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Chemical Studies on the Reactions of Synthetic 1.13-nm-Tobermorite with Alkali Metal Hydroxides at Room Temperature

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Summary. The reaction of alkali metal hydroxides (*M*OH; *M*= Li, Na, K; c = 0.02–1.0*M*) with synthetic 1.13-nm-tobermorite ($Ca_5Si_6H_2O_{18}\cdot 4H_2O$) at 25±2°C was studied. The results obtained indicate that the reactivity highly depends on *pH* and cation field strength and to lesser degree on the ionic radius of *M*. *M*OH has negative effects on the crystallinity of the concerned phase in the following order: KOH > NaOH > LiOH. Furthermore, the hydroxides cause swelling of crystals, attributable to the creation of new cavities due to partial hydrolysis of tetrahedral $SiO_2(OH)_2$ chains in the lattice. Hydrolysis *via* cleavage of Si-O-Si bonds facilitates the cation exchange process $Ca^{2+} \rightleftharpoons M^+$ which probably proceeds by a nucleophilic substitution reaction (S_N2). The observed different affinities of 1.13-nm-tobermorite towards *M*OH could be used for the separation of these cations.

Keywords. 1.13-nm-Tobermorite; Alkali metal; Cation exchange; Hydrolysis of $SiO_2(OH)_2$ chains.

Chemische Untersuchung der Reaktion von synthetischem 1.13-nm-Tobermorit mit Alkalimetallhydroxiden bei Raumtemperatur

Zusammenfassung. Die Reaktion von Alkalimetallhydroxiden (*M*OH; *M* = Li, Na, K; c = 0.02–0.1 *M*) mit synthetischem 1.13-nm-Tobermorit ($Ca_5Si_6H_2O_{18}\cdot 4H_2O$) wurde bei 25±2°C untersucht. Die Ergebnisse zeigen, daß die Reaktivität stark vom *pH*-Wert und von der Kationenfeldstärke, hingegen weniger vom Ionenradius des verwendeten Alkalimetalls abhängt. *M*OH wirkt sich in der Reihenfolge KOH > NaOH > LiOH negativ auf die Kristallinität der betroffenen Phasen aus. Darüber hinaus verursachen Hydroxide eine Schwellung der Kristalle, ausgelöst durch die Erzeugung neuer Hohlräume durch partielle Hydrolyse tetraedrischer $SiO_2(OH)_2$-Ketten im Kristallgitter. Hydrolyse der Si-O-Si-Bindungen erleichtert den Kationenaustauschprozeß zwischen M^+ und Ca^{2+}, welcher wahrscheinlich über einen S_N2-Mechanismus verläuft. Die beobachteten Unterschiede in der Reaktivität zwischen *M*OH und 1.13-nm-Tobermorit eröffnen eine Möglichkeit zur Trennung dieser Kationen.

Introduction

1.13-nm-Tobermorite ($Ca_5Si_6H_2O_{18}\cdot 4H_2O$) is one of the major phases found in hydrothermally treated CaO-SiO_2-H_2O systems. Furthermore, it has been found to be the major component of technically important autoclaved cement-based products. It's structure was first investigated by *Megaw* and *Kelsey* [1] and later by *Hamid* [2]. The basic layer structure consists of a central sheet of Ca^{2+} and O^{2-} ions which is sandwiched by rows of tetrahedral $SiO_2(OH_2)$ moieties that are linked to chains running parallel to the *b* axis direction [3]. The presence of Si-O-Si bridges between the chains has been confirmed by several authors [4–6]

The structure of silicate anions formed hydrothermally from the above system depends on CaO/SiO_2 ratio and reaction time [7]. It's length was found to be independent on preparation temperature, whereas it became with decreasing CaO/SiO_2 ratio. According to ^{29}Si NMR studies [8], the formation and structure of 1.13-nm-tobermorite depends also on the source of silica in the starting reaction. Such information is useful with respect to an elucidation of the probable mechanism of the reaction of the concerned phase with alkali metal hydroxides.

Many investigators [9–13] have examined the chemistry of alkali-silica reactions. In these reactions, hydroxide ions attack the silica, causing Si-O-Si bridges to be replaced by pairs of SiO groups. This process, repeated many times, ultimately fragments the threedimensional silica framework into separate silicate anions. The negative charges, whether on oxygen atoms still being part of the framework or on such ones present in separate silicate ions, are balanced by the most readily available cations (*e.g.* Na^+ and K^+). It has been reported [14] that alkali-silica reactions differ from alkali-CaO-SiO_2-H_2O reactions. In this connection, there is a general agreement that the reaction rate is controlled by the alkali species, the *pH* value, the structural status of the silica compounds, the presence of other ions, and the temperature. According to *Nikonova et al.* [15], the alkalies affect the degree of polymerization of silicon-oxygen anions for some CaO-SiO_2-H_2O phases. The depolymerization effect exerted by alkalies increases with increasing concentration in the order $KOH > NaOH > LiOH$. At hydrothermal conditions, K^+ ions are inserted in the structure of tobermorite according to the reaction $Ca_5(Si_6O_{17})\cdot 4H_2O \rightarrow Ca_5(Si_6O_{18}K_2)\cdot 4H_2O$. The reaction between alkali metal hydroxides (*M*OH) with the crystallographically highly disorded but chemically uniform phase has been studied by *H. Stade* [16]. He found that the amount of incoporated *M*OH increases with decreasing CaO/SiO_2 ratio, temperature, and cation radius of *M*. The uptake of *M*OH was assumed to take place most probably by a reaction of the hydroxide with SiOH groups at the inner surface of the interlayer. With higher concentrations of *M*OH, a $M^+ \rightleftharpoons Ca^+$ exchange within the interlayer would take place to a smaller extent.

In the present work, investigations on the ability of 1.13-nm-tobermorite to incorporate alkali metal hydroxides in its crystal lattice at room temperature have been performed. A proposed reaction mechanism is presented.

Results and Discussion

Powder X-ray diffraction analysis of the synthesized material indicated the presence of 1.13-nm-tobermorite as a single phase (Fig. 1). The results of scanning electron microscope (SEM) showed aggregates of round and plate crystals (Fig. 2) of an approximate chemical formula $Ca_5Si_6O_{16}(OH)_2\cdot 4H_2O$ as obtained from chemical analysis. The ionic Ca^{2+} and Si^{4+} species released from the solid structure to alkali metal hydroxide solutions of different concentrations and the calculated Ca/Si molar ratio of the solid phases after the reaction (on the basis of released Ca^{2+} and Si^{4+} are given in Table 1. The changes of *pH* values as well as those of electrical conductivity and alkali concentration of the reacted solutions are presented in Tables 2 and 3. The relation between Ca^{2+} and Si^{4+} released from the

Table 1. Concentrations of calcium and silicate ions released from 1.13-nm-tobermorite; calculated Ca/Si molar ratio of the solid phase after equilibrium

Molar concentration of alkali	LiOH			NaOH			KOH		
	[Ca^{2+}] (mmol/l)	[Si^{4+}] (mmol/l)	Ca: Si of the solid phase	[Ca^{2+}] (mmol/l)	[Si^{4+}] (mmol/l)	Ca: Si of the solid phase	[Ca^{2+}] (mmol/l)	[Si^{4+}] (mmol/l)	Ca: Si of the solid phase
0.02	0.10	1.01	0.880	0.30	0.520	0.841	0.20	0.874	0.867
0.05	0.20	1.02	0.875	0.40	0.938	0.857	0.40	0.899	0.855
0.10	0.30	0.835	0.858	0.80	0.986	0.835	0.60	0.831	0.838
0.20	0.90	0.801	0.818	1.00	0.970	0.820	0.70	0.717	0.826
0.50	1.90	0.553	0.742	1.20	0.767	0.797	0.90	0.685	0.812
1.00	2.50	0.508	0.702	1.90	0.670	0.748	2.50	0.510	0.702

Table 2. Changes in *pH* values and electrical conductivities of alkali metal solutions due to the solubility of 1.13-nm-tobermorite

Molar concentration of alkali	LiOH			NaOH			KOH		
	Initial *pH*	*pH* eq	Electrical conductivity (μmho· cm^{-1})	Initial *pH*	*pH* (eq)	Electrical conductivity (μmho· cm^{-1})	Initial *pH*	*pH* (eq)	Electrical conductivity (μmho· cm^{-1})
0.02	12.32	11.23	2.0×10^2	12.35	11.04	5.0×10^2	12.40	11.46	6.00×10^2
0.05	12.65	11.87	1.0×10^3	12.67	12.51	5.5×10^2	12.61	12.18	4.70×10^3
0.10	13.05	12.50	3.0×10^3	13.01	12.49	1.4×10^4	13.10	12.35	8.00×10^3
0.20	13.33	12.52	7.0×10^3	13.29	12.07	1.6×10^4	13.33	12.51	1.40×10^4
0.50	13.69	12.59	2.7×10^4	13.72	12.40	2.0×10^4	13.67	12.77	2.80×10^4
1.00	14.00	12.63	3.0×10^4	14.00	12.42	3.4×10^4	14.00	12.80	3.45×10^4

Table 3. Changes in initial molar concentration of alkali metal hydroxides after reaction with 1.13-nm-tobermorite

Initial concentration (mol/l)	Concentration after equilibrium (mol/l)		
	LiOH	NaOH	KOH
0.02	0.0149	0.0147	0.0148
0.05	0.0298	0.0196	0.0246
0.10	0.0847	0.0542	0.0894
0.20	0.1841	0.1290	0.1493
0.50	0.4881	0.4230	0.3991
1.00	0.8675	0.9480	0.8675

lattice is given in Fig. 3 whereas the relation of released Ca^{2+} to ionic radius Å of M^+ is shown in Fig. 4.

The results of X-ray diffraction analysis for selected solid samples reacted with 1.0 *M* of alkali hydroxide are shown in Fig. 1. The data point to changes in the crystal lattice and/or to partial chemical composition. These changes could be

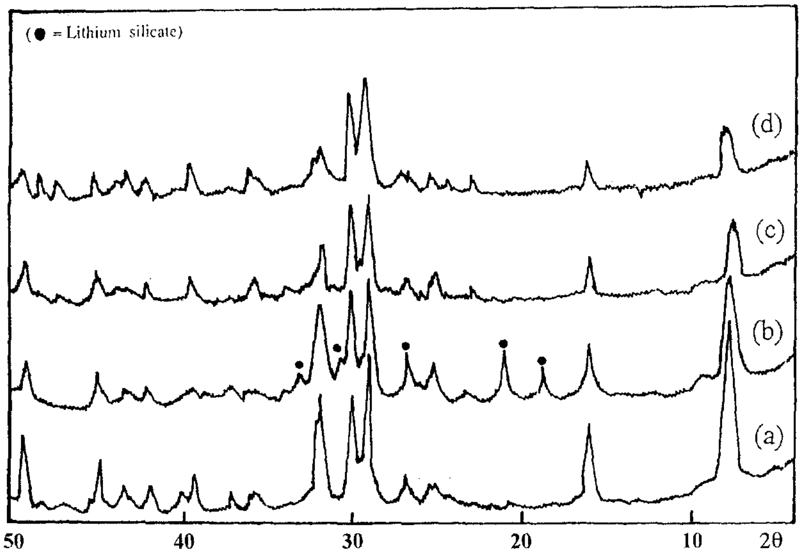

Fig. 1. X-ray diffractograms of synthetic 1.13-nm-tobermorite (a) and 1.13-nm-tobermorite treated with 1.0 *M* of LiOH (b), NaOH (c), and KOH (d)

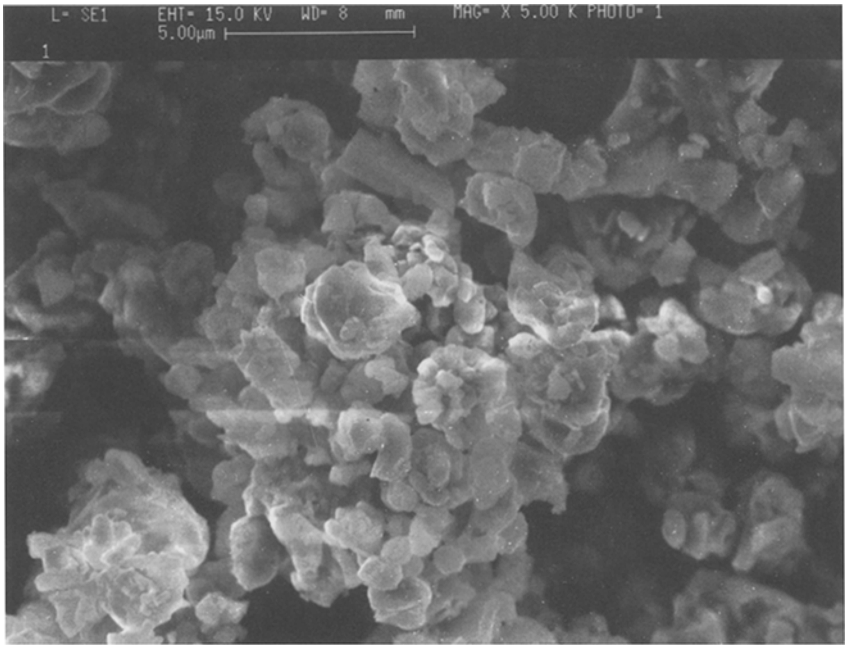

Fig. 2. SEM of synthetic 1.13-nm-tobermorite

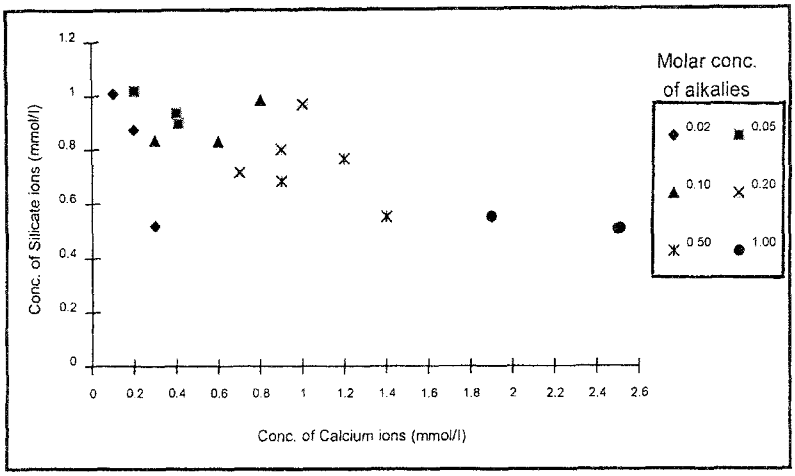

Fig. 3. Calcium ion concentrations against silicate ions released from the solid structure

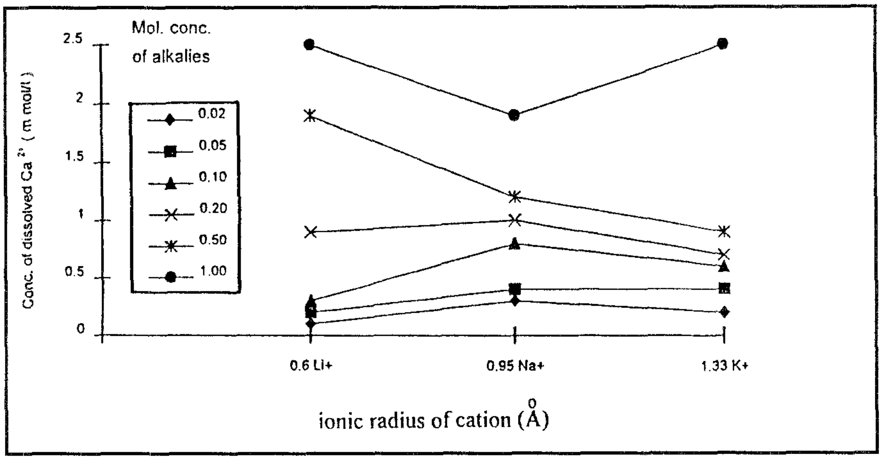

Fig. 4. Relation between the ionic radii of the metal ion of hydroxides and amount of liberated Ca^{2+} ions

attributed to the release of Ca^{2+} and Si^{4+} ions from the lattice structure, in addition to a probable exchange process Ca^{2+} $\rightleftharpoons$ M^+ and/or incorporation of M^+ in lattice. The intensities of (002) d-spacing at 7.8(2θ), (400) or (207) d-spacing at 31.8 (2θ), and (408) d-spacing at 45.3 (2θ) decreases in the order LiOH > NaOH > KOH. The peaks at 7.8 (2θ) are rather sharp, especially those treated with NaOH and KOH. Such changes would indicate that the cations of alkali have been uptaken by the solid *via* an ion exchange process and not as adsorbed entities on the surface. Similar results have been found by *M. Jsuji et al.* [17]. It could be assumed that partial hydrolysis of silicate chains by action of OH$^-$ groups at the silanol groups (Si-OH) takes place; thereby, Si^{4+} ions will be released into solution. It is furtherly assumed that such partial hydrolysis would accelerate the Ca^{2+} $\rightleftharpoons$ M^+ exchange process. Moreover, X-ray analysis pointed to the formation of lithium silicate after LiOH treatment where no sodium or potassium silicates could be detected (may be due to their higher solubility products). The chemical analyses as presented in

Table 1 clearly demonstrated the increase of Ca^{2+} ions released with increasing alkali concentrations in the order $NaOH < KOH < LiOH$ up to 0.2 *M* of *M*OH. At 0.5 *M*, a different trend was observed: $LiOH > NaOH > KOH$. The corresponding increase in the release of Ca^{2+} ions at 1.0 *M* followed the order $LiOH = KOH > NaOH$. On the other hand, it was observed that the Si^{4+} concentration generally decreased with the increase of alkali concentration. It is worth mentioning that the measured Si^{4+} concentrations are lower than should be expected from the amount of actually liberated Si^{4+} ions from the lattice of the solid. This could be explained by the formation of insoluble metal silicates (*e.g.* lithium silicate). As to the electrical conductivity of alkali solutions after their reactions with the solid, a decrease in the measured values of electrical conductivity was noticed. However, such a decrease seems to be insensitive when higher concentrations of alkali are used (Table 2). In this respect, the presence of a partial preexchange reaction $Ca^{2+} \rightleftharpoons M^{+}$ is suggested at higher concentration of alkali metals [18], making the cation exchange process very complicated.

The suggested mechanism would take place by adsorption of OH^{-} ions at the inner surface (or edges) of the solid at silanol groups (Si-OH) and by cleavage of Si-O-Si bonds between paired or bridging $SiO_2(OH)_2$ tetrahedrals (Fig. 5). Cleavage at the bridging $SiO_2(OH)_2$ tetrahedrals would take place if the tobermorite solid is of the anomalous type,*i.e.* substituted with Al [3]. Keeping in mind that the tobermorite under consideration is of the normal type (unsubstituted), this step may be similar to the first step occuring in the alkali-silica reaction mechanism. It differs, however, from calcium silicate hydrates which have a rigid structure based on Ca-O layers [14]. A cleavage of Si-O-Si bonds would consume minor amounts of *M*OH according to

$$\mathrm{Si-O-Si} + 2M\mathrm{OH} \rightarrow 2\mathrm{Si-O}M + \mathrm{H_2O}$$

The negative charges on the silicate chains will be balanced by M^{+} at the cleaved positions. Since all oxygen atoms shared with Si-O chains in the central sheet of CaO_2 in tobermorite, the Ca-O interaction will became weaker. Hence, in this structure calcium (indicated by dotted circles in Fig. 5) will be available to be exchanged with M^{+} ions from solution (irreversible reaction). Moreover, some of the Ca^{2+} ions released may also be created from the interlayer (indicated by solid circles in Fig. 5), and therefore also be available for exchanging with M^{+} ions (probably a reversible reaction). The cleavage of Si-O-Si bonds may lead to small pores or channels of different diameters in the solid structure, and hence may facilitate the exchange of interlayer Ca^{2+} ions. It is worth mentioning that *S. Komarneni* [3] suggested that in Al substituted tobermorite K^{+} ions (from KCl solution) displaced Ca^{2+} ions mainly from the edge and planar surface of tobermorite, whereas the exchange of interlayer Ca^{2+} was uncertain and appeared to depend on the nature of the exchanging cations. *H. Stade* [16] reported that Li^{+} ions with their small cation radius are bounded in a higher amount than K^{+} or Na^{+} in the reaction of *M*OH with the $CaO\text{-}SiO_2{\cdot}H_2O$ system. In the present study, the amount of Ca^{2+} ions released was in general higher than in case of Li^{+} ions, especially at higher concentrations. However, it was difficult to find a relation between the amount of M^{+} ions bound and the ionic radius due to the creation of new cavities with different diameters and the formation of solid metal silicates (*e.g.*

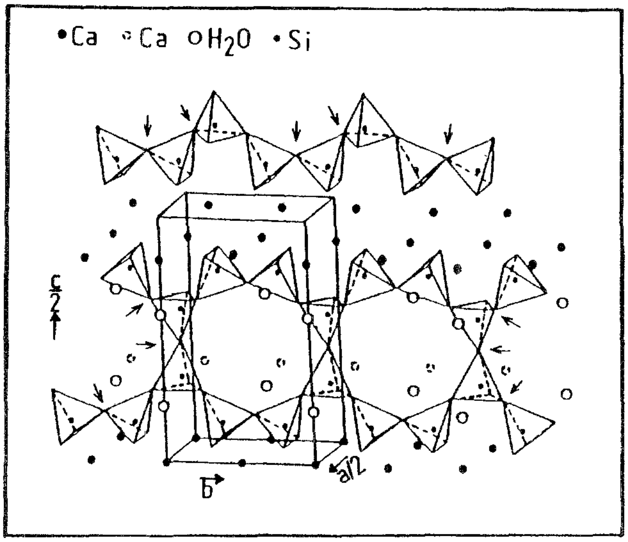

Fig. 5. Three dimensional view of anomalous 1.13-nm-tobermorite with Ca:Si = 0.83]

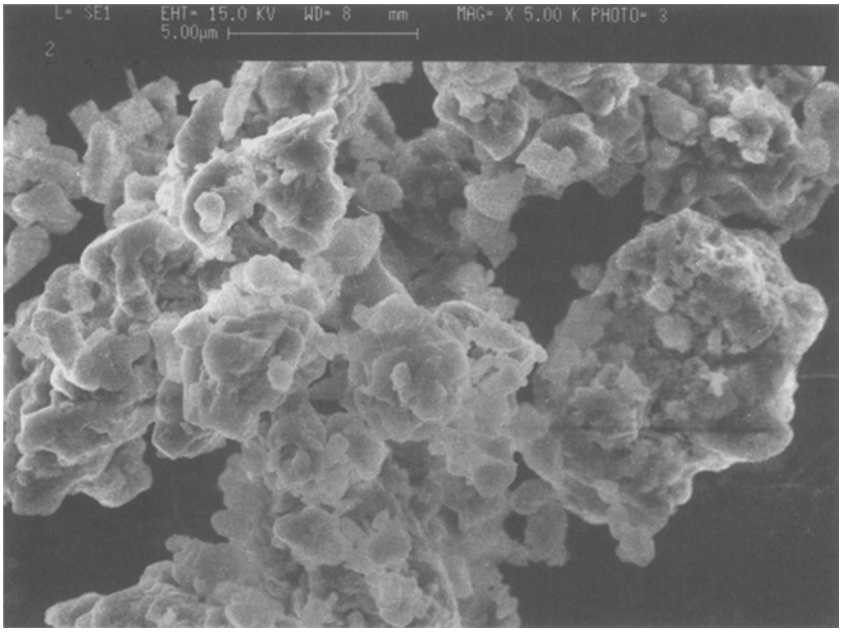

Fig. 6. SEM of synthetic 1.13-nm-tobermorite treated with 1.0 *M* KOH

Li_2SiO_3). Such cavities will accommodate additional M^+ ions in the solid structure. *M. Tsuji et al.* [17] have reported that in certain cases Ca^{2+} is not replaced by K^+ or Rb^+ because of its large hydrated radius and the steric limitations of tobermorite. The creation of cavities, however, will give a relatively open structure, leading to the swelling of the solid as noticed from the SEM examination (Fig. 6). One might be inclined to suggest that the cleavage of surface Si-O-Si bonds between $SiO_2(OH)_2$ tetrahedrals by action of OH^- groups may proceed by a mechanism similiar to that of a nucleophilic substitution reaction (S_N2). The detection of lithium silicate as a solid product together with tobermorite when using LiOH would support this view which may be interpretated in terms of a partial hydrolysis of tetrahydral $SiO_2(OH)_2$ chains as in the case of the alkaline hydrolysis of $SiCl_4$ [19].

Experimental

1.13-nm-tobermorite was prepared by mixing stoichiometric amounts of CaO with quartz (CaO: $SiO_2 = 0.83$ molar ratio). CaO was prepared by ignition of $CaCO_3$ (1050°C, 3h) The solid was added to 10 times its weight of decarbonated deionized water and stirred for 15 min in 250 ml beaker. The content was quantitatively transferred to a stainless steel autoclave bomb (250 cm^3) internally coated with teflon. The autoclave was placed in a manually controlled electrically heated oven, and the temperature was raised gradually to 180°C and kept at this temperature for 144 h. At the end of the run, the autoclave was cooled down and the content was washed with few ml of distilled water and dried at 80°C for 24 h. The solid was characterized by X-ray powder diffraction (Philips diffractometer using Ni filtered CuK_α radiation) scanning electron microscopy, and chemical analysis.

The solutions of LiOH, NaOH, and KOH (0.02–1.0 M) were prepared from analytical grade reagents (BDH). Constant weights (100 mg) of the solids powder (below 45 μm) were suspended in 50 ml of alkali solutions in polyethylene beakers with continual stirring for 24 h at room temperature (25± 2°C). After this time, no significant uptake of *M*OH by the solid was observed as indicated by the unchanged concentrations of *M*OH. The changes of *pH* value electrical conductivity, and alkali concentration were measured before and after each reaction. The solids were filtered off and collected for chemical analysis.

Analysis:

The Ca^{2+} concentration released from the solid structure was determined by titration with a standard *EDTA*; solution the Si^{4+} concentration was estimated using the molybdenum blue photometric method [20]. Unreacted OH^- ions were determined with standard 0.1 M HCl solution using phenolphthaleine as indicator. Some selected solid samples treated with 1.0 M *M*OH were investigated by the same techniques which were used in the characterization of untreated reference samples to clearfiy any possible change in lattice structure or chemical composition of the concerned phase.

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