

THERMAL ANALYSIS OF RAW MEALS DOPED WITH LI, CU AND S FOR BURNING OF PORTLAND CEMENT CLINKER

THEODOR STANĚK^{a,*}, DALIBOR VŠIANSKÝ^b, MICHAELA KREJČÍ KOTLÁNOVÁ^a,
MARTIN BOHÁČ^a, ZDENĚK KREJZA^a, EVA BARTONÍČKOVÁ^c

^a Research Institute for Building Materials, Hněvkovského 30, 617 00 Brno, Czech Republic

^b Masaryk University, Faculty of Science, Department of Geological Sciences, Kotlářská 267, 611 37 Brno, Czech Republic

^c Brno University of Technology, Faculty of Chemistry, Institute of Materials Science, Purkyňova 464, 612 00 Brno, Czech Republic

* corresponding author: stanek@vush.cz

ABSTRACT. The intensification of clinker production is one of the strategies for reducing energy consumption and CO₂ emissions associated with cement manufacturing. This study explores the use of various mineralisers and fluxes, specifically lithium, copper, and sulphur, added to the raw meal for clinker burning. These components can originate from both traditional and alternative fuels and raw materials. The influence of these elements on clinker melt formation, phase composition, and microstructure was investigated in the laboratory. Raw meals prepared from common cement materials were doped with chemically pure compounds Li₂CO₃, CuO, and (NH₄)₂SO₄ in graded amounts. The thermal processes of the raw meals were monitored using differential thermal analysis coupled with a thermogravimetric analysis. The phase composition and microstructure of the resulting clinkers were analysed using X-ray powder diffraction and light microscopy. All dopants were found to lower the melt formation temperature, with lithium having the most significant effect. The dopants also caused changes in the phase composition and microstructure of the clinker, particularly affecting the size and shape of the alite crystals and the volume of the belite unit cell.

KEYWORDS: Clinker, TG/DTA, XRD, phase composition, lithium, copper, sulphur.

1. INTRODUCTION

One effective strategy to reduce the energy consumption and CO₂ emissions in cement production is to lower the burning temperature of the main intermediate product – clinker. This can be achieved through the use of various mineralisers and fluxes [1]. Sulphur oxide (SO₃) significantly alters the physicochemical properties of the clinker melt, reducing its viscosity and surface tension [2, 3]. This results in a reduction in the nucleation of the alite crystals and increase in their growth rate [4], thus promoting the formation of the hydraulically active alite modification M1 [5, 6]. Sulphur is incorporated into all clinker phases, with the most significant impact observed in belite [7]. Excess SO₃ leads to the formation of alkaline sulfates, CaSO₄, and other less common phases. Increasing the SO₃ content in clinker can lead to a negative phenomenon, an increase in belite content at the expense of alite [8, 9].

In combination with other fluxing elements, such as lithium (Li) and copper (Cu), the effects on clinker melt can be even more significant. These elements are recognised for their beneficial impact on clinker mineralisation, as noted in a study by SINTEF [1]. Lithium, distinct from sodium or potassium, tends to form a relatively nonvolatile oxide at elevated kiln temperatures [10]. The addition of Li₂CO₃ lowers the decomposition temperature of CaCO₃, initiating the

process in two steps. At a 1% dopant level, CaO formed at low temperatures reacts with SiO₂ to produce β-C₂S even at 750 °C, with the reaction completing at 1350 °C to form β-C₂S and small amounts of γ-C₂S. A 5% addition further reduces the final reaction temperature to 1290 °C, producing β-C₂S and small quantities of C₃S [11].

Small amounts of lithium oxide improve the raw meal reactivity by lowering the temperature of the initial melt formation. However, exceeding a Li₂O exceeding 1% in the raw meal impairs the combination of free lime with C₂S and inhibits the conversion of C₂S to C₃S [10, 12]. Laboratory tests combining SO₃ and Li₂O demonstrated high mineralisation efficiency, with cement prepared from clinker burned at 1300–1350 °C showing an increase in initial strength of up to 100% compared to commercial OPC (ordinary Portland cement) [13].

Kakali et al. [14] studied the phase formation of Portland cement clinker containing Cu oxide. These authors found 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 crystallisation processes upon cooling the clinker.

Ma et al. [15] reported that alite grains can be up to 3 times larger for clinker with the addition of 3% of CuO than the reference sample without the addition

Component	Content
Pure limestone	52.84
Contaminated limestone	28.04
Clay shale	16.74
Fe correction	1.55
FGD gypsum	0.83
LSF*	96.5
SR**	2.66
AR***	1.34

* Lime saturation factor: $LSF = \frac{100C}{2.8S+1.18A+0.65F}$
** Silica ratio: $SR = \frac{S}{A+F}$
*** Alumina-iron ratio: $AR = \frac{A}{F}$

TABLE 1. Composition of reference raw meal in wt. % and its basic chemical parameters.

of copper. The grains also have much more distinct contours. Kolovos et al. [16] studied clinkers doped with CuO by SEM and electron microprobe and the authors reported a new phase in the form of white rims around the crystals of alite. The EDS analysis showed a high content of Cu and Ca. The CaO:CuO ratio was about 1:2.

Ma et al. [17] found that the addition of 0.1 % of CuO can increase the C₃A content in the clinker and at the same time the addition of 0.1 to 0.3 % of CuO decreases the amount of C₃S. In contrast, the addition of 0.3 to 1.0 wt. % of CuO increases the formation of C₃S. However, Ma et al. [15] reported that the addition of CuO increases the C₄AF content while the C₃A content does not change much.

The addition of 3 % of CuO appears to be redundant. The results showed that excess CuO clusters in the form of Cu₂O, as a cuprite mineral, at a temperature higher than 1085 °C [15, 18]. Cu₂O slows down the formation of alite due to its reduction properties [10]. The high Cu content in the clinker led to the separation of C₃S into C₂S and free lime [19].

CuO, in quantities greater than 1 wt. %, can cause a significantly prolonged induction period and strength decrease in the early hydration stages [20]. On the contrary, a low addition of CuO, below 1 wt. %, with an increased C₄AF content increases the hydration activity of Portland cement [21].

2. MATERIALS AND METHODS

For the experimental work, a reference raw meal was prepared using common cement raw materials. The raw meal consisted of two types of limestone, clay shale, iron correction, and flue gas desulphurization (FGD) gypsum. The composition of the raw meal is detailed in Table 1.

The crushed raw materials, weighed in the proportions shown in Table 1, were combined to a total quantity of 5 kg. These materials were ground together in a laboratory ball mill to achieve a fineness characterised by a residue of 13.2 wt. % on a 0.09 mm mesh. Secondary oxides in the form of chemically pure compounds – (NH₄)₂SO₄, CuO, and Li₂CO₃ – were

then added to this reference raw meal (designation RM). The dosages of these individual compounds are provided in Table 2. Calculations for the additions were performed based on clinker composition, assuming zero loss on ignition, which was taken as 35 wt. % for the raw meal.

The weighted mixtures were homogenised and subjected to monitoring using differential thermal analysis performed on a Perseus STA 449 Netzsch device. The analysis was conducted in the dynamic atmosphere of synthetic air (N₂/O₂ = 80/20), with a temperature rise rate of 10 °C min⁻¹ within a temperature range of 30–1450 °C.

Subsequently, tablets with a diameter of 40 mm and a weight of 20 g were pressed from each raw meal. These tablets underwent burning in a programmable superkanthal furnace with an internal volume of 10 dm³, ramped up at 10 °C min⁻¹ to 1450 °C with a soaking time of 1 hour, followed by removal from the furnace to laboratory conditions (the cooling rate was approximately 200 °C min⁻¹).

X-ray powder diffraction analysis was performed using a Panalytical Empyrean diffractometer equipped with fixed slits and a PIXcel detector at conventional Bragg-Brentano reflection geometry. Operating conditions were 45 kV and 40 mA, using non-monochromated, Ni-filtered CuKα radiation (λ = 1.541718 Å). Scans were conducted from 4.5° to 90° 2θ in 0.013° 2θ increments with a counting time of 192 s per step and a total scan time of 1 hour, 28 minutes, and 8 seconds. Quantitative phase analysis of the crystalline portion of the samples and the refinement of β-C₂S lattice parameters were performed using the Rietveld method with the Bruker AXS Topas 4 software, using the ICDD No. 330302 structure model.

The microstructure of polished sections of clinkers was etched with acetic acid fumes [22] and observed using a Nikon Eclipse LV100 light microscope. The average size of alite crystals was determined based on 100 individual measurements. In this case, the apparent size was measured as the maximum dimension of a randomly oriented section of the crystal.

Designation	CuO	Li ₂ CO ₃	(NH ₄) ₂ SO ₄	RM
0	-	-	-	100
0.5S	-	-	0.532	99.468
1S	-	-	1.061	98.939
2S	-	-	2.100	97.900
3S	-	-	3.117	96.883
4S	-	-	4.114	95.886
5S	-	-	5.090	94.910
0.1Li	-	0.162	-	99.838
0.2Li	-	0.316	-	99.684
0.5Li	-	0.799	-	99.201
1Li	-	1.580	-	98.420
2Li	-	3.117	-	96.883
3Li	-	4.601	-	95.399
0.2Cu	0.130	-	-	99.870
0.5Cu	0.324	-	-	99.676
1Cu	0.646	-	-	99.354
2Cu	1.283	-	-	98.717
3Cu	1.913	-	-	98.087

TABLE 2. Composition of doped raw meals [wt. %] (the number in the sample designation indicates the expected content of dopant oxide in clinker [wt. %]).

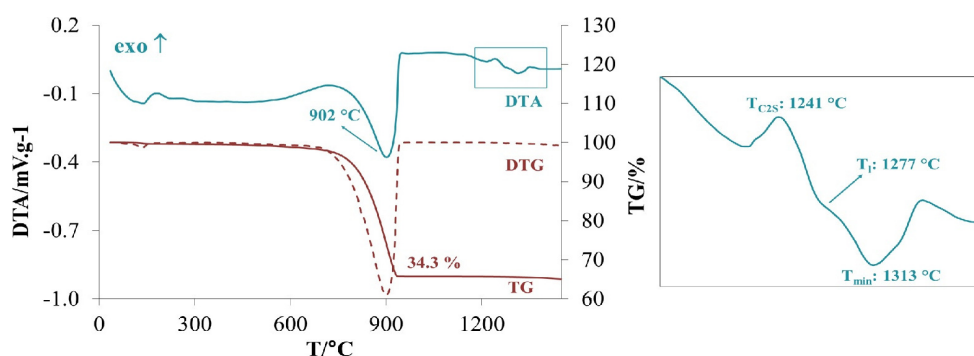


FIGURE 1. Thermogram of the reference raw meal 0 with a detail characterising the clinker melt formation. $T_{C_{2S}}$ – exotherm peak of belite formation, T_l – beginning of clinker melt formation, T_{min} – minimum temperature of endothermic clinker melt formation.

3. RESULTS AND DISCUSSION

3.1. THERMAL ANALYSIS

Differential thermal analysis (DTA) was employed to monitor changes in clinker melt formation temperature induced by the addition of dopants. The formation of the liquid phase is pivotal in the clinker formation process. At the onset of the furnace's sintering zone, prior to liquid phase formation, various decomposition processes of the raw meal occur, including the dissociation of carbonates, dehydration, and dehydroxylation of clay minerals and mica. These reactions predominantly take place in a dispersed state in heat exchangers (or calciners) in current production systems, followed by a bulk state in a rotary kiln, and are notably endothermic. Belite formation occurs during the dissociation of limestone via solid-phase reactions.

At the beginning of the sintering zone, local eutectics form in the regions with elevated Fe contents,

initiating the aggregation of bulk material in these areas. The gradual development of a continuous clinker melt is initially accompanied by a rapid exothermic process of belite formation, which subsequently ceases. The final phase of melt formation exhibits a significant endothermic character [23].

These processes are visible on the DTA curve of the reference raw meal 0 in Figure 1, where the peak of belite formation, the beginning of melt formation, and the minimum of its endotherm are marked. The influence of dopants on these parameters is elucidated in Figure 2.

At higher concentrations of SO_3 and Li_2O , the exothermic nature of belite formation became less pronounced, making it challenging to determine its temperature via DTA. Our investigation revealed that lithium exhibited the most significant reduction in melt formation temperature, whereas sulphur demonstrated the least effect. Specifically, at a Li_2O content of 0.5 wt. %, the temperature was reduced by approx-

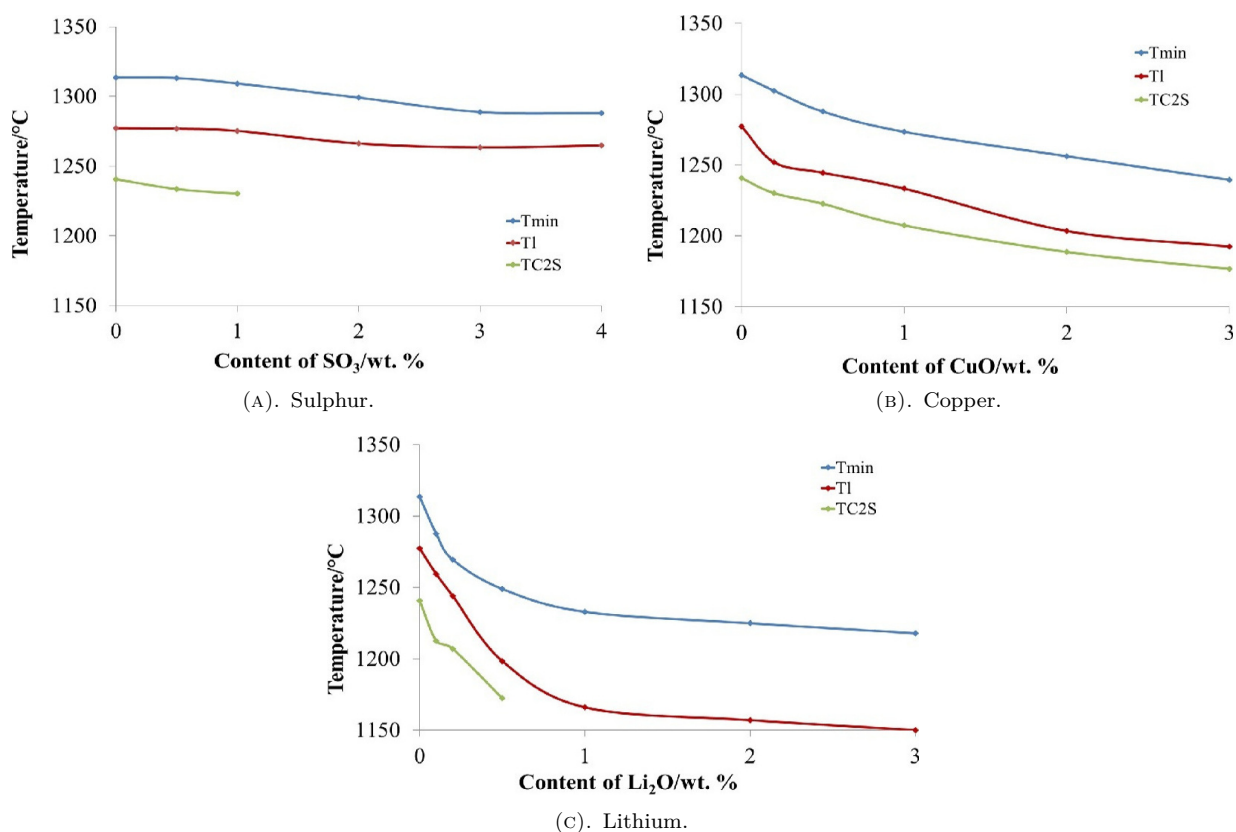


FIGURE 2. Differential thermal analysis – the effect of dopants on the clinker melt formation temperature and belite formation.

imately 80 °C compared to the reference raw meal. A similar reduction in temperature was observed with the addition of 2–3 wt. % of CuO.

Furthermore, lithium was confirmed to lower the decomposition temperature of limestone. At higher Li concentrations, a decarbonation endothermic reaction manifested as a split into two minima (see Figure 3), consistent with previous findings by other authors [11]. The endothermic peak at 643 °C is associated with the decomposition of lithium carbonate.

3.2. PHASE COMPOSITION OF DOPED CLINKERS AND THEIR MICROSTRUCTURE

The quantitative phase composition of the clinkers, as determined by X-ray diffraction analysis, is given in Tables 3–5.

With increasing SO₃ content, the belite content obviously increases and the alite content in the clinker decreases (Figure 4). As is well known, sulphur preferentially enters into the structure of belite, where it replaces Si in the anionic part, thus enabling the entry of a larger proportion of Ca than in the case of the pure C₂S phase [24]. Therefore, the expected increase in the free CaO content with increasing SO₃ content in the clinker did not occur. The increasing volume of the unit cell of belite is related to the entry of sulphur into the belite structure (Figure 5).

Thus, sulfur promotes belite stability and retards alite crystallisation. This is caused both by a change

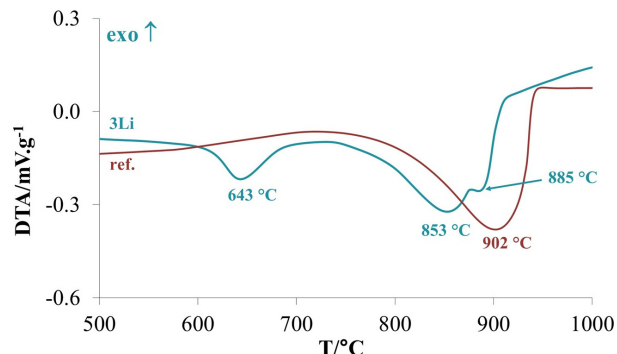


FIGURE 3. Part of the DTA curves of the reference raw meal and the raw meal with a high Li₂O content in the area of calcium carbonate decomposition.

in the physicochemical conditions in the clinker melt (reduction in viscosity and surface tension) and by the entry of sulfur into the belite crystal lattice [25].

Conversely, for the cation-forming elements Cu and Li, an inverse correlation is evident. Given that the lithium cation is smaller than that of copper, the reduction in the unit cell is more pronounced. The minimal change in unit cell volume in the case of copper can also be attributed to the previously observed phenomenon that Cu enters belite in the smallest amount among all clinker phases [1, 26].

In the case of copper, the results reveal a notable increase in the C₄AF content (Figure 6), likely at-

Phase	0	0.5S	1S	2S	3S	4S	5S
C ₃ S	43.9	43.6	42.3	41.5	39.5	37.9	36.9
C ₂ S	35.9	36.7	38.1	39.2	41.7	43.7	44.2
C ₃ A	6.9	6.4	5.9	5.7	5.2	4.7	4.6
C ₄ AF	11.6	12.1	12.3	12.6	12.3	12.4	12.8
C	0.4	0.3	0.3	0.0	0.3	0.2	0.3
CH	0.9	0.5	0.7	0.7	0.7	0.7	0.9
Arcanite	0.4	0.3	0.3	0.3	0.2	0.3	0.2
Suma	100	99.9	99.9	100	99.9	99.9	99.9
Rwp	3.24	3.20	3.17	3.18	3.21	3.22	3.25
GOF	1.50	1.46	1.45	1.45	1.46	1.47	1.48
V C ₂ S [Å ³]*	347.53	347.69	347.76	347.89	348.04	348.15	348.25

* C₂S unit cell volume, Rwp and GOF: parameters characterising the degree of agreement between the measured and calculated diffractometric record.

TABLE 3. Composition of burned clinkers doped with SO₃ determined by X-ray diffraction [wt. %].

Phase	0	0.2Cu	0.5Cu	1Cu	2Cu	3Cu
C ₃ S	43.9	44.6	44.4	43.9	43.0	42.1
C ₂ S	35.9	35.0	35.8	36.6	37.7	38.3
C ₃ A	6.9	6.8	4.8	3.9	1.6	1.2
C ₄ AF	11.6	12.7	14.1	14.9	16.3	16.6
C	0.4	0.3	0.3	0.3	0.4	0.4
CH	0.9	0.5	0.1	0.1	0.3	0.3
Cuprite	0	0	0.1	0.1	0.3	0.8
Arcanite	0.4	0.1	0.3	0.2	0.3	0.3
Suma	100	100	99.9	100	99.9	100
Rwp	3.24	3.26	3.03	3.25	3.20	3.14
GOF	1.50	1.49	1.38	1.49	1.49	1.44
V C ₂ S [Å ³]*	347.53	347.49	347.32	347.19	347.09	347.04

* C₂S unit cell volume, Rwp and GOF: parameters characterising the degree of agreement between the measured and calculated diffractometric record.

TABLE 4. Composition of burned clinkers doped with CuO determined by X-ray diffraction [wt. %].

Phase	0	0.1Li	0.2Li	0.5Li	1Li	2Li
C ₃ S	43.9	45.1	46.0	49.2	49.0	46.5
C ₂ S	35.9	35.9	36.0	33.6	33.3	34.3
C ₃ A	6.9	5.2	3.6	1.9	1.1	1.3
C ₄ AF	11.6	12.4	13.3	13.5	11.1	6.2
C	0.4	0.4	0.4	0.6	2.1	4.8
CH	0.9	0.6	0.3	0	0.5	1.9
Li ₂ SO ₄	0	0	0	0.3	0.8	1.6
LiFeO ₂	0	0	0	0.6	1.6	3.0
Arcanite	0.4	0.3	0.3	0.3	0.4	0.4
Suma	100	99.9	99.9	100	99.9	100
Rwp	3.24	3.21	3.17	3.20	3.13	3.53
GOF	1.50	1.47	1.46	1.47	1.44	1.62
V C ₂ S [Å ³]*	347.53	347.36	347.19	346.94	346.48	346.35

* C₂S unit cell volume, Rwp and GOF: parameters characterising the degree of agreement between the measured and calculated diffractometric record.

TABLE 5. Composition of burned clinkers doped with Li₂O determined by X-ray diffraction [wt. %].

tributed to the incorporation of Cu along with Fe into its structure, as corroborated by other authors [26]. Simultaneously, the C₃A content decreases. A higher Cu content in the clinker results in a slight increase

in the proportion of belite at the expense of alite. Da et al. [27] combined Cu with CaF₂ and found a similar effect in the case of C₄AF and C₃A, but CaF₂ eliminated the negative effect of Cu on the for-

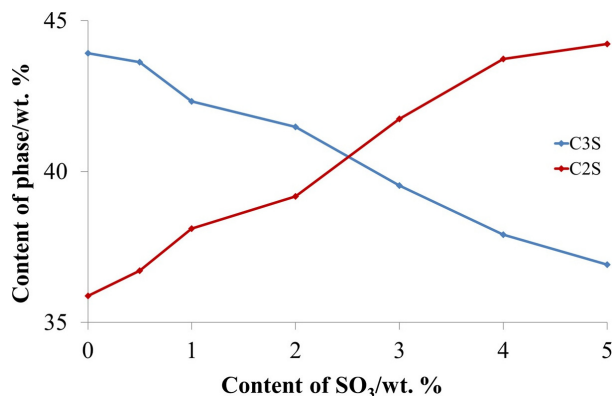


FIGURE 4. Effect of SO₃ addition on the contents of calcium silicates in clinker.

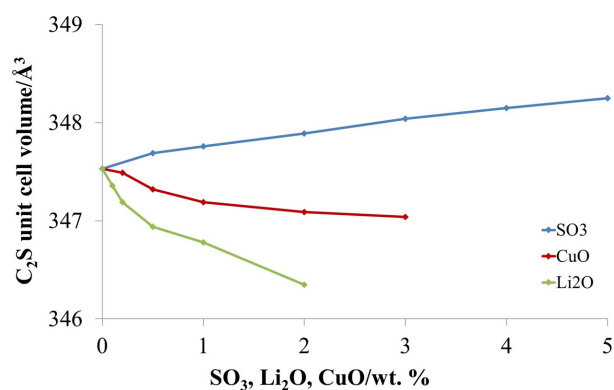


FIGURE 5. Change in the volume of the belite unit cell due to the content of individual dopants.

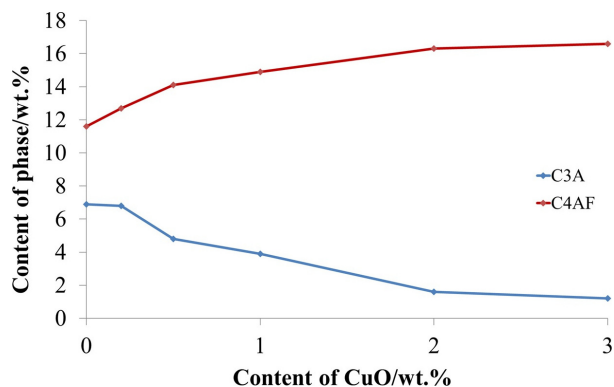


FIGURE 6. Effect of CuO on the interstitial clinker phase content.

mation of alite. Starting from 0.5 wt. % of CuO, a new phase, cuprite (Cu₂O), begins to form. Other studies also affirm that at larger amounts, Cu is in excess and does not integrate into the structures of clinker phases [15, 18].

Doping clinker with lithium initiates the formation of new phases, starting from 0.5 wt. % of Li₂O. These phases are likely Li₂SO₄ and LiFeO₂. The escalating proportion of free CaO with the increasing Li₂O content in the clinker can be partly attributed to the substitution of Li for Ca in the alite structure, which could also be related to the observed increas-

ing alite content in the clinker up to the addition of 1 wt. % of Li₂O. Additionally, the previously established decomposition of alite into a microcrystalline mixture of belite and free lime also occurs to some extent [28].

The introduction of dopants alters the physicochemical conditions within the clinker melt, thereby influencing the growth of alite crystals. Alite crystals demonstrate an increase in size (Table 6), accompanied by a transition in crystal habit from euhedral to subhedral and anhedral forms. The microstructure of burned clinkers is depicted in Figure 7. Alite (C₃S) forms blue crystals, belite (C₂S) forms brown grains, the bright spaces between crystals and grains are interstitial clinker phases (C₄AF + C₃A), the diffuse black areas are open pores, and the grey areas are pores closed filled with epoxy (see Figure 7A–7C). In the case of lithium, anhedral clusters of intergrown alite crystals up to 500 μm in size are formed, with belite between the alite crystals forming small grains and structures referred to as “fishbone” (Figure 7E) [16]. In Figure 7D, one of these alite clusters is visible – a large light blue area with yellow inclusions of free lime, darker areas of decomposition of alite into belite, and free lime (marked by arrows). Cuprite forms in clinker with a high copper content, and its isolated light fine grains in the interstitial mass (marked by arrows) are visible in Figure 7F.

4. CONCLUSION

This study aimed to investigate the influence of sulphur, copper, and lithium on the thermal processes occurring during clinker formation, as well as on its phase composition and microstructure, under laboratory conditions. Chemically pure compounds were used as sources of these elements, while the reference raw meal was prepared using common components for clinker burning.

Sulphur doping in the form of (NH₄)₂SO₄ resulted in:

- (1) A decrease in the clinker melt formation temperature by approximately 15 °C at a theoretical content of 3 wt. % of SO₃ compared to the reference raw meal.
- (2) A decrease of 10 °C in the peak exotherm maximum of belite formation at 1 wt. % of SO₃.
- (3) An increase in belite content at the expense of alite and a decrease in C₃A content.
- (4) An augmentation of alite crystal size and imperfection of crystal habit from euhedral to subhedral.
- (5) At a dosage of 5 wt. % of SO₃, alite crystals reached up to four times the size compared to the reference clinker.
- (6) An increase in the volume of the belite unit cell by 0.2 % at a content of 5 wt. % of SO₃.

Designation of clinker	Average size	Standard deviation	Coefficient of variation	Maximum size
0	28.6	13.62	0.488	65
5S	113.9	55.55	0.509	190
2Li	217.2	91.68	0.433	475*
3Cu	67.8	33.28	0.503	135

* This is a cluster of intergrown alite crystals.

TABLE 6. Average and maximum detected alite crystal size [μm].

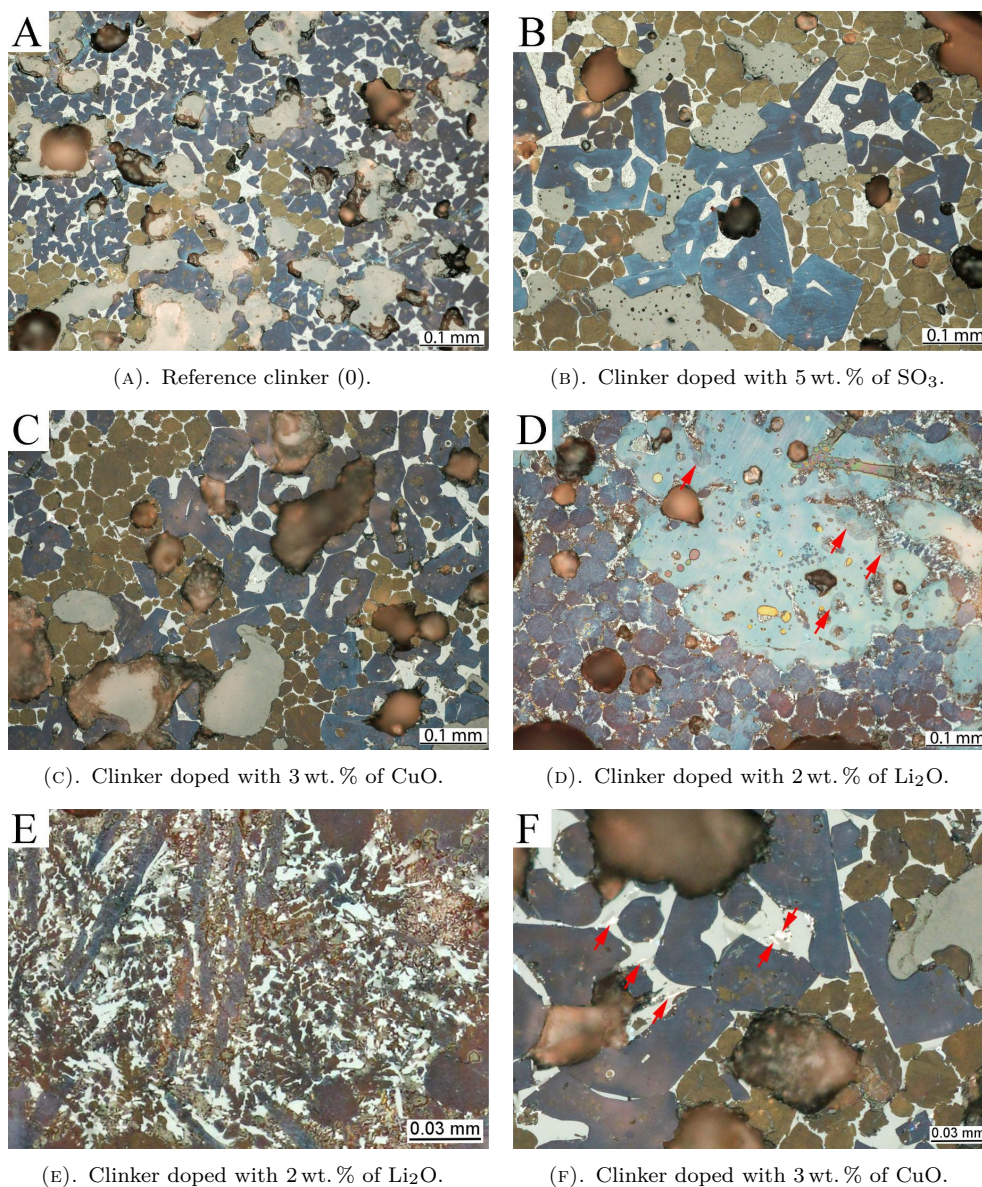


FIGURE 7. Micrographs of polished sections of clinkers etched with acetic acid fumes, reflected light.

Copper doping in the form of CuO led to:

- (1.) A decrease in the clinker melt formation temperature by 85°C at a theoretical content of 3 wt.% of CuO compared to the reference raw meal.
- (2.) A decrease of about 65°C in the peak exotherm maximum of belite formation at 3 wt.% of CuO .
- (3.) An increase in C_4AF content and a decrease in C_3A content.
- (4.) Formation of a new phase – cuprite (Cu_2O).
- (5.) An increase in alite crystal size and imperfection of crystal habit from euhedral to subhedral.
- (6.) At a dosage of 3 wt.% of CuO , alite crystals reached two and a half times the size compared to the reference clinker.
- (7.) A reduction of the belite unit cell volume by 0.14% at a content of 3 wt.% of CuO .

Lithium doping in the form of Li_2CO_3 resulted in:

- (1.) A decrease in the clinker melt formation temperature by up to 80°C at a theoretical content of 0.5 wt. % of Li_2O and by about 130°C at 3 wt. % of Li_2O compared to the reference raw meal.
- (2.) A decrease of about 70°C in the peak exotherm maximum of belite formation at 0.5 wt. % of Li_2O .
- (3.) A decrease of 50°C in the endotherm minimum of CaCO_3 decomposition at 3 wt. % of Li_2O , with a splitting of the endotherm.
- (4.) An increase in the content of C_4AF , alite, and free lime, and a decrease in the content of C_3A .
- (5.) Formation of new phases – Li_2SO_4 , LiFeO_2 (identification of these phases should be verified by other experiments and analyses).
- (6.) An increase in alite crystal size and imperfection of crystal habit from euhedral to anhedral.
- (7.) At a dosage of 2 wt. % of Li_2O , alite crystals and their clusters reached up to seven and a half times the size compared to the reference clinker.
- (8.) A reduction of the belite unit cell volume by 0.34 % at a content of 2 wt. % of Li_2O .

The observed changes in clinker composition, crystal growth, and phase formation highlight the importance of quality control and product development in the cement industry. Manufacturers may need to adjust their production processes and formulations to account for the effects of dopants on the cement properties. Additionally, the development of new cement formulations incorporating dopants could lead to a production of innovative cement products with tailored properties for specific applications.

The insights gained from this study offer opportunities for improving the efficiency, sustainability, and performance of cement production processes, ultimately contributing to the ongoing advancement of the cement industry.

LIST OF SYMBOLS

C	CaO
S	SiO_2
A	Al_2O_3
F	Fe_2O_3
C_3S	Ca_3SiO_5 , alite, tricalcium silicate
C_2S	Ca_2SiO_4 , belite, dicalcium silicate
C_3A	$\text{Ca}_3\text{Al}_2\text{O}_6$, tricalcium aluminate
C_4AF	$\text{Ca}_2(\text{Al, Fe})_2\text{O}_5$, brownmillerite, tetracalcium aluminoferrite
C	CaO , free lime
CH	$\text{Ca}(\text{OH})_2$, portlandite
Rwp	Weighted R-profile residual
GOF	Goodness of Fit

ACKNOWLEDGEMENTS

This research was carried out within project number GA23-05082S, financed by the Czech Science Foundation.

REFERENCES

- [1] C. J. Engelsen. Effect of mineralizers in cement production. Tech. Rep. SBF BK A07021, SINTEF Building and Infrastructure, 2007. [2025-01-30]. https://www.sintef.no/globalassets/sintef-byggforsk/coin/sintef-reports/sbf-bk-a07021_effect-of-mineralizers-in-cement-production.pdf
- [2] V. V. Timašev, A. P. Osokin. Fiziko-khimitcheskie osnovy formirovaniya struktury i svoystv klinkera [In Russian; Physico-chemical basics of the structure formation and properties of clinker]. *Cement* **9**:4–6, 1982.
- [3] A. P. Osokin, E. N. Potapova. Alitbildung in Oxid-Salz-Schmelzen. Struktur und Eigenschaften der flüssigen Klinkerphase [In German; Alite formation in oxide-salt melts. Structure and properties of the liquid clinker phase]. *Silikattechnik* **40**(1):4–6, 1989.
- [4] I. Maki, K. Goto. Factors influencing the phase constitution of alite in Portland cement clinker. *Cement and Concrete Research* **12**(3):301–308, 1982. [https://doi.org/10.1016/0008-8846\(82\)90078-3](https://doi.org/10.1016/0008-8846(82)90078-3)
- [5] T. Staněk, P. Sulovský. The influence of the alite polymorphism on the strength of the Portland cement. *Cement and Concrete Research* **32**(7):1169–1175, 2002. [https://doi.org/10.1016/S0008-8846\(02\)00756-1](https://doi.org/10.1016/S0008-8846(02)00756-1)
- [6] X. Li, H. Huang, J. Xu, et al. Statistical research on phase formation and modification of alite polymorphs in cement clinker with SO_3 and MgO . *Construction and Building Materials* **37**:548–555, 1985. <https://doi.org/10.1016/j.conbuildmat.2012.07.099>
- [7] J. Strunge, D. Knöfel, I. Dreizler. Einfluss der Alkalien und des Schwefels auf die Zementeigenschaften [In German; Influence of alkalis and sulfur on cement properties]. *Zement-Kalk-Gips* **38**(3):150–158, 1985.
- [8] T. Staněk. The influence of SO_3 and MgO on kinetics of alite formation. *Procedia Engineering* **151**:26–33, 2016. <https://doi.org/10.1016/j.proeng.2016.07.353>
- [9] O. Sheshukov, M. Mikheenkov. Peculiarities of Portland cement clinker synthesis in the presence of a significant amount of SO_3 in a raw mix. In H. M. Saleh (ed.), *Cement Industry – Optimization, Characterization and Sustainable Application*. IntechOpen, 2021. <https://doi.org/10.5772/intechopen.94915>
- [10] J. I. Bhatti. Role of minor elements in cement manufacture and use. *Research and Development Bulletin* p. RD109T, 1995.
- [11] I. P. Saraswat, V. K. Mathur, S. C. Ahluwalia. Thermal studies of the CaCO_3 : SiO_2 (2:1) system containing lithium as dopant. *Thermochimica Acta* **97**:313–320, 1986. [https://doi.org/10.1016/0040-6031\(86\)87033-2](https://doi.org/10.1016/0040-6031(86)87033-2)
- [12] V. K. Mathur, R. S. Gupta, S. C. Ahluwalia. Lithium as intensifier in the formation of dicalcium silicate phase. In *Proceedings of the 9th International Congress on the Chemistry of Cement*, vol. 2, pp. 406–412. 1992.
- [13] T. Staněk, I. Khongová, A. Zezulová, et al. Method of intensifying cement clinker production. In *Proceedings of the 16th International Congress on the Chemistry of Cement 2023 – ICC2023*, vol. 1, pp. 62–65. Thailand Concrete Association, 2023.

- [14] G. Kakali, G. Parissakis, D. Bouras, et al. A study on the burnability and the phase formation of PC clinker containing Cu oxide. *Cement and Concrete Research* **26**(10):1473–1478, 1996. [https://doi.org/10.1016/0008-8846\(96\)00143-3](https://doi.org/10.1016/0008-8846(96)00143-3)
- [15] X.-W. Ma, H.-X. Chen, P.-M. Wang. Effect of CuO on the formation of clinker minerals and the hydration properties. *Cement and Concrete Research* **40**(12):1681–1687, 2010. <https://doi.org/10.1016/j.cemconres.2010.08.009>
- [16] K. G. Kolovos, S. Tsvivilis, G. Kakali. SEM examination of clinkers containing foreign elements. *Cement and Concrete Composites* **27**(2):163–167, 2005. <https://doi.org/10.1016/j.cemconcomp.2004.02.003>
- [17] S. Ma, X. Shen, X. Gong, B. Zhong. Influence of CuO on the formation and coexistence of $3\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot\text{CaSO}_4$ minerals. *Cement and Concrete Research* **36**(9):1784–1787, 2006. <https://doi.org/10.1016/j.cemconres.2006.05.030>
- [18] A. Ghosh, T. K. Bhattacharya, B. Mukherjee, S. K. Das. The effect of CuO addition sintering of lime. *Ceramics International* **27**(2):201–204, 2001. [https://doi.org/10.1016/S0272-8842\(00\)00064-X](https://doi.org/10.1016/S0272-8842(00)00064-X)
- [19] N. Gineys, G. Aouad, F. Sorrentino, D. Damidot. Incorporation of trace elements in Portland cement clinker: Thresholds limits for Cu, Ni, S or Zn. *Cement and Concrete Research* **41**(11):1177–1184, 2011. <https://doi.org/10.1016/j.cemconres.2011.07.006>
- [20] M. Boháč, D. Kubátová, M. K. Kotlánová, et al. The role of Li_2O , MgO and CuO on SO_3 activated clinkers. *Cement and Concrete Research* **152**:106672, 2022. <https://doi.org/10.1016/j.cemconres.2021.106672>
- [21] Q. Deng, M. Zhao, M. Rao, F. Wang. Effect of CuO-doping on the hydration mechanism and the chloride-binding capacity of C_4AF and high ferrite Portland clinker. *Construction and Building Materials* **252**:119119, 2020. <https://doi.org/10.1016/j.conbuildmat.2020.119119>
- [22] S. Chromý. Anfärben des freiem CaO und Silikate in anschliffen von Portlandklinker [In German; Etching of free CaO and silicates in polished sections of Portland clinker]. *Zement-Kalk-Gips* **27**:79–84, 1974.
- [23] R. Kondo, S. Choi. Mechanism and kinetics of Portland cement formation for and example of the solid-state reaction in the presence of a liquid phase. In *Proceedings of the 5th International Congress on the Chemistry of Cement 1968 – ICC1968*, vol. 1, pp. 163–171. 1968.
- [24] T. Staněk, P. Sulovský. Dicalcium silicate doped with sulfur. *Advances in Cement Research* **24**(4):233–238, 2012. <https://doi.org/10.1680/adcr.11.00021>
- [25] X. Li, G. Kang, S. Dou, et al. Preparation and properties of sulfur-modified alite calcium sulfoaluminate cement. *Materials* **17**(24):6258, 2024. <https://doi.org/10.3390/ma17246258>
- [26] Y. Tao, W. Zhang, N. Li, et al. Fundamental principles that govern the copper doping behavior in complex clinker system. *Journal of the American Ceramic Society* **101**(6):2527–2536, 2018. <https://doi.org/10.1111/jace.15393>
- [27] Y. Da, T. He, C. Shi, et al. Revealing the co-doping effects of fluorine and copper on the formation and hydration of cement clinker. *Construction and Building Materials* **335**:127516, 2022. <https://doi.org/10.1016/j.conbuildmat.2022.127516>
- [28] T. Staněk, A. Rybová, A. Zezulová, M. Boháč. Formation of clinker containing lithium. *Materials Science Forum* **955**:50–55, 2019. <https://doi.org/10.4028/www.scientific.net/MSF.955.50>