

# **Influence of the type and concentration of sodium alkaline activator on the hydration process of blast furnace slag**

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## 1. Introduction

The importance of so-called alkali activated slag (AAS) has been increasing over the past few dozen years [1-5].

Alkali activated slag is mixes of ground slag and the alkali activator which is introduced during the slag grinding - or (a method applied more frequently) during the mixing of paste, mortar or concrete components. Apart from classical solutions, which are based on the alkaline activation of granulated blast-furnace slag, there are also production technologies utilising other slags with a high degree of vitrifications (e.g. post-copper slags, granulated phosphoric slag) [3]. The back ground of the alkaline activation of granulated blast-furnace slags as presented by Kühl [6] as early as in 1907, and subsequently developed by Purdon [7] in 1940. This research did not, however, results in the industrial application of the above method; the foundations for the development of slag-alkaline binding material production technologies were developed in Gluchowski's works [1, 8]. His works, published in the nineteen fifties and sixties, helped to advance the production technology of clinkerless slag-alkaline binding materials and led to the industrial production stage [8].

In recent years, a relatively small energy consumption required for the production of slag-alkaline binding materials, as well as their considerable strength and excellent corrosion resistance, have made them a very attractive subject of research, resulting in the development of numerous interesting practical applications [2, 3, 5]. The large-scale research started among others in the USA, Canada, the Netherlands, and Australia – it turned out that these materials may play a significant role in the process of utilising numerous noxious industrial waste.

Although alkali activated slag binders have already been the subject of many papers, the description of the phase composition of hydrating slag-alkaline pastes gives rise to numerous difficulties resulting from the amorphous form of products. Numerous research projects have shown that irrespective of the alkaline activator used, the main product of hydration is hydrated calcium silicate (C-S-H) with a low C/S ratio, which comprise as much as 70% of the volume of all hydration products. For alkali activated slag binders, this numerous binders phase remains amorphous even after long maturing periods and usually has the form of a compact gel (type IV of the C-S-H phase according to Diamond's classification) [2, 9-11].

Furthermore, the presence of  $C_4AH_{13}$  (AFm type phase),  $C_2ASH_8$  and hydrotalcite in hydrating pastes has also been confirmed [14]. There are

still certain discrepancies concerning the possibility of appearance of zeolites among the products of hydration. Gluchowski [1, 6], Krivenko [3] and Davidovits [12] have pointed out on numerous occasions the presence of natrolite, analcime and other similar minerals in hydrating slag-alkaline pastes. This has not been confirmed by the research conducted by Wang and Scrivener [9]. The most recent research [13] indicates that the formation of zeolites requires the appropriate chemical composition of slag or the modification of the bath by additives which leads to a system with a relatively high Al/Si ratio and a correspondingly low Ca/Si ratio. The process of zeolite formation is facilitated by conditions of increased pressure and temperature. This has been confirmed by the works of Brylicki, Małolepszy and Deja [15].

## 2. Experimental

In order to enable a comprehensive presentation of the properties of AAR pastes, we have carried out the research of two types of industrial granulated blast-furnace slag activated by  $\text{Na}_2\text{CO}_3$ , sodium water glass or NaOH. The slags used in the research differed considerably as regards  $\text{Al}_2\text{O}_3$  and MgO content, which exerted a significant influence on their hydraulic activity. The properties of slags have been presented in Table 1.

Table 1. Properties of granulated blast-furnace slags

Type of slag	Chemical composition, % by mass						Glass content %	Specific surface $\text{m}^2/\text{kg}$
	$\text{SiO}_2$	CaO	$\text{Al}_2\text{O}_3$	MgO	$\text{Fe}_2\text{O}_3$	$\text{Na}_2\text{O}_{\text{eq}}$		
ZA	35.28	40.02	12.89	8.23	0.23	1.14	95	475
ZK	38.73	45.90	8.18	4.33	0.90	1.22	90	410

Slags were activated by a 5% addition of  $\text{Na}_2\text{CO}_3$ , a 15% addition of water glass with  $M_k = 1.5$ , or a 5 M NaOH solution (27% addition). The properties of pastes were examined after 2 and 28 days of curing in natural conditions ( $20 \pm 2^\circ\text{C}$ ,  $\text{RH} \geq 95\%$ ). Additionally, pastes after heat treatment were also examined ( $180^\circ\text{C}$ , 24 h).

Therefore in the present paper, following designations were used: ZA, ZK – type of slag; NC – activation by sodium carbonate, SW – activation by water glass, 5M – activation by a 5-mole NaOH solution; 2, 28 – time of curing samples in natural conditions, H – samples subjected to heat treatment.

In presented research, the mineral composition of hydrating pastes was determined by means of the following techniques: XRD, ESEM, SEM(EDS) and Nuclear Magnetic Resonance.

## 2.1. XRD analyses

On Figures 1-4 XRD patterns of slags and pastes activated by  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$  are presented. The tests confirmed that independent from the type of slag and activator highly amorphous C-S-H(I) phase is dominating product of activation (very broad peak for  $d=0.307\text{nm}$ ). In the case of samples activated by sodium carbonate  $\text{CaCO}_3$  is also present between the hydration products (CC peaks on XRD patterns).

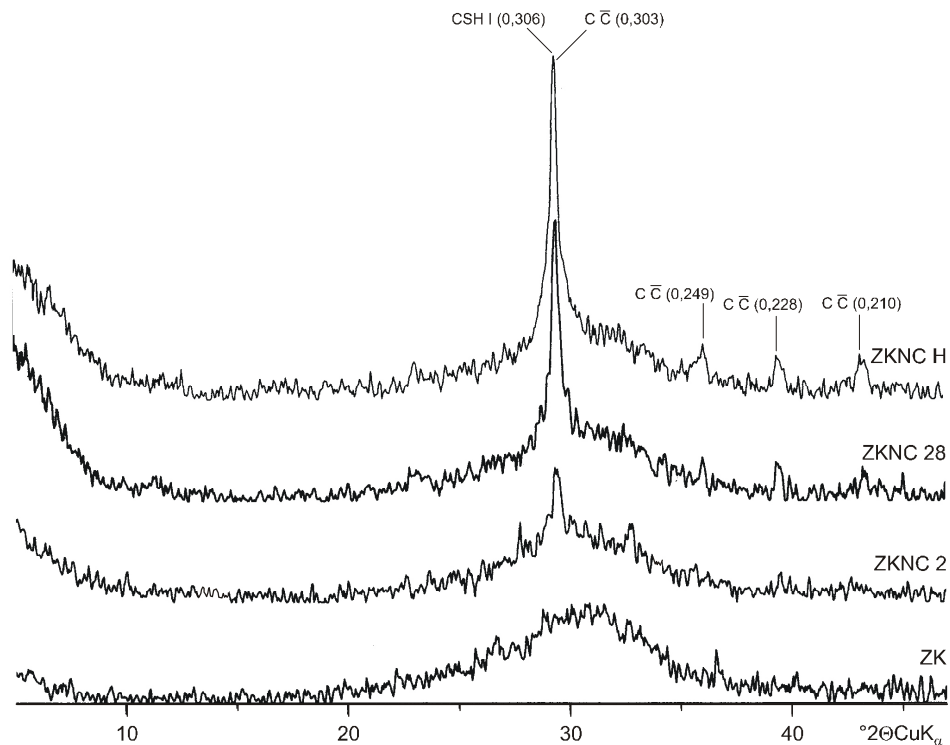


Fig. 1. XRD patterns of ZK slag and pastes activated by  $\text{Na}_2\text{CO}_3$ .

For higher concentration of alkaline activator ( $\text{NaOH}$ ) presence of hydrotalcite is detected (HT,  $d=0.764, 0.386, 0.256$  and  $0.228\text{nm}$ ).

The use of average concentration of alkaline activator (water glass) leads to the presence of high amounts of amorphous C-S-H(I) phase, but hydrotalcite was not detected.

It is also well visible that high content of  $\text{MgO}$  in the slag (even 8.23%) is not the only factor of hydrotalcite formation – high concentration of alkaline activator is decisive. Hydrothermal curing of the pastes causes in

destruction of hydrotalcite (reduction of 0.764 peak) and formation of additional amounts of C-S-H(I) and tobermorite.

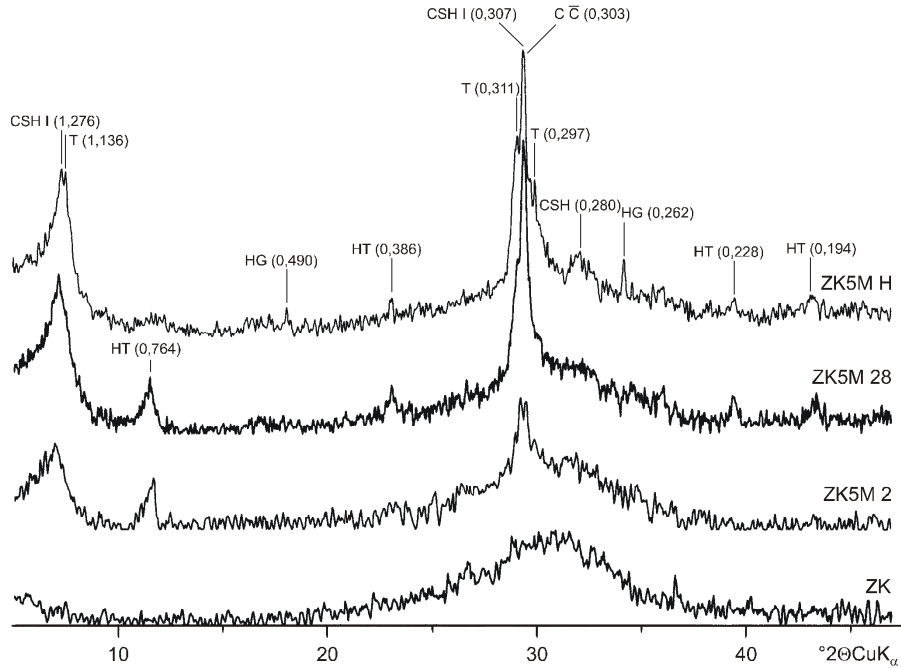


Fig. 2. XRD patterns of ZK slag and pastes activated by 5M NaOH.

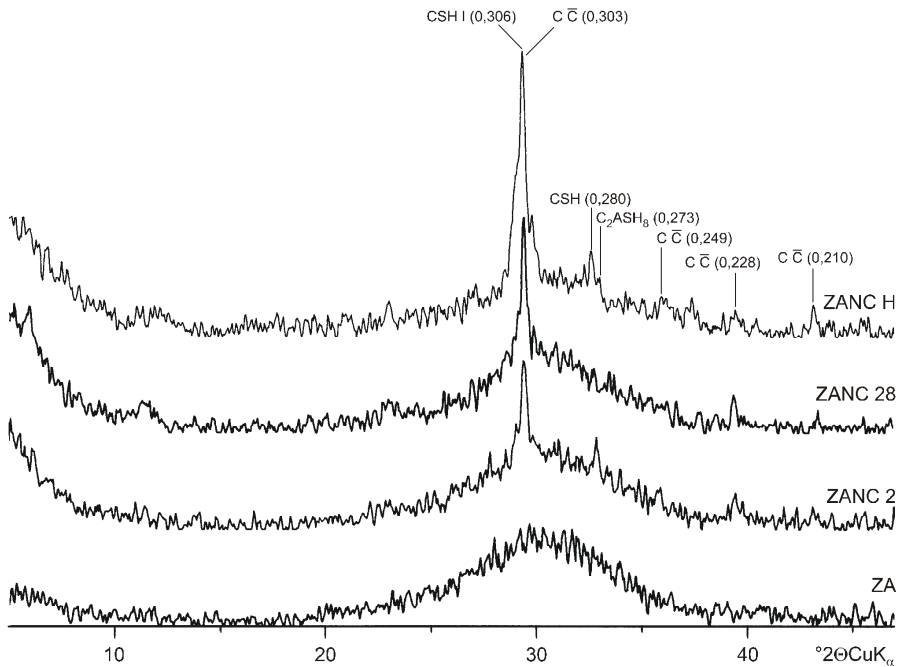


Fig. 3. XRD patterns of ZA slag and pastes activated by  $\text{Na}_2\text{CO}_3$ .

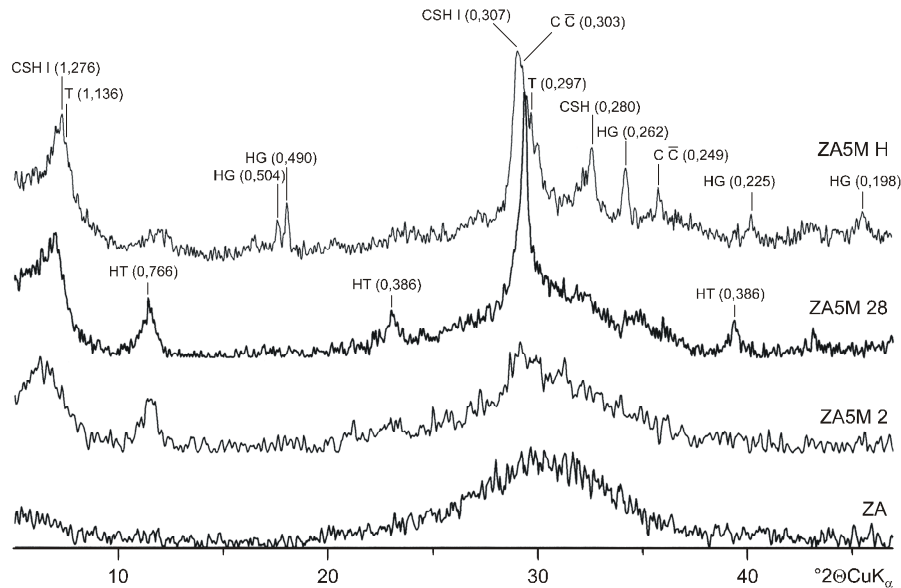


Fig. 4. XRD patterns of ZA slag and pastes activated by 5M NaOH.

## 2.1. Scanning Electron Microscopy

The ESEM observations confirmed that in the initial period of hydration, under the influence of the activator solution, a C-S-H phase with a very low C/S ratio, rich in sodium, aluminium and magnesium, starts to form on the surface of slag grains. The quantity of this C-S-H phase increases considerably when water glass or NaOH is used. The time of hydration impacts the C/S ratio in the C-S-H phase and the Na, Al and Mg content only slightly. This becomes evident when EDS analyses in microareas of samples over a period ranging from 24 hours to 90 days of hydration are compared (Fig. 5).

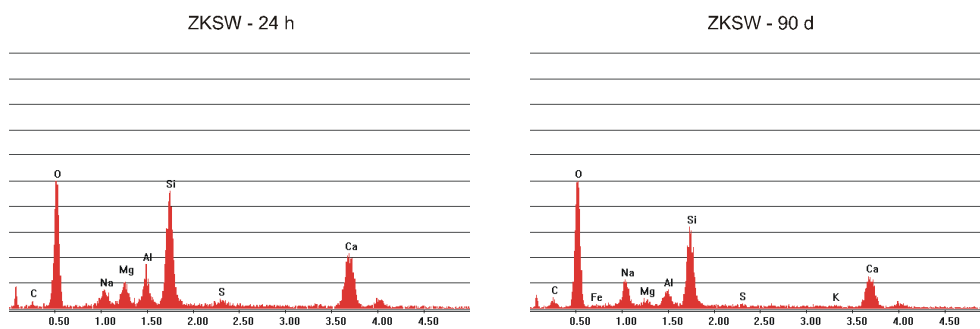


Fig. 5. Analyses in average microareas of samples ZKSW (ESEM + EDS)

Using SEM (EDS) technics the detection of hydrotalcite was not possible. It confirms the results presented by Wang and Scrivener [9] who concluded that hydrotalcite forms very small crystals ( $< 1\mu\text{m}$ ) dispersed in C-S-H phase. Taking into account the EDS results of numerous set of points for C-S-H phase of paste A activated by sodium hydroxide, relationship  $\text{Mg}/\text{Ca} = f(\text{Al}/\text{Ca})$  was prepared (Fig. 6).

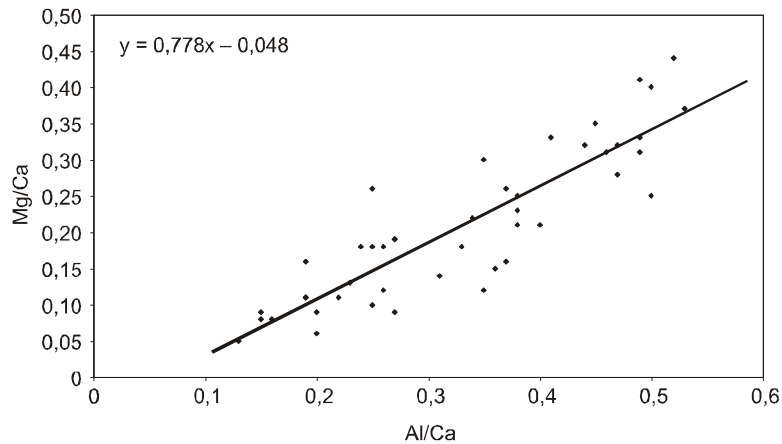


Fig. 6. Relationship  $Mg/Ca = f(Al/Ca)$  for ZA5M 28 paste.

Assume that Mg and the part of Al are bounded in hydrotalcite, it is well visible that significant part of Al ions is located in C-S-H phase. Extrapolation of the plotted line to the value  $Mg/Al = 0$  leads to the conclusion that C-S-H gel contains 6-7% of Al ions. It is in good relation to the results obtained by Richardson and Groves [17].

### 2.3. Nuclear Magnetic Resonance examinations

Using the NMR (Nuclear Magnetic Resonance) technique to analyse the  $^{29}\text{Si}$  spectrum, Schneider et al. [16] confirmed the occurrence in slag-alkaline pastes of the C-S-H phase of the structure close to the model proposed by Richardson and Groves [17-19] and Kersten [20], characterised by the occurrence of a chain structure in which the arrangement of chain elements is repeated at every fourth tetrahedron. This is a characteristic element of the structure of numerous calcium silicates and is known as dreierketten; it is linked to the cationic substructure, and thus to the octahedral oxygen-calcium layer. The two side elements are coordinated directly with the octahedral layer while the middle tetrahedron remains outside. It is precisely this tetrahedron that participates in establishing a bridge between neighbouring octahedral layers [21].

On the basis of measurements of chain average length Schneider [16] concludes that the C-S-H phase in AAR pastes there is a considerable polymerisation of silicon-oxygen tetrahedrons. In the presence of a large quantity of the activator, the degree of polymerisation is so considerable that a great number of chain units longer than octamers occurs in the C-S-H phase (pentamers with a certain quantity of octamers dominate in typical Portland cement and slag cement pastes).

NMR examinations also provide important information on the occurrence of  $\text{Al}^{3+}$  ions in the structure of hydrates [16].

If we assume that a considerable part of  $\text{Si}^{4+}$  ions in bridging tetrahedrons is replaced by aluminium, the presence of a large quantity of  $\text{Na}^+$  ions

incorporated in the C-S-H phase is balancing the charge. This has been confirmed by the research carried out by Nocuń-Wczelik [22].

Taking into consideration the considerable possibilities of NMR in structural researches and the numerous questions concerning the characteristic of products of the hydration of AAR, an attempt has been made to apply this method to the study of ZA and ZK slags and their pastes. MRJ impulse spectrometer of Bruker equipped with a 7T superconductive magnet and a probe, with the sample spinning at a magical angle (MAS) was used. MAS-MRJ spectra were measured of  $^{29}\text{Si}$  (frequency of 59.517 MHz, sample spinning frequency of 4 kHz) and for  $^{27}\text{Al}$  (frequency of 78.066 MHz, sample spinning frequency of 8 kHz). The  $^{29}\text{Si}$  MAS-NMR spectra of initial slag samples contain a broad line at (-80) ppm, which is characteristic for amorphous silicate, covering a range typical for silicon-oxygen anions type  $\text{Q}^1$  and  $\text{Q}^2$  (end and middle tetrahedrons in the chain structure).

Due to the amorphous (vitreous) nature of slags, the splitting of these bands does not occur. Neither do the spectra indicate any presence of a three-dimensional structure ( $\text{Q}^4$ ), cross-linking ( $\text{Q}^3$ ), or isolated tetrahedrons ( $\text{Q}^0$ ). For selected pastes, ZA slag of  $^{29}\text{Si}$  MAS-NMR spectra were measured (Fig.7).

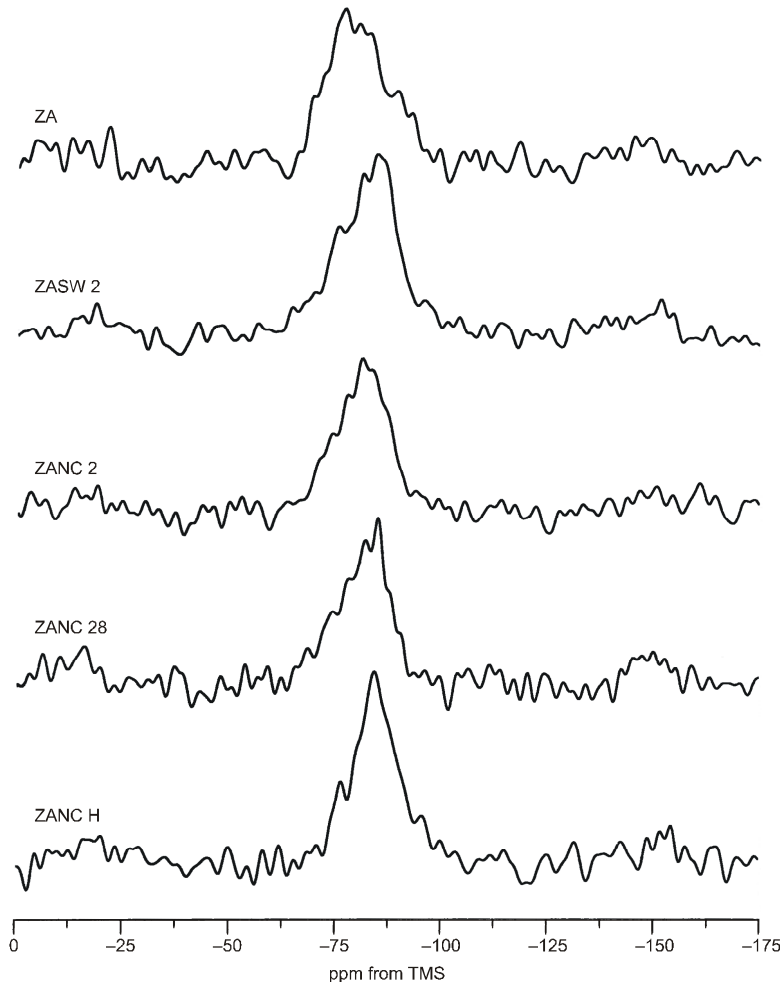


Fig. 7.  $^{29}\text{Si}$  MAS-NMR spectra of alkali-activated ZA slag

The paste spectra correlate very closely with the spectra of slag. There is no visible splitting into individual bands, nevertheless peaks become prominent and shift towards an increase in the share of  $Q^2$  anions, which corresponds to the disintegration of silicate-type glass and the appearance of a larger number of chains, most probably constituting a part of the C-S-H structure. In the case of materials subjected to autoclaving or hydrated for 28 days, band peak becomes more sharpened and shifts towards a range corresponding to  $Q^2$ ; this may be explained by the increase in the chain-like quantity of the product, and also by the increase in the length of chains. As in the case of the initial material, the presence of a three-dimensional structure ( $Q^4$ ), cross-linking ( $Q^3$ ) or isolated tetrahedrons ( $Q^0$ ) was not found. The spectroscopic image of the oxygen-silicate sublattice of hydrated slag appears to be more uniform than in the case of the synthesis of C-S-H type hydrates from silicate gel and calcium hydroxide [22]. The product of slag hydration is monostructural having principally chain structure. It may be assumed that in the further development of the structure, the formation of ribbons through cross-linking, in the aluminium-oxygen tetrahedrons participate.

The  $^{27}\text{Al}$  MAS-NMR spectra of slags correspond to the entirely amorphous phase, with the predominant tetrahedral coordination of aluminium. The process of hydration with activators leads to the appearance of aluminium in an octahedral configuration. Thus, all hydrated samples contain aluminium in both the tetrahedral (peak at approximately 60 ppm) and octahedral (peak at a location of approximately 5 ppm) coordination. The percentage share of octahedral aluminium changes and can be estimated, the information of which has been provided in the breakdown of spectra. These spectra have been presented in Figures 8 and 9.

The increased share of the octahedral configuration of aluminium must definitely be indicative of the formation of a product with a composition similar to that of hydrotalcite ( $[\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2](\text{CO}_3)_{0.125}(\text{OH})_{0.5}$ ). The extension of the time of hydration, as well as of autoclaving, leads to a considerable decrease in the share of aluminium in the octahedral configuration [5].

It would seem that during the hydration process aluminate ions are in the liquid phase and forms two types of products:

- aluminate anions with a tetrahedral coordination which replace silicate anions in the C-S-H phase (the presence of sodium ions ensures charge compensation),
- anions with an octahedral coordination form separate phases (hydrogranates, hydrated carboaluminates, and the previously mentioned hydrotalcite).



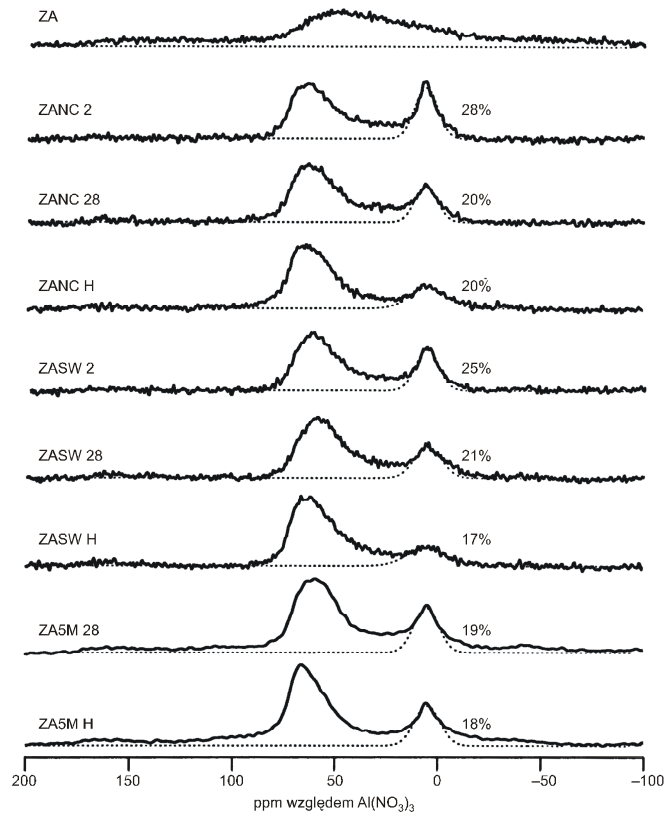


Fig. 8.  $^{27}\text{Al}$  MAS-NMR spectra of alkali-activated ZA slag

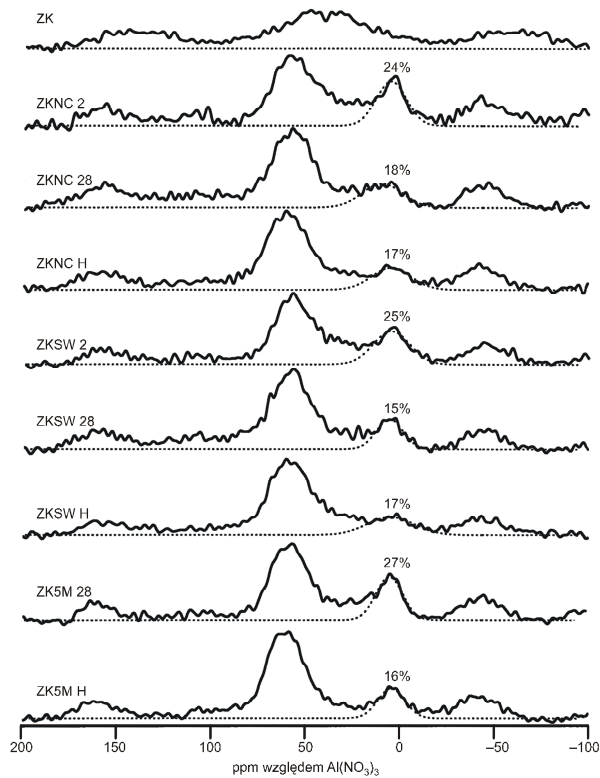


Fig. 9.  $^{27}\text{Al}$  MAS-NMR spectra of alkali-activated ZK slag

One may mention that for both slags, of which the ZA slag contains nearly 13% of aluminium oxide while the ZK slag approximately 8% of  $\text{Al}_2\text{O}_3$ , the shares of the octahedral configuration are more or less similar. After two days of hydration, this totals at most (approximately) 25%, while after 28 days the content decreases by a further few percent. The same or slightly lower values have been determined for autoclaved samples, while in this case the shape of the bands – very broad – additionally indicates that the structure of phases with octahedral configuration is disordered. However, certain differences can be noted, and these may point both to the influence of the quantity of aluminium oxide in slag glass, and the mechanisms that most probably influence the operation of used activators. It would seem that the relative increase of the share of alumina in tetrahedral coordination, together with an extension of the hydration time, is a simple consequence of increasing the quantity of aluminium incorporated into the C-S-H phase due to the advancing disintegration of slag glass which is subjected to the influence of sodium ions. In turn, hydrothermal conditions do not facilitate the crystallisation of phases containing aluminate ions; on the contrary - they facilitate the deterioration of the silicoaluminate network of glass with the formation of a C-S-H phase in which silicon is replaced with aluminium, which supports the formation of a tobermorite structure. The examinations of samples after 28 days of hydration at a temperature of 20°C indicate that in the case of ZK slag activated with a 5M solution of NaOH there is a considerable relative increase in the share of aluminium in the octahedral configuration which points to an increase in the share of hydrotalcite at the expense of aluminium in the C-S-H. Spectra of hydrated ZA slag samples do not show the relative increase in the share of aluminium-oxygen octahedrons at the expense of tetrahedrons, although this does not mean that the content of these phases is lower than in the case of ZK slag. In this instance, the bands are clearly sharp and narrower. Such a band shape testifies the greater order of the structures formed - and in particular of those formed in the autoclaving process [5]. It is also worth noting that the results obtained for both series are similar (as a function of the time and conditions of the hydration process), irrespective of the activator used.

### 3. Conclusions

On the basis of the results the following conclusions can be made:

- the increased time of slag hydration, as well as the application of thermal treatment, leads to an increase in the share of silicate chains in the structure of the C-S-H phase and an extension of their length. This points to the increased ordering of the phase structure, leading towards a tobermorite structure.
- aluminate ions occur in the structure of the C-S-H phase in the form of tetrahedrons replacing anions  $[\text{SiO}_4]^{4-}$ .

- aluminium ions also form separate hydrated phases (hydrogranates rich in silicate anions, hydrated carboaluminates), in which their coordination number of 6.
- increased hydration time leads to a relative decrease the share of aluminium in the octahedral coordination, replaced by aluminium in tetrahedral units in the structure of the C-S-H phase. Research of the author - not presented in this work - has shown that the amorphous C-S-H phase in AAS binders contains approximately 6-7% of aluminium.
- the formation of phases rich in magnesium is determined primarily by the quantity of the alkaline activator. It was established that with increasing addition of activator ensuring a content of Na<sub>2</sub>O in the binding material in excess of 4%, the paste contains hydrotalcite Mg<sub>6</sub>Al<sub>2</sub>CO<sub>3</sub>(OH)<sub>16</sub>·4H<sub>2</sub>O. However, no measurable differences were determined in the hydrotalcite content with different MgO content in slag, namely 4.3 and 8.2%. It is highly probable that a part of the magnesium ions forms solid solutions in the C-S-H phase. The confirmation of this conclusion is difficult because hydrotalcite usually forms nanometric mixtures with C-S-H phase.
- the results of ESEM examination have confirmed that in the initial period of hydration, under the influence of the activator, a C-S-H phase with a very low C/S ratio, rich in sodium, aluminium and magnesium, starts to form on the surface of slag grains. The quantity of C-S-H phase formed increases considerably when a greater concentration of the activator is used. The C/S ratio in the C-S-H phase and the content of Na, Al and Mg therein change only slightly as hydration proceeds.
- the presence of zeolites has not been determined in classical AAS pastes. Their formation is possible only for slags with a low C/S ratio and simultaneously high A/S ratio. Increasing hydration time or heat treatment facilitates the formation of these phases.

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