



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| <b>(54) Title:</b> HYDRAULIC CEMENT AND COMPOSITION EMPLOYING THE SAME<br><br><b>(57) Abstract</b><br><br><p>A hydraulic cement is formed from a Class C fly ash and an alkali metal activator. Mortar and concrete compositions can be prepared with this hydraulic cement. The cement is particularly useful in producing mortar and concrete compositions that achieve high strengths in a short time.</p>                                                                                                                                                                                                                                         |           |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |

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## HYDRAULIC CEMENT AND COMPOSITION EMPLOYING THE SAME

BACKGROUND OF THE INVENTION

Hydraulic cements, such as portland cement and blended hydraulic cements, consisting of portland cement and pozzolans, have, for many years, been used as an essential ingredient of the mortar and concrete used for construction of structures, highways, etc. In many instances, fly ash has been used as the pozzolanic component in blended hydraulic cements, and as a mineral admixture to replace part of the more expensive portland cement used in mortar or concrete. The use of fly ash, in place of part of the portland cement or as a constituent in blended cements reduces the large amount of energy required to produce the hydraulic cements required for mortar and concrete. However, the prior art has taught that no more than 35 to 45 per cent of the portland cement can be replaced with fly ash. According to the teachings of the prior art, when more fly ash than that is employed, the resulting mortars and concretes do not have sufficient strength.

It now has been found, however, according to the present invention, that a hydraulic cement where all of the portland cement or blended hydraulic cement is replaced with fly ash can be formed by activating a Class C fly ash with an alkali metal containing material. There is, consequently, a further reduction of cost and energy requirements.

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BRIEF DESCRIPTION OF THE INVENTION

In accordance with the present invention, a hydraulic cement composition is provided consisting essentially of Class C fly ash and an alkali metal activator. The activator consists of one or more materials selected from the class consisting of potassium hydroxide, potassium carbonate, sodium hydroxide, sodium carbonate and portland cementkiln dust. The amount of alkaline metal activator employed, per 100 parts of the total composition, can vary from about 1/2 to 10 parts, by weight. In general, when one of the listed materials other than portland cement kiln dust is employed, no more than 4 parts by weight are used, preferably, between 1/2 and 3 parts, by weight.

Included in the formulation are appropriate set control materials such as citric acid, borax, Cormix, WRDA, Daracem 100, or other admixtures commonly used in concrete formulations. The admixture should comprise from about 1/2 to 3 parts, by weight, of at least one of the referenced materials per 100 total parts of cement composition.

This hydraulic cement achieves both high early strengths and high ultimate strengths. It can be utilized for rapid concrete repair or construction. This cement can be utilized in the production of precast and prestressed concrete, with or without heat curing.

The cement composition of the present invention includes the following components, by weight:

From 90 to 97 parts Class C fly ash

From 1/2 to 10 parts alkali metal activator

From 1/2 to 3 parts admixture

In addition to the materials in the above formulation, other materials can be added to the composition, as, for example, retarders and water reducers commonly used in concrete formulations. Various substitutions are also possible for

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the required materials. While potassium hydroxide is the preferred alkaline metal activator, sodium hydroxide, sodium carbonate, potassium carbonate, and portland cement kiln stack dust can replace all or part of the potassium hydroxide. As indicated, when any of the referenced materials other than portland cement kiln stack dust is employed, the amount of material is generally from 1/2 to 4 parts, by weight, for each 100 part of the cement composition, preferably from about 1/2 to 3 parts, by weight.

When the hydraulic cement of the present invention is used in concrete or mortar, the resulting hardened material has sufficient strength that it can be put into service a few hours after being placed. This strength can be obtained with or without heat curing.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

The hydraulic cement of the present invention has, as previously indicated, the following components by weight:

90 to 97 parts Class C fly ash

1/2 to 10 parts alkali metal activator

1/2 to 3 parts admixture

The fly ash is a Class C fly ash as classified in ASTM C-618.

When potassium hydroxide is used as the alkali metal activator, it can be in the form of flakes, pellets, or water solution. Sodium hydroxide, potassium carbonate, sodium carbonate, and high alkali kiln stack dusts, such as those collected during the production of portland cement, can also be utilized as a source of alkali metal ions.

A preferred admixture is citric acid which can be in any available grade, such as fine crystal, powder, or liquid. Salts of citric acid can be used.

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Borax, a mineral with the composition  $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ , can be used in any available grade and can be replaced, all or in part, by other available admixtures that control the set of concrete mixtures. The major distinction between the cement of the present invention and prior art is the use of fly ash with an alkali metal activator to produce a hydraulic cement with very early strengths, and without portland cement.

All of the components can be interground or interblended and used as a complete cement without additional admixtures. In an alternative, the sources of the alkali metal ion, citric acid, and borax, or other admixtures, may be added at the concrete mixer, in a dry or liquid form, as an admixture or as a second component. When all of the materials are blended together, so that only water and aggregate are required to obtain a mortar or concrete, the control problems that can occur when materials are mixed in the field are eliminated or minimized. On the other hand, when the various materials are blended in the field, there is an economy of storage and shipping. In addition, the two component procedure does allow for greater control of working time.

The following are given as examples of formulations of the hydraulic cement of the present invention. They should be considered only as illustrative and not as limiting, in any way, the full scope of the invention as covered in the appended claims.

All parts are by weight. The Class C fly ash used in the following examples had the properties set forth below:

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CLASS C FLY ASHCHEMICAL ANALYSIS (AS RECEIVED %)

|                                         |       |
|-----------------------------------------|-------|
| SiO <sub>2</sub>                        | 37.60 |
| Al <sub>2</sub> O <sub>3</sub>          | 20.47 |
| Fe <sub>2</sub> O <sub>3</sub>          | 5.44  |
| CaO                                     | 21.54 |
| MgO                                     | 4.61  |
| SO <sub>3</sub> (by LECO Furnace 2.12%) | 1.71  |
| Na <sub>2</sub> O                       | 2.78  |
| K <sub>2</sub> O                        | 0.52  |
| TiO <sub>2</sub>                        | 1.05  |
| SrO                                     | 0.65  |
| Loss                                    | 0.41  |

FINENESS

SIEVE No. 325 = 82.3% passing

BLAINE = 4270 cm<sup>2</sup>/gX-RAY DIFFRACTION - CRYSTAL STRUCTURES PRESENT:

- 1) SiO<sub>2</sub> (silicon oxide)
- 2) Fe<sub>2</sub>O<sub>3</sub> (iron oxide)
- 3) MgO (magnesium oxide)
- 4) CaO (calcium oxide)
- 5) TiO<sub>2</sub> (titanium oxide)

EXAMPLE 1

A cement mixture was formed consisting of:

- 96.29 parts Class C fly ash
- 1.41 parts potassium hydroxide
- 1.28 parts citric acid
- 1.02 parts borax

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EXAMPLE 2

A concrete was prepared employing the cement of Example 1 and other necessary materials as indicated below:

825 parts of cement as Example 1

1213 parts sand

1820 parts gravel

142 parts water

The various materials were mixed in a concrete mixer. The concrete had an open or working time of 25 minutes. Part of the concrete was cast in molds and cured at ambient temperature (73°F). This concrete had compressive strengths as follows:

| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 3 hours    | 1,800 psi       |
| 4 hours    | 2,000 psi       |
| 1 day      | 4,000 psi       |
| 3 days     | 6,600 psi       |
| 7 days     | 8,800 psi       |
| 28 days    | 10,400 psi      |

The remaining concrete was cast in molds and stored at ambient temperature (73°F) for one hour, then cured in steam at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This concrete had compressive strengths as follows:

| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 3 hours    | 3,600 psi       |
| 4 hours    | 4,800 psi       |
| 1 day      | 5,700 psi       |
| 3 days     | 6,600 psi       |
| 7 days     | 7,600 psi       |
| 28 days    | 9,400 psi       |

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EXAMPLE 3

A cement mixture was formed consisting of:

- 95.98 parts Class C fly ash
- 1.40 parts potassium hydroxide
- 1.28 parts citric acid
- 1.02 parts borax
- 0.05 part Cormix SP-1P

Cormix 2000 SP-1P is a sodium salt of a copolymer of an unsaturated carboxylic acid and the hydroxyaklyl ester of such an acid. Cormix meets the requirements of ASTM C-494 as a Type G admixture (water-reducing, high range, and retarding admixture).

EXAMPLE 4

A concrete was prepared employing the cement of Example 3 and other necessary materials as indicated below:

- 827 parts of cement of Example 3
- 1362 parts sand
- 1669 parts gravel
- 142 parts water

The various materials were mixed in a concrete mixer. The concrete had an open or working time of 20 minutes. Part of the concrete was cast in molds and cured at ambient temperature (73°F). This concrete had compressive strengths of 2,000 psi at 4 hours, 4,200 psi at 1 day, and 7,600 psi at 7 days.

The remaining concrete was cast in molds and stored at ambient temperatures (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This concrete had compressive strengths of 5,000 psi at 4 hours, 6,500 psi at 1 day, and 7,600 psi at 7 days.

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EXAMPLE 5

A cement mixture was formed consisting of:

95.98 parts of Class C fly ash  
1.40 parts potassium hydroxide  
1.28 parts citric acid  
1.02 parts borax  
0.05 part Cormix 2000 cp

The Cormix 2000 is the sodium salt of a copolymer of an unsaturated carboxylic acid and the hydroxyalkyl ester of that acid. The material meets the requirements of ASTM C-494-86, as a type G admixture, one which is water-reducing, high range, and retarding.

EXAMPLE 6

A concrete was prepared employing the cement of Example 5 and other necessary materials as indicated below:

827 parts of cement of Example 5  
1362 parts sand  
1669 parts gravel  
142 parts water

The various materials were mixed in a concrete mixer. The concrete had an open or working time of 32 minutes. Part of the concrete was cast in molds and cured at ambient temperature (73°F). This concrete had compressive strengths of 1,300 psi at 4 hours, 2,800 psi at 1 day, and 5,500 psi at 7 days.

The remaining concrete was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This concrete had compressive strengths of 2,200 psi at 4 hours, 3,200 psi at 1 day, and 4,500 psi at 7 days.

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EXAMPLE 7

A cement mixture was made consisting of:

- 95.98 parts Class C fly ash
- 1.40 parts potassium hydroxide
- 1.28 parts citric acid
- 1.02 parts borax
- 0.05 part WRDA-79P

WRDA 79-P is a modified lignosulfonate, with catalyst. It meets the requirements of ASTM C-494 as a Type A admixture (water-reducing admixture) and Type D admixture (water-reducing and retarding admixture).

EXAMPLE 8

A concrete was prepared employing the cement of Example 7 and other necessary materials as indicated below:

- 827 parts of cement of Example 7
- 1362 parts sand
- 1669 parts gravel
- 142 parts water

The various materials were mixed in a concrete mixer. The concrete had an open or working time of 28 minutes. Part of the concrete was cast in molds and cured at ambient temperature (73°F). This concrete had compressive strengths of 1,900 psi at 4 hours, 3,600 psi at 1 day, and 7,600 psi at 7 days.

The remaining concrete was cast in molds and stored at ambient temperatures (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This concrete had compressive strengths of 2,900 psi at 4 hours, 4,200 psi at 1 day, and 5,800 psi at 7 days.

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EXAMPLE 9

A cement mixture was made consisting of:

- 95.98 parts Class C fly ash
- 1.40 parts potassium hydroxide
- 1.28 parts citric acid
- 1.02 parts borax
- 0.05 part Daracem 100P

Daracem 100P is a dispersion of sulfonated naphthalene formaldehyde condensate, a gluconate, and a lignosulfonate. Daracem 100P meets the requirements of ASTM C-494 as a Type G admixture (water-reducing high range, and retarding admixture).

EXAMPLE 10

A concrete was prepared employing the cement of Example 9 and other necessary materials as indicated below:

- 827 parts of cement of Example 9
- 1362 parts sand
- 1669 parts gravel
- 142 parts water

The various materials were mixed in a concrete mixer. The concrete had an open or working time of 30 minutes. Part of the concrete was cast in molds and cured at ambient temperature (73°F). This concrete had compressive strengths of 1,900 psi at 4 hours, 3,800 psi at 1 day, and 7,700 psi at 7 days.

The remaining concrete was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This concrete had compressive strengths of 3,800 psi at 4 hours, 4,900 psi at 1 day, and 6,200 psi at 7 days.

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EXAMPLE 11

A cement mixture was made consisting of:

- 95.98 parts Class C fly ash
- 1.40 parts potassium hydroxide
- 1.28 parts citric acid
- 1.02 parts borax
- 0.025 part Cormix 2000 cp
- 0.025 part Cormix SP-1P

EXAMPLE 12

A concrete was prepared employing the cement of Example 11 and other necessary materials as indicated below:

- 827 parts of cement of Example 11
- 1362 parts sand
- 1669 parts gravel
- 142 parts water

The various materials were mixed in a concrete mixer. The concrete had an open or working time of 25 minutes. Part of the concrete was cast in molds and cured at ambient temperature (73°F). This concrete had compressive strengths of 2,400 psi at 4 hours and 5,000 psi at 1 day.

The remaining concrete was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This concrete had compressive strengths of 5,100 psi at 4 hours and 7,300 psi at 1 day.

EXAMPLE 13

A mortar was prepared employing the cement of Example 1 and other necessary materials as indicated below:

- 1480 parts of the cement of Example 1
- 2274 parts sand
- 246 parts water

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The various materials were mixed in a mortar mixer. The mortar had an open or working time of 30 minutes. Part of the mortar was cast in molds and cured at ambient temperature (73°F). This mortar had compressive strengths as follows:

| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 2 hours    | 2,000 psi       |
| 3 hours    | 2,300 psi       |
| 4 hours    | 2,700 psi       |
| 1 day      | 5,400 psi       |
| 3 days     | 8,400 psi       |
| 7 days     | 10,000 psi      |
| 28 days    | 13,200 psi      |

The remaining mortar was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This mortar had compressive strengths as follows:

| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 4 hours    | 4,400 psi       |
| 1 day      | 5,800 psi       |
| 28 days    | 12,800 psi      |

#### EXAMPLE 14

A cement mixture was made consisting of:  
96.41 parts Class C fly ash  
1.28 parts potassium hydroxide  
1.28 parts citric acid  
1.03 parts borax

#### EXAMPLE 15

A mortar was prepared employing the cement of Example 14 and other necessary materials as indicated below:  
1479 parts of the cement of Example 14  
2275 parts sand  
246 parts water

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The various materials were mixed in a mortar mixer. The mortar had an open or working time of 37 minutes. Part of the mortar was cast in molds and cured at ambient temperatures (73°F). This mortar had compressive strengths as follows:

| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 2 hours    | 1,800 psi       |
| 3 hours    | 2,200 psi       |
| 4 hours    | 2,400 psi       |
| 1 day      | 4,700 psi       |
| 3 days     | 7,400 psi       |
| 7 days     | 8,500 psi       |
| 28 days    | 12,000 psi      |

The remaining mortar was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This mortar had compressive strengths as follows:

| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 4 hours    | 3,400 psi       |
| 1 day      | 5,000 psi       |
| 28 days    | 12,000 psi      |

#### EXAMPLE 16

A cement mixture was made consisting of:

- 96.53 parts Class C fly ash
- 1.16 parts potassium hydroxide
- 1.28 parts citric acid
- 1.03 parts borax

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EXAMPLE 17

A mortar was prepared employing the cement of Example 16 and other necessary materials as indicated below:

1477 parts of the cement of Example 16

2276 parts sand

247 parts water

The various materials were mixed in a mortar mixer. The mortar had an open or working time of 45 minutes. Part of the mortar was cast in molds and cured at ambient temperature (73°F). This mortar had compressive strengths as follows:

| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 2 hours    | 1,500 psi       |
| 3 hours    | 2,000 psi       |
| 4 hours    | 2,200 psi       |
| 1 day      | 4,200 psi       |
| 3 days     | 6,600 psi       |
| 7 days     | 8,300 psi       |
| 28 days    | 11,700 psi      |

The remaining mortar was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This mortar had compressive strengths as follows:

| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 4 hours    | 3,100 psi       |
| 1 day      | 5,200 psi       |
| 28 days    | 11,100 psi      |

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EXAMPLE 18

A cement mixture was prepared consisting of:

96.66 parts Class C fly ash  
1.03 parts potassium hydroxide  
1.28 parts citric acid  
1.03 parts borax

EXAMPLE 19

A mortar was prepared employing the cement of Example 18 and other necessary materials as indicated below:

1476 parts of the cement of Example 18  
2277 parts sand  
247 parts water

The various materials were mixed in a mortar mixer. The mortar had an open or working time of 60 minutes. Part of the mortar was cast in molds and cured at ambient temperature (73°F). This mortar had compressive strengths as follows:

| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 2 hours    | 1,300 psi       |
| 3 hours    | 1,800 psi       |
| 4 hours    | 2,200 psi       |
| 1 day      | 4,000 psi       |
| 3 days     | 6,300 psi       |
| 7 days     | 8,200 psi       |
| 28 days    | 11,700 psi      |

The remaining mortar was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This mortar had compressive strengths as follows:

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| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 4 hours    | 2,400 psi       |
| 1 day      | 5,300 psi       |
| 28 days    | 11,200 psi      |

EXAMPLE 20

A cement mixture was prepared consisting of:

96.79 parts Class C fly ash  
0.90 part potassium hydroxide  
1.28 parts citric acid  
1.03 parts borax

EXAMPLE 21

A mortar was prepared employing the cement of Example 20 and other necessary materials as indicated below:

1475 parts of the cement of Example 20  
2278 parts sand  
247 parts water

The various materials were mixed in a mortar mixer. The mortar had an open or working time of 110 minutes. Part of the mortar was cast in molds and cured at ambient temperature (73°F). This mortar had compressive strengths as follows:

| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 2 hours    | 160 psi         |
| 3 hours    | 1,200 psi       |
| 4 hours    | 1,600 psi       |
| 1 day      | 3,600 psi       |
| 3 days     | 5,400 psi       |
| 7 day      | 6,900 psi       |
| 28 days    | 9,700 psi       |

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The remaining mortar was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. This mortar had compressive strengths as follows:

| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 4 hours    | 2,000 psi       |
| 1 day      | 5,000 psi       |
| 28 days    | 9,900 psi       |

#### EXAMPLE 22

A cement mixture was prepared consisting of:

96.91 parts Class C fly ash  
0.77 part potassium hydroxide  
1.28 parts citric acid  
1.03 parts borax

#### EXAMPLE 23

A mortar was prepared employing the cement of Example 22 and other necessary materials as indicated below:

1474 parts of the cement of Example 22  
2279 parts sand  
247 parts water

The various materials were mixed in a mortar mixer. The mortar had an open or working time of 135 minutes. Part of the mortar was cast in molds and cured at ambient temperature (73°F). This mortar had compressive strengths as follows:

| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 2 hours    | not set         |
| 3 hours    | 640 psi         |
| 4 hours    | 1,400 psi       |
| 1 day      | 3,100 psi       |
| 3 days     | 4,900 psi       |
| 7 days     | 5,500 psi       |
| 28 days    | 8,900 psi       |

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The remaining mortar was cast in molds and stored at ambient temperature (73°F) for one hour, then cured at 195°F for one and one-half hours. Specimens were then cured in ambient (73°F) air until tested. The mortar had compressive strengths as follows:

| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 4 hours    | 1,000 psi       |
| 1 day      | 3,100 psi       |
| 28 days    | 7,900 psi       |

#### EXAMPLE 24

A mortar was prepared as in Example 19 and cast in molds at ambient temperature (73°F). The specimens were cooled at 5°F and maintained at that temperature until shortly before testing. At that time the specimens were warmed to 73°F and tested for compressive strength. The mortar had strengths of 700 psi at 4 hours, 1,200 psi at 1 day, 1,500 psi at 7 days, and 3,400 psi at 28 days.

#### EXAMPLE 25

A cement mixture was prepared consisting of:

- 96.91 parts Class C fly ash
- 0.77 part sodium hydroxide
- 1.29 parts citric acid
- 1.03 parts borax

#### EXAMPLE 26

A mortar was prepared employing the cement of Example 25 and other necessary materials as indicated below:

- 1467 parts of the cement of Example 25
- 2268 parts sand
- 265 parts water

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The various materials were mixed in a mortar mixer. The mortar had an open or working time of 40 minutes. The mortar was cast in molds and cured at ambient temperatures (73°F). This mortar had compressive strengths of 1,700 psi at 2 hours, 2,000 psi at 3 hours, 2,200 psi at 4 hours, and 4,100 psi at 1 day.

#### EXAMPLE 27

A cement mixture was prepared consisting of:

94.95 parts Class C fly ash  
3.79 parts potassium carbonate  
1.26 parts citric acid

#### EXAMPLE 28

A mortar was prepared employing the cement of Example 27 and other necessary materials as indicated below:

1482 parts cement of Example 27  
2246 parts sand  
272 parts water

The various materials were mixed in a mortar mixer. The mortar had an open or working time of 30 minutes. The mortar was mixed, cast in molds and cured at ambient temperature (73°F). The mortar had compressive strengths as follows:

| <u>Age</u> | <u>Strength</u> |
|------------|-----------------|
| 2 hours    | 1,100 psi       |
| 3 hours    | 1,500 psi       |
| 4 hours    | 1,700 psi       |
| 1 day      | 4,100 psi       |
| 3 days     | 5,800 psi       |
| 7 days     | 8,400 psi       |

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EXAMPLE 29

A cement mixture was prepared consisting of:

90.69 parts Class C fly ash

7.98 parts kiln stack dust

1.33 parts citric acid

The kiln stack dust had the following properties:

Specific Gravity = 2.63

CHEMICAL

Leco  $\text{SO}_3$  = 11.70%

Atomic Absorption  $\text{Na}_2\text{O}$  = 2.25%

Atomic Absorption  $\text{K}_2\text{O}$  = 25.2%

Loss = 12.25%

Moisture Content = 0.57%

Water Soluble Alkali:  $\text{Na}_2\text{O}$  = 2.1%

Water Soluble Alkali:  $\text{K}_2\text{O}$  = 20.4%

FINENESS

Sieves: No. 200 = 90.5%

No. 325 = 86.3%

Blaine: 18,619  $\text{cm}^2/\text{g}$

X-RAY DIFFRACTION; CRYSTAL STRUCTURES PRESENT:

- 1) Calcium Carbonate
- 2) Potassium Sulfate
- 3) Potassium Sodium Sulfate

EXAMPLE 30

A mortar was prepared employing the cement of Example 29 and other necessary materials as indicated below:

1424 parts cement of Example 29

2273 parts sand

303 parts water

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The various materials were mixed in a mortar mixer. The mortar had an open or working time of 30 minutes. The mortar was mixed, cast in molds and cured at ambient temperature (73°F). The mortar had compressive strengths of 1,300 psi at 2 hours, 1,500 psi at 3 hours, and 1,600 psi at 4 hours.

EXAMPLE 31

A cement mixture was prepared consisting of:

92.02 parts Class C fly ash

6.65 parts kiln stack dust

1.33 parts citric acid

EXAMPLE 32

A mortar was prepared employing the cement of Example 31 and other necessary materials as indicated below:

1431 parts cement of Example 31

2284 parts sand

285 parts water

The various materials were mixed in a mortar mixer. The mortar had an open or working time of 30 minutes. The mortar was mixed, cast in molds and cured at ambient temperature (73°F). The mortar had compressive strengths of 1,200 psi at 2 hours, 1,500 psi at 3 hours, 1,800 psi at 4 hours, and 4,000 psi at 1 day.

While specific examples of the present invention have been shown and described, they should be considered as merely illustrative, and not as limiting, in any way, the full scope of the invention as set forth in the appended claims.

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WHAT IS CLAIMED AS NEW IS:

1. A hydraulic cement comprising, by weight:  
From about 90 to 97 parts Class C fly ash  
From about 1/2 to 10 parts alkali metal activator  
From about 1/2 to 3 parts admixture
2. The hydraulic cement of Claim 1 wherein the alkali metal activator is portland cement kiln dust.
3. The hydraulic cement of Claim 1 wherein the alkali metal activator is from 1/2 to 4 parts of at least one material selected from the group consisting of potassium hydroxide, potassium carbonate, sodium hydroxide, and sodium carbonate.
4. The hydraulic cement of Claim 3 wherein the amount is from about 1/2 to 3 parts.
5. The hydraulic cement of Claim 3 wherein the alkali metal activator is potassium hydroxide.
6. The hydraulic cement of Claim 1 wherein the admixture is selected from the class consisting of citric acid, borax, Cormix, WRDA, and Daracem 100.
7. The hydraulic cement of Claim 6 wherein the admixture is from about 1/2 to 1 1/2 parts citric acid and from about 1/2 to 1 1/2 parts borax.

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8. A two part composition for hydraulic cement, wherein said two parts are blended prior to preparation of the cement, comprising:

a. a first part comprising from 90 to 97 parts, by weight, Class C fly ash; and

b. a second part comprising:

(1) from about  $1/2$  to 10 parts alkali metal activator; and

(2) from about  $1/2$  to 3 parts admixture.

9. The composition of Claim 8 wherein the alkali metal activator is portland cement kiln dust.

10. The composition of Claim 8 wherein the alkali metal activator is from  $1/2$  to 4 parts of at least one material selected from the group consisting of potassium hydroxide, potassium carbonate, sodium hydroxide, and sodium carbonate.

11. The composition of Claim 8 wherein the amount is from about  $1/2$  to 3 parts.

12. The composition of Claim 8 wherein the alkali metal activator is potassium hydroxide.

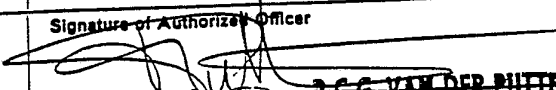
13. The composition of Claim 8 wherein the admixture is selected from the class consisting of citric acid, borax, Cormix, WRDA, and Daracem 100.

14. The composition of Claim 8 wherein the admixture is from about  $1/2$  to  $1\ 1/2$  parts citric acid and from about  $1/2$  to  $1\ 1/2$  parts borax.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 88/04055

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|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|
| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup><br>According to International Patent Classification (IPC) or to both National Classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                                                                                                                                              |                                     |
| IPC <sup>4</sup> :      C 04 B 7/26                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                                                                                                              |                                     |
| <b>II. FIELDS SEARCHED</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                                                                                                                              |                                     |
| Minimum Documentation Searched <sup>7</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                              |                                     |
| Classification System                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Classification Symbols                                                                                                                                                                                                                       |                                     |
| IPC <sup>4</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | C 04 B                                                                                                                                                                                                                                       |                                     |
| Documentation Searched other than Minimum Documentation<br>to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                              |                                     |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                                                                                                                              |                                     |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                                                                                                                              |                                     |
| Category <sup>10</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>                                                                                                                               | Relevant to Claim No. <sup>13</sup> |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | US, A, 4028130 (WEBSTER et al.)<br>7 June 1977<br>see claim 20<br>--                                                                                                                                                                         | 1,2,8,9                             |
| X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | Chemical Abstracts, volume 95, no. 8,<br>August 1981, (Columbus, Ohio, US),<br>A. Derdacka-Grzymek et al.:<br>"Cementless binding material from<br>fly ash", see page 295, abstract<br>66734k, & Cem.-Wapno-Gips 1980,<br>(8-9), 220-2<br>-- | 1,3,8,10                            |
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| <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> * Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"G" document member of the same patent family</p> </div> </div> |                                                                                                                                                                                                                                              |                                     |
| <b>IV. CERTIFICATION</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                                                                                                                              |                                     |
| Date of the Actual Completion of the International Search                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | Date of Mailing of this International Search Report                                                                                                                                                                                          |                                     |
| 27th February 1989                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | 23. 03. 89                                                                                                                                                                                                                                   |                                     |
| International Searching Authority                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | Signature of Authorized Officer                                                                                                                                                                                                              |                                     |
| EUROPEAN PATENT OFFICE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | <br>P.C.G. VAN DER PUTTEN                                                                                                                                |                                     |

| III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET) |                                                                                    |                      |
|----------------------------------------------------------------------------|------------------------------------------------------------------------------------|----------------------|
| Category *                                                                 | Citation of Document, with indication, where appropriate, of the relevant passages | Relevant to Claim No |
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US 8804055

SA 25593

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 16/03/89. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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| GB-A- 1505861                             | 30-03-78            | None                                                                                                                                                                                                      |                                                                                                                                              |
| US-A- 4268316                             | 19-05-81            | None                                                                                                                                                                                                      |                                                                                                                                              |