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NOTE: The country must be indicated by its International Abbreviation - see schedule 4 of the Regulations

54	TITLE OF INVENTION

Method for improving grindability of cement aggregates

57	ABSTRACT (NOT MORE THAN 150 WORDS)

NUMBER OF SHEETS 15

The sheet(s) containing the abstract is/are attached.

If no classification is furnished, Form P.9 should accompany this form.
~~The figure of the drawing to which the abstract refers is attached.~~

A&A P208

(57) Abstract

In order to improve grindability and regulate the hydraulic properties of cement aggregates, especially slags, scots or pozzolans, the cement aggregates are subjected to a treatment at temperatures ranging between 250° C and 1000° C before undergoing grinding.

(57) Zusammenfassung

Zum Verbessern der Mahlbarkeit und zur Einstellung der hydraulischen Eigenschaften von Zementzumahlstoffen, insbesondere Schlacken, Flugaschen oder Puzzolanen, werden die Zementzumahlstoffe vor dem Mahlvorgang einer Temperaturbehandlung zwischen 250 °C und 1000 °C unterworfen.

Method for Improving the Grindability of Cement Aggregates

The invention relates to a method for improving the grindability, and adjusting the hydraulic properties, of cement grinding additives, in particular slags, flue ashes or puzzolans.

Slag cements, in particular blast furnace slag cement or metallurgical cement, are obtained from granulated slags by grinding and, as a rule, are used as grinding additives for cement mixtures. It is known to improve the grinding properties during grinding by chemical additives and, in particular, by socalled grinding aids, which will, however, constitute foreign substances within the grinding material. Likewise, it is known to influence the hydraulic properties and, in particular, the setting behavior and the attainable compressive strength at predetermined points of time by chemical additives which are added either to the cement or during the production of concrete.

The invention now aims to improve and/or influence the grinding properties, and optionally also the hydraulic properties, of cement grinding additives without any assistance of such chemical additives. To solve this object, the method according to the invention essentially consists in that the cement grinding additives are subjected to a temperature treatment at between 250°C and 1000°C prior to the grinding procedure. Surprisingly, it has been shown that, in particular, granulated blast furnace slag exhibits significantly enhanced fracture-mechanical properties after such a temperature treatment. Modification in that case essentially ranges between the socalled glass relaxation temperature and the crystallization temperature, wherein it has been shown that the grinding energy to be input will be reduced by approximately 20% already by a treatment at about 500°C over a period of about 1 hour. Suprisingly, it has yet been shown that even the hydraulic properties and, in particular, the development of strength can be considerably influenced within that temperature range in which the required grinding energy can be reduced on account of the temperature treatment. The treatment of blast furnace slag granulates at temperatures of about 500°C simultaneously with the decrease by approximately 20% of the grinding power to be consumed will result in an increase in the 28 day compressive strength by approximately 15%. Treatment at higher temperatures and, in particular, at, for instance, about 900°C will cause an even more significant reduction of the grinding energy, and it was even feasible to reduce the required grinding energy by half, wherein, however, such a treatment at a temperature of about 900°C led to a decrease of the compressive strength after 7 and after 28 days. The decrease of the grinding energy to be consumed, thus, does not linearly follow the change in compressive strength and the change in hydraulicity with the treatment temperature increasing, whereby also a delayed setting of cement mixtures may yet appear desirable in some cases, such setting in a conventional manner having been obtainable by chemical additives only.

Advantageously, the method according to the invention is carried out in a manner that the temperature treatment is effected between 300° and 900°C, in particular between 300 and 700°C, whereby a decrease of the grinding energy expenditures to approximately a half was feasible within that temperature range and an increase in the compressive strength after 28 days of nearly 20% was feasible within the preferred temperature range, provided such a temperature-treated blast furnace slag was mixed with portland cement at a ratio of 1:1 after or during the grinding procedure. The improvement of the grindability of the treated component, moreover, also led to an improvement of the grindability of a mixture of portland cement clinker and treated blast furnace slag granulates to the effect that a reduction of the grinding energy expenditures or, at the same grinding energy input, a higher grinding fineness, could respectively be observed even when at the combined grinding with portland cement clinker.

In a particularly advantageous manner, the method according to the invention is carried out such that the temperature treatment is effected over a period of time ranging from 15 minutes to 3 hours, preferably 45 minutes to 2 hours. Particularly when using blast furnace slags, the temperatures required for the temperature treatment, as a rule, will be available in the form of waste heat within the reach of the blast furnace. At higher treatment temperatures, the time of treatment may be chosen to be shorter. Thus, it is feasible to utilize, for instance, the residual heat of the regenerator of a blast furnace. The temperature treatment itself may be effected on various places, it being advantageously proceeded in a manner that the heat treatment is carried out immediately upon granulation by the aid of the residual heat of the granulated particles by delayed cooling, the selective influence of the slag quality and the reduction of the grinding work being feasible by the simple adaptation of a standard granulation or pelletizing process and, in particular, by the regulation of the residence time and the temperature control during dry granulation. Blast furnace slag, however, may be uprated also subsequently by being introduced into a drying plant for thermal aftertreatment. Finally, it is conceivable to arrange separate treatment units upstream of a slag mill while, for instance, simultaneously utilizing the waste heat derived from clinker cooling means with the alternative option provided in the zone of a cement rotary tubular kiln clinker cooler, to transfer blast furnace slag into a temperature window suitable for such a treatment. Finally, the grinding temperature may be raised during blast furnace slag grinding.

Besides the opportunity to positively influence the early strength of concrete and the opportunity to render more economical the combined grinding of clinker and slag on account of the improved grindability of the blast furnace slag component, there is also the opportunity to vary and adapt characteristic strength developments of composite cements, it being feasible at the same time to lower, for instance, the 28 day strength and increase the early strength. Such a mode of procedure may be ensured by an elevated slag fineness resulting from the improved grindability and, in particular, from the combined grinding of slag and clinker.

The cement grinding additives in a particularly simple manner may be cooled at air after the temperature treatment and before the grinding procedure, the treatment of blast furnace slags preferably being effected below the melilitic crystallization temperature of about 850°C.

A particularly significant increase in the strength values will be observed, if, as in accordance with a preferred further development, it is proceeded in a manner that the heat treatment is effected between 250°C and the nuclei formation temperature of about 700°C, in particular at about 500°C.

In the following, the invention will be explained in more detail by way of the drawing. Therein, Fig. 1 shows the development of the compressive strength following temperature treatment, Fig. 2 shows the course of the bending strength for different treatment temperatures, and Fig. 3 illustrates the decrease of the required grinding energy for different treatment temperatures.

With reference to the exemplary embodiments elucidated in the drawing, a series of additional measurements was effected, a thermoanalytical measurement of the nuclei formation and crystallization temperatures of the primarily occurring melilitic phases as well as respective determinations of the grinding fineness according to Blaine by laser diffraction or sieve analysis as well as of the hydraulic activity according to Austrian Standard B 3310 using mortar prisms having slag portions of 50%, WC (water to cement) value 0.6, having been carried out, in particular. Control tests revealed that the strength development was adversely affected after the completion of the nuclei formation, yet that negative strength development after completed nuclei formation did not show any change of the glass content in control diffractometer measurements. The tests were carried out in 100° steps regarding treatment temperatures, the results being elucidated in Fig. 1. Fig. 1 illustrates the course of the compressive strength for different treatment temperatures, a ratio of slag to cement of 50:50 having been chosen. From Fig. 1 it is apparent that the strength development and, in particular, the improvement of the 28 day strength is significant over a temperature range of 400 to 600°. The measuring point at 900°C, however, is not to be regarded as representative in the illustration according to Fig. 1, since, in the instant test, the constant fineness of 4500 cm^2/g observed in the other tests could no longer be observed on account of the substantially enhanced grindability. The strongly enhanced grindability in that case had resulted in a fineness of 6700 cm^2/g.

The thermoanalytical analyses of a blast furnace slag showed peak temperatures for nuclei formation at 710°C, for melilitic crystallization at 850°C, for further crystallization at 900°C and the occurrence of a peak temperature of 1190°C for the eutectic melt. A homogenous melt in the thermoanalysis was determined at 1330°C.

The blast furnace slags were treated in a chamber kiln, treatment times of 1 hour each having been chosen at the temperatures indicated in Fig. 1. After completion of the treatment time, the slags were removed from the kiln and cooled at air.

The grinding of the thus treated blast furnace slag is effected in a ball mill, the grinding progress each being determined by measurement of the Blaine fineness.

From the compressive strength development illustrated in Fig. 1, a significant increase in the compressive strength up to a temperature range of about 500°C is apparent. The maximum compressive strength after 28 days is reached at higher temperatures than the early strength maxima. The temperature treatment, thus, leads to a differentiation of the strength values at predetermined points of time, whereby the hydraulicity may altogether be adjusted within wide limits.

After having exceeded the temperature ranges for nuclei formation and crystallization (about 700°C), a decrease of the hydraulic activity (especially 28 day compressive strength) was observed. Surprisingly, also an increase in the 2 day compressive strength could be observed by treatments at higher temperatures.

As already mentioned, the measuring point at 900°C in Fig. 1 is not to be regarded as representative, since grinding to a substantially higher fineness was effected in that case.

It was also feasible to clearly influence the bending tensile strengths by the temperature treatment. Fig. 2 depicts the course of the bending tensile strength for different treatment temperatures, again for a slag cement ratio of 50:50, with the same explanations as given above in respect to the grinding fineness again applying for the measuring point at 900°C. There has been a tendency towards a slight decrease of the bending tensile strength up to the crystallization temperature, a clear drop of the bending tensile strength having been recognized only after exceeding of the crystallization temperature.

Bending tensile strengths and compressive strengths in the early strength range show similar curve progressions and, therefore, again allow for as large an adaptation as possible to the desired hydraulic properties of the end product.

Finally, the grindability was subjected to measurements at the temperatures examined, the results being illustrated in Fig. 3. From Fig. 3, the change of the grinding time as a function of the treatment temperature applied is apparent and it is clearly visible that the grinding time until which the same Blaine fineness of about 4500 cm^2/g could be reached rapidly decreases with the treatment temperature increasing. The measuring value entered for the temperature of 900°C in the instant case is not fully correct, since at that point of time a grinding fineness of 6700 cm^2/g had already been reached, the Blaine fineness of 4500 cm^2/g having occurred aleady at a substantially earlier point of time. The grinding finenesses were additionally verified by a check of the remainders on 45 µm sieves (R45) (and laser diffraction measurements), the results of such determinations being indicated in the Table below.

Treatment temperature	Grinding time	Grinding time	Blaine	R45
(°C)	(min)	(%)	(cm^2/g)	(mass-%)
20 (reference)	270	100	4700	1.27
300	230	85	4600	0.57
400	225	83	4500	0.83
500	225	83	4500	0.53
600	215	80	4500	0.57
700	210	78	4600	0.57
900	180	67	6700	8.87

As is demonstrated by the determination of R45 as well as the measurement of the grain size distribution by laser diffraction, an increased portion of crystalline substances is accompanied by a distinct change in the grain distributions characteristic of slags.

To sum up, it hence follows that already at a temperature treatment at 300 to 500°C the saving of grinding energy will amount to about 15%. A reduction by about 20% is obtained in the nuclei formation temperature range, whereby the grinding time will significantly drop a second time as soon as crystalline portions have formed.

Claims:

1. A method for improving the grindability, and adjusting the hydraulic properties, of cement grinding additives, in particular slags, flue ashes or puzzolans, characterized in that the cement grinding additives are subjected to a temperature treatment at between 250°C and 1000°C prior to the grinding procedure.

2. A method according to claim 1, characterized in that the temperature treatment is effected between 300° and 900°C, in particular between 300 and 700°C.

3. A method according to claim 1 or 2, characterized in that the temperature treatment is effected over a period of time ranging from 15 minutes to 3 hours, preferably 45 minutes to 2 hours.

4. A method according to claim 1, 2 or 3, characterized in that the cement grinding additives are cooled at air after the temperature treatment and before the grinding procedure.

5. A method according to any one of claims 1 to 4, characterized in that the treatment of blast furnace slag is effected below the melilitic crystallization temperature of about 850°C.

6. A method according to any one of claims 1 to 5, characterized in that the heat treatment is effected between 250°C and the nuclei formation temperature of about 700°C, in particular at about 500°C.

7. A method according to any one of claims 1 to 6, characterized in that the heat treatment is effected immediately upon granulation by the aid of the residual heat of the granulated particles by delayed cooling.

8. A method according to claim 1, substantially as herein described and illustrated.

9. A new method for improving the grindability and adjusting the hydraulic properties of cement grinding additives, substantially as herein described.

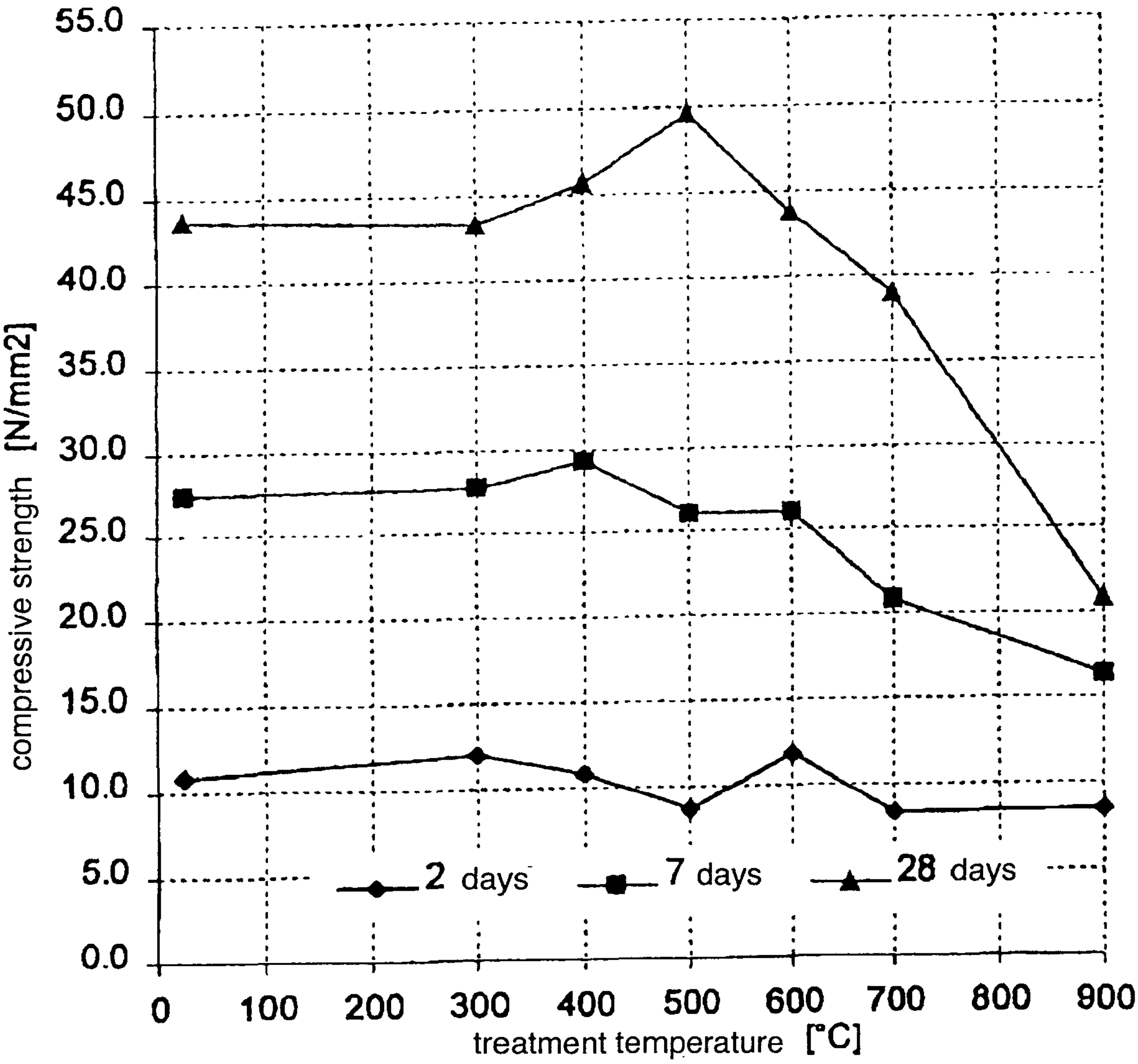
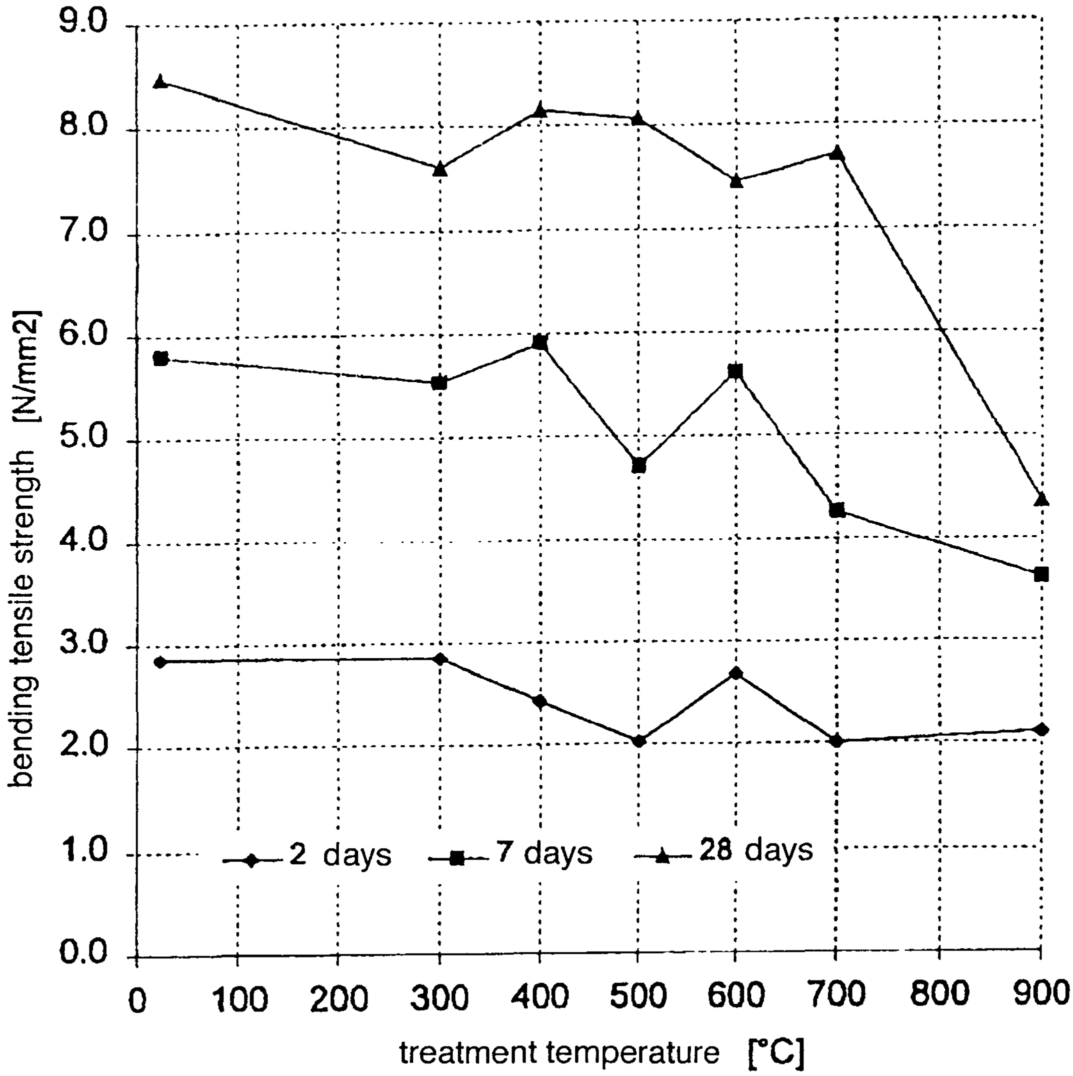

55.0
50.0
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
compressive strength [N/mm2]
2 days
7 days
28 days
0
100
200
300
400
500
600
700
800
900
treatment temperature [°C]

Fig. 1



9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
bending tensile strength [N/mm2]
2 days
7 days
28 days
0
100
200
300
400
500
600
700
800
900
treatment temperature [°C]

Fig. 2

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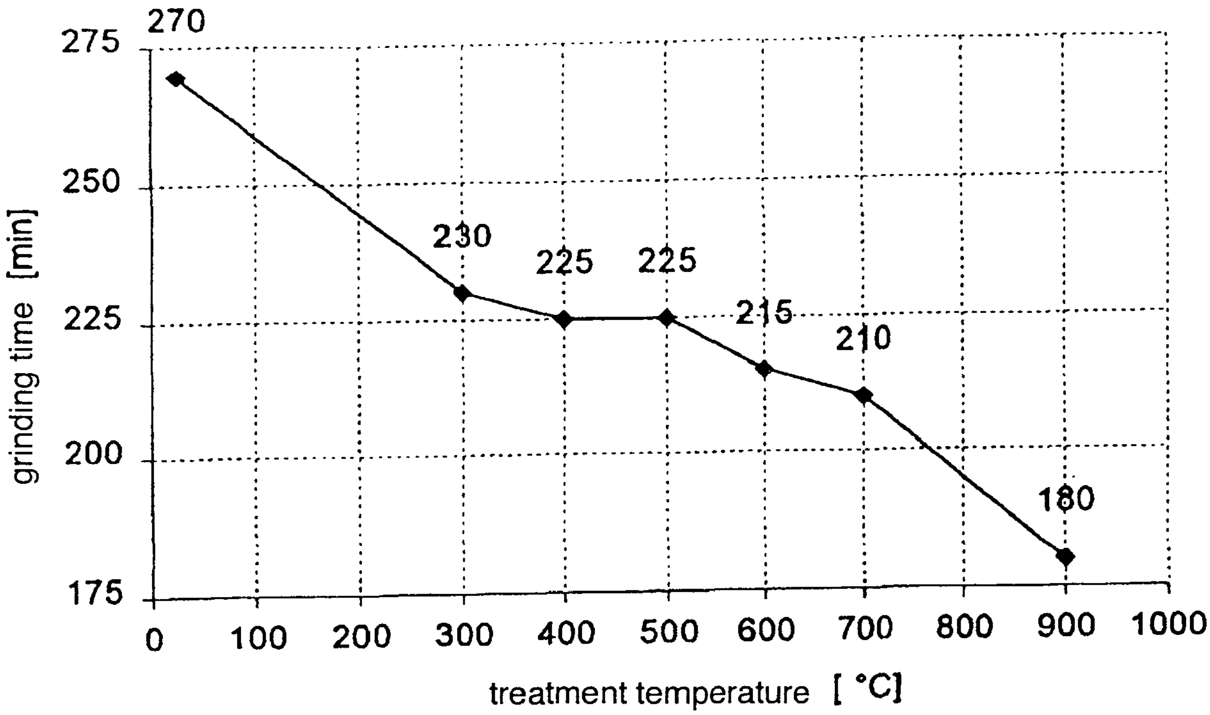

Fig. 3