Arab Gulf J. scient. Res. **4** (1), pp. 95-104 (1986)

Effect of SiO_2 on the Formation of Tricalcium Aluminate

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ABSTRACT. The aim of the present work is to study the effect of SiO_2 on the formation of tricalcium aluminate in relation to firing temperature; up to 1400°C, as well as to determine the metastable phases in this system $CaO-Al_2O_3-SiO_2$. Four mixes having the stoichiometric composition of tricalcium aluminate with 0, 0.5, 1.0 and 1.5 mole of SiO_2 were studied. The compounds formed were investigated by using x-ray diffraction as well as chemical analysis to determine the phases formed and unreacted free CaO.

The results showed that C_3A is formed by firing the stoichiometric composition at 1400°C for 3 hours without any additions of SiO_2. Addition of SiO_2 results in the formation of other phases than C_3A and lower percentage of free lime.

The system $CaO\text{-}Al_2O_3-SiO_2$ is considered the basic system to cement production and its knowledge is essential to cement chemistry. Its three oxides (CaO, Al_2O_3 and SiO_2) form about 90 percent portland cement and over 80 percent high alumina cement (Lea 1970). These oxides interact with one another during sintering process in the rotary kiln to form a series of complex products. It is well known that the first compounds formed at lower temperature are monocalcium aluminate (CA) and $\bar{\alpha}-$dicalcium silicate ($\bar{\alpha}-C_2S$). Formation of tricalcium aluminate does not occur readily, nor does that of tricalcium silicate commence until a temperature of 1300°C is reached. A similar progress of reactions is found when mixes of kaolin and calcium carbonate are heated (Ludwig *et al.* 1960, Lehmann *et al.* 1964 and Quittkat 1965). Gehlenite (C_2AS) starts to form at about 900°C and then decomposes again by 1100°C. The compound ($C_{12}A_7$) is observed between 900°C and 1100°C and converts to C_3A at 1100°C upwards.

Cement notations used in this work are : C = CaO; A = Al_2O_3 and S = SiO_2.

The present work deals with the influence of SiO_2 on the formation of tricalcium aluminate over a range of firing temperatures from 1000°C up to 1400°C.

Experimental

To study the effect of SiO_2 on the formation of tricalcium aluminate, mixes having the stoichiometric composition of tricalcium aluminate with 0, 0.5, 1.0 and 1.5 mole of SiO_2 were prepared. The materials used in this study were BDH analytical grade reagents. The components of each mix were mechanically mixed in a porcelain ball mill for one hour. The blended mixes were calcined for two hours at 900°C in a platinum boat and then ground to pass completely through $< 73\ \mu m$ sieve to attain complete homogeneity. Pellets were made from each mix with the aid of water than dried at 105°C. The dried pellets of each mix were separately fired in an electric furnace at temperature ranges from 1000°C up to 1400°C for a period ranging from two-three hours. After burning, they were quenched in air. The products were ground to below 63 μm and then kept in air tight containers (El-Didamony 1978). The investigation was followed using x-ray diffractometry as well as chemical analysis to determine the reaction product phases and free lime (Kondo *et al.* 1975).

Results and Discussion

X-ray diffraction patterns of the fired stoichiometric composition of tricalcium aluminate with 0.0 mole of SiO_2 as a function of firing temperature are shown in Figure 1. The sample fired at 1000°C shows the presence of $C_{12}A_7$ and monocalcium aluminate (CA) with the pattern of free or unreacted calcium oxide as the predominant phase. At 1100°C for two hours the same compounds were detected. The sample fired at 1200°C illustrates the increase of $C_{12}A_7$ with relatively decrease of monocalcium aluminate (CA) and free CaO. As the temperature increases to 1300°C, the pattern shows the appearance of tricalcium aluminate as the predominant phase. $C_{12}A_7$ is still present but in small amount and CaO is completely consumed. The sample fired at 1400°C for three hours illustrates only the pattern of pure tricalcium aluminate.

Figure 2 illustrates the x-ray diffraction patterns of fired mixes of stoichiometric tricalcium aluminate with 0.5 mole SiO_2. The sample fired at 1000°C shows the patterns of $C_{12}A_7$ and CA with traces of free CaO. At 1100°C $\beta-C_2S$ forms with $C_{12}A_7$, CA and free CaO. Monocalcium aluminate is the predominant phase with $C_{12}A_7$.

The sample fired at 1200°C shows also CA and $C_{12}A_7$ with a limited amount of $\beta-C_2S$ and no detectable free CaO. At 1300°C, the pattern demonstrates the presence the monocalcium aluminate (CA) with small amounts of $C_{12}A_7$ and the

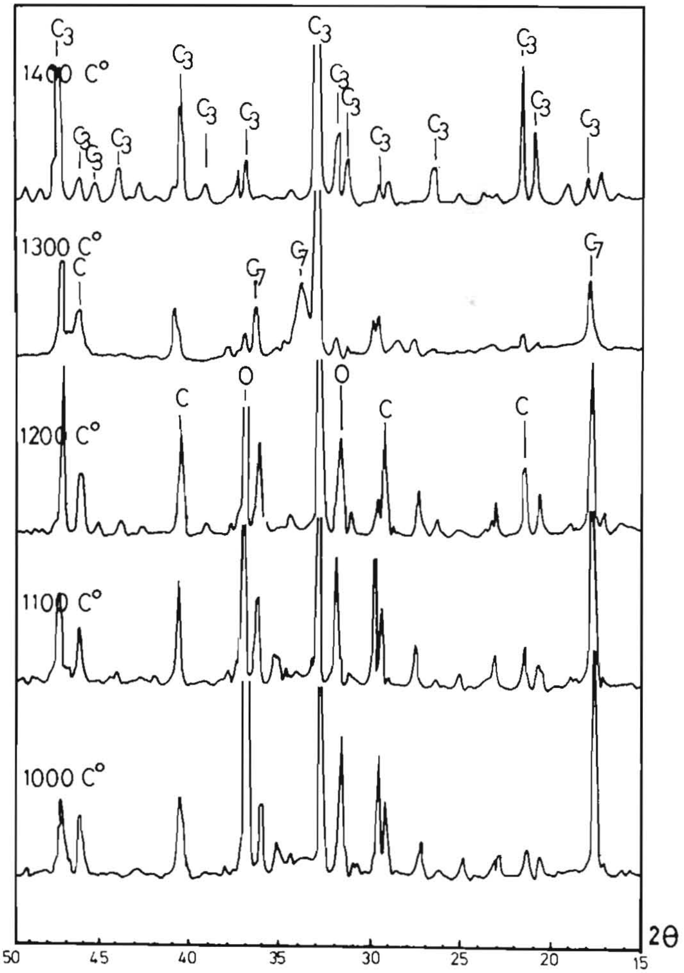

Fig. 1. x-ray diffraction patterns of ignited stoichiometric composition of C_3A with 0.0 mole SiO_2.

disappearance of $\beta-C_2S$. It seems that the presence of 0.5 mole SiO_2 prevents the formation of tricalcium aluminate and that SiO_2 reacts with CaO and Al_2O_3 at higher temperature, forming calcium aluminosilicate.

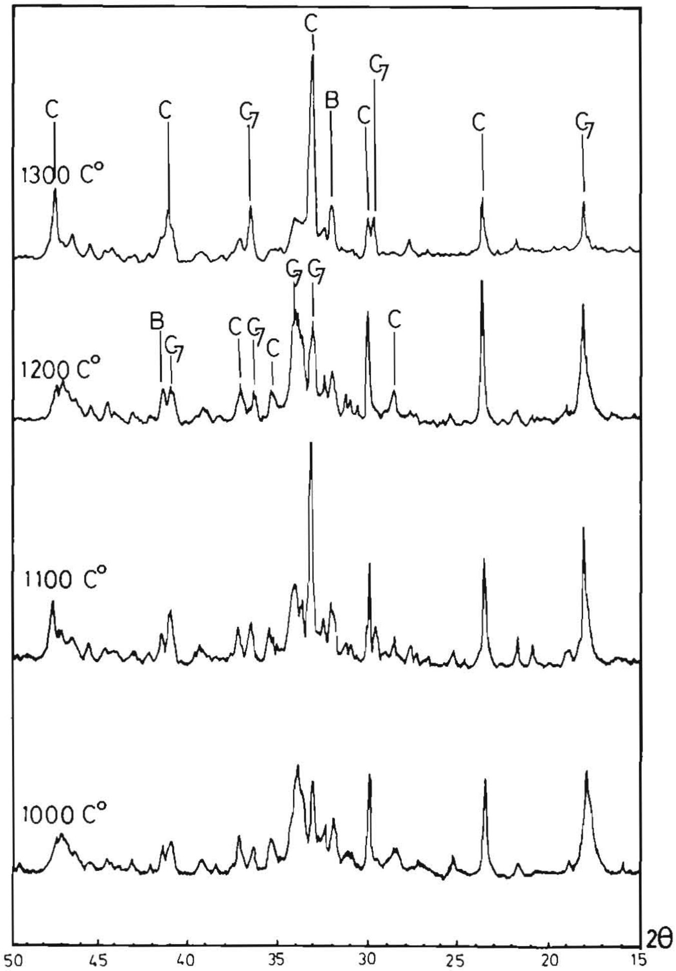

Fig. 2. x-ray diffraction patterns of ignited stoichiometric composition of C_3A with 0.5 mole SiO_2.

Figure 3 shows the x-ray diffraction patterns of the stoichiometric composition of C_3A with one mole SiO_2. The increase of SiO_2 tends to promote the formation of gehlenite (C_2AS) with $C_{12}A_7$, CA and $\beta-C_2S$ at 1000°C. As the firing temperature increases (1200°C) the pattern of gehlenite enhances with $C_{12}A_7$ and $\beta-C_2S$. The sample fired at 1300°C shows the presence of gehlenite and $\beta-C_2S$ with the disappearance of $C_{12}A_7$. No C_3A was detected.

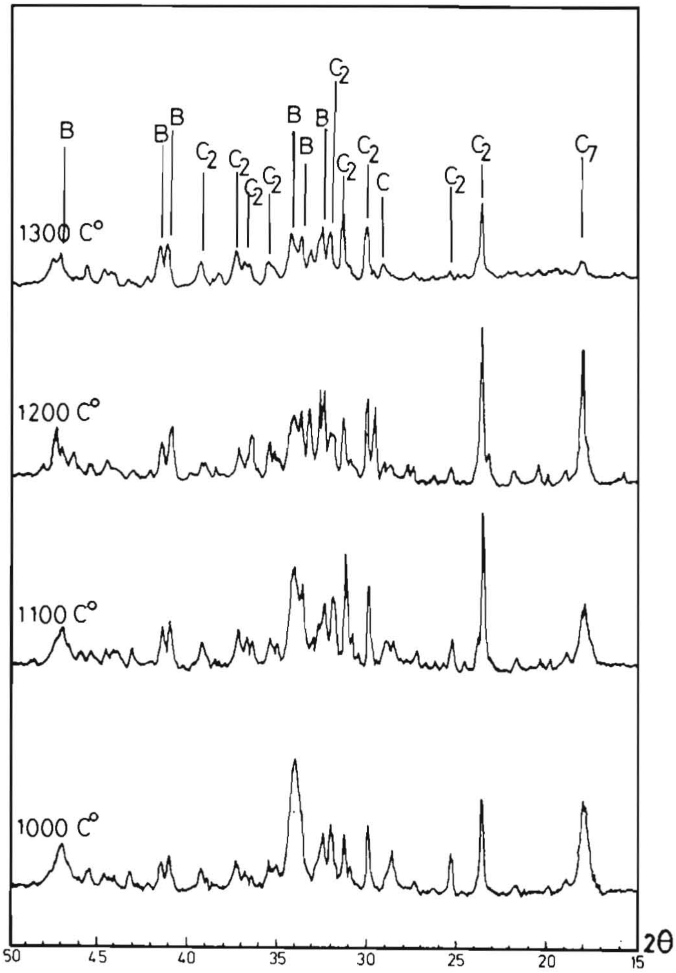

Fig. 3. x-ray diffraction patterns of ignited stoichiometric composition of C_3A with 1.0 mole SiO_2.

Figure 4 shows the x-ray diffraction pattern of the stoichiometric composition of C_3A with 1.5 mole SiO_2 fired at different temperatures. The sample fired at 1000°C shows $C_{12}A_7$ and C_2AS as the main constituents with $\beta-C_2S$ and traces of free CaO. At 1100°C, the gehlenite (C_2AS) increases with the decrease of $C_{12}A_7$. $\beta-C_2S$ exists too. As the firing temperature increases (1200°−1300°C) the gehlenite increases with the disappearance of $C_{12}A_7$. The sample fired at 1300°C shows C_2AS as the main phase with $\beta-C_2S$ and a very small amount of $C_{12}A_7$. It is clear that mixes with 1.0 as well as 1.5 mole SiO_2 show the same phases such as C_2AS, $\beta-C_2S$ and $C_{12}A_7$ and no pattern of C_3A is detected. It is found that calcium aluminosilicate is formed before the calcium aluminate.

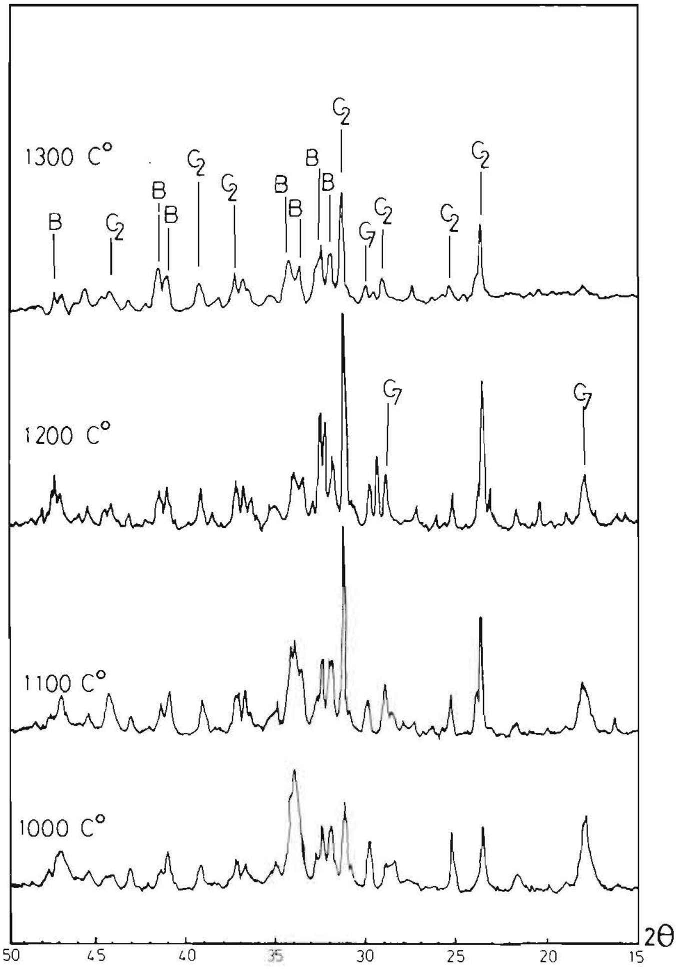

Fig. 4. x-ray diffraction patterns of ignited stoichiometric composition of C_3A with 1.5 mole SiO_2.

The kinetics of reaction were followed by the determination of free CaO in the ignited samples. Figure 5 illustrates the free CaO content of the different mixes as a function of firing temperatures. It was found that the stoichiometric composition of tricalcium aluminate gives free CaO up to 1300°C. These values decrease with firing temperature and amounts to 12 percent of free CaO. It is completely consumed after three hours of firing at 1400°C. By adding SiO_2 to the stoichiometric composition of C_3A, the free CaO is consumed at lower firing temperatures than for the pure mixture. As the SiO_2 content increases, the free CaO disappears at lower temperatures, *i.e.*, 0.5, 1.0 and 1.5 mole SiO_2 show no free CaO at 1250°, 1200° and 1180°C for two hours of firing respectively.

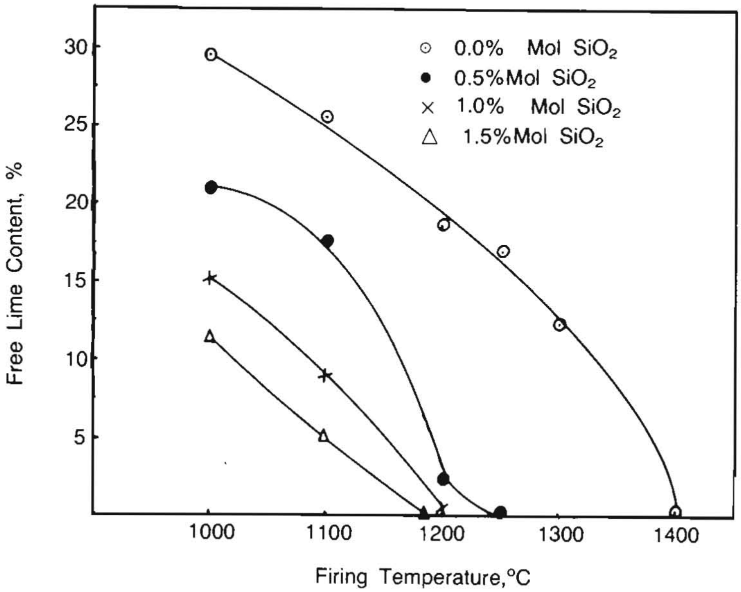

Fig. 5. Free CaO Content of Different Mixes as a Function of Firing Temperature.

Conclusion

It was found that tricalcium aluminate is formed by firing a stoichiometric composition at 1400°C for 3 hours. Addition of 0.5 mole SiO_2 tends to form monocalcium aluminate CA as well as $C_{12}A_7$ with $\beta-C_2S$. Mixes with 1.0 and 1.5

mole SiO_2 show the main phases of gehlenite (C_2AS) with $\beta-C_2S$ and no pattern of C_3A is detected. The kinetics of reaction were followed by the determination of free CaO in the ignited samples. It was also found that the mix with no SiO_2 gives 12.0 percent CaO at 1300°C and the latter is consumed at 1400°C. As the SiO_2 content increases, the free CaO disappears at lower temperatures, *i.e.,* 0.5, 1.0 and 1.5 mole SiO_2 show no free CaO at 1250°, 1200° and 1180°C respectively.

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(Received 30/05/1984;
in revised form 03/08/1985)

Symbols used in x-ray diffraction patterns are :

Ca = C
$C_{12}A_7$ = C_7
C_3A = C_3
C_2AS = C_2
$\beta-C_2S$ = B
CaO = O

تأثير ثاني أكسيد السليكون على تكوين ألومينات ثلاثي الكالسيوم

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يهدف هذا البحث لدراسة تأثير أكسيد السليكون على تكوين ألومينات ثلاثي الكالسيوم الذي يعتبر أحد مكونات الإسمنت الأساسية وذلك عند الحرق حتى ١٤٠٠° م. حضرّت أربعة مخاليط تحتوي على نسب مختلفة من ثاني أكسيد السليكون وهي صفر، ٠,٥ ، ١، ١,٥ جزىء سليكا مع الوزن الجزيئي لهذا المركب. درست المركبات التي تكونت بعد الحرق في كل مخلوط عند درجات الحرارة المختلفة من ١٠٠٠° حتى ١٤٠٠°م وذلك بواسطة جهاز الأشعة السينية والتحليل الكيميائي.

أثبتت النتائج أن وجود السليكا يعمل على عدم تكوين ألومينات ثلاثي الكالسيوم وتكوين مركبات من ألومينات سليكات الكالسيوم مثل الجلينيت. تتكون ألومينات ثلاثي الكالسيوم بعد حرق مخلوط من الحجر الجيري والألومينا عند ١٤٠٠°م لمدة ثلاث ساعات.

وجد أن نسبة الجير الحيّ تقل بزيادة ثاني أكسيد

* معهد أبحاث البناء . . الدقي ـ القاهرة ـ مصر .

السليكون نظراً لأن تفاعل السليكا مع الجير أسرع من الألومينا وذلك لتكوين مركبات السليكا والألومينا. المركبات التي وجدت في هذا النظام هي الجلينيت ـ سليكات ثنائي الكالسيوم ـ أحادي ألومينات الكالسيوم ـ سابع ألومينات الكالسيوم.