

PATENT SPECIFICATION

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(54) A RAPIDLY SETTING PORTLAND CEMENT COMPOSITION AND PROCESS OF FORMING A MODIFIED PORTLAND CEMENT

- (71) We, PORTLAND CEMENT ASSOCIATION, an unincorporated association organized and existing under the laws of the State of Illinois, United States of America, of 5420 Old Orchard Road, Skokie, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to portland cement compositions and processes for making same. The present invention provides a rapidly setting portland cement composition containing one to thirty percent by weight of a calcium halo-aluminate having the formula $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaX}_2$ in which X is a halogen.
- The present invention also provides a process of regulating the set time of portland cement which comprises adding thereto a ground clinker containing a calcium halo-aluminate having the formula $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaX}_2$ in which X is halogen in an amount such that the percent of said calcium halo-aluminate in the cement product is one to thirty percent by weight.
- The present invention further provides a process of forming a modified portland cement which comprises subjecting high alumina portland cement ingredients to burning at 1275 to 1400°C. in the presence of calcium fluoride whereby to form in the resulting product from one to thirty percent by weight of a ternary compound having the formula $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$.
- The present invention also further provides a process of forming a modified portland cement which comprises subjecting high alumina portland cement ingredients to burning at 1380 to 1510°C. in the presence of calcium chloride to form in the resulting product from one to thirty percent by weight of a ternary compound having the formula $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaCl}_2$.
- A characteristic of portland cement is that after mixing with water it sets to a final product having very considerable strength. However, one of the properties of such compositions is that the set time is slow when compared to certain other cementitious products and the initial set strength of the product tends to be low and increases only comparatively slowly during the setting period. These properties have limited the uses to which portland cement can be put in certain applications.
- The relatively slow setting properties of presently used portland cement and portland cement concretes make the forming, casting and form-stripping cycle on job-placed concrete a process requiring at least one and usually several days. A portland cement in which the set can be controlled would speed up the building process. There is also a great need for fast setting concrete in concrete products plants making such products as block, pipe, architectural panels, structural beams and columns, extruded products and various types of sculptured concrete. If, for example, in such a plant the fast set would permit the turnover of moulds three to four times per day instead of once a day, this would decrease a major part of the capital investment three to four times. In certain special uses, such as patching airport pavements, it would be desirable to have a portland cement concrete that could be poured, screeded, and set adequately for traffic in less times than are now possible. Lightweight concrete for roof decks, when pumped from ground to roof level, desirably should set in twenty to thirty minutes to permit working on the roof behind the pouring operation. In most of these instances, the fast setting and curing of concrete would eliminate many of the difficulties attendant to slow setting concrete. In many cases, this would minimize or eliminate the

[Price 5s. 0d. (25p)]

- mixed, in the volume ratio of one part cement to six parts perlite (weight ratio of 356 parts cement to 182 parts perlite), gauged with water and entrained air to a density of 54 pounds per cubic foot and poured. After one hour the composition had set sufficiently to resist a compressive force of 48 pounds per square inch. At two days the composition had set to a strength such that it would support 124 pounds per square inch.

EXAMPLE 3

- One hundred parts by weight of a commercial portland cement kiln feed (Composition A), six parts of hydrated alumina (64.9 percent by weight Al_2O_3) and 2.0 parts of calcium fluoride were interground and burned in an electric muffle at 1350°C . (2462°F .) for thirty minutes. The clinker was ground to a fineness of 4340 cm^2 per gram (Blaine). The analyses of Composition A and the ground clinker (I204K) were as follows in percent by weight:

	Composition	
	A	I204K
SiO ₂	13.7	19.15
Al ₂ O ₃	4.4	11.91
Fe ₂ O ₃	1.7	2.71
CaO	42.5	60.52
MgO	2.2	2.87
K ₂ O	0.6	0.68
Na ₂ O	0.3	0.29
F	—	0.65
Free CaO	—	1.31
Ignition Loss	35.4	0.57

- The amount of the ternary fluoro compound as determined by X-ray analysis in the clinker was 19.30 percent by weight. One hundred parts of the ground clinker were mixed with 2.6 parts anhydrite (CaSO_4) and 2.6 parts calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) to give a cement containing 18.3 percent $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$, 2.8 percent SO_3 and 1.25 percent free lime.

- The resulting cement was mixed with perlite in the ratio one part by volume of clinker to six parts of perlite, gauged with water and entrained air to a density of 49 pounds per cubic foot, and poured. After one hour the composition had set sufficiently to resist a compressive force of 88 pounds per square inch. By the end of two days the concrete had developed strength to resist a compressive force of 130 pounds per square inch.

EXAMPLE 4

- Five hundred thirty-seven parts by weight of commercial calcite (CaCO_3), 198 parts of commercial kaolin (see Example 1 for analysis) and 17.5 parts of anhydrous calcium chloride (CaCl_2) were interground and burned at 1440°C . (2624°F .) for forty minutes in a gas fired furnace. The resulting

product contained calcium silicate and calcium chloro-aluminate having the formula $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaCl}_2$. The amount of the tertiary chloro compound as determined by X-ray analysis in the resulting clinker was 24.6 percent by weight; the analysis of the clinker (B221J) was as follows (percent by weight):

SiO ₂	19.40	70
Al ₂ O ₃	16.07	
Fe ₂ O ₃	0.30	
CaO	61.68	
TiO ₂	0.79	
MgO	0.38	75
K ₂ O	<0.01	
Na ₂ O	<0.01	
Cl	1.24	
Free CaO	0.16	

The clinker was ground to a fineness of 4018 Blaine to form the enriched cement and 35 parts by weight were thoroughly mixed with 65 parts of commercial portland cement (Composition B of Example 1). The resulting portland cement composition embodying this invention and prepared as outlined above contained 8.6 percent $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaCl}_2$, 1.67 percent SO_3 and 1.4 percent free lime.

The final portland cement composition was mixed with expanded perlite, in the ratio of one part by volume of cement to six parts perlite, gauged with water and entrained air to a density of 51 pounds per cubic foot and poured. After two hours the concrete had set sufficiently to resist a compressive force of 62 pounds per square inch. By the end of three days the concrete had developed strength to resist a compressive force of 232 pounds per square inch.

EXAMPLE 5

One hundred parts by weight of a commercial portland cement kiln feed (Composition A of Example 3), six parts of hydrated alumina (64.9 percent by weight Al_2O_3) and 2.32 parts of anhydrous calcium chloride were interground and burned in an electric muffle at 1440°C . (2624°F .) for 35 minutes. The resulting clinker was ground to a fineness of 4038 Blaine. The analysis of the resulting clinker (1220°F .) in weight percent was as follows:

SiO ₂	19.72	
Al ₂ O ₃	11.88	
Fe ₂ O ₃	2.58	
CaO	61.45	115
MgO	2.89	
K ₂ O	0.02	
Na ₂ O	0.02	
Cl	0.85	
Free CaO	0.36	120

The amount of the ternary chloro compound

as determined by X-ray analysis in the clinker was 14.8 percent by weight.

5 The ground clinker was mixed with perlite in the ratio one part by volume of clinker to six parts of perlite, gauged with water and entrained air to a density of 49 pounds per cubic foot and poured. After two hours the composition had set sufficiently to resist a compressive force of 86 pounds per square inch. By the end of three days the concrete had developed strength to resist a compressive force of 288 pounds per square inch.

10 The 28 day strengths of the lightweight perlite concretes (3 day moist cure, subsequent 25 day dry cure) described in Examples 1 to 5 above averaged about 450 pounds per square inch. The expanded perlite used in those examples conformed to ASTM designation: C332-66.

EXAMPLE 6

20 The process of Example 5 was carried out by substituting calcium bromide for the calcium chloride. The resulting cement had a reduced set time when compared with a similar composition having no $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaBr}$ or other halo-aluminate present. Care was taken in the burning step because the fumes of elemental bromine formed may provide a health hazard.

EXAMPLE 7

30 An enriched cement was prepared by mixing 89.6 parts of the compound B200 (Example 1), 89.6 parts of a commercial portland clinker C, 16 parts anhydrite (anhydrous CaSO_4) and 4.8 parts of dehydrated plaster (approx. $\text{CaSO}_4 \cdot 1/10 \text{H}_2\text{O}$). The portland clinker C was ground to $3685 \text{ cm}^2/\text{g}$ (Blaine) and analyzed as follows (percent by weight):

	SiO_2	21.82
40	Al_2O_3	6.02
	Fe_2O_3	2.36
	CaO	64.59
	MgO	3.36
	SO_3	0.22
45	K_2O	0.42
	Na_2O	0.19
	Free CaO	0.87
	Ignition Loss	0.67

50 A normal density mortar was prepared from the enriched cement, the ingredients of which were:

Enriched cement	251 grams
Water	105 grams
Sand	502 grams

55 These ingredients were mixed two minutes and two inch cubes were cast for compressive strength determinations. The handling time for the mortar was 14 minutes; the compressive

strength at one hour was 1000 psi and at one day was 3300 psi.

EXAMPLE 8

A concrete mixture was prepared from the enriched cement previously described in Example 7. The ingredients of the concrete were:

Enriched cement	7.27 pounds	65
Water—(net)	3.17 pounds	
Sand	16.3 pounds	
Gravel (3/4 inch maximum size)	23.1 pounds	

70 These ingredients were mixed for two minutes and 3×6 -inch cylinders cast for compressive strength determinations. The concrete consistency was approximately $2\frac{1}{2}$ inches (slump) and the mixture remained workable for approximately thirteen minutes. The average compressive strength of three cylinders tested at one hour after start of mixing was 607 pounds per square inch and 1560 pounds per square inch at 24 hours.

80 With respect to the percentage of the ternary halo-aluminate, $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaX}_2$, that may be present in the portland cement of this invention, this will depend upon the initial set strength desired and the amount of set retarder, i.e., calcium sulfate, used to control the initial set time. The amount of the ternary compound, or a mixture of the several halo ternary compounds, should be at least one percent by weight of the portland cement to obtain significant results. Economic considerations dictate that the percentage should not exceed thirty percent by weight.

In the foregoing examples, X-ray analyses on the inter-burned cement and the blending cements were used to determine the identity and amount of halo-aluminate. The method is described by Copeland et al., Analytical Chemistry 30, 196 (1958) and was as follows:

95 Silicon was employed as the internal standard, the 111 line ($d=3.14\text{\AA}$) being used. One of the two strongest lines of the halo-aluminates, $d=4.88\text{\AA}$, was chosen as the analytical line for the aluminate. The intensities of the lines were measured by planimetry their areas.

100 The halo-aluminates have X-ray diffraction patterns that are not only almost identical to each other but also to that of pure $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ and all have lines at $d=3.20\text{\AA}$. These lines overlap the $3.14\text{\AA}$ line of silicon to a slight degree. Instead of graphically correcting for this overlap, the combined intensities of these two lines (the area under the double hump) were measured, and the ratio of this combined intensity to the intensity of the $4.88\text{\AA}$ line was calculated for various mixtures (several for each of three compounds) that contained different proportions of silicon. The graphs of intensity ratio versus the

silicon to halo-aluminate, and also to pure $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, were linear, each having a positive intercept, α , on the axis of intensity ratios and a positive slope, β . In each case the intercept is equal to the ratio of the intensity of the 3.20 Å line of the particular aluminate to that of its 4.88 Å lines. These intercepts differ from each other and can be used to identify the particular compound present.

The detailed method of sample analysis follows.

1. If it is not known which halo-aluminate is present, determine the intensity ratio of the 3.2 Å line to that of 4.88 Å line. This ratio, α , by reference to that table below, identifies the halo-aluminate.

2. Intergrind a known quantity of silicon with the sample. Ten percent Si is usually

suitable. Determine the combined intensity of the 3.20 Å and 3.14 Å lines. Also determine the intensity of the 4.88 Å line of the halo-aluminate.

3. Calculate an intensity ratio, R, by dividing the combined intensity of the 3.20 Å and 3.14 Å lines by that of the 4.88 Å line. The intensity ratio so obtained is used to calculate the weight ratio of halo-aluminate to silicon by the equation.

$$\frac{11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaX}_2, \%}{\text{Si, \%}} = \frac{\beta_x}{R - \alpha_x}$$

where α_x is the intercept, and β_x the slope, of the calibration curve determined for the compound sought. The values of the constants are given in the following table.

Compound	X	β_x	α_x
$12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$	$\frac{1}{2} \text{O}$	4.10	0.08
$11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$	F	3.85	.158
$11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaCl}_2$	Cl	2.78	.219

In the foregoing examples the calcium halo-aluminate is prepared by reacting the appropriate calcium halide (e.g., calcium fluoride) with an alumina containing material. However, other halides such as the fluorosilicates or fluoroborates may be used. Accordingly, it is apparent that methods other than those previously outlined may be used for producing the $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ compound or other ternary halide which is added to portland cement for the purposes indicated.

WHAT WE CLAIM IS:—

1. A rapidly setting portland cement composition containing from one to thirty percent by weight of a calcium halo-aluminate having the formula $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaX}_2$ in which X is a halogen.

2. The composition recited in claim 1 having added thereto from one to twelve percent by weight calcium sulfate calculated as SO_3 .

3. The composition recited in claim 1 or claim 2 in which X is fluorine or chlorine.

4. A process of regulating the set time of portland cement which comprises adding thereto a ground clinker containing a calcium halo-aluminate having the formula $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaX}_2$ in which X is halogen in an amount such that the percent of said calcium

halo-aluminate in the cement product is from one to thirty percent by weight.

5. A process of forming a modified portland cement which comprises subjecting high alumina portland cement ingredients to burning at 1275 to 1400°C. in the presence of calcium fluoride to form in the resulting product from one to thirty percent by weight of a ternary compound having the formula $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$.

6. A process of forming a modified portland cement which comprises subjecting high alumina portland cement ingredients to burning at 1380 to 1510°C. in the presence of calcium chloride to form in the resulting product from one to thirty percent by weight of a ternary compound having the formula $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaCl}_2$.

7. A rapidly setting portland cement composition according to claim 1 substantially as described herein.

8. A process of regulating the set time of portland cement according to claim 4 substantially as described herein.

9. A process of forming a modified portland cement according to claim 5 or claim 6 substantially as described herein.

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silicon to halo-aluminate, and also to pure $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, were linear, each having a positive intercept, α , on the axis of intensity ratios and a positive slope, β . In each case the intercept is equal to the ratio of the intensity of the 3.20 Å line of the particular aluminate to that of its 4.88 Å lines. These intercepts differ from each other and can be used to identify the particular compound present.

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halo-aluminate in the cement product is from one to thirty percent by weight.

5. A process of forming a modified portland cement which comprises subjecting high alumina portland cement ingredients to burning at 1275 to 1400°C. in the presence of calcium fluoride to form in the resulting product from one to thirty percent by weight of a ternary compound having the formula $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$.

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7. A rapidly setting portland cement composition according to claim 1 substantially as described herein.

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9. A process of forming a modified portland cement according to claim 5 or claim 6 substantially as described herein.

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