THE INFLUENCE OF THE METAKAOLINITE ADDITION ON THE HYDRATION PROCESS OF THE ALKALI-ACTIVATED SYNTHETIC GEHLENITE GLASSES
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Abstract:

Usage of the MK in concretes has got an advantageous influence on the compressive strength and durability of hardened concretes. As activators of slag - MK, the NaOH, $Ca(OH)_2$, KOH, Na_2SO_4, $CaSO_4$, water-glass or portland cements can be used. In this work two main questions were asked – if and how is the MK addition influencing on the properties of hydrated gehlenite glasses. In samples preparation sodium hydroxide was used. There also the MK after thermal activation was used. In the MK reaction with activators, the C-S-H, C_2ASH_8, C_4AH_{13} and zeolite phases are formed. In this work the properties of the hydration products of the alkali-activated gehlenite glasses with the MK addition presence were examined.

Key words: akermanite, alkaline activation, gehlenite, melilites, metakaolinite, mineral additives, slag

1. Introduction

Alkaline activation of granulated blast furnace slags by highly concentrated solutions of sodium or potassium ions has been a subject of numerous investigations. The research of cements and lime substitutes was terminated by the general utilization of the blast-furnace slags and fly ashes in the binding material technology for many last decades [1-4]. But there are still some interesting parts in the area of slags investigations. Properties of AAS pastes, mortars and concretes strongly depend on the chemical and phase composition of the slags and other minerals additives. Especially according to slags containing the minerals from gehlenite – akermanite solid solution series called melilites. During the last years

a lot of researchers reported that the metakaolinite (MK) was used as the main component of energy-saving cements. MK is a pozzolanic material which is formed during the thermal activation of kaolin clay. During the firing of clays such as kaolin, montmorillonite, illite, or chlorite, there is proceeding the phase transition consisted in emission OH^- groups from the structure. The structure variations obtained in clayey minerals are very large scaled and conducting to form almost amorphous state of matter. The specific for that state is no thermodynamic equilibrium. It is the deciding factor of chemical reactivity that kind of materials.

It was noticed that the chemical composition of MK represents a good correspondence with generally used cement additives. The investigations show that the MK can be used as the main component of the energy-saving cements [3 , 4] and also as the pozzolanic addition for concretes and mortars [7, 8, 11-15]. The 10 - 20% substitution of cement by the MK has a advantageous influence on the compressive strength and the durability of concrete [10]. During the hydration process with the MK addition, the extra C-S-H phase is formed in reaction with $Ca(OH)_2$, which is released during the portland cement hydration process. Like many other cement additives, also the MK needs additional activation to increase the reactivity [3, 4, 9, 10]. The properties of the MK have also got an influence on the final properties of the hydrate. The factors that mainly determinate the properties of the MK based binders:

- sort of the initial raw material – composition, grain distribution, specific surface of kaolin,
- temperature of firing,
- temperature and time of curing,
- water/binder ratio,

During the MK reaction with activators in the water solution, in the first turn the lattice bond breaking of anhydrous kaolin, that is weaken by the water loosing, proceeds by the hydroxyl ions. It creates the possibility of proceeding the reactions that can give the following products: C-S-H, C_2ASH_8, C_4AH_{13} and zeolite phases. Among the reaction products, there can also occur good-mechanical properties inorganic polymers called geopolymers [7, 11]. The most important rate-determining factor in the MK hydration process is the concentration of the used activator. The literature reports that using of one kind of the activator, with the concentration below 10 moles,

yields no significant effects or the process doesn't proceed. The increase of the temperature to 45°C [11] and 85°C [7, 12, 13] is also not beneficially in this case. Only the significant increase of concentration of used activators causes the start or significant increase of hydration process. The samples activated by 12 moles of NaOH have already shown some mechanical strength. That strength is the result of presence of inorganic polymer with approximated formula $Si_2Al_2Na_2H_4O_{10}$ [7]. If the activation process is conducted with 5 moles of NaOH and $Ca(OH)_2$ solutions, the very slow process of MK activation is observed. The main product of this reaction is the gel state of C-S-H phase. In case of using 12 moles activator or above, the main product is the inorganic alkaline polymer. If the concentration is below 12 moles, the main product is the gel phase and low amount of crystalline zeolites [11]. As the literature shows [14], the kinetic of hydration of MK based binders, activated with high concentration of activators, depends on the temperature.

2. Experimental

In present study, for investigations it was used the kaolin clay from the „Surmin-Kaolin S.A." mine of raw minerals. The clay was fired in 750°C for 24h. The chemical composition is shown in table 1, and the mineral composition of kaolin clay is shown in table 2. The XRD diffraction pattern obtained for the MK is shown in fig. 1.

Tab. 1. The chemical composition of the kaolin clay

Component	Amount [%]
SiO_2	52.00
Al_2O_3	34.00
Fe_2O_3	0.40
TiO_2	0.45
CaO	0.15
MgO	0.20
alkalis	0.57
Loss on ignition	12.10

In spite of quite good reactivity of the slag minerals, there is always possibility to improve that reactivity by converting the minerals into vitreous state. In vitreous state the matter doesn't have a long-range order, it only has a local concentration called domains or clusters.

Tab. 2. The mineral composition of the kaolin clay

Component	Mount of the mineral phase [% by weight]
Kaolin	80.00
Illite	9.00
Quartz	9.00

The diameters of domains don't exceed 20 Å, so that kind of materials are not a diffraction grating for X-rays. It is also characteristic for the vitreous state, that the molecules that are constructed from, doesn't have an energetic minimum. Through that fact, the reactivity of glasses is much higher than a crystalline equivalent. According to the text above, the investigation was fixed in the mineral composition samples, in the vitreous state.

The main target of this work is to definite the influence of the activator concentration and the influence of the A/S ratio in slags on the hydration products. To achieve that target, three kinds of alumino-silicate glasses were prepared. The A/S ratio was fixed as 0,25; 1,0 and 1,2. The raw materials ($Al(OH)_3$, $CaCO_3$, SiO_2, $Mg(OH)_2$) were ground (~4000cm^2/g according to Blain), mixed in adequate ratios and homogenized for 24h. The hot melt was poured out into the cold water. The obtained product was grounded again to ~4000cm^2/g and the XRD analyze was carried out. The level of the vitrification of all the glasses was above 96%. Two glasses were gehlenite type and one was fixed as melilite solid solution type. The gehlenite/akermanite ratio in the melilite glass was fixed as $C_2AS/C_2MS_2 = 0,66$ ($Al_2O_3/SiO_2 = 0,25$). The composition of the particular glasses is shown in the tables 3 and 4.

In each glass, the peaks from crystalline gehlenite were observed. Amount of crystalline phases in obtained glasses was below 2%, but even very low amount of crystalline gehlenite gives very intensive peaks.

The pastes were obtained from the prepared glasses and the samples with dimensions 10x10x60 mm were prepared from these pastes. The glasses were activated by NaOH as equivalent amount of Na_2O. The 15M, 7.5M and 3.75M concentrations of NaOH were used. The composition and designation of the samples is shown in the table 5.

Tab.3. Amount of oxides in gehlenite glasses of A/S ratio 1.0 and 2.0

Glass	Content [%]			Amount of moles [per 100g]			Molar ratio Al_2O_3/SiO_2
	CaO	Al_2O_3	SiO_2	CaO	Al_2O_3	SiO_2	
1.0	40.91	37.18	21.91	0.729	0.365	0.365	1.00
1.2	38.08	41.53	20.39	0.679	0.407	0.339	1.20

Tab.4. Amount of oxides in mellilite glass of A/S = 0.25

Glass	Content [%]				Amount of moles [per 100g]				Molar ratio Al_2O_3/SiO_2
	CaO	Al_2O_3	SiO_2	MgO	CaO	Al_2O_3	SiO_2	MgO	
0.66	41.05	14.84	35.23	8.88	0.732	0.146	0.586	0.220	0.25
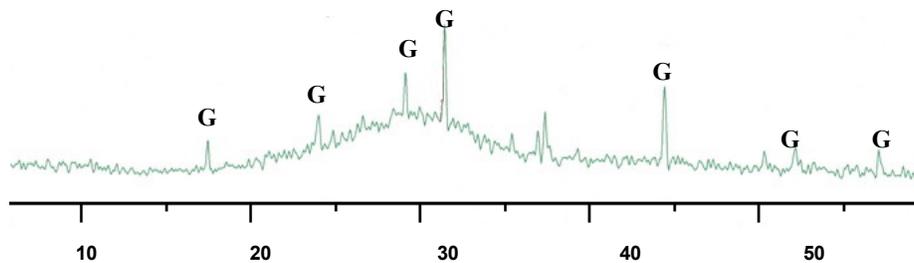
Fig. 1. The diffraction pattern of the gehlenite glass 1,0.

The properties of the particular glasses occurred to be totally different, so that the water/binder ratio has to be fixed for every glass on the basis of the consistency. As a result of that, the obtained strength results include the partial error.

the following examinations were carried out on the prepared samples:
- Setting time
- XRD
- IR
- Summary heat of hydration
- Flexural strength
- Compressive strength

The first investigation was conduct to define the setting time of particular samples. The samples made with gehlenite type glass with molar ratio $Al_2O_3/SiO_2 = 1,0$ showed the shortest setting time. These

samples also showed the highest strengths and summary heats of hydration.

Tab. 5. Designations and compositions of the samples

Designation	%-fraction of the glass			%-fraction of the MK	%-fraction of the activator		
	0.25	1.0	1.2		Na$_2$O		
AN1	100				1.16		
AN3	100					3.49	
AN7	100						6.98
AMN1	80			20	1.16		
AMN3	80			20		3.49	
AMN7	80			20			6.98
BN1		100			1.16		
BN3		100				3.49	
BN7		100					6.98
BMN1		80		20	1.16		
BMN3		80		20		3.49	
BMN7		80		20			6.98
CN1			100		1.16		
CN3			100			3.49	
CN7			100				6.98
CMN1			80	20	1.16		
CMN3			80	20		3.49	
CMN7			80	20			6.98

Tab. 6. Setting times, flexural and compressive strengths of particular samples without MK addition

Designation	Water-cement ratio	Setting time	Compression strength [MPa]	Heat of hardening, Q$_{24h}$, J/g	
AN1	0.24	24h	24.5	55	
AN3	0.24	24h	24.5	81	
AN7	0.24	24h	26.0		121
BN1	0.40	10 seconds	78.5	89	
BN3	0.40	10 seconds	94.5	103	
BN7	0.40	10 seconds	96.0		140
CN1	0.38	120 seconds	20.0	98	
CN3	0.38	30 seconds	48.5	124	
CN7	0.38	10 seconds	47.0		141

In the fig. 2 there is diffraction pattern which shows the comparison of the particular glasses. The patterns show that the gehlenite type glasses are considerable different from the melilite glasses based pastes. In case of melilite pastes, the C-S-H phase is dominant, and the increase in the activator concentration causes the increase in amount of crystalline C-S-H and hydrotalkite ($Mg_6Al_2CO_3(OH)_6{\cdot}4H_2O$) phases. The dominant phase in case of the gehlenite type glasses is the C-A-S-H phase, mainly as the crystalline stratlingite ($Ca_2Al_2SiO_7{\cdot}8H_2O$).

Tab. 7. Setting times, flexural and compressive strengths of particular samples with MK addition

Designation	Water-cement ratio	Setting time	Compression strength After 28 days[MPa]	Heat of hydration, Q_{24h}, J/g
AMN1	0.24	24h	3.0	65
AMN3	0.24	24h	22.0	96
AMN7	0.24	24h	27.0	122
BMN1	0.4	10 s	17.5	94
BMN3	0.4	10 s	10.0	118
BMN7	0.4	<10 s	11.0	156
CMN1	0.38	60 min	21.5	107
CMN3	0.38	45 min	21.0	132
CMN7	0.38	15 min	24.0	115

The amount of stratlingite is significantly higher in case of glass with the Al_2O_3/SiO_2 molar ratio = 1,2 (samples CN1, CN3 and CN7) than in 1,0 (samples BN1, BN3 and BN7). In both cases aragonite was observed as the carbonatization product of C-A-S-H phase, as effect of sample preparation.

After the MK addition (fig .3), the compressive strength has decreased. Such a large changes are probably caused by two factors. The rate of the hydration process is noticeably lower with MK addition. The MK has a very high specific surface, so there is a possibility of activator adsorption. The substances with highly developed surfaces have a high porosity level. Addition of that kind of substances is the reason of increase in the total porosity of samples. In this point, it is necessary to remember that the compressive strength has only got pictorial character for the sake of variable water/binder ratio and difficulty during samples preparation.
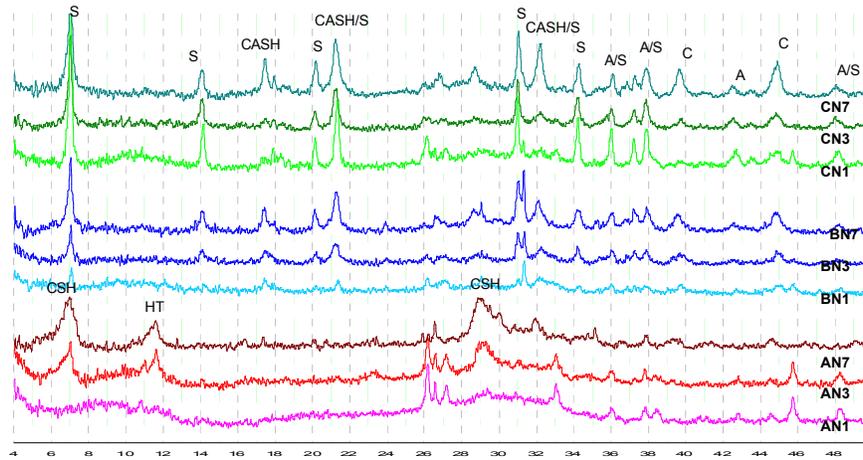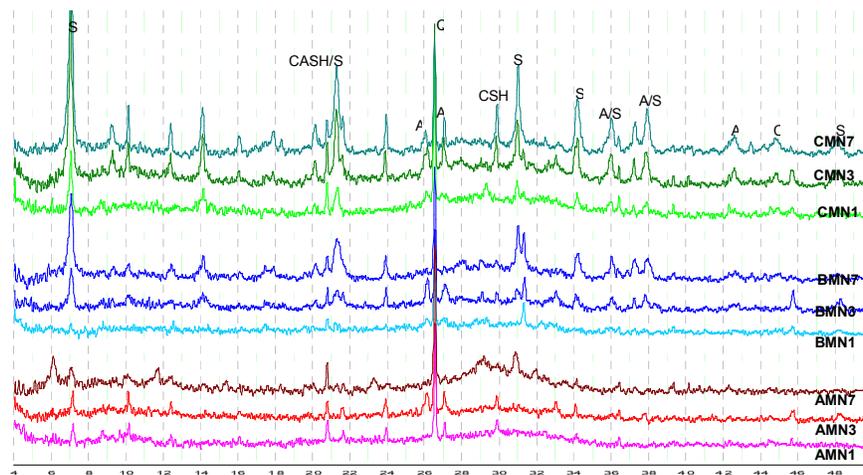
Fig. 2. Comparison of particular products of hydrtation without MK addition. Designations: A - aragonite ($CaCO_3$), C - calcite ($CaCO_3$), S - stratlingite ($Ca_2Al_2SiO_7 \cdot 8H_2O$), HT - hydrotalkite ($Mg_6Al_2CO_3(OH)_6 \cdot 4H_2O$)

Fig. 3. Comparison of particular products of hydration with MK addition. Designations: A - aragonite ($CaCO_3$), C - calcite ($CaCO_3$), S - stratlingite ($Ca_2Al_2SiO_7 \cdot 8H_2O$), HT - hydrotalkite ($Mg_6Al_2CO_3(OH)_6 \cdot 4H_2O$)

The analysis of XRD patterns shows that some zeolite phases were formed. In comparison with the patterns of pastes without MK addition, it is noticed that some zeolite phases are probably formed at the cost of stratlingite. The confirmation of that fact can be IR

analysis (fig. 4), where fading of band in ~540cm^{-1} is observed. The MK addition has a significant influence on the hydration process and on the final hydration products. It looks like that the MK, as a very highly developed surface substance, adsorbs significant amount of the activator, because the process of hydration hardly proceeds with low activator concentration.

With 7,5M activator, the hydration process proceeds with reliable delay. It looks like that after violently adsorption, the further process procee ds through the diffusion. At last, with 15M activator concentration, the rate of hydration process is comparable to the hydration without MK addition.

The SEM analysis (Fig. 6 – 11) shows that in case of MK addition use, the products obtained are rich   in very fine-crystalline phases. Highly developed surface of the MK caused formation of very fine-crystalline or amorphous products. The XRD analysis (Fig. 3) shows a lot of crystalline products. In SEM pictures some crystalline phases are observed with high magnification (Fig. 12).
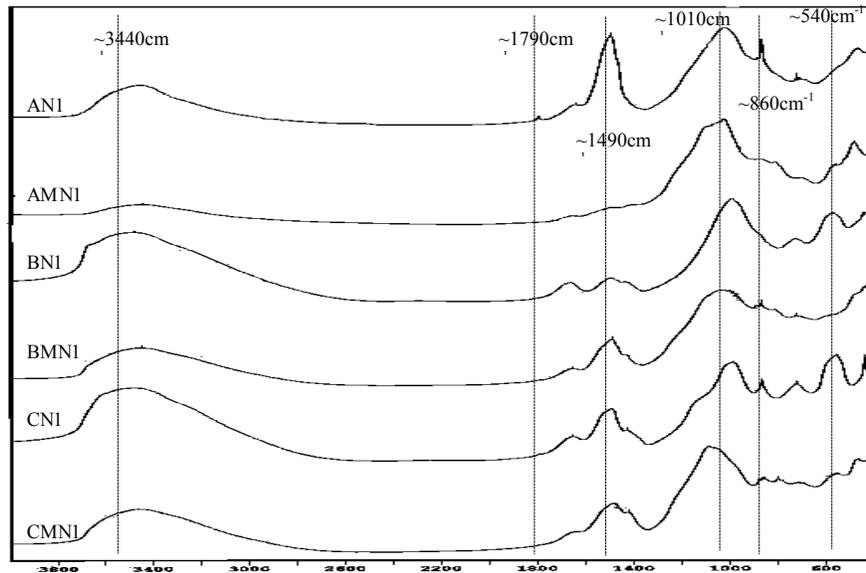

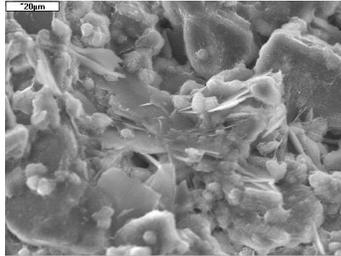Fig. 4. The IR spectrogram of particular samples
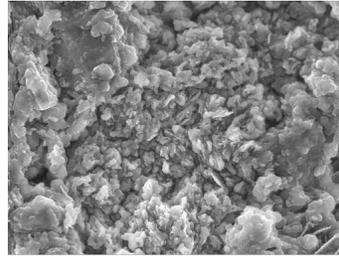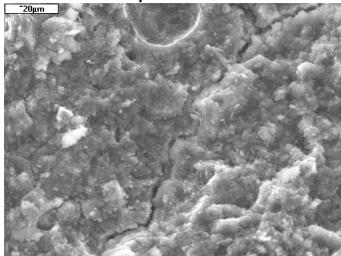
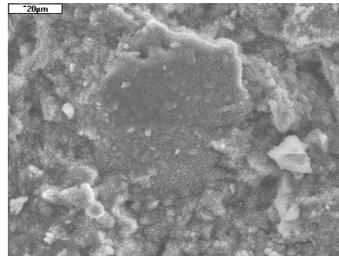Fig. 6. AN3 sample

Fig. 7. AMN3

Fig. 8. BN3 sample

Fig. 9. BMN3 sample
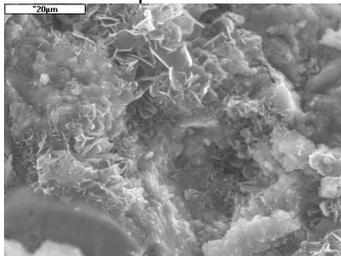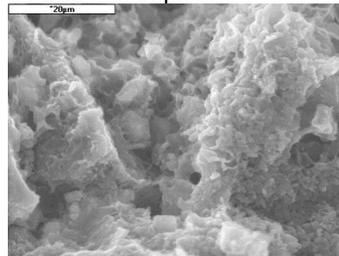

Fig. 10. CN3 sample

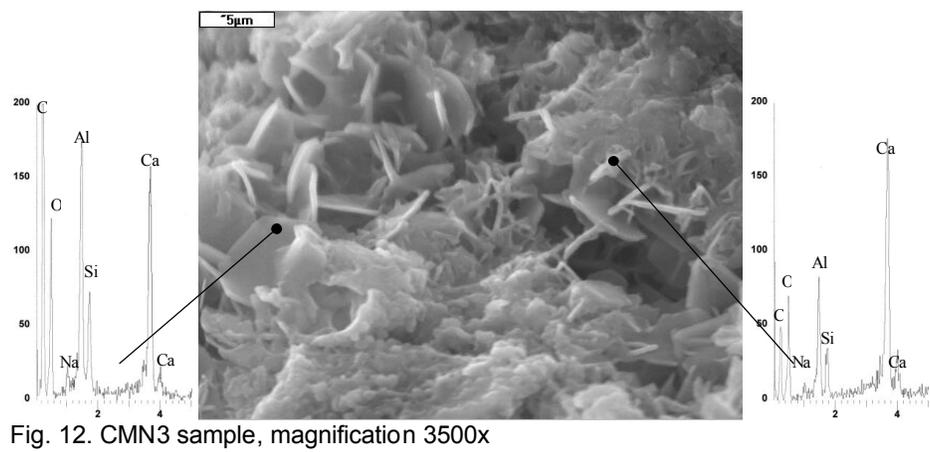Fig. 11. CMN3 sample

Fig. 12. CMN3 sample, magnification 3500x

3. Conclusions

The influence of Al_2O_3/SiO_2 molar ratio is significant. The differences in the rates of hydration and also in the kind of hydration products were observed. When the amount of Al_2O_3 is higher, the crystalline phases are dominant. In case of lower Al_2O_3 amount, the gel phase is dominant – according to the XRD patterns and SEM analysis.

The MK addition has a tremendous influence on the rate of hydration process, and on the properties and kind of forming phases. The highly developed surface of MK, causes decrease of mechanical properties of the samples. The amount of very fine-crystalline products of hydration is higher in this case.

The concentration of activator has a major influence on the rate of hydration process and amount of crystalline phases. The increase of concentration doesn't cause new phases formation. In case of pastes without the MK addition, more crystalline products with lower concentration of activator were observed. This fact is a result of rate of hydration process. With high concentrations, the rate of reaction is too high to form well crystallized phases. In case of the samples without MK addition and with 15M activator, the products were more amorphous then with 7,5M and 3,75M. In case of samples with MK addition, the products of hydration were rich in very fine-crystalline phases, and the crystallization level increased with concentration of the activator. High formation temperature of gehlenite glasses and necessity of using high activators concentration causes difficulty with using that kind of glasses as a bonding materials on the large technological scale. But there are some cases (in mines, injection pastes for the rock mass sealing, immobilization of hazardous wastes etc.), where using very expensive, extremely fast bonding and high strength materials is needed.

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