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## Expansive cement admixture contg. alumina and calcium salts

DE 4447852 C2

### المخلص

A cement admixture comprises an expansive material which is produced by mixing CaO raw material, Al<sub>2</sub>O<sub>3</sub> raw material and CaSO<sub>4</sub> raw material, followed by heat treatment, and which has a CaO/Al<sub>2</sub>O<sub>3</sub> molar ratio of 6.5-18 and a CaSO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 1.5-4. Also claimed are (i) a cement compsn, comprising cement and the above admixture; and (ii) chemically prestressed concrete produced by subjecting a cement mix of compsn. (i) to compaction in a .mould and then hardening

### الوصف مترجمة من الألمانية

The present invention relates to a cement admixture, a cement composition and produced therefrom, chemically prestressed Be ton. This is primarily useful in the .fields of housing, for building and for construction purposes

Cement provides for the construction of residential buildings or for the construction of buildings is an indispensable material. It can be said that one can .produce cost than cement large structures with any other material

In the cured products produced from cement, however slight cracks form, which is .a problem. Such a cracking may be caused by various factors

One of these factors is the drying shrinkage and for the purpose of drying shrinkage compensation of such a number of expansive cement materials has .been proposed

As a second factor for the thermal cracking cracking may be mentioned due to the heat of hydration. As a method for reduction of thermal cracking has been the use of a low heat generating element Ze proposed, that is a cement that generates a small amount of Hy dratationswärme. It has also been proposed a method in which an expansive cement material and a means for suppressing the heat-tion .Hydrata be used in combination

The cement with low heat generation, a sol cher is mainly used in which a large amount of Puzzolanmaterials is incorporated as for example blast furnace slag or fly ash, Portland cement. It is also known that this material is effective to prevent thermal cracking of a concrete mixture for construction purposes, z. B. a dam, and .may be the reason that which occurs at the beginning of hydration Wärmebil tion reduced remarkably to

The cracks formed in a structure are usually a combina tion of thermal cracking and cracking due to drying shrinkage. Therefore, in order to prevent cracking at large, it is common practice to use egg nen cement, low heat generation and an .expansive cementitious material in combination

As expansive cement materials are those of 3CaO. SiO<sub>2</sub> - free CaO; 3CaO. SiO<sub>2</sub> - free CaO - Free CaSO<sub>4</sub>; and 3CaO. 3Al<sub>2</sub>O<sub>3</sub> -CaSO<sub>4</sub> - free CaO - Free CaSO<sub>4</sub> known (Japanese Unexamined Patent publications No. 650/1987 13, No. 31 and .(No. 7 170/1978 171/1976 and German published patent applications DE-OS 21 62 053 and... DE-OS 20 48 127

These expansive cement materials, however, there is the problem that when they are used as cement mixtures, which pozzolan materials are as blast furnace slag, fly ash and silica incorporated, the expansive properties are impaired remarkably. Consequently, this expansive cement materials must if they are to be used for such cement mixtures are used in

### المطالبات (4) مترجمة من الألمانية

1 .cement admixture comprising an expanding material which has been prepared by mixing CaO raw material, Al<sub>2</sub>O<sub>3</sub> and CaSO<sub>4</sub> -Rohmaterial -Rohmaterial, followed by heat treatment, and that after the heat treatment, a CaO / Al<sub>2</sub>O<sub>3</sub> molar ratio of 6 , 5 to 18 and a CaSO<sub>4</sub> / Al<sub>2</sub>O<sub>3</sub> molar ratio of 1.5 to 4, wherein a latent hydraulic material, a thickening agent and a water reducing agent are .incorporated into the cement admixture

2 .cement admixture comprising an expanding material which has been prepared by mixing CaO raw material, Al<sub>2</sub>O<sub>3</sub> and CaSO<sub>4</sub> -Rohmaterial -Rohmaterial, followed by heat treatment, and that after the heat treatment, a CaO / Al<sub>2</sub>O<sub>3</sub> molar ratio of 6 , 5 to 18 and a CaSO<sub>4</sub> / Al<sub>2</sub>O<sub>3</sub> molar ratio of 1.5 to 4, wherein dextrin wt .-% of the cement admixture incorporated with a cold water soluble .content of 10 to 65

3 .A cement composition comprising cement and as defined in any one .of claims 1 or 2 cement admixture

4 .Use of a cement composition according to claim 3 for preparing a .chemically prestressed concrete

large quantities, and they can be practically applied in economic terms hardly. Further, there is a problem in that the  
.Langzeitbe resistance of the concrete may be impaired

In addition to the impairment of the expansive properties occurs when these expansive cement materials are incorporated in  
.large quantities, a delay in the timing of the expansion, the reinforcing effect is reduced and it is easy to expansion cracks

On the other hand, in recent years for the purpose of saving labor and in view of the difficulties in workplace safety of  
construction workers and in view of the continually increasing size of the Kon constructions concrete mixtures have been  
proposed in which orientation no Kompak is required or compacted with low vibration can be. In these, a large amount of a  
thickening agent and an agent for water reduction incorporated and a latent hydraulic material such as fly ash or blast furnace  
.slag is mixed with the cement (Japanes cal Unexamined Patent Publication Nos. [45 522/1991](#) and no. [237 049/1991](#)

These concrete mixture compositions, however, there was a problem per the fact that a substantial shrinkage occurred and  
.the dimensional stability is poor

Prestressed concrete is currently tonkonstruktionen widely used in the field of building and Be. Made of prestressed concrete  
structures are characterized by the feature that the concrete does not crack under the intended load. The resistance is good,  
they have a low weight, the material is strong and can prepare excellent. Prefabricated solid compound structures can be  
easily formed where the connecting portions must be fastened together securely, and they can give the components a safety  
.factor

As a method for introducing bias voltages, a mechanical method, an electrical method and a chemical method is known. A  
chemical method, ie a chemical biasing method, in ERAL nen in the case of concrete pipes or parts of buildings used with  
complicated shape and difficult stages of production. Various Zementbeimisch ments for such chemically prestressed  
concrete have been proposed (eg. As Japanese Unexamined Patent Publication Nos. [171/1976 7](#), no. 13650/1978 and no.  
.[31 170/1978](#)

With respect to an increasing demand for lightweight concrete structures, it has become necessary in recent times,  
increasingly, apply chemical bias. It is used, for example, for the purpose of improving the work efficiency or reducing the  
costs frequently cement mixtures in which a pozzolanic material, such as blast furnace slag or fly ash incorporated is.  
Furthermore, chemical bias voltage is applied in the context of increasing use under adverse environmental conditions, such  
.as the application under ground

In a mixed cement, however, there is the problem that an adequate chemical bias with a conventional Zementbeimisch  
.clothes can not be imported

The inventors have found that it is possible to solve the above problems by using a cement admixture, which comprises a  
.certain specific component. The invention is based on these findings

The present invention thus provides a cement admixture comprising an expanding material which has been prepared by  
reacting CaO raw material,  $Al_2O_3$  -Rohmaterial and  $CaSO_4$  -Rohmaterial mixed, followed by heat treatment, and a CaO /  
 $Al_2O_3$  molar ratio of 6.5 to 18 and a  $CaSO_4 / Al_2O_3$  molar ratio of 1.5 to 4, wherein said cement admixture further relates  
are incorporated into a latent hydraulic material, a thickening agent and a water reducing agent. The invention further relates  
to a cement admixture, wherein the dextrin having a cold water soluble content of 10 to 65 wt .-% in such a cement admixture  
incorporated in cement compositions comprise a cement and the cement admixtures; and the use of this mixture for the  
.preparation of a surface pre-stressed concrete

.In the following the invention is explained in detail

The expansive material in the cement admixture according to the invention gives the mixed cement an effective expansive  
property. The Ma material was improved by adjusting the mixing ratios of CaO Raw,  $Al_2O_3$  and  $CaSO_4$  -Rohmaterial -  
.Rohmaterial in the specified ranges

The raw materials for the expansive material which is used according to the invention can be arbitrarily selected, depending  
on the purity and cost. They are not particularly limited. The material can  $CaO_3$  material or  $Ca(OH)_2$  material be such as  
limestone or hydrated lime for example  $CaCO_3$ ;  $Al_2O_3$  -Rohmaterial may be such as bauxite, aluminum or ash residue and  
.  $CaSO_4$  -Rohmaterial example, anhydrous gypsum, hemihydrate or gypsum dihydrate be

Impurities, such as  $SiO_2$ ,  $Fe_2O_3$ ,  $CaF_2$ , MgO and  $TiO_2$ , present in the raw materials are not particularly limited as long as  
.they do not adversely affect the purpose of the present invention

In the present invention, the mixing ratios of the raw materials have to be adjusted such that the CaO /  $Al_2O_3$  molar ratio in  
the resulting expansive material from 6.5 to 18 and the  $CaSO_4 / Al_2O_3$  molar ratio of 1.5 to 4 is. The CaO /  $Al_2O_3$  molar  
ratio is preferably in front of 8-12 and  $CaSO_4 / Al_2O_3$  molar ratio is preferential from 2 to 3. If the CaO /  $Al_2O_3$  molar ratio  
is smaller than 6.5 is not sufficient expansive property obtained when the expansive material is used for a cement mixture.  
Other hand, if the ratio exceeds 18, are readily formed expansion cracks. Similarly, if the  $CaSO_4 / Al_2O_3$  molar ratio of less

than 1.5, do not receive adequate expansive property and if the ratio exceeds 4, the timing of the expansion is delayed and it may form expansion cracks.

In the present invention, the decomposition temperature of gypsum to form sulfuric acid varies significantly depending on the mixture ratios of the raw material mixtures  $M_i$  or the content of the contaminants. The firing temperature is not particularly limited. In general, the firing temperature is preferably 1100-1600 °C.

A method of mixing the raw materials is not particularly limited and conventional methods are used.

In the following a method for producing the expansive materials is described.

The heat treatment method for producing the Zementbeimischung mixture is not particularly limited and it may be any method, such as oven baking with a rotary kiln or melting with an electric, can be used.

The fineness of the expansive material, the present invention will depend upon the particular purpose or application and is not particularly limited. Usually, however, it is preferable to provide a level of fineness Blainewerts 1500-8000  $\text{cm}^2/\text{g}$ . If this value is to be less than 1500  $\text{cm}^2/\text{g}$ , the reinforcing effect is reduced, and if it exceeds 8000  $\text{cm}^2/\text{g}$ , sufficient expansive property is obtained.

In the case of cement admixture comprising the expansive material and the subsequently mentioned latent hydraulic material, thickening agent, and water reducing agent, the amount of the expansive material parts by weight is usually from 3 to 12 parts by weight, more preferably from 5 to 7 in 100 parts by weight of a binder comprising the below-mentioned cement, the expansive material and the below mentioned latent hydraulic substance. However, depending on the particular use, the ratio can also vary. If the amount is less than 3 parts by weight, an adequate expansive property hardly be obtained and if the amount exceeds 12 parts by weight, it is easy to abnormal expansion.

In the case of cement admixture comprising the expansive material and the dextrin mentioned below, the amount of expansive material is preferably from 80 to 98 parts by weight, more preferably from 90 to 95 parts by weight, in 100 parts by weight of the cement admixture. If the amount is less than 80 parts by weight, the reinforcing property is reduced and if the amount exceeds 98 parts by weight, the effect of the alteration is Verhinder heat generation by hydration small.

The latent hydraulic material which is used according to the invention is the cement to improve the fluidity, stability compared to the separation of the materials and for improving the density. Specifically, it may, for example, a pozzolanic material such as silica dust, fly ash or fine powder of blast furnace slag. The fineness of the latent hydraulic material is not particularly limited, but is preferably at a level of a Blaine value of at least 4000  $\text{cm}^2/\text{g}$ . If the fineness is less than 4000  $\text{cm}^2/\text{g}$ , no sufficient level of fluidity or resistance is obtained against separation of materials.

The amount of the latent hydraulic material is preferably from 10 to 70 parts by weight per 100 parts by weight of the total amount of cement and latent hydraulic material. If the amount is less than 10 parts by weight, the fluidity or resistance to separation of the materials in the cement composition becomes insufficient, and if the amount exceeds 70 weight parts, the fluidity is extremely small.

In the present invention, the thickening agent is used to obtain the fluidity or maintain separation of the materials to a certain extent. Special mention thickeners are nitrid from wasserlöslich union polymers of z. B. methyl cellulose type, polyethylene glycol type, Ethylene, acrylic type, such as polyacrylamide, polyvinyl alcohol and. However, it can also be a commercial product, which is available as an aqueous admixture nichtaufrennbare available used.

The aqueous, non-separable admixture may for example be of methyl cellulose type, such as "Askaclean", "Aqua Eter", or "Denkastabikon A", or the acrylic type, such as "Seabetter", or "Aronsecrete W".

These thickeners may be used in an amount as given by the respective manufacturers. However, in general the amount of such a thickening agent is preferably from 0.01 to 2 kg per  $\text{m}^3$  of concrete. It is advisable to change the amount corresponding to the respective usage purpose or the conditions of use in its intended purposes manner.

The water reducing agent according to the invention to be used under is not particularly limited. However, it is preferred to use a high-performance AE water-reducing agent or a fluidizing agent.

Water reducing agents can be broadly classified into a naphthalene, a melamine, a polycarboxylic acid and aminosulfonic acid.

As typical examples are "Maity WH 2000", "Denka FT-500" or "Denka FT-80" are mentioned as the naphthalene type, "Mermento F-10" or "Sicament 1000H" can be mentioned as the melamine-type; "Darlex super 100PHX" or "super Darlex 200", or "Reobuild SP-8HS" were mentioned as the polycarboxylic acid type; and "Paric FP-100U" can be mentioned as aminosulfonic acid.

These water reducing agents may in such an amount be used provided they are given by the manufacturers respectively. In the case of the naphthalene type or melamine type, the amount, however, preference, from 1 to 4 parts by weight per 100 parts by weight of a binder which comprises cement, the expansive material and the latent hydraulic material.

Similarly, in the case of the polycarboxylic acid type or of the Aminosulfonsäuretyps the amount is preferably from 1 to 2 parts by weight. The amount of the water reducing agent is not particularly limited to these examples

In the present invention, dextrin is used as a means to lower the suppression of hydration of the cement. If only his cold soluble content of 10 to 65 wt.-%, in any dextrin can be used in the present invention, for example, one that is available such by adding a dilute acid to starch, followed by heat decomposition, which obtainable by enzymatic Zerset tion of starch or one which is obtainable by condensation of glucose

With "cold soluble content" of dextrin is understood here as the amount of dextrin, which dissolves in distilled water at a temperature of 21 ° C. Specifically, 10 g of dextrin are introduced into a 200 ml flask. Closing at 150 ml of distilled water are added at a temperature of 21 ° C and the mixture is kept one hour at a temperature of 21 ± 1 ° C, followed by filtration. The filtrate is distilled to dryness, then the ratio of the resulting dextrin is found to the un-age lights as cold soluble dextrin content

In the present invention, the cold soluble content of Dex trin is from 10 to 65 wt.-%, preferably from 15 to 50 wt.-%, more .%- before given to from 20 to 40 wt

The amount of dextrin is preferably from 2 to 20 wt.-%, more preferably from 5 to 10 wt.-% in 100 parts by weight of a cement admixture containing Zementbei or a mixture containing the dextrin, the expansive material and the expansive material, amorphous calcium aluminate and includes the dextrin. If the amount is less than 2 parts by weight, the effect is small in terms of suppressing the heat of hydration, and if the amount exceeds 20 parts by weight, the reinforcing property is .low

In the present invention, the cement admixture is one which comprises the expansive material, the latent hydraulic material, .the Verdickungsmittel and the water reducing agent and one which comprises the expansive material and dextrin

The fineness of the powder of the cement admixture invention depends on the particular application and is not subject specially len restrictions. The fineness but generally preferably at a level of a Blaine 1500 to 8000 cm<sup>2</sup> / g. If the value is .outside this range will not receive sufficient expansive property in some cases

In the case of cement admixture which the expansive material is handled, the amount of the cement admixture is usually preferably from 3 to 12 parts by weight, more preferably 5-7 parts by weight. per 100 parts by weight of the cement, although the amount may vary depending on the particular intended use. If the amount is less than 3 parts by weight, sufficient .expansive property is obtained, and if the amount exceeds 12 parts by weight, it is easy to abnormal expansion

In the case of cement admixture which the expansive material is handled, and when chemical bias voltage is to be introduced, the amount of the cement admixture is usually preferably from 3 to 15 parts by weight, more preferably from 5 to 12 parts by weight in 100 parts by weight of the total amount of cement and cement admixture, although the amount may vary depending upon the particular purpose. If the amount is less than 3 parts by weight, the amount of the introduced prestress is .insufficient, and if the amount exceeds 15 parts by weight, no additional effect can be expect Tet

In the case of cement admixture comprising the expansive material and the dextrin, the amount of the cement admixture is preferably 3 to 12 parts by weight, more preferably from 5 to 9 parts by weight in 100 parts by weight of the total amount of cement and cement admixture . If the amount of clay is ner than 3 parts by weight, sufficient expansive property is obtained, .and if the amount exceeds 12 parts by weight, it is easy to abnormal expansion

With the cement admixture according to the invention can be Expansionseigenschaft adjusted to the specific intended use or the use of the cement, and by adjusting the ratios of the CaO Mischungsver raw material, the Al<sub>2</sub>O<sub>3</sub> -Rohmaterial and .CaSO<sub>4</sub> as the -Rohmaterial raw materials for the expansive material

The cement can use different cements in this context Portland as normal Portland cement, Portland cement with high early strength. Portland cement with ultra high early strength and Portlandze ment with excessive heat (moderate heat portland cement), and various blended cements with a pozzolan, such as blast furnace slag or fly ash such a Portland cement is mixed or cements with low heat generation, which use the blended cements as the basis and alumina cements. The features of the .vorlie inven- become particularly wear when mixed Ze instruments are used

In the present invention, in addition to the research Zementbeimi, one or more members of the group who incorporated the in a region in which the purpose of the invention is not affected surfaces in wesentli. This group consists of Härtingsmodifiziermitteln. Aggregates such as sand and gravel, an AE (water reducing agent from the hydrocarbon sulfonic acid type), an anti-rust agent, antifreeze, a polymer emulsion, clay minerals such as Bento nit and montmorillonite, ion exchangers such as zeolite, hydrotalcite and hydro calumit, inorganic sulfates such as aluminum sulfate and sodium sulfate, .organic phosphates and boric acid

The method of mixing or kneading of the cement admixture, or cement composition is not particularly Beschränkun Gene and there may be a conventional method can be used. The respective en materials may be premixed and then mixed into a cement. They can also be mixed separately cement. The respective en materials can also be mixed at the time of application. .You can also pre-mix some or all of them

As a device for mixing the cement admixture with Ze ment, etc., you can use a conventional mixing apparatus example as an .inclined drum mixer, a Omuni mixer, a mixer with a V-shape, a Henschel mixer or a Nauter mixer

The amount of water to be used can be set at a level to who, as conventionally verwen for ordinary mortar or concrete is det, .and is not particularly limited

The curing process for a cured cement product which has been produced with which it according to the invention cement admixture is not subject spe cial restrictions and can be applied any conventional methods such as curing at normal temperature and normal pressure, curing with steam curing with high temperature and high pressure or curing under .pressure

In the preparation of chemically prestressed concrete, conducted using either cation for cement admixture according to the invention, it is common practice to first dispose a tension insulating core in the mold. The clamping voltage insulating core is used to transmit a tensile stress in the concrete. Specifically, a PC steel material made of steel with a tensile strength or ho forth zugbeanspruchbares material of fiber reinforced plastic (FRP) in which Fa fibers are fixed by an organic substance, are used. The procedures in matters of arrangement of Spannungsisolierkerns is not particularly limited, but is preferably an .arrangement in the direction taken in front of the tension is applied

The method of applying a cement mixture, which was prepared by using Ver the cement admixture according to the invention .is not particularly limited, and a conventional method can be applied

In the following the invention will be with reference to examples in detail erläu tert. It should be noted, however, that the present invention by specific examples, is not limited. The reference examples further revelation, but they are not the subject .of this invention

#### (EXAMPLE 1 (Reference Example

The reagents of CaO raw material, Al<sub>2</sub>O<sub>3</sub> and CaSO<sub>4</sub> -Rohmaterial -Rohmaterial be mixed so that the product assumes a mole ratio, as indicated in Table 1. Subsequently, a baking treatment is carried out in an electric furnace at 1300 ° C during a .de stun, to obtain a clinker

.This clinker was pulverized and adjusted to a Blaine value of 3,000 ± 200 cm<sup>2</sup> / g, to obtain a cement admixture

The molar amounts of CaO, Al<sub>2</sub>O<sub>3</sub> and CaSO<sub>4</sub> of the expansive material who determines the values of the chemical analysis. CaSO<sub>4</sub> is calculated from the chemical's analysis values of SO<sub>3</sub> and CaO is the value obtained by subtracting from .the total CaO in the CaO-CaSO<sub>4</sub> content

Cement cement is used as the α and Zementbeimi mixture obtained is incorporated in an amount as specified in Table 1, on 100 parts by weight of the cement, a mortar with water / (cement cement admixture) = 60% and to obtain (cement + cement admixture) / sand ratio = 1/2. The mortar is then cured in air at 20 ° C under humidity of 80% egg ner. Then the coefficient of .expansion is measured. The results are summarized in Table 1

For comparison purposes, the experiment is carried out in the same manner using a commercially available expansive Ma .terials. The results are given in Table 1

#### Materials used

CaO raw material: calcium carbonate  
Al<sub>2</sub>

O<sub>3</sub>

,Rohmaterial: Alumina-  
CaSO<sub>4</sub>

,Rohmaterial: Anhydrous gypsum-

"Commercially available expansive material δ: "Onada Expan  
:Blaine  
cm<sup>2</sup> 3100

G /

Denka CSA # 20": Commercially available expansive material ε"  
:Blaine  
cm<sup>2</sup> 2950

G /

,Cement α: Normal Portland cement

,Sand: Sand standard

Water: Tap water

Test methods

(Expansion coefficient: According to JIS A6202 (Method B

(EXAMPLE 2 (Reference Example

The experiment is performed in the same manner as in Example 1 results in Runaway with the exception that a cement is used as the cement  $\beta$ . The results are shown in Table 2

Use Tete materials

Cement  $\beta$ : blast furnace slag cement

(EXAMPLE 3 (Reference Example

The experiment is performed in the same manner Runaway leads as in Example 2 with the exception that the raw material of CaO, Al<sub>2</sub>O<sub>3</sub> and CaSO<sub>4</sub> -Rohmaterial -Rohmaterial be changed and the expansive material with a rotary kiln with a maximum firing temperature is fired from 1400 ° C. The results are shown in Table 3

Materials used

,CaO raw material: limestone

Blaine: 3840 cm<sup>2</sup>

G /

Al<sub>2</sub>

O<sub>3</sub>

Rohmaterial: Aluminum ash residue-  
CaSO<sub>4</sub>

,Rohmaterial: Anhydrous gypsum-

Blaine: 4210 cm<sup>2</sup>

G /

(EXAMPLE 4 (Reference Example

The reagents and raw material of CaO-Al<sub>2</sub>O<sub>3</sub> -Rohmaterial, as used in Example 1, in a molar ratio of CaO: 8 mixed, and then in an electric furnace at 1650 ° C: Al<sub>2</sub>O<sub>3</sub> = 10 melted and then quenched to obtain a clinker from amor phen calcium.

.This is pulverized amorphous Cal ciumaluminat with a Blaine value of 3410 cm<sup>2</sup> / g to obtain

The amorphous calcium aluminate (A CA) is incorporated in an amount as indicated in Table 4, namely, per 100 parts by weight of expansionary ven material, which was obtained in Example 1 and to obtain a cement admixture

When the cement of the cement is used, and  $\alpha$  the cement admixture obtained is incorporated in an amount as indicated in Table 4, namely, per 100 parts by weight of the cement. This gives a mortar with water / (cement + cement admixture) = 50% and (cement + Zementbei mix) / sand ratio = 1/2, which is cured in air at 20 ° C under an air humidity of 80%. The Ausdehnungskoeffezient is mea sen. The results are shown in Table 4

Materials used

,Sand: river sand

(EXAMPLE 5 (Reference example

The experiment is performed in the same manner as in Example 4 Runaway leads, one with the exception that 30 parts by weight A-CA is marked with a CaO content as described in Table 5 to 100 parts by weight of expansive material with CaO: Al<sub>2</sub>O<sub>3</sub>: CaSO<sub>4</sub> molar ratio of 10: 1: 2.5 are used. The results are shown in Table 5

Table 5

(EXAMPLE 6 (Reference example

The experiment is performed in the same manner as in Example 4 Runaway leads, with the exception that, cement is used as  $\beta$  cement. The He results are shown in Table 6

The experiment is performed in the same manner as in Example 6 Runaway leads, with the exception that the expansive material, which was obtained in Example 3 is used. The results are shown in Table 7

## EXAMPLE 8

The CaO raw material, the  $Al_2O_3$  and  $CaSO_4$  -Rohmaterial -Rohmate material are changed and the expansive clinker material to be burned to the moving surface manner as in Example 3, using a rotary kiln at a maximum baking temperature of  $1400^\circ C$ , followed by pulverization, to obtain various expansive materials with a Blaine value of  $3,000 \pm 200 \text{ cm}^2/g$

Cement cement is used as the  $\alpha$  and there are 30 parts by weight of a latent hydraulic material in 100 parts by weight of the total amount of cement and latent hydraulic material and 7 parts by weight of the expansive materials so forth provided in 100 wt nents. parts of a binder to sum up the cement, the expansive material and the latent hydraulic Mate rial are mixed to obtain a concrete, where the unit amount of the binder  $460 \text{ kg} / \text{m}^3$ , and the unit amount of the other com- is as follows:  $158.1 \text{ kg} / \text{m}^3$  of water,  $889 \text{ kg} / \text{m}^3$  fine aggregates  $741 \text{ kg} / \text{m}^3$  coarse aggregate,  $20 \text{ g} / \text{m}^3$  thickeners,  $6.9 \text{ kg} / \text{m}^3$  of water reducing agent and  $23 \text{ g} / \text{m}^3$  an AE agent

Using this kneaded concrete flow value of the mass and the VF-value can be measured as indices of the flowability. Further, this concrete is poured into a mold of  $10 \times 10 \times 40 \text{ cm}$ . Twenty hours later, the molded product is removed from the mold, and 24 hours later, the expansion coefficient of the one-day old material is measured. At closing, the product is cured in water and the expan coefficient of only 3 days old material and the 7 day old material to be measured. The results are summarized in Table 8

## Materials used

CaO raw material: limestone powder  
 $Al_2O_3$

$O_3$

Rohmaterial: Bauxite-  
 $CaSO_4$

Rohmaterial: Fabric acid as a byproduct incurred anhydrous gypsum from the production of hydrofluoric-  
Expansive material a:  $CaO: Al_2O_3$

$O_3$

$CaSO_4$  :

,Molar ratio = 5: 1: 2.5

Blaine:  $2990 \text{ cm}^2$

G /

Expansive material b:  $CaO: Al_2O_3$

$O_3$

$CaSO_4$  :

Molar ratio = 6.5: 1: 2.5, Blaine:  $3120 \text{ cm}^2$

G /

Expansive material c:  $CaO: Al_2O_3$

$O_3$

$CaSO_4$  :

,Molar ratio = 10: 1: 2.5

Blaine:  $3140 \text{ cm}^2$

G /

Expansive material d:  $CaO: Al_2O_3$

$O_3$

CaSO<sub>4</sub> :

,Molar ratio = 15: 1: 2.5

Blaine: 3010 cm<sup>2</sup>

G /

Expansive material e: CaO: Al<sub>2</sub>

O<sub>3</sub>

CaSO<sub>4</sub> :

,Molar ratio = 18: 1: 2.5

Blaine: 3100 cm<sup>2</sup>

G /

Expansive material f: CaO: Al<sub>2</sub>

O<sub>3</sub>

CaSO<sub>4</sub> :

,Molar ratio = 20: 1: 2.5

Blaine: 3060 cm<sup>2</sup>

G /

Expansive g Material: CaO: Al<sub>2</sub>

O<sub>3</sub>

CaSO<sub>4</sub> :

,Molar ratio = 10: 1: 1

Blaine 2960 cm<sup>2</sup>

G /

Expansive material h: CaO: Al<sub>2</sub>

O<sub>3</sub>

CaSO<sub>4</sub> :

,Molar ratio = 10: 1: 1.5

Blaine: 3110 cm<sup>2</sup>

G /

Expansive material i: CaO: Al<sub>2</sub>

O<sub>3</sub>

CaSO<sub>4</sub> :

,Molar ratio = 10: 1: 3.0

Blaine: 3050 cm<sup>2</sup>

G /

Expansive material j: CaO: Al<sub>2</sub>

O<sub>3</sub>

CaSO<sub>4</sub> :

,Molar ratio = 10: 1: 4.0

Blaine 2880 cm<sup>2</sup>

G /

Expansive material k: CaO: Al<sub>2</sub>

CaSO<sub>4</sub> :

,Molar ratio = 10: 1: 5.0

Blaine 2920 cm<sup>2</sup>

G /

Latent hydraulic material A: fly ash

Thickener: methylcellulose

"Water reducing agent: "Darlex super 100 PHX

Main component: polycarboxylic acid type

"AE means: "AEA S

:Main component

Sulfonsäurekohlenwasserstoff type

Fine Aggregates: Specific gravity: 2.63, 2.74 FM

Coarse Aggregates: Ge specific weight: 2.67, 6.94 FM

Test methods

Flow value of the mass: The spread of the concrete is measured at two points in vertical direction as outlined in the "Test of Aqueous Inseparable Concrete, slump flow test" in Appendix 1 of Aqueous Inseparable Concrete Manual, published by the Foundation Engan Kaihatsu Gijutsu Center and Gyoko Gyoson Kensetsu Gijutsu Kenkyusho

VF value: Using a VF Consistometer propose of Civil Engineering Association, the cement composition is formed from a perforation at the lower portion of a cylinder without vibration can flow out and the lowering of the upper surface of the cement composition in the cylindrical container at the time when stops the flow is measured. The measured value is taken as the VF value

Filling property: The filling property of concrete is evaluated without vibration. In a transparent acrylic vessel having a horizontal cross-section of 50 x 50 cm and a height of 40 cm, a total of 56 amplis Kung rods with 16 mm diameter disposed, in 8 rows horizontal in horizontal direction and 7 rows in the vertical direction parallel to each other in the horizontal direction with a distance of 50 mm in both the horizontal and vertical directions, in such a way that a space in which no bar is arranged in, is provided at one side of the container. In this space the concrete is filled and the filling properties in the area with Stabanord voltage is evaluated by the time required for complete filling. The assessment is made by symbols x, o and. The symbol x indicates that it takes at least 15 seconds o 10 seconds or less and 7 seconds or less, until the filling is complete

EXAMPLE 9

The experiment is performed in the same manner as in Example 8 Runaway leads with the exception that the amount of the expansive material C in 100 parts by weight of the binder, which comprises the cement, the expansive material and the latent hydraulic material, according to Table 9 is changed. The results are summarized in Table 9

EXAMPLE 10

The experiment is performed in the same manner Runaway leads as in Example 8 with the exception that the expansive material c is used. In addition to the type and the amount of latent hydraulic material can be changed to 100 parts by weight of the total amount of cement and latent hydraulic material, as shown in Table 10. The results are shown in Table 10

Material Used

,Latent hydraulic material B: blast furnace slag

Blaine: 4200 cm<sup>2</sup>

G /

EXAMPLE 11

CaO as limestone raw material powder is used, generated from the Oumimine by Denki Kagaku Kogyo KK, and as Al<sub>2</sub>O<sub>3</sub> is used -Rohmaterial commercially available bauxite. The whole is melted in an electric furnace at 1650 ° C and shrunk in the same manner as in Example 4 from. This gives a clinker from A-CA, is pulverized to obtain A-CA

The experiment is performed in the same manner as in Example 8 Runaway leads, with the exception that cement is used as the cement α, A-CAa is used as CA-A and 30 parts by weight of the latent hydraulic material in 100 wt. parts by the total amount of cement and latent hydraulic material, 7 parts by weight of an expansive material into 100 parts by weight of the binder comprising cement, the expansive material, A-CA and the latent hydraulic material and 5 wt Parts A-CA are mixed. The results are shown in Table 11

Material Used

A CAa: CaO content 40 wt .-%, Blaine: 3120 cm<sup>2</sup>

G /

EXAMPLE 12

The experiment is performed in the same manner as in Example 11 Runaway leads, with the exception that the amount of the expansive material C in 100 parts by weight of the binder, which comprises the cement, the expansive material, A-CA and .latent hydraulic material is changed according to Table 12. The results are shown in Table 12

EXAMPLE 13

The experiment is performed in the same manner as in Example 11 Runaway leads, with the exception that the expansive material c is used, and the type and amount of the latent hydraulic material in 100 parts by weight of the total amount of .cement and latent hydraulic material, is changed according to Table 13. The results are shown in Table 13

EXAMPLE 14

The experiment is performed in the same manner as in Example 11 leads Runaway, except that the type and the amount of A-CA in 100 parts by weight of the binder, which the cement, the expansive material c, A-CA includes latent hydraulic material .can be changed according to Table 14. The results are shown in Table 14

Materials used

A CAb: CaO content 35 wt .-%, Blaine: 3150 cm<sup>2</sup>

G /

A CAc: CaO content 45 wt .-%, Blaine: 3090 cm<sup>2</sup>

G /

EXAMPLE 15

A clinker of the expansive material is obtained in the same manner as in Example 3 and pulveri up to a Blaine value of 3,000 ± 200 cm<sup>2</sup> / g Siert. In this way one obtains different expansive materials. Ze cement is used as a management α and a cement admixture comprising 94 parts by weight of the expansive material and 6 parts by weight of dextrin and A is in an amount of 7 parts by weight in 100 parts by weight of the total amount of cement cement admixture mixed to obtain a mortar with a water / (cement + cement admixture) ratio = 45% (cement + cement admixture) / Sand = 1/2 and with a temperature of 20 ± 0.3 ° C after complete mixing. Thereafter, the temperature in the center of the mortar, and the coefficient of expansion is .measured. The the outcome of these are shown in Table 15

Use Tete materials

Expansive material l: CaO: Al<sub>2</sub>O<sub>3</sub>: CaSO<sub>4</sub> molar ratio = 4: 1: 2.5  
Expansive material m: CaO: Al<sub>2</sub>O<sub>3</sub>: CaSO<sub>4</sub> molar ratio = 6.5: 1: 2.5  
Expansive material n: CaO: Al<sub>2</sub>O<sub>3</sub>: CaSO<sub>4</sub> molar ratio = 10: 1: 2.5  
Expansive material o: CaO: Al<sub>2</sub>O<sub>3</sub>: CaSO<sub>4</sub> molar ratio = 18: 1: 2.5  
Expansive Material p: CaO: Al<sub>2</sub>O<sub>3</sub>: CaSO<sub>4</sub> molar ratio = 20: 1: 2.5  
Expansive material q: CaO: Al<sub>2</sub>O<sub>3</sub>: CaSO<sub>4</sub> molar ratio = 10: 1: 1  
Expansive material r: CaO: Al<sub>2</sub>O<sub>3</sub>: CaSO<sub>4</sub> molar ratio = 10: 1: 1.5  
Expansive material s: CaO: Al<sub>2</sub>O<sub>3</sub>: CaSO<sub>4</sub> molar ratio = 10: 1: 4  
Expansive material t: CaO: Al<sub>2</sub>O<sub>3</sub>: CaSO<sub>4</sub> molar ratio = 10: 1: 5

"Dextrin A: "MF30

%-. soluble in cold water content: 30 wt

Fine aggregates: river sand, 5 mm or less

Measurement Method

The temperature at the center of the mortar: about 3.5 l mortar are charged into a cylindrical container which is made of a foamed styrene and BE has a height of 30 cm. The container has an inner diameter of 13 cm and a thickness of 10 cm. The container is cured at a constant temperature room at 20 ° C. The temperature is automatically measured at the center of the mortar with a .Bimetallthermofühler

EXAMPLE 16

The experiment is performed in the same manner Runaway leads as in Example 15, except that the expansive material N is used, and the amount of the cement admixture, which is incorporated to 100 parts by weight of the total amount of cement

.and cement admixture, is changed. The He results are shown in Table 16

#### EXAMPLE 17

The experiment is performed in the same manner as in Example Runaway leads 15, is used with the exception that the y .cement as the cement. The results are shown in Table 17

Use Tetes material

Cement  $\gamma$ : blast furnace slag cement

#### EXAMPLE 18

The experiment is carried out in the same manner as in Example 17, except that the expansive material used is m and the type of dextrin, and the amount of dextrin in 100 parts by weight of the cement admixture to be changed. The results are .summarized in Table 18

Use Tete materials

%-. Dextrin B: In cold water soluble content: 10 wt

%-. Dextrin C: Cold water soluble content: 45 wt

%-. Dextrin D: Cold water soluble content: 65 wt

#### EXAMPLE 19

A cement admixture comprising 94 parts by weight of expansive material N and 6 parts by weight of dextrin A is mixed in an amount of 7 parts by weight in 100 parts by weight of the total amount of cement and Zementbeimi research. 352 parts by weight of coarse aggregate to 255 parts by weight of incorporated are fine aggregates to obtain a concrete that is set to a water / (cement + cement admixture) ratio of 53% and after complete mixing, a temperature of 20 ° C has. The water mixed concrete is poured into a mold of 50 × 50 × 50 cm, consisting of iron, with four sides are insulated by foamed styrene, with a thickness of 10 cm and two sides for heat dissipation are open. The curing takes place in a constant temperature room at 20 ° C. The temperature in the Zen center of the concrete is automatically measured with a thermocouple. Furthermore, the .expansion coefficient is measured. The results are shown in Table 19

Use Tetes material

Coarse aggregate: river gravel,  $G_{max}$

mm 25 =

#### EXAMPLE 20

It ended the use in Example 4. A CA is used. A cement admixture comprising 69 parts by weight of the expansive material, 25 parts by weight A-CA and 6 parts by weight of dextrin A is in an amount of 10 parts by weight in 100 parts by weight in a total amount (cement + cement admixture) of  $\alpha$  cement and cement admixture mixed to obtain a mortar with a What water / (cement + cement admixture) ratio of 45% and / sand = 1/2. The temperature after complete kneading is  $20 \pm 0.3$  ° C. The temperature at the center of the mortar and the coefficient Ausdehnungskoeff be measured. The results are shown in Table .20

#### EXAMPLE 21

The experiment is performed in the same manner Runaway leads as in Example 20, except that the expansive material N is used and the amount of the cement admixture, which is incorporated to 100 parts by weight of the total amount of cement and .cement admixture, is changed. The results are He as shown in Table 21

#### EXAMPLE 22

The experiment is performed in the same manner as in Example 20 Runaway leads, with the exception that cement is used  $\gamma$ . .The results are shown in Table 22

#### EXAMPLE 23

The experiment is performed in the same manner Runaway leads as in Example 22, except that the expansive material N is used and the amount of A-CA is changed while the amounts of the cement admixture and dextrin in the cement admixture .can be kept constant. The the outcome of these are shown in Table 23

#### EXAMPLE 24

The experiment is performed in the same manner as in Example 22 leads Runaway, the type of dextrin and the amount of dextrin in 100 parts by weight of Zementbeimi change research with the exception that the expansive material is used and n, while the quantities the cement admixture and the A-CA keeps constant in the cement admixture. The results are shown in

## EXAMPLE 25

The experiment is performed in the same manner as in Example 19. Runaway leads with the exception that a cement admixture comprising 69 wt n parts of the expansive material, 65 parts by weight of A-CA and 6 parts by weight of Dex trin A in an amount of 10 parts by weight to 100 parts by weight of Gesamtmenge be incorporated into cement and cement admixture and 352 parts by weight of coarse aggregate to 255 parts by weight of fine aggregate einver be lebt to obtain a concrete of a A composition with a water / (cement + cement admixture) ratio of 49% and was adjusted to a temperature that is after the .complete kneading 20 ° C. The results are shown in Table 25

(EXAMPLE 26 (Reference example

An expansive material is prepared in the same manner as in Example 15 and is used as a cement admixture. Using cement  $\beta$  as the cement, concrete with a water / (cement + cement admixture) ratio of 40% and a content of fine aggregates is to 39% is prepared by adding 1 part by weight of water to moderate reduction per 100 parts by weight of the total amount of cement and Zementbeimi used research, one unit quantity of cement 385 kg / m<sup>3</sup> and unit amounts of cement admixture, fine .aggregates, big ben aggregates and water 45 kg / m<sup>3</sup>, 654 kg / m<sup>3</sup>, 1054 kg / m<sup>3</sup> or 172 kg / m<sup>3</sup>, respectively

Using a PC steel rod as a main reinforcement and a PC steel wire as a spiral reinforcement, a steel Zugisolationskern is arranged with a ratio of 0.4% in a mold. The prepared concrete is poured and formed with centrifugal force to a concrete pipe with a diameter of 20 cm, a length of 25 cm and a wall thickness of 40 ± 1 mm. The whole 24 hours in a room for curing are laser-sen. Then the concrete pipe is scolded and subjected to steam curing at 65 ° C for 10 hours. After the steam curing, the .tube is subjected to an outside Wassersprühhärtung

The voltage is measured with a voltmeter that was previously associated with the spiral reinforcement and the amount of preload tion, which was introduced in the measuring direction of the concrete is determined at a material which has 28 days .old. The results are shown in Table 26

Use Tete materials

"Water reducing agent: "Denka FT-500G

.Fine aggregates: river sand

Coarse aggregate: river gravel, G<sub>max</sub>

mm 15 :

(EXAMPLE 27 (Reference example

Using a cement admixture, which is composed of the expansive material n, a concrete with a water / (cement + cement admixture) ratio of 38% and a content of the fine to aggregates is produced by 39%, and that weight using 1. - part of a water reducing agent per 100 parts by weight of the total amount of cement and cement admixture, materials with a unit amount of cement of 390 kg / m<sup>3</sup> and with unit quantities of cement admixture, fine aggregate, coarse aggregate and water of 50 kg / m<sup>3</sup>, 685 kg / m<sup>3</sup>, 1098 kg / m<sup>3</sup> or 167 kg / m<sup>3</sup>

Using the concrete made a box-shaped channel having an outer dimension of 2340 × 2340 × 1500 mm, a thickness of 170 .mm and a Hüftbereichsdimension of 150 mm is formed

Steel reinforcements are made in double-rod assembly where the steel ratio is at 1.6% in the main reinforcing bar side and 0.25% on the distribution side bar. 3 hours after the introduction of the concrete, a steam curing is conducted at a temperature rise rate of 16 ° C / h and the mold is held at the maximum temperature of 65 ° C for 3 hours. After the steam curing, the mold is allowed to cool naturally Wei se. 24 hours later, the molded product is removed from the mold and allowed to stand at room temperature. When a material is due 14 days old, the voltage is measured with a voltmeter. The results are shown in Table .27

(EXAMPLE 28 (Reference example

Using a cement admixture, consisting of the expansive material N, a mortar with a mortar flow value of 200 ± 20 mm with W / C = 34% is produced. The cement admixture is 8 parts by weight per 100 parts by weight of the total amount of cement and .Zementbeimi mixture and the (cement + cement admixture) sand ratio is 1 / 1.8

By Zentrifugierformen with 25 G at the maximum rotation a steel pipe of 10 cm in diameter × 30 cm lined in a thickness of 0.5 .cm with the prepared mortar

The steel pipe obtained, lined with mortar is 4 hours ste hingelassen and then heated at a temperature increase of 16 ° C / h. .Subsequently, a steam curing is carried out while maintaining the tube for 3 hours at a maximum temperature of 50 ° C

The product is then allowed to cool in a natural way sen Gelas, taken after 24 hours from the mold and then hingelassen

outside Ste. The condition regarding cracks and peeling is observed in a material that is a year old. The results are shown in Table 28.

(EXAMPLE 29 (Reference example

The experiment is performed in the same manner Runaway leads as in Example 26, except that a cement admixture is used, consisting of the expansive material N, and that the amount of Zementbeimi mixture 100 parts by weight of the total amount of cement and Zementbeimi Research is changed according to Table 29. The results are shown in Table 29 shows ge

(EXAMPLE 30 (Reference example

Using cement  $\beta$ , as the cement and A-CAa as in Example 11, 100 parts by weight of an expansive material, which was prepared in the same manner as in Example 15 and 30 parts by weight A-CA mixed, to obtain a cement admixture

The experiment is performed in the same manner as in Example 26 Runaway leads, with the exception that the unit cement amount of  $374 \text{ kg} / \text{m}^3$  and the unit amount of cement of the cement admixture of  $56 \text{ kg} / \text{m}^3$ . The the outcome of these are shown in Table 30

(EXAMPLE 31 (Reference example

The experiment is performed in the same manner as in Example 30 Runaway leads, with the exception that a cement admixture, the n from the expansionary tive material is used and changed the type of A-CA. The result s are shown in Table 31.

(EXAMPLE 32 (Reference example

The experiment is performed in the same manner as in Example 27 Runaway leads, with the exception that a cement admixture, which comprises 100 parts by weight of an expansive material N and 30 parts by weight A-CAa, is used. The unit amount of cement is  $383 \text{ kg} / \text{m}^3$ , the unit amount of Zementbei mix and water amount to  $57 \text{ kg} / \text{m}^3$  or  $176 \text{ kg} / \text{m}^3$  and the water / (cement + cement admixture) ratio is 40%. The results are shown in Table 32

(EXAMPLE 33 (Reference example

The experiment is performed in the same manner as in Example 28 Runaway leads, with the exception that a cement admixture is used which comprises 100 parts by weight of an expansive material N and 30 parts by weight A-CAA. The results are shown in Table 33

(EXAMPLE 34 (Reference example

The experiment is performed in the same manner as in Example 29 Runaway leads, with the exception that a cement admixture comprising 100 parts by weight of n of the expansive material and 30 parts by weight A-CAa is used and the amount of the cement admixture in 100 parts by weight of the total amount of the cement and the cement admixture is changed according to Table 34. The results are shown in Table 34

Using the cement admixture according to the invention can even be mixed in a cement excellent expansive char acteristics and onswärme achieve excellent effects in reducing the Hydratati. It is possible to obtain a concrete with excellent dimensional stability, which does not require compaction

.Further, a chemically prestressed concrete is provided, in which a large quantity was introduced in pre-tension

#### اقتباسات متعلقة ببراءات الاختراع

العنوان	مقدم الطلب	تاريخ النشر	تاريخ التسجيل	براءة اختراع مذكورة
العنوان غير متاح		27 أيار (مايو) 1971	30 أيلول (سبتمبر) 1970	* DE2048127A1
Zement-expandierungsmittel	Denki Kagaku Kogyo Kk	18 كانون الثاني (يناير) 1973	14 كانون الأول (ديسمبر) 1971	* DE2162053A1

\* تم الاقتباس من قبل الفاحص

#### التصنيفات

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