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Kinetic Models of Integrated Solidification and Cementation of Cement-formation Interface with New Method

Jun Gu*, Pei Zhong, Wenzheng Qin, Haoya Liu, Lifei Dong and Yijun Yang

Petroleum Engineering Department, Faculty of Earth Resources, China University of Geosciences, Wuhan 430074, China

Abstract: The isolation failure of cement-formation interface is an important and urgent problem in oil production, while an effective way to solve it is to realize the integrated solidification and cementation of cement-formation interface (ISCCFI). In order to study the kinetics of ISCCFI with MTA (Mud Cake to Agglomerated Cake) method, the Diamond Differential Scanning Calorimetry Analyzer is adopted for experiments with dynamic method and isothermal method. The results show that there is a linear relationship between the solidification reaction temperature and the heating rate of ISCCFI with MTA method. For the first exothermic peak, the initial temperature, peak tip temperature and final temperature are 53 °C, 69 °C and 83 °C respectively, and the apparent activation energy of solidification reaction is 44.39×10^{-3} $kJ\cdot mol^{-1}$, the natural logarithm of preexponential factor is 7.26, the solidification reaction order is 0.88. For the second exothermic peak, the initial temperature, peak tip temperature and final temperature are 83 °C, 92 °C and 114 °C respectively, and the apparent activation energy of solidification reaction is 99.14×10^{-3} $kJ\cdot mol^{-1}$, the natural logarithm of preexponential factor is 24.77, the solidification reaction order is 0.94. The maximum solidification reaction rates at 50 °C, 75 °C and 90 °C are 0.09×10^{-3} s^{-1}, 0.27×10^{-3} s^{-1} and 0.51×10^{-3} s^{-1} respectively. The kinetic models of ISCCFI with MTA method under different temperatures are established. It provides a theoretical and technical support for the isolation improvement of cement-formation interface.

Keywords: Kinetic model, Fluid channeling, Cement-formation interface, MTA method.

1. INTRODUCTION

Along with the secondary development of old oilfields, the oilfield development in China and even the world mainly have two problems. First, the interlayer channeling after the production of oil wells can cause watered-out reservoirs. Second, the fluid magrition after well cementing can usually cause the great danger. An origin of these problems is the isolation failure of cement-formation interface, and it has seriously restricted the effect and benefit of petroleum exploration and development [1-4]. The practice proves that the main pathway of fluid channeling is located in the cement-formation interface [5]. In other words, the cement sheath can be peeled off from the borehole wall so long as the mud cake exists. This will cause microcracks between cement sheath and borehole wall, which reduces the bonding strength of cement-formation interface and provides a path or channel for fluids (oil, gas and water) from the reservoir or formation [6, 7]. So the main factor that causes the isolation failure of cement-formation interface is the interface defects [2]. In order to solve this problem, the MTC (Mud to Cement) method was proposed in the early 1990s [8]. This method can achieve the integrated solidification and cementation of cement-formation interface (ISCCFI) combined with multifunctional drilling fluids [9, 10]. However, it has been questioned by many scholars since 1994, because the MTC solidified body is brittle [11-13]. So, the MTC method can only be used in the well cementing of surface casing and intermediate casing of oil and gas well [14, 15].

In order to improve the bonding quality of cement-formation interface effectively, a scientific concept of Mud Cake to Agglomerated Cake (MTA) was proposed [16]. It attempted to achieve the ISCCFI. The experimental evidences of ISCCFI with MTA method were obtained by mechanical evaluation, microstructural analysis and fluid dissolution test [17, 18]. This method has been applied in 23 adjustment wells in Daqing, Shengli, and Henan oilfields in China. The applications show that this method has a remarkable effect [19, 20]. Based on DSC (differential scanning calorimetry) test, the kinetic models of ISCCFI with MTA method were established.

2. EXPERIMENTAL

2.1. Experimental Material

The mud cake modifier and forming agent of agglomerated cake are made in-house. The spacer is composed of 85 % tap water and 15 % forming agent of agglomerated cake. The drilling fluid is the drilling and completion fluid from Henan oilfield in China with 1 %-3 % mud cake modifier added. The formula of the cement slurry is Class G cement with 0.4 % dispersant and 46 % tap water.

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*Address correspondence to this author at the Petroleum Engineering Department, Faculty of Earth Resources, China University of Geosciences; No. 388, Lumo Road, Wuhan, Postcard: 430074 China;
Tel: +86-27-6784-8569; Fax: +86-27-6788-3051;
E-mail: gujun2199@126.com

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2.2. Sample Preparation

The preparation method of experimental samples can refer to the reference [4]. The permeability and porosity of simulated wellbore (SWB) are 450×10^{-3} μm^2 and 26 % respectively, which simulate the reservoir properties of main bonding section in Henan oilfield. The DSC test samples (100 mg each share) are taken from the agglomerated cake at cement-formation interface of well-prepared SWB with a special tool, and put into the special seal-bags carefully.

2.3. Measurement of DSC Curve

The DSC curve is measured by Diamond Differential Scanning Calorimetry Analyzer from Platinum-Elmer Instruments (Shanghai) Co., Ltd. According to the temperature profiles of most oilfields in China, the heating rates with dynamic method are set at 5°C/min, 10 °C/min and 20 °C/min respectively, and the temperatures range from 50 °C to 130 °C. While based on the temperatures of most reservoirs in China, the temperatures with isothermal method are set at 50 °C, 75 °C and 90 °C respectively, and the temperature will keep constant after reach a setting one at 20 °C/min.

3. RESULTS AND ANALYSIS

3.1. Kinetic Analysis of ISCCFI with Dynamic Method

The DSC curves adjusted by Origin software are showed in Fig. (**1**). Obviously, the DSC curves of various heating rates have two exothermic peaks. The temperature of the first exothermic peak ranges from 50 °C to 100 °C, while the second exothermic peak ranges from 80 °C to 140 °C. The initial temperature T_i, peak tip temperature T_p and final temperature T_f of reaction exothermic peak tend to be higher with the increase of heating rate β. The data from the first and second exothermic peak are listed in Tables **1** and **2** respectively.

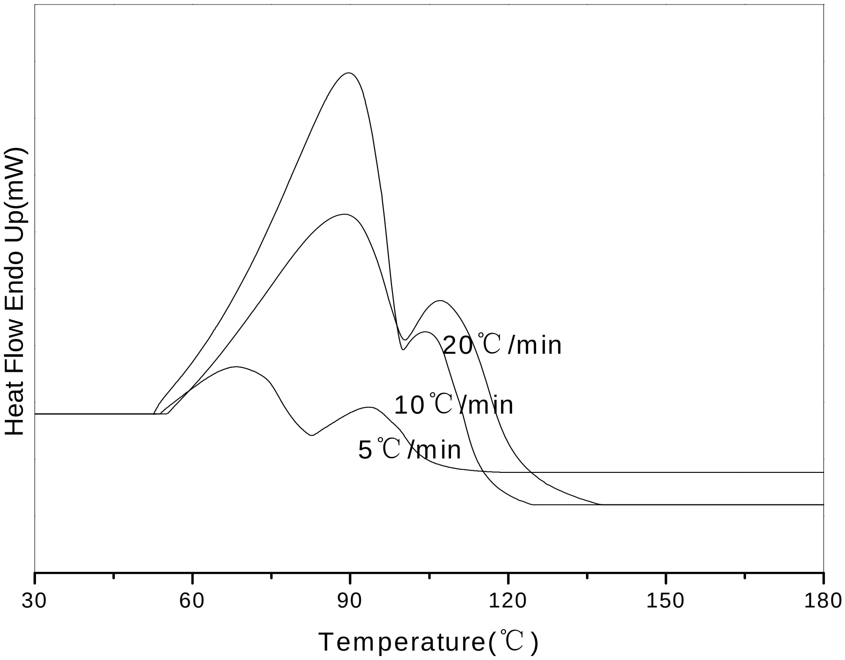

Fig. (1). DSC curves measured with dynamic method.

Table 1. Data from the First Exothermic Peak

B (°C·min^{-1})	T_i (K)	T_p (K)	T_f /K	$1/T_p$ (10^3 K^{-1})	$\ln(\beta/T_p^2)$	$\ln\beta$
5	327.05	341.61	355.82	2.927	-10.058	1.609
10	325.82	362.91	373.28	2.756	-9.486	2.303
20	328.46	362.07	373.46	2.762	-8.788	2.996

Table 2. Data from the Second Exothermic Peak

B (°C·min^{-1})	T_i (K)	T_p (K)	T_f /K	$1/T_p$ (10^3 K^{-1})	$\ln(\beta/T_p^2)$	$\ln\beta$
5	355.82	366.59	393.56	2.728	-10.199	1.609
10	373.28	377.44	397.65	2.649	-9.564	2.303
20	373.46	380.14	410.59	2.631	-8.885	2.996

3.1.1. Determination of Solidification Temperature with Extrapolation

The research shows that there is a linear relationship between the solidification reaction temperature and heating rate [21]. Thus, the solidification temperature of mud cake can be calculated with extrapolation. The results show that T_i, T_p and T_f of the first exothermic peak are 53 °C, 69 °C and 83 °C respectively Fig. (**2**), and T_i, T_p and T_f of the second exothermic peak are 83 °C, 92 °C and 114 °C respectively Fig. (**3**).

3.1.2. Determination of Apparent Activation Energy in Solidification Reaction

Kissinger pointed out that there was a certain mathematical relationship among the apparent activation energy E_a, T_P and β of solidification reaction [21]. Based on Kissinger Equation and data in Table **1**, the relationship between $\ln(\beta/T_P^2)$ and $1/T_P$ from the first exothermic peak can be obtained by linear regression Fig. (**4**), and the fitting degree is 0.33706.

According to the slope of fitting line in Fig. (**4**), E_a/R is 5.33912 K, and E_a is 44.39×10^{-3} kJ·mol^{-1}. From the intercept of fitting line in Fig. (**4**), the natural logarithm of preexponential factor $\ln A_i$ is 7.26.

Similarly, based on Kissinger Equation and data in Table **2**, the relationship between $\ln(\beta/T_P^2)$ and $1/T_P$ from the second exothermic peak can be obtained by linear regression Fig. (**5**), and the fitting degree is 0.75241.

According to the slope of fitting line in Fig. (**5**), E_a/R is 11.93005 K, and E_a is 99.14×10^{-3} kJ·mol^{-1}. From the intercept of fitting line in Fig. (**5**), $\ln A_i$ is 24.77.

3.1.3. Determination of the Solidification Reaction Order

Crane equation can be expressed as below [21]:

$$\frac{d(\ln\beta)}{d(1/T_p)} = -\left(\frac{E_a}{nR} + 2T_p\right) \qquad (1)$$

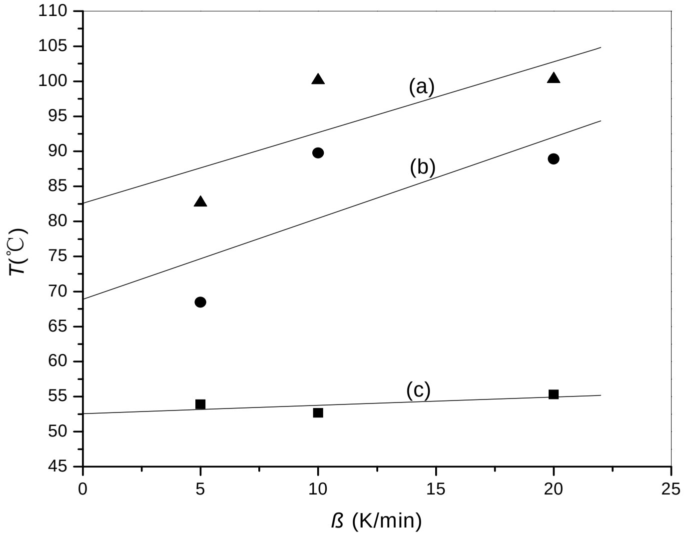

Fig. (2). Relationship between T_i, T_p, T_f and β from the first exothermic peak [(a)T_f, (b)T_p, (c)T_i].

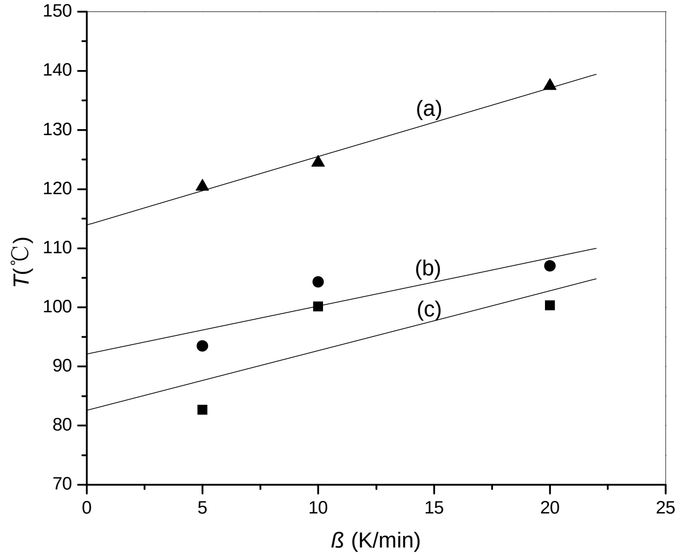

Fig. (3). Relationship between T_i, T_p, T_f and β from the second exothermic peak [(a)T_f, (b)T_p, (c)T_i].

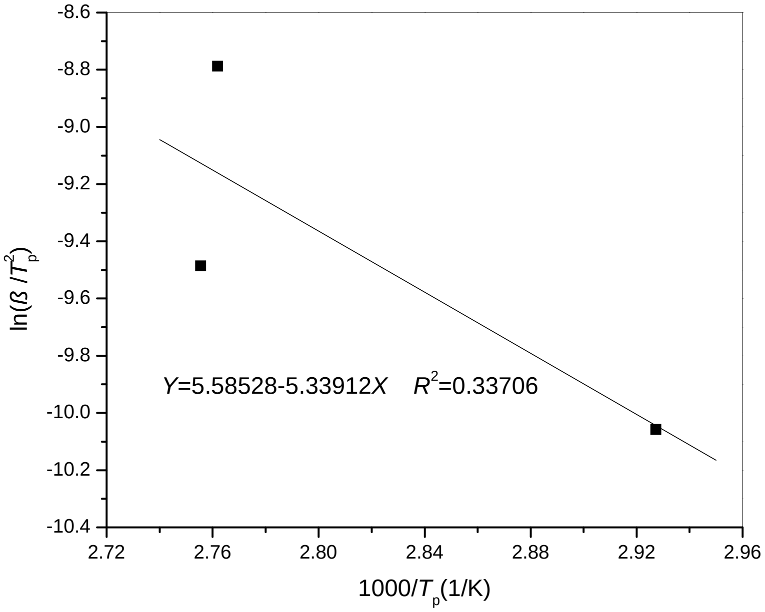

Fig. (4). Relationship between ln (β/T_P^2) and $1/T_P\times10^{-3}$ from the first exothermic peak.

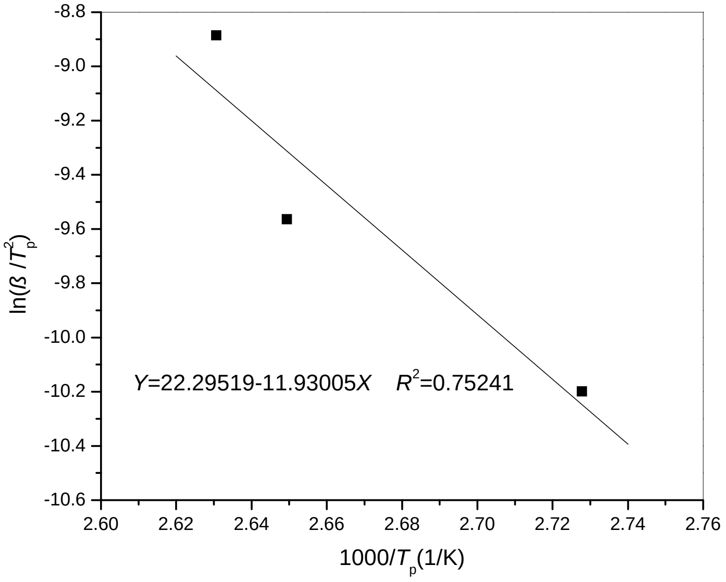

Fig. (5). Relationship between ln (β/T_P^2) and $1/T_P\times10^{-3}$ from the second exothermic peak.

When $E_a/(nR)$ is much bigger than T_p, $2T_p$ can be ignored in Eq. 1.

Substituting the relevant data above into Eq. 1, the calculation results show that the solidification reaction orders n of the first and second exothermic peaks are 0.88 and 0.94 respectively. Thus, the reaction can be considered as a complex reaction.

3.2 Kinetic Analysis of ISCCFI with Isothermal Method

According to the analysis above with dynamic method, T_P's of two exothermic peaks are 69 °C and 92 °C respectively. So, the experimental temperatures with isothermal method are selected at 50 °C, 75 °C and 90 °C respectively. The DSC curves at three different temperatures are showed in Fig. (**6**).

3.2.1. Determination of Solidification Degree and Reaction Rate

By measuring the heat generated in process of solidification reaction, the solidification kinetic parameters of mud cake with isothermal method can be calculated. The reaction heat varies with temperature and time t. In the process of reaction, the consumed amount of active functional groups stands for the extent of the reaction. By assuming that the heat evolved during curing is proportional to the extent of the reaction [22], the released heat is proportional to the consumed amount of active functional groups in process of solidification reaction. Based on this, the solidification degree α and reaction rate $d\alpha/dt$ in process of solidification reaction can be expressed as follows:

$$\alpha = \frac{\Delta H_t}{\Delta H_0} \tag{2}$$

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_0} \cdot \frac{dH}{dt} \tag{3}$$

According to Eqs. 2 and 3, the relationship between α and t at different experimental temperatures is illustrated in Fig. (**7**), and the relationship between $d\alpha/dt$ and α at different experimental temperatures is illustrated in Fig. (**8**).

From Fig. (**7**), within a certain solidification time, the higher the solidification temperature is, the higher α. For a certain temperature, α increases quickly in initial reaction stage, but slowly after reaches 0.6. At last, α keeps constant. It is caused by the growth, branching and crosslinking of chain in the process of mud cake solidification. With the development of solidification reaction, the molecular weight and crosslinking density increase, while the fluidity of reaction molecular decreases, so $d\alpha/dt$ decreases.

From Fig. (**8**), at a certain temperature, $d\alpha/dt$ increases with α in the initial reaction stage. The maximum values of $d\alpha/dt$ at 50 °C, 75 °C and 90 °C are $0.09\times10^{-3}\ s^{-1}$, $0.27\times10^{-3}\ s^{-1}$ and $0.51\times10^{-3}\ s^{-1}$ respectively.

3.2.2. Determination of Reaction rate Function

The solidification reaction of ISCCFI with MTA method can be described by the phenomenological model [23]:

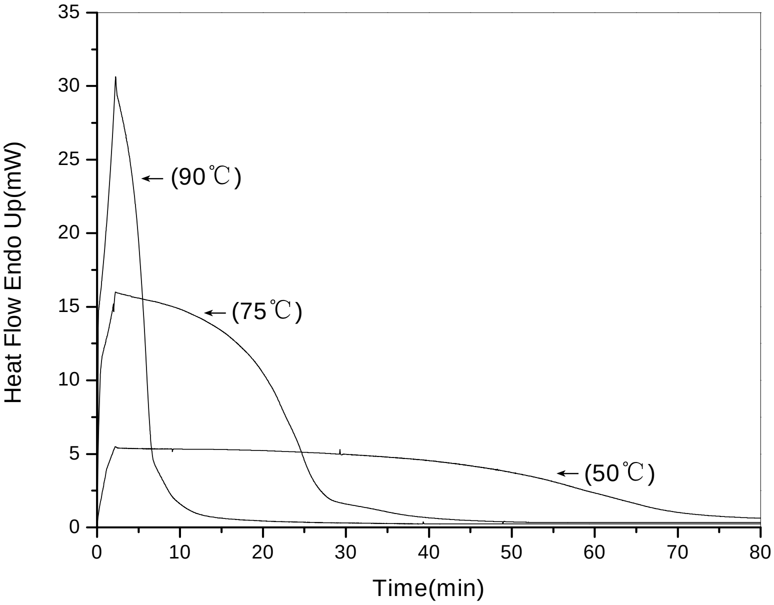

Fig. (6). DSC curves measured with isothermal method.

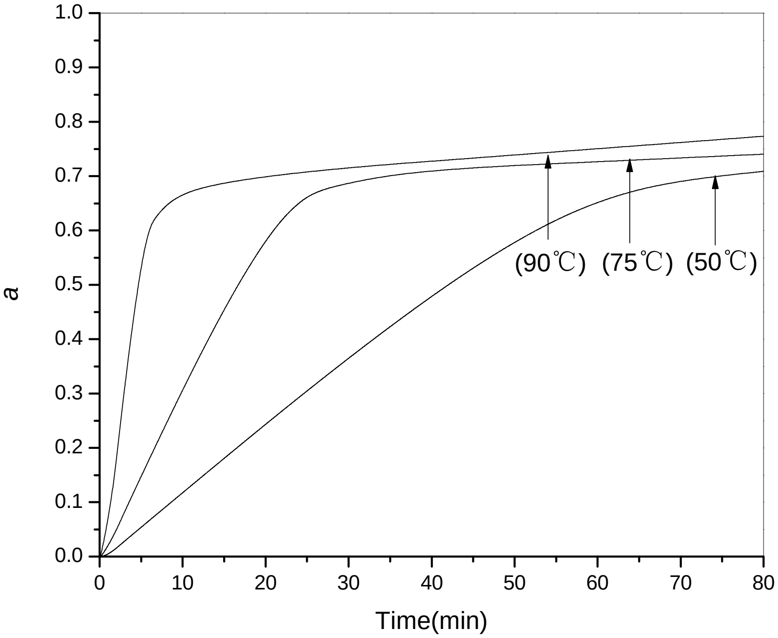

Fig. (7). Relationship between α and t with isothermal method.

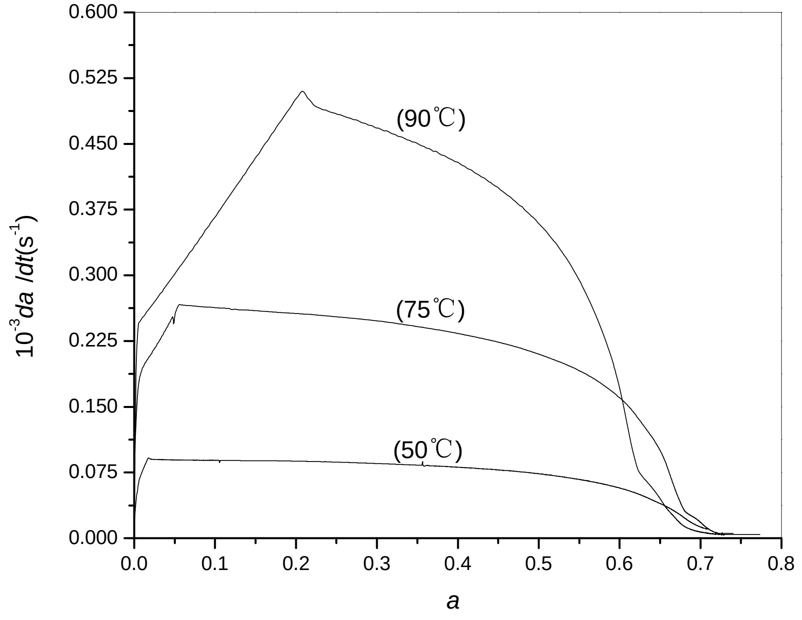

Fig. (8). Relationship between $d\alpha/dt$ and α with isothermal method.

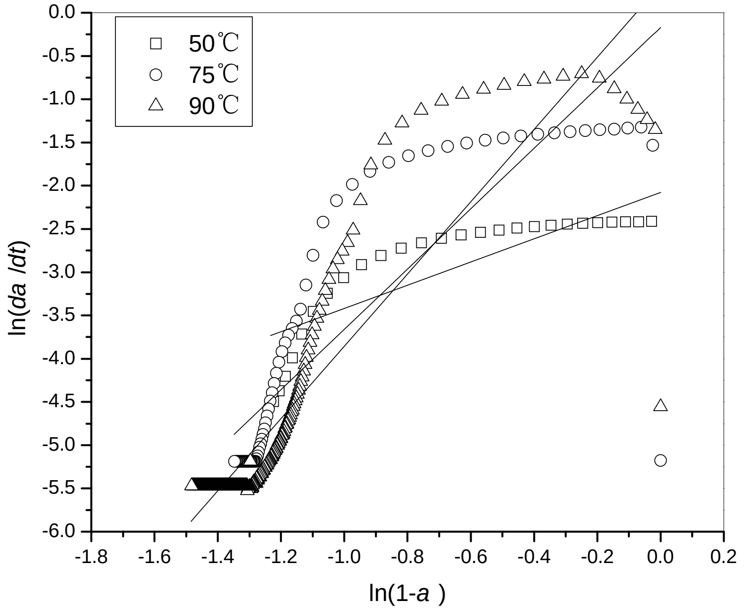

Fig. (**9**). Relationship between ln($d\alpha/dt$) and ln(1-α) with isothermal method.

$$\frac{d\alpha}{dt} = (k_2 + k_3\alpha^m)(1-\alpha)^n \tag{4}$$

Considering the intercept of curve (t = 0) in Figures 7 and 8 as the initial reaction rate, k_2 in Eq. 4 can be calculated as follows:

$$\left[\frac{d\alpha}{dt}\right]_{t=0} = k_2 \tag{5}$$

By taking natural logarithm on each side in Eq. 4, Eq. 4 is transformed into:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(k_2 + k_3\alpha^m) + n\ln(1-\alpha) \tag{6}$$

When α tends to be 1, ln(k_2+$k_3\alpha^m$) is considered as a constant, then $d$ln($d\alpha/dt$)/$d$ln(1-α) is equal to the reaction order. Based on ln(β/T_P^2) and $1/T_P$, Fig. (**9**) can be obtained by regression analysis. The slope of regression curve is equal to $d$ln($d\alpha/dt$)/$d$ln(1-α), then n can be determined.

Eq. 6 can be written as the following style:

$$\ln\left(\frac{d\alpha/dt}{(1-\alpha)^n} - k_2\right) = \ln k_3 + m\ln\alpha \tag{7}$$

Because k_2 and n can be calculated by Eqs. 5 and 6 respectively, the relationship between ln[($d\alpha/dt$)/(1-α)^n-k_2] and lnα can be obtained by regression analysis [Fig. (**10**)]. The reaction order m and k_3 are calculated respectively by the slope and intercept of the curve.

Based on k_2 and k_3, the activation energy and preexponential factor can be calculated by Arrhenius equation [23]:

$$k_i = A_i \exp\left(-\frac{E_{a(i)}}{RT}\right) \tag{8}$$

Eq. 8 can be transformed into the following style by taking natural logarithm on each side:

$$\ln k_i = \ln A_i - \frac{E_{a(i)}}{RT} \tag{9}$$

Based on lnk_i and 1/T, Figs. (**11**) and (**12**) can be obtained. The equations in the figures are established by regression analysis. And the activation energy is obtained by the slope of the line, while the intercept is lnA_i.

From the figures and calculated data above, the kinetic parameters of solidification reaction with isothermal method are obtained (Table **3**).

3.2.3. Kinetic models of ISCCFI with MTA method

Based on the analysis above, the kinetic models of ISCCFI with MTA method under three temperatures can be expressed as follows:

$$\text{At 50 °C } \frac{d\alpha}{dt} = (0.833 + 0.149\alpha^{0.16})(1-\alpha)^{1.34} \tag{10}$$

$$\text{At 75 °C } \frac{d\alpha}{dt} = (5.650 + 1.020\alpha^{0.30})(1-\alpha)^{3.49} \tag{11}$$

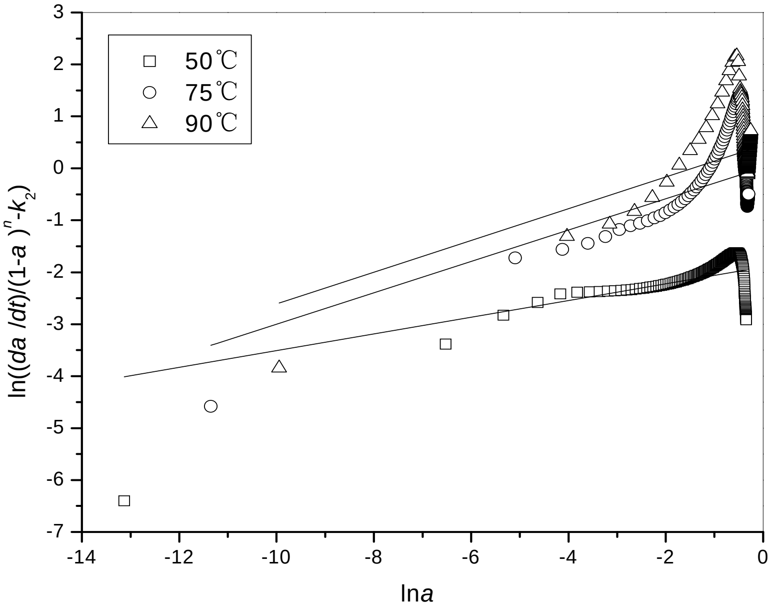

Fig. (10). Relationship between ln[($d\alpha/dt$)/(1-α)^n-k_2] and lnα with isothermal method.

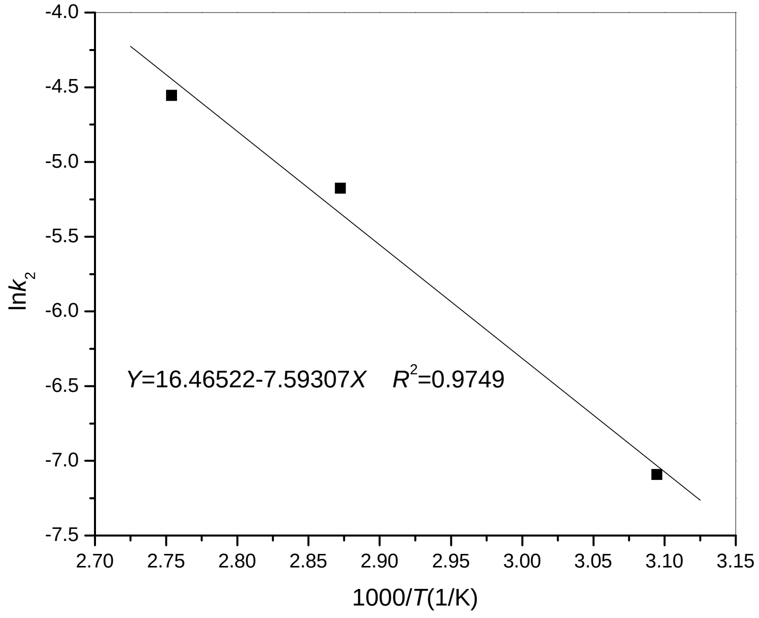

Fig. (11). Relationship between lnk_2 and 1/T with isothermal method.

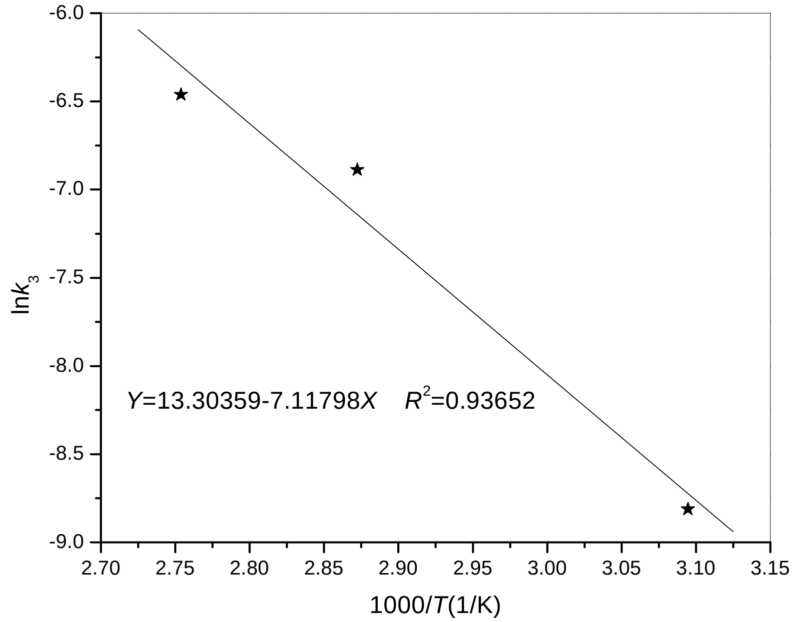

Fig. (12). Relationship between lnk_3 and $1/T$ with isothermal method.

Table 3. Kinetic Parameters Of Solidification Reaction with Isothermal Method

T (°C)	k_2 ($10^{-3}s^{-1}$)	k_3 ($10^{-3}s^{-1}$)	m	n	lnA_1	lnA_2	E_{a1}	E_{a2}
50	0.833	0.149	0.16	1.34	16.49	13.30	63.13	59.18
75	5.650	1.020	0.30	3.49				
90	10.530	1.561	0.31	4.18				

At 90 °C $$\frac{d\alpha}{dt} = (10.530 + 1.561\alpha^{0.31})(1-\alpha)^{4.18} \qquad (12)$$

4. CONCLUSIONS

There is a linear relationship between the solidification reaction temperature and heating rate of ISCCFI with MTA method. For the first exothermic peak, T_i, T_p and T_f are 53 °C, 69 °C and 83 °C respectively, E_a of solidification reaction is 44.39×10^{-3} kJ·mol^{-1}, lnA_i is 7.26, and the solidification reaction order is 0.88. For the second exothermic peak, T_i, T_p and T_f are 83 °C, 92 °C and 114 °C respectively, E_a of solidification reaction is 99.14×10^{-3} kJ·mol^{-1}, lnA_i is 24.77, the solidification reaction order is 0.94. The maximum values of $d\alpha/dt$ at 50 °C, 75 °C and 90 °C are 0.09×10^{-3} s^{-1}, 0.27×10^{-3} s^{-1} and 0.51×10^{-3} s^{-1} respectively. The solidification reaction of ISCCFI with MTA method under different constant temperatures can be described by the phenomenological model. But, as the assumptions given in this paper, the result still have some limitations. So it is necessary to study further on ISCCFI in order to solve the isolation problem of cement-formation interface effectively.

NOMENCLATURE

T_i = Initial temperature °C
T_P = Peak tip temperature °C
T_f = Final temperature °C
β = Heating rate °C·min^{-1}
E_a = Apparent activation energy kJ·mol^{-1}
m, = n Reaction order
R = Universal gas constant 8.314×10^{-3} kJ·mol^{-1}·K^{-1}
R^2 = Fitting degree
α = Solidification degree
$d\alpha/dt$ = Solidification reaction rate s^{-1}
ΔH_0 = Maximum reaction heat measured with isothermal method J·g^{-1}
ΔH_t = Reaction heat during constant time J·g^{-1}
t = Time min
T = Temperature °C
k_2, k_3, k_i = Reaction rate constants
$E_{a(i)}$ = Activation energy
A_i = Preexponential factor

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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