# (12) (19) (CA) **Demande-Application**

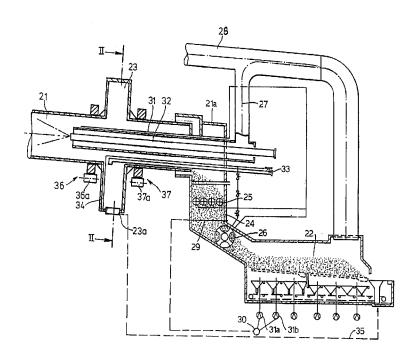




(21) (A1) **2,227,470** 

(86) 1996/07/29 (87) 1997/05/09

- (72) DOUMET, Joseph E., LB
- (71) DOUMET, Joseph E., LB
- (51) Int.Cl.<sup>6</sup> C04B 7/47, F27B 15/02, C04B 7/44
- (30) 1995/10/31 (95117163.6) EP
- (54) PROCEDE ET APPAREIL DE PRODUCTION DE CLINKER DE CIMENT
- (54) METHOD AND APPARATUS FOR PRODUCING CEMENT CLINKER



(57) L'invention se rapporte à un procédé et à un appareil de production de clinker de ciment. Le clinker de ciment est d'abord totalement brûlé dans une zone de combustion, puis refroidi dans une zone de refroidissement. Le refroidissement se fait au moins partiellement par l'amenée de combustible et de vapeur, et se caractérise en ce que, dans une première phase, le combustible introduit est mélangé avec le clinker de ciment et initialement pyrolysé. Les produits de pyrolyse obtenus ont une forte réaction endothermique avec la vapeur de sorte que le clinker de ciment subit un refroidissement tel que 95 % au moins, de préférence la totalité, de la phase liquide qu'il renferme se transforme en verre.

(57) The invention is related to a method and an apparatus for producing cement clinker, in which the cement clinker is first of all burnt in a burning zone and then cooled in a cooling zone, wherein the cooling takes place at least partially by the delivery of fuel and steam, characterised in that in a first cooling phase the delivered fuel is mixed with the cement clinker and initially pyrolysed and the resulting pyrolysis products have a strong endothermic reaction with the steam, so that the cement clinker is quenched in such a way that at least 95 %, preferably all, of the liquid phase contained therein is transformed into glass.

# **PCT**

# WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)			
(51) International Patent Classification <sup>6</sup> :		(11) International Publication Number:	WO 97/16390
C04B 7/47, 7/44, F27D 15/02	A1	(43) International Publication Date:	9 May 1997 (09.05.97)
(21) International Application Number: PCT/IB (22) International Filing Date: 29 July 1996 ( (30) Priority Data: 95117163.6 31 October 1995 (31.10.95) (34) Countries for which the regional or international application was filed:	29.07.9	CA, CH, CN, CZ, DE, DK, EE, IS, JP, KE, KG, KP, KR, KZ, L MD, MG, MK, MN, MW, MX, N SD, SE, SG, SI, SK, TJ, TM, TI VN, ARIPO patent (KE, LS, MV patent (AM, AZ, BY, KG, KZ, MI patent (AT, BE, CH, DE, DK, ES	ES, FI, GB, GE, HU, IL, K, LR, LS, LT, LU, LV, NO, NZ, PL, PT, RO, RU, R, TT, UA, UG, US, UZ, V, SD, SZ, UG), Eurasian D, RU, TJ, TM), European S, FI, FR, GB, GR, IE, IT, tent (BF, BJ, CF, CG, CI,
(71)(72) Applicant and Inventor: DOUMET, Joseph, E. Villa Joseph E. Doumet, P.O. Box 40-124, Yarz (LB).			

#### (54) Title: METHOD AND APPARATUS FOR PRODUCING CEMENT CLINKER

## (57) Abstract

The invention is related to a method and an apparatus for producing cement clinker, in which the cement clinker is first of all burnt in a burning zone and then cooled in a cooling zone, wherein the cooling takes place at least partially by the delivery of fuel and steam, characterised in that in a first cooling phase the delivered fuel is mixed with the cement clinker and initially pyrolysed and the resulting pyrolysis products have a strong endothermic reaction with the steam, so that the cement clinker is quenched in such a way that at least 95 %, preferably all, of the liquid phase contained therein is transformed into glass.

**- 1 -**

### Method and apparatus for producing cement clinker

5

10

15

20

25

30

The invention relates to a method and to apparatus for producing cement clinker according to the preamble to claim 1 and the generic concept of claim 10.

So-called Portland Cement Clinker consists essentially of alite  $(C_3S)$  and belite  $(C_2S)$ , tricalcium aluminate  $(C_3A)$  and tetracalcium aluminate ferrite  $(C_4AF)$ . Further constituents are in particular free magnesium oxide as well as alkalis.

cooling of the cement clinker influences its structure, the mineralogical composition and the properties of the cement produced therefrom. The rate cooling of the clinker has an influence particular on the ratio between the crystalline phase content and the glass phase content in the clinker. With slow cooling, crystal formation takes place for almost all clinker components, whilst rapid cooling impedes the crystal formation and allows the called liquid phase  $(2,95 \text{ Al}_2\text{O}_3 + 2,2 \text{ Fe}_2+\text{MgO} + \text{alkalis})$  to solidify in glass form. The proportion of liquid phase in clinkers from rotary kilns is approximately 20 to 28 %.

The rapid cooling of the clinker increases in particular the sulphate resistance of the cement to sulphates (magnesium, sodium, potassium, etc.) Free alcalis and MgO cristals (periclase) entering in the glass formation. This may be explained by the fact that the  $C_3A$  content which is responsible of the capacity of cement to sulfates resistance, becomes part of the glass and also free alcalis and MgO (periclase), due to

WO 97/16390 PCT/IB96/00956 <sup>-</sup>

- 2 -

rapid cooling of the clinker and therefore will be resistant to attack by sulfates. As free alkali disappear, free alkali will not anymore attack the silica in aggregates.

5

A cement clinker which essentially consists only of alite, belite and glass, i.e. in which  $C_3A$  and  $C_4AF$  are bonded in the glass, could be designated as Glass Portland Cement. It is distinguished in particular by a special capacity for resistance to environmental influences without restriction of its strength.

10

Although the so-called Glass Portland Cement has already been produced in the laboratory, no method has hitherto been known which permits commercial production thereof.

15

The necessary rate of cooling cannot be achieved with the clinker cooling processes which are known in the art, particularly with the aid of so-called grate coolers.

20

25

A method of producing active belite cement is known from DD-A-206 422. In this case the belite clinker from the rotary kiln is delivered to a first cooling stage into which brown coal dust and low-temperature exit gas contains in particular carbon dioxide and steam. This leads to gasification of the supplied fuel with steam or with carbon dioxide, these gasification reactions extracting the necessary reaction enthalpy from the cement clinker.

- 3 -

5

10

15

20

25

30

The object of the invention is to provide a method and apparatus for industrial production of Glass Portland Cement.

This object is achieved by the characterising features of claims 1 and 10. According to the invention the fuel delivered in the first cooling phase is mixed with the cement clinker and initially pyrolysed. The resulting pyrolysis products have a strong endothermic reaction with the steam, so that the cement clinker is quenched in such a way that at least 95 %, preferably all, of the liquid phase contained therein is transformed into glass.

The gaseous pyrolysis poducts resulting from the pyrolysis react directly with the steam. As a result the cement clinker can be quenched from its burning temperature of the order of magnitude of 1.450 °C in a few seconds. This rapid cooling process effects the transformation of the liquid clinker constituents  $C_3A$  and  $C_4AF$  into glass including free alcalis and MgO (periclase).

The further cooling takes place through the generally known gasification of the fuel with steam, which also proceeds endothermically, but this takes place significantly more slowly by comparison with the reaction of the gaseous pyrolysis products with steam.

Further embodiments and advantages of the invention are the subject matter of the subordinate claims and are explained in greater detail with reference to the description and the drawings, in which:

- 4 -

5

10

15

20

25

30

Fig.1 shows a schematic representation of apparatus according to the invention and

Fig.2 shows a sectional representation along the line II-II of Fig.1.

The apparatus according to the invention for producing cement clinker is described first of all with reference to Fig. 1 and 2. It consists essentially of a rotary kiln 21 for burning the cement clinker, a first cooling stage constructed as a reactor 23 and a second cooling stage constructed for example as a grate cooler 22.

In the illustrated embodiment the reactor 23 constructed as a part of the rotary kiln 21 with enlarged diameter and is disposed at the outlet end of the kiln. The rotary kiln 21 has at its outlet end a kiln hood 21a which together with a connecting arrangement 24 constitutes the transition from the kiln 21 to the grate cooler 22.

The kiln hood 21a well as as the connecting arrangement 24 are constructed the conventional in manner. A crusher, preferably a roll crusher 25, which advantageously cooled from the inside by demineralised water, is disposed in the connecting arrangement 24. Here the clinker comminuted for is example to a particle size of 25 mm before it passes to a rotary vane gate 26 which delivers the clinker to the grate cooler 22. The rotary vane gate 26 is preferably also cooled from the inside with demineralised water. In the grate cooler 22 the cement clinker which has already been precooled in the reactor 23 is further cooled by means of air. The cooling air heated thereby

- 5 -

5

10

15

20

25

30

is used in the apparatus as air for combustion in the usual way as secondary air 27 or as tertiary air 28.

A pressure-measuring device 29 is provided in the connecting arrangement 24 shortly before the rotary vane gate 26, and by way of a control device 30 this pressure-measuring device controls the speed of the first two fans 31a and 31b of the cooler 22 in such a way that no pressure builds up in the region of the pressure-measuring device 29.

The secondary air 27 generated by the grate cooler 22 is introduced into the rotary kiln 21 in the region of the kiln hood 21a by way of a secondary air line 31. The secondary air line 31 is of double-walled construction and is cooled with demineralised water. In the middle of the secondary air line 31 there is provided an additional burner 32 for any fuel.

The reactor illustrated in this embodiment is approximately three times greater in diameter than the rotary kiln 21, and the width of the reactor corresponds to approximately 1/5 of its diameter.

In the illustrated embodiment the rotary kiln 21 is supported in the region of the reactor 23 by way of two supporting tyre-rollers stands 36, 37 which are each disposed respectively shortly before and shortly after the reactor. A further supporting tyre-roller stand could be provided if necessary in the region of kiln outlet. With the two supporting roller stands provided before and after the reactor 23 the additional weight due to the reactor 23 can best be distributed. Each supporting roller stand consists of two supporting

- 6 -

5

10

15

20

25

30

rollers. In Fig. 1 supporting rollers 36a, 37a of the supporting roller stands 36, 37 can be seen.

The reactor 23 also has an arrangement constructed as a screw conveyor 33 for delivery of a fuel, in particular a carbonaceous fuel. The screw conveyor is again of double-walled construction and is cooled with demineralised water. The feed point for the fuel lies in the inlet region of the hot bulk material into the reactor 23.

The saturated steam required in the reactor 23 is obtained completely or partially from the cooling water from the various apparatus parts described above. Furthermore, the reactor 23 has an arrangement 34 for blowing steam into the cement clinker which is mixed with the fuel. This arrangement is disposed parallel to the walls delimiting the reactor 23 and is constructed in the form of a plate, the edges of which are chamfered in order to provide the least possible resistance for the clinker coming into the reactor. The steam will preferably stream out in the region of the base of the reactor 23.

At the lower end of the reactor 23 a closable opening 23a is also provided in order to transport the clinker located in the reactor to the cooler outlet by way of a conveying arrangement 35, represented by broken lines, when a longer kiln stop is necessary.

In the production of cement clinker with the aid of the apparatus described above the cement clinker is first of all burnt in the rotary kiln 21 in a burning zone and then passes into the reactor 23. The fuel which is

5

10

15

20

25

30

- 7 -

also delivered there, particularly carbonaceous fuel with a pyrolysable component, is mixed with the cement clinker in a first cooling phase and pyrolysed. The resulting pyrolysis products, such as in particular tar, light hydrocarbons with some CO<sub>2</sub> and CO, have a strong endothermic reaction with the steam which is also delivered. A particularly rapid reaction takes place between the gaseous pyrolysis products and steam, so that the cement clinker is quenched in such a way that at least 95 %, preferably all, of the liquid phase contained therein is transformed into glass.

In this first cooling phase the cement clinker is quenched from the burning temperature of the order of magnitude of 1.450 °C to approximately 1.250 °C, the rate of cooling in the first cooling phase being between 600 K/min and 6.000 K/min.

In the reaction between pyrolysis products and steam, gases such as  $CH_4$ ,  $H_2$ , CO,  $CO_2$  to  $C_4$  hydrocarbons are produced.

In a second cooling phase, which also takes place in the reactor 23, the principal occurrence is a gasification of the delivered fuel as well as the pyrolysis products still present with steam. This gasification reaction again proceeds endothermically and extracts the necessary reaction enthalpy from the cement clinker. In the gasification the following reactions occur in particular:

$$C + H_2O ---> H_2 + CO$$
  
 $CO + H_2O ---> H_2 + CO_2$   
 $C + CO_2 ---> 2CO$ 

10

15

20

25

30

WO 97/16390 PCT/IB96/00956

- 8 -

Thus in the method according to the invention for producing cement clinker the clinker is first of all quenched in a first cooling phase from approximately 1.450 °C to 1.250 °C within a few seconds. in the second cooling phase the further cooling of the cement clinker takes place principally through endothermic gasififaction. In the third cooling phase the cement clinker which has been cooled to approximately 1.000 to 1.100 °C is fed to the grate cooler.

The quantity of coal or the ratio between coal and liquid or gaseous fuel introduced in the reactor to through pyrolysis enough rapid products, is completely independent of the fuel needed for precalcining at preheater outlet (before kilninlet). The air necessary for the combustion process is introduced into the rotary kiln by way of the secondary air line 31. The temperature of the secondary air is approximately 750 °C. The additional burner 32 in the of the secondary air line 31 is used particular when starting the rotary kiln and can also be used when the fuel gas produced in the reactor 23 is not sufficient for sintering the raw meal to clinker in the sintering zone.

In order to achieve the fullest possible transformation of the liquid phase into glass, a thorough mixing of the fuel with the cement clinker and the most uniform possible blowing in of steam is necessary. The arrangement 34 for introducing the steam is normally provided so as to be stationary. However, it can also be disposed so as to be movable to and from in the direction of the rotational movement of the rotary

5

10

15

20

25

30

- 9 -

kiln/reactor arrangement, in order to reach the most effective location for the chemical reactions.

Liquid and/or gaseous fuels react in the first cooling significantly more quickly than carbonaceous fuel, since the latter must first be broken up by pyrolysis. Therefore in order to set a sufficient rate of cooling, additional fuel in liquid and/or gaseous form can 'be introduced into reactor 23. Arangements similar to those used for blowing in the steam are particularly suitable for this. The rate of cooling in the first cooling phase can be set between 600 K/min and 6.000 K/min.

The intermixing of the delivered fuel with the cement clinker takes place particularly reliably reactor according to the invention. Since the reactor moves with the rotary kiln, the introduced cement clinker is constantly moving. In advantageous an embodiment the reactor can be provided internally with ceramic lifters for lifting the cement clinker. This effects an even more intensive intermixing and moreover the lifting and dropping of the cement clinker leads to comminution thereof, so that a homogenisation of the size of the cement clinker lumps takes place. This in turn ensures a uniform cooling of the cement clinker.

When the rotary kiln/reactor arrangement is being started, the additional burner 32 located in the secondary air line 31 is used. If the fuel/hydrogen ratio has adjusted to the gasification capacity of the reactor 23 the combustion process can be operated independently of the additional burner 32, in which case the fuel consumed, the regulation of the flame and

10

15

20

25

30

WO 97/16390 PCT/IB96/00956

- 10 -

the quantitiy of fuel deliverd to the rotary kiln is independent of the fuel needed for precalcining.

With the aid of the reactor 23 described above the hot bulk material passes into the cooler having already been precooled, so that the entire quantity of air to be used in the cooler can be used as secondary air for kiln and tertiary air for precalcining. quantity of air used by the cooler 22 is sufficient and there is no excess quantity of air and then no heat must be given off into the atmosphere. In this way between 75 and 100 kcal/kg of energy can be saved. Furthermore, it is possible to dispense with filters and cleaning arrangements for the quantities of air which would otherwise be given off into the atmosphere. The gas (CO + H<sub>2</sub>) produced in the reactor meets the secondary air with a temperature of 1.000 °C, whilst the secondary and tertiary air is at 750 °C approximately. Therefore the temperature of the flame easily reach temperatures between 2.500 °C. The burning process can be controlled much more easily due to this high temperature of the flame. Also the coating of the clinker which is necessary for the protection of the lining of the burning zone can be controlled much more simply.

Since the cement clinker in the reactor 23 is quenched by 200 to 250 °C within a few seconds only alite and belite crystallise. The only other constituent present is glass in which in particular C<sub>3</sub>A, C<sub>4</sub>AF, alkalis and magnesium oxide are bonded. Such a cement clinker could be designated as Glass Portland Cement.

- 11 -

The fuel ashes used in the gasification reaction do not have to be taken into account in the composition of the raw material. These ahses form a filler in the clinker. Pit coal and brown coal with high proportions of ash as well as coals with high volatile components can therefore be used. The fuel supplied to the reactor 23 does not have to be either dried or crushed and can be delivered in the form of 5 to 10 mm particles.

Due to the rapid quenching the calcium sulphates will not decompose and pass in the clinker as  ${\rm CaSO}_4$  (anhydrite).

This can have a result of reducing sulphur circulation problem in rotary kilns and substantially simplify the sulphur problem leading to the possibility of using fuels with higher sulphur content.

5

10

### <u>Claims</u>

5

10

15

20

25

- 1. Method of producing cement clinker, in which the cement clinker is first of all burnt in a burning zone and then cooled in a cooling zone, wherein the cooling takes place at least partially by the delivery of fuel and steam, characterised in that in a first cooling phase the delivered fuel is mixed with the cement clinker and initially pyrolysed and the resulting pyrolysis products have a strong endothermic reaction with the steam, so that the cement clinker is quenched in such a way that at least 95 %, preferably all, of the liquid phase contained therein is transformed into glass.
- 2. Method as claimed in claim 1, characterised in that carbonaceous fuel with a pyrolysable component is delivered as fuel.
- 3. Method as claimed in claim 1, characterised in that liquid and/or gaseous fuel is added for setting the rate of cooling in the first cooling phase.
- 4. Method as claimed in claim 1, characterised in that the rate of cooling in the first cooling phase is between 600 K/min and 6.000 K/min.
- 5. Method as claimed in claim 1, characterised in that the cement clinker is cooled by approximately 200 K in the first cooling phase.
- 6. Method as claimed in claim 1, characterised in that the cement clinker is quenched in the first cooling

10

25

30

- 13 -

phase from the burning temperature of the order of magnitude of 1.450 °C to 1.250 °C.

- 7. Method as claimed in claim 1, characterised in that during mixing of the fuel with the cement clinker a comminution of the cement clinker takes place simultaneously.
- 8. Method as claimed in claim 1, characterised in that in a second cooling phase a gasification of the delivered fuel with steam takes place, the gasification reaction extracting the necessary reaction enthalpy from the cement clinker.
- 9. Method as claimed in claim 8, characterised in that the fuel gases produced in the gasification reaction are used in the burning of the cement clinker in the burning zone.
- 20 10. Apparatus for producing cement clinker according to the method as claimed in one of claims 1 to 9, with
  - a) a rotary kiln (21) for burning the cement clinker,
  - b) a cooler (22) for cooling the burnt cement clinker,
  - c) an arrangement (33) for delivering a fuel,
  - d) an arrangement (34) for blowing in steam, characterised in that

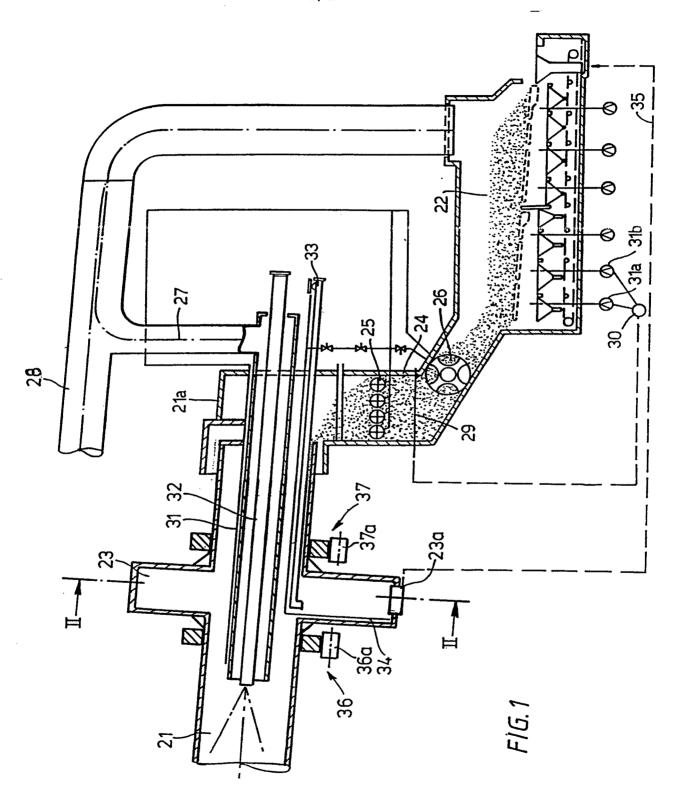
10

15

20

- e) a reactor (23) is provided which has the arrangement (33) for delivery of the fuel and the arrangement (34) for blowing in of the steam, and
- f) the reactor (23) is constructed as part of the rotary kiln and rotates therewith.
  - 11. Apparatus as claimed in claim 10, characterised in that the reactor is constructed as a part of the rotary kiln (21) with enlarged diameter.
    - 12. Apparatus as claimed in claim 10, characterised in that the reactor (23) is disposed substantially immediately before the discharge end of the rotary kiln (21).
    - 13. Apparatus as claimed in claim 10, characterised in that the rotary kiln (21) is supported immediately before and behind the reactor (23).
    - 14. Apparatus as claimed in claim 10, characterised in that the reactor is provided with a further arrangement for introducing liquid and/or gaseous fuel.

1/2



2/2

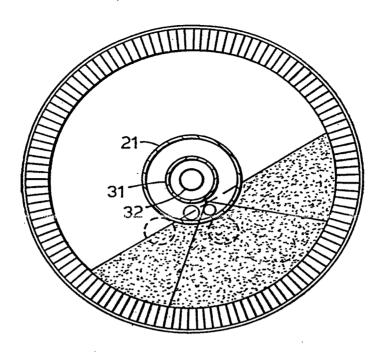


FIG.2

