ASBESTOS INTERNATIONAL ASSOCIATION

(Limited by Guarantee)

68 GLOUCESTER PLACE, LONDON W1H 3HL, ENGLAND

MEMORANDUM

TO: Asbestos Producers Advisory Panel
Medical Advisory Panel

FROM: Director General

OUR REF.: AIA/5/FIB

7 December 1984

cc Executive Committee

TREMOLITE IN CHRYSOTILE

The attached report on a meeting, together with a paper by Dr. Hodgson on Tremolite in Chrysotile, are forwarded for information.

In essence, research is being conducted at the IOM* into the possibilities of testing commercial chrysotile tremolite content.

This matter would appear to be of considerable significance to chrysotile miners.

You will be kept informed.

Sir Neville Stack

Encs. Notes on a Meeting
Paper by Dr. A.A. Hodgson

* Institute of Occupational Medecine, Edinburgh, Scotland

A0130C

NOTES ON A MEETING BETWEEN DOCTORS ELMES, HODGSON AND BROWNE REPRESENTING THE ASBESTOSIS RESEARCH COUNCIL AND SIR NEVILLE STACK, DIRECTOR GENERAL OF THE ASBESTOS INTERNATIONAL ASSOCIATION, TO DISCUSS ASPECTS OF THE PROBLEM OF TREMOLITE CONTAMINATION OF ASBESTOS FIBRE (22 November 1984)

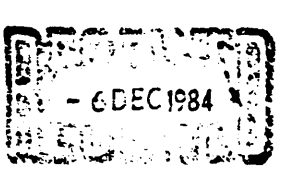
TMS 6/12

Doctor Browne began by explaining the background of the present meeting. At the last meeting of the Scientific Committee of the A.R.C. much time had been spent in discussing recent research which had suggested that tremolite, which was a regular contaminant of chrysotile may be an important cause of some of the morbidity associated with the mining, milling and manufacture of chrysotile. He had been in correspondence with Professor MacDonald, who confirmed that research was being carried out in his Department on the adverse health effects of tremolite, both in vermiculite miners in Montana and in chrysotile miners and textile workers in Quebec and Charleston respectively, as well as examining lung fibre burdens of a wide range of cases in mesothelioma throughout Canada, to assess the importance of tremolite in causation. Some of the results of his work are being presented at the conference on "Inhaled Particles", next September.

Doctor Elmes gave further details of research indicating tremolite as an important cause of asbestos-related disease. He discussed the views of the A.R.C. that an attempt should be made to produce a practical commercial test for assessing the tremolite content of chrysotile. The possibility of producing such a test method was already being explored by Doctor Hodgson in conjunction with the Institute of Occupational Medicine at Edinburgh. Some research funding was being made available by the A.R.C. but this research seems to be of great importance to the asbestos industry, particularly the mining industry and it was felt that the A.I.A. should be urged to participate. He also said that some manufacturing Companies were already beginning to frame a policy of restricting imports of chrysotile to those areas where the tremolite content was known to be minnimal. It was felt that the International Asbestos Industry should be made aware of this development.

Doctor Hodgson had prepared a valuable paper for the meeting, outlining what was known about tremolite as a contaminant of chrysotile and discussing possible schemes for both identification and the separation of tremolite from chrysotile. He pointed out that a wide range of samples of fibre would be required for research on this subject. He mentioned one or two possible sources, one of which was Central Asbestos and undertook to look into the possibility of obtaining fibre from this source. But it was emphasised that collaboration from the mining industry members of the A.I.A. would be very helpful. He and Doctor Elmes gave details of main problems associated with the assessment of the tremolite content and of the health problems associated with it. The Vanderbilt talc mine was quoted. Apparently this contained up to 50% of tremolite but much of it in a massive and splintered form. In Zimbabwe many serpentines were incorrectly labelled tremolite. Chrysotile in the Gobi Desert was said to contain up to 17% of tremolite.

In conclusion, Sir Neville Stack undertook to report the substance of the meeting to the relevant Committees of the A.I.A.



A01301

(J)

Top 5/56

[redacted]

TREMOLITE IN CHRYSOTILE

A. A. HODGSON

It is established that tremolite fibre has high ranking as a carcinogen, and its biological effects are strongly suspected in its association with chrysotile, vermiculite and talc, in some but not all occurrences. Tremolite is not now mined on a commercial scale, the largest producer in Korea having closed some years ago. Exploitable deposits occur in Pakistan, and in northern Italy where a valuable long fibre tremolite is believed to be extracted from time to time.

Presence of tremolite in chrysotile There is growing concern about the tremolite content of chrysotiles in commercial use, but as far as is known studies have never been made to establish the presence of tremolite in chrysotile on a quantitative basis. It is the purpose of these notes to outline the properties and other relevant information concerning both of these fibres, in order to assist towards a quantitative scheme for separating and identifying the tremolite.

The presence of tremolite in chrysotile should be regarded as ubiquitous, even to very small quantities, because the paragenesis of these minerals, which applies also to vermiculite and talc, leads to such a conclusion, as explained later. The ubiquity of tremolite is not upheld by such qualitative researches as have been made on the minerals associated with chrysotile. Butler 1960[1] found tremolite in only 8 out of 128 samples of various chrysotiles, and Gosseye and Hahn-Weinheimer 1971[2] found tremolite in 1 out of 58 samples, that particular one not having been detected by Butler. Both these investigations were made by X-ray diffraction (XRD).

Reasons for the sparse location of tremolite in these samples appear to be two-fold. Although tremolite may be widespread in chrysotiles and serpentinite rocks, it is unlikely to be distributed uniformly. The very small samples taken for XRD could well be unrepresentative, and the chance that any one sample contains tremolite in detectable amounts may be less than one in three. Secondly, and more importantly, the direct analysis of such samples by XRD is hampered by detection limits for tremolite of about 1 %[3]. Fractions of tremolite less than this would be completely unobserved.

Any method for the quantitative analysis of tremolite in chrysotile must therefore have as its first stage a means of concentrating the tremolite, to lift its content in any residues well above the detection limits of XRD and other techniques, and if possible to concentrate it towards 100 %.

A01302

Relation to TLVs The following table sets out the concentration of tremolite in terms of f/ml, which will apply at various levels of TLV for chrysotile and at various assumed tremolite contents.

Possible tremolite content of chrysotile %	at TLV for chrysotile of 2 f/ml	1 f/ml	0.5 f/ml
	tremolite count, f/ml, is:		
1	0.02	0.01	0.005
2	0.04	0.02	0.01
5	0.10	0.05	0.025
10	0.20	0.10	0.05

For the most part the tremolite count is negligable and is below current TLVs for crocidolite. However tremolite is the most intransigent of all asbestos fibres and this distinction is a matter of biological significance in relation to chrysotile. Chrysotile fibre inhaled into the lungs can be partially cleared by a dissolution process, leaving any associated tremolite to become concentrated in lung tissue. Thus, while at the same time natural lung clearance takes place presumably at the same rate for both types of fibre, the relative proportions of tremolite and chrysotile will change, and the effective count of tremolite at lung burden level will progressively increase by several, if not many, times the figures calculated above.

Geology and mineralogy Serpentines and ultimately chrysotiles are products of the thermal metamorphism of both ultrabasic rocks with high magnesium contents, and siliceous dolomites containing magnesium and calcium. Tremolite is an early product of the metamorphism of dolomites (hence tremolitic marbles), but equally it is an accessory mineral along with talc, brucite, magnetite and etc. in the serpentinization of ultrabasic rocks. The latter are usually low in calcium content and consequently the generation of tremolite, of which calcium is an essential part, is limited. On the other hand the dolomites have high calcium contents, and ultimate serpentinization may be expected to yield proportionately high amounts of tremolite.

There is a broad belt of serpentinized ultrabasic rocks in the Northern Hemisphere stretching from Canada to Russia and Siberia. The serpentines of Zimbabwe have a similar origin. Serpentinized dolomites are characteristic of the Mediterranean area, and also of the northern and eastern Transvaal in South Africa. Chrysotile deposits, large and small, are

A01303

located in all these geographical areas, and it follows that these deposits might be expected to contain greater or lesser proportions of tremolite, depending on their regional siting.

Mining and milling Any chrysotile deposit can be expected to contain some tremolite. Apart from its random distribution throughout the deposit, tremolite may occur in pockets, fairly easy to distinguish and hence avoided in mining operations, since it would be considered to degrade the quality of the end product. The more general distribution of tremolite throughout a chrysotile deposit cannot be avoided, and any large scale separation of small amounts of tremolite from chrysotile fibre is hardly practical or even possible in the initial stages of extraction.
However asbestos milling and grading processes must to some degree bring about a differentiation between the two types of fibre. The grading of asbestos fibre is essentially a serial screening and air-lifting process, with longer fibres being lifted first and shorter fibres passing each screen to the next stage. Tremolite has a distinctly higher density than that of chrysotile, and it follows that tremolite fibres have a lesser chance of being air-lifted than have chrysotile fibres, and similarly a greater chance of being screened out. Hence there should be some concentration of tremolite in shorter grades of chrysotile, and of course in tailings.

Chemistry Tremolite and chrysotile are highly distinguishable from each other in terms of chemical and thermal properties. Tremolite is the most acid resistant of all asbestos fibres, while chrysotile possesses complete lack of acid resistance, and indeed can be leached by water. Much of the chemistry concerning the acid resistance of asbestos fibres is well known[4], and it is only necessary here to summarize those aspects which may be of help in formulating a scheme towards a quantitative analysis for tremolite in chrysotile.
The relative acid resistance curves for asbestos fibres refluxed in 4N HCl show that chrysotile decomposes with a 58 % weight loss in ½ hr., while tremolite has a 4 % weight loss under the same conditions. All the MgO and H_2O contents of chrysotile are removed leaving a siliceous residue. The tubular morphology of the chrysotile remains, but the residue is amorphous to X-ray and EM beams. Tremolite may lose up to 22 % of its Ca^{2+} content, these ions being picked off at the ends of cation chains. The loss of other ions is negligable.
These are drastic conditions, and it is possible to reduce the concentration of acid without any effect on the decomposition of the chrysotile, but with

a reduction in the removal of Ca^{2+} from tremolite. Rates of reaction are proportionately decreased with reduction in acid strength, although there is little difference in reaction rates in changing from 1N to 0.1N HCl. This may be an important factor in setting up a scheme to extract chrysotile if many samples are to be involved, but at the same time low acid concentrations will have minimal effect on the decomposition of tremolite. The kinetics of the acid decomposition of chrysotile have been reported in detail by Atkinson and Rickards 1971[5] and by Monkman 1971[6]. In these investigations the chrysotile was ground to a high surface area, which to some extent may be a disadvantage when attempting to preserve the integrity of any tremolite which may be present.

The rate of reaction of H_2SO_4 on chrysotile is slightly greater than that of HCl of the same normality. In this context the choice of H_2SO_4 may be the better one, because the effect of the SO_4^{2-} ion may be to suppress the removal of Ca^{2+} from tremolite, $CaSO_4$ being insoluble.

Chrysotile is vulnerable to alternating acid and alkaline conditions[7]. The reaction of acid removes Mg^{2+} but leaves a layer of orthosilicic acid which effectively controls the rate of diffusion of the reaction acid into the inner layers of the chrysotile. The orthosilicic acid can however be removed in a consecutive reaction with NaOH to give sodium silicate in solution. After each consecutive stage in a series of such extractions the residues require to be washed to remove soluble magnesium salts and sodium silicate. In suitable conditions of acid concentration this may be a way of completely removing chrysotile with negligable effect on tremolite residues. Tremolite will not in any way react to alkaline solutions.

Talc is a frequent accessory mineral in chrysotile and its presence may interfere with the final determination of tremolite contents. Talc is insoluble in acids and therefore will accumulate in extraction residues. If the talc content is high and the tremolite content is low, the former may obscure the latter in the final analysis.

One refinement to the extraction method which might be considered involves the heating of the sample specimen. Chrysotile dehydroxylates and forms a highly disorganised forsterite at about 600°C; talc begins to dehydroxylate at about 700°C; and tremolite remains stable up to about 950°C (a higher temperature than any other type of asbestos). The advantage of pre-heating chrysotile to 600°C lies in its extreme vulnerability to acid decomposition, since there is little residual crystal structure left at this temperature.

Further, regarding the presence of talc, this mineral can be assessed quantitatively byIR analysis, and it has been reported that the IR spectra of many of the minerals associated with chrysotile are rendered less complex by pre-heating them to certain temperatures[8].

Other possible extraction techniques The density of tremolite is 2.9 to 3.2, that of chrysotile 2.55. It is therefore experimentally possible to differentiate between the two minerals by heavy liquid separation, using a medium of suitable intermediate specific gravity. It would be usual to apply this technique to relatively small samples and to make a final separation of the heavier mineral by centrifuge. Complete separation of tremolite from chrysotile might be difficult because of the entanglement of one type of fibre with the other. Again talc may interfere, and samples containing talc may require a secondary heavy liquid separation. The density of talc is 2.65 to 2.9, indicating a slight overlap here between the densities of talc and tremolite. However, the method may be useful as a preliminary assay of samples, to determine approximate tremolite contents.

Following similar lines, it should be possible to obtain a separation of the two minerals, chrysotile and tremolite, by a bench scale flotation process. It is relevant to note in this connection that Cyprus Industrial Minerals Corp. in USA have used a flotation process for the beneficiation of New York state talcs, which are notorious for their high tremolite contents[9]. Anionic surfactants will disperse chrysotile fibres and will also effect a partial, spontaneous, fibrillation of the asbestos. In principle this should lead to the release of tremolite, and permit the separation of both chrysotile and talc by a flotation method. The application of anionic surfactants to chrysotile is an essential step in the wet dispersion process for making chrysotile yarns, as outlined by Gettins and Mallon 1971[10], Heron and Huggett 1971[11] (all four authors associated with TBA), and Otouma and Take 1975[12]. For the purpose of this present exercise it will be useful to approach TBA to ascertain whether there is any feasibility in applying wet dispersion and flotation techniques to the separation of tremolite from chrysotile.

Identification of tremolite by UV light The Cyprus Ind. Min. Corp. patent[9], referred to above, cites an optical sorting method in which talc ore containing tremolite is sorted under UV radiation of wavelength 250 to 340 nm, in which the talc fluoresces white and the tremolite fluoresces orange or red. The principle might be applied to chrysotile/tremolite mixes to give a preliminary indication of high or low levels of tremolite content.

A01306

Outline schemes for separating tremolite from chrysotile

On face value, a chemical separation scheme appears to be absolute, but if many samples are to be investigated it will be tedious and time consuming, unless an automated means of extraction of the chrysotile can be devised. Choice of sample sizes will be important, due to the uneven distribution and variable content of tremolite in chrysotiles from different sources. A preliminary assay of samples by heavy liquid separation or by UV screening (if practical) may be necessary.

The following steps are foreseen in setting up an analytical procedure.

1. Confirm experimentally that chrysotile fibre can be fully decomposed into soluble products, by using alternating acid and alkaline conditions, and by selecting an optimum reaction regime as indicated in the literature. Assess the decomposition of pure tremolite under the same conditions.
2. Determine what advantages lie in pre-milling or pre-heating the samples.
3. Investigate a procedure for the preliminary assay of samples by heavy liquid separation or by UV screening.
4. Draw up plans for an automated bench rig to decompose the chrysotile and leave a residue of tremolite.
5. Prepare an order of sample sizes (1 to 10 gm ?) according to likely tremolite content, and according to choice of final quantitative assessment.
6. Investigate the interference due to other insoluble minerals, particularly talc, in the final assessment of residues.
7. Consider the choice of one or more methods for the final analysis of residues:-

   XRD for positive identification of tremolite from all samples;
   IR for quantitative assessment of talc in the presence of tremolite;
   gravimetric evaluation of large residues;
   EDXA (Ca content) for the evaluation of tremolite in small residues.

Two further approaches should be considered:

(a) If chrysotile samples contain considerably more than 1 % tremolite, it should be possible to analyse them directly by XRD/EDXA, particularly if a set of calibrated mixes has been prepared and examined beforehand. To obtain a statistically acceptable result it would be necessary to assess a number of aliquots of the unknown.

(b) The feasibility of a flotation technique for separating tremolite and chrysotile should be examined as a separate issue. A flotation method would replace chemical separation, and could probably be the means of separating off any interfering talc along with the chrysotile. The T&N

elutriation method, as used in the testing of asbestos fibres, could probably be adapted without difficulty to the partition of chrysotile and talc from tremolite, after preparation of the samples with suitable surfactants.

References

1. M. A. Butler. The physical and chemical characteristics of serpentine rocks and minerals. PhD thesis. University College, Cardiff, 1980.
2. A. Gosseye, P. Hahn-Weinheimer. A comparative study of asbestos minerals. 2nd International Asbestos Conference, Louvain, 1971.
3. E.J.W. Whittaker (Oxford University). Advisory communication to Cape Asbestos Fibres Ltd., 1978.
4. A. A. Hodgson. Fibrous Silicates. Royal Institute of Chemistry, 1965.
5. A. W. Atkinson, A. L. Rickards. Acid decomposition of highly opened chrysotiles. 2nd International Asbestos Conference, Louvain, 1971.
6. L. J. Monkman. Some aspects of the reaction of chrysotile with inorganic and organic acids. 2nd International Asbestos Conference, Louvain, 1971.
7. P. F. Holt, S. G. Clark. Nature, Lond., 1960, 185, p. 237.
8. E. Martinez, R. B. Haagensen, H. L. Lovell. Investigation of the quantitative determination of minerals in serpentine and asbestos samples by infra-red spectroscopy and thermo-analysis. 1st International Asbestos Conference, Oxford, 1967.
9. US Patent 3837582. Beneficiation of New York State talc. Cyprus Mines Corp., 1974. (now Cyprus Industrial Minerals Corp.)
10. R. B. Gettins, F. J. Mallon. Adsorption of surface active agents on chrysotile asbestos. 2nd International Asbestos Conference, Louvain, 1971.
11. G. F. Heron, R. Huggett. Dispersion based textiles. 2nd International Asbestos Conference, Louvain, 1971.
12. T. Otouma, S. Take. Effect of anionic surface active agents on chrysotile. 3rd International Asbestos Conference, Quebec, 1975.

Proceedings of the International Asbestos Conferences are not readily available, and the authors referenced above did not necessarily publish elsewhere. Copies of the relevant papers can be obtained from AAH if so desired.

A. A. H.
30.10.1984.

Copies: Chairman, ARC Research Committee 3
Institute of Occupational Medicine 2

A01308