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Limestone as an accelerator and filler in limestone-substituted alumina cement

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Abstract

The effect of substitution of alumina cement by limestone up to 25% as well as its fineness on the physico-mechanical properties of the hardened cement pastes is studied. The results revealed that the replacement of alumina cement by limestone slightly decreases the water of consistency and the setting times (initial and final). The combined water content increases with the curing time and the fineness of limestone. The total porosity decreases, and accordingly the compressive strength improves with the content and fineness of limestone. Hence, the limestone has a little accelerating action on the hydration process of the alumina cement but acts only as a filler reducing the porosity due to its compact structure. Therefore, the compressive strength of the hardened cement pastes is enhanced. The addition of finely ground limestone filler only up to 15% gives better results on strength. The XRD and DTA analyses of samples cured up to 28 days show that the addition of higher amounts of limestone filler to the aluminous cement tends to decrease the conversion reaction due to the partial carbonation of C_3AH_6.

Keywords: B. X-ray methods; C. Strength; Limestone

1. Introduction

The manufacture of alumina cement is very expensive due to the higher hardness of its clinker, higher energy consumption as well as the high prime cost of raw materials. Therefore, in Egypt, various types of alumina cements are still entirely imported from abroad. The alumina cements yield high strength during the early ages of hydration, but this property is often lost in the conversion reaction of calcium aluminate hydrates with curing time. Moreover, the alumina cements show an anomalous setting behaviour at temperature range 20 and 30 °C. This means that a retardation of the hydration reactions occurs in this temperature range [1–4]. The low alumina cements often contain the $C_{12}A_7$[1] phase which does not show an anomalous setting phenomenon, particulary when used with additives [2,4].

Because the energy conservation has recently acquired a considerable importance, the use of additives is a common practice to achieve a special property of a material impossible to obtain economically by using the material alone. Additives improve the strength development by modification of the hydration system [5–7]. Accordingly, this paper aims to study the effect of limestone and its fineness on the hydration process and strength behaviour of the low alumina cement pastes. The objective is to modify the rate of conversion reaction in order to prepare less expensive building materials having satisfactory cementitious properties.

2. Experimental procedure

2.1. Raw materials

Raw materials are alumina cement (50% Al_2O_3) obtained from the Egyptian Company for Refractories, and limestone provided by Helwan Portland Cement Company, Cairo, Egypt. The limestone was obtained with two degrees of fineness (3050 and 4600 cm^2/g). The mix compositions were made in a porcelain ball mill using porcelain balls of different sizes for 1 h to ensure the complete homogeneity of all mixes. The chemical analysis of the raw materials is shown in Table 1, while the mix composition as well as the Blaine surface area of the starting raw materials are given in Table 2.

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[1] Shorthand notation: C: CaO, S: SiO_2, A: $A1_2O_3$, H: H_2O.

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Table 1
Chemical analysis of raw materials (wt.%)

Raw Materials	Oxides								
	L.O.I.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O and k_2O	SO_3	TiO_2
Alumina cement	0.50	4.20	51.61	5.61	34.89	0.32	0.59	–	2.28
Limestone	41.87	2.64	1.38	0.16	52.68	0.39	0.06	0.12	0.70

Table 2
Mix compositions of alumina cement with limestone and blaine surface area of raw materials

Raw materials	Cement mixes, wt.%						Blaine Area Cm^2/g
	I	II	III	IV	V	VI	
Alumina cement	100	95	90	85	80	75	3200
Limestone	–	5	10	15	20	25	3050 and 4600

2.2. Preparation and methods

The water of consistency and setting time were directly carried out using Vicat apparatus [8,9]. The cement pastes were mixed with the predetermined water of consistency, cast in one inch cubic moulds of internal dimensions 2.5×2.5×2.5 cm^3, cured for 24 h in a humidity chamber at 100% R.H. and constant room temperature (23±1 °C), then demoulded and cured under tap water for 1, 3, 7, 28 and 90 days. The water of curing was renewed every week. The broken specimens from the determination of compressive strength [10] were then immersed in a 1:1 methanol–acetone mixture to stop the hydration. Three samples of cement cubes were measured for each test, and the mean value was considered. The mechanism of hydration was also studied by the classical techniques, namely the chemically combined water measurements [11], XRD (X-ray diffraction) and DTA (differential thermal analysis). The chemically combined water content was carried out on the basis of ignition loss. XRD analysis was performed using a Philips X-Ray Diffractometer Mod. PW 1390, with Ni-filtered, Cu–K_α radiation. DTA analysis was carried out using NETZSCH Geratobau Selb, Bestell-Nr. 348472c at a heating rate 10 °C/min up to 1000 °C.

3. Results and discussion

The main phases of alumina cement are CA, CA_2 and $C_{12}A_7$ depending on the C/A-ratio, while the most predominant hydration products are CAH_{10}, C_2AH_8, C_3AH_6 and AH_3. The only stable hydrates at ordinary temperatures are gibbsite AH_3 and cubic C_3AH_6. Furthermore, the alumina cement provides high strength development in the early period of hydration compared with the ordinary portland cement. However, a part of the high strength is often lost during the conversion reaction of the calcium aluminate hydrates with curing time [3,11]. During this conversion, the porosity increases causing a temporary loss of strength. With time, the porosity that develops due to this conversion may be filled again with the newly formed hydration products resulting in a strength gain. Hence, the rate and extent of this conversion determine the change in strength. [2,3]

The results of water of consistency and setting time (initial and final) of the various cement pastes are plotted in Fig. 1. Generally, as the amount of limestone increases, the water of consistency decreases slightly and the setting time accelerates, i.e. decreases. Alumina cement is slow setting at the beginning of hydration, but the final set occurs more rapidly. This is essentially due to the presence of the predominant phase CA_2 which

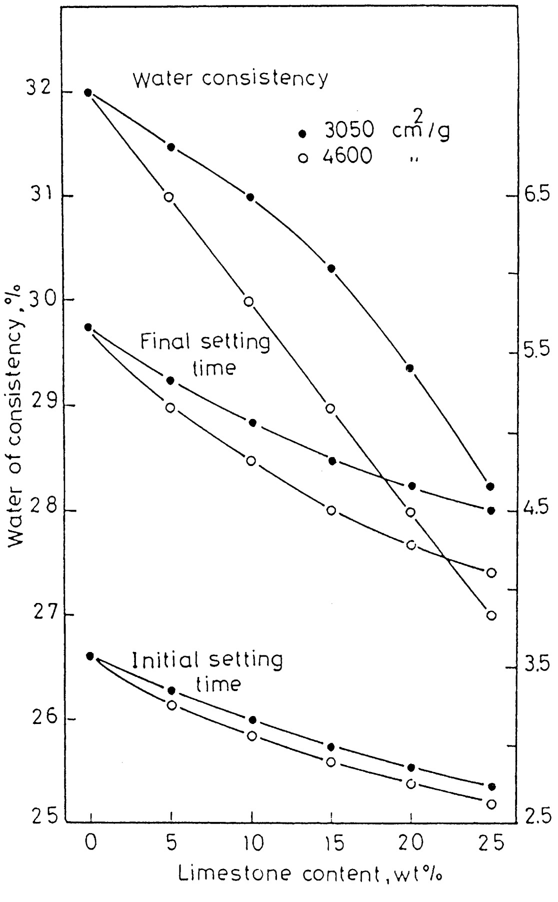

Fig. 1. Water of consistency as well as setting time of alumina cement pastes containing different proportions of limestone powder.

shows a slow rate of hydration, and therefore it has a slow setting because as the C/A-ratio decreases, the setting becomes slower, and vice versa [1,3]. In the presence of limestone filler, the calcium carboaluminate hydrate can be formed which acts as a regulator in controlling the setting properties and has an accelerating action on the rate of hydration which reflected on the setting time [3]. The decrease of water of consistency with the amount of limestone means that the limestone acts as a filler which needs less amount of mixing water. Therefore, the total porosity decreases, and then the setting time shortens. The effect of fineness of limestone on the water of consistency as well as initial and final setting times is also shown in Fig. 1. The finely ground limestone (4600 cm^2/g) has a positive effect on the hydration of alumina cement where it decreases the rate of conversion reaction to a larger extent than the coarse particles (3050 cm^2/g) as clearly shown in Fig. 1. This is mainly attributed to the fact that the finer particles increase the reactivity [11,12].

It is well known that the chemically combined water content is an indirect evidence of the quantitative increase of the newly formed hydration products in the hardened cement pastes [11]. Figs. 2 and 3 show that the amount of chemically combined water of the various cement pastes increases with curing time. The combined water content of the hardened cement pastes increases sharply through the first week of hydration particularly those containing limestone filler with higher fineness (4600 cm^2/g), and then slightly increases onward so that it seems to be nearly constant, i.e. the rate of increase seems to be higher at early ages up to 7 days, followed by a relatively slower or nearly stable rate of hydration during the later ages. This indicates that the hydration of the alumina cement is nearly completed in the first 7 days. The combined water contents of the aluminous cement containing 5–15% limestone are slightly higher than those of the pure alumina cement at all curing ages. This is essentially due to the relatively higher reactivity of aluminous cement particularly in the presence of limestone [3,12,13]. In contrast, the cement pastes containing more than 15% limestone with lower surface area (3050 cm^2/g) exhibited combined water contents lower than those of alumina cement alone (Fig. 2). This is mainly attributed to the presence of lower amounts of the alumina cement compounds responsible for the higher rate of hydration. Consequently, it can be concluded that the use of finely ground limestone (4600 cm^2/g) in the cement mix accelerates the rate of hydration especially during the early ages, and hence the higher the fineness of limestone (Fig. 3) higherly combined water content [11].

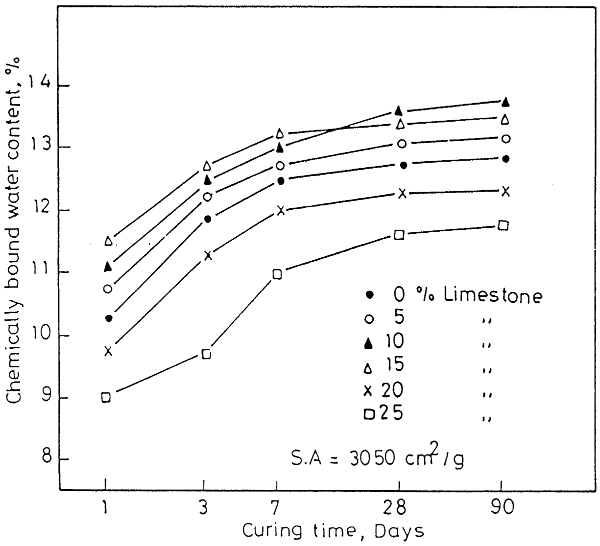

Fig. 2. Chemically-combined water contents of alumina cement pastes containing 3050 cm^2/g limestone powder.

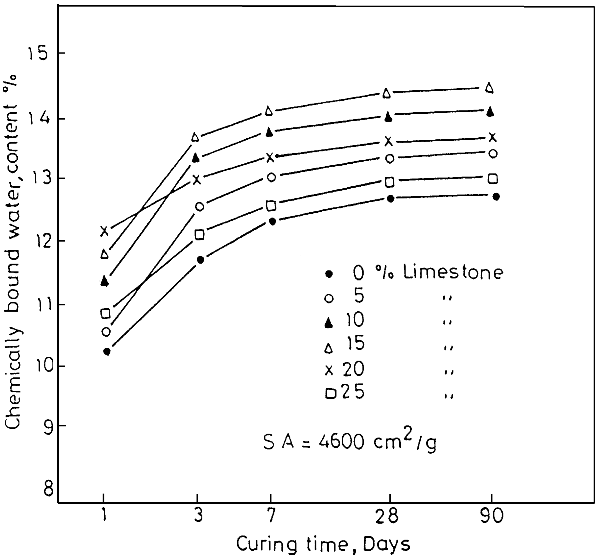

Fig. 3. Chemically combined water contents of alumina cement pastes containing 4600 cm^2/g limestone powder.

The compressive strength values of the hardened cement pastes are plotted as a function of curing time in Figs. 4 and 5 according to the fineness of limestone. The results indicate that the compressive strength of all hardened cement pastes increases continuously with curing time. This is mainly due to the continual formation of hydration products which always deposit inside the available pore structure leading to a decrease in the total porosity. Therefore, the specific volume and bulk density must increase resulting in a clear improvement of compressive strength [11]. Moreover, the cement pastes containing limestone filler give higher initial strength than those of the pure alumina cement specially with finely ground limestone (4600 cm^2/g). This behaviour increases with the amount of limestone filler but only up to 15%. This is essentially due to the acceleration effect of limestone filler related to the formation of calcium carboaluminate hydrate which may be con-

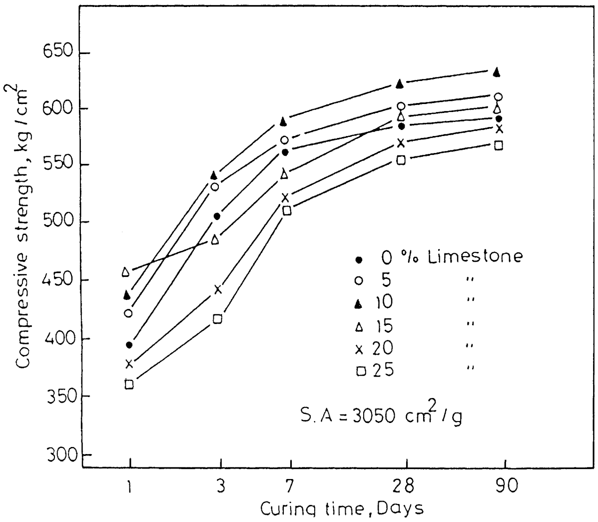

Fig. 4. Compressive strength of alumina cement pastes containing 3050 cm^2/g limestone powder.

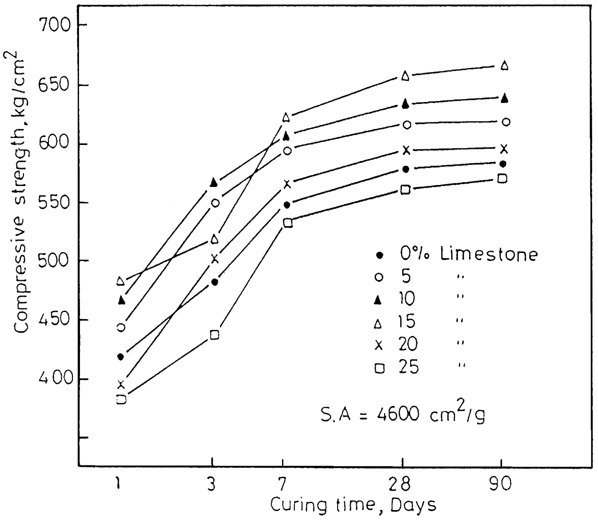

Fig. 5. Compressive strength of alumina cement pastes containing 4600 cm^2/g limestone powder.

tributed to the overall increase in the rate of hydration. Also, the increased binding capacity of carboaluminate is likely due to its compact structure [14]. Furthermore, the consumption of calcite in the formation of carboaluminate hydrates, the accelerating influence on the hydration of CA, the changes in the calcium aluminate hydrates between limestone filler and the cement constituents, in addition to the fineness of limestone are the different factors specific to the reactivity of limestone filler [15]. Also, the limestone filler has been tentatively used to compensate for the loss in strength occurring due to the so-called conversion reaction in the aluminous cement. The addition of limestone more than 15%, the compressive strength of the cement pastes decreases and becomes lower than that of the pure alumina cement at all ages. This is principally due to the lower amount of the main hydration products responsible for the cementing properties of the cement pastes. The strength loss is found to correspond to the conversion reaction of alumina cement, while the strength gain is to the beginning of the conversion reaction of alumina cement and limestone filler [2–4]. Hence, the conversion reaction of aluminous cement could be avoided or at least delayed by adding limited proportions of limestone filler. Thus, it can be concluded that the impact of limestone filler is very important when the fineness of limestone is high [2,4,13], i.e. the fine particles of limestone have a positive action on the specific properties of alumina cement where they decrease the rate of conversion reaction and improve the bond between the cement paste and the filler. So, coarse particles must be avoided and eliminated completely [13,16]. It is well established that although the limestone filler plays an important role in the hydration process and has a positive effect on the hydration mechanism of the aluminous cement, the larger amounts (>15%) must be avoided. This is mainly due to the decrease of calcium aluminate hydrates and may be the increase of carboaluminate hydrate. This is because the formation of higher amounts of calcium carboaluminate hydrate is undesirable due to its adverse influence on the setting and hardening of the cement pastes which reflects adversely on the compressive strength [2,13]. It is thus necessary to fix a maximum content of $CaCO_3$ in the cement.

Consequently, the most common factors responsible for the reactivity of alumina cement by the addition of limestone are the filler effect of the fine particles [14], the acceleration of hydration due to the action of calcite on the aluminate compounds, the formation of monocarboaluminate [3], the development and modification of the microstructure of the cement [17], improvements due to the formation of a carboaluminate bond between the cement paste and the filler [18], and the absence of free lime in the hydrated cement [2,11]. The acceleration effect on the rate of hydration may be due to that the limestone filler modifies the hydrating surfaces of the cement components and serving as crystallization nuclei [19]. This effect increases with the fineness and content of limestone filler [11,12]. The impact of limestone filler also increases in C_3A rich cements. This is mainly due to the fact that limestone fillers physically improve the compactness of composite cements. Furthermore, they are reactive and increase the binding capacity of the cement paste [11,15].

Fig. 6 represents the XRD patterns of the unhydrated and hydrated specimens of the aluminous cement with various proportions of limestone up to 28 days. It is clear that new peaks representing C_3AH_6 and AH_3 are formed which are due to the hydration of the alumina cement. However, few peaks characterizing the unhydrated specimen are still present but with lower intensities. The addition of 5% limestone to the aluminous cement has a marginal effect on the hydration as well

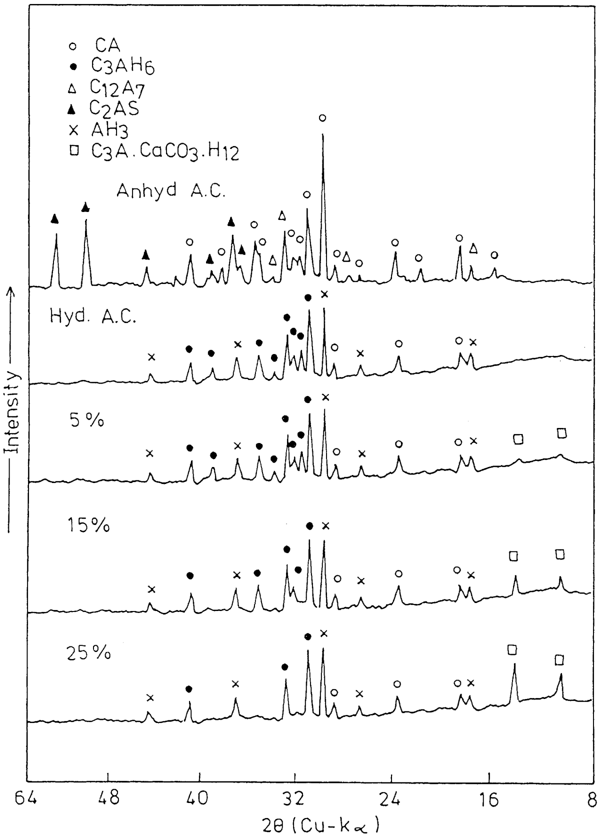

Fig. 6. XRD patterns of anhydrous alumina cement limestone-substituted alumina cement pastes hydrated up to 28 days.

as the formation of carboaluminate hydrate. At higher additions (15 and 25%) of limestone, the carboaluminate hydrate phase is clearly detected which increases with the content of limestone followed by a gradual disappearance of C_3AH_6. Fig. 7 shows the DTA thermograms of the same hydrated specimens. The endothermic peaks at the temperature range (100–135 °C) are due to the decomposition of the intermediate metastable products CAH_{10} and C_4AH_3, while those at temperature ranges 250–280, 405–435 and 698–767 °C are mainly due to the decomposition of the stable hydrates C_3AH_6, AH_3 and $C_3A.CaCO_3.H_{12}$, respectively.

During the hydration of alumina cements, most components convert to cubic C_3AH_6 and gibbsite (AH_3). This is known as conversion reaction. This conversion creates more porosity and leads to a strength loss. In the presence of limestone filler, the carboaluminate hydrate often forms instead of C_3AH_6. The newly formed hydration product tends to deposit into the pore structure of the cement paste resulting in a strength gain. Therefore, the addition of limestone filler modifies the deleterious effect of this conversion [17,18]. The XRD patterns as well as DTA thermograms show a corresponding increase in the amount and intensity of carboaluminate. Hence, the results obtained are in a good agreement with those of XRD and DTA analyses.

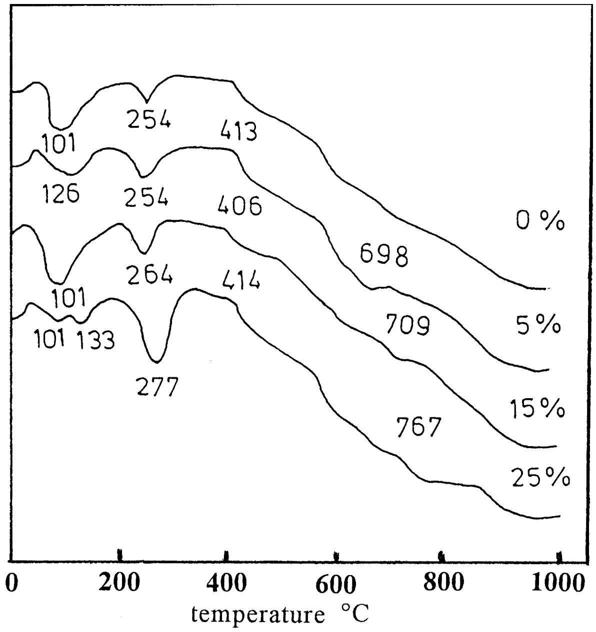

Fig. 7. DTA thermograms of alumina cement and limestone-substituted alumina cement pastes hydrated up to 28 days.

4. Conclusions

1. The strength loss occurring due to the conversion reaction of alumina cement could be reduced and delayed partially by adding limited proportions of limestone up to 15 wt.% of lower fineness, but up to 20 wt.% with higher fineness limestone.
2. The fine particles of limestone filler have a positive effect on the properties of alumina cement. Therefore, the coarse particles of limestone must be completely avoided.
3. The limestone filler acts primarily as an accelerator. It increases the rate of hydration and serves as crystallization nuclei. The rate of hydration increases with the content and fineness of filler in the cement mix.

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