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Effect of Na and Al on the phase composition and morphology of autoclaved calcium silicate hydrates☆

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Abstract

The hydrated materials were synthesized at 160–240°C in hydrothermal conditions. The series of samples with differing CaO/SiO_2 ratios and doped with NaOH and $Al(OH)_3$ (used as Na- and Al-bearing compounds) were produced, yielding materials consisting of the ill-crystallized calcium silicate hydrates and/or more crystalline calcium silicate phases. Generally, in the presence of sodium ions the acceleration of reactions leads to the formation of calcium-silicate-hydrate, which is an intermediate product for many well-defined phases that can appear in this system. A significant amount of sodium additive (although it accelerates the precipitation and to some extent the ordering of calcium-silicate-hydrate structure) seems to hinder the crystallization of well-developed, final phases, which are expected to be formed at assumed CaO-to-SiO_2 ratios. The Ca-Na silicate hydrates are produced at significant sodium content (over 20% by weight), and at SiO_2 content exceeding 50% by weight. When Al is added to the calcium hydroxide, silica, and NaOH water suspensions, the sodium aluminosilicate-analcite ($Na[AlSi_2O_6].H_2O$) is detected, or the formation of more ordered CSH I (transformed subsequent to the tobermorite) is observed.

Keywords: Calcium-silicate-hydrate (C-S-H); Xonotlite; Tobermorite; Pectolite; Analcite; Sodium; Aluminium additives

1. Introduction

Phase composition and properties of products formed at temperatures >100°C under saturated steam pressure (hydrothermal conditions) in water suspensions containing CaO- and SiO_2-bearing components are strongly affected by the CaO-to-SiO_2 ratio in the initial mixture and by the presence of admixtures [1–4]. Among the inorganic admixtures, those containing aluminium and sodium oxides play a significant role in the mechanism and kinetics of hydration. Alumina is a component of Portland cement phases and other materials used as mineral admixtures to cement (e.g., slags and fly ashes) and therefore it takes part in the formation of hydration products. The sodium compounds are not only found in cement phases and many other additional materials, but also they are widely used as alkaline activators, particularly together with the components having poor hydraulic properties [5]. Their effectiveness has been fully exploited in the alkali-activated slag technologies [6].

The system Na_2O-CaO-SiO_2-H_2O was investigated by many authors: Blakeman et al. [7], Nelson and Kalousek [8], and Xi and Dent Glasser [9]. Reports on the phase composition and properties of calcium silicate hydrate have been published recently by the author [10–12]. Blakeman et al. [7] found that at constant $CaO:SiO_2$ molar ratio $= 0.83$ and varying $NaOH:SiO_2$ molar ratio $= 0.05$–0.63, the calcium-silicate-hydrate (C-S-H), tobermorite, pectolite, and xonotlite phases could form as a result of hydrothermal reactions occurring in water suspensions of the oxides mentioned above.

Hydrated calcium silicates are materials with poorly ordered structure and variable chemical composition ($CaO/SiO_2 = 0.8$–2). They are formed as a first precursor of many more ordered, crystalline phases produced at higher temperatures. Tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$), of relatively more ordered structure and stable chemical composition, is discussed in some papers as a second, further precursor. The final product synthesized on hydrothermal curing in lime- and silica-containing water suspensions at CaO/SiO_2 molar ratio close to 1 can be xonotlite ($Ca_6Si_6O_{17}(OH)_2$). The SiO_2 content increase brings about the formation of gyrolite ($Ca_8(Si_4O_{10})_3(OH)_4 \cdot 6H_2O$) and similar phases. When the molar ratio CaO/SiO_2 is higher than 1, one can expect the formation of such phases as foshagite $Ca_4(SiO_3)_3(OH)_2$, afwilite $Ca_3[SiO_3(OH)] \cdot 2H_2O$, a-$C_2SH$ $Ca_2[SiO_3(OH)] \cdot$

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(OH) [2], which depend on the chemical composition and time/temperature parameters of curing. These latter products are normally synthesized using hydrothermal conditions.

In some principal papers concerning the system Na_2O-CaO-SiO_2-H_2O, the authors generally found the acceleration of syntheses occurring in the presence of NaOH, the hindering of C-S-H → tobermorite transition, and the formation of tobermorite of highly disordered structure at high NaOH content [7–9,13]. According to Langton et al. [13], the Na_2O admixture up to 10% by weight, together with the silica content up to 55% by weight, did not produce any other individual phase apart from C-S-H. At higher SiO_2 content pectolite can be detected as a result of autoclaving [13].

Pectolite ($NaCa_2HSiO_3O_9$) is produced in Na_2O-, CaO-, SiO_2-, and H_2O-containing mixtures, subjected to the hydrothermal treatment at relatively low temperatures (slightly over 100°C). Its stability range is rather wide [7–9,13]. The predominant role of pectolite as a sodium-containing calcium silicate phase has been reported in some works [7–9]. The authors found that the crystallization of pectolite was strongly affected by the sufficient, relatively high sodium content and curing conditions. Pectolite can occur in equilibrium together with xonotlite, truscotite ($Ca_7(Si_4O_{10})(Si_8O_{19})(OH)_4 \cdot H_2O$), foshagite, and tobermorite. The fairly good mechanical properties and durability in a corrosive environment make this phase a desirable product of setting and hardening in some underground structures (deep wells, lining-rock mass contact, etc.) [13]. The other metastable Na-containing phase $NaCaHSiO_4$ has also been reported. This phase was detected in some mixtures of different stoichiometry [9,14]. The sodium ions can be incorporated in the C-S-H or tobermorite structure, but they do not form any solid solutions with the other crystalline calcium silicates such as xonotlite or foshagite [8].

In the presence of sodium ions in the liquid phase, degree of condensation of the silicate anions decreases and the content of highly polymerized fractions is reduced. This was reported by Dent Glasser et al. [15], who used the trimethylsilylation procedure, and more recently by the author using the nuclear magnetic resonance method [16]. This observation is consistent with the proposed mechanism of reaction in the system, assuming the disintegration of the SiO_2 network (i.e., considering quartz as the phase of highest silica condensation degree) in the highly alkaline NaOH solution, followed by the crystallization of reaction products [7]. The lower calcium ion concentration resulting from the reduced calcium hydroxide solubility in the liquid phase of highly alkaline pH should favour the formation of a preliminary product or precursor having a lower CaO content.

It has been commonly known that aluminium ions can be incorporated in the structure of hydrated calcium silicates, both at silicon and calcium sites [17,18]. The effect of aluminium on the structure of tobermorite was thoroughly studied by Mitsuda, Taylor, and El-Hemaly [19–20]. The authors emphasize the stabilizing action of Al on this phase. There are also some reports concerning the complex substitution Al + Na, showing that tobermorite substituted in such a way exhibits the properties of an ion exchanger [21].

In the light of the data presented above, it appears that sodium and aluminium admixtures significantly affect the formation and properties of the calcium silicate hydrates. The experiments presented in this work were undertaken as a part of a study on the effect of different additives in the activation of the hydration process.

2. Methods

2.1. Materials, preparation, and methods

The following substances of analytical purity were used: NaOH, $Ca(OH)_2$, and different sources of SiO_2; amorphous, finely dispersed Aerosil, Degussa (specific surface about 20,000 cm^2/g), normal silica-gel of coarser grains and finely ground quartz. The aluminium hydroxide of analytical purity was added as Al-bearing compound. All the reactants, aside from the Aerosil, were produced by POCH-Gliwice in Gliwice, Poland. The components of each sample were thoroughly homogenized with equal amounts of water in an agate mixer for 30 min. The suspensions thus obtained were sealed in Teflon containers and heated in a laboratory autoclave. The experiments were carried out on the series of samples synthesized in different conditions within the temperature range from 160 to 240°C. The time range was from 2 to 48 h.

In the first step the mix proportions were assumed, taking into account the chemical formulae of calcium- and sodium-containing well-defined hydrated silicates. Therefore, apart from the pectolite and the metastable calcium-sodium silicate hydrated phase mentioned above, the compositions given in ASTM data for X-ray diffraction (XRD) Ca-Na silicate hydrates phase identification were also considered.

For this purpose the basic NCS series of mixtures were

Table 1
Chemical composition of samples in the basic NCS series

No.	Final formula	Na:Ca	Na:Si	(Na + Ca)/Si	Ca:Si	SiO_2 (% by weight)	Na_2O (% by weight)
1NCS	$Na_2Ca_2Si_2O_7$aq	1	1	2	1	40.8	21.1
2NCS	$Na_2CaSi_2O_6$aq	2	1	1.5	0.5	50.4	26.1
3NCS	$NaCa_2Si_3O_9$aq	0.5	0.33	1	0.67	55.5	9.9
4NCS	$NaCa_4Si_6O_{17}$aq	0.25	0.17	0.83	0.67	58.4	5.2
5NCS	$Na_4CaSi_3O_9$aq	4	1.33	1.67	0.33	50	34.4

prepared from NaOH, $Ca(OH)_2$, and SiO_2 (silica-gel). The composition of these mixtures is given in Table 1. It is clearly seen that the Ca/Si ratios in sodium-containing hydrate phases are exactly the same as Ca/Si in some well-known calcium silicate hydrates. The subsequent second series was produced by incorporation of additional Al-bearing component calculated as 10% by weight Al_2O_3 to the total mass of oxides $Na_2O + CaO + SiO_2$ in the samples of the first series. The NCAS mixtures thus obtained were autoclaved for 24 h at temperatures of 160, 200, and 240°C, respectively.

The third series of samples was composed exclusively of $Ca(OH)_2$ and SiO_2. The CaO-to-SiO_2 molar ratios in these samples were the same as in the samples of the basic series. These mixtures were autoclaved for 24 h at 200°C.

In the next step the effect of varying the sodium oxide content on the formation of both gyrolite and xonotlite was investigated. A constant amount of aluminium was also introduced into some samples. The mixtures composed of calcium hydroxide and amorphous silica (finely dispersed Aerosil), mixed to give the CaO/SiO_2 molar ratio 0.67 in the case of gyrolite series and 1.00 in the case of xonotlite, were mixed with sodium hydroxide to produce an Na_2O content of 1, 5, 10, and 20% by weight to the total mass of $CaO + SiO_2$ oxides. The reference samples without admixtures were also prepared. The samples with 20% Na_2O were finally mixed with additional $Al(OH)_3$ to produce constant Al_2O_3 content, equal to 10% by weight of $CaO + SiO_2$. Therefore, the third series of six samples thus produced were mixed as follows: (1) 0% Na_2O, (2) 1% Na_2O, (3) 5% Na_2O, (4) 10% Na_2O, (5) 20% Na_2O, and (6) 20% Na_2O + 10% Al_2O_3. The mixtures were subsequently autoclaved for 24 h at a temperature of 200°C.

In the subsequent series of experiments, the formation of xonotlite was studied starting from the mixtures with different SiO_2-bearing components, viz. silica gel of coarser grains as used in NCS series sample preparation, as well as the finely ground quartz. The six-sample series were mixed with sodium (and aluminium) as listed above.

For further studies the mixtures with the silica gel of coarser grains were selected. Several six-sample series were examined to follow the effect of variable time on the formation of xonotlite and on the transitions: CSH → CSH I → tobermorite(?) → xonotlite(?), in sodium- (with and without aluminium) doped systems, at temperatures of 160 and 200°C.

Finally, the reference series without Na_2O was produced. The samples were mixed at CaO/SiO_2 molar ratio corresponding to $(CaO + Na_2O)/SiO_2$ molar ratio in the basic xonotlite series mixed with sodium. In such a way the effect of declination from stoichiometry on the formation of xonotlite was also investigated.

After thermal treatment the materials were ground with acetone to produce the fine-grained specimens for the phase composition determination. The solution of water and acetone was evaporated. This procedure was repeated several times. Finally, the specimens were dried at 60°C. The phase composition of the products was examined by XRD (TUR M64). The phase identification was done based on the ASTM data and some literature data. The semiquantitative estimation was done by comparison of peak height.

The fractured samples for scanning electron microscopy (SEM) observations were placed in alcohol and dried before preparation. The microstructure was observed by means of Tesla BS 300 scanning electron microscope.

3. Results

The results of XRD studies are given in Tables 2 through 8 and the examples of XRD plots are shown in Figs. 1 and 2.

The results of phase composition studies for the reference samples (i.e., corresponding to CaO/SiO_2 molar ratios in NCS and NCAS series) produced from the SiO_2, $Ca(OH)_2$, and H_2O containing mixtures and autoclaved for 24 h at a temperature of 200°C are presented in Table 4. In Table 6, the XRD results dealing with the phase composition of xonotlite series produced with different silica-bearing components are shown. In Table 7, the XRD results dealing with the phase composition of xonotlite series produced at different temperatures (160 or 200°C) within 2 to 48 h are presented.

The phase compositions of autoclaved materials mixed at CaO/SiO_2 molar ratio corresponding to $(CaO + Na_2O)/SiO_2$ molar ratio in the series admixed with sodium are given in Table 8.

Table 2
Phase composition of products in NCS series subjected to hydrothermal treatment

	Phases detected in product after 24 h autoclaving at temperatures (°C)		
No.	160	200	240
1NCS	$N_2C_2S_2$aq, CSHI(T)	CSHI(T)	CSHI(T)
2NCS	CSHI(T)	P	P
3NCS	CSH	CSH, G	CSHI(T)
4NCS	CSHI, G(?)	G, CSH	G, CSHI(T)
5NCS	P, CSHI	P	P

Chemical composition of mixtures is given in Table 1. CSH: poorly crystallized, nearly amorphous calcium silicate hydrate, showing practically only the XRD peak corresponding to $d = 0.307$ nm; CSHI: calcium silicate hydrate of more ordered structure, with further two interplanar spacings (0,307; 0,280; 0,183 nm). T: tobermorite (d = 1, 136; 0,566; 0,357; 0,311; 0,299; 0,283; 0,253 nm); Xo: xonotlite (d = 0,700; 0,425; 0,364; 0,325; 0,308; 0,283; 0,270 nm); P: pectolite (d = 0,385; 0,358; 0,328; 0,308; 0,289; 0,272; 0,258; 0,242; 0,231; 0,228; 0,215 nm); G: gyrolite (d = 2,222; 1,099; 0,840; 0,741; 0,420; 0,366; 0,312; 0,280 nm); Z: Assarson's Z phase, precursor of gyrolite (d = 1,53; 0,838; 0,418; 0,305 nm); $N_2C_2S_2$aq: hydrated metastable sodium-calcium silicate (d = 0,386; 0,285; 0,272 nm); AH_3: unreacted alminium hydroxide residue (d = 0,485; 0,437; 0,432 nm); An: analcite, $NaAlSi_2O_6 \cdot H_2O$ (0,563; 0,345; 0,292; 0,268 nm); Tr: truscottite, calcium silicate hydrate of low CaO content, formed preferentially in the presence of alkalis (d = 1,887; 0,943; 0,763; 0,465; 0,413; 0,380; 0,347; 0,315; 0,300; 0,283; 0,263 nm), α-C_2SH (d = 0,422; 0,390; 0,354; 0,327 nm). The question mark denotes that the phase occurs in negligible amount and that it was detected based on some peaks of poor intensity; it is difficult to prove its presence because of the interferences of stronger peaks.

Table 3
Phase composition of NCS products enriched with 10% Al_2O_3 (NCAS series) subjected to hydrothermal treatment

No.	Phases detected in product after 24 h autoclaving at temperatures (°C)		
	160°C	200°C	240°C
1NCSA	T, AH_3[a]	T	T, AH_3[a]
2NCSA	P, CSH, An(?)	An, AH_3, CSHI	An, AH_3[a]
3NCSA	CSH, P(?)	CSHI	CSHI, AH_3, An
4NCSA	CSH, AH_3	CHS, Z	CSHI, G, An
5NCSA	unknown (?), An	AH_3, An	CHS, P

Same symbols as Table 2.

[a] Small amount.

Examples of microstructure are shown in Figs. 3. The SEM observations give an insight into the phase composition determination. The examples of microstructure in which the well-developed broomlike pectolite forms are visible are shown in Figs. 3a and 3b. The growing analcite crystal and the analcite in its final form with smooth walls are presented in Figs. 4a and 4b. The evolution of the morphology of hydrated phases formed in the presence of sodium is illustrated in Figs. 5a through 5c and 6. The honeycomb structure of C-S-H formed at lower NaOH addition and at lower temperature/shorter time of autoclaving (Figs. 5a, 5b) is followed by the platelike tobermorite when Al is added (Fig. 5c). The needlelike xonotlite forms are formed at prolonged curing at some sodium content (Fig. 6).

4. Discussion

In this work the effects of sodium, as well as of sodium and aluminium acting together, on the processes occurring in the mixtures from the system $CaO\text{-}SiO_2\text{-}H_2O$ cured in hydrothermal conditions were studied.

As the first step the initial batches (NCS and CS series), differing significantly with molar proportions of basic components, were prepared (CaO/SiO_2 in the range 0.33 to 1.00). Sodium oxide content varied from 5 to 35% by weight. At Na_2O content exceeding 20% and at high silica content (more than 50%) the pectolite phase was detected in the products. The characteristic morphology of pectolite crystals is shown in Fig. 3. In one case ($CaO/SiO_2 = 1$, Na/Ca = 1; 160°C/24 h) the metastable $N_2C_2S_2aq$ phase was determined to be present. It was found that when the Na_2O admixture was not higher than 20%, it did not produce any detectable sodium-calcium silicate phase, but only modified the crystallization of the other calcium silicate hydrated products. As one could notice the proportions between the CaO and SiO_2 in these other batches were the same as in gyrolite or xonotlite phases (0.67 and 1.00, respectively; see Table 1). It appeared that xonotlite did not form in the sample doped with over 20% Na_2O, but gyrolite was found as a component in the sample with $CaO/SiO_2 = 0.67$ and at relatively low sodium content as well as in some other samples with $CaO/SiO_2 = 0.67$. This was taken as a starting point in preparation of mixtures composed of $Ca(OH)_2$ and SiO_2 without admixtures. The CaO to SiO_2 molar ratios in these samples were the same as in the samples of basic NCS series. Analyzing the XRD data for these two series (Tables 2 and 3), one can see that at molar ratio $CaO/SiO_2 = 1.00$, in the batch without admixture cured within 24 h at 200°C, the complete (from the XRD method point of view) reaction of xonotlite formation occurs, while at the presence of over 20% Na_2O only the intermediate product, the CSH phase of ordered structure transforming to tobermorite, is detected. Also at lower CaO/SiO_2 ratio (0.67 or less) in the mixtures with no admixture, the formation of gyrolite or Z phase occurs better, while at Na_2O admixture (about 5 and 10%, respectively) a C-S-H residue is present. This proves that

Table 4
Phase composition of products formed in CS series, subjected to hydrothermal treatment (200°C/24 h)

No.	CaO/SiO_2 molar ratio	Phases detected in reaction product
1CS	0.33	Z (G), CSH
2CS	0.5	Z, G, CSH
3CS	0.67	G, (Z), CSH
4CS	1	Xo

Same symbols as Table 2.

Table 5
Phase composition of products in gyrolite series ($CaO/SiO_2 = 0.67$) with admixtures, prepared using Aerosil, subjected to hydrothermal treatment (200°C/24 h)

No.	Admixtures (wt. %)	Products detected by XRD
1	0%	CSH
2	1% Na_2O	CSH
3	5% Na_2O	CSH, Z
4	10% Na_2O	CSHI, G
5	20% Na_2O	CSHI, G
6	20% Na_2O + 10% Al_2O_3	T, CSH

Same symbols as Table 2.

Table 6
Phase composition of products in xonotlite series ($CaO/SiO_2 = 1.00$) with admixtures, produced using different silica-bearing components, subjected to hydrothermal treatment (200°C/24 h)

No.	Admixtures (wt. %)	Products detected by XRD in samples with different SiO_2 source		
		Aerosil	quartz	SiO_2 gel
1	0%	CSH	Xo	Xo
2	1% Na_2O	CSH	Xo	Xo
3	5% Na_2O	Xo, Tr[a]	Xo, $N_2C_2S_2$(?)[a]	Xo
4	10% Na_2O	Xo, Tr[a]	Xo, $N_2C_2S_2$(?)[a]	Xo, CSH
5	20% Na_2O	Xo, Tr[a]	Xo, $N_2C_2S_2$(?)[a]	CSH I, T
6	20% Na_2O + 10% Al_2O_3	T	T, $N_2C_2S_2$(?)[a]	T

[a] Small amount.

Table 7
Phase composition of products in xonotlite series ($CaO/SiO_2 = 1.00$) with admixtures, produced using silica gel component, presented as a function of hydrothermal curing conditions

	Phases detected by XRD as a function of varying time/temperature parameters						
No.	200°C/ 2 h	200°C/6 h	200°C/12 h	200°C/24 h	200°C/48 h	160°C/24 h	160°C/48 h
1	CSH	Xo	Xo	Xo	Xo	CSH	CSH
2	CSH	Xo	Xo	Xo	Xo	CSH	CSH
3	CSH	CSH	CSH	Xo	Xo	CSH	CSH
4	CSH	CSH	CSH	Xo, CSH	Xo	CSH	CSH
5	CSH I	CSH I	CSH I	CSH I, T	CSH I, T	CSH I	CSH I
6	CSH I, T	CSH I, T	T, CSH I	T	T	CSH I	CSH I, T

Sample numbers and contents of admixtures are the same as in Table 6.
Same symbols as Table 2.

there are some effects that hinder the formation of assumed phases. The high concentration of sodium ions in the liquid phase of hydrating suspension can disturb the dissolution and further reaction of calcium hydroxide, although Na ions undoubtedly promote the dissolution of silica-bearing component. Presumably the calcium and silicate ions are removed from the solution giving the C-S-H, which does not transform easily into the assumed final product. Because of the reduced concentration of Ca^{2+}, the CaO/SiO_2 ratio in this C-S-H phase may be lowered.

Some more information dealing with the (Na_2O)-CaO-SiO_2-H_2O system as a model of real cementitious systems cured in hydrothermal conditions can be produced when aluminium hydroxide is added to the hydrating mixtures. As results from many XRD data for NCAS samples show, particularly those autoclaved at lower temperatures, alumina is easily combined by other compounds in this system (see Table 3). However, the phase composition of autoclaved NCS mixtures doped with aluminium becomes more complex. Generally, the synthesis of pectolite is hindered and the transformation of disordered, amorphous C-S-H to CSH I and further on to tobermorite takes place. This can be derived from the evolution of 1.1 nm XRD peak and the occurrence of two other peaks attributed to more ordered C-S-H. The stabilization of tobermorite occurs predominantly in the mixtures with over 20% Na_2O, at CaO/SiO_2 molar ratio 1.00, admixed with 10% Al_2O_3.

In many samples with sufficient sodium content the sodium aluminosilicate-analcite ($NaAlSi_2O_6 \cdot H_2O$) appears. The formation of this phase was reported by Langton et al. [13] in the mixtures containing Na_2O, Al_2O_3, and SiO_2. The large, well-developed, characteristic analcite crystals were observed by SEM and particular stages of their growth have been documented (see Fig. 4).

In the experiments with NC(A)S series it appeared that the phases containing Na as a constituent did not form starting from the mixtures in which CaO/SiO_2 molar ratio corresponded exactly to xonotlite or gyrolite, and more or less ordered C-S-H was found as a component of product after autoclaving. Therefore, in the next step the studies on gyrolite and xonotlite formation were continued at variable content of sodium admixture. Because the gyrolite formation was rather slow under the assumed conditions, only one series of samples was produced and characterized (see Table

Table 8
Phase composition of products in xonotlite series of CaO/SiO_2 molar ratio declined from 1.00, produced in hydrothermal conditions at 200°C

		Phases detected by XRD as a function of time of hydrothermal treatment	
No.	CaO/SiO_2	6 h	48 h
1ref	1,00	Xo	Xo
2ref	1,03	Xo	Xo
3ref	1,14	T	CSH, αC_2SH[a]
4ref	1,27	CSH	CSH, αC_2SH[a]
5ref	1,54	CSH, CH	CSH, αC_2SH[a], CH

[a] Small amounts.

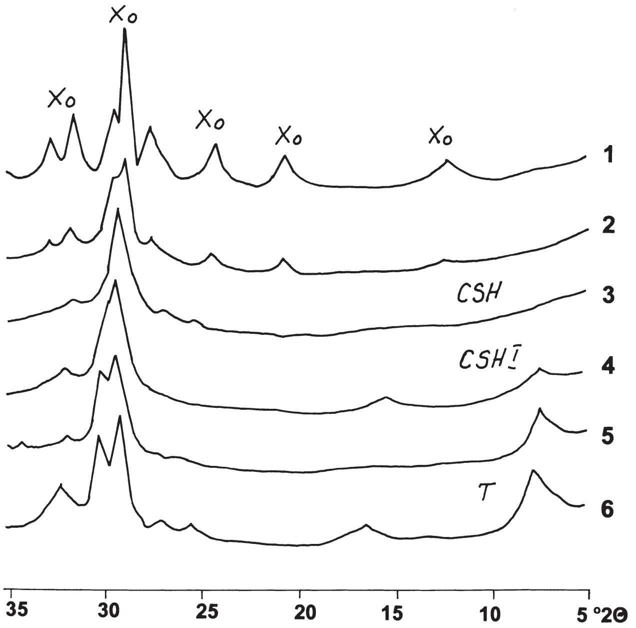

Fig. 1. XRD patterns of samples prepared at 200°C/6 h, $CaO/SiO_2 = 1.00$ with no admixture (1), 1% Na_2O (2), 5% Na_2O (3), 10% Na_2O (4), 20% Na_2O (5), 20% Na_2O + 10% Al_2O_3 (6). See the peaks of xonotlite in (1) markedly reduced in (2) and a continuous transformation of poorly crystallized C-S-H in (3) to better developed ones in (4) and (5) and to poor tobermorite in (6).

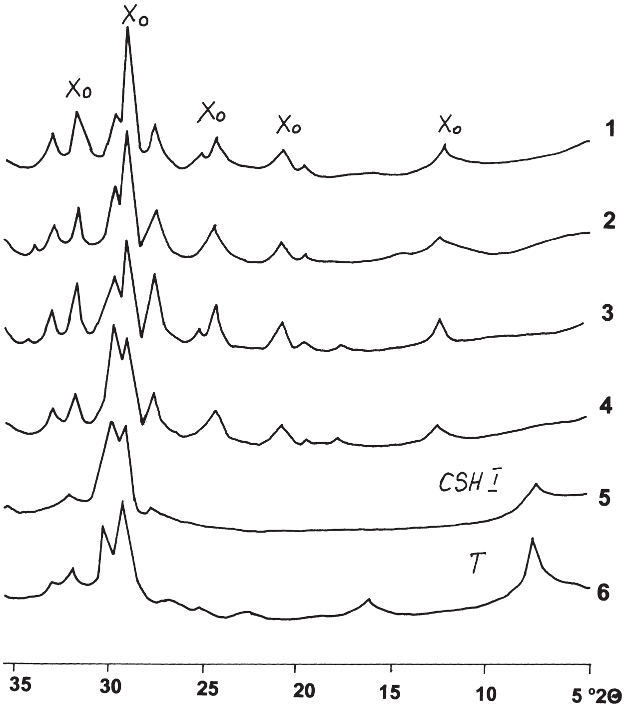

Fig. 2. XRD patterns of samples prepared at 200°C/48 h, $CaO/SiO_2 = 1.00$ with no admixture (1), 1% Na_2O (2), 5% Na_2O (3), 10% Na_2O (4), 20% Na_2O (5), 20% Na_2O + 10% Al_2O_3 (6). See the peaks of xonotlite in (1), (2), (3), and (4), C-S-H I in (5), and tobermorite in (6).

5). The main research focused on the formation of xonotlite. The mixtures with CaO/SiO_2 molar ratio 1 and sodium oxide admixture ranging from 1 to 20% were produced. In some experiments dealing with the xonotlite synthesis, different SiO_2 sources were taken into account (see Table 6). Aluminium hydroxide calculated as 10% Al_2O_3 of (CaO + SiO_2) was added to the samples with 20% Na_2O. In any event, the xonotlite phase seems to be more significant from the practical point of view.

The significant influence of sodium on the processes occurring in the autoclaved CaO-SiO_2-H_2O mixtures has been found. The accelerating effect of sodium, present at a concentration from 1 to 10% Na_2O, on the transformation of highly disordered C-S-H structure to the most ordered one was documented. This effect is visible particularly in case of xonotlite series. The scope of sodium's modifying action depends in turn on the nature of SiO_2-bearing component and/or the time/temperature parameters of hydrothermal process.

In the batches produced from very fine, amorphous silica (Aerosil), heated hydrothermally for 24 h at 200°C, xonotlite was detected at 5% and higher Na_2O admixture. At lower content and without admixture, a disordered C-S-H was formed. One can presume that amorphous silica acts as a nucleating agent and probably does not dissolve partially, but reacts with calcium ions from the solution giving an amorphous, highly disordered C-S-H of low CaO/SiO_2. This first product does not easily transform to the more ordered structures. In other words, Aerosil used in gyrolite and xonotlite synthesis is highly reactive and transforms into C-S-H directly by sorption of calcium hydroxide from the solution. Such a situation has been already described by other authors who investigated the formation of the other calcium silicate hydrates [22].

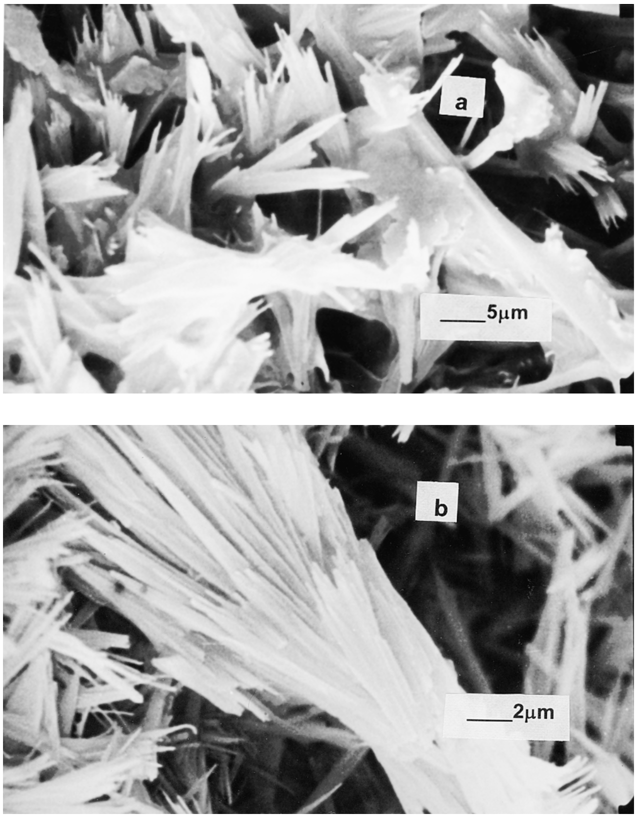

Fig. 3. (a, b) SEM microstructure of sample 2 NCS, cured at 240°C/24 h. See the broomlike forms of pectolite.

On the other hand, when the results produced in experiments with Aerosil are compared to those for NCS and CS samples (produced from ordinary silica gel, see Tables 2 and 4), there are some discrepancies. In the latter case the formation of xonotlite and gyrolite occurs easily without admixture (see Table 4) while at a high (20%) sodium oxide content, an ordered CSH I is detected as a main product (see Table 2). The formation of xonotlite is thus inhibited by the presence of admixture. Taking this into account the analogous xonotlite series of samples were mixed using a silica gel as described previously (of coarser grains) or ground quartz. As has been mentioned earlier, in the mixtures with finely dispersed silica (Aerosil), the xonotlite was not formed in the reference, neat sample at the hydrothermal treatment within 24 h at 200°C. However, this phase was produced in the further samples of this series, admixed with 5 to 20% Na_2O. In the analogous series with silica gel, cured in the same way, the xonotlite was formed in the reference sample and in the samples with 1 to 5% Na_2O. At high Na_2O content (20%) the degradation of structure was observed—only the CSH I (probably mixed with tober-

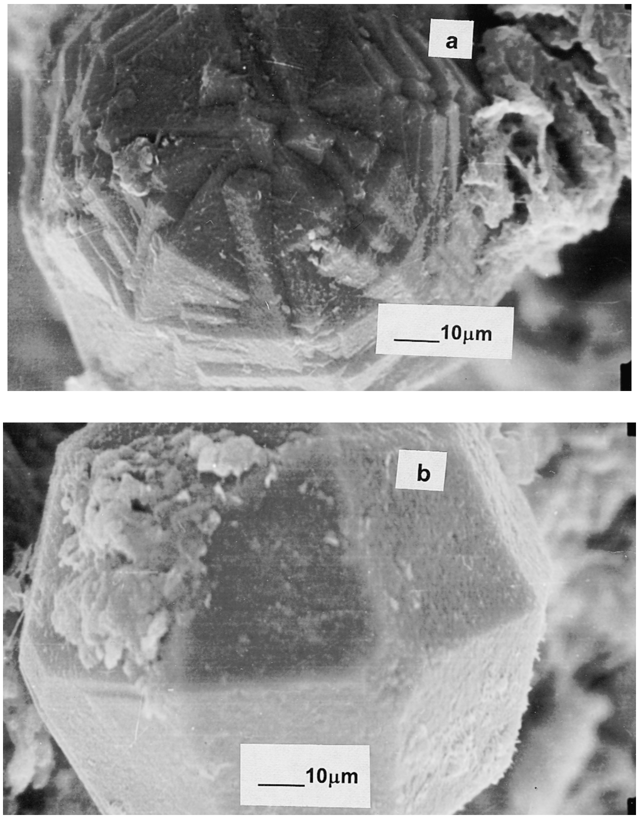

Fig. 4. SEM microstructure of growing analcite crystal (a) and analcite crystal in its final form (b), sample 5 NCAS, cured at 200°C/24 h.

morite) was detected; a noticeable xonotlite content decrease took place at 10% Na_2O. The effect of quartz at the same curing conditions was slightly different. This material is known because of its stimulating role in the formation of tobermorite. The relatively low, moderate rate of reaction between quartz and lime in hydrothermal conditions, as compared with the other forms of silica, was previously reported [20,23]. This could explain the formation of relatively ordered structure of xonotlite in the sample without admixture and at 1 to 10% Na_2O. The other crystalline phase could be also detected, presumably $N_2C_2S_2$ (there is a strong coincidence between the XRD data for xonotlite and for this phase). In the sample with 20% Na_2O, a significant amount of tobermorite was produced (see Table 6). In all the mixtures thus examined, irrespective of the siliceous component, the 10% Al_2O_3 admixture (apart from 20% Na_2O) stabilized the tobermorite phase and other products were not detected.

For the next step of the studies, the mixtures with the silica gel were selected as giving the most clear results. As one could expect, the change of reaction parameters such as time and temperature shed some new light on the effect of alkaline component and the formation of calcium silicate-hydrated phases. First of all it has been found the xonotlite formation did not occur at temperature 160°C even at prolonged time (48 h). One can notice only a slight transformation of poorly crystallized C-S-H to more ordered form in the presence of 20% Na_2O, and further on, when the additional Al-bearing admixture is introduced (see Table 7). On the other hand, the phase composition changes for the mixtures heated hydrothermally at 200°C exhibit some clear regularities. At longer time of treatment, the range of structure ordering or stabilization increases (as can be seen from Table 7). After 2 h of treatment at 200°C, only the C-S-H type products are formed. Their structure becomes more ordered as the sodium content increases. Alumina addition brings about the stabilization of tobermorite. The transfor-

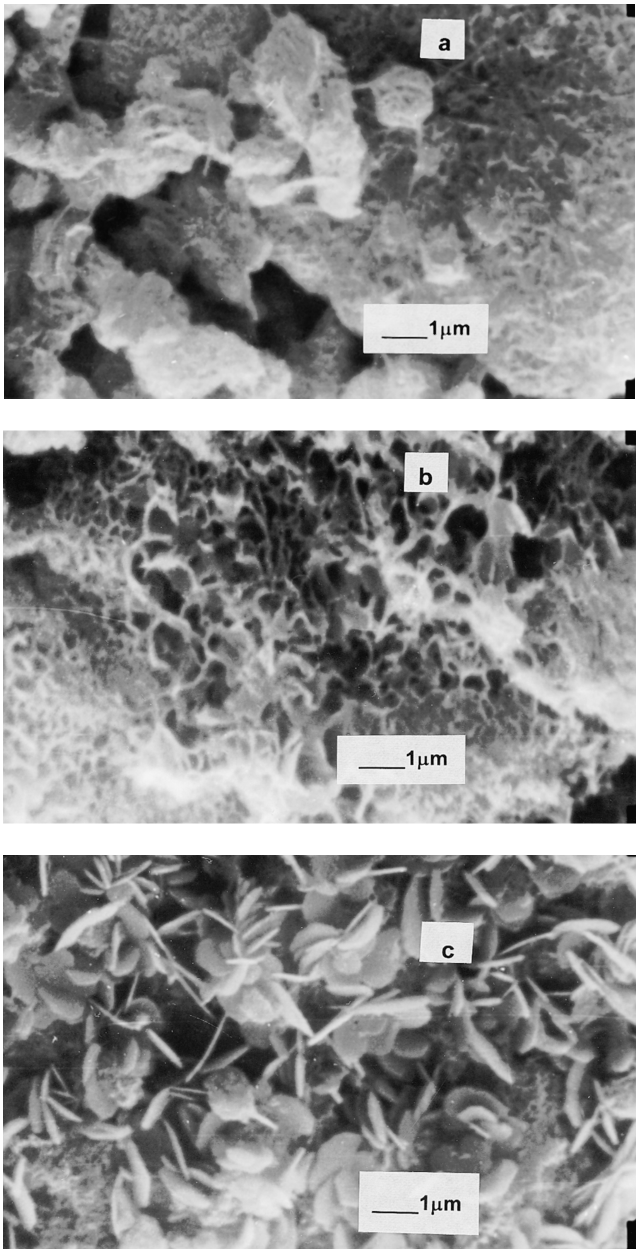

Fig. 5. SEM microstructure of sample cured at 200°C/2 h, $CaO/SiO_2 = 1.00$. (a) The network of poorly crystallized C-S-H is visible (1% Na_2O). (b) The honeycomb structure formation can be noticed (10 % Na_2O). (c) The platelike forms of tobermorite (20% Na_2O + 10% Al_2O_3).

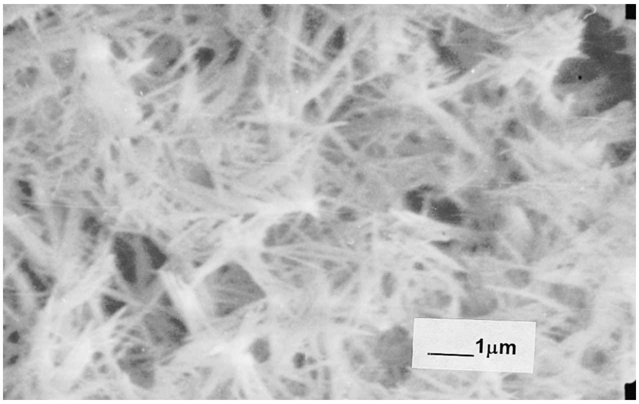

Fig. 6. SEM microstructure of sample cured at 200°C/48 h, $CaO/SiO_2 = 1.00$, 5 % Na_2O. See the network of xonotlite needles.

mation of structure is visible in SEM observations. The areas of interlocked C-S-H fibres and honeycomb structure appear in admixed samples, as can be seen in Figs. 5a and 5b. Further on, the platelike forms, characteristic of the tobermorite-like phase, are visible (Fig. 5c).

In the samples cured for 6, 12, 24, or 48 h at 200°C the xonotlite, tobermorite, and C-S-H were detected. At 6 h of thermal treatment, in the mixture without admixture and in the mixture with 1% Na_2O, xonotlite is formed (as can be seen in Fig. 1). At prolonged time of hydrothermal treatment (48 h), the xonotlite crystallization is found also in the samples with 5 and 10% Na_2O, replacing the poorly crystallized C-S-H present after shorter time of autoclaving (see Fig. 2). At 20% Na_2O only the transformation C-S-H → C-S-H I is observed.

Under SEM the xonotlite phase is visible usually as a network of long, thin needles (Fig. 6). Some amount of sodium seems to favour the formation of well-developed, smooth xonotlite crystals.

In all the series examined, the aluminium addition together with sodium stabilized the formation of tobermorite. From SEM observations one can conclude that the prolonged curing at temperature 200°C promotes the corrosion of tobermorite by alkaline solution.

In the light of the presented results, it seems that in the hydrothermally treated mixtures containing the CaO- and silica-bearing components at CaO/SiO_2 molar ratio close to 1, the transformation C-S-H → xonotlite without an intermediate product, tobermorite, is possible. When the tobermorite is produced, particularly in the presence of sodium and aluminium, the transformation to xonotlite becomes difficult or even impossible. The C-S-H being a precursor of xonotlite must have a specific, xonotlite-friendly composition and structure. Presumably the supersaturation of the liquid phase with silica (as takes place in neat systems or some systems with moderate sodium concentration) promotes the formation of C-S-H, structurally related to xonotlite.

Since it results from the mixtures having the CaO/SiO_2 molar ratio more or less higher than 1, the formation of xonotlite is sensitive for declination from stoichiometry (Table 8). The excess lime is hidden in C-S-H, depending on curing conditions, it enters the calcium silicate-hydrated phases or remains as unreacted residue (at $C/S > 1{,}5$). One can presume that the deficiency of CaO in solid intermediate phase, being in quasi-equilibrium with the liquid (for example, at quick precipitation of C-S-H with low CaO/SiO_2), or lower calcium ions concentration in the presence of sodium ions are not an obstacle in xonotlite structure formation. On the other hand, some excess of calcium ions can effectively hamper the synthesis of xonotlite without disturbing the local formation of tobermorite structure. The direct determination of equilibrium in the solution in contact with the solid in hydrothermal conditions is unrealisable, practically. It is known that the sodium ions in the liquid phase of hydrating suspension can disturb the dissolution and subsequent further incorporation of calcium ions into the structure of products, though undoubtedly they promote the dissolution of siliceous component, unless both the calcium and silicate ions are removed from the solution through the crystallization of products. These mutually opposed processes are of particular importance in the reaction occurring in the $CaO\text{-}SiO_2\text{-}H_2O$ system with admixtures.

5. Conclusions

1. The processes occurring during the hydrothermal treatment of CaO- and SiO_2-bearing components in water suspension are modified by the presence of sodium. Sodium accelerates the formation of poorly crystallized calcium silicate hydrates, but further transformation of this intermediate product into the more-ordered, well-developed crystalline forms can be disturbed at some admixture content.
2. The Ca-Na-containing phases are formed at significant sodium content, over 20% Na_2O by weight and at SiO_2 content exceeding 50% by weight.
3. The xonotlite synthesis is affected by the nature of SiO_2-bearing component (apart from the time/temperature parameters of hydrothermal curing) and by sodium admixed to the hydrating calcium silicate suspension. In the presence of amorphous, very finely dispersed silica the crystallization process is slow. The formation of xonotlite occurs at temperature 200°C in the presence of some Na_2O admixture (up to 10%), depending on the time of hydrothermal treatment and nature of SiO_2-bearing component. The structure of xonotlite is generally destabilized by an excess of Na_2O or CaO.
4. The xonotlite synthesis can occur without tobermorite as an intermediate phase.
5. Al admixed to the calcium hydroxide, silica, and NaOH water suspensions in the form of aluminium hydroxide brings about further changes in phase com-

position of autoclaved product; these changes can be characterized as follows:

- At high sodium and low silica content the sodium aluminosilicate analcite ($Na[AlSi_2O_6] \cdot H_2O$) is produced.
- In cases where Al does not form any Al-containing detectable phase, the formation of better developed CSH I transforming subsequently to the tobermorite takes place, irrespectively of CaO and SiO_2 molar ratio in the batch.
- Tobermorite is stabilized by an additional 10% Al_2O_3 admixture to the all calcium hydroxide, silica ($CaO/SiO_2 = 1$), and 20% Na_2O-containing water suspensions.

Acknowledgments

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