Solid Solution Mechanism of CO_2O_3 During C_3S Formation

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Abstract: Polymorphism of tricalcium silicate were prepared by a calcination method with $Ca(OH)_2$ and SiO_2 as crude materials and Co_2O_3 as doping agent. The solid solution mechanism of Co_2O_3 during C_3S formation were studied by means of chemical analysis, XRD and phase diagram analysis. The results show: according to phase analyse of CaO-CoO and $CoO-SiO_2$, Co_2O_3 accelerated solid reaction of $CaO-SiO_2$. When Co_2O_3 additive was less than 1.5% in mass, the content of f-CaO increased with the increase of Co_2O_3, and the formation rate of C_3S was accelerated by Co_2O_3; when Co_2O_3 addition exceeded 1.5%, the content of f-CaO decreased with the increase of Co_2O_3. By the least square method and defined f-CaO, the molecular formula that Co_2O_3 solidified in C_3S could be deduced: $(Ca_{3-0.86x} Co_{0.86x}) (Si_{1-0.14x}Co_{0.14x}) O_5$ (x=0.0209).

Keywords: C_3S, crystal form, phase diagram, solid solution.

INTRODUCTION

The main components of Portland cement are CaO, SiO_2, Al_2O_3, and Fe_2O_3, and they are responsible for the composition of the main mineral phases, such as alite, belite, aluminate and ferrite phase. Minor components such as MgO, SO_3, and alkalis also have an influence on the clinker formation during the burning process, as well as on the hydration process of the cement. Meanwhile, cement also contains heavy metals in the form of trace elements from the natural sources of the raw materials. Volatile components, such as the compounds of Cu, Pb, and P, can evaporate during the burning process and precipitate in the cooler parts of the kiln. They can be found in the kiln dust. Less volatile compounds are incorporated in the clinker phases during the burning process [1]. Normally, these trace elements have no influence on the burning or hydration process because of very low concentration. However, with more frequent use of alternative fuels and secondary raw materials, their concentration can possibly rise within the typical range of the clinker and its products [2, 3].

In order to estimate the influence of these ions on the formation of clinker and the hydration of cements, tests were done with pure phase composed of raw meals mixed with different concentrations of ions. To show the effects, the amount of added ion oxide was in concentrations two or three dimensions higher than usual in practice.

EXPERIMENTS

(1) Raw Materials

For the experiments the type of crude material with one composition was chosen: one mineral in ordinary Portland

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cement (PC). The sample was taken from the chemically pure agent. To prepare tricalcium silicate with higher concentrations of oxide, Co_2O_3 was added to the crude material to give an ion oxide concentration of approximately 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 wt.% respectively.

(2) Sample Preparation and Methods of Investigation

The oxides were intensively mixed with 200g of crude material and then the cylinders were made (diameter>20mm, height>40mm) to give a regular burnability of the tricalcium silicate. The tricalcium silicate was burned in a platinum crucible in an electrically heated furnace. All samples were thermally treated up to 1550°C (rate:10°C/min and kept for 2h, 4h, 6h and 8h respectively at 1550°C) in an electric furnace and cooled rapidly in air. After burning, the samples were taken out at 1400°C or 600°C and then cooled quickly in air.

Samples were performed in a batch oscillating laboratory mill at equal times and conditions and then analyzed for the content of free lime by Franke's method [4]. These samples were also analyzed by means of X-ray powder diffraction (XRD) and DTA-TG.

Table 1. Content of Co_2O_3 in C_3S

Sample	B	O1	O2	O3	O4	O5	O6
$\omega(Co_2O_3)/\%$	0	0.5	1.0	1.5	2.0	3.0	4.0

RESULTS AND DISCUSSION

(1) The Content of Free Lime

According to Franke's method, the free lime in C_3S was analyzed [5]. In order to judge which ion oxide was incorporated into the C_3S, the concentration of ion oxide in the tricalcium silicate and the change content of free lime during burning were given in Fig. (**1**). The results showed

a. splat cooling

b. furnace cooling

Fig. (1). Effect of doped Co_2O_3 on f-CaO content in C_3S samples.

that a clear mechanism on firstsight, an enlargement tendency and a following decreasing tendency could be seen; they all intersected at the addition of 1.5wt. %.

With the addition of Co_2O_3 up to a concentration of 0.5 wt. %, the content of CaO increased. With more Co_2O_3 addition, the free lime rose sharply. When the addition of Co_2O_3 rose to 1.5wt.%, the free lime reached a peak point. Then with more adding Co_2O_3, the free lime reduced gradually. Some colleagues [6, 7] came to the same results, some ions like Co^{3+}, Cr^{3+}, Cu^{2+} and Sn^{4+} etc could generate liquid phase to form C_3S, and it also showed that a litter content of Co_2O_3 led to a generation of liquid phase that could accelerate to form C_3S. From the observation reduction, the maximum concentration of Co_2O_3 which was incorporated into C_3S at 1550°C was 1.5wt.%, when the adding below 1.5%, during phase diagram of CaO-CoO and $CoO-SiO_2$, it showed that CoO was easier to react with SiO_2 to form Co-Si-O solid solution, so a little Co_2O_3 could make CaO to spare out, with more Co_2O_3 adding, more Co_2O_3 could reduce the eutectic point of $CaO-SiO_2-Co_2O_3$ ternary system. So when the content of Co_2O_3 satisfied the condition that the addition which can accelerate the formation of sosoloid at 1550°C, the free lime down.

By the observation of sample, both the samples with splat cooling (SSC) and the samples with furnace cooling (SFC) were exist with solid body, with some calculations, before the adding of 1.5wt.%, the rate of grade of SFC was a little bigger than the rate of grade of SSC, that was because of the difference of solidification effectiveness by two cooling ways. After 1.5wt.% additon, the tendency change of the rate of grade was revers, since the explanation could be that: the quantity of heat of SFC that come from furnace could promote the absorption of f-CaO in $CaO-SiO_2$ system.

(3) Effect of Co_2O_3 on Formation of Liquid Phase of C_3S

Differential thermal analysis-thermal gravimetry (DTA-TG) analyses of B and O (wtO₂ = 1%) samples were carried out from 20°C-1500°C, 10°C/min.

In all cases the following changes were observed. As an example, a complete description of those changes was shown

for B and O: a first endothermic peak between 380-550°C corresponding to calcium hydroxide decomposition; then the CaO reaction zone with silicates and phosphorous pentoxide as an endothermic band in the 1100-1400°C zone was observed. This band was attributed to the formation of liquid as well as to the formation and development of alite crystals. At last, an exothermal peak was observed at 1400-1440°C assigned to the formation and development of tricalcium silicate.
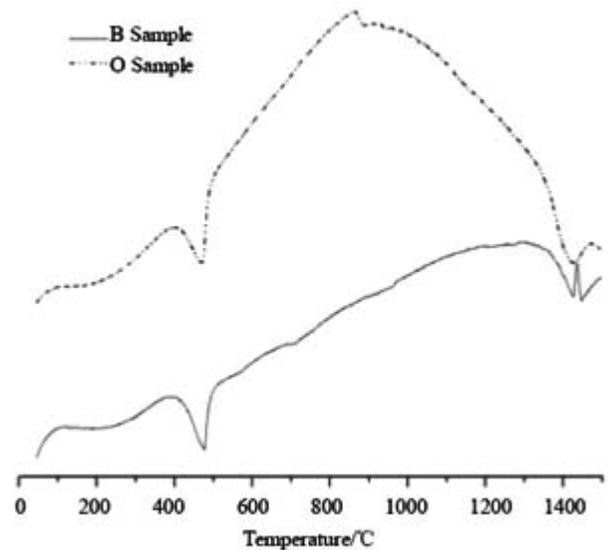
Fig. (2). DTA curves of B and O sample.

By DTA, the starting decomposition temperature of Ca (OH)₂ in samples B and O were 390.6°C and 397.6°C respectively, implying that the decomposition tempera- ture of calcium hydroxide was a little changed by Co_2O_3 addition. In contrast, the formation of the alite and the liquid phase was strongly affected by the presence of Co_2O_3. The starting formation temperatures of liquid phase and Belite in samples B and O were 1300.6°C and 864.6°C respectively, the starting point of temperature was greatly changed by Co_2O_3 addition. The ending formation temperatures of liquid phase

and Belite in samples B and O were about 1424.6°C and 1428.6°C respectively, So the main endothermic peak at 1424.6°C shifted towards a lower temperature by 4°C. These discrepancies were caused by the different reactivity of crude material. It proved that Co_2O_3 as flux could lower the formation temperature of liquid phase, increased quantity of liquid phase, and furthermore promoted the formation of tricalcium silicate mineral. In less reactive materials, the main formation of belite was assumed to take place in one step. The higher reactivity of the samples containing Co_2O_3 in these temperatures, has been confirmed by the determination of the content of $3CaO·SiO_2$.

During the research of the chemical properties of Co_2O_3 at high temperature, there was a deoxidate reaction of Co_2O_3 at 895°C as equation (1).

$$Co_2O_3 \rightarrow CoO + 1/2\ O_2 (895°C) \qquad (1)$$

Therefore, CoO was researched to explain the effect mechanics of Co_2O_3 in CaO-SiO₂ system. According to the phase diagram of CaO-CoO [4] and CoO-SiO₂ [8], CoO was easier to react with SiO_2 to form Co-Si-O solid solution.

According to the proportion of ingredients (assuming Co_2O_3 content is 1.0%): wtCaO = 72.95%, wtSiO2 = 26.05%, wtCoO = 0.99%. In binary reaction system of CaO-CoO: wtCaO: wtCoO = 98.65:1.35; In binary reaction system of SiO2-CoO: wtSiO2: wtCoO = 96.3:3.7.

In binary system of CaO-CoO, solid solution and liquid phase convert at about 2174 °C and in binary system of SiO₂-CoO, solid solution and liquid phase convert at about 1384 °C. Transition temperature of conversion of C₃S and liquid in binary phase diagram of CaO-SiO₂ is 2150 °C, but SiO₂-CoO solid-liquid transition temperature point is only 1384 °C. So there is a conclusion that Co_2O_3 is advantage for formation of liquid in CaO-SiO₂ binary system.

(4) Crystallographic Examination of C₃S

The effect of the Co_2O_3 on the mineralogical state of the C₃S concerned mainly the phases which were crystallized from the melt.

As it can be seen in Figs. (**3**, **4**), the main peaks of tricalcium silicate mineral were at d=0.278, 0.303nm, and secondary peaks of tricalcium silicate mineral were at d=0.219nm. And secondary peaks of tricalcium silicate mineral at d=0.274, 0.261, 0.176nm were coincidence with secondary peaks of dicalcium silicate, so there were some difficulties to appreciate by these coincidence peaks, but it also could be judged data by analyzing the main peaks of tricalcium silicate. Comparing the intensity of diffraction main peaks of tricalcium silicate mineral (d=0.278, 0.303nm), the content of $3CaO·SiO_2$ formed in all samples O were all more than that of the sample B. The experimental results indicated that Co_2O_3 could promote the formation of $3CaO·SiO_2$ mineral. When the addition of Co_2O_3 was below 2.0%, a slowly increase of C₃S content followed by an increase of the Co_2O_3 content. When the addition of Co_2O_3 was greater than 2.0%, the content of $3CaO·SiO_2$ mineral were increased apparently. This may be attributed that addition of Co_2O_3 can lower the formation temperature of the liquid phase.

Comparing the intensity of XRD peaks of SSC and SFC, it could be seen that the intensity of diffraction peaks (d= 0.303, 0.278, 0.274, 0.261, 0.219, 0.176nm) of the Ca_3SiO_5 phase in SSC were higher. It showed that different cooling ways could influence the formation of Ca_3SiO_5, and Ca_3SiO_5 will decompose partly below at 1250°C, so the tricalcium silicate mineral peaks of SSC were higher than those of SFC.

(5) Solidifying Form of Co₂O₃ in C₃S

In conditional C₃S crystal structure [9, 10], $r_{Ca}^{2+}/r_O^{2-} = 99/132 = 0.75$, Ca united with O to form $[CaO_6]$ octahedron; $r_{Si}^{4+}/r_O^{2-} = 41/132 = 0.31$, Si united with O to form $[SiO_4]$ tetrahedron. $r_{Co}^{2+}/r_O^{2-} = 74/132 = 0.56$, $r_{Co}^{3+}/r_O^{2-} = 65/132 = 0.49$, aaccording to Pauling first rule, coordination number of Co ion is 6, and the formation of Co-O is $[CoO_6]$ octahedral. In a coordination structure, the shared edge, especially in the presence of shared surface will reduce the stability of this structure, according to the third rule of Pauling, with the same kind of coordination, roof effect of octahedral of Ca^{2+} is bigger than Co^{3+} because the charge number of Co^{3+} is higher than Ca^{2+}. In addition, coordination number of Co^{2+} is 4, according to Pauling fourth rule, Co^{2+} relative to Ca^{2+}, the same valence but low coordination number of Co^{2+} to form $[CoO_6]$ coplanar octahedral edge effects are increased.
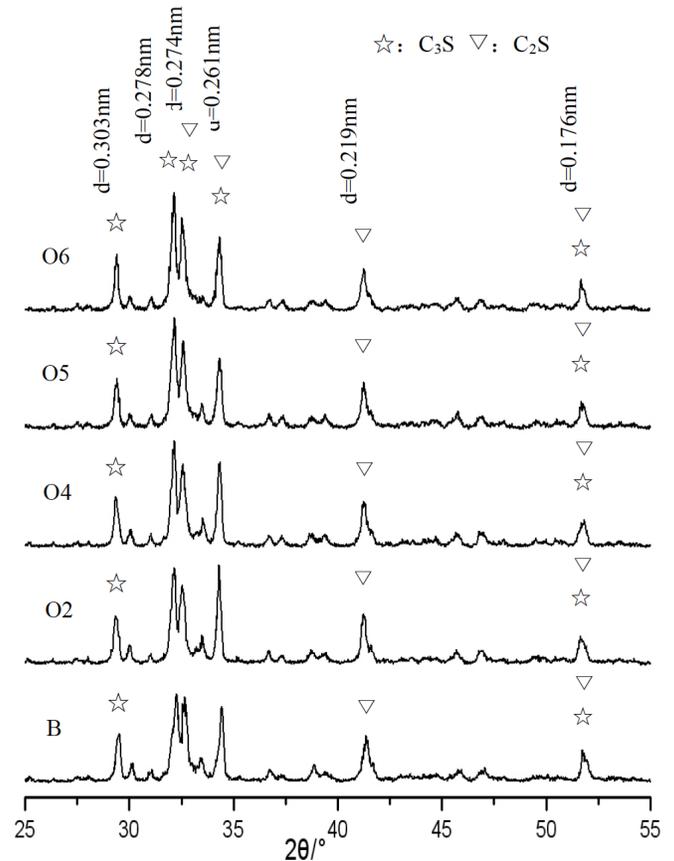
Fig. (3). XRD of C₃S samples through down quenching.

When the orbits of d^0, d^3, d^8, d^{10} and d^5 high spin and d6 low spin which are occupied by electrons are superimposed together, the d-shell electron cloud distribution is symmetric in space. So, they are octahedral position is stable, but spatial

distribution of electron cloud of d4 and d9 ion of d shell is asymmetry. In this way, it leads to further split the d orbital and distortion from symmetrical position. So, the ions are stable [11]. Transition metal ions in the environment will be distorted. After distortion, a more stable electron configuration has been formed because the orbits are occupied to reduce the energy. As shown in Table **2**, stability energy of Co^{2+}, Ca^{2+} in octahedral and tetrahedral crystal is 0, octahedral select potential OSPE is 0. With the third rule of Pauling, the results show Co^{2+} and O^{2-} in the form of coplanar and edges were formed $[CoO_6]$ deformed octahedron. The foregoing analysis shows, Co^{2+} replaced Ca^{2+} solution, the crystal structure of C_3S easily lead to the distortion in the octahedron and octahedron shared edges of surface probability was increased.
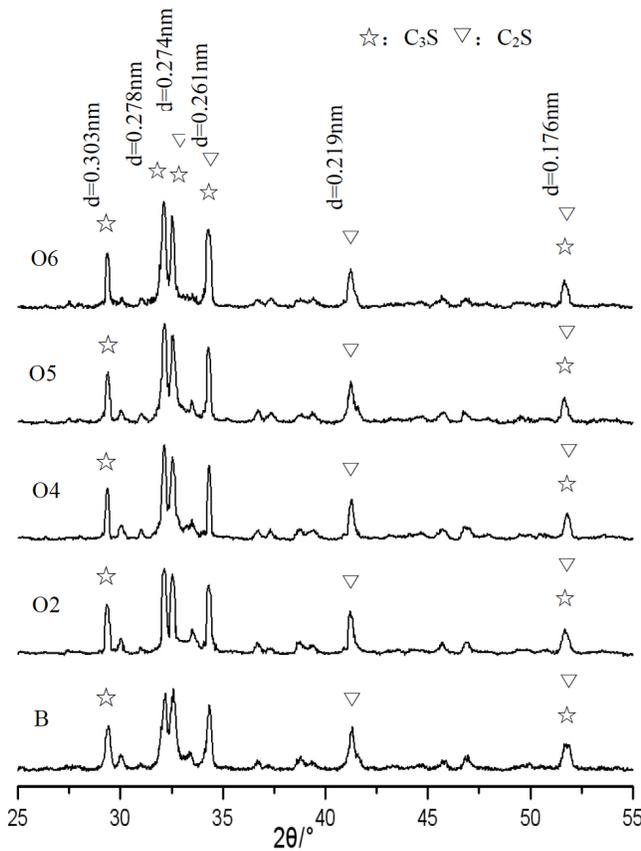
Fig. (4). XRD of C_3S samples through furnace quenching.

(6) Solidifying Equation of Co_2O_3 in C_3S

Samples which had been sintered for 8 h were continued to sintered in an electrically heated furnace at 1550°C, and taken out at 1450°C and then were cooled quickly in air.

Samples were sintered repeatedly to assure that content of f-CaO was invariable. Apply least-squares procedure to statistic the numeric values which can be seen in Table **3**. The essence of least-squares procedure was to define one aligning expressed by equation y=bx+a, it would be maked it better to reflect the variation of data, the data should be satisfied the formula to be minimality.

$$\sum_{i=1}^{n}[y_i - (bx_i + a)]^2 = \min \quad (2)$$

When $b = \dfrac{n\sum_{i=1}^{n}x_iy_i - \sum_{i=1}^{n}x_i\sum_{i=1}^{n}y_i}{n\sum_{i=1}^{n}x_i^2 - (\sum_{i=1}^{n}x_i)^2}$, $a = \bar{y} - b\,\bar{x}$, equation above

set up, so y=bx+a was called equation of linear regression.

Table 3.   The Content of CaO in C₃S

Sample (x_i)	B (x_1)	O1 (x_2)	O2 (x_3)	O3 (x_4)
ω(f-CaO/% (y_i))	0.65	0.70	0.95	1.22

According to Table **3** , substitute numeric value of f-CaO into valuation of x_i and y_i, during some calculation, the results could be getting: b= 0.392, a=0.586. That was to say that numerical data can format one straight-line and the slope coefficient is 0.392. It could be explained that if introduce one gramme Co_2O_3, it will separate out 0.392g CaO, that was also to say that one mol Co_2O_3 can make 0.86 mol CaO separate out. According to the correlation studies about Co_2O_3 doped in C_3S, the solidifying equation of Co_2O_3 in C_3S was seen as followed.

$(Ca_{3-0.86x}Co_{0.86x})(Si_{1-0.14x}Co_{0.}14x)O_5$ (x-solidsolubility)
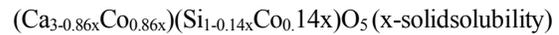
According to the analysis of f-CaO and XRD, when the addition of Co_2O_3 up to 1.5%, it could reach the ultimate solid solution, when the addition was greater than this amount, the sample began to produce melt phase. At this moment, Co_2O_3 was not inserted in C_3S with a solid solution mode [11], but it could response with CaO and SiO_2 to form ternary eutectic system, so it was necessary to definite the ultimate solid solution exactly. Batching crude material at a 1.5% addition, keep at 1550°C for 2h, taken out at 1450°C and assayed the content of f-CaO. Specific parameter could be seen in Table **3**.

Through analysis on Table **4**, the curve of f-CaO has appeared a break, transfer into mole percentage composition that was proportion to $CaO-SiO_2$ system. So the molecular formula of Co_2O_3 solid solution was shown as followed.

$(Ca_{3-0.86x}Co_{0.86x})(Si_{1-0.}14xCo_{0.14x})O_5$ (x=0.0209)
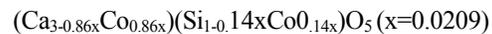
Table 2.   The Stabilizing Power of Transition Ion in Octahedral Coordination

Electronic Configuration	Ion	Stability Energy		
		Elongated Octahedral	**Compressed Octahedral**	**Most Stable Form of Coordination Polyhedron**
$3s^23p^6$	Ca^{2+}	0	0	octahedral
$3s^23p^63d^4$	Co^{3+}	$12/5\Delta_0$	$12/5\Delta_0$	octahedral
$3s^23p^63d^5$	Co^{2+}	$4/5\Delta_0 + 2/3\delta$	$4/5\Delta_0 + 1/3\delta$	elongated octahedral

Table 4.   **Content of CaO in C$_3$S**

$\omega(Co_2O_3)/\%$	1.2	1.3	1.4	1.5	1.6	1.7	1.8
$\omega(f\text{-}CaO)/\%$	3.17	3.29	3.45	3.51	3.25	2.98	2.65

CONCLUSIONS

1. According to the characteristic of Co$_2$O$_3$ which could increase liquid phase, the free lime firstly rose with Co$_2$O$_3$ added, and then decreased if the addition of Co$_2$O$_3$ exceeded 1.5%. Combining with XRD analysis, the adding of the solid solution saturation ratio is about 1.5%. Below this ratio, tricalcium silicate mineral rose slowly with the increase adding, and above this ratio, tricalcium silicate mineral rose apparently with the increase adding.

2. According to crystallochemical theory and Hume-Rothery experimental regulation, Solidifying equation of Co$_2$O$_3$ can be deduced, with least-squares procedure and definiting the ultimate solid solution exactly, the solidifying equation could be derived:
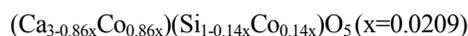
$$(Ca_{3-0.86x}Co_{0.86x})(Si_{1-0.14x}Co_{0.14x})O_5 \ (x=0.0209)$$

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