FORMATION OF CLINKER CONTAINING COPPER

Theodor Staněk[1], Michaela Krejčí Kotlánová[1], Anežka Zezulová[1], Ingrid Khongová[1], Martin Boháč[1], Matej Dzurov[2]
[1]Research Institute for Building materials, Hněvkovského 30/65, 617 00 Brno, Czech Republic, stanek@vustah.cz
[2]CEITEC, Brno University of Technology, Purkyňova 123, 612 00 Brno, Czech Republic

Abstract

Copper is one of many elements present in secondary raw materials. These coppers containing secondary raw materials can be utilized in the production of ordinary Portland cement (OPC). At laboratory conditions, copper significantly influences the formation of clinker melt and the main clinker phase – alite. For the scope of this research, differential thermal analysis (DTA), powder X-ray diffraction analysis (XRD), optical microscopy (OM), and scanning electron microscopy with electron dispersive spectroscopy (SEM-EDS) methods were used for the investigation of the influence of copper on clinker. It has been confirmed, that addition of copper-containing compounds to a raw meal has a significant intensification effect on the clinker melt formation. On the other hand, a decrease in the total alite content in the clinker with increasing CuO content has been observed. Observations were conducted on clinkers with CuO content up to 4 wt. %. The addition of CuO also reduced burning temperatures of alitic clinker from standard industrial burning temperature of 1450 °C to 1250 °C. The decrease of 200 °C in burning temperature has applications for clinker production and reduction of emissions.

Introduction

Nowadays, wastes, and secondary products from industrial production are increasingly used, which can distinctly increase the heavy metal content of the resulting clinker.
Many wastes, such as sewage sludge, copper slag, or fly ash contain a certain amount of copper [1,2].
It is necessary to investigate the effects of copper oxides on the phase composition of clinkers and hydration processes which can help us utilize copper-containing waste in cement production.
Standard clinker is composed of four major phases – C_3S, C_2S, C_3A, and C_4AF. In recent years, it has been found that the addition of heavy metal oxides affects the composition and hydration properties of the clinker [3-6].
Kakali et al. [7] found out that the addition of CuO affects the formation of silicates and aluminates. CuO mainly promotes the formation and growth of alite crystals at lower temperatures and alters the crystallization processes upon cooling clinker.
Kolovos et al. [8] studied clinkers doped with CuO by SEM and electron microprobe and the authors reported a new phase. The ratio of CaO to CuO was about 1:2.
Ma et al. [9] reported that alite grains may be up to 3 times larger in clinker with the addition of 3 % CuO than the reference sample without the addition of copper. They disclosed that the addition of CuO increases the C_4AF content while the C_3A content does not change much.
The excess of CuO results in Cu_2O clusters as a cuprite mineral at a temperature higher than 1085 °C [9,10].
Hou et al. [11] studied a cement clinker composed mainly of C_3S with the addition of 1 % CuO. They confirmed the positive effect on burnability. The burning temperature decreased to temperatures between 1200 and 1450 °C.
It means that CuO is a good additive for special high C_2S and high C_3S clinkers.

Methodology

Composition of reference raw meal from pure chemicals

Raw material	$CaCO_3$	SiO_2	Al_2O_3	Fe_2O_3	K_2CO_3	Na_2CO_3
Content [wt. %]	78.77	14.91	3.28	2.05	0.71	0.28

Addition of CuO – 0; 0.5; 2; 4 wt. %

Thermal properties – Perseus STA 449 Netzsch: 30-1450°C, 10°C/min

Burning – superkanthal furnace, Pt plate, 10°C/min, 1300°C, grinding, pelleting, 10°C/min, 1450°C, hold 60 mins

Phase composition – XRD, Bruker D8 Advance, Rietveld method

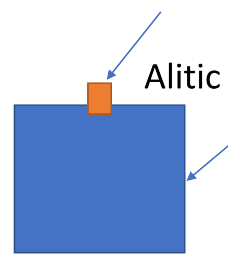
Clinker microstructure – polished cross sections, light microscopy, Nicon Eclipse LV100, reflective light, etched by acetic acid fumes, alite crystals size

SEM-EDS – TESCAN MIRA3-XMU with Oxford Instruments EDS, special samples ("target experiments") from pure clinker phases

Composition of mixtures for "target experiments" in wt. %

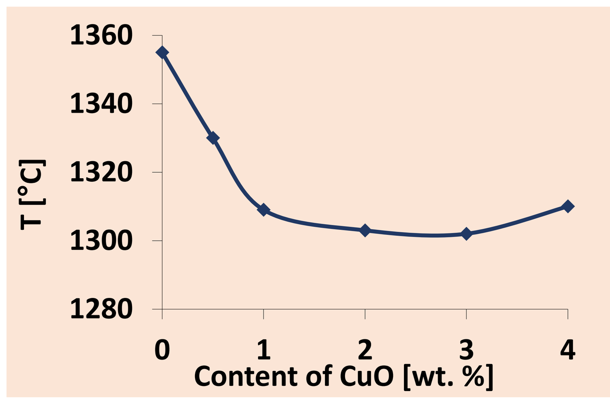
Phase	Alitic clinker	Belitic clinker
C_3S triclinic	80	0
β-C_2S	0	80
C_3A cubic	10	10
C_4AF	10	10

Target experiments
1450°C, 60 mins hold



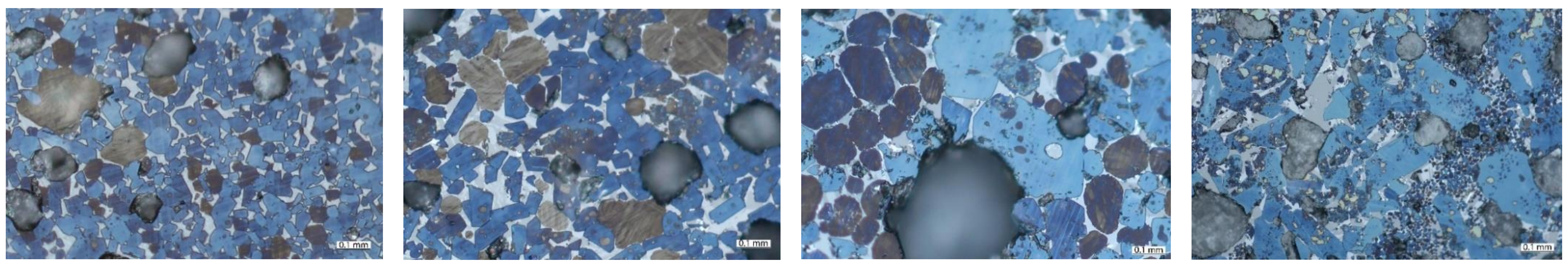
Results

The relationship of the temperature of clinker melt formation on the CuO content



Size of alite crystals in µm depending on CuO content

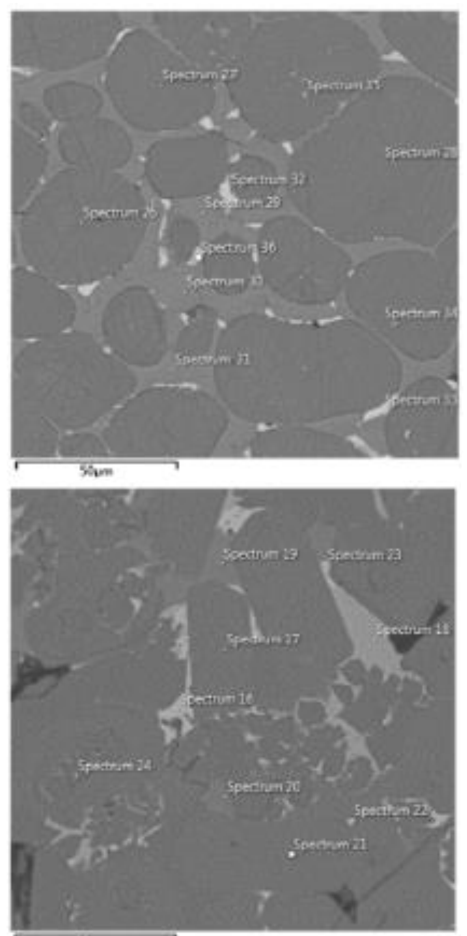
CuO content [wt. %]	0	0.5	2	4
Average size	8	18	23	30
Maximum size	17	36	55	93



Clinker microstructure without addition of CuO (1st foto); clinker microstructure with addition of 2 wt. % CuO (2nd foto) and with 4 wt. % CuO (3rd foto); microstructure of clinker 3CuO 1250 °C 60´ (4th foto) – alite forms blue crystals, belite brown grains and interstitial matter form bright areas between crystals and grains and (reflected light, polished cross sections etched by acetic acid fumes)

Phase composition of clinkers doped with CuO in % determined by XRD analysis

Phase	0CuO	0.5CuO	2CuO	4CuO	3CuO 1250°C 60´
C_3S	69.0	67.9	58.1	46.1	25.6
β-C_2S	10.5	12.5	21.2	32.2	38.2
α´-C_2S	1.9	1.3	1.1	1.4	0.4
γ-C_2S	-	-	-	-	12.0
C_3A cubic	3.0	3.4	3.4	3.9	4.5
C_3A ortho.	10.5	9.3	6.8	4.8	3.5
C_4AF	5.1	5.3	7.3	8.7	9.9
C free	0.0	0.0	1.1	1.3	5.2
Cuprite		0.3	1.0	1.6	0.7



Back-scattered image of analyzed regions of belitic (up) and alitic (down) clinkers

Spectral phase composition and phase identification of the most representative spectra according to SEM-EDS analysis

Point	16	17	19	26
Ca	1.0	51.0	33.4	45.0
Si	0.0	11.9	0.6	17.1
Al	0.0	0.0	9.8	0.0
Fe	0.0	0.0	19.8	0.0
O	10.8	35.8	32.5	37.9
Cu	88.2	1.3	3.9	0.0
Sum	100.0	100.0	100.0	100.0
Phase	Cu_2O	C_3S	C_4AF	β-C_2S

Conclusion

- It has been found that at laboratory conditions, copper in raw meal intended for the burning of Portland clinker causes a reduction in the temperature necessary for the clinker melt formation. It can therefore act as a burning intensifier and can shift clinker production to lower temperatures than the usual 1450 °C.
- By the effect of Cu in the clinker melt, nucleation is reduced and the growth rate of alite crystals increases. With the increasing CuO content, fewer alite crystals of larger dimensions are formed.
- SEM-EDS analysis confirmed the presence of copper-containing compounds in a form of mineral cuprite – Cu_2O. The cuprite phase seems to be dispersed mostly in the interstitial matter along grains of β-C_2S and C_3S. Copper also enters and substitutes atoms in the C_4AF and C_3S phase at a lower degree, while β-C_2S seems to be without copper.
- Results show that a concentration around 0.5 wt. % of CuO positively influences and intensifies the burnability of doped clinker. At these low concentrations, the negative influence of copper on alite formation is marginal or heavily suppressed.
- Thus, the utilization of copper wastes and slags as secondary raw materials can provide a reduction in already significant energy demands and a decrease in emissions accompanied by Portland cement production.

Acknowledgements

This research was carried out within the project No. 19-05762S financed by the Czech Science Foundation. CzechNanoLab project LM2018110 funded by MEYS CR is gratefully acknowledged for the financial support of the measurements at CEITEC Nano Research Infrastructure.

References

1. Fjällborg B., Dave G.: Envi. Int. 28(8), 761-769 (2003).
2. Yang R., Liao W.-P., Lin Ch.-Y.: Envi. Progress & Sustain. Ener. 32(4), 1-8 (2013).
3. Katyal N.K., Parkash R., Ahluwalia S.C., Samuel G., Monsier F., Haehnel C.: Cem. Concr. Res. 29(3), 355-359 (1999).
4. Stephan D., Mallmann R., Knofel D., Hardtl R.: Cem. Concr. Res. 29(12), 1949-1957 (1999).
5. Achternbosch M., Bräutigam K.-R., Gleis M., Hartlieb N., Kupsch C., Richers U., Stemmermann P.: Forschungszentrum Karlsruhe GmbH. Karlsruhe (2003).
6. Kolovos K.G., Barafaka S., Kakali G., Tsivilis S.: Ceram.-Silik. 49(3), 205-2012 (2005).
7. Kakali, G. Parissakis G., Bouras D., Eber B., Härdtl R.: Cem. Concr. Res. 26(10), 1473-1478 (1996).
8. Kolovos K.G., Tsivilis S., Kakali G.: Cem. Concr. Compos. 27 (2), 163-167 (2005).
9. Ma X.-W., Chen H.-X., Wang P.-M.: Cem. Concr. Res. 40(12), 1681-1687 (2010).
10. Ghosh A., Bhattacharya T. K., Mukherjee B., Das S.K.: Ceram. Int. 27(2), 201-204 (2001).
11. Hou G.H., Shen X.D., Xu Z.Z.: J. Wuhan Univ. Technol.-Mater. Sci. Ed. 22(1), 56-60 (2007).