

2504

STEINKAMP

rec'd upon letter dtd

5/18/93

THE ROYAL INSTITUTE OF TECHNOLOGY



THE CHEMISTRY OF DEEP GROUNDWATERS IN
CRYSTALLINE ROCKS

Peter Wikberg

Department of
Inorganic chemistry

S-100 44 Stockholm, Sweden

1987

102.8

9305210274 930518
PDR WASTE PDR
WM-11

Till Händel

Tack för din gåva



**THE CHEMISTRY OF DEEP GROUNDWATERS IN
CRYSTALLINE ROCKS**

PETER WIKBERG

TRITA-OKK-1018

May 25, 1987

**DEPARTMENT OF INORGANIC CHEMISTRY
THE ROYAL INSTITUTE OF TECHNOLOGY
S-100 44 STOCKHOLM, SWEDEN**

ABSTRACT

Equipment for the chemical characterization of deep groundwaters have been developed. This is an integrated system consisting of a mobile field laboratory where groundwater chemical analyses are made and a down-hole measuring sond by which the most sensitive parameters, Eh and pH, of the water are measured in situ.

The analysis of redox sensitive elements are more consistent when analyzed in the field laboratory than analyses made at external laboratories. The other (main) constituents are in good agreement with the results from the external laboratories.

The deep groundwaters encountered at depth in the Swedish crystalline bedrock are mostly of sodium-calcium bicarbonate type, with a TDS value of less than 0.1%. In isolated sections water with a higher concentration of sodium and chloride are found. In areas close to the shore line waters with high sodium, calcium, chloride and sulphate concentrations have been encountered. These waters have a TDS value of more than 1% and are probably of marin origin.

The redox conditions have been studied by in situ field measurements of Eh and analyses of main and redox sensitive elements dissolved in the groundwater. The field observations have also been simulated under well controlled conditions in the laboratory. The deep groundwaters investigated are reducing. The Eh values are determined by equilibria in the water phase which are controlled by the minerals in the rock. On an Eh-pH diagram the measured values lie close to the equilibrium line of magnetite and hematite, and the ferrous/ferric ratio in the silicate mineral solid solutions. The low value of Eh is supported by the fact that no ferric, only ferrous iron and sulphide are the dominant redox sensitive elements present in the groundwaters.

The redox capacity and the rate of the redox buffering reactions seem to be controlled by the initial weathering reactions occurring when the water percolates through the upper parts of the bedrock. Therefore surficial groundwaters mostly have a high concentration of ferrous iron while the deep groundwaters have an appreciable concentration of sulphide and consequently a low iron concentration. The evolution from the surficial to the deep groundwater has involved the precipitation of ferrous iron on the fracture surfaces.

Key words: chemical characterization, deep groundwater, mobile field laboratory, crystalline bedrock, redox conditions, redox capacity, in situ Eh measurements.

CONTENTS

		Page
1	INTRODUCTION	1
2	GROUNDWATER SAMPLING	4
2.1	General	4
2.2	Hydrogeological aspects	4
2.3	Technical aspects	5
2.4	Chemical aspects	6
3	EQUIPMENT FOR SAMPLING AND ANALYSIS	7
3.1	Objective	7
3.2	Hydraulically operated down-hole equipment	7
3.3	Equipment for Eh and pH measurements	9
3.4	The mobile field laboratory	11
3.5	Conclusions	14
4	RESULTS FROM THE SITE INVESTIGATIONS AND THE LABORATORY STUDIES	15
4.1	General chemistry	15
4.2	Redox conditions	19
4.3	Isotope geochemistry	37
4.4	Uranium geochemistry	39
5	DISCUSSION	39
5.1	Natural background	39
5.2	Near field	48
5.3	Radiochemical aspects	48
6	CONCLUSIONS	50
7	ACKNOWLEDGEMENT	53
8	REFERENCES	54

INTRODUCTION

Groundwater is the term used for water existing in the soil and in the fracture systems of the bedrock. Depending on the climate the groundwater table, the depth below ground surface of the groundwater surface, varies from a few meters to several hundreds of meters. In Sweden the groundwater level is mostly at (10 +/-10)m below the ground surface.

The chemistry of the groundwater is influenced by the processes in the soil cover and by the interaction with minerals. The reaction between rock minerals and the infiltrating groundwater may be very slow. If the flux is sufficiently low there might be time for a chemical equilibrium to be established between most of the components of the groundwater and the rock, but if e.g. surficial water has penetrated deep into the rock in a very short time there might be a total disequilibrium in the system, because different reactions need different time to reach equilibrium. For some reactions even the geologic time might not be sufficient for the equilibration. The dissolution and precipitation of calcite is an example of fast reactions as practically all natural groundwater systems are in equilibrium with respect to calcite see e.g. Fergusson (1982) p. 46. An example of the opposite situation is the equilibration of quartz which at low temperatures seems to be a very slow process (see e.g. Siever, 1957, Krauskopf, 1956).

The chemical composition of the groundwater is important for the evaluation of the safety aspects of a nuclear waste repository placed at depth in the bedrock. The corrosion of the waste canisters and the dissolution of the waste form will depend on the chemical composition of the groundwater surrounding the repository. The migration of radionuclides released from the waste form will also be strongly influenced by the chemistry of the groundwater.

In this thesis I will emphasise some fundamental chemical problems which determine the long time safety of the repository system.

The areas of importance can best be understood by looking at the possible chemical interactions in the waste repository and in the surrounding.

- i The groundwater interacts with the minerals in the bulk rock and fracture surfaces giving it a specific chemical composition, altering the rock and precipitating and dissolving fracture filling minerals.
- ii The groundwater interacts with the backfill material changing the composition of the water and affecting the stability of the backfill.

- iii The chemical composition of the groundwater influences the corrosion of the waste canisters.
- iv If the water comes in direct contact with the spent fuel radionuclides the rate of dissolution will depend on the chemical composition of the water.
- v The transport of radionuclides through the near field of the repository and the release of radionuclides to the far field will be influenced by the chemical properties of the groundwater, buffer material, near field rock and possibly also the corrosion and radiolysis products.
- vi The transport of radionuclides through the undisturbed geosphere will be influenced by the chemical composition of the groundwater and structural and chemical properties of fracture and bulk rock minerals.

These different phenomena can be divided into three groups, i.e. natural background aspects (i), near field aspects (ii,iii,iv,v) and radiochemical aspects (vi). These are discussed in chapter 5 in the light of the results from the investigations.

The residence time of the water in the rock is a central issue for the safety evaluation. It should in principle be possible to draw important conclusions on hydraulic conditions from the composition of the groundwater, because many of the weathering reactions in which the groundwater is taking part are slow compared to the water flow. In particular the isotopes should be useful in this respect (see e.g. Davis and Bentley, 1982).

From 1977 and up till now a number of places in Sweden have been investigated in order to collect the necessary geological hydrogeological and chemical data needed for safety analyses of repositories in deep bedrock systems, see Figure 1. Only crystalline rock is considered and in many cases this has been gneisses of sedimentary origin but granites and gabbros are also represented. Core drilled holes have been made at nine sites. Up to 15 holes may be core drilled at one site, the deepest down to 1000 m. In addition to this a number of boreholes are percussion drilled at each site to depths of about 100 m. When possible, the drilling water is taken from percussion drilled holes.

In this thesis I will describe the characterization of the chemistry of the deep groundwaters which has been carried out within the site investigations, supplemented with laboratory studies. This work includes the development of equipment for in situ measurements of Eh, pH and pS, discussed in paper I, which is a part of an integrated system for the chemical characterization of the deep groundwaters, paper II. One issue which is of special interest is the redox conditions of the deep groundwaters, discussed in paper III.

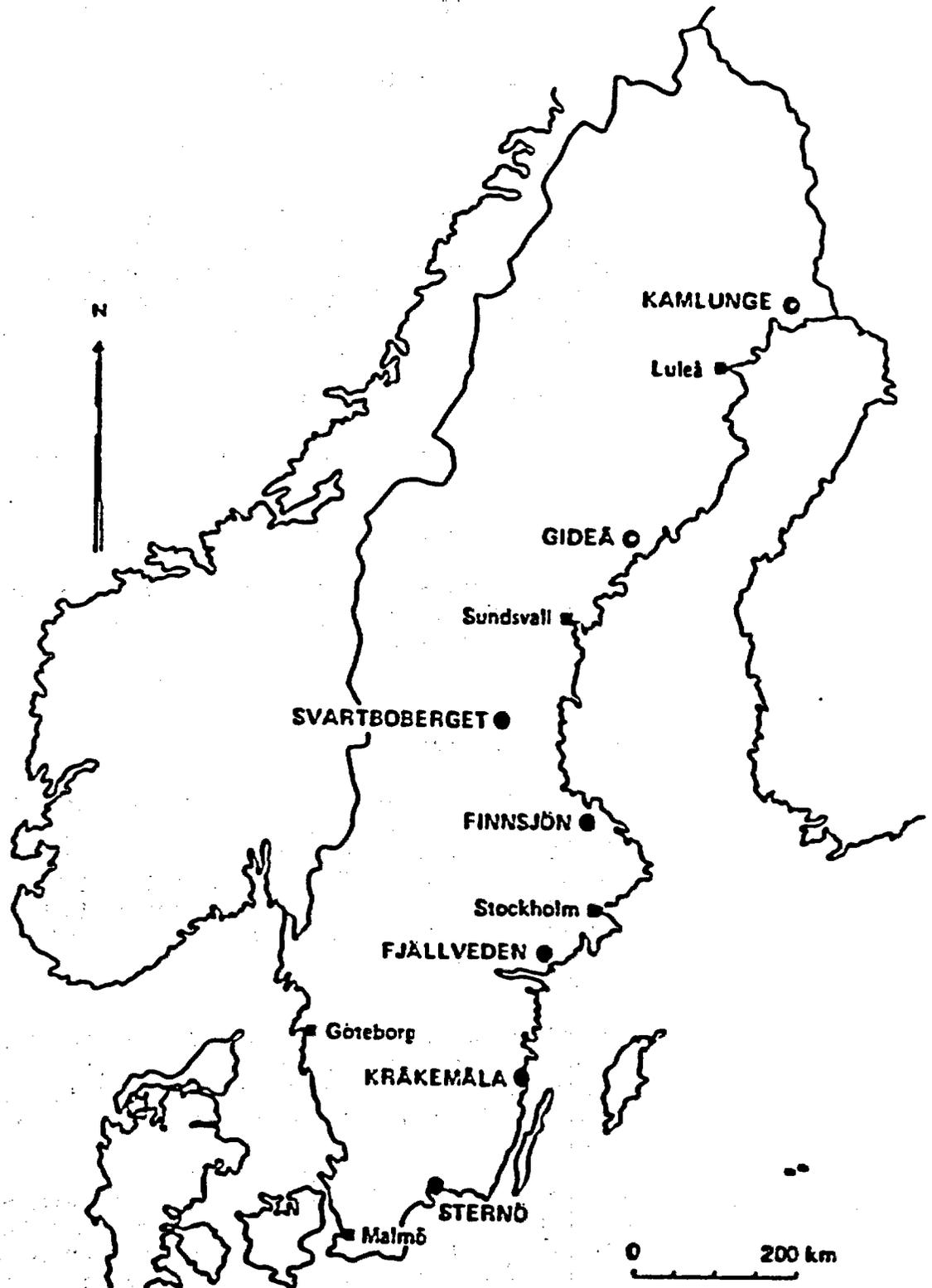


Figure 1. Location of the places in Sweden which have been investigated in order to obtain data for the safety assessment of a repository for a final disposal of spent nuclear fuel in a crystalline bedrock.

2 GROUNDWATER SAMPLING

2.1 General

The sampling of groundwater can in principle be done in many different ways. The method used must be selected so that it will fit the purpose of the investigation and the prevailing (hydrologic) conditions. For groundwater sampling in boreholes there are some aspects which will seriously affect the choice of sampling technique. These are:

- i the hydrogeological situation in the vicinity of the borehole
- ii the number and the hydrology of the water yielding sections in the borehole
- iii the chemical composition of the water

In the following sections the hydrogeological, technical and chemical aspects of importance for the sampling of groundwater will be discussed.

2.2 Hydrogeological aspects

The groundwater flow in the bedrock is determined by the hydraulic conductivity and the hydraulic head conditions. The variations in the hydraulic head is determined by the topography. Therefore the natural groundwater flow is faster in hilly areas as compared to flat ones. The hydraulic conductivity is three to six orders of magnitude larger in the fractured parts of the rock than in the bulk-rock. Consequently the water flow is taking place in the fractured parts of the rock.

Depending on the hydrologic conditions the investigated sites are classified as recharge or discharge areas. In recharge areas the hydraulic head decreases by depth, resulting in a downwards flow of water. In a discharge area the flow is in the opposite direction.

The variations in hydraulic head are mostly small and always regular while the hydraulic conductivity on the other hand, varies irregularly and by several orders of magnitude. Therefore on a local scale the water flow is fast in high conductivity parts of the rock as compared to low conductivity parts. As a consequence of this it is possible to find water which has had a short residence time at considerable depth, down to several hundreds of meters, whereas water with a much longer residence time can be found in low permeability parts of the rock at depths of only a few hundred meters. However, as the over all hydraulic conducti-

vity decreases by depth it is most likely that the waters with long residence times will be found at depth and that the waters with short residence time will be found close to surface.

As one or more boreholes have penetrated the water conducting horizons the hydraulic situation is no longer undisturbed. The boreholes shortcircuit water conducting horizons and will result in a flow of water from sections with a higher to sections with a lower head. In recharge areas this results in a flow of surficial water down the borehole and into deeper laying permeable horizons. In order to avoid these disturbances the water samples should be collected as soon as possible after the holes have been drilled. The different water conducting sections should also be isolated from each other by packers placed around every section which has a hydraulic conductivity of 10^{-8} m/s or higher.

2.3 Technical aspects

The drilling of a borehole in itself is a source of disturbance for the groundwater sampling. The core drilling technique needs large amounts of water to cool the drill bit and to lift the drilling debris. The drilling water which is flushed down is seldom recovered at ground surface. Consequently most of the cooling water is pressed into the more permeable parts of the rock, where it mixes with the groundwater. Our experience is that the water in the high permeability parts of the rock ($K > 10^{-6}$ m/s) is always contaminated by drilling water. This is not surprising since 200 m^3 of drilling water is used for the drilling of a 600 m long borehole. Assuming that the drilling water is mixed with a ten fold volume of groundwater the affected volume is 2000 m^3 . In order to be able to measure the amount of drilling water in the water samples the drilling water can be tagged with a tracer. Uranine is a dye well suited for this purpose mainly because it can be analyzed down to a concentration of less than 1 micro gram/litre by a simple fluorimeter.

Water conducting sections are normally located through hydraulic conductivity measurements. This is a time consuming and expensive procedure which is not only made for the purpose of locating suitable sampling sections of a borehole. Another method, tube wave seismics, has been tested as a quick method of locating water conducting sections. The limited experience indicates that the method is well suited for this purpose.

Contamination with drilling water can be avoided by the use of air flush percussion drilling instead of water cooled core drilling. The compressed air will empty the borehole from water, thus reducing the hydrostatic pressure in the borehole. The result of this will be that water flows from the rock mass into the borehole, i.e. in the opposite direction to what is the case in core drilling. This technique has been tested at Finnsjön. The results are preliminary so far but it seems as if this is a viable

technique for the sampling of highly conductive zones with a hydraulic conductivity above 10^{-6} m/s which are otherwise always contaminated by drilling water. Such fractured zones are normally found in the uppermost 100 meters of the bedrock. At great depth when the air compressors do not manage to keep the borehole free from water air intrudes into the water conducting fracture systems. This intrusion has a much worse effect on the chemistry than the mixing with drilling water. In such situations the normal core drilling technique is preferable.

The pumping of groundwater from a borehole creates an artificial pressure gradient. Especially if the sampling section has a low conductivity the artificial gradient is considerably larger than the natural ones. This will result in a flow of water towards the pump from all directions. In this way a mixed water is pumped to the surface. A severe example of this type occurs when the sealed off section is completely tight and water leaks into the section from above or below the packers.

The mixing of water through the borehole can be minimized if the drilling and sampling is done as a stepwise procedure where the drilling is interrupted at regular intervals or when conductive levels are penetrated. In such situations the sampling is performed below a single packer, placed as close as possible to the bottom of the hole.

2.4 Chemical aspects

The chemical composition of the groundwater is different from surface waters e.g. with respect to the redox condition. Because of this it is necessary to collect the samples without exposing the water to the oxidizing air. Another factor of importance is also the pressure decrease to which the water is subjected when it is pumped up from great depth. Dissolved gases will escape and cause changes in the equilibrium situations, e.g. the pH of the water is increasing when the dissolved carbon dioxide escapes.

We have encountered the largest difficulties to obtain pure samples for the analyses of gases, trace constituents and radioisotopes of atmospheric origin. However, it should be noted that in cases of minor contamination of the deep groundwater with water from the surface or near surface the samples are still representative as far as major components are concerned. This is also true for the trace components which are specific for the deep groundwaters.

3 EQUIPMENT FOR SAMPLING AND ANALYSIS

3.1 Objective

In an early stage of the site investigations it was obvious that an equipment specially designed for these investigations had to be designed. This equipment was developed to meet the following requirements:

- * Main constituents in the groundwater should be analyzed immediately and the results used for guidance of the drilling and sampling program.
- * Redox sensitive trace elements should be analyzed in the field
- * Eh (the redox potential) should be measured in situ

The entire equipment meeting these requirements consists of a mobile field laboratory for analyses of main constituents and redox sensitive trace elements, a down-hole measuring sond equipped with electrodes for Eh, pH and pS measurements connected to a pump and packer system through an umbilical hose and a downhole gas sampling unit. This integrated equipment is described by Almen et.al. (1986) and in paper II. It is also illustrated in Figure 2. Only the main features will be described here.

3.2 Hydraulically operated down-hole equipment

The pump and packer systems are hydraulically operated through pressure tubings in an umbilical hose. The packers used to seal off the sampling section in the borehole, consist of rubber sleeves which are inflated and pressed towards the walls of the borehole. The packers are inflated with a pressure exceeding the hydrostatic one by 0.8 MPa. The groundwater pump is operated with pressure pulses of 3 MPa.

The unit for collecting the gas samples is also hydraulically operated. Evacuated stainless steel sample cylinders are filled when a needle penetrates a rubber plug at the top of them. The cylinders can be emptied in the same way as they have been filled. Consequently there is no risk of contaminating the samples when the gas content is analyzed.

The umbilical hose consists of nine polyamid pressure tubings, three copper conductors with a cross section area of 6 mm² and a 24 conductor signal cable. The multihose is wound on a reel, making the raising and lowering of the equipment convenient and fast. In the centre of the multihose there is a steel wire taking

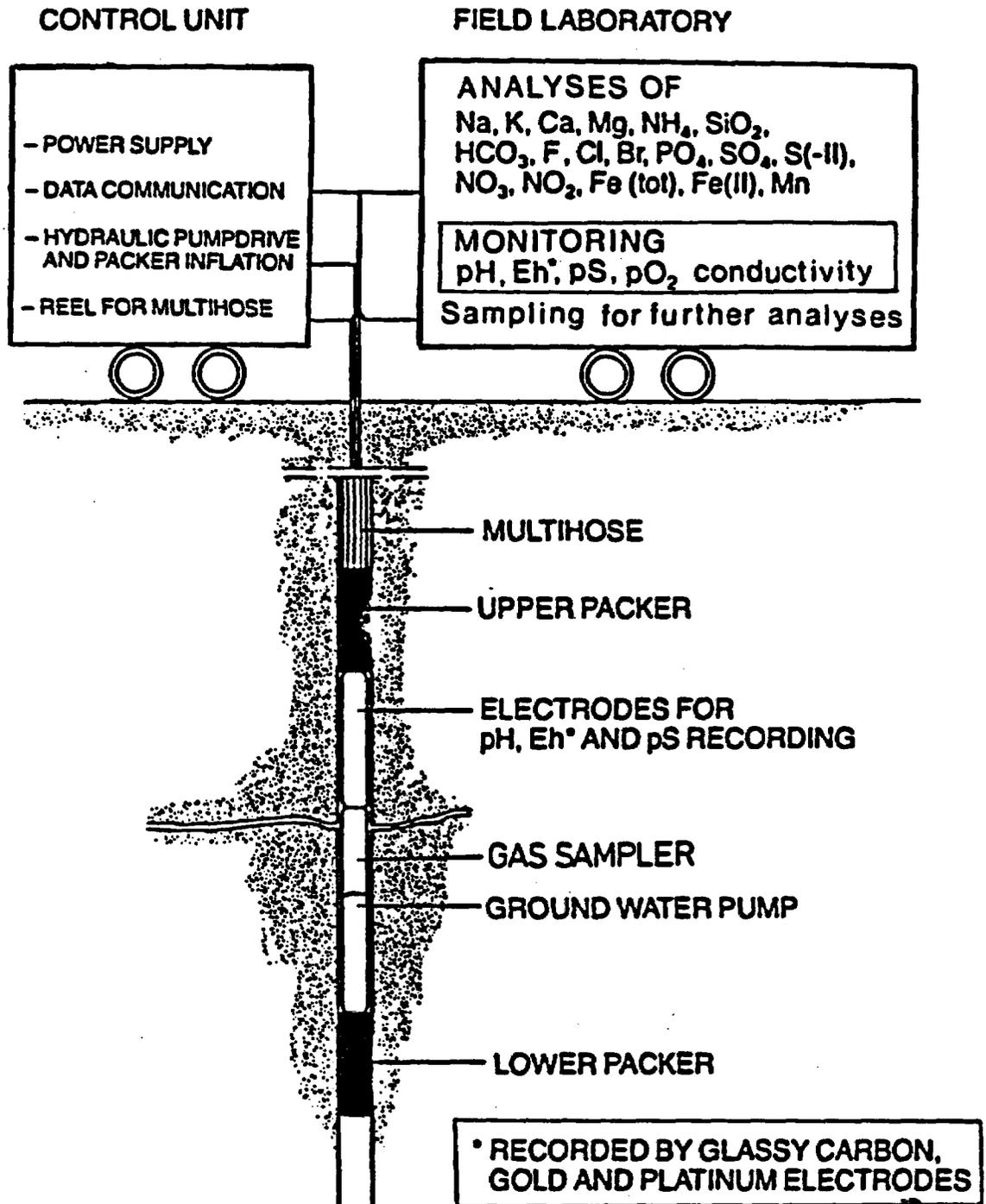


Figure 2. A schematic illustration of the integrated mobile field unit which is used for the chemical characterization of the deep groundwaters sampled from isolated sections in slim boreholes. The water passes through an unbroken plastic liner all the way from the pump to the outlet in the field laboratory.

up the load. The relatively low density of the umbilical hose as compared to the conventionally used steel pipes makes it light in the water filled holes, even when the deep levels are sampled.

3.3 Equipment for Eh and pH measurements

Reliable Eh measurements are notoriously difficult to make and this area is perhaps the one where most of the efforts have been made in order to improve the sampling technique. The different instrumentations and methods which have been tried are discussed in some detail in paper I. Therefore they will only be briefly mentioned here:

- * in situ measurements in open boreholes
- * on surface measurements in cells through which the pumped up water flows
- * in situ measurements in packed off sections in the borehole from which water is pumped out

The in situ measurements in open boreholes were not reproducible and the attempt to measure Eh values in this way was abandoned.

The measurements in the surface flow through cell indicated that reliable values could be obtained even though it took a long time for the electrodes to reach a stable level. In the field investigations proceeding the KBS-3 report (KBS-3, 1983) the Eh and pH were measured in this way. The measuring cell was frequently opened for calibration of the sensors. This resulted in oxygen contamination and because of this there was never time enough for the Eh electrodes to reach a constant level. Also interruptions in the pumping had great influence on the Eh electrode readings.

In order to eliminate these disturbances we constructed a down-hole measuring system which should prevent accidental contamination by oxygen. This equipment consists of a down-hole flow through cell with electrodes connected to an electronics compartment for measuring the potentials and transmitting the signal to a surface computer. The setup is schematically illustrated in Figure 3. The surface flow through cell is principally the same as the down-hole one. The entire measuring system is described in detail in paper I. It is also discussed together with the redox conditions of the deep groundwaters in paper III.

The pH is measured by a pressure equilibrated glass electrode and the sulphide concentration is measured by a silversulphide membrane or a silver/silversulphide electrode. The reference is a gel filled triple junction silver/silverchloride electrode. The down-hole electrodes are all specially designed for our measurements while the electrodes in the surface flow through cell are all commercially available.

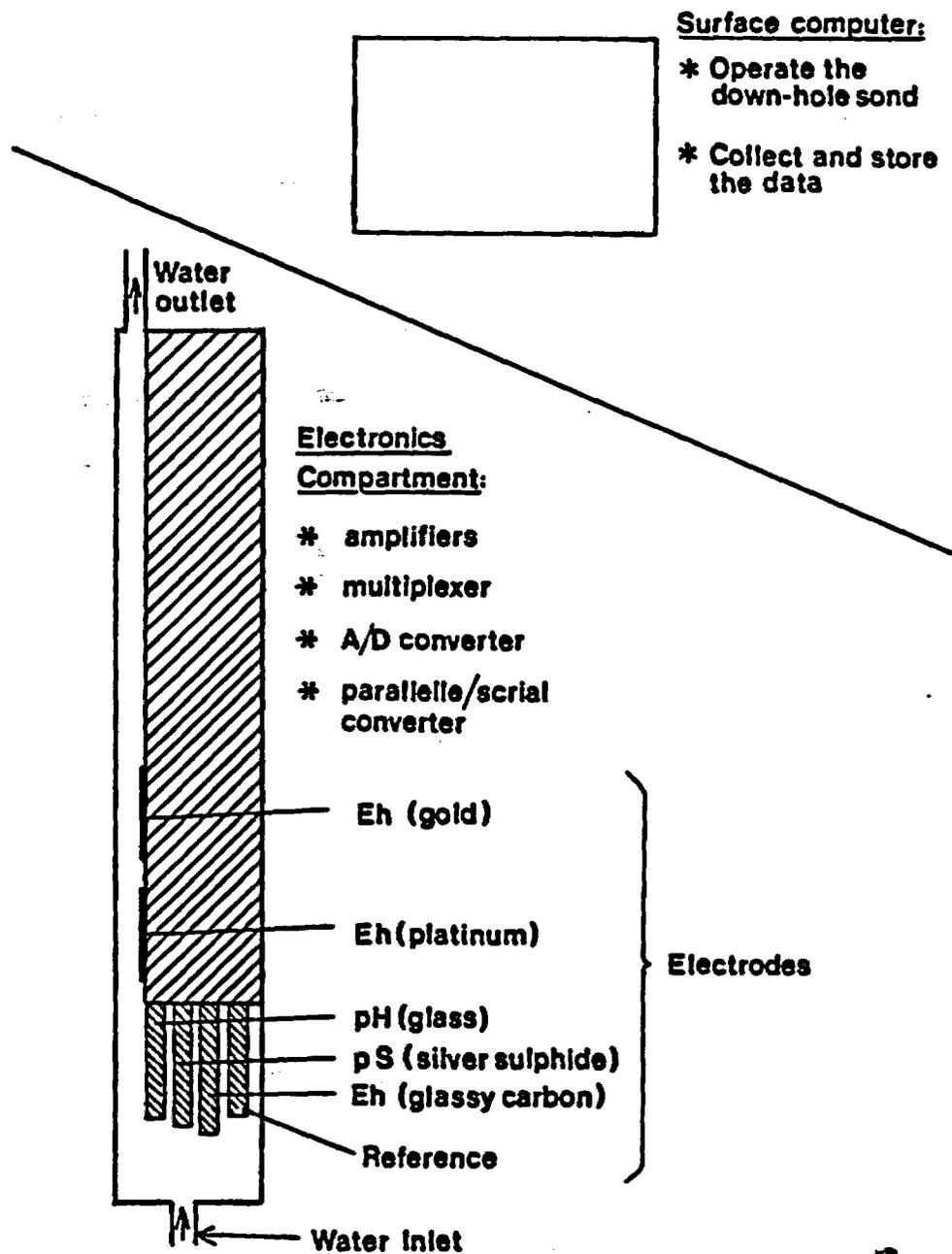


Figure 3. A schematic illustration of the equipment for down-hole Eh, pH and pS(sulphide) measurements. The down-hole sond contains electrodes and electronics which is operated from the surface computer system. The sond is connected to a pump which passes the water up to the surface.

Each of the electrodes is connected to a separate amplifier. In this way very little current is drawn through the electrodes. The amplifiers are connected to a multiplexer which is operated from the surface computer. The multiplexer connects one of the electrodes to an A/D converter. The digital word is then converted into serial form and sent to the surface computer as a frequency shifted signal.

3.4 The mobile field laboratory

The water from the borehole is lead directly into a field laboratory. In this way the water can be analyzed without coming into contact with the atmosphere. In the field laboratory the water passes through cells where the Eh and pH values measured down-hole are checked. The conductivity and the dissolved oxygen content of the water are also measured in these cells. The cells are placed in a refrigerator which is kept at the same temperature as in the down-hole sampling section.

The main ions and redox sensitive trace constituents are also analyzed in the mobile laboratory. The main constituents are used for guiding the investigation and are thus needed immediately. The redox sensitive elements have to be analyzed immediately in order to avoid reactions between the atmospheric oxygen and the reducing elements in the water samples.

The water samples are also analyzed for uranine which is used as a tracer in the drilling water. In this way contamination by drilling water can be traced down to concentrations of less than one per mil in the sampled water.

The groundwater pumped up into the laboratory passes a 0.45 micron online filter before it is collected for analyses. In special cases the water is filtered through membrane filters place in series with 0.4, 0.2, 0.05 and 0.05 micron pore sizes. The particle fractions collected on these filters are analyzed for Fe, Al, Mn, S, Ca and Si. The filtrate is analyzed for total and ferrous iron.

The main instruments/techniques used for the field analyses are an ion chromatograph, a spectrophotometer and titrations. Methods, elements and the detection limits are summarized in the Table 1.

Table 1. Methods and detection limits of the analyses which are performed in the field laboratory.

Method	Element	Detection limit (mg/l)
IC	Na	0.1
IC	K	0.1
IC/SP	NH ₄	0.1/0.005
IC	NO ₃	0.05
IC/SP	NO ₂	0.05/0.001
IC	F	0.1
IC	Cl	0.1
IC	Br	0.05
IC/SP	PO ₄	0.2/0.002
IC	SO ₄	0.05
SP	Fe _{tot} /Fe ²⁺	0.005
SP	Mn	0.01
SP	SiO ₂	1
SP	S ²⁻ tot	0.01
Tit	Ca	2
Tit	Mg	0.4
Tit	HCO ₃	0.6
SF	Uranine	<0.1% drilling water contamination

IC = ion-chromatograph
 SP = spectrophotometer
 Tit = titration
 SF = spectrofluorimeter

The trace constituents, isotopes and gases which are analyzed at external laboratories are listed in Table 2.

The field laboratory is schematically illustrated in Figure 4.

Table 2. Trace elements, isotopes and gases are sampled for external analyses.

Element	Sample Volume	Method
Al		
B	250 ml	AA/AE
Ba		
Sr		
TOC	1 l	
U		
Ra	10 l	
Rn		Activation Analyses
Th		
^2H	100 ml	MS
^3H	1 l	Natural Decay
^{13}C		MS
^{14}C	130 l	Natural Decay
^{18}O	100 ml	MS
$^{234}\text{U}/^{238}\text{U}$	5 l	
Gases	50-200 ml	Gaschromatograph
Fulvic and Humic Acids		Chemical Characterization
AA = Atomic Absorption AE = Atomic Emission MS = Mass Spectrometry		

An extensive calibration/standardization procedure has been made in order to check the results from the field laboratory against two other laboratories (Axelsen et. al, 1986). The results of this work is also presented in some detail in paper II. All the analyses made in the field laboratory were found to give correct results. It was quite clear from this study that the iron and sulphide/sulphate analyses must be made immediately in order to be reliable. The acidification of the samples do not prevent ferrous iron from being oxidized even if the reaction of course is slower than in a neutral solution.

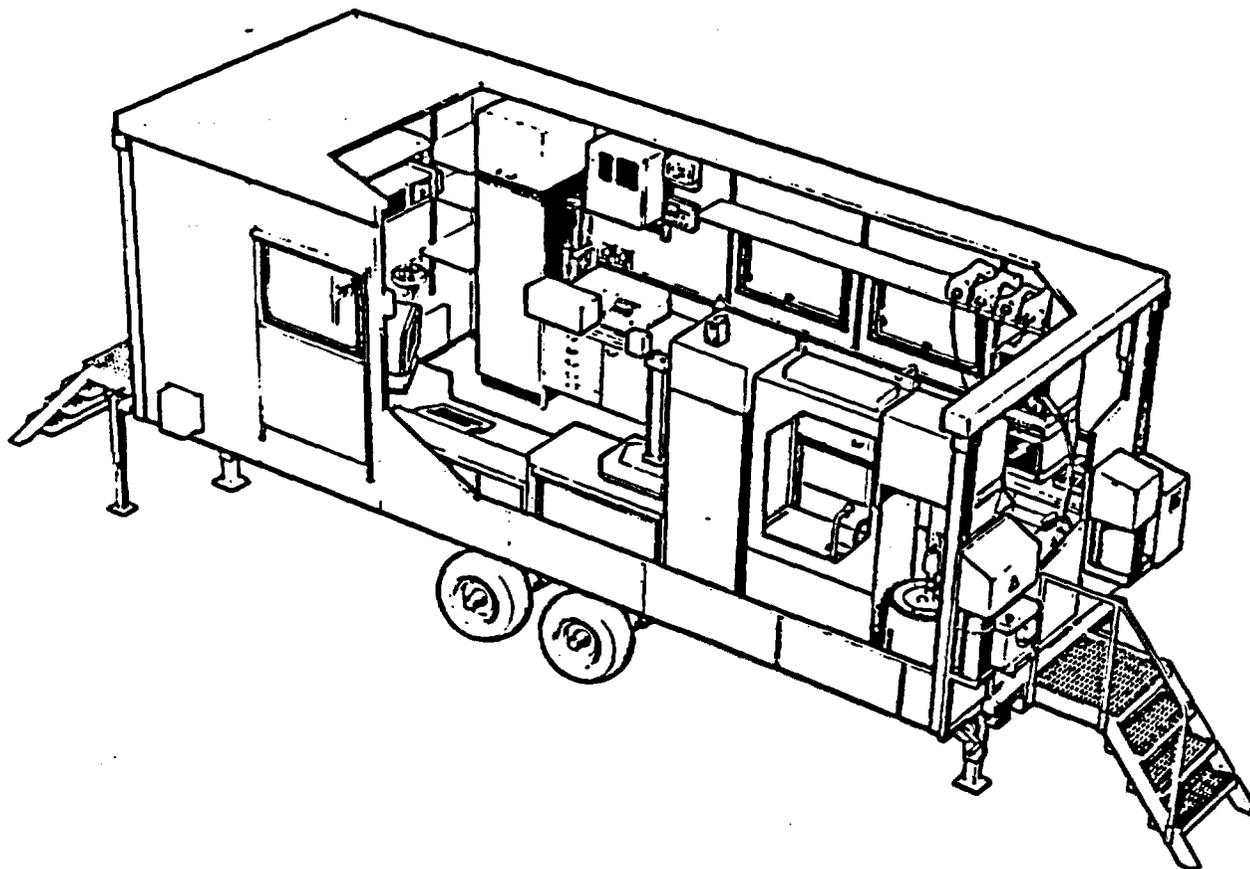


Figure 4. An illustration of the mobile field laboratory with analytical instruments on both long sides used for cation, anion and redox sensitive trace element analyses.

3.5 Conclusions

In conclusion the advantages with the new equipment can be summarized as follows:

- * Sensitive parameters such as pH, Eh and Fe(II) are more accurately obtained by analyses in situ in the field laboratory.
- * Drilling water markers and main constituents are immediately analyzed. Borehole sections which are too heavily contaminated can quickly be identified and avoided all together or, alternatively be the subject to only limited sampling.

- * Longer packer sleeves and controlled pumping prevents water from the borehole to bypass the packers.

The mobile field laboratory was first tested in Fjällveden in 1984. It has been in regular use since then. The entire equipment is described in more detail in paper II.

4 RESULTS FROM THE SITE INVESTIGATIONS AND THE LABORATORY STUDIES

4.1 General chemistry

The sampling is continued at every sampled section until representative water samples are collected. The criterion for a representative water sample has been stable Eh values and constant composition of the main elements. In practice this has been obtained after pumping periods of about two weeks. In some cases it has not been possible to obtain representative samples due to a severe contamination by the drilling water. Such sections are only sampled for main constituents and are then abandoned.

The results of the analyses performed in the field laboratory are given in Table 3. Only major and redox sensitive elements are included in the table.

Table 3. Chemical composition of the groundwaters analysed with the mobile field laboratory. All concentrations are given in mg/l.

Bore hole	level m	Na	K	Ca	Mg	HCO ₃	Cl	SO ₄	S-II	Fe _{tot}	Fe ²⁺	pH	Eh mV	Type
Fj 2	468	36	1.4	27	3.0	182	3.7	2.0	0.2	0.65	0.65	6.9	-220	A
Fj 7	722	300	1.3	40	0.2	16	470	0.5	0.6	0.005	0.004	9.0	-350	C
Kl 1	406	45	1.0	14	2.3	78	45	1.8	0.1	0.013	0.012	8.2	-305	B
Kl 2	326	28	1.1	31	1.0	137	17	0.1	0.08	0.140	0.134	7.6	-290	B
	741	38	1.6	16	2.0	99	23	0.1	0.24	0.045	0.039	8.2	-340	B
	761	12	3.0	23	4.0	106	7	0.5	0.03	0.350	0.345	8.0	-290	A
	860	65	1.6	8.3	1.8	102	51	1.5	0.12	0.043	0.041	8.1	-300	B
Kl 9	696	16	1.3	29	3.0	120	6	4.4	0.02	0.096	0.094	7.6	-275	A
Fi 9	94	410	6.2	101	16	286	670	100	0.22	0.590	0.580	7.5	-245	D
	182	1050	17	708	78	150	2900	220	0.24	0.915	0.915	7.3	-220	D
	360	1600	8	1900	110	33	5200	300	0.01	0.310	0.310	7.7	----	D
FIB1	71	23	3	76	6	220	61	8	<.01	9.01	8.88	6.9	+ 40	A
	234	650	9	320	40	260	1500	140	0.03	0.437	0.432	7.7	-270	D
	439	1700	15	1600	120	48	5500	400	<.01	0.01	<.005	7.0	+400	D
HK 1	89	1500	7	950	170	75	4100	340	<.01	0.470	0.465	7.5	-140	D
HK10	140	1500	16	1100	250	104	5000	490	<.01	5.25	5.25	7.5	+ 50	D

Fj = Fjällveden Kl = Klipperås Fi = Finnsjön HK = Forsmark

From Table 3 it can be seen that there is a great variation in the composition of the different waters. According to the composition they can, however, be grouped as indicated in the last column of Table 3.

Type A is a typical granitic water normally found at depths varying from several tenths of meters down to several hundreds of meters, depending on the local hydrogeology; recharge/discharge, conductive zones etc. Calcites have been dissolved and part of the calcium ions have been exchanged with sodium from sodium rich minerals (Jacks, 1973). The concentration of other elements is often very low. The type A waters are neutral to slightly alkaline, depending on whether the carbonate system is open to input of carbon dioxide or not (Garrels and Christ, 1965 p. 74).

Type B waters have had a longer residence time in the rock than the type A waters. The weathering reactions and perhaps some other processes have given the waters a contribution of sodium and chloride. The pH of these waters are in general slightly higher than that of the type A waters.

Type C waters have been isolated in the rock for long time periods. The interactions with the minerals in the rock have given them a high pH and high concentrations of sodium, calcium and chloride. The high pH and calcium concentrations of the water have resulted in precipitation of calcite and hence a decrease in the bicarbonate concentration.

Type D waters have probably a marine origin. These waters are characterized by a neutral pH and high concentrations of sodium, calcium, chloride and sulphate. The main difference between the type C and type D waters is, besides the amounts of total dissolved solids also the pH and the sulphate concentration.

The boreholes F19 and FiB1 are located in a discharge area while all the others are located in recharge areas. The discharge area Finnsjön was covered by the Litorina Sea between 5000 - 7000 years ago. A probable explanation for the salinity at Finnsjön is therefore that the seawater which seeped into the rock during this time has been isolated by a freshwater pillow. The freshwater is separated from the saline water by a subhorizontal fracture zone. The fracture zone itself holds some mixed water, but due to the difference in density there is very little mixing between the freshwater and the saline water above and below the zone.

The boreholes HK1 and HK10 are located in the bedrock under the Baltic Sea. It is therefore not possible to define the surrounding as a recharge or discharge area because the sea above has levelled out all the local gradients. However, it is interesting to see that the saline water in the boreholes F19, FiB1, HK1 and HK10 all have fairly similar composition, indicating a similar origin.

From Table 3 it can also be seen that the type A, B and C waters can exist at any depth. However, there is a good correlation

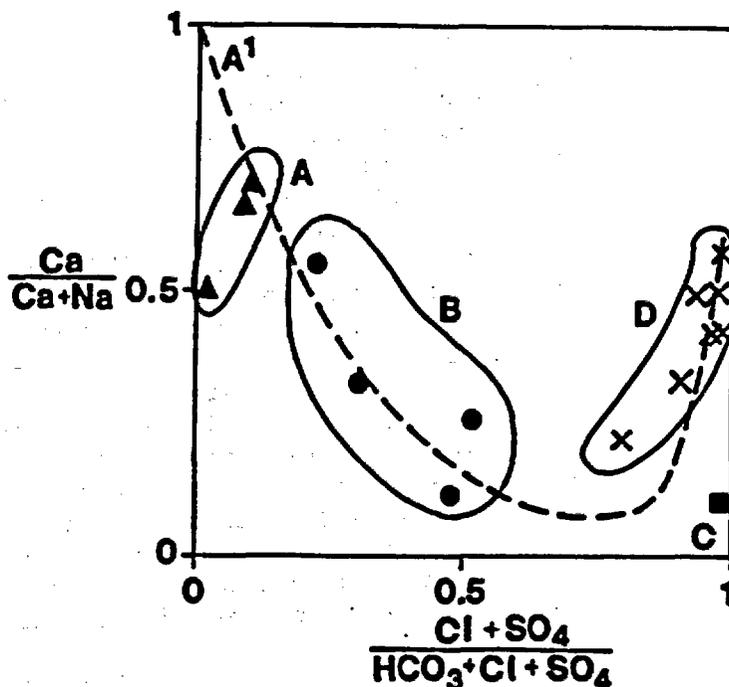


Figure 5. A modified Piper plot based on the concentration of main constituents in the water samples. The letters A to D represent different categories of water which have different residence time in the bedrock.

between the hydraulic conductivity of the rock and the type of water found in it. The A type waters are all sampled in highly water conducting fracture zones whereas the type C water is extracted from the low permeability parts of the rock. The type B waters are mostly obtained from discrete fractures in the rock.

In Figure 5 the waters from Table 3 are plotted on a modified Piper diagram. It can be seen from the figure that the waters of the different categories fall close together in the diagram. The figure also includes the "evolution" line of the groundwaters, indicating the relative residence time of the water in the rock. Water percolating the soil cover takes up carbon dioxide and dissolves calcite when it enters the bedrock (A'). The slower weathering reactions, give the water an increasing sodium chloride character (A → B → C). As the salinity increases there is often a tendency of increasing calcium ratios (C → D). However, in this case the type D waters are expected to have an origin different from the others. It is important to understand how mixing effects will appear in the Piper plot. Water with a composition given by any point on a straight line between two end members of given composition may be obtained from a mixing of water from the end members. In the same way any point within a triangle can be obtained by mixing of water with the characters described by the corners of the triangle.

Even though the waters are of different type, they are all strongly reducing. This is also in good agreement with the total and ferrous iron analyses which indicate that all the iron in the waters is in the ferrous form. Many of the waters also contain detectable amounts of sulphide. There is one exception to this, the F1B1 borehole where both the most shallow and the deepest of the sampled sections gave positive Eh values. The strongly oxidizing conditions at the 439 m level is due to the presence of considerable amounts of oxygen in the water. This is due to the air flush drilling technique tested for this borehole. When the effect of the booster air compressor is no longer sufficient to keep the borehole free from water the pressure at the bottom of the hole increases, which results in a flow of air into the water conducting fracture systems. Large quantities of air can be dissolved due to the high pressure at depth. At 439 m depth 43 times more air can be dissolved than at the same temperature at atmospheric pressure. The positive Eh of the most shallow level is in good agreement with the pH and iron content of the water, assuming that the water is saturated with respect to ferric hydroxide.

All the water which is sampled has passed a 0.45 micron online filter. The amount and the distribution of the particulate material in the water was estimated by filtering through 0.4, 0.2, 0.05 and 0.05 micron membrane filters placed in series. These filters are analyzed for iron, aluminium, calcium, silica and sulphur by an X-ray fluorescence. The results from such analyses show that the amounts of particulate material is in general a few tens of micrograms/l. However, there does not seem to be any systematics in the distribution between the different elements. The reason for this might be that the particulate material results from the mixing of water of different origin. This hypothesis is based on the results from a redox relaxation experiment where the rate of reduction of dissolved oxygen was tested in situ in a field experiment. Guided by results from laboratory studies the test was made in the following way:

1000 l of groundwater was pumped out of a sealed off section at the 468 m level of the borehole Fj2. The water was analyzed in the mobile field laboratory while it was pumped up. The water was aerated, tagged by uranine and stored until the iron hydroxide had precipitated. Afterwards this water was pumped back into the packed off section. Two weeks later the pumping of water was started again, including the analyses in the field laboratory. The results obtained on these two pumping occasions agreed with the results previously reported for the 468 m level of the borehole Fj2 in Table 3. However, the water contained only 4% of the water which had been pumped down. Furthermore the amount decreased rapidly down to 0.2 % within a few days. The explanation to this is that the water in the packed off section had flowed away due to the natural hydraulic gradient. Because of the very low portion of the aerated water it was not possible to see any effects on the Eh electrodes, which rapidly levelled out at a value of -250 mV. The conclusion to be drawn out of this is that the experiment should be repeated in a section with a much lower conductivity.

During the experiment the water was filtered through the filters of different pore size. The results of the analyses of these filters are presented in Figure 6. The three first analyses are made on the water sampled in the first pumping period. The concentrations are constant with small variations between the samples. The other analyses are made on the water pumped out of the section the second time. From the figure it is obvious that the intrusion of the oxidized water has had a dramatic effect on the contents of particulate material in the water. The Al and Si concentrations are not affected while the Fe content is high the first two days and then decreases to "initial" values. The sulphur content is the one which has increased most. It also takes a long time before it decreases to the level of the undisturbed waters. The explanation is that the oxygen in the water which was pumped down reacts with the sulphide in the water oxidizing it to sulphur. If this is a common situation the amount of sulphur collected on the filters might be used to detect the mixing of small portions of oxidizing waters with the reducing deep groundwater.

4.2 Redox conditions

Eh measurements

The possibility of direct Eh measurements in poorly buffered natural waters has been frequently discussed in the literature. Part of this discussion is reviewed in paper III and is therefore not repeated here. However, when we started the investigations we controlled the behaviour of the inert electrodes in solutions which had a good buffering capacity, due to the presence of solid material, but a low concentration of free ions in the solution. To 0.01 mol/l and 0.05 mol/l carbonate-bicarbonate buffer solutions Fe^{2+} and Fe^{3+} was added in quantities large enough to cause precipitation of $\text{Fe}(\text{OH})_3$ and FeCO_3 . In this way the free concentrations of Fe^{2+} and Fe^{3+} are controlled by the free carbonate concentration and the pH, both of which are well defined in a carbonate-bicarbonate buffer solution. The Eh of these solutions can easily be calculated from the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio and compared with the experimentally obtained values. Four different experiments in both of the two solutions gave Eh values of $-(349 \pm 9)\text{mV}$ and $-(384 \pm 11)\text{mV}$ for the 0.05 and 0.01 mol/l carbonate-bicarbonate solutions respectively. The theoretical values are -348 mV and -389 mV respectively. These experiments and calculations are described in more detail by Wikberg et al (1983).

The down-hole Eh measurements turned out to be more stable than those made on the surface. Figure 7 illustrates the difference between the Eh values measured on the surface and down-hole.

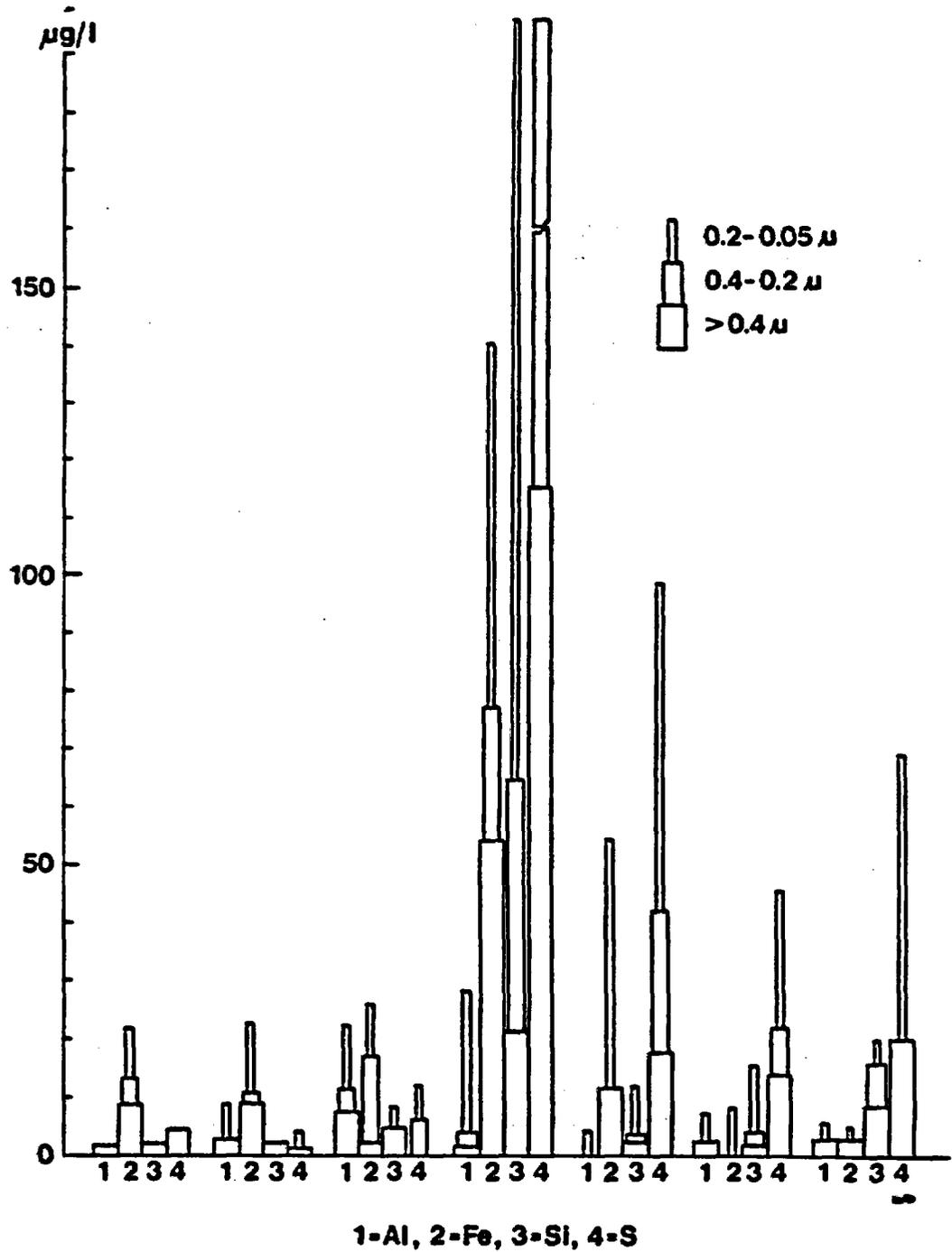


Figure 6. The concentration and size distribution of particulate material filtered off the groundwater in a redox relaxation experiment in Fjällveden 2, 468 m level.

The shaded areas in Figure 7 include readings of all three electrodes, gold, platinum and glassy carbon. The difference between the electrode readings is smaller down-hole than on the surface. However, the surface electrodes also approach the values of the down-hole electrodes, even though this takes a long time. One observes, that the pump failure indicated in the figure has only a marginal effect on the down-hole electrodes, whereas the surface electrodes are strongly affected. This is caused by oxygen diffusion into the surface cell, and the effect of this on the redox processes on the electrodes and in the solution. The down-hole electrodes are not affected because of the total absence of oxygen in the surrounding groundwater.

The most important conclusion to be drawn from Figure 7 is that after the initial equilibration process the electrodes are constant without any drift even in the time scale of several months.

In Figure 8 a plot of Eh versus time is presented for another type of water. A comparison between the two figures indicate that the initial behaviour of the electrodes differ. The most likely reason for this is the large differences in the chemical character between the two waters. c.f. Table 4. The water described in Figure 8 has a high pH and a high sulphide concentration and a correspondingly low iron concentration. Because of the low iron concentration the time needed for the downhole electrodes to reach equilibrium is longer than in the case where the iron concentration is high, Figure 7. On the other hand the difference in the behaviour of the surface and down-hole electrodes are smaller in Figure 8 than in Figure 7. An explanation to this might be that the residual oxygen which causes the disturbances of the surface electrodes is reduced faster in the high pH-sulphide water than in the neutral pH-iron water.

Table 4. The chemical composition of groundwater from boreholes Fjällveden 2, at 468m and with high hydraulic conductivity and Fjällveden 7, at 722 m and low hydraulic conductivity. All concentrations are given in mg/l.

Analysis	Fj 2	Fj 7	Analysis	Fj 2	Fj7
pH	6.9	9.0	Eh(mV)	-220	-350
HCO ₃	182	16	Na	36	300
Cl	3.7	470	K	1.4	1.3
F	0.6	6.2	Ca	27	40
SO ₄	2.0	0.5	Mg	3.0	0.2
S(-II)	0.2	0.6	Mn	0.2	.007
NO ₃	<.001	.009	Fe(II)	1.0	<.005
NH ₂	<.001	<.001	NH ₄	.05	.04

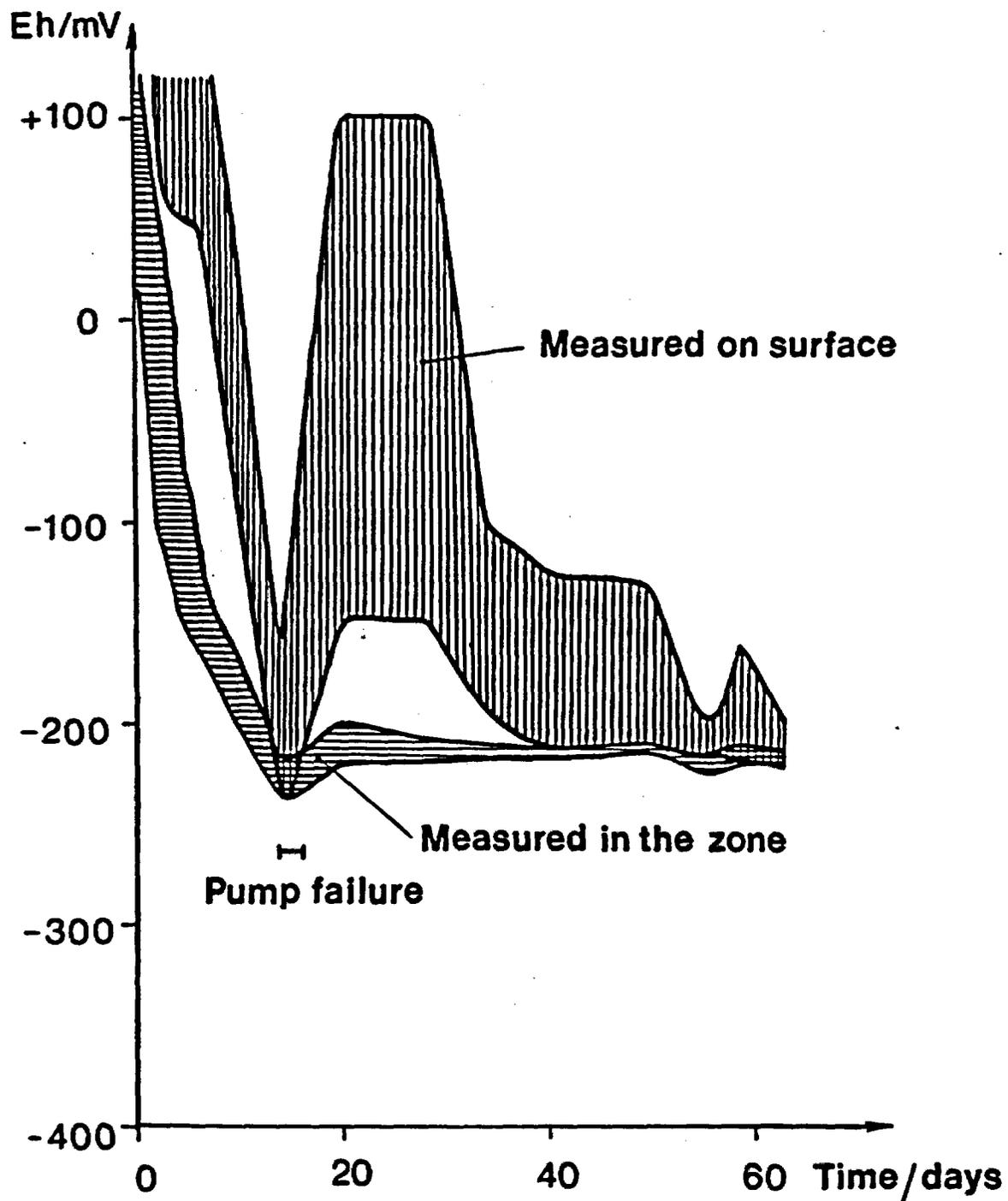


Figure 7. Eh versus time plot of the surface and down-hole measured values. Both measurements are made in continuously flowing water. The dashed fields represent the largest differences between the potentials of the gold, platinum and glassy carbon electrodes. The length of a pumpfailure period is indicated.

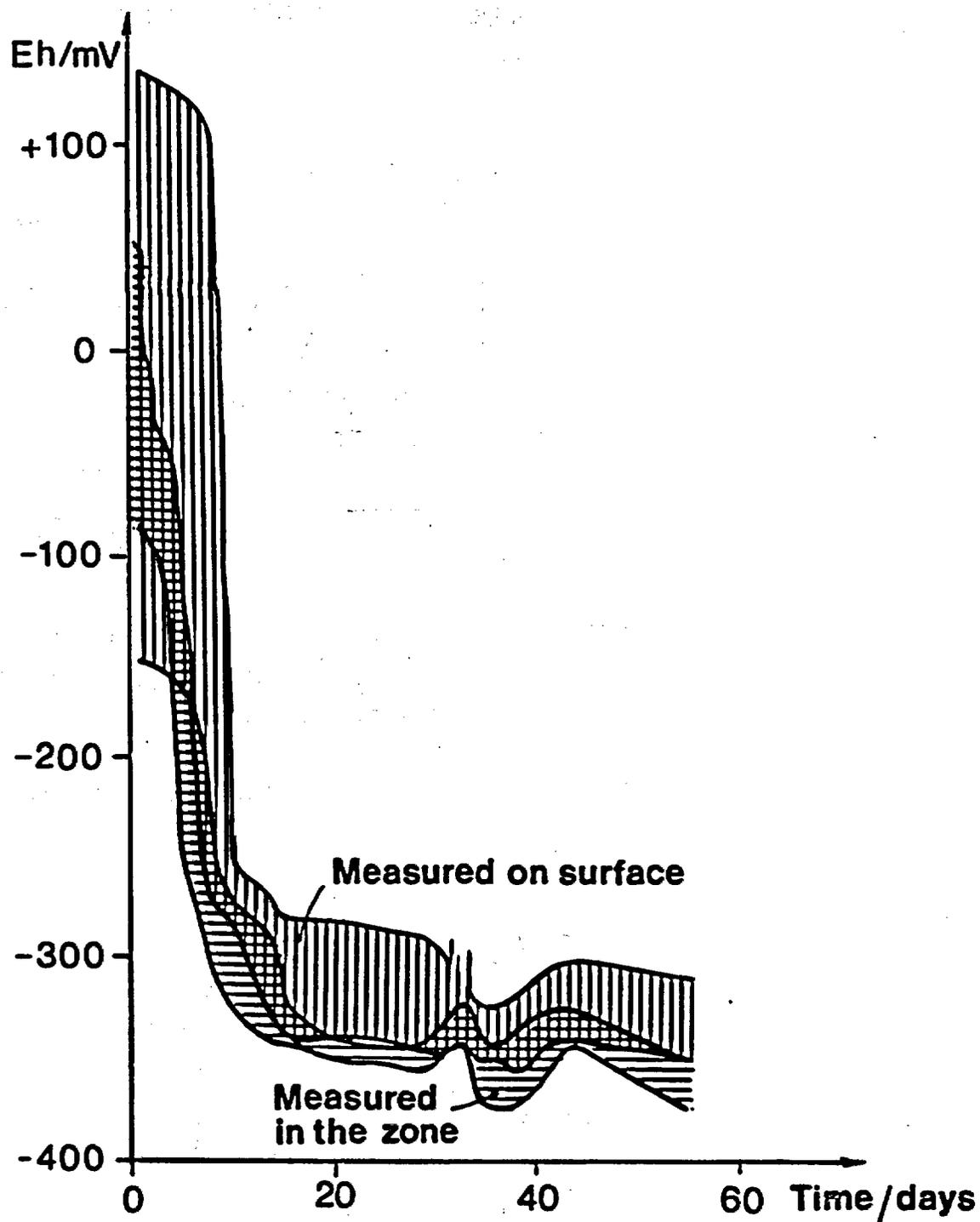


Figure 8. Eh versus time plot of the surface and down-hole measured values. Both measurements are made in continuously flowing water. The dashed fields represent the largest differences between the potentials of the gold, platinum and glassy carbon electrodes.

REDOX POTENTIALS MEASURED ON SURFACE

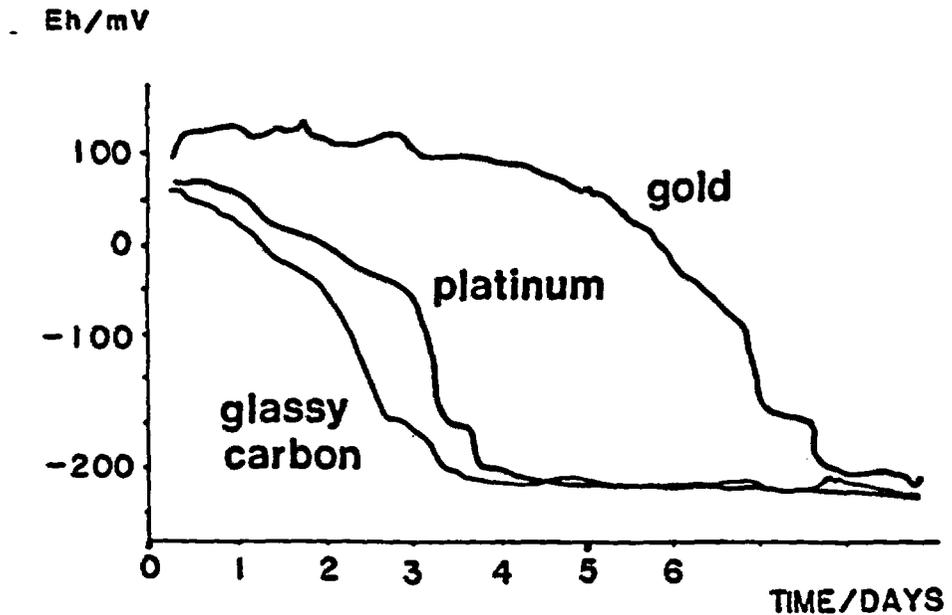


Figure 9. Eh versus time plot of the gold, platinum and glassy carbon electrodes in the surface flow-through-cell at the beginning of a pumping period in borehole Pjällveden 2 at 468 m level.

REDOX POTENTIALS MEASURED ON SURFACE

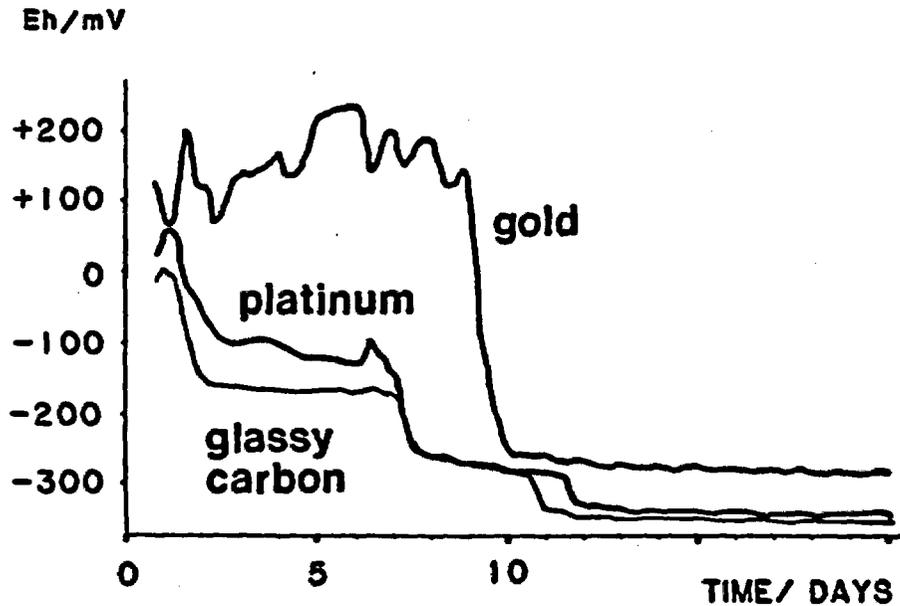


Figure 10. Eh versus time plot of the gold, platinum and glassy carbon electrodes in the surface flow-through-cell at the beginning of a pumping period in borehole Pjällveden 7 at 722 m level.

In some cases mixed potentials have been identified. An example is the effect of small amounts of dissolved oxygen on the electrode readings. This effect is easy to spot because the electrodes always respond in the same way to small portions of oxygen dissolved in the water. Figure 9 and Figure 10 show how the electrodes in the surface flow through cell respond in the beginning of a sampling period. Even though the examples are taken from two different type of waters, see Table 4, the Eh electrodes respond in the same way. The gold electrode always gives a value which is much higher than the other electrodes. The gold electrode is also the one which gave the largest response to the pump failure in Figure 7. This indicates that the electrode processes on gold are more influenced by oxygen than on platinum and glassy carbon. The concentrations of oxygen that causes these changes is not exactly known. However, the results plotted in Figure 11 indicate that concentrations well below the detection limit of the oxygen sensor, 0.03 ppm, still have an effect on the Eh electrodes.

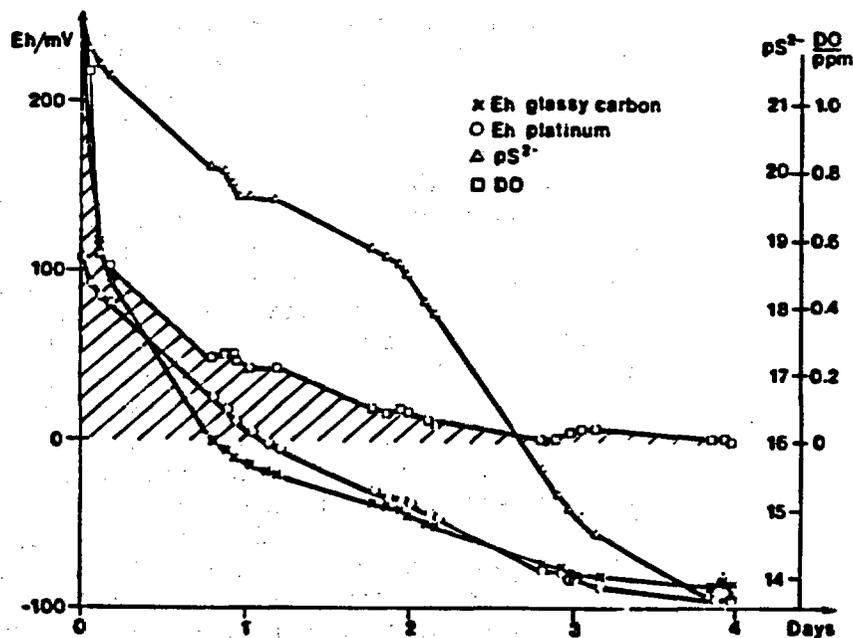


Figure 11. Eh, pS(sulphide) and dissolved oxygen data versus time in the beginning of a pumping period in the early stage of the investigations.

The rate of the reaction between ferrous iron and oxygen in aqueous solutions is well known. In neutral solutions the rate is equal to

$$\frac{-d(\text{Fe}^{2+})}{dt} = -4 \frac{d(\text{pO}_2)}{dt} = k(\text{Fe}^{2+})\text{pO}_2(\text{OH}^-)^2$$

The rate constant k has been found to have a value of approximately $10^{12} \text{ (mol/l)}^{-2} \text{ atm}^{-1} \text{ s}^{-1}$ by several investigators, see e.g. Lawson (1982). With a pH of 8.5 and a constant ferrous content of 0.56 mg/l and a sufficiently low concentration of oxygen this is a pseudo first order rate equation with a half life of about 8 hours. However, the rate is very sensitive to pH and the estimates of the rates of oxygen reduction must be calculated for each situation. There is no doubt from the above estimate that the intrusion of a pulse of oxygen in the sampling section or in the measuring cell will spoil the measurements for several days.

The reproducibility of the Eh measurements was checked on several occasions. The results are compiled in Figure 12. These data indicate that the reproducibility of both the Eh and the pH measurements is good.

The Eh is given as a function of pH in Figure 13. All data where stable Eh values were obtained are included. The bars in the figure represent the largest difference between the measured Eh-values of the different electrodes.

From Figure 13 one observes that there is a difference in the results obtained in the early phases of the field measurements as compared to the later ones. This difference is a result of the improvement of the measuring procedures. In the early phase the Eh-measurements were interrupted frequently by calibrations of the electrodes. Each time oxygen entered into the flow cell, and it was only slowly expelled. A typical situation after a calibration is shown in Figure 11 where Eh and dissolved oxygen values are presented as a function of time. From the figure it is obvious that there is a drift in the readings as long as there is dissolved oxygen left in the measuring cell. In order to eliminate this source of error we decided to continue the pumping without interruptions throughout the whole measuring period in the field studies. This procedure has been used ever since and has resulted in much lower Eh readings as can be seen in Figure 13.

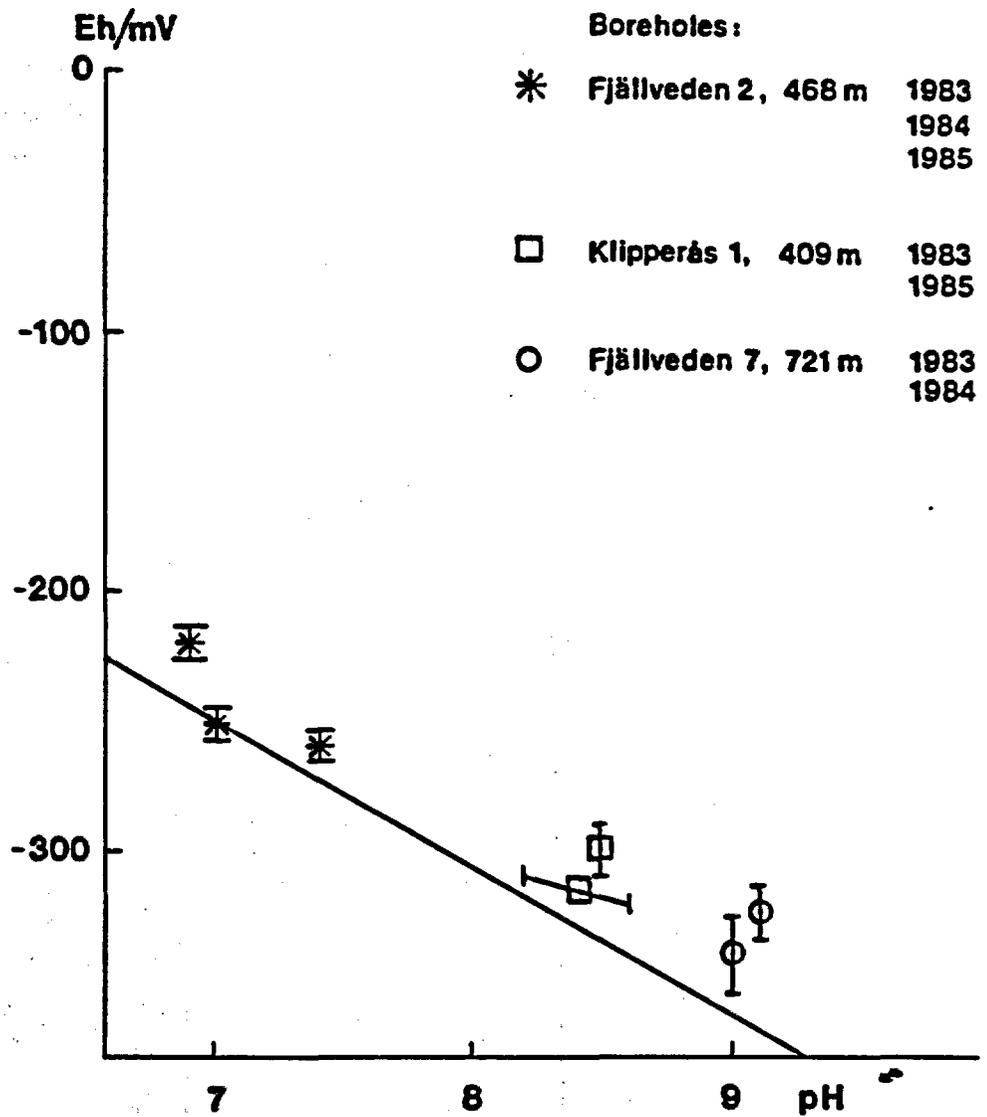


Figure 12. Eh and pH data obtained at repeated groundwater sampling in selected boreholes. The bars indicate the uncertainty in the values.

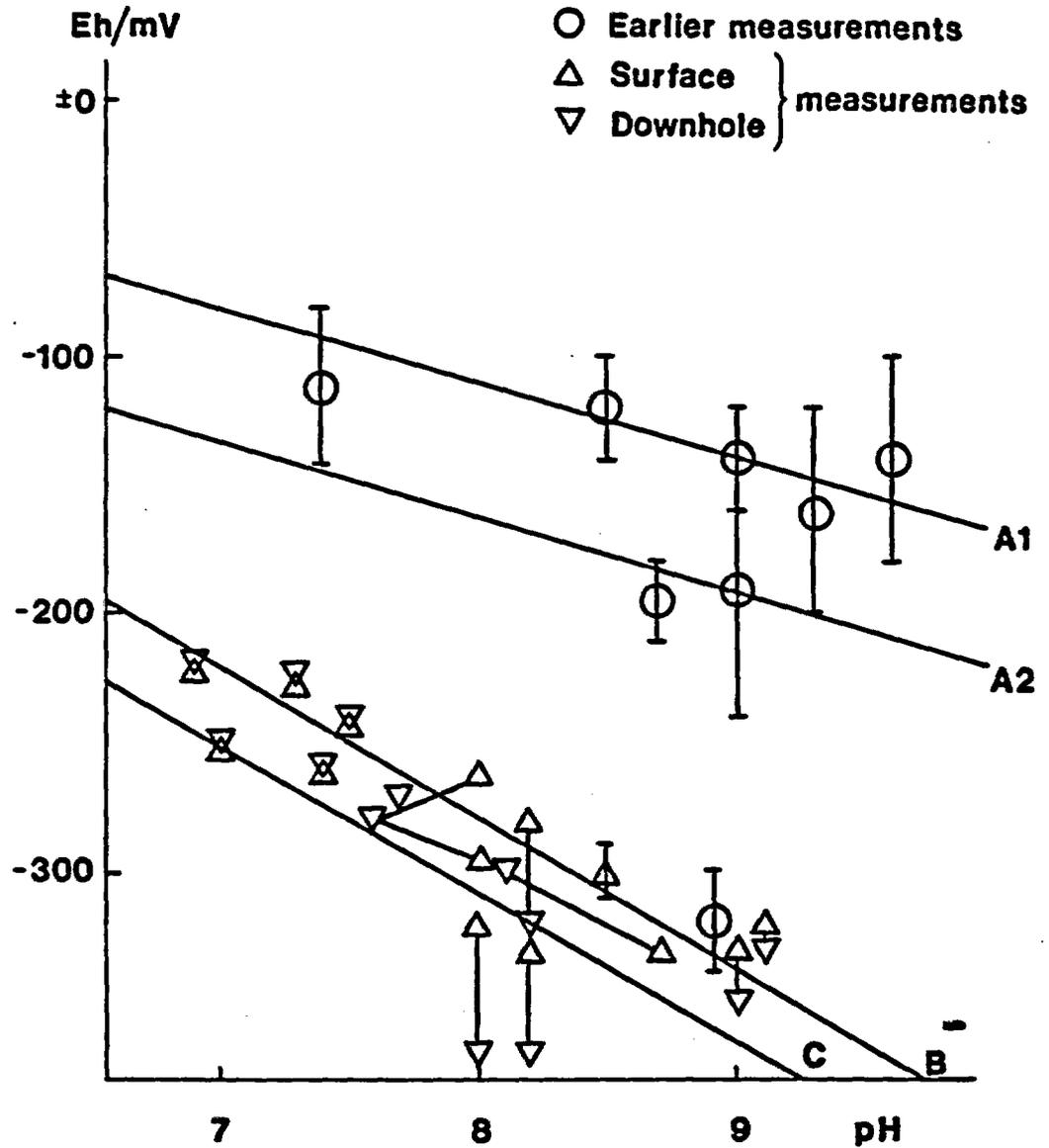


Figure 13. Eh versus pH data of all the groundwater samples which have been considered representative of the environment where they have been sampled.

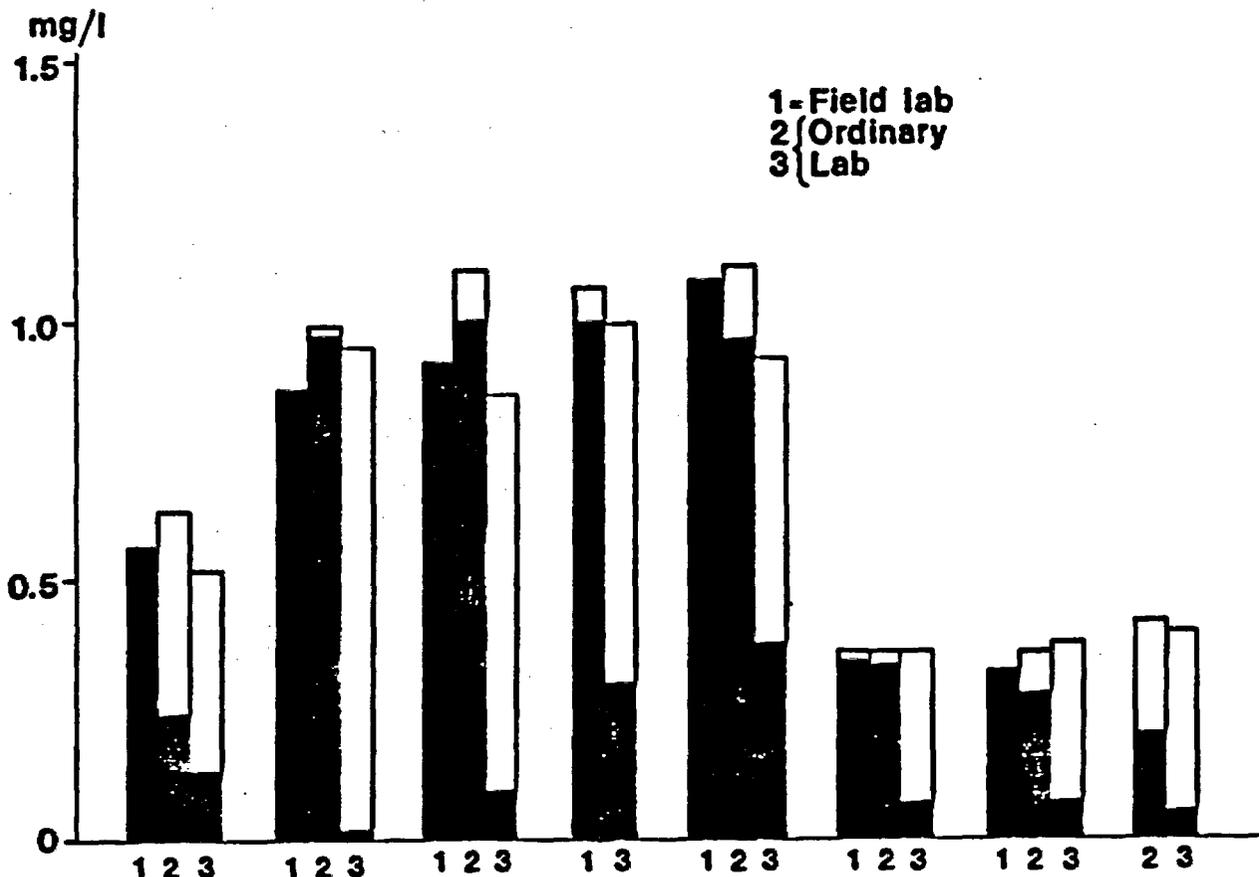


Figure 14. Results of analyses of total and ferrous iron concentrations in the groundwaters at three different laboratories. Filled bars equal the amount of ferrous iron. The full bar equals the amount of total iron.

Analysis of redox sensitive elements

The field laboratory gave results that were more consistent than found previously. The most important improvement was found in the iron analyses. Earlier results, on waters sampled and preserved with hydrochloric acid (Nordstrom et.al., in prep) and sent to laboratories for analyses, showed a notable difference between the amounts of total and ferrous iron. However, this was an artifact due to the time delay between sampling and analyses. The oxidation of ferrous iron to ferric is a slow process in the acidified sample but it does occur, and by time significant quantities are oxidized. The results of analyses made at three different laboratories are presented in Figure 14. One can easily see that the

results from the field laboratory always gives a ferrous iron content which is equal to the total iron content. The results from the other two laboratories vary considerably. However, the results of the total iron analyses agree very well between all three laboratories.

Some of the computer codes used for the equilibrium modelling compute the Eh-value of the solution on the basis of analytical data for ferrous and ferric species. Calculations of this type will be erroneous if a proper analytical method is not used. Our data indicate that the traditional HCl-preservation must be used with great care.

Modelling of the redox conditions of the deep groundwaters

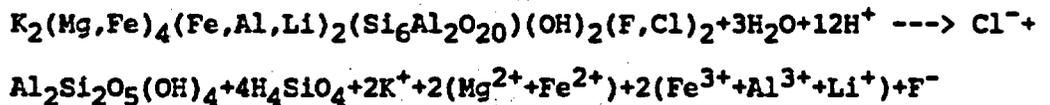
The chemical interaction between the groundwater and the minerals in the crystalline rock investigated, determines the character of the groundwater. The water in the highly permeable parts of the rock are of sodium-calcium bicarbonate type and has a fairly high Fe(II) content, whereas the water in the less permeable parts of the rock are of sodium-calcium chloride type with much lower iron, but a rather high sulphide content. An example of the composition of these two types of water is given in Table 4. From the Eh-values in the table it is obvious that both types of water are strongly reducing.

The results of the Eh measurements made in the early stage of the investigations provide an example of the difficulties in the interpretation. The measurements gave a poor fit to a model based on the ferrous and ferric iron content of the water (Wilkberg et. al, 1983). This was thought to be due to disturbances of oxygen. Later on the same data were modelled by Nordstrom and Puigdomenech who showed that the Eh in fact was controlled by the sulphide, polysulphide and sulphur equilibria (Nordstrom and Puigdomenech, 1986). The formation of polysulphide has taken place through oxidation of sulphide caused by the intrusion of oxygen. Similar phenomena are known from some sulphide rich brines (Boulegue and Michard, 1979). From the EQ3/EQ6 data base (Wolery, 1983) the theoretical Eh-pH dependence for 0.01 ppm and 1 ppm sulphide have been calculated (Puigdomenech pers. comm.) and included in Figure 13, lines A1 and A2. The theoretical Eh-pH dependence for the hematite-magnetite equilibrium is also from the EQ3/EQ6 data base (Puigdomenech pers. comm.), line C.

The more recent field data have not been disturbed by intrusion of oxygen. Therefore they plot close to the theoretical line for the hematite-magnetite equilibrium. As can be seen from Figure 13 the measured values both down-hole and on the surface agree very well. This indicates that the redox condition of the groundwater is controlled by the minerals of the rock. This is reasonable since the large buffering capacity is in the rock and fracture filling minerals and not in the water. However, the fact that a

certain mineral equilibrium agrees with the measured Eh does not mean that the electrodes respond to this reaction. The electrode process must still be mediated by a redox couple in the solution which has a high enough exchange current density on the electrode surfaces. It is reasonable to think that this is the ferrous/ferric redox couple. The ox/red ratio of this redox couple is then controlled by the minerals.

The following scenario might describe the Eh determining processes in the rock - groundwater system. Water which percolates through the fracture systems of the rock slowly dissolves primary minerals of the rock. This process, weathering, occurs on the fracture surfaces in the recharge areas. The weathering results in alteration products which are specific for the process. Such reactions, occurring in granitic rocks, have been frequently discussed in the literature. Edmunds et.al (1984), have studied the chemistry of groundwaters in Carnmenellis granite in the south west of the British Isles. They concluded that the highly saline waters encountered had resulted from the kaolinization reactions of biotite and feldspar. Cramer (1982), also found that the chemical composition of the groundwater in the Lac du Bonnet granite in Manitoba, Canada was described by the alteration of plagioclase, K-feldspar, biotite and muscovite to form kaolinite and illite. These alteration products were also found in the open fractures. The kaolinization reaction as given by Edmunds et.al. is:



This is a process where ferrous iron is dissolved in quantities large enough to explain the amounts in the groundwaters. In cases where oxygen containing water has weathered the rock it is possible to see an increase in the amount of Fe(III) oxides as the ferrous iron released was oxidized to ferric which was precipitated immediately, see e.g. Goldish (1938).

The redox conditions of the groundwater thus reflect the redox conditions of the bedrock even though chemical equilibrium has not been reached between the solid minerals and the dissolved species in the groundwater. As iron is the main redox constituent in the solution it is not surprising that the Eh-values measured in the groundwaters shows a good correlation with Fe(II) and Fe(III) mineral equilibria. Many minerals give equilibrium lines which are close to one another. We have used the magnetite-hematite equilibrium as an example even if these are not the dominating Fe(II) and Fe(III) minerals in the investigated granites. Brotzen has previously described the Eh-values in deep groundwaters in crystalline rock (KBS-1, 1977) as controlled by the ferrous/ferric ratio in silicates. Due to the possible variations of the ratio Fe(III)/Fe(II) in the silicate solid solutions a variation of

+/-100 mV was applied. The Eh-pH relation valid for unity ferrous/ferric ratio is given by the equation

$$\text{Eh(V)} = 0.26 - 0.06 \text{ pH}$$

Results of more recent investigations show that the Fe(II) minerals are by far more common than the Fe(III) minerals in the investigated sites (Torstenfelt et al, 1983). Assuming an average ratio of Fe(III)/Fe(II) of 0.1 the values are 60 mV more negative included as line B in Figure 13. This line is only about 20 mV apart from the magnetite-hematite equilibrium line and as good a model for the measured Eh values as the line C. There are also other phase equilibria which give an Eh-pH relation close to the measured Eh data. An example of such a reaction suggested by Eriksson (1985), p. 76, involves the equilibrium between goethite and pyrite. This reaction has a slope of -75 mV/pH and depends on the concentration of sulphate in the water.

The bedrock is very heterogeneous from a strict chemical point of view. Therefore we do not want to imply that Eh is controlled by one specific reaction but only conclude that the redox conditions are determined by the iron in the rock and fracture minerals. It should also be noted that the measured Eh values in general show that the waters are undersaturated with respect to Fe₂O₃ by approximately three orders of magnitude. These calculations are made using the Eh, ferrous iron and pH data because ferric iron concentrations are not analytically available because practically all the iron in the waters is in ferrous form, c.f. Figure 14.

The water samples from the early phase of the investigation should also have given Eh values close to the latter ones if the measurements had been carried out without interruptions for longer periods. This is indicated by the fact that one single point where the sampling section was pumped for a much longer time than the others due to a very low flow rate plots close to the model lines B and C in Figure 13. In this particular experiment there was time enough for all the dissolved oxygen to be expelled from the measuring cell.

Laboratory simulation of the redox conditions

The results of three consecutive experiments where water was circulated in contact with drill cores in a well sealed glass vessel are illustrated in Figure 15 in the form of Eh versus time plots. The pH is not included since there was no significant change during the course of the experiments. A comparison between the experiments where the water initially was saturated by oxygen and the one where the water was deaerated clearly shows that there is a delay in the Eh drop in the first case. It should also be noted that the platinum electrode is much more sensitive to oxygen than the graphite electrode, c.f. Whitfield (1974). However, when the oxygen is consumed all electrodes level out at about the same

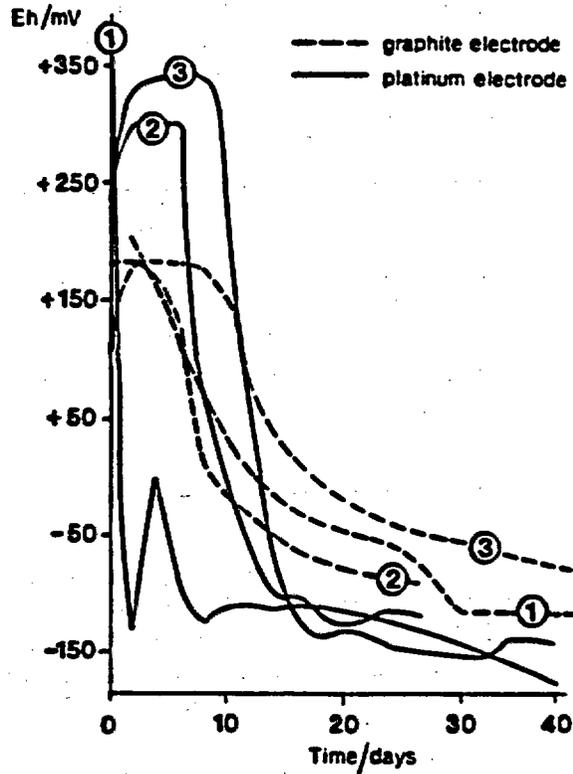


Figure 15. Eh versus time data obtained in the laboratory studies of the redox kinetics. The first run is made with deaerated water, the other two with air saturated water.

values. Similar experiences have been reported by e.g. Jantzen (1985).

During these experiments the water was analyzed for iron and sulphide. The results are presented in Table 5. The analyses were made after terminating the experiments, except for the first run where the natural groundwater was used.

The successively decreasing amounts of iron suggests that the surface of the drill cores is gradually oxidized, leaving a smaller amount of ferrous iron left to be dissolved in the water. However, as the reduction of oxygen proceeds with the same rate in all the experiments it seems as if the reaction occurs on the mineral surfaces and not in the bulk of the solution. If the reaction had taken place in the solution the rate would have been proportional to the amounts of dissolved iron, c.f. p. 26. Consequently the last experiment should have needed a longer time to reach reducing conditions than the two preceding ones, this was not the case.

Table 5. Sulphide and total and ferrous iron contents in the water rock interaction experiments. The 0-values are the concentrations in the natural groundwater used for the first experiment. All concentrations are given in mg/l.

Component	NATURAL GROUNDWATER			DEIONIZED WATER + HCO ₃	
	0-values	1A	1B	2	3
Fe(II)	<.005	.039	.039	.006	<.005
Fe(tot)	<.005	.041	.041	.011	<.005
S(-II)	<.01	----	.03	.02	-----

A constant reduction rate could also be explained by a microbial reduction of the dissolved oxygen. Organic material left on the drill cores from the drilling could constitute the substrate for the bacteria. We do not think that this is the case but the probability will be investigated in the future.

A set of similar experiments has been run with crushed material in a different experimental setup. The result of these four runs are presented in Figure 16. The first three of them are identical. In the fourth the equipment was placed in a box with nitrogen atmosphere. As shown in the figure this made the Eh drop about 200 mV compared to the previous runs. This indicates the extreme oxygen sensitivity of the redox system. The constant Eh values in the three first experiments indicate a steady state situation where the rates of oxygen diffusion into the system is balanced by the rate of reduction by the Fe(II) minerals.

The reduction of oxygen due to chemical interaction between the minerals and the infiltrating groundwater is a commonly accepted theory. Ferrous iron is dissolved from easily weathered minerals and reacts with the dissolved oxygen precipitating ferric hydroxide (Siever and Woodford, 1979). Neretnieks (1986) proposed that the main process for oxygen reduction in the infiltrating water is the diffusion of oxygen into the rock matrix and a subsequent oxidation of Fe(II) minerals. This process probably involves diffusion of carbon dioxide or protons into the micro fractures where the Fe(II) is dissolved and immediately oxidized to an Fe(III) oxide by the oxygen which has also diffused into the micropores. Thus the oxygen reduction takes place in the pore water in the micro fractures. Neretnieks (1986) has used an average flow rate of the water and a diffusion rate of oxygen in the rock matrix, to calculate the depth of oxygen penetration. The result of this calculation agrees well with some experimental findings. He has made the assumption that the oxidation has taken place since last glaciation which may be doubtful.

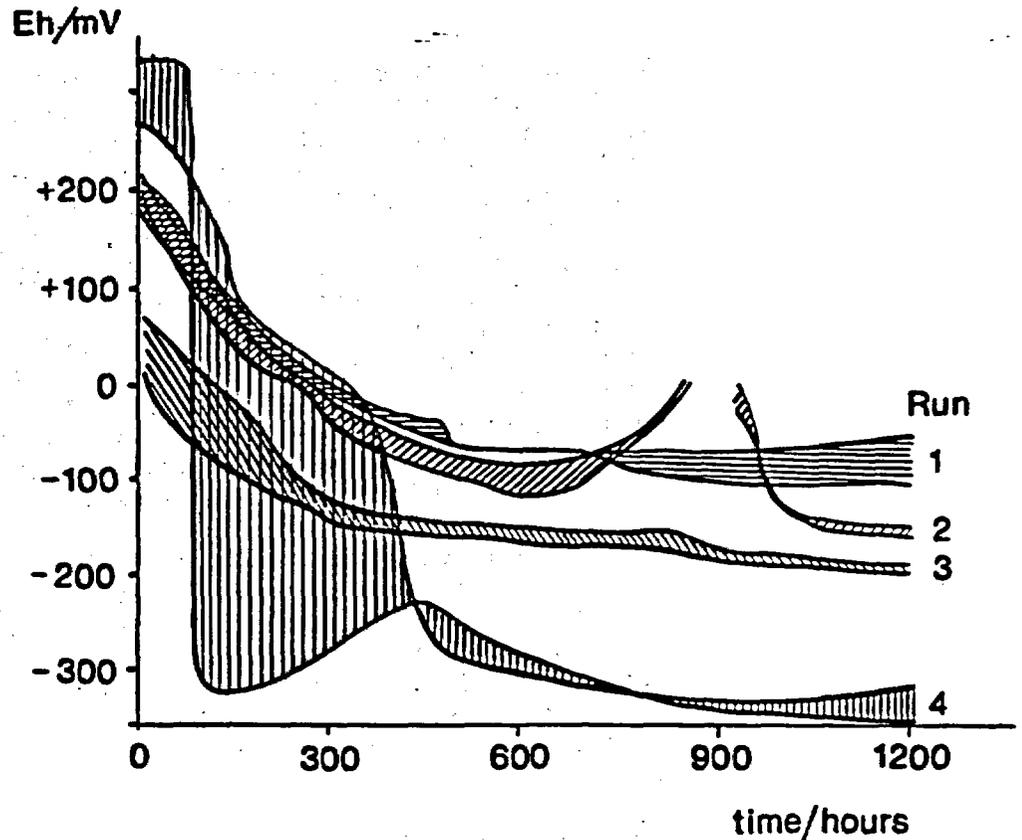


Figure 16. Eh versus time data of four consecutive experiments on redox kinetics. The fourth experiment is made in a totally oxygen free atmosphere.

Investigations of weathering profiles show that the content of total iron is constant, (Cramer, 1982), but the ratio Fe(III)/Fe(II) is high at the surface and decreases gradually into the bulk of the rock (Clauer et.al, 1982). Fergusson (1982) p. 48 and Goldish (1938) have demonstrated how weathering gradually changes the amounts of Fe(II) and Fe(III) oxides. The ferrous oxide decreases and ferric oxide increases. Ferrous iron is dissolved, oxidized and precipitated as ferric hydroxide.

When a large number of experiments have been run with the same drill cores there is a decrease in the reducing capacity. This results in more easily disturbed Eh values and a longer time needed for the initial reduction of oxygen. Polishing the sides of the drill cores when the reducing effect was very low did not improve the capacity significantly. Hence, it seems as if the ability to reduce the oxygen resides mainly in the fracture minerals in these experiments.

In this context it is important to keep in mind the differences between the oxygen reduction taking place a) when the surface water percolates down through the fractures in the upper part of the bedrock, b) in the Eh measuring cells through which the deep groundwater is pumped and c) in the laboratory simulations. The processes are entirely different in all three cases.

The surface water is normally depleted from dissolved oxygen, due to the biological oxidation of organic material, when it percolates through the soil cover. However, when the soil cover is thin, the water which reaches the upper part of the bedrock still contains some dissolved oxygen. Studies of the fracture surfaces in such rocks tell that this residual oxygen has been reduced by Fe(II) dissolved from the minerals in the bulk of the rock. As a result of this reaction the existence of rust can be seen on the fracture surfaces. Another obvious process is also the diffusion of oxygen into the micro pores of the rock matrix, as described previously. The diffusion of oxygen into the rock matrix is a slow process, however, the flow rate of the water in these fractures is also very slow giving the diffusion process time enough to deplete the water from the dissolved oxygen.

In the measuring cells the reduction of oxygen is a homogeneous reaction which occurs in the aqueous phase. Fe(II) species or sulphide (HS^-) reacts with the oxygen. The rate of such reactions is much more rapid as indicated from the calculations of the reduction of dissolved oxygen previously. Also the reactions taking place when a deep reducing groundwater is mixed with a portion of surface or drilling water is of course also of this type.

The reaction taking place in the laboratory is in principle of the same type as the one occurring in the uppermost part of the rock. However, there is one difference. The results of the laboratory studies indicate that the reduction of oxygen is due to reactions with the fracture filling minerals. Such minerals have partly been formed by the precipitates from supersaturated water flowing in the fracture systems. Therefore it is expected that these minerals should be kinetically more accessible to reactions than the bulk rock minerals.

One experiment has also been performed with carbon dioxide saturated water. The pH of this was three units lower than in those previously described. Within two weeks the iron content of the water had reached a level of 0.2 mg/l which is five times higher than what has ever previously been obtained. Therefore there is no doubt that the carbon dioxide weathering is responsible for the high iron concentration in the water. Siever and Woodford (1979) have studied the dissolution kinetics and weathering of mafic minerals. They have divided the dissolution processes into the following steps:

- * a rapid exchange between cations, including Fe^{2+} and Mg^{2+} , and protons in the water
- * a slower incongruent dissolution of silica

Their studies at different pH values indicated that the dissolution rate is strongly dependent on pH. For the results of our field and laboratory investigations this is a fully acceptable model for the most important water-rock interactions.

4.3 Isotope geochemistry

The stable isotopes oxygen-18 and deuterium and the radioactive tritium of the water have been regularly analyzed as well as radioactive carbon-14 and stable carbon-13 of the carbonate dissolved in the water. These results are presented in Table 6 for all the sampled sections where representative samples have been obtained (Smellie et.al, 1985). As compared to the results of general chemistry presented previously in Table 3, Table 6 includes data obtained also from investigations where the field laboratory has not been used. The isotopic data has previously been discussed by Karlsson and Wikberg (1987).

The results in Table 6 will be discussed in some detail in two different categories, stable isotopes and radioactive isotopes since there is a fundamental difference in how these data can be used.

Table 6. Isotopic composition of the groundwaters investigated in the course of the Swedish nuclear waste management research program.

Area	Borehole	Depth m	¹⁴ C PMC	T TU	D ‰ SMOW	¹⁸ O ‰ SMOW
Kamlunge	Km13	197	40.5	10	-	-13.7
Gideå	Gi 2	157	45.3	<3	-90.4	-12.6
	Gi 4	212	23.0	5	-89.7	-12.6
Svartboberget	Sv 4	324	16.0	<3	-95.3	-13.2
The Baltic Sea		50			-57.7	- 7.0
Forsmark	HK 1	90				-12.2
	HK 7	140				- 9.8
	HK10	140				- 9.3
Finnsjön	Fi 9	182	21.9	<3	-86.6	-10.6
	Fi B1	71				-88.2
	Fi B1	169			-85.2	
	Fi B1	234			-85.7	
Fjällveden	Fi B1	439			-88.7	
	Fj 2	506	18.3	<3		-14.1
	FJ 4	131	43.6	<3	-84.7	-11.9
Klipperås	Fj 7	647		<3	-80.3	-11.4
	Kl 1	406	2.9	<3	-86.3	-12.0
	Kl 9	581	2.2	<3		-11.9

Stable isotopes

The data of the stable isotopes deuterium and oxygen-18 are presented as the deviation from the isotopic ratios $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ of the standard mean ocean water (SMOW). Because of climatic conditions these values deviate, the colder the climate the lower are the values. However, it has been globally proved that the water which has a meteoric origin always follows a straight line on a deuterium-oxygen-18 diagram (see e.g. Dansgaard, 1964). Therefore the deuterium and oxygen-18 values are extremely useful for deciding whether the deep groundwaters are of meteoric or metamorphic origin. So far no metamorphic waters have been encountered.

The oxygen-18 value in itself is a good indicator of the climatic condition when the water was precipitated. The data from the northern sites, Kamlunge, Gideå, and Svartboberget tend to have lower oxygen-18 values than the southern sites, Fjällveden and Klipperås. One specific notation on the results is that the oxygen-18 value of the Forsmark groundwaters are much lower than the value of the Baltic Sea at the same chloride concentration. This suggests that the Forsmark groundwaters consist of oceanic seawater mixed with freshwater with a much lower oxygen-18 value than the freshwater which now a days dilutes the oceanic water to form the Baltic Sea water.

Radioactive isotopes

The radioactive isotopes which have been analyzed are tritium and carbon-14. Carbon-14 has a half life of 5730 years and is expressed in Table 6 as the percentage of carbon-14 in relation to the amount in living organisms (per cent of modern carbon = PMC). The very long half life of the carbon-14 makes it a useful tool for detecting water with a long residence time. Tritium was produced in the nuclear bomb tests in the early sixties. Before that the background concentration was insignificant, partly due to the fact that tritium has a half life of only 12.4 years. The tritium data of the groundwaters is given as the arbitrarily defined tritium unit (TU). The precipitation contained at the most, in 1964, about 2000 TU which has continuously decreased to a level of below 100 TU to day. However, there have probably been large differences between the north and the south of Sweden. Nevertheless detectable amounts of tritium in the groundwater simply indicates that the water has been precipitated less than 40 years ago.

The data in Table 6 show that the carbon-14 values are generally around or below 50 PMC indicating that the water has a long residence time in the rock. However, in two of the samples the tritium content is above the detection limit which indicates that there are portions of the water which has been precipitated less than 40 years ago while the carbon-14 value indicate a residence time of

5000 to 10000 years. There are some possible explanations to this situation given in the discussion of groundwater residence time.

4.4 Uranium geochemistry

Uranium is an element which is of interest for two reasons. The first one is that the uranium is the major part of spent nuclear fuel and as such important for the safety assessment of a repository. The chemistry of uranium makes it important also for the evaluation of the redox conditions in the groundwaters. Under reducing conditions uranium exists in an almost insoluble tetravalent form whereas it exists in a very soluble hexavalent form as carbonate complexes under oxidising conditions. The concentrations of uranium as well as the uranium 234/238 activity ratio has been regularly analyzed in the site investigation program. The results and the use of these data has been discussed by Smellie et.al (1985). Mostly the contents of uranium in the waters has been close to or below the detection limit. This is in good agreement with the low Eh-values measured in the waters. The activity ratio 234/238 increases with decreasing uranium concentrations, see e.g. Andrews et.al (1982). This is due to the solution of alpha-recoil Th at the rock-water interface, which has an appreciable impact on the activity ratio at the low uranium concentrations under reducing conditions. It should be noted, however, that the groundwater flow rate affects the activity ratio.

5 DISCUSSION

5.1 Natural background

The ultimate goal of the geochemical investigations is to identify and quantify the results of the groundwater rock interaction. This knowledge is necessary for any safety evaluation of a subsurface nuclear waste repository. One very important part of this work is the identification of water flow paths and the mixing of different groundwater types. For this purpose the chemistry of both surface and deep groundwaters need to be studied in some detail.

The depth investigations include groundwater sampling from water conducting fractures at different depth in boreholes. Samples need to be taken both from sections with extremely high and low permeabilities. The technique used for obtaining these samples will depend the hydraulic conductivity.

In addition to main and redox sensitive elements trace elements which are important for equilibrium modelling; Al, B and Ba, and trace elements which are part of the waste form, e.g. uranium and radium need to be analyzed. These elements are naturally occurring

in the groundwater system and are thus models for the behaviour of the same or similar elements from the waste. Other elements like thorium are analogues to other tetravalent actinides such as Pu(IV). The content of uranium is of interest also for the redox conditions. Tetravalent uranium is very insoluble whereas hexavalent uranium can exist in much higher concentrations as carbonate complexes.

The content of dissolved gas in the groundwater will describe the equilibrium conditions but also the evolution of the groundwater. Gas seeping out from the mantle of the earth can be detected and the deep gas carrying fractures thus located. The different gases and the purpose of analyzing them are:

*	N ₂	main component, sample quality
*	O ₂	redox sensitive, sample quality
*	CO ₂	pH-HCO ₃ ⁻ CO ₂ equilibrium
*	Ar	sample quality
*	He	radioactive decay, deep source
*	H ₂	redox sensitive, deep source
*	CH ₄	redox sensitive, deep source

Oxygen and argon are analyzed only because they indicate whether the samples are contaminated by the air or not.

The groundwater rock interaction is schematically illustrated in Figure 17. The bulk rock minerals are weathered and dissolved in the groundwater which percolates through the upper parts of the rock. The water will be supersaturated with respect to some minerals which will be precipitated in the fracture system.

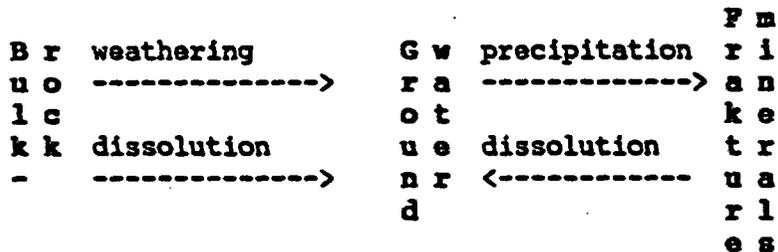


Figure 17. Schematic illustration of the reaction path in the groundwater rock interaction.

If the chemical composition of the groundwater is changed then the fracture minerals will be dissolved etc. This can be seen as a dynamic process including partial equilibria. The weathering which is a non equilibrium process gives a water composition which is depending on the time the water has been in contact with the rock. If the hydrologic situation is changed then the residence time of the water and the water composition are also changed. This will in general result in changes of the fracture minerals. From careful fracture mineral studies and groundwater chemical analyses it is possible to understand how these events have taken place in the past. This is the only information which can be used to make extrapolations into the future. A process that is necessary if one wants to make predictions on how radionuclides will be transported in the groundwater when released from the waste form. It is obvious that extrapolations cannot be made over extensive periods of time. The uncertainty of the predictions will increase with increasing time in much the same manner as the knowledge of the geologic history fades out in the past. However, the knowledge of the geological events taking place since last glaciation are fairly well known and therefore the extrapolation to the end of next glaciation should be fairly safe.

The chemical composition of the groundwater

Groundwater under land is in general of meteoric origin. The chemical composition of groundwater is a result of interactions with soil minerals, soil atmosphere and further interactions with the minerals of the bedrock as the water infiltrates into the recharge areas. The most important reaction is the addition of carbon dioxide in the soil zone which leads to calcite dissolution. The carbon dioxide weathering has been used by e.g. Jacks (1973) to describe the composition of different groundwaters in silicate rocks. By plotting the contents of different elements as a function of the bicarbonate concentration he could easily detect where incongruent dissolution or other processes had occurred. His results are in good agreement with our investigations where the deep groundwaters in general have a calcium content and slowly increasing sodium concentration due to weathering of sodium containing minerals.

Paces (1972) has described the groundwaters from granitic, granodioritic rocks as being in partial equilibrium with respect to K-feldspars, indicating the weathering or dissolution of this to be fairly rapid. Kaolinite and Ca-montmorillonite are frequently stable secondary minerals in the chemical conditions defined by the composition of the groundwater. The waters are in general dominated by sodium, bicarbonate and chloride in decreasing concentrations. The concentrations of sulphate and silica are much lower.

Reactions in the carbon dioxide calcium carbonate system determines the pH of the groundwater. There is a great difference in pH

depending on whether the weathering processes have occurred in an open or closed system (Garrels and Christ, 1965). In an open system carbon dioxide is continuously added during the process. The consequence of this is that large amounts of calcite are dissolved resulting in high concentrations of calcium and bicarbonate. Due to the continuous addition of carbon dioxide the pH of the water is buffered at a value of about 7. In a closed system where no restoring of the consumed carbon dioxide takes place the calcite dissolution stops when an amount equivalent to the initial carbon dioxide concentration has been dissolved. The pH of this water is controlled by bicarbonate at a value of about 8.5. In most of the situations where water has been sampled the pH lies between these values defined by the totally open and the totally closed systems, see Table 3.

The dissolved oxygen from the atmosphere is gradually consumed during the infiltration and reducing conditions are obtained: first due to microbiological decomposition of organic material in the soil zone and later due to reactions with reducing minerals containing iron and sulphur. These changes can be followed by studying the water composition and fracture mineral composition at different depths. Siever and Woodford (1979) have studied the dissolution kinetics and weathering of mafic minerals, c.f. p. 36.

Claesson (1983) found from an extensive study of water-rock interaction at elevated temperatures that weathering shells, formed by the secondary minerals, did not affect the rate of dissolution of the minerals. An other result obtained by Claesson was that he could never detect iron and magnesium dissolved from the minerals. This was thought to be due to an adsorption of these elements in the weathering shell.

Increased salinity is sometimes encountered at depth in crystalline rocks. This has been found both in the Canadian Shield (brine concentrations) (Frape et.al, 1984) and in the Fennoscandian Shield in Sweden (Nordstrom et.al, 1985) and Finland (Hyyppä, 1985). The main components are sodium, calcium and chloride. The origin of these saline waters are being discussed and several explanations have been suggested, such as ancient seawater, dissolved evaporites, released fluid inclusions, leached chloride containing minerals, residual water after deep permafrost etc (see e.g. Nordstrom and Olsson, 1987 and references therein). Two different types of saline water have been encountered throughout the site investigations. The most saline, with chloride concentrations around and above 5 g/l, have been found in the bedrock close to or below the Baltic sea. The other type, with chloride contents of about 500 mg/l, has been found in low conductivity fracture systems at great depth. The main difference between the two types of water is in the pH, the sulphate concentration and in the sodium/calcium ratio. The water in the deep low conductivity parts has a high pH (around 9), a sulphate/chloride ratio of 1/1000 and a sodium/calcium ratio of 10/1 whereas the water with a composition close to sea water has a neutral pH and the values 1/10 and 1/1, respectively, for the ratios. These differences in combina-

tion with the difference in the surrounding where they have been sampled indicate that the waters are of different origin. By the guidance of the oxygen-18 data the saline water in the coastal areas has been found to originate from the Litorina Sea some 5000 years ago (Wikberg, 1986), a similar explanation has been given to the origin of high salinity groundwater found in the bedrock below the Gulf of Finland (Kankainen, 1986 and Nordstrom, 1986).

The composition of deep groundwaters can change considerably from one part of the bedrock to the other. An example of this is the sharp increase in salinity from a few mg/l of chloride to about 5 g/l on passing a subhorizontal fracture zone in Finnsjön (Ahlbom et al., 1986). This is an illustrative example of the role geological features might have on the hydrological regimes.

In conclusion the results of the water analyses can be used to delineate the normal composition of groundwater at a specific site and the variations in the composition due to depth and in/outflow conditions. The results can also be used in combination with information from rock and fracture mineral investigations as input data for geochemical models in order to explain the water composition and predict possible changes in this composition. Important systems in this respect are those which defines pH (HCO^- , calcite and feldspars), redox conditions (Fe^{2+} , HS^- in solution, iron (II) and sulphide minerals) and actinide chemistry (uranium and thorium containing minerals).

Groundwater-rock interaction

The interactions between crystalline rock and water will predominantly take place in the fractures. Fracture filling minerals as well as groundwater chemistry can therefore give information about the geochemical conditions in the fractures. Representative groundwater samples can sometimes be difficult to obtain, especially in inflow areas and at low depth (Smellie et al 1985). One recent investigation (Tullborg, 1986) shows that fractures containing Fe(III) minerals are more frequent in fractured zones whereas calcite fillings are more common in single fractures. The explanation to this is that the water has flowed with different rates in the fracture systems. In fractured zones oxidizing water has reached depth of several hundred meters because the flow rate has been so fast that there has not been time enough for the water-rock processes to reduce the dissolved oxygen until the water has reached considerable depth. Calcite filled fractures on the other hand indicate that the water in them has been supersaturated with respect to calcite indicating that the flow rate has been low and the water has been in equilibrium with the rock minerals.

Most of the Fe-minerals present as fracture fillings are iron oxyhydroxide, hematite and pyrite. These minerals represent different redox states and the distribution of them will therefore give

information about the variation of the redox conditions in the fractures.

From the evidence obtained it seems likely that many of the water conducting horizons sampled are directly associated with dykes, schlieren or bands etc. of rocks characterized by compositions distinct from the overall bedrock; these may also influence the groundwater compositions. For example, at one of the sites (Fjällveden) where waters have been sampled from well-defined greenstone horizons, there is a strong possibility that the exceptionally high iron content is due to contact between the groundwater and the greenstone for some time/distance. Furthermore, large increases in sulphate content were observed in groundwaters collected from an amphibolite bedrock mass at another study-site (Kamlunge).

Alteration and oxidation in the rock immediately surrounding a fracture/fracture zone gives information about the migration of water into the rock itself. This is of importance also for the migration of radionuclides. One pilot study of oxidation profiles from a fracture into a granitic rock is at present carried out. Fe(III)/Fe(II), ^{18}O , D and uranium series isotopes are analysed. The aim of this study is to get 1) an oxidation profile in the rock 2) to characterize the water responsible for the alteration 3) to use the uranium series isotope analyses to get information about the residence time of the water circulation system.

Another very useful approach is to carry out uranium decay series measurements (^{238}U ^{234}U ^{230}Th) on carefully selected fracture zone mineral phases, together with the corresponding groundwaters. Isotopic characterization of the fracture zones can reveal the redox nature of corresponding groundwater, i.e. whether the fracture section (usually selected from a drill core) represents an environment of uranium leaching (high redox potential) or precipitation (low redox potential).

A very specific situation has been encountered in some basic rocks where low temperature interaction has produced calcite and swelling clay minerals like smectites in the fractures. These minerals have sealed the fractures and thus decreased the hydraulic conductivity and the water-rock interaction. Therefore the fracture fillings in the basic rocks have to a large extent preserved their original oxygen-18 values in contrast to the situation in granitic rock (Tullberg, 1986).

Groundwater residence time

Due to the mixing processes it is not possible to assign a single "age" to a groundwater. The water has a residence time distribution. Short lived natural radionuclides may give an indication on the fraction of the water with short residence time, longer lived

nuclides on the fraction with long residence time. Several nuclides with different half lives are needed to get a coherent picture on the residence time distribution of a water. An investigation of the ^{14}C and other isotopes in the groundwater, the organic material of the groundwater and in the calcites in the fractures might give a history of the groundwater from which the residence time of the water can be obtained.

Deuterium and oxygen-18 in general reveal the meteoric origin of the water and the climatic conditions during infiltration. It is therefore a valuable part of the information on groundwater origin. In case of the groundwaters found below the Baltic Sea the oxygen-18 data was sufficient for the dating of these waters. This was due to the fact that this water was stagnant covered by the Baltic Sea which levelled out all possible local gradients which could cause a mixing with other types of water.

Tritium could in principle be used to find cases of rapid infiltration. In practice, however, tritium is used as a measure of sample contamination. Surface waters and near surface waters are rich in fallout tritium from the nuclear bomb tests in the sixties and this may enter deeper sampling levels through the borehole if care is not taken to avoid this.

Carbon-14 in dissolved carbonate is a classic method to measure groundwater "age" and the stable isotope carbon-13 is sometimes used to correct for errors in carbon-14 age due to the dissolution and precipitation of calcite. However, there is a series of circumstances that may affect the carbon-14 age values such as;

- * Mixing of different waters along the flow path (IAEA, 1983)
- * Dissolution and precipitation of carbonate minerals (Wigley 1976)
- * Sorption and exchange with carbonate minerals (Allard et al 1981)
- * Diffusion loss of carbon-14 into the open microfracture system (Neretnieks 1981)
- * Oxidation of carbon-14 deficient organic material

All these processes give an "age" which is higher than the actual residence time of the water in the rock. Therefore the carbon-14 age should be expressed as per cent modern carbon (PMC) instead of in years.

From the discussion on the tritium and carbon-14 data above it is obvious that the water samples occasionally have detectable tritium concentrations even though the carbon-14 values (PMC) are low. In most cases this can be explained by a contamination during the sampling, see section 2. However, there are also situations

when the detectable tritium concentration cannot be explained by sample contamination. E.g. the two samples in Table 6 are considered representative of the location where they have been sampled. There are a few possible explanations to this situation:

- i) The representative water of the sampled horizon consists of a major portion of water with a long residence time and a minor portion of water which has reached the sampling depth very rapidly through natural flow paths.
- ii) The representative water of the sampled horizon has a long residence time but due to the great pressure gradient caused by the pump new flow paths are opened. Such flow paths could then transport surficial water down to the sampling horizon.
- iii) The different processes that affects the carbon-14 content have diluted it to such a degree that the age indicated by the PMC value is totally wrong, whereas the age indicated by the tritium content is correct and valid for the whole water volume.

The explanations i and ii are reasonable. Unfortunately there is no simple way to sort out which one is the correct explanation in the different situations. The third explanation is the most hypothetical one, but nevertheless possible. The processes mentioned above, dissolution of old calcite, sorption and exchange of carbonate and diffusion into microfractures, can easily dilute the carbon-14 content in the infiltrating water by a factor of more than two in some specific situations. Therefore this possibility must be kept in mind when the residence time of the water is evaluated. It is also possible that all three explanations are partly valid. Depending on the hydrogeological conditions the contribution of them will vary. Fortunately there is one indirect way of deciding whether the water has a long or short residence time in the rock. The general chemical composition of the groundwater can be used for this purpose. Neutral calcium bicarbonate waters are young and high pH sodium chloride waters are old.

Equilibrium modelling of ground water evolution

The flow-rate of deep groundwaters is slow. Hence the time for chemical interactions between the water and the mineral components along the flow path is long. This state can often be described by assuming chemical equilibrium between the water and the minerals. Chemical interactions between the infiltrating water and the minerals results in changes both in the minerals and in the groundwater composition. There is thus a continuous chemical evolution of the water along the flow-path. Many attempts (Jenne, 1979) have been made to model these processes.

Equilibrium models are all based on the assumption that there is chemical equilibrium between the various minerals and the ground water. From thermodynamic data for the various solid phases that occur or may form in the system and similar data for the soluble ions and molecules that may form in the aqueous phase one can calculate the chemical composition of both the aqueous and the solid phases. This is a well-established method and several well-tested computer codes exist for the execution of these calculations (Nordstrom et al 1979). The calculations are no better than the assumptions and the quality of the thermodynamic data.

The evolution of a ground water along a flow-path is usually made with "box" models. A given quantity of water is equilibrated with a given quantity of minerals with an equilibrium model. This water is equilibrated with new minerals etc. The box models have been useful for the description of some groundwater systems (Drever, 1982).

Kinetic modelling

The equilibrium models do not take into account that some chemical equilibria are slow even in comparison with the long residence times of deep groundwaters. These equilibria have to be identified otherwise the equilibrium models will give erroneous results.

Weathering processes are slow compared to equilibrium reactions in a solution. Slow weathering reactions can be modelled (Gould, 1971) and these models are capable of a more detailed and precise description of the repository system than the equilibrium models. However, modelling of reaction kinetics has not been made so far on complicated systems like a nuclear-waste repository. Some development work is necessary because kinetic processes may be important for several phenomena of critical importance for the over-all safety of the repository. These are;

- * The rate of reduction of dissolved oxygen and uranium(VI) by the minerals in bedrock and fractures
- * The formation of a skin on the fracture mineral surfaces which will affect the rate of reduction of dissolved oxygen and uranium(VI)
- * The rate of dissolution and re-precipitation and their role in changing the hydrologic path ways
- * The rate of dissolution and re-precipitation and their role for co-precipitation phenomena and colloid formation

5.2 Near field

The near field is defined as the vicinity of the repository which will be chemically and physically affected by the processes and materials in the repository, i.e. the buffer, the waste canister and the waste. The near field processes where the composition of the undisturbed groundwater has an impact will be shortly mentioned.

Buffer stability

It is necessary to know the content of the main components of groundwater and the possible changes in these concentrations in order to assess the long time stability and performance of the backfill. Trace constituents such as aluminium, iron and silica may also be of interest depending on the choice of backfill material.

Canister corrosion

The corrosion of the waste canisters is determined by the properties of the canister material and the chemical composition of the groundwater, and the backfill. The main corroding agent for metallic copper is sulphide-ions present in groundwater c.f. KBS-3 (1983).

Dissolution of the waste form

The most important characteristic for the dissolution of the waste form and the subsequent transport of dissolved radionuclides is the redox properties of the rock-groundwater system. The solubility will in addition be influenced by strong complexing agents, the most important of these are carbonate and possibly naturally occurring organic materials. The dissolution rate may be severely restricted by the rate at which the components may diffuse or flow away from the fuel.

5.3 Radiochemical aspects

The properties of the radionuclides are strongly influenced by the chemical composition of the groundwater, mainly its redox-state and pH. The concentrations of substances which may form insoluble solid phases, or solubilize solids through the formation of soluble complexes, are also important.

Many of the radionuclides may occur in different oxidation states. The relative stabilities of the various oxidation states are determined by the groundwater composition. The chemical properties of the different oxidation states of a given radionuclide are often totally different. Tetravalent actinides are for instance extremely insoluble in groundwater while the penta and hexavalent actinides may have solubilities which are more than one million times higher.

Radiolysis is likely to be important in the near field. The oxygen which is produced will oxidize the nuclides dissolved from the waste form. The extent of these reactions are not known, but some evidence is given from studies of the OKLO formation (Curtis and Gancarz, 1983). The oxidized form will be transported until the point where the interaction between the groundwater and the rock has reduced all the oxidants to a state where actinides are no longer soluble. In this way a redox front will be created which will move downstream from the repository. The propagation of the front is depending on the groundwater flow and the kinetics of the reactions between the oxidants in the groundwater and the reductants in the rock.

The redox capacity of the rock can be expressed in terms of the amount of reducing elements. The bedrock contains 1 to 10 per cent of iron mostly in the ferrous form. The reducing capacity of the rock is certainly lower than this because only a part of the iron is accessible for the interaction with the groundwater. A conservative estimate of the redox capacity of the system is that only the amounts of reducing elements in the fracture surfaces are accessible. In a very long time scale the redox capacity is larger due to the fact that also some of the reducing elements at depth in the fracture minerals and even in the bulk of the rock are available for reaction. This is because the oxidants are diffusing into the rock matrix and the reductants are diffusing out of the rock. As a consequence of this the kinetics and the transport processes of the redox reactions are more important than the total redox capacity.

The immediately available redox capacity of the groundwater-rock system might be determined by the weathering reactions. The high concentration of ferrous iron in the groundwater at shallow depth is thought to be the result of weathering of biotite. This is a fairly rapid reaction indicated by the fact that all the near-surface waters have reached a fairly high iron concentration, up to 10 mg/l. Further processes will change the composition of the groundwater giving it a high pH and a high sulphide content and a correspondingly low ferrous concentration. Practically all the iron which was initially dissolved has been precipitated on the fracture surfaces during this process. The iron is easily available for reaction in case the groundwater composition is changed e.g. due to effects of radiolysis. From the laboratory experiments we have seen that the reduction of oxygen is fast most likely due to the dissolution of fracture minerals. The amount of fracture fillings available is identical to the amount of iron initially

dissolved in the water. This amount should be seen as the immediately accessible redox buffer.

6

CONCLUSIONS

The chemical composition and evolution of the groundwater is a central issue in hydrogeology. It is also of very great importance for all studies concerned with the transport of trace elements and toxic materials, corrosion etc. in groundwater systems. E.g., any type of modelling of the evolution of a repository for radioactive waste materials, including the stability of metallic waste canisters, the dissolution of the waste form, and the subsequent transport of radioactive material with the groundwater, must start with a model for the undisturbed system. The data reported in this study indicates that we have a good understanding of the chemical phenomena responsible for the redox state of deep granitic groundwaters and that we can express this understanding in quantitative terms.

For the modelling of the groundwater chemistry it is necessary to identify the processes which have resulted in the chemical composition observed. These processes are mainly the interaction between the groundwater and the rock but can also include other factors like disturbances due to other activities in the borehole.

For the qualitative modelling it is an advantage to be able to test different hypotheses in a laboratory where the system of interest can be isolated from outside disturbances, something which is very difficult in the field.

The redox buffer capacity in the groundwater-rock system can be described by the surficial weathering processes. Siever and Woodford (1979) have described the dissolution of main cations including Fe(II) as the initial and fast reactions in the weathering processes of mafic rocks. This is in good agreement with the results we have obtained where the water samples taken at shallow depth normally have a higher iron content than the deeper waters. This is due to the fact that the deeper waters have a higher pH and also a sulphide concentration which regulates the iron concentration in the solution. The fact that the water at shallow depth always has a high iron content indicates that the weathering reactions dissolve iron by a rate which is fast in comparison with the flow rate of the infiltrating groundwater. Results of our laboratory studies support these observations. Practically all the iron initially dissolved in the water will be precipitated on the fracture surfaces. This fracture filling material is, however, accessible for reaction in case the chemical conditions in the water are changed. Therefore the redox buffer capacity can be defined as the amount of iron dissolved in the weathering process.

It is well known that redox measurements in weakly buffered systems are difficult to perform. Our studies indicate that reproducible Eh values may be obtained under certain well specified conditions in the deep groundwaters. These are

- * No atmospheric oxygen must be allowed to enter into the measuring system.
- * The hydrology in the borehole and in the vicinity of the borehole must be known, so that waters from different origin are not accidentally mixed in the borehole.
- * The fate of the drilling fluid (preferably pure groundwater) used during the drilling operation must be investigated. It may take a long time to eliminate disturbances in the water chemistry from this source.

Accurate chemical analysis of the redox components of the groundwater provides additional information about its redox status. Such an analysis should always be made because it also provides the necessary information for the chemical modelling of the groundwater composition and evolution. We have pointed out that the traditional HCl conservation method for the analyses of total Fe and Fe(II) has serious drawbacks.

In many of the investigated waters the content of sulphide is of the same order of magnitude as the content of sulphate. The sulphide sample is always preserved by zinc acetate and sodium hydroxide, which seems to be an acceptable method. The sulphate, however, is normally analyzed on an untreated sample where the sulphide at least partly may have been oxidized to sulphate. This might result in errors unless the sulphide is expelled from the sample. This could be done by acidification and flushing by nitrogen at the time when the sample is collected.

The sampling of groundwater from depth is not a straight forward process. In order to fully understand the results obtained from these investigations one needs to consider the hydrological situation in the rock both before and after the boreholes have penetrated the water conducting parts of the rock mass.

Before the boreholes have been drilled the groundwater flows in the natural flow paths. This situation can be modelled from the hydrogeologic data collected from the borehole investigations.

As one or more boreholes have penetrated the water conducting horizons the hydraulic situation is no longer undisturbed. The boreholes shortcircuit water conducting horizons and will result in a flow of water from sections with a higher hydraulic head to sections which have a lower head. In recharge areas this results in a flow of surficial water down the borehole and in to deeper lying permeable horizons.

The drilling in itself is also a source of disturbance for the groundwater sampling. The core drilling technique needs large amounts of water to cool the drill bit and to lift the drilling debris. The drilling water which is flushed down is seldom recovered on the ground surface. Our experience is that the water in the high permeability parts of the rock (with hydraulic conductivities above 10^{-6} m/s) are always contaminated by drilling water.

7 ACKNOWLEDGEMENT

I am grateful to all the people at the department of inorganic chemistry, KTH who have assisted me in different ways by discussions, practical arrangements and technical solutions. I am especially grateful to professor Ingmar Grenthe for his valuable suggestions and the fruitful discussions throughout the writing of this thesis and to my co-workers Karin Axelsen and Folke Fredlund for their careful and patient work through the years we have worked together.

The work presented in this thesis has been fully financed by the Swedish Nuclear Fuel and Waste Management Company (SKB). The encouragement and support by especially Harald Åhagen and Fred Karlsson has been of great importance for the quality of the results which have been obtained.

The practical arrangements in the field have been handled by Karl-Göran (Figge) Nederfeldt throughout most of the time. His enthusiasm, good memory and planning ability have to a great extent contributed to the successful field investigations.

At last, but not least, I wish to thank the persons at SGAB, IPK, IPA, IVL, BAT and SKB who have been involved in the investigations reported here for their skilfull contribution to the co-operation.

REFERENCES

Ahlbom K., Andersson P., Ekman L., Gustavsson E., Smellie J. and Tullborg E-L. (1986), Preliminary investigation of fracture zones in the Brändan area, Finnsjön study site, SKB Technical Report 86-05, Stockholm.

Almen K., Andersson O., Fridh B., Johansson B-E., Sehlstedt M., Gustavsson E., Hansson K., Olsson O., Nilsson G., Axelsen K. and Wikberg P., Site investigation equipment for geological, geophysical, hydrogeological and hydrochemical characterization. (1986), SKB Technical report 86-16., Stockholm.

Allard B., Torstenfelt B. and Andersson K. (1981), Sorption studies of $H^{14}CO_3$ on some geologic media and concrete, Mat. Res. Soc. III, R D Symp. on Scientific Basis for Nuclear Waste Management, Boston.

Andrews J. and Kay L. (1982), $^{234}U/^{238}U$ activity ratios of dissolved uranium in groundwater from Jurassic aquifer in England, Earth Planet. Sci. Lett., 57, 139.

Axelsen K., Wikberg P., Andersson L., Nederfeldt K-G., Lund J., Sjöström T. and Andersson O. (1985) Equipment for deep groundwater characterization: calibration and test run in Fjällveden, SKB Arbetsrapport 86-14, Stockholm.

Boulegue J. and Michard G. (1979), Sulphur speciation and redox processes in reducing environments, in Chemical modelling in aqueous systems, ACS Symp. Ser. 93 Washington D.C. Ed Jenne, E.A.

Claesson T. (1983), Water-rock interaction at elevated temperatures; Chemical changes in water composition, Diss., Chalmers University of Technology, Göteborg, Sweden.

Clauer N., O'Neil J. and Bonnot-Courtois C. (1982), The effect of natural weathering on the chemical and isotopic compositions of biotites, Geochim. Cosmochim. Acta, 46, 1755.

Cramer J. (1982), Effects of rock-water interaction on radionuclide transport, p. 277 in Atomic Energy of Canada Limited Technical Record, TR-201.

Curtis D. and Gancarz A. (1983), Radiolysis in nature: Evidence from the Oklo natural reactors, KBS Technical report 83-10, Stockholm.

Dansgaard W. (1964), Stable isotopes in Precipitation, *Tellus*, 16, 436.

Davis S and Bentley H. (1982), Dating groundwater. A short review, ACS Symp. Ser., 176, Nuclear and chemical dating techniques: Interpreting the environmental resources. Ed. Lloid A Currie.

Drever J. (1982), The geochemistry of natural waters, Precentice Hall, USA.

Edmunds W., Andrews J., Burgess W., Kay R. and Lee D. (1984), The evolution of saline and thermal groundwaters in the Carnmenellis granite, *Mineralogical Magazine*, 48, 407.

Eriksson E. (1985), Principles and applications of hydrochemistry, Chapman and Hall, London.

Fergusson J. (1982) Inorganic chemistry and the earth, Pergamon Press, N.Y.

Frape S., Fritz P. and McNutt R. (1984), Water-rock interaction and chemistry of groundwaters from the Canadian shield, *Geochim. Cosmochim. Acta*, 48, 1617.

Garrels R. and Christ C. (1965), Solutions, mineral and equilibria, Harper & Row, New York.

Goldich S. (1938), A study in rock-weathering, *J. Geol.*, 46, 17.

Gould R. (1971), Non equilibrium systems in natural water chemistry. ACS Advances in Chemistry Series 106.

Hyypä J. (1984), Chemical composition of groundwater in Finnish bedrock, Nuclear Waste Commission of Finnish Power Companies, Report YJT-84-10.

IAEA (1983), Hydrogeological assessment of potential sites for disposal of high level radioactive waste, Technical report Series No 228, Wien.

Jacks G. (1973), Chemistry of some groundwaters in igneous rocks, Nord. Hydrol., 4, 207.

Jantzen, C.M. (1984), "Methods of Simulating low Redox Potential (Eh) for a Basalt Repository", Mat. Res. Symp. Proc., 26, 613.

Jenne E.A.(ed) (1979), Chemical modelling in aqueous systems, ACS Symp. Ser. 93 Washington D.C.

Kankainen T. (1986), On the age and origin of groundwater from the rapakivi granite on the island of Håstholmen, Nuclear Waste Commission of Finnish Power Companies, Report YJT-86-29.

Karlsson F. and Wikberg P. (1987) Some highlights on the isotope geochemistry studies within the Swedish research program on radioactive waste disposal, Applied Geochemistry, in press.

KBS-1 (1977), Handling of spent nuclear fuel and final storage of vitrified high level reprocessing waste, KBS, Stockholm.

KBS-3 (1983), "Final disposal of spent nuclear fuel", SKBF, Stockholm.

Krauskopf K. (1956), Dissolution and precipitation of silica at low temperatures., Geochim. Cosmochim. Acta, 10, 1.

Lowson R.T. (1982), Aqueous oxidation of pyrite by molecular oxygen, Chemical Reviews 5, 461.

Neretnieks I. (1981), Age dating of groundwater in fissured rock. Influence of water in micropores, Water Resources Res. 17, 421.

Neretnieks I. (1986), "Some Uses for Natural Analogues in Assessing the Function of a HLW Repository" in Natural Analogues to the Conditions around a final Repository for high-level radioactive Waste., Chem. Geol., 55, 175.

Nordstrom K., Plummer L., Wigley T., Wolery T., Ball J., Jenne E., Bassett R., Crerar D., Florence T., Fritz B., Hoffman M., Holdren G., Lafon Jr., Mattigod S., McDuff R., Morel F., Reddy M., Sposito G., Thraillkill J., (1979), Comparison of computerized chemical models for equilibrium calculations in aqueous systems, Redox equilibria of iron in acid mine waters, in Chemical modelling in aqueous systems, ACS Symp. Ser. 93 Washington D.C. Ed Jenne E.A.

Nordstrom D.K.(ed), Andrews J., Carlsson L., Fontes J., Fritz P., Moser H. and Olsson T. (1985), Hydrogeological and hydrogeochemical investigations in boreholes - Final report of phase 1: Geochemical investigations of the Stripa groundwaters. Stripa project. Technical report 85-06.

Nordstrom K. and Puigdomenech I. (1986) Redox chemistry of deep groundwaters in Sweden, SKB Technical report 86-03, Stockholm.

Nordstrom K. (1986), Hydrogeochemical interpretation of the groundwater at the Hästholmen site, Finland, Nuclear Waste Commission of Finnish Power Companies, Report YJT-86-32.

Nordstrom K. and Olsson T. (1987), Fluid inclusions as a source of dissolved salts in deep granitic groundwaters, To be published.

Nordstrom K., Ball J., Vivit D. and Chadwick A., Determination of total and ferrous iron in natural waters, In preparation.

Paces T. (1972), Chemical characteristics and equilibration in natural water- felsic rock-CO system., Geochim. Cosmochim. Acta, 36, 217.

Siever R. (1957), Amer. Mineral., 42, 826.

Siever R. and Woodford N. (1979), Dissolution kinetics and weathering of mafic minerals., Geochim. Cosmochim. Acta, 43, 717.

Smellie J., Larsson N-Å., Wikberg P. and Carlsson L., (1985), Hydrochemical investigations in crystalline bedrock in relation to the existing hydraulic conditions: Experience from SKB test sites in Sweden. SKB Technical report 85- 11, Stockholm.

Stumm W. (1967), Redox potential as an environmental parameter; conceptual significance and operational limitations, Adv. in Water Pollution Res., 1, 283.

Stumm W. and Morgan J. (1981), Aquatic Chemistry, 2nd ed, (John Wiley & Sons, New York).

Torstenfelt B., Allard B., Johansson W. and Ittner T. (1983), Iron content and reducing capacity of granites and bentonite, KBS Technical Report 83-36, Stockholm.

Tullborg E-L., (1986), Fissure fillings from Klipperås study site, SKB Technical Report 86-10, Stockholm.

Whitfield M. (1974), Thermodynamic limitations on the use of the platinum electrode in Eh measurements, Limnol. Oceanogr., 19, 857.

Wigley T., (1976), Effect of mineral precipitation on isotopic composition and ^{14}C dating of groundwater, Nature 263, 219.

Wikberg P., Grenthe I. and Axelsen K. (1983), "Redox conditions of groundwaters Fjällveden, Gideå, Svartboberget and Kamlunge. KBS Technical report 83-40, Stockholm.

Wikberg P. (1986), Grundvattenkemi i SFR, SFR Arbetsrapport 86-05.

Wolery T. (1983), EQ3NR A computer program for geochemical aqueous speciation - solubility calculations: Users guide and documentation, Lawrence Livermore National Laboratory, UCRL-53414.

REDOX CONDITIONS OF DEEP GROUNDWATERS

Peter Wikberg and Ingmar Grenthe

Department of inorganic chemistry,
The Royal Institute of Technology
100 44 Stockholm, Sweden

ABSTRACT

The redox conditions of deep groundwaters from crystalline rock have been studied by in situ field measurements of Eh and analyses of main and redox sensitive elements dissolved in the groundwater. The field observations have also been simulated under well controlled conditions in the laboratory. New equipment for the down-hole Eh measurements and a mobile field laboratory have been constructed. The deep groundwaters investigated are reducing. The Eh level being controlled by iron containing minerals in the bedrock. This is also consistent with the analysis of redox sensitive elements in the water.

INTRODUCTION

The redox potential, Eh, is one of the most important master variables used to characterize natural water systems. Eh may be measured experimentally and/or calculated from a chemical analysis of the various redox couples in the water system.

Several attempts have been made to model the measured Eh-values by using equilibrium models. The results of these attempts have often been discouraging, c.f. Stumm and Morgan, and Lindberg and Runnels. On the other hand there are some cases where there is a good agreement between measured and calculated Eh-values. Some of the more interesting studies and discussions of Eh-data in natural water systems are summarized below:

Lindberg and Runnels (1985) have made a comprehensive review of experimental Eh-data. Their study included several hundreds of Eh measurements in various groundwater systems obtained from the records of the US Geologic Survey. They compared the measured values with those calculated for all possible redox couples in the solution and found no correlation. Consequently they stated that "The computed Eh values do not agree with each other, nor do they agree with the single "master" value measured in the field with a platinum electrode" and "Eh values as input to equilibrium hydrogeochemical computer models will generally yield misleading results for normal groundwaters".

Nordstrom et al. (1979) have studied the redox chemistry of acid mine drainage. They found an excellent fit between measured Eh-values and those calculated from the ferric/ferrous ratio in the solution. They stated that the very good fit was due to the high concentrations of iron. The authors also discuss the criteria which must be fulfilled in order to obtain reliable Eh-measurements.

Boulegue and Michard (1979) have studied the redox conditions in sulphur rich brines and found that the redox potential is controlled by polysulphides. They conclude that this can be the case in many natural sulphide rich groundwaters.

Stumm and Morgan (1981) p 490, Stumm (1966) and Morris and Stumm (1967) have discussed the Eh concept and the reliability of Eh-measurements. They point out the experimental difficulties encountered when making Eh-measurements in systems with a low redox buffer capacity and with redox couples which give low exchange current densities at the electrode surfaces.

Whitfield (1974) has studied the behaviour of the platinum electrodes as an Eh measuring device theoretically. He found that the platinum will act as an inert electrode only within a rather narrow interval. In solutions containing dissolved oxygen the electrode will always respond to the platinum oxide potential. In sulphide rich solutions there is a risk of PtS formation on the

electrode surface. In high saline waters PtCl coatings will be formed.

There are some other studies where the authors have discussed the Eh-evolution in aquifers. Edmunds et al. (1984) have investigated redox processes in three British aquifers. They interpreted the results in terms of sequential reactions giving the water a more reduced character in each step. Both the measured Eh and the analyses of redox sensitive elements supported this interpretation. The unconfined sections of all three aquifers contained dissolved oxygen, Eh 350 - 450 mV. After a sharp redox boundary the Eh seemed to be controlled by Fe(II) (Eh 0-100 mV), Fe(II) and sulphide (Eh -200-0 mV) and methane and hydrogen for Eh < -200 mV.

Champ et al. (1979) have also investigated the redox conditions of a groundwater flow path over a certain distance in a confined aquifer. They interpret the results as redox sequences. These different sequences are characterized by the occurrence of oxygen-nitrate, iron-manganese and sulphide, respectively when going from upland recharge to lowland discharge areas.

From the literature survey given above it is obvious that both the measurements and the modelling of the redox conditions of natural groundwaters is not a straight forward process. The limited material reviewed above, indicates that the measurements and modelling of Eh may be successful in the cases where both chemically and hydrologically well defined systems have been investigated. It seems easier to elucidate how the chemical conditions can affect the Eh measurements than to see how the hydrology affects them. In the following will present a brief discussion on both subjects.

The chemical system must have a sufficiently large redox buffer capacity in order to avoid that the system is disturbed by the measuring procedure itself. The system must also contain a redox couple capable of exchanging electrons with the electrode material. The exchange current density decreases proportionally with the concentration of the redox couple. Hence there is no sharp concentration limit below which it is impossible to measure Eh. However, good measuring devices are needed when measurements are made in solutions with low concentrations of redox couples. Disturbances in the form of irreversible reactions at the electrode surfaces will be more important as the concentration of the electroactive species decreases. It is therefore necessary to identify and eliminate such disturbances.

The kinetics of the redox reactions affects the Eh-measurements in two ways. One is that slow redox equilibria, involving structural changes in the molecules, e.g. $\text{SO}_4^{2-} \rightleftharpoons \text{S}_2^{2-}$, cannot be measured at the electrode surfaces due to too low exchange current densities. The other is disequilibria in the bulk phase caused by recent mixing of different types of water with different redox status, e.g. oxic and anoxic.

The mixing of waters with different characters is the hydrologic phenomenon which in many cases might be the (unknown?) reason for the poor results of many attempts to measure and model Eh. Conta-

mination by drilling water may be one important cause of disequilibria when studying samples of deep groundwaters. Most drilling methods use a cooling medium, no matter whether this is pure groundwater or if it contains mud and lubricants it causes a mixing of the water in the fractures of the rock. Due to this mixing the chemical reactions are no longer at equilibrium or representative of the undisturbed medium.

The pumping of water from a specific section which is sealed off from the rest of the borehole is also a source of disturbances. The pressure gradients in the undisturbed rock are small compared to the gradient caused by the pumping. During the pumping the water is subject to different pressure gradients than normally, hence it also flows and mixes in a different way which may result in a mixing of waters from different regions.

The mere existence of the borehole will also result in mixing processes as water conducting levels are shortcircuited. This results in a flow of water from the level with the highest pressure to the ones with the lowest pressure.

We have recently been engaged in a program to study the chemical properties of deep groundwaters, as a part of an integrated effort to study the geological, hydrogeological and geochemical conditions at selected sites in crystalline rocks in Sweden. In connection with this work we have improved both the sampling methods and the analytical procedures. These technical improvements have made it possible to obtain reproducible Eh-data and to describe these data by using equilibrium models. The experimental work has also given us some insight into the sources of errors that might be encountered when measuring Eh-values in deep groundwaters in crystalline bedrock. In order to support our chemical interpretations of the deep groundwater systems we have also made laboratory studies of the groundwater - bedrock chemical interactions.

This paper is intended to describe the results of Eh-measurements and to compare them with the results of analysis of redox sensitive elements in the groundwater. Both the equipment and the procedure used will be discussed as they both have a large impact on the results. The results of the field investigations have been verified by laboratory simulations of the groundwater - rock interaction.

EXPERIMENTAL

Equipment for in situ Eh measurements

A mobile laboratory and bore hole devices have been built (Almen et al., 1986) in order to characterize the groundwater chemistry in deep crystalline bedrock. Different experimental procedures have been used to measure Eh. These are:

- * in situ measurements in open boreholes
- * measurements in cells on the surface through which the pumped up water flows
- * in situ measurements in isolated sections in the borehole from which water is pumped out

The in situ measurements in open boreholes were not reproducible and the attempt to record Eh values in this way was not pursued.

In an early stage of the field investigations we pumped subsurface water from a packed off section in a borehole to a flow-through cell on the surface. In this cell we measured Eh (and pH). The data obtained indicated that reproducible Eh-values could be obtained, even if it took a long time (three to five days) for the electrodes to attain a steady value (equilibrium?). We also found that calibrations of the electrodes and interruptions of the pumping caused large changes in the Eh-readings. These changes were the result of the entry of small amounts of oxygen into the measuring system. The oxygen was then slowly reduced by the strongly reducing groundwater.

In order to eliminate these disturbances we constructed a down-hole measuring system which could totally eliminate the entry of oxygen. This equipment consists of a down-hole flow through cell with electrodes connected to an electronics compartment for measuring the potentials and transmitting the signal to a surface data collection computer system. We kept the surface flow through cell in order to obtain a comparison between the two measuring systems. The setup is schematically illustrated in Figure 1. The surface flow through cell is principally the same as the down-hole one. The entire measuring system is described in detail by Almen et al. (1986).

The down-hole measuring sond contains three different electrode systems for measurement of Eh, pH and pS and a common reference electrode. The reference electrode is a gel filled triple junction Ag/AgCl electrode. The Eh measuring system consists of three different electrodes, made of Pt, Au and glassy carbon, respectively. We have used different electrode materials in order to ascertain whether the measured potential is influenced by the electrode material (electrocatalysis) or not. The most important advantage of using several different types of Eh electrodes is that mixed potentials are more easily identified as the different inert materials catalyze the electrode reactions differently. Consequently a mixed potential is specific for the electrode material. Even if the mixed potentials would be stable in time they would be expected to have different values for the different electrode materials.

The down-hole pH and pS values are measured by using a pressure equilibrated glass electrode and a Ag/Ag₂S or a silversulphide membrane electrode, respectively. The down-hole electrodes are all specially designed for the purpose, while the electrodes in the surface flow through cells are all commercially available. The

measuring system was tested for stability in different ways. At constant temperature the electronics has a drift less than 1 mV, when tested over periods of several weeks. The pH and Eh electrode systems have the same stability when tested against stable buffer solutions. It was not possible to perform such long term tests of the sulphide electrode since the sulphide solutions were not sufficiently stable. The calibration of the electrodes was used as a continuous test of the performance and stability. The electrode system was calibrated before the down-hole equipment was lowered into the hole and immediately after it was taken up. The calibrations were made at the same temperature as in the sampling section in the borehole. The difference between the two calibrations were in general less than 5 mV for all the electrodes. Differences of 10-15 mV are acceptable for our purposes. When the differences were larger the electrodes were exchanged for new ones. Our criterion for stable Eh values during the measuring period was that all the electrodes should lie within a span of 20-30 mV and the change in potential should be less than 10 mV within two days.

Each of the electrodes was connected to a separate amplifier. In this way very little current passed through the electrodes. The amplifiers were connected to a multiplexer which was operated from the surface data collection computer system. The multiplexer connects each of the electrodes to an A/D converter. The digital word was then converted into serial form and sent to the surface as a frequency shifted signal.

The Eh-measurements is one of the parameters used to characterize the redox state and the general chemistry of the groundwater. We have also made extensive chemical analyses of the major chemical components including redox sensitive main and trace elements. The main constituents are necessary in order to understand the flow and mixing processes that might occur down-hole. These data are needed continuously and immediately in the field experiments. The redox sensitive elements have to be analyzed before oxygen has entered into the water samples. In order to obtain this information we have used on site measurements in a mobile field laboratory. As discussed in the next section this was the only possibility to obtain quick and reliable analyses.

Sampling procedures

Sampling holes were in general core drilled. The water yielding fractures were located by hydraulic conductivity measurements. A set of sections were selected for groundwater sampling. These were then sealed off by packers and the water was pumped out continuously. A schematic illustration of the entire equipment is given in Figure 2.

The pumped up water was lead directly into a field laboratory. In this way the water could be analyzed without coming in contact with the atmosphere. In the field laboratory the water passed through cells where the down-hole measured Eh and pH values were checked. The conductivity and the dissolved oxygen contents of the

water were also measured in these cells, which were placed in a refrigerator kept at the same temperature as in the down-hole sampling section.

An ion-chromatograph, a spectrophotometer and various titration methods were used for the field analyses. Methods, elements and the detection limits are summarized in the Table 1 below.

Table 1. Methods and detection limits of the analyses which are performed in the field laboratory.

Method	Element	Detection limit (mg/l)
IC	Na	0.1
IC	K	0.1
IC/SP	NH ₄	0.1/0.005
IC	NO ₃	0.05
IC/SP	NO ₂	0.05/0.001
IC	F	0.1
IC	Cl	0.1
IC	Br	0.05
IC/SP	PO ₄	0.2/0.002
IC	SO ₄	0.05
SP	Fe _{tot} /Fe ²⁺	0.005
SP	Mn	0.01
SP	SiO ₂	1
SP	S ²⁻ tot	0.01
Tit	Ca	2
Tit	Mg	0.4
Tit	HCO ₃	0.6
SF	Uranine	<0.1% drilling water contamination

IC = ion-chromatograph
 SP = spectrophotometer
 Tit = titration
 SF = spectrofluorimeter

Equipment for laboratory simulation of the redox conditions

During the field investigations we have in many cases found water samples which had ten per cent or more of drilling water contamination. Despite of this the waters were mostly reducing with an appreciable concentration of ferrous iron. This indicates that the kinetics for the reduction of the oxygen initially dissolved in the drilling water is fast enough to deplete the water of oxygen within a time span of a few months.

In order to test these observations on a laboratory scale we made a number of experiments where we kept groundwater in contact with drill cores of the rock in well sealed glass vessels. The water phase was circulated continuously by a magnetic piston pump inside the vessel. The pH and the Eh were measured continuously by electrodes. The vessel was filled with approximately 5 litres of water and the surface area of the drill cores were approximately 30 square decimeters, geometrically estimated. The experimental setup is schematically illustrated in Figure 3.

RESULTS AND DISCUSSION

Eh measurements

The down-hole Eh measurements turned out to be more stable than those made on the surface, Figure 4 illustrates these differences.

The shaded areas in Figure 4 include readings of all three electrodes, gold, platinum and glassy carbon. The difference between the electrode readings is smaller down-hole than on the surface. However, the surface electrodes also approach the values of the down-hole ones, even though this takes a long time. One observes, that the pump failure indicated in the Figure has only a marginal effect on the down-hole electrodes, whereas the surface electrodes are strongly affected. This is caused by oxygen diffusion into the surface cell, and the effect of this on the redox processes on the electrodes and in the solution. The down-hole electrodes are not affected because of the total absence of oxygen in the surrounding groundwater.

The most important conclusion to be drawn from Figure 4 is that after the initial equilibration process the electrodes are constant without any drift even in the time scale of several months.

An example of mixed potentials is the effect of small amounts of dissolved oxygen on the electrode readings. This effect is easy to distinguish because the electrodes always respond in the same way to small portions of oxygen dissolved in the water. Figure 5 and Figure 6 show how the electrodes in the surface flow through cell

respond in the beginning of a sampling period. Even though the examples are taken from two different type of waters, see Table 2, the Eh electrodes respond in the same way. The gold electrode always gives a value which is much higher than the other electrodes. The gold electrode is also the one which gave the largest response to the pump failure in Figure 4. This indicates that the electrode processes on gold are more influenced by oxygen than on platinum and glassy carbon. The concentrations of oxygen that causes these changes is not exactly known. However, the results plotted in Figure 9 indicate that concentrations well below the detection limit of the oxygen sensor, 0.03 ppm, still have an effect on the Eh electrodes.

The rate of the reaction between ferrous iron and oxygen in aqueous solutions is well known. In neutral solutions the rate is equal to

$$\frac{-d(\text{Fe}^{2+})}{dt} = -4 \frac{d(p\text{O}_2)}{dt} = k(\text{Fe}^{2+})p\text{O}_2(\text{OH}^-)^2$$

The rate constant k has been found to have a value of approximately $10^{12}(\text{mol/l})^{-2}\text{atm}^{-1}\text{s}^{-1}$ by several investigators, see e.g. Lawson, 1982. With a pH of 8.5 and a constant ferrous content of 0.56 mg/l and a sufficiently low concentration of oxygen this is a pseudo first order rate reaction with a half life of about 8 hours. However, this reaction is very sensitive to pH and the estimates of the rates of oxygen reduction must be calculated for each situation. There is no doubt from the above estimate that the intrusion of a pulse of oxygen in the sampling section or in the measuring cell will spoil the measurements for several days.

The reproducibility of the Eh measurements was checked on several occasions. The results are compiled in Figure 7. These data indicate that the reproducibility of both the Eh and the pH measurements is good.

The Eh is given as a function of pH in Figure 8. All data where stable Eh values were obtained are included. The bars in the Figure represents the largest difference between the measured Eh-values of the different electrodes.

In Figure 8 one observes that there is a difference in the results obtained in the early phases of the field measurements and the later ones. This difference is a result of the improvement of the measuring procedures. In the early phase the Eh-measurements were interrupted frequently by calibrations of the electrodes. Each time oxygen entered into the flow cell, it was only slowly expelled. A typical situation after a calibration is shown in Figure 9 where Eh and dissolved oxygen values are presented as a function of time. From the figure it is obvious that there is a drift in the readings as long as there is dissolved oxygen left in the measuring cell. In order to eliminate this source of error we decided to continue the pumping without interruptions throughout the whole measuring period in the field studies. This procedure

has been used ever since and has resulted in much lower Eh readings as can be seen in Figure 8.

Analysis

The field laboratory gave results that were more consistent than found previously. The most important improvement was found in the iron analyses. Earlier results, on waters sampled and preserved with hydrochloric acid (Nordstrom et al., in prep) and sent to laboratories for analyses, showed a notable difference between the amounts of total and ferrous iron. However, this was an artifact due to the time delay between sampling and analyses. The oxidation of ferrous iron to ferric is a slow process in the acidified sample but it does occur, and by time significant quantities are oxidized. The results of analyses made at three different laboratories are presented in Figure 10. One can easily see that the results from the field laboratory always gives a ferrous iron content which is equal to the total iron content. The results from the other two laboratories vary considerably. However, the results of the total iron analyses agrees very well between all three laboratories.

Some of the computer codes used for the equilibrium modelling compute the Eh-value of the solution on the basis of analytical data for ferrous and ferric species. Calculations of this type will be erroneous if a proper analytical method is not used. Our data indicate that the traditional HCl-preservation must be used with great care.

Modelling of the redox conditions of the deep groundwaters

The chemical interaction between the groundwater and the minerals in the crystalline rock investigated, determines the character of the groundwater. The water in the highly permeable parts of the rock are of sodium-calcium bicarbonate type and has a fairly high Fe(II) content, whereas the water in the less permeable parts of the rock are of sodium-calcium chloride type with much lower iron, but a rather high sulphide content. An example of the composition of these two types of water is given in Table 2. From the Eh-values in the Table it is obvious that both types of water are strongly reducing.

Table 2. The chemical composition of groundwater from boreholes Fjällveden 2, at 468m and with high hydraulic conductivity and Fjällveden 7, at 722 m and low hydraulic conductivity. All concentrations are given in mg/l.

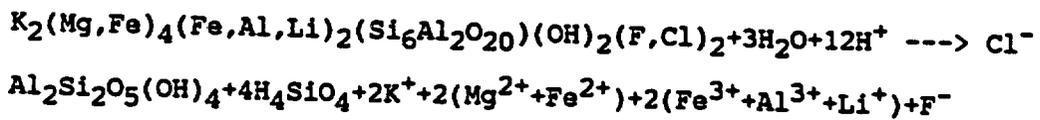
Analysis	Fj 2	Fj 7	Analysis	Fj 2	Fj7
pH	6.9	9.0	Eh(mV)	-220	-350
HCO ₃	182	16	Na	36	300
Cl	3.7	470	K	1.4	1.3
F	0.6	6.2	Ca	27	40
SO ₄	2.0	0.5	Mg	3.0	0.2
S(-II)	0.2	0.6	Mn	0.2	.007
NO ₃	<.001	.009	Fe(II)	1.0	<.005
NO ₂	<.001	<.001	NH ₄	.05	.04

The results of the Eh measurements made in the early stage of the investigations provide an example of the difficulties in the interpretation. The measurements gave a poor fit to a model based on the ferrous and ferric iron content of the water (Wikberg et al., 1983). This was thought to be due to disturbances of oxygen. Later on the same data were modelled by Nordstrom and Puigdomenech who showed that the Eh in fact was controlled by the sulphide, polysulphide and sulphur equilibria (Nordstrom and Puigdomenech, 1986). The formation of polysulphide has taken place through oxidation of sulphide caused by the intrusion of oxygen. Similar phenomena are known from some sulphide rich brines (Boulegue and Michard, 1979). From the EQ3/EQ6 data base (Wolery, 1983) the theoretical Eh-pH dependence for 0.01 ppm and 1 ppm sulphide have been calculated (Puigdomenech pers. comm.) and included in Figure 8, lines A1 and A2. The theoretical Eh-pH dependence for the hematite-magnetite equilibrium is also from the EQ3/EQ6 data base (Puigdomenech pers. comm.), line C.

The more recent field data have not been disturbed by intrusion of oxygen. Therefore they plot close to the theoretical line for the hematite-magnetite equilibrium. As can be seen from Figure 8 the measured values both down-hole and on the surface agree very well. This indicates that the redox condition of the groundwater is controlled by the minerals of the rock. This is reasonable since the large buffering capacity is in the rock and fracture filling minerals and not in the water. However, the fact that a certain mineral equilibrium agrees with the measured Eh does not mean that the electrodes respond to this reaction. The electrode process must still be mediated by a redox couple in the solution which has a high enough exchange current density on the electrode

surfaces. It is reasonable to think that this is the ferrous/ferric redox couple. The ox/red ratio of this redox couple is then controlled by the minerals.

The following scenario might describe the Eh determining processes in the rock - groundwater system. Water which percolates through the fracture systems of the rock slowly dissolves primary minerals of the rock. This process, weathering, occurs on the fracture surfaces in the recharge areas. The weathering results in alteration products which are specific for the process. Such reactions, occurring in granitic rocks, have been frequently discussed in the literature. Edmunds et al. 1984, have studied the chemistry of groundwaters in Carnmenellis granite in the south west of the British Isles. They concluded that the highly saline waters encountered had resulted from the kaolinization reactions of biotite and feldspar. Cramer, 1982, also found that the chemical composition of the groundwater in the Lac du Bonnet granite in Manitoba, Canada was described by the alteration of plagioclase, K-feldspar, biotite and muscovite to form kaolinite and illite. These alteration products were also found in the open fractures. The kaolinization reaction as given by Edmunds et al. is:



This is a process where ferrous iron is dissolved in quantities large enough to explain the amounts in the groundwaters. In cases where oxygen containing water has weathered the rock it is possible to see an increase in the amount of Fe(III) oxides as the ferrous iron released was oxidized to ferric which was precipitated immediately, see e.g. Goldish, 1938.

The redox conditions of the groundwater thus reflect the redox conditions of the bedrock even though chemical equilibrium has not been reached between the solid minerals and the dissolved species in the groundwater. As iron is the main redox constituent in the solution it is not surprising that the Eh-values measured in the groundwaters shows a good correlation with Fe(II) and Fe(III) mineral equilibria. Many minerals give equilibrium lines which are close to one another. We have used the magnetite-hematite equilibrium as an example even if these are not the dominating Fe(II) and Fe(III) minerals in the investigated granites. Brotzen has previously described the Eh-values in deep groundwaters in crystalline rock (KBS-1, 1977) as controlled by the ferrous/ferric ratio in silicates. Due to the possible variations of the ratio Fe(III)/Fe(II) in the silicate solid solutions a variation of +/- 100 mV was applied. The Eh-pH relation valid for unity ferrous/ferric ratio is given by the equation

$$\text{Eh(V)} = 0.26 - 0.06 \text{ pH}$$

Results of more recent investigations show that the Fe(II) minerals are by far more common than the Fe(III) minerals in the investigated sites (Torstenfelt et al., 1983). Assuming an average ratio of Fe(III)/Fe(II) of 0.1 the values are 60 mV more negative included as line B in Figure 8. This line is only about 20 mV apart from the magnetite-hematite equilibrium line and as good a model for the measured Eh values as the line C. There are also other phase equilibria which give an Eh-pH relation close to the measured Eh data. An example of such a reaction suggested by Eriksson, 1985, p. 76, involves the equilibrium between goethite and pyrite. This reaction has a slope of -75 mV/pH and depends on the concentration of sulphate in the water.

The bedrock is very heterogeneous from a strict chemical point of view. Therefore we do not want to imply that Eh is controlled by one specific reaction but only conclude that the redox conditions are determined by the iron in the rock and fracture minerals. It should also be noted that the measured Eh values in general show that the waters are undersaturated with respect to Fe_2O_3 by approximately three orders of magnitude. These calculations are made using the Eh, ferrous iron and pH data because ferric iron concentrations are not analytically available because practically all the iron in the waters is in ferrous form, c.f. Figure 10.

The water samples from the early phase of the investigation should also have given Eh values close to the latter ones if the measurements had been carried out without interruptions for longer periods. This is indicated by the fact that one single point where the sampling section was pumped for a much longer time than the others due to a very low flow rate plots close to the model lines B and C in Figure 8. In this particular experiment there was time enough for all the dissolved oxygen to be expelled from the measuring cell.

Laboratory simulation of the redox conditions

The results of three consecutive experiments where water was circulated in contact with drill cores in a well sealed glass vessel are illustrated in Figure 11 in the form of Eh versus time plots. The pH is not included since there was no significant change during the course of the experiments. A comparison between the experiments where the water initially was saturated by oxygen and the one where the water was deaerated clearly shows that there is a delay in the Eh drop in the first case. It should also be noted that the platinum electrode is much more sensitive to oxygen than the graphite electrode, c.f. Whitfield 1974. However, when the oxygen is consumed all electrodes level out at about the same values. Similar experiences have been reported by e.g. Jantzen (1985).

During these experiments the water was analyzed for iron and sulphide. The results are presented in Table 3. The analyses were made after terminating the experiments, except for the first run where the natural groundwater was used.

Table 3. Sulphide and total and ferrous iron contents in the water rock interaction experiments. The 0-values are the concentrations in the natural groundwater used for the first experiment. All concentrations are given in mg/l.

Component	NATURAL GROUNDWATER			DEIONIZED WATER + HCO ₃	
	0-values	1A	1B	2	3
Fe(II)	<.005	.039	.039	.006	<.005
Fe(tot)	<.005	.041	.041	.011	<.005
S(-II)	<.01	----	.03	.02	-----

The successively decreasing amounts of iron suggests that the surface of the drill cores is gradually oxidized, leaving a smaller amount of ferrous iron left to be dissolved in the water. However, as the reduction of oxygen proceeds with the same rate in all the experiments it seems as if the reaction occurs on the mineral surfaces and not in the bulk of the solution. If the reaction had taken place in the solution the rate would have been proportional to the amounts of dissolved iron. Consequently the last experiment should have needed a longer time to reach reducing conditions than the two preceding ones, this was not the case.

A constant reduction rate could also be explained by a microbial reduction of the dissolved oxygen. Organic material left on the drill cores from the drilling could constitute the substrate for the bacteria. We do not think that this is the case but the probability will be investigated in the future.

A set of similar experiments has been run with crushed material in a different experimental setup. The result of these four runs are presented in Figure 12. The first three of them are identical. In the fourth the equipment was placed in a box with nitrogen atmosphere. As shown in the Figure this made the Eh drop about 200 mV compared to the previous runs. This indicates the extreme oxygen sensitivity of the redox system. The constant Eh values in the three first experiments indicate a steady state situation where the rates of oxygen diffusion into the system is balanced by the rate of reduction by the Fe(II) minerals.

The reduction of oxygen due to chemical interaction between the minerals and the infiltrating groundwater is a commonly accepted theory. Ferrous iron is dissolved from easily weathered minerals and reacts with the dissolved oxygen precipitating ferric hydroxide (Siever and Woodford, 1979). Neretnieks (1986) proposed that the main process for oxygen reduction in the infiltrating water is the diffusion of oxygen into the rock matrix and a subsequent oxidation of Fe(II) minerals. This process probably involves diffusion of carbon dioxide or protons into the micro fractures where the Fe(II) is dissolved and immediately oxidized to an Fe(III) oxide by the oxygen which has also diffused into the

micropores. Thus the oxygen reduction takes place in the pore water in the micro fractures. Neretnieks (1986) has used an average flow rate of the water and a diffusion rate of oxygen in the rock matrix, to calculate the depth of oxygen penetration. The result of this calculation agrees well with some experimental findings. He has made the assumption that the oxidation has taken place since last glaciation which may be doubtful.

Investigations of weathering profiles show that the content of total iron is constant, (Cramer, 1982), but the ratio Fe(III)/Fe(II) is high at the surface and decreases gradually into the bulk of the rock (Clauer et al., 1982). Fergusson (1982) p.48 and Goldish (1938) have demonstrated how weathering gradually changes the amounts of Fe(II) and Fe(III) oxides. The ferrous oxide decreases and ferric oxide increases. Ferrous iron is dissolved, oxidized and precipitated as ferric hydroxide.

When a large number of experiments have been run with the same drill cores there is a decrease in the reducing capacity. This results in more easily disturbed Eh values and a longer time needed for the initial reduction of oxygen. Polishing the sides of the drill cores when the reducing effect was very low did not improve the capacity significantly. Hence, it seems as if the ability to reduce the oxygen resides mainly in the fracture minerals in these experiments.

In this context it is important to keep in mind the differences between the oxygen reduction taking place a) when the surface water percolates down through the fractures in the upper part of the bedrock, b) in the Eh measuring cells through which the deep groundwater is pumped and c) in the laboratory simulations. The processes are entirely different in all three cases.

The surface water is normally depleted from dissolved oxygen, due to the biological oxidation of organic material, when it percolates through the soil cover. However, when the soil cover is thin, the water which reaches the upper part of the bedrock still contains some dissolved oxygen. Studies of the fracture surfaces in such rocks tell that this residual oxygen has been reduced by Fe(II) dissolved from the minerals in the bulk of the rock. As a result of this reaction the existence of rust can be seen on the fracture surfaces. An other obvious process is also the diffusion of oxygen into the micro pores of the rock matrix, as described previously. The diffusion of oxygen into the rock matrix is a slow process, however, the flow rate of the water in these fractures is also very slow giving the diffusion process time enough to deplete the water from the dissolved oxygen.

In the measuring cells the reduction of oxygen is a homogeneous reaction which occurs in the aqueous phase. Fe(II) species or sulphide (HS^-) reacts with the oxygen. The rate of such reactions is much more rapid as indicated from the calculations of the reduction of dissolved oxygen previously. Also the reactions taking place when a deep reducing groundwater is mixed with a portion of surface or drilling water is of course also of this type.

The reaction taking place in the laboratory is in principle of the same type as the one occurring in the uppermost part of the rock. However, there is one difference. The results of the laboratory studies indicate that the reduction of oxygen is due to reactions with the fracture filling minerals. Such minerals have partly been formed by the precipitates from supersaturated water flowing in the fracture systems. Therefore it is expected that these minerals should be kinetically more accessible to reactions than the bulk rock minerals.

One experiment has also been performed with carbon dioxide saturated water. The pH of this was three units lower than in those previously described. Within two weeks the iron content of the water had reached a level of 0.2 mg/l which is five times higher than what has ever previously been obtained. Therefore there is no doubt that the carbon dioxide weathering is responsible for the high iron concentration in the water. Siever and Woodford (1979) have studied the dissolution kinetics and weathering of mafic minerals. They have divided the dissolution processes into the following steps:

- * a rapid exchange between cations, including Fe^{2+} and Mg^{2+} , and protons in the water
- * a slower incongruent dissolution of silica

Their studies at different pH values indicated that the dissolution rate is strongly dependent on pH. For the results of our field and laboratory investigations this is a fully acceptable model for the most important water-rock interaction.

CONCLUSIONS

It is well known that redox measurements in weakly buffered systems are difficult to perform. Our studies indicate that reproducible Eh values may be obtained under certain well specified conditions in the deep groundwaters. These are

- * No atmospheric oxygen must be allowed to enter into the measuring system.
- * The hydrology in the borehole and in the vicinity of the borehole must be known, so that waters from different origin are not accidentally mixed in the borehole.
- * The fate of the drilling fluid (preferably pure groundwater) used during the drilling operation must be investigated. It may take a long time to eliminate disturbances in the water chemistry from this source.

Eh values obtained in this way, may very well be used as input to equilibrium hydrogeochemical computer models. When interpreting the results of such calculations one must of course always test the equilibrium assumption. It is well known that some redox equilibria are extremely slow, and they are of course not properly modelled by the single master variable Eh. The statements of Lindberg and Runnels (1985) thus need to be somewhat modified.

Accurate chemical analysis of the redox components of the groundwater provides additional information about its redox status. Such an analysis should always be made because it also provides the necessary information for the chemical modelling of the groundwater composition and evolution. We have pointed out that the traditional HCl conservation method for the analyses of total Fe and Fe(II) has serious drawbacks.

By comparing the results of field measurements with laboratory experiments under well controlled conditions we have obtained data that strongly indicates that the Eh-values in deep groundwaters are determined by equilibria in the water phase which are controlled by the minerals in the rock. On an Eh-pH diagram the measured values lie close to the equilibrium line of magnetite and hematite, and the ferrous/ferric ratio in the silicate mineral solid solutions. The low value of Eh is supported by the fact that no ferric, only ferrous iron and sulphide are the dominant redox sensitive elements present in the groundwaters.

The redox conditions in the waters with a high concentration of sulphide and where there has been an intrusion of oxygen seems to be controlled by the sulphide/polysulphide equilibria in agreement with the observations of Boulegue and Michard (1979).

The observed behaviour of oxygen which has intruded into the laboratory system is qualitatively in agreement with the general accepted theories for the evolution of groundwaters from oxidizing to reducing, by Edmunds et al. (1984) characterized by oxygen, iron and sulphide systems.

The redox buffer capacity in the groundwater-rock system can be described by the surficial weathering processes. Siever and Woodford (1979) have described the dissolution of main cations including Fe(II) as the initial and fast reactions in the weathering processes of mafic rocks. This is in good agreement with the results we have obtained where the water samples taken at shallow depth normally have a higher iron content than the deeper waters. This is due to the fact that the deeper waters have a higher pH and also a sulphide concentration which regulates the iron concentration in the solution. The fact that the water at shallow depth always has a high iron content indicates that the weathering reactions dissolve iron by a rate which is fast in comparison with the flow rate of the infiltrating groundwater. Results of our laboratory studies support these observations. Practically all the iron initially dissolved in the water will be precipitated on the fracture surfaces. This fracture filling material is, however, accessible for reaction in case the chemical conditions in the water are changed. Therefore the redox buffer

capacity can be defined as the amount of iron dissolved in the weathering process.

The chemical composition and evolution of the groundwater is a central issue in hydrogeology. It is also of very great importance for all studies concerned with the transport of trace elements and toxic materials, corrosion etc. in groundwater systems. E.g., any type of modelling of the evolution of a repository for radioactive waste materials, including the stability of metallic waste canisters, the dissolution of the waste form, and the subsequent transport of radioactive material with the groundwater, must start with a model for the undisturbed system. If one cannot model this it will not be possible to model the more complex repository system. The data reported in this study indicates that we have a good understanding of the chemical phenomena responsible for the redox state of deep granitic groundwaters and that we can express this understanding in quantitative terms.

ACKNOWLEDGEMENT

The work reported here has been financed by the Swedish Nuclear Fuel and Waste Management Company (SKB). The careful work of our co-workers in both the stationary and the field laboratory is gratefully acknowledged. We also wish to thank Dr. Otto Brotzen and professor Erik Eriksson for their valuable suggestions on this manuscript. The present paper is part of P. Wikberg's ph.D thesis The chemistry of deep groundwaters in crystalline rocks.

REFERENCES

Almen K., Andersson O., Fridh B., Johansson B-E., Sehlstedt M., Gustavsson E., Hansson K., Olsson O., Nilsson G., Axelsen K. and Wikberg P. (1986), Site investigation equipment for geological, geophysical, hydrogeological and hydrochemical characterization., SKB Technical report 86-16., Stockholm.

Boulegue J. and Michard G. (1979), Sulphur speciation and redox processes in reducing environments, in Chemical modelling in aqueous systems, ACS Symp. Ser. 93 Washington D.C. Ed Jenne E.A..

Champ D.R., Gulens J. and Jackson R.E. (1979), "Oxidation-Reduction Sequences in Groundwater flow Systems", Can. J. Earth Sci., 16, 12.

Clauer N., O'Neil J. and Bonnot-Courtois C. (1982), The effect of natural weathering on the chemical and isotopic compositions of biotites, *Geochim. Cosmochim. Acta*, 46, 1755.

Cramer J. (1982), Effects of rock-water interaction on radionuclide transport, p.277 in Atomic Energy of Canada Limited Technical Record, TR-201.

Edmunds W.M., Miles D.L. and Cook J.M. (1984), "A comparative Study of sequential Redox Processes in Three British Aquifers from the United Kingdom", in Proceedings of the Uppsala Symposium on Hydrochemical Balances of Freshwater Systems., Ed. Erik Eriksson. IAHS-AISH Publication No.150.

Edmunds W., Andrews J., Burgess W., Kay R. and Lee D: (1984), The evolution of saline and thermal groundwaters in the Carnmenellis granite, *Mineralogical Magazine*, 48, 407.

Eriksson E. (1985), Principles and applications of hydrochemistry, Chapman and Hall, London.

Fergusson J. (1982), Inorganic chemistry and the earth, Pergamon Press, N.Y..

Goldich S. (1938), A study in rock-weathering, *J. Geol.*, 46, 17.

Jacks G. (1973), Chemistry of some groundwaters in igneous rocks, *Nord. Hydrol.*, 4, 207.

Jantzen C.M. (1984), "Methods of Simulating low Redox Potential (Eh) for a Basalt Repository", *Mat. Res. Symp. Proc.*, 26, 613.

KBS-1 (1977), Handling of spent nuclear fuel and final storage of vitrified high level reprocessing waste, KBS, Stockholm.

Lindberg R. and Runnells D. (1984), "Ground Water Redox Reactions", *Science*, 225, 925.

Lowson R.T. (1982), Aqueous oxidation of pyrite by molecular oxygen, *Chemical Reviews* 5, 461.

Morris J., and Stumm W. (1967), Redox equilibria and measurements of potentials in aquatic environment in Equilibrium concepts in natural water systems. *Adv. Chem. Ser.*, 67, 270.

Neretnieks I. (1986), "Some Uses for Natural Analogues in Assessing the Function of a HLW Repository" in Natural Analogues to the Conditions around a final Repository for high-level radioactive Waste., Chem. Geol., 55, 175.

Nordstrom K., Jenne E. and Ball J. (1979), Redox equilibria of iron in acid mine waters, in Chemical modelling in aqueous systems, ACS Symp. Ser. 93 Washington D.C. Ed Jenne E.A.

Nordstrom K. and Puigdomenech I. (1986) Redox chemistry of deep groundwaters in Sweden, SKB Technical report 86-03, Stockholm.

Nordstrom K., Ball J., Vivit D. and Chadwick A., Determination of total and ferrous iron in natural waters, In preparation.

Siever R. and Woodford N. (1979), Dissolution kinetics and weathering of mafic minerals., Geochim. Cosmochim. Acta, 43, 717.

Stumm W. (1967), Redox potential as an environmental parameter; conceptual significance and operational limitations, Adv. in Water Pollution Res., 1, 283.

Stumm W. and Morgan J. (1981), Aquatic Chemistry, 2nd ed, (John Wiley & Sons, New York.).

Torstenfelt B., Allard B., Johansson W. and Ittner T. (1983), Iron content and reducing capacity of granites and bentonite, KBS Technical Report 83-36, Stockholm.

Torstensson B-A. (1984), A new system for ground water monitoring, Groundwater Monitoring Reveiw, Fall 1984, 131.

Whitfield M. (1974), Thermodynamic limitations on the use of the platinum electrode in Eh measurements, Limnol. Oceanogr., 19, 857.

Wikberg P., Grenthe I. and Axelsen K. (1983), "Redox conditions of groundwaters Fjällveden, Gideå, Svartboberget and Kamlunge. KBS Technical report 83-40, Stockholm.

Wolery T. (1983), EQ3NR A computer program for geochemical aqueous speciation - solubility calculations: Users guide and documentation, Lawrence Livermore National Laboratory, UCRL-53414.

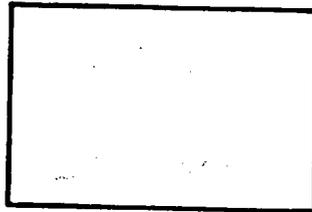
LEGEND TO FIGURES

- Figure 1.** A schematic illustration of the equipment for down-hole Eh, pH and pS(sulphide) measurements. The down-hole sond contains electrodes and electronics which is operated from the surface computer system. The sond is connected to a pump which transports the water up to the surface.
- Figure 2.** A schematic illustration of the integrated mobile field unit which is used for the chemical characterization of the deep groundwaters sampled from isolated sections in narrow boreholes. The water passes through an unbroken plastic liner all the way from the pump to the outlet in the field laboratory.
- Figure 3.** A schematic illustration of the glass vessel and circulation pump system used for the laboratory simulations of the groundwater-rock reactions.
- Figure 4.** Eh versus time plot of the surface and down-hole measured values. Both measurements are made in continuously flowing water. The dashed fields represent the largest differences between the potentials of the gold, platinum and glassy carbon electrodes. The length of a pumpfailure period is indicated.
- Figure 5.** Eh versus time plot of the gold, platinum and glassy carbon electrodes in the surface flow-through-cell at the beginning of a pumping period in borehole Fjällveden 2 at 468 m level.
- Figure 6.** Eh versus time plot of the gold, platinum and glassy carbon electrodes in the surface flow-through-cell at the beginning of a pumping period in borehole Fjällveden 7 at 722 m level.
- Figure 7.** Eh and pH data obtained at repeated groundwater sampling in selected boreholes. The bars indicate the uncertainty in the values.

- Figure 8. Eh versus pH data of all the groundwater samples which have been considered representative of the environment where they have been sampled.
- Figure 9. Eh, pS(sulphide) and dissolved oxygen data versus time in the beginning of a pumping period in the early stage of the investigations.
- Figure 10. Results of analyses of total and ferrous iron concentrations in the groundwaters at three different laboratories. Filled bars equal the amount of ferrous iron. The full bar equals the amount of total iron.
- Figure 11. Eh versus time data obtained in the laboratory studies of the redox kinetics. The first run is made with deaerated water, the other two with air saturated water.
- Figure 12. Eh versus time data of four consecutive experiments on redox kinetics. The fourth experiment is made in a totally oxygen free atmosphere.

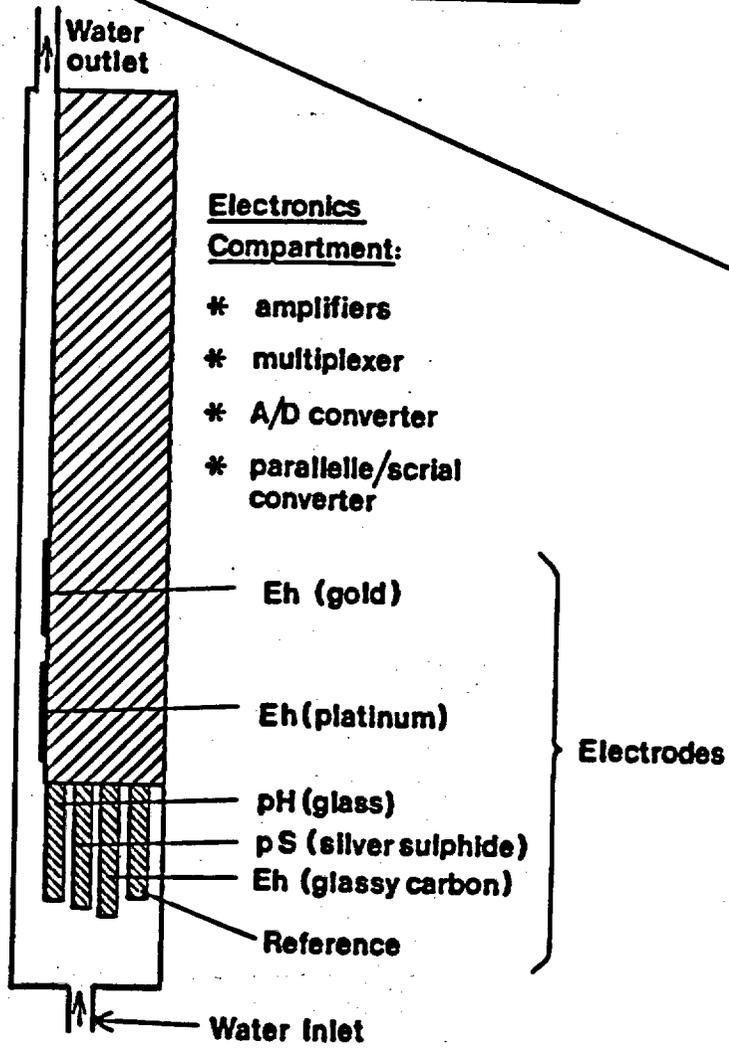
Surface computer:

- * Operate the down-hole sond
- * Collect and store the data



**Electronics
Compartment:**

- * amplifiers
- * multiplexer
- * A/D converter
- * parallele/serial
converter



CONTROL UNIT

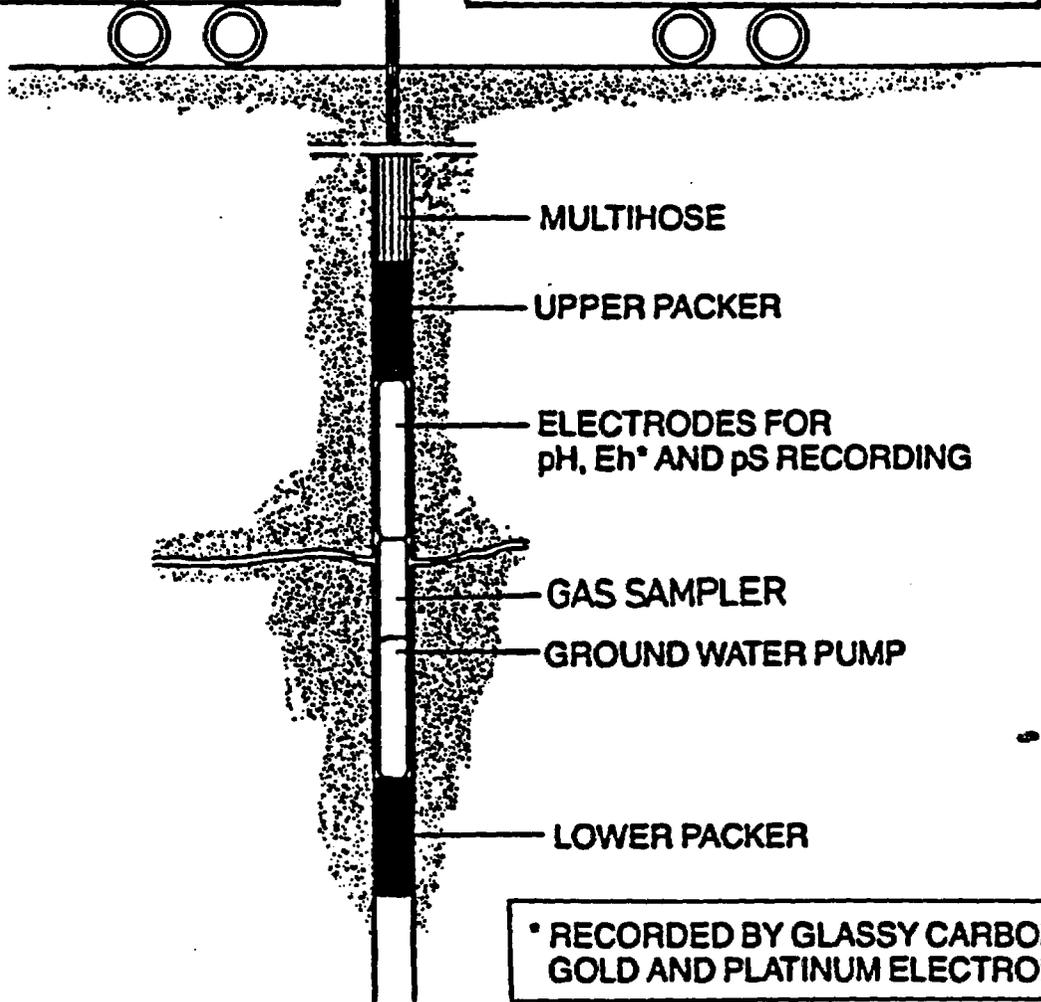
FIELD LABORATORY

- POWER SUPPLY
- DATA COMMUNICATION
- HYDRAULIC PUMP DRIVE AND PACKER INFLATION
- REEL FOR MULTHOSE

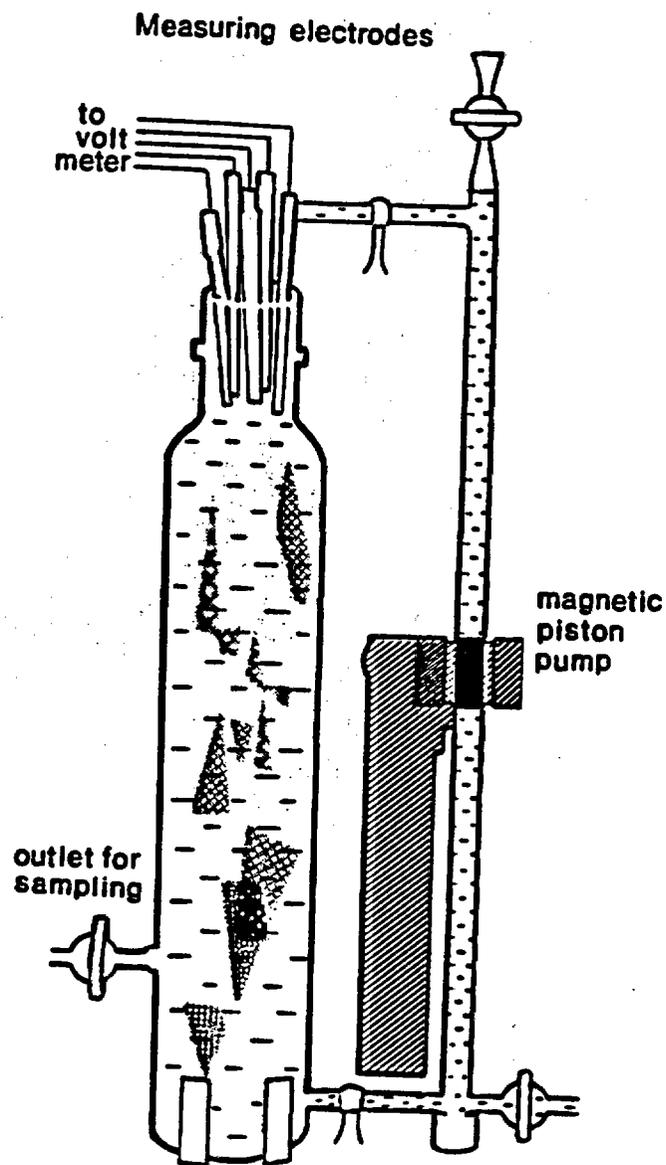
ANALYSES OF
Na, K, Ca, Mg, NH₄, SiO₂,
HCO₃, F, Cl, Br, PO₄, SO₄, S(-II),
NO₃, NO₂, Fe (tot), Fe(II), Mn

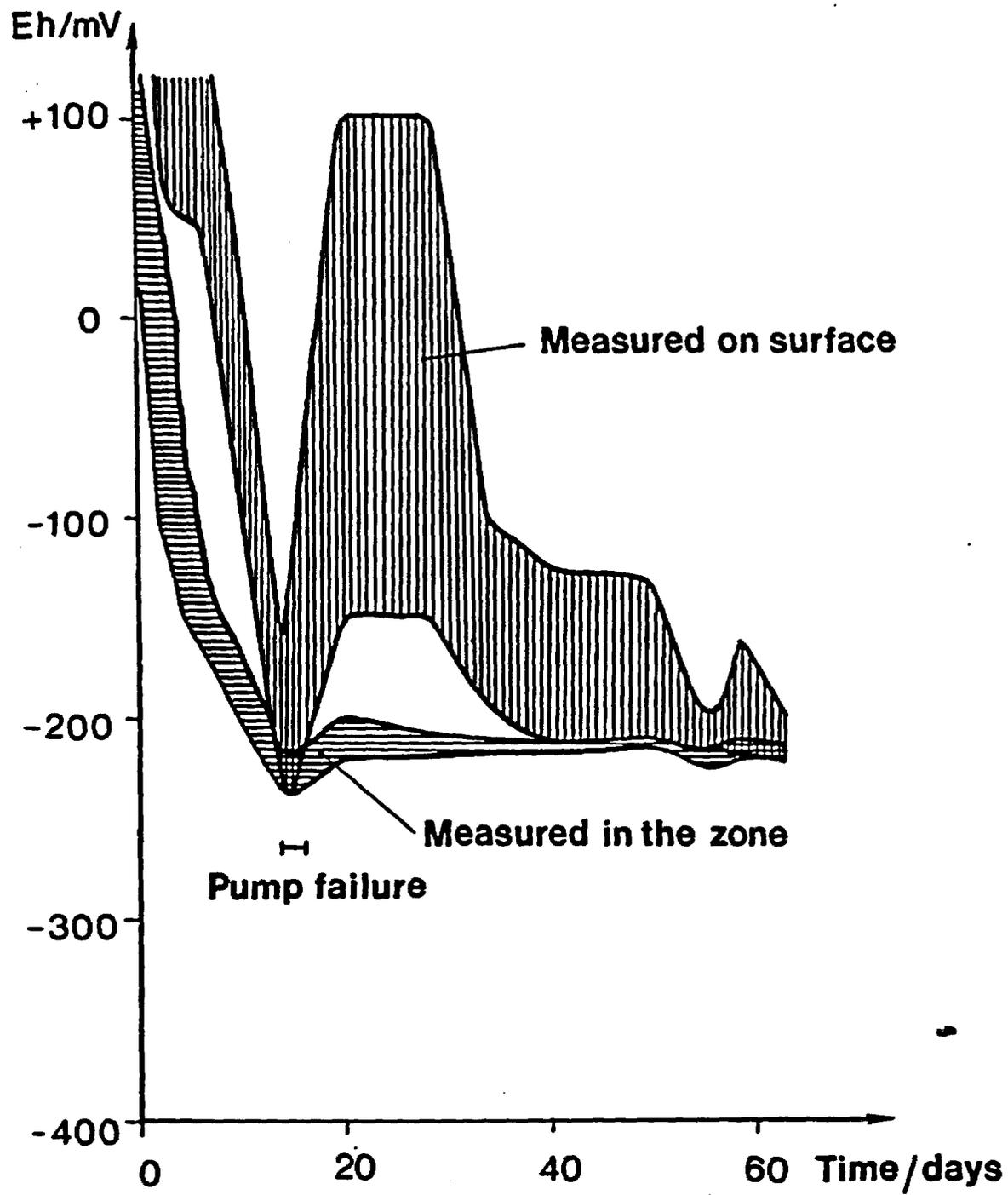
MONITORING
pH, Eh*, pS, pO₂ conductivity

Sampling for further analyses

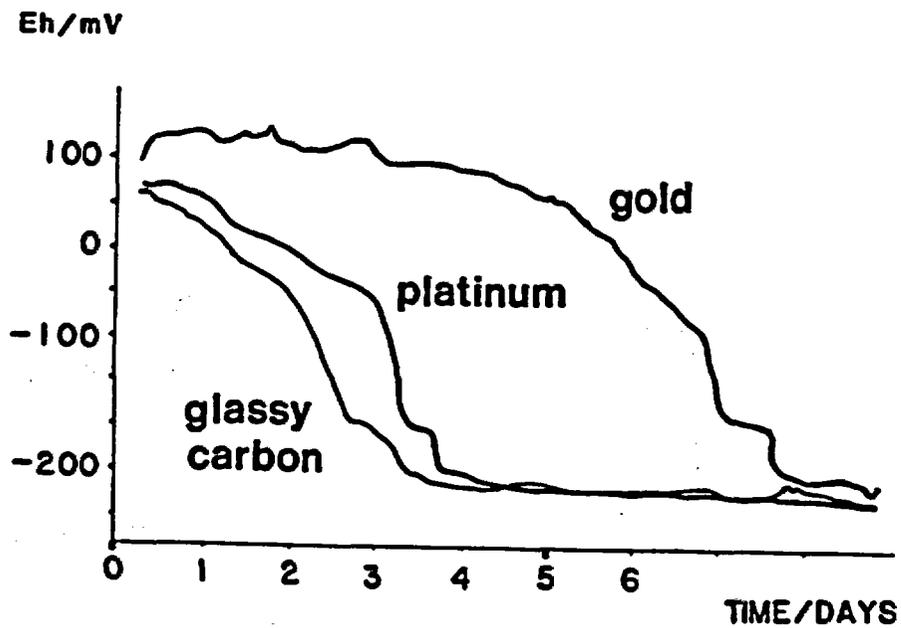


* RECORDED BY GLASSY CARBON,
GOLD AND PLATINUM ELECTRODES

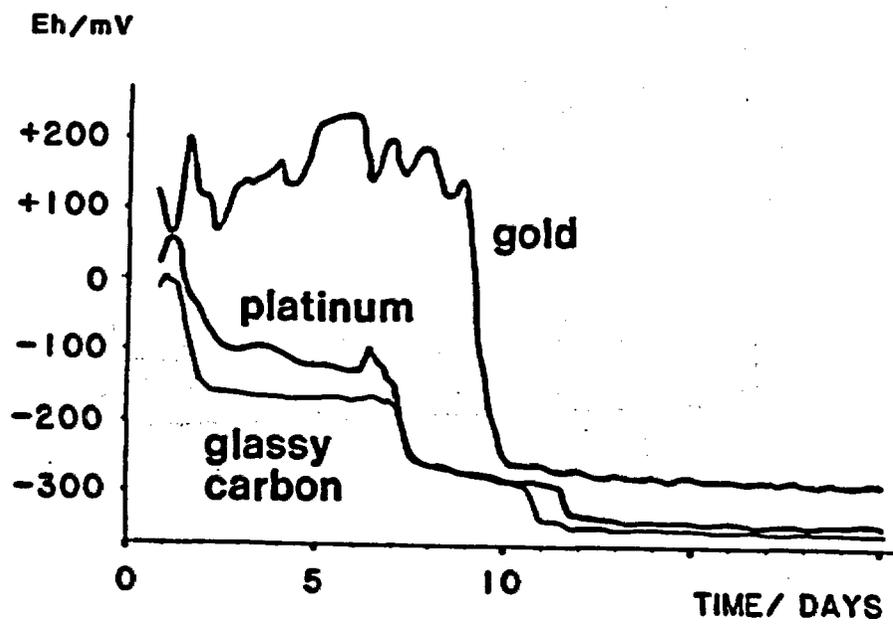


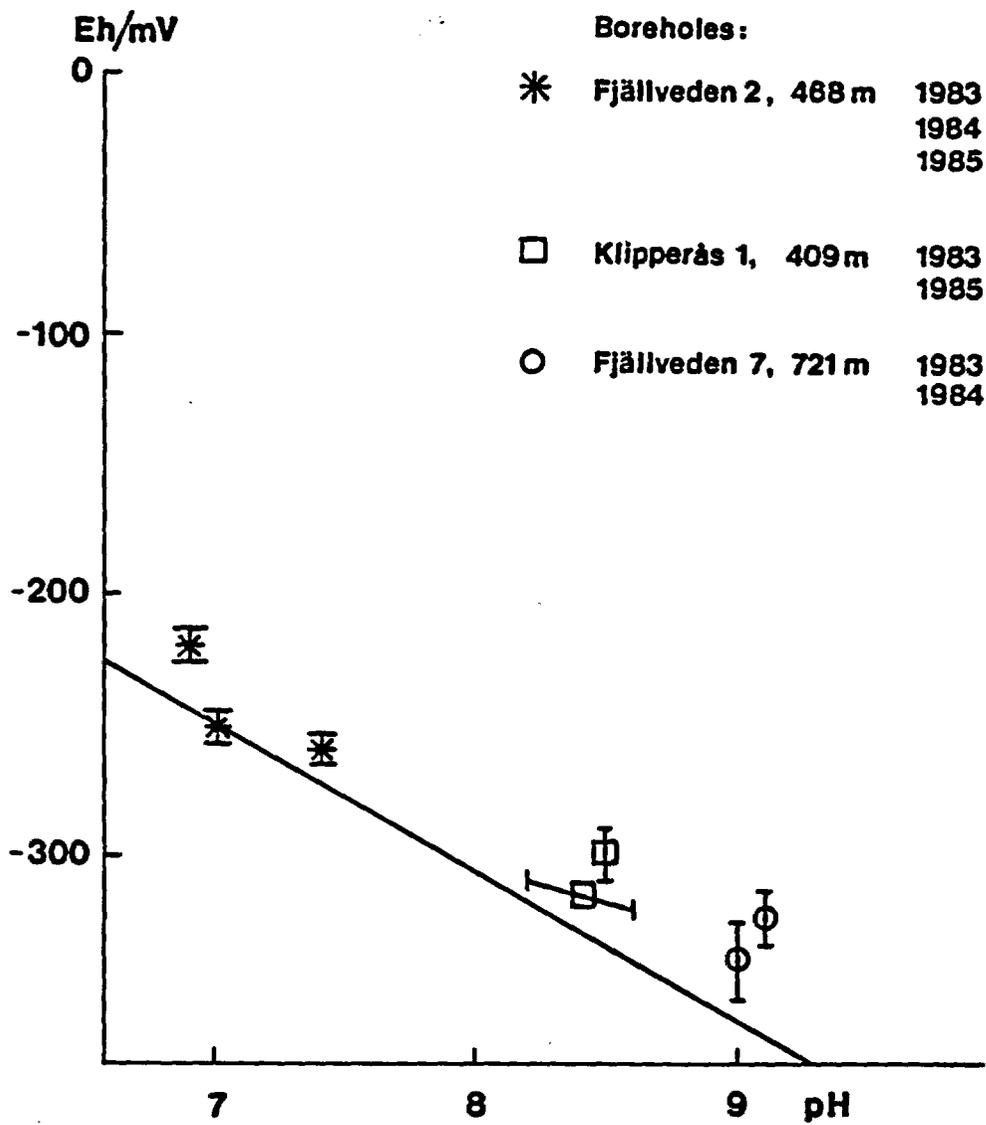


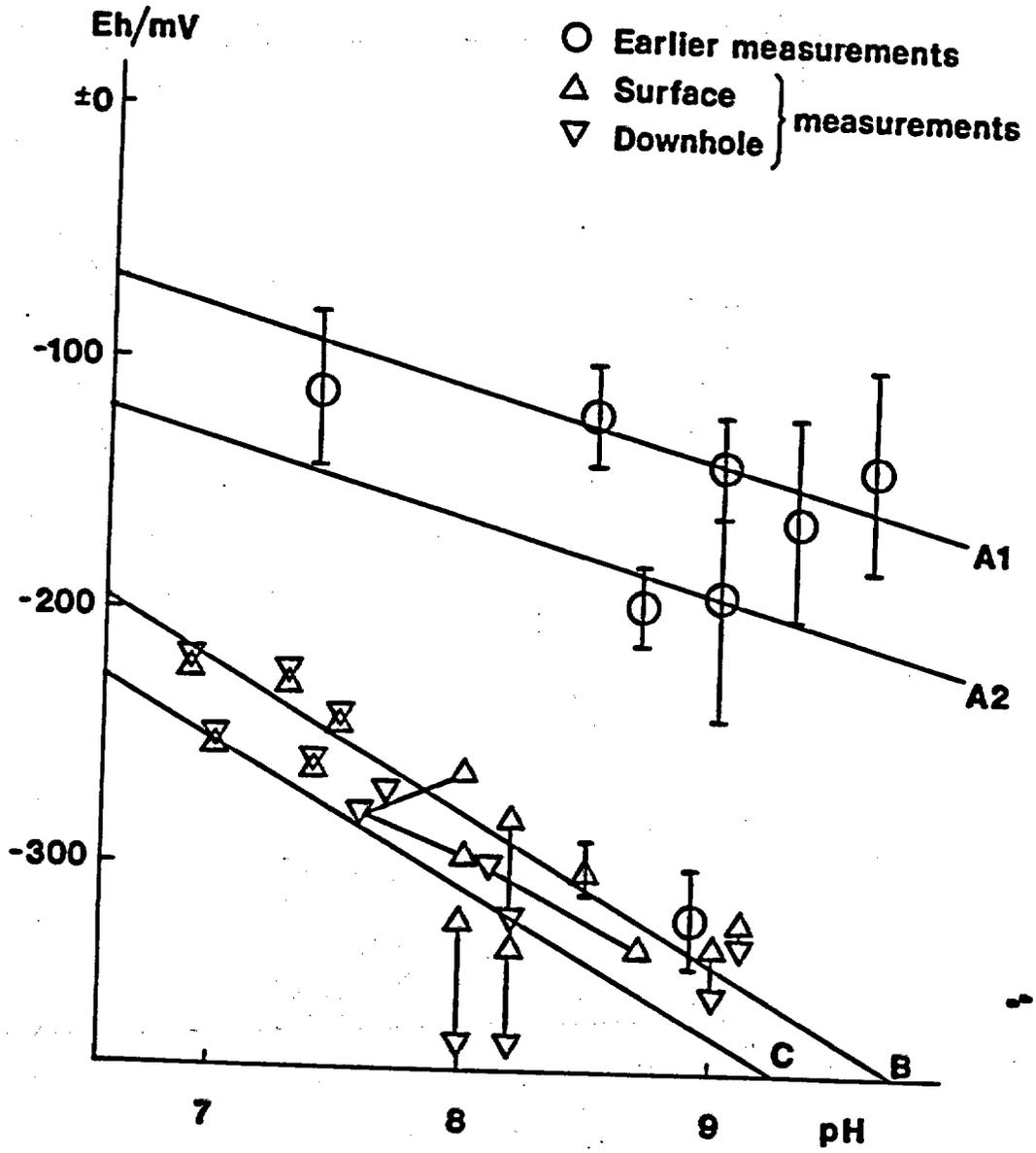
REDOX POTENTIALS MEASURED ON SURFACE

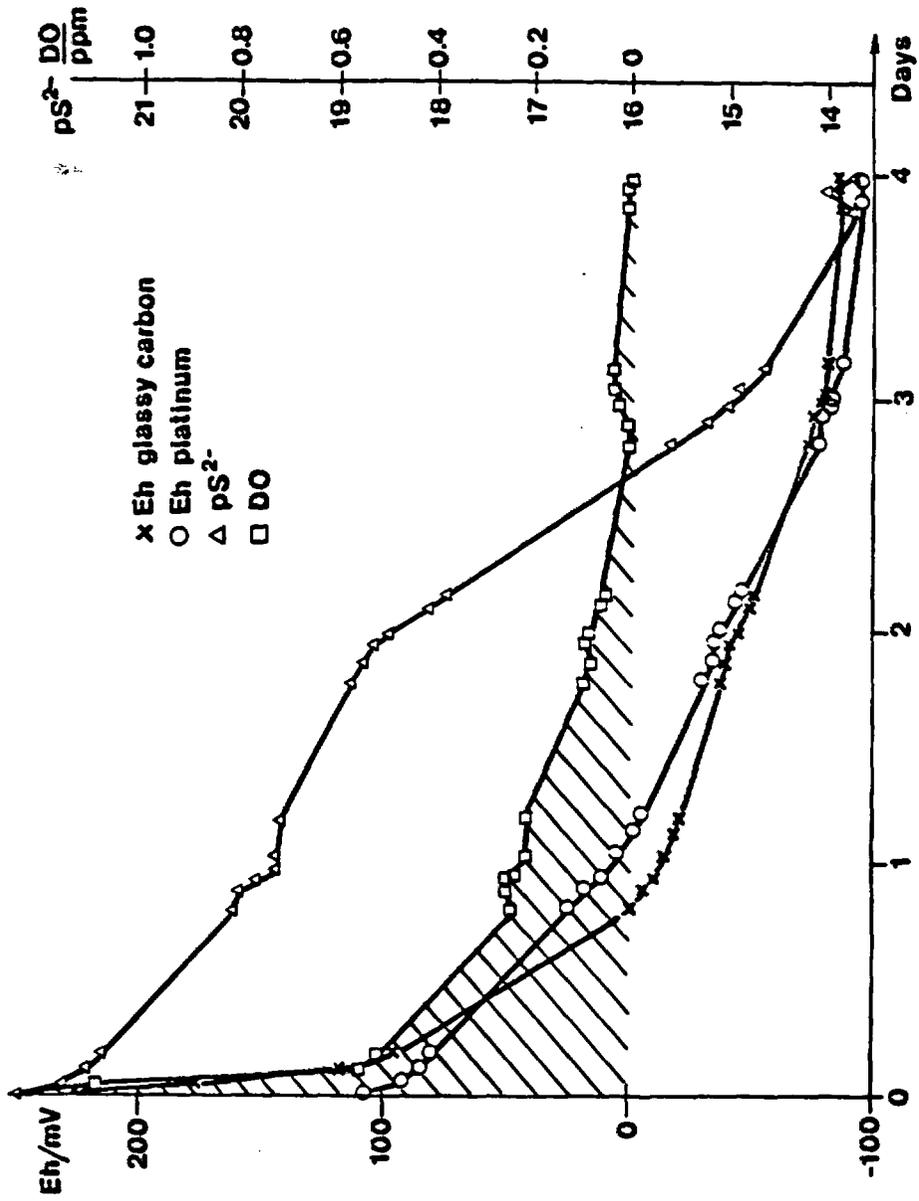


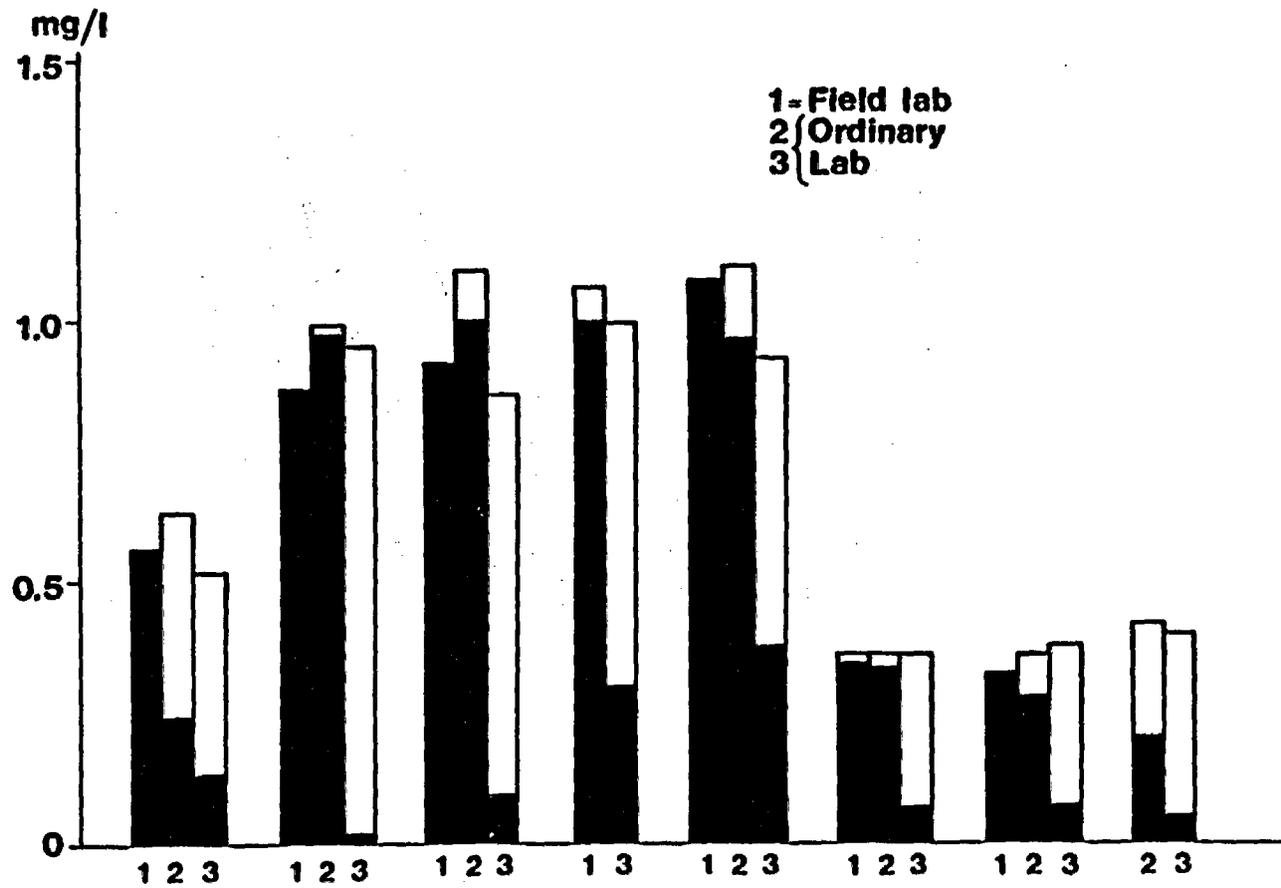
REDOX POTENTIALS MEASURED ON SURFACE

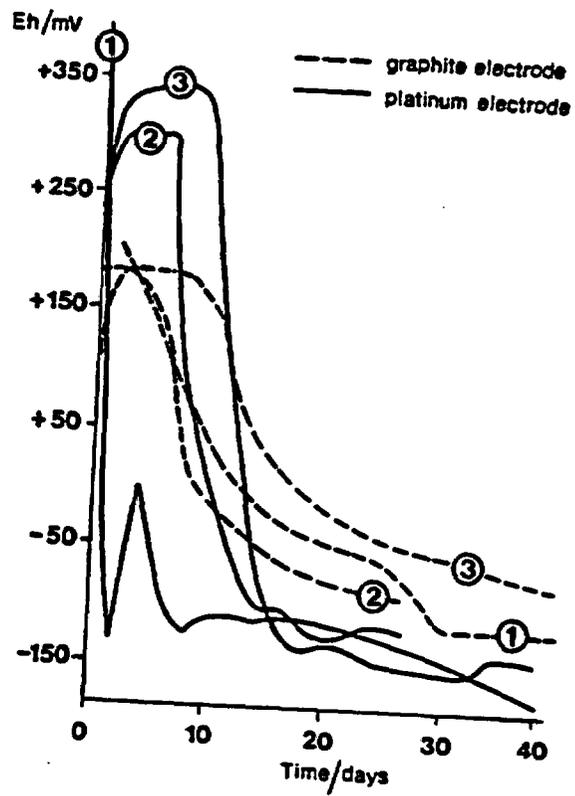


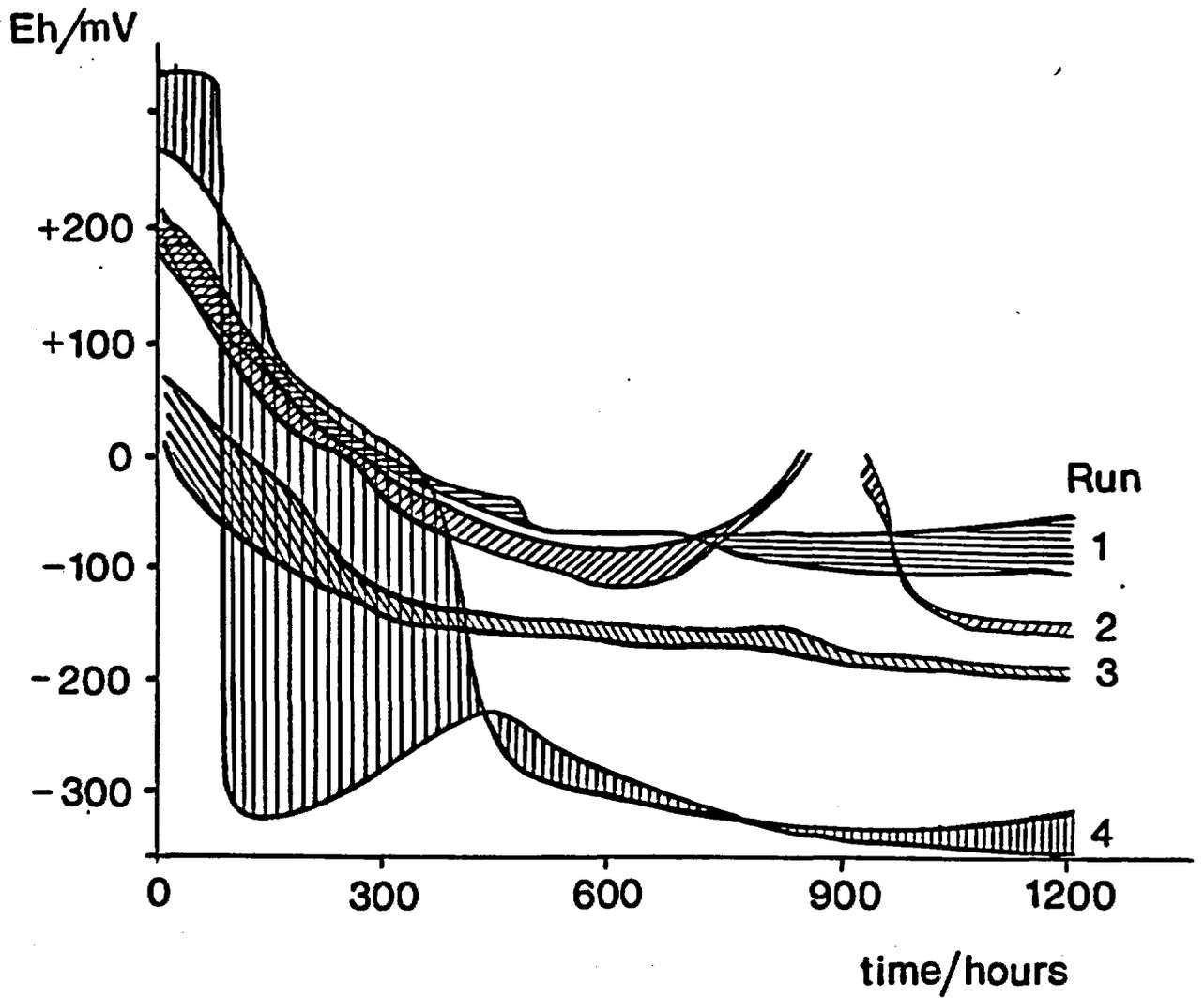












INSTRUMENTATION FOR MEASUREMENTS OF Eh, pH and pS in DEEP GROUNDWATERS

Peter Wikberg and Karin Axelsen
Department of inorganic chemistry, The Royal Institute of Technology,
100 44 Stockholm, Sweden.

Jan Lund, Bengt-Erik Johansson and Olle Olsson, Swedish Geological Company,
Box 118, 930 70 Malå, Sweden.

ABSTRACT

Different methods have been used in order to measure the Eh (redox potential), pH and pS (sulphide concentration) in natural deep groundwaters. A light weight logging tool has been developed for the measurements in open 56 mm boreholes. This equipment is useful for obtaining a chemical profile of a borehole, indicating locations where the character of the water changes. The measurements are not reproducible and therefore useless for a quantitative description of the chemistry of the groundwater. Measurements have also been made in continuously flowing water pumped out from isolated water conducting sections in boreholes. These measurements are reproducible. In conjunction, the water is sampled for further analyses of main and redox sensitive elements. Flow-through-cells have been constructed for measurements both downhole and on the surface. The downhole measurements are not disturbed by atmospheric oxygen as the measurements on the surface.

1. INTRODUCTION

During the past ten years several questions regarding deep groundwaters have been emphasized in the framework of nuclear waste disposal in deep geological formations. Some of the important areas are:

How does the groundwater move in the formation?

How will the water affect the waste package?

How will radionuclides, eventually released from the waste package, be transported by the groundwater?

These questions are fundamental for an evaluation of the over-all safety of a nuclear waste repository located in a deep geological formation. To answer the questions one must have a good knowledge of the groundwater composition and the interaction between the groundwater and the waste package.

Within the Swedish programme for disposal of nuclear wastes, known as the KBS project, the Swedish Nuclear Fuel and Waste Management Company (SKB) has performed investigations of areas, potentially suitable as a repository for underground disposal of spent nuclear fuel (KBS-3, 1983) A number of sites all over Sweden have been studied, cf. fig 1. At some of them, Kamlunge, Gideå, Svartboberget and Fjällveden, thorough geochemical groundwater investigations have been performed. The characterization of the groundwater has been done by three different methods:

- 1) pumping water from packed off sections to the surface and sampling of water for analyses of major and minor elements, trace elements and isotopes. Measurements by electrodes of pH, Eh (redox potential), pS (free sulphide concentration), DO (dissolved oxygen content) and conductivity on the continuously flowing water
- 2) logging of pH, Eh, pS of the water in open coredrilled boreholes
- 3) monitoring of pH, Eh and pS in a packed off sections of the borehole from which water is pumped up. The water is characterized and analyzed as described in 1).

2. INSTRUMENTATION

Increasing emphasis has been put on field measurements and new procedures have successively been developed. As many measurements and analyses as possible should be made in the field, especially those of unstable quantities. There are a number of reasons why such measurements are superior to later analyses made on sampled water. Some of these will be mentioned below.

Many of the critical parameters are changed in contact with the atmosphere, for instance oxygen sensitive parameters like Eh and the concentrations of

ferrous iron, sulphide and dissolved oxygen. The same is true also for carbon dioxide sensitive parameters like pH and alkalinity. Therefore these analyses should be made downhole or at least as soon as possible after the water has been removed from the borehole.

Another important advantage of the field measurements is that they make it possible to obtain a fast estimate of the general chemical character of the ground water. In this way we obtain a check whether mixing or other problems turn up during the sampling. Changes during long pumping periods could also be monitored and the sampling adjusted accordingly.

2.1. Surface measurements

Measurements performed at the surface are made with conventional equipment with commercially available sensors and instruments. The water pumped up passes to flow through cell where pH, Eh, pS, dissolved oxygen and conductivity are measured, cf. fig. 2. The cell is made of stainless steel and polyamid plastic lines are used for transporting the water. The equipment used for this type of measurements consists of:

- o two inflatable packers that are used to seal off a section of a borehole around a conductive fracture or fractured zone
- o a polyamid or teflon liner used to transport the water to the surface
- o a hydraulically operated pump, situated between the packers

This instrumentation has been used to obtain analytical data from the groundwater in the site investigations as mentioned above. The data has been condensed into a table where rather narrow intervals are given for the concentration of the main constituents in the water. In fact more than 90 per cent of all the investigated waters fall within these limits. The remaining waters are mostly saline with a much higher concentration of sodium, calcium, chloride and sulphate.

Table 1.

Average composition of non saline groundwaters in Swedish granitic rock (KBS-3, 1983). The concentrations are given in mg/l.

pH	7 - 9	Ca ²⁺	0 - 40
Eh, V	0 - (-0.45)	Mg ²⁺	2 - 10
HCO ₃ ⁻	90 - 275	Na ⁺	10 - 100
SO ₄ ²⁻	0.5 - 15	K ⁺	1 - 5
HPO ₄ ²⁻	0.01 - 0.2	Fe ²⁺	0.02 - 5
NO ₃ ⁻	0.01 - 0.5	Mn ²⁺	0.1 - 0.5
F ⁻	0.5 - 4	NH ₄	0.05 - 0.2
Cl ⁻	4 - 15	SiO ₂ (tot)	3 - 14
HS ⁻	0 - 0.5	TOC	1 - 8

2.2. Downhole measurements

The instrumentation for the in situ measurements in the boreholes is specially designed for this purpose. Two sets of instrumentation have been developed, one for open hole measurements and one for measurements in a packed off section of the borehole.

2.2.1. Equipment for open hole measurements

The equipment designed for open hole measurements is a light-weight chemical logging system, cf. fig. 3. It consists of a surface unit, a down hole sond and a winch with cable and measuring wheel. The measuring electrodes are of our own construction. Currently the pH, Eh, pS and temperature can be measured with this equipment.

The surface unit is based on a RCA 1802 CMOS microprocessor. The unit transmits a digital word to the downhole unit. The word with the instruction "measure electrode nn" is decoded and the signal from the electrode is sent to the surface unit, also in digital form. From a keyboard the operator can select the electrodes to be measured and add comments in alpha numerical form. All information is stored on paper lists and tape.

The downhole probe consists of a battery package, an electronic compartment and a head for attachment of the electrodes. All units are housed in a 2000 mm long pastic tube with a diameter of 35 mm. The electrode head supports four replacable electrodes and two stationary electrodes (gold and platinum) and a thermistor.

2.2.2. Equipment for measurements in packed off sections

A downhole sond in conjunction with a downhole pump is placed in a zone that is isolated by rubber packers, cf. fig. 4. Water is continuously pumped out of the section and brought to the surface via the sond through a plastic tube. In the downhole section the pH, Eh, pS and temperature are measured. At the surface the same parameters plus the conductivity and the dissolved oxygen concentration are measured, once again in flow through cells, which enable us to check the performance of the downhole equipment.

All measurements are controlled by a surface unit, a RCA:s 1806 CMOS processor. From a keyboard the operator can instruct the unit how to carry out the measurements; name the electrodes, change time between the measurements etc. The software is written in assembler language and consists of an application program and an operative system capable of handling multiple tasks. The communication between the surface and the downhole units is made in frequence shifted serial form with a rate of 300 baud. In combination with a mobile field laboratory (Almen et al., 1986) the operation is made by a MDX-11 computer from Scientific Micro System Inc.

The downhole sond consists of an electronic unit and a measuring chamber. All communication and the power supply to the downhole probe goes through a five conductor cable. The electronics in the downhole unit has the following main tasks:

1. Receive a digital word from the surface unit containing the information "measure electrode mm" and decode it
2. Select the appropriate electrode and convert the analog signal to a digital word
3. Transmit the digital word in a serial form to the surface unit

In the chamber the water flows continuously by the electrodes. Four of the electrode positions are constructed for replaceable electrodes and two electrodes (gold and platinum) are permanently mounted. All the electrodes are connected to separate amplifiers with an extremely high input impedance, 10 Gohms. The temperature is measured by a thermistor with a resolution of 0.01 degree. The electronics and the measuring chamber are housed in a stainless steel tube with a length of 1600 mm and a diameter of 54 mm.

A flow through cell on the surface consists of three chambers, in order to provide separate calibrations of the different electrodes. This unit is placed in a refrigerator in order to obtain a stable temperature. The flow through cell can be equipped with up to eighteen electrodes including the conductivity cell and the DO sensor. The electronics connected to these electrodes are three sets of the same type as used in the downhole probe. All parts of the cell are made of stainless steel and the tubings between the parts are polyamid plastics (Tecalán 6/4).

2.3. Electrodes and sensors

The electrodes and sensors used in the surface flow through cells are listed in table 2. These are all commercially available and reliable under the conditions valid in our experiments.

Table 2.

Electrodes and sensors for measurements in flow through cells

Sensor	Manufacturer	Model	Type
pH	Electrofact	SM 21/AG4	glass electrode
Eh	Metrohm	EA 276	glassy carbon
Eh	Metrohm	EA 281	massive platinum
Eh	Metrohm	EA 284	massive gold
pS	own construction		Ag/Ag ₂ S
reference	Electrofact	SR 20/AP4	gelfilled Ag/AgCl
DO	YSI	57	DO meter
conductivity	Kemotron	802-81	four electrode

For the downhole measurements there are no commercial electrodes available. The high pressure at depth in combination with the limited space in the bore holes are the reasons why we have constructed own downhole electrodes. All electrodes except for the reference have a diameter of less than 10 mm. The pH and the reference electrodes are equipped with a pressure equalisation system so that they can in principle withstand any pressure. Pressure changes do not affect the electrode readings to any significant extent.

3. EVALUATION OF THE MEASUREMENTS

The types of instrumentation described above have been used in very different ways. The use of an equipment for measuring the characteristics of the groundwater when it has been pumped up to surface is a safe way of obtaining data, though in some cases it will be a very time consuming one. The downhole measurements on the other hand is a much better way of obtaining the characteristics in the true surrounding of the water. The downhole measurements, however, need an instrumentation which because of limited space and high pressure in the boreholes need to be specially constructed and hence will become more vulnerable. The experience obtained with the different types of equipment is summarized below:

1) A groundwater pump in combination with a flow through cell on the surface is a sufficient tool for obtaining both master parameters like pH and Eh, and samples for total analyses of the water constituents. The Eh measurements performed in this way are time consuming especially when water with low redox buffer capacities are encountered. It might take a week for the redox electrodes to stabilize after a calibration of the system. This slow drift is probably caused by traces of oxygen that will only slowly be reduced in the water. This assumption is confirmed by laboratory simulations which show that it is possible to obtain stable electrode potentials within one day in solutions with a similar composition as the groundwater (Wikberg et al. 1983).

From a practical point of view the surface flow through cell is convenient to use as the parts are commercially available and they can be exchanged without removing the entire equipment from the borehole.

2) The instrument for measuring the pH, Eh and pS in open boreholes gives a chemical profile of the borehole by measuring these parameters while the instrument is lowered down the hole. However, the reproducibility of the measurements is poor and a quantitative interpretation cannot be made of the measured data. The water in the borehole is not representative of the surrounding rock because of the mixing of shallow and deep waters, and occasionally because of the presence of drilling water in the borehole. On the other hand, the data has a qualitative value as indicator of inflow and outflow of water with different character and the measurements are fast and inexpensive.

3) The best results have been obtained with a quite recently developed equipment which is a combination of the surface and the downhole systems. The pH, Eh and pS values monitored in situ as the water is pumped up are free from disturbances of atmospheric oxygen and therefore even the Eh values stabilize within one day. The same parameter monitored on the surface in a flow through cell shows a different potential to begin with and it lasts about one week before the Eh values monitored on the surface have reached the same level as the electrodes downhole. Fig. 5 illustrates the redox potentials as function of time monitored both downhole and at the surface with three different inert electrode materials.

4. DISCUSSION

The quality and usefulness of the results obtained is depending on the chemical and the hydrological conditions of the investigated system. It is not trivial to identify the one which has the largest impact on the results in different situations. Therefore each of them will be discussed in some detail.

The chemical system in the groundwater of the rock reflects the chemistry of the rock minerals interacting with the water. This interaction is a process which moves towards an equilibrium situation. However, the time needed for the different reactions to reach equilibrium may vary considerably, some equilibria are reached fairly rapidly, e.g. calcite saturation (Fergusson, 1982, p 46), while others are very slow, and equilibrium is, if ever, reached, e.g. quartz saturation (see e.g. Siever, 1957, Krauskopf, 1956).

The internal equilibrium among the redox couples present in the groundwater also need varying time to be established. Hence, different redox couples analyzed in the same water sample give different Eh values (Lindberg and Runnells, 1984). It is essential to identify the different redox couples and to see which of them are reversible and can possibly contribute to the electrode reaction and electrode potential. It is not surprising that one single master Eh value is not obtained from all redox couples present in the water. However, there must be one or more couples which agree with the measured Eh value. This value could be called the effective Eh of the water.

In the case where the Eh level and the buffering capacity are determined by the rock minerals the electrons must be mediated by a redox couple in the solution which has a large enough exchange current density at the electrode. Such a system might easily be disturbed and the Eh measurements have to be made carefully. We have noticed that the measurements in reducing natural groundwaters are extremely sensitive even to trace quantities of dissolved oxygen. It might take days before the effects of the dissolved oxygen have disappeared and the electrode readings are stable.

The prevailing hydrogeological situation determines how the water mixes in an undisturbed situation. In low conductivity parts of the rock the water travels very slowly and is expected to be at equilibrium internally and with the rock minerals. This ideal situation is no longer valid when a borehole has been drilled into the rock. The drilling in itself and the mere existence of the borehole are factors which strongly affect the mixing of waters.

The normal core drilling technique needs large amounts of drilling fluid, pure groundwater or mud, which is pressed down at a high pressure. Most of the drilling fluid is not recovered at the ground surface. Hundreds of cubic meters of water is lost into the conducting sections when a 1000 m deep hole is drilled. Assuming that this water mixes with a ten fold volume of groundwater the volume of mixing water is in the order of thousands of m³. This mixed water is in general not in equilibrium neither internally, nor with the rock minerals. The careless investigator may erroneously take this as characteristic of the deep undisturbed groundwater. A subsequent modelling may reveal its non-equilibrium nature. However, this conclusion is not necessarily valid for the undisturbed water. It is essential to have a good understanding of the possible mixing processes when discussing the chemistry of deep ground water systems.

The borehole shortcircuits conductive parts of the rock mass which mostly have different hydraulic heads. The result of this is that water flows from the parts with the higher heads through the borehole into parts with lower heads. Especially in recharge areas where the hydraulic head decreases by depth this results in a flow of surficial water down the borehole. In this way all the conducting parts in the borehole will be intruded by the surficial water.

The low permeability parts in the rock are normally less contaminated than the high conductivity parts. However, when these sections are sampled a great force is needed to pump out the water. The pressure gradient which is created in this way is orders of magnitude higher than the natural one. Consequently this results in a flow which is different from the natural water flow, i.e. the result is a mixing of water that would not occur in the undisturbed system.

5. CONCLUSIONS

The method one selects for the characterization of the groundwater chemistry must depend on the purpose of the investigation. A quantitative picture of the groundwater chemistry can only be obtained from the investigation of water from an isolated section. The Eh and pH values should be recorded downhole and the analyses of redox sensitive elements should be made in the field.

A qualitative picture of the chemistry can be obtained from a logging of a borehole. The usefulness of the results is in this case dependent of the hydrogeologic conditions.

Before the data are used in equilibrium models one should define the hydrological conditions prevailing when the water sample was taken. A good point is to tag the drilling water with a tracer so that drilling water residues can be detected in the water samples.

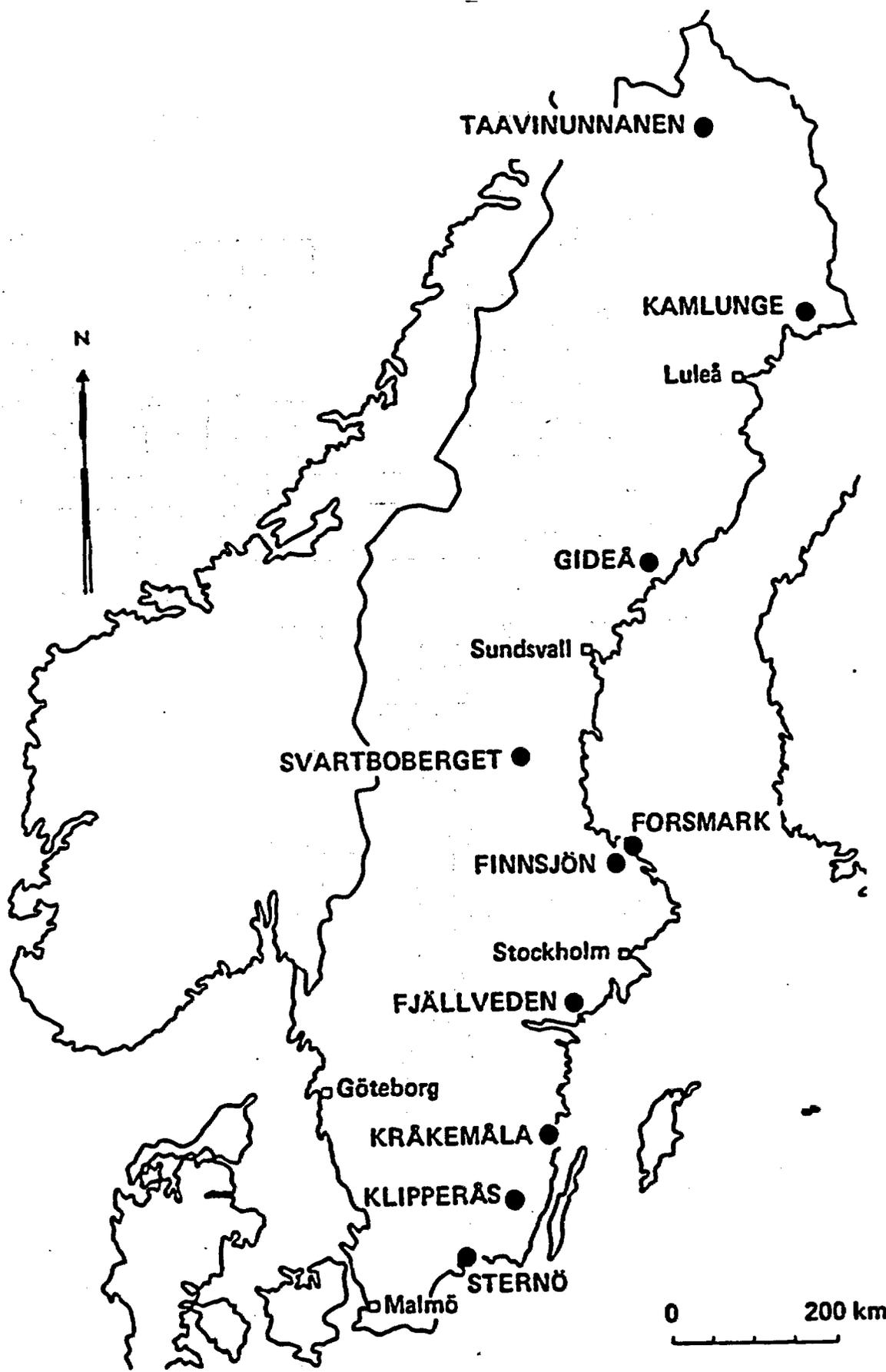
6. ACKNOWLEDGEMENT

The work reported here has been financed by the Swedish Nuclear Fuel and Waste Management Company (SKB). The careful work of our co-workers in both the developing and testing of the equipment is gratefully acknowledged. We are grateful to professor Ingmar Grenthe and Dr Fred Karlsson for their valuable suggestions on this manuscript. The present paper is part of P. Wikberg's ph.D. thesis: The chemistry of deep groundwaters in crystalline rocks.

7. REFERENCES

- Almen, K., Andersson, O., Fridh, B., Johansson, B-E., Sehlstedt, M., Gustavsson, E., Hansson, K., Olsson, O., Nilsson, G., Axelsen, K. and Wikberg, P., Site investigation equipment for geological, geophysical, hydrogeological and hydrochemical characterization. (1986), SKB Technical report 86-16., Stockholm
- Fergusson, J. (1982) Inorganic chemistry and the earth, Pergamon Press, N.Y.
- KBS-3 (1983), "Final disposal of spent nuclear fuel", SKBF, Stockholm
- Krauskopf, K. (1956), Dissolution and precipitation of silica at low temperatures., Geochim. Cosmochim. Acta, 10, 1
- Lindberg, R. and Rummels, D. (1984), "Ground Water Redox Reactions", Science, 225, 925.
- Siever, R. (1957), Amer. Mineral., 42, 826
- Wikberg, P., Grenthe, I. and Axelsen, K. (1983), "Redox conditions of groundwaters Fjällveden, Gideå, Svartboberget and Kamlunge. KBS Technical report 83-40, Stockholm.

- Figure 1.** Location of the places in Sweden which have been investigated in order to obtain data for the safety assessment of a repository for a final disposal of spent nuclear fuel in a crystalline bedrock.
- Figure 2.** A schematic illustration of the groundwater sampling equipment where pH, Eh, pS(sulphide), DO(dissolved oxygen) and conductivity measurements are made in a flow-through-cell on the surface.
- Figure 3.** A schematic illustration of the equipment for down-hole Eh, pH, pS(sulphide) and temperature measurements in open boreholes. The down-hole sond contains electrodes and electronics which is operated from the surface unit.
- Figure 4.** A schematic illustration of the equipment for down-hole Eh, pH and pS(sulphide) measurements. The down-hole sond contains electrodes and electronics which is operated from the surface computer system. The sond is connected to a pump which transports the water up to the surface flow-through-cells where the measurements are checked.
- Figure 5.** Eh versus time plot of the surface and down-hole measured values. Both measurements are made in continuously flowing water.



TAAVINUNNANEN ●

KAMLUNGE ●

Luleå □

GIDEÅ ●

Sundsvall □

SVARTBOBERGET ●

FORSMARK ●

FINNSJÖN ●

Stockholm □

FJÄLLVEDEN ●

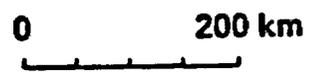
Göteborg □

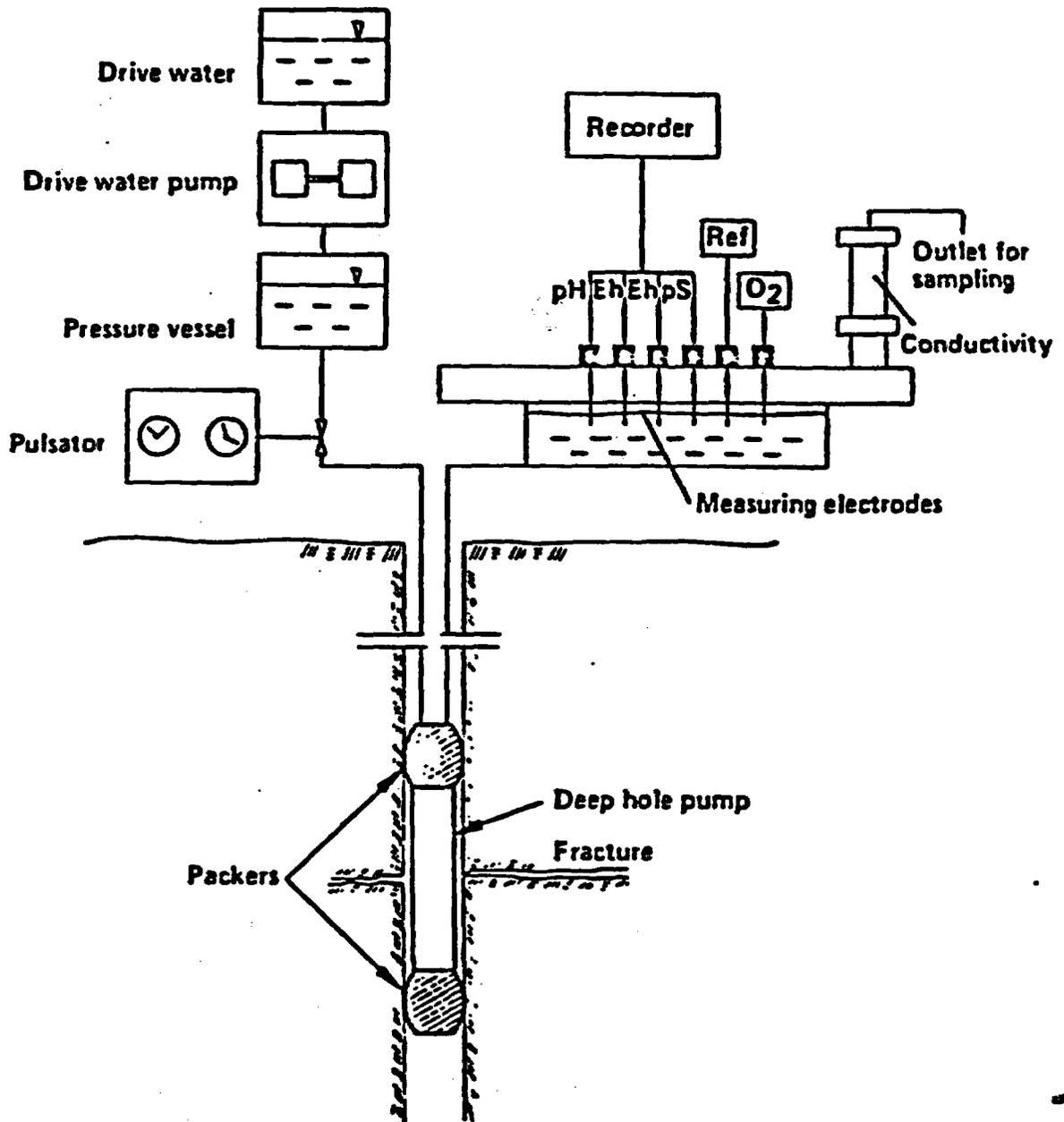
KRÅKEMÅLA ●

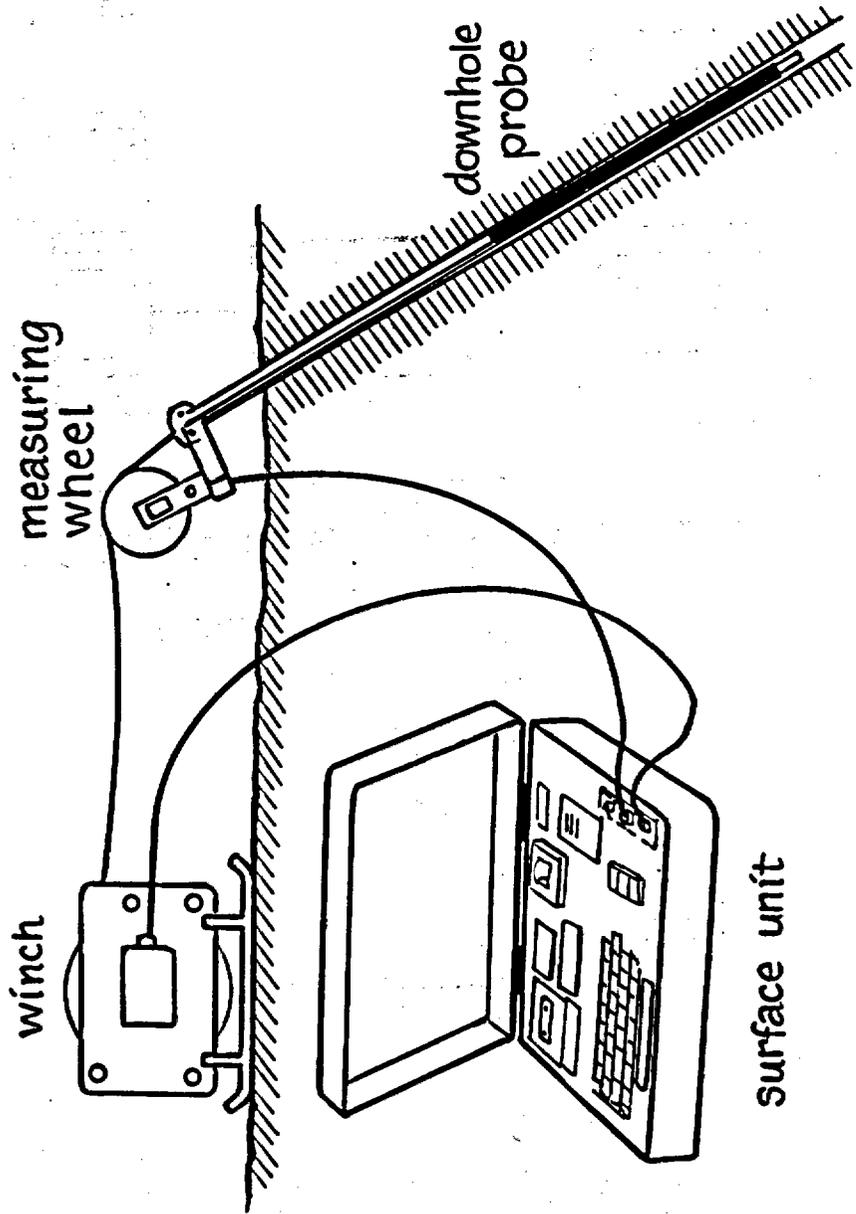
KLIPPERÅS ●

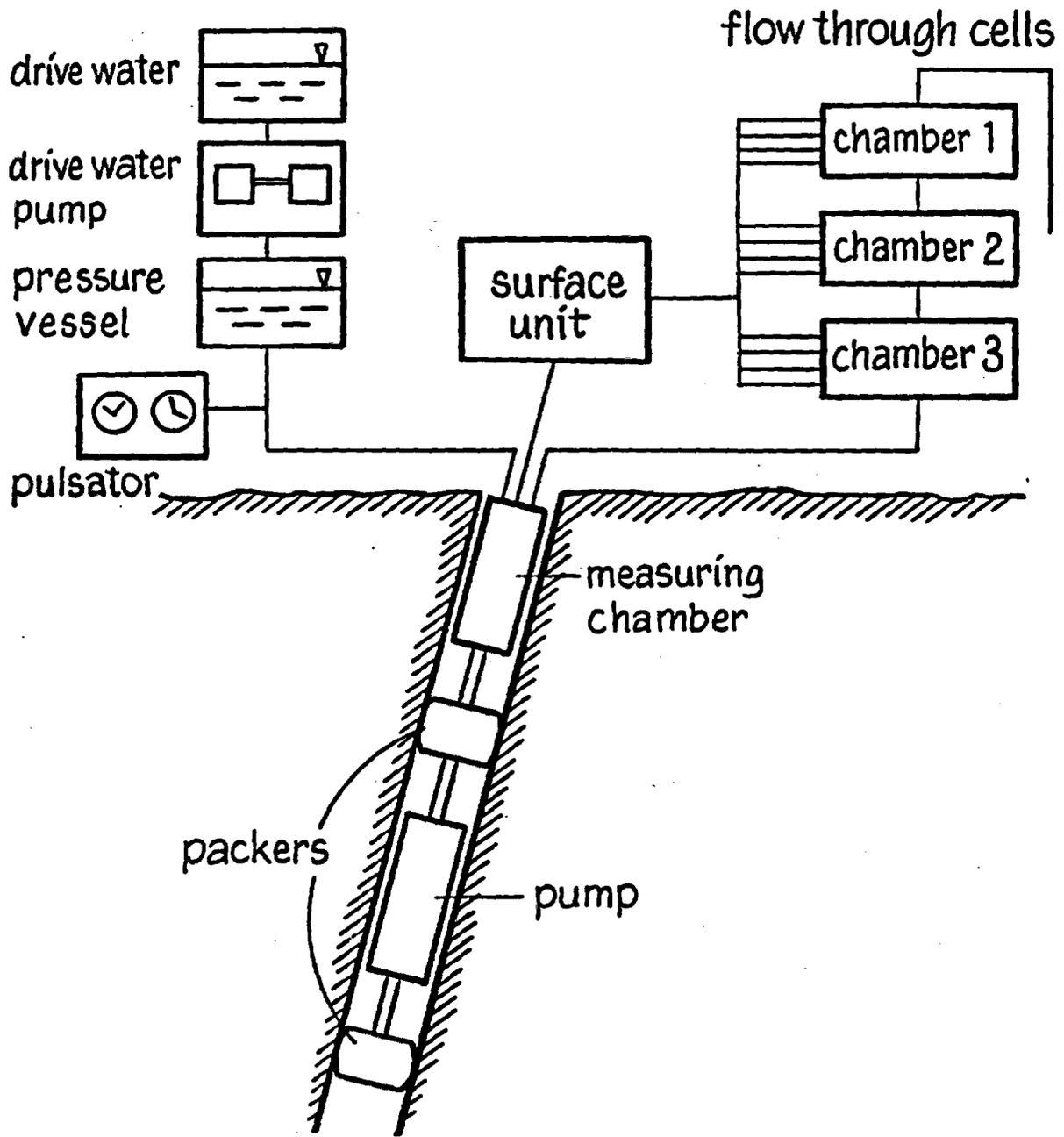
Malmö □

STERNÖ ●







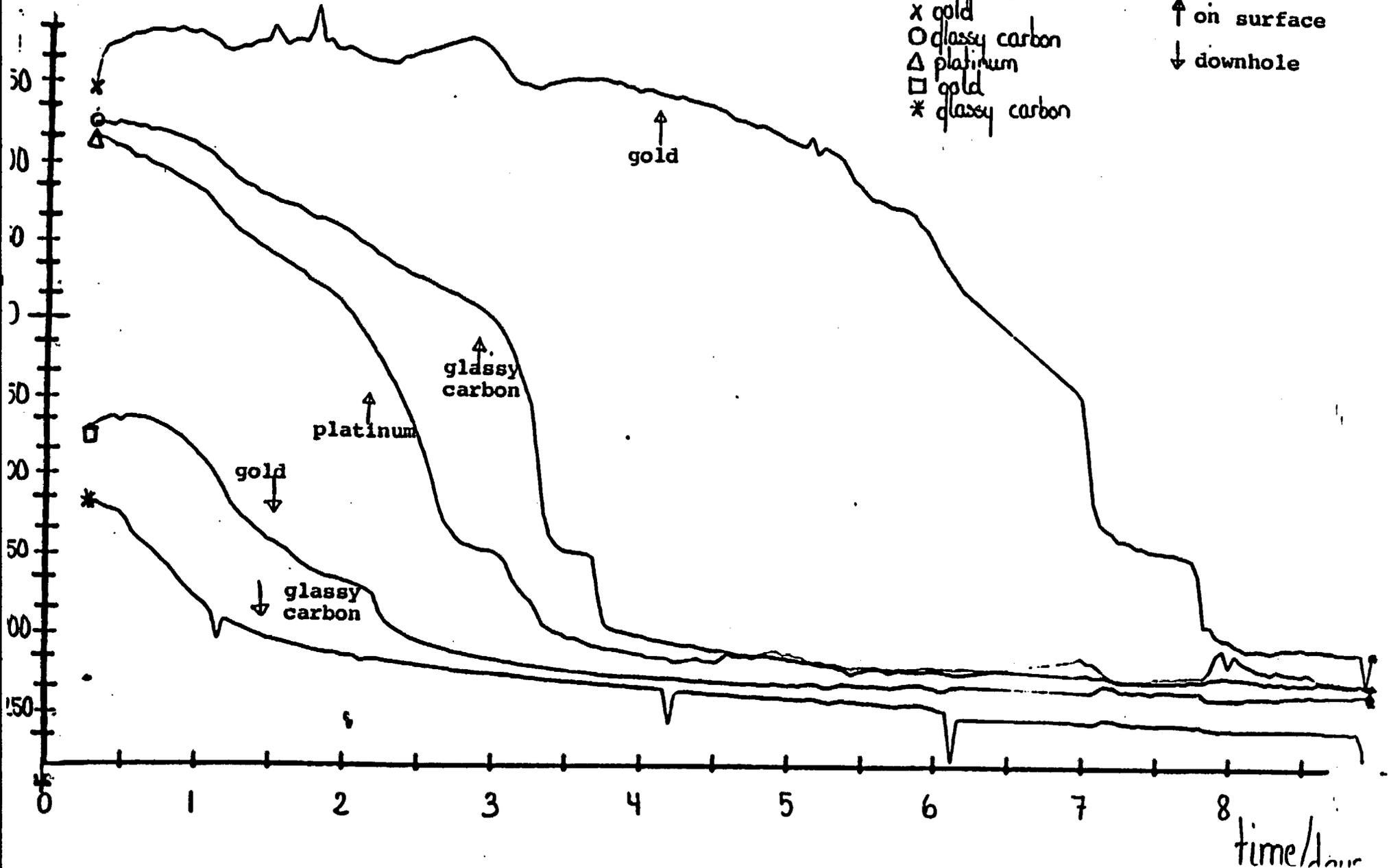


Eh/mV

Legend

- x gold
- O glassy carbon
- Δ platinum
- gold
- * glassy carbon

- ↑ on surface
- ↓ downhole



INVESTIGATION OF THE CHEMISTRY OF DEEP GROUNDWATERS

Peter Wikberg and Karin Axelsen

Department of inorganic chemistry,
The Royal Institute of Technology
100 44 Stockholm, Sweden

ABSTRACT

Equipment for the chemical characterization of deep groundwaters have been developed. This is an integrated system consisting of a mobile field laboratory where groundwater chemical analyses are made and a down-hole measuring sond by which the most sensitive parameters, Eh and pH, of the water are measured in situ.

The analyses made in the field laboratory have been controlled against analyses made at external laboratories. The analysis of redox sensitive elements are more consistent when analyzed in the field laboratory. The other (main) constituents are in good agreement with the results from the external laboratories.

The deep groundwaters encountered at depth in the Swedish crystalline bedrock are mostly of sodium-calcium bicarbonate type, with a TDS value of less than 0.1%. In isolated sections water with a higher concentration of sodium and chloride are found. In areas close to the shore line waters with high sodium, calcium, chloride and sulphate concentrations have been encountered. These waters have a TDS value of more than 1%.

INTRODUCTION

The chemistry of the groundwater is influenced by minerals. The reactions between rock minerals and the infiltrating groundwater may be very slow. If the flux is very low there might be time for a chemical equilibrium to be established between most of the components of the groundwater and the rock, but if e.g. surficial water has penetrated deep into the rock in a very short time there might be a total disequilibrium between the groundwater and the rock. However, different reactions need different time to reach equilibrium. For some reactions even the geologic time might not be sufficient for the equilibration. The dissolution and precipitation of calcite is an example of a fast reaction as practically all natural groundwater systems are in equilibrium with respect to calcite see e.g. Fergusson (1982) p.46. An example of the opposite situation is the equilibration of quartz which at low temperatures seems to be a very slow process (see e.g. Siever, 1957, Krauskopf, 1956).

The sampling of groundwater can in principle be done in many different ways. The method used must be selected so that it will fit the purpose of the investigation and the prevailing hydrogeological conditions. For groundwater sampling in boreholes there are some aspects which will seriously affect the choice of sampling technique. These are:

- i the hydrogeological situation in the vicinity of the borehole
- ii the number and the hydrology of the water yielding sections in the borehole

From the sampling point of view the easiest situation is an artesian borehole with only one water yielding fracture. For the sampling of this water practically no equipment is needed. It is sufficient to collect the water that flows out of the borehole in sample bottles. In all other situations the section which will be sampled has to be sealed off from other sections in order to avoid mixing of different types of water. The worst sampling situation is in recharge areas where the borehole transports the surface water down into water conducting sections at depth in the borehole. An extensive pumping period might be needed in order to get rid of such disturbances before a representative water sample can be obtained.

We have during the past five years been involved in a program to study the chemistry of deep groundwaters. For a nuclear waste repository placed at depth in the bedrock the chemistry of the groundwater is of great importance. The reactions leading to corrosion of the waste canisters and the dissolution of the waste form will depend on the chemical composition of the groundwater. Therefore the chemical character of the groundwater will be one of

the most important factors for the safety assessment. Some chemical parameters are more important than others. These are factors that will speed up the corrosion rate, increase the solubility of the radionuclides due to complexation and affect their migration.

Examples of some repository processes and how they are influenced by the groundwater components are given below.

Copper canister corrosion:	sulphide ions and redox conditions
Bentonite backfill stability:	alkaline and alkaline earth element ions
Spent fuel dissolution:	carbonate ions, pH and redox conditions
Radionuclide migration:	pH, redox conditions, carbonate ions, colloids, humic and fulvic acids

The trace elements that need to be characterized carefully are those which are part of the waste form, e.g. uranium and radium. These elements are naturally occurring in the groundwater system and are thus models for the behaviour of the implaced waste. Other elements like thorium are analogues to the hazardous nuclides with a similar chemistry and are therefore of interest to study.

The migration of the dissolved radionuclides will take place only in the groundwater which has passed through the repository. Hence another group of important parameters are also those which can be used to trace the history of the groundwater, thus indicating the time of the water turn over cycle. It should in principle be possible to draw important conclusions on hydraulic conditions from the composition of the groundwater. In particular the isotopes should be useful in this respect (see e.g. Davis and Bentley, 1982).

The contents of dissolved gas in the groundwater will describe the equilibrium conditions and the evolution of the groundwater. Gas seeping out from the mantle of the earth can be detected and the deep gas carrying fractures thus located.

Due to the conditions shortly described above this type of an investigation needs an instrumentation which is specially designed for the purpose. In this paper we will describe the integrated system we have developed for the investigations. We will also present and discuss some of the experimental results.

EQUIPMENT FOR GROUNDWATER CHEMICAL CHARACTERIZATION

An integrated system of equipment has been developed to improve the sampling and the analysis of deep groundwaters, see Figure 1. This equipment includes a sond for in situ measurements and a fully equipped laboratory. The sond and the field laboratory are connected via an umbilical hose through which the water is pumped to the surface, the packer system and the down-hole pump are hydraulically operated. Data communication and power supply between the surface and the down-hole sond is obtained through three electrical conductors also included in the umbilical hose. The sond contains electrodes for Eh, pH and pS measurements. The pressure is recorded and water for gas analysis can be collected at the in situ pressure by remote control. The pump flow is adjusted according to the pressure drop in the packed off section. The maximum flow is 250 ml/min. Extensive pumping in a low permeability section can decrease the pressure with more than 1 MPa, which can cause an unwanted mixing of water with different origin.

The mobile field laboratory

We found that although many groundwater components can be accurately analyzed at a later stage on well preserved samples, the redox sensitive components are better analyzed in the field before the atmospheric oxygen has altered the redox conditions. In order to perform the investigation most efficiently the analysis of the main constituents and the drilling water residue are needed immediately. Earlier results had clearly shown that sections that were contaminated by drilling water should be avoided and that the time needed for obtaining stable water composition varied considerably. Based on these experiences we constructed a field laboratory for the analyses of major constituents and redox sensitive trace elements.

Interior

The laboratory is installed in a specially designed caravan. The external dimensions are 7 x 2.5 meters. The ceiling is high, 2.5 m, providing an inside space large enough for two people to work in conveniently. The two long sides are supplied with work benches and shelves and the short sides are equipped with doors, one of them used only as an emergency exit and for loading and unloading of large equipment. A plan of the field laboratory is given in Figure 2.

A 200 l teflon coated water tank is connected to a pressure tank. Normal tapwater, deionized water and doubly deionized water is distributed in copper and poly amid plastic pipes, respectively.

A fume cupboard equipped with a fan is connected to a heat exchanger, through which the incoming air also passes. Inside the laboratory there is an air conditioner to which an electrostatic filter is connected. In this way dust is filtered off before the air comes into the laboratory and the small size particles that pass through the dust filters are collected on the electrostatic filter. Due to this precaution we can analyze trace constituents down to ppb levels.

Instruments

The analytical instruments used in the field laboratory are selected on the following basis:

- * because of limited space as many parameters as possible must be analyzed with the same instrument
- * the instruments should not require side equipment such as cooling system, forced ventilation, gas etc

An ion chromatograph, a spectrophotometer, a spectrofluorimeter and titration equipment fulfill the requirements we have on the instruments. The major constituents; sodium, potassium, chloride, fluoride, bromide, sulphate and high concentrations of ammonia, nitrate and nitrite are analyzed on a Dionex 2010i ion chromatograph, to which a Hewlett-Packard integrator model 3392-A is connected. The trace constituents; ferrous and total iron, manganese, phosphate, nitrite, ammonia and sulphide, and also silicate are analyzed on a Perkin-Elmer Lambda 1 spectrophotometer. The alkalinity, calcium and magnesium are titrated with a Metrohm Multidosimat E415 automatic buret. Uranine, the tracer which is added to the drilling water is analyzed with a Perkin-Elmer LS2 Fluorimeter.

Analyses

All the water samples which are collected have passed through an inline 0.45 micron membrane filter. The methods and the quantification limits of the analyses are summarized in Table 1. A more detailed presentation of the analyses is given below.

Major cations and anions are analysed by ion chromatography. The cations are separated in a CS1 column and the anions in a AS4 column. 0.005 mol/l HCl and 0.0029 mol/l - 0.0023 mol/l bicarbonate - carbonate buffer solution are used as eluents for the cation and anion separations respectively. In both systems fiber suppressors are used to decrease the conductivity of the eluents. 0.0125 mol/l H_2SO_4 and 0.08 mol/l tetramethylammonium hydroxide are used for regenerating the fiber suppressors for the

anion and cation systems respectively. The detection limit is 0.1 mg/l for most of the elements.

Ferrous and total iron are analyzed according to the ferrozine method (Nordstrom et.al., in prep). The water sample is filtered into a 100 ml volumetric flask containing 1 ml concentrated ultra-pure hydrochloric acid. By using 5 cm cuvettes a quantification limit of 0.005 mg/l can be reached.

Table 1. Methods and detection limits of the analyses which are performed in the field laboratory.

Method	Element	Detection limit (mg/l)
IC	Na	0.1
IC	K	0.1
IC/SP	NH ₄	0.1/0.005
IC	NO ₃	0.05
IC/SP	NO ₂	0.05/0.001
IC	F	0.1
IC	Cl	0.1
IC	Br	0.05
IC/SP	PO ₄	0.2/0.002
IC	SO ₄	0.05
SP	Fe _{tot} /Fe ²⁺	0.005
SP	Mn	0.01
SP	SiO ₂	1
SP	S ²⁻ tot	0.01
Tit	Ca	2
Tit	Mg	0.4
Tit	HCO ₃	0.6
SF	uranine	<0.1% drilling water contamination

IC = ion-chromatograph
 SP = spectrophotometer
 Tit = titration
 SF = spectrofluorimeter

Manganese is analyzed according to a modified version of the periodate oxidation method according to Hach, 1985 p.154. The quantification limit is 0.01 mg/l.

Sulphide is analyzed according to the methylene blue method (SIS, 1976a) with a quantification limit of 0.01 mg/l. A simplified version of the method (Hach, 1985 p.289) was abandoned due to bad reproducibility of the calibration curves.

Phosphate is complexed with molybdate and antimony(III) in acid solution and reduced to a heteropoly complex (SIS, 1984). The quantification limit is 0.002mg/l as P.

Nitrite is determined as an azo dye according to SIS, (1976b). The quantification limit is 0.001 mg/l as N.

Ammonium is determined by the indophenol blue method according to SIS, 1976c. The quantification limit is 0.001 mg/l as N.

Silica is determined by a simplified version of the silico-molybdate method (Hach, 1985 p.274).

Calcium and magnesium are determined by EDTA titrations according to SIS, (1983) and SIS, (1974).

Alkalinity (=bicarbonate) is titrated with HCl according to SIS, 1981.

Drilling water residues. The water used for the drilling is tagged by uranine (0.5 mg/l). The uranine is analyzed at 520 nm in the fluorimeter. The quantification limit is dependent on the background fluorescence of the sample but always < 0.0005 mg/l, i.e. less than 0.1% drilling water contamination.

The down-hole sond for pH and Eh measurements

Reliable Eh measurements are notoriously difficult to make and this area is perhaps the one where most of the efforts have been made in order to improve the sampling technique. As a result the methods used for the Eh measurements have also been continuously developed. The different methods which have been tried are:

- * in situ measurements in open boreholes
- * on surface measurements in cells through which the water, pumped up from isolated sections, flows
- * in situ measurements in packed off sections in the borehole from which water is pumped out

The in situ measurements in open boreholes were not reproducible and the attempt to measure Eh values in this way was abandoned.

The measurements in the surface flow through cell indicated that reliable values could be obtained even though it took a long time for the electrodes to reach a stable level. In an early stage of the field investigations the Eh and pH were measured in this way. The measuring cell was frequently opened for calibration of the sensors. This resulted in oxygen contamination and because of this there was never time enough for the Eh electrodes to reach a constant level. Interruptions in the pumping also had a great influence on the Eh electrode readings due to leakage of oxygen into the stagnant water in the measuring cell.

In order to eliminate these disturbances we constructed a down-hole measuring system which should prevent accidental contamination by oxygen. This equipment consists of a down-hole flow through cell with electrodes connected to an electronics compartment for measuring the potentials and transmitting the signal to a surface computer. The setup is schematically illustrated in Figure 3. The volume of the down-hole flow through cell is approximately one litre.

Electrodes

For the down-hole Eh measurements three different inert materials are used, gold, platinum and glassy carbon. In this way we can identify erroneous values which are due to reactions catalyzed by the specific electrode material, among them the so called mixed potentials. The gold and the platinum electrodes are permanently mounted whereas the glassy carbon like the rest of the electrodes can easily be disconnected and changed.

The pH is measured by a pressure equilibrated glass electrode and the sulphide concentration is measured by a silversulphide membrane or a silver/silversulphide electrode. The reference electrode is a gel filled triple junction silver/silverchloride electrode. The down-hole electrodes are all specially designed.

Each of the electrodes is connected to a separate amplifier. In this way very little current passes through the electrodes. The amplifiers are connected to a multiplexer which is operated from the surface computer. The multiplexer connects one of the electrodes at a time to an A/D converter. The digital word is then converted into serial form and sent to the surface computer as a frequency shifted signal.

The temperature of the water is sensed by a thermistor. This is mainly because the temperature is needed for the calculations of pH, Eh and the sulphide content from the measuring signals of the electrode systems.

The in situ measurements are checked in a compartment inside the field laboratory, thermostated to the same temperature as in the down-hole measuring cell. The electrical conductivity and the dissolved oxygen content of the water are also monitored. This surface unit is principally the same as the one used down-hole. For the measurements in the surface system ordinary commercial electrodes are used because there are no high demands on pressure resistance or small size.

Both the down-hole and the surface measurements are automatized. The data collection system consists of a MDX-11 computer from Scientific Micro Systems Inc. which is compatible with the digital PDP11/23 computer. This unit has a 1 Mbyte memory and a 15.9 Mbyte Winchester drive.

Calibration and corrections

The electrodes in the down-hole sond are calibrated in a standardized manner. The calibration solution is circulated through the cell by a circulation pump which is connected to the inlet and outlet of the cell. The different calibration solutions and the corresponding calibration values of the electrodes are shown in Table 2.

Table 2. pH, Eh and pS values of the calibration solutions valid at 10°C.

Calibration solution	pH	Eh	pS
pH 4.0 buffer solution + quinhydron	4.0	+487 mV	
pH 7.0 buffer solution + quinhydron	7.0	+316 mV	
pH 10.0 buffer solution	10.2		
0.05 mol/l Na ₂ S in 0.1 mol/l NaOH	(13.3)		2.0
0.01 mol/l Na ₂ S in 0.1 mol/l HCO ⁻			
CO ₃ buffer	(10.5)		5.5

The calibration solutions are all prepared from ampoules and dilution with deionized water. The pH standard buffers are ordinary commercial products whereas the sulphide calibration solutions have been specially made for these calibrations by pH-Tamm Laboratorier AB. The pH buffers are also supplied by the same company.

The conductivity meter in the surface cell is calibrated by 0.01 and 0.1 mol/l KCl solutions and the dissolved oxygen meter is checked against air saturated water.

The temperature has a great influence on the electrode measurements. Therefore we have tried to make the calibrations at a temperature which is close to the temperature of the pumped up water which is normally around 10°C. However, this is not always possible and we therefore use data on the values of the calibration solutions as function of temperature in Table 3.

Table 3. The variation of the calibration values as a function of temperature.

Temp C	pH 4 buffer		pH 7 buffer		pH 10 buffer		sulph pH
	pH	Eh/mV	pH	Eh/mV	pH	pH*	
0	4.00	501.3	7.06	355.5	10.30	10.57	13.67
5	4.00	494.2	7.05	325.4	10.23	10.52	13.49
10	3.99	486.7	7.04	315.9	10.17	10.47	13.31
15	3.99	479.1	7.01	305.9	10.11	10.42	13.13
20	3.99	471.5	6.99	295.9	10.05	10.37	12.94

* pH of the carbonate-bicarbonate buffer containing 0.01 mol/l sulphide

The concentration of the sulphide solutions is not changing due to temperature changes. However, the hydrogen ion activity of the sulphide solutions is dependent on the temperature as indicated by the two last columns in Table 3.

If the calibration of the electrodes has been made at a temperature which is different from the one of the pumped up water a correction must be applied to the data. This correction is specific for the electrode system and must be investigated for all the different electrode systems that are used, i.e. pH, Eh and pS. For our electrode systems the following corrections are relevant:

$$\Delta \text{pH} = 0.02 \times (T_{\text{calibration}} - T_{\text{water}})$$

$$\Delta \text{Eh} = 0.5 \text{ mV} \times (T_{\text{calibration}} - T_{\text{water}})$$

$$\Delta \text{pS} = 0.07 \times (T_{\text{calibration}} - T_{\text{water}})$$

Gas sampling unit

Earlier investigations of the deep groundwaters have included a qualitative-semiquantitative analysis of the gases dissolved in the water. The groundwater has passed a trap where the gas which has escaped from the water is collected. In this way the degree of

oversaturation of the water can be estimated. The gas collected is analysed in a gas chromatograph with respect to the components nitrogen, oxygen, carbon dioxide, helium and argon. However, this technique can not tell how much gas there is left in the water after passing the trap. It is also difficult to know exactly which volume the gas represents since it has been transported a long distance through plastic tubings before it passes the gas trap.

The amounts of gas obtained on different sampling occasions varied considerably. In some cases where water was sampled from a depth greater than 500 m, the gas/water volume ratio was approximately 1, while other waters contained orders of magnitude less gas.

These findings indicated that the difficulties in collecting the gas dissolved in the deep groundwater had to be solved in such a way that the sample also could be transferred to the gas chromatograph in a safe way. Existing in situ sample collectors did not have a satisfactory way to transfer the sample from the collector to the analyzer. The adapters that were needed always had too large a dead volume, the gas content of which was difficult to control. We therefore redesigned the equipment for collecting the pressurized water samples in close collaboration with the laboratory which will perform the analyses. We have tried to develop an unbroken chain of procedures all the way from the sample elevation to the laboratory analyses. The construction of the equipment was made by "BAT AB" in cooperation with "IPA konsult". The design was based on the principles of geotechnical-chemical sampling devices manufactured by "BAT AB" (Torstensson, 1984).

Pressurized sample collector

The gas sampler is placed together with the down-hole sond in close connection to the down-hole pump and packer system, see Figure 1. The sampler consists of two units, one activation unit and one containing sampling flasks. These two can easily be separated when new sampling flasks are loaded.

The sampling flasks are stainless steel cylinders sealed in both ends by flexible rubber discs. The sampling unit can be loaded by either two cylinders with the volumes 50ml and 100 ml or one cylinder with a volume of 200 ml.

Operation and function

The sample cylinders are purged with very pure nitrogen and evacuated several times before they are loaded in the sampler. A sample is collected by applying a pressure on the hose to which the gas sampler is connected. The connection between the inside of the sample cylinders and the outside water, provided by a double-

ended needle, is kept open long enough for the pressure in the cylinder to reach the level in the outside water.

The function of the double-ended needle is illustrated in Figure 4. When the sample cylinder is pressed downwards the needle penetrates the rubber discs, thus creating a hydraulic connection. When the pressure is released springs (not included in the figure) pull the needle out of the rubber discs.

The rubber discs must be capable of withstanding a water pressure of more than 10 MPa, corresponding to a depth of approximately 1000 m. Consequently the composition and the geometry of the parts involved must be carefully selected.

The filling and the emptying of the sample cylinders are the only occasions when the samples can be contaminated. Especially when the sample is transferred from the cylinder into the analytical equipment the connection must be absolutely tight in order not to contaminate the sample by atmospheric gases. Therefore the transfer is made by the same technique as the sampling, i.e. by the use of a double-ended needle and flexible rubber discs.

Pump and packer system

All the down-hole equipment is operated through the umbilical hose which contains nine polyamid plastic tubes with inside diameters from 4 to 10 mm, a 24 conductor signal cable and three copper conductors with a cross-sectional area of 6 mm². The hose is wound up on a reel housed in a trailer, see Figure 1. The tubes and the electrical conductors are connected through a swivel in the center of the reel.

The interface between the umbilical hose and the down-hole equipment consists of a multicoupling for all the nine tubes and five electrical conductors. The electrical connections have been tested to withstand a current of 5 ampere.

The down-hole piston pump has a capacity of maximum 250 ml/min. The flow rate is adjusted by time relays controlling the pressure pulses. The water is pumped up to the surface through the down-hole measuring cell. All parts in the pump which are in contact with the water are made of stainless steel.

The packers that are used are normally one meter long. They consist of inflatable rubber sleeves which are tightly pressed towards the walls of the borehole. The packers can be placed either one above and one below the rest of the equipment giving a section length of about six meters, or they can both be placed below the pump at any desirable spacing. One configuration which we have often used is to seal off the bottom of the hole by only having the upper packer installed.

RESULTS AND DISCUSSION

Performance of the field laboratory

The accuracy of the analyses that were made in the field laboratory was controlled by analyses at two other laboratories. In a calibration and test run two boreholes with different types of water were sampled for a period of two months each. During this test the water was analysed five days a week in the field laboratory and samples were sent to the external laboratories. The results of this "intercalibration" showed that the analyses made in the field laboratory were in most respects as reliable as those made at the two other laboratories. This was very satisfactory since the laboratories have used different methods for many of the analyses. Atomic absorption and atomic emission spectrometers were used for the cation and trace element analyses by the external laboratories while they were analyzed on an ion-chromatograph and calorimetrically in the field laboratory.

The sodium, potassium, calcium, magnesium, chloride, fluoride, silica, bicarbonate and manganese analyses are in good agreement. However, low concentrations of potassium and magnesium in combination with high concentrations of sodium and calcium, respectively, give a large scatter in the results from the field laboratory.

The redox sensitive elements turned out to give more consistent results when they were analyzed in the field laboratory as compared to the results obtained from the two external laboratories. Differences were obtained between total and ferrous iron, sulphate and sulphide. The explanation to this will be discussed in some detail.

The water samples for ferrous and total iron analyses were preserved by hydrochloric acid. The acid was added to the sample bottle before the water. Consequently the water was acidified immediately as it entered the bottle. All samples for iron analyses, also the ones analyzed in the field laboratory were collected in this way. The results show that the field analyses in most cases has the same ferrous and total iron content while there is normally a considerable difference in the ferrous results from the other laboratories. The reason for this is that part of the ferrous iron has been oxidized before the sample was analyzed. The oxidation of ferrous iron to ferric is a slow process in the acidified sample, but it does occur and by time significant quantities are oxidized. The results of analyses made at three different laboratories are presented in Figure 5. It should be noted that the results of the total iron analyses agree very well between all three laboratories.

The sulphate analyses performed in the field laboratory are more stable than those made externally. The reason for this is that the sulphide in the water samples had time to be oxidized to sulphate before the analyses were made at the external laboratories. Some of the investigated waters have a sulphide concentration which is significantly higher than the initial sulphate concentration. If part of this sulphide is oxidized the sulphate concentration might change considerably. In a quick check the sulphate concentration of a water sample changed from 0.43 to 0.63 mg/l within four hours in a refrigerator. This is in good agreement with the half life of sulphide oxidation in seawater which is known to be a few hours, Stumm and Morgan, 1981 p.471. If the sample for sulphate analysis is acidified and purged by nitrogen it should be possible to remove all the sulphide.

The sulphide is analyzed immediately on an untreated sample in the field laboratory. The other sulphide samples are preserved by zinc acetate and sodium hydroxide. The results of the external analyses are more varying than the field analyses.

The fact that the result of the analyses were available immediately made it possible to use them for guiding the drilling and borehole investigations. The most important experiences in this respect are:

- * highly conductive sections ($K=10^{-6}$ m/s) are severely contaminated by drilling fluid. Occasionally the drilling water residues have constituted up to ten per cent of the pumped up water. The amount of drilling water contamination tends to decrease very slowly. Therefore the sampling of such sections were terminated after only a couple of days pumping, because it would take from months to years before the drilling water had been totally removed.
- * Low conductivity sections ($K<10^{-8}$ m/s) have to be sampled for a long time before representative water is obtained. This is because the flow rate normally is very low. Figure 6 is an example of the results from sampling such a section.

General Chemistry

The results of the analyses performed in the mobile field laboratory are given in Table 4. Only major and redox sensitive elements are included in the table.

Table 4. Chemical composition of the groundwaters analysed with the mobile field laboratory. All concentrations are given in mg/l.

Bore hole	level m	Na	K	Ca	Mg	HCO ₃	Cl	SO ₄	S-II	Fe _{tot}	Fe ²⁺	pH	Eh mV	Type
Fj 2	468	36	1.4	27	3.0	182	3.7	2.0	0.2	0.65	0.65	6.9	-220	A
Fj 7	722	300	1.3	40	0.2	16	470	0.5	0.6	0.005	0.004	9.0	-350	C
Kl 1	406	45	1.0	14	2.3	78	45	1.8	0.1	0.013	0.012	8.2	-305	B
Kl 2	326	28	1.1	31	1.0	137	17	0.1	0.08	0.140	0.134	7.6	-290	B
	741	38	1.6	16	2.0	99	23	0.1	0.24	0.045	0.039	8.2	-340	B
	761	12	3.0	23	4.0	106	7	0.5	0.03	0.350	0.345	8.0	-290	A
	860	65	1.6	8.3	1.8	102	51	1.5	0.12	0.043	0.041	8.1	-300	B
Kl 9	696	16	1.3	29	3.0	120	6	4.4	0.02	0.096	0.094	7.6	-275	A
Fi 9	94	410	6.2	101	16	286	670	100	0.22	0.590	0.580	7.5	-245	D
	182	1050	17	708	78	150	2900	220	0.24	0.915	0.915	7.3	-220	D
	360	1600	8	1900	110	33	5200	300	0.01	0.310	0.310	7.7	----	D
Fi 81	71	23	3	76	6	220	61	8	<.01	9.01	8.88	6.9	+ 40	A
	234	650	9	320	40	260	1500	140	0.03	0.437	0.432	7.7	-270	D
	439	1700	15	1600	120	48	5500	400	<.01	0.01	<.005	7.0	+400	D
HK 1	89	1500	7	950	170	75	4100	340	<.01	0.470	0.465	7.5	-140	D
HK10	140	1500	16	1100	250	104	5000	490	<.01	5.25	5.25	7.5	+ 50	D

Fj = Fjällveden Kl = Klipperås Fi = Finnsjön HK = Forsmark

From Table 4 it can be seen that there is a great variation in the composition of the different waters. According to the composition they can however be grouped as indicated in the last column of Table 4.

Type A is a typical granitic water normally found at depths varying from several tenths of meters down to several hundreds of meters, depending on the local hydrogeology; recharge/discharge, conductive zones etc. Calcites have been dissolved and part of the calcium ions have been exchanged with sodium from sodium rich minerals (Jacks, 1973). The concentration of other elements is often very low. The type A waters are neutral to slightly alkaline, depending on whether the carbonate system is open to input of carbon dioxide or not (Garrels and Christ, 1965 p. 74).

Type B waters have had a longer residence time in the rock than the type A waters. The weathering reactions and perhaps some other processes have given the waters a contribution of sodium and chloride. The pH of these waters are in general slightly higher than that of the type A waters.

Type C waters have been isolated in the rock for long time periods. The interactions with the minerals in the rock have given them a high pH and high concentrations of sodium, calcium and chloride. The high pH and calcium concentrations of the water have

resulted in precipitation of calcite and hence a decrease in the bicarbonate concentration.

Type D waters have probably a marine origin. These waters are characterized by a neutral pH and high concentrations of sodium, calcium, chloride and sulphate. The main difference between the type C and type D waters is, besides the amounts of total dissolved solids also the pH and the sulphate concentration.

The boreholes Fi9 and FiB1 are located in a discharge area while all the others are located in recharge areas. The discharge area Finnsjön was covered by the Litorina Sea between 5000 - 7000 years ago. A probable explanation for the salinity at Finnsjön is therefore that the seawater which seeped into the rock during this time has been isolated by a freshwater pillow. The freshwater is separated from the saline water by a subhorizontal fracture zone. The fracture zone itself holds some mixing water but due to the difference in density there is very little mixing between the freshwater and the saline water above and below the zone.

The boreholes HK1 and HK10 are located in the bedrock under the Baltic Sea. It is therefore not possible to define the surrounding as recharge or discharge because the sea above has levelled out all the local gradients. It is, however, interesting to see that the saline water in the boreholes Fi9, FiB1, HK1 and HK10 all have fairly similar composition, indicating the same origin.

From Table 4 it can also be seen that the type A, B and C waters can exist at any depth. However, there is a good correlation between the hydraulic conductivity of the rock and the type of water found there. The A type waters are all sampled in highly water conducting fracture zones whereas the type C water is extracted from the low permeability parts of the rock. The type B waters are mostly obtained from discrete fractures in the rock.

In Figure 7 the waters from Table 4 are plotted on a modified Piper diagram. It can be seen from the figure that the waters of the different categories fall close together in the diagram. The figure also includes the "evolution" line of the groundwaters, indicating the relative residence time of the water in the rock. Water percolating the soil cover takes up carbon dioxide and dissolves calcite when it enters the bedrock (A'). The slower weathering reactions, give the water an increasing sodium chloride character (A -> B -> C). As the salinity increases there is often a tendency of increasing calcium ratios (C -> D). However, in this case the type D waters are expected to have an origin different from the others. It is important to understand how mixing effects would appear in the Piper plot. Water with a composition given by any point on a straight line between two end members of given composition may be obtained from a mixing of water from the end members. In the same way any point within a triangle can be obtained by mixing of water with the characters described by the corners of the triangle.

Even though the waters are of different type, they are all strongly reducing. This is also in good agreement with the total and ferrous iron analyses which indicate that all the iron in the waters is in the ferrous form. Many of the waters also contain detectable amounts of sulphide. There is one exception to the this, the F1B1 borehole where both the most shallow and the deepest of the sampled sections gave positive Eh values. The strongly oxidizing conditions at the 439 m level is due to the presence of considerable amounts of oxygen in the water. This is due to the air flush drilling technique tested for this borehole. When the effect of the booster air compressor is no longer sufficient to keep the borehole free from water the pressure at the bottom of the hole increases, and results in a flow of air into the water conducting fracture systems. Large quantities of air can be dissolved due to the high pressure at depth. At 439 m depth 43 times more air can be dissolved than at the same temperature at atmospheric pressure. The positive Eh of the most shallow level is in good agreement with the pH and iron content of the water, assuming that the water is saturated with respect to ferric hydroxide.

All the water which is sampled has passed a 0.45 micron online filter. The amount and the distribution of the particulate material in the water was estimated by filtering through 0.4, 0.2, 0.05 and 0.05 micron membrane filters placed in series. These filters are analyzed for iron, aluminium, calcium, silica and sulphur by an X-ray fluorescence. The results from such analyses show that the amounts of particulate material is in general a few tens of micrograms/l. However, there does not seem to be any systematics in the distribution between the different elements. The reason for this might be that the particulate material results from the mixing of water of different origin. This hypothesis is based on the results from a redox relaxation experiment where the rate of reduction of dissolved oxygen was tested in situ in a field experiment. Guided by results from laboratory studies the test was made in the following way:

1000 l of groundwater was pumped out of a sealed off section at the 468 m level of the borehole Fj2. The water was analyzed in the mobile field laboratory while it was pumped up. The water was aerated, tagged by uranine and stored until the iron hydroxide had precipitated. Afterwards this water was pumped back into the packed off section. Two weeks later the pumping of water was started again, including the analyses in the field laboratory. The results obtained at these two pumping occasions agreed with the results previously reported for the 468 m level of the borehole Fj2 in Table 4. However, the water contained only 4% of the water which had been pumped down. Furthermore the amount decreased rapidly down to 0.2 % within a few days. The explanation to this is that the water in the packed off section had flowed away due to the natural hydraulic gradient. Because of the very low portion of the aerated water it was not possible to see any effects on the Eh electrodes, which rapidly levelled out at a value of -250 mV. The conclusion to be drawn out of this is that the experiment should be repeated in a section with a much lower conductivity.

During the experiment the water was filtered through the different pore size filters as described above. The results of the analyses of these filters are presented in Figure 8. The three first analyses are made on the water sampled in the first pumping period. The concentrations are constant with small variations between the samples. The other analyses are made on the water pumped out of the section the second time. From the figure it is obvious that the intrusion of the oxidized water has had a dramatic effect on the contents of particulate material in the water. The Al and Si concentrations are not affected while the Fe content is high the first two days and then decreases to "initial" values. The sulphur content is the one which has increased most. It also takes a long time before it decreases to the level of the undisturbed waters. The explanation to this is that the oxygen in the water which was pumped down reacts with the sulphide in the water, oxidizing it to sulphur. If this is a common situation the amount of sulphur collected on the filters can be used to detect the mixing of small portions of oxidizing waters with the reducing deep groundwater.

Eh pH and pS measurements

The redox conditions of the groundwater are controlled by the minerals of the rock. This is reasonable since the buffering capacity is in the rock and not in the water. However, the fact that certain mineral equilibria agree with the measured Eh does not mean that they participate in the electrode reactions. The electrode process must still be mediated by a redox couple in the solution which has a high enough exchange current density. As iron is the dominating redox sensitive element with a high exchange current density it seems likely that the iron redox couple is the mediator. The redox conditions of groundwaters have been discussed by Wikberg and Grenthe, (1987).

The down-hole pH measurements are in general consistent with the surface measurements. Sometimes the down-hole values have been up to 0.6 pH units lower than the surface values. This is probably due to the escape of carbon dioxide when the pressure is reduced.

In all the sampling occasions where the Eh and pH have been measured a sulphide electrode has also been used. From the results obtained it is obvious that this electrode does not respond to the sulphide content unless this is higher than about 10^{-6} mol/l. Too low sulphide concentrations may result in erroneous readings because the silversulphide acts as an inert electrode responding to the Eh of the reducing waters. In situations where low Eh values are measured, lower than -300 mV, the potential of the silversulphide electrode corresponds to a very high concentration of sulphide, mg/l levels.

Gas analysis

The contents of the sample cylinder is sucked into a high vacuum bottle where all the gas dissolved in the water is released and pumped into a gas burette where the volume is measured. From this burette a small volume is extracted for injection into a gas chromatograph. The amounts of nitrogen, carbon dioxide, carbon monoxide, helium, hydrogen, methane, ethane, propane, isobutane, normal butane, argon and oxygen are determined with a typical quantification limit of one ppm (volume gas/ volume sample). However an other limit is also set by the fact that the largest sample volume is 200 ml and the smallest amount of gas needed for the analyses is 1 ml.

The gas sampling unit has recently been taken into operation. So far only one successful sample has been analyzed in order to test the whole sequence of sampling and analyses.

CONCLUSIONS

The investigation of the chemistry of deep groundwaters has been running for five years. During this time a large amount of data have been collected, as well as practical experiences. There are three steps, sampling, analysis and modelling, which are essential for the understanding of the groundwater chemistry. All the steps are equally important and it is useless to do the modelling, the third step, if one of the previous steps is unknown or poorly characterized. As a consequence of this in any groundwater study the initial efforts should be directed towards the problems related to sampling and analysis.

Sampling of groundwater from depth is not a straight forward process. In order to fully understand the results obtained from these investigations one needs to consider the hydrological situation in the rock both before and after the boreholes have penetrated the water conducting parts of the rock mass.

Before the boreholes have been drilled the groundwater flows in the natural flow paths. This situation can be modelled from the hydrogeologic data collected from the borehole investigations.

As one or more boreholes have penetrated the water conducting horizons the hydraulic situation is no longer undisturbed. The boreholes shortcircuit water conducting horizons and will result in a flow of water from sections with a higher hydraulic head to sections which have a lower head. In recharge areas this results in a flow of surficial water down the borehole and in to deeper lying permeable horizons. In order to avoid these disturbances the water samples should be collected as soon as possible after the

holes have been drilled. The different water conducting sections should also be isolated from each other by packers placed around every section which has a hydraulic conductivity of 10^{-8} m/s or higher.

The drilling in itself is also a source of disturbance for the groundwater sampling. The core drilling technique needs large amounts of water to cool the drill bit and to lift the drilling debris. The drilling water which is flushed down is seldom recovered on the ground surface. Our experience is that the water in the high permeability parts of the rock ($K > 10^{-6}$ m/s) are always contaminated by drilling water.

The contamination caused by the drilling water can be avoided if a booster drilling technique is used instead of the diamond drilling technique. In this case the compressed air will empty the borehole from water and thus reduce the hydrostatic pressure in the borehole. The result of this will be that water flows from the rock mass in to the borehole, i.e. in the opposite direction to what is the case in core drilling. Especially for high conductive fracture zones close to the surface this method has proved to be superior. However, at great depth when the capacity of the booster compressor is no longer sufficient to keep the borehole free from water, the compressed air will intrude into the fracture systems in the same way as the drilling water when core drilling techniques is used.

Other methods for obtaining representative water samples from fracture zones with high hydraulic conductivity might be the use of pumps with much higher capacity.

Analyses

All the deep groundwaters we have investigated are reducing. Because of this the following aspects have to be considered:

- * Analyses of ferrous iron must be performed immediately as the sample is taken, because the acidification by hydrochloric acid does not prevent the oxidation of ferrous iron. The deep groundwaters are strongly reducing and there is practically no ferric iron in them. Consequently the water sample acts as a trap for atmospheric oxygen, even though the reaction rate is lower than in a neutral solution. In samples where the ratio between ferrous and ferric iron is around unity the waters are no longer reducing and the hydrochloric acid might be useful for preserving the ferrous-ferric ratio for a longer time.
- * In many of the investigated waters the content of sulphide is of the same order of magnitude as the content of sulphate. The sulphide sample is always preserved by zinc acetate and sodium hydroxide, which seems to be an acceptable method. The

sulphate, however, is normally analyzed on an untreated sample where the sulphide at least partly may have been oxidized to sulphate. This might result in errors unless the sulphide is not expelled from the sample. This could be done by acidification and flushing by nitrogen at the time when the sample is collected.

Modelling

The modelling of the groundwater chemistry should always be made in two steps, the first one being a qualitative modelling of the groundwater chemistry. This includes the identification of the processes which have resulted in the chemical composition observed. These processes are mainly the interaction between the groundwater and the rock but can also include other factors like disturbances due to other activities in the borehole.

For the qualitative modelling it is an advantage to be able to test different hypotheses in a laboratory. The great advantage with the laboratory simulations is that the system of interest can be isolated from outside disturbances, something which is very difficult in the field.

A quantitative modelling performed with the aid of numerical computer codes is the only tool which can be used to test the chemical assumptions made. In order to make a verification one must of course only use data which are representative of the system one wants to model. Otherwise there is always the risk, as in any multivariabel modelling, that the model which is created fits the data even though the assumptions of the system are totally wrong. Mixing of different types of water can create such situations.

ACKNOWLEDGEMENT

The work reported here has been financed by the Swedish Nuclear Fuel and Waste Management Company (SKB). The careful work of our co-workers in both the stationary and the field laboratory is gratefully acknowledged. We also wish to thank Dr. Fred Karlsson and professor Ingmar Grenthe for their valuable suggestions on this manuscript. The present paper is part of P. Wikberg's ph.D thesis The chemistry of deep groundwaters in crystalline rocks.

REFERENCES

Almen K., Andersson O., Fridh B., Johansson B-E., Sehlstedt M., Gustavsson E., Hansson K., Olsson O., Nilsson G., Axelsen K. and Wikberg P., Site investigation equipment for geological, geophysical, hydrogeological and hydrochemical characterization. (1986), SKB Technical report 86-16., Stockholm.

Davis S. and Bentley H. (1982), Dating groundwater. A short review, ACS Symp. Ser., 176, Nuclear and chemical dating techniques: Interpreting the environmental resources. Ed. Lloid A Currie.

Fergusson J. (1982) Inorganic chemistry and the earth, Pergamon Press, N.Y.

Garrels R. and Christ C. (1965), Solutions, mineral and equilibria, Harper & Row, New York.

Hach (1985), Water analysis handbook, HACH Chemical Company, Loveland, Colorado.

Jacks G. (1973), Chemistry of some groundwaters in igneous rocks, Nord. Hydrol., 4, 207.

KBS-3 (1983), "Final disposal of spent nuclear fuel", SKBF, Stockholm.

Krauskopf K. (1956), Dissolution and precipitation of silica at low temperatures., Geochim. Cosmochim. Acta, 10, 1.

Nordstrom K., Ball J., Vivit D. and Chadwick A., Determination of total and ferrous iron in natural waters, In preparation.

Siever R. (1957), Amer. Mineral., 42, 826.

SIS (1974), Swedish Standard SIS 02 81 19, Determination of calcium content of water.

SIS (1976a), Swedish Standard SIS 02 81 15, Determination of sulphide content of pure water and non-polluted natural water: Calorimetric method.

SIS (1976b), Swedish Standard SIS 02 81 32, Determination of the nitrite nitrogen content of water.

SIS (1976c), Swedish Standard SIS 02 81 34, Determination of the ammonium nitrogen content of water.

SIS (1981), Swedish Standard SIS 02 81 39, Determination of alkalinity of fresh water.

SIS (1983), Swedish Standard SIS 02 81 21, Determination of the sum of calcium and magnesium in water - Titrimetric method.

SIS (1984), Swedish Standard SIS 02 81 26, Determination of phosphate in water.

Smellie J., Larsson N-Å., Wikberg P. and Carlsson L., (1985), Hydrochemical investigations in crystalline bedrock in relation to the existing hydraulic conditions: Experience from SKB test sites in Sweden. SKB Technical report 85-11, Stockholm.

Torstensson B-A. (1984), A new system for ground water monitoring, Groundwater Monitoring Review, Fall 1984, 131.

Wikberg P, and Grenthe I. (1987) Redox conditions of deep groundwaters, to be published.

LEGEND TO FIGURES

- Figure 1. A schematic illustration of the integrated mobile field unit which is used for the chemical characterization of the deep groundwaters sampled from isolated sections in slim boreholes. The water passes through an unbroken plastic liner all the way from the pump to the outlet in the field laboratory.
- Figure 2. An illustration of the mobile field laboratory with analytical instruments on both long sides used for cation, anion and redox sensitive trace element analyses.
- Figure 3. A schematic illustration of the equipment for down-hole Eh, pH and pS(sulphide) measurements. The down-hole sond contains electrodes and electronics which is operated from the surface computer system. The sond is connected to a pump which passes the water up to the surface.
- Figure 4. The working principle of the gas sampling unit.
- Figure 5. Results of analyses of total and ferrous iron concentrations in the groundwaters at three different laboratories. Filled bars equal the amount of ferrous iron. The full bar equals the amount of total iron.
- Figure 6. The chemical composition as a function of time when a low conductivity section in the borehole Fjällveden 7 at 722 m level is sampled for a long period. Only main constituents are included.
- Figure 7. A modified piper plot based on the concentration of main constituents in the water samples. The letters A₁ to D represent different categories of water which have different residence time in the bedrock.
- Figure 8. The concentration and size distribution of particulate material filtered off the groundwater in a redox relaxation experiment in Fjällveden 2, 468 m level.

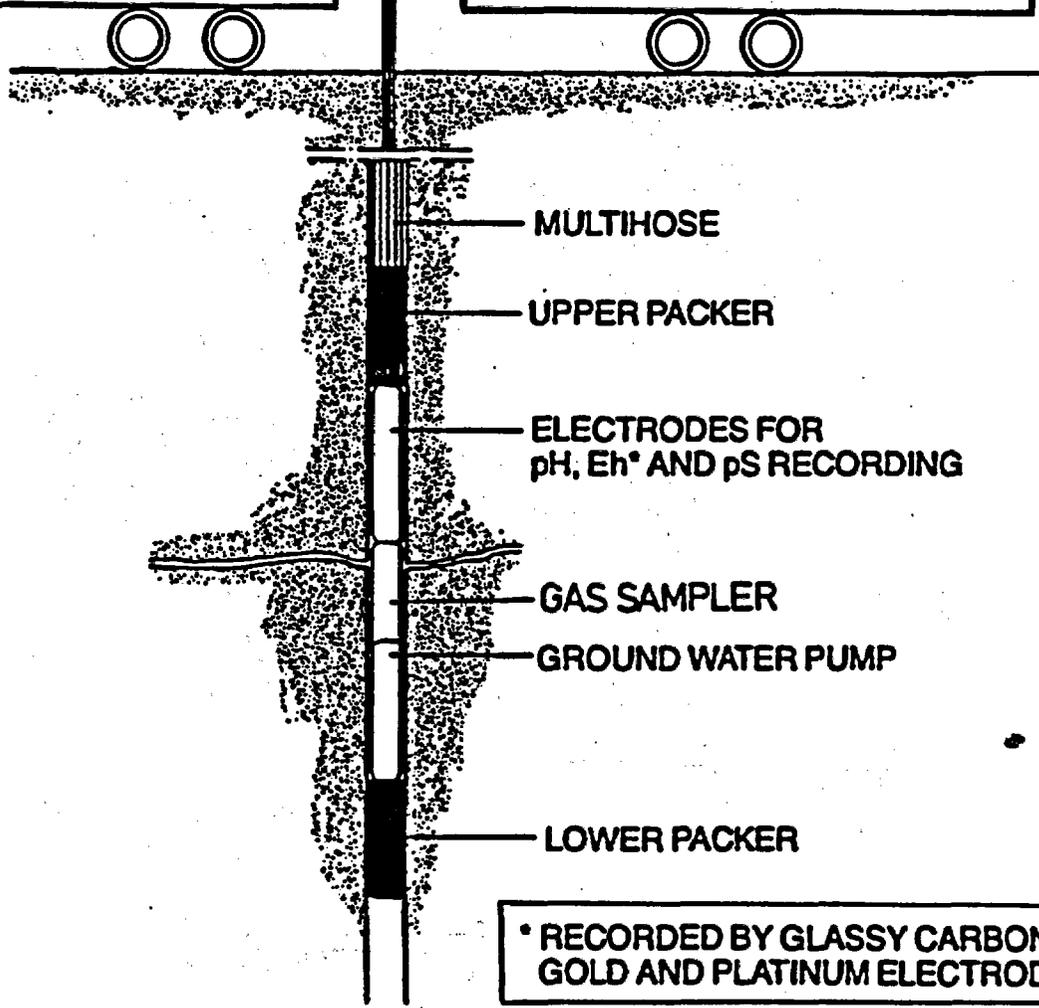
CONTROL UNIT

- POWER SUPPLY
- DATA COMMUNICATION
- HYDRAULIC PUMP DRIVE AND PACKER INFLATION
- REEL FOR MULTHOSE

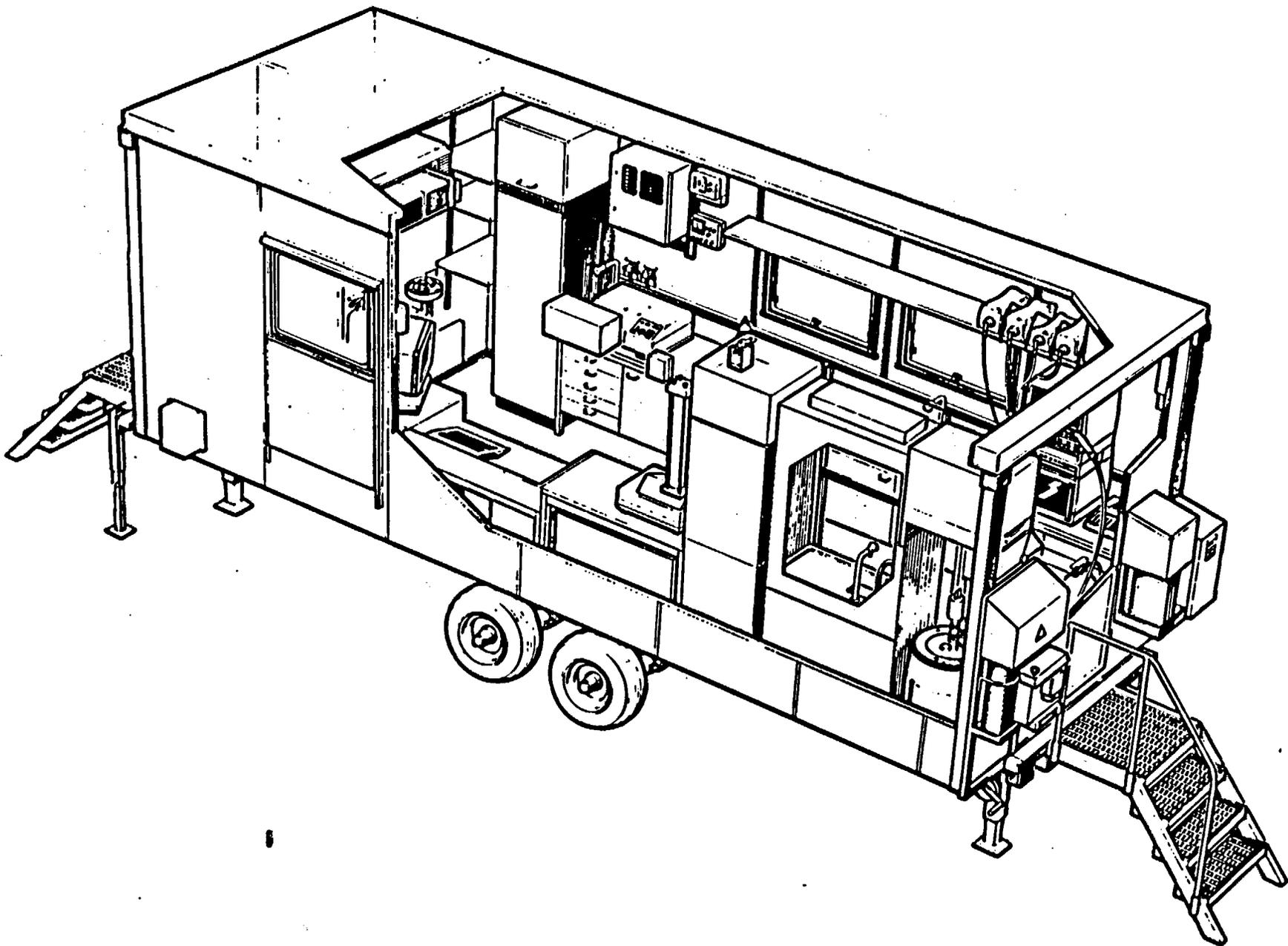
FIELD LABORATORY

ANALYSES OF
Na, K, Ca, Mg, NH_4 , SiO_2 ,
 HCO_3 , F, Cl, Br, PO_4 , SO_4 , S(-II),
 NO_3 , NO_2 , Fe (tot), Fe(II), Mn

MONITORING
pH, Eh*, pS, pO_2 conductivity
Sampling for further analyses

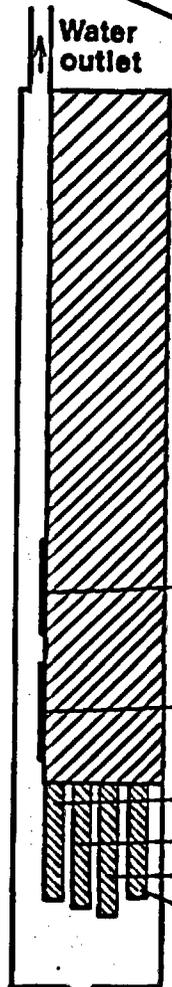
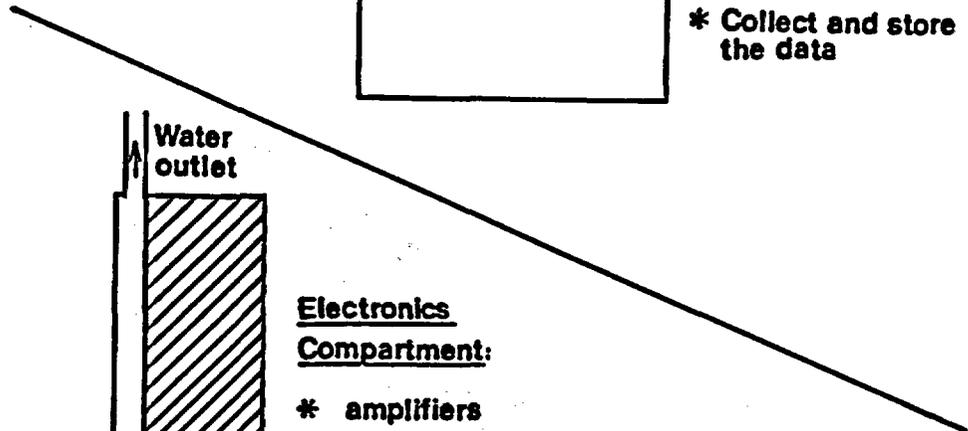
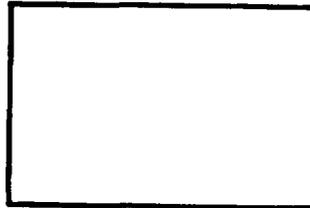


* RECORDED BY GLASSY CARBON,
GOLD AND PLATINUM ELECTRODES



Surface computer:

- * Operate the down-hole sond
- * Collect and store the data



Electronics
Compartment:

- * amplifiers
- * multiplexer
- * A/D converter
- * parallel/serial converter

Eh (gold)

Eh (platinum)

pH (glass)

pS (silver sulphide)

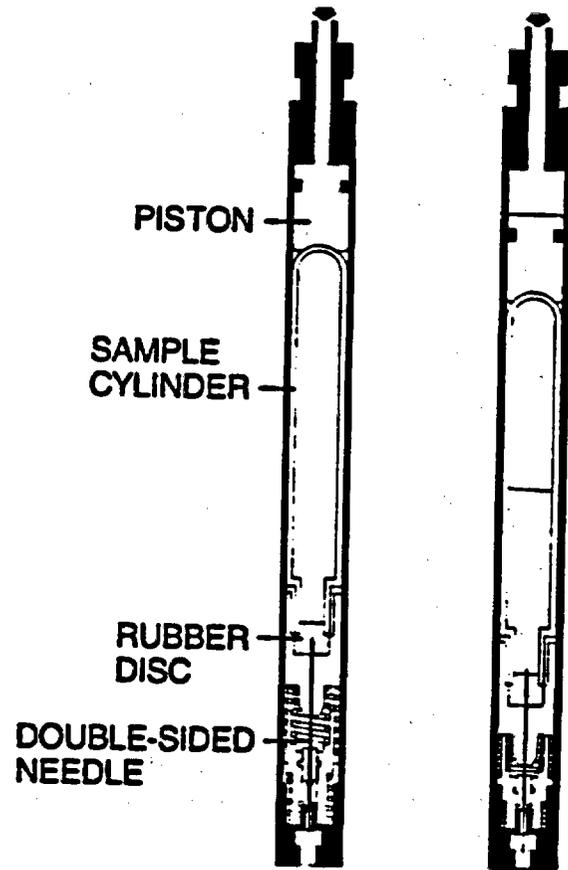
Eh (glassy carbon)

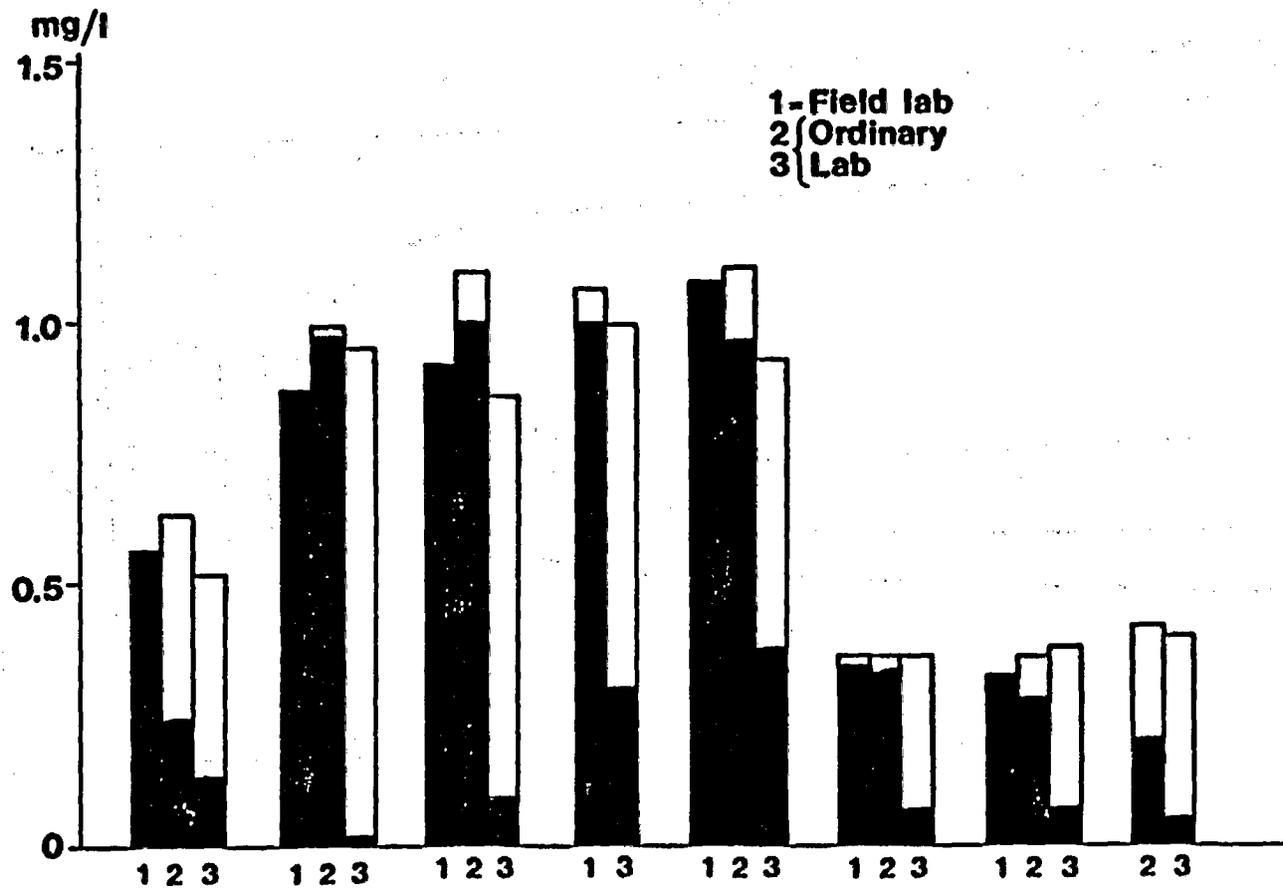
Reference

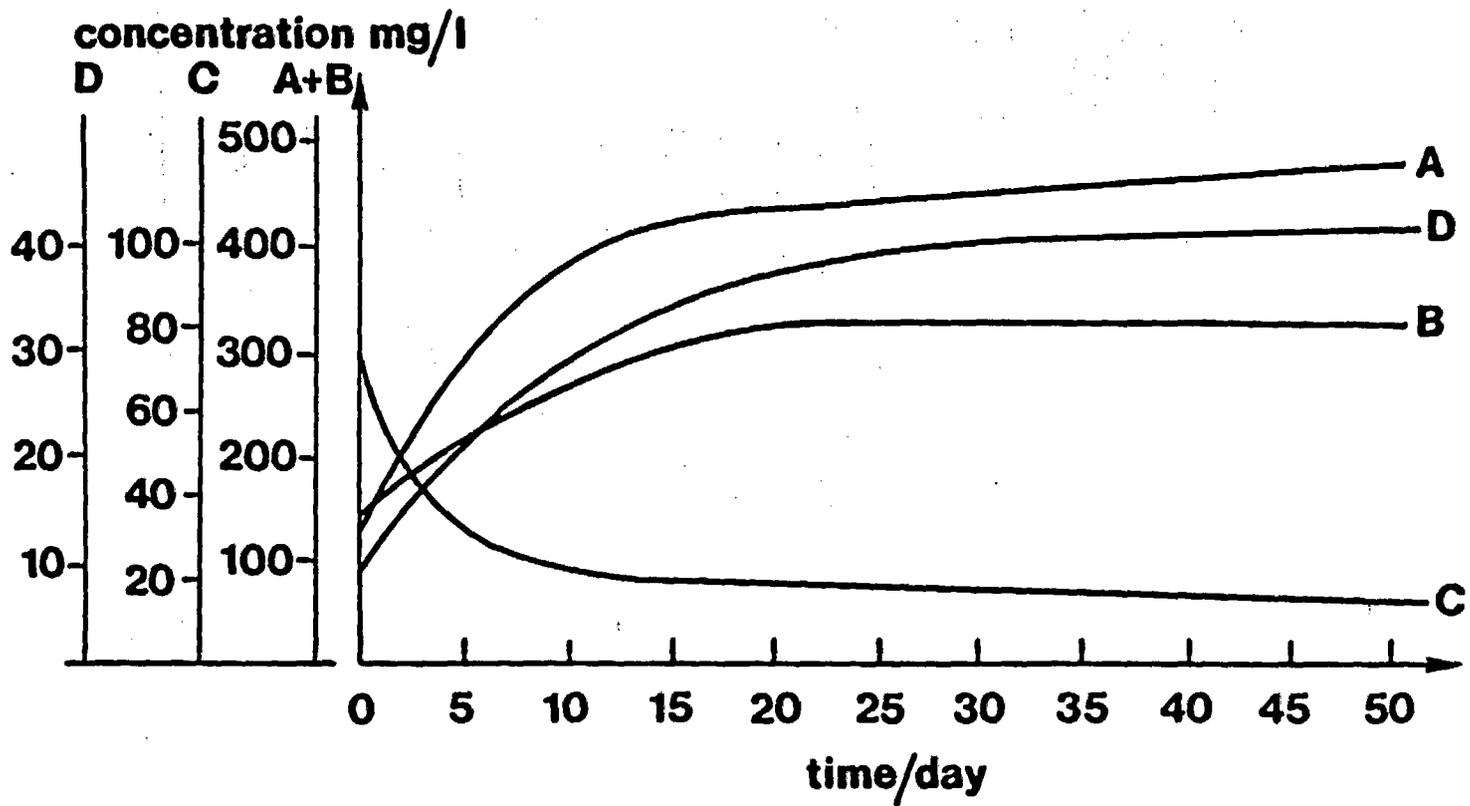
} Electrodes

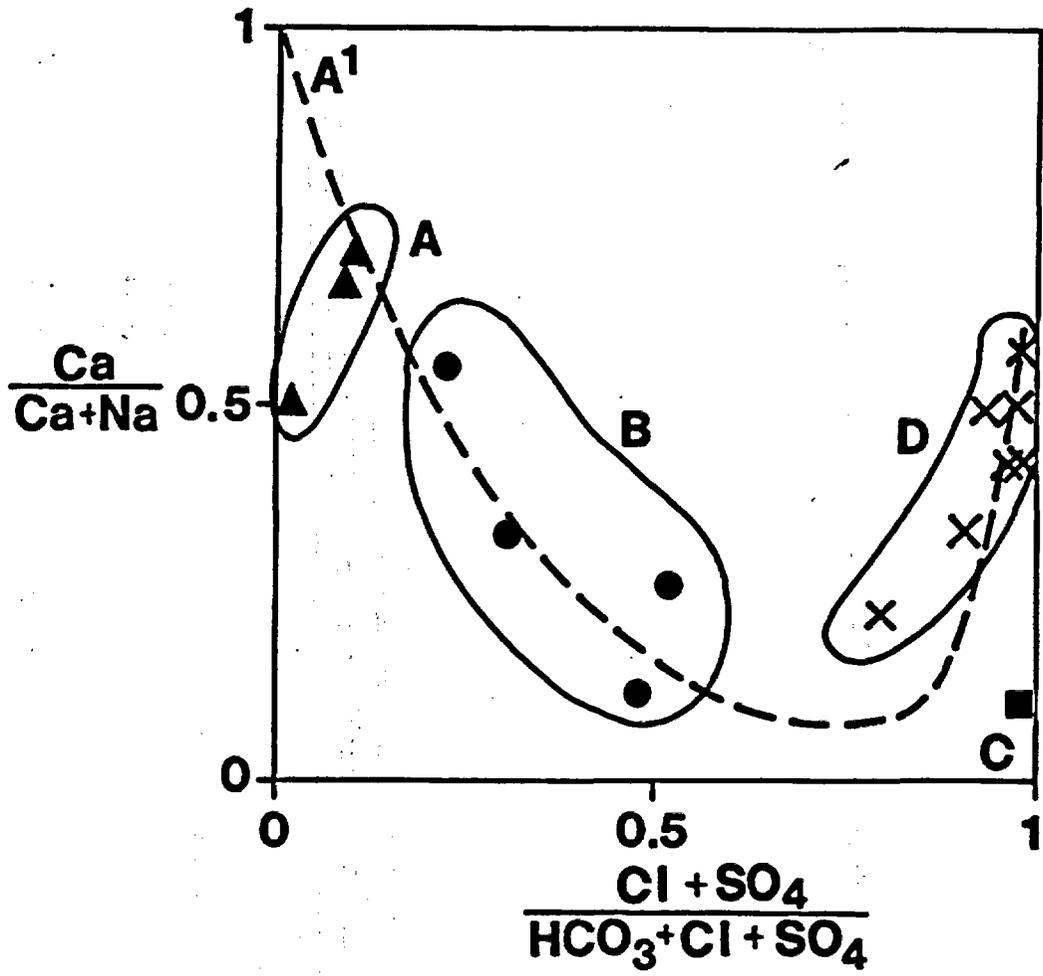
Water Inlet

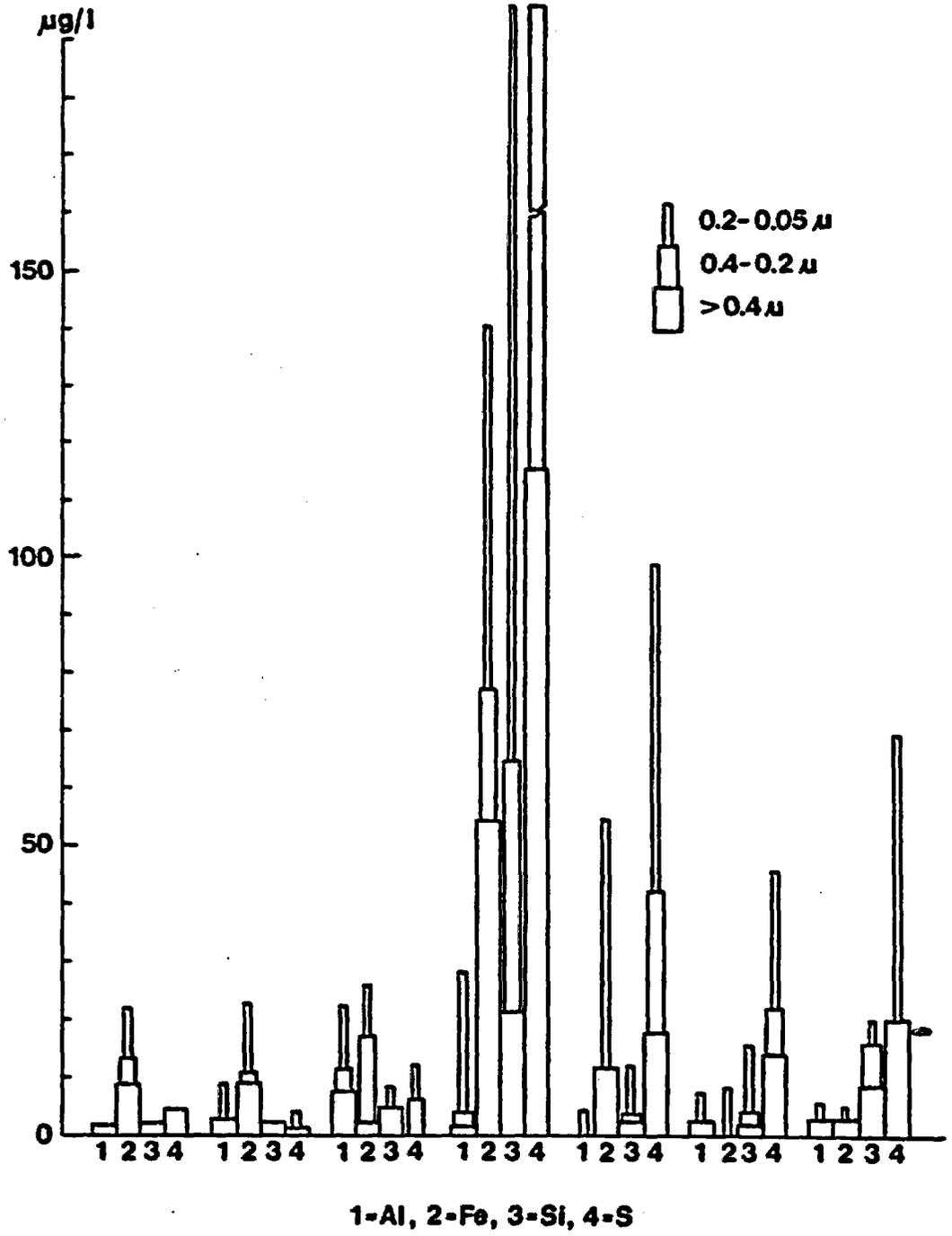
GAS SAMPLER











The following number is for OCRWM Records Management purposes only
and should not be used when ordering this publication:

Accession Number:NN1.880912.0052