

METHOD FOR PRODUCING SLAG WITH HYDRAULIC PROPERTIES

5 The present invention relates to a method for preparing a slag having hydraulically binding properties on the basis of a mixture comprising limestone, fly ash and any additives, which starting materials or raw materials are mixed, melted and pulverised.

Such a method is known from European patent No 0 393 731, one of the inventors of which is also mentioned as an inventor in the present application. According to the method is that is known therefrom, 10 the raw materials, which are based on CaO , SiO_2 and Al_2O_3 , are melted in a vessel at a temperature ranging from 1400 °C to 1550 °C, so that the result is a melt composed of 33-52 wt.% of CaO , 9-25 wt.% of Al_2O_3 and 23-45 wt.% of SiO_2 , which melt is cooled after tapping by passing it between 15 the rollers of a roller cooler (calendar) until a temperature of 500-1000 °C is reached, after which the thus solidified mass is broken and further cooled with air, with the heated cooling air being used for further heating of the raw materials. In practice it has become apparent that such a method leads to a vitrified slag having a high CaO content.

20 Both from Belgian patent application No 766 032 and from German Offenlegungsschrift No 2 122 027 there is known a method for using carbon residues and calcium carbonate, which mixture is heated to a temperature of about of 1300 °C and subsequently baked at a temperature of at least 1500 °C, during which process roasting and sintering occurs. 25 Sintering, however, is a process in which granules fuse at their surfaces, causing them to bond together. This means that in the arrangement as disclosed in the two aforesaid patent publications bonding will take place at or just above the location where the fuel is supplied, which is highly undesirable in practice, causing bonding and clogging of 30 the entire mass of solid materials in the pre-heater already, which is highly undesirable.

In many countries traditional Portland cement is still being produced, the main component of which Portland cement is Portland clinker which is prepared in a shaft furnace. This labour-intensive production process, which hardly complies with the environmental requirements (dust), if at all, and which has limitations as regards the obtained clinker quality, does not hold out much prospects as regards the realisation of adaptations that will lead to improvements or to a higher production. It has now appeared to be possible to adapt the existing infrastructure of the factory, thus making it possible to change over to another production process which likewise provides an inorganic binder for the construction industry which has practically identical properties as regards strength and processing possibilities as Portland cement.

The object of the present invention is to provide a method for preparing a slag having hydraulically binding properties, in which sintering into fist-sized or even larger lumps of the starting materials that have been heated to a high temperature must be prevented as much as possible during the course of the calcination process.

Another object of the present invention is to provide a method for preparing a slag having hydraulically binding properties, in which the starting materials are supplied to a heating furnace in the form of granules having a known composition, which heating furnace prevents sintering of the granules that have already been supplied in the desired specific composition.

Yet another object of the present invention is to provide a method which utilises the existing infrastructure of a clinker production process in which a shaft furnace is used, and which adapts said infrastructure in such a manner that slag is produced instead of clinker, the aim being to achieve a maximum throughput of fired product for the preparation of slag.

Another object of the present invention is to provide a method and apparatus in which no bonding of the granules will take place

at the surfaces thereof and so-called point contacts will occur between the slowly moving granules, as a result of which undesirable clogging of the mass is practically excluded.

The present invention as referred to in the introduction is characterized in that the method comprises the following steps:

i) mixing the starting materials, viz. limestone, fly ash and any additives, in the desired weight ratio,

ii) granulating the mixture from step i), whilst adding a solid fuel,

iii) supplying the granules from step ii) at the upper side of a cylindrical, vertical heat exchanger,

iv) supplying the fired product obtained at the bottom side of said cylindrical vertical heat exchanger to a melting furnace so as to obtain a melted product,

v) quenching the melted product obtained in step iv) so as to obtain the slag having hydraulically binding properties, and subsequently

vi) pulverising the slag obtained in step v) and mixing it with fly ash and any additives, preferably an activator, so as to obtain a binder.

By carrying out the present method in this manner, a slag having hydraulically binding properties is obtained, which, after pulverisation and mixing with fly ash and any additives, preferably an activator, yields a binder which is used as cement. The present invention is in particular suitable for use in the modification of shaft furnaces of cement factories.

An amount of granules already comprising a solid fuel, for example coal or fly ash having a high carbon content, is supplied to the heat exchanger, the composition of each of which granules is already in accordance with the desired specification, so that a slag having the correct chemical composition is obtained at the outlet of the melting

furnace. In specific embodiments it is desirable to use starting materials that have been pulverised in accordance with step i). As a result of the presence of solid fuel in the granules, an intense homogeneous reaction will take place in the granule, in which sintering effects take place only within the granules, so that there will be hardly any bonding at the surfaces thereof, which external bonding might even result in clogging of the mass. Since the granules have been fully decarbonated in the cylindrical vertical heat exchanger, the temperature of the melt is locally not adversely affected by an energy-consuming decarbonisation process. In addition, the granules cause hardly any separation in the melting furnace. Although limestone is consistently mentioned as the starting material herein, it will be apparent to those skilled in the art that besides limestone also industrial waste having a high CaO content, such as Ca(OH)_2 or CaO residues, can be used in step i) of the present method.

After pulverisation, the slag is finally mixed with a substantially identical amount of fly ash to obtain a binder as the final product. The present method has several advantages compared to the clinker production processes according to the prior art. Since the slag is of a high quality, unprocessed fly ash can be added in an amount of up to the own weight of the slag (slag : fly ash = 50 : 50). As a result, the production costs and the energy costs for the present final product are reduced to a level below that of common Portland cement. In addition to that, a significant reduction of the use of limestone per unit of final product is achieved. This leads to a strongly reduced CO_2 emission (a reduction by more than 50%). Another advantage is the fact that the final product can be produced from coal fly ash as an alternative raw material in an amount of up to 70%.

The term additives is understood to include agents such as binders, fillers and correcting agents, which latter agents are considered to be agents which, as a result of their chemical or

mineralogical composition, correct a mixture, in particular a mixture of limestone and fly ash, so as to obtain the intended optimum composition and green strength in the granules. Thus, a correcting agent is added to the raw materials limestone and fly ash in step i) of the present method
5 in order to obtain the desired chemical or mineralogical composition of the granules.

Preferably, the hot gases from the melting furnace are supplied to the cylindrical vertical heat exchanger, which hot gases move through the heat exchanger in counterflow with the package of granules
10 moving in downward direction. Such a hot gas will dry, heat, decarbonate and ignite the components that are present in the granules. From a viewpoint of efficiency it is desirable to obtain the hot gases from the waste gases of the melting furnace in full or in part. It should be understood that the heat exchanger may also be heated by means of other
15 energy sources, such as coal, usual fuels or natural gas.

In the present method it is in particular important that the temperature in the cylindrical vertical heat exchanger be controlled so that sintering together of the granules supplied in accordance with step iii) is prevented and complete decarbonation is achieved. Such a
20 temperature adjustment will effect a minor ceramic binding within the granules during their residence and movement through the heat exchanger, after which the granules are carried to the melting furnace, where they will react in a manner which is known per se.

Furthermore, the temperature at the bottom side of the cylindrical vertical heat exchanger is preferably about 1100-1300 °C and
25 the temperature of the melting furnace is preferably about 1400-1550 °C.

In principle, two partial flows can be distinguished in the cylindrical vertical heat exchanger, viz. the granules being supplied at the upper side and the hot gases from the melting furnace being supplied
30 at the bottom side. Due to the high temperatures of the gases from the melting furnace, the package of granules slowly moving through the

cylindrical vertical heat exchanger will be heated by the hot gases being supplied in counterflow therewith. In order to support the flow of the hot gases in upward direction through the cylindrical vertical heat exchanger, a draught fan is preferably installed at the upper side of the cylindrical vertical heat exchanger. An additional advantage of the package of granules moving in downward direction through the cylindrical vertical heat exchanger is the fact that said package functions as a dust collector. Any fine residual substances can be collected at the upper side of the heat exchanger by conventional dust removing installations.

In a special embodiment it is desirable to use a shaft furnace as the cylindrical vertical heat exchanger and a melting furnace for the preparation of rock wool or glass wool as the melting furnace.

According to the present method, limestone, fly ash and any additives are already present in a desired proportion in the granules that have been formed, which has a positive effect on the chemical and physical processes that take place in the cylindrical vertical heat exchanger and the melting furnace.

In order to obtain a binder having excellent hydraulically binding properties, it is preferred to add an activator, for example a substance exhibiting an alkalic reaction, such as NaOH, Ca(OH)_2 and the like, as an additive in step vi). Another suitable additive to be added in step vi) is dried, natural pozzolan which has been pulverised to the dimension of cement.

The granules to be produced in accordance with the present method in particular vary only to a slight degree as regards their grain diameter, with a diameter of, for example, 1-2 cm being preferred, which granules may be obtained by the possible addition to the starting materials, viz. limestone, fly ash and any additives, of a component which is conducive towards the physical cohesion between the pulverised starting material components. The use of granules is in particular advantageous in order to prevent undesirable variation in the adjusted

proportion of the elements upon entry in the melting furnace.

Although fly ash from coal-fired plants is consistently mentioned herein, it is also possible to use other residual substances, such as incinerator residues, other types of fly ash, purified steel
5 grit, sewage sludge, sludge from sewage treatment plants, asbestos, metallic slags, dredged material and other substances containing impurities. In the preparation of the present slag having hydraulically binding properties it is furthermore important for the melt not to
crystallise but to remain in its vitreous state, because crystallisation
10 would lead to an unusable final product.

CLAIMS

1. A method for preparing a slag having hydraulically binding properties on the basis of a mixture comprising limestone, fly ash and any additives, which starting materials are mixed, melted and pulverised, characterized in that the method comprises the following steps:

i) mixing the starting materials, viz. limestone, fly ash and any additives, in the desired weight ratio,

ii) granulating the mixture from step i), whilst adding a solid fuel,

iii) supplying the granules from step ii) at the upper side of a cylindrical, vertical heat exchanger,

iv) supplying the fired product obtained at the bottom side of said cylindrical vertical heat exchanger to a melting furnace so as to obtain a melted product,

v) quenching the melted product obtained in step iv) so as to obtain the slag having hydraulically binding properties, and subsequently

vi) pulverising the slag obtained in step v) and mixing it with fly ash and any additives so as to obtain a binder.

2. A method according to claim 1, characterized in that the hot gases from the melting furnace are supplied to the bottom side of said cylindrical vertical heat exchanger, which hot gases move through the heat exchanger in counterflow with the package of granules moving in downward direction.

3. A method according to any one of the preceding claims, characterized in that the temperature in the cylindrical vertical heat exchanger is controlled so that sintering together of the granules supplied in accordance with step iii) is prevented and complete decarbonation is achieved.

4. A method according to any one or more of the preceding

claims, characterized in that the temperature of the melting furnace is higher than the temperature of the cylindrical vertical heat exchanger.

5 5. A method according to claim 4, characterized in that the temperature at the bottom side of the cylindrical vertical heat exchanger is about 1100-1300 °C and the temperature of the melting furnace is about 1400-1550 °C.

6. A method according to any one or more of the preceding claims, characterized in that a shaft furnace is used as said cylindrical vertical heat exchanger.

10 7. A method according to any one or more of the preceding claims, characterized in that a melting furnace for the preparation of rock wool or glass wool is used as said melting furnace.

8. A method according to any one or more of the preceding claims, characterized in that pulverized starting materials are used in
15 accordance with step i).

9. A method according to any one or more of the preceding claims, characterized in that the additive in step vi) comprises an activator.

10. A method according to any one of the preceding claims,
20 characterized in that the additive in step i) comprises a correction agent.

11. A method according to any one of the preceding claims, characterized in that the additive in step vi) is dried natural pozzolan, which has been pulverized to the dimension of cement.

25 12. A method according to any one or more of the preceding claims, characterized in that the granules obtained in step ii) vary only to a slight degree as regards their grain diameter, the diameter in particular being 1-2 cm.