Cement and Concrete Research 40 (2010) 1681–1687

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Effect of CuO on the formation of clinker minerals and the hydration properties

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ARTICLE INFO

Article history:
Received 21 June 2010
Accepted 10 August 2010

Keywords:
CuO
C_3S
Cement clinker
Hydration

ABSTRACT

The purposes of this study are to explore the mechanisms of Cu element in clinker burning and hydration processes and to make effective use of waste containing copper in cement production. The effect of CuO on clinker mineral composition, C_3S polymorph and size, Cu element distribution and state, compressive strengths, hydration products, non-evaporable water quantity and hydration heat release rate was analyzed by XRD, SEM, DTA, isothermal heat-conduction calorimetry, etc. Results show that as the amount of CuO increases the formation and growth of C_3S grain are accelerated, R C_3S is gradually transformed into M_3 and the content of C_4AF increases; a small quantity of CuO increases the 3-day and 28-day strengths and the hydration degree of clinker, but excessive CuO has adverse effects. Those effects of CuO on clinker burning process are attributed to the formation of low-melting Cu_2O and the dissolution of CuO in C_4AF which decrease the formation temperature of liquid phase and increase its quantity. The effects on hydration process result from the combined action of the following factors: the induction period is prolonged; the hydration reactions in the initial and acceleration periods are accelerated.

1. Introduction

Cement rotary kiln provides an effective way of harmless treatment and resource utilization for some industrial waste, sludge, municipal solid waste and the soil polluted by heavy metals and many relevant research and practice are carried out [1,2]. Some waste, e.g. copper slag, copper tailings and sewage sludge, contains a certain amount of copper element which will affect on the sintering process of cement raw mix. Cu element in waste is almost incorporated in clinker [3,4] and will also influence on the hydration process. Therefore, it is necessary to study the effects of copper element on the sintering and hydration processes in order to make effective use of waste containing copper in cement production.

At the same time, doping minor elements to cement raw meal is a very important measure for improving the properties of clinker and decreasing in energy consumption in cement production and Cu element has also caused great concern. CuO is found to promote the combination of free lime, especially in the temperature range between 1000 °C and 1300 °C, and lower the clinkering temperature by at least 50 °C [5]. Even though a raw mixture (1%CuO) was prepared according to 70%alite, the clinker burnt at 1450 °C contains only 0.77% of free lime [6]. CuO also accelerates the formation and growth of alite whose crystals are almost larger and prismatic grains [7].

CuO has a great influence on the hydration of clinker. 1%CuO is found to only decrease the early strength but favors the compressive strength after 7 days [8]. 2%CuO, however, strongly delays the hydration of clinker, even at 28 days [9]. Moreover, CuO also affects on the hydration of C_3S: 0.5%CuO promotes the hydration, but more than 1%CuO have a delayed effect [6]. The delayed effect of CuO is generally attributed to the formation of $Cu(OH)_2$ which strengthens the covering layer on the surface of the silicate phase and prevents clinker particles from further hydrating [6,9,10], but no credible evidence is given. In addition, Cu^{2+} is fixed by the hydrates and does not produce an immediate environmental threat [11,12].

Although the above research has obtained the great progress, the reasons why CuO decreases the formation temperature of liquid phase, promotes the formation of C_3S and delays the hydration still need clarification. Moreover, it is very necessary for the application of waste containing copper in cement industry to further study the mechanism of CuO in the burning and hydration process.

In this paper, the effect of CuO on the formation of clinker minerals is analyzed from mineral composition, the polymorph and size of C_3S and the distribution of Cu element in clinker. The hydration properties of CuO clinker are discussed from compressive strength, hydration products, non-evaporable water quantity and heat release rate. In addition, in order to strengthen the effect of CuO and to explain better those phenomena, the amount of CuO added is increased to 3%.

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doi:10.1016/j.cemconres.2010.08.009

2. Experimental

2.1. Sample preparation

Analytical reagent grades $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3 and CuO were used in order to as far as possible eliminate the effect of other impurities. One reference mixture was prepared according to the potential mineral components $C_3S=75\%$, $C_3A=7\%$ and $C_4AF=18\%$ and six modified mixtures were prepared by mixing with the reference, respectively, with 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, and 3.0% (w/w) CuO. Then the raw mixtures were pressed with a pressure of 200 MPa into blocks of 50 mm × 50 mm × 10 mm and dried in an oven at 105 °C for 2 h and put into an electrical furnace (silicon carbide rods). The heating rate was 10 °C/min. The samples were maintained at 1400 °C for 40 min, then cooled at once in air and ground to the residue weight of a 0.08 mm sieve less than 5% with a centrifugal ball mill.

The ground clinkers were mixed with 4.74 wt.% $CaSO_4 \cdot 2H_2O$ (chemical grade). Pastes were prepared at a water-to-solid weight ratio of 0.27, cast in 20 mm × 20 mm × 20 mm molds and vibrated at the time of casting to remove air bubbles. The molded pastes were kept at 20 ± 2 °C and relative humidity exceeding 90% for 24 h, and then removed from the molds. The demolded samples were cured in water at 20 ± 2 °C for 3, 7 and 28 days.

2.2. Sample testing

2.2.1. Free lime tests

The content of free lime in clinker was estimated using glycerin-alcohol method.

2.2.2. XRD

A Rigaku International Corporation D/max 2550 VB3+/PC diffractometer (Cu K_α radiation) was used to identify mineral and hydrated phases of clinker. The measurements were carried out in the range of 10 to 80° (2θ) with a step size of 0.02° (2θ), a counting time of 4 s at each step, an accelerating voltage of 40 kV and a current of 100 mA.

2.2.3. SEM

SEM imaging using backscattered electrons requires a polished specimen for optimum performance [13]. A cut block sample was placed in a plastic mold (32 mm diameter), and then an epoxy resin mixture was pressed into the mold at a suitable vacuum pressure. The molded sample was cured at room temperature for 24 h and then demolded. Scratches of the demolded sample were removed by 600 grit and followed by 1200 grit sandpaper. Final polishing was done on a lap wheel with (9, 3 and 0.25) micrometer diamond paste for 120 s each. After polishing, the sample was cleaned using a clean polishing cloth. The final polished sample was coated with carbon to provide a conductive surface for SEM imaging. Observation of mineral morphological feature, in particular the alite phase, was carried out on a FEI Company Quanta 200 FEG-SEM with a Link EDX system in a backscatter mode. An accelerating voltage and probe current for the images were 12 kV and 3 nA, respectively. The distribution of Cu element in clinker minerals was analyzed by EDAX.

2.2.4. Compressive strength tests

Compressive strength tests were carried out after 3, 7 and 28 days of hydration. Each resultant value of compressive strength was an average calculated from six determinations.

2.2.5. DTA-TG

A Stanton Redcroft STA 780 Simultaneous Thermal Analyzer was used to conduct DTA analyses of non-evaporated water content. The samples hydrated were subjected to acetone and isopropyl ether treatment, then dried for 24 h in a vacuum and ground to a fineness less than 80 μm. The ground samples were placed in an oven at 105 °C and dried to constant weight. Then the dried samples were examined by thermal analyzer at a heating rate of 10 °C/min under flowing nitrogen (100 cm^3/min) from 30 to 1100 °C. The non-evaporable water content was calculated as the difference between the 1050 °C and 105 °C mass measurements. The difference between the mass of the samples at 105 °C and at 1050 °C, divided by the mass of the sample at 1050 °C, and corrected for the loss on ignition of the unhydrated cement gives the non-evaporable water content.

2.2.6. Hydration heat-evolution test

An isothermal heat-conduction calorimetry (TAM air C80, Thermometric, Sweden) was used to measure the hydration heat evolution of clinker. The water/clinker ratio was 0.5 and experimental temperature was 20 ± 0.1 °C. Clinkers and water were tempered for several hours before mixing, then the water was injected into the reaction vessel and the samples were stirred in the calorimeter for several minutes. This procedure allowed monitoring the heat evolution from the very beginning when water was added to clinkers. Data logging was continued for about 12.5 days.

3. Results and discussions

3.1. The effect of CuO on burning process

3.1.1. Free lime (f-CaO) in clinker

Variations in the content of f-CaO in clinker with the amount of CuO at 1400 °C are given in Fig. 1. The content of f-CaO decreases as the amount of CuO rises and this trend is more obvious in the range of CuO amount from 1.5 to 3.0%. For example for 3.0%CuO clinker the amount of f-CaO drops by 70%. The effect of CuO on the content of f-CaO in clinker is considered to be the decrease in the formation temperature of liquid phase [5,6]. Moreover, in our experiment alumina brick as the substrate of samples with CuO was found to be attacked by liquid phase and the attack was more obvious in the position where the samples with 2–3% CuO were placed. This phenomenon indicates that CuO increased the amount of liquid phase.

3.1.2. Clinker mineral

3.1.2.1. Major minerals. XRD patterns of clinkers are shown in Fig. 2. The intensity of C_3S peaks increases as the amount of CuO rises. The intensity of diffractive peak is related to not only the content, but also to the crystallinity and the size of grains. Considered the content of free lime, the variation in the content of C_3S should not be greater, but the grain should crystallize better and the size would be larger. The peaks of C_3S shield some βC_2S peaks, but the unshielded peak of βC_2S at about 31° (2θ) is not obvious. This means that the content of C_2S is

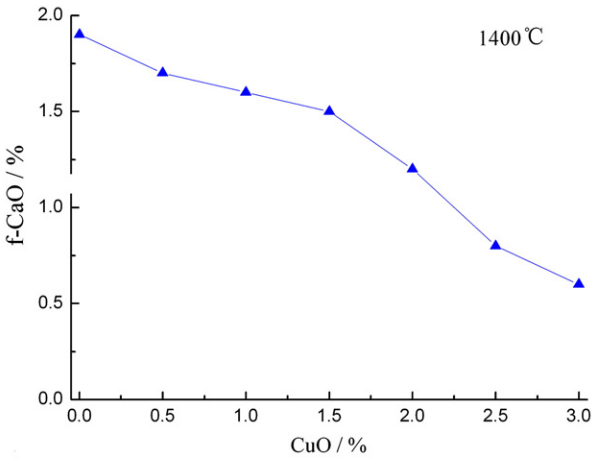

Fig. 1. Change in the content of f-CaO with the amount of CuO.

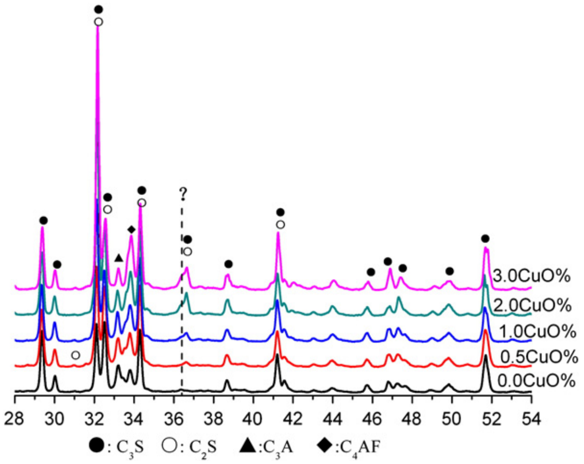

Fig. 2. XRD patterns of clinker.

very low. In contrast, the intensity of C_4AF peak (2θ = 33.8°) with CuO amount obviously increases while that of C_3A (2θ = 33.3°) is almost the same. This variation suggests that CuO promotes the formation of C_4AF, but affects little on C_3A. That result disagrees with Kakali's report that CuO favors the CaO–Al_2O_3 reaction and the formation of C_3A [5]. Generally speaking, liquid phase containing more C_4AF has a lower viscosity when the quantity of liquid phase keeps constant. Therefore, to some extent, CuO decreases the viscosity of liquid phase.

3.1.2.2. Minor minerals. A small shoulder peak (36.4°/2θ) in XRD patterns of samples with more than 2%CuO is found near C_2S and C_3S overlapping peak (36.6°/2θ). By analysis of Jade software, the shoulder peak may be related to Cu_2O or 2CaO·CuO. Moreover, when the sample with 3%CuO was examined by SEM, some white areas are found (Fig. 3) and the analyzed results by EDAX show that the white areas contain higher Cu and O element (1 point in Table 1). Those areas may mainly be a cupreous oxide. In addition, since some researchers thought that the reaction of CaO and CuO would produce CaO·2CuO at 1085 °C [6,8,14], the mixture of CuO and $CaCO_3$ (mole ratio 2:1) was burnt at 1200 °C and 1250 °C, respectively, and their XRD patterns are shown in Fig. 4. From Fig. 4, only the peaks of Cu_2O (PDF card: 05-0667, cuprite, syn.) and CaO are found. Based on the solid solution limit of CuO in clinker minerals of Hornain's report [15], 3%CuO has been beyond the solid solution limit of clinker minerals. Even though his report was incorrect, the result of SEM indicates that CuO is excessive and redundant CuO appears in the form of Cu_2O.

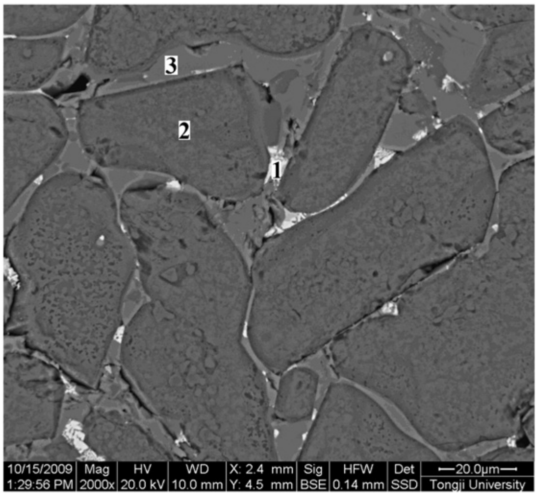

Fig. 3. SEM of the clinker with 3%CuO.

Table 1
Elemental analysis of points in Fig. 3 (at.%).

Element	1	2	3
O	45.34	54.89	53.89
Al	–	1.07	15.68
Si	1.59	11.68	1.57
Ca	6.26	31.01	24.06
Fe	–	0.47	4.13
Cu	46.81	–	0.66

3.1.3. Alite polymorph

Tricalcium silicate exhibits seven polymorphs: three triclinic T_I, T_{II} and T_{III}, three monoclinic M_I, M_{II}, M_{III} and a rhombohedral R. At room temperature, pure C_3S only exists in the form of T_I. The other six modifications are stable only at higher temperature or as solid solutions with stabilizing foreign oxides. Because of high concentrations of impurities in the raw meal, M_I and M_{III} are the most frequently polymorphs observed in commercial clinker. To study the polymorph of alite, especially the angles 2θ = 51–52° and 31–33° are always examined (Fig. 5a and b). The peak of the R alite at about 51.7° is almost a singlet, the corresponding peak of the M_3 alite is a well-defined doublet, and those of T_1 C_3S and T_2 alite are triplets [16]. Due to the very low content of C_2S, the polymorph of C_3S can be identified by the character of peaks in the two angular ranges. The comparative intensities at 32.1° and 32.5° change and the single peak at 51.5° is divided into doublet as the amount of CuO added increases. Those changes mean that the R is transformed into the M_3 when CuO is added.

Moreover, it needs to be noted that the peaks of C_3S at 51–52° and 31–33° obviously shift to the right with CuO amount. This shift indicates that CuO is dissolved in C_3S and leads to decrease in d value due to the difference of their ionic radius ($r_{Cu}^{1+} = 0.96$ Å and $r_{Ca}^{2+} = 0.99$ Å).

3.1.4. Crystal size and crystallinity of C_3S

From Fig. 3, it is also found that the C_3S grains are enclosed by interstitial phases, very great prismatic particles, their lengths are about 50 μm and their outlines are also very clear in the sample with 3%CuO. Compared with the 3%CuO sample, the C_3S grains in the reference are much smaller and most of the particles are smaller than 10 μm. Moreover, the difference of their particle size is very great: the length of the largest particle is up to 30 μm but the smallest is only several microns (Fig. 6a). The difference between the 0.5%CuO sample and the reference is that on the whole the former has more large particles more than 10 μm than the later (Fig. 6b). The above analyses

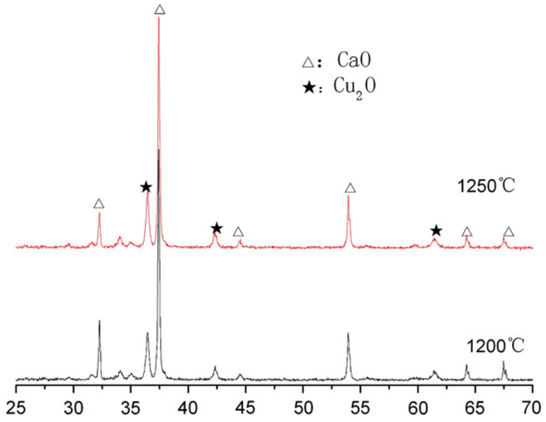

Fig. 4. XRD patterns of mixtures calcined of CaO and CuO (1:2).

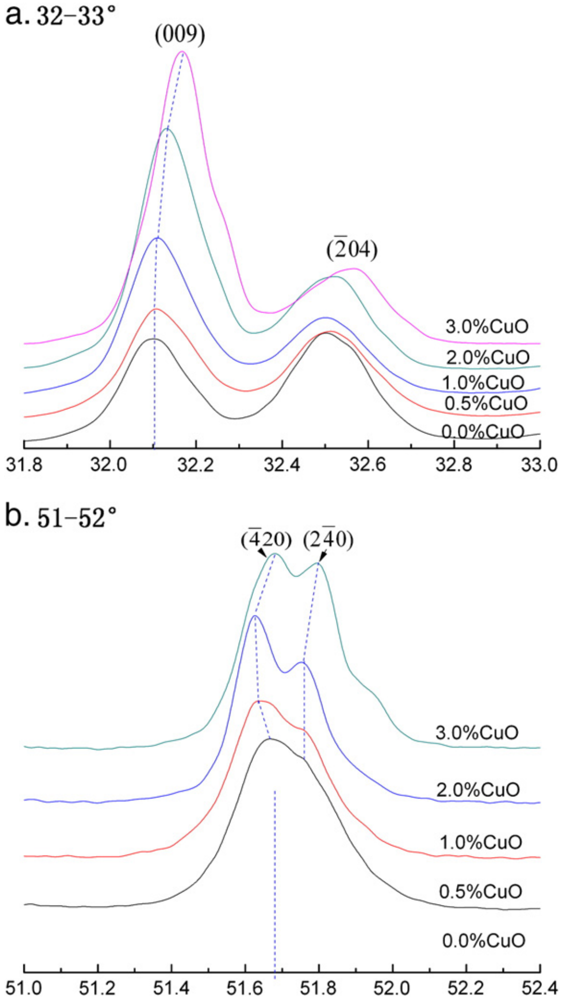

Fig. 5. The change in the C,S polymorphism. a. 32–33°. b. 51–52°.

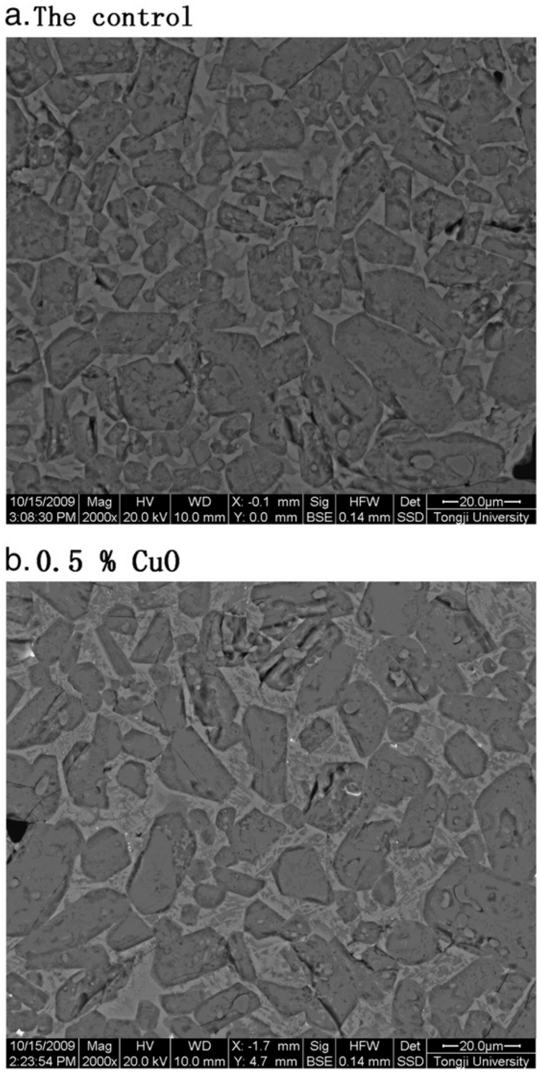

Fig. 6. SEM of clinkers with CuO and the control.

indicate that CuO promotes the growth of the C_3S grain and that effect is strengthened with CuO amount. Those extraordinarily large grains, however, may affect the hydration of clinker.

3.2. *The effect of CuO on hydration process*

3.2.1. *Compressive strength*

Compressive strengths of samples with different CuO contents are shown in Fig. 7. The three dot lines in Fig. 1 were drawn based on the strengths of the reference at the required ages. Notably, the sample with 0.5%CuO has higher strengths than the reference at all ages. However, the strengths obviously decrease as the amount of CuO increase, especially more than 1.5%. For example, the strength of the sample with 3.0%CuO is almost zero after 7 days. Moreover, the samples with more than 2%CuO were found not to be set after 24 h yet. The above results indicate that at the required ages a small quantity of CuO increases the strengths but more CuO evidently decreases the strengths.

3.2.2. *Amount of non-evaporated water*

The amount of non-evaporate water in cement hardened paste is approximately equal to the content of chemical bound water and proportional to the degree of hydration [17]. To estimate the hydration degree of CuO clinker, the amount of non-evaporate water was measured (Table 2). As the amount of CuO increases, change in the non-evaporated water amount is similar to that in compressive strength. In addition, the non-evaporated water amounts of the samples with 1% and 2%CuO are almost the same as that of the reference after 28 days.

3.2.3. *XRD pattern of hydration products*

Since the amount of non-evaporated water only reflects the overall hydration of clinker, the unhydrated C_3S and the hydration product Ca

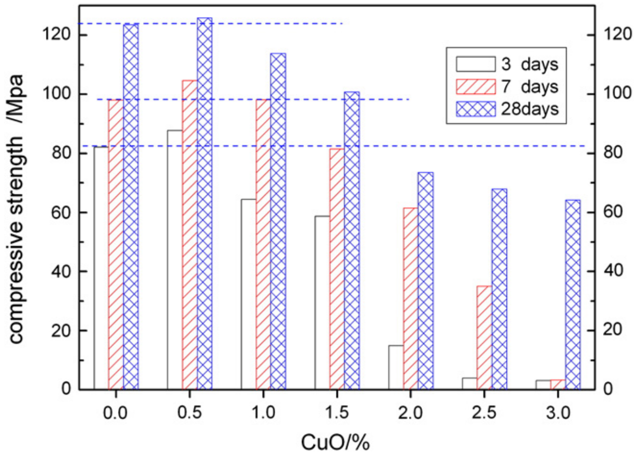

Fig. 7. Compressive strength of samples with different CuO contents/MPa.

Table 2
The quantity of non-evaporated water/%.

	0.0%CuO	0.5%CuO	1.0%CuO	2.0%CuO	3.0%CuO
3 days	13.90	16.30	13.26	11.14	5.85
28 days	17.96	18.36	17.33	17.17	14.81

$(OH)_2$ were examined by XRD as shown in Fig. 8. Although the diffraction peak intensity was not directly proportional to the content of crystalline phases, some important information can be obtained from comparisons of the relative intensity or changes of the intensity with age. After 3 days, it is found from the variation in C_3S peak at 29.3° that 0.5%CuO promotes the hydration of C_3S but more than 0.5% CuO has an evident delayed effect. After 28 days, the same trend appears but their difference becomes unobvious. At the same time, the variation in (100) peak of $Ca(OH)_2$ at 16.8° also reflects the same results. Notably, that peak of the sample with 3%CuO doesn't appear after 3 days. However, those peaks at 16.8° of the samples with 2%CuO and 3%CuO have almost the same intensities as that of the reference after 28 days. In addition, the copper hydroxide was not detected.

3.2.4. Hydration heat

To reflect the effect of CuO on the hydration of clinker in detail, the heat liberation of hydration was also measured during 12.5 days as shown in Fig. 9. Rather intense heat liberation within a few minutes is due to the initial rapid hydration of C_3A and C_3S in the pre-induction period. Soon thereafter, the overall rate of hydration is slowed down and almost zero in the induction period and then a second main exothermic peak appears which is mainly due to the hydration of C_3S (Fig. 9a). The end time of the induction period has an important effect on clinker hydration properties as shown in Table 3. From Table 3, CuO is found to prolong the induction period, especially CuO more than 1%.

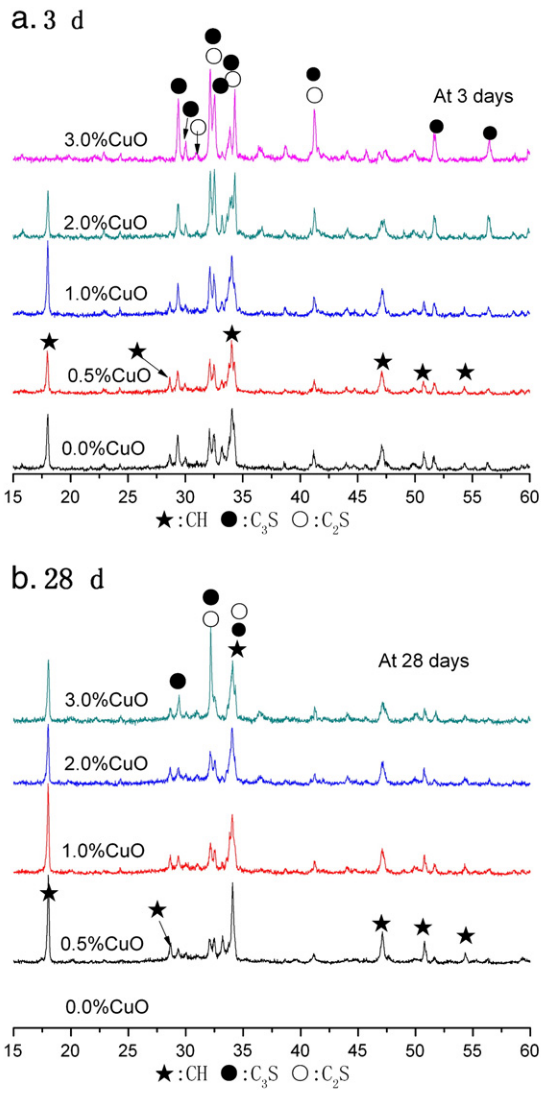

Fig. 8. XRD patterns of clinkers hydrated at the curing ages.

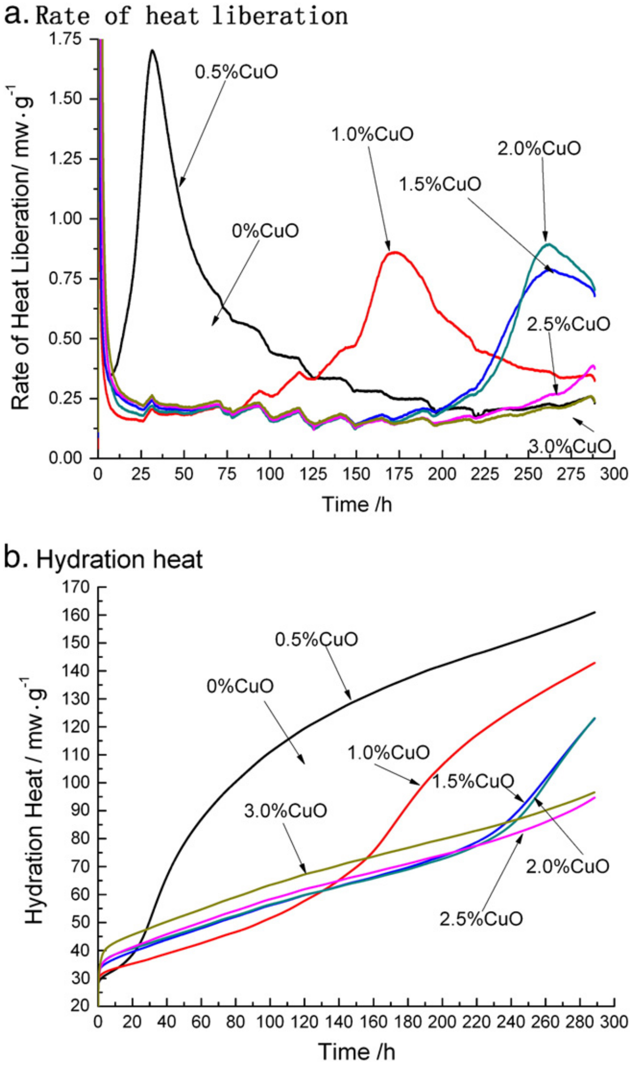

Fig. 9. Rate of clinker heat release with different CuO contents.

In the initial hydration, the amount of heat release slightly rises for the samples with 0.5% and 1%CuO, but for the samples with more than 1%CuO obviously increase compared with the reference. In the induction period, however, the more the amount of CuO added the longer the induction period. For example, the induction period ends after 33.5 h for the sample with 0.5%CuO, but after 195 h for the sample with 2%CuO. After the induction period, the heat release amounts of the samples with 0.5% and 1.0%CuO are more than that of the reference after 40 h and 280 h, respectively. The heat release

Table 3
The end time of the induction period/h.

	0.0% CuO	0.5% CuO	1.0% CuO	1.5% CuO	2.0% CuO	2.5% CuO	3.0% CuO
Duration	5.5	11.3	75	183	185	210	228
End time	8	14.2	82	198	200	235	253

amount of the samples with more than 1.0%CuO will eventually be beyond that of the reference although their heat release amounts are lower than the reference during 1–12.5 days. Moreover, the heat release curve trend shows that the amount of heat release will increase with CuO amount added when the hydration is up to a certain age.

From the above analyses, CuO is found to promote the hydration in the initial and acceleration periods, but to prolong the induction period.

3.3. Discussions

3.3.1. The effects of CuO on formation of clinker

The effects of CuO on formation of clinker are mainly reflected in the following aspects: CuO promotes the consumption of CaO, increases the content of C_4AF, accelerates the formation and growth of C_3S, and causes the transformation of C_3S from R to M_3. Those effects are attributed to the effect of CuO on the quantity and properties of liquid phase: formation temperature, quantity and viscosity.

The effect of CuO is closely related to the decomposition of CuO into Cu_2O at 1095 °C (Figs. 10 and 11). Newly-formed Cu_2O provides the CuO system a low-melting-point mineral (1226 °C), decreases the formation temperature of liquid phase by 130 °C and increases its quantity.

The dissolution of CuO in C_4AF decreases the melting temperature of C_4AF and makes the CuO system form more liquid phase than the reference. Moreover, increase in the content of C_4AF is owing to the replacement of Cu^{1+} in $3Cu_2O$ for Fe^{3+} in C_4AF which means increasing the content of Fe_2O_3 in the raw mixture and decreasing the alumina ratio and causes the quantity of liquid phase to rise and its viscosity to drop. Those changes in the quantity and properties of liquid phase provide a favorable condition for the consumption of CaO and the burning process.

Since the formation of C_3S depends on the quantity and properties of liquid phase, increase in the quantity of liquid phase provides more room for the formation and growth of C_3S and decrease in the viscosity of liquid phase accelerates mass transfer in the liquid phase, so that the size of C_3S in CuO clinkers is larger. In addition, decrease in the viscosity of liquid phase also favors copper ion to enter the structure of C_3S and makes C_3S appear in the form of the M_3 at room temperature.

3.3.2. The effects of CuO on the hydration of clinker

The effects of CuO on the amount of non-evaporated water, the hydration degree of C_3S and the rate of heat release are consistent and reflect the effect on the degree of hydration. The degree of hydration general corresponds with compressive strength. The higher the hydration degree, the higher the strength. The above effects of CuO are closely related to its amount. A small quantity of CuO increases the strengths and hydration degree, but more CuO suppresses those two properties. The more the amount of CuO, the more obvious the suppressed effect. The effects of CuO can be summarized as follows.

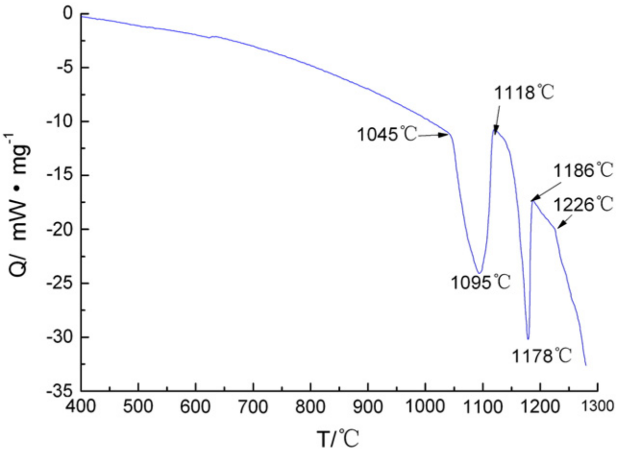

Fig. 10. DTA curve of CuO.

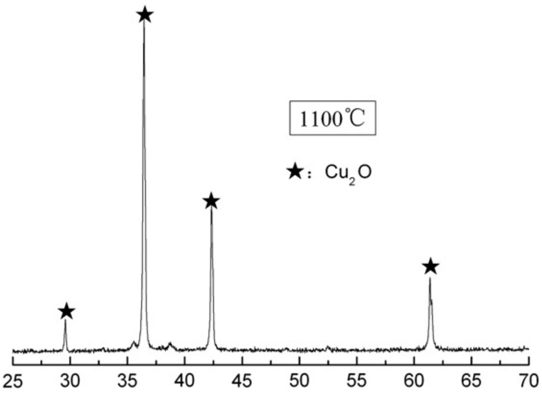

Fig. 11. XRD of CuO at 1100 °C.

3.3.2.1. CuO increases the rate of clinker hydration reaction. CuO is dissolved in C_4AF, C_3S and other clinker minerals and cause their lattice distortions which lead to crystal defects rising. It is well known that crystal defects will raise the hydration activity of crystals. Since the hydrations in the initial and acceleration periods are controlled by the rate of the hydration reaction, the hydrations in those periods are promoted as shown in the curve of heat release. Other factors such as polymorph and particle size will also affect the rate of hydration reaction. The M_3-type C_3S is thought to have a lower hydration activity than the R-type [18,19]. Moreover, some researchers think that the defects may have greater effect on the hydration than the transformation of C_3S polymorphs [16,20–22].The effect of particle size is related to its specific surface areas. The larger the particle, the rapider the hydration. Since the particle size distributions of all samples are mainly in the range of 10–30 μm, the effect of particle size cannot be considered here. Therefore, the contribution of CuO to hydration rate may mainly derive from the formation of crystal defect.

3.3.2.2. CuO prolongs the induction period. The curves of heat release show a very obvious prolonged induction period in CuO clinkers. This is related to the rapid hydrations of C_3S and C_4AF in the initial period which increase the amount of CSH and iron gel and cause the formation of the covering layer on the surface of the particles easier. The covering layer makes the diffusion of ions more difficult and the hydration slower so that it needs a longer time to reach the condition under which the covering layer is broken such as the nucleation and growth of CH or C–S–H and shows a prolonged induction period. Moreover, CuO increases the size of C_3S grains by several or even dozens of times. Since the covering layer has a greater effect on larger grains than small ones, the hydration degree of CuO clinkers decreases and the induction period is also prolonged. Some researchers also find that increase in the size of C_3S grains would decrease the strength [23–25], but others think that the strength would rise or not be affected [26,27]. The difference of the above results may be caused by the difference of the size range studied.

The effect of CuO on the hydration results from the combined action of the above two factors. CuO added increases the hydration rate but prolongs the induction period. When the amount of CuO is lower the effect on the induction period is less and the acceleration period more quickly begins. As a result, the hydration is promoted and the 3-day and 28-day strengths and hydration degree increase. However, when the amount of CuO rises, the longer induction period and the lower hydration rate in the induction period retard the role of CuO in the acceleration period. Thereby, the strength and hydration degree decrease at a shorter time (28 days).

For the components of the covering layer, some researchers thought that $Ca_2(OH)_4 4Cu(OH)_2 \cdot H_2O$ [22] or $Cu(OH)_2$ [5] enters the covering layer and increases its density. But their endothermic peaks in the temperature range of 117 °C, 250–400 °C and 390–430 °C and their reflection peaks were not found on the DTA curve and XRD pattern. In addition, the results of TLCP for CuO samples after 28 days show that the concentrations of Cu^{2+} ion in the leachates are below 5 ppm. Therefore, the components of the covering layer need to be further studied.

4. Conclusions

1. CuO promotes the consumption of CaO and improves the clinkering process.
2. CuO increases the content of C_4AF, accelerates the formation and growth of C_3S and causes the transformation of C_3S from R to M_3.
3. The effects of CuO on the formation of clinker minerals are attributed to the formation of low-melting Cu_2O and the dissolution of CuO in C_4AF which decrease the formation temperature of liquid phase and increase the amount of liquid phase.
4. A small quantity of CuO increases the 3-day and 28-day strengths and the hydration degree of clinker, but excessive CuO has adverse effects. For example, the strength and amount of $Ca(OH)_2$ and non-evaporable water of the clinker pastes increase when the doping amount of CuO is 0.5% but when CuO exceeds 1.0% they decrease at the required ages and when CuO is 3.0% the strength is almost lost and $Ca(OH)_2$ is not detected at 3 days.
5. With doping CuO, the induction period of the clinker is prolonged, and the hydration reactions in the initial and acceleration periods are accelerated. Those two effects result in compressive strength and hydration degree decreasing.

Acknowledgement

The authors gratefully acknowledge the National Science Council of China for its financial support for this study (Contract Nos.: 2009CB623102 and 2009CB623104).

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