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EFFECT OF SOME INORGANIC ADMIXTURES ON THE FORMATION AND PROPERTIES OF CALCIUM SILICATE HYDRATES PRODUCED IN HYDROTHERMAL CONDITIONS

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ABSTRACT

Hydrated calcium silicates have been synthesized at 200°C under saturated steam pressure, giving materials consisting of ill crystallized calcium silicate hydrates, formed as an initial product and/or more crystalline forms. Three series of samples having different CaO/SiO_2 ratios and doped with inorganic compounds such as $CaCl_2$, $AlCl_3$, $CrCl_3$, Na_2CrO_4, NaOH and $Al(OH)_3$ were produced. The phase composition of the samples was examined by XRD. The microstructure was observed with the SEM and porosity measurements. Their thermal behaviour was characterized by DTA/TG methods. It has been found that the CaO/SiO_2 lowering promoted the formation of poorly crystalline C-S-H with high surface area and porosity. The stabilizing effect of Al on tobermorite was generally confirmed. The formation of disordered C-S-H, with relatively high water content, surface area and porosity in the presence of $CrCl_3$ was found. The formation of xonotlite was promoted by $CaCl_2$ and NaOH. *Copyright © 1997 Elsevier Science Ltd.*

Introduction

The formation of many crystalline calcium silicates hydrates using hydrothermal conditions experience an intermediate stage in which the precursor, near amorphous calcium silicate hydrate (C-S-H) is produced, sometimes followed by 1.1nm tobermorite. Tobermorite $Ca_5[Si_6O_{18}H_2].H_2O$ has a relatively stable chemical composition with a CaO to SiO_2 molar ratio equal to 0.83 and a well defined structure. In the CaO to SiO_2 molar ratio mixtures close to 1, the xonotlite phase - $Ca_6SiO_6O_{17}(OH)_2$ can be synthesized as a final product, at a temperature of synthesis not lower than 180°C. When the CaO to SiO_2 ratio falls below 1 the gyrolite phase, having a formula $Ca_8(Si_4O_{10})_3(OH)_4.6H_2O$, is formed as a final product. In practice, most poorly or well crystallized calcium silicate hydrates in the autoclaved mixtures can be detected by XRD and under SEM. The formation, structure and other properties of the "neat" hydrated calcium silicate phases have been reviewed in some works of fundamental importance [1,2] as well as studied in detail by numerous investigators [e.g. 3-6]. For the last 10 years, as new instrumental methods were put into use (NMR), new information concerning the structure of C-S-H have been published [7].

Small amounts of inorganic admixtures can affect substantially the kinetics and mechanism of calcium silicate hydrate synthesis as well as the properties of the products. The foreign cations and anions can act in different ways. They can promote the dissolution of initial lime and silica bearing compounds, and/or accelerate or hinder the crystallisation of products. Some amount of admixture can enter the structure of calcium silicate hydrates. The role of aluminium in the stabilisation of tobermorite has been widely reported [8,9]. There are also some works on the effect of alkalis [10], chromium [11] and other compounds discussed in terms of C-S-H to tobermorite transition [12,13]. For the last few years some admixtures and structures have been studied in the aspect of nuclear and other hazardous wastes immobilisation [14,15].

Materials

Mixtures of calcium hydroxide (analytically pure), silica-gel (pure) and water with CaO to SiO_2 molar ratios equal to 0.67, 0.83 and 1.00, corresponding to gyrolite, tobermorite and xonotlite respectively were prepared. Apart from the reference samples without admixtures, the following compounds of analytical purity (calculated as 5 wt.% of anhydrous $CaO+SiO_2$ substance) were introduced to the batch:

$CaCl_2$, $AlCl_3$, $CrCl_3$, Na_2CrO_4, NaOH and $Al(OH)_3$.

Methods

The samples were subjected to 24 h thermal treatment in a laboratory autoclave at 200°C. After this, the samples were crushed, washed with acetone and dried at 60°C before the further measurements. Some pieces of fractured samples were subjected to the SEM observations (JEOL 5200 with LINK AN 10/5 EDS microanalyser). The phase composition was characterized by XRD (TUR M-62 diffractometer). The thermal decomposition was followed by DTA/TG (Derivatograph Q 1500D). The molybdate complexation method [16] was applied to estimate the silicate anion structure. The surface area and porosity were measured by nitrogen adsorption using the ASAP 2000 equipment.

Results

The XRD patterns for the series of samples having different CaO/SiO_2 ratios are plotted in Figures 1-3.

The effect of CaO/SiO_2 ratio and admixtures is clearly visible. At $CaO/SiO_2 = 0.67$, corresponding to the gyrolite phase, the poorly crystallized material is a predominant product, irrespective of the admixtures used. In the pure mixture, as well as in the samples made with $CaCl_2$, $AlCl_3$ and Na_2CrO_4 the near amorphous C-S-H material is detectable almost exclusively. The samples prepared with $CrCl_3$ and NaOH reveal some Assarson's Z-phase [17]. In the latter case, some 1.1nm tobermorite and xonotlite can also be detected as was the case in the sample made with $Al(OH)_3$. Very small peaks which can be attributed to the crystalline sodium and calcium silicate hydrate - pectolite ($NaCa_2Si_3O_9H$) appear on the pattern of the samples with Na_2CrO_4. At higher CaO/SiO_2 ratios, corresponding to the tobermorite (0.83), the higher degree

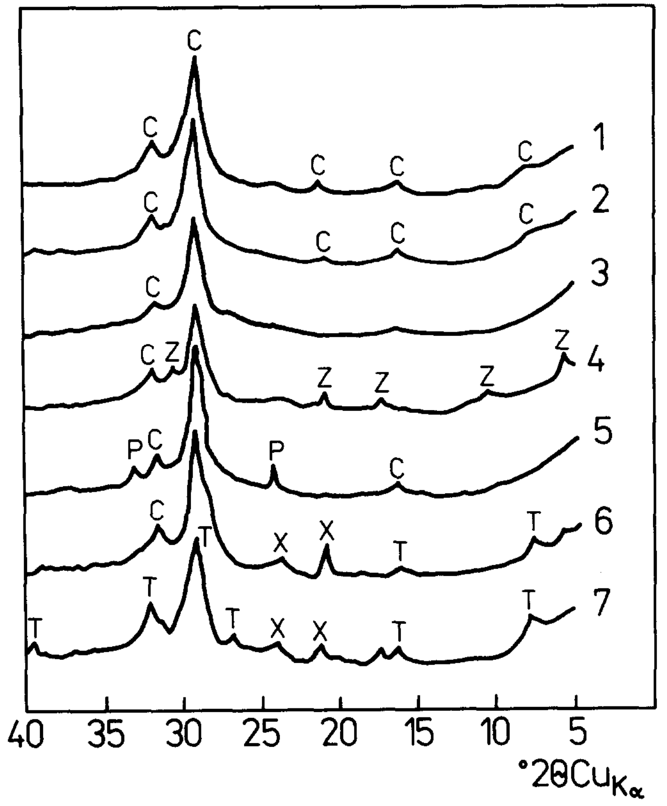

FIG. 1.
XRD patterns of the samples prepared at 200°C/24h, $CaO/SiO_2 = 0.67$ with no admixture (1) and with the following admixtures (5wt. %): 2-$CaCl_2$, 3-$AlCl_3$, 4-$CrCl_3$, 5-Na_2CrO_4, 6-NaOH, 7-$Al(OH)_3$. **C**-C-S-H, **T**-tobermorite, **X**-xonotlite, **Z**-Z-phase.

of crystallinity of the samples thus produced as well as modifying influence of admixtures is evident. The XRD patterns corresponding to the samples prepared with no admixture, with $CaCl_2$, $AlCl_3$ and $Al(OH)_3$ are similar. In the presence of $CaCl_2$, as well as in the unadmixtured sample the small amount of xonotlite, occurring together with tobermorite was found. Tobermorite together with xonotlite is also produced in the samples mixed with Al compounds.The samples with Na_2CrO_4 and NaOH show only the presence of xonotlite and pectolite. In the presence of $CrCl_3$ the C-S-H of low crystallinity is stabilized. At the CaO/SiO_2=1 some further changes are observed. The xonotlite phase is formed as a main component in the samples without admixture, with $CaCl_2$ and NaOH. The tobermorite phase is stabilized in those mixed with $AlCl_3$, $Al(OH)_3$ and accompanied by xonotlite. Small 1.1nm peak at the XRD pattern of $CrCl_3$ proves the transformation of C-S-H structure to tobermorite. The XRD plot of Na_2CrO_4 doped sample exhibits the presence of relatively poorly crystallized C-S-H with some amount of xonotlite.

The SEM observations give interesting insight to the phase composition determination. The example of microstructure in which the well developed plate-like tobermorite forms occur

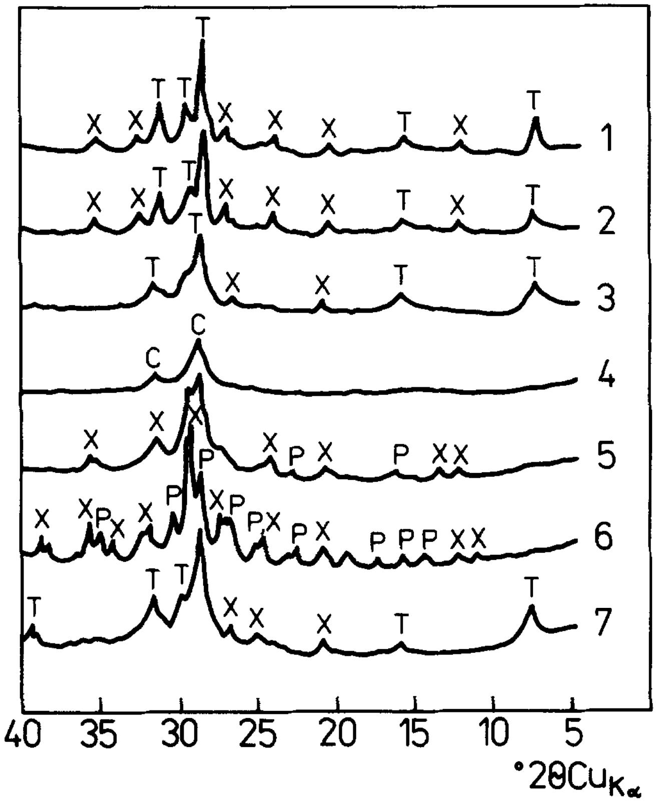

FIG. 2.

XRD patterns of the samples prepared at 200°C/24h, $CaO/SiO_2 = 0.83$ with no admixture (1) and with the following admixtures (5wt. %): 2-$CaCl_2$, 3-$AlCl_3$, 4-$CrCl_3$, 5-Na_2CrO_4, 6-NaOH, 7-$Al(OH)_3$. C-C-S-H, T-tobermorite, X-xonotlite, P-pectolite.

together with poorly crystallized C-S-H and fibres of xonotlite is shown in Figure 4. The results obtained by SEM can be summarized as follows:

- the microstructure of C-S-H and tobermorite is affected by the admixtures used, particularly by those containing Cr and Al,
- the characteristic, thin needle-like xonotlite crystals are found in the presence of $CaCl_2$,
- the well developed forms are not present in the samples with CaO/SiO_2 molar ratio equal to 0.67; only in the presence of $Al(OH)_3$ and NaOH the plate-like tobermorite crystals are visible.

The elements introduced with admixtures seem to be randomly distributed in the products and detectable by EDS analysis.

On the DTA curves the endothermic peaks corresponding to the decomposition of hydrates on heating in the range from 60°C to 200°C occur together with the exothermic peaks attributed to the calcium silicates synthesis from the decomposition products over 800°C. The bound

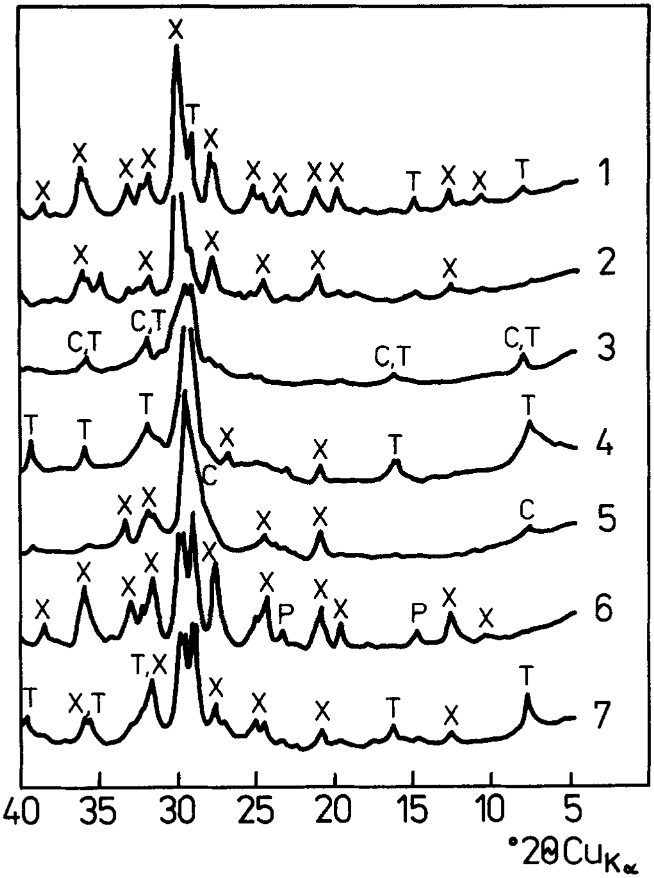

FIG. 3.

XRD patterns of the samples prepared at 200°C/24h, CaO/SiO_2 = 1.00 with no admixture (1) and with the following admixtures (5wt. %): 2-$CaCl_2$, 3-$CrCl_3$, 4-$AlCl_3$, 5-Na_2CrO_4, 6-NaOH, 7-$Al(OH)_3$. **C**-C-S-H, **T**-tobermorite, **X**-xonotlite, **P**-pectolite.

water contents listed in Table 1 reveal a significant variability from about 6% to over 26%. It is not surprising that the bound water content, as measured by thermogravimetry, strongly relates to the structure of products. This, in turn, depends on the phase composition of autoclaved batches, i.e. on the crystalline phases content and on the nature of accompanying C-S-H, influenced by the additives. Theoretically, the bound water content in tobermorite and xonotlite is 14.5% and 8% respectively. A relatively higher percentage of water is connected with the disordered structure of C-S-H phase of low crystallinity, produced in the samples prepared at CaO/SiO_2 ratio equal 0.67. At higher CaO/SiO_2, corresponding to tobermorite, the differences between the samples are more pronounced. The amount of C-S-H occurring together with tobermorite is variable and reveals higher or lower water content. The lowest H_2O percentage was observed in the Na compounds containing samples, the highest - in those prepared with $AlCl_3$ and $CrCl_3$. The formation of xonotlite in the samples with CaO/SiO_2 ratio

FIG. 4.

SEM microstructure of autoclaved sample (200°C/24h). $CaO/SiO_2 = 1.00$, 5% $AlCl_3$. See the poorly crystallized material (C-S-H) with small fibers (xonotlite?) and the plate-like tobermorite forms.

equal to 1 results in the water content decrease, even below the theoretical level. At the presence of $AlCl_3$, $CrCl_3$ and Na compounds the higher values are found.

The silicate anion structure in the autoclaved samples was estimated from the molybdate complexing curves plotted in Figures 5-7, basing on some earlier works [16,18]. Analyzing the sets of curves one should remember that the complexing process takes place after the silicate anions decomposition to monomers with a rate depending on the polimerization degree. Therefore the slope of the curve reflects the highly polimerized fraction residue - the sample is more polimerized as the curve is more parallel to the horizontal axis. Therefore it can be concluded that the condensation process is strongly advanced in the samples with CaO/SiO_2 ratio equal 0.67. Simultaneously, the silicate anion structure is less affected by chemical admixtures than in case of the other two series with higher CaO/SiO_2. The results for the series of samples cor-

TABLE 1

Water Bound in the Products Autoclaved at 200°C/24h (TG measurements)

CaO/SiO_2 ratio	Water content in wt.% as a function of admixture added as 5 wt.%						
	reference	$CaCl_2$	$AlCl_3$	$CrCl_3$	Na_2CrO_4	NaOH	$Al(OH)_3$
0.67	10.1	26.2	16.8	17.1	12.9	12.8	22.9
0.83	10.6	15.1	21.1	22.2	6.4	6.6	17.2
1	7.8	7	19.6	19.7	15.6	14.4	6.8

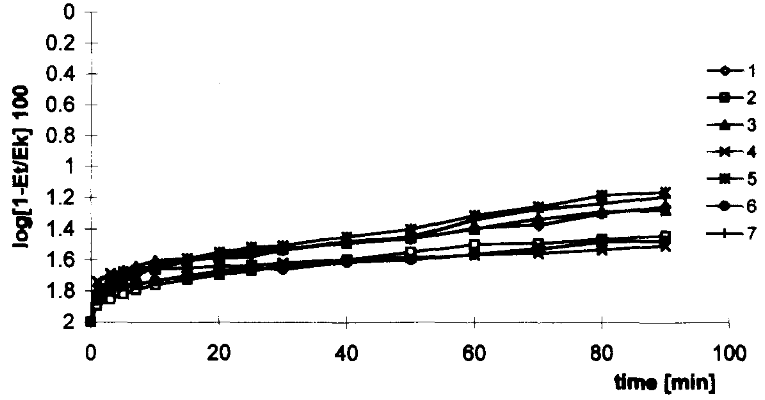

FIG. 5.

Molybdate complexing curves of the samples prepared at 200°C/24h, $CaO/SiO_2 = 0.67$ with no admixture (1) and with the following admixtures (5wt. %): 2-$CaCl_2$, 3-$AlCl_3$, 4-$CrCl_3$, 5-Na_2CrO_4, 6-NaOH, 7-$Al(OH)_3$. Proportion of silica complexed Et/Ek is plotted as log[1 - Et/Ek]100 vs time.

responding to CaO/SiO_2 ratio 1 and 0.83 respectively are relatively scattered but the following remarks can be noted:

- in the "tobermorite" series the amount of polimerized fraction is almost constant and the monomer content varies in a wide range; the highest monomer content occurs in the samples with NaOH and $AlCl_3$,

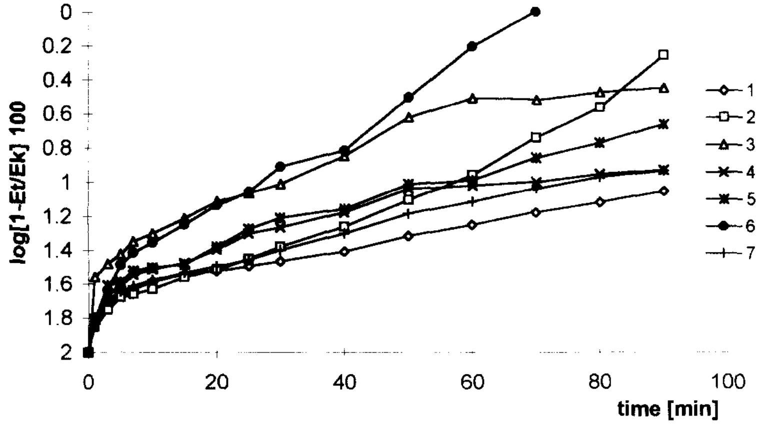

FIG. 6.

Molybdate complexing curves of the samples prepared at 200°C/24h, $CaO/SiO_2 = 0.83$ with no admixture (1) and with the following admixtures (5wt. %): 2-$CaCl_2$, 3-$AlCl_3$, 4-$CrCl_3$, 5-Na_2CrO_4, 6-NaOH, 7-$Al(OH)_3$. Proportion of silica complexed Et/Ek is plotted at

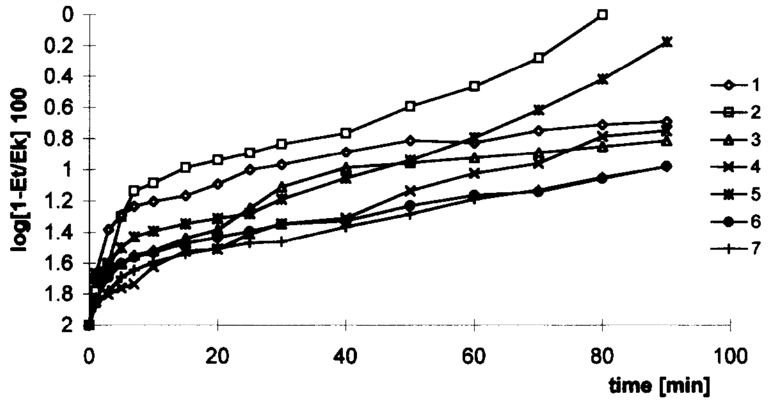

FIG. 7.

Molybdate complexing curves of the samples prepared at 200°C/24h, $CaO/SiO_2 = 1.00$ with no admixture (1) and with the following admixtures (5wt. %): 2-$CaCl_2$, 3-$AlCl_3$, 4-$CrCl_3$, 5-Na_2CrO_4, 6-NaOH, 7-$Al(OH)_3$. Proportion of silica complexed Et/Ek is plotted as log[1 - Et/Ek]100 vs time.

- in the "xonotlite" series the particular samples show significant differences in the degree of silicate anion condensation.

The results of porosity and surface area measurements by nitrogen adsorption are presented in Table 2. The surface areas by BET range from over 10 to almost 140 m^2/g, while the specific pore volumes range from 0.03 cm^3/g to about 0.5 cm^3/g, which corresponds to the relative porosity varying from ca. 7% to over 50%. The pore diameters are in the range to about 100 nm; the mean pore diameter does not exceed 10-20 nm. The surface area of micropores (less than 3 nm) accounts for 10% of total specific surface; in some samples the micropores do not occur. The hysteresis of adsorption - desorption isoterms prove the bottle - neck shape of the pores. Analyzing the data in Table 2 one can conclude that the surface area and porosity of autoclaved samples are strongly affected by chemical composition of the initial batch. The formation of more crystalline phases is accompanied generally by the reduction of surface area. The CaO/SiO_2 ratio decrease results in the production of disordered, nearly amorphous C-S-H, showing high surface area and porosity. In the presence of $CrCl_3$ such a C-S-H occurs, irrespective of the CaO/SiO_2 ratio of the mixture. The NaOH addition gives the hydrated calcium silicate product exhibiting relatively low porosity and surface area. With $CaCl_2$ additions the samples vary over a wide range from those having the highest surface area and porosity (137.9m^2/g at CaO/SiO_2 ratio=0.67) to those having the lowest values (11.1cm^2/g at CaO/SiO_2 ratio = 1.0).

Conclusions

The phase composition and properties of autoclaved calcium silicate hydrates synthesized with and without inorganic admixtures is strongly affected by CaO/SiO_2 ratio and the nature of ad-

TABLE 2.

Specific Surface and Pore Characteristics of Autoclaved Products (200°C/24h).

BET studies	Admixture in sample (5 wt.%)						
	reference	$CaCl_2$	$AlCl_3$	$CrCl_3$	Na_2CrO_4	NaOH	$Al(OH)_3$
$CaO/SiO_2=0.67$							
Surface area [m^2/g]	89	138	104	88	76	48	107
Surface of micropores [m^2/g]	4.5	2.3	4.3	1.2	1.8	0	4.9
Pore volume [cm^3/g]	0.37	0.51	0.44	0.35	0.37	0.19	0.44
$CaO/SiO_2=0.83$							
Surface area [m^2/g]	26	37	82	91	59	22	62
Surface of micropores [m^2/g]	1.1	1.9	3.3	0.7	3.5	0	4.2
Pore volume [cm^3/g]	0.09	0.13	0.32	0.43	0.26	0.06	0.25
$CaO/SiO_2=1.00$							
Surface area [m^2/g]	16.4	11.1	88.4	109	77	16	33
Surface of micropores [m^2/g]	0	0	7.7	1.4	2.5	0	0
Pore volume [cm^3/g]	0.05	0.03	0.33	0.35	0.35	0.05	0.11

mixture used. In spite of the complexity of the autoclaved systems studied the following conclusions can be made:

1. The CaO/SiO_2 decrease from 1.00 to 0.67 brings about the formation of poorly crystalline C-S-H with high surface area and porosity.
2. In the presence of $Al(OH)_3$ tobermorite is stabilized.
3. In the presence of $CrCl_3$ the formation of disordered C-S-H takes place, irrespective of the CaO/SiO_2 ratio. This product exhibits relatively high water content, surface area and porosity.
4. In the presence of NaOH hydrated sodium silicate is formed, occurring together with xonotlite at CaO/SiO_2 ratio=1; Na_2CrO_4 favors the formation of C-S-H.

5. Na containing samples show relatively low water content within the series of samples having different CaO/SiO_2 ratios, irrespective of phase composition and surface area.
6. $CaCl_2$ and NaOH favor the formation of xonotlite.
7. $CaCl_2$ doped autoclaved calcium silicate mixtures differ in bound water content over a wide range, from 26.6% to 7%. This change is accompanied by the change of surface area from 137.9 to 11.1 m^2/g.
8. $AlCl_3$ brings about the formation of tobermorite at CaO/SiO_2 ratio not lower than 0.83. Samples with $AlCl_3$ show relatively high water content and surface area.

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