

# The influence of metakaolin substitution by slag in alkali-activated inorganic binders for civil engineering

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**Abstract.** In this study the effect of metakaolin replacement by milled blast furnace slag in alkali-activated geopolymeric binder was investigated in accordance to their rheological and mechanical properties. It was demonstrated that slag addition into the metakaolin binder can improve mechanical properties of final products. Our investigation was focused on broad interval of metakaolin substitution in the range from 100 to 40 volume per cents of metakaolin so that the volume content of solids in final binder was maintained constant. Prepared binders were activated by alkaline solution of potassium silicate with silicate module of 1.61. The particle size analyses were performed for determination of particle size distribution. The rheological properties were determined in accordance to flow properties by measurements on Ford viscosity cup and by oscillatory measurements of hardening process. For the investigation of hardening process, the strain controlled small amplitude oscillatory rheometry was used in plane-plate geometry. For determination of applied mechanical properties were binders filled by ceramic grog in the granularity range 0-1 mm. The filling was maintained constant at 275 volume per cents in accordance to ratio of solids in dry binder. The mechanical properties were investigated after 1, 7 and 28 days and microstructure was documented by scanning electron microscopy. The results indicate that slag addition have beneficial effect not only on mechanical properties of hardened binder but also on flow properties of fresh geopolymer paste and subsequent hardening kinetics of alkali-activated binders.

## 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, 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 metakaolin 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 their blends [8, 9].

Slag is used as an additive to geopolymers mixtures for improvement of mechanical strength and for decrease of setting time. It is expected that role of  $\text{Ca}^{2+}$  ions in geopolymerization process consists in incorporation into final structure as charge balancing ion and in precipitation of calcium silicate hydrates as nucleation sites which trigger rapid formation of geopolymer network respectively [10, 11].

This study describes the effect of metakaolin substitution by blast furnace slag on hardening rate and compressional and flexural strength of hardened material. For description of hardening rate the small amplitude oscillatory rheometry was used as promising method to detect the sol-gel transition of alkali activated geopolymer suspension to amorphous gel state [12,13].

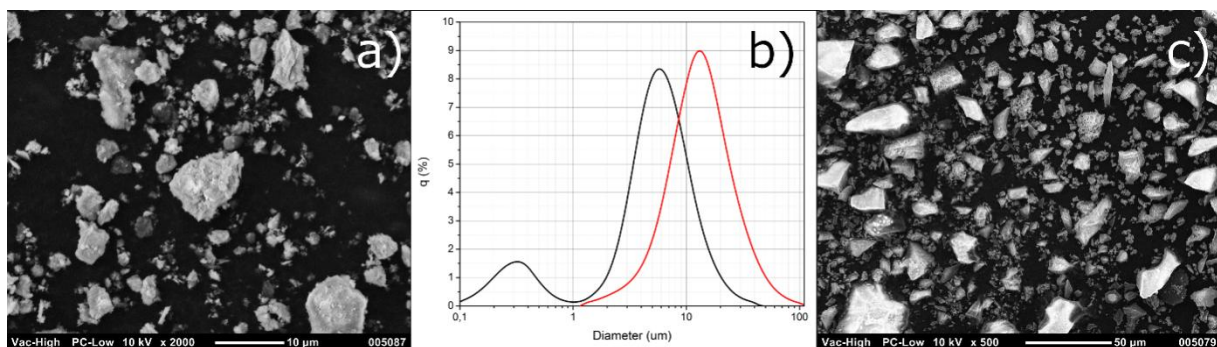
## 2 Materials

In this study, a calcined shale (CS) as a metakaolin source and milled blast furnace slag (MS) were used as raw materials. For determination of mechanical properties calcined chamotte was used as filler. These materials were supplied by Ceske lupkove zavody a.s, Nove Straseci, Czech Republic and by Kotouc Stramberk a. s. in the case of milled blast furnace slag. The chemical compositions were determined by the XRF technique and are listed in Table 1.

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

Composition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	LoI	Others
CS	53.02	39.9	0.11	0.12	2.33	1.22	0.58	2.05	0.67
MS	40.4	6.9	39.2	9.4	-	0.4	-	-	3.7
Activator	17.60	-	-	-	-	-	17.13	65.27	-

Granularity was determined by static light scattering technique and results are graphically presented in figure 1 b). The specific gravities of CS and MS were determined by Archimedes method to be 2.56 and 2.92 g/cm<sup>3</sup> respectively. This data was used for volume fraction substitutions in the range 0-60 wt.%. 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.** SEM images of calcined shale (a), particle size distribution (b) – black (CS) and red (MS) and SEM image of milled blast furnace slag (c)

## 3. Procedures and results

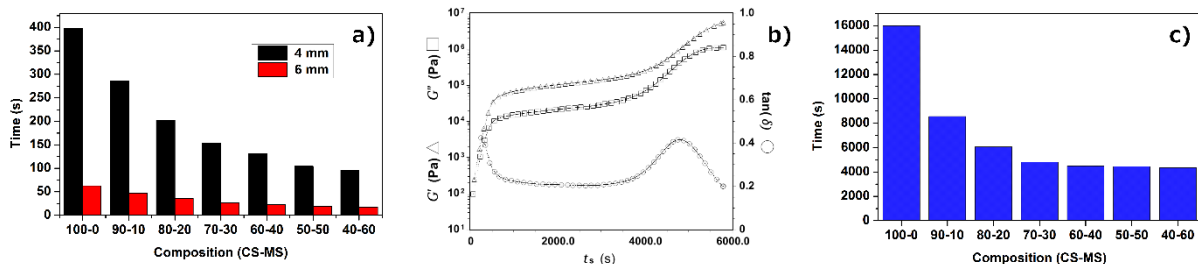
### 3.1 Experimental concept

In this study, the experimental approach was as follows. The geopolymeric binder in the form of fresh paste was prepared by mixing of metakaolin with activator in weight proportion 1:1 for 5 minutes in

laboratory vacuum mixer as a model binder and marked as 100-0. To determination of the substitution effect, metakaolin in this process was substituted by blast furnace slag in 10 vol% steps up to 60 vol% which was marked as binder 40-60. These binders were subsequently used for rheometrical measurements. These binders were filled by calcined chamotte with granularity range of 0-1 mm in accordance to Fuller-Thomson line of granularity for mechanical strength determination.

### 3.2 Rheological measurements

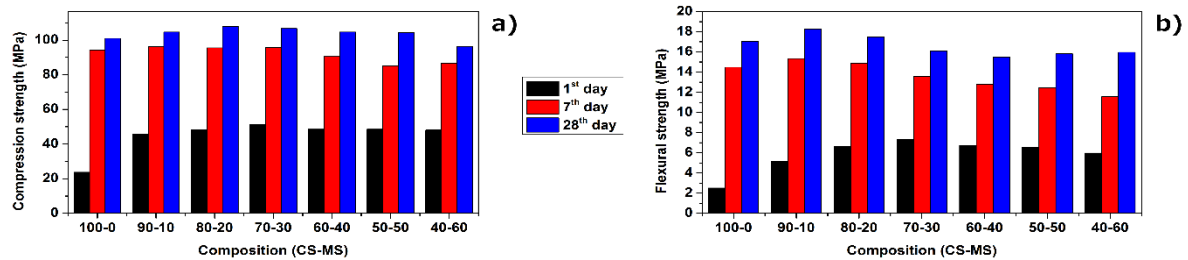
For description of flow properties and workability measurements on fresh pastes with Ford viscosity cups of diameters 4 and 6 mm were conducted. How it can be seen in figure 2 a) increasing metakaolin substitution leads to significant reduction of viscosity which is important to workability. This behavior can be attributed to increasing of overall particle sizes in individual pastes. The determination of setting time by small amplitude oscillatory rheometry was described earlier [13]. The measurements were performed in plain-plate geometry on an Ares G2 rheometer from TA Instruments with working gap of 0.5 mm and strain controlled to 0.01 %. After 15 minutes, isothermal heating at temperature of 30 °C was initiated for a period of time necessary for paste hardening. Subsequently, changes in position of maximum value on loss tangent curve were used for determination of hardening kinetics. The result for binder 70-30 is presented in figure 2 b) and overall results of loss tangent maxima clearly indicate that hardening of individual pastes is accelerated by increasing amount of slag. This effect is significant to the 40% substitution and it can be described as a fast dissolution of amorphous content of slag and subsequent construction of calcium silicate gel together with formation of geopolymer network which have effect on early age mechanical strength [11].



**Figure 2.** Results of flow measurements by Ford cups (a); Standard results of oscillatory measurement (binder 70-30) where  $G'$ ,  $G''$  – storage and loss moduli in torsion,  $\tan(\delta)$  – loss tangent (b); results of individual oscillatory measurements (c)

### 3.3 Measurements of mechanical properties

For flexural and compression strength investigation, binder was prepared according to procedure described in section 3.1 in amount of 200 weight parts and mixed with 275 weight parts of filler. The mixing was performed in planetary mixer for a period of 10 minutes. Subsequently, the mixtures were cast in moulds with dimensions of 20×20×120 mm and 20×20×20 mm for flexural and compressional strength determinations. Before individual tests the samples were cured at ambient temperature in polypropylene bags to prevent humidity loss. Results for individual periods of time are presented in figure 3. The mechanical properties after 1<sup>st</sup> and 7<sup>th</sup> day clearly correspond with findings by rheometrical measurements up to the substitution of 30%. Beyond this limit increasing the amount of slag is not further beneficial for mechanical properties. This is more apparent after 28 days where the best results are between 10 and 20% substitution. However, in all cases at the end of investigated time period the mechanical strength in compression and flexure exceeded 90 and 15 MPa respectively and thus all mixtures represent good binding properties.



**Figure 3.** Results of strength measurements in compression (a) and flexure (b)

#### 4 Conclusions

It can be summarized that the slag addition is beneficial mainly for fast hardening of geopolymeric binders where the 40% substitution of metakaolin by slag reduces setting time by 5 times. This behavior has beneficial effect also on early age mechanical strength up to the 30% substitution. On the contrary higher substitutions slightly decrease mechanical strength. Moreover, after 28 days the best results of mechanical strengths were achieved by 10-20% substitution of metakaolin by slag and it can be related to slower polycondensation of geopolymer network which results in less structural defects. However, in whole investigated range the mechanical properties are suitable for construction applications. Thus, it can be concluded that lower substitutions could be used for casting at construction sites and 30% and higher substitution can be advantage in manufacturing of prefabricated elements where short time of unmolding is significant parameter because of fast hardening and also where saving of natural resources is desirable.

#### Acknowledgments

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