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DETERMINATION OF POZZOLANIC ACTIVITY OF MATERIALS BY THERMAL ANALYSIS*

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Abstract

The results of pozzolanic activity determination using DTA-TG method are presented. This feature was characterised by $Ca(OH)_2$ residue determination in cement pastes admixtured with siliceous earth, consuming the calcium ions from hydrolysis of cement clinker minerals. The rate of pozzolanic reaction was thus estimated. Some results for fly ash containing pastes were also given.

Keywords: calcium hydroxide determination, pozzolanic cement, siliceous earth admixture

Introduction

The applicability of pozzolanic materials used as admixtures in cement technology is determined by the so-called pozzolanic activity. This pozzolanic activity is strongly related to the amount of active components, such as SiO_2 and Al_2O_3 available in reaction with calcium hydroxide formed as a result of calcium silicate hydrolysis [1]. The calcium silicates, as it is commonly known, are the main constituents of Portland cement.

Pozzolanic activity of materials depends generally on the active silica content. In cement paste this active silica dissolves and precipitates in the form of calcium silicate hydrate, so-called C–S–H phase [2]. Thus the calcium hydroxide content in cement paste decreases, as a result of calcium ions consumption by additional silica. Cement pastes produced with pozzolanic admixtures show fairly good strength, long-term durability and corrosion resistance [3–7].

Differential thermal analysis and thermogravimetry is one of the best among various methods of pozzolanic activity characterization, giving the results, which allow to predict the properties of hardened cement material. By using this method one can find the calcium hydroxide content in paste. $Ca(OH)_2$ reduction reflects very well the pozzolanic action of admixture as a function of percentage and time from the beginning of hydration. Of course, the determination of $Ca(OH)_2$ content is based upon the mass loss in the range of calcium hydroxide decomposition at about 450–550°C.

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Experimental

The experiments were carried out for cements with pozzolanic admixtures, such as siliceous earth, diatomite, gaize, zeolite tuff and fly ash. Portland cement without admixture and cement with quartz sand inert filler were used as reference samples. The percentage of admixture components was at constant 45 mass% level. Chemical composition of pozzolanic admixtures is shown in Table 1. In Table 2 the active components (SiO_{2act} and Al_2O_{3act}) contents are given, based on the determination by ASTM C 593-56 method.

Table 1 Chemical composition of pozzolanic admixtures

Type of admixture	Percentage in mass%								
	L.o.i.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
Siliceous earth	8.92	79.99	6.63	1.80	0.67	0.66	0.01	0.62	0.58
Gaize	18.02	56.87	1.58	0.92	20.79	0.49	0.11	0.11	0.71
Diatomite	11.90	74.20	8.25	2.79	0.17	0.58	0.02	0.35	1.19
Zeolite tuff	13.85	63.56	12.17	1.83	3.09	1.03	0.06	2.20	2.00
Fly ash	3.81	49.00	24.30	12.10	4.72	2.86	1.95	0.28	0.80
Silica sand	0.05	99.15	0.37	0.08	0.07	0.01	0.01	0.03	0.05

L.o.i.: loss of ignition

Results and discussion

As one can see in Table 1, different types of pozzolanic materials were used: natural deposit rock of inorganic origin – siliceous earth and gaize, natural deposit rock of organic origin – diatomite, natural volcanic rock – zeolite tuff and industrial by-product – fly ash, being the burned carbon shale. Therefore, the chemical and phase composition of materials differ significantly, as well as the type and percentage of active components.

The highest active silica content was found in case of siliceous earth, as it results from the data presented in Table 2. In Fig. 1a the microstructure of active, amorphous silica, being the main component of siliceous earth, is shown. The chemical composition determined by EDS is given in Fig. 1b.

Table 2 Pozzolanic activity of admixtures as measured by ASTM C 593-56 method

Type of admixture	Percentage in mass%	
	SiO_{2act}	Al_2O_{3act}
Siliceous earth	52.76	0.64
Gaize	14.60	0.20
Diatomite	47.26	0.77
Zeolite tuff	41.59	5.16
Fly ash	20.07	6.41

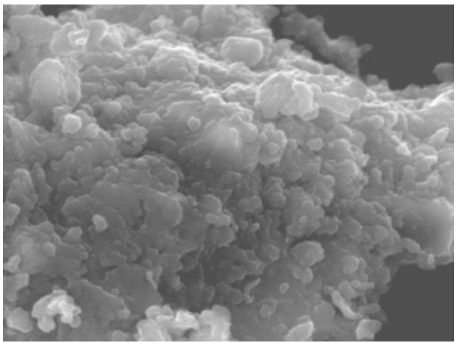

Fig. 1a Microstructure of siliceous earth determined by SEM; 10000×

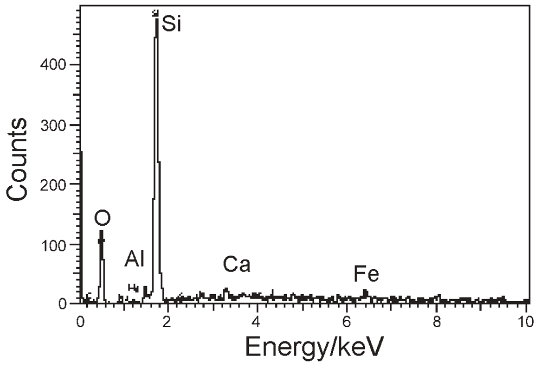

Fig. 1b Chemical composition of siliceous earth determined by EDS

The pastes produced from cement mixtures and control samples at water to cement ratio *w*/*s*=0.5 were subjected to DTA/TG measurements after 1, 3, 7, 28 and 90 days maturing. In Figs 2 and 3 the DTA/TG curves of reference cement paste without admixtures and cement paste containing 45 mass% of siliceous earth are plotted.

In Fig. 4 the problem of $Ca(OH)_2$ determination in the presence of coal residue in fly ash admixtured to cement is illustrated. One should take in consideration that the samples containing pozzolanic admixture with combustible residue of coal (fly ash) should be examined in non-oxidized atmosphere (e.g. in argon), because of the superposition of peaks attributed to coal combustion and calcium hydroxide decomposition.

In Fig. 5 the calcium hydroxide plotted *vs*. hydration time, based on TG data. One can notice that after 1 day hydration the active pozzolanic component reacts with a significant amount of calcium hydroxide from calcium silicate hydrolysis. However, up to 7 days from the beginning of hydration, the rate of calcium hydroxide liberation to the solution is higher than the rate of formation of hydration products with even the very active components of pozzolanic admixtures. The situation is changed at later ages, leading to the relatively rapid, total elimination of $Ca(OH)_2$. The results presented in Fig. 5 show, in fact, the view on reactivity of pozzolanic materials in the mixture with given type of cement. One can also find the type and amount of

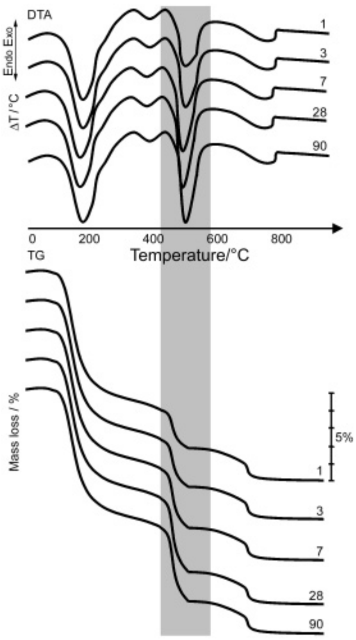

Fig. 2 DTA curves of reference pastes (without admixtures) after 1, 3, 7, 28 and 90 days curing

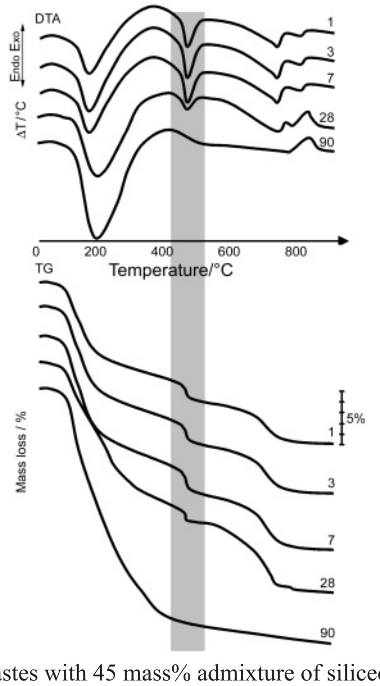

Fig. 3 DTA curves of pastes with 45 mass% admixture of siliceous earth after 1, 3, 7, 28 and 90 days curing

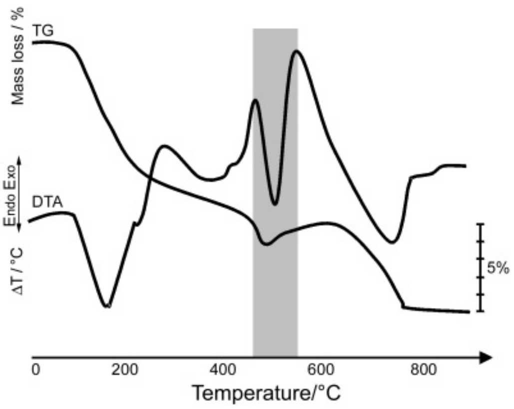

Fig. 4 DTA curves of paste with 45 mass% admixture of fly ash after 7 days curing

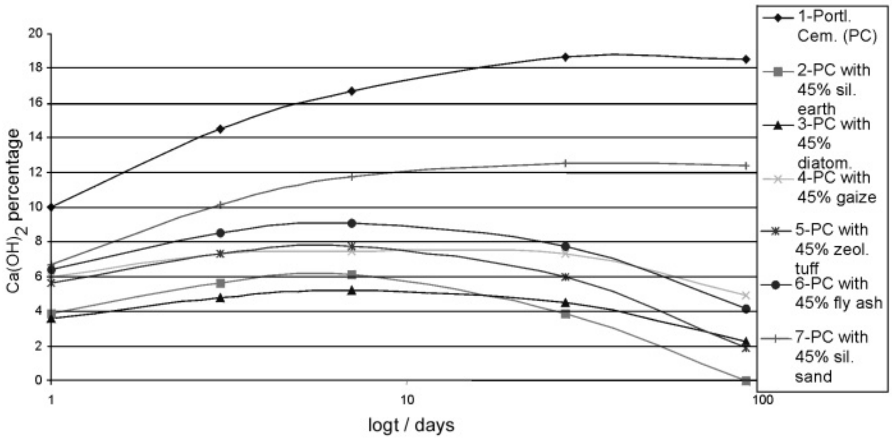

Fig. 5 Pozzolanic activity of different materials determined by thermal analysis

pozzolanic component, which must be used to eliminate the calcium hydroxide and, thus, to protect the paste against the corrosive action, particularly that of sulphates.

Conclusions

DTA/TG measurements may be successfully used in the examination of hydrated cement pastes and particularly in evaluation of pozzolanic activity of admixtures. This pozzolanic activity can be measured as a reduction of portlandite $Ca(OH)_2$ content with time, related to the control paste, without admixture. The results thus presented show very good correlation with the results of analytical evaluation of pozzolanic activity by ASTM C 593-56 method.

DTA/TG method gives the possibility to follow the rate of pozzolanic reaction with time in case of particular pozzolanic material used as admixture to definite kind of cement.

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