

Sorption and Diffusion Behavior of Palladium in Bentonite, Granodiorite and Tuff

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Sorption and Diffusion Behavior of Palladium in Bentonite, Granodiorite and Tuff

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Abstract

Sorption and diffusion behavior of palladium, which has been identified as one of the hazardous radionuclides in performance assessment of HLW disposal, in bentonite, granodiorite and tuff was studied in order to make reliable data set for the performance assessment.

Sorption experiments of Pd on bentonite, granodiorite and tuff were conducted as functions of pH, ionic strength and liquid to solid ratio by batch method under aerobic conditions at room temperature. The distribution coefficients (K_d) of Pd on these solids were almost in the range of 10^{-1} to 10^2 m³/kg and were in the order of bentonite > granodiorite ≈ tuff. The sorption trends with change in pH, ionic strength and liquid to solid ratio are very similar between three solids. The K_d values were the highest at pH 5 and decreased with increasing pH between 5 and 11. The effect of ionic strength on K_d was not found in a range of 10^{-2} to 10^{-1} , but K_d values increased with increasing liquid to solid ratio. The width of variation in K_d was one order of magnitude in a liquid to solid ratio of 0.1 to 1 m³/kg. Sorption behavior of Pd is different from that of divalent metal ions such as Ni and Co etc. and chemical analogy may be inappropriate. The dominant aqueous species of Pd in the experimental conditions studied is estimated to be neutral species, Pd(OH)₂(aq) by the thermodynamic calculations. The K_d values of Pd on three solids were relatively high and uncharged complexes may be more strongly sorbed. The pH dependency of K_d values suggests that Pd sorption is most likely to be occurring onto positively charged S-OH₂⁺ type site which are progressively removed (to form SOH and SO⁻ sites) at higher pH values.

Diffusion behavior of Pd in bentonite was also studied by in-diffusion method as a function of dry density. The D_a values obtained based on the instantaneous planar source model were in the orders of 10^{-13} to 10^{-12} m²/s and decreased with increasing dry density of bentonite. The K_d values in compacted bentonite were derived from the D_a values and were in the order of 10^{-2} to 10^{-1} m³/kg. The K_d values obtained from the D_a were lower than those obtained by batch sorption by 1-2 orders of magnitude. However, the difference between both K_d values is correlated to liquid to solid ratio, and the K_d values decreased with reduction of liquid to solid ratio.

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ベントナイト，花崗閃緑岩，凝灰岩中におけるパラジウムの収着及び拡散挙動

(研究報告)

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要旨

性能評価に用いるデータセットの信頼性を向上させることを目的として、性能評価上の重要核種の一つであり、かつ、実測データがほとんど存在しないパラジウムのベントナイト、花崗閃緑岩、凝灰岩中における収着・拡散挙動に関するデータを取得した。

収着試験については、ベントナイト、花崗閃緑岩、凝灰岩を対象に、pH、イオン強度、液固比をパラメータとしてバッチ法により行った。Pdの分配係数として、 $10^{-1} \sim 10^2$ m^3/kg の範囲の値が得られた。ベントナイトに対する分配係数は花崗閃緑岩、凝灰岩に比べ若干高く、花崗閃緑岩と凝灰岩では同程度であった。分配係数のパラメータ依存性はいずれの固相でも同様の傾向を示した。pH依存性については、pH5で最大の分配係数となり、pHの増加に伴い減少する傾向であった。イオン強度の影響は顕著ではなく、液固比については、液固比が高いほど分配係数は高くなる傾向であった。Pdの収着挙動はNi、Co等の2価の金属イオンのそれとは異なり、これらのデータをアナログとしてPdを評価することは不適切であることが示唆された。本試験条件下におけるPdの支配化学種は、熱力学計算から中性の $\text{Pd}(\text{OH})_2(\text{aq})$ と予想された。Pdの分配係数は $10^{-1} \sim 10^2$ m^3/kg と比較的高い値であり、中性化学種の収着性は高いことが示された。また、分配係数がpHの増加と共に減少する傾向にあることから、Pdの収着は固相表面の S-OH_2^+ サイトとの反応により支配されている可能性が示唆された。

拡散試験については、ベントナイトを対象に密度をパラメータとしてin-diffusion法により行った。薄膜拡散源モデルにより解析された見かけの拡散係数は $10^{-13} \sim 10^{-12}$ m^2/s のオーダーであり、ベントナイト密度の増加と共に減少する傾向であった。見かけの拡散係数から得られた圧縮ベントナイト中での分配係数は $10^2 \sim 10^{-1}$ m^3/kg となり、バッチ収着試験により得られた値よりも1~2オーダー低い値であった。しかしながら、分配係数と液固比との関係には相関が見られ、液固比が低いほど分配係数は低くなる傾向であった。

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1. Introduction

The Japanese high-level radioactive waste (HLW) disposal concept is based on multi-barrier system which consists of containers, buffer materials and surrounding rocks. Radionuclides released from a HLW may be transported through the buffer materials and the surrounding rocks. Radionuclides migrate in these materials with groundwater in connected pore spaces, and are retarded by interacting with the surrounding solid phase. The sorption is one of the most important phenomena in the retardation processes. If groundwater movement is sufficiently slow, radionuclides transport will be controlled by diffusion and sorption. Therefore, understanding the sorption and diffusion behavior of radionuclides is important in the performance assessment of geological disposal system.

Sorption behavior of radionuclides is generally evaluated using the distribution coefficient, K_d , which represents the distribution of radionuclides between solid and aqueous phase. Diffusion behavior of radionuclide is usually evaluated by the apparent diffusion coefficient, D_a , which represents non-steady state diffusion including retardation by sorption, and the effective diffusion coefficients, D_e , which represents steady-state diffusion. Until now, the JNC has obtained these sorption and diffusion data of radionuclides concerned in HLW disposal on bentonite and various geological materials such as granodiorite and tuff (Sato et al., 1992, Sato et al., 1993, Shibutani et al., 1994, Sato and Shibutani, 1994, Baston et al., 1995, 1997, 1999, Tachi et al., 1998). Bentonite is considered as a candidate buffer material for HLW disposal. On the other hand, neither a candidate geological environment nor specific site is selected in Japan at the present time. In the JNC, the sorption and diffusion data for the rocks have been mainly obtained for granodiorite and tuff which are considered as fractured and porous media, respectively.

Palladium, contained in a high-level radioactive waste as Pd-107 which has a long half-life of 6.5×10^6 y, has been identified as one of the hazardous radionuclides (PNC, 1993, Nagra, 1994). However, few experimental studies concerning sorption of Pd on geologic materials have been so far reported. Vandergraaf (1982) cites experimental K_d values of about $0.01 \text{ m}^3/\text{kg}$ for Pd sorption on crushed and sieved granite at pH 7 for performance assessment in Canada. In the NEA Sorption Database

(Ticknor and Rüegger, 1989), K_d data of Pd is in a range 0.006 to 3.2 m^3/kg , which data were obtained for sediment only by Lang and Klotz (1982). In the sorption data sets used for the performance assessments in the other nation's program (Stenhouse, 1995, Brandberg and Skagius, 1991, Vandergraaf et al., 1993, Hakanen and Hölttä, 1992), the recommended K_d values for Pd were based on the above data or chemical analogy of nickel and ruthenium. In the H-3 report (PNC, 1993), K_d parameter of Pd was determined based on chemical analogy of cobalt for bentonite and on Vandergraaf's data for rocks. There is a great discrepancy between K_d values for Pd in those programs (0.001 to 1 m^3/kg) because of the scarcity of experimental data. On the other hand, no report for diffusion of Pd in geological materials is found. Therefore, it is essential that sorption and diffusion studies of Pd on concerned geological materials are performed in order to make reliable data set for performance assessment.

In this study, sorption behavior of Pd on bentonite, granodiorite and tuff was investigated by batch method. Sorption experiments were carried out as functions of pH, ionic strength and liquid to solid ratio under aerobic conditions at room temperature. Diffusion behavior of Pd in bentonite was also investigated by in-diffusion method under aerobic conditions at room temperature. Sorption mechanisms and consistency between K_d values obtained by batch sorption and diffusion experiments are discussed.

2. Experimental

2.1 Materials

Bentonite used in the experiments is Kunigel V1® (Kunimine Industries Co. Ltd., Japan) which is a crude bentonite and a candidate buffer material in Japan. Granodiorite was obtained from Sori, Gunma, which is Japanese standard rock sample(JG-1) selected by the Geological Survey of Japan. Tuff samples used in the experiments were obtained from Toki Lignite-Bearing Formation(AN-4 bore hole, 72.0m below ground level), Tono mine, Gifu, central Japan. The particle sizes, specific surface areas measured by the Brunauer-Emmett-Teller(BET) method, mineralogy determined by X-ray diffraction analysis and thin section observation and chemical composition for these materials are shown in Table 1.

2.2 Sorption experiment

2.2.1 Batch sorption methodology

The sorption experiments were carried out by batch method under aerobic conditions at room temperature. Experimental conditions and procedure are shown in Table 2 and Figure 1, respectively. The samples were contacted with 0.1M and 0.01M-NaCl solutions prepared from distilled water(CPW - 200, Advantec Toyo Co. Ltd., Japan) and reagent grade NaCl(Kanto Chemical, Japan) in polyethylene vessels. The liquid to solid ratios were 0.1 and 1 m³/kg for bentonite and tuff, 0.05 and 0.5 m³/kg for granodiorite. The pH values of the solutions were adjusted to 5, 8 and 11 with HCl and NaOH solutions prepared from distilled water and reagent grade HCl(Tama Chemicals, Japan) and NaOH(Merck, Japan), and were periodically monitored with calibrated combined glass electrodes(F-13, Horiba, Japan) to achieve equilibration for about 30 days. After the pre-equilibration, a tracer solution prepared by diluting a 1000 ppm - Pd Standard Solution(Kanto Chemicals, Japan) was spiked in the solutions. The initial concentration of Pd was 50 ppb in the experiments for bentonite and granodiorite. In the experiments for tuff, the initial concentrations of Pd were 10 ppb at pH values of 5 and 11, and 2 ppb at pH 8. The vessels were frequently shaken and the pH was periodically measured and adjusted if necessary. After the reaction time of 30 days, liquid and solid were separated by filtration with 10,000

Table 1 Description of materials used in Pd sorption and diffusion experiments

Solid	bentonite*	granodiorite	tuff
Source	Tsukinuno, Yamagata (Kunigel V1® from Kunimine Industries Co., Japan)	Sori, Gunma (Japanese standard rock sample (JG-1) selected by Geological Survey of Japan)	Tono, Gifu (Toki Lignite-Bearing Formation, AN-4 bore hole, 72.0m below ground level)
Particle size	<10µm (70.3%) 10µm-22µm (6.2%) >22µm (23.5%)	< 355 µm	< 355 µm
Specific surface area (m ² /s)	10	0.7	24
Mineral composition	smectite 46-49 % quartz 0.5-0.7 % chalcedony 37-38 % plagioclase 2.7-5.5 % calcite 2.1-2.6 % dolomite 2.0-3.8 % analcite 3.0-3.5 % pyrite 0.5-0.7 %	quartz 30.8 % plagioclase 39.2 % K-feldspar 24.5 % biotite 4.32 % chlorite 0.3 % apatite 0.1 %	plagioclase smectite clinoptilolite heulandite quartz kaolinite biotite gypsum pyrite K-feldspar illite sericite chlorite horneblende Fe-oxyhydroxide
Chemical composition	SiO ₂ 70.7 % TiO ₂ 0.20 % Al ₂ O ₃ 13.8 % Fe ₂ O ₃ 1.49 % FeO 0.62 % MnO 0.22 % MgO 2.26 % CaO 2.30 % Na ₂ O 2.56 % K ₂ O 0.33 % P ₂ O ₅ 0.05 % S 2900 ppm CO ₂ 22000 ppm	SiO ₂ 73.92 % TiO ₂ 0.31 % Al ₂ O ₃ 12.21 % Fe ₂ O ₃ 0.16 % FeO 2.38 % MnO 0.07 % MgO 0.89 % CaO 1.66 % Na ₂ O 2.89 % K ₂ O 3.90 % P ₂ O ₅ 0.10 % H ₂ O(-) 0.02 % H ₂ O(+) 0.83 ppm S 80 ppm C 270 ppm CO ₂ 500 ppm	-

* Ito et al. (1993)

Table 2 Experimental conditions for batch sorption

Solid	bentonite	granodiorite	tuff
Initial solution	0.1M, 0.01M - NaCl	←	←
Liquid to solid ratio	0.1, 1 m ³ /kg	0.05, 0.5 m ³ /kg	0.1, 1 m ³ /kg
Atmosphere	Aerobic	←	←
Temperature	Room temperature	←	←
pH	5, 8, 11	←	←
Initial concentration of tracer	50 ppb	←	10 ppb (pH=5, 11) 2 ppb (pH=8)
Reaction time	30 days	←	←
Producibility	2	←	←
Remarks (additional test)	Blank test	Blank test	Blank test Washing test of vessel

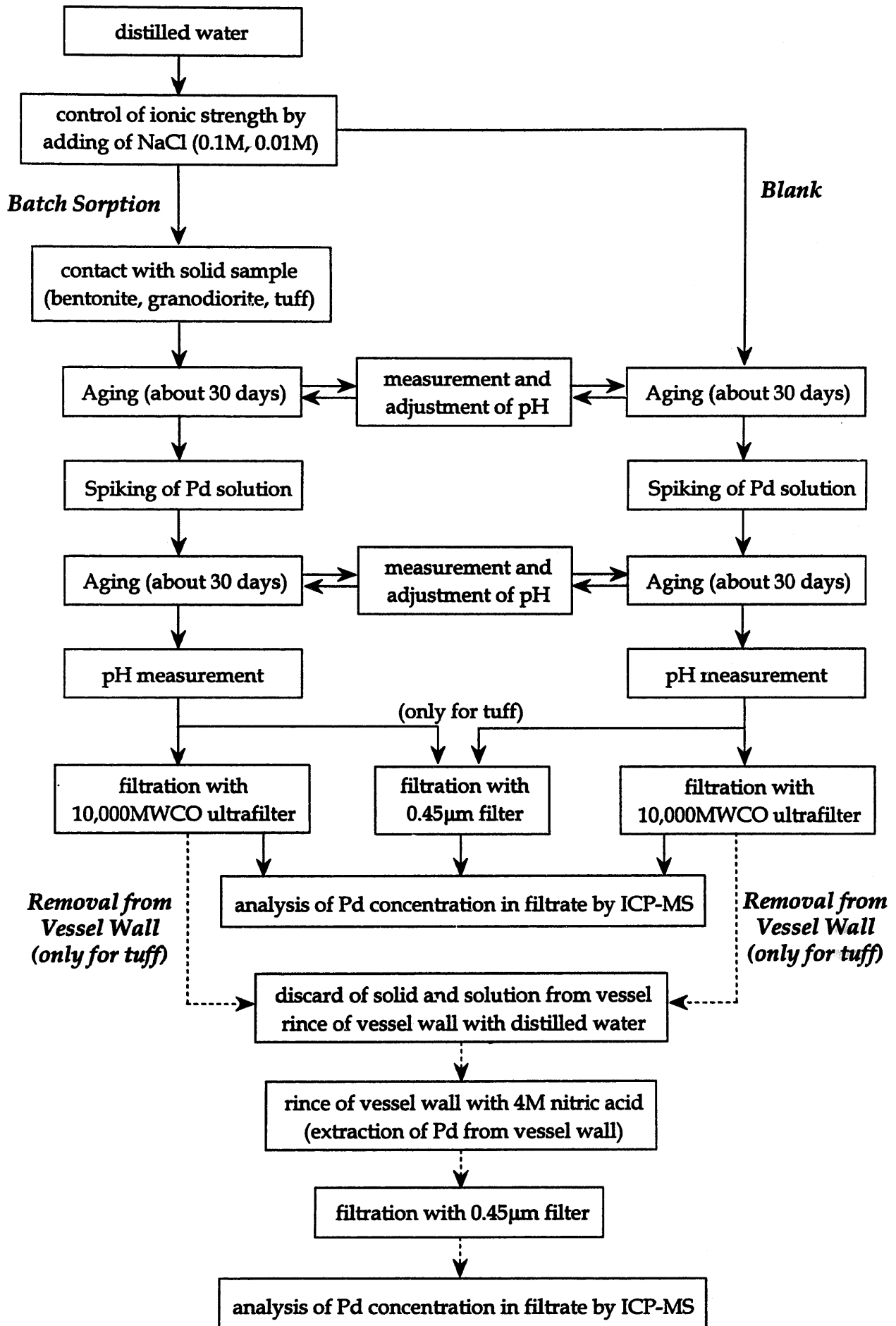


Figure 1 Experimental flow sheet of batch sorption experiment

molecular weight cut-off(MWCO) ultrafilters(USY-1, Advantec Toyo Co. Ltd., Japan). In the experiments for the tuff, phase separation with 0.45 μm membrane filters (DISMIC-25, Advantec Toyo Co. Ltd., Japan) was also carried out in addition to 10,000 MWCO ultrafilters in order to confirm colloid effect on sorption. The concentrations of Pd in the filtrates were analyzed with an inductively coupled plasma mass spectroscopy(ICP-MS) (SPQ6500, Seiko Electronics Co. Ltd., Japan). The batch sorption experiments were performed in duplicate.

2.2.2 Blank test

In the batch sorption experiments, blank tests were also carried out to monitor precipitation and sorption of Pd on vessel walls and filters. A tracer solution was spiked in 0.1M and 0.01M-NaCl solutions without solids to achieve the same initial concentration with the batch sorption experiments. The procedure is also shown in Figure 1. The pH values of the solutions were also adjusted to the same values(5, 8 and 11) with the sorption experiments. The vessels were frequently shaken and the pH values were periodically measured and adjusted if necessary. After 30 days, the solutions were filtered with 10,000 MWCO ultrafilters and the concentrations of Pd in the filtrates were analyzed with the ICP-MS. In the blank test for tuff, solutions were also filtered with 0.45 μm membrane filters.

2.2.3 Measurement of vessel wall sorption

In the batch sorption experiments, the blank test without solid is commonly carried out to monitor precipitation and sorption on vessel walls and filters, and the K_d is derived by correcting the concentration in the blank solution. Several studies indicate that wall sorption induces small effect to the distribution coefficient in sorption experiment with solid, and wall sorption may be important in blank test without solid because no other competing solid phase is present(Morgan et al., 1987, Stenhouse, 1995, Baston et al., 1995). Therefore, when sorption onto the vessel wall is significant, a blank correction will underestimate the calculated K_d .

In the experiments for tuff, removal experiments from vessel wall were carried out in order to measure the quantity of Pd sorbed on the vessel wall. The procedure is also shown in Figure 1. After the sorption experiments, the solid and solution were

discarded from the vessels, and the vessels were rinsed with distilled water, and 4M- HNO_3 solution added in the vessels to extract Pd from the vessel walls. The concentrations of Pd in the HNO_3 solutions were then analyzed by the ICP-MS after filtration by 0.45 μm filter.

2.3 Solubility experiment

Solubility experiments were conducted to validate that initial concentration of Pd in the batch sorption experiments was less than solubility. A tracer solution was spiked in 0.1M and 0.01M- NaCl solutions without solids to achieve the initial concentration of 500 ppb (4.7×10^{-6} mol/l). The pH values of the solutions were adjusted to 5, 8 and 11 with HCl and NaOH solutions. The vessels were frequently shaken and the pH values were periodically measured and adjusted if necessary. After 30 days, the solutions were filtered with 10,000 MWCO ultrafilters and 0.45 μm membrane filters, and the concentrations of Pd in the filtrates were analyzed with the ICP-MS.

2.4 Diffusion experiment

2.4.1 In-diffusion methodology

The diffusion experiments were carried out by the in-diffusion method under aerobic conditions at room temperature. Experimental conditions and procedure are shown in Table 3 and Figure 2, respectively. The schematic view of a diffusion cell is shown in Figure 3. The powder of bentonite was dried at 110 $^{\circ}\text{C}$ for more than 24 hours and compacted into a diffusion cell with the size of 20 mm in diameter and 20 mm in length. Dry densities of the compacted bentonite are 1.4 and 1.8 Mg/m^3 . Compacted bentonite were immersed in distilled water (SA-2000E, Tokyo Rika Kikai, Japan) under low pressure conditions for a month to saturate pore in bentonite with water. A tracer solution of 0.01M- PdCl_2 was prepared by dissolving reagent grade PdCl_2 (Wako Chemicals, Japan) in distilled water and the pH value of the tracer solution was adjusted at 7 by NaOH solution prepared from distilled water and reagent grade NaOH (Kanto Chemicals, Japan). After pH adjustment, precipitation (or suspension) were found. A small amount (25 μl) of the tracer solution containing suspension was put on one surface of saturated bentonite as shown in Figure 3. The diffusion periods

are 7.2 and 48.2 days for a density of 1.4 Mg/m^3 , and 7.2 and 83.1 days for a density of 1.8 Mg/m^3 .

At the end of the diffusion period, the diffusion cell was disassembled and the bentonite was cut into 0.2 or 1 mm thickness (0.2 mm for shorter diffusion period and 1 mm for longer diffusion period). Each slice was weighed before and after drying at 110°C for about 24 hours to determine precise thickness and water content. Then each slice was immersed in 4 or 10 ml of a 1M HNO_3 solution to extract Pd from bentonite for one week. Liquid and solid were separated through 10,000 MWCO ultrafilters (Molecut TGC, Millipore, Japan). The concentrations of Pd in the filtrates were analyzed with an ICP-MS (PH82, Yokogawa Analytical Systems, Japan). The diffusion experiments were performed in single.

2.4.2 Blank test

In the in-diffusion experiment, blank tests were also carried out to determine background concentration of Pd contained naturally in bentonite. The blank experiments was carried out in the same way as diffusion experiments with the exception of putting the tracer solution. The blank tests were performed in single. The bentonite was cut into 1.0 mm thickness both for 1.4 and 1.8 Mg/m^3 .

Table 3 Experimental conditions for in-diffusion

Solid	Bentonite
dry density	1.4, 1.8 Mg/m ³
sample configuration	φ 20 mm x L 20 mm
initial solution	Distilled water
Atmosphere	Aerobic
Temperature	Room temperature
Trace solution	0.1M-HNO ₃ solution containing 0.01M-PdCl ₂
Diffusion time	7 - 83 days
Producibility	1
Remarks (additional test)	Blank test

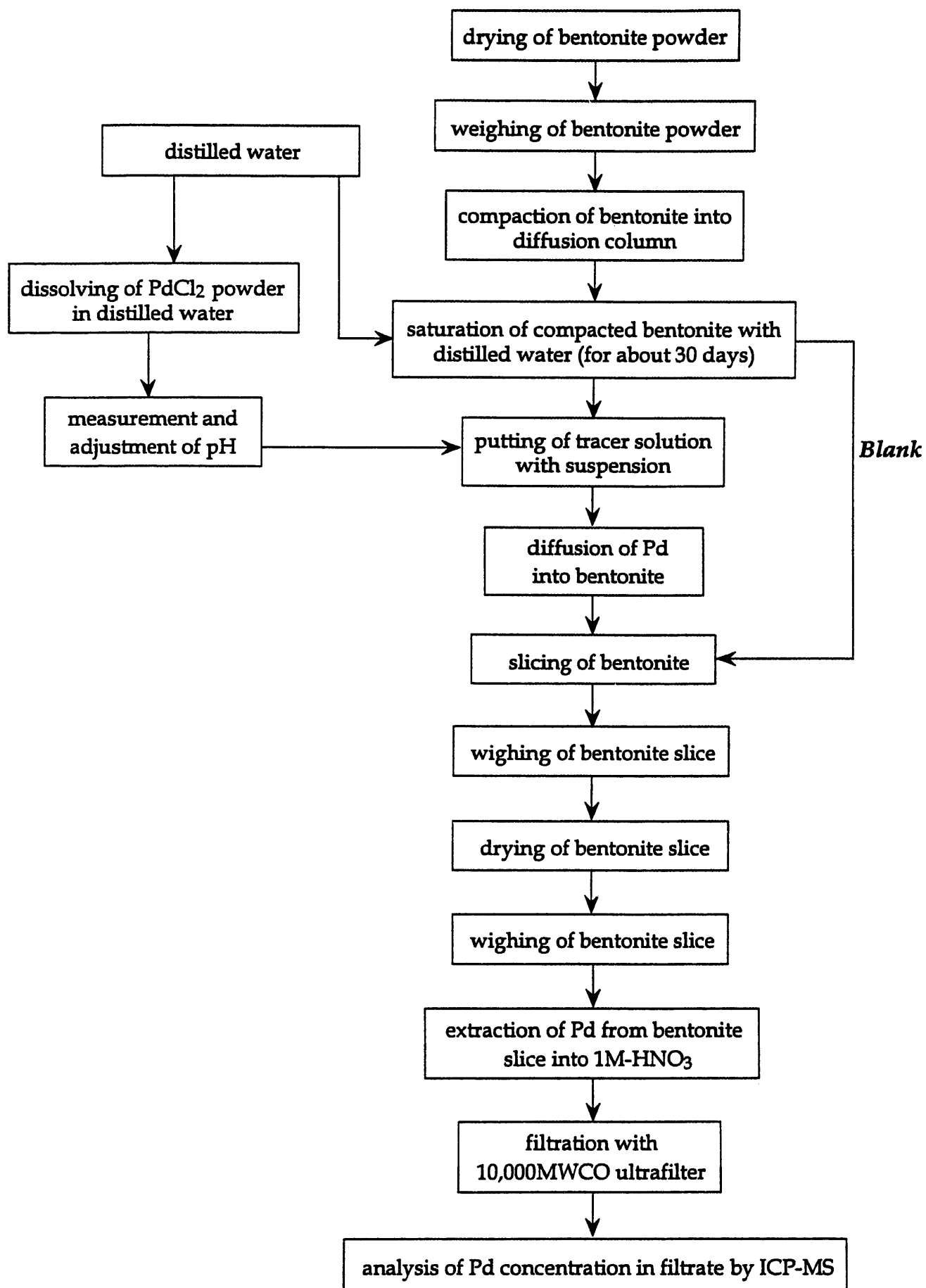


Figure 2 Experimental flow sheet of in-diffusion experiment

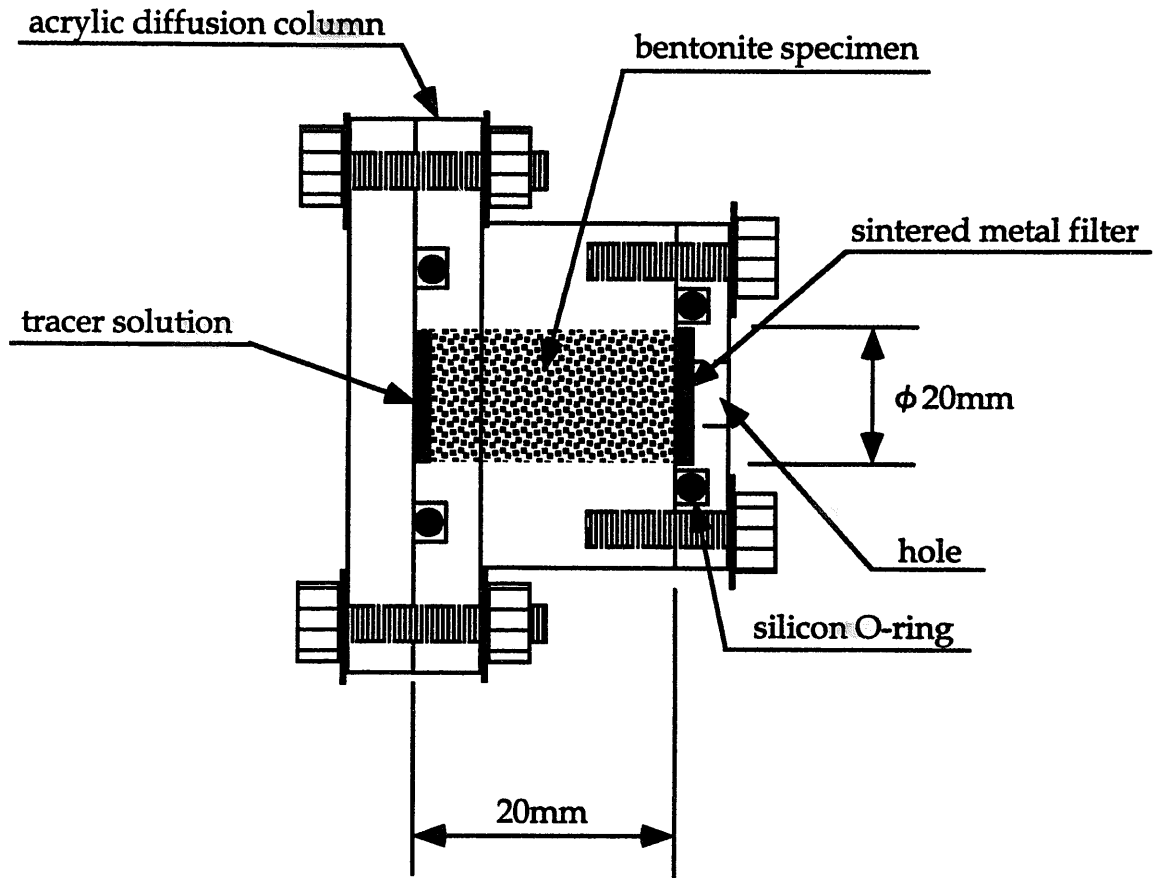


Figure 3 Schematic view of diffusion column

3. Results

3.1 Batch sorption experiment

3.1.1 Data evaluation methodology

The fraction of sorbed Pd and the distribution coefficient are determined using the following equation, respectively,

$$R_s = \frac{C_b(\text{or } C_i) - C_t}{C_b} \times 100 \quad (1)$$

$$K_d = \frac{C_b(\text{or } C_i) - C_t}{C_t} \times \frac{L}{S} \quad (2)$$

where R_s is the fraction of sorbed Pd(%), K_d is the distribution coefficient(m^3/kg), C_b is the final concentration of Pd in the blank solution(kg/m^3), C_i is the initial concentration of Pd in the blank and test solutions(kg/m^3), C_t is the final concentration of Pd in the test solution(kg/m^3), and L/S is the liquid to solid ratio(m^3/kg).

In the batch sorption experiments, the K_d is generally derived by correcting the concentration in the blank solution. On the other hand, several studies indicated that wall sorption induces small effect to the distribution coefficient in sorption experiment with solid, and wall sorption may be important in blank test without solid because no other competing solid phase is present(Morgan et al., 1987, Stenhouse, 1995, Baston et al., 1995). Hence, the fraction of sorbed Pd and the distribution coefficient of Pd are derived both from C_i and C_t . However, in many blank samples, significant decrease of Pd concentration was found(see 3.1.2-4) and the K_d values could not be determined from final concentration in blank solution. According to the results of the removal experiments from vessel walls(see 3.1.5), the K_d values derived from C_i are used for the following results and discussions.

3.1.2 Bentonite

Results of sorption experiments for bentonite are shown in Table 4 with experimental conditions. In the pre-equilibration period of about a month, the pH values of test solutions became steady at the desired values, 5, 8 and 11. The pH

values in test solutions monitored after addition of Pd were approximately constant. Palladium concentration in blank solution significantly decreased from the initial concentration. The K_d values derived from initial concentration are in the range of 17 to >250 m^3/kg at pH 5, 0.67 to 28 m^3/kg at pH 8 and 0.35 to 25 m^3/kg at pH 11. The averaged K_d values of Pd on bentonite derived from initial concentration are shown as a function of pH in Figure 4. Distribution coefficients at pH 5 are more than values plotted in Figure 4 because of the detection limit in ICP-MS analysis. The K_d values were highest at pH 5 and decreased with increasing pH between 5 and 11. Little effect of ionic strength on K_d was not found in a pH range of 5 to 11. The K_d values increased with increasing liquid to solid ratios between 0.1 and 1 m^3/kg . Averaged K_d values at a liquid to solid ratio of 1 m^3/kg are higher than those at 0.1 m^3/kg by one order of magnitude.

3.1.3 Granodiorite

Results of sorption experiments for granodiorite are shown in Table 5. Significant decrease of Pd concentration was also found in blank samples. The K_d values derived from initial concentration are in the range of 2.2 to 83 m^3/kg at pH 5, 0.24 to 12 m^3/kg at pH 8 and 0.14 to 4.8 m^3/kg at pH 11. The averaged K_d values of Pd on granodiorite from C_i are shown as a function of pH in Figure 5. The pH dependency was the same as that of bentonite; the K_d values decreased with increasing pH. Over the pH range studied, the K_d values for granodiorite are lower than those for bentonite. The effect of ionic strength on K_d are significant rather than that for bentonite, the K_d values for 0.01M-NaCl were about 2 times greater than those for 0.1M-NaCl. The K_d values at a liquid to solid ratio of 0.5 m^3/kg are higher than those at that of 0.05 m^3/kg by one order of magnitude.

3.1.4 Tuff

Results of sorption experiments for tuff are shown in Table 6. Significant decrease of Pd concentration was also found in blank samples. The K_d values derived from initial concentration are in the range of >4.9 to >49 m^3/kg at pH 5, 0.23 to 9.0 m^3/kg at pH 8 and 0.096 to 2.2 m^3/kg at pH 11. The averaged K_d values of Pd on tuff derived from C_i are shown as a function of pH in Figure 6. The K_d values at pH 5

Table 4 Results of Pd sorption on bentonite

sample name	solid	solution	L/S (m ³ /kg)	pH	C _i *1 (ppb)	measured pH	C _t *2 (ppb)	C _b *3 (ppb)	sorption rate (%)		K _d (m ³ /kg)	
									by C _b *4	by C _i *5	by C _b *4	by C _i *5 (average)
BSL5-1	bentonite	0.1M-NaCl	0.1	5	50	5.1	< 0.2	29	> 99	100	> 14	> 25 (> 21)
BSL5-2	bentonite	0.1M-NaCl	0.1	5	50	5.1	0.3	29	99	99	10	17
BSL8-1	bentonite	0.1M-NaCl	0.1	8	50	8.0	0.9	5.1	82	98	0.5	5.5 (3.1)
BSL8-2	bentonite	0.1M-NaCl	0.1	8	50	8.0	6.5	5.1	-	87	-	0.67
BSL11-1	bentonite	0.1M-NaCl	0.1	11	50	11.0	7.0	12	42	86	0.07	0.61 (0.48)
BSL11-2	bentonite	0.1M-NaCl	0.1	11	50	11.0	11	12	8	78	0.009	0.35
BSH5-1	bentonite	0.1M-NaCl	1	5	50	5.1	< 0.2	29	> 99	100	> 144	> 250 (> 156)
BSH5-2	bentonite	0.1M-NaCl	1	5	50	5.1	0.8	29	97	98	35	62
BSH8-1	bentonite	0.1M-NaCl	1	8	50	8.1	1.7	5.1	67	97	2.0	28 (16)
BSH8-2	bentonite	0.1M-NaCl	1	8	50	8.1	11	5.1	-	78	-	3.5
BSH11-1	bentonite	0.1M-NaCl	1	11	50	10.9	2.9	12	76	94	3.1	16 (13)
BSH11-2	bentonite	0.1M-NaCl	1	11	50	10.9	4.3	12	64	91	1.8	11
BDL5-1	bentonite	0.01M-NaCl	0.1	5	50	5.1	< 0.2	11	> 98	100	> 5.4	> 25 (> 25)
BDL5-2	bentonite	0.01M-NaCl	0.1	5	50	5.1	< 0.2	11	> 98	100	> 5.4	> 25
BDL8-1	bentonite	0.01M-NaCl	0.1	8	50	8.1	0.7	2.3	70	99	0.23	7.0 (4.0)
BDL8-2	bentonite	0.01M-NaCl	0.1	8	50	8.1	4.7	2.3	-	91	-	0.96
BDL11-1	bentonite	0.01M-NaCl	0.1	11	50	11.0	1.7	9.7	82	97	0.47	2.8 (2.0)
BDL11-2	bentonite	0.01M-NaCl	0.1	11	50	11.0	4.2	9.7	57	92	0.13	1.1
BDH5-1	bentonite	0.01M-NaCl	1	5	50	5.0	< 0.2	11	> 98	100	> 54	> 250 (> 166)
BDH5-2	bentonite	0.01M-NaCl	1	5	50	5.0	0.6	11	95	99	17	82
BDH8-1	bentonite	0.01M-NaCl	1	8	50	8.0	2.8	2.3	-	94	-	17 (9.9)
BDH8-2	bentonite	0.01M-NaCl	1	8	50	8.0	13	2.3	-	74	-	2.8
BDH11-1	bentonite	0.01M-NaCl	1	11	50	10.9	1.9	9.7	80	96	4.1	25 (18)
BDH11-2	bentonite	0.01M-NaCl	1	11	50	10.9	4.2	9.7	57	92	1.3	11

*1 initial concentration of Pd in test solution

*2 final concentration of Pd in test solution after filtration

*3 final concentration of Pd in blank solution

*4 derived by using C_b (Pd final concentration in blank solution)*5 derived by using C_i (Pd initial concentration in test solution)

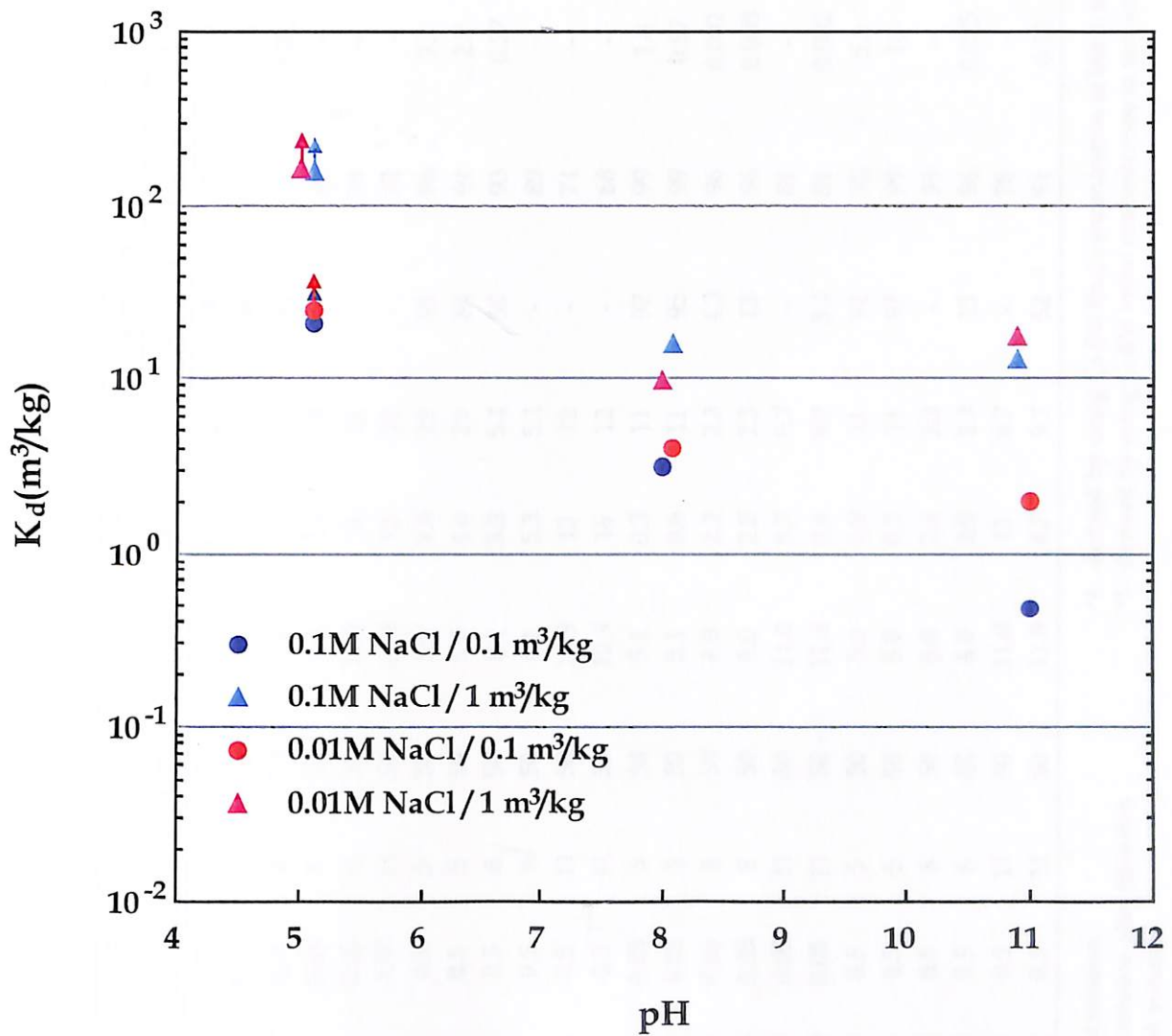


Figure 4 Distribution coefficients (K_d) of Palladium on bentonite

Table 5 Results of Pd sorption on granodiorite

sample name	solid	solution	L/S (m ³ /kg)	pH	C _i *1 (ppb)	measured pH	C _i *2 (ppb)	C _b *3 (ppb)	sorption rate (%)		K _d (m ³ /kg)		
									by C _b *4	by C _i *5	by C _b *4	by C _i *5 (average)	
GSL5-1	granodiorite	0.1M-NaCl	0.05	5	50	5.1	0.7	29	98	99	2.0	3.5	(2.9)
GSL5-2	granodiorite	0.1M-NaCl	0.05	5	50	5.1	1.1	29	96	98	1.3	2.2	
GSL8-1	granodiorite	0.1M-NaCl	0.05	8	50	8.0	3.5	5.1	31	93	0.023	0.66	(0.45)
GSL8-2	granodiorite	0.1M-NaCl	0.05	8	50	8.0	8.5	5.1	-	83	-	0.24	
GSL11-1	granodiorite	0.1M-NaCl	0.05	11	50	10.9	13	12	-	74	-	0.14	(0.14)
GSL11-2	granodiorite	0.1M-NaCl	0.05	11	50	10.9	13	12	-	74	-	0.14	
GSH5-1	granodiorite	0.1M-NaCl	0.5	5	50	5.0	1.9	29	93	96	7.1	13	(8.8)
GSH5-2	granodiorite	0.1M-NaCl	0.5	5	50	5.0	4.6	29	84	91	2.7	4.9	
GSH8-1	granodiorite	0.1M-NaCl	0.5	8	50	8.1	3.3	5.1	35	93	0.27	7.1	(5.6)
GSH8-2	granodiorite	0.1M-NaCl	0.5	8	50	8.1	5.3	5.1	-	89	-	4.2	
GSH11-1	granodiorite	0.1M-NaCl	0.5	11	50	10.9	13	12	-	74	-	1.4	(1.2)
GSH11-2	granodiorite	0.1M-NaCl	0.5	11	50	10.9	16	12	-	68	-	1.1	
GDL5-1	granodiorite	0.01M-NaCl	0.05	5	50	5.1	0.3	11	97	99	1.8	8.3	(6.2)
GDL5-2	granodiorite	0.01M-NaCl	0.05	5	50	5.1	0.6	11	95	99	0.87	4.1	
GDL8-1	granodiorite	0.01M-NaCl	0.05	8	50	8.0	2.2	2.3	4.3	96	0.002	1.1	(1.1)
GDL8-2	granodiorite	0.01M-NaCl	0.05	8	50	8.0	2.0	2.3	13	96	0.008	1.2	
GDL11-1	granodiorite	0.01M-NaCl	0.05	11	50	11.0	9.7	9.7	-	81	-	0.21	(0.21)
GDL11-2	granodiorite	0.01M-NaCl	0.05	11	50	11.0	9.4	9.7	3.1	81	0.002	0.22	
GDH5-1	granodiorite	0.01M-NaCl	0.5	5	50	5.0	0.9	11	92	98	5.6	27	(55)
GDH5-2	granodiorite	0.01M-NaCl	0.5	5	50	5.0	0.3	11	97	99	18	83	
GDH8-1	granodiorite	0.01M-NaCl	0.5	8	50	8.0	2.6	2.3	-	95	-	9.1	(11)
GDH8-2	granodiorite	0.01M-NaCl	0.5	8	50	8.0	2.0	2.3	13	96	0.075	12	
GDH11-1	granodiorite	0.01M-NaCl	0.5	11	50	11.0	11	9.7	-	78	-	1.8	(3.3)
GDH11-2	granodiorite	0.01M-NaCl	0.5	11	50	11.0	4.7	9.7	52	91	0.53	4.8	

*1 initial concentration of Pd in test solution

*2 final concentration of Pd in test solution after filtration

*3 final concentration of Pd in blank solution

*4 derived by using C_b (Pd final concentration in blank solution)*5 derived by using C_i (Pd initial concentration in test solution)

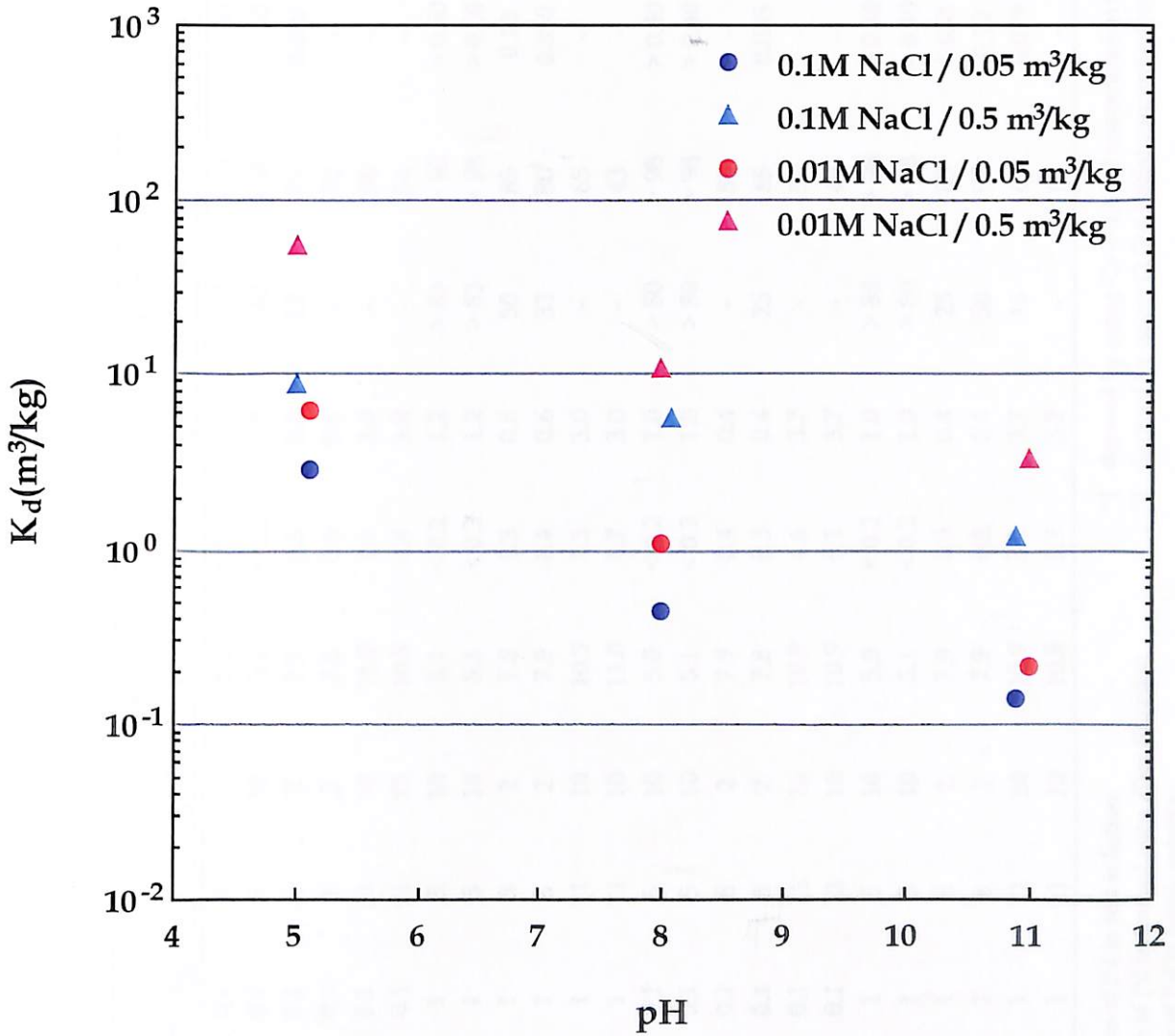


Figure 5 Distribution coefficients (K_d) of Palladium on granodiorite

Table 6 Results of Pd sorption on tuff

sample name	solid	solution	L/S (m ³ /kg)	pH	C _i *1 (ppb)	measured pH	C _f *2 (ppb)	C _b *3 (ppb)	sorption rate (%)		K _d (m ³ /kg)	
									by C _b *4	by C _i *5	by C _b *4	by C _i *5 (average)
TSL5-1	tuff	0.1M-NaCl	0.1	5	10	5.0	< 0.2	1.2	> 83	> 98	> 0.50	> 4.9 (> 4.9)
TSL5-2	tuff	0.1M-NaCl	0.1	5	10	5.0	< 0.2	1.2	> 83	> 98	> 0.50	> 4.9
TSL8-1	tuff	0.1M-NaCl	0.1	8	2	7.9	0.5	0.6	17	75	0.020	0.30 (0.27)
TSL8-2	tuff	0.1M-NaCl	0.1	8	2	7.8	0.6	0.6	-	70	-	0.23
TSL11-1	tuff	0.1M-NaCl	0.1	11	10	11.0	4.6	3.0	-	54	-	0.12 (0.12)
TSL11-2	tuff	0.1M-NaCl	0.1	11	10	10.8	4.6	3.0	-	54	-	0.12
TSH5-1	tuff	0.1M-NaCl	1	5	10	5.1	< 0.2	1.2	> 83	> 98	> 0.50	> 49 (> 49)
TSH5-2	tuff	0.1M-NaCl	1	5	10	5.1	< 0.2	1.2	> 83	> 98	> 0.50	> 49
TSH8-1	tuff	0.1M-NaCl	1	8	2	7.8	0.3	0.6	50	85	0.10	5.7 (4.8)
TSH8-2	tuff	0.1M-NaCl	1	8	2	7.9	0.4	0.6	33	80	0.050	4.0
TSH11-1	tuff	0.1M-NaCl	1	11	10	10.9	3.5	3.0	-	65	-	1.9 (1.3)
TSH11-2	tuff	0.1M-NaCl	1	11	10	11.0	5.7	3.0	-	43	-	0.75
TDL5-1	tuff	0.01M-NaCl	0.1	5	10	5.0	< 0.2	1.0	> 80	> 98	> 0.40	> 4.9 (> 4.9)
TDL5-2	tuff	0.01M-NaCl	0.1	5	10	5.1	< 0.2	1.0	> 80	> 98	> 0.40	> 4.9
TDL8-1	tuff	0.01M-NaCl	0.1	8	2	7.9	0.4	0.4	-	80	-	0.40 (0.48)
TDL8-2	tuff	0.01M-NaCl	0.1	8	2	7.8	0.3	0.4	25	85	0.033	0.57
TDL11-1	tuff	0.01M-NaCl	0.1	11	10	10.9	4.6	3.7	-	54	-	0.12 (0.11)
TDL11-2	tuff	0.01M-NaCl	0.1	11	10	10.9	5.1	3.7	-	49	-	0.096
TDH5-1	tuff	0.01M-NaCl	1	5	10	5.0	< 0.2	1.0	> 80	> 98	> 0.40	> 49 (> 49)
TDH5-2	tuff	0.01M-NaCl	1	5	10	5.1	< 0.2	1.0	> 80	> 98	> 0.40	> 49
TDH8-1	tuff	0.01M-NaCl	1	8	2	7.9	0.3	0.4	25	85	0.033	5.7 (7.3)
TDH8-2	tuff	0.01M-NaCl	1	8	2	7.9	0.2	0.4	50	90	0.10	9.0
TDH11-1	tuff	0.01M-NaCl	1	11	10	10.9	3.1	3.7	16	69	0.019	2.2 (2.0)
TDH11-2	tuff	0.01M-NaCl	1	11	10	10.8	3.7	3.7	-	63	-	1.7

*1 initial concentration of Pd in test solution

*2 final concentration of Pd in test solution after filtration

*3 final concentration of Pd in blank solution

*4 derived by using C_b (Pd final concentration in blank solution)*5 derived by using C_i (Pd initial concentration in test solution)

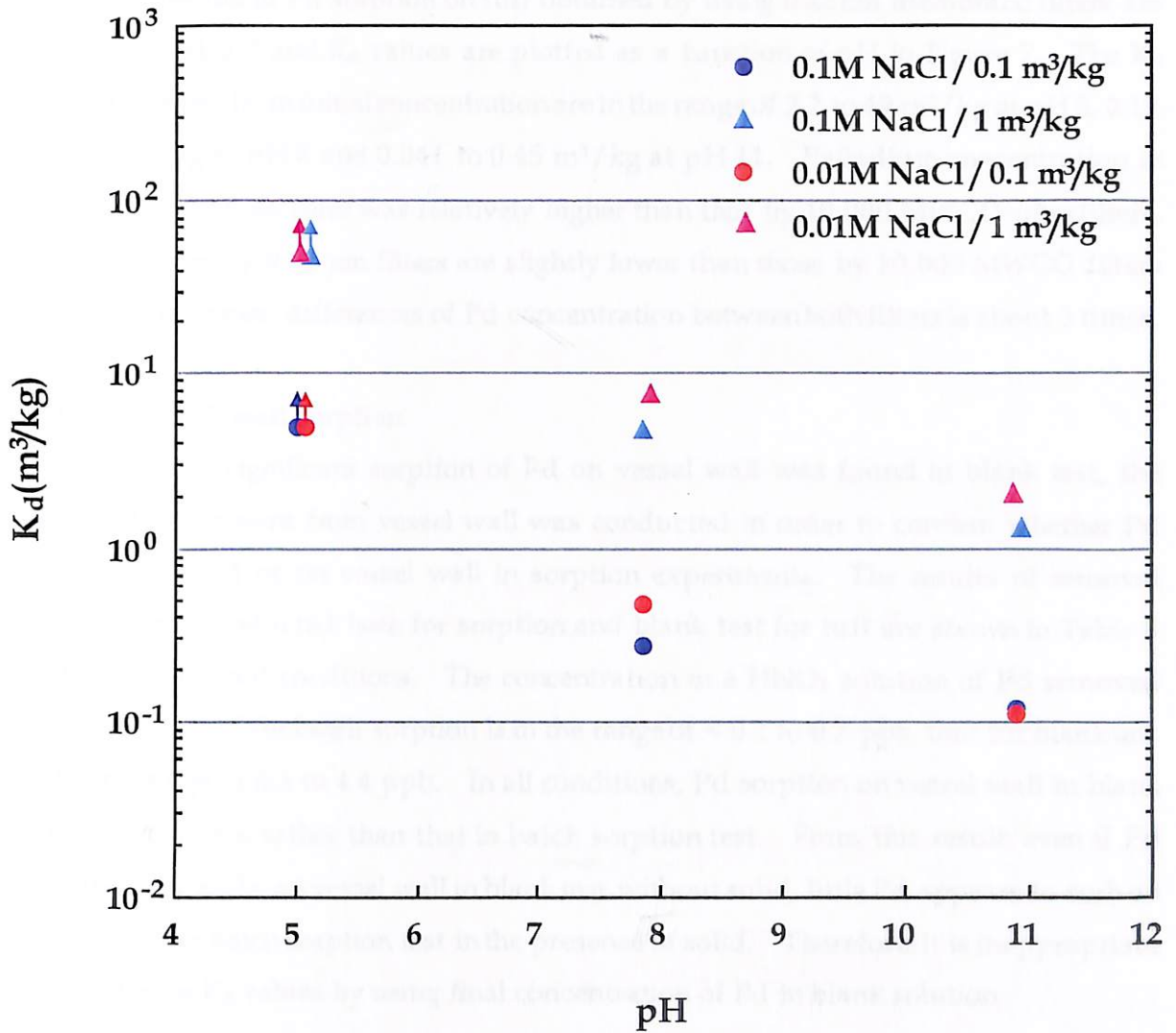


Figure 6 Distribution coefficients (Kd) of Palladium on tuff

are higher than values plotted in Figure 6 because of the detection limit in ICP-MS analysis. The pH dependency was the same as that of bentonite and the K_d values decreased with increasing pH. The K_d values for tuff are almost the same as those for granodiorite. The effect of ionic strength and liquid to solid ratio was similar to that for bentonite as mentioned above.

Results of Pd sorption on tuff obtained by using 0.45 μ m membrane filters are shown in Table 7 and K_d values are plotted as a function of pH in Figure 7. The K_d values derived from initial concentration are in the range of 3.2 to 49 m³/kg at pH 5, 0.19 to 1.9 m³/kg at pH 8 and 0.041 to 0.45 m³/kg at pH 11. Palladium concentration in filtrates by 0.45 μ m filter was relatively higher than that by 10,000 MWCO ultrafilters. The K_d values by 0.45 μ m filters are slightly lower than those by 10,000 MWCO filters and the maximum differences of Pd concentration between both filters is about 3 times.

3.1.5 Vessel wall sorption

Since significant sorption of Pd on vessel wall was found in blank test, the removal experiment from vessel wall was conducted in order to confirm whether Pd sorbed on solid or on vessel wall in sorption experiments. The results of removal experiments conducted both for sorption and blank test for tuff are shown in Table 8 with experimental conditions. The concentration in a HNO₃ solution of Pd removed from vessel wall for batch sorption is in the range of < 0.2 to 0.7 ppb, that for blank test is in the range of 0.5 to 4.4 ppb. In all conditions, Pd sorption on vessel wall in blank test is significant rather than that in batch sorption test. From this result, even if Pd significantly sorbs on vessel wall in blank test without solid, little Pd appears to sorb on vessel wall in batch sorption test in the presence of solid. Therefore, it is inappropriate to determine K_d values by using final concentration of Pd in blank solution.

3.2 Solubility experiment

The results of solubility experiments are shown in Table 9 with experimental conditions, and solubilities are shown as a function of pH in Figure 8. The solubility of Pd is in the range of 180 to 540 ppb (1.7×10^{-6} to 5.1×10^{-6} mol/l) at pH 5, 15 to 47 ppb (1.4×10^{-7} to 4.4×10^{-7} mol/l) at pH 8 and 58 to 200 ppb (5.5×10^{-7} to 1.9×10^{-6} mol/l) at pH 11. The solubilities of Pd in 0.1M-NaCl solutions at pH 5 seem to be higher than initial

Table 7 Results of Pd sorption on tuff by using 0.45 μm filter

sample name	solid	solution	L/S (m^3/kg)	pH	C _i *1 (ppb)	measured pH	C _f *2 (ppb)	C _b *3 (ppb)	sorption rate (%)		K _d (m^3/kg)	
									by C _b *4	by C _i *5	by C _b *4	by C _i *5
TSL5-1	tuff	0.1M-NaCl	0.1	5	10	5.0	0.3	2.7	89	97	0.80	3.2
TSL8-1	tuff	0.1M-NaCl	0.1	8	2	7.9	0.4	1.4	71	80	0.25	0.40
TSL11-1	tuff	0.1M-NaCl	0.1	11	10	11.0	5.2	6.0	13	48	0.015	0.092
TSH5-1	tuff	0.1M-NaCl	1	5	10	5.1	0.2	2.7	93	98	13	49
TSH8-1	tuff	0.1M-NaCl	1	8	2	7.8	0.7	1.4	50	65	1.0	1.9
TSH11-1	tuff	0.1M-NaCl	1	11	10	10.9	6.9	6.0	-	31	-	0.45
TDL5-1	tuff	0.01M-NaCl	0.1	5	10	5.0	0.2	4.6	96	98	2.2	4.9
TDL8-1	tuff	0.01M-NaCl	0.1	8	2	7.9	0.7	1.2	42	65	0.07	0.19
TDL11-1	tuff	0.01M-NaCl	0.1	11	10	10.9	7.1	5.5	-	29	-	0.041
TDH5-1	tuff	0.01M-NaCl	1	5	10	5.0	0.4	4.6	91	96	11	24
TDH8-1	tuff	0.01M-NaCl	1	8	2	7.9	0.9	1.2	25	55	0.33	1.2
TDH11-1	tuff	0.01M-NaCl	1	11	10	10.9	7.7	5.5	-	23	-	0.30

*1 initial concentration of Pd in test solution

*2 final concentration of Pd in test solution after filtration

*3 final concentration of Pd in blank solution

*4 derived by using C_b (Pd final concentration in blank solution)*5 derived by using C_i (Pd initial concentration in test solution)

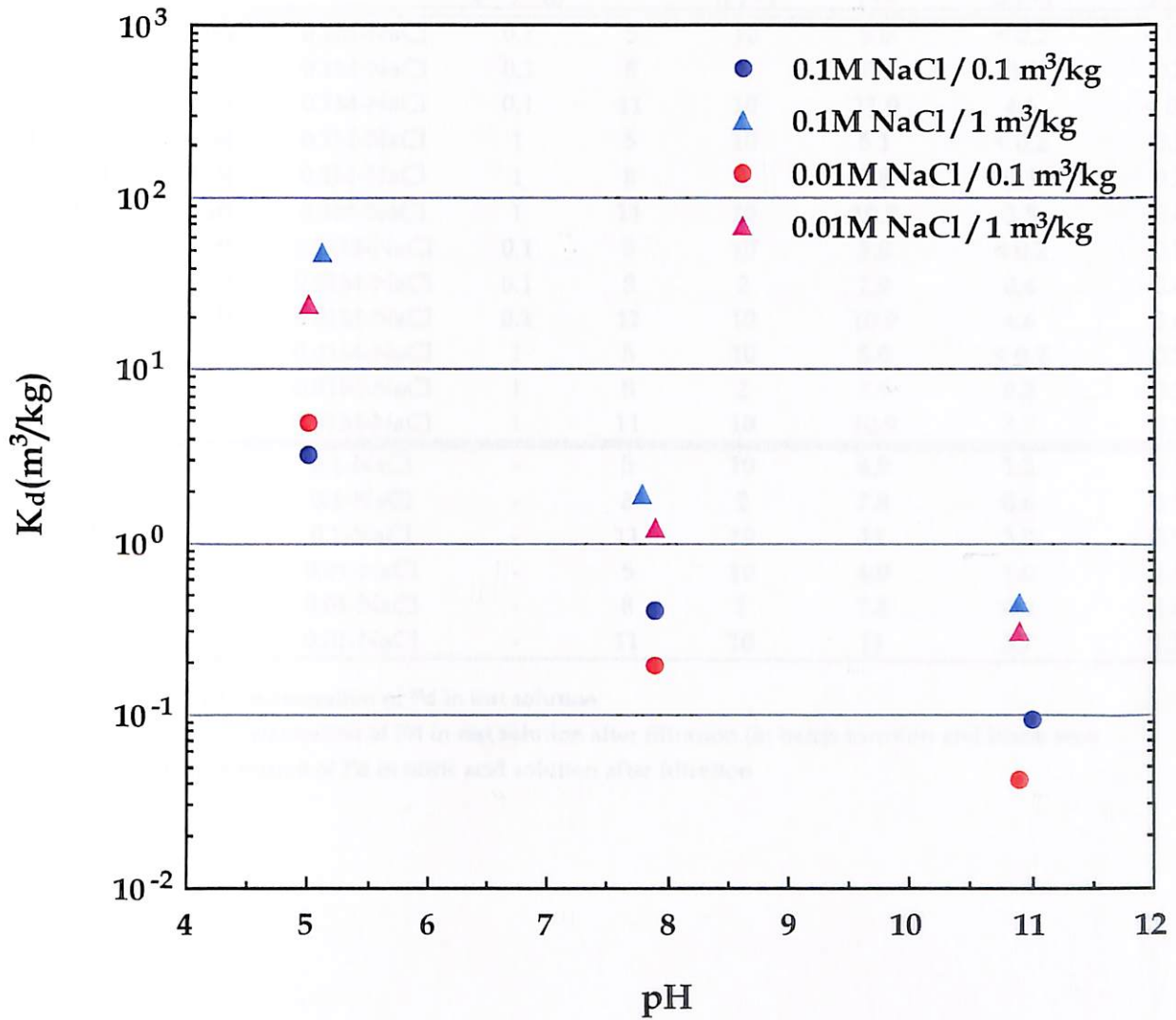


Figure 7 Distribution coefficients (K_d) of Palladium on tuff (by using $0.45\mu m$ membrane filters)

Table 8 Results of vessel wall sorption

sample name	solid	solution	L/S (m ³ /kg)	pH	C _i *1 (ppb)	measured pH	C _f *2 (ppb)	C _r *3 (ppb)
TSL5-1	tuff	0.1M-NaCl	0.1	5	10	5.0	< 0.2	< 0.2
TSL8-1	tuff	0.1M-NaCl	0.1	8	2	7.9	0.5	0.3
TSL11-1	tuff	0.1M-NaCl	0.1	11	10	11.0	4.6	< 0.2
TSH5-1	tuff	0.1M-NaCl	1	5	10	5.1	< 0.2	0.2
TSH8-1	tuff	0.1M-NaCl	1	8	2	7.8	0.3	0.2
TSH11-1	tuff	0.1M-NaCl	1	11	10	10.9	3.5	0.4
TDL5-1	tuff	0.01M-NaCl	0.1	5	10	5.0	< 0.2	0.7
TDL8-1	tuff	0.01M-NaCl	0.1	8	2	7.9	0.4	0.4
TDL11-1	tuff	0.01M-NaCl	0.1	11	10	10.9	4.6	0.6
TDH5-1	tuff	0.01M-NaCl	1	5	10	5.0	< 0.2	0.5
TDH8-1	tuff	0.01M-NaCl	1	8	2	7.9	0.3	0.3
TDH11-1	tuff	0.01M-NaCl	1	11	10	10.9	3.7	0.3
BTS5	-	0.1-NaCl	-	5	10	4.9	1.2	2.3
BTS8	-	0.1-NaCl	-	8	2	7.8	0.6	0.5
BTS11	-	0.1-NaCl	-	11	10	11	3.0	0.9
BTD5	-	0.01-NaCl	-	5	10	4.9	1.0	4.4
BTD8	-	0.01-NaCl	-	8	2	7.8	0.4	0.6
BTD11	-	0.01-NaCl	-	11	10	11	3.7	1.2

*1 initial concentration of Pd in test solution

*2 final concentration of Pd in test solution after filtration (in batch sorption and blank test)

*3 concentration of Pd in nitric acid solution after filtration

Table 9 Results of Pd solubility experiments

sample name	solution	pH	C _i *1 (ppb)	measured pH	solubility			
					10,000 MWCO		0.45 μm	
					(ppb)	(mol/l)	(ppb)	(mol/l)
PTS5-S	0.1-NaCl	5	500	5.1	540	5.1E-06	530	5.0E-06
PTS8-S	0.1-NaCl	8	500	7.8	42	3.9E-07	47	4.4E-07
PTS11-S	0.1-NaCl	11	500	10.9	58	5.5E-07	180	1.7E-06
PTD5-S	0.01-NaCl	5	500	5.1	180	1.7E-06	410	3.9E-06
PTD8-S	0.01-NaCl	8	500	7.8	15	1.4E-07	40	3.8E-07
PTD11-S	0.01-NaCl	11	500	10.9	79	7.4E-07	200	1.9E-06

*1 initial concentration of Pd in test solution

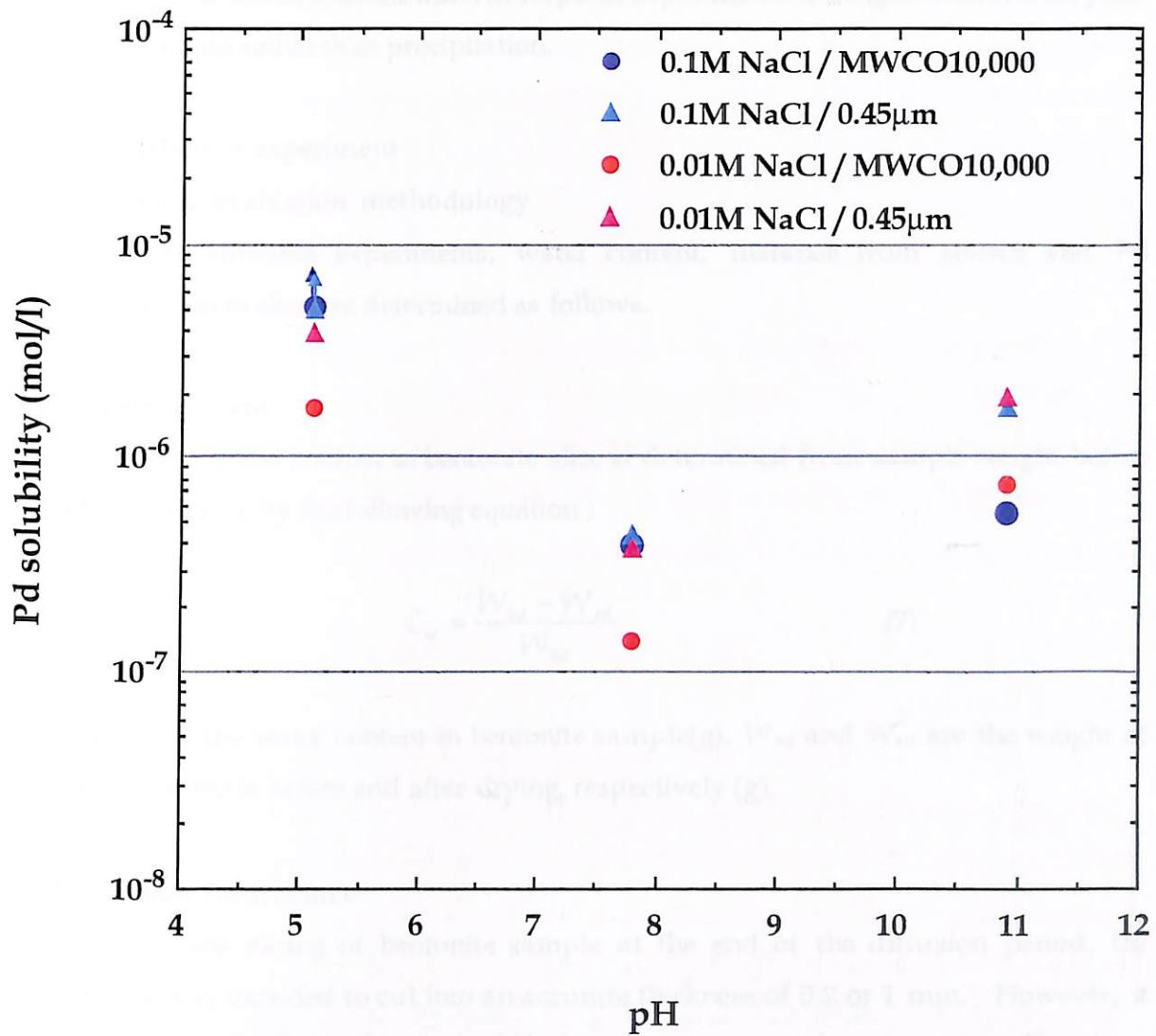


Figure 8 Solubility of Palladium in 0.1M and 0.01M-NaCl solution

concentration. The solubility of Pd is lowest at pH 8 and increases at lower or higher pH. Neither significant effect of ionic strength nor of filtration on Pd solubility is found. The initial concentrations of Pd in sorption experiments at pH 8 for bentonite and granodiorite are slightly higher than solubility. However, the effect of precipitation on sorption could be ignored because the difference of Pd concentration between solubility and initial concentration in sorption experiments is insignificant and sorption is fast reaction rather than precipitation.

3.3 Diffusion experiment

3.3.1 Data evaluation methodology

In diffusion experiments, water content, distance from source and Pd concentration in slice are determined as follows.

(1) Water content

The water content in bentonite slice is determined from sample weight before and after drying by the following equation ;

$$C_w = \frac{W_{bd} - W_{ad}}{W_{bd}} \quad (7)$$

where C_w is the water content in bentonite sample(g), W_{bd} and W_{ad} are the weight of bentonite sample before and after drying, respectively (g).

(2) Distance from source

In the slicing of bentonite sample at the end of the diffusion period, the bentonite was intended to cut into an accurate thickness of 0.2 or 1 mm. However, it is difficult to check whether desired thickness was accurately cut or not. Therefore, the distance from source was determined based on the weight of each slice by the following equation ;

$$X_i = \frac{W_i + W_{i-1}}{2} \times \frac{L}{\sum_{i=1}^n W_i} + X_{i-1} \quad (8)$$

where X_i is the distance from source of i th slice(mm), W_i is the weight of i th slice before drying(g), L is the thickness of bentonite sample(mm), n is the total number of slice for one bentonite sample.

(3) Pd concentration in slice

The Pd concentration in each slice was obtained by considering background concentration as the following equation. In this case, the background concentration was determined as averaged value of concentrations in each slice which obtained in the blank test(see 3.3.2).

$$C_i = \frac{(T_i - T_{bg})V}{W_i} \quad (9)$$

Where C_i is the Pd concentration in i th slice per unit weight(ng/g-bentonite), T_i is the Pd concentration in HNO₃ solution including i th slice(ng/L), T_{bg} is the averaged Pd concentration in blank sample(ng/g-bentonite), V is the volume of HNO₃ solution used for extraction(L), W_i is the weight of i th slice before drying(g). The error in Pd concentration of each slice is also evaluated considering results of blank tests (see 3.3.2).

3.3.2 Blank test

Results of blank tests for in-diffusion experiments are shown in Tables 10 - 11 with the experimental conditions. Averaged Pd concentration, standard deviation and percentage of standard deviation to the averaged concentration are also shown. Figure 9 shows plots of Pd concentrations as a function of distance from one surface of bentonite. Graphs (a) and (b) show the results for 1.4 and 1.8 Mg/m³, respectively. The averaged Pd concentration and standard deviation are also shown as solid and dotted lines, respectively. The averaged Pd concentration, standard deviation and percentage of standard deviation to the averaged concentration are 182, 17.3 and 9.49% in the blank test for 1.4 Mg/m³, 188, 30.8 and 13.0% for 1.8 Mg/m³, respectively. However, the error in Pd concentration by ICP-MS analysis is below about 1%. Therefore, the error in Pd concentration is estimated to have been caused by slicing and extraction from bentonite slice rather than ICP-MS analysis. The width of error for 1.8 Mg/m³ is larger than that for 1.4 Mg/m³ and the error may be also different by the

Table 10 Result of blank test for in-diffusion experiment (1.4 Mg/m³)

Bentonite Solution	Kunigel V1 distilled water	Back ground Pd concentration in slice (ng/g-bentonite)	Standard deviation	Percentage of standard deviation to background
density of sample	1.4 Mg/m ³			
diffusion time	-			
thickness of slice	1.0 mm	181.823	17.256	9.49%

Slice No.	Sample weight before drying (g)	Sample weight after drying (g)	Water content (%)	Distance from source (mm)	Pd concentration in leachant (µg/L)	Pd concentration in slice (C _{Pd}) (ng/g-bentonite)	Square of difference between C _{Pd} and averaged C _{Pd} (C _{Pd} -C _{Pd(average)}) ²
1	0.475	0.330	0.305	0.419	8.900	187.368	30.749
2	0.549	0.404	0.264	1.322	10.000	182.149	0.106
3	0.539	0.401	0.256	2.281	8.365	155.195	709.073
4	0.523	0.394	0.247	3.217	7.388	141.262	1645.217
5	0.543	0.409	0.247	4.157	9.842	181.252	0.326
6	0.550	0.412	0.251	5.121	9.698	176.327	30.206
7	0.542	0.405	0.253	6.084	10.880	200.738	357.769
8	0.607	0.451	0.257	7.097	12.180	200.659	354.786
9	0.572	0.428	0.252	8.136	11.710	204.720	524.275
10	0.580	0.434	0.252	9.152	12.070	208.103	690.650
11	0.599	0.445	0.257	10.191	10.460	174.624	51.823
12	0.561	0.417	0.257	11.214	9.642	171.872	99.034
13	0.576	0.427	0.259	12.217	10.790	187.326	30.285
14	0.586	0.430	0.266	13.241	11.060	188.737	47.803
15	0.620	0.457	0.263	14.304	9.741	157.113	610.600
16	0.595	0.437	0.266	15.376	10.760	180.840	0.966
17	0.588	0.427	0.274	16.419	11.370	193.367	133.267
18	0.570	0.411	0.279	17.440	10.070	176.667	26.590
19	0.563	0.404	0.282	18.439	11.340	201.421	384.071
20	0.604	0.394	0.348	19.467	10.070	166.722	228.051
			(0.267)			(181.823)	

Table 11 Result of blank test for in-diffusion experiment (1.8 Mg/m³)

Bentonite Solution	Kunigel V1 distilled water	Back ground Pd concentration in slice (ng/g-bentonite)	Standard deviation	Percentage of standard deviation to background
density of sample	1.8 Mg/m ³			
diffusion time	-			
thickness of slice	1.0 mm	188.001	30.791	12.99%

Slice No.	Sample weight before drying (g)	Sample weight after drying (g)	Water content (%)	Distance from source (mm)	Pd concentration in leachant (µg/L)	Pd concentration in slice (C _{Pd}) (ng/g-bentonite)	Square of difference between C _{Pd} and averaged C _{Pd} (C _{Pd} -C _{Pd(average)}) ²
1	0.470	0.373	0.206	0.355	9.628	204.851	283.938
2	0.691	0.583	0.156	1.232	10.770	155.861	1032.949
3	0.707	0.596	0.157	2.288	13.560	191.796	14.408
4	0.641	0.540	0.158	3.307	14.760	230.265	1786.297
5	0.665	0.558	0.161	4.294	13.730	206.466	340.977
6	0.664	0.556	0.163	5.298	13.770	207.380	375.543
7	0.720	0.603	0.163	6.343	12.720	176.667	128.458
8	0.809	0.675	0.166	7.498	12.350	152.658	1249.127
9	0.367	0.309	0.158	8.387	9.004	245.341	3287.876
10	0.625	0.524	0.162	9.136	12.570	201.120	172.119
11	0.633	0.530	0.163	10.087	12.390	195.735	59.815
12	0.627	0.523	0.166	11.039	13.640	217.544	872.804
13	0.595	0.494	0.170	11.962	9.246	155.395	1063.128
14	0.658	0.548	0.167	12.909	12.410	188.602	0.361
15	0.621	0.517	0.167	13.875	10.500	169.082	357.909
16	0.621	0.515	0.171	14.813	12.790	205.958	322.473
17	0.616	0.507	0.177	15.748	11.260	182.792	27.127
18	0.602	0.494	0.179	16.668	10.270	170.598	302.850
19	0.637	0.520	0.184	17.604	12.650	198.587	112.075
20	1.267	0.996	0.214	19.043	13.090	103.315	7171.665
			(0.170)			(188.001)	

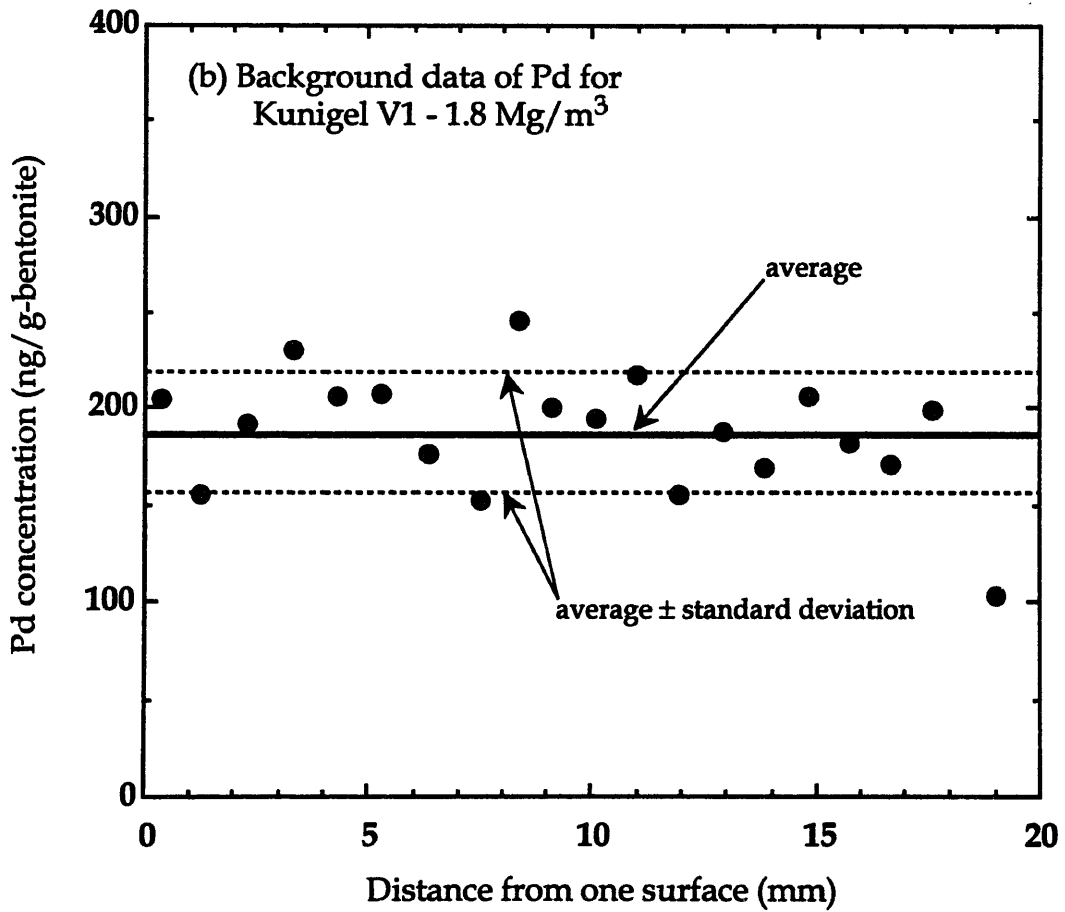
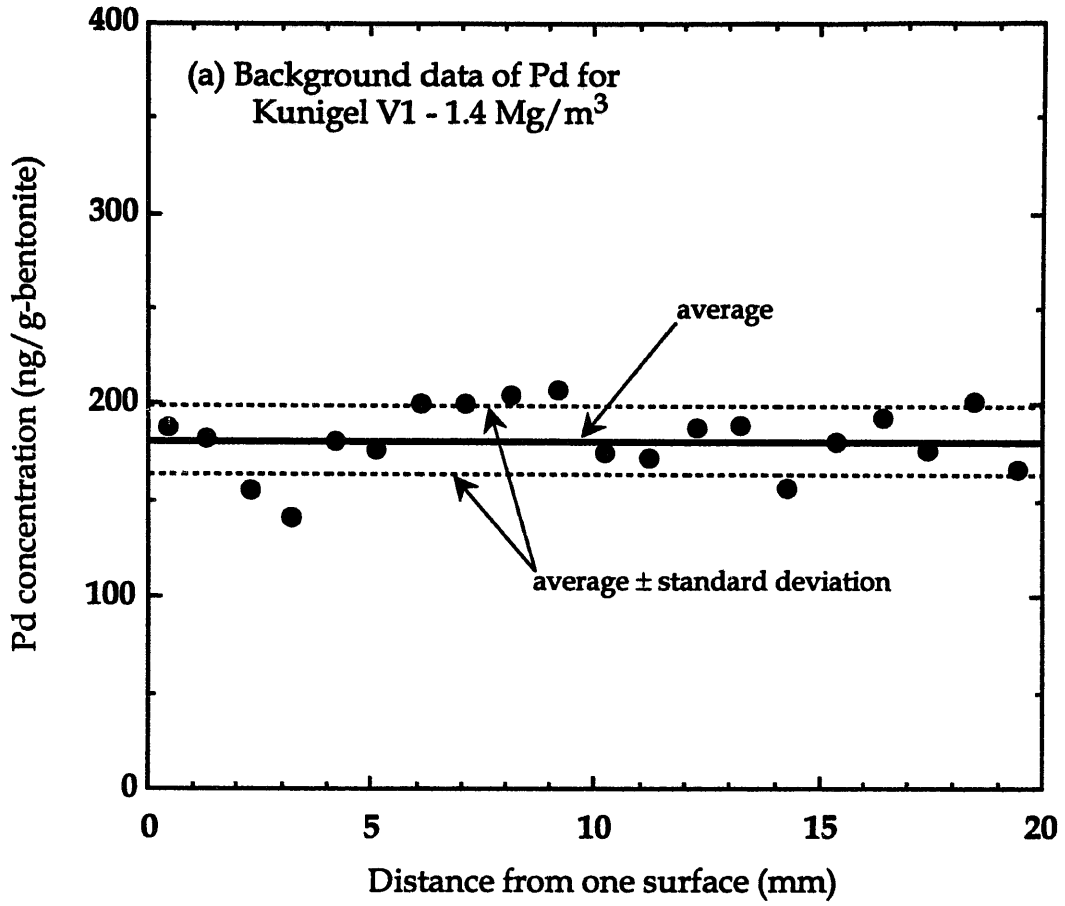


Figure 9 Result of blank test for in-diffusion experiment
(a) 1.4 Mg/m^3 , (b) 1.8 Mg/m^3

thickness of slice(0.2 and 1.0 mm). Hence, the average values of Pd concentration and standard deviation obtained in the blank tests for 1.4 and 1.8 Mg/m³ were used for an estimation of error in Pd concentration in the in-diffusion experiments.

3.3.3 Analytical methodology

The diffusion of nuclides into porous media is interpreted by the following equation based on Fick's second law considering retardation(Crank, 1975),

$$\frac{\partial C_p}{\partial t} = D_a \frac{\partial^2 C_p}{\partial x^2} \quad (3)$$

where C_p is the concentration of tracer element in the porewater(kg/m³), t is the diffusion period(s), x is the distance from the source of tracer element(m), D_a is the apparent diffusion coefficient(m²/s). The apparent diffusion coefficient is related to the effective diffusion coefficient and K_d as follows(Skagius and Neretnieks, 1984),

$$D_a = \frac{D_e}{\epsilon + \rho K_d} \quad (4)$$

where ϵ is the porosity, D_e is the effective diffusion coefficient(m²/s), ρ is the dry density of bentonite(kg/m³). The apparent diffusion coefficient is derived from concentration profile using either instantaneous planar source model or constant source model as follows:

(1) Instantaneous planar source model

The instantaneous planar source model is based on the assumption that the concentration of tracer is lower than solubility in porewater, and a planar source consists of a limited amount of substance. For one-dimensional semi-infinite medium, solving equation (3) based on initial and boundary conditions as follows : initial condition : $C_p(t, x) = 0, t = 0, x > 0$; boundary condition : $C_p(t, x) = 0, t > 0, x = \infty$, the analytical solution is derived as the following equation(Crank, 1975),

$$C = \frac{M}{\sqrt{\pi D_a t}} \exp\left(-\frac{x^2}{4D_a t}\right) \quad (5)$$

$$M = \int_b^{\infty} C dx$$

where C is the concentration of tracer element in the bentonite(kg/m^3), M is the total amount of diffusing element in the bentonite(kg/m^3).

(2) Constant source model

The constant source model is based on the assumption that the concentration of tracer in porewater at the surface where the tracer solution is putted on is constant at the solubility if the concentration of tracer solution is much higher than solubility. In the concentration profiles adapted by the constant source model, a few higher plots by precipitation are generally observed at the surface, and surface concentration is constant with time. In semi-infinite medium, solving equation (3) based on initial and boundary conditions as follows: initial condition : $C_p(t, x) = 0, t = 0, x > 0$; boundary condition : $C_p(t, x) = C_0, t > 0, x = 0$, the analytical solution is derived as the following equation (Crank, 1975).

$$C = C_0 \operatorname{erfc}\left(\frac{x}{2\sqrt{D_a t}}\right) \quad (6)$$

$$\operatorname{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\infty} \exp(-\eta^2) d\eta$$

where C_0 is the constant concentration of tracer element at the interface of the bentonite (kg/m^3).

Hence, the apparent diffusion coefficients were determined based on analytical solutions of both models, and applicability of both model was discussed.

3.3.4 Concentration profile and apparent diffusion coefficient

The results of in-diffusion experiments of Pd in bentonite are shown in Tables 12-15 with the experimental conditions. Concentration profiles of Pd in compacted bentonites are shown in Figure 10-13. The error of Pd concentration in each slice increases with increasing penetration depth, and the concentration level approximately becomes background level around 2 mm from source. The profiles were fitted both based on the instantaneous planar source model and the constant source model by non-linear least squares method. The fitted curves are also shown in each

concentration profile in Figures 10-13. Graphs (a) and (b) show fitting curves by the instantaneous planar source model and the constant source model, respectively. It is difficult to judge, by which model D_a is appropriate to be calculated from concentration profiles shown in Figures 10-13. The D_a values obtained by both models are shown in Table 16 with experimental conditions. The D_a values obtained by both models were in the orders of 10^{-13} to 10^{-12} m^2/s and relatively large error in D_a was found. This is because Pd concentration in bentonite is near background level as described above and error is large. The D_a values tends to decrease with increasing of dry density of bentonite. The D_a values obtained by the constant source model are higher than those by the instantaneous planar source model by a factor of 2. Thinking boundary condition, the concentration of Pd at the surface of bentonite decreased with time as shown in Figures 10-13. If boundary condition is controlled by solubility, the concentration of Pd at the surface of bentonite is constant. Besides, no higher plot by precipitation was observed at the surface in the concentration profiles. From these results, the authors judged that analysis by the planar source model is appropriate to calculate D_a .

Table 12 Result of diffusion experiment (1.4 Mg/m³, 7 days)

Bentonite Solution	Kunigel V1 distilled water	Pd concentration in slice (Background)	Error
density of sample	1.4 Mg/m ³	(ng/g-bentonite)	
diffusion time	7.2 days	185.00	24.00
thickness of slice	0.2 mm		

Slice No.	Sample weight before drying (g)	Sample weight after drying (g)	Water content (%)	Distance from source (mm)	Pd concentration in leachant (µg/L)	Pd concentration in slice (ng/g-bentonite)	Error	Pd concentration in slice (- BG) (ng/g-bentonite)	Error
1	0.135	0.090	0.333	0.116	19.290	571.556	74.302	386.556	78.082
2	0.074	0.053	0.284	0.296	11.720	633.514	82.357	448.514	85.782
3	0.113	0.082	0.274	0.458	14.780	523.186	68.014	338.186	72.124
4	0.108	0.076	0.296	0.648	15.100	559.259	72.704	374.259	76.563
5	0.115	0.086	0.252	0.840	16.580	576.696	74.970	391.696	78.718
6	0.120	0.086	0.283	1.043	10.340	344.667	44.807	159.667	50.829
7	0.112	0.083	0.259	1.242	6.304	225.143	29.269	40.143	37.850
8	0.119	0.086	0.277	1.441	5.731	192.639	25.043	7.639	34.686
9	0.117	0.083	0.291	1.645	5.009	171.248	22.262	-	-
10	0.136	0.098	0.279	1.863	6.071	178.559	23.213	-	-
			(0.283)						

Table 13 Result of diffusion experiment (1.4 Mg/m³, 48 days)

Bentonite Solution		Kunigel V1 distilled water		Pd concentration in slice (Background)		Error				
density of sample	1.4 Mg/m ³				(ng/g-bentonite)	185.00	24.00			
diffusion time	48.2 days									
thickness of slice	1.0 mm									
Slice No.	Sample weight before drying (g)	Sample weight after drying (g)	Water content (%)	Distance from source (mm)	Pd concentration in leachant (µg/L)	Pd concentration in slice (ng/g-bentonite)	Error	Pd concentration in slice (- BG) (ng/g-bentonite)	Error	
1	0.614	0.439	0.285	0.524	17.470	284.528	36.989	99.528	44.093	
2	0.612	0.455	0.257	1.570	16.170	264.216	34.348	79.216	41.902	
3	0.567	0.424	0.252	2.577	15.580	274.780	35.721	89.780	43.035	
4	0.607	0.455	0.250	3.579	15.100	248.764	32.339	63.764	40.272	
5	0.565	0.422	0.253	4.579	12.710	224.956	29.244	39.956	37.832	
6	0.611	0.456	0.254	5.582	12.740	208.511	27.106	23.511	36.204	
7	0.593	0.440	0.258	6.610	11.560	194.941	25.342	9.941	34.903	
8	0.589	0.439	0.255	7.619	10.450	177.419	23.065	-	-	
9	0.606	0.450	0.257	8.639	9.786	161.485	20.993	-	-	
10	0.557	0.414	0.257	9.631	8.852	158.923	20.660	-	-	
11	0.586	0.434	0.259	10.607	9.265	158.106	20.554	-	-	
12	0.599	0.444	0.259	11.618	8.941	149.265	19.405	-	-	
13	0.596	0.440	0.262	12.638	8.551	143.473	18.652	-	-	
14	0.596	0.443	0.257	13.655	8.239	138.238	17.971	-	-	
15	0.577	0.428	0.258	14.656	8.064	139.757	18.168	-	-	
16	0.582	0.430	0.261	15.646	8.343	143.351	18.636	-	-	
17	0.600	0.441	0.265	16.654	7.943	132.383	17.210	-	-	
18	0.563	0.411	0.270	17.647	7.683	136.465	17.740	-	-	
19	0.546	0.394	0.278	18.593	7.434	136.154	17.700	-	-	
20	0.551	0.378	0.314	19.530	7.106	128.966	16.766	-	-	
			(0.263)							

Table 14 Result of diffusion experiment (1.8 Mg/m³, 7 days)

Bentonite Solution	Kunigel V1 distilled water				Pd concentration in slice (Background) (ng/g-bentonite)	Error			
density of sample	1.8 Mg/m ³				185.00	24.00			
diffusion time	7.2 days								
thickness of slice	0.2 mm								
Slice No.	Sample weight before drying (g)	Sample weight after drying (g)	Water content (%)	Distance from source (mm)	Pd concentration in leachant (µg/L)	Pd concentration in slice (ng/g-bentonite)	Error	Pd concentration in slice (- BG) (ng/g-bentonite)	Error
1	0.190	0.152	0.200	0.144	17.210	362.316	47.101	177.316	52.863
2	0.084	0.064	0.238	0.353	12.750	607.143	78.929	422.143	82.497
3	0.155	0.131	0.155	0.534	14.110	364.129	47.337	179.129	53.073
4	0.102	0.086	0.157	0.730	8.760	343.529	44.659	158.529	50.699
5	0.161	0.135	0.161	0.930	11.150	277.019	36.012	92.019	43.277
6	0.122	0.101	0.172	1.145	6.757	221.541	28.800	36.541	37.489
7	0.141	0.115	0.184	1.345	6.502	184.454	23.979	-	-
8	0.120	0.099	0.175	1.543	6.679	222.633	28.942	-	-
9	0.133	0.109	0.180	1.736	6.729	202.376	26.309	-	-
10	0.127	0.104	0.181	1.933	5.759	181.386	23.580	-	-
			(0.180)						

Table 15 Result of diffusion experiment (1.8 Mg/m³, 83 days)

Bentonite Solution	Kunigel V1 distilled water	Pd concentration in slice (Background)	Error
density of sample	1.8 Mg/m ³	(ng/g-bentonite)	
diffusion time	83.1 days	185.00	24.00
thickness of slice	1.0 mm		

Slice No.	Sample weight before drying (g)	Sample weight after drying (g)	Water content (%)	Distance from source (mm)	Pd concentration in leachant (µg/L)	Pd concentration in slice (ng/g-bentonite)	Error	Pd concentration in slice (- BG) (ng/g-bentonite)	Error
1	0.596	0.502	0.158	0.453	16.380	274.832	35.728	89.832	43.041
2	0.670	0.563	0.160	1.417	16.280	242.985	31.588	57.985	39.671
3	0.656	0.555	0.154	2.425	15.300	233.232	30.320	48.232	38.669
4	0.712	0.602	0.154	3.466	14.760	207.303	26.949	22.303	36.087
5	0.640	0.539	0.158	4.494	12.580	196.563	25.553	11.562	35.057
6	0.686	0.579	0.156	5.503	12.620	183.965	23.915	-	-
7	0.652	0.550	0.156	6.521	11.100	170.245	22.132	-	-
8	0.659	0.554	0.159	7.518	10.550	160.091	20.812	-	-
9	0.679	0.571	0.159	8.536	11.870	174.816	22.726	-	-
10	0.653	0.549	0.159	9.550	11.160	170.904	22.217	-	-
11	0.669	0.561	0.161	10.555	11.550	172.646	22.444	-	-
12	0.663	0.557	0.160	11.569	11.400	171.946	22.353	-	-
13	0.632	0.529	0.163	12.554	11.210	177.373	23.059	-	-
14	0.678	0.567	0.164	13.550	11.040	162.832	21.168	-	-
15	0.654	0.549	0.161	14.564	11.240	171.865	22.343	-	-
16	0.698	0.584	0.163	15.592	11.280	161.605	21.009	-	-
17	0.592	0.494	0.166	16.574	10.750	181.588	23.606	-	-
18	0.639	0.536	0.161	17.510	11.240	175.900	22.867	-	-
19	0.707	0.591	0.164	18.534	11.520	162.942	21.182	-	-
20	0.610	0.509	0.166	19.536	10.360	169.836	22.079	-	-

(0.160)

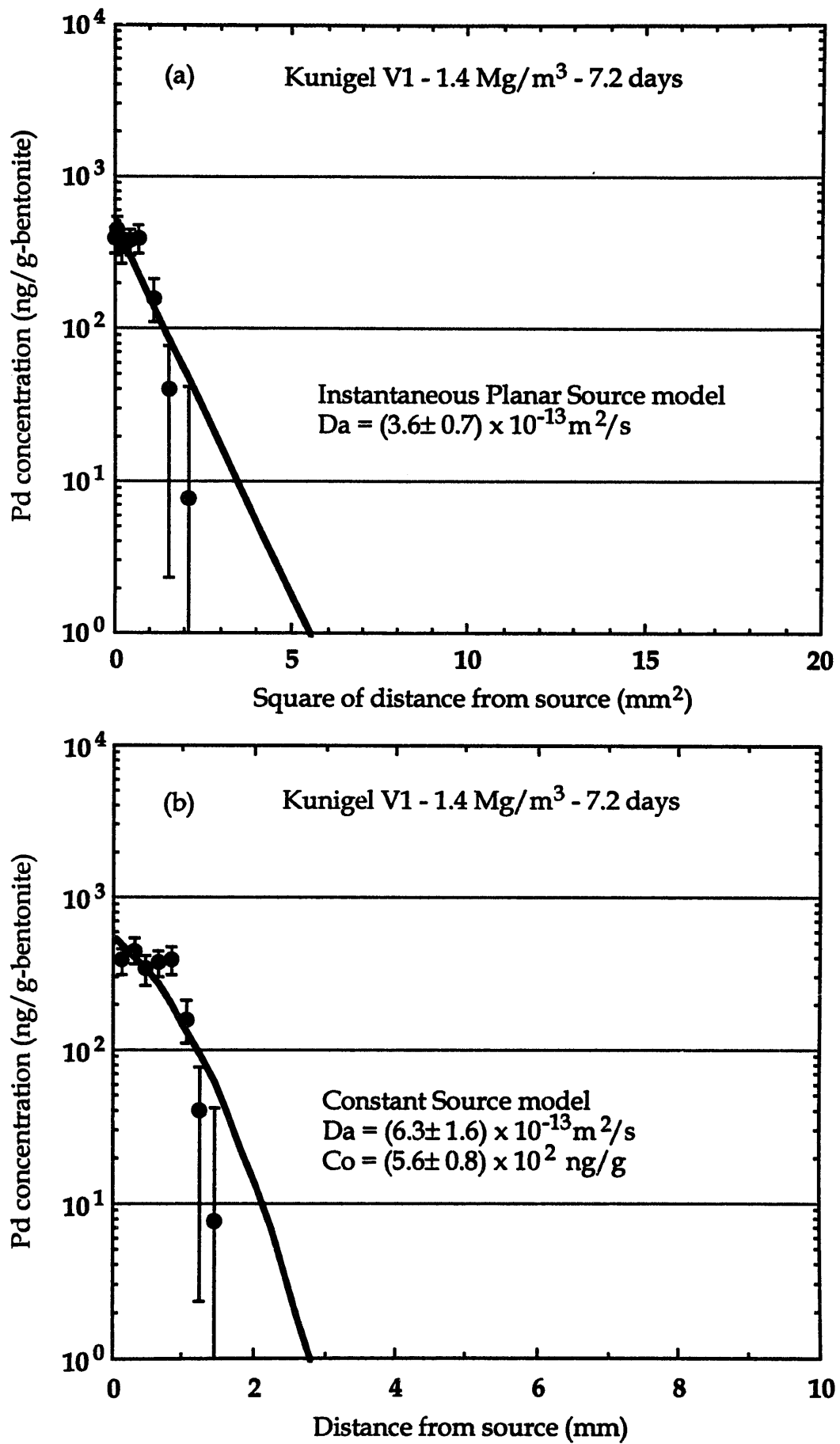


Figure 10 Concentration profile of Pd in bentonite and fitting curves (Kunigel V1 - 1.4 Mg/m³ - 7.2 days)

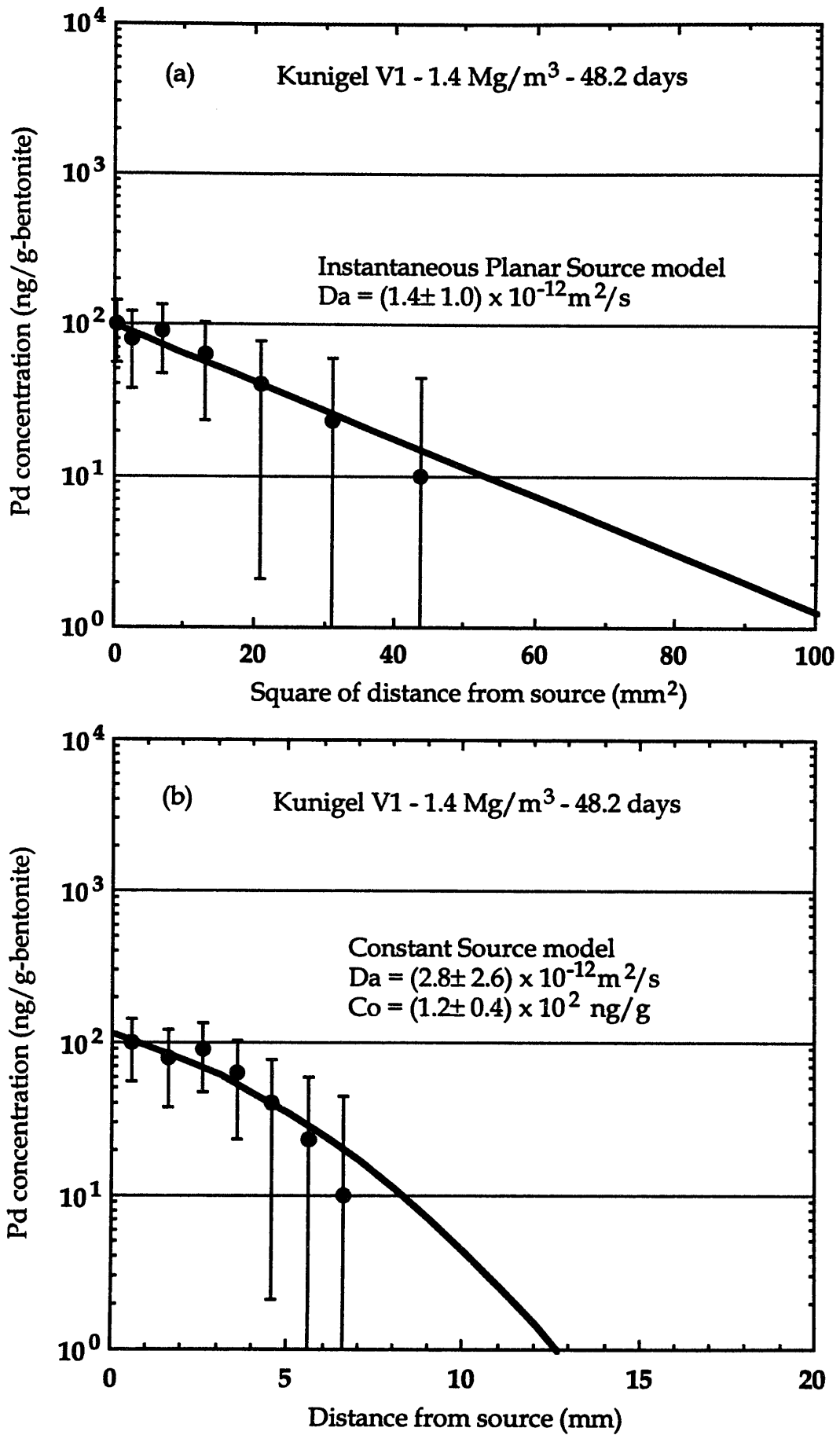


Figure 11 Concentration profile of Pd in bentonite and fitting curves (Kunigel V1 - 1.4 Mg/m³ - 48.2 days)

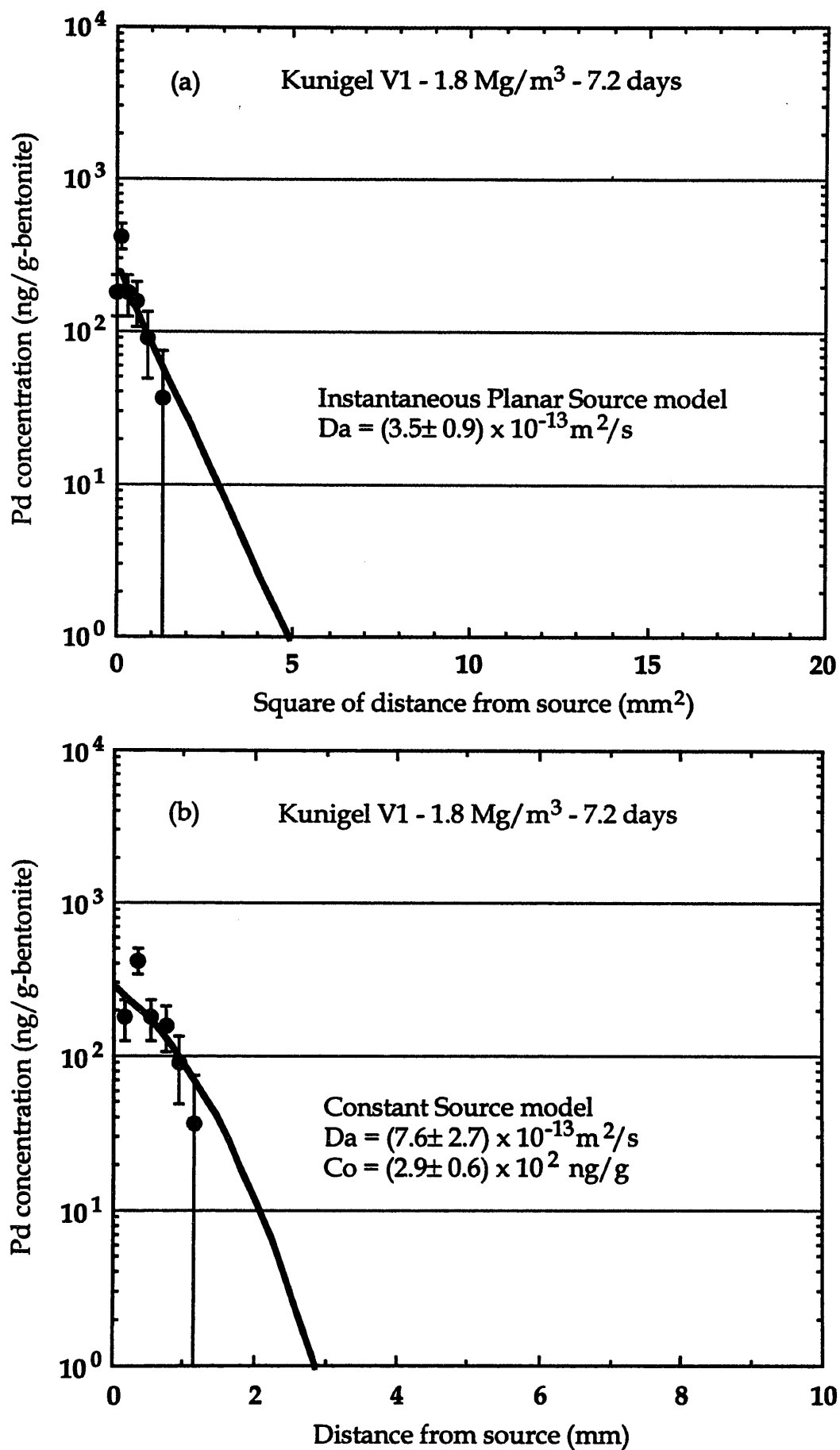


Figure 12 Concentration profile of Pd in bentonite and fitting curves (Kunigel V1 - 1.8 Mg/m³ - 7.2 days)

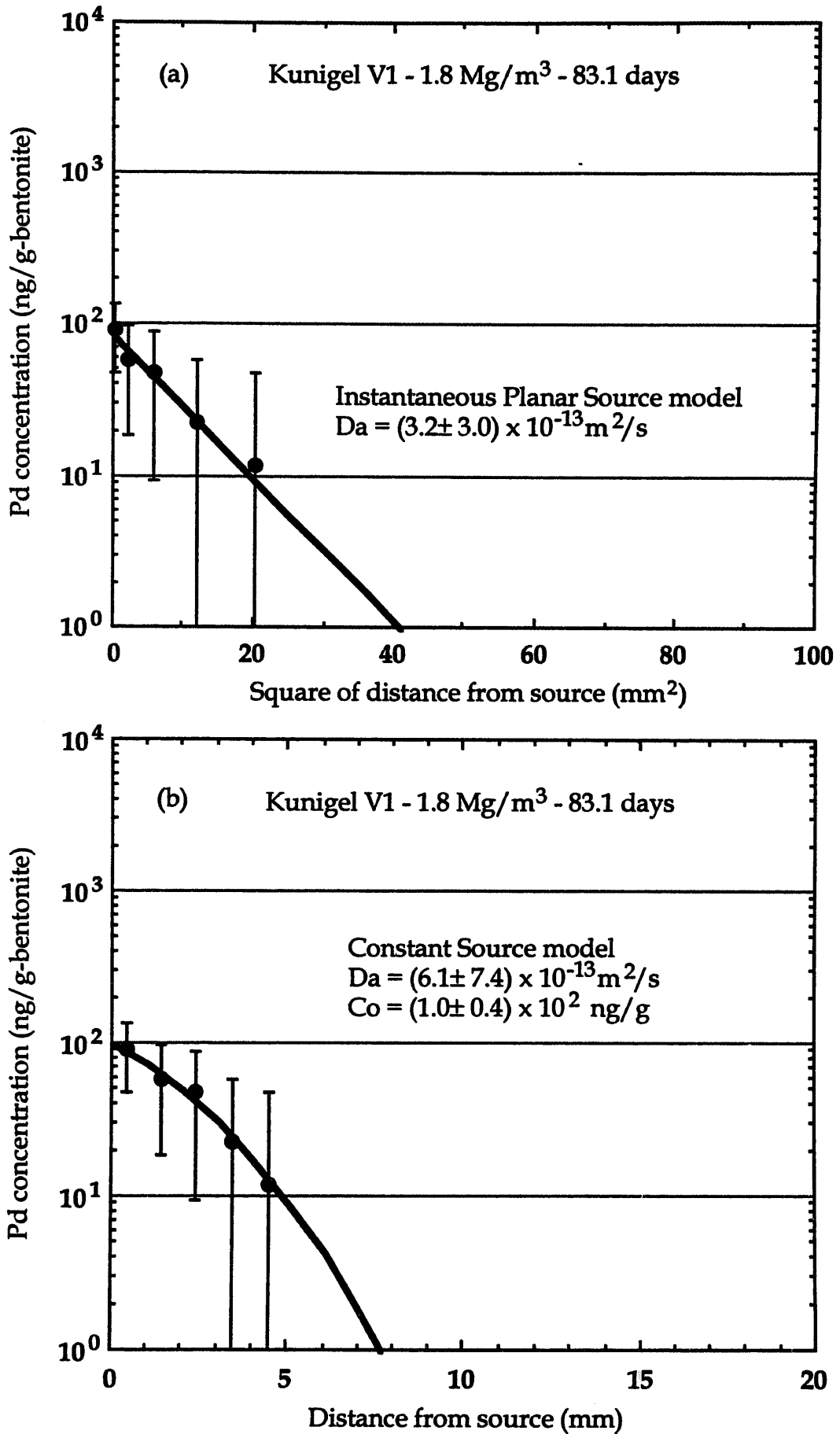


Figure 13 Concentration profile of Pd in bentonite and fitting curves (Kunigel V1 - 1.8 Mg/m³ - 83.1 days)

Table 16 The apparent diffusion coefficients obtained by in-diffusion experiment

dry density (Mg/m ³)	diffusion time (days)	apparent diffusion coefficient (m ² /s)	
		instantaneous planar source model	constant source model
1.4	7.2	$(3.6 \pm 0.7) \times 10^{-13}$	$(6.3 \pm 1.6) \times 10^{-13}$
	48.2	$(1.4 \pm 1.0) \times 10^{-12}$	$(2.8 \pm 1.6) \times 10^{-12}$
	(average)	8.7×10^{-13}	1.7×10^{-12}
1.8	7.2	$(3.5 \pm 0.9) \times 10^{-13}$	$(7.6 \pm 2.7) \times 10^{-13}$
	83.1	$(3.2 \pm 3.0) \times 10^{-13}$	$(6.1 \pm 7.4) \times 10^{-13}$
	(average)	3.4×10^{-13}	6.8×10^{-13}

4. Discussions

4.1 Aqueous speciation

The result of solubility experiments was compared with that obtained by thermodynamic calculation using the geochemical PHREEQE code (Parkhurst et al., 1980) and the thermodynamic database. The aqueous chemistry of Pd has been few studied. In the JNC chemical thermodynamic database (JNC-TDB) (Yui et al., 1999), formation constant of Pd(II) is selected only for chloride and amino complexes. The solubility product of Pd(II) is selected only for Pd(cr). However, formation constant for hydrolysis of Pd(II) is not selected because of complex hydrolysis reaction involving polynuclearization and absence of reliable data (Yui et al., 1999, Lothenbach et al., 1999). The thermodynamic data of Pd selected in the JNC-TDB are shown in Table 17. On the other hand, Baeyens and McKinley (1989) selected formation constants for hydrolysis and solubility product of Pd(OH)₂(am) obtained by Nabivanets and Kalabina (1970) in the thermodynamic database for performance assessment in Switzerland. These data are also shown in Table 17. The solubility and speciation of Pd under the experimental conditions are calculated by thermodynamic data shown in Table 17. Hence, thermodynamic calculations were conducted by using only the formation constants selected by the JNC-TDB and by using all the formation constants in Table 17. In all calculations, the solubility limiting phase was assumed to be Pd(OH)₂(am) selected by Baeyens and McKinley (1989). The calculated solubility are shown in Figure 14 with the experimental results. Solubility calculated by using only the formation constants selected in the JNC-TDB is in the range of 10⁻⁴ to 10⁻¹³ mol/l in a pH range of 5 to 11 and is remarkably dependent on pH and ionic strength. On the other hand, solubility calculated by using all the formation constants in Table 17 is ranging from 10⁻⁴ to 10⁻⁶ mol/l and is independent of pH and ionic strength. The experimental solubility and its dependency on pH and ionic strength are relatively close to those calculated by using all the formation constants in Table 17. The speciations calculated by using only the formation constants selected in JNC-TDB and by using all the formation constants in Table 18 are shown in Figure 15 and 16, respectively. Graphs (a) and (b) show the speciations for 0.1M and 0.01M-NaCl solution, respectively. The speciations calculated by using only the formation constants selected in the JNC-TDB

Table 17 Thermodynamic data of Pd(II) in JNC-TDB selected by Yui et al.(1999) and Baeyens and McKinley(1989)

reactions	log K	Reference
solid		
$\text{Pd(cr)} = \text{Pd}^{2+} + 2\text{e}^-$	-32.9	JNC-TDB/Yui et al.(1999)
$\text{Pd(OH)}_2(\text{s}) = \text{Pd(OH)}_2(\text{aq})$	-1.6	Baeyens and McKinley(1989)
aqueous species		
$\text{Pd}^{2+} + \text{Cl}^- = \text{PdCl}^+$	5.1	JNC-TDB/Yui et al.(1999)
$\text{Pd}^{2+} + 2\text{Cl}^- = \text{Pd(Cl)}_2(\text{aq})$	8.3	JNC-TDB/Yui et al.(1999)
$\text{Pd}^{2+} + 3\text{Cl}^- = \text{Pd(Cl)}_3^-$	10.9	JNC-TDB/Yui et al.(1999)
$\text{Pd}^{2+} + 4\text{Cl}^- = \text{Pd(Cl)}_4^{2-}$	11.7	JNC-TDB/Yui et al.(1999)
$\text{Pd}^{2+} + 3\text{Cl}^- - \text{H}^+ + \text{H}_2\text{O} = \text{PdCl}_3\text{OH}^{2-}$	2.5	JNC-TDB/Yui et al.(1999)
$\text{Pd}^{2+} + 2\text{Cl}^- - 2\text{H}^+ + 2\text{H}_2\text{O} = \text{PdCl}_2(\text{OH})_2^{2-}$	-7.0	JNC-TDB/Yui et al.(1999)
$\text{Pd}^{2+} + \text{NH}_3(\text{aq}) = \text{PdNH}_3^{2+}$	9.6	JNC-TDB/Yui et al.(1999)
$\text{Pd}^{2+} + 2\text{NH}_3(\text{aq}) = \text{Pd(NH}_3)_2^{2+}$	18.5	JNC-TDB/Yui et al.(1999)
$\text{Pd}^{2+} + 3\text{NH}_3(\text{aq}) = \text{Pd(NH}_3)_3^{2+}$	26.0	JNC-TDB/Yui et al.(1999)
$\text{Pd}^{2+} + 4\text{NH}_3(\text{aq}) = \text{Pd(NH}_3)_4^{2+}$	32.8	JNC-TDB/Yui et al.(1999)
$\text{Pd}^{2+} - \text{H}^+ + \text{H}_2\text{O} = \text{PdOH}^+$	-1.8	Baeyens and McKinley(1989)
$\text{Pd}^{2+} - 2\text{H}^+ + 2\text{H}_2\text{O} = \text{Pd(OH)}_2(\text{aq})$	-3.8	Baeyens and McKinley(1989)
$\text{Pd}^{2+} - 3\text{H}^+ + 3\text{H}_2\text{O} = \text{Pd(OH)}_3^-$	-15.9	Baeyens and McKinley(1989)
$\text{Pd}^{2+} - 4\text{H}^+ + 4\text{H}_2\text{O} = \text{Pd(OH)}_4^{2-}$	-29.4	Baeyens and McKinley(1989)

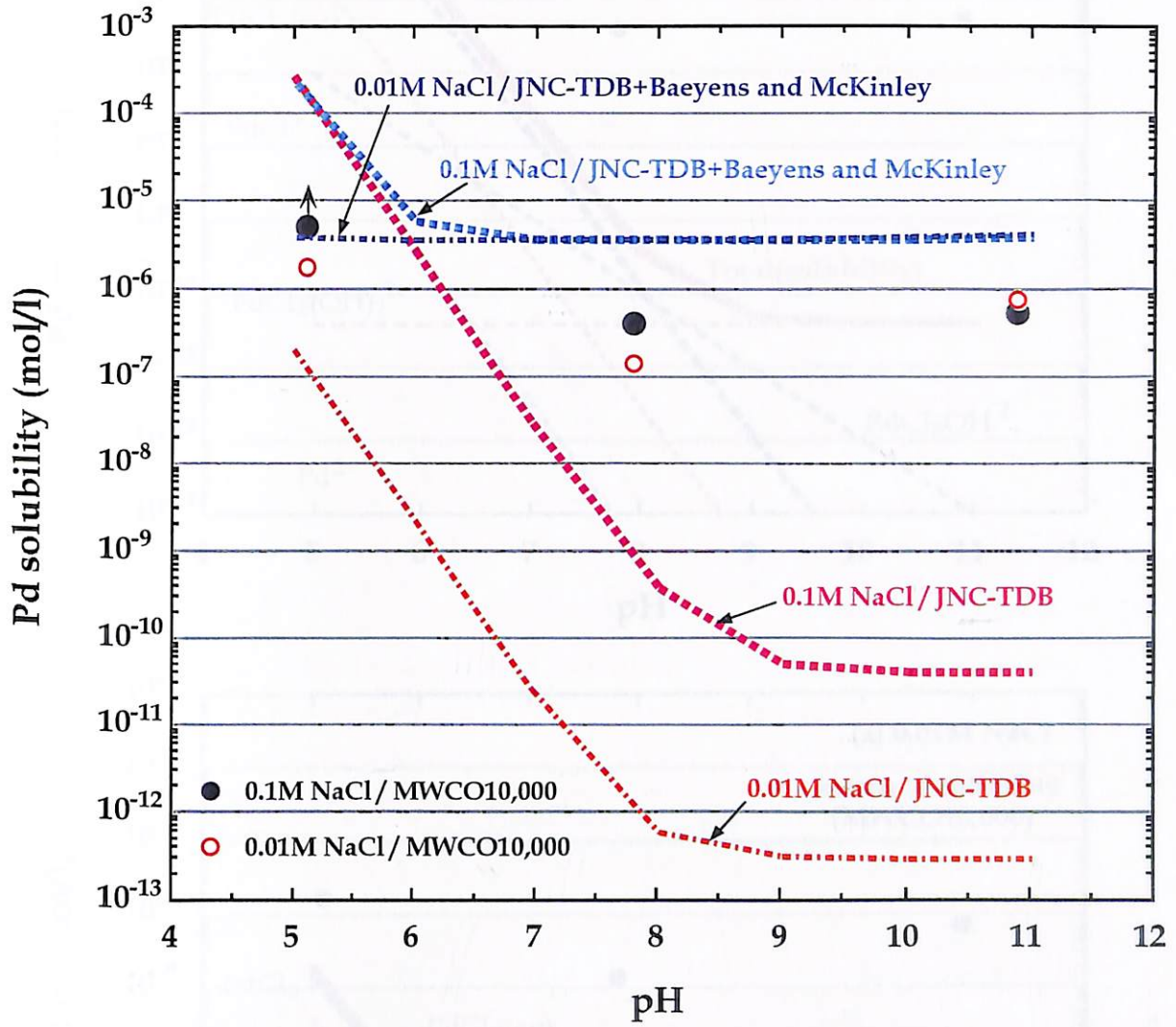


Figure 14 Solubility of Palladium measured and calculated by TDB (formation constants used in calculation are presented in figure and solubility limiting phase was assumed to be Pd(OH)₂(am) in all calculation.)

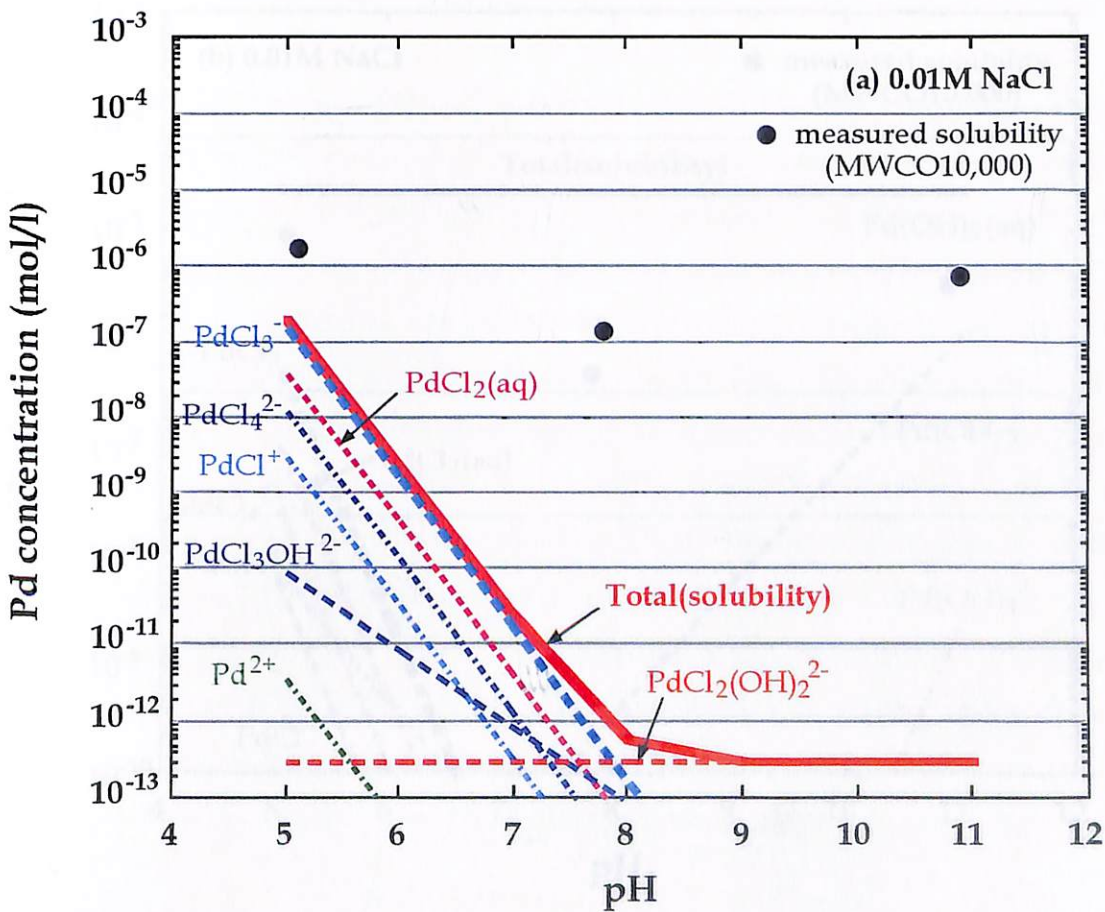
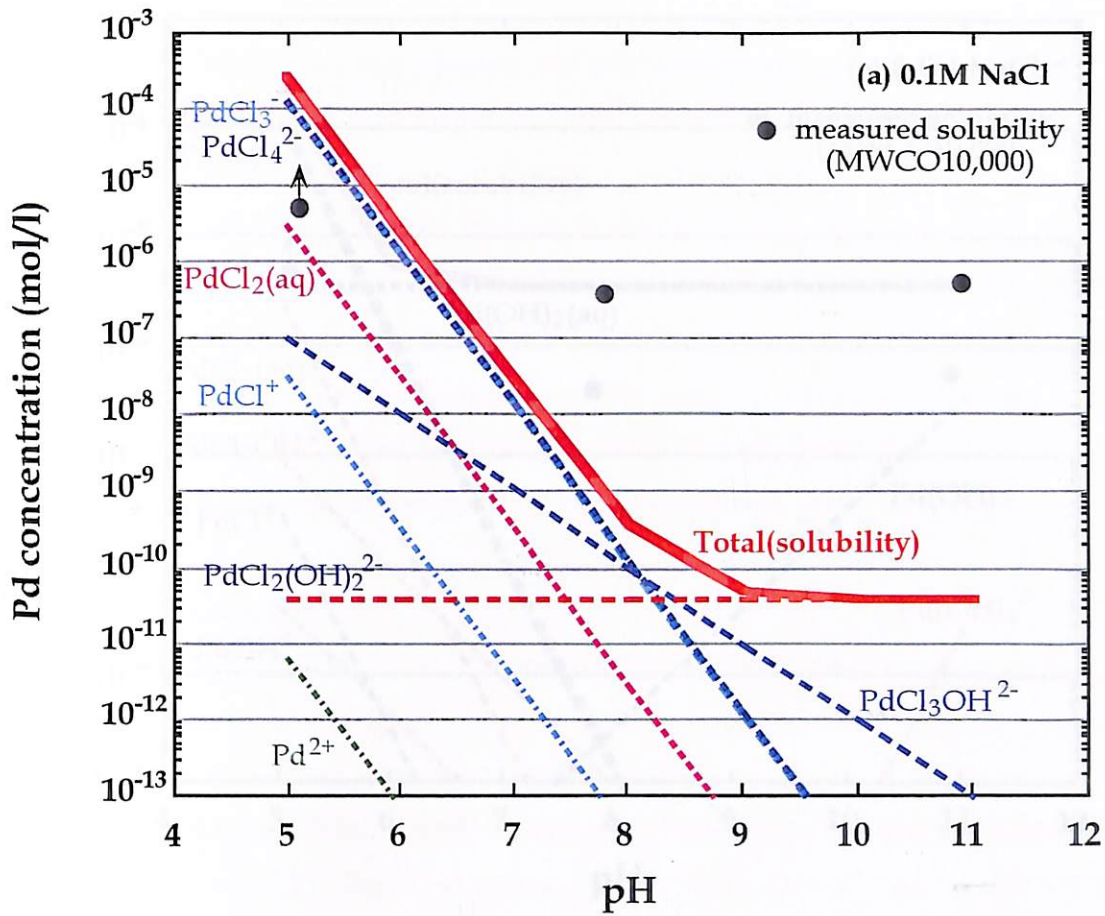


Figure 15 Solubility and speciation calculated by JNC-TDB
(Solubility limiting phases is assumed to be $\text{Pd}(\text{OH})_2(\text{am})$.)

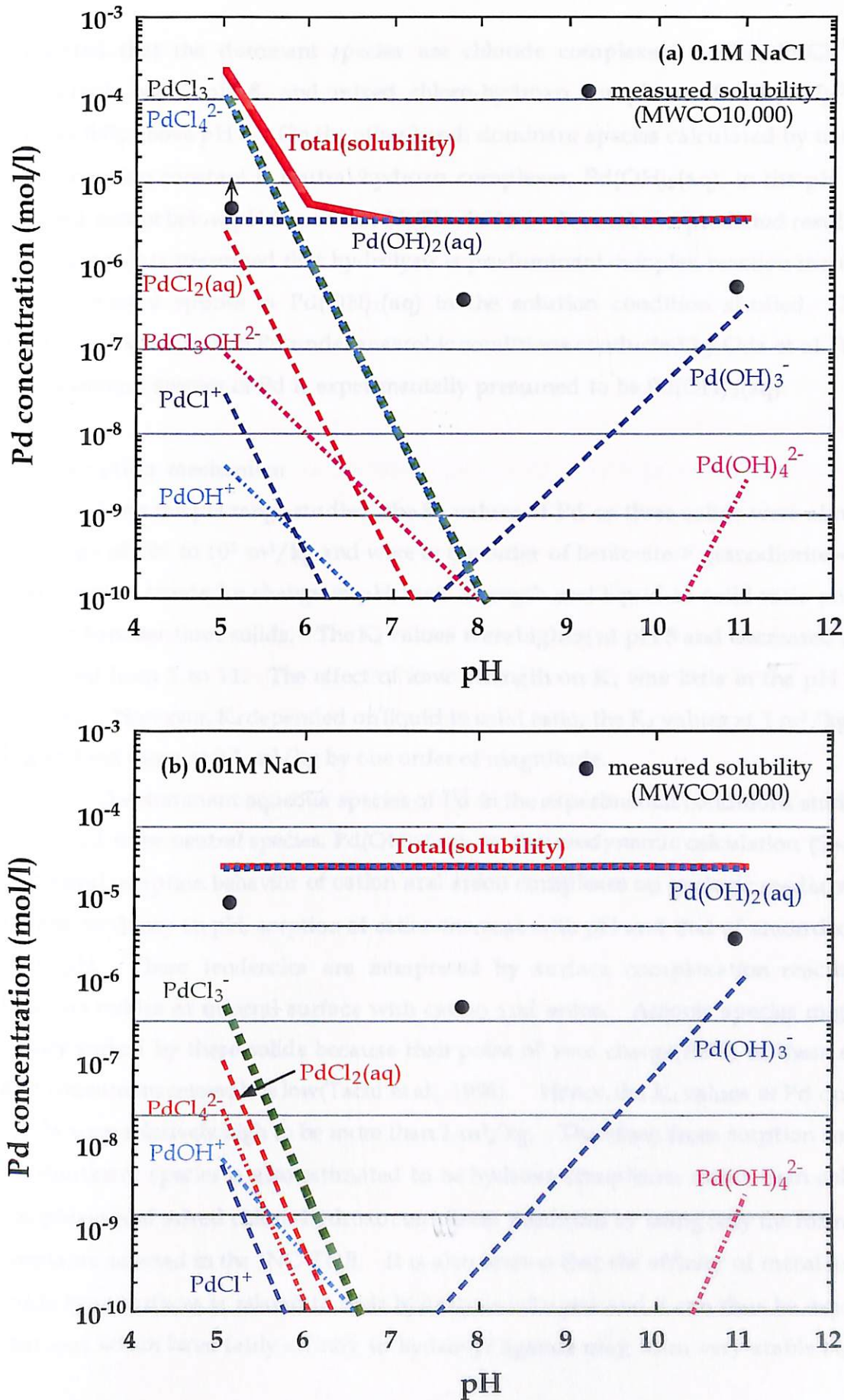


Figure 16 Solubility and speciation calculated by TDB which formation constant for hydrolysis of palladium in Nabivanets and Kalabina(1970) in addition to JNC-TDB. (Solubility limiting phases is assumed to be $\text{Pd}(\text{OH})_2(\text{am})$.)

indicated that the dominant species are chloride complexes; PdCl_3^- , PdCl_4^{2-} and $\text{PdCl}_2(\text{aq})$, below pH 8, and mixed chloro-hydroxo complexes; $\text{PdCl}_2(\text{OH})_2^{2-}$ and $\text{PdCl}_3\text{OH}^{2-}$, above pH 8. On the other hand, dominant species calculated by using all the formation constant is neutral hydroxo complexes, $\text{Pd}(\text{OH})_2(\text{aq})$, in the pH range studied except below pH 6 in a 0.1M NaCl solution. From above predicted results and discussion, it is presumed that hydrolysis is predominant complex reaction in solution and dominant species is $\text{Pd}(\text{OH})_2(\text{aq})$ in the solution condition studied. In the solubility experiment of Pd under anaerobic conditions conducted by Oda et al. (1996), the dominant species of Pd is experimentally presumed to be $\text{Pd}(\text{OH})_2(\text{aq})$.

4.2 Sorption mechanism

Over the pH range studied, the K_d values of Pd on three solids were almost in the range of 10^{-1} to 10^2 m^3/kg and were in the order of bentonite > granodiorite = tuff. The sorption trends for change in pH, ionic strength and liquid to solid ratio are very similar between three solids. The K_d values were highest at pH 5 and decreased as pH increased from 5 to 11. The effect of ionic strength on K_d was little in the pH range studied. However, K_d depended on liquid to solid ratio, the K_d values at 1 m^3/kg were higher than those at 0.1 m^3/kg by one order of magnitude.

The dominant aqueous species of Pd in the experimental conditions studied is estimated to be neutral species, $\text{Pd}(\text{OH})_2(\text{aq})$, by thermodynamic calculation (See 4.1). In general, sorption behavior of cation and anion complexes on geologic media shows reverse tendency on pH, sorption of cation increase with pH and that of anion decrease with pH. These tendencies are interpreted by surface complexation reaction of hydrous oxides at mineral surface with cation and anion. Anionic species might be poorly sorbed by these solids because their point of zero charge (PZC) of these solids and constituent minerals is low (Tachi et al., 1998). Hence, the K_d values of Pd on three solids were relatively high to be more than 1 m^3/kg . Therefore, from sorption results, the dominant species is also estimated to be hydroxo complexes, rather than chloride complexes and mixed chloro-hydroxo complexes predicted by using only the formation constants selected in the JNC-TDB. It is also known that the affinity of metal ions to oxide-type surfaces is related to their hydrolysis behavior and it can thus be expected that ions which have fairly affinity to hydroxyl ligands may form very stable surface

complexes on these types of solids (Schindler and Stumm, 1987). Hence, sorption of divalent metal ions such as Ni and Co etc. on oxide-type surfaces increases with pH and corresponds to their hydrolysis behavior (Schindler and Stumm, 1987, Lothenbach et al., 1997). Therefore, it can thus be expected that Pd(II) which has affinity to hydrolysis may form very stable surface complexes on these types of solids. However, sorption behavior of Pd is different from those of divalent metal ions because sorption of Pd show reverse tendency on pH and data of divalent metal ions may be inappropriate as chemical analogy for Pd. It appears that uncharged complexes may be different from cationic metal ions and may be more strongly sorbed. Baston et al. (1995) indicated that technetium are strongly sorbed under reducing conditions because dominant species changes to Tc(IV) neutral hydroxo complex from Tc(VII) anionic species which is dominant under aerobic conditions. Baston et al. (1995) describes that this may be due to the solvation layer round the aqueous complex being less strongly bound for an charged species, thus making the sorption reaction more energetically favorable. The pH dependency of K_d values of Pd suggests that sorption is most likely to be occurring onto positively charged $S-OH_2^+$ type site which are progressively removed (to form SOH and SO^- sites) at higher pH values.

4.3 Derivation of K_d from D_a and comparison between K_d values by batch sorption and diffusion

The K_d in compacted bentonite is derived from D_a obtained by in-diffusion experiments. The K_d in compacted bentonite is expressed by D_e and D_a from equation (4) as follows;

$$K_d = \frac{1}{\rho} \left(\frac{D_e}{D_a} - 1 \right) \quad (10)$$

where ρ is the dry density of compacted bentonite (kg/m^3), D_e is the effective diffusion coefficient (m^2/s) and D_a is the apparent diffusion coefficient (m^2/s). If there are measured data for both of D_e and D_a , K_d in compacted bentonite can be derived based on equation (10). However, there is no data for D_e of Pd in compacted bentonite. Hence, D_e values for tritiated water (Sato et al., 1993) were used in the derivation of K_d values because the dominant species of Pd was estimated to be neutral.

The K_d values calculated from the D_a based on the instantaneous planar source model are shown in Table 18 and have large error because of large error in D_a values. The average K_d values are $2.7 \times 10^{-1} \text{ m}^3/\text{kg}$ for $1.4 \text{ Mg}/\text{m}^3$ and $1.8 \times 10^{-1} \text{ m}^3/\text{kg}$ for $1.8 \text{ Mg}/\text{m}^3$. On the other hand, K_d values obtained by batch sorption experiments at pH 8 in the 0.1M-NaCl solution which is estimated to be close to porewater in compacted bentonite were 3.1 and $16 \text{ m}^3/\text{kg}$ for liquid to solid ratio of 0.1 and 1 m^3/kg (see Table 4 and Figure 4), respectively, being 1-2 orders of magnitude higher than those calculated from D_a and D_e values. The K_d is not ideally affected by the liquid to solid ratio. However, many experimental studies indicated that K_d values decreased with decreasing the liquid to solid ratio (Meier et al., 1987, 1994, Sato and Shibutani, 1994). This may be because porewater chemistry also changes with changing bentonite density. For example, it is reported that Na and $\text{HCO}_3^- + \text{CO}_3^{2-}$ concentrations changes (Sasaki et al., 1995). The ionic strength of porewater generally increases with decreasing liquid to solid ratio. This indicates that competing ions increase as liquid to solid ratio decreases. Hence, K_d value obtained by batch sorption and diffusion experiments are plotted as a function of liquid to solid ratio in Figure 17. The K_d values are related to liquid to solid ratio and decrease with reduction of the liquid to solid ratio. However, in the results of sorption experiments, the effect of ionic strength in a range of 10^{-2} to 10^{-1} on K_d of Pd was not found. Therefore, this effect may be because sorption site contributing for sorption decreases as liquid to solid ratio decreases.

Table 18 The distribution coefficient derived from D_a obtained by in-diffusion experiment

dry density (g/cm ³)	diffusion time (days)	distribution coefficient, K_d (m ² /s) (from D_a based on instantaneous planar source model)
1.4	7.2	$(4.4 \pm 0.9) \times 10^{-1}$
	48.2	$(1.1 \pm 0.8) \times 10^{-1}$
	(average)	2.7×10^{-1}
1.8	7.2	$(1.7 \pm 0.5) \times 10^{-1}$
	83.1	$(1.9 \pm 1.8) \times 10^{-1}$
	(average)	1.8×10^{-1}

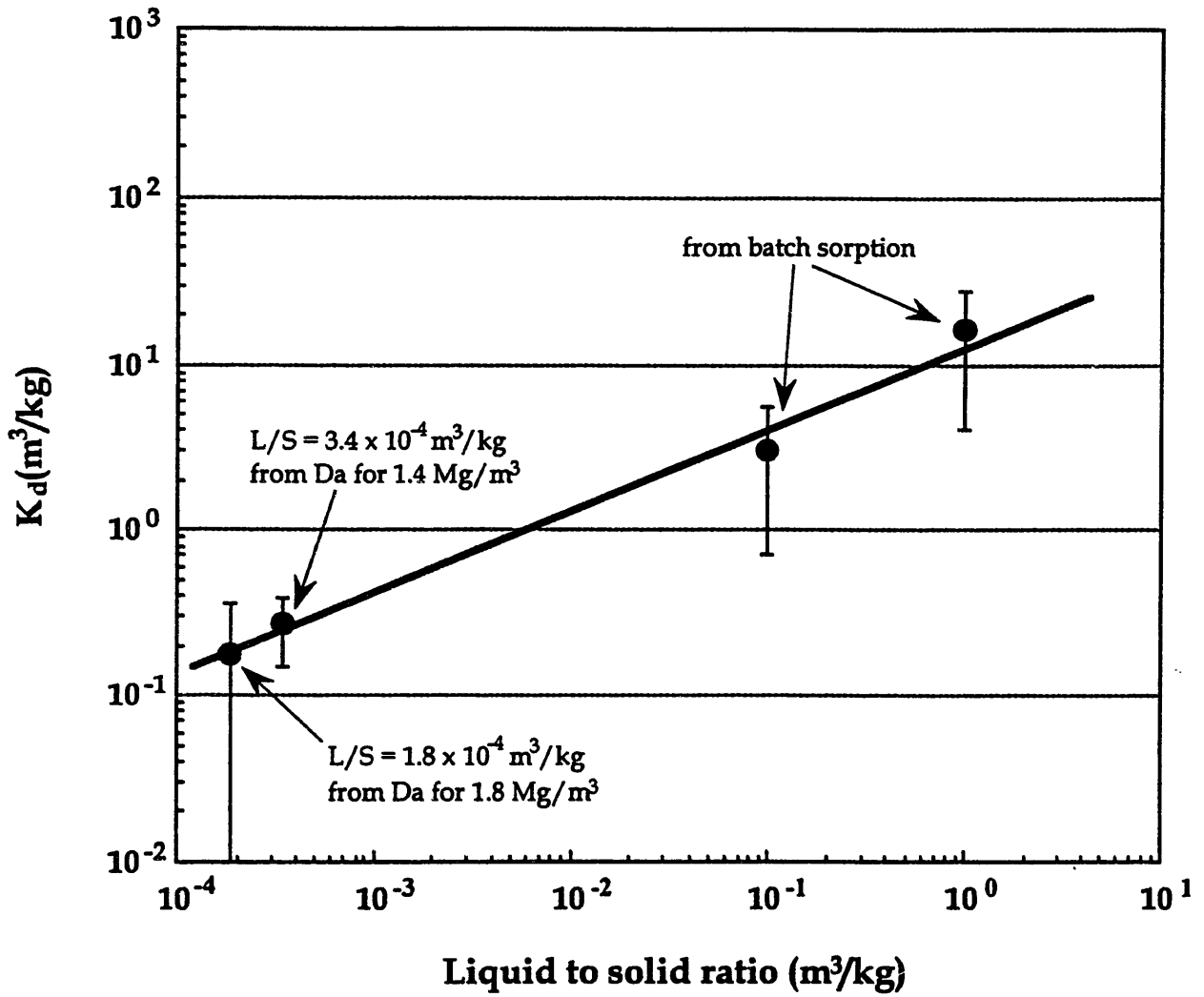


Figure 17 K_d obtained by batch sorption and diffusion experiments as a function of the liquid to solid ratio

5. Conclusions

Sorption behavior of palladium on bentonite, granodiorite and tuff were investigated as functions of pH, ionic strength and liquid to solid ratio by the batch sorption experiment under aerobic condition at room temperature. Over the pH range studied, the K_d values of Pd on three solids were almost in the range of 10^{-1} to 10^2 m³/kg and were in the order of bentonite > granodiorite ≈ tuff. The sorption trends with change in pH, ionic strength and liquid to solid ratio are very similar between three solids. The K_d values were the highest at pH 5 and decreases with increasing pH between 5 and 11. The effect of ionic strength on K_d was not found in a range of 10^{-2} to 10^{-1} , but K_d values increased with increasing liquid to solid ratio. The width of variation in K_d was one order of magnitude in a liquid to solid ratio of 0.1 to 1 m³/kg. Sorption behavior of Pd is different from those of divalent metal ions, Ni and Co etc. and chemical analogy may be inappropriate. The dominant aqueous species of Pd in the experimental conditions studied is estimated to be neutral species, Pd(OH)₂(aq) by the thermodynamic calculation. The K_d values of Pd on three solids were relatively high and uncharged complexes may be more strongly sorbed. The pH dependency of K_d values suggests that Pd sorption is most likely to be occurring onto positively charged S-OH₂⁺ type site which are progressively removed (to form SOH and SO⁻ sites) at higher pH values.

Diffusion behavior of Pd in bentonite was also studied by in-diffusion method as a function of dry density. The D_a values obtained based on the instantaneous planar source model which are selected by comparison with the constant source model were in the order of 10^{-13} to 10^{-12} m²/s and decreased with increasing dry density of bentonite. However, the D_a values have great errors because of large error in Pd concentration which is caused by containing of Pd naturally in bentonite. The K_d values in compacted bentonite were derived from the D_a values and were in the order of 10^{-2} to 10^{-1} m³/kg. The K_d values obtained from the D_a values were lower than those obtained by batch sorption by 1-2 orders of magnitude. However, the difference between both K_d values is correlated to liquid to solid ratio, and K_d values decreased with reduction of liquid to solid ratio. This effect may be because sorption site contributing for sorption decreases as liquid to solid ratio decreases.

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