# THE EFFECT OF ADMIXTURES OF $Na_2CO_3$, SODIUM LIGNOSULPHONATE, GRANULATED BLAST-FURNACE SLAG AND SILICA FUME ON THE PROPERTIES OF GYPSUM-FREE PORTLAND CEMENTS

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*Using the method of mathematical planning od experiments, the effects of $Na_2CO_3$, sodium lignosulphonate, ground granulated blast-furnace slag and silica fume on the properties of pastes of gypsum-free Portland cements were determined. The respective effects differ from those on the properties of pastes of standard Portland cements and exhibit local extremes.*

## INTRODUCTION

Gypsum-free Portland cement (hereinafter GF cement) can be described as the system of Portland cement clinker ground to a specific surface area of 400-600 $m^2\,kg^{-1}$ supplemented with admixtures replacing the effects of gypsum, namely sulphonated polyelectrolyte + salt of an alkali metal [1]. The basic property of GF cements is the possibility of preparing pastes, mortars and concretes with a very low water-to-cement ratio. This characteristic is responsible for attainment of high early and long-term strengths, for the ability to set and harden at low and even subzero temperatures, and for a high resistance to the effects of aggressive environments and high temperatures [1,2,3].

The effect of admixtures which replace gypsum in GF cements is synergic in nature; the respective mechanism has not yet been completely explained, and the effects of ground slag and silica fume have not so far been investigated.

The present study is concerned with the effects of $Na_2CO_3$, sodium lignosulphonate, ground granulated blast-furnace slag (hereinafter BF slag) and silica fume on the properties of pastes of GF cements, and summarizes the results described in [4,5,6]. Similar investigations (also with other admixtures) were carried out in 1987-92 also on mortars and concretes, and their results constituted the basis of industrial formulations for the manufacture and utilization of GF cements in the Czech Republic [3].

## EXPERIMENTAL PART

The raw material for the preparation of GF cements was clinker from standard production of Portland cement. The clinker had the composition [wt.%] $SiO_2$ 20.71, $Al_2O_3$ 5.56, $Fe_2O_3$ 3.21, CaO 63.18, $CaO_f$ 0.49, $Na_2O$ 0.25, $K_2O$ 1.35, MgO 2.99, $SO_3$ 0.69 and ignition loss 0.25. Repeated sampling and analyses of sinter from industrial production showed that the deviations from the above composition did not exceed ±1-3 rel.%. The clinker was ground without gypsum in a laboratory ball mill with an addition of 0.05 % grinding aid Abeson TEA™ to a specific surface area of about 550-570 $m^2\,kg^{-1}$. The granulated blast-furnace slag from Vítkovice Steelworks had the composition [wt.%] $SiO_2$ 39.3, $Al_2O_3$ 8.17, $Fe_2O_3$ 0.43, CaO 43.9, MgO 5.92, $SO_3$ 0.93. The composite cements were prepared by grinding the slag jointly with clinker and Abeson TEA to a surface area of 530-570 $m^2\,kg^{-1}$ (again in the absence of gypsum). In other experiments, use was made of silica fume $SiO_2$ Microsilica produced by Elkem (Norway) which had the composition [wt.%] $SiO_2$ 97.5, $Al_2O_3$ 0.4, $Fe_2O_3$ 0.1, CaO 0.2, MgO 0.1 and $H_2O$ 0.4. The silica fume was homogenized with the ground clinker or the ground clinker-slag mixture.

The pastes with $w$ = 0.25 were prepared with sodium lignosulphonate containing less than 2 % reducing monosaccharides. The admixtures replacing the effects of gypsum, namely $Na_2CO_3$ + sodium lignosulphonate, were always dissolved in advance in the mix water. Specimens 2 × 2 × 2 cm in size were prepared of the pastes, placed for 24 hours in a medium of saturated water vapour and then till the 28th day in water, all at 22 °C. The compressive strength was determined after 4 hours, 24 hours and 28 days. The time of setting was also measured (Vicat).

The rheological properties of the pastes were determined visually according to their workability. This somewhat empirical method was chosen because the differences in the rheological properties at the low water ratio values and with the various amounts of admixtures employed were so great that no single objective method such as that of rotary viscometry could be used. The following empirical scale was employed:

degree 0 – dry paste, unworkable
1 – paste flows only when vibrated at 50 Hz
2 – paste flows only when the mixing is knocked against
3 – paste flows by gravity
4 – paste flows freely.

The following procedure was chosen in the study of the effects of admixtures because of the wide scope of the experiments envisaged: The combinations of admixtures and their concentrations were determined by the method of mathematical planning of experiments (factor analysis with two factors and random approach) using the Statgraphics™ program. The individual pastes were prepared with the combinations of admixture concentrations thus computed (nodal points). The same approach was used in the study of the simultaneous effects of ground BF slag and silica fume. The values of the paste properties (workability, set point, 4-hour, 24-hour, 28-day strength) for the individual nodal points were evaluated by the Winsurfer™ program. The program produces an equidistant data network from non-equidistant nodal points with the use of interpolating algorithms. This equidistant data network allows a spatial 3D network to be created, for instance that of the dependence of strength on the concentrations of $Na_2CO_3$ and lignosulphonate. Projection of this 3D dependence onto a plane yields a 2D system of isolines. These systems of 2D isolines are then presented as a result of the effects of admixtures on the properties of GF cement pastes in another part of the present study. In this way it was possible to reduce significantly the amount of work necessary for establishing the complex relationships between the effects of the individual admixtures and their combinations.

## RESULTS AND DISCUSSION

The main difference between GF cements and Portland cements is based on the absence of gypsum in the former and its substitution with the system of a sulphonated polyelectrolyte (e.g. lignosulphonate or sulphonated polyphenolate) and a hydrolyzable salt of an alkali metal (such as $K_2CO_3$, $Na_2CO_3$, $Na_2SiO_3$). Sulphonated polyelectrolytes act as efficient setting retarders and simultaneously as plasticizers of Portland cement mortars and concretes, and often reduce their early strength. In Portland cement mortars and concretes, salts of alkali metals mostly accelerate the setting and hardening process, increase early strength and often reduce long-term strength. The effects of the admixtures in pastes (but also in mortars and concretes [3]) of GF cements differ from those in Portland cement mixes, but only on the condition *that both types of admixtures (i.e. the polyelectrolyte and the alkali salt) are present simultaneously*. The effects of admixtures replacing gypsum are complex in nature and cannot be attributed the explicit functions known in the case of Portland cements.

The effects of the $Na_2CO_3$ + sodium lignosulphonate admixture on the rheological properties of GF cement pastes (visual workability) at a low water ratio of $w = 0.25$ is shown in figure 1. The plot demonstrates that at a certain concentration of the admixture (designated ▲ in the diagram) the paste achieves the maximum fluidity and that there exists a plastification optimum. At higher contents of the admixtures the workability again worsens.

The effect of the $Na_2CO_3$ + sodium lignosulphonate system on the setting point (cf. figure 3) of GF pastes is monotonous, without exhibiting any extremes. The time of set can be prolonged either by increasing the content of sodium lignosulphonate while keeping the content of $Na_2CO_3$ constant, or by increasing both contents of $Na_2CO_3$ and sodium lignosulphonate. Very rapidly setting pastes can be prepared with the concentrations of admixtures corresponding to the right-hand bottom corner of figure 2.

Likewise monotonous in the effect of the $Na_2C0_3$ + sodium lignosulphonate system on the strength of hardened GF cement pastes after 4 hours of hydration (figure 3). In this case the strength is explicitly reduced by higher additions of sodium lignosulphonate, while being raised by $Na_2CO_3$ concentrations exceeding about 1.5 %. Very high early strengths can be achieved at very low lignosulphonate and very high $Na_2CO_3$ contents (but at the expense of a very short-term workability).

The effect of the $Na_2CO_3$ + sodium lignosulphonate system on the 24-hour strength (figure 4) is quite well-balanced, showing regions of virtually identical strengths at various contents of $Na_2CO_3$ and sodium lignosulphonate. A sharp decrease of strength occurs at very low $Na_2CO_3$ contents and higher lignosulphonate concentrations (left-hand upper corner of the plot).

The 28-day strengths of hardened GF pastes exhibit a maximum in the central region (figure 5) and a significant loss of strength at a low $Na_2CO_3$ content and a higher lignosulphonate concentration.

The relationships in question allow the concentration of the $Na_2CO_3$ + lignosulphonate admixtures to be selected so as to make the properties of the paste meet the given performance requirements. For the system in question, a compromise between the individual properties resulted in the selection of the optimum corresponding to 0.85 % sodium lignosulphonate + 1.7 % $Na_2CO_3$.

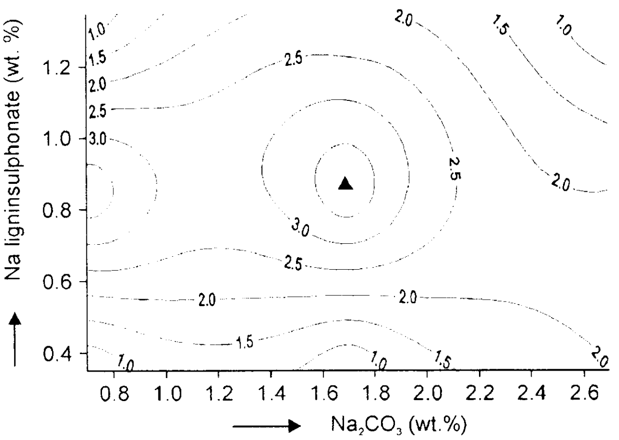


Figure 1. Visual workability of pastes with $w$ = 0.25 vs. $Na_2CO_3$ and sodium lignosulphonate concentration, GF cement with specific surface area of 560 $m^2$ $kg^{-1}$. The symbol ▲ designates the region of maximum paste fluidization.

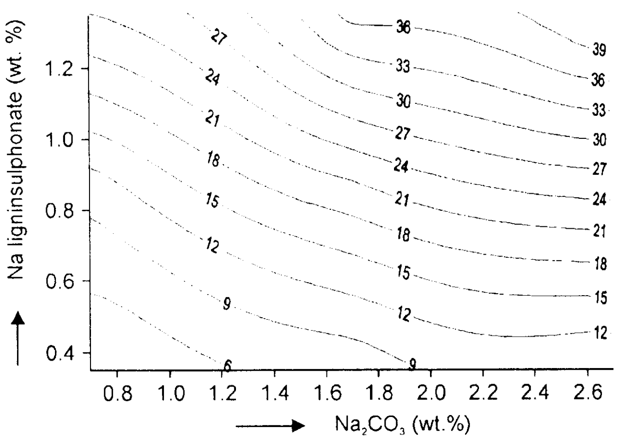


Figure 2. Time of set (minutes) of paste with $w$ = 0.25 vs. $Na_2CO_3$ and sodium lignosulphonate concentration, GF cement with specific surface area of 560 $m^2$ $kg^{-1}$.

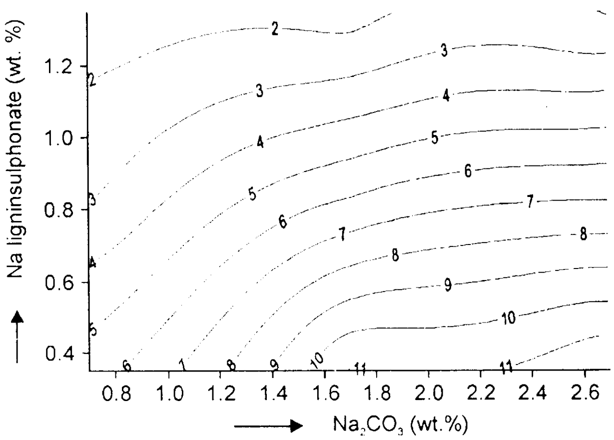


Figure 3. Compressive strength (MPa) after 4 hours for GF cement paste with $w$ = 0.25 vs. $Na_2CO_3$ and sodium lignosulphonate concentration, GF cement with specific surface area of 560 $m^2$ $kg^{-1}$.

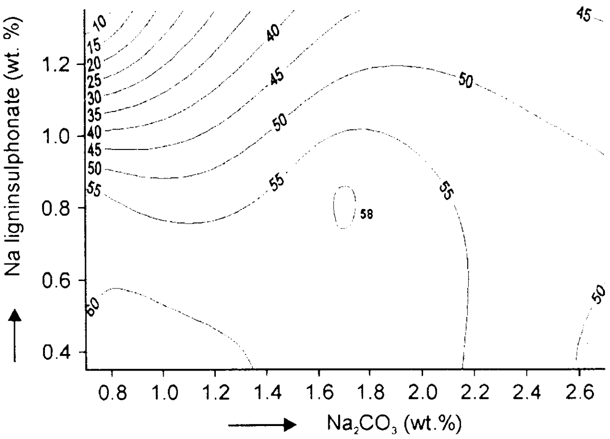


Figure 4. Compressive strength (MPa) after 24 hours for GF cement paste with $w$ = 0.25 vs. $Na_2CO_3$ and sodium lignosulphonate concentration, GF cement with specific surface area of 560 $m^2$ $kg^{-1}$.

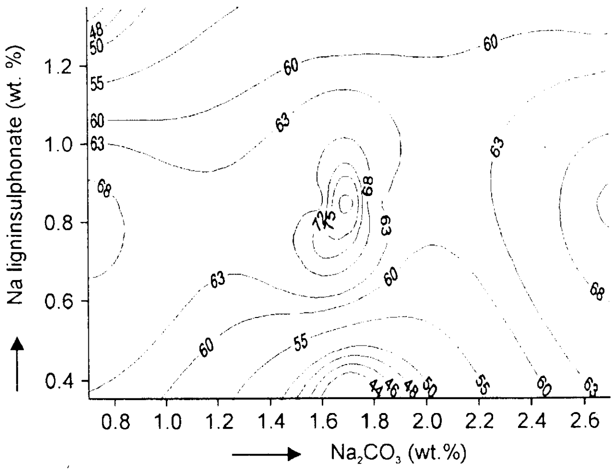


Figure 5. Compressive strength (MPa) after 28 days for GF cement paste with $w$ = 0.25 vs. $Na_2CO_3$ and sodium lignosulphonate concentration, GF cement with specific surface area of 560 $m^2$ $kg^{-1}$.

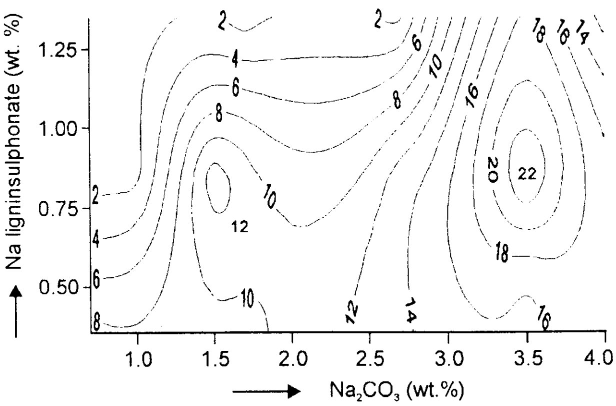


Figure 6. Compressive strength (MPa) after 4 hours for GF cement paste with 5 % slag and $w$ = 0.25 vs. $Na_2CO_3$ and sodium lignosulphonate concentration, GF cement with specific surface area of 570 $m^2$ $kg^{-1}$.

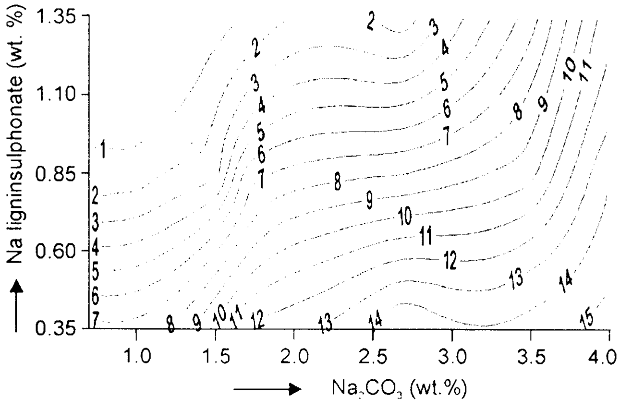


Figure 7. Compressive strength (MPa) after 4 hours for GF cement paste with 10 % slag and $w$ = 0.25 vs. $Na_2CO_3$ and sodium lignosulphonate concentration, GF cement with specific surface area of 550 $m^2$ $kg^{-1}$.

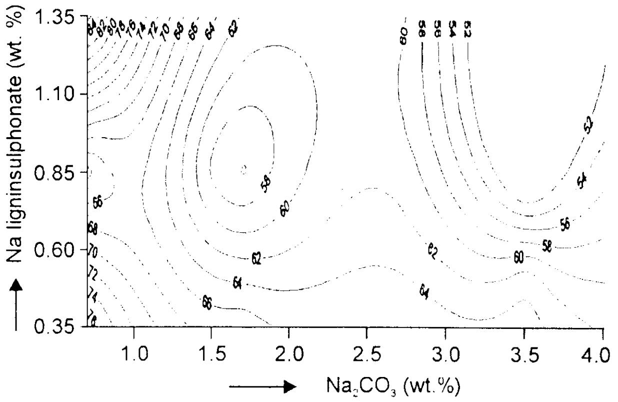


Figure 10. Compressive strength (MPa) after 28 days for GF cement paste with 5 % slag and $w$ = 0.25 vs. $Na_2CO_3$ and sodium lignosulphonate concentration, GF cement with specific surface area of 570 $m^2$ $kg^{-1}$.

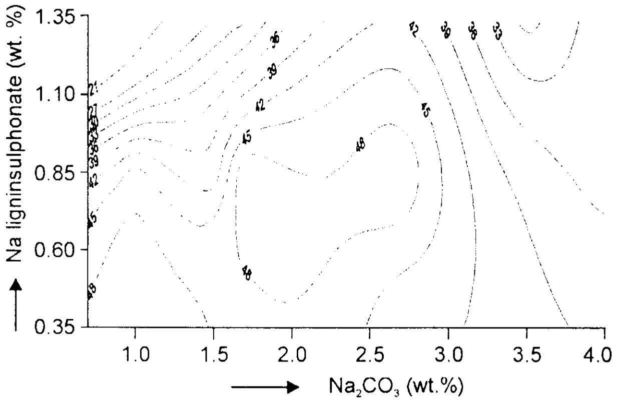


Figure 8. Compressive strength (MPa) after 24 hours for GF cement paste with 5 % slag and $w$ = 0.25 vs. $Na_2CO_3$ and sodium lignosulphonate concentration, GF cement with specific surface area of 570 $m^2$ $kg^{-1}$.

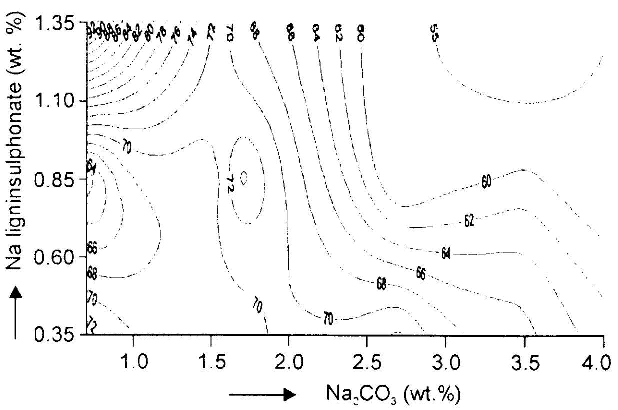


Figure 11. Compressive strength (MPa) after 28 days for GF cement paste with 10 % slag and $w$ = 0.25 vs. $Na_2CO_3$ and sodium lignosulphonate concentration, GF cement with specific surface area of 550 $m^2$ $kg^{-1}$.

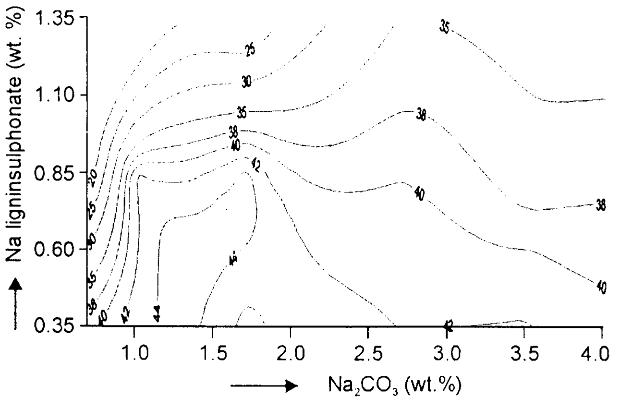


Figure 9. Compressive strength (MPa) after 24 hours for GF cement paste with 10 % slag and $w$ = 0.25 vs. $Na_2CO_3$ and sodium lignosulphonate concentration, GF cement with specific surface area of 550 $m^2$ $kg^{-1}$.

The properties of GF cements are likewise influenced by admixtures exhibiting latent hydraulic properties, in particular by ground granulated blast-furnace slag.

The effect of the system $Na_2CO_3$ + sodium lignosulphonate on the strength of hardened pastes with GF cement containing 5 % slag after 4 hours is characterized by a maximum of strength (figure 6); with 10 % of slag (figure 7), the effect of the $Na_2CO_3$ + sodium lignosulphonate system is monotonous in character, similarly to the single-component GF cement.

The influence of the system $Na_2CO_3$ + sodium lignosulphonate on the strength of hardened pastes of GF cements containing 5 and 10 % BF slag after 24 hours (figures 8, 9) is analogous to that on single-component GF cement. There is again a marked decrease in strength at low $Na_2CO_3$ contents and high sodium lignosulphonate concentrations.

The effect of the $Na_2CO_3$ and sodium lignosulphonate admixture on the 28-day strength (figures 10, 11) is relatively small except for the region with low $Na_2CO_3$ and high sodium lignosulphonate contents where high strengths were achieved (in excess of 90 - 100 MPa, the left-hand top corner). However, this combination yields very low early strengths.

With respect to 4-hour strength of GF cement pastes with 5 and 10 % slag, the optimum concentrations amounted to 0.8 % lignosulphonate and 3.5 % $Na_2CO_3$, while the highest 24-hour strengths resulted from additions of 0.8 % lignosulphonate and 2.5 % $Na_2CO_3$.

Silica fume (extremely fine-grained $SiO_2$) was another substance whose effect on the GF cement was studied. It was found to improve workability, allowing the water ratio to be further reduced (down to the region of $w$ = 0.20 - 0.22). In contrast to Portland cement, the optimum additions were found to be lower, over the range of 2 - 4 %, as higher concentrations were responsible for impaired rheological properties. This was probably due to the coarser particle size of standard Portland cements which allows larger amounts of the fine silica fume to be accommodated in the free spaces.

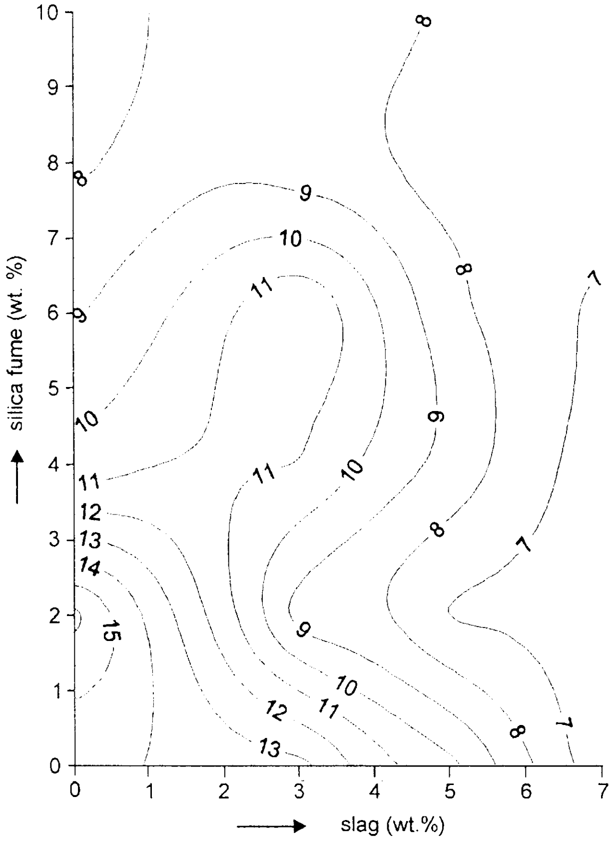


Figure 12. Compressive strength (MPa) after 4 hours for GF cement paste with $w$ = 0.25 vs. content of ground BF Vítkovice slag and silica fume Elkem, GF cement ground for 5 hours (specific surface area 530-550 $m^2$ $kg^{-1}$), 2 % $Na_2CO_3$ + 0.8 % sodium lignosulphonate.

The relationships found for the effect of silica fume and granulated BF slag on the properties of GF cement pastes are plotted in figures 12 and 13. The data were used to derive the optimum concentrations for the highest early strengths, namely up to 2 % silica fume and up to 1 % BF slag. The maximum 28-day strengths were obtained with 6 % or 2 % silica fume and 7 % slag. The optimum workability was achieved with 2 % silica fume.

It may be concluded that the effect of the admixtures on the properties of GF cement pastes is much more sensitive than that of gypsum and other additives on the properties of single-component Portland cement. There is a new phenomenon of the existence of optimum concentrations of the admixtures, which lead to a significant intensification of their effects, i.e. to a synergy.

The relationships described for the pastes in question and for the given clinker hold qualitatively also with other clinkers, as well as for mortars and concretes [3]. The sensitivity of GF cement mortars and concretes to changes in the concentration of admixtures is smaller than that of the pastes. The positions of optimum concentrations of admixtures for mortars and concretes differ from those of pastes and have to be determined experimentally [3].

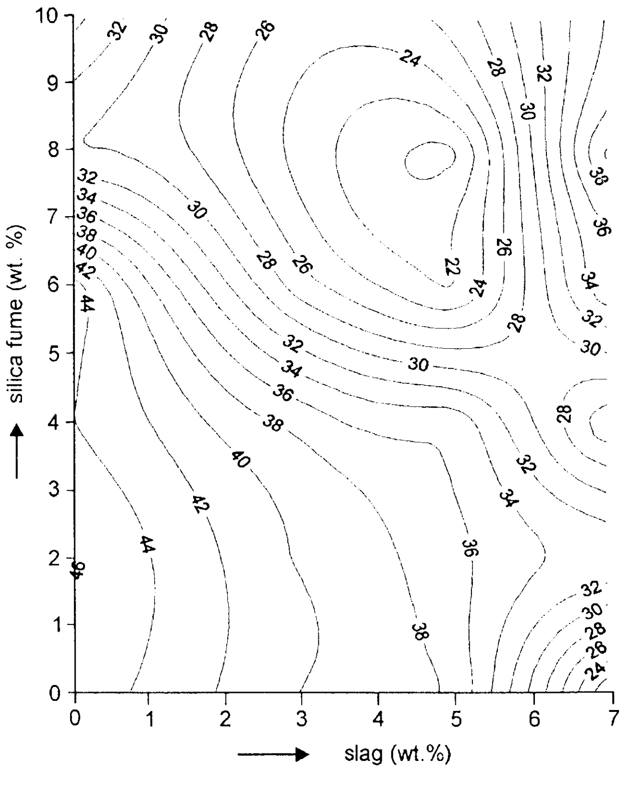


Figure 13. Compressive strength (MPa) after 24 hours for GF cement paste with $w$ = 0.25 vs. content of ground BF Vítkovice slag and silica fume Elkem, GF cement ground for 5 hours (specific surface area 530-580 $m^2$ $kg^{-1}$), 2.5 % $Na_2CO_3$ + 0.8% sodium lignosulphonate.

## CONCLUSION

1. The dependence of the properties of gypsum-free cement pastes on the amount of admixtures of $Na_2CO_3$, sodium lignosulphonate, ground granulated blast-furnace slag and silica fume was determined by the mathematical experiment planning method. The relationships differ from the effect of the admixtures on pastes of Portland cement and were found to exhibit local extreme values.

2. On the basis of a compromise between the values of 4-hour, 24-hour and 28-day strengths, workability and set point, the optimum of 0.85 % sodium lignosulphonate + 1.7 % $Na_2CO_3$ was established.

3. With GF cements containing 5 and 10 % ground BF slag, the optimum concentrations of admixtures were found to be 0.8 % sodium lignosulphonate and 3.5 % $Na_2CO_3$ for 4-hour strength, and 0.8 % lignosulphonate and 2.5 % $Na_2CO_3$ for 24-hour strength.

4. In contrast to conventional Portland cement, the optimum addition of silica fume is lower, namely over the range of 2 to 4 %. The maximum early strength for GF cements containing both slag and silica fume was exhibited with 2 % silica fume and up to 1 % slag. The maximum 28-day strengths were achieved with 6 % or 2 % silica fume and 7 % slag. The optimum workability was obtained with 2 % silica fume.

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## VLIV PŘÍSAD $Na_2CO_3$, LIGNINSULFONANU SODNÉHO, VYSOKOPECNÍ GRANULOVANÉ STRUSKY A ÚLETU $SiO_2$ NA VLASTNOSTI BEZSÁDROVCOVÝCH PORTLANDSKÝCH CEMENTŮ

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Pomocí matematického plánování experimentů byly zjištěny závislosti vlivu přísad $Na_2CO_3$, ligninsulfonanu sodného, mleté vysokopecní granulované strusky a úletu $SiO_2$ na vlastnosti kaší bezsádrovcových portlandských cementů. Tyto závislosti jsou odlišné od působení uvedených přísad na kaše portlandského cementu a existují na nich lokální extrémy. Závislosti byly vyjádřeny pomocí soustav izočar. Pro kaše GF cementu bylo nalezeno na základě kompromisu mezi hodnotami 4 a 24 hodinových, 28 denních pevností, zpracovatelností a počátkem tuhnutí optimum přísad: 0.85 % ligninsulfonan sodný + 1.7 % $Na_2CO_3$. U GF cementů s obsahem strusky 5 a 10 % bylo z hlediska pevností po 4 hodinách nalezeno optimum koncentrací 0.8 % ligninsulfonanu a 3.5 % $Na_2CO_3$, pro pevnosti po 24 hodinách pak 0.8 % ligninsulfonanu a 2.5 % $Na_2CO_3$. Na rozdíl od portlandského cementu se optimum přísady úletu $SiO_2$ projevuje při nižších koncentracích a to do hodnot 2-4 %. Při současném obsahu strusky a úletu $SiO_2$ byla nalezena optimální koncentrace pro maximální počáteční pevnosti a to v oblasti do 2 % úletu $SiO_2$ současně s obsahem strusky do 1 %. Pro maximální 28 denní pevnosti bylo nalezeno optimum s 6 % úletu $SiO_2$ nebo s 2 % úletu $SiO_2$ a 7 % strusky.