

경화촉진제와 억제제의 시멘트 및 시멘트-목재 복합체 양생 효과에 관한 전자현미경적연구^{*1}

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Scanning Electron Microscopic Examination of the Effects of an Inhibitor and an Accelerator on Setting and Hardening of Portland Cement Paste and Wood-Cement Composites (WCC)^{*1}

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적 요

경화촉진제로서 염화칼슘, 경화억제제로서 수크로오즈를 처리한 포트랜드시멘트의 양생효과를 전자현미경에 의해 관찰한 결과, 경화억제제를 처리한 시멘트는 결경을 이루지 못하고 용기상태로 남아있고, 경화촉진제를 처리한 시멘트는 겔형으로 변한후 육각형의 결경을 이루는 것이 관찰되었다.

또한 시멘트-목재 복합체의 양생은 좀 다른양상을 보이고있어 경화제가 처리된 WCC는 포플러·스리버 표면에서 작은 용기가 겔상의 표면에 많이 관찰되나 무처리는 거의 일정한 모양의 입자가 관찰되어 시멘트 경화촉진제와 억제제의 효과를 구명하였다.

Keywords : Accelerator, hydration, portland cement, retarder, wood-cement composites (WCC)

1. INTRODUCTION

The composition of the portland cement is basically calcium silicate mixture predominantly containing tricalcium and dicalcium silicates which can usually be abbreviated as C_3S ($3CaO \cdot SiO_2$) and C_2S ($2CaO \cdot SiO_2$) and tricalcium aluminoferrite (C_4AF) in smaller proportion.

The general composition of the portland cement is in Table 1. High aluminum cement contains mainly monocalcium aluminate($CaO \cdot Al_2O_3$, or CA) and relatively small amount of silicates.

Some technical terms on cement are defined for clarity as follows (14):

Cement paste: the thick slurry formed by mixing a cement with aggregates and water on such

proportion that setting will occur. Also the mixture above and resulting materials at all stages of setting and hardening, even after becoming quite rigid. Setting: the initial stiffening, which usually occurs within a few hours. Hardening: the development of strength which is a slower process of strength development of the paste. The strength of the paste increases at least two years in portland cement under ordinary temperatures. Hydration reaction: the reactions causing and hardening of cement paste. Curing of paste: leaving the paste for setting and hardening. Neat cement: the paste of a cement with water in absence of aggregates.

The silicates in portland cement hydrate form clusters of acicular particles. These clusters are found at the time of initial set of paste and become larger and denser. Interlocking and growing

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Table 1. Potential Phase Composition for Cements of Different Types

Cement		Potential phase composition(%)					Free CaO (%)	CaSO ₄ (%)	Total ¹ (%)
Type	Description	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	MgO			
I	General Use	45	27	11	3	2.9	0.5	3.1	98
II	Moderate Heat of Hardening	44	31	5	13	2.5	0.4	2.8	99
III	High Early Strength	53	19	11	9	2.0	0.7	4.0	99
IV	Low Heat	28	49	4	12	1.8	0.2	3.2	98
V	Sulphate Resisting	38	43	4	9	1.9	0.5	2.7	99

Note: 1. The remaining 1—2% consists mainly of moisture, insoluble residue, and alkali oxides combined in various ways.

Source: Taylor, H.F.W. 1964. The Chemistry of Cements. Vol.1. p.5. Taylor, H.F.W., Ed. Academic Press.

together of the clusters of acicular particles cause final hardening of the cement paste. The development of strength in concrete is the result of chemical reactions—hydration reaction—between the cement constituents and the water added. The consolidation process occurs by the formation of rigid interlocking matrix of hydration products. The hydration products gradually replace the water between the cement grains and finally bind together (2).

2. BACKGROUND

2.1. The Hydration Process of Cement

The estimated necessary curing times of cement paste depend on the water to cement ratio (W/C), for type I cement at standard laboratory condition. It takes one year when W/C is 0.7, half year W/C 0.6, 14 days W/C 0.5, 7 days W/C 0.45 and 3 days W/C 0.40. The volume of the cement gel and other products is about 2.1 times that of the cement from which it was derived. Therefore, hydration products replace not only cement but also some of the water filled space (9).

The hydration of cement takes three basic hydration stages. Just after adding of water into cement, calcium hydroxide and calcium sulfoaluminate so-called "ettringite": $3CaO \cdot 3Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$, are formed at the first stage. The ettringite is a longneedle-like form.

After an hour, crystallization of calcium silicate hydration in long fiber forms—"tobermorite", from tricalcium silicate—"alite", and from dicalcium

silicate—"belite" occurs at second stage. The long fiber-like crystallines of calcium silicate hydrate bridge over the needle-like crystallines of ettringite resulting in huge micropores and give the greater stability to the structure. The length of the fiber is about 1 micron and the range of the diameters is 50 to 1,000 Ångstroms.

At the third stage of hydration the existing pores in volume are filled up with newly forming fine crystallines of calcium silicate hydrate and are made smaller in size-micropores, then the basic structure of cement paste is consolidated and strength of cement paste increases tremendously(1).

The hydrogel developed in a portland cement is an intimate but still heterogeneous mixture of several phases. The predominant phase is a colloidal calcium silicate hydrate of indefinite or variable composition. This material, C-S-H gel phase, is structurally tobermorite. The second major constituent of cement gel is hydrated lime (C-H), dissolved or reprecipitated or otherwise separated in the process of hydration of the calcium silicates. Third gel phase is the groups of compounds formed as products of hydration of the aluminate-bearing and ferrite-bearing clinker constituents in a solution containing calcium and sulphate ions, and also reactive silica complex. This phase is complex of C-A-H gel phase (4).

The size of hydration products of portland cement are all in the range of resolution of the scan-

ning electron microscope (14). Early studies on cement structures were done by reflective optical microscope but the preparation of specimens is extremely difficult(5). Microstructure of cement in fresh paste and cured paste is various forms of crystalline and of amorphous (4).

2.2. The Inhibitor and its Mechanisms on Cement Setting

Certain chemicals affect the setting and hardening of cement. The substances from wood disturbing cement setting and hardening are called inhibitory substances. Even impurity of water itself hinders the cement setting severely. Water soluble sugars such as glucose, fructose, sucrose and galactose present in sapwood disturb the setting and hardening of cement (13).

Saccharinic acid and isosaccharinic acid converted from sugars present in woods under alkaline conditions during setting are one of the main inhibitory substances in cement setting. The saccharinic acids react with calcium giving insoluble salts which cover the growing crystalline particles of cement hydration (3). The critical amount of xyllose, glucose, cellobiose, ascorbic acid and gluconic acid as cement inhibitor is below 0.25 percent and that of raffinose is ca 0.50 percent. Phenols, conidrin, tannin and pentachlorophenol are also critical to cement setting (10).

The quantitative index of inhibition, I , is expressed as:

$$I = 100 Q_s / (Q_s - Q)$$

where Q_s : the time required for uninhibited cement to attain its maximum temperature while setting in a Dewar flask.

Q : the time required for inhibited cement mixture of 200 grams of cement, 15 grams of wood and 90ml of water.

On the same species of wood used, the index decreased with increasing of the wood particle diameters (15).

Usually, the resin acids are more in pines, 3 to 5 percent, than spruce or firs, 1.5 percent. It is necessary to add calcium chloride for saponifica-

tion of resin acids presenting in wood (11).



Addition of 3 percent calcium chloride to the mixture causes the increase of internal bonding and modulus of rupture in Wood-Cement Composites (WCC)(6).

Organic substances such as cellulose products, sugars, carboxylic acids, tannins and lignosulfonic salts, as mentioned above, are the well known inhibitor of cement setting. These compounds have

HO-C-H groups, then the following hypothesis is proposed: Since the compounds are absorbed in the cement stones (grains) of $3CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$, then protection layer of hydration on the cement particles occurs. On the other theory, sugars are converted into calcium saccharides in the water-cement system which have quite poor-dissociation in the system and it causes the increased solubility of aluminum and the aluminium silicate gel covers over the surface of cement particles, the hydration of cement severely retards or ceases. The main reason for this is that the aluminum silicate gel is a material which has hard water penetration properties (12).

3. EXPERIMENTAL

3.1. Materials

Portland cement type 1, *Populus* sp. slivers, 2.7 × 2.7 × 20.0mm in size, 0.1% solution of sucrose as an inhibitor, and 1.0% solution of calcium chloride ($CaCl_2$) as an accelerator were used.

3.2. Procedures

3.2.1. Preparation of Sample Paste and WCC

Wood-cement composites, 10.0 × 15.0 × 100.0mm in dimension and expected density 1.2, were prepared as follows: Wood to cement ratio is 0.3 and water to cement ratio (W/C ratio) 0.4.

Cement paste, 10.0 × 15.0 × 70.0mm in dimension, was mixed in the condition that cement to water ratio was 0.4.

3.2.2. The Mixture

Wood-Cement Composites : Spraying the cal-

culated amount of water having 1% of calcium chloride or sucrose onto that of sivers of poplar and moistening after 10 minutes in a beaker, add the weighted amount of cement into the water-wood mixture. Mix the system and set in form.

Cement paste: Cement pastes are prepared with the water having 1.0% of calcium chloride as an accelerator or 1.0% of sucrose as a retarder of cement setting, and set in forms.

3.2.3. Curing

All the specimens for cement paste and WCC are cured 24 hours under 20°C and saturated relative humidity.

3.2.4 Treatment of Inhibitory Solution:

After 24 hours of cement setting and hardening of specimens are progressed, some of the specimens(accelerator treated one or neat paste without inhibitor) are immersed into 1% sucrose solution for 10 minutes. After the treatment the boards are cured 5 days under the same curing condition.

3.2.5. Electron Microscopic Examination

Preparation of Specimens: The exposing area of specimens for scanning electron microscopy(SEM) is the part of the fresh fracture surface in the range of ca 10×10mm in size.

Drying of the Specimens : Samples of cement powders, specimens having fresh fracture surface and slivers of poplar from WCC were dried 4days under vacuum.

Coating of the Specimen: After mounting the specimens on stubs, all specimens were coated with gold in thickness of 150 Ångstroms under 50 to 100 Torr in vacuum in the spreading device, Hummer 11 Sputting Device.

Kind of Specimens:

- # (2) Paste with water and sugar (1 percent).
- # (3) Paste with water and treated with sugar (1%) 24 hrs later.
- # (4) Paste with water and accelerator(1% Ca-Cl₂).
- # (5) Poplar sliver treated with 1% CaCl₂(Set-

ting Accelerator).

- # (6) Poplar sliver treated no accelerator.

Observation : Observation and photography of the fresh fracture surface of the specimens were done through SEM with the magnification of 500 and 2,000× on specimen #1, 500, 1,200, 3,000, and 10,000× on specimens #2, #3, and #4, and 500, 3,000 and 10,000× on specimen #5 and #6 at 20.0 kV, with Autoscan, ETC Corp. The exposure time was 2 minutes.

4. RESULTS AND DISCUSSION

4.1. Portland Cement

The grains of portland cement are so fine that nearly all of them pass at least through a sieve having 40,000 openings per square inch. The size of each opening in 200 mesh is 0.075mm or 75 microns in diameter. It is obvious that the newly reformed materials exist in the cured cement paste if there is something bigger than 75 microns in diameter. The biggest grains of portland cement are 30 to 40 microns in diameter. These grains are the starting anhydrous compounds for hydration of portland cement. There are two kinds of cement grain in color under the light microscope. The one is clear and transparency and 90 to 95% in amount, and the other is dark in color, and originated from iron ore, an additive to the portland cement at the grinding process, and 5-10 percent in number.

4.2. The Portland Cement Setting with a Retarding Agent

As shown in Explanation of Specimens in page 8, the specimen # 2 is prepared with sucrose, 1% by weight of cement at beginning. The scanning electron micrographs of specimen # 2 are in a series of different magnifications in Plates 1, 2, and 3. The specimen # 3 is the neat cement paste treated with 1% sucrose solution after 24 hours curing at room temperature and almost saturated relative humidity. The scanning electron micrographs of specimen # 3 in different magnifications are arranged in series in Plates 1, 2,

and 3. The specimens #2, #3, #4, #5 and #6 were cured 5 days under the same condition above. Comparing the specimen #2 with that of #3, Plate 2, there are sharp differences in appearance. In #2 many cement grains remained almost in original form, but in #3, cement grains were changed to hydrate to gel phase, and were reprecipitated or reformed to fiber form and plate as shown at the micrograph #2, Plate 1.

In #2, Plate 2, there are crystallites but they are poor and a few in number, whereas in #3 there are many well developed interlocking crystallites in fiber and sheets of hexagonal flakes. These flakes are either calcium hydroxide or calcium sulphoaluminate hydrate. The hexagonal plate is assumed a calcium aluminate hydrate.

On the most well developed part in crystal form in #2, Plate 3, crystallites in small number as well as denser humps in greater number on the surface of cement grains are clearly observed at the higher magnification. The humps are the site of crystallite developing. But in this case growth of the crystallites on the surface of cement grains ceased and became humps at the site. In #3, Plate 3, the broken crystallites of fiber form are easily marked. The diameters of the crystallites are in the range of 0.1 to 0.4 micron. There is no hump on the surface of gel phase. These are the reasons that the specimen #3 is stiff, hard and has strength whereas the specimen #2 is brittle and has no strength.

4.3. The Effects of an Accelerator on Cement Setting

A series of scanning electron micrographs of specimen #4 having an accelerator, 1% CaCl_2 by weight, is shown in Plates 4 and 5. The grains of cement changed to hydrated gel phase at the micrograph #4-A, Plate 4. No individual cement grain is marked in the field of observation. In #4-B, crystallites in fiber, cleavage of calcium hydroxide or calcium sulphoaluminate hydrate and hydrate gel appeared. In #4-C, Plate 5, smaller and denser crystallites between the gel phases

and sheets in form are observed clearly. In #4-D, the broken crystallites in fiber form, crystallites between the gels and the thinnest crystallites on the surface of gel are appeared. The thinnest crystallites on the surface of gel phases are out of resolution of the scanning electron micrographs at the magnification of 10,000 times as shown in #4-D, Plate 5.

The microstructure of the fracture surface in #4, Plates 4 and 5 is quite different from that of #2 and #3, Plates 2, 3, 4 and 5. in appearance.

A scanning electron micrograph of specimen #4, in magnification of 3,000 times, is a crack of cement paste, in Plate 6. In the micrograph, bundles of crystallites, gel phases and sheets of hexagonal flakes or plates in cleavage are observed clearly. It is assumed to crack freshly during the preparation of the specimen fracture surface or by shrinkage during setting and hardening of cement paste.

4.4. The Effect of an Accelerator on Portland Cement Setting in WCC

There is not much difference between unhydrated cement grains and hydrated cement grains in #6, Plate 7. The individual grains having almost the same form and shape of portland cement on surface of poplar sliver from WCC are noticed in #6, Plate 7, but in #5, Plate 9, a smaller amount of cement grains is on the surface of the sliver from WCC and the shape of the grains is changed to hydrate deeply. The difference between the two specimens #5 and #6 is clearly seen in Plate 8.

An accelerator on cement setting and hardening in WCC, especially with poplar wood, resulted in the specific differences between the specimens #5 and #6 in shape and size of the hydration products. In #5, Plate 9, many tiny humps having round ends on the surface of grains are located on the surface of grains and gel phases. This is the results of alkaline degradation products of poplar wood components and alkaline extractives affect

ting the process of cement hydration in WCC. (16):

The composition of a poplar wood is as follows

Table 2. Extractives of *Populus tremuloides*

Ether-Soluble Extractives (%)	Composition of the Extractives		
	Fatty acids (%)*	Fatty esters (%)*	Unsaponfiabiles (%)*
1.0—2.7	35	50	14

Note: *Based on the ether-soluble extractives

Source: Wenzl, H.F.J. 1970. The Chemical Technology of Wood. pp.142—3, Academic Press.

EXPLANATION OF SPECIMENS

Specimen

- # 2 : Cement Paste with water and 1% sucrose by weight of cement.
- # 3 : Cement paste treated with 1% sucrose solution after curing of 24 hours.

- # 4 : Cement paste with an eccelerator (1% CaCl_2).
- # 5 : Poplar sliver in WCC treated with an accelerator (1% CaCl_2)
- # 6 : Poplar sliver in WCC treated with no accelerator.



2 (500X)



3 (500X)

PLATE 1. Scanning Electron Micrographs of the Fresh Fracture Surface of the Specimens # 2 and # 3

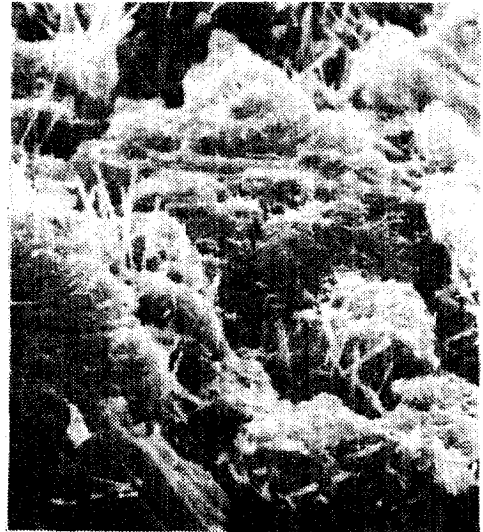
Specimen # 2 : Cement paste having 1% sucrose by weight.

Specimen # 3 : Cement paste immersed in 1% sucrose solution for 10 minutes after curing of 24 hours.

The Difference in appearance between the specimens is quite distinct. In # 2 many cement grains are almost in original form, but in # 3 there is much close contact of gel and hydrates in fiber form.



2 (3,000X)



3 (3,000X)

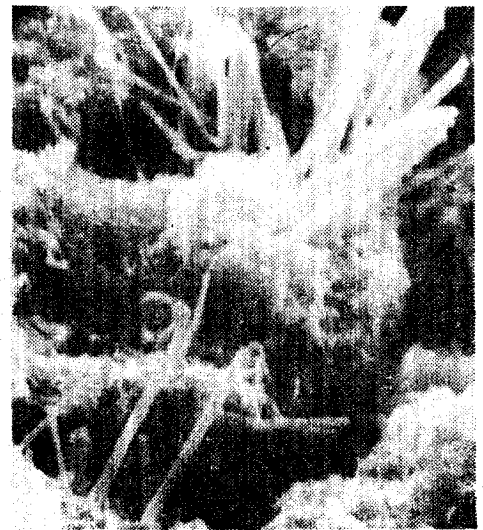
PLATE 2. Scanning Electron Micrographs of the Fresh Fracture Surface Showing the Difference of Crystallites between the Specimens # 2 and # 3

2 : Closed-up of the lower right part of #2, Plate 3. The well crystallized part in #2, Plate 3.
 # 3 : Closed-up of the middle part of # 3, Plate 3.

There are crystallites in specimen # 2 but they are poor and a few in number, whereas in # 3 there are many well developed interlocking crystallites in fiber form and sheets in needle form.



2 (10,000X)



3 (10,000X)

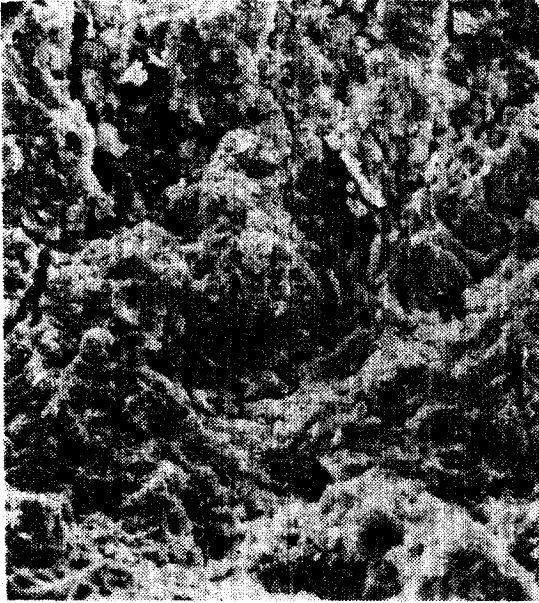
PLATE 3. Scanning Electron Micrographs of the Fresh Fracture Surface Showing the Difference of Crystallites between the Specimens # 2 and # 3 in magnification of 10,000X

2 : Closed-up of the lower middle part of #2, Plate 4. This is the most well developed part showing the most denser crystallines in the specimen.

3 : Closed-up of the upper left part of # 3, Plate 4. The diameters of the fiber form of crystallites are in the range of 0.1 to 0.4 micron. On the fracture surface the broken fiber form crystallites are easily observed in # 3.

The specimen # 2 is brittle in properties and has no strength.

The specimen # 3 is quite stiff and has strength.



4-A (500X)



4-B (1,200X)

PLATE 4. Scanning Electron Micrographs of the Fresh Fracture Surface Showing the Well Developed Crystallites in Specimen #4 Compared with the Specimens #2 and #3 in Plates 2 and 3

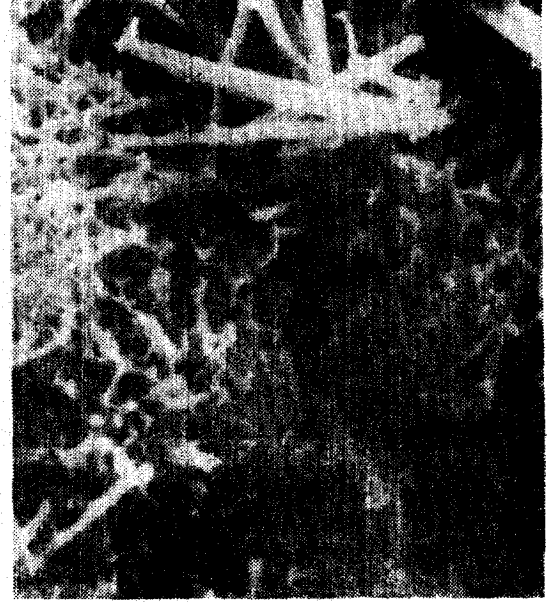
4-A : Cement paste having an accelerator, 1% CaCl_2 .

4-B : Closed-up of the center part of #4-A.

The well developed crystallites are observed in abundance at #4-B.



4-C (1,200X)



4-D (10,000X)

PLATE 5. Scanning Electron Micrographs of the Fresh Fracture Surface on Specimen #4
Abundance of crystallites and gel is noticed.



(3,000X)

PLATE 6. Scanning Electron Micrograph of a Crack in Closed-up in the Middle Left Part of # 4-A, Plate 6

It is assumed to crack freshly during the preparation of specimen fracture surface or shrinkage while setting and hardening of the paste.



5 (500X)



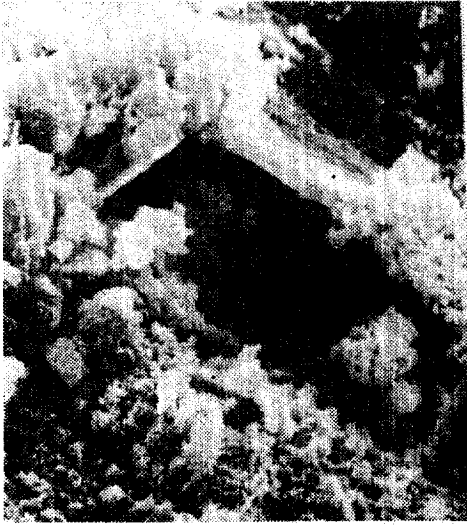
6 (500X)

PLATE 7. Scanning Electron Micrographs of a Sliver Surface Showing the Effects of an Accelerator on Cement Setting

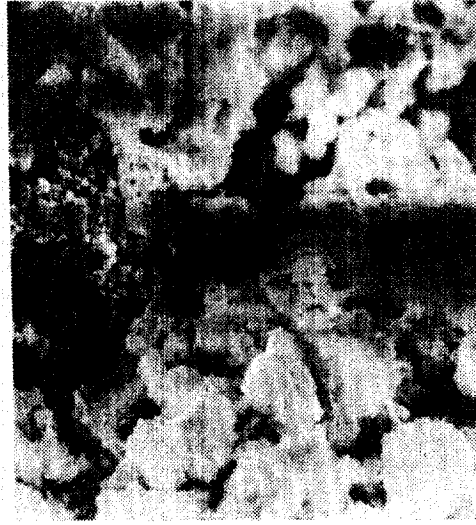
5 : Poplar sliver surface treated with 1% CaCl_2 .

6 : Poplar sliver surface with no accelerator.

Comparing #6 with A, Plate 1, there is not much difference between unhydrated cement grains and hydrated grains in shape. Individual grains having poor forms on poplar sliver surface are seen clearly in #6. In #5 a small amount of cement grains is on the surface of the sliver but the shape of the grains is changed to hydrated.



5 (3,000X)



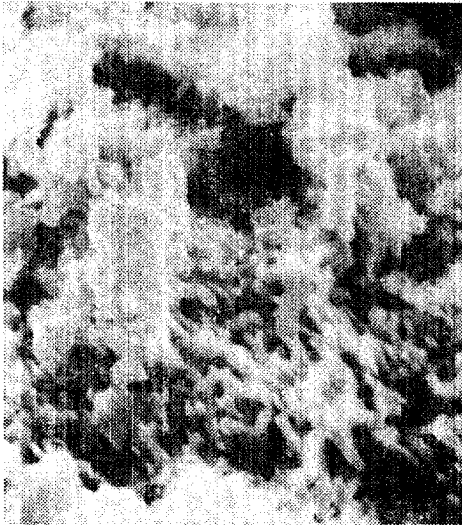
6 (3,000X)

PLATE 8. Scanning Electron Micrographs of a Sliver Surface Showing the Effects of an Accelerator on Cement Setting

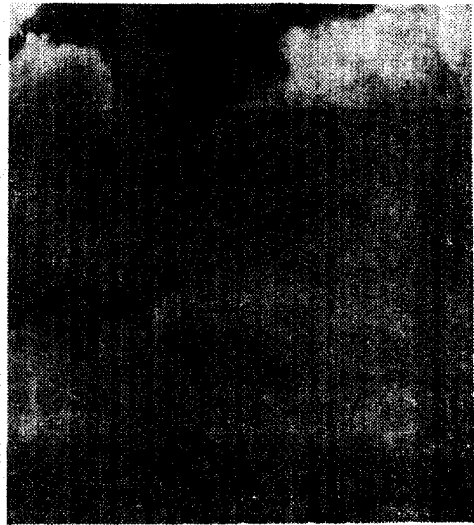
5 : Closed-up of the lower middle part of # 5, Plate 9.

6 : Closed-up of the left middle part of #6, Plate 9.

There are specific differences between the specimens #5 and #6 in shape and size of the developed hydration products.



5 (10,000X)



6 (10,000X)

PLATE 9. Scanning Electron Micrographs of Cement Hydration Products on Poplar Sliver Surface Showing the Effects of an Accelerator on Cement Setting

5 : Closed-up of the lower middle part of #5, Plate 10.

6 : Closed-up of the center part of #6, Plate 10.

The differences in crystalline form and in size are observed. Especially, the crystallites in #5 are specific one.

5. CONCLUSION

The sharp differences in appearance between the fracture surface of a cement paste with 1% sucrose by weight and that of cement paste treated with 1% sucrose solution after curing of 24 hours and between the specimen treated with an inhibitor and that treated with an accelerator. Many cement grains remained almost in an original form or were just covered with the thin gel layer that might be considered the protecting layer of the grains or hindering layer of water penetration for hydration of the grains. So-called protecting layer on surface of cement grains might be reprecipitated from the supersaturated paste of cement at the first stage. The mechanisms of the inhibiting agents on setting and hardening of portland cement are not known in detail. Denser dot-like humps, or humps in higher magnification, were observed clearly on the fresh fracture surface of the specimen having an inhibitor. The humps are the site of crystallite developing. With an inhibitor the growth of crystallites might be ceased and remained humps at the site.

On the fresh fracture surface of the specimen having an accelerator, well developed hydrated gel phases, clear crystallites, hexagonal flakes and hexagonal plates in cleavage were observed. But the short and thinnest crystallites on the amorphous gel surface are out of the resolution at magnification of 10,000 times.

An accelerator on cement setting and hardening between the wood and cement interface in WCC resulted in the specific differences in setting of shape. The individual grains having almost the same shape of portland cement on surface of poplar sliver from accelerator untreated WCC were noticed, but on the fracture surface of accelerator treated poplar sliver from WCC many tiny humps having round end on the surface were located on surface of gel phases. This is the results of inhibiting action of alkaline degradation products from poplar wood components and alkaline extractives from poplar wood.

LITERATURE CITED

1. Bröker, F.W. 1973. Studies on the dimensional change in Wood-Cement Composites (German). Dissertation. Hamburg University, pp. 1—151.
2. Double, D.D. and A. Hellawell. 1977. The solidification of cement. *Sci. Amer.* 237(1) : 82—90.
3. Fischer, Von F., O. Wienhausen, M. Ryssel and J. Olbrecht. 1974. The water-soluble carbohydrates and their influence on the cement setting in WCC(German). *Holztech.* 15(1) : 12—19.
4. Grudemo, A. 1964. Electron microscopy of portland cement paste. *IN the Chemistry of Cements.* Taylor, H.F.W., Ed. Academic Press, New York. Vol. 1 : 371—389.
5. Insley, H. and V.D. Frechette. 1955. Microscopy of ceramic and cements including glasses, slags and foundry sands. Academic Press New York. pp. 177—210.
6. Namioka, Y., T. Takahashi, T. Anasawa and M. Katasawa. 1976. Studies on the wood-cement board manufacture. *Bull. Hokkaido For. Prods. Lab. Japan.* 67 : 86—142(Japanese).
7. Parker, P.N., C. Clement and R. Al. Beirut. 1977. Basic cementing: Today's oil-well cements offer operators a variety of choices. *The Oil and Gas Journ.* Feb. 21, 1977 : 59—63.
8. Portland Cement Association, Structural Bureau. 1963. *Portland Cement.* 5pp.
9. Powers, T.C., L.E. Copeland and H.M. Mann. 1959. Capillary continuity or discontinuity in cement paste. *Jour. PCA Res.* May 1959 : 38—48.
10. Sanderma, W. and M. Brenzel. 1956. Studies on mineral bonded particleboard—The cement inhibiting action of wood components and its dependency of chemical constitutions. *Holz als Roh- u. Werkstoff* 14(8) : 307—313.
11. _____ and U.V. Dehn. 1951. Influence of chemical factors on the strength properties of wood-cement composites (German). *ibid.* 9(3)

- : 97—101.
12. _____ and H. J. Preusser and W. Schweers. 1960. Studies on mineral bonded particleboard. On the action of wood components on internal bonding of WCC (German) Holzfor. 14(3) : 70—77.
 13. Simatupang, M.H. 1969. On the aptitude of some wood species for WCC manufacture (German). Holz-Zentralblatt Nr. 31 : 475—476.
 14. Taylor, H. F. W. 1964. The Chemistry of Cement. Vol. I : 1—24. Taylor, H. F. W. Ed., Academic Press.
 15. Weatherwax, R. C. and H. Tarkow. 1964. Effect of wood on setting of portland cement. For. Prods. J. 14(12) : 567—570.
 16. Wenzl, H. F. J. 1970. The Chemical Technology of Wood. pp. 142—3. Academic Press (Translated into English from the German by F. E. Brauns and D. V. Brauns).