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The reprocessing of advanced mixed lithium orthosilicate/metatitanate tritium breeder pebbles

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HIGHLIGHTS

- The recycling of advanced breeder pebbles without a deterioration of the material properties is possible using a melt-based process.
- The only accumulation of impurities upon reprocessing, results from the platinum crucible alloy used for processing.
- It is possible to replenish burnt-up lithium by additions of $LiOH{\cdot}H_2O$ to the melt during reprocessing.

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ABSTRACT

The recycling of tritium breeding materials will be necessary for any future use of nuclear fusion energy due to economical as well as ecological considerations. In the case of the solid breeder blanket concept, the ceramic pebble beds that are intended for the generation of tritium will eventually need to be restored due to depleted lithium levels as well as due to fractured pebbles, which will cause a deterioration of the pebble bed properties. It is proposed that the pebbles, which are fabricated using a melt-based process, are recycled using the same initial process, by replenishing the lithium levels and reforming the pebbles at the same time. To prove this recycling scheme, advanced ceramic pebbles were fabricated and then re-melted multiple times to prove that the reprocessing did not have any negative effect on the pebble properties and secondly, pebbles were produced with a simulated lithium burn-up and subsequently replenished by additions of LiOH to the melt. It was shown that the re-melting and lithium re-enrichment had no effect on the pebble properties, demonstrating that a melt-based process is suitable for recycling used breeder pebbles.

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1. Introduction

Lithium rich ceramic pebbles are to feature in the solid breeder blanket concepts in the wall of a fusion reactor [1]. During operation, a significant amount of the ^{6}Li will be burnt-up by transmuting to tritium (and helium), which is to be used as a fuel for the fusion reaction. In addition to this, because of the various thermal expansion forces and neutron irradiation, some pebbles may fracture during operation, causing a deterioration of the pebble bed quality. Fractured pebbles, for example, may cause the caking of the purge gas vents, resulting in the decline of the tritium extraction efficacy. Due to the vast amount of ^{6}Li-rich pebbles that is required for the production of tritium in future fusion reactors, it is imperative that a suitable recycling scheme is developed to minimise the costs and waste. Tritium breeding pebbles produced and reprocessed by a shaping and subsequent sintering process require an intricate solvent based recycling process to produce new pebbles [2–5].

If multiple usage cycles are envisioned for the ceramic breeder pebbles, which include a proposed operational period of 3 years, the cool-down period and the reprocessing step, it is crucial to make sure that there is no significant process related accumulation of impurities after each reprocessing cycle. Due to the fact that certain impurities will transmute to radioactive isotopes with exceptionally long half-lives, the length of the cool-down period may strongly be affected by a change in the composition [6,7]. Mukai et al. [7] calculated the activation for multiple reprocessing cycles of lithium orthosilicate with 30 mol% lithium metatitanate and could demon-

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strate that the cool-down period of about 18 years to reach the activation level for remote-handling-recycling (10 mSv/h) after the first use is only marginally increased to 22 years after 15 reprocessing cycles. Furthermore, the total amount of impurities caused by processing and transmutation after 15 cycles, i.e. 45 full power years (fpy) of irradiation, was found to be less than 0.5 wt.% compared to the initial amount of 0.13 wt.% [7].

However, if a direct reprocessing of used pebbles is envisaged and no chemical reprocessing step for the extraction of impurities is considered, it is important to keep in mind that besides the impurities introduced by the raw materials and the processing, or generated by transmutation, impurities may also be added to the material during use via contamination by structural materials that are in direct contact to the outer layer of the breeder pebble bed.

The present European tritium breeding reference material for the HCPB (Helium Cooled Pebble Bed) concept is lithium orthosilicate with an excess of silica, fabricated by a melt-spraying process [8]. Previously, it was already shown that lithium orthosilicate (Li_4SiO_4) pebbles, with a surplus weight of 2.5 wt.% SiO_2 added to the melt to form lithium metasilicate (Li_2SiO_3), could be successfully reprocessed while replenishing the lithium levels by additions of lithium hydroxide hydrate ($LiOH{\cdot}H_2O$) to the melt [9].

In comparison to melt-spraying, the fabrication process for lithium orthosilicate based pebbles has recently been modified in two major ways. Firstly, the pebbles are currently produced by melting the raw materials in a platinum alloy crucible and then ejecting the melt through a nozzle to form a jet [10]. Due to Plateau-Rayleigh instabilities, the jet breaks up into droplets, which are then solidified by cooling with a liquid nitrogen spray to form pebbles. Secondly, advanced lithium rich breeder pebbles are fabricated and consist of lithium orthosilicate with additions of lithium metatitanate (Li_2TiO_3) as a secondary phase (as no solid solutions of these phases seem to exist [11]). This measure gives rise to improved mechanical pebble properties while maintaining a high lithium density [11]. Preliminary tests also indicated that the change in composition of these advanced pebbles does not affect the radiation stability [12] or release characteristics [13].

The objective of this paper is to show the viability of re-melting as an efficient means for the reprocessing of advanced ceramic breeder pebbles and replenishing ^{6}Li levels without any deterioration of the pebble properties. As a demonstration for the re-melting of mixed lithium orthosilicate/lithium metatitanate pebbles, a batch of pebbles with 20 mol% lithium metatitanate (20LMT) was produced and subsequently re-melted five times. For the reprocessing test, a composition that is expected after 3 years in the reactor wall was produced; namely a 15% burn-up of an initial enrichment of 50% ^{6}Li. This material was then re-enriched by additions of a corresponding amount of $LiOH{\cdot}H_2O$ during production to regain the intended composition.

2. Experimental

2.1. Multiple Re-melting

A batch of approximately 400 g of pebbles consisting of lithium orthosilicate with 20 mol% lithium metatitanate (LOS/20LMT) was fabricated using the melt-based process [10]. The starting powders SiO_2 (Alfa Aesar 99.8%, metal basis), TiO_2 (Alfa Aesar 99.8%, metal basis) and ultra-pure $LiOH{\cdot}H_2O$ (Alfa Aesar 99.995%, metal basis) were thoroughly mixed and then filled into a large platinum alloy crucible. Although pebbles to be used in fusion reactors will need to be enriched with ^{6}Li, the isotope ratio does not have an effect on either the production process or the pebble properties. Therefore, due to the substantial increase in the price for ^{6}Li enriched lithium substances, standard $LiOH{\cdot}H_2O$ with a naturally occurring 7.5 at.% ^{6}Li was used for the experiments. The powders were weighed out and reacted together at approximately 1300 °C to form a melt according to the following equation:

$$18LiOH \cdot H_2O + 4SiO_2 + TiO_2 \rightarrow 4Li_4SiO_4 + Li_2TiO_3 + 27H_2O \qquad (1)$$

A controlled pressure was then applied to the crucible, forcing the melt through a 300 μm diameter nozzle to form a liquid laminar jet. As the surface Plateau-Rayleigh instabilities increased, the jet broke into droplets which were then solidified below the oven in a cooling tower using liquid nitrogen. Approximately 400 g of pebbles were produced during the process which were then collected and stored in a dry atmosphere, after which a sufficient quantity was removed for characterisation.

The remaining pebbles were then refilled into the crucible and processed using the same parameters as the initial batch. Again, after this batch, a sample was taken for characterisation and the remaining pebbles were reprocessed. This was repeated until the initial batch had been re-melted a total of five times. Due to a nozzle malfunction during the last re-melting cycle, it was not possible to form a proper jet and hence the physical characteristics of the produced pebbles are not comparable. However, the nozzle malfunction is not expected to have had an effect on the chemical composition of the produced ceramics.

A series of analysis methods were used to characterise the pebbles. The concentrations of the main constituents and a total of 57 impurities were measured for each batch using inductively coupled plasma – optical emission spectroscopy (ICP-OES). The investigated elements included many common impurities found in raw materials such as Al, Ca, Na, K and Fe. Cobalt was additionally measured using inductively coupled plasma – mass spectroscopy (ICP-MS) as even the lowest ICP-OES detectable amount of cobalt will significantly affect the cool-down period for recycling [6,7,14]. ICP-MS analysis of the raw materials, determined that cobalt originated predominantly from the TiO_2 starting powder; however, traces were also found in the SiO_2. Lithium levels were measured using ICP-OES, while silicon and titanium levels were measured using X-Ray Fluorescence Spectroscopy (XRF).

In addition to the chemical analysis, physical characterisation was also performed. In order to establish the mechanical strength of the pebbles, a Zwick-Roell UTS electro-mechanical testing system was used. 40 mono-sized pebbles were measured individually by determining how much force was required to crush the pebbles and the average was calculated. This was performed for pebbles from each batch for both 500 and 1000 μm diameters.

The He-density was determined using He-pycnometry (Porotec, Pycnomatic ATC) and knowing the theoretical density of the material, it was possible to calculate the closed porosity. The pebble microstructure was examined using a scanning electron microscope (Zeiss, Supra 55) on etched cross-sections.

2.2. Re-enrichment

To prove the ability to re-enrich LOS/20LMT breeder pebbles with lithium, a batch of pebbles with a lithium deficit was produced. A schematic representation of the reprocessing cycle is shown in Fig. 1. It is assumed that after 3 fpy operation in the reactor wall, the pebbles (with an assumed enrichment of 50% ^{6}Li) will experience a ^{6}Li burn-up of 15%. This meant that the pebbles would need to have the equivalent composition as LOS/20LMT pebbles with 7.5% of the lithium removed. This resulted in a theoretical lithium content of 20.3 wt.% and in the following composition for the pebbles:

- 66.5 mol% Li_4SiO_4
- 20.0 mol% Li_2TiO_3
- 13.5 mol% Li_2SiO_3

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