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HYDROTHERMAL TRANSFORMATION OF TOBERMORITE GEL TO 10 Å TOBERMORITE

R. Jauberthie*, M. Temimi* and M. Laquerbe*
* Teacher - Researcher
I.N.S.A., Laboratoire G.T.Ma, 20, Avenue des Buttes de Coësmes,
35000 Rennes, France

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ABSTRACT

The tobermorite gel, formed by hydrothermal reaction of silica and lime, is transformed either into "Z" phase if the quantity of lime is less than 37 % or into 10 Å tobermorite if the quantity of lime is between 37 % and 42 %.

The sheets of tobermorite gel are progressively ordered in a direction perpendicular to their plane in a turbostratic way to form "Z" phase. The order is correct in the plane but there is rotations with different angles between planes (large variations of a and b parameters occur).On the contrary, the sheets of tobermorite gel are ordered in a perfect way during the formation of the 10 Å tobermorite and without noticeable modification of parameters a and b.

The 10 Å tobermorite is stable in the presence of gyrolite, whereas "Z" phase is metastable.

1. Introduction

The study of the CaO - SiO_2 - H_2O system by hydrothermal reaction (the temperature limited at 210 °C and the duration less than 1600 h) of silica and of lime for quantities of lime less than 50% has allowed to define 3 distinct domains ; the formed phases in these domains are respectively :

- tobermorite gel ; gyrolite gel ; "Z" phase ; gyrolite [1],
- tobermorite gel ; gyrolite gel ; gyrolite ; 10 Å tobermorite [2], [3],
- tobermorite gel ; 10 Å tobermorite ; xonotlite [4], [5].

In this paper the relations and filiations between the tobermorite gel - 10 Å tobermorite and gyrolite gel - gyrolite from the second domain are examined.

A parallel is drawn between the tobermorite gel - "Z" phase and gyrolite gel - gyrolite transformations studied in a preceding paper [1].

2. Materials and Testing

Materials

Lime. The lime used is the "Merck lime" coming from Prolabo factory (France). The minimum proportion of calcium hydroxide $Ca(OH)_2$ contained in this lime is 96%. Its granulometry attests to the fineness of the grains :

- diameter of the largest particles : less than 50 microns,
- mean diameter : 3.8 microns,
- specific area (B.E.T.) : 10.26 m^2/g.

Silica. The silica is used in an amorphous form (silica gel). The size of particles don't exceed 63 microns.

Testing. The products of synthesis are obtained by hydrothermal reaction of lime and of silica gel in an excess of water. After reactions, an excess of water is always present with products. This synthesis is carried out in teflon cells placed in sealed bombs heated to 60, 90, 120, 150, 180 and 210 °C, under pressure of saturated vapour. The duration of the reaction varies from 25 to 1600 hours in geometric progression (ratio 2). The percentage of lime [$CaO / (CaO + SiO_2)$], computed with regard to the weight, is between 37% and 42%. A systematic study has been carried out for a quantity of lime fixed at 40%. At the end of the experiment, the bombs are hardened in water at 20 °C and the products dried in dessicators without CO_2 (in presence of KOH). After this preparation, they are examined by X- ray diffractions.

3. Results and Discussion

Figure 1 gives the experimental area of synthetic products identified by X- ray diffractions (Fig. 2).

For short reactions or low temperatures, the diffraction pattern shows only a few peaks characteristic of tobermorite gel (Fig. 2). The domain is represented in figure 1 and called GT.

In the sheet, the symmetry is rectangular. The parameters, determined by approximation of the least squares (table 1), are a = 11.24 Å and b = 7.33 Å.

For longer reaction times or higher temperatures, the piling up of sheets having rectangular symmetry of tobermorite gel is progressively ordered in the direction c perpendicular to the plane ; in particular the (002) peak at 10.06 Å appears clearly and the (hkl) peaks are equally visible (Fig.2). This organisation which leads to the formation of 10 Å tobermorite is not accompanied by notable variations of the lattice parameters a and b of the tobermorite gel (a = 11.24 Å stays unchanged and b = 7.32 Å sustains a slight decrease). The 10 Å tobermorite domain is called T 10 in figure 1.

At the same time, a second series of diffraction peaks shows the formation of sheets with hexagonal lattice parameter a = 9.68 Å corresponding to distance 8.38 Å between atomic rows (table 1). This phase, called gyrolite gel (called GG in figure 1), is characterized by a strong diffraction at 4.19 Å (20.) and weaker diffractions at 8.42 Å (10.), 2.42 Å (22.) and

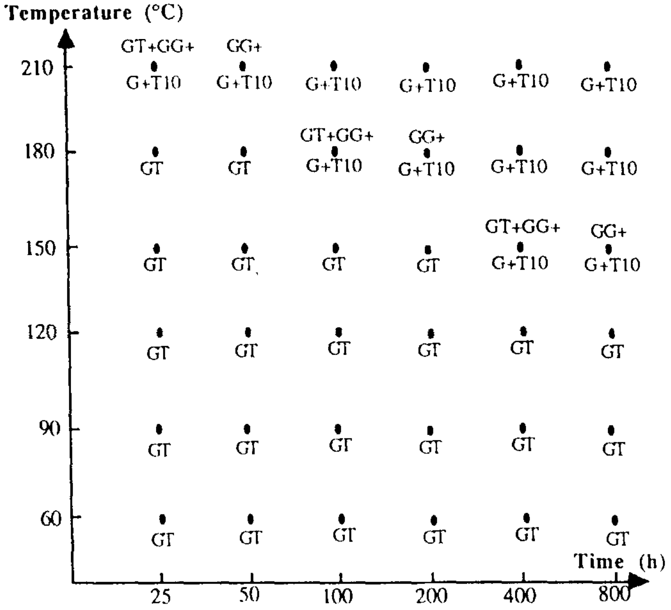

FIG. 1.

Experimental area of synthetic products [$CaO/(CaO + SiO_2) = 0.40$], (GT=Tobermorite gel, T10=10 Å tobermorite, GG=Gyrolite gel, G=Gyrolite).

1.92 Å (32.)*. At first the order in c direction perpendicular to the leaf plane is mediocre : no diffraction is visible at 22 Å (00.6) and at 11 Å the (00.12) peak is very weak. Then, the intensity of the (00.l) peaks increase more rapidly than the (hk) intensities, the gyrolite with parameters a = 9.68 Å and c = 22 Å takes over progressively from the gyrolite gel. The two synthesized phases (10 Å tobermorite and gyrolite) are still present at 210 °C after 600 hours of reaction. The percentage of the two phases present is independent of the temperature and duration of the reaction.

3.1. Comparative study of the genesis of tobermorite gel - gyrolite gel - "Z" phase - gyrolite and tobermorite gel - gyrolite gel - 10 Å tobermorite - gyrolite. With reacting mixtures containing 40% lime, as in the case of mixtures lower in lime, tobermorite gel forms at the beginning and is characterized by sheets with rectangular lattice without periodicity between the sheets. In a second stage, the organisation of sheets in the perpendicular direction becomes apparent. The order is three-directional and the (hkl) peaks diffractions are visible. The piling up of sheets at a reticular distance of 10.06 Å is only accompanied by a very slight reduction of the parameter b (a = 11.24 Å, b = 7.32 Å, c = 10.6 Å).

On the contrary, with mixtures still lower in lime (30%) [1], the arrangement of the tobermorite gel sheets in the c direction takes place with a greater reticular distance (c = 15.2 Å) ; the direction of the sheets in their plane being uncertain, it leads to a turbostratic structure. This transformation of the tobermorite gel into "Z" phase is accompanied by a sharp

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* Indexed in Miller notations in hexagonal sheets ($h\ k\ \overline{h+k}$).

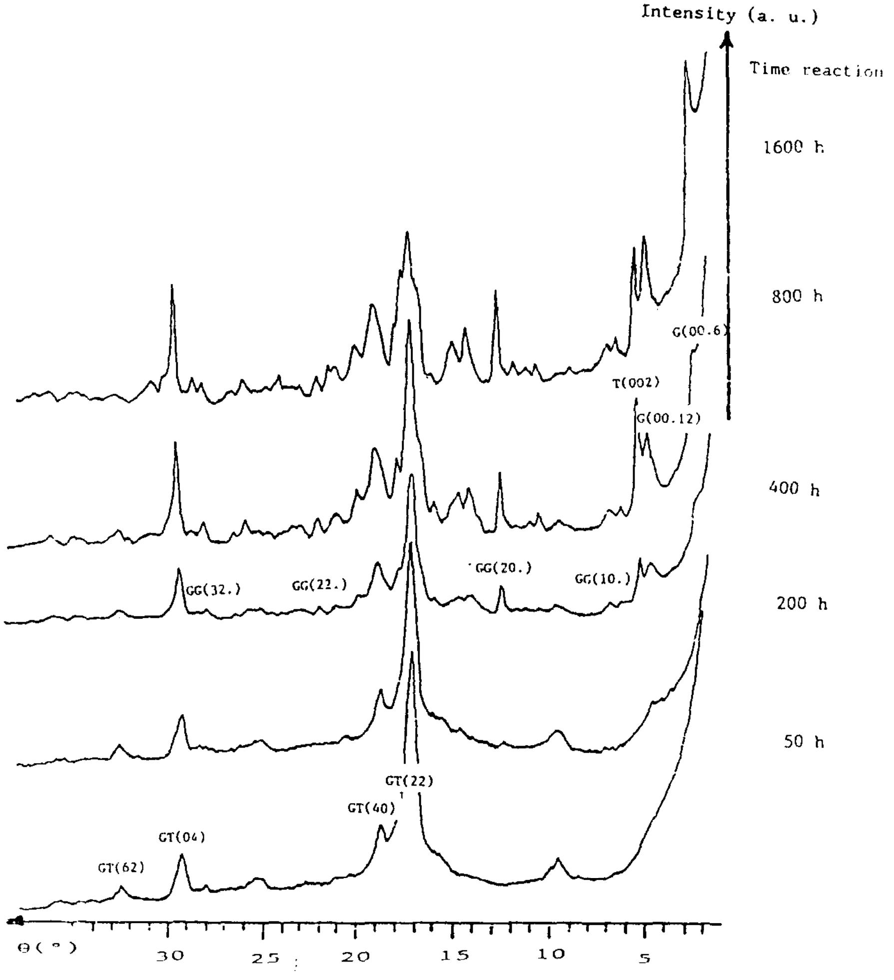

FIG. 2.

X-ray diffraction patterns of synthesized products (KaCo radiation, Fe filter), (GT = Tobermorite gel, T = 10 Å tobermorite, GG = Gyrolite gel, g = Gyrolite).

decrease of the a and b parameters (a = 11.20 Å, b = 7.28 Å, c = 15.2 Å). Finally, whatever the quantity of lime used in the reacting mixture, the gyrolite is always formed from sheets with hexagonal lattice. In a first stage the gyrolite gel is formed and the organization in the c direction appears in the second stage. The formation of gyrolite is always linked to the appearance of an order in the piling up of gyrolite gel sheets.

3.2. Stability of formed phases. The tobermorite gel, then the "Z" phase, disappears progressively when the gyrolite gel is transformed into gyrolite [1]. On the contrary, the 10 Å tobermorite is always present with gyrolite at a temperature of 210 °C and a reaction time of 600 hours. The relative quantity of these two phases stays unchanged. In the case of "Z"

TABLE 1
Synthesized Products Parameters

Tobermorite gel			10 Å Tobermorite			Gyrolite gel		
h k	Obs.D	Cal.D	h k	Obs.D	Cal.D	h k	Obs.D	Cal.D
2 2	3.04	3.07	2 2	3.03	3.07	1 0.	8.42	8.38
4 0	2.81	2.81	4 0	2.80	2.81	2 0.	4.19	4.19
0 4	1.83	1.83	0 4	1.83	1.83	2 2.	2.42	2.42
6 2	1.67	1.67	6 2	1.67	1.67	3 2.	1.92	1.92

phase, the organization of the sheets of tobermorite gel in the perpendicular direction to the plane of the sheets, is of turbostratic type. This organization is accompanied by a relatively significant modification of the a and b parameters in the plane. The "Z" phase is metastable in the presence of gyrolite.

On the contrary, the organization of the sheets of tobermorite gel in the c direction, giving rise to the 10 Å tobermorite, does not bring about the notable variation of the a and b parameters. There are no defects in the piling up such as rotation of the axis perpendicular to the plane, or translation parallel to this plane. The 10 Å tobermorite is stable in the presence of gyrolite.

4. Conclusion

When the proportion of lime is less than 37%, the "Z" phase forms ; the distance between the sheets becomes constant but the direction of a (or b) in the plane is uncertain. This transformation is accompanied by a significant variation of the tobermorite gel parameters.

If the percentage of lime is between 37% and 42%, 10 Å tobermorite forms in which the sheets are organized in a direction perpendicular to their plane. During the transformation of tobermorite gel to 10 Å tobermorite, the a and b parameters of the sheets are practically unchanged. Lastly, if the "Z" phase is metastable in the presence of gyrolite, while the 10 Å tobermorite is always present with the gyrolite.

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