CuO AND ZnO ADDITION IN THE CEMENT RAW MIX: EFFECT ON CLINKERING PROCESS AND CEMENT HYDRATION AND PROPERTIES

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One reference and two modified mixtures, prepared by mixing the reference sample with 1.0 wt.% of chemical grade CuO and ZnO, were studied. The effect of the added oxides was evaluated on the basis of the unreacted lime after sintering, the hydration rate, the cement properties and the leaching behavior of clinkers, cements and cement pastes. The added oxides improve the burnability of the Portland cement raw mix and the strength development of the produced cements, without considerably affecting the hydration rate and the physical properties. Cu^{2+} *and* Zn^{2+} *are not readily leached from hydrated cement products made from Cu- and Zn-containing clinkers, possibly due to the high incorporation degree of* Cu^{2+} *and* Zn^{2+} *cations in the main clinker phases.*

INTRODUCTION

Industrial wastes from several processes have substituted for fuels and alternative raw materials in Portland cement production, incorporating through clinker sintering certain elements that even at low concentration exert a remarkable effect on the sintering process of cement raw mixture. Their subsequent stabilization in cement or mortar also makes a significant environmental contribution. Partial substitution of industrial wastes for raw materials or fossil fuels in cement kilns represents, therefore, an alternative source of energy, while meeting incineration standards and maintains the final product quality. Besides, this integrated activity offers additional revenues to the cement industry, as the disposal of wastes normally receives a financial incentive [1-4].

The behavior of minor elements in the crystallization of clinker phases and cement hydration and properties are fundamental parameters for the evaluation of benefits and risks of burning hazardous wastes. If industrial wastes and secondary fuels are to be permitted as kiln feeds, it is important to demonstrate that clinker properties are not impaired and that toxic heavy metals are not readily leached from hydrated cement products. Data in support of this must be relevant to industrial practice yet contain sufficient fundamental data to permit independent verification and to be of general applicability.

Previous works by the authors demonstrated that certain foreign elements exert a positive effect during burning by accelerating sintering reactions and by improving the reactivity of the raw mix, despite of their low concentration [5, 6]. In this paper, ZnO and CuO were selected in order to introduce Zn and Cu in a Portland cement raw mix and to study their effect on cement hydration and properties. The two metals (Cu and Zn) were chosen using the following criteria: (1) positive effect in clinker sintering, (2) high incorporation degree in clinker structure, (3) literature data about their presence in natural or secondary cement raw materials, (4) literature data about their different reaction path on hydration according to their source in cement and (5) potential environmental risks of a future use of such modified cements.

Zinc oxide can be found in a variety of sources, mainly from waste-derived fuels such as car tyres, the rubber of which contains up to 4 wt.% ZnO [7]. Additional Zn sources are some metallurgical slags, which could contain up to 10 wt.% ZnO. Copper oxide is found in dusts and galvanic sludges recovered after gas treatment in steel factories and foundries, which use scrap as raw material [8]. These wastes are usually treated before disposal by means of solidification/stabilization techniques, using cementitious materials. The potential of reusing these wastes in construction materials is less studied, but some examples can be found in the literature [9].

Thorough literature review on the role of zinc oxide in cement clinkering and hydration has been published by Bolio-Arceo and Glasser [7, 10] and Olmo et al. as well [9]. The cycles of ZnO in the industrial process were studied by Sprung and Rechenberg [11, 12] and a 82-91% retention in clinker was determined, similarly to recently published studies [6, 8]. Generally it is believed that ZnO addition improves the burning behavior of the raw mix and accelerates the clinker formation [6]. ZnO acts both as mineralizer and flux leading to higher activity and promoting the solid reactions as well as the formation of alite by increasing the amount of liquid phase [13-15]. Odler et al. [16] studied the assimilation of zinc oxide in C_3S*, while the incorporation of ZnO in the aluminates has been thoroughly investigated, again by Bolio-Arceo and Glasser [7].

The influence of ZnO on hydration behavior has also been studied [9-12, 17-23]. Arliguie and Grandet [21, 22] reported that an amorphous $Zn(OH)_2$ layer is formed during the hydration of C3S phase in the presence of Zn, thus retarding the hydration of this phase. Mollah et al. [24], also suggested the formation of $CaZn_2(OH)_6 \cdot 2H_2O$ surface layer, which inhibits the water transport to C_3S phase. Soluble zinc salts added to mix water cause retardation [18, 25, 26]. While the reported extent of retardation and its mechanism vary somewhat, the general principle that retardation occurs is not in doubt. Zinc oxide and hydroxides are also retarders of cement hydration, especially at concentrations above 0.3 wt.%, although the long-term strength gain of Zn-rich cement has been reported to be unaffected [9]. Finally, studies concerning the hydration of C_3A phase in the presence of Zn concluded that hydration is influenced by the amount of sulfate in cement. When the concentration of sulfate is higher than 2.5 wt.%, the hydration of C_3A is retarded. Tashiro and Oba [27] reported that the hydration of C_3A phase is partially hindered in the presence of ZnO; when the substitution is 20 mol% ZnO, a very small amount of hydrate is formed, even after 28 days of curing. Retardation of the early hydration of C_3A is also confirmed by Differential Calorimetry. The compressive strength of hardened C_3A is not affected in the presence of 20 mol% ZnO up to 28 days. Of great importance are the remarks by Bolio-Arceo and Glasser [10] who were the first that illustrated the importance of the Zn-source in the cement hydration. They showed that zinc incorporated in clinker follows a different reaction path than Zn from other sources. Setting times and compressive strengths are related to the amount of zinc present and the general chemistry of clinker. In general, small amounts of zinc oxide do not affect setting times or compressive strengths, but as ZnO contents are increased setting times increases and compressive strengths decreases.

Similarly to Zn, the effect of Cu on the clinkering process has also been reviewed in the past, though in a lesser extent [28, 29, 6]. CuO acts both as mineralizer and flux. It decreases the melt temperature by at least 50°C, even for 0.5 wt.% addition in the raw meal, and favours the combination of free lime even at 1100°C [29, 6]. CuO accelerates the C_3S formation whose crystals appear larger in size - compact, prismatic and angular in shape [30]. Although CuO is volatile at kiln temperature (melting point: 1326°C), a 99% incorporation degree in clinker has been found [6, 8].

The effect of Cu on the hydration of cement phases has also been studied. The addition of 2.0 wt.% CuO strongly delays the hydration even after 28 days and its action is related to the formation of $Cu(OH)_2$ during the first days of hydration [18]. Cu retards the setting of cement, due to the formation of compounds, which cover the silicate phases [26]. Soluble copper salts are retarders and give low heat of hydration [28]. The effect is more pronounced on the C_3A phase [27]. According to Miller [31], the addition of Cu also gives low sulfate expansion in certain cases.

The above literature review shows that previous research has been focused either on the effect of CuO and ZnO on the clinkering process and their incorporation in the clinker phases or on the retarding effect of Zn and Cu compounds added directly in cement. This paper concerns the addition of 1.0 wt.% ZnO and CuO in a Portland cement raw meal and their effect on cement hydration and properties. Finally the leaching behavior of these elements in clinker, cement and cement pastes, is evaluated according to the Toxicity Characteristic Leaching Procedure (TCLP).

EXPERIMENTAL

Materials

Portland cement raw meal of industrial origin was used. The raw meal had a residue at 90 micron of 17%. The chemical composition of the raw mix as well as the mineral composition (according to Bogue) and the moduli of the obtained clinker are presented in table 1.

Table 1. Characteristics of the raw mix and the produced clinker.

Raw mix		Clinker			
Chemical composition (wt.%)		Mineral composition (Bogue) (wt.%)		Moduli	
SiO_2	13.76	C_3S	71.1	LSF	0.981
Al_2O_3	3.23	C_2S	7.7	SM	2.42
Fe_2O_3	2.45	C_3A	6.9	AR	1.32
CaO	43.11	C_4AF	11.6	HM	2.22
MgO	0.55				
K_2O	0.28				
LOI	35.62				

Burning procedure and clinker structure

One reference and two modified mixtures, prepared by mixing the reference raw meal with 1.0 wt.% of chemical grade CuO or ZnO, were examined. All samples were pressed to form pellets, sintered at 1450°C for 30 minutes in an electrical furnace and cooled rapidly in air. The unreacted lime (free lime) in clinker was determined according to the standard ethylene glycol method. The sintering reactions in all samples were recorded by means of Differential Thermal Analysis using a Mettler Toledo TGA/SDTA 851 instrument. The temperature was raised at a constant rate (10°C/min) from ambient to 1450°C.

Mineralogical studies of the sintered samples were performed using a Siemens D-5000 X-Ray Diffractometer, with CuKa$_1$ radiation ($\lambda = 1.5405$ Å). Scanning Electron Microscopy was used in order to examine the structure of the obtained clinkers and the distribution of Cu and Zn in its main phases, using a JEOL JSM-5600 Scanning Electron Microscope, interfaced to an OXFORD LINK ISIS 300 Energy Dispersive X-Ray Spectrometer (EDS). Experimental conditions involved 20 kV accelerating voltage and 0.5 nA beam current.

Cement hydration and properties

All clinkers were inter-ground with 5.0 wt.% gypsum in a pro-pilot plant ball mill of 5 kg capacity. The gypsum was of industrial origin (98 wt.% $Ca_2SO_4 \cdot 2H_2O$, 46.7 wt.% SO_3). The fineness of all the produced cements was found to be in the range between 3500 and 3700 cm^2/g (Blaine). The compressive strength of the samples (EN 196-1) as well as the consistency of the standard paste and the setting time (EN 196-3) was determined. The compressive strength is calculated as the arithmetic mean of six individual results. If one result within the six individual results varies by more than ±10 % from the mean, this result is discarded (EN 196-1). In our experiments, no result was discarded and the standard deviation was in the range 1.1-2.0 % (for example, the standard deviation of the 28 days strength of the reference sample was 0.55 N/mm^2 or 1.47 %).

The cements were mixed with water in order to prepare cement pastes. A water-to-cement ratio (*W*/*C*) of 0.4 was retained for all pastes and deionized water was used. After a period of 6 hours the cement cores where put in polyethene containers (vials), sealed hermetically and wet-cured at 20°C. Samples hydrated for periods of 1, 2, 7, and 28 days were subjected to acetone and isopropyl ether treatment and then dried for 24 hours in vacuum. TGA was used for the determination of total compound water, calcium hydroxide and water in the hydration products in dried cement paste samples using the thermobalance Mettler Toledo TGA/SDTA 851 instrument. The samples were heated over the range 20 to 600°C at a constant rate of 15°C/min in air (static) atmosphere. A limited number of samples were treated up to 1000°C in order to confirm that there was no transformation of $Ca(OH)_2$ to $CaCO_3$.

Leaching tests

Leaching tests for Cu and Zn heavy metals were conducted according to the TCLP (Toxicity Characteristic Leaching Procedure) for clinkers, cements and hydrated products at the ages of 1, 2, 7 and 28 days [32, 33]. The leaching solution used was deionized water, *pH*-adjusted to 6.0. All materials were first crushed to pass a 2 mm sieve [34] (clinkers and cement pastes), then mixed with the leaching solution (solid:liquid = = 1:10 w/w) in hermetically sealed polyethene containers (vials), stirred for 24 hours in a stirring device at ambient temperature and then filtered. In all filtered solutions *pH* was kept constant in the range of 11.0-13.0 by feedback control and addition of 0.1N NaOH solution [33], whereas Cu and Zn concentrations were analyzed by Differential Pulse Anodic Stripping Voltammetry (DPASV).

RESULTS AND DISCUSSION

Effect on the burnability of the raw mix

Differentiations on the burnability of the raw mixtures were evaluated on the basis of the unreacted lime (fCaO) content in the sintered products. All fCaO values, mentioned below, are the average values of three burning experiments. fCaO values for control and CuO and ZnO modified clinkers correspond to the values of 2.43, 1.27 and 1.77 % respectively. The decrease of fCaO values (47 % for CuO and 27 % for ZnO doped sample) implies a strong positive effect on the burnability of the Portland cement raw mix for both additions, especially in CuO modified sample. Similar data have been extracted in previous studies [6], where it was confirmed that the overall reactivity of the raw mix could be correlated with the electron configuration of the added ions, in the same way as the properties of the melt. Possibly, the addition of small amount of Zn^{2+} and Cu^{2+} alters extensively the properties of the melt and these modifications of the melt properties are reflected on the reactivity and burnability of the raw mix, which is very important in the case of the cement production.

Calorimetric studies of modified clinkers

Figure 1 presents the DSC curves of pure and raw mixtures containing 1.0 wt.% CuO and ZnO. In all modified samples the reactions associated with the decomposition of $CaCO_3$ (in the temperature range of 800-900°C) and clinkerization (1200-1450°C) are recorded, suggesting satisfactory burning and clinkerization of all samples. Especially in CuO-doped sample, belite formation is segmentally completed at lower temperatures. In both modified mixtures the formation of the melt (endothermic reaction in the range 1300-1400°C) is shifted to lower temperatures and overlapped with the belite formation. That was also confirmed by the accelerated consumption of free lime. This fact indicates that the Cu^{2+} and Zn^{2+} cations are partially dissolved in the liquid phase, affecting mainly the formation and the properties of the melt and therefore change the reactivity of the mixture at high temperatures.

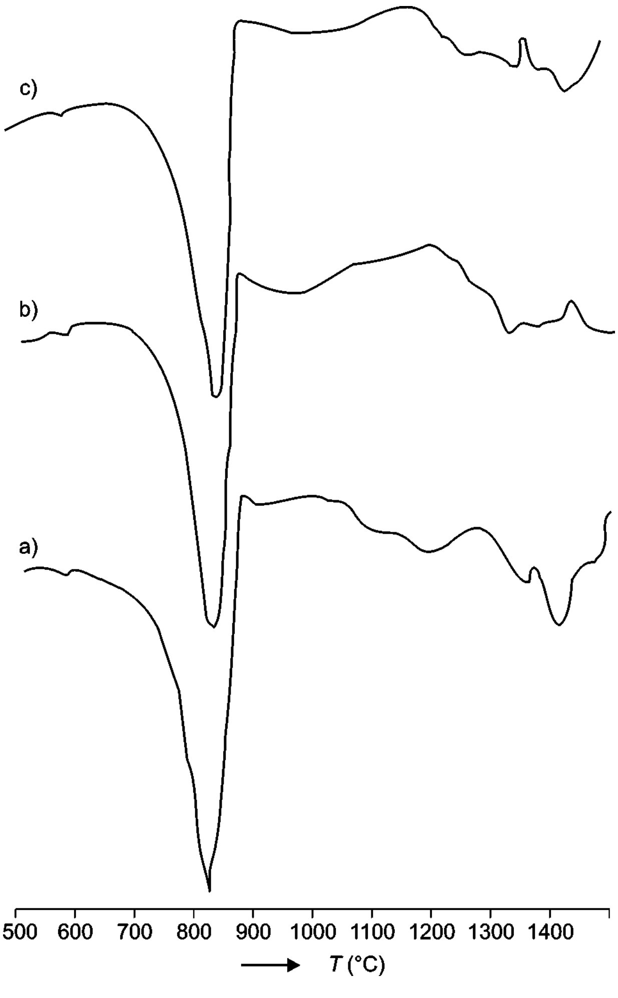


Figure 1. DSC curves of raw samples; a) Reference, b) Ref. + CuO, c) Ref. + ZnO.

XRD and SEM studies of modified clinkers

From the XRD studies (figure 2) it was proved that all sintered samples correspond to the structure of a typical clinker with well-crystallized dominant phases and higher alite percentages. No detection of undesired compounds (γ-C_2S) was recorded. Differentiations among samples were restricted in calcium aluminate and ferrite, due to the selective incorporation of Cu and Zn in these phases and the changes that occur in their chemical composition and structure. Pure clinker and clinkers prepared from raw meal containing 1.0 wt.% Cu and Zn oxides were examined under a Scanning Electron Microscope. Photos of these samples are presented in figure 3. The areas presented in the photos were selected to be representative as far as the size and the shape of alite and belite crystals are concerned. The SEM observations are summarized in table 2.

Table 2. Size and shape of alite and belite crystals in modified clinkers.

Sample	Alite		Belite	
	Size (μm)	Shape	Size (μm)	Shape
Reference	20-30	compact, prismatic, with slightly rounded outline	5-10	Small, roundish
Ref.+CuO	40-60	large compact, prismatic, angular	10-30	roundish
Ref.+ZnO	20-40	large, rounded at the rims	10-20	round

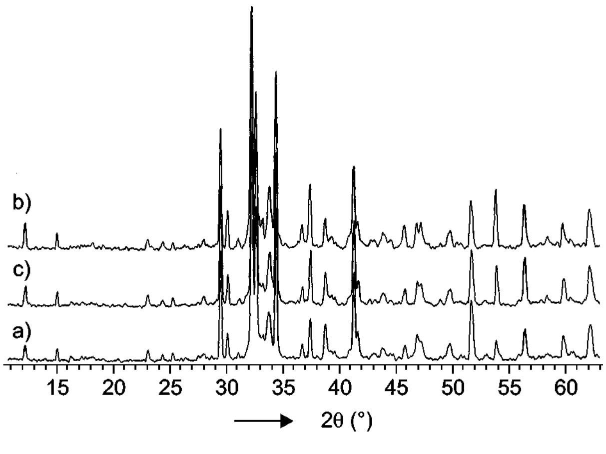
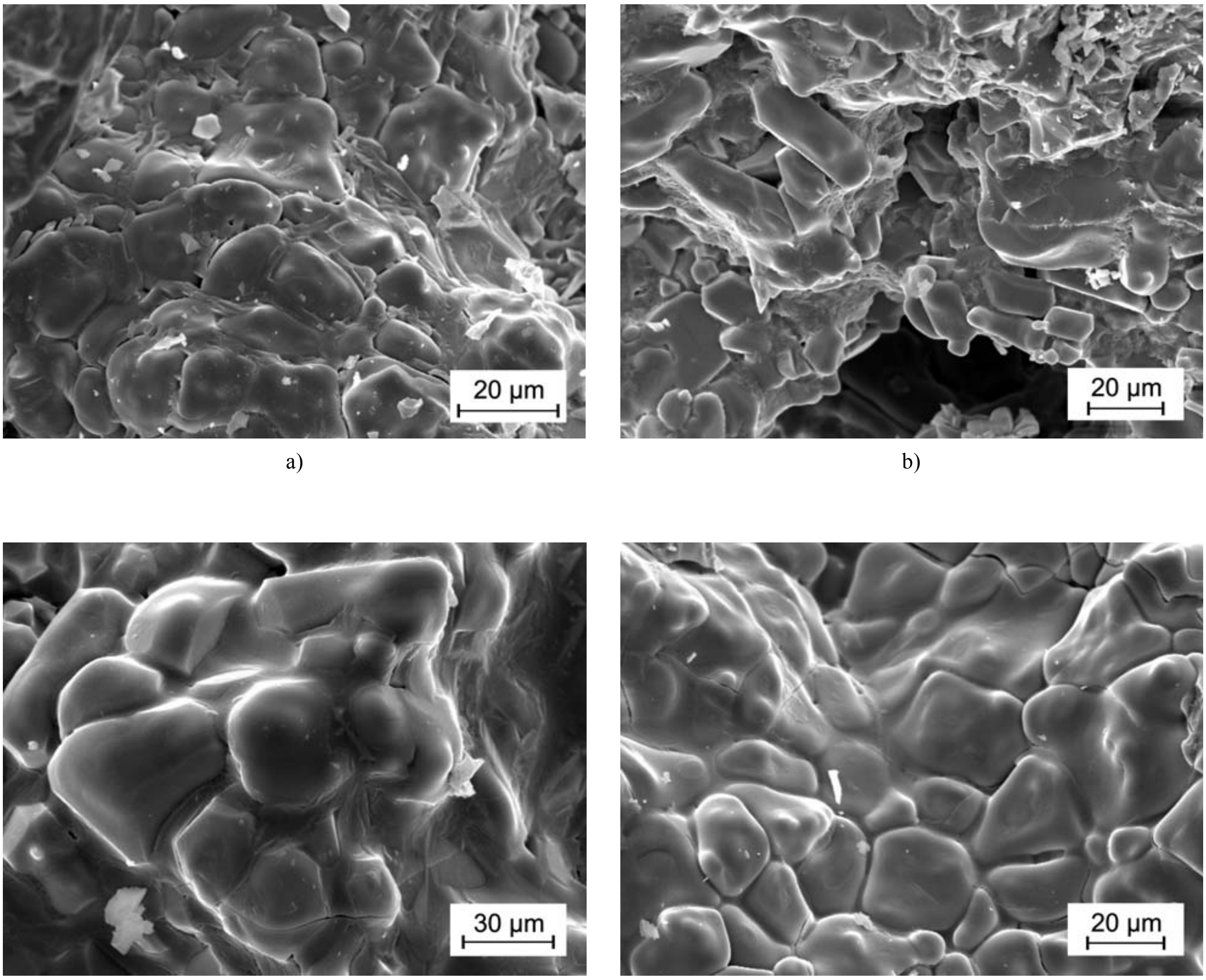


Figure 2. XRD patterns of sintered samples; a) Reference, b) Ref. + CuO, c) Ref. + ZnO.



a) b)

c) d)

Figure 3. SEM photos of reference and modified clinkers; a) Reference, b,c) Ref. + CuO, d) Ref. + ZnO.

Differentiations are related to the size and shape of alite and belite phases. In both modified samples alite was developed in profuse, as large, compact, prismatic and angular crystals in Cu-doped sample, large and rounded in Zn-doped sample. In comparison to the other samples, in Cu-doped sample the packing of silicate grains is so dense that little interstitial phase exists between them. Indications exist about the appearance of a new phase in the form of $CaCu_2O_3$. The detection of the $CaCu_2O_3$ phase was reported in clinkers, originated from a synthetic raw mix, doped with 2.5 wt.% CuO and sintered at 1450°C [30]. Details concerning a similar configuration in CuO and ZnO modified clinkers, originating from chemical grade raw mixes, have also been published in [30].

Hydration rate of cements pastes

Cement pastes were studied by means of a TGA analyzer. The weight loss up to 550°C, which corresponds to the total water incorporated to the cement paste, was determined. The $Ca(OH)_2$ content, which is directly related to the hydration of silicate compounds was also measured. The weight loss in the range of 600-700°C, if any, corresponds to the CO_2 of $CaCO_3$ and it has to be converted to the equivalent $Ca(OH)_2$ and then to equivalent H_2O. The carbonation of the paste is an accidental event that may take place during the preparation of the paste or during the grinding of the paste previous to the TG measurement. The water combined in the hydration products (other than calcium hydroxide) corresponds to the weight loss up to 300°C. Any changes of this amount indicate that the kind and/or the stoichiometry of the hydration products are changed. Table 3 presents the percentage of total compound water, calcium hydroxide and water in the hydration products in relation to the added oxide in the raw sample and the age of hydration.

From table 3 it can be seen that with 1.0 wt.% CuO and ZnO addition in the raw mix the total rate of hydration tends to slow down, compared to reference sample, as it is indicated by the progressive decrease of water and calcium hydroxide content in the pastes. Retardation is more intense in early ages (1 and 2 days) and in samples with CuO. However, in the course of time, hydration accelerates so that differentiations on the wt.% percentage of calcium hydroxide at the age of 28 days are significantly low (less than 9 %). These retardation phenomena, recorded mainly for CuO-enriched samples are probably related with the formation of amorphous salts, originated from the Cu^{2+} ions and the dissolved Ca^{2+} ions from the cement paste that cover the anhydrous grains of clinker phases, especially those of alite, inhibiting their hydration [32]. Especially for copper, in the form of $Cu(OH)_2$, the retardation effect on C_3S is reported in the literature, since it appears not only in the early ages but also at the age of 28 days [35]. Nevertheless, the results for ZnO pastes do not support the well-known retardation act of Zn in the same extent as when ZnO is added directly in cement, making cement setting impossible [10].

Table 3. Total compound water, calcium hydroxide and water in the hydration products of the studied samples.

Sample	Hydration age (days)			
	1	2	7	28
	Compound water (wt.%)			
Reference	10.15	11.17	16.21	21.67
Ref. + CuO	7.33	9.00	15.29	18.27
Ref. + ZnO	10.44	11.6	16.00	18.49
	$Ca(OH)_2$ (wt.%)			
Reference	17.14	19.84	23.78	26.00
Ref. + CuO	13.62	14.96	21.14	23.68
Ref. + ZnO	17.22	17.66	22.21	24.38
	Water in hydrated products (wt.%)			
Reference	5.98	6.34	10.43	15.35
Ref. + CuO	4.02	5.36	10.15	12.51
Ref. + ZnO	6.25	7.30	10.60	12.56

Tests of consistency, setting and strength

CuO and ZnO addition has no effect on the water demand of the cement paste. The consistency of the standard paste for the modified cements varies from 26.1 % to 26.7 % while the relative value for the pure cement is 26.5 %.

Figure 4 presents the setting time of the produced cements in relation to the added oxides. It can be seen that the added oxides lead to a slight increase of the setting time (especially the final setting time) and this phenomenon is more obvious in the case of the CuO modified cement paste. The retardation on setting that was recorded at that particular sample is probably attributed to the Cu^{2+} effect on hydration rate and is in agreement with the TG measurements. The slight increase on setting times observed at the ZnO modified cement paste is undoubtedly weaker than the one published for cements containing free Zn compounds. In any case the recorded setting times lie within the limits settled by the European Standard (EN 197-1).

The soundness of the tested cements is satisfactory. The expansion measured according to Le Chatelier process varies from 0.5 mm to 1.5 mm whilst the limit according to EN 197-1 is 10 mm.

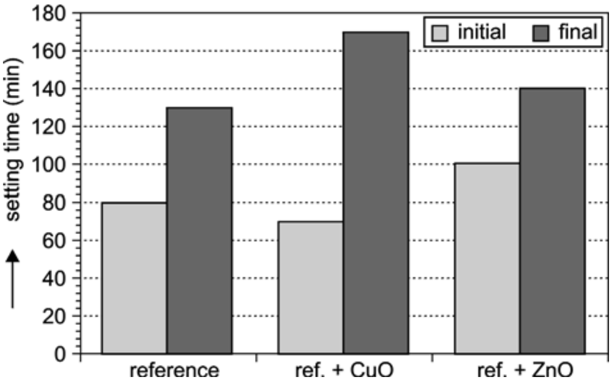


Figure 4. Setting time of the tested cements.

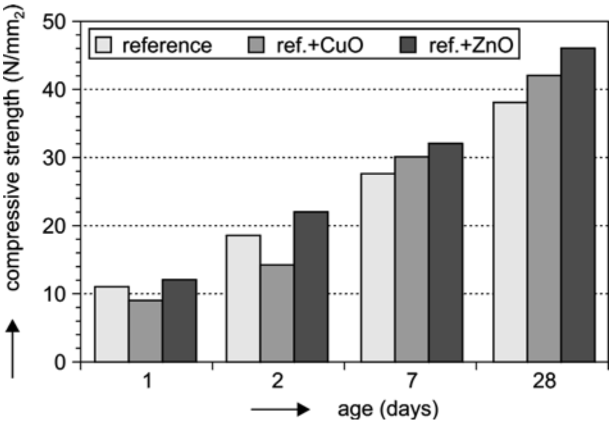


Figure 5. Strength development of the tested cements.

Figure 5 portrays the strength development of the produced cements in relation to the added oxides. Zn-enriched cement exerted the best results. As it is shown the addition of CuO and ZnO affects the compressive strength after 7 and more days in a positive way (a 9.6 and 19.2 % increase was recorded at 28 days respectively compared to the reference cement). Possibly, this is attributed to the positive effect of CuO and ZnO addition on the alite content, also found by the XRD and SEM tests, and the modifications caused on the configuration and development of C_3S crystals toward reference. Such modifications reflected on the properties of the melt influence, decisively, the environment of alite development, leading to a selective formation of more active C_3S polymorphs and, consequently, to a higher hydraulic activity [28]. A decrease of the early ages strength was observed only for CuO sample (20.8 % decrease at 2 days) and is attributed to the retarding effect in the initial stages of hydration, also reflected on setting times. On the contrary, the 2 days strength development for ZnO modified sample exhibits a 16.9 % increase, in comparison to the reference cement.

From the above results it is concluded that CuO and ZnO addition in the cement raw mix favors the mechanical properties of the produced cements and does not affect the physical properties.

Leaching tests

An assessment of a potential environmental risk by a possible application of CuO and ZnO containing cement clinkers as building materials was carried out on the basis of monitoring Cu and Zn release in water matrixes. Since both metals are considered as toxic, their leaching concentrations lie under strict limitations.

All measured values for Cu and Zn leaching concentrations are shown in table 4. As it can be seen, Cu and Zn concentrations in clinker leachates were below the DPASV detection limits (0.5 ppb both for Cu and Zn). A slight increase in Cu and Zn concentrations was recorded at 7 and 28 days cement pastes leaching solutions, especially for Cu. However these values prove to be extremely low, significantly less than permissible levels. Of course, the long term leachability of these materials needs to be further investigated.

Table 4. Cu and Zn concentrations (ppb) in leachates.

Sample	Concentration (ppb)	
	Cu	Zn
Clinker	n.d*	n.d*
Cement	1.3	n.d*
Cement paste 1 day	1.6	0.8
Cement paste 2 days	2.8	1.2
Cement paste 7 days	23.0	3.7
Cement paste 28 days	24.1	3.6

* n.d.: not detected

The low amounts of leached Cu and Zn in all materials (clinkers, cements and hardened pastes) are attributed to the high incorporation degree of Cu^{2+} and Zn^{2+} cations in the main clinker phases. Since much of the Cu^{2+} or Zn^{2+} cations added are occluded within clinker grains, they are only available for release slowly, as hydration progresses.

Solubility data for Zn indicate that zinc held in clinker phases is very insoluble (below 2 ppm in the aqueous phase). This partly explains the lack of retardation as aqueous zinc concentrations are never sufficiently high as to led to significant retardation [10]. Additionally the high alkaline environment of the hardened cement paste is an extra reason for a lower leachability for Cu and Zn, since it is well known that the highest leachability for heavy metals is recorded at acidic pH, contrary to the higher leachability of their oxy-anionic species (e.g. CrO_4^{2-}, MoO_4^-, VO_4^{3-}, AsO_4^{3-}) that is recorded at mild alkaline to neutral pH [33].

CONCLUSIONS

From the present study the following conclusions can be drawn:

- CuO and ZnO, when added in cement raw mix, promote the sintering reactions and improve the burnability of the mixture.
- The added oxides do not alter the mineral composition of the clinker, but they affect the size and shape of alite and belite grains.
- The addition of 1.0 wt.% CuO and ZnO in the cement raw mix exerts a slight retarding effect on the hydration process, especially at the early ages. However, on the course of time, hydration rate increases and after 28 days differentiations are minimized.
- The added oxides exert a small increase in setting times. However, all setting times recorded, lie within the European Standard specifications (EN 197-1) and radically differ with the setting times of cements deriving from Portland cement mixed with CuO and ZnO rich materials.
- CuO and ZnO addition in the cement raw mix favors the cement strength development and does not affect the physical properties of the cements.
- The amounts of leached Cu and Zn in all materials (clinkers, cements and hardened pastes) were extremely low and this is attributed to the high incorporation degree of Cu^{2+} and Zn^{2+} cations in the main clinker phases.

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* Footnote:
Cement chemistry notation: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, C_3S = $3CaO.SiO_2$ (alite), C_3S = $2CaO.SiO_2$ (belite), C_3A = $3CaO.Al_2O_3$ (aluminate), C_4AF = $4CaO.Al_2O_3.Fe_2O_3$ (ferrite).

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PŘÍDAVEK CuO A ZnO V CEMENTÁŘSKÉ SMĚSI: ÚČINEK NA PROCES PŘÍPRAVY SLÍNKU, HYDRATACI CEMENTU A JEHO VLASTNOSTI

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Byly studovány jedna referenční a dvě upravené směsi připravené smíšením referenční směsi s 1.0 hmot.% CuO a ZnO. Účinek přidaných oxidů byl hodnocen na základě nezreagovaného vápence po slinování, rychlosti hydratace, vlastností cementu a vyluhovatelnosti slínků, cementů a cementových past. Přidané oxidy zvyšují účinnost výpalu referenční směsi Portlandského cementu a vývoj pevnosti připravených cementů, aniž by podstatně ovlivňovaly rychlost hydratace a fyzikální vlastnosti. Ionty Cu^{2+} a Zn^{2+} nejsou snadno vyluhovatelné z hydratovaných cementových produktů, pravděpodobně vzhledem k vysokému stupni jejich zabudování do struktury hlavních slínkových fází.