Canadian Mineralogist
Vol. 21, pp. 611-623 (1983)

LEACHING STUDIES OF NATURAL AND SYNTHETIC TITANITE, A POTENTIAL HOST FOR WASTES FROM THE REPROCESSING OF CANADIAN NUCLEAR FUEL†

P.J. HAYWARD, F.E. DOERN, E.V. CECCHETTO AND S.L. MITCHELL
Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba R0E 1L0

ABSTRACT

Glass ceramics (*i.e.*, glasses subjected to controlled crystallization) with synthetic titanite as the major crystalline phase are being considered as potential hosts for the radioactive wastes arising from possible future reprocessing of nuclear fuel in Canada. In order to assess the stability of titanite in the anticipated environment of a disposal vault sited 500–1000 m deep within a granitic pluton in the Canadian Shield, leaching experiments have been performed with natural and synthetic titanite, using a synthetic groundwater whose composition is based on findings from a recent borehole-survey. The results are in qualitative agreement with calculations of solution equilibria for titanite and its main alteration products, and indicate that titanite should be stable and suffer no net leaching under anticipated conditions in the vault.

Keywords: nuclear waste, titanite, stability, solubility, leaching, groundwater.

SOMMAIRE

On étudie actuellement la possibilité d'utiliser, comme hôte, la céramique de verre (c'est-à-dire le verre soumis à une cristallisation contrôlée), dont la titanite synthétique constitue la principale phase cristalline, pour les déchets radioactifs pouvant provenir du retraitement éventuel du combustible nucléaire au Canada. À l'aide d'une eau phréatique synthétique dont la composition est dérivée des données obtenues lors de récentes études de forage, on a procédé à des expériences de lixiviation en utilisant de la titanite naturelle ou synthétique dans le but de connaître la stabilité de la titanite dans le milieu prévu d'une enceinte d'évacuation située à 500–1000 mètres de profondeur, au sein d'un pluton granitique du bouclier canadien. Du point de vue qualitatif, les résultats correspondent aux calculs des équilibres de solutions propres à la titanite et à ses principaux produits d'altération; ils indiquent que la titanite devrait être stable et ne pas subir de lixiviation nette en présence des conditions prévues dans l'enceinte.

Mots-clés: déchets nucléaires, titanite, stabilité, solubilité, lixiviation, eau phréatique.

INTRODUCTION

The Canadian concept for disposing of nuclear fuel wastes is based upon multiple barriers to inhibit the migration of radionuclides from a deep underground vault (Boulton 1978). In addition to the natural geological barriers, various engineered barriers are also being investigated. Two classes of nuclear fuel wastes are being considered for disposal, namely, irradiated CANDU* fuel and also the high-level radioactive wastes that would arise from possible future reprocessing of irradiated fuel from CANDU reactors. High-integrity materials are being developed to immobilize the latter class of wastes, and the disposal concept under investigation involves burial of the high-integrity material ("the waste form") in an engineered vault, at a depth of 500–1000 m, within a granite or granodiorite pluton in the Canadian Shield in Ontario. The waste form would be contained within a metal or ceramic canister surrounded by a suitable "buffer" material (typically bentonite-based), which would swell if contacted by underground water and thus retard access of the water to the waste form. Finally, the vault would be backfilled and sealed.

The purpose of this system of engineered barriers is to retard the release of radionuclides to the biosphere until the radioactivity has decayed to negligible levels. The only credible mechanism for return of radionuclides would be by partial dissolution of the waste form in underground water, followed by solution or colloidal transport to the surface. Consequently, a major criterion in selecting a waste-form material will be its geochemical stability or resistance to leaching in a flooded vault under epithermal conditions.

An additional stipulation arising from the disposal concept under consideration (Boulton 1980, Dixon & Rosinger 1981, Cameron & Strathdee 1979) is that the mean temperature of the vault, which may be varied by design, should not exceed ~100°C. At one proposed spacing of waste canisters, this temperature corresponds to an upper limit of ~ 1 wt.% fission products in the waste form for wastes from irradiated fuel that has been cooled for five years before reprocessing. Cesium-127 and strontium-90 are the major heat-producing radionuclides, each with a half-life of approximately 30 years, so that the vault temperature would approach that of the host rock after several hundred years.

---

*CANDU (*Can*ada *D*euterium *U*ranium) reactors use heavy water as moderator and coolant and natural UO_2 as fuel. A thorium-based fuel cycle is a future possibility.

†Issued as AECL 7856.

CHOICE OF WASTE-FORM MATERIALS

Materials under investigation include borosilicate and aluminosilicate glasses, and glass ceramics based on the mineral titanite ($CaTiSiO_5$). The latter, partly crystalline materials, are produced by controlled crystallization during reheating of precursor glasses from the system Na_2O–Al_2O_3–CaO–TiO_2–SiO_2 (Hayward & Cecchetto 1982). The product consists of 0.5–5 μm titanite crystallites in a matrix of residual aluminosilicate glass. Waste ions incorporated in the parent glass will partition into either the crystalline or the vitreous phase, or may, perhaps, form a separate phase. However, a major factor in the choice of titanite as a candidate phase for waste immobilization is its well-documented ability to take a wide variety of foreign ions into its structure (Ribbe 1980).

In order to understand the leaching behavior of these composite materials, leaching experiments have been performed on representative glass-ceramics and also on specimens of natural and synthetic titanite. This report discusses the results of the leaching experiments on titanite with reference to anticipated conditions in the vault. Results for the glass ceramics will be published separately.

ANTICIPATED CHEMISTRY OF THE GROUNDWATER

A recent survey of more than fifty locations across the Canadian Shield has confirmed that highly saline groundwaters of the Ca–Na–Cl type occur widely at depths below a few hundred metres (Frape & Fritz 1981, 1982), the salinity generally increasing with depth. This trend has been observed in samples from deep boreholes at Sudbury, Ontario, at Thompson, Manitoba, and at Yellowknife, N.W.T., and is illustrated in Figure 1 by groundwater compositions from the Con mine, Yellowknife (Boyle 1979). At depths of 700 metres and below, Ca^{2+} is the dominant cation, and Cl^- is by far the dominant anion. The K^+ and Mg^{2+} concentrations increase slightly with depth, contrary to their behavior at Sudbury and Thompson. At Yellowknife, HCO_3^- and SO_4^{2-} concentrations fall to negligible levels with increasing depth. Concentrations of dissolved silica, which were not measured in the Yellowknife and Thompson data, are likely to lie between the saturation values for quartz (log H_4SiO_4 molality = -4.0) and amorphous silica (log H_4SiO_4 molality = -2.7). Thus, dissolved silica in mine waters in the Sudbury area give a mean log H_4SiO_4 molality of -3.2 for various depths down to 800 m.

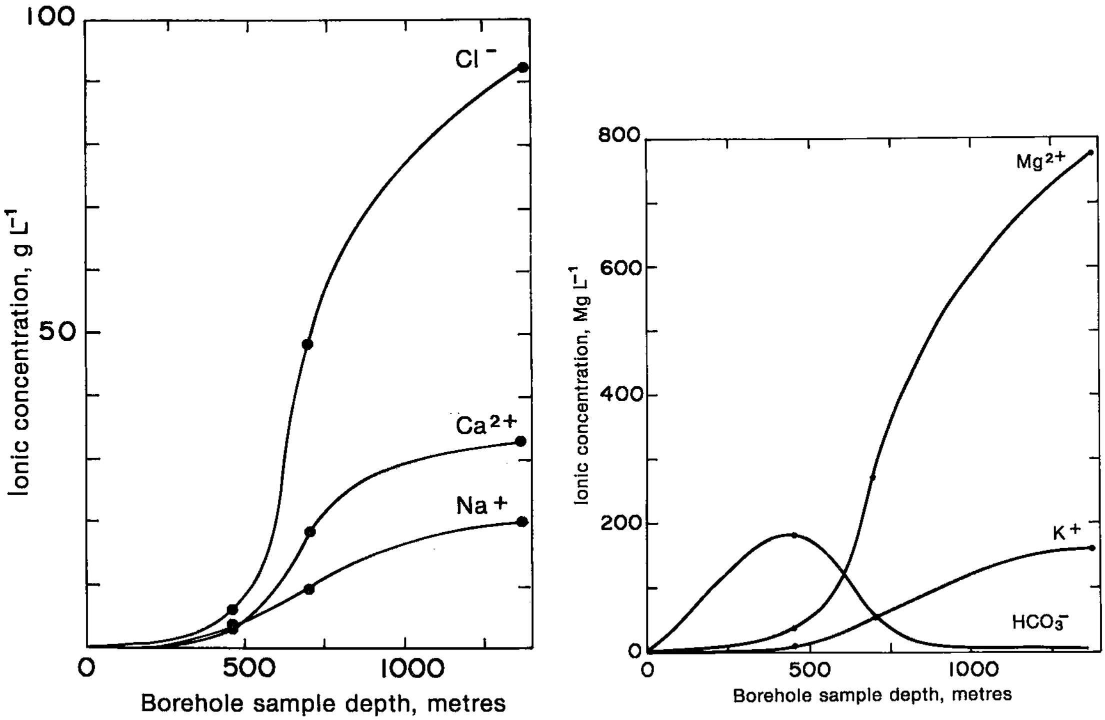

FIG. 1. Variation of groundwater composition with depth at the Con mine, Yellowknife, N.W.T.

It may be concluded from the above that any penetration of the engineered barriers within the vault by groundwater is likely to bring the waste form into contact with solutions rich in Ca^{2+}, Na^+ and Cl^-, and poor in K^+, Mg^{2+}, $SO_4{}^{2-}$ and $HCO_3{}^-$. A standard synthetic groundwater designed to correspond approximately to the Yellowknife groundwater at ~ 700 m depth has, therefore, been prepared for use in leaching experiments. Its composition (in mg L^{-1}) is: Ca^{2+} 15500, Na^+ 5047, Cl^- 34310, SiO_2(aq) 50, Sr^{2+} 20, Mg^{2+} 200, K^+ 50, $SO_4{}^{2-}$ 790, total carbonate as $HCO_3{}^-$ 10, and $NO_3{}^-$ 50, with a total dissolved solids content of 56 g L^{-1}. This synthetic groundwater has also been used as a model composition in the calculations of thermodynamic stability, discussed below.

TITANITE STABILITY IN THE VAULT ENVIRONMENT

Of the species present in natural brines and the synthetic groundwater, reactions might be anticipated between titanite and (a) H_3O^+, (b) sulfate species in solution ($SO_4{}^{2-}$ and $HSO_4{}^-$) and (c) carbonate species in solution ($CO_3{}^{2-}$, $HCO_3{}^-$ and H_2CO_3). In this section, equilibrium conditions for these three classes of reactions are presented, and sample calculations are made for titanite stability in the synthetic groundwater.

Free-energy data for these calculations have been taken from the compilations of Robie *et al.* (1979) and Barner & Scheuerman (1978). High-temperature data for sulfate and carbonate species are taken from Marshall & Jones (1966) and Helgeson (1967), respectively. Saturation solubilities for quartz and amorphous silica, and free-energy data at high temperature for H_4SiO_4 have been computed from Rimstidt & Barnes (1980). Calculations of speciation in solution and of the activities of the resulting species have been made using the computer program SOLMNEQ (Kharaka & Barnes 1973). Activity coefficients are calculated by SOLMNEQ using the $B^{\bullet}$ version of the extended Debye–Hückel equation (Lewis & Randall 1961, Helgeson 1969) and are likely to be in error for high-ionic-strength solutions, such as the synthetic groundwater, by factors of up to 3 for the species considered here (H.W. Nesbitt, pers. comm. 1983). The effect on the equilibrium calculations, however, is expected to be relatively small. Sample calculations for sulfate and carbonate species, described below, confirm that the trends of the results remain unaffected.

Calculated activities of the major ionic species in the synthetic groundwater are listed in Table I. Square brackets are used throughout to denote activities. Species present at very low activities, such as $H_3SiO_4{}^-$, $H_2SiO_4{}^{2-}$ and $HSO_4{}^-$, are ignored in the following calculations.

TABLE 1. CALCULATED ACTIVITIES OF MAJOR IONIC SPECIES IN THE SYNTHETIC GROUNDWATER IN THE TEMPERATURE RANGE 25-150° C

x	−LOG [x]			
	25°C	60°C	100°C	150°C
Ca^{2+}	1.06	1.09	1.16	1.26
Mg^{2+}	2.69	2.73	2.80	2.90
Na^+	0.83	0.85	0.87	0.92
K^+	3.09	3.11	3.13	3.18
Sr^{2+}	4.38	4.43	4.50	4.61
Cl^-	0.21	0.23	0.25	0.29
SO_4^{2-}	3.41	3.57	3.80	4.22
HSO_4^-	8.46	7.85	7.17	6.29
CO_3^{2-}	7.66	8.14	9.00	10.55
HCO_3^-	4.33	4.70	5.23	6.02
H_2CO_3	4.96	5.10	5.19	5.12
NO_3^-	3.29	3.30	3.33	3.37
H_4SiO_4	2.90	2.93	2.94	2.95
$H_3SiO_4^-$	5.54	5.43	5.60	6.24
$H_2SiO_4^{2-}$	10.23	9.92	10.23	11.43
H^+ (pH)	7.00	6.71	6.37	5.81
Eh (volts)	− 0.204	− 0.239	− 0.272	− 0.294
Ionic strength ($1/2\Sigma mZ^2$)	1.457	1.453	1.450	1.446

Reaction with H_3O^+

Activity diagrams for the H^+-H_2O-CaO-TiO_2-SiO_2 system have been published for 25°C (Nesbitt *et al.* 1981a, 1981b) and for 150°C (Hayward & Cecchetto 1982). The corresponding diagram calculated for 100°C is shown in Figure 2. These diagrams demonstrate that, within the temperature range anticipated for the waste vault, and at [SiO_2(aq)] values found in most natural groundwaters, either titanite or rutile is the stable phase in this system, depending on the log ($[Ca^{2+}]/[H^+]^2$) values.

In general, for the reaction

$$CaTiSiO_5 + 2H^+ + H_2O \rightleftharpoons Ca^{2+} + TiO_2 + H_4SiO_4$$

the equilibrium-activity expression is:

$$\log([Ca^{2+}]/[H^+]^2) + \log[H_4SiO_4] = \log K_1 \qquad (1)$$

Values of K_1, the equilibrium constant for the reaction, have been computed as a function of temperature in the range 25–150°C, and used to calculate equilibrium values of log ($[Ca^{2+}]/[H^+]^2$) at log [H_4SiO_4] values corresponding to (a) quartz saturation, and (b) amorphous silica saturation. The

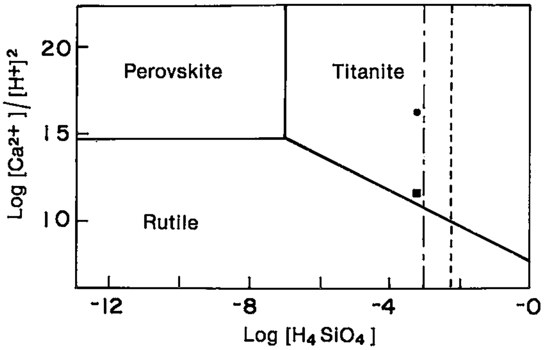

FIG. 2. The system H^+-H_2O-CaO-TiO_2-SiO_2 at 100°C. Dashed lines (a) and (b) represent quartz saturation and amorphous silica saturation, respectively. Square and circle represent the synthetic groundwater at pH 6.37 (unbuffered) and at pH 8.5 (buffered), respectively.

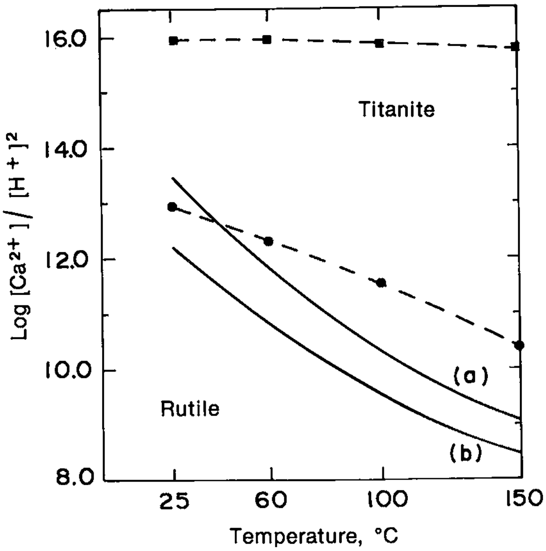

FIG. 3. Equilibrium log ($[Ca^{2+}]/[H^+]^2$) values in the temperature range 25–150°C for the reaction: $CaTiSiO_5 + 2H^+ + H_2O \rightleftharpoons Ca^{2+} + TiO_2 + H_4SiO_4$, at log $[H_4SiO_4]$ values corresponding to quartz saturation and amorphous silica saturation. Dashed line (a) represents log ($[Ca^{2+}]/[H^+]^2$) values for unbuffered synthetic groundwater. Dashed line (b) represents log ($[Ca^{2+}]/[H^+]^2$) values for buffered synthetic groundwater, pH 8.5.

results are shown graphically in Figure 3. Also shown in the figure are the log ($[Ca^{2+}]/[H^+]^2$) values computed for the synthetic groundwater in this temperature range. The groundwater calculations refer to (i) unbuffered conditions, and (ii) solutions buffered to pH 8.5 by addition of a crushed CaO-TiO_2-SiO_2 glass frit (as discussed in the section on experimental procedure).

Providing that the silica content of the groundwater is maintained at a value between the saturation level for quartz and that for amorphous silica, Figure 3 shows that titanite will be stable relative to rutile in the presence of either solution (i) or (ii), the stability increasing at higher temperatures. If a source of Ti ions in solution were made available, as in the case of the groundwater buffered to pH 8.5 by finely powdered glass frit, titanite should precipitate from solution.

Reaction with SO_4^{2-}

For the reactions

$$CaTiSiO_5 + 2H^+ + SO_4^{2-} + H_2O \rightleftharpoons CaSO_4(s) + TiO_2 + H_4SiO_4$$

$$CaTiSiO_5 + 2H^+ + SO_4^{2-} + 1.5H_2O \rightleftharpoons CaSO_4{\cdot}0.5H_2O(s) + TiO_2 + H_4SiO_4$$

$$CaTiSiO_5 + 2H^+ + SO_4^{2-} + 3H_2O \rightleftharpoons CaSO_4{\cdot}2H_2O(s) + TiO_2 + H_4SiO_4$$

computations of the free-energy changes involved in each reaction indicate that anhydrite is the preferred product in the range 150–60°C, with gypsum the preferred product below 60°C. Hemihydrate is metastable with respect to anhydrite or gypsum throughout this temperature range.

The equilibrium expressions for the three reactions all take the form:

$$\log [H_4SiO_4] - \log [SO_4^{2-}] - 2 \log [H^+] = \log K_2 \qquad (2)$$

Equation (2) has been used to calculate values of K_2, the equilibrium constant for the preferred reaction (*i.e.*, to give anhydrite above 60°C and gypsum below 60°C) in the temperature range 25–150°C. By inserting the synthetic groundwater values for log $[SO_4^{2-}]$ into the equation, the equilibrium values of pH for the above reaction at temperatures in this range have been computed for log $[H_4SiO_4]$ values corresponding to (a) quartz saturation, and (b) amorphous silica saturation, and are shown in Figure 4. Also shown is the pH variation of the synthetic groundwater with temperature. The results indicate that titanite should be stable with respect to reaction with sulfate in the goundwater at temperatures above ~25°C, provided that the level of dissolved silica remains close to these saturation values.

Errors in these calculations that result from the use of the B• version of the extended Debye-Hückel equation will be greatest for reactions involving highly charged species in solution, such as SO_4^{2-}.

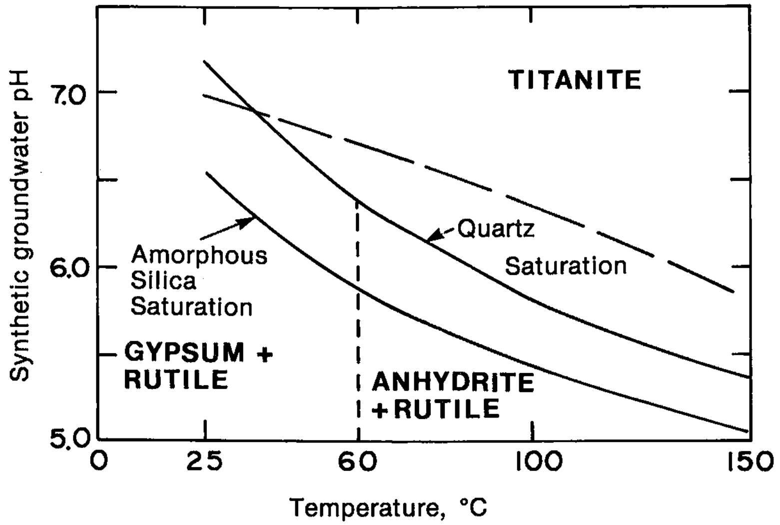

FIG. 4. Variation of equilibrium pH with temperature for the reaction $CaTiSiO_5 + 2H^+ + H_2O + SO_4^{2-} \rightleftharpoons CaSO_4 + TiO_2 + H_4SiO_4$, in synthetic groundwater at specified $[H_4SiO_4]$ values. The dashed line represents the calculated variation in pH with temperature for the unbuffered synthetic groundwater.

Their magnitude and influence may be judged by assuming, as a worst possible case, that the calculated activity-coefficients for SO_4^{2-} are in error by a factor of 3. It then follows from Equation (2) that the boundary between titanite and (rutile + anhydrite) or between titanite and (rutile + gypsum) in Figure 4 will be shifted by ± 0.24 on the pH axis. The temperature for equilibrium between titanite and its reaction products at a given value of $[H_4SiO_4]$ will be altered accordingly. However, the trend shown in Figure 4, namely, the destabilization of titanite with respect to its reaction products as temperature is reduced, remains unchanged.

Reaction with carbonaceous species

The carbonaceous species occurring in groundwaters are CO_3^{2-}, HCO_3^- and H_2CO_3, plus dissolved CO_2. The reactions between titanite and these species are given by:

$$CaTiSiO_5 + CO_3^{2-} + 2H^+ + H_2O \rightleftharpoons CaCO_3 + TiO_2 + H_4SiO_4$$

$$CaTiSiO_5 + HCO_3^- + H^+ + H_2O \rightleftharpoons CaCO_3 + TiO_2 + H_4SiO_4$$

$$CaTiSiO_5 + H_2CO_3 + H_2O \rightleftharpoons CaCO_3 + TiO_2 + H_4SiO_4$$

Equilibrium equations for these three reactions are, respectively:

$$\log [H_4SiO_4] - 2 \log [H^+] - \log [CO_3^{2-}] = \log K_3 \quad (3)$$

$$\log [H_4SiO_4] - \log [H^+] - \log [HCO_3^-] = \log K_4 \quad (4)$$

$$\log [H_4SiO_4] - \log [H_2CO_3] = \log K_5 \quad (5)$$

where K_3, K_4 and K_5 are the equilibrium constants for the reactions. Values for $\log K_3$, $\log K_4$ and $\log K_5$ have been calculated from free-energy data for temperatures in the range 25–150°C, and are shown in Figure 5. Formation of calcite in the reaction products has been assumed, since it is the stable $CaCO_3$ polymorph at atmospheric pressure in this temperature range. Although metastable aragonite is a possible product of reaction at temperatures above ~ 40°C and in the presence of other cations in solution (Deer *et al.* 1962), its formation instead of calcite would have a negligible effect on the above calculations, since the free energies of formation are within ~ 0.1% of each other in the range 25–150°C. Also shown in Figure 5 are the corresponding logarithmic activity-products, $\log AP_3$, $\log AP_4$ and $\log AP_5$, obtained by inserting the activities of the appropriate species in the synthetic groundwater (from Table 1) into Equations 3-5 at several temperatures in this range. For each possible reaction, titanite stability is indicated by the condition $\log AP > \log K$.

The influence of errors in the calculated activity-coefficients for the charged species in solution can

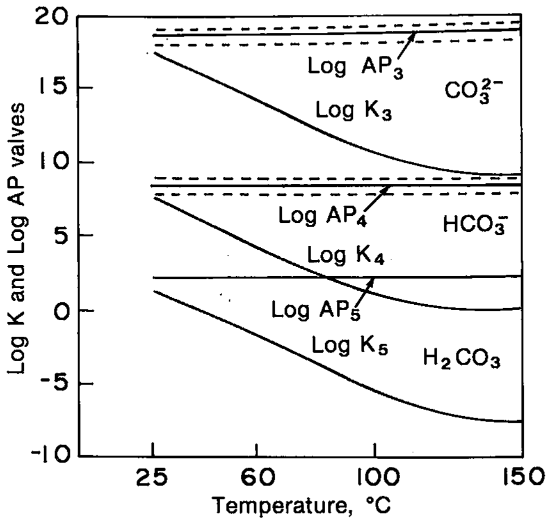

FIG. 5. Variation with temperature of the logarithmic equilibrium-constants, log K_3, log K_4 and K_5, for reaction between titanite and soluble carbonaceous species, calculated from equations 3–5. Also shown is the variation with temperature of the logarithmic activity-products log AP_3, log AP_4 and log AP_5 in unbuffered synthetic groundwater. Dashed lines explained in text.

be estimated, as in the preceding section, by assuming that the values used for CO_3^{2-} and HCO_3^- are in error by a (maximum) factor of 3. It follows, from Equations 3 and 4, that the log AP_3 and log AP_4 curves in Figure 5 may be shifted vertically by up to ± 0.48. This is represented by the areas within the dashed lines.

For all three reactions, a similar trend is seen, namely, convergence of the groundwater activity-products and the equilibrium constants as the temperature falls toward 25°C. The implication from Figure 5 is that titanite should be stable in the presence of the CO_3^{2-}, HCO_3^- and H_2CO_3 in the synthetic groundwater at all temperatures in this range, its stability increasing at higher temperatures.

The conclusion from these simplified thermodynamic analyses is that titanite should be stable in the synthetic groundwater at all temperatures in the range 25–150°C. However, it should be noted that this conclusion may not be directly applicable to a crystalline waste-form based on titanite, since the following factors have not been considered: (i) radiation-damage and transmutation effects in the titanite structure resulting from the incorporation of fission products, (ii) stability-field changes due to the incorporation of fission products and processing chemicals (*e.g.*, Na^+, used for solution-scrubbing and adjustment of plutonium valency during reprocessing), (iii) any grain-boundary segregation of waste ions not easily accommodated in the titanite structure, and (iv) ion exchange at the titanite surface between, for example, fission products in the Ca sites and Ca^{2+} from the groundwater. These complications will need to be addressed in future experimental studies.

The remainder of this report describes leaching experiments with natural and synthetic titanite in deionized water and under conditions designed to simulate a flooded waste-vault. The experiments were intended to measure rates of release of ions from titanite in these leaching solutions, and do not necessarily represent equilibrium situations. Nevertheless, many of the experimental observations are in agreement with thermodynamic predictions, and suggest that the simplified thermodynamic analyses described above may be useful in predicting long-term stability. In contrast, kinetically-based leaching models require extrapolation beyond their time frames to be applicable to predictions of leaching behavior over extended periods of time, and this extrapolation is always open to question.

EXPERIMENTAL PROCEDURES

Sample preparation and analysis

Samples of synthetic (ceramic) titanite were prepared by melting a stoichiometric mixture of $CaCO_3$, TiO_2 and SiO_2 in a platinum crucible at 1450°C, pouring the melt into water, drying the resulting "frit", reheating to 1050°C for one hour to crystallize the "frit", and then grinding under butanol in an alumina jar with alumina grinding media. The product after drying is a fine (< 10 μm) powder, to which was added 1% stearic acid and 3% wax binder in an ether - carbon tetrachloride solution to form a slurry. The slurry was dried and granulated to less than 800 μm, and 10–20 g quantities were pressed into 25-mm diameter pellets in a hardened steel die at 25 MPa. The pellets were sintered by heating at 5°C per minute to 1310°C and held at this temperature for six hours. The final ceramic consists of interlocking $CaTiSiO_5$ crystallites 5–20 μm in diameter, with an estimated porosity of ~ 5–10%. Scanning-electron-microscope (SEM) examination of numerous fracture-surfaces showed that the pores are typically 5–25 μm in diameter and not interconnected. ASTM test C20 (ASTM 1980) was used to confirm that a representative sample is impervious to water.

Analyses have been performed on these ceramics and on similar ceramics prepared with partial replacement of calcium and titanium by simulated fission products, uranium and thorium. Methods included HF-$HClO_4$ dissolution followed by atomic absorption (AA) spectroscopy, or neutron-activation analysis, or X-ray fluorescence (XRF) spectroscopic analysis on powdered and solid specimens. Mean results for the undoped ceramic were CaO 24.4, TiO_2 40.9, SiO_2 30.7, Al_2O_3 2.9, other oxides (principally Na_2O, K_2O and MgO) 1.1 wt.% by difference, indicating that the method of preparation had produced slight loss of calcium and enrichment in aluminum. X-ray-diffraction results showed titanite to be the only detectable crystalline phase, and SEM examination of fractured surfaces showed no inclusions or obvious secondary phases.

Samples of natural titanite from North Crosby Township, Ontario, have also been used in these experiments; electron microprobe and XRF analyses gave CaO 27.7, TiO_2 36.5, SiO_2 30.3, FeO 1.25, MnO 0.25, Al_2O_3 1.7, Na_2O 0.04, V 0.5, La 0.3, Y 0.04, Zr 0.04, Sr 0.02 wt. %.

Leaching experiments

Monolithic samples of both the ceramic and North Crosby Township (NCT) titanite have been used in static leaching experiments, with both deionized water and synthetic groundwater as leachants. The NCT titanite specimens were cut from the massive mineral using a fine diamond saw and light oil as cutting fluid. Orthogonal specimens of 10–20 mm side dimension were ground to 600-mesh finish using carborundum paper and a light oil lubricant, followed by rinsing in acetone. Cylindrical ceramic specimens, approximately 18 mm in diameter and 1–4 mm high, were prepared and ground in a similar manner.

Leaching experiments were performed in 150-ml sealed teflon vessels, heated to 100°C in a circulating oven. In all cases, an apparent ratio of surface area to leachant volume of 0.1 cm^{-1} was maintained. The surface-area measurements were made geometrically, and thus did not take surface roughness or the presence of exposed pores into account. Apparent leach-rates calculated for these samples would, therefore, be higher than true leach-rates. The problem of surface-area measurements in the preparation of ceramic samples for leaching experiments has been discussed by Coles & Bazan (1982), who concluded that alternative methods such as those based on measurements of N_2 or Kr sorption give results at least one order of magnitude too high.

Leaching was followed by weight-change measurements on the samples at 30-day intervals for up to one year, followed by re-immersion of the samples in the leaching solutions. Solution analyses were performed at the termination of each test, and surface examinations of selected specimens were made using SEM combined with energy-dispersion X-ray analysis (EDX). To identify some of the finer surface-precipitates and reaction products, extraction replicas were made using acetyl cellulose foils, which were then used for scanning-transmission electron-microscopy (STEM) EDX analyses of individual grains.

Leaching experiments with the synthetic groundwater were performed in two ranges of pH. Some were done with no added pH buffer (except for dissolved CO_2, introduced during the weight-change measurements); here, the pH remained in the range 6.0–6.5. In some experiments, however, 5 g of a powdered glass (*i.e.*, amorphous) frit of composition 30.8 CaO, 31.4 TiO_2, 37.8 wt.% SiO_2 was added to increase the pH to the range 8.0–9.0 without the addition of foreign ions to the system. The frit also served as a source of Ca, Ti and Si ions, which could dissolve and reprecipitate as crystalline titanite if it were thermodynamically stable under the experimental conditions.

Finally, 5 g of powdered biotite granite (Cold Spring quarry, Lac du Bonnet, Manitoba) were added to each teflon vessel to simulate rock–groundwater interactions. It was anticipated that the major effect of these additions would be rapid saturation of the groundwater with respect to Al^{3+} and SiO_2 (aq). It was also recognized, however, that the use of additions of powdered granite and glass frit allowed the possibility of their adherence to the specimen surfaces and interference with weight-change measurements, and that surface analyses would be required to distinguish this situation.

Experiments involving titanite plus deionized water were performed in the same manner, except that no additions of glass frit or powdered granite were made.

EXPERIMENTAL RESULTS

NCT titanite + deionized water

Determinations of solution concentrations and sample-weight changes were performed in triplicated experiments, terminated after 30, 60 and 90 days, respectively. Elemental leach-rates ($kg{\bullet}m^{-2}{\bullet}s^{-1}$)

TABLE 2. INDIVIDUAL ION AND BULK LEACH-RATES, NATURAL AND SYNTHETIC TITANITE

Material	Leaching Duration in Days	Bulk Rate from wt.loss	Calculated from Leaching Solution Analyses			
			Bulk rate	Ca rate	Si rate	Ti rate
NCT titanite	30	2.4(2.0)	2.4(1.1)	6.6(3.8)	2.0(0.5)	<0.015
	60	5.4(2.9)	2.1(0.9)	5.9(2.2)	1.4(1.1)	0.02(0.02)
	90	2.3(1.4)	1.4(0.2)	3.7(0.1)	1.3(0.5)	0.003(0.002)
synthetic titanite	30	—	4.7(0.9)	4.3(1.3)	11.0(2.2)	<0.24
	60	3.4(0.1)	3.6(0.2)	4.2(0.2)	7.6(0.8)	<0.16
	90	2.7(0.1)	2.7(0.1)	3.2(0.2)	5.7(0.5)	0.003(0.0006)
	120	2.4(0.2)	2.7(0.1)	3.4(0.4)	5.6(0.4)	<0.002

Leach rates (× 10^{-10}) expressed in $kg.m^{-2}.s^{-1}$, with standard deviation in parentheses. Natural titanite from North Crosby Township, Ontario. Leaching was carried out at 100°C in deionized water.

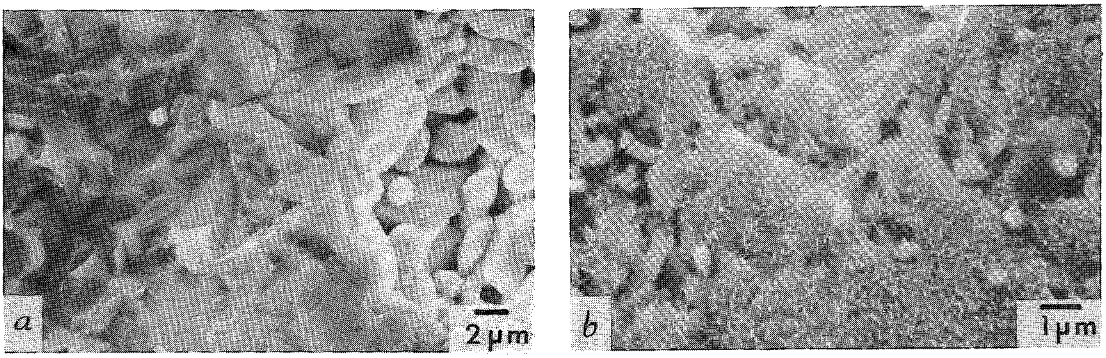

FIG. 6. Scanning-electron photomicrographs of (a) titanite ceramic, fracture surface, and (b) titanite ceramic, leached 120 days in deionized water at 100°C.

were calculated from the equation: leach rate = C_iV/F_iAt, where C_i is the concentration of the analyzed element or ion (kg L^{-1}), V is the leachant volume (L), A is the geometric surface-area (m^2), t is the duration of the leaching experiment (s), and F_i is the element or ion fraction in the mineral as defined by $F_i = X_iW_i/100\ W_{ox}$, where X_i is the weight percent of the oxide of element i in the mineral, W_i is the atomic weight of the element or ion multiplied by the number of ions in the oxide formula, and W_{ox} is the molecular weight of the oxide. F_i relates the ion concentration in solution to the ion concentration in the mineral, and the resulting leach-rate for each element or ion is thus normalized to unit concentration in the mineral.

Bulk leach-rates were calculated both from the weight-loss measurements and from the ion concentrations in solution. Discrepancies between the two may be due to (i) analytical or weighing errors, (ii) precipitation of surface phases from solution, (iii) formation of a hydroxylated layer on the mineral surface and (iv) back precipitation of a leached phase onto the mineral surface.

Leach-rate data for NCT titanite in deionized water are summarized in Table 2. The bulk leach-rates determined from composition of solution and weight-loss measurements are, within experimental error, in agreement. The leach rates of the individual ions demonstrate a preferential removal of Ca^{2+} compared to Si^{4+}, with Ti^{4+} almost immobile, suggesting that a surface layer rich in a titanium oxide species is formed at the mineral surface. Metson *et al.* (1982) independently observed the formation of titanium-rich surface layers and selective leaching of

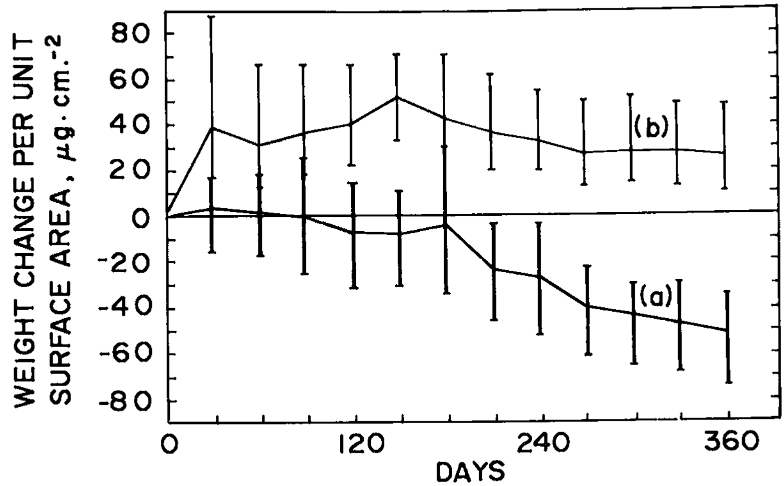

FIG. 7. Leaching results for North Crosby Township titanite using (a) synthetic groundwater plus crushed granite, pH 6.0–6.5, and (b) synthetic groundwater plus crushed granite plus $CaO-TiO_2-SiO_2$ glass frit, pH 8.0–9.0. Static tests at 100°C.

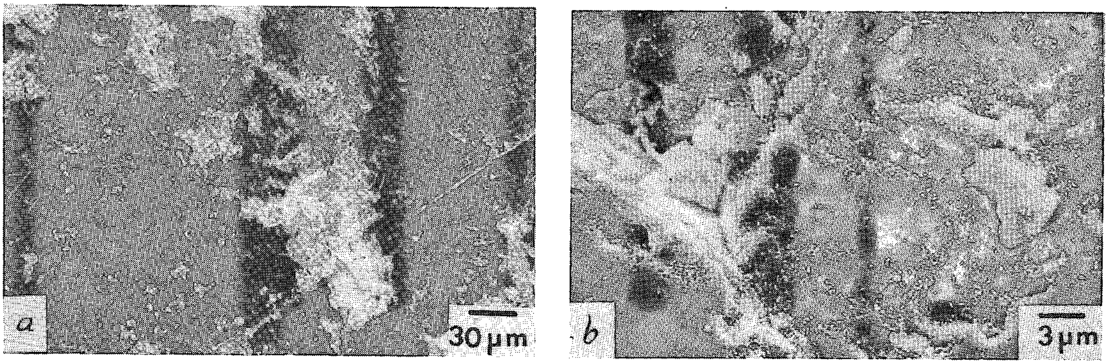

FIG. 8. Scanning-electron photomicrographs of North Crosby Township titanite leached in synthetic groundwater plus crushed granite, pH 6.0–6.5 for 360 days at 100°C.

Ca^{2+} and Si^{4+} on samples of leached titanite using X-ray-photoelectron spectroscopy and secondary ion mass-spectrometry.

Synthetic titanite + deionized water

Compositions of solution and weight-change measurements from triplicated experiments were used to calculate bulk and elemental leach-rates in tests terminated after 30, 60, 90 or 120 days. The leach rates are presented in Table 2, and are in good agreement with those obtained for NCT titanite except for the Si^{4+} rates, which are somewhat larger. The higher rates found for Si^{4+} may be due to loss of Ca^{2+} (and gain of Al^{3+}) during ceramic fabrication, so that the resulting ceramic probably contained stoichiometric $CaTiSiO_5$ plus traces of surplus TiO_2 and SiO_2 together with Al_2O_3. Although $CaTiSiO_5$ was the sole phase identified by XRD and SEM–EDX, considerations of phase equilibria suggest that quartz, rutile, corundum and, possibly, mullite could have been present as minor coexisting phases and may have contributed to an enhanced leach-rate for Si^{4+}.

Scanning-electron photomicrographs of an unleached and a leached ceramic surface are shown in Figure 6. Two distinct phases are seen to have precipitated on the surface of the leached sample. SEM–EDX resolution was not adequate to analyze the fibrous phase. The prismatic phase was identified by EDX as being Al- and Si-rich, although the crystal morphology did not appear to resemble those of hydrothermal aluminosilicates such as kaolinite or pyrophyllite.

NCT titanite + synthetic groundwater + crushed granite, pH 6.0–6.5

The mean results of weight-change measurements made on three specimens in continuous experiments lasting 360 days are shown in Figure 7, curve (a). After an initial gain in weight, a slight but progressively increasing loss was recorded, so that the mean bulk leach-rate between days 90 and 360 was $(2.2 \pm 0.3) \times 10^{-10}$ kg•m^{-2}•s^{-1}.

SEM–EDX examination of the leached surfaces (Fig. 8) showed that little dissolution of the matrix had occurred (original polishing scratches were still

TABLE 3. COMPOSITION OF PARTICLES FROM EXTRACTION REPLICAS OF LEACHED TITANITE

Analysis	Na	Mg	Al	Si	K	Ca	Ti	Fe	Cl	S	Phase identified
(a)											
(i)	-	4	21	50	5	7	-	12	-	-	clay mineral?
(ii)	0.5	7	9	39	0	2	1	41	-	-	chlorite?
(iii)	-	-	20	56	23	-	-	1	-	-	altered? K feldspar
(iv)	1	-	26	65	-	4	1	2	-	-	clay mineral?
(v)	-	-	3	94	-	-	-	3	-	-	quartz
(b)											
(vi)	0.8	-	23	62	1.4	6	3	3	-	-	clay mineral?
(vii)	-	-	26	70	-	3	-	1	-	-	clay mineral?
(viii)	-	-	24	64	6	4	-	2	-	-	clay mineral?
(ix)	-	-	2	96	-	-	-	1	-	-	quartz
(x)	-	10	17	34	12	1	-	27	-	-	chlorite?
(c)											
(xi)	-	-	-	7	-	53	2	-	-	39	gypsum or anhydrite
(xii)	-	-	24	72	-	4	-	-	-	-	clay mineral?
(xiii)	-	-	-	60	-	37	1	1	1	-	xonotlite?
(xiv)	-	-	8	57	2	32	0.8	-	-	-	?
(xv)	-	-	-	29	-	36	34	-	-	-	titanite
(d)											
(xvi)	-	-	25	67	-	6	1	1	-	-	clay mineral?
(xvii)	-	-	-	28	-	34	37	-	-	-	titanite
(xviii)	-	-	2	55	-	35	5	-	-	-	intergrown xonotlite-titanite?
(xix)	-	5	18	69	-	6	1	1	-	-	clay mineral?
(xx)	-	2	0.5	36	-	34	27	1	-	-	titanite

Compositions determined by STEM-EDX analysis, expressed in cation wt. %, excluding oxygen and hydroxyl. (a) North Crosby Township titanite, 360 days in synthetic groundwater plus crushed granite at 100°C, pH 6.0-6.5. (b) Synthetic titanite, same conditions as (a). (c) North Crosby Township titanite, 360 days in synthetic groundwater plus crushed granite plus glass frit at 100°C, pH 8.0-9.0. (d) Synthetic titanite, same conditions as (c).

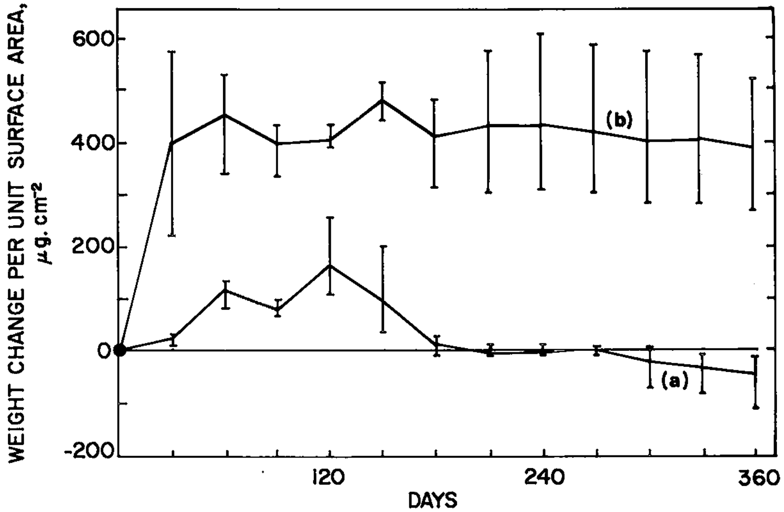

FIG. 9. Leaching results for synthetic titanite using (a) synthetic groundwater plus crushed granite, pH 6.0–6.5, and (b) synthetic groundwater plus crushed granite plus $CaO-TiO_2-SiO_2$ glass frit, pH 8.0–9.0. Static tests at 100°C.

visible). Surface phases, mainly K–Al–Si, were predominantly those of debris from the addition of crushed granite. The fine precipitate visible in Figure 8b was too small to permit EDX analysis.

STEM-EDX measurements were made on five particles adhering to an extraction replica. The EDX measurements, converted to cation weight percents, are given in Table 3a. Although it was not always possible to identify these phases on the basis of the EDX analyses and morphologies, the compositions correspond to granite or altered granite debris. The high content of Fe in composition (ii) may represent reprecipitated Fe leached from either the underlying titanite or the crushed granite.

Synthetic titanite + synthetic groundwater + crushed granite, pH 6.0–6.5

Weight-change measurements were made on three specimens in continuous experiments up to 360 days; the results are plotted in Figure 9, curve (a). A somewhat larger initial weight-gain was found than for NCT titanite, and this persisted up to day 180, after which the ceramic lost weight, with a bulk leach-rate of (0.65 ± 0.36) × 10^{-10} $kg{\bullet}m^{-2}{\bullet}s^{-1}$.

SEM examination of a leached surface after 360 days showed little visible evidence of bulk dissolution of the ceramic: the original polishing scratches were still clearly visible (Fig. 10). The closed pores in the original unleached ceramic (Fig. 6a), which had been exposed during cutting and grinding of the sample, are seen to be largely infilled with debris from the crushed granite; EDX analysis of this debris demonstrate the presence of quartz and K–Al–Si phases.

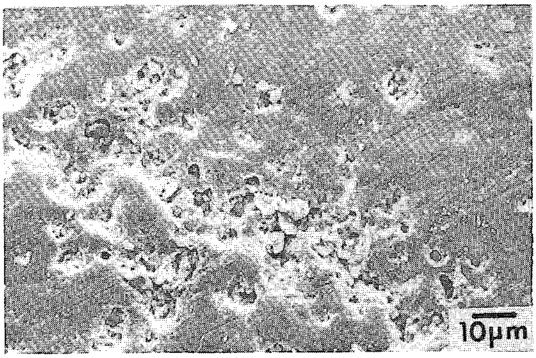

FIG. 10. Scanning-electron photomicrograph of synthetic titanite leached for 360 days at 100°C in synthetic groundwater plus crushed granite, pH 6.0–6.5.

STEM–EDX measurements were performed on five particles from an extraction replica, and the proportions of cations (wt. %) are quoted in Table 3(b). The results confirm the presence of granitic or altered granitic phases, and are similar to those of Table 3(a).

NCT titanite + synthetic groundwater + crushed granite + glass frit, pH 8.0–9.0.

Weight-change measurements were made for three specimens during 360 days of leaching, and the mean

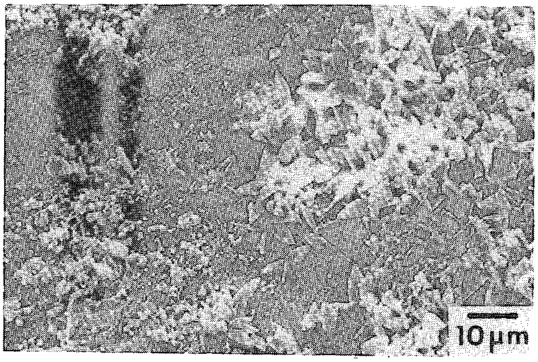

FIG. 11. Scanning-electron photomicrograph of North Crosby Township titanite leached for 360 days at 100°C in synthetic groundwater plus crushed granite plus $CaO-TiO_2-SiO_2$ glass frit, pH 8.0–9.0.

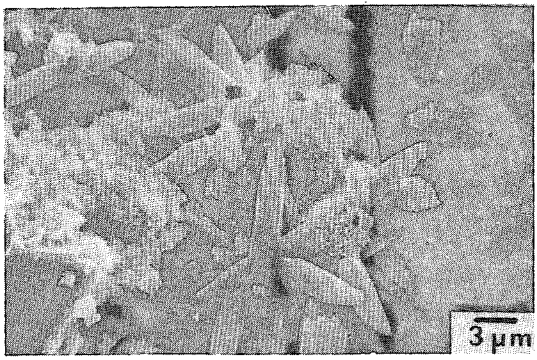

FIG. 12. Scanning-electron photomicrograph of synthetic titanite leached for 360 days at 100°C in synthetic groundwater plus crushed granite plus $CaO-TiO_2-SiO_2$ glass frit, pH 8.0–9.0.

results are shown in Figure 7, curve (b). In contrast to the results of the experiments at pH 6.0–6.5, the initial gains in weight observed after 30 days leaching were maintained for the duration of the experiment.

SEM examination of specimen surfaces after 360 days leaching showed the buildup of a multiphase surface-layer (Fig. 11). The elongate crystals were indentified by EDX as a Ca–Ti–Si phase, and the rhomboidal morphology is characteristic of titanite. Other phases were found to be Al- and Si-rich with some K and Ca and traces of Na and Mg, and most probably represent original or altered granite debris. STEM–EDX analytical data on 5 particles from an extraction replica are given in Table 3(c), and are in general agreement with the SEM–EDX results.

Synthetic titanite + synthetic groundwater + crushed granite + glass frit, pH 8.0–9.0.

Weight-change measurements were made for three specimens during the course of 360 days of leaching, and mean results are shown in Figure 9, curve (b). The observed trend, namely, a significant gain in weight during the first 30 days followed by little weight-change thereafter, is similar to that observed for the NCT titanite samples, but approximately on one order of magnitude larger.

SEM examination of the specimen surfaces after 360 days leaching showed a buildup of a multi-phase layer (Fig. 12). The rhomboidal crystals were again identified by EDX and morphology as titanite. The coral-like growth on the titanite crystals in the figure is a calcium silicate with traces of Mg, Al, K and Cl, possibly xonotlite $Ca_6Si_6O_{17}(OH)_2$ or tobermorite $Ca_5Si_6O_{17}{\bullet}5H_2O$.

Results of STEM–EDX analyses of five grains from an extraction replica of a leached surface are given in Table 3(d), and confirm the presence of titanite. Composition (xviii) may correspond to intergrown titanite plus a hydrated calcium silicate phase, such as the coral-like phase observed in Figure 12. The other compositions probably represent clay minerals or feldspars (or mixtures of the two).

DISCUSSION AND CONCLUSIONS

The results of leaching of the two varieties of titanite with deionized water are similar, and suggest that Ca and Si are preferentially leached to leave a surface layer enriched in Ti. This is consistent with the thermodynamic arguments presented earlier, since rutile or, possibly, anatase or brookite (rutile polymorphs) would be the stable phase under these conditions (Fig. 2). Nesbitt *et al.* (1981a) identified brookite on the surfaces of perovskite leached in deionized water, which may be regarded as a similar reaction involving Ca^{2+} leaching. The buildup of a Ti-rich surface layer would progressively reduce the exposed surface-area of unleached titanite, so that the leach rates of Ca^{2+} and Si^{4+} in deionized water should decrease with time until they reach a value controlled by the rate of dissolution of the TiO_2-enriched surface layer. There is evidence in our experiments of a slight fall with time in the Ca^{2+} and Si^{4+} leach rates, but Figure 6 confirms that the surface TiO_2 layer is not sufficiently coherent to constitute a significant barrier to further leaching. Longer-term experiments are required to confirm this prediction.

The weight losses observed for both NCT and synthetic titanite in the experiments with synthetic groundwater at pH 6.0–6.5 are not easily understood. Figure 3 suggests that titanite should be stable under these conditions, and no visible evidence for leaching, such as etch pits or obvious alteration-products, was found in the SEM examinations of either material. At this pH range, and assuming Al_2O_3 saturation (from the addition of crushed granite), calculations of mineral-solution equilibria using the SOLMNEQ program indicate that the leachant is supersaturated with respect to at least 29 minerals, the majority being clays. The early gains in weight in the experiments are presumably due to precipitation of one or more of these supersaturated phases on the surfaces of the specimens. It is possible that part of the observed weight-losses was the result of repeated drying of the samples prior to weighing, followed by rewetting when the samples were replaced in the groundwater, causing the adhering layer to loosen and separate. It is also possible that the local activity of Ca^{2+} and H^+ at the surfaces of the titanite specimens departed significantly from the mean values in the solution, making titanite a nonequilibrium phase and consequently causing leaching of Ca^{2+} and Si^{4+} ions from the surfaces. The observed weight-losses correspond to removal of approximately 0.1 μm of material from exposed surfaces; it is doubtful whether such a small loss would be visible using SEM.

In the groundwater experiments at pH 8.0–9.0, the addition of the glass frit raised the pH by surface exchange of Ca^{2+} for H^+, and also provided a source of Ca, Si and Ti ions in solution. The observation that fresh titanite crystals formed on the surfaces of both the NCT and the specimens of synthetic titanite confirms that titanite is a stable phase at high Ca^{2+} concentrations in solution or high pH when the H_4SiO_4 activity is at, or close to, saturation values. Thus the gypsum or anhydrite deposited in the surface layers [Table 3(c), analysis (xi)] was produced by precipitation from the groundwater rather than from alteration of titanite. This deduction is supported by SOLMNEQ calculations of solution equilibria for the groundwater at 100°C and pH 8.5, which indicate that the latter was significantly supersaturated with respect to gypsum and to anhydrite, and also by the failure to observe rutile, anatase or brookite in the altered layers. In the same way, the unaltered nature of the titanite surfaces, where visible through the precipitated layers, and the absence of either calcite or aragonite in these layers, suggest a lack of reaction with carbonate species in solution.

The significant difference in magnitude of the weight gains observed for synthetic and NCT titanite at 100°C and pH 8.5 may be due to the differing abilities of the ceramic surfaces and the mineral surfaces to cause precipitation and adherence of supersaturated phases from the groundwater solution, or to permit adherence of debris and alteration products from the crushed granite. It should be noted that the surfaces of the ceramic specimens contain numerous exposed pores, none of which are interconnected, but which could have acted as sites for precipitation from solution or for infilling by granite debris.

The overall conclusion from these experiments is, therefore, that titanite has excellent durability under anticipated conditions in a waste repository. For successful development of a titanite glass-ceramic wasteform, however, it will be necessary to demonstrate that a significant fraction of the waste ions in the parent glass partitions into the titanite structure during controlled crystallization. This aspect is being explored at the Whiteshell Nuclear Research Establishment, McMaster University and the University of Western Ontario using ion-beam or electron-beam microanalytical techniques, in many cases at their limits of spatial and spectroscopic resolution.

ACKNOWLEDGEMENTS

Sincere thanks are due to P.G. Richardson for the STEM/EDX analyses, and to the staff of the Analytical Science Branch at WNRE and J.B. Metson of the University of Western Ontario for the solution and solid analyses. The advice and comments of many colleagues, including B.W. Goodwin, R.J. Lemire, H.W. Nesbitt, J.B. Metson, G.M. Bancroft, J.C. Tait, K.B. Harvey and A.G. Wikjord, are also gratefully acknowledged. The referees' comments were most useful in preparing the final version of this contribution.

REFERENCES

AMERICAN SOCIETY AND MATERIALS (1980): Annual Book of ASTM Standards **17**, C2, 6-8.

BARNER, H.E. & SCHEUERMAN, R.V. (1978): *Handbook of Thermochemical Data for Compounds and Aqueous Species.* John Wiley & Sons, New York.

BOULTON, J., ed. (1978): Management of radioactive fuel wastes: the Canadian disposal program. *Atomic Energy Can. Ltd., Rep.* **AECL-6314.**

______ (1980): Second annual report of the Canadian nuclear fuel waste management program. *Atomic Energy Can. Ltd., Rep.* **AECL-6804.**

BOYLE, R.W. (1979): The geochemistry of gold and its deposits. *Geol. Surv. Can. Bull.* **280.**

CAMERON, D.J. & STRATHDEE, G.G. (1979): Material aspects of nuclear waste disposal in Canada. *In* Ceramics in Nuclear Waste Management (T.D. Chikalla & J.E. Mendel, eds.). U.S. Dep. Energy Rep. **CONF-790420.**

COLES, D.G. & BAZAN, F. (1982): Continuous-flow leaching studies of crushed and cored SYNROC. *Nucl. Tech.* **56,** 226-237.

DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1962): *Rock-Forming Minerals.* V. *Non-Silicates.* Longmans, London.

DIXON, R.S. & ROSINGER E.L.J. (1981): Third annual report of the Canadian nuclear fuel waste management program. *Atomic Energy Can. Ltd., Rep.* **AECL-6821.**

FRAPE, S.K. & FRITZ, P. (1981): A preliminary report on the occurrence and geochemistry of saline groundwaters in the Canadian Shield. *Atomic Energy Can. Ltd., Tech. Rec.* **TR-136.**

______ & ______ (1982): Saline groundwaters in the Canadian Shield, a first overview. *Chem. Geol.* **36,** 179-190.

HAYWARD, P.J. & CECCHETTO, E.V. (1982): Development of sphene-based glass ceramic tailored for Canadian waste disposal conditions. *In* Scientific Basis for Nuclear Waste Management (S.V. Topp, ed.). Elsevier, New York.

HELGESON, H.C. (1967): Thermodynamics of complex dissociation in aqueous solution at elevated temperature. *J. Phys. Chem.* **71,** 3121-3136.

______ (1969): Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *Amer. J. Sci.* **267,** 729-804.

KHARAKA, Y.K. & BARNES, I. (1973): SOLMNEQ: solution-mineral equilibrium computations. *U.S. Geol. Surv. Comp. Contr.* **PB-215-899** (The version used was modified and updated by B.W. Goodwin, Atomic Energy Can. Ltd.).

LEWIS, G.N. & RANDALL, M. (1961): *Thermodynamics (2nd edition).* McGraw-Hill, New York.

MARSHALL, W.L. & JONES, E.V. (1966): Second dissociation constant of sulphuric acid from 25 to 350° evaluated from solubilities of calcium sulphate in sulphuric acid solutions. *J. Phys. Chem.* **70,** 4028-4040.

METSON, J.B., BANCROFT, G.M., KANETKAR, S.M., NESBITT, H.W., FYFE, W.S. & HAYWARD, P.J. (1982): Leaching of natural and synthetic sphene and perovskite. *In* Scientific Basis for Nuclear Waste Management **5** (W. Lutze, ed.). Elsevier, New York.

NESBITT, H.W., BANCROFT, G.M., FYFE, W.S., KARKHANIS, S.N., NISHIJIMA, A. & SHIN, S. (1981a): Thermodynamic stability and kinetics of perovskite dissolution. *Nature* **289,** 358-362.

______, ______, KARKHANIS, S.N. & FYFE, W.S. (1981b): The stability of perovskite and sphene in the presence of backfill and repository materials: a general approach. *In* Scientific Basis for Nuclear Waste Management **3** (C. Northrup, ed.). Plenum, New York.

RIBBE, P.H., ed. (1980): Orthosilicates. *Mineral. Soc. Amer., Rev. Mineral.* **5.**

RIMSTIDT, J.D. & BARNES, H.L. (1980): The kinetics of silica-water reactions. *Geochim. Cosmochim. Acta* **44,** 1683-1699.

ROBIE, R.A., HEMINGWAY, B.S. & FISHER, J.R. (1979): Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascals) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.* 1452.

Received December 9, 1982, revised manuscript accepted April 16, 1983.