

SUPERINDUSTRIA Y COMERCIO
Radicación: 03105205 00000003 Folios: 2
Fecha (AMH): 2004-11-09 17:43:04
Trámite: 002 PATENTES D I REGISTRO/ 530 PETICION
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

SEÑORES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES
E.S.D

REF EXPEDIENTE No. : **03105205**
SOLICITANTE : **CEMEX TRADEMARKS WORDWIDE, LTD**
PATENTE : **CLINKER Y CEMENTO BLANCO CON ALTO**
CONTENIDO DE AZUFRE ...

ASUNTO: SOLICITUD ESTUDIO DE FONDO

DILIA RODRÍGUEZ D'ALEMAN, en mi condición de apoderada de la Sociedad solicitante, por el presente escrito atentamente solicito a Usted que habiéndose surtido la publicación de la presente solicitud, en la Gaceta de la Propiedad Industrial No.543 de fecha Septiembre 1, 2004 se proceda con el estudio de Fondo.

Para tal fin me permito anexar la tasa correspondiente.

Agradezco continuar con el presente trámite.

Señor Jefe,


DILIA RODRÍGUEZ D'ALEMAN
T.P.No. 20824 del CSJ

P-521

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SUPERINDUSTRIA Y COMERCIO
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Folios: 2

NIT : 900176089-2

RECIBO OFICIAL DE CAJA : 04 - 79,732
FECHA : OCTUBRE 12 DE 2004

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CLARKE NODET Y CO. COLOMB	CONSIGNACION	BANCO POPULAR	050-00110-6	23291510	11/10/2004	5,951,000.00

***** C O N C E P T O *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
		05 EXAMEN DE PATENTABILIDAD DE INVEN	353,000.00
		TOTAL :	5 353,000.

SOM: TRESCIENTOS CINCUENTA Y TRES MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 03-105205

EL EXTRACTO DE LA PRESENTE SOLICITUD DE PATENTE DE INVENCION
FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No 543, DE
FECHA 01 DE SEPTIEMBRE DE 2004, EL TERMINO HABIL SEÑALADO POR
LA LEY EXPIRA EL 29 DE NOVIEMBRE DE 2004.

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud calga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____

NO X _____

**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020

Bogotá, D. C., 30 de Agosto de 2006

Doctora

DILIA MARÍA RODRÍGUEZ D' ALEMÁN

Representante **CEMEX TRADEMARKS WORLDWIDE, LTD**

ASUNTO

Radicación No. 03-105205

Trámite 002

Evento 001

Actuación 430

Oficio 10150

Folios 048

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica

1) Documentos estudiados:

- a) Para el presente estudio se tendrán en cuenta el capítulo descriptivo, comprendido en los folios 5 a 22 de la solicitud en estudio.
- b) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 16 reivindicaciones en los folios 23 a 29 de la solicitud en estudio.
- c) Conforme lo establece los artículos 9, 10 y 11 de la decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 28 de noviembre de 2003, y en el momento de la radicación si se reclama prioridad de la primera solicitud presentada en México MX/PA/a/2002/12235

2) Objeto de la Invención

- a) Las reivindicaciones 1 a 16 de la solicitud en estudio se refieren a una composición de clínker de cemento blanco con alta capacidad de fijar el azufre proveniente del coque de petróleo con alto contenido de azufre (>5% S) usado como combustible, y que además dicho clínker presenta bajo consumo energético y el cemento producido tiene rápido fraguado, caracterizado porque contiene las cantidades de las fases del clínker en por ciento peso siguientes: $3\text{CaO} \cdot \text{SiO}_2$ (C_3S): 40 a 75,2 $\text{CaO} \cdot \text{SiO}_2$ (C_2S): 10 a 35, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (C_3A): 0 a 15, $\text{CaO} \cdot \text{SO}_3$ (CS): 0 a 10, $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$ ($\text{C}_4\text{A}_3\text{S}$): 2 a 15, $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ ($\text{C}_{11}\text{A}_7 \cdot \text{CaF}_2$): 0 a 5, % CaF_2 Total: 0.3 a 1.5 medido como CaF_2 , % Fe_2O_3 : 0 a 0.5, y un contenido de SO_3 de entre 1.5 y 5% en peso obtenido por medio de la calcinación de una mezcla cruda que contiene principalmente CaO , SiO_2 , Al_2O_3 , y CaF_2 , usando como combustible coque de petróleo con un contenido de azufre mayor al 5%, a temperaturas de entre 1200 a 1350°C, sin la adición de ningún aditivo que contenga SO_3 en la mezcla cruda.

- b) El anterior producto busca mejorar composiciones de cemento.
- c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a: C 04 B 7/00

3) Claridad de la Solicitud

- a) El artículo 28 de la Decisión 486 de la Comisión de la Comunidad Andina de Naciones establece

"La descripción deberá divulgar la invención de manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla"

La descripción no es clara toda vez que el solicitante emplea unos códigos que no son universalmente aceptados. Aunque en algunas zonas se usan, como Norteamérica, en otras latitudes no lo hacen ni se aceptan. Dado que semejan formulas químicas simples, puede darse una confusión de términos para el lector desprevenido. Por tanto, se le requiere al solicitante para que no haga uso de las abreviaturas como C_3S , C_2S , C_3A , CS , C_4A_3S o $C_{11}A_7.CaF_2$, y en general de los compuestos sobre los que se basa la solicitud.

- b) El artículo 30 de la Decisión 486 de la Comisión de la Comunidad Andina establece que

"Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción. Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior.- Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará reivindicación dependiente múltiple."

El capítulo reivindicatorio no es claro toda vez que:

- i) No se encuentra correctamente redactado. Como se puede observar en dicho capítulo, se encuentran frases largas y prácticamente sin signos de puntuación, por lo que, la idea que quiere expresar el solicitante se torna confusa. Por ejemplo, la reivindicación 1 habla de una composición de clínker de cemento blanco. Se entendería que dicho clínker deberá tener una alta capacidad de fijar azufre, donde el azufre provenga de coque de petróleo, pero no se entiende si el 5% que relaciona corresponde al contenido de azufre en el coque de petróleo o del clínker. Tampoco se entiende cual es el que es usado como combustible. La frase "contiene las cantidades de las fases del clínker" es etérea, imprecisa y confusa. El último párrafo es demasiado confuso también. Todo el problema radica en una errónea redacción.
- ii) Frases ambiguas tales como 'aproximadamente...' deben eliminarse.

- iii) La observación hecha en el punto 3) a) deberá tenerse en cuenta acá.
- iv) La expresión "alta capacidad de fijar" es ambigua. Deberá precisarse la materia contenida en las reivindicaciones
- v) La expresión "bajo consumo energético" es ambigua y no precisa la materia contenida en las reivindicaciones.
- vi) La expresión "rápido fraguado" es ambigua y no precisa la materia contenida en las reivindicaciones
- vii) La expresión "que le confiere una mayor facilidad de molienda" es ambigua, e innecesaria en la reivindicación 9.
- viii) El símbolo @ empleado en algunas reivindicaciones es inaceptable, toda vez que no tiene un sentido claro.
- ix) No son claros los términos empleados por el solicitante en la reivindicación 15. ¿"cenizas volantes"? ¿Los materiales puzolanicos no contemplan los anteriores materiales?

De acuerdo a lo anterior, el capítulo reivindicatorio no cumple con el requisito de claridad de acuerdo a lo establecido en el Art. 30 de la Decisión 486.

4) Determinación del Estado de la Técnica

El artículo 16 de la Decisión 486 de la Comisión establece:

"El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido este incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C 04 B 7/00 y las más cercanas a ellas, se encontró que antes del 10 de diciembre de 2002 (fecha para determinar el estado de la técnica) habían sido publicados los documentos que se enumeran en la siguiente tabla los cuales se relacionan con clínker y cementos blancos.

De acuerdo con lo establecido en el artículo 16 se determinó el estado de la técnica y se encontró el siguiente antecedente:

N°	Documento	Título	Fecha de Publicación
D1	US 5851282	Portland cement clinker and use thereof	1998.12.22
D2	US 5356472	Portland cement clinker and Portland cement	1994.12.18
D3	US 6149724	Hydraulic cement with accelerated high strength development	2000.11.21
D4	US 5374309	Process and system for producing cementitious materials from ferrous blast furnace slags	1994.12.20
D5	US 3767435	Rapid hardening Portland cement clinker composition	1973.10.23
D6	US 4798628	Settable mineral clinker compositions	1987.07.23
D7	EP 0 812811	Hydraulic cement with an accelerated development of high strength	1997.12.17
D8	CA 2193339	Hydraulic cement with accelerated high strength development	1997.12.10

5) Evaluación de los requisitos de patentabilidad

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Los Países Miembros otorgarán patentes para las invenciones, sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas tengan nivel inventivo y sean susceptibles de aplicación industrial".

En cumplimiento con este artículo, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

a) Evaluación del Nivel Inventivo

El art. 18 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en el arte en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica".

El solicitante pretende que le sea protegida una composición de cemento blanco, que comprende $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{SO}_3$, $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$, $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, CaF_2 , y un contenido de SO_3 determinado, donde existen proporciones establecidas. Cada uno de los componentes es posible obtenerlos en cada una de las anterioridades citadas y dichas proporciones, si bien no se encuentran en un único documento, son posibles obtenerlas combinando parejas de documentos citados. En general podría decirse que la presente solicitud carecería de la altura inventiva necesaria para que se le conceda el privilegio solicitado, ya que un técnico podría encontrar lo aquí solicitado partiendo de la técnica conocida

b) Resumen

En conclusión los requisitos de patentabilidad de la presente solicitud se podrían ver afectados así:

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	US 5851282	1 -16	Nivel inventivo
D2	US 5356472	1 -16	Nivel inventivo
D3	US 6149724	1 -16	Nivel inventivo
D4	US 5374309	1 -16	Nivel inventivo
D5	US 3767435	1 -16	Nivel inventivo
D6	US 4798628	1 -16	Nivel inventivo
D7	EP 0 812811	1 -16	Nivel inventivo
D8	CA 2193339	1 -16	Nivel inventivo

6) Notificación

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación debe responder a la notificación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto por el numeral 5.2, literal e) del capítulo quinto del título primero de la Circular Única N° 10 de 2001


ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en la lista, de fecha

07 SET. 2006

Concepto Técnico N°	EXAMINADOR TÉCNICO	EXAMINADOR JURÍDICO
1393	Código No. 202003	Código No.

US005851282A

United States Patent [19] Odler

[11] Patent Number: 5,851,282
[45] Date of Patent: Dec. 22, 1998

[54] PORTLAND CEMENT CLINKER AND USE THEREOF

5,356,472 10/1994 Odler 106/734

[76] Inventor: Ivan Odler, 16 Olde Village Dr.,
Winchester, Mass. 01890

FOREIGN PATENT DOCUMENTS

4204227 2/1993 Germany .
93/21122 10/1993 WIPO .

[21] Appl. No.: 849,641

OTHER PUBLICATIONS

[22] PCT Filed: Nov. 17, 1995

Gimenez et al "Production of cement requiring low energy expenditure", *Zement-Kalk-Gips*, pp. 12-15 Jan. 1991.

[86] PCT No.: PCT/DE95/01621

§ 371 Date: Jul. 18, 1997

§ 102(e) Date: Jul. 18, 1997

[87] PCT Pub. No.: WO96/15996

PCT Pub. Date: May 30, 1996

[30] Foreign Application Priority Data

Nov. 23, 1994 [GB] United Kingdom P 44 41 614.8

[51] Int. Cl.⁴ C04B 7/04; C04B 11/00

[52] U.S. Cl. 106/733; 106/709; 106/735;
106/736; 106/739; 106/763; 106/765; 106/767;
106/768; 106/772; 106/775

[58] Field of Search 106/733, 735,
106/736, 739, 763, 765, 767, 768, 772,
775, 709

[56] References Cited

U.S. PATENT DOCUMENTS

4,036,657 7/1977 Mehta 106/757
4,042,408 8/1977 Murray et al. 106/744

[57] ABSTRACT

A Portland cement clinker free of $C_4A_3\bar{S}$ having the following proportions of clinker phases, in % by wt.:

— C_3S : 40 to 80

— C_2AF : <20

— C_2S : <30

— C_4A : <20

and a SO_3 content from 1.0 to 3.0% by wt., based on the clinker, obtained by burning a mixture of raw materials containing CaO , SiO_2 , Al_2O_3 , Fe_2O_3 and an additive containing SO_3 at temperatures from 1200° to 1350° C. centigrade, the use thereof and a Portland cement.

11 Claims, No Drawings

5,851,282

1

PORTLAND CEMENT CLINKER AND USE THEREOF

The invention concerns a Portland cement clinker, the use thereof and a Portland cement. Portland cement usually consists of a Portland cement clinker and a sulphate carrier, normally gypsum.

A Portland cement clinker is made from a mixture of raw materials containing mainly certain proportions of calcium oxide (CaO), silica (SiO₂), alumina (Al₂O₃) and iron oxide (Fe₂O₃). New compounds, the so-called clinker phases, are formed therefrom by heating the mixture up to sintering. Their typical quantities, in percent by weight, may be given as follows:

—C₃S (3 CaO x SiO₂) 40 to 80

—C₂S (2 CaO x SiO₂) 20

—C₄AF (4 CaO x Al₂O₃ x Fe₂O₃) 4 to 15

—C₃A (3 CaO x Al₂O₃) 7 to 15

The cement mixed with water and hardened has its strength due to the clinker phase C₃S.

Producing the cement clinker requires a considerable expenditure of energy. The latter consists partly of thermal losses in burning (particularly by radiation, exhaust gas losses and hot clinker outputted at the end of the furnace). Another portion of energy is consumed in endothermal reactions, especially in the decomposition of calcium carbonate (important CaO carrier) into calcium oxide.

Accordingly, one endeavors to decrease the energy costs.

First, it seemed to be logic that this goal could be achieved most simply by decreasing the proportion of CaO-rich clinker phases (C₃A, C₂S) and increasing the proportion of the content of the phases with less CaO (C₃S, C₄AF) accordingly.

However, the disadvantage would be that the corresponding cement would fall far behind the usual Portland cements in its development of strength, because the hydration of C₂S and C₄AF proceeds much more slowly than that of C₃S and C₃A.

In this context, it was attempted to replace the clinker phase C₃S by C₄A₂S (wherein S stands for SO₃), because C₄A₂S hydrates relatively fast. In this case, a separate addition of a sulphate carrier into the mixture of raw materials is necessary, the largest part of the sulphate (expressed as SO₃) becoming bound within the phase C₄A₂S.

With this known cement (clinker), it is disadvantageous that C₃S is not formed at all in the burning process, because the formation to C₃S is hindered or prevented by the presence of the sulphates (SO₃). "Zement-Kalk-Gips, 4/1990, p. 199" already describes that the C₃S (alite) content decreases with an increasing SO₃ content in the clinker. Additionally, at burning temperatures as low as about 1250° to 1300° centigrade required for the formation of C₄A₂S no C₃S is formed in the presence of the high SO₃ proportions (3-10% by wt.) required for the formation of C₄A₂S. An increase of temperature is out of the question, because then C₄A₂S becomes unstable and cannot be formed any more.

The DE 42 04 227 C1 describes a Portland cement clinker having a SO₃ content of 3-8% by wt. In addition to C₄A₂S it contains also 30-80% by wt. C₃S. The synthesis of this clinker is achieved by addition of a F⁻ containing additive to the mixture of raw materials. In addition to thermal energy also electrical energy is required for the grinding of the clinker.

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The object of the invention is to provide a Portland cement, the clinker of which is producible at lower burning temperatures and grindable with decreased expenditure of energy than for a conventional Portland cement, the Portland cement formed therefrom showing, after mixing with water, a development of strength which at least equals that of a conventional Portland cement.

Surprisingly, it was found that such a Portland cement clinker is producible with a C₃S content from 40 to 80% by wt. and can be burned at low temperatures of 1250° to 1350°, if a SO₃ containing additive is mixed into the mixture of raw materials, the SO₃ content of the clinker having to be >1.0 to <3.0% by wt. The addition of an additive containing fluorine (e.g. CaF₂ or ZnO) for the acceleration of the burning process is not necessary but possible.

The following advantages result:

By a lower burning temperature the consumption of energy for the clinker production decreases.

The clinker may have higher values of free lime than the clinker burned at higher temperatures, but with the clinker (cement) according to the invention even contents of up to 5.0% by wt. of CaO do not lead to appearances of unsoundness during setting or to losses in strength. Obviously, this is connected with the increased reactivity of the CaO formed at lower temperatures, which, before the setting process, reacts to Ca(OH)₂ and is therefore harmless. With the same lime saturation factor and the same grinding fineness a higher initial strength of the clinker (cement) with regard to conventional Portland cements was found. A part of the calcium oxide necessary for the formation of the clinker phases is added by the sulphate carrier, for example anhydrite (CaSO₄), instead of the calcium carbonate, whereby, with the same lime standard, the energy consumption further decreases.

All important advantage is the high (total) porosity of the clinker, which leads to an easy, energy saving and therefore inexpensive grind. It is usually higher than 8.0 percent by volume.

The development of strength is higher than in the usual Portland cements.

The total SO₃ content of the cement should to be from 2 to 4% by wt.

A cement clinker having the following portions of clinker phases, in % by wt., is preferred:

—C₃S: ~70 (65-75)

—C₂S: ~10 (7-13)

—C₄AF: ~10 (7-13)

—C₃A: ~10 (7-13)

A preferred SO₃ content in the clinker can be given with 1.5 to 2.5% by wt., based on the clinker.

The necessary SO₃ containing component is preferably added in the form of a calcium sulphate carrier. This carrier may be gypsum or anhydrite. But it is also possible to use sulphite and/or sulphate containing industrial residues, like an ash from a fluidized-bed combustion and/or a stabilizate from the flue gas desulfurization. By adding a sulphite containing product a further saving of fuel results, because the oxidation of sulphite to sulphate is an exothermic process.

The respective calcium sulphate carriers may also be used for the production of the finished Portland cement from the described clinker.

To optimize the setting reaction an advantageous embodiment proposes to grind the clinker to a specific surface area

of 2500 to 4000 cm²/g (according to Blaine), wherein the grinding can be effected with little expenditure of energy or a shorter grinding time due to the high porosity of the clinker.

The lower consumption of fuel being possible with the production of the clinker according to the invention has already been pointed out. It was shown by experiments that the consumption of energy decreases by up to 10%.

Furthermore the lining of the furnace (rotary kiln) is worn less because of the lower burning temperature. This also affects the costs advantageously.

Finally, less molten phase develops in burning the clinker (also due to the low burning temperature), which results in the described high porosity clinker. The improved grindability results in a saving of energy in grinding, which may be up to 50%.

As well, harmful emissions, for example emissions of CO₂ and NO_x, are reduced by the lower burning temperatures. Industrial residues containing sulfur like ashes from fluidized-bed combustion may also be processed as component of the raw meal.

The invention will be explained below in more detail by various embodiments.

Sample 1 describes a sulphobeltic cement which is C₂S free but has a C₄A₃S proportion of 20% by wt.

Sample 2 describes a cement according to the invention which is free from C₄A₃S.

Sample 3 concerns a cement according to DE 42 04 227 Cl.

The proportions of the clinker phases, the SO₃ content of the clinker, the selected burning temperature and the total SO₃ content of the cement as well as the values of the compressive strength after 1, 3, 7, 28 and 365 days are indicated in table 1 below.

As a result, the samples according to the invention have a clearly improved initial strength, and, partly, also the further development of strength is drastically higher than that of the comparative sample 1.

In order to show clearly the advantages achievable by the Portland cement according to the invention, a conventional Portland cement which was burned at 1480° centigrade is indicated as sample 4.

The improved development of strength results in the following advantages with regard to the known Portland cements:

Production of cements of higher value with the same lime saturation factor and grinding fineness.

Grinding to a smaller specific surface area with the same development of strength.

Production of blended cements with good development of strength or a higher content of grinding additives.

1. A Portland cement clinker, free of C₄A₃S, having the following proportions of clinker phases, in % by wt.:

—C₂S: 40 to 80

—C₄AF: <20

—C₂S: <30

—C₃A: <20

and a SO₃ content from 1.0 to 3.0% by wt., based on the clinker, obtained by burning a mixture of raw materials containing CaO, SiO₂, Al₂O₃, Fe₂O₃, and an additive containing SO₃ at a temperature from 1200° centigrade to 1350° centigrade.

2. The Portland cement clinker according to claim 1 having a SO₃ content from 1.5 to 2.5% by wt., based on the clinker.

3. The Portland cement clinker according to claim 1, wherein the additive containing SO₃ was added in the form of a calcium sulphate carrier.

4. The Portland cement clinker according to claim 3, wherein the additive containing SO₃ was added in the form of gypsum, anhydrite and/or industrial residues.

5. The Portland cement clinker according to claim 1, wherein the proportions of the C₂S and C₃A clinker phases add up to less than 5% by wt.

6. The Portland cement clinker according to claim 1 having a content of free CaO from 0.5 to 5.0% by wt.

7. The Portland cement clinker according to claims 1 having a total open porosity >8% by vol.

8. The Portland cement clinker according to claim 4, comprising an ash from a fluidized-bed combustion and/or a stabilisate from a flue gas desulfurization as an industrial residue.

9. A Portland cement comprising

a Portland cement clinker, the Portland cement clinker being free of C₄A₃S and having the following proportions of clinker phases in % by wt.:

—C₂S: 40 to 80

—C₄AF: <20

—C₂S: <30

—C₃A: <20

and a SO₃ content from 1.0 to 3.0% by wt., based on the clinker, obtained by burning a mixture of raw materials containing CaO, SiO₂, Al₂O₃, Fe₂O₃, and an additive containing SO₃ at a temperature from 1200° centigrade to 1350° centigrade,

TABLE 1

Nr.	clinker phases (% by wt.)					SO ₃ in the clinker (% by wt.)	burning temperature	total SO ₃ (% by wt.)	compressive strength (N/mm ²)				
	C ₂ S	C ₂ S	C ₃ A	C ₄ A ₃ S	C ₄ AF				1 d	3 d	7 d	28 d	365 d
1	0	60	0	20	20	7.5	1200	14.5	21.0	27.0	29.0	32.5	77.5
2	80	0	10	0	10	2.9	1280	3.9	47.2	59.0	67.0	73.7	89.9
3	40	0	0	30	30	5.9 ¹⁾	1190	16	36.0	37.0	43.5	46.5	49.0
4	80	0	10	0	10	0.0	1480	2	21.5	49.7	72.5	81.5	85.0

¹⁾0.5% by wt. of CaF₂ was added to the mixture of raw materials of these samples

I claim:



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the Portland cement further including up to 2% by wt. of SO_3 in the form of gypsum and/or anhydrite, the Portland cement having a specific surface area according to Blaine from 2,500 to 4,000 cm^2/g .

10. A Portland cement comprising,

a Portland cement clinker having the following proportions of clinker phases, in percent by wt.:

— A_3S : 40 to 60

— C_2AF : <20

— C_2S : <30

— C_3A : <20

and a SO_3 content from 1.0 to 3.0% by wt., based on the clinker, obtained by burning a mixture of raw materials containing CaO , SiO_2 , Al_2O_3 , Fe_2O_3 and an additive containing SO_3 at temperatures from 1200° to 1350° centigrade,

the SO_3 content being from 1.5 to 2.5% by wt., based on the clinker,

the additive containing SO_3 being a calcium sulphate carrier selected from gypsum, anhydrite and/or industrial residues

the Portland cement clinker being free of $\text{C}_4\text{A}_3\text{S}$, wherein the proportions of the C_2S and C_3A clinker phases add up to less than 5% by wt.,

the Portland cement clinker having a content of free CaO from 0.5 to 5.0% by wt., and

the Portland cement clinker having a total open porosity >8% by vol., and

up to 2% by wt. of SO_3 in the form of gypsum and/or anhydrite, having, a specific surface area according to Blaine from 2500 to 4000 cm^2/g .

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11. A method of producing a blended cement, comprising the steps of

forming a Portland cement clinker having the following proportions of clinker phases, in percent by wt.:

— C_2S : 40 to 60

— C_2AF : <20

— C_2S : <30

— C_3A : <20

and a SO_3 content from 1.0 to 3.0% by wt., based on the clinker, obtained by burning a mixture of raw materials containing CaO , SiO_2 , Al_2O_3 , Fe_2O_3 and an additive containing SO_3 at temperatures from 1200° to 1350° centigrade,

the SO_3 content being from 1.5 to 2.5% by wt., based on the clinker,

the additive containing SO_3 being a calcium sulphate carrier selected from gypsum, anhydrite and/or industrial residues

the Portland cement clinker being free of $\text{C}_4\text{A}_3\text{S}$,

wherein the proportions of the C_2S and C_3A clinker phases add up to less than 5% by wt.,

the Portland cement clinker having a content of free CaO from 0.5 to 5.0% by wt., and

the Portland cement clinker having a total open porosity >8% by vol., and

adding to the Portland cement clinker granulated blast-furnace slag, pozzolans or other latent hydraulic materials individually or in blends.

* * * * *

[54] HYDRAULIC CEMENT WITH
ACCELERATED HIGH STRENGTH
DEVELOPMENT

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[*] Notice: This patent based on a continued pro-
visional application filed under 37 CFR
1.53(a), and is subject to the twenty year
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154(a)(2).

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[22] Filed: Dec. 4, 1996

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[31] Int. Cl.⁷ C04B 09/28

[32] U.S. Cl. 106/680; 106/682; 106/715;
106/720; 106/736; 106/739

[36] Field of Search 106/680, 681,
106/682, 715, 726, 736, 739, 737, 768,
772

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[57] ABSTRACT

A method of manufacturing cement based on calcium silicates by forming a clinker through calcining a solution of typical cement precursor raw materials to temperatures of more than 1200° C. in an industrial kiln, preferably with a preheater (typicality of the cementing system type) and providing, selected in such a manner that the clinker from produced has a high content of calcium silicates, calcium aluminates and disilicates aluminates with an other calcium silicates out, preferably during or prior to the grinding thereof, adding to the clinker from produced (with the above recited basic components), effective amounts of calcium sulfate or hydroxide and calcium sulfate, in order to activate said clinker upon said grinding, thus making sure that the clinker sulfate present in the clinker obtained cement product is in a condition to react rapidly during the hydration of said cement, thereby giving rise to the early formation of strength, for which the presence of a pit above 12 is needed. Also claimed is the novel activated cement resulting from the calcination and grinding methods of this invention.

11 Claims, 10 Drawings

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HYDRAULIC CEMENT WITH
ACCELERATED HIGH STRENGTH
DEVELOPMENT

FIELD OF THE INVENTION

The invention relates to the production of high early strength cement which develops high-strength in a short time with reliable predictability; more particularly, the invention relates a method of producing such cement and also relates to the cement itself.

BACKGROUND OF THE INVENTION

Hydraulic cements are known which are composed of materials formed by calcine and defined clinkers from the field of inorganic chemistry, the use of which is based on the chemical reaction of the calcine and other constituents of the cement with water in order to form hydrated compounds which applications to form a mass volumetric mass or form rigid mechanical strength are developed. Within the general concept of "hydraulic cements" there are on the market cements of the above-mentioned type, some capable of very fast development of mechanical strength. There are known as "ultrafast cements".

Said ultrafast cements are substantially composed of calcine silicates of the formula $CaO \cdot Al_2O_3$, and other amounts of calcine silicates ($CaO \cdot Al_2O_3$, Fe_2O_3 , as well as traces of other calcine silicates of the formula $2CaO \cdot 7Al_2O_3$).

The invention of this application is not aimed to such ultrafast cements but rather to those cements based on the calcine silicates/silicates compound of the formula $4CaO \cdot 3Al_2O_3 \cdot 3SiO_2$.

The closest reference to cements based on calcine silicates was made in a French patent granted in 1954 to the firm Pullet et Chassagne, Paris, France, which invention had its origin in the research of Henri Lander. These cements, based on calcine silicates, have their firm known known as Lander cements.

By 1941 the above-mentioned French firm was manufacturing what is known as "expansive and contraction cements", produced from a clinker obtained through calcination of a mixture of suitable compositions, based on gypsum, chips and limestone.

By 1958, in the United States, Klein submitted a paper during the 51st Annual Meeting of the ASTM, wherein he stated that a compound, non-polymerized (which seemed to correspond to an anhydrous calcium silicates), was the cause of the behavior of these expansive cements. Since then practically, such expansive cements based on calcine silicates are known as K cements by ASTM and follow specification No. C-940: Expansive hydraulic cements.

Expansive cements, such as those mentioned above, were manufactured in a mass or less capable way until the Fifth International Congress on the Cement Chemistry, held at Tokyo in 1958, where in the presence of various nations there was agreement identifying the main component of such cements as being calcium silicates (having the formula $4CaO \cdot 3Al_2O_3 \cdot 3SiO_2$).

According to the prior art teachings to obtain such expansive cements, the clinker based on calcine silicates was obtained with Portland clinker, as well as with ground slag from blast furnace, in order to obtain a "non-metallurgical" product. Since then, the cement research-

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on became aware that these cements based on calcine silicates/clinker exhibited earlier and greater strength relative to those obtained with the use of Portland cement alone (as was clearly established, for instance, in U.S. Pat. No. 4,597,556 to Hiram Kinsberg).

Regarding the Kinsberg's invention and according to the teaching derived therefrom, it is particularly important to determine accurately the setting time of the cement by the Vicat method, as the setting time is very fast, thus making the manipulation of the concrete produced from such cement very difficult, even though the use of citric acid is recommended as a setting retardant.

Another problem of the cement produced according to the Kinsberg patent is that the development of the strength thereof is unpredictable and, although in certain instances the anticipated compressive strength can be obtained, frequently much lower strengths are obtained. This problem is due basically to three materials forming the Kinsberg cement, as defined in the corresponding U.S. Patent.

Also regarding the Kinsberg patent, it is pointed out at columns 3 and 4 that the calcine silicates is not thermodynamically stable, and when heated to an industrial kiln, decomposition at temperatures higher than 1200° C.

On the other hand, the Kinsberg patent clearly states at column 5 that, due to the thermodynamic properties of the calcine silicates, it is highly difficult, if not impossible, to obtain clinker resulting from calcination of the raw materials in produce cement containing effective amounts of calcine silicates, calcium aluminates and disilicates aluminates. As a consequence of which, it is pointed out in said patent that clinker thus produced must be admixed with a separate hydraulic clinker containing trisilicates aluminates and disilicates aluminates.

Finally, with respect to the Kinsberg patent, there are doubts about the fact that the compressive strength measured through the use of the test methods identified as ASTM-C-109 or ASTM-C-109-1 (the latter being the standard for the European Community), the required values for such strengths can be obtained. It is also not clear what would be the actual value for such strength, above in the context of the above-mentioned patent the strength of the cement produced according to the Kinsberg method is compared to the strength of Portland cement.

Furthermore, with respect to the problem of measuring the strength as developed by Kinsberg cement, it is not clear which in his method he used to determine the cement setting at different ages thereof, which leads one to believe that such measurements are equivalent to those made regarding Portland cements and in any case he states that they are equivalent. This in fact is not true, since the value of the mechanical strength of any type of hydraulic cement is not an absolute value (such as might be said for the specific gravity or the chemical composition thereof). On the contrary, the value for such strength basically depend on the method employed to evaluate the same. Mechanical strength, in case of hydraulic cements, is a function of the water/cement ratio as well as of the contraction rate. Thus, when any of said ratios are changed, the results in the measuring methods are not comparable.

According to the ASTM method, the conventional ratio is 1:2.75 and the water/cement ratio is about 0.49 for Portland cements. In Kinsberg's patent a conventional ratio of 1:1 is employed and, of course, the water/cement ratio that is used is not clear.

FEATURES OF THE INVENTION

Therefore, it is a feature of the invention to obtain a cement based on calcine silicates, in the process of

Handwritten mark resembling a stylized 'X' or '8'.

TABLE I-continued

Age	High-strength cement 50% Compressive Strength	Portland cement Type I 50% Compressive Strength
42 hrs.	245	Run 2 245
54 hrs.	245	245

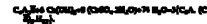
Note: The cement paste in test cylinders that show water absorption during dry cement cure is subjected to the compressive test. Run 2 through its value but the value does not, as it was not tested as soon as possible is applied. Thus, no cement can be used as cement.

All of the results of the compressive strength in the above table are expressed in MPa (kilopascals) and have been obtained by ASTM-C-109 method: Standard Test Method for Compressive Strength of Hydraulic Cement Mortars.

As with other cements based on metakaolin, it is possible to delay the setting of the cement of this invention by means of the use of organic products, such as ethyl acid, as disclosed in the above related article by Collaps and Thierbach.

Based on the studies carried out by the inventors, on the cement hydration reactions, it has been concluded that the fast development of strength with the cement of this invention is due to the formation of straight crystals, which are present from the very moment when the water addition is started. It is believed that only mild compound contributes to the fast development of the cement strength, as the diacid and trisilicic silicates act at the beginning only as inhibitors for the main reaction, due to their slow contribution of calcium ions Ca^{2+} to the solution thus helping in a high pH value substitution, which, as above stated, is important for the development of the main reaction. Said diacid and trisilicic silicates later contribute to a slower and gradual manner, to the further development of the mechanical strength, all due to their slower hydration reaction.

It is hereby agreed regarding the conclusions established by Collaps and Thierbach, that the main reaction for:



However, the authors agree that the contribution of $Ca(OH)_2$ was due to the hydration of calcium silicates, which reaction, as already discussed hereinafter, generates in a manner which is too slow (whereby the contribution of $Ca(OH)_2$ is needed in a more direct manner) to obtain the rapid strength development of the cements of this invention based on calcium metasilicates, (never attained by said authors).

On the other hand, it is possible to track the hydration reactions of the cement of this invention, by means of techniques that are common for the study of hydration reactions in other hydraulic cements. One can consult the suitable literature for such techniques and, therefore, the technique chosen in this disclosure was considered unnecessary.

Some aspects of tracking the hydration reactions (by means of the X-ray diffraction technique) will be described.

The tracking of said reaction is stated one minute after the reaction begins, when water and cement are brought into contact, starting with the diacid in the diffraction diagrams of the X-ray identifying the presence of straight lines

the very first moment. With the passage of time, the lines will be more precise and will grow wider, conversely, these lines corresponding to the calcium metasilicates will be disappearing in short intervals.

For the purposes of this invention, the optimal composition of the invention would be such that, the straight lines would be present from the very first moment and increase rapidly in the following hours, while from then identifying calcium metasilicates would regularly disappear their intensity down to the complete disappearance thereof 24 hours after the hydration reaction starts, thus allowing the total information of straight on the basis of calcium metasilicates. It is obvious that the real behavior of cement must differ slightly from that just herein disclosed, but in essence would be highly similar.

It is to be clearly noted from the above that the teachings of Kinsinger differ clearly from that above stated, since said processes established in his patent that the fast strength developed by the cement based on metasilicates was due to the calcium silicate reaction, as it occurs with silicate cements. In cements according to the present invention, based on calcium metasilicates, there is an calcium silicate present. Moreover, in this invention provision is made for the quantification of the cement composition in order to prevent the presence of any possible composition of calcium silicates (e.g. CSA, CSA/7, etc.).

What is claimed is:
1. A method of producing a calcium metasilicate-containing cement clinker, comprising subjecting a mixture of cement raw materials, to calcining temperatures sufficiently above 1200° C. to assure the consistent consistent formation of diacid silicates and trisilicic silicates in an industrial kiln; said kiln having a preheater; said raw materials being sources of CaO , SiO_2 , Al_2O_3 , and Fe_2O_3 , and being added so as to obtain clinker having a content of 25% to 40% of calcium metasilicates, 10% to 30% of diacid silicates, at least 1% of trisilicic silicates, at least 1% of oxybisilicates so as to assure the suppression of the presence of any silicates apart from calcium metasilicates, and less than 0.5% of free calcium oxide, all percentages being based on the total weight of said clinker obtained.

2. The method of producing cement clinker according to claim 1, wherein the content of diacid silicates is from 10% to 30%.

3. The method of producing cement clinker according to claim 2, wherein said industrial kiln has a preheater.

4. The method of producing cement clinker according to claim 1, wherein said industrial kiln has a preheater.

5. The method of producing cement clinker made according to claim 1, further comprising pulverizing said clinker obtained by addition of an amount of about 1% to 6% of calcium oxide to hydratable and about 3% to 7% calcium sulfate, the latter percentage being in terms of SO_3 present, and subjecting the resulting mixture to grinding, leaving a significant percentage of particles smaller than 45 μ m and maintaining a grinding temperature sufficient to effectively achieve the hemihydrate phase of calcium sulfate.

6. The method of producing cement according to claim 5, wherein the grinding temperature is maintained between 100° and 120° C.

7. The method of producing cement clinker according to claim 1, wherein the calcining temperature is between 1200° and 1300° C.

8. The method of producing cement according to claim 8, wherein said clinker activation through the addition of calcium oxide or hydratable is carried out prior or during the grinding step of said clinker.

9. A calcium metasilicate-containing cement, produced by the method of claim 8.

10. The calcium metasilicate-containing cement, produced by the method of claim 8, wherein said cement upon hydration has a pH higher than 12 and develops a compressive strength of about 30 mpa within a period of about 5 hours due to the formation of straight lines said calcium metasilicates reacts with calcium and sulfate ions.

11. The method of producing cement clinker according to claim 1, wherein the mixture of cement raw materials is selected from the group consisting of limestone, silica, calcium sulfate and clay.

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[31] Int. Cl. _____ C08G 7/14
[32] U.S. Cl. _____ 306/714; 106/721;
106/729; 106/747; 106/789; 106/790
[33] Field of Search _____ 306/714, 721, 729, 747,
106/789, 790; C08G 7/14

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Primary Examiner—Mark L. Bell
Assistant Examiner—Paul Marcotullio
Attorney Agent & Firm—Baker & Botts

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20 October 3: Reading: Elster

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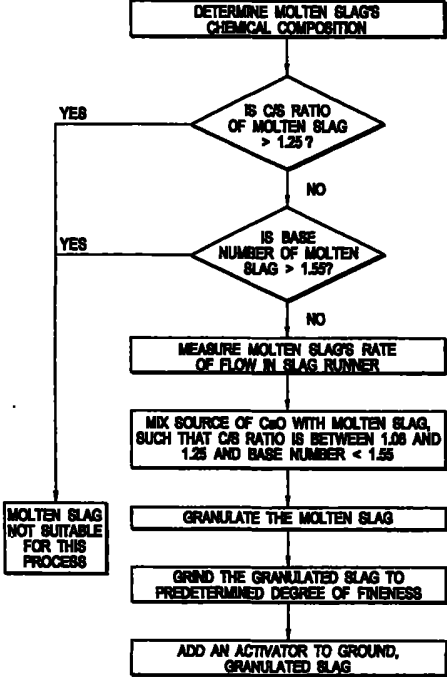
"Methods of Testing Cement: Determination of

ABSTRACT

Process and systems for producing conventional materials from waste have been developed. The conventional melting of a source of CaO with molten slag flowing from at least one slag tap hole of a blast furnace. Sufficient CaO is mixed with the molten slag to make the ratio of CaO to SiO₂ in the C/S Ratio of the slag to be between about 1.05 and 1.25, while maintaining the Base Number of the molten slag less than about 1.80. The slag is then poured into a ladle and ground to a product. The product is then added to a second granulated slag and the C/S Ratio of the granulated slag determines the degree of fluxing to which the granulated slag must be ground to achieve a desired hydration rate in the resultant cementitious material. Conventional materials with C/S Ratios in this range may be ground into fly ash, yet possess the same hydration rates, as other same fly ash ground conventional materials.

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FIG. 1



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FIG. 2

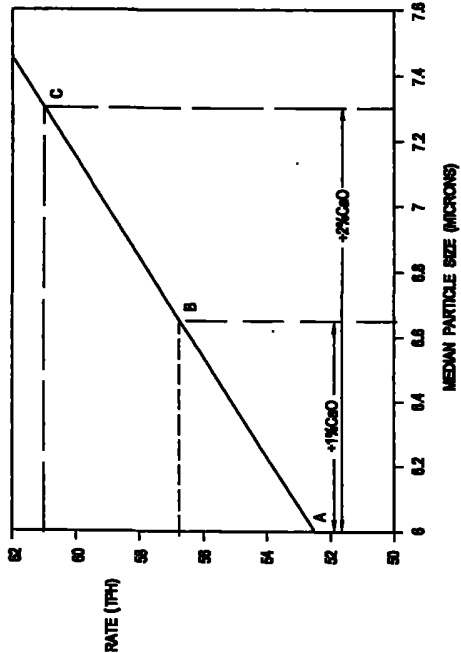
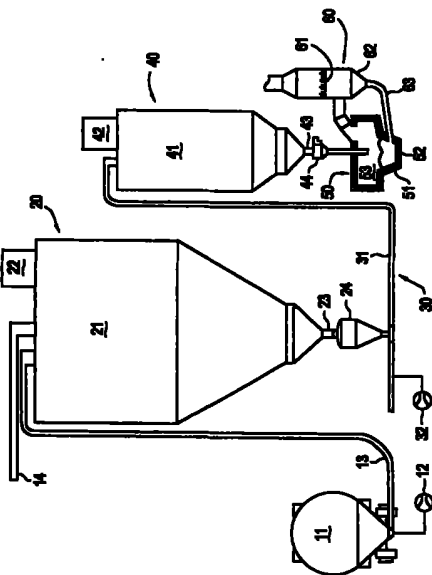


FIG. 3



PROCESS AND SYSTEM FOR PRODUCING CEMENTITIOUS MATERIALS FROM FERROUS BLAST FURNACE SLAG

BACKGROUND OF THE INVENTION

1. Field of the Invention
This invention relates to improvements in the cementitious properties of granulated, furnace blast furnace slag used to produce cementitious materials. Specifically, it relates to a process for making a mixture of calcium oxide (CaO) with surface treatments that form a dry, granular material. When such dry is ground, cementitious properties that are the same as or similar to those of most finely ground cementitious materials can be achieved at a lower specific surface area, thereby saving production and energy costs. Moreover, improved properties can be achieved by grinding such dry to the same or smaller specific surface area as that of a ground, granulated blast furnace slag produced without the addition of a source of CaO. The invention further relates to a system for performing the addition.

2. Description of the Related Art
Portland Cement is the most widely used cementitious material. It is manufactured by heating a finely ground and controlled blend of raw materials (for example, CaO, such as shell, and SiO₂, such as silica sand) with an equivalent amount of CaO, such as shell, in a temperature of about 1100° F. (593° C.). When necessary, other sources of CaO, such as lime, and other sources of SiO₂, such as sand, and other sources of Al₂O₃, such as bauxite, and other sources of Fe₂O₃, such as iron, may also be added. After it is cooled, the resulting clinker is added with gypsum for a mixture of sulphate and gypsum and ground to a fine powder.

There are a number of different processes for making cementitious materials. In a wet process, the mixture of materials is ground with water to produce a slurry which is then fed to a rotary kiln. In this process, the fuel consumption in the kiln is generally high due to the need to dry, as well as to heat the materials. In a traditional dry process, the materials are ground dry to form a powder which is then fed to a kiln. This process generally has a lower fuel consumption than wet processes. Variants of these processes include a semi-dry process, in which water is partially removed from the slurry by fluidization to form a cake of ground material which then is fed to the kiln, or the Lurgi process, in which a dry powder is first combined with the addition of some water after which the mixture is fed to the kiln.

In a conventional granular process, the materials are ground dry to form a powder which is passed through a series of cyclones before it enters the kiln. In these cyclones, the powder is heated with waste gases from the kiln and is gradually heated, such that the powder may be made a temperature of about 1200° F. (650° C.). As a consequence of this preheating, the fuel consumption in this process may be lower than in the processes described above.

The improvement in granular process may be realized by the addition of a cementitious material between the cyclones and the rotary kiln in which about 30 percent of the total fuel required to produce a clinker can be saved. This process is known as a granular process. In this process, the powder may be heated to about 1200° F. (650° C.) before it enters the kiln. An advantage of this process is that a higher output may be achieved for a given kiln size. There is the same chemical efficiency

improvement in granular and granular processes, however, the clinker forming step is usually the most energy intensive in processes for making cementitious materials.

When the finely ground blend of materials is heated in any of the above processes, the cementitious materials usually begin to dehydrate at about 1275° F. (690° C.), and the cementitious materials may dehydrate at about 1300° F. (705° C.). At about 1300° F. (705° C.) the mixture usually begins to melt, so that by about 1350° F. (730° C.) about 35 percent of the mixture is molten. This liquid encourages the formation of clinker and promotes chemical reactions between the CaO, SiO₂, Al₂O₃ and Fe₂O₃ to form four chemical compounds commonly referred to as clinker minerals, which are described in Table I. All percentages expressed herein are by weight.

TABLE I

Chemical Formula	Estimated Percent	Typical Levels in Ordinary Portland Cement (wt. %)
C ₃ S	55-65	45-55
C ₂ S	35-45	35-45
C ₃ A	5-10	5-10
C ₄ A	1-3	1-3
C ₃ A ₂ S ₂ Fe ₂ O ₃	0-1	0-1

When clinker containing these minerals is ground to a fine powder and mixed with water, the clinker reacts rapidly causing the mixture to set. For this reason, clinker may be ground with about five (5) percent gypsum for another appropriate source of calcium sulfate (CaSO₄) to control the reaction, so that green, mature, or setting cement from cementitious materials can be placed and compacted (or poured) before hardening commences.

After setting, the cementitious material gains strength as the clinker minerals compounds hydrate. After 10 days the strength gained is about 70 percent of the ultimate strength. In Portland Cement, according to both early and late strengths, clinker is less reactive and only contributes to strength typically between 10 days after placement for strength. Both materials react with water to form a non-crystalline, calcium silicate hydrate or C-S-H gel. In this gel, the ratio of CaO to SiO₂ (denoted as the "C/S Ratio") is less than that in the unhydrated clinker minerals, and the CaO liberated in the reaction hydrates clinker with water to form calcium hydroxide (Ca(OH)₂).

Cementitious material uses are particularly increased in setting and strength development characteristics, and for this reason, clinker strengths and both clinker and cementitious setting times are specified in the ASTM (American Society For Testing and Materials) C150 standard specification for Portland Cement. In addition to the clinker minerals described in Table I, there are a number of other components which form in the clinker from hydration in the raw materials or fuel. These other components can influence both the clinker setting process and the hydraulic reactivity and cementitious properties of the resulting cementitious material. The level of clinker, mainly SiO₂ and Fe₂O₃, present in Portland Cement may be of particular concern. If cementitious materials are combined with aggregates containing reactive SiO₂ to make concrete, the clinker from the cementitious material may react with

3 this RCN to form an expansive effect which can lead to the cracking and break up of the concrete structure. Densifying and curing the use of compressive containing reactive RCN is difficult. Therefore, in order to avoid this problem, compressive materials with a specific low alkali content are commonly used. Thus, a material equivalent Na₂O of about 0.60 percent is included as an optional limit in the ASTM C150.

One way of solving using compressive materials containing more than about 0.60 percent equivalent Na₂O with aggregates containing reactive RCN, and of avoiding expansive expansion within the mass thus reducing the total energy stresses due to expansion, the compressive materials, is to mix the Portland Cement with other materials which are not compressive by themselves, but which are capable of reacting with the alkali and Ca(OH)₂ formed in the Portland Cement system to form additional compressive hydrates. Suitable materials for this purpose include pozzolanic materials, such as power station fly ash and certain types of naturally occurring volcanic material, or latently hydroscopic materials, such as ground, granulated blast furnace slag.

Slag is used herein, refers to the material that remains after the smelting of a suitable ore, a process which entails the reduction of the ore to a molten state. Smelting of iron ore generally involves the combination of iron ore, a source of carbon, generally coke and a flux, such as limestone, in a blast furnace. The term "blast furnace" or "blast iron furnace" refers to the slag that remains after the smelting of iron ore.

Pozzolanic materials are generally low in CaO and contain SiO₂ and Al₂O₃ in an amorphous or vitreous form, which react with the Ca(OH)₂ released by the hydrating Portland Cement. Latently hydroscopic materials contain sufficient CaO, SiO₂, and Al₂O₃ to form their own calcium silicate and aluminum hydrates. The materials may only be activated in suitable reaction conditions, such as are achieved in the presence of hydrating Portland Cement or by adding small amounts of alkali, such as sodium hydroxide or sodium carbonate, to the latently hydroscopic material.

Consequently, pozzolanic and latently hydroscopic materials, even when mixed with Portland Cement, do not react as fast as Portland Cement and as a result, contribute more to the late strength than to the early strength of a compressive material. An advantage of their lower early reactivity, however, is that pozzolanic and latently hydroscopic materials produce less heat than hydrating Portland Cement during the early reaction stages. If only Portland Cement were to be used, the heat produced in large structures could subject the structure to excessive thermal stresses during the initial hardening and result in crack formation.

In addition to the advantages outlined above, adding Portland Cement with ground, granulated blast furnace slag can improve the workability of concrete, mortar, or grout, thereby making it easier to place and compact (or pump). Mixing can also reduce the possibility of localized expansion, mortar, or grout, thereby improving its durability. At high percentages slag volume, a consistent concrete, mortar, or grout may have volume stability properties equal to or better than an ASTM Type V cement, as defined in ASTM C150.

Grounded blast furnace slag may be mixed with Portland Cement in various ways. The slag may be incorporated with the Portland Cement either as a separate to produce a compressive material. This is a com-

mon practice in conventional concrete. Alternatively, it may be ground alone and then mixed with Portland Cement and is generally preferred in the United States of America and the United Kingdom. An advantage of having the ground, granulated blast furnace slag available separately is that it can be selected by the addition of alkali, such as sodium hydroxide or sodium carbonate, without any Portland Cement, for certain specific applications such as soil stabilization, as described in U.S. Pat. Nos. 4,370,185, and the substitution of sand for well cementing operations, as described by Cowan et al. in Paper 8725 presented at the 67th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers held in Washington, D.C. in October 1992.

In order to optimize hydrating properties, blast furnace slag must be quenched rapidly to preserve the molten slag in a vitreous state. Two processes that are commonly used are granulation and pulverization. In granulation, the slag is quenched by the injection of a large quantity of water under pressure into the slag, i.e., water granulation. If the slag temperature prior to quenching is above the liquidus, water granulation yields a molten slag material with a high degree of vitrification. The water is injected under pressure and at a sufficiently low temperature to quench the slag and break up the molten slag into small pieces. Because of its increased surface area, the molten slag reacts quickly in a pulverization process, the molten slag is directed into a pulverizing device together with a small quantity of water. The slag is then projected into the air and solidifies as small, round, and frequently hollow pellets. As a consequence of the slower quench rate, the degree of vitrification of pulverized slag is usually lower than that of granulated slag. If pulverized to unit closely or different from large, slow cooling pieces, molten slag may react more rapidly than or as compressive material.

Despite the advantages gained by adding Portland Cement with ground, granulated blast furnace slag, through development of suitable an important property, and for this reason, it has been traditional in the United States of America to compare the strength measured in psi after about seven (7) and twenty-eight (28) days curing of a 28/28 blend of Portland Cement and slag, with the strength of a 28/28 blend of Portland Cement, as outlined in ASTM C595. This comparison has been expressed as a slag activity index (SAI). This ratio of strengths provides the comparison of the hydration rates of various types of compressive materials.

The glass content and the composition of the slag, however, will also provide a guide to its hydrating reactivity, and it is also essential to consider the C/S Ratio, or the ratio of the combined CaO, MgO, and Al₂O₃ contents to the SiO₂ content (hereinafter the "hydraulic index"). In general, slag with the highest glass content, the highest C/S Ratio, and Hydroscopic Index is preferred for use with Portland Cement. Nevertheless, the higher the C/S Ratio and Hydroscopic Index the higher the slag melting temperature and the more difficult it is to quench the molten slag to a vitreous state, vitrification of crystalline phases. Because slag is a by-product from the iron making (and steel-making) process, its composition is largely dictated by the composition of the iron ore, which and other raw materials and the efficiency of furnace operation.

Process slag produced in the United States of America, however, usually has a C/S Ratio of about 1. How-

ever, in the C/S content and then, the C/S Ratio of the slag increases, the viscosity of the slag also increases. As the viscosity of the slag increases, however, the efficiency of separation of the blast furnace may decline. Further, sources of CaO may be relatively expensive components in the making of iron, blast furnaces, blast furnaces, may seek to limit the amount of any source of CaO that they add to the molten process, so that they can maintain the costs of making and maintain the efficiency of their furnace.

For example in the United States of America, blast furnaces will commonly consider the Blast Number of the molten slag produced by their furnace.

Blast Number = CaO + MgO + SiO₂

When the Blast Number exceeds about 1.50 and the C/S Ratio exceeds about 1.50, the viscosity of the slag may have significant adverse effects on blast furnace operation and efficiency. In the United States of America, where competition in the iron and steel industry is intense, blast furnaces generally operate their blast furnaces to produce slag with relatively low C/S Ratio and Blast Numbers. In other countries, however, C/S Ratio or Blast Numbers may be higher due to furnace and raw material differences. As a consequence, the hydraulic reactivity of blast furnace slag may be below its potential and is often variable. To produce a suitable granulated blast furnace slag having suitable slag, it is necessary to study grind the slag to achieve very high surface areas to ensure it conforms with ASTM C595 and to vary the fineness of the grind, so that the viscosity of the slag is reduced to a level acceptable to pour. This results in high energy costs to grind the slag, lower output, and higher fueling and manpower costs to meet the slag quality and to adjust slag grinding operation.

Applicant has developed a process and system for incorporating a source of CaO into molten slag such that the C/S Ratio of the slag does not, but the slag can still be successfully granulated to produce a highly vitreous state. Such slag exhibits improved hydraulic reactivity. Therefore, Applicant's process permits low energy ground, granulated slag to be used to produce compressive materials possessing qualities previously available only from more finely ground, granulated slag. This process permits the production of ground granulated slag with improved properties over previous granulated slag which were ground in the same furnace. With such slag, it is possible to utilize applications to suit some general, granulated blast furnace slag with the Portland Cement and still produce high quality compressive materials.

SUMMARY OF THE INVENTION

This invention relates to a process for producing a compressive material from molten furnace slag. In this process, a source of CaO is mixed with the molten slag at a suitable point, so that a ratio of CaO to SiO₂, the C/S Ratio, in the molten slag is a range of about 1.20 to 1.50 is obtained, and the slag has a Blast Number less than about 1.50. The molten slag is then granulated, and the granulated slag is ground to a predetermined degree of fineness. The degree of fineness is determined by the desired composition of the granulated slag and the hydraulic qualities desired in the compressive material. As a solvent, which may be an alkali selected from a group consisting of potassium hydroxide, sodium hy-

droxide, and sodium hydroxide, may then be added to the ground, granulated slag to produce the compressive material.

The source of CaO may be quicklime, such as dehydrated quicklime, lime, or limestone. Quicklime is a natural material the major portion of which is CaO (or CaO in natural combination with a lesser amount of MgO). Lime generally refers to hydrated or slaked lime which is a dry powder obtained by treating quicklime with enough water to satisfy its chemical affinity for water under the conditions of its hydration. Lime also may be associated with some water, resulting in a moist or slaked state. Limestone is a natural material which the major component of which is calcium carbonate (CaCO₃).

Additionally, the molten slag's chemical composition can be determined, and the molten slag's rate of flow can be measured before the source of CaO is mixed with the molten slag.

In addition, the slag can be granulated by injecting a fluid, such as water, or a combination of fluids, such as water and air, into the slag at a sufficiently low temperature, in sufficient quantity, and under sufficient pressure to quench and break up the molten slag.

If the source of CaO is lime, it may also be necessary to add a low volatile fluid, e.g., coke fines or fine balls, with the lime and the molten slag, whereby sufficient heat is generated in the molten slag to dehydrate the lime. It also may be necessary to add oxygen (O₂) to the molten slag to further conditions of this low volatile fluid. Alternatively, if the source of CaO is limestone, it may be necessary to add a low volatile fluid, e.g., coke fines or fine balls, with the limestone and the molten slag, whereby sufficient heat is generated in the molten slag to decompose the limestone. It again may also be necessary to add oxygen (O₂) to the molten slag to further conditions of the low volatile fluid. Further, even when the source of CaO is quicklime, it may be necessary to add a low volatile fluid to the molten slag to generate heat in the slag to promote faster.

Further, a volatile fluid, e.g., wood, may be added to the molten slag, whereby the slag is granulated by gases released during the combustion of the volatile fluid. This granulation may sometimes the mixing of the molten slag and the source of CaO and serve to break up any crystalline layer created by the addition of an excess quantity of lime of the source of CaO to the molten slag.

This invention also relates to a system for producing a compressive material from molten furnace slag flowing from a source of such slag, e.g., a furnace blast furnace. It is of course possible to convert furnace slag that has previously been granulated and allowed to cool. This, however, adds additional energy costs.

The system comprises a slag mixer for directing the molten slag to a mixing point, an injection line means for delivering a source of CaO to a centrally located mixing bin, and means for transferring the source of CaO from this storage bin to the injection line, whereby the quantity of lime of the source of CaO that can be produced during the transfer is suitably controlled. If some slag flow are produced and mixed with the molten slag, they will cause the C/S Ratio at the surface of the slag to also supply. The surface of the molten slag may then crystallize and prevent mixing of the source of CaO with molten slag beneath this crystallized surface.

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Examples of means suitable for delivering the stream of CaO to the centrally located storage bin may include a pneumatic pipeline and a spout and valves fitted with shut-off means for delivering said dry material. Suitable means may include several means capable of carrying about one hundred tons of a stream of CaO . The system further may comprise means for measuring the stream flow rate in the dry stream and means for determining the stream flow's chemical composition. A flowmeter is an example of a mechanism suitable for measuring the stream flow rate of flow. The stream flow's rate of flow in the dry stream may also be less accurately, but adequately, measured by determining the depth of the stream flow in the dry stream, such as by depth gauges on the dry stream, and by determining the rate of flow of the stream flow past a point on the dry stream. Means for determining the stream flow's chemical content may comprise a sampling device, a sample measuring device, and testing equipment capable of measuring and measuring the quantity of chemical components within a sample of stream flow. The system further may comprise means for adding the stream of CaO with the stream flow in the dry stream at a predetermined rate, means for providing the stream flow, means for measuring the quantity of stream flow, and means for providing the stream flow to a predetermined depth of stream flow. In one embodiment, the means for providing may comprise a measuring station at which a fluid at a temperature sufficiently low to quench the dry can be injected into the stream flow in sufficient quantity and at sufficient pressure to quench the stream flow.

Additionally, the system may comprise means for cooling and measuring stream flow, e.g., fluid containing CaO released during the mixing of the stream of CaO with the stream flow. This means for cooling and measuring this waste gas may comprise a ducting chamber surrounding the mixing point, a fan, whereby air and the dust are drawn from the chamber, and a condenser or dry dust collector, whereby the dust and air drawn from the chamber are separated.

In addition, the means for transferring the stream of CaO from the storage bin to the injection bin may comprise a pressure transfer vessel in communication with the storage bin and capable of receiving a quantity of the stream of CaO under pressure from the storage bin. It may further comprise at least one dry air compressor to provide the stream transfer vessel and for providing the stream of CaO through the piping connecting the vessel to the injection bin and a junction for providing dry, compressed air from the dry air compressor or compressors to the piping.

As noted above, the stream of CaO may be quiescent, such as dolomite quiescent lines or flowmeters. If the stream of CaO is flow, the system can further comprise means for adding a low velocity fluid with the flow and the stream flow, whereby sufficient heat is provided in the dry to dehydrate the flow. It also can comprise means for injecting oxygen (O_2) into the stream flow, such as by a sample oxygen lance coupled with a stream of oxygen (O_2).

If, however, the stream of CaO is flowmeters, the system may further comprise means for adding a low velocity fluid with the flow and the stream flow, whereby sufficient heat is provided in the dry to dehydrate the flow. It also can comprise means for injecting oxygen (O_2) into the stream flow, such as by a sample oxygen lance coupled with a stream of oxygen

(O_2). Further, even when the stream of CaO is quiescent, it may be necessary to add a low velocity fluid or oxygen (O_2), or both, to the stream flow in the manner described above, to generate heat in the stream flow. A suitable mechanism for adding a low velocity fluid with the stream flow could include a volumetric feeder of sufficient capacity located adjacent to the adding point. Alternatively, the low velocity fluid may be added with the stream of CaO in a single feeder and added simultaneously with the stream flow.

It is an object of this invention to save energy and energy costs in the construction of conventional materials. It is a feature of this invention that a stream of CaO is added with stream flow to achieve fusion. It is an advantage of this invention that depending on the stream of CaO chosen little or no fuel need be added in this process (or by this system) to achieve the desired fusion nor need the operation of the blast furnace be altered to produce stream flow at a higher temperature.

It is also an object of this invention to reduce energy use, energy cost, work, and expense associated with the production of the stream flow. It is a feature of this invention that dry CaO having a purity of about 1.06 and 1.23 and flow number less than about 1.53 that have been generated by the injection of a sufficient quantity of fluid(s) at a temperature sufficiently low to quench the stream flow and under sufficient pressure have improved hydraulic reactivity over other granulated dry CaO of all degrees of purity. It is an advantage of this invention that conventional materials produced by this process and in this system process the same quality as other more finely ground conventional materials. This also results in higher production rates of conventional materials by this system.

It is a further object of this invention that conventional materials are produced with hydraulic qualities similar to Portland Cement, but at a lower cost. It is a feature of this invention that the conventional material is manufactured from blast furnace slag. Further, advantages of this invention are that stream flow—a waste product—can be recycled and that the operation of the blast furnace need not be modified to produce dry suitable for this process.

It is an additional object of this invention to utilize dry produced from blast furnace which produce dry with lower C/S Ratio and lower flow number, such as those currently operated in the United States of America, to manufacture conventional materials exhibiting improved hydraulic reactivity. It is a feature of this invention that the predominant amount of a stream of CaO are added with the stream flow after it leaves the blast furnace to improve the hydraulic qualities of a conventional conventional material. It is an advantage of this invention that blast furnace can continue to operate within the parameters required by competitive market forces and produce stream flow suitable for the manufacture of conventional materials presenting qualities similar to those of Portland Cement.

Other objects, features, and advantages will be apparent when the detailed description of the invention and the drawings are considered.

BRIEF DESCRIPTION OF THE DRAWINGS
FIG. 1 is a flow chart for a description of a preferred embodiment of the process of the invention.

FIG. 2 is a graph depicting the relation between stream particle size and ball mill grinder production rate in a preferred embodiment of the process.

FIG. 3 is a schematic view showing a preferred embodiment of the system of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, the flow chart indicates, a preferred embodiment of the process for enhancing the hydraulic properties, e.g., the hydration rate or hydraulic reactivity, of stream blast furnace slag. The process may save energy costs by reducing the grinding and/or the quantity of additive, particularly Portland Cement, required to produce conventional materials presenting predominant hydraulic qualities.

Blast furnace slag is a by-product of the smelting of iron, and most blast furnaces are equipped with one or more dry runners, i.e., channels made of fire brick, refractory materials, or other materials, which are built with constant gradients, to direct stream flow away from the blast furnace to a temperature of between about 1800° and 2000° F. (1000° and 1100° C.). The amount of stream flow produced and to chemical composition may depend on the quality of the iron ore used and the amount of iron produced by the blast furnace operation. Further, the chemical composition of the slag may also depend on the quality of the type-steel used in the smelting process. For example, ferro-silicon is commonly used as a deoxidizing agent. If more ferro-silicon is added to the furnace, the CaO content of the resultant slag may increase.

Blast slag commonly has a C/S Ratio in the range of about 0.80 to 1.40. As noted above, however, as the C/S Ratio of slag increases, its viscosity may also increase. Because of the competitive market for iron and steel in the United States of America, U.S. iron conditions strive to operate that blast furnace efficiently, i.e., to produce "lean" slag with low C/S Ratio, low flow number, and, consequently, low viscosity. For example, at Bethlehem Steel's Sparrows Point Facility in Sparrows Point, Md., U.S.A., slag C/S Ratio are generally in the range of about 0.80 to 1.00. When furnace operating conditions are very variable, slag may be produced with higher C/S Ratio. Slag with C/S Ratio greater than about 1.25 or with flow number greater than about 1.50, however, are not suitable for this process.

It is preferred that the chemical content of the stream flow is determined before the stream of CaO is added with it. This may be done by standard sampling techniques and laboratory analysis. Blast furnace operators commonly use standard chemical analysis on each sample, so that the efficiency of the blast furnace operation can be continuously monitored. Nevertheless, for this process, sampling equipment, laboratory testing equipment, and related laboratory personnel are probably available for and thus testing of the stream flow's composition. Automated testing equipment capable of continuously testing and reporting the chemical composition is preferred for accomplishing this step. While various chemical tests can be performed, it is also preferred that at least the CaO , MgO , SiO_2 , and Al_2O_3 contents are measured, and the C/S Ratio and flow number are calculated.

It is also preferred that the rate of flow of the stream flow is measured. The rate of flow of the stream flow can be measured in tons per minute (TPM). For example, at

Bethlehem Steel's Sparrows Point Facility, the rate of flow of the slag may average about three (3) TPM per dry runner, but may range between about one (1) and ten (10) TPM. The rate of flow of the slag may be adequately calculated by observing the depth of the slag in the dry runner and determining the rate of the flow of stream flow past a point on the dry runner. Preferably, however, the rate of flow of the stream flow may be measured by an automatic flowmeter which can provide continuous measurement of the rate of flow of the stream flow.

If the chemical composition and rate of flow of the stream flow are known or can be calculated by the means described above, the stream of the stream of CaO required to achieve a desired range of C/S Ratio and flow number can be calculated. The preferred stream of CaO is quiescent, and dolomite quiescent is the preferred type of quiescent. Quiescent is preferred because it flows with the stream flow at temperatures in the range of about 1800° to 2000° F. (1000° to 1100° C.). Therefore, no additional heat or fuel to produce heat may need to be added to the stream flow to produce the process. When using quiescent as the source of CaO , current tests have shown that blast furnace in the CaO content of the stream flow of up to about 4.0 percent +/- 0.5 percent may be obtained without the addition of fuel to generate additional heat in the stream flow.

If, then, such as dolomite or hydrated lime, is the source of CaO , it may be necessary to add a low velocity fluid, e.g., water flow or air flow, to the stream flow in order to generate sufficient heat to dehydrate the flow. It also may be necessary to add oxygen (O_2) to the stream flow to facilitate the dehydration of the low velocity fluid.

If, however, limestone is the source of CaO , it may be necessary to add a low velocity fluid to the stream flow in order to generate sufficient heat to dehydrate the limestone, i.e., remove the CaCO_3 to CaO and CO_2 . It also may be necessary, to add oxygen (O_2) to the stream flow to facilitate the dehydration of the low velocity fluid.

The mixing of the stream of CaO and the stream flow can be accomplished in several ways. The least expensive and, therefore, a preferred method is to supply a stream of CaO ground to various degrees of fineness, such that the stream of CaO will flow into the stream flow and disperse throughout the stream flow as it discharges. It is preferred that if quiescent is the source of CaO , the quiescent should be crushed or ground to an average diameter of about 0.075 inches (60 mesh). It is also preferred that the stream of CaO does not contain an excessive amount of fines. Fines tend to float on the surface of the stream flow and to remove the surface layer of the stream flow with CaO , as they discharge. This tend to remove may cause the C/S Ratio and the viscosity of the surface layer of the stream flow to increase rapidly. The increase in the C/S Ratio also may cause the crystalline phase properties of the surface layer to increase. A layer of crystalline slag may then form on the surface of the stream flow and prevent the desired mixing of the stream flow with the crystalline layer and the stream of CaO .

There are several methods to inhibit the formation of such a crystalline layer and to encourage proper mixing, including the physical mixing of the stream flow and the stream of CaO and the addition of means for creating turbulence in the stream flow at the mixing point. A preferred method is to add a velocity fluid, such as a wooden board, to the stream flow at the mixing point.

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In the case of difficulty in grinding the slag sample, and the relative amounts of energy necessary to grind the sample to a predetermined degree of fineness.

TABLE IV
Slag No. 1

Slag No.	Grinding Time, min.	Grinding Time, min.	Grinding Time, min.	Grinding Time, min.
157	15	15	15	15
158	15	15	15	15
159	15	15	15	15
160	15	15	15	15
161	15	15	15	15
162	15	15	15	15
163	15	15	15	15
164	15	15	15	15
165	15	15	15	15
166	15	15	15	15
167	15	15	15	15
168	15	15	15	15
169	15	15	15	15
170	15	15	15	15
171	15	15	15	15
172	15	15	15	15
173	15	15	15	15
174	15	15	15	15
175	15	15	15	15
176	15	15	15	15
177	15	15	15	15
178	15	15	15	15
179	15	15	15	15
180	15	15	15	15
181	15	15	15	15
182	15	15	15	15
183	15	15	15	15
184	15	15	15	15
185	15	15	15	15
186	15	15	15	15
187	15	15	15	15
188	15	15	15	15
189	15	15	15	15
190	15	15	15	15
191	15	15	15	15
192	15	15	15	15
193	15	15	15	15
194	15	15	15	15
195	15	15	15	15
196	15	15	15	15
197	15	15	15	15
198	15	15	15	15
199	15	15	15	15
200	15	15	15	15

Based on the information provided in Tables III and IV, it can be concluded that over a fineness range of about 200 to 800 mesh, the slag to which addition was added requires about four (4) percent less energy to grind to a predetermined degree of fineness than untreated slag. Further, by adding addition with the molten slag, the hydraulic viscosity of the slag increased such that it is easier to achieve the same rates (7) dry strength, normal dry strength is about 1000 psi. This would result in a saving of about 25 percent of the energy required for grinding. Moreover, in practice ground, granulated slag with the same rates (7) dry strength as normal slag with a surface area of 2000 mesh, the surface area of the ground slag could be lowered by at least about 300 mesh. This would result in a saving of about 25 percent over the energy required for grinding normal slag.

FIG. 3 represents a preferred embodiment of a system for producing the process described above. The structure and operation indicated are detailed in part by the flow diagram operation contained in FIG. 4, which is incorporated herein by reference. FIG. 5, shows the following a source of CaO 20, preferably comprises a roller 21 and a hopper (not shown) and piping 22 for discharging the source of CaO from roller 21 to a rotary burner 23. Alternatively, a rotary burner 23 may be used to give a source of CaO from a ship, barge, or other facility to storage bin 24. Preferably, burner 23 has a diameter of at least about 2 inches (5.1 cm). A dry air compressor 25 provides dry compressed air to piping 26 for pneumatically transferring the source of CaO from roller 21 to storage bin 24.

Storage bin 24 comprises a bulk storage chamber 25, a pneumatic transfer vessel 26, and piping 27 for placing storage chamber 25 in communication with transfer vessel 26. Storage chamber 25 is provided with dry compressed air, so that the source of CaO can be transferred from storage chamber 25 to transfer vessel 26, it

is preferred that storage chamber 25 has a capacity of about 200 to 800 short tons. A dust collector 28 is connected on storage chamber 25 to collect the source of dust released during the delivery of the source of CaO to storage chamber 25.

Means of transferring the source of CaO 20 from transfer vessel 26 to injection bin 40 comprises transfer piping 31 which joins transfer vessel 26 to injection chamber 41 and at least one, but preferably two, dry air compressors 32 supply dry compressed air to pneumatically transfer the source of CaO from transfer vessel 26 to injection chamber 41. It is further preferred that at least one dry air compressor 32 provides dry compressed air at pressure sufficient to transfer the source of CaO at a rate of about 10 (10) TPD.

Injection bin 40 comprises injection chamber 41, a volumetric feeder 44, and piping 45 for connecting injection chamber 41 to volumetric feeder 44. Preferably, injection chamber 41 has a capacity of about 10 short tons. It is preferred that the source of CaO is transferred from injection chamber 41 to volumetric feeder 44 by means of dry compressed air. Alternatively, however, injection chamber 41 can be connected above volumetric feeder 44, and the source of CaO can be gravity fed to volumetric feeder 44. It is further preferred that volumetric feeder 44 is capable of delivering a source of CaO at delivery rates between about 10 (10) and 100 (100) TPD. A variety of suitable volumetric feeders, such as the Anderson 1502, are commercially available. Preferably, suitable volumetric feeders should be capable of feeding the source of CaO at variable rates up to about 100 cubic feet (2.83 m³) per hour. Alternatively, however, the source of CaO may be added with the molten slag by a feeder that measures the weight, rather than the volume, of the CaO to be added. A dust collector 46 is connected on injection chamber 41 to collect source dust released during the transfer of the source of CaO to injection chamber 41.

The source of CaO is mixed with molten slag 33 in a dry mixer 34 at a mixing point 35. Dry mixer 34 is preferably constructed of the batch or outside rotating method. Preferably, mixing is accomplished by using a rotating drum mixer. The drum mixer 34 may also be employed with a source for cooling the source of CaO at point of mixing 35. A preferred source for cooling the source of CaO is a water-cooled roller (not shown) located in dry mixer 34. It may not always be possible to add molten slag to an existing dry mixer because the position of the dry mixer was established when the plant layout was built. In these cases, it may be preferred that a batch processor (not shown) is mounted on the side of dry mixer 34 or a batch processing processor (not shown) is mounted on the floor of dry mixer 34. These wedge-shaped processors may cause dry 35 to hit back on itself and create the desired turbulence in mixing point 35.

Dry mixer 34 may be replaced with means for supplying (not shown) dry 35 to it from the plant furnace. These means for supplying are a component of the means for desiccating the molten slag's chemical composition (not shown). Dry mixer 34 may also be replaced with means for measuring the rate of flow (not shown) of dry 35 in dry mixer 34. Preferably, the means for desiccating the chemical composition of the molten slag are capable of the continuous sampling of

slag 33 and the continuous analysis of such slag samples. It is also preferred that the means for measuring the rate of flow of dry 35 is a flowmeter (not shown) capable of continuously measuring the rate of flow of dry 35 in dry mixer 34. It is further preferred that the output from the means for desiccating the chemical composition of dry 35 and the output from the means for measuring the rate of flow of dry 35 are provided to a volumetric feeder control unit (not shown) such that volumetric feeder 44 can be automatically adjusted to provide sufficient amounts of the source of CaO to maintain the C/S Ratio of dry 35 to the range of about 1.05 to 1.25.

Preferably, means for collecting and removing source dust released during mixing of the source of CaO and slag 33 are located at mixing point 35. Dry mixer 34 is preferably enclosed in a dusting chamber 36. A fan (not shown) draws air and source dust from dusting chamber 36 and into a scrubber 37. It is preferred that scrubber 37 is equipped with means for expelling the air and the source dust 38, such as water spray heads. It is further preferred that scrubber 37 is equipped with means for collecting the source dust 38 and a return line 39 for returning the collected source dust to dry 35. Alternatively, a dry dust collector (not shown) could be used to remove source dust from the air. In a dry dust collector, air and dust are passed through a permeable fabric on which the dust collects. Dust is then removed from the fabric by use of compressed air or by mechanical means, e.g., shaking. Use of dry dust collector, however, is limited by the heat to which the fabric can be subjected.

It is preferred that dry mixer 34 discharges dry 35 to a granulating system (not shown). The granulating system is preferably equipped with at least one field for molten (not shown) for heating (not shown) at a temperature sufficiently low to quench the molten slag and in sufficient quantity and under sufficient pressure into the molten slag. This field injection system and breaks up the slag, thereby granulating it. Preferably, the field is water at ambient temperature, and it is injected into the molten slag at a rate of about two (2) times the rate of flow of the molten slag and at a pressure of about 20 psi (1381 kPa).

Although wet granulated slag can be ground, it is preferred that the granulated slag is desiccated as part of the step of grinding the granulated slag. This can be accomplished by heating the granulated slag to promote evaporation of the source water. Desiccated by this method, however, may require the expenditure of additional energy and the creation of additional structures in which to heat the wet, granulated slag. The preferred method of desiccating the granulated slag is simply to transfer the granulated slag to a filter bed run in which the source water can drain from the granulated slag naturally. Alternatively, the granulated slag may be desiccated by use of a rotating slag drum which can operate at a relatively low speed and use gravitational force to desiccate the slag.

It is further preferred that as part of the step of grinding the granulated slag, the water content of the granulated slag is reduced to a range of about two (2) to three (3) percent. If necessary, a dryer or heated granular drying chamber may be a preferred means of reducing the water content to the desired range.

Before the granulated slag is ground, its chemical composition should be determined and the degree of fineness required to obtain a predetermined reactivity

should be calculated. Means for measuring the granulated slag's chemical composition (not shown) preferably comprise a means for drawing a sample of the slag after granulation and means for analyzing the sample to determine its chemical composition. It is further preferred that the measuring of the chemical composition is continuous and that the output of this measuring is provided to a granular control unit (not shown). Preferably, the granular control unit will instruct the granular (not shown) as to the degree of fineness desired, given the desired characteristics of the cementitious material and the chemical composition of the granulated slag.

It is also preferred that the granular (not shown) is a ball mill (or tube) grinder. Such grinders can provide continuous grinding and are available from a variety of commercial sources. A ball mill grinder comprises a large diameter, steel cylinder which is filled with cast alloy balls of steel that vary in size between about 0.625 and 4 inches (1.58 and 10.16 cm) in diameter. The granulated slag enters one end of the cylinder and is ground between the balls as the cylinder is rotated. The ground, granulated slag discharged from the other end of the cylinder is separated into two categories. Slag that has been sufficiently ground can be added together with an activator to form a cementitious material. Slag that is too coarsely ground is returned to the granular for further grinding. Alternatively, a high pressure roll compressor granular may be used instead of or in conjunction with the ball mill grinder.

The preferred means of adding an activator to the ground granulated slag is to mix it with Portland Cement and add water. The reaction of the Portland Cement and the water produces a mixture of calcium hydroxide. The adding of the ground granulated slag with the appropriate amount of Portland Cement is preferably performed by continuously variable proportions.

The dimensions and capabilities provided for the various components of the system may be varied to accommodate different plant layouts, facilities, and production capacities. Although a detailed description of the present invention has been provided above, it is understood that the scope of the present and the system are not to be limited thereby, but are to be determined by the claims which follow.

1. claim

2. A process for producing a cementitious material from molten slag, said molten slag from a source of CaO, MgO, and SiO₂, comprising:

3. adding a source of CaO with said molten slag, said source of CaO to SiO₂ in said molten slag is a range of about 1.05 to 1.25 is obtained and said molten slag has a Basic Number less than about 1.25, wherein said Basic Number equals (CaO+MgO)/SiO₂;

4. granulating by breaking up and quenching said molten slag and

5. grinding said granulated slag to a degree of fineness to obtain a granulated slag.

2. The process of claim 1 further comprising the steps of:

3. adding an activator to said ground, granulated slag.

3. The process of claim 2 wherein the step of granulating said molten slag comprises heating said slag to a temperature effective to quench said molten slag into said molten slag at a sufficient rate and at a sufficient pressure to granulate said molten slag.

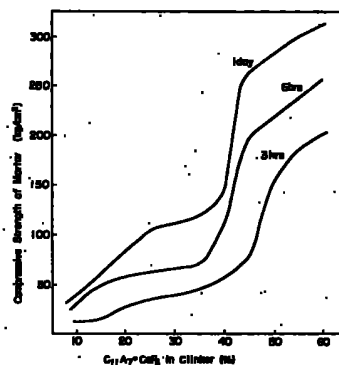
4. The process of claim 3 wherein said solvent is selected from an ester group consisting of potassium hydroxide, sodium hydroxide, and calcium hydroxide.
5. The process of claim 3 wherein said solvent is Portland Cement.
6. The process of claim 1 wherein said source of CaO is dolomitic oxidation.
7. The process of claim 6 further comprising the step of:
adding an activator to said ground, granulated slag.
8. The process of claim 7 wherein the step of granulating said molten slag comprises injecting water at a temperature effective to granulate said molten slag into said molten slag at a rate about ten times said rate of flow of said molten slag and at a pressure of about 30 psi (1381 torr).
9. The process of claim 8 further comprising the step of:
adding a low volatile fuel with said oxidation and said molten slag, whereby heat is generated in said molten slag.
10. The process of claim 1 wherein said source of CaO is lime and further comprising the step of:
adding a low volatile fuel with said lime and said molten slag, whereby sufficient heat is generated in said molten slag to dehydrate said lime.
11. The process of claim 10 further comprising the step of:
adding oxygen to said molten slag to facilitate combustion of said low volatile fuel.
12. The process of claim 11 further comprising the step of:
adding an activator to said ground, granulated slag.
13. The process of claim 13 wherein the step of granulating said molten slag comprises injecting water at ambient temperature into said molten slag at a rate about ten times said rate of flow of said molten slag and at a pressure of about 30 psi (1381 torr).
14. The process of claim 1 wherein said source of CaO is limestone and further comprising the step of:
adding a low volatile fuel with said limestone and said molten slag, whereby sufficient heat is generated in said molten slag to decompose said limestone.

15. The process of claim 14 further comprising the step of:
adding oxygen to said molten slag to facilitate combustion of said low volatile fuel.
16. The process of claim 10 further comprising the step of:
adding an activator to said ground, granulated slag.
17. The process of claim 15 wherein the step of granulating said molten slag comprises injecting water at a temperature effective to granulate said molten slag into said molten slag at a rate about ten times said rate of flow of said molten slag and at a pressure of about 30 psi (1381 torr).
18. The process of claim 1 further comprising the step of:
adding a volatile fuel to said molten slag whereby said molten slag is granulated and formation of a layer of crystalline slag on said molten slag's surface is prevented.
19. The process for producing a nonmetallic material from molten slag flowing from at least one slag tap hole of a furnace blast furnace comprising:
dehydrating said molten furnace slag's attached composition, said molten slag containing CaO, MgO, and SiO₂,
removing said molten slag's rate of flow from said tap hole,
mixing oxidation with said molten slag, so that a ratio of CaO to SiO₂ in said slag is a range of about 1.05 to 1.25 is obtained and said slag has a flow Number less than about 1.25, wherein said flow Number equals (CaO+MgO)/SiO₂,
granulating by breaking up and quenching said molten slag by injecting water at ambient temperature into said molten slag at a rate of about ten times said molten slag's rate of flow and at a pressure of at least about 30 psi (1381 torr),
granulating said water granulated slag to a degree of fineness to obtain a hydraulic cement, and
adding an activator to said ground, granulated slag.

[54] RAPID HARDENING PORTLAND CEMENT CLAYER COMPOSITION
[73] Inventors: Shigefumi Mori, Kazumichi Hiroaki, Osamu, Fushiki, Shinobu, Ueda, Tokyo, all of Japan
[72] Assignee: Onoda Cement Company, Ltd., Onoda-shi, Yamaguchi, Japan
[32] Filed: Dec. 18, 1971
[21] Appl. No.: 288,669
[30] Foreign Application Priority Date: Dec. 21, 1970 Japan 45/120529
[52] U.S. Cl.: 105/89, 105/100, 105/104
[51] Int. Cl.: C04B 7/02

[58] Field of Search: 105/89, 915, 100, 105/104
[56] References Cited: UNITED STATES PATENTS 3,038,973 12/1971 Gansley 105/89
Primary Examiner—James E. Poir
Attorney—Morris F. O'Brien et al.
[57] ABSTRACT
A rapid hardening portland cement comprising 40 – 60 percent by weight of $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ phase and 20 – 30 percent by weight of K_2CO_3 solid solution phase as the main mineral composition thereof and a process for manufacturing it.
4 Claims, 6 Drawing Figures

FIG. 1



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FIG. 2

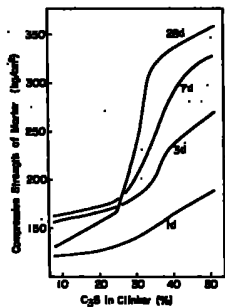


FIG. 3

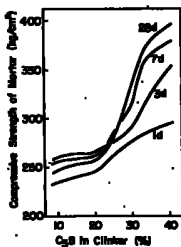


FIG. 4

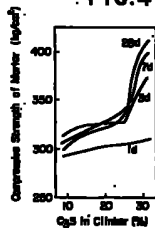


FIG. 6

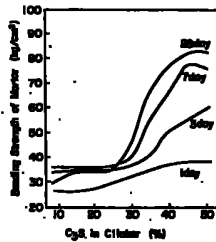


FIG. 5

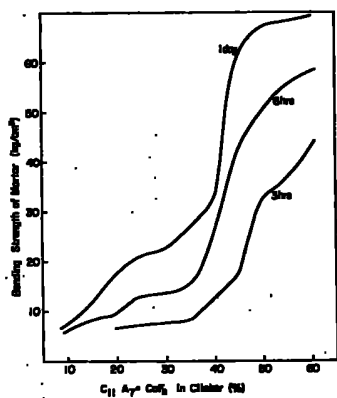


FIG. 7

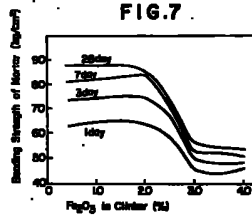
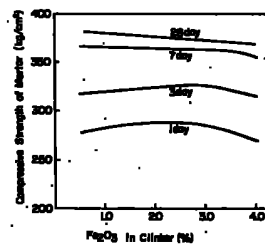


FIG. 8



FIELD OF THE INVENTION

FIELD OF THE INVENTION

The present invention also provides a suitable composition comprising whatever product by such a method; a hardened mass formed by the setting of a conventional composition; and dry mixtures from which the compositions may be produced by the addition of water.

The present invention also provides, as a novel composition of matter, a mineral composition that consists at least 10% by weight of CaO , CaSO_4 , SiO_2 , and not more than 10% by weight of free lime, and less than 25% by weight of Ca(OH)Cl , and not more than 10% by weight of NaOH .

BACKGROUND OF THE INVENTION

The mineral compositions of this invention may be produced, initially as a slinker, by a process in which a suitably proportioned mixture of a source of Cr_2O_3 , a source of Al_2O_3 , and a source of H_2O is heated to at least the temperature of liquid fusion under conditions that are suitable with respect to time. The resultant slinker may be melted and then ground, that is to say reduced to particulate form, by any appropriate means.

BRIEF DESCRIPTION OF THE DRAWING[illegible]

SUMMARY OF THE DIVERSION

The present invention provides a method of producing a suitable cementitious composition wherein a ground mineral composition is mixed in the presence of water with a source of alkali metal or alkaline earth metal under alkaline conditions, the acid mineral composition containing the phase $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SO}_3$.

The mineral composition to be used in the present method may be described as "multimineral." The mineral phase $\text{CaO} \cdot \text{SiO}_2 \cdot \text{SO}_3$ is known as Kiehl's compound and may also be represented by $\text{CaO} \cdot \text{SiO}_2 \cdot \text{SO}_3 \cdot \text{CaO}$ or $\text{Ca}_2\text{O} \cdot \text{SiO}_2 \cdot \text{SO}_3$. Chalks containing Kiehl's compound, their production and their use as expensive agents in Portland cement compositions are known as U.S. Pat. Nos. 1,152,326 (Kiehl), 1,251,701 (Kiehl) and 1,357,714 (Kiehl) and 4,419,136 (Kiehl). However, in the practice of the present invention, it is preferred to employ the novel mineral composition described above.

The mineral composition to be used in the present invention will comprise usually at least 25% by weight, preferably at least 50% by weight and capacity at least 45% by weight, of CaSO_4 . In principle, by using very low water contents in the chemical reversionary furnace it is possible to obtain a chemical reversionary furnace with a low water content, for example a furnace with a content of CaSO_4 of about 100% (about 90% production waste would be relatively high. A CaSO_4 content of up to 50% by weight of the mineral composition, typically about 20%, is adequate for many applications, but it may be appropriate to have a CaSO_4 content of up to 65.60%, or even up to 50%, by weight in certain cases. The percentage-by-weight figures are determined from the abstract analysis by calculation of the potential phase composition and are denoted by X-co-

It has been found that the presence of a significant quantity of free iron (FeO) is undesirable, as it may lead to premature aging of a cement composition incorporating the mineral composition. Accordingly, it is preferred that the content of free iron be less than 0.5%, especially less than 0.2%, by weight of the mineral composition; ideally, free iron should be substantially absent from the mineral composition.

It has also been found that the presence of a significant quantity of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (abbreviated to CoCl_2) can seriously impair the setting time and the development of strength of a cement composition produced from the mineral composition. Preferably, the content of CoCl_2 is not more than 10%, more preferably not more than 5% and especially not more than 3%, by weight of the mineral composition. Usually, CoCl_2 is substantially absent. However, relatively high levels of CoCl_2 , e.g. 20% or more, can be tolerated if slow development of strength and long setting times can be tolerated or if relatively high levels of the mineral composition are used in the slurry.

The solvent system $\text{CH}_2\text{Cl}_2/\text{THF}$ (abbreviated to CzA) reacts gently with water to produce H_2O accordingly, in order to avoid premature sintering. It is appropriate to have only a low content, preferably less than 5% by weight, of CzA in the mineral composition. However it has been found to be beneficial, especially with regard to the strength development of the cement composition, to retain a small quantity of CzA within the mineral composition, preferably in an amount of at least 0.5% and typically up to 4%, especially about 2%, by weight. Nevertheless, the use of a mineral composition from which CzA is substantially absent is also possible.

[illegible]

Surprisingly, when it is wished to maintain the content of CaO , the presence of a minimal quantity of $\text{Ca}_2\text{Al}_2\text{O}_7$ (abbreviated to CA), in the mineral composition, for example up to 20% by weight without a remainder or up to 60%, e.g. up to 40%, by weight with a remainder, can be tolerated without seriously modifying the low reactivity of the mineral composition with water.

It is preferred that the mineral composition should contain no SO_2 in excess of that supplied to form the CaSO_4 ; thus, it is preferred that calcium sulfate (CaSO_4) or CaO should be substantially absent from the mineral composition. However, an excess of CaSO_4 may be desirable to assist in such treatment in a melt process for the production of the mineral slaker if the corresponding addition of physical properties of the product is acceptable. A preferred class of mineral compositions according to the present invention is characterized by a maximum SO_2 content of 4.5% by weight.

The mineral composition according to the present invention can be manufactured by either dissolving or melting the raw materials in any suitable furnace, for example a Portland cement clinker rotary kiln or a reverberatory hearth furnace, in general at a temperature of at least 1200° C.

Normally, the new materials will be selected and prepared in order to produce the maximum possible level of Kelen's component; this will usually require the use of one or more materials having a relatively high purity. An approximate source of CO is Synthane. A suitable source of CO_2 is carbonic acid, the various types of hydrocarbons or aldehydes; however, it is also possible to produce the mixture from other sources, for example by using a fuel having a high sulphur content for firing the furnace. A suitable source of Al_2O_3 is bauxite; however, it would also be possible to use an alternative metal, e.g. zircon, aluminium, the combination of which would contribute energy to the breaking of the ether molecule.

It may be necessary to adjust the limits of the new records in order to ensure that the free time content of the final effort is as low as possible. For example, when a starting problem is a rotary kiln is employed, a time corresponding to 20% passing through a British Standard 50-mesh sieve should generally be adequate, whereas another new material could be substituted if a starting problem is used.

In order to obtain the maximum benefit, careful control of the mineral composition within the above-mentioned parameters is important. Such control, and the selection and proportioning of the raw materials, should be well within the competence of the skilled cement manufacturer. When the type of process used dictates the quantity of CaSO_4 that can be obtained, such as a clinkering process in a Portland cement clinker sintering line (which, unless specially altered, generally uses a patented feed system that causes the clinker to be present during burning for many days of initial clinkering), the manufacturer should be aware of the above-mentioned situation. CA rather than the sodium silicate, Ca_2Si , is less toxic than that, in order to avoid the formation of CaF_2 in the clinker, the composition should be adjusted towards the low-dust region of CaO , preferably such that it is in 5% by weight of CaO is present.

It is necessary to assume that the burning environment contains oxidizing with respect to iron, since the reduction of $\text{Fe}(\text{III})$ will give $\text{Fe}(\text{II})$ which will act as a CaO equivalent, while Ca_2AF will no longer form, and the Ca_3A content will become excessive and undesirable quantities of free lime may form. The presence of FeO in the clinker phase of the clinker may impair the strength development of the cement composition.

It should be mentioned that, under of course conditions in the furnace, carbon oxides could decompose into carbon monoxide and carbon dioxide, having undesirable balances of flow line in the final effluent and possibly giving rise to high levels of CO_2 . However, the oxygen level in the furnace or lift can be regulated in order to adjust (probably indirectly) the rate of oxidation of CO from the carbon surface, and can thus be used to control the amount of CO or then the flow line of CO_2 . The amount of CO flow rate can also be maintained avoiding excess oxidation of the raw material mix.

When coal is used as a fuel, the ash content should be regarded as one of the raw materials in order to ensure that the appropriate balance of components in the composition is maintained.

(19)



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(11) EP 0 812 811 B1

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EUROPEAN PATENT SPECIFICATION

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(51) Int. Cl.: C04B 7/32

(21) Application number: 97500028.6

(22) Date of filing: 04.02.1997

(54) Hydraulic cement with an accelerated development of high strength
Hydraulischer Zement mit beschleunigter hoher Festigkeitsentwicklung
Ciment hydraulique à développement de haute résistance accélérée

(84) Designated Contracting States: DE ES FR GB IT (30) Priority: 10.08.1996 MX 9602271 (43) Date of publication of application: 17.12.1997 Bulletin 1997/51 (73) Proprietor: CEMEX, S.A. DE C.V. 64000 Monterrey, Nuevo Leon (MX) (72) Inventors: - Pae Uthairi, Ramon Garcia Garcia, 66230, Nuevo Leon (MX) - Lopez Gonzalez, Walter Monterrey, 64000, Nuevo Leon (MX) - Villafraa Torres, José Sacramento S. Nicolas d. I. Garza, 66460 Nuevo Leon (MX) (74) Representative: Davila Baz, Angel c/o Claris, Modet & Co., Goya, 11 28001 Madrid (ES)	(56) References cited: WO-A-8804815 DE-A- 4 227 815 DE-B- 1 388 478 FR-A- 2 188 442 US-A- 3 251 701 US-A- 4 957 558 - CHEMICAL ABSTRACTS, vol. 108, no. 14, 6 October 1988 Columbus, Ohio, US; abstract no. 116700a, T.A. ATAKUZIEV ET AL.: page 302; XP002941126 & SU 1 244 121 A (ID.) - CHEMICAL ABSTRACTS, vol. 108, no. 10, 5 September 1988 Columbus, Ohio, US; abstract no. 76968z, X. LI, ET AL.: page 340; XP000019927 & CN 103 848 A (ID.) 6 December 1987 Remarks: The file contains technical information submitted after the application was filed and not included in this specification
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Description

FIELD OF THE INVENTION

[0001] The invention object of the present application relates to the production of cements which, in short times, develop high predictable strength, more specifically the invention provides a method for the production of such cements as well as the cement itself.

BACKGROUND OF THE INVENTION

[0002] Hydraulic cements are known to be constituted by materials composed by oxides and defined chemical compounds belonging to the inorganic chemistry, the use of which is based upon the chemical reaction of said oxides and other constituents of the cement with water, thus forming hydrated compounds which agglutinate with each other, resulting in a mass which, faster or slower, develops mechanical strength. There are cements of the kind mentioned previously in the market, encompassed within the general term "hydraulic cements", which are capable of developing mechanical strength very rapidly, and which are widely known as "high alumina cements".

[0003] Said high alumina cements are constituted essentially by calcium aluminate of formula $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and smaller quantities of calcium aluminoferrite $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ as well as traces of another calcium aluminate of formula $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$.

[0004] The invention object of this application has no relation with high alumina cements, but it does with cements based upon the calcium sulfoaluminate compound of formula $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$.

[0005] The earliest mention to cements based upon calcium sulfoaluminate was made in a French patent, issued in the year 1938, to the company Poliet et Chausson of Paris, the invention of which originated from the research of Henry Leclerc, thus being cements based on the calcium sulfoaluminate compound known up to this date as Leclerc cements.

[0006] By the year 1941 the aforementioned French company manufactured on demand "expansive cements with no contraction", produced from a clinker obtained by the burning of a mixture of the appropriate composition, formed by gypsum, ferruginous bands and limestone.

[0007] In 1958, in the United States, Klein presented a work at the seventy-first Annual Meeting of the ASTM in which he established that a compound that was not precisely identified, but which seemed to correspond with an anhydrous calcium sulfoaluminate, was the reason for the behavior of these expansive cements. Virtually since that time, said expansive cements, based upon calcium sulfoaluminate, are known as K cements by the ASTM, and are governed by specification C-848: expansive hydraulic cements.

[0008] The expansive cements mentioned earlier were manufactured in a more or less empirical manner until, during the Fifth International Congress on Cement Chemistry, held in Tokyo in the year 1963, the works of several authors coincided in pointing out that the main component of these cements is constituted by calcium sulfoaluminate of formula $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$.

[0009] According to the teachings of the prior art for the obtaining of said expansive cements, the calcium sulfoaluminate based clinker was mixed with Portland clinker as well as with granulated blast-furnace slag, so as to obtain a "controlled expansion" product. Since that time cement researchers realized that cements based upon a calcium sulfoaluminate clinker produced early strength cements, greater than those obtained by the sole use of Portland cement, as is clearly established in the United States Patent No. 4,257,558 of Hassan Kumbargi.

[0010] In relation to the invention by Kumbargi and according to the teachings derived from it, it is virtually impossible to accurately determine the setting of the cement by the Vicat method, as said setting is extremely fast, which greatly increases the difficulty in handling the concrete produced with this cement, even and although the use of citric acid is recommended as a setting retardant.

[0011] Another problem presented by the cement produced according to Kumbargi's patent is that the development of strength by the same is unpredictable and, even though in some cases the offered compressive strengths are obtained, frequently much smaller strengths are obtained. This problem, of course, basically derives from the materials which constitute Kumbargi cement as defined in the respective United States Patent.

[0012] Also in relation to Kumbargi's patent, in its columns 3 and 4, the fact is emphasized that calcium sulfoaluminate is not thermodynamically stable and that it decomposes when heated in an industrial bin at temperatures above 1200 °C.

[0013] On the other hand, in said Kumbargi patent, column 5, it is clearly established that due to the thermodynamic properties of calcium sulfoaluminate, it is extremely difficult, if not impossible, that the clinker resulting from the burning of the raw materials involved in the production of the cement, may contain calcium sulfoaluminate, tricalcium silicate and dicalcium silicate, reason for which it is established in said patent that it is necessary to mix a hydraulic clinker which contains tricalcium silicate and dicalcium silicate with the clinker produced in said manner.

[0014] Finally, in relation to the Kumbargi patent, it is doubted that the compressive strengths mentioned therein are

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real, particularly under the assumption that by the use of the ASTM-C-109 method or the EN196-1 method, the latter being the standard of the European Community, the value of said strengths are not obtained, without clearly establishing the real value of said strengths, as in the context of the patent in question, the strength of the cement produced by the Kumbargi method is compared against the strength of Portland cement.

[0016] Going even further into the problem of the measurement of the strength developed by Kumbargi cement, the method employed for the determination of the different setting ages of the cement is not exactly clear, allowing the belief that such measurements are equivalent to those performed with respect to Portland cements, announcing them in any case as equivalent, which in fact is not so, as the value of the mechanical strength of any type of hydraulic cement is not an absolute value as could be the case of the specific weight or the chemical composition, considering that the values of said strength depend, basically, upon the method employed for its assessment. In the case of hydraulic cement the mechanical strength is a function of the water : cement ratio as well as of the cement : sand ratio, and when any of said ratios is changed, the results between the different measurement methods are not comparable.

[0016] According to the ASTM method, the cement : sand ratio is 1:2.75 and the water : cement ratio is about 0.49 for Portland cements. In the case of the Kumbargi patent, a 1:1 cement : sand ratio is used, and, of course, the water : cement ratio employed is not clear, however, it is a fact that Kumbargi cement presents far greater strengths than those obtained by Portland cements, but the determinations carried out according to the ASTM method are not comparable.

OBJECTIVES OF THE INVENTION

[0017] It is therefore a main objective of the invention to obtain a cement, based on calcium sulfoaluminate, in the manufacturing process of which the raw materials are clinkered at temperatures above 1200 °C, without this resulting in a reduction in the content of calcium sulfoaluminate in the clinker due to the decomposition of the same.

[0018] It is another objective of the invention to obtain a cement based on calcium sulfoaluminate containing, apart from an adequate amount of calcium sulfoaluminate, dicalcium silicate and tricalcium silicate, thus eliminating the need, according to Kumbargi's teachings, of having to mix the sulfoaluminous clinker with a hydraulic clinker which contains tricalcium silicate and dicalcium silicate.

[0019] It is yet another objective of the invention to produce a clinker, by the use of a clinkering kiln fitted with a preheater and a preclinker, in the composition of which calcium sulfoaluminate, tricalcium silicate and dicalcium silicate are present, as well as other components in smaller amounts, as the result of a single burning operation in an industrial kiln.

[0020] It is yet an additional objective of the present invention to provide a method for the preparation of a calcium sulfoaluminate based cement with improved handling characteristics and rapid development of strength, all as a result of the composition of the clinker to which, as a previous or simultaneous step to the grinding, other components are introduced, thus obtaining a cement with very high and rapid strengths, with a better setting time and particularly, with the guarantee that the strengths which develop will always remain within the preset control parameters.

[0021] As a summary of the advantages provided by the invention object of this application, the following can be mentioned:

a) a clinker is produced which was impossible to produce according to the prior art.

b) the total chemical composition of the clinker produced allows that it may conveniently be activated by other components during a further grinding process,

c) by means of the process for the obtaining of the cement of the invention, it is possible to produce, in a totally controlled and predictable manner, a cement which rapidly develops very high mechanical strengths.

d) the cement object of the present application exhibits characteristics such as to permit the elaboration of concrete pavements which can be opened to heavy truck traffic no more than 8 hours after its construction. This application can be clearly extended to the laying of landing courses, repair of bridges or concrete structures, these applications being only listed for the purpose of illustration and not limitation.

[0022] In aid of simplicity in writing, throughout the description of the invention object of the present application, abbreviated notations will be employed for the chemical compounds, which are widely employed commonly, worldwide, in the cement industry:

S will serve to identify SiO_2 ,

A for Al_2O_3

F for Fe_2O_3

C for CaO

M for MgO

S for SO_3

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N for Na_2O
 K for K_2O and
 H for H_2O

SUMMARY OF THE DESCRIPTION

[0022] As mentioned earlier, the invention of this application consists in the obtaining of a clinker resulting from the burning of the raw materials which form the cement, the chemical composition of which had not been possible to obtain industrially. Said composition consists fundamentally of a high content in calcium sulfoaluminate $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$, tricalcium silicate $3\text{CaO} \cdot \text{SiO}_2$ and dicalcium silicate $2\text{CaO} \cdot \text{SiO}_2$, adding, during the grinding stage, to said clinker, optimum amounts of calcium oxide or hydroxide (limestone or hydrated limestone) and some of the different forms of calcium sulfate, natural, produced industrially or as an industrial by-product. The addition of the latter ingredients brings about the activation of the clinker.

[0023] The addition of the previously mentioned ingredients can, of course, be carried out prior to the grinding or throughout the same, providing the sulfoaluminous clinker, the lime or hydrated lime and the calcium sulfate of the necessary fineness to be employed as a cement with the essential characteristics of the same, namely, the development of high strengths in very short times.

[0024] As raw materials for the production of the clinker, any type of material of the kind normally used in the production of calcium sulfoaluminate based cements can be employed, which, when dosed adequately, provide the adequate chemical composition to the mixture, which, prior to grinding, will be fed into an industrial kiln, of the kind usually known in the cement industry, for its burning at a temperature above 1200°C . This produces a sulfoaluminate clinker as part of the process for the obtaining of the cement of the invention.

[0025] As an example of the raw materials which can be used are those which are usually employed in the production of Portland cement, such as limestone, shale, calcareous material, and any of the natural forms of calcium sulfate, such as gypsum or anhydrite; different types of clay such as kaolin and aluminas and any of the different types of basidia, if it were necessary.

[0026] It is also possible to use raw materials which are the result of industrial processes, such as wastes, with the only limitation of complying with the requirements in relation to environmental law. Hence, it is possible to use gypsum obtained as a by-product of some industrial process, such as phosphogypsum, which is marginally obtained in the industrial production of phosphoric acid.

[0027] The amounts of raw material used in the making of the clinker are subject to the condition that, after their burning at temperatures above 1200°C , the following percentages will be complied with:

- 1.- The calculated amount of calcium sulfoaluminate will be comprised preferably between 20 and 40% of the total weight of the cement composition.
- 2.- The calculated amount of dicalcium silicate shall be comprised preferably between 10 and 30%.
- 3.- The calculated amount of tricalcium silicate shall necessarily always be of at least 1%, but it will preferably be comprised between 10 and 30%.
- 4.- The calculated amount of anhydrite CaSO_4 , shall be of at least 1%.
- 5.- In no case shall the content of combined lime in the clinker, calculated as total lime minus free lime, give rise to C3S values departing those specified in point three.
6. The content in free lime will preferably be below 0.6%, but it shall in no case be as high as to exceed what is stated in points 3 and 5.

[0028] According to the teachings of the invention, the coexistence of calcium sulfoaluminate and tricalcium and dicalcium silicates in the clinker produced is extremely important. Therefore, it is necessary that the temperature in the hottest area of the kiln exceeds 1200°C , and that the combination reaction of the calcium oxide with the other oxides be as complete as possible, this means that the control of the operation of the kiln is carried out by determining the amount of calcium oxide which remains uncombined, being such compound known as free lime in the cement industry. In order to analytically determine the amount of calcium oxide which remains uncombined, the most recommended method is that described in ASTM-C114: Chemical Analysis of Hydraulic Cement. This determination method allows a precise control of the operation of the kiln, assuring that the chemical reactions that take place in the inside the kiln are carried out in the desired manner, thus guaranteeing the formation of the predetermined amounts of calcium sulfoaluminate and dicalcium and tricalcium silicates.

[0029] Once the clinker has been produced, the optimum amounts of calcium hydroxide and calcium sulfate to be added to the clinker during the grinding process, will have to be determined in the laboratory, so as to obtain the desired compressive strengths.

[0030] The dosing of the calcium hydroxide and calcium sulfate to the clinker may be carried out, as mentioned

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earlier, prior to or during the grinding of the materials to a predetermined fineness, being it possible to employ as calcium sulfate any of the several forms which exist of this compound, with the only condition that the temperature within the mill is such that the cement attains a temperature of approximately between 100 and 125 °C during the grinding, and that the retention time in said mill will be sufficiently long to convert gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ into the hemihydrate $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, thus ensuring that the calcium sulfate present in the cement will be in a condition to react rapidly during the hydration of cement, and that the same develops the desired strength.

[0032] The presence of calcium hydroxide added prior to or during the grinding of the cement, as well as the fact that calcium sulfate is found in the composition of the cement in the form of the hemihydrate are teachings which are totally unknown in the description and claims of the Kurbargi patent, this being the main reason for which the calcium sulfoaluminate based cement consistently develops the rapid strengths which are sought and for which the setting time is more retarded, which facilitates the use of the concrete.

DETAILED DESCRIPTION OF THE INVENTION

[0033] As it has already been established in the previous text, the invention object of this claim is particularly related to the controlled industrial production of a calcium sulfoaluminate based cement, which develops in a predictable manner very high strengths in a short time.

[0034] For informative purposes it is pointed out that the cements of the prior art, based upon calcium sulfoaluminate, were classified exclusively as a function of their expansive properties and that in the invention which we are dealing with, this expansive characteristic is not relevant.

[0035] Also in the way of clarification, attention is drawn to the fact that when mention is made to a solution, reference is being made to the paste which results from adding water to cement, in which certain substances are dissolved as a result of the hydration reactions of the cement.

[0036] Essentially, the rapid development of strength in the cement of the invention is based particularly upon the formation of the chemical compound, so called Ettringite, the formula of which is $\text{C}_3\text{A}_3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$, the conditions for the formation of which will be described in detail in the description of the invention which will be given subsequently, and which is the result of the chemical reaction between calcium sulfoaluminate, calcium sulfate and calcium hydroxide when the cements becomes hydrated.

[0037] It is of vital importance, as derived from the teachings of the invention, that the Ettringite is produced from the very beginning of the hydration of the cement, thus being essential for the same that the necessary amounts of calcium ions Ca^{2+} , sulfate ions SO_4^{2-} and hydroxyl ions OH^- are present in solution. Said amounts must be sufficient to produce an oversaturation of the respective ions in the solution which forms the cement paste, the calcium and sulfate ions react with the calcium sulfoaluminate to form Ettringite and the hydroxyl ions will maintain a pH above 12, which permits the formation of ettringite.

[0038] Some of the restrictions placed upon the composition of the clinker, and which are established as derived from the present invention, are derived from what has been previously mentioned briefly, and can be summarized as follows:

1.- All the aluminum oxide present in the clinker must be found in the form of sulfoaluminate, in order to guarantee the maximum formation of Ettringite in the shortest possible time, starting from a single compound during the hydration of the cement, by the development of a single chemical reaction. If there was tricalcium aluminate in the clinker, Ettringite could still be formed, derived from the reaction between tricalcium aluminate and calcium sulfate, but this would change both the reaction velocity and the chemical equilibrium, as there would be two compounds competing simultaneously, at a different velocity, for the sulfate ion.

2.- In order to ensure that all the aluminum oxide present in the clinker is found in the form of sulfoaluminate, a slight excess of SO_3 must be provided, that is, there must be a minimum amount of anhydrite, therefore, all the SO_3 which may react with the aluminum oxide will form sulfoaluminate. If there is an excess of aluminum oxide, due to a sulfate ion deficiency, tricalcium aluminate will be formed, the presence of which compound is undesirable in the cement, as was explained in the previous paragraph.

3.- With the object of ensuring that the formation of Ettringite takes place rapidly, it is necessary to maintain a highly alkaline medium, i.e. at a pH of at least 12 or above, which is guaranteed by the presence of OH^- ions originating from the addition to the cement of hydrated lime during or before grinding. Additionally, the calcium ions also present due to the addition of hydrated lime help maintain the oversaturation of calcium ions, necessary for the rapid formation of Ettringite.

The presence of free lime in the clinker provides an additional supply in the amount of calcium ions present in the solution of hydration of the cement, and is equally a factor in maintaining a high pH level in the same, but the speed at which it will get into solution depends upon a number of factors, for example the burning temperature of the clinker takes the calcium oxide to a lower state of reactivity (lime burnt to death) than that of properly burnt

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lime. In the clinker the free lime granules are of different sizes, and are generally surrounded by the rest of the chemical compounds which form part of the clinker. Hence their availability to react is not immediate. In fact, it is not exactly known at what speed and at what time the residual free lime in the clinker will start reacting, this being the reason for establishing that the residual free lime in the clinker (calcium oxide) must remain at a minimum level, that is, at a value below 0.5%. In this way the formation of the maximum possible amount of dicalcium and tricalcium silicate is also ensured.

4.- If as a result of burning the value of free lime exceeds 0.5%, this factor must be corrected during the clinker activation tests, avoiding in any case the excess in free lime as derived from what is described in the previous paragraph, as an excess in free lime can lead to the occurrence of the following additional problems:

- a) An undesirable and uncontrolled expansion might take place during hydration of the cement, which would be the result of the hydration and untimely reaction of said free lime. In case of the latter taking place, the formation of Ettringite would be delayed, occasioning such delay the destructive expansion of the cement.
- b) The calculation of the compounds, may lead to a negative value for tricalcium silicate, with the subsequent alteration in the conditions of the chemical equilibrium which one desires to obtain with the specific chemical composition of the invention, making that the cement produced will tend to fall within the specification and behavior problems of Kunberg cements. Hence, due to the problems analyzed above, the free lime shall not exceed a value such as to obtain a negative tricalcium silicate.

[0038] Apart from the characteristics described previously in relation to the chemical composition of the clinker, it is very important that the operational conditions of the kiln are adequate to obtain the formation of the desired compounds, within the quantity parameters determined. In relation to the operational parameters of the kiln, the temperature which the material attains in the warmest area of the same, shall be above 1200°C, and shall preferably be between 1200°C and 1500°C.

[0040] An additional operational characteristic of the kiln is that it will have to be operated in such a way that the material remains at the maximum temperature the necessary time to ensure that the resulting free lime content in the clinker is below 0.5%. The chemical composition of the clinker produced shall be determined following any method of chemical analysis used in the cement industry, for example by X-ray fluorescence, however, in case of discrepancy among results, the method to be used shall be that described in ASTM-C-114: Chemical Analysis of Hydraulic Cement. For the determination of free lime content during the operation of the kiln, the recommended, and most convenient, analytical method is that described in ASTM-C-114: Chemical Analysis of Hydraulic Cement-84, section 27.

1.- The chemical analysis expressed in percentages by mass shall be expressed in moles, for which purpose the percentage of each oxide is divided by its molecular weight:

Moles of silicon oxide	$SiO_2 = \%SiO_2 / 60.07$
Moles of aluminum oxide	$Al_2O_3 = \%Al_2O_3 / 101.96$
Moles of ferric oxide	$Fe_2O_3 = \%Fe_2O_3 / 159.89$
Moles of total calcium oxide	$CaO_{\text{total}} = \%CaO_{\text{total}} / 56.08$
Moles of free calcium oxide	$CaO_{\text{free}} = \%CaO_{\text{free}} / 56.08$
Moles of sulfur trioxide	$SO_3 = \%SO_3 / 80.06$

2.- From the total content of moles of calcium oxide, CaO_{total} , the content in moles of free calcium oxide, CaO_{free} , will be subtracted. This value shall be considered as the combined calcium oxide CaO_{cp} .

3.- It is considered that all the content in aluminum oxide, Al_2O_3 , is found combined as calcium sulfoaluminate $4CaO \cdot 3Al_2O_3 \cdot SO_3$.

4.- The moles of SO_3 and CaO which are found forming calcium sulfoaluminate, $4CaO \cdot 3Al_2O_3 \cdot SO_3$, are calculated:

moles of SO_3 combined in the sulfoaluminate: $SO_3 = \text{moles } Al_2O_3 \cdot 3$
moles of CaO combined in the sulfoaluminate: $CaO(1) = \text{moles } Al_2O_3 \cdot (4 \cdot 3)$

5.- The content of calcium sulfoaluminate, in moles, in the clinker shall be equal to the number of moles of SO_3 in the calcium sulfoaluminate.

6.- The content of anhydrite, $CaSO_4$, in the clinker will be equal to the excess in moles of SO_3 : moles of anhydrite: $CaSO_4 = \text{total moles of } SO_3 - SO_3 \text{ in calcium sulfoaluminate}$. $CaO \text{ in anhydrite} = CaO(2) = \text{moles of } SO_3 \text{ in anhydrite}$.

7.- All the Fe_2O_3 shall be considered as $2CaO \cdot Fe_2O_3$.

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8.- Calculate the CaO necessary to form the $2\text{CaO.Fe}_2\text{O}_3$: moles of CaO in $2\text{CaO.Fe}_2\text{O}_3$: $\text{CaO}(3)$ = moles of $\text{Fe}_2\text{O}_3 \times 2$.

9.- Calculate the moles of calcium oxide which remain uncombined at this moment: moles of CaO which remain uncombined: $\text{CaO}(4) = \text{CaO}(1) - \text{CaO}(2) - \text{CaO}(3)$.

10.- Calculate the molar ratio $\text{CaO}(4) / \text{SiO}_2$. If this ratio is smaller than 2, the clinker departs from specifications. End of the calculation.

11. The calcium oxide found as C28 will be: $\text{CaO}(5) = \text{moles of SiO}_2 \times 2$.

12.- The content in moles of C38 will be: $\text{CaO}(4)$ minus CaO in C28: moles of C38 = $\text{CaO}(4) - \text{CaO}(5)$.

13.- The content of C28 will equal the total content of moles of SiO_2 minus the moles of C38.

14.- Finally, to transform the results of the calculation of compounds into percentages by mass, the value obtained for each compound shall be multiplied by its molecular weight: percentage of calcium sulfoaluminate, $4\text{CaO}.3\text{Al}_2\text{O}_3.\text{SO}_3 \times 610.28$. Percentage of anhydrite, CaSO_4 , moles of $\text{CaSO}_4 \times 136.14$. Percentage of calcium ferrite, $2\text{CaO.Fe}_2\text{O}_3$, moles of $2\text{CaO.Fe}_2\text{O}_3 \times 271.85$. Percentage of tricalcium silicate, C38, moles of C38 $\times 228.2$. Percentage of dicalcium silicate, C28, moles of C28 $\times 172.23$.

[0041] The coexistence within the clinker, at the output of the kiln, of both calcium sulfoaluminate and of dicalcium and tricalcium silicates, can be determined by several different analytical methods, for example, by optical microscopy or by scanning electron microscopy. The coexistence of the previously mentioned compounds can also be checked by x-ray diffraction, notwithstanding, although any of these methods can be used as a complementary control, their use is not essential for process control, which will have to be focused upon the control of the free lime by the previously mentioned analytical method.

[0042] It is recommended that the chemical composition of the clinker be controlled from the point of the grinding of the raw materials, carefully controlling the composition of the crude powder, stage of the process during which the proportioning of the different materials, such as limestone or shale, clays, kaolin, bauxite, gypsum, etc., is carried out, this being the usual way of controlling the composition of the clinker in the cement industry.

[0043] It is obvious that there is no problem in using, in the production of clinker, different materials which result as industrial wastes or by-products from other industries, for instance, it is possible to use sand from foundry molds, phosphogypsum, etc. The method for the grinding of the raw material can be carried out by any procedure of those normally employed in the cement industry, i.e. by means of ball mills, tube mills, roller-presses or some combinations thereof.

[0044] The kiln employed in the production of the clinker can also be of any type usually employed for the production of clinker for Portland cement. For example, it is possible to use, without any restrictions, straight kilns, kilns with a preheater of any of the different types of cyclone or grate, kilns with a preheater and a preburner, etc. Equally, any of the different systems in existence for the cooling of the clinker, which are common in the cement industry, may be used during the unloading of the kiln. One may mention, for instance, grate or planetary coolers.

[0045] Once the clinker has been produced it shall have to be assessed and assayed in the laboratory by means of activation tests by the addition of calcium oxide or hydroxide and some form of calcium sulfate. The clinker produced industrially shall not necessarily result, when ground to any fineness, in a cement capable of rapidly developing high strengths, generally this is not the case.

[0046] The rapid development of high strengths will result from the adequate composition of the clinker, but also from the adequate chemical composition of the cement so as to allow the rapid formation of ettringite crystals, the formation of which will take place by means of the reaction of calcium sulfoaluminate with calcium hydroxide and calcium sulfate.

[0047] Contrary to what was established by Collapardi and Turidani in 1972, this reaction will depend upon the concentration of SO_4^{2-} and OH^- ions in the solution (the term solution stands for the paste formed by the addition of water to the cement). The time of formation of Ettringite crystals will depend upon the near immediate availability of these ions in the solution, and, hence, so will also the development of high strengths, it is for this reason that an adequate dosification of $\text{Ca}(\text{OH})_2$ is important, without thus having to depend upon the appearance of this compound as a function of the free lime or of the generation of, $\text{Ca}(\text{OH})_2$ from the hydration of C3S, as proposed by Kurbarg in his patent No. 4,957,568, the reaction velocity for which purpose is virtually impossible to calculate or predict.

[0048] Something similar happens with the presence of SO_4^{2-} ions in the solution, the behavior of which is mistakenly evaluated in laboratory tests by the direct addition of gypsum to the clinker, without taking into account the real behavior of these materials in the industrial practice, as it is a common practice to calculate, in the laboratory, the presence of SO_4^{2-} ions as derivatives of gypsum and not as hemihydrate.

[0049] During industrial grinding, the temperature of the materials in the grinding circuit must be raised to temperatures between 100 and 130 °C. Under these temperature conditions, the gypsum $\text{CaSO}_4.2\text{H}_2\text{O}$ loses one and a half molecules of water and becomes the hemihydrate: $2\text{CaSO}_4.\text{H}_2\text{O}$, whose solubilization and SO_4^{2-} saturation equilibrium velocities are different from those of gypsum and anhydrite, this being the reason for the inadequate dosification of the

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amount of SO_3 , being it necessary to add gypsum to the clinker in order to optimize the development of its strength, as a consequence of which, according to the previous art, unpredictable results are obtained.

[0050] Laboratory activation tests, prior to grinding, will consequently be carried out on a sample of clinker which is representative of the lot to be ground, on a sample gypsum which is representative of the lot to be used and which has been kept, for at least 24 h, in a laboratory oven at 120 °C, verifying by means of differential thermal analysis, thermogravimetry and X-ray diffraction, its transformation into the hemihydrate $2CaSO_4 \cdot H_2O$, and also on a representative sample of the lot of hydrated lime which will be used in the grinding. The materials mentioned previously will be previously ground to a fineness similar to that to which one expects to produce the cement, this fineness being expressed as the percentage of cement particles with a size under 45 microns.

[0051] Once the materials have been fully identified, one shall proceed to determine the optimum content in hydrated lime and hemihydrate that shall be dosed into the clinker for its activation. Mixtures of the clinker and hemihydrate are prepared varying the content in SO_3 added, for example, 3%, 5%, 7% SO_3 , subsequently dosifying, for each of the mixtures, increasing amounts of hydrated lime, starting from, for instance, 1% and with 1% increments, as in this case the variation in the content of lime is critical. Thus, the following series of samples will be obtained, identified as follows:

- 1.- +3% SO_3 and 1,2,3,4,5 and 6% hydrated lime
- 2.- +5% SO_3 and 1,2,3,4,5 and 6% hydrated lime, etc.

[0052] One shall proceed to determine the compressive strength of each of the samples by the method ASTM-C109 - Standard Test Method for Compressive Strength of Hydraulic Cement Mortars, only taking into consideration that the water to cement ratio shall be adjusted by the use of the fluidity table and not by the constant water to cement ratio specified for Portland cements. The strengths developed can be verified at the ages which are considered convenient, for example, one and a half hours, three hours, etc, after the water for mixing was added. Following this method it is easy to relate with the strengths which, at the same age, would be developed by a reference hydraulic cement, such as for example, a Portland cement.

[0053] As example of the compressive strengths which can be obtained by following the teachings of the present invention, the following table is presented in which the strengths of Portland cement are also shown.

Age	High Strength Cement MPA Compressive Strength	Type I Portland Cement (MPa) Compressive Strength
1.5 hours	5.0	Note 1
3.0 hours	7.5	Note 1
5.0 hours	10.0	Note 2
24.0 hours	20.0	10.0

[0054] Note 1: The mortar cubes do not maintain their shape when removed from the mould and hence they could not even be subjected to the compression test.

[0055] Note 2: Although the cubes maintained their shape when removed from the mould, these collapsed as soon as pressure was applied. It is not possible to measure any strength.

[0056] All the compressive strength results in the previous table are expressed in MPA (Megapascals) and have been obtained by the ASTM-C-109 method: Standard Test Method for Compressive Strength of Hydraulic Cement Mortars.

[0057] As with other sulfoaluminate based cements, it is possible to delay the setting of the cement of the invention by the use of organic products such as citric acid, as described in the previously mentioned article by Collapard and Turitziani.

[0058] Based upon the studies carried out by the inventors of the hydration reactions of cement, it has been concluded that the rapid development of strength in the cement of the invention is caused by the formation of Etringite crystals, which are present from the very moment that the addition of water is commenced. The rapid development of strength by the cement is attributed exclusively to this compound, as dicalcium and tricalcium silicates initially only act as stabilizers of the main reaction, as a consequence of their slow input of Ca^{2+} ions to the solution, helping in this manner to stabilize a high pH value, which, as mentioned earlier, is essential for the development of the main reaction. Solid dicalcium and tricalcium silicates do subsequently contribute in a slower and more gradual manner, to the development of mechanical strength, all due to their slower hydration reaction.

[0059] There is agreement with what was established by Collapard and Turitziani in that the main reaction is: $C_4A_3S + 8Ca(OH)_2 + 8CaSO_4 \cdot 2H_2O + 74H_2O = 3(C_3A_3CS_3 \cdot 32H_2O)$.

[0060] Notwithstanding, they defended that the provision of $Ca(OH)_2$ is due to the hydration of the calcium silicates,

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reaction which, as mentioned previously, takes place very slowly, thus being it necessary to have a more direct supply of $\text{Ca}(\text{OH})_2$, leading to the obtaining of the rapid strength exhibited by the calcium sulfoaluminate based cements of the invention, which they were never able to obtain.

[0061] On the other hand, it is possible to follow the hydration reactions of the cement object of the present application by means of techniques which are common to the study of the hydration reactions of other hydraulic cements, being it possible to consult the appropriate bibliography in relation to said techniques, hence it has been considered unnecessary to include them here.

[0062] Some aspects of this monitoring by an X-ray diffraction technique will be described next.

[0063] The monitoring of the reaction must be commenced one minute after the beginning of the same, due to the putting together of the water and the cement. The lines which identify the presence of ettringite begin to become defined in the diffraction pattern from said first moment. With the passage of time, said lines will increase and become more defined, whereas on the contrary, the lines corresponding to calcium sulfoaluminate will decrease in intensity.

[0064] For the purposes of the present invention, the optimum composition of the invention will be such that apart from presenting Ettringite lines from the first minute and regularly increase in intensity thereafter, the lines which identify calcium sulfoaluminate shall decrease regularly in intensity and disappear completely after 24 hours of the beginning of the hydration reactions, which indicates the total formation of Ettringite from calcium sulfoaluminate. It is obvious that the real behavior of the cement may differ slightly from what has been described herein, but in essence it should be very similar.

[0065] In relation to the latter it shall be clearly noted that what was expressed by Kunberg differs completely from what has been exposed above, as in his patent he established that the rapid strength developed by sulfoaluminate based cements was due to the reaction of calcium aluminates, as it occurs in the case of high alumina cements. There is no calcium aluminate present in calcium sulfoaluminate based cements, moreover, provisions are made in the present invention for the quantification of the composition of the cement, in order to prevent the presence of any of the possible compositions of calcium aluminates, CSA, C12A7, etc.

Claims

1. A method of producing a calcium sulfoaluminate-containing cement clinker, comprising subjecting a mixture of cement raw materials, to calcining temperatures sufficiently above 1200°C to assure the consistent consistent formation of dicalcium silicate and tricalcium silicate in an industrial kiln; said kiln having a preheater; said raw materials being sources of CaO , SiO_2 , Al_2O_3 and SO_3 and being mixed so as to obtain clinker having a content of 20% to 40% of calcium sulfoaluminate, 10% to 30% of dicalcium silicate, at least 1% of tricalcium silicate, at least 1% of enhydrite so as to assure the suppression of the presence of any aluminates apart from calcium sulfoaluminate, and less than 0.5% of free calcium oxide, all percentages being based on the total weight of said clinker obtained.
2. The method of producing cement clinker according to claim 1, wherein the content of tricalcium silicate is from 10 to 30%.
3. The method of producing cement clinker according to any of claims 1 and 2, wherein the calcining temperature is between 1200°C and 1500°C .
4. The method of producing cement clinker according to any of claims 1 to 3, wherein said industrial kiln has a preclinker.
5. The method of producing cement from clinker made according to any of claims 1 to 4, further comprising activating said clinker obtained by addition of an amount of about 1% to 6% of calcium oxide or hydroxide and/or about 3% to 7% of calcium sulfate, the later percentage being in terms of SO_3 present, and subjecting the resulting mixture to grinding, having a significant percentage of particles smaller than $45\text{ }\mu\text{m}$ and maintaining a grinding temperature sufficient to effectively achieve the hemihydrate phase of calcium sulfate.
6. The method of producing cement according to claim 5, wherein the grinding temperature is maintained between 100°C and 130°C .
7. The method of producing cement according to any of claims 5 and 6, wherein said clinker activation through the addition of calcium oxide or hydroxide is carried out prior or during the grinding step of said mixture.

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8. The method of producing cement clinker according to any of claims 5 to 7, wherein the mixture of cement raw materials is selected from the group consisting of limestone, calcium sulfate and clays.
9. A calcium sulfoaluminate-containing cement, produced by the method of any of claims 5 to 8, wherein said cement upon hydration has a pH higher than 12 and develops a compressive strength of about 10 MPa within a period of about 5 hours due to the formation of ettringite when said calcium sulfoaluminate reacts with calcium and sulfate ions.

10 Patentansprüche

1. Verfahren zur Herstellung von Calciumsulfoaluminat enthaltendem Zementklinker, bei dem ein Gemisch eines Zementrohmaterials bei einer Kalzinierungstemperatur von hinreichend über 1200°C behandelt wird, um die konsistente koexistierende Bildung von Dicalciumsilikat und Tricalciumsilikat in einem industriellen Brennofen zu gewährleisten, der einen Vorheizler aufweist, wobei die Rohmaterialien Quellen von CaO, SiO₂, Al₂O₃ und SO₂ sind und gemischt werden, um Klinker zu erhalten, die einen Gehalt von 20% bis 40% Calciumsulfoaluminat, 10% bis 30% Dicalciumsilikat, wenigstens 1% Tricalciumsilikat, wenigstens 1% Anhydrit, um die Anwesenheit von jeglichem Aluminat außer von Calciumsulfoaluminat zu unterdrücken, und von weniger als 0,5% freiem Calciumoxid aufweisen, wobei alle Prozentangaben auf dem Gesamtgewicht des erhaltenen Klinkers basieren.
2. Verfahren zur Herstellung von Zementklinker nach Anspruch 1, wobei der Gehalt an Tricalciumsilikat zwischen 10 und 30 % beträgt.
3. Verfahren zur Herstellung von Zementklinker nach einem der Ansprüche 1 oder 2, wobei die Kalzinierungstemperatur zwischen 1200°C und 1500°C beträgt.
4. Verfahren zur Herstellung von Zementklinker gemäß einem der Ansprüche 1 bis 3, wobei der Brennofen einen Preheizer aufweist.
5. Verfahren zur Herstellung von Zement aus gemäß einem der Ansprüche 1 bis 4 hergestelltem Klinker, das zusätzlich die Aktivierung des erhaltenen Klinkers durch Zusatz einer Menge von etwa 1% bis 6 % Calciumoxid oder -hydroxid und/oder etwa 3% bis 7 % Calciumsulfat umfasst, die letztgenannte Prozentangabe in Bezug von vorhandenem SO₂, und das resultierende Gemisch gemahlen wird, wobei ein wesentlicher Prozentsatz von Partikeln kleiner als 45 µm ist und eine hinreichende Mahltemperatur aufrechterhalten wird, um wirksam die Hemihydrat-Phase von Calciumsulfat zu erhalten.
6. Verfahren zur Herstellung von Zement gemäß Anspruch 5, wobei die Mahltemperatur zwischen 100°C und 130°C gehalten wird.
7. Verfahren zur Herstellung von Zement nach einem der Ansprüche 5 oder 6, wobei die Aktivierung des Klinkers durch den Zusatz von Calciumoxid oder -hydroxid vor oder während des Mahlchritzes des Gemisches erfolgt.
8. Verfahren zur Herstellung von Zementklinker gemäß einem der Ansprüche 5 bis 7, wobei das Gemisch des Zementrohmaterials aus der aus Kalkstein, Calciumsulfat und Ton bestehenden Gruppe ausgewählt wird.
9. Calciumsulfoaluminat enthaltender Zement, hergestellt nach einem Verfahren der Ansprüche 5 bis 8, wobei der Zement nach der Hydratation einen pH-Wert über 12 aufweist und eine Druckfestigkeit von etwa 10 MPa innerhalb einer Zeitdauer von etwa 5 Stunden infolge der Bildung von Ettringit entwickelt, wenn das Calciumsulfoaluminat mit Calcium- und Sulfationen reagiert.

10 Revendications

1. Procédé de production d'un clinker contenant du sulfoaluminat de calcium, comprenant les étapes consistant à soumettre un mélange de matériaux bruts de ciment à des températures de calcination suffisamment supérieures à 1200 °C pour permettre la formation coexistante conséquente de silicate bicalcique et de silicate tricalcique dans un four industriel ; ledit four étant équipé d'un réchauffeur ; lesdits matériaux bruts étant des sources de CaO, SiO₂, Al₂O₃ et SO₂ et étant mélangés de façon à obtenir un clinker avec une teneur en sulfoaluminat de calcium

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comprise entre 20% et 40%, une teneur en silicate bicalcique comprise entre 10% et 30%, une teneur en silicate tricalcique d'au moins 1%, une teneur en anhydrite d'au moins 1% de façon à permettre la suppression de tout aluminat présent à l'exception du sulfoaluminat de calcium, et une teneur en oxyde de calcium libre de moins de 0,5%, tous les pourcentages étant basés sur le poids total dudit clinker obtenu.

2. Procédé de production d'un clinker selon la revendication 1, dans lequel la teneur en silicate tricalcique est comprise entre 10% et 30%.
3. Procédé de production d'un clinker selon l'une quelconque des revendications 1 et 2, dans lequel la température de calcination est comprise entre 1200 °C et 1500 °C.
4. Procédé de production d'un clinker selon l'une quelconque des revendications 1 à 3, dans lequel ledit four industriel est équipé d'un four de préchauffage.
5. Procédé de production d'un ciment à partir du clinker obtenu selon l'une quelconque des revendications 1 à 4, comprenant en outre les étapes consistant à activer ledit clinker obtenu par addition d'une quantité d'environ 1% à 6% d'oxyde ou d'hydroxyde de calcium et/ou environ 3% à 7% de sulfate de calcium, ce dernier pourcentage étant exprimé en termes de présence en SO_3 , et à soumettre le mélange obtenu au broyage, avec un pourcentage significatif de particules dont la taille est inférieure à 45 μm et à maintenir une température de broyage suffisante pour réaliser de manière efficace la phase semi-hydrate du sulfate de calcium.
6. Procédé de production d'un ciment selon la revendication 5, dans lequel la température de broyage est maintenue entre 100 °C et 130 °C.
7. Procédé de production d'un ciment selon l'une quelconque des revendications 5 et 6, dans lequel ledite activation du clinker est réalisée par ajout d'oxyde ou d'hydroxyde de calcium avant ou pendant l'étape de broyage dudit mélange.
8. Procédé de production d'un clinker selon l'une quelconque des revendications 5 à 7, dans lequel le mélange de matériaux bruts de ciment est choisi dans le groupe comprenant du calcaire, du sulfate de calcium et de l'argile.
9. Ciment contenant du sulfoaluminat de calcium, produit par le procédé de l'une quelconque des revendications 5 à 8, dans lequel ledit ciment a un pH supérieur à 12 par hydratation et développe une résistance à la compression d'environ 10 Mpa en une période d'environ 5 heures en raison de la formation d'étringite lorsque ledit sulfoaluminat de calcium fait réagir les ions de calcium et de sulfate.



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 (54) CIMENT HYDRAULIQUE A DEVELOPPEMENT ACCELERE
 HAUTE RESISTANCE
 (55) HYDRAULIC CEMENT WITH ACCELERATED SET
 STRENGTH DEVELOPMENT

(57) L'invention consiste en une méthode de fabrication de ciment à base de sulfates de calcium, consistant en la formation d'un clinker par calcination des matières premières à des températures supérieures à 1 200 degrés °C de telle manière que le clinker ainsi produit présente une fraction élevée en sulfates de calcium, en vitesses très rapides et en absence d'additifs, durant un court laps de temps de cuisson, en l'absence de clinker sans produit des composés de base conventionnels, des quantités optionnelles d'oxyde ou d'hydroxyde de calcium et de sulfate de calcium, de manière à obtenir un clinker. Pendant le broyage, on garde une température d'environ 100 à 125 °C et la durée de l'opération doit être suffisante pour convertir le gypse en semi-hydrate, faisant ainsi en sorte que le sulfate de calcium présent dans le produit ainsi obtenu soit en état de réagir rapidement durant l'hydratation du ciment, ce qui permet ainsi la formation d'un ciment, pour lequel un pH supérieur à 12 est nécessaire. Évidemment, le ciment ainsi obtenu est susceptible de subir une réaction de durcissement de la période de prise et d'hydratation accélérée.

(57) The invention consists in a method of manufacturing cement based on calcium sulfates, consisting in the formation of a clinker through the roasting of raw materials to temperatures of more than 1200°C in such a manner that the clinker thus produced has a high content of calcium sulfates, in extremely rapid and in absence of additives, during the short cooking period, in the absence of clinker without product of basic conventional, optional amounts of calcium oxide or hydroxide and calcium sulfate, in order to obtain said clinker. Upon said milling, a temperature of about 100 to 125°C is to be observed and a time enough to convert gypsum to hemihydrate, thus making that the calcium sulfate present in the thus obtained product be in a condition to react quickly during the hydration of said cement, thus giving place to the formation of a cement, for which the presence of a pH above 12 is needed. Of course, it is also claimed as a novelty the accelerated cement, resulting from the addition and milling methods of this invention.



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ABSTRACT OF THE DISCLOSURE

The invention consists in a method of manufacturing cements based on calcium sulfoaluminate, consisting in the formation of a klinker through the reacting of raw materials to temperatures of more than 1200°C in such a manner that the klinker thus produced has a high content of calcium sulfoaluminate, trisulfate silicate and dicalcium silicate and, during the milling thereof or prior to the milling thereof, adding to the klinker thus produced, with the above recited basic components, optimal amounts of calcium oxide or hydroxide and calcium sulfate, in order to activate said klinker. Upon said milling, a temperature of about 100 to 125°C is to be observed and a time enough to convert gypsum to hemihydrate, thus making that the calcium sulfate present in the thus obtained product be in a condition to react quickly during the hydration of said cement; thus giving place to the formation of ettringite; for which the presence of a pH above 12 is needed. Of course, it is also claimed as a novelty, the obtained cement, resulting from the calcination and milling methods of this invention.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method of preparing a high strength, fast setting calcium sulfoaluminate cement from a suitable raw material at a temperature above 1200°C to obtain a klinker having a high content of calcium sulfoaluminate, tricalcium silicate and dicalcium silicate and having less than 0.5% free lime, adding calcium oxide or hydroxide and calcium sulfate to activate the klinker and milling the klinker mixture so obtained at a temperature of between 100 and 130°C.
2. A method according to Claim 1, wherein the roasting temperature of the raw material is between 1200 and 1300°C.
3. A method according to Claim 1, wherein the chemical composition of the klinker obtained from the roasting of the raw material is: calcium sulfoaluminate content, between about 20 and 40%; dicalcium silicate content, between about 10 and 30%; tricalcium silicate content, greater than 1%, anhydrite CaSO_4 content, at least 1%; with the proviso that the content of combined lime in said klinker, calculated as total lime minus free lime, is such that the value of $3\text{CaO} \cdot \text{SiO}_2$ is within said value given for tricalcium silicate, and further that the free lime content is within the combined value of the sum of the tricalcium silicate content and combined lime content.

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**HYDRAULIC CEMENT WITH ACCELERATED HIGH STRENGTH
DEVELOPMENT**

FIELD OF THE INVENTION

The invention forming the subject matter of this application relates to the production of cements which develop predictable high-strengths in brief periods of time; more particularly, the invention provides a method of producing such cements and also relates to the cement itself.

BACKGROUND OF THE INVENTION

Hydraulic cements are known constituting materials formed by oxides and defined chemically belonging to the field of the inorganic chemistry, the use of which is based on the chemical reaction of said oxides and other ingredients of said cement with water in order to form hydrated compounds which are valued forming a mass wherein more or less rapid mechanical strengths are developed. Within the general concept of "hydraulic cements" there are in the market cements of the above mentioned type, capable of, very fast developing mechanical strengths, which are broadly known as "aluminous cements".

Said aluminous cements are substantially constituted by calcium aluminate of the formula $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and minor amounts of calcium sulfinate of the formula $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, as well as traces of other calcium silicates of the formula $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$.

The invention of this application is not related to said aluminous cements but to those cements based on the calcium sulfaluminate compound of the formula $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$.

The oldest reference to cements based on calcium sulfaluminate was made in a French patent granted on 1936 to the firm Pollet et Chausson, Paris, France, which invention was the origin of the searching works of Henri Lesclapart, these cements based on calcium sulfaluminate being known, since that date, as Lesclapart