Physical stability and durability of heavy-ion irradiated crystalline zirconolite $CaZrTi_2O_7$ ceramic designed for minor actinide disposition

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Abstract *– External irradiation studies with heavy ions Pb^{3+} accelerated at 510 keV were conducted on non radioactive zirconolite ceramic pellets, containing actinide surrogates such as Rare Earth Elements (REE). Ion irradiation of ceramic pellet surfaces has transformed the outermost several tenths of nanometers of the surface into a metamict state. The chemical durability in water of the irradiated zirconolite ceramics was measured at 100°C. The dissolution behavior is similar to that for the fully crystalline materials, and natural zirconolite minerals as well, which are at least several hundred million years old and self-irradiated up to 10^{20} alpha decay/g due to the presence of appreciable quantities of Th and U. The amorphisation process of the crystalline structure by the alpha decay does not modify the high chemical durability of zirconolite.*

INTRODUCTION

Zirconolite is a potential inorganic matrix that is currently being investigated with a view to provide durable containment of the trivalent and tetravalent minor actinides like neptunium, curium, americium and small quantities of unrecyclable plutonium separated from other nuclear wastes. The radiation stability of zirconolite is currently being studied by combining four avenues of research:

(1) Examination of zirconolite doped with short lived actinide isotopes,
(2) Examination of very old natural metamict crystals of Th and U-zirconolite,
(3) Atomistic modeling of the collision cascades induced by the recoil nucleus,
(4) Examination of Nd-zirconolite after external bombardment with heavy ions primarily simulating alpha-recoil radiation damage from alpha-emitting radionuclide.

This paper focuses on the fourth topic. The initially crystalline structure will gradually amorphise, as a consequence of α-decay of the actinides, and the cascades of collision induced by the recoil nuclei. The goal of the present study is to elucidate any significant differences in the physical stability and in the chemical durability of the undamaged crystalline surface versus the damaged surface.

METHODOLOGY

Ceramic pellets of the composition of $(Ca_{0.8}Nd_{0.1}Ce_{0.1})(Zr_{0.94}La_{0.03}Gd_{0.03})(Ti_{1.86}Al_{0.14})O_7$ and $Ca_{0.8}Nd_{0.2}ZrTi_{1.8}Al_{0.2}O_7$ were prepared by pressureless sintering at 1400°C for 96 hours [1]. Zr, Al and Ti alkoxides were mixed with nitrate solutions of Ca and REE. The mixture was dried, calcined at 750°C for one hour, wet-milled, cold-pressed and then sintered in air at about 1400°C (Figure 1). The final pellets were dense (92-95% of the theoretical density).

The pellets, 25 mm in diameter, were then cut to discs with a thickness of 1 mm. The discs were polished on both sides with SiC under alcohol.

The discs were bombarded on both surfaces (about 90% of the total surface of the discs) with Pb^{3+} ions accelerated at 510 keV. The curved surface of the discs was not irradiated. These irradiations were performed at the Centre de Spectrométrie de Masse et de Spectroscopie Nucléaire (CSNSM) at Orsay, with the IRMA tool. Three doses were achieved :

- 3×10^{14} ions/cm² (i.e. 0.07 dpa)
- 2×10^{15} ions/cm² (i.e. 0.44 dpa)
- 2×10^{16} ions/cm² (i.e. 4.43 dpa)

Two pellets were bombarded on both sides at each dose. The fully damaged zone is equal to about 50 nm in depth from the outer surface of the pellets, for the lowest dose (Figure 2).

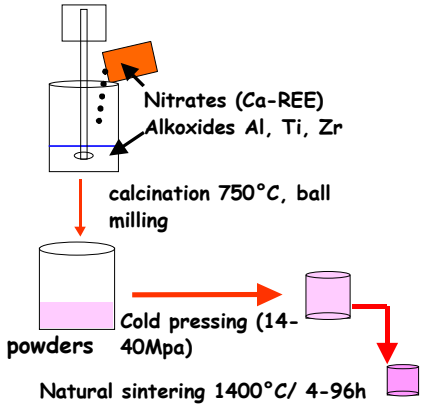

Figure 1. Ceramic process to prepare zirconolite pellets.

The surfaces of the ceramics were examined by Scanning Electron Microscopy (SEM), X-ray Diffractometry (XRD - glancing angle), X-ray

Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM), before and after irradiation, and after leaching as well.
The chemical durability of the zirconolite was studied using a soxhlet apparatus. One disc of ceramic was placed under a permanent renewal of the leachate (deionised water) at 100°C, for a total duration of 28 days. Small aliquots of leachate (5 mL) were recovered from the boiling part of the leaching reactor, every day during the first 15 days, and thereafter every 7 days. A total number of 6 soxhlet tests were carried out. The tests on the non-irradiated discs and those irradiated at 3 x 10^{14} ions/cm² were carried out in duplicate , whilst single tests were conducted for the two highest dosed specimens.
Sub-samples of the leachates were analysed by ICP-MS for cations Ca, Ti, Al, Zr, Ce, Nd, La, Hf and Gd. The calcium released in the leachate is consider as the major kinetic tracer. All elemental masses determined were then normalised to the geometric surface area of the ceramic, and normalised to the amount of each element in the ceramic matrix, using the following equation:

$$NL(i) = mi/[(SA)\times fi]$$

With :
NL(i) = normalised mass loss for element i ($g.m^{-2}$)
mi= mass of element i released (g)
SA= total surface area of exposed ceramic disc (m^2)
Fi=mass fraction of element i in the ceramic.

RESULTS

Physical properties

SEM results show that prior to leaching and irradiation, the zirconolite was homogeneous, contained no detectable minor phases. SEM examinations of the irradiated surfaces do not reveal any modification by sputtering, compared to the un-damaged materials.

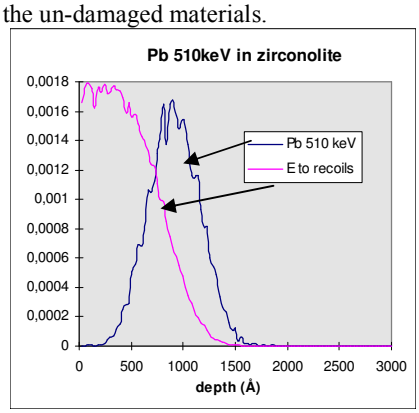

Figure 2. SRIM-2000 calculation of the damaged zone as a function of the depth in zirconolite (blue line : distribution of the implanted Pb^{3+} ions; pink line : distribution of the displaced atoms).

The amorphisation of the damaged zone is confirmed by XRD analyses conducted with various glancing angles (between 0.6 to 1°).

As shown in Figure 3, the ceramic irradiated at 3 x 10^{14} ions/cm² is characterised by a broad peak at about 2θ ~ 30°, which is typical for an amorphous material. The amorphous zone is located at the outermost surface of the discs, and not in the internal zone where Pb ions are implanted, as shown also by cross-sectional TEM examinations (Figure 4). The thickness of the amorphous layer is at least 150 nanometers.
All these surface characterisations confirm that the surface areas of the zirconolite discs have been transformed from a crystalline to an amorphous structure.

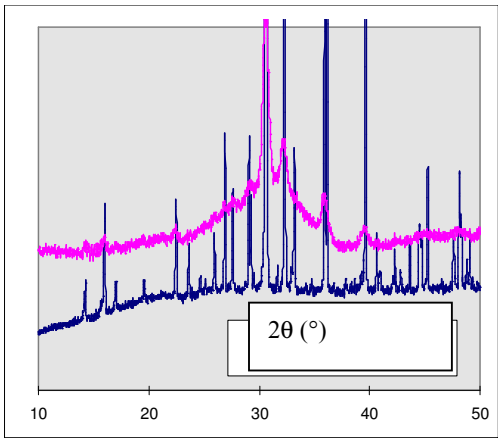

Figure 3. XRD spectra (glancing angle of 0.5°) of zirconolite, before irradiation (blue) and after irradiation (pink) at 3 x 10^{14} Pb^{3+} ions/cm².

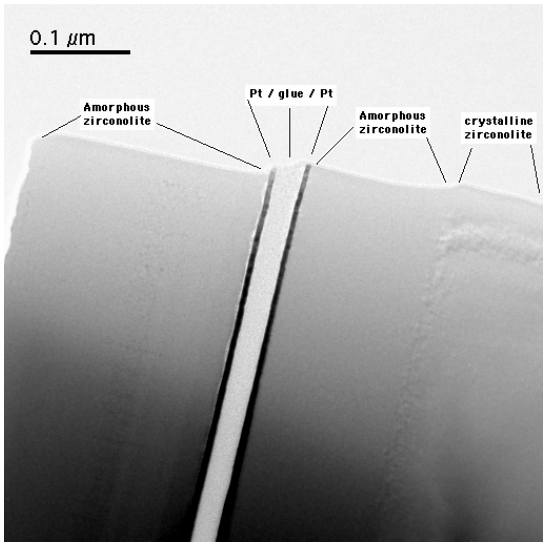

Figure 4. TEM examination of the Pb^{3+} irradiated zirconolite at a dose of 3.10^{14} ions/cm², before leaching.

Chemical durability

Only the reported analytical concentration data for Ca and Al were above the instrument minimal detection limits. The mass amount released for Ti,

Zr, Ce, Nd, Gd, Hf and La were too low to be detected (less than 2-5 ppb).
The normalised mass losses of Ca are shown in Figure 5 for the non-irradiated samples and after irradiation at a dose of 3 x 10^{14} ions/cm².

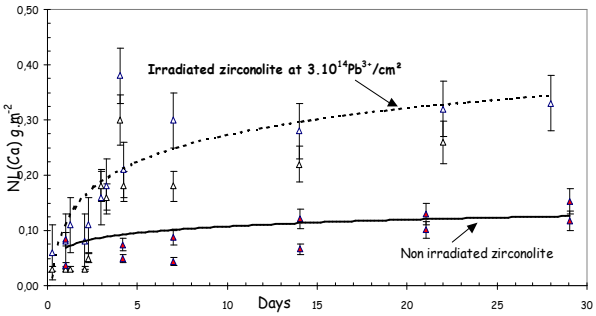

Figure 5. Chemical durability of zirconolite before and after irradiation at a dose of 3 x 10^{14} ions/cm² (Soxhlet test at 100°C, permanent renewal of water)

Before and after irradiation up to the critical amorphisation dose (3.10^{14} ions/cm²), the Ca normalised mass losses NL(Ca) show almost the same trend over time. There is an initial instantaneous linear release of Ca during the first few days. The corresponding initial dissolution rates r_0 for non-irradiated and damaged zirconolite are equivalent, i.e. approximately 8.10^{-2} g.m^{-2}.d^{-1}. Steady state NL(Ca) values are then achieved after about 5 days. This evolution indicates a diminution of the zirconolite dissolution rate, even under highly renewed conditions. Compared to the un-damaged material, the steady state NL(Ca) values for the irradiated zirconolite are 1.5 times higher after 5 days of interaction with water.
The effects of higher irradiation doses were also examined, up to 2 x 10^{16} ions/cm² equivalent to 66 times the critical amorphisation doses (Figure 6). As already observed, after a few days, the alteration rate dropped significantly for all samples. Again, the same trend as a function of time is obtained: the initial dissolution rate corresponds to a very short transitory stage, followed by a rapid decrease of the dissolution rate.
The corresponding NL(Ca) values for the irradiated samples were almost equivalent to those for the unirradiated one (Figure 6). All the data points measured on the irradiated samples are distributed around the data points for the unirradiated samples.
It is also important to point out that the equivalent thickness of altered zirconolite is less than a few tenths of nanometers (NL(Ca)/ω, ω=zirconolite specific weight 4.5 x 10^6 g/m^3). This value is lower than the thickness of the metamict damaged layer (Figure 4), thus confirming that the diminution of the dissolution rate is not related to the alteration of the underlying undamaged material.

XPS analysis indicated that the surface composition of the Pb^{3+} ion-irradiated samples (top layer <5 nm), after leaching, was similar to that of the unleached sample, irrespective of the dose.
As shown in Table 1, Ca and Al concentrations on the leached surface layer decreased slightly with respect to Zr. On the other hand, surface Ce, La and Ti concentrations (with respect to Zr) did not change much after leach testing. Similar results were also observed for the unirradiated samples, before and after leaching: the leached surface composition of the non-irradiated zirconolite is similar to that of the irradiated specimens. These surface analysis results confirm the analytical results of the elemental releases in solution: Ca is the most mobile element of the system.

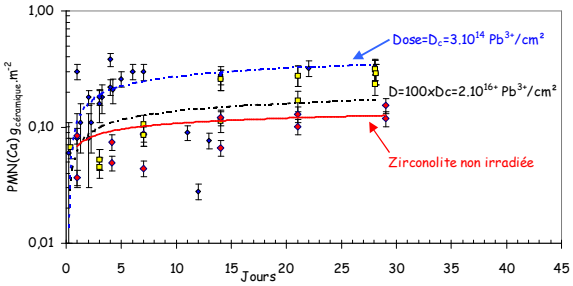

Figure 6. Chemical durability of zirconolite before and after irradiation at a dose up to 2.10^{16} ions/cm² (Soxhlet test at 100°C, permanent renewal of water).

Table 1. XPS analysis of the Pb^{3+} irradiated zirconolite ceramic at a dose of 3.10^{14} ions/cm².

	Ca/Zr	Ce/Zr	Ti/Zr	La/Zr	Al/Zr
Before leaching	0.70	0.06	1.19	0.02	0.15
After leaching	0.49	0.07	1.06	0.03	0.10

DISCUSSION

The primary aims of these experiments were to test zirconolite durability after ion irradiation up to and beyond the critical amorphisation dose. The leach rates at 100°C, under a high renewal rate of the leachate, of the irradiated and unirradiated zirconolite were very similar, given the errors in measurement (Figure 5 and Figure 6).
Similar results were obtained with 2 and 3 MeV Au^{2+} irradiated zirconolite pellets leached at a lower temperature (90°C), low pH (2) and under static conditions, by Smith et al. [2]. The normalised Ca release rates (g.m^{-2}.d^{-1}) reported by these authors

are reported on the Figure 7. The comparison with the previous data obtained at 100°C (Figure 5 and Figure 6) is not direct : the normalised Ca release rates reported on the Figure 7 were calculated by dividing NL(Ca) ($g.m^{-2}$) by the duration (days).

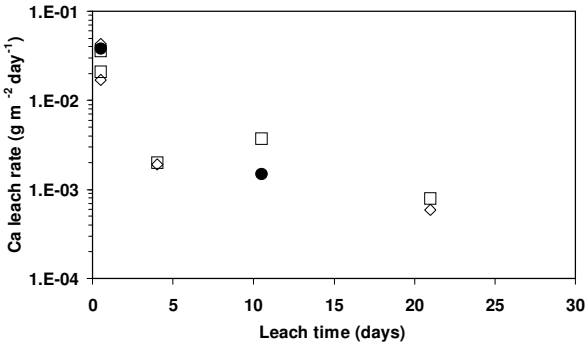

Figure 7. Nd-zirconolite leached under static conditions at 90°C, pH 2 (from Smith et al. [2]). Black dot : unirradiated zirc.; Square : 2MeV Au^{2+} irradiated zirc.; Losange : 3MeV Au^{2+} irradiated zirc.

All the trends in the leaching rates of all samples give a decrease with time with the leaching approaching very low levels after several days, despite the aggressive leaching conditions.

Radiation damaged natural analogues, where the damage occurs throughout the material over a long time frame, of titanate still appear to be very durable ([4], [5]). When reported in an Arrhenius diagram (Figure 8), the heavy-ion irradiated zirconolite ceramics are as durable as the unirradiated samples, and as the fully metamic natural Th and U-rich zirconolite samples as well. This fact is clearly demonstrated by the similar values of the initial dissolution rates r_0 reported on the graph.

Metamictisation is a transformation at the atomic scale, where the lengths and the angles of the coordination polyhedras are slightly modified. However, it does not seem to notably modify the strength of the atomic bonds between the cations (Ti, Zr, Ca, etc.) and the oxygen network : the chemical resistance of these bonds does not change, as quantified at the macroscopic scale with the leaching tests.

CONCLUSIONS

Zirconolite is an extremely durable actinide host phase.

Radiation damage does not affect the elemental leach rates of Nd, Ti, Ca, Al & Zr from REE-bearing zirconolite. This important conclusion is based on leaching experiments conducted under aggressive leaching conditions (dynamic leach tests at 100°C at pH=6 and static leach tests at 90°C, 0.01M nitric soln. at pH=2).

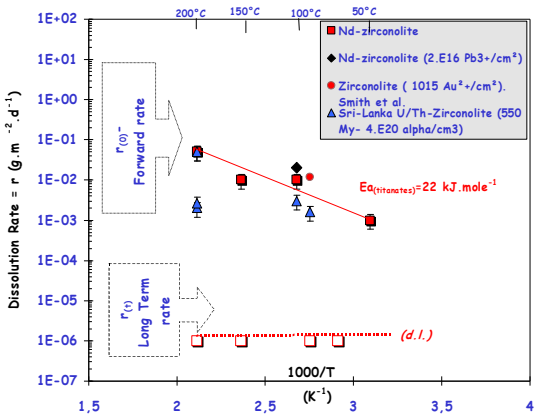

Figure 8. Arrhenius diagram for the unirradiated synthetic zirconolite, heavy-ion bombarded synthetic zirconolite and fully metamict natural Th-zirconolite.

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