BLENDED GYPSUM BINDER WITH HYDRAULIC PROPERTIES

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Blended gypsum binder comprising ß-$CaSO_4.1/2H_2O$ and small proportions of a mixture of Portland cement and ground fly ash, or ground blast-furnace slag, is a binding agent with distinct hydraulic properties which shows strength increments also when cured in water. The hydraulic features of the blended gypsum binder are due to formation of less soluble ettringite-type phases and the C-S-H phase on the surface of gypsum crystals.

INTRODUCTION

The issue of gypsum-based cements has recently been paid considerable attention resulting from the ever-increasing amounts of waste gypsum produced by desulphurization processes of flue gas. At present, manufacture of various types of gypsum-based bonding agents from waste gypsum has been mastered and the products find wide fields of application. However, the applications are restricted by the essential property of hardened gypsum binders, which is a poor resistance to the effects of water (non-hydraulicity of the material). Elimination of this problem (aimed at finding new applications for waste gypsum) is subject to extensive research. In the literature (as well as in practice) one encounters a number of methods how to render gypsum products hydrophobic. There are the external waterproofing methods, such as the protection of products by coatings (of resin [1], wax [2], polymer [3]) or other protective layers (Al foil [4]). Another way is based on internal waterproofing when the product is impregnated with hydrophobic (mostly organic) substances (paraffin wax emulsion [5]). Still another way of rendering gypsum resistant to water is based on precipitation of insoluble substances on the surface of gypsum crystals (gypsum + siloxanes [6, 7]), (gypsum + wax emulsion + H_3BO_3 + vinyl alcohol [8]). A certain improvement of resistance to water was established for example in the systems gypsum hemihydrate - lime - fly ash [9], gypsum hemihydrate - b.f. slag [10], gypsum hemihydrate - slag - $Al_2(SO_4)_3$ [11]), gypsum hemihydrate - magnesite - waste Fe_2O_3 - $MgCl_2$ [12]. Interesting results were obtained in the study of the system anhydrite - fly ash (slag) - Portland cement [13-15], where significant long-term increases in water resistance were achieved.

The present study is concerned with the system ß-$CaSO_4.1/2H_2O$ - ground fly ash (b.f. slag) - Portland cement - H_2O [16] and with the properties of the hardened blended binding agent, in particular under the conditions of water curing.

EXPERIMENTAL PART

Commercial ß-$CaSO_4.1/2H_2O$ of standard quality conforming to Czech standard ČSN 72 2301 was used in the experiments. The secondary raw materials employed were fly ash Chvaletice having the composition (wt.%) 55.1 SiO_2, 26.7 Al_2O_3, 3.1 CaO, 1.1 MgO, 2.1 TiO_2, 0.87 SO_3, 0.37 Na_2O, 1.64 K_2O, 1.26 combustible substances, and blast-furnace granulated slag Vítkovice composed of 39.30 SiO_2, 8.17 Al_2O_3, 0.43 Fe_2O_3, 43.90 CaO, 5.92 MgO, 0.93 SO_3. Further used was standard Portland cement CEM I 32.5 R Prachovice with the composition (wt.%) 66.1 CaO, 21.2 SiO_2, 5.2 Al_2O_3, 2.3 Fe_2O_3, 2.0 MgO, 2.8 SO_3, specific surface area (Blaine) 300 $m^2 kg^{-1}$. The fly ash employed in the study had a surface area (Blaine) of 200 $m^2 kg^{-1}$, and for the experiments was ground in a ball mill to a surface area (Blaine) of 320 $m^2 kg^{-1}$ and 480 $m^2 kg^{-1}$ respectively. The slag was ground in a vibration mill to a surface area (Blaine) of 310 $m^2 kg^{-1}$. The pastes were plasticized with agents based on lignine sulphonate and naphtalene sulphonate, produced by Adiment (FRG) and Holderchem (Switzerland).

The study of the blended gypsum binder was launched by comparatively extensive introductory experiments aimed at finding the approximate composition of a binder having acceptable rheological properties, an adequate setting point and satisfactory strengths. These experiments were to a significant degree concerned with selection of suitable plasticizers which would at the same time allow an acceptable time of initial set to be achieved. The best results were achieved with the plasticizer Eucoplast 200 VZ, Holderchem (lignine sulphonate type with a small amount of accompanying monosaccharides), figures 1 and 2.

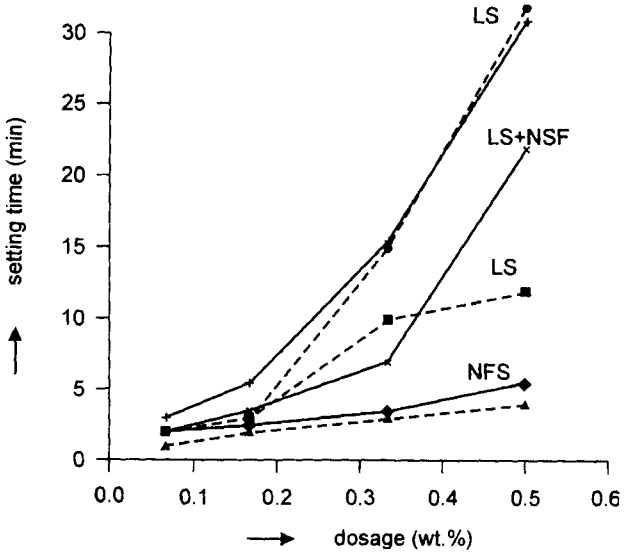


Figure 1. The effect of additive type and concentration on the time of initial set of pastes (w =0.40) of blended binder 80 wt.% β-$CaSO_4$.1/2H_2O – 10 wt.% ground fly ash (320 m^2 kg^{-1}) – 10 wt.% Portland cement.
LS - lignine sulphonate, NSF - derivative of naphthalene sulphonate, LS+NSF - mixed plasticizer

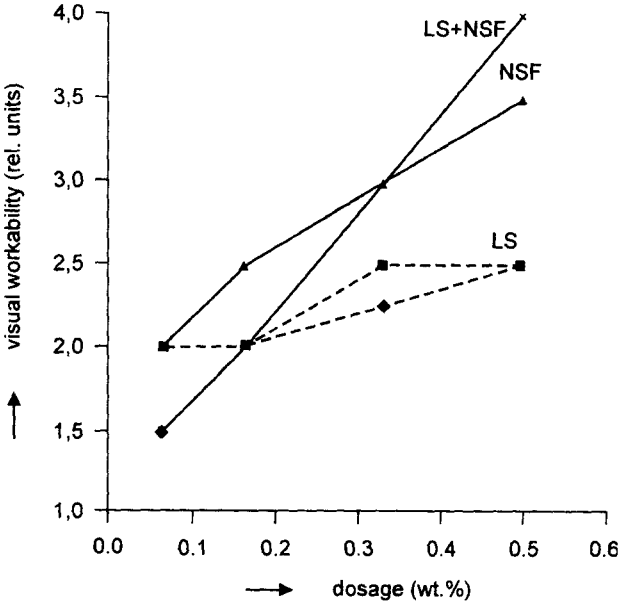


Figure 2. The effect of plasticizer type and concentration on visual workability of pastes (w = 0.40) of blended binder 80 wt.% β-$CaSO_4$.1/2H_2O – 10 wt.% ground fly ash (320 m^2 kg^{-1}) – 10 wt.% Portland cement.
LS - lignine sulphonate, NSF - derivative of naphthalene sulphonate, LS+NSF - mixed plasticizer

The actual experiments with the system β-$CaSO_4$.1/2H_2O - ground fly ash (slag) - Portland cement -H_2O were carried out with an addition of 0.5 wt.% (in terms

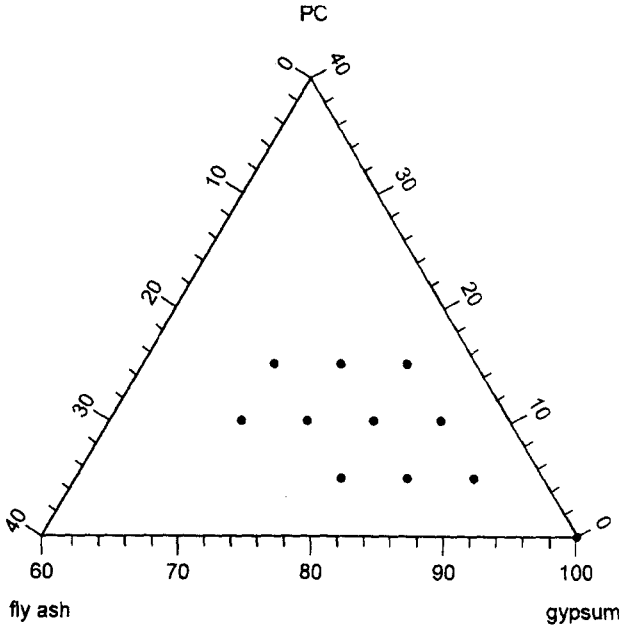


Figure 3. The composition range of blended gypsum binders studied by the experiments.
● - points corresponding to the mix compositions

of total binder) of Eucoplast 200 VZ using a water-to-cement ratio w = 0.40. The plasticizer was added to the mix water. The study of the system was restricted (on the basis of preliminary experiments) to the range of 70 to 100 wt.% β-$CaSO_4$.1/2H_2O, 0 to 15 wt.% Portland cement and 0 to 15 wt.% ground fly ash (ground slag), cf. figure 3.

The blended binder was prepared by mixing the individual components and their subsequent homogenizing (a PE vessel fitted in a device revolving around three axes) for 10 minutes. The pastes prepared were tested for the time of initial set (Vicat), apparent visual workability according to an empirical scale (0 ... unworkable paste to 4 ... freely flowing paste). Test specimens 20×20×20 mm in size for compressive strength determination were prepared. The moulds with the paste were kept for 2 hours in a medium of 100 % relative humidity (R.H.) and then demoulded. A part of the specimens were cured in the medium of saturated water vapour and a part were kept in water, all at 20 °C. The strength in compression was tested at time intervals from 1 to 28 days. The specimens cured at 100 % R.H. were dried at 40 °C before testing. The specimens cured in water were not dried prior to testing. Specimens kept continuously in water for 6 months were also prepared within the framework of preliminary tests.

The results of the strengths established were expressed as isolines in ternary diagrams plotted by means of the Grapher and Surfer® software (Golden Software, USA).

The fractions from compression test specimens were used for studying the composition of hydration products by thermal analysis, X-ray diffraction and scanning electron microscopy. The surface of specimens exposed to the effects of water for 6 months was studied by means of light imaging analysis.

RESULTS AND DISCUSSION

The system ß-$CaSO_4.1/2H_2O$ - ground fly ash (slag) - Portland cement - H_2O exhibits a behaviour different from that of the system ß-$CaSO_4.1/2H_2O$ - H_2O in that the former is capable of attaining higher strength even when cured in water.

A small addition of PC and ground fly ash or slag increases significantly the strength of the blended binder when compared to gypsum alone. Increasing the content of the individual additives (fly ash or slag, PC) has no distinct effect on further rise in strength, as demonstrated by the ternary diagrams in figures 4, 5 and 6. The character of the quantitative relations between strength and binder composition given in the ternary diagrams for the conditions of moist curing and subsequent drying remained virtually unchanged for the conditions of wet curing. The course of strength development for the blended binder and for gypsum hemihydrate alone under the respective curing conditions is plotted in figures 7 and 8. In our experiments, the optimum composition of the blended binder corresponded to an addition of 7 to 12 wt.% of a mixture of Portland cement with ground fly ash or ground slag.

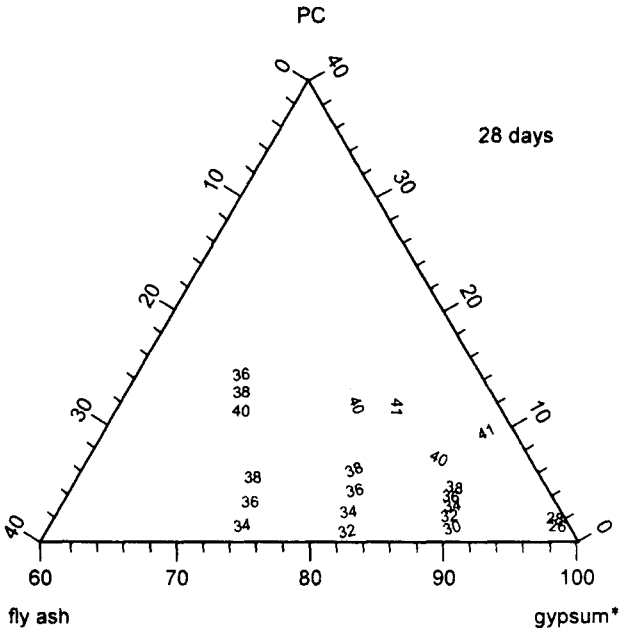


Figure 5. Ternary diagram of the system β-$CaSO_4.1/2H_2O$ - ground fly ash (320 $m^2 kg^{-1}$) - Portland cement, with compression strength isolines in MPa, after 28 days of curing (100 % R.H., specimens dried before testing).
* Gypsum without admixtures 24.8 MPa

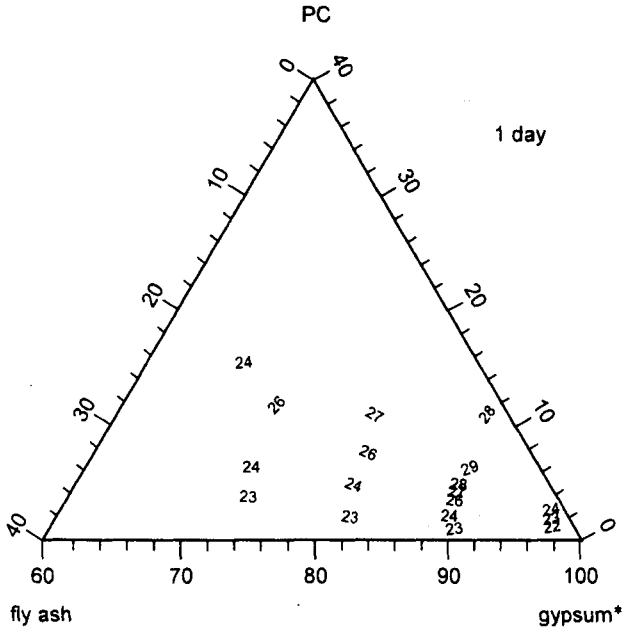


Figure 4. Ternary diagram of the system β-$CaSO_4.1/2H_2O$ - ground fly ash (320 $m^2 kg^{-1}$) - Portland cement, with compression strength isolines in MPa after 1 day of curing (100 % R.H., specimens dried before testing).
* Gypsum without admixtures 20.7 MPa

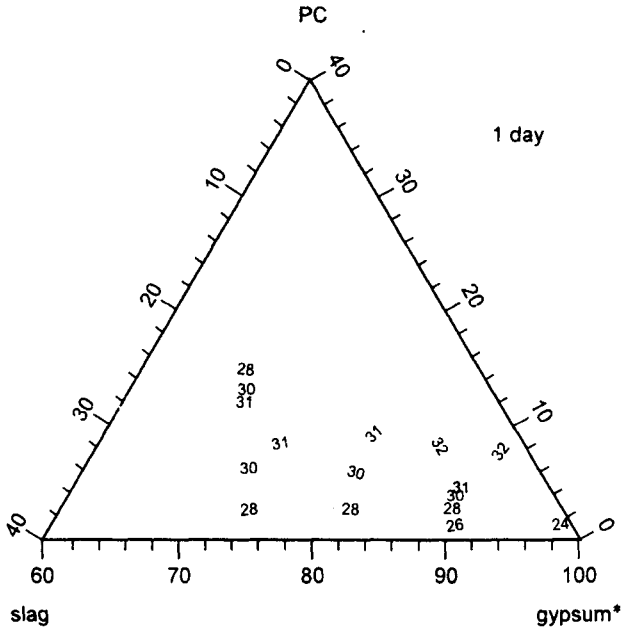


Figure 6. Ternary diagram of the system β-$CaSO_4.1/2H_2O$ - ground b.f. slag (310 $m^2 kg^{-1}$) - Portland cement with compression strength isolines in MPa, after 1 day of curing (100 % R.H., specimens dried before testing).
* Gypsum without admixtures 20.7 MPa

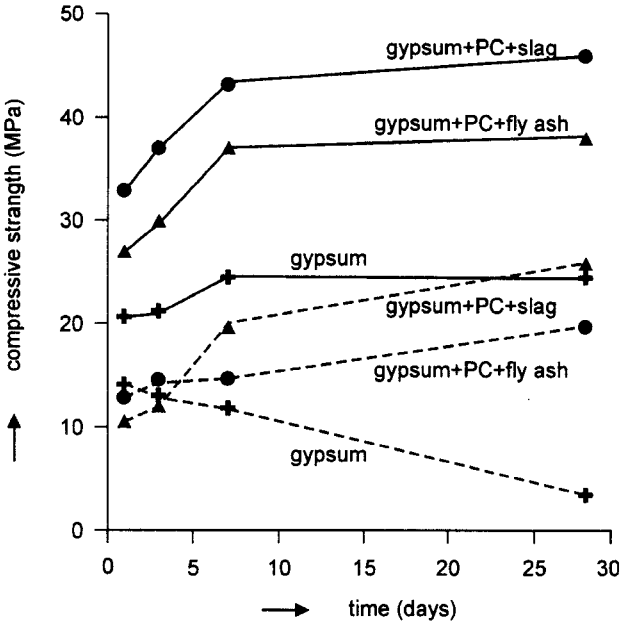


Figure 7. Compressive strength in terms of time after curing in 100 % R.H., in water, and after subsequent drying, for blended binder β-$CaSO_4.1/2H_2O$ - ground fly ash (320 m^2 kg^{-1}) or ground b.f. slag (310 m^2 kg^{-1}) - Portland cement.

The increase in the fineness of fly ash used in the blended binder resulted in a higher strength. However, this increase in strength was not substantial and in our opinion no extra fine grinding of fly ash is necessary. The addition of ground slag to the blended gypsum binder brings about a distinct improvement of the hydraulic properties (continuous increase in strength on water curing, figure 8).

Study of the products of hydration of blended gypsum binders (figures 9 and 10) showed that apart from $CaSO_4.2H_2O$ only small amounts of other hydration products are formed. Besides gypsum and ettringite, also the C-S-H phase was probably identified in the hydrated blended binder. The morphology of fracture surfaces of hardened blended binder pastes revealed that the characteristic gypsum crystals were coated with hydration products (ettringite, and probably the C-S-H phase). Unlike the structure of hardened hemihydrate, that of the gypsum skeleton of the blended binder appears to be much more closely packed. The hardened blended binder containing ground slag as its component had a distinctly more uniform microstructure than that prepared with ground fly ash (study of the morphology is to be continued).

Preliminary long-term study [16] of the effect of water storage on the properties of the blended gypsum binder was carried out within the framework of our experiments. On the basis of visual examination and image analysis of specimen surfaces it may be concluded that the surface of blended binder specimens kept in water for 6 months remained unchanged whereas the surface of specimens prepared from ß-hemihydrate was seriously eroded and about 30 % of the specimen weight has dissolved.

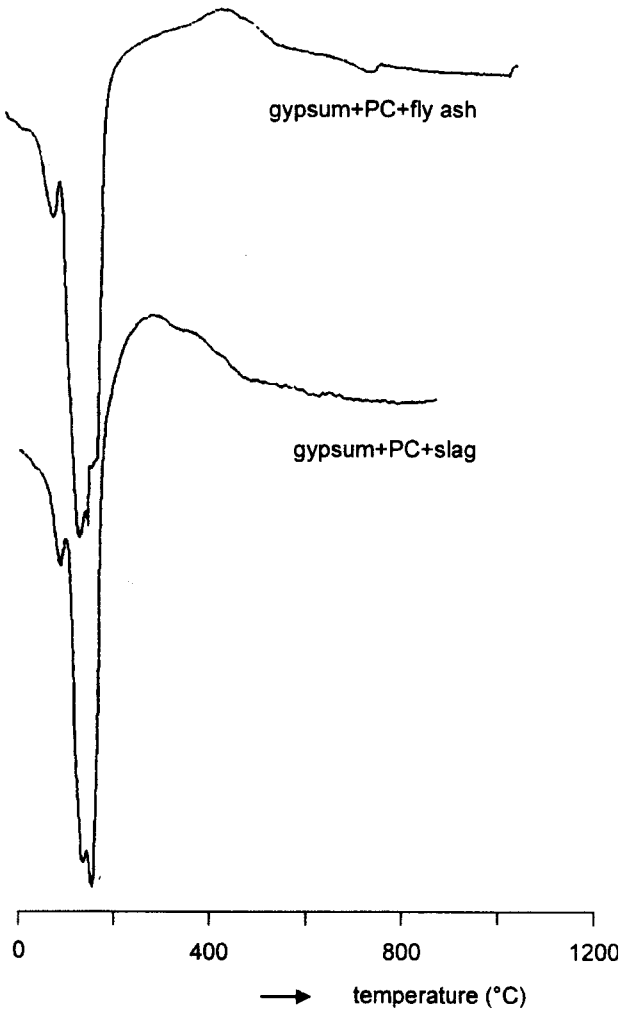
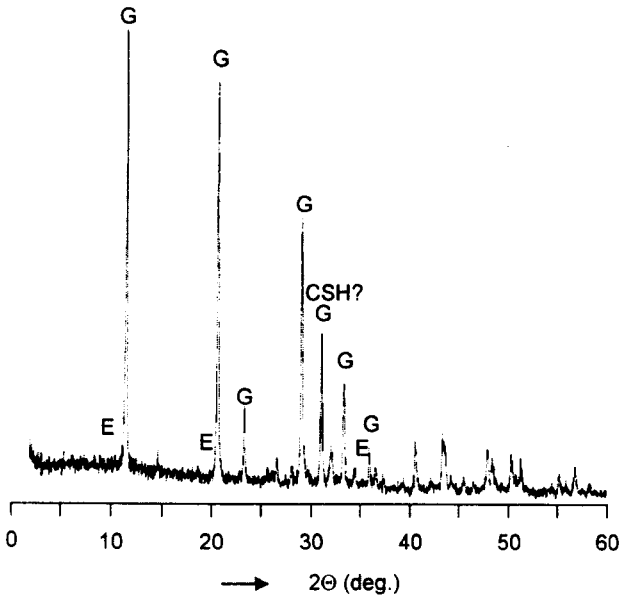


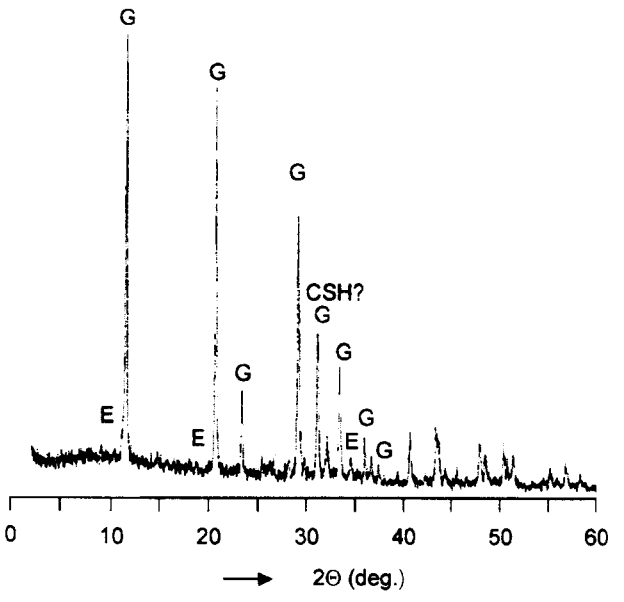
Figure 8. DTA curves for mixed binder β-$CaSO_4.1/2H_2O$ - ground fly ash (320 m^2 kg^{-1}) - or ground b.f. slag (310 m^2 kg^{-1}) - Portland cement, after 28 days of hydration.

The blended gypsum binder composed of ß-$CaSO_4.1/2H_2O$ and a small amount of Portland cement and ground fly ash or slag is a binding agent exhibiting hydraulic properties, as demonstrated by the increase in strength when cured in water. The properties are due to a difference in the structure of the hardened material as compared to the microstructure of hardened gypsum. Hydration of the blended binder at first produces a skeleton of gypsum crystals (typical of hardened gypsum). During the subsequent stage of hydration, the Portland cement and fly ash or slag form additional

hydrates, in particular ettringite and the C-S-H phase, and possibly also C_2ASH_8 (gehlenite hydrate). These hydrates precipitate preferentially on the surface of gypsum crystals and reinforce the critical points of the gypsum matrix, namely the points of contact between the gypsum crystals. In this way it is possible to explain the hydraulic features of this blended binder.



a)



b)

Figure 9. X-ray diffraction patterns for the blended binder containing 80 wt.% β-$CaSO_4$.1/2H_2O, 10 wt.% Portland cement and *a*) 10 wt.%ground fly ash (320 m^2 kg^{-1}) or *b*) ground b.f. slag (310 m^2 kg^{-1}) , after 28 days of hydration. G – $CaSO_4$.2H_2O, E -ettringite.

Data from the literature and our other findings indicate that mixing hemihydrate with a small amount of Portland cement or fly ash alone does not yield any significantly improved resistance to water compared to gypsum. Satisfactory results are obtained solely with additions of Portland cement-slag or Portland cement-fly ash mixtures. This is probably due to formation of more C-S-H phase and less $Ca(OH)_2$ during hydration of a Portland cement/slag or Portland cement/fly ash mixture than during hydration of Portland cement alone. The resistance to water results more from the effect of the C-S-H phase than from that of $Ca(OH)_2$.

The study of blended gypsum binders with internal inorganic waterproofing appears to be a prospective way towards improving the performance properties and thus the possibility of finding use for the continuously increasing amounts of waste $CaSO_4$.2H_2O. And this is the direction our future experimental work, aimed at other inorganic systems, will take.

CONCLUSION

1. A binding agent with distinct hydraulic properties can be prepared by adding a small amount of Portland cement and ground fly ash or ground blast-furnace slag to ß-$CaSO_4$.1/2H_2O.

2. The blended binding agent of this type must further contain a setting retarder to achieve an acceptable time of initial set. This purpose was best met by a mixture of lignine sulphonate with naphthalene sulphonate, which moreover allowed a low ater ratio to be employed thanks to its plasticizing effect.

3. The blended gypsum binder exhibits satisfactory increases in strength when cured in dry, moist (100% R.H.) medium, as well as in water. The strengths achieved are significantly higher than those of gypsum alone.

4. The optimum properties were achieved with a binder composed of ß-$CaSO_4$.1/2H_2O and 7 to 12 wt.% of a mixture of Portland cement and ground fly ash or ground slag.

5. The microstructure of the hardened blended binder differs from that of hardened gypsum. The hydration products found apart from $CaSO_4$.2H_2O were ettringite and the C-S-H phase. The latter cover the gypsum crystals and are responsible for increased strength and suppression of solubility of gypsum crystals in water.

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SMĚSNÉ SÁDROVÉ POJIVO S HYDRAULICKÝMI VLASTNOSTMI

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Přídavkem malého podílu portlandského cementu a mletého popílku resp. mleté strusky do β-$CaSO_4.1/2H_2O$ lze vytvořit směsné sádrové pojivo s výrazně hydraulickými vlastnostmi. Směsné sádrové pojivo tohoto typu musí dále obsahovat zpomalovač tuhnutí pro dosažení akceptabilního počátku tuhnutí. Jako optimální řešení byla nalezena směs ligninsulfonanu s naftalensulfonanem, která svým plastifikačním účinkem dále umožnila zpracování pojiva při nízkém vodním součiniteli. Směsné sádrové pojivo vykazuje nárůst pevností při vlhkém (100% R.H.) i vodním uložení. Toto pojivo dosahuje výrazně vyšších pevností než samotná sádra. Optimálních vlastností bylo dosaženo při složení pojiva obsahující vedle β-$CaSO_4.1/2H_2O$ 7-12% hm. směsi portlandského cementu a mletého popílku resp. mleté strusky. Mikrostruktura zatvrdlého směsného sádrového pojiva je odlišná od mikrostruktury zatvrdlé sádry. Jako hydratační produkty ve směsném pojivu byly kromě $CaSO_4.2H_2O$ nalezeny ettringit a C-S-H fáze. Tyto fáze pokrývají krystalky sádrovce a způsobují zvýšení pevností a snížení rozpouštění sádrovcových krystalů při vodním uložení.