SOLID SOLUTIONS OF CALCIUM ALUMINATES C_3A, $C_{12}A_7$ AND CA WITH SODIUM OXIDE

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Abstract

The research concerns the influence of a substantial range of sodium ion concentrations on the structure of the calcium aluminates C_3A[**], $C_{12}A_7$ and CA until CaO is emitted. The research also shows the influence of sodium ions of the cell parameters of each calcium aluminate and what reaction occur in mixtures of Na_2O and calcium aluminates at elevated temperatures.

Keywords: calcium aluminates, substitution of sodium, X-ray diffraction

Introduction

Elucidation of the structure of clinker materials doped with various additives is very important in the chemistry of cements. It is often the basis for development of new technologies for the production of high strength building materials. Moreover, this problem gains ever greater significance, because of the necessity for the utilization of various industrial waste materials.

Calcium aluminates are important components of aluminium and portland cements. The formation of calcium aluminate phases during the clinkerization process and their modification by different ions present in the raw materials used for the clinker production are important problems in the chemistry of cements. Moreover, the formation of calcium aluminates is also essential in the production of aluminium oxide, and in particular, when leaching aluminium hydroxide from calcium aluminates. Alkalies present in cement grouts influence the rate of binding, modify the structures formed, and affect the properties of the hydration products formed. According to Bensted, the alkalies initiate pozzolane reaction in cement [1].

Investigations of the binding and hardening of calcium aluminates in the systems $C_{12}A_7$–C_3A and $C_{12}A_7$–CA have indicated that rapid binding of cement grout can be explained by the presence of large quantity of $C_{12}A_7$ and C_3A, while the strength, after a long hardening time, comes from the presence of CA. By the appro-

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**   The following abbreviations have been applied in this work for designation of the particular calcium aluminates calcium–sodium aluminates and sodium aluminate: C_3A: $3CaO\ Al_2O_3$ ($Ca_3Al_2O_6$); $C_{12}A_7$: $12CaO\ 7Al_2O_3$ ($Ca_{12}Al_{14}O_{33}$); CA: $CaO\ Al_2O_3$ ($CaAl_2O_4$); NC_8A_3: $Na_2O\ 8CaO\ 3Al_2O_3$ ($Na_2Ca_4Al_3O_9$); $N_2C_3A_5$: $2Na_2O\ 3CaO\ 5Al_2O_3$ ($Na_4Ca_3(AlO_2)_{10}$); NA: ″ $Na_2O\ Al_2O_3$ ($NaAlO_2$).

priate choice of the component ratios, cements with relatively short binding time and rapid hardening can be obtained.

It is a common notion that the presence of alkalies in cement is harmful [2–5]. However, there are discrepancies between opinions of different authors about acceptable alkali contents. Many investigators working on this problem are convinced that the acceptable range of alkali concentrations is determined by the alkali form existing in the clinker. Concurrently, it is pointed out that the influence of alkalies on cement properties clearly depends on the type of raw materials and the technology used for the cement production [6, 7]. Literature data indicate that the influence of sodium on the structure of calcium aluminates $C_{12}A_7$ and CA has not been studied sufficiently enough as only the effect of sodium on the structure of C_3A in small concentrations has been established [8, 9].

The lack of data concerning the reaction mechanisms occurring in calcium aluminates $C_{12}A_7$ and CA in the presence of sodium ions stimulated our interest in this topic. Hence, we decided to carry out research aimed at the synthesis of different crystalline forms of solid solutions of Na_2O in C_3A, CA and $C_{12}A_7$. Moreover, we undertook an attempt at synthesise hypothetical compounds NC_8A_3 and $N_2C_3A_5$.

The purpose of these studies was to determine the influence of a broad range of sodium ion concentrations sodium ions on the structure of calcium aluminates C_3A, $C_{12}A_7$ and CA within up to the separation point of free calcium oxide in addition the determination of the influence of sodium ions on crystal lattice parameters of the particular aluminates, and establishing the reactions which occur in the mixtures of Na_2O with the calcium aluminates at high temperatures was targeted. The scope of this work covers the synthesis of pure calcium aluminates $3CaO\ Al_2O_3$, $12CaO\ 7Al_2O_3$ and $CaO·Al_2O_3$ (i.e., C_3A, $C_{12}A_7$ and CA) at the temperatures above 1200°C and the synthesis of the particular aluminates doped with sodium oxide.

The calcium aluminates $3CaO\ Al_2O_3$, $12CaO\ 7Al_2O_3$, $CaO\ Al_2O_3$ and their solid solutions with Na_2O were obtained within the concentration range of 1.8% of Na_2O (by mass) up to the point where free CaO started to separate (i.e., to about 20–25% of Na_2O) at 1 or 2% intervals. The synthesis of solid solutions within the particular pseudo-systems $C_3A–Na_2O$, $C_{12}A_7–Na_2O$ and $CA–Na_2O$ was carried out by calcination of homogenized mixtures of the calcium aluminates (C_3A, $C_{12}A_7$, CA) with a predetermined amount of sodium oxide added in the form of sodium carbonate Na_2CO_3. Each sample was homogenized in an agate mill and then calcinated for 10 to 20 h. After the calcination, the sodium content in the samples was determined by atomic absorption spectroscopy.

Experimental methodology

The following methods have been applied for analysis of the prepared compounds:
- X-ray diffractometry
- Fourier-transform infrared spectroscopy (FT-IR)
- Atomic absorption spectroscopy
- Chemical analysis

The data from the X-ray diffraction patterns obtained for powders were applied for the calculation of the lattice parameters of elementary cells of the solid solutions, using the software packet 'Proszki' developed at Jagiellonian University, and, the packet DHN/PDS owned by Institute of Inorganic Chemistry and Technology PK [10, 11].

The determination of CaO content in the samples studied was done by the glycol method, according to a normalized procedure. [12].

Results and discussion

Effect of sodium ions on the structure of tricalcium aluminate (C₃A)

Previous studies of tricalcium aluminate doped with sodium oxide allowed us to conclude that the sodium oxide formed solid solutions with C_3A [9, 13–15]. Depending on the sodium content, different crystallographic forms were obtained. The polymorphic forms of the C_3A–Na_2O solid solutions were identified by XRD, microscopy and infrared spectroscopy. However, the solubility limit of Na_2O in C_3A and the existence of the compound NC_8A_3 are still questionable.
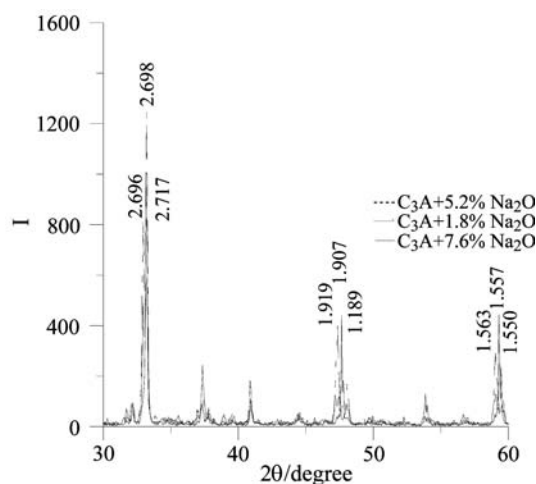

Fig. 1 X-ray diffractograms comparison of the C_3A samples with 1.8, 5.2 and 7.6 mass% Na_2O

Our results from X-ray diffractometry and FT-IR spectroscopy obtained for solid solutions of Na_2O in C_3A are generally consistent with the literature data [9, 15, 16]. In the case of 1.8% Na_2O in C_3A, practically no change was observed in the diffraction patterns and IR spectra of the C_3A–Na_2O solid solution in comparison to pure C_3A. This indicates that no significant changes occurred in the crystal structure of C_3A containing that amount of sodium oxide as the sample retained its regular crystallographic structure. The same was observed for the sample containing 2.5% of Na_2O in C_3A.

At the sodium oxide concentrations of 3.5, 4.2 and 5.2% (by mass) the changes in the diffraction patterns and infrared spectra became significant. The main diffrac-

tion lines of C_3A at d_{hkl} values 2.698, 1.907 and 1.557 Å split into doublets in the diffraction patterns of C_3A–Na_2O solid solutions to yield the d_{hkl} values 2.717, 2.696, 1.919, 1.890, 1.563 and 1.550 Å respectively, as shown in Fig. 1.

The splitting was also observed in the diffraction pattern of the sample containing 7.6% of Na_2O, which equalized the Na_2O content in the compound NC_8A_3. Moreover, we observed that the intensity of the diffraction line corresponding to d_{hkl} value 890 Å increased with the increase of sodium content in C_3A (i.e., at least up to 7.6% of Na_2O), relative to the intensity of the line with d_{hkl} value 1.920 Å.

On the basis of literature data and indexing of the obtained diffraction patterns, we found that the sample of C_3A containing 3.5% of Na_2O was an orthorhombic form of C_3A–Na_2O solid solution. The same occurred at 4.2% of Na_2O. However, the sample containing 5.2% of Na_2O in C_3A was monoclinic. The results obtained are summarized in Table 1.

Table 1 Parameters of unit cells for cubic, orthorhombic, monoclinic of solid solution C_3A–Na_2O

Change of crystalline solid solution C_3A–Na_2O	Na_2O content/ mass%	Parameters of cells/Å	Volume of unit cells/Å^3
Cubic	0	a=15.259 (0.0009)	3552.93
Cubic	1.8	a=15.2569 (0.0019)	3551.39
Cubic	2.5	a=15.2469 (0.0018)	3544.41
Orthorhombic	3.5	a=10.8414 (0.0056) b=10.8720 (0.0097) c=15.1752 (0.0083)	1788.66
Orthorhombic	4.2	a=10.8590 (0.0039) b=10.8545 (0.0040) c=15.1323 (0.00430)	1784.89
Monoclinic	5.2	a=10.8090 (0.0036) b=10.8388 (0.0015) c=15.0846 (0.0037) =90.203 (0.029)	1767.25

As shown in Table 1, at 1.8 and 2.5% of Na_2O the elementary cell is still regular, but the parameter a starts changing. Figure 2 shows the changes of the elementary cell volume, determined from the X-ray data.

In order to answer the question whether the C_3A–Na_2O solid solutions obey the Vegard law, Figs 2 and 3 show plots of the change of the elementary cell volume $vs.$ Na_2O concentration (in mass%). In the system studied, the cell volume changes within a range of Na_2O concentrations that can be represented by a straight line. At higher Na_2O contents however, (i.e., above 1.8% in Fig. 2 and above 4.2% in Fig. 3) the volume changes stepwise.

The sudden bend in the curve representing dependence of the elementary cell volume on the concentration of Na_2O introduced into the calcium aluminate structure indicates a deviation from the Vegard law. It can be stated, that such a phenomenon occurs when C_3A–Na_2O solid solution undergoes change of its elementary cell from regular to orthorhombic (Fig. 2). According to other researchers, this lies within the range of coexistence of two phases: regular and orthorhombic, or, when the change of the cell structure from regular to orthorhombic is in progress (Fig. 3).

For the comparison of our results with literature data, all the data obtained for C_3A–Na_2O solid solutions are collated in Table 2, while Table 3 shows the d_{hkl} values of some of the solid solutions.

Infrared spectroscopy of C_3A–Na_2O solid solutions indicates, that starting at 3.5% of Na_2O (by mass), the IR spectra exhibit large changes in comparison to the spectra of the regular 1.8 and 2.5% solid solutions. The IR spectra of the C_3A–Na_2O solid solutions containing 3.5, 4.2, 5.2 and 7.6% of Na_2O are similar. Hence, by infra-

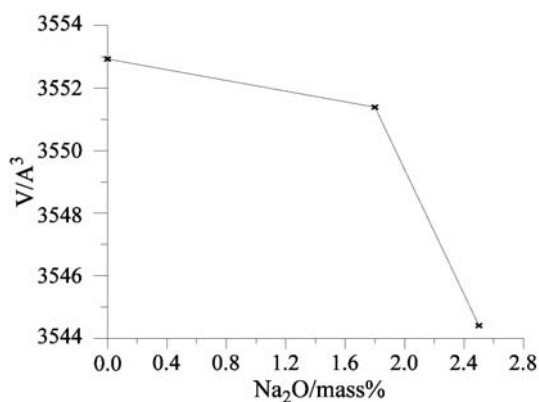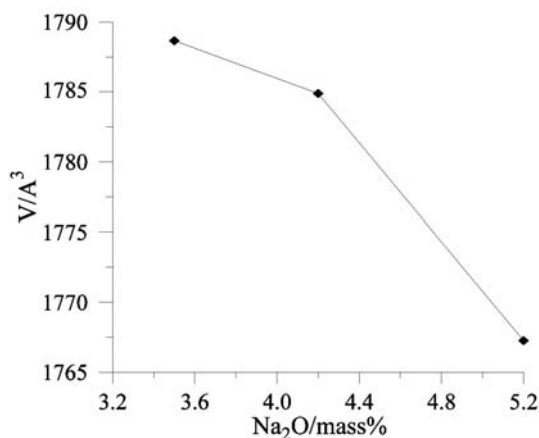**Fig. 2** Change of the volume of the C_3A regular cell in the solutions of C_3A– Na_2O

Fig. 3 Change of the volume of the C_3A cell in the solutions of C_3A–Na_2O

red spectroscopy it is not possible to distinguish orthorhombic form of C_3A–Na_2O solid solution from the monoclinic one.

   The observed significant difference between IR spectra of C_3A–Na_2O solid solutions, containing 3.5% or more Na_2O, in comparison to the spectrum of pure C_3A,

Table 2 Parameters of unit cells for cubic, orthorhombic, tetragonal and monoclinic of solid solution C_3A–Na_2O

Change of crystalline solid solution C_3A–Na_2O	Author	Na_2O contents/ mass%	Parameters of cells/Å	Volume of unit cells/Å^3
Cubic	Regourd et al. [13, 18]	2.0	a=15.243	3541.70
	Bojkowa et al. [9, 15]	2.43	a=15.25	3546.58
	Nishi et al. [19]	2.4	a=15.248	3545.18
	Żelazny [21, 22]	1.8	a=15.255	3551.39
	Żelazny [21, 22]	2.5	a=15.246	3544.41
Orthorhombic	Regourd et al. [13, 18]	4.2	a=10.862 b=10.845 c=15.106	1779.46
	Regourd et al. [13, 18]	5.3	a=15.330 b=15.394 c=15.123	3568.89
	Bojkowa et al. [9, 15]	3.81	a=10.88 b=10.85 c=15.14	1787.25
	Nishi et al. [19]	3.3	a=10.879 b=10.845 c=15.106	1784.43
	Nishi et al. [19]	3.8	a=10.875 b=10.859 c=15.105	1783.77
	Żelazny [21, 22]	3.5	a=10.8414 b=10.8720 c=15.1752	1788.66
	Żelazny [21, 22]	4.2	a=10.8690 b=10.8545 c=15.1323	1784.89
Tetragonal	Regourd et al. [13]	4.5	a=10.854 b=15.115	1780.69
	Bojkowa et al. [9, 15]	4.85	a=10.85 b=15.12	1779.96
Monoclinic	Regourd et al. [13]	5.0	a=10.862 b=10.862 c=15.123 =90.24°	1784.24

Table 2 Continued

Change of crystalline solid solution C_3A–Na_2O	Author	Na_2O contents/ mass%	Parameters of cells/Å	Volume of unit cells/Å^3
Monoclinic	Bojkowa *et al.* [9, 15]	5.72	a=10.87 b=10.87 c=15.13 =90.14°	1787.71
	Nishi *et al.* [19]	5.7	a=10.877 b=10.854 c=15.135 =90.1°	1786.82
	Żelazny [21, 22]	5.2	a=10.8090 b=10.8388 c=15.0846 =90.203°	1767.25

was attributed by Bojkowa *et al*. to changes in configuration of the Al_6O_{18} ring on influence of sodium ions, while the transition of the orthorhombic form into the monoclinic one occurs practically without change of the Al_6O_{18} ring (i.e., with no change in IR) [15].

Broadening of the IR bands resulting from the structural disorder caused by replacement of Ca^{2+} by Na^+ considerably simplifies the spectrum. The bands located at the following wave numbers are observed: 870, 790, 730, 537, 523 and 494 cm^{-1}.

The formation of C_3A–Na_2O solid solution occurs via the following ion exchange: $Ca^{2+}\Leftrightarrow 2Na^+$. Hence, the introduction of sodium oxide into C_3A structure causes release of free CaO. The concentrations of free CaO found in the solid solutions containing 1.8, 2.5, 3.5, 4.2, 5.2 and 7.6% of Na_2O confirmed the proposed mechanism of formation of the C_3A–Na_2O solid solution.

Table 4 compares concentrations of free CaO in the C_3A–Na_2O solid solutions found experimentally with those calculated from the following reaction equation:

$$3Ca_3Al_2O_6+Na_2O \quad Na_2Ca_8Al_6O_{18}+CaO \quad (3C_3A+N \quad NC_8A_3+C) \qquad (1)$$

At the concentration 7.6% Na_2O in C_3A, we should obtain the compound NC_8A_3, but according to the majority of researchers, synthesis of such a compound is not possible. The attempts to synthesise NC_8A_3 ended with failure, while the final product contained free CaO. It is a common notion that the solubility limit of Na_2O in C_3A equals 5.9% (by mass), which is below 7.6% of Na_2O calculated for NC_8A_3 [23, 24].

The possibility of the formation of NC_8A_3 solid solution was also investigated by Tavasci, Massazza and Costa [25]. They obtained the NC_8A_3 solid solution with orthorhombic structure, but their samples were heterogeneous (i.e., the samples were composed of free CaO and a mixture of orthorhombic and monoclinic forms of C_3A–Na_2O solid solution).

Table 3 D_{hk} of C_3A with Na_2O after Bojkowa [9, 15] and Regourd [13, 18] and Żelazny [22]

No	C_3A		Bojkowa						Regourd						Żelazny	
			Cubic cell with 2.43 mass% Na_2O		Rhombic cell with 3.81 mass% Na_2O		Monoclinic cell with 5.72 mass% Na_2O		Cubic cell with 1.8 mass% Na_2O		Rhombic cell with 4.2 mass% Na_2O		Monoclinic cell with 5.3 mass% Na_2O		Monoclinic cell with 5.2 mass% Na_2O	
	d_{hkl}/Å	I/%	d_{hkl}/Å	I/%	d_{hkl}/Å	I/%	d_{hkl}/Å	I/%	d_{hkl}/Å	I/%	d_{hkl}/Å	I/%	d_{hkl}/Å	I/%	d_{hkl}/Å	I/%
1	2.696	100	2.783	6	2.697	100	2.697	96	2.694	100	2.692	100	2.716	36	2.717	57
			2.696	100	2.714	45	2.702	100			2.716		2.698	100	2.696	100
					2.721	43	2.721	72			2.712	56	2.691			
2	1.906	32	1.906	30	1.906	4	1.926	20	1.904	40	1.918	40	1.924	41	1.919	21
			1.889	3	1.920	32	1.918	19			1.903	7	1.915		1.890	14
					1.892	14	1.903	5			1.898	20	1.901	3		
							1.891	18					1.890	20		
3	1.557	32	1.556	30	1.551	13	1.566	19	1.556	40	1.563	42	1.565	42	1.563	23
					1.562	21	1.562	24			1.561		1.562		1.550	9
					1.565	18	1.552	18			1.550	19	1.551	19		

Table 4 Mount free CaO participated from the solid solutions of Na_2O in C_3A analyzed chemically and calculated on the basis of the reaction (1)

Contents of Na_2O in C_3A		Contents of CaO analyzed chemically		Contents of CaO calculated on the reaction (1)/ mass%
mass%	mol%	mass%	mol%	
1.83	0.029	1.60	0.028	1.63
2.48	0.040	2.20	0.039	2.26
3.52	0.057	3.18	0.057	3.17
4.20	0.068	3.90	0.069	3.80
5.24	0.084	4.80	0.085	4.70
7.59	0.122	11.30	0.201	12.96

As indicated in our further studies, introduction of Na_2O into C_3A ranging from 7.6 to 20% causes transformation of the initially formed monoclinic C_3A–Na_2O solid solution into sodium aluminate ($NaAlO_2$) and free calcium oxide (CaO), as shown in Figs 4 and 5.

Table 5 Determination of the amount of free CaO displaced by Na_2O in Na_2O–$Ca_3Al_2O_6$, Na_2O–$CaAl_2O_4$ and Na_2O–$Ca_{13}Al_{14}O_{33}$ systems

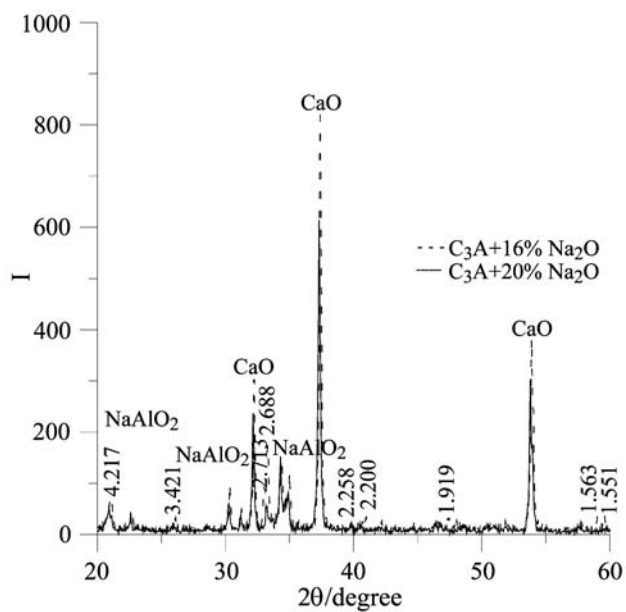| Na_2O–$Ca_3Al_2O_6$		Na_2O–$CaAl_2O_4$		Na_2O–$Ca_{13}Al_{14}O_{33}$	
Na_2O/ mass%	free CaO*/ mass%	Na_2O/ mass%	free CaO*/ mass%	Na_2O/ mass%	free CaO*/ mass%
1.80	1.60	1.80	–	1.80	–
2.50	2.20	3.50	–	3.50	–
3.50	3.18	5.20	–	4.20	–
4.20	3.90	7.60	–	5.20	–
5.20	4.80	8.00	–	8.00	0.13
7.60	11.60	9.00	–	10.00	0.30
7.90	12.80	10.00	0.10	15.00	5.40
8.00	12.98	15.00	0.60	20.00	13.91
9.00	14.99	20.00	1.49	25.00	26.39
10.00	20.10	25.00	4.80		
12.00	26.28	28.20	8.40		
14.00	30.00				
16.00	40.11				
18.00	45.00				
20.00	48.00				

* found experimentally

Fig. 4 X-ray diffractograms comparison of the C_3A sample with 16 and 20 mass% Na_2O. X-ray diffractogram C_3A with 20 mass%. Na_2O sample, where we have diffraction lines characteristic for phases $NaAlO_2$ and CaO
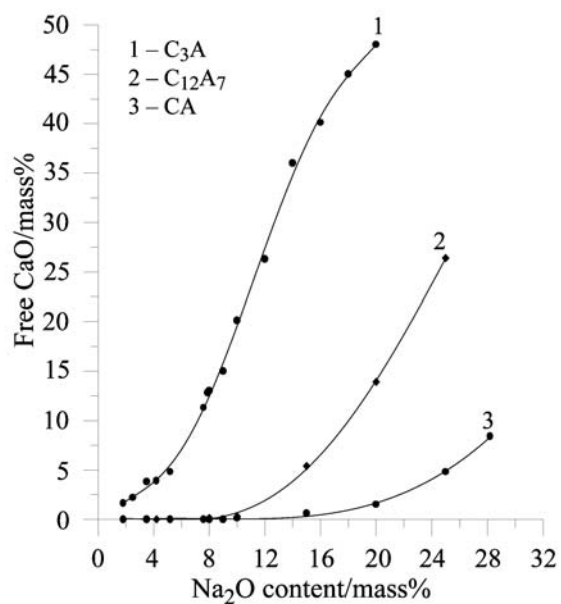

Fig. 5 Graph dependences given off free CaO from contents Na_2O in systems: $Na_2O–C_3A$, $Na_2O–C_{12}A_7$ and $Na_2O–CA$

With increase of sodium oxide content in C_3A, the diffraction lines characteristic for the monoclinic phase formed initially at 5.2% of Na_2O, gradually disappear from the diffraction patterns of C_3A–Na_2O solid solutions. The same happens with the corresponding IR bands in the IR spectra. On the other hand, intensities of the diffraction lines and the IR bands characteristic for $NaAlO_2$ and CaO increase. This phase transformation is complete at about 20% of Na_2O in C_3A, according to the following reaction:

$$Ca_3Al_2O_6 + Na_2O \quad 2NaAlO_2 + 3CaO \qquad (C_3A + N \quad NA + 3C)$$

Upon incorporation of sodium oxide into C_3A up to about 8% of Na_2O, the amount of free CaO increases gradually. However, at 9% of Na_2O a rapid increase in the released amount of free CaO is noticeable due to formation of sodium aluminate. Figure 5 shows the plot of the amount of free CaO released from $Ca_3Al_2O_6$ *vs.* the concentration of Na_2O (curve 1 and Table 5).

Effect of sodium ions on the structure of calcium monoaluminate (CA)

Our studies of the products from CA synthesis containing different amounts of Na_2O have indicated that at low sodium contents, up to 10% of Na_2O, $C_{12}A_7$ and $N_2C_3A_5$ phases are formed. The amount of $C_{12}A_7$ and $N_2C_3A_5$ phases reaches a maximum at 10% of Na_2O (by mass).

The elementary cell parameters determined from the diffraction patterns of CA containing 1.8, 3.5 and 5.2% of Na_2O are shown in Table 6. In the results, these parameters

Table 6 The parameters of monoclinic unit cell, calculated from the diffractograms of CA with 1.8; 3.5 and 5.2 mass% Na_2O

Na_2O content in CA/mass%	Parameters of monoclinic cell CA; a, b, c/Å and /°	Volume of monoclinic cell CA/ Å^3
0	a=8.6820 (0.0012) b=8.1048 (00013) c=15.2117 (0.0029) =90.189 (0.0019)	1070.61
1.8	a=8.6877 (0.0030) b=8.0808 (0.0024) c=15.1927 (0.0053) =89.874 (0.0045)	1066.58
3.5	a=8.6729 (0.0056) b=8.0964 (0.0025) c=15.2011 (0.0072) =90.326 (0.0081)	1067.39
5.2	a=8.6752 (0.0070) b=8.1118 (0.0050) c=15.2141 (0.0031) =90.174 (0.0076)	1070.63

vary within the limits of experimental errors (i.e., there are only small differences in the values of the parameters of the order of 0.0020–0.0080). The errors resulted from different intensities of the diffraction patterns used for the parameter calculation, because with increase of Na_2O the CA content decreased when the new phase $N_2C_3A_5$ formed.
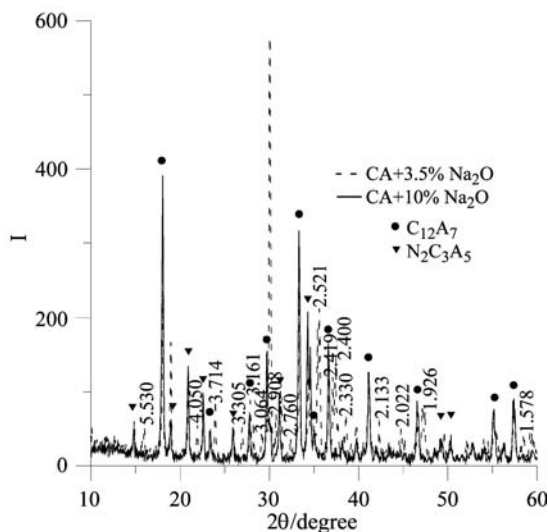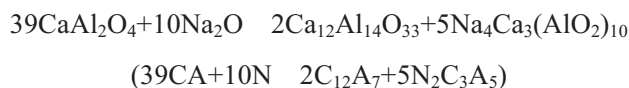

Fig. 6 X-ray diffractograms CA with 3.5 and 10 mass% Na_2O samples. Described diffractions lines belong to phases CA. X-ray diffractogram CA with 10 mass%. Na_2O sample, that is mixture $C_{12}A_7$ and $N_2C_3A_5$ phases

At 10% of Na_2O in $CaO\ Al_2O_3$, practically all the $CaO\ Al_2O_3$ is converted into $12CaO\ 7Al_2O_3$ and $Na_4Ca_3(AlO_2)_{10}$ (i.e., $N_2C_3A_5$), as shown in Fig. 6. Hence, we can write the following reaction:

$$39CaAl_2O_4 + 10Na_2O \rightarrow 2Ca_{12}Al_{14}O_{33} + 5Na_4Ca_3(AlO_2)_{10}$$

$$(39CA + 10N \rightarrow 2C_{12}A_7 + 5N_2C_3A_5)$$

With 15% Na_2O (by mass) the phase C_3A–Na_2O solid solution forms, while the amount of $C_{12}A_7$ decreases. Simultaneously, the amount of $N_2C_3A_5$ also decreases. At 15% of Na_2O, the phase C_3A–Na_2O solid solution dominates.

The large amounts of $C_{12}A_7$ phase formed in the reaction of CA with Na_2O undergo further changes at higher sodium contents corresponding to 20 and 28.2% of Na_2O, as shown in Fig. 7.

With an increase of the sodium content to 25% of Na_2O, the amount of C_3A–Na_2O solid solution decreases, while the amounts of sodium aluminate ($NaAlO_2$) and free calcium oxide increase. The content 28.2% of Na_2O in CA (by mass) is sufficient to bind the aluminium from CA almost entirely into sodium aluminate, according to the reaction:
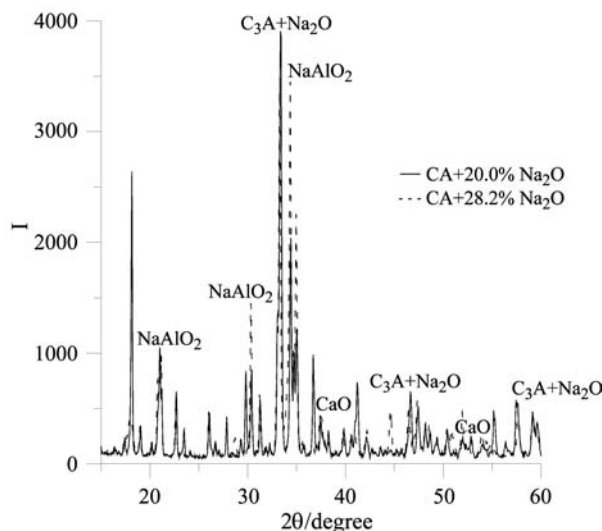
$$CaAl_2O_4 + Na_2O \rightarrow 2NaAlO_2 + CaO \qquad (CA + N \rightarrow NA + C)$$
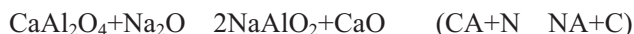
Fig. 7 X-ray diffractograms comparison of the CA samples with 20 and 28.2 mass% Na_2O

Analysis of free CaO content in the CA–Na_2O samples allowed us to affirm that practically free CaO appeared at 20% of Na_2O. In this sample, beside the large amounts of the phase of C_3A–Na_2O solid solution, sodium aluminate ($NaAlO_2$) was also present. The amount of free CaO considerably increased with increase of Na_2O concentration to 25%, where the content of C_3A–Na_2O solid solution was modest, while the amount of $NaAlO_2$ phase was large. This indicates that the phases of C_3A–Na_2O solid solution changed to sodium aluminate and free CaO. Figure 7 shows the dependence of the concentration of the released free CaO on the amount of Na_2O doped into the CA (curve 3 in Fig. 5 and Table 5).

The CA–Na_2O samples were also studied by IR spectroscopy. These studies indicate that under the influence of sodium ions on $CaO\ Al_2O_3$, the phase $12CaO\ 7Al_2O_3$, and to lesser extent, $2Na_2O\ 3CaO\ 5Al_2O_3$ are formed. The former phase was indicated by IR bands at 455 and 570 cm^{-1}, while the latter one was detected by the bands at 662, 840 and 930 cm^{-1}. At Na_2O contents above 10%, intensities of the bands characteristic for the phase $2Na_2O\ 3CaO\ 5Al_2O_3$ decreased. Moreover, at that high Na_2O contents, the bands at 411, 637 and 683 cm^{-1} belonging to $CaO\ Al_2O_3$ also disappeared. These observations are consistent with the data obtained by Grzeszczyk *et al.* [26].

Up to 10% of Na_2O, the amount of $12CaO\ 7Al_2O_3$ phase increases with increase of sodium content in the sample, while above that Na_2O content the amount of $12CaO\ 7Al_2O_3$ phase decreases. Above 10% of Na_2O, C_3A–Na_2O solid solution forms. Starting at 20% of Na_2O this undergoes transformation into $NaAlO_2$ and free CaO.

Effect of sodium ions on the structure of dodecacalcium septaaluminate ($C_{12}A_7$)

Our studies of the products from synthesis of $C_{12}A_7$ with different sodium contents have indicated that under the influence of sodium ions, $C_{12}A_7$ transforms into the

phase sodium–calcium aluminate (C_3A–Na_2O), while at low sodium contents (i.e., 5.2, 7.6 and 10% of Na_2O), small amounts of $NaAlO_2$ phase are also formed. Up to 10% of Na_2O (by mass), the amount of C_3A–Na_2O phase successively increases with increase of the sodium content in $C_{12}A_7$.

With further increase of the sodium content, the C_3A–Na_2O phase transforms into sodium aluminate and free calcium oxide, as shown in Fig. 8. Similar results were obtained by Grzeszczyk [27].
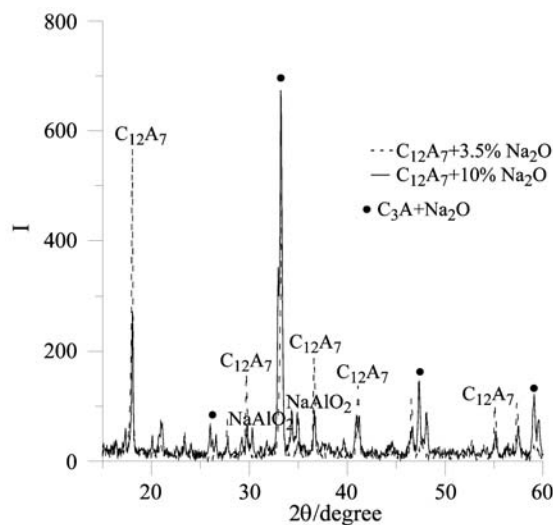

Fig. 8 X-ray diffractograms comparison of the $C_{12}A_7$ samples with 3.5 and 5.2 mass% Na_2O

In the case of the samples containing 1.8, 3.5, 4.2, 5.2, 8 and 10% of Na_2O in $C_{12}A_7$, also the parameter a of $C_{12}A_7$ elementary cell changes, as shown in Table 7.

Table 7 The parameters of unit cell $C_{12}A_7$, calculated from diffractograms of $C_{12}A_7$ with 1.8; 3.5; 4.2; 5.2; 8 and 10 mass% Na_2O

Na_2O content in $C_{12}A_7$/mass%	Parameter of cubic cell $C_{12}A_7$, a/Å	Volume of cubic cell $C_{12}A_7$/ Å^3
0	11.9846 (0.0009)	1721.35
1.8	12.0191 (0.0017)	1736.26
3.5	12.0130 (0.0012)	1733.62
4.2	12.0138 (0.0015)	1733.97
5.2	12.0027 (0.0018)	1729.17
8	11.9975 (0.0011)	1726.92
10	11.9919 (0.0008)	1724.50

The effect of sodium on $C_{12}A_7$ discussed above is further confirmed by analysis of the amount of free CaO formed by the reaction of $C_{12}A_7$ with Na_2O. No free CaO was found in the solid solution containing up to 5.2% of Na_2O in $C_{12}A_7$. This is justified by the fact that at those Na_2O concentrations, $C_3A–Na_2O$ phase is formed, which contains more CaO than that in $C_{12}A_7$.

At 8% of Na_2O in $C_{12}A_7$ the content of free CaO was 0.3%, which gradually increased to 13.91% (by mass) when the Na_2O content was increased to 20%. At 25% of Na_2O, the amount of free CaO considerably increased up to 26.39%, due to decomposition of the $C_3A–Na_2O$ phase into $NaAlO_2$ and CaO. The changes in the amount of released free CaO as a function of the amount of Na_2O doped into $C_{12}A_7$ are represented by curve 2 in Fig. 5 and Table 5.

On the basis of the volume of the $C_{12}A_7$ elementary cell, we can say that up to 1.8% of Na_2O in $C_{12}A_7$, the sodium oxide forms solid solutions in $C_{12}A_7$. With further increase of Na_2O content, the volume of $C_{12}A_7$ elementary cell slightly decreases. However, these data are within the experimental errors (i.e., there are small deviations of the calculated parameters of the order of 0.0020–0.0080). These errors come from different intensities of the diffraction patterns used for calculation of the elementary cell parameters, resulting from the fact that with increase of Na_2O content, the amount of $C_{12}A_7$ phase decreased, while the new phase $N_2C_3A_5$ containing sodium formed.
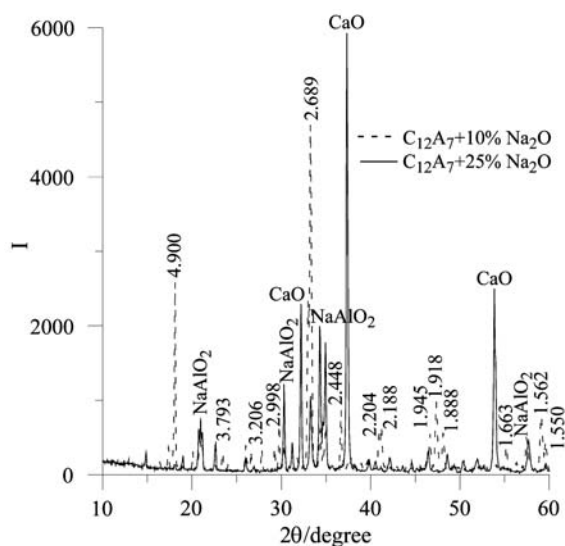

Fig. 9 X-ray diffractograms comparison of the $C_{12}A_7$ samples with 10 and 25 mass% Na_2O

In the case of the sample containing 25% of Na_2O, the amount of sodium oxide was sufficient to bind the entire amount of aluminium from dodecacalcium septaaluminate into sodium aluminate by the following reaction, as confirmed by Fig. 9.

$$Ca_{12}Al_{14}O_{33}+7Na_2O \quad 14NaAlO_2+12CaO \quad (C_{12}A_7+7N \quad 7NA+12C)$$
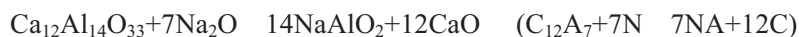
The data obtained indicate that at 10% of Na_2O (by mass), the maximum amount of C_3A–Na_2O phase is formed, while at higher Na_2O contents the C_3A–Na_2O phase initially formed decomposes into $NaAlO_2$ and CaO.

Infrared studies of the $C_{12}A_7$–Na_2O samples have indicated that with increase of Na_2O content in $C_{12}A_7$ the bands at 464, 577, 780 and 847 cm^{-1} belonging to $C_{12}A_7$ gradually disappear, while the bands at 720 and 872 cm^{-1} characteristic for C_3A–Na_2O solid solution initially appear and then disappear at Na_2O contents above 10%. The band that appears and increases in intensity continuously is that of $NaAlO_2$ at 830 cm^{-1}.

Composition of the phases in the system CaO–Al$_2$O$_3$–Na$_2$O

The results obtained are also presented in the phase diagram of CaO–Al_2O_3–Na_2O, by plotting them on the only diagram reported so far for the tri-phase system by Brownmiller and Bogue [28] (Fig. 10). As shown in Fig. 10, the points are representing compositions of the particular samples of C_3A–Na_2O, $C1_2A_7$–Na_2O and CA–Na_2O lie on the straight lines connecting the compositions of pure C_3A, $C_{12}A_7$ and CA with the point corresponding to 100% of Na_2O.
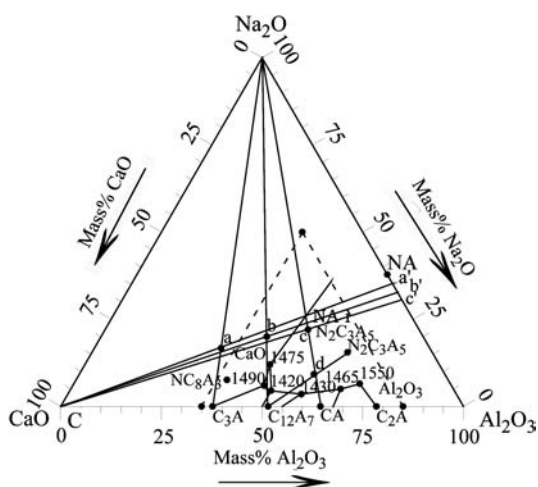

**Fig. 10** Composition of the phases in the system CaO–Al$_2$O$_3$–Na$_2$O

The points from the C_3A–Na_2O system lie within the crystallization area of C_3A and CaO, but the location of this area is not established accurately, because the study of that system has not been sufficient. On the basis of our study, it has been found that after mixing of C_3A with 20% of Na_2O (by mass), the starting composition corresponds to point *a*. However, it has turned out that after the reaction at 1250°C, two practically pure phases of $NaAlO_2$ and CaO were formed by the following reaction.

$$Ca_3Al_2O_6 + Na_2O \quad 2NaAlO_2 + 3CaO \quad (C_3A + N \quad NA + 3C)$$
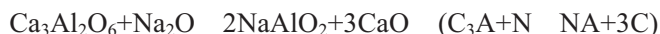
Hence, on the basis of the lever rule we can say that two phases (i.e, $NaAlO_2$ and CaO with the compositions at the points C and a') are formed from the composition at the point a in Fig. 10. Moreover the amount of the formed CaO phase is 48 mass%, which allows us to estimate the ratio of the phases from the following equation:

$$\frac{m_{CaO}}{m_{NaAlO_2}} = \frac{aa'}{aC}$$

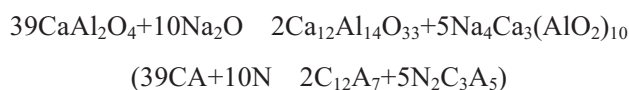On the other hand, the data from the system $C_{12}A_7$–Na_2O lie within the crystallization area of C_3A and CaO, as well as that of C_3A–Na_2O solid solution, but exact location of these areas is not known. Our results show that the composition of the mixture of $C_{12}A_7$ with 25% of Na_2O is at the point b, while after the reaction at 1250°C, almost pure phases of $NaAlO_2$ and CaO occur, due to the following reaction:

$$Ca_{12}Al_{14}O_{33}+7Na_2O \quad 14NaAlO_2+12CaO \qquad (C_{12}A_7+7N \quad 7Na+12C)$$
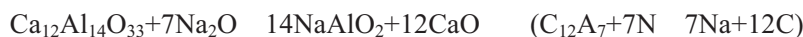
Thus, on the basis of similar reasoning as that described previously we can state, that according to the lever rule, the phases $NaAlO_2$ and CaO with compositions corresponding to the points C and b' are formed from the phase with the composition at the point b. Moreover, from the amount of CaO phase equal to 26.4%, we can estimate the ratio of the phases, using the following equation:

$$\frac{m_{CaO}}{m_{NaAlO_2}} = \frac{bb'}{bC}$$

Accordingly, the data from the CA–Na_2O system are already located within the crystallization area of $C_{12}A_7$, as well as that of NA and $N_2C_3A_5$. We have established that at the point corresponding to 10% of Na_2O in CA, there are two phases: $C_{12}A_7$ and $N_2C_3A_5$, resulting from the following reaction:

$$39CaAl_2O_4+10Na_2O \quad 2Ca_{12}Al_{14}O_{33}+5Na_4Ca_3(AlO_2)_{10}$$

$$(39CA+10N \quad 2C_{12}A_7+5N_2C_3A_5)$$

Hence, according to the lever rule, the phases $C_{12}A_7$ and $N_2C_3A_5$ are formed from the initial composition corresponding to the point d, while their amounts can be calculated from the ratio of the following line segments:

$$\frac{m_{C_{12}A_7}}{m_{N_2C_3A_5}} = \frac{dN_2C_3A_5}{dC_{12}A_7}$$

Moreover our data show that at 28.2% of Na_2O in CA there are also almost exclusively two phases: $NaAlO_2$ and free CaO, because of the following reaction:

$$CaAl_2O_4+Na_2O \quad 2NaAlO_2+CaO \qquad (CA+N \quad NA+C)$$
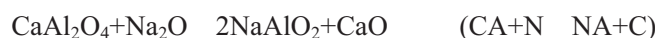
Hence, on the basis of the lever rule we can conclude that the phases $NaAlO_2$ and CaO are formed from the phase located at the point c in Fig. 13. Moreover, we

know that the amount of the formed CaO phase is 8.4%. From that we can estimate the ratio of the phases formed, by the following equation:

$$\frac{m_{CaO}}{m_{NaAlO_2}} = \frac{cc'}{cC}$$

Conclusions

On the basis of the literature data and the experimental results obtained in this study, the following can be concluded.

The solid solutions formed at high temperature (1250°C) by isomorphic substitution of calcium ions with sodium ions in the C_3A–Na_2O pseudo-system crystallize in the following crystallographic forms:

- cubic – at the Na_2O contents 1.8 and 2.5% (by mass),
- orthorhombic – at 3.5 and 4.2% of Na_2O,
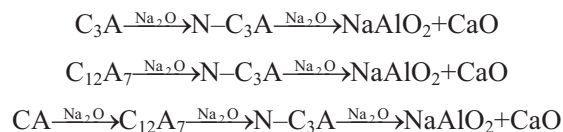- monoclinic – at 5.2% of Na_2O.

When C_3A is doped with higher than 5.2% Na_2O, the monoclinic solid solution initially formed transforms into sodium aluminate ($NaAlO_2$) and free calcium oxide (CaO), according to the reaction: $C_3A+N \rightleftharpoons NA+3C$.

Doping of calcium aluminate (CA) with sodium ions up to 10% of Na_2O increases the contents of $C_{12}A_7$ and $N_2C_3A_5$ phases by the following reaction: $39CA+10N \rightleftharpoons 2C_{12}A_7+5N_2C_3A_5$. With further increase of sodium content (i.e., above 10% of Na_2O), the following reaction between the $C_{12}A_7$ phase and Na_2O takes place: $C_{12}A_7+7N \rightarrow (4N–C_3A)+3NA$.

By indexing of the diffraction pattern of one of the C_3A–Na_2O solid solutions formed in the system CA–Na_2O at 20% of Na_2O, the presence of an orthorhombic solid solution formed in the system C_3A–Na_2O was also detected.

The solid solutions formed in the system $C_{12}A_7$–Na_2O have similar composition to those in the system C_3A–Na_2O. Moreover, it has been found that in the system $C_{12}A_7$–Na_2O there is a possibility of the formation of solid solutions with cubic symmetry. In these solutions, as sodium ions are built into the $C_{12}A_7$ structure, the parameter a of the regular elementary cell successively decreases from 12.0191 Å at 1.8% of Na_2O to 11.9975 Å at 8% of Na_2O in $C_{12}A_7$. At higher Na_2O contents, gradual conversion of the initially formed phases into $NaAlO_2$ and CaO occurs, according to the reaction: $C_{12}A_7+7N \rightleftharpoons 7NA+12C$.

Thus, in the reactions of C_3A, $C_{12}A_7$ and CA with Na_2O, always C_3A–Na_2O solid solutions of different symmetry form, which upon doping with larger amounts of Na_2O decompose into $NaAlO_2$ and CaO, as summarized in the following reaction set:

$$C_3A \xrightarrow{Na_2O} N–C_3A \xrightarrow{Na_2O} NaAlO_2+CaO$$

$$C_{12}A_7 \xrightarrow{Na_2O} N–C_3A \xrightarrow{Na_2O} NaAlO_2+CaO$$

$$CA \xrightarrow{Na_2O} C_{12}A_7 \xrightarrow{Na_2O} N–C_3A \xrightarrow{Na_2O} NaAlO_2+CaO$$

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