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Phase equilibria studies of $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3$-MgO system using CALPHAD

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ABSTRACT

A detailed CALPHAD (CALculation of PHAse Diagram) based thermodynamic study on CaO- $SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3$-MgO system (C-A-S-F-M) has been carried out to study the evolution of phases during heating and to investigate the effects of individual oxides. The important phases present at high temperature in the system are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), dicalcium ferrite (C_2F) and a liquid phase. The evolution of liquid phase and other important phases predicted by CALPHAD closely matches with the experimental results. It was observed that in C-A-S-F-M system, there is a critical percentage of CaO and SiO_2 at which C_3S is maximum. Both Fe_2O_3 and Al_2O_3 significantly increase the amount of liquid phase. Both Fe_2O_3 and Al_2O_3 reduce C_3S and increase C_2S in the system. Up to 1.5 wt%, MgO also helps in increasing liquid phase. A mathematical model to predict phases has been developed as an alternative to the Bougue's equation which is very effective in predicting phase fractions.

1. Introduction

$CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3$-MgO (C-S-A-F-M) system is a very important system for having huge applications in various ceramics and metals industries such as Portland cement, high alumina cement, steel slag, tiles and bricks, refractories, glasses, etc [1–4]. Understanding the thermodynamics of this system and the complex interactions among these oxides is very much crucial in view of its applications. Conventionally, it is done by using well known binary or ternary diagrams where interactions between two or three component are considered at a time [5]. Therefore, there has always been a gap as the interactions of all the oxides present in the system cannot be considered together because of its practical limitations. So, for such higher order complex system, it is very difficult to study the same using conventional phase diagrams and to predict the phases precisely. It is most convenient to use advanced computational thermodynamic based CALPHAD (CALculation of PHAse Diagram) [6] method to calculate the phase formation.

CALPHAD is a semi-empirical technique used to simulate unknown phase diagrams and to calculate thermodynamic properties on a given equilibrium condition [7]. This technique can predict phases for complex higher order systems using available lower order systems using extrapolation method in a few seconds. Now a days, it is routinely used in many industries and research institutes for various applications in metallurgy [8], ceramic [9] and cement [10] to predict phases, design new materials and for various route cause analysis.

To produce cement, the raw materials such as limestone, clay, etc. as a source of these five oxides (CaO, SiO_2, Fe_2O_3, Al_2O_3 and MgO) are mixed, grinded in a ball mill or a vertical roller mill to produce raw mix which is followed by firing the raw mix at high temperature (1350–1500 °C) in a rotary kiln [3]. The raw mix contains 61–67 wt% CaO, 19–23 wt% SiO_2, 2.5–6 wt% Al_2O_3, 0–6 wt% Fe_2O_3 and 0–5 wt% MgO [3,5]. The final product (clinker) contains mainly four phases, tricalcium silicate (Ca_3SiO_5), also known as C_3S, dicalcium silicate (Ca_2SiO_4) which is commonly known as C_2S, tricalcium aluminate ($Ca_3Al_2O_6$), known as C_3A and tetra calcium alumino ferrite which is mostly identified as C_4AF [11]. Typical range of these phases in Portland cement are given in Table 1. C_4AF is a secondary solid solution of dicalcium ferrite ($Ca_2Fe_2O_5$) known as C_2F and hypothetical-C_2A [12]. Therefore, C_4AF is not modelled in the Thermo-Calc oxide database as a separate compound, but as a solid solution of C_2F. Apart from these four phases, two important minor halite phases are also very common in cement clinker namely, unreacted or free MgO and free CaO. Both, free MgO and free CaO are not desirable in cement as it causes crack formation during setting due to the formation of $Mg(OH)_2$ and $Ca(OH)_2$ respectively of higher volume. During hydration of the product, different phases react differently with water based on their reactivity and generates interlocking microstructure which gives final strength. The final properties like strength [5], durability [13], heat of hydration [14], flow ability [15,16], etc. of the cement are directly linked to the

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Table 1
Range of major phases obtained in Portland cement clinker.

Phase	C_3S	C_2S	C_3A	C_4AF/C_2F
Wt(%)	50–70	15–30	5–10	5–15

Table 2
Oxide percent in a typical cement composition.

Oxides	CaO (g)	SiO_2 (g)	Al_2O_3(g)	Fe_2O_3(g)	MgO(g)	Others
Typical Composition	63.44	20.91	5.5	4.15	3.2	2.8
Range Calculated	55–75	16–30	0–10	0–10	0–5	–

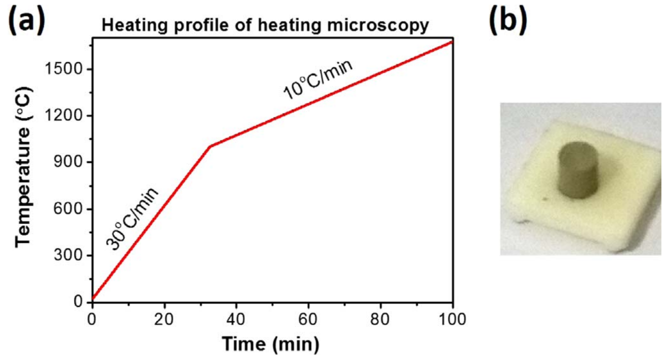

Fig. 1. (a) Heating profile and (b) cylindrical sample used for heating microscopy experiments.

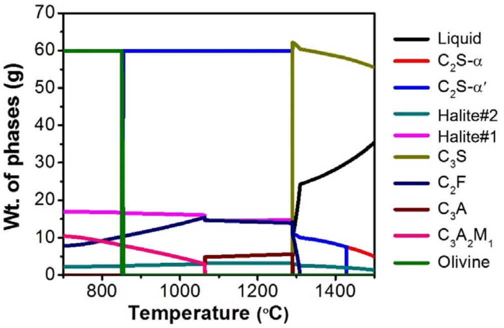

Fig. 2. Evolution of phases as a function of temperature for C-A-S-F-M system given in Table 2.

phases formed after firing the raw materials. C_3S contributes to the early strength (3 days strength) whereas, C_2S mostly contributes to the later strength (28 days strength). C_3A exothermically reacts with water immediately after mixing with water and a larger amount of heat forms during reaction. This excessive heat can cause damage in bulk construction. It can also lead to flash setting which is responsible for poor workability and impedes easy construction. Although, C_3A and C_2F do not contribute significantly in the development of strength but, their presence is required for C_3S formation as during firing they form liquid phase which helps in completing the formation of C_3S. So, it is always targeted to keep the levels of C_3A and C_2F as low as possible which are essential to complete C_3S formation and increase percentage of C_3S and C_2S in the system. The proportion of C_3S and C_2S is also negotiable depending on the area of application for the better performance as both of them have different role in strength development as described earlier. For a particular application, the desired percentages of phases are obtained by varying the level of input oxides. Thus, it is of paramount importance to have a proper understanding of the phase formation in order to have a good control over the final phases formed after the firing. Amounts of the phases in final product are generally predicted using well known Bogue's [17] equations (Eqs. (1)–(4)) which are temperature independent. However, there is always some discrepancy between the Bogue's equation and XRD results depending on the reaction conditions and raw materials composition.

$$C_3S = 4.0710 \times CaO - 7.6024 \times SiO_2 - 1.4297 \times Fe_2O_3 - 6.7187 \times Al_2O_3 \tag{1}$$

$$C_2S = 8.6024 \times SiO_2 + 1.0785 \times Fe_2O_3 + 5.0683 \times Al_2O_3 - 3.0710 \times CaO \tag{2}$$

$$C_3A = 2.6504 \times Al_2O_3 - 1.6920 \times Fe_2O_3 \tag{3}$$

$$C_4AF = 3.0432 \times Fe_2O_3 \tag{4}$$

2. Methodology and experimental procedure

In the current study, five major oxides (CaO, SiO_2, Fe_2O_3, Al_2O_3 and MgO) have been considered for the calculations. Initially, thermodynamic simulation has been used to study the phase evolution for a typical cements composition during firing in rotary kiln. Subsequently, effects of individual oxides have been studied through thermodynamic simulation. Finally, the phase formation of typical composition has been validated using experimental results.

2.1. Simulation methodology

A typical Portland cement composition is given in Table 2 which was considered as the reference composition. All the thermodynamic calculations were carried out using Thermo-Calc Software (version 2016b) TCOX Metal Oxide Solutions database version 6 [18,19]. Temperature vs. phase fraction diagram was calculated with the composition given in Table 2 in a temperature range 700 °C to 1500 °C. To study the effect of each oxide individually, each oxide was varied in a particular range as given in Table 2, while remaining oxides contents were kept fixed. For an illustration, to study the effect of CaO, CaO was varied from 55 g to 75 g with a step size 1 while the compositions of SiO_2, Fe_2O_3, Al_2O_3 and MgO were fixed at 20.91 g, 4.15 g, 5.5 g and 3.2 g, respectively.

A Design of Experiment (DOE) [20] was employed to study the overall effect of oxides on phase formation. To generate the DOE, each set of oxides was varied in a particular range given in Table 2. Finally, the phase fractions corresponding to each composition were calculated using Thermo-Calc software with oxide database.

To establish the regression model, a DOE was generated in a composition range given in Table 2 with step size 1. Total no of element of the DOE matrix is $11 \times 11 \times 5 \times 5 \times 5 = 15{,}125$. The equilibrium calculation of 15,125 different compositions was then calculated using Thermo-Calc software. Liquid phase, C_3S, C_2S phases were calculated at 1400 °C whereas, C_3A and C_2F were calculated at 1200 °C. The DOE matrix along with corresponding phase obtained by calculation is given in supplementary file (S1.xlsx). Finally, multiple regression analysis has been carried out using Minitab [17] software.

2.2. Experimental procedure

The initial raw precursor was prepared with limestone, laterite, lithomarge and bauxite by mixing them in proper proportions and grinding in an in house ball mill (maximum capacity 5 kg) for 2 h. This raw mix was mixed with little water (15 wt%) and nodules of 5–6 cm diameter were prepared. Finally, the nodules were kept in dryer (110 °C) for overnight. Firing was carried out in a platinum crucible covered with a lid in a Carbolite Down Hearth furnace with a heating rate 10 °C/min up to 1400 °C followed by a holding for 1hr and air quenching to room temperature. The sample was analyzed using heating microscopy and X-Ray Diffraction (XRD). Bruker's D8 advance