Aqueous dissolution behaviour of Nd-bearing zirconolite in citric acid at 90°C

P.J. McGlinn, T. McLeod, Z. Aly, Z. Zhang, T. Advocat*, M.G. Blackford, H. Li, G. Leturcq*

Australian Nuclear Science & Technology Organisation: New Illawarra Road, Lucas Heights, NSW, 2234.
* Commissariat de l'Energie Atomique, Marcoule, 30207 Bagnols-sur-Cèze, France
pjm@ansto.gov.au

Abstract – *The capacity for zirconolite to incorporate actinides, combined with a very high chemical durability, makes zirconolite-rich ceramics potential candidates for the containment of minor actinides from reprocessing of nuclear spent fuel. Our studies examine the chemical durability of sintered Nd-bearing zirconolite under simulated geological repository conditions, demonstrating the effect of citric acid (at varying concentrations), as an organic complexing agent, on the leaching behaviour of zirconolite under a low flow regime. The complexation limit of zirconolite at pH5 in citrate media appears to be reached by 0.001M citric acid concentration. Secondary phase development (titania and possibly titania-rich hydrolysed species) was evident on the zirconolite leached in 0.0001M citric acid, similar to that on zirconolite leached in water.*

INTRODUCTION

Zirconolite ($CaZrTi_2O_7$) is one of a group of structurally related minerals able to contain the rare earth elements (Nd, Ce, La, Hf, Gd) and the actinides (U, Np, Am, Cm, Pu) by substitution at Ca and Zr sites. Combined with a very high chemical durability, this makes zirconolite-rich ceramics potential candidates for the containment of minor actinides from reprocessing of nuclear spent fuel.

Our studies examine the chemical durability of sintered Nd-bearing zirconolite (Nd simulating the trivalent actinides) under simulated geological repository conditions, demonstrating the effect of citric acid, as an organic complexing agent common in groundwaters (typically 0.001M), on the leaching behaviour of zirconolite under a low groundwater flow regime.

This paper is an extension of previous studies [1] into zirconolite behaviour in citrate-bearing solutions and gives an overview of the effect of varying citric acid strength on elemental releases from zirconolite and alteration products on the leached surfaces.

METHODOLOGY

The synthesis route for making the zirconolite, the preparation of the samples for leaching and for microscopy examination, and the measurement of surface area of the powders are detailed in [1]. The nominal composition of the zirconolite was $Ca_{0.8}Nd_{0.2}ZrTi_{1.8}Al_{0.2}O_7$, with density approximating 95% of the theoretical value.

Zirconolite was leached for 139 days in citric acid of varying strengths – 0.0001M, 0.001M and 0.01M, with parallel tests in deionised water, under dynamic, single-pass-through conditions (to simulate a low groundwater flow) at 90°C (modified MCC-4 protocol [2]). Blank tests i.e. identical tests without zirconolite samples, were carried out simultaneously for all tests to provide background elemental concentrations. Citric acid in solution degrades fairly quickly with time [3], so a fresh batch of citric acid solution was prepared every 3-4 days to ensure its effectiveness as a leachant. The pH of the citric acid leachant was adjusted to 5 (from an initial pH of about 3.3) using KOH to reflect the pH of deionised water used in the parallel tests, thereby avoiding pH effects on zirconolite solubility. Leachates were collected daily, apart from weekends, for the first 29 days of leaching, and thereafter weekly. Elemental concentrations were measured using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

Each test cell contained a 0.5g powdered specimen providing a high surface area for reaction. The cell for the 0.0001M citric acid test also contained a monolith and an IBT (Ion Beam Thinned) specimen. The increase in the overall zirconolite surface area caused by the inclusion of the monolith and IBT specimens in this cell was negligible.

The monolith and IBT specimens were used to examine surface alteration as a result of leaching using Scanning Electron Microscopy (SEM)/ Energy Dispersive X-ray Spectrometry (EDS), TEM (Transmission Electron Microscopy)/ EDS and X-ray Photoelectron Spectroscopy (XPS). Previous studies [1] showed that leaching in

0.001M citric acid produced no detectable surface alteration features, whilst leaching in water showed some signs of secondary phase formation at the surface of the monolith and the IBT specimens. It was suggested in our earlier work that citric acid concentrations of 0.001M provided complexation conditions which prevented formation of alteration products. It was thereby considered redundant in our latest work to study the surface of specimens leached under higher cit ric acid concentration conditions. However, it was possible that such alteration could have occurred at a concentration much lower (0.0001M), so examination of these specimens was undertaken.

The details of the SEM, TEM, XPS and ICP-MS instrumentation are given in [1].

RESULTS

The normalised release rates of Ti, Zr, Nd, Al and Ca are shown in Figure 1 (legend for all graphs shown in the first). Gaps in the data correspond to results that are either below the detection limit of the ICP-MS, or blank levels that are approaching or greater than those in the tests containing zirconolite samples.
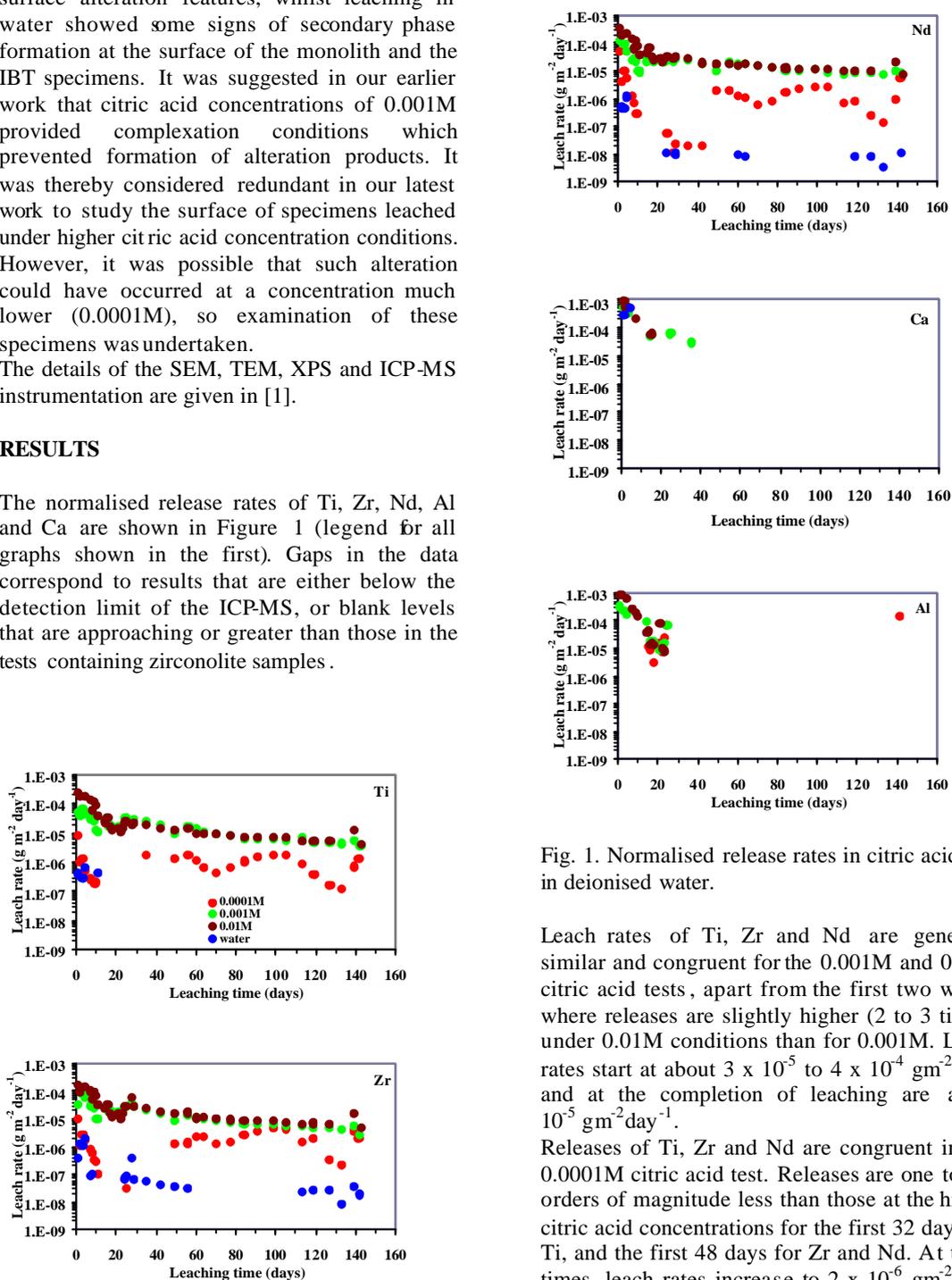
Fig. 1. Normalised release rates in citric acid and in deionised water.

Leach rates of Ti, Zr and Nd are generally similar and congruent for the 0.001M and 0.01M citric acid tests, apart from the first two weeks where releases are slightly higher (2 to 3 times) under 0.01M conditions than for 0.001M. Leach rates start at about 3×10^{-5} to 4×10^{-4} $gm^{-2}day^{-1}$ and at the completion of leaching are about 10^{-5} $gm^{-2}day^{-1}$.

Releases of Ti, Zr and Nd are congruent in the 0.0001M citric acid test. Releases are one to two orders of magnitude less than those at the higher citric acid concentrations for the first 32 days for Ti, and the first 48 days for Zr and Nd. At these times, leach rates increase to 2×10^{-6} $gm^{-2}day^{-1}$ for Ti, Zr and Nd. Thereafter, leach rates fluctuate with a similar range (from 2×10^{-6} to $\sim 10^{-7}$ $gm^{-2}day^{-1}$) and periodicity for all three elements. There is no explanation for these fluctuations.

In deionised water releases are commonly undetectable. For Nd, Zr and Ti leach rates are similar for the first few leach periods at around 10^{-6} $gm^{-2}day^{-1}$. After ten days Ti is no longer detected. Zirconium and Nd releases by the end of leaching are similar and extremely low at about 10^{-8} $gm^{-2}day^{-1}$.

Calcium results are few for the 0.01M, 0.001M and water tests, and were not detectable in the 0.0001M leachates. For the 0.01M test this reflects relatively high background levels, whilst for the other tests it is generally a matter of detectability.

Releases of Al under 0.001M and 0.01M citric acid conditions are higher than for Ti, Zr and Nd initially (first two weeks). For the ensuing one to two weeks releases are similar to those for Nd, Zr and Ti, before dropping off to undetectable levels for the remainder of the tests. Releases were only detectable for the period 14 to 24 days, and for the final period, for the 0.0001M test. No Al releases were detected in the water tests.

The pH of the 0.01M leachates, and the corresponding blanks, were generally static at 5 (see Figure 2). For the 0.001M test the pH rose to 5.5 in the first week, then returned to 5 during the following week, and maintained this level for the remainder of the experiment; the pH of the corresponding blank experiments remained at ~5 for the entire leaching time.

The pH of the 0.0001M test remained at about 5 to 42 days, then fluctuated between 0.2 to 0.5 units higher for the rest of the leaching time; the pH levels remained slightly higher (up to 0.4 pH units) than those of the blank throughout the entire leaching time.

The pH of the leachates of the water tests mimic those of the blanks, starting at 4.5, increasing to 5.3 after 30 days, then, like the leachates from the 0.0001M tests, fluctuate slightly at between 5.2 and 5.5 for the remainder of the test.
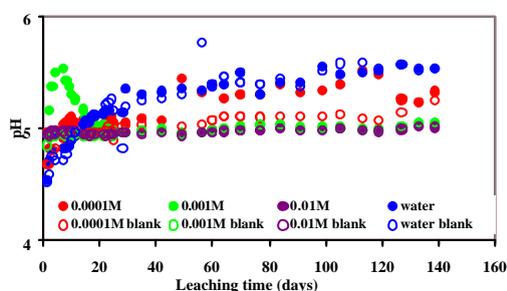

Fig. 2. Change in pH with time.

SEM results show that prior to leaching the zirconolite was homogeneous and contained no detectable minor phases. After leaching in 0.0001M citric acid for 139 days there were round, sub-micron particles on the surface, sparsely distributed and too small to identify by SEM/EDS.

TEM examinations were more definitive of secondary phase development on the zirconolite IBT specimen leached in 0.0001M citric acid. Figure 3 shows Ti-rich particles approximately 100nm in diameter on the surface of the IBT specimen.
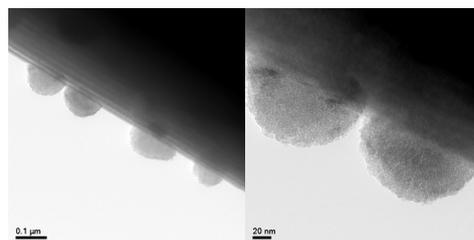

Fig. 3. Example of aggregate of Ti-rich particles covering surface of IBT specimen (image on right at higher magnification).

Selected area electron diffraction analysis indicated that the grains were probably TiO_2 polymorphs and possibly hydrolysed Ti-rich species (as per previous work [1]).

XPS results showed that leaching in 0.0001M citric acid caused very small changes in the surface composition of the zirconolite. Calcium and Al surface concentrations decreased slightly with respect to Zr. The changes in surface composition lie between those leached in deionised water and 0.001 M of citric acid (reported in [1]).

DISCUSSION

The primary aim of these experiments was to test zirconolite durability under repository-type conditions where infiltrating groundwater contained typical levels of citric acid (0.001M), and to see how durability changed if significantly higher (0.01M) or lower (0.0001M) citric acid levels were present. A secondary aim was to examine possible mechanisms to explain zirconolite leaching behaviour under these different citric acid concentration conditions.

Zirconolite leached congruently under all conditions tested (0.01M, 0.001M, 0.0001M, and deionised water) with releases under 0.01M and 0.001M conditions the greatest (by up to two

orders of magnitude from 0.0001M citric acid). Over the longer term, releases in deionised water were lower by up to two orders of magnitude than under 0.0001M citric acid conditions.

The results from these tests concur with those from previous studies using 0.001M citric acid and water [1].

Citrate ions characteristically form very stable complexes in solution, particularly with Zr^{4+}, Nd^{3+} and Ti^{4+} ions [4]. This is reflected in our results which show, compared to deionised water, leaching in citric acid maintains mobility of all elements released from the zirconolite to a high order (particularly at citric acid concentrations $\geq 0.001M$).

'Alteration' products on zirconolite leached in 0.0001M citric acid were too sparsely distributed and too fine to characterise by SEM/EDS. TEM/EDS analysis suggested that the secondary phase consists of titania and possibly hydrolysed Ti-rich products. These results are similar to those of zirconolite in water from our previous studies [1].

XPS results indicate that there is a small decrease in Ca and Al surface concentrations, although no widespread Ti-, Zr-enriched secondary layer. The decrease in Ca and Al is less than that observed under identical leaching conditions using deionised water [1].

Previous work [5] proposed that hydroxide layers form on the surface of zirconolite leached in water at 90°C and that the apparent cessation of surface alteration/leaching is due to the solubility limit being reached with respect to these hydrolysed phases rather than with the zirconolite *per se*. This was extrapolated to our previous studies [1] of zirconolite leached in water. Further, based on the similarities of the secondary phase developed between the previous work and our current results, it is suggested that similar mechanisms may be acting here as well. Although there is no evidence from our studies that a (continuous) enriched 'passivating' layer exists, it is hypothesised that oxide bonds (with Ti and Zr for example) at the surface may be broken during leaching in water with addition of hydrogen ions to form (Ti-, Zr-) hydroxides. This imparts to the surface the appearance of hydroxide species, effectively forming hydrolysed zirconolite. Equilibrium between these species and the leachates would then lead to cessation of dissolution of the zirconolite matrix.

By contrast to the tests in water and in 0.0001M citric acid, there was no development of any secondary phases under stronger citric acid conditions (0.001M) in our previous studies [1]. This suggests, from the hypothesis just described, that complexation by citrate ions at these concentrations prevents control by surface hydrolysed species on zirconolite solubility.

CONCLUSIONS

Simulated groundwater containing various levels of citric acid have demonstrated variable zirconolite dissolution behaviour. At citric acid concentrations of 0.01M and 0.001M the leaching behaviour, as depicted by leach rates, is almost identical and releases congruent. Increasing citric acid concentration above 0.001M has no additional effect on elemental releases from the zirconolite. Effectively the complexation limit of zirconolite at pH5 in citrate media appears to be reached by 0.001M citric acid concentration. By contrast, 0.0001M citric acid has a much less complexation potential, and water virtually none.

In terms of mechanisms controlling the leaching behaviour of the zirconolite, it is proposed that hydroxide species may form in situ, effectively forming hydrolysed zirconolite. This may inhibit further dissolution of the zirconolite matrix due to the solubility limit being reached with respect to the hydrolysed phases rather than with zirconolite. In contrast, complexation by citrate ions, where leachants contain concentrations of citric acid of 0.001M or more, prevents such control by hydrolysed species on zirconolite solubility. Control is less apparent at citric acid concentrations an order of magnitude lower.

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