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INFLUENCE OF CEMENT TYPE AND ADMIXTURES ON RHEOLOGICAL PROPERTIES OF CEMENT PASTE

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Abstract. The article aims to research the influence of the chemical admixtures on the rheological properties of Portland cement paste and determine their impact on the effectiveness of hydration induction period. Materials used in the study: Portland cement CEM I 42.5 (N and R early strength), limestone Portland cement CEM II/A-LL 42.5 N, plasticizer Centrament N3, the latest generation superplasticizer MC-PowerFlow 3140 and water. Investigations focused on effects of Plasticizer and superplasticizer on water and cement (W/C) ratio and Portland cement paste flow characteristics. Portland cement pastes with the same water-cement ratio with and without chemical admixtures were tested. Investigations were carried out using a Suttard viscometer and rotation viscometer Rheotest NH 4.1 with coaxial cylinders. It was observed that viscosity of Portland cement paste can be controlled by chemical admixtures during the hydration induction period. Investigations of effectiveness of the chemical admixtures on the rheological properties of the Portland cement pastes, comparing it with a control composition of the Portland cement paste were provided in the article. Diagrams show changes of the viscosity of the Portland cement pastes depending on the type and amount of the used chemical admixtures. Obtained results were compared with the same consistence without admixtures. After making the regressive analysis of research results of Portland cement paste with and without chemical admixtures, empirical equations were produced.

Keywords: Portland cement paste, chemical admixtures, viscosity, plasticizer, superplasticizer, rheological properties, rotational viscometer.

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Introduction

The new generation of concrete is very sensitive to production conditions: ambient temperature, mixing parameters, water quality and others. Sometimes, efforts to produce a high quality product result in failure. For this reason, it is important to ensure the stability and characteristics of the mixture: to assess the effects of admixtures on the rheological properties of cement paste, select the composition of mixtures, which would assuredly regulate paste rheology control at nanostructural level and the formation of the initial cement hydration period. Using various modifiers, it is possible to achieve the desired characteristics of cement pastes (Ragaišytė *et al.* 2012).

Cement pastes are complex dispersion systems having considerable specific surfaces where complex time-related hydration reactions take place. The structure of such a system mainly depends on the water-to-cement ratio, ranging from 0.3 to 1.0, depending on the literature source (Gonet *et al.* 2004).

Cement paste is not a homogeneous fluid and is itself composed of particles (cement grains) in a liquid (water).

Because cement paste on a macroscopic scale flows as a liquid, equation as for liquid is applicable.

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If a shear force is applied to a liquid, a velocity gradient is induced in the liquid. The proportionality factor between the force and the gradient is called viscosity.

Pastes rheological properties are influenced by the free water content in them (chemically or physically bound water is not affected). Over time, the water in the bound form is changing. The mineral matrix hydration leads to increase chemically and physically bound water content and a proportional decrease in the quantity of free water (Skripkiūnas 2007).

At the beginning of the hydration process of cement paste and before the induction period (duration of the period amounts to 15–20 min), the cement particles are unchanged. At this early period of the solution saturated with Na^+, K^+, Ca^{2+}, OH^-, SO_2^{2-} ions, reactions between formed hydrates bear cement particles. Once the induction period starts, it lasts for several hours. In the supersaturated solution, portlandite ($Ca(OH)_2$) crystallizes and interaction between SO_4^{2-} ions and C_3A as well as formed ettringite crystal whiskers film which slows the rapid coagulation of C_3A structure formation and allows cement to bind at the right speed (≥60 min). After the induction period, the crystallisation of calcium hydrate and accelerated hydration of alite results in a considerable growth of viscosity of the paste. The rheological properties of the cement paste gradually change with time (Eisinas, Baltakys 2009).

In recent years, the new generation of plasticizer admixtures – dispersants-deflocculant (polycarboxylate esters PCE) are widely used to regulate the rheological properties of paste. As new deflocculant manufacturers and researchers (Hommer, Wutz 2005) explain PCE deflocculant, the polymer backbone and side chain lengths depends on the nano scale and size 3–20 nm (main chain) and 3–40 nm (side chains). In the system of water and cement they case a double effect of dispersion – the spatial and electrostatic (Fig. 1). Their use prevents the cement particles from sticking together, even when exposed to the original cement hydrates.

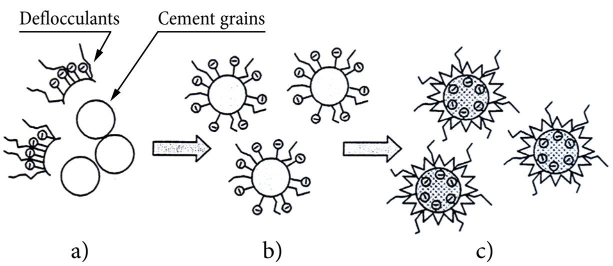

Fig. 1. Dual dispersion mechanism by PCE: electrostatic + steric repulsion = electrosteric repulsion (Hommer, Wutz 2005)

Polycarboxylate esters not only disperse the material, but also active in the cement hydration process – the first two periods of hydration of the cement paste remain plastic and buried, might be regulated by chemical and mineral admixtures (Puertas *et al.* 2005; Hanehara, Yamada 1999).

PCE was studied in two flocculants, possessing different structure (different lengths of the side chains), the effect of cement hydration process. Comparative cement paste deflocculant studies show (Hommer, Wutz 2005), that suspension without deflocculant hydration induction period lasts about 30 minutes (later to begin a massive hydrate deposition), and the suspensions deflocculant induction period lasts about 2–3 hours, depending on the side chain length. Some authors state that the cement hydration process depends of deflocculant side chains length – the longer are side chains, the shorter is time of cement hydration and the higher is early compressive strength (Hommer, Wutz 2005; Puertas *et al.* 2005).

Numerous methodologies can be used to determine rheological properties of cementitious paste. For this purpose, various viscometers could be used, which vary according to the mode of operation (Saak *et al.* 2001; Ferraris, Gaidis 1992). One of the most widespread cement paste rheological characterization techniques is based on the use of a rotational viscometer with coaxial cylinders.

Comparison of results obtained using different geometric parameters of rotational viscometer with coaxial cylinders indicated that geometric parameters of the viscometer affect the results on rheological properties of the cement paste that can be directly and quantitatively compared not by the plastic viscosity but by the relative viscosity of the plastic (Lapasin *et al.* 1983; Banfill 2003; Nehdi, Rahman 2004).

This work aims to investigate the effects of chemical admixtures on rheological properties of Portland cement paste and determine their impact on the effectiveness of hydration during induction period.

1. Materials used for research

The studies used cements produced the cement factory that meet the requirements of LST EN 197-1:2011, the characteristics given in Table 1.

Characteristics of MC-Bauchemie (Germany) chemical admixtures are shown in Table 2.

Table 1. Technical information on cements types
(AB "Akmenės cementas")

Type of cement	Mark of cement	Compressive strength after 7 and 28 days, MPa		The initial and final setting time of cement paste, min		Amount of H_2O for normal consistency of cement paste, %	Fineness		Loss on ignition, %	Insoluble residue, %	SO_3, %
							Blaine, m^2/kg	>90 µm, %			
CEM I 42,5 N	CN	25.5	55.0	120	175	25.9	327	2.7	1.32	0.29	2.74
CEM I 42,5 R	CR	28.9	54.6	150	200	26.0	356	1.1	1.43	0.22	3.10
CEM II/A-LL 42,5 N	CLN	23.7	51.1	190	285	25.4	408	4.3	5.79	–	2.69

Table 2. Technical information on chemical admixtures

Name of the admixture	Centrament N3	PowerFlow 3140
Type of the admixture	Plasticizer on a basis of lignosulphonate	Superplasticizer on a basis of polycarboxylate ester (PCE)
Mark of the admixture	P	SP
pH (20 °C)	6.0	5–7
Density, kg/dm^3	1,17	1.07
Max. amount of chlorides, %	<0.10	<0.10
Conc. of active material in solution, %	50	30

2. Research methodology

Portland cement paste was mixed according to LST EN 196-1:2005 requirements for dosing by weight of cement, and water and chemical admixtures by volume. Chemical admixtures, plasticizer and superplasticizer content in paste was constant — 0.75% of the cement weight.

Normal consistency of Portland cement paste was determined by Vicat apparatus with the plunger according to LST EN 196-3.

Suttard viscometer was used to study the effect of plasticizer and superplasticizer on water and cement (W/C) ratio and their flow characteristics of Portland cement paste. Paste dispersion was measured in two perpendicular directions and the average measure was determined.

Investigate changes in viscosity of the same water-cement ratio (W/C = 0.33 to 0.34) of Portland cement paste with and without chemical admixtures. Paste viscosity was measured in 5 min, 15 min, 30 min, 45 min, 60 min, 90 min, 120 min since cement was mixed with water for 30 s at a constant velocity gradient (149 s^{-1}). Experimental studies were carried out using a rotary viscometer Rheotest NH 4.1 with coaxial cylinders (Fig. 2).

Fig. 2. Illustration of the rheometer used
(shown with coaxial cylinders)

3. Test results and discussion

3.1. Testing the plastification of Portland cement paste

The compositions of Portland cement pastes, used for investigation (amount per 1 m^3 of paste) are given in Table 3.

Compositions of paste with chemical admixtures and W/C ratio equal to spread-flow are given in Table0. 4 for pastes. The water content reduction due to the effect of the chemical admixtures in the identical spread-flow cement pastes (130±10 mm) shown in Figure 3.

Table 3. Compositions of cement pastes, kg/m^3

Mark of the cement paste	CN			CR			CNL		
Mark of the admixtures	–	P	SP	–	P	SP	–	P	SP
Cement, kg	485	485		485	485		493	493	
Watter, kg	166	166		166	166		164	164	
Chemical admixtures, kg	–	3.64		–	3.64		–	3.70	
W/C	0.34			0.34			0.33		

Table 4. The influence of cement type and chemical admixtures on W/C ratio in the identical spread-flow cement pastes

Mark of the specimen*	CN	CNP	CNSP	CR	CRP	CRSP	CLN	CLNP	CLNSP
W/C	0.34	0.32	0.24	0.34	0.33	0.24	0.33	0.31	0.25
Flow, mm	130±10								
*Mark of the specimen consists of mark of cement paste and of admixture.									

Figure 3 shows that the chemical admixtures in Portland cement paste can reduce required amount of water: plasticizer – 5–6%, superplasticizer – 24–30%. Comparing the influence of different chemical admixtures on Portland cement paste and paste flow characteristics, it was found that effective plasticizer Portland limestone CLN is more efficient than Portland cement paste CN or CR. Superplasticizer is effective for Portland cement paste CN and CR than for limestone Portland cement CNL.

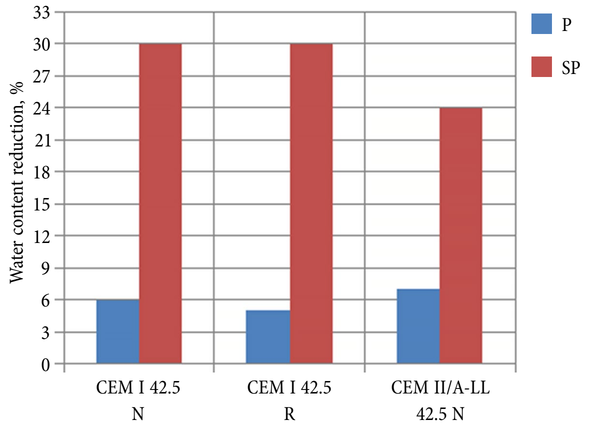

Fig. 3. The water content reduction due to the effect of the chemical admixtures in the identical spread-flow cement pastes (130±10 mm)

3.2. Portland cement paste viscosity studies

Changes in viscosity of Portland cement paste describe changes in rheological properties of Portland paste – technological nature of deterioration during the hydration process and the formation of hydration products.

Results of the impact on viscosity of chemical admixtures to Portland pastes CN, CR and CNL (in 5 min from the start of mixing the paste) are presented in Figure 4. It appears that initial viscosity values of the Portland cement paste without chemical admixtures are similar as well as the water-cement ratio (W/C = 0.33 to 0.34).

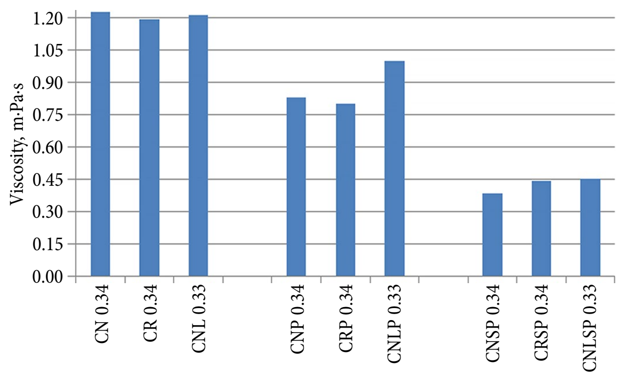

Fig. 4. The impact of chemical admixtures on initial viscosity of Portland cement pastes

Viscosity of all Portland cement pastes with plasticisers CNP, CRP, CNLP decreases. Comparing the impact on the dynamic viscosity of Portland cement paste, the plasticiser reduces the viscosity by about 33% in CN and CR, CNL – 17%. Thus, the plasticizer in Portland cement paste CN, CR reduces the viscosity by 50% more efficiently than the limestone Portland (CNL) paste.

Portland cement pastes with superplasticizer CNSP, CRSP and CNLSP demonstrated uniform viscosity reduction – viscosity of superplasticizer Portland cement paste CN, CR and CNL had greater efficiency of approx. 67–50% compared to a plasticizer such as Portland cement paste compositions.

Viscosity results of Portland cement paste were statistically processed by a computer program Statistica. Statistical correlation and trends are evident by drawing the shape variables versus time scale used to assess the strength of the connection correlation coefficients (R) and coefficients of determination (R^2).

Figures 5–7 are presented in a scatter plot, which shows the evolution of Portland cement paste with chemical admixtures and without viscosity over time.

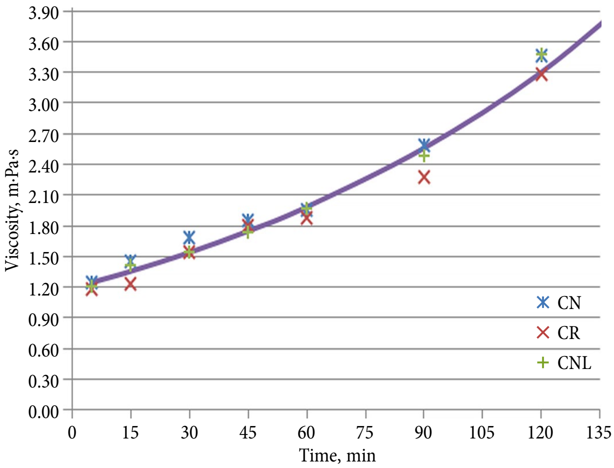

Fig. 5. Viscosity of common cement pastes without admixtures

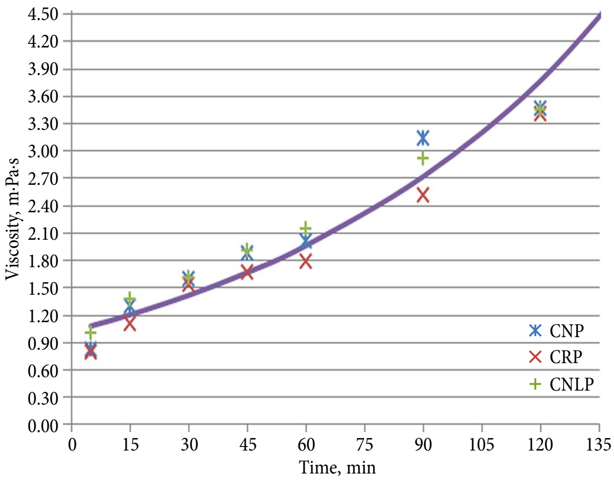

Fig. 6. Change in viscosity of common cement pastes with plasticizer

Figure 8. The chemical admixtures of Portland cement paste impact the effectiveness of the induction hydration period. It appears that effectiveness of some chemical admixtures is limited in duration.

Multiple regression analysis led to an equation of dependable variables, where x is time in minutes, correlation and determination coefficients (Table 5, Equations 1–3). Dependent variables in the equation can be used to calculate the viscosity of Portland cement paste with and without admixtures in known time.

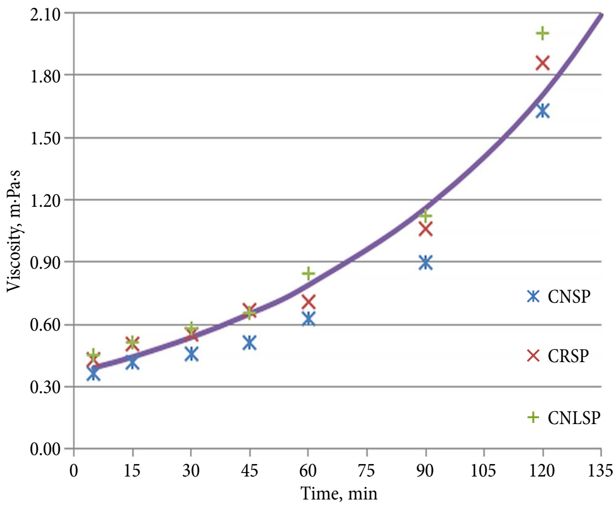

Fig. 7. Change in viscosity of common cement pastes with superplasticizer

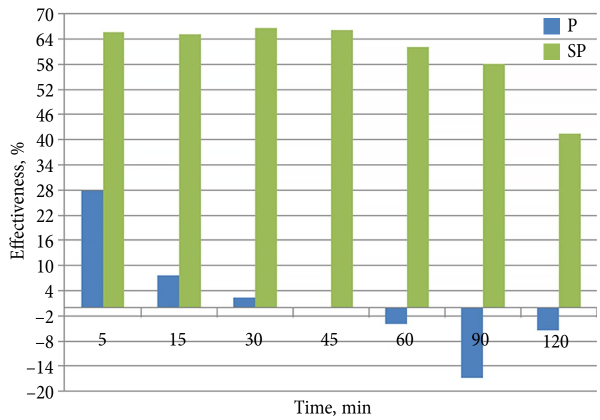

Fig. 8. The changes of effectiveness of chemical admixtures in cement pastes within the time span of two hours

Table 5. Empirical equations and coefficients of correlation and determination on cement pastes with and without chemical admixture

Pastes / Parameters	Without chemical admixtures	With plasticizer	With superplasticizer
	1	2	3
Empirical equations (where x – time in minutes; y – viscosity)	y = 1.1926·exp(0,0085·x)	y = 1.0198·exp(0,0109·x)	y = 0.365·exp(0,0129·x)
Coefficients of correlation	0.986	0.995	0.93
Coefficients of determination	0.9725	0.9901	0.8649

Conclusions

1. Chemical admixtures enable the reduction in the amount of water needed for preparation of Portland cement pastes: respectively, plasticizer Centrament N3 – 5–6%, superplasticizer PowerFlow 3140 – 24–30%, for pastes with the same flow.
2. Comparison of the impact on flow characteristics of chemical admixtures in Portland cement paste revealed that the plasticizer Centrament N3 is more efficient for limestone Portland cement (CLN) than CN or CR portlandcement pastes. Superplasticizer PowerFlow 3140 is more effective for Portland cement pastes CN and CR, than limestone Portland (CNL).
3. Viscosity of Portland cement paste can be controlled by chemical admixtures during all hydration induction period.
4. The equations obtained by regression analysis of the dependent variables can be used in the calculation of Portland cement paste viscosity, known as the time variable.

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CHEMINIŲ ĮMAIŠŲ POVEIKIS REOLOGINĖMS CEMENTO TEŠLOS SAVYBĖMS

M. Macijauskas, A. Gailius

Santrauka. Šio darbo tikslas – ištirti cheminių įmaišų poveikį reologinėms portlandcemenčio tešlų savybėms ir nustatyti jų poveikio veiksmingumą indukcinio hidratacijos periodo metu. Tyrimams naudotos šios medžiagos: AB „Akmenės cementas“ gamyklos portlandcementis CEM I 42,5 (N ir R ankstyvojo stiprumo), klinties portlandcementis CEM II/A-LL 42,5 N, plastiklis Centrament N3, naujausios kartos superplastiklis MC-PowerFlow 3140 ir vanduo. Ištirtas plastiklio ir superplastiklio poveikis vandens ir cemento (V/C) santykio pokyčiams ir portlandcemenčio tešlų sklidumui naudojant Sutardo viskozimetrą. Buvo tiriamos vienodo vandens ir cemento santykio portlandcemenčio tešlos su cheminėmis įmaišomis ir be jų. Tyrimai atlikti naudojant rotacinį viskozimetrą Rheotest NH 4.1 su bendraašiais cilindrais. Nustatytas cheminių įmaišų portlandcemenčio tešlose veiksmingumas. Pastebėta, kad portlandcemenčio tešlų dinaminė klampa gali būti reguliuojama cheminėmis įmaišomis viso indukcinio hidratacijos periodo metu. Atlikus portlandcemenčio tešlų su cheminėmis įmaišomis ir be jų tyrimų rezultatų regresinę analizę, gautos empirinės lygtys.

Reikšminiai žodžiai: portlandcementis, cemento tešla, cheminės įmaišos, klampa, plastiklis, superplastiklis, reologinės savybės, rotacinis viskozimetras, sklidumas.

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