CERAMICS — Silikáty *34*, s. 307—314 (1990)

THE EFFECT OF GRINDING AIDS ON THE PROPERTIES OF GYPSUM-FREE CEMENTS

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Received 9. 2. 1990

The effects of four grinding aids on the process of grinding Portland clinker and on the properties of gypsum-free cements prepared from the clinker were investigated with respect to particle size distribution, the surface area obtained, apparent viscosity of the cement pastes, the time course of the hydrating reactions and the compressive strength. The results indicate that from the standpoint of early and long-term strength, the ABESON-TEA aid is superior to the LIGRASOL aid used so far.

INTRODUCTION

Gypsum-free Portland cements (GFC) are inorganic binders in which the retarding effect of gypsum is replaced by a control system comprising the combination of an alkaline metal salt and a surface-active substance (SAS). This change in the chemical composition of cement, jointly with finer grinding, allows pastes with a very low cement-water ratio ($w = 0.20$) to be prepared; the corresponding mortars and concretes show high early strength and chemical durability.

The Portland clinker from which the GFCs are prepared is ground to a specific surface area of 400 to 700 m^2kg^{-1} (Blaine) with the use of efficient grinding aids. In this way the substances become a part of the cement and influence its properties, such as rheology, time course of hydration and the mechanical properties.

THEORETICAL

The significance of grinding aids in the grinding process

An addition of surface-active substances (SAS) and grinding in a certain defined medium (inert gases) allows the efficiency of the grinding process to be raised, and thus the energy per unit surface can be reduced [1]. The effect of grinding aids on the process is explained in two ways:

1. By affecting the grinding proper where the energy consumption is cut down as a result of decreasing the surface energy.
2. By the anti-agglomerating effect where adsorption on the surface of fracture areas inhibits rejoining of the surfaces by repulsive forces which do not allow them to approach one the other to a distance of intermolecular forces.

On the basis of practical experience, some authors have established the regions of optimum concentrations of grinding aids, which depend on the type of the aid, the grinding pebs, the mill, etc. [3].

Grinding aids and GFC

Brunauer [4] points out that grinding aids are used not only to achieve a higher fineness of the ground clinker, but also to influence the workability and strength of pastes, mortars and concretes based on GFCs. In this respect, the best results are obtained with the SAS-type aids containing both polar and non-polar groups. The polar groups are attracted by ions on the clinker surface while the non-polar parts of the SAS molecules are directed outwards from the clinker surface. The clinker grains are therefore somewhat hydrophobized, thus slowing down hydration and allowing the Newtonian behaviour of the paste to be approached in spite of the high fineness of the ground clinker. The grinding aid itself is not capable of controlling the consistency of the binder but has this effect in conjunction with the plasticizer and the alkali metal salt. It seems that the hydrophobic film formed in the course of grinding on the surface of clinker grains inhibits at first access of water to the clinker grain surface and in this way retards hydration, of course in dependence on the type of the grinding aid employed. The retarding effect proper is therefore a result of the joint effects of the grinding aid, the plasticizer and the alkali metal salt. In the case of GFCs, this combination substitutes the retarding effect of gypsum in classical Portland cements, producing a qualitatively novel type of cement with different physico-chemical properties.

Triethanolamine, which is known as an efficient aid for the grinding of Portland cement, was used as a typical representative of liquid grinding aids in the present study. Special attention was paid to a triethanolamine derivative manufactured in this country under the trade name ABESON-TEA. This compound belongs among anionic SAS forming negatively charged surface-active ions on dissociation in water. It was chosen as a suitable grinding aid for GFC because of its great surface activity, i.e. the ability to form surface adsorption layers. Sodium lignosulphonate (trade name LIGRASOL), so far considered the most suitable grinding aid for GFC [5], and amorphous SiO_2 (trade name KOMSIL), which was expected to have an anti-agglomerating effect and a favourable influence on the stability and rheological properties of GFC [6], were selected from the group of powdered grinding aids.

EXPERIMENTAL

Clinker from the Lochkov cement works was precrushed, homogenized, and its 0—2 mm fraction used for grinding. The chemical and mineralogical composition of the clinker is given in Tables I and II. The grinding was carried out under constant conditions in a ball mill with a chamber capacity of 23 dm^3. The clinker was always precrushed in a jaw crusher. Table III lists the values of specific surface area attained after 5 hours of grinding. The amounts of grinding aids are given in wt. % of ground clinker.

Table I

Chemical composition of the Portland clinker (wt. %)

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O + + K_2O	free CaO	ign. loss
66.10	21.16	5.25	2.30	2.01	1.05	0.85	1.0	0.13

Table II
Mineralogical composition of the portland clinker [wt . %]

C_3S	C_2S	C_3A	C_4AF	free CaO
73.1	7.8	14.6	2.9	1.2

Table III
Specific surface area of the ground clinker

Grinding aid	Dose (wt. %)	Specific area (m^2kg^{-1})	State
triethanolamine	0.05	510	l
ABESON-TEA	0.05	560	l
LIGRASOL	0.3	540	s
KOMSIL	0.3	490	s

Pastes of GFC were prepared with additions of anhydrous sodium carbonate and the KORTAN-FM compound, which is a sodium-ferric salt of the condensed product of phenol with formaldehyde, where a technical mixture of bivalent phenols serves as the initial raw material. All of the pastes were prepared by mixing 100 g of the ground clinker with 23 ml of aqueous solution (in distilled water), containing 0.4 g of KORTAN-FM and 1 g of sodium carbonate.

The particle size distribution and frequency function was determined by the Couler Counter AII instrument.

The initial setting time of the cement pastes was established by a conduction calorimeter which was found suitable for the GF-type of cement. The theoretical explanation and a description of the function of the instrument is given in [7, 8]. The time course of the hydration was likewise measured by a conductivity calorimeter.

The apparent viscosity of the cement pastes was measured by the RN 211 viscometer (GDR).

Some of the paste was cast into a steel mould with six compartments $2 \times 2 \times 2$ cm in size. After the respective time of hydration, the copmressive strength of the specimens was measured, always 2, 24 hours, 7, 28 and 180 days after the time of initial set, using the ZD 10/90 (GDR) tester. For 24 hours after casting, the specimens were kept in a medium of saturated water vapour, after 24 hours they were immersed in water.

DISCUSSION OF THE RESULTS

The grain size frequency functions are plotted in Fig. 1. The frequency functions of clinker ground with ABESON-TEA and LIGRASOL are very similar in spite of the fact that the substances are completely dissimilar as regards state, chemical composition as well as the concentrations employed. As the amount of LIGRASOL applied was six times that of ABESON-TEA, the latter can be considered a very efficient grinding aid, intensifying the grinding process better than LIGRASOL used in finely powdered form. The above grain size functions differ sharply from those of clinkers ground with triethanolamine and KOMSIL. In the former case, the peak value of the function is the highest, while in the latter it is the lowest and in addition to this, it is shifted to a lower value of particle size *d*. The comparatively sharp course of the grain size function for the sample with triethanolamine is a possible explanation of the highest value of apparent viscosity of the respective cement paste (Table IV).

Table IV
Apparent viscosity η_z of the cement pastes

Grinding aid	triethanolamine	ABESON-TEA	LIGRASOL	KOMSIL
η_z [Pa s]	3.14	1.94	1.62	1.22

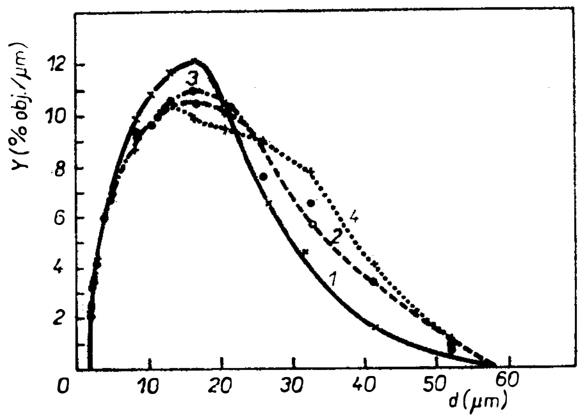

Fig. 1. The course of grain size frequency functions Y'(d) 1 — triethanolamine, 2 — ABESON-TEA, 3 — LIGRASOL, 4 — KOMSIL.

The times of initial set of the cement pastes are given in Table V and the time course of the hydrating reaction is plotted in Fig. 2. The shortest initial set is exhibited by the paste of clinker ground with triethanolamine and the longest by that of clinker ground with KOMSIL. An exception is provided by the paste with clinker ground with LIGRASOL where the retarding effect of KORTAN-FM was superimposed by that of LIGRASOL. The same phenomenon can be observed on the curves of time dependence of hydration and on those of compressive strength (Fig. 2 and Table V). The hydration time course curves show two peaks except for that of the paste with triethanolamine, where the thermal effect in the initial stage overlaps the other peak. The hydrating reaction of ground clinker in aqueous suspension is known to proceed in two stages [9], indicated by two peaks on the curve of time dependence of the liberated heat. The first is explained by hydration of a small proportion of C_3A to C_4AH_{19}, and the other corresponds to hydration of C_3S, C_2S and the other solid phases to cement gel. The disproportionate size

Table V
Initial set and compressive strength of the cement pastes

Grinding aid	Initial set, min.	Compressive strength (MPa)				
		2h	24h	7 days	28 days	180 days
triethanolamine	39	14.5	56.0	62.5	86.3	122.5
ABESON-TEA	49	9.3	68.5	88.5	99.0	176.0
LIGRASOL	106	4.0	63.5	77.0	102.5	161.0
KOMSIL	153	4.5	68.0	80.0	102.5	170.0

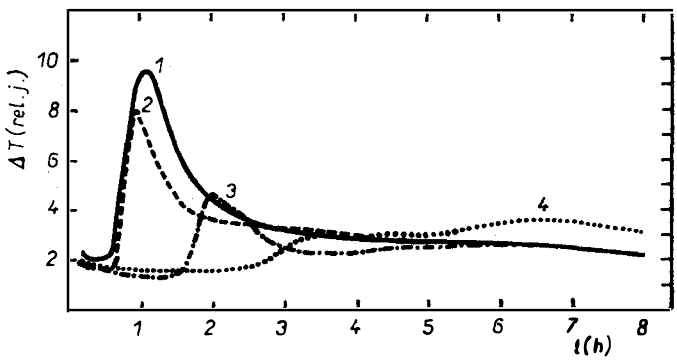

Fig. 2. Time course of the hydration reactions of ground clinker 1 — triethanolamine, 2 — ABESON-TEA, 3 — LIGRASOL, 4 — KOMSIL.

of the first peak of the sample with triehanolamine can be explained by an accelerating effect of triethanolamine on the hydration of C_3A [10]. In the case of the sample with KOMSIL, the second peak is even larger than the first one, this being obviously associated with the effect of amorphous SiO_2 [6].

The development of compressive strength (Table V) gives evidence for the advisability of using triethanolamine when early high strength is required, whereas the use of ABESON-TEA represents a certain optimum, providing considerable early- as well as long-term strength, which is not the case of the other aids.

CONCLUSION

The study of clinker ground with selected grinding aids allows the following conclusions to be formulated:

1. a) The efficiency of the grinding aids expressed in specific area attained after 5 hours of grinding decreases in the sequence ABESON-TEA > > LIGRASOL > triethanolamine > KOMSIL.
   b) The effect of the grinding aids on the rheological properties of cement pastes, characterized by apparent viscosity at water-cement ratio $w = 0.23$, increases in the sequence KOMSIL > LIGRASOL > ABESON-TEA > triethanolamine.

1. c) The influence of the grinding aids on mechanical properties of hardened cement pastes, characterized by the development of compressive strengths, is expressed by the sequence
triethanolamine > ABESON-TEA > KOMSIL > LIGRASOL
d) The effect of the grinding aids on the development of the heat of hydration, characterized by the heat liberated during the initial stage of the hydration reaction, is expressed by the sequence
triethanolamine > ABESON-TEA > LIGRASOL > KOMSIL.
2. a) Compared to the other cement pastes studied, that prepared from clinker ground with triethanolamine exhibits the highest apparent viscosity; this can be explained by the specific shape of the grain size distribution curve (Fig. 1). On the other hand, the lowest apparent viscosity is shown by the paste of clinker ground with KOMSIL, because the presence of amorphous SiO_2 of high fineness (mean grain size 0.1 μm) in the liquefied paste reduces its apparent viscosity.
b) The use of triethanolamine and ABESON-TEA as grinding aids for GFC results in high early strengths of the cement pastes and the heat liberated during the initial stage of hydration is likewise considerable, which is obviously associated with accelerated hydration of C_3A and C_3S to cement gel.
3. From the standpoint of practical application in building construction practice, ABESON-TEA appears to be the most suitable of the four types of grinding aids tested, as the cement paste exhibits a convenient time of set, a low apparent viscosity, and attains high early as well as long-term strengths.

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VLIV MLECÍCH PŘÍSAD NA VLASTNOSTI BEZSÁDROVCOVÝCH PORTLANDSKÝCH CEMENTŮ

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Byl sledován účinek čtyř vybraných mlecích přísad na proces mletí portlandského slínku a na vlastnosti bezsádrovcových portlandských cementů z tohoto slínku připravených. Vybrané přísady reprezentují základní typy z širšího souboru látek, jež byly studovány. Vhodnost mlecí přísady byla diskutována z hlediska rozdělení velikosti částic, dosaženého měrného povrchu, zdánlivé viskozity cementových kaší, časového průběhu hydratačních reakcí a pevností v tlaku. Ze studia slínků umletých s vybranými mlecími přísadami vyplývají tyto závěry:

1. a) Účinnost přísad na proces mletí vyjádřená velikostí měrného povrchu dosaženého po 5 hodinách mletí klesá v řadě ABESON-TEA > LIGRASOL > triethanolamin > KOMSIL
   b) Účinek mlecích přísad na reologické vlastnosti cementových kaší charakterizovaný velikostí zdánlivě viskozity kaše při vodním součiniteli w = 0,23 roste v řadě KOMSIL < LIGRASOL < ABESON-TEA < triethanolamin
   c) Vliv mlecích přísad na mechanické vlastnosti zatvrdlých cementových kaší vyjádřený rychlostí nárůstu pevností v tlaku znázorňuje řada triethanolamin > ABESON-TEA > KOMSIL > LIGRASOL
   d) Vliv mlecích přísad na vývoj hydratačního tepla charakterizovaný velikostí vybaveného tepla v počáteční etapě hydratační reakce vystihuje řada triethanolamin > ABESON-TEA > LIGRASOL > KOMSIL
2. a) Cementová kaše připravená ze slínku umletého s triethanolaminem má oproti ostatním zkoumaným kaším největší zdánlivou viskozitu, což lze vysvětlit specifickým tvarem zrnitostní křivky (obrázek 1). Naopak, nejmenší zdánlivou viskozitu má kaše ze slínku umletého s KOMSILEM, protože přítomnost amorfního SiO_2 o vysoké jemnosti (průměrná velikost zrna je 0,1 μm) ve ztekucené kaši snižuje její zdánlivou viskozitu.
   b) Užitím triethanolaminu a ABESONU-TEA jako mlecí přísady pro BPC se dosahuje vysokých počátečních pevností v tlaku cementových kaší a rovněž tak vybavené teplo v počáteční fázi hydratační reakce je značné, což zřejmě souvisí s urychlením hydratace C_3A a C_3S na cementový gel.
3. Z hlediska použití ve stavební praxi je ze čtyř záměrně vybraných mlecích přísad pro BPC nejvhodnější ABESON-TEA, neboť cementová kaše má při reálné době zpracovatelnosti poměrně nízkou zdánlivou viskozitu a je dosaženo vysokých krátkodobých i dlouhodobých pevností.

Obr. 1. Průběh zrnitostních frekvenčních funkcí Y'(d); 1 — triethanolamin, 2 — ABESON-TEA, 3 — LIGRASOL, 4 — KOMSIL.

Obr. 2. Časový průběh hydratačních reakcí umletého slínku; 1 — triethanolamin, 2 — ABESON-TEA, 3 — LIGRASOL, 4 — KOMSIL.

ВЛИЯНИЕ ИЗМЕЛЬЧАЮЩИХ ДОБАВОК НА СВОЙСТВА БЕЗГИПСОВЫХ ПОРТЛАНДСКИХ ЦЕМЕНТОВ

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Исследовали действие четырех подобранных измельчающих добавок на процесс измельчения портландского клинкера и на свойства безгипсовых портландских цементов, приготовленных из приводимого клинкера. Подобранные добавки представляют собой основные типы широкого набора веществ, подвергаемых исследованию. Пригодность измельчающей добавки рассматривали с точки зрения распределения размера частиц, полученной поверхности, кажущейся вязкости цементных тест, временного хода гидратационных реакций и прочностей при сжатии. На основании исследования клинкеров, молотых с подобранными измельчающими добавки выводится, что:

1. а) Действие добавок на процесс измельчения, выраженное величиной удельной поверхности, полученной после 5 часов измельчения понижается в ряде ABESON < TEA < LIARASOL < триэтаноламин < KOMSIL

б) Действие измельчающих добавок на реологические свойства цементных тест, характеризуемое величиной кажущейся вязкости теста при водяноm коэффициенте w = 0,23 растет в ряде
KOMSIL < LIGRASOL < ABESON — TEA < триэтаноламин

в) Влияние измельчающих добавок на механические свойства застывших цементных тест, выраженное скоростью роста прочности при сжатии, изображает ряд триэтаноламин < ABESON — TEA < KOMSIL < LIGRASOL

г) Влияние измельчающих добавок на выделение гидратационного тепла, характеризуемое величиной выделяемого тепла в начальном этапе гидратационной реакции, выражает ряд
триэтаноламин < ABESON — TEA < LIGRASOL < KOMSIL

2. а) Цементное тесто, приготовленное из клинкера, молотого с триэтаноламином обладает по сравнению с остальными исследуемыми тестами наибольшей кажущейся вязкостью, что можно объяснить специфичной формой кривой зернистости (рис. 1). Наоборот, наименьшей кажущейся вязкостью обладает тесто из клинкера, молотого с комсилом, так как присутствие аморфного SiO_2 высокой тонкости (средняя величина зерна 0,1 μм) в сжижженном тесте понижает его кажущуюся вязкость.

б) Использование триэтаноламина а ABESON — TEA в качестве измельчающей добавки для безгипсовых портландских цементов обеспечивает высокую начальную прочность при сжатии цементных тест и также выделяемое тепло в начальной фазе гидратационной реакции значительно, что очевидно связывается с ускорением гидратации C_3A и C_3S в цементный гель.

3. С точки зрения использования на строительной практике из четырех целесообразно подобранных измельчающих добавок, предназначенных для производства безгипсовых портландских цементов наиболее пригодной добавкой является ABESON — TEA, так как цементное тесто при реальном времени обрабатываемости обладает сравнительно низкой кажущейся вязкостью и кроме того таким образом достигается высокой кратковременной и долгосрочной прочности.

Рис. 1. Ход частотных функций зернистости $Y'(d)$: *1 — триэтаноламин, 2 —* ABESON — TEA, *3 —* LIGRASOL, *4 —* KOMSIL.

Рис. 2. Временный ход гидратационных реакций молотого клинкера: 1 — триэтаноламин, 2 — ABESON — TEA, *3 —* LIGRASOL, *4 —* KOMSIL.