

BURNUP PERFORMANCES OF BORON NITRIDE AND BORON COATED NUCLEAR FUELS

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ABSTRACT

The nuclear fuels of urania (UO₂) and 5% and 10% gadolinia (Gd₂O₃) containing UO₂ previously produced by sol-gel technique were coated with first boron nitride (BN) then boron (B) thin layer by chemical vapor deposition (CVD) and also by plasma enhanced chemical vapor deposition (PECVD) techniques to increase the fuel cycle length and to improve the physical properties.

From the cross-sectional view of BN and B layers taken from scanning electron microscope (SEM), the excellent adherence of BN onto fuel and B onto BN layer was observed in both cases.

The behavior of fuel burnup, depletion of BN and B, the effect of coating thickness and also Gd₂O₃ content on the burnup performances of the fuels were identified by using the code WIMS-D/4 for Pressurized Water Reactor (PWR) and Boiling Water Reactor (BWR) cores. The optimum thickness ratio of B to BN was found as 4 and their thicknesses were chosen as 40 µm and 10 µm respectively in both reactor types to get extended cycle length.

The assemblies consisting of fuels with 5% Gd₂O₃ and also coated with 10 µm BN and 40 µm B layers were determined as candidates for getting higher burnup in both types of reactors.

Key words: boron, boron nitride, CVD, PECVD, urania, gadolinia, reactivity, burnup

INTRODUCTION

The use of burnable absorbers in ceramic nuclear fuels in order to increase the reactor cycle length has been acquired much importance during the last two decades. For this reason they have been utilized in boiling water reactors (BWRs) and western and Russian type Pressurized Water Reactors (PWRs and VVERs). In early times boric acid (H₃BO₃) was added into the moderator. Later boron carbide (B₄C) was used in the fuel bundles as burnable poison [1,2]. H₃BO₃ changes the properties of the moderator and causes the control problems in the case of large removal.

These adverse effects are removed by using burnable absorber bearing fuels. One is Gd₂O₃ containing and the other is zirconium diboride (ZrB₂) coated UO₂ fuel. First type has been produced by mixing of UO₂ and Gd₂O₃ powders mechanically. In this study, the fuel pellets were produced by sol-gel technique to provide mixing at molecular level and to minimize the radioactive dust problem seen in mechanical mixing [3-6]. The difficulties both in the fabrication technique and in the solubility of zirconium in the reprocessing stage of the spent fuel are the disadvantages of the second type fuel [7].

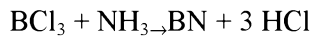
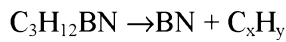
Neutrons coming from the moderator are faced with the B layer and some of them are absorbed. Since B has relatively low absorption cross-section, it must exist on the surface of the fuel to deplete out by the end of the cycle. Gadolinium has significantly high absorption cross-section ($\approx 49,000$ b), hence it burns out at a very high rate. Therefore it must be mixed with the fuel.

In this research work the fuel pellets were coated with first BN, which has good physical, chemical and mechanical properties. It has high strength against thermal shocks, resistance to corrosion, chemical inertness and neutronic advantages. The BN layer was then coated with B layer which is denser than BN. Thus, it provides more effective neutron absorption compared with the BN layer. The BN layer stands as the buffer zone between the fuel and B layer to prevent the chemical interaction between B and fuel which lowers the vitrification temperature of fuels because of its fluxing effect. The burnup characteristics of B in each layer and the effect of burnable absorber on the effective multiplication factor (reactivity) of a typical (17x17) PWR and (8x8) BWR fuel assemblies were investigated with the lattice code WIMS-D/4 [8]. The results were compared with the standard fuel assemblies without burnable absorber and conventional $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel coated with BN and B thin layers.

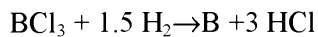
EXPERIMENTAL WORKS AND RESULTS

(i) Coating Methods:

BN coating on the pellets of UO_2 -only and (5% and 10%) Gd_2O_3 containing UO_2 fuels by CVD technique was performed in a tube furnace assembly from the thermal decomposition of BTMA complex vapor and also from the reaction of BCl_3 with ammonia at 875 K and 1200 K according to the reactions shown below [9]:



B coating on previously BN coated pellets was accomplished by CVD technique at 1250 K in the same furnace according to the chemical reaction [9]:



The fuel pellets were also coated with BN thin layer by PECVD method [10]. Coating was performed in an inductively coupled plasma(ICP) apparatus in which an argon plasma medium created at 750 W by the reaction taking place between BCl_3 and NH_3 . Then BN coated pellets were coated with B thin layer at the plasma power of 500 W by the reaction between BCl_3 and H_2 [11].

(ii) Infrared (IR) Analysis:

The IR spectrum of BN powder exhibited a strong peak at 1400 cm^{-1} and two weaker peaks at 880 cm^{-1} and 800 cm^{-1} . The strong peak of B-N stretching while the weak peaks are of B-N-B bond bending [9,12]. The IR spectrum of B has peaks at 1080 , 800 and 750 cm^{-1} . All the peaks are of B-B vibrations and agree with the literature values[13].

(iii) X-Ray Diffraction (XRD) Analysis:

In the literature [14,15] the main peak was reported at $2\theta = 26^\circ$. This indicates the hexagonal and turbostratic crystal structure. In this study, this peak was shifted to $2\theta = 28^\circ$ due to the presence of carbonaceous material in BN from BTMA [9].

(iv.) Microstructure Analysis (SEM):

The morphological structure of the BN and B coated surfaces was examined by the pictures taken from scanning electron microscope (SEM). The grainy and rod like BN structures on the fuels [9,10] and also similar B structures on the BN layers were observed [11]. The fuel/BN/B intersections in CVD and PECVD cases are seen in Fig.1 and Fig.2 respectively. The adherence of B onto BN layer is seen from the boundary line between BN and B layers as seen in Fig.1. In the PECVD case while the BN layer on the fuel is being smooth, the B layer is not being smooth as seen in Fig.2.

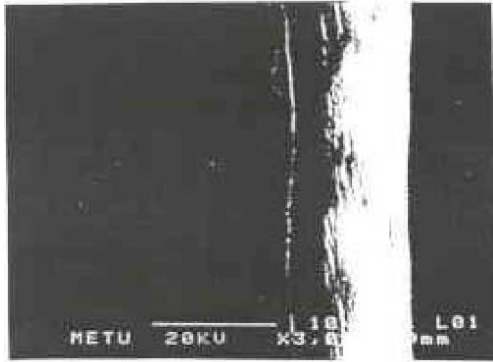


Figure 1. Fuel/BN/B layers (CVD)

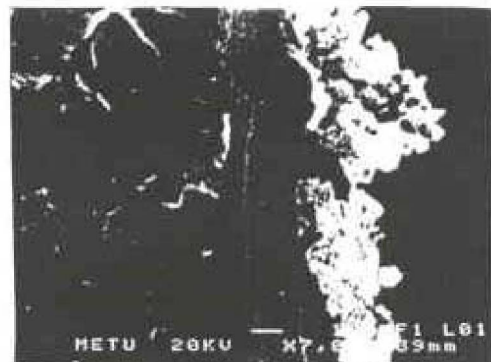


Figure 2. Fuel/BN/B layers (PECVD)

RESULTS AND DISCUSSION ON FUEL PERFORMANCE ANALYSIS

In the calculations neutrons having 18 energy groups were considered. These are 5 thermal, 6 intermediate and 7 fast groups. The data used in performance calculations are shown in Table 1.

Table .1. Data Used in Performance Calculations

Reactor type	PWR	BWR
Fuel	UO ₂ , UO ₂ -Gd ₂ O ₃	UO ₂ , UO ₂ -Gd ₂ O ₃
Moderator	H ₂ O	H ₂ O
Cladding material	Zr-4	Zr-2
Fuel rod pitch	12.6 mm	16.3 mm
Fuel assembly type	17x17	8x8
Fuel pellet diameter	8.05 mm	10.4 mm

Cladding thickness	0.66 mm	0.86 mm
Density of UO_2 ,	10.36 g/cm^3	10.36 g/cm^3
Density of $\text{UO}_2\text{-Gd}_2\text{O}_3$ (W%)	$10.36 - (0.04*W)$	$10.36 - (0.04*W)$
Density of (BN/B/Zr)	$(1.5/2.35/6.45) \text{ g cm}^3$	$(1.5/2.35/6.45) \text{ g cm}^3$

In PWR modeling, each assembly was assumed as consisting of (17x17) fuel rods and 8 fuel rods contain Gd_2O_3 in an assembly. In BWR modeling however, each assembly consisted of (8x8) fuel rods and 6 fuel rod with Gd_2O_3 were used.

In the calculations also the fuel enrichment in U-235 was assumed as 3%. The calculations to find the optimum B/BN ratio and thickness were done for one UO_2 -only fuel rod. In all other works assembly modeling was used. In both PWR and BWR modeling a symmetric fuel bundle plane was used. Gadolinia content in the fuels was taken as 5 wt % and 10 wt %.

(i) Depletion Characteristics of Coated Layers:

Nuclear fuels are generally classified as Conventional (UO_2 -only), integral Fuel Burnable Absorber (IFBA) which contains Gd_2O_3 and alternative IFBA with BN-B hybride coating (here) in addition to Gd_2O_3 .

Performance of IFBAs mainly depends on the depletion behavior of both the fuel and burnable absorbers. Depletion rates of burnable absorber which is B in BN and in B layers is an important parameter in the determination of optimum thicknesses of each layer.

The principal reason for having a BN layer before a B layer is to avoid any chemical interaction between B and the fuel material causing undesired vitrification and therefore a decrease in the melting point of fuel. The BN layer will serve as a buffer zone as well as it is utilized as a burnable absorber due to its absorption capability.

The BN and B coating thickness should be adjusted such that boron in the B layer depletes faster than that of in the BN layer to prevent the possibility for B atoms to diffuse into the fuel region. Therefore, the B layer should be sufficiently thick such that it will be consumed before the BN layer. This is desired since BN is not an effective absorber as much as B owing to its low B-10 content.

If either outer B or inner BN layer thickness is not sufficient, then depletion of boron in BN is promoted. Therefore, its role as a buffer zone is not performed.

The variation of boron ratio as a function of burn up is analyzed to see the relative depletion of B-10 in the B and BN layers. The boron ratio is defined as the ratio of the number density of B-10 in the B layer to that of in the BN layer. The B ratio has been evaluated for various thickness combinations as shown in Fig.3. and Fig.4. for PWR and Fig.5. and Fig.6. for BWR to obtain optimum thicknesses.

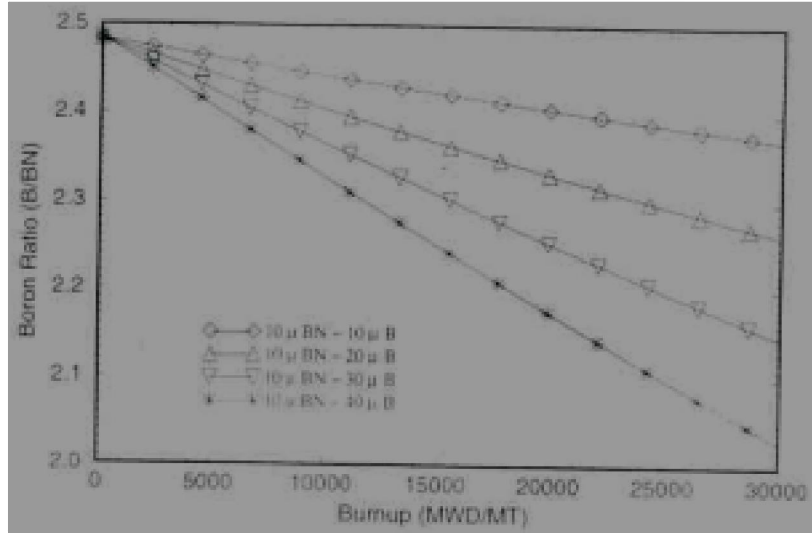


Figure 3 .Boron Depletion in PWR with Constant BN Layer

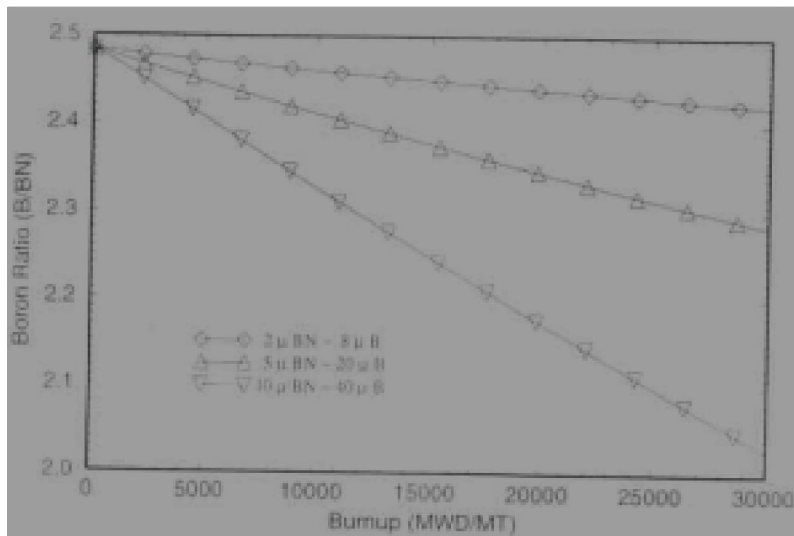


Figure 4. Boron Depletion in PWR with Variable BN Layer

It is easily seen from Fig.3. and Fig.4. that the depletion of boron becomes comparable in both layers as the thickness of B layer decreases. Here the thickness of BN layer was taken as 10 μm for various B layer thicknesses since the depletion behavior of B is important from the neutron absorption point of view.

In the thin layer (less than 30 μm) of B coating case, the layer becomes transparent to incoming neutrons, so the depletion of BN layer may take short time, and the probability of interaction of B layer with the fuel increases.

As the thickness of outer layer increases, its shielding effect for neutrons becomes more effective and the depletion of BN layer may take longer time. If the thickness of B layer is increased over 40 μm , the majority of the neutrons are held and the quantity of neutrons for

fission is reduced. This is undesired from the burn up (criticality) point of view, so the optimum thickness ratio of B to BN was chosen as 4.

If we compare Fig.3 with Fig.5 the same behavior is observed. Initial (start up) B ratios are the same in each figure. But as the burn up proceeds the slopes of the lines for the same thickness ratio change slightly due to the type of the reactor (PWR or BWR).

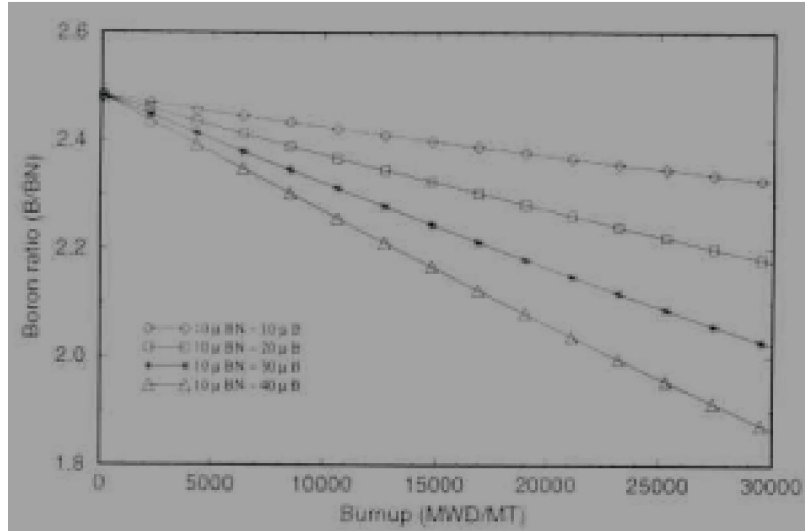


Figure 5. Boron Depletion in BWR with Constant BN Layer

At the burn up value of 30,000 MWD/MT, the B ratio values are 2.37, 2.27, 2.16, and 2.05 in PWR and 2.33, 2.18, 2.02, and 1.87 in BWR for the BN-B coating thickness of 10-10, 10-20, 10-30, and 10-40 μm respectively. The depletion rate of B in PWR cores is larger than that of BWR cores because of harder neutron energy spectrum observed in BWRs. This results in lower depletion rates of burnable poison in BWR cores as seen in Fig. 5 and Fig.6.

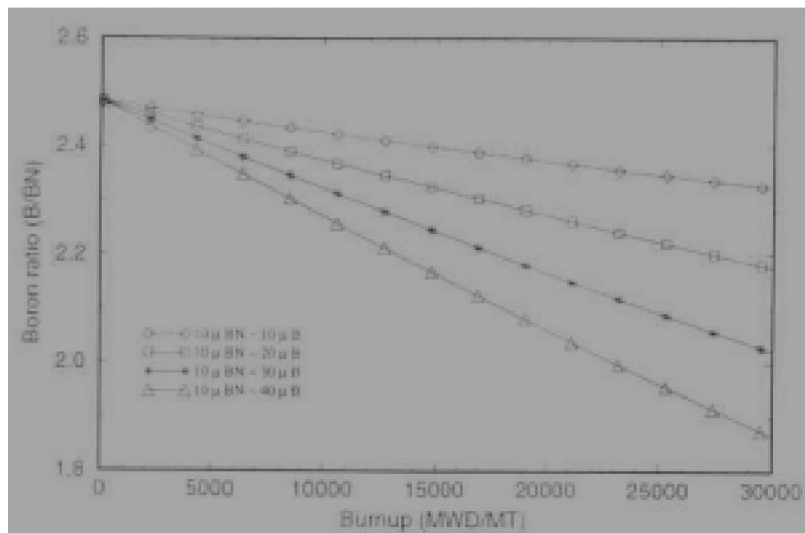


Figure 6. Boron Depletion in BWR with Variable BN Layer

After determining the optimum thickness ratio as 4, it is also necessary to find the optimum thickness of each layer. In this case, the thickness of BN layer was changed also. As seen from Fig.4 and Fig.6 the B layer is not effective in shielding the neutrons when the thickness of the layer is not large enough. The depletion rates of B in both layers are not considerably different if the B layer thickness is less than 20 μm . Then we have decided to choose the thickness of the layers as 10 μm and 40 μm for BN and B respectively.

(ii) Reactivity Calculations:

Calculations were done for both a PWR assembly with 17x17 square array containing 8 fuel rods bearing Gd_2O_3 and a BWR assembly with 8x8 type containing 6 fuel rods with Gd_2O_3 to analyze the reactivity behavior. Fuel used was 3% enriched in U-235. The results were shown in Fig. 7 and Fig. 8 for a PWR and a BWR core respectively.

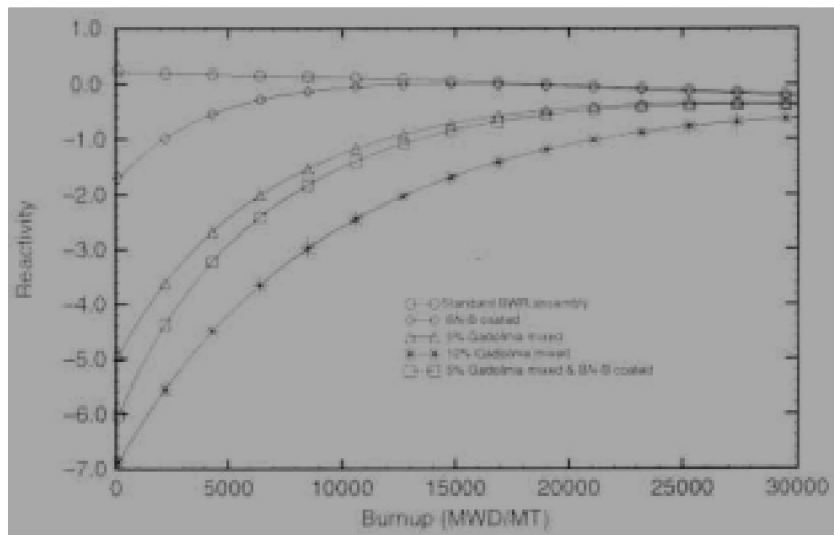


Figure 7. Reactivity vs. Burn up in PWR Core.

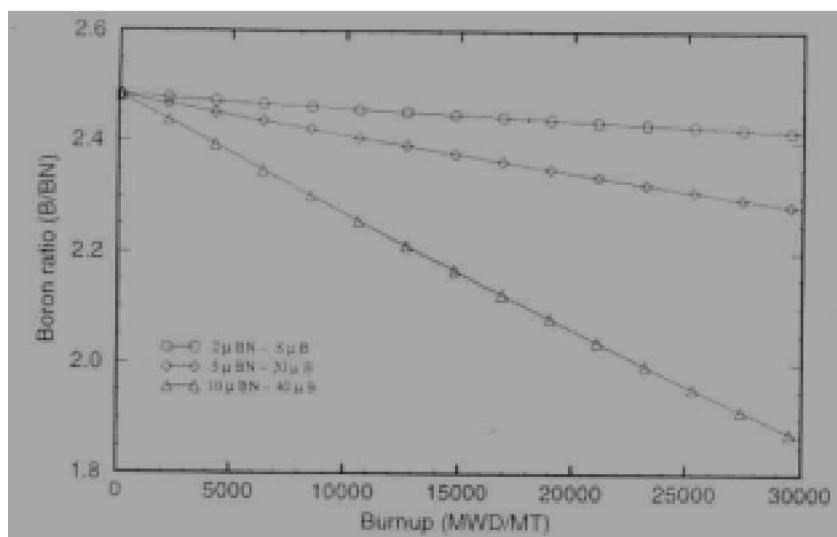


Figure 8. Reactivity vs. Bum up in BWR Core.

All reactors are started up with excess reactivity for sustaining criticality and to compensate the negative reactivity coming from fuel depletion and poisonous fission products. The standard assembly curves in both figures show this behavior. Initially they have sufficient reactivity. The reactivity decreases due to fuel burnup and fission products. The assembly becomes subcritical beyond the burnup values of 8500 MWD/MT in PWR and 17000 MWD/MT in BWR. The reason for higher burnup value in BWR assembly is harder neutron spectrum, so higher Pu-239 (fissile) production.

The area between the curve of standard assemblies and any one of the curves of the assemblies with burnable absorber shows the negative and positive reactivity insertion during the reactor operation. That means the reactivity corresponding to this area would have been controlled by control rods, if the burnable absorbers were not used.

The number of control rods are decreased and more fuel are loaded into the place of eliminated rods, so the length of the cycle is increased.

In both Fig.7 and Fig.8 the initial reactivity values of burnable absorber containing assemblies are negative and as the time proceeds, the reactivity increases due to the depletion of burnable absorbers and then the behavior of the curve is governed mainly by the depletion of fuel isotope.

As the burnup increases, the reactivity decrease in the standard fuel assemblies will be compensated by the positive reactivity addition of IFBA assemblies because of the higher burnup rate of burnable absorber compared to the fuel isotopes. Therefore, the reactor will have sufficient positive reactivity for longer period of time that means the cycle length will be extended.

The assembly with 10% Gd_2O_3 bearing fuels introduces more negative reactivity compared to that of 5% Gd_2O_3 mixed assembly and the corresponding peak reactivity value is high in case of 5% Gd_2O_3 mixed assembly, Also the thermal conductivity of the fuel with higher Gd_2O_3 content decreases significantly.

If the burnup behavior of 5% Gd_2O_3 mixed assembly is compared with the BN-B hybride coated assembly, it is seen that they have the same depletion characteristics after 15000 MWD/MT of burn up. Their residual absorption effect is less at the high burnup region, and the measure of net saving which is the area between the standard assembly case and the 5% Gd_2O_3 mixed and BN-B coated assembly case is high, so we can conclude that the optimum choice is 5% Gd_2O_3 mixed and BN-B coated assembly in PWR as seen in Fig. 7.

The burnup behavior of assemblies in BWR seen in Fig.8 is different than that of PWR. In this case the higher negative reactivity is introduced by 10% Gd_2O_3 mixed assembly. Standard assembly and BN-B coated assembly both have the same burnup value of 17000 MWD/MT. The depletion characteristics of 5% gadolinia mixed assembly, and 5% gadolinia mixed and BN-B coated assembly are similar to each other. Here the effect of Gd_2O_3 is much higher compared to PWR case since the number of fuel rods is less but the number of gadolinia bearing

fuel rods is almost the same. The higher fuel utilization is accomplished in the type of 5% gadolinia mixed and BN-B coated assembly also.

CONCLUSIONS

1. A new IFBA fuel with BN-B hydride coating has been introduced.
2. Both the BN and B coating were accomplished by CVD and PECVD techniques.
3. Depletion calculations showed that optimum thickness of coating layers to avoid chemical interaction of B with fuel material are 10 μm and 40 μm for BN and B layers respectively in both PWR and BWR core assemblies.
4. The assemblies which consist of fuels with 5% gadolinia and also coated with 10 μm BN and 40 μm B layers were determined as candidates for getting higher burnup in both types of reactors.

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