

POSIVA-96-24

# Deep groundwater redox reactions in the Palmottu uranium deposit:

The role of uranium and iron in these processes

Jordi Bruno  
Esther Cera  
Lara Duro  
QuantiSci, Spain

Lasse Ahonen  
Geological Survey of Finland

December 1996

---

POSIVA OY

Annankatu 42 D, FIN-00100 HELSINKI, FINLAND

Phone (09) 228 030 (nat.), (+358-9-) 228 030 (int.)

POSIVA-96-24

# Deep groundwater redox reactions in the Palmottu uranium deposit:

The role of uranium and iron in these processes

Jordi Bruno  
Esther Cera  
Lara Duro  
QuantiSci, Spain

Lasse Ahonen  
Geological Survey of Finland

December 1996

---

POSIVA OY

Annankatu 42 D, FIN-00100 HELSINKI, FINLAND

Phone (09) 228 030 (nat.), (+358-9-) 228 030 (int.)

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

**ISBN 951-652-023-5**  
**ISSN 1239-3096**



# Posiva-raportti – Posiva report

Posiva Oy  
Annankatu 42 D, FIN-00100 HELSINKI, FINLAND  
Puh. (09) 2280 30 – Int. Tel. +358 9 2280 30

Raportin tunnus – Report code

POSIVA-96-24

Julkaisuaika – Date

December 1996

Tekijä(t) – Author(s) Jordi Bruno, Esther Cera, Lara Duro, QuantiSci, Spain Lasse Ahonen, Geological Survey of Finland	Toimeksiantaja(t) – Commissioned by  Posiva Oy
Nimeke – Title  DEEP GROUNDWATER REDOX REACTIONS IN THE PALMOTTU URANIUM DEPOSIT: THE ROLE OF URANIUM AND IRON IN THESE PROCESSES	
Tiivistelmä – Abstract  <p>The reduction oxidation properties of the deep bedrock and groundwater are important geochemical factors with respect to the chemical stability of the multibarrier system, which isolates the disposed nuclear fuel from biosphere. In this report we describe the results of the redox experiments carried out in the field using the natural groundwaters of Palmottu, in Nummi-Pusula, Finland.</p> <p>The experiments include 1) measurements of natural water redox potential values during four to eight hours continuous pumping; 2) monitoring of the redox-potential response to an artificial change of pH of the groundwater. Separate tests were made in iron and uranium-rich groundwaters, respectively. The data of the field experiments were used in the redox-modelling of the iron and uranium systems.</p> <p>In accordance with earlier knowledge, we show that dissolved iron is an important redox electrolyte in natural waters, at least at concentration levels of milligrams per liter. However, a striking observation was that - in the absence of dissolved iron - dissolved uranium (in concentrations of about 200 nM or more) seems to be able to give nernstian response on platinum electrode in acid/base titrations.</p> <p>The effective redox properties of the bedrock-groundwater system depend on the availability and reactivity of solid phases able to exchange electrons with dissolved redox electrolytes. The present results indicate that, in the bedrock/groundwater system of the Palmottu uranium mineralization, uranium minerals are important redox buffers.</p>	
ISBN ISBN 951-652-023-5	ISSN ISSN 1239-3096
Sivumäärä – Number of pages 26	Kieli – Language English



# Posiva-raportti – Posiva report

Posiva Oy  
Annankatu 42 D, FIN-00100 HELSINKI, FINLAND  
Puh. (09) 2280 30 – Int. Tel. +358 9 2280 30

Raportin tunnus – Report code

POSIVA-96-24

Julkaisuaika – Date

Joulukuu 1996

Tekijä(t) – Author(s) Jordi Bruno, Esther Cera, Lara Duro, QuantiSci, Spain Lasse Ahonen, Geologian tutkimuskeskus	Toimeksiantaja(t) – Commissioned by  Posiva Oy
Nimeke – Title  PALMOTUN URAANIMINERALISAATION KALLIO-POHJAVESISYSTEEMIN REDOX- REAKTIOT: URAANIN JA RAUDAN MERKITYS	
Tiivistelmä – Abstract  <p>Kallioperä-pohjavesisysteemin hapetus-pelkistysominaisuudet ovat tärkeä geokemiallinen tekijä loppusijoitettua ydinpolttoainetta eristävän moniestesysteemin kemiallisen stabiilisuuden kannalta. Tässä raportissa esitetään tulokset Nummi-Pusulan Palmotussa luonnon kalliopohjavedellä tehdyistä kokeista.</p> <p>Kokeissa mitattiin 1) luonnon pohjaveden redox-potentiaalia jatkuvan pumppauksen aikana; 2) redox-potentiaaliarvon reagoimista keinotekoisesti aiheutettuun veden pH-arvon muutokseen. Kokeita tehtiin sekä rauta- että uraanipitoisissa vesissä. Kenttämittausten tuloksia käytettiin sekä rauta- että uraanisysteemien redox-mallinnuksessa.</p> <p>Aikaisempien tutkimustulosten kanssa yhtäpitävästi liuennut rauta osoitettiin tärkeäksi luonnon-vesien redox-elektrolyytiksi, ainakin pitoisuustason ollessa suuruusluokkaa 1 mg/l. Huomion-arvoinen havainto oli, että rautaköyhässä vedessä liuennut uraani (ainakin pitoisuustasolla 200 nM) voi antaa Nernstin lain mukaisen vasteen platinaelektrodilla muutettaessa vesinäytteen pH-arvoa hapolla tai emäksellä.</p> <p>Kallio/pohjavesisysteemiin vaikuttavat redox-ominaisuudet riippuvat niiden kiinteiden faasien määrästä ja reaktiivisuudesta, jotka voivat vaihtaa elektroneja liuenneiden redox-elektrolyyttien kanssa. Tämä tutkimuksen tulokset osoittavat, että uraanimineraalit ovat tärkeä redox-puskuri Palmotun uraanimineralisaation kallio/pohjavesi-systeemissä.</p>	
ISBN ISBN 951-652-023-5	ISSN ISSN 1239-3096
Sivumäärä – Number of pages 26	Kieli – Language Englanti

## LIST OF CONTENTS

1. INTRODUCTION	7
1.1 General	7
1.2 Discussion on the concepts	8
2. METHODS	10
2.1 Methodology of the redox field measurements	10
2.2 Methodology of the chemical determinations	11
3. RESULTS	12
3.1 Analytical data	12
3.2 Kinetics of the redox measurement. Equilibrium vs. Disequilibrium	13
4. THERMODYNAMIC CONSIDERATIONS	16
4.1 A brief discussion about some critical thermodynamic data and the modelling codes used	16
4.2 Redox equilibrium pairs. Thermodynamic calculations	16
4.3 Redox buffers in the system. Thermodynamic calculations	19
5. DISCUSSION	22
6. REFERENCES	25

## **PREFACE**

This study is based on research contract between Posiva Oy and QuantiSci, a part of the study is based on research contract between Posiva Oy and the Geological Survey of Finland (GTK).

The contribution of GTK in the modelling work was partially funded by the Finnish Ministry of Trade and Industry, while the field measurements were carried out within the Palmottu Natural Analogue project under the auspices of the Finnish Centre for Radiation and Nuclear Safety (STUK).

The work has been performed by Jordi Bruno, Esther Cera and Lara Duro from QuantiSci, Spain and by Lasse Ahonen from GTK. The contact persons in this study were Margit Snellman and Juhani Vira from Posiva Oy, Jordi Bruno from QuantiSci, and Lasse Ahonen from GTK.

## 1. INTRODUCTION

### 1.1 General

The main role of the geosphere in a nuclear waste repository is to provide the geological, hydrological and chemical conditions required to maintain the stability of the engineered barrier system (EBS). The radionuclide retardation capability of the geosphere additionally improves the overall safety of the deep disposal.

The geochemical stability of the repository environment largely depends on the fact that appropriate conditions are found and maintained for the stability and performance of the successive barriers of the repository system: bentonite buffer - metallic canister - solid matrix of the spent fuel - radionuclide retardation by the bedrock.

Geochemically stable conditions for the various components are partially defined in terms of various intensive parameters, e.g., concentrations, temperature, pH and Eh. However, the capability of the disposal system to react against chemical disturbances is not completely described by the intensive parameters, because their persistence depends on the associated extensive parameters. Large alkalinity (pH) and redox (Eh) buffering capacities are two of the main chemical conditions required in a geological system to ensure that both the internal (arising from the waste and the barriers) and external perturbations (i.e. glaciation/ de-glaciation periods) do not perturb the performance of the EBS.

The reduction/oxidation (redox) properties of the bedrock-groundwater system are important geochemical factors with respect to the stability of the EBS, and with respect to the radionuclide mobilization/retardation behaviour. The present nuclear waste disposal programs carried out in many countries have had a large impact on the studies of redox conditions of the deep bedrock, as well as on the development of the redox-measurement technology (e.g., Wikberg 1987). It has been found that, in redox electrolyte-poor groundwaters, stable potentials are not readily attained, but measuring times of several weeks may be required. It has been also found that different types of electrodes may have dissimilar response to dissolved redox electrolytes.

Recently Grenthe et al. (1992b) surveyed the literature on redox measurements and concluded that the measurement of redox potentials in the laboratory and in the field, and their interpretation in terms of chemical reactions, are possible in systems where the redox properties are determined by the solid Fe(III)/ dissolved Fe(II) couple. They also indicated that the kinetics of redox reactions constrain the use of the redox potential as a master variable of a natural water system.

Our purpose in the present report is to further elucidate the role of redox chemistry in the definition of the geochemically stable environment for the disposal of nuclear waste. We will base our discussions on the on-line redox measurements performed at the Palmottu uranium deposit. Kinetics of the response of platinum electrode was studied in two different water types: iron-rich slightly acidic water, and uranium rich, slightly basic water. In both cases, we studied the change of potential on platinum electrode, when the pH of water was artificially changed during sampling.

Another purpose of this work is to demonstrate that the Palmottu uranium ore deposit constitutes a Natural Analogue to the reducing capacity of the  $\text{UO}_2$  spent fuel matrix. For that purpose, we are comparing modelling calculations of uranium system with results of field measurements from different boreholes in Palmottu.

## 1.2 Discussion on the concepts

The definition and use of a natural water redox potential (Eh) is still controversial. The use of Eh as a master variable of natural water system was anathematised by Lindberg and Runnells (1984). After comparing the theoretical (equilibrium) and measured redox potentials of more than 600 normal groundwaters, these authors concluded that: *The concept of Eh remains a valuable tool for theoretical and pedantic purposes. However, in the apparent absence of internal redox equilibrium, investigators should abandon the use of any measured Eh for predicting the equilibrium chemistry of redox reactions in normal groundwaters.* The same authors conclude their anathema with the following sentence: *If any measured Eh is used as input for equilibrium calculations, the burden rests with the investigator to demonstrate the reversibility of the system.*

As the definition of the master variables is intimately linked to the concept of thermodynamic equilibrium, it only applies to those situations where equilibrium conditions may be assumed. A universal equilibrium Eh-value can not be measured for a natural bedrock-groundwater system, because these systems are never in complete thermodynamic equilibrium. However, there may be subsystems, in which redox equilibrium is readily attained, and can be easily measured.

In this report, we are discussing on the potential-controlling redox couples using two partially different approaches:

1) (dissolved) equilibrium redox couples (redox mediators). They are in equilibrium with the electrode so that the measured potential and distribution of redox species are those predicted by the Nernst law. In this case we can say that the electrode is poised for the couple, meaning that the electrode is able to react relatively rapidly to changes in redox speciation of the couple.

2) Potential controlling redox couples (redox buffers). They are affecting on the measured redox-potential level, these couples may consist of solid phases. Potential-controlling couples and redox mediators are not necessarily same couples.

The parallelism between pH and pe ( $\text{pe} = -\log[\text{e}^-] = (\text{RT}/\text{nF})\ln(\text{Eh})$ ), as master variables has been previously derived and the relationship between proton and electron activities, pH and pe, with their corresponding buffering capacities has been established (e.g., Stumm and Morgan, 1996).

The alkalinity of a system is defined by the total concentration of species able to react with the excess protons. This can be described by the following expression:

$$[\text{Alk}] = \sum_i q [\text{R}(\text{OH})_q] - \sum_j p [\text{RH}_p] \quad (1)$$

where  $\text{R}(\text{OH})_q$  and  $\text{RH}_p$  describe the species able to react with and release protons, respectively. While  $p$  and  $q$  are the number of alkalinity or acid equivalents involved.

The reductive capacity, or oxidant neutralising capacity can be described by the following expression:

$$[RDC] = \sum_i n_i [Red]_i - \sum_j n_j [Oxd]_j \quad (2)$$

Where Red and Oxd describe the individual reductants and oxidants, while  $n_i$  and  $n_j$  are the number of equivalent electrons transferred in the reactions.

These capacities are related to the pH and pe intensities by the following expressions:

$$\begin{aligned} [Alk] &= \int \beta_{acid} \partial pH \\ [RDC] &= \int \beta_{red} \partial pe \end{aligned} \quad (3)$$

where  $\beta_{acid}$  and  $\beta_{red}$  are the acid and redox buffer intensities, respectively.

The definition of alkalinity and reductant capacities precludes the establishment of a zero state of the system. The zero state for the alkalinity of the near field (and the geosphere) is the one given by distilled water equilibrated with  $CO_2$  at the partial pressure under repository conditions. Therefore,  $CO_2$  is considered to be a neutral species not able to either transfer or exchange protons.

The definition of a zero state for the redox capacity of the near field is far more complex. There are many redox processes which occur. However, if our objective is to describe the redox stability of the spent fuel, we should establish a zero state which is directly related to the stability of the spent fuel.

The spent fuel matrix is mainly constituted by  $UO_2$  and the radionuclide release is largely dependent on the stability of the matrix. In principle, it would be logical to set the zero redox state at the  $UO_2$  to  $UO_{2+x}$  boundary. Where,  $UO_{2+x}$  describes the various states of oxidation of the  $UO_2$  matrix prior to its disruption. This upper limit has been established by different investigators to be in the range  $UO_{2.67}$ , which corresponds to the stoichiometry  $U_3O_8$ .

## 2. METHODS

### 2.1 Methodology of the redox field measurements

The methodology of the groundwater sampling and chemical analysis has been previously reported (e.g., Ahonen et al., 1993, 1995, Laaksoharju et al. 1995). Basically, it consisted of the isolation of hydraulically conductive groundwater fractures with a double packer system. In normal groundwater sampling, water was pumped using cyclic pressure pulses of nitrogen driving out the uppermost column of water, which was then replaced by water flowing from the packered off section. There was a moving water column (length about 5 to 10 meters) in the pressure tube, which isolated nitrogen gas from the sampled water. In water sampling, flow rates of 500 ml/min to 1500 ml/min were normally used, continuous pumping times were usually from 4 to 8 hours. Total water volume of the tube system was about 5 l / 100 m of tube, water volume of the normal packer interval (6 meters) was about 10 liters (drill-hole diameter of 46 mm).

On the surface, a part of the sampled water was flown through a gas-tight measurement cell, in which the redox potential, electrical conductivity, pH, dissolved oxygen were continuously monitored. Groundwater samples were obtained from an another outlet parallel to the measurement cell, when the pH and redox potentials reached steady-state.

We also studied the response of the redox electrode measurements, as the pH of the groundwater was changed by adding a strong acid (HCl) or base (NaOH) to the solution. This was done in a sealed on-line measurement cell, under inert gas ( $N_2$ ) atmosphere (Figure 1). In the experiment, new groundwater was continuously flowing into the measuring cell: in borehole 302 natural overflow of the borehole was utilised, while in borehole 324 groundwater was pumped into the cell by means of nitrogen gas. The rate of flow entering the measuring cell was about 50 ml/min and 150 ml/min in boreholes 302 and 324, respectively. The volume of the measuring cell was 200 ml.

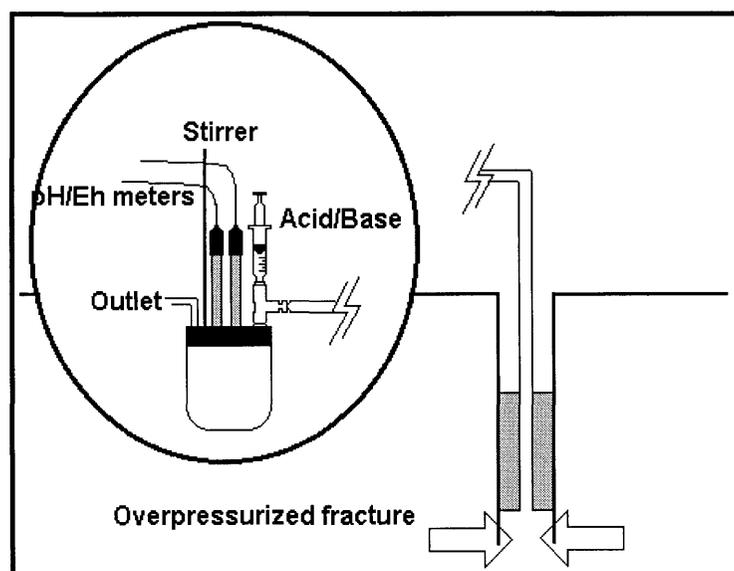


Figure 1. Experimental set up of pH titration in field, drillhole 302.

The redox potential cell consisted of a combined Ag/AgCl reference electrode and a Pt-foil (WTW Pt 4805). The standard potential of the reference electrode vs. the hydrogen electrode is of  $207 \pm 2$  mV. The pH was measured with a combined glass electrode (WTW E-50). The calibration was done by using standard buffer solutions at pH 7 and 10. Dissolved oxygen was measured by means of a WTW Oxi-96 oxymeter (detection limit 0.01 mg/l). The data was recorded every two seconds by a microcomputer system.

## **2.2 Methodology of the chemical determinations**

Once steady state was attained the sampled groundwater was filtered through a 0.45 mm Millipore filter and analysed for various chemical parameters. Major anion and cation concentrations were determined by flame AAS or ICP-AES methodology. The total bicarbonate concentration was determined by alkalimetric titration in laboratory. The uranium concentration was analysed by alpha spectroscopy measurements. The determination of the redox states of uranium was performed by the selective co-precipitation of U(IV) with  $\text{Nd}_3\text{F}$ . The separation of the U(IV) and U(VI) fractions was done in the field, under inert gas atmosphere. Total uranium was determined by the previous reduction of the sample with  $\text{TiCl}_3$ , to ensure that all uranium in solution was present in the IV redox state. The uranium (VI) concentration was calculated as the difference between total uranium and uranium(IV). The  $^{232}\text{U}$  tracer was added to both sample fractions after separation of the redox states. Uranium analyses were also carried out in the particulate fraction retained by the 0.45 mm filter. The details of the procedure are given in (Ahonen et al., 1995).

### 3. RESULTS

#### 3.1 Analytical data

The analytical data for the sampled groundwaters are given in Table 1. The data concerning the uranium analyses, pH and Eh measurements are given in Table 2.

*Table 1. Analytical data for major component chemistry of the selected groundwater samples from Palmottu (mmol·dm<sup>-3</sup>).*

<i>Sample</i>	<b>Na</b>	<b>K</b>	<b>Ca</b>	<b>Mg</b>	<b>Fe</b>	<b>HCO<sub>3</sub></b>	<b>SO<sub>4</sub></b>	<b>Si</b>	<b>Cl</b>	<b>F</b>
302 (90-95m)	0.97	0.03	0.45	0.18	<0.001	1.40	0.31	0.16	0.04	0.019
324 (95-101m)	0.60	0.04	0.77	0.19	0.048	1.80	0.18	0.19	0.12	0.007
346 (65-71m)	0.42	0.08	0.89	0.30	<0.001	2.30	0.17	0.13	0.09	0.007
346 (122-128m)	2.30		0.53	0.32	<0.001	2.70	0.35	0.20	0.61	
346 (122-128m)	18.00	0.11	0.65	0.19	<0.001	1.00	8.20	0.15	2.00	0.070
348 (200-225m)	20.00	0.08	0.70	0.22	0.001	1.00	8.70	0.10	1.90	0.050

*Table 2. pH, Eh and uranium concentrations and determined uranium redox state speciation for the selected groundwater samples from Palmottu*

<i>Sample</i> <b>drill hole (depth)</b>	<b>pH</b>	<b>Eh</b> <b>(mV)</b>	<b>[U(IV)]</b> <b>(mol·dm<sup>-3</sup>)</b>	<b>[U(VI)]</b> <b>(mol·dm<sup>-3</sup>)</b>
302 (90-95m)	8.42	-55	2.2·10 <sup>-8</sup>	7.8·10 <sup>-7</sup>
324 (95-101m)	6.87	+5	1.5·10 <sup>-8</sup>	2.5·10 <sup>-7</sup>
346 (65-71m)	8.05	-11	2.8·10 <sup>-8</sup>	4.0·10 <sup>-7</sup>
346 (122-128m)	8.40	-70	3.0·10 <sup>-9</sup>	3.9·10 <sup>-8</sup>
346 (122-128m)	8.40	-80	2.0·10 <sup>-8</sup>	1.5·10 <sup>-8</sup>
346 (240-246m)	9.05	-92	6.1·10 <sup>-9</sup>	4.5·10 <sup>-10</sup>
348 (200-225m)	8.82	-70	5.0·10 <sup>-10</sup>	6.8·10 <sup>-9</sup>

In Figure 2 we show a typical profile for the on-line pH and Eh measurements. As a rule, the measured pH and electrical conductivity attained stable values within a couple of minutes, if the actual water composition in the tubes and between packers was homogenous. A redox electrode, stored in contact with air, initially gave high redox potential readings, which decreased relatively rapid during the first hours of pumping. Figure 2 shows the time-course of redox readings measured during pumping from a section under a single packer at the depth of 90 meters in drill hole 302, the pumping rate was about 1 l/min. After the removal of the pumping system, this same overpressurized section was isolated by one packer, and the outlet tube was connected to the measuring chamber. Water was then allowed to flow (100 ml/min) through the measuring cell during five days time. In this case, first readings were taken after the weekend, and stable values were already attained, being about 30 - 40 mV lower than those obtained at end of the initial pumping of Figure 2.

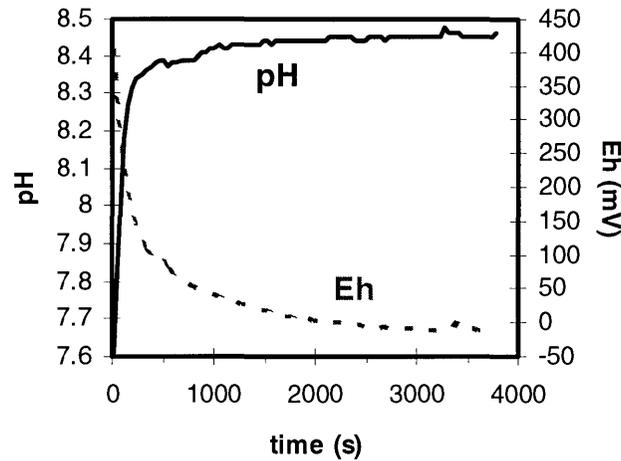


Figure 2. Profile of Eh/pH measurements as a function of time. Borehole #302.

At this point it is important to evaluate to which extent the redox measurements are representative of an equilibrium condition of the sampled waters.

### 3.2 Kinetics of the redox measurement. Equilibrium vs. Disequilibrium

Figures 3a, 3b and 4 are plots of the variation of the on-line measured pH and Eh as a function of time, due to changes in pH of the sampled groundwaters 302 and 324. The change of pH was caused by carefully adding acid or base to the water entering the flow-through cell, and then, after reaching the ultimate values, by allowing fresh water replace the water in the measuring cell. This experiment was preceded by a pumping (or natural flow) until apparently stable redox-values were achieved.

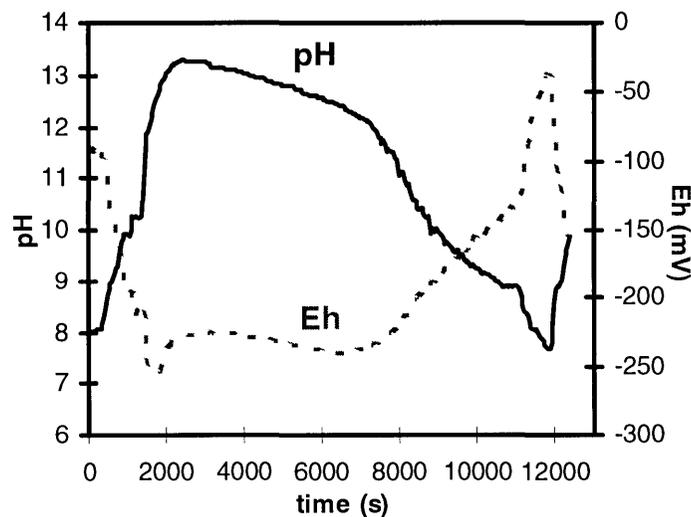


Figure 3a. Base addition experiment carried out by continuing water flowing of borehole #302. Water temperature about 10° C.

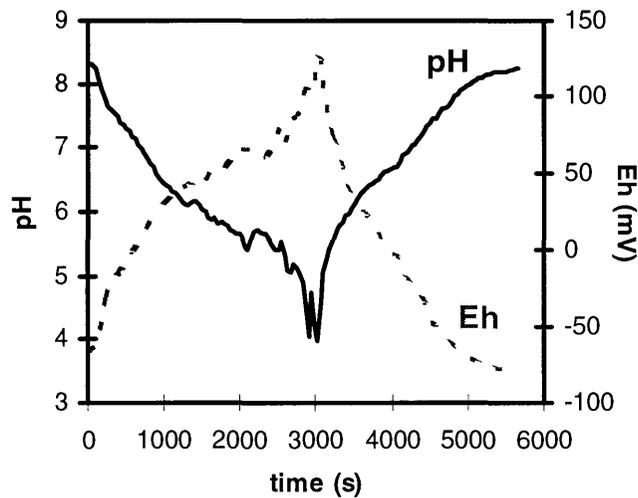


Figure 3b. Acid addition experiment carried out by continuing water flowing of borehole #302. Water temperature about 10° C.

In Figure 3a, we show the variation on pH and Eh on the sampled groundwater 302 as a result of an increase on alkalinity. During the first 2000 seconds the pH increases to a value close to 13, while the measured Eh approaches a -300 mV level. In the subsequent 8000 seconds, the system relaxes slowly back to the initial pH and Eh values. Figure 3b shows the evolution of pH and Eh of the groundwater 302 caused by addition of acid into the sample. In the first 3000 seconds the pH decreases down to a value close to 4, while the Eh increases to values around +100 mV. At pH of about 5, all bicarbonate is titrated to carbonic acid and, due to the lack of buffering capacity of  $\text{HCO}_3^-$ , rapid decrease of pH may take place. During the next 3000 seconds the system is allowed to relax back to the initial pH and Eh values. Figure 4 is an acidification experiment performed with groundwater from borehole 324. This borehole, which has the largest iron content of the sampled waters, was selected to check the rôle of the Fe(III)/Fe(II) couple in the overall redox system. The addition of acid to the sampled waters disturbs the initial pH and Eh, but the system relaxes back to the initial Eh and pH values in approximately 3000 seconds.

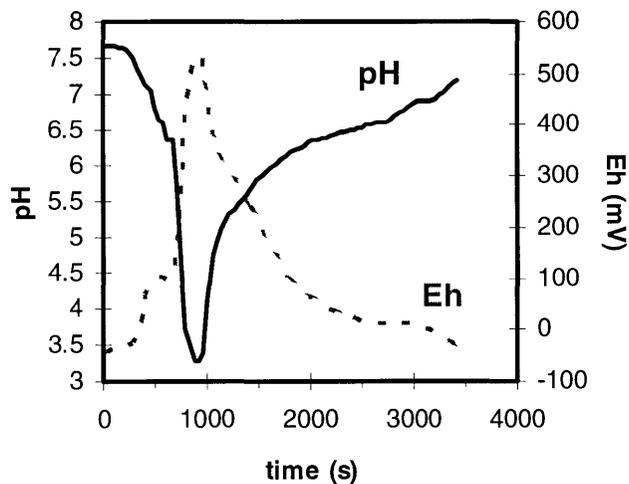


Figure 4. Acid addition experiment carried out by pumping water from borehole #324.

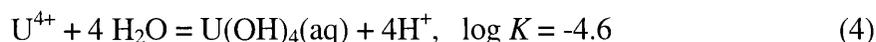
The outcome of these kinetic experiments is quite encouraging. In spite of the size and sign of the perturbation of the initial condition, the redox potential of the sampled groundwaters return to their original values. This is a clear proof of the reversibility of the measured redox potential and a clear indication of the alkalinity and redox capacity of the sampled groundwaters. Furthermore, the characteristic reaction times for the recovery of redox equilibrium are in the range: 3000-11000 seconds.

## 4. THERMODYNAMIC CONSIDERATIONS

### 4.1 A brief discussion about some critical thermodynamic data and the modelling codes used

Thermodynamic data on the hydrolysis of U(IV) is of crucial importance for the interpretation of the present results. Tetravalent uranium has a strong tendency to hydrolyse. The hydrolysis of cations is normally investigated by determining the solubility of oxide-/hydroxide precipitates as a function of pH: in case of amphoteric compounds, solubility increases both towards acid and basic solutions, while the solubility minimum represents the predominance area of the neutral hydrolytic species, which in case of U(IV) is  $\text{U}(\text{OH})_4(\text{aq})$ . The first hydrolytic step of uranium is well known; there are several mutually independent determinations available, which are in accordance with each others. The second and third hydrolytic steps are of less importance. Observations of (Gayer and Leider, 1957) were interpreted as an indication of the formation of  $\text{U}(\text{OH})_5^-$  in basic solutions, but this interpretation has been questioned in later reviews (e.g., Grenthe et al., 1992a).

The stability constant of  $\text{U}(\text{OH})_4(\text{aq})$  could be determined by studying the solubility of thermodynamically well-characterised uranous oxide or hydroxide minerals in reducing conditions. However, their solubility is extremely low and the sensitivity to oxic conditions very high. This makes the analytical determinations extremely difficult. Bruno et al. (1987) studied the solubility of an amorphous form of  $\text{UO}_2$ , the work being the source from which Grenthe et al. (1992a) derived the thermodynamic properties of the species  $\text{U}(\text{OH})_4(\text{aq})$ . According to their data, reaction with corresponding stability constant is:



The value is close to that used in the SKBU1 database (Bruno and Puigdomènech 1989:  $\log K_{s0} = -5.13$ ), while there is a clear discrepancy between this value and those proposed by Ryan and Rai (1983) as well as by Rai et al. (1990), which are up to 9 log units lower. This potential inconsistency in thermodynamic data was discussed by Grenthe et al. (1992a, p.129)

In the thermodynamic calculations, we have used the HALTAFALL based INPUT/SED/PREDOM code package (Puigdomenech, 1983) in conjunction with the SKBU1 uranium thermodynamic data base (Bruno and Puigdomènech, 1989).

### 4.2 Redox equilibrium pairs. Thermodynamic calculations

Once we have established that the measured redox potentials correspond to an equilibrium redox potential of the sampled groundwaters, we have to ascertain which are the redox couples responsible for the redox potential of the measured sample. It is well known from earlier experiments that ferric/ferrous iron couple is able to give nernstian response at iron concentrations of 0.1 mM or less. In this redox pair, the transfer of one electron is associated with the transfer of three protons and, consequently, a slope of about 170 mV / pH unit can be seen on an Eh-pH graph. Grenthe et al.(1992b) plotted the redox potential values measured from deep groundwater samples against  $(3\text{pH} + \log[\text{Fe}^{2+}])$ , and showed that the experimental values agree fairly well with the equilibrium between solid ferric

oxyhydroxide and dissolved ferrous iron. In Figure 5, we have made a similar plot using the data from the pH-variation experiment with iron-rich water of borehole 324. The results indicate that the water sample is in a redox equilibrium with a ferric oxyhydroxide mineral, which according to the discussion of Grenthe et al. (1992b) would be a crystalline phase, probably goethite. However, the experimental data plotted in Figure 5 is from the pH-titration experiment, which was carried out in a flow-through chamber. Consequently, we know that crystalline ferric oxyhydroxide minerals were not present in the system considered. By only considering the dissolved iron species, we obtain the theoretical predominance diagram of Figure 6. It can be seen that the observed response of the pH titration experiment can be explained by the dissolved ferric/ferrous couple at pH range from about 3 to about 10. The trace of the experimental data points is about 2 to 3 pe units below the boundaries defining the equilibrium activity of ferric and ferrous species. Consequently, the 'nernstian' ferric/ferrous ratio in this water should be between 1/100 and 1/1000. It is well known that the solubility of ferric iron is very low at intermediate to basic pH values ( $7 < \text{pH} < 10$ ). At pH values of above 8 even ferrous iron precipitates. Consequently, it is evident that the measured redox pair to which the inert electrode is responsible is 'lost' during the titration towards the basic pH-range, indicating that the soluble species are indeed responsible of the electron transfer and that no sufficient iron was present in the system to provide the necessary redox buffering capacity.

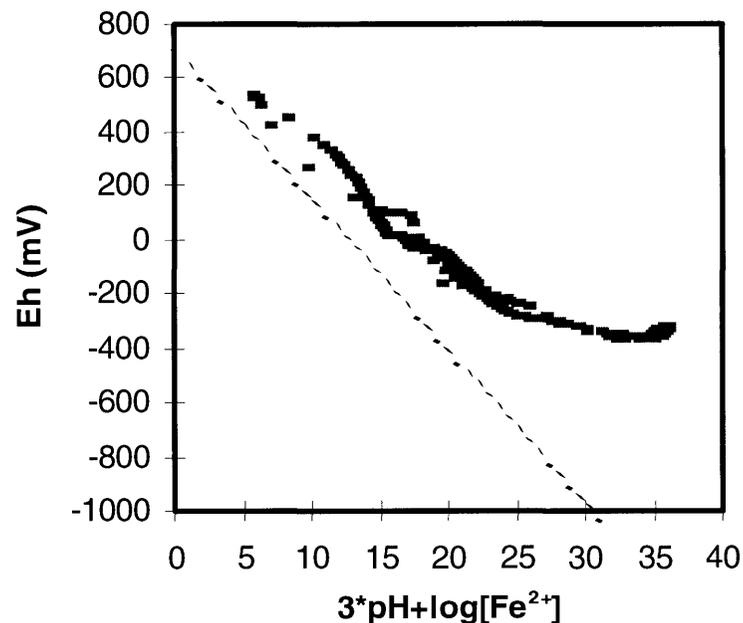


Figure 5. Values of redox potential versus  $3\text{pH} + \log[\text{Fe}^{2+}]$  measured from the groundwater of drill hole #324. Dotted line is the theoretical trend of the  $\text{Fe(II)}/\text{Fe(OH)}_3(\text{s})$  redox couple (Grenthe et al., 1992b).  $[\text{Fe}^{2+}]$  was assumed to be equal to  $\text{Fe}(\text{tot})$  in Table 2.

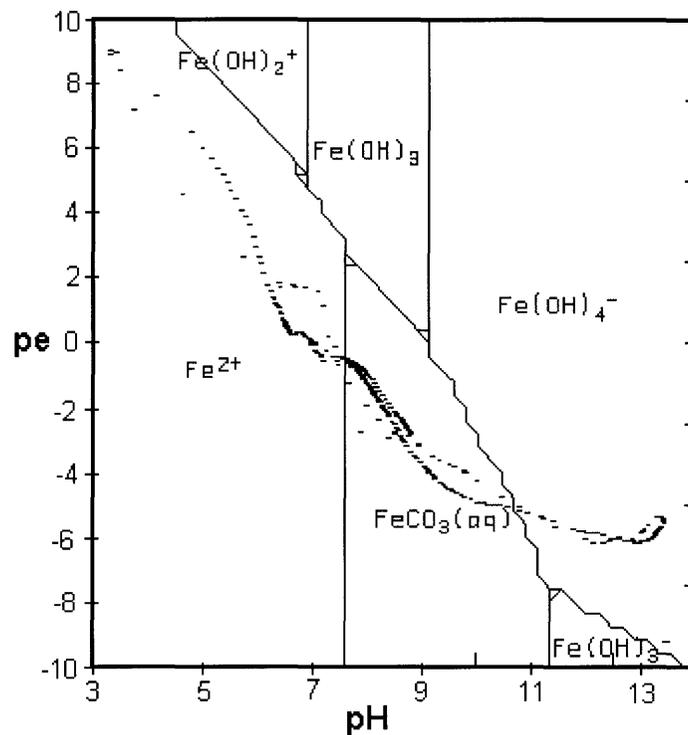


Figure 6. Aqueous speciation of the Fe system. Superimposed are the experimental *pe* versus *pH* values taken from *pH* titration in borehole #324.

Figure 7 shows the results of *pH* variation experiment carried out using the uranium-rich, iron-poor water of borehole 302. The slope on the Eh-*pH* is slightly less than 60 mV / *pH* unit, differing clearly from that seen with iron rich water. In the same diagram we have included the theoretical speciation of dissolved uranium; the experimental slope of observations agree well with the model, indicating that the measured redox potentials can be explained by assuming equilibrium in the U(VI)/U(IV) system. However, if we assume that the analysed U(VI)/U(IV) ratio of about 35:1 (Table 2) is correct, the experimental data should plot about 1.5 *pe* units above the theoretical diagram drawn for equal activity of the redox species of uranium. The diagram was calculated using the stability constant value  $\log K = -5.13$  for the formation of  $\text{U}(\text{OH})_4(\text{aq})$ . Decrease of this value by about 1 to 2 log units would give an ideal fit between the experimental data and uranium speciation model within the *pH*-range 4 - 11. The present speciation model is not able to completely explain the observed behaviour at *pH*-values higher than 11. However, experiments with both iron and uranium rich waters displayed similar behaviour in the *pH* range 11 to 13, and the water in drillhole 324 also contains relatively high amounts of uranium (250 nM in drillhole 324 vs. 780 nM in drillhole 302).

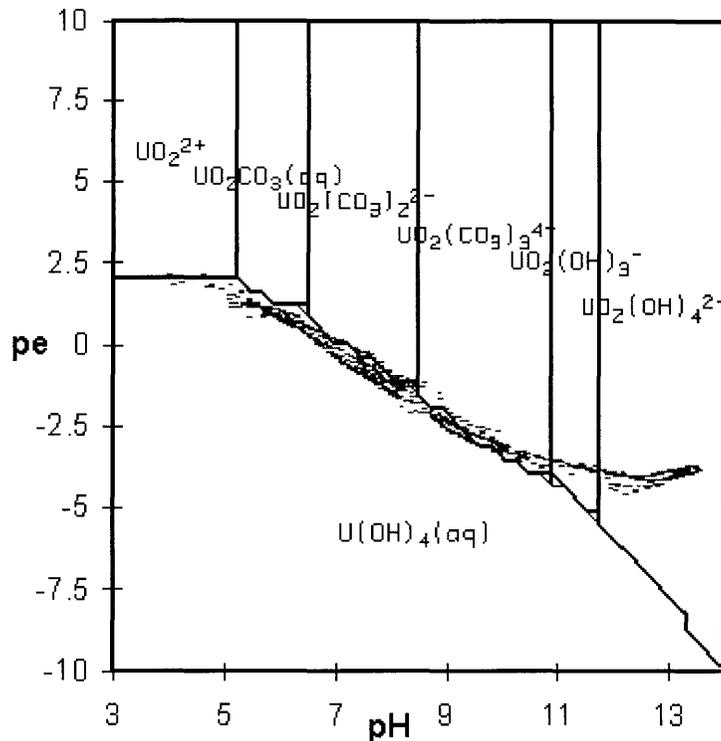


Figure 7. Aqueous speciation of the U system. Superimposed are the experimental *pe* versus *pH* values taken from *pH* titration in borehole #302.

At this point, we have shown that there are at least two possible redox pairs available in the groundwaters of Palmottu, which may be able to have nernstian response on the redox electrode. The dissolved redox couples act as mediators, which provide information on the redox potential of the system, but the redox capacity properties of the system may have to be derived from the availability of the reactive solid phases, redox buffers. In order to have the link between the measured redox potential values and the 'redox state' of the system, we have to be able to show that the system contains redox buffers, which give rise to the observed redox potential values.

### 4.3 Redox buffers in the system. Thermodynamic calculations

In Figure 5 we already demonstrated the possible effect of one important redox -buffering mineral, ferric oxyhydroxide. In Figure 8, the representative *Eh* - *pH* values are plotted together with the ferric oxyhydroxide - dissolved ferrous iron boundary. The graph has been drawn using the activity value of  $4.8 \times 10^{-5}$ , corresponding to the analysed dissolved iron concentration of the water of borehole 324; concentration of iron in other boreholes was below detection limit of  $1 \times 10^{-6}$  M. According to Figure 8, the redox-buffering role of ferric oxyhydroxide is well established in case of the iron-rich water, while very little can be concluded with respect to the other samples.

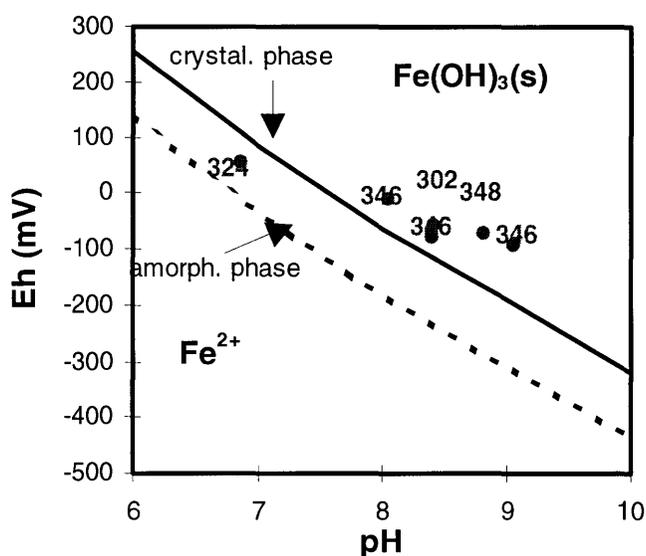


Figure 8. Boundary between  $Fe^{2+}$  and  $Fe(OH)_3(s)$ , solid and dotted lines limit the stability field of microcrystalline ( $\log K=3$ ) and amorphous ( $\log K=5$ ) phases, respectively (Stumm and Morgan, 1996). Superimposed are experimental values from different boreholes.

The possible role of uranium minerals as a redox buffer at Palmottu was earlier discussed by Ahonen et al. (1993) by studying thermodynamic stability boundaries between uranium minerals and groundwater. In Figure 9, we have presented the phase boundaries of the  $UO_{2+x}$ -minerals as a function of pH and Eh. The measured Eh/pH values lie within the  $UO_2$  to  $U_3O_7$  phase transition, this would indicate that this surface oxidation is mainly responsible of the reducing capacity of the Palmottu groundwaters.

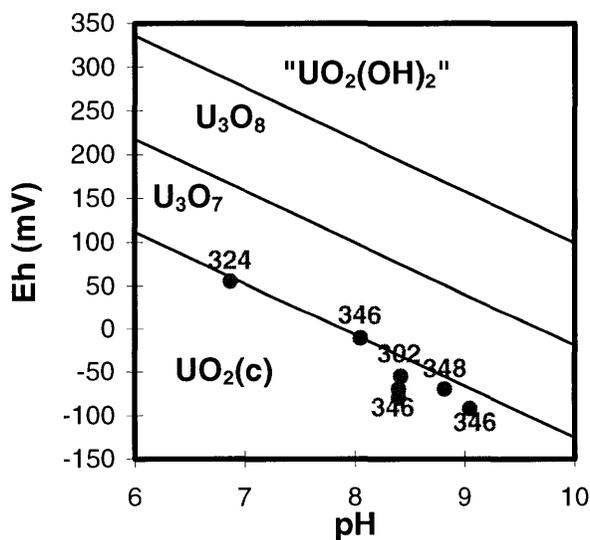


Figure 9. Boundaries between the  $UO_{2+x}$ -phases. Stability constants taken from SKBUI database (Bruno and Puigdomènech, 1989),  $UO_2(c)$  stability constant taken from the NEA database (Grenthe et al., 1992a). Superimposed are the measured values from the different boreholes.

However, one of the striking observations from Palmottu is that redox equilibrium is also obtained for U(VI)/U(IV) in the aqueous phase. How is this justified by thermodynamic models ?

In Figure 10, we have compared the analysed uranium concentration with the activity of dissolved uranium assuming that there is an equilibrium between the minerals  $\text{UO}_2(\text{c})$  and  $\text{U}_3\text{O}_7$ . We can see that the model reproduces satisfactorily the observed parameters in case of groundwater samples from deeper parts of boreholes 346 and 348, while the analysed uranium concentrations of the groundwater of borehole 302 are two decades higher than predicted by this model. However, the uranium concentration in this water is particularly high compared to the level of uranium in the drill holes of Palmottu in general. It is also known that this overflowing borehole penetrates granite, which is rich in iron oxyhydroxides. According to the hydrogeological investigations, the groundwater is very probably flowing relatively fast along this granite. The high concentration of uranium may thus be due to leaching of uranium associated to iron oxyhydroxides.

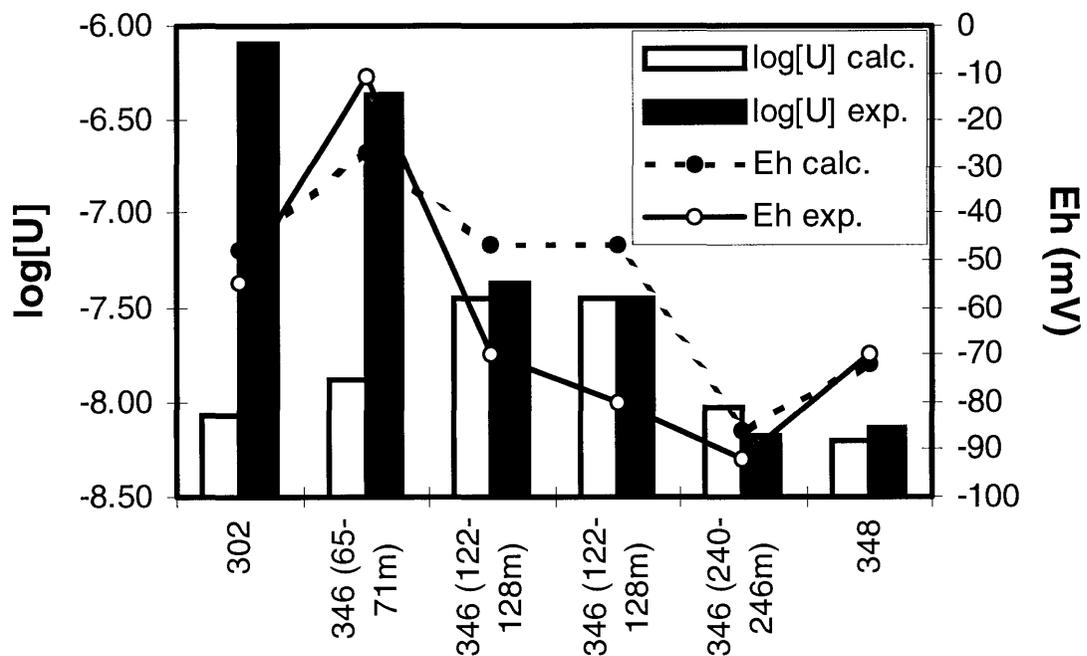


Figure 10. Comparison between calculated and experimental data by assuming the equilibrium between  $\text{UO}_2(\text{c})$  and  $\text{U}_3\text{O}_7$  solid phases.

## 5. DISCUSSION

The entire basis of our discussion is the fact that equilibrium redox potentials can only be measured for redox pairs at equilibrium. Redox disequilibrium is a well established fact in Natural Systems, because the characteristic reaction times of many redox reactions are quite large, this is particularly true for redox pairs that involve transfer from the molecules having strong covalent bonds and/or requiring multielectron transfer and structural rearrangement (e.g., CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, MnO<sub>7</sub><sup>-</sup>). Furthermore, most of the biosphere lives from this apparent redox disequilibrium. However, we are becoming more and more aware of the advantage of looking at redox buffer capacities rather than redox intensities, to describe the redox evolution of a Natural System.

Active solid phases constitute a large pool of redox buffering capacity, provided that the necessary time is given to reach redox equilibrium. This necessary time to reach equilibrium can be assessed by using the concept of characteristic reaction times of slow processes and compare it to the residence times of the water in the system under consideration.

Table 3 is a summary of characteristic reaction times for relevant geochemical processes in Natural Systems from a recent monography on the Trace Element Geochemical Modelling (Bruno, 1996).

This should be compared to the residence times of water in different reservoirs as shown in Table 4.

*Table 3. Characteristic reaction times for geochemical processes. Data from (Baes and Mesmer, 1976), (Choppin and Clark, 1991), (Davidson and Seed, 1980), (McKibben and Barnes, 1986), (Bruno et al., 1991), (Rimstidt and Barnes, 1980), (Busenberg et al., 1976), (Helgeson et al., 1984), (Lasaga et al., 1994)*

Reaction type	Example	log $\tau_{\text{char}}$ (s)
<i>Homogeneous reactions</i>		
<b>Inorganic complexation (OH, CO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, ...)</b>	$\text{Me}^{z+} + q \text{H}_2\text{O} \Rightarrow \text{Me}(\text{OH})^{(z-q)+} + q \text{H}^+$	-6 - -1
<b>LMW organic complexation</b>	$\text{Me}^{z+} + \text{EDTA} \Rightarrow \text{MeEDTA} + z \text{H}^+$	-2 - 2
<b>Humic and fulvic acids</b>	$\text{Me}^{z+} + \text{HA} \Rightarrow \text{MeHA}$	-1 - 3
<b>Redox reactions one electron transfer, minor structural rearrangement</b>	$\text{Fe}(\text{II}) + \text{O}_2 \Rightarrow \text{Fe}(\text{III})$	3 - 8
<b>Redox reactions multielectron transfer, structural rearrangement</b>	$\text{Cr}(\text{III}) + \text{O}_2 \Rightarrow \text{Cr}(\text{VI})$	8 - 11
<i>Heterogeneous reactions</i>		
<b>Oxyhydroxide dissolution</b>	$\text{Fe}_2\text{O}_3(\text{s}) + 3 \text{HCO}_3^- + 2\text{H}^+ \Rightarrow \text{Fe}(\text{OH})\text{CO}_3(\text{aq}) + \text{Fe}(\text{CO}_3)_2^- + 2\text{H}_2\text{O}$	9 - 12
<b>Oxyhydroxide precipitation</b>	$\text{Fe}^{3+} + 3 \text{H}_2\text{O} \Rightarrow \text{Fe}(\text{OH})_3(\text{s}) + 3 \text{H}^+$	-12 - 10
<b>Carbonate dissolution</b>	$\text{CaCO}_3(\text{s}) + \text{H}^+ \Rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$	3 - 5
<b>Carbonate precipitation</b>	$\text{Ca}^{2+} + \text{HCO}_3^- \Rightarrow \text{CaCO}_3(\text{s}) + \text{H}^+$	0 - 2
<b>Aluminosilicate dissolution</b>	$\text{KAlSi}_3\text{O}_8(\text{s}) + 4\text{H}^+ + 4\text{H}_2\text{O} \Rightarrow \text{K}^+ + \text{Al}^{3+} + 3\text{H}_4\text{SiO}_4$	12 - 14
<b>Redox reactions one electron transfer</b>	$>\text{FeO}-\text{Fe}^+ + \text{e}^- \Rightarrow >\text{FeO}-\text{Fe}$	2 - 4
<b>Redox reactions multielectron transfer</b>	$\text{FeS}_2 + 3.5 \text{O}_2(\text{g}) + \text{H}_2\text{O} \Rightarrow \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 2 \text{H}^+$ $\text{UO}_2(\text{s}) + 0.5 \text{O}_2(\text{g}) + 2 \text{HCO}_3^- \Rightarrow \text{UO}_2(\text{CO}_3)_2^{2-}$	9 - 11

*Table 4. Average residence times of water in the main reservoirs*

Reservoir	log $\tau_R$ (s)
<b>Oceans and seas</b>	11
<b>Lakes and reservoirs</b>	8.5
<b>Swamps</b>	7.5 - 8.5
<b>Rivers</b>	6
<b>Soil moisture</b>	6 - 7.5
<b>Shallow groundwaters</b>	6 - 8.5
<b>Deep groundwaters</b>	9.5 - 12
<b>Icecaps and glaciers</b>	8.5 - 11.5
<b>Atmospheric water</b>	5.9
<b>Biospheric water</b>	5.8

By comparing the average residence times of water in the various reservoirs with the characteristic reaction times of chemical processes which are relevant to the geochemistry of natural water systems it is possible to derive the following general rules:

1) Most homogeneous redox reactions in aqueous media are fast compared to the average residence times of water, therefore they can be treated as equilibrium reactions. The only exception are redox reactions which involve multielectron transfer and/or structural rearrangement (i.e. Se(IV)/Se(VI), Cr(III)/Cr(VI), V(III)/V(V)). These homogeneous processes have to be approached kinetically and the influence of potential catalysts (solid surfaces, biota) has to be considered.

2) Most heterogeneous, water/rock, interactions have characteristic reaction times larger than, or comparable to the average residence time of water. Therefore, most heterogeneous processes have to be kinetically approached. The exceptions are the precipitation and dissolution of amorphous oxides (i.e.  $\text{Fe}(\text{OH})_3(\text{am})$ ,  $\text{SiO}_2(\text{am})$ ,  $\text{UO}_3 \cdot x\text{H}_2\text{O}(\text{am})$ ) and the precipitation and dissolution of carbonates ( $\text{CaCO}_3$ ,  $\text{MnCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{FeCO}_3$ ). These processes can be treated by assuming equilibrium, particularly for the reservoirs with longer residence times of water (oceans, deep groundwaters)

By comparing the characteristic reaction times of the redox processes we are discussing we may extract the following:

1) In oxic shallow groundwaters the redox chemistry will be basically controlled by the Fe(III)/Fe(II) redox process. These waters have residence times in the range of  $10^6 - 10^{8.5}$  seconds which is comparable to the characteristic reaction times of the Fe(III)/Fe(II) redox reaction :  $10^3 - 10^8$  seconds, and therefore redox equilibrium is attained and measured (Grenthe et al, 1992b).

2) In deep anoxic, basic groundwaters, other redox couples are active. In the presence of uraninite, as in Palmottu, the potential redox pair may be given by the  $\text{UO}_2$  to U(VI) transition. The characteristic reaction time for this process is :  $10^9 - 10^{11}$  seconds, which is comparable to average residence times of these deep groundwaters:  $10^{9.5} - 10^{12}$  seconds and therefore, equilibrium is attained.

As a consequence, in the spent fuel repository, in the presence of large amounts of  $\text{UO}_2$  and with long residence times of water, the redox capacity of the  $\text{UO}_2$  matrix is expected to play a critical rôle in neutralising the oxidants produced by the radiolysis of water. In this context the redox information so far collected in the Palmottu ore deposit indicate that this is a plausible and quantifiable phenomenon.

## 6. REFERENCES

- Ahonen, L., Ervanne, H., Ruskeeniemi, T., Jaakkola, T. and Blomqvist, R. 1993. Uranium mineral - Groundwater equilibration at the Palmottu natural analogue study site, Finland. *Mater. Res. Soc. Symp. Proc.*, 294, p. 497-504.
- Ahonen, L., Ervanne, H., Jaakkola, T. and Blomqvist, R. 1995. Redox chemistry in uranium-rich groundwater of Palmottu uranium deposit, Finland. *Radiochim. Acta* 66/67, p. 115-121.
- Baes, C.H. and Mesmer, R.E. 1976. *The hydrolysis of cations*. John Wiley & Sons, New York.
- Bruno, J., Casas, I., Lagerman, B. and Muñoz, M. 1987. The determination of the solubility of amorphous  $\text{UO}_2(\text{s})$  and the mononuclear hydrolysis constants of uranium (IV) at 25°C. *Mater. Res. Soc. Symp. Proc.*, 84, p. 153-161.
- Bruno, J., Casas, I., Puigdomènech, I. 1991. The kinetics of dissolution of  $\text{UO}_2$  under reducing conditions and the influence of an oxidized surface layer ( $\text{UO}_{2+x}$ ). Application of a continuous flow-through reactor. *Geochim. Cosmochim. Acta*, 55, p. 647-658.
- Bruno J. 1996. Principles and applications of trace element geochemical modelling, Chapter XI in *Applications of thermodynamic modelling* (Grenthe, I. and Puigdomènech, I. eds.) NEA OCDE, *In preparation*.
- Bruno, J. and Puigdomènech, I. 1989. Validation of the SKBU1 uranium thermodynamic data base for its use in geochemical calculations with EQ3/6. *Mater. Res. Soc. Symp. Proc.*, 127, p. 887-896.
- Busenberg, E. and Clemency, C.V. 1976. The dissolution kinetics of feldspars at 25°C and 1 atm  $\text{CO}_2$  partial pressure. *Geochim. Cosmochim. Acta*, 41, p. 41-49.
- Choppin, G.R. and Clark, S.B. 1991. The kinetic interactions of metal ions with humic acids. *Mar. Chem.*, 36, (1-4), p. 27-38.
- Davidson, W. and Seed, G. 1980. The kinetics of oxidation of ferrous iron in synthetic and natural waters. *Geochim. Cosmochim. Acta*, 47, p. 67-79.
- Gayer, K.M. and Leider, H. 1957. *Canadian J. Chem.*, 35, p. 5-7.
- Grenthe, I., Fuger, J., Konings, R.J.M., Lemire, R.J., Muller, A.B., Nguyen-Trung, C. and Wanner, H. (1992a); *Chemical Thermodynamics Vol.1. Chemical Thermodynamics of Uranium*. NEA. (Wanner and Forest ed.) Elsevier.
- Grenthe, I., Stumm, W., Laaksoharju, M., Nilson, A.-C. and Wikberg, P. 1992b. Redox potentials and redox reactions in deep groundwater systems. *Chem. Geol.*, 98, p. 131-150.
- Helgeson, H.C., Murphy, W.M. and Aagaard, P. 1984. Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions. II. Rate constants,

effective surface area, and the hydrolysis of feldspar. *Geochim. Cosmochim. Acta*, 48, p. 2405-2432.

Laaksoharju, M., Ahonen, L. Blomqvist, R. 1996. Handheld double packer equipment for water sampling and hydraulic measurements in deep boreholes. *Groundwater Monitoring & Remediation* 15, (2), p. 125-133.

Lasaga, A., Soler, J.M<sup>a</sup>, Ganor J., Burch, T. and Nagy, K. 1994. *Geochim. Cosmochim. Acta*, 58, p. 2361-2386.

Lindberg, R.D. and Runnels, D.D. 1984. Ground water redox reactions: an analysis of equilibrium state applied to Eh measurements and geochemical modeling. *Science*, 225, p. 925-927.

McKibben, M.A. and Barnes, H.L. 1986. Oxidation of pyrite in low temperature acidic solutions: Rate laws and surface textures. *Geochim. Cosmochim. Acta*, 50, p. 1509-1520.

Puigdomènech, I. 1983. Input, sed and predom computer programs drawing equilibrium diagrams. PhD Thesis TITRA-OOK-3010. RIT, Stockholm.

Rai, D., Felmy, A.R. and Ryan, J.L. 1990. Uranium (IV) hydrolysis constants and solubility product of  $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ . *Inorg. Chem.*, 29, p. 260-264.

Rimstidt, J.D. and Barnes, H.L. 1980. The kinetics of silica-water reactions. *Geochim. Cosmochim. Acta*, 44, p. 1683-1699.

Ryan, J.L. and Rai, D. 1983. The solubility of uranium (IV) hydrous oxide in sodium hydroxide solutions under reducing conditions. *Polyhedron*, 2 (9), 947-952.

Stumm, W. and Morgan, J.J. 1996. *Aquatic chemistry*. John Wiley & Sons. Third ed. New York.

Wikberg, P. 1987. The chemistry of deep groundwaters in crystalline rocks. PhD Thesis. Royal Institute of Technology (KTH), Department of Inorganic Chemistry. Stockholm.

## LIST OF POSIVA REPORTS PUBLISHED IN 1996

- POSIVA-96-01      Determination of U oxidation state in anoxic (N<sub>2</sub>) aqueous solutions –  
method development and testing  
Kaija Ollila  
VTT Chemical Technology  
June 1996  
ISBN 951-652-000-6
- POSIVA-96-02      Fault plane solutions of microearthquakes in the Loviisa region in  
south-eastern Finland  
Jouni Saari  
IVO International Ltd  
Ragnar Slunga  
Försvarets Forskningsanstalt, Stockholm, Sweden  
June 1996  
ISBN 951-652-001-4
- POSIVA-96-03      Thermal optimisation of the final disposal of spent nuclear fuel  
Heikki Raiko  
VTT Energia  
June 1996  
(in Finnish)  
ISBN 951-652-002-2
- POSIVA-96-04      On the origin and chemical evolution of groundwater at the  
Olkiluoto site  
Petteri Pitkänen  
Technical Research Centre of Finland  
Margit Snellman  
Imatran Voima Oy  
Ulla Vuorinen  
Technical Research Centre of Finland  
June 1996  
ISBN 951-652-003-0
- POSIVA-96-05      Seismic emissions induced by the excavations of the rock repository  
in Loviisa  
Jouni Saari  
IVO International Ltd  
June 1996  
ISBN 951-652-004-9
- POSIVA-96-06      Geochemical modelling study on the age and evolution of the  
groundwater at the Romuvaara site  
Petteri Pitkänen  
Technical Research Centre of Finland  
Margit Snellman  
Imatran Voima Oy  
Ulla Vuorinen, Hilkka Leino-Forsman  
Technical Research Centre of Finland  
September 1996  
ISBN 951-652-005-7

- POSIVA-96-07      Boring of full scale deposition holes using a novel dry blind boring method  
Jorma Autio, Timo Kirkkomäki  
Saanio & Riekkola Consulting Engineers  
November 1996  
ISBN 951-652-006-5
- POSIVA-96-08      Production methods and costs of oxygen free copper canisters for nuclear waste disposal  
Harri Aalto, Hannu Rajainmäki, Lenni Laakso  
Outokumpu Poricopper Oy  
October 1996  
ISBN 951-652-007-3
- POSIVA-96-09      Characterization of the excavation disturbance caused by boring of the experimental full scale deposition holes in the Research Tunnel at Olkiluoto  
Jorma Autio  
Saanio & Riekkola Consulting Engineers  
December 1996  
ISBN 951-652-008-1
- POSIVA-96-10      Gamma and neutron dose rates on the outer surface of the nuclear waste disposal canisters  
Markku Anttila  
VTT Energy  
December 1996  
ISBN 951-652-009-X
- POSIVA-96-11      Criticality safety calculations for the nuclear waste disposal canisters  
Markku Anttila  
VTT Energy  
December 1996  
ISBN 951-652-010-3
- POSIVA-96-12      Assessment of alternative disposal concepts  
Jorma Autio, Timo Saanio, Pasi Tolppanen  
Saanio & Riekkola Consulting Engineers  
Heikki Raiko, Timo Vieno  
VTT Energy  
Jukka-Pekka Salo  
Posiva Oy  
December 1996  
ISBN 951-652-011-1
- POSIVA-96-13      Design report of the canister for nuclear fuel disposal  
Heikki Raiko  
VTT Energy  
Jukka-Pekka Salo  
Posiva Oy  
December 1996  
ISBN 951-652-012-X

- POSIVA-96-14      Final disposal of spent nuclear fuel in the Finnish bedrock, technical research and development in the period 1993-1996  
Posiva Oy  
December 1996  
(in Finnish)  
ISBN 951-652-013-8
- POSIVA-96-15      The Hyrkkölä native copper mineralization as a natural analogue for copper canisters  
Nuria Marcos  
Helsinki University of Technology  
Laboratory of Engineering Geology and Geophysics  
October 1996  
ISBN 951-652-014-6
- POSIVA-96-16      Final disposal of spent fuel in the Finnish bedrock, scope and requirements for site specific safety analysis  
Posiva Oy  
December 1996  
(in Finnish)  
ISBN 951-652-015-4
- POSIVA-96-17      Interim report on safety assessment of spent fuel disposal  
TILA-96  
Timo Vieno, Henrik Nordman  
VTT Energy  
December 1996  
ISBN 951-652-016-2
- POSIVA-96-18      Sorption of protactinium on rocks in groundwaters from Posiva investigation sites  
Seija Kulmala, Martti Hakanen  
University of Helsinki  
Department of Chemistry  
Radiochemistry laboratory  
Antero Lindberg  
Geological Survey of Finland  
December 1996  
ISBN 951-652-017-0
- POSIVA-96-19      Final disposal of spent fuel in the Finnish bedrock, detailed site investigations 1993-1996  
Posiva Oy  
December 1996  
(in Finnish)  
ISBN 951-652-018-9
- POSIVA-96-20      Suitability of Hästholmen Loviisa for final disposal of spent fuel - Preliminary study  
Posiva Oy  
December 1996  
(in Finnish)  
ISBN 951-652-019-7

- POSIVA-96-21      Hydrogeochemistry of deep groundwaters of mafic and ultramafic rocks in Finland  
Timo Ruskeeniemi, Runar Blomqvist, Antero Lindberg, Lasse Ahonen  
Geological Survey of Finland  
Shaun Frapé  
University of Waterloo  
December 1996  
ISBN 951-652-020-0
- POSIVA-96-22      Helium gas methods for rock characteristics and matrix diffusion  
Juhani Hartikainen, Kari Hartikainen  
University of Jyväskylä, Department of Physics  
Aimo Hautojärvi  
VTT Energy  
Kalle Kuoppamäki, Jussi Timonen  
University of Jyväskylä, Department of Physics  
December 1996  
ISBN 951-652-021-9
- POSIVA-96-23      Sorption of cesium, radium, protactinium, uranium, neptunium and plutonium on Rapakivi granite  
Tuula Huitti  
Martti Hakanen  
University of Helsinki  
Antero Lindberg  
Geological Survey of Finland  
December 1996  
ISBN-951-652-022-7
- POSIVA-96-24      Deep groundwater redox reactions in the Palmottu uranium deposit:  
The role of uranium and iron in these processes  
Jordi Bruno, Esther Cera, Lara Duro  
QuantiSci, Spain  
Lasse Ahonen  
Geological Survey of Finland  
December 1996  
ISBN-951-652-023-5