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(71) Applicant: **HEIDELBERGCEMENT AG** [DE/DE]; Berliner Str. 6, 69120 Heidelberg (DE).

(72) Inventors: **BEN HAHA, Mohsen**; Sandgasse 10, 69117 Heidelberg (DE). **BULLERJAHN, Frank**; Bodelschwinghstraße 2, 69181 Leimen (DE).

(74) Agent: **WAGNER, Jutta**; Zellentin & Partner GbR, Rubensstraße 30, 67061 Ludwigshafen/Rhein (DE).

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(54) Title: MINERALIZER FOR CALCIUM SULFOALUMINATE TERNESITE CEMENTS

(57) **Abstract**: The present invention relates to a method for the production calcium sulfoaluminate (belite, ferrite) ternesite clinker using fluxes/mineralizers comprising the following steps: providing a raw meal comprising at least sources of CaO, SiO_2, Al_2O_3, SO_3, sintering the raw meal in a kiln at >1200 to 1400 °C to provide a clinker, cooling the clinker, wherein a mineralizer comprising at least one compound containing chrome is added prior to sintering providing an amount of chrome calculated as Cr_2O_3 of at least 500 mg/kg in the raw meal. The invention further relates to the clinker obtained, as well as to calcium sulfoaluminate (belite, ferrite) ternesite cements and binders produced from the clinker.

Mineralizer for calcium sulfoaluminate ternesite cements

[0001] The present invention relates to a method for production of calcium sulfoaluminate (belite, ferrite) ternesite clinker and cement types (CSA(B,F)T). The invention further relates to calcium sulfoaluminate (belite, ferrite) ternesite cements produced from the clinker and binders comprising the cement.

[0002] To simplify the description below, the following abbreviations, which are common in the cement industry, will be used: H – H_2O, C – CaO, A – Al_2O_3, F – Fe_2O_3, M – MgO, S – SiO_2 and \$ – 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 chemistry 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.

[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 the hydraulically reactive phase ye'elimite ($Ca_4(AlO_2)_6SO_4$ or $C_4A_3\$$ in cement chemist's notation) and ternesite ($Ca_5(SiO_4)_2SO_4$) or $C_5S_2\$$ in cement chemist's notation). 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 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] The cement industry is known to consume a large quantity of raw materials and energy. In order to reduce the environmental impact industrial wastes have been promoted as raw materials and fuels to replace the naturally available raw materials for manufacturing. From the prior art it is further known to use fluxes and mineralizers for producing Portland cement clinker. Fluxes and mineralisers are defined as materials that promote the formation of melt and of intended clinker phases, respectively, already at lower burning temperatures during sintering, thereby allowing a reduction of sinter temperature or an increased conversion at the same temperature. The differentiation between fluxes and mineralisers is typically not applied strictly, as many materials show both effects. GB 1 498 057 is an example for a method of manufacturing clinker using fluxes/mineralizers. According to this method fluorine and sulphur are added during the raw mix preparation, usually in the form of fluorite (CaF_2) and gypsum ($CaSO_4 \cdot 2H_2O$).

[0005] Calcium fluoride is a typical flux used in the cement industry for reducing the temperature at which Portland cement (OPC) clinker is burnt. Cement manufacturers usually add calcium fluoride during the preparation of the raw mix to produce white cements, to optimize the production of grey cements and to reduce CO_2 emissions.

[0006] Calcium sulfate is another flux/mineralizer that has gained practical importance for OPC. As is well known, the cement industry also uses calcium sulfate (natural gypsum, chemical gypsum and anhydrite) as a setting regulator (typical addition rate is 3-5 %) adding it upon clinker grinding.

[0007] The development of alternative cements has been another focus besides optimizing the manufacturing of Portland cement. Over the past 35 years or so, energy saving or "low-energy" cement have been studied. To this end, calcium sulfoaluminate and belite cements were investigated.

[0008] Calcium sulfoaluminate cements or clinkers contain mainly polymorphs of ye'elimite. Depending on the raw materials used and the applied burning temperature they typically also contain belite, ferrites and/or aluminates, and anhydrite. A specifically desirable clinker further contains ternesite, see e.g. WO 2013/023728 A2. Methods of manufacturing the calcium sulfoaluminate ternesite (CSA(BF)T) clinkers and cements are known from WO 2013/023731 A2 and WO 2013/023729 A2. 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 sulfate and/or calcium sulfoaluminate and optionally some 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 sulfate can be gypsum, bassanite, anhydrite, ternesite or mixtures thereof whereby anhydrite is commonly used. CSA(BF)T cements are produced at lower temperatures than Portland cement and require less energy for grinding. Furthermore, they require less limestone in the raw mix than Portland cement, so there are less CO_2 emissions.

[0009] It is further known from EP 2 801 557 A1 to add glass and/or copper as flux/mineralizer in the manufacture of aluminate or calcium sulfoaluminate ternesite clinkers.

[00010] The use of industrial side products (e.g. slag, embers) as substitute raw-materials for calcium sulfoaluminate cement is known from the prior art, too. Such raw materials usually contain a higher amount of various impurities than mineral raw materials, wherein the impurities can act as flux/mineralizer, but the effect is almost never considered.

[00011] One important aspect of manufacturing calcium sulfoaluminate ternesite clinkers is the correlation between the optimum temperature for the clinker formation and the thermal stability of the intended clinker phases. Ye'elimite ($C_4A_3\$$) is generally stable up to temperatures of around 1250 °C. At higher

temperatures like e.g. above 1300 °C a faster formation of $C_4A_3\$$ is normally observed but followed by a fast decomposition. At 1350 °C this process is even more pronounced. The phase $C_5S_2\$$ shows a similar behaviour but at significant lower temperatures of about 1100 to 1200 °C.

[00012] US 2007/0266903 A1 describes the use of mineralizers, mainly borax and calcium fluoride, for the production of BCSAF clinker with the following mineralogical composition: 5 to 25 % $C_2A_xF_{(1-x)}$, 15 to 35 % $C_4A_3\$$, 40 to 75 % C_2S (with at least 50% as alpha) and 0.01 to 10 % in total of minor phases.

[00013] EP 2 105 419 A1 describes an additive compound, based on a water soluble calcium salt and an alkanolamine, as grinding aid as well as an performance enhancing agent for a BCSAF clinker with the following mineralogical composition: 5 to 25 % $C_2A_xF_{(1-x)}$, 15 to 35 % $C_4A_3\$$, 40 to 75 % C_2S (with at least 50% as alpha) and 0.01 to 10 % in total of minor phases.

[00014] The article "Characterization of mortars from belite-rich clinkers produced from inorganic wastes", Chen et al., Cement & Concrete Composites 33 (2011), 261-266 reports the successful use of an electroplating sludge, containing 55826 ppm Cr, as a major raw material for the production of belite-rich OPC (BRC) at lab-scale.

[00015] The article "Reuse of heavy metal-containing sludges in cement production", Shih et al., Cement and Concrete Research 35 (2005), 2110-2115 also reports the successful use of heavy metal-containing sludges, containing around 4000 to 40000 ppm Cr, as a raw material for the production of OPC at lab-scale.

[00016] Engelsen describes in "Effect of mineralizers in cement production", SINTEF REPORT No SBF BK A07021 dated 7.6.2007 the use of chrome as a mineralizer for OPC production.

[00017] The article “The effect of Cr_2O_3 and P_2O_5 additions on the phase transformations during the formation of calcium sulphoaluminate $C_4A_3\$$”, Benarchid and Rogez, Cement and Concrete Research (2005), reports the use of a combination of P_2O_5 and Cr_2O_3 for the synthesis of $C_4A_3\$$ clinker. Neither an information about the use of chrome as mineralizer for the formation of ternesite clinker nor a beneficial effect on the thermal stability of ternesite (i.e. stability towards higher sintering temperatures like > 1200 °C up to 1400 °C) is presented. The effect of the combination on the formation of $C_4A_3\$$ is split, higher concentrations were found to stabilize CA and thus decrease the $C_4A_3\$$ content, i.e. hinder its formation. As a result, uncombined anhydrite will be left in the clinker which is thermodynamically not stable at ≥ 1300 °C. This leads to the undesired volatilization of SO_2 and the formation of free CaO within the clinker.

[00018] It is an object of the present invention to produce a ternesite containing clinker having an improved clinker mineralogy, i.e. formation and thermal stability of ternesite, in a single sintering step above 1200 °C, and preferably around 1250 °C to 1350 °C and most preferably around 1300 °C. Furthermore, it is an objective of this invention to present an alternative method for the treatment or use of heavy metal, mainly chromium, contaminated materials.

[00019] Surprisingly it was found that ternesite is formed in a broad range of solid solutions in the presence of chrome whereby for example mainly sulphate but also silicon can be partly replaced by chromium. Chrome significantly improves the thermal stability of ternesite towards higher sintering temperatures compared to the state of the art. As a result ternesite bearing clinker can be formed at temperatures suitable or even optimum for the formation of ye'elimite. Furthermore, magnesium sources can be added to enable the formation of chromate-bearing spinel-type phases and permanently store / fix chromate in phases that are inert during hydraulic reaction and in the hardened paste. Thus, raw materials

can be used which heretofore typically had to be treated as hazardous waste and stockpiled, as they contain heavy loads of for example chrome.

[00020] Accordingly the above object is solved by a method for producing ternesite or calcium sulfoaluminate (belite, ferrite) ternesite clinker comprising the following steps:

- providing a raw meal comprising at least sources of CaO, SiO_2, Al_2O_3, SO_3 and preferably also of Fe_2O_3 and/or MgO, - sintering the raw meal in a kiln at a temperature ranging from > 1200 to 1400 °C, preferably from 1200 to 1350 °C, to provide a clinker, and
- cooling the clinker,

wherein at least one compound containing chrome is added prior to or during the sintering providing a total content of chrome in the raw meal of ≥ 500 mg/kg, preferably ≥ 1000 mg/kg and most preferred ≥ 2000 mg/kg. Conditions are preferably chosen such that all or almost all heavy metals, mainly chrome, are bound in clinker minerals.

[00021] Preferably the raw meal is made from one or more raw materials providing the following amounts of the components calculated as oxides:
CaO: 35 to 65 % by weight,
preferably from 40 to 60 % by weight, most preferred from 45 to 55 % by weight;
Al_2O_3: 7 to 45 % by weight,
preferably from 10 to 35 % by weight, most preferred from 15 to 25 % by weight;
SO_3: 5 to 25 % by weight,
preferably from 7 to 20 % by weight, most preferred from 8 to 15 % by weight;
SiO_2: 3 to 30 % by weight,
preferably from 5 to 25 % by weight, most preferred from 10 to 20 % by weight;
Fe_2O_3: 0 to 30 % by weight,
preferably from 3 to 20 % by weight, most preferred from 5 to 15 % by weight,
MgO: 0 to 10 % by weight,

preferably from 1 to 5 % by weight, most preferred from 2 to 4 % by weight; Cr_2O_3: ≥ 500 mg/kg, preferably ≥ 1000 mg/kg, most preferred ≥ 2000 mg/kg; wherein all components present, including those not listed above, sum up to 100 %.

[00022] The cooling of the clinker can take place fast or slowly in the known manner. Typically, fast cooling in air is applied. But it is known and can be beneficial for some clinkers to apply a slow cooling over specific temperature ranges, i.e. a tempering step before cooling. Thereby, the content of desired phases can be increased and unwanted phases can be converted into desired ones like e.g. $C_5S_2\$$ and/or $C_4A_{3-x}F_x\$$.

[00023] The compound containing chrome acts as mineralizer. It can be added to the raw meal, e.g. to the raw materials, or be contained in at least one raw material, whereby raw materials and mineralizers are ground together. It can be added after grinding the raw materials to the raw meal at the feed part or in the pre-heater. By adding the mineralizers into the raw material they can be homogenized directly with the raw meal. Alternatively, the mineralizers can be added as powders and/or as silt to sand-like fractions during the processing like e.g. feeding via the kiln inlet, injecting through the burners or at any other suitable point right up to the sintering zone.

[00024] The term "compounds containing chrome" means any material containing chrome metal, chrome ions or chemically bound chrome. The compounds containing chrome are preferably, but not exclusively, selected from the group consisting of industrial side products and wastes like slags (e.g. steel slag, ladle slag, converter slag), ashes (siliceous or calcareous fly ash, waste incineration ash), ore residues, alloys, pigments, slurries and muds (e.g. red mud) or chrome minerals like Cr_2O_3, chromite ($FeCr_2O_4$ to $MgCr_2O_4$ and the solid solutions with other elements like Al), $Na_2[Cr(CO)_5]$, $Na_2[Cr_2(CO)_{10}]$, $Cr(C_6H_6)_2$, $K_3[Cr(CN)_5NO]$, $CrCl_2$, $CrCl_3$, K_2CrF_6, K_3CrO_8, K_2CrO_4, $KCrS_2O_8$, $[CrCl_2(H2O)_4]Cl$, $[CrCl(H_2O)_5]Cl_2$,

$[Cr(H_2O)_6]Cl_3$, $Cr(OH)_3$, CrF_4, CrF_6, $CrBr_4$, CrO_2Cl_2, $Cr_2S_3O_{24}H_{24}$, chromic acid, acetate and formate of chromium. The industrial side products and wastes are most preferred as compound containing chrome. They can contain chrome or chrome oxide as well as mixtures of two or more of the mentioned compounds.

[00025] The amount of compounds containing chrome added in the method according to the invention is usually chosen such that the content of chrome, calculated as Cr_2O_3, is ≥ 500 mg/kg, preferably ≥ 1000 mg/kg, most preferred ≥ 2000 mg/kg with respect to the total weight of the raw meal (including the material added during pre-heating or sintering).

[00026] For Cr metal and compounds with high amount of Cr like Cr_2O_3, chromite ($FeCr_2O_4$ to $MgCr_2O_4$ and solid solutions with other elements like Al), $Na_2[Cr(CO)_5]$, $Na_2[Cr_2(CO)_{10}]$, $Cr(C_6H_6)_2$, $K_3[Cr(CN)_5NO]$, $CrCl_2$, $CrCl_3$, K_2CrF_6, K_3CrO_8, K_2CrO_4, $KCrS_2O_8$, $[CrCl_2(H2O)_4]Cl$, $[CrCl(H_2O)_5]Cl_2$, $[Cr(H_2O)_6]Cl_3$, $Cr(OH)_3$, CrF_4, CrF_6, $CrBr_4$, CrO_2Cl_2, $Cr_2S_3O_{24}H_{24}$, chromic acid, acetate and formate of chromium, and Cr-rich industrial (side) products like e.g. alloys the resulting absolute amount of an added compound will be from a few tenths to a few percent. Typical ranges for additions of compounds like e.g. slags or ashes, that contain low amounts of Cr, are up to 50 % by weight and even more. It is preferred to use industrial side products and waste materials as chrome containing compound.

[00027] In one embodiment, the mineralizer additionally comprises glass powder. The glass powder is preferably a borosilicate glass or an alkali-rich glass. Window glass, borosilicate glass and other glass wastes can be used. The glasses can be composed of

- SiO_2 35 to 85 %, typically from 40 to 80 %
- CaO 0 to 30 %, typically from 7 to 20 %
- Na_2O 0 to 20 %, typically from 4 to 15 %
- B_2O_3 0 to 20 %, typically from 10 to 15 %

- Al_2O_3 0.1 to 10 %, typically from 0.5 to 5 %
- K_2O 0 to 8 %, typically from 0.1 to 2 %
- MgO 0 to 10 %, typically from 0.1 to 5 %
- Fe_2O_3 0 to 1 %, typically from 0.01 to 0.2 %
- SO_3 0 to 1 %, typically from 0.01 to 0.2 %
- others 0 to 5 %, typically from 0.1 to 2 %.

[00028] The glass powder is used in an amount ranging from 0.1 to 5 % by weight, preferably from 1 to 4 % by weight and most preferred from 1.5 to 3 % by weight relative to the total weight of the raw meal.

[00029] It is advantageous when further one or more minor elements are present in the raw meal, preferably added with the mineralizers. These elements are preferably selected from the group consisting of Zn, Ti, Mn, Ba, Sr, V, Cu, Co, Ni, P, fluoride, chloride, and mixtures thereof. Usually they will be added as ZnO, TiO_2, MnO, BaO, SrO, VO, CuO, CoO, NiO, P_2O_5, CaF_2, $CaCl_2$, $FeCl_3$ and mixtures thereof. The elements can be also added in the form of e.g. ashes, slags (e.g. copper or phosphor slag), alloys, red mud or other industrial by-products and residues. They can be added in amounts from 0.1 to 5 % by weight, preferably from 0.5 to 3 % by weight, and most preferred from 1 to 2 % by weight, calculated as oxides or calcium salts, respectively, relative to the total weight of the raw meal.

[00030] The invention is beneficial to all kinds of ternesite and calcium sulfo-aluminate ternesite cements both belite-rich and poor ones as well as with differing amounts of aluminates and ferrites.

[00031] The ternesite and calcium sulfoaluminate (belite, ferrite) ternesite clinker usually comprises
10 - 95 % 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,

5 – 90 % by weight preferably 10 to 60 % by weight and most preferred 15 to 40 % by weight $C_5S_2\$$,
0 - 85 % by weight, preferably 10 to 60 % by weight, 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 calcium sulfate
and up to 20 % by weight minor phases, especially C_3S, C_3A, and one or more X-ray amorphous phases,
all with respect to the total weight of the clinker. The ternesite and calcium sulfoaluminate (belite, ferrite) ternesite cement typically comprises the same phases. However, in case there is little or no calcium sulfate and/or less than the desired amount of $C_4A_{3-x}F_x\$$, those are added. Calcium sulfate is added such that the content of calcium sulfate in the CSA cement ranges from 1 to 30 % by weight, preferably from 5 to 25 % by weight and most preferred from 8 to 20 % by weight of the ternesite and CSA(BF)T cement.

[00032] Furthermore, a part of the total chrome can be bound in mainly magnesium and / or iron bearing chromites.

[00033] The clinker obtained in accordance with the invention can be processed further similarly to the known clinkers, to form cement or binder mixtures. The cement 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.

[00034] The ternesite and calcium sulfoaluminate (belite, ferrite) ternesite cement obtained by grinding the clinker made according to the invention preferably possesses 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. The Rosin Rammler Parameter (slope) n can preferably vary from 0.7 to 1.5, especially from 0.8 to 1.3 and most preferably from 0.9 to 1.15.

[00035] It is preferred to use grinding aids during grinding of the clinker made according to the method of the invention. The efficiency of grinding aids can be enhanced as a more uniform material hardness is achieved and a possible segregation of bulk material during the grinding process is reduced or even completely avoided. Additionally, the grinding aids can be specifically chosen for example for clinkers being low or high in iron and/or ternesite.

[00036] Preferred grinding aids are: Alkanolamines like e.g. monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA) or triisopropanolamine (TIPA), sugars and sugar derivates, glycols like e.g. monoethylene glycols or diethylene glycols, carboxylic acids like e.g. sodium gluconate, oleic acid, sulphonic acids or (lingo)sulphonate. Typical dosages range from 0.01 % to 1.5 % by weight, preferably 0.02 % to 0.5 % by weight, relative to the weight of clinker.

[00037] Preferably, a chromate reducing agent can be added to the cement. The chromate reducing agent can be added before, during or after the cement grinding. Alternatively, the agent can be added during the concrete mixing. The chromate reducing agent can be chosen for example, but not exclusively, from the group of ferrous sulphates, stannous sulphates, stannous chlorides, stannous oxides, sodium sulphates, and mixtures thereof.

[00038] The clinker produced with the method according to the invention can have a reduced hardness gradient, due to the depletion of belite, by the formation of ternesite and the depletion of ferritic phase by formation of an iron-rich solid solution of ye'elimite. This improves the grindability of the produced clinker. Additionally, a significantly enhanced formation of a liquid phase, improved clinker

mineralogy, already at low temperatures of around 1200 °C as well as at 1250 °C can be observed, allowing a unique phase composition/combination.

[00039] Thus, the invention also relates to the clinker obtainable according to the method described and to the cement and binder produced from this ternesite and calcium sulfoaluminate (belite, ferrite) ternesite clinker.

[00040] As known for prior art ternesite and CSA(BF)T cements and binders, further possible substances are e.g. admixtures which are added to the cement / binder but also to concrete and mortar. Typical useful admixtures / accelerators are: calcium nitrate and/or calcium nitrite, CaO, $Ca(OH)_2$, $CaCl_2$, $Al_2(SO_4)_3$, KOH, K_2SO_4, $K_2Ca_2(SO_4)_3$, K_2CO_3, NaOH, Na_2SO_4, Na_2CO_3, $NaNO_3$, LiOH, LiCl, Li_2CO_3, $K_2Mg_2(SO_4)_3$, $MgCl_2$, $MgSO_4$.

[00041] The binder can further contain supplementary cementitious materials in amounts ranging from 10 to 90 % by weight. The supplementary cementitious materials are selected from latent hydraulic materials and/or pozzolanic materials, preferably but not exclusively from latent hydraulic slags like e.g. ground granulated blast furnace slag, natural puzzolans, silica rich (type-C) and/or calcium rich (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.

[00042] The cement and binder according to the invention are useful as binder for concrete, mortar, etc. and also as binder in construction chemical mixtures such as plaster, floor screed, tile adhesive and so on. It can be used in the same way as known CSA and CSA(BF)T cement, whereby it provides improved phase composition and resulting reactivity and/or reduces the environmental impact due to an improved energy utilization.

[00043] 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.

[00044] The invention further includes all combinations of described and especially of preferred features that do not exclude each other. A characterization such as "approximately", "around" and similar expressions 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.

[00045] Example 1

The raw mixes were prepared from reagent grade materials (i.e. Al_2O_3, $CaCO_3$, $CaSO_4 \cdot 2\ H_2O$, Cr_2O_3, Fe_2O_3, SiO_2). The composition of the basic / reference raw mix was 61.58 % $CaCO_3$, 14.06 % SiO_2, 11.96 % Al_2O_3, 10.54 % Fe_2O_3 and 1.86 % $CaSO_4 \cdot 2H_2O$ for a targeted clinker composition of approximately 60 % belite (C_2S), 30 % ye'elimite ($C_4A_3\$$), 6 % ferrite (C_4AF) and 4 % anhydrite ($C\$$). Sample "Ref" comprised no mineralizer, "Cr-0.5" and "Cr-1.0" comprised 0.5 wt.-% and 1.0 wt.-% Cr_2O_3, respectively. The total amount of chrome in the reference raw meal, based on reagent grade materials, was 146 mg/kg (ppm) which corresponds to around 209 mg/kg in the clinker assuming the loss on ignition is about 30 %. The clinkers were fired at 1250 °C or 1300 °C.

[00046] The raw meals were heated up during approximately 30 min from 20 °C to the intended temperature and sintered for 1 hour followed by a rapid cooling in air. The mineralogical phase composition of the comparison clinkers "Ref" and the clinkers according to the invention "Cr" are presented in Table 1, all amounts are in % by weight relative to the total clinker weight

[00047] Table 1

Sample	Ref	Cr-0.5	Cr-1.0	Ref	Cr-0.5	Cr-1.0
mineralizer	none	Cr_2O_3	Cr_2O_3	none	Cr_2O_3	Cr_2O_3
sintering temp.	1250 °C			1300 °C		
Σ C_2S	58.7	47.9	42.6	60.8	48.0	44.0
Σ $C_4A_3\$$	29.2	30.8	32.2	29.6	31.6	32.7
Σ ferrite	6.6	5.4	5.1	5.7	4.9	5.6
$C_5S_2\$$	--	14.5	20.1	--	14.7	17.7
C$	4.2	1.1	--	3.0	0.4	--
C	0.4	--	--	--	--	--
M	0.3	0.3	--	0.3	--	--
S	--	--	--	0.1	--	--
C_2MS_2	0.6	--	--	0.5	0.4	--

[00048] From table 1 it can be seen that additions of 500 and 1000 mg Cr_2O_3 per kg clinker stabilised ternesite ($C_5S_2\$$) towards higher sintering temperatures and further increased the amount of formed ye'elimite ($C_4A_3\$$) at the expense of the ferritic phases, i.e. it enhanced the formation / stabilisation of a cubic iron-rich $C_4A_{3-x}F_x\$$. The presence of around 200 mg/kg chrome in the reference clinker was not enough to provide this effect, as shown by the absence of ternesite in the reference sample. One additional feature is that the ferritic phases in the reference sample are mainly present as approximately C_4AF. In the case of the chrome bearing samples, the ferritic phases are mainly present as approximately C_2F, CF and CF_2.

[00049] These results prove that chrome is a powerful mineralizer for the formation and stabilisation, i.e. towards higher sintering temperatures, of ternesite and furthermore promotes the formation of additional iron-rich ye'elimite.

[00050] Example 2

Raw mixes were prepared from natural raw material sources and industrial by products. The composition of the raw materials is presented in table 2 (in % by weight). The composition of the basic / reference raw mix was 55.55 % by weight ladle slag, 11.00 % by weight LD slag, 13.82 % by weight gypsum, 10.08 % by weight limestone and 9.56 % by weight sand for a targeted clinker composition of (by weight) approximately 45 % belite (C2S), 35 % ye'elimite (C4A3$), 15 % ferrite (C4AF) and 5 % anhydrite (C$). The clinkers were fired at 1250 °C and 1300 °C, respectively. The mineralogy was chosen to be as close as possible to the mineralogy of example 1 but allows at the same time the use of the highest quantity of industrial by products to achieve a sufficient quantity of chrome.

[00051] Table 2

	Limestone	Gypsum	Sand	Ladle slag	LD slag
LOI 1050 °C	43.40	20.95	0.66	6.53	-3.35
SiO_2	0.67	1.78	97.66	3.47	12.92
Al_2O_3	0.20	0.55	0.77	31.00	2.22
TiO_2	0.01	0.02	0.11	0.36	0.32
MnO	0.01	0.00	0.00	0.30	4.96
Fe_2O_3	0.10	0.24	0.19	0.99	32.26
CaO	54.57	32.06	0.09	52.42	31.08
MgO	0.26	0.28	0.02	3.86	8.04
K_2O	0.04	0.10	0.46	0.01	0.00
Na_2O	0.00	0.09	0.07	0.00	0.00
SO_3	0.01	43.61	0.00	0.61	0.01
P_2O_5	0.04	0.03	0.02	0.03	1.10
Sum-XRF-1050°C	99.31	99.71	100.05	99.58	89.56
Cr (IPC-OES) [ppm]	< 2	< 2	8.7	2340.0	222.0

[00052] The raw mixes were placed in corundum crucibles, heated up during approximately 30 minutes from 20 °C to the intended temperature and sintered for 1 hour followed by a rapid cooling in air. The chemical composition of the raw materials and of the two clinkers are presented in Table 3, the mineralogical phase compositions of the two clinkers are presented in Table 4, all amounts are in % by weight relative to the total anhydrous material.

[00053] Table 3

	Raw mix (free of LOI)	Clinker 1250 °C	Clinker 1300 °C
LOI 1050 °C	0.00	0.17	0.13
SiO_2	14.47	14.62	14.90
Al_2O_3	19.03	18.95	18.97
TiO_2	0.29	0.28	0.29
MnO	0.91	0.92	0.95
Fe_2O_3	6.38	5.95	6.03
CaO	48.13	48.37	49.17
MgO	3.40	3.41	3.47
K_2O	0.02	0.02	0.02
Na_2O	0.02	0.01	0.01
SO_3	7.19	6.64	6.11
P_2O_5	0.17	0.17	0.17
Sum-XRF-1050°C	100.00	99.51	100.22
Cr (IPC-OES) [ppm]	522.46	533.50	540.00

[00054] Table 4

Sample	Clinker	Clinker
sintering temp.	1250 °C	1300 °C
Σ C_2S	30.3	30.3
Σ $C_4A_3$$	29.1	29.2
Σ ferrite	10.1	11.7
$C_5S_2$$	11.4	8.2
Minors (including an X-ray amorphous fraction)	19.1	20.6

[00055] From table 4 it can be seen that Cr_2O_3 stabilised ternesite ($C_5S_2$$) towards higher sintering temperatures, as already shown in example 1. Using a mix which contains around 530 mg/kg chrome, it was possible to obtain around 11% and 8% of ternesite at 1250 °C and 1300 °C. This proves that chrome is a powerful mineralizer for the formation and stabilisation towards higher sintering temperatures of ternesite.

Claims

1. A method for producing a ternesite or calcium sulfoaluminate (belite, ferrite) ternesite clinker comprising the following steps
   - providing a raw meal comprising at least sources of CaO, SiO_2, Al_2O_3, and SO_3,
   - sintering the raw meal in a kiln at a temperature ranging from >1200 to 1400 °C to provide a clinker
   - cooling the clinker

   wherein a mineralizer comprising at least one compound containing chrome is added to the raw meal prior to or during sintering providing a total amount of chrome calculated as Cr_2O_3 of at least 500 mg/kg in the raw meal.

2. The method according to claim 1, wherein the sintering temperature ranges from 1250 to 1350 °C.

3. The method according to claim 1 or 2, wherein the total amount of chrome in the raw meal is adjusted to ≥ 1000 mg/kg and preferably to ≥ 2000 mg/kg.

4. The method according to at least one of claims 1 to 3, wherein sources for Fe_2O_3 are additionally provided in the raw meal.

5. The method according to at least one of claims 1 to 4, wherein sources for MgO are additionally provided in the raw meal.

6. The method according to at least one of claims 1 to 5, wherein the mineralizer is added to the raw materials used to provide the raw meal, or enriched in at least one of them, or is added as powder or silt to the raw meal before feeding and/or during feeding at the kiln inlet or is added to the kiln, preferably through the burner, before or at the sintering zone.

7. The method according to at least one of claims 1 to 6, wherein the compound containing chrome is chosen from industrial side products containing chrome.

8. The method according to claim 7, wherein the industrial side products containing chrome are selected from ashes, slags, embers, ores (residues), chrome alloys or mixtures thereof.

9. The method according to at least one of claims 1 to 8, wherein glass powder, which is preferably selected from window glass powder, borosilicate glass powder, powdered waste glass or mixtures thereof, is used as additional mineralizer.

10. The method according to at least one of claims 1 to 9, wherein additionally one or more minor elements selected from the group consisting of Zn, Ti, Mn, Ba, Sr, Cu, V, Co, Ni, P, fluoride, chloride and mixtures thereof is/are used as mineralizer.

11. Clinker obtainable by the method according to any one of claims 1 to 10.

12. Clinker according to claim 11, containing
10 - 95 % 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,
5 – 90 % by weight preferably 10 to 60 % by weight and most preferred 15 to 40 % by weight $C_5S_2\$$,
0 - 85 % by weight, preferably 10 to 60 % by weight, 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 calcium sulfate
and up to 20 % by weight minor phases, especially C_3S, C_3A, and one or more X-ray amorphous phases,
all with respect to the total weight of the clinker.

13. Method of manufacturing a ternesite or calcium sulfoaluminate (belite, ferrite) ternesite cement, wherein a clinker obtainable by the method according to any one of claims 1 to 10 is subjected to grinding.

14. Method according to claim 13, wherein a calcium sulphate source is added.

15. Method according to claim 14, wherein at least one calcium sulphate or mixtures of various calcium sulphates are added in an amount in the range of 1 to 25 % by weight, preferably in the range of 2 to 20 % by weight and most preferred in the range of 4 to 15 % by weight, relative to the total weight of the cement.

16. Method according to claim 14 or 15, wherein the calcium sulphate is added prior to the grinding or a the separately ground calcium sulphate is blended and homogenized with the ground clinker.

17. Method according to at least one of claims 13 to 16, wherein a chromate reducing agent is added, preferably selected from ferrous sulphates, stannous sulphates, stannous chlorides, stannous oxides, sodium sulphates, and mixtures thereof.

18. Method according to at least one of claims 13 to 17, wherein a grinding aid, preferably selected from alkanolamines e.g. monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA) or triisopropanol-amine (TIPA), sugars and sugar derivate, glycols e.g. monoethylene glycols or diethylene glycols, carboxylic acids like e.g. sodium gluconate,

oleic acid, sulphonic acids or (lingo)sulphonate and mixtures thereof, especially DEA or TIPA or mixtures thereof, is used.

19. Cement obtainable by the method according to at least one of claims 13 to 18.

20. Binder comprising a cement according to claim 19.

21. Binder according to claim 20, further containing at least one supplementary cementitious material, preferably in an amount ranging from 10 to 90 % by weight of the binder.

22. Binder according to claim 21, wherein the supplementary cementitious material is selected from latent hydraulic materials and/or pozzolanic materials, preferably from latent hydraulic slags, especially ground granulated blast furnace slag, natural pozzolans, 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, especially rice husk ash, or mixtures thereof.

23. Binder according to claim 20, 21 or 22, further comprising a chromate reducing agent, preferably chosen from the group of ferrous sulphates, stannous sulphates, stannous chlorides, stannous oxides, sodium sulphates and mixtures thereof.

24. Binder according to at least one of claims 20 to 23, further comprising an activator, preferably selected from calcium nitrate, calcium nitrite, CaO, $Ca(OH)_2$, $CaCl_2$, $Al_2(SO_4)_3$, KOH, K_2SO_4, $K_2Ca_2(SO_4)_3$, K_2CO_3, NaOH, Na_2SO_4, Na_2CO_3, $NaNO_3$, LiOH, LiCl, Li_2CO_3, $K_2Mg_2(SO_4)_3$, $MgCl_2$, $MgSO_4$ and mixtures thereof, in an amount in the range of 0.01 to 10% by weight, preferably in the range of 0.1 to 5 % by weight and most preferred

in the range of 0.5 to 2 % by weight, relative to the total weight of the binder.

25. Binder according to at least one of claims 20 to 24, further comprising Portland cement clinker or Portland cement in an amount in the range of 1 to 30 % by weight, preferably in the range of 5 to 25 % by weight and most preferred in the range of 10 to 20 % by weight, relative to the total weight of the binder.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/001013

A. CLASSIFICATION OF SUBJECT MATTER
INV. C04B7/32
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	EP 2 842 923 A1 (HEIDELBERGCEMENT AG [DE]) 4 March 2015 (2015-03-04) paragraphs [0030], [0031], [0033], [0035], [0037] -----	7,8, 11-13, 19-25
X	EP 2 842 924 A1 (HEIDELBERGCEMENT AG [DE]) 4 March 2015 (2015-03-04) paragraphs [0022], [0023] -----	7,8, 11-13, 19,20
X	EP 2 842 922 A1 (HEIDELBERGCEMENT AG [DE]) 4 March 2015 (2015-03-04) paragraphs [0022], [0033], [0034], [0036], [0048]; claim 1 ----- -/--	1-6,9, 10,13-18

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

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Roesky, Rainer

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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.
A	BENARCHID ET AL: "The effect of Cr2O3 and P2O5 additions on the phase transformations during the formation of calcium sulfoaluminate C4A3S@?", CEMENT AND CONCRETE RESEARCH, PERGAMON PRESS, ELMSFORD, NY, US, vol. 35, no. 11, 1 November 2005 (2005-11-01), pages 2074-2080, XP005158766, ISSN: 0008-8846, DOI: 10.1016/J.CEMCONRES.2005.06.005 cited in the application the whole document -----	1-25

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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