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Transformation of silicon-bearing minerals during CaC_2 production and its effect on CaC_2 formation

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ABSTRACT

Silicon carbide (SiC) and ferrosilicon are the main solid by-products in the production of calcium carbide (CaC_2) from coke and lime. Both of these silicon compounds are formed from silicon-bearing minerals in the raw materials but the routes of their formation are unclear. This paper presents a detailed study about transformation of the silicon-bearing minerals in a CaC_2 furnace and its influence on CaC_2 formation. The research was carried out in a thermogravimetric analyzer coupled with a mass spectrometer. It is found that the silicon-bearing minerals transform to SiC via reduction by C when the raw materials are large in size or to calcium silicates via reaction with CaO when the raw materials are pulverized and well mixed. The main calcium silicate, Ca_3SiO_5, reacts further with coke to form SiC and CaC_2 via an intermediate Ca_2SiO_4. At exhaustion of coke, the calcium silicates react with CaC_2 to form SiC. SiC may react with Fe to form ferrosilicon which is the main route for ferrosilicon formation in industrial furnaces. Low-temperature eutectics are formed from calcium silicates and CaC_2. Calcium silicates inhibit the reaction of C and CaO to CaC_2.

1. Introduction

Calcium carbide (CaC_2) is an important reagent for organic synthesis for acetylene chemistry [1] and has been produced in industry for several decades. The raw materials for its production, coal-derived coke and lime, usually contain various non-Ca minerals at contents as high as 10 wt%. These minerals and their reaction products may mix in the molten product CaC_2 to reduce its purity or accumulate in the furnace bottom to cause operation problems. Compared with the traditional electric arc process for CaC_2 production, the auto-thermal process, heated by oxygen-combustion of coke, saves more than 37% energy but consumes about 3 times more coke [2–4], which results in more minerals or their reaction products in the furnace. The transformation and effect of minerals therefore are crucial issues in CaC_2 production. However, little information in this aspect, except limited practical data and our recent report [5], is available in the literature.

Practical operation shows that the main silicon-bearing products are silicon carbide (SiC) and ferrosilicon [6]. Most of them accumulate in the furnace bottom while a small portion of them mixes in the molten product CaC_2. The main iron-bearing and aluminum-bearing products are ferrosilicon and aluminates, respectively, which mainly accumulate in the furnace bottom. The magnesium-bearing product is element magnesium (Mg), which volatilizes and reacts with carbon monoxide (CO) or nitrogen (N_2) in the gas phase. These experiences, although important, do not show detailed transformation routes of these minerals to promote advancement of the technology. Our recent research [5] on individual influence of a few minerals on CaC_2 production indicated that (1) Fe_2O_3 and MgO are reduced by coke to form elemental Fe and Mg prior to CaC_2 formation and the elemental Fe and Mg have little influence on CaC_2 formation; (2) SiO_2 and Al_2O_3 react with CaO to form Ca_3SiO_5 and $Ca_2Al_2O_5$, respectively, which then react with C to form CaC_2 at rates lower than that for CaO. Both the practical experience and laboratory data suggest that the influence of magnesium-bearing minerals can be ignored during CaC_2 production. A comprehensive understanding on the combined effect of silicon-, aluminum- and iron-bearing minerals is necessary since it may be different from the effect of single mineral, especially when the ash is rejected in the molten state as suggested in studies of high temperature coal gasification [7,8].

The silicon-, aluminum- and iron-bearing minerals in coke include quartz (SiO_2), silicate, aluminosilicate (mainly kaolinite, $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$), aluminum hydroxide ($Al(OH)_3$), iron oxides and iron sulphide (FeS_2) [9]. Experimental study of these molten minerals in a CaC_2 furnace is needed but is difficult because the high reaction temperatures, generally above 2000 °C. In recent years, many phase diagrams have been formulated for the development of high temperature pulverized coal gasification technologies, and

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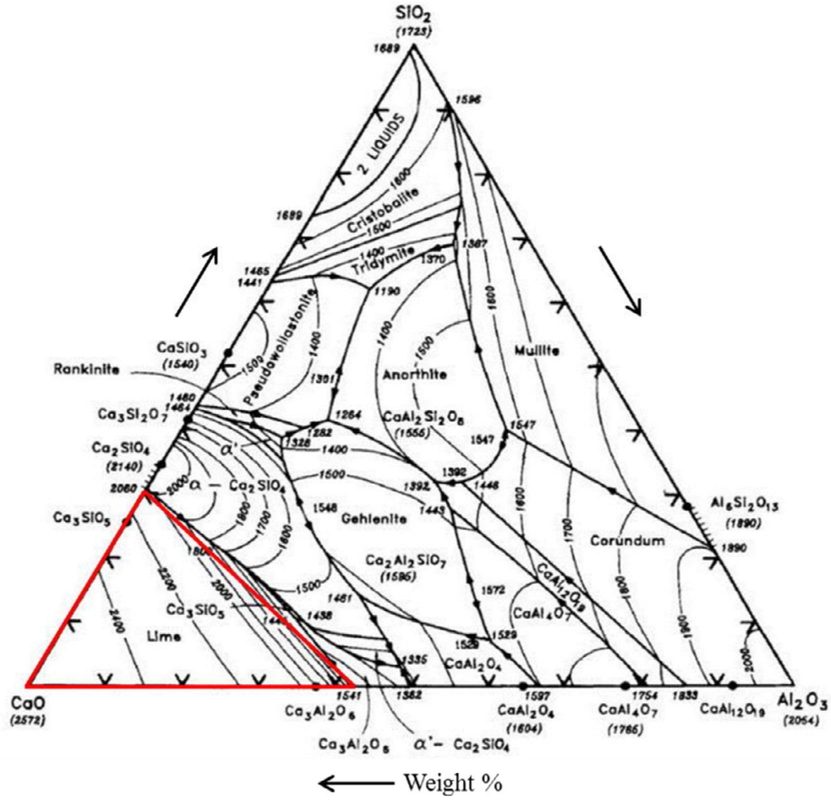

Fig. 1. A CaO-SiO_2-Al_2O_3 phase diagram (in °C) from literatures [20–22].

found to be effective to understand the detailed transformation process and fusibility behavior of minerals [7,8]. With the aid of phase diagram of CaO-SiO_2-Al_2O_3 and literature knowledge, transformation of silicon-, aluminum- and iron-bearing minerals in a CaC_2 furnace is analyzed preliminarily below.

2. Current understanding on transformation of silicon-, aluminum- and iron-bearing minerals

For the electric arc CaC_2 process, the raw materials lime and coke are usually 30–50 and 10–25 mm in size, respectively [6], where the minerals in coke are surrounded by C. For the powdery feeds used in the auto-thermal process, quantities of minerals will be exposed to the powders including the powdery lime, which would certainly increase their contact. For these reasons, transformation of the minerals in a CaC_2 furnace is analyzed in two circumstances: with the initial contact with C or with lime.

It is generally accepted that kaolinite dehydrates at temperatures of 480–600 °C through Eq. (1) and then decomposes to mullite ($3Al_2O_3{\cdot}2SiO_2$) and SiO_2 at 1000 °C through Eq. (2) [10,11]. $Al(OH)_3$ may decompose to its oxide at temperatures higher than 950 °C [12]. FeS_2 may transform to magnetite (Fe_3O_4) and hematite (Fe_2O_3) by oxygen in coke [13], which then react with SiO_2 to form Fe_2SiO_4 [14]. All the final compounds are usually termed ash.

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O = Al_2O_3 \cdot 2SiO_2 + 2H_2O \tag{1}$$

$$3(Al_2O_3 \cdot 2SiO_2) = 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2 \tag{2}$$

If these minerals were surrounded by C, SiO_2 would be reduced quickly to SiC at 1500 °C (Eq. (3)) [15], mullite would react with C in two stages (Eqs. (4) and (5)) to form SiC and Al_4C_3 [16–19], and the iron-bearing compounds, such as Fe_2O_3 and Fe_2SiO_4, would be reduced to elemental Fe by C at temperatures of 650–1100 °C [13,14]. These carbides and Fe are likely to be inert to CaC_2 and CaO if they accumulate at the bottom of furnace, although details are not found in the literature.

$$C + SiO_2 = SiC + CO \tag{3}$$

$$3Al_2O_3 \cdot 2SiO_2 + 6C = 3Al_2O_3 + 2SiC + 4CO \tag{4}$$

$$2Al_2O_3 + 9C = Al_4C_3 + 6CO \tag{5}$$

If these minerals were in contact with lime, Fe_2O_3 and Fe_3O_4 would react with CaO and Al_2O_3 to form compounds like $CaFe_2O_5$ and $Ca_2(AlFe)O_5$, which are then reduced by C at 1100 °C to form Fe [14]. SiO_2, Al_2O_3 and mullite would react with CaO to form calcium-silicate, aluminate or aluminosilicate at about 1300 °C [20]. To identify their composition in a CaC_2 furnace, a CaO-SiO_2-Al_2O_3 phase diagram (Fig. 1) widely used in researches of pulverized coal gasification and cement production [21–23] is referenced. It can be seen that when CaO is in excess and the temperature is higher than 1500 °C, *i.e.* the conditions for initiation of CaC_2 formation [5], the mixture can be expressed by a simple ternary phase diagram of silicate-aluminate-CaO in the lower left corner highlighted in red, which does not include aluminosilicate. The calcium silicates include mainly tricalcium silicate (Ca_3SiO_5) and a small amount of dicalcium silicate (Ca_2SiO_4). The calcium aluminates include mainly tricalcium aluminate ($Ca_3Al_2O_6$). Transformation of these compounds in a CaC_2 furnace needs to be studied.

Based on the above analysis, this work studies the interaction of SiC with Fe and transformation of Ca_3SiO_5 to comprehensively understand transformation of silicon-bearing minerals in CaC_2 production.