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The cementitious binder derived with fluorogypsum and low quality of fly ash

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Abstract

The possibility of using the low quality of fly ash that is economically supplied countrywide in China instead of the high quality of fly ash in the production of the binder of fly ash-fluorogypsum-Portland cement was studied. The influence of the composition and curing conditions on the properties of the binder was investigated. The superior composition of this binder results because the content of Portland cement is in the range of 15 to 20%. The content of fluorogypsum is not higher than 40% and the content of fly ash must be more than that of fluorogypsum. Steam curing increases the early strength and enhances the rate of strength increase of the binder. The hydration mechanism of the binder is changed in elevated temperatures. This binder is suitable to manufacture precast products such as wall elements.

Keywords: Fluorogypsum; Fly ash; Curing; Strength

1. Introduction

It is very important for the sustainable development of our industry and the protection of environment that the appropriate and economical disposal of industrial by-products would increase every year. Two major by-products are fly ash and chemical gypsum, which are produced in annual magnitude of over a hundred million tons in China. Only about 40% of fly ash and much less of chemical gypsum are properly reutilized in China presently. Therefore, there is continuing interest in establishing suitable processes in which they can be valuably reused.

The main way to reuse fly ash and chemical gypsum is manufacture of building materials or products [1,2]. Some attempts were made to produce gypsum-cement-pozzolana binder [3–6] with phosphogypsum or fluorogypsum. Fluorogypsum also was used as an activator in the recycling process of lower hydraulicity cementitious solid wastes [7].

In our previous work, a new binder with high strength, good volume stability, and excellent water resistance has been developed using high-quality fly ash, fluorogypsum, and Portland cement as raw materials [8,9]. Because of the scarcity and high price of high-quality fly ash in China, this binder has weak competitive power compared to other cementitious materials. In this paper, the possibility of replacement of high-quality fly ash by low-quality fly ash that is economically supplied countrywide in China in the production of this binder was studied.

2. Methods

The fluorogypsum and Portland cement used were similar to those described previously. A fly ash complying with the quality requirement of Chinese National Standard GB 1596-91 (Table 1) for the second class was used instead of the first class of fly ash used in previous work [8,9]. The chemical compositions of three raw materials are listed in Table 2. Fluorogypsum was ground to the fineness similar to cement. Raw fly ash was used. Binders with different mixing proportions were prepared (Table 3). The Chinese standard for silica sand was used to prepare the strength-testing specimens. The sand-to-binder ratio of mortars was 2.5. The water-to-binder ratio of mortars was 0.41.

Fluorogypsum, fly ash, and Portland cement were blended. The mortars were mixed by machine for 3 min, cast into 40 × 40 × 160-mm moulds for the strength test and free volume variance test, then vibrated for 2 min. The samples were kept in humid air at 20 ± 2°C for 24 h. After

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Table 1
The quality requirement for fly ash in GB 1596-91 and the data of the fly ash used in this work

	1st class	2nd class	Fly ash used in this work
Fineness (%)(residue on the 0.045-mm sieve)	<12	<20	17
The ratio of water demand (%)	<95	<105	102
Loss on ignition (%)	<5	<8	4.18
Water content (%)	<1	<1	<1
SO_3 (%)	<3	<3	0.58
The ratio of compressive strength at 28 days[a] (%)	>75	>62	66

[a]The ratio of compressive strength is determined with the mortar whose cement content is substituted by fly ash in the amount of 30% and the mortar consisting of pure cement.

demoulding, the initial length of the mortar prisms was measured. Then, half of the samples were cured in ambient air in the temperature range of 16 to 23°C; the other half were cured underwater at 20 ± 2°C. Three mortars (nos. 1, 5, and 9) also were cured with steam at 60°C for 6 h. After steam curing, samples were cured in the same conditions as other non-steam-cured samples. The strength and volume variance of mortars were determined at the scheduled ages. The corresponding pastes were prepared and cured in the same conditions for determination of hydrate phases by X-ray diffraction (XRD). The morphologies of the hydration products were investigated on the fresh surface of mortars using scanning electron microscopy (SEM).

Concrete for testing was made with binders nos. 1, 5, and 9. The mixing proportion is shown in Table 4. Crushed limestone with size range of 5 to 20 mm and natural river sand with fineness modulus of 2.7 were used as coarse and fine aggregate. Concrete mixes were prepared in a 30-L drum mixer, then cast into 100 × 100 × 100-mm moulds for strength test and carbonation test. The specimens were kept in ambient air for at least 24 h. After demoulding, half of the specimens were cured in humid air with 95% relative humidity at 20 ± 2°C; the other half were cured with steam at 60°C for 6 h, then in the same condition described above. The compressive strength test was made at 7, 28, and 56 days. The carbonation test was made on the specimens cured for 28 days. The specimens were laid in a sealed chamber with 20% of CO_2 and 70% relative humidity at 20 ± 3°C. After 28 testing days, the carbonated depth was determined with a colorimetric test on the split fracture. The strengths of the carbonated specimens were determined also.

Table 3
The proportion of the binder of fluorogypsum, fly ash, and Portland cement (wt%)

No.	Fluorogypsum	Fly ash	Portland cement
1	31	53	16
2	40	44	16
3	50	34	16
4	31	57	12
5	40	48	12
6	50	38	12
7	31	49	20
8	40	40	20
9	50	30	20

Table 4
The mixing proportion of concrete

Binder (kg/m^3)	Aggregate (kg/m^3)	Sand (kg/m^3)	Water (L/m^3)	Water/ binder ratio
580	1186	434	203	0.35

3. Results and discussion

3.1. Strength development of non-steam-cured specimens

The compressive and flexural strengths of the specimens cured in air and underwater are shown in Figs. 1 and 2. The binder of fly ash-fluorogypsum-Portland cement possesses low strength in early ages, but with a satisfactory strength increase rate. It has been determined that the strength gain of this binder is due to the hydration of anhydrite contained in the fluorogypsum, the pozzolanic reaction of fly ash and the hydration of Portland cement [9]. The first two reactions progress slowly but continuously when there is an adequate water supply. The strength of the specimens cured in air does not increase after 28 days, and even decreases in some, which have the lowest content of cement because the reactions do not continue due to the lack of water. The strengths of the specimens cured underwater are almost the same as those cured in air at early ages, but increase to a much higher level in later ages, based on the sustainable pozzolanic reaction of fly ash. Thus this binder is a hydraulic one that is different from ordinary gypsum binders.

Along with the increase of proportion of Portland cement, the strengths of the binders increase obviously. The content of cement in specimens nos. 4, 5, and 6 is too little (12%) to produce enough C-S-H and $Ca(OH)_2$ hydrates to stimulate the pozzolanic reaction of fly ash and stabilize the gypsum hydrate. They have the lowest strength, which declines after 28 hydrating days when they stay in air. In the groups of binders

Table 2
Chemical composition of raw materials (%)

	CaO	Fe_2O_3	SiO_2	Al_2O_3	MgO	SO_3	TiO_2	Na_2O	K_2O	CaF_2	Loss on ignition
Fluorogypsum	38.19	0.31	1.84	0.41	0.13	52.15	0.02	0.10	0.12	4.30	2.99
Fly ash	3.51	3.77	47.76	39.16	0.52	0.58	1.55	0.10	0.49	–	4.18
Portland cement	60.87	3.16	22.17	5.43	1.67	2.3	0.25	0.07	1.10	–	2.63

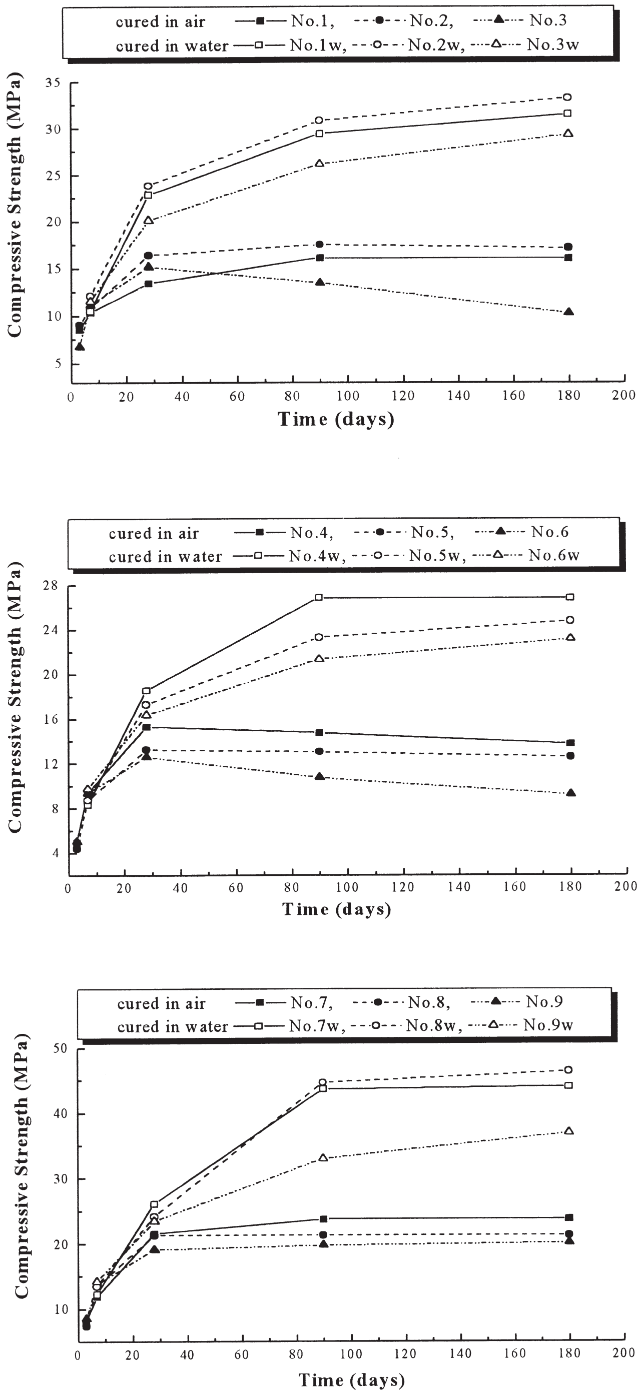

Fig. 1. The compressive strength development of the specimens cured initially without steam, then in air or underwater.

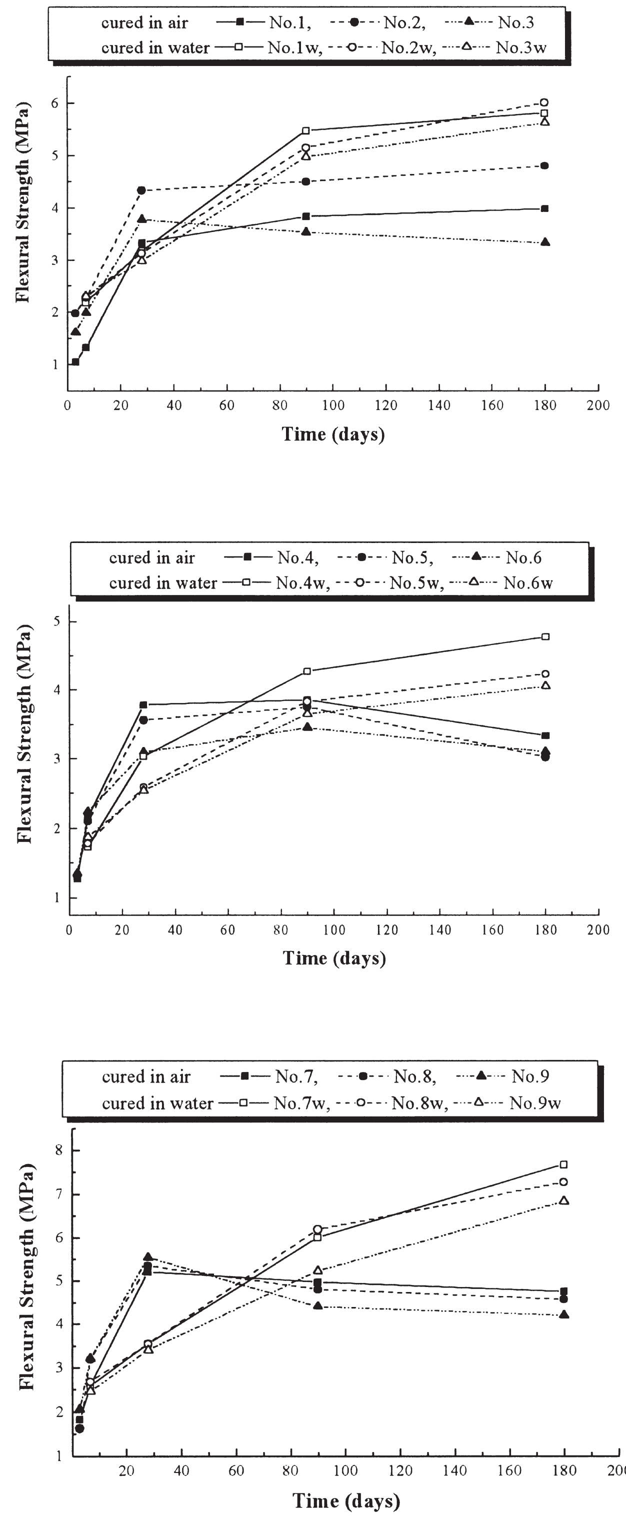

Fig. 2. The flexural strength development of the specimens cured initially without steam, then in air or underwater.

possessing identical cement proportion, those containing 50% fluorogypsum and less fly ash always gain the lowest strength; on the contrary, those containing 31 or 40% fluorogypsum and more fly ash gain the highest strengths. Thus the content of cement in the binder cannot be lower than 15%, but 20% of cement content is enough for the binder to gain good properties. The content of fluorogypsum cannot be more than 40% and the proportion of fly ash must be larger than that of fluorogypsum.

3.2. Strength development of specimens cured initially with steam

Curing specimens with steam at 60°C for 6 h greatly increases their strength at early ages, but cannot markedly im-

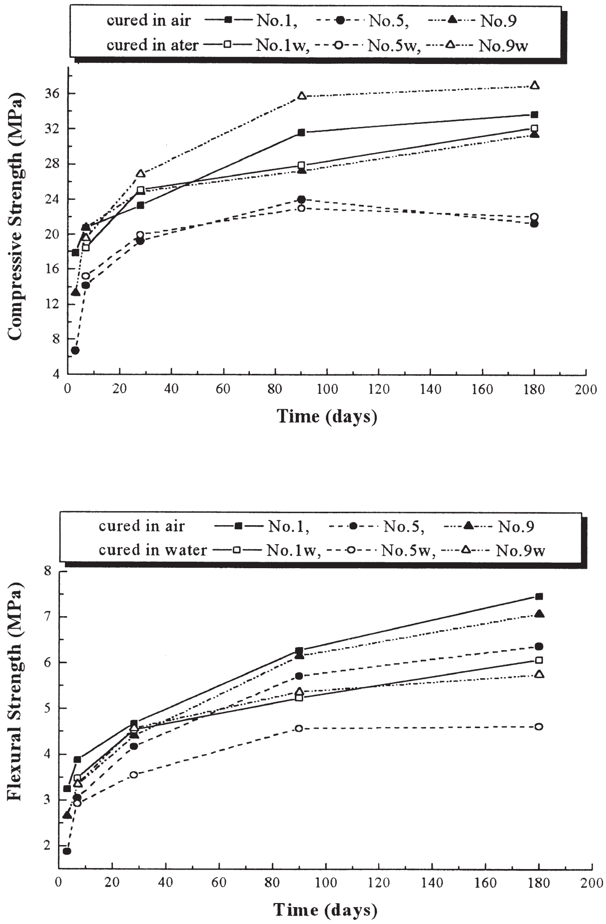

Fig. 3. The strength development of the specimens cured initially with steam, then in air or underwater.

prove their long-term properties. The long-term strengths of the specimens cured in air at later periods increase and those underwater decrease (Fig. 3), compared to the non-steam-cured specimens in the same curing condition in later periods. The compressive strengths of the specimens cured underwater at later periods are higher than those cured in air; their flexural strengths are only 70 to 80% of those cured in air. The longer the curing age is, the larger the difference of the flexural strengths. Steam curing can stimulate the hydration of Portland cement and the pozzolanic reaction of fly ash to increase the strength of binders at early ages.

The XRD patterns of steam-cured paste no. 1 are shown in Fig. 4. Their hydration mechanism is different from that of the non-steam-cured paste [9]. The steam curing retards the transformation of anhydrite into gypsum. A large quantity of anhydrite remains after the steam-curing process ends and a little is transformed into gypsum at the later periods. A weak peak of ettringite can be identified only in the sample cured under water for 28 days or longer. There are no characteristic peaks of $Ca(OH)_2$ produced during the hydration of Portland cement. All of it has been consumed by the pozzolanic reaction of fly ash. The steam-cured specimens have high hydration rate in early ages (Fig. 5), but

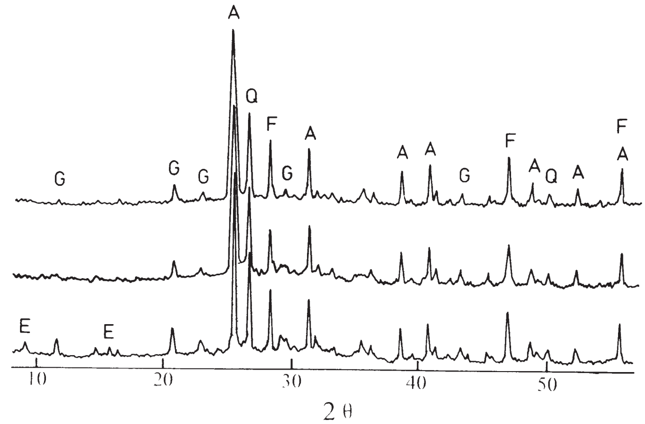

Fig. 4. XRD patterns of paste no.1 cured initially with steam. (upper pattern) in air for 3 days; (middle pattern) in air for 28 days; (lower pattern) underwater for 28 days. A, anhydrite; E, ettringite; G, gypsum; F, CaF_2; Q, quartz.

gains a minor increase in later ages, which restricts their long-term strength development.

The flexural strength is very sensitive to the microcracks, which may be introduced by the formation of expansive ettringite in the hardened mortars. Ettringite forms gradually with the curing prolongation in the mortars cured initially with steam and then underwater. Their flexural strengths increase less and are lower in later periods than those cured in air.

3.3. The volume stability of the mortars

The volume stability of the binder of fly ash-fluorogypsum-Portland cement is characterized with the free longitudinal variance of mortars (Figs. 6 and 7). The non-steam-cured mortars have a large shrinkage in the first 7 days of hydration and soon enters the stable equilibrium. The mortars cured underwater have smaller shrinkage than ones

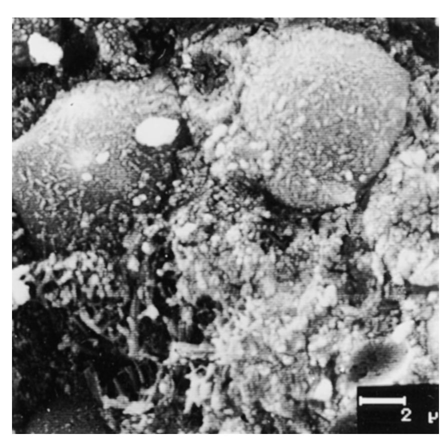

Fig. 5. Morphology of mortar no. 1 cured initially with steam, then in air for 3 days. There is a lot of gel-like hydrate between the fly ash particles, which are covered by a thick hydration product layer.

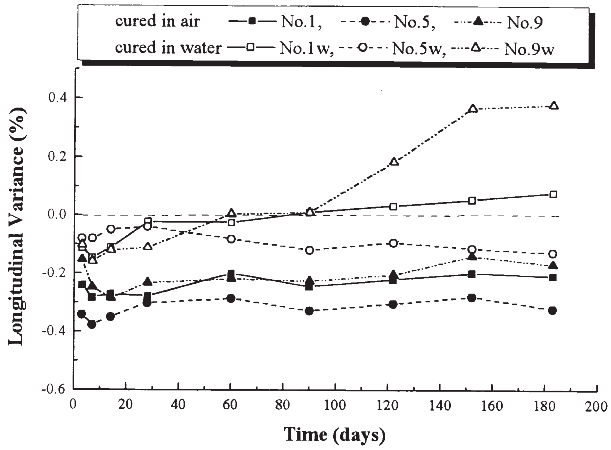

Fig. 6. The longitudinal variances of the specimens cured initially without steam, then in air or underwater.

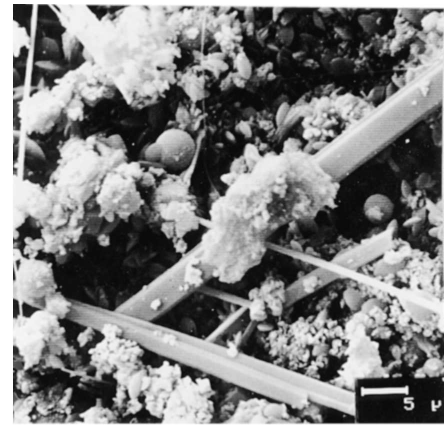

Fig. 8. Morphology of mortar no.1 cured initially with steam, then under water for 28 days. There are single smooth stick-like ettringite crystals and nontransformed anhydrite microcrystal clusters.

cured in air. The volume of the steam-cured mortars varies little till 180 days. Thus they have good volume stability. Mortar no. 9 cured underwater is an exception. It expands significantly after 90 days due to its high content of cement and fluorogypsum, which results in many expansive hydration products (Fig. 8) in the case of a rich water supply.

3.4. The properties of concrete prepared with the binder of fly ash-fluorogypsum-Portland cement

As much as possible fluorogypsum and fly ash must be used to eliminate the pollution of solid waste. Thus the proportion of the binder in the mix is higher than that in ordinary cement concrete. The slump of the fresh concrete is smaller than 1 cm. The compressive strengths of concrete cured with and without steam are shown in Fig. 9. The strengths increase markedly from 7 to 28 days and little after 28 days. Steam curing increases the early strength and enhances the increase rate. The strengths of steam-cured specimens can be over 40 MPa, 20 to 80% higher than ones of non-steam-cured specimens and they do not decline in the later periods.

The carbonated depths of concrete prisms cured initially with or without steam vary in the range of 40 to 50 mm after 28 days of carbonation. The strength of carbonated specimens is not affected. It is equal to that of the control specimens. The carbonation resistance of the binder is not good. This binder is not suitable for production of reinforced concrete. It is proper for the manufacture of precast products, for example wall elements.

4. Conclusions

A binder with satisfactory strength and high-volume stability can be fabricated mainly using industrial by-products fluorogypsum and low quality of fly ash that is supplied economically countrywide in China. The superior composition of this binder results because the content of Portland cement is in the range of 15 to 20%. The content of fluoro-

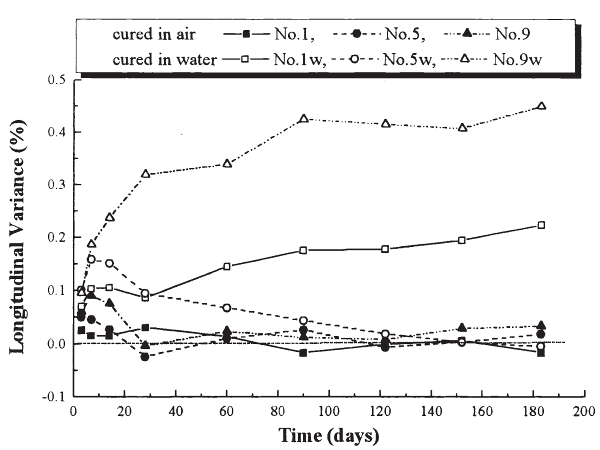

Fig. 7. The longitudinal variances of the specimens cured initially with steam, then in air or underwater.

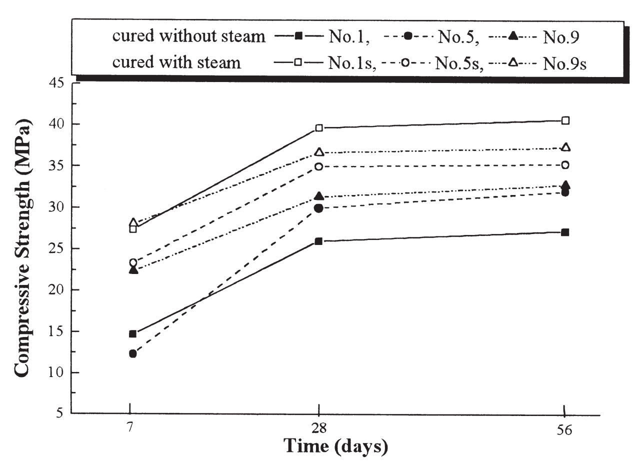

Fig. 9. The strength development of concrete cured initially with or without steam, then in standard condition.

gypsum is not higher than 40% and the content of fly ash must be more than that of fluorogypsum.

Steam curing increases the early strength and enhances the strength increasing rate of the binder. The transformation of anhydrite into gypsum is hindered by elevated temperatures. The hydration mechanism of the binder is changed in this condition.

This binder is suitable to manufacture of the precast products, such as wall elements, but it is not proper to production of reinforced concrete. Steam curing can be used to enhance the strength development both in early and later ages.

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