(12) UK Patent Application (19) GB (11) 2 188 922 (13) A

(43) Application published 14 Oct 1987

(21) Application No 8608715

(22) Date of filing 10 Apr 1986

(71) Applicant
Fosroc International Limited,

(Incorporated in United Kingdom),

285 Long Acre, Nechells, Birmingham B7 5JR

(72) Inventor
Roderick Macdonald Smart

(74) Agent and/or Address for Service
Laurence Shaw, George House, George Road, Edgbaston, Birmingham B15 1PG

(51) INT CL[4]
C04B 28/06

(52) Domestic classification (Edition I)
C1H 120 610 620 717 724 735 739 742 744 747 757
U1S 1747 C1H

(56) Documents cited
None

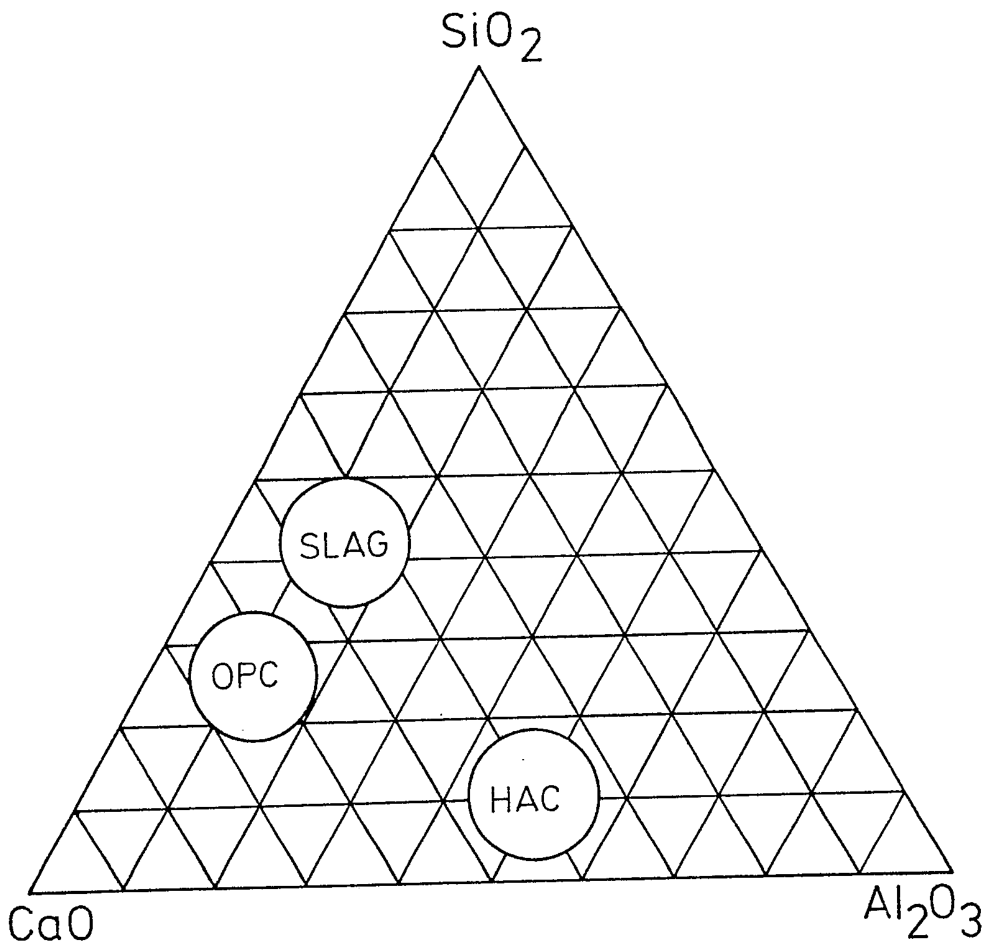
(58) Field of search
C1H
Selected US specifications from IPC sub-class C04B

(54) Self-setting cementitious compositions

(57) A capsule contains in separate compartments the interactive components of a self-setting composition which comprise as base component a paste of high alumina cement, retarders, water, and a source of CaO and SiO_2 – e.g. preferably granulated blast furnace slag or alternatively fly ash, silica fume, a pozzolan or diatomaceous earth; and as a catalyst component a paste of lime, water and a water-soluble lithium salt. When reacted the components form a set cement containing hydrated phases typical of an OPC.

GB 2 188 922 A

The drawing(s) originally filed was (were) informal and the print here reproduced is taken from a later filed formal copy.
The claims were filed later than the filing date within the period prescribed by Rule 25(1) of the Patents Rules 1982.


SiO2
SLAG
OPC
HAC
CaO
Al2O3

SPECIFICATION

Capsules of self-setting cementitious compositions

The invention relates to capsules containing the interactive components of a self-setting composition, the components being housed in separate compartments until the capsule is broken. Such a capsule may be used for example to anchor an element in a borehole, e.g. in a mine gallery roof.

Capsules of this class are known, and they fall into different types dependent on the nature of the self-setting composition. The composition may be organic as in the case of polyester systems or inorganic as in the case of cementitious systems. This invention is concerned with capsules containing a cementitious system the interactive components of which comprise a cement and water or cement and a catalyst therefor. The components are typically a base component (the cement) and a catalyst component.

A cementitious composition may be based on Ordinary Portland Cement (OPC). This has the disadvantage of a slow rate of set. There is claimed in our European patent 0113593 (case CPB139) a capsule containing a cementitious composition based on high alumina cement (HAC) the rate of set of which can be controlled. The use of HAC has its limitations, in particular a tendency for the hydrated cement to undergo HAC conversion which may lead to problems caused by loss of strength.

It is an object of this invention to provide a capsule containing a cementitious composition which has the advantages of the use of HAC without the disadvantages. In particular, a long shelf life and controlled rate of set, without any substantial deterioration in the ultimate strength or other adverse effect.

The invention is based on the realisation that the incorporation in the base component of a filler which is substantially inert with respect to the other ingredients of the base component but which will be activated by the catalyst component when the components are mixed, will secure these advantages.

According to one aspect of the invention there is provided a frangible capsule containing in separate compartments the interactive components of a self-setting cementitious composition, one component being a base component and comprising high alumina cement, retarders and water, and the other component being a catalyst component and comprising lime, an accelerator and water, is *characterised in that* the base component also includes CaO and SiO_2 in sufficient quantities such that on hydration of the cement, the hydrate phases of a hydrated Portland cement are found.

The CaO and SiO_2 may be provided by separate sources or a single source may be used. Preferred single sources are pulverised fly ash, silica fume and pozzolans such as Tripoli (available in the USA) and diatomaceous earths. It is a much preferred feature of the invention that the additives are supplied in a form which is non reactive with water, and for this purpose we prefer to use ground granulated blast furnace slag. The ground granulated blast furnace slag preferably has a minimum fineness of 275m^2/kg, and a bulk density of 1200 kgm^{-3} and an approximiate specific gravity of 2.9. Such slags are made from rapidly cooled blast furnace slag which is the ground to the degree of fineness indicated.

The hydrated phases in a set OPC cement are (cement chemistry notation) typically

CSH
C_4AH_{13}
$Ca(OH)_2$
C_2ASH_8

whereas in a set HAC cement the hydrated phases are typically

CAH_{10}
C_2AH_8
C_3AH_6
C_2ASH_8 (minor amount).

It is a surprising feature of the invention that by adding sources of CaO and SiO_2 in sufficient quantities to an HAC cement the hydrated phases typical of an OPC are formed. The effect is illustrated in the oxide composition diagram of the accompanying drawing. The three main oxides which occur in cement systems are CaO (lime), Al_2O_3 (alumina) and SiO_2 (silica). It will be seen that the oxide phases in the OPC and in the slag are relatively low in Al_2O_3, whereas that of the HAC is high. According to the invention by adding slag in sufficient quantity to the HAC, the set cement has an oxide composition more typical of OPC.

Blast furnace slag is a well known reactive filler often used in OPC compositions. So far as we are aware, no-one has previously proposed its use in a HAC composition, probably because its rate of reactivity conferred no benefit. The use of this filler in the base component containing the HAC and the isolation of these two materials from a catalyst component which causes both to set is, in our view, both new and non-obvious.

The blast furnace slag may be of any known type, and derived from any commercial source. The particle size may vary widely but the size should be related to that of the cement particles.

It is a surprising feature of the invention that the proportion of the blast furnace slag may be varied widely relative to the HAC without substantially affecting the rate of set of the interacted self-setting composition. It is a preferred feature of the invention that the composition undergo an initial set within less than 15 minutes, ideally about 4 minutes. In our evaluations we have been able to use ratios from about 1:1 up to about 8:1 by weight and keep the rate of set within the preferred time scale.

One advantage of the capsule of the invention is the prolonged shelf life, of at least 6 months and often for a year.

The interacted components are capable of achieving initial set times between about 1 and 10 minutes, preferably about 3 to about 5 minutes. The set composition after 30 minutes, will have a shear strength of about 7.5N/mm^2 and a compressive strength of about 17N/mm^2.

The cementitious material in the composition is so-called high alumina cement. This material is known under a variety of names in different countries, for example "Cement Fondue" and "alumina cement" or "super alumina cement". The content of alumina in the cement varies from country to country, sometimes being as low as 30% and other times being over 77%. The invention is applicable to all such alumina cements.

The catalyst component most preferably comprises a catalyst for the cement together with a base material, such as lime. A catalyst for the high alumina cement is preferably a lithium derivative which is preferably lithium carbonate, lithium sulphate or lithium hydroxide. Any lithium salt may be used provided it is water soluble and compatible with the other ingredients. Trisodium nitrilotriacetate, which will prevent the lime from forming a thick paste, in a proportion of about 0.5 to 2 parts relative to the base, is preferably present.

As taught in our European patent publication 0113593 (my ref: CBP 139) sequestrants and the like may be present.

The base component preferably has a pH of the order of about 8.5. When components are mixed the set composition will have a pH of the order of about 11.

The composition may include other ingredients, e.g. water reducing agents, expanding agents, surfactants, colourants, latex emulsions, anti-foaming agents and plasticisers. Other accelerators may be present, e.g. sodium carbonate, sodium sulphate, calcium chloride, sodium hydroxide, ferrous sulphate, sulphuric acid, acetic acid, calcium sulphate, etc. A thixotropic, thickening agent or air entraining agent may be present if water bleed on storage and a loss of grout composition is to be minimised, a point especially important in overhead or fissured rock applications. Polymeric additives such as cellulose ethers,polyacrylamides and polyethylene oxides, or montmorillonite type clays may be present.

The capsule may be of any suitable shape so long as the two interactive components are housed in separate compartments for storage. When required and in known manner, an anchoring element is used to rupture the capsule, open the compartments and intermix the interactive components. The capsule may range from 20 to 40 mm in diameter and 200 to 600 mm in length, and may be used in boreholes ranging from about 25 mm to about 50 mm in diameter. The boreholes may be drilled in the wall or roof of a coal mine, gold mine, iron ore mine, quarry or civil engineering structures.

In order that the invention may be well understood, it will now be described by way of example with reference to the following examples, in which parts are by weight unless otherwise indicated.

Example 1

A catalyst component was made as a paste of

ingredient	*parts*
slaked lime	53.1
water	35.4
lithium hydroxide	6.6
magnesium sulphate	2.7
trisodium nitroloacetate	1.8
citric acid	0.4

A range of base compositions were made up as shown in Table I. The compositions were stored for several months and then the interactive components mixed. The set times, shear strengths and compressive strengths were measured as shown in Tables II and III. From these results it is clear that the set composition has excellent characteristics.

Example II

Capsules according to selected formulations of Example I were made up and allowed to set in comparison with two commercially available capsules

– LOKSET LF6, according to patent publication EP0046037 (LOKSET is a registered trade mark.)
– EC PHIX W, available from Celtite Ltd., Alfreton, Derbyshire.

The shear strength and rate of strength development are shown in Tables IV and V respectively from which it can be seen that the capsules of the invention have much better properties.

TABLE I

Composition	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*
high alumina cement	(control) 68.4	58.4	48.9	42.7	38.6	34.0	30.8	28.0	25.7	19.3	15.4	13.0
blast furnace slag (ground granulated	0	14.6	24.5	32.0	38.6	42.5	46.3	49.1	51.4	57.8	61.6	65.0
water	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4	18.4
silica fume	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6
zinc borate	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3
EDTA (sodium salt)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
water soluble polymers	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

EDTA=ethylene diamine tetraacetic acid

TABLE II

Set times and shear strengths of grouts

Composition No.	*Initial Set (minutes)*	*Shear strengths (N/mm2^{2}*						
		1/2 Hr.	*2 Hrs.*	*24 Hrs.*	*7 d.*	*28 d.*	*2 mnth*	*6 mnth*
1 Control	4	7.5	9.3	11.1	16.8	21.2	25.6	28.9
2	3.1/2	6.6	8.5	12.1	18.1	24.1	26.7	30.9
3	3.1/2	6.0	8.2	12.0	19.6	24.0	25.4	31.2
4	3	5.8	7.8	12.5	19.6	23.1	27.2	29.4
5	3	5.0	6.7	11.6	18.8	23.2	26.5	33.4
6	3	4.6	5.6	12.5	17.0	22.9	25.7	28.3
7	2.1/2	4.1	4.9	11.5	16.9	22.5	27.4	34.2
8	2.1/2	3.7	4.6	10.4	16.4	21.7	25.8	29.8
9	2.1/2	3.0	4.5	10.0	15.6	20.8	28.8	29.3
10	5	1.6	3.5	7.1	16.1	20.3	27.8	30.2
11	6	1.1	2.5	5.0	13.0	19.0	24.0	29.4
12	7	0.9	2.1	4.3	11.6	18.9	22.4	28.6

TABLE III

Compressive strengths of grouts

Formulation No.	Compressive strengths (N/mm2^2)						
	1/2 Hr.	2 Hrs.	24 Hrs.	7 d.	28 d.	2 month	6 month
1 Control	18.2	21.2	25.4	38.3	47.4	53.3	60.8
2	16.1	17.8	25.6	38.0	55.0	60.4	70.3
3	13.5	18.0	19.9	39.2	52.1	53.1	71.4
4	10.7	14.4	22.6	34.9	48.2	54.4	73.2
5	9.4	12.7	22.4	34.0	43.6	53.1	66.7
6	8.7	11.7	21.9	25.2	46.6	57.4	67.2
7	7.3	9.0	17.7	35.5	41.5	59.0	70.2
8	6.9	9.7	17.7	28.8	40.0	51.9	68.4
9	5.1	9.7	17.0	26.3	40.6	50.9	66.9
10	5.2	9.7	17.5	25.8	43.6	45.6	71.8
11	4.0	4.9	14.6	24.9	48.9	51.0	70.1
12	2.8	4.4	9.7	28.0	47.9	54.6	69.8

TABLE IV

Strength development rate of differing capsules of Example II

GROUT	Time after mixing				
	15 m.	1/2 Hr.	1 Hr.	2 Hrs.	3 Hrs.
COMPOSITION 1 OF TABLE I	4.7	7.4	8.5	9.2	9.7
COMPOSITION 5 OF TABLE I	3.0	5.0	6.1	6.7	7.1
COMPOSITION 9 OF TABLE I	1.9	3.0	4.0	4.7	5.3
LOKSET LF6	10.6	12.6	13.6	13.9	14.0
CELTITE EC PHIX W	3.2	5.3	6.6	7.2	7.3

TABLE V

Strength of different capsules of Example II

GROUT	Shear strengths (N/mm2^2)		
	7 DAY	28 DAY	2 MONTH
COMPOSITION 1	16.8	21.2	25.6
COMPOSITION 5	18.8	23.2	26.5
COMPOSITION 9	15.6	20.8	28.8
LOKSET LF6	15.0	15.0	15.0
CELTITE EC PHIX W	9.0	9.0	9.0

CLAIMS

1. A frangible capsule containing in separate compartments the interactive components of a self-setting cementitious composition, one component being a base component and comprising high alumina cement, retarders and water, and the other component being a catalyst component and comprising lime and water, in which the base component includes both CaO and SiO_2 in sufficient quantity such that when the interactive components are interacted the hydrate phases of a hydrated Portland cement are formed.

2. A capsule according to Claim 1, in which a single source of the CaO and SiO_2 is present.

3. A capsule according to Claim 2, in which the CaO and SiO_2 are provided by pulverised fly ash, silica fume, a pozzolan or diatomaceous earth.

4. A capsule according to any preceding Claim, in which the CaO and SiO_2 are supplied as a material which

is substantially non-reactive with water.

5. A capsule according to Claim 4, in which the CaO and SiO_2 are provided by granulated blast furnace slag.

6. A capsule according to Claim 5, in which the granulated blast furnace slag has a minimum fineness of $275m^2/Kg$, a bulk density of 1200 Kgm^{-3} and an approximate specific gravity of 2.9.

7. A capsule according to any preceding Claim, in which the CaO and SiO_2 are present in a combined weight ratio of from about 1:1 to about 8:1 relative to the high alumina cement.

8. A capsule according to any preceding Claim, in which the base component includes sufficient water to form a paste.

9. A capsule according to any preceding Claim, in which the catalyst component comprises lime, water and a water soluble lithium salt.

10. A frangible capsule containing in separate compartments the interactive components of a self setting composition, substantially as described herein.

Printed for Her Majesty's Stationery Office by Croydon Printing Company (UK) Ltd, 8/87, D8991685.
Published by The Patent Office, 25 Southampton Buildings, London WC2A 1AY, from which copies may be obtained.