THERMODYNAMIC STUDY OF YE'ELIMITE FORMATION

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ABSTRACT: The production of Calcium Sulfo-aluminate cements (CSA) involves lower CO_2 emissions compared to the ordinary Portland cement (OPC). Ye'elimite ($Ca_4Al_6O_{16}S$) is the main phase in CSA clinkers. Some solid-state reactions proposed in literature to discuss ye'elimite formation may not been thermodynamically verified. The purpose of the current work is the equilibrium calculations of standard Gibbs free energy changes for the reactions involved during ye'elimite formation.

Keywords: Ye'elimite, Calcium Sulfo-aluminate Cement, Thermodynamic, Standard Gibbs free energy of formation

1. INTRODUCTION

Concrete is the most widely used construction material in the world. Ordinary Portland Cement (OPC) has traditionally been used as the binder material in concrete [1]. However, the production of OPC cements contributes of approximately 5% of global anthropogenic CO_2 emissions [2]. Calcium Sulfoaluminate Cements (CSA) [3], Belite-CalciumSulfoaluminate-Ferrite cements (BCSAF) [4,5] and Alite-Sulfoaluminate cements (ACSA) [6] are potential alternative cementitious binder for OPC cements. The production of CSA, BCSAF or ACSA clinkers involves lower embodied energy and CO_2 emissions compared to the Ordinary Portland Clinker (OPC), because they require less limestone, lower grinding energy and lower clinkering temperatures than OPC clinker [7].

Ye'elimite ($Ca_4Al_6O_{16}S$ or $C_4A_3\overline{S}$)* is the main phase in CSA clinkers and also a key component in BCSAF and ACSA clinkers [7]. Ye'elimite is considered as a simple model system for CSA clinkers. Therefore, the detailed understanding of ye'elimite formation may be the key for solving burnability† encountered in the production of CSA clinkers. The formation mechanism of ye'elimite has been discussed in literature by many solid-state reactions deduced from the mineralogical analysis using X-ray diffraction (XRD). Table 1 shows the possible reactions involved during ye'elimite formation in different temperature ranges [8]. Solid-state formation of ye'elimite from pure raw materials starts at 1000°C and it continues until 1300 °C through reactions between calcium aluminate phases (CA, CA_2) and $CaSO_4$ until 1300°C. Above 1300°C, ye'elimite decomposes into calcium aluminate phases, O_2 gas and SO_2 gas.

Thermodynamic calculations are proving extremely useful in cement research [9]. This work presents the equilibrium calculations of standard Gibbs free energy change of the involved reactions. With the data obtained, the spontaneity of the various involved reactions processes is discussed.

Table 1. The possible reactions involved during ye'elimite formation based experimental XRD results.

* The cement phase notations are used in this work (C= CaO, A = Al_2O_3, $\overline{S}$ = SO_3, $\overline{C}$ = CO_2, H = H_2O).
† The burnability is the facility with which the components of CSA cements raw mixture are combined.

Solid-state reaction		Temperature range	Ref.
$C\overline{S}H_2 \rightarrow C\overline{S} + 2\ H$	(R1)	T < 1000 °C	[8,10]
$C\overline{C} \rightarrow C + \overline{C}$	(R2)		[8,10]
$C + A \rightarrow CA$	(R3)	1000 °C < T < 1100 °C	[8]
$3\ C + 3\ A + 1\ C\overline{S} \rightarrow C_4A_3\overline{S}$	(R4)		[8,10]
$CA + A \rightarrow CA_2$	(R5)		[8]
$3\ CA + 1\ C\overline{S} \rightarrow C_4A_3\overline{S}$	(R6)	1100 °C < T < 1300 °C	[8,10,11]
$3\ C + 3\ CA_2 + 2\ C\overline{S} \rightarrow 2\ C_4A_3\overline{S}$	(R7)		[8]
$C\overline{S} \rightarrow C + \overline{S} \rightarrow C + SO_2\uparrow + ½\ O_2\uparrow$	(R8)	T > 1300 °C	[8,10,12]
$C_4A_3\overline{S} \rightarrow 1/5\ C_{12}A_7 + 8/5\ CA + SO_2\uparrow + 1/2\ O_2\uparrow$	(R9)		[8,10,12]

2. THERMODYNAMIC CALCULATION

Based on the second law of thermodynamics, the spontaneity of the reaction process can be determined [13]. Changes in standard Gibbs free energy helps to predict whether a reaction will be spontaneous in the forward or reverse direction under standard conditions (solids are pure and gases pressures equal to 1 atm). Thermodynamic equilibrium calculations of the Gibbs energy of the reactions involved during ye'elimite formation were performed using a suitable thermochemical data. Thermochemical data taken from literature which include standard enthalpy (ΔH^0), standard entropy (ΔS^0) and heat capacity (Cp) for the involved phases are collected in Table 2.
In the calculation, the standard enthalpy of substances is given as [14]:

$$\Delta H^0(T) = \Delta H_f^0(298) + \int_{298}^{T} Cp(T)\ dT \qquad \text{Eq (1)}$$

where $\Delta H_f^0(298)$ is the standard enthalpy of formation at 298 K, Cp(T) is the heat capacity at constant pressure (given in Eq 2), T is temperature.

$$Cp(T) = a + bT + cT^{-2} + dT^2 \qquad \text{Eq (2)}$$

Standard entropy values can be calculated using equation (3):

$$\Delta S^0(T) = \Delta S_f^0(298) + \int_{298}^{T} \frac{Cp(T)}{T}\ dT \qquad \text{Eq (3)}$$

where $\Delta S_f^0(298)$ is the standard entropy of formation at 298 K. The standard Gibbs energy change (ΔG_r^0) for a chemical reaction is calculated as:

$$\Delta G_r^0(T) = \Delta H_r^0(T) - T\ \Delta S_r^0(T) \qquad \text{Eq (4)}$$

where $\Delta H_r^0(T)$ is the standard enthalpy change of the reaction and $\Delta S_r^0(T)$ is the corresponding standard entropy change.

Table 2. Thermochemical data of the phases involved during ye'elimite formation.

Phase	$\Delta H_f^0(298)$ ($kJ.mol^{-1}$)	$S_f^0(298)$ ($J.mol^{-1}.K^{-1}$)	a ($J.mol^{-1}.K^{-1}$)	b x 10^{-3} ($J.mol^{-1}.K^{-1}$)	c x 10^5 ($J.mol^{-1}.K^{-1}$)	d x 10^{-6} ($J.mol^{-1}.K^{-1}$)	Ref.
C	0	0	57.753	-10.779	-11.51	5.328	[15]
$C\overline{C}$	-1206.600	91.710	99.544	27.136	-21.479	0.002	[16]
$\overline{C}$	0	0	29.314	39.970	-2.484	-14.783	[15]
H	-285.830	69.950	186.884	-464.247	-19.565	548.631	[17]
SO_2	0	0	54.779	3.350	-24.745	-0.241	[16]
O_2	0	0	34.859	1.312	-14.140	0.163	[18]

A	0	0	115.977	15.654	-44.290	-2.358	[19]
CA	-2326.304	114.223	150.62	24.94	-33.3	0	[20]
CA_2	-3999.067	177.820	276.511	22.944	-74.469	-0.006	[17]
$C_{12}A_7$	-19429.998	1046.837	1263.401	274.052	-231.375	0	[21]
$C_4A_3\bar{S}$	-8393.19	450.2	554.05	143.34	-113.4	0	[22]
$C\bar{S}$	-1437.622	106.692	115.894	39.335	-25.102	-0.003	[23]
$C\bar{S}H_2$	-2022.629	194.100	91.379	317.984	0	0	[17]

3. RESULTS AND DISCUSSION

Fig. 1 shows curves of the standard Gibbs free energy change of the involved reactions (Table 1) at a temperature range of from 200 °C to 1400 °C. The chosen temperature range is justified by the fact that ye'elimite starts to melt above 1400 °C [8]. As it is shown in Fig.1, between 200 °C and 1400 °C, the standard Gibbs free energy changes of the reactions (R1), (R3), (R4), (R5), (R6) and (R7) are negative, indicating that the reactions may occur spontaneously under standard conditions. It is positive for reaction (R9), showing that the reaction is unlikely to proceed thermodynamically in the studied temperature range (from 200 °C to 1400 °C). The reaction (R2) is thermodynamically unfavoured between 200 °C to 900 °C since the standard Gibbs free energy change is positive, while it starts to be spontaneously possible above 900 °C. Similarly, for reaction (R8), the standard Gibbs free energy change of the reaction is positive between 200 °C to 1200 °C, to be negative above 1200 °C. These thermodynamic calculations enable to predict if the reaction can take place under standard conditions. The next stage will to examine the effect of gas partial pressures on the decomposition temperatures, especially SO_2, O_2 partial pressures on the ye'elimite decomposition (R9).

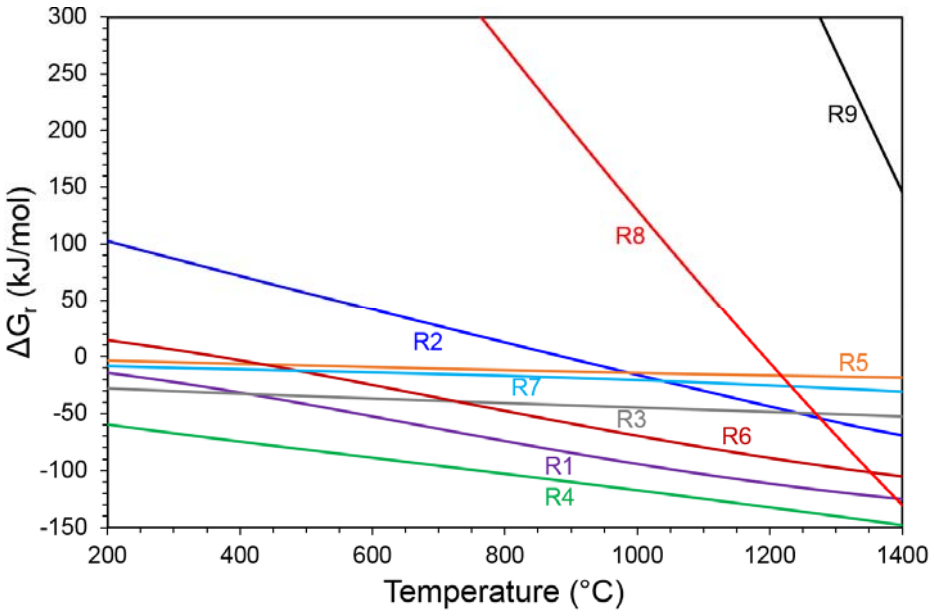

Fig.1. Evolution with temperature of the standard Gibbs energy change (ΔG_r) of the reactions given in Table 1.

4. CONCLUSIONS

With equilibrium calculations of standard Gibbs free energy change according to the temperature ranging from 200 °C to 1400 °C, the thermodynamic process spontaneity of the reactions involved during ye'elimite formation is studied for the first time. The results can be used to discuss thermodynamically the suggested reactions reported in literature relevant to ye'elimtie formation, which could help CSA cement manufacturers to optimize the burnability process.

Through the calculations of standard Gibbs free energy change, it is found that most of the suggested solid-state reactions for ye'elimite formation taken from literature are feasible thermodynamically under standard

conditions. Meanwhile, the thermodynamic calculations indicate that the ye'elimite decomposition reaction $C_4A_3\overline{S} \rightarrow 1/5\ C_{12}A_7 + 8/5\ CA + SO_2\uparrow + 1/2\ O_2\uparrow$ (R9) has a positive standard Gibbs free energy change over the studied temperature range, which is not in line with the experimental results published in literature. The effect of SO_2 partial pressure generated from sulfate decomposition (R8) on ye'elimite decomposition (R9) was not investigated. It should be reminded that thermodynamic calculation of standard Gibbs free energy changes assuming ideal gases and pure solid phases of small volume involved.

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