

# Alkali-Activated Slag concrete development and their practical use

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## Abstract

New inorganic binders are searched which are able to substitute Portland cement in some branches of the building industry. The reason is the lowering of emissions of carbon dioxide and use of some secondary materials. Alkali-activated slag (AAS) concretes - relatively well-known composites - are one of the perspective binders. They show good mechanical properties and good resistance to the attack of a variety of chemical media but for practical application various different problems must be solved; the optimum content of alkaline activator and its nature; the composition of the activator for optimum setting and hardening time, good workability, smallest volume exchanges and maximum strength and high durability. These problems are discussed in the present paper. The aim of the paper is to design an appropriate mixture for producing AAS concrete and for performing actual pilot tests in a concrete plant.

## 1. Introduction

Alkali-Activated Slag (AAS) composites are composites prepared from Ground Granulated Blast furnace Slag (GGBFS) activated through appropriate alkali solution. Usually it is water glass and/or sodium hydroxide sometimes also potassium hydroxide. Especially different forms of CSH gel arise as main binding phases [1,2]. Sometimes also some geopolymers occur. Some authors [3] recommend to use the term „geopolymers“ for AAS composites. In any case, they show good mechanical properties, good resistance to the attack of a variety of chemical media and some other suitable properties but for practical purposes it is necessary to solve any problems [4], especially the setting of the AAS concretes and high shrinkage of AAS concretes which results in cracking, especially at the surfaces of elements.

Some authors [2] published results about quickness of setting and hardening in dependence on the nature of the activator. A very high strength was obtained for water glass activated composites, lower for NaOH or Na<sub>2</sub>CO<sub>3</sub> activated composites. The different strengths are a consequence of different form of CSH gel; which is confirmed by NMR analysis. The properties of CSH gel and binding of alkalis were studied for example in [2,5].

The shrinkage is a topic of interest of many researchers. Occurrence of cracks is affected by the presence of silica in alkali-silicate activator [6]. The larger amount of silica, the bigger autogenous shrinkage. The influence of storage condition is also very important for the cracks occurrence and strength development [7]. Significantly lower strengths were obtained for specimens exposed to laboratory conditions (23°C and 50% r.h.) than for sealing or bath specimens.

The results may be affected by properties of slag. For this reason it is not possible to adopt the results without any study with particular slag and also alkali activator. Some important results were shown in other papers [4,8]. They show that minimum 6% of Na<sub>2</sub>O is necessary for a reasonable course of setting and hardening for our specific condition. As was shown in [8] the setting and hardening is strongly affected by the ratio Na<sub>2</sub>O/SiO<sub>2</sub> in activator (water glass and sodium hydroxide). During hardening the significant efflorescence take place on the surface of specimen. It is necessary to avoid the efflorescence. The use of K<sup>+</sup> ions instead Na<sup>+</sup> ions in activator can be an appropriate way.

During the investigation three main ways were kept:

1. designed AAS concretes must to be easy to produce – without problems with setting and hardening, with number of compounds (minimum new containers for materials); the formulae should be as simple as possible.
2. designed AAS concretes should have workability similar to Self-Compacting Concrete. The AAS concretes can be useful in competition with SCC concretes because alkalis and SiO<sub>2</sub> bring good workability.
3. AAS concretes should be cheaper or as expensive as usual concrete

## 2. Materials

The used GGBFS is produced near Ostrava in the Czech Republic and milled in Stramberk cement plant to specific surface 350 or 420 m<sup>2</sup>/kg. The finer fraction, 420 m<sup>2</sup>/kg, was used in this paper. The RDA pattern of the slag (Fig. 1) shows that the slag is glassy, only merwinite peaks are recorded. The chemical composition of the slag is also shown in figure 1. It is possible to use different kinds of water glasses which differ by silicate modulus M<sub>s</sub>. In literature [2,6,7] authors usually use water glass with M<sub>s</sub> = 1.5. But this water glass is very sensitive to low temperatures; the solid sodium silicate can arise. For this reason the water glass with M<sub>s</sub> = 1.8 and dry mass content about 45% was used. For the modification of M<sub>s</sub> of water glass during mixing the solution of NaOH (concentration 50%) was

formerly used [8,9]. The NaOH solution is relatively cheap but this brings some problems – especially efflorescence on the surfaces of beams. For this reason, the replacement of solution of NaOH by solution of KOH (concentration 50%) was tested.

Grounded limestone was sometimes used with fineness similar to GGBFS fineness. Originally, lowering of concrete mixture price was the reason for this but later also some better properties of these mixtures were recorded. Drinking water and usual sand and aggregates were also used to prepare mortars and concretes.

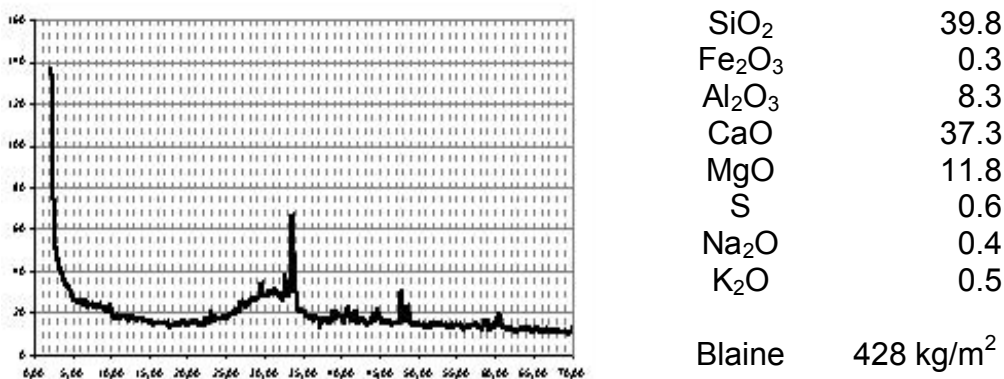


Figure 1: RDA pattern and chemical composition of used slag

### 3. Searching for best activator composition

A number of possibilities as to retarding the setting of AAS composites is known in the theoretical studies. The setting and hardening of the pastes made from slag, sodium water glass ( $M_s=1.8$ ), 50% KOH and drinking water (water/slag = 0.35) was investigated. The amount of dry mass of activator to mass of slag and limestone ( $\text{SiO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O}$ ) / slag + limestone) is 6% or 10%. The reason of replacement of limestone is discussed below. The setting (start of setting and time of setting) was measured by Vicat apparatus.

It is evident that courses of setting differ for different amounts of alkali activator, for NaOH or KOH and for the replacement of slag by limestone. There are two possibilities to mix AAS mortars and concretes with convenient time of setting. It is possible to use ratio  $(\text{Na}_2\text{O} + \text{K}_2\text{O}) / \text{SiO}_2$  between 50/50 or 60/40 or use only KOH as activator respectively – 100% K<sub>2</sub>O. As the content of Na<sub>2</sub>O must to be minimum 6%, see [4], the content Na<sub>2</sub>O + SiO<sub>2</sub> in activator (total dry mass in activator) must to be minimum 10% (see peak of grey dashed curve in figure 2). For the optimum combination of sodium water glass and solution

of KOH, 10% of solid dry mass of activator represents 5% of alkalis ( $K_2O + Na_2O$ ) and 5% of  $SiO_2$ .

A very important result is the retarding of setting by limestone which replaces slag. The start of setting is twice as long for pastes with replacement of 1/3 of amount of slag by limestone.

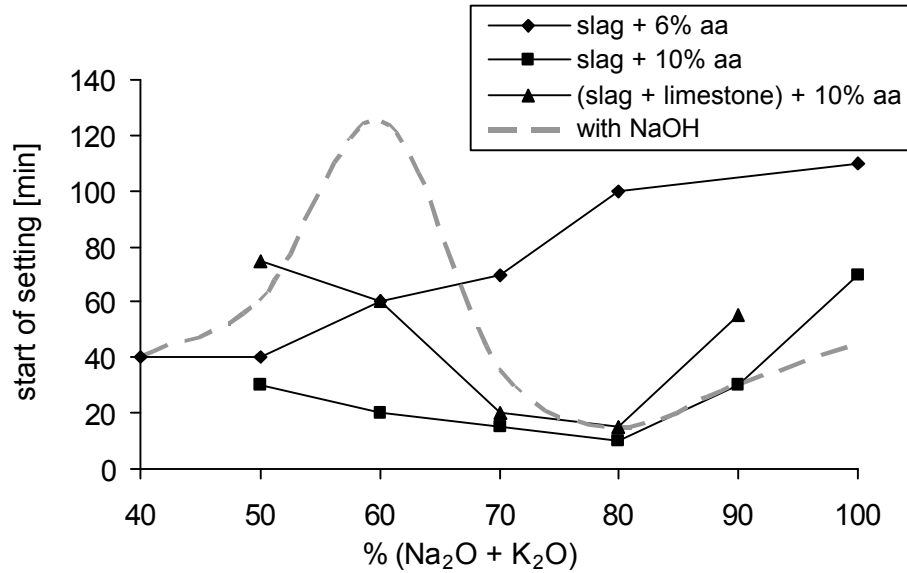


Figure 2: Start of setting of AAS pastes in dependence on alkali activator (aa) composition. The dry mass content  $Na_2O+K_2O+SiO_2$  is 6 or 10%

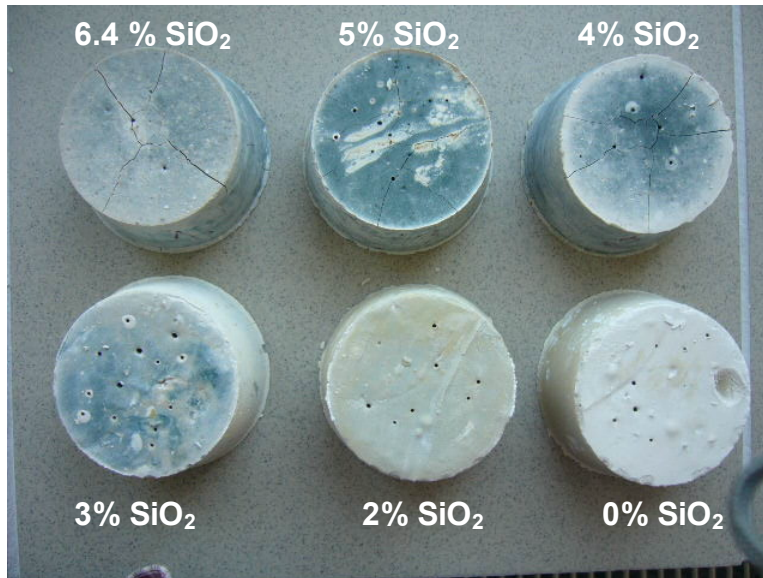


Figure 3: Cracking of samples after measurement of setting through Vicat apparatus. The dry mass content in activator ( $Na_2O+K_2O+SiO_2$ ) is 10%

There is some basic insight into cracking of AAS composites in figure 3. The samples after Vicat test are conspicuously cracked if  $\text{SiO}_2$  content increases. No cracking is observed for only  $\text{K}_2\text{O}$  activated pastes. But it is important to note the cracking is not the result of shrinkage only, but also tensile strength and modulus of elasticity.

#### 4. NMR study

Setting results evokes some question concerning the nature of hydration products. It is also interesting to know if it is possible to consider investigated AAS composites as geopolymers.

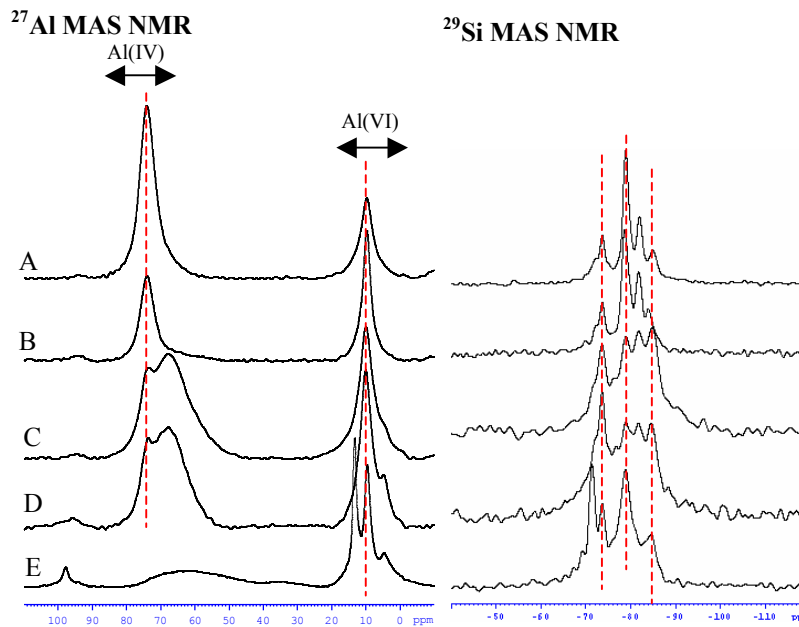


Figure 4: A - 10%  $\text{K}_2\text{O}$ ; B - 6%  $\text{K}_2\text{O}$ ; C – 5%( $\text{K}_2\text{O}+\text{Na}_2\text{O}$ )+5% $\text{SiO}_2$ ;  
D - 3%( $\text{K}_2\text{O}+\text{Na}_2\text{O}$ )+3% $\text{SiO}_2$ ; E – CSH (white cement and water)

It was found from  $^{27}\text{Al}$  MAS NMR analysis (Fig. 4) that tetrahedral groups exist in AAS pastes and their amount increase with increasing alkali content (paste A,B). These groups are dominant compounds of geopolymers. But in AAS pastes the resonance of  $\text{Al}^{\text{IV}}$  groups occurs at 72 ppm and not at 58-60 ppm as it is obvious for geopolymers. The signal at 72 ppm indicates tabular structures with periodically alternating  $\text{Al}^{\text{IV}}$  and  $\text{Al}^{\text{VI}}$  units. It is not possible to consider these structures as geopolymers; they are characterised by 3-dimensional network. If water glass is a part of activator (pastes C and D) the  $^{27}\text{Al}$  MAS NMR analysis shows increase of  $\text{Al}^{\text{IV}}$  inordinate units, see signals around 68 ppm. It indicates tetrahedrally coordinated Al-atoms in amorphous phase which can correspond to  $\text{Q}^4(3\text{Al})$  groups of geopolymeric mass. The water glass ( $\text{SiO}_2$  presence) facilitates the creation of 3-dimensional geopolymer similar network.  $^{29}\text{Si}$

MAS NMR analysis confirms the presence of  $Q^4(3Al)$  in pastes activated by KOH and water glass and the absence of  $Q^4(3Al)$  in only alkali (mix of NaOH and KOH) activated pastes.

Detected signals correspond to  $Q^0$ ,  $Q^1$  and  $Q^3$  structural units which are also present in usual CSH gel (see sample E). Nevertheless it is evident that alkali activation induces polymerization of  $Q^0$  and  $Q^1$  and the origin of short polymeric Si-O-Si chains. Generally, the observed results are in accordance with other results [10,11].

### 5. Workability of mortars

On the basis of optimum course of setting and hardening some mortars were prepared with a different replacement of  $Na_2O$  by  $K_2O$ .

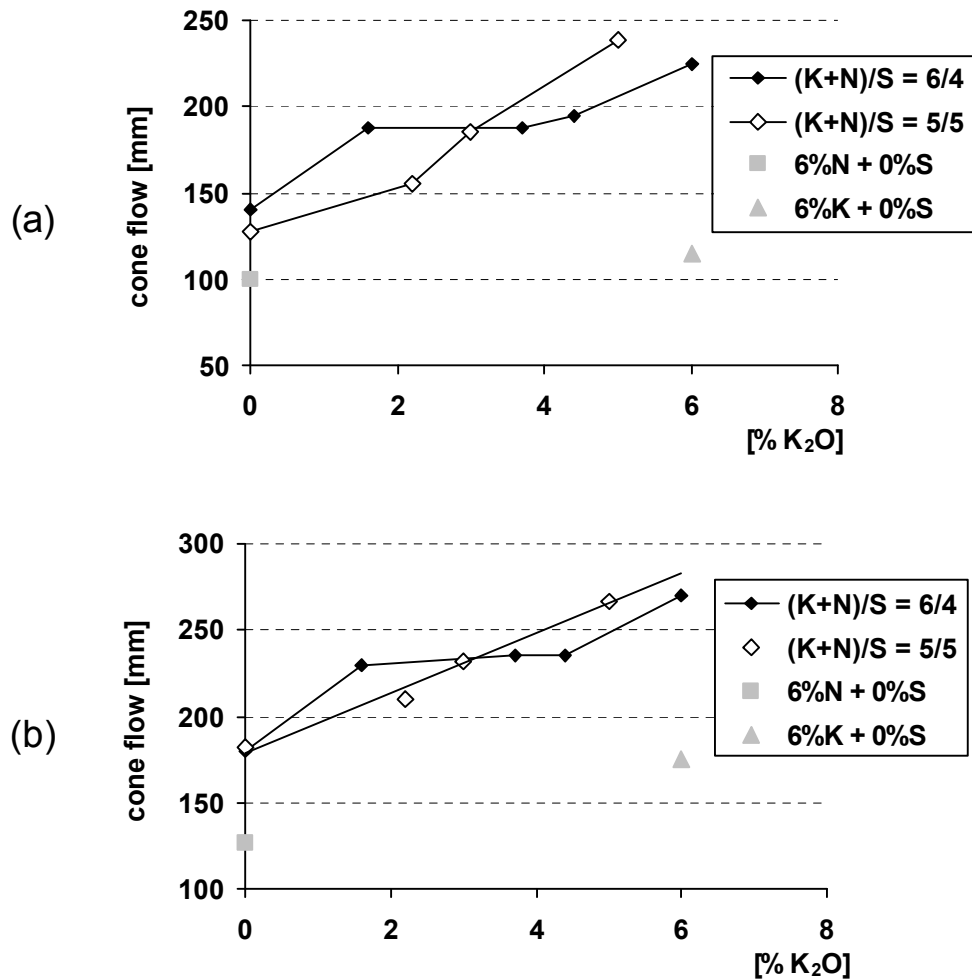


Figure 5: Cone flow (a) and cone flow after 15 blows of table (b).

The ratio  $(K_2O+Na_2O)/SiO_2$  was kept 6/4, the ratio  $(K_2O+Na_2O+SiO_2)/(slag+ limestone)$  was 10%. Also mixtures activated by only  $Na_2O$  and  $K_2O$  were prepared and mixtures with  $(K_2O+Na_2O)/SiO_2$  ratio 5/5. Water/(slag + limestone) ratio was 0.6.

It follows from the figure 5 that alkalis enhances workability, see also [4]. It is evident that workability is significantly better for the increasing of amount of  $K_2O$  in activator. This is true of  $(K_2O+Na_2O)/SiO_2$  ratio 6/4 (advantageous for  $Na_2O$  in activator) and also of the ratio 5/5 (advantageous for mix of  $Na_2O$  and  $K_2O$  in activator). Also  $SiO_2$  content probably play a role because mixtures with 5% of  $SiO_2$  show better workability than mixture with 4%  $SiO_2$ . These results are very important because they permit to lowering of water/slag ratio.

## 6. Strengths development

With respect to early strengths it can be seen in figure 6 the minimum content of alkali activator should be 10%. The content of slag has not got some any mayor effect. However, for self-compacting concrete some minimum amount of fine particles should be present in the mixture. The alkali and water glass presence brings good plasticity and the amount of fine particles content can be reduced but not below  $450 \text{ kg/m}^3$  for used aggregates. For this reason the replacement of slag by limestone was tested.

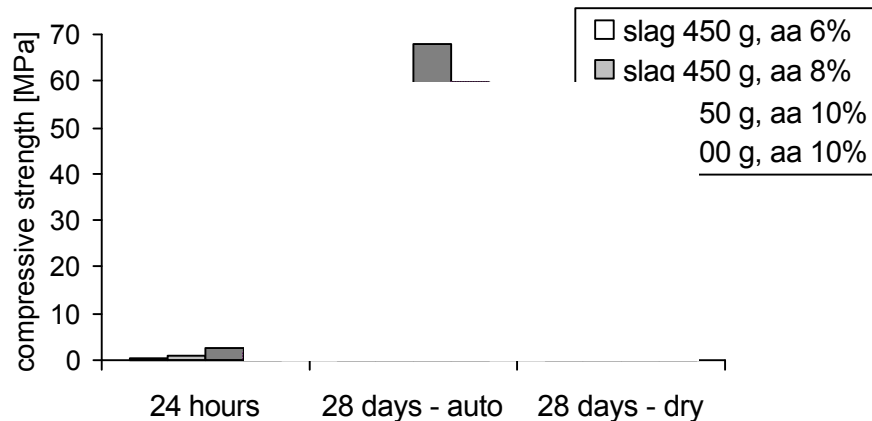


Figure 6: Influence of amount of slag and amount of alkali activator on compressive strength of mortars (beams 160x40x40 mm)

Compressive strength development for mortars with different replacement of slag by limestone is shown in figure 7 for two different amounts of alkali activator dry mass –  $(K_2O + Na_2O + SiO_2)/(slag + limestone)$  is 10% and 15% respectively. Ratio  $(K_2O + Na_2O)/SiO_2$  is 5/5 or 7.5/7.5 respectively.

It is interesting that mortar with the replacement of 100 kg of slag by limestone shows higher strengths than that made from slag only. Probably the limestone affects the strength only a little and the effect of higher actual ratio  $(K_2O+Na_2O+SiO_2)/\text{slag}$  plays important role for strength development. While this ratio is only 10% or 15% for mixture with only slag, it increases to 12.8% or 15% respectively for mixture where 100 kg or 150 kg of slag were substituted by limestone. The effect of storage conditions (covering by PE-foil or dry storing in  $t \approx 20^\circ\text{C}$  and  $r.h. \approx 60\%$ ).

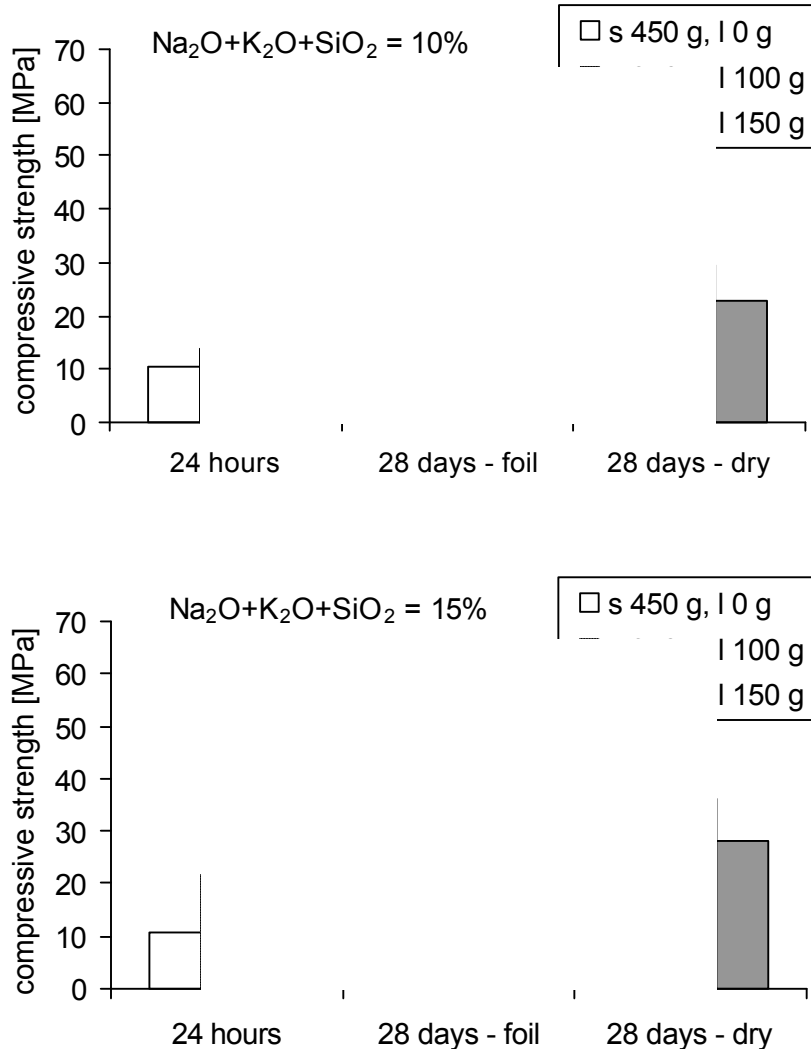


Figure 7: Development of compressive strength of AAS mortars with replacement GGBFS by limestone (beams 160x40x40 mm)

Strength development for mixtures tested for workability is shown in figure 8. The combine effect of  $K_2O + Na_2O$  mixture is evident; the mixture of these brings higher strengths than either one of them used separately. The composition for 1.6% of  $K_2O$  and 4.4% of  $Na_2O$  is convenient



because it is cheaper than the others. This ratio is one of the ratios used for concrete preparation.

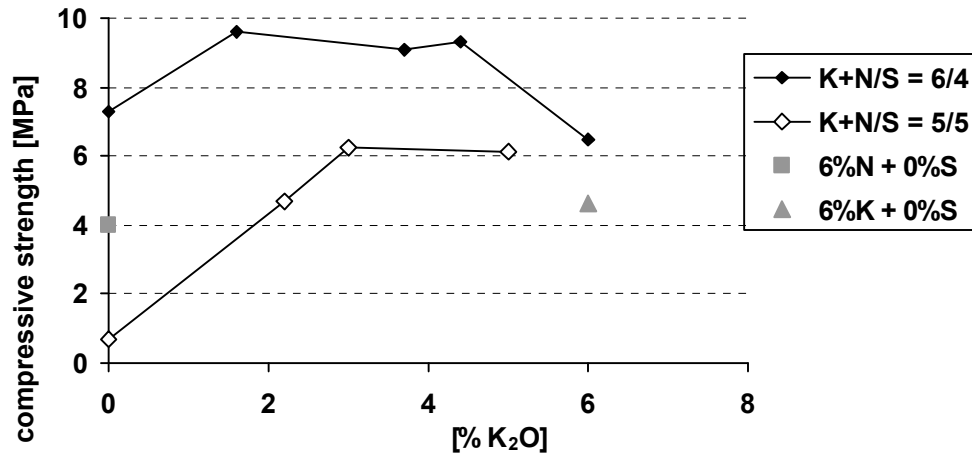


Figure 8: 24-hour's strength development of mortars used for workability measurement (beams 160x40x40 mm)

## 7. AAS concretes

On the basis of previous experiments the concretes were prepared in a laboratory mixer and some tests were performed. The 1m<sup>3</sup> composition and some results are shown in table 1.

Table 1: Composition and some properties of AAS concretes designed on basis of the above mentioned tests

	NK6/4	NK5/5-1	NK5/5-2	NK5/5-3
Na <sub>2</sub> O+K <sub>2</sub> O+SiO <sub>2</sub>	10%	7.8 %	10%	10%
(Na <sub>2</sub> O+K <sub>2</sub> O) /SiO <sub>2</sub>	6 / 5	5 / 5	5 / 5	5 / 5
Water/(slag+limestone)	0.50	0.55	0.52	0.52
GGBFS 420 m <sup>2</sup> /kg	450	350	350	300
Limestone (450 m <sup>2</sup> /kg)	0	100	100	150
Na-water glass M <sub>s</sub> 1.8	62	60	78	78
50% solution KOH	60	28	36	36
Water	150	175	167	167
Sand 0/4 mm	790	790	775	775
Crushed aggr. 4/8 mm	240	240	260	260
Crushed aggr. 8/16 mm	550	550	515	515
workability - cone flow	585x580	620x600	580x600	580x580
Compressive str. 24 h.	5.6	3.6	4.2	3.7
Bending strength 24 h.	1.8	0.9	1.1	1.0
Compressive str. 28 d.	73.5	54.5	59.6	58.0

Workability was measured as Abram's cone flow; bending strength was measured on beams 400x100x100mm, compression strength was measured on 100 mm cubes. Specimens were stored in wet condition (r.h.  $\approx$  95%,  $t \approx 20^\circ\text{C}$ ).

All of the concretes show low early strength which is the biggest disadvantage of these materials. Workability is good as well as 28-days strengths. Cracking can occur (dry cured samples) but this is not a problem if the concrete is wet cured.

## 8. Conclusions

On the basis of experiments which were performed on the AAS pastes, mortars and concretes some of these important conclusions can be emphasized:

- Combination of sodium water glass and potassium hydroxide is a convenient way for efflorescence avoidance
- Combination of sodium water glass and potassium hydroxide is a convenient way for enhancement of workability
- The optimum  $(\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{SiO}_2$  ratio has been found for both - appropriate course of setting and strengths development
- Concretes were designed which can be used in practice. Problems can represent some early strength
- Cracks occurrence is minimalised by careful curing
- NMR study shows that term „geopolymers“ is not very convenient for this type of AAS composites because only a little part of binding products can be consider as geopolymer-like products

Despite some problems, some elements were made from the above mentioned AAS concrete mixtures. The investigation continues to reach better properties and to avoid mentioned problems.

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