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Lithium titanate pebbles reprocessing by wet chemistry

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Abstract

An original dissolution method for irradiated Li_2TiO_3 in aqueous H_2O_2 was developed. One could easily obtain fine Li_2TiO_3 powders from the solution through drying and calcination. Li_2TiO_3 pebbles (size ~0.6 mm, above 90% TD) were obtained from the 'reprocessed' powders. These solutions were also suitable for the formation of a sol emulsion in 2-ethyl-hexanol-1, from which gelled microspheres of lithium titanate could be obtained. Locally prepared Li_2TiO_3 reprocessed and supplied pebble batches were tested for tritium release by temperature programmed desorption (TPD) methods in He + 0.1%H_2 (R-gas) after their short irradiations in a thermal neutron flux. The relative TPD data were compared. A qualitative correlation was developed between peak characteristics and pebble microstructure.

1. Introduction

A review of the preparation, properties, irradiation performance and tritium release of lithium containing ceramics has been recently published [1]. Li_2TiO_3 pebbles are now undergoing extensive investigation because of their good tritium release properties [2,3], chemical stability, and low activation under irradiation, in the frame of the European 'helium cooled pebble bed blanket' (HCPBB) program for the DEMO reactor (Li_4SiO_4 pebble bed was originally considered [4]).

The aim of this paper is to report our preliminary investigations about the feasibility of reprocessing Li_2TiO_3 breeder pebbles in order to recover the remaining ^6Li isotope at 'end-of-life' condition. The 'refabricated' pebbles are also tested for their tritium release characteristics and compared to the 'reference' material supplied by CEA/CEREM (France) also in the frame of European Fusion Technology Program that supported this work. These studies were also conducted in collaboration with other world wide institutes like CRNL (Canada), CCHEN (Chile) and IChTJ (Poland).

2. Li_2TiO_3 pebbles reprocessing by acid attack

The first attempts to reprocess Li_2TiO_3 pebbles by dissolution in nitric acid resulted in the formation of an insoluble titania phase and $LiNO_3$. The decomposition of $LiNO_3$ and solid state reaction between Li_2O and undissolved titania [5], were unsatisfactory from the point of view of obtaining reactive powders to fabricate highly density pebbles (above 90% of TD) as required for HCPBB project [6]. Only low density pebbles with fully open porosity could be obtained (FN1) [5].

3. Li_2TiO_3 pebbles reprocessing by Li–Ti peroxo-complexes

We explored new routes to completely dissolve Li_2TiO_3 pebbles looking at Ti(IV) wet chemistry. Orange coloured acidic solutions of Ti(IV) in H_2O_2 were discovered more than a century ago [7] and exploited for

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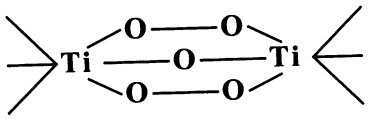
analytical purposes. Depending on the pH, mononuclear cationic and dinuclear anionic species with general formula TiO_2OH^+ (pH = 1) and $Ti_2O_5(OH)_x^{(2-x)}$ where $x = 2$ at pH 3 and $x = 6$ at pH 9 are known. By using Li_2TiO_3 a final pH of about 9 was measured. The following reaction schematically suggests what may be taking place:

$$2Li_2TiO_3(s)+2H_2O_2(aq)+H_2O(l)\rightarrow Li_4Ti_2O_5(OH)_6(aq) \quad (1)$$

The dinuclear unit is bonded through a μ-oxygen and two μ-peroxy groups.



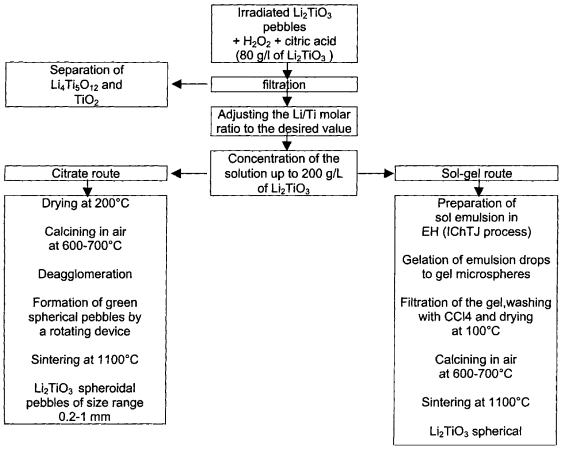
(2)

Both mononuclear and dinuclear compounds are not stable in time, they tend to transform into the insoluble peroxotitanium hydrate $TiO_3(H_2O)_x$ with a decrease in pH for the cationic species and an increase in pH for the anionic ones.

Stabilisation of the solution was achieved by addition of a terdentate chelating agent, like citric acid, to the H_2O_2 as suggested from the particular configuration (2) of the Ti-dinuclear unit.

On this basis we were able to dissolve Li_2TiO_3 powders in a few hours and sintered pebbles in 1–2 days in aqueous H_2O_2 (30% vol) + citric acid. Traces of $Li_4Ti_5O_{12}$ and TiO_2, eventually present in the starting material, was found to constitute the insoluble phases (Fig. 1) and could be separated by filtration. The clear solution of the Li–Ti-peroxocomplex could be subsequently handled without phase separation.

Two procedures were tested for the preparation of Li_2TiO_3 dense pebbles: (i) the citrate route and (ii) the sol–gel route as shown in the following schematic flow sheet:



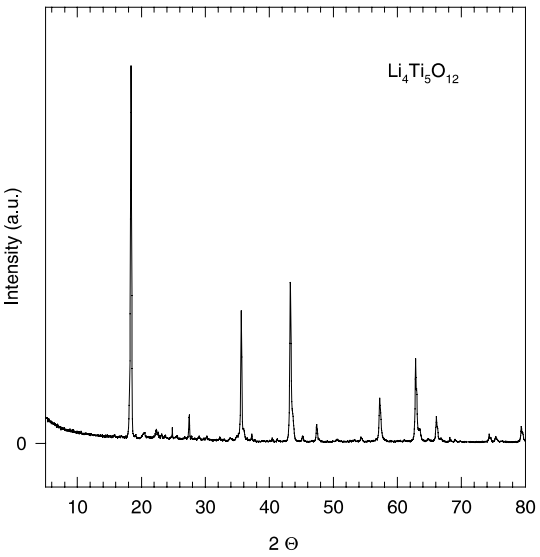


Fig. 1. X-ray diffraction pattern of the insoluble residue (about 4 wt% of the starting Li_2TiO_3 powder). The principal phase is $Li_4Ti_5O_{12}$, traces of TiO_2 are also present.

3.1. Citrate route

The stable citric acid solution could be concentrated up to 200 g/l of titanate and dried at 200°C without any phase separation. After heating the organic substance in air at 650°C, well below the normal solid state temperature reaction between TiO_2 and lithium salts, a very soft microcrystalline powder of Li_2TiO_3 was produced. The relative X-ray diffraction pattern is shown in Fig. 2.

To form green pebbles the de-agglomerated powder was sprayed with an hydro-alcoholic solution of a binder (methocel A-411) and tumbled in a planetary mill without grinding media. By optimising the binder amount, the rotation speed, and the filling factor of the mill, spheroidal pebbles with size 0.4–1 mm were obtained. After sintering for 2 h at 1100°C a density of about 92% of TD could be reached owing to the high sinter-activity of the powder. More details about these processes and material characterisation are reported elsewhere [8]. Fig. 3 reports an image of a sample of a batch (named FN5) prepared in this way. Some of its characteristics can be found in Table 1.

3.2. Sol–gel route

The potential for preparation of spherical pebbles through the water extraction variant of sol–gel process [9] was tested at IChTJ of Warsaw. The purpose of this activity was to prepare spherical pebbles in the small size range (10–100 μm) without using the classical powder technology. This procedure was based on the formation of an emulsion between 2-ethylhexanol-1 containing

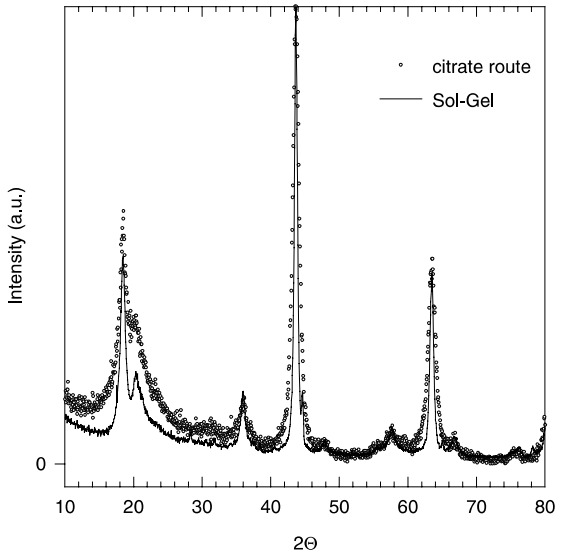


Fig. 2. X-ray diffraction pattern of Li_2TiO_3 powders fired for 2 h at 650°C.

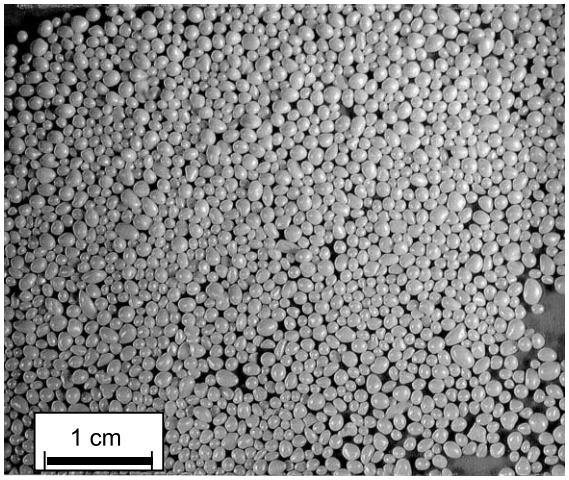


Fig. 3. Li_2TiO_3 sintered pebbles of the batch FN5.

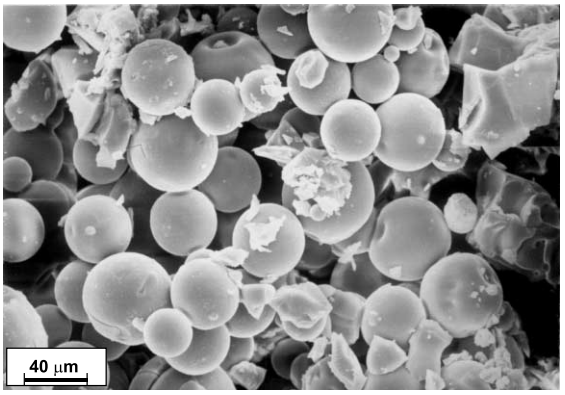


Fig. 4. SEM image of dried gelled pebbles.

surfactants like Span-80 + Ethomen S-15 (EH) and the concentrated citric acid solution of titanate. The gelation of the emulsion droplets was carried out by water extraction with partially dehydrated EH. The gelled particles were then separated, dried, calcined at 650°C and sintered for 2 h at 1100°C. Like the citrate route, the formation of Li_2TiO_3 could be observed after the organic burning at 650°C as revealed by X-ray diffraction pattern shown in Fig. 2.

While the gelation step was successful in producing spherical pebbles, (see Fig. 4) later heat treatments caused sticking of the spheres and sintering to an irregular particle shape. Optimisation of the process parameters will be investigated further. Some characteristics of a batch called 'SOL–GEL' are reported in Table 1.

4. Pebble irradiation and their out of pile tritium release characteristics

Functional properties of Li-ceramics have to be tested by in situ tritium release irradiation experiments under conditions simulating those foreseen for the HCPBB, including high Li-burnup. However, fast, qualitative evaluations on specimens differing in density,

Table 1
High- and low-density Li_2TiO_3 pebbles: main characteristics and relative tritium release TPD parameters

Pebble bed batch	Av. diam. (mm)	Density (% TD)	Sintering temper. (°C)	Nominal Li/Ti at. ratio	Grain size range (μm) min–max	T_t (°C) 5%	T_m (°C) 50%	T_f (°C) 90%
FN1	1.56 ± 0.06	56	1300	1.9	10–30	372	452	598
SOL–GEL	Irr. particles 0.01–0.1	Not evaluated	1100	2	1–10	340	465	626
FN5	0.6 ± 0.3	92	1100	2	3–20	390	510	656
CTI30C7	1.3 ± 0.1	93	1100	1.95	2–4	355	491	682

purity, grain size, and phase composition may give screening information and understanding of some basic aspects underlying tritium transport phenomena in these systems. Therefore, in addition to low and high density pebbles FN1, SOL–GEL and FN5, out-of-pile tritium release experiments were tested for the high density pebbles CTI30C7 supplied by CEA (considered as reference). The reference pebbles were prepared by the extrusion–spheronization–sintering process described in [10]. Table 1 reports some characteristics of the above described specimens. Moreover, we examined several well characterised pebble batches supplied by CRNL (Canada) and CCHEN (Chile).

About 0.2 g of each 'as received' pebbles were irradiated in the TRIGA reactor 'lazy Susan' rotating device (neutron flux $\sim 2 \times 10^{16}$ n/m^2/s, irradiation time $\sim$30 h). The irradiated specimens were tested out-of-pile for tritium release by exploiting a CREATE [11] equipment in the typical TPD mode, the resulting data are shown in Fig. 5 for the FN5 pebble-bed.

Two or three runs were performed for each specimen in order to check the test-reproducibility that was found to be very good (peaks overlap within ± 5°C $\cong 1$ min $\times \beta$). The reproducibility also compared favorable to the originally reported TPD peak [11] as obtained in near the same conditions on the same CRNL specimen.

Generally, a single peak (may be including several convoluted peaks) was observed for all the tested specimens under these conditions. Fig. 6 shows the TPD traces as 'normalized' to their peak value in order to show comparison with nominally identical irradiation conditions. As reported in Table 1, three characteristic temperatures were defined: T_t (ranging from 340°C to 400°C), T_m (from 450°C to 550°C) and T_f (from 600°C to

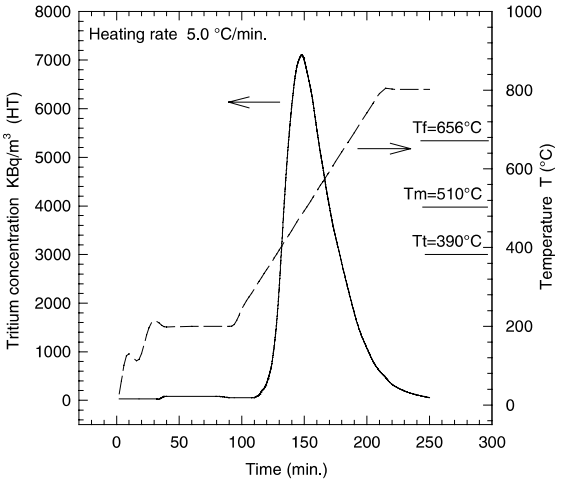


Fig. 5. Concentration of released tritium (left ordinate) in the R-gas purge during a typical temperature programmed run (right ordinate) on FN5 pebble bed.

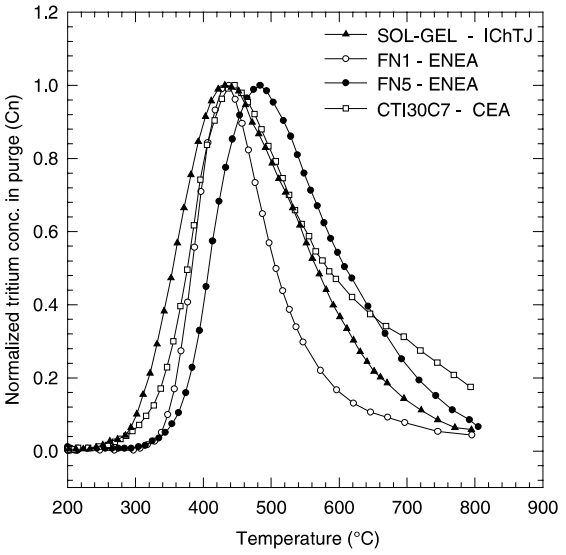


Fig. 6. Concentration of released tritium 'normalized' to the peak values (C_n) versus temperature for TPD runs in R-gas purge. Heating rate $\beta = 5$°C/min.

700°C) at which the fraction of the tritium removed resulted to be 5%, 50% and 90%, respectively.

A ranking criterion was developed in order to relate the pebble tritium release performances to characteristic temperatures and pebble characteristics. Pebble size (as varied from 0.01 to 2.5 mm) was not found to have a significant influence. T_t was found to depend on the lower value of the material grain size fraction, while not on density. CEA specimens CTI-30C7 and CTI15C7 (g.s. = 2–5 μm and density 93% TD) showed the lowest T_t. Hence, this material exhibits excellent tritium release at lowest temperature which assures the minimum allowed tritium inventory during HCPBB operation. T_f was found to depend mainly on density with grain size playing some role. The highly porous FN1 pebbles showed the narrower TPD single peak characterised with the lowest $T_f = 596$°C. Among the high density samples, those with the biggest grain size showed a slightly lower T_f, indicating the role of grain boundary surface on the total tritium removal. The T_m values were correlated to the pebbles grain size once the density was near the same. For high density fine grained CTI30C7(CEA), its T_m was slight lower (491°C) than the large grained samples FN5 ($T_m = 510$°C). However, these data cover a region in which the tritium inventory is negligible for the HCPBB design.

5. Conclusions

A new reprocessing 'citrate route' was investigated for Li_2TiO_3 pebbles yielding material which could be

re-fabricated at dimensions and density within HCPBB specifications. The performance of this pebble bed (ENEA specimen FN5) under irradiation is being tested in the EXOTIC-8 experiment [12]. A SOL–GEL process was tested using the same feed solution from the view of taking advantage of avoiding powder handling. However, this process necessitates a further optimization to get pebbles with the specified size and shape.

The out of pile TPD technique was used to study several 'as received' Li_2TiO_3 pebble beds for a rough evaluation of their tritium release performance. The resulting data was characterized by TPD peak shapes correlated to the material grain size, open porosity and density. Grain size exhibits the greatest influence. Tritium release rates are improved for the finest grained pebbles up to 50% of its total recovery; a 90% recovery value was reached at temperature slightly lower for the largest grained materials. Therefore, surface grain boundary extension certainly plays a role in the rate determining step tritium release. When decreasing the grain size, the lowest temperature limit for tritium release decreased. This correlation seems to be reversed at the high temperatures; however, at these higher temperatures tritium inventory is not significant.

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