

POSIVA 98-12

# Sorption of plutonium on rocks in groundwaters from Posiva investigation sites

**Seija Kulmala, Martti Hakanen**  
Laboratory of Radiochemistry  
Department of Chemistry  
University of Helsinki

**Antero Lindberg**  
Geological Survey of Finland

**December 1998**

---

**POSIVA OY**

Mikonkatu 15 A, FIN-00100 HELSINKI, FINLAND

Phone (09) 2280 30 (nat.), (+358-9-) 2280 30 (int.)

Fax (09) 2280 3719 (nat.), (+358-9-) 2280 3719 (int.)

POSIVA 98-12

# Sorption of plutonium on rocks in groundwaters from Posiva investigation sites

**Seija Kulmala, Martti Hakanen**  
Laboratory of Radiochemistry  
Department of Chemistry  
University of Helsinki

**Antero Lindberg**  
Geological Survey of Finland

**December 1998**

---

**POSIVA OY**

Mikonkatu 15 A, FIN-00100 HELSINKI, FINLAND

Phone (09) 2280 30 (nat.), (+358-9-) 2280 30 (int.)

Fax (09) 2280 3719 (nat.), (+358-9-) 2280 3719 (int.)

**ISBN 951-652-050-2**  
**ISSN 1239-3096**

The conclusions and viewpoints presented in the report are those of author(s) and do not necessarily coincide with those of Posiva.

Radiokemian laboratorio  
Kemian laitos  
PL 55 (A.I.Virtasen aukio 1)  
00014 Helsingin yliopisto

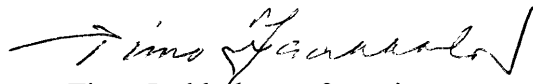
Helsinki 27.11.1998

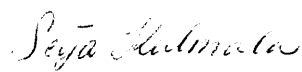
Tutkimussopimus TVO9197/95/LPn

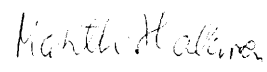
PLUTONIUMIN JA PROTAKTINIUMIN SORPTIO TVO:N TUTKIMUSALUEIDEN  
KALLIOPERÄSSÄ

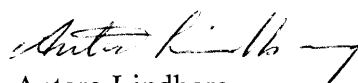
Raportti POSIVA-98-12

SORPTION OF PLUTONIUM ON ROCKS IN GROUNDWATERS FROM POSIVA  
INVESTIGATION SITES

  
Timo Jaakkola, professori

  
Seija Kulmala.

  
Martti Hakanen

  
Antero Lindberg  
Geologian tutkimuslaitos  
PL 96  
02151 ESPOO

1  
10.12.1998  
2.12.1998  
KUS



# Posiva-raportti – Posiva Report

Posiva Oy  
Mikonkatu 15 A, FIN-00100 HELSINKI, FINLAND  
Puh. (09) 2280 30 – Int. Tel. +358 9 2280 30

Raportin tunnus – Report code

POSIVA 98-12

Julkaisuaika – Date

December 1998

Tekijä(t) – Author(s) Seija Kulmala, Martti Hakanen, University of Helsinki Antero Lindberg, Geological Survey of Finland	Toimeksiantaja(t) – Commissioned by  Posiva Oy
Nimeke – Title  SORPTION OF PLUTONIUM ON ROCKS IN GROUNDWATERS FROM POSIVA INVESTIGATION SITES	
Tiivistelmä – Abstract  <p>Sorption of plutonium was studied as part of an investigation into the sorption and diffusion of nuclides of spent nuclear fuel in Finnish bedrock. The sorption of Pu was studied for rocks and groundwaters from three areas in Finland under consideration by Posiva Oy as locations for the repository of spent nuclear fuel. These areas are Olkiluoto at Eurajoki, Romuvaara at Kuhmo and Kivetty at Äänekoski.</p> <p>Sorption percentages and the mass distribution ratios, <math>R_d</math> values, were determined for crushed rock by batch method. Polished rock thin sections were studied by autoradiographic method. The experiments were performed under both oxic and anoxic (nitrogen atmosphere) conditions.</p> <p>The <math>R_d</math> values under oxic conditions were <math>\geq 1.0</math> m<sup>3</sup>/kg, (0.05 - 0.4) m<sup>3</sup>/kg and (0.2 - 0.6) m<sup>3</sup>/kg for Olkiluoto, Romuvaara and Kivetty rock samples, respectively. Under anoxic conditions the values were (0.91 - 18) m<sup>3</sup>/kg for Olkiluoto, (0.38 - 9.1) m<sup>3</sup>/kg for Romuvaara and (1.0 - 5.9) m<sup>3</sup>/kg for Kivetty samples. The oxidation/reduction equilibrium for the anoxic atmosphere was checked with some crushed rock/groundwater samples spiked with Tc.</p>	
Avainsanat – Keywords sorption, plutonium, bedrock, oxic and anoxic conditions, radioactive waste disposal, autoradiography, batch method	
ISBN ISBN 951-652-050-2	ISSN ISSN 1239-3096
Sivumäärä – Number of pages 52	Kieli – Language English



# Posiva-raportti – Posiva Report

Posiva Oy  
Mikonkatu 15 A, FIN-00100 HELSINKI, FINLAND  
Puh. (09) 2280 30 – Int. Tel. +358 9 2280 30

Raportin tunnus – Report code

POSIVA 98-12

Julkaisuaika – Date

Joulukuu 1998

Tekijä(t) – Author(s) Seija Kulmala, Martti Hakanen, Helsingin yliopisto Antero Lindberg, Geologian tutkimuskeskus	Toimeksiantaja(t) – Commissioned by  Posiva Oy
Nimeke – Title  PLUTONIUMIN SORPTIO POHJAVEDESTÄ KIVEEN POSIVAN TUTKIMUSALUEILLA	
Tiivistelmä – Abstract  <p>Plutoniumin sorptiota tutkittiin osana laajempaa tutkimusohjelmaa ydinpolttoaineen nuklidien sorptio- ja diffuusio-ominaisuuksista Suomen kallioperässä. Plutoniumin sorptiota tutkittiin kolmen paikkakunnan: Eurajoen Olkiluodon, Kuhmon Romuvaaran ja Äänekosken Kivetyn kallioperä-näytteillä laboratorio-olosuhteissa.</p> <p>Sorptioprosentit ja massajakaantumiskertoimet, <math>R_d</math>-arvot määritettiin eräkokeilla kivimurskeille. Kivien eri mineraalien sorptioaffiniteettia tutkittiin autoradiografisesti. Kokeita tehtiin sekä hapellisissa että hapettomissa (typpiatmosfääri) olosuhteissa.</p> <p>Sorptio oli korkea kaikille näytteille. Hapellisissa olosuhteissa <math>R_d</math>-arvot olivat <math>\geq 1,0</math> m<sup>3</sup>/kg Olkiluodon kivimurskeille, (0,05 - 0,4) m<sup>3</sup>/kg Romuvaaran kivimurskeille ja (0,2 - 0,6) m<sup>3</sup>/kg Kivetyn kivimurskeille. Hapettomissa olosuhteissa <math>R_d</math>-arvot olivat myös korkeita; (0,91 - 18) m<sup>3</sup>/kg Olkiluodon, (0,38 - 9,1) m<sup>3</sup>/kg Romuvaaran ja (1,0 - 5,9) m<sup>3</sup>/kg Kivetyn kivimurskeille. Hapettomien olosuhteiden hapetus/pelkistys-tasapainoa seurattiin teknetiumilla leimatuilla kivi-murske/pohjavesi-näytteillä.</p>	
Avainsanat - Keywords sorptio, plutonium, kallioperä, hapelliset ja hapettomat olosuhteet, radioaktiivisen jätteen loppusijoitus, autoradiografia, eräkoemenetelmä	
ISBN ISBN 951-652-050-2	ISSN ISSN 1239-3096
Sivumäärä – Number of pages 52	Kieli – Language Englanti

## TABLE OF CONTENTS

Abstract	
Tiivistelmä	
PREFACE	8
1 INTRODUCTION	9
2 MATERIALS	10
2.1 Rock samples	10
2.2 Groundwaters	10
2.3 Radionuclides	11
3 METHODS	13
3.1 Sorption experiments	13
3.2 Radioactivity measurements	14
4 RESULTS AND DISCUSSION	16
4.1 Sorption of Pu under oxic conditions	16
4.2 Sorption of Pu with added Cs under oxic conditions	18
4.3 Sorption of Pu under anoxic conditions	19
4.4 Verification of redox conditions by sorption of Tc under anoxic conditions	22
4.5 Sorption of Pu on polished rock surfaces	23
5 SUMMARY AND CONCLUSIONS	26
REFERENCES	29
APPENDIX A: Materials used in the study	31
APPENDIX B: Methods for the sorption studies	36
APPENDIX C: Sorption of plutonium on rocks from Posiva investigation sites where sorption was from the corresponding groundwaters. Values are for individual samples.	42

## **PREFACE**

This study was commissioned by Posiva Oy and was carried out in the Laboratory of Radiochemistry, Department of Chemistry, University of Helsinki. The contact persons at Posiva Oy were Margit Snellman and Aimo Hautojärvi. The responsible researchers and authors were Seija Kulmala and Martti Hakanen from the Laboratory of Radiochemistry. The rock samples were chosen and analysed for mineral composition and the autoradiograms were examined by Antero Lindberg of the Geological Survey of Finland.



## **1 INTRODUCTION**

This study is part of a wide investigation into the behaviour of spent fuel waste nuclides in Finnish bedrock. The investigation is being carried out by Posiva Oy, the company responsible for the final disposal of spent nuclear fuel in Finland. Posiva Oy is studying four different sites in Finland: Olkiluoto, Hästholmen, Romuvaara and Kivetty.

The aim of the present experiments was to investigate the sorption of plutonium in the laboratory conditions simulating the geosphere at Olkiluoto, Romuvaara and Kivetty. The experiments were carried out under both oxic (ambient) and anoxic (nitrogen) conditions.

## **2 MATERIALS**

### **2.1 Rock samples**

The rocks were mica gneiss (Ol1), tonalite (granodiorite, Ol2A) and granite (granodiorite, Ol2B) from Olkiluoto, tonalite (Ro1A), granite (Ro1B) and mica gneiss (Ro1C) from Romuvaara and porphyritic granite (Ki4A) and porphyritic granodiorite (Ki4B) from Kivetty. All samples were cut from 42-mm drill core samples. Rock samples are characterized in detail in Kulmala et al. (1996) and briefly in Appendix A.

A part of each rock sample was crushed and sieved to grain size  $\varnothing < 2$  mm. Also some polished rock thin sections were prepared for each sample.

The specific areas of the crushed rock samples were measured at the Helsinki University of Technology by N<sub>2</sub>/BET method. The cation exchange capacities were determined at the Laboratory of Radiochemistry by silver-thiourea (AgTU) method (Chhabra et al. 1975). The cation exchange capacity was also measured for caesium. The results and methods are presented in detail in Kulmala et al. (1996) and are reproduced in part in Appendix A.

### **2.2 Groundwaters**

The waters used in the study were natural groundwaters from the same areas and depths as the rock samples. The groundwaters for the anoxic experiments were sampled under N<sub>2</sub> atmosphere and transported to field laboratory where the groundwater was added to individual samples. The samples and remaining waters were transported to the laboratory glove box. All this was done under nitrogen atmosphere within a portable glove box. The concentrations of selected solutes in the groundwaters are presented in Table 1 and the detailed chemical compositions in Appendix A and Kulmala et al. (1996).

**Table 1.** Chemical composition of the natural groundwaters (Imatran Voima Oy, Chem. Lab.).

	Romuvaara, RoKR4 187 - 190 m	Kivetty, KiKR4 436 - 468 m	Olkiluoto, OIKR5 446 - 558 m
pH*	7.9	8.2	7.0
E <sub>h</sub> (Pt) (mV) *	-71	-61	-157
KMnO <sub>4</sub> (mg/l)	2.8	2.9	80.0
CO <sub>2</sub> (tot) (mg/l)	53.8	58.2	4.20
Br (mg/l)	0.10	0.03	58.0
Cl (mg/l)	4.3	3.2	9200
SO <sub>4</sub> (mg/l)	3.9	2.00	3.30
Ca (total, mg/l)	2.1	13.0	2100
Fe (total, mg/l)	0.059	0.520	0.230
K (mg/l)	0.69	0.87	15.0
Mg (mg/l)	0.08	3.0	67.0
Mn (mg/l)	0.001	0.210	0.360
Na (mg/l)	39.0	18.0	3330
Cs (mg/l)	< 0.005	< 0.005	0.008
ionic strength, M	$1.5 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	$3.1 \cdot 10^{-1}$

\* pH and E<sub>h</sub> (Pt) (mV) were field measurements.

Other values were measured at the laboratory.

### 2.3 Radionuclides

The radionuclides were Pu-236 ( $T_{1/2} = 2.85$  a) and Pu-242 ( $T_{1/2} = 3.8 \cdot 10^5$  a). Pu-236 was used as tracer and Pu-242 was a carrier to achieve higher concentrations of plutonium. The Pu concentrations in the samples are presented in Table 2. The Pu spike was dried onto a teflon platelet and the platelet added to the crushed rock/groundwater sample (Kulmala et al. 1996). It is assumed in the calculations that all the spike dried onto the teflon platelet is dissolved.

**Table 2.** Concentrations of plutonium in the sample (mol/l), assuming that all the Pu dried onto the teflon platelet is dissolved. All Pu concentrations are lower than the estimated solubility of plutonium (Vuorinen et al. 1998).

Concentration	Pu-236 (mol/l)		Pu-242 (mol/l)	
	oxic	anoxic	oxic	anoxic
Concentration 1	$3.3 \cdot 10^{-13}$	$1.9 \cdot 10^{-12}$	-	-
Concentration 2	$3.3 \cdot 10^{-13}$	$1.9 \cdot 10^{-12}$	$2.9 \cdot 10^{-11}$	$5.0 \cdot 10^{-11}$
Concentration 3	$3.3 \cdot 10^{-13}$	$1.9 \cdot 10^{-12}$	$5.7 \cdot 10^{-10}$	$1.1 \cdot 10^{-9}$

Some of the crushed rock/groundwater samples were spiked with Tc(VII) to verify the redox conditions. At pH of about 7 the  $E_h$  for Tc(VII) to reduce to Tc(IV) is about -50 – -150 mV (Lieser & Bauscher, 1987, Allard et al., 1979). The use of Tc was due to low ionic strength of RoKR5 and KiKR4 groundwaters where the lack of suitable redox pair may cause the measured  $E_h$  values to be inaccurate. The amount of Tc(VII)-99 used was equal to  $9.5 \cdot 10^{-9}$  mol/l, with the same assumption made as in Table 2.

### 3 METHODS

#### 3.1 Sorption experiments

The sorption experiments were performed by batch method for crushed rock samples and rock thin sections and by autoradiographic method for rock thin sections. The batch method for crushed rock is based on ASTM Standard and has been described in many earlier reports (ASTM Designation: D 4319-93, Kulmala et al. 1996). The autoradiographic method is described in Lindberg et al. (1983).

The sorption experiments done by batch method were executed with rock mass/water volume (m/V) ratio of 1/10 at room temperature and under oxic (ambient) or anoxic (nitrogen atmosphere) conditions. The O<sub>2</sub> concentration in the glove box was lower than 2 ppm when the sample bottles were opened for subsampling and pH and E<sub>h</sub> measurements. The experimental procedures are presented in Appendix B, along with the equations used to calculate the sorption percentages and mass distribution coefficients.

The sorption experiments with polished rock thin sections were performed by first equilibrating the thin section with groundwater for about one hour. The Pu-236 spike was evaporated gently to dryness on a liquid scintillation counter bottle and the residue was dissolved in groundwater. Part of the groundwater spike solution was used to spike the rock thin sections and the rest was used as standard sample for the activity measurements. After about one day, the spike was removed and the thin section dried.

The pH values of the samples were measured with a combination glass electrode (Radiometer, pHC2401). The system was calibrated before every measurement period with pH 4 and pH 10 standard buffer solutions (Radiometer). The E<sub>h</sub> values were measured with a Pt-electrode (Radiometer, M21Pt) against calomel electrode (Radiometer, REF401) as reference. The Pt-calomel electrode system was calibrated with pH standard solutions saturated with kinhydron (Kokholm).

### 3.2 Radioactivity measurements

The first subsamples were measured for total alpha activity by low level liquid scintillation counting (LSC) with a Wallac Quantulus 1220 using  $\alpha/\beta$  separation. Tc-99 was measured by LSC with a Wallac Rackbeta 1217.

In some samples, natural alpha-active radionuclides in the groundwaters and radionuclides possibly leached from the crushed rock were suspected to make a considerable contribution to the alpha counts in LSC. Second subsamples were therefore taken. Subsamples of the non-saline groundwaters (Romuvaara and Kivetty) were evaporated to near dryness, the residue was dissolved in dilute nitric acid, and Pu was co-precipitated with neodymium fluoride and collected on a 0.1  $\mu\text{m}$  Millipore filter for alphaspectrometric measurement with a surface barrier semiconductor detector. This method could not be applied to the more saline Olkiluoto groundwater because of its relatively high Ca concentration.

Plutonium in the saline Olkiluoto groundwater was separated by an anion exchange method (Appendix B, Hakanen et al., 1984). The counting samples were prepared the same way as the counting samples for non-saline groundwater. The chemical yield of the separation method was determined for new 10 ml groundwater samples by using Pu-236 spike and LSC for monitoring of the radioactivity (the effectivity of  $\alpha$  measurement with LSC is  $\sim 100\%$ ). The yield of Pu was over 90%, and this was the figure used in derivation of the Pu-236 activities in sorption samples analysed. The chemical purity of the Pu fraction was good according to determination by alpha spectrometry for some real Olkiluoto samples where Pu-242 (1 dpm/sample) was used as the yield tracer. The radioactivity of Pu-242 added as carrier (see page 12) was negligible relative to the amount of yield tracer Pu-242.

The samples prepared for anoxic conditions were mainly measured by low level liquid scintillation counting using  $\alpha/\beta$  separation. Some samples were anyhow analysed with

isotope diluting technique using Pu-242 as yield monitor. The samples were measured by alpha counting with semiconductor detector.

The standard deviation of radioassay ( $\pm 1\sigma$ ) for an individual result was indicated from the error percentage of the measurement. The minimum detectable activity (MDA) of the samples was calculated according to ASTM Standard D 3648-95. With LSC without ion exchange separation the MDA was 0.4 dpm for Kivetty and Romuvaara samples and 1.3 dpm for Olkiluoto samples.

Autoradiograms were prepared from the spiked thin sections. The film was Kodak X-OMAT MA X-ray film and the exposure time was about one month. The sorption of Pu onto different minerals on the rock thin sections was described by Antero Lindberg at the Geological Survey of Finland. All the experiments with rock thin sections were performed under oxic conditions.

## 4 RESULTS AND DISCUSSION

### 4.1 Sorption of Pu under oxic conditions

The sorption percentages and the  $R_d$  and  $R_{d,des}$  values for sorption and desorption under oxic conditions are presented in Table 3. The equations used to calculate the  $R_d$  and  $R_{d,des}$  values are presented in Appendix B. The sorption percentages are the mean values of three parallel determinations while the  $R_d$  and  $R_{d,des}$  values, where they exceed the limit of detection, are the ranges for the three samples. The results for the individual samples are presented in Appendix C.

The sorption was high for all samples. Under oxic conditions the amount of plutonium spike on the teflon platelet after the experiment was in all samples less than 1%. For Olkiluoto samples the  $R_d$  values were higher than  $1.0 \text{ m}^3/\text{kg}$ , for Romuvaara samples they varied from  $0.1 \text{ m}^3/\text{kg}$  to  $2.0 \text{ m}^3/\text{kg}$  and for Kivetty samples from  $0.2 \text{ m}^3/\text{kg}$  to  $0.6 \text{ m}^3/\text{kg}$ . The  $R_d$  values for Olkiluoto samples were higher than that for the minimum detectable activity, MDA. In Appendix C, where the results for individual samples are presented, the  $R_d$  values are calculated directly from the measured activities.

The concentration of Pu had no effect on the sorption. The ranges of the  $R_d$  values for parallel samples were about the same for three different Pu concentrations.

The desorption mass distribution ratios,  $R_{d,des}$  values, were  $\geq 1.0 \text{ m}^3/\text{kg}$  for all samples. The higher  $R_{d,des}$  values than the  $R_d$  values suggest the sorption of plutonium to be partly irreversible.



**Table 3.** Sorption percentages and  $R_d$  values for the sorption and desorption of plutonium, on Olkiluoto, Romuvaara and Kivetty crushed rock samples. Experiments were made with the local groundwater under oxic conditions. The given error is the standard deviation of the mean value of the results for three parallel samples.

Rock	Undissolved fraction (%)	$S_s$ (%)	$R_d$ (m <sup>3</sup> /kg)	$S_{s,des}$ (%)	$R_{d,des}$ (m <sup>3</sup> /kg)
Ol1, mica gneiss					
[Pu] = $3.3 \cdot 10^{-13}$ mol/l	$0.27 \pm 0.24$	$\geq 99.1$	$\geq 1.0$	$\geq 99$	$\geq 1.0$
[Pu] = $2.9 \cdot 10^{-11}$ mol/l	$0.37 \pm 0.08$	$\geq 99.1$	$\geq 1.0$	$\geq 99$	$\geq 1.0$
[Pu] = $5.7 \cdot 10^{-10}$ mol/l	$0.38 \pm 0.17$	$\geq 99.1$	$\geq 1.0$	$\geq 99$	$\geq 1.0$
Ol2A, tonalite					
[Pu] = $3.3 \cdot 10^{-13}$ mol/l	$0.17 \pm 0.02$	$\geq 99.1$	$\geq 1.0$	$\geq 99$	$\geq 1.0$
[Pu] = $2.9 \cdot 10^{-11}$ mol/l	$0.17 \pm 0.03$	$\geq 99.1$	$\geq 1.0$	$\geq 99$	$\geq 1.0$
[Pu] = $5.7 \cdot 10^{-10}$ mol/l	$0.39 \pm 0.31$	$\geq 99.1$	$\geq 1.0$	$\geq 99$	$\geq 1.0$
Ol2B, granite					
[Pu] = $3.3 \cdot 10^{-13}$ mol/l	$0.41 \pm 0.04$	$\geq 99.1$	$\geq 1.0$	$\geq 99$	$\geq 1.0$
[Pu] = $2.9 \cdot 10^{-11}$ mol/l	$0.50 \pm 0.19$	$\geq 99.1$	$\geq 1.0$	$\geq 99$	$\geq 1.0$
[Pu] = $5.7 \cdot 10^{-10}$ mol/l	$0.91 \pm 0.21$	$\geq 99.1$	$\geq 1.0$	$\geq 99$	$\geq 1.0$
Ro1A, tonalite					
[Pu] = $3.3 \cdot 10^{-13}$ mol/l	$0.10 \pm 0.02$	$96.0 \pm 1.5$	0.18 - 0.41	$\geq 99$	$\geq 1.0$
[Pu] = $2.9 \cdot 10^{-11}$ mol/l	$0.25 \pm 0.10$	$95.5 \pm 0.8$	0.18 - 0.28	$\geq 99$	$\geq 1.0$
[Pu] = $5.7 \cdot 10^{-10}$ mol/l	$0.19 \pm 0.16$	$96.3 \pm 0.9$	0.21 - 0.35	$\geq 99$	$\geq 1.0$
Ro1B, granite					
[Pu] = $3.3 \cdot 10^{-13}$ mol/l	$0.09 \pm 0.06$	$88.1 \pm 5.1$	0.048 - 0.11	$\geq 99$	$\geq 1.0$
[Pu] = $2.9 \cdot 10^{-11}$ mol/l	$0.18 \pm 0.08$	$90.7 \pm 7.1$	0.050 - 0.13	$\geq 99$	$\geq 1.0$
[Pu] = $5.7 \cdot 10^{-10}$ mol/l	$0.09 \pm 0.07$	$92.6 \pm 1.3$	0.11 - 0.15	$\geq 99$	$\geq 1.0$
Ro1C, mica gneiss					
[Pu] = $3.3 \cdot 10^{-13}$ mol/l	$0.15 \pm 0.07$	$93.1 \pm 2.5$	0.10 - 0.23	$\geq 99$	$\geq 1.0$
[Pu] = $2.9 \cdot 10^{-11}$ mol/l	$0.29 \pm 0.20$	$93.9 \pm 0.6$	0.15 - 0.18	$\geq 99$	$\geq 1.0$
[Pu] = $5.7 \cdot 10^{-10}$ mol/l	$0.35 \pm 0.20$	$93.7 \pm 0.8$	0.14 - 0.18	$\geq 99$	$\geq 1.0$
Ki4A, porph. granite					
[Pu] = $3.3 \cdot 10^{-13}$ mol/l	$0.11 \pm 0.04$	$97.0 \pm 1.2$	0.27 - 0.61	$\geq 99$	$\geq 1.0$
[Pu] = $2.9 \cdot 10^{-11}$ mol/l	$0.16 \pm 0.08$	$96.5 \pm 1.4$	0.20 - 0.42	$\geq 99$	$\geq 1.0$
[Pu] = $5.7 \cdot 10^{-10}$ mol/l	$0.33 \pm 0.19$	$96.5 \pm 1.2$	0.22 - 0.47	$\geq 99$	$\geq 1.0$
Ki4B, porph. granodiorite					
[Pu] = $3.3 \cdot 10^{-13}$ mol/l	$0.12 \pm 0.06$	$96.2 \pm 1.4$	0.22 - 0.46	$\geq 99$	$\geq 1.0$
[Pu] = $2.9 \cdot 10^{-11}$ mol/l	$0.20 \pm 0.05$	$96.0 \pm 2.0$	0.18 - 0.56	$\geq 99$	$\geq 1.0$
[Pu] = $5.7 \cdot 10^{-10}$ mol/l	$0.30 \pm 0.26$	$97.2 \pm 0.9$	0.26 - 0.47	$\geq 99$	$\geq 1.0$

## 4.2 Sorption of Pu with added Cs under oxic conditions

Some Olkiluoto samples were prepared with higher caesium concentration to study the affect of a nuclide sorbing by cation exchange on the sorption of plutonium. The spiking concentration of Pu was  $3.3 \cdot 10^{-13}$  mol/l and the Cs concentrations were  $1.6 \cdot 10^{-4}$  mol/l and  $1.6 \cdot 10^{-6}$  mol/l (OIKR5 groundwater already contained  $6.0 \cdot 10^{-8}$  mol/l of Cs). The results are presented in Table 4.

**Table 4.** Sorption percentages and  $R_d$  values for the sorption of plutonium in the presence of caesium on Olkiluoto crushed rock samples. Experiments were made with OIKR5 groundwater under oxic conditions. The error is the standard deviation of the mean value of three parallel samples.

Rock	Undissolved fraction (%)	Sorption (%)	$R_d$ (m <sup>3</sup> /kg)
Ol1, mica gneiss			
[Cs] = $1.6 \cdot 10^{-4}$ mol/l	$0.83 \pm 0.16$	$\geq 99.1$	$\geq 1.0$
[Cs] = $1.6 \cdot 10^{-6}$ mol/l	$0.72 \pm 0.17$	$\geq 99.1$	$\geq 1.0$
Ol2A, tonalite			
[Cs] = $1.6 \cdot 10^{-4}$ mol/l	$0.89 \pm 0.50$	$\geq 99.1$	$\geq 1.0$
[Cs] = $1.6 \cdot 10^{-6}$ mol/l	$0.61 \pm 0.26$	$\geq 99.1$	$\geq 1.0$
Ol2B, granite			
[Cs] = $1.6 \cdot 10^{-4}$ mol/l	$1.98 \pm 0.74$	$\geq 99.1$	$\geq 1.0$
[Cs] = $1.6 \cdot 10^{-6}$ mol/l	$0.95 \pm 0.45$	$\geq 99.1$	$\geq 1.0$

Addition of caesium had no significant effect on the sorption of plutonium. The measured activities were  $\leq$  MDA (minimum detectable activity).

### 4.3 Sorption of Pu under anoxic conditions

The sorption of Pu under anoxic conditions is described in terms of sorption percentages and mass distribution ratios ( $R_d$  values) in Tables 5-7. The pH and  $E_h$  values are measured values at the end of the experimental period. The contact time was six months for the first samples and one year for the second samples.

Results for the Olkiluoto samples measured by semiconductor detector after the ion exchange procedure (Appendix B) are presented in Table 5 for three individual samples (O11, O12A and O12B) for Pu concentration of  $5 \cdot 10^{-11}$  mol/l.

The amount of Pu left on the teflon platelet varied a lot and was higher (9% - 40%) under anoxic conditions than under oxic conditions. The lower solubility under anoxic than oxic conditions was probably due to the strong hydrolysis or the lower oxidation states of Pu (Vuorinen et al. 1998). The pH value of the samples increased and the  $E_h$  value decreased during the experiment.

**Table 5.** Sorption percentages and  $R_d$  values for the sorption of plutonium on Olkiluoto crushed rock samples. Experiments were made with OlKR5 groundwater under anoxic conditions. The error is the standard deviation of the mean value of results for three parallel samples. The given error is the standard deviation of the mean of three parallel samples.

Rock	Contact time (days)	Undissolved fraction (%)	pH	$E_h$ (Pt) (mV)	$S_s$ (%)	$R_d$ (m <sup>3</sup> /kg)		
Ol1, mica gneiss	[Pu] = $1.9 \cdot 10^{-12}$ mol/l	237	33.9 ± 0.2	8.61	-156	99.9 ± 0.1	16	
		237	35.7 ± 0.2	8.20	-234	99.2 ± 0.1	1.3	
		410	16.8 ± 0.1	8.12	-325	99.6 ± 0.2	2.7	
	[Pu] = $5.0 \cdot 10^{-11}$ mol/l	237	14.2 ± 0.1	8.55	-166	99.9 ± 0.1	15	
		410	16.4 ± 0.1	7.80	-280	99.6 ± 0.1	2.9	
	[Pu] = $1.1 \cdot 10^{-9}$ mol/l	237	9.70 ± 0.1	8.44	-138	99.9 ± 0.1	18	
		410	8.48 ± 0.1	7.87	-303	99.8 ± 0.1	5.7	
	Ol2A, tonalite	[Pu] = $1.9 \cdot 10^{-12}$ mol/l	237	39.7 ± 0.2	8.45	-180	99.7 ± 0.1	4.3
			410	32.3 ± 0.2	7.78	-428	99.2 ± 0.4	1.4
		[Pu] = $5.0 \cdot 10^{-11}$ mol/l	237	24.1 ± 0.1	8.56	-186	99.7 ± 0.1	3.2
			410	9.57 ± 0.07	7.85	-338	99.3 ± 0.1	1.5
		[Pu] = $1.1 \cdot 10^{-9}$ mol/l	237	17.5 ± 0.1	8.55	-202	99.8 ± 0.1	4.5
410			8.35 ± 0.06	8.12	-323	99.4 ± 0.1	1.8	
Ol2B, granite		[Pu] = $1.9 \cdot 10^{-12}$ mol/l	237	26.0 ± 0.1	8.61	-202	99.7 ± 0.1	3.5
			410	29.8 ± 0.2	8.15	-316	98.8 ± 0.1	0.91
	[Pu] = $5.0 \cdot 10^{-11}$ mol/l	237	25.7 ± 0.1	8.41	-192	99.7 ± 0.1	3.5	
		410	28.6 ± 0.2	8.20	-320	99.0 ± 0.1	0.99	
	[Pu] = $1.1 \cdot 10^{-9}$ mol/l	237	8.30 ± 0.1	8.55	-153	99.8 ± 0.1	5.3	
		410	8.29 ± 0.06	8.13	-321	99.6 ± 0.1	2.9	
	[Pu] = $5.0 \cdot 10^{-11}$ mol/l	Ol1	491	-	6.6	-340	99.40±0.04	<b>1.8</b>
		Ol2A	491	-	6.7	-304	99.23±0.05	<b>1.4</b>
Ol2B		491	-	6.7	-297	98.72±0.05	<b>0.80</b>	

- not measured

**Table 6.** Sorption percentages and  $R_d$  values for the sorption of plutonium on Romuvaara crushed rock samples. Experiments were made with RoKR4 groundwater under anoxic conditions. The given error is the standard deviation of the mean value of parallel samples.

Rock	Contact time (days)	Undissolved fraction (%)	pH	$E_h$ (Pt) (mV)	$S_s$ (%)	$R_d$ ( $m^3/kg$ )	
Ro1A, tonalite	[Pu] = $1.9 \cdot 10^{-12}$ mol/l	218	15.2 ± 0.1	9.68	-144	99.3 ± 0.1	1.4
		391	59.8 ± 0.2	9.40	-272	97.2 ± 0.2	0.38
	[Pu] = $5.0 \cdot 10^{-11}$ mol/l	218	-	9.59	-225	99.4 ± 0.1	1.7
		391	24.9 ± 0.1	9.26	-325	99.1 ± 0.1	1.1
	[Pu] = $1.1 \cdot 10^{-9}$ mol/l	218	11.5 ± 0.1	9.64	-198	99.1 ± 0.1	1.1
		391	6.78 ± 0.06	9.27	-345	98.9 ± 0.1	0.98
Ro1B, granite	[Pu] = $1.9 \cdot 10^{-12}$ mol/l	218	37.5 ± 0.2	9.68	-234	98.8 ± 0.1	0.83
		391	19.2 ± 0.1	9.22	-363	98.7 ± 0.1	0.75
	[Pu] = $5.0 \cdot 10^{-11}$ mol/l	218	12.9 ± 0.1	9.71	-212	99.5 ± 0.1	2.1
		391	25.8 ± 0.1	9.30	-346	98.7 ± 0.1	0.79
	[Pu] = $1.1 \cdot 10^{-9}$ mol/l	218	13.3 ± 0.1	9.68	-173	99.3 ± 0.1	1.5
		391	17.4 ± 0.1	9.45	-358	98.4 ± 0.1	0.64
Ro1C, mica gneiss	[Pu] = $1.9 \cdot 10^{-12}$ mol/l	218	32.0 ± 0.2	9.71	-221	99.0 ± 0.1	1.1
		391	9.68 ± 0.07	9.30	-343	98.9 ± 0.1	0.89
	[Pu] = $5.0 \cdot 10^{-11}$ mol/l	218	26.6 ± 0.1	9.66	-227	99.9 ± 0.1	9.1
		391	6.57 ± 0.05	9.40	-362	99.5 ± 0.1	2.3
	[Pu] = $1.1 \cdot 10^{-9}$ mol/l	218	6.19 ± 0.1	9.72	-236	99.6 ± 0.1	2.9
		391	27.0 ± 0.2	9.16	-346	99.6 ± 0.1	2.4

- not measured

**Table 7.** Sorption percentages and  $R_d$  values for the sorption of plutonium on Kivetty crushed rock samples. Experiments were made with KiKR4 groundwater under anoxic conditions.

Rock	Contact time (days)	Undissolved fraction (%)	pH	$E_h$ (Pt) (mV)	$S_s$ (%)	$R_d$ ( $m^3/kg$ )	
Ki4A, porph. granite [Pu] = $1.9 \cdot 10^{-12}$ mol/l	204	$31.5 \pm 0.2$	9.55	-274	$99.1 \pm 0.1$	1.1	
	377	$18.8 \pm 0.1$	9.41	-235	$99.5 \pm 0.1$	1.9	
	[Pu] = $5.0 \cdot 10^{-11}$ mol/l	204	$8.07 \pm 0.1$	9.47	-302	$99.5 \pm 0.1$	2.1
		377	$24.1 \pm 0.1$	9.75	-360	$99.0 \pm 0.1$	1.0
	[Pu] = $1.1 \cdot 10^{-9}$ mol/l	204	$12.1 \pm 0.1$	9.66	-280	$99.8 \pm 0.1$	5.9
		377	$19.9 \pm 0.1$	9.60	-361	$99.8 \pm 0.1$	5.0
Ki4B, porph. granodiorite	[Pu] = $1.9 \cdot 10^{-12}$ mol/l	204	$34.1 \pm 0.2$	9.71	-270	$99.3 \pm 0.1$	1.5
		377	$33.8 \pm 0.2$	9.54	-330	$99.1 \pm 0.1$	1.2
	[Pu] = $5.0 \cdot 10^{-11}$ mol/l	204	$11.7 \pm 0.1$	9.69	-280	$99.1 \pm 0.1$	1.2
		377	$18.6 \pm 0.1$	9.13	-340	$99.7 \pm 0.1$	4.0
	[Pu] = $1.1 \cdot 10^{-9}$ mol/l	204	$26.3 \pm 0.1$	9.65	-267	$99.8 \pm 0.1$	5.8
		377	$27.4 \pm 0.2$	9.45	-357	$99.5 \pm 0.1$	2.4

#### 4.4 Verification of redox conditions by sorption of Tc under anoxic conditions

Anticipating difficulties in interpretation of the measured  $E_h$  values, we prepared several crushed rock/groundwater samples with Tc(VII)-99 spike to check the redox conditions of the rock/water system. Under oxic conditions Tc exists in anionic  $TcO_4^-$  form, which is nearly non-sorbing, whereas under reducing conditions it exists as Tc(IV), which is readily hydrolysed and strongly sorbing (Allard et al. 1979, Lieser & Bauscher, 1987). The amount of Tc sorbed on the solid phase rock or on vessel walls is presented in Table 8 and the results for individual samples are given in Appendix C.

**Table 8.** Fraction of Tc-99 spike in crushed rock in groundwater/crushed rock samples under anoxic conditions. The pH and  $E_h$  values are measured at the end of the experiment. The given error is the standard deviation of the mean value of parallel samples.

Groundwater	Rock	pH	$E_h$ (meas.)	Tc-99 in rock (%)
OIKR5 (saline)	no rock	8.21	- 371	78.3 ± 28.4
	Ol1, mica gneiss	8.36	- 233	98.7 ± 0.2
	Ol2A, tonalite	8.40	- 257	98.6 ± 0.2
	Ol2B, granite	8.28	- 250	98.7 ± 0.2
RoKR5 (non-saline)	no rock	9.42	- 217	78.8 ± 27.9
	Ro1A, tonalite	9.66	- 264	96.2 ± 2.9
	Ro1B, granite	9.74	- 272	88.0 ± 14.4
	Ro1C, mica gneiss	9.68	- 284	96.6 ± 1.9
KiKR4 (non-saline)	no rock	9.63	- 269	98.0 ± 0.1
	Ki4A, porph. granite	9.76	- 332	98.2 ± 0.6
	Ki4B, porph. granodiorite	9.72	- 319	97.6 ± 1.0

The measured distribution of Tc indicates that the anoxic (nitrogen atmosphere) conditions in the glove box were reducing for technetium and thus Tc occurred in the Tc(IV) form. This is in accord with the measured pH/ $E_h$  conditions. In samples without crushed rock (only groundwater and Tc-spike) most of the Tc was sorbed, but there were significant amounts of Tc in the water, although the measured redox conditions did not differ from the other samples.

#### 4.5 Sorption of Pu on polished rock surfaces

The ranges of  $R_a$  values for the sorption of Pu on polished rock thin sections under oxic conditions are presented in Tables 9 - 11. Values for the individual samples are given in Appendix C.

**Table 9.** Sorption (sorption percentages and  $R_a$  values) of plutonium on polished Olkiluoto rock thin sections from saline and non-saline groundwater under oxic conditions. The given error is the standard deviation of the mean value of three rock thin section samples.

Rock	OIKR5 saline groundwater		KiKR4 non-saline groundwater	
	Sorption %	$R_a \cdot 10^{-4}$ ( $m^3/m^2$ )	Sorption %	$R_a \cdot 10^{-4}$ ( $m^3/m^2$ )
O11, mica gneiss	56.2 ± 1.6	20.4 - 22.1	37.1 ± 0.9	7.73 - 10.4
O12A, tonalite	50.5 ± 1.8	15.9 - 18.9	36.9 ± 0.5	8.90 - 9.70
O12B, granite	47.0 ± 3.0	13.2 - 18.2	36.6 ± 1.5	8.60 - 9.46

**Table 10.** Sorption (sorption percentages and  $R_a$  values) of plutonium on polished Romuvaara rock thin sections from saline and non-saline groundwater under oxic conditions. The given error is the standard deviation of the mean value of three rock thin section samples.

Rock	RoKR5 non-saline groundwater		OIKR5 saline groundwater	
	Sorption %	$R_a \cdot 10^{-4}$ ( $m^3/m^2$ )	Sorption %	$R_a \cdot 10^{-4}$ ( $m^3/m^2$ )
Ro1A, tonalite	57.3 ± 1.4	21.2 - 26.7	38.7 ± 1.8	10.3 - 11.5
Ro1B, granite	59.4 ± 1.4	22.4 - 23.7	33.2 ± 2.8	7.53 - 9.14
Ro1C, mica gneiss	62.2 ± 1.3	26.4 - 26.7	35.7 ± 2.2	7.60 - 9.42

**Table 11.** Sorption (sorption percentages and  $R_a$  values) of plutonium on polished Kivetty rock thin sections from saline and non-saline groundwater under oxic conditions. The given error is the standard deviation of the mean value of three rock thin section samples.

Rock	KiKR4 non-saline groundwater		OIKR5 saline groundwater	
	Sorption %	$R_a \cdot 10^{-4}$ ( $m^3/m^2$ )	Sorption %	$R_a \cdot 10^{-4}$ ( $m^3/m^2$ )
Ki4A, porph. granite	45.1 ± 1.5	10.8 - 12.0	34.4 ± 0.8	7.99 - 8.55
Ki4B, porph granodiorite	46.7 ± 2.6	11.9 - 12.4	39.1 ± 4.9	7.09 - 11.5

In saline groundwater no mineral specific sorption was observed in the autoradiograms of any samples. In the case of fresh groundwater the autoradiograms revealed some tendency to mineral specific sorption.



In the autoradiograms of Kivetty rock thin sections with non-saline groundwater the darker spots more or less corresponded to the dark minerals, biotite and amphibole. Likewise the darker areas of the Romuvaara rock autoradiograms corresponded to biotite and amphibole. The Ro1B granite autoradiograms showed some of the Pu activity to be associated with plagioclase grains altered to sericite. High sorption of Pu was observed on dolomite.

In the Olkiluoto thin section autoradiograms only OI2B granite with non-saline groundwater showed some mineral specific darkening. The darker spots corresponded to sericite (muscovite), possibly calcite, lying between K-feldspar and quartz grains.

## 5 SUMMARY AND CONCLUSIONS

The sorption of plutonium was high on all rocks. Under oxic conditions the  $R_d$  values were  $\geq 1.0 \text{ m}^3/\text{kg}$ ,  $0.05 \text{ m}^3/\text{kg} - 0.4 \text{ m}^3/\text{kg}$  and  $0.2 \text{ m}^3/\text{kg} - 0.6 \text{ m}^3/\text{kg}$  for Olkiluoto, Romuvaara and Kivetty rock samples, respectively. Virtually all of the spike that dried onto a teflon platelet was dissolved; less than 1% of the initial spike was left on the teflon platelet.

Addition of caesium to the spiking solution had no significant effect on the amount of the undissolved fraction, nor on the sorption percentages or  $R_d$  values. Either Pu and Cs favour different sorption sites or there was insufficient Cs to fill the sorption places.

Under oxic conditions the  $R_d$  values were  $\geq 1.0 \text{ m}^3/\text{kg}$  for Olkiluoto rock samples,  $(0.05 - 0.4) \text{ m}^3/\text{kg}$  for Romuvaara samples and  $(0.2 - 0.6) \text{ m}^3/\text{kg}$  for Kivetty samples. Under anoxic (nitrogen atmosphere) conditions the high sorption of Tc indicated that the conditions were reducing for technetium when Tc occurred in the Tc(IV) oxidation state. The amount of Pu left on the teflon platelet was considerably greater than under oxic conditions: the undissolved fraction varied between 13% and 40%. Also, the sorption of Pu was slightly higher than under oxic conditions. The  $R_d$  values were  $(0.9 - 18) \text{ m}^3/\text{kg}$ ,  $(0.8 - 14) \text{ m}^3/\text{kg}$  and  $(1 - 6) \text{ m}^3/\text{kg}$  for Olkiluoto, Romuvaara and Kivetty crushed rock samples, respectively.

The  $R_d$  values of plutonium measured in this study correspond fairly well to the  $R_d$  values measured earlier for basic plutonic rocks and vulcanite (Kaukonen et al. 1993).

**Table 12.** Sorption of plutonium (mass distribution coefficients,  $K_d$  values ( $m^3/kg$ )) on basic plutonic rocks and vulcanite under oxic conditions according to Kaukonen et al. (1993).

[Pu] (mol/l)	Mäntsälä	Sodankylä	Syyry	
	Allard 1:10	Allard 1:10	Allard 1:10	Syyry gw
$(1.5 \pm 0.5) \cdot 10^{-12}$	0.11 - 0.31	0.23 - 0.36	0.015 - 0.14	0.082 - 1.1
$(0.97 \pm 0.11) \cdot 10^{-10}$	0.12 - 0.30	0.079 - 0.33	0.15 - 0.33	0.57 - 1.2
$(0.89 \pm 0.14) \cdot 10^{-8}$	0.28 - 0.39	0.44 - 0.92	0.16 - 0.35	0.97 - 1.6

Mäntsälä = Mäntsälä plutonic rock

Syyry = Syyry plutonic rock

Sodankylä = Sodankylä vulcanite

Syyry gw = Syyry groundwater (slightly saline)

Allard 1:10 = Allard 1:10 ( $HCO_3^-$  1:1) simulated granitic groundwater

**Table 13.** Sorption of plutonium ( $K_d$  values,  $m^3/kg$ ) from Syyry groundwater onto finely crushed ( $\phi \leq 2$  mm) basic plutonic rocks and vulcanite under anoxic conditions according to Kaukonen et al. (1993).

[Pu] (mol/l)	Syyry plutonic rock	Sodankylä vulcanite
$(2.2 \pm 0.04) \cdot 10^{-12}$	$\geq 9.9$	$\geq 16.5$
$(4.2 \pm 0.03) \cdot 10^{-10}$	$\geq 12.4$	$\geq 25.5$
$(4.2 \pm 0.02) \cdot 10^{-8}$	$\geq 24.4$	$\geq 16.4$

Huitti et al. (1996) measured, for plutonium,  $R_d$  values of (0.56 - 1.6)  $m^3/kg$  and  $\geq 0.38$   $m^3/kg$  for Hästholmen rock samples under oxic and anoxic conditions, respectively (Table 14).

**Table 14.**  $R_d$  values ( $m^3/kg$ ) for sorption of plutonium from Hästholmen brackish groundwater onto Hästholmen rapakivi granite according to Huitti et al. (1996).

Rock	[Pu] (mol/l)	Oxic conditions	Anoxic conditions
YT5-1 fresh	$10^{-13}$	0.86 - 1.0	$\geq 0.54$
	$10^{-11}$	$\geq 0.56$	
	$10^{-9}$	1.3 - 1.4	
YT5-2 weathered	$10^{-13}$	$\geq 0.65$	$\geq 0.38$
	$10^{-11}$	0.86 - 1.0	
	$10^{-9}$	1.1 - 1.6	
YT5-3 altered	$10^{-13}$	$\geq 0.66$	$\geq 0.89$
	$10^{-11}$	0.67 - 1.1	
	$10^{-9}$	1.0 - 1.6	

For polished rock thin sections the  $R_a$  values were  $(7.7 - 22) \cdot 10^{-4} m^3/m^2$ ,  $(7.5 - 27) \cdot 10^{-4} m^3/m^2$  and  $(7.1 - 12) \cdot 10^{-4} m^3/m^2$  for Olkiluoto, Romuvaara and Kivetty samples, respectively. The  $R_a$  values were slightly lower for saline groundwater than for fresh groundwater except for Olkiluoto thin sections. Koskinen et al. (1988) measured  $R_a$  values of  $81 \cdot 10^{-4} m^3/m^2$  for rapakivi granite thin sections and  $R_a$  values of  $(250 - 1700) \cdot 10^{-4} m^3/m^2$  for rock coupons from fresh reference (Allard) water. Suksi et al. (1989) measured  $R_a$  values of  $(26 - 260) \cdot 10^{-4} m^3/m^2$  for drill core cup samples from Allard water.

## REFERENCES

*Allard, B., Kigatsi, H. & Torstenfelt, B., 1979:* Technetium: reduction and sorption in granitic bedrock. *Radiochem. Radioanal. Letters* Vol. 37(4-5), pp 223 - 230, ISSN 0079-9483.

*ASTM Designation: D 4319 - 93:* Standard Test Method for Distribution Ratios by the Short-Term Batch Method. American Society for Testing and Materials, Philadelphia, 6 p. August 1993.

*ASTM Designation: D 3648 - 95:* Standard Practices for the Measurement of Radioactivity. American Society for Testing and Materials, Philadelphia, 27 p, June 1995.

*Chhabra, R., Pleysier, J. & Cremers, A., 1975.* The measurement of the cation exchange capacity and exchangeable cations in soils: a new method. *Proc. Int. Clay Conf. 1975*, Applied Publishing Ltd, Wilmele, Illinois 60091, USA.

*Hakanen, M., Jaakkola, T. & Korpela, H., 1984.* Simultaneous determination of Pu-241, Pu-238 and Pu-239, 240 in low activity environmental samples. In: Glover, K.M., Ivanovich, M. & Lally, A.E. (ed.). *Proceedings of the Second Seminar on Alpha-Particle Spectrometry and Low-Level Measurements*, Harwell, England. May 10-13, 1983. In: Siegbahn, K. & Karlsson, E. (ed.). *Nuclear Instruments & Methods in Physics Research. Section A: Accelerators, spectrometers, detectors and associated equipment.* Vol. 223, Nos 2,3, pp 382-385. ISSN 0167-5087.

*Huitti, T., Hakanen, M. & Lindberg, A., 1996.* Sorption of cesium, radium, protactinium, uranium, neptunium and plutonium on rapakivi granite. Report POSIVA-96-23, 57 p, ISBN 951-652-022-7, ISSN 1239-3096.

*Kaukonen, V., Hakanen, M. & Lindberg, A., 1993.* Sorption of Cs, U, Np and Pu and diffusion of water, Cs and Np in basic plutonic rocks and vulcanite. Nuclear Waste Commission of Finnish Power Companies, Report YJT-93-13, 36+24 p, ISSN 0359-548X.

*Kokholm, G.:* Redox measurements their theory and technique. 3rd revised edition, Copenhagen, Denmark: Radiometer A/S 918-139 8103D, 29 p.

*Koskinen, A., Hakanen, M. & Lindberg, A., 1988.* Sorption experiments at oxic and anoxic conditions. Nuclear Waste Commission for Finnish Power Companies, Report YJT-88-05, 27 p, ISSN 0359-548X.

*Kulmala, S., Hakanen, M. & Lindberg, A., 1996.* Sorption of protactinium on rocks in groundwaters from Posiva investigation sites. Report POSIVA-96-18, 44 p, ISBN 951-652-017-0, ISSN 1239-3096.

*Lieser, K.H. & Bauscher, Ch., 1987: Technetium in the hydrosphere and in the geosphere 1. Chemistry of technetium and iron in natural waters and influence of the redox potential on the sorption of technetium. Radiochimica Acta 42, pp 205 - 213, ISSN 0033-8230.*

*Lindberg, A., Pinnioja, S. & Nikula, A., 1983. Sorption of radionuclides in rock, mineralogic factors and autoradiography. Nuclear Waste Commission of Finnish Power Companies, Report YJT-83-02, 78 p, (in Finnish), ISSN 0359-548X.*

*Suksi, S., Siitari-Kauppi, M., Hölttä, P., Jaakkola, T. & Lindberg, A., 1989. Sorption and diffusion of radionuclides (C, Tc, U, Pu, Np) in rock samples under oxic and anoxic conditions. Nuclear Waste Commission of Finnish Power Companies, Report YJT-89-13, 68 p, ISSN 0359-548X.*

*Vuorinen, U., Kulmala, S., Hakanen, M., Ahonen, L. & Carlsson, T., 1998. Solubility database for TILA-99. Report POSIVA-98-14, to be published.*

**APPENDIX A: Materials**

Table 1.	Rock samples.	32
Table 2.	Mineral composition of thin sections (Vol.-%) calculated by point counting method (500 points/sample).	33
Table 3.	Cation exchange capacities (CEC values) of crushed rock samples measured by AgTU method.	34
Table 4.	Chemical composition of the Olkiluoto, Romuvaara and Kivetty groundwaters.	35

**Table 1.** Rock samples. Crushed rock samples and polished thin sections were prepared at the Geological Survey of Finland and specific areas were measured at the Helsinki University of Technology, Laboratory of Mechanical Processing and Recycling. Ol=Olkiluoto study site, Ro=Romuvaara study site and Ki=Kivetty study site.

Rock	Depth of the rock thin section (m)	Depth of the crushed rock sample (m)	Specific area of the crushed rock (m <sup>2</sup> /g)
Ol1, mica gneiss	561	520 - 586	0.95
Ol2A, tonalite	355	346 - 390	0.22
Ol2B, granite	417	417 - 455	0.36
Ro1A, tonalite	337	335 - 412	0.28
Ro1B, granite	559	547 - 654	0.23
Ro1C, mica gneiss	753	724 - 793	0.18
Ki4A, porphyritic granite	301	255 - 328	0.21
Ki4B, porphyritic granodiorite	385, 439	371 - 442	0.22



**Table 2.** Mineral compositions of thin sections (Vol.-%) calculated by point counting method (500 points/sample).

Minerals	O11, mica gneiss	O12A, tonalite	O12B, granite	Ro1A, tonalite	Ro1B, granite	Ro1C, mica gneiss	Ki4A, porph. granite	Ki4B, porph. granodiorite
K-feldspar	19.2	16.6	15.2	-	30.2	0.2	26.4	36.6
Plagioclase	14.8	38.6	38.4	25.4	24.8	27.0	23.6	25.4
Quartz	16.6	26.0	35.8	44.4	36.4	38.8	39.0	20.0
Biotite	32.4	6.6	0.2	16.4	2.6	31.2	5.4	12.0
Muscovite	2.4	3.6	9.2	12.2	3.8	0.2	0.8	0.8
Chlorite	-	6.4	0.2	+	0.6	0.2	-	-
Hornblende	-	-	-	-	+?	-	4.0	4.4
Apatite	?	1.0	-	0.2	+	0.8	0.2	0.2
Epidote	+	0.4	+	1.0	1.2	0.6	-	0.2
Calcite	-	-	-	-	+	3-	-	-
Sphene	-	+	-	+	-	-	-	0.2
Zircon			-	?	?	+		
Garnet	-	0.6	+	-	-	-	-	-
Sillimanite	3.2	-	1.0	-	-	-	-	-
Cordierite	9.8	-	-	-	-	-	-	-
Fluorite	-	-	-	-	0.2	-	-	-
Opaques	1.6	0.2	-	0.4	+	1.0	0.6	0.2

- not observed  
 + optically observed  
 ? uncertain observation

O11 is relatively fresh, even-grained mica gneiss with clear schistosity

O12A is medium-grained (0.6 - 3 mm) granodiorite which is slightly schistose; plagioclase alteration to sericite has been relatively strong.

O12B comes from a white granite vein (granodioritic composition on the basis of point counting), which contains muscovite as dark mineral and some sillimanite and garnet marking the metamorphic origin and influence of sedimentary content.

Ro1A is a medium-grained (0.5 - 1.0 mm) tonalite, with some indications of deformation and recrystallization.

Ro1B is from a leucocratic tonalite containing abundant potassium feldspar, which puts it in the granite field in the IUGS classification. Relatively coarse muscovite flakes and very fine-grained (cloudy) sericite are abundant.

Ro1C is a fine-grained (0.2 - 1.6 mm) unaltered mica gneiss with clear schistosity.

Ki4A is a porphyritic granite with grain size from 1 to 7 mm. The texture shows some deformation but no alteration. Deformation has produced recrystallized, fine-grained groundmass.

Ki4B is very similar to the Ki4A sample, but here large potassium feldspar phenocrysts make the composition even more granitic (quartz monzonite). Deformation has been stronger and plagioclase is moderately sericitized.

**Table 3.** Cation exchange capacities, CEC values, of the crushed rock samples measured by AgTU-method.

Rock	$\Sigma$ exchangeable cations (meq/100 g)	Ag <sup>+</sup> (meq/100 g)	Cs <sup>+</sup> (meq/100 g)
O11, mica gneiss	3.3 ± 0.3	1.5 ± 0.4	1.6 ± 0.1
O12A, tonalite	1.4 ± 0.2	2.1 ± 0.4	0.66 ± 0.07
O12B, granite	2.0 ± 0.1	1.8 ± 0.4	0.54 ± 0.17
Ro1A, tonalite	9.5 ± 0.4	1.8 ± 0.6	0.76 ± 0.06
Ro1B, granite	5.1 ± 0.3	1.8 ± 0.3	0.51 ± 0.08
Ro1C, mica gneiss	8.9 ± 0.5	1.3 ± 0.4	0.66 ± 0.17
Ki4A, porph, granite	2.9 ± 0.1	1.2 ± 0.4	1.1 ± 0.1
Ki4B, porph. granodiorite	2.8 ± 0.3	1.9 ± 0.2	1.3 ± 0.2

**Table 4.** Chemical composition of Olkiluoto, Romuvaara and Kivetty groundwaters (IVO Chem. Lab.)

	Romuvaara, RoKR4 187 - 190 m	Kivetty, KiKR4 436 - 468 m	Olkiluoto, OIKR5 446 - 558 m
Eh(Pt) (F) (mV)	- 71	-61	-157
O <sub>2</sub> (F) (mg/l)	2.70	0.00	0.00
Cond (F) (mS/m)	16.0	14.0	1981
Cond (L) (mS/m)	18.0	17.0	2330
pH (F)	7.9	8.2	7.0
pH (L)	9.3	8.2	8.2
Alk (F) (m) (meq/l)	1.52	1.40	0.30
Alk (F) (p) (meq/l)	0.28	0.24	0.10
DIC (mg/l)	15.8	15.1	1.30
DOC (mg/l)	2.0	7.2	1.2
Fe <sub>tot</sub> (Fz) (mg/l)	0.050	0.600	0.084
Fe <sub>tot</sub> (AAS) (mg/l)	0.059	0.520	0.230
Fe <sup>2+</sup> (Fz) (mg/l)	< 0.01	0.150	0.076
SiO <sub>2</sub> (mg/l)	13.0	13.0	6.3
Al (mg/l)	0.071	0.030	0.032
Na (mg/l)	39.0	18.0	3330
K (mg/l)	0.69	0.87	15.0
Ca (mg/l)	2.1	13.0	2100
Mg (mg/l)	0.08	3.0	67.0
Mn (mg/l)	0.001	0.210	0.360
Cs (mg/l)	< 0.005	< 0.005	0.008
S <sub>tot</sub> (mg/l)	1.44	0.73	1.50
S(-II) <sub>tot</sub> (F) (mg/l)	0.066	0.025	0.160
S(-II) <sub>tot</sub> (L) (mg/l)	0.04	0.04	0.30
SO <sub>4</sub> (mg/l)	3.9	2.00	3.30
P <sub>tot</sub> (mg/l)	0.15	< 0.01	< 0.01
PO <sub>4</sub> (mg/l)	0.44	0.02	< 0.01
Cl (mg/l)	4.3	3.20	9200
F (mg/l)		3.00	1.30
Br (mg/l)	0.10	0.03	58.0
Uranine (FL) (µg/l)	4.0	4.0	< 1
H-3 (TU)	0.9	1.9	2.0
U-238(H <sub>2</sub> O) (mBq/l)	5.4	39.0	0.32
U-238(H <sub>2</sub> O) (ppb)	0.439	3.190	0.026
U-234/U-238	3.83	3.44	2.07
U-238(part.) (mBq/l)	< 0.2	< 0.07	< 0.11
U-238(part.) (ppb)	< 0.02	< 0.01	< 0.01
Ionic strength	$1.5 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	$3.1 \cdot 10^{-1}$

F = field measurement or analysis in the field

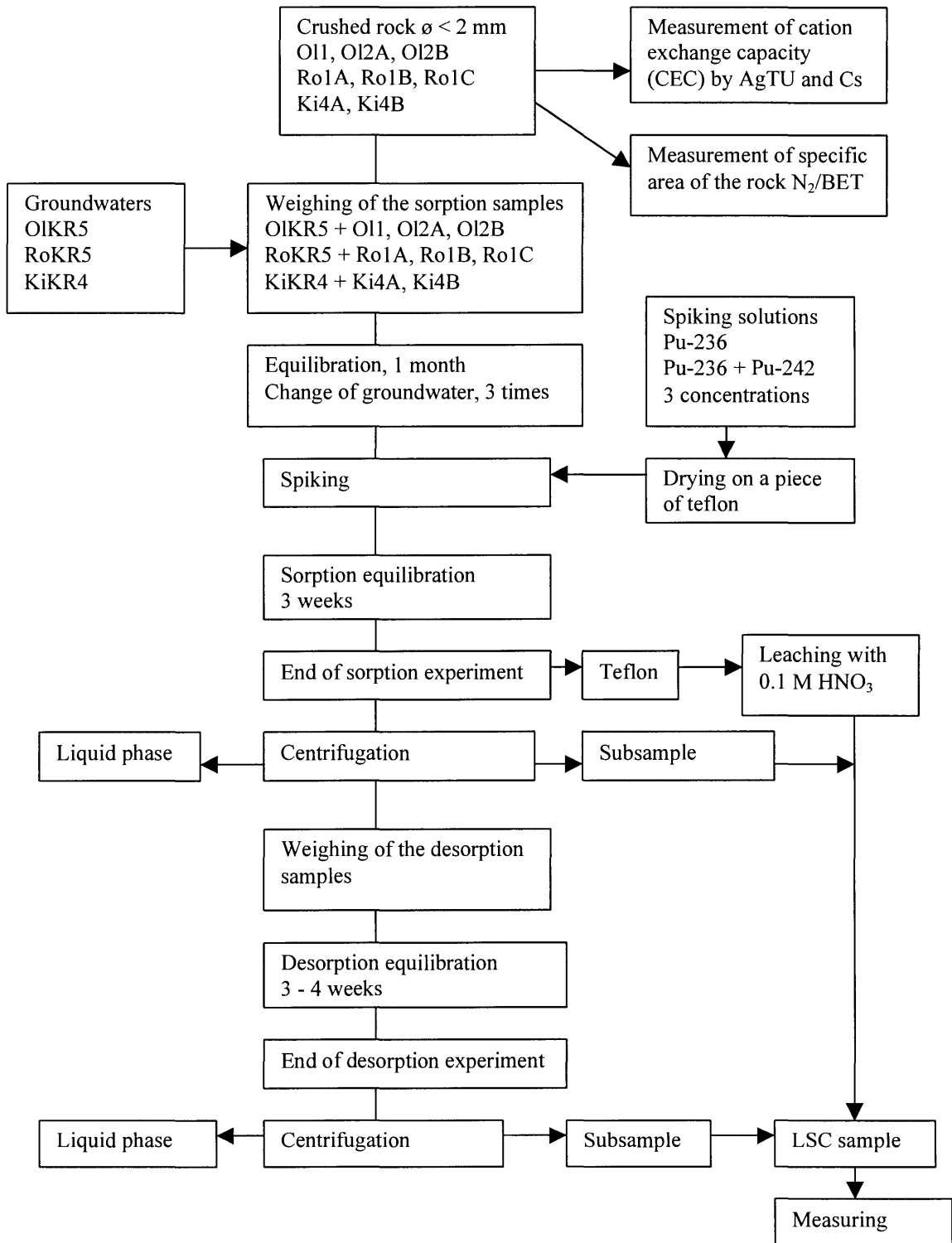
L = laboratory measurement or analysis

FL = fluorimetry

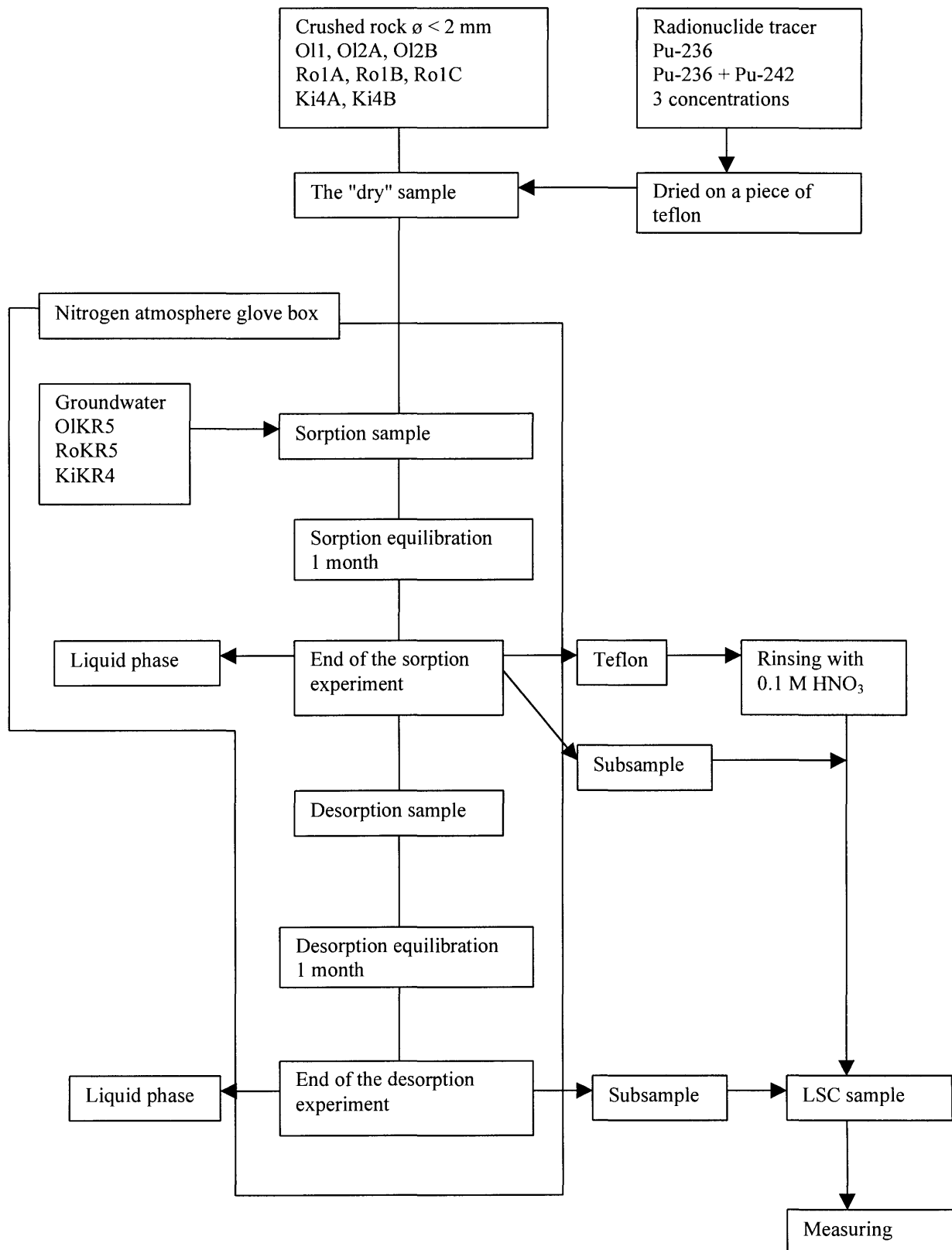
Fz = ferrozine analytical method

**Appendix B: Methods for the sorption studies.**

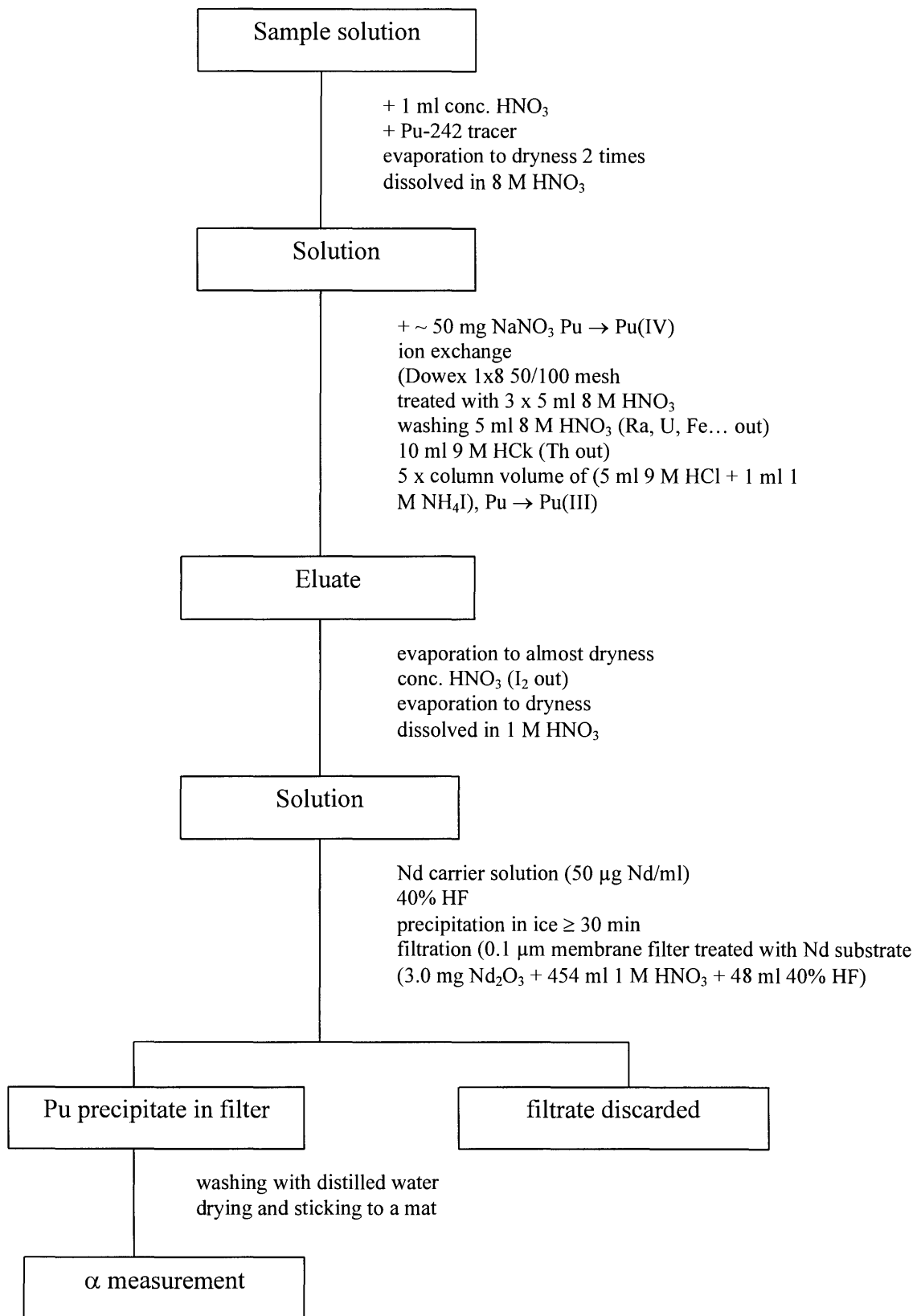
Figure 1.	Experimental procedure for the studies on crushed rock under oxic conditions	37
Figure 2.	Experimental procedure for the studies on crushed rock under anoxic conditions	38
Figure 3.	Ion exchange diagram for Pu separation from OIKR5 groundwater samples	39
B.1	Equations used to calculate the sorption percentages and mass distribution ratios.	40



**Figure 1.** Experimental procedure for the studies on crushed rock under oxic conditions.



**Figure 2.** Experimental procedure for the studies on crushed rock under anoxic conditions.



*Figure 3. Ion exchange diagram for Pu separation from OlKR5 groundwater samples.*

### B.1 Equations used to calculate the sorption percentages and mass distribution ratios

The sorption percentages,  $S_s(\%)$ , are calculated from the measurements with Equation (1):

$$S_s(\%) = \frac{\frac{A_{tracer} - A_{teflon}}{V_{total}} - \frac{A_{sample}}{V_{sample}}}{\frac{A_{tracer} - A_{teflon}}{V_{total}}} * 100\% \quad (1)$$

where  $A_{tracer}$  = activity dried on the teflon platelet  
 $A_{teflon}$  = activity left on the piece of teflon (undissolved fraction)  
 $V_{total}$  = total volume of the solution  
 $A_{sample}$  = activity of the measured subsample  
 $V_{sample}$  = volume of the measured subsample

The mass distribution ratio,  $R_d$ , was calculated with Equation (2):

$$R_d = \frac{S_s(\%)}{100 - S_s(\%)} * \frac{V}{m} \quad (2)$$

where  $S_s(\%)$  = sorption percentage  
 $V$  = volume of the water in the sample ( $m^3$ )  
 $m$  = mass of the solid in the sample (kg)

$$R_d \text{ (ml/g)} = 10^3 * R_d \text{ (m}^3\text{/kg)}$$

When the liquid phase is removed from the sorption sample, some of the spiking solution is unavoidably left in the crushed rock. This is taken into account when calculating the sorption percentages in desorption experiments.



The sorption percentages for desorption experiments ( $S_{s,des}$ ) are calculated by Equation (3):

$$S_{s,des} (\%) = \frac{A_{tracer} * \frac{S_s (\%)}{100\%} + \frac{V_r * A_{tracer}}{V_{s,total}} * \left(1 - \frac{S_s (\%)}{100\%}\right) - \frac{A_{de,sample}}{V_{de,sample}} * V_{de,total}}{A_{tracer} + \frac{S_s (\%)}{100\%} + \frac{V_r * A_{tracer}}{V_{s,total}} * \left(1 - \frac{S_s (\%)}{100\%}\right)} * 100\% \quad (3)$$

where  $A_{tracer}$  = activity of the spiking solution  
 $S_s(\%)$  = sorption percentage  
 $V_r$  = volume of the spiking solution left with the solid phase  
 $A_{de,sample}$  = activity of the measured desorption subsample  
 $V_{de,sample}$  = volume of the measured desorption subsample  
 $V_{de, total}$  = total volume of the desorption sample  
 $V_{s,total}$  = total volume of the sorption sample

The mass distribution ratio,  $R_{d,des}$ , was calculated with Equation (4):

$$R_d = \frac{S_{s,des} (\%)}{100 - S_{s,des} (\%)} * \frac{V}{m} \quad (4)$$

where  $S_{s,des} (\%)$  = sorption percentage of desorption  
 $V$  = volume of water in the desorption sample ( $m^3$ )  
 $m$  = mass of the solid in the sample (kg)

With polished rock thin sections the surface ratio,  $R_a$ , is calculated by Equation (5):

$$R_a = \frac{\frac{S(\%)}{L(\%)} = \frac{S(\%)}{100 - S(\%)} * \frac{V}{A}}{V} \quad (5)$$

where  $S(\%)$  = amount of the radionuclide sorbed on the thin section as a percentage of the spiking solution  
 $L(\%) = 100 - S(\%)$  = amount of the radionuclide left in the spiking solution  
 $A$  = geometric surface area of the sample ( $m^2$ )  
 $V$  = volume of the solution ( $m^3$ )

**Appendix C: Sorption of plutonium on rocks from Posiva investigation sites where sorption was from local groundwater. Values are for individual samples.**

Table 1.	Sorption and desorption of plutonium from OIKR5 groundwater onto Olkiluoto rock samples under oxic conditions.	43
Table 2.	Sorption of plutonium from OIKR5 groundwater onto Olkiluoto rock samples under oxic conditions with added caesium	44
Table 3.	Sorption and desorption of plutonium from RoKR5 groundwater onto Romuvaara rock samples under oxic conditions.	45
Table 4.	Sorption and desorption of plutonium from KiKR4 groundwater onto Kivetty rock samples under oxic conditions.	46
Table 5.	Sorption of plutonium from OIKR5 groundwater onto Olkiluoto rock samples under anoxic conditions.	47
Table 6.	Sorption of plutonium from RoKR5 groundwater onto Romuvaara rock samples under anoxic conditions.	48
Table 7.	Sorption of plutonium from KiKR4 groundwater onto Kivetty rock samples under anoxic conditions.	49
Table 8.	Concentration of Tc-99 in crushed rock in groundwater/crushed rock samples under anoxic conditions.	50
Table 9.	Sorption percentages and $R_a$ values for the sorption of plutonium on Olkiluoto rock thin sections under oxic conditions.	51
Table 10.	Sorption percentages and $R_a$ values for the sorption of plutonium on Romuvaara rock thin sections under oxic conditions.	51
Table 11.	Sorption percentages and $R_a$ values for the sorption of plutonium on Kivetty rock thin sections under oxic conditions.	52

**Table 1.** Sorption and desorption of plutonium from OlKR5 groundwater on Olkiluoto rock samples under oxic conditions.

Sample	Undissolved fraction (%)	Sorption $S_s$ (%)	$R_d$ (m <sup>3</sup> /kg)	$S_{s,des}$ (%)	$R_{d,des}$ (m <sup>3</sup> /kg)
O11Pu1-1	0.54	99.997	289	≥ 99	≥ 1.0
O11Pu1-2	0.11	99.990	104	≥ 99	≥ 1.0
O11Pu1-3	0.15	99.989	94.4	≥ 99	≥ 1.0
O11Pu2-1	0.35	99.995	193	≥ 99	≥ 1.0
O11Pu2-2	0.31	99.993	141	≥ 99	≥ 1.0
O11Pu2-3	0.45	99.992	124	≥ 99	≥ 1.0
O11Pu3-1	0.21	99.995	217	≥ 99	≥ 1.0
O11Pu3-2	0.54	99.987	75.9	≥ 99	≥ 1.0
O11Pu3-3	0.38	99.993	141	≥ 99	≥ 1.0
O12APu1-2	0.15	99.993	153	≥ 99	≥ 1.0
O12APu1-3	0.18	99.990	105	≥ 99	≥ 1.0
O12APu2-1	0.18	99.992	124	≥ 99	≥ 1.0
O12APu2-2	0.15	99.996	261	≥ 99	≥ 1.0
O12APu2-3	0.16	99.981	53.7	≥ 99	≥ 1.0
O12APu3-1	0.11	99.984	64.4	≥ 99	≥ 1.0
O12APu3-2	0.73	99.994	173	≥ 99	≥ 1.0
O12APu3-3	0.33	99.985	67.8	≥ 99	≥ 1.0
		99.982	54.5		
O12BPu1-1	0.41	99.993	138	≥ 99	≥ 1.0
O12BPu1-2	0.44	99.997	401	≥ 99	≥ 1.0
O12BPu1-3	0.37	99.990	106	≥ 99	≥ 1.0
O12BPu2-1	0.47	99.994	158	≥ 99	≥ 1.0
O12BPu2-2	0.33	99.982	58.0	≥ 99	≥ 1.0
O12BPu2-3	0.70	99.989	88.7	≥ 99	≥ 1.0
O12BPu3-1	0.70	99.992	124	≥ 99	≥ 1.0
O12BPu3-2	0.94	99.994	168	≥ 99	≥ 1.0
O12BPu3-3	1.10	99.982	56.1	≥ 99	≥ 1.0

**Table 2.** Sorption of plutonium from OlKR5 groundwater on Olkiluoto rock samples under oxic conditions with added caesium.

Sample	Undissolved fraction (%)	Sorption (%)	$R_d$ (m <sup>3</sup> /kg)
Ol1CsPu1-1	0.71	99.986	67.4
Ol1CsPu1-2	1.01	99.986	71.1
Ol1CsPu1-3	0.76	99.985	66.6
Ol1CsPu2-1	0.61	99.989	93.0
Ol1CsPu2-2	0.64	99.989	93.3
Ol1CsPu2-3	0.91	99.982	55.8
Ol2ACsPu1-1	0.98	99.985	67.8
Ol2ACsPu1-2	0.36	99.988	83.7
Ol2ACsPu1-3	1.34	99.980	51.9
Ol2ACsPu2-1	0.53	99.987	81.4
Ol2ACsPu2-2	0.40	99.986	70.4
Ol2ACsPu2-3	0.90	99.988	84.5
Ol2BCsPu1-1	1.23	99.976	43.3
Ol2BCsPu1-2	2.02	99.949	20.0
Ol2BCsPu1-3	2.70	99.995	186
Ol2BCsPu2-1	0.65	99.987	77.5
Ol2BCsPu2-2	0.73	99.979	47.2
Ol2BCsPu2-3	1.47	99.963	27.4

**Table 3.** Sorption and desorption of plutonium from RoKR5 groundwater on Romuvaara rock samples under oxic conditions. The presented error is the standard deviation of radioassay.

Sample	Undissolved fraction (%)	$S_s$ (%)	$R_{d,s}$ (m <sup>3</sup> /kg)	$S_{des}$ (%)	$R_{d,des}$ (m <sup>3</sup> /kg)
Ro1Apu1-1	0.09	96.0 ± 0.6	0.255	≥ 99.9	≥ 1.0
Ro1Apu1-2	0.11	97.5 ± 0.3	0.407	≥ 99.9	≥ 1.0
Ro1Apu1-3	0.11	94.5 ± 0.4	0.179	≥ 99.9	≥ 1.0
Ro1Apu2-1	0.19	96.2 ± 0.3	0.275	≥ 99.9	≥ 1.0
Ro1Apu2-2	0.36	95.6 ± 0.2	0.225	≥ 99.9	≥ 1.0
Ro1Apu2-3	0.19	94.6 ± 0.7	0.178	≥ 99.9	≥ 1.0
Ro1Apu3-1	0.11	96.5 ± 0.6	0.284	≥ 99.9	≥ 1.0
Ro1Apu3-2	0.08	97.1 ± 0.3	0.349	≥ 99.9	≥ 1.0
Ro1Apu3-3	0.37	95.3 ± 0.8	0.208	≥ 99.9	≥ 1.0
Ro1Bpu1-1	0.15	91.6 ± 1.0	0.114	≥ 99.9	≥ 1.0
Ro1Bpu1-2	0.06	90.4 ± 1.0	0.0975	≥ 99.9	≥ 1.0
Ro1Bpu1-3	0.06	82.2 ± 0.3	0.0481	≥ 99.9	≥ 1.0
Ro1Bpu2-1	0.12	82.8 ± 0.3	0.0504	≥ 99.9	≥ 1.0
Ro1Bpu2-2	0.27	96.4 ± 1.0	0.0653	≥ 99.9	≥ 1.0
Ro1Bpu2-3	0.16	92.8 ± 0.9	0.128	≥ 99.9	≥ 1.0
Ro1Bpu3-1	0.05	93.1 ± 0.6	0.140	≥ 99.9	≥ 1.0
Ro1Bpu3-2	0.05	93.5 ± 0.4	0.147	≥ 99.9	≥ 1.0
Ro1Bpu3-3	0.16	91.2 ± 0.8	0.107	≥ 99.9	≥ 1.0
Ro1Cpu1-1	0.12	95.6 ± 0.3	0.229	≥ 99.9	≥ 1.0
Ro1Cpu1-2	0.22	93.1 ± 0.4	0.141	≥ 99.9	≥ 1.0
Ro1Cpu1-3	0.10	90.6 ± 0.9	0.101	≥ 99.9	≥ 1.0
Ro1Cpu2-1	0.27	93.3 ± 0.7	0.146	≥ 99.9	≥ 1.0
Ro1Cpu2-2	0.50	94.3 ± 0.3	0.175	≥ 99.9	≥ 1.0
Ro1Cpu2-3	0.10	94.0 ± 0.3	0.165	≥ 99.9	≥ 1.0
Ro1Cpu3-1	0.52	94.5 ± 0.7	0.180	≥ 99.9	≥ 1.0
Ro1Cpu3-2	0.39	93.0 ± 0.3	0.140	≥ 99.9	≥ 1.0
Ro1Cpu3-3	0.13	93.7 ± 0.6	0.156	≥ 99.9	≥ 1.0

**Table 4.** Sorption and desorption of plutonium from KiKR4 groundwater on Kivetty rock samples under oxic conditions. The presented error is the standard deviation of radioassay.

Sample	Undissolved fraction (%)	$S_s$ (%)	$R_{d,s}$ ( $m^3/kg$ )	$S_{s,des}$ (%)	$R_{d,des}$ ( $m^3/kg$ )
Ki4APu1-1	0.07	$98.3 \pm 0.5$	0.612	$\geq 99.9$	$\geq 1.0$
Ki4APu1-2	0.15	$96.2 \pm 0.7$	0.268	$\geq 99.9$	$\geq 1.0$
Ki4APu1-3	0.10	$96.6 \pm 0.2$	0.303	$\geq 99.9$	$\geq 1.0$
Ki4APu2-1	0.19	$97.6 \pm 0.3$	0.420	$\geq 99.9$	$\geq 1.0$
Ki4APu2-2	0.22	$95.0 \pm 0.7$	0.201	$\geq 99.9$	$\geq 1.0$
Ki4APu2-3	0.07	$96.8 \pm 0.2$	0.316	$\geq 99.9$	$\geq 1.0$
Ki4APu3-1	0.14	$97.8 \pm 0.5$	0.470	$\geq 99.9$	$\geq 1.0$
Ki4APu3-2	0.34	$96.1 \pm 0.5$	0.257	$\geq 99.9$	$\geq 1.0$
Ki4APu3-3	0.51	$95.5 \pm 0.9$	0.220	$\geq 99.9$	$\geq 1.0$
Ki4BPu1-1	0.18	$97.8 \pm 0.6$	0.464	$\geq 99.9$	$\geq 1.0$
Ki4BPu1-2	0.12	$95.4 \pm 0.8$	0.218	$\geq 99.9$	$\geq 1.0$
Ki4BPu1-3	0.06	$95.5 \pm 0.6$	0.225	$\geq 99.9$	$\geq 1.0$
Ki4BPu2-1	0.23	$98.2 \pm 0.2$	0.563	$\geq 99.9$	$\geq 1.0$
Ki4BPu2-2	0.22	$94.4 \pm 0.5$	0.177	$\geq 99.9$	$\geq 1.0$
Ki4BPu2-3	0.14	$95.4 \pm 0.4$	0.215	$\geq 99.9$	$\geq 1.0$
Ki4BPu3-1	0.30	$97.8 \pm 0.4$	0.473	$\geq 99.9$	$\geq 1.0$
Ki4BPu3-2	0.05	$97.5 \pm 0.4$	0.412	$\geq 99.9$	$\geq 1.0$
Ki4BPu3-3	0.56	$96.2 \pm 0.5$	0.264	$\geq 99.9$	$\geq 1.0$

**Table 5.** Sorption of plutonium from OlKR5 groundwater on Olkiluoto rock samples under anoxic conditions. The presented error is the standard deviation of radioassay.

Sample	pH	Eh (mV)	Undissolved fraction (%)	Sorption, $S_s$ on teflon (%)	Sorption, $S_s$ on rock (%)	$R_d$ ( $m^3/kg$ )
Ol1Pu1-1	8.61	-156	$33.9 \pm 0.2$	0.077	$99.9 \pm 0.1$	15.5
Ol1Pu1-2	8.20	-234	$35.7 \pm 0.2$		$99.2 \pm 0.1$	1.32
Ol1Pu1-3	8.12	-325	$16.8 \pm 0.1$		$99.6 \pm 0.2$	2.66
Ol1Pu2-1	8.55	-166	$14.2 \pm 0.1$	0.20	$99.9 \pm 0.1$	14.5
Ol1Pu2-2	7.80	-280	$16.4 \pm 0.1$		$99.6 \pm 0.1$	2.93
Ol1Pu3-1	8.44	-138	$9.70 \pm 0.1$	0.049	$99.9 \pm 0.1$	17.7
Ol1Pu3-2	7.87	-303	$8.48 \pm 0.06$		$99.8 \pm 0.1$	5.74
Ol2APu1-1	8.45	-180	$39.7 \pm 0.2$	0.021	$99.7 \pm 0.1$	4.26
Ol2APu1-3	7.78	-428	$32.3 \pm 0.2$		$99.2 \pm 0.4$	1.41
Ol2APu2-1	8.56	-186	$24.1 \pm 0.1$	0.12	$99.7 \pm 0.1$	3.17
Ol2APu2-2	7.85	-338	$9.57 \pm 0.07$		$99.3 \pm 0.1$	1.52
Ol2APu3-1	8.55	-202	$17.5 \pm 0.1$	0.44	$99.8 \pm 0.1$	4.46
Ol2APu3-2	8.12	-323	$8.35 \pm 0.06$		$99.4 \pm 0.1$	1.83
Ol2BPu1-1	8.61	-202	$26.0 \pm 0.1$	0.046	$99.7 \pm 0.1$	3.49
Ol2BPu1-2	8.15	-316	$29.8 \pm 0.2$		$98.8 \pm 0.1$	0.910
Ol2BPu2-1	8.41	-192	$25.7 \pm 0.1$	0.070	$99.7 \pm 0.1$	3.52
Ol2BPu2-2	8.20	-320	$28.6 \pm 0.2$		$99.0 \pm 0.1$	0.993
Ol2BPu3-1	8.55	-153	$8.30 \pm 0.1$	0.091	$99.8 \pm 0.1$	5.31
Ol2BPu3-2	8.13	-321	$8.29 \pm 0.06$		$99.6 \pm 0.1$	2.89

**Table 6.** Sorption of plutonium from RoKR5 groundwater on Romuvaara rock samples under anoxic conditions. The presented error is the standard deviation of radioassay.

Sample	pH	Eh (mV)	Undissolved fraction (%)	Sorption. $S_s$ on teflon (%)	Sorption. $S_s$ on rock (%)	$R_d$ ( $m^3/kg$ )
Ro1APu1-1	9.68	-144	15.2 ± 0.1	0.051	99.3 ± 0.1	1.35
Ro1APu1-2	9.40	-272	59.8 ± 0.2		97.2 ± 0.2	0.381
Ro1APu2-1	9.59	-225	- *		99.4 ± 0.1	1.74
Ro1APu2-2	9.26	-325	24.9 ± 0.1		99.1 ± 0.1	1.12
Ro1APu3-1	9.64	-198	11.5 ± 0.1	0.047	99.1 ± 0.1	1.08
Ro1APu3-2	9.27	-345	6.78 ± 0.06		98.9 ± 0.1	0.984
Ro1BPu1-1	9.68	-234	37.5 ± 0.2	0.095	98.8 ± 0.1	0.829
Ro1BPu1-2	9.22	-363	19.2 ± 0.1		98.7 ± 0.1	0.753
Ro1BPu2-1	9.71	-212	12.9 ± 0.1	4.45	99.5 ± 0.1	2.08
Ro1BPu2-2	9.30	-346	25.8 ± 0.1		98.7 ± 0.1	0.793
Ro1BPu3-1	9.68	-173	13.3 ± 0.1	16.5	99.3 ± 0.1	1.47
Ro1BPu3-2	9.45	-358	17.4 ± 0.1		98.4 ± 0.1	0.637
Ro1CPu1-1	9.71	-221	32.0 ± 0.2	6.31	99.0 ± 0.1	1.06
Ro1CPu1-2	9.30	-343	9.68 ± 0.07		98.9 ± 0.1	0.892
Ro1CPu2-1	9.66	-227	26.6 ± 0.1	0.12	99.9 ± 0.1	9.05
Ro1CPu2-2	9.40	-362	6.57 ± 0.05		99.5 ± 0.1	2.29
Ro1CPu3-1	9.72	-236	6.19 ± 0.1	22.9	99.6 ± 0.1	2.87
Ro1CPu3.2	9.16	-346	27.0 ± 0.2		99.6 ± 0.1	2.35

\* not analyzed



**Table 7.** Sorption of plutonium from KiKR4 groundwater on Kivetty rock samples under anoxic conditions. The presented error is the standard deviation of radioassay.

Sample	pH	Eh (mV)	Undissolved fraction (%)	Sorption, $S_s$ on teflon (%)	Sorption, $S_s$ on rock (%)	$R_d$ ( $m^3/kg$ )
Ki4APu1-1	9.55	-274	$31.5 \pm 0.2$	0.073	$99.1 \pm 0.1$	1.14
Ki4APu1-2	9.41	-235	$18.8 \pm 0.1$		$99.5 \pm 0.1$	1.94
Ki4APu2-1	9.47	-302	$8.07 \pm 0.1$	0.24	$99.5 \pm 0.1$	2.05
Ki4APu2-2	9.75	-360	$24.1 \pm 0.1$		$99.0 \pm 0.1$	1.03
Ki4APu3-1	9.66	-280	$12.1 \pm 0.1$	2.16	$99.8 \pm 0.1$	5.91
Ki4APu3-2	9.60	-361	$19.9 \pm 0.1$		$99.8 \pm 0.1$	4.96
Ki4BPu1-1	9.71	-270	$34.1 \pm 0.2$	0.056	$99.3 \pm 0.1$	1.45
Ki4BPu1-2	9.54	-330	$33.8 \pm 0.2$		$99.1 \pm 0.1$	1.17
Ki4BPu2-1	9.69	-281	$11.7 \pm 0.1$	0.21	$99.1 \pm 0.1$	1.17
Ki4BPu2-2	9.13	-340	$18.6 \pm 0.1$		$99.7 \pm 0.1$	3.96
Ki4BPu3-1	9.65	-267	$26.3 \pm 0.1$	0.079	$99.8 \pm 0.1$	5.79
Ki4BPu3-2	9.45	-357	$27.4 \pm 0.2$		$99.5 \pm 0.1$	2.44

**Table 8.** Concentration of Tc-99 in crushed rock in groundwater/crushed rock samples under anoxic conditions. The presented error is the standard deviation of radioassay.

Groundwater	Rock	Tc-99 in water (%)	pH	Eh(Pt) (mV)
OIKR5	no rock	98.3 ± 0.1	8.35	-412
		58.2 ± 0.3	8.07	-330
	Ol1, mica gneiss	98.7 ± 0.1	8.55	-156
		98.7 ± 0.1	8.16	-310
	Ol2A, tonalite	98.6 ± 0.1	8.64	-182
		98.6 ± 0.1	8.16	-331
	Ol2B, granite	98.6 ± 0.1	8.55	-165
		98.7 ± 0.1	8.00	-334
RoKR5	no rock	59.0 ± 0.3	9.24	-60
		98.5 ± 0.1	9.60	-374
	Ro1A, tonalite	94.2 ± 0.2	9.75	-170
		98.2 ± 0.1	9.56	-358
	Ro1B, granite	77.8 ± 0.3	9.88	-190
		98.2 ± 0.1	9.60	-353
	Ro1C, mica gneiss	95.2 ± 0.1	9.82	-220
		97.9 ± 0.1	9.54	-347
KiKR4	no rock	98.0 ± 0.1	9.63	-269
	Ki4A, porphyritic granite	97.8 ± 0.1	9.86	-340
		98.6 ± 0.1	9.66	-323
	Ki4B, porphyritic granodiorite	96.9 ± 0.1	9.84	-284
		98.2 ± 0.1	9.60	-353

**Table 9.** Sorption percentages and  $R_a$  values for the sorption of plutonium on Olkiluoto rock thin sections under oxic conditions. The presented error is the standard deviation of radioassay.

from saline OIKR5 groundwater			from non-saline KiKR5 groundwater		
Sample	$S_s$ (%)	$R_a \cdot 10^{-4}$ (m <sup>2</sup> /m <sup>3</sup> )	Sample	$S_s$ (%)	$R_a \cdot 10^{-4}$ (m <sup>2</sup> /m <sup>3</sup> )
O11-4	57.3 ± 0.5	22.1	O11-12	36.2 ± 0.4	7.73
O11-5	55.1 ± 0.5	20.4	OL1-13	37.1 ± 0.4	10.3
O12A-4	51.7 ± 0.5	18.9	O11-14	38.0 ± 0.4	10.4
O12A-5	49.2 ± 0.5	15.9	O12A-12	37.4 ± 0.4	8.90
O12B-4	49.1 ± 0.5	18.2	O12A-13	36.4 ± 0.4	9.23
O12B-5	44.9 ± 0.5	13.2	O12A-14	36.8 ± 0.4	9.70
			O12B-12	36.6 ± 0.4	8.60
			O12B-13	35.1 ± 0.4	8.90
			O12B-14	38.1 ± 0.4	9.46

**Table 10.** Sorption percentages and  $R_a$  values for the sorption of plutonium on Romuvaara rock thin sections under oxic conditions. The presented error is the standard deviation of radioassay.

from non-saline RoKR4 groundwater			from saline OIKR5 groundwater		
Sample	$S_s$ (%)	$R_a \cdot 10^{-4}$ (m <sup>2</sup> /m <sup>3</sup> )	Sample	$S_s$ (%)	$R_a \cdot 10^{-4}$ (m <sup>2</sup> /m <sup>3</sup> )
Ro1A-4	58.2 ± 0.3	26.7	Ro1A-12	36.6 ± 0.5	10.3
Ro1A-5	56.3 ± 0.4	21.2	Ro1A-13	39.6 ± 0.5	11.5
Ro1B-4	60.3 ± 0.3	23.7	Ro1A-14	39.9 ± 0.5	11.5
Ro1B-5	58.4 ± 0.3	22.4	Ro1B-12	32.8 ± 0.5	7.86
Ro1C-4	61.3 ± 0.3	26.4	Ro1B-13	36.2 ± 0.5	9.14
Ro1C-5	63.1 ± 0.3	26.7	Ro1B-14	30.7 ± 0.5	7.53
			Ro1C-12	35.2 ± 0.5	9.16
			Ro1C-13	38.0 ± 0.5	9.42
			Ro1C-14	33.8 ± 0.5	7.60

**Table 11.** Sorption percentages and  $R_a$  values for the sorption of plutonium on Kivetty rock thin sections under oxic conditions. The presented error is the standard deviation of radioassay.

from non-saline KiKR4 groundwater			from saline OIKR5 groundwater		
Sample	$S_s$ (%)	$R_a \cdot 10^{-4}$ (m <sup>2</sup> /m <sup>3</sup> )	Sample	$S_s$ (%)	$R_a \cdot 10^{-4}$ (m <sup>2</sup> /m <sup>3</sup> )
Ki4A-1	46.1 ± 1.2	12.0	Ki4A-10	34.6 ± 0.5	8.14
Ki4A-2	43.4 ± 1.2	10.9	Ki4A-11	35.0 ± 0.5	8.55
Ki4A-3	45.7 ± 1.2	10.8	Ki4A-12	33.5 ± 0.5	7.99
Ki4B-1	48.5 ± 1.2	12.4	Ki4B-10	44.7 ± 0.4	11.5
Ki4B-2	47.9 ± 1.1	12.1	Ki4B-11	36.8 ± 0.4	8.03
Ki4B-3	43.7 ± 1.2	11.9	Ki4B-12	35.7 ± 0.4	7.09

**POSIVA REPORTS 1998, situation 12/98**

- POSIVA 98-01      Bentonite swelling pressure in strong NaCl solutions  
- Correlation of model calculations to experimentally determined data  
*Ola Karnland*  
Clay Technology, Lund, Sweden  
January 1998  
ISBN 951-652-039-1
- POSIVA 98-02      A working groups conclusions on site specific flow and transport  
modelling  
*Johan Andersson*  
Golder Associates AB, Sweden  
*Henry Ahokas*  
Fintact Oy  
*Lasse Koskinen, Antti Poteri*  
VTT Energy  
*Auli Niemi*  
Royal Institute of Technology, Hydraulic Engineering, Sweden  
(permanent affiliation: VTT Communities and Infrastructure, Finland)  
*Aimo Hautojärvi*  
Posiva Oy  
March 1998  
ISBN 951-652-040-5
- POSIVA 98-03      EB-welding of the copper canister for the nuclear waste disposal –  
Final report of the development programme 1994-1997  
*Harri Aalto*  
Outokumpu Poricopper Oy  
October 1998  
ISBN 951-652-041-3
- POSIVA 98-04      An isotopic and fluid inclusion study of fracture calcite from borehole  
OL-KR1 at the Olkiluoto site, Finland  
*Alexander Blyth, Shaun Frapce*  
University of Waterloo, Waterloo, Ontario, Canada  
*Runar Blomqvist, Pasi Nissinen*  
Geological Survey of Finland  
*Robert McNutt*  
McMaster University, Hamilton, Ontario, Canada  
April 1998  
ISBN 951-652-042-1
- POSIVA 98-05      Sorption of iodine on rocks from Posiva investigation sites  
*Seija Kulmala, Martti Hakanen*  
Laboratory of Radiochemistry  
Department of Chemistry  
University of Helsinki  
*Antero Lindberg*  
Geological Survey of Finland  
May 1998  
ISBN 951-652-043-X

- POSIVA 98-06      Dissolution of unirradiated UO<sub>2</sub> fuel in synthetic groundwater –  
Progress report '97  
*Kaija Ollila*  
VTT Chemical Technology  
June 1998  
ISBN 951-652-044-8
- POSIVA 98-07      Geochemical modelling of groundwater evolution and residence time  
at the Kivetty site  
*Petteri Pitkänen, Ari Luukkonen*  
VTT Communities and Infrastructure  
*Paula Ruotsalainen*  
Fintact Oy  
*Hilkka Leino-Forsman, Ulla Vuorinen*  
VTT Chemical Technology  
August 1998 (to be published)  
ISBN 951-652-045-6
- POSIVA 98-08      Modelling gas migration in compacted bentonite  
- A report produced for the GAMBIT Club  
*P.J. Nash, B.T. Swift, M. Goodfield, W.R. Rodwell*  
AEA Technology plc, Dorchester, United Kingdom  
August 1998  
ISBN 951-652-046-4
- POSIVA 98-09      Geomicrobial investigations of groundwaters from Olkiluoto,  
Hästholmen, Kivetty and Romuvaara, Finland  
*Shelley A. Haveman, Karsten Pedersen*  
Göteborg University, Sweden  
*Paula Ruotsalainen*  
Fintact Oy  
August 1998  
ISBN 951-652-047-2
- POSIVA 98-10      Geochemical modeling of groundwater evolution and residence time  
at the Olkiluoto site  
*Petteri Pitkänen, Ari Luukkonen*  
VTT Communities and Infrastructure  
September 1998 (to be published)  
ISBN 951-652-048-0
- POSIVA 98-11      Sorption of cesium on Olkiluoto mica gneiss, granodiorite and granite  
*Tuula Huitti, Martti Hakanen*  
Laboratory of Radiochemistry, Department of Chemistry,  
University of Helsinki  
*Antero Lindberg*  
Geological Survey of Finland  
September 1998  
ISBN 951-652-049-9

- POSIVA 98-12 Sorption of plutonium on rocks in groundwaters from Posiva investigation sites  
*Seija Kulmala, Martti Hakanen*  
Laboratory of Radiochemistry, Department of Chemistry,  
University of Helsinki  
*Antero Lindberg*  
Geological Survey of Finland  
December 1998  
ISBN 951-652-050-2
- POSIVA 98-13 Solubilities of uranium for TILA-99  
*Kaija Ollila*  
VTT Chemical Technology  
*Lasse Ahonen*  
Geological Survey of Finland  
November 1998  
ISBN 951-652-051-0
- POSIVA 98-14 Solubility database for TILA-99  
*Ulla Vuorinen*  
VTT Chemical Technology  
*Seija Kulmala, Martti Hakanen*  
University of Helsinki, Laboratory of Radiochemistry  
*Lasse Ahonen*  
Geological Survey of Finland  
*Torbjörn Carlsson*  
VTT Chemical Technology  
November 1998  
ISBN 951-652-052-9
- POSIVA 98-15 Normal evolution of a spent fuel repository at the candidate sites in Finland  
*M.B. Crawford, R.D. Wilmot*  
Galson Sciences Ltd, United Kingdom  
December 1998  
ISBN 951-652-053-7