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Basic Mechanical and Neutron Shielding Performance of Mortar Mixed with Boron Compounds with Various Alkalinity

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Abstract: This study conducted fundamental tests on mortars using the boron compounds recycled industrial wastes to replace uneconomic boron products. The boron compounds were three types according to the pH and the physical and neutron shielding performance of mortar mixed with boron compounds was examined. The adopted boron compounds classified as acid, slightly alkaline, and strongly alkaline with respect to the pH are acidic boric acid, alkali borax, and high alkali borax, respectively. The physical properties were evaluated by measuring the compressive strength and setting time as well as the thermal neutron shielding performance. The measured compressive strength revealed that the strengths of the specimens mixed with boron compounds were generally lower than that of the basic specimen made of control specimen. In addition, the initial and final setting times were longer than those of the control specimen. The thermal neutron shielding performances of the specimens mixed with boron compounds were higher than that of the control specimen. Consequently, the differences of the type and chemical composition of boron compounds influenced the physical properties and thermal neutron shielding performance of mortar, including its compressive strength, setting time, and neutron shielding performance. Therefore, it is important to determine the optimal amount of boron compounds in the fabrication of mortar.

Keywords: boron compound; compressive strength; setting time; thermal neutron shielding performance

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1. Introduction

Recently, Korea has witnessed increasing exploitation of radiation-generating devices such as accelerators in the medical, research, and industrial sectors [1,2]. The accompanying release of high-level radioactive energy stresses the importance of shield and protection technologies for corresponding facilities [3,4]. In particular, concrete is widely exploited for shielding containers in facilities using radioactive substances owing to the low price of this highly dense and heavy material as well as its outstanding shielding performance. Moreover, studies are actively being conducted on improving the shielding performance of concrete by mixing with hydrogen (H)-based macromolecule compounds that can slow down the fast neutrons into the slow neutrons or by adding materials such as boron that can capture neutrons [5–8]. However, the utilization of such macromolecule compounds and boron compounds is difficult due to problems related to the increase of the initial construction cost and the loss of physical properties. Especially, because of the rarity of boron mines worldwide, boron is very expensive and its exploitation in concrete is limited because of its effect on the physical properties, including the setting delay and loss of strength [9,10].

Among boron compounds, boron carbide presents strong molecular bonds and does not affect the durability of concrete, because it becomes inactive in concrete. However, beyond a definite amount, this compound provokes steep degradation of the mechanical

properties and is so expensive that it becomes economically unaffordable [9,10]. Apart from admixing boron directly, there are also methods to admix boron indirectly by using minerals including boron. For example, one method replaces the aggregates with minerals such as colemanite [11,12] but is difficult to apply due to the limited number of producing mines and the ever-present loss of physical properties. Ongoing studies focusing on the utilization of boron carbide or colemanite as a replacement material are being conducted, but the lack of research on the exploitation of other boron compounds or their improvement is noteworthy.

Accordingly, this study performs a series of fundamental tests on mortars using three types of boron compounds with respect to the alkalinity, considering recycled industrial wastes that can be easily supplied. In addition, the boron compound used in this paper is about 95% cheaper than existing boron products and has excellent economic efficiency (Boric acid price: 1500 $/ton, Borax price: 1000 $/ton, based on 2013 values).

Moreover, tests are performed to evaluate the physical properties of mortar mixed with boron compounds with respect to the alkalinity with reference to the previous literature, pointing out the possibility to improve the physical performance of concrete according to the alkalinity level of specimens admixed with boron compounds [13].

In physical experiments, compressive strength and setting time tests were performed for each age, and the neutron shielding test was conducted on thermal neutrons to examine the shielding performance.

2. Materials and Methods

2.1. Summary of Tests

The series of tests conducted for the analysis of the physical properties and neutron shielding performance of mortar mixed with boron compounds in this study are listed in Table 1. Three types of boron compounds were considered according to the alkalinity and acidity. The mortar mixtures were produced in the thirteen mix proportions according to the type and replacement ratio of boron compounds.

Table 1. Experimental plan.

	Factor	Type
Mixture	W/C	0.485
	Boron content (wt%)	0.2/0.4/0.6/0.8
	Boron compound types	• Acidic boric acid (AA) • Alkali borax (AB) • High alkali borax (HB)
Experiment	Physical properties	• Compressive strength • Setting time test • Thermal neutron shielding performance

The content of boron compounds was set to less than 1% of the fine aggregates with reference to regulations of ASTM C637 and C638, previous literature, and the results of preliminary tests [14–18]. The replacement rations of boron compound are 0.2%, 0.4%, 0.6%, and 0.8% of fine aggregates.

In the experiment, compressive strength and setting test mixtures are measured at 3, 7, and 28 days according to the type and content of boron. The neutron shielding test is performed by selected boron based on the results of the physical properties.

2.2. Materials and Mixtures

Type-1 Ordinary Portland Cement (OPC, specific gravity: 3.15 g/cm^3, fineness: 3800 cm^2/g) was used and the fine aggregate was produced by company A in Korea. Tables 2 and 3 arrange the details of the adopted cement and aggregate.

Table 2. Chemical composition of OPC.

Cement	Main Components (%)				
	SiO_2	Al_2O_3	MgO	SO_3	CaO
OPC	21.01	6.40	3.02	2.14	61.33

Table 3. Physical properties of the aggregate (agg.).

Type	Size (mm)	Density (g/cm^3)	Water Absorption (%)	Fineness Modulus (FM)
Fine agg.	2.56	1.09	1.83	2.59

In addition, the pH was measured in solutions in which the boron compounds were preliminarily mixed with distilled water [18]. The compounds were then classified into acid, alkaline, and highly alkaline according to the measured pH. The adopted compound products are acidic boric acid (AA) from company B of China for the acid type, and low alkali borax (AB) and high alkali borax (HB) from company C of Turkey for the alkaline and highly alkaline compounds, respectively. The compositions of the considered boron compounds are shown in Table 4.

Table 4. Physical properties of the aggregates (%).

	AA	AB	HB
B_2O_3	56.3	22.8	40
$Ca(OH)_2$			40
Al_2O_3		0.038	
CaO		0.057	20
K_2O		0.042	
Na_2O		40.36	
Fe_2O_3	0.0007	0.026	
$S(SO_4)$	0.05	3.18	
Cl	0.001		
pH	3.9 (Acid)	9.2 (Alkali)	12.8 (High alkali)
Density (g/cm^3)	1.49	1.72	2.5

The boron (B_2O_3) contents of the compounds were 56.3% for AA, 40% for HB, and 22.8% for AB. Compound HB also contains $Ca(OH)_2$ and CaO, which is expected to produce remarkable hydration and strength compared to the mortar mixtures using other compounds [13,19–21]. On the other hand, compound AB has the smallest content of boron and includes large quantities of impurities, which are expected to make the mixtures mixed with AB less prone to the boron-induced setting delay [7,8].

Table 5 arranges the details of the thirteen mix proportions considered according to the type and replacement ratio of boron compounds.

Table 5. Details of tested mortar mixtures.

	W/C (%)	Cement [kg/m^3]	Fine Aggregate [kg/m^3]	Boron Compound [kg/m^3]	Boron Compound Content (%)
Control	48.5	568.35	1392.45	0	0
AA-0.2			1389.66	1.62	0.2
AA-0.4			1386.88	3.24	0.4
AA-0.6			1384.09	4.86	0.6
AA-0.8			1381.31	6.48	0.8
AB-0.2			1389.66	1.87	0.2
AB-0.4			1386.88	3.73	0.4
AB-0.6			1386.09	5.60	0.6
AB-0.8			1381.31	7.46	0.8
HB-0.2			1389.66	2.73	0.2
HB-0.4			1386.88	5.46	0.4
HB-0.6			1386.09	8.19	0.6
HB-0.8			1381.31	10.92	0.8

2.3. Fabrication of Specimens and Testing Method

The compressive strength of hardened mortar was measured in compliance with KS L 5105 on three 50 × 50 × 50 mm^3 cubes per mix at 3, 7, and 28 days [22]. The setting time of mortar was defined as the period of time from early to final setting corresponding to penetration resistances of 3.5 and 28 MPa, respectively. The test was interrupted when final setting did not occur within 48 h [23]. The neutron irradiation specimen was manufactured cross-section of 15 × 15 cm and a thickness of 5 cm on considering the size of neutron irradiation test equipment. The curing was carried out wet curing a constant temperature of 23 ± 2 °C.

The shielding performance tests of boron compounds to thermal neutrons were conducted using a method available in the literature. A neutron transmission test was performed using a combination of a ^{241}Am/Be neutron source and a ^{3}He proportional counter (SP-9). In addition, the test was conducted at the Radiation Source Standards Center, Korea Research Institute of Standards and Science. The ^{241}Am/Be neutron source is one of the four calibration standard sources presented in ISO 8529-1 and the spectrum of the source is shown in Figure 1. Figure 2 shows the thermal neutron shielding experiment [24]. The experiment was conducted by wrapping a neutron source (^{241}Am/Be neutron source) with polyethylene and decelerating a high-speed neutron to change it into a thermal neutron and then irradiating it to the specimen to measure (using the ^{3}He proportional counter) the number of thermal neutrons that passed through the specimen.

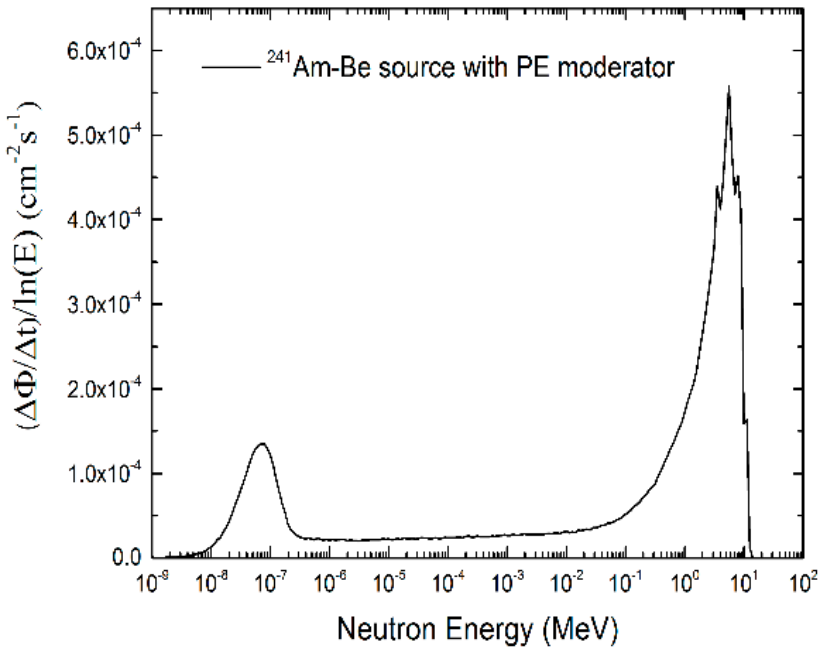


Figure 1. Neutron spectrum of the ^{241}Am-Be source.

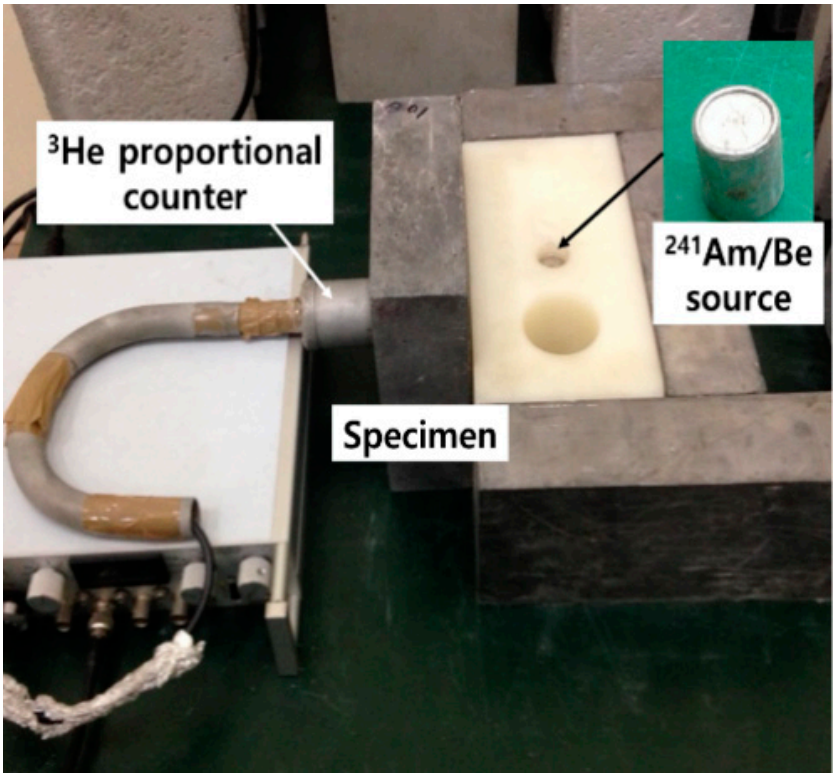


Figure 2. Thermal neutron measurement.

3. Results and Discussion

3.1. Compressive Strength Test

Figures 3–5 show the measured compressive strength in the mortar mixed with the boron compounds. Overall, the compressive strength of the mixtures tended to decrease more than the control specimen. The analysis showed that the compressive strengths of the mortar mixed with boron compounds were different according to the type and content of the boron compound. Compared to the control specimen, mixes AA and AB

resulted in reduced compressive strength, but the strength of HB increased as the boron content increased.

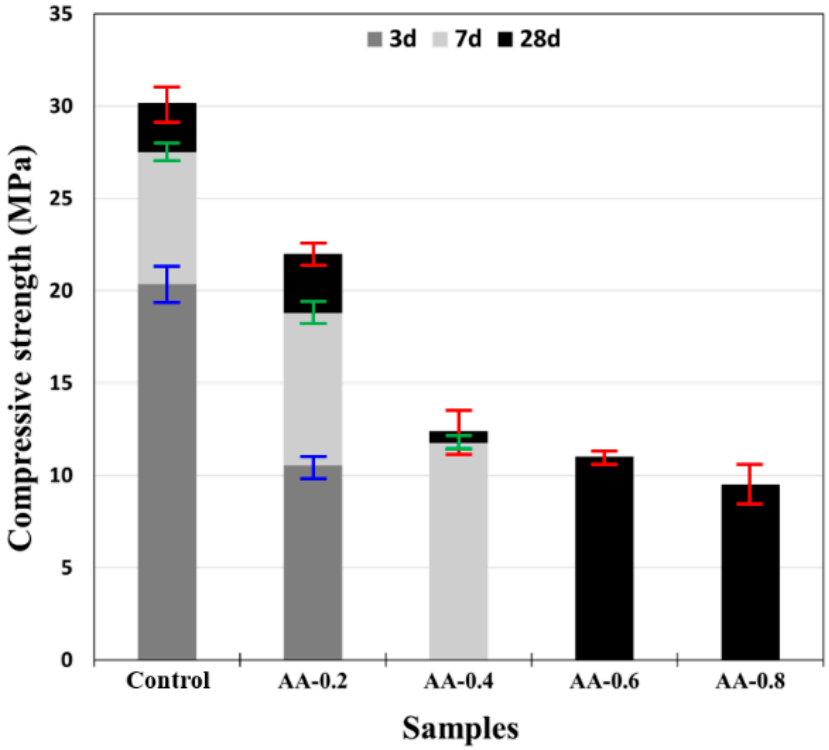


Figure 3. Compressive strength of AA.

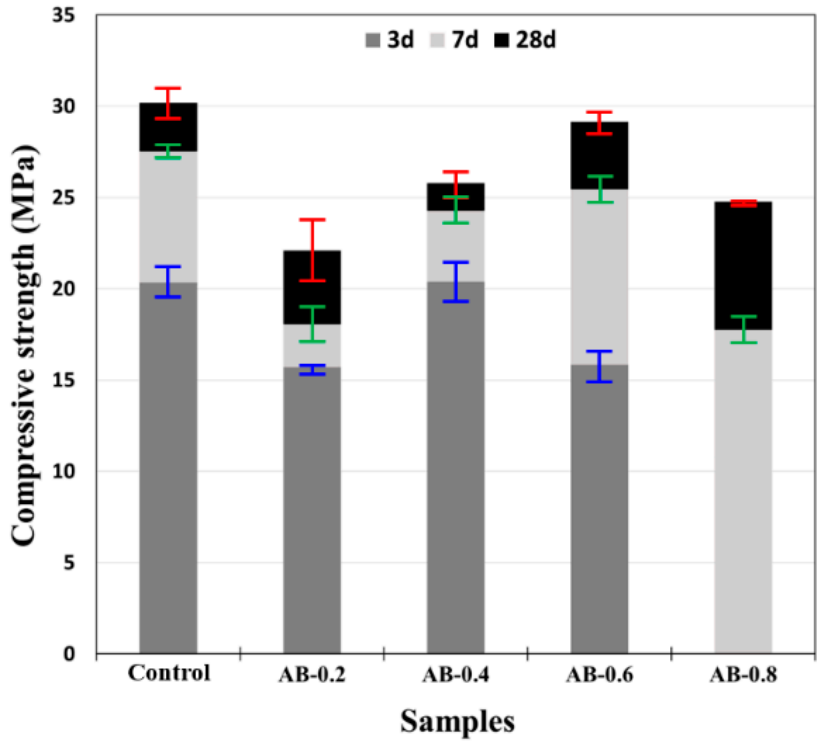


Figure 4. Compressive strength of AB.

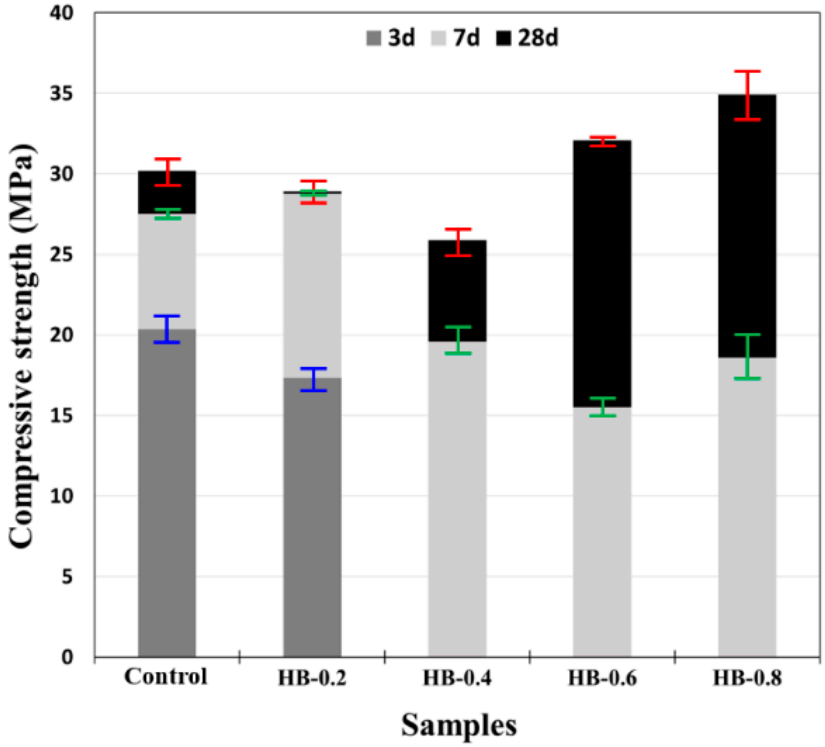


Figure 5. Compressive strength of HB.

Figure 3 plots the compressive strength of the specimen containing AA and it showed a decreasing tendency with increased content of boron. In particular, the loss of the compressive strength was at least 3% to a maximum of 27% compared to the control specimen at 28 days of age. In addition, when the boron compound content was 0.4% or more, the strength was not measured because the concrete was not hardened until 3 or 7 days of age. The reason for this is that the boron compound AA has the highest boron content (B_2O_3) among the boron compounds, and the boron content (B_2O_3) affected the hydration and hardening of the cement [13,19–21].

Figure 4 shows the compressive strength of AB and it shows a different trend than AA. The specimens of AB also showed that the compressive strength was decreased compared to the control specimen, but AB showed a tendency to increase up to 0.6% and then decrease. In particular, the boron content of AB exceeds 0.6% and the hardening of the mortar did not occur until day 3. It appears that the delay of hardening had an effect on the overall compressive strength.

The compressive strength of boron HB is shown in Figure 5. The compressive strength of the HB specimen tended to increase as the content of HB increased. The HB boron also did not cause hardening until 3 days when the boron content was more than 0.4%, so the compressive strength was not measured at 3 days. However, unlike AA and AB, the strength at 28 days was excellent. In particular, in the case of HB-0.6 and HB-0.8, the strengths at 28 days of age were 7% and 16% higher respectively, than that of the basic test specimen, even though it did not cure until 3 days of age. The compressive strengths of the HB mixtures can be attributed to the large contents of $Ca(OH)_2$ and CaO of compound HB [13,19]. Even if the HB mixtures had delayed setting, the $Ca(OH)_2$ and CaO components contributed to the generation of hydrates, which mitigated the loss of the compressive strength.

It was confirmed that the strength and setting properties differed depending on the component of the boron compound. Therefore, it is desirable to determine the optimal mixing amount after examining the characteristics.

3.2. Setting Test

Table 6 shows the setting test results of the mortar specimens mixed with boron compounds. The initial and final setting times appear to occur later than those of the control specimen, regardless of the type and dosage of the boron compound [9,10]. In particular, as the B_2O_3 content of the boron compound and the boron content increased, the initial and final times were delayed.

Table 6. Setting times of cement paste with boron components.

Sample	Initial Setting Time (Hour:Min)	Final Setting Time (Hour:Min)
Control	4:20	8:10
AA-0.2	26:55	45:30
AA-0.4	over 48 h	over 48 h
AA-0.6	over 48 h	over 48 h
AA-0.8	over 48 h	over 48 h
AB-0.2	7:35	18:10
AB-0.4	3:40	27:25
AB-0.6	over 48 h	over 48 h
AB-0.8	over 48 h	over 48 h
HB-0.2	12:20	14:12
HB-0.4	16:45	over 48 h
HB-0.6	over 48 h	over 48 h
HB-0.8	over 48 h	over 48 h

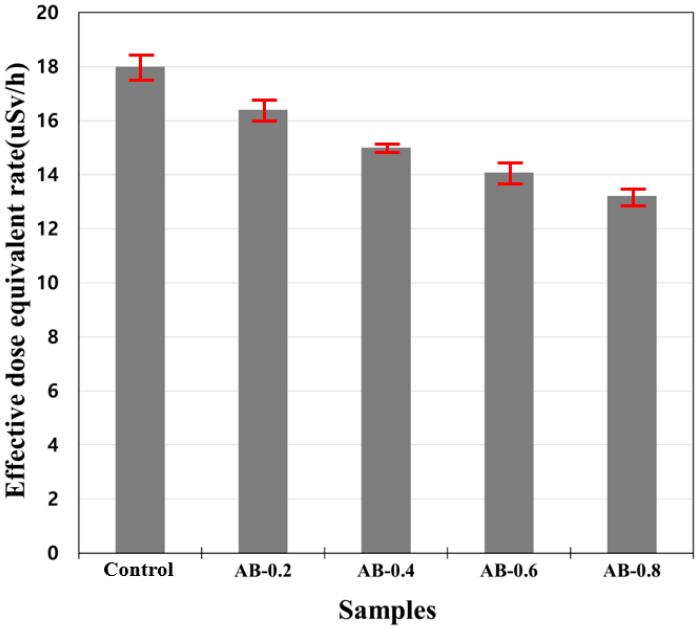
The AA specimens exhibited the latest initial setting times, and mix AA-0.4 did not initiate setting even after 48 h. The AB mixtures showed the fastest initial setting, and the initial setting of mix AB-0.4 occurred earlier than MOR. Mix HB-0.2 had the shortest time between the initial and final setting times, but the specimens with contents exceeding 0.2% were over 48 h. Specimen HB showed the longest setting delay despite its highly alkaline environment (Table 5). This is in contradiction with the well-known reduction of the setting delay of the mortar mixed with boron in a highly alkaline environment reported in the literature [25]. This setting delay already reported in the work of Davraz is due to the delay of the hydration and other chemical reactions caused by the $Ca[B(OH)_4]_2$ compounds generated by the reaction of Ca^{2+} and OH^-, which block any contact with the water enclosing the surface of cement [13,19]. Consequently, this indicates the need for further studies on other factors governing the setting of mortar, apart from the alkalinity resulting from the admixing of boron compounds.

3.3. Thermal Neutron Shielding Test

Thermal neutron shielding experiments were performed on the AB and HB specimens selected based on the compressive strength and setting tests. The thermal neutron shielding test was performed as discussed in Section 2.3 by measuring the thermal neutrons passing through the specimen using the ^{3}He proportional counter.

Figures 6 and 7 show the effective dose equivalent and the shielding performance of the specimens. In the graphs, the x- and y-axes represent the type of specimen and the dose equivalent rate, respectively. In addition, the shielding rate was compared to the control specimen for each specimen.

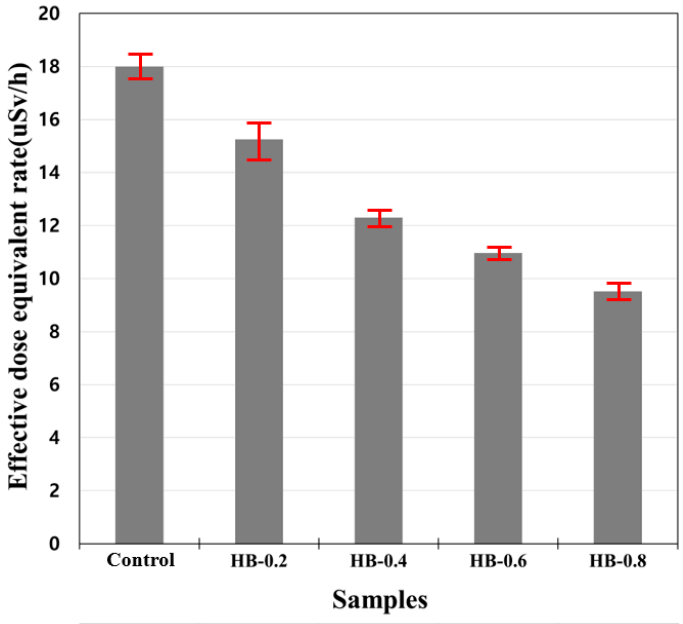
The effective dose equivalent of the control specimen was 18 uSv/h, whereas that of AB was from 13.2 to 16.4 uSv/h and that of HB was from 9.5 to 15.3 uSv/h. In other words, the specimen containing the boron compound was observed to have a lower effective dose equivalent than the control specimen and the shielding performance tended to increase as the amount of the boron compound was increased.



	AB-0.2	AB-0.4	AB-0.6	AB-0.8
Neutron shielding* (%)	9	17	22	27

*Was compared to the neutron shielding performance in the Control

Figure 6. Thermal neutron shielding performance of AB.



	HB-0.2	HB-0.4	HB-0.6	HB-0.8
Neutron shielding* (%)	15	32	39	47

*Was compared to the neutron shielding performance in the Control

Figure 7. Thermal neutron shielding performance of HB.

The thermal neutron shielding performance of AB showed an improvement of at least 9% and up to 28% compared to the basic specimen. HB had improved shielding performance of at least 15% and up to 47% compared to the control specimen. In particular, HB showed about a 2 times higher shielding rate than AB [26,27].

The reason for this is considered to be that the boron (B_2O_3) of HB is about twice that of AB [26–28]. In addition, the density of HB boron is higher than AB and this affects thermal neutron shielding. The component of boron is also considered to have an effect on the neutron shielding performance. The $Ca(OH)_2$ content of HB is higher than other specimens, which affects durability and density, including strength [13,19–21]. Therefore, these effects can be verified in the thermal neutron shielding performance results shown in Figures 6 and 7. Consequently, in the case of mortar mixed with boron compound, it is recommended to determine the optimal dosage of boron considering the fact that the physical and thermal neutron shielding performance depend on the type and composition of the boron compound.

4. Conclusions

The physical characteristics of boron compounds and neutron shielding performance were analyzed in mortar mixed with various boron compounds. The following conclusions can be drawn from the results.

The compressive strength of AA and AB was decreased, but HB was increased. The compressive strength characteristics of boron compound showed differences according to the dosage and composition of boron. These characteristics should be considered when determining the optimal boron content.

The mortars mixed with boron compounds underwent longer setting delays compared to the control specimen. In particular, when the content of boron compounds exceeded 0.2%, it did not harden within 48 h.

The thermal neutron shielding performance of the boron compounds was at least 9% and up to 47% higher than the basic specimen, regardless of the type of boron compound. This performance depended on the content and composition of the boron compound.

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