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Expert Working Group Meeting on
Fibro-cement Composites

Vienna, 20 - 24 October 1969

SOME CONDITIONS OF ASBESTOS SUBSTITUTION IN ASBESTOS-CEMENT PRODUCTS 1/

by

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Institute for the Silicate Industry,
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SUMMARY

SOME CONDITIONS OF ASBESTOS SUBSTITUTION IN ASBESTOS-CEMENT PRODUCTS [1]

by

József Talabér
Director of the Central Research and Design
Institute for the Silicate Industry,
Budapest, Hungary

The paper reviews the traditional method of asbestos-cement production and examines the possibility of replacing asbestos with other mineral fibres. The characteristics of the raw materials used in asbestos-cement production and the effect of variations or changes in the quality level is given for conventional asbestos-cement production. Theoretical observations are based on the aim to partially substitute asbestos in asbestos-cement compositions.

The Hungarian plant-scale experience is related in connexion with the use of varying asbestos batches and different cement qualities, particularly since the rise of using short fibre asbestos for the production of roofing and corrugated plates.

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The results of tests carried out in Hungary showed that standard quality roofing slates can be manufactured with considerable safety without any changes in the manufacturing technology by omitting asbestos type P-3 and increasing the P-5 and P-6 asbestos.

Apart from conventional asbestos-cement production some theoretical aspects of the partial substitution of asbestos has been reviewed. It is considered that different artificial inorganic fibrous materials can only partially substitute asbestos fibres according to the presently known manufacturing process applied to asbestos-cement products, i.e. only up to that limiting value where it acts as a reinforcing agent.

Glass wool, slag wool and basalt wool are discussed in detail as possible substitutes for asbestos.

The results of tests carried out in Hungary with these inorganic fibres proved that asbestos fibres can be partially substituted by fine mineral wool which has the most favourable technical characteristics in the following ratio:

Roofing slate	10-17%
Corrugated plates	10-14%
Drain pipes	10-17%
Pressure water tubing	10-17%

1. Introduction

According to the classic definition asbestos-cement is an artificial stone, produced by mixing of asbestos and cement and the hardening of the obtained homogeneous product. Generally hardening is carried out at room temperature in compliance with the hydraulic strength of cement, however there is also an accelerated solidification process /steam curing, known from the concrete technology/.

Asbestos fibres embedded into cement have a similar role as the steel in reinforced concrete. This is quite obvious. Tensile strength of chrysotil-asbestos which is generally used in the asbestos-cement industry amounts to 6000-8000 kg/cm^2; that of the best quality asbestos, so-called blue asbestos is 20,000 - 22,000 kg/cm^2. High strength asbestos framework, comparable with best quality steels, surpassing them even in some cases lend very useful characteristics to cement. From the peculiar interaction of these two materials we obtain a very useful product surpassing considerably strength characteristics of cement; this product is called asbestos-cement. The original patent had been registered in 1900 by Ludwig Hatschek under the denomination of fibrous cement /Faserzement/. The patent description contains interesting data being important at a farther stage and according to which fibrous cement is an artificial stone consisting of fibres, binding material and in some cases of fine additives. The uniformly distributed quantity of fibres used for this product must guarantee the required strength.

No doubt, the original patent had been built up on asbestos. By the fact, however, that the general term "fibre" is mentioned in the patent as a skeleton forming material, it has paved the way for a series of subsequent experiments which aimed at full or partial substitution of asbestos in that product which from then onwards is known under the denomination of asbestos-cement in literature.

The widespread propagation of asbestos-cement products has justified Ludwig Hatschek's expectations since this branch of industry developed all over the world. In spite of the fact that the number of additional patents having been registered in the past decades is immeasurably high, determinations of the basic patent and the principles having been laid down in it are still valid.

2. Basic materials

2.1 Cement

It appears to be superfluous to deal at this place in detail with the strength characteristics of cement. At the production of asbestos-cement generally cement quality 275, eventually 375 is used/symbols according to the DIN Standard/. Strength characteristics of the cement are unanimously defined in the standards of the different nations, thus there is no need to raise this question herewith.

However, it appears to be necessary to complete our respective knowledge by mentioning a few facts.

According to Soviet researchers, Sokolov and Medvedev /1960/ the bonding strength between asbestos and cement is a function of the saturation factor of the cement i.e. of the $3\,CaO.SiO_2$ /C_3S/ content; higher C_3S content generally increases bonding strength.

Kitaev /1959, 1961/ arrived at similar results stressing the importance of the particle size distribution of the cement. According to him the bonding strength between asbestos and cement may be described by the following formula

$$R_x = K_x \frac{F_s^3}{d} \cdot \frac{\tau}{\tau + \alpha x}$$

where

R_x = strength kg/cm^2

K_x = factor depending on asbestos content

F_s = cement saturation factor

d = average diameter of cement grain size, μ

τ = hardening time, days

α_x = factor depending on the method cement strength test

/ tensile - 4.7;
bending - 3.0/

2.1.1. Chemical and mineral composition of cement

Numerous researchers /Sokolov 1960, Kitaev 1959,1961, Berkovich 1962, etc./ have studied the effect of the mineral composition of cement on the characteristics of asbestos-cement and on the output of the slate manufacturing machine both on a laboratory and plant scale. It has been determined that cements with a high C_3S and a low C_3A content should be used. Increase of C_3S content tends to increase strength, reduce water absorbing capacity, improve density, frost resistance and other characteristics of the asbestos-cement /Table 1./

The increase of C_3S very favourably influences manufacturing facilities too; consequently precipitate content of the clarifying water decreases, which on the one hand increases the bonding strength between the asbestos fibre and the cement grains, on the other hand decreases raw material losses.

By increasing C_3S content the dewatering of the raw asbestos cement layers becomes more favourable, thus possibility is offered to work with asbestos-cement layers of a higher thickness i.e. to increase output of the slate manufacturing machine /Table 2./

Table 1.

Variation of asbestos-cement characteristics in the function of C_3S-content of the cement

Cement		Bending strength kg/cm²			Water abs. capacity %			Bulk weight G/cm		
F_s	C_3S %	3	7	14	3	7	14	3	7	14
		days of hardening								
0.80	35.3	127.1	134.5	145.6	30.5	29.5	29.0	1.40	1.43	1.47
0.82	40.1	133.7	140.2	150.2	30.0	39.0	28.1	1.42	1.45	1.48
0.85	45.2	140.2	150.1	154.9	29.0	28.0	27.7	1.45	1.48	1.40
0.88	50.5	145.1	157.3	160.7	28.9	27.6	27.5	1.48	1.50	1.51
0.90	56.1	159.5	162.6	167.2	27.3	27.0	26.8	1.50	1.52	1.53
0.92	61.7	165.3	169.1	172.5	26.2	26.0	25.1	1.53	1.55	1.56

Applying of cements with a high C_3S content is particularly important when using short fibre asbestos.

Adsorption ability of asbestos represents one of its important characteristics. Thus the asbestos adsorbs intensively lime hydrate having been released in the course of cement /mainly C_3S/ hydration and some other hydration products in consequence of which a strong connection is brought about between the asbestos fibre and the cement. This phenomenon plays an outstanding role in the initial and the later period of hardening. Thus all hydraulic additives /e.g. trass, acid fly ash/ which bind the lime-hydrate, decrease bonding strength between asbestos and cement, thus deteriorating the asbestos-cement product.

By increasing C_2S content /on the expense of C_3S/ the strength of asbestos-cement decreases and its water absorption increases.

Summarizing the fact one may determine that applying cements of a higher C_3S content gives a higher output of the slate manufacturing machine besides an improved quality of the product.

Increasing of C_3A content not only impairs the quality of the product but it has also a detrimental effect on the manufacturing technology. It is a well known fact that among the four clinker minerals /C_3S, C_2S, C_3A and C_4AF/ C_3A reacts most quickly with water, and its hydration products are of a colloidal character.

The considerable quantity of colloidal formations deteriorates filtration characteristics of the asbestos-cement suspension, thus leading to a forced decrease of the asbestos-cement layer thickness, which at the same time cuts the output of the slate manufacturing machine.

By increasing C_3A content the bonding strength between

Table 2.

Effect of the C_3S content of the cement on the output of the slate manufacturing machine

F_s	Mineral Composition				Precipitate content in clarifying water	Thickness of the asbestos-cement layer	Out-put of the slate manufacturing machine per hour	
	C_3S	C_2S	C_3A	C_4AF	%	mm	in std.size pieces	in kilograms
0.80	35.3	40.0	10.0	10.3	2.0	0.6	2495	2600
0.82	40.1	35.2	9.3	10.0	1.5	0.7	2825	2960
0.85	45.2	30.7	10.0	10.1	1.0	0.8	3175	3550
0.88	50.5	24.5	10.0	10.0	0.8	1.0	3750	4000
0.90	56.1	18.2	10.2	10.0	0.5	1.1	4216	4570
0.92	61.7	16.6	10.1	9.8	0.3	1.2	4684	5150

asbestos and cement decreases i.e. strength and compactness of the ready product also decrease and its water absorption capacity increases. According to the literature this phenomenon may to a large extent be due to the fact that hydration of C_3A is mainly taking place already in the suspension and during the moulding process /on the machine/. /According to some researchers good quality asbestos-cement is obtained if hydration takes place mainly after moulding/. Tables 3. and 4. illustrate in which way C_3A content effects product quality as well as the output of the slate manufacturing nachine.

2.1.2. Cement fineness

From the quality point of view of the product the second most important factor is the fineness of cement. Thus increasing of the specific surface of cement with a simultaneous high C_3S content improves both quality of the product as well as the output of the slate manufacturing machine /Tables 5. and 6./

By increasing the specific surface the bonding strength between asbestos and cement also increases, in consequence of which facilities are given for moulding thicker asbestos-cement layers. In addition precipitate content of the clarifying water /i.e. raw material loss/ also decreases; moreover strength and density of the final product are improving with the simultaneous decrease of the water absorption capacity.

Another question arises when applying cements with a high C_3A content, when the overgrinding of cement /higher then 3500 cm^2/g/ may already become detrimental. The latter is connected with the fact that the hydration processes are taking place rather speedely and, as a consequence the filtration properties of asbestos-cement suspensions are de-

Table 3.

Variation of asbestos-cement product properties as a function of C_3A content of cement

C_3A content %	Bending strength kg/cm²			Water absorption capacity, %			Bulk weight g/cm		
	3	7	14	3	7	14	3	7	14
	days of hardening								
3,0	183,1	200.5	210.3	25	24	23	1.61	1.66	1.70
7.3	173.4	181.5	191.1	26	25	24	1.57	1.62	1.66
10.1	165.3	169.1	172.5	25.2	26	25	1.53	1.55	1.56
13.0	143.8	150.2	157.3	29	28	27	1.49	1.51	1.55
17.0	129.7	135.3	145.2	31	30	29	1.43	1.45	1.47

Table 4.

Effect of C_3A content of cement on the output of the slate manufacturing machine

C_3A content %	Precipitate content in clarifying water %	Thickness of the asbestos-cement layer mm	Out-put of the slate manufacturing machine per hour in std.size pieces	in kilograms
3.0	0.2	1.31	5100	6130
7.0	0.2	1.24	4850	5730
13.0	1.0	1.13	4400	4730
17.0	2.0	1.05	4100	4300

Table 5.

Effect of C_3A content of cement on the output of the slate manufacturing machine

F_s	Specific surface cm^2/g	Precipitate content in clarifying water %	Thickness of the asbestos-cement layer mm	Out-put of the slate manufacturing machine per hour in std.size pieces	in kilograms
0.80	2800	3.0	0.51	2150	2190
	3515	1.7	0.70	2800	2950
	4120	1.0	0.95	3600	3870
0.85	2760	2.0	0.71	2880	3020
	3520	0.8	0.90	3500	3710
	4270	0.3	1.10	4220	4620

Table 6.

Variation of physical properties of the asbestos-cement product as a function of cement fineness

F_s	Specific surface cm^2/g	Bending strength kg/cm^2 3	7	14	Water absorption % 3	7	14	Bulk weight g/cm^3 3	7	14
		days of hardening								
	2800	120.3	125.7	140.9	32.0	31.5	30.0	1.35	1.40	1.45
0.8	3515	135.2	141.2	150.9	30.0	28.1	27.5	1.42	1.44	1.50
	4120	149.3	155.4	161.5	28.5	28.0	26.1	1.45	1.47	1.51
	2750	130.5	141.2	150.1	31.0	30.0	28.8	1.43	1.45	1.45
0.85	3520	154.3	154.9	160.3	28.2	27.1	27.0	1.46	1.47	1.52
	4270	155.0	162.5	167.2	27.0	25.0	25.0	1.49	1.49	1.55
	2810	140.3	155.9	162.2	28.3	28.0	27.7	1.47	1.49	1.52
0.90	3530	163.9	166.7	171.5	27.0	27.0	26.0	1.52	1.53	1.54
	4250	175.3	185.5	188.1	26.5	26.0	25.0	1.55	1.57	1.58

teriorating. Accordingly the layer thickness of the asbestos decreases i.e. output of the slate manufacturing machine also becomes less /Table 7./

Formation of a higher quantity of colloids impairs dewatering properties and densification of the asbestos-cement layer which finally leads to the quality deterioration of the asbestos cement product /Table 8./

Summarizing the above one may state that the right selection of the mineral composition and specific surface of the cement forms the basis of the manufacturing technology of the asbestos-cement product. Therefore it is not a mere incident that in the USSR, being one of countries with a highest asbestos-cement production, a special standard has been called into life which prescribes cement quality to be applied for the manufacture of asbestos cement products.

For the production of the asbestos-cement products the USSR standard GOST 9835 prescribes 400 and 500 brand cements. As to the chemical and mineral composition of the cement the following is compulsory:

free CaO	max. 1 %
MgO	max. 5 %
C_3S	min. 50 %
C_3A	max. 8 %
SO_3	between 1.5 - 3.5

In addition it prescribes setting time and fineness of the cement

Setting time, initial: 1 h 30 min
Setting time, final : not over 12 h
Oversize 4900 /i.e. 90μ/ = 7 %

Table 7.

Effect of the fineness of cement with a high C_3A content on the output of the slate manufacturing machine

/ C_3A - 14.5 % /

Specific surface cm²/g	Precipitate content in clarifying water	Thickness of the asbestos-cement layer	Out-put of the slate manufacturing machine per hour	
	%	mm	in std.size pieces	in kilograms
2800	3.5	0.51	2100	2150
3500	2.0	0.61	2600	2700
4150	2.0	0.56	2300	2300

Table 8.

Effect of cement fineness on the physical properties of asbestos-cement products

/ C_3A - 14.5 % /

Specific surface cm²/g	Bending strength kg/cm²			Water absorption %			Bulk density g/cm³		
	3	7	14	3	7	14	3	7	14
	days			days			days		
2800	120.0	126.0	135.0	31.7	31.0	30.0	1.36	1.40	1.42
3500	130.1	141.7	149.3	29.0	27.7	27.0	1.41	1.45	1.49
4150	123.0	130.6	140.0	31.5	30.6	30.0	1.37	1.40	1.45

2.2 Asbestos

Asbestos crystallizes either in nests or in layers in a socalled "matrix". Chemical composition of the matrix is identical with that of the asbestos,but not its crystallinity.

The original rock of the matrix is of volcanic origin. In case of amphibol asbestos it is mainly olivine with more or less pyroxene /augite/. In fact the matrix is formed from olivine by high temperature and high pressure steam.

In case of chrysotil-asbestos the matrix is serpentine: chrysotil-asbestos is crystallizing within geological ages in the fissures of the serpentine rock. Composition of chrysotile asbestos can be written as:

$$Mg_6/OH/_6./Si_4O_{11}/.H_2O$$

The most frequent kinds of the amphibol-asbestos used in the asbestos-cement industry are the following:

Crocidolite or blue asbestos
/Amosita /iron aluminium magnesium silicate/.

In addition asbestos may occur as:

Tremolite /calcium magnesium silicate/
Actinolite /calcium magnesium iron silicate/
Antophillite /magnesium silicate/.

Composition of this group may be expressed by the formula

$$Ca_2Mg_5/OH/_2./Si_4O_{11}/_2$$

In spite of the similarity in the formation conditions there is a vital difference between the asbestos types belonging into the two main groups. The fibres of chrysotile-asbestos are vitreous those of amphibol asbestos, however, present a compact substance. The former one is soft and flexible, the latter is hard and brittle. Both asbestos kinds contain a considerable quantity of structural water, which leaves at a high temperature only. This is the reason for the high refractoriness of these kinds of asbestos.

Strength of blue asbestos is rather high, but it occurs on few places only /South Africa and to a lesser extent in Australia and Bolivia/. The blue colour of this sort of asbestos is due to the iron compounds contained in it.

In practice chrysotile asbestos is a magnesium silicate containing structural water. Its hardness is 3-4, /Mohs scale/, density 2,5 g/cm^3. Its strength is far below that of amphibolite asbestos. Its chemical composition in a pure state is approximately as follows:

MgO = 43,0 %

SiO_2= 43,0 %

H_2O = 12-13.0 %

Other= 12 % /mainly CaO/

Its strength is 6000 - 8000 kg/cm^2 as compared to that of amphibole asbestos /blue asbestos/ of 20,000-22,000 kg/cm^2. To give a complete survey of the characteristics of all asbestos kinds would be too far reaching, thus we are giving only some vital data on basis of the literature /1/.

Tables 9. and 10 indicate composition of some characteristic sorts of chrysotile and amphibol-asbestos, respectively.

Table 11. is rather interesting and offers information without any special discussion about the fact what special effect of asbestos is acting on strength.

The extraordinary thinness and the enormous specific surface of the chrysotile-asbestos is striking. This may explain those enormous surface forces which are effective between set cement and the reinforcing asbestos which finally result in the favourable strength characteristics of the asbestos-cement products.

Table 9.

Chemical composition of some chrysotile asbestos types

%	Canada		U.S.S.R		Rhodesia	Cyprus
	Thetford	Donville	Ural	Siberia		
SiO_2	39–43	41.8 - 42.8	42.5–43.5	41.5–42.0	40–43	40.6
Al_2O_3	1.5–3.5	-	Traces 0.5	-	0.6–1.7	1.0
Fe_2O_3	0.2–2.5	2.2 - 3.7	0–0.15	6–7	Traces–4.5	4.9
MgO	40.0–41.5	39.5–42	41.8–42.6	35.1–36	38.3–39.6	39.0
H_2O	14.0–14.5	14.0–14.5	14.3–15.3	16.0–16.5	11.7–14	14.5
FeO	-	-	-	-	-	-
Alkali oxides	-	-	-	-	-	-

Table 10.

Chemical composition of amphibole asbestos

%	Blue asbestos Australia	Amosite Transvaal	Tremolite Finland	Tremolite Italy	Antophillite USA
SiO_2	51.1	50.24	62.02	55.1	57.6
Al_2O_3	-	-	2.08	3.4	0.9
Fe_2O_3	-	7.8	-	-	-
MgO	2.3	3.96	27.20	29.5	31.2
H_2O	3.9	3.0	5.04	5.0	4.5
FeO	35.8	32.0	3.54	4.6	5.8
Alkali oxides	6.9	2.12	0.71 CaO	2.4 CaO	

Table 11.

Physical properties of different fibres

Kind of fibres	Fibre diameter mm	Number of fibres on 1 mm length	Fibre surface cm^2/g
Nylon	0.0075	132	3100
Cotton	0.01	100	7200
Silk	-	-	7600
Wool	0.02 - 0.0275	36 - 50	9600
Viscosa	-	-	9800
Chrysotile asbestos	0.000018-0.000029	34,000-56,000	130,000-220,000
Glass fibre	0.0065	153	-
Slag wool	0.00355 - 0.0071	141-282	-

As a fact worth mentioning we would point out that the fibre diameter of blue asbestos is by one order of magnitude higher than that of the elementary fibre of chrysotile asbestos. /elementary fibre diameter of blue asbestos is 0,0001 mm/. Over and above the difference in the physical characteristics this may serve as an explanation for the flexibility of chrysotile asbestos. In addition data contained in Table 11 offer likewise explanation for the fact why the strength characteristics of products made of glass fibre and cotton slag wool are lower than those with asbestos reinforcement.

Fibre length is one of the very interesting and extremely important characteristics of the various asbestos kinds. This depends to a very great extent on the field of application. Besides the asbestos quality its fibre length /measurements of which are fixed by standards/ depend first of all on the processing method. An investigation of these questions, however, would go beyond the topic dealt with herein.

2.21. Qualitative and quantitative effect of asbestos

In the course of the physico-mechanical study of the asbestos-cement properties Sokolov /1960/ stated that the strength of the asbestos-cement system is determined by the ratio of the average length /l/ and the average diameter /d/ of the asbestos fibre. According to the above, strength of the asbestos-cement does not depend on the asbestos quality if in the course of the processing of different asbestos kinds an identic value of $\frac{l}{d}$ is attained. In the scope of this assumption which may be subject to discussion from different angles, asbestos types of shorter fibres may also be used successfully, provided preparation /degree of shredding/ is adequate. In view of this fact the socalled "wet shredding" process had been elaborated.

In order to determine optimal asbestos content, Lukoskina and Davidova /1951/ have made series of experiments on a laboratory scale based on asbestos kinds according to the USSR classification i.e. P-3, P-4, P-5 and P-6. The authors have determined that the increase of asbestos quantity over an optimal limit is no longer advantageous from the point of view of asbestos-cement quality. An exagerrated asbestos feed causes a decrease of bulk weight as well as the increase of water absorption. They have further determined that the value of the optimal quantity depends also on the asbestos quality. Thus optimal value may vary if different types of asbestos are applied.

The quantitative effect of asbestos has also been studied by Kitaev /1961/. He used the following asbestos mixture:

P-5-50	40 %
P-6-45	20 %
M-5-60	40 %

Quantity of the asbestos amounted to 10-12-14-16 %. The specific surface of cement used was 3200 cm^2/g; its mineral composition:

C_3S	61.7 %
C_2S	20.0 %
C_3A	3.0 %
C_4AF	10.4 %

In Tables 12-13 the effect of asbestos quantity on the output of the slate manufacturing machine as well as on the asbestos-cement characteristics is shown based on the above experiments.

It can be seen that by increasing asbestos quantity from 10 % to 16 %, bonding strength between the cement grains and the asbestos fibres increases in consequence of which precipitate content of clarifying water decreases. This

Table 12.

Effect of asbestos quantity on the output of the slate manufacturing machine

Asbestos quantity %	Precipitate content in clarifying water	Thickness of the asbestos-cement layer	Out-put of the slate manufacturing machine per hour	
	%	mm	in std.size pieces	in kilograms
10	1.0	1.18	4600	5530
12	0.5	1.24	4850	5880
14	0.2	1.31	5100	5130
16	0.2	1.37	5350	6450

Table 13.

Effect of asbestos quantity on the characteristics of the product

Asbestos quantity %	Bending strength kg/cm²				Water absorption				Bulk weight g/cm³			
	3	7	14	28	3	7	14	28	3	7	14	28
	days				days				days			
10	145.0	100.0	167.0	130.0	23	21	21	21	1.65	1.70	1.72	1.7
12	165.0	177.2	139.0	200.0	24	22	21	21	1.63	1.67	1.71	1.7
14	183.1	200.5	210.3	224.0	25	24	23	21	1.61	1.66	1.70	1.7
16	200.0	225.3	238.6	256.7	26	25	24	21	1.58	1.64	1.69	1.7

renders possible an increased layer thickness of asbestos cement i.e. an increased output of the slate manufacturing machine. Quantitative increase of asbestos of an identic quality has a favourable effect on the strength of the asbestos product, however, it impairs to a certain extent its bulk weight and its water absorption.

Furthermore Kitaev has very thoroughly studied the qualitative effect of asbestos on the output of the slate manufacturing machine and on the product quality. P-5, P-6, M-5 and K-6 types of asbestos generally used in the USSR for the production of corrugated sheet and roofing slate were tested; in the course of these tests asbestos content amounted to 14 %. The relative test results are shown in Tabl.14/a-14/b.It may be ascertained that when using low quality asbestos, precipitate content of the clarifying water as well as the moisture content of the asbestos plates increases, and the layer thickness of the asbestos cement i.e. output of the slate manufacturing machine decreases. These variations are of special importance if asbestos of the M-6 type gets into the mixture.

Low quality asbestos impairs the quality of the product.

Thus, strength is decreasing, bulk weight and water absorption are increasing. A considerable deterioration of the product occurs if the quantity of M-6 type asbestos in the mixture reaches 20 %.

In case of applying low quality asbestos due care must be given to its preparation /improvement of shredding/ and to adhere to the cement quality standard.

In summary it can be stated that the asbestos quality bears a considerable effect both on the technological process as well as on the quality of product. /Studying the respective literature it appears that in the USSR a mixture consisting of asbestos types P-5, P-6, M-5 and K-6 is used for the

Table 14/a

Effect of asbestos quality on the output of the slate manufacturing machine

Asbestos quality	%	Precipitate content in clarifying water %	Moisture of asbestos-cement layer		Thickness of the asbestos - cement layer mm	Moisture of asb. slate %	Out put of the slate manufacturing machine per hour	
			before vacuum	after vacuum			In std. pieces	In kilograms
P-5-50	100	0.2	33	30	1.35	21	5250	6770
P-6-45	100	0.2	38	30	1.34	21	5200	6540
P-5-50 P-6-45	70 30	0.2	40	30	1.34	22	5200	6600
P-5-50 P-6-45	50 50	0.2	40	30	1.32	22	5150	6350
P-5-50 M-5-60 P-6-45	40 40 20	0.2	42	32	1.31	22	5100	6180
P-5-50 M-5-60	50 50	0.5	45	35	1.16	25	4500	5250
M-5-60	100	1.0	48	38	1.03	26	4000	4600
P-5-50 M-5-60 M-6-40	50 40 10	2.0	50	40	0.90	27	3500	3920
P-5-50 M-5-60 M-6-40	40 40 20	3.5	55	45	0.75	29	2900	3160

Table 14/b

Effect of asbestos quality on the characteristics of products

Asbestos quality	%	Bending strength, kp/cm²			Water absorption, %			Bulk weight, g/cm³		
		3	7	14	3	7	14	3	7	14
		days of hardening			days of hardening			days of hardening		
P-5-50	100	230.1	240.6	260.7	20	19	18	1.72	1.77	1.80
P-6-45	100	205.0	221.5	258.9	22	21	20	1.65	1.70	1.75
P-5-50	70	210.0	227.3	240.8	22	20	19	1.68	1.72	1.76
P-6-45	30									
P-5-50	50	200.5	220.1	230.7	24	22	21	1.63	1.65	1.73
P-6-45	50									
P-5-50	40									
M-5-60	40	183.1	200.5	210.3	25	24	23	1.61	1.66	1.70
P-6-45	20									
P-5-50	50									
M-5-60	50	170.5	185.0	193.9	26	25	24.2	1.58	1.59	1.63
M-5-60	100	150.0	165.3	179.1	27.7	26	25.1	1.55	1.57	1.61
P-5-50	50									
M-5-60	40	145.0	150.9	160.3	29.3	28	27	1.50	1.52	1.55
M-6-40	10									
P-5-50	40									
M-5-60	40	130.1	135.7	143.9	31.5	30	29.3	1.44	1.46	1.50
M-6-40										

production of corrugated sheet and roofing slate.

2.22 Experiments made in Hungary on a plant scale

In the period between 1968-1969 experiments were carried out at the "Eternit Works" controlled by the research workers of the Central Research and Design Institute for the Silicate Industry with a view to the production of roofing and corrugated plates made with varying asbestos batches and different cement qualities.

The experiments on a plant scale aimed at determining what changes are brought about in the manufacturing technology and in the product quality by increasing the ratio of short fibre asbestos in the batch used for the production of roofing plates. The adjustment of the asbestos batch composition was made by taking as a basis the generally used asbestos batch for the production of roofing slates in which the ratio of the short-fibre asbestos was gradually increased.

Composition of the cement used for the experiments was always the same and the asbestos-cement ratio was also always constant i.e. 14 w. % asbestos and 86 w. % cement.

Manufactured slate has been submitted to durability tests according to standard prescriptions. The test results are shown in Tables 15, 16, 17 and 18.

Table 15.

Composition of experimental asbestos batches

Batch	Brand of asbestos and its quantity in %				
	P-3-70	P-4-35	P-5-65	P-6-40	K-6-30
1+	9,5	-	75,0	15,5	-
2++	9,5	-	75,0	9,5	6,0
3	-	9,5	75,0	9,5	6,0
4	-	-	85,0	15,0	-
5	-	-	50,0	50,0	-
6			50,0	25,0	25,0

+ Batch used most frequently by the works

++ basic batch suggested by the works.

Table 16.

Strength of experimental roofing slates /Test No.1./

No. Batch	Bending strength kg/cm² 5 days II	5 days ⊥	8 days II	8 days ⊥	28 days II	28 days ⊥	90 days II	90 days ⊥	Ratio II/⊥ in % 5 days of hardening	8	28	90
1	462	291	437	247	520	292	512	309	62	56	56	60
2	407	279	452	259	438	286	422	306	68	57	65	72
3	439	265	359	247	472	289	476	288	60	68	61	60
4	446	295	496	277	450	290	438	294	66	56	64	67
5	398	284	396	258	425	270	435	276	71	65	63	63
6	340	230	407	253	360	250	362	262	67	62	69	72

⊥ = perpendicular to direction of manufacture

II = parallel " " " "

Table 17.

Water absorption and bulk weight of experimental roofing slates - Test No.1.

No. of test batch	Water absorption %	Bulk weight kg/m³
1	12,6	1750
2	13.0	1760
3	14.1	1766
4	12.9	1815
5	13.7	1730
6	13.6	1850

Table 18.

<u>Durability of experimental roofing slates /Test No.1./</u>

/ after 10 cycles /

Test-piece dimension: 9.50 x 9.50 x 40 cm.

No. of batch	Bending strength kg/cm²		Loss of strength %
	Nontreated	Treated	
2	392.1	353.9	9.8
3	355.0	310.0	12.7
4	313.3	287.0	8.4
5	298.1	252.6	15.3
6	260.0	248.7	4.4

Sample marked 1 had not been tested

General conclusions of these tests:

2.221 Each of the experimental asbestos batches /Nos 3, 4, 5 and 6 in Table 15/ are suitable to manufacture roofing slates fulfilling, and even surpassing the quality requirements of the Hungarian Standard Specification MSZ 1197-56 concerning strength, water absorption, water penetration and bulk weight.

2.222 When applying asbestos batch No.6 a strong sticking was experienced on the collecting cylinder in consequence of which waste increased.

2.223 From the point of view of strength changes during durability tests there is no vital difference in the roofing slates made with the basic and the experimental asbestos batches. Strength of the test pieces was in every case superstandard even after the durability tests.

2.224 It may be stated that by omitting asbestos type P-3 and by increasing P-5 and P-6 asbestos quantities standard quality roofing slates can be manufactured with due safety without any disturbances in the manufacturing technology.

In the course of the experiments great stress was put on the questions in connection with cement quality and manufacturing technology. The latter one is linked to the arrangement of the asbestos fibres, being determined by manufacturing circumstances. Thus, for instance, by increasing the rate of revolution of the dipping cylinder the fibres are better oriented in the direction cylinder rotation, in consequence of which strength value measured perpendicularly to fibre orientation is also increasing. Increasing of the average length of the fibre i.e. applying long-fibre asbestos results in the same effect. Fibre orientation may be regulated by changing the number of revolutions of the mixer too. Thus by means of thorough mixing unidirectional fibre orientation may be decreased and the strength parallel to the manufacturing direction can be increased. The question of mixing is particularly important when using long-fibre asbestos /P-3, p-4/.

Going into more details with a view to this question would surpass the limits of the present study; therefore I wanted to point out some possibilities only based on experiments.

3. Endeavours aimed at the partial substitution of asbestos

3.1 Reasons of the endeavours aimed at the partial substitution of asbestos

Taking into consideration facilities offered by the original Hatschek patent very soon the intention became more and more acute to substitute partly or eventually fully asbestos fibres by different natural or artificial fibrous materials. During these experimental and realisation activities research work was carried on since about 1930 for the production of artificial /synthetic/ asbestos fibres.

Endeavours and research activity aimed at the substitution of asbestos were first of all based on economic considerations. Economic considerations arose for the following reasons: all over the world there is a scarcity in asbestos which is due to the fact that the natural occurences of asbestos are limited and more significant ones are concentrated in some countries of the world only. At the same time comparing the asbestos reserves of all the deposits of the world with the speedly increasing requirements of the processing industry /asbestos-cement, insulating, spinning and paper industries, etc./ endeavour makes itself apparent to substitute asbestos fibres by different fibrous materials. In consequence of the steady increase of asbestos consumption asbestos substitution is a problem even in those countries which have considerable asbestos deposits /as e.g. in the USSR/.

The other economic reason is the fact that only a lesser part of the available asbestos stocks can be used by the processing industry as the respective industrial branches are rather exacting with a view to the asbestos quality. The present method of exploitation of the asbestos mines as well as the introduction of the mechanical classification of asbestos fibres resulted in the fact that a considerable part of asbestos, having been mined does not meet quality requirements for further processing. This circumstance acted as a double incentive for researchers and industrial experts: namely to create possibilities for the utilization of substandard asbestos /worse than grade 6/; on the other hand, however, tó research and utilize adequate fibrous material with a view of a partial substitution of asbestos. Among the economic reasons one may also mention that the majority of countries processing and utilizing asbestos can cover their requirements only by way of imports.

Over and above the targets of an economic character mentioned above there were also endeavours to decrease or even cease the disadventageous properties of raw asbestos fibres /different fibre diameter, tensile and bending strength, high specific weight, bad wettability in the case of some asbestos types/ by using partially or fully artificial or natural fibres or fibrous materials of more uniform quality and characteristics.

Numerous studies and patents deal with the question of the asbestos. However, the opinion of some of the authors with a view to the evaluation of fibrous materials suitable for the purpose is often diverging.

3.2 Asbestos characteristics in the asbestos-cement products

In the asbestos cement products asbestos fibres have to fulfil the following three functions:

a./ to attract cement grains,

b./ to form a filtrating layer on the supporting sieve,

c./ to bring about setting of the product thus lending it high grade tensile and bending strength.

Condition of the first two properties is the cement carrying ability which is just a characteristic feature of the asbestos fibres. Research was not succesful yet to fully clear the question wether the cement carrying ability is exclusively due to a surface adherence or is a function of the chemical composition or something else. The third characteristic of asbestos applies to the resistance of the reinforcing frame, mainly against the corrosion effect of the cement hydration products.

The aforementioned triple function of asbestos should partly or fully be met by the different artificial fibrous materials to be used for substitution of asbestos. Therefore only those fibrous materials are suitable for the /partial/ substitution of asbestos which can take over fully or at least partly functions of asbestos in the products.

3.3 Theoretical conditions of the partial substitution of asbestos

In the course of laboratory investigations of different fibrous materials applied for the partial substitution of asbestos, some of the researchers came to find that in the course of manufacture a certain minimum quantity of asbestos fibres is necessary in the batch. This quantity should be of that order which can succesfully prevent the setting of cement during mixing. This minimum asbestos quantity was different in the case of the various kinds of asbestos used for the batch and according to the method of asbestos preparation. All this proves that essentially the so-called cement carrying capacity is a function of the specific surface of asbestos fibres. Consequently in such asbestos-cement batches where there is only asbestos and no other substituting fibrous material, only a part of asbestos serves as the reinforcing of the product /i.e. increasing its strength/. At the same time this reinforcing part need not meet the two further basical functions of asbestos fibres /carrying of cement and the forming of a filtrating layer on the sieve cylinder/.

After these preliminaries it can be stated that the part of asbestos fibres which reinforces /i.e. increases strength/ need not be cement carrying. At the same time, however, the reinforcing part has to dispose of all those preconditions which are required for perfect reinforcement i.e. it has to be flexible and has to have an excellent tensile strength and a good resistivity against cement.

These theoreticalassumptions were satisfactorily met by numerous artificial inorganic fibrous materials which were used for the partial substitution of asbestos in the manufacture of asbestos-cement products. Such fibrous materials are: basalt wool, glass-wool, etc.

From the theoretical assumptions it clearly appears that different artificial inorganic fibrous materials can only partly substitute asbestos fibres according to the presently known manufacturing process applied for asbestos cement products i.e. only up to that limiting value where it acts as a reinforcing agent.

On basis of pilot plant test results as well as the respective literature references the final measure of the substitution of asbestos fibres by artificial, fibrous materials has been determined at 40 % in the case of slate manufacturing.

3.4 Kinds, grouping and basic physical properties of fibrous materials which can be applied for partial substitution of asbestos

The different fibrous materials used and applied for the full or partial substitution of asbestos fibres may be classified according to the following:

a./ artificial /synthetic/ asbestos
b./ natural organic fibrous materials
c./ artificial organic fibrous materials
d./ artificial inorganic fibrous materials.

The four groups contain the following materials:

a./ different kinds of artificial asbestos
b./ peat fibres
flax fibres
rayon
wood-pulp
c./ cellulose fibres
spun viscose
d./ glass wool
basalt wool
slag wool

With some of the different fibrous materials mentioned under items a./, b./ and c./ experiments were carried on in order to terminate asbestos shortage which made itself apparent during World War II; some of them, for instance artificial /synthetic/ asbestos and cellulose fibres were even used at a plant scale for the manufacture of asbestos cement products.

After the War, however, utilization of artificial asbestos and of different organic fibres for the purposes of the asbestos-cement industry was almost completely stopped on account of the disadvantageous properties of these fibres.

Among the artificial inorganic fibrous materials it has been tried to make use of glass wool, slag wool and basalt wool for the partial substitution of asbestos in the manufacture of products of the asbestos-cement industry.

3.41 Glass wool

For the partial substitution of asbestos, glass wool up to 10-15 % is used in some of the asbestos-cement products in quite a number of countries. Investigating the properties of glass wool it was determined that the hydration products of cement have a "corrosive" effect on the glass fibres, in consequence of which a jelly-like film is formed on the surface of the glass fibres which hinders further deterioration. In view of this it is suggested for part of the asbestos cement products to be substituted by a highly basic glass wool. According to some experiences, the water bearing capacity of glass wool is rather weak; thus it often occurs that it does not dissolve uniformly in the batch and tends to float on the surface; in addition this is also in relation with the operating length of the glass wool. Furthermore the filtrating effect of glass wool is rather bad which renders possible for the cement to float away thus causing a decrease of strength in the product.

Elasticity constants of glass wool change in time: elongation and strength of glass fibres gradually decrease causing a drop in strength of the product.

Average diameter of the industrially manufactured glass wool fibre amounts to 10-15μ : its working length has to be 30-40 mm.

3.42 Slag wool

Slag wool was used for the partial substitution of asbestos on an experimental scale in the manufacture of asbestos-cement products.

There are diverging opinions in the literature on the characteristics and the suitability of slag wool to be used for this purpose.

Average length of slag wool fibres amounts to approx. 7-20 mm or less; its average fibre diameter is between 4-10μ . In the course of the slag wool manufacture melt pearls are formed on some of the fibres /up to a quantity of 40 %, depending on the system /which are not drawn out into fibres; their average diameter may vary from the average fibre diameter up to 500μ . Utilisation of slag wool for the purposes of the asbestos-cement industry depends first of all on the fact how far the quantity of the non-fibrous part /melt pearl/ can be decreased. Obviously the separation of melt pearl content results in the decrease of fibre length. Elasticity constant of slag wool is $E = 7.10^5$ kg/cm^2.

According to I. Taichmann slag wool fibres are very brittle, their chemical composition is not suitable; in the course of investigations this resulted in the fact that the slag wool fibres deteriorated with time in the asbestos-cement in consequence of cement formation. Resistivity of slag wool fibres against alkalis is also rather poor and their hydrolytic resistance is 2-3-times lower than that of basalt wool. In the case of slag wool a sulfuric or limy decomposition often occurs resulting in the complete deterioration of the fibres.

Investigations made by P.P. Budnikov and K.E. Goryainov proved on the other hand that slag wool fibres in cement mixtures had shown favourable characteristics. On the surface of slag wool fibres kept in a saturated lime solution hydration products have formed /as proved by microscopic investigation/, which dispersed more or less uniformly on the fibre surface. The hydration products were mainly calcium silicate hydrates and calcium aluminium silicate hydrates. On account of the hydration products formed on the slag wool surface the average fibre diameter may not be less than 2μ, because, as a consequence of surface hydration, the average diameter will soon decrease to 0.5-1μ. The "microconcrete" theory of V.N. Yung may also be applied to slag wool fibres according to which clinker grains and the hydration products of the surface layers of slag wool fibres bring about a new hydration product similarly as in the case of slag concrete. This product is the so-called "transitory layer" to which cement grains are adhering with an extraordinary strength.

3.43 Basalt wool

In the manufacture of asbestos-cement products basalt wool fibres are used in a considerable quantity for substituting asbestos.

Average fibre diameter of basalt wool fibres is between 7-35μ, depending on the fibre forming system. Materials of an average fibre diameter of 7-15μ have the most favourable characteristics. Average tensile strength of basalt wool amounts to 6000-8000 kg/cm^2. Chemical resistivity of basalt wool fibres compares with that of the best glass fibres, their resistivity against alkalis is also excellent; their resistivity against water is more favourable than that of slag wool; some of the basalt wool fibres show a satisfactory resistivity against cement attack. In the course of the basalt wool manufacture there is also melt-pearl formation, quantity of which, however, does not surpass 20 % in the majority of cases.

The Czechoslovak standard No. ČSN 727,311 does not permit a melt-pearl content higher than 10 % in first grade basalt wool.

In the case of a higher pearl content than the above the artificial inorganic fibrous materials which may be used for the partial ubstitution of asbestos have to be freed from pearls.

3.5 Experiments carried out abroad with a view to the partial substitution of asbestos

In the latter years experiments were made in the USSR, Czechoslovakia, Roumania and Hungary with different artificial inorganic fibrous materials with a view to the partial substitution of asbestos. In the USSR slag wool has been used for this purpose and basalt wool in the other countries. Technical indexes of the experimental asbestos-cement products made by partial substitution almost reach the values having been determined for the products without substitution.

In the course of the application of slag wool Czechoslovakian researchers have found that the slag wool fibres are brittle, their melt-pearl content is rather high nor is their chemical composition suitable; thus below acidity index 1.2 fibres are deteriorating by the alkalinity of cement, consequently the strength of these products is also decreasing considerably. Glass wool, if its chemical composition is unsuitable, is indurable, thus by applying this material strength decrease of the product cannot be prevented.

Foreign research workers obtained rather favourable results by using basalt wool. According to these experiences asbestos-mainly the long one - can be subsituted up to at least 30 % by good quality basalt wool; this has far more favourable fibre characteristics than has slag wool. Fibres of basalt wool are not destroyed by cement alkalinity nor by moisture or weather effects, thus strength values of products made of this material do not decrease in the function of time.

3.6 Hungarian experiments

Research project was executed at the Central Research and Design Institute for the Silicate Industry on a plant scale in the period between 1966-1968 aimed at finding a suitable solution for the partial substitution of asbestos. These experiments were made with the following artificial inorganic fibrous materials;

a./ slag wool /Hungarian/
b./ basalt wool /Hungarian/
c./ basalt wool /Czechoslovakian/
d./ mineral wool /Swedish/

No mention will be made of the numerical evaluation of the investigations; we shall merely limit ourselves to final conclusions which may be drawn as follows:

Among the artificial, inorganic fibres which may be used for the partial substitution of asbestos the Swedish mineral wool "Rockwool 113" or a fine fibre basalt wool of identical quality and technical characteristics are the most favourable. The most important technical characteristics of these fibrous materials are as follows:

Chemical composition:

SiO_2	45-46 %
Al_2O_3	14-15 %
CaO	16-17 %
MgO	8- 9 %
Fe_2O_3	10-12 %

Acidity index:

$$\frac{SiO_2 + Al_2O_3}{CaO + MgO} = 2.3$$

Resistivity against water:

not more than 19.6 mg/100 g fibrous material,

Physical characteristics:

Average fibre diameter	4 -6 μ
Melt-pearl content /above 0.2 mm/	max. 1 %
Surface treatment	1 % organic material to prevent dust formation.

On basis of plant scale experiments it can be stated that asbestos fibres can be partially substituted in the following ratio by mineral wool of the quality mentioned above;

Roofing slates	10 - 17 %
Corrugated plates	10 - 14 %
Drain pipes	10 - 20 %
Pressure water tubing	10 - 17 %

Primarily P-3, P-4 and P-5 grade asbestos qualities can be substituted by a suitable quality of mineral wool.

Generally one can state that for the partial substitution of asbestos artificial inorganic fibrous materials can be used acidity index of which is above 2.3, and which have a low quantity of melt-pearl contents /maximum 10 %/, and their fibre diameter is rather thin /4-6 μ/.

Mention must be made here of the "A" fibre having been tested in the Czechoslovakian Research Institute of Brno and which is probably a mineral fibre stabilized with ZrO_2. We are not in possession of the data bearing on the chemical composition and physical properties of the "A" fibre but according to some Czechoslovakian reports it can be used with a rather good efficiency in all asbestos-cement products in a quantity of about 20 %. In spite of this we understand that "A" fibre is not used in the Czechoslovakian asbestos-cement industry on a plant scale.

3.6 Cost questions

It would serve no purpose to mention in this report such self-cost data which have a specific character in the individual countries, and their use in some other countries would bear out in rather doubtful results.

Nevertheless we should like to point to three fundamental principles in this matter:

a./ Asbestos occurences are rather limited. A prime target should be to discover possibilities by which asbestos share can be decreased in the asbestos-cement products.

b./ Endeavours aimed at decreasing asbestos proportion can by no means result in a quality deterioration of the product.

c./ In case of adhering to conditions under b./ costs of substituting materials used cannot be higher than that of the substituted asbestos.

To adhere to these three principles is a "must" in all future work.

List of References:

1./ Asbestzement — H. Klos, Springer Verlag 1967

2./ Utilization of low quality asbestos for the manufacture of asbestos-cement products. Research report by Mrs. P. Opoczky — SZIKKTI Report, 1968

3./ Partial substitution of imported asbestos in asbestos-cement products by artificial inorganic fibrous materials. Research report by J. Bakos — SZIKKTI Report, 1968

4./ Theoretical and experimental research on the basic characteristics of asbestos-cement products — Report of the Technical University, Budapest, 1966

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