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(54) Title: A CEMENT FORMULA COMPOSITION FOR CONSTRUCTING A MULTIPLE LAYERED OBJECT

Fig. 2

(57) Abstract: It is the objective of the present invention to provide a cement formula composition that can be used for constructing a multiple layered object having a structural shape that is more flexible when compared to those obtained from the traditional extrusion methods. A cement formula composition for constructing a multiple layered object having at least one referenced layer and an adjacent stacked layer disposed over said referenced layer which are formed by extrusion of said composition through an extruder head, comprising a hardening accelerator and fibers wherein the amount of said accelerator is in the range of 0.1 to 5 % by weight and comprises an aluminate composition having alumina content in the range of 30 to 98 % by weight and wherein the fibers have a length from 0.5 millimeters to half of the diameter of the extruder head and the amount of said fibers is in the range of 0.1 to 1.0 % by volume thereby allowing the overlap of layers.

[Continued on next page]

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A CEMENT FORMULA COMPOSITION FOR CONSTRUCTING A MULTIPLE LAYERED OBJECT

FIELD OF INVENTION

The present invention relates generally to a cement formula composition for constructing a multiple layered object, and more particularly to the construction of objects having non-geometrical shapes.

BACKGROUND

There have been prior attempts in applying 3D printing techniques in the field of construction. Such applications primarily include the method of dispensing the preferred construction material through the printing head's nozzle and depositing the same on one horizontal layer at a time before moving upwards to begin a new layer thereby forming a growing workpiece. The movement is generally under computer control in which the set of instructions related to a desired shape is recorded in the computer memory. A binder is normally incorporated into the material used during the process in order to harden layers. One of the particular techniques is known as extrusion and considered as one of the common 3D printing techniques. However, even within the scope of one particular technique, there are substantial differences when it comes to the selection of materials and the criteria for using the same to achieve the desired shape without compromising the structural strength and integrity.

Certain compositions have been disclosed in the prior arts. These include Chinese application No. CN 104230289 A regarding "3D printing composition as well as preparation method and applications thereof." The said prior art discloses a 3D printing composition comprising gypsum powder, gasification enhancer, binding material, enhancer, additives, solid lubricant, and preservatives. However, the said composition is not intended for use in the field of construction, thereby the strength achieved is not sufficiently high.

The other composition has been disclosed as per Chinese application No. CN 104891891 A for "3D printing cement-based material and preparation method thereof." The said disclosure refers to 3D printing cement-based materials comprising powdered cementitious material and aggregate. The powdered cementitious material includes cement, superplasticizer, active admixture, early
strength agent, retarding agent, expanders, transfer coagulant, extenders, binders, air-entraining agent, plasticizer, water-repellant agents, starch ethers, powders fillers, and fibers. However, certain limitations are encountered as the said composition suffers from the issue of fast fluidity loss thereby affecting the extrusion performance.

It therefore can be seen that the prior arts do not sufficiently address the issue regarding the balance between the hardening behavior of material and the appropriate time for such behavior. Hence, they are not able to support the construction of non-standard structures, particularly in the continuous or semi-continuous extrusion-based construction process. The non-standard structures, in this case, refer to structures having at least one curvature section and/or structures having a non-geometrical shape. Hence, it is necessary to develop a particular formula of the construction material that can be hardened at the appropriate time and the corresponding method of using such material in order to obtain the desired initial setting time and working time for forming such non-standard structures.

**SUMMARY OF THE INVENTION**

It is therefore the objective of the present invention to provide a cement formula composition that can be used for constructing a multiple layered object having a structural shape that is more flexible when compared to those obtained from the traditional extrusion methods. A cement formula composition for constructing a multiple layered object having at least one referenced layer and an adjacent stacked layer disposed over said referenced layer which are formed by the extrusion of said composition through an extruder head, comprising a hardening accelerator and fibers wherein the amount of said accelerator is in the range of 0.1 to 5% by weight and comprises an aluminate composition having alumina content in the range of 30 to 98% by weight and wherein the fibers have a length from 0.5 millimeters to half of the diameter of the extruder head and the amount of said fibers is in the range of 0.1 to 1.0% by volume thereby allowing the positions of the outermost edges of the referenced layer and the layer adjacent to have a horizontal overlap based on the relationship that the percentage of said overlap is equal or higher than two times the ratio between the thickness and the width of the referenced layer. In the other aspect, the accelerator can be calcium sulfoaluminate cement (CSA) or high alumina cement (HAC). In the preferred embodiment where HAC is used, it is preferable to have the amount of HAC in the range of 0.1 to 3% by weight.
In the preferred embodiment, in the other aspect, fibers can be one or more fibers selected from a group of polymer fibers such as polypropylene (PP) fiber and polyvinylalcohol (PVA) fiber, and natural fibers such as refined or unrefined cellulose fiber or chemically treated cellulose fiber, particularly those having low water absorption, and other fiber types such as glass fibers.

In the other aspect, the cement formula further comprises at least one or more materials and chemical additives including aggregate, supplementary cementitious material, superplasticizer, retarder, rheology modifier, and water. The aggregate can be selected from a group of sand, limestone, and recycled concrete aggregate. The supplementary cementitious material can also be selected from a group of metakaolin, fly ash, rice husk ash, bottom ash, slag, and silica fume.

The objectives and unique characteristics and other aspects of this invention will be described in more detail by way of the examples and drawings included and the best mode will also be further described.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Fig. 1 shows the overlap between layers according to this invention.

Fig. 2 shows the measurement of degrees of the constant vertical slope between the positions of the outermost edges of the referenced layer and the other layers of one of the possible embodiments.

**DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS**

For a better understanding of the preferred embodiment and to show how it may be performed, it will now be described in more detail by way of examples only with reference to the accompanying drawings. The parts shown in the drawings will be represented by the referenced number. The description, however, does not imply to any limitation, and the scope of the invention will be in accordance with the claims attached herein.

According to this invention, a cement formula composition for constructing a multiple layered object having at least one referenced layer and an adjacent stacked layer disposed over said referenced layer which are formed by the extrusion of said composition through an extruder's head, comprising a hardening accelerator and fibers wherein the amount of said accelerator is in the range of 0.1 to 5% by weight and comprises an aluminate composition having alumina content in the
range of 30 to 98% by weight and wherein the fibers have a length from 0.5 millimeters to half of the diameter of the extruder head and the amount of said fibers is in the range of 0.1 to 1.0% in volume thereby allowing the positions of the outermost edges of the referenced layer and the layer adjacent to the said layer to have a horizontal overlap based on the relationship that the percentage of said overlap is equal or higher than two times of the ratio between the thickness and the width of the referenced layer. In the preferred embodiment, the accelerator is HAC and the preferred amount of HAC in the range of is 0.1 to 3% by weight. From the experiment, it was found that the composition without HAC had the initial setting time of 195 minutes (following ASTM C807) and the working time at 25°C and 58% relative humidity of 120 minutes. The addition of HAC reduced the initial setting time and working time to the levels as deemed appropriate for the extrusion. For the addition of HAC using the minimum amount of 0.1%, this would yield the initial setting time of 148 minutes and working time of 110 minutes. For the addition of HAC using the maximum amount of 3%, this would yield the initial setting time of 26 minutes and working time of 16 minutes. However, it should be noted that the appropriate levels may be varied according to the other factors such as the speed of the movement of the nozzle head.

In the preferred embodiment, in the other aspect, fibers can be one or more fibers selected from a group of polymer fibers such as polypropylene (PP) fiber and polyvinylalcohol (PVA) fiber, and natural fibers such as refined or unrefined cellulose fiber, or chemically treated cellulose fiber, particularly those having low water absorption, and other fiber types such as glass fibers or a combination of the aforementioned.

Different types of fibers can be used. However, certain amounts are preferred depending on the type of fibers. For example, the amount of PP fiber should be in the range of 0.1 to 0.5% by volume and preferable in the range of 0.1 to 0.2% by volume. The amount of PVA fibers should be in the range of 0.1 to 0.6% by volume and preferable in the range of 0.1 to 0.3% by volume. The amount of chemically treated cellulose fiber, particularly those having low water absorption should be in the range of 0.1 to 0.5% by volume and preferably in the range of 0.1 to 0.2% by volume. The amount of glass fiber should be in the range of 0.1 to 0.5% by volume and preferable in the range of 0.1 to 0.2% by volume. From the experiment, the addition of fibers significantly increased the yield stress of each layer. The said addition also increased the extension distance before the layer yielded in a flexural test.
The preferred cement formula further comprises at least one or more materials and chemical additives including aggregate, supplementary cementitious material, superplasticizer, retarder, rheology modifier, and water. The aggregate can be selected from a group of sand, limestone, and recycled concrete aggregate. The supplementary cementitious material can also be selected from a group of metakaolin, fly ash, rice husk ash, bottom ash, slag, and silica fume.

Different types of aggregate can be used. These include sand, limestone, and recycled concrete aggregate. Certain amounts of such aggregate are also preferred based on the type of aggregate. In case that sand is selected, the amount of sand should be in the range of 0.1 to 60% by weight. In case that limestone is selected, the amount of limestone should be in the range of 20 to 70% by weight and is preferable to be in the range of 35 to 60% by weight. In case that recycled concrete aggregate is used, the amount of recycled concrete aggregate should be in the range of 0.1 to 50% by weight and is preferable to be in the range of 0.1 to 50% by weight.

Different types of supplementary cementitious material can also be used. These include metakaolin, fly ash, rice husk ash, bottom ash, slag, and silica fume. If metakaolin is used, the amount of metakaolin should be in the range of 0.1 to 8% by weight. If fly ash, rice husk ash, and bottom ash are used, the amount of ash should be in the range of 4 to 10% by weight. If slag is used, the amount of slag should be in the range of 6 to 8% by weight. In case that silica fume is used, the amount of silica fume should be in the range of 2 to 10% by weight and is preferable to be in the range of 3 to 5% by weight.

The amount of superplasticizer should be in the range of 0.1 to 0.2% by weight. The amount of retarder should be in the range of 0.01 to 0.05% by weight and is preferable to be in the range of 0.01 to 0.02% by weight. The amount of rheology modifier should be in the range of 0.1 to 0.5% by weight and is preferable to be in the range of 0.1 to 0.3% by weight. The amount of water should be in the range of 8 to 20% by weight and is preferable to be in the range of 9 to 15% by weight.

One may use the composition according to this invention by providing a chamber containing a cement composition; dispensing said cement composition from the said chamber; consolidating cement composition into a first layer to form a first cross-section of the object; dispensing a cement composition onto the said first layer and repeating the consolidation to form a second cross-section of said object; Repeating the dispensing, consolidating steps to build a successive layers in a layer-wise fashion in accordance with said design for forming a multiple layered object. During such process, it is important to control the consolidation of said composition by measuring the speed of
the movement of the dispenser and the time against the predefined threshold and controlling stability of the layered construction.

The said control of the stability includes the monitor of horizontal difference between the positions of the outermost edges of the referenced layer and the layer adjacent based on the relationship that the percentage of said difference is equal or higher than two times the ratio between the thickness and the width of the referenced layer. The said arrangement can be described using the formula:

$$\text{% of Overlap} \times \left( \frac{\text{Width}}{\text{Thickness}} \right) \geq 2.0$$

FIG. 1 shows the overlap between layers according to the aforementioned formula.

One of the significant technical effects is that, by overlapping layers based on the criteria as described in this disclosure, the acceptable level of compressive strength can still be achieved. This provides a level of flexibility for construction that cannot be expected from the traditional extrusion method without the cement formula composition according to this present invention. From the experiments, an non-geometrical shape having different levels of the slope between the upper and lower layers was constructed. It was found from the said experiments that the vertical slope measuring from the positions of the outermost edges of the referenced layer and the layer adjacent to the said layer can be varied from less than 90 degrees to 50 degrees. It is easier to demonstrate the flexibility of the arrangement when the slopes between different pairs of layers are constant. A sample of which is shown in FIG. 2. However, this sample does not in any way limit the possibility to position layers having inconsistent vertical slope.

Four examples of the invention are shown below, which are not intended to limit the invention. In the examples, "%" means a weight basis unless otherwise specified. The amount of HAC and fibers are varied within the ranges specified according to this invention. The desired effects including setting time and compressive strength that correspond to each example are also shown below.
<table>
<thead>
<tr>
<th>Material</th>
<th>Example 1</th>
<th>Example 2</th>
<th>Example 3</th>
<th>Example 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ordinary Portland Cement</td>
<td>28.00%</td>
<td>28.00%</td>
<td>26.50%</td>
<td>25.00%</td>
</tr>
<tr>
<td>HAC</td>
<td>0.00%</td>
<td>0.00%</td>
<td>1.50%</td>
<td>3.00%</td>
</tr>
<tr>
<td>Fly ash</td>
<td>8.00%</td>
<td>8.00%</td>
<td>8.00%</td>
<td>8.00%</td>
</tr>
<tr>
<td>Silica fume</td>
<td>4.00%</td>
<td>4.00%</td>
<td>4.00%</td>
<td>4.00%</td>
</tr>
<tr>
<td>Limestone</td>
<td>60.00%</td>
<td>60.00%</td>
<td>60.00%</td>
<td>60.00%</td>
</tr>
<tr>
<td>Sum</td>
<td>100.00%</td>
<td>100.00%</td>
<td>100.00%</td>
<td>100.00%</td>
</tr>
<tr>
<td>Superplasticizer</td>
<td>0.12%</td>
<td>0.12%</td>
<td>0.13%</td>
<td>0.10%</td>
</tr>
<tr>
<td>Retarder</td>
<td>0.01%</td>
<td>0.01%</td>
<td>0.01%</td>
<td>0.01%</td>
</tr>
<tr>
<td>Fiber having the length in the range of 3 to 6 mm (% by volume)</td>
<td>0.00%</td>
<td>0.20%</td>
<td>0.20%</td>
<td>0.20%</td>
</tr>
<tr>
<td>Shot fiber having the length less than 1mm (% by volume)</td>
<td>0.00%</td>
<td>0.20%</td>
<td>0.10%</td>
<td>0.25%</td>
</tr>
<tr>
<td>Total</td>
<td>100.13%</td>
<td>100.53%</td>
<td>100.44%</td>
<td>100.56%</td>
</tr>
<tr>
<td>Compressive strength (MPa)</td>
<td>Example 1</td>
<td>Example 2</td>
<td>Example 3</td>
<td>Example 4</td>
</tr>
<tr>
<td>1-Day</td>
<td>37.8</td>
<td>32.6</td>
<td>34.1</td>
<td>34.3</td>
</tr>
<tr>
<td>3-Day</td>
<td>61.1</td>
<td>49.2</td>
<td>56.7</td>
<td>58.5</td>
</tr>
<tr>
<td>7-Day</td>
<td>72.7</td>
<td>53.6</td>
<td>58.8</td>
<td>60.6</td>
</tr>
<tr>
<td>28-Day</td>
<td>76.0</td>
<td>59.9</td>
<td>70.2</td>
<td>68.1</td>
</tr>
<tr>
<td>Initial setting time (min)</td>
<td>195</td>
<td>195</td>
<td>35</td>
<td>26</td>
</tr>
<tr>
<td>Working time (min)</td>
<td>120</td>
<td>120</td>
<td>35</td>
<td>16</td>
</tr>
<tr>
<td>Extension of 3-point bending (mm)</td>
<td>Example 1</td>
<td>Example 2</td>
<td>Example 3</td>
<td>Example 4</td>
</tr>
<tr>
<td>1-Day</td>
<td>0.4</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>3-Day</td>
<td>0.6</td>
<td>2.4</td>
<td>2.2</td>
<td>2.4</td>
</tr>
<tr>
<td>Yield stress (10^4 Pa)</td>
<td>61.8</td>
<td>102</td>
<td>102</td>
<td>103</td>
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</table>
Percentage of an overlap * (width / thickness) | Number of layers
--- | ---
| Example 1 | Example 2 | Example 3 | Example 4
2.16 | 2 | 2 | 8 | not collapse
2.42 | 5 | 12 | not collapse | not collapse
2.64 | 10 | 30 | not collapse | not collapse

It will be appreciated by persons skilled in the art that the present inventions are not limited by what has been particularly shown described hereinabove. Rather the scope of the present invention includes both combinations and sub-combinations of the features described hereinabove as well as modifications and variations thereof which would occur to a person of skill in the art upon reading the foregoing description and which are not in the prior art.
CLAIMS

1. A cement formula composition for constructing a multiple layered object having at least one referenced layer and an adjacent stacked layer disposed over said referenced layer which are formed by the extrusion of said composition through an extruder head, comprising a hardening accelerator and fibers wherein the amount of said accelerator is in the range of 0.1 to 5% by weight and comprises an aluminate composition having alumina content in the range of 30 to 98% by weight and wherein the fibers have a length from 0.5 millimeters to half of the diameter of the extruder head and the amount of said fibers is in the range of 0.1 to 1.0% by volume thereby allowing the positions of the outermost edges of the referenced layer and the layer adjacent to the said layer to have a horizontal overlap based on the relationship that the percentage of said overlap is equal or higher than two times the ratio between the thickness and the width of the referenced layer.

2. The cement formula as cited in Claim 1 wherein the relationship is described by the formula:

\[
\% \text{ of Overlap} \times \left( \frac{\text{Width}}{\text{Thickness}} \right) \geq 2.0
\]

3. The cement formula as cited in Claim 1 wherein the accelerator is calcium sulfoaluminate cement (CSA).

4. The cement formula as cited in Claim 1 wherein the accelerator is high alumina cement (HAC).

5. The cement formula as cited in Claim 4 wherein the range of HAC is 0.1 to 3% by weight.

6. The cement formula as cited in Claim 1 wherein fibers are polymer fibers, natural fibers, glass fibers, or combination of any of the said fibers.

7. The cement formula as cited in Claim 1 further comprising at least one or more of the materials and chemical additives selected from the group of aggregate, supplementary cementitious material, superplasticizer, retarder, rheology modifier, and water.

8. The cement formula as cited in Claim 7 wherein the aggregate is one or more aggregates selected from a group of sand, limestone, and recycled concrete aggregate.

9. The cement formula as cited in Claim 7 wherein supplementary cementitious material is selected from a group of metakaolin, fly ash, rice husk ash, bottom ash, slag, and silica fume.
Fig 1.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. B28B1/00 C04B28/04

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

B. FIELDS SEARCHED

Minimum documentation searched classification system followed by classification symbols

B28B C04B

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tbody>
<tr>
<td>X</td>
<td>JP 2002 249365 A (DENKI KAGAKU KOGY0 KK) 6 September 2002 (2002-09-06) paragraphs [0008], [0013] [0029] [0032]</td>
<td>1-9</td>
</tr>
<tr>
<td>X</td>
<td>CN 104 891 891 A (UNIV TONGJI) 9 September 2015 (2015-09-09) cited in the application example 3</td>
<td>1,6-9</td>
</tr>
<tr>
<td>A</td>
<td>CN 104 310 918 A (CHINA STATE CONSTRUCTION CO) 28 January 2015 (2015-01-28) the whole document</td>
<td>1-9</td>
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</table>

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) on which the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

3 January 2017

Date of mailing of the international search report

18/01/2017

Name and mailing address of the ISA:

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Fax. (+31-70) 340-3016

Authorized officer

Theodori dou, K
### DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family</td>
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<td>JP 2002249365 A</td>
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<td>09-09-2015</td>
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<td>CN 104310918 A</td>
<td>28-01-2015</td>
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<td>KR 20150138608 A</td>
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<td>10-04-2014</td>
<td>CN 104684667 A</td>
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<td>EP 2903762 A2</td>
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