ELSEVIER

Microstructural Changes Due to Elevated Temperature in Cement Based Grouts

Danielle Palardy,* Maria Onofrei,† and Gerard Ballivy*
*Université de Sherbrooke, Département de Génie Civil, Sherbrooke, Québec, Canada; and
†AECL, Whiteshell Laboratories Pinawa, Pinawa, Manitoba, Canada

The durability of type K and H cement based grouts under conditions potentially found to be in high level nuclear waste repositories was studied. Tests have been carried out to determine the effects of temperature on the hydraulic conductivity and the leaching resistance of the grouts. Measurements of mercury intrusion porosimetry and scanning electron microscopy with energy dispersive X-ray analysis have been used to investigate the changes in the pore structures of both grouts as function of leaching and permeating time. Type K and type H cement based grouts, made with low water to cementitious materials ratio, silica fume, and superplasticizer, were exposed to high temperature and pressure. Preliminary results indicate that both hydraulic properties and leaching behavior of the grouts investigated are affected by the increase in temperature. However, data show that leaching rate and hydraulic conductivity of the grouts decrease with time. The results showed clearly that chemical reactions, presumably accelerated by the elevated temperatures (100°C), led to the formation of a precipitate in the microcracks and on the surface of the leached specimens. This precipitate is likely the cause of the observed decrease in the hydraulic conductivity and leaching rate. ADVANCED CEMENT BASED MATERIALS 1998, 8, 132–138. *© 1998 Elsevier Science Ltd.*

KEY WORDS: Cement based grout, High temperature, Microstructure modifications, Permeability, Static leaching, Type K cement, Type H cement

Current repository designs for the disposal of radioactive waste envisage extensive use of cement based materials (i.e., grouts, concrete) [1–4]. These materials may be used for the waste form matrix, as construction materials for walls and floor, as a grout to fill in gaps between waste packages, and to seal boreholes, shafts, tunnels, and natural fractures or fractures generated during vault excavation. The cement based materials will fulfil different functions in each of these applications. They are used in these applications due to inherent strength, durability, and versatility.

Cement based grouts have been identified as potential grouting materials. The required performance of cement based grouts includes not only an ability for the material to penetrate and seal very fine fracture, but also a potential for long-term mechanical and chemical stability in disposal vault environment. Under many conditions, the deterioration of cement based materials is not attributed to any single cause, but arises from the combined action of a number of potentially destructive agents. There are many possible environmental factors and processes by which the design properties of the cement based grouts may change over long periods of time. These include reaction with the environment through the aqueous phases, internal microstructural changes, temperature, action of microorganism, and radiation (i.e., radiolysis). It is commonly held that the hydraulic performance of cement based grouts would change as water passed through the pores in the materials. The cement will dissolve in a saturated environment, and porosity and hydraulic conductivity would increase with time. The rates of change would be influenced by spontaneous changes in microstructure of the material. It is obvious that the hydraulic dynamics in the vicinity of the grout are an important factor in estimating the long-term durability of cement based grouts.

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. Durability is an important parameter; it is defined as the capacity of a cementitious material to resist under given environmental conditions [5]. This article presents the results of laboratory studies carried out to determine the effects of temperature, type of cement, and hardened grout porosity on the hydrau-

Address correspondence to: Dr. Gerard Ballivy, Civil Engineering Department, Université de Sherbrooke, Rocks Mechanics Laboratory, Sherbrooke, Quebec J1K 2R1, Canada.
Received December 5, 1997; Accepted March 20, 1998.

655 Avenue of the Americas, New York, NY 10010

ISSN 1065-7355/98/$19.00
PII S1065-7355(98)00016-9

TABLE 1. Composition of grouts studied

Mix	Type of Cement	Ratio W/C	Silica Fume (%)	Super plasticizer (%)
1	K	0.5	10	1
2	H	0.3	15	1

lic conductivity and leaching behavior of cement based grouts.

Materials

Type K cement is the most common expansive cement used today [6,7]. In this cement, the aluminate source for the ettringite formation is calcium sulfoaluminate (C_4A_3S). An expansive cement normally is used in a situation where shrinkage of the cement based material cannot be tolerated [8]. In the case of cement based grout, the required expansion is higher than the shrinkage to create a contact force between the grout and its environment. This balance between expansion and shrinkage reduces cracking.

Type H cement is an oil-well cement; specifications were established by the American Petroleum Institute. It is a slow-setting cement that is used to seal deep wells under high temperature and pressure. Type H cement can be used as a basic well cement from the surface to depths of 2500 m. Its typical fineness is about 160 m^2/kg. This cement is a high sulfate resistance cement, as determined by C_3A content (maximum 3%).

Two different grout mixes, one with type K cement and the other with type H cement, were studied. The mixes are shown in Table 1. Silica fume and a naphthalene based superplasticizer were added to each cement to improve grout properties such as low permeability and long-term leaching resistance. All the grout components (cement, distilled water, silica fume, and superplasticizer) were mixed for 300 s at a speed of 40 rpm with a laboratory mixer. After the mixing, the grout specimens were cast in molds and placed in a humid chamber for 24 hours. The samples were demolded and cured under a saturated $Ca(OH)_2$ water at 20°C for 28 days.

Experimental Procedures

Permeability Tests

The hydraulic conductivity tests were carried out in a specially constructed permeameter (Figures 1 and 2) [9,10]. It is a radial flowing permeameter and allows the study of samples under high temperature and pressure. This permeameter permits the creation of medium depth conditions. Cylindrical samples with a central cylindrical opening parallel to the longitudinal axis were tested. The dimensions of the samples are 50 mm in diameter and 110 mm in length with an axial hole diameter of 13 mm. Before testing, the samples were saturated, for at least 2 days, with deionized, deaerated water. Tests were done by the convergent method, which forces the flow from the outside to the inside. In other words, the sample is subjected to a radial compressive stress field. The samples were tested at three different temperatures (20°, 50°, and 100°C) in a sequential manner with a 10-MPa pressure differential. The temperature was increased as soon as the hydraulic conductivity reached a constant value. In general, the test at each temperature was carried out for approximately 30 days.

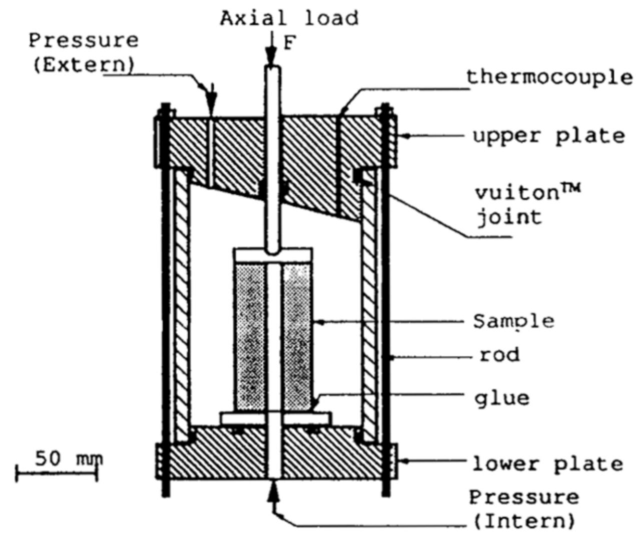

FIGURE 1. Radial-type permeametric cell [9,10].

Static Leaching Tests

The full description of the experimental design and method has been given elsewhere [11]. The test is used

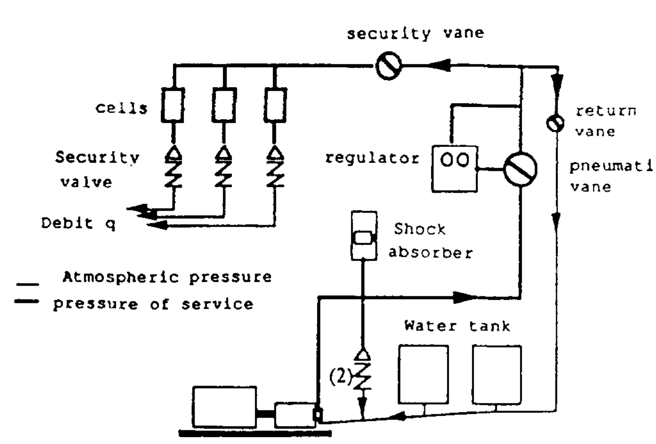

FIGURE 2. Environmental permeameter [9,10].

TABLE 2. Nominal composition and pH of Whiteshell N-1 synthetic groundwater

Ion	Concentration (mg/L)	Ion	Concentration (mg/L)
Ca	1890	Si	4
Na	1830	Cl^-	5790
Mg	55	SO_4^{2-}	1000
Sr	22	HCO_3^-	40
K	13	pH	7

to investigate the behavior of cement based grouts under various conditions of temperature, water chemistries, and lengths of time in contact with the leachant. The leaching tests were carried out at 25°, 50°and 100°C in Teflon containers of 90-mL volume. The grout specimens were placed on Teflon grids at the bottom of each container to ensure full contact between the sample and the solution. Leachant was added to yield a sample surface area to solution volume ratio of 0.1 cm^{-1}. Prismatic-shaped samples were cut to obtain a surface area of approximately 6 cm^2. The amount of water used in each container was about 60 mL. The leachants used in this study included deionized distilled water and Whiteshell N-1 synthetic groundwater; they were not renewed during the test. Table 2 shows the composition and pH of the synthetic groundwater used. Leach times of 7, 14, 28, and 35 days were used. The grout samples were removed from the container at their predetermined leaching times.

Analytical Method

Characterization of the microstructure and the chemical properties were done before and after the permeability tests and the static leaching tests to find any changes in the cement grouts attributable to different test conditions. Any changes in porosity, chemical composition of the samples, or liquids deriving from the leaching tests were determined. Optical, chemical, and microstructural methods were used to measure these changes occurring as a result of the durability tests.

Microstructure Characterization

Surface analysis of the test specimens at the termination of the hydraulic conductivity and leaching tests were performed by scanning electron microscopy (SEM). Before the analysis began, the grout specimens were impregnated with epoxy based resin and polished with increasingly finer diamond powders (15, 3, and 1 μm). The microscope used was a JEOL JMS 840A connected to a microprobe LINK 10,000.

Techniques such as mercury intrusion porosimetry have also been used to investigate the changes in pore structure of both grouts. Before measurements, the grout samples were dry by placing them in acetone for 4 hours and then in an oven at 60°C for 12 hours.

Chemical Characterization

Crystalline phases were determined by X-ray diffraction (XRD). Samples were crushed under a controlled

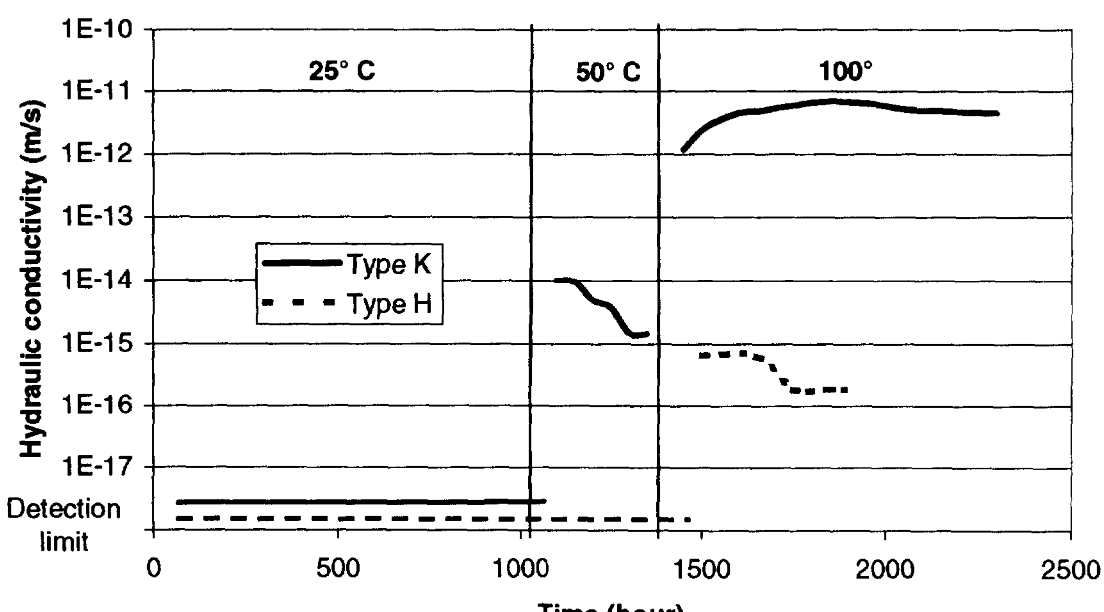

FIGURE 3. Effect of percolating time and temperature on the hydraulic conductivity of the grouts studied.

TABLE 3. Variation of water viscosity with temperature [12]

Temperature (°C)	Viscosity ($\nu \cdot 10^6$ m²/s)
20	0.995
60	0.480 ($\Delta\nu = -50\%$)
100	0.290 ($\Delta\nu = -70\%$)

nitrogen atmosphere to prevent carbonation and analyzed by a Rigaku DMAXB apparatus. Solution analyses were performed at the termination of each static leaching test. Calcium was analyzed by inductively couple plasma spectroscopy.

Results and Discussion

Permeability Tests

Hydraulic conductivity was assessed with grout specimens under compression. Figure 3 presents the effects of percolating time and temperature on hydraulic conductivity of both grouts under investigation. A mean hydraulic conductivity was calculated for each temperature.

The results show that, under the test conditions, both grouts had a permeability lower than the detection limits ($< 10^{-17}$ m/s) at 25°C and even at 50°C for the type H cement based grout (Figure 3). Type K cement based grout has shown a moderate flow at 50°C and a more important hydraulic conductivity at 100°C. As a comparison, the conductivity measured for this grout at 100°C (10^{-12} m/s) corresponds to the conductivity at 25°C of sound granite. The important fact to notice is the considerably low hydraulic conductivity of type H cement based grout.

As expected, permeability increases along with the temperature increases. The observed increase in hydraulic conductivity may be attributed to changes in microstructure and the decrease in the viscosity of permeated water. The viscosity of water is lower (Table 3) and it moves easily through the grout samples.

A high permeability was measured at the initiation of the tests. Temperature can bring thermal expansion that creates fractures and cracks. Examination of the specimens after the tests revealed the presence of cracks parallel to their longitudinal axis. The presence of these cracks may explain the high permeability at the initiation of the tests. However, this increase in hydraulic conductivity is observed for a short period of time, after which the hydraulic conductivity decreases with time. This was attributed to the self-sealing properties of the grouts. Microscopic examination of the grouts at the termination of the tests showed that chemical reaction, accelerated by the elevated temperature, led to the formation of a precipitate in the cracks in the grout specimens. This precipitate is the likely cause of the temperature-induced decrease in the hydraulic conduc-

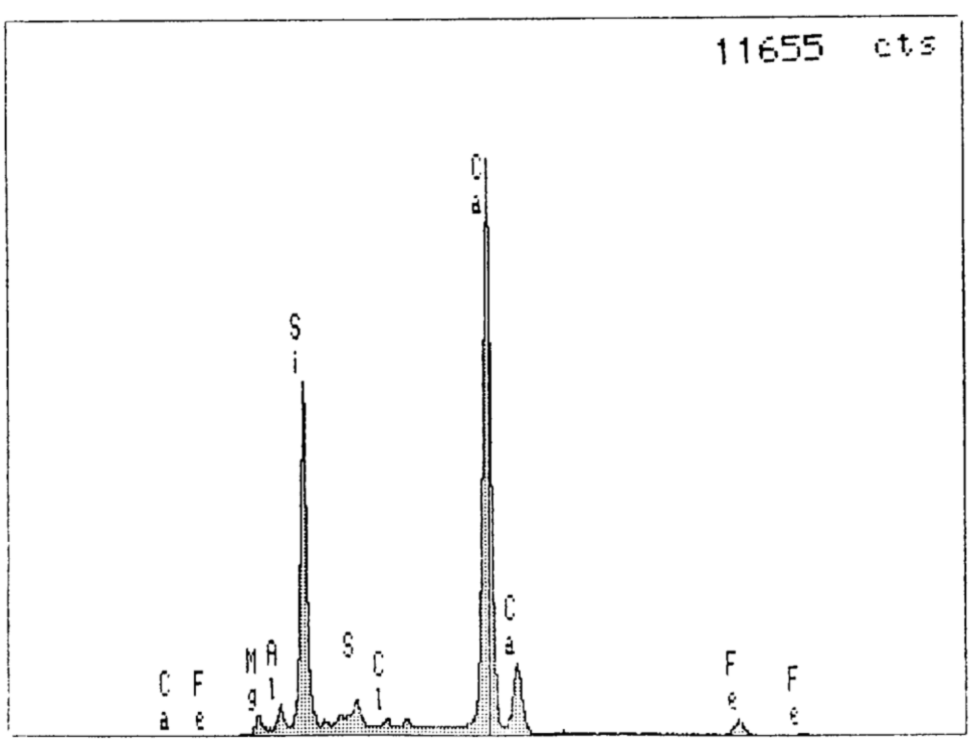

FIGURE 4. SEM/energy dispersive X-ray analyses of the deposit in a crack from the type K cement based grout.

tivity of the grout. The mechanism of self-sealing of cracks in the cement based materials is not well understood even though the phenomenon is well-established. Several authors have indicated that the most likely mechanisms responsible for the crack sealing are deposition of calcium carbonate and/or formation of new hydration products [13–15]. Under the experimental conditions used in this study, the results suggest that the most likely process responsible for the crack sealing is continued hydration reaction. The SEM/energy dispersive X-ray analyses of the filling material indicated that it consisted mainly of Ca and Si (Figure 4). The morphology and the chemical composition of the filling material suggest CSH. Figure 5 shows a general view of a fracture observed in the type K cement based grout and filled up with reaction product.

It is a known fact that the pore structure of cement paste controls to a large extent the permeability of the material. Therefore, any factors affecting either the total porosity or the pore size distribution of hardened grout should affect the hydraulic properties of the material. Medium size capillary pores (0.01 to 0.05 μm) and large pores (0.05 to 10 μm) control permeability [16]. As shown in Figures 6 and 7, each grout has a low percentage of large capillary pores due to the use of silica fume admixture. This may explain the very low results obtained for permeability. However, the type K cement based grout contains a higher percentage of medium capillary pores, which may explain the higher hydraulic conductivity in comparison with the other one. Classification used in these figures comes from [17].

An increase in total porosity is observed in both grouts relative to the initial values obtained for the control specimens: 6% for the type K cement based grout and 4% for the type H (Figures 6 and 7). However, despite the fractures observed, classes 1 and 2 have not increased excessively: a slight increase was observed in type K cement paste. This may be attributed to the formation of precipitate. Class 3 shows no change, whereas for the fourth one, an increase of 5% is measured (Figure 6). The increase in class 4 may indicate the increase in the CSH gel as the result of continue hydration. Finally, the type H cement based grout shows a low increase for classes 3 and 4 (Figure 7).

FIGURE 5. Deposit in a crack from the type K cement based grout (2,200×).

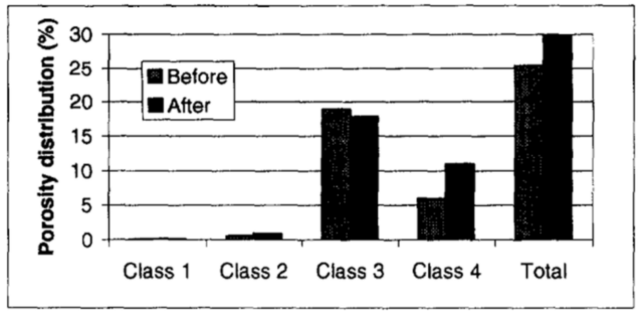

FIGURE 6. Pore size distribution of type K grout before and after the permeability tests (see nomenclature).

SEM in backscattered electron induced mode examinations revealed the presence of unhydrated phases in the hardened grouts: approximately 10% of the matrix for the type K cement based grout and 25% for the type H grout. Some particles have an hydrated layer on their margin, whereas others show only a remnant of their initial structure. The hydration of these unhydrated phases when in contact with the permeating water may explain the delay before the water flowed through the grout. In the control samples, the initial unhydrated phases represented approximately 20% in the type K cement based grout and 40% in the type H grout.

The increase in classes 2 and 3 in type K grout may be attributed to ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 25H_2O$] decomposition above 60°C. These observations have been confirmed by XRD analysis performed on the specimen after the permeability tests. The results show the presence of katoite [$Ca_3Al_2(SiO_4)(OH)_8$]. This min-

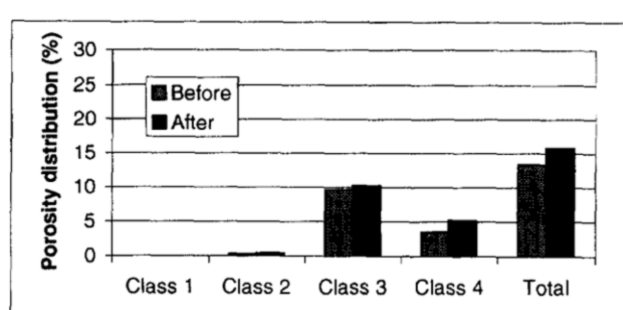

FIGURE 7. Pore size distribution of type H grout before and after the permeability tests.

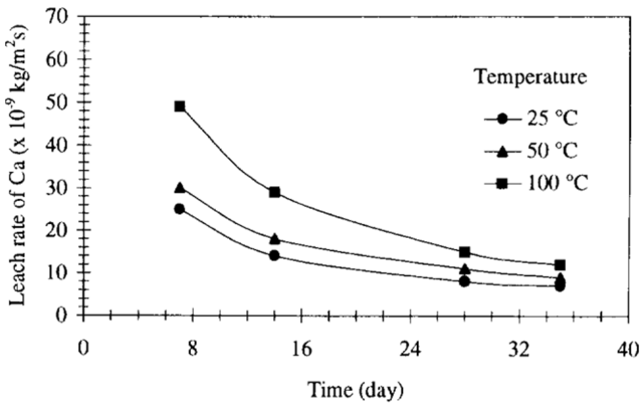

FIGURE 8. Effect of leaching time and temperature on the leach rate of calcium for the type K grout reacted with deionized water.

eral and calcium sulfates, $CaSO_4xH_2O$, appear after the decomposition of ettringite.

Static Leaching Tests

As for the permeability tests, the increase in temperature to 100°C brings more important changes in the grout in comparison to 25°C or 50°C. In fact, at 100°C, the results show higher calcium leaching rates, leaching depth, and porosity. Figures 8 and 9 show the calcium leaching rate for the type K and type H grouts submerged in deionized water: leaching increases at higher temperatures. However, after a certain period of time, the system tends to approach a steady state attributed to calcium concentration approaching solubility limits and/or due to formation of a surface protective layer. SEM examination confirmed the formation of a precipitate layer on the surface of the leached specimens. This layer was identified, by XRD, as being in major part composed of calcium carbonate. The samples leached in

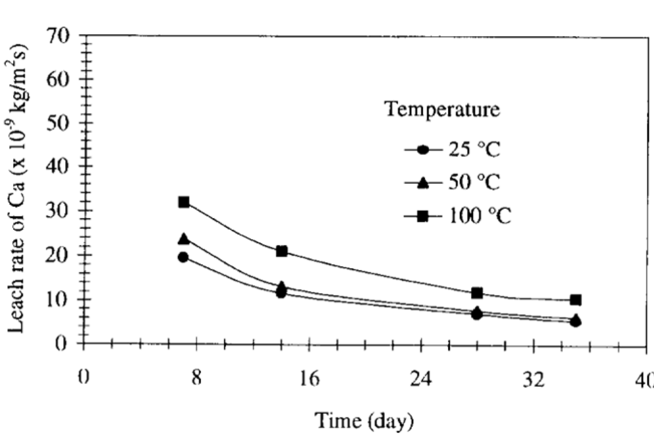

FIGURE 9. Effect of leaching time and temperature on the leach rate of calcium for the type H grout reacted with deionized water.

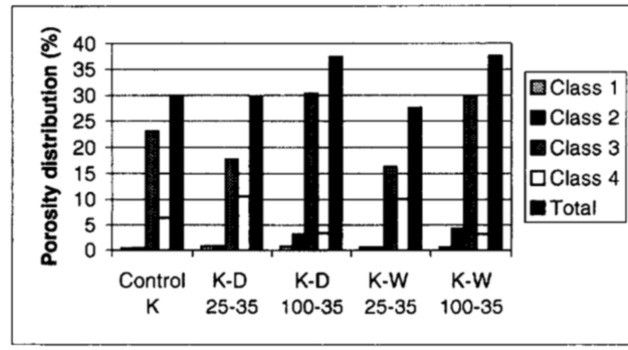

FIGURE 10. Porosity distribution in the type K cement based grout after 35 days of leaching (see nomenclature).

synthetic groundwater also show traces of $Mg(OH)_2$ on the external surface. A solution with $MgSO_4$ or $MgCl_2$ leaches the calcium hydroxide and brings the formation of brucite deposits [18].

The calcium leaching originates mostly from the portlandite $Ca(OH)_2$, of which the decrease can be seen semi-quantitatively by XRD. The dissolution of this mineral increases the porosity of the grouts and may affect their long-term durability. Figures 10 and 11 show the pore size distribution in the type K and type H cement based grouts. The porosity does not change significantly at 25°C in comparison with the control sample, but at 100°C, a significant difference is observed.

The decomposition of ettringite at high temperature also may contribute to the increase in porosity. This is more important in the type K grout, because it contains agglomerations of ettringite crystals. This may explain the increase of class 2 at 100°C for this grout.

Furthermore, fewer differences are observed in the porosity classes between 25°and 50°C; it is at 100°C that the changes are really important. At the two first temperatures, the hydration is more important, which is represented by an increase for class 4. However, at 100°C, it is class 3 (and 2) that increases: leaching is more important than hydration.

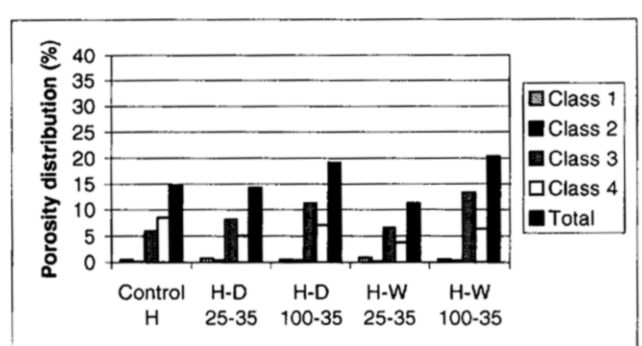

FIGURE 11. Porosity distribution in the type H cement based grout after 35 days of leaching.

Finally, SEM observations show that the leaching depths increase with temperature, especially at 100°C, and duration of test. This results in higher porosity.

Conclusions

The study shows that both, hydraulic conductivity and leaching properties of the grouts investigated, were affected by the increase in temperature. However, the results show that both leaching and hydraulic conductivity of the grouts tend to decrease with time. The observed changes were attributed to the formation of new hydration products resulting from the increase in the degree of hydration and associated reactions.

The work discussed here revealed that the porosity of the grout does change with leaching time, but in the limits that depend on grout composition, temperature and initial porosity. The results confirm that the grouts investigated have the potential to self-seal.

Nomenclature

Class 1 (%)	300–0.9 μm
Class 2 (%)	0.9–0.06 μm
Class 3 (%)	0.06–0.009 μm
Class 4 (%)	0.009–0.003 μm
K and H	Cement type
D and W	Water type
25 and 100	Temperature (°C)
35	Test duration (days)

Acknowledgments

The authors wish to thank Atomic Energy of Canada Limited for providing financial support during this project.

References

1. Atkinson, A.; Hearne, J.A. *An assessment of long-term durability of concrete in radioactive waste repositories.* AERE-R 11467, UK Atomic Energy Authority Harwell, Oxfordshire, 1984.
2. Push, R. *Waste Disposal in Rock*; Elsevier Science: Amsterdam, The Netherlands, 1994.
3. Coons, W.; Bergstorm, A.; Gnirk, P.; Gray, M.; Knecht, B.; Push, R.; Steadman, R.; Stillborg, J.J.; Tokonami, M.; Vaajasa, M. *State-of-the-art report on potential useful materials for sealing nuclear waste repository.* Stripa Project Technical Report 87-12, Swedish Nuclear Fuel and Waste Management Company, Stockholm, 1987.
4. Roy, D.M.; Langton, C.A. *Longevity of borehole and shaft sealing materials.* ONWI-202, 1982.
5. Mehta, P.K.; Monteiro, P.J.M. *Concrete, Structure Properties and Materials*; Prentice-Hall: Englewood Cliffs, NJ, 1993.
6. Folliard, K.J.; Ohta, M.; Rathje, E.; Collins, P. *Cement and Concrete Research* **1994,** 24, 424–432.
7. Kurdowski, W. In *7ième Congrès International de la Chimie des Ciments, Paris, France.* 1980; pp V.2/1–V.2/11.
8. Derucher, K.N.; Heins, C.P. *Materials for Civil and Highway Engineers*; Prentice-Hall: Englewood Cliffs, NJ, 1981.
9. Colin, J.C. MsA thesis. Université de Sherbrooke, Quebec, 1990.
10. Ballivy, G.; Colin, J.C.; Mnif, T. In *Grouting, Soil Improvement and Geosynthetics*, GT Div/ASCE Proceedings, New Orleans, LA, 1992; pp 588–600.
11. Onofrei, M.; Gray, M.N.; Breton, D.; Ballivy, G. In *Scientific Basic for Nuclear Waste Management XIV*, Mater. Res. Soc. Proc., Pittsburgh, PA, 1991; pp 417–425.
12. Welty, J.R.; Wicks, C.E.; Wilson, R.E. *Fundamentals of Momentum, Heat and Mass Transfer*, Third Edition; John Wiley & Sons: New York, 1984; p 803.
13. Onofrei, M.; Gray, M.N.; Keil, L.D.; Push, R. In *Pore Structure and Permeability of Cementitious Materials*, Mater. Res. Soc. Proc., Pittsburgh, PA, 1989; pp 349–358.
14. Onofrei, M.; Gray, M.N.; Coons, W.E.; Alcorn, S.R. *Waste Management* **1992,** 12, 133–154.
15. Brodersen, K.; Nilsson, K. *Cement and Concrete Research* **1992,** 22, 405–417.
16. Mindess, S.; Young, J.F. *Concrete*; Prentice-Hall: Englewood Cliffs, NJ, 1981.
17. Revertegat, E.; Richet, C.; Gégout, P. *Cement and Concrete Research* **1992,** 22, 259–272.
18. Frigione, G.; Sersale, R. *Cement and Concrete Research* **1989,** 19, 885–893.