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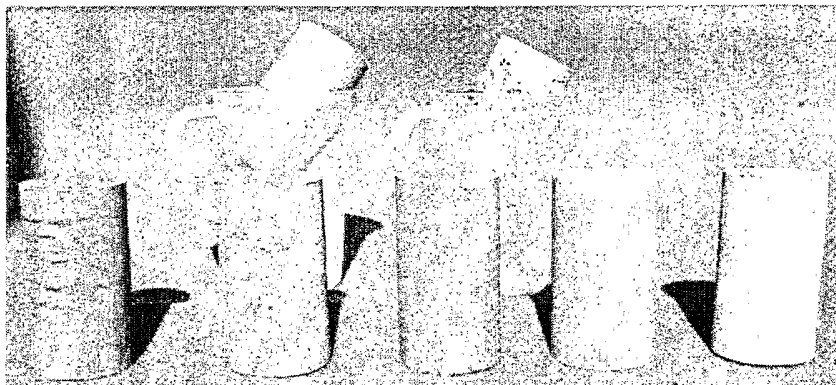
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(54) Title: PULP SLUDGE ASH COMPOSITION FOR PRODUCING BUILDING MATERIALS



(57) Abstract: Disclosed is a pulp sludge ash composition for producing building materials, which comprises pulp sludge ash combined with modified sodium silicate having an acidic group. The pulp sludge ash composition shows excellent water resistance and strength as well as improved physical properties, and thus is useful for various industrial fields as a building material, a civil engineering material, an interior material, a filler for a safe, or the like.

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【DESCRIPTION】**【Invention Title】****PULP SLUDGE ASH COMPOSITION FOR PRODUCING BUILDING MATERIALS****【Technical Field】**

<1> The present invention relates to a pulp sludge ash composition for producing building materials. More particularly, the present invention relates to a pulp sludge ash composition for producing building materials, which comprises pulp sludge ash obtained by incineration of pulp sludge generated from a paper manufacturing process after a wastewater treatment step, and further comprises modified sodium silicate having an acidic group. The pulp sludge ash composition according to the present invention allows fast curing with no need for additional baking or sintering. Additionally, the above pulp sludge ash composition further comprising a polymer emulsion shows excellent strength and water resistance.

【Background Art】

<2> In general, pulp sludge is generated from a paper manufacturing process after a wastewater treatment step, in a great amount. Most of the pulp sludge has been discarded in a landfill. However, pulp sludge itself is not suitable to be discarded as landfill because it is not solidified with ease due to its high water content. Therefore, a recent tendency has been for pulp sludge to be dumped in the sea.

<3> To solve the above-mentioned problem, there has been an attempt to subject pulp sludge to incineration so as to recover any remaining heat energy from pulp sludge and to reduce the amount of waste to be discarded in a landfill. Pulp sludge ash generated from such incineration has been thought to have low industrial applicability, and thus has been utilized in limited use (for example, a supplementary additive for cement).

<4> Additionally, many attempts have been made to develop use of pulp sludge ash. For example, Korean Patent Publication No. 1989-0002566 discloses a method for producing building materials using ash generated from the

incineration of paper-manufacturing sludge. More particularly, the method comprises adding slaked lime, asbestos, paper-manufacturing sludge, or the like to the pulp sludge ash, further adding sodium silicate thereto to accomplish preliminary bonding, and curing the resultant product with steam under high temperature and high pressure conditions to provide building materials. The method permits the initial molding work to be performed quickly due to the curing reaction of metal oxides and sodium silicate added to the pulp sludge ash. However, there is a problem in that because sodium silicate *per se* has poor water resistance, the bonding force between sodium silicate and metal oxides is weakened after curing of the pulp sludge ash, due to the absorption of ambient water or moistures into the cured material. There is another problem embedded in this method because it includes a steam-curing step performed at high temperature, which is not cost-efficient and has low industrial applicability.

<5> Therefore, there is a continuous need for a method for recycling pulp sludge ash. This may be in the form of the creation of a pulp sludge ash composition, which has excellent bonding strength and water resistance and is cost-efficient, or in the form of the same pulp sludge ash composition.

<6>

【Disclosure】

【Technical Problem】

<7> Therefore, the present invention has been made in view of the above-mentioned problems. It is an object of the present invention to provide a pulp sludge ash composition for producing building materials, wherein the pulp sludge ash composition comprises pulp sludge ash and modified sodium silicate having an acidic group added thereto, allows fast curing with no need for additional baking or sintering, and shows excellent strength and water resistance.

<8> It is another object of the present invention to provide a pulp sludge ash composition for producing building materials, which uses sodium silicate modified to provide improved water resistance, so that the water absorptivity can be reduced significantly.

<9> It is still another object of the present invention to provide a pulp sludge ash composition for producing building materials, which comprises modified sodium silicate having an acidic group, combined with aggregate or light aggregate, and thus shows more improved strength or significantly reduced specific gravity.

<10>

【Technical Solution】

<11> According to an aspect of the present invention, there is provided a pulp sludge ash composition for producing building materials, which is obtained by mixing pulp sludge ash with modified sodium silicate having an acidic group.

<12> According to another aspect of the present invention, there is provided a pulp sludge ash composition for producing building materials, which is obtained by mixing pulp sludge ash with modified sodium silicate having an acidic group, combined with a polymer emulsion.

<13> Particularly, the modified sodium silicate having an acidic group is obtained by mixing sodium silicate with any one selected from the group consisting of: aqueous sodium sulfate, copper sulfate, iron sulfate, aluminum sulfate, magnesium sulfate, potassium bicarbonate, chrome alum, sulfuric acid and hydrochloric acid solutions; and mixtures thereof; and then adding caustic soda thereto as a catalyst.

<14> In a preferred embodiment of the present invention, the modified sodium silicate having an acidic group is obtained by introducing sodium silicate and each aqueous solution of copper sulfate, sodium sulfate, caustic soda and chrome alum into an agitator, followed by agitation.

<15> In another preferred embodiment of the present invention, the modified sodium silicate having an acidic group is obtained by introducing sodium silicate, 10% aqueous sodium lauryl sulfate solution, caustic soda and aqueous sulfuric acid solution into an agitator, followed by agitation.

<16> Particularly, the polymer emulsion is any one selected from the group consisting of latex, silicone resin, gum arabic, acrylic resins and epoxy resins.

<17> In the pulp sludge ash composition according to the present invention, the pulp sludge ash and the modified sodium silicate having an acidic group are mixed in a ratio of 1: 1.2~2.

<18> To increase the strength, the pulp sludge ash composition may further comprise any one selected from the group consisting of dust, fly ash, sand, slag, gypsum, lime and molding sand.

<19> To reduce the specific gravity, the pulp sludge ash composition may further comprise any one light-weight additive selected from the group consisting of wood powder, perlite, vermiculite, Styrofoam particles and a foaming agent.

<20> When the above-mentioned additives are added to the pulp sludge ash composition, organic bentonite or methyl cellulose is further added thereto in order to accomplish a uniform distribution.

<21> Additionally, to improve the bending strength, the pulp sludge ash composition may further comprise any one selected from the group consisting of wire mesh, waste fiber and fiber.

<22>

【Advantageous Effects】

<23> As can be seen from the foregoing, the cement-like composition according to the present invention, which comprises pulp sludge ash and the modified sodium silicate, shows excellent water resistance and strength, and thus is useful for various industrial fields as a building material, etc. The composition may further comprise various kinds of additives, if desired, to conform to the particular use thereof. Additionally, it is possible to transform various kinds of industrial wastes into the composition according to the present invention. Therefore, the present invention contributes to recycling of wastes and the protection of environment, and is cost-efficient and time-efficient.

<24> While this invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not limited to the disclosed

embodiment and the drawings. On the contrary, it is intended to cover various modifications and variations within the spirit and scope of the appended claims.

<25>

【Description of Drawings】

<26> The foregoing and other objects, features and advantages of the present invention will become more apparent from the following detailed description when taken in conjunction with the accompanying drawings in which:

<27> FIG. 1 is a photograph showing various building materials obtained from the pulp sludge ash compositions according to preferred embodiments of the present invention.

<28>

【Best Mode】

<29> Hereinafter, the present invention will be explained in more detail.

<30> The present inventors have found that addition of an aqueous acidic solution to pulp sludge ash results in fast curing within a time of 1 hour or less. Based on this finding, there is provided modified sodium silicate to improve the strength of a pulp sludge ash composition, wherein the modified sodium silicate is obtained by adding sodium silicate to an acidic solution, such as an aqueous solution of sodium sulfate, copper sulfate, iron sulfate, aluminum sulfate, magnesium sulfate, potassium bicarbonate, chrome alum, sulfuric acid or hydrochloric acid solutions. Additionally, caustic soda (sodium hydroxide) is added to the pulp sludge ash composition, as a catalyst that helps blending of pulp sludge with the aqueous acidic solution.

<31> Due to the acidic group contained in the modified sodium silicate, pulp sludge ash can be cured quickly and the modified sodium silicate shows more improved water resistance compared to non-modified sodium silicate.

<32> Particular examples of the aqueous acidic solution that may be used to provide the modified sodium silicate include aqueous solutions with pH 7 or less, such as an aqueous sodium sulfate, copper sulfate, iron sulfate, aluminum sulfate, magnesium sulfate, potassium bicarbonate, chrome alum,

sulfuric acid and hydrochloric acid solutions, and mixtures thereof.

<33> Although various combinations of the above aqueous acidic solutions may be used to provide modified sodium silicate, it is preferable to use modified sodium silicate 1 and modified sodium silicate 2 as described hereinafter so as to improve the water resistance to the highest degree.

<34> (1) Modified Sodium Silicate 1

<35> Modified sodium silicate 1 having an acidic group is obtained by introducing sodium silicate, copper sulfate, sodium sulfate and chrome alum into an agitator in a mixing ratio of 30:4:3:20, further introducing caustic soda into the agitator in the same proportion as chrome alum, and agitating the resultant mixture for 30 minutes.

<36> (2) Modified Sodium Silicate 2

<37> Modified sodium silicate 2 having an acidic group is obtained by adding 10% aqueous sodium lauryl sulfate solution and caustic soda to sodium silicate, agitating the resultant mixture for 30 minutes, and further adding aqueous sulfuric acid solution thereto with stirring. Preferably, sodium silicate, 10% aqueous sodium lauryl sulfate solution, caustic soda and aqueous sulfuric acid solution are mixed in a ratio of 10:3:10:3.

<38> The modified sodium silicate having an acidic group, obtained as described above, is added to pulp sludge ash to provide the composition for producing building materials according to the present invention. Preferably, the pulp sludge ash has a fine size of 150 mesh or less, and the mixing ratio of pulp sludge ash to the modified sodium silicate is 1: 1.2~2, on the weight basis.

<39> Additionally, the cement-like composition according to the present invention, comprising pulp sludge ash and the modified sodium silicate having an acidic group, may further comprise various additives, so as to improve the water resistance, to prevent deformation such as shrinkage, to increase the strength, to reduce the specific gravity, or to improve the bending strength.

<40> More particularly, in order to improve the water resistance, the composition optionally further comprises a polymer emulsion selected from the

group consisting of latex, silicone oil, gum arabic, acrylic resins and epoxy resins; in addition to the modified sodium silicate having an acidic group.

<41> For example, 3~25 g of latex, as a polymer emulsion, may be further added to 100 g of the above modified sodium silicate 1 having an acidic group with stirring, and then the resultant combination may be added to pulp sludge ash. However, addition of the latex in an amount of 25 g or more inhibits fast curing.

<42> In a variant, 0.3~15 g of silicone oil, as a polymer emulsion, may be further added to 100 g of the above modified sodium silicate 1 having an acidic group with stirring, and then the resultant combination may be added to pulp sludge ash. However, addition of the silicone oil in an amount of 15 g or more inhibits fast curing.

<43> In another variant, 5~15 g of gum arabic and 0.5~3g of silicone oil, as polymer emulsions, may be further added to 100 g of the above modified sodium silicate 1 having an acidic group with stirring, and then the resultant combination may be added to pulp sludge ash. However, addition of the gum arabic in an amount of 15 g or more inhibits fast curing.

<44> In still another variant, 5~25 g of an acrylic resin and 0.5~3 g of silicone oil, as polymer emulsions, may be further added to 100 g of the above modified sodium silicate 1 having an acidic group with stirring, and then the resultant combination may be added to pulp sludge ash. However, addition of the acrylic resin in an amount of 25 g or more inhibits fast curing.

<45> Meanwhile, in order to prevent deformation such as shrinkage, the cement-like composition, comprising pulp sludge ash and the modified sodium silicate having an acidic group, may further comprise calcium carbonate, lime, a metal oxide such as magnesium oxide or zinc oxide, or the like.

<46> In order to increase the strength, the cement-like composition, comprising pulp sludge ash and the modified sodium silicate having an acidic group, may further comprise dust, fly ash, sand, slag, gypsum, lime, molding sand, or the like.

<47> In order to reduce the specific gravity, the cement-like composition, comprising pulp sludge ash and the modified sodium silicate having an acidic group, may further comprise light-weight aggregate, such as wood powder, pearlite, vermiculite or Styrofoam particles, or may be provided with air bubbles obtained from pressurized air with a vegetable foaming agent. When such light-weight aggregate or air bubbles are added to the composition, a thickening agent such as organic bentonite or methyl cellulose may be further added thereto so as to accomplish uniform blending.

<48> Additionally, in order to improve the bending strength, the cement-like composition, comprising pulp sludge ash and the modified sodium silicate having an acidic group, may further comprise wire mesh, waste fiber, fiber, or the like.

<49>

【Mode for Invention】

<50> Reference will now be made in detail to the preferred embodiments of the cement-like composition, comprising pulp sludge ash and the modified sodium silicate having an acidic group, according to the present invention. Test results for each composition are also provided.

<51> **Example 1**

<52> First, 60 parts of pulp sludge ash were provided. Next, 85 parts of modified sodium silicate were prepared by mixing 1,500g of sodium silicate with an aqueous acidic solution with stirring. The acidic solution was obtained by introducing 200g of copper sulfate, 150g of sodium sulfate, 1,000g of caustic soda and 1,000g of chrome alum into an agitator, each in the form of an aqueous solution, and agitating the materials for 30 minutes. Then, 60 parts of pulp sludge were mixed with 85 parts of the modified sodium silicate to obtain a cement-like composition.

<53> The pulp sludge ash composition was injected into a cylindrical mold having a diameter of 50mm and a depth of 100 mm. Then, a bar having a weight of 1kg and a diameter of 10mm was placed on the mold at different times, and determined the initial curing completion time, when the molded product showed

no physical changes in its surface and permitted demolding and handling. The composition removed from the mold was cured naturally for 7 days. Then, the composition was measured for its weight and strength. Additionally, the composition was dipped into a water bath for 24 hours and removed from the water bath. Then, the composition was dried for 1 hour, and then was measured for its weight and strength to determine the water absorptivity and strength of the composition. The results are shown in the following Table 1.

<54> **Example 2**

<55> First, 60 parts of pulp sludge ash were provided. Next, 85 parts of modified sodium silicate were prepared by adding 300g of 10% aqueous sodium lauryl sulfate solution and 1,000g of aqueous caustic soda to 1,000g of sodium silicate, agitating the materials for 30 minutes and further adding 300g of 10% aqueous sulfuric acid solution thereto and further agitating the materials. Then, 60 parts of pulp sludge were mixed with 85 parts of the modified sodium silicate to obtain a cement-like composition.

<56> The composition obtained in this Example was tested in the same manner as described in the above Example 1. The results are shown in the following Table 1.

<57> **Example 3**

<58> First, 60 parts of pulp sludge ash were provided. Next, 85 parts of modified sodium silicate were prepared by mixing 1,500g of sodium silicate with an aqueous acidic solution with stirring. The acidic solution was obtained by introducing 200g of copper sulfate, 150g of sodium sulfate, 1,000g of caustic soda and 1,000g of chrome alum into an agitator, each in the form of an aqueous solution, and agitating the materials for 30 minutes. Further, 30g of latex and 3g of silicone oil were added to 1,000g of the acidic solution. Then, 60 parts of pulp sludge were mixed with 85 parts of the modified sodium silicate to obtain a cement-like composition.

<59> The composition obtained in this Example was tested in the same manner as described in the above Example 1. The results are shown in the following Table 1.

<60> Example 4

<61> First, 60 parts of pulp sludge ash were provided. Next, 85 parts of modified sodium silicate were prepared by mixing 1,500g of sodium silicate with an aqueous acidic solution with stirring. The acidic solution was obtained by introducing 200g of copper sulfate, 150g of sodium sulfate, 1,000g of caustic soda and 1,000g of chrome alum into an agitator, each in the form of an aqueous solution, and agitating the materials for 30 minutes. Further, 30g of silicone oil were added to 1,000g of the acidic solution. Then, 60 parts of pulp sludge were mixed with 85 parts of the modified sodium silicate to obtain a cement-like composition.

<62> The composition obtained in this Example was tested in the same manner as described in the above Example 1. The results are shown in the following Table 1.

<63> Example 5

<64> First, 60 parts of pulp sludge ash were provided. Next, 85 parts of modified sodium silicate were prepared by mixing 1,500g of sodium silicate with an aqueous acidic solution with stirring. The acidic solution was obtained by introducing 200g of copper sulfate, 150g of sodium sulfate, 1,000g of caustic soda and 1,000g of chrome alum into an agitator, each in the form of an aqueous solution, and agitating the materials for 30 minutes. Further, 30g of an acrylic polymer emulsion and 3g of silicone oil were added to 1,000g of the acidic solution. Then, 60 parts of pulp sludge were mixed with 85 parts of the modified sodium silicate to obtain a cement-like composition.

<65> The composition obtained in this Example was tested in the same manner as described in the above Example 1. The results are shown in the following Table 1.

<66> Comparative Example

<67> A composition was prepared by adding 100 parts of non-modified sodium silicate solution to 60 parts of pulp sludge ash.

<68> The composition obtained in this Comparative Example was tested in the

same manner as described in the above Example 1. The results are shown in the following Table 1.

[Table 1]

Test Results for Compositions Comprising Pulp Sludge Ash and Modified Sodium Silicate

Sample	Curing time (min.)	Weight before dipping (g)	Weight after dipping (g)	Strength before dipping (kg/cm ²)	Strength after dipping (kg/cm ²)
Ex. 1	21	301.6	358.9	93	89
Ex. 2	19	303.0	360.6	87	85
Ex. 3	32	302.1	311.6	118	104
Ex. 4	43	301.4	310.4	117	110
Ex. 5	36	301.5	320.0	135	130
Comp. Ex.	280	348.4	351.2	136	0

As can be seen from Table 1, the compositions comprising pulp sludge ash and the modified sodium silicate having an acidic group are capable of fast curing within 1 hour, thereby providing products that can be demolded, transported and loaded with ease. Such compositions are amenable to mass production. After the water bath dipping test, it can be seen that addition of a polymer emulsion can provide the compositions with excellent water resistance, as compared to the sample free from a polymer emulsion, which shows a relatively high water absorptivity and a relatively low strength. On the contrary, the sample according to the above Comparative Example, comprising non-modified sodium silicate, is not capable of fast curing and causes cracking and deformation on the surface during drying. Moreover, the comparative sample shows such poor water resistance that the sample may be dissolved in the water bath dipping test, thereby making it impossible to measure the strength after dipping. Therefore, it can be seen that the sample according to the above Comparative Example has no industrial applicability.

Meanwhile, in order to improve the water resistance of the composition according to the present invention, it is also possible to apply a polymer emulsion onto the surface of the composition.

<74> Additionally, in order to determine whether harmful heavy metals generally contained in pulp sludge ash are leached out of each composition according to the above Examples and Comparative Examples, each composition was crushed after measuring the compression strength, and then subjected to the test methods for waste process evaluation. The results are shown in the following Table 2.

<75> [Table 2]

<76> Results for Heavy Metal Leaching in the Inventive Compositions

Item	pH	Results (expressed in ppm units)								
		Pb	Cu	As	Hg	Cd	Cr	Zn	Ni	Mn
Quality Standard	7	3	3	1.5	0.005	0.3	1.5	3	3	3
Pulp sludge ash	5.8	52	43	0.01	ND	0.2	10	206	13	16
Ex. 1	10.5	0.03	0.01	ND	ND	ND	ND	0.4	ND	ND
Ex. 2	10.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ex. 3	10.3	16	8	ND	ND	ND	0.04	34	0.01	0.02
Ex. 4	10.4	ND	ND	ND	ND	ND	ND	0.03	ND	0.04
Ex. 5	10.0	ND	ND	ND	ND	ND	ND	0.02	ND	0.01
Comp. Ex.	11.5	1.4	0.6	ND	ND	ND	0.03	3.5	ND	1.8

<77>

<78> As can be seen from Table 2, although pulp sludge ash contains a large amount of heavy metals such as lead, zinc, etc., the inventive composition comprising the modified sodium silicate having an acidic group in addition to pulp sludge ash does not allow the heavy metals to leach out of the composition. On the contrary, the composition according to the Comparative Example allows several heavy metals to leach out of the composition. As demonstrated by the above results, the cement-like composition according to the present invention is capable of fast curing and does not cause environmental pollution. Therefore, it is thought that the present invention may be applied to solidify any other heavy metal-containing industrial wastes in a short time, or to transform the same wastes into industrially useful products.

<79> Hereinafter, the composition comprising pulp sludge ash and the modified sodium silicate, and further comprising various additives, if desired, according to another preferred embodiment of the present invention will be described.

<80> **Example 6: Composition Further Comprising Fly Ash**

<81> First, 60 parts of pulp sludge ash was provided. Next, 130 parts of modified sodium silicate having an acidic group was prepared by introducing 1,500g of sodium silicate No. 3, 200g of copper sulfate, 150g of sodium sulfate, 1,000g of caustic soda and 1,000g of chrome alum, each dissolved in hot water, into an agitator, stirring the materials for 30 minutes to provide 1,000g of an acidic solution, further adding 100g of a polymer emulsion latex and 3g of silicone oil thereto with stirring. Then, 60 parts of pulp sludge ash was mixed with 130 parts of the modified sodium silicate to obtain a cement-like composition. Finally, 30 parts of fly ash was further added to the cement-like composition.

<82> The final composition was injected into a cylindrical mold having a diameter of 100mm and a depth of 200 mm. Then, a bar having a weight of 1kg and a diameter of 10mm was placed on the mold at different times, and determined the initial curing completion time, when the molded product showed no physical changes in its surface and permitted demolding and handling. The composition removed from the mold was cured naturally for 3 days. Then, the composition was measured for its weight and strength. Additionally, the composition was dipped into a water bath for 24 hours and removed from the water bath, and then was measured for its weight and strength to determine the water absorptivity and strength of the composition. The results are shown in the following Table 3.

<83> **Example 7: Composition Further Comprising Dust Generated from Steel-Manufacturing Process**

<84> A cement-like composition was prepared by mixing 60 parts of pulp sludge ash with 120 parts of the modified sodium silicate having an acidic group, obtained in the same manner as described in Example 6. Then, 100 parts of dust generated from a steel-manufacturing process was added to the composition. The composition was tested according to the method as described in Example 6. The results are shown in the following Table 3.

<85> **Example 8: Composition Further Comprising Iron Powder**

<86> A cement-like composition was prepared by mixing 60 parts of pulp sludge ash with 120 parts of the modified sodium silicate having an acidic group, obtained in the same manner as described in Example 6. Then, 300 parts of iron powder generated after a surface treatment process for iron panels was added to the composition. The composition was tested according to the method as described in Example 6. The results are shown in the following Table 3.

<87> Example 9: Composition Further Comprising Copper Slag

<88> A cement-like composition was prepared by mixing 60 parts of pulp sludge ash with 120 parts of the modified sodium silicate having an acidic group, obtained in the same manner as described in Example 6. Then, 170 parts of copper slag generated during a copper refining process was added to the composition. The composition was tested according to the method as described in Example 6. The results are shown in the following Table 3.

<89> Example 10: Composition Further Comprising Waste Molding Sand

<90> A cement-like composition was prepared by mixing 60 parts of pulp sludge ash with 120 parts of the modified sodium silicate having an acidic group, obtained in the same manner as described in Example 6. Then, 100 parts of waste molding sand with a size of 7 mm or less, generated during a molding process, was added to the composition. The composition was tested according to the method as described in Example 6. The results are shown in the following Table 3.

<91> [Table 3]

<92> Test Results for Physical Properties of Compositions Further Comprising Various Kinds of Aggregate

Sample	Curing time (min)	Weight before dipping (g)	Weight after dipping (g)	Strength before dipping (Kg/cm ²)	Strength after dipping (Kg/cm ²)
Ex. 6	31	295.9	304.6	121	120
Ex. 7	28	364.6	375.1	126	130
Ex. 8	25	869.5	879.6	166	161
Ex. 9	30	469.1	473.8	181	180
Ex. 10	48	387.6	396.6	176	175

<93>

<94> As can be seen from Table 3, each composition according to Examples 6~10 conform to the constitution of the cement-like composition according to the present invention due to the presence of the modified sodium silicate in addition to pulp sludge ash. However, addition of fly ash results in a slightly delayed curing time. Therefore, it can be seen that addition of fly ash controls the curing time. Also, it can be seen that addition of steel-manufacturing dust and other aggregate contributes to realization of fast curing and improved strength. Particularly, because industrial wastes such as steel-manufacturing dust containing a large amount of heavy metals can be incorporated into the composition according to the present invention, it is possible to recycle various types of harmful wastes into curable cement. Meanwhile, besides the above-described wet process wherein mortar is injected into a mold and cured therein, it is also possible to obtain a composition according to the present invention via a pressurized molding process by incorporating aggregate into the composition. The following Examples 11~13 illustrates the compositions further comprising light-weight aggregate for the purpose of weight-down.

<95> **Example 11: Composition Further Comprising Wood Powder**

<96> A composition was prepared by mixing 80 parts of pulp sludge ash with 100 parts of the modified sodium silicate having an acidic group, obtained in the same manner as described in Example 6. Then, 60 parts (based on the weight of the above composition) of wood powder (sawdust), as light-weight aggregate, was added to the composition, and 1.5 parts (based on the weight of the above composition) of organic bentonite was further added thereto, so that the light-weight aggregate can be distributed and blended uniformly in the resultant mortar. The final composition was injected into a cylindrical mold with a diameter of 50mm and a depth of 100mm. Then, the composition was measured for its demoldable strength and initial curing time. Additionally, the composition was cured naturally for 3 days and was measured for its specific gravity. Also. The composition was measured for its weight before and after dipping it into a water bath for 12 hours. The results are shown in

the following Table 4.

Example 12: Composition Further Comprising Pearlite

A composition was prepared by mixing 80 parts of pulp sludge ash with 130 parts of the modified sodium silicate having an acidic group, obtained in the same manner as described in Example 6. Then, 40 parts (based on the weight of the above cement-like composition) of pearlite, as light-weight aggregate, was added to the composition, and 1.5 parts (based on the weight of the above composition) of organic bentonite was further added thereto. The final composition was measured in the same manner as described in Example 11. The results are shown in the following Table 4.

Example 13: Composition Further Comprising Styrofoam Particles

A composition was prepared by mixing 80 parts of pulp sludge ash with 130 parts of the modified sodium silicate having an acidic group, obtained in the same manner as described in Example 6. Then, light-weight aggregate, comprising 1,000cc of Styrofoam particles with a size of 3mm or less and 1.2 parts (based on the weight of the above cement-like composition) of methyl cellulose, was added to the composition. The final composition was measured in the same manner as described in Example 11. The results are shown in the following Table 4.

[Table 4]

Test Results for Physical Properties of Compositions Further Comprising Various Kinds of Light-Weight Aggregate

Sample	Initial curing time (min)	Specific gravity	Weight before dipping (g)	Weight after dipping (g)
Ex. 11	60	8.9	211.4	231.8
Ex. 12	55	7.3	173.1	180.6
Ex. 13	50	6.8	162.5	180.0

As can be seen from Table 4, each composition further comprising light-weight aggregate to reduce the weight also allows fast curing. Moreover, a greater amount of light aggregate may be used to reduce the weight to a higher degree, so that the composition is amenable to pressurized molding.

Additionally, it can be seen that use of a thickening agent such as organic bentonite or methyl cellulose permits uniform blending of light-weight aggregate. In a variant, the composition according to the following Example 14 comprises air bubbles for the purpose of weight-down.

Example 12: Composition Further Comprising Air Bubbles

A pulp sludge ash composition was prepared by mixing 80 parts of pulp sludge ash, containing 1.5 parts of methyl cellulose added thereto, with 100 parts of the modified sodium silicate having an acidic group, obtained in the same manner as described in Example 6. Then, 1,000cc of air bubbles, obtained from pressurized air with a vegetable foaming agent, were added to the composition with stirring to provide a final composition. The final composition was injected into a cylindrical mold with a diameter of 50mm and a depth of 100mm. Then, the composition was measured for its demoldable strength and initial curing time. Additionally, the composition was cured naturally for 3 days and was measured for its specific gravity. Also. The composition was measured for its weight before and after dipping it into a water bath for 12 hours. The results are shown in the following Table 5.

[Table 5]

Test Results for Physical Properties of Compositions Further Comprising Air Bubbles

Sample	Initial curing time (min)	Specific gravity	Weight before dipping (g)	Weight after dipping (g)
Ex. 14	160	4.3	11.6	121.8

As can be seen from Table 5, addition of air bubbles does not adversely affect the composition according to the present invention.

As described in the above Examples 1~14, addition of the modified sodium silicate having an acidic group to pulp sludge ash can provide a cement-like composition, which is capable of fast curing, and has excellent strength and water resistance. Additionally, because the composition according to the present invention may further comprise fly ash, aggregate, light-weight

aggregate and air bubbles, it is possible to provide a cost-efficient composition that can be used in various industrial fields, as a building material, a civil engineering material, an interior material, a filler for a safe, or the like. Particularly, the pulp sludge ash composition is useful for solidifying harmful industrial wastes promptly. Further, the composition may further comprise wire mesh, waste fiber, fiber or pulp sludge in order to improve the bending strength. To prevent a shrinking phenomenon of the composition, it is possible to add calcium carbonate, lime, a metal oxide such as magnesium oxide or zinc oxide, or the like. Besides sodium silicate, silicate salts (such as potassium silicate and lithium silicate) and modified sodium silicate, obtained by adding boron, phosphoric acid or aluminum to sodium silicate during its preparation, provide the same effect as sodium silicate. Further, the composition may further comprise a dye, a pigment, an additional waterproofing or water-repellant agent for Portland cement, or the like, if desired.

【CLAIMS】**【Claim 1】**

<114> A pulp sludge ash composition for producing building materials, which comprises pulp sludge ash combined with modified sodium silicate having an acidic group.

【Claim 2】

<115> The pulp sludge ash composition for producing building materials according to claim 1, wherein the modified sodium silicate having an acidic group further comprises a polymer emulsion.

【Claim 3】

<116> The pulp sludge ash composition for producing building materials according to claim 1, wherein the modified sodium silicate having an acidic group is obtained by mixing sodium silicate with any one selected from the group consisting of aqueous sodium sulfate, copper sulfate, iron sulfate, aluminum sulfate, magnesium sulfate, potassium bicarbonate, chrome alum, sulfuric acid and hydrochloric acid solutions, and mixtures thereof.

【Claim 4】

<117> The pulp sludge ash composition for producing building materials according to claim 3, wherein caustic soda is further added as a catalyst.

【Claim 5】

<118> The pulp sludge ash composition for producing building materials according to claim 1, wherein the modified sodium silicate having an acidic group is obtained by introducing sodium silicate, 10% aqueous sodium lauryl sulfate solution, caustic soda and aqueous sulfuric acid solution into an agitator, followed by agitation.

【Claim 6】

<119> The pulp sludge ash composition for producing building materials according to claim 2, wherein the polymer emulsion is any one selected from the group consisting of latex, silicone resin, gum arabic, acrylic resins and epoxy resins.

【Claim 7】

<120> The pulp sludge ash composition for producing building materials according to claim 3, wherein the pulp sludge ash and the modified sodium silicate having an acidic group are mixed in a ratio of 1: 1.2~2.

【Claim 8】

<121> The pulp sludge ash composition for producing building materials according to claim 1, which further comprises any one selected from the group consisting of dust, fly ash, sand, slag, gypsum, lime and molding sand, in order to increase the strength.

【Claim 9】

<122> The pulp sludge ash composition for producing building materials according to claim 1, which further comprises any one light-weight additive selected from the group consisting of wood powder, perlite, vermiculite, Styrofoam particles and a foaming agent, in order to reduce the specific gravity.

【Claim 10】

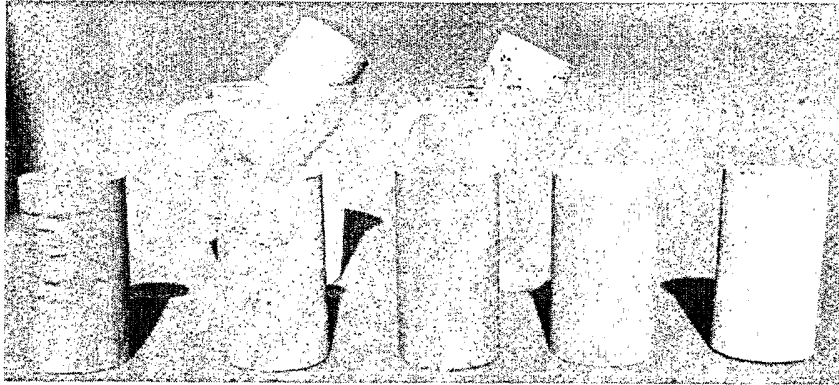
<123> The pulp sludge ash composition for producing building materials according to claim 9, which further comprises organic bentonite or methyl cellulose, in order to accomplish a uniform distribution when adding the additives.

【Claim 11】

<124> The pulp sludge ash composition for producing building materials according to claim 1, which further comprises any one selected from the group consisting of wire mesh, waste fiber and fiber in order to improve the bending strength.

<125>

【Figure 1】



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2005/003736

A. CLASSIFICATION OF SUBJECT MATTER**D21H 17/01(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8 C04B 29/00, C04B 18/06, A01G 1/00, D21J 1/08, C04B 18/04,

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKIPASS, USPTO, PAJ, "PULP SLUDGE ASH" "PAPER SLUDGE ASH" "SODIUM SILICATE"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 59137362 A (1984.08.07.) Fuji Funen Kenzai Kogyo KK Abstract, claim 1-5	1, 2, 4
A	KR 10-1988-0006422 A (1988.07.22.) Jeonju Paper Making CO. See the whole document	1 - 11
A	JP 06-315671 A (1994.11.15.) Hirose Masanao etc. See the whole document	1 - 11
A	KR 10-1995-17811 A (1995.07.20.) HANSOL PAPER CO., LTD. See the whole documents	1 - 11
E, A	KR 10-2005-0008417 A (2005.01.21.) Park Jong Won See the whole documents	1 - 11

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2005/003736

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP59137362A2	07.08.1984	AU2383584A1	02.08.1984
		AU573562B2	16.06.1988
		CA1207806A1	15.07.1986
		DE3481908C0	17.05.1990
		EP0115306A2	08.08.1984
		EP115306A2	08.08.1984
		EP115306B1	11.04.1990
		EP115306A3	08.01.1986
		JP59137362	07.08.1984
		KR1019840007394	07.12.1984
		KR9102580B1	27.04.1991
		US04586958	06.05.1986
		US04812169	14.03.1989
		US4586958A	06.05.1986
		US4812169A	14.03.1989
KR1019880006422	22.07.1988	KR8902566B1	18.07.1989
JP06315671	15.11.1994	JP06315671	15.11.1994
		JP6315671A2	15.11.1994
KR1019950017811	20.07.1995	KR9611327B1	22.08.1996
KR1020050008417	21.01.2005	None	