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57	ABSTRACT (NOT MORE THAN 150 WORDS)

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The sheet(s) containing the abstract is/are attached.

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~~The figure of the drawing to which the abstract refers is attached.~~

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(54) Title: HIGH BELITE-CONTAINING SULFOALUMINOUS CLINKER, METHOD FOR THE PRODUCTION AND THE USE THEREOF FOR PREPARING HYDRAULIC BINDERS.

(54) Titre : CLINKER SULFOALUMINEUX A HAUTE TENEUR EN BELITE, PROCEDE DE FABRICATION D'UN TEL CLINKER ET SON UTILISATION POUR LA PREPARATION DE LIANTS HYDRAULIQUES

(57) Abstract: The invention relates to a belite-sulfoaluminous clinker, to a method for the Production and the use thereof for preparing hydraulic binders comprising the following mineralogical composition: 5 to 35 %, preferably 10 to 20 % a calcium aluminoferrite phase whose composition corresponds to a general formula C2AXF(1-X), wherein X ranges from 0.2 to 0.8, 15 to 35 %, preferably 20 to 30 % a calcium sulphoaluminate phase "yee' limite" (C4A3S), 40 to 75 %, preferably 45 to 65 % belite (C2S), 0.1 to 10 % one or several mineral phases selected form calcium sulphates, alkali sulphates, perovskite, calcium aluminates, gehlenite, free lime, periclase and/or a vitreous phase and at least a secondary element selected from sulfur, magnesium, sodium, potassium, boron, phosphorus, zinc, manganese, titanium, fluorine, chlorine, wherein the total content of said secondary elements is equal to or less than 15 %.

(57) Abrégé : L'invention concerne un clinker bélite sulfoalumineux, à son procédé de fabrication et à son utilisation pour la préparation de liants hydrauliques, et comprenant comme composition minéralogique : - 5 à 25%, préférentiellement 10 à 20%, de phase aluminoferrite calcique d'une composition correspondant à la formule générale C2AXF(1-X), avec X compris entre 0,2 et 0,8, - 15 à 35%, préférentiellement 20 à 30%, de phase sulfoaluminate de calcium « yee' limite » (C4A3S), - 40 à 75%, préférentiellement 45 à 65% bélite (C2S), - de 0,01 à 10% d'une ou plusieurs phases mineures choisies parmi les sulfates de calcium, les sulfates alcalins, la perovskite, les aluminates de calcium, la gehlénite, la chaux libre et la périclase, et/ou une phase vitreuse, - et au moins un élément secondaire choisi parmi le soufre, le magnésium, le sodium, le potassium, le bore, le phosphore, le zinc, le manganèse, le titane, le fluor, le chlore, la teneur totale desdits éléments secondaires étant inférieure ou égale à 15%.

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HIGH BELITE-CONTAINING SULPHOALUMINOUS CLINKER, METHOD FOR THE PRODUCTION AND THE USE THEREOF FOR PREPARING HYDRAULIC BINDERS

The present invention concerns a belite-rich sulphoaluminous clinker, a method for producing such a clinker and its use for preparing hydraulic binders.

Most modern concretes are made with hydraulic cements generally obtained from Portland cement clinkers.

Portland cement is produced by heating a fine, intimate mixture of limestone, clay, silica and iron ore, to a temperature of over 1400°C in a rotary oven. The calcined mixture, the clinker, takes the form of hard nodules which, after cooling, are ground with calcium sulphates and other added minerals to form the Portland cement.

The mixture of raw materials put into the oven needs to be very rich in limestone in order to obtain a clinker for which the main mineral phase is alite.

Alite is an impure form of calcium trisilicate, Ca_3SiO_5, for which the conventional notation is C3S.

A high percentage of alite, generally over 50%, is indispensable in the mineralogical composition of modern cements, because this is what allows the strength properties to develop rapidly just after setting, and allows the strength properties at 28 days and over to develop sufficiently, in order to meet the specifications, in this area, of most cement standards.

For the remaining of the description of the invention, the following abbreviated notations will be used, unless explicitly stated otherwise, to designate the mineral components of the cement.

- C represents CaO,
- A represents Al_2O_3,
- F represents Fe_2O_3,
- S represents SiO_2,
- $ represents SO_3.

Over the last decades, the level of carbon dioxide, CO_2, in the atmosphere has increased considerably and continues to grow increasingly rapidly. This is linked to human activity, and scientists are unanimous in recognizing that this increase will have important effects on climatic conditions in the future.

Many governments today are taking steps to reverse the trend and are studying how to reduce CO_2 emissions, particularly industrial emissions. The cement industry contributes greatly to these emissions, being responsible for 5% of all industrial emissions of CO_2.

CO_2 emissions in Portland cement clinker production can be reduced by about 10% if the alite is almost totally eliminated. This can be done if the quantity of limestone introduced into the oven is reduced by 10%; the quantity of CO_2 linked to the decarbonatation of limestone during calcination is reduced, as is the amount of fuel necessary for supplying the energy to decarbonate the limestone.

This is accompanied by a reduced oven temperature, which has advantages, as described by E. Gartner, Cement and Concrete Research, "Industrially interesting approaches to low CO_2 cements", 2004, article in press CEMCON-02838.

Portland cement clinkers with a low alite content are always rich in belite, an impure form of calcium disilicate, Ca_2SiO_4, for which the conventional notation is C2S. But the belite-rich Portland cements obtained do not make it possible to obtain sufficient mechanical strength properties in the short term to meet standard requirements, nor to obtain the performance required at present from modern concrete applications.

For these reasons the production of belite-rich Portland cement clinkers are not a satisfactory solution for reducing industrial CO_2 emissions by 10% or less.

In order to develop commercially useable cements, the production of which is associated with low industrial emissions of CO_2, it is necessary to examine other types of hydraulic cement clinkers among these, systems based on calcium aluminates and/or calcium sulphates.

Alumina-rich cements, such as "Fondu Cement" by LAFARGE, are known for their property of acquiring high resistance in the short term; but they sometimes present the well-known problem of "conversion", which is accompanied by a drop in the mechanical strength properties, and moreover highly specialised equipment is needed for their production, and a high fuel consumption, in spite of the low limestone content in the raw materials, and relatively expensive raw materials such as bauxite.

Besides, sulphate-based cements, such as gypsum and anhydrites, are inexpensive and generate little CO_2 during their production, but cannot be used in most concrete applications, due to their low mechanical strength properties and their poor resistance to water.

However, certain types of cements based on calcium sulphoaluminates, written as CSA, are very important because they have simultaneously the positive effects of calcium aluminates and of calcium sulphates in terms of low industrial CO_2 emission without having to use expensive raw materials, to the extent that the use of high quality bauxites could be minimised or be substituted by other materials.

Over the last 30 years, the Chinese cement industry has developed technology and set up a series of national standards concerning sulphoaluminous cements known as the "TCS series", described by Zang L., Su M.Z., and WONG Y.M., in the journal "Advances in Cement Research", Volume 11, n°1, 1999.

However, these cements have not been developed with the intention of reducing industrial emissions of CO_2; they have mainly been developed for application in which high strength had to be obtained in the short term, as for prefabrication.

These "TCS series" sulphoaluminate cements are very rich in the calcium sulphoaluminate C4A3$ phase, known as "Klein salt" or "yee' limit", which makes it possible to obtain high resistance in the short term, but in order to be formed during production, they necessitate introducing into the oven large quantities of high quality bauxite as a raw material. The cost of these cements is prohibitive for them to be used in many applications. Nevertheless, they can be produced with conventional rotary ovens.

The typical formulations of CSA aluminate cements are given in Table 1 below.

Table 1

Phases	C4A3$ (%)	C2S (%)	C4AF (%)
CSA (low ferrite content)	55 to 75	15 to 30	3 to 6
CSA (high ferrite content)	35 to 55	15 to 35	15 to 30

CSA: Sulphoaluminous cement

At the same time, P.K. Mehta in the USA developed other clinkers, the composition of which is based on the calcium sulphoaluminate phase C4A3$ "yee' limit", and described in the journal "World Cement Technology" of May 1980, pp 166-177, and the journal "World Cement Technology" of July/August 1978, pp 144-160.

The clinkers described by Mehta differ from the "TCS series" mainly by their very high free calcium sulphate content in the form of anhydrite.

Although the clinkers described by Mehta have never been marketed, the clinker # 5 reference quoted seems to correspond to the requirements of low industrial emission of CO_2 and have performances that are roughly those of modern Portland cements.

This clinker contains 20% of C4A3$ "yee' limit", 20% anhydrite C$, 45% belite C2S and 15% tetracalcium aluminoferrite C4AF.

However, in spite of the good performances obtained in the laboratory, this clinker and the others quoted by Mehta in his publications, have the disadvantage linked to their high calcium sulphate content; indeed, it is well known that calcium sulphate is unstable at high temperatures at which it dissociates, generating a gas, sulphur dioxide SO_2, particularly in a reducing atmosphere or when the oxygen pressure is low, as is the case in rotary ovens. Therefore the clinkers proposed by Mehta would be difficult to produce in conventional rotary ovens without creating serious environmental problems related to the emission of sulphur dioxide SO_2.

The clinker # 5 quoted by Mehta in the journal "World Cement Technology" of May 1980, pp 166-177 has the following mineralogical composition, by weight compared with the total weight of clinker:

C2S: 45 % C4A3$: 20 % C4AF: 15 % C$: 20 %

with C$: calcium sulphate (anhydrite).

It would nonetheless be desirable to have clinkers leading to reduced industrial CO_2 emissions during their productions, also requiring reduced energy consumption that would make it possible to give added value to industrial by-products which are not usually used as raw materials that enter into their formulation, and which at the same time would make it possible to obtain hydraulic binders with rheological and mechanical strength properties at least equal to those of conventional Portland cements, particularly as to the mechanical performance when young and the development of resistances in the medium and long term.

The aforementioned aims are met according to the invention, by a belite-sulphoaluminous clinker which has, compared with the total weight of the clinker, the following mineralogical composition:

- 5 to 25%, preferably 10 to 20%, of a calcium aluminoferrite phase with a formulation corresponding to the general formula C2AXF(1-X), with X comprised between 0.2 and 0.8.

-15 to 35%, preferably 20 to 30%, of a calcium sulphoaluminate phase "yee' limit" (C4A3$),

- 40 to 75%, preferably 45 to 65% belite (C2S),

- from 0.01 to 10% of one or several minor phases selected from calcium sulphates, alkaline sulphates, perovskite, calcium aluminates, gehlenite, free limestone and periclase, and/or a vitreous phase such as a blast furnace slag or a hydraulic glass.

According to the invention, the clinker contains one or several secondary elements selected from among sulphur, magnesium, sodium, potassium, boron, phosphorus, zinc, manganese, titanium, fluorine, chlorine, present in the following quantities:

- from 3 to 10% of sulphur expressed in sulphuric anhydride,

- up to 5% of magnesium expressed in magnesium oxide,

- up to 5% of sodium expressed in sodium oxide,

- up to 5% of potassium expressed in potassium oxide,

- up to 3% of boron expressed in boron oxide,

- up to 7% of phosphorus expressed in phosphoric anhydride,

- up to 5% of zinc, manganese, titanium or mixtures of these, expressed in oxides of these elements,

- up to 3% of fluoride, chloride, or mixtures of these, expressed in calcium fluoride and calcium chloride,

the total content of said additives being less than or equal to 15%.

Preferably, the clinker according to the invention comprises as secondary elements in the chemical formulation:

- from 4 to 8% of sulphur expressed in sulphuric anhydride,

- from 1 to 4% of magnesium, expressed in magnesium oxide,
- from 0.1 to 2% of sodium, expressed in sodium oxide,
- from 0.1 to 2% of potassium, expressed in potassium oxide,
- up to 2% of boron, expressed in boron oxide,
- up to 4% of phosphorus expressed in phosphoric anhydride,
- up to 3% of zinc, manganese, titanium or mixtures of these, expressed in oxides of these elements,
- up to 1% of fluoride, chloride, or mixtures of these, expressed in calcium fluoride and calcium chloride,

More preferably, the clinker according to the invention comprises as secondary elements in the chemical formulation:

- from 0.2 to 1% of sodium, expressed in sodium oxide,
- from 0,2 to 1% of potassium, expressed in potassium oxide,
- from 0,2 to 2% of boron, expressed in boron oxide,
- a fluorine plus chlorine content less than or equal to 1%, expressed in calcium fluoride and chloride.

Preferably in the preferred clinker above the sodium and the potassium are both present.

The preferred element according to the invention is boron which, introduced into the raw mix in the form of borax, encourages the formation of the belite α' phase during clinkerisation.

Thus, advantageously the belite phase of the clinker is partially or totally crystallised in the α' form.

Preferably, at least 50% by weight of the belite phase of the clinker, is in the α' form.

The clinker comprises at least the following main oxides present in the relative proportions expressed in % of the total weight of the clinker:

CaO:	50 to 61%
Al_2O_3 :	9 to 22%
SiO_2 :	15 to 25%
Fe_2O_3 :	3 to 11%

By comparing with the alite phase (C3S), the main component of Portland cements, a larger amount of belite phase (C2S) in the clinker is totally beneficial. It leads to the reduction of industrial emissions of CO_2 and of the energy consumption. Moreover, the belite contributes to the development of the long term strength of belite-sulphoaluminous cement.

The cement can be obtained by co-grinding the clinker with an adequate quantity of gypsum or other forms of calcium sulphate determined by trials or theoretical calculations. In the case where an excess of calcium sulphate is introduced into the raw mix in order to obtain anhydrite in the clinker, the cement can be prepared directly by grinding the clinker without additional gypsum added to the clinker.

These belite-sulphoaluminous cements can be used with one or several dispersing agents selected from polynaphthalene sulphonates, polymelamine sulphonates, hydroxycarboxylic acids, (poly)acrylic acids, their derivatives and corresponding salts, derivatives of phosphonic acid, and mixtures of these.

These admixtures are commercially available products. As an example, mention can be made of the products OPTIMA 100® and OPTIMA 175®, marketed by CHRYSO®.

The sulphoaluminous clinker according to the invention can advantageously comprise an accelerator or retarder for setting and/or hardening.

Another object of the invention is to provide a production method of a sulphoaluminous clinker comprising:

a) the preparation of a raw mix comprising a raw material or a mixture of raw materials able by clinkerisation to provide the phases C2AXF(1-X), with X comprised between 0.2 and 0.8, C4A3$ and C2S in the required proportions;

b) adding to and mixing into the raw mix at least one additive supplying a secondary element selected from sulphur, magnesium, sodium, potassium, boron, phosphorus, zinc, manganese, titanium, fluorine, chlorine, or mixtures of these, in quantities calculated so that, after clinkerisation, the quantity corresponding to secondary elements, expressed as indicated above, is less than or equal to 15% by weight compared with the total weight of clinker; and

c) calcinating the mixture at a temperature of 1150°C to 1350°C, preferably from 1220°C to 1320°C, for at least 15 minutes in an atmosphere that is sufficiently oxidising to avoid the calcium sulphate being reduced to sulphur dioxide.

Thus, the emission of CO_2 is decreased by more than 25% with respect to that resulting from the clinkerisation of a typical Portland cement.

The raw materials used in the production of the clinker according to the invention are selected among phosphate limestone, magnesium limestone, clays, fly ash, hearth ash, fluidised bed ash, laterite, bauxite, red mud, slag, clinker, gypsum, desulphogypsum, phosphogypsum, desulphurisation mud, industrial slag, and mixtures of these.

The additives supplying secondary elements can be raw materials themselves to the extent that they contain the required secondary elements in appropriate proportions or particular compounds of these secondary elements, for example oxides such as the oxides of sodium, potassium, magnesium, boron (particularly borax), zinc, magnesium, titanium, halides such as calcium fluoride and chloride and sulphates particularly calcium sulphate.

The term "additive supplying secondary elements" as used for the present invention is understood to mean compounds that improve the clinkerisation capacity of the mixture of raw materials, and that stabilise a required crystalline form of the phase in order to improve its reactivity.

The production of the binder, in particular of the clinker according to the invention, consists in grinding the clinker with gypsum until it is fine enough to activate its hydraulic properties. The greater the specific surface of the clinker, the better its reactivity from a hydraulic point of view.

Preferably, the clinker is ground until a Blaine specific surface of over 3000 cm^2/g is obtained, advantageously over 3500 cm^2/g.

The binder can comprise source materials of calcium sulphate and/or calcium oxide.

Advantageously, the binder according to the invention comprises as much as 15% by weight of the total weight of the binder, of a material selected from gypsum, anhydrites and hemihydrates.

According to another advantageous embodiment, the binder according to the invention can also comprise as much as 30% by weight of binder based on the total weight, of at least one material selected from limestone, pozzolana, fly ash and blast furnace slag.

The binder according to the invention can also comprise at least one setting retarder.

Such setting retarders can be selected from gluconates, saccharides, retarders of the phosphoric acid or carboxylic acid type or mixtures of these.

Preferably, the binder according to the invention comprises at least one dispersing agent selected from polynaphthalene sulphonates, polymelamine sulphonates, hydroxycarboxylic acids, (poly)acrylic acids and their corresponding salts, derivatives of phosphonic acid, and mixtures of these.

The invention also includes the production of a slurry, a concrete or a mortar using the binder according to the invention.

The invention is illustrated by the following examples.

In these examples, and unless otherwise indicated, all quantities and percentages are expressed by weight.

Figure 1 presents the evolution over time of mechanical strength properties of different mortars prepared according to the invention compared to that of a reference mortar.

EXAMPLE 1: Preparation of a raw mix of sulphoaluminous clinker

For the production of a sulphoaluminous clinker according to the invention, raw materials are used that are selected from among Orgon limestone marketed by MEAC, BS4® brand alumina-rich clay and/or BS5® brand clay that is less rich in alumina marketed by AGS-BMP, and crushed natural gypsum from Villiers. Small quantities of iron oxide or iron ore, indicated in Table 3, are also used to adjust the ferrite phase content of the clinker.

The chemical formulations of the raw materials used are given in Table 2.

Table 2

%	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	TiO_2	K_2O	Na_2O	Loss on ignition
Orgon fines	55.71	0.01	0.08	0.03	0.05	0.19	0.01	0.01	0.01	43.67
BS4 clay	0.14	41.88	40.26	0.66	0.34	0.08	0.87	0.16	0.12	16.03
BS5 clay	0.38	51.04	32.78	1.30	0.20	0.18	1.33	1.02	0.08	11.92
Gypsum	32.68	1.05	0.15	0.08	44.64	0.11	0.02	0.02	0.02	21.43

The raw materials are dried at 100°C for 4 hours (except gypsum), then ground so that they can be passed through a sieve with a 80 μm mesh.

The crushed and ground gypsum and the BS4 clay have been previously sieved with a 100 μm sieve before incorporating them into the mixture of raw materials.

However, all the particles with a size of over 80 µm account for less than 5% of the mixture of raw materials.

Thus the basic raw mixes are obtained by mixing together limestone, clay, gypsum and iron oxide, for example with BS4 clay following the proportions given in Table 3.

Table 3

% by weight	Orgon limestone	"BS4" clay	Villiers gypsum	Fe_2O_3
Clinker without anhydrite	60.1	28.34	6.58	5.07

From these basic raw mixtures, different raw mixtures are produced by adding an additive or a mixture of additives selected from borax, zinc oxide, magnesium oxide and gypsum (SO_3). The proportions of additives are indicated in Table 4.

Table 4

Raw mix obtained	Additive		Basic raw mix (% by weight)
	Type	% by weight	
Basic raw mix	-	-	100
Raw mix + borax	Borax	4.03	95.97
Raw mix + ZnO	ZnO	2.17	97.83
Raw mix + MgO	MgO	2.40	97.60
Raw mix + SO_4	Gypsum	6.98	93.02

The raw mixes obtained are mixed and homogenised by successive dilutions.

The raw mixes obtained are then conditioned in the form of nodules using a rotary granulator until nodules are obtained with a diameter of 5 to

10 mm.

The nodules obtained in this way are placed in a oven at 100°C for 12 hours.

EXAMPLE 2: Preparation of a sulphoaluminous clinker

250 g of raw mix from Table 4 are placed in crucibles with a diameter of 7 cm and a height of 10 cm.

The crucibles are first brought up to a precalcination temperature comprised between 950 and 975°C, with a rate of heat increase of about 15°C/min. The raw mix is precalcined for 30 minutes.

Then the crucibles are rapidly transferred to a high temperature oven which has previously been heated to a temperature comprised between 950 and 975°C.

The crucibles transferred in this way are brought to thermal equilibrium to be at between 950 and 975°C, then the temperature is increased by 5°C/min, until it reaches a temperature comprised between 1150 and 1350°C during a period of time comprised between 30 and 60 minutes.

After the baking time, the clinkers obtained in this way are cooled in the open air until they reach ambient temperature.

The reduction of CO_2 emission during clinker production is more than 25% compared with ordinary Portland cements, as is shown in Table 5.

Table 5

	Quantity of limestone needed (Kg/t clinker)	Emission of CO_2 from raw materials (Kg/t clinker)	% reduction of CO_2
Sulphoaluminous clinker according to the invention	880	387	26%
Clinker from typical Portland cement	1200	528	—

Moreover, the low clinkerisation temperature and the use of large proportions of gypsum in these sulphoaluminous clinkers, also contribute to the reduction of the emission of CO_2 and the reduction of the amount of energy needed for the clinkerisation of over 20%.

EXAMPLE 3: Preparation of sulphoaluminous cement

The cements corresponding to the different clinkers are obtained by co-grinding, using a laboratory grinder with a capacity of 1 kg, with 8% of gypsum as a setting regulator, except for the clinker corresponding to the raw mix $+SO_4$ in Table 4 which already contains the required amount of gypsum.

EXAMPLE 4: evaluation of the consistency, setting time and mechanical strength properties on mortar.

Using the different cements obtained from the clinkers in example 2, mortars are produced having the following composition:

500 g of cement

500 g of sand-lime with a granulometric size of 0/0.315 mm

250 g of water

After successively introducing the three components into a Kenwood mixer, the mixture is mixed for 30 seconds at low speed, then for 30 seconds at high speed.

These two speeds correspond to those of a standardised mixer used for trials on mortar according to standard EN 196-1.

The mortars obtained are evaluated for their consistency and for their setting time at 20°C.

The setting tests are carried out with a Vicat device, according to standard EN 196-3.

The consistency is evaluated according to the mini-slump method described in the publication Aïtcin P.C, Jolicoeur C, and MacGregor J.G., "Superplasticizers: How they work and why they occasionally don't", Concrete International, vol.16, n° 15, 1994, pp 32-45.

Their mechanical strength properties are measured on 2x2x10 cm^3 test specimens of prismatic mortar prepared at 20°C using metal moulds and unmoulded after 6 hours or 24 hours depending on the case. The test specimens are then kept in water at 20°C until the end of the measurement.

The resistance of the samples obtained is tested according to standard EN 196-1.

EXAMPLE 5: Comparative tests on samples of mortars according to the invention.

A mortar comprising a Portland cement "Saint Pierre la Cour" (SPLC), CPA CEM I, 52 .5 according to standard EN 197-1, is produced according to the method in example 4, to be used as a comparative sample for the different tests.

The results of these tests are given in Table 6 below:

Table 6

Cement	Consistency	Setting time (h)	Compression resistance at 6h (Mpa)	Compression resistance at 24h (MPa)	Compression resistance at 28 days (MPa)
CPA SPLC	Firm	~ 5 .0	0	20.2	62.7
Basic CSA	Plastic	Not measured	14.5	15.0	27.0
CSA Borax	Fluid	~ 4.0	3.2	20.0	53.5
CSA SO_3	Plastic	~ 3.5	3.8	18.0	34.0
CSA ZnO	Firm	~2.0	9.6	18.2	28.0

CPA SPLC: Saint Pierre La Cour Portland Cement

CSA: Sulphoaluminous cement

Basic CSA: Sulphoaluminous cement without additives

The results obtained show that the preferred formulation CSA Borax, according to our invention, has performances comparable to those of SPLC Portland cement.

They also show the influence of the additive on the setting time and the acquisition of mechanical strength properties, particularly for the CSA Borax compound.

EXAMPLE 6: Comparative tests.

A new raw mix of basic sulphoaluminous clinker was prepared in the same way as in example 1, using the same raw materials. Starting from this basic raw mix, five modified raw mixes are produced, in the same way as in example 1, by adding a finely ground additive or mixture of additives. These additives are chemically pure compounds.

Six sulphoaluminous clinkers were prepared from the basic raw mix and from the five modified raw mixes following the operating parameters described in example 2. and using a maximum clinkerisation temperature of 1300°C for 30 minutes.

The chemical formulations of the six CSA clinkers were determined by combining the direct ultimate analyses with calculation methods. The results are given in Table 7:

Table 7: Estimated formulations of clinkers expressed in % by weight of oxides

	Cement used	CaO	Al_2O_3	SiO_2	Fe_2O_3	SO_3	MgO	TiO_2	K_2O	Na_2O	P_2O_5	B_2O_3
1	Basic CSA	52.5	16.9	17.6	7.8	4.5	0.2	0.4	0.1	0.1	0.0	0.0
2	2% Borax	51.5	16.6	17.2	7.6	4.4	0.2	0.4	0.1	0.7	0.0	1.4
3	1%P_2O_5+2%Borax	51.3	16.5	17.2	7.2	4.3	0.2	0.3	0.1	0.6	1.0	1.4
4	2%K_2SO_4+2%Borax	50.8	16.3	16.8	7.4	5.1	0.2	0.3	1.1	0.6	0.0	1.4
5	2%K_2SO_4+2%Borax + 2%$CaSO_4$	50.9	16.0	16.5	7.3	5.8	0.2	0.3	1.1	0.6	0.0	1.4
6	1%P_2O_5+2%Borax + 2%K_2SO_4 +2%$CaSO_4$	50.1	15.8	16.5	6.9	6.1	0.2	0.3	1.1	0.6	1.0	1.3

Entries 2 to 6 Basic CSA + additives

The clinkers obtained are then ground so as to obtain cements with a Blaine specific surface of 3800 ± 100 cm²/g, according to the method described in example 3, except that the weight of gypsum is 12% compared to the clinker in each case.

Six mortars were prepared from these six cements, and their properties were tested (consistency, setting time, mechanical strength properties) in the same way as in example 4.

As a comparison, a new batch of the same Portland cement as that used in example 5 (St. Pierre La Cour CEM I 52.5) was used for the entry 7 mortar.

The results of these mortar tests are given in Table 8 and in Figure 1

Table 8: Mechanical properties of prepared mortars

	Cement used	Fluidity at 15 minutes	Mechanical strength properties (MPa) Time in days				
			0.25	1	7	14	28
1	Basic CSA	normal	6	19	20	24	32
2	2% Borax	normal	2	24	26	50	64
3	1% P_2O_5+2% Borax	high	3	23	29	28	53
4	2%K_2SO_4+2% Borax	fairly high	10	23	31	29	47
5	2%K_2SO_4+2%Borax+2%$CaSO_4$	fairly high	10	24	34	36	36
6	1%P_2O_5+2%Borax+2%K_2SO_4+2% $CaSO_4$	normal	15	29	37	39	40
7	CPA SPLC (CEM I 52.5)	normal	0	15	48	56	67

Entries 2 to 6: Basic CSA + additives

Table 8 and Figure 1 show clearly that all the CSA-based cements lead to better mechanical strength properties at short times than the control Portland cement (N° 7). However at 28 days, the control Portland cement leads to a slightly better mechanical strength (67 Mpa) than that of the best modified CSA cement (64 Mpa). Nevertheless, all the CSA cements modified by additives lead to mechanical strengths in an acceptable range for Portland cements according to European cement standards (> 35 MPa).

All the mixtures produced, except for the one prepared from a mixtures of alkalis, possess an acceptable initial fluidity and setting time.

CLAIMS

1. A sulphoaluminous clinker, characterised in that it contains as phase formulation, compared with the total weight of clinker: 5 to 25%, preferably 10 to 20%, of a calcium aluminoferrite phase with a formulation corresponding to the general formula C2AXF(1-X), with X comprised between 0.2 and 0.8.

- 15 to 35%, preferably 20 to 30%, of a calcium sulphoaluminate phase "yee' limit" (C4A3$),
- 40 to 75%, preferably 45 to 65% belite (C2S),
- from 0.01 to 10% of one or several minor phases selected from calcium sulphates alkaline sulphates, perovskite, calcium aluminates, gehlenite, free limestone and periclase, and/or a vitreous phase,
- and in that it contains one or several secondary elements selected from sulphur, magnesium, sodium, potassium, boron, phosphorus, zinc, manganese, titanium, fluorine, chlorine, present in the following quantities:
- from 3 to 10% of sulphur expressed in sulphuric anhydride,
- up to 5% of magnesium expressed in magnesium oxide,
- up to 5% of sodium expressed in sodium oxide,
- up to 5% of potassium expressed in potassium oxide,
- up to 3% of boron, expressed in boron oxide,
- up to 7% of phosphorus expressed in phosphoric anhydride,
- up to 5% of zinc, manganese, titanium or mixtures of these, expressed in oxides of these elements,
- up to 3% of fluoride, chloride, or mixtures of these, expressed in calcium fluoride and calcium chloride,

the total content of said additives being less than or equal to 15%.

2. A sulphoaluminous clinker according to claim 1, characterised in that it comprises one or several secondary elements in the following quantities, by weight compared to the total weight of the clinker:

- from 4 to 8% of sulphur expressed in sulphuric anhydride,
- from 1 to 4% of magnesium, expressed in magnesium oxide,
- from 0.1 to 2% of sodium, expressed in sodium oxide,
- from 0.1 to 2% of potassium, expressed in potassium oxide,
- up to 2% of boron, expressed in boron oxide,
- up to 4% of phosphorus expressed in phosphoric anhydride,

- up to 3% of zinc, manganese, titanium or mixtures of these, expressed in oxides of these elements,
- up to 1% of fluoride, chloride, or mixtures of these, expressed in calcium fluoride and calcium chloride,

3. A sulphoaluminous clinker according to claims 1 or 2, characterised in that it comprises the following secondary elements, in the following quantities, by weight compared to the total weight of the clinker:
- from 0.2 to 1% of sodium, expressed in sodium oxide,
- from 0.2 to 1% of potassium, expressed in potassium oxide,
- from 0.2 to 2% of boron, expressed in boron oxide
- a fluorine plus chlorine content less than or equal to 1%, expressed in calcium fluoride and chloride.

4. A sulphoaluminous clinker according to any one of claims 1 to 3, characterised in that it comprises at least the following main oxides present in the relative proportions expressed in % of the total weight of the clinker:

CaO:	50 to 61%
Al_2O_3 :	9 to 22%
SiO_2 :	15 to 25%
Fe_2O_3 :	3 to 11%

5. A sulphoaluminous clinker according to any one of claims 1 to 4, characterised in that the belite phase of the clinker is partially or totally crystallised in the α' form.

6. A sulphoaluminous clinker according to any one of claims 1 to 5, characterised in that the belite phase of the clinker in the α' form accounts for at least 50% by weight of the clinker.

7. A sulphoaluminous clinker according to any one of the preceding claims, characterised in that it comprises an accelerator or retarder of setting and/or hardening.

8. A production method of a clinker according to any preceding claim, characterised in that it comprises:
a) the preparation of a raw mix comprising at least one raw material or a mixture of raw materials able by clinkerisation to provide the phases C2AXF(1-X), with X comprised between 0.2 and 0.8, C4A3$ and C2S in the required proportions;
b) adding to and mixing into the raw mix at least one additive supplying a secondary element selected from sulphur, magnesium, sodium, potassium, boron,

phosphorus, zinc, manganese, titanium, fluorine, chlorine, or mixtures of these, in quantities calculated to provide a clinker according to any one of claims 1 to 4;
c) calcinating the mixture at a temperature of 1150°C to 1350°C, preferably from 1220°C to 1320°C, for at least 15 minutes in an atmosphere that is sufficiently oxidising to avoid the calcium sulphate being reduced to sulphur dioxide.

9. A production method for a sulphoaluminous clinker according to claim 8, characterised in that the raw materials used in the production are selected from among phosphate limestone, magnesium limestone, clays, fly ash, hearth ash, fluidised bed ash, laterite, bauxite, red mud, slag, clinker, gypsum, desulphogypsum, phosphogypsum, desulphurisation mud, industrial slag, and mixtures of these.

10. A production method of a clinker according to claim 8 or 9, characterised in that the clinker obtained is then ground with or without calcium sulphate, in the form of gypsum, or hemihydrate, or anhydrite, until a Blaine specific surface of over 3000 cm^2/g is obtained, advantageously over 3500 cm^2/g.

11. A hydraulic binder comprising a mixture of clinker according to any one of the claims 1 to 7 and source materials of calcium sulphate and/or calcium oxide.

12. A binder according to claim 11 characterised in that it contains as much as 30% by weight of the total weight of the binder, of at least one material selected from limestone, pozzolana, fly ash and blast furnace slag.

13. A binder according to claims 11 or 12, characterised in that it contains as much as 15% by weight of the total weight of the binder, of a material selected from gypsum, anhydrites and hemihydrates.

14. A binder according to any one of claims 11 to 13, characterised in that it contains at least one setting retarder selected from among gluconates, saccharides, retarders of the phosphoric acid or carboxylic acid type or mixtures of these.

15. A binder according to any one of claims 11 to 14, characterised in that it contains at least one dispersing agent selected from polynaphthalene sulphonates, polymelamine sulphonates, hydroxycarboxylic acids, (poly)acrylic acids, their derivatives and their corresponding salts, derivatives of phosphonic acid, and mixtures of these.

16. A binder according to any one of claims 11 to 15, characterised in that it is used to produce a slurry, mortar or cement.

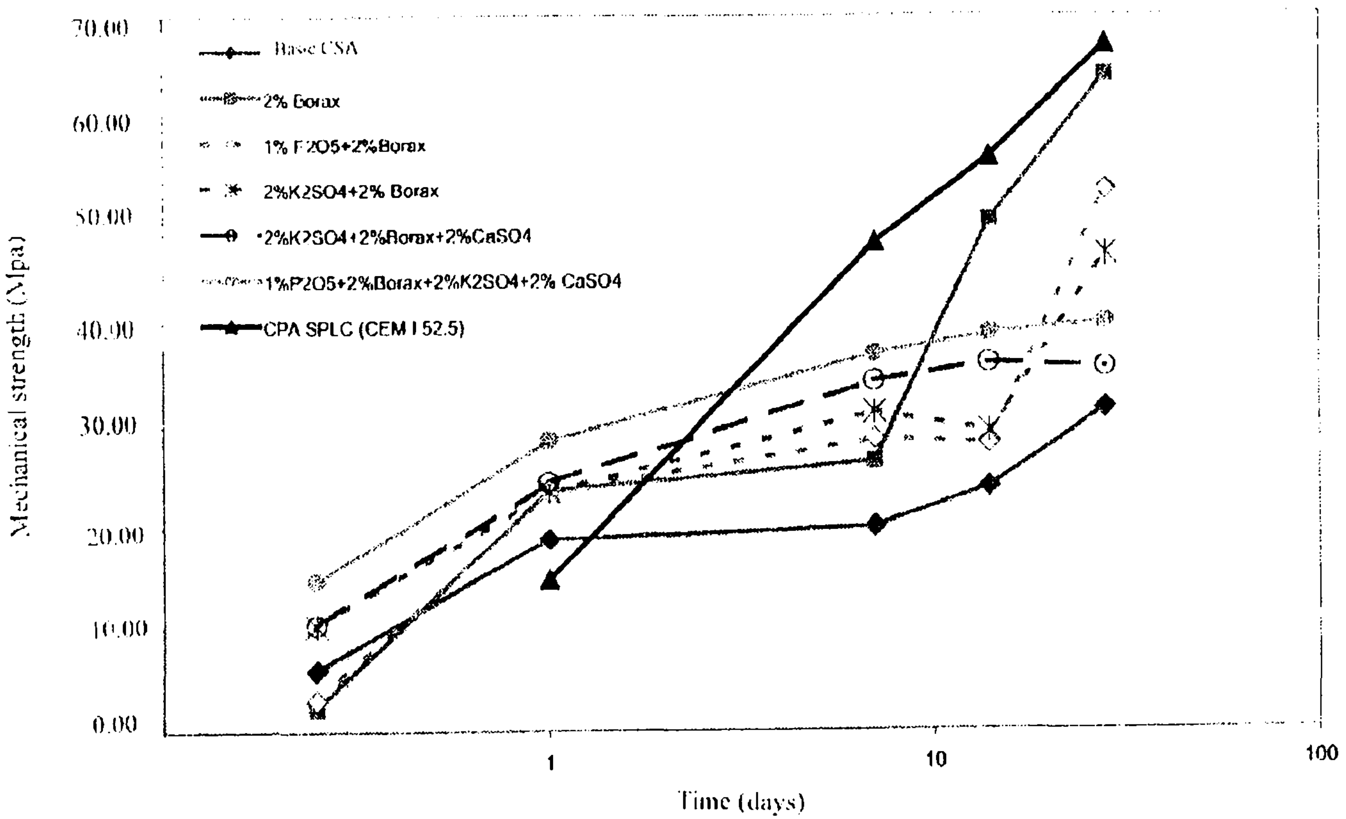

Figure 1

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