Neutronics of MAX phase materials

Christopher Grove, Daniel Shepherd, Mike Thomas, Paul Little
National Nuclear Laboratory, Preston Laboratory, Springfields, UK

Abstract

This paper examines the neutron absorption properties of atomic elements that have been identified as constituents of MAX phase materials and provides a method to estimate the neutron absorption properties of any MAX phase material. A literature review identified 24 possible constituent elements across the MAX phase group of materials; for each element, an analysis was performed to identify neutron absorption properties – elements were modelled in the core of both a thermal-spectrum and fast-neutron spectrum reactor system. The neutron absorption of each element is quantified relative to currently used cladding materials (zirconium-alloy for thermal systems and stainless-steel for fast systems) and elements are ranked relative to each other. Further analyses were performed in order to identify each individual element's sensitivity to neutron absorption with change in single-element-material density; this data was then used in combination with a method developed to estimate the neutron absorption properties of any MAX phase material. An analysis of the neutron activation of individual element is also presented.

The study has identified lowest absorption elements: Zr and Cr ('M' elements), Bi and Pb ('A' elements) and C ('X' elements). Highest neutron absorption elements were identified as: Hf and Ta ('M' elements), In, Cd, As ('A' elements) and N ('X' elements). Therefore, of currently known or postulated MAX phase materials, Zr_2PbC is estimated to have the lowest neutron absorption. However, reactor components, when manufactured to the required mechanical robustness, would not necessarily have the lowest overall neutron absorption due to the effects on neutron absorption of material mass and density – an increase in either will result in an overall increase in neutron absorption.

Introduction

MAX phase materials have been identified as potential materials for use in current and future reactor systems. They have desirable properties that make them potentially suitable including: high thermal conductance, mechanical robustness, damage tolerant, resistant to thermal shock. This study examines the potential of MAX phase materials for use primarily as fuel cladding for advanced fuels, in addition to potential structural and control rod material applications. As well as structural/mechanical properties of the materials, the neutron interaction properties of the materials need to be considered; low neutron absorption is desirable for clad and core component structural materials and high neutron absorption is desirable for control rod materials. If neutron absorption of clad material is too high, there is a detrimental effect on the performance of the reactor.

The ideal clad material is one that is extremely robust mechanically, chemically inert and has high neutron transparency. The purpose of this study was therefore to identify low and high neutron absorbing MAX phase materials ahead of materials being developed specifically for use in nuclear reactors.

Due to the number of 'MAX phases' identified, it was decided not to attempt to model each material individually. An alternative approach was adopted in that each individual element was modelled as a single-element-material forming the cladding material in a reactor. The individual elements included were identified from lists of MAX phases given in reference [1] and [2]. In addition, It was discovered that a new set of MAX phase materials had been synthesised using bismuth as a constituent element [3]. Bismuth is a post-transition metal, falling into the 'A' category of MAX phase elements. In the newly synthesised materials, Bi was present as a substitutional constituent of the 'A' element of MAX phases, partially taking the place of another majority 'A' element. Natural Bi consists of a single quasi-stable nuclide Bi-209 (half-life ~10^{19} years) and therefore elemental Bi is modelled as this single nuclide.

The comprehensive list of MAX phase constituent elements plus bismuth comprises twenty four elements in total. The neutron absorption of each element is examined through modelling of the clad material in a reactor model. The clad material is changed to consist of 100% natural composition of the element. The effect on the neutron multiplication factor, k, is then examined. In addition, the radiation through neutron activation is examined for each element.

The method also examined the sensitivity to a change in density of the neutron absorption properties of each individual element. Once these data have then been obtained, it is possible to estimate the overall level of neutron absorption for any MAX phase material - if the density of the material and its constituent elements are known.

Method

To calculate the thermal spectrum absorption properties of MAX phase materials the neutron lattice code CASMO-5 [5] was used for thermal reactor systems calculations and ERANOS [6] was used for fast reactor systems.

Whilst modelling a clad as consisting of a single element is physically non-sensical, data obtained from this initial part of the method is used to estimate the neutron absorption properties of MAX phase materials – comprising of elements examined in the initial part of the study. The benefit of this method is that it allows the neutron absorption of any MAX phase element to be estimated, without implicit modelling, provided that the material's constituent elements and density are provided.

Table 1: Identified constituent elements of MAX phase materials

M	A	X
Sc	Al	C
Ti	Si	N
V	P	
Cr	S	
Zr	Ga	
Nb	Ge	
Mo	As	
Hf	Cd	
Ta	In	
	Sn	
	Tl	
	Bi	
	Pb	

The input parameters of the modelling tools in use all require materials to be broken down into constituent nuclides: therefore the structure and element phases etc. of a compound would have no bearing at all on the results obtained – only the constituent nuclides and material density have any effect. It should be noted that experimental data for MAX phase densities are often scarce [4] and they are difficult to predict *ab initio* due to their complex crystal structures. Modelling individual nuclides should enable a 'tool kit' for estimating the neutron interaction properties of any MAX phases in existence – or yet to be discovered.

In addition to neutron transparency of material, the FISPIN code [7] has been used to consider the neutron activation behaviour in a similar manner. FISPIN is capable of modelling the neutron interactions and decay processes that occur in a material. When exposed to a neutron flux, materials may become activated potentially leading to creation of nuclides that form a radiation hazard persisting after the material's exposure to the neutron flux, experienced during operation of the reactor, has ceased. For example, neutron activation of Cr-59 present in some steels leads to creation of Cr-60, a gamma emitter with half-life of ~5.3 years.

Considering cladding materials, obviously, the radiation field from the spent fuel contained within vastly dominates anything emitted from the cladding and therefore neutron activation will only be of concern in reprocessing scenarios where the clad is separated from the spent fuel post-discharge from the reactor. However, for materials with the potential to be otherwise used in the structure of the reactor core, it is important to consider the effects of neutron activation as use of such materials may have implications for plant maintenance and decommissioning operations.

Neutron absorption calculations – thermal spectrum

The lattice code CASMO-5 has been used to model an infinite 2-D array of typical PWR fuel assemblies. The standard Zircaloy clad material is replaced with each MAX phase element in a series of runs. The neutron multiplication factor for the infinite array (K_{inf}) is examined in each run. As the fuel composition and all other parameters remains consistent between runs, only the neutron

absorption properties of the clad effect the K_{inf} value. A K_{inf} value below that achieved with Zircaloy clad indicates the element tested has a higher neutron absorption and vice-versa.

The neutron absorption properties of a material at the very beginning of the reactor cycle (BOC) – when the fuel contains no fission products or non-uranium actinides - may be different from that after a period of irradiation: the neutron flux in the core may interact with isotopes in the clad which causes them to transmute to other isotopes which may have higher or lower neutron absorption characteristics. For this reason, the assembly is depleted to simulate irradiation in the reactor core. The value of K_{inf} after the fuel reaches a burn-up of 50 GWd/tHM (EOC) is examined.

Although the clad materials modelled, in most cases, are physically nonsensical the modelling gives an insight into the element's neutron absorption properties when included as part of a clad material. To test an element's sensitivity to change in density, CASMO-5 has also been used to carry out three sets of the runs for three different clad densities. The nuclear data library used with CASMO is based on ENDF/B-VII Rel. 0.

Neutron absorption calculations – fast spectrum

The method for fast spectrum calculations is broadly similar to that for thermal spectrum calculations. An ERANOS full core R-Z model of a Sodium-cooled Fast Reactor reactor is used. The steel clad material is replaced with each element from the MAX phase list in a series of runs. The value of K_{eff} is examined (K_{eff} as opposed to K_{inf} as a discrete core model is used rather than an infinite array) at the beginning of an irradiation cycle (BOC) and after 2000 days irradiation.

Generally, neutron absorption in a fast spectrum is lower than that for thermal due to the large reduction in capture cross-section with increasing neutron energy. The fast spectrum results are expected to show less variation in K_{eff} than thermal spectrum results. The underlying nuclear data library used for the fast spectrum calculations is based on JEF 2.2.

Neutron activation calculations

In core irradiation leads to transmutation of isotopes in the clad material. The clad material will generate a radiation field, the strength and type of which will depend upon the level of total transmutation and the precise isotopes created. The radiation emitted from an element is calculated using FISPIN. The materials are modelled experiencing a typical in-core neutron flux lasting for the duration of a typical fuel element dwell time.

The radioactivity of the clad material following irradiation has been modelled using NNL's fuel inventory code 'FISPIN'. Although neutron absorption cross-sections are typically much lower at fast spectrum neutron energies, fast reactors irradiate fuel to much higher burn-up than thermal reactors. The thermal spectrum modelled is that from a PWR, taking fuel to a burnup of 50 GWd/tHM. The fast spectrum is for an SFR and simulates fuel burnup of 150 GWd/t. For this reason, activation in the fast spectrum results is expected to be higher as the clad experiences much greater total neutron flux during its time in the core.

Material degradation and changes in material properties due to transmutation of nuclides and/or irradiation damage are additional issues to be considered in the selection of materials for nuclear applications, however, consideration of these issues are beyond the scope of this study.

Results – Neutron Absorption

Figures 1 and 2 show the calculated values of neutron multiplication for the thermal and fast cores respectively at beginning of cycle (BOC) and end of cycle (EOC) with lines included for the reference zirconium alloy and steel cladding materials respectively at the same clad thickness. Where the bars exceed the line, this indicates lower neutron absorption than the same thickness of reference clad and indicates higher absorption when the bars are below the line. The clad material is modelled as consisting entirely of the natural composition of each element listed. No changes have been made to any other aspect of the model between cases.

Figure 1 : K_{inf} values for MAX phase constituent elements in thermal spectrum

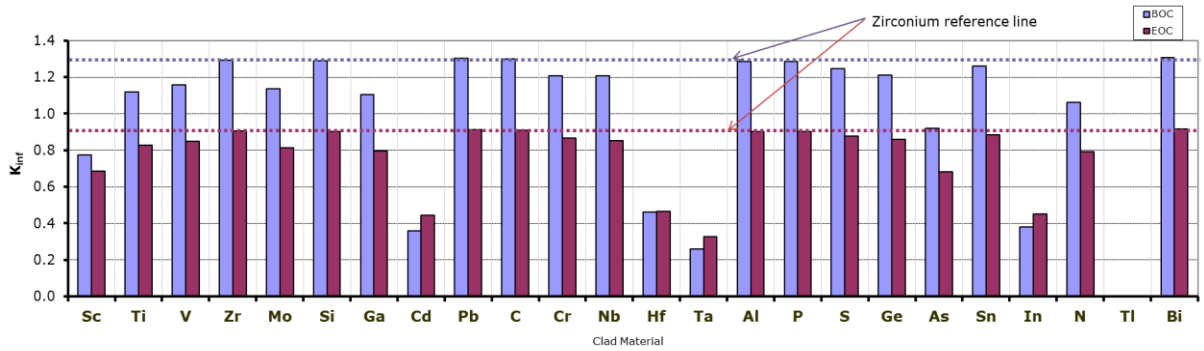
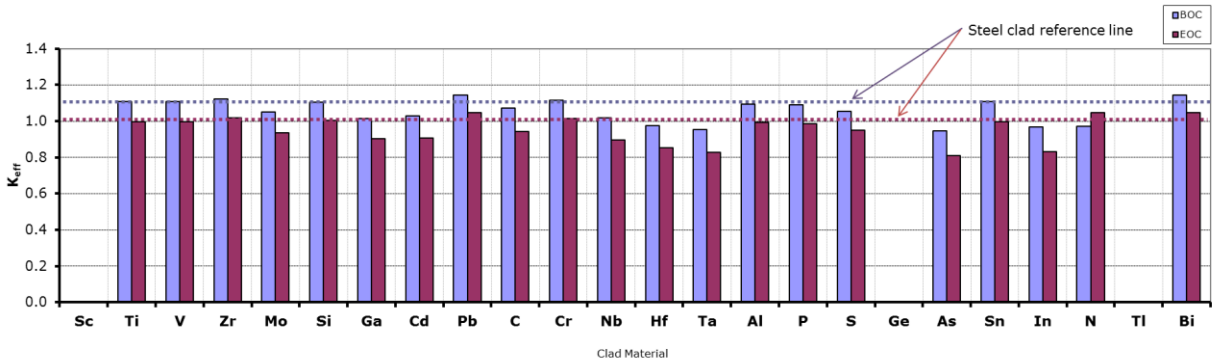


Figure 2 : K_{eff} values for MAX phase constituent elements in fast spectrum



Note that neutron multiplication values should not be compared between the thermal and fast cases as the core geometry, operation, power etc. are completely different between the two models.

As some of the elements modelled are not usually relevant to in-core reactor materials, there is some missing data in the libraries used to provide the underlying neutron cross-section data for use with the codes. Where data was lacking, the requested element could not be included in the model. For CASMO-5, the only element of the twenty three which could not be modelled was thallium (Tl). For ERANOS, scandium (Sc), germanium (Ge) and thallium (Tl) could not be modelled. For this reason, Tl is not included in Figures 1 and 2. Sc and Ge data in Figure 2 is also missing. In practice, thallium would be unlikely to be used owing to its toxicity.

To obtain an estimation of the neutron absorption properties of elements missing from the data libraries used by CASMO and ERANOS, the neutron capture cross-section at a single, representative, thermal and fast energy is obtained. For thermal energy cross-sections values are obtained at 0.025

eV; fast spectrum cross-sections, at 1 MeV. These values are obtained via interrogation of major libraries (ENDF/B-VII, JEF 3.2, JENDL4.0). An estimate of the K_{inf}/K_{eff} values that would have been obtained had the data been included in the relevant libraries has been made.

Table 1 shows the current clad K_{inf}/K_{eff} values divided by the same value for the currently used cladding material; a value greater than 1 therefore indicates lower neutron absorption properties, whilst a value less than one indicates the material has higher neutron absorption properties. Elements are ranked by thermal-spectrum BOC k_{inf} with the most neutron transparent element at the top; 'M' elements are highlighted in grey. As can be seen, there are relatively few MAX phase elements that offer a benefit in terms of increased neutron transparency.

Table 1 : Element neutron multiplication value/current clad neutron multiplication value

	Thermal		Fast	
	BOC	EOC	BOC	EOC
Bi	1.0107	1.0112	1.0341	1.0412
Pb	1.0085	1.0090	1.0358	1.0431
C	1.0067	1.0038	0.9696	0.9364
Zr	1.0007	1.0006	1.0153	1.0145
Si	0.9978	0.9987	0.999	0.9987
Al	0.9943	0.9959	0.9884	0.9881
P	0.9936	0.9976	0.9853	0.9823
Sn	0.9760	0.9791	1.0009	0.9935
S	0.9645	0.9702	0.9528	0.9465
Ge	0.9363	0.9518	0.9602*	
Cr	0.9352	0.9586	1.0097	1.0081
Nb	0.9341	0.9421	0.9223	0.8933
V	0.8950	0.9369	1.0012	0.9915
Tl	0.8825*		0.9628*	
Mo	0.8784	0.8977	0.9507	0.9324
Ti	0.8670	0.9163	1.0023	0.9912
Ga	0.8542	0.8784	0.9184	0.8979
N	0.8221	0.8751	0.8788	0.8495
As	0.7116	0.7538	0.8553	0.8069
Sc	0.5988	0.7575	0.9680*	
Hf	0.3583	0.5130	0.8826	0.8475
In	0.2940	0.4997	0.8762	0.8278
Cd	0.2773	0.4926	0.9295	0.9020
Ta	0.2010	0.3619	0.8639	0.8244
Current	1.0000	1.0000	1.0000	1.0000

*Indicates value estimated by other means

Table 2 shows the elements ranked from highest neutron transparency to lowest for both the fast and thermal spectrum results. The table predicts that the best clad material, from a neutronics perspective, would be Zr_xPb_xC for both thermal and fast reactors (although including Bi as a partial consitituent of the 'A' element ; $Zr_2(Pb,Bi)C$ would be better in a thermal reactor). The worst combinations would be Ta_xCd_xN for thermal reactors and Ta_xAs_xN for fast reactors, though these would be the best combinations for control rod applications.

To allow direct comparison of neutron absorption, these results have been prepared with a standard material density. However, the material density and the material properties (for example, minimum thickness of the clad that could be used) effect neutron absorption and therefore play an important role in determining the suitability of clad material.

Table 2 : Ranking of MAX phase elements by neutron absorption (thermal and fast)

Thermal			
Rank	**M**	**A**	**X**
1	Zr	Bi	C
2	Cr	Pb	N
3	Nb	Si	
4	V	Al	
5	Mo	P	
6	Ti	Sn	
7	Sc	S	
8	Hf	Ge	
9	Ta	Ga	
10		Tl	
11		As	
12		In	
13		Cd	

Fast			
Rank	**M**	**A**	**X**
1	Zr	Pb	C
2	Cr	Bi	N
3	Ti	Sn	
4	V	Si	
5	Sc	Al	
6	Mo	P	
7	Nb	Tl	
8	Hf	Ge	
9	Ta	S	
10		Cd	
11		Ga	
12		In	
13		As	

Variation with density

For the thermal spectrum results, the modelled clad materials were given a density of 6.5 g/cm^3 (approximately the material density of typical zirconium-alloy clad). To test the sensitivity to density, a series of sensitivity runs were performed changing the density of the modelled clad material. Clad density was varied between 1 g/cm^3 and 10 g/cm^3. The change in reactivity with change in material density (reactivity density coefficient) was then calculated in units of pcm/g/cm^3. The results have been plotted in Figure 3 against the BOC K_{inf} values (calculated with material density of 6.5 g/cm^3).

The higher the initial K_{inf} value, then the lower the sensitivity to change in material density. Note that these values are unique to this particular core configuration and are not applicable to a fast spectrum reactor. The relative ranking however is likely to be little affected by the particular core configuration (as it is the underlying neutron absorption cross-sections which determine the ranking). The anomalous point seen just above -10000 pcm/g/cm^3 is Cd, which has an extremely high capture cross-section, an order of magnitude above the other elements tested in this study.

Figure 3 : Thermal spectrum reactor k_{inf} vs density

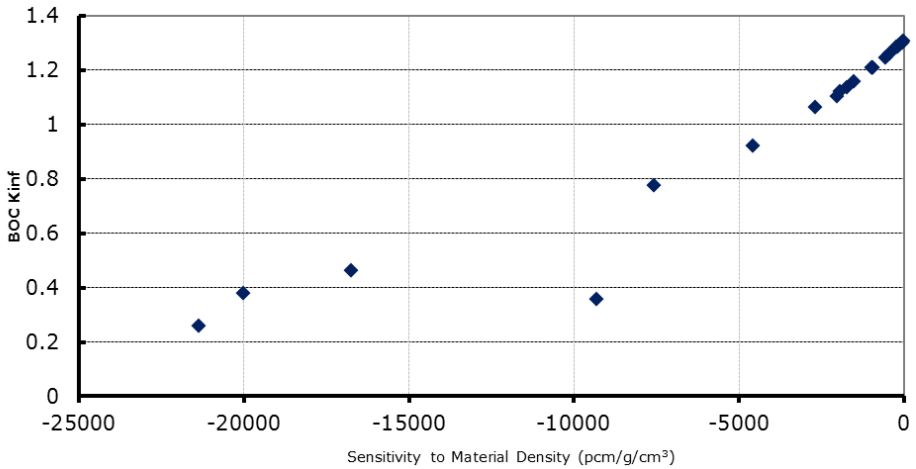


Table 3 : Reactivity density coefficients

Rank	M		A		X	
	Element	pcm/g/cm^3	Element	pcm/g/cm^3	Element	pcm/g/cm^3
1	Zr	-127	Bi	-10	C	-44
2	Cr	-955	Pb	-36	N	-2687
3	Nb	-978	Si	-158		
4	V	-1508	Al	-201		
5	Mo	-1716	P	-210		
6	Ti	-1931	Sn	-427		
7	Sc	-7580	S	-564		
8	Hf	-16756	Ge	-933		
9	Ta	-21363	Ga	-2010		
10			As	-4569		
11			Cd	-9308		
12			In	-20012		

It can be seen that the relative neutron absorption rankings given previously in Table 2 do not change significantly for the reactivity density coefficient rankings. In general, it should be noted that MAX phases are ceramics and have lower densities than equivalent metals (e.g. zirconium alloys or steels) on account of their less densely packed crystal structure. The values from Table 3 have been used to provide an estimate of the predicted K_{inf} values for five individual MAX phase materials.

Modelling of individual MAX phase materials

Five MAX phase materials were modelled explicitly in CASMO-5 as clad material for a typical PWR fuel assembly. Estimated neutron transparency properties for these five MAX phase materials are calculated using data obtained from the first part of the study. These values can then be compared against the results from CASMO-5. This tests the validity of the assumption that individual element results, when combined, give a suitable guide to the neutron absorption properties of the MAX phase materials. The five materials modelled were: Ti_2AlC, Nb_2SnC, Ta_2GaC, Zr_2PbC and Zr_2InN.

To allow comparison, a reference value of reactivity is calculated with clad density set to zero (effectively the clad is removed). This value is determined as 23528 pcm (k_{inf} = 1.30766) for the thermal reactor model used in the study. The reactivity deficit caused by including the MAX phase cladding is then calculated and this is then converted to a k_{inf} value. Reactivity, ρ, is related to the fractional change in neutron population and is given by :

$$\rho = \frac{k_{inf} - 1}{k_{inf}} \quad (1)$$

Values of ρ are multiplied by $1x10^5$ to give units termed ‘pcm’.

The procedure to estimate the reactivity when using a MAX phase material is as follows. Firstly the material composition and density are obtained from reference [1] or [2]. In addition the standard atomic weight of each element is obtained. The mass fraction of each element within the MAX phase is calculated; this allows the effective density of each element within the compound to be calculated. Note that calculations have assumed that MAX phases are 100% pure and with no deviation in stoichiometry.

Next the reactivity change due to the addition of each element (at the effective density within the MAX phase) is calculated by multiplying the effective density by the reactivity density coefficient values (for the thermal reactor system modelled in this study, values are shown in Table 3). The sum of these values for each constituent of the MAX phase material is then deducted from the reference reactivity value (23528 pcm) to give an estimated value of reactivity with the MAX phase material used as the cladding. These reactivity values can then be converted to a neutron multiplication factor using the relationship:

$$k = \frac{1}{1-\rho} \tag{2}$$

These values give an estimate of the level of neutron absorption that a MAX phase material may have and are shown in Table 4 in column 'Predicted K_{inf}'. These materials have then been modelled in CASMO-5 and the predicted/modelled values compared.

Table 4: Data to predicted K_{inf} values of MAX phase cladding

	Atomic Weight	Mass Fraction	Density (g/cm^3)[1][2]	Reactivity density coeff. (pcm/g/cm^3)	Reactivity Change (pcm)	Baseline Reactivity (pcm)	Predicted Reactivity (pcm)	Predicted K_{inf}
Ti_2AlC			4.1					
Ti	47.9	0.7107	2.91	-1931	-5626.2			
Al	27.0	0.2003	0.82	-201	-165.2			
C	12.0	0.0890	0.36	-44	-16.0			
					-5807.5	23528	17720	1.2154
Nb_2SnC			8.4					
Nb	92.9	0.5870	4.93	-978	-4823.6			
Sn	118.7	0.3751	3.15	-427	-1344.1			
C	12.0	0.0379	0.32	-44	-14.0			
					-6181.7	23528	17346	1.2099
Ta_2GaC			13.05					
Ta	181.0	0.8105	10.58	-21363	-225945.9			
Ga	72.6	0.1627	2.12	-2010	-4265.7			
C	12.0	0.0269	0.35	-44	-15.4			
					-230227.0	23528	-206699	0.3261
Zr_2PbC			9.2					
Zr	45.6	0.2939	2.70	-127	-342.9			
Pb	207.2	0.6675	6.14	-36	-218.5			
C	12.0	0.0387	0.36	-44	-15.6			
					-577.0	23528	22950	1.2979
Zr_2InN			7.53					
Zr	45.6	0.4146	3.12	-127	-396.0			
In	114.8	0.5218	3.93	-20012	-78624.3			
N	14.0	0.0636	0.48	-2687	-1287.6			
					-80307.9	23528	-56780	0.6378

The five MAX phase clads were modelled with clad thickness equal to that of current PWR zirconium-alloy clad ('Zircaloy'). The change in reactivity with change in density assumes a linear relationship between reactivity and material density. This relationship appears to hold true for the majority of elements modelled with the exception of the very highly absorbing materials : Cd, In and Ta. These elements suppression of reactivity is under-predicted at higher material densities. However, any MAX phase with more than trace quantities of these elements would not be suitable for clad materials. From the five MAX phases calculated in this study, in most cases the reactivity deficit is dominated by one particular element.

Table 5 compares the K_{inf} values calculated using the CASMO-5 lattice neutronics code and those calculated using the method presented in this study. For MAX phases containing large amounts of the very high neutron absorbing elements (Ta and In) the agreement is not as close, however, the method still predicts a very high level of neutron absorption. For the other MAX phases, there is very good agreement between CASMO-5 results and predicted K_{inf}.

Table 5 : Comparison of predicted vs. calculated k_{inf} value for five MAX phases

	Predicted K_{inf} (BOC)	CASMO-5 K_{inf} (BOC)
Ti_2AlC	1.21536	1.21171
Nb_2SnC	1.20986	1.20881
Ta_2GaC	0.32605	0.21654
Zr_2PbC	1.29787	1.29605
Zr_2InN	0.63783	0.51703
Zircaloy		1.29204

Results – Neutron Activation

Figures 4 and 5 show the calculated values of neutron activation for the thermal and fast cores respectively alongside the reference cladding material ('Zirc' = Zircaloy-4 and 'SS' = AIM1 stainless steel). The charts show the gamma energy emission from each clad material post irradiation at cooling times of 2, 20 and 50 years; giving broad coverage of the time periods at which reprocessing of fuel may occur. 2 years might be expected for very rapid reprocessing, such as that expected for a fast reactor breeding cycle. 20 years represents a more realistic, intermediate cooling and reprocessing time. 50 years corresponds to spent fuel which languishes in storage at the reactor site for timescales similar to the operational life of the reactor. Typically, gamma emission from activation of fuel cladding is from nuclides with fairly short half-lives with respect to spent fuel storage and reprocessing timescales.

Figure 4: Total gamma radioactivity: post thermal spectrum exposure

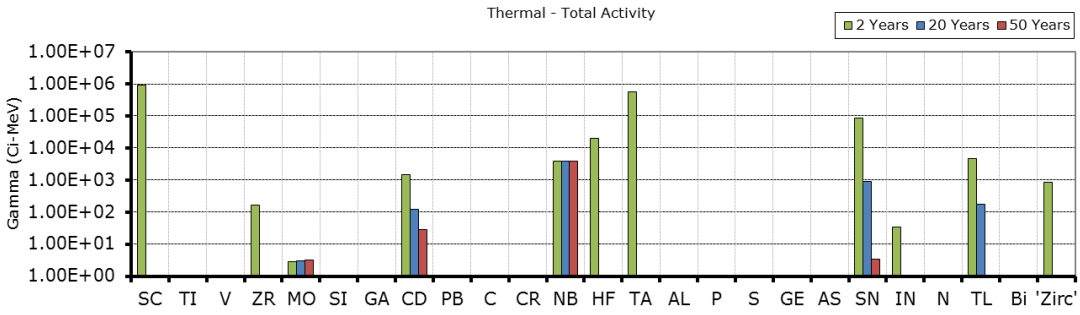
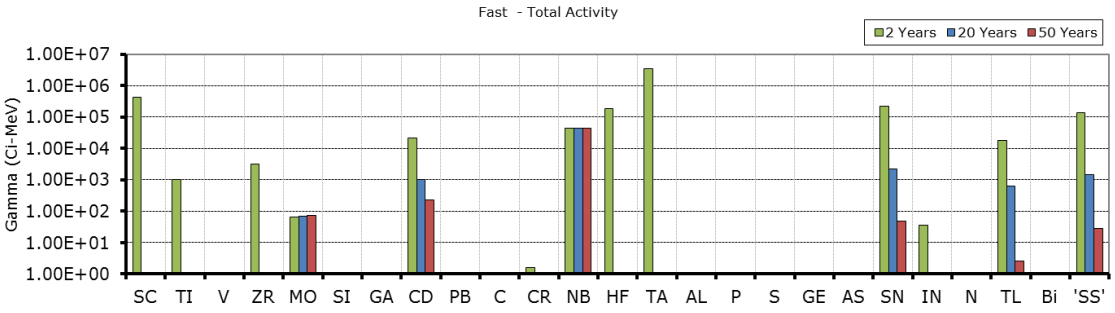


Figure 5 : Total gamma activity: post fast-spectrum exposure



Some elements produce zero gamma as a result of activation (nuclides produced through activation are either short-lived, stable or produce no gamma). Other elements (Bi, Cr, Pb, S, and V) have data-points which are too small to be seen on the current charts; these elements have still been included in the charts as this data still constitutes results.

Table 6 shows the ranked performance of the various elements by total gamma radioactivity after 2 years cooling, which would correspond to the timescale of most concern i.e. as part of a fast reactor breeding fuel cycle. Elements with zero gamma emission have equal first ranking and have been included in the table in alphabetical order. In general, the elements with higher neutron absorption are likely to have a higher level of activity post-irradiation: a higher level of neutron capture by the clad creates higher levels of activation products. Therefore the rankings given below in Table 6 with respect to activity and gamma emission are not drastically different compared with those by neutron absorption given previously in Table 2. The elements modelled are pure with no attempt to include impurities.

Table 6 : Ranking of MAX phase elements by total gamma radioactivity after 2 years cooling

	Gamma Energy (Ci-MeV)											
	Thermal						Fast					
	M		A		X		M		A		X	
Rank		γ (Ci-MeV)		γ (Ci-MeV)		γ (Ci-MeV)		γ (Ci-MeV)		γ (Ci-MeV)		γ (Ci-MeV)
=1	Ti	0.00E+00	Al	0.00E+00	C	0.00E+00	V	5.92E-06	Al	0.00E+00	C	0.00E+00
			As	0.00E+00					As	0.00E+00		
			Ga	0.00E+00					Ga	0.00E+00		
			Ge	0.00E+00	N	0.00E+00			Ge	0.00E+00	N	0.00E+00
			Pb	0.00E+00					P	0.00E+00		
			Si	0.00E+00					Si	0.00E+00		
2	V	1.10E-10	S	6.84E-07			Cr	1.57E+00	S	3.39E-08		
3	Cr	1.75E-03	Pb	0.000322			Mo	6.60E+01	Pb	1.44E-02		
4	Mo	2.84E+00	Bi	0.0614			Ti	1.03E+03	Bi	7.97E-01		
5	Zr	1.62E+02	In	34.8			Zr	3.23E+03	In	3.53E+01		
6	Nb	3.83E+03	Cd	1460			Nb	4.44E+04	Tl	1.76E+04		
7	Hf	1.98E+04	Tl	4770			Hf	1.82E+05	Cd	2.11E+04		
8	Ta	5.60E+05	Sn	88300			Sc	4.35E+05	Sn	217000		
9	Sc	9.43E+05					Ta	3.51E+06				

Discussion

The neutron absorption properties of the MAX phase materials are determined by the underlying neutron capture cross-sections of the constituent elements. It is clear that the best clad materials, from a neutron absorption perspective, will comprise of elements with low capture cross-sections and have the lowest possible material density. Optimum clad thickness is therefore a balance between thermal performance, the minimum tolerable mechanical robustness under irradiation conditions and minimising neutron absorption.

The clad thickness modelled in this study was fixed between all materials. Depending upon the mechanical properties of the material, fuel/reactor engineers may be able to exploit more robust materials by reducing clad thickness or be forced to increase clad thickness to compensate for poorer performing materials. Materials that show a moderate, like-for-like detriment in neutron absorption (compared with current clad materials) may still prove to be good clad materials if they show enhanced mechanical robustness. In general, the high strength and stiffness of MAX phases in common with other engineering ceramic materials mean that a thinner clad may be tolerable as long as sufficient mechanical properties can be maintained.

In the case of materials containing moderate amounts of very high neutron absorbing elements (such as Cd, In, Ta, and Hf), it is unlikely that clad can be reshaped to such a degree as to avoid unacceptably detrimental reactor performance.

The mechanical properties of the clad are also linked, to an extent, to the operating scheme of the reactor. It may be possible to improve the performance of a reactor through use of cladding materials with more robust mechanical characteristics: for example, through tolerating higher fuel and/or coolant temperatures in the core.

Elements with more extreme neutron absorption characteristics (high or low) have already been exploited extensively in nuclear reactor design: low neutron absorption Zr forms the bulk of zirconium alloy cladding which is used in thermal spectrum light water reactors around the world. Lead-bismuth has also been used as a coolant in fast reactors and carbon as a moderator in numerous reactor types. Recognised neutron absorbing materials such as Cd and In are used in reactor control rods and Hf has been used as a burnable absorber: added to fuel to reduce reactivity during the early stages of irradiation.

The materials ranked as having high neutron absorption properties may be potentially useful as control rod materials. In fact, all of the materials identified in this study as having high neutron absorption (Hf, Ta, In, Cd) have already been, and continue to be, used in current reactors as reactivity control materials (with the exception of Ta which is excluded as a result of high gamma emission due to neutron activation). Control rod materials are significantly less sensitive to material strength compared with clad materials as it is the convention to manufacture the control rod material as a solid rod (contained within a metal clad) compared with clad tubes; in addition control rods experience less extreme temperature ranges during normal operation and do not come into contact with the range of isotopes/fission products which clad materials must withstand. As a result, the main drivers for considering a MAX phase control rod would be a higher melting point than current metallic control rod materials (important in accident conditions) or improved mechanical properties with respect to current ceramic, high melting point control rod materials e.g. boron carbide. Maintaining control rod material, and most importantly, control rod clad integrity (depending upon the design of control rod) would also require consideration of possible material interactions between guide thimble, clad and control rod material.

Conclusions

The constituent elements of all MAX phase materials identified have either been modelled as discrete clad material or had the resulting value of neutron multiplication for the system estimated using cross-section data.

For thermal reactor systems, only one pure MAX phase material - 'Zr_2PbC' - has been identified as having lower neutron absorption than current zirconium-alloy based clad. From a neutron absorption and activation perspective, Zr_2PbC appears to be the best choice for a pure MAX phase material, which can also be identified from NNL's earlier work with respect to a specific thermal reactor scenario [11**Error! Reference source not found.**]. In addition, this work has identified that the neutron absorption of $Zr_2(Pb,Bi)C$ would be even lower, with Bi, Pb and Zr also all ranking well with respect to low dose. Although Bi is known to produce highly radioactive polonium-210, with a half-life of 138 days, a post shutdown cooling time of two years is sufficient to significantly deplete this isotope such that it would no longer be of concern. In fast systems, the neutron absorption properties are slightly less of a concern when selecting clad material due to the generally lower neutron absorption cross-sections at higher neutron energies. Although reduced neutron absorption is desirable, the materials' ability to maintain mechanical robustness in a high neutron flux and liquid metal coolant environment is also of high importance in selecting a clad material. Hence the use of stainless steel in fast systems compared to zirconium alloy in thermal systems.

The radioactivity (in terms of total activity and gamma emission) resulting from a period of irradiation has been calculated for each constituent element in both a thermal and fast reactor spectrum. The activation of clad material is a trivial concern in a once-through fuel cycle where the clad is never intended to be separated from the fuel post-irradiation. In a closed fuel cycle, clad activation may be a minor concern alongside the more major concerns surrounding the handling and disposal of separated fission products/actinides. In addition, the activation of MAX phase materials if used as structural components in-core may pose some concerns for reactor maintenance/decommissioning if certain, more highly activating, elements are used. Results have shown that elements with high neutron absorption properties also have higher levels of neutron activation.

This study developed a 'tool kit' to aid the initial selection of MAX phases for further development by means of combining the neutron absorption and activation properties of individual constituent elements. Final selection of neutronically suitable MAX phases should include consideration of impurities. The MAX phases modelled have not included impurities which, in a real world application, will arise and may have an effect on the neutron absorption and activation properties.

References

[1] Z.M. Sun (2011), 'Progress in research and development on MAX phases: a family of layered ternary compounds', International Materials Reviews, Volume 56 (3), pp.143-166.

[2] C. Hu et al. (2012), "New phases' discovery in MAX family", International Journal of Refractory Metals & Hard Materials, Volume 36, pp.300-312.

[3] D. Horlait et al. (2015), "Development of MAX phases for nuclear fuel cladding applications", ICACC-S12-038-2015, 39th International Conference and Exposition on Advanced Ceramics and Composites, 25-30th January 2015.

[4] P. Eklund et al. (2010), “The Mn+1AXn phases: Materials science and thin-film processing”, Thin Solid Films, Volume 518, pp.1851-1878.

[5] “CASMO-5 – A Fuel Assembly Burnup Program – User’s Manual”, SSP-07/431 Revision 3, Studsvik Scandpower, (2011).

[6] G. Rimpault et al. (2002), “The ERANOS code and data system for fast reactor neutronic analyses”, Proceedings of the International Conference on Physics of Reactors, Seoul, Korea, 2002.

[7] R. F. Burstall (1979), “FISPIN – A Computer Code for Nuclide Inventory Calculations”, ND-R-328(R), UK Atomic Energy Authority.

[8] S.F. Mughabghab (2003), “Thermal Neutron Capture Cross Sections Resonance Integrals and G-Factors”, IAEA INDC.

[9] K. Koebke et al. (1985), “Principles and application of advanced nodal reactor analysis methods”, Atomkernenergie, Volume 46(4).

[10] T. El-Raghy et al. (2000), “Synthesis and characterization of Hf_2PbC, Zr_2PbC and M_2SnC (M = Ti, Hf, Nb or Zr)”, Journal of the European Ceramic Society, Volume 20, pp.2619-2625.

[11] P. Little (2014), “Investigation into the use of ceramics as a reactor cladding material”, NNL Technical Memorandum, DE08287/06/10/05.