100. PVA繊維で補強された繊維セメントの耐久性について

DURABILITY OF CEMENT SHEET REINFORCED WITH PVA FIBER

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〔ABSTRACT〕 高強力タイプのPVA繊維は、セメントシート分野で用いられている石綿の代替物として良く知られている。本報では、ミニハツェックマシンを用いてPVA繊維を補強材とするモデルシートを作り、耐久性について曲げ強度の面から検討したので、繊維自身の耐久性と共に報告する。

長期間の屋外曝露の後では、セメントシートの曲げ強度は若干低下したが、このシートから取り出されたPVA繊維自身の引張強度や、化学構造の面に変化は見られなかった。これとは別に、モデルシート及びそれに用いた繊維について加速試験により耐久性を調べた。セメントシート、繊維とも高い温度の条件下では時間の経過と共に、強度が低下する傾向を示した。屋外曝露と加速テストとの関係は明確でないが、セメントのアルカリ性の度合いは時間と共に低下し、繊維自身の耐アルカリ性は本質的には優れたものであるので、少なくともPVA繊維のセメントシート中での耐アルカリ性についての危惧は不要と思われる。

PVA繊維で補強されたセメントシートの耐久性は優れたものであり、このシートは外装用建材としての実使用が可能であると考えられる。

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1. INTRODUCTION

In Europe and America, hazardous nature of asbestos against human body has been pointed out [1] and investigation for its substitute started at the end of 70's. Also in Japan, programs for reducing consumption of asbestos have been carried out both on industrial voluntary regulation basis and under governmental guidance.[2]

In the field of asbestos cement products, polyvinyl alcohol(PVA) fiber has been successfully used as a substitute for asbestos, mostly in Europe, on an industrial scale. This paper deals with durability of PVA fiber used as a substitute for asbestos and reports the results of test on fiber reinforced cement products, as well as reinforcing fiber itself.

2. EXPERIMENT

2.1 Materials used

(1)Fiber

Fibers usable for reinforcing cement should have sufficient adhesiveness with cement, good dispersibility in cement matrix, high tensile strength and relatively high Young's modulus.[3] Kuraray Co. has developed high-tenacity fiber made from polyvinyl alcohol, as a substitute for asbestos for reinforcing cement. Table 1 shows the properties of PVA fiber.

Table 1 Properties of PVA fiber for fiber cement

Description	Kuraray Vinylon RM182×6
Diameter	14 μm
Length	6mm
Strength	1.5GPa
Young's Modulus	36GPa

(2)Pulp

Asbestos is a fibrillate material which has also the function of a process facilitating agent or a filtrability adjusting agent. Since synthetic fibers do not have this function, wood pulp is added for filtrability adjustment. In our experiments, conifer kraft pulp (NUKP) was used, with its C.S.F. being adjusted to100 to 150 ml.

(3)Cement

Standard grade cement produced by Onoda Cement Co. (Braine value: 3,400) was used.

(4)Others

To maintain a high yield, a process agent (Silica Flour; specific surface area: 28m²/g) and a coagulating agent were used.

2.2 Test methods

(1)Preparation of fiber cement sheet

Sheets having a thickness of about 5 mm were prepared with a mini-Hatschek machine (Table 2), and the sheets were pressed under a pressure of 75kg/cm^2 for 30 minutes to give green sheets.

The green sheets were wrapped in PVC sheet and aged for 28 days in a constant temperature room, to give sample sheets.

Table 3 shows the composition of sample sheets and Figure 1 shows the flexural stress/strain curves of the sheets in which a linear stress is applied in a direction perpendicular to the lengthwise direction of samples. The sheet reinforced with RM182x6 shows nearly the same strength as that of asbestos cement and has the interesting feature of markedly large strain until breakage.

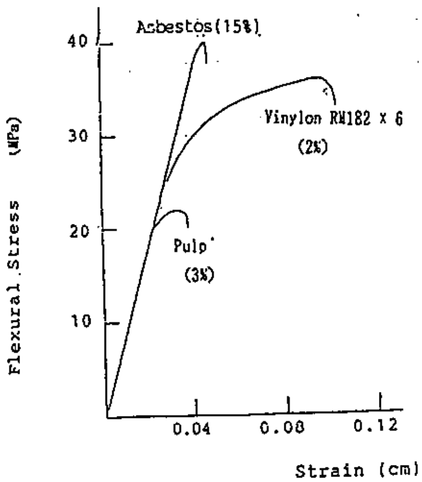
Table. 2 KURARAY's mini-Hatschek machine

Produced by	Matsumoto Iron Work
Type	Uni-Drum Sieve Type
Speed	14m/min
Sheet Breadth	30cm

Table 3 Composition of sample sheet (wt%)

Composition	Sample	Reference 1	Reference 2
RM182 6	2	-	-
Asbestos(5R)	-	15	-
Pulp	3	3	3
Silica Flour	5	-	5
O.P.Cement	90	82	92

Fig. 1 Stress/Strain curve on bending.



(2)Weathering test

A test of exposure to natural weather was conducted in Okayama. Sample sheets were fixed at a height of 1.5m above the ground on a steel frame. The sheets were positioned being inclined at an angle of 45° with the ground surface and facing the south. Since then, and 0.5-, 2-, 3- and 6-year samples were tested for the flexural strength.

(3)Accelerated test

It has been an important subject how to predict the durability of fiber cements and studied at ECC and other institutions [4], with seemingly no generally accepted methods. The authors carried out a test which comprises, repeating a cycle of immersing sample sheets in warm water at 60C° for 1 week and allowing them to stand in an oven kept at 60C° for the next 1 week. This cycle was repeated for 1 year.

To 1 kg of Portland cement, 4 liters of tap water was added and the mixture was stirred at 20C° for 4 hours, after which the supernatant was obtained by filtration. The test solution thus obtained had a pH of 12.8. The endless fiber before cutting was wrapped around a stainless steel frame having a span of 20 cm. The set thus prepared was subjected to a test which comprises a cycle of immersion in the test solution at 60C° for 1 week and standing in an oven at 60C° for the next 1 week.

The cement sheets and fiber samples thus tested for 1 year were measured for flexural strength and tensile strength respectively.

3. RESULTS

3.1 Weathering test of cement sheets

Fig. 2 Featherbility of PVA Fibre Reinforced Cement Sheet

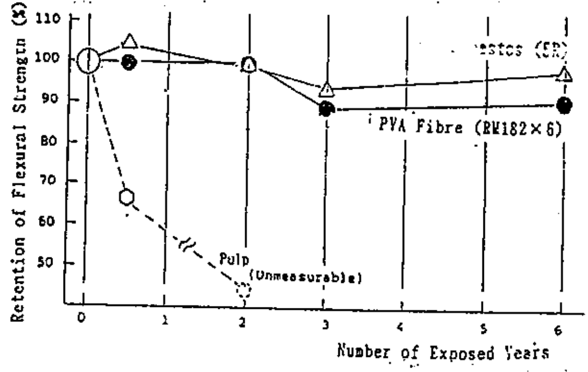


Figure 2 shows how the flexural strength changed during 6-years weathering. It may be said that the strengh decreased to about 90% of original strength at around the third year with, however, no change being observed thereafter. The asbestos cement sheet, prepared under the same conditions, showed similar behavior. A slight drop of flexural strength obsreved on PVA fiber reinforced mini-Hatschek sheets after exposure to natural weathering is statistically not significant due to the small number of specimen and the large scatter of bending test. Thus, there may be little fear about durability. Anyway, such a drop doesn't reflect out 12 year experience of Eternit in Europe with industrial products.

Cement sheet samples having been exposed for 2 years were subjected to a chemical treatment to remove cement component and withdraw PVA fiber. The fiber thus taken out was tested for its properties (see Table 4).

Table 4 Analysis of PVA fiber extracted from the cement sheet

Condition of treatment(PVA Fiber)	Tensile Strength *2 (GPa)	Crystalinity (%)	Content of 1,2-glycohol *3
From un-exposed sheet	1.21	63	1.9
From 2years-exposed sheet	1.19	63	1.8
Virgin RW182 *1 (Control)	1.24	63	1.8

*-1 Virgin PVA fiber was treated by the same chemical and same method which was applied to the cement sheet to separate fiber.
*-2 n=30, Gauge length is 1 mm.
*-3 mol%

Tensile test on 6-mm fiber samples showed no decrease in the strength, and neither did X-ray analysis for crystallinity. NMR spectrometry was conducted to determine the content of 1,2-glycol bond, which is an index for possible scission of PVA molecule, and it revealed no difference between the original fiber, the fiber withdrawn from the cement sheets exposed to weather for 2 years and the fiber withdrawn from unexposed cement sheets.

It is understood from these results that the high-tenacity PVA fiber showed no physical or chemical change under weathering conditions in Okayama at least within 2 years.

For longer exposure, there are available data obtained after 5-year exposure (in Okinawa) and those after 12 years (in Europe), of flexural strength of cement sheets and the properties of the PVA fiber (RM182x6) withdrawn from the cement sheets. These data show no appreciable change in the properties.

3.2 Accelerated test

Figure 3 shows the results of the repeated wet-dry tests at 60C°.

Various attempts have been made to accelerate durability test to predict the durability in practice of fiber cements. See for example a detailed report on alkali-resistant glass fiber[5] and a paper on the durability of cellulose fiber reinforced cement composites.[6] In the present experiment, a cycle of wet and dry treatments at 60C° was repeated during 1 year, without definite knowledge of how this condition correlates to natural weathering. The wet condition at 60C° may hardly take place in practice, but employment of the high-temperature condition may be of some meaning in shortening the test period.

From Figure 3, it is noted that the flexural strength of cement sheet slightly decreased. The figure also showed how the tensile property characteristics of the tested fiber itself changed under the same conditions in a cement extracted solution. It is understood that the constant-length test gave results in a good agreement with the flexural strength data of cement sheet.

Figure 4 shows how the tensile characteristics of PVA fiber immersed in an aqueous solution having pH=12.8 at 20C° during 24 months. It is understood that the high-tenacity PVA fiber, showed no change at all when placed under high alkali condition.

Table 5 shows the results

Figure 3 Accelerated test of PVA fiber reinforced cement sheet and PVA fiber

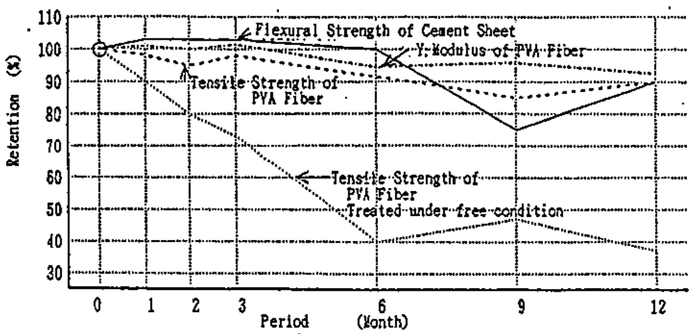


Fig. 4 Alkali resistance of High-tenacity PVA Fiber
· Protracted immersion to aq. soln., extracted from cement slurry

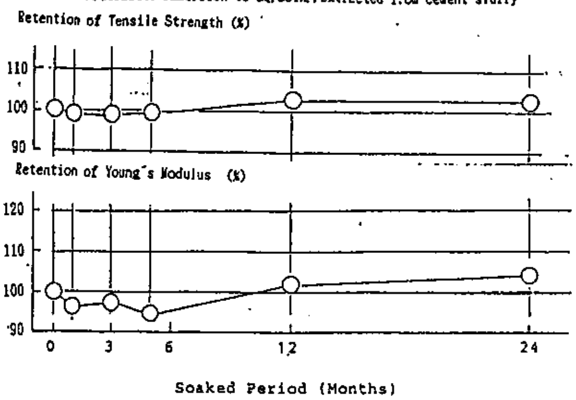


Table 5 X-Ray analysis of PVA fiber after accelerated test

Treated period	Degree of Crystallinity X_c (%)	Crystallite size Breadth (100) Å	Crystallite size Length (020) Å	Orientation Factor (%)
0 month	74	73	109	97
1	75	75	110	98
2	73	73	108	97
12	72	75	112	98

of structural analysis by X-ray diffractometry on PVA fiber during the acceleratedtest.

It is understood from this table that this type of PVA fiber, suffered no change in terms of fiber structure detectable within accuracy of X-ray analysis. These results support the fact that, under the accelerated condition semployed in this test, influence on the strength factor of the fiberwas very small.

4.DISCUSSION

Cement products must have longperiod durability to serve their purposes. In dealing with PVA fiber, what may have to taken into consideration is long-period contact with alkali, which is however, gradually neutralized in the course of long perioid of time by action of carbon dioxide in air. Table 6 shows the results of X-ray analysis on the cement sheet having undergone weathering and accelerated test.

Table 6 X-ray diffraction analysis of exposed cement sheet

Deffraction Angle 2θ (deg)	Assignment of Crystalline (ASTM)	Diffraction Intensity (C.P.S.)		
		Reference	Natural Weathering (2 Years)	Accelerated Aging Test (1 Year)
29.45	$CaCO_3$	176	300	350
32.2	$54CaO-16SiO_2-Al_2O_3-MgO$	300	240	224
34.15	$Ca(OH)_2$	300	280	204

As seen from the table, 2-year exposure decreases $Ca(OH)_2$ component and increases $CaCO_3$ component. This tendency is more marked with the acceletated test. This means the problem of alkali resistance associated with PVA fiber is lightened with elapse of time, and the accelerated test condition was so severe compared with the natural aging.

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