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First principles review on the options for tritium breeder and neutron multiplier materials for breeding blankets in fusion reactors

First principles review on the options for tritium breeder and neutron multiplier materials for breeding blankets in fusion reactors

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Abstract. The current breeding blankets proposed in the different conceptual fusion power plants are based mainly on the use of Li_4SiO_4 and/or Li_2TiO_3 as tritium breeder and $Be/Be_{12}Ti$ as neutron multiplier or an eutectic $Li_{17}Pb_{83}$ for as a hybrid tritium and neutron multiplier. The selection of these functional materials has offered up to know possible solutions for the problem of the tritium self-sufficiency in a fusion reactor. However, the options for functional materials are reduced and some of them, especially the use of Be, raises several key feasibility questions. The selection of these functional materials dates from several decades ago. In the meanwhile, our current understanding in material science and technology has been significantly improved and comprehensive databases exists nowadays with many new compounds that may trigger the revision of such selection. Also, the rapid and vast improvement in computational power since then allows nowadays to perform more reliable detailed 3D heterogeneous neutronic simulations of a fusion reactor with different functional materials in relatively short time. The goal of this paper is to perform a revised screening for all tritium breeder and neutron multiplier materials from first principles that can be found in the current material databases and assess the tritium breeding performance of the selected compounds. The screening has updated the selection of potential tritium breeder and neutron multipliers and revealed several new options. Given the new multipliers found, a new subdivision between solid and liquid multipliers is proposed. For the selected compounds detailed 3D heterogeneous neutronic analyses have been performed with MCNP5-1.60 assuming the architecture of the current EU DEMO Helium Cooled Pebble Bed (HCPB) as a benchmark breeding blanket. The assessment has concluded that several Li compounds can enhance the tritium breeding capabilities of Li_4SiO_4 and that realistic and very promising alternatives to Be and beryllium compounds exist, resulting in a comparable tritium breeding performance as the current reference material choices.

Keywords: breeding blanket, tritium breeding, TBR, neutron multiplier, DEMO

1. Introduction

A Fusion Power Plant (FPP) based on the fusion of deuterium (D) and tritium (T) to give He and a 14.1 MeV neutron ($D+T \rightarrow He+n$) necessitates of an *in-situ*, continuous production of T, due to the practical unavailability of such element in our environment. This is one of the basic functions of the so-called Breeding Blanket in a future FPP and in particular in the demonstration FPP (EU DEMO) [1], together with the extraction of thermal power and its contribution as neutron shield. This T breeding function is accomplished by irradiating a so-called breeder material with neutrons, which by means of a (n,T) nuclear reaction will transmute elements of the material into T and some other byproducts. However, not all neutrons from the $D+T$ fusion are available, as some part is lost due to parasitic absorptions in the structural and non-functional materials of the blanket, or due to streaming and leaking through the blanket gaps and the blanket thickness respectively. Therefore, the breeding blanket necessitates of a so-called neutron multiplier to generate additional neutrons to compensate for these loses.

Since the 1980s, the EU has directed several studies regarding different breeding blanket concepts, which are mainly divided on liquid or solid concepts depending on the aggregate state of the functional materials. The most remarkable due to their extension and coherence towards an integrated study of a power plant are the DEMO conceptual study in the 1990s (e.g. [2]) and the EU Power Plant Conceptual Study [3]. In the former, four breeding blanket concepts were proposed: the Self Cooled Lithium Lead (SCLL), the Water Cooled Lithium Lead (WCLL) and two Helium Cooled Pebble Bed (HCPB) concepts, a Breeder In Tube (BIT) and a Breeder Out of Tube (BOT). While the SCLL and WCLL were based on the use of a liquid $Li_{17}Pb_{83}$ eutectic as combined mixture of breeder (Li) and multiplier (Pb), the HCPB-BOT was based on the use of (solid) pebbles of Li_4SiO_4 as T breeder and Be as neutron multiplier and the HCPB-BIT on pellets of $LiAlO_2$ or Li_2ZrO_3 as breeders and again Be as multiplier material. However, the study did not offer a clear rationale on the selection of these functional materials. Similarly, the PPCS study proposed again the WCLL, HCPB (only the BOT version) and SCLL and added two more concepts, the Helium Cooled Lithium Lead (HCLL) and the Dual Cooled Lithium Lead (DCLL), which in any case were also based on the use of LiPb and no further investigation was carried out on possible alternative functional materials. A second EU DEMO pre-conceptual study started in 2014 [4][5] have been newly proposed [6], proposing again the HCPB, HCLL, WCLL and DCLL based on similar functional materials as in PPCS, with the exception of a proposal for an advanced ceramic breeder material based on Li_4SiO_4 with additions of Li_2TiO_3 in order to improve its mechanical properties [50].

The choices for the functional materials in the EU were also in part influenced by the comprehensive studies previously performed in the US, especially during the Blanket Comparison Selection Study [7]. Here the most complete list to date of promising functional materials in different configurations of breeder, multiplier and coolants for solid and liquid breeding blankets can be found. However, it lacks from an *ab initio* search for those functional materials, especially for the neutron multipliers, where the options have been always very reduced. Broadening the choice of multipliers is then a central point of this paper.

Since those studies from the 1980s and 1990s our knowledge in material science and technology has been improved and global material databases have been developed and are readily accessible online. This, coupled with the exponential increase in computational power and the vastly improved level of detail of the in-vessel components of a FPP and DEMO, allows us to revise and complete the palette of options for breeder and neutron multiplier materials for breeding blankets. This paper aims at revising the search for neutron multiplier and breeder materials from first principles, setting first several basic requirements, scanning for adequate elements and investigating possible material mixtures in each case, leading to a choice of promising compounds. The choice is then verified with a 3D neutron transport code (MCNP 5) by simulating the T breeding ratio in a highly detailed model of the latest design HCPB breeding blanket for the current EU DEMO.

2. Basic requirements for candidate functional elements

Despite the many elements and their possible combinations in different compounds that exists, any of them has to fulfill the following list of counter-acting requirements.

3.1 Safety (toxicity, reactivity, non-radioactivity)

The functional materials must minimize its toxicity, reactivity with air and water and the structural materials of the blanket. Also, the candidate materials should minimize any volatile

or mobilizable element produced during their lifetime in the blanket (by means of e.g. irradiation, mechanical failure, etc.) that can be a safety concern.

In this regard, alkali and alkaline metals are on their own readily reactive, with increasing reactivity for higher period elements, which includes Li and Be, therefore they should be ideally used as compound to reduce their reactivity. Elements after Bi should be discarded under this requirement due to their natural radioactivity. The chemical toxicity of elemental Be (acute Be disease) is a safety concern already raised during the BCSS [7] and care must be taken to minimize the inventory of such material while designing a blanket containing Be.

3.2 Low activation

One of the basic requirements in FPPs is that it is qualified as a low activation, i.e. the selection of materials that are to be under fusion environment meet a series of low activation characteristics, which include waste management, accident safety, maintenance and routine effluents, as defined in [12].

Of course, in order to obtain a qualified answer, a neutronic analysis of the reactor activation must be performed. However, a good indication if an element will meet such criterion is by checking its waste and recycling classification. Although this classification is strongly dependent on the host country where the reactor is [18], Figure 1 shows as a model the usage limits of the elements depending on its quantity when placed in an in-vessel component and their incident neutron spectrum for near-surface burial following the US convention. Following this chart and for practical reasons, elements that can only be used in too low amounts (e.g. less than 1%) should not be considered, e.g. Al, Nb, Mo, Ag, Cd, Hf, Au, Bi, etc.
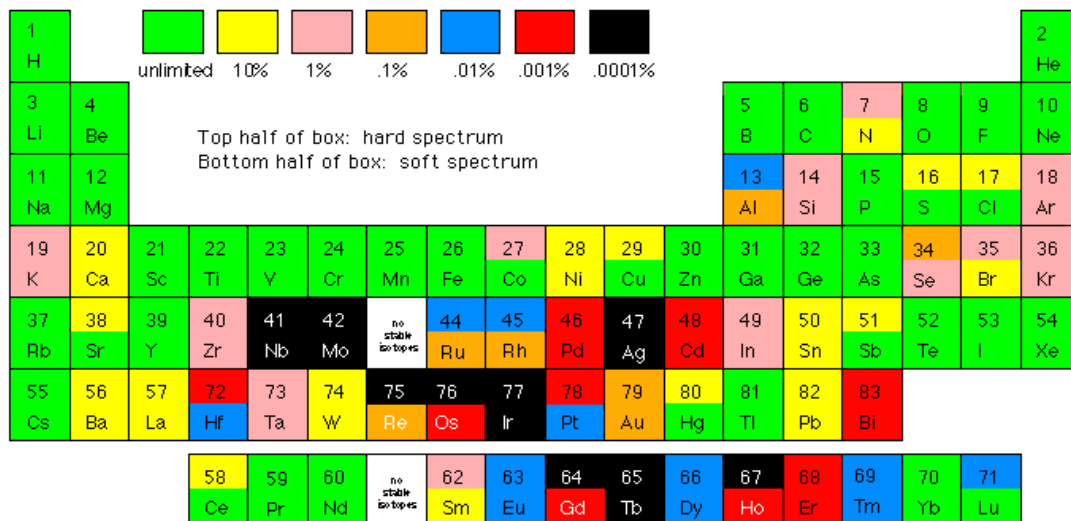
Figure 1. Limits on the use of elements for near-surface burial after US methodology [12]

Although not appearing in the chart of Figure 1, fertile elements like U and Th are also excluded, as their use in a blanket would produce different high-level waste actinides (Pu, Am, Cm).

Especial attention must be taken to impurities that may be contained in the raw materials or that can be introduced during manufacturing processes. Even if in low quantities, due to the large amounts of functional materials these impurities may become nevertheless important. In

this regard, care must be taken again with Be, as the raw material contains U impurities and high purity Be is then required (<30 wppm U in Be after ITER safety standards) if this material is to be used in a blanket [17].

3.3 Availability and cost

Figure 2 shows a periodic table of endangered elements [11]. From this table it can be concluded that the use of elements in "serious" or "rising" threat is very questionable, e.g. Zn, Ga, Ge, As, Nb, etc. On the other side, the volume for functional materials in a breeding blanket will be necessarily high due to the large size of the machine. For the case of the current EU DEMO and with characteristic major radius of 9 m ÷ 9.5 m [5], it is estimated that this volume is ~700 m³. Such a large volume will require the use of several hundreds of tons of functional materials, therefore the candidates should be readily available and their resources large enough in order not to pose mid to long-term sustainability concerns. This is the case of the use of Be, in which its limited reserves has already raised concerns about it sustainability as blanket functional material [13][14], and will most probably require recycling to ensure the economic sustainability of a blanket working on the basis of this material [17].

In the same way, the cost is a factor also tightly related to the availability. Precious metals like Au, Pt, Pd, Ir and Ag are therefore obviously out of the scope of any practical use as functional material. However, the case of Be is especial because, despite its availability is not immediately at risk, its cost as finished product is known to be high (e.g. estimation in [15]), mostly because of the stringent safety issues during its handling due to its high toxicity, especially when inhaled as dust form.
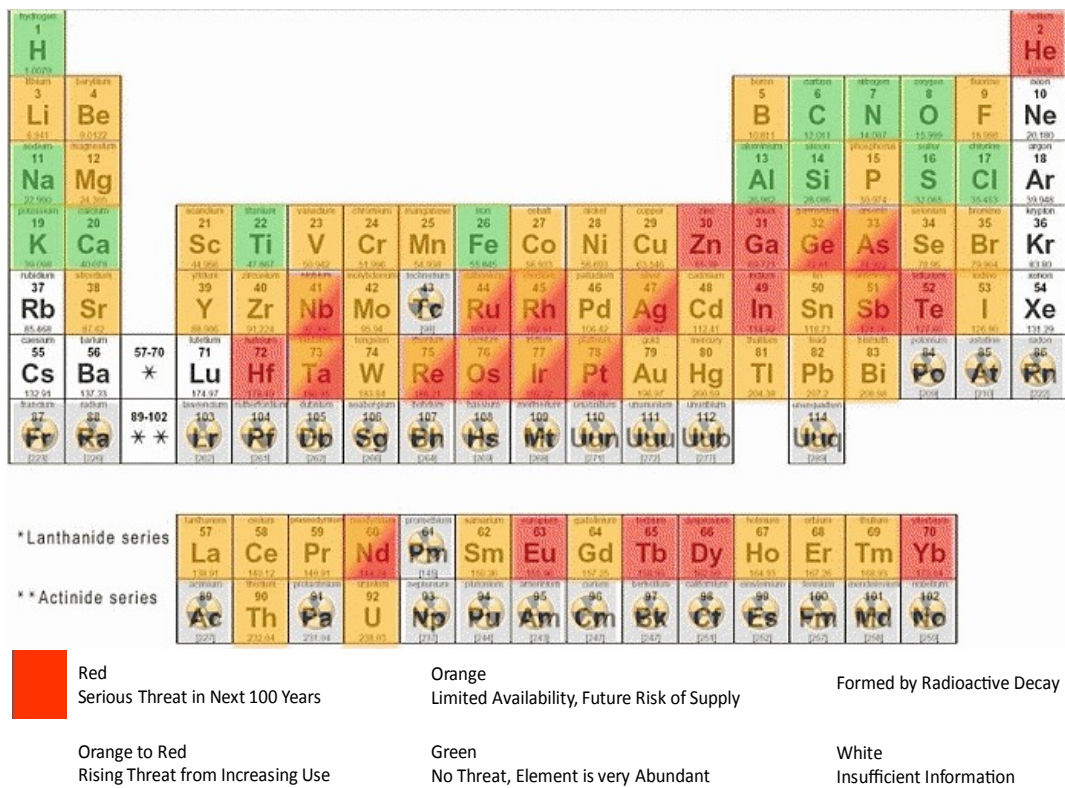

Figure 2. Periodic table of endangered elements [11]

3. Screening and selection of tritium breeder materials

While many elements of the periodic table interact with an incident neutron to form T via a (n,T) reaction, paradoxically only very few of them have significant (n,T) reaction rates (Figure 3 left). Only ^{6}Li and ^{10}B show a significant (n,T) cross section for a range of high energy neutron spectrum at least from 14 MeV down to about 1 MeV. Unfortunately, ^{10}B is about two orders of magnitude lower than ^{6}Li for <10^{-1} MeV neutrons. For fast neutrons, ^{7}Li, ^{14}N, ^{19}F, ^{11}B and ^{9}Be behave similarly, though with different and probably too high threshold energies for a practical use on their own.
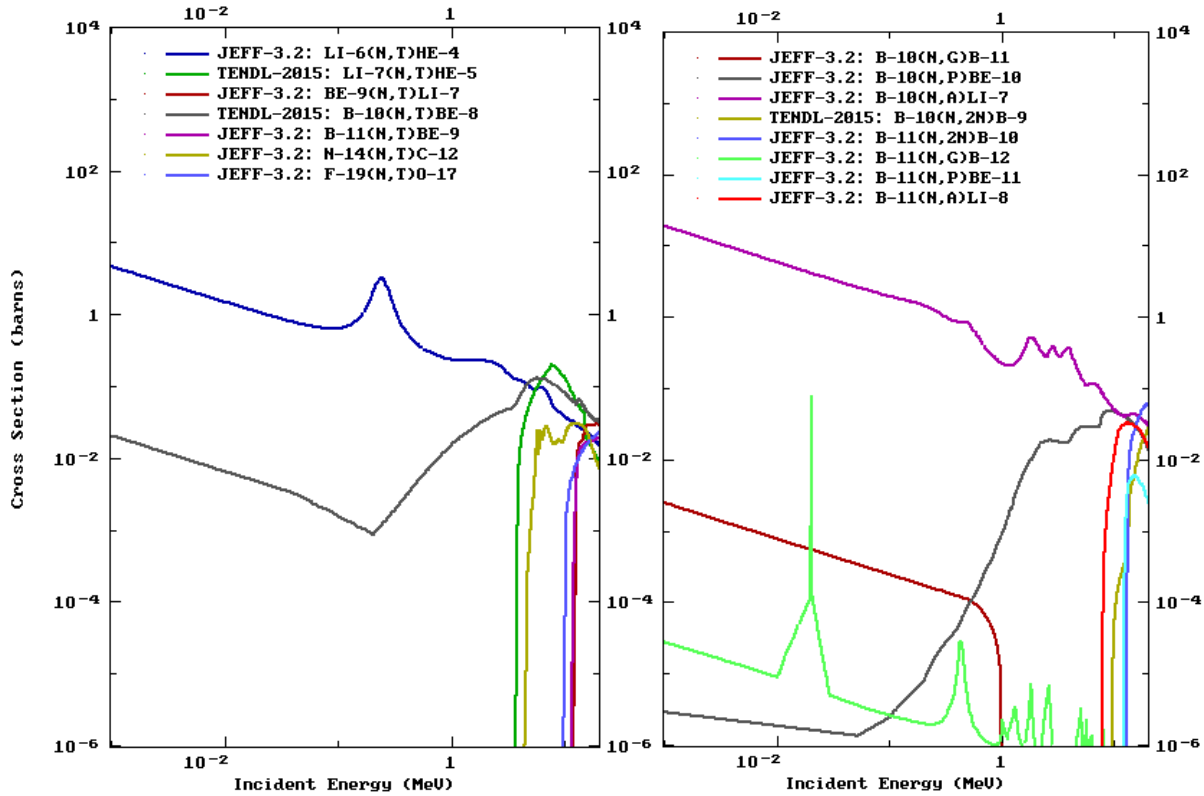
Figure 3. Left: Elements with significant (n,T) reaction cross section. Right: different neutron capture cross sections for ^{10}B and ^{11}B

The proximity of B to Be and Li in the periodic table makes that element interesting. Indeed the neutron interaction of ^{10}B (one of the highest among the elements) and ^{11}B by means of (n,p) and (n,α) captures "breeds" efficient neutron shifters and multipliers (^{9}Be, ^{10}Be) and additionally the breeder element ^{7}Li respectively (Figure 3 right). The incident neutrons in B will be then indirectly used for breeding (through bred ^{7}Li) or for multiplying (through bred Be), further helping to increase the T yield in B, but unfortunately ^{7}Li is not as efficient as ^{6}Li for T breeding and it is not expected that B will offer a practical use in combination with a multiplier.

Therefore, Li (and in particular its isotope ^{6}Li) is actually the only element capable of producing enough T on its own so as to achieve the reactor T self-sufficiency. It must be said that, while ^{6}Li consumes a neutron to produce a T, the reaction of ^{7}Li is of the type $(n,n'\alpha)T$ and therefore no neutron is consumed in this case (only its energy is decreased). Pure Li with a clever tailoring of the ^{6}Li/^{7}Li mixture inside the blanket can then theoretically suffice, but achieving the T self-sufficiency has been proven to be in this case still difficult without the

addition of moderators or multiplier materials [10]. Moreover, its reactivity with water, air and possibly also with the surrounding structural materials poses critical safety issues, especially if other in-vessel components are to be water-cooled. Its low melting point would force its use in a liquid form, bringing additional problems of pressure losses due to Magnetohydrodynamic (MHD) phenomena in the liquid metal while flowing in the high magnetic fields of the tokamak magnet system, therefore rendering this material as unpractical for DEMO or a first generation FPP.

All the above forces a breeding blanket to use some compound of Li that can mitigate or solve the safety and material compatibility concerns of using pure Li. At this point, theoretically a large spectrum of possibilities are opened, based mostly on the use of intermetallic alloys, salts or ceramic compounds with Li. In all these cases, a material that will multiply neutrons via $(n,2n)$ is then necessary and the eligible Li compounds will be then those with the best neutron economy, i.e. elements different than Li in the compound must be elements with low parasitic absorption or neutron multipliers by themselves and the compound itself maximizes the volume fraction of Li atoms.

4.1   Li compounds

Already in the 1980s and after recognizing the safety issues of pure Li, many options for Li compounds as T breeders were already identified [7][8][9]. These were the (liquid) $Li_{17}Pb_{83}$ and $LiBi_5Pb_4$, the $LiF-BeF_2$ salt (FLIBE), the (solid) intermetallic alloy Li_7Pb_2 and the Li ceramics Li_2O, $LiAlO_2$, Li_2SiO_3, Li_4SiO_4, Li_2ZrO_3 and Li_2TiO_3.

$LiBi_5Pb_4$ was early discarded due to the high activation of Bi. FLIBE was found to have critical issues with material compatibility and chemistry control. The rest, only eutectic $Li_{17}Pb_{83}$ for liquid blankets and Li_4SiO_4 or Li_2TiO_3 for solid blankets are nowadays the reference in the majority of blankets worldwide. Due to the high atomic density of Li, Li_2O is a good T breeder, but its high reactivity with water and the compatibility problems with steels reduce the attractiveness of this compound. $LiAlO_2$ was an early ceramic candidate, but its low Li density and the activation of Al rendered it as unpractical. Li_4SiO_4 has a higher Li density and therefore is superior to Li_2TiO_3 in terms of T breeding. However, Li_2TiO_3 is more resilient to mechanical loads in comparison with Li_4SiO_4, which shows a rather brittle behavior. This has been a main motivation to pursue a modified Li_4SiO_4 breeder material with addition of Li_2TiO_3 in order to improve the mechanical properties of the resulting compound [50]-[52], leading to the so-called advanced ceramic breeder material, which is currently being developed for the EU DEMO HCPB.

While the cubic ($Fm\overline{3}m$) Li_2O is the Li ceramic with the highest Li volume fraction (0.079 Li atoms/Å³), other compounds based on tetragonal or tri/hexagonal crystal structures show also a very high Li density. Such is the case of Li_8ZrO_6 (trigonal $R\overline{3}$) with 0.059 Li atoms/Å³ and Li_8PbO_6 (trigonal $R\overline{3}$) with 0.0575 Li atoms/Å³. These compounds have been already proposed and investigated by several authors [53]-[58] and have been subject of irradiation campaigns (Li_8ZrO_6 in the EXOTIC experiment series [58] and Li_8PbO_6 in the JRR-4 reactor [54]).

Taking into account this past work and the main figures of merit of the most attractive breeder materials, an extended research exploring more possible high Li density compounds has been performed and it is reported in the next section.

4.1.1   Eligible Li compounds with potential high T breeding performance

For the initial material scan, the Materials Project[1] software [60] has been used for the calculation of possible compounds. The search for eligible Li compounds has been divided in 2 groups. Non-ceramic (binary) Li compounds (borides, nitrides, silicides…) and ceramic (ternary) Li compounds. For each combination of elements selected, a minimum energy above hull of 0.003 has been set, in order to discard calculated compounds with chances not to be stable already at room temperature. Elements that have not a practical use as (solid) T breeder due to a too low melting temperature, safety/reactivity concerns (e.g. Li_2O, $Li_{21}Si_5$) and/or due to a low Li atomic density have been mainly discarded. The threshold for the low melting temperature has been set to 800 °C. This value has been choosen taking into account the case of Li_4SiO_4, as its melting point is 1258 °C [62] but a maximum allowable temperature of 920 °C is commonly accepted [63], which represents a factor of about 0.75 with respect to the melting point. Applying the same factor to the threshold of 800 °C would result in a maximum allowed temperature for the material of about 600 °C. This leaves a practical operating temperature window of about 250-300°C for the breeder material, between a minimum of 300-350 °C (set by the minimum temperature of the structural material that encloses the breeder material and which is normally considered to be the low activation steel EUROFER97 [64]) and the maximum of 600 °C, to obtain still a reasonable T release rate. For the Li atomic density, a threshold of 0.037 Li atoms/Å³ is considered, which is the Li density for Li_2TiO_3, taken as well as a reference of a material with low density but yet fair T breeding. This threshold has not been applied nevertheless for Li borides, as B is considered after Section 3 as a breeder material.

After a first scan and preliminary selection with the Materials Project software, a literature review have been performed to verify the existence and stability of such element and its density. If the density has not been found in the literature, the calculated value from the software has been assumed plus a ~3% deviation to take into account the typical underestimation of the density in the software [61]. The elements found are listed in Table 1.

Table 1. Properties (room temperature, RT) of selected Li compounds as T breeders

Compound	Compound atomic density [at/Å³]	Atomic density of Li [at/Å³]	% Li atomic density	Compound density RT [kg/m³]	Melting point [°C]	Ref.
Non-ceramics						
Li_3N	0.0899	0.0674	75.0	1.30	813	[67]
LiF	0.1223	0.0612	50.0	2.64	848	[65]
Ceramics						
Li_2TiO_3	0.1129	0.0376	33.3	3.43	1533	[79]
Li_4TiO_4	0.0998	0.0444	44.5	2.57	>1000	[69]
Li_4SiO_4	0.1085	0.0482	44.4	2.40	1258	[62]
Li_8SiO_6	0.1106	0.0590	53.3	2.20	830*	[62]
$Li_6Zr_2O_7$	0.0957	0.0383	40.0	3.56	1267	[68]
Li_8ZrO_6	0.1109	0.0591	53.3	2.98	1336	[68]
Li_8PbO_6	0.1077	0.0575	53.4	4.28	>800	[54]
Li_4GeO_4	0.1031	0.0463	44.9	3.16	1298	[73]
Li_8GeO_6	0.1062	0.0567	53.4	2.64	n/a	[74]
Li_8CeO_6	0.1006	0.0537	53.3	3.25	n/a	[75]
Li_5AlO_4	0.1078	0.0539	50.0	2.25	1047	[72]

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[1] www.materialsproject.org

Li₆CoO₄	0.1113	0.0607	53.2	2.77	n/a	[71]
Li₈CoO₆	0.1060	0.0565	53.3	2.47	n/a	[78]
Li₈SnO₆	0.1140	0.0608	53.3	3.41	1050	[76]
Li₆ZnO₄	0.1116	0.0609	54.6	2.86	n/a	[80]
Li₂MnO₂	0.1053	0.0420	39.9	3.90	n/a	[81]
Li₆MnO₄	0.1031	0.0562	54.5	2.50	n/a	[71]
Li₅FeO₄	0.1028	0.0514	50.0	2.64	n/a	[71]

*Decomposition of the compound before melting

Of the non-ceramic compounds, Li_3N has the highest Li atomic density and should result in very high T breeding ratios. However, its relatively low melting temperature, and most important, its high reactivity with water hinders its practical use in a reactor. Next in the list with a large Li density is LiF, where F atoms may also slightly contribute to the breeding. Contrarily to Li_3N, LiF has a very high molecular stability and therefore a negligible reactivity with water, which would make its use attractive. However, its relatively low melting point may be a technical drawback.

The borides LiB (density 1.51 g/cm³, melting point 1000 °C [66]) and LiB_3 (density 1.75 g/cm³, melting point about 1760 °C [67]) have a lower Li density, nevertheless the one of LiB it is still higher than the well-known Li_4SiO_4. The Li density of LiB_3 is low, but the content of B is large and may compensate that. These compounds have the key advantage of a higher melting point, especially LiB_3. The synthesis of many borides of the type Li_xB_{1-x} with $0.3<x<0.9$ have been reported in [83]. A drawback of these compounds may be their reactivity with air and water. Lewis [84] shows nevertheless that the reactivity of these compounds is related to their Li content, but since the melting point of the borides is much larger than that of pure Li (especially for LiB_3), their reactivity is less than metallic Li. These borides have been nevertheless discarded as breeder material in combination with multiplier due to the high neutron capture of B and its consequent transmutation to the low T breeding performant ^7Li.

Of the other possible discarded compounds (not shown in Table 1), $Li_{13}Si_4$ (density 1.25 g/cm³, melting point about 750 °C [82]) is worth mentioning. It has not been included due to its low melting point, however its Li atomic density is as high as 0.1084 at/Å³, significantly higher than the well-known Li_2O and therefore could be used without a neutron multiplier. However, and as it happens with Li_2O, this compound may have reactivity concerns if water ingress occurs during an accidental condition.

Regarding the ceramic compounds, many have been found to have larger Li atomic densities than Li_4SiO_4 and they should lead to larger T breeding performances than that reference compound. In several of them, the oxide anion is formed by a metal or metalloid element that has properties of a multiplier, i.e. high $(n,2n)$ with low neutron capture (see Section 4): this is the case of Li_8PbO_6, Li_8ZrO_6 and Li_8SnO_6. While being an advantage in terms of T breeding, octalithium compounds are prone to decompose at high temperatures [57]. Several of them decompose before reaching 1000 °C such as Li_8SiO_6 and most probably Li_8PbO_6. Li_8ZrO_6 and Li_8SnO_6 melt congruently, but Li_8ZrO_6 does it at a significantly higher temperature than Li_8SnO_6 that is even higher than Li_4SiO_4, making this compound very interesting, albeit the activation of Zr may be a concern (Figure 1). The compounds Li_8GeO_6, Li_8CeO_6, Li_8CoO_6, Li_6CoO_4, Li_6ZnO_4, Li_6MnO_4 and Li_5FeO_4 have also excellent Li atomic densities and should perform a priori even better than Li_4SiO_4, yet their melting points could not be found in the literature and therefore the authors cannot make any statement about their practical use in a

blanket. However, many of them are being studied for their use as cathode materials for batteries [71], so they may be worth to further, deeper study on their basic thermo-physical properties.

The T breeding performance will be numerically in Section 5 validated using 3D neutronic transport analyses for the compounds listed in Table 1 for the current EU DEMO HCPB solid breeding blanket, as benchmark blanket.

4. Screening and selection of neutron multiplier materials

From a purely neutronics point of view, a good neutron multiplier material is any that has a large $(n,2n)$ cross-section while minimizing the parasitic absorption, mainly (n,γ), and ideally fulfills the basic requirements listed in Section 2. For this, it is useful to plot the relative reaction rate (RRR) of $(n,2n)$ and (n,γ) as function of the elements as shown in Figure 4 [19]. In this figure, the reaction rates have been determined using the characteristic neutron spectrum in a HCLL-type EU DEMO as example. The dark red vertical stripes indicates elements failing to meet the low activation requirement. The exclamation mark on the names of the elements indicates an availability risk and/or elevated cost of the material. The green vertical stripes indicates elements with high $RRR(n,2n)$ and $RRR(n,\gamma)$ of at least 2 orders of magnitude lower than $RRR(n,2n)$ and the elements typed in green are those which $RRR(n,\gamma)$ is at least an order of magnitude lower than $RRR(n,2n)$ and $RRR(n,2n)$ is only about an order of magnitude lower than the maximum achievable (Bi).

When all these factors are taking into account, the choice of a neutron multiplier is largely reduced to just a few of options. Only Be and Pb manage to show a large enough neutron multiplication together with a very low absorption so as to be considered on their own practical neutron multipliers. CUriosly enough, if Ar had the density of a solid or liquid or if it would form compounds, it may probably be also a good neutron multiplier, comparable to Pb. Bi may be slightly better multiplier than Pb but, unfortunately, its activation into the alpha emitter [210]Po prevents it to be considered as functional material.
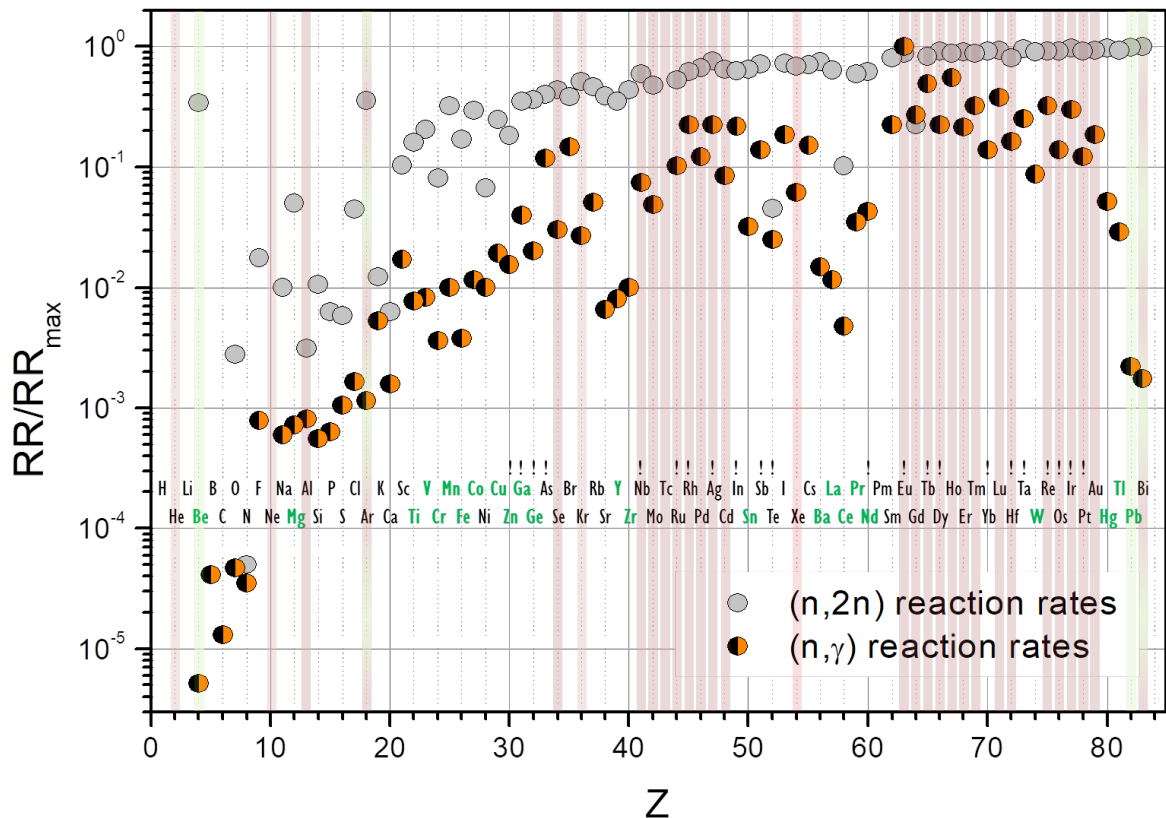
Figure 4. $(n,2n)$ and (n,γ) relative reaction rates for the elements up to Bi (Z=83).

Be on its own, and despite some of the shortcomings mentioned in Section 2, can be used as neutron multiplier in a solid breeding blanket due to its high melting point. However, its use as compound is more desired in order to reduce its reactivity. Elementary Pb could be also used but its melting point is too low and would force its use as liquid multiplier, so alloying is needed keep it in solid state at high temperatures (at least about 1000 °C ÷ 1500 °C).

Fortunately, a relatively large list of elements show a low enough absorption with a high enough multiplication so as to be considered good alloying elements to form Be and/or Pb compounds: Mg, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Ga, Ge, Y, Zr, Sn, Ba, La, Ce, Pr, Nd, W, Hg and Tl.

4.1   Compounds of Be

Eligible compounds of Be are all those that maximize the volume fraction of Be inside the compound. They should have a high melting point (ideally higher than 1000 °C) for an appropriate use in a solid breeding blanket and their melting should be congruent, i.e. the solid and liquid phases have the same composition along the whole range of temperatures.

After a research in different databases of phase diagrams of binary Be alloys, it has been found that Pb form stable compounds with Ti, Cr, W, Zr, Y, V, Mg, Ba, Mn and C, having high and congruent melting points. Figure 5 shows these phase diagrams (retrieved from ASM International[2]) except for C and Mn. For these binary systems, the following are the compounds with the highest Be content with a congruent melting: $Be_{12}Ti$, $Be_{12}Cr$, $Be_{22}W$, $Be_{13}Zr$, $Be_{13}Y$, $Be_{12}V$, $Be_{13}Mg$, $Be_{13}Ba$, Be_2C, $Be_{12}Mn$. The atomic densities, mass and melting point of these compounds are summarized in Table 2.

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[2]http://mio.asminternational.org/apd/index.asp

Table 2. Properties (room temperature, RT) of selected Be compounds as neutron multipliers

Compound	Compound atomic density [at/Å³]	Atomic density of Be [at/Å³]	% Be atomic density	Compound density RT [kg/m³]	Melting point [°C]	Ref.
$Be_{12}Ti$	0.1144	0.1056	92.3	2.28	1520	[23]
$Be_{12}Cr$	0.1188	0.1096	92.3	2.43	1338	[26]
$Be_{22}W$	0.1170	0.1119	95.6	3.23	1520	[26]
$Be_{13}Zr$	0.1104	0.1025	92.8	2.73	1800	[26]
$Be_{13}Y$	0.1043	0.0968	92.8	2.55	1920	[26]
$Be_{12}V$	0.1176	0.1085	92.3	2.39	1700	[23]
$Be_{13}Mg$	0.1066	0.0990	92.9	1.79	960	[26]
$Be_{13}Ba$	0.1186	0.1102	92.9	3.59	1807	[26]
Be_2C	0.1142	0.0762	66.7	1.90	2100	[27]
$Be_{12}Mn$	0.1152	0.1063	92.3	2.40	n/a	[28]
Be	0.1234	0.1234	100	1.85	1285	[29]

$Be_{12}Ti$ and $Be_{12}V$ are well known neutron multipliers, e.g. [20], [21] and [22]. They are known to mitigate some key issues associated with the use of pure Be, namely the slightly low melting point, the radiation induced swelling and oxidation in the presence of water. $Be_{22}W$ can be found mentioned in [22], nevertheless the T breeding performance is shown to be significantly lower than $Be_{12}Ti$. The authors in [22] also mention $Be_{12}Mo$ as a possible option, nevertheless Mo has been discarded in the present work as it does not meet the low activation criteria.

From all the compounds, $Be_{22}W$ shows the highest atomic density in Be. However and interestingly enough, the authors in [22] show that the T breeding performance with this material is significantly lower (30÷40% lower) than with $Be_{12}Ti$. This indicates that the T breeding does not seem to directly correlate with the atomic density and the nature of the alloying element (in this case W) plays a decisive role in the multiplier performance and indeed Figure 4 shows that the $RRR(n, \gamma)$ for W is high.

The melting point of the alloys is higher than pure Be, except for $Be_{13}Mg$ which is rather low for a practical application in a blanket and being $Be_{13}Y$, $Be_{13}Ba$ and $Be_{13}Zr$ the highest among the intermetallics, in that order.

Later in this paper (Section 5), the T breeding performance will be benchmarked using 3D neutronic transport analyses for all these compounds in the current EU DEMO HCPB solid breeding blanket, as benchmark blanket.
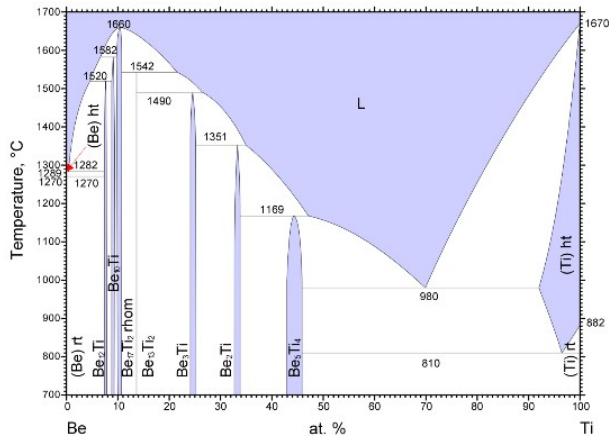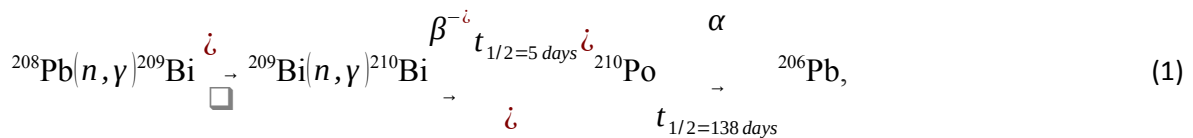
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Figure 5. Phase diagrams of binary Be compounds

4.2 Compounds of Pb

As defined in the last section, eligible compounds of Pb are also all those that maximize the volume fraction of Pb in the compound. However, the key difference is the melting point of Pb compared to Be.

Indeed if a solid neutron multiplier is wanted, the low melting point of Pb forces to look for alloying elements that increase the melting point of the compound. However, the fact of the low melting point of Pb opens also the possibility to think about having a liquid multiplier. A key motivation for that would be the possibility to have a material without a solid structure, making it immune to radiation damage. One may be tempted to think that such material will inherit the MHD issues of liquid metal functional materials, nevertheless another key difference of a liquid Pb multiplier would be the lack of a need to circulate such material at any speed, as virtually no T is produced here, eliminating these concerns. A very low or stagnant Pb would greatly reduce as well the known corrosion issues of flowing liquid Pb or Pb alloys [31]. Additionally, the use of Pb minimizes the problem of the production of ^{210}Po, as this is a two-step process in Pb

$$^{208}\text{Pb}(n,\gamma)^{209}\text{Bi} \xrightarrow{¿}_{\square} {}^{209}\text{Bi}(n,\gamma)^{210}\text{Bi} \xrightarrow[¿]{\beta^{-¿}\, t_{1/2=5\,days}\, ¿} {}^{210}\text{Po} \xrightarrow[t_{1/2=138\,days}]{\alpha} {}^{206}\text{Pb}, \tag{1}$$

and generates 1000 less ^{210}Po than systems using Bi or lead-bismuth eutectic (LBE), where the concern has been originally identified [30], therefore the need for an online ^{210}Po removal would be a matter of discussion, further simplifying the system. On the other side and contrarily than for a solid multiplier, an even lower melting point may be wanted (especially if water is envisaged as the breeding blanket cooling fluid) if a liquid form is pursued and in this case alloying elements that reduce the melting point are therefore desirable.

Compounds for both strategies have been found and are reported in the following Sections 4.2.1 and 4.2.2.

4.2.1 Compounds of Pb for a solid neutron multiplier

Similarily as for Be, different alloy phase diagram databases have been researched and it has been found that Pb forms high and congruent melting point compounds with at least Zr, Ba, Nd, Ce, S, Ca, Y and La. The list could be larger, but some compounds have not been selected due to several reasons. E.g. compounds with alkali metals like $RbPb_3$ or Sr_5Pb_3 are possible, but are likely to be rather reactive with water. Also, compounds with low atomic fraction of Pb, especially if the alloying element does not have an advantageous ratio $RRR(n,2n)$-to-$RRR(n,\gamma)$, are likely to perform poorly, e.g Sc_6Pb_5 (melting point >1200 °C), YbPb (melting point >1100 °C) or PbO (melting point >1600 °C), as it will be shown later in the paper for other selected compounds with higher Pb atomic fractions.

Following the above, the following binary intermetallic alloys have been found: Zr_5Pb_3, Zr_5Pb_4, Ba_5Pb_3, Nd_5Pb_3, Nd_5Pb_4, $CePb_3$, SPb, CaPb, YPb_2, YPb_3, $LaPb_3$, $PrPb_3$ and $SmPb_3$. The atomic, mass densities and melting point of these compounds are summarized in Table 3 and the phase diagrams (except for SPb and CaPb) are shown in Figure 6 (retrieved from ASM International[3]).

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[3] http://mio.asminternational.org/apd/index.asp

Table 3. Properties (room temperature, RT) of selected solid Pb compounds as multipliers

| Compound	Compound atomic density [at/Å³]	Atomic density of Pb [at/Å³]	% Pb atomic density	Compound density RT [kg/m³]	Melting point [°C]	Ref.
Zr_5Pb_3	0.0433	0.0162	37.4	9.69	1650	[33]
Zr_5Pb_4	0.0436	0.0227	52.1	10.33	1200	[33]
Ba_5Pb_3	0.0233	0.0087	37.3	6.32	970	[32]
Nd_5Pb_3	0.0318	0.0119	37.4	8.86	1550	[35]
Nd_5Pb_4	0.0339	0.0151	44.5	9.70	1452	[35]
$NdPb_3$	0.0350	0.0262	75.1	11.13	1106	[35]
$CePb_3$	0.0345	0.0259	75.1	10.91	1170	[26]
SPb	0.0384	0.0192	50.0	7.62	1118	[36]
CaPb	0.0340	0.0170	50.0	6.98	965	[37]
YPb_2	0.0360	0.0240	66.7	10.03	970	[38]
YPb_3	0.0359	0.0269	74.9	10.58	721	[38]
$LaPb_3$	0.0339	0.0225	66.4	10.72	1170	[39]
$PrPb_3$	0.0348	0.0261	75.0	11.03	1120	[26]
$SmPb_3$	0.0354	0.0265	74.9	11.34	1050	[26]
Pb	0.0330	0.0330	100	11.35	325	[40]
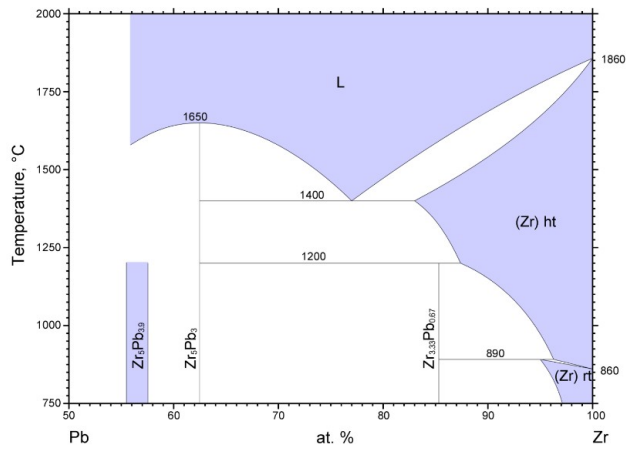
Figure 6. Phase diagrams of eligible Pb compounds (I).

From this list, the only compound that can be found in the literature related to fusion breeding blankets is Zr_5Pb_3. This compound was already proposed in the 1980s for the so-called Starfire US DEMO design [49], but the resulting T breeding performance was rather marginal in comparison to blankets based on Be. However, some research performed during the 90s with the Pb-Zr system showed that the interstitial phase Zr_5Pb_4 also exists [34]. Indeed it will be shown later (Section 5) that Zr_5Pb_4 slightly improves the T production in comparison to Zr_5Pb_3 due to the higher density of Pb. As for the Be compounds, T breeding assessments are also performed with the rest of compounds in Section 5.

4.2.2 Compounds of Pb for a liquid neutron multiplier

Contrarily to the search methodology in Section 4.2.1, here the aim has been to find binary systems of Pb showing an eutectic composition that lowers the melting point of that of pure Pb, while still keeping Pb as the primary multiplying element. Again, a relatively large list of eligible compounds have been found under this criterion, comprising the following alloying elements: Zr, Hg, Ga, Mn, Ba, As, Sn, Sm, Sb and Mg. Table 4 summarizes the atomic, mass densities and melting point of these eutectic alloys and their phase diagrams (retrieved from ASM International[4]) are depicted in Figure 7.

Binary systems of Pb with the alkali metals Li, Na, K and Rb contains also eutectic compositions with attractive melting temperatures of 276 °C, 307 °C, 235 °C and 300 °C respectively. However, they are not further considered due to their reactivity with water, which is believed to rise with increasing period. Pb-Li is a very well known functional material and it is the reference worldwide for liquid metal blankets. Its reactivity with water is only mild and could be taken into account, but due to its dual function as multiplier and breeder, it is not suitable to include this compound in this list.

Table 4. Properties of selected liquid Pb compounds as multipliers

Compound	Compound atomic density [at/Å³]	Atomic density of Pb [at/Å³]	% Pb atomic density	Compound density RT [kg/m³]	Melting point [°C]	Ref.
Pb	0.0330	0.0330	100	11.35	325	[40]
$Pb_{98.5}Zr_{1.5}$	0.0311	0.0306	98.5	11.23	315	[41]
$Pb_{80}Hg_{20}$	0.0329	0.0263	80	11.79	260	[42]
$Pb_{85}Hg_{15}$	0.0324	0.0275	85	11.68	277	[42]
$Pb_{94}Ga_6$	0.0334	0.0314	94	11.02	313	[43]
$Pb_{90}Mn_{10}$	0.0339	0.0305	90	10.81	290	[44]
$Pb_{95}Ba_5$	0.0324	0.0307	95	10.95	290	[32]
$Pb_{93}As_7$	0.0332	0.0309	93	10.92	286	[45]
$Pb_{80}Sn_{20}$	0.0333	0.0266	80	10.48	280	[46]
$Pb_{90}Sm_{10}$	0.0327	0.0294	90	10.93	280	[26]
$Pb_{83}Sb_{17}$	0.0329	0.0273	83	10.53	250	[47]
$Pb_{83}Mg_{17}$	0.0331	0.0275	83	9.69	248	[48]

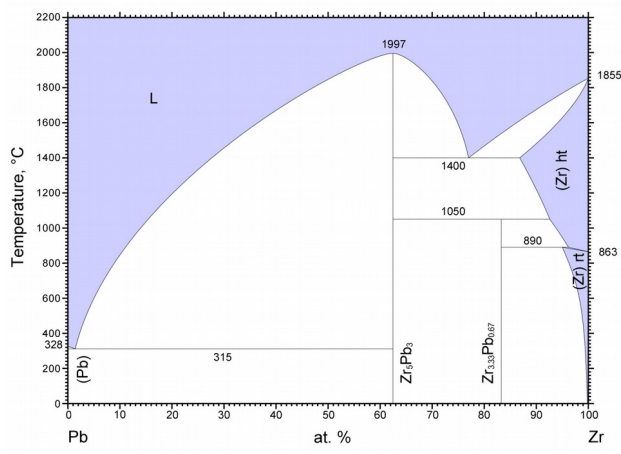[4] http://mio.asminternational.org/apd/index.asp

Figure 7. Phase diagrams of eligible Pb compounds (II).

5. Tritium breeding performance assessment: example for the EU DEMO

For the assessment of the nuclear performance of the selected T breeder and neutron multiplier compounds of Sections 3 and 4, 3D neutron transport analyses with the MCNP5-1.60 code have been performed. The analyses have been run with nuclear data from JEFF-3.2 library on a 1 sector out of the 18 of the current baseline EU DEMO design [5] (Figure 8 left), taking the HCPB concept in its current design [86] as the benchmark solid breeding concept.

The current HCPB breeding blanket concept consists of a series of inboard (IB) and outboard (OB) blanket segments in a multi-module arrangement (Figure 8 right). Each module has a sandwich-like configuration of cooling plates and alternate layers of a T breeder material (11 mm thick layer) and a neutron multiplier (33 mm thick layer). The reference functional materials are Li_4SiO_4 as T breeder and Be as neutron multiplier. Both materials are in a pebble bed form (polydisperse Li_4SiO_4 bed of Ø(0.25÷0.63) mm pebbles and Ø1 mm pebble bed for Be, both with 63% packing factor), which permits a purge gas to sweep the beds to collect and transport the generated tritium out of the modules to the Tritium Extraction and Removal (TER) system.

As reported in [86], two configurations for the breeder zone (BZ) radial thickness have been considered: (1) OB thickness 820 mm, IB thickness 450 mm (version v1) and (2) OB thickness 520 mm and IB thickness 230 mm (version v2). The version v2 optimizes (reduces) the inventory of functional materials, which is of especial importance for Be. A further v3 with 15 mm and 40 mm as breeder and multiplier bed thicknesses respectively is considered in [86] as reference for the HCPB, however, v2 is taken in this study for a better comparison with v1. Further details of the HCPB architecture are reported in [86].
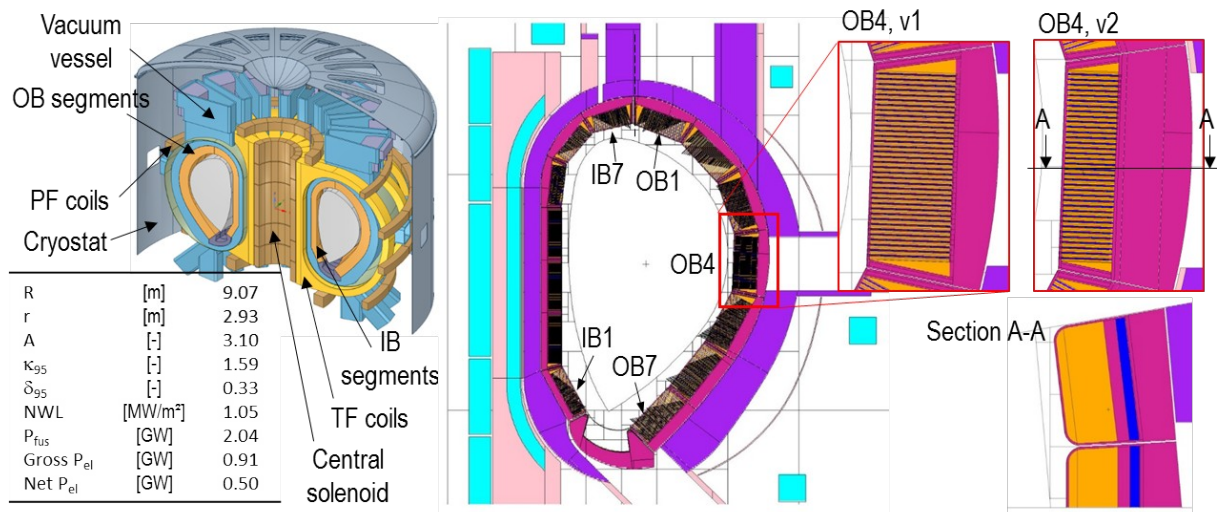

R	[m]	9.07
r	[m]	2.93
A	[-]	3.10
κ_{95}	[-]	1.59
δ_{95}	[-]	0.33
NWL	[MW/m²]	1.05
P_{fus}	[GW]	2.04
Gross P_{el}	[GW]	0.91
Net P_{el}	[GW]	0.50

Figure 8. Current EU DEMO baseline design with main tokamak parameters(left), poloidal-radial cross-section view of the tokamak with close-up views of the equatorial module (right)

For the neutronic modeling of the EU HCPB-DEMO in MCNP5 in this Section, the same methodology as described in [87] has been followed, with the only difference that here a water-cooled has been taken into account instead of the He-cooled one modeled in [87]. Generally speaking, the fact of introducing a water-cooled divertor softens the neutron spectrum globally, worsening the TBR by a factor of ~0.966.

In the present work, the reference functional materials have been systematically substituted by the pre-selected compounds in Sections 3 and 4. Therefore, for the T breeding assessment of T breeders, the Li_4SiO_4 has been substituted by the compounds in Table 1, assuming the v2 configuration and the same form of pebble beds due to the requirement of the T extraction from the T breeder beds. In this case, the reference Be beds have been kept as neutron multiplier and the original layers' thicknesses of the sandwich structure in v2 have not been altered.

In the case of the assessment of the T breeding performance of the different neutron multiplier compounds of Table 2 and Table 3, the original Li_4SiO_4 pebble beds has been left as breeder material. Due to the production of T in the case of Be intermetallic compounds, pebble beds and purge gas for the T extraction and transport is needed. However, the Pb intermetallics have a negligible T production and there is no need for a purge gas sweeping in the material, hence both pebble bed and slabs have been considered for some of these compounds, but the TBR has been calculated in a slab form only when the TBR as pebble bed has been more than 0.9.

5.1 Tritium breeders

Table 5 shows the TBR for the selected potential breeder compounds, which has been sorted by decreasing TBR. It can be observed that the oxo-lithium compounds are generally superior than orto- and meta-lithium ones. Indeed, when the TBR is plotted against the atomic density of Li in the compound (Figure 9 left), a clear positive correlation between both can be observed.

Table 5. T breeding performance of the selected T breeder compounds

Compound	Atomic density of Li [at/Å³]	% Li atomic density	Compound density RT [kg/m³]	Melting point [°C]	^{6}Li enrichment [%]	TBR
Non-ceramics						
Li_3N	0.0674	75.0	1.30	813	60%	1.23
LiF	0.0612	50.0	2.64	848	60%	1.21
Ceramics						
Li_8PbO_6	0.0575	53.4	4.28	>800	60%	1.21
Li_8SiO_6	0.0590	53.3	2.20	830*	60%	1.20
Li_8ZrO_6	0.0591	53.3	2.98	1336	60%	1.20
Li_8GeO_6	0.0567	53.4	2.64	n/a	60%	1.19
Li_8CeO_6	0.0537	53.3	3.25	n/a	60%	1.19
Li_5AlO_4	0.0539	50.0	2.25	1047	60%	1.19
Li_8SnO_6	0.0608	53.3	3.41	1050	60%	1.19
Li_6ZnO_4	0.0609	54.6	2.86	n/a	60%	1.19
Li_6MnO_4	0.0562	54.5	2.50	n/a	60%	1.18
Li_5FeO_4	0.0514	50.0	2.64	n/a	60%	1.18
Li_4TiO_4	0.0444	44.5	2.57	>1000	60%	1.17
Li_6CoO_4	0.0607	53.2	2.77	n/a	60%	1.17
Li_8CoO_6	0.0565	53.3	2.47	n/a	60%	1.17
Li_4SiO_4	0.0482	44.4	2.40	1258	60%	1.15
$Li_6Zr_2O_7$	0.0383	40.0	3.56	1267	60%	1.15
Li_4GeO_4	0.0463	44.9	3.16	1298	60%	1.15
Li_2TiO_3	0.0376	33.3	3.43	1533	60%	1.12

Li₂MnO₂	0.0420	39.9	3.90	n/a	60%	1.12

*Decomposition of the compound before melting

However, the absolute quantity of Li in the blanket is not the responsible *per se* of this behavior. Figure 9-right shows as an example the saturation of the TBR depending on the packing factor of the pebble bed, ranging from 20% to a perfectly solid slab (100%). In this case, the TBR reaches a maximum at values around 60% and drops slightly with packing factors/densities larger than 70%. This indicates that the effect of the other elements in the compound plays also an important role at higher packing factors and that the relative amount of Li content in the BZ plays a central role. A key factor for the importance of a high relative amount of Li in the breeder compound is the fact that Li is a light atom and, as such, it is a very good neutron moderator after its main role as T breeder. This characteristic helps to thermalize the incident neutrons, increasing the probability of further (n, T) reactions, provided that the compound does not have much density of other materials competing for neutron interactions.
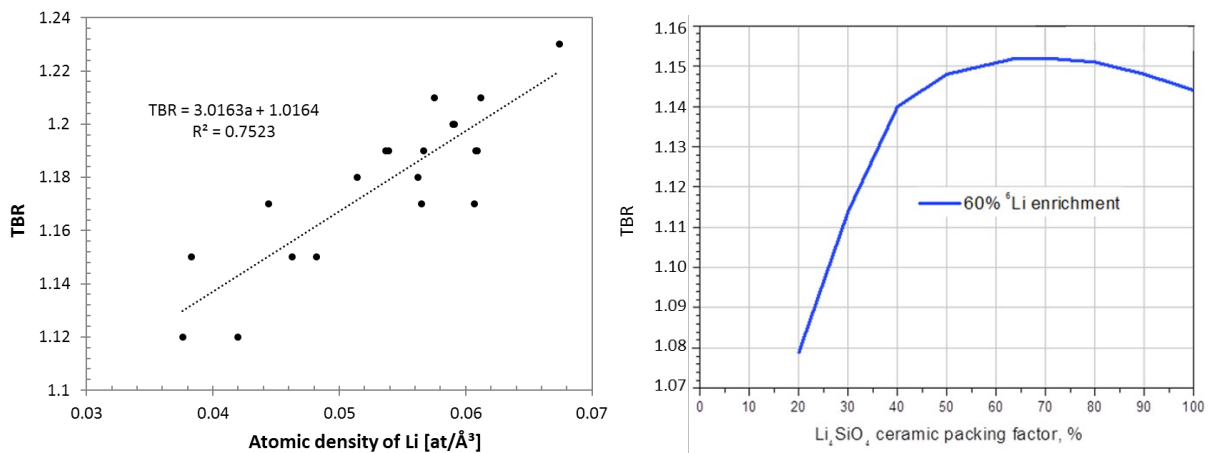

Figure 9. Relationship between TBR and Li atomic density in the compounds (left) and TBR as function of the pebble bed packing factor

The reference breeder compound Li_4SiO_4 already shows a fairly good T breeding performance, being 3% better than Li_2TiO_3, which is the other reference material proposed in several solid breeder blankets in the fusion community. In this respect, mixing Li_4SiO_4 with some additions of Li_2TiO_3 up to 30% as proposed in [50], [51] and [52] should not affect the TBR in a significant way, as shown in Figure 10, and it is expected to reduce the TBR up to less than 1%. As an exercise, and without taking into account the technical feasibility of such mixtures (with the exception of the known Li_2TiO_3), Figure 10 shows the TBR of the reference HCPB with Li_4SiO_4 mixed with increasing amounts of Li_8PbO_6 or Li_8SnO_6. Together with the mixture with Li_2TiO_3, a nearly lineal behavior in the TBR can be observed and therefore, only those mixtures with significantly larger (or lower) TBR will make a sensible effect in the T breeding already at relatively low mixing ratios.
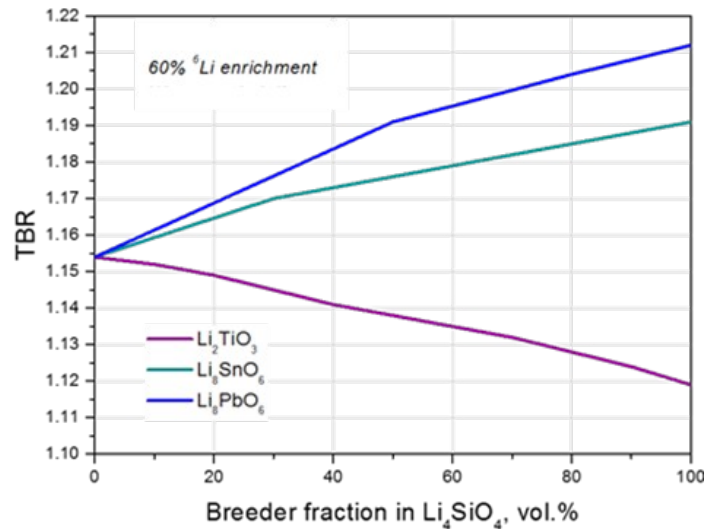
Figure 10. Effect of TBR in the reference HCPB v3 when adding increasing amounts of Li_2TiO_3, Li_8SnO_6 and Li_8PbO_6 to the reference Li_4SiO_4

Li_3N scores the highest in the list, but the presence of N may reduce the attractiveness of this compound due to the increasing production of ^{14}C through $^{14}N(n,p)^{14}C$ in the long run, apart from its relatively modest melting point. LiF is the next most interesting compound in terms of T breeding performance, but it offers practically the same advantage as Li_8PbO_6, Li_8SiO_6 and Li_8ZrO_6. However, LiF presents a risk of dissociation under neutron radiation, potentially releasing highly reactive fluorine.

Among the three best performing ceramics, Li_8ZrO_6 is very attractive in many ways. First, its high melting point (higher than Li_4SiO_4) allows larger bed thicknesses or reduced cooling requirements at the region with highest power densities. It is also a relatively well known compound, whose mechanical properties and irradiation behavior has been already assessed in the past (e.g. [59] and [58]). The only drawback of any lithium zirconate compound may be the long term activation of Zr, nevertheless Zr in Li_8ZrO_6 represents a small volume fraction percent with respect to other zirconates with lower Li densities. Li_8PbO_6 and Li_8SiO_6 may be attractive only for regions at the back of the BZ that are at low temperatures (600 °C÷700 °C).

Several other compounds are also very attractive. The resulting TBR with Li_8GeO_6, Li_8CeO_6 and Li_8ZnO_6 is comparable to that of Li_8ZrO_6. Contrarily to Li_8GeO_6 and Li_8ZnO_6, the activation of Ce in Li_8CeO_6 may be problematic. On the other side, the current resources of Zn and Ga may pose some concern to the use of Li_8ZnO_6 and Li_8GaO_6 in the long term. Another compound worth mentioning is Li_5FeO_4, whose tritium breeding performance is moderately superior to Li_4SiO_4 and may offer a reduced activation, cost effective option. Unfortunately, the melting point of all these compounds could not be found in the literature and therefore no basic judgement can be given about the feasibility of their use in a solid breeding blanket.

5.2 Solid neutron multipliers
The upper part of Table 6 shows the TBR performance with the selected beryllide compounds, together with the reference Be for the comparison. The four best beryllides are then $Be_{12}Cr$, $Be_{12}V$, $Be_{12}Ti$ and $Be_{12}Zr$. From these compounds, $Be_{12}Ti$ is becoming a relatively well known compound, already being proposed by some breeding blanket concepts due to its different advantages in comparison to pure Be in terms of increased T release,

reduced T retention, swelling and reactivity with water, to mention some. $Be_{12}V$ is starting to be thoroughly investigated and recent characterization studies shows even better behavior than $Be_{12}Ti$ in terms of H_2 production, T retention and desorption temperature [24]. The T breeding performance of $Be_{12}Zr$ is equivalent to that of $Be_{12}Ti$, nevertheless the long term activation of Zr may pose questions about its use in the blanket, especially due to the large amount of multiplier required in the blanket (about 200 m³ of bulk multiplier for the HCPB v2). Likewise, $Be_{12}Cr$ and $Be_{12}V$ have an equivalent TBR but given the higher melting point of $Be_{12}V$ and the recent very promising T behavior characteristics and improved safety in this compound, makes it the most attractive among the beryllides.

Even considering the best candidate, $Be_{12}V$, the TBR is significantly lower (about 5%) when compared to the reference Be. However, the TBR assessment has been performed taking into account the cooling plate configuration of the HCPB v2, which is appropriate for Be but it is not necessarily suitable for beryllides. Indeed the maximum Be layer thickness is driven by the maximum temperature that this material is able to withstand under neutron radiation, which is about 650 °C [86]. However, $Be_{12}Ti$ and $Be_{12}V$ seems to shift this limit up to 900 °C [24] and therefore larger bed thicknesses would be possible, reducing the TBR difference with respect to Be.

Table 6. T breeding performance of the selected solid neutron multiplier compounds

Compound	Atomic density of NMM [at/Å³]	% Be or Pb atomic density	Compound density RT [kg/m³]	Melting point [°C]	^6Li enrichment [%]	TBR pebble bed form	TBR slab form
Beryllide intermetallics							
$Be_{12}Cr$	0.1096	92.3	2.43	1338	60%	1.09	n/a
$Be_{12}V$	0.1085	92.3	2.39	1700	60%	1.09	n/a
$Be_{12}Ti$	0.1056	92.3	2.28	1520	60%	1.08	n/a
$Be_{13}Zr$	0.1025	92.8	2.73	1800	60%	1.08	n/a
$Be_{13}Y$	0.0968	92.8	2.55	1920	60%	1.07	n/a
$Be_{13}Mg$	0.0990	92.9	1.79	960	60%	1.07	n/a
$Be_{13}Ba$	0.1102	92.9	3.59	1807	60%	1.06	n/a
$Be_{12}Mn$	0.1063	92.3	2.40	n/a	60%	1.02	n/a
Be_2C	0.0762	66.7	1.90	2100	60%	1.00	n/a
$Be_{22}W$	0.1119	95.6	3.23	1520	60%	0.94	n/a
Be (ref.)	0.1234	100	1.85	1285	60%	1.15	n/a
Plumbide intermetallics							
$LaPb_3$	0.0225	66.4	10.72	1170	60%	0.85	n/a
					90%	0.94	1.02
YPb_3	0.0269	74.9	10.58	721	60%	0.86	n/a
					90%	0.94	1.00
YPb_2	0.0240	66.7	10.03	970	60%	0.85	n/a
					90%	0.93	0.98
$CePb_3$	0.0259	75.1	10.91	1170	60%	0.83	n/a
					90%	0.92	0.97
Zr_5Pb_4	0.0227	52.1	10.33	1200	60%	0.84	n/a
					90%	0.93	0.96
Zr_5Pb_3	0.0162	37.4	9.69	1650	60%	0.82	n/a
$PrPb_3$	0.0261	75.0	11.03	1120	60%	0.82	n/a

NdPb₃	0.0262	75.1	11.13	1106	60%	0.81	n/a
Nd₅Pb₄	0.0151	44.5	9.70	1452	60%	0.74	n/a
Nd₅Pb₃	0.0119	37.4	8.86	1550	60%	0.72	n/a
Ba₅Pb₃	0.0087	37.3	6.32	970	60%	0.76	n/a
SPb	0.0192	50.0	7.62	1118	60%	0.75	n/a
CaPb	0.0170	50.0	6.98	965	60%	0.73	n/a
SmPb₃	0.0265	74.9	11.34	1050	60%	0.66	n/a
Pb (ref.)	0.0330	100	11.35	325	90%	n/a	1.02

The lower part of Table 6 shows the T breeding performance with the selected plumbide compounds, showing as well Pb as a reference for the comparison. Clearly, Pb is not as efficient as Be at the given enrichments and pebble bed configuration of v2. However, the table already offers a good relative comparison basis and it can be identified that $LaPb_3$, YPb_3, YPb_2, $CePb_3$ and Zr_5Pb_4 are the most promising compounds, in this order. The melting point of YPb_3 is yet probably too low for a practical use as a solid multiplier. For the first five best performant compounds, the TBR has been also assessed with a 90% ^6Li enrichment, boosting the TBR about 10%. This confirms the need of such an enrichment for plumbide compounds, which is in line to the ^6Li enrichment of the current proposed liquid eutectic $Li_{17}Pb_{83}$ blankets worldwide.

In order to evaluate the potential of the plumbide intermetallics, a parametric study has been performed, considering the most promising solid multiplier plumbide compound, $LaPb_3$. In a first step, a better configuration for the BZ radial depth has been assessed and the results are plotted in Figure 11-left. Here it can be seen that significant larger TBR performances are still possible by extending the BZ depth: extending only the OB BZ 300 mm with respect to the depth in v2 a TBR increment of 0.06 is obtained, while extending the IB BZ about 220 mm, an additional TBR increment of 0.04 can be achieved. In total, setting a v1-like configuration for $LaPb_3$ brings the TBR to an acceptable 1.10.

Additionally, further T breeding performance improvements can be achieved by choosing appropriate thicknesses of the ceramic and plumbide multiplier beds. Figure 11-right shows the results of a parametric analysis of the TBR with $LaPb_3$ as function of the multiplier and breeder bed thicknesses. It can be observed that for increasing breeder bed thicknesses, higher TBR maxima can be achieved for a certain multiplier bed thickness. The reason for the positive effect is the fact that the plumbides are not efficient moderator materials, contrarily as Be or beryllides, and therefore this function is undertaken by the Li atoms in the breeder bed, accelerating the thermalization of the neutron field in the BZ.
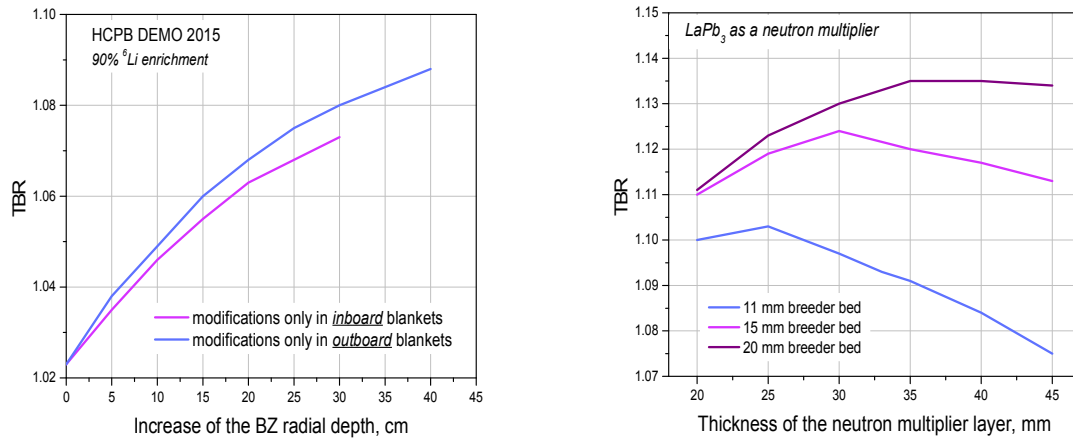
Figure 11. TBR as function of the radial thickness of the BZ (left) and TBR as function of the multiplier and breeder beds thicknesses for LaPb$_3$

In this respect, selecting a breeder bed thickness of 20 mm (maximum thickness about which the temperature of the reference breeder material reaches its design maximum) and a LaPb$_3$ multiplier bed thickness of 40 mm, a further TBR boost up to 1.14 can be achieved, a comparable performance to that of the reference HCPB v2 with Be.

As a final note, *Figure 12* depicts the relationship between TBR and the atomic density of Be in the beryllides (left) and of Pb in the plumbides (right). Due to the very large parasitic absorption of W in Be$_{22}$W and Sm in SmPb$_3$, these alloys score significantly worse than the rest and they have not been included in the fitting lines, as they have been considered as outliers. Similarly to the Li compounds, there is a dependence on the Be and Pb atomic density for beryllides and plumbides, though the effect is less pronounced in the beryllides, indicating that the alloying element is of key importance in the T breeding performance of the blanket with these compounds than for plumbides.
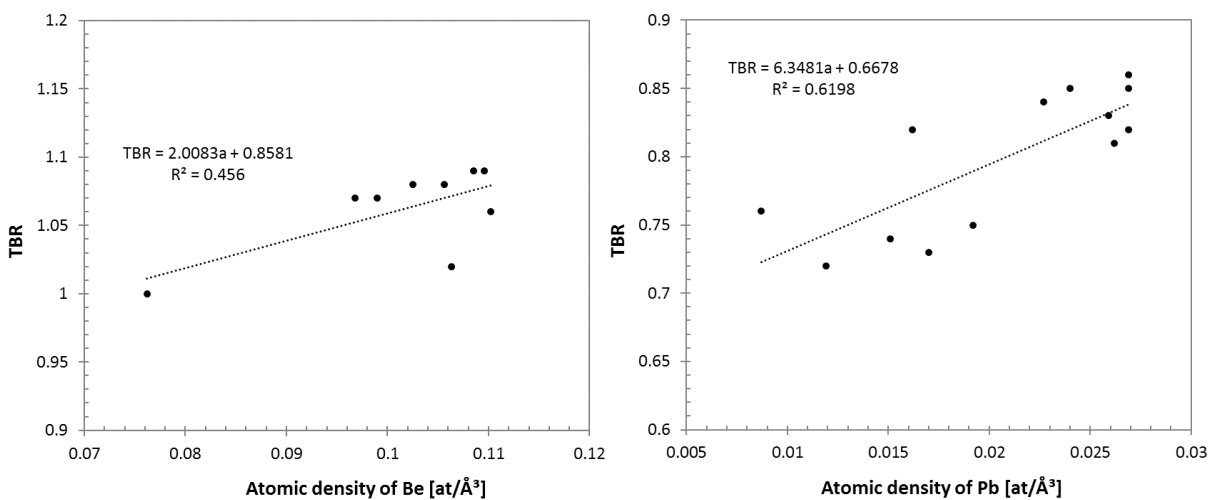

Figure 12. Relationship between TBR and Be atomic density (left) and Pb atomic density (right) in the intermetalic compounds

5.3   Liquid neutron multipliers

The TBR studies with the liquid neutron multipliers have been performed assuming the optimized configuration found for LaPb$_3$ in the last Section 5.2, which is assumed to be representative for all Pb-alloys in general. Table 7 shows the T breeding performance with each of the selected liquid Pb-alloy multiplier compounds.

Table 7. T breeding performance of the selected liquid neutron multiplier compounds

Compound	Atomic density of Pb [at/Å^3]	% Pb atomic density	Compound density RT [kg/m^3]	Melting point [°C]	^{6}Li enrichment [%]	TBR
Pb$_{98.5}$Zr$_{1.5}$	0.0306	98.5	11.23	315	90%	1.14
Pb$_{94}$Ga$_6$	0.0314	94	11.02	313	90%	1.13
Pb$_{90}$Mn$_{10}$	0.0305	90	10.81	290	90%	1.13
Pb$_{95}$Ba$_5$	0.0307	95	10.95	290	90%	1.13
Pb$_{85}$Hg$_{15}$	0.0275	85	11.68	277	90%	1.10
Pb$_{80}$Sn$_{20}$	0.0266	80	10.48	280	90%	1.09
Pb$_{80}$Hg$_{20}$	0.0263	80	11.79	260	90%	1.08
Pb$_{93}$As$_7$	0.0309	93	10.92	286	90%	1.08
Pb$_{83}$Mg$_{17}$	0.0275	83	9.69	248	90%	1.02
Pb$_{90}$Sm$_{10}$	0.0294	90	10.93	280	90%	1.01
Pb$_{83}$Sb$_{17}$	0.0273	83	10.53	250	90%	1.00
Pb (ref.)	0.0330	100	11.35	325	90%	1.15

First, pure Pb results in a TBR performance which is as good as for the reference HCPB v2 with Be. From the Pb-alloys, the best performing are Pb$_{98.5}$Zr$_{1.5}$, Pb$_{94}$Ga$_6$, Pb$_{90}$Mn$_{10}$ and Pb$_{95}$Ba$_5$, which are practically at par with pure Pb. The activation problem of Zr in Pb$_{98.5}$Zr$_{1.5}$ may be reduced as for its beryllide counterpart due to the very low fraction of Zr in the alloy. However, the reduction of melting point is not much significant. In this respect, Pb$_{90}$Mn$_{10}$ and Pb$_{95}$Ba$_5$ are more attractive, as the melting point is reduced below 300 °C, which would minimize the problem with phase change during operation. Yet, Pb$_{95}$Ba$_5$ may rise a question about its reactivity with water, probably making Pb$_{90}$Mn$_{10}$ the best choice among the Pb compounds.

The Li atomic density has a certain influence on the TBR as shown in Figure 13, though weak, meaning that the alloying element is playing in these cases a relatively sensible role.
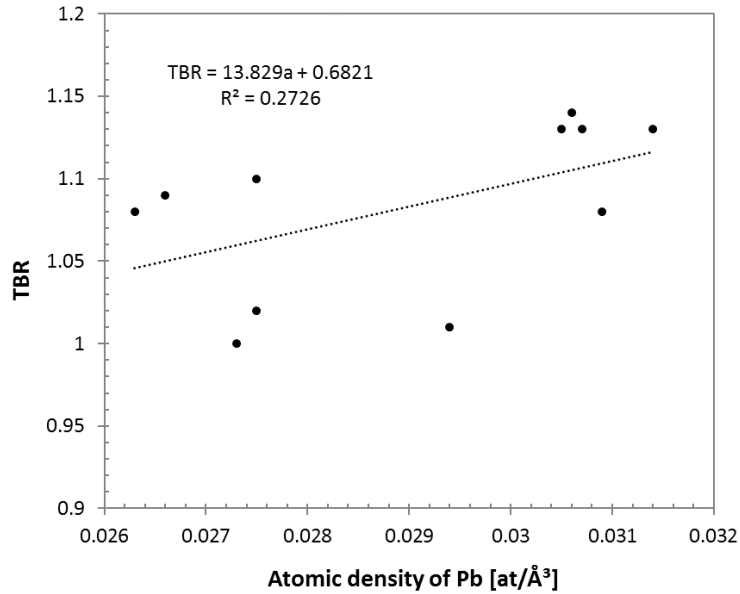
Figure 13. Relationship between TBR and Pb atomic density in the liquid Pb-alloy compounds

6. Summary, conclusions and outlook

This paper has reviewed the options available for T breeder and neutron multiplier from first principles, beginning from a brief recap on basic functions and requirements of these functional materials and performing then an exhaustive screening on the possible elements and compounds that can accomplish such conditions.

For T breeding, and although other elements have a certain sensible T production, the key element is the well known Li and its compounds. In this respect, two types of compounds, ceramic and non-ceramic, have been identified, the former being the most numerous, known and promising. Taking as a reference the current EU DEMO HCPB breeding blanket for the comparison (Li_4SiO_4 as breeder, Be as multiplier, TBR=1.15), several Li ceramics have been found largely outperforming the reference Li_4SiO_4. Among them, Li_8ZrO_6 is highlighted due to its high T breeding performance (1.20) and high melting point. Moreover, this compound has been relatively well characterized in the past, also under neutron irradiation. Other high performing options have been identified as well (Li_8PbO_4, Li_8SiO_6), though they may be only be used in regions of the BZ with lower temperatures due to their low melting or dissociation points.

As for multipliers, the screening has revealed two practical types: the known beryllides (including Be) but also novel plumbides (including Pb). Particularly, the low melting point of Pb has motivated to propose a better classification of neutron multipliers depending on their aggregate state during the operation in the blanket, i.e. solid and liquid neutron multipliers. In this respect and regarding solid multipliers, a list of beryllide and plumbide compounds have been found. As for beryllides, $Be_{12}V$ and $Be_{12}Ti$ offers the best T breeding (1.09 and 1.08 respectively) after Be. For plumbides it has been demonstrated that a more adequate BZ configuration than the reference HCPB v2 is needed, with a larger BZ, multiplier slabs instead of pebble beds and larger ^6Li enrichments (90%). After the appropriate changes, it has been found that $LaPb_3$ (TBR=1.14) can be contender to Be and beryllides. Regarding liquid multipliers, plumbides (best TBR=1.14) and pure Pb (TBR=1.15) are also remarkable options. From the (liquid) plumbides, $Pb_{90}Mn_{10}$ (TBR=1.13) offers an interesting alternative to Pb due

to its low melting point (290 °C) and comparable breeding performance (TBR=1.13), especially if water cooling and/or a typical coolant inlet temperature around 300 °C is envisaged.

After the present research, the authors highlight the following conclusions and recommendations:

- Despite the current reference Li_4SiO_4 breeder material offers a fairly good T breeding performance, some oxo-lithium compounds score significantly better. In particular, a further investigation of Li_8ZrO_6 is highly recommended in view of the higher melting point and possible better thermal conductivity and mechanical properties.
- Despite the apparent poorer TBR performance of the beryllides in comparison to pure Be, the higher design temperature limit of beryllides (900 °C vs 650 °C) can compensate the TBR, as larger bed thicknesses are possible for comparable thermal conductivity values at their respective highest temperatures. In this way, a reduced sacrifice in TBR performance will be compensated by key safety and functional advantages that beryllides have in front of pure Be.
- Some plumbide compounds (e.g. $LaPb_3$ and YPb_2) are credible contenders to Be-based solid multipliers, offering a very similar performance but with the key advantages of: (1) larger availability, (2) reduced toxicity, (3) more cost effective and safer, (4) non-T breeding and therefore no need for T-extraction and purging in mutliplier, (5) simpler production with slabs (no need pebble bed form).
- For a best T breeding performance, solid plumbide multipliers should be used in slab form. This raises a question to ensure the thermal contact to the surrounding structural steel. A possible solution could be to have an interfacial pebble bed layer of a few mm made by the same or other materials with low neutron interaction (graphite, SiC…) to ensure such contact. Such layer would act as a compliant (pebble bed) layer to accommodate the differential thermal expansion between both materials, ensuring a thermal contact and a controlled heat transfer between them.
- The liquid plumbide multipliers may have a competitive advantage against the solid ones due to their assembly and functional simplicity. As they do not require to keep a structural form during operation, they are immune to neutron irradiation and they eliminate the problematic with thermal contact issues with the surrounding structures.
- Blankets based on Pb or plumbide neutron multipliers needs larger BZ depths to reach comparable TBR performance as blankets based on Be or beryllide multipliers, which will penalize the weight of the blanket. However, it has been shown that increasing the presence of a moderating material in the BZ rapidly enhances the TBR with Pb and plumbides. This indicates that the quantity of Pb or plumbide multiplier may be potentially reduced at the back of the blanket by substituting it by a moderator material. The moderator should act as well as neutron reflector, improving the neutron economy and the shielding characteristics. Used in combination with a high T breeding materials like Li_8ZrO_6, Pb or plumbide-based blankets can be engineered with similar BZ depths as with Be/beryllide-based ones, obtaining equivalent TBR performances.
- Due to the large potential benefits of the high T breeder performance materials and the Pb-based neutron multipliers, dedicated R&D programs are recommended to bridge current knowledge gaps in the thermo-physical, material compatibility and, where applicable, T transport characterization in these compounds, in order to be able to have a last word on their technical feasibility in a blanket. These programs should culminate

with dedicated in-pile irradiation campaign, so as to understand the behaviour of the selected compounds under DEMO relevant in-pile conditions.

To conclude, the results of the present research can bring enhancements and new ideas to the current solid breeding blankets and opens the possibility for a new generation of more cost effective solid and hybrid solid/liquid breedingblankets with enhanced safety features. Future research will be then conducted to apply some of these findings to revise and realize innovative, improved breeding blanket concepts.

Acknowledgments

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