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RESEARCH ARTICLE

Study of the chemical durability of a hollandite mineral leached in both static and dynamic conditions

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ABSTRACT

Hollandite is a ceramic used for the confinement of cesium. In this study, we synthesized a hollandite of chemical formula: $K_{0.28}Ba_{0.76}Ti_{7.10}Cu_{0.9}O_{16}$, where K simulates cesium. This new formulation of a copper-containing hollandite was synthesized by a double calcination; the first one at 950°C during 18 h, and the second one at 1000°C during 6 h. The mineral was identified by X-ray diffraction. Various leaching tests are employed in order to assess the chemical durability of this mineral. The static test MCC1 gave elemental leaching rates of: 7.097 10^{-5} g cm^{-2} d^{-1} for Cu, 5.592 10^{-7} g cm^{-2} d^{-1} for Ti and 4.630 10^{-6} g cm^{-2} d^{-1} for Ba, after 42 days. This corresponds to dissolved elements percentages of: 5.7% Cu, 0.0007% Ti and 0.2% Ba. The equivalent amount of dissolved K is 0.0029%. A static test in the presence of a clay barrier, gave the best leaching rates (at 42nd day, NR<3.704 10^{-7} g cm^{-2} d^{-1} of Cu, and <1.11 10^{-9} g cm^{-2} d^{-1} of Ti and <3.67 10^{-9} g cm^{-2} d^{-1} of Ba). This corresponds to 0.030% of Cu, 10^{-6} % of Ti and 0.002 % of Ba, and about 0.002% of K. In MCC5 dynamic test, the leaching rates of Cu, Ti and Ba reached 2 10^{-6}, 1,468 10^{-7}, and 1.084 10^{-5} g cm^{-2} d^{-1}, respectively, corresponding to 0.028% Cu, 0.0003% Ti, and 0.082% Ba, after seven days. The estimated K leaching rate is 3.613 10^{-6} g cm^{-2} d^{-1}, ie 0.082% K dissolved in the leachate. There is no passivation layer formation. The MCC5 test is considered as a dissolution test.

Keywords: Hollandite, cesium, leaching, MCC1, MCC5, clay

1. INTRODUCTION

Alkaline isotopes raising from many intermediate radioactive waste, such as 137 Cs, 134 Cs and 90 Sr are an issue in an environmental point of view, and their confinement for long periods of time, in durable matrix is a concern for the scientific community [1].

Many nuclear glasses and ceramic matrix as well, have been proposed to embed such radioactive elements. The ceramics have the advantage to be more chemically durable and are highly resistant to radiations damages, resulting from radionuclides disintegrations in the materials during waste disposal. Among the proposed confinement materials for these alkaline elements, borosilicate, aluminosilicate and phosphate glasses, ceramics (NZP: $NaZr_2(PO_4)_3$, phosphated apatites such as $Ca_8NdCs(PO_4)_6F_2$, silicated apatitessuch as $Ca_7Nd_2Cs(PO_4)_5(SiO_4)F_2$), zeolite cenospheres, $KCsFeZrP_3O_{12}$, etc.), and aluminosilicate glass-ceramics, have suitable properties[1–4].

Synroc ceramics which are mainly composed of hollandite, perovskite, zirconolite, and rutile can also confine Cs and Sr in the crystalline lattice of their minerals. Hollandite is a mineral belonging to Synroc. It can easily accommodate cesium in its structure. Hollandite can vary in its chemical composition leading to various material properties [5].

Natural hollandite has the chemical formula: $BaAl_2Ti_6O_{16}$. It is dedicated to the confinement of radioactive alkaline earth elements, such as cesium (Cs), rubidium (Rb) and barium (Ba) [6]. The general formula of hollandite is: $A_x(B,C)_8O_{16}$, $x \leq 2$, where A cations are mono or bivalent, C cations, usually bi or trivalent, and B cations tetravalent. C cations compensate the charge for the incorporation of A cations into the structure [7]. This structure is derived from that of rutile, and consists of double chains of BO_6 octahedron. The structure symmetry can be

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monoclinic (I2/M) or quadratic (I4/M), depending on the ionic radii of A, B or C cations [8–12]. According to J. Zhang et al. [13], the most widespread crystalline structure for hollandite is tetragonal, with a (I4/M) space group.

Many studies have dealt with the hollandite optimal composition.

F. Angeli et al. [14] synthesized a hollandite with the chemical formula: $Ba_x^{2+}Cs_y^{2+}M_{2x+y}^{3+}Ti_{8-2x-y}^{4+}O_{16}$ ($x \leq 2$) where M is a trivalent cation (Ti^{3+}, Al^{3+} or Fe^{3+}) providing the charge compensation required for Ba and Cs loading. When M= Fe^{3+} or Fe^{3+} + Al^{3+} in Ba_xCs_y (Fe, Al)$^{3+}{}_{2x+y}Ti^{4+}{}_{8-2x-y}O_{16}$) hollandite, the most significant amounts of Cs were loaded in the structure, under oxidizing sintering conditions [7, 15–18].

Joint investigations between the ANSTO (Australian Nuclear Science and Technology Organisation) and the French CEA (Commissariat àl'Enérgie Atomique)report the loading of high amounts of Cs ions within $Ba_1Cs_{0,28}Al_{1,46}Fe_{0,82}Ti_{5,72}O_{16}$ hollandite [19].

Several synthetic methods, dry and wet ones, are used to synthesize hollandite. However, most of them are wet route processes, based on sol-gel reactions in which the precursors mixtures are obtained by the alkoxide route [14, 18, 20, 21]. Otherwise, the dry method employs sintering processes, called 'oxides route' [15, 16]. This last is based on a calcination, under air or inert atmosphere, of a mixture of oxides and carbonates, followed by a sintering between 1200 and 1400 °C [16, 17].

For an optimal confinement of Cs, under the frame of (Ba-Cs) hollandite investigations, many studies seek to vary the charge compensating element (C), among many metals. Till today, copper has not been studied yet.

This study investigates the synthesis of a titaniferous hollandite with copper (Cu^{2+}) as a charge compensating element, with the chemical formula of: $K_{0.28}Ba_{0.76}Cu_{0.9}Ti_{7.10}O_{16}$, by a dry method. The precursor mixture contains titanium (Ti), barium (Ba), and copper (Cu) oxides, and potassium (K) carbonate. The ionic radii of Ti^{4+} and Cu^{2+} are relatively close to each other [7] and the tolerance factor, th, has been verified, such that one can expect a stable structure of hollandite [22].

On the other hand, to avoid process constraints due to the chemical properties of Cs_2O (low melting temperature (490°C) and high volatility), potassium is used as Cs simulator, to validate the process; and to check the possibility of formation of hollandite mineral under the chosen operating conditions.

One can note that the optimization of sintering conditions has been the subject of a previous work in our laboratory [23].

The chemical durability of hollandite is assessed by three leaching tests: the MCC1 static test, a static test in the presence of a clay barrier, and the MCC5 soxhlet dynamic test. The leaching kinetics is monitored by ICP-OES spectroscopy. The evolution of the concentration, the mass loss, and the elemental leaching rate of Cu, Ti and Ba, are calculated; and make conclusions valuable, on the leaching behavior of the as-prepared hollandite.

2. MATERIALS & METHOD

The following commercial reagents are employed: K_2CO_3 (99% Merck), BaO (99.6% Fluka), TiO_2 (99% Merck) and CuO (99% Merck). They are dried separately in an oven at 100°C overnight, crushed using a manual agath mortar, and sieved to reach a particle size less than 60 μm. A mixture of powders, according to the stoichiometric conditions of the chosen chemical formula, is weighed. 8 wt.% of zinc stearate (Sigma-Aldrich) is added as organic binder. The mixture is homogenized using a D 4030 Controls Automatic Sieve Shaker. Pellets with 14.3 mm diameter, and of different heights are compacted using a Sodemi RD uni-axial press, at 6 t. They are calcined at 950°C for 18 h in a RHF-1600 Carbolite furnace, with a heating and cooling rate of 5 and 10 ° min^{-1}, respectively. The calcined pellets are similarly crushed, pelletized, then sintered under air at 1000°C, for 6 h, with both a heating and cooling step of 5 ° min^{-1}. Both green (d_c) and sintered (d_f) geometrical densities are measured.

The materials phases' identification is performed by X-ray diffraction analysis (XRD) with a Philips X-Pert Pro spectrometer. The X'Pert High Score Plus software, 4.1 version, is used for phase' identification [24].

The MCC1 leach test is performed in a small volume of leachate during a relatively short time period. The mineral pellets are immersed in dark opened glass vials, containing ultra-pure water (18 MΩ cm^{-1}) at ambient temperature (≅25°C). Regular samplings of 1 mL are performed at know times, not exceeding 42 days. A drop of 1N nitric acid solution is added to each sample to prevent the formation of solid layers on the sampling tubes walls.

After each sampling, the leachate volume is completed to its initial value, with ultra-pure water, in order to maintain (S_0/V_0) surface to volume ratio constant.

The starting leachate immersion volumes are calculated considering S_0/V_0= 30. This last is an important test parameter. S0: is the material surface effectively in contact with the leachate, and V_0 is the leachate volume.

The static test, performed in presence of a clay barrier, simulating an engineering barrier in storage conditions, is similar to MCC1 test. The samples are immersed in water into a clay container. This last is synthesized by calcination at 750°C in air, of natural Algerian kaolin.

The MCC5 test employs a 250 mL soxhlet extractor, working under air.Cylindrical pellets, of both known dimensions and weight, are continuously immersed in the leachate. The balloons are filled with 30 mL of ultra-pure water excess (18 MΩ cm^{-1}), to prevent both evaporation and samplings water losses.

Daily leachates samplings of 1 mL are performed in the balloon during 7 days. The balloon residues are collected after the last sampling. The balloon is further cleaned with a 1N HNO_3 (Merck) acid solution, in order to remove walls likely deposits. The whole of liquid' residues are analyzed.

All leachates are analyzed by a32 Jobin Yvon ICP-OES spectrometer, after establishing the calibration curves of the interest elements, leached from the mineral, namely: Cu, Ti et Ba.

Standard solutions are prepared using ICP/DCP Fluka standards. The chosen concentrations are: 10, 20, 50, 80 and 100 ppm. The elemental calibrations curves of the measured intensity (I) versus the i element concentration (C_i), are fitted using LabView equipment software.

The elemental mass loss, for each i element, NLi traduces the dissolution of a known i element [25]. It is expressed in kg m^{-2}, and given by the equation (1).

$$NL_i = \frac{C_i V_0}{S_0 F_i} \quad (1)$$

Where C_i: is the total concentration of the i element (kg m^{-3}), V0: the total volume of the leachate solution (m^3), S0: the sample initial surface effectively in contact with the liquid (m^2) and Fi: the i element weight fraction in the solid phase (wt.%).

The elemental normalized leaching rate (NR_i) as a function of time expresses the material normalized dissolution rate (in kg m^{-2} s^{-1}). It is given by the equation (2)[25].

$$NR_i = \frac{dM_i}{dt} = \frac{1}{F_i S_0}\frac{dm_i}{dt} \quad (2)$$

The i element average leaching rate is calculated by dividing the normalized mass loss by a mean time interval (Δt) starting from the initial time of leaching. It is given by the equation (3).

$$NR_{imoy} = \frac{\Delta M_i}{\Delta t} = \frac{1}{F_i S_0}\frac{\Delta m_i}{\Delta t} \quad (3)$$

3. RESULTS & DISCUSSION

3.1. Density of the synthesized material

The hollandite crud density, dc, is of 2.72. After the first thermal treatment, it is of 2.02; and the final sintered density is of 2.56. After the first thermal treatment, the materials density decreases highlighting the fact that a second thermal treatment is required. This last improved the material density.

V. Aubin-Chevaldonnet et al. [15] found sintered densities in the interval of 3.92-4.55, for different Ba-hollandites. These values are higher than those of the present study, due to the synthesis processemployed by these authors,which involves a sintering pressure, and thus increases density, and reduces the internal porosity. Adding to the difference in the used elements, such as Cu, which have a low atomic weight, and contributes to decreasing the sintered density.

3.2. Phases identification

Both the calcined and sintered materials XRD spectra are given in Fig 1. The calcined material phases identificationshows a main tetragonal phase, identified as $BaTi_7MgO_{16}$ hollandite skeleton, associated to the JCPDS card number: 01-073-0499, with over 60 % [26]. The calcined pellets appear to be homogeneous. An excess of TiO_2 appears as a secondary phase, identified by the JCPDS standard number 03-065-0191.

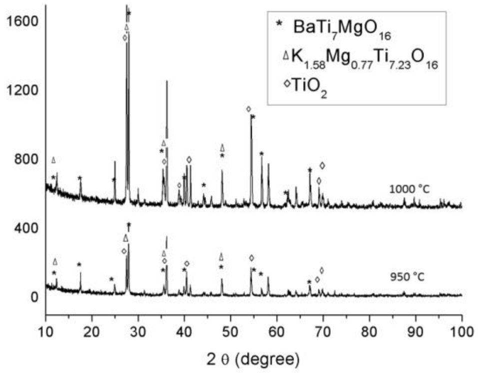

Fig 1. XRD spectra of both calcined (950 °C) and sintered (1000 °C) materials

A similar semi-quantitative composition is identified for the sintered material, with over 65 % of hollandite skeleton, shared in two phases: 46 % of tetragonal $BaTi_7MgO_{16}$ (JCPDS 01-073-0499) and 19 % of tetragonal $K1.58Mg0.77Ti_{7.23}O_{16}$ (JCPDS 01-084-0976). One can also observe 35 % of tetragonal TiO_2 (JCPDS 01-089-4202).

3.3. Leaching tests

MCC1 static test

During this test, the evolution of Ba, Ti and Cu concentrations as a function of time show that for the whole of elements, the elemental concentrations (Ci) are low during the first seventh days, then increase (Fig 2). They are high between the 28th and the 35th day, with maximum values. Copper is the most water-soluble element, with a maximum concentration at the 35th day: C_{Cu}=3.8335 kg m^{-3}. At this time, C_{Ba}=0.6985 kg m^{-3}, and C_{Ti}=0.0221 kg m^{-3}; being in mind that this last element is the most abundant in the solid phase.

For all elements, these values decrease at the 42nd day (1 day=86400 s).

The evolution of normalized mass losses, N_{Li}, in Ba, Ti and Cu seems to follow that of concentrations (Table 1). Until the 7th day, the values are very low. Beyond, NL_{Cu} increases rather quickly, till the 35th day, and then decreases significantly. For Ba, this evolution goes in the same way but is slower than that for Cu. For Ti, the evolution of NL_{Ti} is absent.

During this leaching stage, there is a certain balance, which shows that the leaching is very slow, or that there is a balance between the leached elements and those that eventually return to the matrix. This is probably due to a solubility competitiveness of Cu and Ba elements in the water.

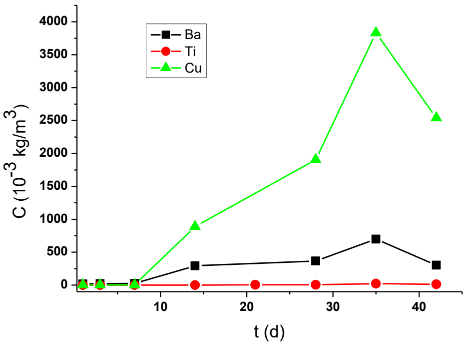

Fig 2. Evolution of Ba, Ti and Cu concentrations as a function of time, for $K_{0.28}Ba_{0.76}Ti_{7.10}Cu_{0.9}O_{16}$ hollandite leached by MCC1 test

Table1. Evolution of the normalized elemental mass loss as a function of time for Ba, Ti and Cu, for $K_{0.28}Ba_{0.76}Ti_{7.10}Cu_{0.9}O_{16}$ hollandite in MCC1 test

t (days)	NL_{Ba} (10^{-2} kg m^{-2})	NL_{Ti} (10^{-2} kg m^{-2})	NL_{Cu} (10^{-2} kg m^{-2})
1	0.0113	0.0770	0.0036
3	0.0145	0.0632	0.0018
7	0.0154	0.0672	0.0019
14	0.1885	0.2113	1.0423
21	---	0.9805	---
28	0.2354	0.0011	2.2365
35	0.4493	0.0044	4.4995
42	0.1944	0.0024	2.9807

In general, Cu is more soluble than Ba, which in turn is more soluble than Ti. The maximum elemental mass losses observed are at day 35: NL_{Ba}=0.4493 10^{-2} kg m^{-2}, NL_{Ti}=0.0044 10^{-2} kg m^{-2}, NL_{Cu}=4.4995 10^{-2} kg m^{-2}. These low values show that the matrix is less soluble in water, especially since its major element, Ti, is released in the smallest amount.

Beyond the 35th day, NLi values increase for the three elements, then decrease. At the 42nd day, they are of: 2.9807 10^{-2} kg m^{-2} for Cu, 0.1944 10^{-2} kg m^{-2}for Ba, 0.0024 10^{-2} kg m^{-2} for Ti. At this stage, the matrix elements are likely redeposited around the material, slowing down the leaching speed. A passivation layer starts to form around the material, leading the leaching medium to a steady state.

F. Angeli et al. [14] have leached a Cs-doped hollandite ceramic ($BaCs_{0.28}Fe_{0.82}Al_{1.46}Ti_{5.72}O_{16}$) at 90°C. A Ba-layer has formed around the material, and coated it, after several months of leaching. It is poor in Cs, and probably formed by $BaCO_3$, where carbon is coming from air CO_2. This layer re-dissolves when the water is renewed in the medium [27,28].

During the leaching process, there is a strong displacement of alkalis from the materials surface. G. Leturq et al. [29] show a zirconolite decalcification after leaching at 150 °C in an acidic medium, and formation of a passivation layer, rich in the least soluble alkalis (Ba). This passivation layer has been evidenced in other studies [30, 31].In this study, NL_{Cs} is similar to that of Ba (19 10^{-5} g cm^{-2}).

In the present test, one can suppose that Cs and K moved during surface alteration, and formed Cs and/or K-reach minerals, as layers deposited on the material surface, like hydrated titanates ($Ti(OH)_4$) [29, 32].

T. Suzuki-Muresan et al. [33] conduct leaching experiments in static mode of (Cs, Ba)-hollandite during 240 days, at various pH in NaCl aqueous solutions.

The steady-state is established between 45 and 240 days, and the average NL_{Cs} ranges between (8.2 ± 0.3) 10^{-6} kg m^{-2} (pH 2.5) to (4.1 ± 0.2) 10^{-6} kg m^{-2} (pH 8.6), and NL_{Ba} from (3.7 ± 0.4) 10^{-6} kg m^{-2} (pH 2.5) to (4 ± 2) 10^{-7} kg m^{-2} (pH 8.6). These values are higher than our results, which are of NL_{Ba}=0.1944 10^{-2} kg m^{-2}, after 42 days of test in a neutral medium.

These authors have loaded hollandite with (^{137}Cs and ^{133}Ba) isotopes, and perform sorption experiments on hollandite pre-leached in aqueous solutions. Cs and Ba release is controlled by surface reactions. Leaching experiments and isotopic addition experiments (^{137}Cs and ^{133}Ba-radiotracers) indicate that Cs behavior is independent on pH-values, at the opposite of that of Ba which strongly depend on it.

The NR_i evolution for Ba, Ti and Cu as a function of time, expresses the mineral dissolution rate. The corresponding speed curves are shown in Fig 3.

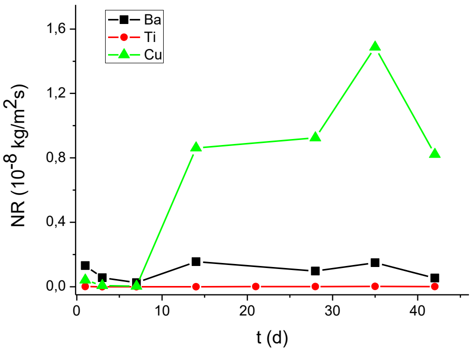

Fig 3. Evolution of the leaching rate as a function of time for Ba, Ti and Cu, for $K_{0.28}Ba_{0.76}Ti_{7.10}Cu_{0.9}O_{16}$ hollandite in MCC1 test

The maximum rates of leaching are at the 35th day, for Ti and Cu, namely: NR_{Ti}=1.157 10-4 kg m^{-2} s^{-1} and NR_{Cu}=1.4884 10^{-8} kg m^{-2} s^{-1}. At the end of the test, ie at the 42nd day, NR_{Cu}=8.2176 10^{-9} kg m^{-2} s^{-1}, and NR_{Ti}=6.4718 10-11 kg m^{-2} s^{-1}.That is a solids content of: 5.7% Cu, and 0.0007% Ti.

NR_{Ba} has a random evolution. The maximum value is at the 14th day. It is of: NRBa=1.5625 10^{-9} kg m^{-2} s^{-1}. At the end of test, ie at the 42nd day, NR_{Ba}=5.3241 10^{-10} kg m^{-2} s^{-1}. That is a solid content of: 0.2%.

Taking into account the stoichiometry of the molecule, the K dissolved amount is of 0.2064 %.

F. Angeli et al. [14] have studied the aqueous corrosion behavior of Cs-doped hollandite ceramic ($BaCs_{0.28}Fe_{0.82}Al_{1.46}Ti_{5.72}O_{16}$) at 90°C, using several static protocols, at both various pH and S_0/V_0 ratios, for times periods ranging from six months to three years. They report that after a rapid initial Cs release, the alteration rate is extremely low over the pH range from 2 to 10 (10^{-5} g m^{-2} d^{-1}≅1.1574 10^{-9} kg m^{-2} s^{-1}), and reaches 510^{-3} g m^{-2} d^{-1} at pH=1. In these experiments S_0/V_0 ratios are from 0.1 to 1200 cm^{-1}. The alteration thicknesses are of a few nanometers per year. These values are about 105 times lower than NR_{Ba} in the present study, which is about 5.3588 10^{-6} kg m_{-2} s_{-1}, instead of the low temperature (25°C).Whilst, after 261 days of test, aCs depletion is evidenced at the surface,when leachates are replenished with fresh deionized water. The presence of a soluble Ba-bearing secondary phase was inferred.

Solomah et al. [34] perform a MCC1 test, during 120 days. They found a value of: NR_{Ba}=6.94 10^{-7} kg m-2 s^{-1}. This value is lower than our result (5.3588 10^{-6} kg m^{-2} s^{-1} at the 42th day).

B.B. Shabalin et al. [32] assessed NR_{Cs} for $Ba_{0.9}Cs_{0.2}Fe_{2.0}Ti_{6.0}O_{16}$ ceramic, by MCC2 test at 150°C, in distilled water, during 1, 3, 7, 10, and 14 days; with S/V=0.01 mm^{-1}(≅ 10^{-5} m^{-1}). After 10 days, NRCs slows down: NR_{Cs}=1.1574 10^{-9} kg m^{-2} s^{-1}.

3.4. Static test in the presence of a clay barrier

The evolution of Ba and Cu concentrations as a function of time shows two minimums on the concentration curves (Fig 4). C_{Ba} stabilizes at the 42nd day at: C_{Ba}=2.288 10^{-3} kg m^{-3}. This low concentration shows the affinity of this alkaline earth element for the clay.

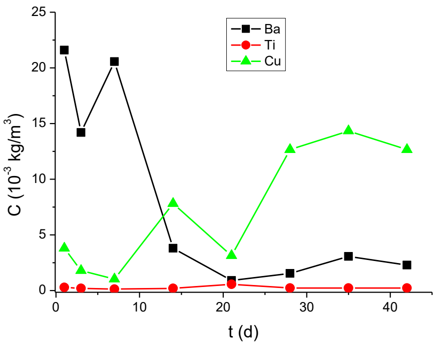

Fig 4. Evolution of the concentration as a function of time for Ba, Ti and Cu, for $K_{0.28}Ba_{0.76}Ti_{7.10}Cu_{0.9}O_{16}$ hollandite in the clay container test

In the clay container test, changes in C_{Ti} as a function of time show that C_{Ti} are the lowest concentrations. There are very weak during the whole period of test.

In opposite, for Cu, two maximum concentrations are observed on the 14th and 35th day. The final C_{Cu} value attains 12.66 10^{-3} kg m^{-3}. Cu does not have any affinity for clay.

The NL_i values follow the evolution of C_{Ba}, C_{Ti} and C_{Cu} values (Table 2), confirming that the clay slows the leaching over the 28th day of test; Ti and Ba (thus K simulator of Cs) having an affinity for the clay, at the opposite of Cu which dissolves in water. At the 42th day, NL_{Ba}=0.0015 10^{-2} kg m^{-2}, NL_{Ti}=4.6526 10^{-7} kg m^{-2} and NL_{Cu}=0.0156 10^{-2} kg m^{-2}.

Table 2. Evolution of the elemental mass loss as a function of time for Ba, Ti and Cu, for $K_{0.28}Ba_{0.76}Ti_{7.10}Cu_{0.9}O_{16}$ hollandite in the clay container test

t (days)	NLBa (10-2 kg m-2)	NLTi (10-7 kg m-2)	NLCu (10-2 kg m-2)
1	0.0145	5,9966	0.0047
3	0.0096	4,1356	0.0022
7	0.0139	2,6881	0.0013
14	0.0026	4,0942	0.0096
21	0.0006	11.9312	0.0039
28	0.0010	4.71458	0.0156
35	0.0021	4.77662	0.0176
42	0.0015	4.65255	0.0156

The evolution of NR_{Ba} and NR_{Cu} as a function of time are shown in Fig 5. It follows an exponential law for the three studied elements. The NR_{Ti} values remain very low over time.

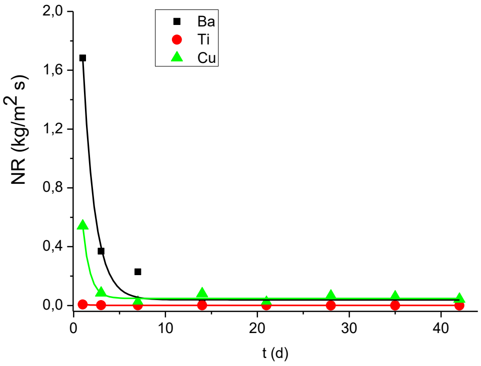

Fig 5. Evolution of the leaching rate as a function of time for Ba, Ti and Cu, for $K_{0.28}Ba_{0.76}Ti_{7.10}Cu_{0.9}O_{16}$ hollandite in the clay container test

The corresponding mathematical relations (4 and 5) are calculated by Origin 8.0 software.

$$NR_{Ba} = 3.8592\ 10^{-11} + 3.5312\ 10^{-9} exp^{\left(\frac{-t}{1.30534}\right)}\ R^2=0.9848 \qquad (4)$$

$$NR_{Cu} = 4.7931\ 10^{-11} + 1.7984\ 10^{-9}\ exp^{\left(\frac{-t}{0.7722}\right)} R^2= 0.9866 \qquad (5)$$

The leaching rates at the end of the experiments are: NR_{Ba}=4.2455 10^{-12} kg m^{-2} s^{-1}, NR_{Ti}=1.2822 10^{-13} kg m^{-2} s^{-1} and NR_{Cu}=4.2869 10^{-11} kg m^{-2} s^{-1}. Therefore, the dissolved amounts are of: 0.0016 % Ba, 10-6 % Ti and 0.0299 % Cu. That is a quantity of dissolved K estimated to 0.0016 %.

3.5. The MCC5 dynamic test

The curves of the evolution of the concentration of Ba, Ti and Cu as a function of time are gathered in Fig 6. During the soxhlet leaching, Ba is the most trained element into the leaching waters. Its concentration reaches 22.62 10^{-3} kg m^{-3} in the first day. Then, the evolution of C has a saw teeth form. The concentration curve shows two minima, the first to the 3rd day

($17.51\ 10^{-3}$ kg m^{-3}) and the 2nd, at the 6th day of test, is much more significant ($1.14\ 10^{-3}$ kg m^{-3}). Then, C_{Ba} is again up to a value of $11.79\ 10^{-3}$ kg m^{-3}. This indicates that this element is still dissolving around the 7nd day.

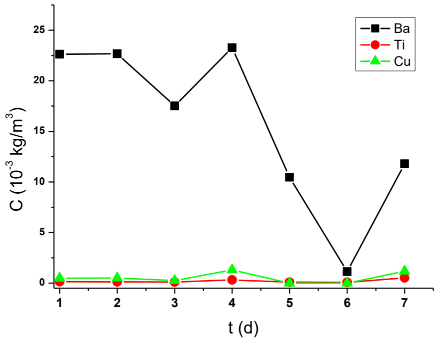

Fig 6. Evolution of the concentration as a function of time for Ba, Ti and Cu, for $K_{0.28}Ba_{0.76}Ti_{7.10}Cu_{0.9}O_{16}$ hollandite in MCC5 test

The evolution of C_{Ti} and C_{Cu} as a function of time shows that these two concentrations are very low during the whole of test, with a slight maximum on the 4th day: $C_{Timax}=0.320\ 10^{-3}$ kg m^{-3} and $C_{Cumax}=1.31\ 10^{-3}$ kg m^{-3}, respectively.

The evolution of NL_{Ba}, NL_{Ti} and NL_{Cu} as a function of leaching follows that of concentrations (Table 3). One can note two minimums on $NL_{Ba}=f(t)$ curve, the most important is at the 6th day with: $0.0073\ 10^{-2}$ kg m^{-2}. The NL_{Ti} and NL_{Cu} values are very low, with a maximum of $0.0154\ 10^{-2}$ kg m^{-2} at the 4th day. At the end of test, Ba, Ti and Cu continue to dissolve. On day 7, $NL_{Ba}=7.59\ 10^{-4}$ kg m^{-2}, $NL_{Ti}=1.0\ 10^{-5}$ kg m^{-2} and $NL_{Cu}=1.40\ 10^{-4}$ kg m^2.

Table3. Evolution of the elemental mass loss as a function of time for Ba, Ti and Cu, for $K_{0.28}Ba_{0.76}Ti_{7.10}Cu_{0.9}O_{16}$ hollandite in MCC5 test.

t (days)	NL_{Ba} (10^{-2} kg m^{-2})	NL_{Ti} (10^{-6} kg m^{-2})	NL_{Cu} (10^{-2} kg m^{-2})
1	0.14556	2.76674	0.0058
2	0.14595	2.56911	0.0059
3	0.11268	2.17386	0.0029
4	0.14975	6.32397	0.0154
5	0.06738	1.97624	*
6	0.00734	1.58099	*
7	0.07587	10.3000	0.0140

S.P. Kumar and B. Gopal [4] have synthesized a langbeinite phosphate powder: $KCsFeZrP_3O_{12}$ by a wet route. After one month of test, the MCC5 test applied to langbeinite phosphate powder: $KCsFeZrP_3O_{12}$ gave normalized mass losses in the order of $NR_K=10^{-7}$-10^{-6} kg m^{-2}, $NR_{Fe}=10^{-9}$-10^{-7} kg m^{-2}, $NR_{Zr}=10^{-8}$-10^{-6} kg $m^{-2}$and $NR_P=10^{-7}$-10^{-6} kg m^{-2}, respectively; and negligible Cs rate of leaching. These values are lower than our values.

The evolution of NR_{Ti} and NR_{Cu} as a function of time is represented in Fig 7. The maximum values are at the 1st day, where they reach: $NR_{Timax}=3.2022\ 10^{-11}$ kg m^{-2} s^{-1} and $NR_{Cumax}=6.7130\ 10^{-10}$ kg m^{-2} s^{-1} for Cu. Then, they decrease, and become undetectable for Cu at the 5th and 6th days.

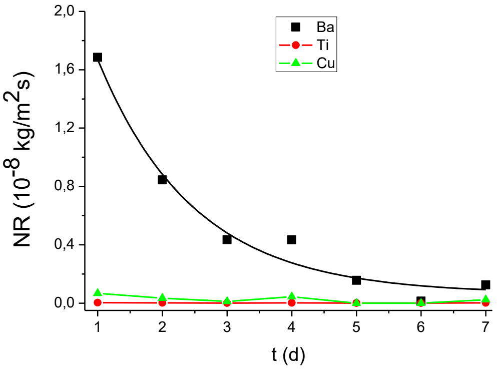

Fig 7. Evolution of the normalized rate of leaching as a function of time of Ba, Ti and Cu, for $K_{0.28}Ba_{0.76}Ti_{7.10}Cu_{0.9}O_{16}$ hollandite in MCC5 test

At the end of MCC5 test, both NR_{Ti} and NR_{Cu} increases again: $NR_{Ti}=1.6992\ 10^{-11}$ kg m^{-2} s^{-1} and $NR_{Cu}=2.3148\ 10^{-10}$ kg m^{-2} s^{-1}, ie 0.00034% Ti and 0.0276% Cu, contained in the mineral.

The evolution of NR_{Ba} as a function of time follows an exponential decay law, calculated by the Origin 8.0 software ($NR_{Ba}=3.1508\ 10^{-8}\exp(-t/1.48452) + 6.3535\ 10^{-10}$, $R^2=0.98973$). At the end of test, $NR_{Ba}=1.25\ 10^{-9}$ kg m^{-2} s^{-1}, corresponding to 0.0820% of the Ba contained in the mineral. The amount of dissolved K is therefore about 0.0822%.

Since Ba is in the geometric position of K (Cs simulator) inside the hollandite crystal, and regarding the Ba/K ratio in the mineral, the dissolution of K can be estimated to the third of $1.25\ 10^{-9}$ kg m^{-2} s^{-1}, is $0.4167\ 10^{-11}$ kg m^{-2} s^{-1}.

These results show that there is no passivation layer, formed during soxhlet leaching; this test being considered as an aggressive one.

In general, the literature surveys show that among the ceramics studied for Cs immobilization, the leaching tests prove the good stability of the matrices against Cs release [4, 35].

Cs-tetra-ferri-annite, $CsFe^{(II)}_3$-$Fe^{(III)}Si_3O_{10}(OH)_2$, leached by soxhlet, in neutral medium, (pH=7.05), with: m/V_0 = 1 mg cm^{-3} , gave 0.82 wt.% of Cs release [35]. Compared to the soxhlet test results in the present study (0.0820 wt.% Ba and 0.0822 wt.% K, after 7 days; m/V_0 = 7.79 mg cm_{-3}), our values are ten times lower compared to those of Cs-tetra-ferri-annite leaching. One can note that in our study, the main amounts of K and Ba, are released in the first day (24 h) of leaching.

4. CONCLUSIONS

In this study, we have synthesized a hollandite mineral with the chemical formula: $K_{0.28}Ba_{0.76}Ti_{7.10}Cu_{0.9}O_{16}$, where K simulates Cs. This new formulation contains copper. After a double calcination at 950°C for 18 h and a sintering at 1200°C for 6 h, the final product presents a sintered density of

2.56. XRD analysis reveals a polyphasic material with 65% of tetragonal hollandite, namely: 46% $BaTi_7MgO_{16}$ and 19% $K_{1.58}Mg_{0.77}Ti_{7.23}O_{16}$; and 35% of TiO_2.

In order to test the hollandite confinement ability, itschemical durability was assessed using three leaching tests: MCC1, MCC5 and a test in the presence of a clay barrier.

On the basis of the results, the leaching in the presence of a clay barrier shows the lowest leaching rates (at the 42nd day, $NR_{Ba}<4.2555\ 10^{-12}$ kg m^{-2} s^{-1}, and $NR_{Ti}=1.2822\ 10^{-13}$ kg m^{-2} s^{-1} and $NR_{Cu}=4.2869\ 10^{-11}$ kg m^{-2} s^{-1}).

MCC1 test gives slightly larger values (42nd day, $NR_{Ba}=5.3241\ 10^{-10}$ kg m^{-2} s^{-1}, $NR_{Ti}=6.4718\ 10^{-11}$ kg m^{-2} s^{-1}and $NR_{Cu}=8.2176\ 10^{-9}$ kg m^{-2} s^{-1}). Finally, the MCC5 test dissolves the most quantities (at the 7th day, $NR_{Ba}=1.25\ 10^{-9}$ kg m^{-2} s^{-1}, $NR_{Ti}=1.6992\ 10^{-11}$ kg m^{-2} s^{-1}and $NR_{Cu}=2.3148\ 10^{-10}$ kg m^{-2} s^{-1}). Obviously, Ti, Ba and therefore K have an affinity for kaolin clays.

Globally, the mineral currently studied has a good chemical durability, which is suitable in disposal conditions.It is able to well embed K (Cs simulator). Indeed, it shows K released contents less than 0.0029% in MCC1, 0.0016% in the presence of a clay barrier and 0.0822% in MCC5.

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