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(54) **PROCEDE DE PRODUCTION DE CIMENT**

(54) **METHOD FOR PRODUCING CEMENT**

(57) L'invention concerne un procédé de production de ciment, selon lequel les matières de départ du ciment sont frittées dans un four. Ce procédé comprend l'injection ou la pulvérisation de sols métalliques ou composés métalliques de préférence dans le dernier tier d'un four afin d'obtenir des ciments colorés tout en excluant les étapes d'oxydation indésirables des métaux (notamment des chromates).

(57) The invention relates to a method for producing cement, in which the starting materials of the cement are sintered in a furnace. Metal sols or metal compounds are sprayed in or injected preferentially in the last third of a kiln, so as to obtain, in this way, coloured cements, as well as to exclude undesirable oxidation steps of metals (particularly chromates).



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(54) Title: METHOD FOR PRODUCING CEMENT (54) Bezeichnung: VERFAHREN ZUM HERSTELLEN VON ZEMENT (57) Abstract The invention relates to a method for producing cement, in which the starting materials of the cement are sintered in a furnace. Metal sols or metal compounds are sprayed in or injected preferentially in the last third of a kiln, so as to obtain, in this way, coloured cements, as well as to exclude undesirable oxidation steps of metals (particularly chromates). (57) Zusammenfassung Das erfindungsgemäße Verfahren zum Herstellen von Zement, bei welchem die Ausgangsstoffe der Zemente in einem Ofen gesintert werden, umfaßt das Eindüsen oder Einsprühen von Metallsolen oder Metallverbindungen bevorzugt in das letzte Drittel eines Brennofens, um auf diese Weise sowohl farbige Zemente zu erzielen als auch unerwünschte Oxidationsstufen von Metallen (insbesondere Chromate) auszuschließen.				

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Process for Producing Cement

The invention relates to a process for producing cements, in which the cement raw materials are burnt or sintered in a furnace after the dry or wet process while introducing
5 reducingly acting substances into the furnace.

Heating, or reaching accordingly high burning temperatures, of the furnaces (usually rotary tubular kilns) may be effected by
10 aid of oils, gases, solid fuels or the like while generally operating at an excess of oxygen, whereby a largely oxidizing furnace atmosphere usually prevails throughout the furnace length.

15 Natural cement raw materials occur at different purities. Depending on the raw materials used, a number of heavy metals other than iron may be additionally contained in the starting materials, wherein, in particular, the presence of metals of side-groups III to VIII may give rise to various problems
20 during the sinter process in an oxidizing atmosphere.

Thus, chromium might, for instance, be present in cement clinker both in the trivalent and in the hexavalent oxidation stages. Yet, an excessive burden by chromium VI of the end
25 product is undesired. It is, therefore, sought to avoid undesired oxidation stages, in particular, of chromium. A partially reducing furnace atmosphere, as a rule, is feasible only by means of specific furnace control and incomplete combustion.

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Also when using complexly composed fuels (e.g., sewage sludges, used tires, etc.) foreign substances may occur in undesired oxidation stages. Moreover, it is desired to produce cements always in stable basic colorings dyed with oxides.

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From DD 246 983 A1 it has become known to introduce reducingly acting substances into the rotary tubular kiln. No examples of

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such substances have been given. The use of Fe(II) sulfates after burning is supposed to have a retarding effect on setting.

- 5 DD 153 816 A1 proposed to nozzle ammonium salts, optionally along with phosphoric acid esters, as a solution or emulsion into the rotary tubular kiln.

10 The invention aims at providing a process for producing cements of the initially defined kind, by which the occurrence of undesired oxidations stages of metals (e.g., the oxidation to chromates) can be restricted or prevented without affecting the economy of furnace control. The formation of toxic organic substances and the formation of SO₂ or other gaseous noxious
15 matter are to be avoided, in particular. At the same time, the process according to the invention aims at adjusting the coloration of the obtained cement during or after the sintering process in a simple and concerted manner such that cements of different colors may be directly produced.

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To solve this object, the process according to the invention essentially consists in that metal oxide, metal hydroxide, metal oxide hydrate and/or metal sols, or metal phosphates, metal silicates or sols thereof are nozzled or sprayed into
25 the furnace.

Such metal oxide, metal hydroxide, metal oxide hydrate and/or metal sols or metal compounds are capable of safeguarding reducing zones in an oxidizing furnace atmosphere, utilizing
30 redox reactions without affecting furnace control, said reducing zones being precisely definable in terms of space. The furnace can, thus, be operated in a usual manner while applying the energetically most favorable mode of operation, an appropriate reducing zone being formed only in that furnace
35 region in which reduction is sought. When adding metal compounds or sols thereof, the analysis of the raw products may be taken into consideration so as to adjust the redox

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effect precisely to the analysis of the starting products. Advantageously, the process according to the invention may be realized in that the metal oxide, metal hydroxide, metal oxide hydrate and/or metal sols or metal compounds or sols thereof
5 are introduced into the furnace in the last third of the path of the cement clinker, whereby it is ensured that undesired oxidation stages are excluded upon emergence from the furnace. Moreover, the above-mentioned sols or metal compounds may also be directly sprayed on the clinker leaving the
10 furnace (mostly 80 to 120°C) so as to display a uniformly reducing effect.

By means of the metal oxide, metal hydroxide, metal oxide hydrate and/or metal sols or metal phosphates or silicates or
15 sols thereof used according to the invention, it is also feasible to lastingly influence the coloring of the cement. In addition to the conventional colors, which usually go back to iron oxide, color tones that have hitherto been obtainable by cumbersome subsequent process steps only may be realized by a
20 number of metals and metal oxides etc. At the same time, it is feasible by the purposeful selection of such metal oxide, metal hydroxide, metal oxide hydrate and/or metal sols or metal phosphates, silicates or sols thereof to adjust within predetermined limits also the surface quality of the cement
25 particles to come as well as their setting behavior.

Advantageously, monomers, heteropolymers or polymers of metal oxide, metal hydroxide and/or metal oxide or metal oxide hydrate sols are used as sols. Advantageously, these are
30 metals and/or oxides thereof, hydroxides, oxihydrates or phosphates or silicates of metals of the third to eighth side-groups of the Periodic Table, the sols being able to enter into action in a concerted manner.

35 According to a particularly preferred further development of the process according to the invention, only those metals which have suitable reduction potentials are employed, thereby

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ensuring effective reduction (e.g., of Cr^{6+}). According to the invention, the basic condition required therefor (in particular, in order to prevent the formation of the chromate stage) is met if and when the metals and/or metal compounds
5 have redox potentials sufficient for the reduction of Cr^{6+} to Cr^{3+} .

In addition, a great number of different colors of the color spectrum may be obtained by choosing suitable metals or metal
10 compounds for dyeing a thus produced cement (and hence, for instance, colored mortars or plasters in a subsequent step).

Finally, the sols may be employed in the grinding of cement clinker, thereby also enabling a reduction of undesired
15 oxidation steps (e.g., Cr^{6+} to Cr^{3+}).

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Claims:

1. A process for producing cement, in which cement raw materials are burnt or sintered in a furnace while introducing
5 reducingly acting substances into the furnace, characterized in that metal oxide, metal hydroxide, metal oxide hydrate and/or metal sols, metal phosphates, metal silicates or sols thereof are nozzled or sprayed into the furnace.
- 10 2. A process according to claim 1, characterized in that the sols and/or the metal compounds or sols thereof are introduced in the last third of the path of the cement through the furnace.
- 15 3. A process according to claim 1, characterized in that monomers, heteropolymers or polymers of metal oxide, metal hydroxide and/or metal oxide or metal oxide hydrate sols are used as sols.
- 20 4. A process according to claim 1, 2 or 3, characterized in that the metals are selected from the third to eighth side-groups of the Periodic Table.
- 25 5. A process according to any one of claims 1 to 4, characterized in that the metals and metal compounds have redox potentials sufficient for the reduction of Cr^{6+} to Cr^{3+} .
- 30 6. A process according to any one of claims 1 to 5, characterized in that the compounds or sols nozzled or sprayed into the furnace subsequently are added both prior to and during clinker grinding.