



# Reduction of impurities and activation of lithium orthosilicate breeder materials

Regina Knitter<sup>a,\*</sup>, Ulrich Fischer<sup>b</sup>, Stefan Herber<sup>b</sup>, Christel Adelhelm<sup>a</sup>

<sup>a</sup>Institute for Materials Research, Forschungszentrum Karlsruhe GmbH, Postfach 3640, D-76021 Karlsruhe, Germany

<sup>b</sup>Institute for Reactor Safety, Forschungszentrum Karlsruhe GmbH, Postfach 3640, D-76021 Karlsruhe, Germany

## A B S T R A C T

The fabrication of lithium orthosilicate pebbles by melt-spraying enables a facile reprocessing of irradiated material by direct remelting. However, the necessary waiting period for the reprocessing is determined by the long-term activation of the material under irradiation that is dominated by the impurities. The activation characteristics for the current composition of lithium orthosilicate pebbles were assessed on the basis of three-dimensional activation calculations for a fusion power reactor. The calculations were used to identify critical amounts of impurities and were compared to the results of a hypothetical, pure material without impurities, as well as to a calculated Li-6 enriched OSi composition.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Slightly hyperstoichiometric lithium orthosilicate (OSi) is one of two lithiated ceramics that have been chosen as possible tritium breeders for the European Helium Cooled Pebble Bed (HCPB) blanket [1]. For the application of these breeder materials in future fusion technology, the recycling is an important issue due to the high costs of Li-6-enriched materials as well as waste considerations. For lithium orthosilicate ( $\text{Li}_4\text{SiO}_4$ ) pebbles, fabricated by a melt-spraying process, the direct remelting without any additional wet-chemical recycling step has been proposed as a facile reprocessing process [2]. However, the amount of impurities in solid breeders dominates the activation under neutron irradiation and also determines the necessary waiting period for the reprocessing. In previous activation calculations for OSi pebbles Co- and Al-impurities were identified as dominant for the long-term activation [3]. According to these calculations, a waiting period of 50–100 years should be sufficient for hands-on recycling of lithium orthosilicate pebbles.

In the melt-spraying process for OSi pebbles the Pt-crucible is supposed to be the only source of contamination. Therefore, the amount of impurities of the final product, besides Pt, only depends on the impurities of the raw materials. Currently  $\text{LiOH} \cdot \text{H}_2\text{O}$  and  $\text{SiO}_2$  are used as raw materials for the fabrication of OSi pebbles [4]. Thereby the impurities could be reduced compared to formerly produced pebbles, so that a decreased waiting period for recycling was expected for the new material. Taking into account that ceramic breeder materials have to be enriched in Li-6 to ensure a sufficient tritium yield in a fusion reactor, other raw materials were investigated to further decrease the impurities of  $\text{Li}_4\text{SiO}_4$  pebbles.

In the present study the activation characteristics for different OSi compositions were assessed to identify critical amounts of impurities.

## 2. Experimental

### 2.1. Materials and methods

The impurities of the current OSi pebbles with an excess of 2.5 wt%  $\text{SiO}_2$  were measured by ICP-OES (inductively coupled plasma – optical emission spectrometry) after digestion in acids. The calibration solutions matched the sample solutions concerning acid and main compound concentration. The values given in Table 1 either represent conservatively estimated maximum values of different batches produced in the recent past, or the determination limits of chemical analysis. With the exception of Pt, all impurities were converted to stable oxides, and normalised Li, Si and O contents were then calculated according to the theoretical values, because the Li/Si ratio of the pebbles is slightly varying from batch to batch [2].

While a variety of  $\text{SiO}_2$  powders and natural enriched Li-containing raw materials with different grades of purity are commercially obtainable, the availability of Li-6-enriched components is rather limited. The only Li-6 component available was metallic lithium with an enrichment of 95.4% (Cambridge Isotope Laboratories, USA, delivered by Euriso-Top, France). As a presumably very pure  $\text{SiO}_2$  powder Aeroperl 300 Pharma (Degussa, Germany) was chosen, a granulated Aerosil powder for pharmaceutical applications. The chemical analyses of these materials exhibit very low impurities of Al and Co, but partly quite high contents of alkali and earth alkali elements (Table 2). Based on these analyses, a composition of Li-6 OSi was calculated (Table 1). The impurities were calculated according to amounts of raw materials necessary

\* Corresponding author.

E-mail address: [regina.knitter@imf.fzk.de](mailto:regina.knitter@imf.fzk.de) (R. Knitter).

**Table 1**  
Composition of different lithium orthosilicate materials used for the calculation of activation.

Element	Pure OSi (hypothetical composition) (wt%)	OSi Pebbles (impurities from chemical analysis) (wt%)	Li-6 OSi (calculated from Li-6 and SiO <sub>2</sub> ) (wt%)	Former OSi (from [3]) (wt%)
Li	22.587	22.4985	22.493623	22.345
Si	24.017	23.9231	23.917848	24.179
O	53.396	53.4585	53.451869	53.302
C	–	0.1000	0.100000 <sup>a</sup>	0.113
Al	–	0.0030	0.000312	0.006
Ba	–	0.0001	0.000016	n.a.
Ca	–	0.0020	0.004825	0.0037
Co	–	<0.0001	0.000074	0.0004
Cr	–	<0.0001	0.000097	0.003
Cu	–	<0.0001	0.000467	0.0003
Fe	–	0.0004	0.005034	0.0106
K	–	0.0010	0.006924	0.0041
Mg	–	0.0002	0.001760	0.0020
Mn	–	<0.00002	0.000016	0.00025
Na	–	0.0020	0.005750	0.0020
Ni	–	<0.0002	0.000148	0.001
Pt	–	0.0090	0.009000 <sup>a</sup>	n.a.
Sr	–	0.000025	0.000030	n.a.
Ti	–	0.0004	0.001758	0.0206
Zn	–	0.0002	0.000372	0.0006
Zr	–	0.0010	0.000074	0.0066

Determination limits (double detection limits) are indicated by '<'.  
<sup>a</sup> Values of OSi pebbles are used.

**Table 2**  
Chemical analysis of the impurities of Li-6 metal and SiO<sub>2</sub>.

Element	Li-6 metal (95.4% <sup>6</sup> Li) (μg/g)	SiO <sub>2</sub> (Aeroperl 300 Pharma) (μg/g)
C	n.a.	90
Al	<7	<3
Ba	<0.5	<0.1
Ca	107	47
Co	<1	<1
Cr	<2	<1
Cu	18.4	<1
Fe	4.5	96
K	302	<2
Mg	64	6.3
Mn	<0.5	<0.1
Na	205	22
Ni	<2	<2
Pt	<5	<5
Sr	1	0.15
Ti	<0.5	34
Zn	14	<1
Zr	<1	<1

Determination limits are indicated by '<'.  
<sup>a</sup> Values of OSi pebbles are used.

to form hyperstoichiometric Li<sub>4</sub>SiO<sub>4</sub>, while for C and Pt the actual values detected for OSi pebbles were used. (C-impurities are mainly due to the absorption of CO<sub>2</sub> after fabrication, Pt is mainly caused by the crucible.) The main constituents were calculated as in case of the OSi pebbles.

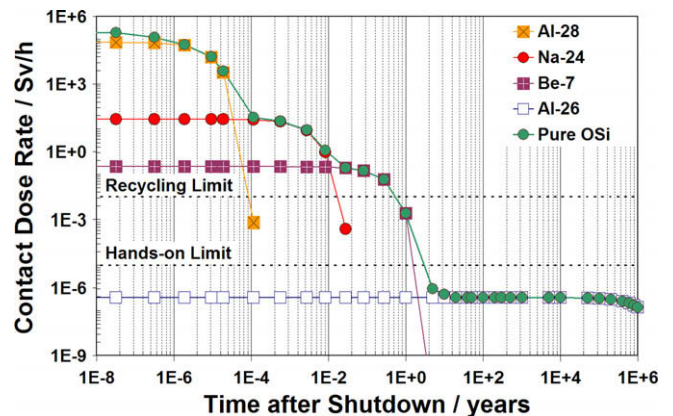
## 2.2. Calculations of activation

The activation of different OSi materials was calculated for a thin front layer in the central outboard blanket module of a fusion power reactor based on the HCPB blanket concept, i.e. the material was considered to be subjected to the highest radiation level. The assumed fusion power amounts to 3300 MW. The neutron spectrum was calculated by a 3D Monte Carlo calculation with the MCNP5 code [5] in a 175 energy group structure. The total flux calculated by MCNP is at  $8.86 \times 10^{14}$  n/s cm<sup>2</sup>. The activation calculations were performed with the FISPACT inventory code [6] using

EAF-2007 activation data [7] and the neutron flux spectrum provided by the MCNP calculation. It was assumed that 1 kg Li<sub>4</sub>SiO<sub>4</sub> as pebble bed with a bulk density of 1.51 g/cm<sup>3</sup> is irradiated over one full power year (1 fpy). A natural isotope composition was assumed for lithium, because the contribution to the dose rate is almost independent of the isotope composition. The contact dose rate (CDR) depending on the time after shutdown was assessed for a hypothetical, pure OSi without impurities, for the current OSi pebble composition, as well as for the calculated composition of Li-6 OSi. For better comparison, the activation of former OSi pebbles with the composition given in [3] was recalculated for the irradiation conditions mentioned above.

## 3. Results and discussion

During neutron irradiation of Li<sub>4</sub>SiO<sub>4</sub> not only the transmutation of Li to T and He takes place, but other isotopes are formed as well. Fig. 1 displays the CDR versus time after shutdown for pure OSi, which mainly results from the production of Al-28, Na-24, Be-



**Fig. 1.** Contact dose rate versus time after shutdown of pure OSi without impurities, and the main contributors Al-28, Na-24, Be-7, and Al-26 (from top to bottom).

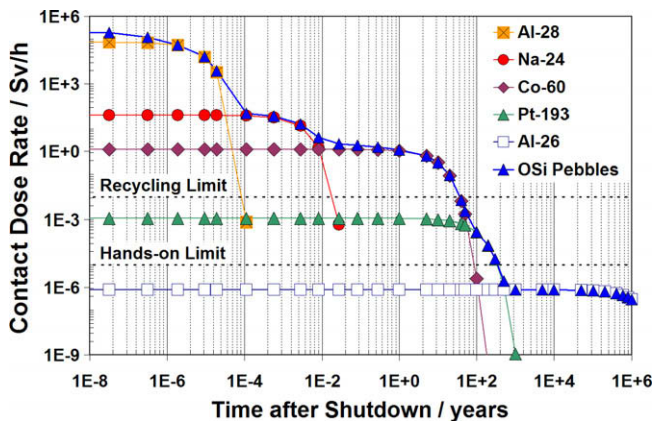


Fig. 2. Contact dose rate versus time after shutdown of current OSi pebbles, and the main contributors Al-28, Na-24, Co-60, Pt-193, and Al-26 (from top to bottom).

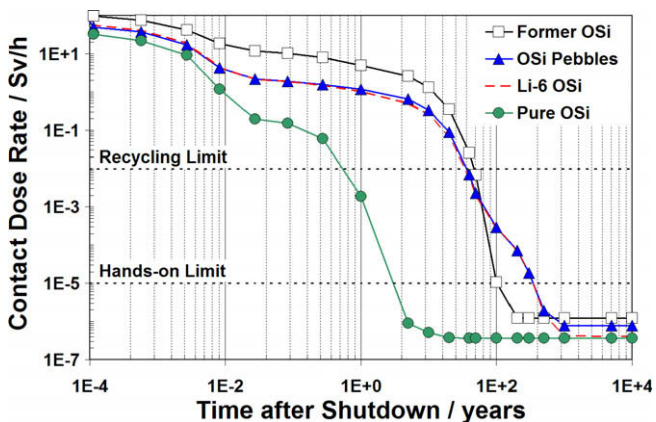


Fig. 3. Comparison of contact dose rates of former and current OSi pebbles, of Li-6 OSi, and of pure OSi.

7, and Al-26. Due to the activity of Be-7, the recycling limit for remote handling (10 mSv/h) and the hands-on limit (10  $\mu$ Sv/h) are reached after <1 and <4 years, respectively.

For the current OSi pebbles these limits are achieved after significantly longer times (Fig. 2). While there is no considerable difference in the activation during the first day ( $\sim 3 \times 10^{-3}$  years), the activation for up to 50 years is dominated by Co-60 originating from the assumed 1  $\mu$ g/g Co-59 in the OSi pebbles, which is the determination limit in the current chemical analysis. The recycling limit is therefore only reached after nearly 40 years. After this time the CDR is dominated by Pt-193 that is responsible for reaching the hands-on limit after almost 400 years.

In Fig. 3 the CDR of pure OSi and OSi pebbles are compared to the results gained for Li-6 OSi and the recalculated former OSi pebbles. In the time up to 1 day the activation is dominated by Na-24. As the matrix effect of Na-24 is about 58%, due to the activation of Si-28, and only 42% of its activation is caused by Na-impurities, the higher Na-content in Li-6 OSi has no considerable influence on the total CDR. Additionally, Na-24 originates from Al-27, so that the lower Al-content in Li-6 OSi somewhat compensates the effect of the higher amount of Na-impurities. The slightly lower Co-content in Li-6 OSi also has no significant effect on the CDR, and the

waiting period for remote handling is barely changed compared to the current OSi pebbles. The hands-on limit is also reached after the same time, as the same Pt-content was assumed for Li-6 OSi. The activity of Al-26, dominant at very long times, depends besides the matrix effect also on the Al-content in the material. The CDR of Li-6 OSi at times  $>10^3$  years is therefore smaller than in case of the current OSi pebbles, but both are well below the hands-on limit. The CDR of the former OSi material recalculated from [3] displays a different behaviour. Because of the higher Co-content of 4  $\mu$ g/g, the limit for remote recycling is only reached after about 50 years. The most significant difference, however, is due to the fact that Pt-impurities were not considered in the former composition. This is why the limit for hands-on recycling is *apparently* reached after shorter times of 100 years. The higher amount of Al-impurities leads in this case to a notably higher activation at times  $>200$  years that is yet below the hands-on limit.

#### 4. Conclusions

The contact dose rates of different  $\text{Li}_4\text{SiO}_4$  materials were assessed for the highest radiation level in a fusion power reactor for 1 fpy. The activation of OSi is strongly influenced by impurities. Compared to former OSi pebbles, the reduced amount of Co in the current OSi pebbles leads to a decrease of the waiting period for remote recycling from 50 to less than 40 years. It has to be emphasized, however, that 1  $\mu$ g/g Co is the determination limit in the current chemical analysis by ICP-OES. That also means that no definitive statement can be made for the waiting period for remote recycling, and the current limit of detection may lead to an over-prediction of activity [8]. The reduced Al-content results in a lower activation at times  $>10^3$  years, but as for both materials the value is below the hands-on limit, no significant improvement for the recycling is accomplished. The activation of the calculated Li-6 enriched OSi exhibits no relevant differences to the current OSi pebbles.

The most significant result of the present study is the activation of OSi by – formerly neglected – Pt-impurities. It was shown that due to these impurities the waiting period for hands-on recycling is considerably increased from about 100 to almost 400 years. The study reveals that the activation of breeder materials is very sensitive to the smallest amounts of impurities. For reliable statements on the waiting period for recycling, the impurities of the raw materials, and all possible contaminations by processing or handling have very carefully to be considered.

#### References

- [1] L. Giancarli, V. Chuyanov, M. Abdou, M. Akiba, B.G. Hong, R. Lässer, C. Pan, Y. Strebkov, J. Nucl. Mater. 367–370 (2007) 1271.
- [2] R. Knitter, B. Löbbecke, J. Nucl. Mater. 361 (2007) 104.
- [3] U. Fischer, H. Tsige-Tamirat, J. Nucl. Mater. 307–311 (2002) 798.
- [4] R. Knitter, G. Piazza, J. Reimann, P. Risthaus, L.V. Boccaccini, in: M. Enoeda (Ed.), Proceeding of the 11th International Workshop on Ceramic Breeder Blanket Interactions, Japan Atomic Energy Research Institute, 2004, p. 108.
- [5] X-5 Monte Carlo Team, MCNP – A general Monte Carlo N-particle Transport Code, Version 5, LA-UR-03-1987, 2003.
- [6] R.A. Forrest, FISPACT 2007: User Manual, UKAEA Fusion, Report UKAEA FUS 534, 2007.
- [7] R.A. Forrest, J. Kopecky, J.-Ch. Sublet, The European Activation File: EAF-2007 Neutron-induced Cross Section Library, UKAEA Fusion, Report UKAEA FUS 535, 2007.
- [8] M. Zucchetti, L.A. El-Guebaly, R.A. Forrest, T.D. Marshall, N.P. Taylor, K. Tobita, J. Nucl. Mater. 367–370 (2007) 1355.