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HIGH-PERFORMANCE CEMENT-BASED GROUTS FOR USE IN A

NUCLEAR WASTE DISPOSAL FACILITY

L'UTILISATION DE COULIS PERFORMANTS À BASE DE CIMENT

DANS UNE INSTALLATION DE STOCKAGE PERMANENT

DE DÉCHETS NUCLÉAIRES

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AECL RESEARCH

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RÉSUMÉ

Des organismes canadiens et de pays étrangers ont identifié des matériaux à base de ciment comme principaux candidats retenus pour le scellement d'étanchéité des enceintes d'isolement des déchets de combustible nucléaire de la biosphère. À l'heure actuelle, on ne dispose pas d'assez de renseignements pour permettre une analyse correcte du comportement à long terme de ces matériaux de scellement d'étanchéité dans une enceinte. On a entrepris un programme combiné de recherches en laboratoire et par modélisation pour fournir les renseignements nécessaires à la mise au point spéciale d'un coulis performant à base de ciment. Les résultats montrent que le coulis se comportera probablement d'une façon acceptable pendant des milliers d'années et vraisemblablement pendant des périodes beaucoup plus longues. Il est établi que les matériaux, qui se sont avérés efficaces dans des applications sur le terrain, sont pratiquement imperméables et fortement résistants à la lixiviation dans les conditions existant dans une enceinte. Des adjuvants plastifiants spéciaux faisant partie de la composition améliorent les caractéristiques physiques du coulis sans porter atteinte à sa résistance chimique. Ni la modélisation ni les essais en laboratoire ont permis une évaluation définitive de la longévité du coulis. Cependant, aucun des résultats de ces études n'ont été en opposition avec l'emploi de coulis performants à base de ciment à des fins de scellement d'étanchéité d'une enceinte.

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ABSTRACT

National and international agencies have identified cement-based materials
as prime candidates for sealing vaults that would isolate nuclear fuel
wastes from the biosphere. Insufficient information is currently available
to allow a reasonable analysis of the long-term performance of these seal-
ing materials in a vault. A combined laboratory and modelling research
program was undertaken to provide the necessary information for a specially
developed high-performance cement grout. The results indicate that accept-
able performance is likely for at least thousands of years and probably for
much longer periods. The materials, which have been proven to be effective
in field applications, are shown to be virtually impermeable and highly
leach resistant under vault conditions. Special plasticizing additives
used in the material formulation enhance the physical characteristics of
the grout without detriment to its chemical durability. Neither modelling
nor laboratory testing has yet provided a definitive assessment of the
grout's longevity. However, none of the results of these studies have
contraindicated the use of high-performance cement-based grouts in vault
sealing applications.

CONTENTS

1. BACKGROUND

The geological disposal of nuclear fuel wastes is recognized internation-
ally as probably the only viable method of protecting man and the environ-
ment from the hazards presented by these materials. Nearly all countries
that now generate electricity through the use of nuclear energy have ongo-
ing programs to develop concepts for waste disposal vaults. The wide vari-
ety of geological formations proposed as appropriate media in which vaults
can be constructed reflect the range of geologies of the countries in-
volved. In all cases, once vaults are closed and sealed, the most likely
mechanism through which waste can escape to the biosphere is through dis-
solution in, and movement through, the groundwater. The materials used to
seal vaults must be affordable, emplaceable and effective in a wide range
of environmen.s. Moreover, the probable performance of the sealing mate-
rials and systems over millenia has to be understood since the hazardous
materials in nuclear fuel wastes are very long lived.

In 1986, a task force of technical representatives from each of the member
countries (Canada, Finland, Japan, Sweden, Switzerland, the United Kingdom
and the United States of America) of the OECD/NEA International Stripa
Project was established to review the current knowledge of sealing materi-
als, to recommend candidate materials and methodologies for use in sealing
vaults and to identify technical issues requiring detailed attention. More
specifically, the task force was required to focus on materials, methodolo-
gies and performance issues related to grouting fractured rock. The task
force recommended that studies should focus on clay and cement-based grout-
ing materials and practices (Coons 1987). For both of these materials, it
was noted that insufficient information was available to allow for reason-
able analyses of the performance of the sealing materials and the systems
of which they form a part. A coordinated series of laboratory, in situ and
theoretical studies was undertaken to provide much of this information.
This report describes the work being carried out on cement-based grouts by
AECL Research in Canada in collaboration with RE/SPEC Inc. in the U.S.,
with an emphasis on the laboratory and theoretical studies into the longev-
ity of the materials.

Numerical models for cement-grout longevity depend on the complexity of the
conceptual model adopted for their formulation. Necessarily, both concep-
tual and numerical models become more complex and, thereby, more realistic
as results from physical and numerical experimentation become available.
The parallel programs of laboratory and theoretical research that form the
joint Canada/U.S. program have led to such developments.

Recent advances in cement technology have led to the development of high-
performance grouts designed for their ability to penetrate fine fissures in
rock (Gray and Keil 1989, Benmokrane et al. 1988, Onofrei et al. 1989) and,
in the specific instance of nuclear fuel waste disposal, for their likely
acceptable long-term performance characteristics. Specific features of the
grouts studied include their fine particle size, the inclusion of pozzo-
lanic material to limit the amount of CH* in the hardened grout and super-

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*   The following nomenclature is used in cement chemistry:
    $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $H = H_2O$.

plasticizer to provide the workability at low ratios of water to cementitious materials (*W/CM*).

While superplasticizers decrease porosity by reducing the *W/CM* ratio, and should thereby decrease the hydraulic conductivity and improve the longevity of the grout, insufficient direct information existed to support this hypothesis. Furthermore, concerns were raised that the superplasticizers could be released from the hardened grouts and increase the mobility of radionuclides in the geosphere.

In conventional civil engineering practice, high-performance cements containing superplasticizer and silica fume are manufactured using any one of five commonly employed portland cement types (ASTM Types I to V). However, earlier studies (Hooton and Mukerjee 1982) indicated that Type V (sulfate-resistant portland cement (SRPC)) was likely to prove most desirable from the perspective of long-term performance. Other cement products designed for sulfate resistance, such as Class H (oil-well) cements and blast furnace slag cements (BFSC), may prove equally acceptable. Proprietary grouting products based on these latter two materials are available commercially. However, the generic nature of the research program and the general lack of ability to obtain detailed information on prop-ietary products led to the selection of a cement based on SRPC. A finely reground and well-characterized SRPC was selected. A less well-characterized proprietary product based on BFSC was also chosen for examination.

The laboratory and modelling research program served a number of major functions. The laboratory tests carried out by AECL Research in Canada allowed a conceptual model to be developed for the morphology and long-term performance parameters of high-performance grouts comprised of reground SRPC, silica fume, superplasticizer and water, and the results could be compared with those for a proprietary BFSC product. Tests would be conducted to determine the effects of superplasticizer on the long-term properties of the grouts. Specifically, the hydraulic conductivity/porosity relationships for the material would be determined to improve our understanding of the material and to provide input to the numerical model. Leaching tests would be carried out to provide details of solid/water reaction processes to improve conceptual models of the material properties and to allow comparisons to be made with the predictions from the numerical models. In turn, RE/SPEC Inc. in the U.S. would use data available at the outset of the investigation to develop a numerical model combining geochemical and permeability modelling, and use it to determine the long-term performance of a grout. The database used for the numerical modelling and the conceptual model used to formulate the numerical model would be upgraded as further data became available through the laboratory work.

This report describes some of the major results from the laboratory and modelling programs.

2. DEVELOPMENT OF THE REFERENCE HIGH-PERFORMANCE GROUT

2.1 MIX DESIGN AND LABORATORY TESTING

Cement-based grouts are fabricated by mixing water with portland cement and often with other additives to produce cement grouts with certain desired properties. Portland cements consist of a mixture of calcium silicates, aluminates, aluminoferrites, lime and calcium sulfate (gypsum) phases. A number of variations in the type of cement have been developed to meet specific requirements such as rapid hardening, low rate of heat evolution and resistance to sulfates, but these variations reflect relatively minor modifications in composition. All cement compounds are hydrophillic, that is, they have a chemical affinity for water, and tend to react with, absorb and retain the water. Specifically, the addition of water to any cement causes exothermic reactions and leads to the formation of a plastic paste that sets and eventually hardens to a hard, rocklike mass. Hardening is associated with the formation of a rigid interlocking matrix of hydration products, especially hydrated calcium silicates (CSH), which gradually replace the water between the cement grains and finally bind the composite cement mass together. Under normal conditions, the hydration reaction in a cement paste does not usually go to completion. The microstructure of historic concretes typically shows (Mallison and Davies 1987) residual grains of unreacted cement embedded in a matrix composed mainly of calcium-silicate-hydrate gel. This reaction does not go to completion because the reaction products form coatings around the cement grains during hydration, and the coatings progressively inhibit the access of water to the anhydrous material. The physical characteristics (such as permeability and strength) developed by the hardened cement product depend in part on the degree of hydration, the temperatures reached during the hydration reactions and the degree to which the CSH phases fill space efficiently. These factors also affect the chemical stability of the hardened product and the permeability of the hardened material, which is a function of material's macro/micro-porosity and the degree of macrocracking caused by thermal strain induced during curing. The physical and chemical requirements are met through a process of mix design where the grout mix is optimized by examining the effects of variations in the type of cement, the W/CM ratio, and the type and quantity of additives on the material properties. A single adjustment tends to affect more than one performance property, and so it was necessary to select a reference material for investigation to make the studies described here practicable.

The purpose of the cement-based grout in a vault is to seal fractures for long time periods to mitigate any dispersal of dissolved nuclear waste to the environment. To do this, the grout must have these properties:

1. acceptably low hydraulic conductivity (e.g., $<10^{-10}$ m/s),

2. an ability to penetrate very fine fissures within the host rock, and

3. physical and chemical compatibility with the host environment.

It is also desirable for the grout to form an effective bond with the host rock (to minimize flow at the rock/grout interface), possess an ability to self-seal internal or interfacial fractures that could arise from physical disturbances (e.g., movement and stresses of the rock, drying and shrinkage), resist leaching, and not alter the groundwater chemistry significantly.

A cement grout reference formulation was developed with these objectives and the practical requirements of emplacement in mind; the work was done under the Canada/U.S. cooperative program of research associated with in situ experiments at AECL Research's Underground Research Laboratory (URL). Full details of the testing program leading to the selection of the reference grout are provided by Al-Manaseer and Keil (1990), Gray and Keil (1989) and Ballivy et al. (1988). Three types of cement were included in this investigation: SRPC (Canadian Type 50), expansive cement (Canadian Type K), and ALOFIX-MC (MC-500), a commercially available slag cement with extremely fine particle size. Since the penetration of very fine fractures was being studied, both the Type 50 and Type K cements were investigated at their normal fineness and after regrinding.

Silica fume was incorporated in all mixes. The addition of silica fume as pozzolanic material minimizes the amount of readily soluble residual lime and the CH liberated during cement hydration and converts it to less leachable CSH. While the prime benefit is enhanced durability, grouts with silica fume additive also exhibit less bleeding and segregation (Figure 1).

Superplasticizer was also incorporated into all mixes to reduce the W/CM ratio of the grout while achieving a viscosity that is low enough to permit emplacement (Figure 2). Low W/CM ratios in a grout maximize the density of the grout and consequently minimize its porosity. Low W/CM ratios may also favor autogenous sealing.

The laboratory studies showed that low-viscosity nonsegregating grouts could be prepared using any of the three basic cement types investigated. The amount of superplasticizer could be varied to achieve the desired viscosity, without significant impacts on the setting time. The reground Type 50 cement with 10% silica fume appeared to require slightly less water than either the Type K with 10% silica fume, or the MC-500, for the equivalent viscosity. Moreover, Type 50 cement is widely available, its engineering properties are well documented in the open literature, and so it meets the requirements of a generic research program. Thus, the reference grout mixture adopted for further use in field trials and in the laboratory for the longevity studies consisted of SRPC (Canadian Type 50) reground to a Blaine fineness of 600 m^2/kg (90% by mass), silica fume (10% by mass), and 1% superplasticizer (sodium salt of sulfonated naphthalene formaldehyde condensate) mixed at W/CM ratios between 0.4 and 0.6. The chemical composition of the cement is given in Table 1. This Type 50 cement was obtained from Cement Canada Lafarge Ltd., Montreal, Quebec, Canada. The silica fume was obtained from SKW Canada, Bécancour, Quebec, Canada. The chemical and physical properties of this silica fume are given in Table 2. The superplasticizer used was a proprietary sodium salt of sulfonated naphthalene formaldehyde condensate (Na-SNFC) supplied by Handy Chemicals Ltd., La Prairie, Quebec, Canada. The chemical formula of the Na-SNFC is

shown in Figure 3. Table 3 shows the composition and selected properties
of the reference high-performance grout investigated in Canada.

2.2   FIELD TRIALS

In 1987, attempts were made to inject the reference grout into rock frac-
tures at the URL. These grout trials provided practical information to aid
in the planning and execution of a larger field experiment presently
planned for 1993. The general layout of the URL is shown in Figure 4.
Figure 5 shows the plan of grout and observation boreholes installed at the
240 Level. The 240 Level sits above a fracture zone in the host granite
rock body, and the grout was injected into this fracture zone through bore-
holes GH1, GH2 and HC9. The fracture zone in the vicinity of holes GH1 and
GH2 exhibited a very low hydraulic conductivity (of the order of 10^{-8} m/s).
We anticipated that these holes would accept only limited volumes of grout.
The fracture zone in the vicinity of hole HC9 was locally more pervious
(hydraulic conductivity of 10^{-6} m/s) and we expected to be able to inject
larger grout volumes. The fracture zone contained groundwater under a
static head of roughly 2.0 MPa. Full details of the field trials were
provided by Gray and Keil (1989). No problems were encountered in the
field trials in mixing, handling or pumping the grout.

Geochemical monitoring was performed throughout the grouting period. The
results obtained were not totally conclusive since mine water, contaminated
by cement, had been injected into the formation during the drilling asso-
ciated with the grouting work. However, it was clear that the geochemical
signature of the grout injected into the rock was very limited both in
lateral extent and in duration. For example, a rise in pH was not detected
in nearby holes except in those where the grout itself had migrated. The
lack of a geochemical signature is likely because these grouts exhibited no
segregation or bleeding during or after injection.

Hydrogeological testing before and after grouting indicated that the hy-
draulic conductivity of the fracture zone decreased by between one and two
orders of magnitude.

A shaft was sunk adjacent to borehole GH2 through a region of the grouted
fracture zone. An examination of the shaft wall revealed that the grout
had penetrated fractures with a wide range of apertures. Thin-section
analyses of grouted specimens recovered from the excavation showed no evi-
dence of voids or segregation within the grout. The grout totally con-
formed to the irregular boundaries of the rock. Moreover, the grout had
penetrated microfissures in the granite with apertures smaller than 20 μm
(Figure 6).

The field data indicate that the reference superplasticized cement-based
grout can be injected successfully into the rock mass using conventional
grouting practices.

3. LONGEVITY STUDIES

In assessing the performance of sealing materials for a nuclear waste repository, it is usually assumed that the material will continue to perform over the design lifetime more or less as demonstrated in short-term tests. A convincing technical basis for either justifying an assumption of no significant degradation in engineering properties or for assessing the extent of plausible degradation over thousands of years remains to be established.

The collaborative studies between AECL Research and RE/SPEC have the broad objective of resolving these longevity issues. The work focused on developing an improved understanding of the potential degradation modes for cement-based grout materials, particularly the potential degradation processes affecting the performance of the reference grout.

3.1   LABORATORY INVESTIGATIONS

The reference high-performance grout contains SRPC (Canadian Type 50). The formation of ettringite enhances leaching because of an expansive reaction that can cause cracks to appear in the grout. Alumina in the SRPC is bound in an iron complex and is thus not free to form ettringite. The cured cement is dominantly hydrated calcium silicate (CSH), which has less susceptibility to complexation and dissolution by SO_4^{2-} than CH and the hydrated phases. The reference grout also includes silica fume as an additive. Silica fume provides a reactive material that generates silicate at the high pH imposed by cement hydration. Silicate reacts readily with the available lime and/or portlandite (CH) to form CSH phases. CH is the most soluble of all the cement hydration products, and so the addition of silica fume should create a hardened grout with improved leach resistance. Moreover, an excess of residual silica in the hardened grout should not impair and may improve the long-term leach resistance of the grout. This arises from the expectation that the groundwater associated with granitic rock is saturated with silica; the pH and saturation with respect to silica (SiO_2) fixes the chemical activity of silica in the groundwater. However, the pH of the groundwater will be buffered by the large volume of rock. Thus, there is no chemical potential for dissolving any residual silica from the grout. It is anticipated that the calcium content of the groundwater will also be controlled chemically to a certain extent by minerals in the rock, e.g., portlandite ($Ca(OH)_2$) or calcite ($CaCO_3$). $CaCO_3$ is likely to be the predominant natural mineral in grouted rock fissures. In either case, the activity of calcium complexes is likely to be fixed, and the chemical potential for dissolution of CSH is expected to be small. Hence, by design, the reference grout will resist leaching. The degree to which this can be achieved is being measured through laboratory studies.

Superplasticizers are organic agents added to the reference cement grout to decrease the viscosity of the mixture. They are used so that low *W/CM* ratios can be achieved without compromising the emplaceability of the grout. The superplasticizer must allow the grout to set in a matter of several hours and should not cause it to lose density after emplacement by either causing or enhancing dispersal in the groundwater. In addition, the superplasticizer should not be released in bleed water or be readily leached from the hardened grout by groundwater. If the superplasticizer is

released into groundwater in substantial concentrations, either by bleed or leaching, then the issue of organometallic complexing of radioactive waste components may need to be evaluated. At the outset of the investigation it was not clear whether the potential engineering benefits gained by using superplasticizers would be offset by decreased longevity of the superplasticized grout in a repository setting. Laboratory studies were carried out to address these issues.

3.1.1   Superplasticizer Sorption

A series of studies (Aitcin et al. 1989; Onofrei and Gray 1989a, 1990) has already been performed to review the mechanistic function of the superplasticizer, to test superplasticizer sorption in unset cement grouts, and to investigate the microstructure of hardened grouts containing superplasti- ... che retention of superplasticizer in hardened cement pastes.

3.1.1.1   Mechanistic Function of Superplasticizers

Several explanations are available to account for the fluidifying effects of superplasticizers on cement-water pastes (Aitcin et al. 1989, Onofrei et al. 1991). The two most popular hypotheses are the pellicle hypothesis and a hypothesis based on colloid theory. The pellicle hypothesis suggests that superplasticizers initially coat the cement grains and allow the mixing water to lubricate the cement particles. The liberated water becomes available as a lubricant, and so fluidifies the cement paste. In the colloid theory, electrochemical forces between the cement particles are affected by the superplasticizer, resulting in interparticle repulsion and particle dispersion. This dispersion is assumed to be sufficient to account for the modified rheological properties.

The pellicle theory is qualitative and cannot be verified through measurement. The application of colloid theories explains some of the observed phenomena, but requires other qualitative descriptions of particle-superplasticizer interactions to explain deviations of the actual behavior of unset cement-water pastes from the predicted behavior.

It appears that superplasticizers do not significantly interfere with the long-term hydration reactions. The reactions appear to proceed to completion with only minor alterations in crystal sizes in the hardened cement, and the final phase distributions in the hardened pastes are only slightly different when superplasticizers are used. Little information could be found in the literature to describe particle-superplasticizer interactions in unset pastes containing silica fume. Moreover, little is known about the location and distribution of superplasticizers in the hardened materials, the persistence of the superplasticizer at these sites, and the effects of the superplasticizer on the long-term properties − such as leaching and dissolution − of the hardened materials, in particular, potential releases of organic materials into the repository environment.

3.1.1.2   Superplasticizer Sorption in Unset Cement Grouts

The dispersive action of a superplasticizer in a grout mix is related to its interaction with cement and other secondary cementitious materials such

as pozzolans. Information about the rate at which superplasticizers are sorbed on hydrating materials during grout mixing and settling is fundamental to understanding the interactions between the superplasticizers and the cementitious solids. Knowing the rates of sorption of superplasticizer on a variety of cementitious materials would allow a qualitative description of the effects of cement composition on superplasticizer-particle interactions in "green" grouts, i.e., freshly mixed unset materials. Such a study was undertaken to determine the nature of interactions in high-performance grouts containing silica fume (Onofrei and Gray 1989, 1990).

The data from the sorption studies in unset cement grouts, shown in Figure 7, indicate that the cement sorbs superplasticizer preferentially to the silica fume and the pore space in the hardened pastes could contain free superplasticizer that may be readily liberated during leaching. However, it is likely that the free superplasticizer will become increasingly immobilized as the degree of hydration of the cement in unset and possibly hardened pastes increases. The superplasticizer content required to produce adequate workability in the grout is approximately 1%; at this concentration, approximately 40% of the added superplasticizer will remain in the pore fluid after the grout reaches its initial set. It thus appears that the water-filled pores left in the hardened pastes may liberate superplasticizer to the surrounding media if they are flushed by permeating water or are exposed through dissolution of the hydrated solid cement phases.

3.1.1.3   Superplasticizer Sorption in Hardened Cement Grouts

The location of the superplasticizer and its retention in hardened grouts was investigated in the reference grout containing up to 3% Na-SNFC superplasticizer labelled with ^{35}S, a beta emitter (Onofrei and Gray 1989b).

Electron microautoradiography combined with scanning electron microscopy and energy dispersive X-ray spectroscopy were used to identify the cement phases containing the labelled superplasticizer. Typical scanning electron microscope (SEM) micrographs and associated energy-dispersive X-ray (EDX) analyses for specimens containing 3% Na-SNFC at a *W/CM* ratio of 0.2 are presented in Figure 8. The bright spots on the electron micrographs indicate the location of the labelled Na-SNFC superplasticizer. The analyses indicate that the superplasticizer resides on phases rich in calcium (spectra b_1 and b_2 in Figure 8) and phases containing aluminum, calcium, silicon and iron (spectra d in Figure 8). No superplasticizer could be detected on the silicon-rich areas (spectra g_1 in Figure 8).

Portland cement is a complex mixture of four principal compounds: tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF), tricalcium silicate (C_3S), and dicalcium silicate (C_2S). All these constituents react with water; however, the rates of hydration decrease approximately in the following order: $C_3A > C_3S > C_4AF > C_2S$. Dicalcium silicate reacts slowly, taking weeks to attain appreciable hydration. The hydration of C_3S is primarily responsible for the early strength of the cement-water system. Because C_3A reacts rapidly with water, its hydration also plays an important role in the early setting behavior of cement. Superplasticizers principally affect the rheology of cement-water mixtures for the first few hours after mixing. To achieve these effects, the superplasticizers appear to interfere primarily with the fastest hydration reactions.

Ramachandran (1982) partially confirmed this hypothesis in his studies on
the adsorption of superplasticizer on C_3A and C_3S in an aqueous medium.
Immediately after mixing, only a small amount of superplasticizer is ad-
sorbed on the C_3A. However, the adsorption increases significantly about
5 h later. Other studies (Collepardi et al. 1981) on the adsorption of
sulfonated naphthalene formaldehyde condensate on various types of indus-
trial cement have shown that the amount of superplasticizer adsorbed de-
pends on the C_3A content - to obtain the same workability, a higher dosage
of superplasticizer is required for Type 10 cement (ordinary portland ce-
ment) than for Type 50 cement (SRPC). The C_3A content is higher in Type 10
cement than in Type 50 cement.

The observations from this study indicate that the Na-SNFC is retained
within the structure of the C-A-H and calcium-rich C-S-H phases after
hardening has occurred. The ratio of the calcium/silicon peaks in both the
EDX spectrum and the X-ray diffraction (XRD) data indicates that the
calcium-rich phase is C_3S hydrate. XRD data also suggest that the phase
containing aluminum and calcium as major constituents is a C_3A hydrate.

Thus, the adsorption of Na-SNFC on, and its incorporation in, the two fast-
est hydrating components of the cement have been confirmed. The principal
mechanism of adsorption appears to be by association with the water mole-
cules hydrating the C_3A and C_3S, although other mechanisms of incorporation
are possible. C-S-H can incorporate significant amounts of other ions
(e.g., sulfate, aluminum and iron) into its structure. The hydration of
C_3A involves reactions with sulfate ions supplied by the dissolution of
gypsum in cement. However, the sulfate group contained in the superplas-
ticizer molecules may also react with C_3A during the hydration reaction,
and the adsorption of Na-SNFC on the C_3A phase may be partly attributed to
this interaction.

Adsorption studies of Na-SNFC in unset grout pastes indicate that the addi-
tion of silica fume to the cement increases the quantity of superplastici-
zer adsorbed. However, our studies of the distribution of superplasticizer
in hardened cement revealed that the superplasticizer is not associated
with silica-rich phases (unreacted silica fume particles). This suggests
that the initial adsorption of superplasticizer on silica fume was tempo-
rary and did not involve a chemical reaction.

Overall these data support the hypothesis that the adsorption of superplas-
ticizer on the hydrated cement phases involves chemical reactions.

3.1.1.4 Superplasticizer Leaching Studies

The retention of adsorbed superplasticizer in hardened cement pastes was
investigated by monitoring the release of the ^{35}S during leaching. Har-
dened grouts containing the labelled superplasticizer were subject to a
series of quasi-static leach tests (Onofrei and Gray 1989). The leachants
used in this study included three synthetic granitic groundwaters: granitic
groundwater (GG), WN-1 synthetic groundwater and standard Canadian Shield
saline solution (SCSSS). Table 4 shows the composition, ionic strength,
and the pH of these groundwaters. They represent the range of groundwater
compositions expected to be encountered up to depths of 1000 m in the
granitic rocks of the Canadian Shield.

Temperature effects, the ratio of the surface area of the grout to the volume of the leachant, and the effect of the ionic strength of the groundwater on the cumulative fraction of release (CFR) of Na-SNFC into solution were examined in the analysis of the results from the leach tests. The CFR data were calculated for a leaching period of 30 d according to the equation

$$CFR_{i,n} = (SA \cdot f_i)^{-1} \left[C_{i,n} \cdot V_n + \sum_{k=0}^{n-1} (C_{i,k} \cdot V_s) \right] \tag{1}$$

where $C_{i,n}$ is the measured concentration of the Na-SNFC in the nth sample (kg/m^3), SA is the geometric surface area of the grout sample (m^2), f_i is the fraction (by weight) of the Na-SNFC in the grout, and V_n is the volume of the solution given by

$$V_n = V_o + (1 - n)V_s \tag{2}$$

where V_o is the starting volume (m^3) and V_s is the sampling volume (m^3). The summation term in Equation (1) accounts for the amount of the Na-SNFC removed by sampling.

The results are shown in Figures 9 to 11. The data show that superplasticizer can be leached from the grouts. However, the cumulated releases are very small (10^{-12} kg/m^2). Figure 9 compares the CFR of Na-SNFC from the reference grout with and without silica fume added to the mixture at low W/CM ratios (= 0.2) for an Na-SNFC content of 2%. The addition of silica fume to the cement increases the release of superplasticizer in solution. We noted earlier that unset cement/silica fume mixtures adsorb more superplasticizer than those without silica fume: this is presumably related to the large specific surface area of silica fume, which is approximately 30 times greater than that of cement. However, the microstructural studies revealed that superplasticizer does not reside on silica-rich phases in hardened cement. This suggests that the sorbtion of superplasticizer by the silica fume is not strong in fresh mixes and, like any free superplasticizer in the capillary pore space of the grout, the superplasticizer is not retained and is readily removed by leaching from the silica fume surfaces.

Figure 10 shows that increasing the quantity of superplasticizer in the mixtures increases the quantity of superplasticizer released to solution. The grout adsorbed less than the total amount of superplasticizer added. The excess superplasticizer remains in the accessible free pore water.

The CFR of superplasticizer increases inversely with the W/CM ratio (Figure 11). The increased release of superplasticizer to solution at lower W/CM ratios can be attributed to the nonhomogeneous distribution of superplasticizer in the grout. As the water content in the cement decreases, and with it the W/CM ratio, the distribution and availability of superplasticizer for adsorption on or reaction with the grout phases also decreases. The unabsorbed and/or unreacted superplasticizer will remain in the pore water.

The results in Figure 11 also indicate that the CFR of superplasticizer increases directly as the temperature and the ionic strength of the groundwater increase, and inversely with the ratio of the surface area of the grout to the volume of solution. The leachability of the grout phases shows a similar functional dependence (Collepardi et al. 1981). Thus, the increasing release of superplasticizer with increasing temperature and ionic strength of groundwater and decreasing surface-area-to-volume ratio would appear to be associated with the dissolution of the hydrated phases of C_3A and C_3S in which it resides. It is also associated with the increasing exposure of accessible pores, whi_h contain leachable Na-SNFC, to the leachate.

The results confirm that superplasticizer can be leached from the hardened grout, albeit in small quantities. The released quantities are derived from the capillary porosity of the hardened cement, although release appears also to occur concomitantly with the gradual dissolution of hydrated C_3A and C_3S phases.

The microstructural analyses and leaching test data indicate a strong chemical bond between the superplasticizer and the C_3A, C_3S and CSH phases on which it is adsorbed or in which it is incorporated.

3.1.2   Leaching Studies of Hardened Grouts

The mechanisms and the rates of the leaching/dissolution processes taking place when a grout is exposed to an aqueous environment are determined by a combination of physical parameters (such as the temperature), microstructure and chemical factors (such as composition of the grout and of the aqueous medium in contact with the grout). The two chemical factors mentioned can control the grout leaching/dissolution processes independently or in combination, depending on the extent to which the aqueous medium is affected by the accumulation of grout dissolution products. The extent of the interaction is determined in turn by the rate at which the water in contact with the grout is replaced and by the ratio between the exposed surface of the grout and the volume of water in contact with it.

Characteristics of cement such as density and porosity will control the rate of water penetration into the pores and capillaries of the matrix. The principal action of external water is to dissolve the portlandite ($Ca(OH)_2$) formed during hydration reactions. When all the soluble $Ca(OH)_2$ is dissolved in water, the remaining calcium silicate hydrate (C-S-H) will decompose to restore the equilibrium, changing as a consequence the pH of the solution. Through leaching studies, the kinetics of the release of calcium have been measured to provide an indication of the extent of grout matrix decomposition under different environmental conditions.

3.1.2.1   Static Leach Tests

Hardened samples of the reference grout mixed at *W/CM* ratios of 0.4 and 0.6 and ALOFIX-MC (MC-500) mixed at *W/CM* ratios of 0.5 and 0.7 were subjected to a series of static leach tests. The full description of the experiment design and method is given by Onofrei et al. (1989).

The Box-Behnken fractional factorial statistical method (Box and Behnken 1960) was used to design a series of static leach tests covering a wide range of conditions that could occur in a nuclear waste disposal vault. The values of the three independent variables (temperature, ionic strength of the groundwater and the cation exchange capacity of clay present in the leachate) used in these leach tests are given in Table 5. The corrosion performance was determined by measuring the leach rates of Ca^{2+} and Si^{4+}. Figures 12 and 13 show typical results from these leach tests.

The cumulative fractional release rate (CFR) of Ca^{2+} is virtually constant over the range of W/CM ratios investigated for the reference grout, and tends to increase marginally with temperature and groundwater salinity. However, the CFR for Ca^{2+} exhibits a marked increase with increasing temperature for MC-500. This is particularly pronounced when the grout is leached in highly saline groundwater (SCSSS). In the most extreme conditions of high temperature (150°C) and groundwater with high salinity (SCSSS), the MC-500 releases Ca^{2+} at approximately six times the rate of the reference grout.

Leaching studies on Type 50 cement grout without silica fume revealed that the amount of Ca^{2+} released is similar in magnitude and functional dependence to that of the reference grout. Consequently, the difference between Ca^{2+} releases from the MC-500 grout and the reference grout cannot be attributed to the addition of silica fume to the reference grout.

Over the range investigated, the results also indicate that the W/CM ratio does not significantly influence Ca^{2+} release into solution for either the reference grout or the MC-500. SEM/EDX examination of the leached cement samples showed a buildup of a multiphase layer on the surfaces of both cement grouts. Figure 14 shows electron micrographs of the leached surfaces of the MC-500 and the reference grout after 56 d in a brackish groundwater, WN-1, at 150°C. The precipitate layer consisted of two distinct phases. The elongated crystals (area a in Figure 14) were identified by EDX as a Ca-rich phase, with the rhombohedral morphology characteristic of calcite ($CaCO_3$). The second phase was found to be a fibrous Mg-Ca-Si phase (area b in Figure 14). The $CaCO_3$ crystals are larger and more abundant for the MC-500 grout. These large quantities of $CaCO_3$ were attributed to a relatively fast removal of Ca^{2+} from the calcium silicate hydrate phase by reaction with the groundwater constituents and/or carbonation of initially large quantities of $Ca(OH)_2$ that were not involved in the pozzolanic reactions. The presence of large quantities of $CaCO_3$ likely explains the faster leaching of the MC-500 grout relative the reference grout.

The cation exchange capacity (CEC) of the clay present in the leachate does not significantly influence Ca^{2+} releases for either of the grouting materials.

The CFR data for Si^{4+} from MC-500 and the reference grout (Figure 12) indicate that the release of Si^{4+} from each of the cements is similar and increases with groundwater salinity. When the grouts are leached with WN-1 groundwater, the CFR for Si^{4+} for the MC-500 is virtually independent of temperature, whereas the reference grout exhibits an increase in Si^{4+} release with increasing temperature. The relatively high releases of Si^{4+}

from the reference grout can be attributed to the silica fume added to this grout. Furthermore, the Si^{4+} release values are much lower than the calcium release values. This suggests that Si^{4+} release is not controlled by the hydration reaction and is mainly the result of dissolution of unreacted silica fume.

3.1.2.2   Dynamic Leach Tests

Static leach tests suffer from the problem of potential solution-saturation effects at both low and high temperatures. The measured leach rates can be artificially low because of reduced chemical potential differences as leached constituents accumulate in the static solution. In cement leaching/dissolution studies, the saturation of the leaching solution with Ca^{2+} is particularly important since matrix leaching plays an important role in cement leaching/dissolution. When cement is exposed to water, $Ca(OH)_2$ is the first phase leached. Once the free calcium hydroxide is removed, Ca^{2+} is leached preferentially from the CSH and from other phases containing calcium. At first, the groundwaters will usually be unsaturated in calcium relative to cement. Consequently, any leach test that allows the leachate concentration of calcium to reach the saturation limit (e.g., $[Ca^{2+}]$ = 0.013 mol/L in water saturated with $Ca(OH)_2$) could result in artificially low leach rates.

While essentially static conditions would likely exist in a sealed vault system, grout leaching was also studied under nonstatic conditions simulating a range of possible groundwater flow rates. Leach tests under dynamic conditions were also carried out in an attempt to understand the role of solution-saturation effects in cement dissolution.

The effect of flow rate and temperature on the leaching performance of cement grouts was investigated in specially designed leach test systems. Figure 15 shows a schematic of the single-pass continuous-flow leach test arrangement used for tests at high temperatures and pressures. The system was designed to provide a continuous flow of leachant through the cell where the grout sample was located. The response of the cement grout to changes in the leachant composition resulting from interactions between the grout and the leachant could also be investigated.

Figure 16 shows the rate of Ca^{2+} leaching in the reference grout as a function of time. The grout has been hardened for 56 d and mixed at a *W/CM* ratio of 0.6. The leaching tests were carried out at temperatures from 25 to 100°C and low (12 mL/d) and high (240 mL/d) flow rates with distilled deionized water as the leachant. The leach rates decreased steadily with time at 25°C, tending to a constant value; this suggests that the leaching process is controlled by the presence of a surface layer that acts as a protective barrier to retard the release of the cement constituents. The data from tests carried out at 50 and 100°C show that the leaching rates increase with time, indicating that leaching may be controlled at these temperatures by a continuous corrosion process in which the surface layer formed is not protective. The reference grout had a similar leaching behavior at a low *W/CM* ratio (0.4), but the rate of leaching was lower than for a *W/CM* ratio of 0.6. This may reflect a higher proportion of capillary space in the reference grout mixed at the higher *W/CM* ratio. The SEM/EDX analyses show the precipitation and redeposition of a calcium

phase identified as calcite ($CaCO_3$) on the outer surface of the leached cement samples, suggesting that the leaching/dissolution rate of the grout phases is sufficiently high to saturate the solution.

At low flow rates (12 mL/d), corresponding to longer contact times between the grout and the surrounding solution, the leach rates are about one order of magnitude lower than those obtained in the high-flow-rate leach tests. At low flow rates, the concentrations of the elements in solution may approach saturation more rapidly than in the high-flow-rate tests. The SEM/EDX analyses of the leached samples from the low-flow-rate tests again revealed the formation of the precipitate layer. The precipitate layer consisted of two phases, a Ca-Si phase and a Ca-rich phase.

As indicated previously, leaching under both static and dynamic conditions was accompanied by precipitation and growth of an assemblage of secondary alteration phases. The composition of the precipitate layer may reflect the chemical transformation in cement as well as compositional changes in the groundwater with which it is in contact. The long-term performance of grouts will depend strongly on the thermodynamic stability of the altera-tion phases formed subsequent to the initial grout dissolution. The precipitate or alteration products that form on the cement surface can arise from a number of sources. Many groundwaters are already supersatu-rated with respect to many possible alteration phases. Moreover, the dissolution/leaching of the grout may lead to the supersaturation of the groundwater with respect to alteration phases (e.g., $Ca(OH)_2$, $CaCO_3$, $Mg(OH)_2$). The pH increase itself may also initiate precipitation. Altera-tion solids of intermediate stability (metastable) may form instead of the most stable ones. The transformation of metastable phases is commonly re-cognized in the alteration of natural minerals and glasses under both static and dynamic system conditions as described by the Ostwald step-rule, or "rule of stages," based on the kinetics of nucleation and crystal growth. The Ostwald step-rule states that "the transition of a chemical system from an unstable state to a stable state typically occurs via a series of irreversible metastable states."

The formation of a precipitate layer on the surface of the grout likely affects the long-term leach rates. It appears to control the leaching/ dissolution behavior of cement grouts under both static and dynamic condi-tions. Therefore, the thermodynamic stability of the alteration/precipi-tate phases may influence the long-term performance of cement grouts.

3.1.3   <u>Hydraulic Conductivity and Porosity of the Reference High-
Performance Grout</u>

It is generally known that the durability of hardened cement exposed to aggressive aqueous environments is related to permeability and thereby to the pore structure of the hardened cement. Permeability is an indicator of the ease of transport of liquids and gases in a grout. Whereas the total porosity of hardened cement paste is not related uniquely to permeability, the maximum continuous pore radius is. The maximum continuous pore radius is representative of the size of pores through which the water flows. The permeability coefficient of a liquid flowing through a porous solid can be expressed by the following form of the Darcy equation:

$$Q = -k \cdot A/\mu \ (dP/dx) \qquad\qquad\qquad (3)$$

where Q is the volumetric flow rate (m³/s), A is the total cross-sectional area (m²), and μ is the viscosity of the liquid. P is the component of the pressure capable of causing flow, and k is the permeability coefficient characteristic of the porous medium and is independent of the fluid, provided that the fluid flow is laminar. When considering water flow in cement, it is common to calculate the hydraulic conductivity, K, as given by

$$Q = A \cdot K \ (dh/dx) \qquad\qquad\qquad (4)$$

where dh/dx is the hydraulic gradient (i) across a specimen and is dimensionless.

The permeability of a hardened cement can be reduced by decreasing the porosity, the maximum pore size, and the extent of the interconnectedness of the pores. Reducing the *W/CM* ratio is also an effective means of decreasing the permeability. However, significant decreases in the *W/CM* ratio can result in difficulties with placing and consolidating the cement. These difficulties can be overcome by using water reducers (such as super-plasticizers) and by adding pozzolanic materials. The addition of pozzolanic material alters the microstructure of the cement that forms on hydration. Studies by Sellevold et al. (1982) and Huang and Feldman (1985) indicate that pozzolans, such as silica fume, do not influence the total porosity significantly. They reduce the volume of the capillary pores, while increasing the hydrated product porosity, and significantly decrease the volume of interconnected pores. By producing smaller and more discontinuous pores, silica fume markedly decreases the permeability of cements (Al-Manaseer et al. 1990).

In addition to the *W/CM* ratio and compositional effects, other factors can have a significant effect on the pore structure of the hardened cement. The microstructure in any given system is also a function of time. At early stages of curing, the microstructural features develop rapidly as the cement reacts with water. The hydration processes in most cement systems are rarely fully completed, with residual unhydrated cement remaining in all mixtures. Hydration processes may continue over long periods of time, and concomitant changes in microstructure may occur from the formation of new hydration products. Changes in microstructure may also take place because of solid-solid phase changes and a chemical breakdown of the hydrated and unhydrated phases of hardened cements. The chemical breakdown may occur through processes such as leaching/dissolution, precipitation and reprecipitation of certain previously existing components, and may be independent of any additional hydration.

Leaching by water involves the penetration of the grout by water or aqueous solutions, the dissolution of soluble constituents of the hydrated grout and transport of the dissolved species through the pore structure to the surrounding water. The depth to which the water or aqueous solution will penetrate into the grout is largely controlled by the permeability of the grout and the chemical potentials in the free water and the pore water. The permeability of the grout is important in limiting the mass transport

of corrosive agents such as sulfates or chlorides into the grout and leach-
ing of the cement components from the grout.

The hydraulic conductivity (K) and permeability were determined on the
reference grout at *W/CM* ratios between 0.4 and 0.8. K was assessed for
grout specimens under compressive and tensile stress using specially
designed radial flow permeameters (Figure 17). The apparatus was designed
to withstand hydraulic pressures of up to 10 MPa. Hydraulic gradients of
up to 40 000 can be applied radially across the 25-mm-thick wall of the
grout specimen. Al-Manaseer et al. (1990) described the experimental
design and methods.

Results from the compressive test series for grouts with no silica fume and
10% silica fume revealed that both grouts tend to store some water over the
ranges of time and pressure investigated. Under hydraulic pressure differ-
ences greater than 4000 kPa (i > 16 500), grout with no silica fume trans-
mitted water in the i direction (see Figure 18). Hydraulic pressure dif-
ferences equal to or greater than 8600 kPa (i > 35 000) were needed to
obtain a measurable through-flow of water at the outflow end of the speci-
men containing silica fume (Figure 19).

Figure 20 shows flow data for the grout containing 10% silica fume at a
W/CM ratio of 0.4 with the specimen in tension and hydraulic pressure
differences up to 2000 kPa. The results show there is no measurable
through-flow of water. The grout has a very low hydraulic conductivity
($<10^{-14}$ m/s). These findings are similar to those obtained from grout
samples that had similar compositions and had been subjected to a compres-
sive radial flow. The water flow did not follow Darcy's Law under either
compressive or tensile stress conditions. Only very high hydraulic gradi-
ents, which could only be applied under compressive stress conditions,
caused water to flow through the specimens.

Also, the data show that silica fume decreases the apparent hydraulic con-
ductivity of the grout, which is approximately 10^{-15} m/s for the grout
containing silica fume and is little influenced by the *W/CM* ratio (see
Figure 21). For mixtures without silica fume, K increases with the *W/CM*
ratio for *W/CM* > 0.6. Below this value, K is of the order of 10^{-14} m/s
and is not significantly influenced by the *W/CM* ratio.

Ongoing investigations on the permeability of cement grouts have confirmed
that the reference grouts containing silica fume have very low hydraulic
conductivities ($<10^{-14}$ m/s). Also, the data show that grouts with *W/CM*
ratios of 0.4 and 0.6 are practically impermeable under hydraulic gradients
up to 36 000. This is very much higher than the gradients expected in a
disposal vault, which may be as low as 10^{-2} (Chan 1989). Water did not
pass through the specimen at these low gradients, and both grouts showed a
tendency to take up and store water.

A number of possible explanations, such as the presence of entrained air in
the pore spaces, continued hydration reactions, and morphological trans-
formation of hydrated cement minerals, could account for the total resis-
tance to the through-flow of water at gradients (up to 36 000) higher than
the gradients expected in a disposal vault (0.01). Results from the tests

conducted on specimens contained in the systems from which air has been virtually excluded show that the air entrapment does not appear to be a major factor affecting flow resistance (Figure 22).

Laboratory studies carried out to assess the effect of leaching/dissolution of cement phases on the pore structure of the reference high-performance grouts partially explain the findings in the permeability and hydraulic conductivity tests (Onofrei et al. 1990). The decrease in hydraulic conductivity caused by the decrease in the W/CM ratio and the addition of silica fume is a consequence of the decrease in pore size and the decrease in the connected capillary pore space.

The porosity studies in deionized distilled water reveal that the porosity of hardened grout changes during leaching, but only within limits that depend on the grout composition and initial porosity. The decrease in the pore radius during leaching (Figure 23) depends on the total porosity of the grout and, more importantly, on the reactivity of the cement and the volume and the type of hydration products developed in the grout during leaching. Changes in porosity during leaching are related mainly to changes in the volume of solids caused by the formation of new hydration products as a result of the increase in the degree of hydration. Microscopic analysis of leached grout samples provided evidence to support these findings. The microscopic examination showed that most of the large pores contained solid hydration products. Figure 24 shows an electron micrograph of the fractured cross section of a sample of reference grout at a W/CM ratio of 0.4 after 32 d of leaching. The solid hydration product observed in the pore was identified as a calcium silicate phase; the lamellar morphology is characteristic of Type 4 calcium silicate hydrate.

In the past, durability models developed to estimate the long-term performance of cement grouts were based on the assumption that the grout would degrade through pore-water exchange and associated leaching processes. A decrease in the performance of cement grouts was considered to be the result of increased porosity. Our laboratory studies on the porosity and permeability of grouts tend to suggest that the distribution of pore sizes rather than total porosity provides a measure through which longevity can be assessed. The smaller pores do not make a significant contribution to permeability, and thus do not appear to allow for efficient pore-water exchange and cement dissolution. Furthermore, observations from the permeability and porosity studies tend to indicate that the conventional models, which suggest that porosity will increase as water flows through and dissolves the cement, may not be appropriate to describe the bulk performance of the reference grout.

3.2   NUMERICAL MODELLING

The description of the microstructure and properties of high-performance cement grouts developed through the laboratory work described in Section 3.1 was not available at the outset of our investigations, and so the initial model developed to predict grout performance was necessarily simplistic. Further work was essential to allow for numerical simulation, the results of which would be used together with those from laboratory tests to guide the assessment of the performance of cement-based grouts. Critical

parameters and data deficiencies would be identified and returned as feed-
back to the assessment programs.

Alcorn et al. (1989) proposed that a numerical assessment of the long-term
performance of cement-grout sealing systems would require a coupled analy-
sis of the materials' chemical and physical properties. Specifically, the
effects of chemical changes on the hydraulic performance of the material
would have to be analyzed. Two sub-models were developed. The first — the
permeability model — attempted to relate porosity to hydraulic conducti-
vity. The second — the grout composition model — attempted to simulate the
effects of long-term geochemical change on the porosity of the grout.
These models would then allow the time-dependent changes in porosity to be
related to performance.

3.2.1   The Permeability Model

It is clear from Section 3.1 that flow through high-performance grouts is
complex and is not simply related to the total porosity. However, Coons
and Alcorn (1989) used data available in the open literature on ordinary
cements and concretes to show that, in general, the relationship in Equa-
tion (5) can be used to express the effects of a change in hydraulic con-
ductivity (dK) on the change in porosity (dn):

$$dK = (K\star)10 \exp[(11.14)(dn)] - K\star \qquad\qquad (5)$$

where $K\star$ is the initial hydraulic conductivity of the grout.

This equation is based on the implicit assumptions that all porosity is
connected and contributes to flow, and that the relationship is valid in-
definitely. These assumptions introduce conservative and nonconservative
factors into the analysis, and the combined effects of these on the vali-
dity of the longevity model remain to be assessed.

3.2.2   The Grout Composition Model

A simplified representation of the initial chemical system was developed
assuming a composition of crystalline solids in fixed chemical proportions
(Alcorn et al. 1989, Coons and Alcorn 1989). Fundamental input parameters
such as Gibb's free energy, molar entropies, solubilities and volumes of
interacting phases allowed likely changes in the chemical system to be
calculated. Uncertainties existed in these calculations in that thermo-
dynamic predictions could not be made with confidence until specific data
for specific formulations were available. The analysis used thermodynamic
data available in the open literature and, whenever possible, from the
ongoing laboratory studies.

The normative composition for the theoretical grout shown in Table 6 was
developed on the basis of the known composition of Type V portland cement
and the fact that excess silica would be included in the reference grout in
the form of silica fume. This neglects the presence of magnesium and other
components in smaller quantities in the material. The normative composi-
tion was sequentially developed by partitioning all the sulfate into et-
tringite, making hydrogarnet from all the remaining alumina, assuming the
iron to be ferric and using it in place of aluminum to produce more

ettringite and hydrogarnet, and using the remaining calcium to make tober-
morite. The full rationale for this sequencing and mineral selection is
given by Coons and Alcorn (1989).

3.2.3 Coupled Performance Modelling

To establish the maximum consequences of dissolution for the upper bound,
groundwater was assumed to saturate the grout and exit the grout with the
dissolved constituents. Precipitation was suppressed. Flow through the
grout and associated increases in porosity were simulated by repeatedly
equilibrating 1.0 L of groundwater with the grout phases and progressively
dissolving them. The time it would take this volume of groundwater to
permeate the grout was calculated using the hydraulic conductivity of the
grout in Darcy's Law and assuming various values for the hydraulic gradi-
ents. Stepwise calculations yielded the time it would take to dissolve
enough grout so the hydraulic conductivity of the grout would exceed a spe-
cified minimum performance value. The calculations assumed that the ini-
tial K of the grout is 10^{-12} m/s and that the hydraulic gradient for the
first 100 a in a vault is 1000, after which it reverts to a value of 1.
The hydraulic gradients are higher than anticipated at a depth of 1000 m in
a vault in granitic rock after sealing (Chan 1989), and conservatively re-
flect the uncertainty during an assumed initial 100-a period when the vault
would be unsealed and could cause a drawdown in the water table. It was
also necessary to assume that the grout contains cryptocrystalline phases,
with thermodynamic properties described by the EQ3NR/EQ6 database but en-
hanced, where possible, for known grout phase properties. The model pre-
dicts acceptable grout performance (K < 10^{-9} m/s) for at least 300 000 a
(Coons and Alcorn 1989).

The laboratory leaching studies showed that the precipitation of portland-
ite, carbonate and CSH tends to clog the pores of both high-performance and
other grouts. An equilibrium model was developed as a possible lower-bound
case to account for this observation (Alcorn et al. 1989). In general, a
disposal vault is expected to be sited in hydrogeological conditions where
the groundwater flow is very small. In such conditions, the water flow
through low-permeability sealing materials will likely be slow enough to
favor the attainment of geochemical equilibrium. An equilibrium model
similar to the upper-bound model was established where the precipitation of
secondary phases would not be suppressed. Changes in porosity were
calculated in this model as the net change caused by an increase resulting
from dissolution minus the decrease due to precipitation (Alcorn et al.
1989). This model predicted an acceptable performance for hundreds of
thousands to millions of years.

4. SUMMARY AND CONCLUDING REMARKS

Parallel developments in conceptualizing the factors affecting the long-
term properties of high-performance cement-based grouts are being made
through laboratory experimentation and numerical simulation. Neither ap-
proach has yet provided a definitive assessment of the longevity of the
grout material when it is used to seal a nuclear fuel waste disposal vault.
However, both approaches have provided evidence to suggest that the perfor-

mance is likely to be acceptable for at least thousands of years and pro-
bably for much longer periods. These performance estimates are based on
numerical modelling studies and are supported by the laboratory investiga-
tions.

Uncertainties in the numerical modelling arise from a number of sources.
These are largely related to the assumptions made in developing the model.
These assumptions were necessary because the thermodynamic properties of
the phases, particularly the CSH phases and also the CAH phases and sul-
fates, are not known completely in high-performance cement. Our under-
standing of the relationships between phases, structure and porosity dis-
tribution in the grout is limited, and our knowledge about the hydraulic,
mineralogical and mechanical properties of the grout-rock interface is un-
certain. Furthermore, a need exists to determine the relationships between
porosity and hydraulic conductivity, and to understand the differences that
are expected between the properties of the grouts tested in the laboratory
and those of materials placed in situ (e.g., segregation).

These uncertainties are being addressed through coordinated laboratory stu-
dies and further numerical simulations. Our leaching tests on hardened
grout have shown that models not accounting for the precipitation and the
dissolution of solids are simplistic and likely underestimate the grout
longevity. Recognizing that precipitation would likely occur, the numeri-
cal models were modified to include precipitation effects and predicted a
10- to 100-fold increase in the period over which the grout's performance
could be acceptable. The microstructural analyses of leached samples also
indicated the presence of a CH phase that was not originally included in
the normative composition of the hardened grout used in the numerical
model. The model is now being modified to include this phase. In this
context, it is noteworthy that the microstructural investigations have
identified many of the secondary phases predicted by the numerical
modelling to be reaction products.

The laboratory studies have shown that the porosity/hydraulic conductivity
relationships for high-performance grouts are more complex than those es-
tablished for normal cements and concretes, and the materials may be re-
garded as virtually impermeable at the hydraulic gradients anticipated in a
vault. In these circumstances, the longevity predicted on the basis of the
porous-medium approach becomes questionable. The modelling approach may
have to be revised to accommodate the nature of the flow in fractures ex-
pected to form in the grout, the effects of precipitates and secondary re-
action products forming on the surfaces of these fractures, and the possi-
bility that diffusion through the grout and the rock may be a major mecha-
nism changing the microstructure of the grout and ultimately the perfor-
mance of the grouted rock mass.

It has been shown that the superplasticizers needed to produce the high-
performance grout are bound chemically within the microstructure of the
hardened materials. In particular, they are held in the high-calcium CSH
and CAH phases of the grout. Superplasticizer will likely be released
slowly as these phases become exposed to and react with groundwater. A
faster release rate can be expected from freshly exposed high-silica phases
on which superplasticizer is only physically absorbed. In general, super-
plasticizers improve the physical properties of a grout because of their

retention in the grout structure, and so should be considered for use in vault-sealing applications.

None of the results of the studies to date have contraindicated the use of high-performance cement-based grouts containing silica fume and superplasticizer in vault-sealing applications. Ongoing and future research is planned to address current uncertainties in both the conceptual and numerical modelling approaches.

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TABLE 1

CHEMICAL COMPOSITION OF TYPE 50 REGROUND CEMENT

Chemical Composition	Type 50 Reground	ASTM C 150 Specifications
Silicon Dioxide (SiO_2)	20.9	—
Aluminum Oxide (Al_2O_3)	3.00	—
Iron Oxide (Fe_2O_3)	4.40	—
Calcium Oxide (CaO), total	59.7	—
Calcium Oxide (CaO), free	0.18	—
Magnesium Oxide (MgO)	4.10	6.0 max
Sulfur Trioxide (SO_3)	3.96	2.3 max
Loss on Ignition	3.20	3.0 max
Alkalies ($Na_2O + 0.658K_2O$)	0.55	—
Compound Composition		
Tricalcium Silicate (C_3S)	46.8	—
Dicalcium Silicate (C_2S)	27.5	—
Tricalcium Aluminate (C_3A)	0.66	—
Tetracalcium Aluminoferrite (Ca_4AF)	13.4	—

TABLE 2

CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF SILICA FUME

Chemical Composition	Percent by Dry Mass
Silicon Dioxide (SiO_2)	94.0
Aluminum Oxide (Al_2O_3)	0.80
Iron Oxide (Fe_2O_3)	0.30
Calcium Oxide (CaO)	0.30
Magnesium Oxide (MgO)	0.40
Available Alkalies as Na_2O	0.20
Available Alkalies as K_2O	0.80
Carbon (C)	1.00
Sulfur (S)	0.20
Loss on Ignition	2.80

Physical Characteristics	
Specific Surface Area (m^2/kg)	18 000 to 20 000
Specific Gravity	2.22
Bulk Density (kg/m^3)	250-300
Fineness (average diameter) (μm)	0.1-0.2
Percent Passing 45-μm Sieve	95-100
Particle Shape	spherical
Form	amorphous
Blaine Fineness (m^2/kg)	6000

Chemical composition and physical data provided
by SKW Canada Inc.

TABLE 3

COMPOSITION AND SELECTED PROPERTIES OF REFERENCE CEMENT GROUT

Mix Composition	
Solids	90% Canadian Type 50 } by dry mass; cement re- 10% silica fume } reground to Blaine fine- ness of 600 m²/kg
W/CM	0.4-0.6
Superplasticizer	Na-sulfonated naphthalene formaldehyde

Selected Properties	
Viscosity	As desired with *W/CM* and superplasticizer content
Setting Time	Initial — varies with temperature, 10-16 h Final — varies with temperature, 12-20 h
Strength	Varies with *W/CM*, time and temperature — 20-60 MPa at 28 d
Hydraulic Conductivity	$<10^{-12}$ m/s

TABLE 4

NOMINAL COMPOSITION OF GROUNDWATERS

Ion	Concentration (mg/L)		
	GG	WN-1	SCSSS
Na	8.3	1910	5 050
K	3.5	14	50
Mg	3.9	61	200
Ca	13	2130	15 000
Sr	—	24	20
Fe	—	0.56	—
Si	—	—	15
HCO_3	—	68	10
Cl	5.0	6460	34 260
SO_4	8.6	1040	790
NO_3	0.62	33	50
F	0.19	—	—
pH	6-7	6.5-7.5	6.5-7.5
Ionic Strength	0.0015 mol/L	0.26 mol/L	1.37 mol/L

TABLE 5

VALUES OF INDEPENDENT VARIABLES USED IN THE LEACH TESTS

Independent Variable	Leach Test Variable	Dimensions	Value of Coded Variable		
			-	0	+
x_1	Ionic Strength	mol	0.0015	0.26	1.37
x_2	Temperature	°C	25	85	150
x_3	Clay Cation Ex-change Capacity	meq/kg	no clay	160	800

TABLE 6

SIMPLIFIED MODEL CEMENT COMPOSITION

Type V Portland Cement (wt.%)		Normalized Composition (wt.%)	Normative Composition (mol%)	
SiO_2	25.0	25.8	Ettringite	1.7
Al_2O_3	3.4	3.5	Fe-ettringite	0.9
Fe_2O_3	2.8	2.9	Hydrogarnet	13.3
CaO	64.1	66.1	Fe-hydrogarnet	6.4
MgO	1.9	—	Tobermorite	77.7
SO_3	1.6	1.7		100.0
	98.8	100.0		
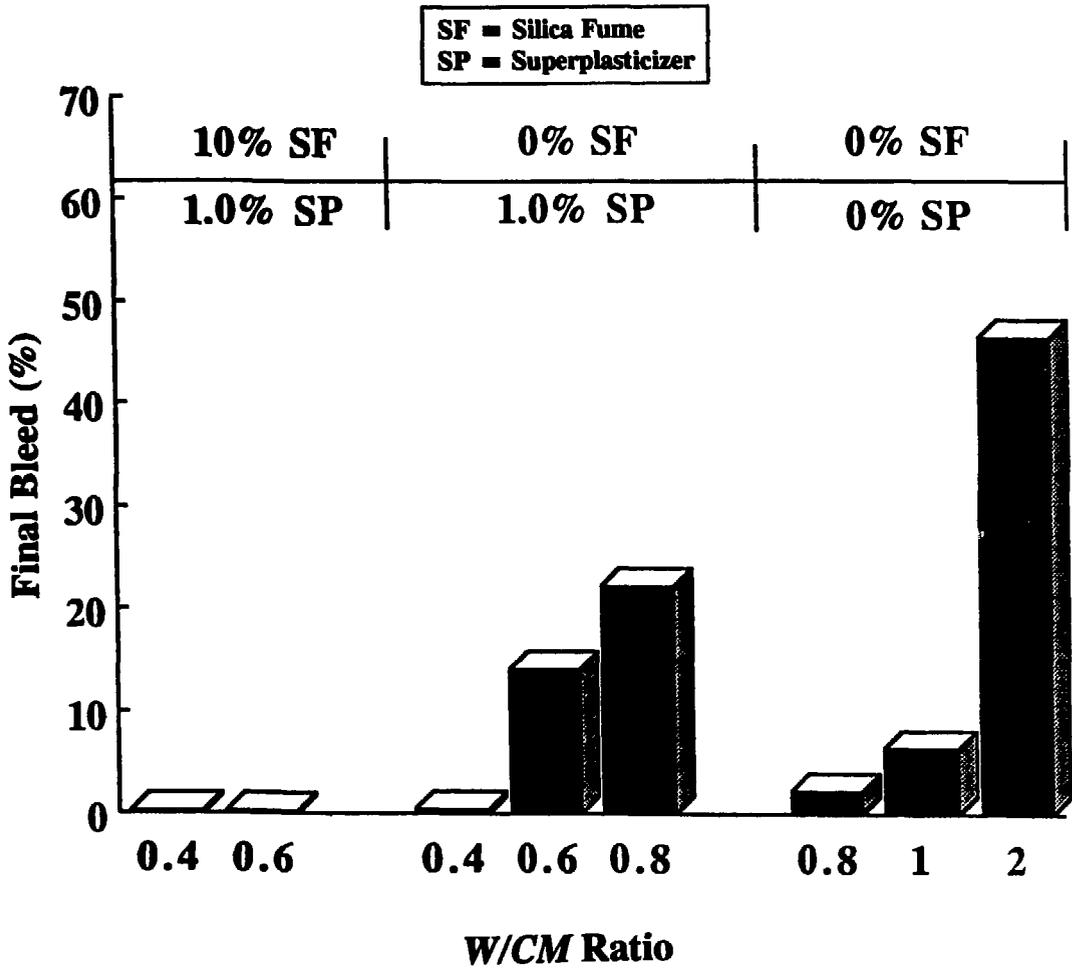
FIGURE 1: Final Bleed Observed for Various Grout Mixes
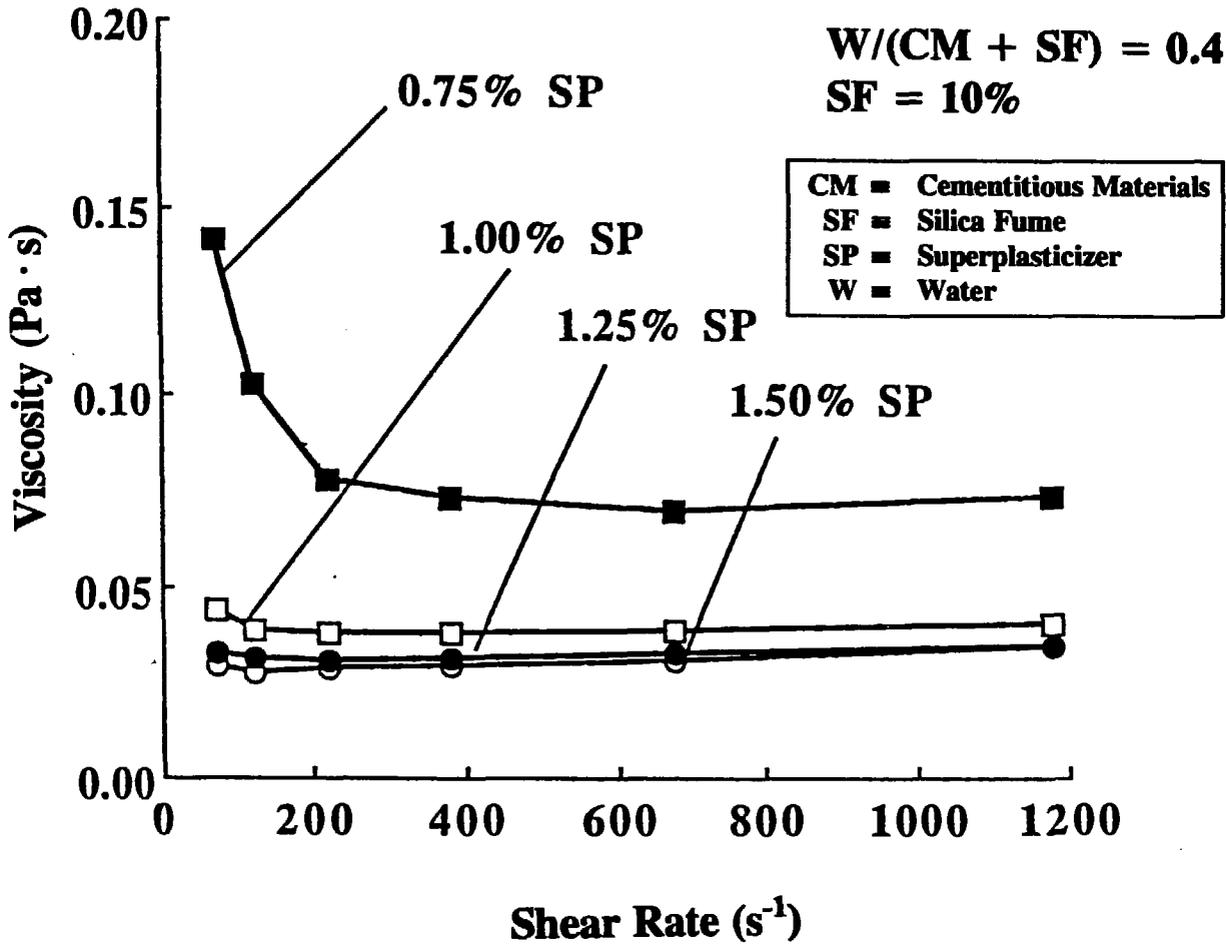
FIGURE 2: Viscosity vs. Shear Rate for Grout Containing 10% Silica Fume
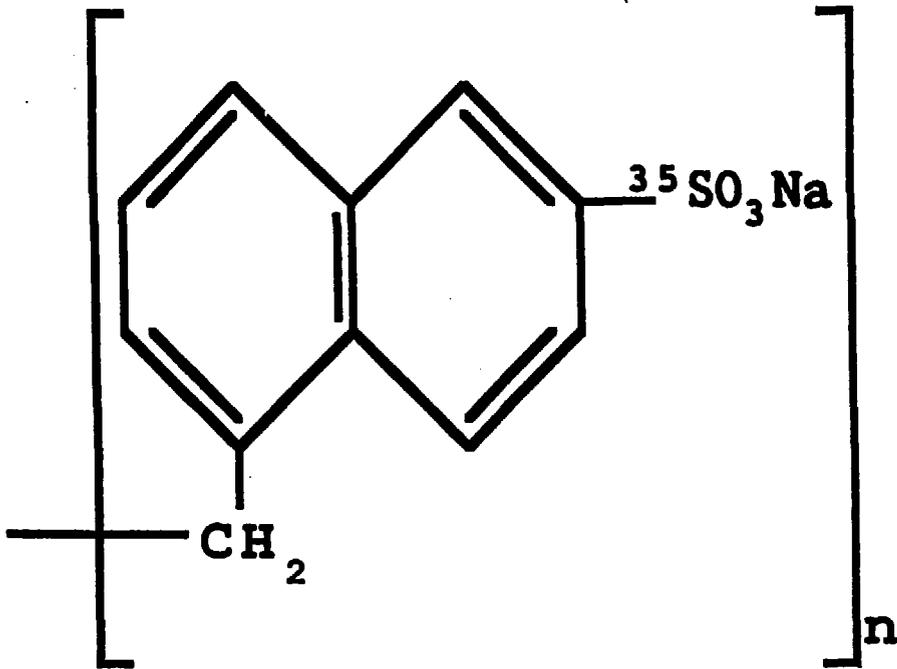
FIGURE 3: Chemical Formula of Na-SNFC

130 Level
Shaft Station

Ventilation Raise

Location of
Grout Trials

240 Level
Development

300 Level
Shaft Station

440 Level
Shaft Station
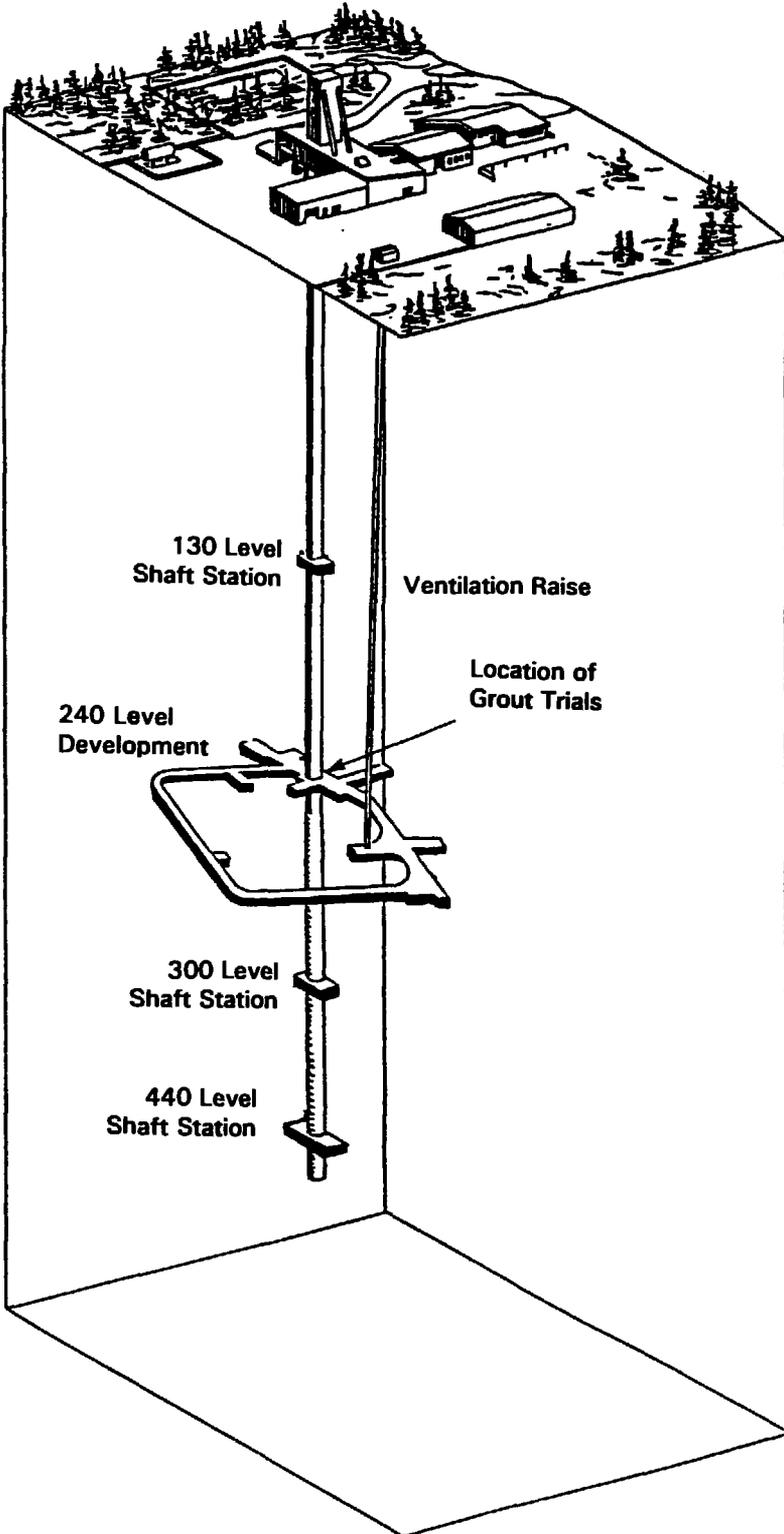
FIGURE 4: General Arrangement of the Underground Research Laboratory
in Manitoba, Canada
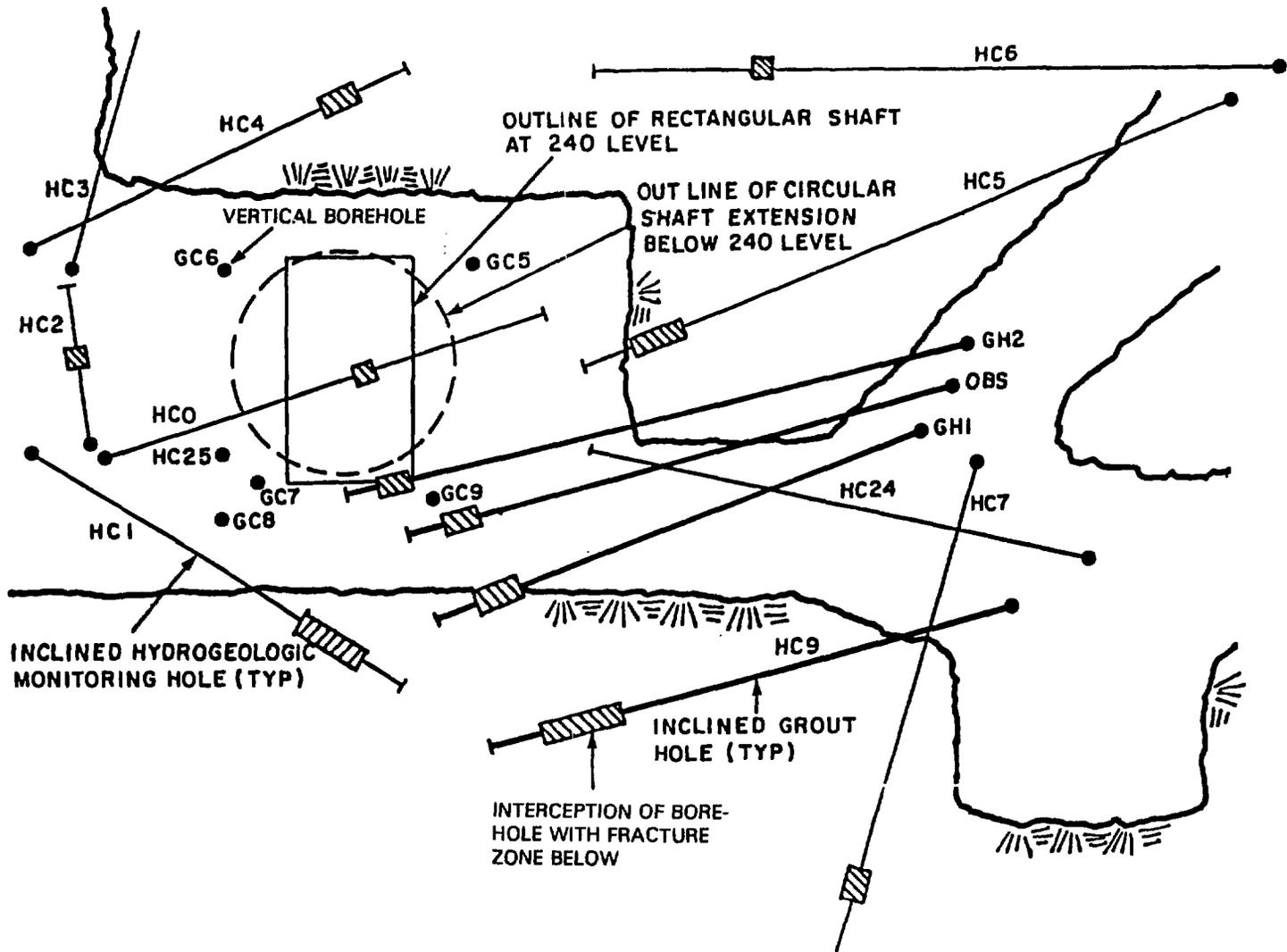
FIGURE 5: Plan View of Boreholes for URL Grout Trials

(a)

(b)

FIGURE 6: Photomicrographs of Thin Sections of Grouted Rock
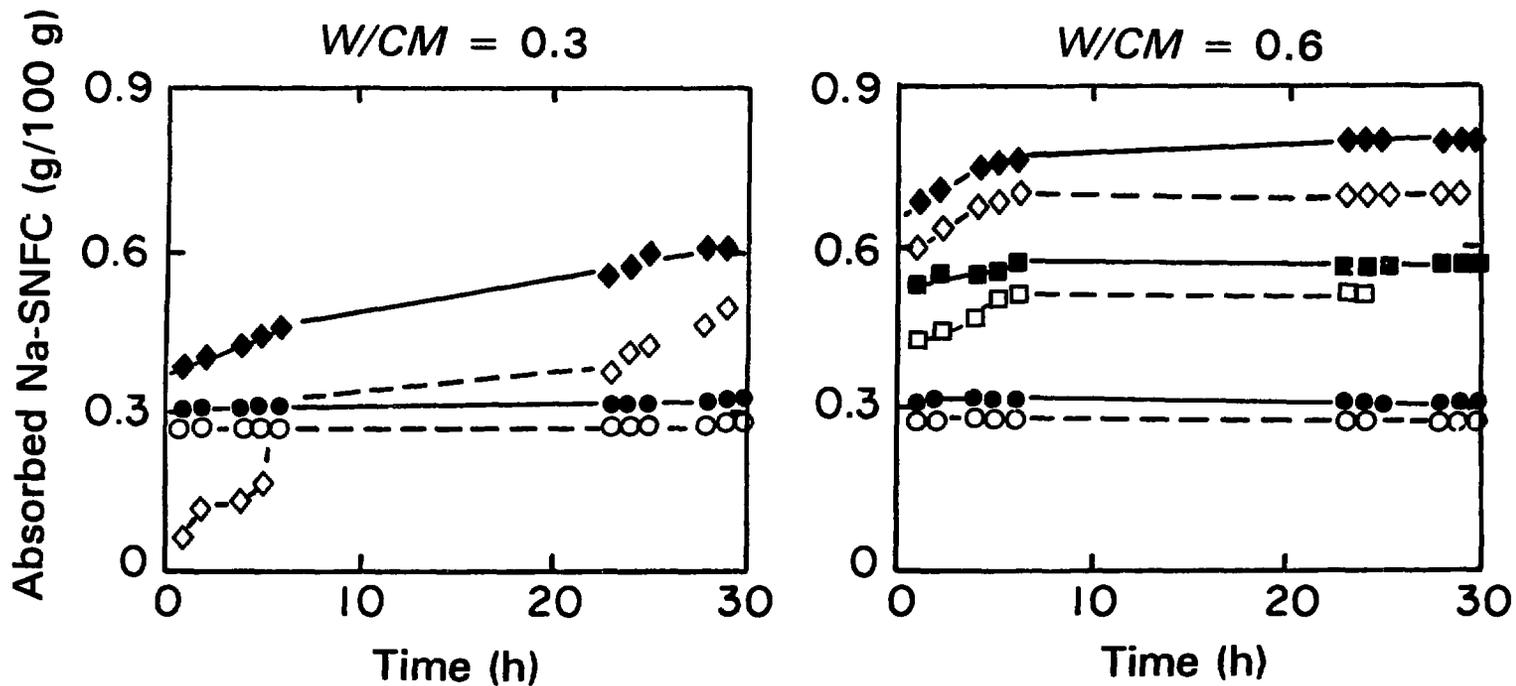
FIGURE 7: Influence of W/CM Ratio, Superplasticizer Content, Silica Fume Addition and Time on the Quantity of Na-SNFC Sorbed by Fresh Grout
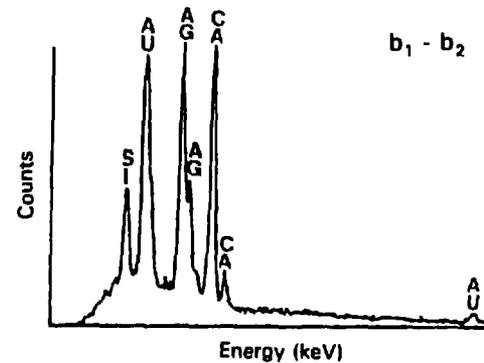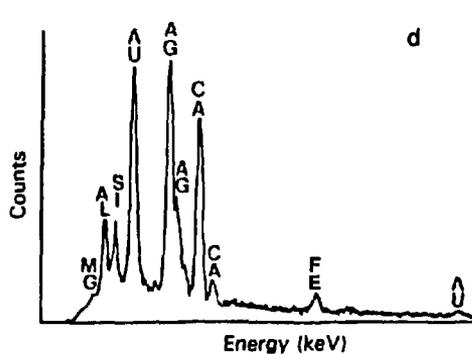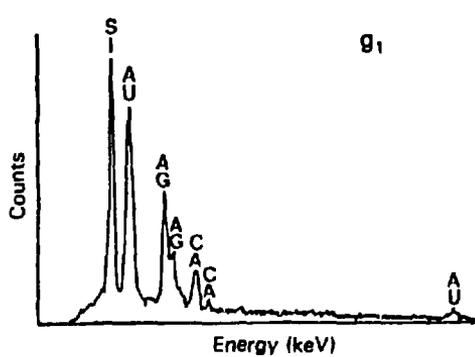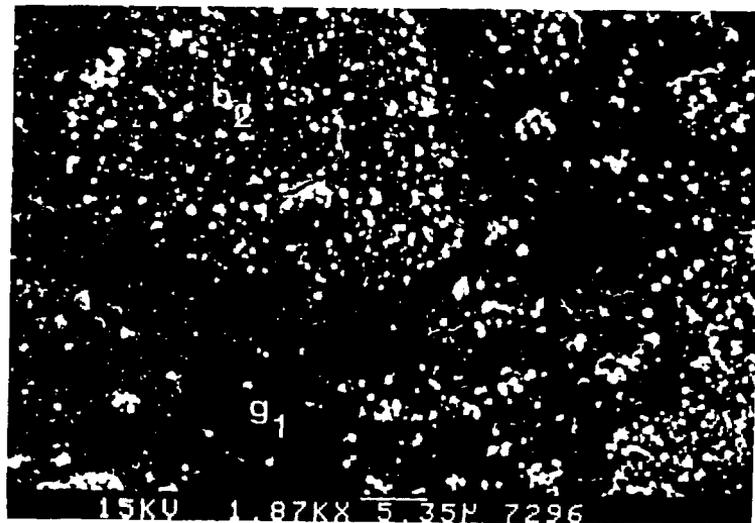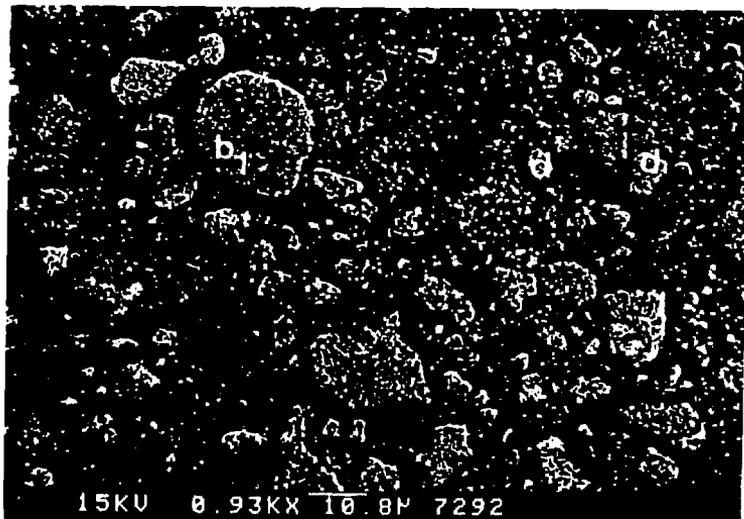
FIGURE 8: Electron Micrographs and EDX Spectra of Polished Surfaces of the Reference Grout at *W/CM* = 0.2, with 10% Silica Fume and 3% ^{35}S-Labelled Na-SNFC

Cement type
Blaine fineness
Silica fume
Superplasticizer
W/CM

50-600-10(2.0)-0.2 ----
50-600-0(2.0)-0.2 ——   SA/Volume = 0.05 cm^{-1}
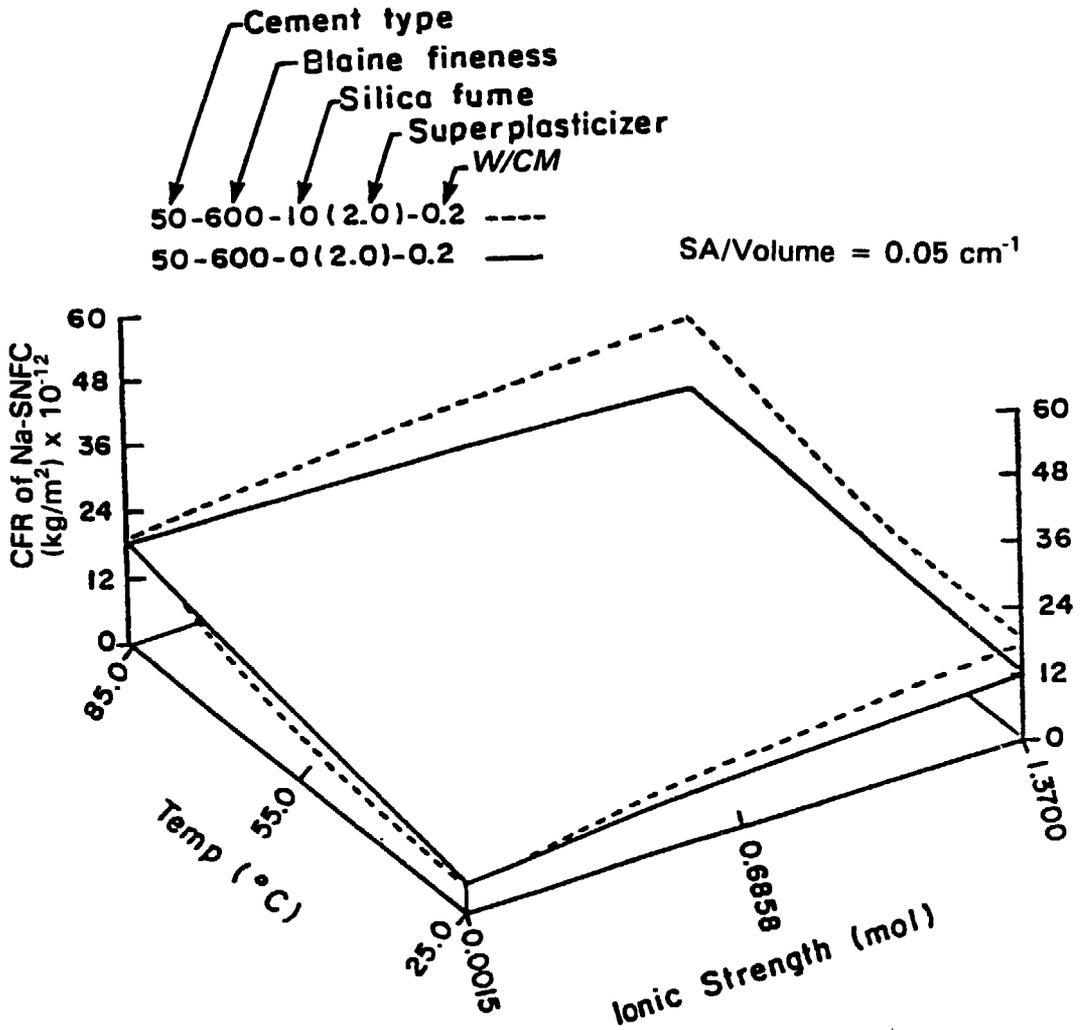
FIGURE 9: Cumulative Fractional Release of Na-SNFC from Reference
Cement Grout at *W/CM* = 0.2

50-600-10(2.0)-0.4 ----
50-600-10(0.5)-0.4 ———

Temperature = 85°C
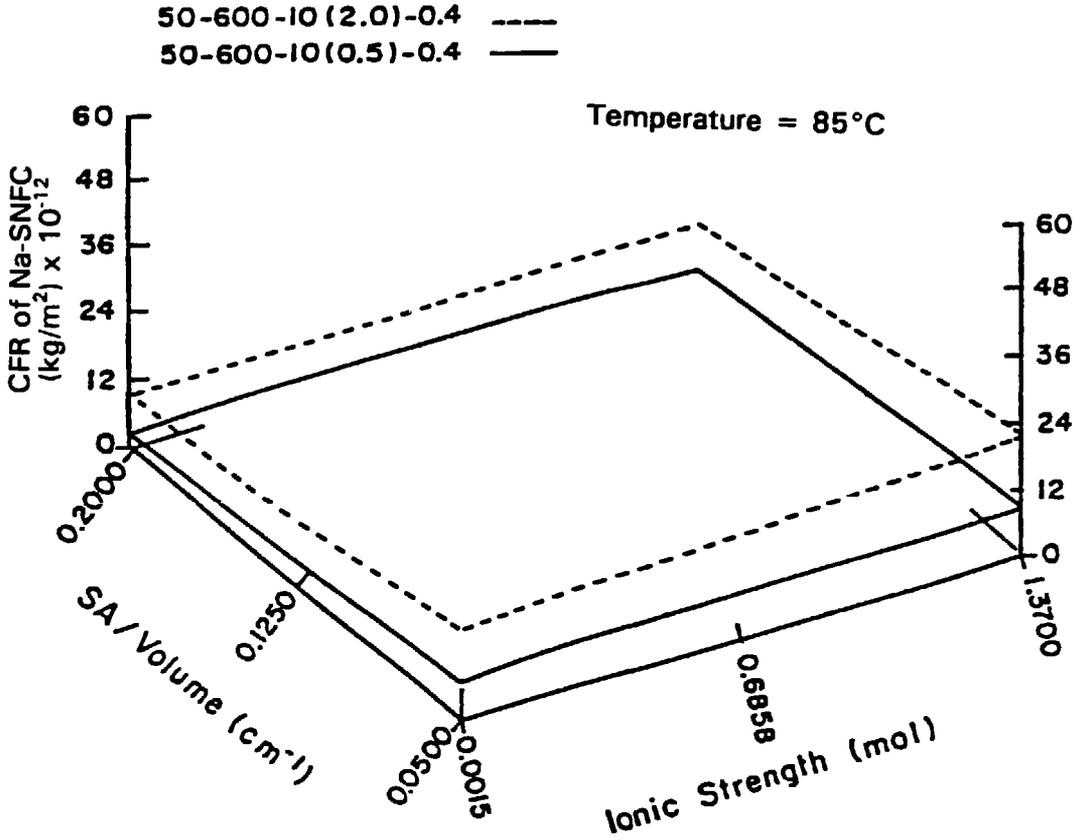
FIGURE 10:   Cumulative Fractional Release of Na-SNFC from Reference
Cement Grout at *W/CM* = 0.4, with 10% Silica Fume and 0.5
and 2.0% Na-SNFC

50-600-10(2.0)-0.4 ----
50-600-10(2.0)-0.2 ——

Ionic Strength = 1.37 mol

CFR of Na-SNFC (kg/m²) x 10⁻¹²

SA/Volume (cm⁻¹)

Temp (°C)

50-600-10(0.5)-0.2 ----
50-600-10(0.5)-0.4 ——

SA/Volume = 0.05 cm⁻¹

CFR of Na-SNFC (kg/m²) x 10⁻¹²

Temp (°C)

Ionic Strength (mol)
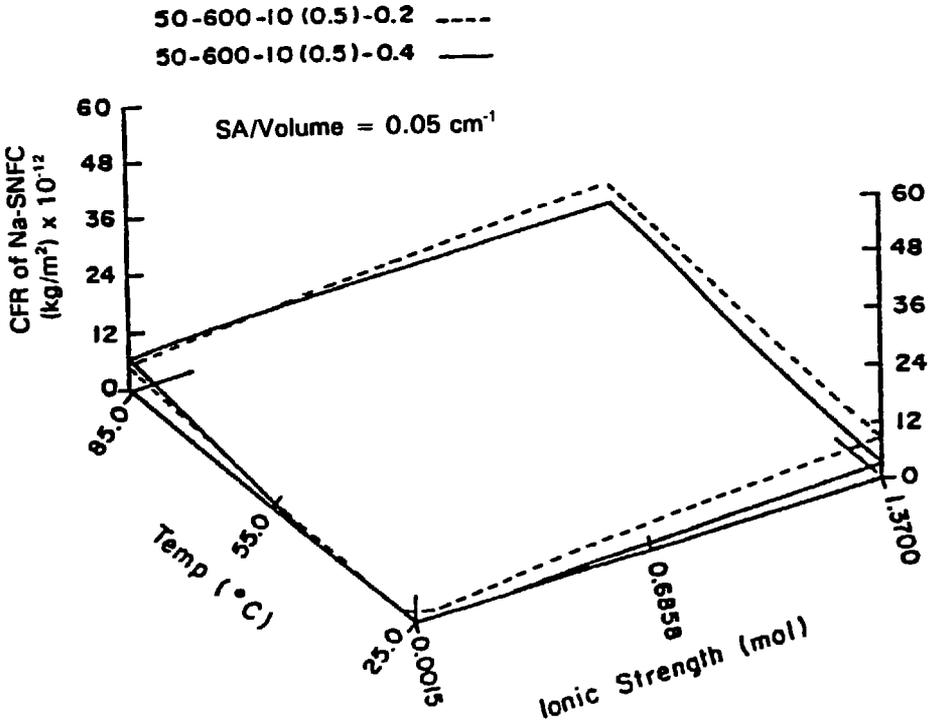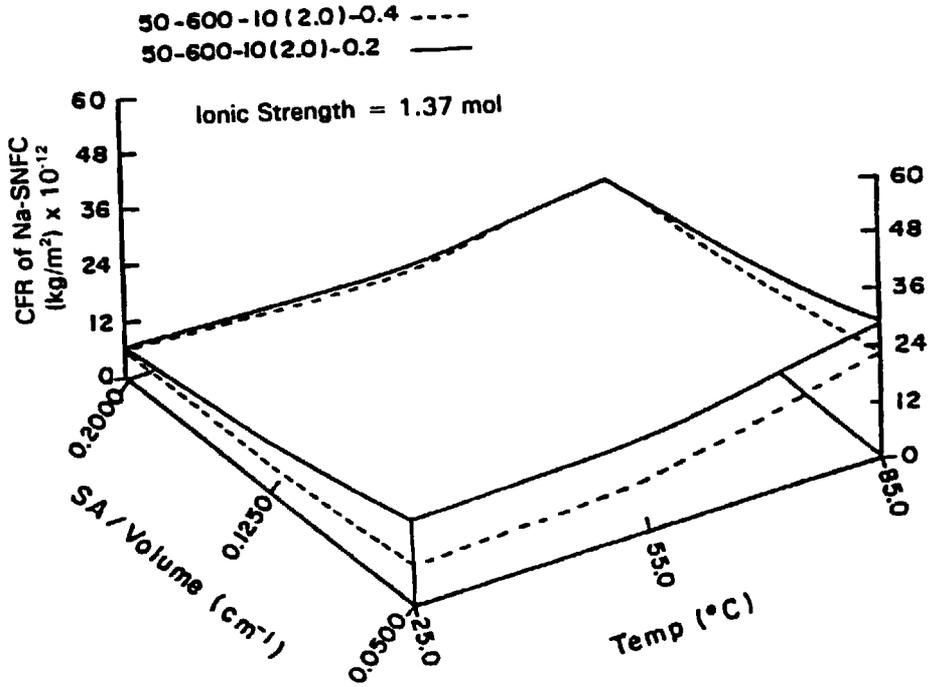
FIGURE 11: Cumulative Fractional Release of Na-SNFC from Reference Cement Grout at *W/CM* = 0.4 and 0.2 with 10% Silica Fume and 0.5 and 2.0% Na-SNFC
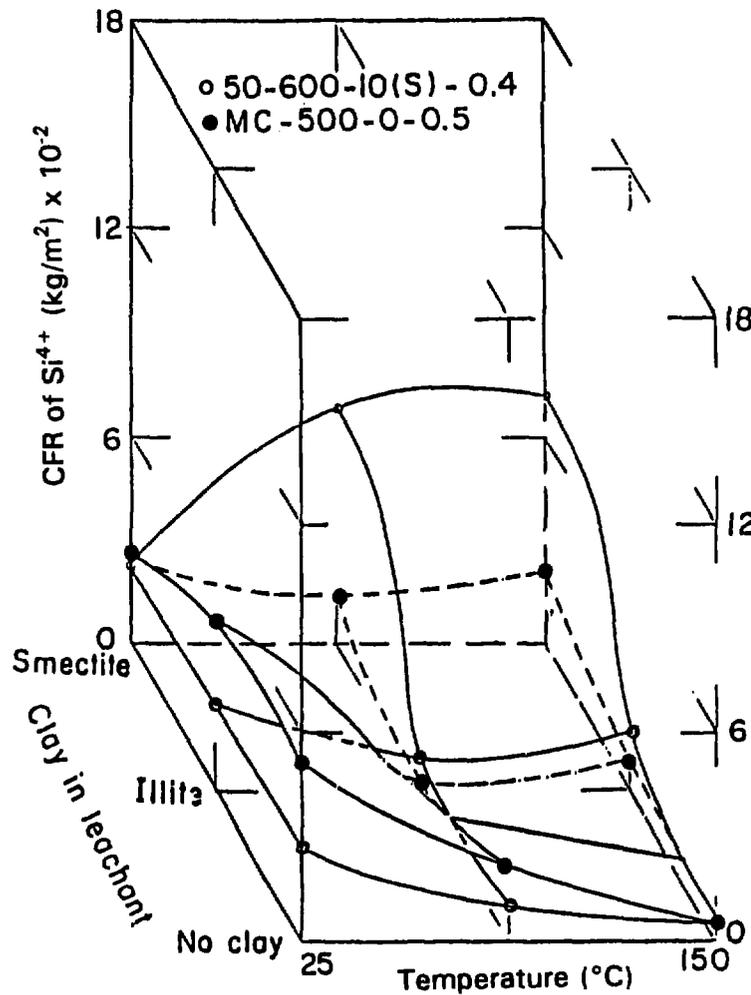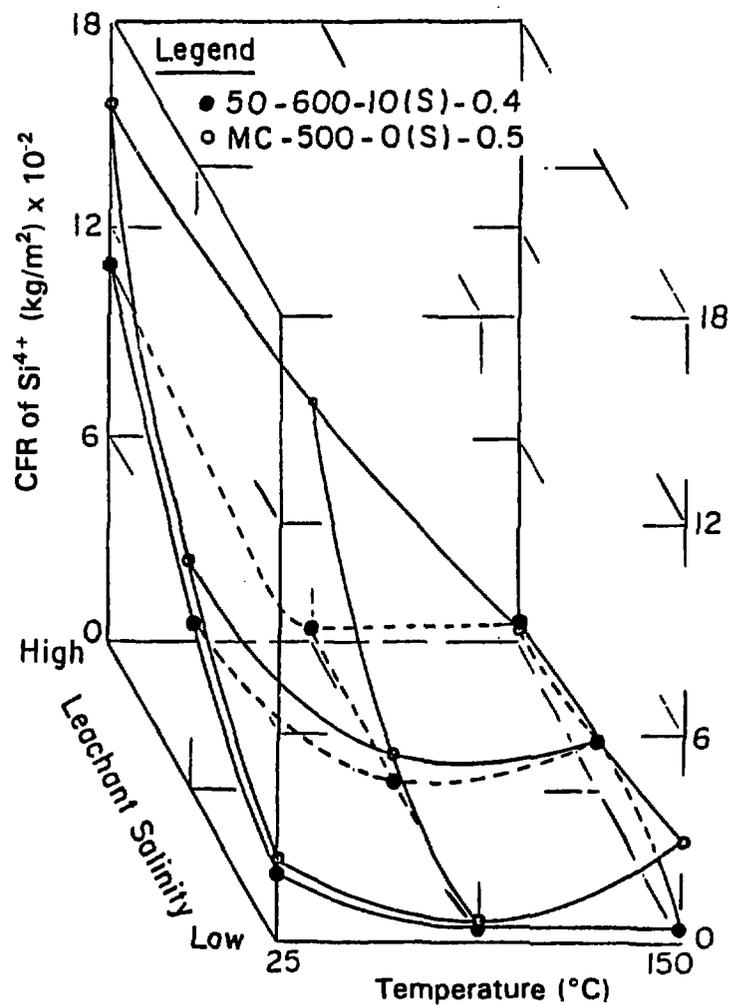
FIGURE 12: Effects of Leachant Salinity and Temperature on the Release of Calcium from the Reference Cement Grout and MC-500 in the Presence of Illitic Clay
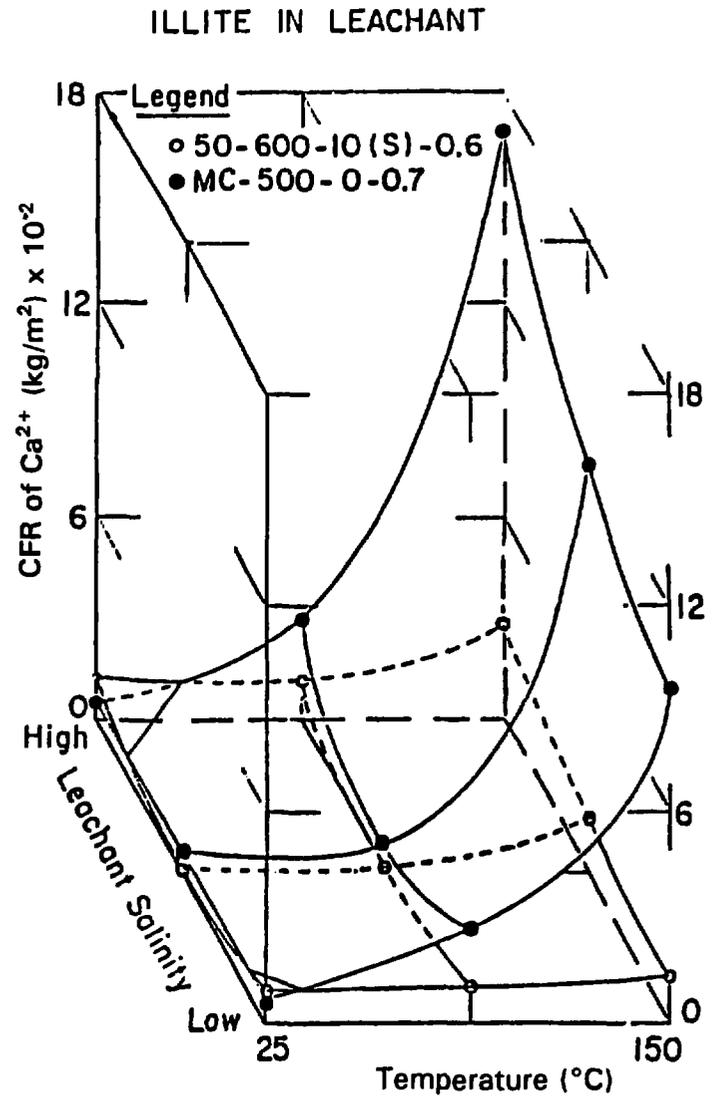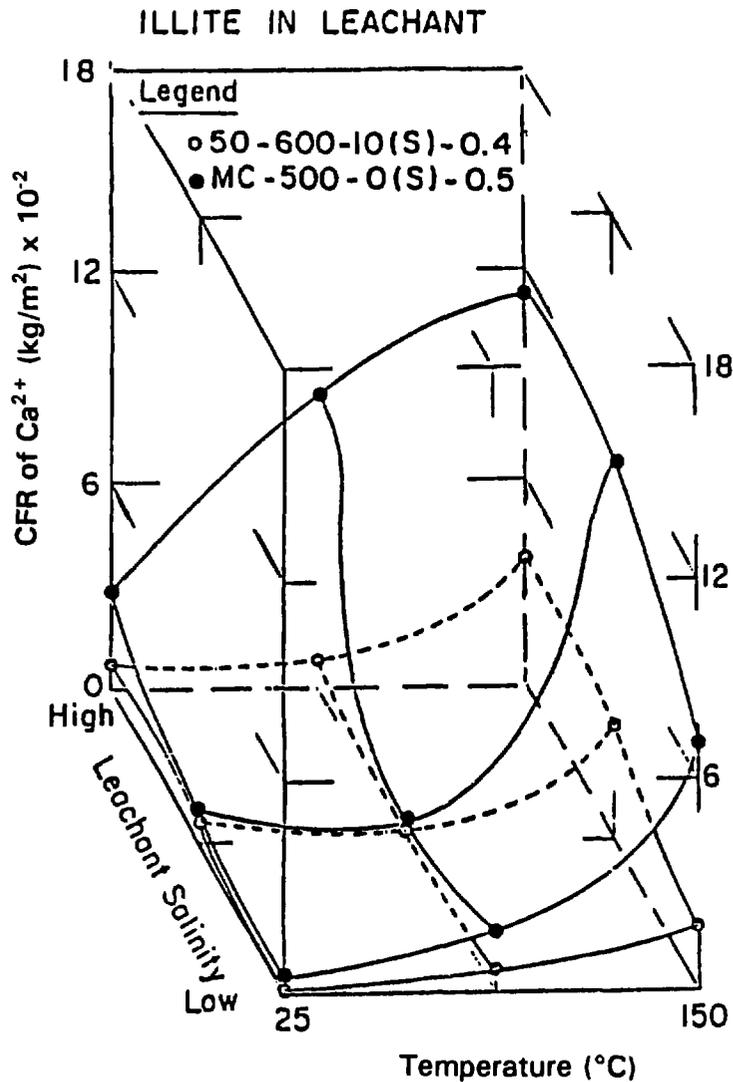
FIGURE 13: Effects of Temperature, Leachant Salinity and Clay Activity on the Release of Silica from the Reference Cement Grout and MC-500
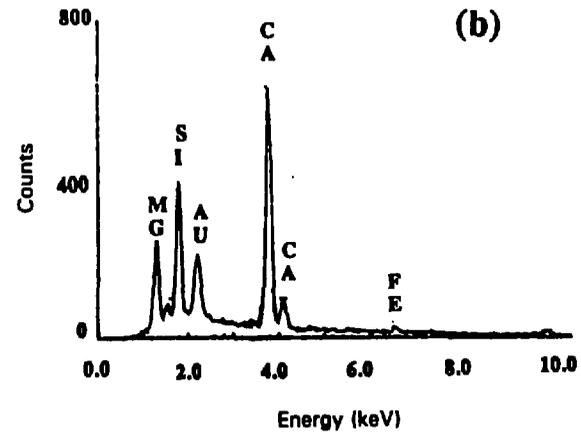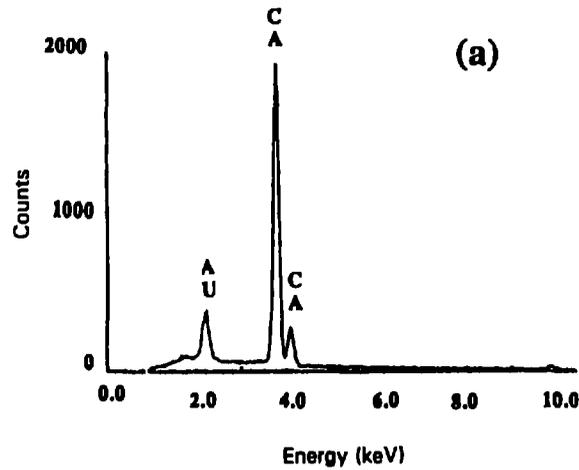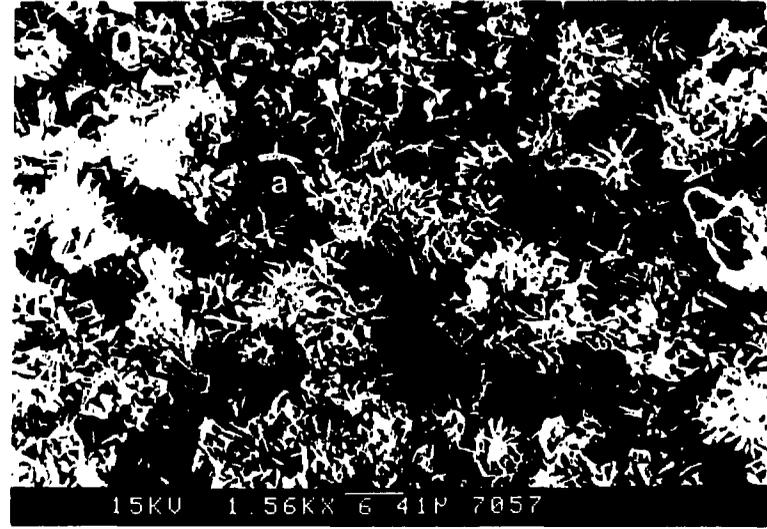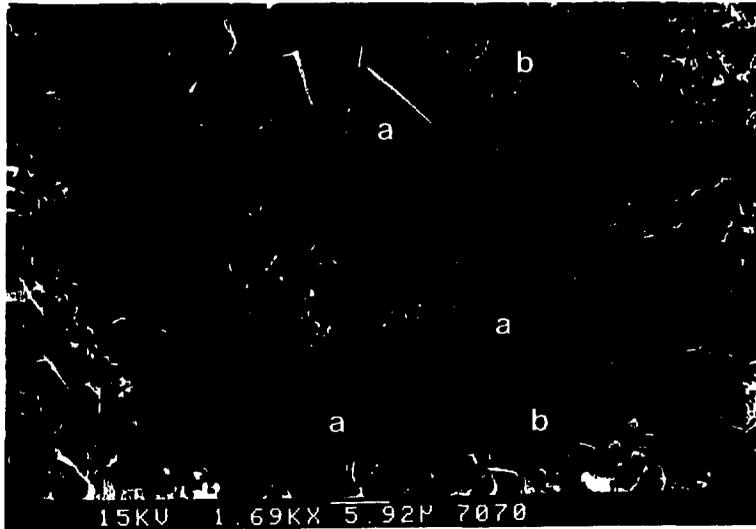
FIGURE 14: SEM Photomicrographs and Associated EDX Spectra Showing the Nature of the Surfaces (a) MC-500 and (b) the Reference Grout after Leaching in WN-1 at 150°C
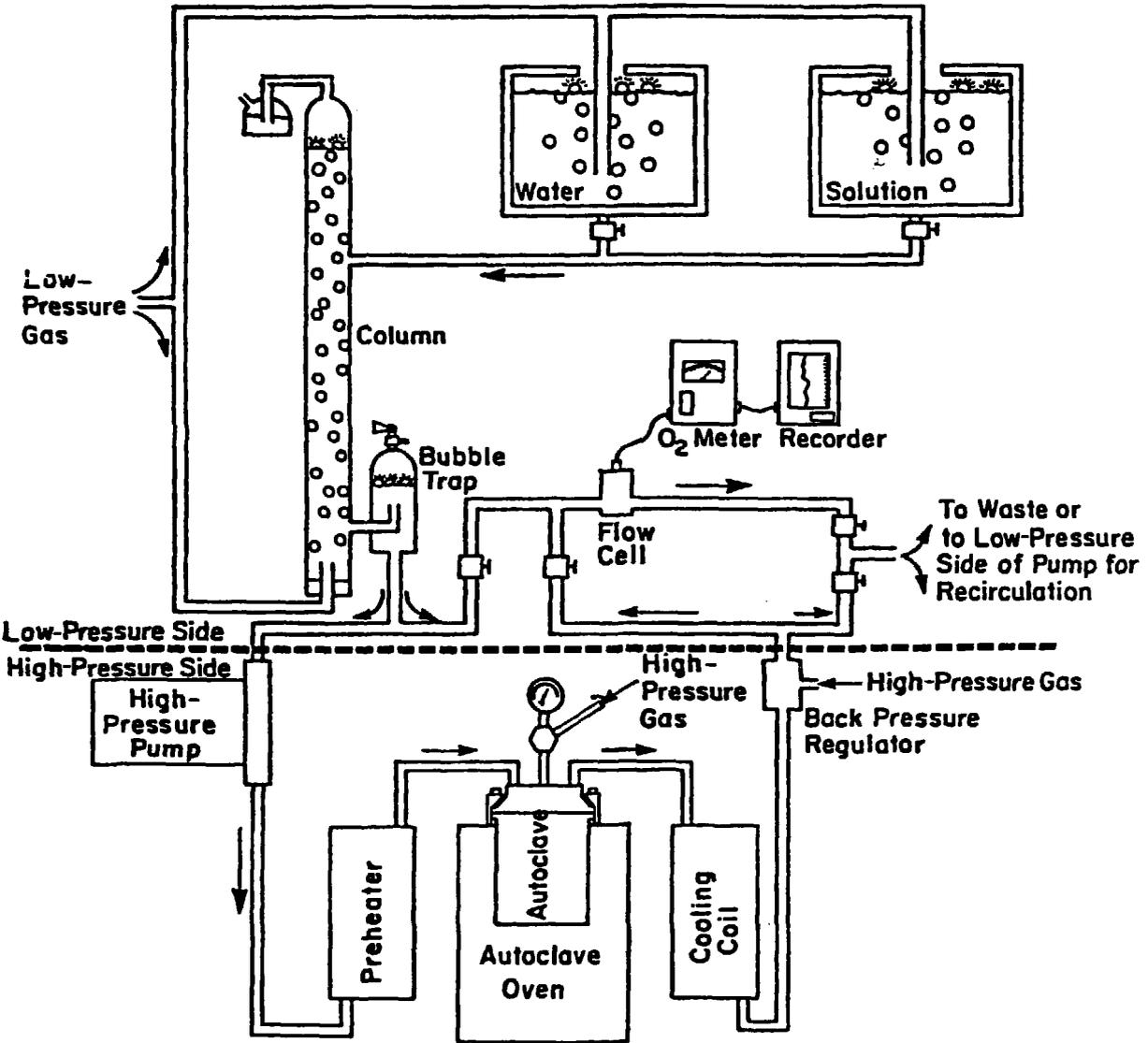
FIGURE 15: Single-Pass Continuous-Flow Leaching Concept
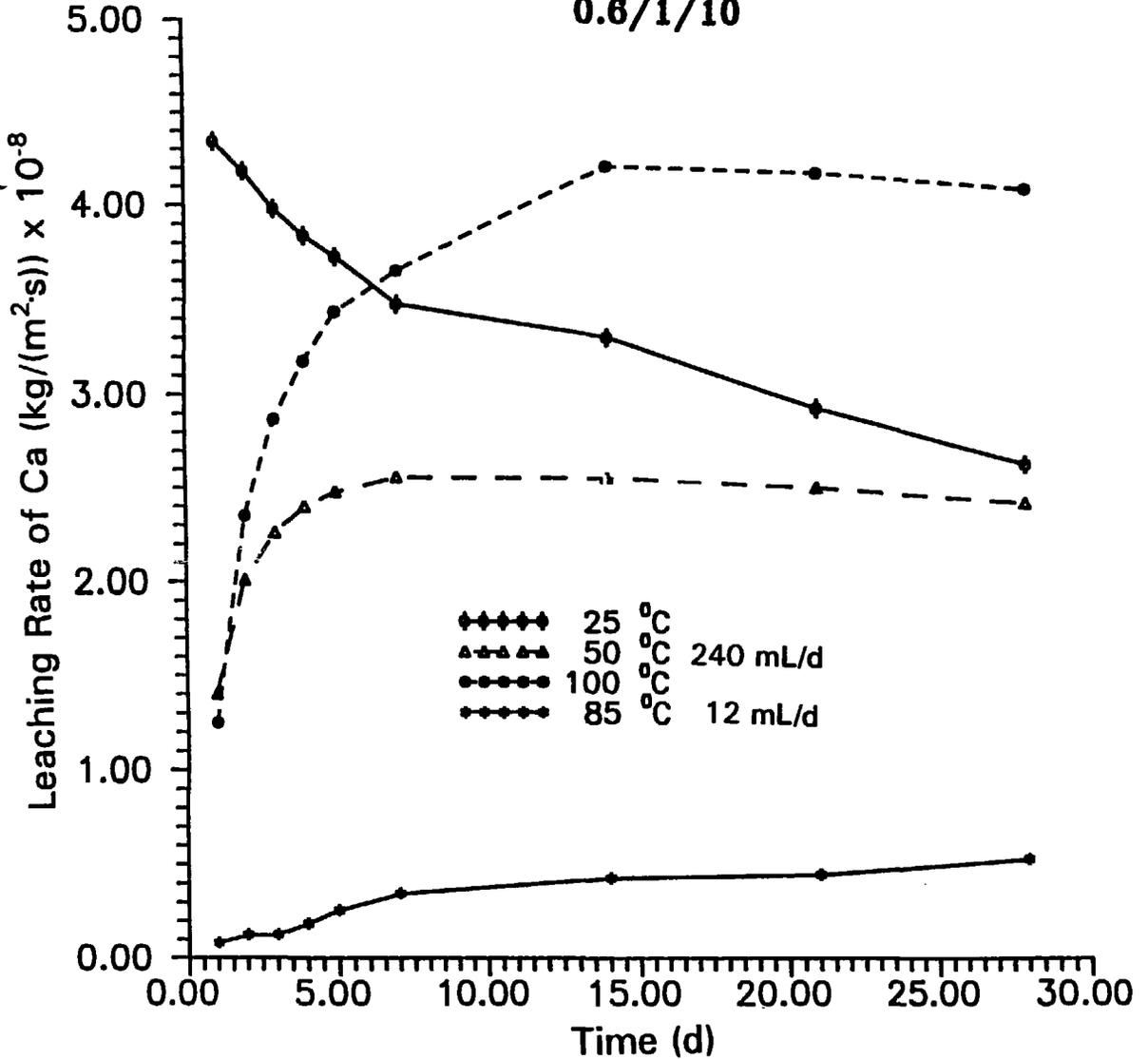
FIGURE 16: Effects of Time, Temperature and Flow Rate on the Leaching Rate of Calcium into Distilled Deionized Deaerated Water from the Reference Grout at *W/CM* = 0.6

1. Center retaining bolt
2. Water inlet/outlet
3. Air bleed fitting
4. Cell top
5. Center retaining bolt O-ring
6. Upper end cap
7. Neoprene gasket
8. Specimen chamber
9. Grout specimen
10. Lower end cap
11. Lower end cap O-rings
12. Specimen chamber O-ring
13. Water outlet/inlet
14. Cell bottom
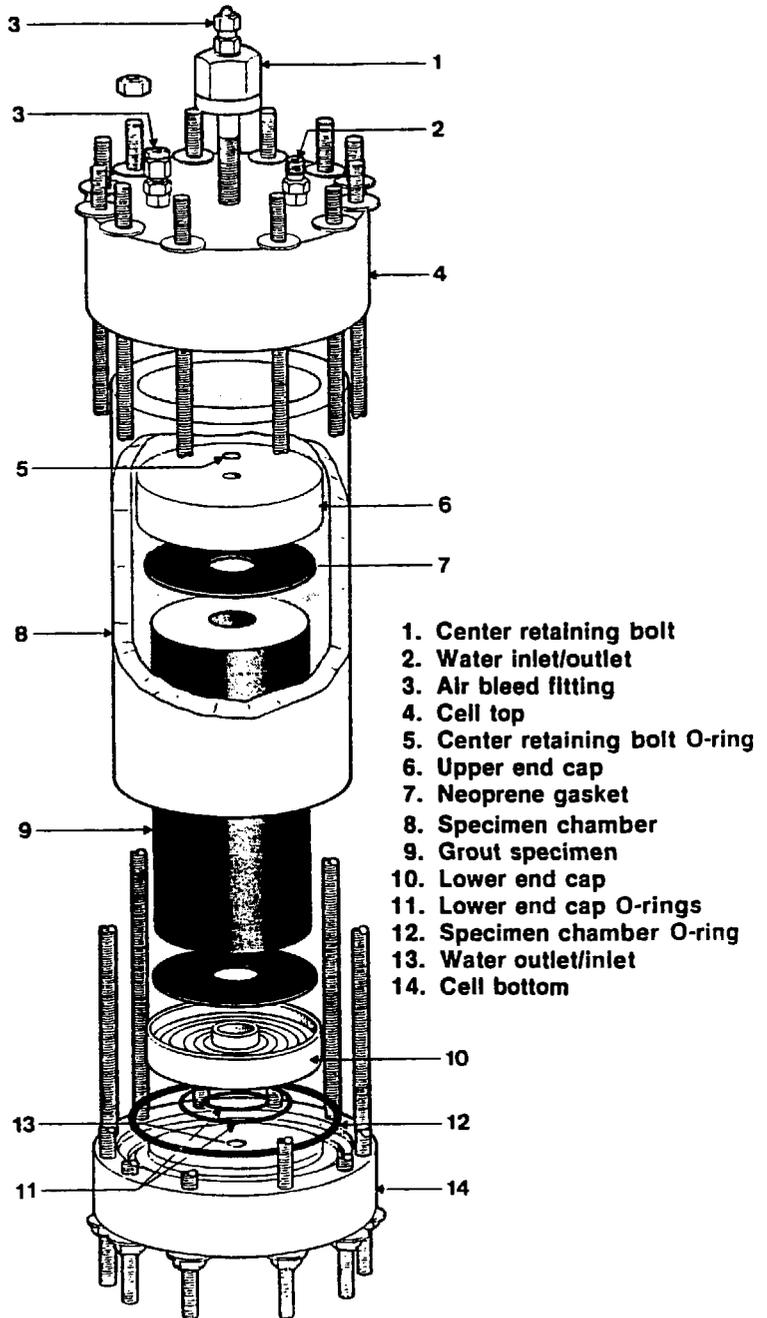
FIGURE 17: Hydraulic Conductivity Test Cell

LEGEND:

Inlet pressure   2200 kPa ▲
                        4200 kPa ■
                        7200 kPa ●

Note: Outlet pressure constant at 200 kPa
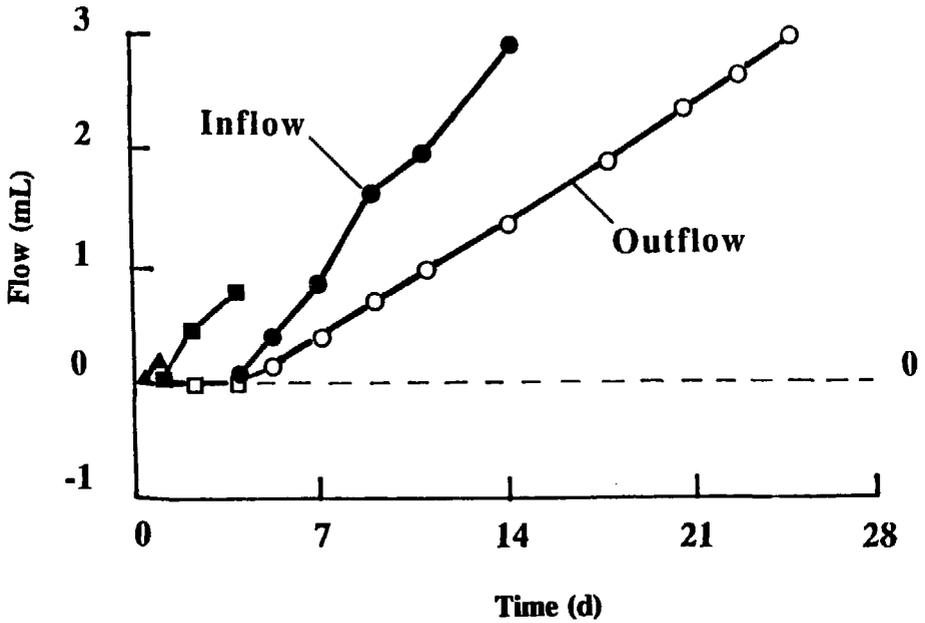
FIGURE 18:   Effect of Hydraulic Pressure on Time-Dependent Flow Through Grout Under Compression (*W/CM* = 0.4 and 0% Silica Fume)
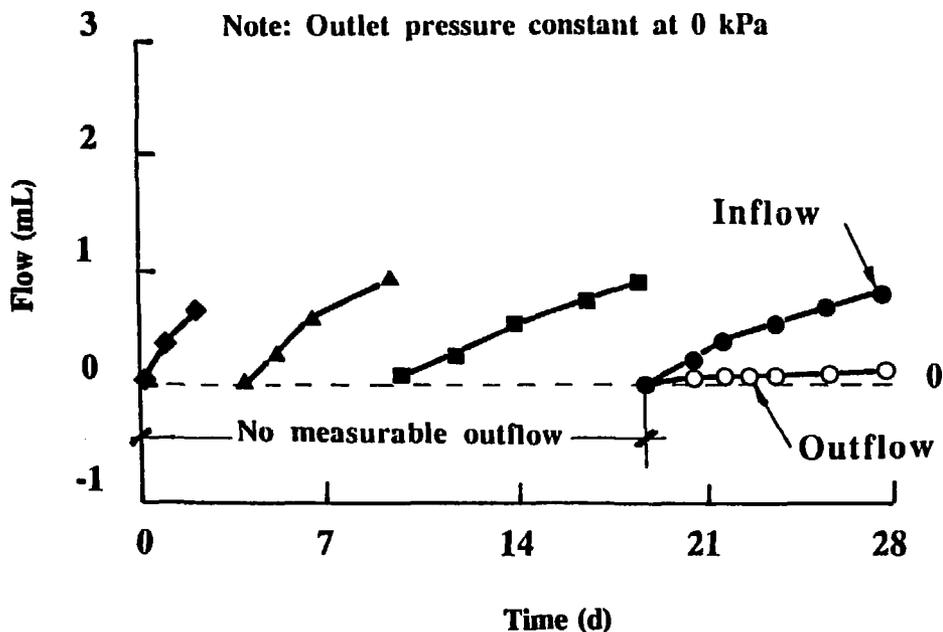
FIGURE 19: Effect of Hydraulic Pressure on Time-Dependent Flow Through Grout Under Compression (*W/CM* = 0.4 and 10% Silica Fume)
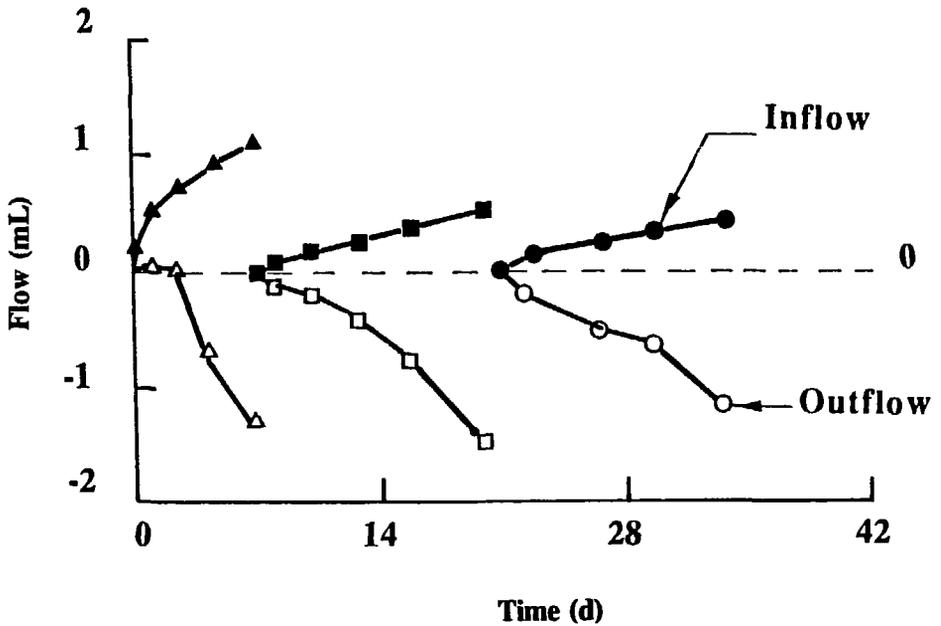
FIGURE 20: Effect of Hydraulic Pressure on Time-Dependent Flow Through Grout Under Tension (*W/CM* = 0.4 and 10% Silica Fume)
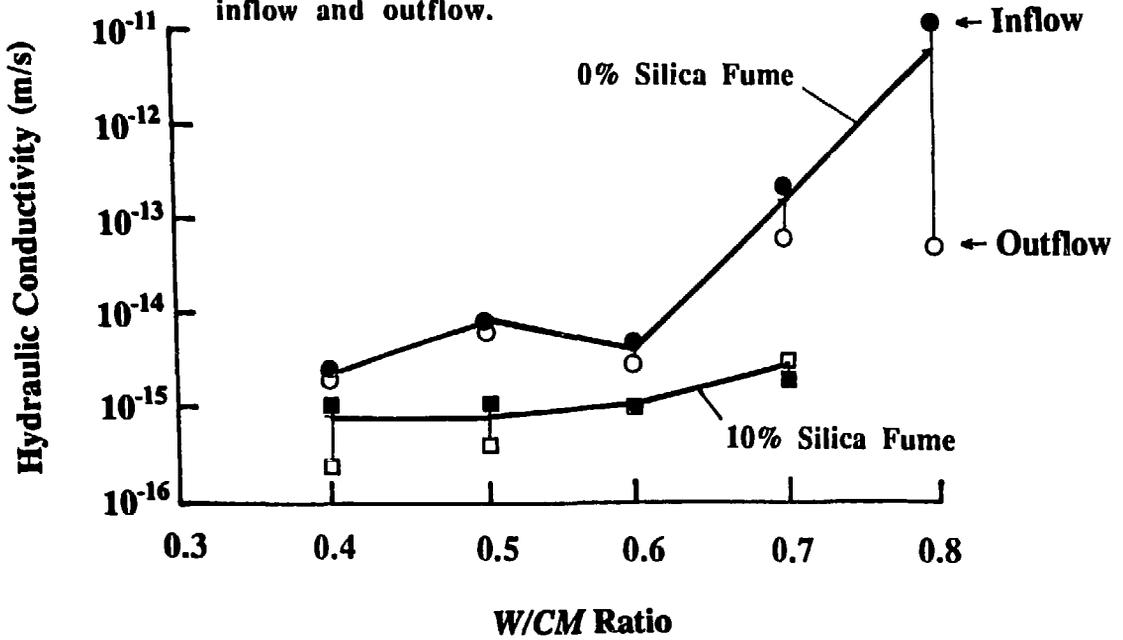
FIGURE 21: Effect of Silica Fume and *W/CM* on the Hydraulic Conductivity of Grout (i > 28 500 for 0% Silica Fume and i > 35 000 for 10% Silica Fume)
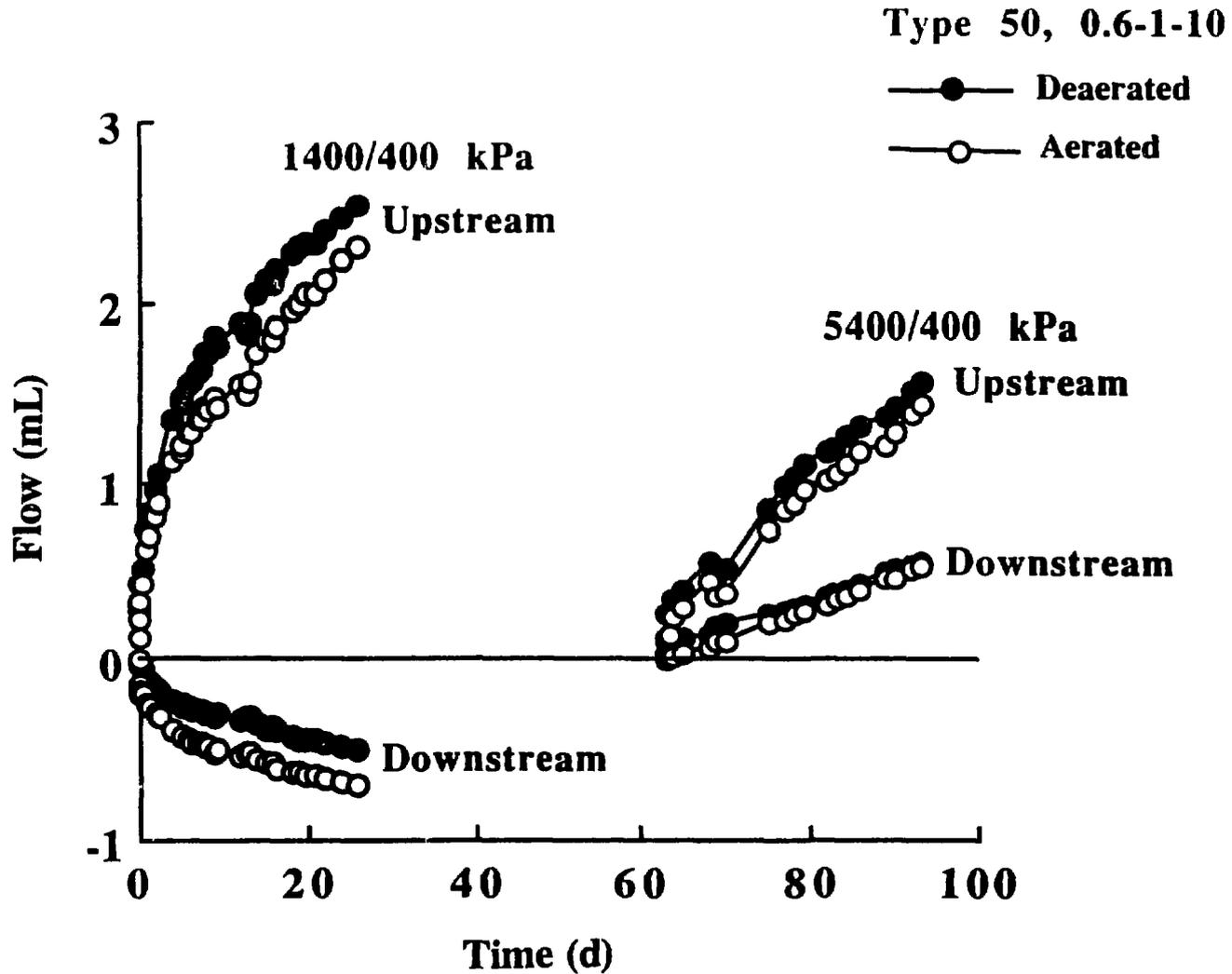
FIGURE 22:   Effect of Hydraulic Pressure on Time-Dependent Flow Through Grout Under Deaerated and
Aerated Conditions (*W/CM* = 0.6 and 10% Silica Fume)
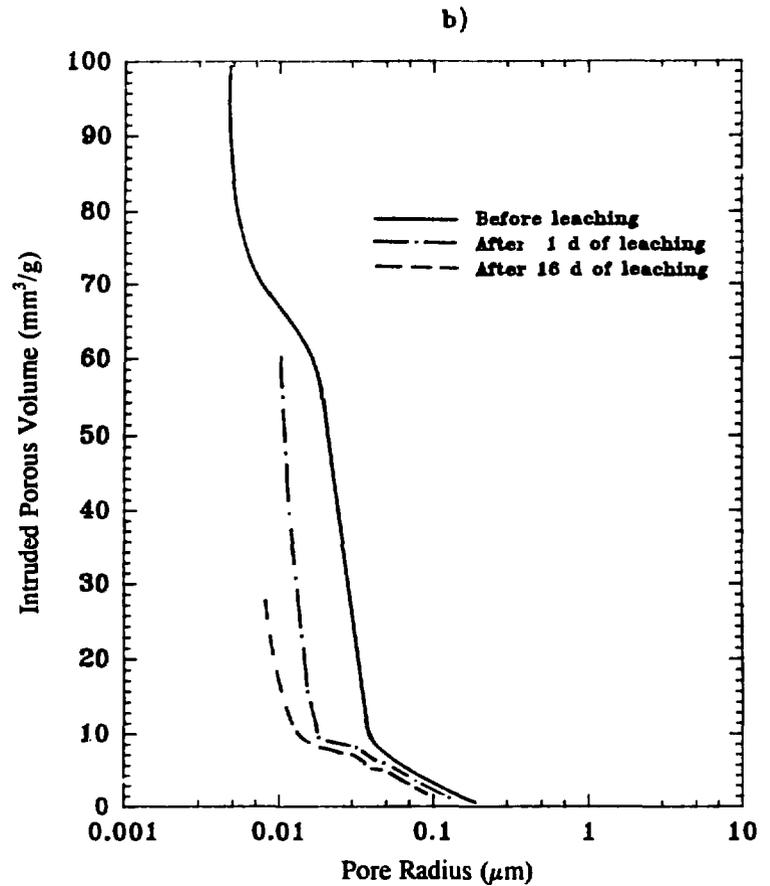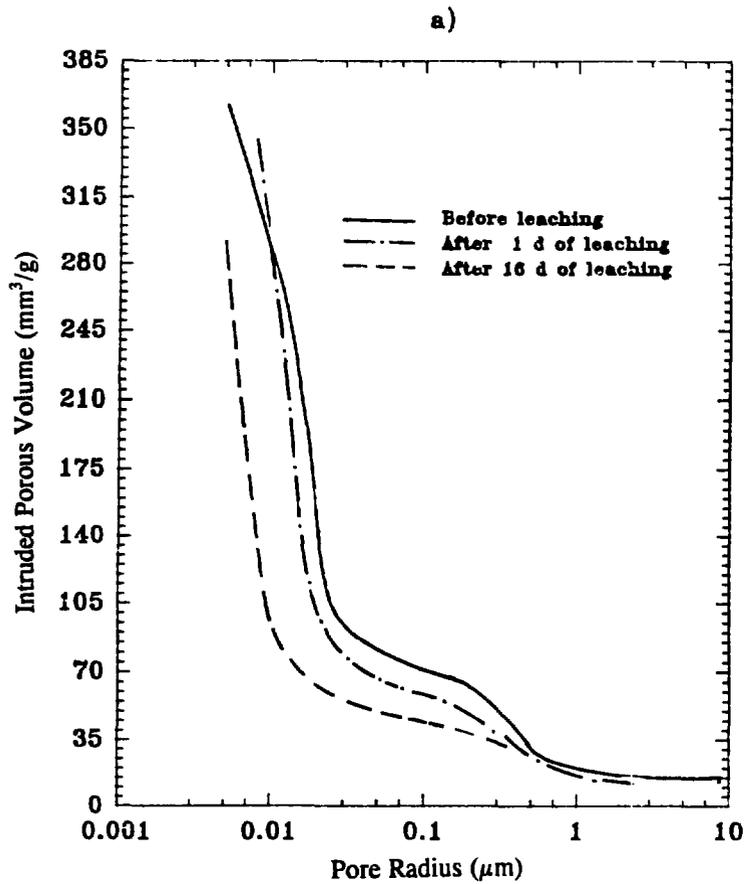
FIGURE 23: Effect of Leaching Time on Cumulative Pore Size Distribution Measured by Mercury Intrusion Porosimetry for a) ALOFX - MC Grout (MC-500, 0:7/1/10), and b) Reference Grout (Type 50, 0:4/1/10.)
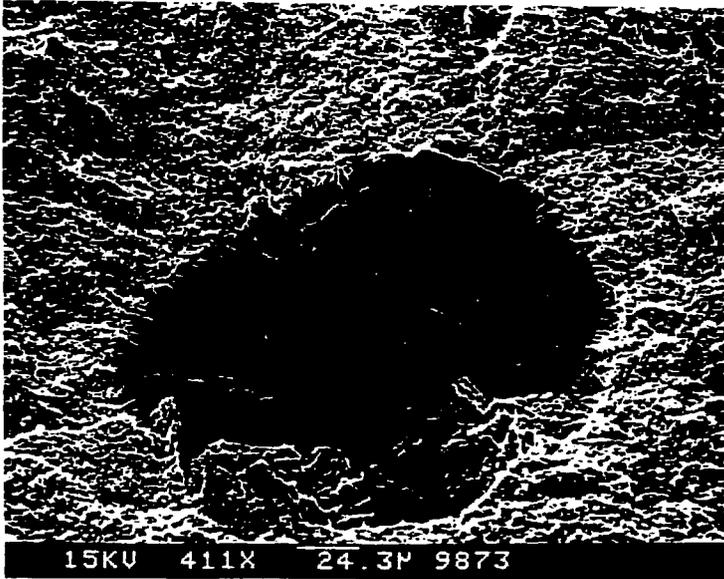
FIGURE 24:   Electron Micrograph of the Fractured Cross Section of
            ALOFIX-MC (MC-500, 0:7/1/10) Grout After 32 d of Leaching
            (A = calcium silicate hydrate, Type 4)