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6.4 GEOCHEMICAL FACTORS INFLUENCING VAULT DESIGN AND LAYOUT

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ABSTRACT

The design and construction of a vault for used nuclear fuel in crystalline rock may be influenced by a number of geochemical factors. During the siting stage, information is needed regarding the rock type, heterogeneities in its composition and the mineralogy of permeable zones because these will cause variations in thermal conductivity, strength and radionuclide sorptive properties of the rock. These factors may affect decisions regarding depth of vault construction, tunnel dimensions and spacing of panels and waste containers. The decision on whether groundwaters are allowed to flow freely into a planned excavation may depend on measurements of their chemical compositions, microbiological contents and presence of hazardous or corrosive constituents (e.g., hydrogen, methane, radon, chloride salts, trace metals). During site characterization, borehole drilling from the surface and subsequent hydraulic testing will introduce both chemical and microbiological contaminants that may further influence this decision.

During vault construction, the geochemistry of the rock may cause changes to the characterization, design and construction of the vault. For example, high salinity fluids in micropores in the rock could prevent the use of radar surveys to detect fractures in the surrounding rock. High rock salinity may also cause unacceptably high total dissolved solids loadings in water discharged from the facility. Again, the presence of toxic, corrosive or radioactive constituents in inflowing groundwater may require grouting or, if inflow is needed for service operations, development of treatment facilities both above and below ground. In addition, the use of explosives will cause high organic and nitrate loadings in service water as well as the possible impregnation of these chemicals in the damaged wall-rock surrounding an excavation. These chemicals may remain despite cleaning efforts and act as nutrients to promote microbial activity in the post-closure phase.

In the operational phase, further design and construction changes may need to be considered if groundwater composition is found to change with time. For instance, inflow of increasingly saline groundwater may affect predicted container corrosion rates and buffer and grout stabilities following vault resaturation and increase in temperature. This, in turn, may affect designs for container materials and spacing. Microbial growths and slime development on vault walls and at groundwater inflow points may extend into the rock mass and may require skimming of wall-rock before closure.

Following closure of the vault, monitoring of groundwater compositions and radionuclide contents will likely be needed in any permeable fracture zones surrounding a vault. This may require the development of remote sensing and telemetry equipment for installation in and around the vault and should be incorporated in vault design plans.

1. INTRODUCTION

Several industrialized nations that operate nuclear power reactors are now considering disposing of their nuclear fuel wastes or reprocessed fuel wastes in deep underground vaults in suitable geologic formations. Many factors will influence the location, design and construction of such a vault. In previous publications and meetings on factors affecting vault design, there has been only limited consideration of the possible impact of geochemistry. In this paper, potentially important geochemical variables are presented and discussed. These are set in the context of the different phases of developing a disposal system, i.e., site characterization and siting, vault excavation, facility operation and waste emplacement, and closure and monitoring. For the purposes of this paper, the term 'geochemical' is used in its broadest sense and includes aspects such as rock geochemistry, groundwater composition, microbiology, rock-water-vault materials interactions and anthropogenic influences (i.e., those caused by drilling, testing, excavating, etc.).

The regulator of nuclear fuel wastes in Canada, the Atomic Energy Control Board, has specified an overall risk criterion for assessing the long-term performance of a geological disposal system. Consequently, there is a need to set design requirements in an iterative manner by evaluating their impact on the overall performance of the system. Some design specifications can be set separately for other purposes such as operational factors. In the Canadian program, for example, a minimum lifetime of 500 a for the waste containers was set primarily to ensure isolation during the operational phase of the disposal vault. It would also allow for retrieval.

In order to meet the regulatory risk criteria to licence a nuclear fuel waste disposal system in Canada, it will be necessary to do an overall performance assessment of the disposal system. This will include the use of geochemical data relating to the expected rate of release and mobility of radionuclides from a vault, corrosion of containers, long-term retention of radionuclides in the vault and retardation of their migration in the geosphere. Geochemical factors have major impacts on these aspects. In the Canadian program, these are not usually separated out; however, in this [6~er, their importance is highlighted. Examples are drawn largely from experiences in operating the Underground Research Laboratory (URL) near Lac du Bonnet, southeastern Manitoba.

2. SITE CHARACTERIZATION FACTORS

The detailed characterization of a site preferred for vault location would be preceded by geoscience studies and performance assessments of a large candidate siting area to identify the preferred vault location. These studies would include examination of archived data from national sources, surface and airborne surveys, and shallow and deep bedrock drilling at grid areas distributed across the candidate siting area. All of these activities would include a geochemical component. For example, the drilling of exploratory boreholes will involve collecting information that influences vault design and construction. Drilling will provide information on rock and groundwater compositions, which will help to delineate favourable areas for the vault and zones to avoid, and it will introduce contaminants into the deep environment that could eventually influence vault performance.

2.1 Rock Geochemical Properties

The geochemistry of the rock mass surrounding a disposal vault has an impact on a number of design factors. Heterogeneities in rock composition (e.g., layering of different rock types and variations in composition in and adjacent to fracture zones) result in a variable distribution of minerals and cause variations in physical properties such as rock strength. These factors may affect vault design by influencing the depth chosen for vault construction, tunnel shape and dimensions, and the spacing of tunnels and waste containers. Variations in the mineral content of the rock influence:

- thermal conductivity, especially by variations in quartz content,

- groundwater composition, especially the total dissolved solids and the redox buffering capacity,

- sorptive properties and the degree of retardation of radionuclide migration, and

- physical and chemical properties of the rock mass that govern the advective and diffusive properties of regions of rock between the waste emplacement areas of the vault and any major fracture zones or significant hydrogeologic features. Examples of important properties are the permeability and porosity for advective transport, the diffusive porosity and tortuosity, and the sorptive capacity for radionuclides.

An example of the variability in mineral content of fracture zones is shown in Fig. 1 for three depth layers in the granitic Lac du Bonnet batholith. The differences in mineral content directly influence rates of migration and retardation of radionuclides and so were used in setting the sorption coefficients for the geosphere transport model in the Canadian performance assessment program.

2.2 Groundwater Chemistry

Variations in the composition of groundwater with depth and across a site may have implications for the design and construction of a vault. Numerous reports (Fritz and Frape 1982, Gascoyne et al. 1987, Nordstrom et al. 1990, Bottomley et al. 1990) have shown that groundwaters in crystalline Shield rocks typically become more saline at depth and vary in salinity depending on location in the hydrogeological flow path. This variation is indicated in Fig. 2 for groundwaters of the Canadian Shield, and is shown in detail in Fig. 3 for the URL lease area on the granitic Lac du Bonnet batholith in southeastern Manitoba. A generalized evolution is shown from a dilute, slightly alkaline Ca-HCO_3 groundwater in shallow environments (or at depth in recharge areas), to a saline, near-neutral Na-Ca-Cl-SO_4 groundwater below about 400 m (or at shallower depths in discharge areas). Between 500 and 1000 m depth, groundwaters in permeable fractures have salinities ranging from 5 to 50 g/L. The likelihood of encountering saline groundwaters at this depth interval clearly needs to be considered in the design and operation of a vault because a decision must be made whether or not to allow these groundwaters to inflow freely into the facility. Complications due to such inflow likely would include corrosion of equipment and machinery, and a need to treat the water before discharge to the surface.

Part of the site characterization program will determine if potential geochemical hazards exist at the site. These include the presence of toxic or flammable gases (e.g., Rn, H_2S, H_2, CH_4) and the presence of certain dissolved species that have toxic or corrosive properties (e.g., As, U, Ra, F and Fe- and S- related bacteria). Some of these gases and dissolved species have been described in Canadian Shield groundwaters by Fritz et al. 1987 (CH_4, C_2H_6), Betcher et al. 1988 (U), Gascoyne and Barber 1992 (Rn, U), and Stroes-Gascoyne et al. 1994 (bacteria). It is important to monitor for these potential hazards as part of the site characterization phase so that any implications for vault design (e.g., additional venting and water treatment facilities) can be considered and incorporated at an early stage.

Drilling of exploratory boreholes during site characterization invariably causes changes to the composition of groundwater in permeable fractures by introducing contaminants. Although unlikely to impact directly on vault design, this may cause complications to subsequent excavation, testing or operational stages. For instance, the use of a surface-derived water during core drilling will cause contamination of groundwaters by introduction of oxygen, organics, micro-organisms and dissolved species not found in the existing groundwaters (see also section 2.3). These potential contaminants and their sources and effects are summarized in Table 1. To minimize these effects, in the early stages of site characterization or when developing drilling plans for vault design purpose, it may be necessary to reduce the number of boreholes drilled or to take special precautions during drilling. One such precaution might be to use low-O_2 groundwater obtained from a nearby borehole that is not hydrogeologically connected to the features of the site under investigation. Alternatively the use of drilling techniques which reduce the amount of drill water introduced into permeable zones might be considered (Almén and Zellman 1991).

2.3 Microbiology

The science of subsurface microbiology has undergone rapid development in the past 15 a (Stroes-Gascoyne and West, 1994) and the new information resulting from this increased effort has led to the realization that the occurrence of microbes in deep granitic groundwaters may have implications for the design and construction of a vault. Microorganisms require water, space, nutrients and a source of energy for growth. Microbiological characterization of an environment should be evaluated on the basis of these requirements.

TABLE 1

THE CONTAMINATING EFFECTS OF BOREHOLE DRILLING ON GROUNDWATER COMPOSITION

CONTAMINANT	SOURCE	EFFECT*
O_2	drillwater	high dissolved O_2 high Eh
natural organics	drillwater (surface-derived)	high DOC
drillwater	surface water bodies	changes δ^2H, $\delta^{18}O$ introduces ^3H, ^{85}Kr, fluorocarbons, etc.
man-made organics	oil and grease surfactants, fuels	high DOC high VOC
rock flour	bedrock	increased colloids, SiO_2; reduced permeability
trace metals	steel drill rods drill bits	high Fe^{2+}, presence of Co, Cr, Mn
micro-organisms	surface drillwaters	high bacterial counts, growth of biofilms, reduced permeability, odour (H_2S, etc).

* DOC = dissolved organic carbon
VOC = volatile organic carbon

Microbial characterization of a rock environment attempts to determine:
1) natural levels of nutrients and energy sources for microbial growth;
2) population size, physiology and species distribution of indigenous microorganisms in the groundwater of the rock and 3) how the indigenous groups of bacteria present are influencing the geochemistry of the groundwaters.

For instance, deep groundwaters from crystalline rocks in Sweden are anoxic with a pH above 7 and a low redox potential, implying that bacterial metabolism here must depend on fermentation or anaerobic respiration (Pedersen, 1993). Electron acceptors available in these groundwaters for respiration are SO_4 (for SO_4-reducing bacteria) and CO_2 (for methanogenic bacteria). Groundwaters at the URL also are reducing with a pH above 8 and contain SO_4 ions and dissolved CO_2, but concentrations of H_2 (needed by methanogenic bacteria) and CH_4 are generally below detection limits. This indicates that methanogenic bacteria are probably not prolific in URL groundwaters. Oxidized chemical species such as Fe^{3+}, Mn^{4+} and U^{6+} can also be used as electron acceptors instead of O_2 by many bacteria in anaerobic systems. The composition of the rock and fracture fillings should be evaluated for electron donors and acceptors such as pyrite in the rock and ferric iron in fracture fillings that may be important in microbial processes. Organic C levels are generally low in groundwaters in granitic rocks, so this will limit the growth of those bacteria that need organic matter as a nutrient and energy source.

In URL groundwaters, microbial populations of 10^3 to 10^5 cells/mL have been found, and the presence of SO_4-reducing (SRB), Fe-related and slime-forming bacteria has been confirmed (Brown and Hamon 1994, Stroes-Gascoyne et al. 1994). The presence of SRB in the generally SO_4-rich groundwaters at the URL shows that there is a potential for significant SO_4-reducing activity in rock fractures, although the SRB populations found in the URL groundwaters are generally small and a good correlation between SRB and HS^- concentration has not been observed (Stroes-Gascoyne et al., 1994). However, HS^- was present in measurable quantities in a number of URL groundwater samples which suggests some SRB activity. The production of sulphides by SRB may have implications for metal corrosion (e.g., stainless steel, Cu). In fact, mackinawite was found on stainless steel parts of a packer system removed from a borehole at the URL which is a direct indication of SRB-influenced corrosion (McNeil and Little, 1990; Stroes-Gascoyne et al., 1994).

Pseudomonas and related species (aerobes that can grow anaerobically in the presence of NO_3 as electron acceptor) were found to be dominant in several URL groundwater samples, indicating the possibility of significant denitrifying activity in groundwaters from this environment (Jain et al., 1995). Other tests showed that the bacteria in the groundwater sample from the URL exhibited imbalanced growth due to lack of a necessary nutrient or nutrients in the environment (i.e., starvation stress) (Jain et al., 1995). This is an important observation because any disturbance through drilling or excavation may introduce nutrients, and bacterial growth may become more prolific if more nutrients are being supplied.

The effect of drilling on the naturally-present microbial population should be evaluated at an early stage of site characterization. In fact, this population may be instantly affected by the drilling activities, and it may be very difficult to assess properly the natural microbiology of the site and hence its potential implications. In order to minimize the effects of drilling or at least to estimate the effects of contamination, it is desirable to drill with an appropriate water source. It is not feasible to demand that drill water should be sterile. Good alternatives are groundwater taken from a nearby but not hydrogeologically connected borehole, or a nutrient-poor drill water (e.g., potable water) that has been tagged with a tracer (e.g., latex microspheres) so that the extent of contamination can be evaluated.

Once the microbial characterization has been performed, the suitability of the site can be evaluated with respect to microbial effects. Site characterization will include assessment of several potential geochemical hazards that may have a microbiological component in their origin. These include the occurrence of H_2S and CH_4 (section 2.2) and large amounts of pyrite in the host rock, which may cause problems such as acid mine drainage (section 3.3). In addition to characterizing existing conditions, it is important to consider whether or how the development of a vault could intensify undesirable microbiological effects. For example some reducing groundwaters have high Fe concentrations. Upon drilling, O_2 is introduced into such a system, In the presence of certain bacterial species, large amounts of Fe precipitates can form, resulting in reduced permeability and fouling of the borehole. This has been observed in several surface boreholes at the URL, even though dissolved Fe concentrations are generally quite low.

3. EXCAVATION FACTORS

Following the selection of a preferred site for the disposal vault, the excavation of shafts and levels will begin at locations and depths identified by the earlier site characterization work. The excavation provides more geochemical information to aid in exactly locating the levels and orientation of a vault but also causes a greater impact on the environment, which may need to be considered in the design process.

3.1 Rock Properties

During the excavation for a disposal facility, the more global aspects of geochemical factors need to be considered. The large surface areas of rock exposed by excavation of the shaft(s), headings, and large rooms and in-floor boreholes permit detailed mapping of variations in the geology and geochemical composition. It is at this stage that inhomogeneities, possibly missed in the borehole investigations, become evident. In the URL, the presence of clusters of xenoliths and large-scale foliation features were observed in the unaltered granite at depth. The full extent of the geochemical nature of these spatial differences could impact on rock mechanical properties and hence vault design and construction. Another influence is the general composition of the rock mass. If it contains a high proportion of hard minerals such as quartz, this will significantly increase excavation costs and the rate of progress.

Other rock geochemical factors such as toxicity and radiation hazards may influence vault design and construction during the excavation stage. For instance, the presence of sulphide minerals at weight-percent concentrations in the host rock or fracture infillings may require special procedures to prevent formation of H_2S or SO_2 gases, or sulphuric acid, when exposed to moisture or micro-organisms. Similarly, high concentrations of radon and related γ radiation may emanate from fresh rock faces and pulverized rock piles if the host rock contains significant amounts of natural U and Th. Regular monitoring at the URL has not indicated any problems in these areas, probably because sulphide- and U/Th-mineral contents are low in rocks of the Lac du Bonnet batholith and mineralization of fractures is limited. Significant sulphide concentrations are only found in xenoliths of country rock that had been included in the granite during the early magma emplacement.

A recently recognized property of deep plutonic rocks of the Canadian Shield is that they may contain considerable quantities of soluble salts which can be released from the rock by fracturing, microcracking and pulverising during blasting and excavation operations. The salts, typically of a Na-Ca-Cl composition, are usually derived from residual magmatic or deuteric fluids and were incorporated as separate phases during cooling and crystallization of the rock. Alternatively, they may have permeated the rock at a later stage due to saline groundwater penetration from sediments or seas which previously overlay the rocks (Gascoyne et al. 1989a).

The presence of salts in the rock matrix will profoundly affect the ability of radar-penetration surveys to detect fractures in the rock surrounding an excavated vault. This is because high salinity reduces the resistivity of the rock which, in turn, attenuates the radar energy and reduces reflections from fracture surfaces. The presence of saline fluids in the rock matrix will, therefore, limit the distance around a vault that intact rock may be confidently predicted.

Several studies at the URL have identified and quantified these salts and demonstrated their ability to migrate through the rock matrix. These studies include the measured depletion of leachable Cl in crushed samples of core from a transect of a permeable fracture zone (Gascoyne et al. 1989b), the rapid, linear increase in salinity of initially-pure waters placed in boreholes in unfractured, pristine granite (Fig. 4) and, recently, direct collection of pore fluids draining from open boreholes in unfractured granite (Gascoyne, unpub. results). This work shows that saline fluids can be readily leached from the rock during excavation.

Leaching of saline pore fluids accounts for the water quality observations made at the URL over the period 1984-1993 for water discharged from the holding pond (Fig. 5). This water inflows continuously to the URL through natural fractures in the shaft and ventilation raises and is stored in the holding pond for use as a service water (for rock-face washing, drilling, etc.) and for fire prevention. The holding pond is discharged approximately weekly and is monitored and sampled for a number of parameters including electrical conductivity. Excavation of the grey granite, which contains more soluble salts than the upper, pink granite, caused a pronounced increase in conductivity (Fig. 5), suggesting leaching of these salts by service water used in the excavation process. Corresponding high chloride concentrations in the pond water supported this interpretation.

Although not essential during the excavation of the grey granite at the URL, maintaining dissolved salt contents to within imposed limits may be required during the construction of a nuclear waste disposal vault. Various design changes (e.g., minimize pulverising activity, construct water treatment facilities, optimize groundwater inflow rate) may be required, therefore, to meet these standards.

There are several other implications of the presence of soluble salts in rocks at a repository site and these are considered further in the relevant sections below.

3.2 Fluid Compositions

Several types of 'fluids' are used and encountered during the excavation stage and their compositions and impacts are considered in this section.

Groundwater inflows into the vault from fractures in the rock need to be monitored throughout the excavation stage to determine if they contain hazardous constituents such as radon, methane, hydrogen, hydrogen sulphide, etc. The presence of these gases in significant quantities may require special venting of the inflow area or separate aeration of the water with provisions for gas removal. Similarly, the presence of high levels of dissolved ionic species such as uranium and radium may require the construction of in situ treatment facilities to remove the ions at source, before mixing with other inflows. An example of the need for this type of facility in the excavation and operation of the URL is given in section 4.1. If the concentrations of hazardous constituents are found to be significant, or if they change unpredictably with time during vault excavation, it may be necessary to grout and seal-off the inflows. This requirement may need to be considered if natural groundwater inflows are to provide the main source of water for operations in the vault.

Inflow of saline groundwaters to the vault, if permitted, is likely to have significant effects on pipes, equipment and machinery in the vicinity of the inflow (due to corrosion, salt-encrusting, etc). If this water is collected and used as a service supply, these effects will be exacerbated because they will occur throughout the vault. Experience at the URL has shown that corrosion of carbon-steel ducting and storage tanks is a problem underground even when dilute waters are used in supply lines. Frequent replacement of pipes or the use of stainless steel or plastic materials must be included in vault design, especially if they are likely to carry saline waters.

As mentioned in section 3.1, construction of water treatment facilities may be needed before or during the excavation stage so that discharges to the surface from the vault meet environmental limits imposed by provincial or federal authorities. Table 2 lists the maximum acceptable concentrations in Canadian drinking water for a number of dissolved species (Guidelines, 1989), and a comparison is made with target concentrations for holding pond discharges for the URL. Experience has shown that these criteria may be exceeded during the excavation stage when soluble salts are leached from crushed rock (section 3.1) and when blasting residues are dissolved by service water (see below). Increased monitoring of holding pond water may be required during construction, with provisions for treatment, if necessary.

There are several anthropogenic effects of vault excavation which must also be considered during the period of vault design because they may lead to a change in excavation procedure or the use of specific materials. For instance, blasting using conventional explosives causes emission of large amounts of nitrogen oxides (from decomposition of ammonium nitrate) and significant levels of organics (from other explosives). These compounds are largely removed as off-gases but some become dissolved in the service water used to wash down rock faces, etc. after blasting. In the latter case, NO_3 concentrations, especially, will increase in the service water and may exceed limits for discharge to the surface (Table 2). The amount of residual explosives-NO_3 that becomes incorporated into service water is difficult to quantify but some indication is given by the results of monitoring URL holding pond concentrations during a three-month period of excavation of a level in the URL (Fig. 6) in 1993/94. Nitrate concentrations exceeded discharge limits (45 mg/L) for several months during this period but, in the first three months of monitoring were kept at lower levels than normal because of additional inflow of low-NO_3 groundwater from an underlying fracture zone for much of this time. Nevertheless, of the 3.8 Mg of ammonium nitrate explosive used, 160 kg of NO_3 were discharged to the surface from the holding pond, for a total excavated tunnel length of 120 m. This represents 1.3 kg nitrate discharged per metre length of excavation, a figure that may be useful in meeting environmental criteria in the future.

A second anthropogenic effect of vault excavation is the influence of conventional grout on the composition of groundwaters in permeable zones intersected by drilling and blasting activities and on service waters used for washing down concrete walkways, residues, etc. Conventional grout is highly alkaline (pH >12) and can contribute significant amounts of dissolved ions (e.g., hydroxyl, sulphate, potassium, calcium) to contacting groundwater before it sets. Hydrochemical monitoring of boreholes adjacent to a freshly grouted portion of a fracture zone in the URL during May 1987 showed that an increment of 1-3 pH units occurred in groundwaters adjacent to the grouting (Fig. 7). New grouts are being developed as part of AECL's sealing program and these cause a much lower initial pH shift and have no long-term hydrochemical effects (M. Onofrei, pers. comm.).

Other anthropogenic effects include the introduction of oil and grease, fuel, and organic residues into the floor materials and micro-cracked wall rock. These are unlikely to require changes in design and construction.

TABLE 2

STANDARDS FOR WATER QUALITY IN CANADIAN DRINKING WATER AND URL HOLDING POND DISCHARGES

Element	Maximum* Acceptable Concentration (mg/L)	URL Objective (mg/L)
Arsenic	0.05	0.05
Ammonia (NH_3)	--	0.2
Cadmium	0.005	0.01
Chloride	250	150
Cobalt	--	0.05
Copper	1	0.06
Iron	0.3	0.3
Lead	0.1	0.007
Mercury	0.001	0.0006
Nickel	--	0.06
Nitrate (NO_3)	45	45
Oil & grease	--	None visible
pH	6.5 - 8.5	6.5 - 9
Radium-226	1 Bq/L	1 Bq/L
Sulphate	500	250
Uranium	0.1	0.1
Total Dissolved Solids	500	500
Zinc	5	0.2

* Source: Canadian Drinking Water Quality Guidelines

3.3 Microbiology

During the excavation stage of a vault a number of microbial effects may occur. As mentioned in section 3.1, the presence of sulphide minerals at weight-percent concentrations in the excavated and crushed host rock or fracture infillings may require special procedures to prevent a problem commonly known as acid mine drainage. Bacterial oxidation of pyrite is of great significance in the development of acidic conditions in mines and mine drainages. The oxidation of pyrite is a combination of spontaneous and bacterially catalyzed reactions. When pyrite is first exposed, as in a mining operation or vault excavation, a slow spontaneous reaction with molecular oxygen occurs (Brock and Madigan, 1991):

$$FeS_2 + 3\ 1/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4{}^{2-} + 2H^+ \quad .$$

This reaction leads to the development of acidic conditions under which Fe^{2+} is relatively stable in the presence of oxygen. However, *Thiobacillus ferrooxidans* catalyzes the oxidation of ferrous to ferric ions. The ferric ions formed under these acidic conditions can readily react spontaneously with more pyrite:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4{}^{2-} + 16H^+ \quad .$$

Because O_2 is present in the aerated drainage, bacteria will continue to oxidize ferrous to form ferric precipitates. The low-pH waters (often less than pH 3) generated as a result of this process may attack other minerals in the rock and cause release of toxic or undesirable elements (an example is Al, which is only soluble at low pH).

Groundwater may flow into excavated tunnels and rooms from permeable fractures. If this water is of neutral pH, Fe-rich and anaerobic, the sudden transition to aerobic conditions will result in oxidation of Fe^{2+} to Fe^{3+} and subsequent precipitation of insoluble hydroxides. In addition to the chemical process, organisms such as *Gallionella* and *Leptothrix* contribute to the oxidation of Fe^{2+} at this redox front. For example, during the excavation of the access tunnel to the underground Aspö laboratory in Sweden, massive growth of *Gallionella* on the wet tunnel walls was observed (K. Pedersen, pers. comm.). *Gallionella* growth has not been observed in the URL, presumably because of the very low dissolved Fe levels in the URL groundwaters.

Only a small amount of energy is available from Fe-oxidation for bacteria, and they must therefore oxidize large quantities of iron in order to grow. *Gallionella* is a true autotrophic organism, which uses CO_2 as a C source to produce cell material and iron oxidation as an energy source. Thus the presence of optimal conditions for this organism may result in massive Fe precipitates and production of organic material, both of which may be undesirable.

During the earlier stages of excavation of the URL, some walls were covered with algae, and mosses were found growing in moist places on the gravel floor (Fig. 8). Algae and mosses produce organic matter from CO_2 and H_2O

using light as energy source, which is provided at the URL on a 24 hr basis from electric lights. Increased ventilation and installation of concrete floors subsequently dried out and covered these areas at the URL, and growth is no longer observed here.

The introduction of bacterial nutrients such as nitrates and organics from explosives during the excavation stage was discussed in section 3.2. These nutrients are largely removed as dissolved species in the service water used to wash rock faces, etc., and they are pumped to a surface holding pond. However, some of these nutrients may remain in the damaged rock zone behind the rock walls. In the presence of water, these nutrients may induce bacterial growth in the form of biofilms during operation of a vault. Biofilm formation is further discussed in section 4.2.

4. OPERATION FACTORS

The period of operation of a nuclear waste vault is likely to be at least 50 years. During this time, the main geochemical effects that might influence vault design and construction are changes in groundwater inflow composition, microbiological growth, and interaction of vault materials with groundwater. These effects are described below.

4.1 Water Chemistry

Long-term changes in the composition of groundwater inflows to a vault might occur as a result of the gradual dissolution and removal of a mineral phase in the flow path that controls the concentration of certain ions, or as a result of inflow of increasing amounts of dilute (or saline) water from shallower (or deeper) permeable zones in the area of the vault. These changes may not be easy to predict, even with a prior knowledge of the rock mineralogy and hydrogeological flow paths.

For example, although the hydrogeological influence of excavation of the URL shaft in 1985 was found to have stabilized within a few months after the completion of excavation and the major ion composition of inflowing groundwaters to the shaft has remained stable since then, concentrations of U in the inflows dramatically increased in 1992, some 7 years after shaft excavation was completed. The increase was attributed to gradual lowering of the U 'redox' front in the granite around the URL shaft location (Fig. 9). Prior to excavation of the URL shaft, the uranium redox front had existed as a boundary of about 100 to 200 m below the surface in this area (Fig. 9a). Dissolved U moving downwards in solution in naturally recharging groundwaters would precipitate or sorb onto other solids as it crossed the redox front, resulting in lower U concentrations in groundwater at depth than near the surface. The excavation of the URL shaft altered the local hydrological conditions, however. Drawdown of the water table, coupled with the higher flow rates through fractures, caused the U redox front to move slowly downwards as surfaces or minerals that could sorb or precipitate U were gradually consumed. After about 7 years the front intersected inflow locations in the URL shaft (Fig. 9b), causing rapid increases in U concentration in inflow and, consequently, in holding pond water. To meet environmental discharge regulations (Table 2) a filter unit that was specific for U (the EXPURRT filter, Gascoyne 1986) was installed at a suitable location in the URL and has helped to lower U concentrations in discharged waters to acceptable levels again.

A localized depression in a redox front and an accompanying increase in U concentration in inflowing groundwaters is probably a common feature of many large excavations at depth, such as mines, but the phenomenon is undetected because U concentration generally is not measured in inflows. In the design of a nuclear waste vault, considerations should be given to limiting groundwater inflow or constructing treatment facilities close to the point of groundwater entry if it is anticipated that the excavation and operation of the vault will alter the geochemistry in inflowing groundwaters in undesirable ways. Additional installations or design changes may be required if there are long-term changes in major ion concentrations or other trace elements, and these would need to be addressed on a case-by-case basis.

4.2 Microbiology

During the operational phase of a vault, microbes may form biofilms and may grow on wet walls and in stagnant pools of water. The interaction of microbes with vault materials may result in microbially influenced corrosion of metal structures and degradation of concrete and wood structures.

At the URL, biofilms have been observed only in a few (wet) places, such as in the ventilation raise, at the base of a free-draining borehole and on the side of a large borehole (Brown and Hamon 1994). Such biofilms, if allowed to grow, can produce anaerobic layers that are unsightly and cause unpleasant odours if disturbed. If they grow on a wet floor, they are a slipping hazard. They are unlikely to be a problem in dry conditions, as witnessed by their sparse occurrence at the URL. At a wet site, permeable fractures may need to be grouted to control water inflow and so reduce the potential for biofilm formation. Boreholes in the floors of rooms may collect water and produce odour, which can be controlled by either plugging or draining the hole or adding hydrogen peroxide or household bleach to the water. In a wet environment under anaerobic conditions corrosion of iron takes place by the following reaction:

$$4Fe^0 + 8H^+ \rightarrow 4Fe^{2+} + 4H_2 \quad .$$

Usually, the H_2 film protects the iron from further corrosion, but in the presence of SO_4 and SO_4-reducing bacteria (SRB), Fe is oxidized, even in the absence of O_2 (Schlegel, 1972), as follows:

$$4Fe^0 + SO_4{}^{2-} + 4H_2O \rightarrow FeS + 3Fe(OH)_2 + 2OH^-$$

The presence of SRB's and SO_4 in waters draining into a vault may indicate that corrosion of Fe structures can be expected even under anoxic conditions.

In a disposal vault, cements would be used in grouts and concretes for a variety of sealing applications. Biodegradation of concrete materials under aerobic conditions is a well-known process. Sulphate-producing bacteria (*Thiobacillus* sp.) are capable of oxidizing sulphur, sulphides and thiosulphates (S^0, S^{2-}, $S_2O_3{}^{2-}$) to sulphuric acid in a relatively short period under aerobic conditions. Nitrifying bacteria (*Nitrosomonas*, *Nitrobacter*) can transform ammonia into nitric acid under aerobic conditions. The inorganic acids that are produced attack the concrete by dissolving $Ca(OH)_2$ and CSH (calcium silicate hydrate) gel from cement. During the operational phase of a vault, aerobic degradation of concrete surfaces could occur, and precautions should be taken to prevent this (Stroes-Gascoyne and West, 1994).

Microbially-influenced degradation of concrete sewer lines has been observed in many countries. This process begins when SRB's in sewage produce H_2S, which escapes to the surrounding air and provides a substrate (a usable energy source) for sulphur oxidizers. In turn, the sulphur oxidizers produce sulphuric acid, which corrodes the cement matrix of the concrete. A similar process could occur in a vault, in a biofilm on a concrete surface. The groundwater may contain SO_4, and anaerobic conditions in the biofilm may support SRB growth and H_2S production which may then serve in another, aerobic location as an energy source for S-oxidizing bacteria resulting in acid production and attack of the concrete (Rogers et al., 1993). Preventive measures would be removal of biofilms, inducing a dry environment and ensuring SO_4-poor groundwaters.

Mine construction often involves the use of wood beams which need to be kept wet to prevent cracking. However, a moist environment may induce attack of the wood by fungi, as has been observed at the URL. Preventive measures, such as treatment with wood preservatives or cleaning with household bleach, may be necessary to prevent organic build-up.

4.3 Vault Materials

During the operational phase, groundwaters will begin to interact with emplaced vault materials in the completed, backfilled segments of the vault as the process of resaturation begins. For the most part, these groundwaters will likely be pore fluids migrating from the bedrock matrix and driven, initially, by the large hydraulic gradient existing between fluids in interconnected pores at depths of 500 - 1000 m, and an excavated, backfilled cavity (at ~1 atm. pressure). In addition, there will be chemical interaction between the fluids in the buffer and backfill that are introduced to achieve required moisture contents for compacting operations.

Because the pore fluids at vault depths in the Canadian Shield are likely to be quite saline (Ca-Na-Cl brines, Gascoyne et al. 1995) and the clay-based buffer fluids will be compositionally different and less saline (Na-SO_4, Oscarson and Dixon 1989), there will likely be complex interactions between these two types of fluids and buffer, backfill, container metals, grout and minerals in the host rock. For instance, the high SO_4 and Ca concentrations achieved on mixing the fluids may cause precipitation of gypsum. Silica is likely to become more soluble under the elevated temperatures of a vault. Because of its availability in buffer and backfill and its ease of release during clay mineral transformations, silica probably will dissolve near the waste containers and will precipitate further away. Influx of bedrock pore fluids during vault operation and then chemical diffusional gradients following reflooding may cause a gradual changes in clay mineral composition and, consequently, changes in swelling and radionuclide sorption capacities.

These types of transformations need to be considered during the early stages of vault design and construction in order to minimize adverse impacts on vault performance.

5. CLOSURE AND MONITORING

Following the operational stage of a vault, there will be a period when all access drifts and shafts are backfilled and sealed with a combination of clay, crushed rock and, in some areas, concrete. These materials will interact with resaturating fluids (section 4.3). To monitor these interactions as well as to allow for sampling of radionuclides, it will be necessary to be able to collect samples of groundwater from permeable fractures both upstream and downstream of the facility. This would require including monitoring boreholes in the vault design plans or, alternatively, using some form of non-intrusive monitoring. An example of remote monitoring might be a system based on geochemical sensors and a power source emplaced during the closure stage with radio-induction monitoring at the surface.

An important effect of the presence of salts in the rock matrix is that they will greatly influence the salinity of resaturating groundwater after vault closure and thereby affect container corrosion rates, clay stability, wasteform stability, radionuclide solubility and speciation and their sorption in the vault environment. In addition, high salinities may develop because the crushed rock is likely to be used as a component of backfill on closure of the vault and it might be necessary to select rock from areas of the excavation site with the lowest salt content to minimize the salinity effect.

During the resaturation process fluids entering the vault from the rock matrix may also carry with them salts that have accumulated in the excavation disturbed zone (surrounding all underground cavities) over the period of operation of the vault. These salts will have migrated towards the vault as pore fluids but will have crystallized out in the aerated, fractured wall-rock due to evaporation by the forced-air ventilation of the operating vault. A 'salt-halo' may therefore be formed around the vault openings (Fig. 10). The halo is expected to redissolve under resaturation conditions to produce extremely saline fluids in contact with vault materials soon after closure. This scenario is supported by rock leaching studies and pore-fluid sampling experiments that are currently underway at the URL. The extent and significance of the phenomenon is still being evaluated in AECL's research program, but its effect is being included in current geosphere and vault performance models and may impact on eventual vault design and construction.

6. CONCLUSIONS AND RECOMMENDATIONS

A number of geochemical properties and effects have been described in this paper which might affect the design and construction of a nuclear waste vault in crystalline rocks of the Canadian Shield. These include rock mineralogy and heterogeneities in composition, variations in groundwater salinity and content of micro-organisms and hazardous constituents, and influences of grout, explosives and organics introduced during the lifetime of the vault. Of particular significance are the influences that are believed to be of importance but that are not yet fully substantiated or readily quantified. These include microbiological activities in the sealed vault, significance and quantity of nutrients emplaced in the vault, pore fluid resaturation and salt-halo effects. If they cannot be quantified, or cannot be shown to be of negligible effect, they may need to be minimized by using special procedures before sealing the vault, such as screening buffer/backfill materials for microbes and nutrients, by minimizing the use of explosives or grout, and by skimming rock walls to remove salt accumulations. In addition, vault design plans may need to allow for construction of in situ or surface-based water treatment facilities to meet environmental regulations and the use of alternative water supplies service operations. Understanding the chemistry of groundwater inflows to a vault is particularly important because some of the inflows could introduce difficulties such as increased corrosion of piping and equipment and the need for pretreatment to remove hazardous constituents.

This paper has summarized, with examples, the geochemical factors that may influence every phase of activities associated with a nuclear waste vault. Geochemical factors need to be integrated with all other factors affecting vault design. To illustrate this, a number of examples have been cited where the geochemistry or a variation in a related factor has a major impact on disposal system design. Most of these emphasize the impact of the geosphere on the operation and post-closure performance of the engineered disposal vault. However, another area being addressed in the research for the Canadian Nuclear Fuel Waste Management Program is the long-term geochemical impact of the vault and its contents on the geosphere. For example, to what extent is the geosphere's ability to retard radionuclide migration modified by geochemical perturbations caused by the vault?

In the Canadian illustrative case study included in the Environmental Impact Statement being submitted in 1994 for technical and public review, the physical and chemical properties of the rock surrounding the vault have been found to be important in isolating the waste containers from a major permeable fracture zone. These properties, therefore, potentially have major impacts on the design and construction of the vault. Engineers and designers should be aware of the importance of geochemical input so that potential problems can be recognized and difficulties that arise throughout the lifetime of a vault can be resolved.

In preparing this report, it has become clear how pervasive geochemical factors are in the design and performance assessment of nuclear fuel waste disposal facilities. Geochemical factors need to be considered in all aspects of design, both in the direct operational sense and also through the integrated performance assessment feedback loop to design testing and optimization. However, not all geochemical factors have been reviewed or mentioned. This was an intentional choice, the focus being primarily on those shown to be important in the disposal concept developed by AECL for Canada's nuclear fuel wastes, namely disposal in an engineered vault at a depth of 500 m to 1000 m in rocks of the Canadian Shield. It is possible that for other concepts, sites and designs, additional geochemical factors could be more important.

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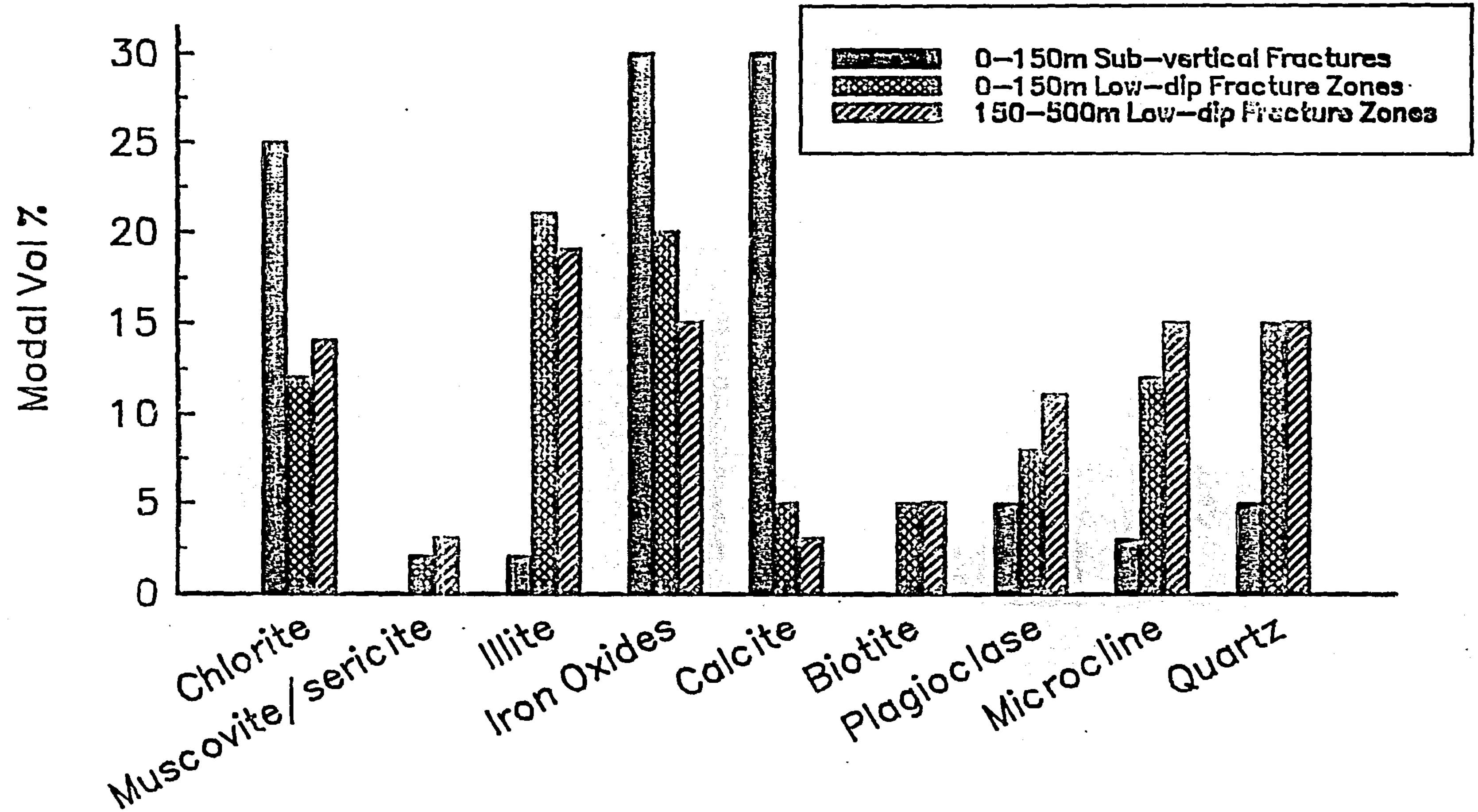

FIGURE 1: Alteration Mineralogy of Permeable Zones

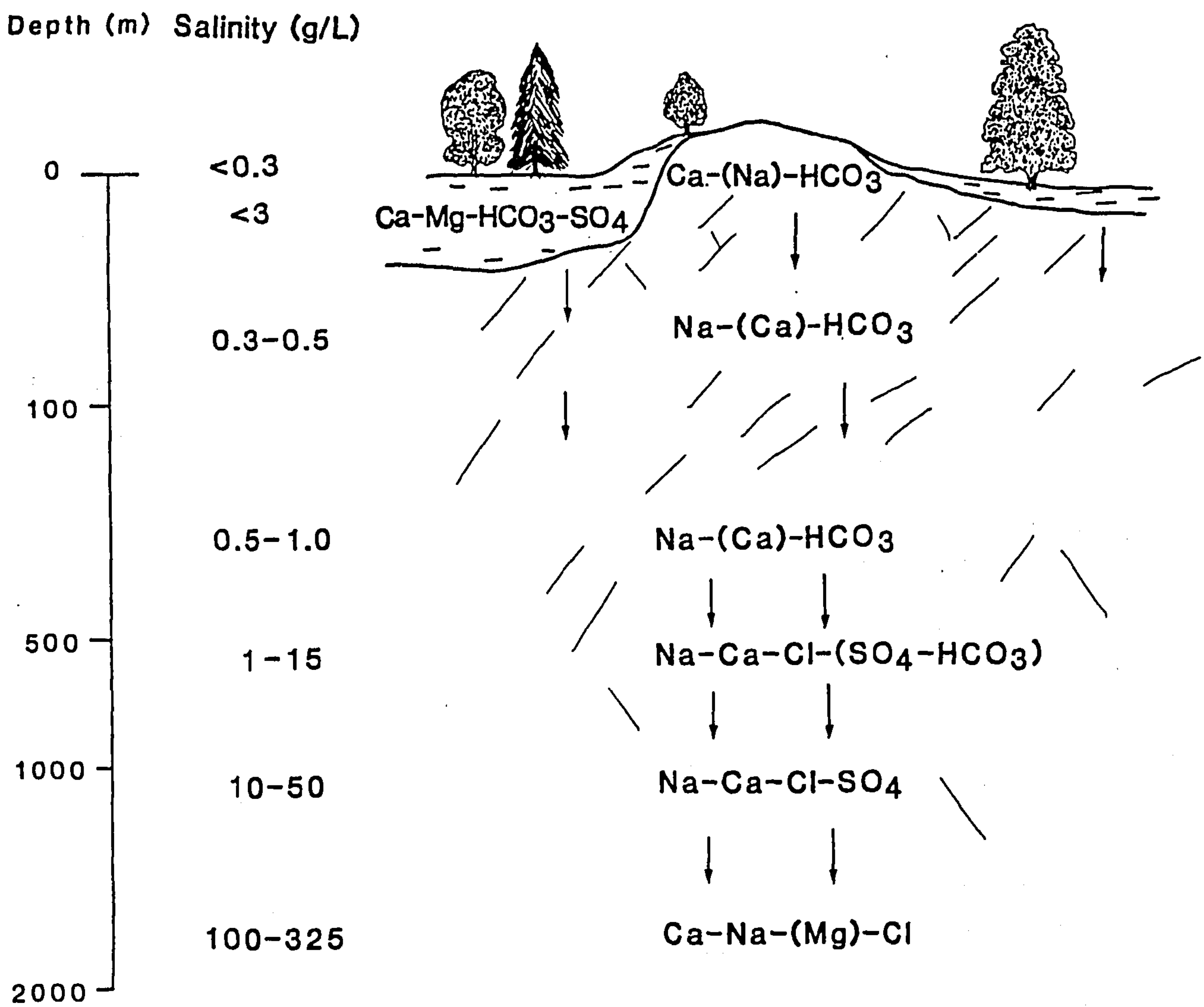

FIGURE 2: Generalized Evolution of Groundwater Chemistry with Depth

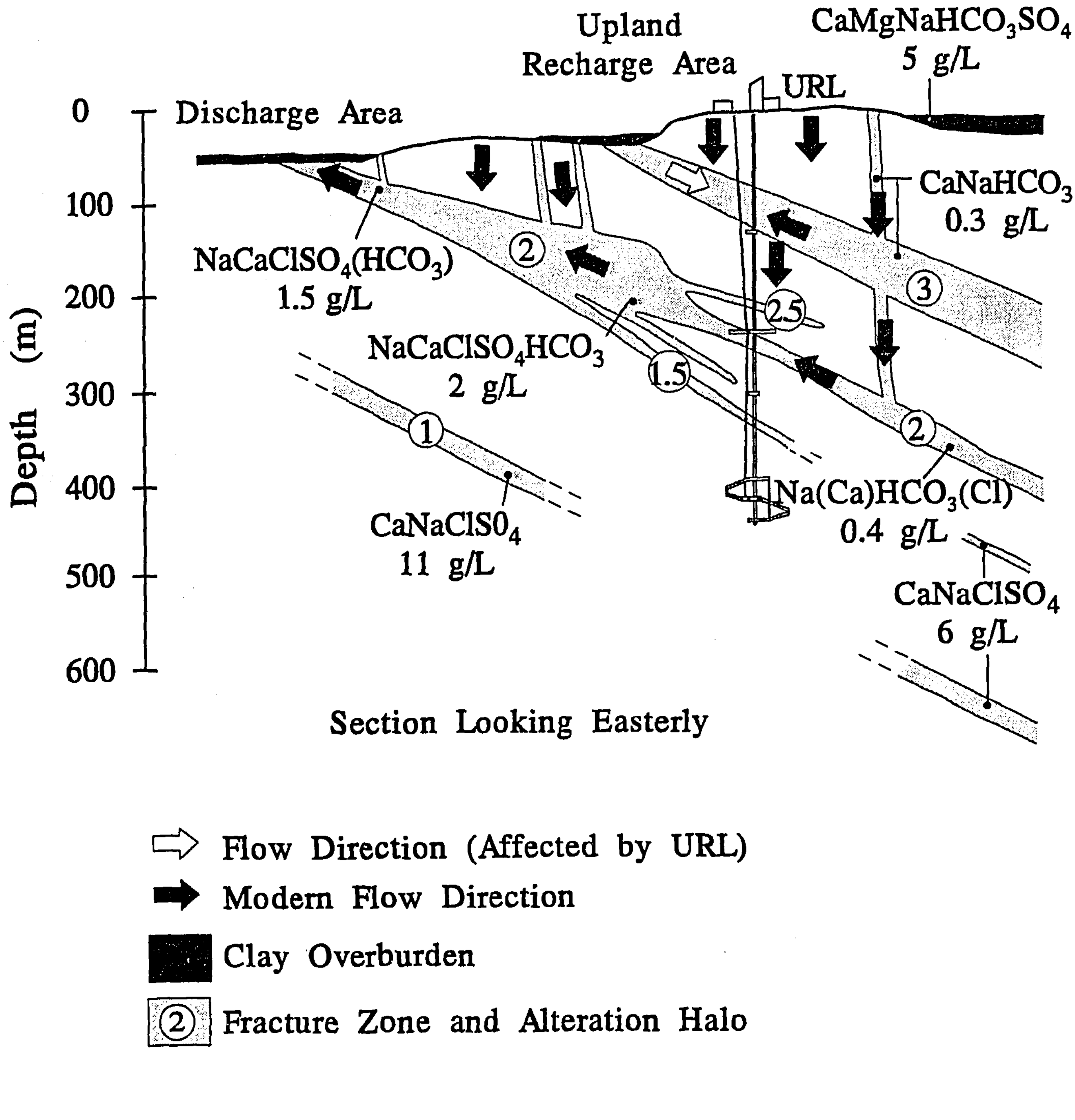

FIGURE 3: URL Groundwater Chemistry

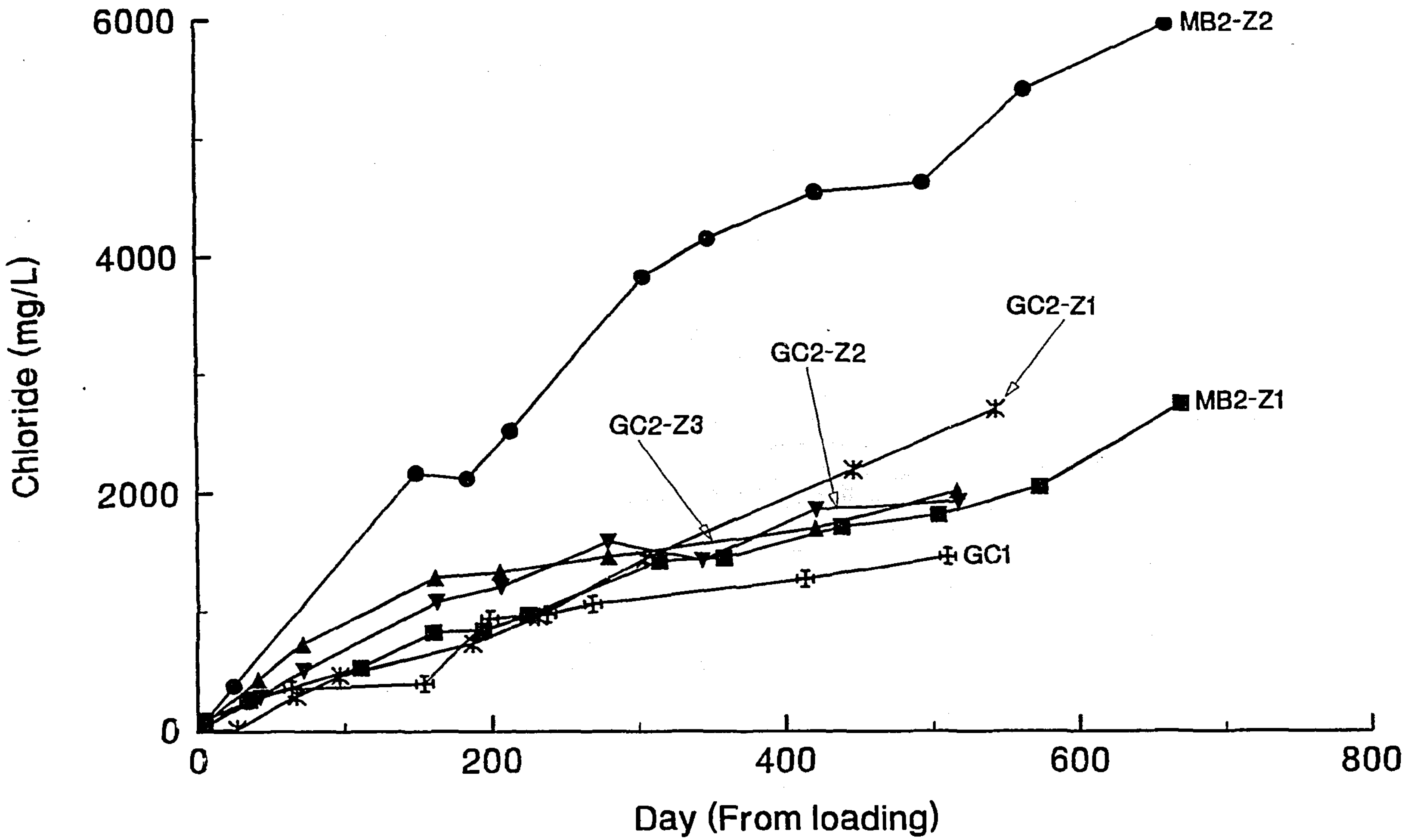

FIGURE 4: Variations of Cl with Time in the Borehole Leach Test at the URL 420 m Level

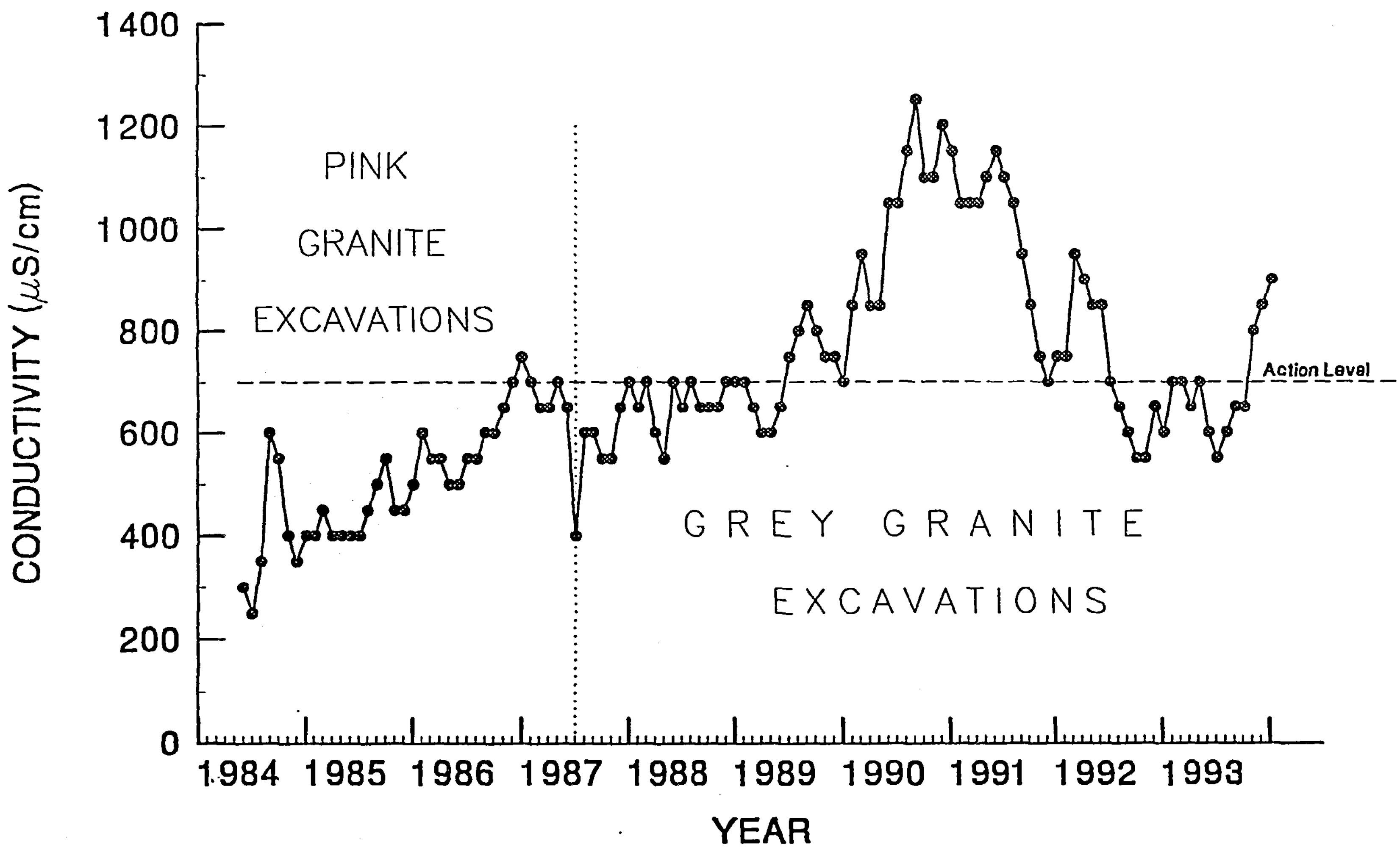

FIGURE 5: Variation of Electrical Conductivity in URL Holding Pond Water

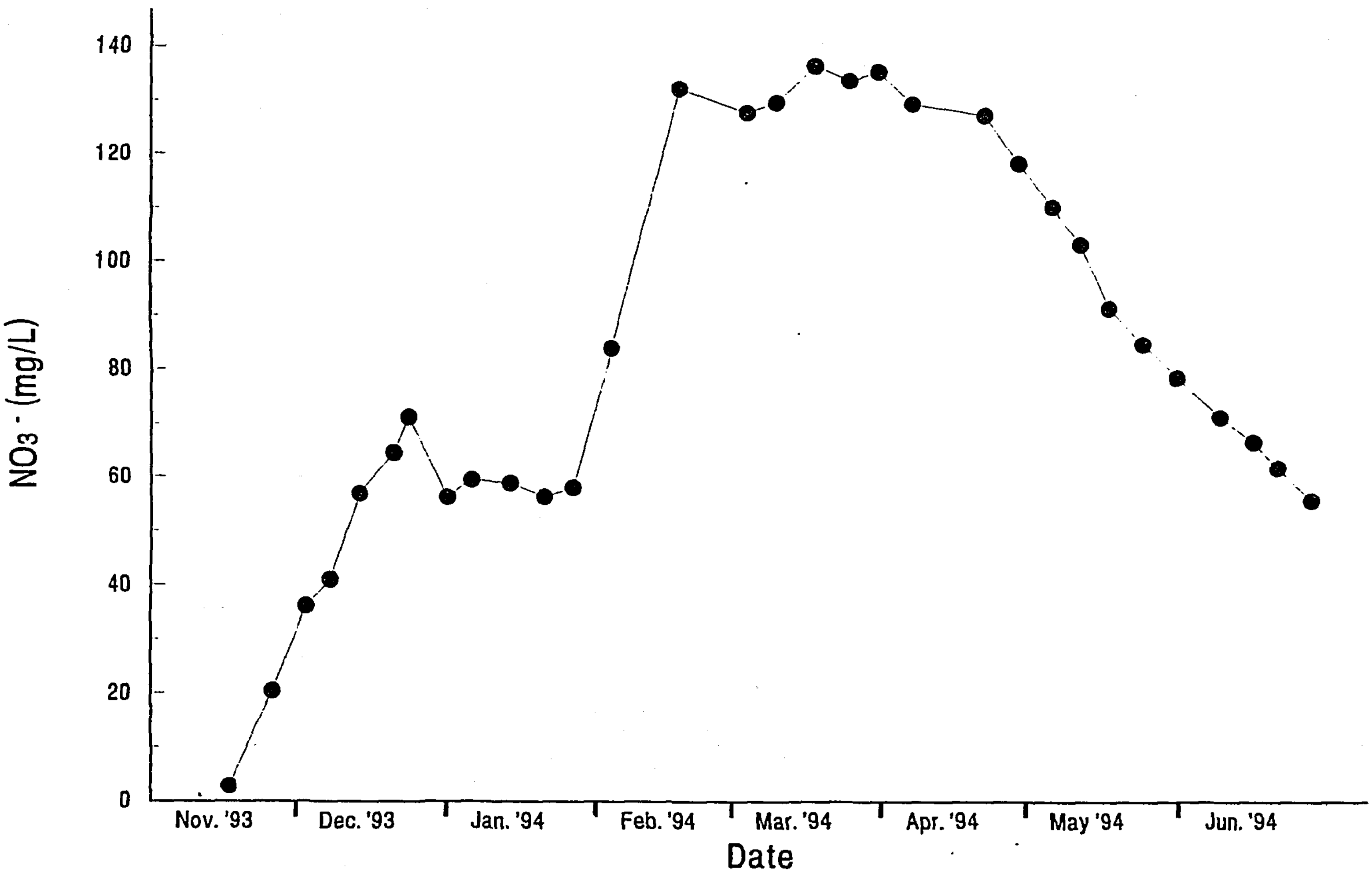

FIGURE 6: Variation of NO_3 in Holding Pond water at the URL

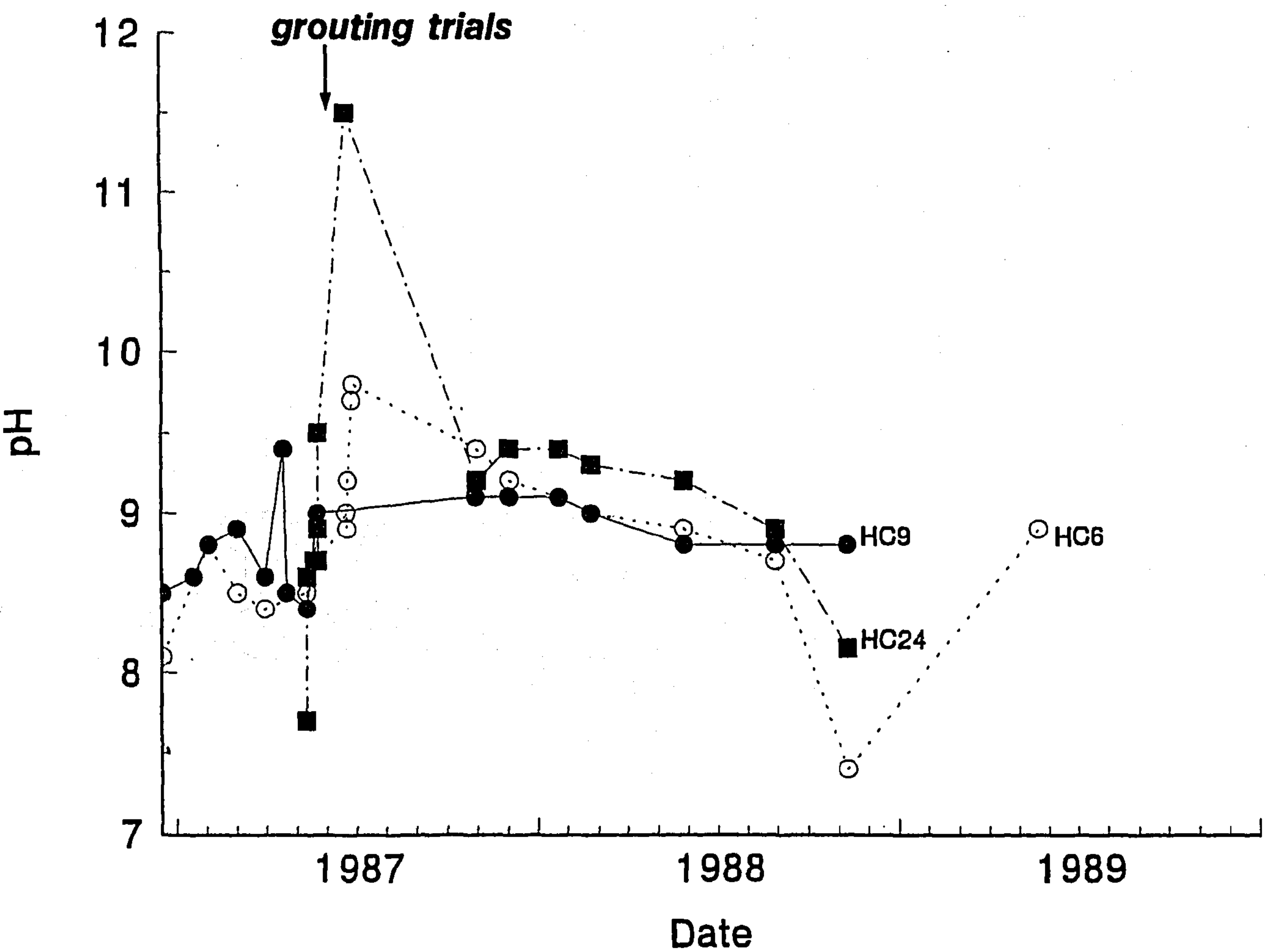

FIGURE 7: Variation in pH of Groundwaters in Boreholes Adjacent to the Grouting Trials at the URL 240 m Level (May 1987)

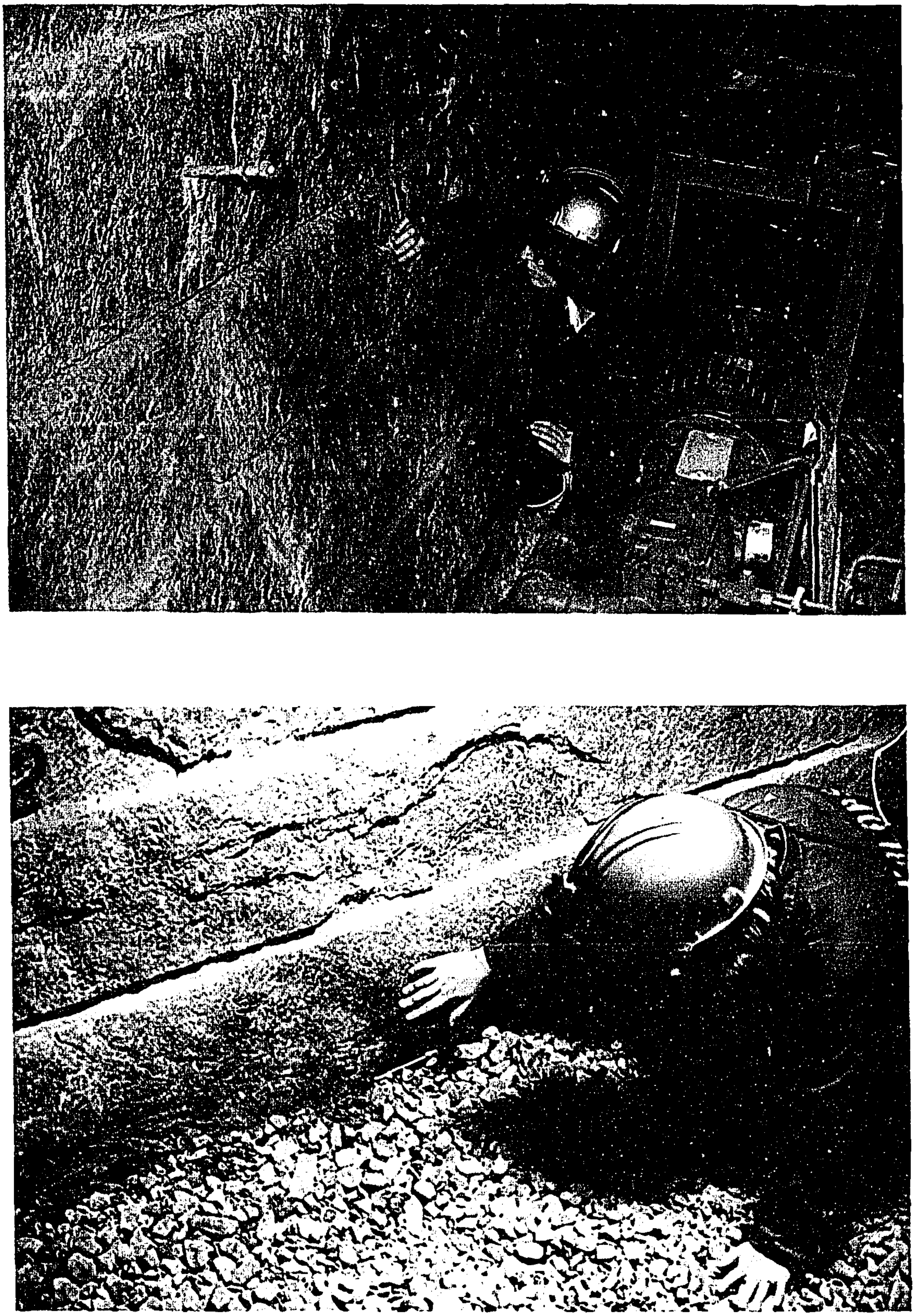

FIGURE 8: Growths of a) Algae and b) Mosses, on Walls in the URL at the 240 m Level

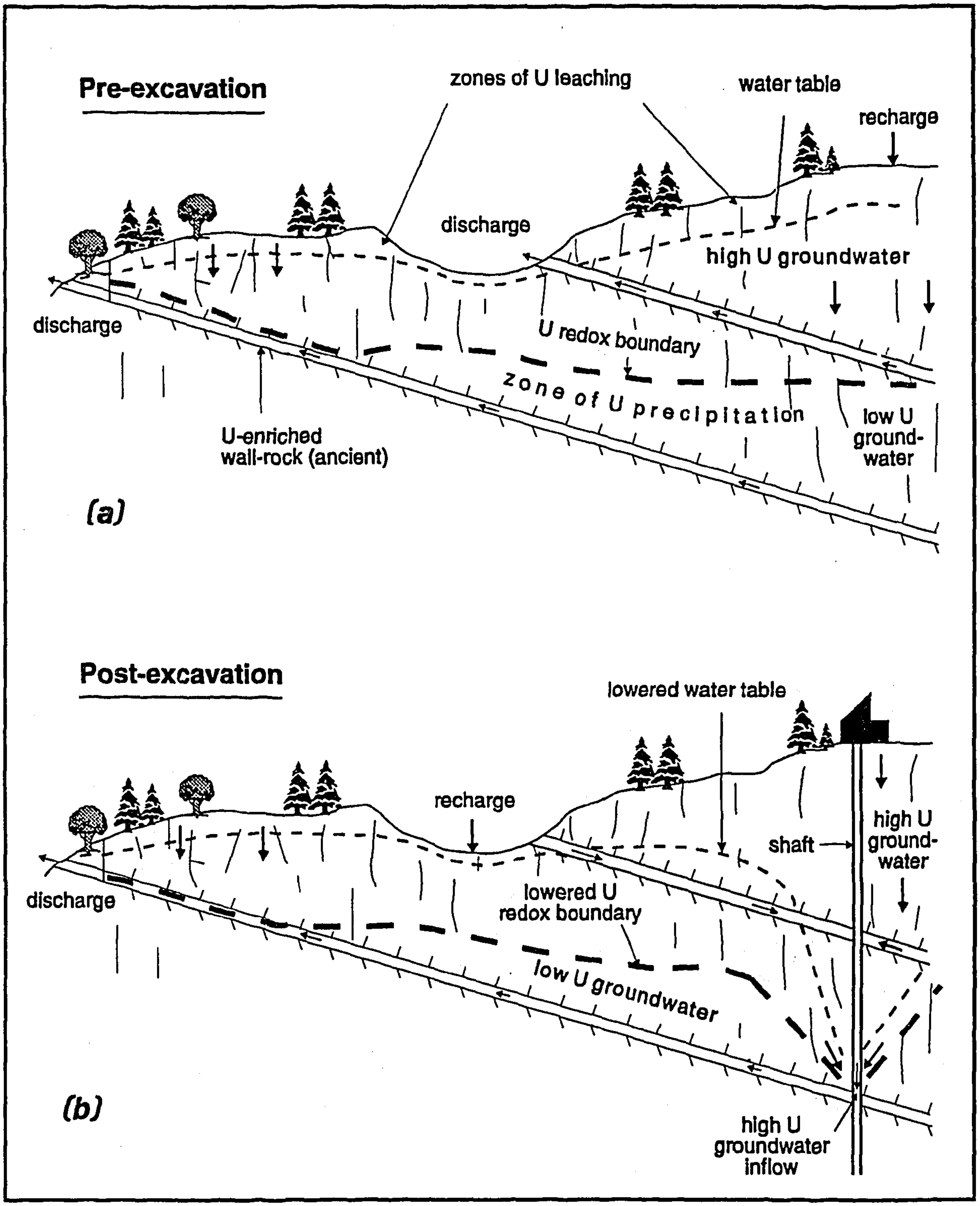

FIGURE 9: Zones of Uranium Mobility and Retardation in Groundwaters, Pre- and Post-Excavation

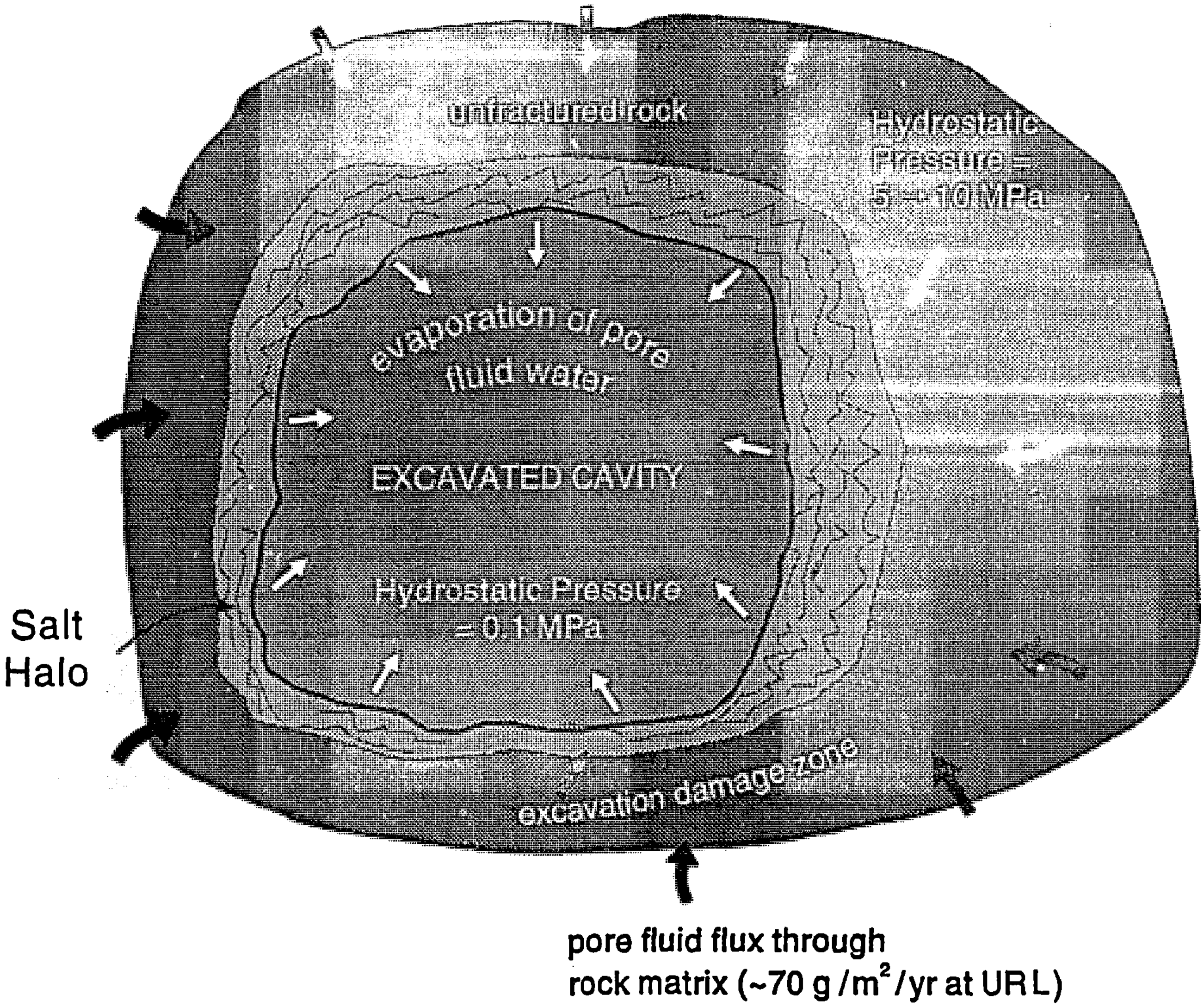

FIGURE 10: The 'Salt Halo Effect' in which Saline Pore Fluids Migrate Through the Rock Matrix and Accumulate in Distrubed Rock Surrounding an Underground Cavity