eds.), pp.13-35, ASA & SSSA, Madison.
- Monsallier, J.-M. and Choppin, G. R. (2003) Influence of humic acid size on actinide complexation. *Radiochim. Acta*, **91**, 135-139.
- Moulin, V. and Moulin, C. (1995) Fate of actinides in the presence of humic substances under conditions relevant to nuclear waste disposal. *Appl. Geochem.*, **10**, 573-580.
- Nagao, S. (1995) Characteristics of humic substances and TRU-humate complexes in groundwater. *Radioactive Waste Res.*, **1**, 231-242 (Japanese with English abstract).
- Nagao, S. and Sakamoto, T. (2001) Effects of dissolved organic materials on radionuclide migration. In: *Studies on Groundwater Flow and Radionuclide Migration at Underground Environments- Final Report of Collaboration Research between JAERI and AECL-* (H. Ogawa et al., Eds.), pp.51-64, JAE-RI-Research, 2000-052.
- Nagao, S. and Senoo, M. (1995) Migration behavior of carbonate- ^{14}C in tuffaceous soil. *Mat. Res. Soc. Symp. Proc.*, **353**, 1093-1100.
- Nagao, S., Rao, R. R., Killey, R. W. D. and Young, J. L. (1998) Migration behavior of Eu(III) in sandy soil in the presence of dissolved organic materials. *Radiochim. Acta*, **82**, 205-211.
- Nagao, S., Fujitake, N., Kodama, H., Matsunaga, T. and Yamazawa, H. (2003) Association of Am with humic substances isolated from river waters with different water quality. *J. Radioanal. Nucl. Chem.*, **255**, 459-464.
- Nagao, S., Sakamoto, Y., Tanaka, T. and Rao, R. R. (2007) Molecular size distribution of Pu in the presence of humic substances in river and groundwaters. *J. Radioanal. Nucl. Chem.*, **273**, 135-139.
- Niitsu, Y., Sato, S., Ohashi, H., Sakamoto, Y., Nagao, S., Ohnuki, T. and Muraoka, S. (1997) Effects of humic acid on the sorption of neptunium(V) on kaolinite. *J. Nucl. Mat.*, **248**, 328-332.
- Righetto, L., Bidoglio, G. and Belbonno, I. R. (1991) Competitive actinide interactions in colloidal humic acid-mineral oxide systems. *Environ. Sci. Technol.*, **25**, 1913-1919.
- Sakamoto, Y., Nagao, S., Ohnuki, T., Senoo, M., Ohashi, A., Sato, S. and Ohashi, H. (1995) Influence of humic acid on sorption of neptunium(V) onto soil. *Mat. Res. Soc. Symp. Proc.*, **353**, 997-1004.
- Sakamoto, Y., Nagao, S., Ogawa, H. and Rao, R. R. (2000) The migration of Np(V) in sandy soil and granite media in the presence of humic substances. *Radiochim. Acta*, **88**, 651-656.
- Tanaka, T., Nagao, S., Sakamoto, Y., Ohnuki, T., Ni, S. and Senoo, M. (1997) Distribution coefficient in the sorption of radionuclides onto ando soil in the presence of humic acid-influence of the molecular size of humic acid-. *J. Nucl. Sci. Technol.*, **34**, 829-834.
- Tanaka, T., Nagao, S., Sakamoto, Y. and Ogawa, H. (2002) Sorption behavior of plutonium(IV) onto soils in the presence of humic acid. *J. Nucl. Sci. Technol.*, **Suppl. 3**, 524-527.
- Thorn, K. A., Folan, D. W. and MacCarthy, P. (1989) *Characterization of the International Humic Substances Society standard and reference fulvic and humic acids by solution state carbon-13 (^{13}C) and hydrogen-1 (^1H) nuclear magnetic resonance spectroscopy*. Water-Resources Investigations Report 89-4196, p.93, U.S. Geol. Survey.
- Thurman, E. M. and Malcolm, R. L. (1981) Preparation isolation of aquatic humic substances. *Environ. Sci. Technol.*, **15**, 463-466.
- Thurman, E. M. (1985) Humic substances in groundwater. In: *Humic Substances in Soil, Sediment, and Water* (G. R. Aiken, D. M. McKnight, R. L. Wershaw, P. MacCarthy, eds.), pp. 87-105, Wiley Interscience, New York.
- Ticknor, K. V. (1993) Actinide sorption by fracture-infilling minerals. *Radiochim. Acta*, **60**, 33-42.
- Tochiyama, O., Endo, S. and Inoue, Y. (1995) Sorption of neptunium(V) on various iron oxides and hydrous iron oxides. *Radiochim. Acta*, **68**, 105-111.