

PROPERTIES OF GYPSUM-FREE PORTLAND CEMENT PASTES WITH A LOW WATER-TO-CEMENT RATIO

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Gypsum-free Portland cement is a hydraulic binder based on ground Portland clinker in which the controlling effect of gypsum has been replaced by a synergistically acting mixture of an anion-active tenside (usually a sulphonated polyelectrolyte) and an inorganic salt (usually Na_2CO_3). The properties of pastes of the cements depend on concentrations of the additives replacing the effects of gypsum. In the dependence of paste viscosity (at a low water-to-cement ratio) on the concentration of additives (e.g. lignin sulphonate and soda) there exists an optimum where the suspension exhibits minimum viscosity. The presence of gypsum in the system ground clinker-sulphonated electrolyte-salt of an alkali metal- H_2O leads to a worsening of rheological properties where an initial liquefaction is followed by a rapid increase in paste viscosity. The rheological properties of the pastes are also affected by the particle size distribution where there holds a direct relationship between viscosity and deviation from the ideal Fuller curve. This effect is demonstrated by differences in workability (viscosity) of pastes of GF cements prepared in various types of grinding equipment. The time course of strength development of the hardened system ground clinker-sulphonated polyelectrolyte-alkali metal salt- H_2O depends on the type of the sulphonated electrolyte. Distinctly higher early strengths were achieved with the system sulphonated polyphenolate- Na_2CO_3 compared to the system lignin sulphonate- Na_2CO_3 . The effect can be explained by a higher pH of the aqueous solutions of the former system.

INTRODUCTION

Gypsum-free Portland cements (hereafter GF cements) are based on the idea published by Rebinder [1] who in 1957 suggested that gypsum in Portland cement could possibly be replaced with the system calcium lignosulphonate - K_2CO_3 . The principle was further elaborated by Brunauer [2] who achieved excellent results with pastes showing very low water ratios (of down to 0.20). The results of experiments carried out in the Czech Republic [3,4] resulted in the development of GF Portland cements which have been commercially produced since 1989 and found application in special building construction works.

GF cement can be described as a system comprising ground Portland cement clinker (specific surface area 350 - 700 $\text{m}^2 \text{kg}^{-1}$), an anion-active tenside (such as lignin sulphonate, sulphonated lignin, sulphonated polyphenolate), a hydrolyzable salt of an alkali metal (carbonate, hydrogen carbonate, silicate). The difference between GF and standard Portland cement lies only in the grinding (absence of gypsum, larger surface area, use of a grinding aid) and in replacement of gypsum with another setting regulator. The properties of GF cements were described in earlier publications, e.g. [5,6].

The present study deals with the system "ground Portland cement clinker - sulphonated polyphenolate (or lignin sulphonate) - alkali metal salt - H_2O ".

EXPERIMENTAL PART

In the experiments, use was made of clinker from commercial Portland cement production by the dry process. The clinker composition was as follows (wt. %): CaO 66.1, SiO_2 21.4, Al_2O_3 5.6, Fe_2O_3 2.3, MgO 1.85, $\text{Na}_2\text{O}+\text{K}_2\text{O}$ 0.85, CaO 1.0, loss of ignition 0.13. The pre-crushed clinker was ground in a ball mill (100-liter capacity) in the presence of a liquid grinding aid consisting for the most part of alkanolamine of dodecylbenzenesulphonic acid. The specific surface area was 450 - 600 $\text{m}^2 \text{kg}^{-1}$. In additional experiments, samples of GF cements were taken during their grinding in industrial-scale equipment (vibration mill, ball mill with classifier, etc.). The particle size distribution of the GF cements of both laboratory and commercial origin was determined by the Analysette 22TM laser grain size meter (Fritsch). The data obtained was used in calculating the deviations of granulometric composition from Fuller's idealized particle size distribution curve. The pastes were prepared with additions of Na_2CO_3 , Na_2SiO_3 or NaHCO_3 , the Kortan FMTM anion-active tenside (sodium-ferric sulphonated polyphenolate) or commercial sodium lignin sulphonate. In some instances, also gypsum in amounts of up to 5 wt.% of the cement was added. For the sake of comparison, Portland cement of classes PC 42.5 and 52.5, made from clinker stemming from the same locality and ground to specific surface areas of 350 and

550 m² kg⁻¹ respectively, was also used. The GF cement pastes were prepared with $w = 0.22 - 0.30$, the Portland cement ones with $w = 0.60$. The rheological properties of the pastes were determined by the coaxial rotary viscometer which measured their viscosity and rheological characteristics (rheological hysteresis loops). The strength of hardened pastes was studied over the range of 1 hour to 180-270 days after hardening. The specimens 2 × 2 × 2 cm in size were kept for 24 hours in saturated water vapour (100 % relative humidity), then in water at 20 °C, and after 28 days in air at a 35 % to 45 % relative humidity. Another series of experiments were concerned with preparation of solutions of additives replacing gypsum over the concentration ranges corresponding to those used in the processing of GF cement. The pH of the solutions was measured at +20 °C.

RESULTS AND DISCUSSION

The system "sulphonated polyelectrolyte (lignin sulphonate, polyphenolate)-alkali carbonate" acts as a powerful plasticizing (liquefying) agent in aqueous suspensions of ground Portland cement clinker. The effect of the two additives is given by their joint influence (synergy), as lignin sulphonate, polyphenolate and alkali carbonate alone cause the suspensions to set very rapidly without bringing about any marked plasticizing. The significant plasticizing effect of the synergic system polyelectrolyte- carbonate allows pastes (and also mortars and concretes) with a much lower water-to-cement ratio to be prepared than in the case of Portland cement pastes (figure 1). The synergic system likewise favourably affects the rheological character of the pastes (figure 2). Portland cement pastes are typical non-Newtonian materials with a flow limit and an inner structure (given by the area of the rheological hysteresis curve). The GF cement pastes (with the synergic additives) are virtually Newtonian fluids with a minimum flow limit and a minimum area of the hysteresis loop. This effect is then projected into a favourable workability of the pastes (and mortars and concretes) at low water ratios.

The rheological properties of ground clinker suspensions depend on the concentration of the polyelectrolyte and the alkali carbonate. Figure 3 shows the course of curves of identical viscosity in terms of concentrations of sodium lignin sulphonate and Na₂CO₃ for GF cement with a specific surface area of 500 m² kg⁻¹. Similar relationships were established for sulphonated polyphenolate and K₂CO₃. The relationships show that there exists an optimum concentration of additives at which the system exhibits a minimum viscosity. This optimum concentration depends on the type of the polyelectrolyte, on the cation of the

carbonate, and on the specific surface area of the cement. This concentration was usually in the respective ranges of 0.6 to 0.8 % of the polyelectrolyte, and 0.8 to 1.0 % of the alkali carbonate.

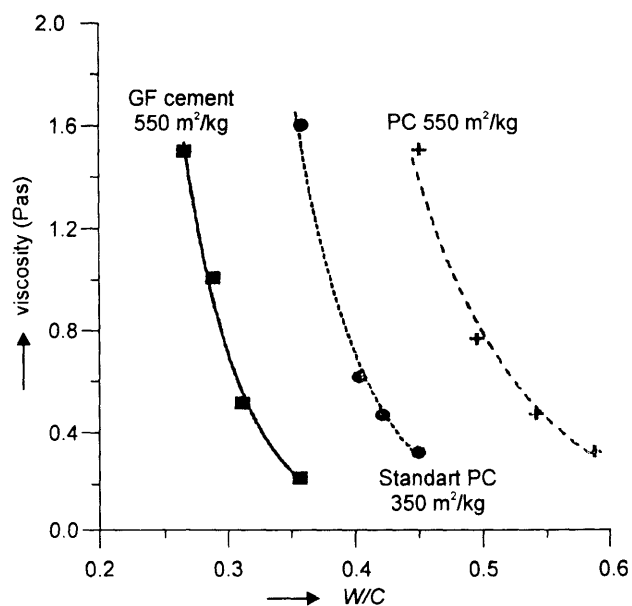


Figure 1. Viscosity of cement suspensions in terms of water-to-cement ratio (GF cement with lignin sulphonate + Na₂CO₃).

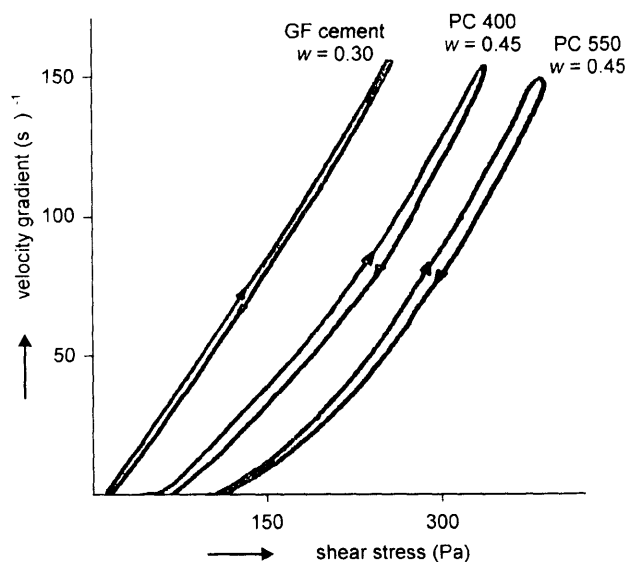


Figure 2. Rheological hysteresis loops of GF cement suspensions and of standard Portland cement suspensions.

The rheological properties of aqueous suspensions of ground clinker with additions of the polyelectrolyte and alkali carbonate are virtually constant (as is their viscosity) prior to the onset of setting (figure 4). However, a different time course of viscosity is exhibited

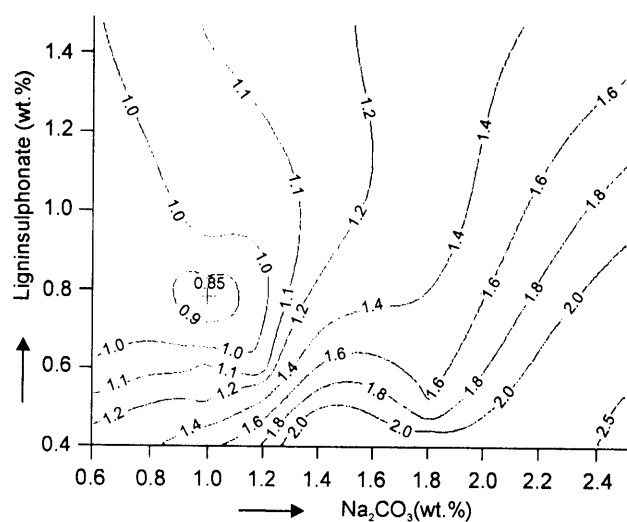


Figure 3. Viscosity of ground clinker ($550 \text{ m}^2 \text{ kg}^{-1}$) suspensions vs. concentration of lignin sulphonate and Na_2CO_3 , $w = 0.26$

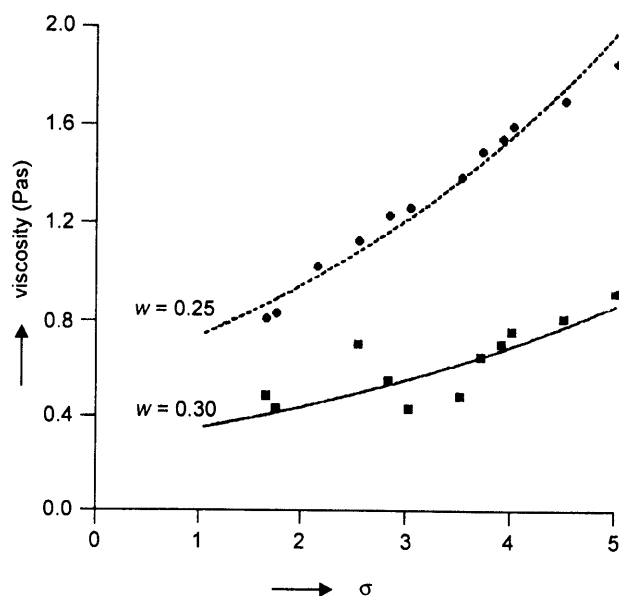


Figure 5. Viscosity of GF cement suspensions (with lignin sulphonate and Na_2CO_3) vs. deviation σ from idealized Fuller's curve of particle size distribution.

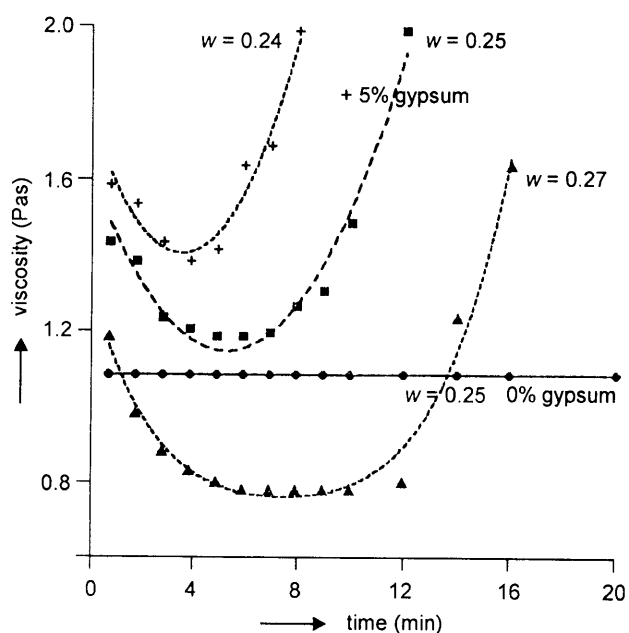


Figure 4. Time course of viscosity of ground clinker suspensions with additions of lignin sulphonate, Na_2CO_3 and 0 % and 5 % of gypsum.

by suspensions containing the polyelectrolyte and carbonate to which gypsum has been added. The suspensions show a distinct time minimum of viscosity where within several minutes the viscosity increases abruptly (a free-flowing paste turns into a ill-formable one). The results indicate that the presence of gypsum in GF cements is undesirable and inhibits attainment of low water-to-cement ratios. The addition of gypsum to GF

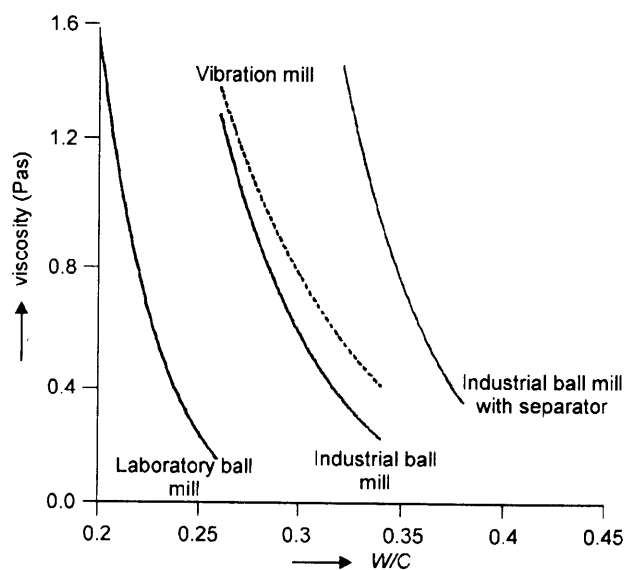


Figure 6. Viscosity of GF cement suspensions vs. water-to-cement ratio for GF cements ground in various types of mills.

cements obviously leads to a destruction of the whole regulating system (precipitation of the carbonate, formation of insoluble calcium forms of the polyelectrolyte by the effect of Ca^{2+} ions from gypsum).

The synergic effect of the polyelectrolyte and the alkali salt has not yet been satisfactorily explained. It may be assumed that the salt strengthens the linear part of the double layer on clinker particles, thus raising the

zeta potential value. The effect was actually found in the studies by Collepardi [7]. It is still unclear why the synergic effect is restricted to hydrolyzable alkali salts with CO_3^{2-} , HCO_3^- and SiO_4^{2-} anions. For example, the system lignin sulphonate-NaCl does not have any plasticizing effects on ground clinker suspensions. Additional experiments are needed in this respect.

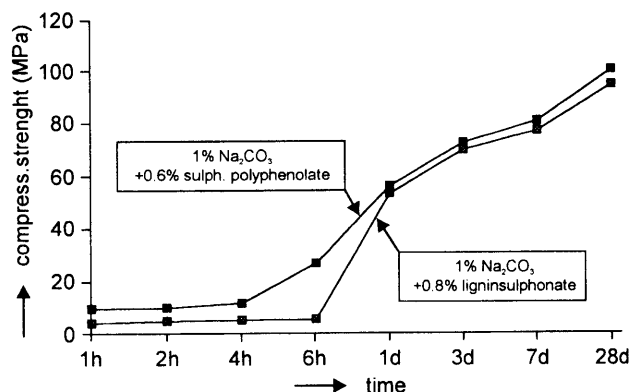


Figure 7. Typical time course of strength of GF cement pastes at $w = 0.25$.

The rheological properties of pastes (and also mortars and concretes) of GF cements depend on cement grain size distribution. Figure 5 shows the viscosity of GF cement pastes vs. deviation σ from Fuller's curve representing idealized densest particle size distribution. The curves demonstrate clearly that viscosity increases, and workability at low water ratios decreases with increasing deviation from the idealized particle size distribution (a system of spheres). The relationship becomes steeper with decreasing water-to-cement ratio. The effect was also found to play its role in the properties of GF cements prepared by grinding in various types of mills. Figure 6 shows the dependence of viscosity of pastes (containing the same concentrations of lignin sulphonate and Na_2CO_3) for GF cements ground in various laboratory and full-scale industrial mills. The workability of pastes (mortars, concretes) of GF cements at low water ratios can thus be also affected by the choice of the grinding equipment (by influencing the particle size distribution).

The additives replacing the effects of gypsum influence the course of the setting and hardening processes, and thus also the strength. Figure 7 shows a typical time course of GF paste strength development with the use of Na_2CO_3 + lignin sulphonate (or sulphonated polyphenol) regulating systems. The curves demonstrate that the initial period of relatively low strength is followed by a period of very fast strength increments. A distinct difference in the initial period exists between the effects of lignin sulphonate and sulphonated polyphenolate additives. The Na_2CO_3 -sulpho-

nated polyphenolate combination gives substantially higher initial strength values (within 4 to 8 hours, the difference can amount to as much as 20 MPa). This effect is independent of the type of lignin sulphonate employed and also applies to GF cements prepared from different clinkers [8]. The phenomenon can be explained by different effects of the solutions of Na_2CO_3 + lignin sulphonate and Na_2CO_3 + sulphonated polyphenolate on the course of hydration of GF cements. The solutions may have different physico-chemical properties. Figures 8 and 9 show the respective dependencies of iso- pH lines

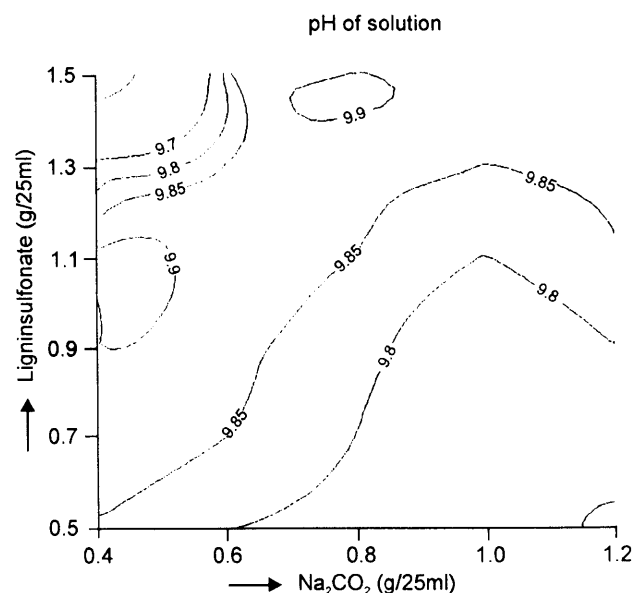


Figure 8. pH of the regulating solutions vs. concentration of lignin sulphonate and Na_2CO_3 .

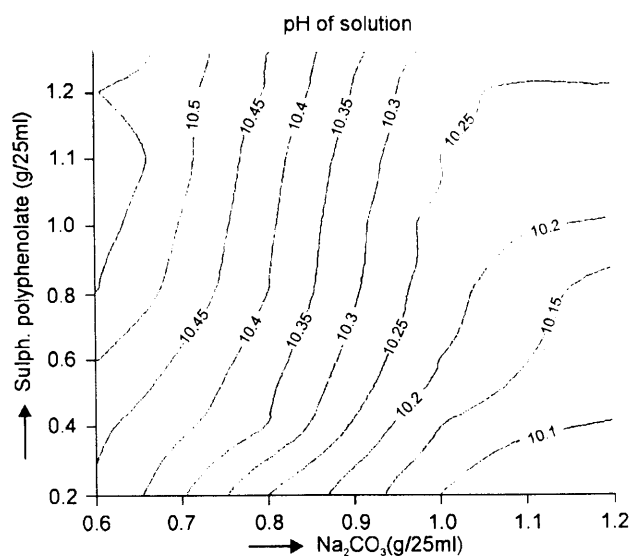


Figure 9. pH of the regulating solutions vs. concentration of sulphonated polyphenolate and Na_2CO_3 .

on the concentration of sodium lignin sulphonate and sodium-ferric polyphenolate in mixture with Na_2CO_3 . The relationship indicates that within the concentration range utilized with GF cements, the two systems form solutions whose pH changes very little with concentration. The only difference between the two system was in the pH value which was higher in the system Na_2CO_3 -sulphonated polyphenolate. The higher pH of the solutions replacing gypsum may be responsible for the higher early strength exhibited by the system Na_2CO_3 -sulphonated polyphenolate as compared to the system Na_2CO_3 -lignin sulphonate, as a result of a stronger alkaline activation in the suspension of ground clinker.

CONCLUSIONS

1. The system ground clinker-sulphonated polyelectrolyte-alkali metal salt- H_2O is qualitatively different from the system ground clinker-gypsum- H_2O .
2. The rheological properties of the system ground clinker-sulphonated polyelectrolyte-alkali metal salt- H_2O depend on concentration of the sulphonated polyelectrolyte and that of the alkali metal salt. At a low water-to-cement ratio, the dependence of paste viscosity on the concentration of the additives (e.g. lignin sulphonate and soda) exhibits an optimum at which the suspension has a minimum viscosity. The presence of gypsum in the system brings about worsening of the rheological properties.
3. The rheological properties of suspensions of the system ground clinker-sulphonated polyelectrolyte-alkali metal salt- H_2O depend to a large degree on cement grain size distribution.
4. The time course of strength after setting of the system ground clinker-sulphonated polyelectrolyte-alkali metal salt- H_2O depends on the type of sulphonated polyelectrolyte. Substantially higher early strengths are obtained with the system sulphonated polyphenolate- Na_2CO_3 than with the system sulphonated lignin- Na_2CO_3 . This effect can be explained by the higher pH of the solutions of the former system.

Acknowledgement

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VLASTNOSTI KAŠÍ BEZSÁDROVCOVÉHO PORTLANDSKÉHO CEMENTU S NÍZKÝM VODNÍM SOUČinitelem

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Bezsádrovcový portlandský cement je nízkoporézní hydraulické pojivo založené na mletém slínku portlandského cementu, kde je regulační účinek sádrovce nahrazen synergicky působící směsí anionaktivního tenzidu (obvykle sulfonovaného polyelektrolytu) a hydrolyzovatelné anorganické soli (obvykle Na_2CO_3). Vlastnosti kaší bezsádrovcového portlandského cementu závisí na koncentraci přísad nahrazující působení sádrovce. V závislosti viskozity kaší při nízkém vodním součiniteli na koncentraci přísad (na př. ligninsulfonanu a sody) existuje optimum, kdy suspenze dosahuje minimální viskozity. Přítomnost sádrovce v systému mletý slínek-sulfonovaný polyelektrolyt-sůl alkalického kovu- H_2O vede ke zhoršení reologických vlastností, kdy po počátečním ztekucení dochází k rychlému zvýšení viskozity kaše. Na reologické vlastnosti kaší má také vliv rozdělení velikostí částic, kde existuje přímá souvislost mezi viskozitou a odchylkou od ideální Fullerovy křivky. Tento vliv se projevuje v různé zpracovatelnosti (viskozitě) kaší GF cementů vyrobených na různých mlecích zařízeních. Časový průběh pevnosti po zatvrdnutí systému mletý slínek-sulfonovaný polyelektrolyt-sůl alkalického kovu- H_2O je závislý na typu sulfonovaného polyelektrolytu. Výrazně vyšší počátečních pevností (po 4-8 hodinách) bylo dosaženo u systému sulfonovaný polyfenolát - Na_2CO_3 ve srovnání se systémem ligninsulfonan- Na_2CO_3 . Tento efekt může být vysvětlen vyšším pH roztoků sulfonovaného polyfenolátu- Na_2CO_3 ve srovnání s roztoky ligninsulfonan- Na_2CO_3 .