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MINERALOGICAL CHANGES OF VARIOUS CEMENT FORMULATIONS DURING REACTION WITH GROUNDWATER IN THE PRESENCE OF Ca- AND Na-BENTONITE AT 150°C*

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ABSTRACT

A commercially available, sulfate-resisting Portland cement (SRPC) and two cement formulations derived from it by addition of 20 vol.% silica fume and 35 vol.% fly-ash, respectively, were leached in Standard Canadian Shield Saline Solution (SCSSS) containing Ca-bentonite or Na-bentonite at 150°C for 14 days. The presence of clay accelerates the rate of release of various elements from the cements. The pH of the leach solutions plays a dominant role in the kinetics of element release.

Keywords: cement, groundwater, bentonite, hydrothermal alteration.

SOMMAIRE

Un ciment disponible sur le marché, résistant aux sulfures et de type Portland (SRPC) et deux autres ciments dérivés, par addition de 20% de farine de SiO_2 ou de 35% de cendres volantes, ont été lessivés en eau salée (Standard Canadian Shield Saline Solution) en présence de bentonites de Ca et Na à 150°C pendant deux semaines. En présence d'argile, le taux de libération de plusieurs éléments de ces ciments est accéléré; le pH de ces solutions influence la cinétique du lessivage des éléments.

Mots-clés: ciment, eau salée, bentonite, altération hydrothermale.

INTRODUCTION

The Canadian Nuclear Fuel Waste Management Program is focusing on assessing the concept of the disposal of nuclear fuel waste deep in a body of plutonic rock (Rummery & Rosinger 1983). The engineered barriers around a disposal vault may include cement- and clay-based materials for grouting water-bearing rock fractures, plugging boreholes, and sealing shaft bulkheads (Bird & Cameron 1982). The sealing materials may comprise high-density, high-strength cements resistant to aggressive chloride- and sulfate-containing groundwater at elevated temperatures. The cementitious materials could be in contact with clay minerals used as components of the buffer and backfill and with saline groundwaters ubiquitous in granitic rocks of the Canadian Shield (Frape *et al.* 1984). In the Canadian concept of disposal, the temperatures in the near-field of the disposal vault could be as high as 150°C (Bird & Cameron 1982).

Although cements have a tradition as building and sealing materials, questions have been raised about their long-term durability and geochemical stability (Pihlajavaara 1980). The present paper describes parts of a program to develop and evaluate cements for use as a component in sealing, containment and construction materials in a disposal vault for nuclear fuel waste (Burnett *et al.* 1985).

It is expected that the cement will react with the clay and groundwater, and that amorphous or poorly crystallized calcium silicate hydrates in the cement matrix will undergo hydrothermal transformation into thermodynamically more stable phases. These reactions are likely to be quite sluggish at temperatures below 100°C. To increase the rate of reaction, a temperature of 150°C was used in the experiments.

MATERIALS AND SAMPLE PREPARATION

A sulfate-resisting Portland cement (SRPC, CSA type 50, Kalicrete, Canada Lafarge) was selected (Hooton & Burnett 1986) as the base cement to provide resistance to the sulfate ions contained in highly saline groundwaters commonly observed in the Canadian Shield at depths of 800 to 1000 m. However, these groundwaters also contain high concentrations of chloride ions. Since there is evidence that SRPC is less resistant to concentrated chloride solutions than normal Portland cement (Feldman 1981), supplementary materials such as silica fume or fly ash were added to the SRPC paste to increase the resistance of SRPC to deterioration by aggressive ions such as chloride (Hooton 1986). Table 1 shows the composition of the SRPC base cement (labeled 303 in this study) and two different formulations derived from it by adding 20 vol.% condensed silica fume (labeled 311) and 35 vol.% ASTM Class F fly-ash (labeled 306). The pastes were made with a water/solid weight ratio of 0.25 and contained 3%

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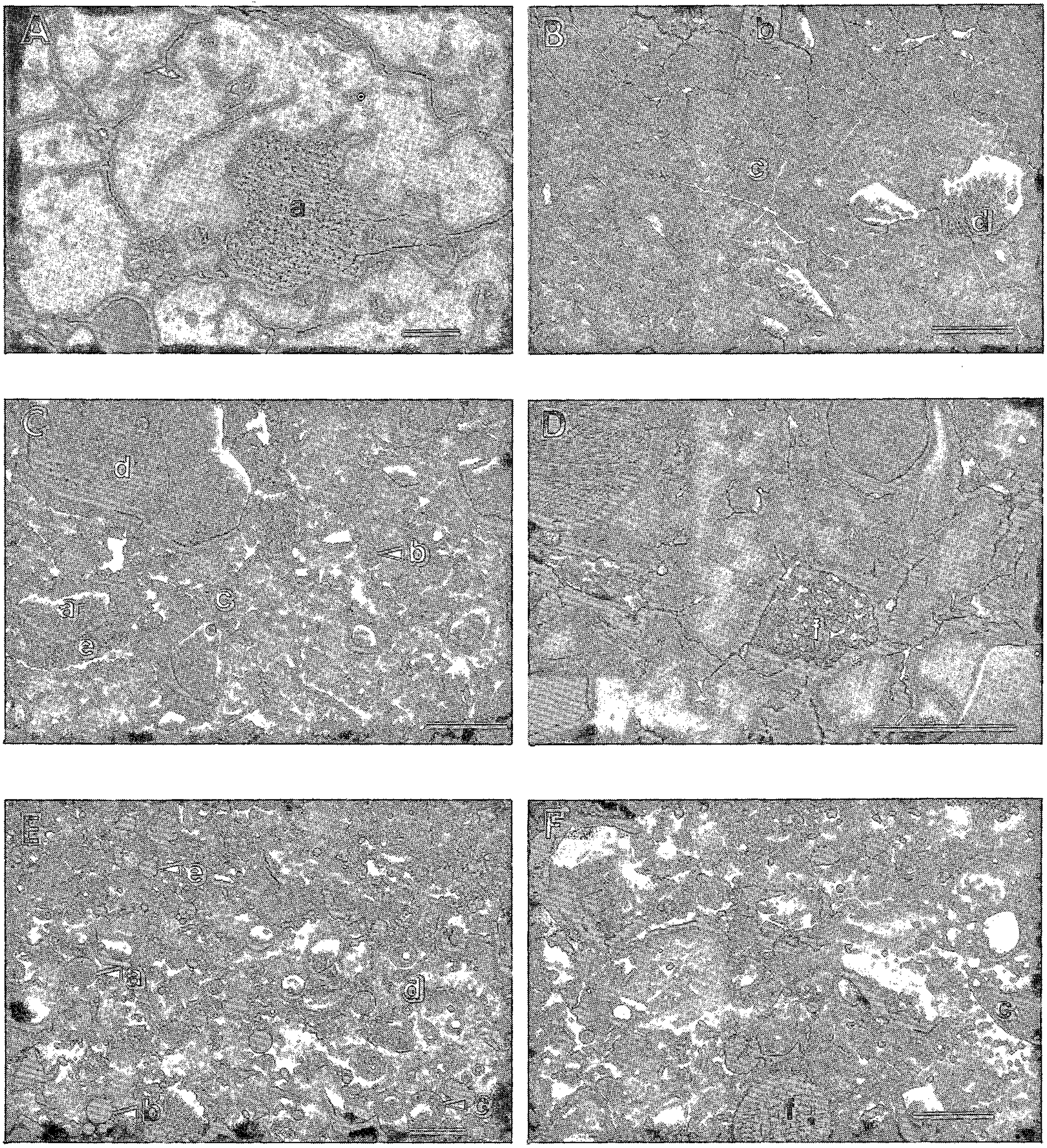

FIG. 1. Robinson backscattered-electron micrographs of polished surfaces of cement. The bar corresponds to 25 μm. A,B: cement 303 (base SRP cement). C,D: cement 311 (SRPC + 20 vol.% silica fume). E,F: cement 306 (SRPC + 35 vol.% fly ash). For an explanation of the labels, see text.

by weight of cementing material Melment L–10 superplasticizer. The samples were moist-cured at 23°C in a 100% relative humidity fog-room for 6 months.

Table 2 shows the chemical composition of the two bentonite clays used in this study. The Ca-dominated bentonite has a mineralogical composition (Quigley 1984) of 80% montmorillonite, 10% smectite–illite mixed-layer mineral, 6% quartz, 3% gypsum and 1% carbonate. This material comes from the Pembina Member of the Vermillion River Formation of Upper Cretaceous age, in southern Manitoba. The Na-dominated bentonite is similar in composition but also contains approximately 3% plagioclase. It comes from the Bearpaw Formation of Upper Cretaceous age in southern Saskatchewan. Both the Ca- and Na-

TABLE 1. CHEMICAL COMPOSITION OF CEMENT SAMPLES

Oxides	303 control SRPC*	311 (SRPC + 20% silica fume)	306 (SRPC + 35% fly ash)
SiO_2 wt.%	17.4 ± 1.0	24.6 ± 1.4	21.5 ± 1.2
Al_2O_3	2.22 ± 0.10	1.90 ± 0.09	6.95 ± 0.40
Fe_2O_3	3.0 ± 0.1	2.7 ± 0.1	5.74 ± 0.08
CaO	49.4 ± 1.4	44.3 ± 1.3	40. ± 2
MgO	2.55 ± 0.18	2.34 ± 0.16	2.25 ± 0.06
K_2O	0.17 ± 0.02	0.38 ± 0.04	0.61 ± 0.02
Na_2O	0.29 ± 0.01	0.39 ± 0.02	0.20 ± 0.03
Mn_2O_3	0.060 ± 0.002	0.056 ± 0.002	0.056 ± 0.006
TiO_2	0.118 ± 0.006	0.103 ± 0.005	0.30 ± 0.03
P_2O_5	0.04 ± 0.01	0.04 ± 0.01	0.10 ± 0.01
SO_3	1.67 ± 0.08	1.42 ± 0.08	1.58 ± 0.08
$H_2O(-)$	8.2 ± 0.2	10.2 ± 0.2	9.5 ± 0.2
$H_2O(+)$	12.4 ± 0.3	8.8 ± 0.3	11.7 ± 0.3

* Bogue composition of water-free SRPC:
54% tricalcium silicate (C_3S, alite)
25% β-dicalcium silicate (C_2S, larnite)
11% tetracalcium ferroaluminate (C_4AF, brownmillerite)
2% tricalcium aluminate (C_3A)

bentonites are commercially mined, and are sold under the brand names of Filtaclay 75 and Avonseal, respectively.

Before the experiments, the clays were treated with a solution of either 1 mol/L $CaCl_2$ or 1 mol/L NaCl to remove potassium ions in interlayer positions, and to produce saturated Ca- or Na-bentonites.

The composition of the Standard Canadian Shield Saline Solution (SCSSS) is shown in Table 3. This solution simulates the composition of saline groundwater commonly found in granitic rocks of the Canadian Shield at depths of 800 to 1000 m (Frape *et al.* 1984, Sargent 1982). Such high-salinity groundwaters have also been found in rock of other cratonic areas such as the Fennoscandian Shield and the Russian Platform (Vovk 1985).

Cement cubes were cut with a diamond-blade saw to produce slices 25 × 25 × 11 mm. After cutting, the samples were ultrasonically cleaned and kept moist to prevent cracking.

Scanning electron micrographs in Robinson backscatter mode were obtained from polished cement surfaces, and energy-dispersion X-ray (EDX) spectroscopy was used to determine the mineral phases present (Fig. 1). Figures 1A and B show the microstructure of the as-received SRPC cement (303). The

TABLE 2. CHEMICAL COMPOSITION OF CLAYS (WEIGHT %) AND CATION-EXCHANGE CAPACITY IN meq/100 g

Oxides or Parameter	Ca-Bentonite*	Na-Bentonite**
SiO_2	57.1	60.3
Al_2O_3	17.5	16.6
CaO	1.24	3.00
MgO	3.45	1.42
Na_2O	0.44	1.93
K_2O	1.04	0.72
Fe_2O_3	2.88	4.86
MnO	0.03	0.18
TiO_2	0.57	0.36
P_2O_5	0.15	0.13
H_2O^+ ***	15.9	6.73
H_2O^-		3.27
CEC	136	82

* X-ray fluorescence spectrometry, X-ray Assay Labs, Toronto, Ontario.

** Whiteshell Nuclear Research Establishment, Pinawa, Manitoba.

*** H_2O^+ refers to the amount of water released by heating at a temperature > 110°C.

H_2O^- refers to the amount of water released at a temperature < 110°C.

TABLE 3. COMPOSITION* OF STANDARD CANADIAN SHIELD SALINE SOLUTION (SCSSS) IN mg/L (SARGENT 1982)

Element or Parameter	Value
Ca	13 800 ± 300
Na	5 000 ± 155
Mg	210 ± 4
K	44 ± 3
Sr	19 ± 0.5
Fe	0.7 ± 0.1
Si	19 ± 1
Cl	34 300 ± 1 700
SO_4	790 ± 10
pH	7.18
Ionic Strength (mol/L)	1.37

* Composition based on known incidence of saline waters in the Canadian Shield.

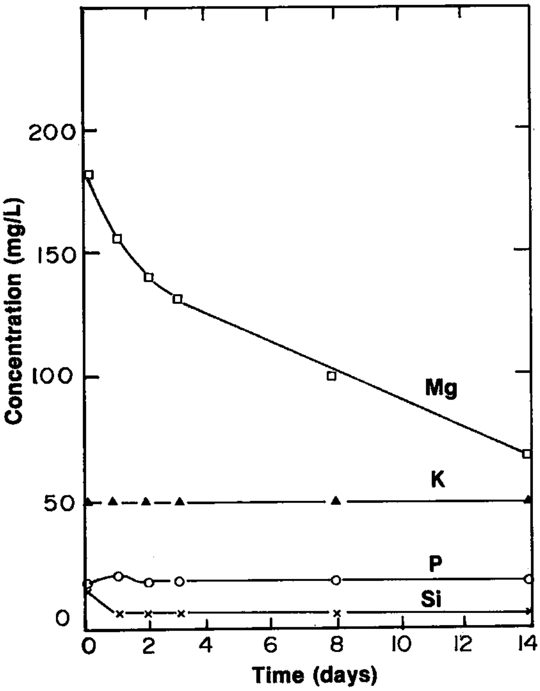

FIG. 2. Concentrations of Mg, K, P and Si in solution obtained by leaching SRPC in Standard Canadian Shield Saline Solution at 150°C (experiment 1, CEM-6-303).

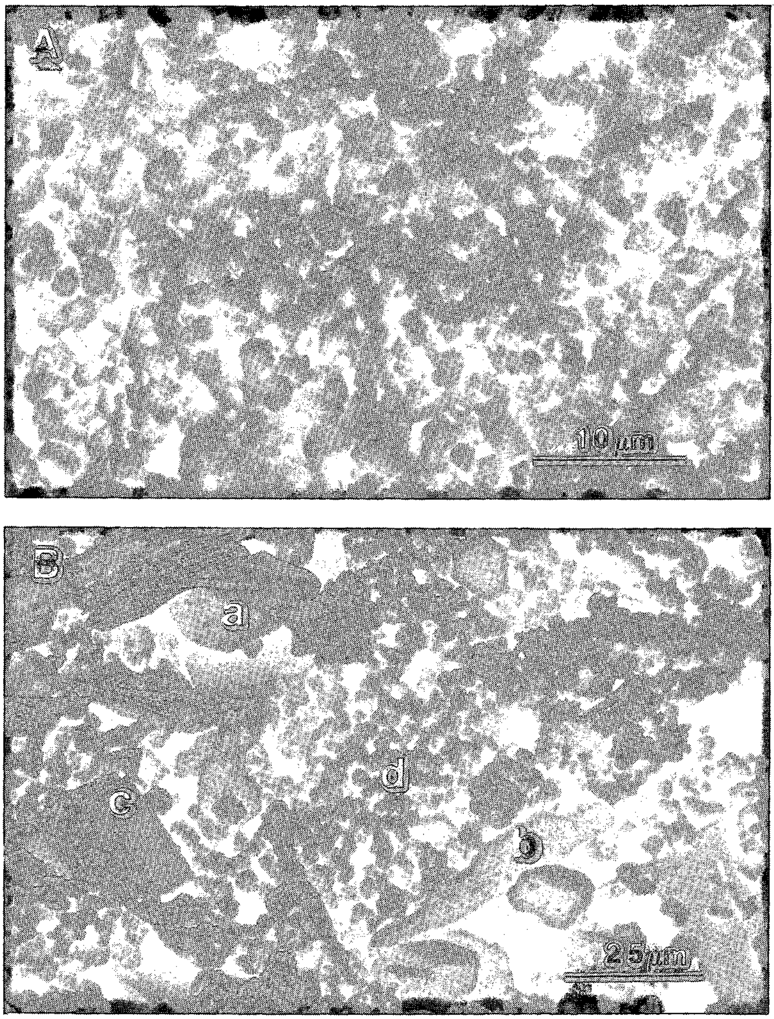

FIG. 3. Electron micrographs of leached surface of cement in experiment 1. A: Ditrigonal prisms of brucite, $Mg(OH)_2$. B: Scalenohedra (a) and lath-shaped (b) crystals of calcite, cube of Mg-containing compound (c), and spherical Ca–Mg-silicate particles (d).

dried sample exhibits extensive cracking of the Ca-silicate matrix (c). Lighter particles (b) were identified with EDX spectroscopy as brownmillerite, C_4AF in the cement-chemistry notation: C = CaO, S = SiO_2, A = Al_2O_3, Fe = Fe_2O_3, H = H_2O. Needle-like crystals in area (d) suggest portlandite (CH) according to EDX data. Area a is likely a hydrated Ca-silicate, as inferred from its microstructural appearance.

Figures 1C and 1D show the microstructure of cement 311. According to the EDX data, there are six different phases present: portlandite (a) with a reaction rim (e) of dicalcium silicate hydrate (C_2SH), brownmillerite (b), larnite (c), alite (d) and calcite (f).

Figures 1E and 1F show the microstructure of cement 306, which is dominated by spherical particles of fly ash and shows considerably less cracking than cement 303. There are three phases present with spherical morphology: K–Al-silicate (a), magnetite or hematite (b), and hollow, very silica-rich particles (c). The matrix is composed of C_3S (d) and contains also some brownmillerite (e). Spherule 'f' in Figure 1F shows iron oxide dendrites in an alkali silicate matrix.

EXPERIMENTAL

Five experiments were performed to evaluate the interaction of the various cements with saline groundwater and clay. They were: (1) SRPC + SCSSS (CEM-6-303), (2) SRPC + SCSSS + Ca-bentonite (CEM-1-303), (3) (SRPC + 20% silica fume) + SCSSS + Ca-bentonite (CEM-4-311), (4) (SRPC + 20% silica fume) + SCSSS + Na-bentonite (CEM-7-311), and (5) (SRPC + 35% fly ash) + SCSSS + Ca-bentonite (CEM-2-306).

The cement samples were reacted with the groundwater and the bentonite in 1-L stainless steel autoclaves (Parr Instruments Company, Moline, Illinois) at 150°C for 2 weeks. All samples were suspended from a platinum wire attached to the sampling dip-tube of the autoclave. Experiment 1 was performed in a Teflon liner. The ratio of the surface area of the solid sample to the volume of the solution was 3 m^{-1} for experiments 2, 3 and 5 and 1.4 m^{-1} for experiments 1 and 4. The clay/groundwater ratio was 50 g/L for all experiments. Sampling was performed after 1, 2, 3, 4, 7 and 14 days according to the schedule recommended by a panel of experts convened by the International Atomic Energy Agency (Hespe 1971).

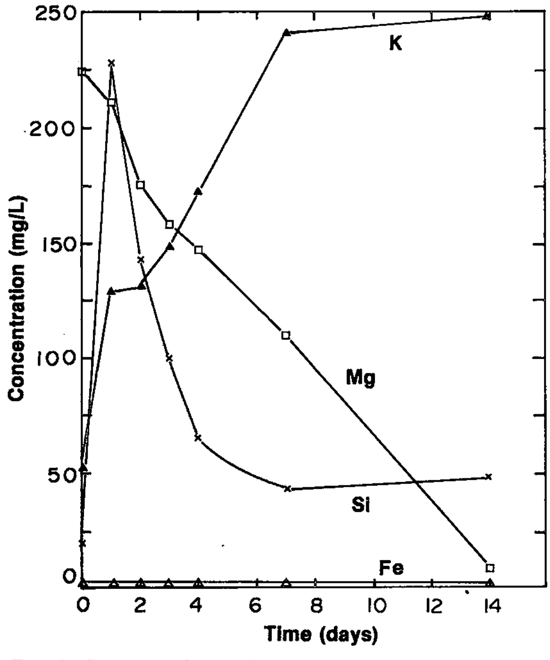

FIG. 4. Concentrations of K, Mg, Si and Fe in solution obtained by leaching SRPC in Standard Canadian Shield Saline Solution + Ca-bentonite (50 g/L) at 150°C (experiment 2, CEM-1-303).

The pH of the leach solutions was measured at 25°C, and these values were used to calculate the pH at 150°C using an algorithm provided by the SOLMNQ code (Goodwin & Munday 1983). The solutions were acidified with 200 μL HNO_3, centrifuged, filtered through 0.45-μm Millipore filters, and analyzed by atomic absorption spectroscopy (AAS) for Si, Mg, Fe and K, and by inductively coupled plasma spectrometry (ICPS) for Al and P.

Surface analyses of the samples of leached cement were performed by scanning electron microscopy (SEM) in conjunction with energy-dispersion X-ray spectroscopy (EDX), and by X-ray powder diffraction (XRD).

RESULTS

Experiment 1: SRPC + SCSSS

Figure 2 shows the concentrations of Mg, K, P and Si in the leach solution as a function of the reaction time. The concentration of Mg decreased with time, suggesting precipitation of a Mg-bearing compound. The concentration of Si was constant with time, corresponding to 0.2 mmol/L SiO_2. This value was very much lower than the saturation concentration, calculated to be 6.5 mmol/L SiO_2 from the Setchenow equation, as given by Chen & Marshall (1982). The K concentration was constant at 50 mg/L, corresponding to its value in the original saline groundwater (see Table 3).

The electron micrograph of the leached surface of the cement (Fig. 3A) shows ditrigonal prisms whose EDX spectrum revealed only Mg. XRD data confirmed that this phase is brucite $Mg(OH)_2$. Other areas of the leached surface (Fig. 3B) exhibit a more complex morphology of the precipitate, and contain calcite scalenohedra (a), lath-shaped calcite crystals (b), Mg-bearing cubes (c) and spherical particles of an unidentified precipitate containing Ca, Si and Mg (d). The presence of brucite as a precipitated phase is consistent with the rapid decrease in Mg concentration in solution shown in Figure 2.

Experiment 2: SRPC + SCSSS + Ca-bentonite

The concentrations of K, Mg, Si and Fe in the leach solution (Fig. 4) show clearly how the presence of clay affects the leaching behavior of the cement. After one day leaching time, the silicon concentration increased to 230 mg/L (8 mmol/L SiO_2), after which it decreased rapidly to a constant value of 50 mg/L (1.8 mmol/L SiO_2) after about six days. The Mg concentration showed a linear decrease to very low values after 2 weeks leaching time, indicating precipitation of a magnesium compound, likely a

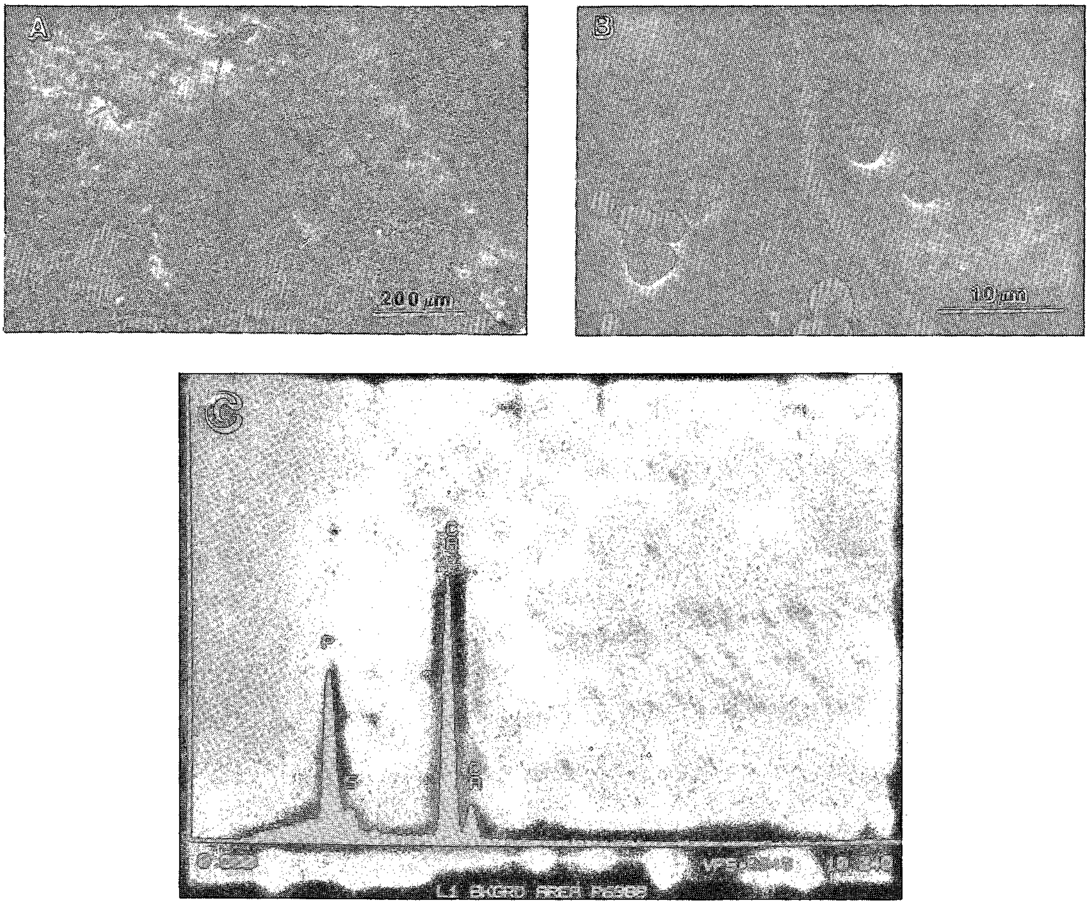

FIG. 5. Electron micrographs of leached surface of cement in experiment 2. A: Smooth surface-layer with hairline cracks. B: Enlargement of layer shown in A showing calcium hydroxide spherules. C: EDX spectrum of reaction layer.

magnesium silicate. SEM examination of the leached surface of the cement indicated precipitation of a plate-like magnesium silicate compound, presumably sepiolite or talc. This assumption is based on the difference in relative magnitude of the calculated solubility-products of talc (log K_t 12.04), sepiolite (log K_t 12.77), and chrysotile (log K_t 21.50) at 150°C (Goodwin & Munday 1983). The concentration of K rose to a relatively high value, and leveled off after 7 days, suggesting that the release was inhibited, possibly due to the formation of a protective surface-layer.

This surface layer is shown in Figure 5A; it has a smooth appearance and contains fine cracks. Figure 5B shows this layer at higher magnification. EDX results indicate that the layer consists of a calcium phosphate (Fig. 5C). X-ray powder-diffraction data of surface scrapings, however, do not give unequivocal evidence of a distinct crystalline compound but suggest the presence of a poorly crystallized calcium phosphate hydrate or calcium phosphate silicate. The small spheres visible in Figure 5B contain predominantly Ca and traces of S, suggesting a calcium hydroxide precipitate with some contamination with anhydrite.

Experiment 3: (SRPC + 20% silica fume) + SCSSS + Ca-bentonite

As shown in Figure 6, the Si concentration in the leach solution rose within a day to 200 mg/L but decreased after about 7 days of leaching to a constant value of 135 mg/L (4.8 mmol/L SiO_2), somewhat below the saturation concentration of 180 mg/L Si (6.5 mmol/L SiO_2) at 150°C in SCSSS calculated according to the equation provided by Chen & Marshall (1982).

In contrast with the results obtained from experi-

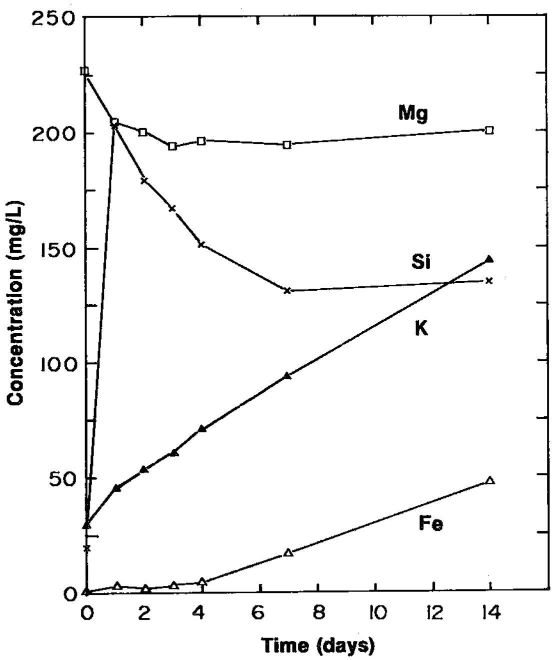

FIG. 6. Concentrations of Mg, Si, K and Fe in solution obtained by leaching cement 311 in Standard Canadian Shield Saline Solution + Ca-bentonite (50 g/L) at 150°C (experiment 3, CEM-4-311).

ments 1 and 2, the Mg decreased slightly in concentration initially, and then remained constant at about 200 mg/L.

The release of K from the cement is linear with time. The increase in iron concentration in solution after 4 days is probably related to the low pH attained in this experiment. The calculated pH at 150°C decreased from 5.0 at the beginning of the experiment to 4.5 at day 4. Below this value, iron dissolution from the austenitic stainless steel pressure vessel was apparently accelerated. The calculated final pH at 150°C, after leaching for 14 days, was 3.8.

Electron micrographs of the leached sample (Fig. 7) indicate the presence of a relatively thick, coarse-grained layer of reaction products. XRD data confirm the presence of calcium hydroxyapatite $Ca_5[(PO_4)_3OH]$ as a major constituent of the layer.

Experiment 4: (SRPC + 20% silica fume) + SCSSS + Na-bentonite

Figure 8 shows that after an initial rapid increase, the silicon concentration reaches about 150 mg/L (5.4 mmol/L SiO_2). The Mg concentration decreases in an exponential fashion, whereas the K concentration remains constant with time at 100 mg/L after two days. Comparison of the leaching data for experiments 3 and 4 shows that the nature of the clay present in the leach solution affects the release kinetics of the elements. The different behavior of the Mg concentration in experiments 3 and 4 seems to be related to the pH of the solution. The pH of the leach solution in the presence of Na-bentonite at 150°C after 2 weeks is 5.2 compared with 3.8 in the presence of Ca-bentonite. The Ca-bentonite used in this study acidifies any groundwater solution owing to large amounts of exchangeable Al^{3+}, which hydrolyze on contact with groundwater, producing protons (Heimann & Stanchell 1984). This leads to pH values in SCSSS as low as 3 at temperatures between 90 and 200°C (Heimann, in prep.). In all leach solutions with pH less than 5, Mg remains dissolved (experiments 3 and 5), whereas in solutions with pH greater than 5 (experiments 1, 2 and 4), Mg is precipitated, as either hydroxide or silicate.

Figure 9 shows the surface of the leached sample covered with the relatively thick layer of reaction products. It has the appearance of a gel (Fig. 9A, region i). The composition of the layer shows the presence of a calcium silicate phase containing minor amounts of Mg and Al, and trace amounts of Fe and Mn (Fig. 9B). Round particles (Fig. 9A, region ii) are composed of Mg and Si (Fig. 9C).

In contrast with experiments 1 to 3, in which no transformation of the primary minerals in the cement was observed, almost complete transformation took place in experiment 4, forming 11-Å tobermorite $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$. Although calculations of Gibbs free energies of the possible reactions for the conversion showed that hydration of the primary phase alite Ca_3SiO_5 should produce hillebrandite $Ca_2SiO_3(OH)_2$, excess reactive silica, as present in cement 311, favors the formation of high-silica phases, predominantly tobermorite or, at temperatures exceeding 180°C at 100 kPa pressure, xonotlite $6CaSiO_3 \cdot 2H_2O$ (Sarkar *et al.* 1982). From a published plot of the basal interplanar spacing of tobermorite against the degree of replacement of silicon by aluminum in the chain of $SiO_2(OH)_2$ tetrahedra in the tobermorite structure (Diamond *et al.* 1966), about 7 mol.% of the silicon is replaced by aluminum in the tobermorite observed in the present work. This finding is consistent with the results of Komarneni & Roy (1983) during the hydrothermal reaction of cement - montmorillonite mixtures with distilled water at 100 and 200°C.

It should be noted that the type of calcium silicate transformation phase has a profound influence on the mechanical properties of the cement. At elevated temperatures exceeding 150°C, crystalline tobermorite or xonotlite (or both) will be formed; their relative proportion increases with increasing

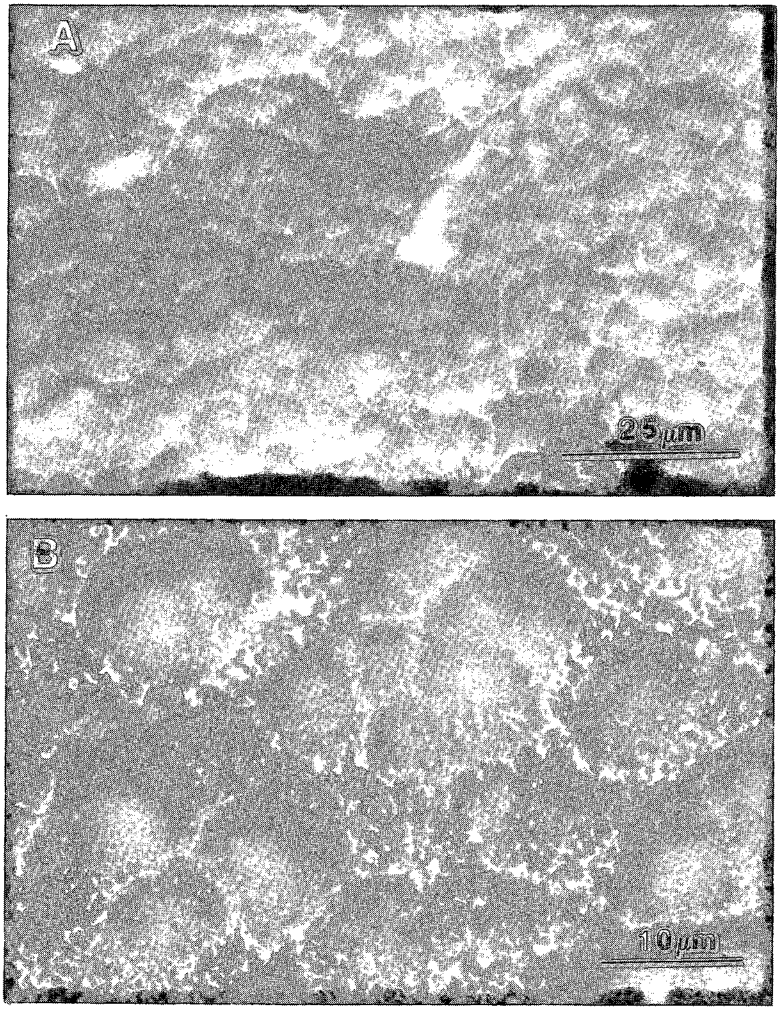

FIG. 7. Electron micrograph of leached surface of cement in experiment 3 at different magnifications.

reaction-time. Because the porosity of the cement matrix increases with the degree of transformation, the compressive strength of the cement body tends to decrease (Taylor 1967). Lower temperatures, around 100°C, produce predominantly a semicrystalline CSH (I) phase (Funk 1967) whose compressive strength is roughly three times that of tobermorite (Butt *et al.* 1960). Thus, temperatures around or below 100°C, realistically expected in a disposal vault for nuclear fuel waste (Baumgartner, in prep.) could increase the mechanical strength and in turn the longevity of cement-based grouting and sealing materials.

In the absence of clay, cement 311, when reacted with SCSSS, forms a compound resembling killalaite $Ca_6Si_4O_{14}{\cdot}H_2O$ (Nawaz 1974) and when reacted with low-salinity "granitic" groundwater (GGW, Sargent 1982) forms dicalcium silicate hydrate ($Ca_2SiO_4{\cdot}H_2O$, Heller 1952). These findings are at variance with the transformation of primary minerals in the cement to tobermorite in the presence of Na-bentonite. In the presence of Na-bentonite, the activity of silica in solution is considered to increase owing to the dissolution of either amorphous silica present in the bentonite or silica in the structure of the montmorillonite. Thus, the Ca/Si atomic ratios of the reaction products decreased from 2 (in $Ca_2SiO_4{\cdot}H_2O$) to 1.5 (in killalaite) to 0.83 (in tobermorite) during reaction of the cement with GGW, SCSSS, and SCSSS + Na-bentonite, respectively.

Experiment 5: (SRPC + 35% fly ash) + SCSSS + Ca-bentonite

In this experiment (Fig. 10), the concentrations of Mg, Si and Fe follow trends similar to those observed for the silica-fume-tempered cement (experiment 3). The K concentration, however, increases steeply within a day to 120 mg/L, and then more slowly within two weeks to 250 mg/L. This high concentration of potassium may be related to the presence of relatively soluble K-aluminosilicate spheres in the fly-ash component of cement 306 (Fig. 1E).

Figure 11A shows a smooth layer of products whose EDX spectrum (Fig. 11B) reveals Ca, P, and trace amounts of Cl. The existence of hydroxyapatite has been also confirmed by XRD. The small amounts of Cl detected in the EDX spectrum may be related to isomorphous replacement of OH by Cl.

DISCUSSION

Because of the complexity of the system, no element could be found whose measured concentration in solution could be used to accurately assess the durability of the cements. However, monitoring the release of potassium can give some indication of durability because, in Ca-rich saline groundwater, no significant ion-exchange of potassium on the clay surface is expected to take place, owing to the much larger selectivity of the montmorillonite structure for Ca^{2+} than for K^+ (Benson 1982, Bruggenwert & Kamphorst 1979).

Thus, the Cumulative Fraction of Release CFR of potassium was calculated to compare the durability of the various cement pastes under different environmental conditions. The CFR values are plotted in Figure 12 for experiments 2 to 5, as well as for SRPC leached in deionized water without addition of clay (CEM-5-303). The latter values serve as a reference to estimate the influence of the saline groundwater and the Ca- and Na-bentonite clays on the release kinetics of potassium. The CFR of potassium from experiment 1 (CEM-6-303) has not been included in Figure 12 because the concentration of potassium in the leach solution remained constant at its original value in the saline groundwater (Table 3) over the entire duration of the leach (Fig. 2). This finding suggests that SRPC in contact with SCSSS without clay has a very low rate of leaching.

The highest CFR of potassium, 50 kg/m^2, was found for SRPC in contact with SCSSS and Ca-bentonite (experiment 2, CEM-1-303). Addition of either silica fume or fly ash decreased the CFR. The SRPC + 20% silica fume in contact with SCSSS and Na-bentonite (experiment 4, CEM-7-311) showed a constant CFR of 10 kg/m^2 throughout the entire leach-period. Fly-ash-tempered SRPC (experiment 5, CEM-2-306) and silica-fume-tempered SRPC (experiment 3, CEM-4-311) in contact with SCSSS and Ca-bentonite show an increasing CFR with time, and appear to attain a value of around 10 kg/m^2 asymptotically.

The CFR of potassium from SRPC in deionized water without addition of clay (CEM-5-303) increases steadily with leach time, and attains a value of 5 kg/m^2 after 14 days.

The shapes of the curves in Figure 12 for the experiments containing Ca-bentonite. *i.e.*, 2, 3 and 5, show a decrease of the rate of CFR of potassium, presumably caused by the formation of some kind of protective layer. Electron microscopy in conjunction with EDX analysis of the leached surfaces of the cement from these three experiments revealed the formation of a hydroxyapatite layer. The sources of phosphate are the Ca-bentonite (0.15% P_2O_5, Table 2) and the cement pastes (0.04 - 0.10% P_2O_5, Table 1). The Ca-bentonite appear to promote precipitation of hydroxyapatite, as indicated by its absence, despite the relatively high phosphate concentration in the original SCSSS of experiment 1 (40 mg/L P_2O_5). Throughout the entire leach-period, the phosphate level in the leach solution of experiment

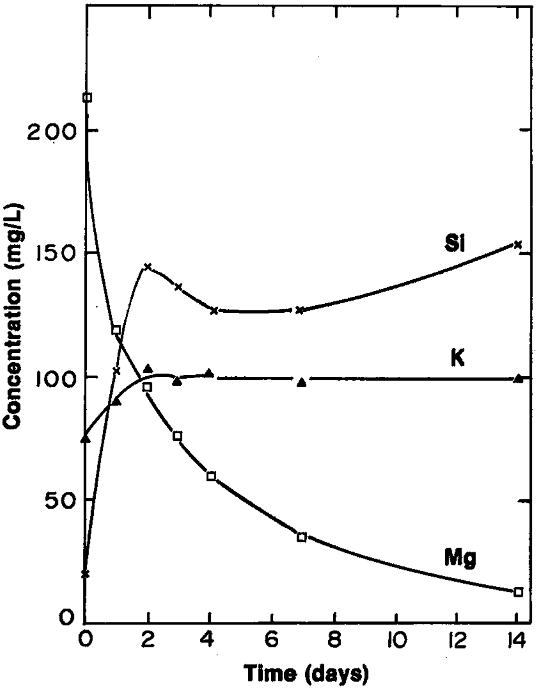

FIG. 8. Concentrations of Si, K and Mg in solution obtained by leaching cement 311 in Standard Canadian Shield Saline Solution + Na-bentonite (50 g/L) at 150°C (experiment 4, CEM-7-311).

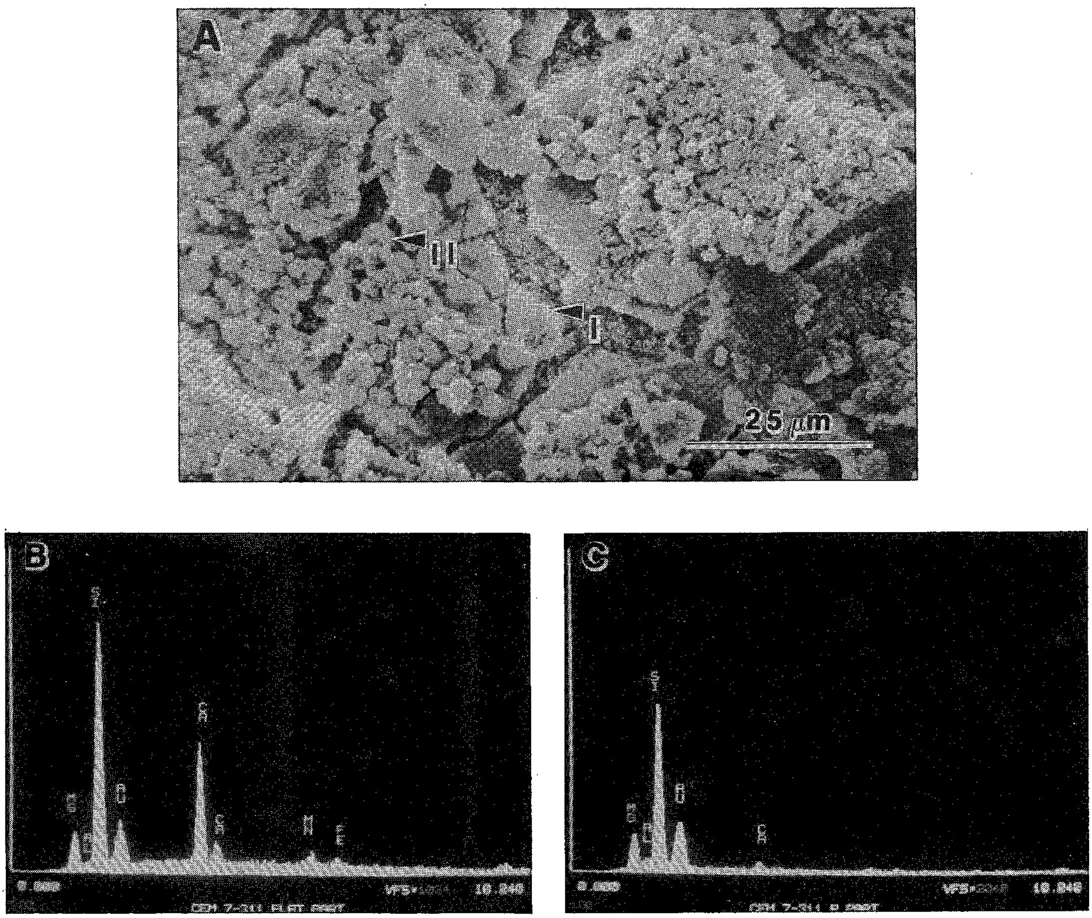

FIG. 9. Electron micrograph of leached surface of cement in experiment 4. A: Gel-like alteration crust (i) and spherical particles (ii). B: EDX spectrum of alteration crust (i). C: EDX spectrum of spherical particles (ii).

1 remained at the original phosphorus concentration in the SCSSS (Fig. 2).

In contrast with the results of the experiments involving Ca-bentonite, experiment 4 (CEM-7-311), involving Na-bentonite, showed a constant CFR throughout the entire leach-time. Although the Na-bentonite contains roughly the same amount of phosphate as the Ca-bentonite (Table 2), no hydroxyapatite layer was found on the leached surface of the cement. However, magnesium silicate and calcium magnesian silicate had precipitated (Fig. 9). An experiment identical to 4, but conducted for 42 days, showed essentially the same result: the K concentration increased steeply to 120 mg/L within two days and then more gradually to a constant level of 145 mg/L within seven days. This level of concentration of K is comparable to that attained by leaching a dense concrete, produced by adding magnetite and hematite to the cement paste SRPC + 20% silica fume, in the presence of SCSSS and Na-bentonite at 100°C (Onofrei, in prep.). It appears that in the presence of Na-bentonite, the CFR of potassium is controlled by residual potassium released from the clay, presumably as a result of the higher pH in the leach solution compared with the experiments involving Ca-bentonite.

SUMMARY

1. In the presence of Ca-bentonite in simulated saline groundwater solution (SCSSS), the concentration of potassium released from cement increases continuously compared with that in leach solutions without clay. In the presence of Na-bentonite, the concentration of potassium released from cement also increases, but attains a constant level after a leach time of two days.

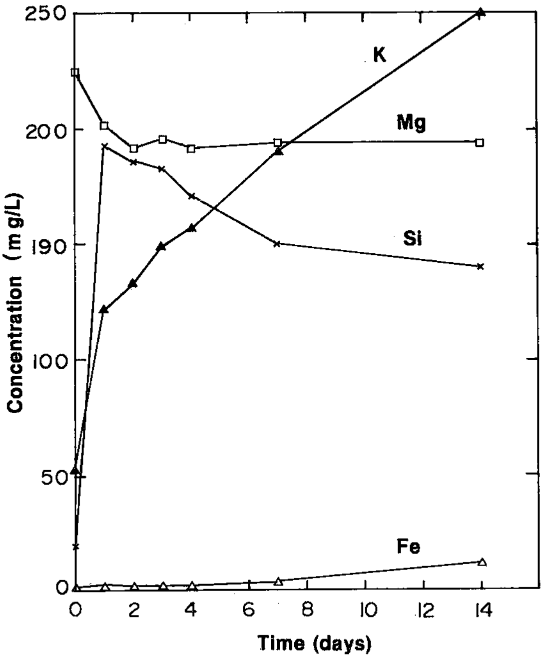

FIG. 10. Concentrations of K, Mg, Si and Fe in solution obtained by leaching cement 306 in Standard Canadian Shield Saline Solution + Ca-bentonite (50 g/L) at 150°C (experiment 5, CEM-2-306).

2. Ca-bentonite produced a lower pH in solution than Na-bentonite, presumably owing to the presence of exchangeable Al^{3+} ions adsorbed onto the clay-mineral sites of the Ca-bentonite. On contact with groundwater, Al^{3+} ions undergo hydrolysis, producing protons.
3. Brucite precipitation was observed on the cement surface after leaching in SCSSS in the absence of clay.
4. In experiments involving Ca-bentonite, a hydroxyapatite layer was formed on the cement surface. Although P_2O_5 contents in the cement pastes are below 0.1 wt.%, calcium phosphate appears at the cement–solution interface because of its very low solubility. Ca-bentonite seems to promote precipitation of hydroxyapatite compared with Na-bentonite.
5. Na-bentonite favors the conversion of the primary calcium silicates in the cement, such as alite or β-larnite, to Al-substituted 11-Å tobermorite.

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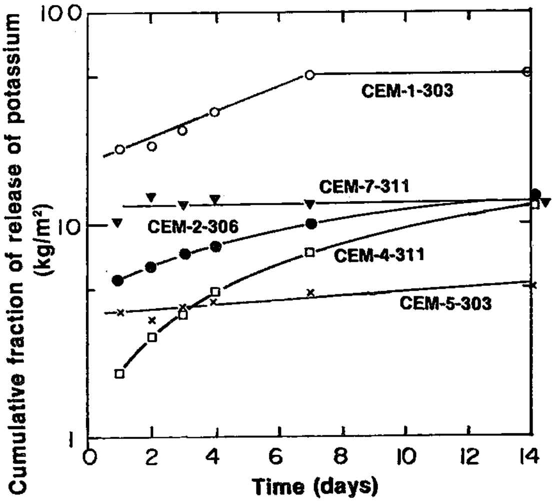

FIG. 12. Cumulative fraction of release (CFR) of potassium as a function of reaction time. CEM-1-303: experiment 2, CEM-4-311: experiment 3, CEM-7-311: experiment 4, CEM-2-306: experiment 5, CEM-5-303: control experiment with deionized water.

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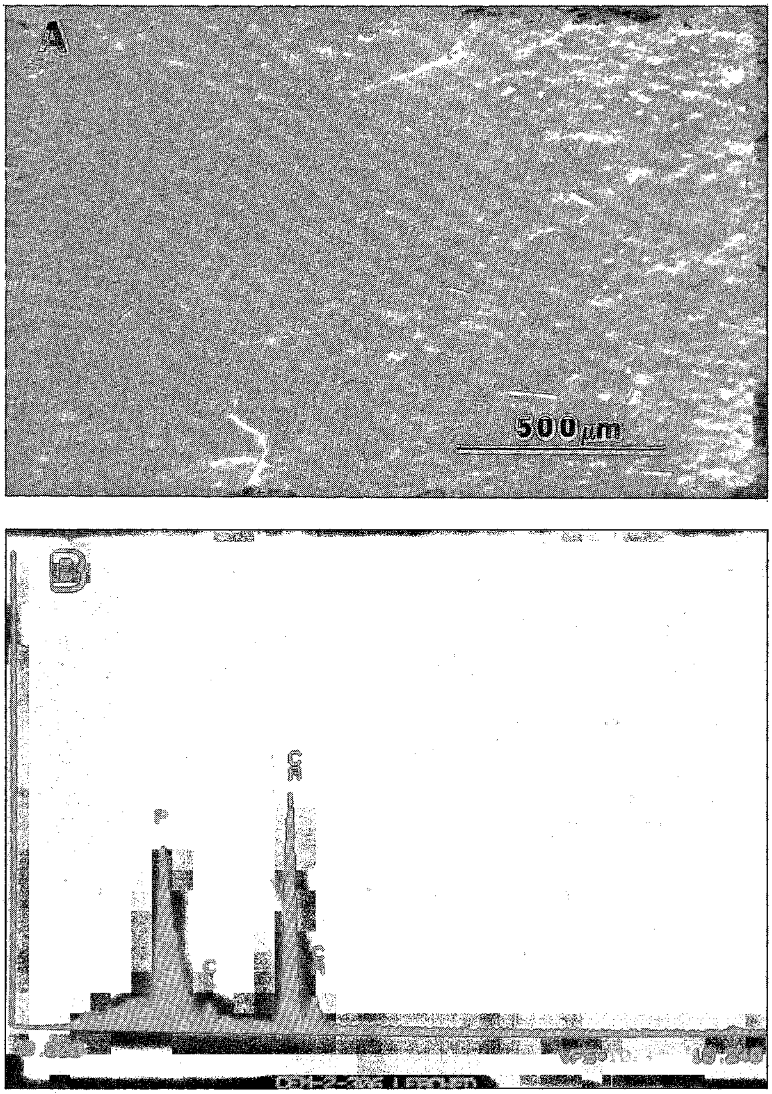

FIG. 11. Electron micrograph of leached surface of cement in experiment 5. A: Smooth layer of hydroxyapatite. B: EDX spectrum of reaction layer.

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