Strength and Microstructures of Hardened Cement Pastes Cured by Autoclaving

S. AKAIWA and G. SUDOH, Chichibu Cement Co., Ltd., Japan

•IT IS well known that autoclave curing is suited for manufacturing secondary products of cement such as asbestos-cement pipe, precast or lightweight concrete products, and sand-lime products. In many cases, the hardening process and properties of autoclaved products differ from those of products cured at ordinary temperature. By autoclave curing the calcium silicate hydrates are formed most prominently, and it may fairly be said that the properties of those hardened bodies are mainly dependent on the kinds and amount of calcium silicate hydrates formed.

The purpose of the present paper is to identify the kinds of calcium silicate hydrates formed and to determine their effects on the mechanical strength or other properties of the autoclaved test specimens. From the results of these tests, binding capacities of several hydrate compounds, as well as suitable conditions for autoclave curing of cements, are discussed.

MATERIALS

The materials used in this study were three cements, ordinary portland cement (OPC), portland blast-furnace slag cement (PBC) and specially prepared cement (SMC). OPC and PBC were of plant manufacture. The content of blast-furnace slag in PBC was 45 percent by weight. SMC was prepared by mixing 60 percent OPC and 40 percent siliceous rock powder by weight. The properties of each cement are indicated in Tables 1, 2 and 3. The chemical composition of the siliceous rock powder is included in Table 1.

METHODS

Preparation of Specimen and Curing Conditions

Cement pastes were made at a water-cement ratio of 0.30, mixed for 3 min, and molded into 4-×4-×16-cm prisms. After 1 day moist curing at room temperature (20 C, 98 percent RH), the prisms were removed from the molds and immediately placed in an autoclave. Four curing temperatures and vapor pressures were used: 110 C, 1.5 kg/cm^2; 150 C, 4.8 kg/cm^2; 200 C, 15.9 kg/cm^2 and 250 C, 40.6 kg/cm^2. Five autoclave curing periods, 5, 10, 16, 24 and 72 hr, respectively, were also used at each temperature and vapor pressure. The time needed for temperature rise in the autoclave and the time needed for cooling it down to room temperature were always kept constant (about 2.5 hr). Three prisms were prepared for examination at each curing condition. For preparing one test prism, about 500 g of cement was required in the cases of OPC and PBC, and about 450 g in the case of SMC.

Chemical Analysis

Specimens for chemical analysis were prepared by grinding the hardened prisms finely and drying to constant weight at 105-110 C.

Only ignition loss and free $Ca(OH)_2$ were determined. Ignition loss was determined by heating the specimen powder at 900 C for 20 min in the cases of OPC and SMC, and by heating at 650 C for 30 min in the case of PBC. Free $Ca(OH)_2$ was determined by using the method of tribromphenol extraction (1), but was calculated as free CaO on ignited base.

TABLE 1

RESULTS OF CHEMICAL ANALYSES ON STARTING MATERIALS

Item / Material	Chemical composition (%)														Potential phase composition (%)			
	ig.loss	insol.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Mn_2O_3	S	Total	F.CaO	C_3S	C_2S	C_3A	C_4AF
OPC	0.50	0.39	21.75	5.18	3.08	65.45	1.61	1.53	0.40	0.62	nd.	nd.	100.51	0.68	54.6	21.2	8.5	9.4
PBC	0.43	1.01	24.47	10.45	2.25	54.75	2.76	2.08	0.53	0.74	0.56	0.36	100.39	0.67	—	—	—	—
SMC	0.38	nd.	49.52	4.73	2.33	39.27	1.51	1.42	0.51	1.02	nd.	nd.	100.69	nd.	—	—	—	—
Siliceous rock powder	0.21	nd.	91.18	4.06	1.20	tr.	1.34	tr.	0.68	1.62	nd.	nd.	100.29	—	—	—	—	—

TABLE 2

RESULTS OF PHYSICAL TESTS ON CEMENTS

Item / Cement		OPC	PBC	SMC
Specific gravity		3.16	3.05	2.95
Fineness	Blaine specific surface area (cm^2/g)	3,420	3,850	3,450
	Sieve 88μ residue (%)	0.5	0.7	3.3
Time of set (hr.— min.)	Initial	1 — 45	1 — 53	2 — 40
	Final	2 — 45	2 — 56	3 — 40
Soundness (Pat test)		sound	sound	sound
Modulus of rupture in flexure (kg/cm^2)	3 days	33.4	33.6	26.5
	7 days	48.8	44.9	33.6
	28 days	72.0	69.8	42.1
Compressive strength (kg/cm^2)	3 days	116	113	75
	7 days	191	190	101
	28 days	370	352	161

Note: The tests complied with JIS R 5201 — Physical Testing Method of Cement (Japanese Industrial Standard; Specimen 4×4×16cm, water-cement ratio 0.65, Mix 1:3).

TABLE 3

STRENGTH OF HARDENED CEMENT PASTES
CURED AT 20 C FOR 28 DAYS

Item / Cement	W/C (%)	Flow (mm)	Modulus of rupture in flexure (kg/cm^2)	Compressive strength (kg/cm^2)	Coefficient of brittleness
OPC	30	222	113.6	680	6.0
PBC	30	201	102.5	693	6.8
SMC	30	231	100.0	434	4.3

Notes: 1. Dimension of test specimen; 4×4×16cm

2. Coefficient of brittleness = [Compressive strength] / [Modulus of rupture in flexure]

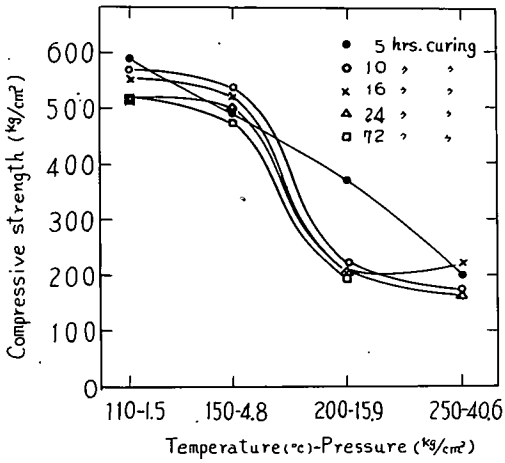


Figure 1. Curing condition vs compressive strength of OPC.

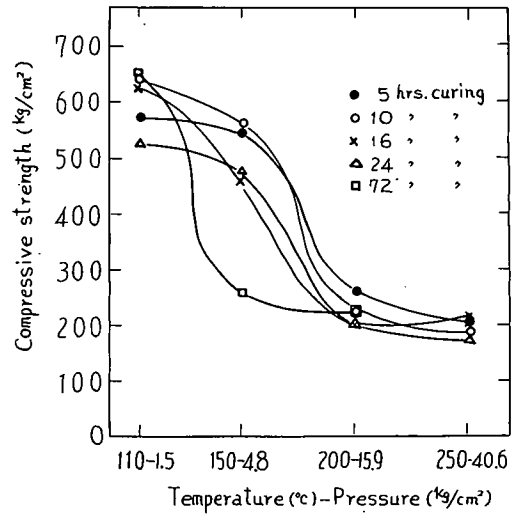


Figure 2. Curing condition vs compressive strength of PBC.

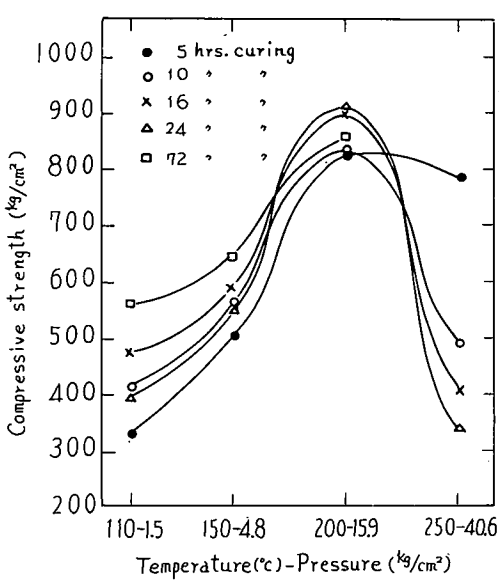


Figure 3. Curing condition vs compressive strength of SMC.

Measurement of Mechanical Strength

Both flexural and compressive strengths were determined. The flexure test was performed on three prisms for each curing condition of respective cement. The compressive strength was measured on the broken pieces of the prism from the flexure test, averaging the strength values of the six test pieces for each curing condition. The error in measurement of compressive strength was fairly small, and was estimated to be less than ± 10 kg/cm^2 in general.

X-Ray Diffraction Analysis and Microscopic Observation

The X-ray apparatus used was a Geiger counter diffractometer made by Rigaku Denki Co., Ltd., in Japan. Operating conditions for all specimens were as follows: CuKα (Ni-filtered); 30-40 kV; 15 mA; scale factor, 8; time constant, 4 sec; multiplier, 1; scanning speed, 0.5 deg/min; chart speed, 1 cm/min. The specimens for X-ray diffraction analyses were prepared in the same manner as those for chemical analyses.

The microscopic examination of the internal structure of the hardened prism was carried out by using both optical and electron microscopes.

The specimens for optical microscope observation were etched with 1 percent HNO_3 in alcohol for 1-3 sec after surface polishing.

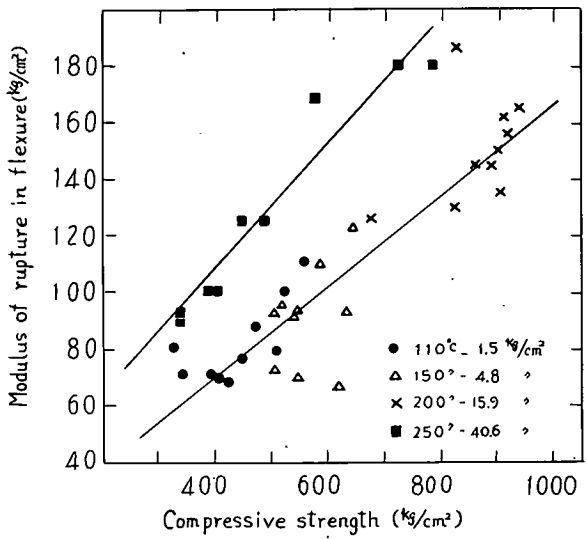


Figure 4. Relationship between flexural and compressive strengths of SMC prism.

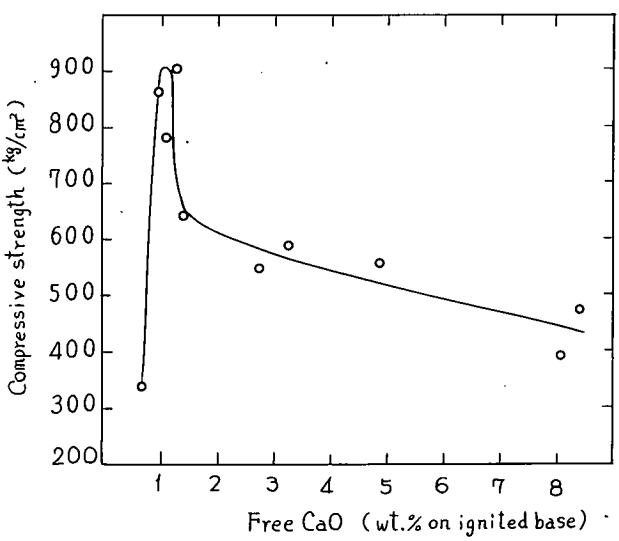


Figure 5. Free lime content vs compressive strength of SMC prism.

For the electron microscope observation, the Filmy Replica technique developed by Fukami (2) was applied on the fractured surface of the prism. The replica in this method is a kind of two-step positive replica using plastic material of high swelling character such as acetylcellulose. In this study chromium-shadowed acetylcellulose-aluminum replicas were used. The electron microscope employed was made by Japan Optics Laboratory Co., Ltd.

RESULTS

Mechanical Strength of Hardened Prisms

The results of measurements of compressive strength are shown in Figures 1, 2 and 3. The effect of temperature and pressure on strength is severe, but that of duration of cure seems to be rather mild.

TABLE 4

ANALYTICAL RESULTS OF IGNITION LOSS AND FREE $Ca(OH)_2$ ON TYPICAL PRISMS AS COMPARED WITH COMPRESSIVE STRENGTH

Cement \ Item	Curing condition: Temperature (°C)	Pressure (kg/cm²)	Time (hr.)	Ig. loss (%)	F. CaO (%)	Compressive strength (kg/cm²)
OPC	110	1.5	5	16.71	14.14	585
	110	1.5	24	16.45	14.77	518
	110	1.5	72	16.07	13.43	516
	150	4.8	5	15.73	14.64	491
	150	4.8	24	14.93	15.17	494
	150	4.8	72	15.05	14.00	475
	200	15.9	5	12.99	13.40	371
	200	15.9	10	11.54	11.72	224
	250	40.6	5	8.84	9.10	201
	250	40.6	24	8.83	9.35	167
PBC	110	1.5	10	16.77	7.55	638
	110	1.5	24	17.08	7.57	523
	110	1.5	72	17.22	6.44	649
	150	4.8	10	14.74	7.24	559
	150	4.8	72	13.45	4.08	256
	200	15.9	5	11.93	3.82	258
	200	15.9	72	11.07	3.22	221
	250	40.6	5	9.81	2.93	201
	250	40.6	24	9.61	2.87	176
SMC	110	1.5	16	13.22	8.40	476
	110	1.5	24	13.66	8.05	395
	110	1.5	72	13.79	4.88	558
	150	4.8	16	13.16	3.22	589
	150	4.8	24	13.26	2.72	549
	150	4.8	72	11.55	1.39	644
	200	15.9	16	15.73	1.33	900
	200	15.9	72	14.44	0.98	862
	250	40.6	5	12.42	1.08	783
	250	40.6	24	10.31	0.62	338

Note: Free $Ca(OH)_2$ is indicated as free CaO on ignited base.

The optimum curing conditions for each cement are: 110 C, 1.5 kg/cm², 5 ~ 10 hr for OPC; 110 C, 1.5 kg/cm², 10~16 hr for PBC; and 200 C, 15.9 kg/cm², 16~ 24 hr for SMC. The expected compressive strengths of each cement corresponding to these curing conditions are above 500 kg/cm², 550 kg/cm² and 900 kg/cm² for OPC, PBC and SMC, respectively.

SMC shows the highest strength and seems to be one of the most suitable cements for autoclave curing.

A few strength values indicated in Figures 1, 2 and 3, such as the values of 200 C. 15.9 kg/cm², 5-hr curing of OPC, or at 150 C, 4.8 kg/cm², 72-hr curing of PBC, deviate considerably from other strength values. X-ray identification, described later, shows that these deviations are not due to error in measurement of compressive strength, but are attributed to the difference in kinds of calcium silicate hydrates formed, originating in different curing times.

The error in measurement of flexural strength was fairly large, probably because of air voids in the prisms.

Air bubbles in the molded cement paste, though initially small, will swell with rising temperature, and may occasionally make continuous pores within the prism. If these swollen pores or voids are situated near the middle of the span of the prism, the apparent flexural strength will be low. However, in testing for compressive strength, pressure is equally distributed over the upper and lower surfaces of the prism, thus reducing the effects of pores and voids.

Figure 4 shows the relationship between flexural and compressive strengths of SMC prisms. The relationship for the prisms cured in the range of 110 C, 1.5 kg/cm^2 ~200 C, 15.9 kg/cm^2 differs from those cured at 250 C, 40.6 kg/cm^2.

The reason for there being two distinct relationships is thought to be that two different kinds of calcium silicate hydrates are formed. In prisms of OPC and PBC, there was no fixed correlation between flexural strength and compressive strength.

Ignition Loss, Free $Ca(OH)_2$ and Their Relation to Compressive Strength

The amounts of ignition loss and free $Ca(OH)_2$ in the prisms of OPC and PBC showed a tendency to decrease with increasing curing temperature and pressure. The reduction of free $Ca(OH)_2$ content is thought to be due to the formation of more lime-rich hydrated compounds at higher temperature and pressure. The amount of ignition loss depends on the amounts of free $Ca(OH)_2$ and hydrated compounds formed, as well as the amount of combined water in the hydrates. Table 4 gives the amounts of ignition loss and free $Ca(OH)_2$ of the sample prisms and their corresponding compressive strengths. The relationships between amount of ignition loss and compressive strength or between amount of free $Ca(OH)_2$ and compressive strength show fair linearity in the cases of OPC and PBC. For specimens made with OPC and PBC, the compressive strength increases with increasing amounts of free $Ca(OH)_2$ or ignition loss.

In the case of SMC the amount of ignition loss is nearly constant in the range between 110 C, 1.5 kg/cm^2 and 200 C, 15.9 kg/cm^2 even though the amount of free $Ca(OH)_2$ decreases with increase of temperature and pressure. This is because of the formation of more hydration product that contains much combined water. As indicated in Figure 5, the existence of a larger amount of free $Ca(OH)_2$ gives comparatively lower strength, owing to the incomplete reaction between siliceous rock powder and $Ca(OH)_2$ liberated by the hydration of calcium silicates in cement. The decrease in the amount of free $Ca(OH)_2$, due to adequate progress of the reaction, may be accompanied by either a decrease, or an increase, in strength. Higher strength is obtained from the formation of hydrate with good binding capacity, whereas lower strength is obtained from the formation of hydrate with poor binding capacity. X-ray identification shows the high-strength compound to be tobermorite phase and the low strength compound to be xonotlite.

X-Ray Identification of Hydrated Compounds

The results of X-ray diffraction analyses show that free $Ca(OH)_2$ or calcium silicate hydrates are predominant in the prisms. No separate hydrated aluminate, ferrite or sulfoaluminate phases were detected. Aluminum-bearing hydrogarnet was recognized, but only in the PBC prism cured at 250 C, 40.6 kg/cm^2. These results are summarized in Table 5.

Microstructure of the Hardened Prism

Results of Observations by Optical Microscope. —The microstructures of hardened OPC prisms cured between 110 C, 1.5 kg/cm^2 and 200 C, 15.9 kg/cm^2 are similar to each other, showing the unhydrated clinker minerals as phenocryst and the hydrated phase as matrix.

However, blackish reaction rims around the clinker minerals become characteristic as the time of curing is prolonged (Fig. 6-a). The prism cured at 250 C, 40.6 kg/cm^2 shows a microstructure of the hydrated phase, for the most part, and of small unhydrated clinker minerals lying scattered in the matrix.

TABLE 5

PHASES DETECTED BY X-RAY IN THE HARDENED PRISMS

Item / Cement	Curing condition Temp.— Pres. (°C) (kg/cm²)	Phases detected: Unhydrated: clinker minerals	Unhydrated: α-SiO_2	Hydrated: f. $Ca(OH)_2$	Hydrated: tobermorite phase	Hydrated: xonotlite	Hydrated: $C_2SH(A)$	Hydrated: $C_2SH(B)$	Hydrated: $C_2SH(C)$	Hydrated: C_3SH_2	Hydrated: gismondite	Hydrated: plazolite	Unknown phase
OPC	110 — 1.5	◎	—	◎	●→○	×	×	×	×	×	×	×	◍
	150 — 4.8	○	—	◎	◍→●	×	×→◍	×	×	×	×	×	●
	200 — 15.9	◍	—	◎	×	×	●→○	×	×	◍→○	×	×	●
	250 — 40.6	◍→●	—	◎	×	×	×	×	◍	○	×	×	●
PBC	110 — 1.5	○→◍	—	◎	◍→○	×	×	×	×	×	×	×	◍
	150 — 4.8	○→◍	—	○	●→○	×	×→◎	×	×	×	×	×	●
	200 — 15.9	◍→●	—	○	◍	×	◎	?	×	×	?	?	◍
	250 — 40.6	◍→●	—	○→◍	×	×	○→◍	×	×	?	×	◍→○	●
SMC	110 — 1.5	○→●	◎	○	●	×	×	×	×	×	×	×	◍
	150 — 4.8	◍→●	◎	○→◍	●→◍	×	●?	×	×	×	×	×	●
	200 — 15.9	●	◎→●	×	○→◎	●	×	×	×	×	×	×	●
	250 — 40.6	●→×	○→●	×	○→●	●→◎	×	×	×	×	×	×	●

Notes: 1. *Peak intensities of each phase are as follows:*
◎; strong, ○; moderate, ◍; weak, ●; very weak

2. *"?" means uncertain existence of peak, and also "X" means absence of peak of corresponding compound.*

3. *"◎→○" means the change of peak intensity from "strong" to "moderate" with increasing curing time. Use of other symbols with arrow indicates corresponding change.*

The microstructures of hardened PBC prisms consist of fine fragments of blast-furnace slag, unhydrated clinker minerals and hydrated phase. The fragments of blast-furnace slag, however, are eroded even by curing at 110 C, 1.5 kg/cm^2 for 10 hr (Fig. 6-b), and no slag fragments of primary form are observed at all in the micro-structures of prisms cured at 250 C, 40.6 kg/cm^2 for 1 day.

The microstructures of hardened SMC prisms consist of fine fragments of silica, unhydrated clinker minerals, and hydrated phase. The fragments of silica show re-action rims when cured at 110 C, 1.5 kg/cm^2 (Fig. 6-c). When cured at 200 C, 15.9 kg/cm^2, these silica fragments are heavily eroded and become very fine, indicating that the reaction is fairly advanced (Fig. 6-d).

Results of Observations by Electron Microscope.—The electron microscope reveals the microstructure of the hydrated phase. In the OPC prisms the hydrated compound presumed to be tobermorite phase is found at 110 C, 1.5 kg/cm^2 curing (Figs. 6-e, 6-f). The prisms cured at 200 C, 15.9 kg/cm^2 show rather porous structure consisting of large grains of crystals and a small amount of platy crystalline matter. By curing at 250 C, 40.6 kg/cm^2, the structure of the prism consists mainly of fibrous or oblong platy crystals (Fig. 6-g).

In the case of PBC prisms, the foils of tobermorite phase and free $Ca(OH)_2$ which show the layer structure are recognized at 110 C, 1.5 kg/cm^2 curing (Figs. 6-h, 6-i). But at 250 C, 40.6 kg/cm^2, many globular crystals are developed in the structure cured for only 16 hr (Fig. 6-j). This globular compound is presumed to be plazolite, $3CaO \cdot Al_2O_3 \cdot 2(SiO_2, CO_2) \cdot 2H_2O$.

In the case of SMC prisms, pliant platy tobermorite phase is found in the structure of the hardened prisms cured at 150 C, 4.8 kg/cm^2. At 200 C, 15.9 kg/cm^2 curing,

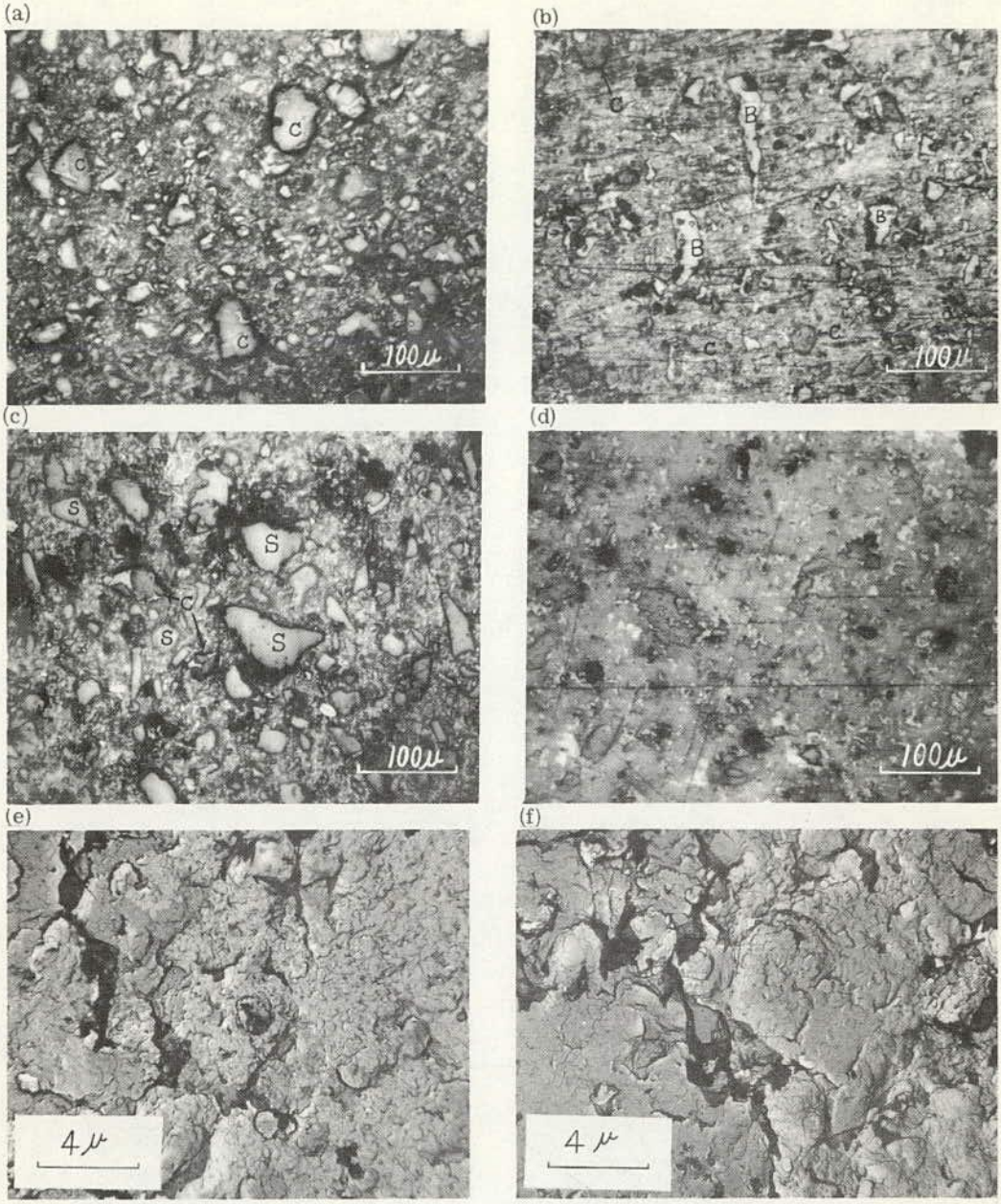


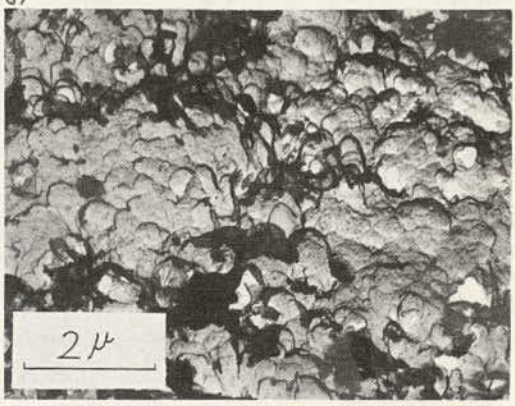
Figure 6. Internal structures of the hardened prisms. (a) OPC prism cured at 110 C, 1.5 kg/cm^2 for 72 hr; C indicates unhydrated clinker minerals (optical micrograph). (b) PBC prism cured at 110 C, 1.5 kg/cm^2 for 10 hr; B indicates the fine fragment of blast-furnace slag, C is as above (optical micrograph). (c) SMC prism cured at 110 C, 1.5 kg/cm^2 for 24 hr; S indicates the grain of silica, C is as above (optical micrograph). (d) SMC prism cured at 250 C, 40.6 kg/cm^2 for 5 hr (optical micrograph). (e) OPC prism cured at 110 C, 1.5 kg/cm^2 for 16 hr (electron micrograph). (f) OPC prism cured at 110 C, 1.5 kg/cm^2 for 16 hr (electron micrograph).

(g)

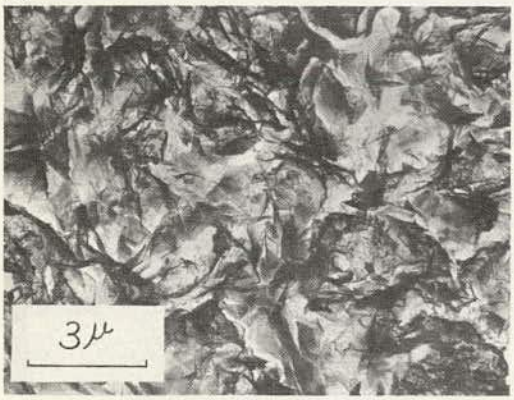
(h)

(i)

(j)



(k)



(l)

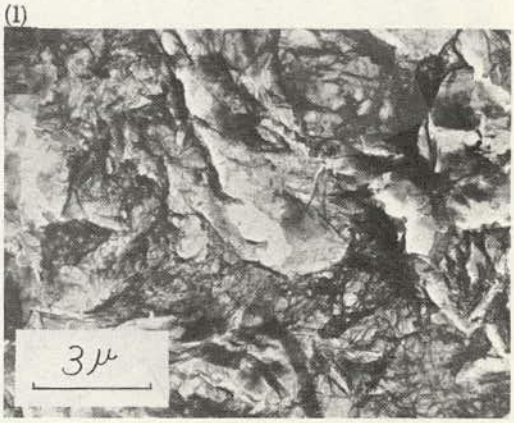


Figure 6 (continued). (g) OPC prism cured at 250 C, 40.6 kg/cm^2 for 5 hr (electron micrograph). (h) PBC prism cured at 110 C, 1.5 kg/cm^2 for 16 hr (electron micrograph). (i) PBC prism cured at 110 C, 1.5 kg/cm^2 for 72 hr (electron micrograph). (j) PBC prism cured at 250 C, 40.6 kg/cm^2 for 16 hr (electron micrograph). (k) SMC prism cured at 200 C, 15.9 kg/cm^2 for 16 hr (electron micrograph). (l) SMC prism cured at 200 C, 15.9 kg/cm^2 for 16 hr (electron micrograph).

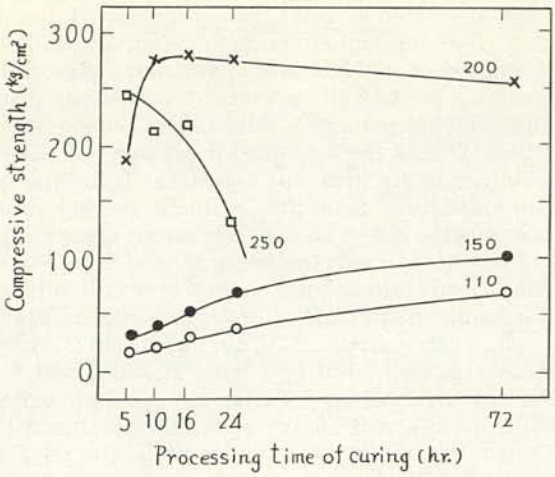


Figure 7. Curing condition vs compressive strength of the specimen made with blast-furnace slag powder (numbers in the diagram indicate the curing temperatures, deg C).

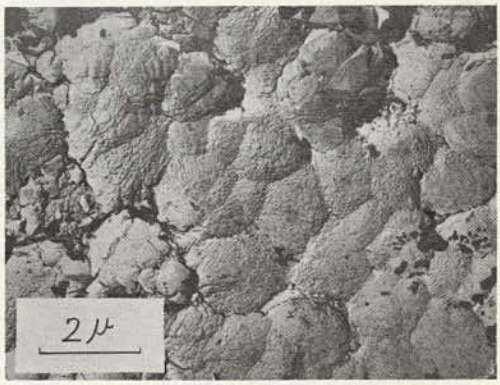


Figure 8. Electron micrograph of plazolite formed in the hardened blast-furnace slag powder.

the tobermorite phase is extremely well developed (Fig. 6-k), but a small amount of fibrous crystals presumed to be xonotlite is also present (Fig. 6-l). At 250 C, 40.6 kg/cm^2 curing, fibrous crystals are developed which are clearly identified as xonotlite, and constitute the structure of the prisms.

DISCUSSION

The properties of the hardened prisms depend mainly upon the hydrated phase, especially calcium silicate hydrates. The hardened OPC prisms show high compressive strength after curing between 110 C, 1.5 kg/cm^2 and 150 C, 4.8 kg/cm^2, and at such conditions the tobermorite phase develops predominantly. By curing at higher temperature and pressure, the tobermorite phase gradually decreases and other calcium silicate hydrates such as lime-rich phase appear, showing lower strength. The hardened PBC prism cured at 110 C, 1.5 kg/cm^2 also consists mainly of tobermorite phase, and it gives high compressive strength. But if the curing time is protracted at 150 C, 4.8 kg/cm^2, the formation of $C_2SH(A)$ proceeds and the compressive strength goes down. If curing is done at higher temperature and pressure, the amount of tobermorite phase is gradually reduced and $C_2SH(A)$, or plazolite, appears, bringing decreased strength in the hardened prisms.

In the hardened SMC prisms cured at 200 C, 15.9 kg/cm^2, the amount of tobermorite phase becomes largest and gives the highest compressive strength. But if cured at 250 C, 40.6 kg/cm^2, the amount of tobermorite phase decreases and xonotlite starts to appear, giving lower strength. In the SMC prisms, tobermorite phase forms to a greater extent than in other cement prisms. This is the reason why SMC shows higher strength than OPC and PBC. One of the authors (3) earlier postulated that the cementing capacities of several calcium silicate hydrates are in the following order: tobermorite phase > xonotlite > gyrolite >afwillite >dicalcium silicate hydrate group. In this study it is also concluded that tobermorite phase has the strongest cementing power and that formations of other calcium silicate hydrates bring strength retrogression of hardened pastes. Hydrogarnet, such as plazolite, also causes strength retrogression. According to other work by Sudoh (4), molded specimens (ϕ30 × 20 mm) of blast-furnace slag powder give maximum compressive strength by curing at 200 C, 15.9 kg/cm^2, when tobermorite phase is most developed. But by curing at 250 C, 40.6 kg/cm^2 plazolite is formed and strength falls with prolonging of curing time. Figure 7 shows the relationship between curing condition and compressive strength. Figure 8 is the electron micrograph of plazolite formed in the hardened specimen of blast-furnace slag powder cured at 250 C, 40.6 kg/cm^2 for 24 hr.

As already mentioned, the hardened prisms of OPC and PBC show good linearity between compressive strength and the amounts of ignition loss or free $Ca(OH)_2$. A large amount of ignition loss indicates sufficient progress of hydration and formation of a hydration product, such as tobermorite phase, that has much combined water in its crystal structure. A small amount of free $Ca(OH)_2$ indicates inadequate progress of hydration, or formation of lime-rich calcium silicate hydrates which commonly have smaller amounts of combined water and low grade cementing capacities. The reason for the good linear relationships between ignition loss content and compressive strength, as well as between free $Ca(OH)_2$ content and compressive strength, can be explained as above.

But in the hardened prisms of SMC, the relationship between compressive strength and the amount of free $Ca(OH)_2$ is different; that is, hardened prisms containing a large amount of free $Ca(OH)_2$ give low compressive strength, but those containing a small amount of free $Ca(OH)_2$ may give either high or low strength, as already discussed.

CONCLUSIONS

From this series of experiments, then, the following may be concluded:

Compressive strength of hardened paste cured by autoclaving depends on temperature, pressure and duration of curing. The effects of temperature and pressure are especially severe. Duration of curing does not affect strength severely, but too-long curing brings strength retrogression. No relationship is recognized between flexural and compressive strengths in the hardened prisms of OPC and PBC, but there is a fairly linear relationship between them in the hardened prisms of SMC.

The amounts of ignition loss and free $Ca(OH)_2$ in cured prisms of OPC and PBC show a tendency to decrease with rise of curing temperature and pressure. Larger amounts of ignition loss and free $Ca(OH)_2$ are related to higher strength of the hardened prisms. In hardened SMC prisms, a large amount of free $Ca(OH)_2$ is related to rather low strength. On the other hand, a small amount of free $Ca(OH)_2$ gives high or low strength, depending on the constitution of the calcium silicate hydrates formed.

According to X-ray identification, the hydration products are mainly calcium silicate hydrates and free $Ca(OH)_2$. No other products are recognized clearly except plazolite in the hardened specimens of PBC. The existence of tobermorite phase gives the highest strength; other hydrated compounds bring strength retrogression.

SMC is considered to be the cement most suited for autoclave curing.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Professor G. Yamaguchi of Tokyo University for his invaluable advice. Thanks are also due to M. Horiguchi, managing director of Chichibu Cement Co., Ltd., for permission to publish this paper.

REFERENCES

1. Fujii, K. Semento Gijutsu Nempo, Vol. 3, p. 93, 1949; Vol. 4, p. 167, 1952.
2. Fukami, A. Jour. Electronmicroscopy, Vol. 4, No. 1, p. 36, 1955.
3. Yoshii, T., and Sudoh, G. Sement Gijutsu Nempo, Vol. 16, p. 97, 1962.
4. Sudoh, G. In preparation.