An Attempt of Steam Curing on Haüyne-Belite Cement

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Abstract

This paper provides a possible application of steam curing on haüyne-belite cement made from blast furnace slag, gypsum and calcium carbonate for the manufacture of prefabricated materials. Cements blended with gypsum and anhydrite have been solidified under equilibrated vapour with boiling water and then bending and compressive strengths have been tested in terms of blending amount and age up to 20 percent and 4 weeks.

1. Introduction

As previously reported cements burnt along the join $C_4A_3\bar{S}$-C_2S generally give so high strength that can be used in practice.[1),2)] However, bauxite is needed for real production, when high early strength cements are desired. If we can make use of this type of cements without bauxite it will be of great benefit for the effective use of blast furnace slag as well as by-product gypsum. In this point of view, in previous work improvement of strength by the addition of calcium sulphates was studied on the cement called mix 0.4, whose raw meal contained no bauxite or extra alumina[3)]. As a result of enhancement of ettringite formation, remarkable increasings were achieved on compressive strength.

Fig. 1 shows a general profile for the development of compressive strength in early time up to 24 hours in 20°C air with saturated humidity on the cement mix 0.4 in neat state, i.e., without additives. Although the setting is considerably rapid, it takes at least 6 to 12 hours for demoulding. Nearly the same trend was observed, when additives of

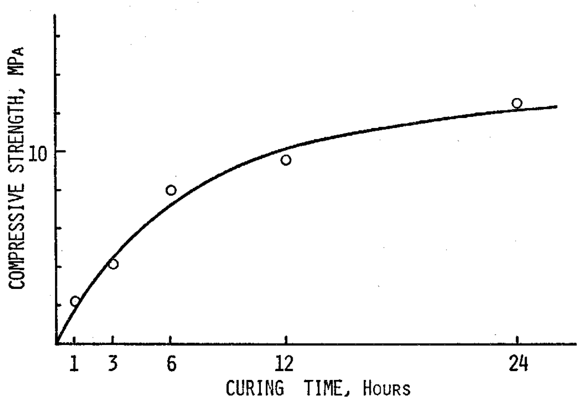

Fig. 1 Development of the compressive strength of the neat cement, mix 0.4, at early age up to 24 hours—paste with W/C 0.40 in 20°C saturated humid air.

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Cement chemical notations are used in this paper. C CaO, A Al_2O_3, S SiO_2, $\bar{S}$ SO_3 and H H_2O.

calcium sulphates were introduced to the cement in small amount. Therefore, curing at ambient temperature is not so beneficial in practice. In this paper steam curing will be attempted to examine a possible application of haüyne-belite cement* for the manufacture of prefabricated materials.

2. Experimental

The cement, mix 0.4, was prepared from the mixture of blast furnace slag, gypsum and calcium carbonate, following the previous method at 1200°C[1], employing a platinum crusible and a silicon carbide resistance furnace. After burning for 1 hour with an intermediate grinding to ensure the completion of burning, charges were pulverized to the fineness of 2500 cm^2/g, Blaine. Additives of gypsum and II-anhydrite were blended independently as much as 5, 10, 15, and 20 percent to the cement, respectively. Chemical composition and constituent minerals of clinker are shown in Table 1 and the neat cement and the additives are specified in Table 2. Then laboratory scale setting times of each cement newly prepared with blending the additives were measured beforehand for the measure of determination of precuring duration, using 10 gram pastes with W/S 0.40[1]. The results were summarized in Table 3, showing perceptible prolongations and the influence of the additives is a little.

Steam curing was performed, following the scheme shown in Fig. 2, using pastes

Table 1 Chemical composition and mineral proportion of the cement, mix 0.4.

SiO_2	Al_2O_3	CaO	MgO	SO_3	Fe_2O_3	MnO	TiO_2	Total (wt %)
26.30	10.75	51.43	5.20	4.74	0.52	0.25	0.81	100.00

Clinker minerals —	$C_4A_3\bar{S}$	α'-C_2S	CA	$C\bar{S}$	Mineralizers[b] — $C\bar{S}$	Others
(mole %)	17.8[a]	74.2	tr.	1.2	2.9	3.9

[a] CA. $1/3C\bar{S}$ is taken as molecular unit. [b] Indicating the potentials estimated to be incorporated into clinker minerals and others comprizing Fe_2O_3, MnO and TiO_2.

Table 2 Specifications of the neat cement and the additives.

Materials	Remarks	Fineness, Blaine, cm^2/g
Neat cement (mix 0.4)	Slag 80.13%, Gypsum 4.84% as $CaSO_4$, $CaCO_3$ 15.03% as CaO, burnt at 1200°C for 1 hour.[c]	2500
Gypsum (G)	$CaSO_4 \cdot 2H_2O$, JIS 1st grade chemical.	2310
II-anhydrite (AII)	$CaSO_4$, decomposed the gypsum at 1000°C for 20 min in air.	2070

[c] Water quenched glassy slag and JIS 1st grade chemicals were used.

* One of the special cases of "supersulphated alumina-belite cements" composed of $C_4A_3\bar{S}$, C_2S and CA as major constituents[1]. The cement, mix 0.4, in present study is particularly called "haüyne-belite cement" due to scarce presence of CA.

Table 3 Setting times of the cements blended with the additives—W/S 0.40 at 20°C. See also the reference about the laboratory scale method.[1]

Addition	Gypsum series		Anhydrite series	
	Initial	Final	Initial	Final
0 %	17 min	32 min	17 min	32 min
5	18	37	19	33
10	19	39	19	35
15	20	41	18	35
20	22	41	19	35

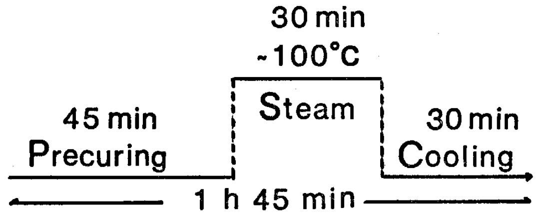

Fig. 2 Scheme of steam curing performed.

with W/S 0.40 in small scale moulds of $1 \times 1 \times 4$ cm dimension, regarding the additives as cement. Since the pastes reveal relatively short final setting times, high temperature steam equilibrated with boiling water can be directly applicable after precuring in 20°C humid air saturated. After cured for 1 hour and 45 minutes in total, includig precuring and cooling times, bending and compressive strengths were tested immediately. Test pieces were also stored in both 20°C air with 51 percent R. H. and in 20°C water for 28 days, respectively, in order to test advancement of strength after the steam curing. Hydrates were identified by means of XRD. Averages of two test pieces are represented in Figs. 3 and 4, i. e., two times for bending strength and four times for compressive strength.

3. Results and discussion

By the addition of gypsum compressive strength over 10 Mpa is easily reached just after the steam curing. With advancement of storage ages both in air and in water, the compressive strength increases markedly. Blending of 5 to 10 percent gypsum would be effectable (Fig. 3). In all hardened cements just after the steam curing, no remaining of $C_4A_3\bar{S}$ was found, i. e., complete hydration. In the case of 5 percent addition gypsum was consumed completely due to hydration under the steam to react with $C_4A_3\bar{S}$ to from ettringite. In the case of 10 percent blending, however, slight amount of gypsum was detected just after the steam curing, remaining unreacted. This was completely wasted in 28-day water curing. In the cases of 15 and 20 percent additions, unreacted gypsum is always found due to excess blending, since 12 percent admixing of gypsum is theoretically required to the present content of $C_4A_3\bar{S}$ to form pure ettringite.

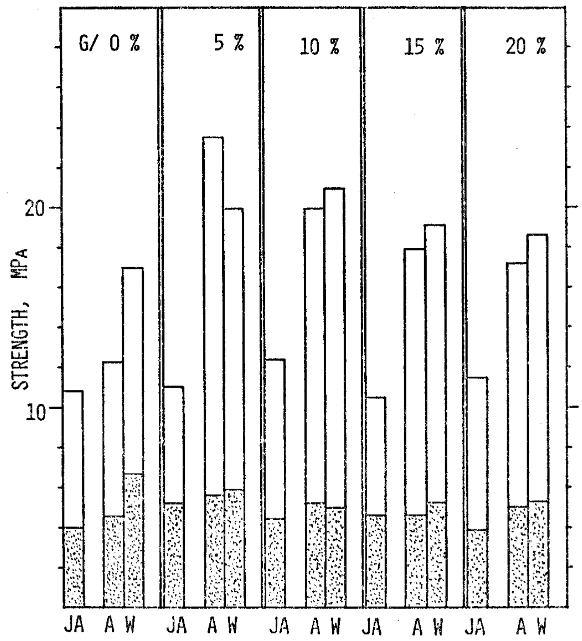

Fig. 3 Representative bending and compressive strengths of the hardened cement added with gypsum (G). JA: just after the steam curing, A: stored in 20°C air with 51% R.H. for 28 days, W: stored in 20°C water for 28 days. Bending strength dotted.

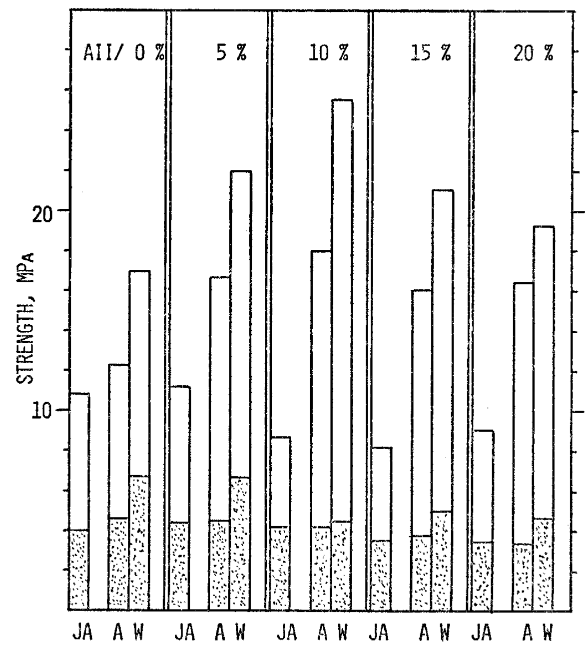

Fig. 4 Representative bending and compressive strengths of the hardened cement added with II-anhydrite (AII). Notations are the same as in Fig. 3.

Table 4 Relative amount of hydrates detected by XRD. Calcium sulphates are also represented for the measure of hydration. Note the augmentation of gypsum and anhydrite in 28-day air curing after the steam curing. Notations; − nil, ± scarce presence suspected, + slight, ++ medium, +++ enhanced. Other notations in Fig. 3.

Addition	Gypsum series			Minerals	Anhydrite series		
	JA	A	W		JA	A	W
0%	++	+	+++	$C_6A\bar{S}_3H_{32}$	++	+	+++
	−	+	−	$C_4A\bar{S}H_{18}$	−	+	−
	+	+	+	$C_4A\bar{S}H_{12}$	+	+	+
	±	−	±	AH_3	±	−	±
	−	+	+	C-S-H	−	+	+
				$C\bar{S}H_2$			
				$C\bar{S}$			
5%	++	++	+++	$C_6A\bar{S}_3H_{32}$	++	+	+++
	−	+	+	$C_4A\bar{S}H_{18}$	−	+	−
	+	±	±	$C_4A\bar{S}H_{12}$	−	−	±
	±	±	−	AH_3	±	±	±
	±	+	+	C-S-H	±	+	+
	−	−	−	$C\bar{S}H_2$			
				$C\bar{S}$	+	+	+
10%	++	+	+++	$C_6A\bar{S}_3H_{32}$	++	+	+++
	+	−	−	$C_4A\bar{S}H_{18}$	±	±	−
	±	+	−	$C_4A\bar{S}H_{12}$	±	±	−
	−	±	±	AH_3	−	−	±
	−	+	+	C-S-H	−	+	+
	+	++	−	$C\bar{S}H_2$			
				$C\bar{S}$	+	++	+
15%	++	+	+++	$C_6A\bar{S}_3H_{32}$	++	+	+++
	−	+	−	$C_4A\bar{S}H_{18}$	−	−	−
	+	−	+	$C_4A\bar{S}H_{12}$	−	+	+
	±	±	−	AH_3	−	±	−
	±	+	+	C-S-H	±	+	+
	++	+++	+	$C\bar{S}H_2$			
				$C\bar{S}$	++	++	++
20%	++	++	+++	$C_6A\bar{S}_3H_{32}$	++	+	+++
	−	−	−	$C_4A\bar{S}H_{18}$	−	+	±
	+	+	+	$C_4A\bar{S}H_{12}$	+	+	+
	−	−	±	AH_3	−	±	±
	±	+	+	C-S-H	±	+	+
	++	+++	++	$C\bar{S}H_2$			
				$C\bar{S}$	++	++	++

Note : anhydrite originally included in small amount in the clinker is neglected (Table 1).

By the addition of II-anhydrite similar trend of strength is noticed, although too much addition spoils the initial strength (Fig. 4). Air curing gives not so high strength as in the case of blending gypsum. On the contrary, water curing reveals relatively so high strength. Addition of 5 to 10 percent II-anhydrite would be suitable. Anhydrite remained more or less unreacted in all hardened cements due to relatively low reactivity of II-anhydrite compared with gypsum. $C_4A_3\overline{S}$ was not detected in all hardened cements just after the steam curing.

Hydrates encountered are ettringite sometimes associated with slight amount of calcium monosulphates both of 18-hydrate and 12-hydrate, C-S-H and probably poorly crystallized gibbsite as summarized in Table 4 in terms of relative amount and age. In early age XRD diagrams sharp reflections of ettringite were observed in specimens added with gypsum, whereas broadened reflections in specimens of neat cement and in specimens added with II-anhydrite, indicating the difference of crystallinity of ettringite derived. In some specimens stored in air weakening or broadening of XRD peaks were observed on ettringite due to relatively dry environment of storage, resulting slight disintegration into calcium monosulphates (18-hydrate and/or 12-hydrate) and calcium sulphates (gypsum or anhydrite), probably accompanied with aqua released. This process can be ex-

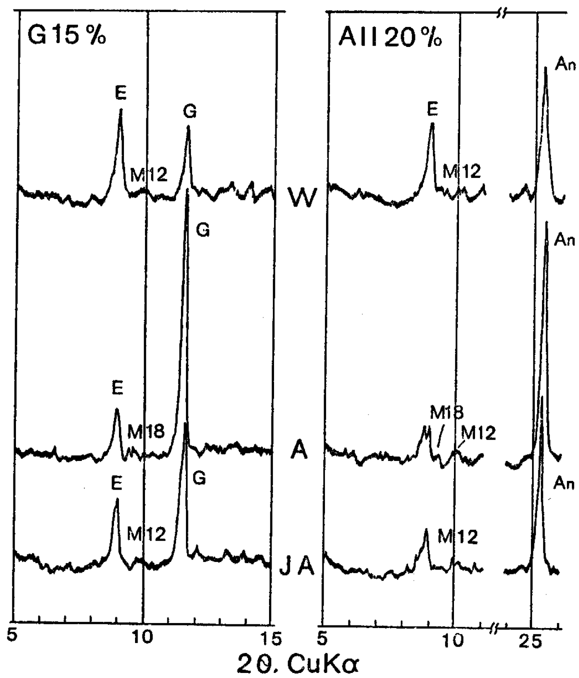

Fig. 5 XRD charts indicating two examples of trisulphate-monosulphate conversion occurred in air storage. Note the increasing of gypsum and anhydrite peaks and the decreasing of ettringite peaks in the diagrams. E: ettringite, M 18: calcium monosulphate 18-hydrate; M 12: calcium monosulphate 12-hydrate, G: gypsum, An: anhydrite. Other notations are in Figs. 3 and 4. Slight contamination of ettringite reflection is suspected on M 12 peaks, but negligible.

pressed as follows:

$$C_6A\bar{S}_3H_{32} \longrightarrow \begin{matrix} C_4A\bar{S}H_{12} \\ \text{and / or} \\ C_4A\bar{S}H_{18} \end{matrix} + \begin{matrix} 2C\bar{S}H_2 \\ \text{or} \\ 2C\bar{S} \end{matrix} + aq.$$

where incorporation of $Ca(OH)_2$ potentially estimated as solid solutions due to hydration of C_2S are neglected. When gypsum is admixed to the cement, gypsum appears as one of the disintegration products in the specimens stored in air, whereas anhydrite appears, when II-anhydrite is blended (Fig. 5). These phenomena are of interest to note. No appreciable influence was detected on the strength of hardened cements due to this conversion.

4. Conclusion

Though the scheme of steam curing, both in temperature and in duration, should be improved more, present haüyne-belite cement made from blast furnace slag, gypsum and calcium carbonate (limestone) has a potential of application for manufacturing water resistant prefabricated materials having moderately high strength in short period of time by means of high temperature steam curing. Although admixing II-anhydrite is also effectable, different from the result of water curing at ambient temperature[3], admixing gypsum may be preferable to admixing II-anhysrite to the neat cement as an additive for increasing compressive strength, as a whole, in stability of strength. Present haüyne-betite cement intends to do effective utilization of industrial wastes, both of blast furnace slag and by-product gypsum and is of interest in comparison with the similar cements now being studied by Sudoh et al[4]., by Mehta[5] and by Viswanathan et al[6]., independently, at the same time from different point of view. Further study will be reported elsewhere.

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