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Short Communication

Influence of CuO on the formation and coexistence of $3CaO \cdot SiO_2$ and $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ minerals

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Abstract

The influence of CuO on the formation and coexistence of $3CaO \cdot SiO_2$ and $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ minerals in Portland cement containing $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ mineral is reported in this paper. The results show that a suitable amount of CuO can lower the clinkering temperature and improve the burn-ability of clinkers. It can also promote the formation of $3CaO \cdot SiO_2$ and $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ minerals and facilitate the coexistence of the two minerals in the clinkers. But adding 1% CuO to the raw material can cause the decomposition of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$.

Keywords: CuO; $3CaO \cdot SiO_2$; $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$; Coexistence

1. Introduction

The main minerals in Portland cement containing $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ are $3CaO \cdot SiO_2$, $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and $2CaO \cdot SiO_2$. The cement manufactured is characterized by rapid hydration, high early strength, small volume shrinkage during hydration and corrosion resistance. But the key problem in the production of the cement containing $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ is how to make the two minerals ($3CaO \cdot SiO_2$ and $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$) coexist in the clinker. Many investigations on this issue have been reported [1–7] since 1978. Researchers [8,9] considered that adding CuO to the raw material can lower the formation temperature of liquid and $3CaO \cdot SiO_2$ mineral, and increase the content of $3CaO \cdot SiO_2$ to as much as 70% of the total amount of clinker. However, for Portland cement containing $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$, little research has investigated the influence of CuO on the mineral formation of the clinker. In the present work, the influence of CuO on the mineral formation and coexistence of $3CaO \cdot SiO_2$ and $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ in the clinker has been investigated by adding different contents of CuO to the raw material.

2. Experimental

The limestone, gypsum, clay, fly-ash and pure chemicals such as CaF_2 and CuO were used as starting materials. The composition of raw materials is shown in Table 1.

The starting materials were ground in a laboratory ball mill respectively to obtain fineness of 6%–8% over 0.08 mm sieve. The raw mixture was prepared by mixing the starting materials according to present proportions (the contents of SO_3 and Al_2O_3 are about 2.0% and 3.5–3.8% respectively and the lime saturation ratio is 0.96). The chemical composition of raw meal is shown in Table 2, and the amount of CuO added to the samples is shown in Table 3.

The raw mixtures were mixed with 8% water and pressed with pressure of 13 MPa into discs using a mould with the size of 25 mm in diameter and 40 mm in thickness. The discs were

Table 1
Chemical composition of raw materials (wt.%)

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	Loss
Limestone	1.88	0.46	0.30	54.14		41.45
Clay	65.75	14.47	5.49	0.61		7.87
Gypsum	2.86	0.62	0.12	30.77	41.19	16.5
Fly ash	51.06	30.54	3.49	2.98		1.70

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Table 2
Chemical composition of raw meal (wt.%)

No.	CaO	Fe_2O_3	Al_2O_3	SO_3	SiO_2	Loss
D	43.35	1.16	3.71	2.16	13.70	34.41

dried in an oven, and burned in a Nabertherm resistance furnace at different temperatures (1300 °C, 1350 °C, 1400 °C) for 30 min, then removed from the furnace at once and cooled rapidly by fan. The discs without CuO and those with 1.0% CuO were burned in the same furnace at different temperatures from 1150 °C to 1300 °C for 30 min, then removed from the furnace at once and cooled rapidly by fan.

In order to investigate clinker formation at different temperatures, the content of free lime in the clinkers was determined chemically after dissolving the clinker with ethanol-glycerin. The mineral compositions of the clinkers burned at different temperatures were analyzed by XRD (Cu,Ka, $\lambda=0.154$ nm). The contents of $3CaO·3Al_2O_3·CaSO_4$ and $3CaO·SiO_2$ were determined by chemical analysis and XRD respectively.

3. Results and discussion

3.1. The burn-ability of the clinker

The free lime contents of clinkers burned at different temperatures are shown in Fig. 1. It can be seen that the free lime contents of clinkers with CuO are lower than that without CuO. This shows that minor amount of CuO can enhance the absorption of free lime, improve the burn-ability of Portland Cement containing $3CaO·3Al_2O_3·CaSO_4$ obviously and accelerate the mineral formation in the clinker.

3.2. Thermal analysis

The DTA curves of raw mixes without CuO (D_0) and with 1% CuO (D_{C4}) are given in Fig. 2. The expected endothermic effect between 600 °C and 800 °C is attributed to the decomposition of $CaCO_3$. The endothermic reaction at about 1250 °C is ascribed to the formation of liquid as well as to the formation and development of alite crystals. By DTA, the starting decomposition temperature of $CaCO_3$ in samples D_0 and D_{C4} are 719 °C and 726 °C respectively, implying that the decomposition temperature of limestone is not changed by CuO addition. This conclusion is in agreement with Kakali et al. [8]. In contrast, the formation of the alite and the liquid phase is strongly affected by the presence of CuO. The formation temperatures of liquid phase and alite in samples D_0 and D_{C4} are about 1274 °C and 1241 °C, respectively. So the main endothermic peak at about 1250 °C shifts towards a lower temperature by 33 °C. It proves that CuO as flux can lower the formation temperature of liquid phase, increase quantity of liquid phase, and furthermore promote the formation of $3CaO·SiO_2$ mineral. The burn-ability of the raw material can also be improved.

Table 3
CuO content in the samples (wt.%)

Sample no.	D_0	D_{C1}	D_{C2}	D_{C3}	D_{C4}
CuO	0	0.1	0.3	0.5	1.0

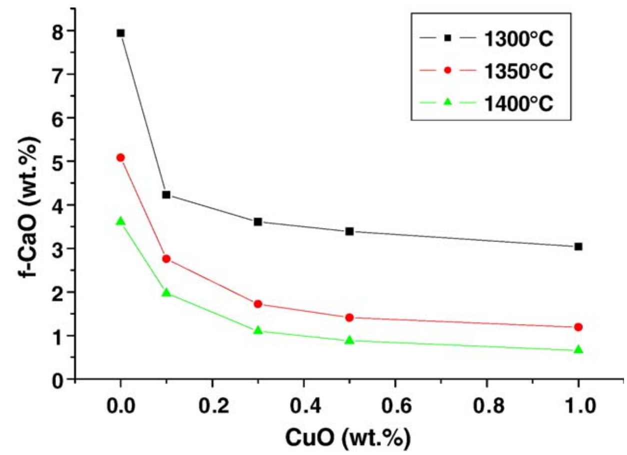

Fig. 1. The effect of amount of CuO on free lime content in clinker.

3.3. Effect of CuO on the minerals formation

3.3.1. Effect of CuO on the formation of $3CaO·SiO_2$

The XRD patterns of the clinkers burned at different temperatures from 1150 °C to 1300 °C are shown in Fig. 3. From Fig. 3, by comparing the intensity of diffraction peaks of $3CaO·SiO_2$ mineral ($d=0.303$ nm), the content of $3CaO·SiO_2$ formed in the samples with CuO is more than that of the sample without CuO. It is also shown that $4CaO·Al_2O_3·Fe_2O_3$ mineral is present for sample D_{C4} burned at 1150 °C which can be dissolved to liquid phase during burning, and the formation of $3CaO·SiO_2$ can be speeded up. The results indicate that CuO can promote the formation of $3CaO·SiO_2$ mineral. Researches [10–12] have demonstrated that SO_3, Fe_2O_3, ZnO and so on can favor the coexistence of $3CaO·SiO_2$ and $3CaO·3Al_2O_3·CaSO_4$. The present work shows that CuO can also favor the coexistence of two minerals.

The contents of $3CaO·SiO_2$ in clinkers burned at 1300 °C were determined by XRD. The results are shown in Table 4. From Table 4, it can be seen that in comparison with the sample D_0, addition of CuO can increase the content of $3CaO·SiO_2$ in clinkers. This may be attributed that addition of CuO can lower

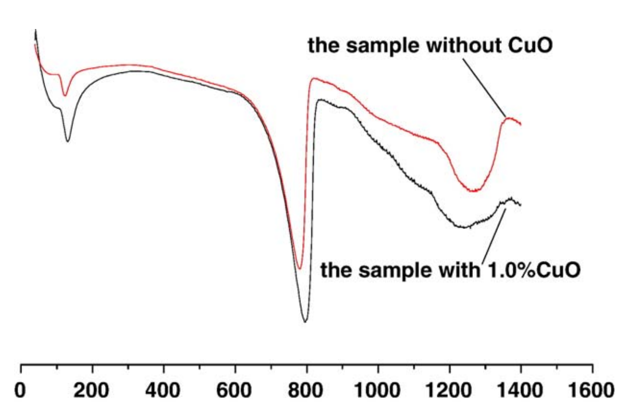

Fig. 2. The DTA curves of samples without CuO and that with 1.0% CuO.

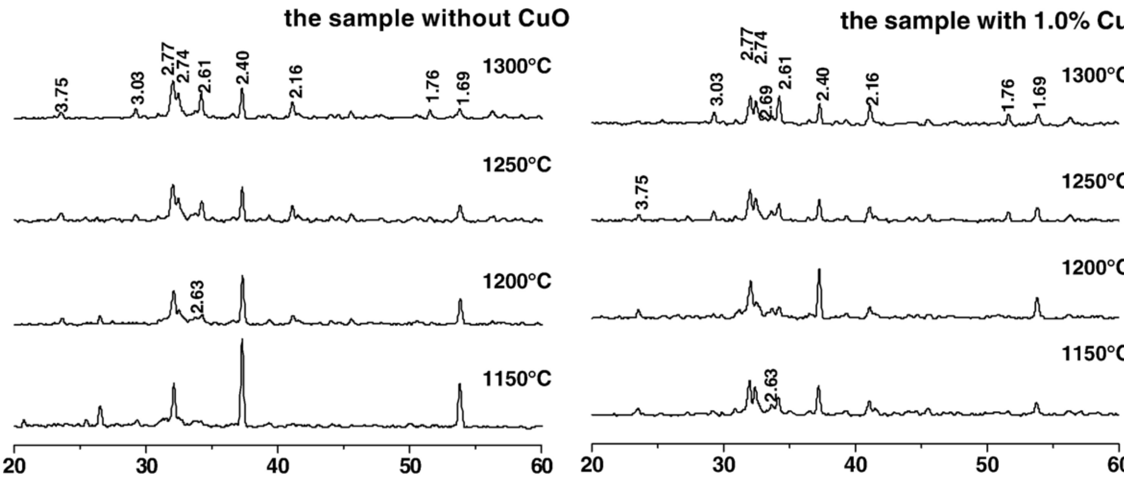

Fig. 3. The XRD of sample without CuO and with 1.0% CuO.

the formation temperature of the liquid phase. With the increase of CuO addition from 0.3% to 1.0%, the content of $3CaO·SiO_2$ mineral increases. This shows that CuO can promote the formation of $3CaO·SiO_2$, and help improve the coexistence of $3CaO·3Al_2O_3·CaSO_4$ and $3CaO·SiO_2$.

3.3.2. Effect of CuO on the formation of $3CaO·3Al_2O_3·CaSO_4$

From XRD analysis (Fig. 3), it can be seen that for sample D_0 burned at 1150 °C, the XRD diffraction peak of $3CaO·3Al_2O_3·CaSO_4$ (d=0.375 nm) is not present. However for sample D_{C4} with 1.0% CuO burned at 1150 °C the XRD diffraction peak of $3CaO·3Al_2O_3·CaSO_4$ is found. Hence, CuO can lower the formation temperature of $3CaO·3Al_2O_3·CaSO_4$ by about 50 °C. For sample D_0 burned at 1300 °C, there is $3CaO·3Al_2O_3·CaSO_4$ mineral in the clinker, while $3CaO·3Al_2O_3·CaSO_4$ mineral is not seen for sample D_{C4} and the diffraction peak of $3CaO·Al_2O_3$ (d=0.269 nm) can be seen at this temperature. It shows that addition of CuO may decrease the decomposition temperature of $3CaO·3Al_2O_3·CaSO_4$ by about 50 °C. This may be ascribed to the fact that $3CaO·3Al_2O_3·CaSO_4$ mineral decomposes to $CaO·Al_2O_3$, and $3CaO·Al_2O_3$ is produced by the reaction of $CaO·Al_2O_3$ with CaO, as expressed by Eq. (1). Excessive amount of CuO does not facilitate the coexistence of $3CaO·3Al_2O_3·CaSO_4$ and $3CaO·SiO_2$.

$$3CaO \cdot 3Al_2O_3 \cdot CaSO_4 + 6CaO \rightarrow 3Ca_3Al_2O_6 + CaSO_4 \quad (1)$$

The contents of $3CaO·3Al_2O_3·CaSO_4$ in the clinkers are also shown in Table 4. From Table 4, it is shown that when the addition of CuO is lower than 0.1%, the amount of $3CaO·3Al_2O_3·CaSO_4$ in the clinker is larger than that in sample D_0, indicating that a minor amount of CuO can promote the formation of $3CaO·3Al_2O_3·CaSO_4$. However, when the addition of CuO reaches 1.0%, the amount of $3CaO·3Al_2O_3·CaSO_4$ decreases remarkably. Appropriate amount of CuO favors the coexistence of $3CaO·SiO_2$ and $3CaO·3Al_2O_3·CaSO_4$.

Table 4
The contents of $3CaO·SiO_2$ and $3CaO·3Al_2O_3·CaSO_4$ in the clinker burned at 1300 °C (wt.%)

No.	D_0	D_{C1}	D_{C2}	D_{C3}	D_{C4}
$3CaO·SiO_2$ content	42.9	60.9	56.6	57.0	59.7
$3CaO·3Al_2O_3·CaSO_4$ content	6.7	7.0	5.9	4.7	0.2

4. Conclusions

1. The addition of CuO into raw material can lower the formation temperature of liquid phase, promote the absorption of f-CaO, and furthermore improve the burn-ability of raw material.
2. 1.0% CuO added to the raw material can lower not only the formation temperature but also the decomposition temperature of $3CaO·3Al_2O_3·CaSO_4$ mineral in clinkers. Appropriate amount of CuO can promote the formation of $3CaO·3Al_2O_3·CaSO_4$ and increase the content of $3CaO·3Al_2O_3·CaSO_4$ mineral.
3. Addition of 0.1% CuO into raw material can increase the content of $3CaO·3Al_2O_3·CaSO_4$ mineral as well to that of C_3S in the clinker. So minor amount of CuO can promote the coexistence of $3CaO·SiO_2$ and $3CaO·3Al_2O_3·CaSO_4$, and favor the formation of Portland cement clinker containing $3CaO·3Al_2O_3·CaSO_4$.
4. At 1300 °C, when the addition of CuO into the raw material is 0.1%, the content of $3CaO·SiO_2$ reach the peak. Increasing content of CuO (from 0.1% to 0.3%) gradually decreases the amount of $3CaO·SiO_2$ formed. But the contents of $3CaO·SiO_2$ increases when the addition of CuO exceeds 0.3%.

Acknowledgments

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