

PROPERTIES OF A CEMENT BASED ON ALKALI-ACTIVATED SLAG

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Received June 21, 1996.

Alkaline activation of slags by alkali hydroxide, carbonate or silicate is an effective way of utilizing their hydraulic activity. The present study was concerned with alkaline activation of granulated blast-furnace slags by sodium silicate (water glass with various $\text{SiO}_2/\text{Na}_2\text{O}$ ratios) in the presence of a plasticizer (lignine sulphonate), with the effect of specific surface area of the ground slag, and with that of the concentration of additives on the rheological properties, the time of initial set and the time development of strength.

INTRODUCTION

Nowadays, a number of technologies and materials are undergoing reassessment from the standpoint of their energy demands and environmental impacts. In the building construction industry, increasing attention is paid to the utilization of waste inorganic materials such as slags, fly-ash, pozzolanes and the like. This trend has brought about introduction of new types of binding agents, in particular blended cements (ternary as well as quarternary ones). Another field of interest is aimed at increasing the "binding potential" of hydraulically active materials such as slags. Considerable efforts have been devoted in particular to the problem of activating ground granulated blast-furnace slags. The literature shows that one of the most effective ways of activating the slags is represented by alkaline activation, e.g. with alkali hydroxide, carbonate or preferably silicate [1,2,3,5,7]. Alkaline activation of slags splits the Si-O-Si bonds and the hydrated siloxane groups then condense, forming spatial polymeric microstructures. The processes, taking place in the presence of Na^+ and Ca^{2+} cations, yield hydrated sodium or sodium-calcium aluminosilicates. These substances resemble natural zeolites and have been given the name geopolymers [4]. At present, these substances with a great binding power are paid considerable attention, because, unlike the case of cement clinker, no carbon dioxide is liberated during their formation. As certain emission limits for CO_2 are likely to be specified for cement works in future, the respective studies have to be regarded as very topical ones.

The present work had the purpose to investigate alkaline activation of ground granulated slags in the presence of a plasticizer (lignine sulphonate), and to determine the effect of the specific surface area of ground slags and that of the concentrations of the additives.

EXPERIMENTAL PART

In the experiments, use was made of granulated blast-furnace slag from Vítkovice steelworks. The slag had the following chemical composition (wt.%): 39.9 SiO_2 , 8.17 Al_2O_3 , 0.43 Fe_2O_3 , 43.9 CaO , 5.9 MgO , 0.93 SO_3 . The X-ray diffraction pattern showed a wide diffusion peak with its centre at $d = 0.297$ nm, corresponding to a vitreous phase, and the crystalline phase probably contained α -quartz. The slag was ground in a laboratory vibration mill with additions of various grinding aids (triethanolamine, ethylene glycol, powdered lignine sulphonate, salts of naphthalene- sulphonic acid). The powdered materials were characterized by their specific surface area (Blaine) and by their particle size distribution (Fritsch Analysette 23). Samples with specific surface areas of 320, 416, 480 and 510 $\text{m}^2 \text{kg}^{-1}$ were used in the experiments.

Pastes of acceptable workability were prepared from the ground slag samples, mostly at $w = 0.35 - 0.45$. The additives employed were water glass solution of $M_s = 1.5$ and sodium lignosulphonate Zewa S1TM (content of monosaccharides up to 2 wt.%). The silicate modulus M_s was adjusted by additions of solid NaOH to values ranging from 1.5 to 0.5. In the early experiments, up to 2.0 wt.% of lignosulphonate were added, but the amount was eventually optimized at 0.1 wt.% and the substance was introduced as a grinding aid.

The rheological properties of the pastes were assessed according to visual workability as follows: degree 5 - freely flowing to sedimenting paste, degree 4 - freely flowing paste, degree 3 - paste flowing out of dish by gravity only, degree 2 - paste flowing out of dish when tapped, degree 1 - paste flowing only when vibrated at 50 Hz. The range of rheological properties of ground slag pastes was so wide that objective viscosity measurement (such as with a rotary viscometer) was not viable.

The pastes prepared were then tested for the time of initial set (Vicat), and for compressive strength after 7 and 28 days of hydration at 20 - 22 °C. The specimens 2 × 2 × 2 cm in size were kept for 24 hours in a medium of saturated water vapour and then till the 7- or 28-day testing in water.

The course of hydration heat generation was determined on a multichannel semiadiabatic calorimeter.

Following the 28-day destructive tests, the fractured specimens were used in determining the composition of the hydration products by X-ray phase analysis, and the morphology of the fracture surfaces was assessed under a scanning electron microscope.

RESULTS AND DISCUSSION

In grinding the slag it was possible to confirm the known fact that attainment of specific surface areas in excess of 250 - 300 m² kg⁻¹ requires the time of grinding to be extended even when using a vibration mill (up to 45 - 60 min). None of the grinding aids employed was found to have any intensifying effect, with the exception of a mild one exhibited by powdered lignosulphonate. It should be noted that both the expert and patent literature [8-11] brings very little information on grinding aids in connection with blast-furnace slag. It seems that the problem of grinding granulated slag to high fineness will have to be resolved by using special technology (high-pressure cylinder mills with classifiers [11]) rather than by means of any grinding aids.

The system ground blast-furnace slag - water glass behaves as a quick-setting cement, in particular when the slag is ground to high specific surface area values. Sodium lignosulphonate containing at the most 2 wt.% accompanying monosaccharides (ZEWA S1™) was found to be a suitable setting regulator for the system ground slag - water glass. As illustrated by figure 1, it is possible to control the time of initial set by adjusting the concentration of lignosulphonate, over the wide range from minutes to days. For the purposes of studying the hydration and strength, the optimum addition was established at 0.1 wt.% lignosulphonate.

The rheological properties of pastes in the system ground granulated slag - water glass - sodium lignosulphonate (figures 2, 3, 4) depend on concentration and silicate modulus M_s of the water glass. The degree of plastification increases with decreasing M_s and decreasing water glass content, up to the degree of sedimenting paste. At $M_s = 0.5$ (figure 4) it was possible to reduce the water ratio while maintaining an acceptable workability down to $w = 0.30$, while in the other instances it was necessary to use $w = 0.45$. The effect of specific surface area on the rheological properties of pastes in the system ground granulated slag - water glass - sodium lignosulphonate was found to be minimum.

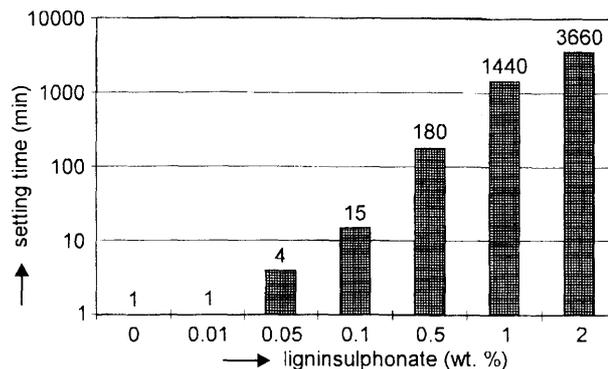


Figure 1. Initial set of pastes $w = 0.45$ of ground slag (416 m² kg⁻¹), additive: 2 wt.% Na₂O (water glass with $M_s = 1.5$) in terms of lignosulphonate (Zewa S1) concentration.

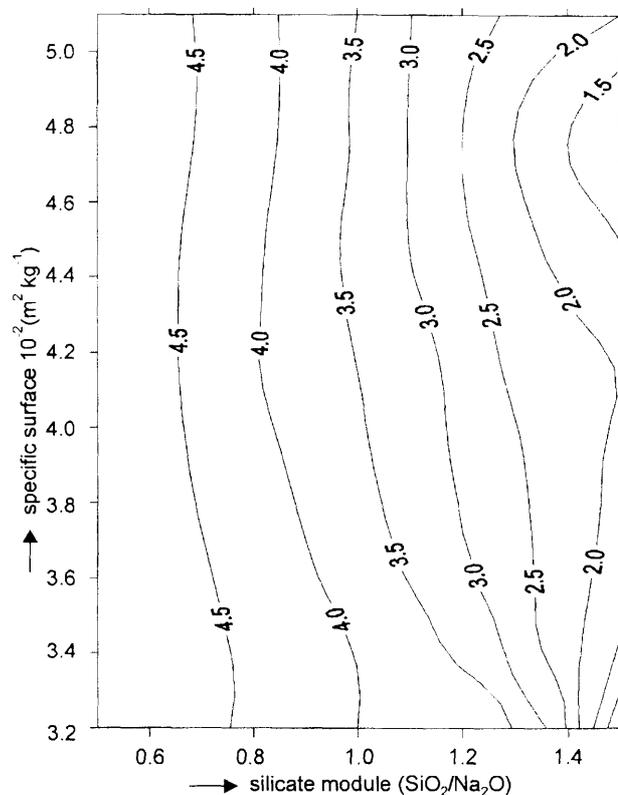


Figure 2. Visual workability of pastes $w = 0.45$ of ground slag with 2 wt.% Na₂O (water glass) and 0.1 wt.% lignosulphonate (Zewa S1) vs. specific surface area of slags and silicate modulus M_s of water glass.

The time of initial set of the system ground granulated slag - water glass - sodium lignosulphonate depends on the specific surface area of the ground slag, on silicate modulus M_s of water glass, on the amount of water glass added (calculated as Na₂O content), as shown by figures 5 and 6. The time of initial set decreases with increasing specific surface area of the ground slag and with increas-

ing content of water glass. The time of initial set can be controlled over a wide range (of the order of minutes to 1-2 days) by adjusting the silicate modulus M_s of the water glass.

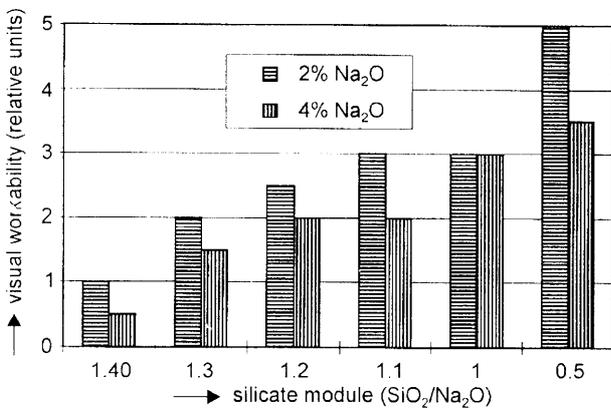


Figure 3. Visual workability of pastes $w = 0.45$ of ground slag ($416 \text{ m}^2 \text{ kg}^{-1}$) with 2 wt.% and 4 wt.% Na_2O (water glass) and 0.1 wt.% lignosulphonate (Zewa S1) vs. silicate modulus M_s of water glass.

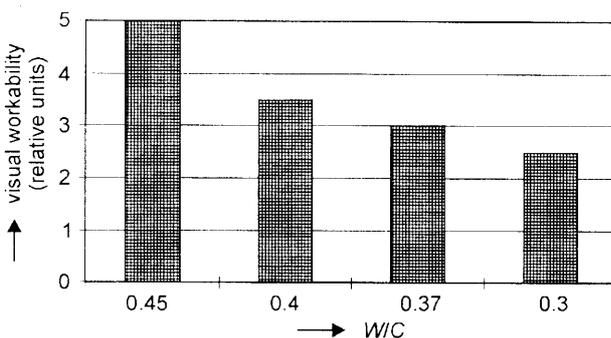


Figure 4. Visual workability of pastes of ground slag ($416 \text{ m}^2 \text{ kg}^{-1}$) with 2 wt.% Na_2O (water glass with $M_s = 0.5$) and 0.1 wt.% lignosulphonate (Zewa S1) vs. water ratio.

Generation of the heat of hydration in the system ground granulated slag - water glass - sodium lignosulphonate is very small, and also very slow when compared to the hydration of Portland cement. The series of calorimetric measurements performed show that the generation of hydration heat in the system ground granulated slag - water glass - sodium lignosulphonate proceeds in two or three waves (after approx. 500, 1500 and 2500 min), regardless of the silicate modulus M_s and the specific surface area of the ground slag. Interpretation of these results is rather difficult and would require additional data and information.

The 7-day and 28-day strengths (figures 7, 8, 9, 10) depend on the specific surface area of the ground slag and on water glass concentration. The strength increases

with increasing specific surface area and increasing water glass concentration. The dependence of strength on silicate modulus is virtually minimum up to the value of $M_s = 1$, where substantially lower strengths are achieved with lower M_s values.

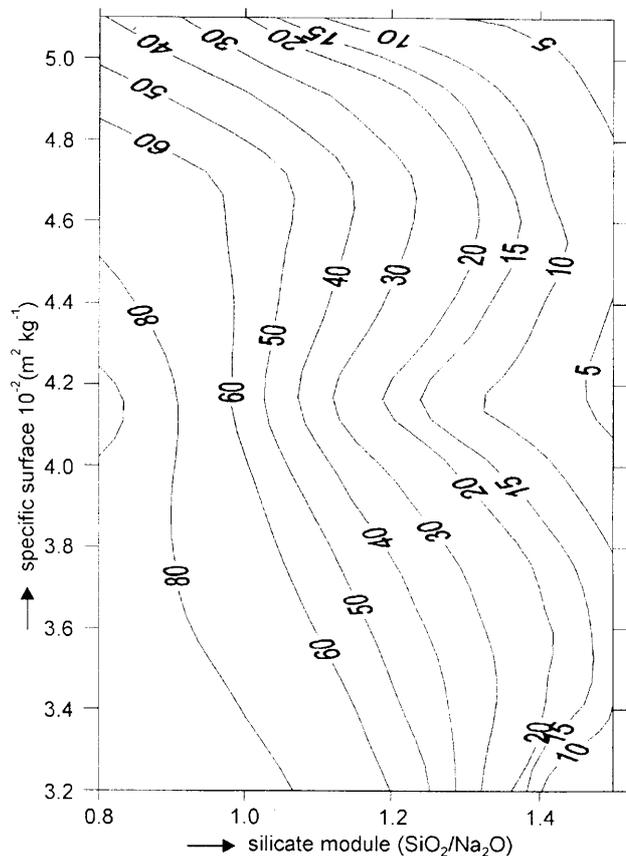


Figure 5. Initial set of pastes ($w = 0.45$) of ground slag with 2 wt.% Na_2O (water glass) and 0.1 wt.% lignosulphonate (Zewa S1) vs. specific surface area of slag and silicate modulus M_s of water glass.

From the standpoint of practical technological properties (workability, initial set, strength), use of water glass with silicate modulus $M_s = 1$ appears viable. This value corresponds to a theoretical water glass composition of Na_2SiO_4 . It should be pointed out that also with other types of alkali activated systems, such as gypsum-free cements, the optimum compositions employed likewise corresponded to Na_2CO_3 , K_2CO_3 and also Na_2SiO_3 . With respect to activation of ground slag [3], an important role is played not only by the pH of the silicate, but also by the character of the silicate component whose composition depends on silicate modulus M_s as well as on water glass concentration. At $M_s = 2$, the polymeration degree of the silicate component amounts to 2.5, while at $M_s = 4$ it is already 27 [3]. At the lower

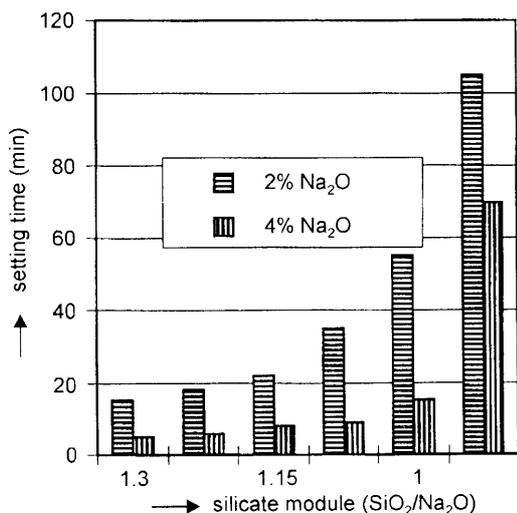


Figure 6. Initial set of pastes of ground slag ($416 \text{ m}^2 \text{ kg}^{-1}$) with 2 wt.% and 4 wt.% Na_2O (water glass) and 0.1 wt.% lignosulphonate (Zewa S1) vs. silicate modulus M_s of water glass. At $M_s = 0.5$, the time of initial set amounts to 1 or 2 days respectively.

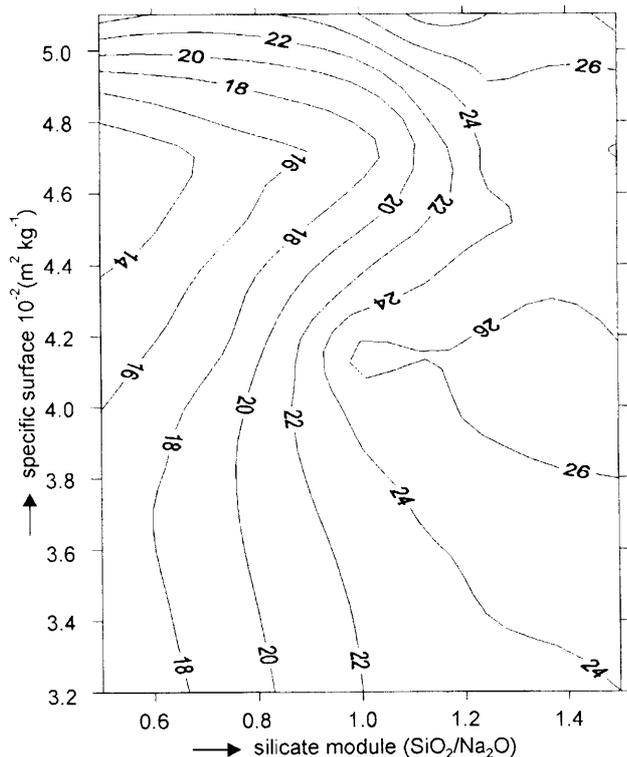


Figure 7. 7-day compressive strength of ground slag pastes $w = 0.45$ with 2 wt.% Na_2O (water glass) and 0.1 wt.% lignosulphonate (Zewa S1) vs. specific surface area of slag and silicate modulus M_s of water glass.

M_s values, the water glass contains for the most part monomers which are distinctly more reactive with respect to cations Ca^{2+} , Al^{3+} and others.

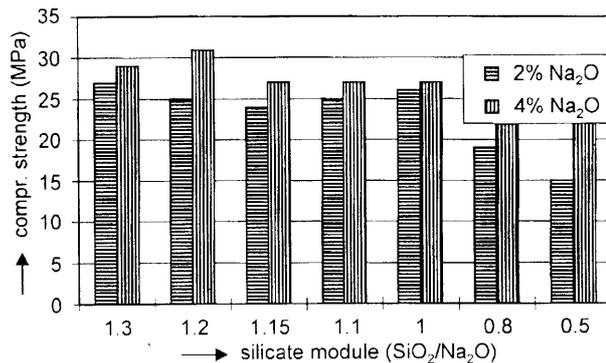


Figure 8. 7-day compressive strength of ground slag ($416 \text{ m}^2 \text{ kg}^{-1}$) pastes with 2 wt.% and 4 wt.% Na_2O (water glass) and 0.1 wt.% lignosulphonate (Zewa S1) vs. silicate modulus M_s of water glass.

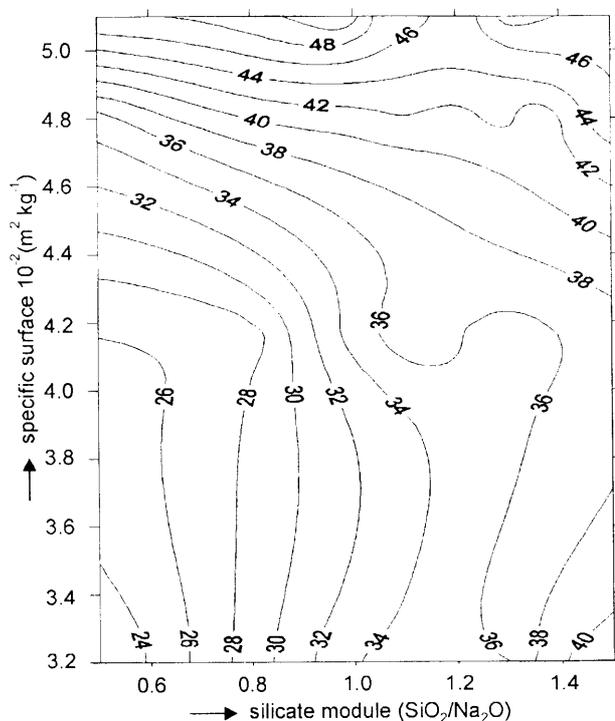


Figure 9. 28-day compressive strength of ground slag pastes ($w = 0.45$) with 2 wt.% Na_2O (water glass) and 0.1 wt.% lignosulphonate (Zewa S1) vs. specific surface area of slag and silicate modulus M_s of water glass.

The following hydration products (figure 11) were determined in hydrated pastes of the system ground granulated slag - water glass - sodium lignosulphonate: CSH phase, hydronepheline $Na_2(Al_2Si_2O_8) \cdot 2H_2O$, thomsonite $CaNa_2(Al_2Si_2O_8) \cdot 2.5H_2O$, and possibly also chabazite $(Na_2Ca)Al_2Si_4O_{12} \cdot 6H_2O$ and analcime $Na(AlSi_3O_6) \cdot H_2O$. Analogous hydration products (in dependence on the conditions of hydration and on slag composition) were also determined by other authors [1-5]. Increasing

specific surface area of the ground slag obviously leads to more profound hydration and formation of a larger number of hydration products. The effect of the silicate modulus on the occurrence of hydration products is not significant.

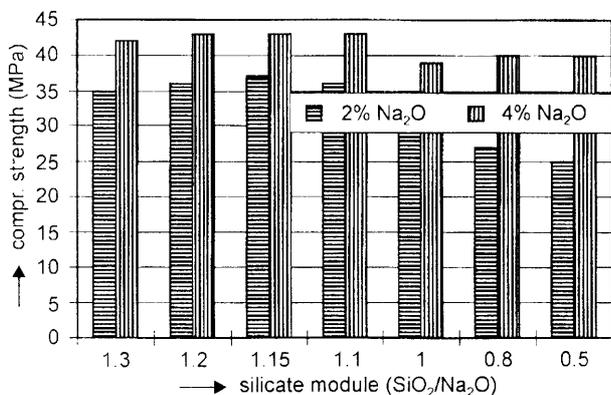


Figure 10. 28-day compressive strength of ground slag ($416 \text{ m}^2 \text{ kg}^{-1}$) pastes with 2 wt.% and 4 wt.% Na_2O (water glass) and 0.1 wt.% lignosulphonate (Zewa S1) vs. silicate modulus M_s of water glass.

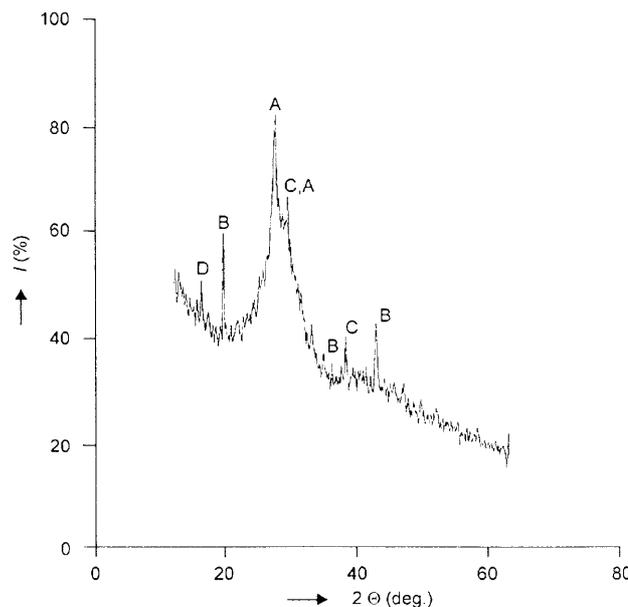


Figure 11. X-ray diffraction pattern of hardened ground slag ($416 \text{ m}^2 \text{ kg}^{-1}$) paste ($w = 0.45$) after 28 days of hydration, additives: 2 wt.% Na_2O (water glass, $M_s = 1$) and 0.1 wt.% lignosulphonate (Zewa S1). Designation: A - CSH phase, B - hydronepheline, C - thomsonite, D - chabazite.

Table 1. Results of X-ray diffraction analyses of hydrated alkali-activated cement pastes in terms of specific surface area of slag and silicate modulus ($M_s = \text{SiO}_2/\text{Na}_2\text{O}$) after 28 days of hydration, $w = 0.40$, admixtures: 2 wt.% Na_2O (in silicate) + 0.1 wt.% Zewa S1.

	$320 \text{ m}^2 \text{ kg}^{-1}$	$416 \text{ m}^2 \text{ kg}^{-1}$	$480 \text{ m}^2 \text{ kg}^{-1}$	$510 \text{ m}^2 \text{ kg}^{-1}$
$M_s = 1.5$	CSH	CSH, thomsonite, hydronepheline	CSH, thomsonite, hydronepheline chabazite?	CSH, thomsonite, hydronepheline chabazite?
$M_s = 1.0$	CSH, thomsonite, hydronepheline	CSH, thomsonite, hydronepheline chabazite?	CSH, thomsonite hydronepheline chabazite? analcime?	CSH, thomsonite hydronepheline chabazite?
$M_s = 0.5$	CSH	CSH hydronepheline chabazite?	CSH hydronephelin thomsonite?	CSH, thomsonite hydronepheline chabazite?

The morphology of fracture surfaces of hardened cement pastes in the system ground granulated slag - water glass - sodium lignosulphonate after 28 days of hydration is quite uniform and corresponds to a mostly gel-like character of the hydration products (in agreement with earlier study [6]). No crystalline formations characteristic of hydrated Portland or slag cement were found on the fracture surfaces. More detailed evaluation of the morphology would require additional information, obtained in particular from EDAX analyses.

Research of hydraulic cements other than the classical Portland types, which offer the opportunity of a higher degree of utilization of so-called waste materials, is an activity with good prospects.

CONCLUSION

1. The system ground granulated slag - water glass is a quick setting and hardening binder. Sodium lignosulphonate allows the setting to be controlled over the range of several minutes to several days.

2. The rheological properties of pastes in the system ground granulated slag - water glass - sodium lignosulphonate depend on concentration and silicate modulus M_s of water glass.
3. The time of initial set of pastes in the system ground granulated slag - water glass - sodium lignosulphonate depends on the specific surface area of the ground slag, on silicate modulus M_s of water glass, and on its amount.
4. The generation of hydration heat during hydration of the system ground granulated slag - water glass - sodium lignosulphonate is very small, and also very slow when compared to the hydration of Portland cement.
5. The compressive strengths after 7 and 28 days of hydration depend on the specific surface area of the ground slag and on the concentration of water glass. The dependence of strength on silicate modulus is virtually minimum up to the value of $M_s = 1$, where the strengths for lower M_s are significantly lower.
6. With respect to the practical properties (workability, time of set, strength), use of water glass with a silicate modulus $M_s = 1$ appears prospective.
7. X-ray diffraction analysis of hydrated pastes in the system ground granulated slag - water glass - sodium lignosulphonate established the presence of the following hydration products: CSH phase, hydronepheline, thomsonite, and possibly also chabazite and analcime.
8. The morphology of fracture surfaces of hardened pastes in the system ground granulated slag - water glass - sodium lignosulphonate after 28 days of hydration is quite uniform and corresponds to the character of gel-type hydration products. No crystalline formations characteristic of hydrated Portland and blended slag cements were found on the fracture surfaces.
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Translated by K. Němeček.

VLASTNOSTI POJIVA
NA BÁZI ALKALICKY AKTIVOVANÝCH STRUSEK

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Systém umletá granulovaná vysokopecní struska - vodní sklo je rychle tuhnoucí pojivo. Použitím ligninsulfonátu sodného lze nastavit počátek tuhnutí v rozmezí několika minut do několika dnů. Reologické vlastnosti kaší systému umletá granulovaná struska - vodní sklo - ligninsulfonan sodný závisí na koncentraci a silikátovém modulu M_s vodního skla. Počátek tuhnutí kaší systému umletá granulovaná struska - vodní sklo - ligninsulfonan sodný je závislý na měrném povrchu umleté strusky, na silikátovém modulu M_s vodního skla, a přídavku vodního skla. Vývoj hydratačního tepla při hydrataci systému umletá granulovaná struska - vodní sklo - ligninsulfonan sodný je velmi nízký a ve srovnání s hydratací struskoportlandského cementu i velmi pomalý. Pevnosti v tlaku po 7 a 28 dnech hydratace závisí na měrném povrchu mleté strusky a na koncentraci vodního skla. Závislost pevností na silikátovém modulu je prakticky minimální až do hodnoty $M_s = 1$, kdy pro nižší hodnoty M_s jsou pevnosti výrazně nižší. Z hlediska praktických vlastností (zpracovatelnost, počátek tuhnutí, dosažené pevnosti) se ukazuje použití přísady vodního skla se silikátovým modulem $M_s = 1$. V hydratovaných kaších systému umletá granulovaná struska - vodní sklo - ligninsulfonan sodný byly nalezeny na základě RTG difrakční analýzy tyto hydratační produkty: CSH fáze, hydronefelin, thomsonit, a pravděpodobně i chabazit a analcim. Morfologie lomových ploch zatvrdlých kaší systému umletá granulovaná struska - vodní sklo - ligninsulfonan sodný po 28 dnech hydratace je dosti uniformní a odpovídá spíše gelovému charakteru hydratačních produktů. Na lomových plochách nebyly nalezeny krystalické útvary charakteristické pro hydratovaný portlandský a struskoportlandský cement.

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