New Binder for Refractory Castables

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The possibility of increasing the hydraulic activity of CA_2 phase through applying solid solutions of some alkali- and alkaline-earth metals as well as iron and silicium has been examined. Results have shown that their influence on the CA_2 reaction with water is insignificant. However, a small amount of CA in CA_2 samples greatly accelerates the CA_2 hydration. The application of calcium hydroxide solution as mixing water gives also good results.

1 Introduction

A shift from the use of shaped refractories to monolithics has been observed for many years [1]. This approach is simultaneously related to the application of calcium aluminate cements (CAC), which contain a large amount of Al_2O_3. It is common practice in order to increase the cement refractoriness. The production of CAC with high alumina content is difficult; therefore, several producers of these cements make mixtures of alu-
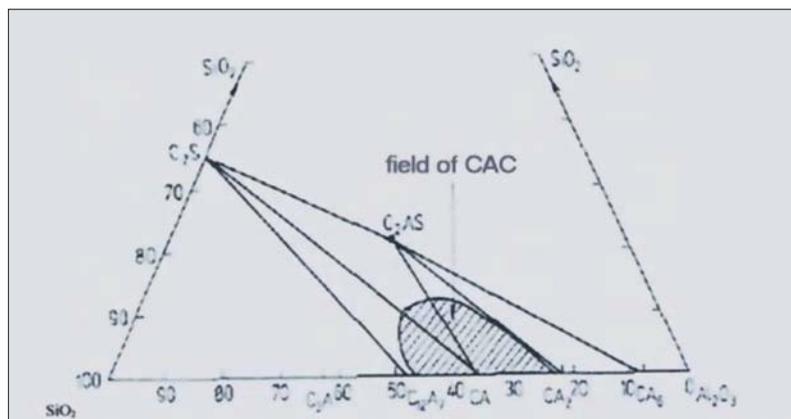
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Fig. 1 The field of CAC in CaO-Al_2O_3 system

minate cement with aluminium oxide so as to increase its content in this product.

In the system CaO–Al_2O_3 there are several phases with high hydraulic activity, nevertheless only mono-calcium aluminate is used in CAC production. However, no method has been invented, which increases hydraulic activity of two phases with greater Al_2O_3 content (namely CA_6 and primarily CA_2 that contains 78,5 % of aluminium oxide). This phase could be used in high alumina cement production as it has higher hydraulic activity at ambient temperature.

The reason for low hydraulic activity of CA_2 is not clear. The thermodynamic analysis of CA_2 reaction with water shows that the free enthalpy of this reaction is significant (273 kJ/kg) and much greater than in case of CA (194 kJ/kg), which is the phase with very good hydraulic properties [2]. *Taylor* [3] claims that the probable reason for a slow calcium bialuminate reaction with water is related to covering the surfaces of crystals by means of hydration products, chiefly of aluminium hydroxide. The explanation of this problem requires research.

Little is known about CA_2 capabilities of isomorphic replacements and their influence on hydraulic properties. Nevertheless, there is a common belief that a specific surface increases and the presence of phases, which quickly react with water, for example CA or $C_{12}A_7$, significantly accelerate the reaction of

CA_2 with water [4]. On the other hand, even in this case after several months of curing, a significant amount of this phase can be detected by the use of X-ray [4].

In the technical literature only a few studies on CA_2 hydraulic properties and attempts to improve hydraulic activities of CA_2 can be found [4, 5]. To control setting additions, for example by using lithium salts [5], or specific heat treatment are applied. In India, the HAC with good properties is produced and contains about 76 % of CA_2. It is also applied as one raw material component, namely calcium hydroxide instead of limestone [6]. This cement has a small content of admixtures and apart from CA_2 and CA (of 22 % content) it has only 2 % of other phases including $C_{12}A_7$ [6].

The aim of this research is to study the influence of chosen minor components on the hydraulic properties of CA_2. The influence of mixing water pH on hydration of CA_2 samples and on physical properties of hardened pastes has been examined.

2 CA$_2$ phase

The phase composition of CAC can be evaluated on the basis of their field in three components CaO–Al_2O_3–SiO_2 system depicted on Fig. 1. Their main component is CA, regardless of chemical composition, which can be variable. In case of cements with high refractoriness, with high alumini-
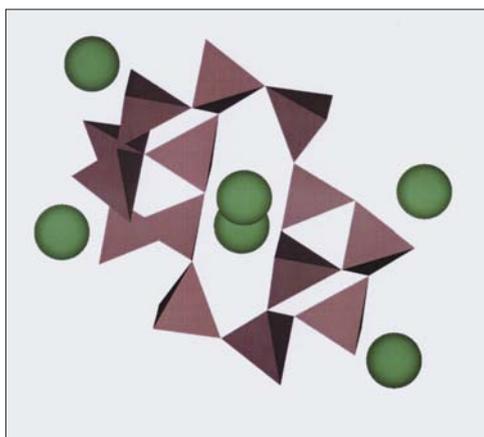
Fig. 2 The structure of CA_2

Fig. 3 The system $CaO - Al_2O_3$

um oxide content (even in the range of 80 %), the content of other phases is low. But it is an interstitial material which contains Fe^{3+} cations with the simplified formula $Ca_2(Al_xFe_{1-x})_2O_5$ [7]. The white interstitial material contains Fe^{2+}, and its composition is very complicated. It is admitted close to $23\ CaO \cdot 13\ Al_2O_3 \cdot 3\ FeO \cdot 3,5\ SiO_2$ [8].

In cements containing not more than 70 % of Al_2O_3 the main phase is CA, and CA_2 is present in small quantities [8]. The producers add corundum powder to cements high in alumina (used for production of high refractory castables) to obtain the desired properties. The cements produced in India, which have already been mentioned, are the exception [6].

The CA_2 phase was discovered by *Rankin* and *Wright* [9] and given the symbol C_3A_5. Later, *Tavasci* [10] found that it has a content corresponding to the formula CA_2. Two years later, this composition was confirmed by *Lagerqvist, Wallmark* and *Westgreen* [11]. CA_2 has a monoclinic symmetry and the elementary cell has the following dimension: a = 128,4 pm, b = 88,6 pm, c = 5,3 pm and belong to the space group C2/c [4].

In the CA_2 structure the alumina atoms are in a thetrahedra coordination by four oxygen

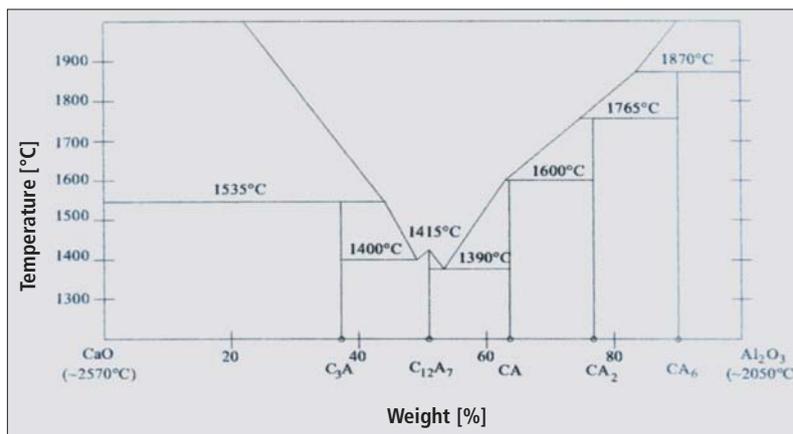(Fig. 2) and thetrahedra is linked in four or six-member rings.

The CA_2 is crystallized from the melt in forms of needles as well as pseudo-tetragonal crystals [12]. It has been established that CA_2 melts at (1762 ± 5) °C (Fig. 3), however, it was controversial if it melts congruently or incongruently. It has been found that it melts incongruently and decomposes into CA_6 and a melt is having in composition 22 % of CaO and 78 % of Al_2O_3 [4].

The calcium aluminates have different reactivity towards water, and therefore they have variable influence in a different manner on setting time of cement and the strength of the paste. The reactive phases have a high heat of hydration, which increases the cement paste temperature and accelerates the reaction with water of less reactive phases. $C_{12}A_7$ phase hydrates quickly and its content accelerates the setting of CAC. This aluminate causes quick hydrate crystallization, because the solution becomes oversaturated in relation to the hexagonal hydrates. The CA phase hydrates quickly, but the setting process runs with a moderate rate because of low nucleation of hydrates. In case of CA_2 the hydration is slow at ambient temperature. *Buttler* and *Taylor* [13] have established that CA_2 reacts at 5 °C very slowly with water and the reaction is quicker at higher temperatures and with the solution of higher pH. The CA hydration at ambient temperature can accelerate the reaction of CA_2 with water. In order to accelerate the reaction of CA_2 with water, it is recommended to increase its specific surface area and increase the temperature to 30 – 40 °C. On the basis of Buttler and Taylor's [13] results it can be expected that the presence of a

small amount of alkalis may also accelerate its hydration. *Rodger* and *Double* [14] recommend the application of lithium hydroxide, where cations play a role of heterogeneous nuclei for hexagonal hydrates which result from very quickly hydrated lithium aluminate precipitation.

3 The calcium bialuminate synthesis in pure form and with admixtures
3.1 Materials

The materials used for CA_2 synthesis were pure chemical reagents and only aluminium oxide was a commercial material, known as MR32. This material contains over 99,8 % of Al_2O_3 and is composed of very fine grains < 10 µm. The maximum on the grain distribution curve is at about 5 µm. The composition of all raw mixtures exactly corresponded to the stoichiometry of CA_2 and the additions of minor components were taken into account. In order to produce the homogeneous composition the samples were mixed for 24 h in water suspension and then dried at 70 °C. From the mixtures tablets were moulded under 10 MPa and fired at 1550 °C for 4 h. The firing was repeated twice, with intermediate grinding in a corundum mill.

No examples of research concerning solid solutions in CA_2 phase have been found, with the exception of Fe^{3+} solution [15]. Therefore, the isomorphism of C_3A was taken as an example. The basis for this approach has some similarities of both structures, principally the Na^+ location at the centre of the rings, formed of AlO_4 tetrahedra. It was not possible to choose the quantity of minor components so the constant addition

Tab. 1 Chemical composition of the phases in the sample with magnesium

Phase	Content of component [mass-%]		
	Al_2O_3	CaO	MgO
CA	65,0	33,4	1,60
CA_2	78,5	20,7	0,75
MA	71,7	1,2	27,1

Tab. 2 The content of minor components in solid solution at 1550 °C

Minor component	Phase and admixture content [mass-%]		
	CA	CA_2	CA_6
Na_2O[1]	0,48	0,40	-
K_2O	1,88	0,80	1,44
Fe_2O_3[2]	2,70	3,17	6,86
SiO_2[3]	-	7,90	0,77
SrO[4]	1,88	4,24	-
BaO[5]	-	2,03	-

1 – small content of the phase rich in sodium, 2 – addition of Fe_2O_3 equal 6,42 %, 3 – small content of gehlenite, 4 – addition of SrO 4,3 %, 5 – low content of phases rich in barium

was used, namely 10 g of alkali metals and alkaline-earth metal carbonates for 155,8 g of CA_2. It must be noted that the concentration of minor components in the aluminate phase will increase altogether with its content in the process of sintering [15]. For this reason, the addition close to saturation can cause the formation of minor components proper phases. In the case of their formation they can be used as examples for quantitative determination of minor components in the solid solution. The following admixtures were used: alkali metals – lithium, sodium, potassium; alkali-earth metals – barium, strontium, magnesium, and additionally iron and silicium. The last two were added as oxides.

Chromium, whose isomorphism with aluminium is known, was not used because the recent decisions concerning legal solutions related to the reduction of Cr^{6+} content rules (2 ppm) pose serious production problems and force producers to use special reducing agents.

3.2 X-ray samples phase composition

The results of X-ray analyses show that all samples contain at least two phases, with the exception of the sample with potassium, which was composed only of CA_2. The second phase was CA or CA_6. Therefore, the content of these secondary phases is very small, not exceeding 3 %. It is probably caused by the lack of liquid phase, which equals CA_2 in the mixture of composition and is formed at 1760 °C, thus at about 200 °C higher than the burning temperature. The formation of CA is the result of this tendency. The melting point of CA is approx-

imately 160 °C lower. Yet, the formation of CA_6 is not so clear; it can only be supposed that this phase is formed as a result of aluminate layer formation on the surface of aluminium oxide grains as a reaction product with CaO [17]. On the basis of balance results it can be deducted that if CA is formed, some amount of CA_6 must also be formed and conversely.

X-ray examinations have shown that the replacement of aluminium and calcium ions in the lattice by minor components causes the increase of elementary cell dimensions. This phenomenon was observed in case of iron, silicium, strontium and barium. This is shown in Fig. 4. All these cations have the radius greater than calcium (Ba and Sr) or aluminium (Fe). Only silicium has lower radius than aluminium, but the difference in valence causes the necessity of vacation formation or appearance of ions in intersticial positions. The largest change of volume was found for iron, whose content in CA_2 was high.

3.3 X-ray microanalyses

The observation of polished sections, prepared from all specimens after burning, were analysed by scanning electron microscopy SEM and X-ray microanalyses were conducted. By using these microanalyses the concentration of minor components were measured in calcium aluminates, chiefly in CA_2. The methods of specimen examination are shown through the example of calcium bialuminate with magnesium addition (specimen D1). Some other examples are also included, for instance, specimens in which minor phases were present. In other specimens only the content of minor components in solid solution is depicted in Tab. 2.

In Fig. 5 the picture of the polished section of specimen D1 is shown. It can clearly be seen that the specimen contains three phases. Small crystals of spinel MA were found (point 3) and two aluminate phases: CA (brighter micro-areas, on point 1) and CA_2 (darker micro-areas, points 2 and 5). The semiquantitative analyses and the results of X-ray microanalyses are presented in Figs. 6 – 8 and in Tabs. 1 and 2.

The content of magnesium in aluminate phases is:

Phase   Mg content as MgO
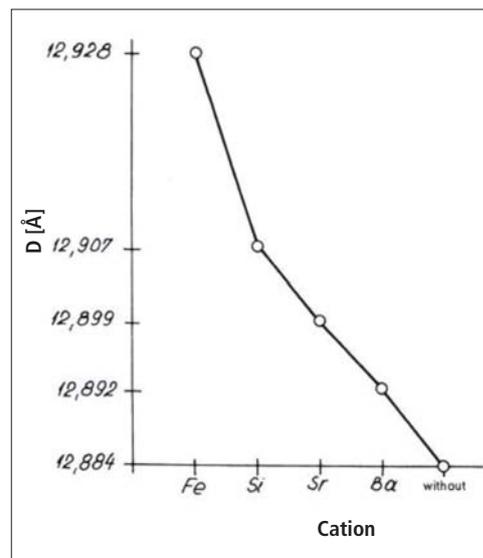CA_2 0,75 mass-%
CA   1,60 mass-%

Fig. 4 Change of lattice parameter caused by calcium and aluminium replacement

The magnesium content was corrected on the basis of spinel analysis. The content of all remaining examined minor components in solid solution is depicted in Tab. 2.

No lithium was found in the sample because it sublimates during heating. Lithium appeared to be a good mineraliser because this sample was practically composed only of CA_2 with an extremely small admixture of CA.

The sample with sodium addition was also composed almost exclusively of CA_2 with a very small admixture of CA. Sporadically, small inclusions of three component phases, which is sodium-calcium aluminate, were found.
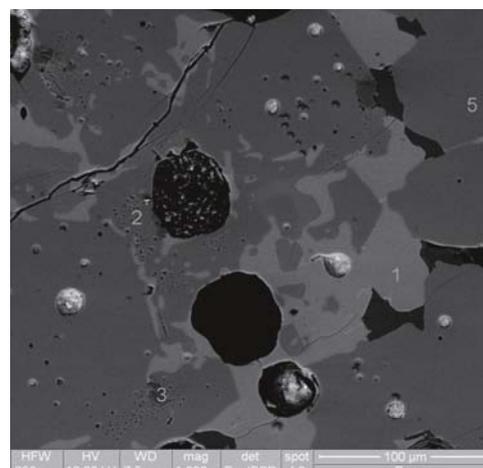

Fig. 5 Polished section of the fragment of D1 specimen with magnesium addition: darker micro-areas designed 2 and 5 CA_2, brighter micro-areas (point 1) of CA, dark crystal of MA (point 3)

Tab. 3 Microhardness of the pastes prepared of samples with different admixtures

Admixture	Microhardness [MPa]		
	After 3 d	After 7 d	After 28 d
Lithium	12,5	6,9	8,3
Sodium	18,5	24,6	42,7
Potassium	14,2	24,6	49,7
Silicium	4,6	9,4	14,8
Without admixture	9,6	9,6	36,3

Tab. 4 Microhardness of the pastes after 7 d of maturing

Admixture	Microhardness [MPa]
Potassium	22,4
Magnesium	65,9
Barium	33,2
Without admixtures**	09,7
Without admixtures*	62,7
Without admixtures**	9,1

*) X-ray detectable admixture of phase CA in burned specimens

**) X-ray detectable admixture of phase CA_6 in burned specimens

In the sample with potassium admixture a definite majority of CA_2 occurs, with a very small content of CA and CA_6. Also small particles of corundum were very seldom found. The specimen with iron has pseudotetragonal crystals of CA_2 with Fe^{3+} in a solid solution. The matrix is poorer in these cations, and pseudotetragonal crystals are richer. The content of this admixture in a solid solution in several calcium aluminate phases is also shown in Tab. 2. The results of the examination of the specimen with strontium admixture have shown that the solid solution of this minor component in CA_2 has 4,24 % of SrO. However, the content of strontium in CA_2 is higher, and even 4,57 % of SrO was found in some crystals of this phase. Yet, the content of strontium in CA is lower and the highest measured concentration was 1,88 %. In the specimen containing 6 % of SiO_2 a small admixture of gehlenite was detected by the use of X-ray. The content of silicium, calculated as SiO_2 is depicted in Tab. 2. The results of X-ray microanalyses of the specimen with BaO admixture indicate that the content of this cation is very changeable in CA_2 aluminate and is in the range from 0,7 % to 2,0 % of BaO. However, barium demonstrates a strong tendency for proper phase formation as barium aluminate or calcium-barium aluminate. The presence of both phases was proved in some specimens by means of X-ray diffraction.

4 Physical properties of pastes

The pastes were prepared from the fired samples with w/c ratio equal to 0,4 and the microhardness was measured by using Vickers' method. The results are presented in Tabs. 3 and 4.

In Tab. 4 the microhardness of pastes produced from fired specimens with a half of the quantity of admixtures is shown. The specimens contained lower addition of potassium, magnesium and barium.

The analysis of the results leads to several suggestions. The general observation is that the measured microhardness of the specimens is relatively good. The tested specimens can be divided into three groups. The specimens with potassium and sodium admixtures have a very good microhardness throughout the whole period when they were being examined. They have a very good hardness, and as a result the compressive strength just after two days and it is still increasing throughout the period of 28 d. The specimen with sodium has slightly better properties after two days, but after 7 d the microhardness of both samples is the same and after 28 d is higher for the specimen with potassium. Both specimens contain as a minor phase CA, which is known to have good early strength, but also after longer periods, i.e. after 28 d. In technical literature it was stated that the presence of CA phase in the paste accelerates the CA_2 hydration. Thus admixture of CA in cement very rich in CA_2 is a good technological method to accelerate its [4] hydration. These samples, which produce the paste with the best properties have small admixtures of sodium and

Tab. 5 Microhardness of the pastes

Sample	After 7 d		After 28 d	
	Microhardness [MPa]	Standard deviation	Microhardness [MPa]	Standard deviation
Water	5,5	1,4	7,6	2,0
VIa	8,1	1,2	9,6	1,7
VIb	9,3	1,4	7,2	1,1
VIc	5,1	0,7	6,8	1,5

potassium which also can have a positive effect on cement hydration, producing solutions with higher pH. The sample with magnesium shows the untypical behaviour, its microhardness is drastically decreasing after 7 d of maturing and then slightly increasing after 28 d. The explanation of this change needs further investigations.

The X-ray examination of paste phases composition after 7 d of hydration has shown that all the specimens contained high amount of unreacted CA_2 which were mainly hydrated hydrogarnet and aluminium hydroxide.

5 Hardening rate of CA_2 in mixing water solution of different composition

This experiment covered the sample without admixture, which was fired again at 1550 °C and heated at this temperature for 4 h. Its X-ray composition was as follows: CA_2 98,4 % and CA_6 1,6 %. The sample, after grinding to 400 m²/kg was mixed with the solution, which contained successively KOH [VIa], NaOH [VIb] and $Ca(OH)_2$ [VIc] in concentration of 1 mole of hydroxide in 1 liter of water. The w/c ratio was: for KOH 0,34, 0,39 for NaOH and 0,38 for $Ca(OH)_2$ and water. The pastes were moulded to have the dimensions 20 x 20 x 100 mm³ and the microhardness as well as bending strength were measured. The results are depicted in Tabs. 5 and 6.

The obtained results can be discussed in the following way. The solution of sodium an potassium hydroxide (increase of pH to 13,5) accelerates significantly the reaction of CA_2 with water and increases the bending strength after 3 and 7 d. However, after 28 d the strength decreases, which must lead to the destruction of specimens. It is probably related to the formation of water-soluble sodium and potassium aluminates. The strength of the samples, which mature in calcium hydroxide is systematically growing throughout the period of 28 d. This solution

could be applied in the production of refractory castables as mixing water.

X-ray examination of the phase composition of the pastes after 7 d of hardening in different solutions gave the following results:

• water – 62,4 % CA_2, 4,4 % CA_6, 33,2 % gibbsite

• VIa – 35,7 % CA_2, 2,1 % CA_6, 14,5 % hydrogarnet, 47,7 % gibbsite

• VIb – 43,8 % CA_2, 3,0 % of CA_6, 7,7 % hydrogarnet, 45,5 % gibbsite

• VIc – 43,2 % CA_2, 3,7 % CA_6, 53,1 % gibbsite.

The hydration acceleration in solutions of high pH can be clearly deduced from the phase paste composition. It correlates well with the measured microhardness and strength of the specimens. No X-ray detectable calcium aluminate hydrates were found in the samples hydrated by water and $Ca(OH)_2$. However, the presence of gibbsite is the proof that calcium aluminate hydrates must be formed in these pastes, probably in amorphous form.

6 Conclusions

The important conclusions, which can be drawn from the results of experiments, are the following:

• Synthesis can result in obtaining CA_2 with CA phase admixtures because it accelerates the hydration of CA_2. It is the simplest technological method, which can be applied in the production of high alumina cement; it assures high hydraulic activity.

• In the production of castables the solution of calcium hydroxide can be used as mixing water, or the addition of 2 – 3 % of active lime in relation to cement.

• The synthesis of CA_2 occurs only at high temperature, at about 1550 °C, and even at that temperature it is of the solid-state reaction. However, CA_2 can be formed at lower temperature, namely at 1400 °C, but this requires complicated technology, which consists in the hydration of CA or pure CAC rich in this phase with the addition of $Al(OH)_3$ and burning of the obtained hydrates.

• The phase CA_2 takes a small amount of minor ions in the form of solid solution, the exceptions being iron and strontium. This result can be predicted for both ions on the basis of previous research. It demonstrated that strontium substitutes calcium in several phases, and relatively
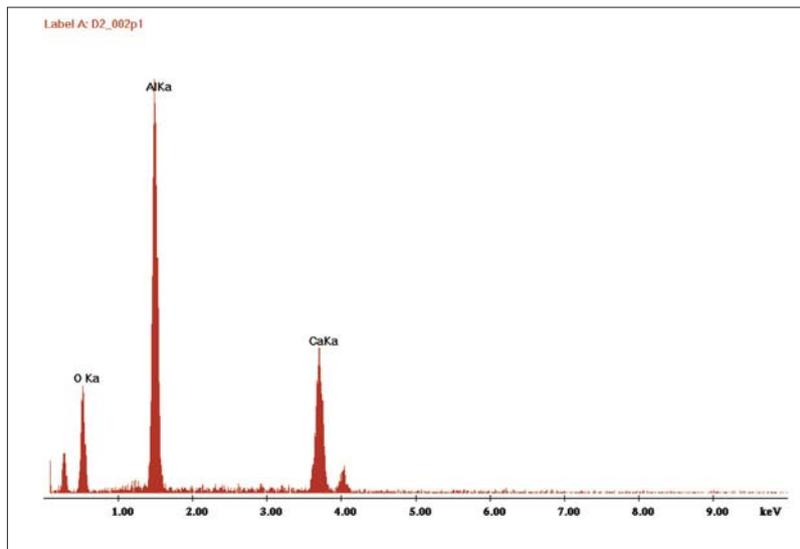

Fig. 6 Semiquantitative analysis in point 1 of D1 sample; analysis corresponds to CA
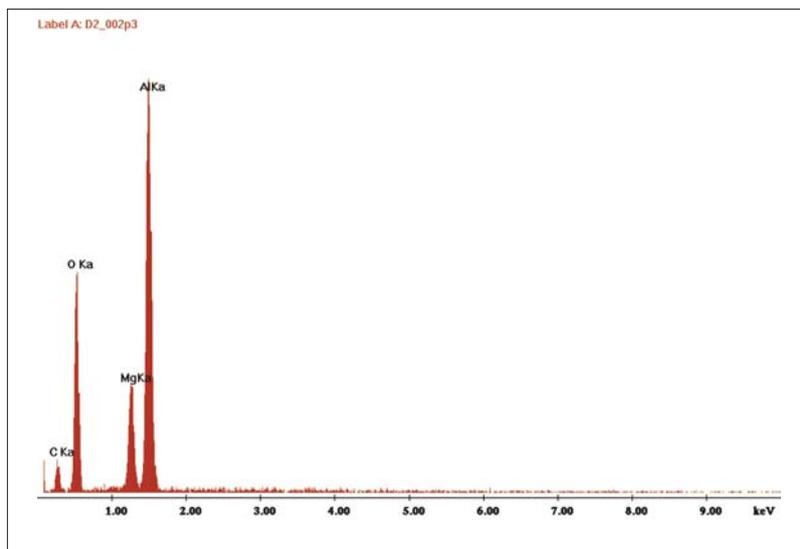

Fig. 7 Polished section of D1; SEM analysis in point 3 of the MA crystal

rarely forms its own phases. However, the iron tendency to replace aluminium in different compounds is well known, particularly in the $CaO – Al_2O_3 – Fe_2O_3$ system.

• The admixtures, which were tested in this study, form solutions with CA_2 in concentration depicted in Tab. 2. The values shown in this table have been discussed. The iron can form the solid solution of high concentration, which could be expected from easy substitution of this ion with aluminium ions. Also *Dayal* [16] found 5,7 % of Fe_2O_3 in solid solution in CA_2. Also strontium can form the solid solution of high concentration because it can replace calcium in several phases.

Tab. 6 Bending strength of the pastes

	Bending strength [MPa]		
	After 3 d	After 7 d	After 28 d
Water	1,93	5,78	8,26
VIa	-	22,6	2,13
VIb	25,0	29,2	1,29
VIc	5,3	6,78	11,27

While discussing the content of potassium in solid solution it must be remembered that potassium is known for having great vapour pressure at elevated temperature and can easily sublimate, which causes its content in solid solutions to

be very changeable and rather low. Yet, the solid solution of silicium can have only limited concentration because it has the tendency for gehlenite formation, which is inert in water at normal conditions. Also the barium aluminates easily forms, whose presence was found in the sample with this addition, so its concentration in solid solution must be low. Finally, lithium completely sublimated at 1550 ℃.

- All used minor components in solid solutions had no remarkable influence on hydraulic activity of calcium bialuminate. The controversial effect of sodium solid solutions in tricalcium aluminate on its hydration rate can be remained here [17]. As it is known some of sodium ions are located at the centres of the Al_6O_{18} rings. There is a hypothesy [5] that these ions in interstitial sites decrease the rate of hydration of C_3A.

- The water solutions with high pH of about 13,5 for sodium and potassium and 12,5 for $Ca(OH)_2$ significantly accelerate the CA_2 hydration. The calcium hydroxide can principally have a practical application, because the two remaining hydroxides cause rapid decrease of strength after 7 d as a result of potassium and sodium formation, which are soluble in water.

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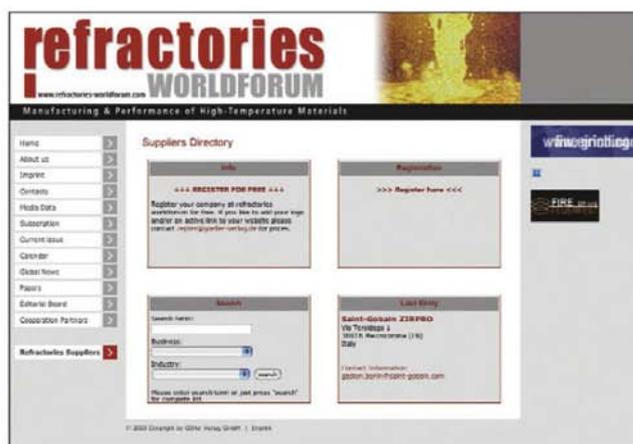[17] Kurdowski, W.; Wieja,K.; Handke, M.: The influence of solid solution with SiO_2 on properties C_3A. Ceramika 38 (1989) 61–77