

ADDITIVES FOR GEOPOLYMER CEMENTS**CROSS REFERENCE TO RELATED APPLICATIONS**

[0001] The present application is a non-provisional application of U.S. Provisional Application No. 62/755431, entitled “ADDITIVES FOR GEOPOLYMER CEMENTS”, filed November 3, 2018, the disclosure of which is hereby incorporated by reference in its entirety.

Field of the Disclosure

[0002] This disclosure relates to chemical additives for geopolymer cements. More specifically, this disclosure relates to sulfates and selenates of a specific formula as well as hydroxycarboxylic acid salts of Li, Na, and K including but not limited to glycolic, lactic, citric, mandelic tartaric, and malic acids used as additives for geopolymer cements.

Background

[0003] Geopolymer cements, also known as alkali activated cements, are very low carbon emission replacements for Portland cement. There are two basic types of geopolymer cements: (1) those that are self-setting and gain strength without addition of external energy; and (2) those that require heat curing to set and gain strength. The first type of geopolymer cement usually consists of a finely divided powder containing ground granulated blast furnace slag, blended or interground with a pozzolan usually class F fly ash. The second type of geopolymer cement usually consists of any combination of finely divided pozzolonic materials including class F fly ash, clay, volcanic glass, waste glass, and silica fume. Both basic types of geopolymer cements can be activated with the same chemicals which include alkali silicate, alkali hydroxide, and/or alkali carbonate.

[0004] Unfortunately, geopolymer cements have been mostly limited to the manufacture of precast concrete shapes due to their rapid loss of workability and poor rheological properties that make concrete made with them difficult to mix, place, and finish by conventional methods. In addition, high alkali activator dosage is often needed to achieve desired compressive strength. This can lead to short working time and setting time (e.g., as short as 10 minutes). Geopolymer cements can be made more rheologically friendly by the addition of typical chemicals that retard the chemical reactions responsible for setting. However, these typical additives can slow timely setting and strength development which limits the number of applications for which geopolymer cements can be used.

Summary

[0005] Provided are chemical additives for geopolymer cements that can improve the rheological properties of geopolymer cements without retarding the time setting or the early strength development. Such chemical additives can provide a significant environmental benefit by allowing for more Portland cement to be replaced by lower carbon emission cements. In addition, the chemical additives for geopolymer cements disclosed herein can facilitate the uniform mixing, increase the time mixtures can be transported, and improve the ability to place and finish concrete and mortars made with the geopolymer cements.

[0006] Reference to “about” a value or parameter herein includes (and describes) variations that are directed to that value or parameter per se. For example, description referring to “about X” includes description of “X”. In addition, reference to phrases “less than”, “greater than”, “at most”, “at least”, “less than or equal to”, “greater than or equal to”, or other similar phrases followed by a string of values or parameters is meant to apply the phrase to each value or parameter in the string of values or parameters. For example, a statement that the cementitious compositions disclosed herein can have less than about 1 wt.%, about 0.5 wt.%, about 0.1 wt.%, or about 0.01 wt.% Portland cement, is meant to mean that the Portland cement in the cementitious composition can be less than about 1 wt.%, less than about 0.5 wt.%, less than about 0.1 wt.%, or less than about 0.01 wt.%.

[0007] As used herein, the singular forms “a,” “an,” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise. It is also to be understood that the term “and/or” as used herein refers to and encompasses any and all possible combinations of one or more of the associated listed items. It is further to be understood that the terms “includes,” “including,” “comprises,” and/or “comprising,” when used herein, specify the presence of stated features, integers, steps, operations, elements, components, and/or units but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, units, and/or groups thereof.

[0008] Additional advantages will be readily apparent to those skilled in the art from the following detailed description. The examples and descriptions herein are to be regarded as illustrative in nature and not restrictive.

Brief Description of the Drawings

[0009] Exemplary embodiments are described with reference to the accompanying figures, in which:

[0010] Figure 1 is a chart illustrating the sodium lactate percentage versus the working time, the set

time, and 1D compressive strength of mortar formed with sodium lactate additive. [0010] Figure 2 is a chart illustrating the alum percentage versus the working time, the set time, and 1D compressive strength of mortar formed with alum additive.

[0011] Figure 3 is a chart illustrating the aluminum sulfate percentage versus the working time, the set time, and 1D compressive strength of mortar formed with aluminum sulfate additive.

Detailed Description

[0012] Provided are chemical additives for geopolymer cements that can produce a flow-able concrete that is easy to mix, place, and finish. In addition to being suitable for normal construction and precast applications, concrete made with the geopolymer cements disclosed herein can be resistant to sulfate and/or chloride attacks because of its chemical composition.

Accordingly, concretes made with the geopolymer cements disclosed herein can be well-suited for use in high sulfate soils, construction, and marine structures such as ports and seawalls. In addition, the chemical additives for geopolymer cements disclosed herein can improve the rheological properties of geopolymer cements without retarding the time setting or the early strength development properties.

[0013] Like fly ash, Ground Granulated Blast Furnace Slag (GGBFS) is another pozzolanic material used in Portland cement concrete. It is the by-product of the iron and steel making industries. It can be obtained by quenching molten iron slag from a blast furnace in water or steam to produce a glassy, granular product that can be dried and ground into fine powder. The Portland cement industry has for some time elected to inter-grind Portland clinkers with GGBFS (slag) typically in the 30-50% range. In some markets, ready-mix concrete (RMC) plants are also blending fine slag powder with Portland cement.

[0014] As stated above, the principal limitation to the successful commercialization of alkali activated slag cement (AASC) concrete is due to its poor workability. Specifically, its inability to provide sufficient working and placing time. Applicants have discovered chemical additives for alkali activated cements (i.e., geopolymer cements) that improves rheological properties such as working time, placing time, pot life, flow-ability, flow retention of mortar, and slump retention of concrete.

[0015] The cementitious compositions disclosed herein can include slag. In some embodiments, the slag is ground granulated blast furnace slag ("GGBFS") or any other metallurgical slags such as steel, copper or silica. In some embodiments, the slag is in powder form. In some embodiments, the

slag is greater than or equal to about 5 wt% of the cementitious composition.

[0016] In some embodiments, the cementitious compositions can also include a pozzolanic material. In some embodiments, the pozzolanic material can include fly ash, bottom ash, clay calcined clay, glass, volcanic glass, pumice, diatomaceous earth, silica fume, other alumino-silica glass, or combinations thereof. In some embodiments, the pozzolanic material is Class F fly ash. In some embodiments, the pozzolanic material can be a finely divided glassy alumino-silicate powder. In some embodiments, the pozzolanic material is in powder form. In some embodiments, the pozzolanic material can be less than or equal to 95 wt% of the cementitious composition.

[0017] In some embodiments, the slag to pozzolanic material in the cementitious composition can be in a certain weight ratio. In some embodiments, the weight ratio of slag to pozzolanic material can be about 100/0 to about 40/60, about 90/10 to about 50/50, about 87/13 to about 60/40, about 85/15 to about 65/35, about 80/20 to about 70/30, or about 75/25. The mixture of slag and pozzolanic material can be a blend of dry powders.

[0018] In some embodiments, the cementitious compositions can include alkali activators or blends of alkali activators to activate the cementitious compositions. These alkali activators can include hydroxides, carbonates, and/or silicates. In some embodiments, the alkali activators can include sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium silicate, and/or potassium silicate. In some embodiments, the alkali activators can include sodium/potassium hydroxide and sodium/potassium carbonate or sodium/potassium silicate. In some embodiments, the alkali activators can include sodium hydroxide and sodium silicate or sodium carbonate.

[0019] In some embodiments, the sodium or potassium hydroxide can be about 0.1-20 wt%, about 0.1-10 wt%, about 0.1-5 wt%, about 1-5 wt%, about 1-4 wt%, about 2-4 wt%, or about 2-3 wt% the cementitious composition. In some embodiments, the sodium or potassium carbonate can be about 0.1-20 wt%, about 0.1-15 wt.%, about 1-10 wt.%, about 1-9 wt%, about 2-8 wt.%, about 3-6 wt.%, about 4-6 wt.%, or about 4-5 wt.% the cementitious composition. In some embodiments, the sodium or potassium silicate can be about 0.1-20 wt%, about 0.1-15 wt.%, about 1-10 wt.%, about 1-9 wt%, about 2-8 wt.%, about 3-6 wt.%, about 4-6 wt.%, or about 4-5 wt.% the cementitious composition.

[0020] Besides the above components in the cementitious composition, Applicants have unexpectedly discovered that including a chemical additive can improve the workability of the subsequent geopolymer cements. Specifically, the chemical additives can facilitate the mixing, increase the time mixtures can be transported, and can improve the ability to place and finish the

geopolymer concrete mixtures. These chemical additives can include sulfate and selenate compounds of the following formulas:

(1) $AB(SO_4, SeO_4)_2 \cdot XH_2O$, where A = K, Na, or NH_4 ; B = Al, Cr, Fe, or Co; and X = 0-12 (preferably 12).

(2) $B_2(SO_4, SeO_4)_3 \cdot XH_2O$, where B = Al, Cr, Fe, or Co.

[0021] In some embodiments, the chemical additive of formula (1) is an alum. For example, the chemical additive of formula (1) can be $KAl(SO_4)_2$. In some embodiments, the chemical additive of formula (2) is aluminum sulfate (i.e., $Al_2(SO_4)_3$).

[0022] In some embodiments, the chemical additives can be about 0.1-5 wt.% or about 0.1-4 wt.% the cementitious composition. In some embodiments, a chemical additive of formula (1) can be about at least 0.1 wt.% the cementitious composition. In some embodiments, a chemical additive of formula (2) can be about at least 0.4 wt.% the cementitious composition. In some embodiments, a chemical additive of formula (1) or (2) can be about less than 5 wt.% but more than 0.1 wt.% the cementitious composition.

[0023] In some embodiments, the chemical additives can be hydroxycarboxylic acid salts of Li, Na, and K including but not limited to glycolic, lactic, citric, mandelic tartaric, and malic acids. In some embodiments, the chemical additives can be hydroxycarboxylic acids including but not limited to glycolic, lactic, citric, mandelic, tartaric, acetic, and lactic neutralized with Li, Na, or K hydroxides or carbonates. For example, the chemical additive can be sodium lactate. The sodium lactate can be in liquid form. In some embodiments, the sodium lactate can have a 60% solids content.

[0024] In some embodiments, a hydroxycarboxylic acid salt chemical activator can be at least about 1 wt.% of the cementitious composition.

[0025] In some embodiments, the cementitious compositions disclosed herein can be substantially free from Portland cement. In some embodiments, the cementitious compositions disclosed herein can have less than about 1 wt.% Portland cement. In some embodiments, the cementitious compositions disclosed herein can have no Portland cement.

[0026] In some embodiments, stable dry powders of these chemical additives can be interblended or interground with the finely divided powders of geopolymers. The chemical additives that cannot be supplied as powders can be added as liquids to the concrete or mortar mixture containing the finely divided powders.

[0027] In some embodiments, the chemical additives can be added to the blend of dry finely divided

slag-pozzolan powders to make concrete or mortar with mixing water into a suitable mixer or can be interground in a grinding mill. When interground with the slag- pozzolan blend, the resulting powder can be used as any other cementitious powder to make concrete or mortar.

[0028] The chemical additives added to geopolymer cements can improve the rheological properties of concrete and mortars made with the cements without retarding the time of setting or strength development of concrete with which they are made.

[0029] Mortar formed from the cementitious compositions described herein can have improved flow (ASTM C 1437), working time/pot life (time interval between addition of water to the time when mortar flow is reduced to 50%), set time (ASTM C 403), and compressive strength (ASTM C 109).

[0030] In some embodiments, the flow of mortar produced using the cementitious compositions described herein can be greater than 100% as determined by test method ASTM C1437.

[0031] In some embodiments, the working time of mortar produced using the cementitious compositions described herein can be at least about 30 minutes, about 45 minutes, about 50 minutes, about 55 minutes, about 60 minutes, about 65 minutes, about 70 minutes, about 75 minutes, or about 80 minutes. In some embodiments, the working time of mortar produced using cementitious compositions described herein can be at most about 5 hours, about 4.5 hours, about 4.25 hours, about 4 hours, about 3.75 hours, about 3.5 hours, or about 3 hours. In some embodiments, the working time of mortar produced using the cementitious compositions described herein can be about 30-300 minutes, about 45-275 minutes, or about 60-240 minutes.

[0032] In some embodiments, the set time of mortar produced using the cementitious compositions described herein can be at least about 3 hours, about 3.5 hours, about 3.75 hours, about 4 hours, about 4.5 hours, about 5 hours, or about 6 hours. In some embodiments, the set time of mortar produced using the cementitious compositions described herein can be at most about 14 hours, about 13 hours, about 12.5 hours, about 12 hours, about 11 hours, about 10 hours, about 9 hours, or about 8 hours. In some embodiments, the set time of mortar produced using the cementitious compositions described herein can be about 2-15 hours, about 3-13 hours, or about 4-12 hours.

[0033] In some embodiments, the 1D compressive strength of mortar produced using the cementitious compositions described herein can be at least about 1500 psi, about 1600 psi, about 1700 psi, about 1800 psi, about 1900 psi, or about 2000 psi. In some embodiments, the 7D compressive strength of mortar produced using the cementitious compositions described herein can be at least about 3000 psi, about 3250 psi, about 3500 psi, about 3750 psi, or about 4000 psi. In

some embodiments, the 28D compressive strength of mortar produced using the cementitious compositions described herein can be at least about 4000 psi, about 4500 psi, about 4750 psi, about 5000 psi, about 5250 psi, about 5500 psi, or about 5750 psi.

[0034] Concrete formed from the cementitious compositions described herein can have improved slump (ASTM C 143), working time (time interval between addition of water to concrete to reach 2 inch slump), set time (ASTM C 403), compressive strength (ASTM C 39); flexural strength (ASTM C 78); splitting tensile strength (ASTM 496); modulus of elasticity (ASTM 469); bond strength (slant shear) (ASTM C 882); length change (ASTM C 157); and rapid chloride permeability (ASTM C 1202).

[0035] In some embodiments, the slump of concrete produced using the cementitious compositions described herein can be .0-10 inches.

[0036] In some embodiments, the working time of concrete produced using the cementitious compositions described herein can be 45-90 minutes.

[0037] In some embodiments, the set time of concrete produced using the cementitious compositions described herein can be 3-7 hours.

[0038] In some embodiments, the compressive strength of concrete produced using the cementitious compositions described herein can be 2000-8000 psi.

[0039] In some embodiments, the flexural strength of concrete produced using the cementitious compositions described herein can be 500-700 psi.

[0040] In some embodiments, the splitting tensile strength of concrete produced using the cementitious compositions described herein can be 500-700 psi.

[0041] In some embodiments, the modulus of elasticity of concrete produced using the cementitious compositions described herein can be 4-5 million psi.

[0042] In some embodiments, the bond strength of concrete produced using the cementitious compositions described herein can be . 700-800 psi.

[0043] In some embodiments, the length change of concrete produced using the cementitious compositions described herein can be 0-0.04%.

[0044] In some embodiments, the rapid chloride permeability of concrete produced using the cementitious compositions described herein can be less than 1000 coulombs.

[0045] The cements disclosed herein are alternatives to the traditional clinker based Portland cements. Given that no or minimal CO₂ is emitted during the production of the cements disclosed

herein, the adaptation of this technology can significantly reduce carbon emissions. Beyond the benefit of a zero or minimal carbon footprint, the cements disclosed herein can also enable greater beneficial use of waste materials (both slag and fly ash). Finally, due to its excellent resistance to chloride and sulfate attacks, the cements disclosed herein can have a longer life cycle than traditional Portland cements.

EXAMPLES

[0046] Mortar Examples

[0047] Cement ingredients: slag (GGBFS); ASTM Class F Fly Ash; Sodium Hydroxide; Sodium Silicate or Sodium Carbonate; and a chemical additive such as Alum ($KAl(SO_4)_2$), Aluminum Sulfate, or Sodium Lactate Liquid (60% solids content).

[0048] Mortar ingredients: 1 part cement; 2 parts ASTM C33 Sand; and water 38.5% of cement weight (i.e., water/cement = 0.385).

[0049] Mortar Test Methods: Flow Test = ASTM C 1437; Working time/Pot life time = time interval between addition of water to the time when mortar flow is reduced to 50%; Set Time = ASTM C 403; and Compressive Strength = ASTM C 109.

[0050] The following Table 1 provides the working time, set time, and compressive strength for mortar produced using alkali activators sodium hydroxide and sodium carbonate with chemical additive sodium lactate (liquid).

TABLE 1

Sodium hydroxide and Sodium Carbonate with Sodium Lactate (liquid)							
Slag (GGBFS) activation							
Example	Data	Working time, Min	Final set, Min	Compressive strength, Psi			
				24H	3D	7D	28D
Comp. Example 1	Slag/classF (87/13), Sodium Hydroxide 1%, Sodium Carbonate 9%	22 Min	7H:08M	2591	2D:4563	6784	7437
Example 1	Slag/classF (87/13), Sodium Hydroxide 1%, Sodium carbonate 9%, Sodium Lactate (Liq) 3%	70 Min	3H:05M	2859	4219	5399	7343
Example 2	Slag/F (87/13), Sodium Hydroxide 1%, Sodium Carbonate 7%, Sodium Lactate 3% (Liq)	75 Min	13H:58M	614	4669	6540	7491
Example 3	Slag/F (87/13), Sodium Hydroxide 1%, Sodium Carbonate 5%, Sodium Lactate 3% (liquid)	105Min	16H:25M	356	4474	5954	7702
Example 4	Slag/classF (87/13), Sodium Hydroxide 1%, Sodium carbonate 9%, Sodium Lactate (Liq) 1%	<30 min	5H:45M	2431	4897	6523	7235
Example 5	Slag/classF (87/13), Sodium Hydroxide 1%, Sodium carbonate 9%, Sodium Lactate (Liq) 2%	30 Min	5H:20M	2561	4419	6599	7243
Example 6	Slag/classF (87/13), Sodium Hydroxide 1%, Sodium carbonate 9%, Sodium Lactate (Liq) 4%	75 Min	3H	1520	3620	4850	7015

[0051] As shown in Table 1 above, the control Mortar mixture (comparative example 1) provides only 22 minutes of working time. In contrast, example 1 provides 70 minutes working time without affecting strength.

[0052] Table 2 provides the working time, set time, and compressive strength for mortar produced using alkali activators sodium hydroxide and sodium silicate with chemical additive sodium lactate (liquid).

TABLE 2

Sodium hydroxide and Sodium silicate with Sodium Lactate (liquid)							
Slag (GGBFS) activation							
Example	Data	Working time, Min	Final set, Min	Compressive strength, Psi			
				24H	3D	7D	28D
Comparative Example 2	Slag/classF (87/13), Sodium Hydroxide 3%, Sodium silicate 5% Control Mix (No chemical additive)	20 Min	2H:17M	3000	2D:3555	5819	7750
Example 7	Slag/classF (87/13), Sodium Hydroxide 1%, Sodium Silicate 2%, Sodium Lactate (liquid) 3%,	2H:30M	<20H	1339	4067	5602	7488
Example 8	Slag/classF (87/13), Sodium Hydroxide 1%, Sodium Silicate 3%, Sodium Lactate (liquid) 3%,	2H:30M	18H:10M	2D:2684	4356	6434	7779
Example 9	Slag/classF (87/13), Sodium Hydroxide 1%, Sodium Silicate 5% , Sodium Lactate (liquid) 3%,	1H:16M	14H:25M	2D:437	3242	6236	8733
Example 10	Slag/classF (87/13), Sodium Hydroxide 3%, Sodium Silicate 5%, Sodium Lactate (liquid) 3%,	82 min	5H:19M	2440	NA	5202	7241
Example 11	Slag/classF (87/13), Sodium Hydroxide 3%, Sodium Silicate 8% , Sodium Lactate (liquid) 3%,	80 min	8H:30M	3697	NA	7181	9855
Example 12	Slag/classF (87/13), Sodium Hydroxide 3%, Sodium Silicate 10% , Sodium Lactate (liquid) 3%,	75 min	6H:20M	3619	NA	7180	8673

[0053] As shown in Table 2 above, the control Mortar mixture (comparative example 2) provides only 20 minutes of working time. In contrast, example 10 provides 82 minutes working time without affecting strength.

[0054] Table 3 provides the working time, set time, and compressive strength for mortar produced

using alkali activators sodium hydroxide and sodium silicate with chemical additive Alum.

TABLE 3

Sodium hydroxide and Sodium Silicate with chemical additive, Alum							
Slag (GGBFS) activation, ASHVC-L Mortar formula							
Examples	Data	Working time, Min	Final set, Min	Compressive strength, Psi			
				24H	3D	7D	28D
Comparative Example 3	Slag/classF (87/13), Sodium Hydroxide 3%, Sodium silicate 5% Control Mix (No chemical additive)	20 Min	2H:17M	3000	2D:3555	5819	7750
Example 13	Slag/classF (87/13), Sodium Hydroxide 3%, Sodium Silicate 5%, No Lactate, Alum 0.25%	4H	12H:52M	2148	2D:3313	5425	7895
Example 14	Slag/classF (87/13), Sodium Hydroxide 3%, Sodium Silicate 5%, No Lactate, Alum 0.5%	6H	16H	1588	4D:4163	4813	7755
Example 15	Slag/classF (87/13), Sodium Hydroxide 3%, Sodium Silicate 5%, No Lactate, Alum 1%	>8H	20H:20M	780	4D:4885	6D:5238	8738

[0055] Table 4 provides working time, set time, and compressive strength for mortar produced using alkali activators sodium hydroxide and sodium silicate with chemical additive Aluminum Sulfate.

TABLE 4

Sodium hydroxide and Sodium Silicate with chemical additive, Aluminum Sulfate							
Slag (GGBFS) activation							
Example	Data	Working time, Min	Final set, Min	Compressive strength, Psi			
				24H	3D	7D	28D
Comparative Example 4	Slag/classF (87/13), Sodium Hydroxide 3%, Sodium silicate 5% Control Mix (No chemical additive)	20 Min	2H:17M	3000	2D:3555	5819	7750
Example 16	Slag/classF (87/13), Slag lot 020516 (Rowen/Essroc) Sodium Hydroxide 3%, Sodium Silicate 5%, Aluminum Sulfate 0.25%	1H:10M	5H:39M	2001	3083	4227	5850
Example 17	Slag/classF (87/13), Sodium Hydroxide 3%, Sodium Silicate 5%, Aluminum Sulfate 0.5%	1H:40M	7H	1858	4D:4314	4674	6383
Example 18	Slag/classF (87/13), Sodium Hydroxide 3%, Sodium Silicate 5%, Aluminum Sulfate 1%	2H:27M	10H:36M	2258	4625	5910	7530
Example 19	Slag/classF (87/13), Sodium Hydroxide 3%, Sodium Silicate 5%, Aluminum Sulfate 1.5%	>8H	26H	0	4D:5427	6646	8549

[0056] The following Table 5 provides the flow retention for various slag mortars.

TABLE 5

Slag Mortar flow % (ASTM C 1437) at different strokes and different time												
	(Comp. Example 5)				(Example 20)				(Example 21)			
	NaOH 2.75% Na Silicate 4.5%				NaOH 2.75% Na Silicate 4.6% Sodium Lactate 2.6%				NaOH 2.75% Na Silicate 4.6% Alum 0.5%			
Time	0 stroke	5 stroke	10 stroke	25 stroke	0 stroke	5 stroke	10 stroke	25 stroke	0 stroke	5 stroke	10 stroke	25 stroke
Initial	9	56	82	122	8	62	92	136	8	58	85	123
30 Min	4	12	15	32	4	20	38	70	4	32	53	96
1H	Not workable				Not workable				4	22	32	67
1H:30 M									4	20	28	50
2H									Not workable			

[0057] Additional Slag Mortar Examples:

[0058] Example 22:

GGBFS (Slag) : 78.38%

Class F fly ash : 11.72%

Sodium Hydroxide : 2.70%

Sodium Silicate : 4.5%

Sodium Lactate (liq) : 2.70%

Total Slag Cement : 100%

Slag Mortar

1 part Slag Cement + 2 part ASTM C 33 sand

Water: 38.5% of Slag cement

Results:

Working time : 82 minutes

Final Set time : 5H:19M

Compressive strength

1-day : 2440 psi

7-day : 5202 psi

28-day : 7241 psi

[0059] Example 23:

GGBFS (Slag) : 80.17%

Class F fly ash : 12%

Sodium Hydroxide : 2.76%

Sodium Silicate : 4.61%

Alum : 0.46%

Total Slag Cement : 100%

Slag Mortar

1 part Slag Cement + 2 part ASTM C 33 sand

Water : 38.5% of Slag cement

Results:

Working time : 4H

Final Set time : 9H:30M

Compressive strength

1-day : 2148 psi

7-day : 5425 psi

28-day : 7895 psi

[0060] Example 24:

GGBFS (Slag) : 79.81%

Class F fly ash : 11.93%

Sodium Hydroxide : 2.75%

Sodium Silicate : 4.59%

Aluminum Sulfate : 0.92%

Total Slag Cement : 100%

Slag Mortar

1 part Slag Cement + 2 part ASTM C 33 sand

Water : 38.5% of Slag cement

Results:

Working time : 2H:27M

Final Set time : 10H:36M

Compressive strength

1-day : 2258 psi

7-day : 5910 psi

28-day : 7510 psi

[0061] From the various Slag Mortar Examples above, Figures 1-3 were produced to illustrate the preferred amount of sodium lactate, alum, and aluminum sulfate in the cementitious composition with respect to working time, set time, and 1D compressive strength.

[0062] Concrete Examples:

[0063] Cement ingredients: slag (GGBFS); ASTM Class F Fly Ash; Sodium Hydroxide; Sodium Silicate or Sodium Carbonate; and a chemical additive such as Alum ($KAl(SO_4)_2$), Aluminum Sulfate, or Sodium Lactate Liquid (60% solids content).

[0064] Concrete mix proportions were prepared as per the guideline of ACI 211. The following Table 6 provides various concrete mix proportions and properties.

TABLE 6

Concrete Mix Proportion			
	Specific gravity	lb/cy	kg/m3
Cement	2.85	750	445
Fine agg, ASTM C 33	2.63	1220	724
Coarse agg. ASTM #57, Lime stone	2.72	1685	999.7
Water	1	258	153

[0065] Concrete Test Methods: Slump = ASTM C 143; Working time = time interval between addition of water to concrete reach 2 inch slump; Time of Set = ASTM C 403; Compressive Strength = ASTM C 39; Flexural Strength = ASTM C 78; Splitting Tensile Strength = ASTM 496; Modulus of Elasticity = ASTM 469; Bond Strength (slant shear) = ASTM C 882; Length Change = ASTM C 157; Rapid Chloride Permeability = ASTM C 1202.

[0066] The following Table 7 provides the slump retention of slag concrete created with the chemical additives disclosed herein.

TABLE 7

Concrete Slump Retention							
All mixes:75:25slag:flyash 750 lb/yd3	Initial slump. Inch	Slump at 30 Min, inch	Slump at 1H, Inch	Slump at 1.5H, Inch	Slump at 2H, Inch	Slump at 3H, Inch	Time to retain 2" slump
Sodium hydroxide:Sodium Silicate 2.5:4.6	6.5	1.5	1				Less than 30 Min
Sodium hydroxide:Sodium Silicate 2.5:4.6 Sodium Lactate 2.6	8.25	6	5	2.75	2		2H
Sodium hydroxide:Sodium Silicate 2.5:4.6 Alum 0.5%	4.5	4	4	4	4	3	Greater than 3H
Sodium hydroxide:Sodium Silicate2.5:4.6 Aluminum sulfate 0.5%	5	5	4	4	4	3	Greater than 3H

[0067] Table 7 indicates that workability retention of concretes made with the cementitious

compositions described herein is more than 3 hours at 73°F. The control alkali activated slag cement concrete loses workability in less than 30 minutes.

[0068] Portland cement can be tested with ASTM C 150, “Standard Specification for Portland Cement”. All other non-Portland cements can be tested with a performance based specification ASTM C 1157. The following Table 8 provides results of slag cement with alum as the chemical additive. The Example 25 tested in Table 8 has the following weight percentages: GGBFS (slag) = 69.13%; Class F fly ash = 23.04 %; Sodium Hydroxide = 2.77%; Sodium Silicate = 4.6%; Alum = 0.46%.

TABLE 8

Property	Method	Slag Cement Data					Example 25
		General Use specification	High Early strength Specification	Moderate Sulfate Resistance Specification	High Sulfate Resistance Specification		
Flow	ASTM C1437	110 +/- 5 %	110 +/- 5 %	110 +/- 5 %	110 +/- 5 %		110%
Vicat Set Time, min	ASTM C191	45 -- 420	45 -- 420	45 -- 420	45 -- 420		180
1-day compression, psi	ASTM C109	N/A	1450 - 2900	NA	NA		1688
3 - day compression, psi	ASTM C109	1450 -- 2900	2465 -- 4350	1450 -- 2900	725- 2175		2470
7 - day compression, psi	ASTM C109	2465 -- 4350	N/A	2465 -- 4350	1450- 2900		2654
28-day compressive strength	ASTM C109	NA	NA	NA	2465-4350		3464
Mortar Bar Expansion	ASTM C1038	Max 0.02% @ 14 days	Max 0.02% @ 14 days	Max 0.02% @ 14 days	Max 0.02% @ 14 days		0.007%
Air Content of Mortar	ASTM C185	Report value	Report value	Report value	Report value		5%
Fineness: Residue on 325 mesh	ASTM C430	Report value	Report value	Report value	Report value		15%
Fineness: Blaine	ASTM C204	Report value	Report value	Report value	Report value		3500 cm ² /g
Autoclave Expansion	ASTM C151	0.8% max	0.8% max	0.8% max	0.8% max		(-)0.065%
Sulfate expansion (Sulfate resistance), %	ASTM C 1012	NA	NA	Max 0.1%	Max 0.05%		0.02%
6 Months							
1 year				NA	Max 0.1%		0.03%

[0069] As indicated in the above Table 8, the cement of Example 25 meets and exceeds the ASTM C 1157 standard (a performance based specification of hydraulic cement) for all four categories: (1) general use; (2) high early strength; (3) moderate sulfate resistance; and (4) high sulfate resistance.

[0070] Additional Slag Concrete Examples:

[0071] Example 26:

GGBFS(Slag) :69.13%

Class F fly ash	: 22.05%
Sodium Hydroxide	: 2.76%
Sodium Silicate	: 4.6%
Alum	: 0.46%
Total Slag Cement	: 100%

Concrete Mix proportion

Slag Cement	: 750 lb/Y ³ (445 kg/m ³)
Fine aggregate	: 1120 lb/Y ³ (724 kg/m ³)
Coarse Aggregate	: 1685 lb/Y ³ (100 kg/m ³)
Water	: 31.1 gallon/Y ³ (153 lit/m ³)

Results:

Slump	: 5 inches
Working time	: 90 min
Initial set time	: 3H:0M
Final set time	: 7H:50M
Compressive strength (ASTM C 39)	
1-day	: 2227 psi
7-day	: 4217 psi
28-day	: 5643 psi

Flexural Strength (ASTM C-78)

7-day	: 610 psi
28-day	: 661 psi

Splitting Tensile (ASTM C 496)

7-day	: 483 psi
28-day	: 604 psi

Modulus of Elasticity (ASTM C 469)

7-day	: 4.54 millions psi
28-day	: 4.63 millions psi

Bond Strength (Slat shear) (ASTM C

882) 7-day	: 773 psi
28-day	: 797 psi

Length Change (ASTM C 157)

7-day	: -0.034%
28-day	: -0.041%

Rapid Chloride Permeability (ASTM C 1202): 549 Coulombs

[0072] This application discloses several numerical ranges in the text and figures. The numerical ranges disclosed inherently support any range or value within the disclosed numerical ranges, including the endpoints, even though a precise range limitation is not stated verbatim in the specification because this disclosure can be practiced throughout the disclosed numerical ranges.

[0073] The above description is presented to enable a person skilled in the art to make and use the disclosure, and is provided in the context of a particular application and its requirements. Various modifications to the preferred embodiments will be readily apparent to those skilled in the art, and the generic principles defined herein may be applied to other embodiments and applications without departing from the spirit and scope of the disclosure. Thus, this disclosure is not intended to be limited to the embodiments shown, but is to be accorded the widest scope consistent with the principles and features disclosed herein. Finally, the entire disclosure of the patents and publications referred in this application are hereby incorporated herein by reference.

Claims

1. A cementitious composition comprising:
 - a slag;
 - a pozzolanic material;
 - an alkali activator comprising at least one of sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium silicate, or potassium silicate;
 - and
 - a sulfate or selenate compound of the formulas:
 - (1) $AB(SO_4, SeO_4)_2 \cdot XH_2O$, where $A = K, Na, \text{ or } NH_4$; $B = Al, Cr, Fe, \text{ or } Co$; and $X = 0-12$; or
 - (2) $B_2(SO_4, SeO_4)_3 \cdot XH_2O$, where $B = Al, Cr, Fe, \text{ or } Co$ and $X = 0-12$.
2. The cementitious composition of claim 1, wherein $A = K$, $B = Al$, and $X = 12$.
3. The cementitious composition of claim 1 wherein $B = Al$.
4. The cementitious composition of claim 1, wherein the sulfate or selenate compound is $KAl((SO_4)_2 \cdot XH_2O)$.
5. The cementitious composition of claim 4, wherein the weight percentage of $KAl((SO_4)_2 \cdot 12H_2O)$ in the cementitious composition is 0.1-10 wt.%.
6. The cementitious composition of claim 1, wherein the sulfate or selenate compound is $Al_2(SO_4)_3$.
7. The cementitious composition of claim 6, wherein the weight percentage of $Al_2(SO_4)_3$ in the cementitious composition is 0.1-10 wt.%.
8. The cementitious composition of claim 1, wherein the slag is a ground granulated blast furnace slag.
9. The cementitious composition of any of claims 1-8, wherein the pozzolanic material is selected from the group consisting of class F fly ash, metallurgical slag, silica fume, natural pozzolans, glass calcined clay and mixtures thereof.

10. The cementitious composition of claim 1, wherein the weight ratio of slag to pozzolanic material in the cementitious composition is 100/0-90/10 and 50/50-0/100.
11. The cementitious composition of claim 1, wherein the alkali activator comprises sodium hydroxide and sodium silicate or sodium carbonate.
12. The cementitious composition of claim 11, wherein the sodium hydroxide is 1-5 wt.% the cementitious composition and the sodium silicate or sodium carbonate is 1-9 wt.% the cementitious composition.
13. A mortar produced using the cementitious composition of claim 1.
14. The mortar of claim 13, wherein the working time of the mortar is 60-240 minutes.
15. The mortar of claim 13, wherein the set time is 4-12 hours.
16. The mortar of claim 13, wherein the 1D compressive strength is greater than 1500 psi, the 7D compressive strength is greater than 3000 psi, and the 28D compressive strength is greater than 4000 psi.
17. A concrete produced using the cementitious composition of claims 1.
18. A cementitious composition comprising:
 - slag;
 - pozzolanic material;
 - an alkali activator comprising at least one of sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium silicate, or potassium silicate;
 - and
 - a hydroxycarboxylic acid salt of Li, Na, or K including glycolic, lactic, citric, mandelic, tartaric, or malic acids.
19. The cementitious composition of claim 18, wherein the hydroxycarboxylic acid salt is sodium lactate liquid with 60% solid content.
20. The cementitious composition of claim 19, wherein the weight percentage of sodium lactate in the cementitious composition is 2-4 wt.%.

21. The cementitious composition of claim 18, wherein the slag is a ground granulated blast furnace slag.
22. The cementitious composition of claims 18, wherein the pozzolanic material is class F fly ash.
23. The cementitious composition of claim 18, wherein the weight ratio of slag to pozzolanic material in the cementitious composition is 100/0-90/10 and 50/50-0/100.
24. The cementitious composition of claim 19, wherein the alkali activator comprises sodium hydroxide and sodium silicate or sodium carbonate.
25. The cementitious composition of claim 24, wherein the sodium hydroxide is 1-5 wt.% the cementitious composition and the sodium silicate or sodium carbonate is 1-9 wt.% the cementitious composition.
26. A mortar produced using the cementitious composition of claim 18.
27. The mortar of claim 26, wherein the working time of the mortar is 60-240 minutes.
28. The mortar of claim 26, wherein the set time is 4-12 hours.
29. The mortar of claim 26, wherein the 1D compressive strength is greater than 1500 psi, the 7D compressive strength is greater than 3000 psi, and the 28D compressive strength is greater than 4000 psi.
30. A concrete produced using the cementitious composition of claim 18.