

THE PROPORTION OF LONG FIBRES IN ATTAPULGITE AND SEPIOLITE CONTAINING ADSORPTION GRANULATES

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INTRODUCTION

In the Federal Republic of Germany every year more than one million tons of adsorption granulates are used by consumers as animal bedding, adsorption material for oil, or as additive in colours and glues. The majority of these granulates consists of the fibrous minerals attapulgite resp. palygorskite and sepiolite. Depending on the location of the mine, rather different lengths and compositions of the fibres can be found. It is suggestive that the content of fine fibres ($D < 0.1 \mu\text{m}$) may have carcinogenic properties.⁴ Intraleurally and intraperitoneally injected attapulgite fibres of the long type caused cancer in rats whereas the short type was not effective.^{3,4,5,6,7} In addition, Spanish sepiolite proved to be ineffective as revealed by intrapleural injection experiments.^{6,7} Nevertheless, a Finnish sample of a remarkably long fibrous sepiolite, supposedly a rarity, was found to cause cancer in intraperitoneal injection experiments. (Pott et al. unpublished) Thus, the durability of the fibres in the lung has at least to be considered.

Morbidity and mortality studies on employees of American attapulgite mines and mills as well as X-ray examinations of workers in decomposition and processing factories of sepiolite in Turkey have been published.^{1,8} However, even mortality studies, conducted during the processing of short fibrous attapulgite deposits in Georgia, distinctively neither excluded nor supported any tumour risk.⁸

Thus, carcinogenic properties of the minerals attapulgite and sepiolite can only be excluded by the use of injection experiments. Especially the content of long fibres in commercially available products has to be kept at least as small as in the tested samples. This communication describes the mineralogical composition and the content of fibres with a length of $L \geq 5 \mu\text{m}$ of adsorption granulates, used as animal bedding.

MATERIALS AND METHODS

Mineralogical Investigations

The mineralogical composition of 75 commercially available samples of adsorption granulates used as animal bedding was studied by means of:

- X-ray diffraction

- polarization—and phase contrast microscopy
- differential thermoanalysis.

Samples supposedly composed of fibrous components were subsequently classified according to number and length of fibres.

Scanning Electron Microscopy (SEM) Classification of Fibre Quality

Of each sample, by the use of sonication (30'), 5 mg were suspended in 50 ml distilled water. Aliquots were filtered with nucleoporefilters (poresize $0.2 \mu\text{m}$, previously sputtered with gold) to obtain a substrate density of $5 \mu\text{g}/\text{cm}^2$. These specimens were analysed by SEM (13000 \times). In addition to the mineralogical study, the specimens were also investigated by energy dispersive X-ray analysis to obtain the elemental composition of each sample.

Qualification of Fibres by Scanning Transmission Electron Microscopy (STEM)

The concentration of fibres contained in 5 samples was revealed by the use of STEM. As described above, an aqueous suspension of the sample was prepared and filtered on an untreated nucleoporefilter (poresize $0.2 \mu\text{m}$). Subsequently, the specimen was sputtered with carbon, the filter material dissolved in a Jaffe washer, and the remaining transmission sample was analyzed at a magnification of 29000 times (STEM) for fibres of any length and at a magnification of 10000 times (TEM) for fibres with a length of $L \geq 5 \mu\text{m}$.⁴

RESULTS

Attapulgite resp. palygorskite were characterized as main components in 7 samples and sepiolite in 19 samples, (Figure 1). In 9 other samples sepiolite was also found in minor quantities. These 35 products as well as 14 other samples containing various calciumsilicahydrates were analyzed for their fibrous components by the use of scanning electron microscopy. Twenty six products which were mainly composed of attapulgite and sepiolite proved to be aggregated of fine fibres. Although the overwhelming majority of these fibres did not exceed the length of $L \geq 5 \mu\text{m}$, a smaller portion of the fibres was longer than $5 \mu\text{m}$ in all cases.

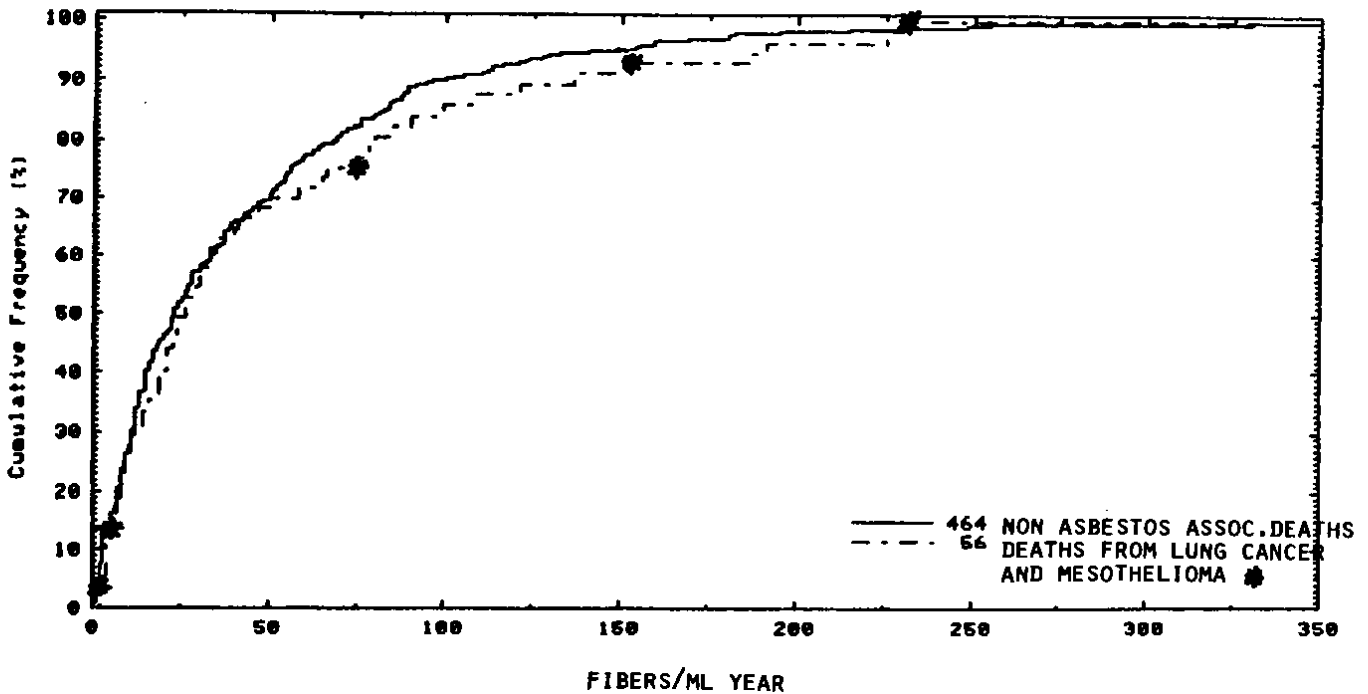


Figure 1. Cumulative doses of cases of lung cancer, mesothelioma and non-asbestos-associated deaths.

The results of X-ray diffraction and differential thermo-analysis studies were confirmed by the elemental analysis which showed a higher Al, Fe portion in attapulgite. However, the distinction between attapulgite and sepiolite with elemental analysis was not completely feasible.

Of the 26 products, 4 samples with relatively long and 1 sample with short fibres as revealed by qualitative fibre characterization were selected for a quantitative analysis by scanning transmission electron microscopy (STEM). The results are summarized in Table I. The median length of the fibres was measured as $L = 0.7$ to $1.3 \mu\text{m}$, the median diameter as $D = 0.03$ to $0.05 \mu\text{m}$ and the ratio was calculated as $L/D = 20$ to 29 . The remarkably constant number of all fibres was counted as 71 to $135 \cdot 10^9$ F/mg. Despite the generally short fibres, longer fibres ($L \geq 5 \mu\text{m}$) were found in all samples. The concentration of fibres with a length of $L \geq 5 \mu\text{m}$ was found to be 1.8 and $26.4 \cdot 10^6$ F/mg for attapulgite and 12.2 , 12.7 , and $1240 \cdot 10^6$ F/mg, respectively, for sepiolite. The latter one was already found to consist of more long fibres than all other products by the use of SEM-analysis.

DISCUSSION AND CONCLUSION

The concentration of fibres longer than $5 \mu\text{m}$ in 5 adsorption granulates achieve a crucial importance if compared with results obtained from experimentally injected attapulgite and sepiolite in animals.⁴ Figure 2 summarizes a comparison between the findings of both investigations. In 4 of the adsorption granulate samples the concentration of fibres longer than $5 \mu\text{m}$ was lower than the concentration yielding carcinogenic effects in the injection experiment. However, it

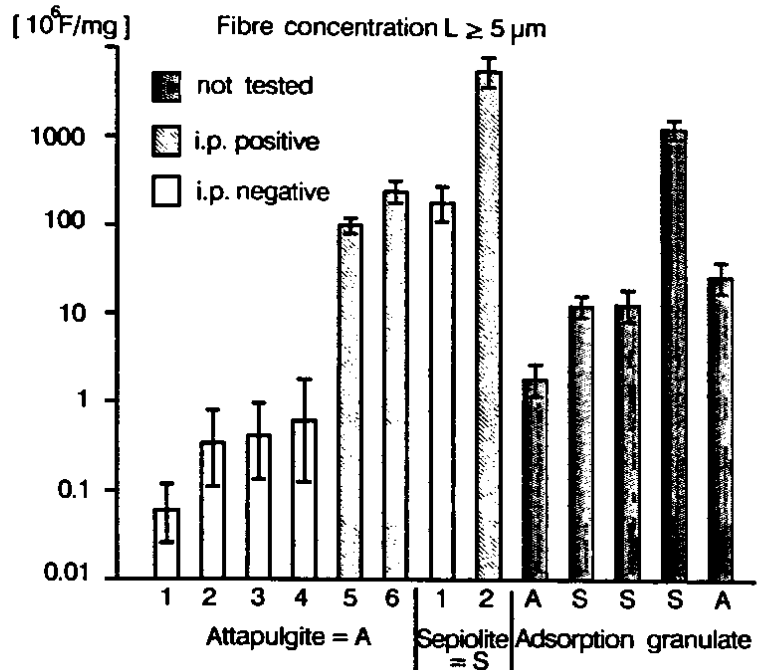


Figure 2. Number of fibres with a length of $L \geq 5 \mu\text{m}$ in 5 selected adsorption granulates as revealed by TEM at a magnification of $10,000\times$. Comparison of samples of attapulgite (Mormoiron 1, Lebria 2, Georgia 3, 4, Torrejon 5, Cacérés 6) and sepiolite (Spain 1, Finland 2) intraperitoneally or intrapleurally examined for carcinogenicity in rats, c. f.⁴

Table I
Causes of Death (ICD 9th Revision) 1950–1987

	Official diagnosis (best information)	Additional diagnosis
<u>Malignant neoplasias</u>		
Respiratory organs, intrathoracic organs (160-165)	59(58)	
lungs (162)	50(52)	
pleura (163)	7(4)	
larynx (161)	1(1)	
other (nose)	1(1)	
Organs of digestion, peritoneum (140-159)	58(59)	
stomach (151)	34(35)	1
intestine (152, 153)	3(4)	
rectum (154)	4(4)	
esophagus (150)	2(2)	
liver (155)	1(1)	
gallbladder (156)	3(3)	
pancreas (157)	4(5)	1
oral cavity and pharynx (140-149)	4(4)	
peritoneum (158)	3(1)	
Other	31(33)	
urinogenital organs (179-189)	14(14)	1
other locations	17(19)	
Primary location poorly designated Neoplasias of unknown character (239)	4(5) 1(0)	
Diseases of the respiratory organs (460-519)	32(33)	
chronic bronchitis (491)	4(5)	3
emphysema (492)	6(6)	4
asthma (493)	8(9)	2
tuberculosis (011, 012)	6(5)	-
pneumoconiosis (500-505)	1(2)	8
other chronic diseases	0(0)	2
pneumonia (480-486)	4(4)	11
other acute (infectious) diseases	3(3)	-
Diseases of the circulatory system (390-459)	203(201)	
myocardial infarction	61(62)	2
other ischemic heart diseases	31(31)	9
cor pulmonale	7(6)	3
other cardiac diseases	39(37)	13
diseases of cerebral vessels	40(40)	6
other circulatory diseases	25(25)	25
Diseases of the organs of digestion (520-579)	47(47)	
gastric and duodenal ulcer	7(7)	6
hepatic cirrhosis	29(29)	1
other	11(11)	-
Other diseases	27(25)	11
Accidents (E 800-949)	54(55)	2
Suicide and violent cause of death (E 950-999)	19(19)	-
Unknown causes of death	5(5)	

still higher than the concentration found to be ineffective. The concentration of fibres with a length of $L \geq 5 \mu\text{m}$ was clearly raised in a fifth adsorption granulate sample of sepiolite. Sepiolite from Spain is reported to be non carcinogenic.^{6,7} The authors state that in their investigated products no fibres longer than $5 \mu\text{m}$ were found.⁷ Yet, in a suspension of this sepiolite which was prepared from respirable dust to perform intrapleural injections, the proportion of fibres with a length of $L \geq 4 \mu\text{m}$ was found to be 10.5%. In contrast, a concentration of 5.5% of fibres with a length $\geq 4 \mu\text{m}$ was found in attapulgite from Torrejon which proved to cause mesotheliomas. In accordance with these findings, in Figure 2 the content of fibres with a length $L \geq 5 \mu\text{m}$ in Spanish sepiolite tested by Wagner was rather high ($180 \cdot 10^6$ F/mg); whereas a Finnish sample containing $5500 \cdot 10^6$ fibres/mg longer than $5 \mu\text{m}$ and also anthophyllite was found to cause mesothelioma. (Pott et al., unpublished).

In summary, the concentration of fine fibres longer than $5 \mu\text{m}$ in adsorption granulates composed of attapulgite and/or sepiolite was lower with a factor of 4 to 100 in the majority of the samples than concentrations significantly carcinogenic in injection experiments. Only one animal experiment with a relatively high number of long sepiolite fibres shows a lower carcinogenic effect than experiments with long attapulgite fibres. However, the main component of adsorption granulates often resembles attapulgite as shown by analytical tests or it cannot be excluded as minor component or impurity. Thus, it is requested that the physical properties and biological effects of fibrous clays are investigated before deposits are handled.⁷ In particular, the carcinogenic effects of the adsorption granulate of sepiolite with $1240 \cdot 10^6$ fibres per mg longer than $5 \mu\text{m}$ has to be tested in an animal experiment by intraperitoneal injection. Furthermore, the persistency of these long fibres has to be studied by intratracheal tests.³

Table II
Lung Cancer Mortality 1950–1986: Observed (O), Expected (E); Standardized Mortality Rate (SMR=O/E) with 95% Confidence Interval (95% c.i.)

Lung cancer (ICD 162)	O	E	SMR (95% c.i.)	p
Total	49	28,50	1,72 (1,21-2,57)	< 0,01
Total smoker-adjusted	49	47,04	1,04 (0,79-1,41)	n.s.
≤ 25 F/ml year	25	12,80	1,95 (1,17-3,74)	< 0,01
≤ 25 smoker-adjusted	25	19,91	1,26 (0,83-1,95)	n.s.
>25 F/ml year	24	15,04	1,60 (1,01-2,96)	< 0,05
>25 smoker-adjusted	24	26,16	0,96 (0,64-1,43)	n.s.

Table III
Crocidolite Exposure of 4 Mesotheliomas (verified by autopsy) and Controls Matched for Sex, Age and Time of First Employment and Duration of Employment

	high	high/medium	medium	negligible	unknown
mesothelioma	xx	x	x		
lung cancer (without asbestosis)		x	x	xx	
non-malignant respiratory disease		x		xx	x
cardiovascular disease	x		xx	x	
alive (1987)			x	xxx	

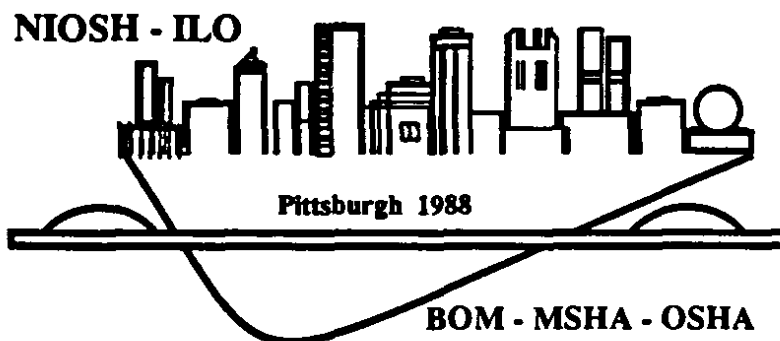
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Part **I**
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Parte



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