

Hardening kinetics investigation of alkali-activated binder by small amplitude oscillatory rheometry

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Abstract. In this study, the rheological behavior of geopolymeric inorganic binder was determined. This binder was synthesized by alkaline activation of mixture, comprising calcined claystone powder and milled blast furnace slag. As an alkaline activator of hardening process, the potassium silicate solution was used. For the investigation of hardening kinetics, the strain controlled small amplitude oscillatory rheometry was used with strain of 0.01%. The reproducibility and versatility of this method is demonstrated for determination of hardening process evolution. The changes of loss tangent shape were studied in this experiment and applied for determination of gelation time. All experiments were conducted at isothermal conditions in temperature range 27-70°C and parallel plate geometry. The results indicate that reaction kinetics is directly depending on temperature. The hardening kinetics was mathematically described and these calculations were compared with self-contained experiment conducted at 2°C. This experiment is described in details and the results of gelation time measurements confirmed calculated data.

1. Introduction

Inorganic polymer cements can be synthesized by alkali-activation of a variety of materials including thermally activated clays, coal fly ash and blast furnace slag to produce a hardened material with mechanical and thermal properties potentially suitable for wide range of industrial applications [1], especially for building applications, as a binder [2]. Alkali-activated pozzolan material was discovered by Purdon and Glukhovsky in the 1940s and systematically studied by them up to the 1960s [3]. Davidovits entitled this type of materials as “geopolymers” and introduced pioneering alkali-activated calcium-free systems based on calcined clays [4]. From a general point of view, geopolymers are classified as aluminosilicate binders activated by solutions of alkali metal hydroxides, carbonates and silicates. Sodium silicate solutions are widely used as geopolymer constituent controlling the dissolution processes of the solid phase via cleavage of the Si-O and Al-O bridging oxygen bonds. The dissolution rate depends on the pH, chemical composition, concentration, structural state, and distribution of silicate species in the system [5]. The following gel precipitation and solid phase formation is driven by polycondensation mechanism and this process is leading to the formation of amorphous aluminosilicate matrix [6]. The most used is kaolinite calcined to metakaoline which leads to increase of reactivity [7]. Not only calcined kaolinite, but many aluminosilicates, also containing alkaline earth oxides as CaO, can be hardened with this mechanism. Examples can be shales and other clay minerals, fly ashes, slags and theirs blends [8].

The effect of temperature in the phase of hardening was also studied by conventional furnace heating, autoclaving and by some nontraditional heating methods where the results indicate, that temperature have effect on both, the reaction rate and mechanical properties [9, 10].



The reaction kinetics was in recent years studied by conventional techniques, mainly by X-Ray diffraction, FTIR and NMR and by some non-traditional methods like micro-mechanical analysis including nanoindentation and non-direct measurements by an open porosity investigation, was used. Also rheometrical measurements are for many years used for investigation and monitoring of hardening reactions in an industry of concretes and polymers. In the concrete science, thixotropic and flow properties measurements by rotary rheometry are widely used as a parameter of workability. Rotary rheometry is sometimes used also in geopolymers for setting time estimations. But often is used high share rate and material can be disturbed. But in polymer research, oscillatory rheometry with small amplitude is helpful approach to degree of reaction estimations. Oscillatory rheometry of crosslinking polymers for tracking of sol-gel transition is widely used form many years and in recent years are pioneering researches for tracking similar transition of alkali activated geopolymer suspension solution to amorphous gel state [11, 12].

In this study, the effect of temperature on setting time of the preliminary calcined clay mineral shale, mixed together with calcium-rich slag has been investigated with using of precision rheometrical measurement in strain controlled small amplitude oscillation mode. Changes in setting times on different temperatures and estimation of reactivity on important technological temperatures are presented.

2. Materials and instrumentation

2.1. Instrumentation

The elemental analysis of the initial material was carried out by XRF using a Bruker AXS S4 Explorer spectrometer calibrated for aluminosilicate materials. The granularity of powder was measured by static light scattering technique on instrument Horiba partica LA-960 and scanning electron microscopy was conducted by microscope JEOL JCM-5000. The loss on ignition was determined by thermogravimetric measurement on TA Instruments Q500. The setting time and reaction kinetics were determined by time-resolved dynamic rheometric measurements with small amplitude on an Ares G2 rheometer from TA Instruments in plane-plate geometry.

2.2. Materials

In this study, a mixture of calcined shale and slag (SSM), supplied by Ceske lupkove zavody a.s, Nove Straseci, Czech Republic, was examined. The shale is a material rich in kaolinite mineral and pre-calcined to metakaolin state and is then mixed with fine amorphous slag for modification of setting time. The chemical composition was determined by the XRF technique and is listed in Table 1.

Table 1. Chemical composition of raw materials [mass %]

Composition	SiO ₂	Al ₂ O ₃	CaO	MgO	TiO ₂	Fe ₂ O ₃	K ₂ O	LoI	Others
SSM	46.37	28.72	15.46	3.40	2.01	0.92	0.56	1.93	0.63
Activator	17.60	-	-	-	-	-	17.13	65.27	-

Granularity of the mixture was determined by static light scattering technique with D50v of 7.046 μm and results are graphically presented in Figure 1 a). In Figure 1 b) can be seen micrograph of the mixture taken by SEM with small particles of shale and coarse particles of slag.

For alkaline activation an aqueous solution of potassium silicate with silicate module 1.61 and content of water soluble solids 34.73% was used.

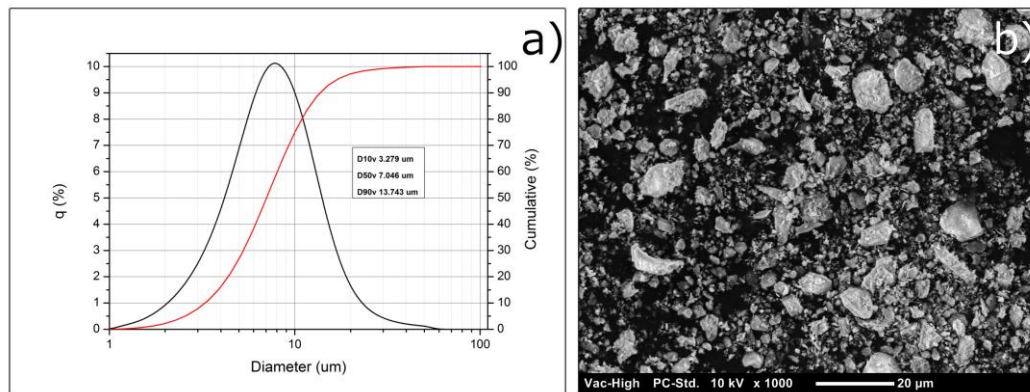


Figure 1. Particle size distribution of binder (a) and SEM image of individual particles (b)

3. Measurements and results

3.1. Measurements of oscillatory rheometry

For determination of setting time by small amplitude oscillatory rheometry we used our procedure described earlier [12].

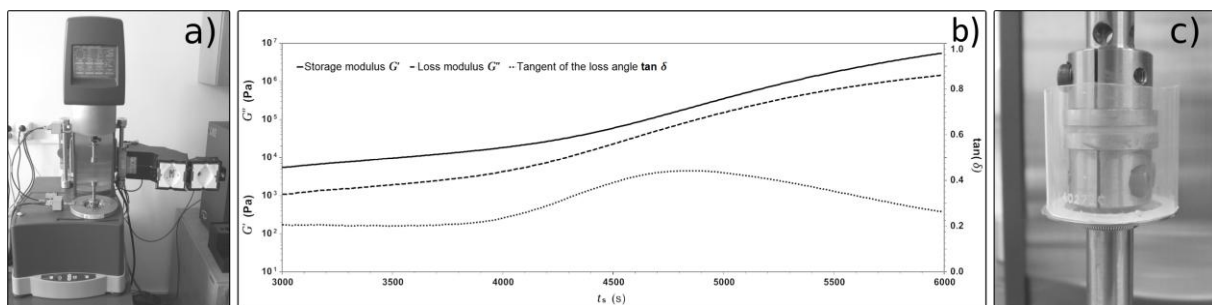


Figure 2. (a) Setup of rheometrical measurement, (b) results of paste measurement at isotherm 30°C (G' , G'' – storage and loss moduli in torsion, $\tan(\delta)$ – loss tangent), (c) sample with protective layer and air deflector before measurement

For all experiments standard mixing ratio of 10:8 by weight was used. This corresponds to ratio of charge balancing atoms $(K_2O+MeO)/Al_2O_3$ of 2.34 and Si/Al ratio of 1.77 in final hardened geopolymer. The mixtures were blended in laboratory vacuum mixer for 2 minutes and immediately transferred into the rheometer. The measurements were performed in plain-plate geometry so that the mixture in an amount of approximately 500 μl was placed into the middle of plain plates and the gap was set to a working distance of 0.8 mm. Then was geometry set to work distance and the edges of mixture were protected by thin layer of silicone oil to avoid evaporation of water and air deflector was used to shielding air vortex in furnace, as can be seen in Figure 2 c). After 6 minutes, isothermal heating at selected temperature in the range 27-70°C was initiated for a period of time necessary for mixture hardening. The measurements were performed at radial velocity 10 rad/sec and strain 0.01% to ensure a minimal influence on the hardening process. Subsequently, the maximum of loss tangent was traced and this point can be considered as transition of inner structure from pseudoliquid solution to inorganic polymer network. For the measurement at 2°C modified method was selected and prepared. Prepared mixtures were shock cooled between 2 metal plates precooled to temperature of 2°C and after selected time were measured. From residual time of transition was deduced the overall of transition at temperature 2°C. All measurements for better statistics were repeated 4 times.

Results of individual measurements are presented in Table 2 a) and dependencies are expressed by logarithmic plot in figure 2 b). The temperature interval of 27-40°C was used to curve fitting, because of side effects at higher temperatures. The results can be expressed by equation:

$$t = 10^{-8.15654 + 3592.77/T} \quad (1)$$

where t represents time of transition in seconds and T temperature in kelvins. According to this equation, the time of transition at 2 °C was calculated as 79607.85 seconds and was compared with measured value 83119.6 seconds. The measured and calculated value has reasonable difference 4.22% and so we think that this procedure can be useful for hardening predictions.

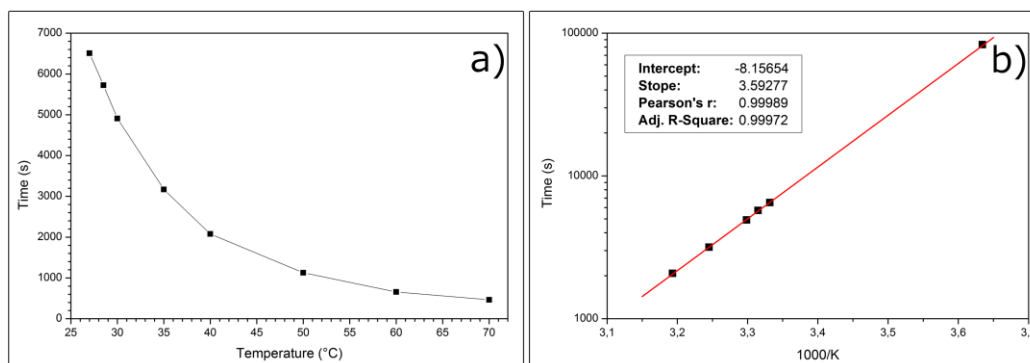


Figure 3. Average measured values of transition time (a), fitting with measured value at 2°C

4. Conclusions

In this paper, we were demonstrating oscillatory rheometry as useful method to determination of geopolymer reactivity by strain controlled measurements with small strain of 0.01%. Data collected by measurements in range 27-40°C were used to mathematical description of reactivity dependency on temperature and for measured and calculated values at temperature 2°C is difference 4.22%. From this point of view the oscillatory rheometry can be considered as reliable method for investigation of geopolymers.

Acknowledgments

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