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**Redox Conditions in Groundwaters  
from Svartoberget, Gideå, Fjällveden  
and Kamlunge**

Peter Wikberg  
Ingmar Grenthe  
Karin Axelsen

Royal Institute of Technology  
Stockholm, Sweden 1983-05-10

**SVENSK KÄRNBRÄNSLEFÖRSÖRJNING AB / AVDELNING KBS**

*POSTADRESS: Box 5864, 102 48 Stockholm, Telefon 08-67 95 40*

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Peter Wikberg  
Ingmar Grenthe  
Karin Axelsen

Dept of Inorganic Chemistry  
Royal Institute of Technology  
S-100 44 Stockholm  
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## SUMMARY

Granitic rock at four different places in Sweden - Svartboberget, Gideå, Fjällveden and Kamlunge - have been investigated in order to find out if they are suitable for the disposal of spent nuclear fuel.

As a part of these investigations groundwaters have been sampled down to depth of about 600 m. Water bearing sections have been isolated with packers, and the water has been pumped up to the surface for the monitoring and sampling. The redox potential  $E_h$  was measured with a platinum and a glassy carbon electrode.

The field measurements have been simulated in the laboratory. These experiments have shown that the  $E_h$  can be measured under conditions valid for deep ground waters.

The field experiments are complicated by the fact that stable electrode potentials are only slowly obtained. However the measured  $E_h$  values show that the ground water at depth in the bedrock is reducing. This picture is confirmed by the low level of uranium present in the waters.

The redox status of the waters has also been calculated using the analytical data obtained from the analysis of sampled water and thermodynamic data for the iron(II)/iron(III) redox couple, and solids of iron(III) oxide hydrate and iron(II) carbonate.

1      INTRODUCTION

The redox potential,  $E_h$ , and pH are the two main variables describing the interactions between the components of a nuclear repository and groundwater. These variables are of prime importance for the corrosion of metallic materials, for the solubility and migration of actinides and therefore of great importance for the assessments of the overall safety of the nuclear waste storage system /1, 2/.

This report describes the measurement and interpretation of  $E_h$ -data obtained in the field, data which may be important for the selection of a nuclear repository site.

2      REDOX POTENTIAL ( $E_h$ ) MEASUREMENTS

## 2.1    THE REDOX STATUS OF NATURAL WATERS

A large number of investigations of the redox status of various natural water systems have been published. The interpretation of these data has often proved difficult and the general consensus seems to be that  $E_h$ -data should be given a qualitative significance only. There are several reasons for this:

- natural waters may contain several different redox systems such as O(0)/O(-II), Fe(III)/Fe(II), S(VI)/S(-II), N(V)/N(III), As(V)/As(III), and true equilibrium between these is not attained because the rate of some of the redox reactions are extremely slow. Thus it may not be clear neither if a measured  $E_h$  represents an equilibrium quantity, nor to what reaction it refers.
- most natural water systems are non equilibrium systems. Groundwaters are oxidizing in recharge areas, and are then gradually rendered more reducing as a result of microbiological activities. In discharge areas they are in general reducing. These changes from recharge to discharge areas are usually fairly stable. However, the variations in the different flow systems may be large e.g. as a result of local mixing of water of different composition. Mixing phenomena may be extreme in lake systems. Streams, soil waters and shallow groundwater systems. Most experimental studies have been made on systems of this type, and the difficulty to interpret the experimental results is thus understandable.
- it is also a difficult problem to measure  $E_h$  in systems with very low concentrations of electroactive redox species. The ex-

change current density at the electrode may be so low, that even an extremely small polarization results in a potential significantly different from the equilibrium value. The electrode material and the possible formation of deposits on it are very important under these conditions.

## 2.2 MEASUREMENTS AND INTERPRETATION OF $E_h$ IN DEEP GROUNDWATERS

Groundwater in deep bedrock of low permeability in regions of low hydraulic gradient represents systems quite different from those previously described. In order to assess the significance of measured  $E_h$ -values it is necessary to understand how these data are affected by factor such as:

- local mixing of different waters, e.g. mixing of deep water with surface water
- slow attainment of equilibrium, e.g. as a result of mixing of waters of different chemical composition. The slow reduction of oxygen from surface or drillwater is particularly important
- the magnitude of the redox buffer capacity of the ground water, particularly the influence of the Fe(II) concentration, because the Fe(II)/Fe(III) system is expected to be the potential determining redox couple.

Field data of  $E_h$ , pH and the chemical composition from a number of different site have been obtained as described in section 4. In order to facilitate the interpretation of these data we have also made a series of laboratory simulations of the field measurements of  $E_h$  as described in section 3.

## 3 LABORATORY SIMULATION OF FIELD MEASUREMENTS OF $E_h$

### 3.1 GENERAL

The redox potential has been measured in the field with a platinum and an amorphous graphite electrode. A silver-silver chloride electrode has been used as a reference.

Groundwater at great depth is expected to be reducing due to the interaction with reducing minerals such as magnetite, biotite, chlorite and sulphides, containing ferrous iron or sulphide ions. The solubility of ferrous iron in groundwater is limited by pH, carbonate ions and in some cases sulphide ions in the water.

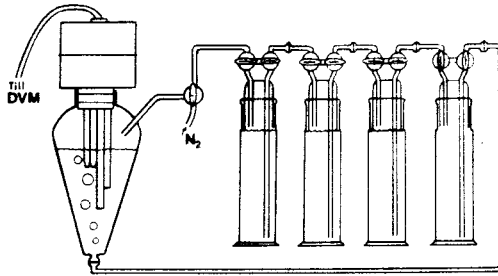


Fig 3-1. The all-glass equipment used for the laboratory measurements. The solutions are prepared in the washbottles and transported to the measuring cell by nitrogen gas.

Therefore the groundwater in general has a low redox buffer capacity.

The field measurements have been simulated in the laboratory by measurements of the redox potential in solution containing solid phases of Fe(III)-oxide and Fe(II)-carbonate in bicarbonate-carbonate pH buffers. By using solutions of known composition it is possible to test the reliability of the field electrodes, and to determine both the potential determining reactions and the minimum redox buffer capacity necessary to obtain reproducible  $E_h$ -readings.

### 3.2 EXPERIMENTAL DESIGN

The experiments have been performed in an all-glass system in order to avoid oxidation of the solutions by oxygen.

Three different electrode materials: gold, platinum and graphite were tested together with a  $Ag/Ag_2S$ -electrode. In the field tests the graphite was replaced by glassy carbon. The different electrode materials were used to establish whether the measured potentials are dependent on the electrode material or not. Such a dependence might be an indication of insufficient redox buffer capacity of the solution and/or that a "mixed" potential is monitored. Some ground waters contain sulphide and it is also necessary to establish whether this affects the electrode readings or not.



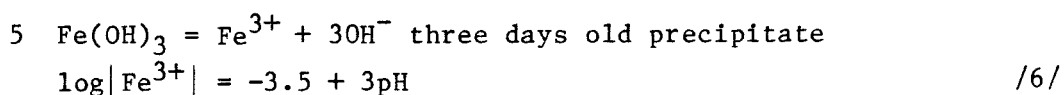
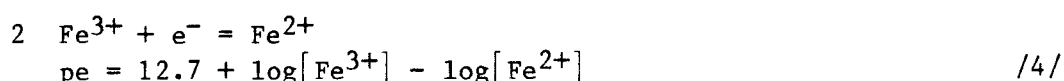
All electrodes are made in the form of a cylindric plug, with a diameter of 5-8 mm and a length of 5-10 mm. The electrode body is made of PVC or polycarbonate. The electrical contact is maintained via a brass screw through the electrode body connected to the electrode.

The silver-silver sulphide electrode is prepared by electrolysis in a sulphide solution using a low current density (0,1 mA/cm<sup>2</sup>).

### 3.3 E<sub>h</sub> DETERMINING CHEMICAL EQUILIBRIA IN GROUNDWATER

Chemical analyses of groundwaters from the sites investigated in the present phase of the KBS project indicate the presence of Fe<sup>2+</sup>(II) and particulate material containing iron and sulphur.

We have used data for some different equilibrium reactions for the calculation of E<sub>h</sub> for the system of natural groundwater and bedrock.



In the equilibrium reactions (1)-(5) the activities and the concentrations are separated so that the negative logarithm of the activity is indicated by a p whereas the concentrations are given within brackets. The equilibrium constants based on concentrations are valid at 0.1 M ionic strength.

The redox potential in the presence of goethite and free Fe<sup>2+</sup>, where the latter quantity is known from chemical analysis, can be calculated from eq (1). From equations (1) and (3) one can in the same way calculate E<sub>h</sub> in the presence of two solid phases, goethite and siderite.

The amorphous Fe(III)-oxide hydrate transforms slowly to goethite. The solubility for such a non-equilibrium system is not thermodynamically defined. However, the numerical value is probably

intermediate between the values given by eqn (4) and (5), where (4) refers to a freshly precipitated Fe(III)-oxide hydrate, while (5) is valid for a three day old precipitate, as reported by Langmuir and Whittemore /6/. By using the data in eqns (1)-(5), we can calculate the  $E_h$  for three different models. From eqns (2), (3) and (4) we obtain:

$$E_{h1} = (RT/F)\ln 10 (26.5 - 3pH + \log[CO_3^{2-}])$$

which is the redox potential of an aqueous system in equilibrium with freshly precipitated Fe(III)-oxide hydrate and Fe(II)-carbonate.

Equilibrium with a three day old Fe(III)-oxide hydrate and Fe(II)-carbonate is in the same way obtained from eqns (2), (3) and (5):

$$E_{h2} = (RT/F)\ln 10 (25.9 - 3pH + \log[CO_3^{2-}])$$

Eqns (1) and (3) give  $E_h$  in equilibrium with crystalline goethite and siderite,  $FeCO_3(s)$ :

$$E_{h3} = (RT/F)\ln 10 (25.1 - 3pH + \log[CO_3^{2-}])$$

The unknown degree of crystallization of the Fe(III)-oxide hydrate results in an uncertainty of approximately  $\pm 40mV$  in the calculated value of  $E_h$ .

### 3.4 RESULTS AND DISCUSSION

The experiments were made with two different concentrations of carbonate buffer; 0.05 mol/l and 0.01 mol/l of  $HCO_3^- - CO_3^{2-}$ . In this way pH was constant while  $pCO_3^{2-}$  varied. The experiments were repeated four times in order to estimate the reproducibility.

The results of the experiments together with the theoretical values calculated from the equations in section 3.3, are listed in Table 3-1. The calculated value of  $E_{h2}$ , valid for a solution in equilibrium with a three day old Fe(III)-oxide hydrate gives the best agreement with the experimentally obtained values. This is reasonable as it took about 24 hours to obtain stable redox potentials in all the laboratory tests.

We observed that the silver-silver sulphide electrode gave very near the same potential as the redox electrodes in sulphide free solutions, however the time for attainment of stable potentials were always longer than for the other electrodes. Under these conditions it seems to function as an "inert" redox electrode, a fact that may be used in the field measurements /7/.

Table 3-1. Theoretical and experimental  $E_h$  (platinum) values in the Fe(III)-oxide hydrate, Fe(II)-carbonate system. The theoretical values are calculated as described in section 3.3.

Solution $\text{HCO}_3^-$ - $\text{CO}_3^{2-}$	Calculated values in mV			Experimental values in mV for different runs			
	$E_{h1}$	$E_{h2}$	$E_{h3}$				
0.05 mol/l	-313	-348	-394	-351	-355	-351	-340
0.01 mol/l	-354	-389	-435	-382	-373	-388	-392

#### 3.4.1 Characteristics of electrode systems used

The  $E_h$ -values given in Table 3-1 were those obtained by the platinum electrodes. The gold electrode gave within a few millivolts the same readings in sulphide free systems. On the other hand, the porous graphite electrodes gave a potential that usually was up to 50 mV more positive than the Pt and Au-electrodes. The reason for this large discrepancy is probably the presence of oxygen in the pores of the electrode. This diffuses very slowly, and results in a non-equilibrium system over the time periods studied. This conclusion is supported by the fact that the non-porous glassy carbon electrodes used in the field measurements always agreed well with the Pt-electrodes.

Table 3-2 gives a comparison between  $E_h$ -readings obtained with a platinum and a glassy carbon electrode under field conditions during two days of the pumping period at the 512 m level in Gi 4.

Both the stability and the agreement of the  $E_h$ -readings are excellent.

Table 3-2. Redox potentials measured in the water pumped from the 512 m level in the bore hole Gi 4.

Week	Day	Time	$E_{hC}$ (mV)	$E_{hPt}$ (mV)
29	1	8.15	- 85	- 81
		10.15	- 90	- 86
		12.15	- 92	- 88
		14.15	- 98	- 93
		16.20	-101	- 97
		17.15	-100	- 97
		29	2	8.10
11.50	-102	- 99		
14.20	-102	-102		

The electrode potentials are normally stabilized within one day. A stable electrode potential seems to be attained more quickly in freshly prepared solutions, than those a few days old. Treatment of the electrodes with 1 mol/l NaOH also results in a faster electrode response. This effect is probably due to removal of oxygen adsorbed on the electrode surface /8/.

Sulphide was shown to have an adverse effect on the Au-electrode. This was tested by adding sulphide to the test solution and then replacing it with fresh solutions. The effect of this sulphide treatment on various electrodes investigated are shown in Table 3-3.

Table 3-3. The influence of sulphide on Au and Pt-electrode potentials.

Electrode material	Electrode potentials in mV at different number of sulphide treatments			
	0	1	2	3
Platinum	-382	-379	-388	-392
Gold	-382	-354	-307	-302
Silver-silver sulphide	-	-373	-375	-370

### 3.5 CONCLUSIONS OF THE LABORATORY MEASUREMENTS

From the results of the previous section we can draw the following conclusions:

- stable and reproducible redox potentials can be measured by using platinum and glassy carbon electrodes in solutions of a redox buffer capacity comparable with those of many groundwaters.
- gold electrodes seems to be poisoned by sulphide and should thus be avoided as electrode material.

In a previous study /2/ we indicated that Au-electrodes were to be preferred in comparison with Pt-electrodes. This conclusion was based on measurements in solutions which did not contain sulphide. Furthermore, no precautions had to be made to remove the oxide layer on the Pt-surface. From the more extensive studies reported here, we conclude that Pt and glassy carbon are the most suitable electrode materials for redox measurements in ground water.

## 4 RESULTS AND DISCUSSION OF FIELD MEASUREMENTS

### 4.1 INVESTIGATED AREAS

Four geographically different areas have been investigated geologically, geophysically and geochemically. These areas are Svartboberget, Gideå, Fjällveden and Kamlunge, and a detailed geological description of them are given in /9, 10, 11, 12/.

The general aim have been to chose at least two boreholes on each site for ground water sampling in recharge as well as discharge areas. In each drillhole 4-5 water bearing zones between 90 and 700 m have been selected for water sampling. The selected zones were sealed off by rubber packers spaced 2,7 m apart. The boreholes were core-drilled with a diameter of 56 mm. The sampling pump was positioned immediately above the sealed off section. In the Fjällveden area an extra drillhole was sampled in two sections. The positions of the sampled sections discussed in this report are presented in the table below.

Data from the boreholes Km 3 and Km 13 in Kamlunge became available at the time when this report was finished. These data are discussed in a separate section 5.2 at the end of this report.

### 4.2 SAMPLING CONDITIONS

Each section has been pumped for 12-13 days with a capacity of 120-360 l/day, except for the section in Gi 4 at 596 m which was pumped for five weeks with a capacity of 1-2 l/day. During the first 4-5 days of a pumping period neither sampling nor field measurements were made. During the rest of the pumping period 7-8 samples were taken for analysis of water characteristics.

The field parameters were monitored with 1-2 hour intervals every day. During the sampling period the water flow through the measuring vessel was stopped 3-4 times, in order to calibrate the electrodes and sensors. The pH was measured with a glass electrode, the  $E_h$  with a platinum and an amorphous graphite electrode. The whole equipment is described in KBS TR 83-44 /13/.

#### 4.2.1 Hydrologic conditions

The drilling of a borehole will affect the hydrology of the rock. While drilling, the drill head is flushed with drilling fluid in order to flush away crushed material. The fluid is injected with a high pressure, which will result in a flow of the fluid into the fissure system of the rock. The water used as drilling fluid is taken from another borehole in the surrounding

Area	Borehole	Length <sup>a</sup> (m)	Depth (m)
Svartboberget	Sv 4	96	82
		376	324
		430	373
		630	551
Gideå	Gi 2	178	157
		328	228
		400	353
		544	478
		602	528
Gideå	Gi 4	96	91
		222	212
		404	385
		512	498
		616	596
Fjällveden	Fj 2	123	106
		342	293
		483	409
		605	506
Fjällveden	Fj 4	151	131
		317	272
		410	349
		496	420
Fjällveden	Fj 8	470	402
		666	562
Kamlunge	Km 3	219	106
		445	375
Kamlunge	Km 13	670	555

<sup>a</sup> Length is the position of the sampling equipment measured along the borehole.

area in order to avoid extensive chemical changes of the minerals and the ground water. However, this always results in a mixing of waters with slightly different characteristics. A comparable mixing will take place when the water injection tests are performed.

Another possible source of mixing of water is that the open borehole will shortcircuit the different flow paths crossing it. This shortcircuiting results in a flow of water from cracks

with a positive piezometric pressure through the drill hole and into cracks with a negative piezometric pressure.

A third possible way of mixing of water might occur when low water bearing cracks are pumped. If the walls of the borehole are not very smooth, a leakage between the packers and the wall might occur, due to the underpressure evolved between the packers due to the low water flow.

The piezometric pressure is the pressure difference between the ground water level and the packed off section in the borehole. A positive piezometric pressure indicates that water flows out of the formation into the borehole when the borehole is open. A negative piezometric pressure indicates an opposite flow. The hydraulic conductivity of a section of the borehole determines the flow rate of water in the section at a certain pressure difference. Combinations of the piezometric pressure and the hydraulic conductivity can be used to calculate the undisturbed flow in a specific section of the borehole. The result is only valid for an open borehole, but will under these circumstances indicate whether a negative or positive flow exists and also the flow rate of the water in the particular section of the borehole.

Both the piezometric pressure and the hydraulic conductivity are obtained from the water injection tests performed prior to the groundwater characterizations. The piezometric pressure, the hydraulic conductivity and the tritium and iodide content of the sampled water are listed in Table 4-1. The use of these parameters will be discussed to some extent.

#### 4.2.2 Tritium content

Tritium is a good indicator of the presence of young water. Tritium levels above the detection limit (3 TU) indicate recent intrusion of shallow water. There is a strong correlation between negative undisturbed flow (discussed above) and high tritium content, which could be due to natural percolation of young water in the undisturbed rock, contamination of drilling fluid or intrusion of surface water through the open drill hole.

#### 4.2.3 Iodide tracer

The drilling fluid has been marked with iodide, ( $10^{-5}$  mol/l). The amounts of iodide left in the water that is sampled are astonishingly high, despite the efforts to clean the drill hole by mammoth pumping and a pumping period of 4-5 days before the sampling is started (see Table 4-1). These very high iodide concentrations might also indicate a certain background of iodide in the formation water /14/. Though it is difficult to see any general pattern in the comparison of the iodide and tritium analyses and the undisturbed flow, some special cases could, however, be mentioned:

Table 4-1. The hydraulic conductivity, the piezometric pressure and the tritium and iodide content in the investigated areas.

Borehole	Depth (m)	log K (m/s)	P (kPa/10)	Flow (l/day)	TU	I <sup>-*</sup> (%)
Sv 4	82	- 7.1	+ 1.0	+181	5(2)	1.0
	324	- 7.6	+22.5	+223	<3	4.2
	373	- 7.7	-	-	<3	0.6
	551	- 9.2	-	-	<3	0.6
Gi 2	157	- 6.6	+ 3.2	+774	<3	0.4
	228	- 9.8	- 1.6	- 0	<3	<0.4
	353	- 9.6	- 9.2	- 2	<3	<0.4
	478	-10.7	-	-	<3	<0.4
	528	-10.5	-	-	<3	<0.4
Gi 4	91	- 7.4	- 5.1	-474	36(2)	0.6
	212	- 8.0	- 4.9	- 21	5(2)	1.7
	385	- 8.3	-26.6	- 23	8(2)	11.8
	498	-11	-	-	49(2)	<0.4
	596	-10.4	-	-	10(2)	16.5
Fj 2	106	- 6.7	- 0.3	- 27		1.7
	293	- 8.8	+ 0.2	+ 0	19(2)	8.7
	409	- 6.4	- 0.9	-130	19(2)	7.9
	506	- 8.5	- 0.8	- 1	<3	5.5
Fj 4	131	- 6.6	+ 0.1	+ 2	9(1)	6.0
	272	- 9.1	- 1.1	- 2	21(2)	4.4
	349	- 8.9	- 1.5	- 4	12(2)	4.3
	420	-10.7	-	-	6(2)	0.6
Fj 8	402	- 8.9	-12.2	- 6	8(2)	5.5
	562	- 7.7	-16.1	-112	10(2)	4.7

\* The values are given as per cent drilling fluid.

- Gi 2, at 157 m depth has a large positive flow, and low tritium and iodide contents. The sections below 157 m have also tritium and iodide concentrations close to the detection limits. This can be interpreted as a result of a protecting water flow from the 178 m level, that prevents contamination through the open borehole. There seems to be a similar but not so pronounced effect in Sv 4, at 324 m depth.

- Gi 4, at 91 m depth has a very large negative flow, low iodide concentration and a high tritium content, indicating an infiltration of young shallow water through the open borehole. All the sections in Gi 4 have a high tritium content, caused by the fact that there is no positive flow at depth that



could prevent shallow water from streaming downwards in the open borehole. The fact that detectable amounts of tritium and iodide are found in the waters indicate that oxygenated water has been mixed with the formation water. Due to the reducing capacity of the rock, the amount of dissolved oxygen is reduced to a value lower than the detection limit. Very small amounts of oxygen can, however, still be present even in the presence of Fe(II), c f 4.3.3 and will affect the  $E_h$  measurements.

#### 4.3 REDOX DEPENDENT QUANTITIES

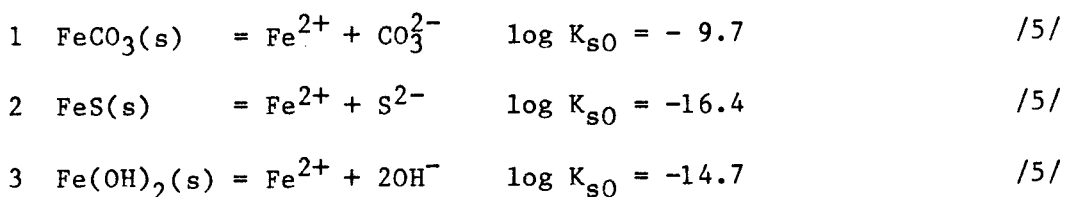
##### 4.3.1 The content of Fe(II) and Fe(III) in ground water

Three different types of analysis have been made, the Fe(II) content, the total iron concentration and analysis of the particle bound iron fraction. All samples were sent to two different laboratories, (SGU-Lab, Uppsala and Hydroconsult, Stockholm), in order to check the occurrence of possible systematic errors in the analytical procedure used. The analytical procedures for the analysis are described elsewhere /14/.

Two different sampling techniques were utilized, either preservation of the field samples by addition of HCl, or sampling in filled borosilicate glass bottles with ground glass stoppers.

The determination of total iron and Fe(II) was made on 5-6 samples from each borehole section investigated. The particle bound iron was determined on two samples from each section. The fraction of particle bound iron was determined by X-ray emission technique on material collected on 0,45  $\mu\text{m}$  membrane filters. Some of the analytical data are presented in Table 4-2. (The data in Table 4-2 correspond to sampling made close to periods of stable field data for pH and  $E_h$ . Average, min and max values are presented in ref /15/.

The analytical data can be used together with information on the values of the solubility products to establish the degree of saturation of the water with respect to the  $\text{FeCO}_3(\text{s})$ ,  $\text{FeS}(\text{s})$  and  $\text{Fe}(\text{OH})_2(\text{s})$ . The following solubility products have been used:



All of them are valid at ionic strength of 0.1 M. Figures 4-1, 4-2 and 4-3 contain plots of  $\text{pFe}^{2+}$  vs  $\text{pCO}_3^{2-}$ ,  $\text{pS}^{2-}$  and  $\text{pOH}^-$ , respectively. The lines represent the equilibrium conditions (1)-

Table 4-2. Redox sensitive parameters measured in the field; pH,  $pS^{2-}$ ,  $E_h(\text{meas})$ , and analyzed in sampled water; Fe(II),  $\text{HCO}_3^-$ , Mn, U. Models for calculated  $E_h$ -values are given in section 4.4.1.

Borehole	Depth (m)	Week-day	pH	Fe(II)* (mg/l)	$\text{HCO}_3^-$ (mg/l)	$pS^{2-}$ (mg/l)	Mn (mg/l)	U (ug/l)	$E_h(\text{Fe})$ (mV)	$E_h(\text{CO}_3)$ (mV)	$E_h(\text{meas})$ (mV)
Sv 4	82	14-7	8.4	0.05(0.04)	137	22.0	0.05	3.5(2)	-129	-227	
	324	16-3	9.6	0.16(0.17)	120	12.9	0.03	<0.1	-355	-365	-140 $\pm$ 40
	373	18-4	9.1	0.28(0.06)	131	16.2	0.05	<0.2	-285	-306	- 80 <sup>c</sup>
	551	21-2	9.0	0.32(0.14)	124	12.9	0.05	<0.1	-273	-298	-140 $\pm$ 20
G1 2	157	21-1	8.8	0.13(0.11)	161	10.6	0.01	0.2(1)	-218	-283	-100 <sup>c</sup>
	228	25-1	8.8	0.64(0.08)	162	13.3	0.02	1.3(2)	-256	-268	- 85 <sup>c</sup>
	353	27-3	8.7	0.54(0.23)	165	13.7	0.02	0.3(1)	-236	-256	- 90 <sup>c</sup>
	478	29-3	8.9	0.24(0.23)	156	14.5	0.06	0.3(1)	-249	-280	- 90 <sup>c</sup>
	528	31-1	8.7	(0.16)	156	11.9	0.02	0.2(1)	-207	-257	-100 <sup>c</sup>
G1 4	91	23-2	8.0	0.75(0.80)	146	12.1	0.22	1.0(2)	-128	-182	- 30 <sup>c</sup>
	212	25-1	9.0	0.25(0.11)	133	11.0	0.02	1.0(2)	-268	-294	-120 <sup>c</sup>
	385	26-4	9.3	0.06(0.06)	18	10.0	0.01	<0.2	-283	-372	-160 $\pm$ 40
	498	28-4	8.5	7.4 (6.1 )	120	14.5	0.27	<0.2	-266	-241	-120 <sup>c</sup>
	596	36-6	8.9	(0.40)	46	9.2	0.05	<0.1	-262	-309	-320 $\pm$ 20
Fj 2	106	34-7	8.1	1.0 (0.08)	160	11.0	0.20	0.6(2)	-152	-191	- 80 <sup>c</sup>
	293	37-1	7.3	(7.6 )	141	22.0	0.50	0.2(1)	- 69	-106	- 90 $\pm$ 20
	409	39-1	7.4	6.5 (5.1 )	165	19.7	0.45	<0.1	- 82	-113	-110 $\pm$ 30
	506	40-4	8.8	0.40(0.06)	89	10.7	0.08	<0.2	-246	-282	-115 $\pm$ 25
Fj 4	131	27-1	8.2 <sup>b</sup>	1.1 (0.61)	220	12.1	0.30	3.7(2)	-118	-194	- 90 <sup>c</sup>
	272	28-3	7.7 <sup>b</sup>	6.5 (5.2 )	192	12.7	0.25	3.0(2)	-131	-142	-110 <sup>c</sup>
	349	31-2	8.0 <sup>b</sup>	1.78(0.99)	194	11.3	0.10	0.6(1)	-150	-175	-100 <sup>c</sup>
	420	35-2	8.7 <sup>b</sup>	1.3 (0.75)	200	11.0	0.10	<0.2	-257	-250	-170 <sup>c</sup>
Fj 8	402	39-2	8.5	2.4 (2.23)	129	13.3	0.15	1.1(2)	-239	-240	-120 $\pm$ 20
	562	40-4	9.0	2.7 (2.21)	129	12.1	0.15	0.4(1)	-324	-296	-190 $\pm$ 50

\* The values within parenthesis are results of analysis of untreated samples whereas the others are from samples conserved by HCl.

b pH measured in laboratory, due to failure in the field equipment.

c Erratic readings with variations in measured potentials, due to mixed waters.

(3). From figure 4-1 it is obvious that all water samples except one are supersaturated with respect to  $\text{FeCO}_3(\text{s})$ . Figure 4-2 show that many samples are also saturated with respect to  $\text{FeS}(\text{s})$ . Figure 4-3 indicates that all water samples are undersaturated with respect to  $\text{Fe}(\text{OH})_2(\text{s})$ .

The concentration of soluble Fe(III) species should be negligible at the pH-values observed. Hence one should expect the ratio between total iron and Fe(II) to be close to unity. The experimental values are always larger, 1.2 - 1.5, indicating the presence of some particle bound Fe(III) fraction.

The spread in the analytical data for total and particle bound iron is much larger than for Fe(II). One also finds that the particle bound fraction, in general, decreases with time. These effects may be due to oxidation of Fe(II) by oxygen containing pump water and an irreproducible sorption/desorption of material on the walls of the tubings carrying the water to the surface.

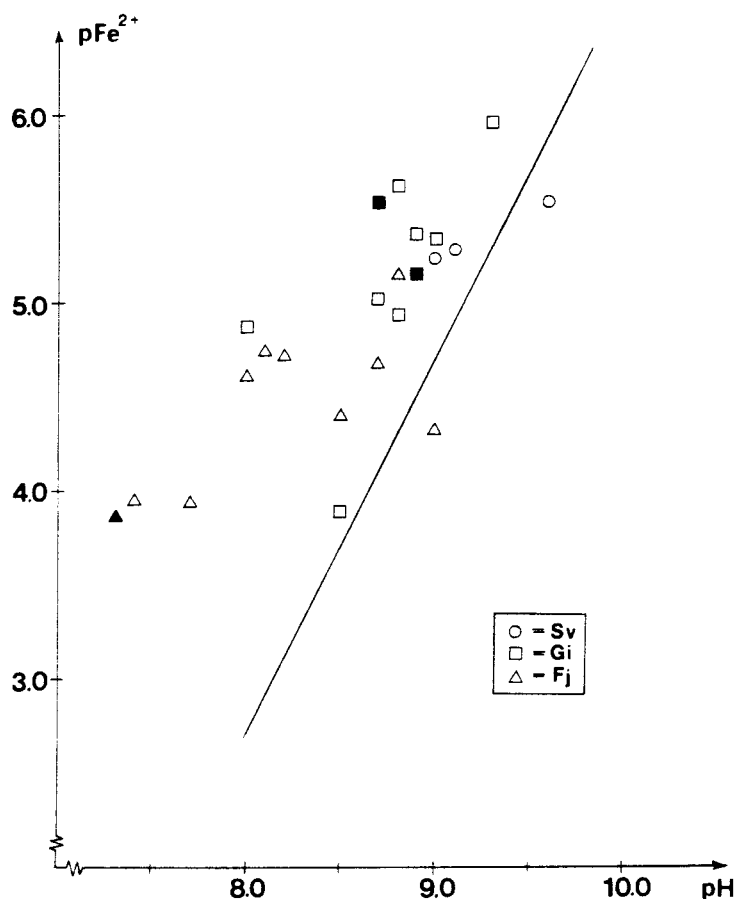


Figure 4-1. A plot of  $p\text{CO}_3^{2-}$  versus  $p\text{Fe}^{2+}$  for waters sampled at Svartboberget, Gideå and Fjällveden. The filled marks indicate that the iron content is analyzed on unpreserved samples. More details are given in section 4.3.1.

#### 4.3.2 The content of manganese(II) in groundwater

All water samples contain  $\text{Mn}^{2+}$ , c.f Table 4-2. This is in agreement with the known chemical properties of manganese, which is expected to be present as Mn(II) at values of  $E_h$  less than +344 mV according to:

$$E_h < (RT/nF)\ln_{10} (20.8 - 2\text{pH} + 1/2[\text{Mn}^{2+}]) \quad /16/$$

#### 4.3.3 The content of S(-II) in groundwater

S(-II) in the form of  $\text{HS}^-$  will reduce oxygen. The presence of  $\text{HS}^-$  will also be important to the corrosion of copper /2/.

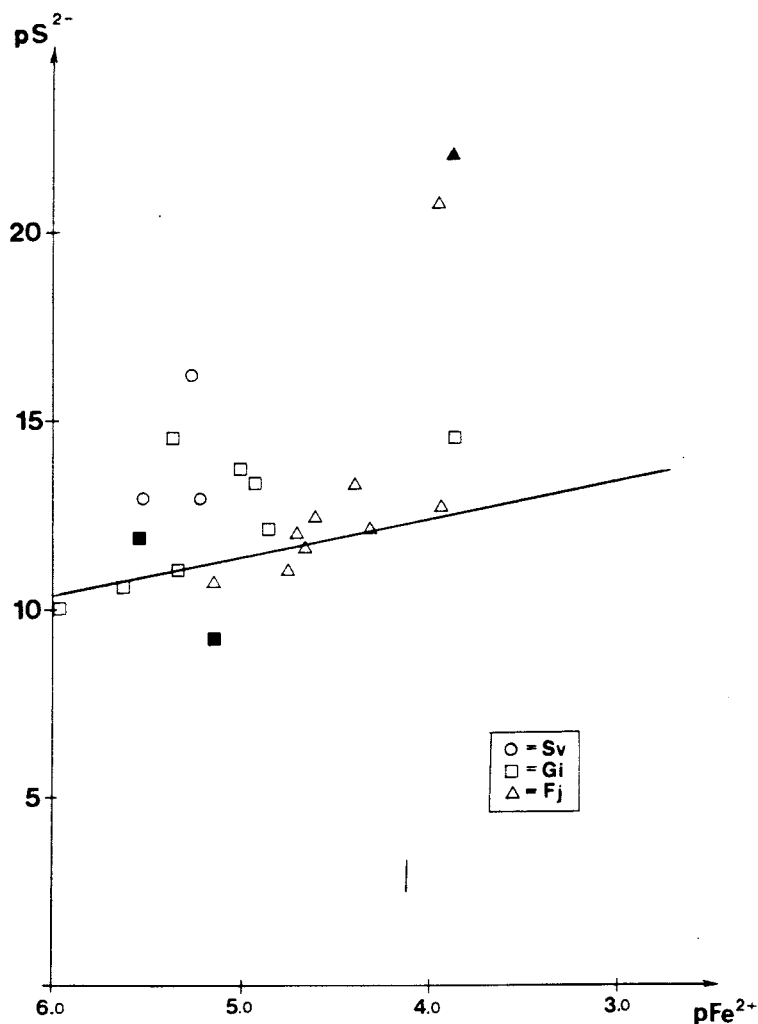


Figure 4-2. A plot of  $pS^{2-}$  versus  $pFe^{2+}$  for waters sampled at Svartboberget, Gideå and Fjällveden. The filled marks indicate that the iron content is analyzed on unpreserved samples. For more details c f section 4.3.1.

The total concentration of S(-II) has been measured as  $S^{2-}$  in the field by using an  $Ag/Ag_2S$  electrode. The total concentration of S(-II) is then calculated from the measured  $pS$  and  $pH$  by using the value  $lgK = 14$  for the protolysis constant of  $S^{2-}$ .

The total S(-II) has also been analyzed in the laboratory, 5-6 water samples were taken from each section. The sulphide concentration was measured by using a commercial ionic selective electrode on samples to which zinc, acetate and sodium hydroxid had been added.

Most water samples contained only very small amounts of S(-II), less than 0.05 mg/l. Table 4-3 presents data for some samples where large amounts of S(-II) were found. This table also shows

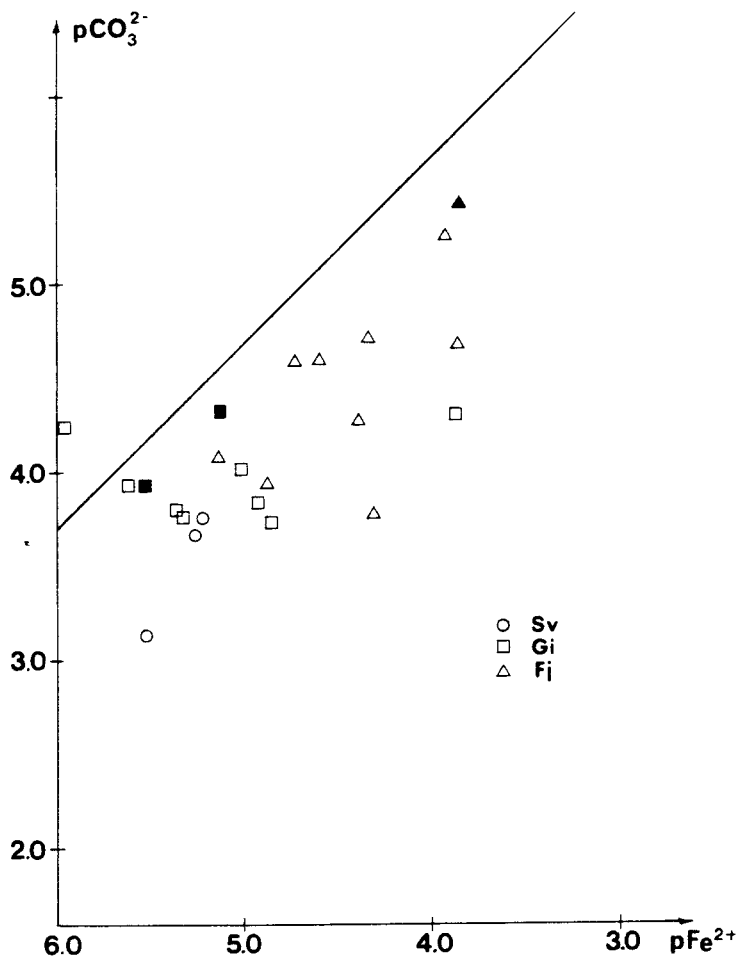


Figure 4-3. A plot of  $p\text{Fe}^{2+}$  versus pH for waters sampled at Svartboberget, Gideå and Fjällveden. The filled marks indicate that the iron content is analyzed on unpreserved samples. For more details c f section 4.3.1.

that the agreement between the field measurements and the laboratory analyses is quite good.

From the calibrations the uncertainty in the pS measurements can be estimated to be within  $\pm 0.5$  pS units, and the uncertainty in the pH measurements to be  $\pm 0.1$  pH units. With these limitations at the differences between the field measurements and the laboratory analyses fall within the experimental error, except for Fj 8 at 562 m depth.

Table 4-3. Comparison between field measured and laboratory analyzed total sulphide content.

Borehole	Depth (m)	pH	pS	HS <sup>-</sup> calc (mg/l)	HS <sup>-</sup> anal (mg/l)
Gi 4	212	9.0	11.0	0.03	0.13
	385	9.3	10.0	0.17	0.23
	596	8.9	9.2	2.7	-
Fj 2	106	8.1	11.0	0.27	0.06
	506	8.8	10.7	0.11	0.11
Fj 4	131	8.2*	12.2	0.02	0.03
	349	8.3*	11.0	0.15	0.20
	420	8.5*	11.0	0.10	0.13
Fj 8	562	9.0	12.1	0.003	0.08

\* pH measured in laboratory.

#### 4.3.4 The oxygen content in groundwater

Oxygen is measured with an oxygen sensitive electrode, which unfortunately has a fairly high detection limit, 0.05 mg/l. It is well known that the presence of oxygen in lower amounts will cause disturbances in the  $E_h$ -readings, and may also lead to slow redox processes, where e.g. Fe(II) is oxidized to insoluble Fe(III)-oxide hydrate.

Oxygen is not expected to be present in the groundwater, but it may be introduced through mixing with surface and drilling water as discussed in section 4.2.3.

The oxygen analyses give very little information of the occurrence of phenomena of this type. Mixing of water may instead be detected indirectly e.g. from age dating or from experimental variations in the  $E_h$ -readings. The latter variations may be due to a decrease in the concentration of dissolved Fe(II) through oxidation by  $O_2$ . The rate and mechanism of this process is fairly well known, and the reaction is slow under the conditions found in the groundwaters. The rate of the oxidation of Fe(II) by dissolved oxygen is /17/:

$$-\frac{d[Fe]}{dt} = -4 \frac{dP_{O_2}}{dt} = K[Fe]P_{O_2}[OH]^{-2}$$

where  $K \approx 10^{12} \text{ (mol/l)}^{-2} \text{ atm}^{-1} \text{ s}^{-1}$

As the oxygen concentration is much lower than the Fe(II) concentration, the latter can be considered constant while the oxygen is decreased. The time needed to decrease the oxygen concentration from 0.06 mg/l to different concentrations are given in Table 4-4.

Table 4-4. The time needed for the reduction of oxygen from  $P_{O_2} = 10^{-3}$  (0.06 mg/l) to different  $P_{O_2}$  values in a solution of pH 8.5,  $Fe = 10^{-5}$  mol/l = 0.56 mg/l.

$\log P_{O_2}$	-4	-5	-6
time/days	1	2	3

This slow rate of reaction seems to be one possible explanation for the slow drifts of  $E_h$  towards more negative values observed in the field.

#### 4.3.5 Content of uranium in groundwater

Small amounts of uranium, usually uraninit, are present in most granitic bedrocks. The solubility of uranium in ground water is to a large extent determined by the redox potential and the carbonate concentration of the water /18/.

Analyses of the uranium content of the groundwaters from the regions investigated in the present phase of the KBS-programme, are given in table 4-2. The concentration of U is usually around 3  $\mu$ g/l.

We have calculated the equilibrium concentration of uranium in the various water samples, by using the analytical values of pH and total carbonate together with the data given in /19/. The calculated solubilities fall in the range  $10^{-8}$  -  $10^{-7.5}$  mol/l (2.4 - 7.4  $\mu$ g/l), i e in good agreement with the measured values. This result is a strong indicator that the groundwater is reducing, c f Fig 4-4.

### 4.4 COMPARISON OF MEASURED AND CALCULATED REDOX POTENTIALS

#### 4.4.1 Models

The dominating reducing species in the groundwaters investigated is  $Fe^{2+}$ . The granitic bedrock and some of the fracture filling minerals contain Fe(II) and Fe(III) minerals, and it seems likely that the Fe(II)/Fe(III) system determines the redox potential of the ground water and the redox potential measured by the elec-

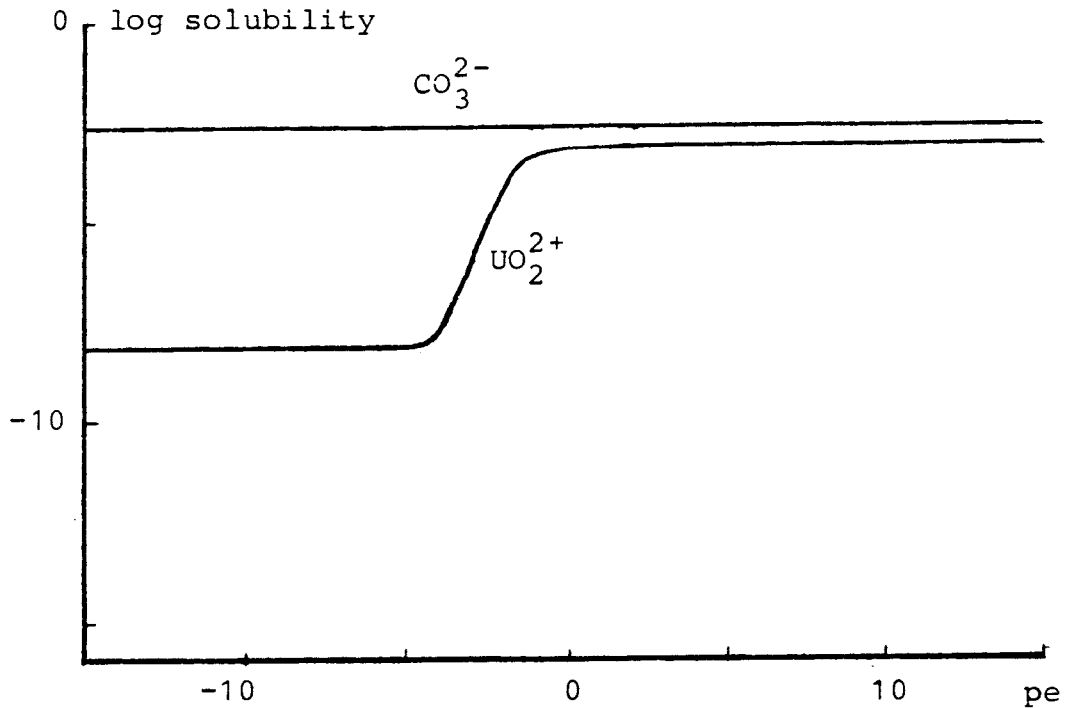


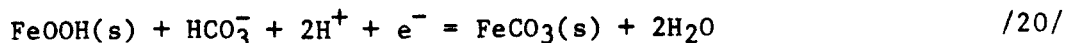
Figure 4-4. The solubility of  $\text{UO}_2^{2+}$  as a function of  $pe$  at  $\text{pH} = 8.45$  and  $\text{HCO}_3^- = 2.2 \text{ mM}$  and  $U_{\text{tot}} = 1 \text{ M}$ .

trode systems. The latter point is given additional support by the results of the laboratory experiments reported in section 3.

The  $E_h$  values for the groundwater samples may then be calculated, by using the known analytical composition of the water. However, we do not know which solid phases are present in the system, and the  $E_h$  calculations will thus be subject to some uncertainty.  $E_h$  is measured at the surface. Hence we cannot tell whether the value is still a characteristic of the formation, or not. However, a span of possible  $E_h$ -values may be obtained as follows:

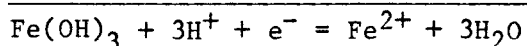
A lower limit of  $E_h$  is obtained by assuming that this quantity is determined by the solubility of the minerals goethite and siderite. An upper limit is obtained by using the solubility of freshly precipitated ferric hydroxide and the analytical concentration of ferrous iron. The source of the ferric hydroxide will in this case be the oxidation of free ferrous iron by traces of oxygen that has leaked into the measuring vessel.

With the two models described above the  $E_h$  will be given by the reactions:



$$E_h (\text{goethite/siderite}) = \frac{RT}{F} \ln 10 (15.3 - 2\text{pH} + \log[\text{HCO}_3^-])$$





$$E_h \text{ (Ferric hydroxide)} = \frac{RT}{F} \ln 10 (16.8 - 3\text{pH} - \log[\text{Fe}^{2+}])$$

The equilibrium constants have been selected for calculations using concentrations instead of activities and are valid at ionic strength 0.1 M.

#### 4.4.2 Measured $E_h$ potential

The electrodes are strongly affected by the presence of oxygen, and it is impossible to avoid contamination during the calibration procedure. This results in drifts and erroneous values of the electrode potentials for about three days after a calibration due to traces of oxygen left c f section 4.3.4.

Typical readings are presented in Table 4-5. The slow drift makes it difficult to decide when equilibrium has been attained.

The experimental procedure used in the field measurements does not always avoid the inadvertent introduction of oxygen. Each level is pumped continuously for 12 days. However, the measurements are interrupted by calibration routines three to four times during this period. During the calibrations it is impossible to avoid introduction of oxygen in the measuring system. We now know that the electrodes are stable for long periods, and have thus changed our calibration routines so that only two calibrations are made, one before and one after the pumping period. However, this new calibration technique has not been used in measurements presented here, c f Table 4-2.

The data presented in Table 4-2 also indicate a non-equilibrium situation in most of the experimental sites. These data will now be discussed in more detail.

- at 373 m in Sv 4; The water in the measuring system contains oxygen, and consequently no stable  $E_h$ -readings can be obtained, c f 4.3.4.
- the bore hole Gi 2; This site is special in many ways. From Table 4-1 and the discussion in section 4.2.3 it is obvious that water from 157 m fills the whole borehole. This will cause some mixing of waters of different origin, which in turn may cause the slow drift of the measured  $E_h$  values. The mixing of waters of different origin was confirmed by a sulphide analysis. A sulphide containing water was present in the borehole during the first 2 weeks of pumping, while sulphide free water was obtained during the following 2 weeks. No analysis samples

Table 4-5. Measured  $E_h$  values in a period between two calibrations, at Gi 2 the 400 m level.

Datum (w-d)	Time	Temp (°C)	Cond (mS/m)	pH	DO (mg/l)	$E_h$ C (mV)	$E_h$ Pt (mV)	pS
26-6	1 200	6.80	27.4	8.50	1.40	226	112	22.32
26-6	1 300	7.20	27.2	8.52	1.10	179	96	21.86
26-6	1 430	7.20	27.2	8.54	.56	119	89	21.61
26-6	1 555	7.20	-	8.56	.52	96	85	21.43
26-7	645	6.10	27.0	8.63	.25	1	28	20.11
26-7	850	6.10	27.0	8.63	.26	- 4	22	20.00
26-7	1 005	6.20	27.0	8.62	.26	- 9	15	19.85
26-7	1 230	6.20	27.0	8.64	.24	- 13	8	19.66
26-7	1 445	6.20	27.0	8.62	.22	- 17	1	19.63
26-7	1 640	6.20	27.0	8.61	.22	- 19	- 2	19.59
27-1	655	6.20	27.0	8.64	.10	- 36	- 28	18.87
27-1	905	6.80	27.0	8.62	.09	- 38	- 31	18.76
27-1	1 100	7.00	27.0	8.60	.10	- 39	- 32	18.67
27-1	1 200	7.00	27.0	8.60	.09	- 43	- 35	18.49
27-1	1 445	7.00	27.0	8.62	.07	- 47	- 41	18.10
27-1	1 540	7.00	27.2	8.62	.06	- 49	- 45	17.92
27-2	650	6.30	27.1	6.91	.01	- 71	- 73	15.62
27-2	950	6.80	27.1	8.64	.01	- 74	- 76	15.23
27-2	1 120	7.10	27.1	8.61	.03	- 77	- 80	15.00
27-2	1 215	7.10	27.1	8.60	.04	- 78	- 81	14.89
27-2	1 520	7.30	27.1	8.59	.04	- 80	- 85	14.66
27-3	800	6.30	27.1	8.66	.01	- 87	- 94	13.74
27-3	1 000	6.80	27.1	8.66	.01	- 84	- 94	14.01
27-3	1 110	7.00	27.1	8.64	.00	- 84	- 95	13.71

were taken during the first period, so no detailed comparison of the two waters can be made.

- at 91 m, 212 m and 498 m in Gi 4; Table 4-1 indicates a negative flow in these sections. This will increase the likelihood of contamination from surface water streaming down the borehole into the fracture system. The section at 498 m has a very low permeability, and is probably also contaminated by water from the borehole through leakage between the packers and the walls of the borehole.
- the Fjällveden area; High concentrations of drilling fluid and high tritium contents are found in all water samples. There was also a change in the experimental equipment used. Fj 2 and Fj 8 were investigated by using new and improved equipment.

## 4.5 CONCLUSIONS OF FIELD MEASUREMENTS

### 4.5.1 Field experiments

The experimental investigations have revealed a number of possible sources of errors, that have to be taken into consideration in order to obtain reliable  $E_h$  results. These are;

- the hydrology of the rock ought to be well characterized, so that the levels selected for water sampling have a suitable hydraulic conductivity and a positive piezometric pressure. In this way one reduces the risk of contamination of the fracture water by water from the borehole. Boreholes with high piezometric pressure close to surface (depth < 100 m) and negative piezometric pressures beneath should not be selected.
- the drilling fluid used is not totally removed by mammoth pumpings. The presence of drilling fluid up to several ten per cent can sometimes be obtained in the sampled water, c f table 4-1. On the other hand a positive and undisturbed flow seems to flush away the drilling fluid. This implies that the larger water bearing zones in the borehole should be isolated by packers so that the drilling water is removed from the water bearing zones through natural flow. The borehole should not be opened again until the water sampling is started.
- as few calibrations of the electrodes as possible should be made in order to avoid oxygen contamination.

### 4.5.2 Comparison between measured and calculated $E_h$ values

The measured  $E_h$  values in general deviate considerably from the  $E_h$  values calculated from chemical models' only in three cases did we observe a reasonable agreement: These are at 596 m in Gi 4 and at 293 m and 409 m in Fj 2. The two sections in Fj 2 have a rather high concentration of Fe(II), and the section at 596 m depth in Gi 4 has a high sulphide content, that will reduce traces of oxygen faster than in waters with low content of the elements. We expect that the deviations observed in the other cases are mainly due to experimental shortcomings and to the selection of unsuitable sampling regions c f section 4.2.1. This conclusion implies that a better agreement between measured and calculated values might have been attained if the measurements were continued without interruption for a longer time c f section 4.5.1.

5 RESULTS FROM MEASUREMENTS PERFORMED WITH IMPROVED TECHNIQUE

5.1 IMPROVED INVESTIGATION PROCEDURE

The data discussed so far in this report imply that the agreement between measured and calculated  $E_h$ -values is in most cases rather poor. We suspect that this is partly caused by traces of oxygen left in the measuring vessel, and have accordingly made some changes in the former investigation procedure which might improve the results. The main changes are:

- calibration of the probes are made only in the beginning and at the end of a two week period
- the pumping of the sealed off water bearing sections has in some cases been prolonged to four weeks instead of two

With these changes we expect to eliminate the problem caused by entering of oxygen into the system every time it is opened.

5.2 RESULTS

The levels investigated with this new procedure and the results are listed in Table 5-1. The data show a better agreement between theoretical and experimental values than previously.

Table 5-1. Redox sensitive parameters measured in the field; pH,  $pS^{2-}$ ,  $E_h(\text{meas})$ , and analyzed in sampled water; Fe(II),  $HCO_3^-$ , Mn. Models for calculated  $E_h$ -values are given in section 4.4.1. Data from the other sites are presented in table 4-2.

Borehole	Depth (m)	Week-day	pH	Fe(II)* (mg/l)	$HCO_3^-$ (mg/l)	$pS^{2-}$ (mg/l)	Mn (mg/l)	U ( $\mu\text{g/l}$ )	$E_h(\text{Fe})$ (mV)	$E_h(\text{CO}_3)$ (mV)	$E_h(\text{meas})$ (mV)
Km 3	106	06-1	7.9	0.18(0.12)	65	22.4	0.02	18 (9)	- 77(- 67)	-190	+ 55±25
	375	01-2	8.7	0.75(0.65)	65	13.0	0.14	4.0(2)	-243(-240)	-279	-195±15
Km 13	555	13-2	7.6	8.5	32	16.4	0.35	-	-120	-174	-131

\* The values between parentheses are results of analysis on filtered samples (0.45 $\mu\text{m}$ ), whereas the others are results from unfiltered samples. Both samples are acidified with HCl on sampling.

In the two deep section at 375 m in Km 3 and 555 m in Km 13 the agreement between the measured and the calculated  $E_h$  values is very good. However, in the upper sections at 106 m in Km 3 the deviation between the field measured and the calculated  $E_h$  values is large. We believe that this is due to a mixing with oxygenated water. Possibly traces of oxygen are left in the water already as it is pumped up from the packed off section.

No stable  $E_h$  readings were obtained at 555 m in Km 13. The reason for this is probably the observed variation in the chemical composition of the water.

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