THE PROPERTIES OF GYPSUM-FREE PORTLAND CEMENTS WITH AN ADMIXTURE OF ABESON-TEA GRINDING AID

JAROSLAV HRAZDIRA

Institute of the Chemistry of Glass and Ceramic Materials, Czechoslovak Academy of Sciences, Sokolská 38, 120 00 Prague 2

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The effects were examined of the ABESON-TEA grinding aid on the properties of gypsum-free Portland cements. The influence of the grinding aid on apparent viscosity of cement pastes, the time course of the hydration reactions and the compressive strength was studied. It was found that for a given specific surface of the cement, there exists an optimum amount of the grinding aid which improves the strength characteristics of binders.

THEORETICAL

During manufacture of gypsum-free Portland cements (GFC), the Portland clinker is ground to a specific surface area of 400 to 550 m^2kg^{-1} (Blaine) in the presence of efficient grinding aids. In this way, these substances become a component of the cement and influence its properties: the rheological properties, the time course of hydration and the development of strength. According to Brunauer [1], surface-active agents (SAA) containing both polar and non-polar groups are the best grinding aids for GFC. The mechanism by which the substances perform is closely associated with the processes taking place at the interface during hydration of the cement particles. The grinding aid alone cannot control the properties of the cement, but can do this jointly with a plasticizer and an alkali metal salt, thus replacing the retarding effects of gypsum which is used in standard Portland cements. In the course of grinding, the SAA becomes adsorbed in the surface of clinker grains. In aqueous dispersions, the hydrophilic and hydrophobic parts of the SAA may take up various configurations under the effect of Van der Waals forces, also being influenced by the amount of SAA in the system. Monomolecular layers of a surface film are formed at lower concentrations. Once the so-called critical concentration is attained, the SAA molecules will spontaneously aggregate into larger formations called micelles. At higher than critical concetrations, lamellar, cylindrical or spherical structural arrangement of the micelles with multimolecular configuration may form [2].

As has already been mentioned, the control systems for GFC comprise a grinding aid and a suitable combination of a plasticizer and an alkali metal salt. The plasticizers employed for GFC are sulphonated polyelectrolytes, mostly ligninsulphonates or polyphenolates, which also belong among SAAs with a high capillary activity. What has been said above on the behaviour of SAA-based grinding aids in aqueous dispersions, also applies to sulphonated polyelectrolytes, so that, in aqueous dispersions of ground clinker, there act two different SAAs whose effect on the hydration process and creation of strong structure in the paste may differ as a result of various thickness and stability of the adsorption films being formed.

In an earlier study, a substance with the trade name ABESON-TEA was used as a suitable grinding aid [3]. This substance belongs among anionic SAAs which, on dissociation in water, form negatively charged surface-active ions exhibiting a high surface activity.

The present study had the aim to establish to what extent the amount (concentration) of the ABESON-TEA grinding aid affects the hydration of GFC and the properties of cement pastes prepared from these cements.

EXPERIMENTAL

Clinker from the Lochkov cement works was pre-crushed, homogenized, and its 0–2 mm fraction was used for grinding. The chemical and mineralogical composition of the clinker is given in Tables I and II. The clinker was ground with various additions of ABESON-TEA (ranging from 0 to 0.1% by weight of clinker) for 4 hours in a 23-litre capacity ball mill.

The pastes of GFC were prepared with anhydrous Na_2CO_3 and two different plasticizers:

a) KORTAN-FM – a sodium-ferric salt of the condensed product of sulphonated phenol with formaldehyde, where a technical mixture of bivalent phenols is used as the initial raw material, and
b) BORRESPERSE-NA – sodium ligninsulphonate, made by the Norwegian BORREGAARD company.

In the case of pastes with KORTAN-FM, 100 g of ground clinker were mixed with 24 ml of aqueous solution containing 0.4 g of the plasticizer and 1 g of Na_2CO_3. In that of pastes with ligninsulphonate, the same amount of ground clinker was mixed with 24 ml

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	Loss on ignition
66.10	21.16	5.25	2.30	2.01	1.05	0.85	1.15	0.13

Table III

The properties of cement pastes with KORTAN-FM in terms of the amount of the ABESON-TEA grinding aid

Amount of grinding aid (wt. %)	Specific surface (m^2kg^{-1})	Setting time (min.)	Compressive strength (MPa)					
			3h	5h	24h	7d	28d	180d
0	450	83	3.3	18,0	55	75	85.5	107.5
0.02	455	78	5.0	23.5	57	86	110	123.5
0.04	466	76	9.0	20.5	58	88	95	105.5
0.06	454	68	9.5	23.0	59	75	90.5	109.5
0.08	446	42	11.0	27.0	59	77	95	105
0.10	446	52	7.3	17.0	54	63	P1.5	100

h – hours, d – days

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

of aqueous solution containing 0.9 g of the plasticizer and 1.2 g of sodium carbonate.

The setting time of the cement pastes was determined by a conduction calorimeter, which had been proved very suitable for these purposes owing to simple operation and considerable precision [4, 5].

The time course of the hydration process was also established by the conduction calorimeter.

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

The prepared paste was cast into a steel mould with 6 compartments 2 × 2 × 2 cm in size. After the respective times of hydration, the compressive strength of the specimens was measured, namely 3, 5, 24 hours and 7, 28 and 180 days after preparing the paste, using the ZD 10/90 tester (FRG). For the first 24 hours, the specimens were kept in a saturated water vapour medium, and afterwards immersed in water.

RESULTS AND DISCUSSION

1. Cement pastes containing KORTAN-FM

Fig. 1 shows that over the entire concentration range of the grinding aid employed (0.02–0.1 wt. %), the values of apparent viscosity of the cement pastes increased with increasing concentration of ABESON-TEA. In this case, the rheological properties of the paste were unfavourably affected by the increasing amounts of ABESON-TEA as a result of increasing internal friction.

Table III lists the values of the specific surface area of the ground clinker (Blaine), the setting time and

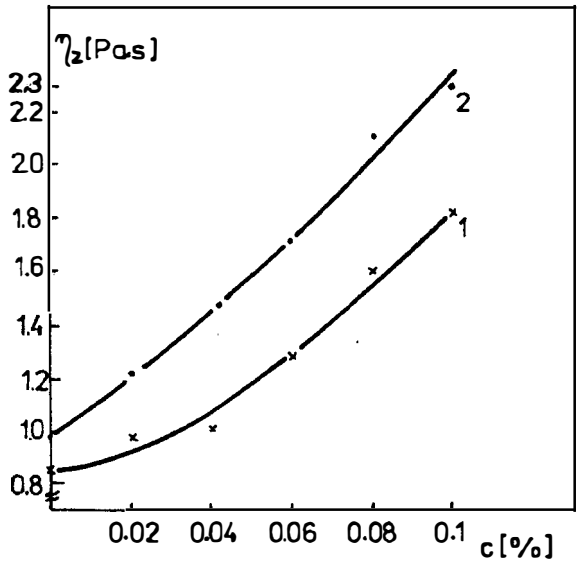

Fig. 1. Apparent viscosity of the cement pastes vs. the amount of ABESON-TEA grinding aid.
1 - KORTAN-FM
2 - BORRESPERSE-NA

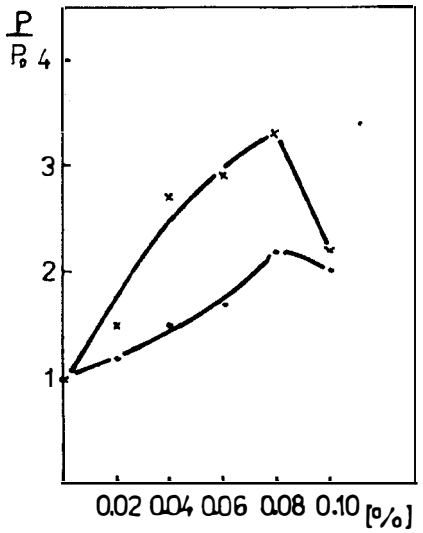

Fig. 2. Dependence of the ratio of compressive strength to the amount of ABESON-TEA grinding aid.
1 - KORTAN-FM
2 - BORRESPERSE-NA
P_0 - compressive strength within 3 hours of mixing the paste without the grinding aid
P - compressive strength within 3 hours of mixing the paste containing various amounts of the grinding aid

the development of compressive strength for the cement pastes in terms of the amount of the grinding aid. The specific surface does not change very much in dependence on the concentration of the grinding aid, which is of course associated with the grinding properties of the clinker and the grinding equipment. Qualitatively different results have been obtained with clinker from a different cement works (Prachovice), [6]. One can see, however, that both short-term and long-term strength increases, and the setting time shortens, with increasing concentration of the grinding aid (Fig. 2). However, at doses of 0.1 wt. % of ABESON-TEA, the strength decreases and the time of initial set increases.

The time course of the hydration reactions of the cement with various amounts of ABESON-TEA is plotted in Fig. 3. The size of the peak increases with rising concentration of the grinding aid, attaining a maximum at 0.08 wt. %. The peak diminished at a dose of 0.1 wt. %. This peak on the curve of time dependence of the liberated heat of hydration is explained by the hydration of C_3A to C_4AH_{19} [7]. From this it follows that in the case of pastes containing KORTAN-FM, the ABESON-TEA grinding aid accelerates hydration of C_3A in a way similar to that of triethanolamine [8]. The hydration of C_3S, C_2S and the other solid phases to cement gel is probably likewise promoted, as indicated by the higher short- as well as long-term compressive strength, compared to clinker free of ABESON-TEA.

Two different surfactants are active during the hydration of GFC: the grinding aid firmly fixed in the surface of clinker grains, and the electrolyte constituting a part of the retarding system. In the absence of the grinding aid, the retarding components start immediately to react with the cement particles and the performance of the polyelectrolyte is free to proceed, so that the setting time is retarded and the hydration reactions are slowed down. In the presence of the grinding aid, however, the clinker grains are coated with a thin film which prevents the polyelectrolyte from acting instantaneously. The polyelectrolyte will thus penetrate to the clinker grains with a delay. The simultaneous effects of the grinding aid combined with a small amount of the retarder should therefore be given preference. In consequence of this, the hydration is speeded up, the setting time shortens and the apparent viscosity of cement pastes increases.

2. Cement pastes containing sodium ligninsulphonate

Fig. 1 shows a plot of apparent viscosity vs. the concentration of the grinding aid for cement pastes containing ligninsulphonate. Similarly to the case of KORTAN-FM, also here the apparent viscosity increases with increasing concentration of ABESON-TEA.

Table IV gives the values of the setting time and the development of compressive strengths for cement

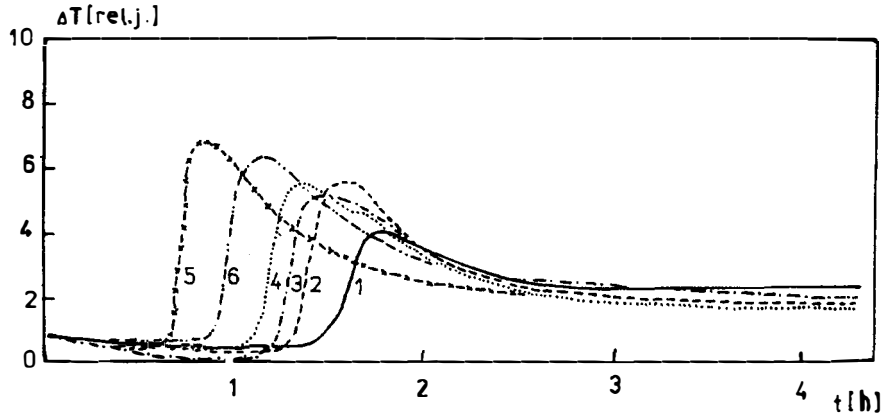

Fig. 3. Time course of hydration reactions of the cements with KORTAN-FM and various concentrations of the ABESON-TEA grinding aid.

1 - 0% *4 - 0.06%*
2 - 0.02% *5 - 0.08%*
3 - 0.04% *6 - 0.10%*

Table IV

The properties of cement pastes with sodium ligninsulphonate in terms of the amount of the ABESON-TEA grinding aid

Amount of grinding aid (wt. %)	Specific surface (m^2kg^{-1})	Setting time (min.)	Compressive strength (MPa)					
			3h	5h	24h	7d	28d	180d
0	450	34	5.3	20.0	66.5	83	109	110
0.02	455	29	6.3	24.5	67	88	103	107
0.04	466	24	8.0	33.5	64	76	93	112
0.06	454	24	8.8	27.5	63.5	81	86	101
0.08	446	18	11.4	24.0	55	72	78	84
0.10	446	24	10.5	25.5	53	65	78	86

h – hours, d – days

pastes in terms of the amount of the grinding aid. In view of the poorer retarding effects of the ligninsulphonate employed, the setting times are shorter; none the less, the relationship established was the same as that found with pastes containing KORTAN-FM, namely that the setting time gets shorter and the early compressive strength increases with increasing concentration of ABESON-TEA (Fig. 2). However, in the case of pastes containing ligninsulphonate, there was a decrease of long-term strength values, i.e. those after more than 24 hours since mixing the paste, over the entire range of the grinding aid concentrations. In other words, formation of the cement gel is activated for only 24 hours from the beginning of the hydration.

The time course of hydration reactions of cements with various amounts of ABESON-TEA is shown by Fig. 4. The size of the peak also increases with increasing concentration of the grinding aid; in this case, however, the maximum is attained at a dose of 0.04 wt. %, above which the peak again begins to decrease.

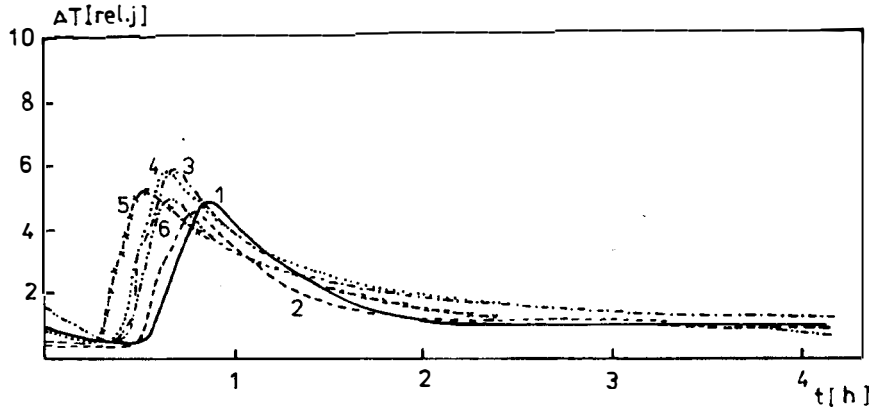

Fig. 4. Time course of hydration reactions of the cements with BORRESPERSE - NA and various concentrations of the ABESON-TEA grinding aid.

1 - 0% *4 - 0.06%*
2 - 0.02% *5 - 0.08%*
3 - 0.04% *6 - 0.10%*

CONCLUSION

The following conclusions can be formulated from the study of gypsum-free Portland cement ground with various amounts of the ABESON-TEA grinding aid:

1. Apparent viscosity of the cement pastes increases with increasing concentration of the grinding aid.
2. Increasing amounts of ABESON-TEA in the cement result in an acceleration of the hydration reactions which is revealed by
   a) shortening the setting time;
   b) greater amounts of heat generated in the initial stages of hydration;
   c) a higher rate of compressive strength development, particularly during the first 24 hours after mixing.
3. For a given grinding equipment and a specific surface of the cement, there exists a certain optimum amount of the ABESON-TEA grinding aid which, at a practical workability of the cement paste, allows the strength characteristics to be distinctly improved, particularly during the first 24 hours of hydration. In the present case, for a specific surface of 450–470 m^2kg^{-1} of the ground clinker, this optimum amount of the grinding aid was 0.04 wt. % by weight of the clinker.

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VLASTNOSTI BEZSÁDROVCOVÝCH PORTLANDSKÝCH CEMENTŮ S PŘÍMĚSÍ MLECÍ PŘÍSADY ABESON-TEA

JAROSLAV HRAZDIRA

Ústav chemie skelných a keramických materiálů ČSAV, Sokolská 38, 120 00 Praha 2

Byl sledován vliv různého množství mlecí přísady ABESON-TEA na vlastnosti bezsádrovcových portlandských cementů. Působení mlecí přísady bylo zkoumáno z hlediska zdánlivé viskozity cementových kaší, časového průběhu hydratačních reakcí a pevností v tlaku.

Z dosažených výsledků vyplývají tyto poznatky:

1. S rostoucí koncentrací mlecí přísady vzrůstá zdánlivá viskozita cementových kaší.
2. Zvyšující se množství ABESONU-TEA v cementu má za následek urychlení hydratačních reakcí, jež se projevuje:
   a) zkrácením počátku tuhnutí cementových kaší;
   b) zvýšením množství vybaveného tepla v počáteční etapě hydratační reakce;
   c) zvýšením rychlosti nárůstu pevností v tlaku, zvláště během 24 hodin od rozmíchání.

3. Pro dané mlecí zařízení a měrný povrch cementu existuje optimální množství mlecí přísady ABESON-TEA, jež při reálné zpracovatelnosti cementové kaše umožňuje výrazně zlepšit pevnostní charakteristiku zatvrdlých pojiv, obzvláště do 24 hodin od přípravy. V našem případě, pro měrný povrch slínku 450–470 m^2/kg (Blaine) je vhodné množství přísady 0.04% hm., přepočteno na hmotnost slínku.

Obr. 1. Závislost zdánlivé viskozity cementových kaší na množství mlecí přísady ABESON-TEA.
1 – KORTAN-FM
2 – BORRESPERSE-NA

Obr. 2 . Závislost poměru pevností v tlaku na množství mlecí přísady ABESON-TEA.
1 – KORTAN-FM
2 – BORRESPERSE-NA

P_0 – pevnost v tlaku po 3 hodinách od rozmíchání kaše bez mlecí přísady
P – pevnost v tlaku po 3 hodinách od rozmíchání kaše s různým množstvím mlecí přísady

Obr. 3. Časový průběh hydratačních reakcí cementů s KORTANEM-FM a s rozdílnou koncentrací mlecí přísady ABESON-TEA.
1 – 0% *4 – 0.06%*
2 – 0.02% *5 – 0.08%*
3 – 0.04% *6 – 0.10%*

Obr. 4. Časový průběh hydratačních reakcí cementů s BORRESPERSE-NA a s rozdílnou koncentrací mlecí přísady ABESON-TEA.
1 – 0% *4 – 0.06%*
2 – 0.02% *5 – 0.08%*
3 – 0.04% *6 – 0.10%*

Recenze knih

CERAMICS IN SUBSTITUTIVE AND RECONSTRUCTIVE SURGERY (Keramika v substituční a rekonstrukční chirurgii). Editor: P. Vincenzini, Materials Science Monographs, 69. Elsevier Amsterdam-Oxford-N.York-Tokyo 1991. 649 stran, cena 231,50 US $.

Kniha je sborníkem textů přednášek ze satelitního stejnojmenného symposia, jež se konalo u příležitosti 7. Světového keramického kongresu (7th CIMTEC) v Montecatini Terme (Itálie) ve dnech 27.–30. června 1990. Symposium mělo výrazně interdisciplinární charakter, jak je zřejmé nejen z účasti sponsorských organizací z oblasti materiálů i institucí lékařských, ale také ze široké škály odborných sdělení, jichž je ve sborníku zahrnuto 66, vč. 8 pozvaných souborných referátů. Články jsou rozděleny do 4 hlavních sekcí: 1. Příprava materiálů; 2. Charakterizace materiálů; 3. lnterakce materiálů s živými tkáněmi; 4. Klinické aplikace.

Sborník se soustřeďuje na nejnovější vývoj biomateriálů nejen na bázi keramiky v užším slova smyslu, ale také skel, speciálních cementů, povlaků atd. V jednotlivých referátech se pojednává o důležitých aspektech přípravy a charakterizace materiálů, i o výrobních technikách. Jsou zde zahrnuty bioinertní keramické materiály, povrchově aktivní a resorbovatelné materiály, kompozity s částicovou, vláknovou i viskrovou výztuží, tenké vrstvy a povlaky. Značná pozornost je věnována interakci biomateriálů s živými tkáněmi; tyto interakce byly sledovány pokusy „in vivo“ i „in vitro“, zejména u materiálů bioaktivních. Význační lékaři a chirurgové referovali o klinických aplikacích v dentální, maxillofaciální a ortopedické oblasti. Sborník představuje všestranný a ucelený přehled současných trendů ve vývoji a aplikaci biomateriálů náležejících do oboru skla a keramiky.

J. Hlaváč