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# Study of leaching of a 2M-Zirconolite (Ca<sub>0,83</sub>Ce<sub>0,17</sub>ZrTi<sub>1,66</sub>Al<sub>0.34</sub>O<sub>7</sub>) in acidic and basic media

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Zirconolite is a mineral intended for actinides elements confinement and is known for its good chemical durability. In this work, 2M-zirconolite, with the chemical formula:  $Ca_{0,83}Ce_{0,17}ZrTi_{1,66}Al_{0,34}O_7$  have been synthesized at 1400 °C by the metallurgical route at a laboratory scale. This stoechiometry corresponds to a CeO<sub>2</sub> loading of 8.61 m.%. Ce is employed as an actinide surrogate. The effect of both pH and temperature on the chemical durability of this mineral has been studied. Phase identification and micrography observations have been done by X-ray diffraction, scanning electronic microscopy, and Fourrier transform infra-red spectroscopy. The end-product has a monophasic structure of 2M-zirconolite. Its density is about 4.013 g/cm<sup>3</sup>, and its relative density is of 96 %TD. It has a microhardeness of 370 MPa. The Ce behavior in leaching media of extreme pH values: acidic medium (pH = 2) and basic medium (pH = 12), at 23 °C and 70 °C, shows that the Ce dissolution speeds are faster at 70 °C compared with those obtained at 23 °C. The 2M-zirconolite matrice presently studied appears to have a good chemical durability.

Key words: 2M-zirconolite, Ce, Solid state synthesis, Leaching.

## Introduction

Radioactive waste (noted: RW) from nuclear power plants pose a serious problem for both the health and the environment. These wastes are composed of highly toxic radionuclides.

Transmutation of minor actinides (MA) and fission products (FP) by bombardment with fast neutrons in reactor could be an ideal solution to deal with their toxicity, because it would provide new stable nuclides and / or shorter half-life ones. The second solution would be confinement in a ceramic matrix, which is chemically stable toward hydrothermal alteration, and resistant against self-radiations [1].

The use of synthetic confinement matrices is inspired by the presence in some natural minerals of radioactive elements over thousands of years. These containment matrixes include pyrochlore, zirconolite, SYNROC, etc. [2]. In order to confine radioactive elements in durable matrices, the method currently adopted is the vitrification, which involves trapping radionuclides in a glassy matrix. However, thermodynamically, the glass remains metastable and non-selective towards the whole of the radionuclides to be confined into it, and consequently, many researches are in progress to investigate the possibility of sequestering these radionuclides in resistant ceramics [3].

The zirconolite is one of the best single phase ceramic that has been proposed and retained as a host phase for the immobilization of separated minor actinides. This is due to its performances (high waste loading, aqueous durability, chemical flexibility, radiation resistance, existence of natural analogues, etc.). Natural zirconolite is a rare mineral with many chemical compositions.

Its general formula is:  $ABC_2O_7$ . The A site can be occupied by divalent cations and trivalent rare earth elements (REE). The B site can be occupied by tri and tetravalent cations such as:  $Hf^{4+}$ ,  $Gd^{3+}$ ,  $U^{4+}$ , etc. Titanium element occupies the C site. The cations:  $Al^{3+}$ ,  $Fe^{3+}$  et  $Mg^{2+}$  act as charge compensators.

Zirconolite doped with lanthanides (Ln) and actinides (An) can be written: (Ca,Ln,An)Zr(Ti,Nb,Fe)<sup>III</sup><sub>2</sub>O<sub>7</sub>. It has interesting features for the containment of MA elements (Np, Am and Cm), and a good chemical durability in hydrothermal alteration conditions [1]. Tri and tetravalent actinides are introduced into the mineral by replacing both the Ca<sup>2+</sup> and Zr<sup>4+</sup> sites by coupled substitution of Al<sup>3+</sup> or Fe<sup>3+</sup> for Ti<sup>4+</sup>. Ca<sup>2+</sup> divalent is most weakly bounded to the crystal structure, as demonstrated by leaching studies. Indeed, a (Zr, Ti)-reach passivation layer formed around the material, in a similar analogous to the formation of a Si-rich layer around leached glasses; which prevents rapid dissolution of borosilicate glasses [4, 5].

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From a crystallographic point of view, several polytypes of zirconolite have been identified [6]. The zirconolite mineral can crystallize in different structures, as: 2M, 4M, 3O, 3T and 6T; the zirconolite with the chemical formula  $CaZr_xTi_{3-x}O_7$  (with 0.7 < x < 1.3) crystallizes in a 2M (GS C2/c) monoclinic structure. [7-9].

A classical way to synthesize zirconolite is the dry metallurgical route. However, many precautionary measures are taken during the synthesis, to avoid the zirconolite polytypes phases' formation, or other phases, as: rutile, baddeleyite or perovskite.

Therefore, an appropriate stoechiometry of the product, powders reagents granulometry and sintering temperatures have to be optimized, in order to obtain the good crystalline zirconolite structure, and thus avoid the formation of secondary phases [10-12].

The 2M-zirconolite with the chemical formula:  $Ca_{0,83}Ce_{0,17}ZrTi_{1,66}Al_{0.34}O_7$  has been synthesized by the metallurgical route at a laboratory scale, at 1400 °C. Cerium (Ce) is used as an actinide chemical analogue. The material was characterized by many spectroscopic techniques. Phase identification and micrography observations have been done by X-ray diffraction (XRD), scanning electronic microscopy (SEM), and Fourrier transform infra-red spectroscopy (FTIR).

Both the density and hardness of the material are measured. The behavior of the material against leaching was investigated by the Ce dissolution kinetics in an environment of extreme leaching pH: acidic (pH 2) and basic (pH = 12). The technique of X-ray fluorescence spectrometry (XRF) was used to follow the Ce rate of dissolution in the leachates.

# **Experimental**

The synthesis is carried out by sintering a mixture of oxides: CaO (MERCK, 99%), ZrO<sub>2</sub> (ALDRICH, 98%), TiO<sub>2</sub> (MERCK, 99.5%), CeO<sub>2</sub> (ALDRICH, 99.999%) and Al2O3 (MERCK, 100%). They are manually grounded in an agath mortar until a granulometry below 63  $\mu$ m, then sieved, and dried overnight at 130 °C, to remove moisture and volatile impurities. CaO has been heated at 900 °C overnight, to remove all traces of calcium carbonate.

Adequate amounts of reagents are weighed in agreement with the stoichiometry of the final product. The reagents mixture was homogenized using an automatic shaker for 8 h to achieve good particles dispersion. The powders are compacted into cylindrical pellets, using a uniaxial press at pressure of 580 MPa, to obtain green pellets of 14 mm diameter. They were sintered at 1400 °C for 16 h, in a high-temperature 1600-RHF Carbolite furnace. The heating and cooling steps were of 4 and 3 °C/min, respectively. The geometrical density of green (dg) and sintered (ds) pellets is measured. Vickers microhardeness (H) was

measured using a Wolpert universal equipment, according AFNOR A 03-154 norm [13].

The X-ray diffraction (XRD) analysis is carried out using a PanAnalytical X'Pert Pro diffractometer equipped with a copper anticathode, with a wavelength  $\lambda$  (K $\alpha$ ) of 1.5418 Å, with a voltage of 40 kV and a current intensity of 40 mA, for 2 $\theta$  ranging between 5 and 90 °. The phases' identification is performed using a Philips X'Pert High Score Plus software, version 4.1 [14]. The micrographic observations are made by a Philips XL'30 scanning electron microscope (SEM), equipped with an ESEM-FEG EDX probe.

The material structure was characterized by Fouriertransform infrared (FTIR) spectroscopy using a NICOLET 380 FTIR spectrometer. The measurements were made at wavelengths between 400 cm<sup>-1</sup> and 4000 cm<sup>-1</sup>. Thin pellets were prepared for FTIR measurements by mixing a small quantity of grinded material with spectroscopic grade dry KBr powder. All measurements were run at 4 cm<sup>-1</sup> resolution.

A batch static leach test was performed on the whole of the pellets according with ISO/6961standard leach test [15]. The samples are weighed in order to reach a constant solid/liquid ratio of 1/50, and a constant surface / volume ratio of  $0.06 \text{ cm}^{-1}$ .

Two pH media, acidic and basic (pH = 2 and 12) and two temperatures of 23 °C and 70 °C, are considered. The tests are conducted in 4 dark closed bottles. The leaching solutions are prepared with HNO<sub>3</sub> acid (Merck p.a., d = 1.40, 65%) and NH<sub>4</sub>OH solution (Merck p.a, d = 0.91, 25%), for the acid and basic media, respectively.

The contacting time of the pellets with the solutions represents the test starting time  $(t_0)$ . The dissolution of the matrices is followed by the Ce dissolution (actinide surrogate) in the leachates.

The Ce normalized elemental mass loss in this solution (NL) is defined by the mathematical formula:

$$N_{L} = C_{Ce} V_{0} / S_{0} F_{Ce}$$
(1)

With:

C<sub>ce</sub>: is the total concentration of leached Ce (kg.m<sup>-3</sup>),
V<sub>0</sub>: the total volume of the leaching mixture (m<sup>3</sup>),
S<sub>0</sub>: the sample initial surface effectively in contact with the leachate (m<sup>2</sup>),

 $F_{Ce}$ : the Ce weight fraction in the material, And the normalized leaching rate is expressed by the relation:

$$\tau_{Ce} = 1/(F_{Ce}S_0) \times (dmCe/\Delta t)$$
<sup>(2)</sup>

with:

 $\tau_{Ce}$ : the Ce normalized leaching rate (kg.m<sup>-2</sup>.d<sup>-1</sup>), m<sub>Ce</sub>: the leached mass during a  $\Delta t$  time interval (kg),  $\Delta t$ : is the leaching time interval (d),

The XRF technique is used to measure the Ce dissolution

rate in all the aqueous leachates. The employed XRF spectrometer is a Magix-Pro PANAnalytical equipment.

#### **Results and Discussion**

#### Physical and mechanical properties

The measured geometrical density of the sintered product is of  $4.01 \pm 0.38$  g/cm<sup>3</sup>. This result agrees with those reported by Ojovan for SYNROC materials (4.35 g/cm<sup>3</sup>) [16], and by P. Pöml *et al.* [17] who synthesized two Ce-zirconolites, with the chemical formulas of: Ca<sub>1x</sub>Ce<sub>x</sub>ZrTi<sub>22x</sub>Al<sub>2x</sub>O<sub>7</sub>, x = 0.13 and 0.15, respectively. These last authors report densities of 4.56 and 4.63 g/cm<sup>3</sup>, for x = 0.13 and 0.15, respectively.

The measured Vickers hardness of the product was of  $366 \pm 29$  MPa for a 3 t load. N. Kamel *et al.* [18] synthesized a CaZrTiO<sub>7</sub> zirconolite by a dry route at 1200 °C, and found a hardness of  $300 \pm 10$  MPa. This value is close to our results.

## **Microstructural properties**

The material XRD analysis gives the diffractogrammes gathered in Fig. 1. The phase identification reveals a substantially pure 2M-zirconolite monoclinic phase CaZr<sub>0.92</sub>Ti<sub>2.08</sub>O<sub>7</sub>, identified to the stallion of JCPDS number (81-0759) [14]. The corresponding lattice parameters, determined by TREOR logiciel [19] are: a = 12.441 A, b = 7.239 A, c = 11.341 A et  $\beta = 100,694^{\circ}$ .

One can note the absence of other zirconolite polytype structures or secondary phases.

Other studies report the formation of secondary phases such as: perovskite, rutile, hollandite, etc. [20-24].

In Table 1 are reported the lattice parameters of many zirconolites synthesized by other authors:  $CaZrTi_2O_7$  and



Fig. 1. XRD diffractogramm of  $Ca_{0,83}Ce_{0,17}ZrTi_{1,66}Al_{0.34}O_7$  2M-zirconolite.

**Table 1.** Comparison of the 2M-zirconolite  $Ca_{0,83}Ce_{0,17}ZrTi_{1,}$ <sub>66</sub>Al<sub>0.34</sub>O<sub>7</sub> lattice parameters with those of other published results.

Chemical formula	a (Å)	b (Å)	c (Å)	β (°)
Ca <sub>0,83</sub> Ce <sub>0,17</sub> ZrTi <sub>1,66</sub> Al <sub>0.34</sub> O <sub>7</sub>	12.441	7.239	11.341	100.694
CaZrTi <sub>2</sub> O <sub>7</sub> [26]	12.4436	7.2742	11.3813	100.554
Ca <sub>0.8</sub> Nd <sub>0.2</sub> ZrTi <sub>1.8</sub> Al <sub>0.2</sub> O <sub>7</sub> [19]	12.4685	7.2697	11.3589	100.654
CaHfTi <sub>2</sub> O <sub>7</sub> [24]	12.420	7.262	11.343	100.57
$\begin{array}{l} Ca_{0,83}Ce_{0,17}ZrTi_{1,66}Al_{0.34}O_7\\ CaZrTi_2O_7 \ [26]\\ Ca_{0.8}Nd_{0.2}ZrTi_{1.8}Al_{0.2}O_7 \ [19]\\ CaHfTi_2O_7 \ [24] \end{array}$	12.441 12.4436 12.4685 12.420	7.239 7.2742 7.2697 7.262	11.341 11.3813 11.3589 11.343	100.6 100.5 100.6 100.5

Ca<sub>0.8</sub>Nd<sub>0.2</sub>ZrTi<sub>1.8</sub>Al<sub>0.2</sub>O<sub>7</sub> were synthesized by sintering, and CaHfTi<sub>2</sub>O<sub>7</sub> by the alkoxide method [19, 24-26].

All the published results are similar to our values. Indeed, the same rule of cations substitution in the materials is observed, and thus it leads to comparable lattice parameters in all the materials.

The calculated theoretical density of the mineral is 96%TD, which confirms the success of the sintering and a good crystallization of the material. Based on the obtained theoretical and geometrical densities, we obtain a relative density of 86.17%. This confirms a good densification of the material during sintering.

Polished 2M-zirconolite pellets examined by SEM microscopy show typical shape features of the zirconolite grains of monoclinic structure (Fig. 2).

The grains structure is uniform and narrow, indicating a good densification of the materials. Several studies in the literature illustrate the morphology of common phases appearing on the zirconolite micrographies (zirconolite, perovskite, hollandite, rutile and brannerite) [20-23].

The observed microstructure is little porous and the distribution of the grains and pores is uniform. The average grains size is about 2 to 3  $\mu$ m, with few grains sizes up to 20  $\mu$ m.

The room temperature FTIR transmittance spectrum of the investigated ceramic exhibit the broad transmittance bands at 412.97 and 473.47 cm<sup>-1</sup> (Fig. 3),



Fig. 2. SEM micrographs of  $Ca_{0,83}Ce_{0,17}ZrTi_{1,66}Al_{0.34}O_7$  2M-zirconolite.



Fig. 3. FTIR spectrum of  $Ca_{0.83}Ce_{0.17}ZrTi_{1.66}Al_{0.34}O_7$  2M-zirconolite.

	Leachate pH					
t (d)	2		12			
	T (°C)					
0	23	70	23	70		
0	$N_L (10^{-3} \text{ Kg.m}^{-2})$					
0	0	0	0	0		
1	2.820	5.200	2.820	0.218		
3	5.920	8.680	5.920	0.973		
5	10.120	10.620	10.120	1.290		
8	10.700	12.100	10.700	1.510		
10	11.320	12.440	11.320	1.82		
11	12.260	12.500	12.260	2.172		
15	12.540	12.650	12.540	2.570		
17	13.205	13.000	13.205	2.830		
22	13.550	13.200	13.550	2.962		
25	13.970	13.450	13.970	3.020		
28	14.300	13.750	14.300	3.068		
30	14.540	13.860	14.540	3.100		
32	15.300	14.050	15.300	3.147		
34	15.260	14.300	15.260	3.266		

Table 2. Evolution of the Ce normalized mass loss  $N_L$  in the leachates, as a function of time and temperature.

corresponding to Ca-O and Ca-O-Ti vibrations of, respectively. The elongation vibrations at 516.69 and 646.34 cm<sup>-1</sup> can be attributed to Ti-O (and/or Zr-O) and TiO<sub>6</sub> characteristic absorption bands. One can also note the Ca-O-Ca vibration at 685.23 cm<sup>-1</sup> [27-29]. A broad band in the mid IR peaking around 1500 cm-1 reveals the OH elongation vibration.

# Chemical durability of the material

The variation of the Ce-normalized elemental mass loss ( $N_L$ ) and the Ce leaching rate ( $\tau_{Ce}$ ) are calculated using the formulas (1) and (2), respectively.

For all the tests, the results of the evolution of  $N_L$  versus time are shown in Table 2.

The results of  $N_L$  show a Ce rapid release in the acidic leachate (pH = 2) for both the two temperatures

(23 °C and 70 °C), until the 10<sup>th</sup> day.

Then, a steady state (equilibrium) is reached, with  $N_L$  values around 12.5  $10^{-3}$  kg.m<sup>-2</sup>. Thus, the temperature has a significant effect on the Ce normalized elemental mass loss.

At pH = 12 and for T = 23 °C, a steady state is reached at the 10<sup>th</sup> day of test, with a value of  $N_L$  of 2.5  $10^{-3}$  kg.m<sup>-2</sup>.

For the temperature of 70 °C, and after the  $10^{\text{th}}$  day of test, one can note an increase of the Ce mass loss until the  $25^{\text{th}}$  day, for which an equilibrium value of  $12.5 \ 10^{-3}$  kg.m<sup>-2</sup>, is observed.

This stabilization of the leaching phenomenon is probably due to the formation of insoluble inorganic coating layers, containing the superficial elements of the matrix, which provoke the appearance of a steady state.

This phenomenum has already been reported for the zirconolite leaching behavior, where insoluble alteration titaniferrous layers, of 1 to 10 nm thickness, form.

These films are decalcified and contain Zr and lanthanides. They are probably constituted by oxy-hydroxide of Zr and Ti. [5, 18, 30, 31].

The results of the evolution of the Ce leaching rate  $(\tau_{Ce})$  as a function of time at 23 °C, for pH values of 2 and 12 are gathered in fig. 4.

On can remark that the dissolution rates are low in the basic medium compared to those in the acidic medium.

For pH 2 and 12 media, and at 23 °C and 70 °C temperatures, and after reaching the steady state (34 d) the values of  $\tau_{Ce}$  are 2.82 10<sup>-3</sup> kg.m<sup>-2</sup>.d<sup>-1</sup> at pH 2 (70 °C); 12 10<sup>-3</sup> kg.m<sup>-2</sup>.d<sup>-1</sup> at pH 2 (23 °C)); 2.73 10<sup>-3</sup> kg.m<sup>-2</sup>.d<sup>-1</sup> at pH 12 (70 °C) and 0.37 10<sup>-3</sup> kg.m<sup>-2</sup>.d<sup>-1</sup> at pH 12 (23 °C).

This stabilization of the leaching phenomenon is probably due to the formation of insoluble inorganic layers containing the superficial matrix elements, which signals the occurrence of the steady state.

Leturcq and al. have synthesized a zirconolite with



Fig. 4. Evolution of the Ce leaching rate of 2M-zirconolite as a function of time and pH, for the temperatures of 23 °C and 70 °C.

Table 3. Mathematical relations of the Ce normalized leaching rate (10-7 kg.m-2d-1) as a function of time (d).

T (°C)	pН	$\tau = \tau_0 + A_1  e^{(-\iota \prime b 1)} + A_2 e^{(-\iota \prime b 2)}$	Error on the coefficients
23	2	$\tau = 5.75194.10^{-8} - 1.72511.10^{-10} e^{(t/5.77799)} + 5.04593.10^{-7} e^{(-t/5.87197)}$	$\begin{array}{l} \Delta \ \tau_0 = 4.88646.10^{-8} \\ \Delta A_1 = 1.80647.10^{-10} \\ \Delta A_2 = 5.04593.10^{-7} \\ \Delta b_1 = 9.79415 \\ \Delta b_2 = 1.49721 \\ R^2 = 0.96769 \end{array}$
	12	$\tau = 8.40685.10^{-8} - 2.95424.10^{-10} e^{(t/5.94131)} + 5.01615.10^{-7} e^{(-t/4.71268)}$	$\begin{array}{l} \Delta \ \tau_0 = 4.19712.10^{-8} \\ \Delta A_1 = 45.86307 \\ \Delta A_2 = 2.68519.10^{-6} \\ \Delta b_1 = 2213.42836 \\ \Delta b_2 = 0.83017 \\ R^2 = 0.95679 \end{array}$
2 70 12	2	$\tau = 1.78101.10^{-9} + 5.1658.10^{-4} e^{(-t/\ 0.15789)} + 5.4591.10^{-6} e^{(-t/\ 3.01954)}$	$\begin{array}{c} \Delta  \tau_0 = 4.96113.10^{-8} \\ \Delta A_1 = 2.04864.10^{-10} \\ \Delta A_2 = 4.43471.10^{-8} \\ \Delta b_1 = 6.93112 \\ \Delta b_2 = 1.22807 \\ R^2 = 0.99058 \end{array}$
	12	$\tau = 2.64895.10^{-8} + 2.77971.10^{-7} e^{(-t/5.4795)} + 2.77971.10^{-7} e^{(-t/5.47239)}$	$\begin{array}{l} \Delta \ \tau_0 = 2.20033.10^{-8} \\ \Delta A_1 = 1.12333 \\ \Delta A_2 = 1.12333 \\ \Delta b_1 = 14466.16261 \\ \Delta b_2 = 14447.20652 \\ R^2 = 0.94592 \end{array}$

the chemical formula  $Ca_{0.8}Nd_{0.2}Zr-Ti_{1.8}Al_{0.2}O_7$  at 1400 °C and shows that the dissolution rate increases with the medium acidity [5].

Dissolution rates are fast at T = 70 °C for both pH 2 and 12. Therefore, one can conclude that the higher is the leachates temperature the higher is the Ce dissolution rate of the zirconolite.

The Ce rate of leaching decreases rapidly as a function of time, following a second order exponential decay mathematical law. The corresponding calculated formulas are given in Table 3. The error on the coefficients:  $\tau_0$ , (A<sub>1</sub>), (A<sub>2</sub>), (b<sub>1</sub>) and (b<sub>2</sub>) is very low. All the values of the correlation coefficient are satisfactory (0.94592- 0.99058).

#### Conclusions

In this work, a 2M-zirconolite with the formula  $Ca_{0.83}Ce_{0.17}ZrTi_{1.66}Al_{0.34}O_7$  has been synthesized by sintering at 1400 °C. The pellets of 2M-zirconolite have an average density of 4.013 g/cm<sup>3</sup> and a hardness of 366 MPa. These results confirm good densification properties of the synthesized material. The measured physical properties are satisfactory and are close to that required for RW confinement materials. The phase identification of the material showed that the main crystalline structure of the product is a monophasic 2M-zirconolite. One can conclude that the synthesized zirconolite has a good rate of incorporation of CeO<sub>2</sub>, which is 10.85%. The SEM analysis reveals a homogeneous, compact and less porous material. The FTIR analysis showed the typical vibration bonds of

the mineral.

A static leach test was used to quantify the amounts of extracted Ce as a function of pH and temperature. The Ce leached amounts are greater in the acid medium of pH = 2, than in the basic one of pH = 12, at both room temperature (23 °C) and 70 °C.

The leaching equilibrium is reached after 34 days. The Ce dissolution rates are faster at 70 °C compared to those obtained at 23 °C, for both the leachates pH of 2 and 12; the Ce speed of dissolution increasing with the leachate temperature.

On can remark that the dissolution rates are low in the basic medium compared to those in the acidic medium. The best values areof  $2.82 \ 10^{-3} \text{ kg.m}^{-2} \text{.d}^{-1}$  at pH 2 (70 °C) ; and of 0.37  $10^{-3} \text{ kg.m}^{-2} \text{.d}^{-1}$  at pH 12 (23 °C), at the steady-state.

One can conclude that the synthesized 2Mzirconolite matrix can be considered as a candidate for the MA confinement.

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