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STABILIZATION OF COPPER REFINING WASTE IN CEMENT MATRIX USING THERMAL ANALYSIS

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Abstract

The objects of the paper are the results of the study on the compatibility of copper refining waste with cement system. The study based on the use of thermal analysis and the comparison of its results with further applied methods (tests of setting, compressive strength and pore analysis) showed good compatibility of the waste up to 20% dose opposite to the cement. It seems that the waste action in cement paste with the $Ca(OH)_2$ binding, produced in the cement process hydration, is connected.

Keywords: copper, *p*-cement, waste isolation

Introduction

The utilization of various types of environmentally harmful industrial waste as components in cement materials represents one of the possibilities of their liquidation or isolation from the environment. The basic condition for a successful application of this method is compatibility between the industrial waste and the cement systems. In this connection, it is important to specify the effects of the interfering compounds on the process of cement hydration [1]. A special attention is being paid to the immobilization of heavy metal compounds. The application of Portland cement and its blended species for the purpose of waste stabilization is adequately documented [2]. In general, the compounds of transition elements like PbO and ZnO delay the setting and hardening of cements, while chromium compounds accelerate both processes [3].

The presented work is part of the series of studies concerning the effects of heavy metal compounds on the hydration of cement-based materials and their properties [4, 5].

The paper presents the results of the study on the effects of copper refining waste on the hydration of cement paste by means of thermal analysis and evaluation the compatibility between the studied waste and the hydrating cement in combination with other research methods.

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Experimental

The materials applied: cement paste containing various doses of waste with a constant value of cement-water ratio 0.3.

The properties measured and the methods applied: the phase composition of cement paste was determined by means of a derivatograph OD 102 MOM Budapest and a Philips diffractograph completed by the tests of setting (according to ČSN 7221 15), the bulk density, compressive strength, and pore structure (using mercury porosimeter Model 2000 and a macroporosimeter 120 Erba Science Milano).

Specific weight by pycnometric method, specific surface by BET method (SORPTOMATIC, Erba Science Milano) and morphology of particles (JEOL JS M35 raster electron microscope), of the studied waste were determined.

Results and discussion

Results of the study of the waste

The waste studied is a product of the chloridizing roasting of copper concentrate at a temperature of 700°C, held up in the form of light ash. The waste contained Fe (4.76%), Cu (6.33%), As (1.49%), S (3.76%), Sb (19.61%), NH_4^+ (29%) and Cl^- (34.1%). According to our measurements, the copper processing waste had loose bulk density of 580 kg m^{-3} (Portland cement PC approx. 1.400–1.700 kg m^{-3}), specific surface of 219 m^2 kg^{-1} (PC approx. 280–320 m^2 kg^{-1}), specific weight of 4.500 kg m^{-3} (PC approx. 3.000 kg m^{-3}), with water-soluble proportion of 8%, and *pH*-value of water extract of 1.68. It is evident that the physical properties of the waste material more or less converge to those of Portland cement. According to raster electronmicroscopy the waste is morphologically a heterogeneous material consisting of particles of globular and irregular shape, occurring predominantly in agglomerates. The physical properties of the waste appear to be compatible with those of cement. Another favourable property of the waste is its relatively low water solubility, representing a reduced demand for the binding of water-soluble components within the cement systems in the presence of waste. However, the acidic character of the waste is in full contrast with the hydrating cement systems which show a relatively strong alkaline character (their *pH*-values are approx. 12). However, the acidity of the waste can be effectively eliminated by $Ca(OH)_2$ produced during the process of cement hydration, and in principle, it does not represent a factor threatening the hydration of hardening of cement and excluding chemical compatibility between the waste and the cement system.

The TG, DTG and DTA curves of the waste material is illustrated in Fig. 1.

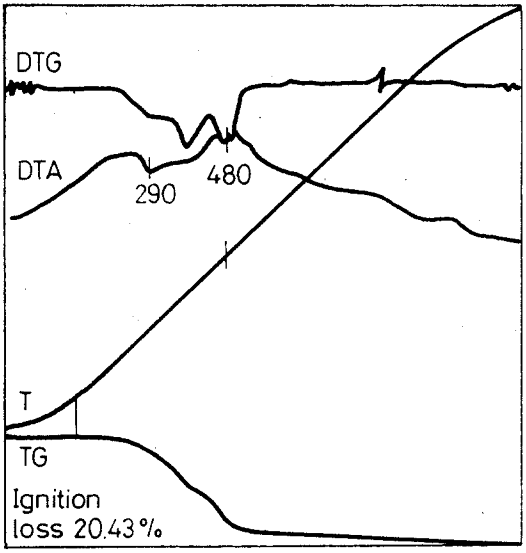

Fig. 1 TG, DTG and DTA curves of the copper refining waste

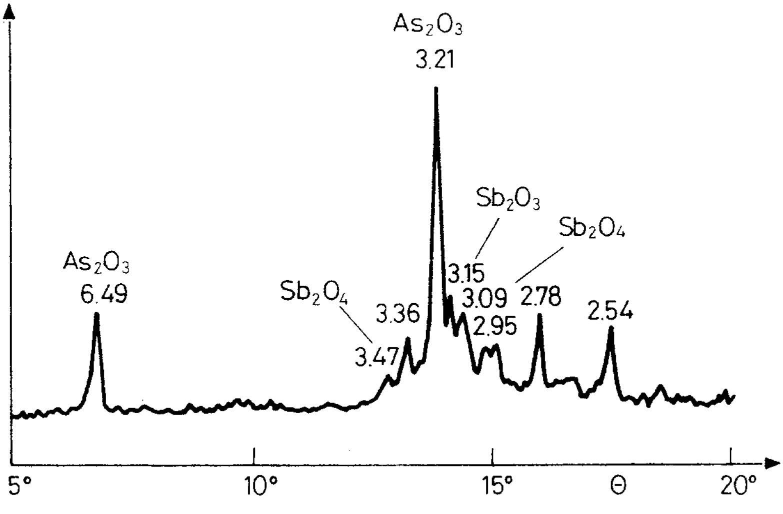

Fig. 2 Diffractogram of the copper refining waste

According to the results of X-ray analysis, the waste contained As_2O_3, Sb_2O_4, and Sb_2O_3 oxides (Fig. 2). With regard to the well known fact that the thermal decomposition of oxides takes place at a temperature substantially higher than the temperature of endothermic peaks at 290 and 480°C occurring on the curves of the waste material, their relevance to oxides found in the waste by X-ray analysis is very much unlikely. The determination of the relevance the mentioned peaks requires further research, which exceeds the framework of this study. However, it is possible to state that these endothermic peaks were caused by the process of thermal decomposition of waste components. It is indicated by a relatively high weight loss 20.43% in the interval delimited by the temperatures of the given peaks. This fact also indicates that the waste material contains a so-far undefined component with thermal stability relatively lower than, e.g. commonly occurring in cement material calcite, with a temperature of decomposition about 700°C. The endotherm at 480°C of the waste is identical with the endotherm of $Ca(OH)_2$, a common component in cement materials. The weight loss which within the given interval, in the case of cement materials represents chemically bound water in the hydration products of cement, or their contents respectively. This fact may hamper the application of gravimetric thermal analysis (TG), for the study of cement materials with the admixture of copper refining waste.

Results of the study of cement pastes

On the basis of results obtained by TG, it was possible to determine a significant characteristic of the process of cement hydration, i.e. the contents of hydration products in the cement paste. This by the weight loss within an interval ranging from 100°C to approx. 450°C. According to Table 1, the content of chemically bound water was not reduced by the presence of waste in the cement paste, on the contrary, it was slightly increased. At the same time, the results obtained by TG showed a decrease in the content of CaO bound in $Ca(OH)_2$ and $CaCO_3$ under the influence of the waste. This change with the disappearance of $Ca(OH)_2$ and $CaCO_3$ content decrease was connected. Similar changes were recorded on DTA curves, which indicated the disappearance of the $Ca(OH)_2$ endothermic peak at 440°C, and the decrease of $CaCO_3$ endothermic peak at 760°C (Fig. 3).

In whole, these changes represent calcium hydroxide content decrease. This is a characteristic product of the hydration of Portland cement (the presence of $CaCO_3$ in the cement paste is a result of the carbonation of $Ca(OH)_2$. The decrease in the content of this phase in hydrating cement materials is usually due to the effects of the presence of hydraulic materials (e.g. ashes, silica fume, slag, etc.). In the case of copper waste application as a potential reaction partner of $Ca(OH)_2$ binding Cr and Sb oxides and the so-far unidentified phase in the waste corresponding to 20.43% weight loss can be considered. Only a further detailed study could enable a definite evaluation. For the time being, it is evident from the results of thermal analysis that the presence of studied waste does not disturb the hydration of cement, on the contrary, it seems that waste admixture moderately supports this process. This favourable effect is indicated by the slight increase of hydration products content waste cement pastes. It is

Table 1 The results of TG and porosimetric analysis of hardened cement pastes

Waste dose / %	Chemically bound water / %	CaO bound / %		Pore volume / $mm^3\ g^{-1}$	Pore median / nm	Total porosity / %
		$Ca(OH)_2$	$CaCO_3$			
0	7.7	2.2	2.2	96	46	17.9
5	8.3	–	2.0	108	46	19.4
20	9.0	–	1.2	–	–	–
40	–	–	–	119	16	23.9

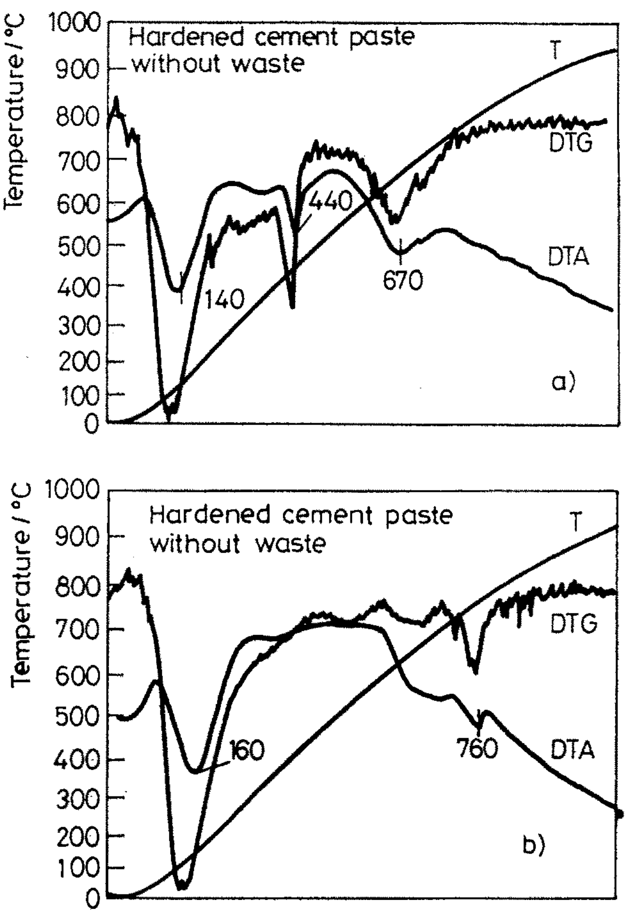

Fig. 3 DTA curves of hardened cement pastes

evident even when the possibility of the influencing of the results by own weight loss of the studied waste is considered.

The supplementary tests fully confirmed the results of thermal analysis. The setting tests have proved that the waste in 5 to 40% doses shortens the beginning of setting by as much as 90%, and its end by up to 60%. After 28 days of hardening, the specimens of cement pastes with 5 to 10% waste content reached values of compressive strength higher by 23 to 112%, while specimens with 40% waste content showed values 45% lower than the control specimens of cement paste without waste. The quality of the pore structure of cement paste containing 5% copper waste was nearly at the level of the control specimen (near values of pore median and total porosity). In the case of 40% dose, however, the total porosity of the cement paste increased, which indicates that the quality of the pore structure of the cement paste by the waste admixture was decreased. This is evidently one of the reasons why the compressive strength of the cement paste with 40% waste decreased. It is evident that the studied waste in optimum doses accelerates the setting and hardening of cement paste and the waste practically is with cement system compatible.

Conclusions

The results of thermal analysis as well as the results of setting test, compressive tests, and the pore structure analysis have shown that compatibility between copper refining waste and materials based on Portland cement is good. According to the obtained results, the optimum doses of waste are up to 20% of the cement weight. It is necessary to determine the long-term stability of the final waste-cement material. This stability represents a decisive criterion of the reliability and applicability of the stabilization and isolation of environmentally harmful industrial waste in practice.

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