ELSEVIER

Journal of Nuclear Materials 283–287 (2000) 99–109

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Ceramic breeder research and development: progress and focus

J.G. van der Laan [a,*], H. Kawamura [b], N. Roux [c], D. Yamaki [d]

[a] NRG Petten, P.O. Box 25, 1755 ZG Petten, The Netherlands
[b] JAERI-Oarai, Japan
[c] CEA Saclay, France
[d] JAERI-Tokai, Japan

Abstract

The world-wide efforts on ceramic breeder materials in the last two years concerned Li_2O, Li_4SiO_4, Li_2TiO_3 and Li_2ZrO_3, with a clear emphasis on the development of Li_2TiO_3. Pebble-manufacturing processes have been developed up to a 10 kg scale. Characterisation of materials has advanced. A jump-wise progress is observed in the characterisation of pebble-beds, in particular of their thermo-mechanical behaviour. Thermal property data are still limited. A number of breeder materials have been or are being irradiated in material test reactors like HFR and JMTR. The EXOTIC-8 series of in-pile experiments is a major source of tritium release data. This paper discusses the technical advancements and proposes a focus for further research and development (R&D) : pebble-bed mechanical and thermal behaviour and its interactions with the blanket structure as a function of temperature, burn-up, irradiation dose and time; tritium release and retention properties; determination of the key factors limiting blanket life.

1. Introduction

A number of ceramic breeder materials are being investigated for fusion blanket application. The status of research and development (R&D) was most recently summarised by Roux et al. [1] and Johnson et al. [2]. This paper is therefore mainly devoted to new results published or presented since ICFRM-8. The main events for information exchange have been the 20th Symposium on Fusion Technology (SOFT), held in Marseille, September 1998 [3]; the IEA Workshop on Ceramic Breeder Blanket Interactions (CBBI-7), held in Petten, September 1998 [4], and most recently the International Symposium on Fusion Nuclear Technology (ISFNT-5) in Rome, September 1999, and the CBBI-8 Workshop in Colorado Springs, October 1999. The world-wide efforts in the past two years concerned lithium oxide, -orthosilicate, -metatitanate and -metazirconates; however, most of the technological work has clearly been devoted to the development and characterisation of lithium metatitanates. Throughout this paper the materials will be denoted by the chemical formulae, although mostly compositions substoichiometric in lithium are used in practice.

2. Developments in fabrication technologies

The development of breeder fabrication technology has been exclusively devoted to manufacturing processes for pebbles, since most solid breeder blanket designs are based on pebble-beds. Table 1 summarises the fabrication methods and results for the breeder materials of current interest.

Wet processing routes have been applied by Tsuchiya et al. [5–8] and Alvani et al. [9]. Tsuchiya et al. developed with NFI sol–gel type processes to produce 1 mm Li_2O [5] and 1.5 mm Li_2TiO_3 pebbles [6,7]. After sintering densities of 80–85% TD (theoretical density) were obtained. Tsuchiya et al. [8] improved the process of dropping gel spheres in a cold bath by introducing a vibratory dropping system. It was demonstrated that in

* Corresponding author. Tel.: +31-224 56 4744; fax: +31-224 56 1883.
E-mail address: vanderlaan@nrg-nl.com (J.G. van der Laan).

0022-3115/00/$ - see front matter
PII: S 0 0 2 2 - 3 1 1 5 (0 0) 0 0 3 5 2 - 4

Table 1
Recent developments in fabrication of ceramic breeder pebbles

Party	Group	Materials	Fabrication process	Diameter (mm)	Density (% TD)	Grain size (μm)
Japan	JAERI	Li_2O	Melting granulation	~1.0	80–85	50
		Li_2TiO_3	Rotating granulation	~1.0	80–85	~5
			Wet method – dehydration	0.5–3.0	80–90	5–20
			Wet method and TiO_2 addition	0.5–3.0	80–93	5–25
			Wet method – substitution	0.2–0.3	93	15
EU	CEA	Li_2ZrO_3	Extrude/spheronization	0.8–1.2	~86	1–1.5
		Li_2TiO_3	Agglomeration	0.6–1.0	89–90	1–2.5
		Li_2TiO_3	Extrusion/spheronization	0.8–1.5	90–94	1–2
	FZK	Li_4SiO_4	Melting/spraying	0.25–0.63	~98	5–15
	ENEA	Li_2TiO_3	Wet Methods	0.2–1.0	~90	3–20
China	SWIP	γ-$LiAlO_2$	Rotation technique	1–4	70–80	
		Li_2ZrO_3	Sol–gel and solid state methods	1–5	60–80	
Chile	CCHEN	Li_2TiO_3	Extrusion/spheronization	2.1	60	3–4
Russia	VNIINM	γ-$LiAlO_2$, Li_2SiO_3, Li_4SiO_4		1–4	80–90	

this way smaller pebbles could be obtained with typical diameters of 1 mm and sphericity better than 1.1. The process is considered to comply with mass fabrication requirements [10]. Stoichiometric MTi pebbles were produced with densities of about 80% TD and grain size over 20 μm after sintering for 4 h at 1300°C.

Alvani et al. [9] tried three different 'wet' routes. By investigating the possibility of setting up a real 'sol–gel' procedure for the preparation of Li_2TiO_3, the wet Ti-peroxo-complexes chemistry have shown the most promising results to date taking into account its applicability to future reprocessing of breeder material. Among the different wet-routes, 'dewatering' and 'acetate-gel' are yet in their initial stage of investigation. The promising results of the resin-forming 'citrate' route has encouraged efforts on optimising the process parameters leading to the preparation of dense pebbles on lab-scale. Several hundred grams of stoichiometric metatitanate ('FN5') pebbles have been produced. A density of about 90% TD is reached after sintering at 1100°C for 2 h. The diameter ranges from 0.2 to 1 mm and grain size from 3 to 20 μm.

The extrusion-spherodisation process has been further developed by Lulewicz et al. in close collaboration with industry [11,12]. The method has been used to fabricate Li_2ZrO_3 and Li_2TiO_3 pebbles (substoichiometric in lithium), typically 0.8–1.2 mm in diameter. Li_2ZrO_3 pebbles were produced with 86% TD and 1 μm grain size. Li_2TiO_3 pebbles had 93% TD and 1–2 μm grains. Current optimisation steps concern the minimisation of closed porosity and grain size by lowering the sintering temperature. Considering the first results of in-pile tritium release (discussed in Section 4) a little lower density of about 90% TD has been set to guide further development.

Tsuchiya et al. [13] performed an experimental study with gamma-aluminate fabricated from starting material with lithium originating either from ore or from seawater. In the latter case much higher concentrations of Ca, Na and Fe were found, but this did not affect any of the basic physical properties.

Breeder material development work in China has been reported by Qiang [14]. It concerns production of pebbles of $LiAlO_2$ by a rotating melting method, as well as Li_2ZrO_3 by sol–gel and solid state reaction methods. In both cases pebbles of 1–4 mm were obtained with densities up to 80% TD. Davydev et al. [15] have reported on breeder R&D in Russia. γ-$LiAlO_2$, Li_2SiO_3, Li_4SiO_4 pebbles have been produced with 1–4 mm diameter and 80–90% TD.

Munakata et al. [16] have explored catalyst additives like Pd and Pt to enhance the tritium release rate of Li_4SiO_4 at lower temperatures. Tritium doping of samples has been performed at the Kyoto University reactor with subsequent T-release using stepwise isothermal desorption [17]. They have found that the isotope exchange reactions between molecular protium and gaseous pre-deuterated water were much faster than that over non-catalytic $LiAlO_2$, Li_2ZrO_3 and Li_4SiO_4, even at temperatures as low as 300°C.

Tellurium doping of Li_4SiO_4 as proposed by Dalle Donne et al. [18] appeared to be unstable at high temperature in a reducing atmosphere (reference purge gas) [19]. Tritium release characteristics were obtained in EXOTIC-8/4 and appeared to be practically identical to the undoped Li_4SiO_4 up to 1.4% total Li-burnup [20].

3. Characterisation

3.1. Base properties (pebbles)

Several properties of breeder materials are considered of primary relevance, either in view of the application or as a characterisation means during the material development stage. Some of the properties are more or less fixed while others may be influenced by specific treatments and enable material optimisation. Basic characteristics for ceramic breeder pebbles are size, shape, density and porosity, microstructure and grain-size. Size and shape are clearly determined by the basic shaping and forming processes during manufacturing. Generally speaking a smaller size and a spherical shape of the pebbles enables higher bed packing factors (for mono-sized beds). The bed packing factor and the actual pebble density jointly form the so-called smear density which is the engineering quantity that determines the achievable Li-densities.

On the more microscopic level, pebbles are characterised by microstructural features like pore size and shape, grain size, phase composition and homogeneity. Mercury porosimetry is applied to batches of pebbles, but some particular measuring difficulties arise due to inter-pebble porosity. In most cases pebble densities are derived from cross-sectional micrographs along with pebble dimensions. It is clear that for materials produced with a sintering step a variety of densities are achievable. In manufacturing lithium metatitanate pebbles, sintering temperatures are quoted from 950°C to 1400°C. A particular means of improving the microstructural stability is the use of compositions that are substoichiometric in lithium [11,12]. During material development the fracture strength of single pebbles is typically measured (requiring of course statistical treatments) as well as thermal shock tests.

Piazza et al. [21,22] investigated the ageing behaviour of Li_4SiO_4, Li_2TiO_3 (pebbles by agglomeration) and Li_2ZrO_3 (pebbles by extrusion), candidates for the Helium-cooled Pebble-Bed (HCPB) blanket concept being developed in Europe. Specimens received different pretreatments and were then held at 970°C in the reference purge gas environment for three months. Crush load tests and chemical analyses were performed at several intervals. Some degradation of mechanical properties was found for all materials during the test period. Some grain growth and densification was observed for the Li_2TiO_3 and Li_2ZrO_3. Uniaxial compression tests (see Section 3.2) after 96 days of annealing did not show significant differences for any of the three ceramic materials [22].

Yamawaki et al. [51,52] reported on the vaporisation behaviour of Li-containing oxides as studied by high temperature mass spectrometry using a Knudsen-cell. The partial pressures were measured for Li_4SiO_4, $LiAlO_2$, Li_2TiO_3, Li_2ZrO_3 and Li_2O by means of atmosphere controlled high temperature mass spectrometry. The enhancement of Li vaporisation and the formation of LiOD as a result of deuterium addition were confirmed. From the results of vapour pressure measurement, the summation of the partial pressures of lithium containing species were calculated. As far as the lithium loss is concerned, it has been established that $LiAlO_2$ is best, Li_2O is worst. Li_2TiO_3, Li_4SiO_4 and Li_2ZrO_3 showed small differences with Li_2TiO_3 and Li_2ZrO_3 being the best and the worst, respectively, among these three at 1000 K.

Casadio et al. [19,23] studied the effect of pebble microstructure and exposure temperature-time on Li_4SiO_4 – moisture interactions. Te-doped large grained pebbles were compared with undoped small grained material. The adsorption and desorption of water vapour from Li_4SiO_4 pebbles exposed to a moist He purge have been examined. Above 650°C, the adsorption/desorption process was found to be independent of material microstructure and material composition. The process could be described as simple dissociative water solubility that appears to follow Henry's law. Thermodynamic analysis showed the system to exihibit positive deviation from ideal behaviour, yielding an activity coefficient for dissolved LiOH of $\sim 10^3$. Below 650°C, segregation of water vapour at grain boundary interfaces was observed to contribute to the equilibrium water concentration; the water concentration decreased with increasing grain size and decreasing temperature. Large grain Te-doped pebbles showed lower water segregation and faster water transport than pure Li_4SiO_4 pebbles with smaller grain sizes (larger grain boundary interface).

Tritium release properties can be well determined from pebble batches. Often specimens are irradiated in a thermal neutron flux for a short time. The tritium produced is subsequently removed by controlled means like isothermal or ramp annealing. Both temperature programmed and isothermal desorption studies have been performed [17,19,23–26].

Casadio et al. [24] reported on out-of-pile tritium annealing studies on a variety of Li_2TiO_3 pebbles. Temperature programmed desorption (TPD) measurements revealed that tritium was released at lower temperatures as HTO. Results suggest that both density and grain size are key parameters determining tritium release rates. The main TPD spectra characteristics (threshold, maximum and decay temperatures) were found to be selectively correlated to the material grain size distribution, open porosity and density. For dense pebbles with low open porosity (above 85% TD), grain size plays a main role in tritium release rate, which is increased by decreasing grain size and consequently increasing grain boundary interface. The titanate pebbles obtained by the extrusion method [11] were found to perform well against TPD criteria in spite of their high density. Peña et al. [25] performed out-of-pile isothermal annealing tests on a similar variety of Li_2TiO_3 pebbles.

It is possible to derive physico-chemical quantities from annealing tests like activation energies. However, in-pile tests under more representative conditions – like temperature, purge gas environment, neutron fluences and lithium burn-up – are required to obtain data on radiation effects.

3.2. Properties of pebble-beds

A definite highlight of the recent breeder R&D is the testing of the thermo-mechanical properties of pebble-beds by Reimann et al. [27–30]. The basic principle is the compression of a ceramic pebble-bed at various temperatures, pressure levels and loading patterns. The main features of the observed pebble-bed behaviour are non-linear elasticity, partially irreversible deformation due to compaction and creep effects. Uniaxial compression tests have been performed with different materials in a temperature range from ambient to 700°C, and for orthosilicate up to 900°C [27,28]. Correlation's for the uniaxial moduli of deformation were established both for the first pressure increase and decrease. In a first stage they were to be considered temperature independent [29], in a second stage this was revised when more data became available [30]. The non-linear elasticity has been explained by Bühler [31], using modifications of previous models based on Hertz theory.

A general observation by Reimann et al. [27–30] is that a higher packing density of the pebble-bed results in a much stiffer behaviour. Such higher packing density is achievable when the pebble-surfaces are smooth. By sieving specific pebble size fractions, it was also shown that a pebble-bed with smaller pebbles is much stiffer than the one with larger pebbles. A so-called binary-bed also results in a higher deformation modulus, but this appears to depend very much on the actual filling fractions and procedures, as has been shown by Reimann et al. [29] for binary beds of beryllium pebbles. Creep data have been obtained for a number of material, temperature and pressure combinations.

A number of results have been obtained on thermal properties of pebble-beds [32–34]. Piazza et al. [32] measured heat transfer properties in a set-up with a cylindrical pebble-bed (51 mm outer diameter (OD), 16 mm inner diameter (ID) and 53 cm height) and a central axial heating rod. Data were derived for a temperature range from 70°C to 815°C, and fitted to give an effective thermal conductivity and heat transfer coefficient. The test also showed a slightly higher conductivity after a longer heating time, which was found to be attributable to local agglomeration caused by sintering of the pebbles. The data showed fair consistency with the so-called Schluender correlation [32]. No pressure dependence on conductivity was found for helium pressures of 1–3 bar.

Sato et al. [33] and Enoeda et al. [34] applied the hot wire method to a number of breeder materials. Unfortunately, the data obtained by these two methods cannot be compared directly, since the data analyses have a different treatment of the heat transfer at the bed-wall interface. Further results from a round robin exchange of specimens are necessary to arrive at a consistent data set. Such data are needed for blanket design purposes and for experiment design and data analyses.

All data on the present day pebbles have been obtained under conditions of low or unknown mechanical constraints. The effects of high pressures and pebble-contact deformation have not yet been systematically examined.

4. Irradiation performance

A number of irradiation experiments have been performed or are still running [35–40]. All these experiments are in-pile tests, and have on-line monitoring of the purge gas exit lines for tritium release. A main feature of in-pile tests is the possibility to derive the specimen's tritium release characteristics from temperature transients. A further value is that the tritium inventory, which is specific for the end-of-irradiation condition, can be determined from post-irradiation examinations (PIE). With the objective of providing input data for the design of an ITER breeding blanket, Van der Laan et al. [35] have reviewed various data analysis methods. A consistent analysis of tritium release properties has been developed and applied to all available European data on pebbles and pellets of Li_4SiO_4, Li_2TiO_3 and Li_2ZrO_3. These data have been obtained mainly in EXOTIC-6, 7 and 8 and some in TRIDEX and LISA. They comprise both in-pile and post-irradiation results for the reference purge gas helium +0.1% H_2. The data compilation includes tentative correlation's for design purposes of the type $\tau = 10^{A+B*1000/T}$, where τ is the tritium residence time, T the (local) breeder temperature and A and B are material dependent quantities [35,36]. The EXOTIC-8 series in the HFR at Petten started June 1997, and a number of six irradiations have been completed, while four additional ones are running. The high burnup (BU) experiments E-8/7 (Li_2TiO_3) and E-8/8 (Li_4SiO_4) have been extended to new targets of 15% and 10% total lithium burnup, respectively, following new HCPB parameters [20]. The EU database has since expanded:

- Li_4SiO_4: data up to 3% BU; larger BU (10%) only for small pebbles (0.1–0.2 mm). The 1-day residence time is about 400°C; new data for 0.25–0.63 mm pebbles are being obtained in EXOTIC-8 up to 3% and 10% BU.

- Li_2TiO_3 [59]: data for pebbles are up to 2% BU (agglomeration method), 2% BU (extrusion method, density 93% TD); about 15% BU will be reached in EXOTIC-8 for pebbles produced by the agglomeration method; 1.4% BU has been achieved with 80% TD annular pellets. The data suggest that the upper- and lower bounds seem to be established: temperatures for a 1-day residence time vary from below 350°C up to 450°C. Slower release is observed for higher densities, and in particular when a significant fraction of the porosity is closed.
- Li_2ZrO_3: data for 'old' pebbles to 13% BU, many data for pellets up to 14% BU. In-pile data for newly developed pebbles (extrusion method) are up to 3% BU. The Li_2ZrO_3 pebbles irradiated in E-8/6 show the fastest release rates with a 1-day residence time below 300°C. This is consistent with older, mostly pellet-base, data.

Tsuchiya et al. [37–39] performed an in-pile test with Li_2TiO_3 pebbles in JMTR at Oarai, Japan up to about 175 full power days (FPD). The pebbles have been fabricated by the rotating granulation method and were about 1 mm in diameter, had a density of 80% TD and an average grain size of about 3 μm. The irradiation volume was 20 mm in diameter and 26 cm in height. Tritium release (HT + HTO and HT separately), moisture and temperatures were monitored continuously. The lowest temperatures achieved at the capsule outer side were as low as 120°C. Central temperatures reached up to 500°C. During the first reactor start-up a clear effect of moisture was observed to enhance the tritium release. Later on and in the subsequent cycles the capsule was purged with various H_2 contents between 10 ppm and 1% and flow rates of 10 to 1000 ml/min. Steady state T-release rates were obtained only when the central temperature was about 450°C and higher [39].

The CRITIC-III irradiation was performed in the AECL Chalk River NRU reactor and concluded after 334 FPD [40]. Lithium titanate pebbles with an average size of 1.2 mm and 81% TD were irradiated in an annular volume (38 mm OD, 10 mm ID and 90 mm height). The material was depleted in Li-6 to a level of 1.85 at.% and a total burnup of about 0.9% was reached. Temperatures at the outer side were varied between 200°C and 380°C; central temperatures were about 500°C higher. The capsule was purged with He + 0.1% H_2 at a pressure of 1 bar and a flow rate of 95 ml/min. Tritium release, neutron flux and temperatures were monitored continuously. Calculations of tritium inventory suggest values over 12 wppm for the lowest temperature case and below 1.2 wppm when the outside temperature was 375°C. Post-irradiation examination has not been done. The temperature records are consistent with predictions for pebble-bed conductivity and do not suggest evidence of pebble disintegration.

Bakker et al. [41] analysed the effects of purge gas composition on Li_4SiO_4 and Li_2ZrO_3 materials irradiated in EXOTIC-6. For these materials both in-pile and out-of-pile tritium release experiments were performed in pure helium purge gas and helium purge gas with 0.001%, 0.01%, 0.1% and 1% H_2. Using the approach described in [35] (discussed above) relations have been obtained for the temperature and hydrogen partial pressure dependence of the tritium residence time in these materials. A clear transition is observed, from diffusion limited release for high hydrogen partial pressure, to desorption limited release for low hydrogen partial pressures. A fairly consistent quantitative picture has been derived for hydrogen contents in a range up to 1% and lithium burnup to about 3%.

Post-irradiation X-ray microanalysis studies were made by Kleykamp et al. [42,43] on selected samples of the MANET steel lined capsule 28.2 of the EXOTIC-7 experiment. A mixture of Be pebbles and SiO_2 doped Li_4SiO_4 pebbles with 52% ^6Li enrichment has been irradiated in the HFR up to 18% burnup [44]. A Li/Si decrease was observed due to Lithium burnup which results in higher amounts of Li_2SiO_3 in the Li_4SiO_4 pebbles. Furthermore, oxygen is released which oxidises the surface of the Be pebbles to BeO. Direct BeO–Li_2SiO_3 contact results in the formation of Li_2BeSiO_4. The predominant Li_2O vapour species is transported to the colder, inner liner surface and recondenses as stratified Li_2O and Li_8SiO_6 layers. Such effects are well known from post-irradiation studies on oxide fuels for fission reactors. The chemical reactions between the MANET steel liner and the breeder materials play a minor role.

5. Fundamental studies

5.1. Hydrogen isotope material interaction (bulk/surface)

Taniguchi and Tanaka [45] studied the dissociative adsorption of H_2 on the surface of Li_2O by an ab-initio quantum-chemical calculation technique using the CRYSTAL92 code. The potential energy surface for the dissociative adsorption of H_2 on Li_2O is obtained by calculating the total energy of the system. The activation energy for dissociation of H_2 becomes larger when an oxygen vacancy exists adjacent to the adsorption sites. This might be caused by the excess charge, which is localised near the defect structure.

Tanigawa et al. [46] studied surface processes in tritium release from solid breeders by ab-initio quantum-chemical calculations. The interaction between hydrogen isotopes and defects in Li_2O has been investigated using Fourier transform infrared absorption spectroscopy (FT-IR). Multiple peaks were observed in the O–D stretching vibration region with Li_2O single crystals, which were treated by thermal absorption and quenching. These peaks had different dependencies on temperature and were attributable to the stretching vibrations of O–D in bulk Li_2O with or without defects. The influence of defects on hydroxyl groups is discussed. They also investigated the electric state of Li_2O with or without defects by X-ray photoelectron spectroscopy (XPS). XPS spectra obtained on Li_2O single crystals were changed by production or recovery of oxygen vacancies.

Yamaguchi et al. [47] introduced work function measurements as a tool to study interactions of hydrogen with breeder material surfaces. The work function change of Li_2ZrO_3 and Li_2TiO_3 was measured in an atmosphere of various gas compositions using a high temperature Kelvin probe, which measures the change of contact potential difference (CPD) between the sample and a reference (Pt) electrode. The work function change of Li_2ZrO_3, due to a change in the chemical composition of the sweep gas, was found to consist of two steps: a rapid change of work function, followed by a gradual change to a steady-state value; whereas in the case of Li_2TiO_3, the work function change was very slow. The observed difference in the work function change was discussed in terms of possible surface phenomena; i.e., production/annihilation of thermal defects, adsorption/desorption of hydrogen, etc. Later work addressed the addition of an in situ particle beam irradiation technique [48].

Fedorov et al. [49] presented a simplified physical model for tritium release, which describes tritium diffusion inside the bulk and tritium recombination at the surface with hydrogen present in the purge gas. The model proved to be capable of simulating the in-pile tritium release measurements and the out-of-pile ramp annealing measurements obtained for Li_4SiO_4 pebbles irradiated in EXOTIC-6 [41]. On the basis of the simulation results a list of the parameters which provide the best consistency with the experimental data was determined. It was found that in the case of in-pile experiments with hydrogen partial pressures $p > 300$ Pa (0.1%), tritium release is limited by bulk diffusion.

Nishikawa et al. [50] reported on their model which describes the tritium release behaviour in a breeder blanket in terms of four main processes inside the material as well as system effects. In this study, a tritium behaviour estimation code is presented, which considers the effects of (1) apparent diffusion of tritium in the grain, (2) adsorption of water vapour on the surface of grain, and (3) isotope exchange reaction between tritium on the grain surface, and gaseous hydrogen, H_2, and water vapour, H_2O, in the purge. In order to analyse the in situ experiments it is necessary to know not only outlet concentrations of H_2, T_2, H_2O and T_2O but also the details of the experimental system containing the reaction tube, piping, and measurement system.

Magnacca et al. [53] presented results of spectroscopic and micro-calorimetric characterisation of $LiAlO_2$. They showed the presence of various phases like $LiAl_5O_8$ at the material surfaces.

A dynamic adsorption and desorption model for tritium desorption from lithium oxide, which was constructed in 1994, was improved by Yamaki et al. [55]. The new assumptions for H_2 and H_2O adsorption/desorption are as follows: (1) the dissociative adsorption of H_2O generates two OH^- s, (2) the dissociative adsorption of H_2 generates one OH^- and one LiH, (3) one H_2O desorbs by recombination of two OH^- s, and (4) one H_2 desorbs by recombination of one OH^- and one LiH. It is also assumed that tritium generated by neutron irradiation exists as OT^- or LiT on the surface, and the surface tritium desorbs as HT or HTO by recombination processes similar to H_2 or H_2O desorption, and as HT by an exchange reaction with an H_2 molecule in the sweep gas. The transient behaviour of tritium release for temperature and sweep-gas composition change and the surface tritium residence time were calculated and compared with earlier experimental results.

5.2. Radiation defects and damage simulations and irradiation parameters

The aim of irradiation experiments is to arrive at irradiation conditions close to those of a fusion reactor with respect to specific parameters like burnup, fluence, etc. While this is straightforward with regard to the burnup, it is somewhat complex when considering displacement damage. The different neutron spectra of fission and fusion reactors in general will result in different PKA-spectra (PKA = Primary Knock-on Atom) and hence in qualitatively different lattice defect structures even if the quantitative dpa accumulation is at the same level. Leichtle and Fischer obtained dpa cross-sections on the basis of an improved Binary Collision Approximation (BCA) computer simulations of the displacement damage in poly-atomic lattices, initially for Li_4SiO_4 [56]. These dpa cross-sections properly include contributions from all kinematically allowed neutron induced reactions, considering as primary knock-on atoms (PKA) the recoil nuclei generated by elastic, inelastic and neutron absorbing reactions as well as secondary charged particles (T, ^4He). With this approach, there is no need to separate the dpa into thermal (T, ^4He) and fast components. The model has subsequently been extended to Li_2O and Li_2TiO_3 [57,58].

Nuclear irradiation parameters relevant to displacement damage and burnup of the breeder materials Li_2O, Li_4SiO_4 and Li_2TiO_3 have been evaluated and compared for spectra in a fusion power demonstration reactor and the high flux fission test reactors HFR Petten, ATR and JMTR [58]. Based on detailed nuclear reactor calculations and the aforementioned dpa approach, it has been shown that breeder material irradiations in these fission test reactors are well suited to simulate fusion power plant conditions provided the neutron spectrum is well tailored and the ^{6}Li-enrichment is properly chosen. In particular, a reduction or cut-off of the thermal neutron spectrum and decrease of the ^{6}Li-enrichment is required to get a response comparable to a fusion power reactor. Requirements for the relevant nuclear irradiation parameters – such as the displacement damage accumulation, the lithium burnup and, furthermore, the damage production function $W(T)$ – can be met when taking into account these prerequisites. The $W(T)$ function indicates the cumulative probability that damage will be caused by a PKA with an energy less than a given value of T [58]. It can be readily calculated from the PKA-spectrum, it is a smooth function of the PKA-energy and is probably the most suitable quantity to judge the qualitative character of the displacement damage as calculated for the different spectra. The lay-out of the actual irradiation experiment requires additional considerations. These include thermo-mechanics, thermo-hydraulics, experiment operation, and cost [54]. Only limited work is ongoing on damage simulations, and two groups have recently made a start: Yamaguchi et al. [48] and Fedorov et al. [54].

6. Evolution in blanket design and development tools

It is necessary as background to review the evolution in solid breeder blanket design, as it has been a focal point for technological research and development. Recent and ongoing design efforts concern breeding blankets for ITER/Next Step and DEMO [60–67].

The ITER Breeding Blanket is based on the use of ceramic breeder pebbles contained in poloidal tubes that are surrounded by beryllium pebble bed columns [60,61]. All three candidate breeder materials (Li_2ZrO_3, Li_2TiO_3 and Li_4SiO_4) satisfy the TBR (Tritium Breeding Ratio) requirement of 0.8 for 1 MWy/m^2 of exposure, and do not present specific important drawbacks or advantages from a functional and performance point of view.

In Japan two basic designs for solid breeder blankets exist [62,63]. The first concept is a water cooled ceramic breeder blanket based on PWR technology (pressure 15 MPa; inlet/outlet coolant 280°C/320°C). The alternative concept uses high temperature helium gas cooling (8.5 MPa; 360°C/480°C), with inherent safety features and potential higher efficiency. Both of them utilise small pebbles, and a layered configuration of breeder and beryllium beds is applied to maximise the tritium breeding performance.

The Helium Cooled Pebble-Bed (HCPB) is one of the two blanket concepts that the EU selected for further development, aimed at the insertion of test blankets in ITER [65]. Meanwhile further design improvements have been made [66]. A more advanced concept based on SiC/SiC as a structural material is now being developed [67]. Boccaccini et al. [68] elaborated on the design considerations for the HCPB DEMO blanket and discussed in particular requirements for TBR, breeder density, and performance limits. Tritium release rates and inventory are considered of less importance for DEMO blankets, while the densities of pebbles and beds can be chosen to optimise their integral mechanical/swelling behaviour.

The development of a concept for an ITER Breeding Blanket and the so-called 'test blanket modules' (TBM) of the ITER partner's DEMO concepts has clearly had an impact on the breeder technology R&D. The TBM's are being designed to address the critical blanket engineering issues in the ITER testing programme. Not only did the manufacturing and assembly processes have to be worked out in detail, but in particular the various scaling steps and their performance analyses require the development of new tools and tests. Work on thermo-mechanical models, that eventually should enable blanket performance analyses, is performed by Ying et al. and Bühler et al. [69–71]. In the EU HCPB programme scaling steps being taken are to prepare for (a) out-of-pile testing of a helium cooled module and (b) a test of subsized modules under neutron irradiation [72–77].

In preparation for the in-pile testing of HCPB pebble-bed assemblies, a simplified test-element has been designed to allow pre-testing of key components and development of thermo-mechanical modelling tools. The basic set-up, denoted SCATOLA, is a cylindrical pebble-bed assembly. The ceramic pebble-bed is enclosed between two plates that are fixed at their circumference. Experimental results in terms of plate displacements have been obtained for Li_4SiO_4 pebble-beds constrained by plates of 3.0 to 5.5 mm thickness. Typical temperatures of 600–650°C and test durations up to 140 h have been applied. Modelling activities have begun at FZK Karlsruhe and NRG Petten to provide thermal–mechanical analysis of the in-pile behaviour of pebble-bed assemblies. The models have been calibrated with experimental results from uniaxial and triaxial tests [27–30] and have then been applied to the SCATOLA configuration. A comparison of numerical and experimental SCATOLA results showed that fair agreement could be obtained for the displacement of the plates when bed compaction and plastic flow are considered [77]. Even the description of creep effects was found to be sufficient to apply the model for analysis of the in-pile test. The SCATOLA test device will be exploited further for pre-testing components and for benchmarking pebble-bed models being developed for blanket design evaluations.

7. Discussion

7.1. Progress

7.1.1. Manufacturing technologies for pebbles (and reprocessing options)

The development of breeder fabrication technology has been devoted exclusively to manufacturing processes for pebbles, which is the selected product form in current blanket concepts. The world-wide efforts in the past two years has had a clear emphasis on the development of Li_2TiO_3. Current processes and facilities concern a scale up to tens of kilograms [8,12,78]. It is to be noted that in these cases industry is involved, either as a subcontractor or as a co-developer. This is important for any judgement on the costs of blanket technology, both on a shorter term for a Next Step (driver) blanket and on a longer term for a DEMO or prototype Fusion Power Plant (FPP). Long-term perspectives include consideration of reprocessing routes and costs.

7.1.2. Properties of pebbles and basic temperature limits

Extensive pebble characterisation techniques are applied by the various research groups involved. An exchange of materials and specimens has improved the general progress of knowledge, although more seems to be possible. However, the specimens used are often rather different and the test conditions are not always directly comparable. Li-compound vaporisation and high temperature annealing are available for out-pile conditions [21,22,51,52]. Basic temperature limits for the various pebble candidates have been derived for design purposes [61,80].

7.1.3. Compatibility with structural materials

The compatibility of ceramic breeders with various structural materials seems of no real concern for the presently considered combinations. However, the supporting data typically have been obtained under out-of-pile conditions.

7.1.4. Elastic/plastic behaviour of pebble-beds

A jump in progress has been obtained in the characterisation of the thermo-mechanical behaviour of pebble-beds. Quite a number of data have already been generated on pebble-bed deformation behaviour, including elevated temperatures.

7.1.5. Thermal conductivity (at low constraint)

Limited thermal property data are available for pebble-beds and are restricted to low constraint conditions. From the various irradiation experiments, which typically have significant temperature gradients, no signs of deterioration of pebble-beds or stack conductivity have been observed yet.

7.1.6. Irradiation effects

In-pile and post-irradiation data are available for some of the currently considered breeder ceramics. So far appreciable, DEMO-like lithium burn-ups are of major concern. High (fast) fluence data do not exist for the currently considered pebbles.

7.2. Focus

7.2.1. Optimised pebble and pebble-bed properties: density or strength?

In order to optimise pebble properties, it is necessary to determine whether pebble density or strength (crush-load) must be maximised. This requires a close interaction with results of pebble-bed tests along with (blanket) performance analyses. Such analyses should focus on single size or monodisperse pebble-beds, as binary beds probably have smaller performance margins (less accommodation of swelling). Such analyses further require a rapid expansion of the data base on creep/plasticity effects, on pebble-bed conductivity, and on their interaction. To date no consistent picture is available for these complex thermo-mechanical interactions. This uncertainty is enhanced by the unknown interaction with neighbouring beryllium pebble-beds and structure.

7.2.2. What are the effects of high (fast) neutron fluences?

Although a number of irradiation data exist, they are limited to, at best, representative lithium burnups. Fast neutron effects have to be determined for the currently considered pebble candidates up to a level of about 5×10^{26} n/m^2. The focus should be on swelling and creep properties, microstructural stability (sintering, phase changes), thermo-mechanics and thermal conductivity. Furthermore, helium and tritium retention along with characterisation of irradiation defects are clear issues [81]. It is necessary to accompany more technology-oriented irradiation tests with other experimental damage simulations along with modelling [48,54,79].

At present most operational temperature and interface-temperature (compatibility) limits for the various breeder-structure combinations are based on out-of-pile tests. It is evident that they need to be evaluated at appropriate irradiation conditions.

8. Conclusions

- Characterisation and fundamental breeder material studies have focused on four main systems: Li_2O, Li_4SiO_4, Li_2TiO_3, Li_2ZrO_3. Manufacturing technology for pebbles appears to be developing well, with most efforts on Li_2TiO_3 and options for re-processing. Further fine-tuning will rely on performance characterisation.
- Clear progress has been made in characterisation methods, particularly in high temperature annealing tests and thermo-mechanical tests on pebble-beds; in addition non-linear elasticity, compaction and creep data are being generated. In-pile tests have provided data on tritium release characteristics.

Designers and materials researchers are working closely together toward an optimised approach in breeder development. International collaboration is essential and is being established.

In the future, ceramic breeder R&D should answer the following questions:

- How can operational windows be enhanced, and what performance margins can be allowed?
- What are the life-limiting factors for a pebble-bed blanket?

References

[1] N. Roux, S. Tanaka, C. Johnson, R. Verrall, Fus. Eng. Des. 41 (1998) 31.
[2] C.E. Johnson, K. Noda, N. Roux, J. Nucl. Mater. 258–263 (1998) 140.
[3] B. Beamont et al. (Ed.), in: Proceedings of the 20th SOFT, Marseille, September 1998.
[4] J.G. van der Laan (Ed.), in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, Petten, February 1999.
[5] K. Tsuchiya, S. Saito, H. Kawarnura, K. Watarumi, K. Fuchinoue et al., J. Nucl. Mater. 253 (1998) 196.
[6] K. Tsuchiya, H. Kawamura, K. Fuchinoue, H. Sawada, K. Watarumi, J. Nucl. Mater. 258–263 (1998) 1985.
[7] K. Tsuchiya, H. Kawamura, K. Fuchinoue, H. Sawada, K. Watarumi, in: Proceedings of the CBBI-6, Report JAERI-Conference 98-006, 1998, p. 245.
[8] K. Tsuchiya, H. Kawamura, K. Watarumi, K. Fuchinoue, H. Sawada, in: Proceedings of the 20th SOFT, Marseille, 1998, p. 1293.
[9] C. Alvani et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 3, Petten, February 1999, p. 9.
[10] K. Watarumi et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 3, Petten, February 1999, p. 1.
[11] J.-D. Lulewicz et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 5, Petten, February 1999, p. 11.
[12] J.D. Lulewicz et al., these Proceedings, p. 1361.
[13] K. Tsuchiya, H. Kawamura, Fus. Eng. Des. 39&40 (1998) 731.
[14] J.P. Qiang, The blanket technology investigation in China, paper presented at ISFNT-5, Rome, September 1999.
[15] Davydev et al., Paper presented at ISFNT-5, Rome, 1999.
[16] K. Munakata et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 3, Petten, February 1999, p. 17.
[17] K. Munakata et al., Enhancement of tritium relaese rates from ceramic breeders with impregnated catalytic additives, paper presented at ISFNT-5, Rome, September 1999.
[18] M. Dalle Donne et al., in: Proceedings of the 19th SOFT, Lisbon, 1996, p. 1483.
[19] S. Casadio, C. Alvani, C.E. Johnson, F. Pierdominici, in: Proceedings of the 20th SOFT, Marseille, 1998, p. 1211.
[20] J.G. van der Laan, R. Conrad, K. Bakker, J.G. Boshoven, S. Casadio, G. Piazza, N. Roux, E. Schuring, M.P. Stijkel, Irradiation performance and tritium release characteristics of solid breeder materials – an update on results from EXOTIC-8, in: A. Ying (Ed.), Proceedings of CBBI-8, UCLA, Feb. 2000.
[21] G. Piazza et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 5, Petten, February 1999, p. 25.
[22] G. Piazza et al., A. Ying (Ed.), Proceedings of CBBI-8, UCLA, Feb. 2000.
[23] S. Casadio et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 5, Petten, February 1999, p. 57.
[24] S. Casadio et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 4, Petten, February 1999, p. 69.
[25] L. Peña et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 4, Petten, February 1999, p. 21.
[26] J.G. van der Laan, R.P. Muis, J. Nucl. Mater. 271&272 (1999) 401.
[27] J. Reimann, S. Müller, in: Proceedings of the 20th SOFT, Marseille, 1998, p. 1337.
[28] J. Reimann, E. Arbogast, S. Müller, K. Thomauske, in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 5, Petten, February 1999, p. 1.
[29] J. Reimann, E. Arbogast, M. Behnke, S. Müller, K. Thomauske, Fus. Eng. Des., to be published.
[30] J. Reimann et al., private communication.
[31] L. Bühler, in: Proceedings of the 20th SOFT, Marseille, 1998, p. 1345.
[32] G. Piazza et al., Measurements of the effective thermal conductivity of a Li_4SiO_4 pebble-bed, paper presented at ISFNT-5, Rome, September 1999.
[33] S. Sato, M. Enoeda, T. Kuroda, S. Kikuchi, H. Takatsu, Y. Ohara, in: Proceedings of the 20th SOFT, Marseille, 1998, p. 1199.
[34] M. Enoeda et al., Effective thermal conductivity measurements of the ceramic breeder pebble beds using the hot wire method, Contribution to CBBI-8, Colorado Springs, 6–8 October 1999.

[35] J.G. van der Laan et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 4, Petten, February 1999, p. 9.
[36] J.G. van der Laan, R. Conrad, K. Bakker, S. Casadio, N. Roux, G. Piazza, M.P. Stijkel, H. Werle, J. Nucl. Mater., to be submitted.
[37] H. Kawamura, K. Tsuchiya, M. Nakamichi, Y. Nagao, J. Fujita, T. Saito, Y. Ikejima, in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 4, Petten, February 1999, p. 1.
[38] H. Kawamura, K. Tsuchiya, M. Nakarnichi, J. Fujita, H. Sagawa et al., in: Proceedings of the 20th SOFT, Marseille, 1998, p. 1289.
[39] K. Tsuchiya, M. Nakamichi, Y. Nagao, J. Fujita, H. Sagawa, S. Tanaka, H. Kawamura, Integrated experiment of blanket in-pile mockup with Li_2TiO_3 Pebbles, paper presented at ISFNT-5, Rome, September 1999, Fus. Eng. Des., to be published.
[40] R.A. Verrall, J.M. Miller, P. Gierszewski, in: Performance of a Li_2TiO_3 pebble-bed in the CRITIC-III irradiation, in: A. Ying (Ed.), Proceedings of CBBI-8, UCLA, Feb. 2000.
[41] K. Bakker et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 4, Petten, February 1999, p. 33.
[42] H. Kleykamp, in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 5, Petten, February 1999, p. 65.
[43] H. Kleykamp, J. Nucl. Mater. 273 (1999) 171.
[44] J.G. van der Laan et al., J. Nucl. Mater. 233–237 (1996) 1446.
[45] M. Taniguchi, S. Tanaka, in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 6, Petten, February 1999, p. 25.
[46] H. Tanigawa et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 5, Petten, February 1999, p. 19.
[47] K. Yamaguchi, A. Suzuki, M. Yamawaki, in: Proceedings CBBI-7, NRG Report 21099/99.23482, vol. 6, Petten, February 1999, p. 21.
[48] K. Yamaguchi et al., Contribution to CBBI-8, in: Proceedings of the CBBI-8 Workshop, Colorado Springs, 6–8 October 1999, to be published.
[49] A.V. Fedorov et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 6, Petten, February 1999, p. 29.
[50] M. Nishikawa, A. Baba, K. Munakata, in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 6, Petten, February 1999, p. 39.
[51] M. Yamawaki, A. Suzuki, M. Tonegawa, M. Yasumoto, K. Yamaguchi, in: Proceedings of the 20th SOFT, Marseille, 1998, p. 1321.
[52] M. Yamawaki et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 5, Petten, February 1999, p. 49.
[53] G. Magnacca et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 5, Petten, February 1999, p. 77.
[54] J.G. van der Laan, R. Conrad, K. Bakker, S. Casadio, A.V. Fedorov, U. Fischer, S. Malang, G. Piazza, B.J. Pijlgroms, N. Roux, A. van Veen, On the irradiation performance of HCPB candidate ceramic breeder materials to DEMO – like conditions – an approach with neutron and particle irradiations, in: A. Ying (Ed.), Proceedings of CBBI-8, UCLA, Feb. 2000.
[55] D. Yamaki et al., Model calculation of transient tritium release behavior from lithium oxide, Contribution to CBBI-8, Colorado Springs, 6–8 October, 1999.
[56] D. Leichtle, U. Fischer, in: Proceedings of the 20th SOFT, Marseille, 1998, p. 1179.
[57] D. Leichtle, U. Fischer, Paper presented at ISFNT-5, Rome, September 1999, Fus. Eng. Des., to be published.
[58] U. Fischer, S. Herring, A. Hogenbirk, D. Leichtle, Y. Nagao, B.J. Pijlgroms, A. Ying, J. Nucl. Mater. 280 (2000) 151.
[59] J.G. van der Laan, R. Conrad, K. Bakker, N. Roux, M.P. Stijkel, in: Proceedings of the 20th SOFT, Marseille, 1998, p. 1239.
[60] M. Ferrari et al., Fus. Eng. Des. 46 (1999) 177.
[61] M. Ferrari et al., in: Proceedings of the CBBI-7, NRG Report, vol. 1, 21099/99.23482, Petten, February 1999, p. 1.
[62] H. Takatsu, H. Kawamura, S. Tanaka, Fus. Eng. Des. 39–40 (1998) 645.
[63] M. Enoeda et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 1, Petten, February 1999, p. 9.
[64] V. Kovalenko et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 1, Petten, February 1999, p. 15.
[65] S. Malang, Fus. Eng. Des. 46 (1999) 193.
[66] S. Hermsmeyer, K. Schleisiek, Improved HCPB concept, FZK Report, 1999.
[67] L.V. Boccaccini, U. Ficsher, S. Gordeev, S. Malang, Advanced HCPB blanket with SiCf/SiC as structural material, paper presented at ISFNT-5, Rome, September 1999, Fus. Eng. Des., to be published.
[68] L.V. Boccaccini et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 1, Petten, February 1999, p. 21.
[69] A.Y. Ying, Z. Lu, M.A. Abdou, Fus. Eng. Des. 39–40 (1998) 759.
[70] A. Ying, in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 6, Petten, February 1999, p. 11.
[71] L. Bühler, J. Reimann, E. Arbogast, K. Thomauske, Mechanical behaviour of Li_4SiO_4 pebble beds in a blanket typical geometry, paper presented at ISFNT-5, Rome, September 1999, Fus. Eng. Des., to be published.
[72] G. Dell'Orco et al., in: Proceedings of the 20th SOFT, Marseille, 1998, p. 1305.
[73] M. Simoncini et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 6, Petten, February 1999, p. 1.
[74] S. Hermsmeyer et al., in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, vol. 4, Petten, February 1999, p. 55.
[75] J.G. van der Laan, R. Conrad, K. Bakker, J.H. Fokkens, S. Hermsmeyer, S. Malang, B.J. Pijlgroms, K. Schleisiek, C. Sciolla, R. van Tongeren, in: Proceedings of the 20th SOFT, Marseille, 1998, p. 1243.
[76] J.G. van der Laan, R. Conrad, K. Bakker, J.H. Fokkens, S. Hermsmeyer, S. Malang, B.J. Pijlgroms, K. Schleisiek, C. Sciolla, R. van Tongeren, in: Proceedings of the CBBI-7, NRG Report 21099/99.23482, Petten, February 1999.

[77] J.G. van der Laan, R. Conrad, K. Bakker, L.V. Boccaccini, J.G. Boshoven, L. Bühler, J.H. Fokkens, M.A.C. van Kranenburg, B.J. Pijlgroms, J. Reimann, Design analyses and pre-tests for the irradiation of HCPB pebble-bed assemblies, Fus. Eng. Des., to be published.
[78] W. Pannhorst, V. Geiler, G. Räke, B. Speit, D. Sprenger, in: Proceedings of the 20th SOFT, Marseille, 1998, p. 1441.
[79] V. Grismanovs, T. Tanifuji, T. Nazakawa, D. Yamaki, K. Noda, in: Proceedings of the 20th SOFT, Marseille, 1998, p. 1183.
[80] K. Ioki, M. Ferrari, Design description document WBS 1.6B: tritium breeding blanket system, ITER Final Design Report G 16 DDD 2 98-06-10 W0.4, p. 225.
[81] C.E. Johnson, J. Nucl. Mater. 270 (1999) 212.