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Asbestos on textiles: is there an endangering during washing and wearing?

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Abstract

Asbestos is a ubiquitous environmental pollutant despite the ban of its use since about 10 years ago. Textiles may be contaminated by asbestos fibres from drinking water or household chemicals, and so a health risk could be possible. To obtain knowledge on the real hazard of asbestos fibres deposited on textiles, the behaviour of asbestos during washing, rinsing and drying of textiles has been investigated using an asbestos-like model fibre, i.e. fluff of cationically modified cellulose fibres. The results showed only small amounts of about 10% of contaminating fibres remained after washing and drying. Some special investigations were also made using asbestos fibres themselves. The simultaneous influence of mechanical and thermal energy, increased by addition of detergents leads to a continuous fibrillation of the asbestos fibres reducing their length below that believed to be hazardous to health. The results cannot be transferred to highly contaminated protective clothing without additional investigations. However asbestos contamination of textile from drinking water or household chemicals in washing processes is highly unlikely to give rise to a health hazard. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The use of asbestos has been prohibited in Germany and many other countries for over 10 years. Very big amounts of this fibrous mineral have, however, been used as building materials, non-inflammable clothing, as filters in the beverage industry, or as

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diaphragms of the chlorine-alkali electrolysis in the chemical industry because of its thermal and chemical resistance. Four million tons of asbestos were used worldwide alone in 1990 [21], most of which still in exist.

Substitutes with suitable properties have been found for nearly all applications (e.g. Dolan 10 in fibre-reinforced cement plates [1]). But to replace the existing asbestos-containing materials by asbestos-free ones and so to remove the sources of a permanent latent contamination is only gradually attainable.

The aim of this work, as supported by the Saechsisches Ministerium fuer Wirtschaft und Arbeit, was to find out the possible sources of the contamination of textiles by asbestos fibres, to estimate the real hazard by small amounts of asbestos deposited on textiles and to show possibilities to minimize any risk. The results shall give arguments against the psychosis brought about by 'Yellow Press' publications.

Asbestos cement in buildings and water mains appears as one source of the contamination. In 1986, the watermain network in the United States contained more than 60% of such tubes [2,3]. Furthermore, as a result of the sometimes still used asbestos diaphragms in the chlorine-alkali electrolysis, we found asbestos fibres in sodium hydroxide (1.3 millions of fibres of the critical length in an 1N solution) as well as in substances produced by using sodium hydroxide. So a usable solution of a commercially available liquid detergent contained about 2.8 millions of asbestos per litre.

The health hazard by asbestos orally taken in with liquids is negligible [3,4]. So in the past it was assumed that asbestos fibres in drinking water from erosion of the asbestos-containing cement pipes caused no danger. After a lengthy use, water from old asbestos-cement pipes may contain considerable amounts. American studies [2,3] quote numbers in the range of 100 000 up to 170 millions asbestos fibres/l drinking water. Up to 11 million fibres/l are found in drinking water in some regions of Germany [5]. However, the quoted literature does not contain any information about the portion of these fibres in the critical range for human health (5 μ m < L < 100 μ m; *D* ≤ 2 μ m). In spite of the low direct hazard from asbestos in drinking water one can theoretically imagine a scenario where a hazard could arise:

Asbestos in drinking water	⇒	Release of asbestos fibres in the air by evaporation, e.g. after spraying in air conditioners and humidifiers
\Downarrow washing		
Deposition on textiles during washing and rinsing processes		
↓ drying		
Possibility to breathe in asbestos fibres		
located on the washed textiles		
promoted by the thermal and		
mechanical energy during wearing		

There are only few published results of investigations about asbestos fibres on textiles. But a paper by Chatfield [6] showed detectable contamination under specific conditions.

The working hypothesis for minimizing the residual risk was as follows: the adhesion between asbestos and textile fibres is favoured by the electrostatic attraction between the positively charged asbestos fibres and the textile fibres with negative surface charges. By changing the charge distributions, i.e. same charges of the adhesion partners, the attraction forces decrease, leading to smaller adhesion between asbestos and fabric.

2. Composition and properties of asbestos

'Asbestos' is the generic term for a number of mineral silicates, of which the most widely used is the fibrous chrysotile or serpentine of the general formula,

 $Mg_3[(OH)_4/Si_2O_5]$

The hydroxylic groups on the surface can be exchanged easily giving rise to a positive excess charge which can be characterized by the electrokinetic or zeta potential (ζ -potential), a special kind of the surface potential [7].

The point of zero charge (pzc) that means the pH value in the ζ -pH plot (streaming potential) of asbestos where the z-potential changes from a positive to a negative value is 11.8. All other organic and inorganic fibres possess an excess of negative surface charges in the acidic area, i.e. already at a pH of ≥ 4 (see Fig. 1).



Fig. 1. The zeta potential of asbestos and unmodified or cationically modified cellulose fibres (pH dependence).

The macroscopically visible fibres are formed by a different number of monofibrils with diameters between 200 and 500 nm. The fibres may split to smaller units down to the monofibrils.

Asbestos fibres of 'critical' lengths between 5 and 100 μ m are the cause of 'asbestosis'. This disease of the lung changes the tissue of the lung (scars, cancer) and leads so to the loss of their function [8]. Asbestos is therefore in Germany classified into group I of the carcinogenic substances ('very strong endangering substances') [9].

Although the noxious effect of asbestos was known at the beginning of this century, it was used in enormous amounts (see Section 1) until the 1990s because of its outstanding insulating properties [21].

3. Methods of investigation and materials

The usual method to determine the number of asbestos fibres in gases or liquids is to collect and to concentrate the fibres on filters followed by plasma ashing and investigating the residue with the scanning or transmission electron microscope (SEM or TEM) [7,10–14]. From the counts in the analysed area one can calculate the amount on the whole filter or in the liquor volume.

The energy dispersive X-ray analysis (EDXA) permits to distinguish between organic and inorganic fibres without ashing the organic part [15].

The direct counting of asbestos fibres on textiles is practically impossible. It succeeds with microscopic methods only by chance to find a few asbestos fibres in an oversized number of textile fibres: an asbestos fibre may be deposited as well on the textile surface as in the voids formed by the textile bond or between the single monofibres in the yarn.

To estimate the contamination of textiles, it is recommended to remove the asbestos fibres mechanically from the textile, e.g. by ultrasonic methods, before investigating the eluate. It is also possible to ash the organic part followed by investigating the residual inorganic part [16]. It has to be assumed that the contaminating fibres are completely removed and are not changed in number and size by the pre-treatment of the samples. These prerequisites are only valid with reservations (see Section 4.1). But nevertheless in this work the investigations of the behaviour of asbestos fibres during different treatments were carried out as described: eluting the polluted fabric by ultrasound, collecting the particles from the liquor or eluate on nuclear pore membrane filters, counting in the transmission electron microscope.

 Table 1

 Size distribution of the asbestos-like model fibres (modified cellulose after cutting and milling)

< 5 µm	46.2%	
5–10 μm	19.5%	critical area: 5–100 µm
10–20 µm	19.5%	
20–50 μm	13.0%	
50–100 μm	1.2%	
100–200 μm	0.6%	

Table 2					
Comparison of selected	properties	of asbestos	and	model	fibres

	Asbestos fibres	Model fibres (fluff cationically modified with a non-
		stoichiometric polyelektrolyte complex)
Geometry - critical dimensions	length $> 5-100 \mu$ m, diameter $< 3 \mu$ m, slimming degree > 3	length $> 5-100 \mu$ m, diameter $< 10 \mu$ m, Slimming degree > 3 , portions of greater fibres exist
Supramolecular structure and topography	pronounced fibrillary structure, easy fibrillation during mechanical influences	fibrillary structure, fibrillation needs strong mechanical influences
Affinity of anionic surfactants	high	medium
Adsorbed amount from solutions of 2×10^{-4} m sodium dodecyl sulphate	22.6×10^{-6} moles/g	1.2×10^{-6} moles/g (unmodified: 0.1×10^{-6} moles/g)
Surface charge (zeta potential)	positive	positive
Mechanical properties		
Strength	$0.22-0.37 \text{ Ntex}^{-1}$	0.30–0.42 Ntex ⁻¹
Brittleness	25%	35-67%
(ratio of maximal tensile strength of loops)		

In our investigations asbestos fibres could be used only in exceptional circumstances because of safety. So we searched for a model fibre with similar properties but without the hazard of asbestos, which is quantitatively estimable with a simple method. Fibre and method had to meet some demands:

Demands on the model fibre are as follows:

- · size distribution and geometry similar to asbestos,
- · Positive zeta potential over a wide range of pH,
- · Visible on the textile surface by optical microscopy,
- No further fibrillation in laundering.
- Demands on the method are:
- · Acceptable time needed for the investigation of extensive test series;
- Reproducible but distinguishing results when the process engineering parameters are varied;
- · Results with model fibres have to be transferable to the behaviour of asbestos fibres.

As a result of comprehensive preliminary examinations of different materials, we chose a cellulosic fibre spun from a solution in N, N'-methyl morpholinium oxide which was modified afterwards [17]. By a series of grinding and fibrillation processes (Table 1) it was possible to produce a fibre fluff with about 50% of the average size of chrysotile. This material was kindly given by Dr. Hengstberger, Institut fuer Chemiefasern, Denkendorf/Germany [18]. After the fibres were dyed with a blue indanthrene dyestuff they were visible under the optical microscope. By means of repeated alternating treatments of the fibres in solutions of an anionic [poly(sodium-4-styrene-sulphonate)] and a cationic [poly(dimethyl-diallyl-ammonium chloride)] polyelectrolyte [19], a non-stoichiometric polyelectrolyte complex was formed. That complex gives a positive zeta potential to the fibre fluff over a wide pH range (Fig. 1).

Table 2 contains the comparison of the properties of asbestos fibres and the modified fibre fluff. The adsorption properties (adsorbed amount of an anionic surfactant) of the model fibres clearly approach those of asbestos after cationic modification.

The laundering tests in this work are carried out with a model washer 'Scourotester' (Computex, Hungary): It contains eight high-grade steel vessels with a volume of 500 ml, each filled with 20 g cotton fabric and 18 steel balls. The liquor ratio was 1:6 (i.e. 6 g of laundering solution to 1 g of fabric). The laundering took 30 min at 60°C and 40 rpm in the Scourotester.

To investigate a series of contamination experiments with the model fibres, the textile surface was directly observed by optical microscopy (reflected dark field). More exact investigations were made with the SEM.

4. Results and discussion

4.1. Laundering experiments with asbestos fibres

Table 3 and Fig. 2, respectively, show the influence of ultrasonic treatments on the size distribution of asbestos dispersions. Table 4 presents the results of 'blind' laundering experiments in the model washer without textile fabric. An exactly known small amount of asbestos fibres was dispersed in the bath. This amount was more than 100

Time of	Fibers							
treatment (min)	$ \frac{0.5 \ \mu m \le 1}{\le 1 \ \mu m} $	1 μm ≤ 1 ≤ 2.5 μm	2.5 μm ≤ 1 ≤ 5 μm	5 μm ≤ l ≤ 10 μm	10 µm ≤ l			
0	6.8	17.7	7.1	8.0	5.7			
1	837	771	619	304	162			
4	2242	1329	984	380	259			
60	2638	2602	1557	746	421			

Influence of ultrasonic treatment on the number of asbestos fibers in aqueous dispersions (fibres/ml)

Table 3

times higher than the average asbestos pollution in drinking water or in solutions of household chemicals, as prescribed in the literature or found in our own measurements (see Section 1).

The results show that asbestos fibres in aqueous solutions fibrillate into smaller particles under the complex influence of mechanics, temperature, and in presence of surfactants acting as dispersing agents by their surface activity. Systematic experiments to investigate the influence of the detergent composition on the fibrillation tendency of suspended asbestos fibres have not yet been carried out. The results however indicate that the fibrillation is stronger in the detergent liquor 2 where the model fibres received the highest negative zeta potential.

The results led to the finding that laundering experiments in defined asbestos-containing water are unsuitable for the quantitative assessment of the effect of washing processes with regard to the deposition or removing of the asbestos fibres. Their



Fig. 2. Influence of ultrasonic treatment on the fibrillation (multiplying) of asbestos fibres.

Table 4 Concentration of asbestos fibres in aqueous dispersions, influence of detergents and mechanics

	Fibres/litre $\times 10^6$ (confidence region $S = 95\%$)					
	0.5 μm ≤ 1 < 2.5 μm	2.5 μm ≤ 1 < 5 μm	5 μm ≤ 1 < 40 μm	40 μm ≤ 1 <100 μm	$l \ge 100 \ \mu m$	$\Sigma \le 40 \ \mu m$
Bath before contamination (initial concentration)	28 (23–35)	21 (16–27)	23 (18–30)	1 (0–3)	0 (0–1)	72
Bath after 'washing' without detergent and textiles	45 (36–55)	16 (11–22)	19 (14–26)	0 (0–1)	0 (0–1)	80
Bath after 'washing' with detergent 1 ^a , without textiles	74 (60–90)	25 (17–35)	20 (12–30)	1 (0–4)	0 (0–2)	119
Bath after 'washing' with optimized detergent 2 ^b , without textiles	281 (240–332)	20 (14–26)	26 (20–34)	0 (0–1)	0 (0–1)	327

^aDetergent 1: mixture of an anionic (sodium dodecyl benzolsulphonate) and a nonionic (ethoxylated fatty alcohol) surfactant, pH 10-11.

^bDetergent. 2: mixture like detergent 1, addition of 10 wt.% of an anionic polyelectrolyte.

continuous splitting makes it impossible to compare the numbers of fibres before and after the treatment.

4.2. Laundering experiments using cotton fabric contaminated with model fibre fluff

Safety reasons as well as the instability of asbestos fibres (see Section 4.1) led to the use of the modified cellulose fibre fluff described in Section 3 as an asbestos-like model fibre for the investigation of the behaviour of asbestos in laundering and rinsing processes:

- Laundering and rinsing of polluted fabric in particle-free water (effect of the laundering conditions on the removal of the pollutant).
- Laundering and rinsing of non-polluted fabric in definedly contaminated liquors (investigation of the deposition on textiles from liquors).

The backing fabric for the laundering tests was a standardized cotton fabric [20]. It was a compromise between the fact that single fibres or fragments of fibres split off from fabrics made of spun yarn and the requirement of a measurable contamination and adhesion, which cannot be attained by a fabric made of filament yarn.

To prepare the polluted cotton fabric, clean fabric was treated during 40 min at 60° C in a surfactant-free suspension of the model fibre fluff. By the laundering tests with this polluted fabric are expected statements to the effectiveness of detergents, optimal laundering and rinsing conditions to remove the polluting fibres as well as to the residual contamination after a tumbler drying.

A blank value was taken in the calculation, that means the number of released fibres from the unpolluted cotton fabric during the treatments. The investigations did, however, include a relatively high error, e.g. by the accumulation of the polluting fibres in creases or wrinkles of the fabric at conditions which are approached to the practice (e.g. low liquor ratio).

The results allow some general conclusions:

- Laundering and rinsing of textiles are processes where the decontamination is superimposed by a 'recontamination' of previously released particles.
- The rinsing in particle-free water may be considered as a dilution process of the polluted solution.
- The contamination of the fabric after laundering and rinsing consists of the portions of adsorption, filtration, and migration, and of the number of particles in the liquid remaining on the fabric.

Results of faundering experiments with cotton cloud, previously containinated with model note num					
Zeta potential of the model fibre	Positive	Positive	Negative		
Initial contamination (fibres/cm ²)	17.2 ± 5.2	19.3 ± 4.2	16.5 ± 6.3		
Detergent (see Table 4)	1	2	1		
Residue contamination (%):					
after laundering	67.8	86.4	60.6		
After 1. rinsing	50.9	63.1	39.7		
After 2. rinsing	39.1		27.8		
After drying	4.7		9.5		

Table 5

Results of laundering experiments with cotton cloth, previously contaminated with model fibre fluff



Fig. 3. Influence of the laundering treatment with anionic surfactants on the zeta potential of asbestos and cationically modified cellulose fibres (pH dependence).

The results of laundering experiments with previously contaminated fabrics, shown in Table 5, indicate that about 2/3 of the polluting fibres are removed from the fabric in laundering and rinsing processes. The number of remaining fibres decreases during the subsequent drying in a tumbler to less than 10% of the initial value. The cationically modified model fibres behaved in the experiments negligibly different compared to the unmodified fibres. We assume the causes in the relatively high error of the counting method but also in the recharging of the positive charged modified fibres in the anionic detergent solution to negative values. This charge reversal is observed also on asbestos fibres (Fig. 3).

The influence of the detergent's properties on contamination and decontamination has yet to be investigated systematically.

Laundering experiments with clean fabric in polluted wash solutions showed that the deposition of the fibre fluff is poor. An equilibrium establishes between deposition and removal as described before in the case of laundering of polluted fabric.

5. Summary and conclusions

Asbestos fibres are found in drinking water or household chemicals in spite of the prohibition of its use for more than 10 years. These fibres can contaminate textiles during laundering.

By contaminating and laundering experiments in solutions polluted by asbestos or by a asbestos-like model substance, it could be shown that deposition takes place on cotton fabric. During the laundering with anionic detergents, the positive surface potential of both the asbestos and the modified model fibre becomes negative as a result of the adsorption of anionic surfactant. Thus, repulsive forces are formed between contaminating fibres and textile with a likewise negative charge. The investigations showed that it is possible to release about 2/3 of the contaminating fibres by laundering and rinsing and additionally 20-25% by drying in a tumbler. The residue of about 10% is obviously so strongly bound that mechanical movement and body heat in wearing are not sufficient enough to remove it from the cloth.

A continuous splitting of the asbestos fibres of critical size into a large number of smaller particles up to the subcritical length of less than 5 μ m takes place during the laundering by supplying thermal, mechanical and chemical energy. We assume that the possible health hazard by asbestos on textiles significantly is diminished by this process.

The detergent formulation seems to influence the laundering effect of the contaminated textiles: the more negatively the adhesion partners are charged, the smaller is the likelihood that asbestos will be deposited out of liquors and the easier it is to remove the asbestos from textile fabrics.

Overall, we have established that the hazard posed by textiles treated in washing baths containing small amounts of asbestos fibres from drinking water, detergents, or softeners, is rather small. This we conclude from the fact that asbestos fibres fibrillate during laundering into smaller particles of at least undercritical sizes and that the portion of fibres not removable by laundering and rinsing is so strongly bond that a release in wearing is improbable.

The results do not permit statements on the behaviour of protective clothes polluted by large amounts of asbestos in the commercial laundry. In this case the complete release of the asbestos cannot be assumed and a considerable hazard may remain from the textile and the waste water.

References

- [1] H. Hähne, U. Schuster, Hochfeste Acrylfasern, Melliand Textilber. 5 (1985) 430-432.
- [2] R. Lemen, T. Meinhardt, G. Becking et al., Report on Cancer Risks Associated with the Ingestion of Asbestos, NTIS Order Nr. PB90-130527/XAD, National Inst. for Occupational Safety and Health, Cincinnati, OH, USA.
- [3] J.S. Webber, S. Syrotynski et al., Asbestos-contaminated drinking water: its impact on household air, Wadsworth Cent. Lab. Res., New York State Dept., USA, Environ. Res. (1988), 46(2), pp. 153–167.
- [4] B.T. Commins, Asbestfasern im Trinkwasser unter besonderer Berücksichtigung der Verwendung von Asbestzementrohren, Gas Wasser Wärme 7th of July 1985, pp. 248–252
- [5] Fasern aus dem Wasserhahn, Ingenieur Digest 4 (1993) p. 60.
- [6] E.J. Chatfield, Analytical protocol for determination of asbestos contamination of clothing and other fabrics, Microscope 38 (1990) 221–222.
- [7] R.S. Feldman, Development of an asbestos reference suspension, Natl. Bureaus of Standard Spec. Publ. 619. Proc. of the NBS/EPA Asbestos Standards Workshop 1980, pp. 68–76.
- [8] Asbest, special issue of the Mitteilungsblatt 'sicher arbeiten', Maschinenbau- und Kleineisenindustrie-Berufsgenossenschaft, Düsseldorf, Germany, 1989.

- [9] Decree for the protection from dangerous substances, Gefahrstoffverordnung—GefStoffV, i.e., Materials Safety Data Sheet, Carl Heymanns Verlag, Köln, Germany, 1993.
- [10] Chatfield: Analytical procedures and standardization for asbestos fiber counting in air, water, and solid samples, Natl. Bureaus of Standard Spec. Publ. 619. Proc. of the NBS/EPA Asbestos Standards Workshop 1980, p. 91 ff.
- [11] Verfahren zur getrennten Bestimmung von lungengängigen Asbestfasern und anderen anorganischen Fasern—Rasterelektronenmikroskopisches Verfahren—ZH 1/120.46, Ed. by Hauptverband der gewerblichen Berufsgenossenschaften, Sankt Augustin, Carl Heymanns Verlag Köln, Germany, 1991.
- [12] Instructions of the VDI 3492 leaf 1: Messen anorganischer faserförmiger Partikel in der Auβenluft, Rasterelektronenmikroskopisches Verfahren, Beuth-Verlag, Berlin, Germany, 1991.
- [13] J.R. Milette, P.J. Clark et al., Methods for the Analysis of Carpet Samples for Asbestos, Environmental Protection Agency, Cincinnati, OH, USA, NTIS Order Nr.: PB93-194355/XAD.
- [14] K. Saito, Y. Takizawa et al. Conc. and Form of Asbestos Fibers in Tap Water Contaminated from Asbestos–Cement Water Pipes, Sch. Med., Akita Univ., Akita, Japan, Nippon Eiseigaku Zasshi 47 (1992) 4, pp. 851–860.
- [15] G. Kurz, TEM-Asbestfaser-Analysen an Textilien und zugehörigem Umfeld, internal report, Institute Fresenius, 1994.
- [16] J.R. Kominsky, R.W. Freyberg et al. Two Cleaning Methods for Removal of Asbestos Fibers from Carpet, NTIS Order Nr.: PB91-125740/XAD, PEI Associates, Cincinnati, OH, USA.
- [17] K.-P. Mieck et al., Contribution to the judgement of fibrillability of cellulosic fibres, Chem. Fibers Internatl. 45 (1995) 44–46.
- [18] M. Hengstberger, Die Bildung von atembarem Feinstfaserstaub bei der Verspinnung und Weiterverarbeitung von Polyblends, AIF-report 9729, 1996.
- [19] S. Schmidt, H.-M. Buchhammer, K. Lunkwitz, Oberflächenmodifizierung von Glas- und Viskosefasern mit nichtstöchiometrischen Tensid/Polyelektrolytkomplexen und Polyelektrolyt/Polyelektrolytkomplexen, Tenside Surf. Det. 34 (1997) 4, pp. 267–271.
- [20] DIN 53 919 Teil 1: Standardbaumwollgewebe zur Beurteilung von Waschverfahren (Mai 1980).
- [21] ACS Minerals Yearbook, Vol. I, 1994, pp. 81-87.