SKB TECHNICAL REPORT

87-07

Deep groundwater chemistry

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June 1987

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ABSTRACT

The chemical conditions of deep groundwaters in granitic rock is described. A large number of groundwater analyses have been made throughout the Swedish nuclear waste management program, directed by SKB, for studying possible high level radioactive waste repository sites. The prime objective of this report is to present the redox potential measurements and to relate them to possible chemical reactions in the groundwater/rock system. Laboratory simulations have been performed in order to understand and support the field observations.

A mobile field laboratory has been constructed and found to give results which are more reliable with respect to redox sensitive constituents than previous analyses.

A down-hole sond has been used for Eh measurements. These measurements are not disturbed by atmospheric oxygen. The results of the measurements indicate that the deep groundwater is strongly reducing. This fact is also supported by the analyses of redox sensitive elements.

1   INTRODUCTION

The chemical composition of the groundwater will determine the corrosion of the waste canisters and the dissolution of the waste form. It will also influence the migration of released radionuclides. The chemical character of the groundwater is therefore a very important factor for the safety assessment of a subsurface repository.

Examples of some repository processes and the corresponding groundwater components of importance 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

These processes are thoroughly discussed in the KBS-3 report, 1983.

The chemistry of the groundwater is influenced by 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. surfical water has penetrated deep into the rock in a very short time there might be a total disequilibrium between the groundwater and the rock, 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 precipita-

tion of calcite is an example of fast reactions as practically all natural groundwater systems are in equilibrium with respect to calcite (Nordstrom et.al. 1985). An example of the opposite situation is the equilibration of quartz which in low temperature systems seems to be a slow process (see e.g. Siever, 1957).

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).

Starting in 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 drilling water is taken from percussion drilled holes.

The first objective is to survey the hydraulic conditions. Core drilled boreholes and sections selected for sampling of deep groundwater are summarized in Table 1.

Table 1. Boreholes and sections where groundwater samples have been taken as a part of the site investigation program.

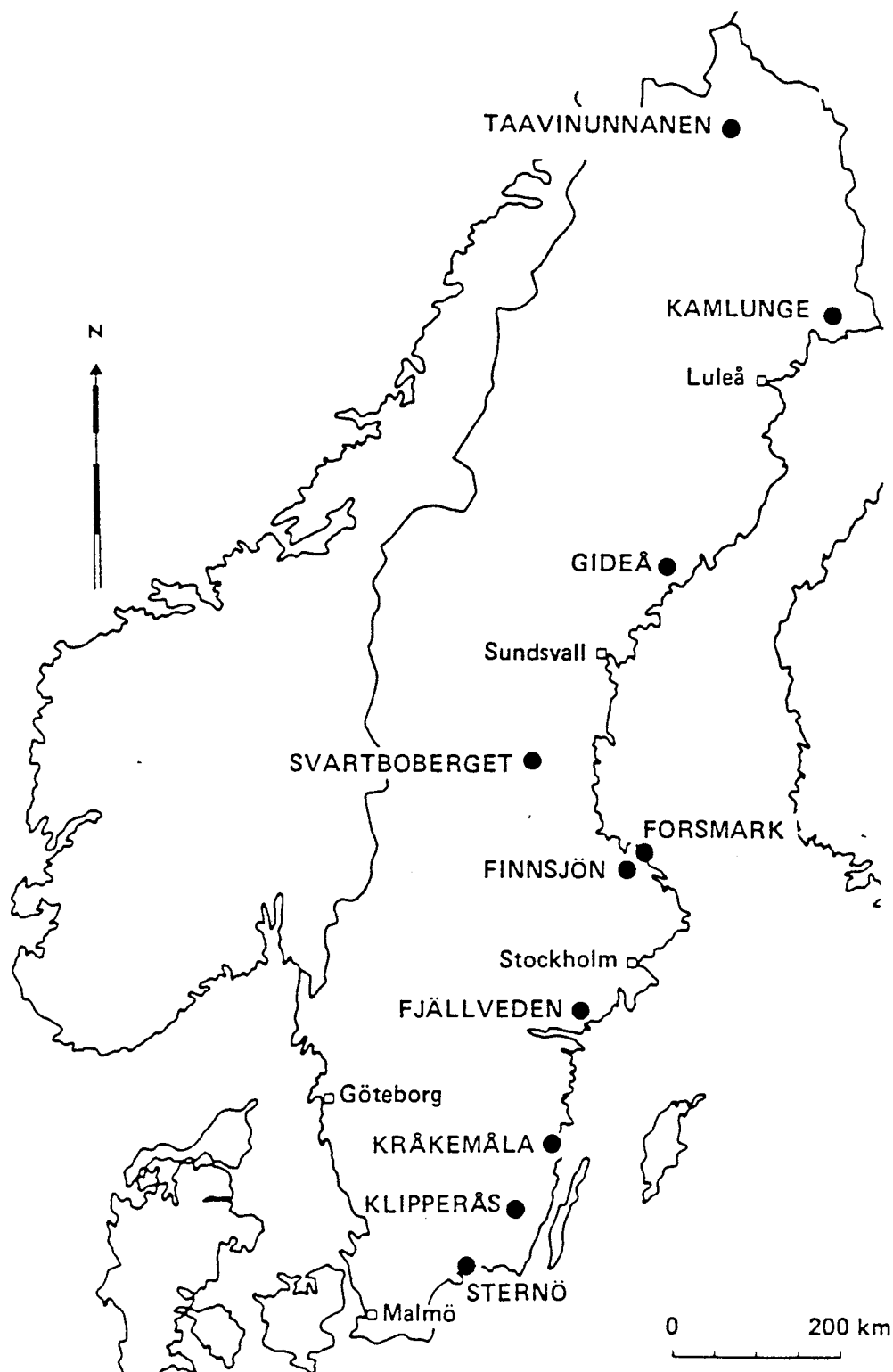| Area	Started	Boreholes	Sections	Depth (m)
Taavinunnanen	1981	1	2	493 - 651
Kamlunge	1982	2	3	106 - 555
Gideå	1982	2	10	91 - 596
Svartboberget	1981	2	8	82 - 718
Finnsjön	1977	8	34	94 - 688
Fjällveden	1982	4	13	107 - 647
Kråkemåla	1977	2	5	103 - 510
Klipperås	1983	3	7	320 - 843
Sternö	1977	2	7	226 - 397

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 SAMPLING TECHNIQUE

2.1 General considerations

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 hydrological 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.

Sampling holes are in general core drilled. In order to trace drilling water contamination, iodine or organic dyes such as Uranine have regularly been used to mark the drilling water. The water yielding fractures are located by hydraulic conductivity measurements. A set of sections are selected for groundwater sampling. These sections are sealed off by packers and the water is pumped out continuously. The most sensitive parameters like Eh and pH have always been measured in the field.

2.2   Experience from previous sampling

A critical analysis has been made of the sampling activities 1982-
1984 at six of the investigation sites: Taavinunnanen, Gideå,
Svartboberget, Fjällveden and Klipperås, by Smellie et
al. (1985). Results of the hydrogeological and hydrogeochemical
investigations were compared to assess the quality of the water
samples.

Four major causes for not obtaining representative water samples
were identified:

1   Drilling water contamination: Considerable amounts of dril-
     ling water can be lost in conductive parts of the rock and
     virgin conditions may then be impossible to restore.

2   Open hole effect: Boreholes left open may create a path for
     mixing between different levels of the hole. Water from
     surface may e.g. reach an inflow section deeper in the hole
     and change the water composition there.

3   Connected holes: Boreholes drilled too close together may
     become connected by horizontal conductive fracture zones
     which create a path for contamination from the open hole
     nearby to the sampling section in the other hole.

4   Packer failure: A technical failure of the packer is unusual.
     However, when excessive pumping in sections with low water
     yield are made the packers may not be sufficiently tight to
     prevent the water from above or below the isolated section to
     leak in. It is even more likely that a large pressure
     gradient will force water to bypass the packers through tiny
     fractures in the surrounding rock.

We have encountered the largest difficulties to obtain pure samp-
les for the analyses of gases, trace constituents and radioiso-
topes 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 relevant as
far as major components are concerned. This is also true for the
trace components which are specific for the deep groundwaters.

2.3   New sampling technique

A mobile field laboratory has been developed to improve the samp-
ling and the analysis of deep groundwaters, see Figure 2. The
equipment is described by Almen et al. (1986). This equipment
includes a sond for in situ measurements and a fully equipped
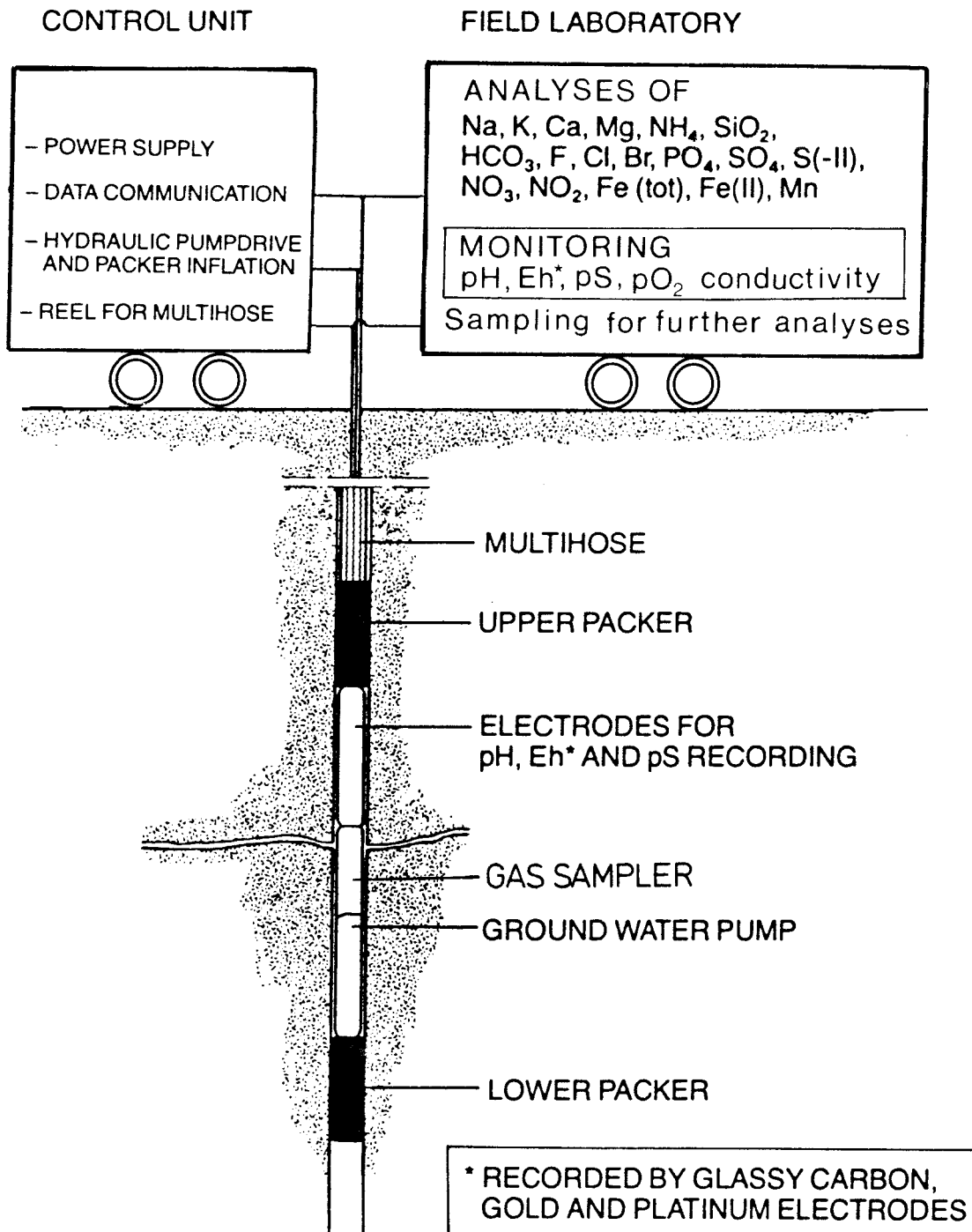laboratory. The sond and the field laboratory are connected via an

CONTROL UNIT   FIELD LABORATORY

CONTROL UNIT

- POWER SUPPLY

- DATA COMMUNICATION

- HYDRAULIC PUMPDRIVE
  AND PACKER INFLATION

- REEL FOR MULTIHOSE

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

MULTIHOSE

UPPER PACKER

ELECTRODES FOR
pH, Eh* AND pS RECORDING

GAS SAMPLER

GROUND WATER PUMP

LOWER PACKER

* RECORDED BY GLASSY CARBON,
  GOLD AND PLATINUM ELECTRODES

Figure 2.   A schematic illustration of the integrated mobile
field unit which is used for the chemical characte-
rization 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 labo-
ratory.

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 drawdown 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.

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.

In the centre of the multihose there is a steel wire taking 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.

The water from the bore hole is lead directly into a field laboratory. In this way the water can be analyzed without coming in to 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 in to the lab 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, Mg 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 2 below.

Table 2. **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 = Spectro Photometer
Tit= Titrations
SF = Spectro fluorimeter

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). All the analyses made in the field laboratory were found to be reliable. 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.

The field laboratory is schematically illustrated in Figure 3.

The trace constituents, isotopes and gases which are analyzed at external laboratories are listed in Table 3.
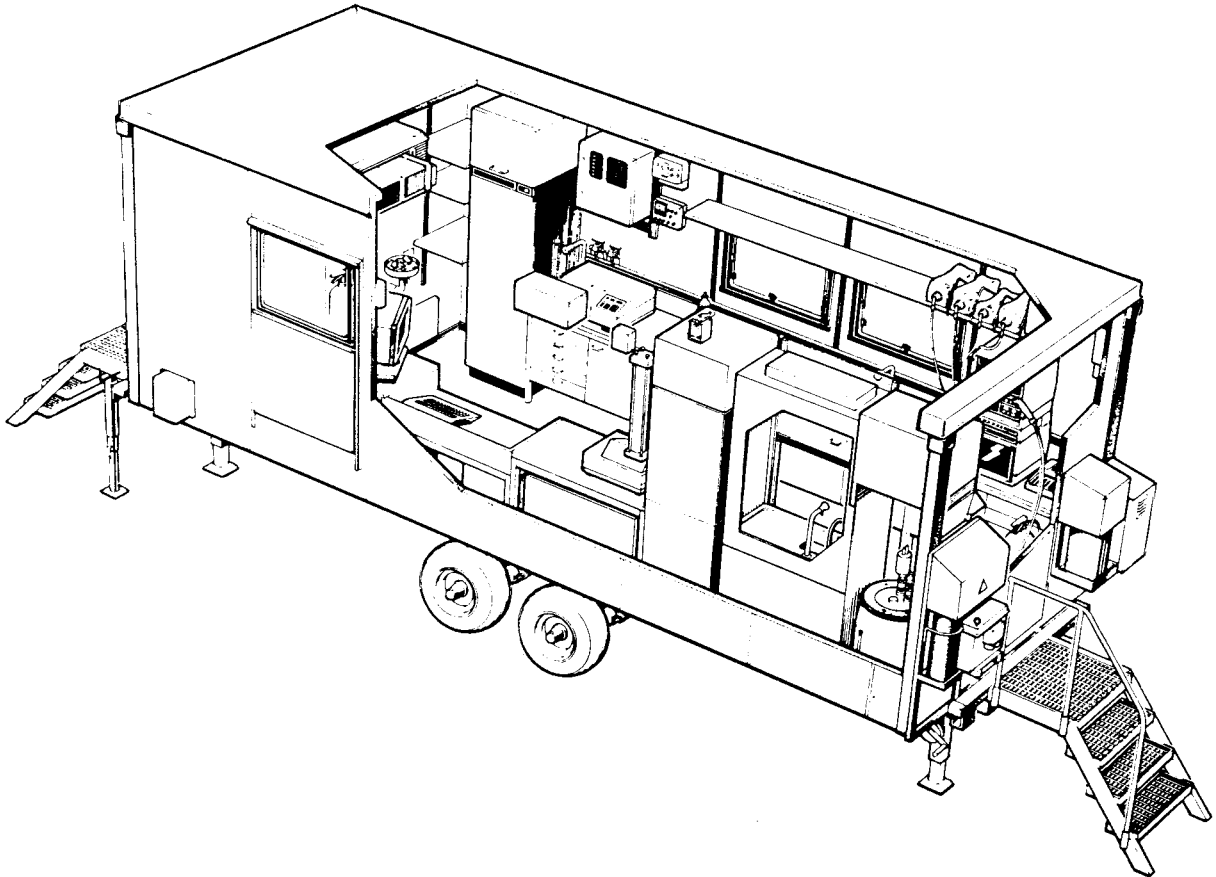
Figure 3. An illustration of the mobile field laboratory with analytical instruments for cation, anion and redox sensitive trace element analyses.

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. Sections which are too heavily contaminated can quickly be identified and avoided all together or 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 by Almen et al. (1986).

Table 3. 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
$^{234}U/^{238}U$	5 l	
Gases	50-200 ml	Gaschromatograph
Fulvic and Humic Acids		Chemical Characterization

AA = Atomic Absorption
AE = Atomic Emission
MS = Mass Spectrometry

Other development efforts have also been made to improve the
quality of the groundwater samples. An example of this is the
early sampling of the water conducting sections in order to mini-
mize the "open hole effect". Tube wave seismic 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.

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 bore-
hole. 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. 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 compres-
sor 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 are
used. The booster percussion drilling technique has been tested at
Finnsjön. The drillings were stopped at regular intervals for
sampling between a packer and the bottom of the borehole. 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.

2.4 Equipment for Eh and pH measurements

Reliable Eh measurements are notoriously difficult to make and this area is perhaps the one were most of the efforts have been put 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 the 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 preceding the KBS-3 report 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 4. 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).

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. Our criterion for stable Eh values is when all the electrodes lie within a span of 20 -30 mV and when the change in potential is less than 10 mV within a period of two days.
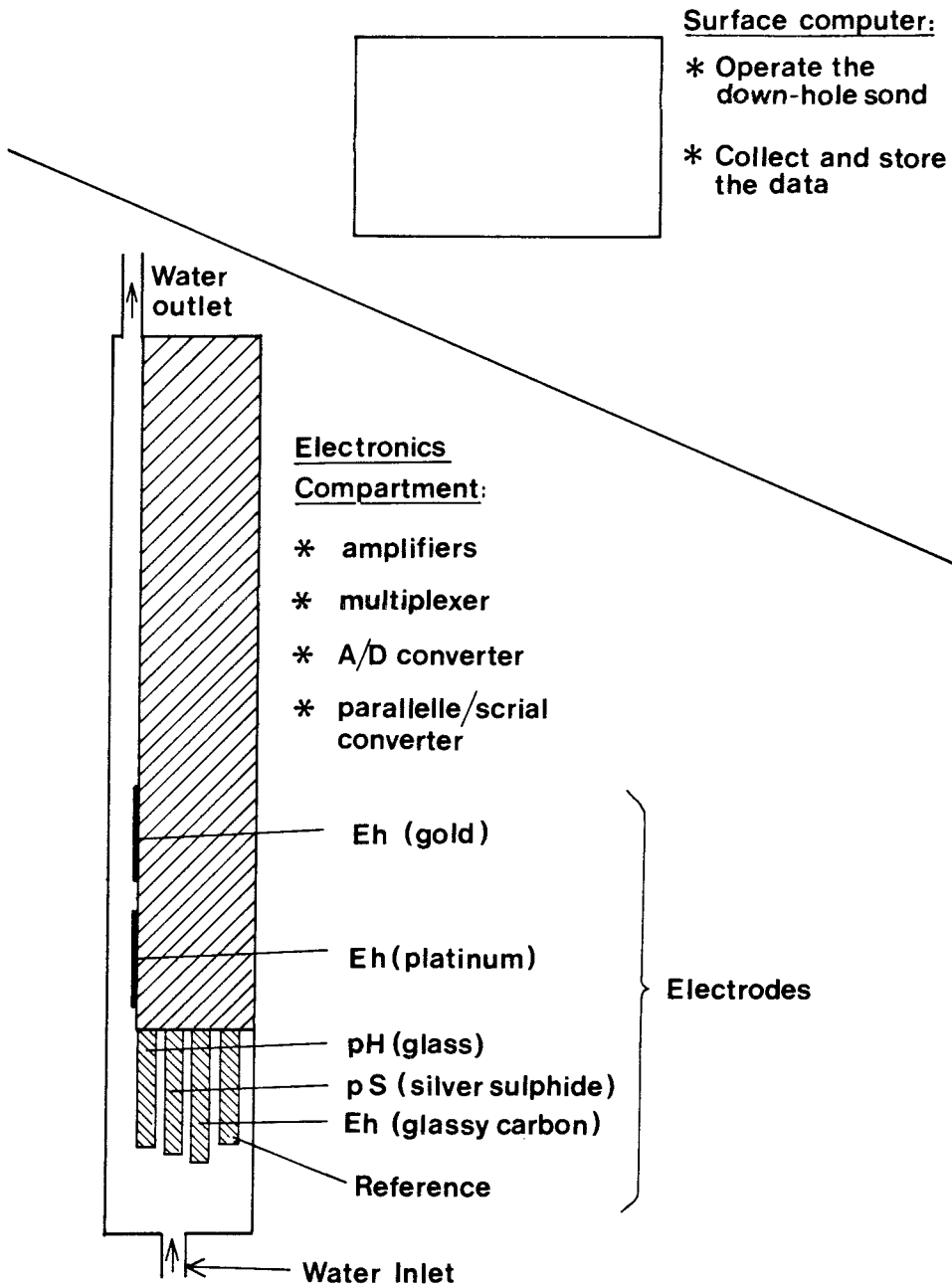
12

Surface computer:

* Operate the
  down-hole sond

* Collect and store
  the data

Water outlet

Electronics Compartment:

* amplifiers

* multiplexer

* A/D converter

* parallelle/scrial converter

Eh (gold)

Eh (platinum)

pH (glass)

pS (silver sulphide)

Eh (glassy carbon)

Reference

Electrodes

Water Inlet

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 passes the
water up to the surface.

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. The down-hole electrodes are all specially designed for our measurements while the electrodes in the surface flow through cell are all commercially available.

Each of the electrodes is connected to a separate amplifiers. In this way very little current, $\sim 10^{-15}$A, 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   RESULTS

3.1   General chemistry

The sampling is to be 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 new 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	F	SO_4	S(-II)	Fe_{tot}	Fe^{2+}	pH	Eh mV	Type
Fj 2	468	36	1.4	27	3.0	182	3.7	0.6	2.0	0.2	0.65	0.65	6.9	-220	A
Fj 7	722	300	1.3	40	0.2	16	470	6.2	0.5	0.6	0.005	0.004	9.0	-350	C
Kl 1	406	45	1.0	14	2.3	78	45	3.8	1.8	0.1	0.013	0.012	8.2	-305	B
Kl 2	326	28	1.1	31	1.0	137	17	2.8	0.1	0.08	0.140	0.134	7.6	-290	B
	741	38	1.6	16	2.0	99	23	4.4	0.1	0.24	0.045	0.039	8.2	-340	B
	761	12	3.0	23	4.0	106	7	2.7	0.5	0.03	0.350	0.345	8.0	-290	A
	860	65	1.6	8.3	1.8	102	51	5.3	1.5	0.12	0.043	0.041	8.1	-300	B
Kl 9	696	16	1.3	29	3.0	120	6	3.0	4.4	0.02	0.096	0.094	7.6	-275	A
Fi 9	94	410	6.2	101	16	286	670	3.0	100	0.22	0.590	0.580	7.5	-245	D
	182	1050	17	708	78	150	2900	10	220	0.24	0.915	0.915	7.3	-220	D
	360	1600	8	1900	110	33	5200	7.4	300	0.01	0.310	0.310	7.7	----	D

Fj = Fjällveden
Kl = Klipperås
Fi = Finnsjön

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 hydrology; 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 (Allard et al. 1983).

Type B waters have had a longer residence time in the rock than the type A waters. Weathering of feldspars, leakage of fluid inclusions or some other possible slow processes have given the waters a contribution of sodium and chloride. The pH of these waters are in general slightly higher than found in 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 concentration 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 borehole Fi9 is 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 therefor that the seawater which seaped 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.

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 mass and the type of water obtained there. The type A 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.
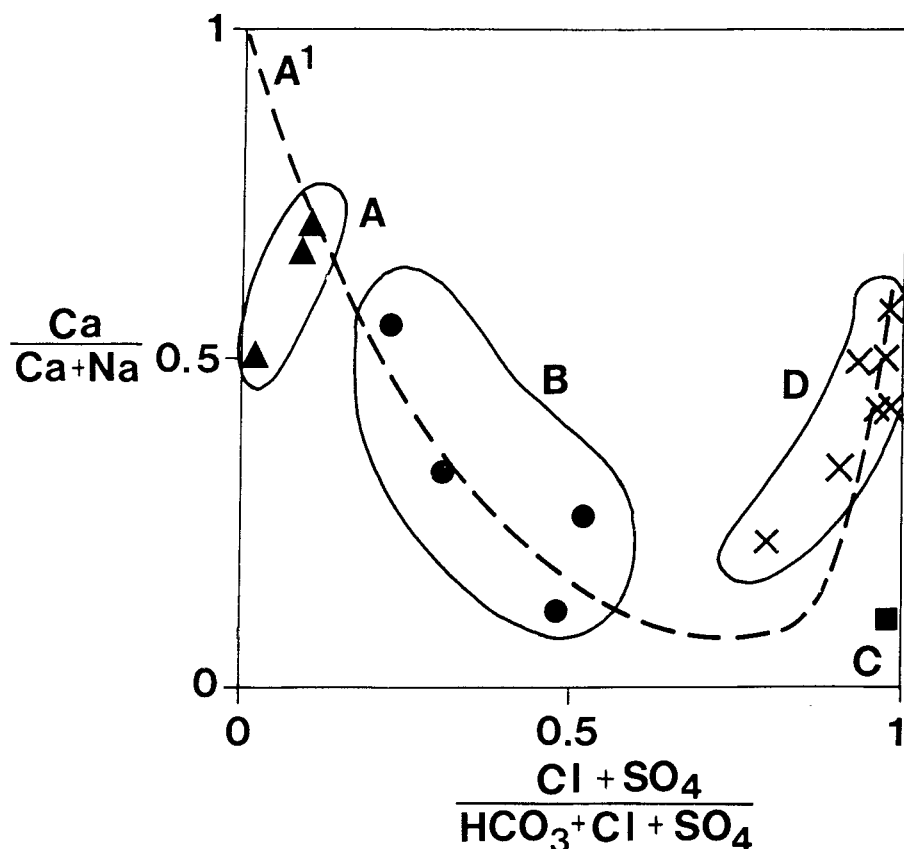
Figure 5. A modified piper plot based on the concentration of main constituents in the water samples. The letters A to D represent different categories of water.

In Figure 5 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. In the figure is also included 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 reactions, weathering etc., gives 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).

Even though the waters are of different type it can be seen that 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. These waters also contain detectable amounts of sulphide.

Earlier results, where waters were sampled and preserved with hydrochloric acid and then sent to laboratories for analyses, showed that there in most cases were a difference between the amounts of total and ferrous iron in the investigated waters. This was, however, an artefact due to the time delay between sampling and analyses. The oxidation of ferrous iron to ferric is a slow
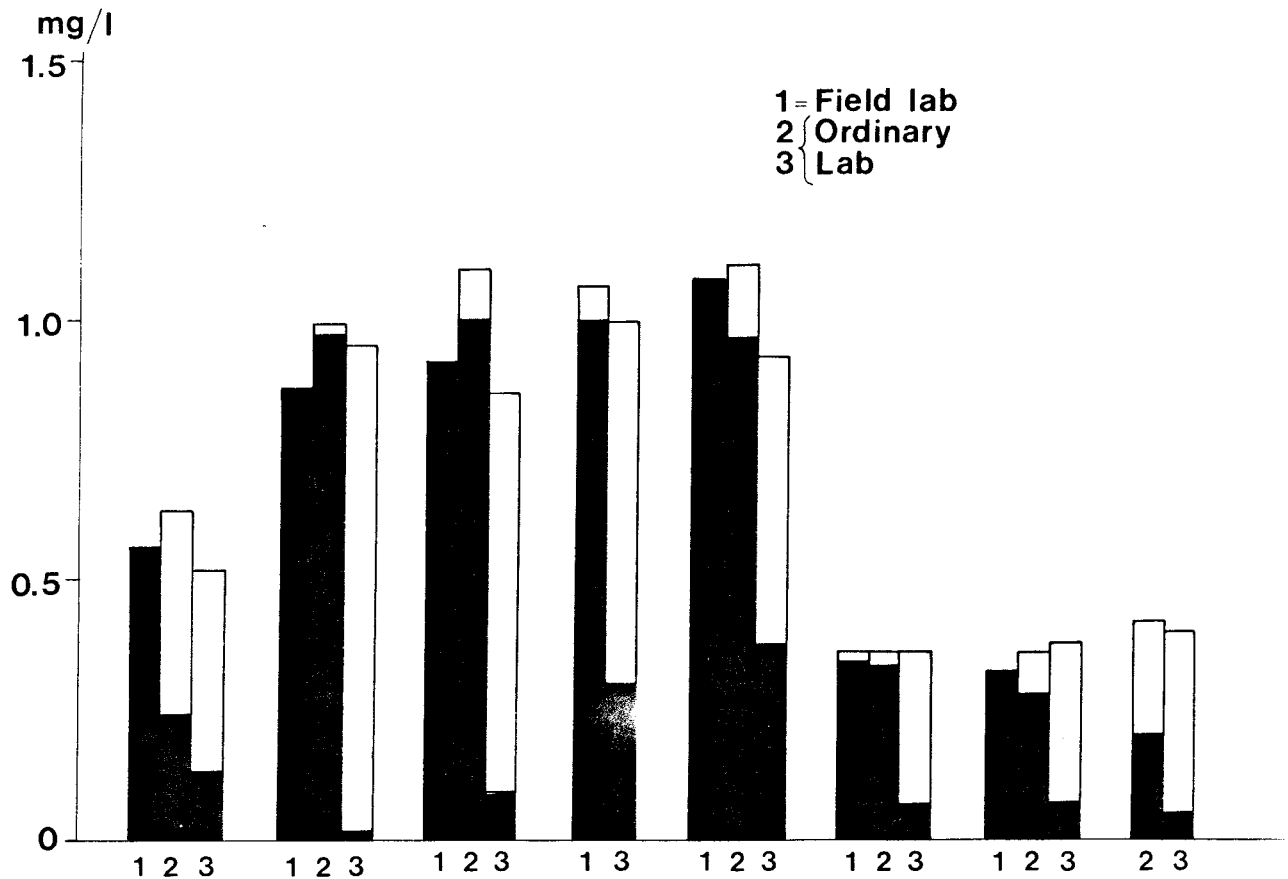
Figure 6.   Results of analyses of total and ferrous iron concentrations in the groundwaters made at three different laboratories. Filled bars equal the amount of ferrous iron. The full length of the bar equals the amount of total iron.

process in the acidified sample, but it does occur and by time significant quantities are oxidized. In Figure 6 results of ana-lyses made at three different laboratories are presented. 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. It should be noted that the results of the total iron analyses agree very well between all three laboratories.

3.2   Eh and pH measurements

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

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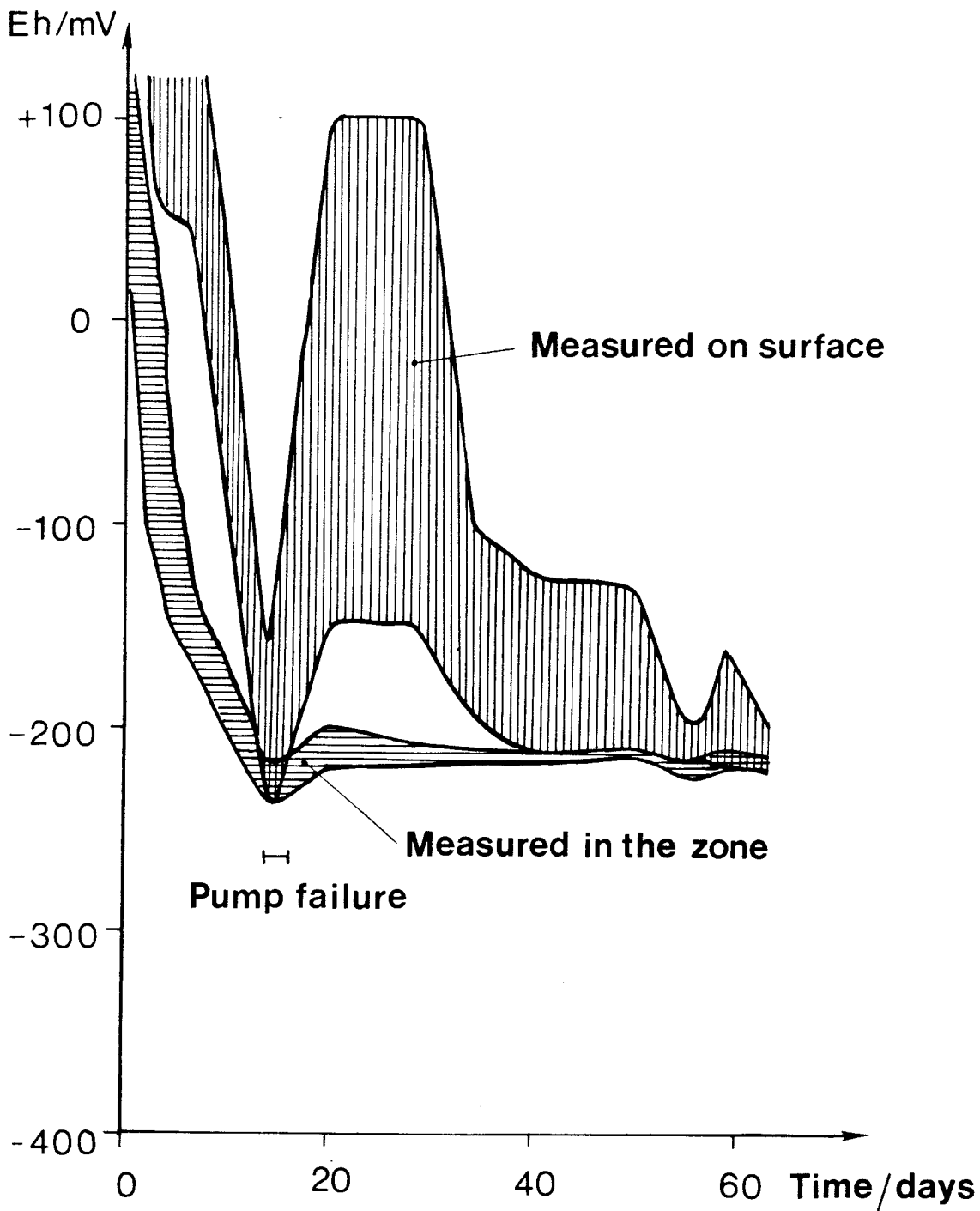
Figure 7.   Eh versus time plot of the surface and down-hole measured values. Both measurements are made in continuously flowing water. The dashed fields represent the largest differences between the potentials of the gold, platinum and glassy carbon electrodes. The length of a pumpfailure is indicated.

electrode readings is smaller down-hole than on the surface. However, the surface electrodes also approach the level of the down-hole electrodes even though it takes longer time. It can also be seen that the pump failure indicated in the figure has a marginal effect on the down-hole electrodes whereas the surface electrodes are influenced very strongly. This is because oxygen diffuses into the surface cell and affects the electrodes. The down-hole electrodes are not affected due to the total absence of oxygen.

The last, but perhaps the most important conclusion to be drawn out of Figure 7, is that after the initial equilibrating process the electrode readings are constant without any drift even in the time scale of months.

The effect that dissolved oxygen has on the Eh electrodes is easy to spot. This is because the electrodes always respond in the same way to small portions of oxygen dissolved in the water. Figure 8 and Figure 9 show how the electrodes in the surface flow through cell respond in the beginning of a sampling period. Even though

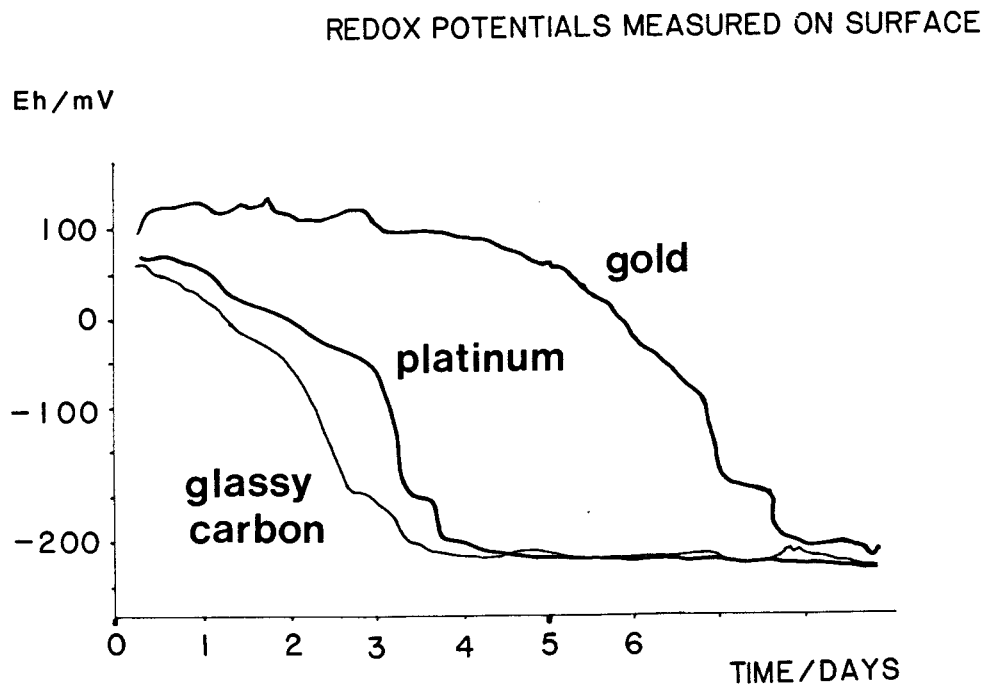REDOX POTENTIALS MEASURED ON SURFACE

Eh/mV

Figure 8.   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.

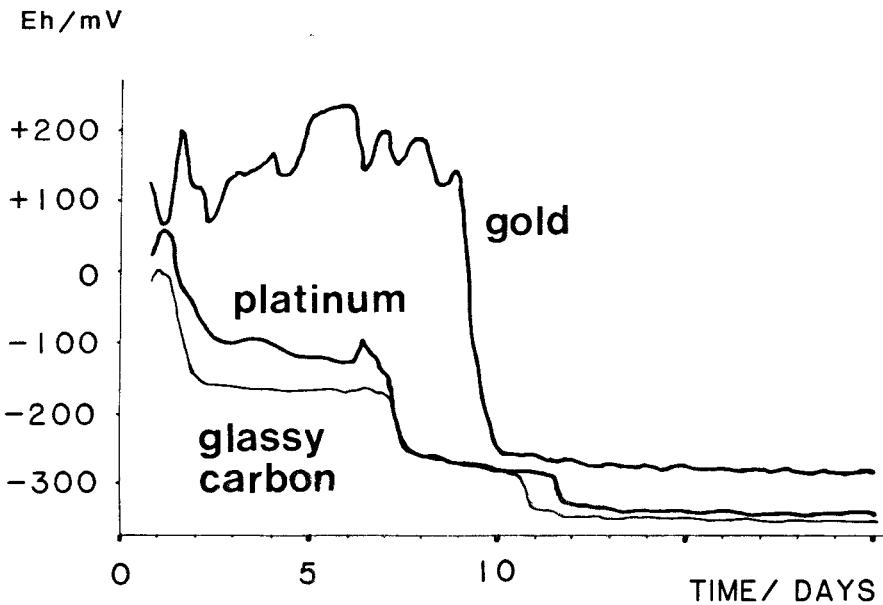REDOX POTENTIALS MEASURED ON SURFACE

Eh/mV

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 Fjällveden 7 at 722 m level.

the examples are taken from two different type of waters, A and C
in Table 4, the Eh electrodes responsed in the same way. The gold
electrode always gives a reading 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 6. One possible
explanation to this is that the reduction of dissolved oxygen is
more strongly catalyzed by gold than by platinum and glassy car-
bon. The concentrations of oxygen that causes these changes is not
exactly known. However, we have results that indicate that con-
centrations well below the detection limit of the oxygen sensor,
0.03 ppm, still have an effect on the Eh electrodes, see Figure
12.

The reproducibility of the Eh measurements have been checked at
several times. The results are compiled on an Eh-pH diagram in
Figure 10. From the figure it can be seen that the reproducibility
of the Eh as well as the pH measurements is good and there is no
major change in the chemistry of the water even when several years
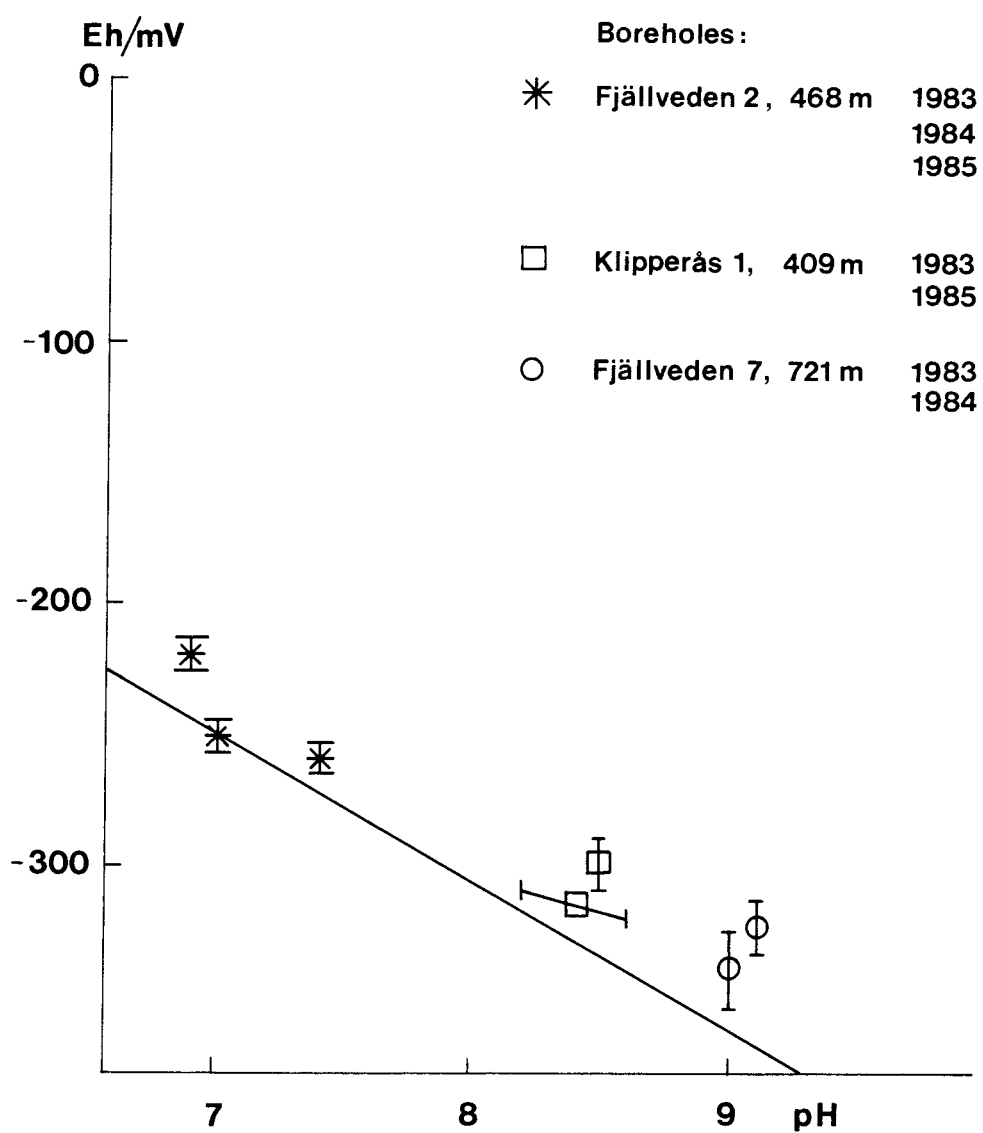have elapsed between the sampling occasions.

Figure 10.   Eh and pH data obtained at repeated groundwater sampling in selected boreholes. The bars indicate the uncertainty in the values.
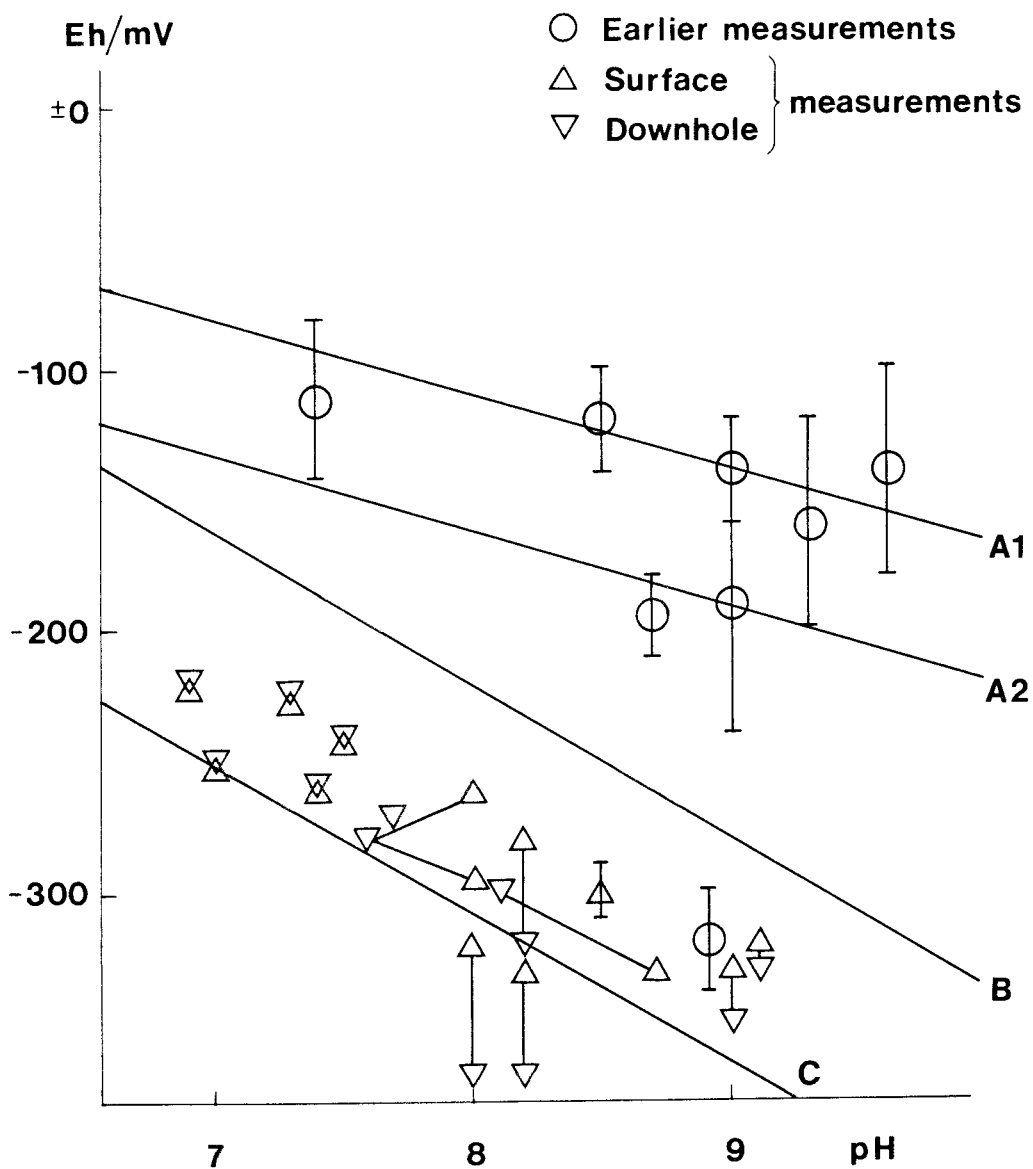
Figure 11. Eh versus pH data of all the groundwater samples which have been considered representative of the environment where they have been sampled. The lines A to C are theoretically calculated Eh-pH relations for different reactions.
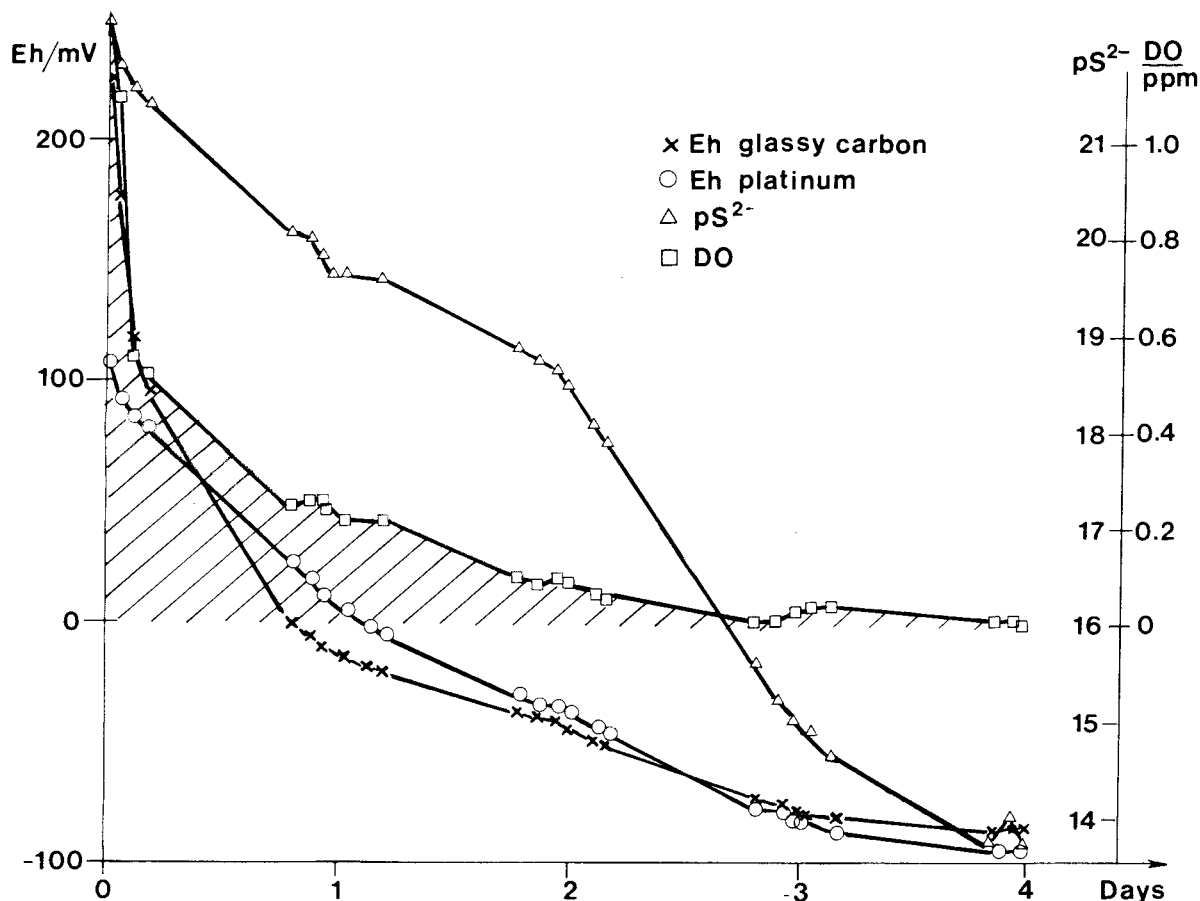
Figure 12. Eh, pS(sulphide) and dissolved oxygen data versus time in the beginning of a pumping period in the early stage of the investigations.

The Eh is presented as a function of pH in Figure 11. In the figure is included all the results were stable Eh values have been obtained. The bars in the figure represents the greatest difference between the highest and the lowest values of the different electrodes.

From Figure 11 it can be seen that there is a difference in the results obtained during the KBS-3 phase as compared to the results obtained later. This difference is significant and is a result of the improvement of the measuring procedures. In the KBS-3 phase the measurements were interrupted frequently by calibrations of the electrodes. At each time oxygen entered the flow cell from which it was only slowly expelled. A typical situation after a calibration is shown in Figure 12 in which 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. Because of this we decided to keep on pumping without interruptions throughout the whole period. This procedure has been used ever since and has resulted in the much lower Eh readings as can be seen in Figure 11. The down-hole pH measurements are in general consistent with the surface measurements. Sometimes the down-hole values have been up to 0.3 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 mea-
sured 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 a certain minimum
concentration. 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.

3.3   Modelling of the redox conditions of the deep groundwaters

The results obtained in the field investigations and which were
subsequently used in the KBS-3 report provide an example of the
difficulties to interpret Eh measurements. The measurements gave a
poor fit to a model which was based on the ferrous and ferric iron
content of the water (Wikberg et al., 1983). This was thought to
be due to disturbances by oxygen. Later on the same data were
modelled by Nordstrom and Puigdomenech who showed that the Eh was
a result from the sulphide sulphur equilibrium (Nordstrom and
Puigdomenech, 1986). The oxidation of sulphide has taken place
through the intrusion of oxygen. Similar phenomena are known from
some hot springs (Boulegue and Michard, 1979). From the EQ3/EQ6
data base (Puigdomenech pers. comm.) the theoretical Eh-pH depen-
dence for 0.01 ppm and 1 ppm sulphide have been calculated and
included in Figure 11. The theoretical Eh-pH dependence for the
hematite-magnetite equilibrium is also from the EQ3/EQ6 data base.

The down-hole data have not been disturbed by the intrusion of
oxygen. They plot close to the theoretical line for the hematite-
magnetite equilibrium. As can be seen from the figure the measured
values both down-hole and on the surface agree very well. This
indicate that the redox conditions of the groundwater are control-
led by the minerals of the rock. This is very reasonable since the
buffering capacity is in the rock and not in the water. However,
the fact that a mineral equilibria agrees 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 ex-
change current density it seems obvious that the iron redox couple
is the mediator. The modelling indicates that the waters are not
saturated with respect to Fe_2O_3 because an Eh level determined by
the Fe^{3+}/Fe^{2+} ratio would, assuming the water saturated by Fe_2O_3,
be about 200 mV higher than the measured ones. This fact is furt-
her supported by the analyses of the iron content which show that
all the dissolved iron is in the ferrous form.

We are confident that the undisturbed water also in the KBS-3
phase would have given Eh values close to the hematite-magnetite
line if the measurements had been carried out for longer periods
without interruptions. This was also the case for one single point
which plot close to the hematite-magnetite line. This sampling
section was pumped for a much longer time than the others due to
very low flow rate.

3.4   Laboratory simulation of the redox conditions

During the field investigations we have in many cases sampled water with ten per cent or more drilling water contamination. Despite this the water has mostly been reducing with an appreciable concentration of ferrous iron. This simply indicates that the kinetics for the reduction of 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 have run a number of experiments where we have had groundwater in contact with drill cores of the rock in well sealed glass vessels. The water phase is circulated continuously by a magnetic piston pump inside the vessel. The pH and the Eh measured by electrodes are continuously monitored. The vessel is filled with approximately 5 litres of water and the surface area of the drill cores are approximately 30 square decimeter. The experimental setup is schematically illustrated in Figure 13.

The results of three consecutive experiments are illustrated in Figure 14 in the form of Eh versus time plot. The pH is not included since there was no significant change during the duration of the experiments. A comparison between the experiments where the water initially was saturated by oxygen and the one where the water was deoxygenated clearly show that there is a delay in the Eh drop in the case where air saturated water was used. It should also be noted that the platinum electrode is much more sensitive to oxygen than the graphite electrode. This is also our experience from the field investigations c.f. 3.2. However, when the oxygen is consumed all electrodes level out at about the same level. Similar results have been reported by 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 the experiments, except for the first run where the natural groundwater was used. In this experiment the first sampled volume was replenished.

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

Component	NATURAL GROUNDWATER			DEIONIZED WATER + HCO_3	
	0-run	1A	1B	2	3
Fe(II)	<.005	.039	.039	.006	<.005
Fe(tot)	<.005	.041	.041	.011	<.005
S(-II)	<.01	----	.03	.02	-----

Measuring electrodes

to
volt
meter

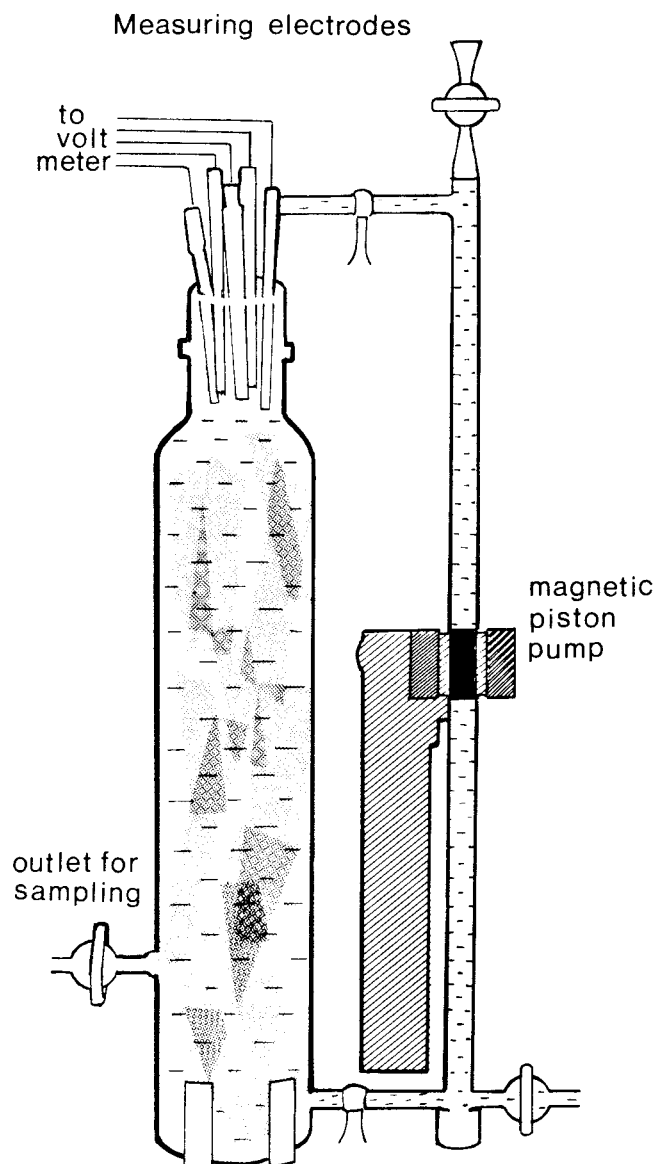magnetic
piston
pump

outlet for
sampling

Figure 13.   A schematic illustration of the glass vessel and
circulation pump system used for the laboratory
simulations of the groundwater-rock reactions.
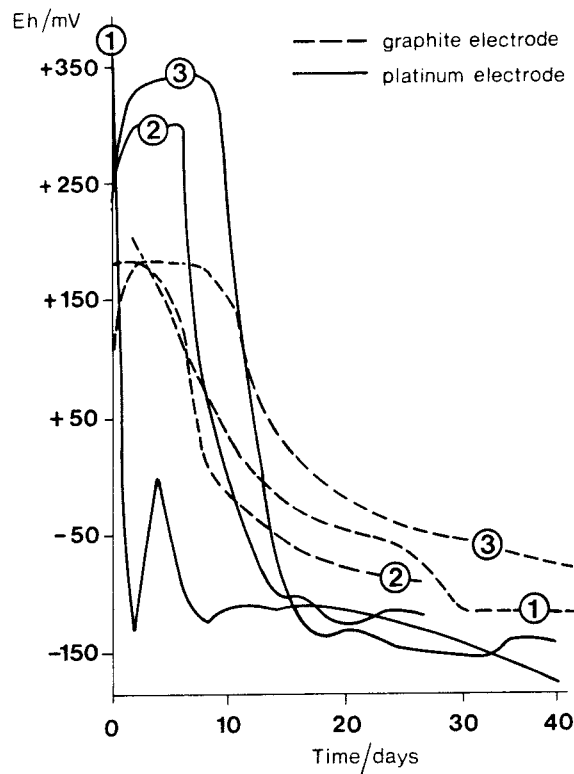
Figure 14.   Eh versus time data obtained in the laboratory
              studies of the redox kinetics. The first run is
              made with deaerated water, the other two with air
              saturated water.

The successively decreasing amounts of iron suggests that the
surface of the drill cores are gradually oxidized, leaving a
smaller amount of ferrous iron left to be dissolved in the wa-
ter. 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 solution. If the reaction had
taken place in the solution the rate would have been proportional
to the amount of dissolved iron. Therefor the last experiment
should have needed a longer time to reach reducing conditions than
the two preceding ones. This conclusion is not valid if the reduc-
tion is caused by biological activities. However, the reduction of
oxygen on mineral surfaces has also been suggested from studies of
natural analogues (Neretnieks, 1986).

Another set of similar experiments has been made with crushed
material in a different experimental setup. The result of these
four runs are presented in Figure 15. The first three of them are
identical. In the forth 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 indicate that the
value at which the Eh electrodes level out in this type of expe-
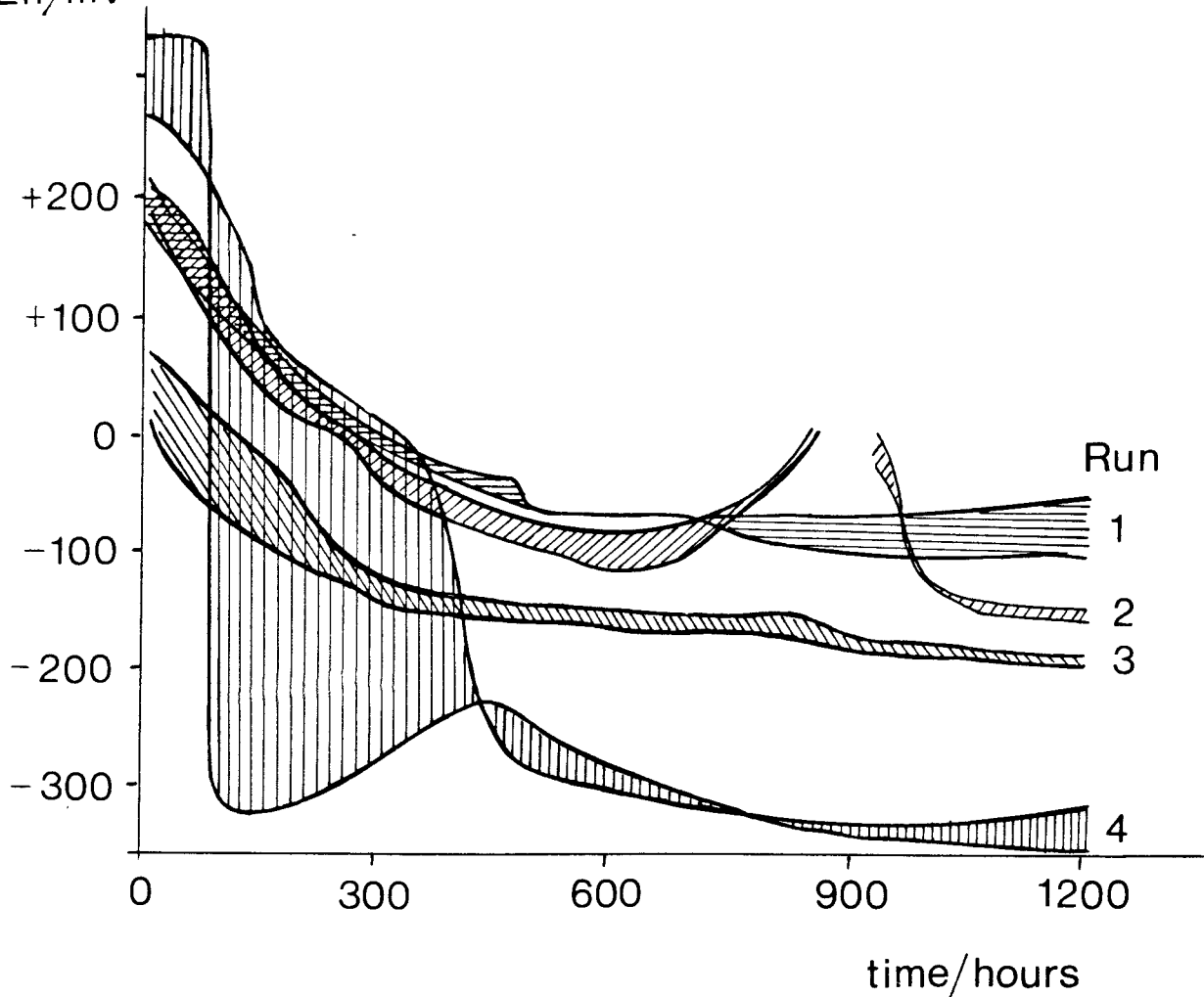riments is not an equilibrium value but a steady state value where

Figure 15. Eh versus time data of four consecutive experiments on redox kinetics. The fourth experiment is made in a totally oxygen free atmosphere.

the dissolution of reducing species from the rock is balanced by the diffusion of oxygen into the measuring cells.

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 at an occasion when the reducing effect was very low did, however, not improve the capacity significantly. Consequently it seems as if the ability to reduce the oxygen resides mainly in the fracture minerals. One should remember though that this is the fast effect which can be studied in the laboratory. There are reasons to believe that also other mechanisms like dissolution (weathering) of primary minerals and matrix diffusion will result in a reduction of oxidants. However, these effects are not as fast as the reaction with the fracture minerals.

3.5   In situ field test

The rate of reduction of dissolved oxygen was tested in situ in a
field experiment. Based on the results of the laboratory studies
the test was made in the following way:

1000 l of groundwater was pumped out of the 468 m level of the
borehole Fj2. The water was analyzed in the mobile field labora-
tory while it was pumped up, stored, aerated and tagged by uranine
before it was pumped back into the packed off section. Two weeks
later the water was pumped back up to surface again and analyz-
ed. The results of the analyses agree with the results previously
reported for the 468 m level of the borehole Fj2 in Table 4.

When the water was pumped up again the second time it contained
only 4% of the water which had been pumped down. Furthermore the
amount decreased rapidly down to 0.2 % within a few days. Because
of the very low portion of the aerated water it was not possible
to see any effects on the Eh electrodes, which rapidly leveled 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 0.4, 0.2,
0.05 and 0.05 micron membrane filters placed in series. These
filters were analyzed for the content of Fe, Al, Si and S. The
results of these analyses are presented in Figure 16. 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 drama-
tic effect on the contents of particulate material in the wa-
ter. Al and Si concentrations are not affected while the Fe con-
tent is high the first two days and then goes down to "initial"
values. The sulphur content is the one which has increased
most. It also takes a long time before it decreases to levels in
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 ground-
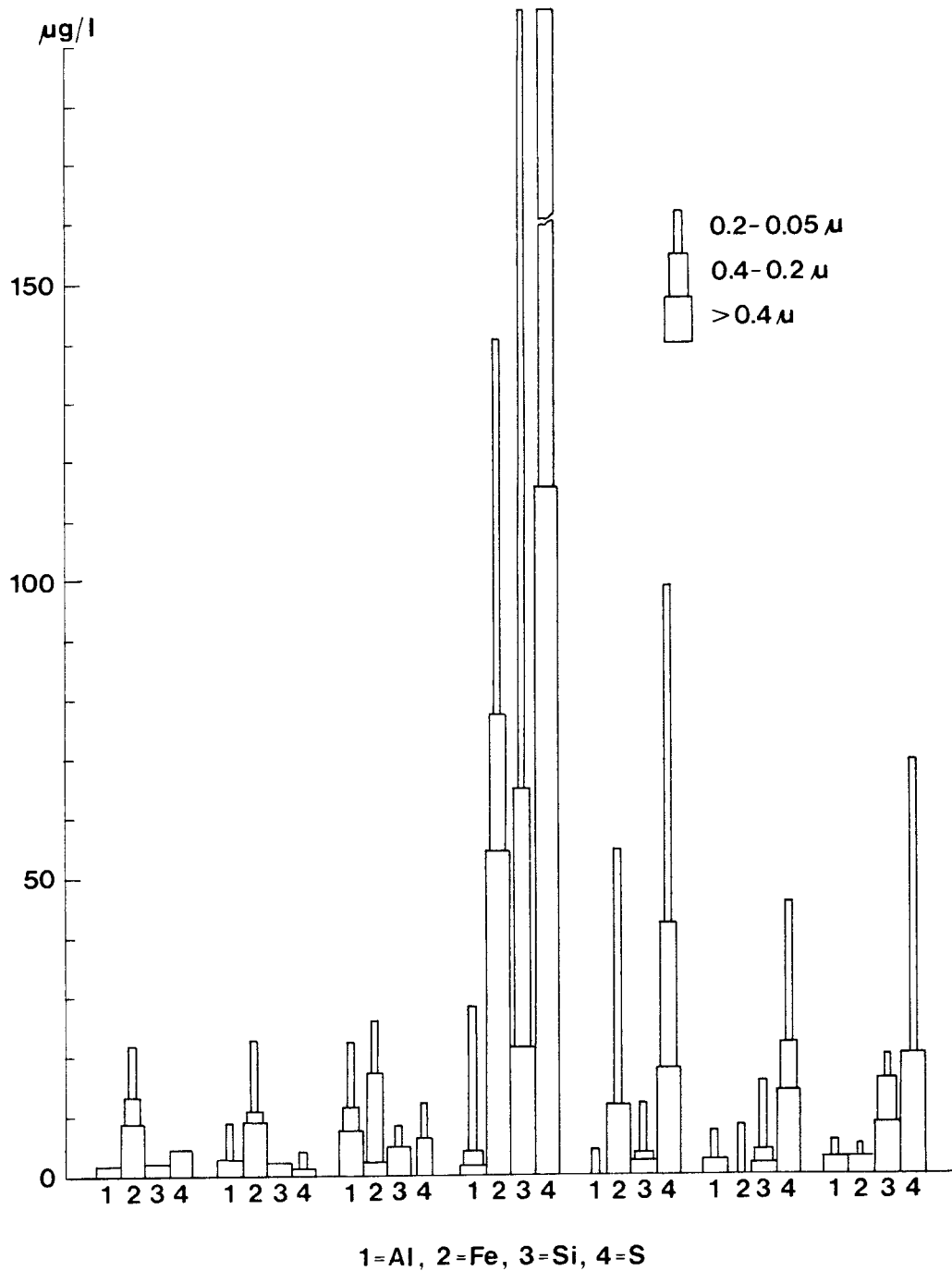water.

Figure 16.   The concentration and size distribution of particu-
late material filtered off the groundwater in a
redox relaxation experiment in Fjällveden 2, 468 m
level.

4   CONCLUSIONS

The SKB groundwater chemical characterization program has been running for five years. During this time a large amount of data have been collected. The conclusions are divided into sampling, analysis and modelling, the first, second and third steps in the process of understanding the groundwater chemistry. It is essential to know all the steps and it is therefore useless to do the modelling, the third step, if one of the previous steps is unknown or poorly characterized. As a consequence of this the efforts have initially been directed towards the problems related to sampling and analyses.

Sampling

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. 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 to 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. 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.

The contamination caused by the drilling water can be avoided if a booster drilling technique is used in stead of the diamond drilling technique. In this case the compressed air will empty the borehole from water, thus reducing the hydrostatic pressure in the borehole. The advantage of the booster percussion drilling is most prominent at shallow depth.

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

For the sampling of water from fractures with a hydraulic conductivities in the range 10^{-8} - 10^{-10} m/s new sampling equipment need to be constructed. This equipment must have the following characteristics:

*   a minimum volume between the packers (less than 1l)

*   easily filled and emptied sample cylinders

Analyses

All the deep groundwaters 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 reason for this is that the deep groundwaters are strongly reducing and there is practically no ferric iron in them. Consequently the water sample acts like 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 contents of sulphide is in 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 the qualitative modelling of the groundwater chemistry. This includes the identification of the processes which has 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 or erroneous sampling or analyses.

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.

The quantitative modelling performed with the aid of numerical computer codes should be made only on those results where the samples are representative. It also seems reasonable to focus this type of work on some specific item at a time. An example of this is the work by Nordstrom and Puigdomenech c.f. 3.3.

The modelling of redox conditions in the deep groundwater has shown that the Eh level in the waters agrees with the equilibrium between the magnetite and hematite, two minerals that are common in the rock. This implies that the redox character of the rock is reflected by the groundwater. This very low Eh level is also supported by the fact that the waters mostly contain sulphide and ferrous iron. The uranium concentrations are below the detection limit.

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