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Synthetic Fibers in Thin-Section Cement Products: A Review of the State of the Art

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Synopsis:

Since the turn of the century, thin-section asbestos-cement sheet and pipe products have been manufactured by the Hatschek Process. Health and environmental concerns with the use of asbestos has led to a worldwide search for alternative fibers. This paper reviews the state-of-the-art in using synthetic fibers to replace asbestos in fiber-cement products.

<u>Keywords</u>: Aramids; <u>asbestos</u>; carbon; cellulose fibers; <u>durability</u>; esters; <u>fiber reinforced</u> <u>concretes</u>; nylon fibers; <u>pipes (tubes</u>); polyethylene; polypropylene fibers; polyvinyl alcohol; pulp; reinforcing materials; <u>sheets</u>; <u>synthetic fibers</u> Dr. David M. Gale is a Senior Research Associate for the DuPont Co. in Wilmington, Delaware, specializing in fiber reinforcement. He is currently active in ACI Committees 440, 544 (Executive Sub-Committee) and 549. In addition, he is Chairman of ASTM Committee C-17, Fiber-Cement Products, and active in ASTM Sub-Committee C09.42, Fiber Reinforced Concrete.

INTRODUCTION

A process for making sheet and pipe asbestos-reinforced cement products was invented in Austria at the turn of the century. The so-called Hatschek Process is similar to paper-making, wherein a slurry of asbestos and cement is picked up on a drum, transferred to a belt and dewatered. Thin layers are collected on an accumulator roll and further processed into a wide variety of sheet and pipe product shapes. The "green" products are cured at ambient conditions or in a steam autoclave. Typical applications are roofing, siding, high pressure water, drain and sewer pipes.

Recent concern with health and environmental issues has led the industry to seek substitutes for the asbestos in these products. During the 1970's, several asbestos-cement manufacturers, for example, the Swiss and Belgium Eternit groups, Dansk Eternit in Denmark, and James Hardie in Australia, led extensive efforts to replace asbestos with synthetic and natural fibers. Ultimately, collaborative efforts with fiber producers such as Kuraray in Japan, Hoechst in Germany and Du Pont in the U.S., led to products which contain synthetic fibers, whereas other developments produced products with natural fibers, particularly highly refined wood cellulose. This paper will focus on the state of the published art with respect to synthetic fiber developments.

In order to replace asbestos with synthetic fibers (which act as reinforcing agents), it is necessary to include other fibers that retain cement fines and hence act as "filter" fibers. Many synthetic reinforcing fibers have been studied, e.g., acrylic, polyvinyl alcohol (PVA), rayon, polyester, nylon, polypropylene, aramid, and carbon. Because of a combination of cost and other properties, acrylic, PVA and polypropylene are most popular today. Popular filter fibers consist of refined wood cellulose, polyethylene pulp, and acrylic pulp. One brand of polyethylene pulp, which is molecularly oriented, has both reinforcing and filter characteristics.

When asbestos is replaced with synthetic fiber systems, the ambient cure version of the Hatschek Process must be employed; synthetic fibers generally cannot withstand the 170-190°C temperatures of the autoclave cure. In general, for systems that replace asbestos, synthetic fibers impart highest ultimate flexural strengths (modulus of rupture) to the cement products. With both synthetic and cellulose fibers, first crack and ultimate strengths as well as rigidity tend to be lower than for asbestos systems.

Today, asbestos replacement is limited to sheet and low pressure pipe products, regardless of whether synthetic or natural fibers are employed.

Replacement fibers in the pressure pipe application have not yet been found because these products require high hoop strengths at low cost.

DISCUSSION

Asbestos-Cement Technology

Thin-section asbestos-cement building products have been known since the turn of the century, when, in Austria, Ludwig Hatschek formed sheets on a modified cardboard paper-making machine. By the beginning of the last decade this industry had grown to consume 1.5 million metric tons of asbestos fibers annually (Vinson and Daniel, 1990). The asbestos-cement products, although they use Portland cement, are quite different from typical aggregate-filled concrete products. A typical asbestos-cement product contains 40-90% Portland cement, 0-50% fine silica and the rest asbestos fibers, typically 7-15% by weight. Sometimes, for less critical applications, cheap diluents (fillers), such as fly-ash and calcium carbonate, are used. High silica content is usually reserved for products prepared by curing in a steam autoclave at 170-190°C. The silica is needed to combine chemically with the cement to form a stable silica-cement phase that is different from the hydrated cement product obtained when Portland cement is cured at ambient temperatures. When the silica is present, the cure can be achieved over night at the elevated autoclave temperatures. Otherwise, without silica, a normal 28-day ambient temperature cure is typical.

In the Hatschek process, a dilute aqueous slurry of cement and asbestos fibers, usually 5-10% solids, are mixed in a tank and transferred to vats containing one or more rotating sieved drums (Hannant, 1978), (Figure 1, after Coutts and Mitchell, 1983). A broad distribution of asbestos fiber lengths is used, the shorter to form an elementary web layer on the drum which will trap cement fines and the longer for reinforcement in the final cured product. As the elementary layer forms, hydrostatic pressure causes the slurry to be filtered through the sieves into center of the drum as solids are removed. The filtered fluid is returned to the mixing tank for recycle, while the asbestos-cement layer is held by the rotating drum until it is transferred to a moving fabric belt. If more than one vat is employed, layers are plied on one another as the belt passes. Suction is applied to the reverse side of the belt to dewater the cement layers, which then are transferred to a large accumulator roll; the roll builds up layers until a desired thickness is achieved. At this point, a knife is used to cut the roll into sheets. (If pipe is desired, the roll of product can be removed and a new mandrel inserted in an automated process.)

"Green" asbestos-cement sheets can be further shaped, cut or otherwise processed. For example, a sheet may be individually pressed (to achieve better properties such as higher flexural strength), stack pressed between steel divider sheets, corrugated, embossed, or even hand molded into accessories such as the peak of a roof or a downspout pipe. Once the final shape is obtained, the green product is cured before shipping and ultimate use. Final product properties depend on whether the high cement content/ambient cure or silica-cement/ autoclave cure has been employed. In general, the higher cement/ambient cured products have higher flexural strengths, whereas the silica-cement/autoclave cured products have better dimensional stability.

Health Concerns with Asbestos-Cement Products

Although enormously successful throughout the 20th Century, the validity of asbestos-cement products began to be seriously doubted because of health concerns (Gilson, 1972). These problems are well known because of the anti-asbestos legislation that ensued. In the U.S.A., for example, asbestos will be phased out completely by 1997. Also, more recently, health concerns have been extended to the fine silica used in autoclaving (Westerholm, et al, 1986). In any case, the asbestos health concerns of the 1970's caused major asbestos-cement producers worldwide, e.g., the Swiss and Belgium Eternit groups, Dansk Eternit in Denmark, James Hardie in Australia, and others to earnestly seek alternative fibers. Collaborations with fiber producers, such as Kuraray in Japan, Hoechst in Germany and Du Pont in the U.S.A., followed initial scouting studies. Much of the details of this work is still considered proprietary and has not been published or discussed openly. Fortunately, however, a sufficient amount has been published to provide a useful overview of the state of the art.

Problems with Replacing Asbestos

In order to understand the difficulties encountered with trying to replace asbestos, it is important to understand the properties of asbestos and its function in the cement matrix. Asbestos fibers are very strong and stiff (Table 1) whereas cement paste is relatively weak, especially in tension or flexure. The abundant tensile strength of asbestos is put to good use in the cement composite and makes up for an inherent defect in cement. Another important property of asbestos is to act as a filter fiber in the Hatschek process. The smallest of cement fines must be trapped on the sieve for transfer to the belt in the Hatschek process. Otherwise, they will accumulate in the water that is returned for recycle. The trade uses the term "dead" to describe cement that has lost its ability to hydrate because it has been recycled too many times through the process before getting incorporated into the product. Fine asbestos fibers are included in the recipe to trap cement fines before they die. Compare, for example, the retention of solids for asbestos fiber vs. other filter fibers (Figure 2, after K. Saimen, Kuraray, quoted with permission in Gale, 1990-Milan). Note that asbestos is particularly effective at trapping solids at low flocculent concentrations; this is because asbestos usually carries both positive and negative charges as measured by zeta-potentials, and so is self-flocculating.

In addition to imparting strength and retaining cement fines, asbestos is chemically inert and a close relative of calcium silicate, the major chemical species in Type I Portland cement. Most asbestos fibers are largely magnesium and aluminum silicates. Because of its inertness and natural compatibility, asbestos-cement products have served in weathering environments for decades without being replaced. Indeed the only drawback to the product prior to discovery of the health issue, is that asbestos-cement products have lower than desired toughness. Also, embrittlement increases with age and sometimes weakens structures with fatal results.

In summary, although asbestos-cement products would be more desirable if they where tougher, the major needs of a replacement product are strength, cement retention and durability. In order to meet these major needs, most

formulations use more than one fibrous ingredient to replace asbestos. This paper will focus on formulations that employ synthetic fibers and are used for ambient cure products. Since most synthetic fibers can not survive at full strength in the highly alkali environment of cement during an autoclave cure, commercial systems using synthetics tend to be limited to ambient cure products. Where installed autoclaves are available as part of an existing asbestos plant, the usual course of action in converting away from asbestos is to install a cellulose-cement process. These products do not contain synthetic fibers.

Typical Formulations Using Synthetics

Today, most commercial systems that use synthetic fibers to replace asbestos use a reinforcing fiber, most usually polyvinyl alcohol (PVA) or acrylic (polyacrylonitrile, PAN) and to a lesser extent polypropylene (PP), and one or more filter fibers, most usually a combination of refined wood cellulose and a polyethylene pulp (PE pulp). For the reinforcing fibers, a special high strength. high modulus grade is preferred. The exact percentages of these ingredients tend to be held in secret by the manufactures, but a typical formulation might contain 2% of reinforcing fiber and 4% of the filter fiber combination. The rest of the formulation can be Portland cement or a mixture of mostly Portland cement and locally available fillers, e.g., fly-ash, mineral wools, sand, limestone, gypsum, etc. Fumed (microscopic) silica is sometime used to control the moisture content of the green cement product and/or to improve fiber-matrix adhesion. In most cases, only modest modifications of commercial Hatschek asbestos-cement equipment is required, however, asbestos-free systems tend to run slower. Also, it is usually necessary to use a dispersant to help open the fibers in the mixing tank and then a flocculent to coagulate the fibers and cement fines in the vat prior to being filtered by the sieve roll. One filter fiber, a molecularly oriented polyethylene pulp, has been reported as having both reinforcement and filter fiber characteristics (Gale, et al, 1990-ACI, 1990-Milan, 1990-Lyon).

In addition to the commercial formulations discussed above, many synthetic fibers have been studied in connection with asbestos replacement (Studinka, 1986 and 1989; Zhou, 1986; Okuda, 1986; Miko, et al, 1986; Hikasa, et al, 1986; Haehne, 1986; Gale, et al, 1986; Koenig, 1987). In addition to those already discussed, synthetic reinforcing fibers studied are carbon, aramid, nylon-66, polyethylene (PE), polyester and rayon. Additional filter fibers include polypropylene and acrylic pulps. In discussing the advantages and disadvantages of various synthetic reinforcing fiber ingredients, the authors cited do not always agree. For example, concerning the alkali stability of polyester fibers, Studinka (1989), Hikasa (1986) and Gale (1986) consider it poor, whereas Zhou (1986) considers it good. But for the most part, the authors do tend to agree. A consensus listing is offered (Table 2). Significant differences in opinion are indicated by the code "NC" for "no consensus." The table format is taken from Studinka (1989). Note that fiber form can effect fiber properties and hence its function in cement. For example, polyethylene staple fiber (generally has a round cross-section) has generally poor adhesion, where as pulp forms of polyethylene have good adhesion owing to the irregular shapes in pulps that promote mechanical adhesion.

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Cement Product Properties

Asbestos-free cement product properties can be varied considerably by controlling the amount of Portland cement vs. inert fillers, the amount of fibers, their type, the treatment of the green cement product prior to cure, for example, whether or not it is pressed. And, if it is pressed in the green state, the conditions of pressing can markedly control properties. For this reason, generalizations stated herein should not be relied on without experimental verification.

In comparing ambient-cured asbestos-free cement products to those containing asbestos, the asbestos-free products will tend to have lower tensile or flexural strength and higher elongation-at-break or toughness. Pressed products will tend to have higher properties vs. unpressed, the better properties associated with higher densities. Thinner products will tend to have higher strengths than the identical product in thicker form. The range of properties expected in synthetic fiber reinforced cement products tends to be in the higher grade range as defined by ASTM Standards. Typical properties for synthetic systems are given in Table 3 (after Gale et al, 1990-ACI).

ASTM Standards and Test Methods

ASTM Committee C-17 has recently set detailed specifications for flat asbestos-free sheets (C 1186), along with test methods for strength and durability (C 1185). Four different grades of product, with flexural strength that varies from Grade I at 580 psi (4 MPa) to Grade IV at 2610 psi (18 MPa) wet strength, or 580 to 3190 psi (22 MPa) equilibrium strength, respectively. The flexural strength referred to is not an average strength, but a more statistically significant 4% acceptable quality level (AQL) at 90% confidence; in other words, no more than 4% of specimens in a specified number tested can have strengths lower than the minimum strengths indicated to make the specified grade. Flexural strength of asbestos-free thin section products are measured by 3-point bending and not the normal third (or 4-point) bending used in most concrete standards. The main reason for this is that industry has used this method for many years and all previous asbestos-cement standards use 3-point bending.

Supplementary requirements on moisture movement, water absorption, moisture content, water tightness, frost resistance, warm water resistance and heat/rain resistance are included for sheets intended for exterior applications. These supplementary requirements are intended to provide a measure of long term durability.

Durability

While some asbestos-cement products have been in service since the turn of the century, synthetic fiber reinforced products are relatively new so that anecdotal information concerning long term durability in the field is not readily available. In addition to tests provided in the new ASTM standards, and the expert opinions found in brief tables or in general discussions referenced above,

a few fuller reports have appeared outside commercial trade bulletins. Akers et al (1989) discuss the long term durability of PVA reinforcing fibers in cement, and relate accelerated tests to fibers extracted after up to 7 years in the cement composite. While loss in tensile strength is noted, the authors conclude that it appears that the PVA fibers are adequately durable. Hachne (1986) studied the alkali resistance of PAN fibers in pH 12 alkali media. He found a 10% decrease in tensile strength, and 15% loss in elastic modulus in the first few months of a 12 month test under ambient conditions. However, the loss in properties leveled off, so it was concluded that the fiber has adequate durability. Gale et al (1990-ACI) studied the durability of cement products reinforced with an oriented PE pulp using accelerated tests. Retention of composite properties was reported as excellent, consistent with the known alkali stability of PE. Keer (1990) studied the property retention of PP (network) reinforced cement and predicted at least a 30 year lifetime. Ando et al (1990) reports excellent retention of properties for carbon fiber reinforced cement composites based on freeze-thaw and hot water accelerated tests.

Applications

Typical applications for fiber-cement products are roofing (slates and corrugated), siding, clapboards, fascia, backer-board, high pressure water pipes, drain pipes, and sewer pipes.

Asbestos-cement products are useful in both sheet and pipes. In substituting asbestos, synthetic fiber reinforced systems have been generally successful (Studinka, 1986 and 1989). High pressure pipes, where the combined requirements of high hoop strengths and low cost are not easily met, have no asbestos-free equivalents. Also, for pressure pipes, crack-free performance is required to prevent leaks. For this reason, first crack stress must be high. With asbestos cement, first crack and ultimate stresses are almost indistinguishable (Hannant, 1976), whereas for synthetic reinforced systems, first crack stresses are generally less than ultimate. In practical terms, high fiber loadings are required to raise first crack stresses, and this becomes too costly.

In summary, to date, synthetic systems have been successful in replacing most asbestos-cement systems, sheets, such as roofing, siding, fascia, clapboards, backer-boards, and low pressure pipes, such as drain and sewer pipes. High pressure pipes, such as water pipes, however, are not currently found in non-asbestos compositions.

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TABLE 1 — MECHANICAL PROPERTIES OF ORDINARY PORTLAND CEMENT PASTE, MORTAR, ASBESTOS CEMENT AND CHRYSOTILE ASBESTOS (STUDINKA, 1989; HANNANT, 1978)

	Flexural Strength, MPa	Tensile Strength, MPa	Elastic Modulus, GPa	Tensile Strain to Failure, %
Cement Paste	7-8	3-6	15	0.01-0.05
Cement Mortar		2-4	25-35	
Asbestos Cement	30-40	17-20	28-35	0.4-0.5
Chrysotile Asbestos		200-3600	150-164	0.1-3.0

TABLE 2 — SYNTHETIC FIBERS FOR ASBESTOS REPLACEMENT: PROPERTIES OF VARIOUS REINFORCING FIBERS USED FOR CEMENT REINFORCEMENT (CONSENSUS OF MANY AUTHORS)

	Tensile Strength, MPa	Tensile Modulus, GPa	Tensile Strain, %	Fiber Diameter, micron	Adhesion to Matrix, relative	Alkali Stability, relative
Asbestos	600-3600	69-150	0.1-0.3	0.02-30	excellent	excellent
Carbon	590-3000	30-500	<1-2	8-18	poor	excellent
Aramid	2700	62-130	3-4	11-12	fair	good
PP	200-700	0.5-9.8	10-15	10-150	poor	excellent
Polyamide	700-1000	3.9-~6	~15	10-50	good	NC
Polyester	800-1300	up to 15	8-20	10-50	fair	NC
Rayon	450-1100	up to 11	7-15	10-50	good	fair
PVA	1150-1470	21-36	15	4-14	good	good
PAN	850-1000	17-18	9	19	good	good
PE	400	2-4	100-400	40	poor	excellent
PE pulp (oriented)				1-20	good	excellent

TABLE 3 — TYPICAL PROPERTIES OF SYNTHETIC FIBER REINFORCED CEMENT VERSUS OTHER REINFORCED CEMENT PRODUCTS

Cement Product	Flexural Strength, MPa (1)	Flexural Toughness, KJ/sq m (2)	
2.0 wt % PAN and 2.5 wt % Oriented PE Pulp	28.0	0.92	
2.0 wt % PVA and 2.5 wt % Oriented PE Pulp	23.7	2.44	
Commercial Asbestos (Ambient Cure)	30.2	0.19	
Commercial Asbestos (Autoclaved)	14.1	0.06	
Commercial Cellulose (Autoclaved)	13.5	0.78	

(1) Ultimate flexural strength (modulus of rupture) in 3-point bending.

(2) Area under load-deflection curve to point of maximum stress, divided by the cross-sectional area of the specimen.





