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(54) Title: CALCIUM SULFOALUMINATE COMPOSITE BINDERS

(57) Abstract: The present invention relates to composite binders containing calcium sulfoaluminate cement and supplementary cementitious material, wherein a weight ratio of calcium sulfate to the sum of ye'elimite, aluminates and ferrites ($R_{\$/(Y+A+F)}$) ranges from 0.5 to 0.85, to a method of manufacturing them comprising the steps: a) providing at least one calcium sulfoaluminate cement b) providing at least one supplementary cementitious material c) mixing 10 to 90 % by weight calcium sulfoaluminate cement(s) with 10 to 90 % by weight supplementary cementitious material(s), and to their use for making hydraulically setting building materials and special construction chemical compositions.

Calcium sulfoaluminate composite binders

[0001] The present invention relates to binders comprising calcium sulfo-aluminate based cement / clinker types and supplementary cementitious materials, a method of manufacturing composite binders and to their use for making hydraulically setting building materials or special construction chemical compositions.

[0002] Calcium sulfoaluminate (CSA) cements are made from clinkers that include ye'elimite ($Ca_4(AlO_2)_6SO_4$ or $C_4A_3\$$ in cement chemist's notation) as a major phase. These binders are used as constituents in expansive cements, in ultra-high early strength cements and in "low-energy" cements. Hydration of CSA cements leads to the formation of mainly ettringite and/or monophases as e.g. monosulfate. Aluminium hydroxide may probably be another hydration product of this binder. The amount and kinetics of formation strongly depend on the cement composition as e.g. the amount and type of sulfate bearing phases being present. Special physical properties (such as intentional expansive behaviour or rapid reaction) are obtained by the adjustment of the availability of calcium and sulfate ions. The use of CSA cement as a low-energy alternative to Portland cement has been pioneered in China, where several million tons per year are produced. The energy demand for production is lower because of the decreased kiln temperatures required for reactions, the better grindability and the lower amount of limestone in the raw mix, which needs to be endothermically decarbonated. In addition, the lower limestone content and lower fuel consumption leads to a CO_2 emission around half of that of Portland cement clinker.

[0003] Within the context of the present invention, clinker shall mean a sinter product which is obtained by burning a raw material mixture at an elevated temperature and which contains at least one hydraulically reactive phase. Cement denotes a clinker that is ground with or without adding further components. Binder or binder mixture denotes a mixture hardening hydraulically and comprising cement and typically, but not necessarily, additional finely ground components, and which is used after adding water, optionally admixtures and/or additives and aggregate. A clinker may already contain all the necessary or desired phases and be used directly as a binder after being ground to cement.

[0004] Another approach to save energy and valuable raw materials is the application of secondary raw materials or industrial by-products as raw meal components to replace primary mineral based raw materials during clinker production.

[0005] In a further approach supplementary cementitious materials, which are often industrial by-products or wastes, are used to replace parts of the clinker during cement production and therefore save energy and primary raw material sources. These materials most often possess a pozzolanic or latent hydraulic reactivity and contribute to the mechanical performance of these composite binders.

[0006] Constituents that are permitted in Portland-composite cements are artificial pozzolans (like e.g. blastfurnace slag, silica fume, synthetic glasses and fly ashes) or natural pozzolans (like e.g. siliceous or siliceous aluminous materials such as volcanic ash glasses, calcined clays and shale). Portland blastfurnace cement contains up to 70% ground granulated blast furnace slag, the rest being Portland clinker and a little sulfate as e.g. gypsum. These composite cements typically produce high ultimate strength, but as slag content is increased, early strength is reduced, while potentially sulfate resistance increases and heat evolution diminishes. Portland fly ash cement contains up to 35% fly ash. The fly ash possesses a pozzolanic behaviour, so that ultimate strength is maintained or even increased. Because fly ash addition allows a lower water to binder ratio and as a result thereof a lower total water content, early strength can also be maintained.

[0007] Supplementary cementitious materials can be divided into latent hydraulic materials and pozzolans. Latent hydraulic materials are not hydraulic on their own or react only very slowly. They need an activation to undergo hydraulic reaction within useful time periods. Activation is typically achieved by (addition of) earth alkali metal or alkali metal compounds (e.g. $Ca(OH)_2$, NaOH, KOH, etc.) or sulfate providing materials ($CaSO_4$, Na_2SO_4, K_2SO_4, etc.), which are able to support the formation of calcium (aluminium) silicate hydrates and/or ettringite and/or others like e.g. AF_m-phases (strätlingite, monosulfate, monocarbonate hemicarbonate etc.) or zeolite-like mineral. Pozzolans are siliceous or alumino-siliceous materials that react with calcium hydroxide from other components of a binder to form calcium silicate hydrates. The foregoing distinction is not always applied strictly, i.e. many fly ashes contain considerable amounts of calcium and are latent hydraulic materials, therefore, but usually they are designated pozzolans, nonetheless. For the present invention the distinction is not important and both are summarized as supplementary cementitious materials, partly abbreviated SCM herein.

[0008] Typical supplementary cementitious materials are natural or artificial pozzolans and latent hydraulic materials, e.g. but not exclusively ground granulated blast furnace slag, and natural or artificial pozzolans, e.g. but not exclusively type-C and/or type-F fly ashes, calcined clays or shales, trass, brick-dust, artificial glasses, silica fume, and burned organic matter residues rich in silica such as rice husk ash or mixtures thereof.

[0009] A problem of portland cement and portland-composite cements is the increasing demand of high early strength. Time granted for construction is continuously decreasing. In the manufacturing of building elements a fast form removal is desired to optimize investment return. Therefore, binders providing high early strength are required, of course without decreasing ultimate strength, durability or workability. There further remains the object to provide cements that have a minimal environmental impact with regard to energy and natural raw materials.

[00010] There have been some proposals to add SCM to calcium sulfoaluminate cements.

[00011] According to GB 2490010 describes cementitious compositions containing (a) 60-94% of at least one pozzolanic material; (b) at least 0.5% calcium sulfoaluminate; (c) 1.2-11%, expressed as SO_3, of at least one inorganic sulfate; and (d) a total sulfate content, expressed as SO_3, of at least 3 %, wherein the cementitious composition includes, at most 3% natural lime, and at most 10% alumina cement. Strength development of this system is mainly based on ettringite, it is a so called super sulfated system with a ratio of calcium sulfate to ye'elimite + aluminates + ferrites of more than 1, the CSA and at least one source of CaO / $Ca(OH)_2$, originating from the addition of e.g. CaO or OPC, is used as activator for early strength.

[00012] In Zivica V., "Possibility of the modification of the properties of sulfo-aluminate belite cement by its blending", Ceramics - Silikaty 45 (1), 24-30, (2001) the addition of 5 %, 15 % and 30 % SCM to a CSA cement containing about 53 % C_2S, 34 % $C_4A_3\$$, 8 % C_4AF and 5 % C$ is studied. From the explanations it is apparent that overburned or "dead burned" anhydrite is part of the clinker and that the SCMs are mostly performing as inactive fillers. Consequently, the article suggests that SCM contents below 15 % are optimal. A significant energy saving seems not possible therewith.

[00013] In Quillin K., BRE "Low-CO_2 Cements based on Calcium Sulfoaluminate" (http://www.soci.org/News/~/media/Files/Conference%20Downloads/Low%20Carbon%20Cements%20Nov%2010/Sulphoaluminate_Cements_Keith_Quillin_R.ashx, status June 2013), the impact of adding 30 or 50 % ground granulated blast furnace slag or 30 % fly ash as well as the impact of sulfate

content to a CSA cement containing about 22 % C_2S, 60 % $C_4A_3\$$, 7 % C_4AF, 8 % C_3S and 5 % C_3A is studied. The ratio of calcium sulfate to the sum of $C_4A_3\$$, aluminates and ferrites is adjusted to 0, 0.35, 0.93 or above 1.

[00014] Surprisingly it was now found that composite binders comprising calcium sulfoaluminate cement and supplementary cementitious materials with a weight ratio $R_{\$/(Y+A+F)}$ of calcium sulfate to the sum of ye'elimite, aluminates and ferrites in the range from 0.5 to 0.85 provide good early and ultimate strength, while further diminishing the environmental impact compared to binders based on calcium sulfoaluminate cements without addition of SCMs. $R_{\$/(Y+A+F)}$ especially stands for $CaSO_4$ / (Σ ye'elimite + Σ aluminates + Σ ferrites), wherein

- $CaSO_4$ represents the quantity of anhydrous calcium sulfate originating from $CaSO_4$, $CaSO_4 \cdot 0.5H_2O$, or $CaSO_4 \cdot 2H_2O$ present in the binder
- Ye'elimite represents $C_4A_{3-x}F_x\$$ with x ranging from 0 to 2, $C_4A_3\$$ with other substitutions with one or more foreign ions, or mixtures thereof
- ∑ Aluminates represents the sum of all phases based on calcium aluminates, preferably it means CA, $C_{12}A_7$, CA_2, C_3A, amorphous aluminate phases and mixtures thereof
- ∑ Ferrites represents the sum of all phases based on calcium oxide and iron oxide, preferably it means $C_2A_yF_{1-y}$, with y ranging from 0.2 to 0.8, C_2F, CF, CF_2, amorphous ferritic phases and mixtures thereof.

Phases such as $C_4A_{3-x}F_x\$$, $C_2A_yF_{1-y}$, CA, $C_{12}A_7$, CA_2, C_3A, C_2F, CF, CF_2 etc. can be crystalline, partly crystalline or amorphous. The phases mentioned could and typically do contain substitutions with foreign ions (or other/additional foreign ions than those stated explicitly), as is common with technical materials. In the case of phases containing C, A and F it does not matter whether they are considered as aluminates or as ferrites, as long as they are included and not calculated twice.

[00015] Calcium sulfate can also be present within the supplementary cementitious materials or in the CSA clinker. This calcium sulfate also has to be

taken into account for the calculation of $R_{\$/(Y+A+F)}$. Amorphous aluminate or ferritic phases are special forms of e.g., but not exclusively, $C_{12}A_7$, CA, C_4AF, CF. Aluminates and/or ferrites introduced by the addition of further components like calcium aluminate or Portland cements to the binder have to be considered as well for the calculation of $R_{\$/(Y+A+F)}$.

[00016] The present invention solves the above mentioned problems with a composite binder comprising calcium sulfoaluminate cement and supplementary cementitious materials with a weight ratio of sulfate to the sum of ye'elimite, aluminates and ferrites in the range from 0.5 to 0.85, wherein preferably
- calcium sulfate means the quantity of anhydrous calcium sulfate originating from $CaSO_4$, $CaSO_4 \cdot 0.5\ H_2O$, and $CaSO_4 \cdot 2\ H_2O$ present in the binder,
- ye'elimite means the content of $C_4A_{3-x}F_x\$$, with x ranging from 0 to 2, $C_4A_3\$$ with other substitutions with one or more foreign ions, or mixtures thereof
- aluminates stands for the content of e.g., but not exclusively, CA, $C_{12}A_7$, CA_2, C_3A, amorphous aluminate phases or mixtures thereof, and
- ferrites stands for the content of e.g., but not exclusively, $C_2A_yF_{1-y}$, with y ranging from 0.2 to 0.8, C_2F, CF, CF_2, amorphous ferritic phases or mixtures thereof
and their use to make hydraulically setting building materials or special construction chemical compositions. It further meets the object with a method of manufacturing a composite binder comprising the steps:
a) providing at least one calcium sulfoaluminate cement
c) providing at least one supplementary cementitious material
d) mixing 10 to 80 % by weight calcium sulfoaluminate cement(s) with 20 to 90 % by weight supplementary cementitious material(s), wherein the weight ratio $R_{\$/(Y+A+F)}$ of sulfate to the sum of ye'elimite, aluminates and ferrites ranges from 0.5 to 0.85.

[00017] To simplify the description, the following abbreviations, which are common in the cement industry, are used: H – H_2O, C – CaO, A – Al_2O_3,

F – Fe_2O_3, M – MgO, S – SiO_2 und \$ – SO_3. Additionally, compounds are generally indicated in the pure forms thereof, without explicitly stating series of solid solutions/substitution by foreign ions and the like, as are customary in technical and industrial materials. As any person skilled in the art will understand, the composition of the phases mentioned by name in the present invention may vary, depending on the chemism of the raw meal and the type of production, due to the substitution with various foreign ions, such compounds likewise being covered by the scope of the present invention.

[00018] The supplementary cementitious materials can be chosen from all available materials showing latent hydraulic and/or pozzolanic properties. Preferred are ground granulated blast furnace slag, fly ashes type C and F and natural pozzolans, calcined clays or shales, trass, artificial glasses, other slags than ground granulated blast furnace slag, brick-dust and burned organic matter residues rich in silica such as rice husk ash. Especially preferred are calcium-rich artificial glasses, type C fly ashes and ground granulated blast furnace slags.

[00019] Calcium sulfoaluminate clinkers contain mainly polymorphs of ye'elimite. Depending on the raw materials used and the burning temperature they typically also contain belite, ferrites and/or aluminates, anhydrite and may further contain ternesite, see e.g. WO 2013/023728 A2. Calcium sulfoaluminate cements are obtained from CSA clinkers by grinding, usually calcium sulfate is added. Manufacturing of the calcium sulfoaluminate cements takes place in a manner known per se. Typically raw materials are mixed in appropriate amounts, ground and burnt in a kiln to give a clinker. Usually, the clinker is then ground together with calcium sulfate and optionally some or all of the other components to give the cement. A separate grinding is also possible and may be advantageous when the grindability of the components is largely different. The calcium sulfate can be gypsum, bassanite, anhydrite or mixtures thereof. Anhydrite is preferably used.

[00020] A calcium sulfoaluminate cement can be obtained by grinding a CSA clinker when that already contains the desired amount of calcium sulfate. Typically, it is obtained by combining CSA clinker with adequate amounts of calcium sulfate. This means that as defined for the present invention the component CSA cement provides ye'elimite and sulfate, as well as optionally aluminates, ferrites, belite and other components, regardless of whether they originate from the CSA clinker or from a mixing of CSA clinker with them, either before, during or after grinding of the CSA clinker. Of course, sulfate, ye'elimite, aluminates, and ferrites can also originate from the SCM component or the optional additional components of the composite binder, so that less is desired in the CSA cement. This means that for manufacturing the binder the sulfate (and also any other phase) can originate from the CSA clinker, the CSA cement, the SCM and even from additional components. With respect to the the sulfate it does not matter whether it is added to the CSA clinker before mixing with the SCM or during mixing, i.e. the CSA cement can be added as one component or as two components, namely ground CSA clinker and ground sulfate.

[00021] Calcium sulfoaluminate clinkers and cements containing $C_4A_3\$$ as a main phase are known and available in different qualitites / compositions. For the present invention all are suitable. For example, the following CSA cements are (commercially) available / known:

Lafarge BCSAF:

Belite (α; +/-β) C_2S	40 – 75%;	Ye'elimite $C_4A_3\$$	15 – 35%;
Ferrite $C_2(A,F)$	5 – 25%;	Minor phases	0.1 – 10%

Lafarge Rockfast®:

Belite (α; +/-β) C_2S	0 – 10%;	Ye'elimite $C_4A_3\$$	50 – 65%
Aluminate CA	10 – 25%;	Gehlenite C_2AS	10 – 25%;
Ferrite $C_2(A,F)$	0 – 10%;	Minor phases	0 – 10%

Italcementi Alipre®:

Belite (α; +/-β) C_2S	10 – 25%;	Ye'elimite $C_4A_3\$$	50 – 65%;
Anhydrite $C\$$	0 – 25%;	Minor phases	1 – 20%

Cemex CSA:

Belite (α; +/-β) C_2S	10 – 30%;	Ye'elimite $C_4A_3\$$	20 – 40%
Anhydrite $C\$$	>1%;	Alite C_3S	>1 – 30%;
Free lime CaO	<0.5 – 6%;	Portlandite $Ca(OH)_2$	0 – 7%;
Minor phases	0 – 10%		

Denka® CSA

Belite (α; +/-β) C_2S	0 – 10%;	Ye'elimite $C_4A_3\$$	15 – 25%;
Anhydrite $C_2(A,F)$	30 – 40%;	Portlandite $Ca(OH)_2$	20 – 35%;
Free lime CaO	1 – 10%;	Minor phases	0 – 10%

China Type II & III CSA

Belite (α; +/-β) C_2S	10 – 25%;	Ye'elimite $C_4A_3\$$	60 – 70%;
Ferrite $C_2(A,F)$	1 – 15%;	Minor phases	1 – 15%

Barnstone CSA

Belite (α; +/-β) C_2S	22%;	Ye'elimite $C_4A_3\$$	60%;
Aluminate $C_{12}A_7$	5%;	Alite C_3S	8%;
Ferrite $C_2(A,F)$	4%;	Minor phases	1%

HeidelbergCement BCT

Belite (α; +/-β) C_2S	1 – 80%;	Ye'elimite $\Sigma C_4A_3\$$	5 -70%;
Ternesite $C_5S_2\$$		5 – 75%; Minor phases 0 – 30%;	

[00022] The calcium sulfoaluminate clinker or cement usually comprises 10 - 100 % by weight, preferably 20 – 80 % by weight and most preferred 25 to 50 % by weight $C_4A_{3-x}F_x\$$, with x ranging from 0 to 2, preferably from 0.05 to 1 and most preferably from 0.1 to 0.6. It typically further comprises 0 - 70 % by weight, preferably 10 to 60 % by weight and most preferred 20 to 50 % by weight C_2S, 0 - 30 % by weight, preferably 1 to 15 % by weight and most preferred 3 to 10 % by weight aluminates, 0 - 30 % by weight, preferably 3 to 25 % by weight and most

preferred 5 to 15 % by weight ferrites, 0 – 30 % by weight preferably 3 to 25 % by weight and most preferred 5 to 15 % by weight ternesite, 0 - 30 % by weight, preferably 5 to 25 % by weight and most preferred 8 to 20 % by weight calcium sulfate and up to 20 % minor phases. As indicated, phases can be present in the CSA clinker or added for obtaining the CSA cement.

[00023] The invention is beneficial to all kinds of calcium sulfoaluminate cements both belite rich and poor ones as well as with differing amounts of aluminates and ferrites as long as the weight ratio $R_{\$/(Y+A+F)}$ in the composite binder is maintained in the range from 0.5 to 0.85. With a ratio below 0.5 only minor or even no contribution of the cementitious material is observed as regards strength development. With a ratio above 0.9 an expansion accompanied by the formation of fine to even large cracks has been observed already after 24 hours of hydration of mortar prisms made with the composite cements. Higher levels of sulfate addition lead to even more pronounced expansion and cracking. Preferably, the weight ratio according to the invention is set from 0.55 to 0.85, especially preferred from 0.6 to 0.85. Within the ranges a higher ratio leads to a higher increase of strength within shorter times, i.e. a higher ratio accelerates the strength development. Any sulfate, aluminate, ferrite or ye'elimite from the supplementary cementitious materials and other components is taken into account when calculating the ratio.

[00024] The supplementary cementitious materials can be added according to the invention in amounts of at least 10 % and up to 90 % by weight, preferably 20 to 80 % by weight are added. The quantity of latent hydraulic materials in the SCM usually ranges from 0 to 100 % by weight, preferably from 20 to 80 % by weight and most preferably from 30 to 70 % by weight of the of the total amount of SCM. The content of pozzolanic materials ranges from 0 to 40 % by weight, preferably from 5 to 35 % by weight and most preferably from 10 to 30 % by weight of the total amount of supplementary cementitious materials.

[00025] The preferred amount of SCM in the binder depends on the reactivity of the SCM. If the SCM is only or mainly latent hydraulic materials the preferred amount of addition ranges from 10 to 90 % by weight, most preferred 30 to 60 % by weight. When only or mainly pozzolanic materials are used, the SCM is preferably added in an amount of 10 to 40 % by weight, most preferred 20 to 30 % by weight. The preferred amounts of SCMs that are mixtures of latent hydraulic and pozzolanic materials depends on the reactivity of the SCM mixture used. Namely, more reactive SCM mixtures are preferably used in higher amounts than those with a low, mainly pozzolanic reactivity.

[00026] In a further embodiment of the invention the calcium sulfoaluminate cement or binder therefrom has a fineness, according to the particle size distribution determined by laser granulometry, with a $d_{90} \leq 90$ µm, preferably a $d_{90} \leq 60$ µm and most preferred a $d_{90} \leq 40$ µm, whereby the Rosin Rammler Parameter (slope) n can vary from 0.7 to 1.5, preferably from 0.8 to 1.3 and most preferably from 0.9 to 1.15.

[00027] The cement according to the invention is obtained by grinding the clinker, with or without addition of further substances. Usually, calcium sulfate is added before or during grinding when its content in the clinker is not as desired. It can also be added after grinding.

[00028] Further components chosen from e.g. but not exclusively calcium aluminate cements, portland cement or portland cement clinker, lime stone, dolomite, ternesite, alkali and/or earth alkali salts can be added in amounts of 0.01 to 20 % by weight, preferably in amounts ranging from 0.5 to 15 % by weight. It is especially preferred when a content of portland cement clinker, limestone, ternesite and/or dolomite ranges from 0.01 to 20 % by weight, preferably from 3 to 20 % by weight and most preferred from 5 to 15 % by weight and a content of alkali salts and earth alkali salts ranges from 0 % to 5 % by weight, preferable from 0.1 to 3 % by weight and most preferred from 0.5 to 2 % by weight.

[00029] Furthermore, common admixtures and/or additives can be present. Admixtures are preferably added in an amount of up to 20 % by weight, additives in an amount of up to 3 % by weight. Naturally, the amounts of all components of one specific mixture add up to 100 %.

[00030] Admixtures are usually added to concrete, mortar etc. made of a binder, but can also be added to the binder. Typical admixtures are:

- Accelerators, which speed up the hydration (hardening), like CaO, $Ca(OH)_2$, $CaCl_2$, $Ca(NO_3)_2$, $Al_2(SO_4)_3$, KOH, K_2SO_4, K_2CO_3, NaOH, Na_2SO_4, Na_2CO_3, $NaNO_3$, LiOH, LiCl, Li_2CO_3, $MgCl_2$, $MgSO_4$.
- Retarders that slow the hydration. Typical polyol retarders are sugar, sucrose, sodium gluconate, glucose, citric acid, and tartaric acid.
- Air entrainments which add and entrain air bubbles, which reduces damage during freeze-thaw cycles, increasing durability.
- Plasticizers that increase the workability of plastic or "fresh" concrete, allowing it be placed more easily, with less consolidating effort. A typical plasticizer is lignosulfonate. Plasticizers can be used to reduce the water content of a concrete while maintaining workability and are sometimes called water-reducers due to this use. Such treatment improves its strength and durability characteristics.
- Superplasticizers (also called high-range water-reducers) that are a class of plasticizers that have fewer deleterious effects and can be used to increase workability more than is practical with traditional plasticizers. Compounds used as superplasticizers include sulfonated naphthalene formaldehyde condensate, sulfonated melamine formaldehyde condensate, acetone formaldehyde condensate and polycarboxylate ethers.
- Pigments can be used to change the color of concrete, for aesthetics.
- Corrosion inhibitors are used to minimize the corrosion of steel and steel bars in concrete.
- Bonding agents are used to create a bond between old and new concrete (typically a type of polymer).

- Pumping aids improve pumpability, thicken the paste and reduce separation and bleeding.

Preferably, (super)plasticizers and/or retarders are comprised. Typically, (super)plasticizers and/or retarders are added in the commonly known amounts, e.g. 0.05 to 1 % by weight, preferably 0.05 to 0.5 % by weight, relative to the sum of CSA cement, SCM and, if applicable, any additional hydraulic components added.

[00031] Typical additives are for example but not exclusively fillers, fibres, fabrics / textiles, silica fume and crushed or ground glass. Fillers are e.g. quartz, limestone, dolomite, inert and/or crystalline fly ashes. Fibres are e.g. steel fibres, glass fibres or plastic fibres.

[00032] The method according to the invention can be carried out with devices known per se. The CSA cement can be mixed with SCM and further components, if applicable, directly after production. Alternatively, the components can be stored prior to mixing. The binder can be stored and transported as known, e.g. packaged into a cement silo or into cement bags or delivered as ready mix concrete after adding aggregate, water and any other desired addition, possibly after having been stored for some time.

[00033] As mentioned before, the method is described as mixing CSA cement and SCM, which shall include a situation where a ground CSA clinker with little or even no sulfate is used and sulfate is admixed as separate component together with eventual additional components to provide the binder. With other words, CSA cement includes a single component comprising at least ground ye'elimite and sulfate as well as the separate components sulfate and ground CSA clinker with no or too little sulfate.

[00034] It would even be possible to mix CSA clinker and unground SCM and perfom the grinding on the mixture, but that is not preferred. The grindability usually differs. A separate grinding also provides more flexibility.

[00035] The binder according to the invention can be used to make concrete, mortar, plaster and other hydraulically setting building materials. It is also useful for manufacturing special construction chemical compositions like tile adhesives, floor screeds, etc. The use can take place in the same manner as that of known binders or cements. The binder is specifically suitable for applications that benefit from a lowered heat of hydration, i.e. especially for massive structures like dams. It is also very useful for ready mix concrete for all purposes.

[00036] The binder according to the invention provides significant further energy saving compared to binders based only on CSA cement. It shows an enhanced strength development compared to the binders comprising CSA and SCM known from the prior art.

[00037] The invention will be illustrated further with reference to the examples that follow, without restricting the scope to the specific embodiments described. If not otherwise specified any amount in % or parts is by weight and in the case of doubt referring to the total weight of the composition/mixture concerned.

[00038] The invention further includes all combinations of described and especially of preferred features that do not exclude each other. A characterization as "approximately", "around" and similar expression in relation to a numerical value means that up to 10 % higher and lower values are included, preferably up to 5 % higher and lower values, and in any case at least up to 1 % higher and lower values, the exact value being the most preferred value or limit.

[00039] Example 1

Composite binders according to the invention and for comparison were formed from a clinker comprising around 45 g/100 g of beta-C_2S, 35 g/100g of $\Sigma C_4A_{3-x}F_x\$$ and 11 g/100g aluminate (C_3A, CA). The content of ferrites was below 1 g /100 g. Natural anhydrite was used as sulfate source. As supplementary cementitious material either slag or a mixture of slag and limestone was used. To provide comparison mixtures, quartz was used as an inert compoment instead of the SCM. The composite binder mixture, the ratio $R_{\$/(Y+A+F)}$ and their strength development is shown in table 1. The strength development was measured as described in EN 196-1 on mortar cubes of 2 cm edge length from a mixture of 2 parts (by weight) cement, 3 parts sand (ISS1, Ø size of 1 mm) and 1 part water. The water/binder ratio was 0.5. The loading velocity was adjusted to 0.4 kN/s.

[00040] It can be seen, that at low $R_{\$/(Y+A+F)}$ values like e.g. 0.25 or 0.35 no (measureable) contribution of the slag to the strength development was observed during the investigated period of time. For the samples with $R_{\$/(Y+A+F)}$ values of 0.55 and 0.74 already after 90 days of hydration an increase of strength of around 7 MPa (0.55) to 12 MPa (0.74) compared to the quartz containing reference was achieved.

[00041] Table 1

No.	clinker (incl. sulfate)	slag	limestone	quartz	$R_{\$/(Y+A+F)}$	strength [MPA] after				
						1d	2d	7d	28d	90d
1	70 %	30 %			0.74	23.8	n.d.	28.5	35.3	50.0
2	70 %	25 %	5 %		0.74	23.7	n.d.	27.8	36.2	49.1
3	70 %	20 %	10 %		0.74	23.0	n.d.	27.3	35.4	45.0
4	70 %			30 %	0.74	15.0	n.d.	28.4	34.1	37.7
5	74.5 %	25.5			0.55	20.3	23.5	34.9	37.2	45.4
6	74.5 %			25.5	0.55	19.1	21.5	32.8	38.6	37.7
7	73 %	27 %			0.35	19.2	n.d.	22.9	28.6	31.2
8	73 %	18 %	9 %		0.35	21.2	n.d.	26.0	30.3	31.3
9	73 %			27 %	0.35	21.6	n.d.	24.3	29.4	29.6
10	65 %	35 %			0.25	12.8	14.7	17.6	20.6	23.7
11	65 %	30 %	5 %		0.25	13.4	15.2	17.8	21.2	24.8
12	65 %	25 %	10 %		0.25	14.2	15.5	18.0	21.1	24.7
13	65 %			35 %	0.25	15.4	17.0	21.9	26.9	33.4

n.d. – not determined

[00042] Example 2

Composite binders according to the invention and for comparison were formed from a clinker comprising 60 g/100 g of beta-C_2S, 22 g/100g of $\Sigma C_4A_3\$$ and 11 g/100g ferrites (C_4AF and C_2F). No calcium aluminate phases was detectable. Natural anhydrite was used as sulfate source. Slag was used as supplementary cementitious material and quartz to provide a comparison. The binder mixtures and the ratio $R_{\$/(Y+A+F)}$ are shown in table 2. Strength development was measured as for example 1.

[00043] Table 2

No.	cement	slag	quartz	ratio	strength [MPA] after				
					1d	2d	7d	28d	90d
13	55 %	45 %		0.85	3.0	6.5	21.8	31.2	32.6
14	55 %		45 %	0.85	2.5	6.1	15.4	19.5	19.6
15	70 %	30 %		0.77	6.7	11.5	20.5	32.0	33.0
16	70 %		30 %	0.77	6.5	12.4	18.7	25.0	25.8
17	100 %			0.77	16.1	17.6	31.5	39.7	46.4
18	50 %	50 %		0.11	2.2	2.7	3.4	4.0	5.3
19	50 %		50 %	0.11	1.9	2.2	3.2	3.2	10.1

[00044] It can be seen that at low $R_{\$/(Y+A+F)}$ values like e.g. 0.11 no (measureable) contribution of the slag to the strength development was observed during the investigated period of time and the quartz containing reference achieved even a higher final compressive strength. For the samples with $R_{\$/(Y+A+F)}$ values of 0.77 and 0.85 already after 7 days of hydration a clear increase of strength of around 2 MPa (0.77) to 6 MPa (0.85) compared to the quartz containing reference was achieved. At 28 days of hydration the increase was around 7 MPa (0.77) to 12 MPa (0.85) and at 90 days 7 MPa (0.77) to 13 MPa (0.85) compared to the quartz containing reference.

Claims

1. Composite binder containing at least one calcium sulfoaluminate cement and at least one supplementary cementitious material, wherein a weight ratio of calcium sulfate to the sum of ye'elimite, aluminates and ferrites in the composite binder ranges from 0.5 to 0.85.

2. Composite binder according to claim 1, wherein the supplementary cementitious material is chosen from latent hydraulic materials and/or natural or artificial pozzolanic materials, preferably latent hydraulic slags like ground granulated blast furnace slag, type-C and/or type-F fly ashes, calcined clays or shales, trass, brick-dust, artificial glasses, silica fume, and burned organic matter residues rich in silica such as rice husk ash, and combinations thereof.

3. Composite binder according to claim 1 or 2, wherein the weight ratio of calcium sulfate to the sum of ye'elimite, aluminates and ferrites ranges from 0.55 to 0.85, preferably from 0.6 to 0.85.

4. Composite binder according to at least one of claims 1 to 3, wherein the calcium sulfoaluminate cement comprises 10 - 100 % by weight $C_4A_{3-x}F_x\$$, with x ranging from 0 to 2, 0 - 70 % by weight C_2S, 0 - 30 % by weight aluminates, 0 - 30 % by weight ferrites, 0 – 30 % by weight ternesite, 0 - 20 % by weight calcium sulfate and up to 20 % minor phases, wherein the sum of all phases adds up to 100%, with the proviso, that calcium sulfate is provided as separate component and/or comprised in the supplementary cementitious material when it is not contained in the calcium sulfoalumnate cement.

5. Composite binder according to at least one of claims 1 to 4, wherein the content of calcium sulfoaluminate cement ranges from 10 to 90 % by weight, preferably from 20 to 70 % by weight and most preferably from 30 to 60 % by weight of the binder.

6. Composite binder according to at least one of claims 1 to 5, wherein the supplementary cementitious materials comprise 0 to 100 % by weight, preferably from 20 to 80 % by weight and most preferably from 30 – 70 % by weight latent hydraulic materials and 0 to 40 % by weight, preferably from 5 to 35 % by weight and most preferably from 10 – 30 % by weight pozzolanic materials with respect to the total amount of supplementary cementitious materials.

7. Composite binder according to claim 6, wherein the content of the supplementary cementitious materials ranges from 30 to 60 % by weight, of the binder for supplementary cementitious materials comprising at least 70 % by weight latent hydraulic materials.

8. Composite binder according to claim 6, wherein the content of the supplementary cementitious materials ranges from 10 to 30 % by weight of the binder for supplementary cementitious materials comprising at least 70 % by weight pozzolanic materials.

9. Composite binder according to at least one of claims 1 to 8, wherein it comprises at least one of calcium aluminate cement, portland cement, portland cement clinker, limestone, dolomite, ternesite, alkali salts, earth alkali salts, admixtures, and additives

10. Composite binder according to claim 9, wherein the content of a contained calcium aluminate cement, portland cement, portland cement clinker, limestone, ternesite and/or dolomite ranges from 0.1 to 20 % by weight, preferably from 3 to 20 % by weight and most preferred from 5 to 15 % by weight of the binder.

11. Composite binder according to claim 9 or 10, wherein the content of contained alkali salts and/or earth alkali salts ranges from 0.05 % to 5 % by weight, preferably from 0.1 to 3 % by weight and most preferred from 0.5 to 2 % by weight of the binder.

12. Composite binder according to at least one of claims 8 to 11, wherein it contains one or more admixtures chosen from accelerators, retarders, air entrainment agents, plasticizers, super plasticizers, pigments, corrosion inhibitors, bonding agents, and pumping aids.

13. Composite binder according claim 12, wherein the content of a contained admixtures ranges from 0.01 to 5 % by weight, preferably from 0.1 to 3 % by weight and most preferred from 0.5 to 1.5 % by weight.

14. Composite binder according to at least one of claims 8 to 13, wherein it contains additives chosen from fillers, fibres, fabrics / textiles, silica fume, and crushed or ground glass.

15. Method of manufacturing a composite binder comprising the steps:
a) providing at least one calcium sulfoaluminate cement
b) providing at least one supplementary cementitious material
c) mixing 10 to 90 % by weight calcium sulfoaluminate cement(s) with 10 to 90 % by weight supplementary cementitious material(s), wherein the weight ratio of calcium sulfate to the sum of ye'elimite, aluminates and ferrites ranges from 0.5 to 0.85.

16. Use of a binder according to at least one of claims 1 to 14 to make hydraulically setting building materials such as concrete and mortar or special construction chemical compositions such as tile adhesive and floor screed.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
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ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ARJUNAN P ET AL: "Sulfoaluminate-belite cement from low-calcium fly ash and sulfur-rich and other industrial by-products", CEMENT AND CONCRETE RESEARCH, PERGAMON PRESS, ELMSFORD, NY, US, vol. 29, no. 8, 2 January 1999 (1999-01-02), pages 1305-1311, XP002320781, ISSN: 0008-8846, DOI: 10.1016/S0008-8846(99)00072-1 abstract; table 2 -----	1-4,6
X	FR 2 949 112 A1 (LAFARGE SA [FR]) 18 February 2011 (2011-02-18) claims 1,7,8; table IV -----	1-16

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

"&" document member of the same patent family

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	GB 2 489 981 A (GREEN BINDER TECHNOLOGIES LTD [IL]) 17 October 2012 (2012-10-17) the whole document -----	1-16
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/002368

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权利要求书2页 说明书9页

(54) 发明名称

硫铝酸钙复合粘结剂

(57) 摘要

本发明涉及复合粘结剂，所述复合粘结剂含有硫铝酸钙水泥和补充性胶结材料，其中硫酸钙与天然硫铝酸钙、铝酸盐和铁素体之和 ($R_{S/(Y+A+F)}$) 的重量比的范围是从 0.5 至 0.85，涉及一种制造所述复合粘结剂的方法，该方法包含以下步骤：a) 提供至少一种硫铝酸钙水泥 b) 提供至少一种补充性胶结材料 c) 混合 10 至 90 重量%硫铝酸钙水泥与 10 至 90 重量%补充性胶结材料，以及涉及所述复合粘结剂用于制作水硬性建筑材料和特殊建筑物化学组合物的用途。

CN 105658598 A

1.复合粘结剂,其含有至少一种硫铝酸钙水泥和至少一种补充性胶结材料,其中在所述复合粘结剂中,硫酸钙与天然硫铝酸钙、铝酸盐和铁素体之和的重量比的范围是从0.5到0.85。

2.根据权利要求1所述的复合粘结剂,其中所述补充性胶结材料选自潜在水硬性材料和/或天然或人工凝硬性材料、优选潜在水硬性矿渣类研磨颗粒化高炉矿渣、C型和/或F型粉煤灰、煅烧粘土或页岩、粗面凝灰岩、砖渣、人工玻璃、硅粉、和诸如谷壳灰之类富含二氧化硅的燃烧有机物残渣以及它们的组合。

3.根据权利要求1或2所述的复合粘结剂,其中硫酸钙与天然硫铝酸钙、铝酸盐和铁素体之和的重量比的范围是从0.55到0.85,优选0.6至0.85。

4.根据权利要求1至3中至少一项所述的复合粘结剂,其中所述硫铝酸钙水泥包含:10-100重量%$C_4A_{3-x}F_x\$$,并且x的范围从0至2、0-70重量%C_2S、0-30重量%铝酸盐、0-30重量%铁素体、0-30重量%ternesite、0-20重量%硫酸钙和至多20%次生相,其中所有相相加之和至多100%,前提条件是硫酸钙作为单独组分提供,和/或当其未被包含在所述硫铝酸钙水泥中时,被包含在所述补充性胶结材料中。

5.根据权利要求1至4中至少一项所述的复合粘结剂,其中硫铝酸钙水泥的含量的范围是从所述粘结剂的10至90重量%、优选20至70重量%并且最优选地30至60重量%。

6.根据权利要求1至5中至少一项所述的复合粘结剂,其中关于补充性胶结材料的总量,所述补充性胶结材料包含0至100重量%、优选20至80重量%且最优选地30-70重量%潜在水硬性材料以及0至40重量%、优选5至35重量%且最优选地10-30重量%凝硬性材料。

7.根据权利要求6所述的复合粘结剂,其中对于包含至少70重量%潜在水硬性材料的补充性胶结材料,所述补充性胶结材料的含量的范围是从所述粘结剂的30至60重量%。

8.根据权利要求6所述的复合粘结剂,其中对于包含至少70重量%凝硬性材料的补充性胶结材料,所述补充性胶结材料的含量的范围是从所述粘结剂的10至30重量%。

9.根据权利要求1至8中至少一项所述的复合粘结剂,其中其包含铝酸钙水泥、波特兰水泥、波特兰水泥熔块、石灰石、白云石、ternesite、碱金属盐、碱土金属盐、掺加物和添加剂中的至少一种。

10.根据权利要求9所述的复合粘结剂,其中所含铝酸钙水泥、波特兰水泥、波特兰水泥熔块、石灰石、ternesite和/或白云石的含量的范围是从所述粘结剂的0.1至20重量%、优选3至20重量%且最优选5至15重量%。

11.根据权利要求9或10所述的复合粘结剂,其中所含碱金属盐和/或碱土金属盐的含量的范围是从所述粘结剂的0.05至5重量%、优选0.1至3重量%且最优选0.5至2重量%。

12.根据权利要求8至11中至少一项所述的复合粘结剂,其中其含有选自加速剂、缓凝剂、引气剂、塑化剂、超级塑化剂、颜料、抗蚀剂、粘结剂和泵送助剂中的一种或多种掺加物。

13.根据权利要求12所述的复合粘结剂,其中所含掺加物的含量的范围是从0.01至5重量%、优选0.1至3重量%且最优选0.5至1.5重量%。

14.根据权利要求8至13中至少一项所述的复合粘结剂,其中其含有选自填料、纤维、织物/纺织品、硅粉和压碎或研磨玻璃的添加剂。

15.制造复合粘结剂的方法,所述方法包括以下步骤:

a)提供至少一种硫铝酸钙水泥

b)提供至少一种补充性胶结材料

c)混合10至90重量％硫铝酸钙水泥与10至90重量％补充性胶结材料，其中硫酸钙与天然硫铝酸钙、铝酸盐和铁素体之和的重量比的范围是从0.5至0.85。

16.根据权利要求1至14中至少一项所述的粘结剂用于制作诸如混凝土和灰浆之类水硬性建筑材料或诸如瓷砖粘合剂和地台砂浆底层之类特殊建筑物化学组合物的用途。

硫铝酸钙复合粘结剂

[0001] 本发明涉及包含硫铝酸钙基水泥/熔块型和补充性胶结材料的粘结剂,一种制造复合粘结剂的方法以及其用于制备水硬性建筑材料或特殊建筑物化学组合物的用途。

[0002] 硫铝酸钙(CSA)水泥是由熔块制得,所述熔块包括作为主要相的天然硫铝酸钙(ye′elimite)($Ca_4(AlO_2)_6SO_4$或$C_4A_3\$$,水泥化学家标记法(cement chemist′s notation))。这些粘结剂在膨胀水泥、超高早期强度水泥和″低能″水泥中用作成分。CSA水泥的水合导致主要形成钙钒石和/或单相(例如单硫酸酯)。氢氧化铝有可能是该粘结剂的另一种水合产物。形成的量和动力学强烈地取决于水泥组合物(例如,存在的含硫酸盐相的量和类型)。通过调整钙和硫酸盐离子的可用性来获得特殊物理性质(例如有意的膨胀行为或快速反应)。在中国,已率先将CSA水泥用作波特兰水泥(Portlandcement)的低能替代形式,并且每年生产数百万吨。因为反应所需炉温降低、可磨性更佳以及原料混合物中石灰石含量更低(该原料混合物需要吸热地除去碳酸),所以生产所需能量更低。另外,更低石灰石含量和更低燃料消耗导致CO_2排放物为波特兰水泥熔块的约一半。

[0003] 在本发明的背景下,熔块应该是指烧结产物,其通过在升高的温度下燃烧原材料混合物而获得并且包含至少一种水硬反应性相。水泥表示在添加或不添加其他组分的情况下研磨的熔块。粘结剂或粘结剂混合物表示一种混合物,其水硬性硬化并且包含水泥和通常但非必需的额外细磨组分,并且其在添加水、任选掺加物和/或添加剂和聚集体之后使用。熔块可能已包含所有必需或期望的相,并且在研磨成水泥之后作为粘结剂直接使用。

[0004] 节约能量和有价值原材料的另一个方法是将次级原材料或工业副产物应用作为生料组分来在熔块生产期间代替初级矿物基原材料。

[0005] 在其他方法中,补充性胶结材料(其常常为工业副产物或废物)被用于在水泥生产期间代替熔块的部分,并因此节约能量和初级原料资源。这些材料大多数常常具有凝硬性或潜在水硬性反应性,并且有助于这些复合粘结剂的机械性能。

[0006] 波特兰-复合水泥中允许的成分为人工火山灰(例如高炉矿渣,硅粉,合成玻璃和粉煤灰)或天然火山灰(例如硅质或硅铝质材料,诸如火山灰玻璃、煅烧粘土和页岩)。波特兰高炉水泥含有至多70%研磨颗粒化高炉矿渣,其余为波特兰熔块和少量硫酸盐(例如石膏)。这些复合水泥通常产生高极限强度,但随着矿渣含量增加,早期强度降低,而潜在地抗硫酸盐性增加并且放热减弱。波特兰粉煤灰水泥含有至多35%粉煤灰。该粉煤灰具有凝硬性行为,以使得极限强度得以维持或甚至增大。因为粉煤灰添加允许更低的水与粘结剂比率,并且因此允许更低的总水含量,所以早期强度也可以维持。

[0007] 补充性胶结材料可被分为潜在水硬性材料和火山灰。潜在水硬性材料并非其自身具有水硬性,或者仅极缓慢反应。它们需要活化以在可用时间周期内发生水硬性反应。活化通常是通过(添加)碱土金属或碱金属化合物(例如$Ca(OH)_2$、NaOH、KOH等)或硫酸盐提供材料($CaSO_4$、Na_2SO_4、K_2SO_4等)来实现,所述碱土金属或碱金属化合物或硫酸盐提供材料能够支持形成硅酸(铝)钙水合物和/或钙钒石和/或其他类似物,例如AF_m-相(水铝黄长石(strätlingite)、单硫酸酯、一碳酸盐半碳酸盐等)或沸石类矿物。火山灰为硅质或铝硅质材料,其与来自粘结剂的其他组分的氢氧化钙反应而形成硅酸钙水合物。上述区别并不总是

严格适用,即,许多粉煤灰含有相当多量的钙,并且为潜在水硬性材料,但尽管如此,通常将它们称为火山灰。对于本发明而言,所述区别并不重要,并且这两者皆被归纳为补充性胶结材料,本文部分地缩写为SCM。

[0008] 典型的补充性胶结材料为天然或人工火山灰和潜在水硬性材料,例如但非排他地,研磨颗粒化高炉矿渣,以及天然或人工火山灰,例如但非排他地,C型和/或F型粉煤灰、煅烧粘土或页岩、粗面凝灰岩、砖渣、人工玻璃、硅粉和富含二氧化硅的燃烧有机物残渣(诸如谷壳灰)或它们的混合物。

[0009] 波特兰水泥和波特兰复合水泥的问题为对高早期强度不断增加的需求。给予进行建筑的时间正不断地减少。在建筑物元件的制造中,需要快速拆模来优化投资回报。因此,需要可提供高早期强度的粘结剂,这当然是在不减小极限强度、耐久性或可加工性的情况下实现。另外还存在的目的是提供就能量和天然原材料而言具有最小环境影响的水泥。

[0010] 已存在一些将SCM加入硫铝酸钙水泥的提议。

[0011] 根据GB 2490010描述,水泥质组合物含有:(a)60-94%至少一种凝硬性材料;(b)至少0.5%硫铝酸钙;(c)1.2-11%至少一种无机硫酸盐,表达为SO_3;和(d)至少3%的总硫酸盐含量,表达为SO_3,其中所述水泥质组合物包括至多3%天然石灰和至多10%矾土水泥。此体系的强度发展主要基于钙钒石,所述体系为所谓的超硫酸化体系,其中硫酸钙与天然硫铝酸钙+铝酸盐+铁素体的比率大于1,CSA以及$CaO/Ca(OH)_2$的至少一种来源(来源于例如CaO或OPC的添加)被用作针对早期强度的活化剂。

[0012] 在Zivica V.,"Possibility of the modification of theproperties of sulfoaluminate belite cement by its blending",Ceramics-Silikaty 45(1),24-30,(2001)中,研究了向含有约53%C_2S、34%$C_4A_3\$$、8%C_4AF和5%C$的CSA水泥添加5%、15%和30%SCM。从阐释中来看,显而易见的是,过烧或“死烧”的硬石膏是熔块的一部分,并且SCM大多数地作为非活性填料起作用。因此,该文章建议,低于15%的SCM含量是最佳的。在这种情况下,显著的能量节约似乎是不可能的。

[0013] 在Quillin K.,BRE"Low-CO_2Cements based onCalcium Sulfoaluminate"(http://www.soci.org/News/~/media/Files/Conference%20Downloads/Low%20Carbon%20Cements%20Nov%2010/Sulphoaluminate_Cements_Keith_Quillin_R.ashx,status June 2013)中,研究了30或50%研磨颗粒化高炉矿渣或30%粉煤灰的添加以及硫酸盐含量对含有约22%C_2S、60%$C_4A_3\$$、7%C_4AF、8%C_3S和5%C_3A的CSA水泥的影响。硫酸钙与$C_4A_3\$$、铝酸盐和铁素体总和之比被调整至0、0.35、0.93或高于1。

[0014] 意外地,现已发现,包含硫铝酸钙水泥和补充性胶结材料并且硫酸钙与天然硫铝酸钙、铝酸盐和铁素体的总和之重量比$R_{\$/(Y+A+F)}$处于0.5至0.85范围内的复合粘结剂提供了良好早期强度和极限强度,同时与基于硫铝酸钙水泥而未添加SCM的粘结剂相比,进一步减弱了环境影响。$R_{\$/(Y+A+F)}$尤其代表$CaSO_4$/(Σ天然硫铝酸钙+Σ铝酸盐+Σ铁素体),其中-$CaSO_4$表示来源于粘结剂中存在的$CaSO_4$、$CaSO_4\cdot0.5H_2O$、或$CaSO_4\cdot2H_2O$的无水硫酸钙的量

-天然硫铝酸钙表示:$C_4A_{3-x}F_x\$$,其中x范围从0至2;$C_4A_3\$$,具有以一种或多种外来离子的其他取代;或它们的混合物

-Σ铝酸盐表示基于铝酸钙的所有相之和,优选地,其是指CA、$C_{12}A_7$、CA_2、C_3A、非晶形铝酸盐相以及它们的混合物

-Σ铁素体表示基于氧化钙和氧化铁的所有相之和,优选地,其是指:$C_2A_yF_{1-y}$,并且y的范围从0.2至0.8;C_2F;CF;CF_2;非晶形铁素体相;以及它们的混合物。

诸如$C_4A_{3-x}F_x\$$、$C_2A_yF_{1-y}$、CA、$C_{12}A_7$、CA_2、C_3A、C_2F、CF、CF_2等的相可以是结晶的、部分结晶的或非晶形的。所述相可能并且通常的确含有外来离子(或除明确说明的那些之外的其他/额外外来离子)的取代,这是技术材料所共同的。就含有C、A和F的相的情况,所述相被视为铝酸盐或铁素体并不重要,只要所述相被包括并且未被计算两次。

[0015] 硫酸钙也可存在于补充性胶结材料内或CSA熔块内。该硫酸钙还必须考虑计算$R_{\$/(Y+A+F)}$。非晶形铝酸盐或铁素体相是(例如但非排他地)$C_{12}A_7$、CA、$C_4AF$、CF的特殊形式。对于$R_{\$/(Y+A+F)}$的计算,还必须将通过向粘结剂添加其他组分如铝酸钙或波特兰水泥而引入的铝酸盐和/或铁素体纳入考虑。

[0016] 本发明用复合粘结剂以及所述复合粘结剂用于制作水硬性建筑材料或特殊建筑物化学组合物来解决了上述问题,所述复合粘结剂包含硫铝酸钙水泥和补充性胶结材料,其中硫酸盐与天然硫铝酸钙、铝酸盐和铁素体之和的重量比是在0.5至0.85的范围内,其中优选地

-硫酸钙是指来源于粘结剂中存在的$CaSO_4$、$CaSO_4\cdot0.5H_2O$和$CaSO_4\cdot2H_2O$的无水硫酸钙的量,

-天然硫铝酸钙是指以下的含量:$C_4A_{3-x}F_x\$$,其中x范围从0至2;$C_4A_3\$$,具有以一种或多种外来离子的其他取代;或它们的混合物-铝酸盐代表(例如但非排他地)CA、$C_{12}A_7$、CA_2、C_3A、非晶形铝酸盐相或它们的混合物的含量,和

-铁素体代表例如但非排他地以下的含量:$C_2A_yF_{1-y}$,其中y的范围从0.2至0.8;C_2F;CF;CF_2;非晶形铁素体相;或它们的混合物。本发明进一步用一种制造复合粘结剂的方法来满足所述目的,所述方法包括以下步骤:

a)提供至少一种硫铝酸钙水泥

c)提供至少一种补充性胶结材料

d)混合10至80重量%硫铝酸钙水泥与20至90重量%补充性胶结材料,其中硫酸盐与天然硫铝酸钙、铝酸盐和铁素体之和的重量比$R_{\$/(Y+A+F)}$的范围是从0.5至0.85。

[0017] 为了简化描述,使用水泥工业中常见的以下缩写:H-H_2O、C-CaO、A-Al_2O_3、F-Fe_2O_3、M-MgO、S-SiO_2和\$-$8O_3$。另外,化合物一般以其纯形式示出,而不明确说明固体溶液/外来离子等等取代的系列,这是技术和工业材料中的惯常做法。如任何本领域技术人员应理解,取决于生料的化学机理和生产的类型,由于各种外来离子的取代,本发明中通过名称提及的所述相的组合物可以变化,这种化合物同样由本发明的范围所涵盖。

[0018] 补充性胶结材料可选自显示出潜在水硬性和/或凝硬性特性的所有可用材料。优选的是研磨颗粒化高炉矿渣、粉煤灰C型和F型和天然火山灰、煅烧粘土或页岩、粗面凝灰岩、人工玻璃、除研磨颗粒化高炉矿渣之外的其他矿渣、砖渣和富含二氧化硅的燃烧有机物残渣(诸如谷壳灰)。尤其优选的是富钙人工玻璃、C型粉煤灰和研磨颗粒化高炉矿渣。

[0019] 硫铝酸钙熔块主要含有天然硫铝酸钙的多晶型物。取决于所用原材料和燃烧温度,所述硫铝酸钙熔块通常还含有斜硅钙石、铁素体和/或铝酸盐、硬石膏,并且还可以含有ternesite,参见例如WO 2013/023728 A2。硫铝酸钙水泥可通过研磨得自CSA熔块,通常添加硫酸钙。硫铝酸钙水泥的制造按本身已知的方式来进行。通常,原材料以适当量混合,研

磨并且在炉中燃烧以得到熔块。通常，熔块随后与硫酸钙和任选的其他组分中的一些或所有一起研磨，以得到水泥。当组分的可磨性极大不同时，单独研磨也是可能的，并且可能是有利的。硫酸钙可以为石膏、烧石膏、硬石膏或它们的混合物。优选使用硬石膏。

[0020] 当CSA熔块已含有所需量的硫酸钙时，可通过研磨CSA熔块获得硫铝酸钙水泥。通常，其通过将CSA熔块与足够量的硫酸钙混合来获得。这意味着，如对本发明所定义，在研磨CSA熔块之前、期间或之后，所述组分CSA水泥提供天然硫铝酸钙和硫酸盐，以及任选的铝酸盐、铁素体、斜硅钙石和其他组分，无论所述组分是否源自CSA熔块或源自CSA熔块与其的混合。当然，硫酸盐、天然硫铝酸钙、铝酸盐和铁素体也可源自SCM组分或复合粘结剂的任选的附加组分，以使得在CSA水泥中所需更少。这意味着，为制造粘结剂，硫酸盐(以及任何其他相)可源自CSA熔块、CSA水泥、SCM并且甚至源自附加组分。关于所述硫酸盐，是否其在与SCM混合之前或在混合期间被加入CSA熔块并不重要，即，CSA水泥可作为一种组分或作为两种组分(即，研磨CSA熔块和研磨硫酸盐)来添加。

[0021] 含有$C_4A_3\$$作为主相的硫铝酸钙熔块和水泥是已知的，并且可以不同品质/组成获得。对于本发明，所有均合适。例如，以下CSA水泥是(市售)可得/已知：

Lafarge BCSAF：

斜硅钙石(α；+/-β)C_2S 40-75％；天然硫铝酸钙$C_4A_3\$$15-35％；

铁素体$C_2(A,F)$5-25％；次生相0.1-10％

Lafarge **Rockfast®**:

斜硅钙石(α；+/-β)C_2S 0-10％；天然硫铝酸钙$C_4A_3\$$50-65％

铝酸盐CA 10-25％；钙黄长石C_2AS 10-25％；

铁素体C2(A,F)0-10％；次生相0-10％

Italcementi **Alipre®**:

斜硅钙石(α；+/-β)C_2S 10-25％；天然硫铝酸钙$C_4A_3\$$50-65％；

硬石膏C$0-25％；次生相1-20％

Cemex CSA：

斜硅钙石(α；+/-β)C_2S 10-30％；天然硫铝酸钙$C_4A_3\$$20-40％

硬石膏C$＞1％；硅酸三钙石$C_3S$＞1-30％；

游离石灰CaO＜0.5-6％；氢氧钙石$Ca(OH)_2$0-7％；

次生相0-10％

Denka®CSA

斜硅钙石(α；+/-β)C_2S 0-10％；天然硫铝酸钙$C_4A_3\$$15-25％；

硬石膏$C_2(A,F)$30-40％；氢氧钙石$Ca(OH)_2$20-35％；

游离石灰C_aO 1-10％；次生相0-10％

China Type II&III CSA

斜硅钙石(α；+/-β)C_2S 10-25％；天然硫铝酸钙$C_4A_3\$$60-70％；

铁素体$C_2(A,F)$1-15％；次生相1-15％

Barnstone CSA

斜硅钙石(α；+/-β)C_2S 22％；天然硫铝酸钙$C_4A_3\$$60％；

铝酸盐$C_{12}A_7$5％；硅酸三钙石C_3S 8％；

铁素体$C_2(A,F)$4%;次生相1%

HeidelbergCement BCT

斜硅钙石(α;+/-β)C_2S 1-80%;天然硫铝酸钙Σ$C_4A_3\$$5-70%;

ternesite$C_5S_2\$$5-75%;次生相0-30%;

[0022] 硫铝酸钙熔块或水泥通常包含10-100重量%、优选20-80重量%和最优选25至50重量%$C_4A_{3-x}F_x\$$,并且x的范围从0至2,优选0.05至1且最优选0.1至0.6。其通常还包含0-70重量%、优选10至60重量%且最优选20至50重量%C_2S,0-30重量%、优选1至15重量%和最优选3至10重量%铝酸盐,0-30重量%、优选3至25重量%且最优选5至15重量%铁素体,0-30重量%、优选3至25重量%且最优选5至15重量%ternesite,0-30重量%、优选5至25重量%且最优选8至20重量%硫酸钙,以及至多20%次生相。如所指出的那样,多个相可存在于CSA熔块中,或被添加以用于获取CSA水泥。

[0023] 本发明对所有种类的硫铝酸钙水泥均有益,包括斜硅钙石富含和稀少的硫铝酸钙水泥以及铝酸盐和铁素体的量不同的硫铝酸钙水泥,只要复合粘结剂中的重量比$R_{\$/(Y+A+F)}$维持在0.5至0.85的范围内。在低于0.5的比率情况下,关于强度发展,仅观察到胶结材料的微弱贡献或甚至无贡献。在高于0.9的比率情况下,在使用复合物水泥制作的灰浆棱柱水合24小时之后,已观察到伴随形成细微至甚至很大的破裂的膨胀。硫酸盐添加的更高水平导致甚至更明显的膨胀和破裂。优选地,将根据本发明的重量比设定为0.55至0.85,尤其优选0.6至0.85。在所述范围内,比率越高导致在越短时间内强度的增加越高,即,更高的比率加速了强度发展。当计算该比率时,将来自补充性胶结材料和其他组分的任何硫酸盐、铝酸盐、铁素体或天然硫铝酸钙纳入考虑。

[0024] 补充性胶结材料可根据本发明以至少10重量%且至多90重量%的量来添加,优选添加20至80重量%。SCM中潜在水硬性材料的量通常的范围是从SCM的总量的0至100重量%,优选20至80重量%且最优选30至70重量%。凝硬性材料的含量的范围是从补充性胶结材料的总量的0至40重量%,优选5至35重量%且最优选10至30重量%。

[0025] 粘结剂中SCM的优选量取决于SCM的反应性。如果SCM仅为或主要为潜在水硬性材料,则优选的添加量的范围是从10至90重量%,最优选30至60重量%。当使用仅或主要凝硬性材料时,优选以10至40重量%、最优选20至30重量%的量来添加SCM。SCM(其是潜在水硬性和凝硬性材料的混合物)的优选量取决于所用SCM混合物的反应性。即,与低、主要凝硬性的反应性的SCM混合物相比,优选以更高量使用更具反应性的SCM混合物。

[0026] 在本发明的另一个实施方案中,根据通过激光粒度测定法测得的粒度分布,硫铝酸钙水泥或来自其的粘结剂的细度为$d_{90} \leq 90\mu m$,优选$d_{90} \leq 60\mu m$且最优选$d_{90} \leq 40\mu m$,由此,RosinRammler参数(斜率)n可从0.7至1.5、优选0.8至1.3且最优选0.9至1.15变化。

[0027] 在添加或不添加其他物质的情况下,通过研磨所述熔块来获得根据本发明的水泥。通常,当熔块中的硫酸钙含量未如所需时,在研磨之前或在研磨期间添加硫酸钙。硫酸钙也可在研磨之后添加。

[0028] 选自(例如但非排他地)铝酸钙水泥、波特兰水泥或波特兰水泥熔块、石灰石、白云石、ternesite、碱金属盐和/或碱土金属盐的其他组分可以按0.01至20重量%的量来添加,优选按范围从0.5至15重量%的量来添加。这在波特兰水泥熔块、石灰石、ternesite和/或白云石的含量的范围是从0.01至20重量%、优选3至20重量%且最优选5至15重量%并且碱

金属盐和碱土金属盐的含量的范围是从0%至5重量%、优选0.1至3重量%且最优选0.5至2重量%时是尤其优选的。

[0029] 此外，可存在普通掺加物和/或添加剂。优选地，掺加物以至多20重量%的量添加，添加剂以至多3重量%的量添加。当然，一种特定混合物的所有组分的量增加到至多100%。

[0030] 掺加物通常被加入由粘结剂制成的混凝土、灰浆等中，但也可被加入粘结剂中。典型的掺加物是：

-加速剂，其加快水合(硬化)诸如CaO、$Ca(OH)_2$、$CaCl_2$、$Ca(NO_3)_2$、$Al_2(SO_4)_3$、KOH、K_2SO_4、K_2CO_3、$NaOH$、Na_2SO_4、Na_2CO_3、$NaNO_3$、$LiOH$、$LiCl$、Li_2CO_3、$MgCl_2$、$MgSO_4$。

-缓凝剂，其减缓水合。典型的多元醇缓凝剂为糖、蔗糖、葡萄糖酸钠、葡萄糖、柠檬酸和酒石酸。

-引气物，其添加并夹带气泡，从而减少在冻-融循环期间的损坏，增加耐久性。

-增塑剂，其增加塑料或"新鲜"混凝土的可加工性，从而使其在进行更少强化努力的情况下更易被放置。典型的增塑剂为木质素磺酸盐。增塑剂可用于降低混凝土的水含量，同时维持可加工性，并且因这种用途而有时被称为减水剂。这种处理改善其强度和耐久性特性。

-超级增塑剂(也称高效减水剂)，其为这样一类增塑剂，其具有更少有害效应并且可用于提高可加工性，比传统塑化剂更实用。用作超级增塑剂的化合物包括磺化萘甲醛缩聚物、磺化三聚氰胺甲醛缩聚物、丙酮甲醛缩聚物和聚羧酸酯醚。

-为了美观，可使用颜料来改变混凝土的颜色。

-使用抗蚀剂来使对混凝土中的钢和钢条的腐蚀最小化。

-使用粘结剂以在老和新混凝土之间产生结合(通常为一类聚合物)。

-泵送助剂提高可泵送性、稠化糊剂并且减少分离和渗出。优选地，将(超级)增塑剂和/或缓凝剂包含在内。通常，关于CSA水泥、SCM和(如果适用)所加任何附加水硬性组分之总和，按通常已知的量，如0.05至1重量%、优选地0.0S至0.5重量%来添加(超级)增塑剂和/或缓凝剂。

[0031] 典型的添加剂例如但非排他地为填料、纤维、织物/纺织品、硅粉以及压碎或研磨玻璃。填料为诸如石英、石灰石、白云石、惰性和/或结晶的粉煤灰。纤维为诸如钢纤维、玻璃纤维或塑料纤维。

[0032] 根据本发明的方法可用本身已知的装置来实施。CSA水泥可在生产之后直接与SCM和其他组分(如果适用)混合。或者，所述组分可在混合之前储存。粘结剂可按已知方式储存并运送，例如包装到水泥筒仓中或水泥袋中，或在添加聚集体、水和任何其他所需添加物之后，可能在已储存一些时间之后，作为预拌混凝土递送。

[0033] 如之前所提及的，该方法被描述为混合CSA水泥和SCM，其应该包括这样一种情况，其中使用具有极少或甚至无硫酸盐的研磨CSA熔块，并且硫酸盐作为单独组分与最终附加组分一起混合以提供粘结剂。换句话说，CSA水泥包括：单个组分，其包含至少研磨天然硫铝酸钙和硫酸盐；以及单独组分硫酸盐和不具有或具有极少硫酸盐的研磨CSA熔块。

[0034] 甚至可能混合CSA熔块和未研磨SCM并且在混合物上进行研磨，但这并不优选。可磨性通常有区别。单独研磨还提供更多灵活性。

[0035] 根据本发明的粘结剂可用于制备混凝土、灰浆、石膏和其他水硬性建筑物材料。所述粘结剂对于制造特殊建筑物化学组合物如瓷砖粘合剂、地台砂浆底层等而言也是有用

的。该用途可按与已知粘结剂或水泥相同的方式发生。该粘结剂特别适用于从水合热量降低中受益的应用,即,尤其适用于大规模结构,如围堤。还极其可用于所有用途的预拌混凝土。

[0036] 相比于仅基于CSA水泥的粘结剂,根据本发明的粘结剂提供显著更进一步的能量节省。相比于现有技术中已知的包含CSA和SCM的粘结剂,所述粘结剂显示增强的强度发展。

[0037] 本发明将进一步参照以下实施例来说明,但不将范围局限于所述的具体实施方案。如果未另外指定,则以%或份数计的任何量是以重量计,且如有质疑,所述重量是参照所关注组合物/混合物的总重量。

[0038] 本发明还包括彼此不排斥的所述特征且尤其是优选特征的所有组合。与数值有关的表征如"约"、"大约"和类似表达意味着,包括更高和更低至多10%的值,优选更高或更低至多5%的值,并且在任何情况下,更高或更低至少至多1%的值,所述确切值为最优选值或极限。

[0039] 实施例1

根据本发明的和用于比较的复合粘结剂是由包含大约45g/100gβ-C_2S、35g/100g Σ$C_4A_{3-x}F_x\$$和11g/100g铝酸盐(C_3A,CA)的熔块形成。铁素体的含量低于1g/100g。将天然硬石膏用作硫酸盐来源。作为补充性胶结材料,使用矿渣或者矿渣和石灰石的混合物。为提供比较混合物,将石英代替SCM用作惰性组分。复合粘结剂混合物、比率$R_{\$/(Y+A+F)}$和其强度发展示于表1中。按EN 196-1中所述,在由2份(以重量计)水泥、3份砂(ISS1,直径1mm)和1份水的混合物制作的2em边长的灰浆立方体上,测量强度发展。水/粘结剂比率为0.5。将加载速度调整至0.4kN/s。

[0040] 可见,在低$R_{\$/(Y+A+F)}$值例如0.25或0.35下,在研究时间段内未观察到矿渣对强度发展的(可测量)贡献。对于$R_{\$/(Y+A+F)}$值为0.55和0.74的样品,已经在水合90天之后,实现相比于含石英参照物的大约7MPa(0.55)至12MPa(0.74)的强度增加。

[0041]

表 1

No.	熔块(包括硫酸盐)	矿渣	石灰石	石英	$R_{\$/(Y+A+F)}$	以下时间之后的强度[MPA] 1天	2天	7天	28天	90天
1	70 %	30 %			0.74	23.8	n.d.	28.5	35.3	50.0
2	70 %	25 %	5 %		0.74	23.7	n.d.	27.8	36.2	49.1
3	70 %	20 %	10 %		0.74	23.0	n.d.	27.3	35.4	45.0
4	70 %			30 %	0.74	15.0	n.d.	28.4	34.1	37.7
5	74.5 %	25.5			0.55	20.3	23.5	34.9	37.2	45.4
6	74.5 %			25.5	0.55	19.1	21.5	32.8	38.6	37.7
7	73 %	27 %			0.35	19.2	n.d.	22.9	28.6	31.2
8	73 %	18 %	9 %		0.35	21.2	n.d.	26.0	30.3	31.3
9	73 %			27 %	0.35	21.6	n.d.	24.3	29.4	29.6
10	65 %	35 %			0.25	12.8	14.7	17.6	20.6	23.7
11	65 %	30 %	5 %		0.25	13.4	15.2	17.8	21.2	24.8
12	65 %	25 %	10 %		0.25	14.2	15.5	18.0	21.1	24.7
13	65 %			35 %	0.25	15.4	17.0	21.9	26.9	33.4

n.d. - 未测定

[0042] 实施例2

根据本发明的和用于比较的复合粘结剂是由包含60g/100gβ-C_2S、22g/100g $\Sigma C_4A_3\$$和11g/100g铁素体(C_4AF和C_2F)的熔块形成。无铝酸钙相是可检测的。将天然硬石膏用作硫酸盐来源。将矿渣用作补充性胶结材料，并且使用石英来提供比较。粘结剂混合物和比率$R_{\$/(Y+A+F)}$示于表2中。强度发展如实施例1中所测量。

[0043] 表2

No.	水泥	矿渣	石英	比率	以下时间之后的强度[MPA]				
					1 天	2 天	7 天	28 天	90 天
13	55 %	45 %		0.85	3.0	6.5	21.8	31.2	32.6
14	55 %		45 %	0.85	2.5	6.1	15.4	19.5	19.6
15	70 %	30 %		0.77	6.7	11.5	20.5	32.0	33.0
16	70 %		30 %	0.77	6.5	12.4	18.7	25.0	25.8
17	100 %			0.77	16.1	17.6	31.5	39.7	46.4
18	50 %	50 %		0.11	2.2	2.7	3.4	4.0	5.3
19	50 %		50 %	0.11	1.9	2.2	3.2	3.2	10.1

[0044] 可见，在低$R_{\$/(Y+A+F)}$值例如在0.11下，在研究时间段内未观察到(可测量)矿渣对强度发展的贡献，并且含石英参照物实现甚至更高的最终压缩强度。对于$R_{\$/(Y+A+F)}$值为0.77和0.85的样品，已经在水合7天之后，实现相比于含石英参照物的大约2MPa(0.77)至6MPa(0.85)的清晰的强度增加。相比于含石英参照物，在水合28天时，所述增加为大约7MPa(0.77)至12MPa(0.85)，并且在90天时，为7MPa(0.77)至13MPa(0.85)。