

## Study on hydrothermal synthesis dynamics of nanoscale xonotlite fibers

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**Abstract.** The xonotlite crystals were synthesized via the hydrothermal synthesis manner from CaO and SiO<sub>2</sub> as the raw materials with their Si/Ca molar ratio of 1.0. Hydrothermal synthesis dynamics of nanoscale xonotlite fibers was explored by masterly measuring the electrical conductivities and the calcium concentrations of product slurries synthesized at various reaction temperature in this paper. The results indicated that the calculated values of the products' quality at various reaction temperatures were consistent with the measured values. Based on chemical reaction kinetic, using fourth-order Runge-Kutta method, spline interpolation and least-squares fitting method, the dynamic relationship of xonotlite fibers synthesized via hydrothermal synthesis process is of  $-dc_A / dt = kc_A^{4/5}$ .

### 1. Introduction

Xonotlite crystal belongs to monoclinic system ( $a=1.67\text{nm}$ ,  $b=0.73\text{nm}$ ,  $c=0.695\text{nm}$ ), and it is a mineral of calcium silicate hydrate with the lowest crystalline water content, the best heat resistance and thermal stability (decomposition temperature of 1050-1100 °C) [1]. In general, the xonotlite products used in industry were fabricated using dynamic process from CaO and SiO<sub>2</sub> as the raw materials with their Si/Ca molar ratio of 1.0[2-6]. Due to the dissolution characteristics of siliceous material, the xonotlite crystals from H<sub>2</sub>SiO<sub>3</sub> and K<sub>2</sub>SiO<sub>3</sub> as siliceous materials could grow to form the various morphologies of spherical particles and fibers respectively. Actually, it was difficult to synthesize xonotlite crystals (specially xonotlite fibers) because of the harsh conditions such as the high reaction temperature and pressure, resulting in the extremely low synthetic efficiency [7-11]. It can be confirmed by many scholars' research that the synthesis of xonotlite crystals was feasible based on the hydrothermal synthesis thermodynamics. But since the invisibility of the reaction and the harsh conditions of xonotlites' formation, the dynamics data of xonotlite crystals was hardly possible to obtain so that few people took the hydrothermal synthesis dynamics into account [12]. Accordingly, in this paper, with K<sub>2</sub>SiO<sub>3</sub> solution and Ca(OH)<sub>2</sub> suspension as siliceous material and calcareous material respectively, hydrothermal synthesis dynamics of nanoscale xonotlite fibers was explored by masterly measuring the electrical conductivities and the calcium concentrations of product slurries, aiming to study on the dynamics of xonotlite fibers, to improve the synthetic efficiency of it and to make the morphologies of the xonotlite crystals be controllable.

### 2. Experiment

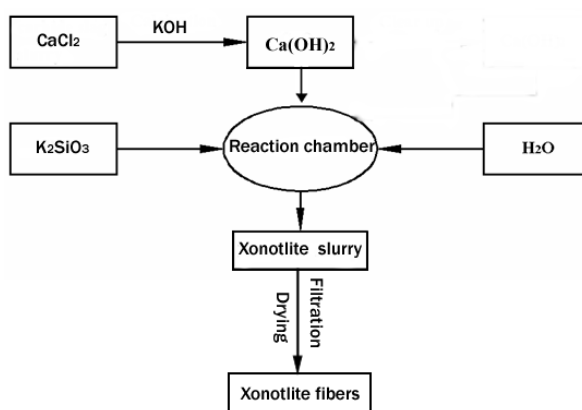


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### 2.1 Materials and methods

The xonotlite fibers were synthesized via the dynamic hydrothermal synthesis method.

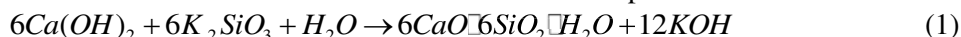
$K_2SiO_3$  solution and  $Ca(OH)_2$  suspension were used as siliceous material and calcareous material respectively.  $K_2SiO_3$  solution was prepared by mixing  $H_2SiO_3$  solution with  $KOH$   $100g \cdot L^{-1}$  at the molar ratio of 1:2.  $Ca(OH)_2$  suspension was prepared by mixing  $CaCl_2$  with  $KOH$   $100g \cdot L^{-1}$  at the molar ratio of 1:2. The calcareous material, distilled water, and siliceous material were homogeneously mixed, and then the mixture was transferred into a reaction chamber with a stirrer at a heating rate of  $1.5 \text{ } ^\circ C \cdot min^{-1}$  and a stirring rate of 200 rpm. The hydrothermal treatment proceeded under the following conditions: the Ca/Si molar ratio of 1.0, the reaction temperature of 190  $^\circ C$ , 210  $^\circ C$  and 230  $^\circ C$  respectively. After the hydrothermal treatment, the suspensions were filtrated and washed three times by distilled water. The resultant powders were dried at 75  $^\circ C$  for 12 h. Technological flow diagram of hydrothermally synthesizing xonotlite products was shown in Figure 1.



**Figure 1.** Technological flow diagram of hydrothermally synthesizing xonotlite fibers.

### 2.2 The Determination Method of Samples

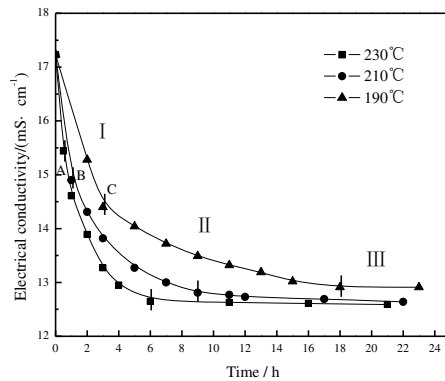
The reaction equation for the formation of the xonotlite fibers could be simplified as:



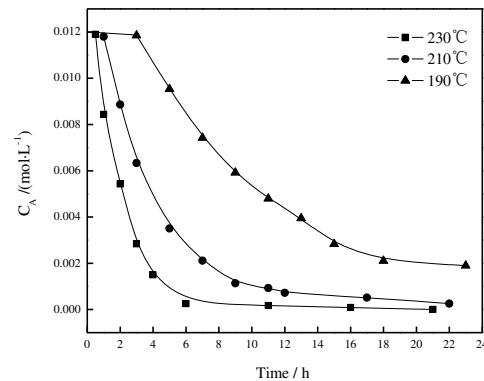
The above equation (1) was only a simplified final reaction equation for the preparation of xonotlite fibers, but the whole reaction was actually made up of a series of complex chemical reaction steps. Due to the invisibility of the hydrothermal synthesis reaction, it was impossible to observe the reaction process directly. When  $K_2SiO_3$  solution was used as siliceous material, with increasing reaction time, the number of ions in the system would be reduced so that the reduction of these conductive ions would cause the changes in the conductivity of the reaction system. Therefore, the dynamic test of the hydrothermal synthesis process of the xonotlite can be achieved by measuring the change of the electrical conductivity during the reaction process.

The product slurries synthesized by hydrothermal synthesis process at various reaction temperatures and time were kept at 25  $^\circ C$  in thermostat water bath cauldron, and the electrical conductivities of various slurries were measured using a DDS-12A digital conductivity meter. The EDTA titration method was used to determine the calcium concentrations of various product slurries formed by hydrothermal synthesis process under various reaction temperature and time. The product slurries were accurately weighed by FA2004 electronic balance after drying. After the induction time ( $t_0$ ), the qualities of the products obtained under various reaction times can be defined as  $m(\text{Total}) = m(KCl) + m(Ca(OH)_2) + m(C-S-H(I)) + m(\text{xonotlite})$ .

## 3. Results and discussion



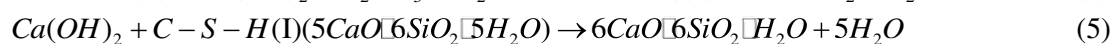
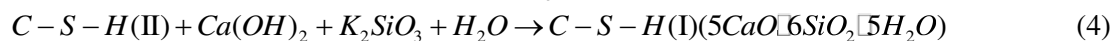
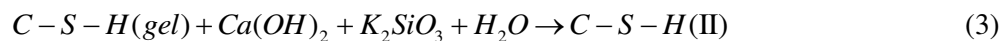
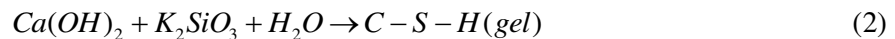
**Figure 2.** Time dependence of the electrical conductivities of hydrothermally synthesized products at various temperatures.



**Figure 3.** Time dependence of the calcium concentrations of the products hydrothermally synthesized at various temperatures.

The electrical conductivities and calcium concentrations of the system were respectively measured after various reaction times, shown in Figure 2 and Figure 3 respectively. It can be seen from Figure 2, with prolonging reaction time, the electrical conductivities of hydrothermally synthesized products at various temperatures decreased, and its descending trend can be divided into three stages. The descending trend of these three curves in the first stage was fastest, in the second stage was relatively slow, obviously, the slowest of the descending trend existed in the third stage. And in the third stage, the conductivities tended to a certain value. The descending trend of these three curves indicated that the reaction rate in the first stage was fastest, then it became slightly slow in the second stage, and the slowest reaction speed appeared in the third stage.

In the hydrothermal synthesis process of xonotlite fibers, the reaction process can be expressed by the following reaction steps:



Equation (2) represented the formation of amorphous C-S-H gels at the initial stage of the reaction. With the progress of the reaction, as shown in equation (3), C-S-H gels were transformed into calcium-rich hydrated calcium silicate C-S-H (II). Then due to the silicon-rich state in the reaction system, as shown in equation (4), C-S-H (II) would be transformed into the silicon-rich C-S-H(I) which owned a structure that similar to the tobermorite ( $5CaO \cdot 6SiO_2 \cdot 5H_2O$ ). Finally, the silicon-rich C-S-H(I) directly transformed into the fibrous xonotlite crystals, as shown in equation (5). According to the reaction process of the xonotlite fibers and Figure 2, it can be assumed that the above-mentioned chemical equation (2, 3 and 4) occurred in the first stage of Figure 2 to form C-S-H. And there was no formation of the fibrous xonotlite crystals in the first stage. Moreover, the reaction time of the first stage was assumed to be the induction time ( $t_0$ ) required for the formation of fibrous xonotlite crystals. Assuming that the chemical reaction of above equation (5) occurred in the second stage, at this moment, the nucleation and growth of xonotlite fibers took place on the surface of the C-S-H, and there was no C-S-H formation in this stage. As before, we also supposed that most of the xonotlite fibers had formed before the third stage. So in the third stage, the reaction rate decreased to the minimum, which led to the conductivities decreased slowly and tended to a certain value.

Based on the above assumptions and the data of calcium concentrations in Figure 3, the qualities of the products under various reaction temperatures and times during the second stage can be calculated,

as shown in Tables 1, 2 and 3. According to the experimental method of 2.2, the quality-time values of the products at various reaction temperatures were measured, as shown in Tables 4, 5 and 6. At the same reaction temperature, the quality-time calculated values of the products were compared with the measured values, and the results were as shown in Figure 4.

**Table 1.** Calculated data of quality-time of products hydrothermally synthesized at 230 °C.

t/[h]	m(KCl)/[g]	m(Ca(OH) <sub>2</sub> )/[g]	m(C-S-H(I))/[g]	m(Xonotlite)/[g]	m(Total)/[g]
0.5	7.4500	0.8806	6.0833	0.0000	14.4139
1	7.4500	0.6241	4.3117	1.7328	14.1186
2	7.4500	0.4017	2.7749	3.2360	13.8625
3	7.4500	0.2101	1.4515	4.5304	13.6419
4	7.4500	0.1112	0.7684	5.1984	13.5281
6	7.4500	0.0185	0.1281	5.8247	13.4213
11	7.4500	0.0124	0.0854	5.8665	13.4142
16	7.4500	0.0062	0.0427	5.9082	13.4071
21	7.4500	0.0000	0.0000	5.9500	13.4000

**Table 2.** Calculated data of quality-time of products hydrothermally synthesized at 210 °C.

t/[h]	m(KCl)/[g]	m(Ca(OH) <sub>2</sub> )/[g]	m(C-S-H(I))/[g]	m(Xonotlite)/[g]	m(Total)/[g]
1	7.4500	0.8806	6.0833	0.0000	14.4139
2	7.4500	0.6557	4.5296	1.5197	14.1550
3	7.4500	0.4689	3.2392	2.7818	13.9399
5	7.4500	0.2592	1.7908	4.1985	13.6985
7	7.4500	0.1563	1.0797	4.8939	13.5800
9	7.4500	0.0839	0.5794	5.3833	13.4966
11	7.4500	0.0686	0.4740	5.4864	13.4790
12	7.4500	0.0534	0.3687	5.5894	13.4615
17	7.4500	0.0381	0.2633	5.6924	13.4439
22	7.4500	0.0191	0.1317	5.8212	13.4219

**Table 3.** Calculated data of quality-time of products hydrothermally synthesized at 190 °C.

t/[h]	m(KCl)/[g]	m(Ca(OH) <sub>2</sub> )/[g]	m(C-S-H(I))/[g]	m(Xonotlite)/[g]	m(Total)/[g]
3	7.4500	0.8806	6.0833	0.0000	14.4139
5	7.4500	0.7055	4.8734	1.1834	14.2123
7	7.4500	0.5498	3.7979	2.2354	14.0330
9	7.4500	0.4379	3.0249	2.9914	13.9042
11	7.4500	0.3552	2.4535	3.5503	13.8089
13	7.4500	0.2919	2.0166	3.9776	13.7361
15	7.4500	0.2092	1.4452	4.5365	13.6409
18	7.4500	0.1557	1.0755	4.8981	13.5793
23	7.4500	0.1556	1.0753	4.8983	13.5792

**Table 4.** Experimental data of quality-time of products hydrothermally synthesized at 230 °C.

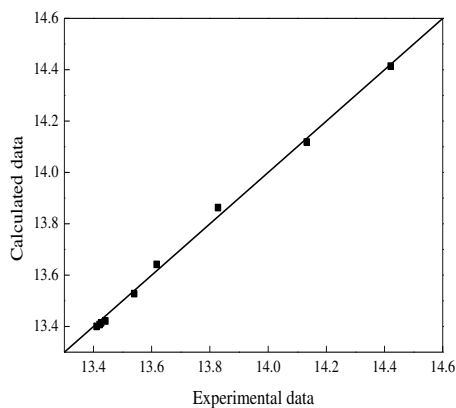
t/[h]	0	0.5	1	2	3	4	6	11	16	21
m(Total)/[g]	15.05	14.42	14.13	13.82	13.61	13.54	13.44	13.42	13.42	13.41

**Table 5.** Experimental data of quality-time of products hydrothermally synthesized at 210 °C.

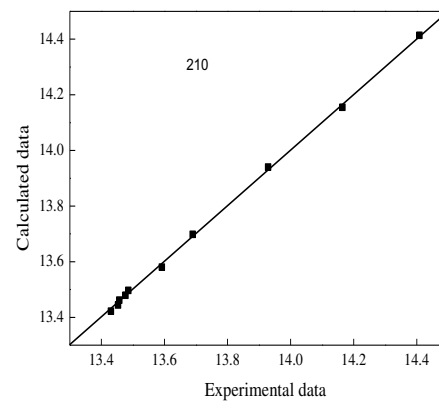
t[h]	0	1	2	3	5	7	9	11	12	17	22
m(Total)/[g]	15.05	14.40	14.16	13.92	13.68	13.59	13.48	13.47	13.45	13.45	13.43

**Table 6.** Experimental data of quality-time of products hydrothermally synthesized at 190 °C.

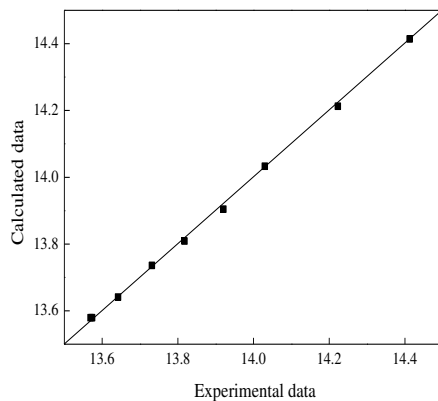
t[h]	0	1	2	3	5	7	9	11	12	17	22
m(Total)/[g]	15.05	14.60	14.41	14.22	14.02	13.92	13.81	13.73	13.64	13.57	13.56



(a) 230 °C



(b) 210 °C



(c) 190 °C

**Figure 4.** The experimental data comparison with calculated data of xonotlite fibers hydrothermally synthesized at different temperatures.

It can be seen from Figure 4 that when the reaction temperature was 230, 210 and 190 °C respectively, the quality-time calculated values were consistent with the measured values after the reaction time of 0.5 h, 1 h and 3 h respectively, so the reaction time of 0.5 h, 1 h and 3 h can be defined as the induction time required for the formation of fibrous xonotlite crystals at 230 °C, 210 °C and 190 °C respectively, as indicated by points A, B and C in Figure 2. There was no formation of fibrous xonotlite crystals before the induction time. At the same time, the above analysis also showed that the above hypotheses were confirmed, that was, the second stage, beginning with the induction time, was the stage of the formation of xonotlite fibers, and there was no C-S-H produced in this stage.

According to the above analytical results, the equation (5) can be simplified as the following chemical reaction:



In the equation:  $A \text{—} Ca(OH)_2$

$B \text{—} C - S - H(I)(5CaO \cdot 6SiO_2 \cdot 5H_2O)$

$C \text{—} 6CaO \cdot 6SiO_2 \cdot H_2O$

$D \text{—} H_2O$

According to the equation (6), the rate equation usually has the following form:

$$-dc_A / dt = k_A c_A^{n_A} c_B^{n_B} \quad (7)$$

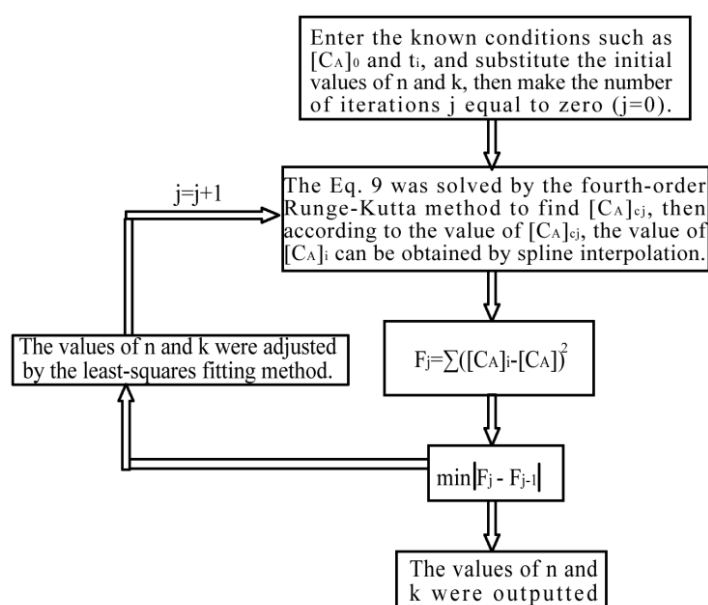
Because  $A=B$ , that is,  $B=C$ . Thus, equation (7) can be simplified as:

$$-dc_A / dt = kc_A^n \quad (8)$$

In the equation,  $k = k_A$  was the total rate constant of the reaction,  $n = n_A + n_B$  was the total order of reaction.

In this equation, the kinetic parameters were only  $k$  and  $n$ , therefore, the rate equation can be established by determining the two parameters. Since there was only one constant in the equation, the form of the rate equation only depended on  $n$ , so the key to determine the rate equation was to determine the reaction order. In order to determine the reaction order, it was necessary to know the concentrations of the reactants ( $C_A$ ) at different times ( $t$ ) at a definite temperature, that was, to know the relationship of  $C_A$ - $t$  in this chemical reaction.

In this paper, the internal performance function provided in Matlab were used, then the reaction order ( $n$ ) and the rate constant ( $k$ ) were determined and calculated respectively by dealing with the dynamic data ( $C_A$ - $t$ ) corresponding to the different temperatures in Figure 3 using the differential method. The values of  $n$  and  $k$  were used as the iterative initial values in the process of solving the fourth-order Runge-Kutta method, and the detailed solving process was shown in figure 5. It should be noted that a series of  $(t_i - [C_A]_{ci})$  values obtained by the fourth-order Runge-Kutta method may not have a corresponding value  $([C_A]_i)$ , therefore, it was necessary to use spline interpolation to solve the values of  $[C_A]_i$ .



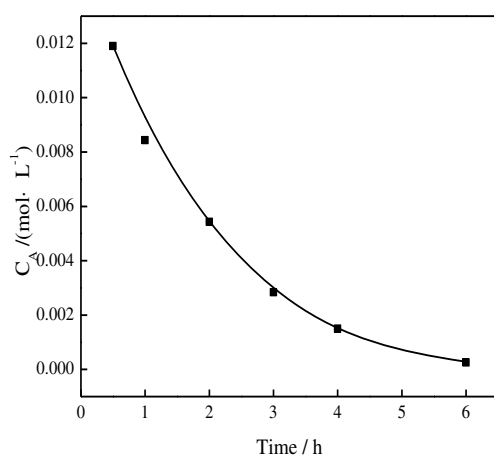
**Figure 5.** Flow chart for program of kinetic parameters.

Firstly, the values of  $[c_A]_i$  were calculated by using Matlab which completed the loop iteration of the fourth-order Runge-Kutta method and the spline interpolation. Then according to  $\min F = \sum ([c_A]_i - [c_A])^2$ , the optimum solution of  $k$  were obtained by the least-squares fitting method.

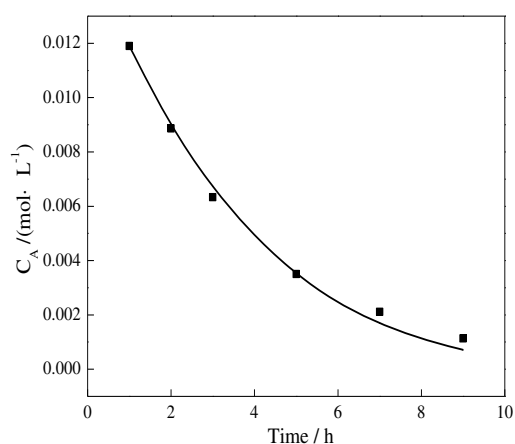
$$\begin{cases} y_{n+1} = y_n + \frac{h}{6} [k_1 + (2 - 2^{\frac{1}{2}})k_2 + (2 + 2^{\frac{1}{2}})k_3 + k_4] \\ k_1 = f_n \\ k_2 = f(t_n + \frac{1}{2}h, y_n + \frac{1}{2}hk_1) \\ k_3 = f[t_n + \frac{1}{2}h, y_n + \frac{2^{\frac{1}{2}} - 1}{2}hk_1 + (1 - \frac{2^{\frac{1}{2}}}{2})hk_2] \\ k_4 = f[t_n + h, y_n - \frac{2^{\frac{1}{2}}}{2}hk_2 + (1 + \frac{2^{\frac{1}{2}}}{2})hk_3] \end{cases} \quad (9)$$

According to the above-mentioned method, the initial values of kinetic parameters  $n$  and  $k$  at hydrothermal synthesis temperature of 230 °C were 0.7993 and  $0.1976(\text{mol} \cdot \text{m}^{-3})^{1/5} \cdot \text{s}^{-1}$  respectively. Since the errors of experimental measurement and the errors of calculation,  $n=0.8$  and  $k=0.1976(\text{mol} \cdot \text{m}^{-3})^{1/5} \cdot \text{s}^{-1}$  were taken as the iterative initial values after rounded the reaction order, then according to  $\min F = \sum ([c_A]_i - [c_A])^2$ , the value of  $k$  that obtained by a least-squares fitting method was of  $0.1976(\text{mol} \cdot \text{m}^{-3})^{1/5} \cdot \text{s}^{-1}$ .

Similarly, when the hydrothermal synthesis temperature was 210 °C or 190 °C respectively, according to  $\min F = \sum ([c_A]_i - [c_A])^2$ , the values of  $k$  were  $0.1109 (\text{mol} \cdot \text{m}^{-3})^{1/5} \cdot \text{s}^{-1}$  and  $0.0411(\text{mol} \cdot \text{m}^{-3})^{1/5} \cdot \text{s}^{-1}$  respectively. When the hydrothermal synthesis temperature was of 230 °C, 210 °C and 190 °C respectively, the value of  $n$  was of 0.8, and the values of  $k$  were of  $0.1976(\text{mol} \cdot \text{m}^{-3})^{1/5} \cdot \text{s}^{-1}$ ,  $0.1109 (\text{mol} \cdot \text{m}^{-3})^{1/5} \cdot \text{s}^{-1}$  and  $0.0411(\text{mol} \cdot \text{m}^{-3})^{1/5} \cdot \text{s}^{-1}$  respectively. The fitting results of the fourth-order Runge-Kutta method were shown in Figure 6.

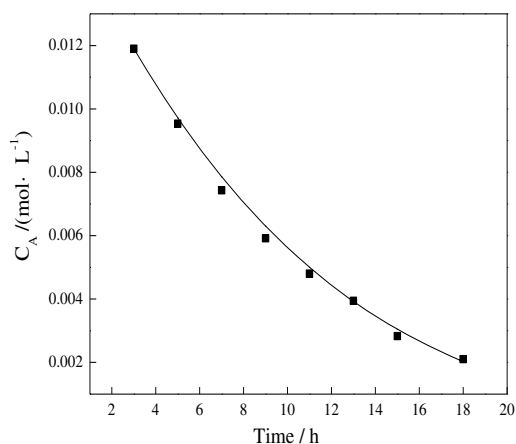


(a) 230 °C



(b) 210 °C





(c) 190 °C

**Figure 6.** The curves of concentration-time fitted by fourth-order Runge-Kutta method at different temperatures.

It can be seen from the Figure 6 that the curves of reaction concentration-time fitted by fourth-order Runge-Kutta method at different temperatures were consistent with the experimental data, obviously, the results showed that the values of  $n$  and  $k$  obtained by aforementioned computational method had a high accuracy. Therefore, the rate equation of xonotlite fibers hydrothermal reaction could be confirmed as  $-dc_A / dt = kc_A^{4/5}$ .

#### 4. Conclusions

- (1) With  $\text{K}_2\text{SiO}_3$  solution and  $\text{Ca}(\text{OH})_2$  suspension as siliceous material and calcareous material respectively, the dynamic test of the hydrothermal synthesis process of the xonotlite fibers can be achieved by measuring the change of the electrical conductivity during the reaction process.
- (2) By measuring the electrical conductivities and the calcium concentrations of product slurries synthesized at various reaction temperature, it can be assumed that the hydrothermal synthesis process of xonotlite fibers can be divided into three stages, that was, the stage forming amorphous C-S-H gels, the stage forming the most of fibrous xonotlite crystals, the stage forming a little xonotlite fibers.
- (3) According to the data of calcium concentrations, the calculated values of the products' quality at various reaction temperatures were consistent with the measured values, showing that the hypotheses dividing the formation process of fibrous xonotlite crystals into three stages were confirmed.
- (4) Based on chemical reaction kinetic, using fourth-order Runge-Kutta method, spline interpolation and least-squares fitting method, the dynamic relationship of xonotlite fibers obtained by direct conversion of silica-rich C-S-H (I) is of  $-dc_A / dt = kc_A^{4/5}$ .

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**Acknowledgments**

We gratefully acknowledge the supports of this work by the National Natural Science Foundation of China (Grant No. 21666007), Science Technology Foundation of Guizhou (Grant No. 2014-2007) and Program for “Hundred” High-level Talents in Guizhou (Grant No. 2016-5655).