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

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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.

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.
Materials under investigation include borosilicate and aluminosilicate glasses, and glass ceramics based on the mineral titanite (CaTiSiO₃). The latter, partly crystalline materials, are produced by controlled crystallization during reheating of precursor glasses from the system Na₂O-Al₂O₃-CaO-TiO₂-SiO₂ (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.

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, Ca²⁺ is the dominant cation, and Cl⁻ is by far the dominant anion. The K⁺ and Mg²⁺ concentrations increase slightly with depth, contrary to their behavior at Sudbury and Thompson. At Yellowknife, HCO₃⁻ and SO₄²⁻ 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 H₂SiO₄ molality = −4.0) and amorphous silica (log H₂SiO₄ molality = −2.7). Thus, dissolved silica in mine waters in the Sudbury area give a mean log H₂SiO₄ molality of −3.2 for various depths down to 800 m.

![Figure 1. Variation of groundwater composition with depth at the Con mine, Yellowknife, N.W.T.](image-url)
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 Ca²⁺, Na⁺ and Cl⁻, and poor in K⁺, Mg²⁺, SO₄²⁻ and HCO₃⁻. 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: Ca²⁺ 15500, Na⁺ 5047, Cl⁻ 34310, SiO₂(aq) 50, Sr²⁺ 20, Mg²⁺ 200, K⁺ 50, SO₄²⁻ 790, total carbonate as HCO₃⁻ 10, and NO₃⁻ 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) H₂O⁺, (b) sulfate species in solution (SO₄²⁻ and HSO₄⁻) and (c) carbonate species in solution (CO₃²⁻, HCO₃⁻ and H₂CO₃). 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 H₂SiO₄ 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 B¹ 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 H₂SiO₄⁻, H₂SiO₄²⁻ and HSO₄⁻, are ignored in the following calculations.

<table>
<thead>
<tr>
<th>Ionic strength</th>
<th>1.457</th>
<th>1.453</th>
<th>1.450</th>
<th>1.446</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1/2moles⁻¹)</td>
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</tbody>
</table>

**Activity with H₂O⁺**

Activity diagrams for the H⁺-H₂O-CaO-TiO₂-SiO₂ 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 [SiO₂(aq)] values found in most natural groundwaters, either titanite or rutile is the stable phase in this system, depending on the log ([Ca²⁺]/[H⁺]²) values.

In general, for the reaction

CaTiSiO₄ + 2H⁺ + H₂O = Ca²⁺ + TiO₂ + H₄SiO₄

the equilibrium-activity expression is:

\[ \log \left( \frac{[Ca^{2+}]}{[H^+]^2} \right) + \log [H_4SiO_4] = \log K_1 \]  (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
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

\[
\begin{align*}
CaTiSiO_5 + 2H^+ + SO_4^{2-} + H_2O &\rightleftharpoons CaSO_4(s) + TiO_2 + H_4SiO_4 \\
CaTiSiO_5 + 2H^+ + SO_4^{2-} + 1.5H_2O &\rightleftharpoons CaSO_4\cdot0.5H_2O(s) + TiO_2 + H_4SiO_4 \\
CaTiSiO_5 + 2H^+ + SO_4^{2-} + 3H_2O &\rightleftharpoons CaSO_4\cdot2H_2O(s) + TiO_2 + H_4SiO_4
\end{align*}
\]

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:

\[
\log [H_4SiO_4] - \log [SO_4^{2-}] - 2 \log [H^+] = \log K_2
\]

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 groundwater at temperatures above \( \sim 25°C \), 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 \( SO_4^{2-}\).
Their magnitude and influence may be judged by assuming, as a worst possible case, that the calculated activity-coefficients for \( SO_{2}^{2-} \) 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 \( \pm 0.24 \) 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:

\[
\begin{align*}
\text{CaTiSiO}_5 + CO_3^{2-} + 2H^+ + H_2O &\rightarrow CaCO_3 + TiO_2 + H_4SiO_4 \\
\text{CaTiSiO}_5 + HCO_3^- + H^+ + H_2O &\rightarrow CaCO_3 + TiO_2 + H_4SiO_4 \\
\text{CaTiSiO}_5 + H_2CO_3 + H_2O &\rightarrow CaCO_3 + TiO_2 + H_4SiO_4
\end{align*}
\]

Equilibrium equations for these three reactions are, respectively:

\[
\begin{align*}
\log [H_4SiO_4] - 2 \log [H^+] - \log [CO_3^{2-}] &= \log K_3 \\
\log [H_4SiO_4] - \log [H^+] - \log [HCO_3^-] &= \log K_4 \\
\log [H_4SiO_4] - \log [H_2CO_3] &= \log K_5
\end{align*}
\]

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 \( \sim 40^\circ C \) 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 \( \sim 0.1% \) 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
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 CaCO₃, TiO₂, and SiO₂ 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 39% 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 CaTiSiO₅ 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-HClO₄ 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, TiO2 40.9, SiO2 30.7, Al2O3 2.9, other oxides (principally Na2O, K2O 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, TiO2 36.5, SiO2 30.3, FeO 1.25, MnO 0.25, Al2O3 1.7, Na2O 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 lechant 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 N2 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 CO2, 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 TiO2, 37.8 wt.% SiO2 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 Al³⁺ and SiO₂ (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·m⁻²·s⁻¹)

<p>| Table 2. Individual Ion and Bulk Leach-Rates, Natural and Synthetic Titanite |</p>
<table>
<thead>
<tr>
<th>Leaching</th>
<th>Bulk Rate</th>
<th>Calculated from Leaching Solution Analyses</th>
<th>Elemental Duration</th>
<th>from wt. loss</th>
<th>Bulk rate</th>
<th>Ca rate</th>
<th>Si rate</th>
<th>Ti rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCT</td>
<td>2.4(±0.3)</td>
<td>2.6(±1.1)</td>
<td>3.4(±1.2)</td>
<td>2.6(±0.3)</td>
<td>2.1(±0.3)</td>
<td>1.4(±0.2)</td>
<td>3.7(±0.1)</td>
<td>4.1(±0.2)</td>
</tr>
<tr>
<td>titanite</td>
<td>2.3(±1.0)</td>
<td>3.4(±0.7)</td>
<td>4.2(±0.9)</td>
<td>4.8(±0.7)</td>
<td>3.7(±0.3)</td>
<td>3.7(±1.0)</td>
<td>4.6(±0.8)</td>
<td>5.1(±0.4)</td>
</tr>
<tr>
<td>spring</td>
<td>2.4(±0.2)</td>
<td>3.7(±0.2)</td>
<td>4.5(±0.3)</td>
<td>5.3(±0.5)</td>
<td>4.5(±0.3)</td>
<td>4.6(±0.4)</td>
<td>5.8(±0.6)</td>
<td>6.1(±0.2)</td>
</tr>
<tr>
<td>n. c.</td>
<td>3.4(±0.2)</td>
<td>4.7(±0.2)</td>
<td>5.8(±0.4)</td>
<td>7.0(±0.3)</td>
<td>5.2(±0.2)</td>
<td>5.2(±0.2)</td>
<td>5.6(±0.2)</td>
<td>5.9(±0.1)</td>
</tr>
<tr>
<td>sandstone</td>
<td>1.7(±0.2)</td>
<td>2.1(±0.1)</td>
<td>2.7(±0.3)</td>
<td>3.5(±0.4)</td>
<td>3.0(±0.2)</td>
<td>3.0(±0.2)</td>
<td>3.5(±0.3)</td>
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<tr>
<td>titanite</td>
<td>2.4(±0.2)</td>
<td>3.4(±0.2)</td>
<td>4.2(±0.3)</td>
<td>5.0(±0.4)</td>
<td>4.2(±0.3)</td>
<td>4.3(±0.4)</td>
<td>5.3(±0.5)</td>
<td>5.8(±0.2)</td>
</tr>
</tbody>
</table>

Leach rates (±10⁻¹⁵) expressed in kg·m⁻²·s⁻¹, with standard deviation in parentheses. Natural samples from North Crosby Township, Ontario. Leaching was carried out at 100°C in deionized water.
were calculated from the equation: leach rate = $C_i V / F_i A$, 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 $F_i = X_i W_i / W_{ox}$, 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...
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\(_4\) plus traces of surplus TiO\(_2\) and SiO\(_2\) together with Al\(_2\)O\(_3\). Although CaTiSiO\(_4\) 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 \((2.2 \pm 0.3) \times 10^{-10} \text{ kg m}^{-2} \text{s}^{-1}\).

SEM-EDX examination of the leached surfaces (Fig. 8) showed that little dissolution of the matrix had occurred (original polishing scratches were still present) while dissolution of the matrix was observed. The mean results of weight-change measurements are presented in Table 2.

**Table 3. Composition of Particles from Extraction Replicas of Leached Titanite**

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
<th>Cl</th>
<th>S</th>
<th>Phase Identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td></td>
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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 8.0–8.5. (d) Synthetic titanite, same conditions as (c).
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 \((0.65 \pm 0.36) \times 10^{-10} \text{ kg m}^{-2} \text{s}^{-1}\).

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.

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
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 indetified 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 xenotlite $\text{Ca}_9\text{Si}_4\text{O}_{17}$(OH)$_2$ or tobermorite $\text{Ca}_2\text{Si}_2\text{O}_7$·5H$_2$O.

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$_2$O$_3$ 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 $H_2SiO_4$ 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.

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REFERENCES


DIXON, R.S. & ROSINGER E.I.J. (1981): Third annual
LEACHING STUDIES OF NATURAL AND SYNTHETIC TITANITE


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


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