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(57) **Abrégé/Abstract:**

In a method for producing photocatalytically active clinker, TiO_2 -containing materials are reacted to calcium titanates, particularly CaTiO_3 , with clinker raw meal or clinker raw mix.



Abstract:

In a method for producing photocatalytically active clinker, TiO_2 -containing materials are reacted to calcium titanates, particularly CaTiO_3 , with clinker raw meal or clinker raw mix.

Method for producing photocatalytically active clinker

The invention relates to a method for producing photocatalytically active clinker.

Photocatalysis in this context means reactions in which a catalyst is brought into an excited state by the exposure to light of a suitable wavelength, which state enables the catalysis of various degradation reactions of different organic molecules. The catalyst in such reactions returns to the initial state and can be reexcited by light.

A number of construction materials in which the photocatalytic phenomenon is utilized are already known, with titanium dioxide in the anatase form being used in the first place. European Patent EP 1 535 886 discloses a hydraulic binder containing titanium dioxide together with additives and water in the form of photocatalytic particles, at least 5% by weight of the titanium dioxide particles having anatase structure. In the hydraulic binder according to EP 1 535 886, anatase portions of the titanium dioxide phase of up to 70% are, moreover, provided, the balance of the titanium dioxide primarily comprising rutile. In that hydraulic binder, the share of the anatase form in the total amount of the present titanium dioxide is thus extremely important for its photocatalytic action such that the selection and sourcing of suitable titanium dioxide is problematic.

It is, therefore, the object of the present invention to provide a method that enables the production of photocatalytically active clinker, and hence photocatalytically active cement, in which titanium dioxide can be used irrespectively of its origin and anatase content. To solve this object, the method according to the invention essentially consists in that TiO_2 -containing materials are reacted to calcium titanates, particularly CaTiO_3 ,

with clinker raw meal or clinker raw mix. The method according to the invention enables TiO_2 -containing materials of any origin to be directly introduced into the clinker during the clinker production process and reacted to the photocatalytically active species referred to as calcium titanate or CaTiO_3 . These compounds, besides CaTiO_3 , also comprise other compounds such as CaTiO_4 , $\text{Ca}_3\text{Fe}_2\text{TiO}_8$, CaTi_4O_9 , $\text{Ca}_2\text{Ti}_5\text{O}_{12}$, $\text{Ca}_4\text{Ti}_3\text{O}_{10}$, $\text{CaTi}_2\text{O}_4(\text{OH})_2$, $\text{NaK}_2\text{Ca}_2\text{TiSi}_7\text{O}_{19}(\text{OH})$, CaTiSiO_5 , BaCaTiO_4 , $\text{Ca}_3\text{Fe}_2\text{TiO}_8$, $\text{Ca}_2\text{TiO}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$, $\text{Mg}_2\text{TiO}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$, $\text{Fe}_2\text{TiO}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$, $\text{Al}_2\text{TiO}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$, $\text{Ca}_3\text{Fe}_3\text{O}_{12}$, $\text{Ca}_3\text{Ti}_3\text{O}_{12}$, $\text{Ca}_3(\text{Ti}_2\text{Si})_3\text{O}_{12}$, $\text{Ca}_3\text{Fe}_2\text{TiO}_4(\text{OH})_8$, $\text{MgAl}_2\text{TiO}_3\text{O}_{10}$, $\alpha\text{-Al}_2\text{TiO}_5$, Al_2TiO_5 , $\text{Mg}_2\text{Al}_6\text{Ti}_7\text{O}_{25}$ and $\text{BaTi}_4\text{Al}_2\text{O}_{12}$. All of these compounds are photocatalytically active and improve the photocatalytic activity of the clinker and the cement, respectively, and they are formed depending on the availability of oxides like Al_2O_3 , Fe_2O_3 , BaO , SrO , Mn_2O_3 , SiO_2 , Na_2O , K_2O or the like.

The method according to the invention is advantageously further developed to the effect that the TiO_2 -containing materials are charged into, and burned in, a rotary kiln together with the clinker raw mix, which will be of particular advantage if the titanium dioxide is present in powder form, thus enabling easy mixing with the raw meal for the production of clinker. Alternatively, it may, however, preferably be provided that the TiO_2 -containing materials and the clinker raw mix are separately charged into the rotary kiln, and reacted and burned together in the rotary kiln. Such a process control will be advantageous if the titanium dioxide is present in the form of a suspension such that mixing with the calcined raw meal appears to be infeasible. The moist or wet TiO_2 -containing materials in this case can be introduced into the rotary kiln by the aid of known injection devices, thus causing thorough mixing of the TiO_2 -containing materials with the raw meal only in the rotary kiln during the conversion of TiO_2 to CaTiO_3 or any of the above-mentioned compounds.

The method according to the present invention is advantageously further developed such that the combustion occurs at temperatures above 1250°C, preferably at 1350°C, and in a particularly preferred manner at 1450°C. It was experimentally found that the formation of CaTiO_3 from CaO and TiO_2 started at temperatures above 1250°C, the complete reaction of the used titanium dioxide with the excess CaO to CaTiO_3 having been observed at combustion temperatures of 1450°C

In order to provide a sufficient photocatalytic action of the cement made with the clinker produced by the method according to the invention, a suitable amount of CaTiO_3 must be present in the clinker, wherein an overdose of CaTiO_3 would jeopardize the physical integrity of the cement. The method according to the present invention is, therefore, preferably further developed to the effect that the TiO_2 -containing materials are added to the clinker raw mix in amounts producing a TiO_2 content of 2% by weight to 5% by weight and, in particular, 3% by weight, from which CaTiO_3 portions of approximately 4% by weight to 10% by weight will result in the clinker. If required, the portion of used titanium dioxide may, however, also be chosen to be higher.

As already mentioned in the beginning, the method according to the invention enables the use of TiO_2 -containing materials of the most different origins, and it is preferably provided in the context of the method according to the present invention that waste substances such as dye sludge, waste dye, kiln ashes, synthetic materials and/or consumed TiO_2 catalyst are used as TiO_2 -containing materials. Such starting materials are available on the market at extremely low cost and even involve disposal problems in some industrial branches, so that the present invention allows for the production of photocatalytic clinker in an extremely cost-effective manner. When using dye sludge, waste

dye and synthetic materials, the solvent residues, or residues of other organic compounds, possibly still contained in these materials may even provide additional benefits to the effect that the compounds present besides TiO_2 may serve as secondary fuels in the clinker process.

The method according to the invention is suitable for the production of photocatalytically active clinker based on already known clinker compositions, said method advantageously being further developed to the effect that a raw mix for calcium sulfoaluminate clinker is used as clinker raw mix. The CaTiO_3 formed by the method according to the invention will not adversely affect the setting and strength characteristics of the finished clinker, thus enabling the clinker produced by the method according to the invention to be processed in a known manner. Alternatively, it may advantageously proceed such that a raw mix for Portland cement clinker is used as clinker raw mix.

According to a further object of the present invention, photocatalytically active clinker is provided, which is characterized in that the photocatalytically active phase comprises calcium titanates, particularly CaTiO_3 . The group of calcium titanates comprises the above-mentioned compounds. As described in the beginning, titanium dioxide and, in particular, titanium dioxide in the anatase form has so far been used for photocatalytically active clinker or photocatalytically active cement. It has now turned out in a surprising manner that also CaTiO_3 possesses outstanding photocatalytic properties, wherein CaTiO_3 can be directly produced during the clinker process in an extremely cost-effective manner by the above-identified method. For the production of CaTiO_3 it may alternatively also be proceeded in a manner that CaTiO_3 -containing materials and, in particular, materials indicated above as being preferred for carrying out

the method according to the invention are reacted with CaO at temperatures above 1250°C and, in particular, at 1450°C.

In order to ensure both a sufficient photocatalytic activity and the required strength characteristics in the clinker according to the invention, the clinker according to the invention is advantageously further developed such that CaTiO_3 is contained in amounts of 2% by weight to 10% by weight and, in particular, in amounts of 6% by weight.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for producing photocatalytically active clinker, wherein TiO_2 -containing materials are reacted to calcium titanates with clinker raw meal or clinker raw mix, via charging the TiO_2 -containing materials into, and burning them in, a rotary kiln together with the clinker raw mix or via charging the TiO_2 -containing materials and the clinker raw mix separately into the rotary kiln, and reacting and burning them together in the rotary kiln, whereby the combustion occurs at temperatures above 1250°C and wherein dye sludge, waste dye, kiln ashes, synthetic materials and/or consumer TiO_2 catalyst are used as the TiO_2 -containing materials.
2. A method according to claim 1, wherein the calcium titanates are CaTiO_3 .
3. A method according to claim 1 or 2, wherein the combustion occurs at a temperature of 1350°C .
4. A method according to claim 3, wherein the combustion occurs at a temperature of 1450°C .
5. A method according to any one of claims 1 to 4, wherein the TiO_2 -containing materials are added to the clinker raw mix in amounts producing a TiO_2 content of 2% by weight to 5% by weight.

6. A method according to claim 5, wherein the TiO_2 -containing materials are added to the clinker raw mix in amounts producing a TiO_2 content of 3% by weight.

7. A method according to any one of claims 1 to 6, wherein a raw mix for calcium sulfoaluminate clinker is used as the clinker raw mix.

8. A method according to any one of claims 1 to 7, wherein a raw mix for Portland cement clinker is used as the clinker raw mix.