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Use of secondary mineralizing raw materials in cement production. A case study of a wolframite–stibnite ore

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Abstract

It has been found that certain foreign elements, despite their low concentration in cement raw mix, improve the reactivity of the cement raw mix. The aim of this research is to investigate the possibility of introducing small amounts of minerals, containing these elements, into the cement raw mix. A stibnite–wolframite mineral was selected in order to introduce W, Sb and S in the cement raw mix. One reference mixture and four modified mixtures, containing 0.5%, 1.0%, 1.5% and 2.0% w/w of the above mineral, were examined. The reactivity of the mixture, the sintering reactions, and the structure of the products were studied. In addition, the hydration rate and some typical properties of cements, produced from the modified clinkers, were measured. It was concluded that the added mineral improves the burnability of the cement raw mixture without affecting significantly the hydration rate and the cement properties.

Keywords: Cement; Clinker; Mineralizers; Wolframite; Stibnite

1. Introduction

Cement production requires a high input of energy mainly because of the thermal treatment of the raw mixture at high temperature. The efforts to decrease the energy demand have been focused on three areas: technological improvement of cement plants, utilization of alternative fuels and raw materials and improvement of cement raw meal reactivity [1–3]. The use of alternative raw materials in cement industry, in order to improve the burnability of the raw mix, has been broadly discussed in the past and it is expected to attract more attention in the future [4–8]. An attractive approach to energy conservation is the addition of small amounts of selected mineralizing materials in the raw mix, aiming either to the decrease of the final burning temperature or the acceleration of the sintering reactions. Secondary materials that can be used as mineralizers or fluxes are industrial by-products, industrial wastes and minerals. These materials contain certain elements that even at low concentration exert a remarkable effect on the sintering process of cement raw mixture. The effect of minor components on the formation of the clinker has been discussed and reviewed adequately [9–13].

This work is part of a project concerning the use of selected Greek minerals as burning aids in cement raw mix. In this paper a wolframite–stibnite mineral is used in order to introduce the elements W, Sb and S in the cement raw mix. According to our studies, these elements have a positive effect on the reactivity of the cement raw mix [12,13].

Sulfur and sulfides from raw materials and fuel are oxidized and incorporated into the phases of clinker as sulfates. In practice, sulfate addition to the raw mix is limited because of the restrictions concerning the SO_3 content in the cement and its volatility, which causes the formation of build-ups in the kiln and the preheaters. A procedure of predicting sulfate distribution in clinker has been developed and tested [14]. An optimum addition of 6.0% $CaSO_4$ has been reported [15,16]. Very little

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work has been reported on the effect of antimony and tungsten on the clinker formation and the properties of the cement [8,17]. It must be noted, however, that when several elements are jointly present in the mixture, the reactivity is not additively changed and any secondary material that is expected to have a positive effect on the reactivity must be individually investigated.

In this work, a varying content of the studied ore was introduced in cement raw meal. The reactivity of the mixture, the sintering reactions and the structure of the products were investigated. In addition, the effect of the added mineral on the hydration rate and some of the mechanical–physical properties of the produced cements were examined.

2. Experimental

2.1. Materials

A wolframite–stibnite assemblage (coming from Kilkis region, Greece) was chosen in order to introduce the elements W, Sb and S in the cement raw mix. The exploitation of wolframite deposits in this area was interrupted after the 2nd World War. The material used in this study was manually selected from mineral accumulations left in front of the deserted galleries. The main constituents of the mineral were (FeMn)WO_4 and Sb_2S_3, while quartz and shale were also present (W: 30% w/w, Sb: 7.5% w/w).

Ordinary Portland cement raw meal of industrial origin was used (residue at 90 μm: 15%). 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.

2.2. Burning procedure

One reference and four modified mixtures, prepared by mixing the reference sample with 0.5%, 1.0%, 1.5% and 2.0% w/w of the wolframite–stibnite mineral, were examined. The samples were pressed to form pellets, they were thermally treated at 1000, 1100, 1200, 1300, 1350, 1400 and 1450 °C for 20 min in an electrical furnace and then they were rapidly cooled. Sintering and cooling conditions were kept constant for all samples. The effect on the burnability was evaluated on the basis of the unreacted lime content in samples sintered at the above-mentioned temperatures. Specifically, the sintered pellets were ground and analyzed by the ethylene glycol method in order to estimate the free CaO (fCaO) content.

In addition, 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. Mass sample was approximately 50 mg. The experiments were conducted in a static atmosphere.

The sintered samples were examined using a Siemens D-5000 X-ray diffractometer, with nickel-filtered Cu Kα_1 radiation ($\lambda = 1.5405$ Å) in order to identify the compounds formed during sintering.

Scanning electron microscopy (SEM) was used in order to examine the texture of the obtained clinkers and the distribution of the foreign elements in its main phases. A JEOL JSM-5600 Scanning Electron Microscope, interfaced to an OXFORD LINK ISIS 300 energy dispersive X-ray spectrometer (EDS) was used. Experimental conditions involved 20 kV accelerating voltage and 0.5 nA beam current.

2.3. Cement hydration and properties

The clinkers were interground with 5% w/w gypsum in a pro-pilot plant ball mill of 5 kg capacity. The gypsum was of industrial origin (98% w/w $Ca_2SO_4 \cdot 2H_2O$). 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 standard paste, the setting time and the soundness (EN 196-3) was determined.

Table 1
Characteristics of the raw mix and the produced clinker

Raw mix		Clinker			
Chemical composition (% w/w)		Mineral composition (Bogue) (% w/w)		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				

LSF = C/(2.8S + 1.18A + 0.65F), SM = S/(A + F), AR = A/F, HM = C/(S + A + F); C, S, A, F: % content of CaO, SiO_2, Al_2O_3 and Fe_2O_3respectively, in cement raw mix.

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 h the cement cores where put in polythene 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 h in vacuum. The hydrated samples were ground to pass through a 54 microns sieve and were studied by means of XRD in order to identify the hydrated products. In addition, TGA was used for the evaluation of the hydration rate. The samples were heated from 20 to 600 °C at a constant rate of 15 °C/min in an atmosphere of carbon dioxide free nitrogen, flowing in 50 cm^3/min. Mass sample was approximately 50 mg. A limited number of samples were treated up to 1000 °C in order to find out if there was any carbonation of $Ca(OH)_2$.

3. Results and discussion

3.1. Burnability of the raw mix

The reactivity of the raw mixtures was evaluated on the basis of the unreacted lime (fCaO) content after sintering at varying temperatures. Table 2 presents the fCaO content in relation to the sintering temperature and the mineral content in the raw mix.

Using the fCaO values of the sintered samples, the burnability capacity (BC) of the raw mix can be estimated from Eqs. (1) and (2).

$$\begin{aligned} C = {} & fCaO_{1000\,°C} + 2fCaO_{1100\,°C} + 2fCaO_{1200\,°C} \\ & + 3fCaO_{1300\,°C} + 4fCaO_{1350\,°C} + 4fCaO_{1400\,°C} \\ & + 2fCaO_{1450\,°C} \end{aligned} \tag{1}$$

$$BC = 600/C \tag{2}$$

The resulted values of BC are given in Table 2.

As can be seen (Table 2), the effect of the added mineral on the fCaO content is marginal at temperatures below 1200 °C. Surprisingly, a negative effect is recorded at 1200 °C, probably attributed to the partial displacement of Ca by Sb in the intermediate compounds formed at this temperature. On the contrary, a significant decrease in the fCaO content is recorded at 1400 and 1350 °C (by 29–74% and 39–47% respectively), implying a remarkable impact of the added mineral on the reactions that proceed in the presence of the liquid phase. This is also reflected on the BC values (Table 2), which are mainly based on the fCaO content at 1400 and 1350 °C. Overall, even 0.5% of mineral addition is considered to improve the burnability of the raw mix, especially at high temperature. The positive effect of this mineral is proportional to the doping concentration.

3.2. Calorimetric studies of modified clinkers

In the DSC curve of a cement raw mix the following stages are distinguished:

- a broad endothermic effect attributed to the dehydroxylation of clays (200–600 °C),
- a strong endothermic effect around 900 °C caused by the decomposition of the limestone,
- one or more exothermic reactions (1200–1350 °C) connected with the belite (C_2S) formation,
- an endothermic reaction just after the last exothermic reaction (1300–1400 °C) associated with the partial melting of the sample.

The first two stages depend on the chemical and mineralogical characteristics of the clay and the limestone respectively, and as it was expected, they are identical in all samples. The most important stages are the third and the fourth which are directly associated with the clinkerization process.

Fig. 1 presents the DSC curves of the pure sample and the sample containing 2% of the mineral. The evaluation of the DSC curves of the modified samples led to the following observations:

- 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.

Table 2
fCaO and BC values of modified clinkers

Mineral content (%)	fCaO (%)							BC
	Temperature (°C)							
	1000	1100	1200	1300	1350	1400	1450	
–	39.21	35.00	20.01	10.00	6.95	4.00	2.12	2.64
0.5	36.62	33.83	24.21	8.18	4.23	2.85	1.94	2.86
1.0	36.33	33.26	23.12	7.83	4.20	2.82	1.82	2.94
1.5	35.53	32.69	22.52	7.56	3.87	2.34	1.32	3.06
2.0	33.84	32.15	15.23	6.75	3.71	1.04	1.41	3.52

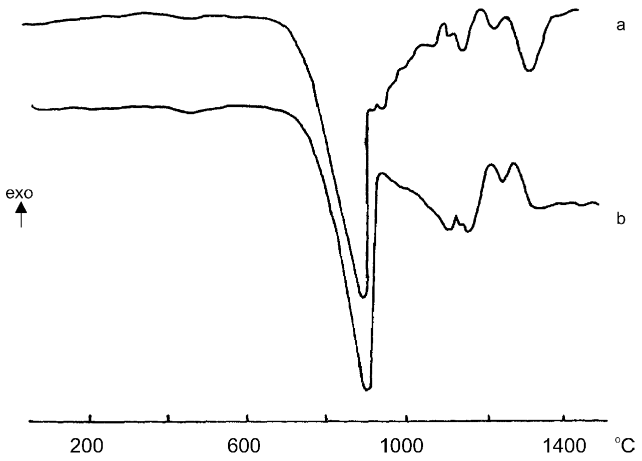

Fig. 1. DSC curves of pure (a) and 2% doped sample (b).

- The added mineral did not affect the decomposition of $CaCO_3$ or the belite formation. In modified mixtures the formation of the melt was shifted to lower temperature and overlapped with the belite formation. This fact indicates that the constituents of the added mineral are 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.

3.3. XRD studies of modified clinkers

All samples sintered at 1450 °C have the structure of a typical clinker. The dominant phases (alite, belite, calcium aluminate and ferrite) were well crystallized, giving peaks at the expected 2θ values. Additionally, no detection of undesired compounds (γ-C_2S) was recorded. Differentiations among samples were restricted in calciumaluminate and ferrite, due to the selective incorporation of the constituents of the mineral in these phases and the changes that occur in their chemical composition and structure.

3.4. SEM studies of modified clinkers

SEM studies were conducted in order to examine the structure of the obtained clinkers and the distribution of the foreign elements in its main phases. The SEM observations are summarized in Table 3, while the SEM photos of some clinkers, burned at 1450 °C, are given in Fig. 2. The photos were selected to be representative as far as the size and the shape of alite and belite crystals are concerned.

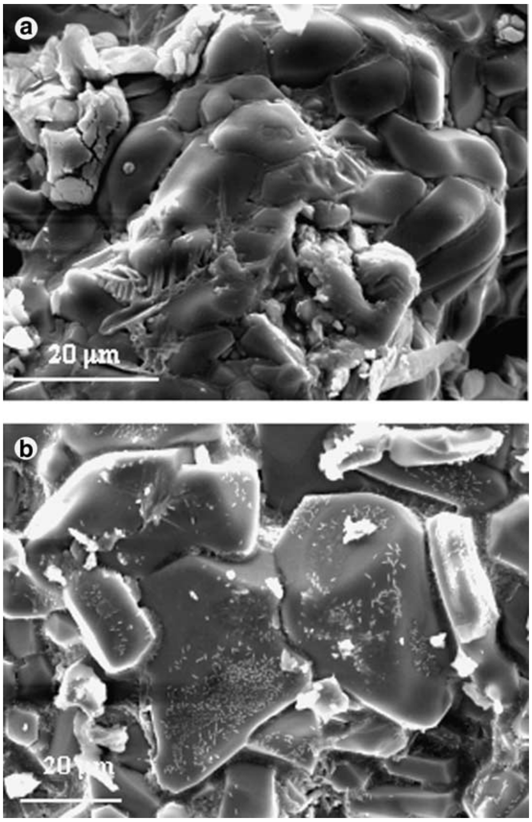

Fig. 2. SEM photos of pure (a) and doped (b) clinker.

In reference sample (Fig. 2a) alite was formed as compact prismatic crystals of slightly rounded polygonal outline, with particle size ranging from 20 to 30 μm. Belite is uniformly distributed as small roundish grains of 10–20 μm in size. The amount of interstitial matrix is generally adequate, having a fine-crystalline structure.

Sample doped with 2.0% w/w wolframite–stibnite is presented in Fig. 2b. Alite was formed as angular, rather expanded big prismatic crystals. EDS analyses performed in alite crystals suggest that W is not incorporated in this phase. On the contrary, the interstitial material exhibited high concentrations of W and Sb, leading to the conclusion that W and Sb are selectively incorporated in the interstitial matrix. DSC and XRD studies also confirmed this result, as it was discussed above.

Table 3
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
Reference + 2% wolframite–stibnite	40–60	Angular, big prismatic	5–15	Round

From Fig. 2 it is concluded that alite crystals appear different in size and shape. Alite crystals are formed and developed in the melt. Since burning and cooling conditions were kept strictly constant for all samples, these changes can only be attributed to the effect of the added minerals on the properties of the liquid phase (viscosity and surface tension on the solid–liquid interface).

3.5. Hydration rate of cements pastes

All pastes were studied by means of a TG analyzer. The weight loss up to 550 °C, which corresponds to the total water incorporated in 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 600–700 °C, if any, corresponds to the decomposition 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 pastes 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 4 presents the content of the total compound water, calcium hydroxide and water in the hydration products in relation to the content of the added mineral in the raw sample and the age of hydration.

As it is shown, small additions of the added mineral (up to 1%) do not significantly affect the extend of hydration. As the mineral content in the raw mix increases, the hydration tends to slow down, as it is indicated by the progressive decrease of water and calcium hydroxide content in the pastes. The stronger effect of the added mineral on the calcium hydroxide content indicates that it affects especially the hydration of silicate compounds.

3.6. XRD studies of hydrated samples

In all samples, a gradual increase of $Ca(OH)_2$ content, accompanied by a corresponding decrease of the anhydrous calcium silicate compounds was observed. The formation of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$), which is the first reaction product between calcium aluminates and gypsum, is confirmed in all samples even after 1 day of hydration. Differentiations are observed after the age of 2 days. The transformation of ettringite to the monosulfate salt ($Ca_4Al_2SO_{10} \cdot 12H_2O$) seems to be delayed, proportionally to the percentage of wolframite–stibnite addition in the raw meal. The monosulfate was initially detected in the pure and the 0.5% doped samples after 2 days of hydration, in the 1.0% and 1.5% doped samples after 7 days and in the 2% doped sample after 28 days. The rest of the calcium silicate and calcium aluminate hydration products do not present distinct peaks due to their low degree of crystallinity and/or their small amounts.

3.7. Cement properties

Fig. 3 presents the strength development of the cements produced in relation to the content of the added

Table 4
Total compound water, calcium hydroxide and water in the hydration products in relation to the content of the added mineral in the raw sample and the age of hydration

Mineral content (% w/w)	Hydration age (days)			
	1	2	7	28
Compound water (% w/w)				
–	15.24	18.08	19.71	24.29
0.5	17.10	17.79	18.75	24.88
1.0	15.72	16.00	17.89	23.36
1.5	14.78	15.26	17.48	23.94
2.0	14.49	15.75	16.78	22.50
$Ca(OH)_2$ (% w/w)				
–	21.35	23.43	26.09	26.80
0.5	20.56	21.38	23.93	24.98
1.0	18.99	19.30	24.17	23.68
1.5	18.34	21.54	23.18	23.68
2.0	18.91	20.10	22.69	22.12
Water in hydrated products (% w/w)				
–	10.05	12.38	13.36	17.77
0.5	12.10	12.59	12.93	18.80
1.0	11.10	11.31	12.01	17.60
1.5	10.32	10.02	11.84	18.18
2.0	9.89	10.86	11.26	17.12

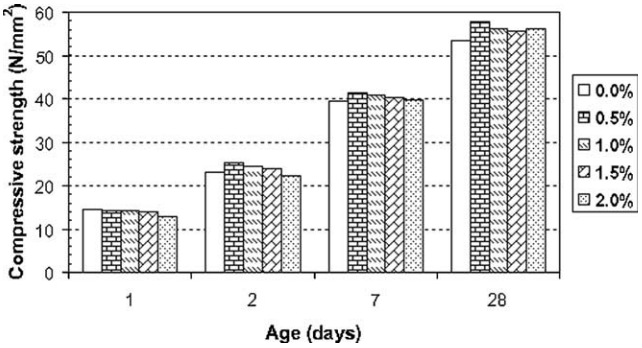

Fig. 3. Strength development of cements in relation to the percentage of the added mineral.

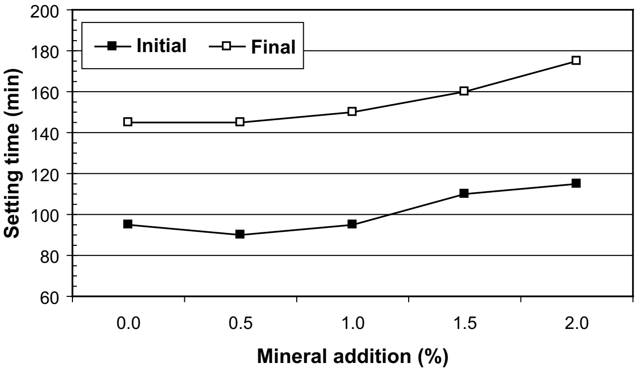

Fig. 4. Setting time of the cements in relation to the percentage of the added mineral.

mineral. The cements prepared from modified raw mixtures present slightly lower initial strengths (1 day), while after 2 and 7 days the strength in all samples is approximately the same. A marginal positive effect is observed at 28 days. The 0.5% w/w addition seems to have the optimum effect.

Fig. 4 presents the setting time of the produced cements in relation to the percentage of the added mineral. It is seen that the mineral addition leads to a slight increase of the setting time proportionally to the mineral content.

The mineral has no effect on the water demand of the cement paste. The standard consistency of the paste varies from 25.9% to 26.5% in all samples.

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

4. Conclusions

From the present study the following conclusions can be drawn:

- The wolframite–stibnite assemblage promotes the consumption of free lime and improves the burnability of the raw mix, especially during the final stage of the sintering. This positive effect is proportional to the doping concentration.
- The elements W and Sb are preferentially concentrated in the melt affecting the growth environment of alite crystals and modifying their shape and size.
- Despite the slight retarding effect on the hydration process, the added mineral does not affect the strength development and the physical properties of the cement.

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