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(54) **Neutron-shielding hydraulic hardening material and method of manufacturing neutron shields using the same**

(57) The present invention provides a neutron-shielding hydraulic hardening material containing 10-50% by weight of hydraulic cement, 30-88% by weight of aluminum hydroxide, and 0.1-35% by weight of boron carbide. The invention also provides a method of manufacturing a neutron shield. The method includes the steps of mixing 100 parts by weight of the hydraulic hardening material, 15-50 parts by weight of water, and not more than 5 parts by weight of at least one chemical admixture selected from the group consisting of air-entraining agents, air-entraining and water reducing agents, high-range water reducing agents, plasticizers, air-entraining and high-range water reducing agents, and foaming agents; and kneading the resultant mixture. The neutron-shielding hydraulic hardening material of the invention has an excellent neutron shielding effect, satisfactory strength of afterhardening product, and has good workability of fresh mortar. Therefore,

when neutron shields are manufactured according to the method of the present invention, neutron shields with enhanced uniformity can be obtained.

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**Description**

## Field of the Invention:

5 The present invention relates to a neutron-shielding material which is useful in the fields of nuclear power plants, reprocessing of spent nuclear fuels, spent nuclear fuel disposal, medicine, etc., and particularly useful for shielding neutrons generated from various sources in such fields. The invention also relates to a method of manufacturing neutron shields.

## 10 Background Art:

In recent years, the percentage of electric power generated by nuclear power plants has been increasing steadily. However, from the viewpoints of nuclear nonproliferation and, particularly in a country like Japan which has very limited natural resources, from the viewpoint of the need to secure effective natural resources, recycling of spent nuclear fuels  
15 has become one of the top priority issues. In the processes of nuclear power generation, a considerable amount of neutrons are generated by active nuclear reactions. Moreover, spent nuclear fuels and nuclear fuel wastes generate neutron rays during self-decay of the resultant fission products.

In order to shield such highly energetic neutrons, it is required that the energetic neutrons be slowed down to thermal neutrons using elements having a small atomic mass number, e.g., hydrogen (H), and that the thermal neutrons be  
20 absorbed by a suitable substance such as boron (B). Thus, a material containing both hydrogen and boron at high concentrations is considered to be effective as a neutron shield.

Cement is a relatively good material for shielding neutrons because, when transformed into mortar or concrete, it is mixed with water so as to form a hydrate that traps water therein. However, the amount of water bound as a constituent of hydrate is small, and the greater part of mixed water is free water, which is likely to be lost due to evaporation,  
25 etc. Plastics such as polyethylene may also contain a relatively large amount of hydrogen. However, generally speaking, plastics are weak against heat and have poor long-term durability. In addition, they are difficult to form into large members of high density. For these reasons, uses of plastics are limited.

Exemplary substances containing boron include natural minerals such as colemanite ( $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) and kurnakovite ( $2\text{MgO} \cdot 3\text{B}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ ). In order to shield neutrons, use of these minerals as aggregate of concrete may  
30 be conceivable. However, the boron content in these minerals is as low as 12-17% by weight, so it is difficult to secure boron content at a high concentration. Moreover, these minerals release  $\text{B}_2\text{O}_3$ , which inhibits cement from setting or hardening. To suppress release of  $\text{B}_2\text{O}_3$ , there has been made an attempt to coarsen the grain size of aggregate to thereby reduce specific surface area. This approach, however, cannot avoid uneven distribution of boron in concrete. In addition, control of grain size of powdery aggregate is difficult. As a result, it is not only impossible to obtain highly plasticized concrete, but it also becomes difficult to place concrete into a formwork uniformly.  
35

As described above, conventional neutron shields and materials therefor have the following drawbacks: Limited hydrogen content and boron content; low strength against heat and external physical force; a tendency to leave large voids in concrete products; difficulty in forming large members or members having complex shapes; and difficulty in obtaining shields having a uniform composition. Therefore, they are not satisfactory as neutron shields around nuclear  
40 reactors or high level radioactive waste.

Under the above circumstances, the inventors of the present invention conducted careful studies, and found that hydraulic hardening materials containing hydraulic cement, aluminum hydroxide, and boron carbide at certain proportions have excellent neutron shielding properties, strength of afterhardening products, and workability of fresh mortar, and that they are capable of forming uniform shields. The present invention was accomplished based on these findings.  
45

## Summary of the Invention:

Accordingly, the present invention provides a hydraulic hardening material for shielding neutrons (hereinafter may be referred to as neutron-shielding material) characterized by containing 10-50% by weight of hydraulic cement, 30-  
50 88% by weight of aluminum hydroxide, and 0.1-35% by weight of boron carbide.

The present invention also provides a method of manufacturing a neutron shield including the steps of mixing 100 parts by weight of the above-mentioned neutron-shielding hydraulic hardening material, 15-50 parts by weight of water, and not more than 5 parts by weight of at least one chemical admixture selected from the group consisting of air-entraining (AE) agents, air-entraining and water reducing agents, high-range water reducing agents, plasticizers, air-  
55 entraining and high-range water reducing agents, and foaming agents; and kneading the resultant mixture.

## Detailed Description of the Invention

Among the constituents of the neutron-shielding hydraulic hardening material of the present invention, the hydraulic

cement provides the target afterhardening structure with strength when mixed with water, aluminum hydroxide provides hydrogen atoms that slow down highly energetic neutrons to thermal neutrons, and boron carbide provides boron atoms that absorb thermal neutrons which have been slowed down by hydrogen atoms. These three constituents work together so as to exert a function as a neutron shield.

5 Hydraulic cements are not particularly limited so far as they harden when mixed with water to thereby develop strength. For example, they may be any one of Portland cements such as ordinary Portland cement and high-early-strength Portland cement; blended cements such as Portland blast-furnace slag cement, Portland pozzolan cement, and Portland fly-ash cement; or ultra-rapid-hardening cement (Jet cement). In addition to these types of cement, there may be used admixtures such as blast-furnace slag, silica fume, fly ash, limestone powder, and gypsum. If needed,  
10 there may also be used additives that are ordinarily used in mortar and concrete; e.g., expansive additives, accelerator, corrosion inhibitor, and waterproofing agents.

Aluminum hydroxide may take a polymorphism such as diaspore, boemite, and gibbsite. In consideration of stability at high temperatures, gibbsite is most preferred. The theoretical hydrogen content of gibbsite is 3.8% by weight.

Boron carbides take the form of  $B_4C$ ,  $B_8C$ ,  $B_{13}C_2$ , etc. Under general circumstances,  $B_4C$  is the easiest one to  
15 obtain. Moreover,  $B_4C$  is preferred because of its good stability. The theoretical boron content of  $B_4C$  is as high as 78% by weight.

When a neutron-shielding hydraulic hardening material neutrons is mixed with water and thereby hardens to develop enough strength as a structure, it is necessary that hydraulic cement be present in the amount of at least 10% by weight.

20 If hydrogen and boron are both co-present, the neutron absorbing effect may be exerted more effectively. Therefore, it is concluded that proper ranges for the content of hydraulic cement, aluminum hydroxide, and boron carbide are 10-50% by weight, 30-88% by weight, and 0.1-35% by weight, respectively. In this case, if  $^{10}B$  is extremely concentrated (in nature,  $^{10}B$  is present in an amount of about 20%), 0.1% by weight of boron carbide would yield an effect, whereas if boron present in nature is used, it must be incorporated in amounts of at least 0.5% by weight.

25 Hydraulic cement is obtained through grinding the clinker that has been burned in a rotary kiln, and mixing it with suitable admixtures such as gypsum. Aluminum hydroxide is usually manufactured using a Bayer's process for industrial production. Boron carbide is normally manufactured through carbonizing of boron oxide ( $B_2O_3$ ) using carbon, and the resultant mass is used after being pulverized. Generally, hydraulic hardening materials obtained by the mixture of these heterogeneous powders have poor fluidity when mixed with water. In extreme cases, flow and slump are barely  
30 obtainable. In addition, ordinary tamping bars cannot achieve uniform filling of the cement into a flow cone or a slump cone; therefore a vibrator is usually required for achieving a uniform placing. Thus, in order to improve fluidity of mortar after the above-mentioned complexed powder has been mixed with water, the powder in a dry state preferably has a filling ratio of not lower than a threshold value.

Specifically, it is preferred that the filling rate be not less than 55%, more preferably not less than 60%, when measured  
35 in such a manner that the powder in a dry state is put in a hollow cylindrical container having an inner diameter of 5 cm and a height of 5 cm, and then compacted by 180 tapings from the height of 2 cm.

In order to enhance the filling ratio of the constituent powdery materials in a dry state to thereby improve the mortar fluidity, it is effective to broaden the distribution of the particle size of the powders.

Alternatively, groups of powders, having peaks at different positions of particle size distribution (i.e., at smaller particle  
40 sizes and at larger particle sizes) that are widely apart from one another, may be used. Specifically, it is preferred that the particles, when sieved through a mesh of 1 mm, be of such distribution that oversize particles are present in an amount of not more than 5% by weight, particles having a diameter of equal to or smaller than 100  $\mu m$  are present in an amount of 60-80% by weight, and particles having a diameter of 60-90  $\mu m$  are present in an amount of not more than 20% by weight.

45 The neutron-shielding hydraulic hardening material of the present invention provides a neutron-shielding product after being mixed with water and then setting. It is not necessarily preferred if the mixing ratio of powders to water is defined by the ratio of water content to cement content as in the case of ordinary mortar and cement.

Instead, it is proper that the ratio be defined in terms of the entirety of powders and water. The ratio is preferably such that water is used in an amount of 15-50 parts by weight with respect to 100 parts by weight of the neutron-shielding  
50 hydraulic setting material of the present invention. If the water content is less than 15 parts by weight, uniform mortar cannot be obtained, whereas if the water content is in excess of 50 parts by weight, not only is strength of the afterhardening product reduced significantly, but there is also caused considerable separation of materials at the time of concrete placement.

Also, if even more improved fluidity is desired for the neutron-shielding hydraulic hardening material of the present  
55 invention when it is mixed with water, this may be achieved by the addition of water reducing agents or high-range water reducing agents. If lighter neutron-shielding products are desired, this may be achieved by adding air-entraining agents, foaming agents, or similar agents to thereby introduce very fine air bubbles in the material while maintaining the uniformity of the composition. That is, the neutron-shielding hydraulic hardening material of the present invention may contain at least one chemical admixture selected from the group consisting of air-entraining agents, air-entraining and

water reducing agents, high-range water reducing agents, plasticizers, air-entraining and high-range water reducing agents, and foaming agents. Preferably, these are incorporated in a total amount of not more than 5 parts by weight per 100 parts by weight of the neutron-shielding hydraulic hardening material of the present invention. If the total amount of the additives is in excess of 5 parts by weight, the additives may become separated when mixed with water; thus these amounts are not preferred.

A fresh mortar obtained through mixing neutron-shielding hydraulic hardening material of the present invention with water is uniform and has an appropriate softness and fluidity. Therefore, it can be uniformly placed into a formwork without the application of violent mechanical vibration as generated by a vibrator. This is advantageous because mortar can be placed uniformly and without leaving large voids into complex members to which rod type vibrators cannot be inserted. Consequently, placing work can be considerably simplified, dispersion in quality of afterhardening product that tends to occur due to the application of vibration is reduced, and separation of materials that tends to occur due to the application of vibration can also be avoided.

Examples:

The neutron-shielding hydraulic hardening material of the present invention and the method of manufacturing neutron shields of the present invention will next be described in detail by way of example, which is given for the purpose of illustration only, and should thus not be construed as limiting the invention.

Example 1:

The neutron-shielding hydraulic hardening materials shown in Table 1 were prepared. The hydraulic cement employed was an high-early-strength Portland cement having a specific surface area of not less than 4,000 cm<sup>2</sup>/g. Three types of aluminum hydroxide having different particle sizes were used including A (particle size centered between 1 and 5 μm), B (particle size centered between 10 and 20 μm), and C (particle size centered between 90 and 110 μm). The boron carbide employed was B<sub>4</sub>C (particle size centered between 100 and 150 μm). Given proportions of powders were mixed using a Henschel mixer for 10 minutes.

Each of the obtained dry powder samples was evaluated in terms of the filling ratio [filling ratio(%) = 100 x mass per unit volume / density] using a powder tester (model PT-D, manufactured by K.K. Hosokawa Tekkojo) and particle-size distribution graded through sieves. Briefly, each sample was placed in a hollow cylindrical container having an inner diameter of 5 cm and a height of 5 cm, and was tapped 180 times from the height of 2 cm within a period of 216 seconds. For all samples, the residue on the sieve having a mesh of 1 mm was less than 1% by weight.

Next, each powder sample was mixed with water at a water/powder ratio of 27% by weight, and a flow value was determined in accordance with the flow test method provided in JIS R5201, to thereby assess the fluidity.

Separately, mortar samples obtained through mixing under the same conditions as those described above were independently placed in a cylindrical formwork having an inner diameter of 10 cm and a height of 20 cm, and the samples were compacted for 5 seconds with vibration of a rod type vibrator. Subsequently, the compacted samples were cured for 14 days, after which time the compressive strength of each afterhardening product was measured. The cross section of the afterhardening product was also observed, and the size of voids were visually determined in accordance with the following criteria.

(Criteria for determining size of pores)

A: Pores measuring 1 mm or greater are not present

B: Pores measuring 1 mm or greater are present; but pores measuring 2 mm or greater are not present

C: Pores measuring 2 mm or greater are present; but pores measuring 4 mm or greater are not present

D: Pores measuring 4 mm or greater are present.

The results are shown in Table 1.

Table 1

Sample No.	Ratio of starting powders (wt.%)			Dry powder filling ratio (%)	Particle size distribution (wt.%) ----- <100 μm   60-90 μm	Flow value (mm)	Compressive strength (N/mm <sup>2</sup> )	Evaluation of voids			
	Cement	Aluminum hydroxide									
		B <sub>4</sub> C	B <sub>4</sub> C								
									A	B	C
1	8	0	0	84	8	53.5	51	27	-	2.0	D
2	15	0	0	77	8	54.2	57	25	-	5.7	D
3	15	12	25	40	8	62.7	71	17	221	6.0	B
4	20	0	0	72	8	58.1	56	24	186	9.5	C
5	20	22	0	50	8	69.0	65	21	217	9.6	B
6	20	20	7	45	8	55.2	69	21	187	9.2	C
7	20	10	20	42	8	63.9	70	9	223	9.4	A
8	30	0	0	62	8	65.1	61	22	215	18.8	B
9	30	10	12	40	8	63.1	72	8	236	18.0	A
10	40	0	0	52	8	70.0	66	16	232	35.0	B
11	40	10	10	32	8	63.1	76	8	221	34.4	A

practice.

When the filling ratio of dry powder is not less than 55% (Samples 3 through 11), flow values can be measured. However, when it is less than 55% (Samples 1 and 2), mortar placed in a flow cone develops cracks after being tapped 15 times. Thus, measurement of flow values cannot be performed. When the filling ratio is not less than 60% (Samples 3, 5, and 7 through 11), the flow values are 200 or greater, affording a good fluidity. Moreover, in the cases where the filling ratio is not less than 60%, particles having a diameter of not more than 100  $\mu\text{m}$  are present in an amount of 60-80% by weight, and particles having a diameter of between 60 and 90  $\mu\text{m}$  are present in an amount of not more than 20% by weight (Samples 3, 7, and 9 through 11), the flow values are 220 or greater, with the mortar exhibiting even more improved fluidity with excellent results of visual observation of voids.

Example 2:

Among the samples of neutron-shielding hydraulic hardening material of the present invention tested in Example 1, a typical sample that exhibited excellent fluidity (Sample 7) was used. This sample was mixed with water and additives at the indicated water/powder proportions and in the amounts indicated in Table 2. The high-range water reducing agent employed was a product of Onoda Cement Corporation (SP-X), and the air-entraining agent was a product of Yamaso Chemical Co., Ltd. (Vinsol W).

The air volume and the flow value without tapping (unit: mm) of the fresh mortar were determined. The flow value without tapping indicates the diameter of mortar spread in a circle on a plane when a cone filled with mortar was placed on the plane and the cone was then removed by being lifted upward. In addition, a mortar sample having the same composition was placed into a formwork having an inner diameter of 10 cm and a height of 20 cm without the application of vibration, and was then cured for 14 days. The size of voids in the cross section of the resultant afterhardening product was determined in the manner described in Example 1. The results are shown in Table 2.

Table 2

Sample No.	Water/powder ratio (wt.%)	High-range water reducing agent* (parts by weight)	Air-entraining agent* (parts by weight)	Flow value without tapping (mm)	Air content (vol.%)	Evaluation of voids
21	27	0	0	105	2	B
22	23	0.4	0	220	0	A
23	27	0	0.04	113	9	B
24	25	0.4	0.04	214	5	A

\*: Amounts (parts by weight) added to 100 parts of neutron-shielding hydraulic hardening powder material.

The following can be seen from Table 2.

Sample 21, representing the standard in which no additives were added, exhibited a flow value without tapping of 105, which was almost the same as that of the bottom size of the flow cone, and an air volume of 2% by volume. In con-

trast, Sample 22 (in which a high-range water reducing agent had been added in an amount of 0.4% by weight) exhibited an increased flow value without tapping of 220 even though the water/powder ratio had been reduced to 23% by weight. Thus, fluidity was greatly improved. Sample 23 (in which an air-entraining agent had been added in an amount of 0.04% by weight) exhibited a high air content at 9% by volume. The air in this case was so finely dispersed that it could not be observed visually. Therefore, this did not result in an uneven composition. Sample 24 (in which a high-range water reducing agent and an air-entraining agent were simultaneously added) exhibited slightly reduced effect of the additives, but still was considered satisfactory in terms of achievement of fluidity and a reduction in weight.

Samples 22 and 24 (in which a high-range water reducing agent was added) show sufficient fluidity, and uniform afterhardening products having no large voids have been obtained by placing without being applied mechanical vibration.

As described above, the neutron-shielding hydraulic setting material of the present invention is a material that provides an excellent neutron shielding effect, satisfactory strength of afterset product, and good workability of fresh mortar. Therefore, when neutron shields are manufactured by the method of the present invention, neutron shields with enhanced uniformity can be obtained.

## Claims

1. A neutron-shielding hydraulic hardening material characterized by containing 10-50% by weight of hydraulic cement, 30-88% by weight of aluminum hydroxide, and 0.1-35% by weight of boron carbide.
2. A hydraulic hardening material for shielding neutrons as described claim 1, which has a filling rate of not less than 55% as measured in such a manner that the material in a dry state is put in a hollow cylindrical container having an inner diameter of 5 cm and a height of 5 cm, and then compacted by 180 tappings from the height of 2 cm.
3. A neutron-shielding hydraulic hardening material as described in claim 1 or 2, which is constituted by particles comprising, when sieved through a mesh of 1 mm, not more than 5% by weight of oversize particles, 60-80% by weight of particles having a diameter of equal to or smaller than 100  $\mu\text{m}$ , and not more than 20% by weight of particles having a diameter of 60-90  $\mu\text{m}$ .
4. A method of manufacturing a neutron shield characterized by comprising the steps of mixing 100 parts by weight of a neutron-shielding hydraulic hardening material as described in any one of claims 1 through 3, 15-50 parts by weight of water, and not more than 5 parts by weight of at least one chemical admixture selected from the group consisting of air-entraining agents, air-entraining and water reducing agents, high-range water reducing agents, plasticizers, air-entraining and high-range water reducing agents, and foaming agents; and kneading the resultant mixture.
5. A method of manufacturing a neutron shield as described in claim 4, wherein the kneaded material is placed into a formwork without being applied mechanical vibration.





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# EUROPEAN SEARCH REPORT

Application Number  
EP 96 11 8207

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	FR 2 546 331 A (ROBATEL SLPI) 23 November 1984	1	G21F1/04
A	* page 2, line 2 - line 34 * ---	3	
Y	DATABASE WPI Section Ch, Week 8929 Derwent Publications Ltd., London, GB; Class A93, AN 89-210259 XP002023882 & JP 01 147 399 A (KURARAY KK) , 9 June 1989 * abstract *	1	
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The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		7 February 1997	Capostagno, E
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... &amp; : member of the same patent family, corresponding document</p>			

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