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Technical article

Research on Neutron Shielding Materials with Metallic Compounds in Storage Casks for Long-term Storage of Spent Nuclear Fuel

TaeHoon Jeon[1], Minsu Ju[1], Seong hyun Kim[2], Sang hyuk Yoon[2], and JaeHak Cheong[3,*]

[1]BRnC Inc., 79-4, Mullae-ro Yeongdeungpo-go, Seoul 07294, Republic of Korea
[2]Korea Radioactive Waste Agency, 174, Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea
[3]Kyung Hee University, Department of Nuclear Engineering, 1732, Deogyeong-daero, Giheung-gu, Yongin-si, Gyeonggi-do 17104, Republic of Korea

ABSTRACT In this study, a compounding technology of additives used in a neutron shielding material was developed, and a particle surface treatment method was obtained by dispersing the inorganic additives in the polyester resin. This process involves two major parts they are (1) Hydroxylation of as received $Mg(OH)_2$ powder by using hydrogen peroxide (H_2O_2) and (2) Surface modification of hydroxyl-modified $Mg(OH)_2$ by using sodium oleate (SOA). As with $Al(OH)_3$ and $Mg(OH)_2$ the zinc borate powder was also modified by direct single SOA modification. The as-received zinc borate powder is a hydrated one because of this we avoid the hydroxylation step. For this initially start with a small quantity (5 g) of zinc borate. In this process 2 wt. % of the as-received zinc borate powder was dissolved in 0.5% of SOA (dissolved in deionized water) under constant temperature at 60°C with a magnetic stirrer. Further, maintain the temperature and agitation for 3 h later allow it to room temperature, and measured the pH by using a universal pH paper range (1-11). The initial pH was 9 and adjusted to pH 5-6 by adding 1 N HCl solution. Finally, the resulting solution was subjected to vacuum filtration and wash with acetone finally dried at 50°C to remove the residual solvent present in the compound. Further, the as-received zinc borate and SOA-modified zinc borate powders were taken in 2 individual 50 mL vials each containing 20 mL of deionized water and 20 mL of toluene. it is clear that the as-received zinc borate powder is dispersed in the water (bottom) layer whereas, the SOA-modified zinc borate was dispersed in the toluene (upper) layer. From the above results, we can conclude that only SOA-modified zinc borate surface is also modified and it is good for dispersion in organic solvents.

Key words: Spent Nuclear Fuel, Cask, Canister, Neutron Shielding Material, Long-term storage

1. Introduction

In the spent fuel storage system, the neutron shielding has technical importance and high value. Develop products that use a polymeric resin that is easy to secure long-term integrity according to demands from markets. In addition, it is necessary to solve the difficulty of resin compound in the manufacturing process and to meet the requirements of domestic and overseas markets in the future [1]. Defects occurring in the manufacturing process are usually caused by crack. The main cause of cracking is the thermal stresses that develop due to the exothermic nature of the curing process. The primary factors that determine the extent of the cracking are the size of the cross-section, the temperature of the resin at the start of the pour and the cure rate [2-3]. The size of the cross-section is critical because the cure rate is highly temperature-dependent. As the resin cures the center of the volume is higher than that of the periphery due to heat loss to the environment. As a result of the cure rate of the center increases which increases the temperature which further increases the cure rate, as so forth. The larger the volume of material being poured at once becomes, the greater the temperature difference becomes, and therefore the thermal stresses increase, leading to cracking. Among other important safety measures in nuclear power plant, neutron shielding is very important. The interaction of neutron causes ionization of the media through a complicated mechanism involving the emission of energetic secondary charged particles. For this purpose, different polymer composites are employed as neutron shielding materials.

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***Corresponding author:** JaeHak Cheong
Tel: +82-31-201-3689, Fax: +82-31-204-8106, E-mail: jhcheong@khu.ac.kr

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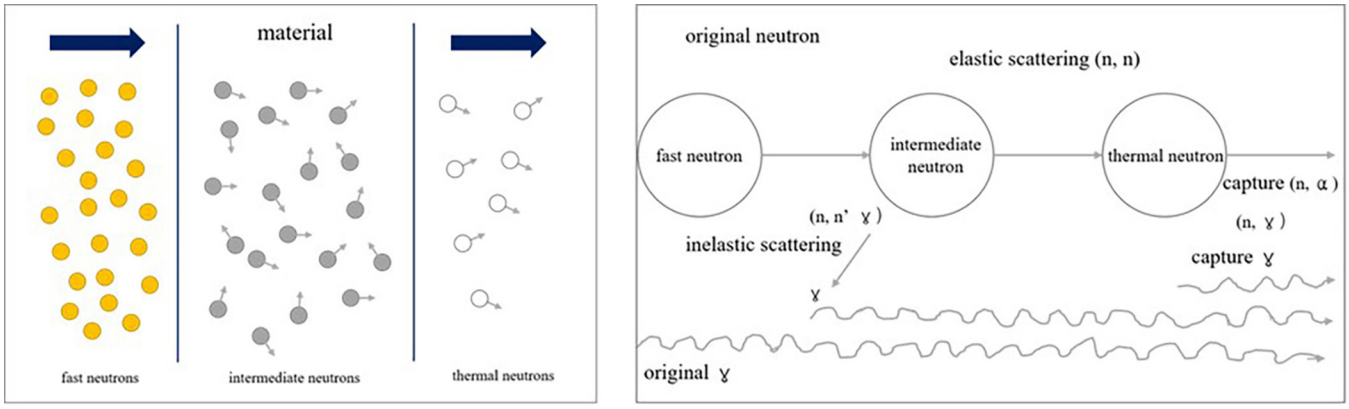

(a) the transportation of neutrons in materials

(b) the brief interaction mechanism

Fig. 1. In polyester resin, the hydrogen capture of thermal neutrons is through the ^{1}H (n, γ) ^{2}H reaction

Mostly thermoplastics, including low- and high-density polyethylene or their composites are commercially available. They have their own inherent advantages, i.e., it can be molded into desired shapes and it occupies less space. Polyester resin is a very effective neutron shielding material and displays excellent attenuation behavior because of its hydrogen content and its density. It is an inexpensive, sealable material and resistant to many chemicals. Another advantage is its hydrophobic nature which reduces the possibility of superficial contamination to a minimum. In polyester resin, the hydrogen capture of thermal neutrons is through the ^{1}H (n, γ) ^{2}H reaction. What we have done is to fabrication a shielding material of high performance that secures spent fuel storage (Cask) from radiation. In the left of Fig. 1(a), fast neutrons roll towards the right. Some of them, trapped by hollows disappear, the others have collided against the rocks scatter with lower energy, only a few of them may go across holding thermal neutrons. Nuclear reaction cross sections determine the probability of trapping and collision. The following Fig. 1(b) is the brief interaction of neutrons with other materials. Nowadays, many kinds of materials were employed as nuclear radiation shielding material, while, the requirements of radiation shielding become more and more strictly. Especially in spent fuel storage (cask), the radiation shielding materials must have high effective shielding properties for the sake of the restriction of the materials' weight and volume. Also, shielding materials have to serve for a long time in a quite inclement environment with high temperature, corrosion, and so on [4-7]. Neutron shielding materials are very important for nuclear safety. Their function is to provide the sufficient protection of the public and of the operators, to keep the integrated dose ALARA. Moreover, storage materials used in installations or in radioactive material packaging must have high-performance for neutron shielding [8-9].

2. Material and Methods

In this study, we have been choosing polyester resin as the basic material for neutron shielding, considering shielding performance, thermal and mechanical properties. We fabricated neutron shielding material that can effectively shield neutrons by mixing additives such as flame retardant, a reinforcing agent in polyester resin. The mechanical properties of shielding materials were then evaluated. The cross-section of the neutron shield boxes is determined by drawing requirements but if this type resin were poured into a large bucket for example cracking would be virtually inevitable. Polyesters are one of the most multi-purpose synthetic copolymers. Polyester are produced in high volume worldwide. They are widely used commercially as plastics., composites, coatings and for shielding application. They are polymer macromolecules that have carboxyl ester groups as a vital component of their polymer basis. Polyesters have received a great deal of attention since the early work, which initiated a study on many step-growth polymerizations. An unsaturated polyester is a macromolecule (average molecular weight between 1,000 and 3,000), built by a polycondensation reaction from dicarboxylic acids and dialcohols. Some of the dicarboxylic acids contain carbon double bonds (C=C), so called unsaturated bond. At room temperature, the unsaturated polyester is a highly viscous liquid or a delicate glasslike product with a low melting point. Unsaturated polyester resin is a solution of the unsaturated polyester in a low-viscosity monomer, which also contains carbon double bonds.

2.1. Fabrication of Neutron Shielding Material

The neutron shielding materials are an unsaturated polyester cross-linked with styrene, which is about 50 wt.% mineral and reinforcement. The components are a polyester resin, styrene product, neutron absorption material, flame retarding material etc. The neutron shielding material provides neutron and gamma shielding. The shielding performance is entirely a function of density and chemistry. In order to satisfy design assumption, cured neutron shielding material must have a density of acceptance level and composition rate. We have set the experimental apparatus and fabrication procedure as shown in Fig. 3. A variable speed mixer was used to mixing liquid resin, curing agent, and additives, which are the basic materials for making neutron shielding materials. In the case of mixing, each compound is prepared at a specified weight ratio and mixed at an equivalence ratio.

2.2. Development of Particle Technology in Neutron Shielding Resins

Neutron shielding materials used in spent fuel storage casks require metal additives in addition to the polymeric compounds of unsaturated polyester resin and styrene monomer. Boron compounds are added for neutron shielding, and inorganic aluminum hydroxide ($Al(OH)_3$) is needed for mechanical properties and as a flame retardant. In this study, aluminum hydroxide was subjected to a surface treatment involving hydrogen peroxide and sodium oleate (SOA) with the objective of enhancing its dispersion in organic materials, specifically polyester resin and styrene monomer. We have identified a catalyst ratio that can induce a stable reaction at room temperature. Cyclonox® is used as a catalyst for the reaction of styrene monomer to polystyrene, and since the catalyst has a bond form of R-O-O-H, Co 6%, a metal-based accelerator, is used to break the bond easily in the form of R-O· and H-O· at room temperature. The mixing ratio of catalyst (Cyclonox®) : accelerator (Co 6%)=24 : 1, with 1.2 mL of catalyst and 0.05 mL of accelerator. The surface treatment of aluminum hydroxide was performed as follows; 1) Add 1 g of $Al(OH)_3$ to 1 to 10 g of hydrogen peroxide and reflux for 4 hours. 2) Filter the hydroxyl group treated $Al(OH)_3$. 3) Hydroxylated $Al(OH)_3$ should be added to distilled water containing 0.5 wt.% SOA, and the solution should be heated at 90°C for a period of three hours. 4) After cooling the solution, add 1N HCl until the pH is 5 to 6 using a pH sheet. 5) After filtering, put the surface-treated $Al(OH)_3$ into the toluene and distilled water layers to check the $Al(OH)_3$ dispersed in the toluene layer only. The results of the surface treatment indicate that prior to the treatment, $Al(OH)_3$ is present in the distilled water layer. However, following the surface treatment, it is observed to migrate to the toluene layer. The hydroxyl group (-OH) of hydrogen peroxide is bound to $Al(OH)_3$, and the hydroxyl group then reacts with the carboxyl group (-COOH) of SOA, resulting in esterification. This process renders the material hydrophobic and well dispersed in toluene, an organic solvent. To identify the efficacy of the surface treatment, the IR spectra were subjected to a comparative analysis, with the data obtained before the surface treatment serving as the baseline. The emergence of new peaks in the range of 3,000 to 2,800 cm^{-1} following the surface treatment serves as confirmation that the procedure was executed correctly (Fig. 2).

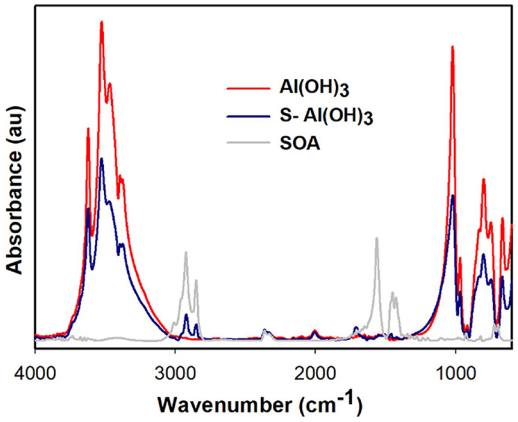

Fig. 2. FTIR spectroscopy analysis of $Al(OH)_3$ powder before and after surface modification by a single step

3. Results and Discussion

3.1. Development of Enhanced Surface Ttreatment Techniques for Neutron Shielding Material

We have improved the surface treatment technology based on the results obtained from the experiments on surface treatment of $Al(OH)_3$ particles. In the previous study, only $Al(OH)_3$ particles, a flame retardant, were surface treated using an excessive amount of hydrogen peroxide (H_2O_2) to perform the surface treatment. In this study, we improved the surface treatment technology to be more efficient and were able to surface not only metal hydrides ($Al(OH)_3$, $Mg(OH)_2$) but also metal oxides (zinc borate) without hydrogen peroxide treatment.

(a) Mixing (b) Drying (c) $Al(OH)_3$

Fig. 3. Representation of a surface modification of as received $Al(OH)_3$ by direct step

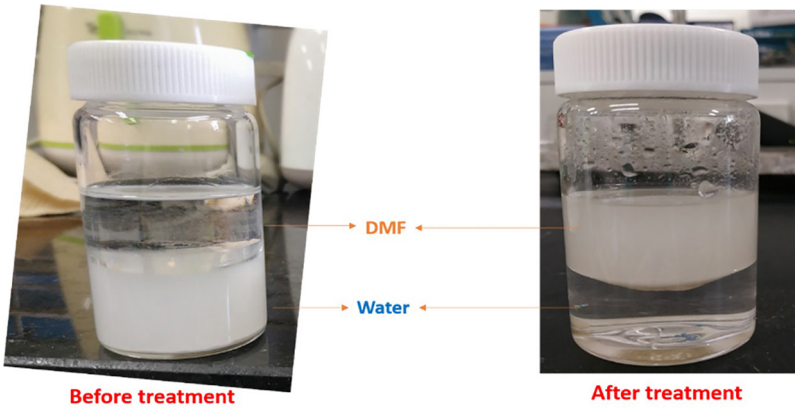

Fig. 4. Optical images of before SOA treatment of $Al(OH)_3$ and after SOA treatment of $Al(OH)_3$ powders in a mixture of water and toluene

3.1.1. Surface modification of $Al(OH)_3$

3.1.1.1. Surface modification of $Al(OH)_3$ by a single step

Based on previous other research ($Mg(OH)_2$ surface modification) $Al(OH)_3$ also followed single-step sodium oleate (SOA) modification. This initially started with a small quantity as of $Al(OH)_3$. In this process 2 wt. % of the as-received $Al(OH)_3$ powder was dissolved in 0.5% of SOA (dissolved in deionized water) under constant temperature at 60°C with a magnetic stirrer. Further, maintain the temperature and agitation for 3 hour later allow to room temperature and measured the pH by using universal pH paper range (1-11). The initial pH was 9 and adjusted to pH 5-6 by adding 1 N HCl solution. Finally, the resulting solution was subjected to vacuum filtration and wash twice with acetone finally dried at 50°C for overnight to remove residual solvent present in the compound the complete schematic representation was shown in Fig. 3.

The as-received $Al(OH)_3$ and SOA modified $Al(OH)_3$ powders were taken in 2 individual 50 mL vials each containing 20 mL of deionized water and 20 mL of toluene as shown in Fig. 4. It is clear that the as-received $Al(OH)_3$ powder is dispersed in the water (bottom) layer whereas, the SOA modified $Al(OH)_3$ was dispersed in the toluene (upper) layer. From the above results, we can conclude that only SOA modified $Al(OH)_3$ surface is also modified and it is good for dispersion in organic solvents. Further, we examine the surface modifications before and after modifications of powder by FTIR spectroscopy as shown in Fig. 2. Based on the FTIR results clearly, we can observe that the as-received $Al(OH)_3$ powder and as received SOA FTIR spectra peaks were co-existing in surface-modified $Al(OH)_3$ powder (labeled as S-$Al(OH)_3$) this confirms that $Al(OH)_3$ is modified by SOA.

3.1.1.2. Upgrade to large scale surface modification by a single step

Further, we upgrade the setup for up to 4 kg per batch, for this, we taken 60 liters of deionized water and dissolved 300 g of SOA and added 4 kg of as received $Al(OH)_3$ powder under constant temperature at 60°C and mechanical stirring and rest of the process same surface modification of $Al(OH)_3$ by a single step and the schematic representation as shown in Fig. 5. In this process, we can observe that after acidity is adjusted to pH

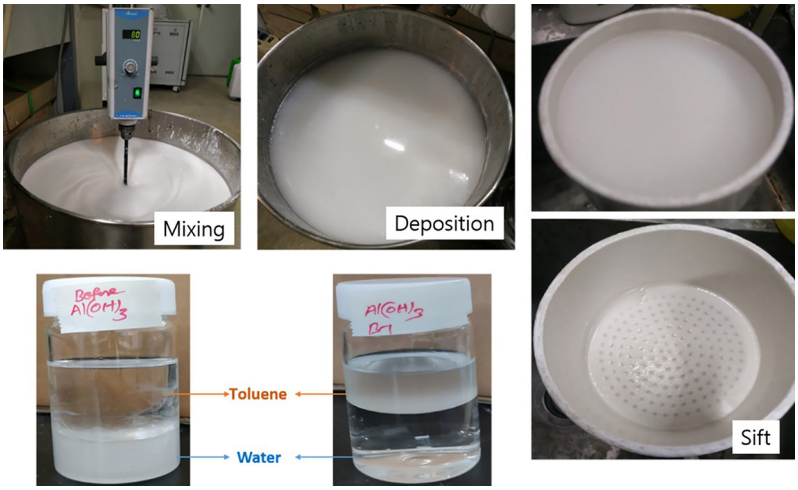

Fig. 5. Schematic representation of a surface modification of as received $Al(OH)_3$ by direct step for large scale

Fig. 6. Schematic representation of a surface modification of as received zinc borate by direct step

5 and allowed to settle we can't see a clear solution on the top like $Mg(OH)_2$. Initially, we thought that there is some $Al(OH)_3$ powder dispersion but we noticed that after filtration there no precipitate observed on the funnel as shown in Fig. 5.

3.1.2. Surface modification of Zinc Borate (ZnB)

3.1.2.1. Surface modification of Zinc Borate by a single step

As with $Al(OH)_3$ and $Mg(OH)_2$ the zinc borate powder was also modified by direct single SOA modification. The as-received zinc borate powder is a hydrated one because of this we avoid the hydroxylation step. This initially start with a small quantity (5 g) of zinc borate. In this process 2 wt. % of the as-received zinc borate powder was dissolved in 0.5% of SOA (dissolved in deionized water) under constant temperature at 60°C with a magnetic stirrer. Further, maintain the temperature and agitation for 3h later allow to room temperature and measured the pH by using universal pH paper range (1-11). The initial pH was 9 and adjusted to pH 5-6 by adding 1N HCl solution. Finally, the resulting solution was subjected to vacuum filtration and wash twice with acetone finally dried at 50°C for overnight to remove residual solvent present in the compound the complete schematic representation was shown in Fig. 6. Further, the as-received zinc borate and SOA modified zinc borate powders were taken in 2 individual 50 mL vials each containing 20 mL of deionized water and 20 mL of toluene as shown in Fig. 6. From Fig. 6 it is clear that the as-received zinc borate powder is dispersed in the water (bottom) layer whereas, the SOA modified zinc borate was dispersed in the toluene (upper) layer. From the above results, we can conclude that only SOA modified zinc borate surface is also modified and it is good for dispersion in organic solvents. Further, we examine the surface modifications before and after modifications of powder by FTIR spectroscopy as shown in Fig. 7. Based on the FTIR

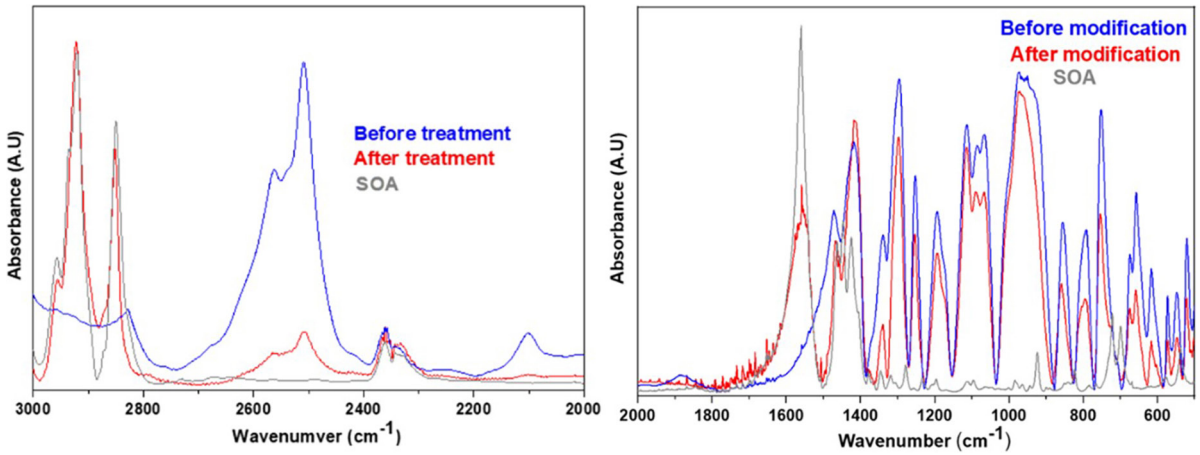

Fig. 7. FTIR spectroscopy analysis of zinc borate powder before and after surface modification by a single step

results clearly, we can observe that the as-received zinc borate powder (Blue color) and as received SOA (grey color) FTIR spectra peaks were co-existing in surface-modified zinc borate powder (Red color).

3.1.2.2. Upgrade to large scale surface modification by a single step

Further, we upgrade the setup for up to 4 kg per batch, for this we taken 60 L of deionized water and dissolved 300 g of SOA and added 4 kg of as received zinc borate powder under constant temperature at 60°C and mechanical stirring and rest of the process same surface modification of Zinc Borate by a single step and the schematic representation as shown in Fig. 6.

3.2. Computer Simulation Performance Evaluation of Neutron Shielding Materials

In order to evaluate the performance of neutron shielding materials, this task makes use of a specific topic report on the metal cask KORAD-21, which was published by the Korea Nuclear Energy and Environment Agency (KORAD). The spent nuclear fuel is mounted within the cask in the form of a square pipe, and neutron absorbers are installed on the outer surface of the cask. A total of 21 spent fuel casks are stored collectively within a single cask. Fig. 8. illustrates the configuration of the canister assembly of KORAD-21. The canister assembly is installed within a cask, which is comprised of a cylindrical side, bottom, and top structure. The outer shell of the cask is designed to accommodate the length of the spent fuel and is equipped with neutron shielding. The cask incorporates a number of engineering designs to facilitate the safe and efficient transportation of the spent fuel. Fig. 9 illustrates the configuration of the cask [8].

3.2.1. Modelling

The structure of spent nuclear fuel casks is highly complex. In order to evaluate the performance of the neutron shielding material developed in this study, the complex cask was simplified and analyzed. The MCNP-6 computer code was employed to assess the performance of the neutron shield, with the spent fuel assumed to be WH17×17 RFA fuel. This is due to the fact that it contains the highest proportion of uranium among the target spent fuel. The spent fuel was assumed to be UO_2 enriched to 4.5 wt.%, with the components that make up the fuel assemblies excluded from the calculations. The empty space within the cask is assumed to be filled with helium for normal operation. The neutron shielding is installed on the outside of the cask with heat transfer fins, but these are also excluded from the evaluation model (Fig 10). Fast neutrons have a greater influence than thermal neutrons due to the fact that neutrons are primarily produced through spontaneous fission, and there is an absence of deceleration material in the surrounding area. The higher the burnup of the nuclear fuel, the higher the emission rate due to the production of transuranic nuclides that undergo spontaneous fission. Therefore, the highest emission rate is observed in the midpoint of the burnup, where the burnup is most advanced. In this analysis, it is assumed that the neutron emission rate varies with burnup along the axial direction of the spent fuel, but remains constant in the transverse direction. The present study did not analyze the areas on the bottom, lid, and

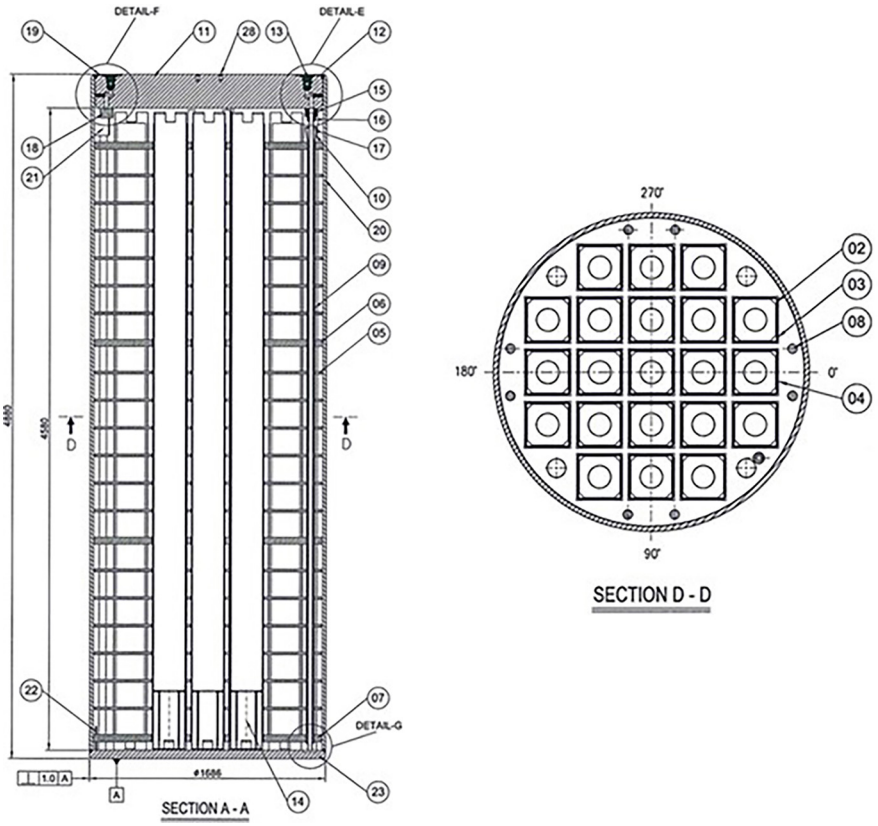

Fig. 8. Drawing of KORAD-21 Canister

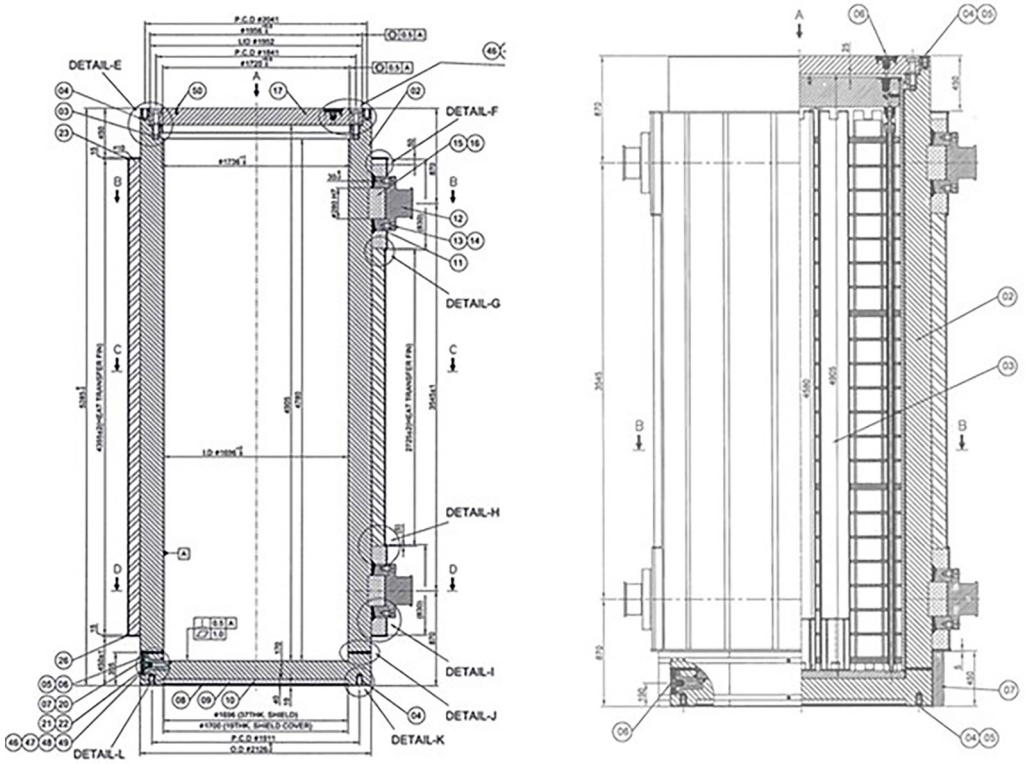

Fig. 9. Drawing of KORAD-21 Cask

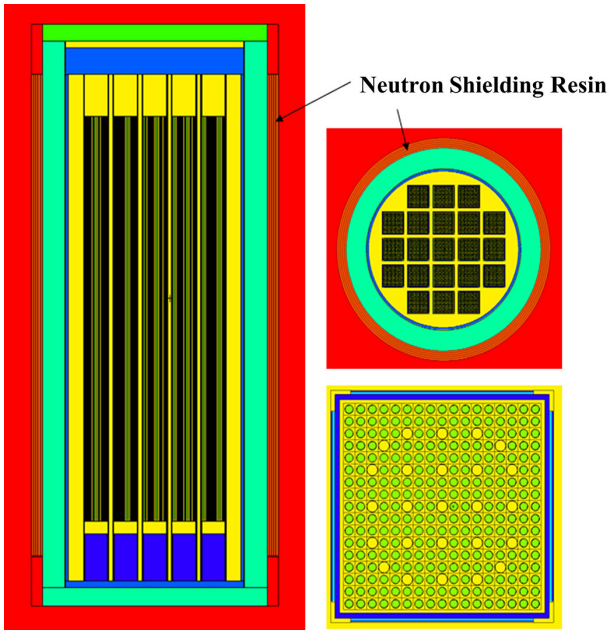

Fig. 10. MCNP-6 Modelling

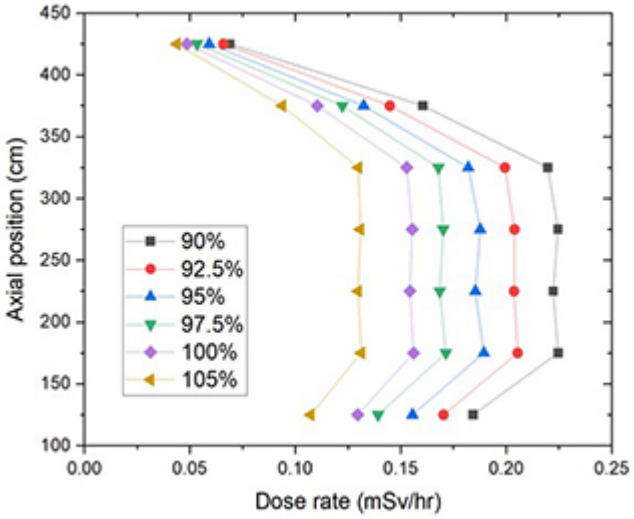

Fig. 11. Surface dose rate as a function of neutron shielding material density

sides of the cask where neutron shielding is not located. The surface neutron flux in areas where shielding is installed was calculated, and dose conversion was performed using factors from ICRP-74. To validate the methodology and model employed in this study, the findings were compared with those of the KORAD-21 Specific Topic Report, as illustrated in Table 1 [8].

3.2.2. Evaluation of Neutron Shielding Material

The material has a density of 1.62 g/cm^3. The primary constituents of the neutron shielding material are hydrogen, carbon, boron, aluminum, oxygen, and zinc. As evidenced in the KORAD-21 Cask Topical Report, a substantial majority (i.e., greater than 90%) of neutrons present in spent nuclear fuel are fast neutrons with energies exceeding 1 MeV. Given the relatively modest absorption cross-section in the fast neutron region, it is recommended that a mixture of materials with high deceleration capability and a substantial neutron absorption cross-section be employed for shielding purposes. In the case of this neutron shielding material, hydrogen plays a role in slowing down neutrons, while boron, which has a large neutron absorption cross-section, absorbs neutrons, thereby improving the overall shielding performance. The efficacy of neutron shielding materials was assessed based on two key variables. First, the performance of the neutron shielding material was evaluated in accordance with the observed change in density. Secondly, the change in the content of the main components was also considered. Fig. 11 illustrates the correlation between neutron shielding material density and dose variation. The evaluation of the surface dose of the neutron shielding material demonstrated

Table 1. Dose Assessment on Cask Side Surfaces

Contents	KORAD-21 Topical Report [8]		Results	
	Position	Dose rate (max)	Axial Position (cm)	Dose rate (Avg)
Cask Side Surface	Upper	0.22	400~450	0.06
			350~400	0.12
			300~350	0.16
	Middle	0.28	250~300	0.17
			200~250	0.17
			150~200	0.17
			100~150	0.14

*Units: mSv h^{-1}

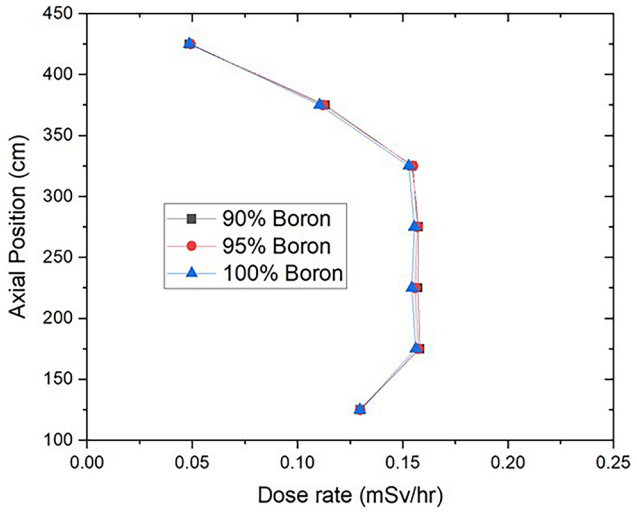

Fig. 12. Surface dose rate as a function of boron contents in neutron shielding material

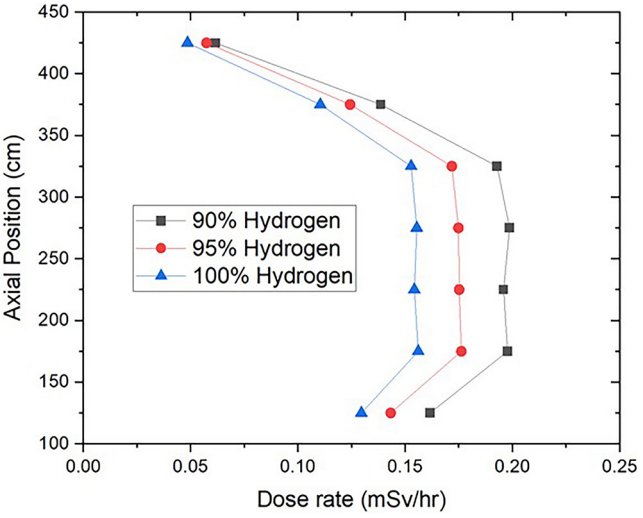

Fig. 13. Surface dose rate as a function of hydrogen contents in neutron shielding material

that the dose was higher in the center of the axial direction. This is due to the fact that the neutron emission rate of spent fuel is higher in the center of the axial direction. It is evident that the efficacy of the neutron shielding diminishes as the density of the material in question is reduced. The mean surface dose of the existing material in the central axial region of the neutron shield was determined to be 0.167 mSv/hr, whereas the mean surface dose of the neutron shield utilized in this investigation was found to be 0.1547 mSv/hr, indicating an enhancement in neutron shielding efficacy of approximately 7.4%. The surface dose was evaluated in relation to the content of boron and hydrogen, the primary components incorporated into the shielding material mixture for neutron shielding. As illustrated in Figs. 12 and 13, the impact of boron is nearly inconsequential, whereas the influence of hydrogen is pronounced. This indicates that the energy of neutrons generated from spent nuclear fuel is relatively high, thereby underscoring the importance of mechanisms designed to decelerate high-speed neutrons for the effective performance of neutron shielding materials. Accordingly, when developing neutron shielding materials, it is advisable to prioritize the inclusion of hydrogen over that of boron.

4. Conclusion

We have developed a multi-functional, high-efficiency shielding material technology in which a boron compound and flame retardant that can shield neutrons are combined with an unsaturated polyester resin containing a large amount of hydrogen that can effectively shield fast neutrons. The technology developed in this study is a nanocomposite material technology with improved structural integrity, mechanical properties, and shielding performance compared to existing products, and will be able to be used as a competitive technology that can be commercialized as a domestic model material.

Given that spent fuel casks will be managed within a controlled area, there is currently no established standard for dose. Nevertheless, it is established that in the United States, 10 CFR 72 permits a dose rate of 0.2 to 4.0 mSv per hour at the surface of the cask. Furthermore, it is customary to design for an annual dose limit of 0.25 mSv at the boundary of the controlled area. In this study, the surface dose rates specified in 10 CFR 72 were found to be adequate for normal operations.

Acknowledgments

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