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Äspö Hard Rock Laboratory

In-Situ determination of O_2 uptake by geological media: Field data for the redox experiment in detailed scale (REX)

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May 2000

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ABSTRACT

The redox conditions of Swedish groundwaters in crystalline rocks are of consequence for the performance of a spend nuclear fuel repository. Molecular oxygen (O_2) would affect both the corrosion of the canister, and the migration of radionuclides eventually released from a damaged canister.

The REX project (Redox Experiment in Detailed Scale) has been carried out within the frame of of SKB's Äspö Hard Rock Laboratory. The aim was to determine how O_2 trapped in the closed repository would react with the rock minerals in the tunnel and deposition holes and in the water conducting fractures.

The field REX experiment consisted of injection and monitoring of O_2 uptake in a confined fracture surface under *in-situ* conditions. The results of this experiment were to be compared with those of the *Replica* experiment: a laboratory study using the other half of the fracture surface used for the *in situ* experiment.

The results from the *in-situ* experiment are presented here. Several O_2 pulses were performed, ranging from ≈1 to 26 mg/ℓ. The data obtained consisted of O_2 concentrations, pH, E_H, temperature, pressure. Furthermore several samples were taken for chemical and microbial characterisation. The data shows that O_2 uptake took place in a time frame of one or two weeks, and that both microbial and inorganic processes contributed to the total O_2 uptake. These results may be used to estimate the fate of molecular oxygen in relation to nuclear waste repository performance.

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1 INTRODUCTION

The SKB concept for disposal of high level nuclear waste is based on isolation of spent fuel in copper canisters buried approximately 500 meters deep in granitic bedrock. A critical safety aspect is the mechanical and chemical stability of engineered barriers: canisters, compacted bentonite in the deposition holes between canister and rock, and sand/bentonite mixtures as backfill in tunnels and shafts. Performance assessment must assess the long-term stability and consequences of eventual failure of these barriers.

Repository performance assessment issues related to groundwater redox chemistry are:

1. The presence and fate of molecular oxygen, O_2, in the deep environment at the time of repository closure. Oxygen affects the corrosion of copper metal
2. Production of hydrogen sulphide, HS^-, from sulphate reduction in the deep environment after the closure of the repository. The presence of sulphide would negatively affect the corrosion properties of the copper canister.
3. Dissolved oxygen in the repository or in fracture zones in the case of radionuclide release. Several long-lived radionuclides, such as Np, Pu, Tc, and U, are much more soluble and mobile under oxygenated conditions. Glacial recharge waters are likely to contain dissolved oxygen, and the capacity of the geological environment to reduce molecular oxygen is of importance.

The REX project has been started at the Äspö Hard Rock Laboratory in order to resolve some of these issues. The project was sponsored by the following organisations:

- SKB (Swedish Nuclear Fuel and Waste Management Co., Sweden).
- JNC (Japan Nuclear Cycle Development Institute).
- ANDRA (Agence Nationale pour la Gestion des Déchets Radioactifs, France)

The results from the *in-situ* experiment are presented here.

1.1 OBJECTIVES

The main objective of the REX project was to investigate dissolved O_2 depletion by creating a controlled oxidising perturbation to the deep rock environment at the Äspö Hard Rock Laboratory which is representative of a deep repository environment.

The aims were:

1. Assess the capacity of the host rock system to buffer against an oxidising disturbance.
2. Determine the kinetics (half-life) of oxygen uptake.
3. Develop quantitative descriptions of these processes that can be used in performance assessment of the repository redox stability for the post-closure phase.

1.2 THE REX PROJECT CONCEPT

The REX project was based on two lines of research:

1. Well-controlled *laboratory studies* using minerals, rock samples, groundwater, and microbes from the Äspö site. The laboratory experiments include both batch experiments and flow-through column experiments. The results of these investigations are reported elsewhere

2. *Underground field experiments* at Äspö, which were compared with the laboratory results. Because of uncertainties in hydraulic parameters, the field experiment focused in injection and monitoring of O_2 into a borehole reaching a hydraulically isolated fracture surface. This concept excluded the complications and costs associated with hydraulic multi-hole experiments.

2 FIELD-EXPERIMENT CONFIGURATION

The concept for the field REX experiment was based on injection and monitoring of non-reactive tracer(s) and dissolved oxygen. These tracers and reactants were to be injected into a wide borehole reaching a fracture surface which had to be made hydraulically isolated, for example by packing a borehole section with a steel cap as shown in Figure 1. The fracture being investigated had to be located in the deep environment at Äspö in order to avoid inflow of organic carbon from the soil or marine sediments.

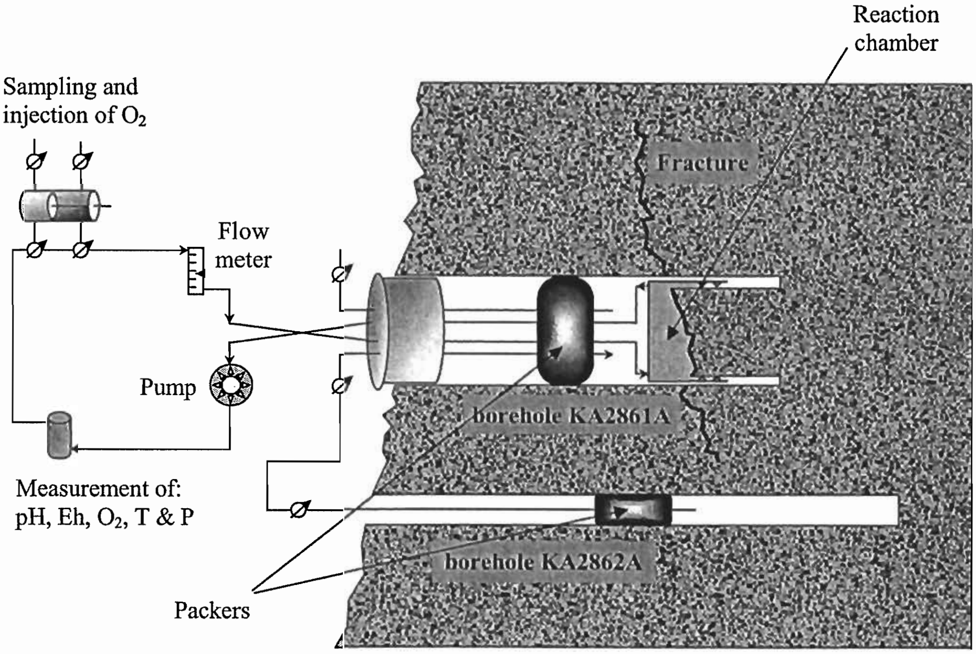


Figure 1. A simple diagram of the experimental configuration for the REX *in situ* experiment.

The experimental concept involved the following aspects:

1. Monitoring of a conservative tracer to assess the hydraulic confinement.
2. Assessment of the chemical composition and mineralogy of the fracture surface in order to identify reaction products from oxygen removal.
3. Microbial studies, to ascertain the relative importance of biological processes.
4. Groundwater composition chosen to avoid if possible dissolution of carbonate fracture filling minerals.

5. Determination of O_2 uptake rates by pulse injection and monitoring of dissolved oxygen. The time dependence of oxygen concentration was expected to depend on the initial oxygen content of the injected solutions.
6. Assessment of O_2 uptake capacity by mass balance of oxygen lost during the experiment until the time when no more oxygen can be depleted.
7. Study of the changes in reactive surfaces and fracture mineralogy. The extent of matrix diffusion of oxygen had to be checked by mineralogical studies of thin sections to find evidence of oxygen penetration.

2.1 SITE SELECTION AND SITE CHARACTERISATION

The REX niche is located 380 m below ground surface at ≈2860 m in the tunnel, *cf.* Figure 2. The criteria for site selection, as well as a complete geological, mineralogical, and geochemical description of the REX site are given in (Puigdomenech et al., 1999). The main characteristics may be summarised as follows

- A simplified structural-geological model for the REX site is shown in Figure 3.
- The rock type at the REX niche is Äspö diorite with a narrow pegmatite dike
- Minor groundwater inflows detected in borehole KA2862A, between 7 and 13.4 m. An inflow of 2 ℓ/min was found at the end of the borehole, at 16 m.
- Chemical characterisation of groundwaters sampled in the vicinity of the REX site are reported in the Appendix. The waters are of Na-Ca(Mg) Cl-SO_4 type and have a relatively high salinity (*cf.* Figure 4). Although only at a depth of 380 m, the stable oxygen and hydrogen isotope data show that the REX groundwaters are amongst the lightest at Äspö, indicating a more ancient cold-climate origin.
- Gas analysis of Äspö of KA2862A groundwaters show concentrations of H_2 and CH_4 in order of 1 μM.
- Geochemical equilibrium calculations performed with PHREEQC (Parkhurst, 1995) and the WATEQ4F database (Ball and Nordstrom, 1991) showed that the waters are close to calcite saturation as shown in Figure 5.
- The redox potential, E_H, measured in the Äspö tunnel with an air-tight flow-through cell holding a Pt electrode shows reducing conditions, *cf.* Table A.1.
- The microbiological characterisation of the groundwaters is given in (Kotelnikova and Pedersen, 2000).

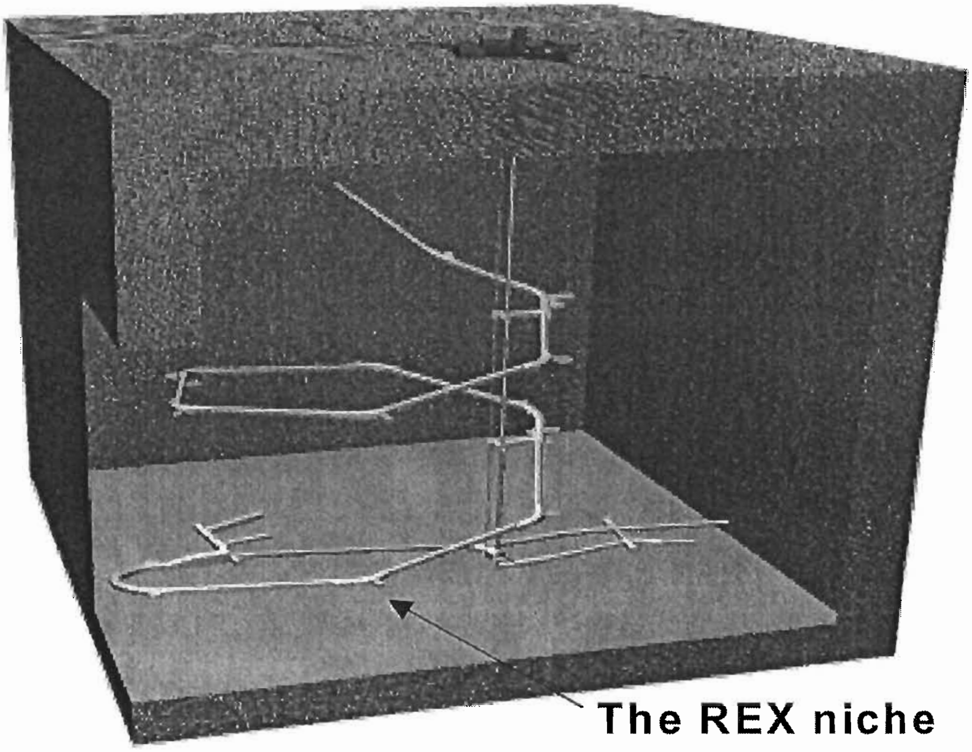


Figure 2. The REX niche located in the tunnel system of the Äspö Hard Rock Laboratory.

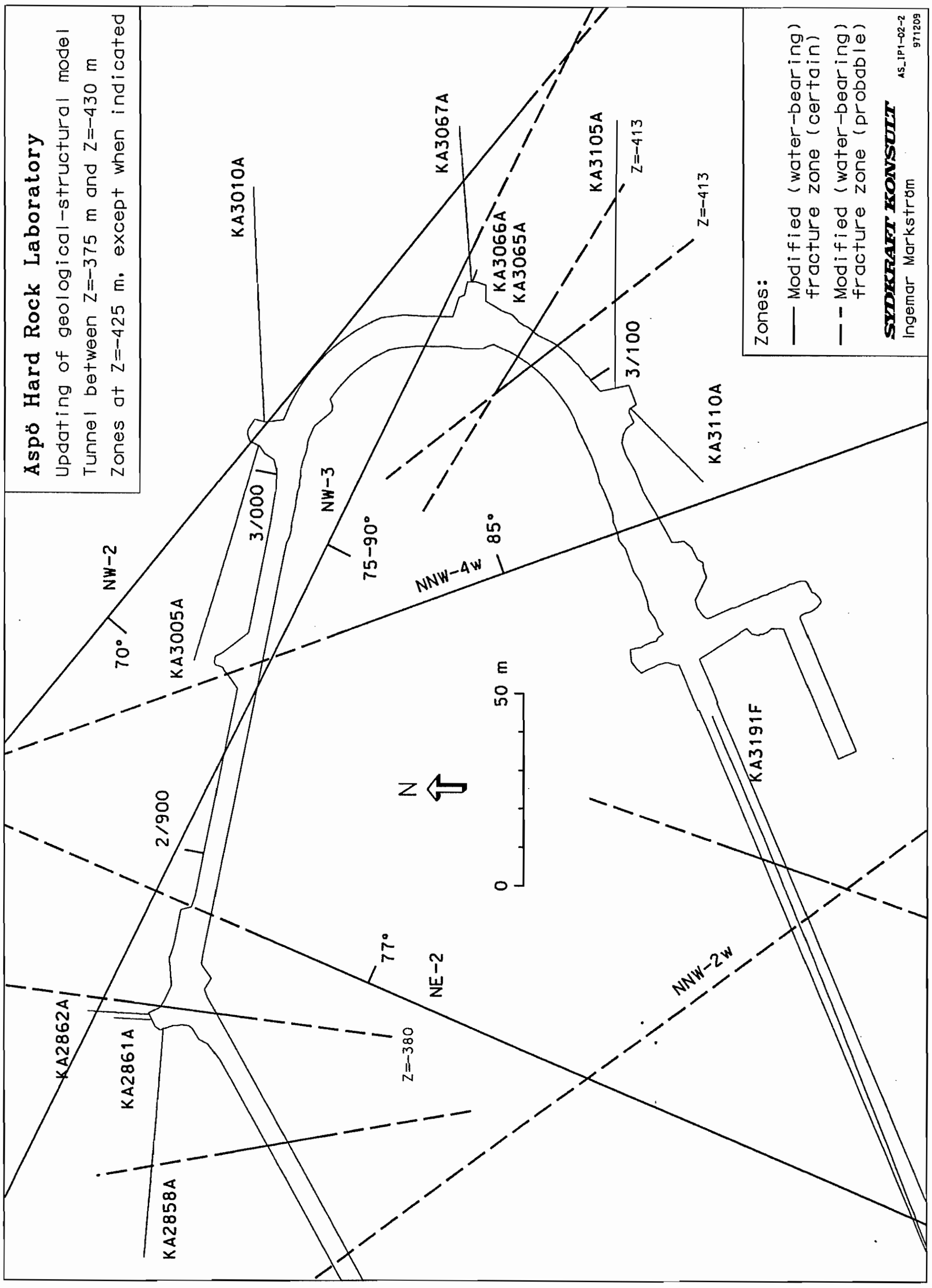


Figure 3. Geological-structural model for the REX site.

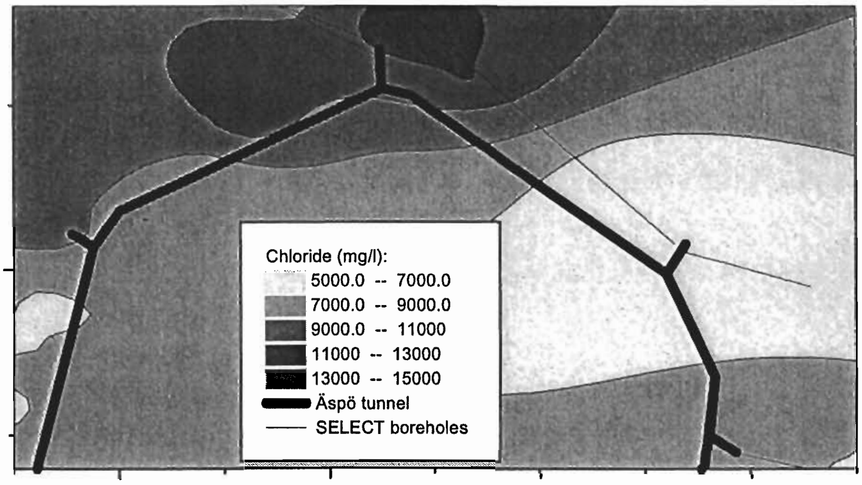


Figure 4. Chloride concentrations in the vicinity of the REX niche at Äspö.

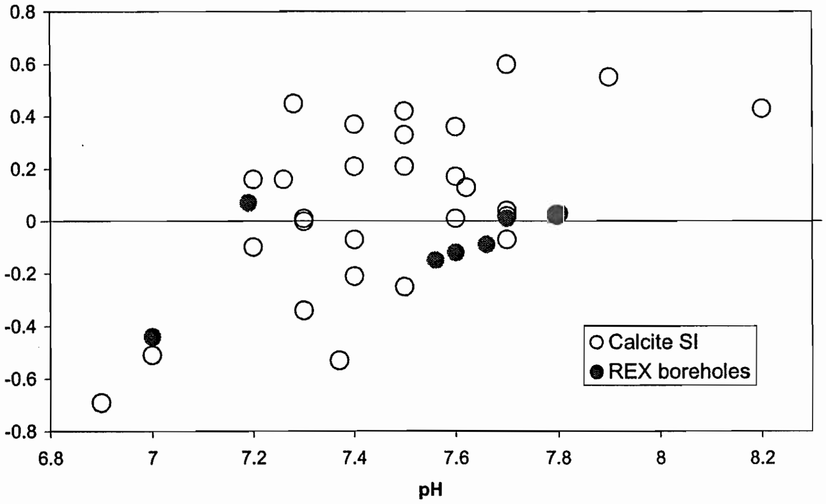


Figure 5. Calculated saturation indices for calcite, $CaCO_3$(cr), as a function of pH for groundwaters in the vicinity of the REX niche at Äspö.

2.2 THE EXPERIMENT BOREHOLE

The experimental concept for the *in situ* REX experiment is injection and monitoring of non-reactive tracer(s) and dissolved O_2 (Section 1.2). These tracers and reactants are to be injected into a wide borehole reaching a fracture surface which had to be made hydraulically isolated, for example by packing a borehole section with a steel cap as shown in Figure 1.

The experimental concept therefore required the drilling of a new wide borehole in the REX niche. The new borehole was to have a diameter of ≈200 mm in order to maximise the fracture surface to groundwater ratio. It was planned that the drilling would leave half of the fracture surface inside the borehole, attached to the rock matrix, as shown in Figure 1. The matching fracture surface was to be extracted with the drill core. The core then would be quickly photographed, and sent to the CEA laboratory at Cadarache, France, inside an airtight package under nitrogen gas. The package was designed and constructed specially for this purpose by the CEA. The drillcore and its fracture surface had to be studied by the CEA and used for the laboratory replica experiment (Trotignon et al., 1999).

Site selection and drilling of the experiment borehole, KA2861A, were described in a status report (Puigdomenech et al., 1999).

The final borehole had a diameter of 196 mm, and the drilling was finalised on Oct. 28, 1996. The new borehole, named KA2861A, is directed towards north, *cf.* Figure 3, ant it was drilled with a downward inclination of 4.6°, so that under most conditions it would remain filled with groundwater. The borehole was drilled at about 1.2 m closer to the tunnel entrance than KA2862A, and it has a slight deviation to bring it closer to the existing KA2862A as the drilling progressed. The calculated distance between the two boreholes is 0.7 m at a distance of 7 m from the tunnel wall.

At 9.34 m the core was withdrawn, and was found to have at its end a fracture surface showing small amounts of fracture filling minerals and signs of alteration. This fracture is located at a depth of 8.81 m in the borehole. The other half of the fracture surface remained in the part of the drillcore that was attached to the rock matrix. The extracted drillcore was sawed some distance from its end, and this part, containing the fracture surface, was packed in a special container provided by Laurent Trotignon. This core sample was sent to CEA (Cadarache, France). The core is described in more detail in the next Section, and may be seen in Figure 6, showing that an epidote-sealed fracture crosses the sampled fracture surface at an angle of about 60°.

The KA2861A borehole produces only small amounts of groundwater (≈0.005 ℓ/min). The groundwater was sampled on Febr. and March 1998, after the installation of the packer, and the results of the chemical analyses are given in the Appendix. This water has a relatively high salinity (13 – 15.6 g/ℓ) supporting a long residence time in the bedrock. According to the classification of groundwaters at Äspö this water is a mixture of glacial meltwaters (or cold recharge waters) with a brine water.

2.2.1 Description of the KA2861A Core

A detailed description of the drillcore was already reported in (Puigdomenech et al., 1999). The most prominent characteristics are as follows. The host rock was foliated, porphyritic Äspö diorite with K-feldspar phenocrysts in the size 1-2 cm. The section between 6.8 to 7.6 m was red stained and tectonised and there were several sealed fractures in this section of the drillcore. These sealed fractures carried epidote and calcite.

At 7.05 m there was an open fracture with very thin and non-continuous fracture coating. When drilling through this fracture, a week response was observed in the hydraulic pressure of the isolated section of KA2862A, indicating a possible connection between the two boreholes. At 7.9 m there is a chlorite coated, probably open fracture.

The sampled fracture is perpendicular to the core axis and a corresponding (parallel and sealed) fracture is found at a distance of 2 cm. The fracture coating is extremely thin and consists of minor spots of chlorite and calcite. A sealed epidote filled fracture transects the sampled fracture surface. The host rock to the fracture is tectonised and the feldspars are red-stained. The biotite is chloritised.

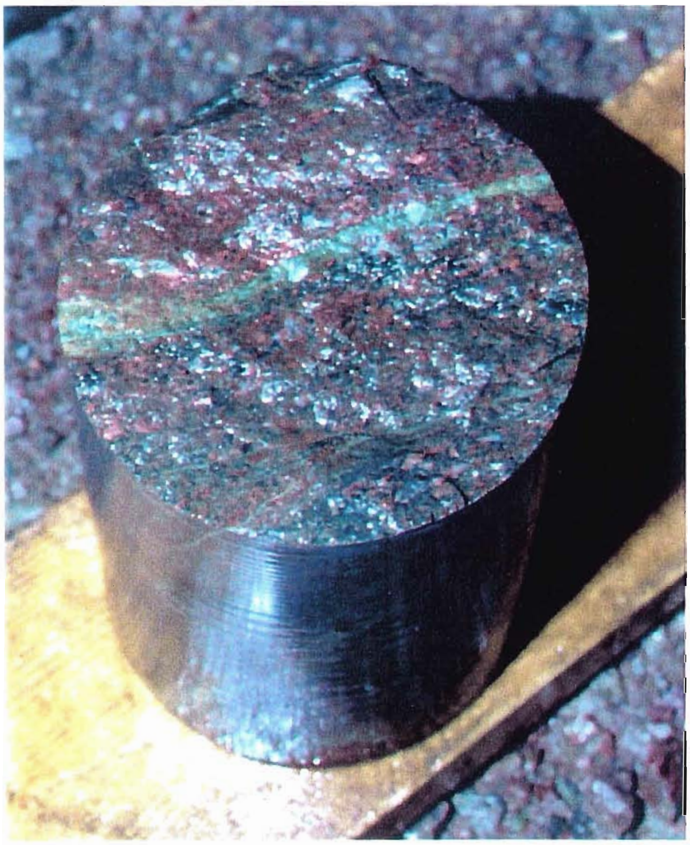


Figure 6. Photograph of the end portion of the core from the KA2861A borehole, which was sent to CEA Cadarache, France, to be used in the replica laboratory experiment.

2.3 FIELD EQUIPMENT

Although the description of the field equipment was reported already in a previous progress report {Puigdomenech, 1999 #3339}, it is reproduced here because of its relevance in judging the experimental data. The figures and text are essentially unchanged.

2.3.1 Design of the Equipment

Based on the experimental concept for the REX *in situ* experiment, as shown in Figure 1, the field equipment was designed to be able to inject and monitor non-reactive tracer(s) and dissolved oxygen.

The final design is shown in Figure 7, Figure 8, and Figure 9.

Because oxygen electrodes continuously consume small amounts of O_2, it is required that the solution being monitored is under stirring. Because of the possibilities of malfunction during the experiment, it was early decided that an external pump would circulate the solution through an external flow circuit. Flow-through cells would be used for the measuring electrodes.

All equipment (pumps, tubing, valves, electrodes, etc) has been designed and tested to withstand the *in situ* pressure of ≈35 bar. To avoid temperature variations of the external flow-through circuit, the tubing and the measuring cabinet shown in Figure 7 are thermally insulated, and a cooling loop in the measuring cabinet uses groundwater from the KA2858A borehole to keep approximate *in situ* temperature for the measuring electrodes.

A gear pump is used to circulate the groundwater from the reaction chamber to the measuring electrodes. The pump is magnetically coupled to the motor so there are no dynamic shaft seals to wear, leak, and lead to oxygen contamination of the experimental set-up. The pump head is a Micropump®, type 1802R.125, with 316 stainless steel pump body and Ryton® (polyphenylene sulphide) gears. The pump motor speed control unit allows circulation flow rates within 0 – 200 cm^3/min.

In order to perform O_2 or tracer injection without disturbing the hydraulic pressure and volume of the closed system, a double piston is used. In this manner the same amount of solution is injected and withdrawn simultaneously. This injection cylinder was manufactured by E2 Systems AB, it had a volume of 1200 mℓ, and it was made of stainless steel with Nitrile Rubber (NBR) sealings.

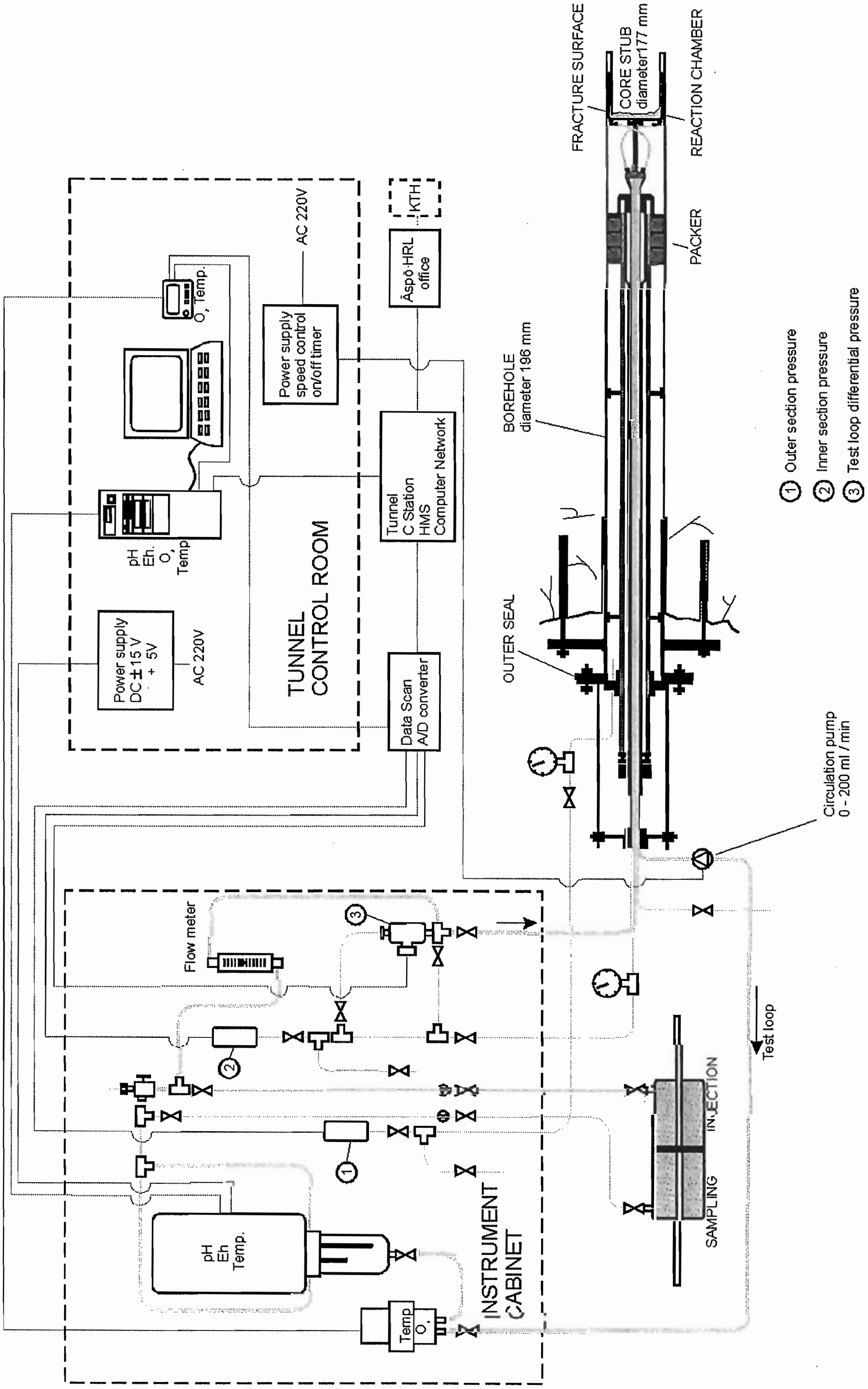


Figure 7. The REX field experiment set-up.

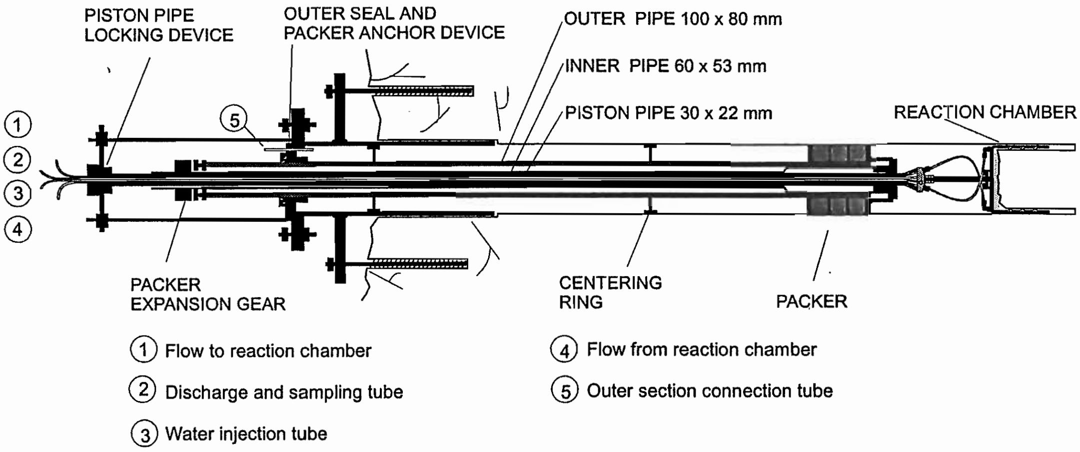


Figure 8. The REX field experiment set-up. The KA2861A borehole.

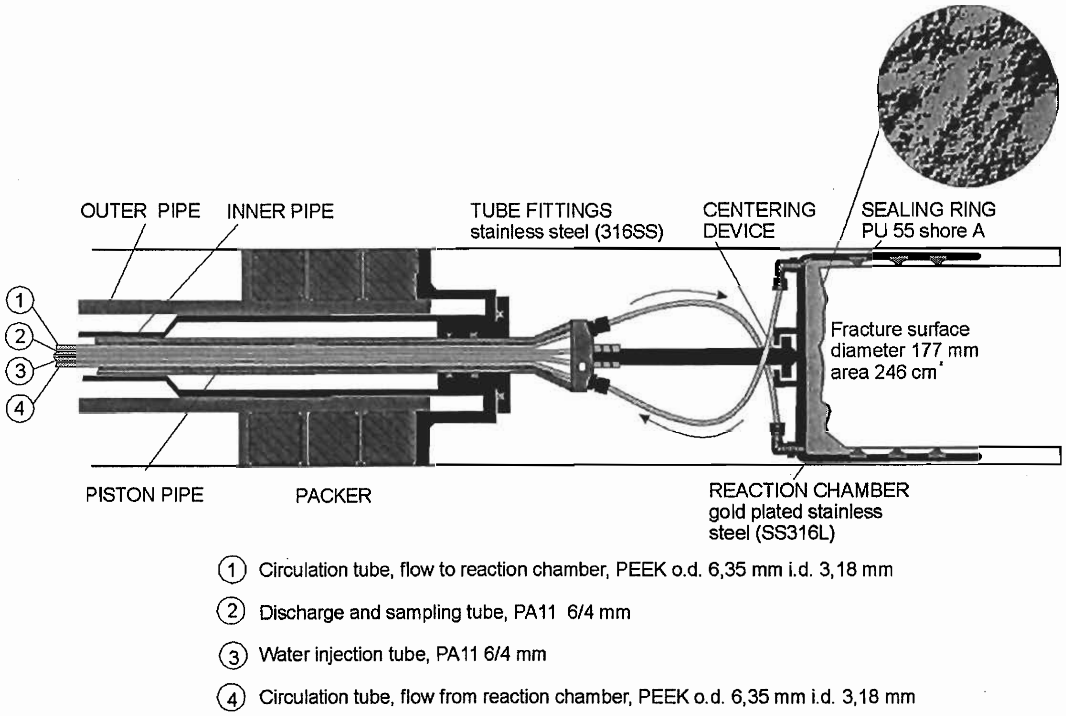


Figure 9. The REX field experiment set-up. Packer and reaction chamber.

The O_2 measuring device is an Orbisphere sensor and flow-through cell, connected to a MOCA analyser and fitted with a 29552A membrane (50 µm thick; measuring range: 2 ppb to 80 ppm; recommended flow rate: 50 cm^3/min).

Electrodes for pH and E_H measurements under *in situ* pressure have been developed and manufactured at the Royal Institute of Technology, Stockholm, Sweden. The pH probe essentially consists of a dismantled commercial glass electrode (Russel pH Ltd., UK, type UU7/9.5/43). Their glass membranes are fitted to specially made Ag/AgCl internal electrodes, and the internal solution is confined by o-rings between the glass membrane and a plastic body of either PVC (polyvinyl chloride) or PPS (also known as Ryton® or polyphenylene sulphide). The glass membrane is allowed to slide on the o-rings in response to pressure changes. The reference electrode is a "home made" Ag/AgCl with a plastic body (PVC or PPS) a Teflon (PTFE = polytetrafluoroethylene) tube and an electrolyte junction of sintered plastic (PVC). The plastic body of the reference electrode is not affected by pressure changes because of its flexibility. These electrodes are connected to specially designed electronic amplifiers and a data collection system supplied by a Swedish commercial company. A low-volume flow-through cell was constructed to accommodate the electrodes. The electrodes are shown in Figure 10.

The measuring instruments were placed inside a measuring cabinet near to the KA2861A borehole, in the REX niche, *cf.* Figure 11.

2.3.2 Choice of Materials

Owing to its chemical and physical properties, molecular oxygen imposes some special difficulties.

The high chemical reactivity of O_2 has as a consequence that it will react with most metals to produce corrosion products, especially in the presence of water. Chloride ions will act as complexing agents of dissolved metal cations and favour corrosion processes.

Microbes use the high reactivity of oxygen to mediate chemical processes and use the resulting energy in their metabolic processes. The most common oxygen consumption reaction mediated by microbes is the consumption of dissolved organic carbon. In its absence, other reductants are used: iron(II), manganese(II), and dissolved molecular hydrogen and methane.

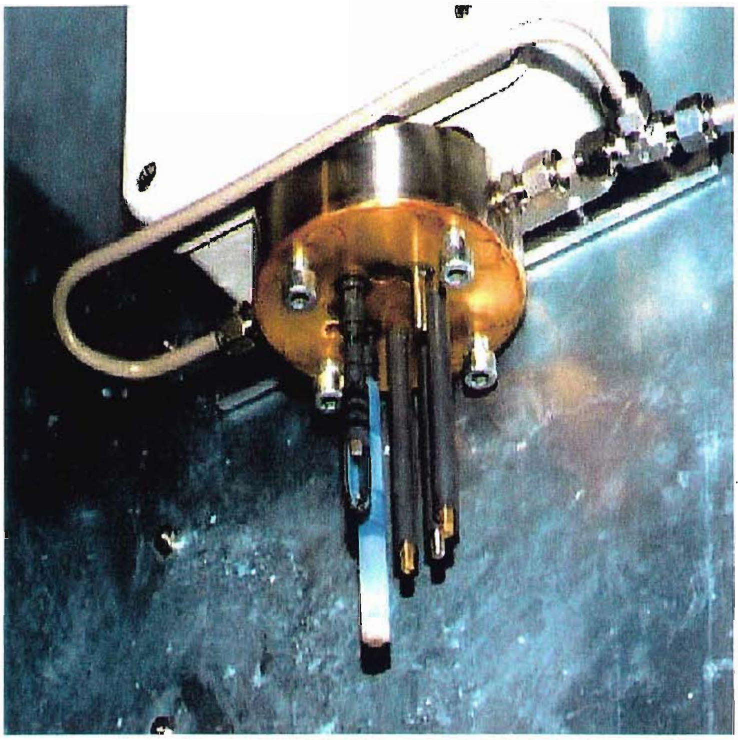


Figure 10. The reference (Ag/AgCl), pH, and E_H electrodes (Pt and Au) disclosed when the lid of the flow-through cell is removed.

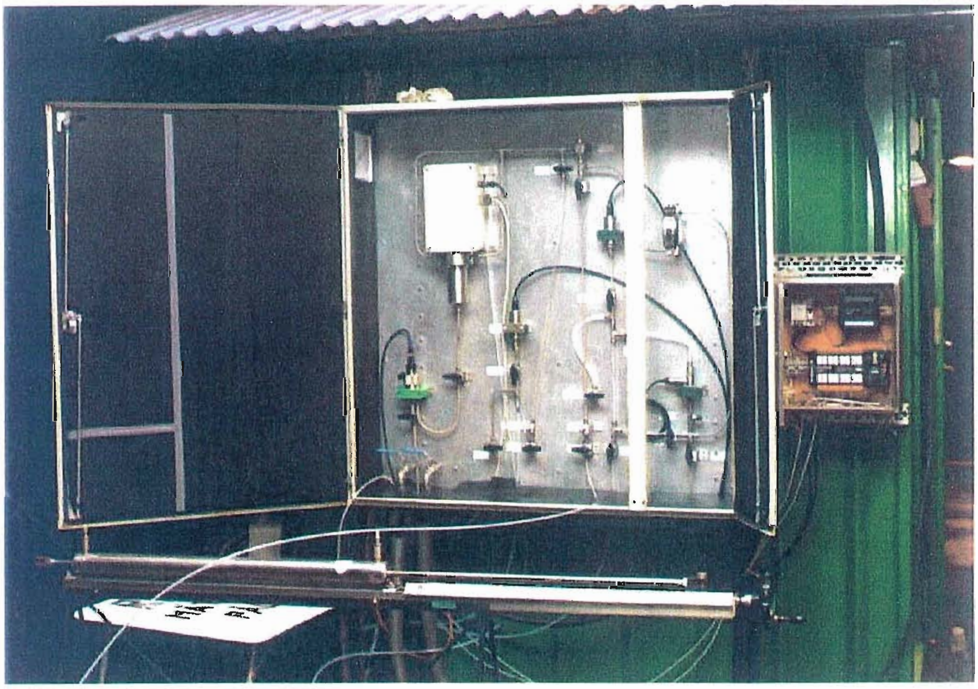


Figure 11. Photograph of the measuring cabinet in front of the REX container. The cabinet contains the pH/E_H flow-through measuring cell, the O_2 sensor, the flow meter, and several manometers. Inside the container, a personal computer collected the measurements, and was connected to the Internet through a optical cable. In the lower part of the picture, the injection cylinder is located in front of the cabinet.

As a small and electrically neutral molecule, O_2 diffuses easily into plastics. Because oxygen is present in the atmosphere, diffusion of O_2 through the walls of plastic tubing must be avoided. Plastic containers can also act as buffers, accumulating oxygen by diffusion when the plastic is in contact with a solution saturated with O_2, and releasing the accumulated oxygen when the concentration in the aqueous phase decreases.

To avoid diffusion of oxygen from the atmosphere PEEK (poly-ether-ether-ketone) is used as the material for all plastic tubing in the REX field experiment set-up. All tubing in the reaction-chamber / measuring electrodes loop has the dimensions 6.35 mm and 3.15 mm as outer and inner diameters respectively.

Metal parts could not be avoided. For example, the flow meter contains a short tube (≈15 cm) of stainless steel. Tubing connections and valves are also stainless steel. To avoid corrosion problems, surfaces of stainless steel were kept to a minimum. Larger areas are needed in the electrode flow-through cell and reaction chamber. These were gold plated to avoid slow but perhaps noticeable corrosion processes.

Three o-rings ensure hydraulic confinement of the investigated fluid by fitting the reaction cap to the borehole core. These o-rings are shown in Figure 9, and they were made of polyurethane, because this material may be manufactured at many different degrees of flexibility.

2.3.3 Installation of Packer, Reaction Chamber, and Instrument Cabinet

The REX packer and the borehole outer seal were installed in the KA2861A borehole for testing purposes on 20-January-1997. The packer was steam-cleaned before insertion in the borehole to avoid excessive microbial contamination of the borehole. On 25-November-1997 the experiment borehole was rinsed from drill cuttings and debris under nitrogen atmosphere, using water from a neighbour borehole, KA2598A.

Tests of the packer and reaction chamber were performed on 16-December 1997. It was then found that the drillcore, which had been attached to the rock matrix after the drilling procedure, had separated and it was lying on the bottom of the borehole. A centring device was designed and manufactured with stainless steel, which could sustain the drillcore at the centre of the borehole. This centring device, the reaction chamber and the packer were finally installed on the 26-March 1998 (Figure 12).

The circulation pump, and the instrument cabinet, containing the sensors (pH, Eh, O_2, temperature, pressure, shown in Figure 11), were installed in the REX niche on 27-April 1998.

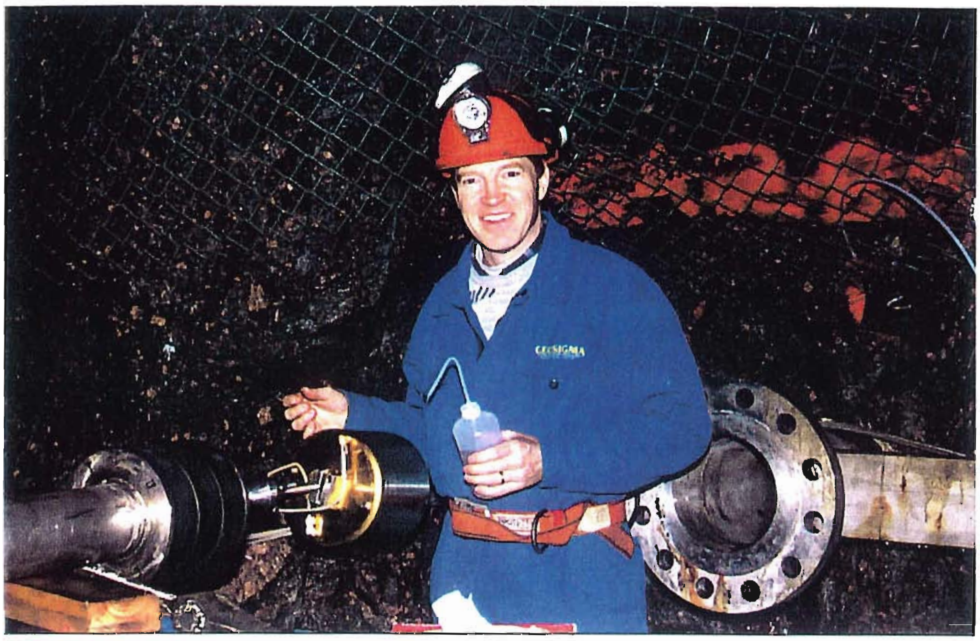


Figure 12. The field equipment being cleaned with an alcoholic solution to avoid bacterial contamination of the borehole

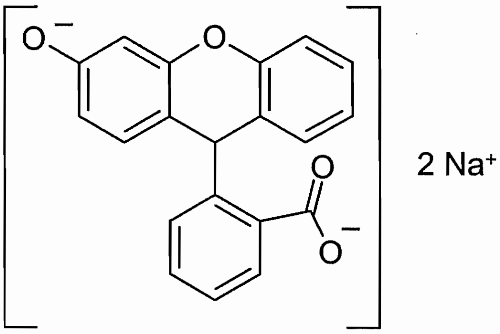
3 RESULTS

3.1 TESTS FOR LEAKAGES

3.1.1 Hydraulic Containment

Tests for hydraulic containment were performed by injecting a tracer solution into the test loop of KA2861A. This was performed with the simultaneous removal of an equal amount of groundwater from the reaction loop. The whole process was performed under *in-situ* pressure (≈35 bar).

The tracer used was uranine ($C_{20}H_{10}O_5Na_2$, CAS-No. [518-47-8]):



which was dissolved in KA2862A groundwater to a concentration of ≈200 mg/ℓ.

Samples of groundwater were removed under *in-situ* pressure at specific time intervals and analysed for uranine contents with a spectrofluorimeter. Samples were taken with the simultaneous addition of the same volume of KA2862A groundwater.

On the second tracer test, which started on 19 March 1999, it was discovered that *uranine decayed* in the samples. The results of that tracer test could not be used, and a new test was started on 28 April 1999, were samples were analysed on the same day.

The discovery of the instability of uranine in the REX samples, even when kept in the dark, conveys a large mistrust on the use of this tracer in the drilling fluids to test for contamination in groundwater samples at Äspö and elsewhere.

The results from the tracer test started on 28 April 1999 are shown in Figure 13. Sampling occurred with the simultaneous dilution with equivalent volumes of uranine-free water, and this is reflected as "steps" in the calculated curve in Figure 13.

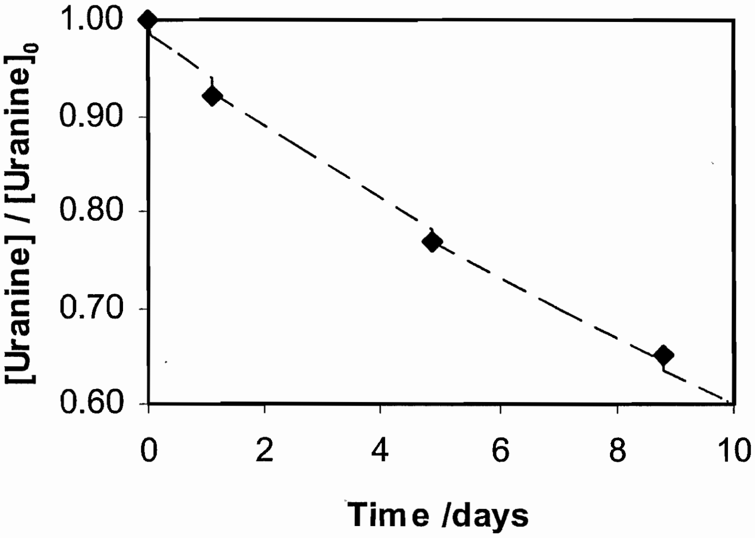


Figure 13. Results from the tracer test started on 28 April 1999.

The results of the tracer tests were interpreted as first order kinetics, and gave as a result a total volume of 0.960 ℓ for the test loop, and a leakage rate constant of 0.041 day^{-1}. The equation describing the leakage is:

$$C = C_0\, e^{-k_{\text{leak}}\, t}$$

where C is the tracer concentration, C_0 is the initial concentration of tracer, k_{leak} is the leakage rate constant, and t is the elapsed time.

As Figure 13 illustrates, a substantial amount of tracer is lost, through the o-rings of the steel cap, to the surrounding section. For periods larger than 10 days, almost 50% of the fluid in the reaction loop is interchanged for groundwater from the surrounding section of KA2861A.

All data from the O_2 pulses was corrected for this leakage before modelling, plotting, *etc.*

3.1.2 Leakage of Atmospheric Oxygen

It was mentioned in Section 2.3.2 that molecular oxygen easily diffuses through plastic materials, *etc.* A test for leakage of atmospheric O_2 into the groundwater circulating through the reaction loop was performed starting on 8 April 1999. The test consisted in purging the circulating loop with "fresh"

KA2862A groundwater, followed by the isolation of the tunnel part of the circulating loop as shown in Figure 14.

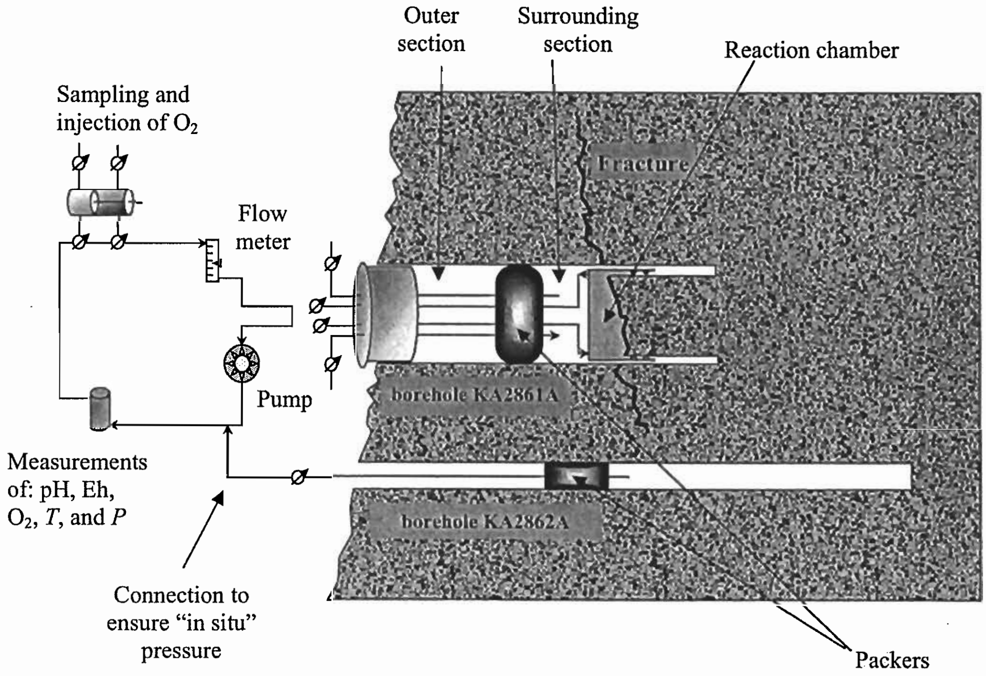


Figure 14. A simple diagram of the experimental configuration for the test of atmospheric O_2 leakage in the REX *in situ* experiment. The diagram should be compared to that of Figure 1.

The data showed that atmospheric O_2 did contaminate the groundwater in the reaction loop at a rate that amounted to ≈1 mg/ℓ in a one-week period, *cf.* Figure 15.

3.1.3 Experimental Constrains Due to Leakage

The leakages described in this section, that is, the interchange of groundwater between the reaction chamber and the surrounding section, combined with the leakage of atmospheric O_2 into the circulation loop, made impossible to reach anoxic conditions in the field experiment set-up. Furthermore, monitoring of the O_2 pulses for periods longer than about one week would not provide information that could be subject to interpretation or modelling.

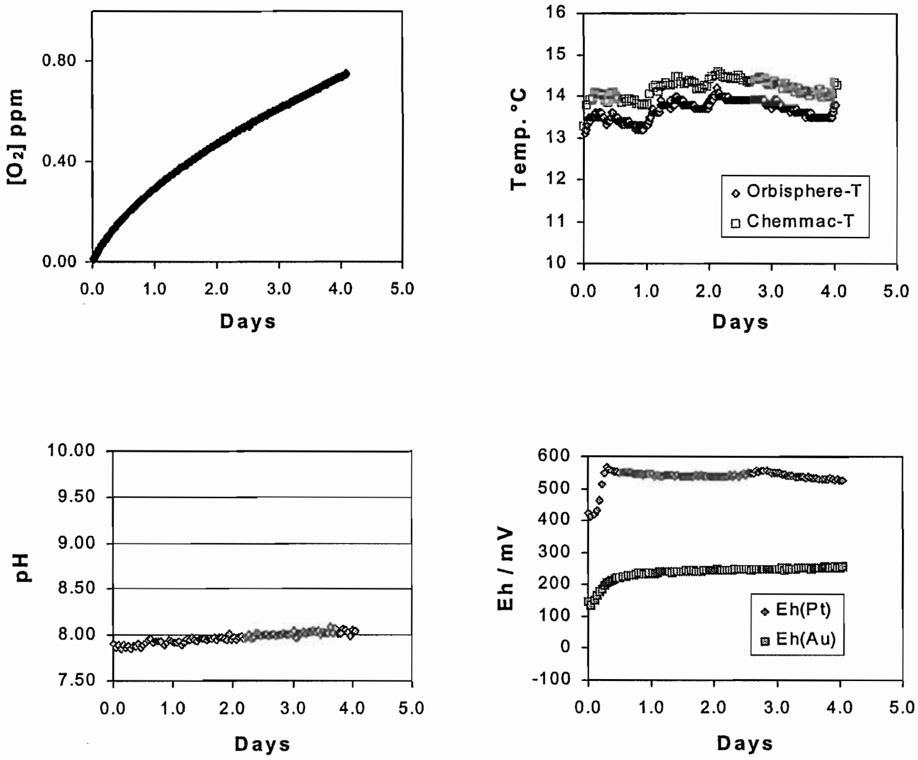


Figure 15. Results from the atmospheric O_2 leakage test started on 8 April 1999.

3.2 DESIGN OF THE O_2-PULSE PROCEDURE

Because the REX borehole produces only small groundwater quantities (≲0.005 ℓ/min), groundwater from the inner section of the KA2862A borehole were used to perform the REX field and replica experiments.

The following actions preceded each O_2 pulse:

- The oxygen electrode was calibrated.
- Groundwater from the neighbour borehole, KA2862A, was allowed to flow through the reaction chamber and tunnel loop. The readings from the O_2-sensor showed dissolved oxygen concentrations below 0.01 mg/ℓ. The flowing was performed under pressure (≈30 bar). A large amount of KA2862A groundwater (about 30 ℓ) was allowed to flow though the section surrounding the reaction chamber. This was performed to ensure O_2-free initial conditions before an experiment.
- Air or oxygen gas was bubbled through a groundwater sample from the KA2862A borehole. The final O_2 contents, as shown by the O_2-sensor, was either ≈8 mg/ℓ (air bubbling) or >30 mg/ℓ (O_2-gas bubbling)

These procedures were followed by the injection of a precalculated amount of the O_2-enriched groundwater through the injection cylinder. This was performed with the simultaneous removal of an equal amount of liquid from the reaction loop. The whole process was performed under *in-situ* pressure (≈35 bar).

An exception to the procedure outline above was the second part of the ≈26 mg/ℓ pulse (Table 1), where the injection of O_2-enriched groundwater was not preceded by either the calibration of the sensor or by the purging of the reaction chamber with "fresh" KA2862A groundwater.

It must be noted that the procedure generally followed in the REX field experiments *differs* from that followed in the Replica experiment (Trotignon et al., 1999), where the groundwater in the reaction chamber and circulation loop was not renewed, and reaction products were allowed to accumulate in the fluid as more O_2-pulses were performed. The reason for this discrepancy between the field and replica experiments was that without purging of the reaction chamber in the KA2861A borehole, initial O_2-free conditions could not be achieved due to the leakages described in Section 3.1. The interchange of groundwater between the reaction chamber and the surrounding section, combined with the leakage of atmospheric O_2 into the circulation loop, made impossible to reach anoxic conditions. This also adds a difference between the REX field and replica experiments: in the field experiment the reaction chamber was saturated with the natural gas content of the KA2862A groundwaters at *in-situ* pressure. In the replica experiment some of this gas content was lost when the pressure in the groundwater bottle was released.

3.3 RESULTS FROM THE O_2 PULSES

3.3.1 Data Overview

The chronology of the different O_2 pulses, tracer tests, etc, is given in Table 1.

Owing to malfunctioning of the O_2-sensor, no results could be obtained from the initial pulses performed in July 1998.

The data from the rest of the pulses are given in Figure 16 to Figure 26.

Some characteristics may be pointed out

- The temperature varied between 13 and 16°C.
- The redox potentials measured with the Au-electrode where consistently higher than the data obtained from the Pt-electrode.
- pH increased from an initial value of ≈7.8 up to 10.
- Dissolved oxygen decreased in an exponential manner, but as expected from the leakage tests (Section 3.1), full anoxic conditions could not be reached.

Table 1. Chronology of the field experiment.

Date	O_2-Pulse Number	Action
26 May 1998		Start of Tracer Test
7 July 1998		Start of ≈0.5 mg/ℓ O_2 pulse
22 July 1998		Start of ≈5 mg/ℓ O_2 pulse
10 Sep. 1998	1	Start of ≈1 mg/ℓ O_2 pulse
29 Oct. 1998	2	Start of ≈1 mg/ℓ O_2 pulse
24 Nov. 1998	3	Start of ≈1 mg/ℓ O_2 pulse
9 Dec. 1998	4	Start of ≈4.5 mg/ℓ O_2 pulse
15 Jan. 1999	5	Start of ≈4.5 mg/ℓ O_2 pulse
29 Jan. 1999	6	Start of ≈4.5 mg/ℓ O_2 pulse
18 Feb. 1999	7	Start of ≈7.5 mg/ℓ O_2 pulse
2 March 1999	8	Start of ≈7.5 mg/ℓ O_2 pulse
12 March 1999	9	Start of ≈1 mg/ℓ O_2 pulse
19 March 1999		Start of Tracer Test
12 April 1999		Start of ≈5 mg/ℓ O_2 pulse on tunnel loop
28 April 1999		Start of Tracer Test and ≈8 mg/ℓ O_2 pulse
11 May 1999	10a	Start of ≈26 mg/ℓ O_2 pulse
19 May 1999	10b	Added more O_2 to reach ≈26 mg/ℓ again
1 June 1999	11	Start of ≈8 mg/ℓ O_2 pulse with microbial inhibitors

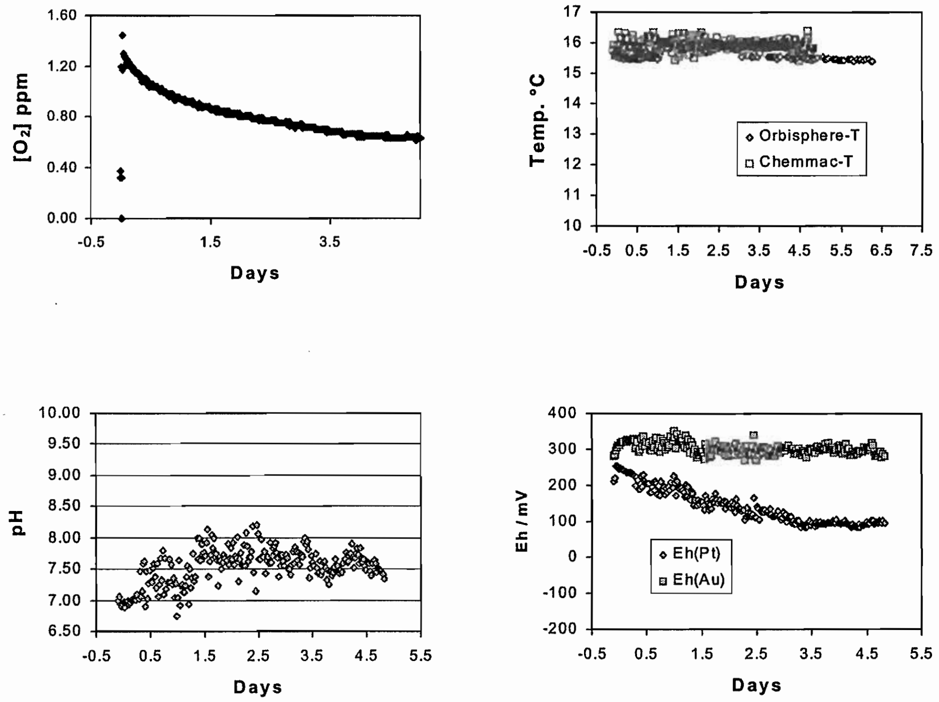


Figure 16. Results from the O_2-pulse started on 10 Sept. 1998.

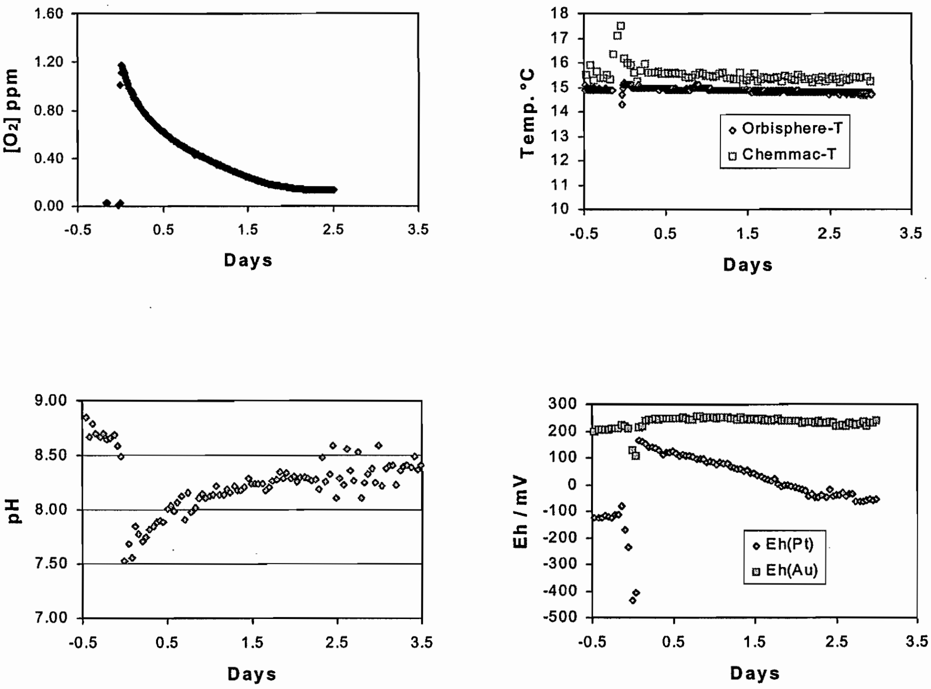


Figure 17. Results from the O_2-pulse started on 29 Oct. 1998.

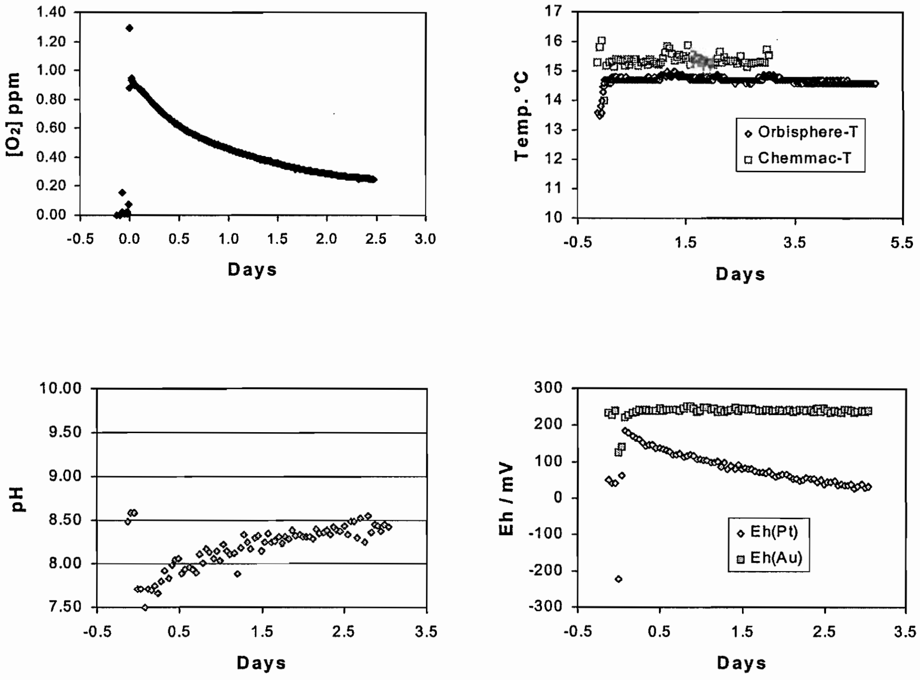


Figure 18. Results from the O_2-pulse started on 24 Nov. 1998.

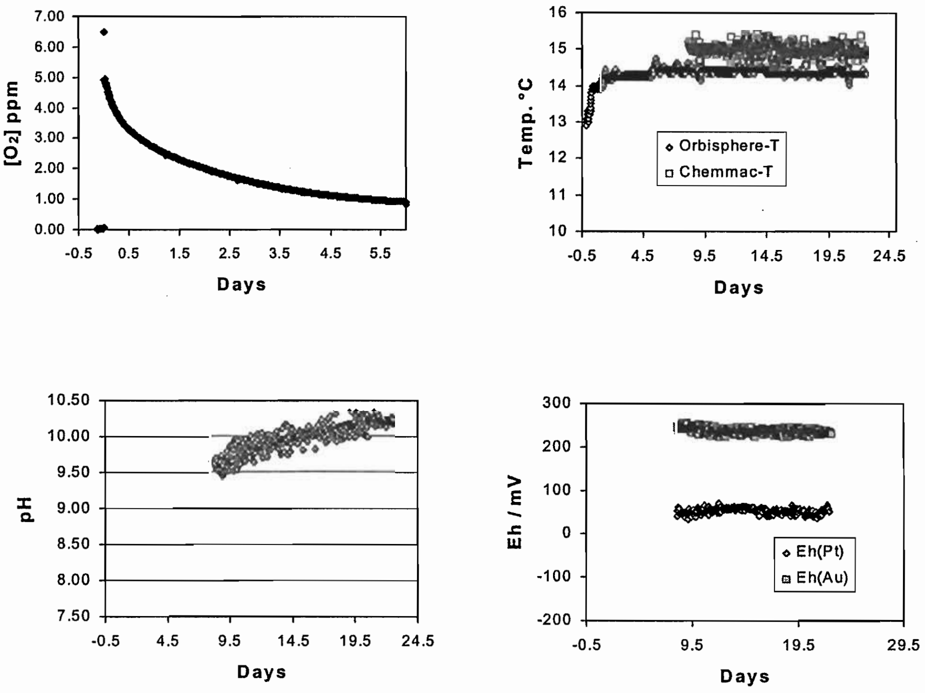


Figure 19. Results from the O_2-pulse started on 9 Dec. 1998.

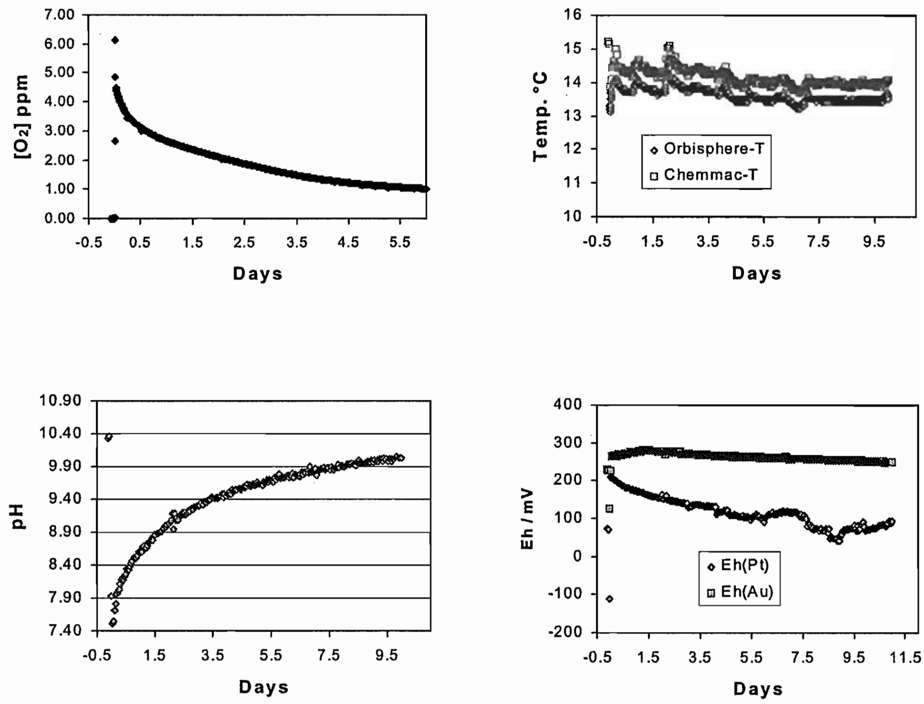


Figure 20. Results from the O_2-pulse started on 15 Jan. 1999.

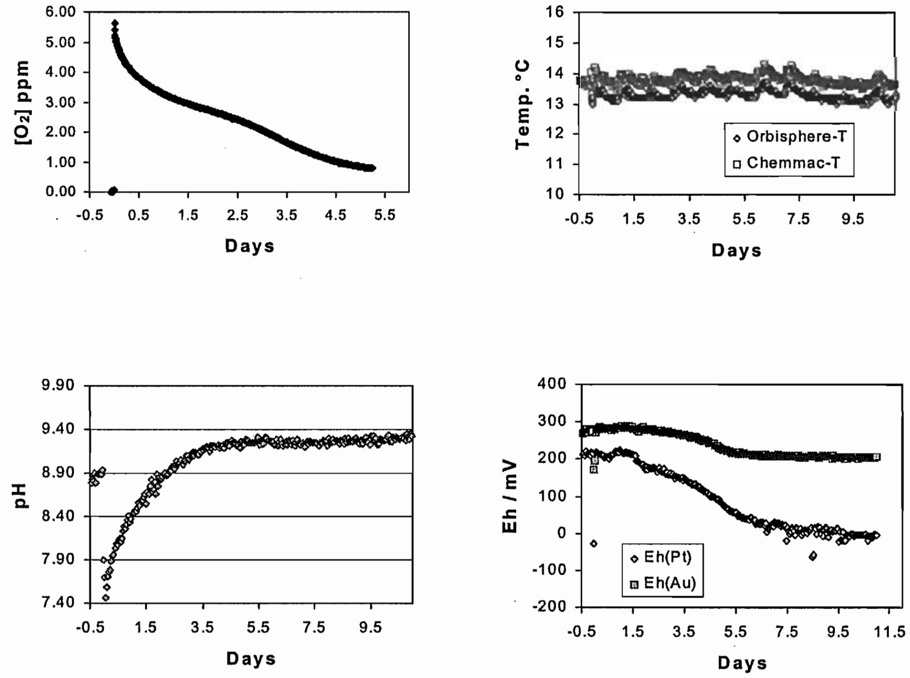


Figure 21. Results from the O_2-pulse started on 29 Jan. 1999.

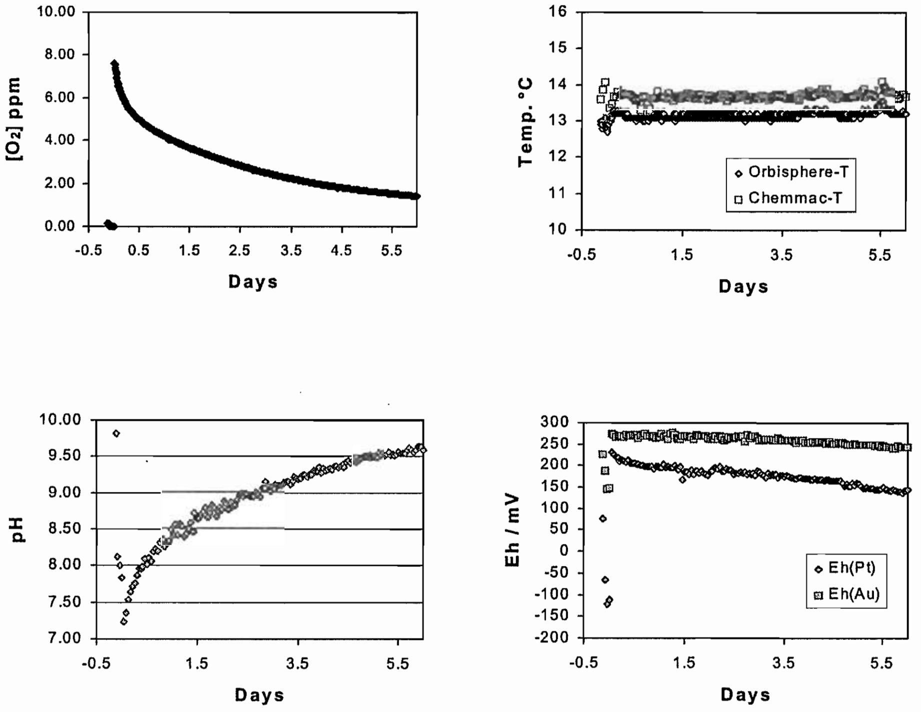


Figure 22. Results from the O_2-pulse started on 18 Feb. 1999.

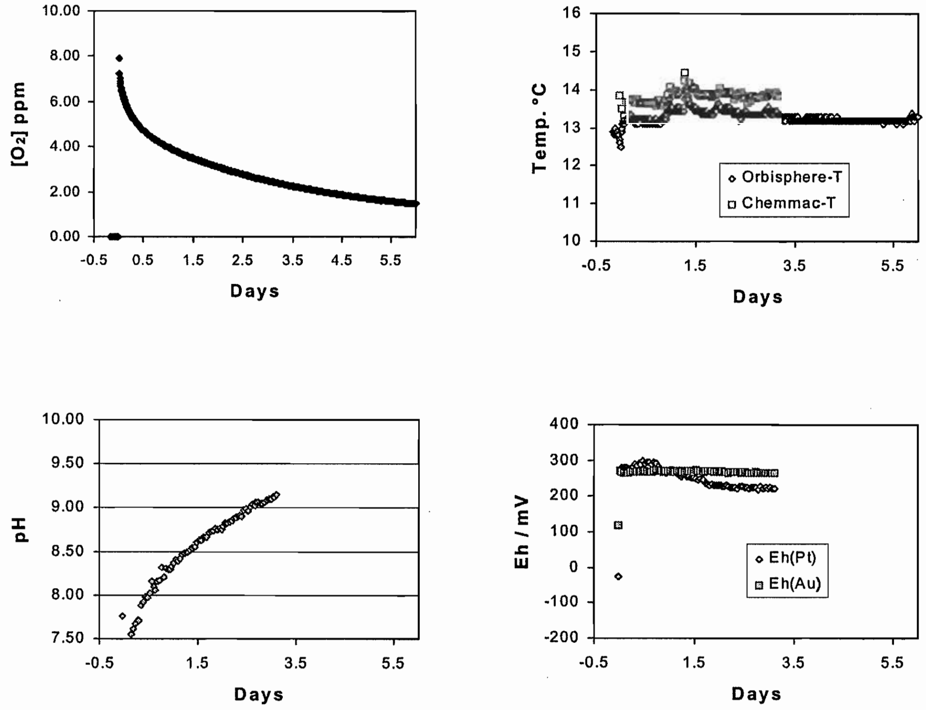


Figure 23. Results from the O_2-pulse started on 2 March 1999.

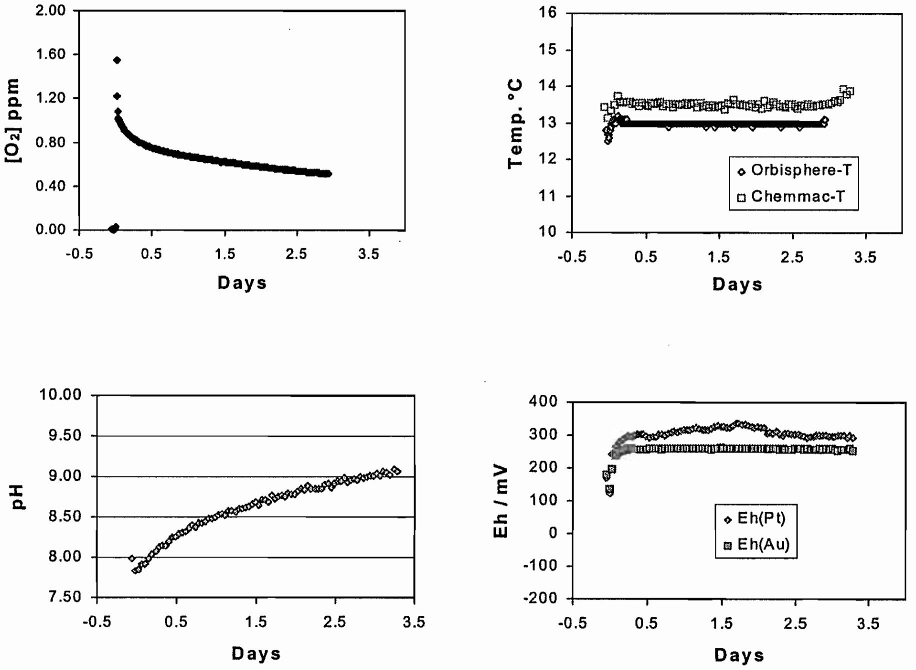


Figure 24. Results from the O_2-pulse started on 12 March 1999.

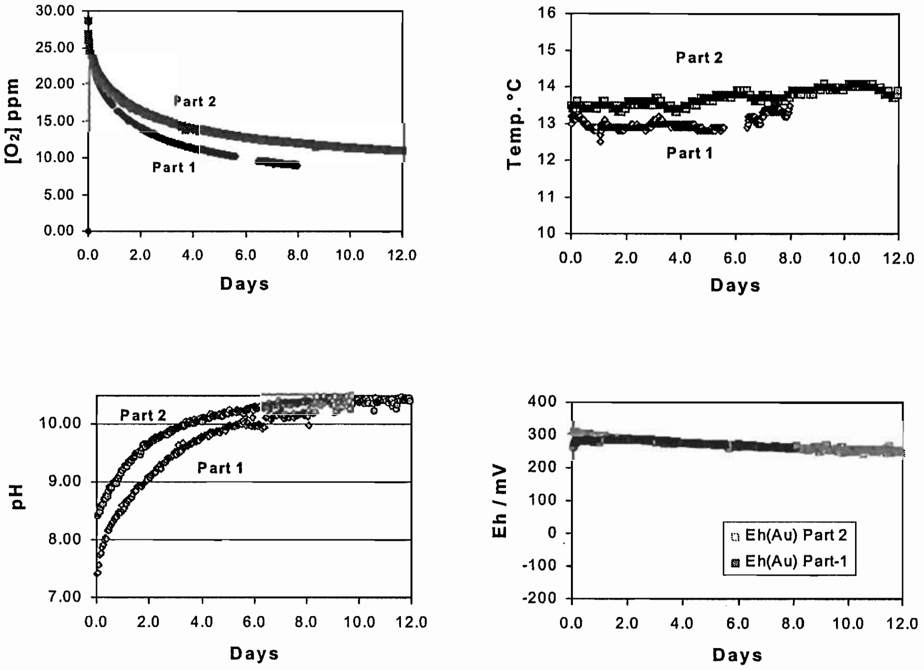


Figure 25. Results from the O_2-pulse started on 11 May 1999.

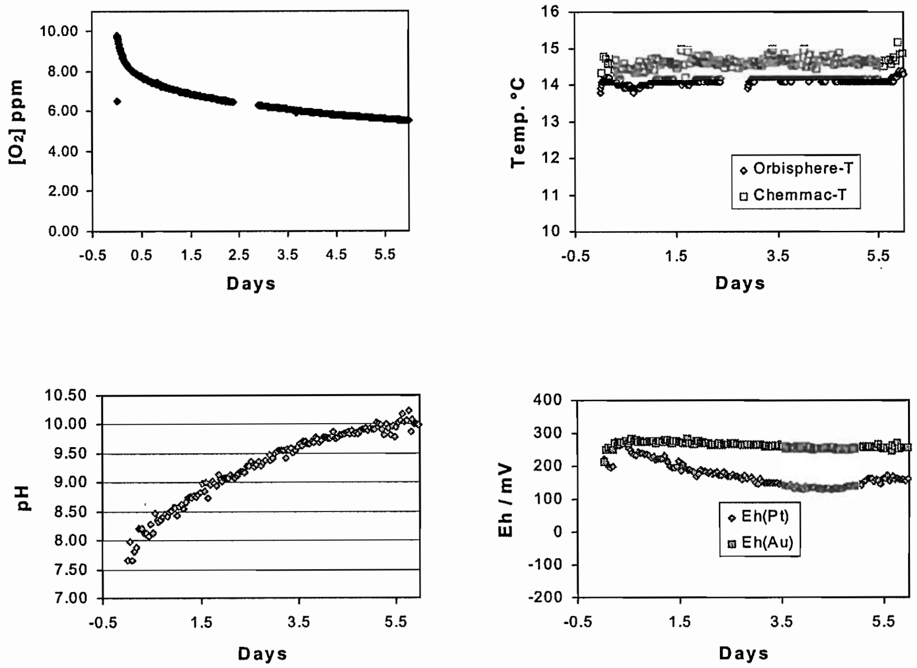


Figure 26. Results from the O_2-pulse started on 1 June 1999, with microbial inhibitors.

3.3.2 Groundwater Chemical and Microbiological Monitoring

Groundwater samples were collected to determine what chemical and microbial changes took place during the O_2-pulse experiments. Results and conclusions from the microbial analyses are reported elsewhere (Kotelnikova and Pedersen, 2000).

The samples from the KA2862A borehole were analysed to check that the chemical and microbial properties of the borehole showed no trends with time. This groundwater was used as the starting fluid in the reaction loop of the REX set-up. The chemical analyses for KA2862A are given in the Appendix. The general trend seems to be a slight increase in the concentration of most components as a function of time.

The data for samples from KA2861A are reported in the Appendix. The first two samples (980204 and 980313) were taken to characterise the groundwaters penetrating the borehole from its own fractures. Chemically these groundwaters are similar to those from KA2862A, as could be expected from the short distance separating these two boreholes ($\leq$1 m). All other samples from KA2861A were taken from the reaction loop of the REX experiment.

The KA2861A sample dated 990707 was taken after a calibration of the pH/Eh electrodes and before an O_2-pulse. However, because the O_2-sensor was inadvertently malfunctioning, there is no information on the oxygen contents at the time of sampling. The sample dated 980722 was taken between two O_2-pulses, *cf.* Table 1, but the O_2-sensor was still malfunctioning. The sample dated 981029 was taken before the O_2-pulse No. 1.

All other samples from KA2861A were taken from the test loop after an O_2-pulse. A comparison between the analysis of KA2862A groundwaters reveals the following chemical changes taking place during the O_2-pulses:

- Alkalinity increases from ≈7 mg/ℓ to >15 mg/ℓ.
- pH increases from ≈7.8 to ≈10.
- Fe and Mn disappear.
- DOC (dissolved organic carbon) increases from ≲3 mg/ℓ to ≳5 mg/ℓ.
- Cr and Ni levels are low.

It must be pointed out that the KA2861A groundwaters are relatively unbuffered with respect to pH, because of their low alkalinity. Therefore, any reaction taking place in the experiments is quickly reflected in the change of alkalinity and pH.

Microbiological characterisation and quantitative tests of microbial oxygen respiration were performed during the *in situ* REX experiment. The groundwater was sampled and analysed 12 times during the experiment, and was compared with the anaerobic groundwater sampled simultaneously from the inner section of neighbouring borehole KA2862A. A detailed description of the results is given in (Kotelnikova and Pedersen, 2000), and they may be summarised as follows.

- Anaerobic and microaerophilic organisms comprised a high fraction of the unattached KA2862A microbial population
- Total counts of free-living microbes increased from $(1\pm3)\times10^5$ up to $\approx8\times10^5$ cells ml^{-1} with the oxidation of the KA2862A groundwater in the REX chamber.
- Oxygenation induced a succession of the microbial population from anaerobic to microaerophilic and aerobic. Methanogens, microaerophilic heterotrophic, sulphate-and iron-reducing bacteria were replaced with methanotrophs, H_2-oxidising and aerobic heterotrophic bacteria after the oxygen pulses in the REX field experiment.
- Aerobic organisms comprised a high fraction of the unattached REX chamber population. Methanotrophs, hydrogen-oxidising and heterotrophic organisms constituted up to 12%, 52% and 75% of total microbial count in the REX groundwater, respectively.
- O_2 uptake rate *in situ* exceeded the rates measured *in vitro* batch experiments by 2 orders of magnitude. The batch experiments registered the oxygen reduction only by free-living cells.
- The presence of biofilms on the surface of the PEEK tubes, drill core and gold cap were established. The number of attached and unattached cells inside the REX chamber, in the PEEK tubing, on the granite core,

and on the gold cap surfaces was ≈7×10^{10} cells. The viable numbers of attached cells exceeded the numbers of unattached cells. Viable counts in biofilms on the PEEK tubes constituted 91% of the whole microbial population. The drill core and the gold cap biofilms contained 8% while the groundwater microorganisms constituted only 1% of the total microflora.
- The microbial inhibitors used in the last O_2 pulse reduced partly the oxygen consumption in the REX chamber (Table 1, Figure 26). Culturing results showed that the microbial activity was not inhibited completely. Inhibition of viable microbial cells was ≈50% in the REX groundwater and ≈90% on PEEK tubes. The numbers of Fe-reducing organisms increased as a result of the inhibition both in the groundwater and on tubes.
- Model calculations and the results of the inhibiting experiment suggest that attached and unattached organisms could be responsible for the O_2 uptake observed under *in situ* conditions.

3.3.3 Modelling the Kinetics of O_2 Uptake

In order to inter-compare the results from the different O_2-pulses were interpreted as first order kinetics. The equation is:

$$[O_2] = [O_2]_0 \, e^{-k_1 t}$$

where $[O_2]$ is the dissolved oxygen concentration, $[O_2]_0$ is the initial concentration of O_2, k_1 is the first order rate constant, and t is the elapsed time. The results of this data treatment are shown in Figure 27 for all O_2-pulses.

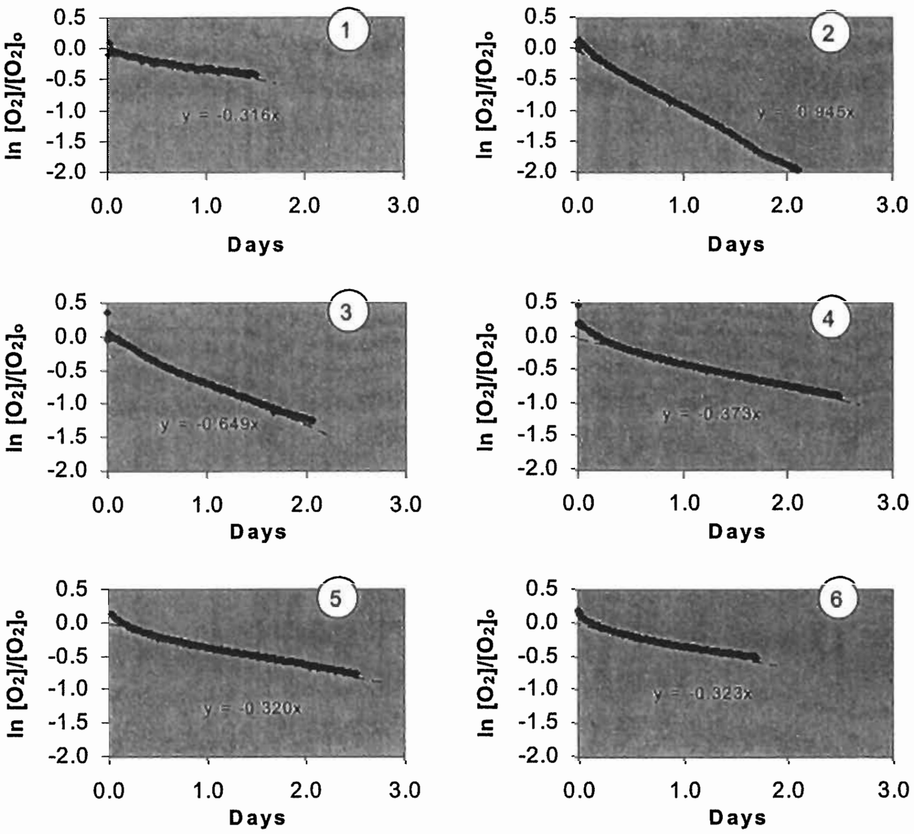


Figure 27. First order kinetic diagrams for the different O_2-pulses listed in Table 1.

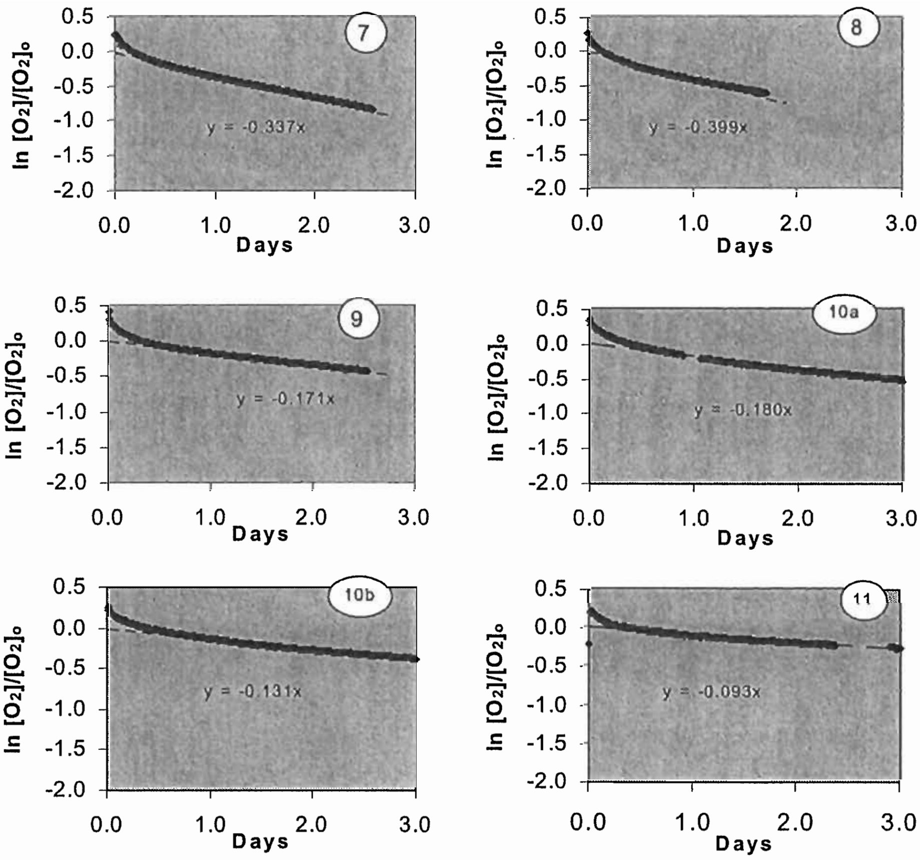


Figure 27. (Continued).

The resulting first order rate constants are summarised in the following table:

Pulse	Start	End	$[O_2]_o$ mg/ℓ	k_1 (day^{-1})
1	1998-09-10	1998-09-15	1.3	−0.316
2	1998-10-29	1998-11-02	1.0	−0.945
3	1998-11-24	1998-11-30	0.9	−0.649
4	1998-12-09	1998-12-18	4.0	−0.373
5	1999-01-15	1999-01-28	3.8	−0.320
6	1999-01-29	1999-02-06	4.6	−0.323
7	1999-02-18	1999-03-01	6.0	−0.337
8	1999-03-02	1999-03-11	6.0	−0.399
9	1999-03-12	1999-03-15	0.8	−0.171
10a	1999-05-11	1999-05-19	20	−0.180
10b	1999-05-19	1999-05-31	21	−0.131
11	1999-06-01	1999-06-08	8	−0.093
0	1999-04-12	1999-04-20	4	−0.119

Excepting the first O_2-pulse, there is a general tendency of decreasing values for k_1 as function of time. This may reflect a change in microbial population, or an gradual change in the reactivity of the fracture surface. Furthermore, it may be seen that although the rate of O_2 uptake in the microbially inhibited experiment was the lowest, the rate was not negligible.

It may be seen in Figure 27 that there is an initial period of faster O_2 uptake. This may be described by a combination of first order kinetics and a Monod term (enzymatic catalysis). However, because of the experimental limitations of the field experiment due to atmospheric O_2 leakage, a further refinement of the mathematical model would be excessive.

3.3.4 Possible Mechanisms for O_2 Uptake

A mechanism for the observed uptake of O_2 must take into account the observed variations in groundwater chemistry for the field and replica experiments:
- the pH in the field experiment increases with O_2 uptake, while in the replica experiment pH decreases,
- alkalinity in the field experiment increases,
- dissolved organic carbon and total microbial population increase,
- an important part of the O_2 uptake is due to microbial processes.

Both inorganic and microbial processes may be responsible for the observed uptake of O_2. These reactions are listed below.

3.3.4.1 Inorganic Processes

The following inorganic reactions may be invoked to reduce dissolved O_2:
- The oxidation of Fe(II), Mn(II) and sulphide are acidity producing processes:

$$\begin{aligned} Fe^{2+} + \tfrac{1}{4}\,O_2 + 2.5\,H_2O &\rightarrow Fe(OH)_3(s) + 2\,H^+ \\ Mn^{2+} + \tfrac{1}{2}\,O_2 + H_2O &\rightarrow MnO_2(s) + 2\,H^+ \\ HS^- + 2\,O_2 &\rightarrow SO_4^{2-} + H^+ \end{aligned}$$

- Corrosion:
  - Under reducing conditions, most metals react with water. For example, for iron the following two reactions take place:

$$\begin{aligned} Fe(cr) + 2\,H^+ &\rightarrow Fe^{2+} + H_2(aq) \\ Fe(cr) + {}^4\!/_3\,H_2O &\rightarrow {}^1\!/_3\,Fe_3O_4(cr) + {}^4\!/_3\,H_2(g) \end{aligned}$$

    The first reaction results in an increase of pH.
  - However, in the excess of O_2 the acidity is unchanged:

$$Fe(cr) + \tfrac{3}{4}\,O_2 + 1.5\,H_2O \rightarrow Fe(OH)_3$$

- One of the pathways for uptake of O_2 by reducing minerals proposed by (White and Yee, 1985) was the direct reaction at the mineral surface according to the following reaction

$$[Fe^{II}, {}^1\!/_Z\,M^{+Z}]_{silicate} + H^+ + \tfrac{1}{4}O_2 \rightarrow [Fe^{III}]_{silicate} + {}^1\!/_Z M^{+Z} + \tfrac{1}{2}H_2O$$

  where M is a cation of charge +Z. This is also a process that would increase the pH.

3.3.4.2 Carbon Balance

Both the inorganic and organic carbon content of the groundwater in the REX chamber increased during the O_2 pulses. Thus the initial inorganic and organic carbon content are 115 μM (alkalinity 7 mg/ℓ) and (17 to 290) μM (DOC = 0.2 to 3.5 mg/ℓ), giving a total initial carbon content in the range 130 to 400 μM.

At the end of an O_2 pulse the final inorganic and organic carbon content are 280 to 640 μM (alkalinity 17 to 39 mg/ℓ) and (416 to 3250) μM (DOC = 5 to 11 mg/ℓ), giving a total initial carbon content in the range 700 to 3900 μM.

The most plausible explanation for this increase is leaching, or bacterial degradation, of plastic materials such as electrode components, o-rings, and PEEK tubing.

3.3.4.3 Microbial Processes

Several processes may be catalysed by micro-organisms. The oxidation of organic matter, either by O_2, sulphate, or Fe(III) are candidate reactions:

- Sulphate reduction by organic matter

$$SO_4^{2-} + CH_3COOH \rightarrow HS^- + 2\,HCO_3^- + H^+$$

- Oxidation of organic matter would decrease the pH:

$$CH_3COOH + 2\,O_2 \rightarrow 2\,HCO_3^- + 2\,H^+$$

- However, oxidation of organic matter by iron-reducing bacteria should increases the pH:

$$CH_3COOH + 8\,Fe(OH)_3 + 14\,H^+ \rightarrow 2\,HCO_3^- + 20\,H_2O + 8\,Fe^{2+}$$

These reaction stoichiometries are however misleading oversimplifications. When bacteria oxidise compounds, they generally obtain energy and need cell constituents for growth (Rittmann and Vanbriesen, 1996). Implicit in the microbial activities related to access of energy and cell constituents there is a process of biosynthesis and growth. The overall stoichiometry must therefore include two parallel processes:

- biomass formation
- respiration

It may be shown that in some cases biomass formation consumes CO_2, and therefore it increases the pH. This will be exemplified using some assumptions:

- The stoichiometry of biomass is assumed to be $C_5H_7O_2$. Nitrogen is neglected here because analytical data on dissolved nitrogen species (other than N_2) is in general not available for groundwaters at Äspö.
- The fraction of electrons available in the organic carbon used for biosynthesis is taken as ≈40%. The rest of the electrons are used for respiration.

Two examples for organic matter with different reducing capacities are chosen: acetate and methane.

Respiration (the reaction producing the energy needed by microbes) is here exemplified by the oxidation of acetate, methane, and biomass:

$$\begin{aligned} CH_3COOH + 2\,O_2 &\rightarrow 2\,HCO_3^- + 2\,H^+ \\ CH_4 + 2\,O_2 &\rightarrow HCO_3^- + H^+ + H_2O \\ C_5H_7O_2 + 5.75\,O_2 + 1.5\,H_2O &\rightarrow 5\,HCO_3^- + 5\,H^+ \end{aligned}$$

Biomass synthesis for our two examples is given as:

$$\begin{aligned} 2.875\,CH_3COOH &\rightarrow C_5H_7O_2 + 1.5\,H_2O + 0.75\,H_2CO_3 \\ 2.875\,CH_4 + 2.125\,H_2CO_3 &\rightarrow C_5H_7O_2 + 4.375\,H_2O \end{aligned}$$

The combination of both processes: If for example ≈40% of the electrons provided by the organic matter are used for biomass synthesis, the overall reactions become:

$$CH_3COOH + 0.3118\,O_2 \rightarrow$$
$$0.2936\,C_5H_7O_2 + 0.4404\,H_2O + 0.532\,HCO_3^- + 0.532\,H^+$$
$$CH_4 + 0.3118\,O_2 + 0.468\,HCO_3^- + 0.468\,H^+ \rightarrow$$
$$0.2936\,C_5H_7O_2 + 1.4404\,H_2O$$

The main characteristics for these reactions are:

- Twice as much organic carbon is needed to build up biomass for acetate as compared with methane. This is due to the fact that acetate it is a less reduced form of organic matter.
- With methane as the substrate a reduction in alkalinity (and an increase in pH) are expected. The reverse (a pH decrease) is expected if the substrate is more oxidised (e.g. acetate).

3.3.4.4 Available Amounts of Reductants

The amount of O_2 initially added in an experiment pulse was in the range $(16 - 810) \times 10^{-6}$ M (*i.e.*, 1 to 26 mg/ℓ). This reacted with equivalent quantities of one or more reductants (electron donors). The available amounts of possible electron donors for the different processes might shed some light on the possible reaction mechanisms.

Reductant	Groundwater concentration		O_2 uptake capacity
	mg/ℓ	μM	μM
Fe(II)	0.02 to 0.13	0.4 to 2	0.1 to 0.5
Mn(II)	0.2 to 0.4	4 to 7	2 to 3.5
H_2		0.01 to 1	0.005 to 0.5
CH_4		0.09 to 1	0.2 to 2
DOC	0.2 to 3.5	17 to 290	2 to 580
		Total:	4.3 to 580

Other reductants are available in unknown amounts: Fe(II) silicates, corroding metal parts, leaching (or degrading) plastic components.

3.3.4.5 O_2 Uptake Mechanisms: Summary

While it is clear that microbial processes were dominant in the REX field experiment (Kotelnikova and Pedersen, 2000), a combination with inorganic processes can not be excluded.

Two inorganic processes may be invoked to raise the pH of the groundwater as a response to O_2 injection: corrosion and Fe(II)-silicate oxidation. However, while these processes would explain an increase in pH, they would fail to explain an increase in alkalinity and organic carbon in the field experiments.

Corrosion has been a subject of concern within the project. Simple mass balance shows that $>3.7\times10^{-3}$ mol O_2 were added to the REX chamber in the course of the experiment (excluding possible leakage of atmospheric oxygen into the test loop). If all this oxygen had been used in corrosion, 0.2 g of Fe should have been dissolved (or comparable quantities of Cr or Ni). This would amount to ≈ 100 mm^3 of steel. No evidence was found to indicate such an extended corrosion after dismantling of the equipment. Nevertheless, a small contribution from corrosion processes can not be excluded.

Several microbial processes may explain an increase in alkalinity (CO_2 production) and dissolved organic carbon. Although most processes would decrease the pH of the solution, some would increase the pH values. As shown in the previous Section, the nature of the organic matter (the electron donor), the oxidant (electron acceptor), and the proportion of biomass synthesised will be important factors determining the pH behaviour of the process.

4 DISMANTLING OF THE REX FIELD EXPERIMENT

The KA2861A drillcore was extracted from the borehole on 11 August 1999. As described in Section 2.3.3, the drillcore had detached from the rock, and therefore it could be extracted when the packer and steel cap were withdrawn from the borehole. Samples of PEEK tubing and fracture surface were taken for microbial analysis. These results are reported elsewhere {Kotelnikova, 2000 #3469}. A photograph of the surface is shown in Figure 28.

Figure 28. Photograph of the fracture surface of KA2861A after termination of the REX field experiment.

Because anoxic conditions could not be reached in the REX field experiment, due to leakage of atmospheric O_2, stainless steel parts were well protected against corrosion by a layer of chromium oxide. This however does not exclude the risk for pitting and crevice corrosion. Both the flow-though cell, containing the pH and E_H electrodes, and the drillcore cap, were gold-plated. Upon dismantling of the field equipment no evidence for corrosion was observed on the flow-though cell. A small pit was however observed in the inner surface of the drillcore cap.

4.1 DESCRIPTION OF THE KA2861A DRILLCORE: THE REX FRACTURE SURFACE

After the REX field experiment the drillcore was examined in respect of possible recent (and old) precipitates.

The host rock to the fracture consists of altered and tectonised Äspö diorite. A mylonite perpendicular to the fracture surface is visible as a 5-10 mm wide epidote rich vein. Thin, partly sealed chlorite-calcite+epidote and fluorite coated fractures are also displayed in the host rock.

The altered Äspö diorite is red stained and the magnetite partly hematised. Breakdown of biotite and plagioclase has resulted in formation of chlorite, epidote and albite. Based on earlier studies on Äspö (cf Banwart et al., 1995 and Puigdomenech et al., 1999) the chlorite has a relatively high portion of Fe(II) (50-80% of total Fe), which means that, despite the oxidation in combination with the hydrothermal alteration, the reducing capacity of the host rock in terms of available Fe(II) is still considerable.

The fracture surface exposed to oxygenated water in the REX in situ experiment, has a very thin and non-continuous fracture coating consisting of spots of calcite, a thin layer of chlorite, only visible in some parts. Minor pyrite crystals were observed in the fracture coating. Where coating exists it is less than 100 μm thick and some of the pyrite grains are even smaller (a few microns only). The stable isotope ratios of the calcite coating indicate a possible low temperature origin (−7.9 ‰ ^{13}C and −9.7 ‰ ^{18}O). The present ground water in the fracture has ^{18}O values around −12.5 to −13.0 ‰. At ambient temperatures (12-15°C) the calcite coating is not equilibria with the present groundwater. The relatively high δ^{13}C values do not show any indication of in situ biogenic activity.

There is no visible changes (alteration or precipitation) related to recent oxidation in the REX experiment. No Fe(III) precipitates or alteration of the micro-grains of pyrite can be seen. Small portions of loose material were found in the golden REX cap. This material was sampled and examined in stereomicroscope. It seems to be debris from the drilling or loose material transported with the groundwater in the fracture. It contained fine grained quartz, feldspar and mica. No indications of recent oxidation were found in the loose material.

Samples of the fracture surface were prepared (gold-plated) for SEM examination, which showed that:

- The calcite patches contains well-crystallised calcite partly with later small micro precipitates on top (Figure 29). These late precipitates have probably formed prior to the experiment but a partly recent formation can not be excluded. Dissolution textures of the calcite was not observed.
- Pyrite grains in different sizes have been observed spanning from 100 µm down to less than 1 µm (Figure 30). There were no indications of dissolution or oxidation of the pyrite.
- Flakes of chlorite and Fe-containing clay minerals are present on the surface.
- As the fracture coating is non-continuous, the water is in contact with the altered wall rock minerals: albite, epidote, chlorite, quartz, K-feldspar, fluorite and micrograins of hematite.

Thin sections perpendicular to the fracture surface were prepared for quantitative analyses of the chlorite and clay minerals, but the coating was found to be too thin to be used for any analyses.

Connected porosity measurement (water absorption) was carried out on a 4 centimetre thick slice of the wall rock from the fracture surface. The porosity is 0.47 volume-% and the density 2744 kg/m^3 (measurements performed by the Swedish National Testing and Research Institute.

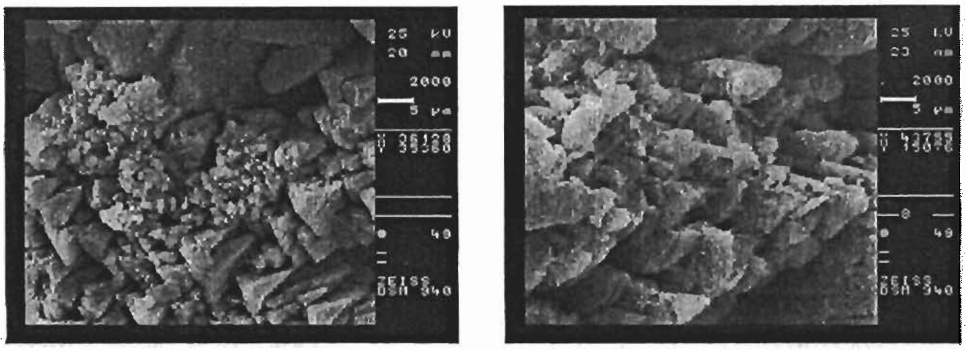


Figure 29. Calcite precipitates on the fracture surface of KA2861A after termination of the REX field experiment (SEM photographs).

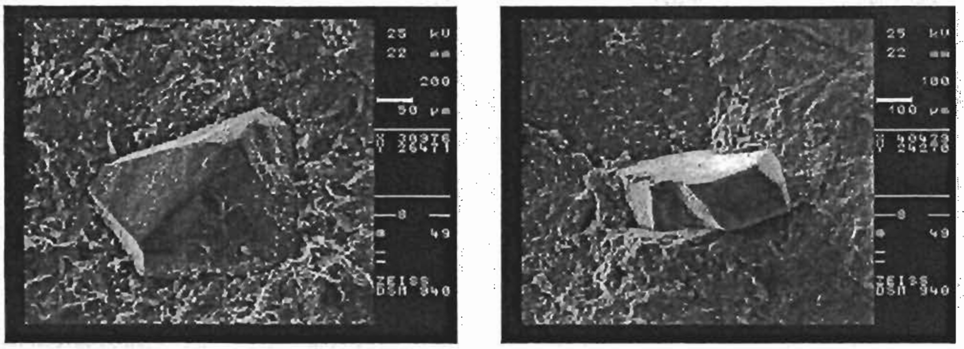


Figure 30. Pyrite grains on the fracture surface of KA2861A after termination of the REX field experiment (SEM photographs).

5 DISCUSSION AND CONCLUSIONS

5.1 LIMITATIONS OF THE FIELD EXPERIMENT

Several difficulties were encountered in the field experiment:

- Possible corrosion of stainless-steel parts and leaching (or degradation) of plastic components.
- The hydraulic confinement was not adequate. The experience was useful in the way that better technical solutions are being applied in other experiments. However, full hydraulic confinement can not be expected because the drill core contains micro-fractures that allow the diffusion of reactants and tracers.
- Leakage of atmospheric oxygen. This problem should be further investigated before other redox sensitive experiments are undertaken.
- The location of the experiment: wet and generally unclean conditions in the Äspö tunnel promoted the failure of electrical equipment, that was intended otherwise to work continuously for long periods of time. The remoteness of the site increased the time at which problems like power cuts could be addressed.

These processes introduced extra uncertainties on the conclusions that could be extracted from the data.

5.2 CONCLUSIONS FROM THE FIELD EXPERIMENT

The results obtained in the REX field experiment, lead to the following conclusions for performance assessment of nuclear waste repositories in granitic rock:

- O_2 uptake takes place in periods of one to two weeks under the present experimental conditions.

- The time scales for O_2 uptake observed are in the same order of magnitude as those found in the Replica experiment (Trotignon et al., 1999).
- Microbial processes consuming O_2 are a substantial part of the observed uptake rate. However, the overall stoichiometry of the process is unknown.
- The mechanism for O_2 uptake in the field experiment and in the replica experiment must be different, because of the contradictory pH-variation during the O_2-pulse experiments. Two main differences exist between the field and replica experiments that may contribute to these differences: the materials for the reaction chamber (plastic versus gold-plated stainless steel), and the gaseous contents of the groundwater.

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APPENDIX

Table A.1. Chemical composition of groundwaters sampled in boreholes of the REX niche.

Borehole:	KA2858A[a]			
Section (m):	39.8-40.8		*39.8-40.8*	*39.8-40.8*
Date (yymmdd):	950310	*960412*	*970917*	*970917*
Sampling flow rate (ℓ/min):	0.14			
Charge imbalance %	2.7	*2.5*	*0.2*	*2.1*
Temp. field (°C)			*14.1*	*14.2*
Conductivity (mS/m):	2650		*2440*	*2920*
Eh field (mV)			*+210*[b]	*+247*[b]
pH field			*8.04*	*8.25*
pH lab.	7.8	*7.26*	*6.74*	*7.16*
Main Components (mg/ℓ):				
Li^+	2.17	*3.02*	*2.36*	*2.96*
Na^+	2630	*2900*	*2680*	*2920*
K^+	9.7	*11.5*	*11.0*	*12.2*
NH_4^+				
Mg^{2+}	49.7	*46.7*	*49.7*	*50.1*
Ca^{2+}	3360	*4270*	*3670*	*4350*
Sr^{2+}	47.5	*68.4*	*56.1*	*79.9*
Ba^{2+}		*0.088*	*0.072*	*0.088*
Fe-tot (ICP-AES)	0.088	*0.06*	*0.07*	*0.07*
(spectr.)	0.090			
Fe(II)	0.090	*0.07*	*0.13*	*0.14*
Mn	0.39	*0.324*	*0.354*	*0.369*
Al		*2.12*	*0.29*	*0.25*
HCO_3^- (alkalinity)	9	*< 20*	*16*	*12*
F^-		*1.43*	*1.32*	*1.29*
Cl^-	10300	*12300*	*10309*	*12405*
SO_4^{2-}	577	*684*	*612*	*664*
S reduced (µg/ℓ)			*13.5*	*< 3*
Br^-	70.1	*88.4*	*77.4*	*94.3*
HPO_4^{2-}		*0.12*	*0.09*	*0.12*
Si	5.5	*4.61*	*4.00*	*3.81*
B		*1.12*	*1.19*	*1.10*
DOC	1.3	*< 1.0*	*<1.0*	*1.03*
D (‰ dev. from SMOW)	–96.6		1	
^{18}O (‰ dev. from SMOW)	–13.1			

a: Values in *italics* are for groundwaters sampled and analysed by the British Geological Survey (West et al., 1998), and financed by JNC.

b: See also the Eh measurement performed in the field on the KA2862A borehole with date 990625, later in this Table.

Table A.1. Chemical composition of groundwaters (continued).

Borehole:	KA2861A				
Section (m):	8.7–9.8	0–8.5	8.7–9.8	8.7–9.8	8.7–9.8
Date (yymmdd):	980204	980313	980707	980722	981029
Sampling flow rate (ℓ/min):	≈0.001	≈0.001			
Charge imbalance %	1.6	4.3			
Conductivity (mS/m):	3050	3220	3250	2860	3330
pH	7.19	7.00	7.80	7.80	7.70
Main Components (mg/ℓ):					
Li^+	3.14	2.78	4.08	4.04	3.40
Na^+	3260	3190	3530	3540	3500
K^+	26.3	12.2	15.2	14.8	13.7
NH_4^+		0.04			
Mg^{2+}	43.2	49.7	29.7	30.7	33.4
Ca^{2+}	4970	4460	5580	5520	5440
Sr^{2+}	69.4	66.6	88.9	85.3	72.2
Fe-tot (ICP-AES)	0.540	0.081	0.015		0.127
(spectr.)					0.129
Fe(II)					0.136
Mn	0.43	0.38	0.51	0.42	0.54
HCO_3^- (alkalinity)	29	15	18	16	7
F^-			10.1	8.9	7.9
Cl^-	13086	13600	15400	15600	15700
SO_4^{2-}	566	638	715	692	692
Br^-	92.5	108	126	136	126
Si	4.3	3.9	3.4	4.1	4.1
PO_4^{3-}	0.71				
DOC	2.9				
D (‰ dev. from SMOW)					
^{18}O (‰ dev. from SMOW)					

Table A.1. Chemical composition of groundwaters (continued).

Borehole:	KA2861A[a]				
Section (m):	8.7–9.8	*8.7–9.8*	*8.7–9.8*	8.7–9.8	8.7–9.8
Date (yymmdd):	990218	*990507*	*990519*	990519	990531
Sampling flow rate (ℓ/min):					
Conductivity (mS/m):	3170			3340	
pH	9.77			10.10	
Main Components (mg/ℓ):					
Li^+	3.60				
Na^+	3640	*3260*			3780
K^+	12.5	*15.4*			15.3
NH_4^+					
Mg^{2+}	33.2	*31.1*			22.6
Ca^{2+}	5590	*5535*			5890
Sr^{2+}	72.3	*94.9*			107
Fe-tot (ICP-AES)		*0.016*			0.009
(spectr.)					
Fe(II)					
Mn		*0.003*			0.0008
Al		*0.048*			0.013
Cr		*0.032*	*<0.45*		0.011
Ni		*0.034*	*0.35*		0.002
HCO_3^- (alkalinity)	17		*13*	39	
F^-					
Cl^-	1600	*15932*			
SO_4^{2-}	710	*685*			773
Br^-					
Si	3.4	*2.9*			2.1
PO_4^{3-}					
DOC	11.0		*5*		
D (‰ dev. from SMOW)					
^{18}O (‰ dev. from SMOW)					

a: Values in *italics* are used for groundwater analyses by the CEA at Cadarache.

Table A.1. Chemical composition of groundwaters (continued).

Borehole:	KA2862A[a]					
Section (m):	0–16	15–16		7.4–16	6.8–6.9	7.4–16
Date (yymmdd):	950127	950310	960412	961210	980312	980312
Sampling flow rate (ℓ/min):	0.58	0.58			0.01	0.4
Charge imbalance %	1.1	1.9			3.9	3.7
Conductivity (mS/m):	3150	3150			3923	3870
pH	7.56	7.60	*6.99*	6.45	7.70	7.66
Main Components (mg/ℓ):						
Li^+	3.24	3.12	*3.92*		3.73	3.82
Na^+	3230	3160	*3270*	3281	3490	3510
K^+	13.6	13.6	*15.3*	16.4	12.0	13.5
NH_4^+			*0.30*		0.02	0.03
Mg^{2+}	41.4	46.5	*32.7*	38.3	35.6	37.6
Ca^{2+}	4720	4600	*4130*	5571	5340	5250
Sr^{2+}	80.5	64.9	*65.4*	92.1	86.7	87.4
Ba^{2+}			*0.098*			
Fe-tot (ICP-AES)	0.119	0.146	*0.08*	0.148	0.044	0.107
(spectr.)	0.132	0.130			0.037	0.118
Fe(II)	0.124	0.120	*0.09*			0.114
Mn	0.38	0.39	*0.270*		0.24	0.34
Al			*2.54*	0.005		
HCO_3^- (alkalinity)	8	8	*< 20*		8	7
F^-			*1.27*			
Cl^-	13300	13200	*14400*	13940	15600	15400
SO_4^{2-}	666	667	*755*	550	766	764
Br^-	102	95	*112*		140	133
HPO_4^{2-}			*0.15*			
Si	6.6	5.2	*4.21*	3.66	4.5	4.4
B			*0.99*			
DOC	0.7	3.1	*< 1*		3.5	0.5
D (‰ dev. from SMOW)	−90.8	−91.3				−89
^{18}O (‰ dev. from SMOW)	−12.7	−12.5				−12.5

a: Values in *italics* are for groundwaters sampled and analysed by the British Geological Survey (West et al., 1998), and financed by JNC. The sample with date 961210 was analysed within the *Replica* experiment at the CEA in Cadarache (Puigdomenech et al., 1999).

Table A.1. Chemical composition of groundwaters (continued).

Borehole:	KA2862A					
Section (m):	7.4–16	7.4–16	7.4–16	7.4–16	7.4–16	7.4–16
Date (yymmdd):	980512	980707	980722	990412	990519	990531
Sampling flow rate (ℓ/min):		2.8	1.34	1.8		
Temp. field (°C)						14.0^b
Conductivity (mS/m):		3320	3360	3080	3350	
Eh field (mV)						−395^b
pH field						7.77^b
pH lab.	7.65	7.70	7.70	7.80	7.80	
Main Components (mg/ℓ):						
Li^+		4.10	3.96	3.59		
Na^+	3800	3540	3610	3690		3840
K^+	18.13	15.1	13.1	12.0		15.6
NH_4^+				0.03		
Mg^{2+}	36.0	29	31.2	32.3		31.7
Ca^{2+}	5040	5500	5670	5530		6000
Sr^{2+}	95	88.2	85.1	73.8		108.0
Ba^{2+}						
Fe-tot (ICP-AES)		0.121	0.152			0.074
(spectr.)		0.126		0.124		
Fe(II)	0.015	0.121		0.117		
Mn	0.22	0.34	0.34	0.31		0.29
Al	0.035					
HCO_3^- (alkalinity)		2	2	7	7	
F^-		16.4	3.6			
Cl^-	15440	15400	15700	15900		
SO_4^{2-}	850	716	716	704		
Br^-		123	142			
HPO_4^{2-}						
Si	3.99	4.6	4.6	3.8		4.7
B						
DOC	1.47	0.2	0.3	1.0		
D (‰ dev. from SMOW)		−87.6	−94.1	−88.1		
^{18}O (‰ dev. from SMOW)		−12.4	−12.2	−12.3		

a: The sample with date 980512 was analysed within the *Replica* experiment at the CEA in Cadarache.

b: Eh was measured with the flow-through cell of the REX field experiment during the period 990625 to 990628.

Table A.1. Chemical composition of groundwaters (continued).

Borehole:	KA2865A	
Section (m):	17.5–20	25.3–27.7
Date (yymmdd):	990420	990427
Sampling flow rate (ℓ/min):	6.2	
Conductivity (mS/m):	3180	1590
pH lab.	7.2	7.5
Main Components (mg/ℓ):		
Li^+		1
Na^+	3800	1990
K^+		11.4
Mg^{2+}		67.1
Ca^{2+}		1858
Sr^{2+}		23.2
HCO_3^- (alkalinity)	13	123
Cl^-	14970	6570
SO_4^{2-}		205
Br^-		22
Si		4.4
D (‰ dev. from SMOW)	−88.8	−77.3
^{18}O (‰ dev. from SMOW)	−12.1	−10.1

Table A.2. Trace metal compositions for groundwaters from boreholes in the REX site.

Borehole:	KA2861A	KA2862A	KA2862A
Section (m):	0–8.52	6.8–6.9	7.4–16
Date (yymmdd):	980313	980312	980312
pH	7.00	7.70	7.66
Main Components: see Table A.1.			
Trace Metals (µg/ℓ):			
U	0.27	0.025	0.017
Th	0.002	0.002	0.002
Rb	59.3	66.2	66.7
Y	0.646	0.786	0.841
Cs	4.12	4.99	5.27
Ba	101	107	118
Cr	1.53	2.2	1.2
Ni	24.4	7.7	0.13
La	0.14	1.02	1.27
Ce	0.073	0.349	0.740
Pr	0.020	0.038	0.071
Nd	0.090	0.155	0.287
Sm	0.013	0.014	0.020
Eu	0.006	0.009	0.006
Gd	0.010	0.025	0.047
Tb	0.009	0.011	0.015
Dy	0.026	0.032	0.029
Ho	0.020	0.024	0.028
Er	0.008	0.008	0.007
Yb		0.006	0.006