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RHEOLOGICAL BEHAVIOUR OF THE SYSTEM PORTLAND CLINKER – Na_2CO_3 – SULPHONATED POLYPHENOLATE – H_2O

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The effect of soda and sodium sulphonated polyphenolate (SSP) on the setting of cement based on Portland clinker was investigated by means of the time dependence of consistency established by the penetrometric method. The results were used to determine the length of incubation periods for the hydration of C_3A *and* C_3S *)*. The incubation period of* C_3A *hydration* (t_1) *exhibits a non-zero value only for the reaction of* C_3A *with the solution of SSP and soda. At a suitable addition of SSP, its value increases with increasing soda addition. On the other hand, the incubation period of* C_3S *hydration* (t_2) *decreases with increasing soda additions. The soda addition, at which for a given amount of SSP* $t_1 = t_2$, *then represents the longest attainable time of initial set of the cement. The optimum addition of SSP is very probably that capable of ensuring steric stabilization of the suspension by creating a protective adsorption layer. The time of early set is distinctly reduced by increasing the time and intensity of mixing. The impossibility of maintaining an identical mechanical history of the binding agent during its preparation and forming is probably the main cause of the poor reproducibility of its behaviour observed earlier.*

1. INTRODUCTION

In 1957, Lukyanova et al. [1] reported that gypsum in the classical Portland cement can be replaced by a mixture of sodium lignosulphonate and potash. The binder obtained can be used to prepare cement pastes, mortars an concrete with a very low water-to-cement ratio, attaining much higher strengths that those prepared with classical Portland cement. Brunauer [2] succeeded in increasing substantially the rate of strength growth of such a cement by grinding the clinker to a much higher specific surface area, thus developing a quite new technology of high-strength cements [3]. As already pointed out by Jawed, the new cement has the disadvantage of being "sensitive" to the way of its preparation, incomparably more so than the binding system based on Portland cement. Research has so far been concerned with finding the optimum formula for preparing the new binding system [5, 6, 7], with developing its practical applications, and with elucidating the functions of the additives employed [8, 9, 10].

Whereas the first two problems have been resoved with comparatively good results, there is as yet no satisfactory explanation of the actual effects of the admixtures. Above all, however, there is no exact description of the effect of the admixtures on the time course of setting which would allow this effect to be evaluated quantitatively. Provision of such information was the aim of the present study.

2. EXPERIMENTAL

2.1 Materials

Clinker

Use was made of clinker from the Lochkov cement works (Czech Republic). The sample was ground, without using any grinding aid, to a surface area of 450 $m^2\ kg^{-1}$ (Blaine). The phase composition was calculated after Boque: 73.1% C_3S, 7.8% C_2S, 14.6% C_3A, 2.9% C_4AF, 1.2% C (free lime). The clinker was kept in a sealed polyethylene bag in the desiccator.

C_3A and C_3S

were prepared from pure oxides, contained only 0.2% of free lime and their specific surface area (Blaine) was 300 $m^2\ kg^{-1}$.

Sodium sulphonated phenolate (SSP)

Use was made of a condensation product (trade mark Kortan FM) of the reaction between sulphonated pyrocatechol and formaldehyde whose assumed formula is shown in Fig. 1.

With the use of an UV detector record ($\lambda = 254$ nm) it was found by capillary isotachoforesis (cf. Fig. 2) that the product contains several ion species (see peaks 1, 2, 3, 4). The absolute molecular weight

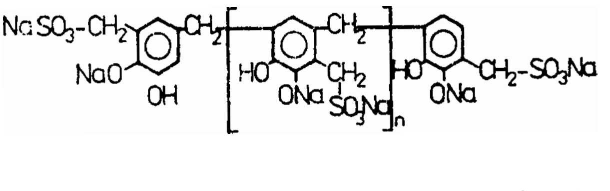

Fig. 1. Assumed formula of the sulphonated polyphenolate.

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*) Use is made of the abbreviated notation where C represents CaO, A...Al_2O_3, H...H_2O, and $\bar{C}$...CO_2.

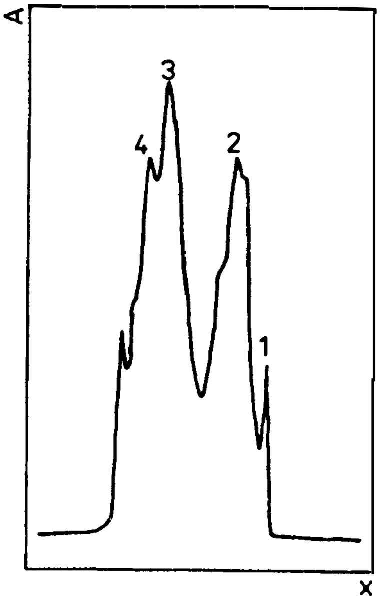

Fig. 2. Isotachoforesis record of SSP (A – absorption in UV region, x – transport rate).

values of the individual fractions were unknown, but the proportion of fractions with a higher molecular weight was obviously larger than that of those with a low molecular weight.. To determine the number and nature of acidic groups, the SSP preparation was converted to the H-form by means of and H-ion exchanger (Dowex). The titration curve of a solution containing 16 g $l^{-1}$of the H-form is shown in Fig. 3. The shares of ionized SO_3H and OH groups are obviously approximately identical so that a half of the phenolic groups remains non-ionized.

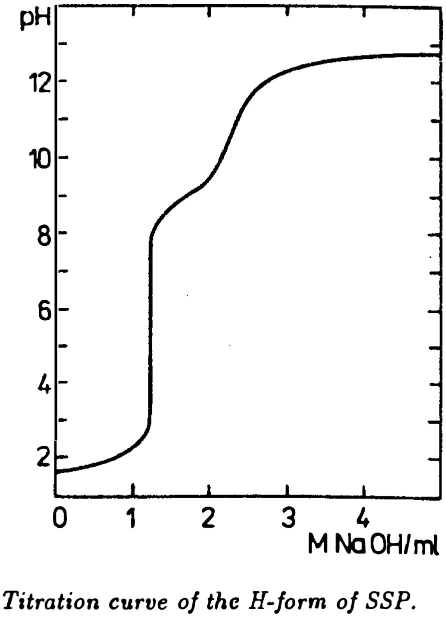

Fig. 3. Titration curve of the H-form of SSP.

2.2 Method

Preparation of the cements

In order to achieve a satisfactory reproducibility of the rheological measurements, a standard way of mixing the components had to be rigorously observed. The clinker (usually 20g), or pure C_3A or C_3S, was always introduced into the amount of aqueous solution of the admixtures corresponding to the water to cement ratio required, that is the ratio of the weight of the solution to the weight of the clinker: (hereafter, the ratio will be designated w). The mixture was mixed for 1 minute and then poured into the vessel for consistency measurement and kept in a sealed vessel at saturated water vapour pressure. The ratio of the admixtures is expressed in % of the clinker weight.

Rheological monitoring of the setting process

The behaviour of a cement can be simulated by the model of transformation of a Newtonian viscous liquid into a Bingham's body. The process can be conveniently followed by means of "consistency" which, according to Bingham [11], is a property of material describing its resistance to a change in shape brought about by an external force. Consistency can be explicitly defined from the relation between the force and the flow of the material. The "mechanical history of the cement paste" has a significant influence on the course of its setting, and the consistency has therefore to be measured on a material which has been motionless from the onset of the process. This condition is met by the method of measuring the resistance offered by the material to impression of a steel needle, described in our earlier study [12]. The stress (σ) required for the needle to penetrate into an intact specimen of the cement paste tested is taken as the measure of consistency. A picture of the solidification process is then provided by the time dependence of this stress, constructed from a sequential series of consistency measurements always carried out in an intact region of the specimen tested.

2.3 The results

2.3.1. The effect of soda and SSP admixtures on the behaviour of cement pastes prepared from pure clinker minerals

The time dependence of the consistency of an aqueous C_3A suspension ($w = 0.4$) is shown by curve *1* in Fig. 4. The reaction of C_3A with water starts immediately after mixing the reactants, that is without any incubation period. In the soda solution (curve *2*), the reaction proceeds in the same way, but the consistency attained is distinctly higher. The SSP admixture brings about liquefaction which, however, disappears within 1 or 2 minutes, while the rate of consistency increase is lower than in the two previous cases.

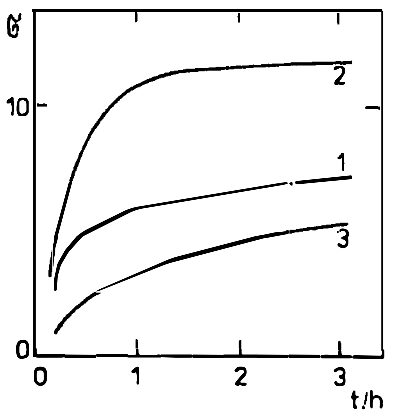

Fig. 4. Time dependence of the consistency of C_3A suspensions ($w = 0.4$) : 1 - $C_3A + H_2O$, 2 - C_3A + 1% Na_2CO_3, 3 - C_3A + 0.4% SSP.

A quite different course is shown by the reaction of C_3A with the soda-SSP solution, as demonstrated by the curves in Fig. 5. A spontaneous increase in consistency takes always place only after a certain incubation period t_1, whose length increases with the amount of soda added, then again decreasing as a result of superfluous soda additions.

The time course of consistency of C_3S suspension is shown in Fig. 6. Mixing with water brings about an immediate reaction which, however, has no effect on the consistency (cf. curve *1*). A spontaneous increase in consistency occurs only after an incubation period, t_2. The SSP admixture prolongs this incubation period (curve *2*), while soda shortens in (curves *3* and *4*). However, in the course of t_2 the consistency of the system containing soda increases slowly, i.e. the hydration of C_3S is not completely stopped. The simultaneous presence of both admixtures (curve *5*) brings the hydration of C_3S to an almost complete standstill, and the sharp bend in this dependence may also be regarded as the end of the incubation period, which we have designated t_2. The value of t_2 decreases with increasing soda additions at a constant addition of SSP.

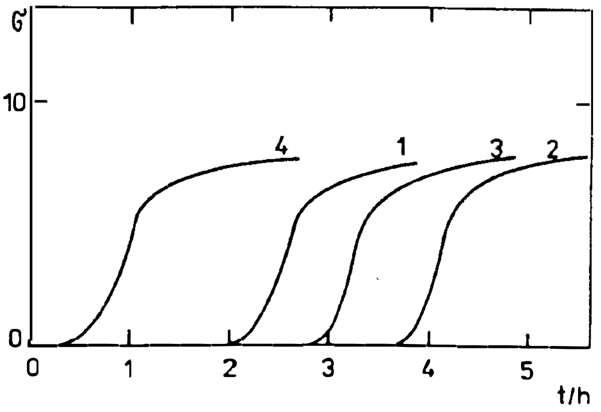

Fig. 5. Time dependence of the consistency of C_3A suspensions ($w = 0.4$) : 1 - C_3A + 0.4% SSP + 0.5% Na_2CO_3, 2 - C_3A + 0.4% SSP + 1% Na_2CO_3, 3 - C_3A + 0.4% SSP + 1.5% Na_2CO_3, 4 - C_3A + 0.4% SSP + 3% Na_2CO_3.

2.3.2 The effect of soda and SSP additions on clinkerffi pastes

The time course of consistency of a clinker suspension in water ($w = 0.25$) is shown by curve *1* in Fig. 7. On comparing the shape of this curve with Figs. 4 through 7, one may reasonably assume that the first

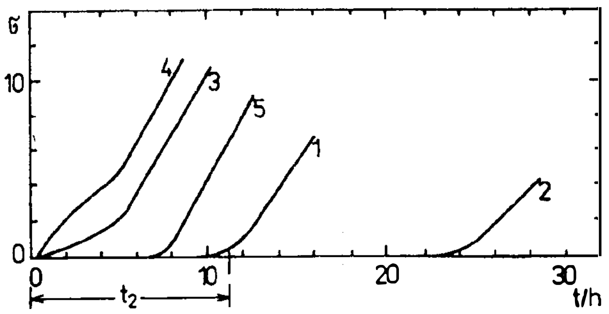

Fig. 6. Time dependence of the consistency of C_3S suspensions ($w = 0.4$) : 1 - $C_3S + H_2O$, 2 - C_3S + 0.4% SSP, 3 - C_3S + 1% Na_2CO_3, 4 - C_3S + 2% Na_2CO_3, 5 - C_3S + 0.4% SSP + 1% Na_2CO_3.

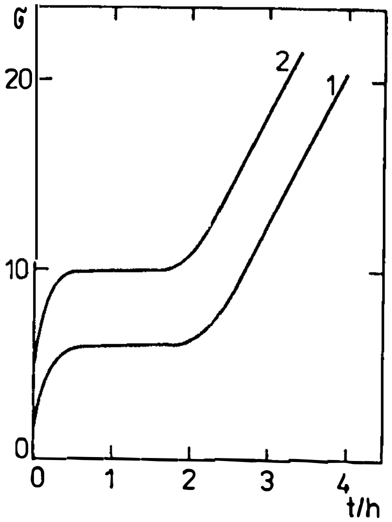

Fig. 7. Time dependence of the consistency of clinker suspensions ($w = 0.4$) : 1 - clinker + H_2O, 2 - clinker + 10% C_3A + H_2O.

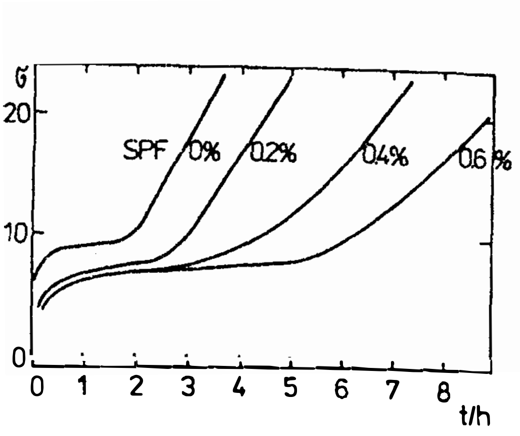

Fig. 8. The effect of SSP addition on the time dependence of the consistency of clinker suspensions (w = 0.25).

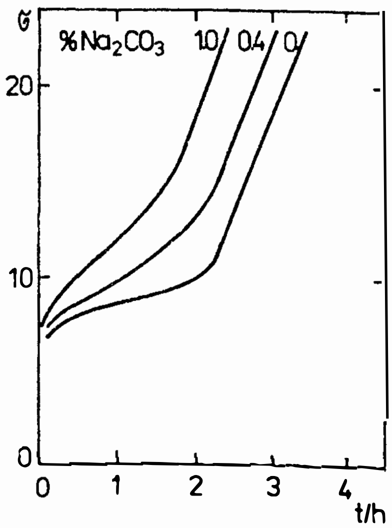

Fig. 9. The effect of soda addition on the time dependence of the consistency of clinker suspension (w = 0.25).

sudden change in consistency is due to hydration of C_3A, and the other to hydration of C_3S. This assumption is also justified by the course of curve *2* in Fig. 7. As demonstrated by the curves in Fig. 8, the length of the incubation period t_2 increases with increasing additions of SSP. The effect of soda additions follows from Fig. 9. The first sudden change in consistency may again be ascribed to the reaction of C_3A, and the subsequent slow rise very probably to the slow reaction of soda with C_3S (compare with curve *4* in Fig. 6). The next bend is probably due to spontaneous hydration of C_3S and corresponds to the end of incubation period t_2.

A quite different character is exhibited by the curves in Fig. 10, showing the time course of consistency for clinker suspensions with variable soda additions and a constant SSP addition. Whereas the incubation period t_1 of C_3A hydration increases with increasing soda content, there is a decrease of incubation period t_2, ascribed to hydration of C_3S. In the case when the soda addition results in an incubation period $t_1 \geq t_2$, the system sets as a result of hydration of both C_3A and C_3S solid phases. The dependence of t_1 and t_2 on soda additions for a given addition of SSP is shown by Fig. 11. It demonstrates that by increasing the soda addition it is possible to prolong the workability stage only up to a certain limit.

Jawed et al. [4] have demonstrated that reproducible results of setting point determination can only be achieved when the admixtures are added in a strictly standard way. Fig. 12 shows that the time

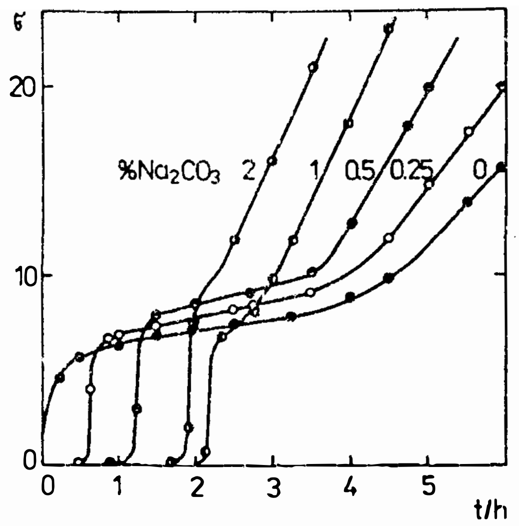

Fig. 10. The effect of soda on the time dependence of the consistency of clinker suspensions with an addition of 0.4% SSP (w = 0.25).

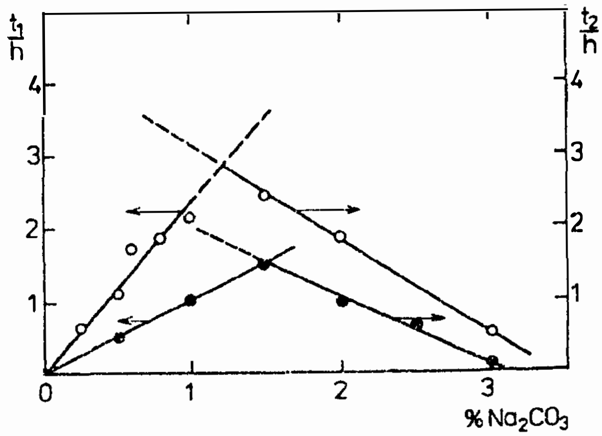

Fig. 11. The dependence of incubation periods t_1 and t_2 on soda additions (w = 0.25) : full rings – 0.3% SSP, empty rings – 0.4% SSP.

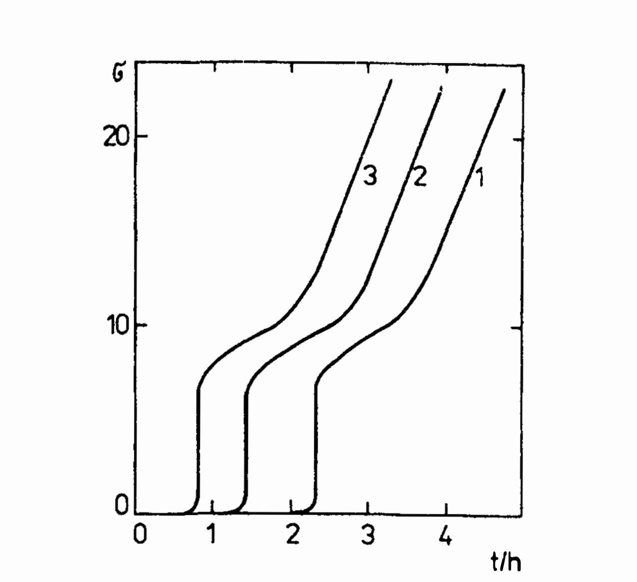

Fig. 12. The effect of the time of mixing on the course of the time dependence of consistency of a suspension containing 0.4% SSP and 0.7% Na_2CO_3 *(w = 0.25) : 1 – mixed for 1 min., 2 – mixed for 2 min., 3 – mixed for 5 min.*

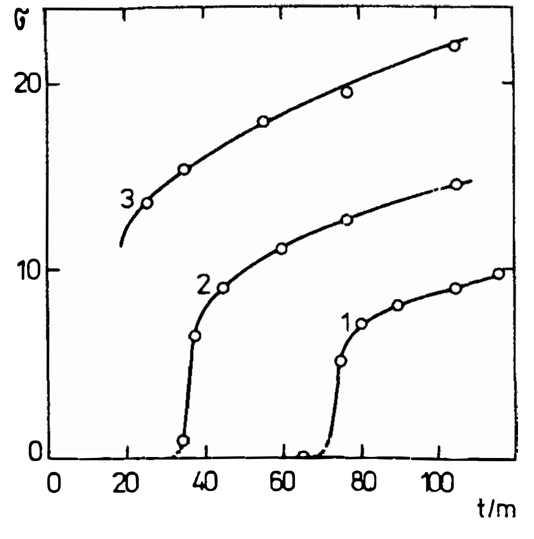

Fig. 13. Time dependence of the consistency of clinker suspension containing 0.4% SSP and 0.5% Na_2CO_3 *(w = 0.25) on the mechanical history (see text).*

of mixing also plays an important role, reducing significantly both t_1 and t_2. Repeated measurements exhibited a considerable dispersion of results, obviously due to the difficulty of keeping the intensity of mixing constant. Moreover, a still greater shortening of t_2 is brought about by mixing the suspension during the incubation period, as demonstrated by the diagram in Fig. 13. This represents the behaviour of a suspension prepared in the standard manner and manner and divided into three equal parts; one was kept motionless and its consistency development measured in terms of time (curve *1*), one was remixed for 1 minute after standing idle for 5 minutes and then its consistency development measured (curve *2*), and one was remixed for 1 minute after standing for 10 minutes motionless, and its further consistency development is shown by curve *3*. The time of initial set, i.e. incubation period t_1, thus depends on the "mechanical history" of the paste over the entire $(0, t_1)$ interval.

3. DISCUSSION

The greates advantage of the new cement is base on its workability at a very low water-to-cement ratio (w=0.25). As shown by Škvára [5], up to the earle set the behaviour of such a clinker suspension is close to that of a Newtonian liquid, which indicates that the dispersed solid particles are mutually repulsed. Most authors [3, 10, 11] assume that this is due to an electrostatic stabilization of the suspension and point out the non-zero zeta potential of the particles as evidence. However, the ionic force of the solution, in which the clinker particles are dispersed, usually exceeds 0.9 and the thickness of electric double layers enclosing the particles is thus smaller than 1 nm [15]. The range of London-Van der Waals forces acting between the particles is thus greater by a factor of ten than the range of electrostatic repulsive forces, and the electrostatic stabilization is therefore ineffective. However, steric stabilization, which is independent of the ionic force, may be effective.

As we found by the isotachoforesis method, SSP contains chain-like molecules with a molecular weight exceeding 2000, which corresponds to the dimensions comparable to the range of Van der Waals forces. Their adsorption on the surface of clinker particles may thus bring about steric stabilization. There is of course the question of anchoring this polymer to the surface of clinker particles. One might easily imagine adsorption of polymeric anions if the clinker particles had a positive charge. Several authors [8, 9, 13] actually established that both C_3A and C_3S particles have a positive charge in the initial stage of hydration, so that the conditions for the existence of steric stabilization are met.

Stabilization of the clinker suspension also ensures its workability till the clinker particles hydrate and new solid phases precipitate, causing the consistency to increase. To extend the time of workability, the hydration of C_3A must therefore take place only after a certain incubation period. This requirement is met by hydration in an aqueous solution of soda and SSP. The effect of soda and SSP admixtures on the setting point of clinker suspensions was studied by Škvára [5]. The author came to the conclusion that at a constant amount of SSP there is always an optimum soda addition corresponding to the longest time of initial set. On taking the time of initial set as being equal to the length of incubation period t_1, this optimum soda addition conforms to the condition $t_1 = t_2$ (cf. Fig. 11).

Similarly to the optimum soda addition, the author assumes the existence of an optimum SSP addition. Our results indicate that this is most probably such an amount of SSP which is necessary for creating a protective layer on the surface of clinker particles (or more correctly, on the surface of all solid phases in the given system), ensuring steric stabilization of the dispersion system. Excess SSP retards and slows down the hydration of both C_3A and C_3S, thus affecting the properties of the binding system in an undesirable way.

The finding that the initial set of the new binding system shows a strong dependence on the mechanical history of its preparation (mixing) may be regarded as significant. Although it is easy to conform to a specified time of mixing and the way of introducing the admixtures, it is virtually impossible to ensure always the same mixing intensity. This fact is probably the main cause of the poor reproducibility of behaviour of the new cement, observed by a number of authors.

The physico-chemical causes of the changes in the rheological behaviour of clinker suspensions, brought about by soda and SSP additions, will be dealt with in a communication which is to follow.

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REOLOGICKÉ CHOVÁNÍ SYSTÉMU PORTLANDSKÝ SLÍNEK – SULFONOVANÝ POLYFENOLÁT – NA_2CO_3 – H_2O

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K vyšetření vlivu přímėsi sody a sulfonovaného polyfenolátu sodného (SPF) na tuhnutí pojiva na bázi portlandského slínku bylo využito časových závislostí konzistence stanovených penetrometrickou metodou. Z nich pak byly odečteny délky inkubačních period hydratace C_3A a C_3S*.

Inkubační perioda hydratace C_3A (t_1) vykazuje nenulovou hodnotu, pouze při reakci C_3A s roztokem sody a SPF. Při vhodné přímėsi SPF její hodnota roste s rostoucí přímėsí sody. Inkubační perioda hydratace C_3S (t_2) s rostoucí přímėsí sody naopak klesá. Přímės sody, pro kterou je při dané přímėsi SPF $t_1 = t_2$, představuje pak nejdelší dosažitelnou dobu počátku tuhnutí pojiva. Optimální přímės SPF je nejspíše taková,. která zajistí vytvořením ochranné adsorpční vrstvy stérickou stabilizaci suspense.

Prodloužením doby a intenzity míchání při přípravě pojiva hodnota počátku tuhnutí výrazně klesá. Nemožnost dodržet stejnou mechanickou historii pojiva při jeho přípravě a tvarování je pravděpodobně hlavní příčinou nereprodukovatelnosti jeho chování, které bylo dříve pozorováno.

Obr. 1. Předpokládaný vzorec sulfonovaného polyfenolátu.

Obr. 2. Záznam izotachoforézy SPF (A – absorpce v UV oblasti, x – rychlost transportu).

Obr. 3. Titrační křivka H-formy SPF.

Obr. 4. Časová závislost konzistence suspenzí C_3A ($w = 0{,}4$) 1 – $C_3A + H_2O$, 2 – C_3A + 1% Na_2CO_3, 3 – C_3A + 0,4% SPF.

Obr. 5. Časová závislost konzistence suspenzí C_3A ($w = 0{,}4$). 1 – C_3A + 0,4% SPF + 0,5 Na_2CO_3, 2 – C_3A + 0,4% SPF + 1% Na_2CO_3, 3 – C_3A + 0,4% SPF + 1,5% Na_2CO_3, 4 – C_3A + 0,4% SPF + 3% Na_2CO_3.

Obr. 6. Časová závislost konzistence suspenzí C_3S ($w = 0{,}4$). 1 – $C_3S + H_2O$, 2 – C_3S + 0,4% SPF, 3 – C_3S + 1% Na_2CO_3 4 – C_3S + 2% Na_2CO_3, 5 – C_3S + 0,4% SPF + 1% Na_2CO_3

Obr. 7. Časová závislost konzistence suspenze slínku ($w = 0{,}25$). 1 – slínek + H_2O, 2 – slínek + 10% C_3A + H_2O

Obr. 8. Vliv přímėsi SPF na časovou závislost konzistence suspenzí slínku ($w = 0{,}25$).

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[*] Použito zkráceného zapisu, kde C znamená CaO, A...Al_2O_3, S...SiO_2, H...H_2O a $\bar{C}$...CO_2.

Obr. 9. Vliv přímėsi sody na časovou závislost konzistence suspenze slínku ($w = 0,25$).

Obr. 10. Vliv přímėsi sody na časovou závislost konzistence suspenzí slínku s přímėsí 0,4% SPF ($w = 0,25$).

Obr. 11. Závislost inkubačních period t_1 a t_2 na přímėsi sody ($w = 0,25$). černé kroužky 0,3% SPF, prázdné kroužky 0,4% SPF.

Obr. 12. Vliv doby míchání na průběh časové závislosti konzistence suspenze slínku obsahující 0,4% SPF a 0,7% Na_2CO_3 ($w = 0,25$). 1 – mícháno 1 min., 2 – mícháno 2 min., 3 – mícháno 5 min.

Obr. 13. Časová závislost konzistence suspenze slínku obsahující 0,4% SPF a 0,5% Na_2CO_3 ($w = 0,25$) na její mechanické historii.

Book Review

PROCEEDINGS OF THE FIRST INTERNATIONAL CONFERENCE ON INTELIGENT MATERIALS. Edited by Toshinori Takagi, Kioshi Takahashi, Masuo Aizawa, Seizo Miyata, Technomic Publishing Company, Inc., 851 New Holland Avenue, Box 3535, Lancaster, Pennsylvania 17604, USA.

The publication summarizes the papers read at the conference held in Japan in March 1992. It represents the cross-section of a new field of materials research dealing with materials exhibiting a combination of several functions (most frequently sensors and processors) and spontaneously reflecting changes in operating conditions by a flexible change in properties. In view of the variety of their chemical composition and the diversity of their applications, the research of these materials is distinctly interdisciplinary in character. It is therefore very difficult to summarize generally the contents of the more than 100 contributions.

The classification of the publication into the individual parts is based partly on the subjective and partly on the functional aspects. Some sections are devoted to problems arising in design and tailoring, manufacture and application of the materials. Altogether eleven quite heterogeneous thematic subjects thus indicate the very fast development of this new branch of materials research.

The reader who is just seeking his way in the field of problems of "intelligent materials" will particularly appreciate the introductory papers devoted to the prospects of these new materials. Also valuable is the information on the research of "intelligent materials" at the French National Centre of Scientific Research (CNRS).

Most of the papers deal with very narrowly specialized subjects, often quite remote for workers in traditional fields of materials research. A great deal of attention is paid to new materials for optics and electronics, application of the materials in pharmacy, and to the possibilities offered to them in the sphere of biomaterials. From the point of view of chemical composition, most of the materials are polymers whose molecular composition can be controlled over a wide range. Inorganic materials are represented to a limited extent, in most cases in combination with organic polymers.

The proceedings of the conference of "intelligent materials" offer new incentives, approaches and concrete solutions of problems associated with the development of materials which, owing to the flexibility of properties and defined responses to stimulations from the environment, may significantly influence the development of many fields of science and technology.

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