LOW ENERGY CEMENTS PREPARED FROM MODIFIED SO_3 DOPED CLINKERS

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Abstract

Clinkers doped with optimized combinations of SO_3 and Li_2O or CuO or MgO were synthetized in laboratory furnace at 1350 °C. Clinkers were characterized by light and scanning electron microscopy. Chemical and phase composition of clinkers is discussed with respect to early hydration properties of cements. Hydration of cement pastes was monitored by isothermal calorimetry and reaction kinetics corelated with early strengths. Flexural and compressive strengths of cements were determined after 2, 7, 28, 90 and 365 days of hydration according to EN 196 on mortars. At high CuO contents, Cu-rich phases form inclusions in C_2S. The limited incorporation of MgO into the structure of clinker phases is rep-resented in the form of inclusions in C_3S. Due to formation of $Cu(OH)_2$, hydration slows down significantly, while Li salts accelerate early hydration. For the studied modified SO_3 doped cements, there is a good correlation between heat development during the first 2 days and strength development during 1 year. Proposed four low-energy cements based on SO_3 doped clinkers burned at 100 °C lower temperature meet the requirement for CEM I strengths.

Introduction

SO_3 doped clinker is one of the ways to reduce energy consumption, CO_2 emissions and limestone mining. The clinker is prepared at temperatures 100 - 150 °C lower than Ordinary Portland cement (OPC) clinker. Despite the low alite content, this clink-er is reactive due to the stabilization of M1 alite modification by SO_3 and the presence of reactive forms of belite. Li_2O, CuO and MgO were selected as binary co-dopants.

Lithium is a strong mineralizer and supports the formation of melt decreasing its formation temperature, which is important for the formation of alite. Furthermore, it significantly reduces the viscosity of the melt, which leads to the formation of large grains of alite. Lithium salts accelerate the initial hydration and are also associated with higher initial strengths of the resulting materials. The reactivity of CuO doped clinker depends on its concentration and distribution in the clinker phases. CuO is preferably incorporated in ferrite and, at higher concentrations also alite, belite and aluminate [7–10]. The delayed effect of CuO on hydration 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. The combination of MgO and SO3 doping leads to stabilization of M1 or M3 depending on several factors but mainly on SO_3/MgO ratio. MgO itself promotes the formation of M3, but its incorporation into the clinker phases is small and an excess is in the clink-er in the form of periclase (MgO). The main influence of MgO on the reactivity of clinker and the resulting strength has the modification of alite or the ratio of M1 and M3.

The paper focuses on comparing the effect of Li_2O, CuO and MgO doping on low-energy SO_3 doped clinker prepared at 1350 °C. The role of selected dopants on clink-er phase composition, microstructure, reactivity and strength development is discussed.

Methodology

Materials

Common cementitious materials limestone, slate (quarry of the Mokrá cement plant) and Fe correction were used for clinker preparation in laboratory (see **Table 1**). Three mixtures modified by 0.5% Li_2O or 1% CuO or 2% MgO were prepared by mixing the reference sample doped with 4% of SO_3. Chemical grade $MgCO_3$, CuO, $LiCO_3$ and FGD gypsum were used. Preparation and synthesis were done in following steps: grinding of raw mix on 13 wt.% rest on 90 µm sieve, homogenization and compacting of raw mix, verification of~ 30 wt. % of C3S by equilibrium burning at 1350 °C of 100 g of material, fast cooling, grinding, homogenization and compacting, second burning at 1350 °C for with rate 10°C/min, fast cooling, compacting and third burning at 1350 °C for 2 hours. When the C_3S content was proved to be around 30 wt.%, the final burning of larger amount of material (6 kg) was carried out. The final burning was at 1350 °C with rate of 10 °C/min and 60 min hold. Cements were prepared by grinding clinker in the laboratory ball mill to fineness 400 $cm^2.g^{-1}$. Chemical grade $CaSO_4.2H_2O$ (G) was added to cement in an amount that was balanced according to early strengths and heat flow development.

Methods

Polished cross-section specimens from doped clinkers were used for light microscopy (LM) and scanning electron microscopy (SEM) investigation. Light microscope NIKON Eclipse LV 100ND was used for microstructural observation in reflected light. SEM analysis were performed by ZEISS EVO LS10 with an OXFORD X-Max 80 mm^2 EDS. The chemical composition of alite and belite was studied using point analyses. The distribution of sulfur, major and minor oxides was monitored using x-ray maps.

Quantitative X-ray (QXRD) diffraction analysis of sample was performed on Bruker D8 Advance apparatus with Cu anode ($\lambda K\alpha$ = 1.54184 Å) and variable diver-gence slits at Θ-Θ reflection Bragg-Brentano para focusing geometry. Quantitative phase analysis was done by Rietveld method with addition of inner standard. As a standard, fluorite (CaF_2) was used in amount of 20 wt. %.

Heat development related to early hydration was studied by isothermal calorimetry at 25 °C on cement pastes with w/c=0.4. Cements were mixed with deionized water ex-situ and placed in the calorimeter after few second of hydration.

Compressive and flexural strength after 2, 7, 28 and 365 days of hydration were determined according to EN 196 on mortars.

Table 1. Raw mix design

	B93 S4	B93 S4 Li0.5	B93 S4 Cu1	B93 S4 Mg2
		(g)		
Limestone (Coral)	2754.0	2754.0	2754.0	2754.0
Limestone (Dark)	1615.2	1615.2	1615.2	1615.2
Slate	1200.6	1200.6	1200.6	1200.6
Fe correction	94.2	94.2	94.2	94.2
FGD gypsum	336.0	336.0	336.0	336.0
$MgCO_3$	-	-	-	163.2
CuO	-	-	39.0	-
Li_2CO_3	-	48.3	-	-
Total	6000.0	6048.3	6039.0	6163.2

Table 2. Chemical and phase composition of doped clinkers

	B93 S4	B93 S4 Li0.5	B93 S4 Cu1	B93 S4 Mg2
	Chemical composition – wet chemistry (wt. %) (*mg/kg)			
SiO_2	22.98	22.95	22.92	22.59
CaO	61.45	61.1	61.28	60.44
Al_2O_3	4.92	4.89	4.93	5.01
Fe_2O_3	3.87	3.71	3.76	3.82
TiO_2	0.28	0.28	0.28	0.28
P_2O_5	0.06	0.07	0.07	0.06
Na_2O	0.26	0.27	0.26	0.26
K_2O	0.93	0.98	0.95	0.95
MgO	1.00	1.01	0.98	2.71
MnO	0.089	0.09	0.087	0.088
CaO (free lime)	0.38	0.47	0.39	0.47
Li_2O	-	0.63	-	-
CuO	-	-	0.90	-
SO_3 total	3.67	3.58	3.44	3.42
LOD	0.05	0.08	0.04	0.07
LOI	0.26	0.16	0.14	0.22
Cu	-	-	*7200	
Li	-	*2932	-	-
	Phase composition - QXRD / PM point counting (wt.%)			
ß-C_2S	57.7 / 57.5	52.1 / 50.6	53.8 / 53.4	54.9 / 54.7
C_3S (M1)	28.4 / 26.4	32.4 / 31.6	31.7 / 31.7	26.8 / 27.8
C_4AF	10.4 / 13.3	11.5 / 15.4	11.6 / 12.3	10.1 / 15.2
C_3A cubic	3.4 / 2.4	2.7 / 2.2	1.1 / 2.6	3.8 / 1.8
C_3A ortho.	0.1	0.2	0.4	0.2
CaO (free lime)	0 / 0.4	0 / 0.2	0.2 / 0.1	0 / 0.4
Anhydrite	0	1.1	1.2	1.1
Periclase	0	0	0	3.1
Lithium silicate		+		
Lithium aluminum silicate		+		

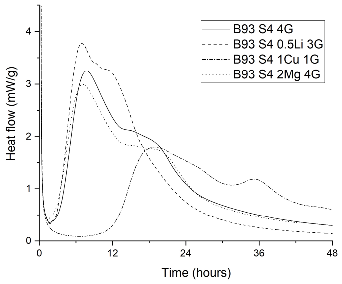

Fig. 1. Heat flow development of cement pastes, w/c=0.4

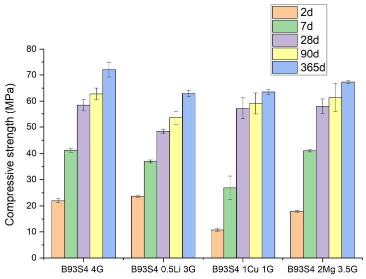

Fig. 2. Compressive strength development of mortars

Results

Phase composition.

QXRD results show that M1 C_3S and beta-C_2S are main silicate modifications in all clinkers. Microscopical examination revealed zonal or twinned crystals of alite in Li_2O and MgO doped clinker which are described as coexistence of M1 and. M1 C_3S and distorted crystals of C_2S in studied doped clinkers are sign of activation by SO_3 which does not only lead to formation of C_2S high-temperature modifications (α'_H and α). Chemical and phase composition of doped clinkers is given in **Table 2**.

Scanning electron microscopy.

Chemical composition of C_3S and C_2S was studied by point analyses and x-ray maps by SEM EDS. Compared to ordinary Portland cement clinker, reference SO_3 doped clinker has increased Ca/Si ratio in the structure of C_2S caused by substitution of SO_4^{2-} for SiO_4^{4-}. In the sample B93 S4 0.5Li, the Ca/Si ratio in C_2S is lower due to the smaller degree of substitution of SO4 into its structure. Along with SO_4, lower contents of Al_2O_3 and Fe_2O_3 are incorporated in the structure of C_2S. Direct determination of Li is not possible, but in terms of alkali content, it is clear that C_2S has higher K_2O and lower Na_2O contents. EDS analysis indicates that due to doping with CuO the incorporation of SO_4 and Fe_2O_3 into the C_2S structure is less extensive and results in lower Ca/Si ratio. The decrease in Ca concentration compared to the reference could be partly attributed to the substitution of CuO for CaO. The increased Cu content in C_2S (0.9 wt.%) is in this case caused by insufficient resolution of the point analysis. Upon closer observation on BSE images, it is evident that Cu phase is enclosed in belite grains in the form of inclusions. Inclusions with the size of tenths of a micron in belites are well distinguishable due to the higher backscattered electron coefficient η of the Cu phase. The incorporation of CuO into the C_3S structure results in substitution for CaO. Furthermore, CuO inhibits substitution of SiO_4 by SO_4. The lower Ca/Si ratio and lower concentrations of SO_3, Al_2O_3, Fe_2O_3 and MgO are the result of these two effects of CuO. Except for higher K_2O contents, the chemical composition of C_2S in MgO doped clinker is the same as in the reference clinker. The Ca/Si ratio in the C_3S is similar for the reference sample and the doped Li_2O and MgO sample. Part of the MgO can be found in C_3S in the form of inclusions. The rest of MgO is in the interstitial matter.

Hydration vs strength development.

The course of hydration was studied by isothermal calorimetry (**Fig. 1**) on cement pastes. Cements prepared from doped clinkers with optimal gypsum content (G) were investigated. Gypsum content was optimized based on mutual position of main silicate peak and 2nd aluminate peak and 2d strengths. As with OPC, a significant initial exotherm followed by a period of slow reactions, a major exotherm associated with C-S-H formation, and a major peak shoulder associated with a second stage of aluminate hydration after gypsum depletion can be observed for cements prepared from doped clinkers. Compared to the reference sample doped only with SO_3, the sample doped with Li_2O shows an accelerated development of heat during the first day of hydration. Then there is a very sharp slowdown in heat development after one day of hydration. As with OPC [6, 12], lithium is strong hydration accelerator for SO_3 doped cements. This accelerating effect is also evident in the strength development, where the lithium doped sample exhibits higher initial strengths, but this rapid increase is compensated by the subsequent slower strength development and lower long-term strengths (see **Fig. 2**).

Conclusion

- Higher concentrations of CuO in SO_3 doped clinker, similarly to OPC clinker, are accompanied by crystallization of Cu-rich compounds in interstitial matter, but al-so in the form of inclusions in C2S.
- The possibility of MgO incorporation in the clinker phases is considerably limited in SO_3 doped clinkers. MgO in excess exceeds in the form of periclase in interstitial matter or as inclusions in C_3S.
- During cooling, the Li rich melt is stable at lower temperatures than in normal or SO_3 doped clinker, which leads to decomposition of C_3S at the same cooling rate. The result of interaction of C_3S with the melt during cooling can be observed as microcrystalline mixture of CaO and C_2S on decomposed C_3S edges.
- The retarded hydration due to CuO and acceleration due to Li_2O is similar to that described for OPC. The role of CuO and Li_2O doping on strength development is similar for both SO_3 doped and OPC clinker. In case of MgO as co-dopant, the effect on hydration is ambiguous.

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