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Harpur Hill, Buxton
Derbyshire, SK17 9JN
T: +44 (0)1298 218000
F: +44 (0)1298 218590
W: www.hsl.gov.uk

HEALTH & SAFETY LABORATORY

Investigation of the chrysotile fibres in an asbestos cement sample

HSL/2007/11

Project Leader: **G.Burdett**

Author(s): **G Burdett,**

Science Group: **Science Group 5**

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EXECUTIVE SUMMARY

Objectives

To investigate whether claims of a physical and chemical change to chrysotile fibres in a cement matrix (A/C), are valid and merit further investigation.

Main Findings

As would be expected in a sample of asbestos cement most of the chrysotile fibres were encapsulated in the cement matrix, often as quite large fibre bundles which are clearly visible to the eye.

When the cement is broken or crushed the chrysotile fibres are released from the cement. The fibres released were examined by analytical transmission electron microscopy (TEM) to determine whether they had been altered and were no longer identifiable as chrysotile asbestos.

The fibres found in both the bulk and air samples had the characteristic morphology and appearance of chrysotile asbestos. The very fine fibres (fibrils), when viewed at higher magnification, showed the characteristic tubular structure associated with chrysotile fibrils and showed no evidence of surface alteration.

Individual fibres analysed by energy dispersive X-ray (EDX) analysis showed chemistry similar to a reference standard of chrysotile and for published compositions for chrysotile from various mines around the world (when adjusted for water content).

Different sections of the same fibres, also gave the characteristic selective area electron diffraction patterns associated with the chrysotile structure. Three electron diffraction patterns were indexed and gave a close match to the published d-spacings for chrysotile. This demonstrated conclusively that there was no structural alteration of the atomic lattice of the chrysotile asbestos.

The analysis carried out showed that the asbestos cement contained fibres of chrysotile asbestos and released chrysotile asbestos fibres to air when sufficiently disturbed.

Many small particles of the cement matrix were present in the bulk preparations; some of these small particles would be close to or attached to the chrysotile fibres. These particles were calcium rich and added calcium to the spectra depending on how close they were to the electron beam / probe.

Only a small percentage of the fibres released from the cement could be described as being coated or altered and it may be more accurate to consider them as still encapsulated in the cement matrix.

There is no evidence from this examination to support claims that all the chrysotile asbestos in asbestos cement is significantly altered so that fibres present or released should no longer be considered to be chrysotile.

Claims being made in Internet articles and in some sections of the newspaper industry are not supported by this investigation.

Epidemiology has shown that chrysotile is a human carcinogen. Animal experiments have shown no evidence that the chrysotile asbestos extracted from the weathered surface of A/C products is less carcinogenic than UICC standard chrysotile asbestos.

Recommendations

The lack of evidence for any significant changes to chrysotile fibres recovered from the cement matrix and released to air in the samples analysed for this report, argues against the need for any further consideration of the regulatory position of asbestos cement.

If there is any scientific data which could lead someone to believe that a new mineral has been formed, the appropriate procedure is to present the data for a review to the International Mineralogical Association.

It must be borne in mind that asbestos cement may also contain crocidolite and amosite asbestos as well as chrysotile and these types of asbestos are also category 1 carcinogens and are considered by HSE to pose a greater risk to health than chrysotile asbestos. No claims have been made that these other types of asbestos are altered.

Well-controlled secondary work with asbestos cement generally results in low airborne exposures to workers but some further sampling of typical work on friable weathered surfaces of asbestos cement should be considered, to see if exposures are increasing due to increased time of weathering.

1 INTRODUCTION

Claims have been made in correspondence to HSE and in various media outlets (Bridle and Stone, 2006), that the chrysotile asbestos in asbestos cement products is altered, by an unexplained process, into a non-asbestos fibrous material. The claims being made suggest that this process is 100% efficient and no chrysotile asbestos remains in the matrix and also no "actionable release" of airborne asbestos fibres can occur. The outcome of these claims would be to show that, " if white asbestos cement products are seen as no longer containing the chemical which has been banned, this should eventually exempt such products from many regulations". There is also the underlying assumption that the, " fibres have been rendered safe by the attendant chemical process".

These observation are reported to be based partly on changes to the appearance of some of the fibres recovered from the matrix of the cement when viewed at high magnifications in a transmission electron microscope (TEM) and changes to the fibre chemistry as detected using energy dispersive x-ray analysis (EDXA) attached to the TEM (unpublished report by Pooley, F.D., 2004). More specifically the claim made was; "The conclusions which emerged from Professor Pooley's report were unequivocal. They confirmed that mixing with cement induces chemical and structural change to the chrysotile fibres. Increased levels of calcium and silicon and an increased tendency to aggregate leaves the fibre definitively altered."

The aim of the work in this report was to investigate whether the claims that have been made are readily and uniformly observed and merit further investigation. Alternatively, if they occur only partially or are artefacts of the sampling and analytical procedures used, can they be discounted as a significant effect. The examination was carried out using similar methods to those that were been used to claim that changes to the chrysotile asbestos had occurred. Some additional electron diffraction analysis has also been carried out.

The issue appears to be similar to previous claims (e.g. Deruyterre et al., 1980) that asbestos cement converted the chrysotile to a less hazardous material, which behaves more like a cement dust than an asbestos dust because small individual particles of cement were attached to the surface of the fibres.

2 DESCRIPTION OF ASBESTOS CEMENT

2.1 Component materials

Asbestos cement is usually a mixture of about 10% asbestos and 90% Portland cement. The types of asbestos used may vary, chrysotile is normally always present but crocidolite and amosite (asbestos grunerite) were also added to many products. Some sources of chrysotile asbestos also contain small amounts of tremolite asbestos but this is unlikely to be detected during routine examination. The product's performance requires that the cement matrix adheres to the outside of the fibres and fibre bundles so that the high tensile strength of the fibres is used to create a stronger product, than if just cement alone was used. The asbestos is added to the cement and wet mixed before being formed, compressed and cured to produce the end product. The addition of crocidolite and amosite was also used to help dewater the product quicker (e.g. increase production rate) and / or to allow greater compression to produce a product of greater strength (e.g. pressure pipes).

Portland cement is a complex mixture of calcium silicates and aluminates that is made by heating a mixture of clay and limestone to about 1,500 °C in a kiln. The mixture is then cooled, pulverized, and gypsum ($CaSO_4 .2H_2O$) is added. When the powder is mixed with water, complex reactions take place and the cement sets to a solid, consisting of many small particles. After adding gypsum, the final cement reaction in the kiln is a mixture of 50% tricalcium silicate (Ca_3SiO_5), 25% dicalcium silicate (Ca_2SiO_4), 10% tricalcium aluminate ($Ca_3Al_2O_6$), 10% tetracalciumaluminoferrate ($Ca_4Al_2Fe_2O_{10}$), and 5% gypsum ($CaSO_4.2H_2O$). When water is added, the components of cement undergo a chemical reaction known as hydration. As this occurs, the silicates are transformed into silicate hydrates and calcium hydroxide ($Ca(OH)_2$), and the cement slowly forms a hardened paste. This process is complex and not complete, so a range of cement particles of different compositions will occur. A typical cement matrix in asbestos cement products consists of: $Ca(OH)_2$ calcium hydroxide (10 – 12 %), calcium silicate hydrates (60 – 80%), calcium aluminate hydrates (3 – 10%), calcium aluminate sulphate hydrates (0 – 5%) and unreacted cement.

Most occurrences of chrysotile (white) asbestos form when rocks from deep in the earths crust and upper mantle undergo recrystallisation under circumstances where there is relatively high pressure and low temperature and a relative abundance of water. This process is known as serpentisation and occurs over a geological timescale of millions of years. The asbestos forms in veins usually only a few centimetres wide and while it has a similar chemistry to the surrounding rock, it differs due to the fibrous habit of the particles formed. Particles which show similar degrees of growth on all the crystal axis are called equant (e.g. grains of salt) but the asbestos is an example of a particle formed from unequal growth along one crystal axis, to form an elongated particle (fibre). Asbestos fibres are regarded as being at the extreme end of particle shape continuum and this is sometimes referred to as the asbestiform habit. The individual fibres (known as fibrils) may be up to several centimetres in length but the fibril width is around 0.03 μm (about one million times less). These thin individual fibrils often form larger fibres and bundles of longitudinally aligned fibres,

sometimes consisting of many thousands of fibrils. The fibres and fibre bundles can divide longitudinally to release thinner fibres and fibrils.

Chrysotile is a recognised mineral type by the International Minerals Association (IMA) and its (almost unique) structure has been widely described in many textbooks. The basic structure is a sheet silicate, formed from a layer of silica tetrahedra and magnesium hydroxide. The packing arrangement has caused a structural deformity that causes the sheet to roll up to form a scroll structure, for each individual fibril. This structure produces a characteristic electron diffraction pattern, which (again, almost uniquely) will not change with the orientation of the fibre. For any significant change to the chemistry to take place throughout the fibre (e.g. the replacement of magnesium with calcium, as suggested by Pooley, 2004) it would be impossible for the characteristic scroll structure to remain intact or the crystal lattice spacings to remain unchanged.

Chrysotile does not have a unique chemistry. Two other sheet silicate serpentine minerals have identical chemistry (antigorite and lizardite) but due to differences in their crystallisation conditions and minor differences in the packing at the atomic level, do not form rolled up scrolls like chrysotile and give a different electron diffraction pattern. Other serpentine minerals have the same elements present as does chrysotile but the oxide weight percentages are significantly different (and also the electron diffraction patterns).

Amosite and crocidolite asbestos have different geological origins to chrysotile and a different structure and chemistry but also occur as fibre bundles and display an asbestiform habit. Like chrysotile only the asbestos forms of the minerals are listed as a human carcinogens by a number of international and national agencies.

2.2 Typical appearance of AC

Asbestos cement sheet can be flat or corrugated (profiled), is usually a light grey colour and about 6 mm thick or greater. Dust reducing coating were applied to the surface of some asbestos cement sheet products to reduce fibre release when handling new sheet materials, which would be slid over each other when stacked. Asbestos cement roofing slates were made from smaller flat sheets that were often both coated and coloured. Many other moulded products were made; e.g. guttering, down pipes, flues, vents, tiles, pressure pipes etc. (see MDHS 100).

As the cement, contains approximately 10 – 13% of asbestos by weight, the larger asbestos bundles are usually readily visible by eye especially at newly fractured edges. A typical example of a chrysotile bundle present in a sample of asbestos cement is given in figure 1a. Although the matrix material will 'cement' particles together, the bundles of chrysotile fibre contain many fibres and fibrils, which are not in direct contact with the cement matrix. Cement by its nature is a relatively hard and resistant material but the asbestos is added to further strengthen and reinforce it .

Also, the relatively short time for the cement to hydrate and cure would limit the ability for chemical changes and substitution to take place in any fibre that was in direct contact with the cement.

In many ways the cement surrounding and encapsulating the fibre will act as a protection for much of the asbestos fibres from the effects of weathering.

2.3 Effect of weathering on the surface fibres

Primarily, the weathering of an asbestos cement sheet is based on its major component (90% cement) and the more resistant asbestos is left increasingly free of the cement matrix. Therefore weathered asbestos cement often has the potential to release more fibres from the surface than unweathered asbestos cement because there are much greater numbers of loosely bound fibres exposed on the surface. In more extreme cases, weathering may cause the surface to flake or crack, giving a greater area from which asbestos may be released into the air.

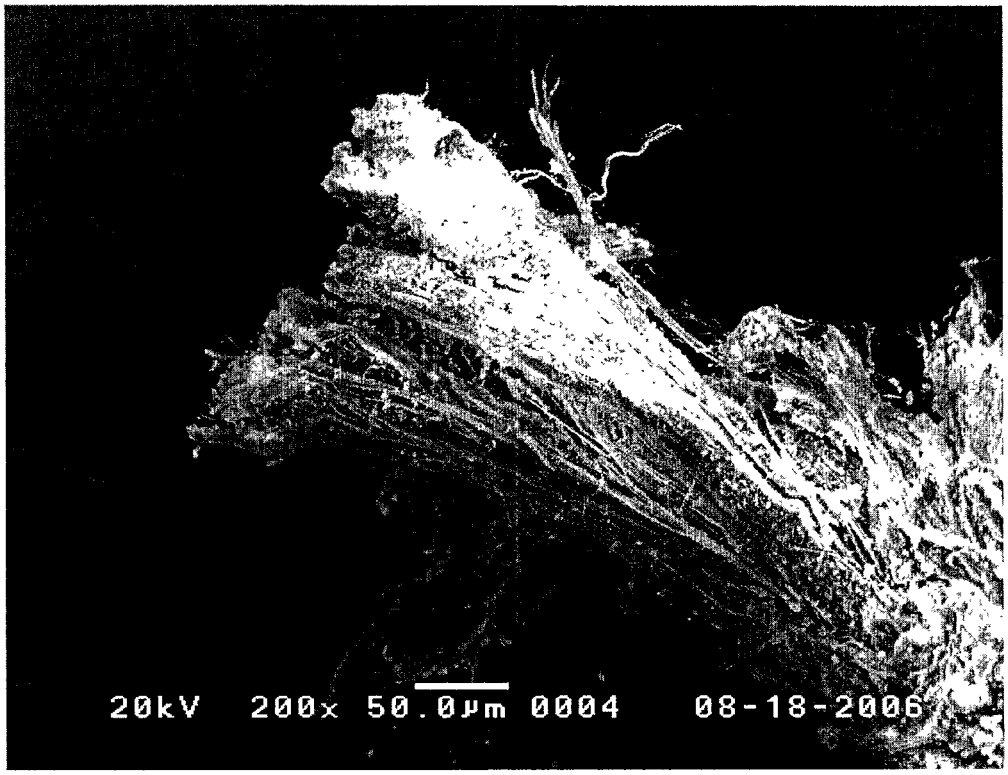


Figure 1a: Chrysotile fibre bundle projecting from a broken segment of the asbestos cement sample (scanning electron microscopy image at x200). Fine cement particles and larger pieces of matrix material can also be seen.

All materials are subject to weathering when exposed to the atmosphere and moisture. A range of processes takes place; as the surface is exposed to electromagnetic waves, moisture, frost fracture, chemicals, gases and biological organisms. Chrysotile is known to have limited resistance to acid attack and both acid rain (sulphuric acid) and organic acids from moulds, mosses and lichen (Favero-Longo et al., 2005) will react with the exposed chrysotile asbestos to progressively remove magnesium hydroxide from the structure (Hodgson, 1979). The fibrous surface of weathered cement also acts as a very good trap for molecules, enabling chemical reactions to take place. Analysis of the surface fibres on asbestos cement sheets show that a wide array of polycyclic aromatic hydrocarbons were present and these materials may even increase the potential carcinogenicity of the fibres (Spurny, 1989). The other types of asbestos are more acid resistant.

Cement is also subject to weathering and a number of chemical reactions will occur. The most water-soluble component of cement is calcium hydroxide and this is dissolved and washed out by water. However, the calcium hydroxide also reacts with carbon dioxide to form less soluble calcium carbonate, but further reactions result in calcium carbonate being turned into more soluble calcium bicarbonate.

Increasing acidity, and the presence of sulphate and carbonate ions will increase the solubility and removal of all the chemical components of cement from the exposed surface layer. The duration of exposure and the acidity of the environment will largely determine the rate of dissolution and wash out of the surface cement matrix, leaving asbestos fibres only loosely attached to the surface and more able to become airborne. Sulphur dioxide emissions from fossil fuel burning are responsible for most acid rain and the sulphate and sulphite compounds formed by chemical reactions with the cement (e.g. calcium sulphate) take up a larger volume than the original components, leads to further disruption of the cement surface and increases the rate of removal of the cement surface layer. The rate of corrosion of the surface of asbestos cement has been estimated at 0.024 mm/year (Spurny, 1989) in cleaner environments and about 1 mm/year in urban environments where higher acidity is expected (Bornemann and Hildebrand, 1986).

Other environments, may also change the chemistry and rate of weathering of the cement. An abundance of chloride ion (e.g. near to the sea) or the material being continuously wet (e.g. in cooling towers of power stations, Sakara et al., 1987) has been reported to result in increased weathering of cement. Mosses, lichen and other flora can readily grow on the surface of asbestos cement and these primarily cover the surface and prevent airborne release. However, these often produce an acidic environment and will retain moisture and over the long term and may increase the weathering of the surface layer and the chrysotile (Dyczek, 2006).

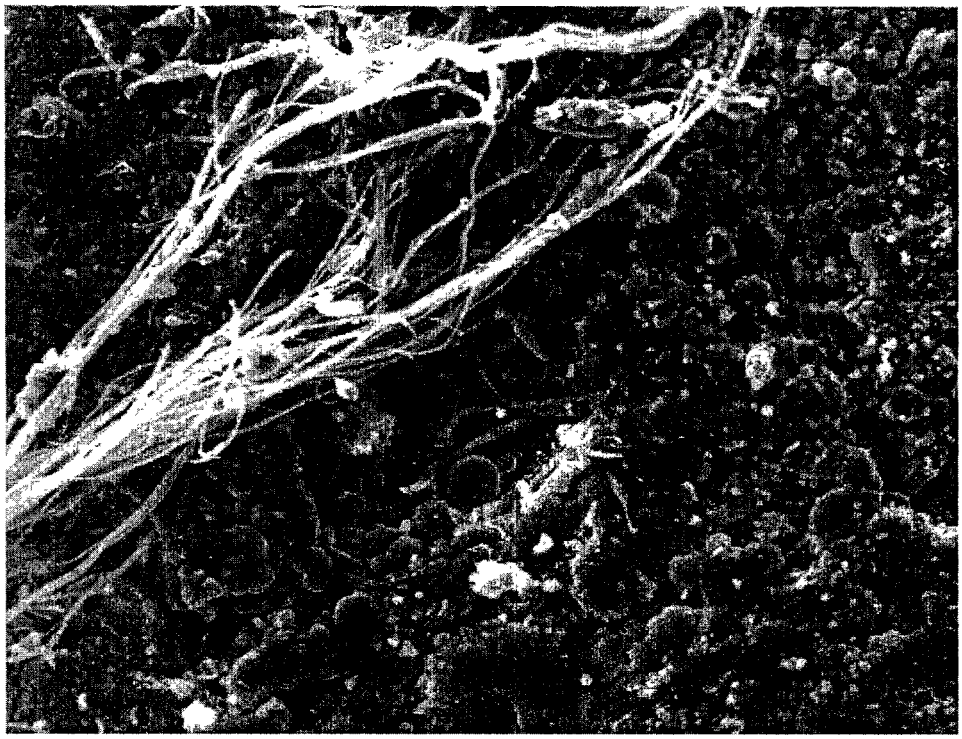


Figure 1b: Chrysotile fibre bundle exposed on the surface of a weathered cement sheet (scanning electron microscopy image at approx X600, picture courtesy of J. Dyczek). Fine cement particles are visible underneath.

2.4 Effects of mechanical breakage

Any physical breaking and cracking of asbestos cement material exerts high mechanical forces to the fracture surface and tends to pull out asbestos fibres and bundles, thus making them more able to become airborne. Fires and very high temperatures causes the hydrated cement to release water vapour and the cement sheet to expand internally, leading to explosive failure where the sheet will crack and spall extensively, leaving areas of pulled-out fibres. A proportion of the fibres disturbed during mechanical breakage will be made airborne at the time. Mechanical attrition of the cement will also lead to release of airborne asbestos fibres and cutting of the cement sheets with saws and angle grinders are particularly able to release fibres from inside the AC. Similarly, mechanical cleaning of dry surfaces of asbestos cement sheets are also known to release substantial numbers of airborne asbestos fibres.

3 EXAMINATION OF ASBESTOS CEMENT: SAMPLE SOURCE AND PREPARATION

A well-characterised sample of asbestos cement sheet (AIMS Round 28 Sample 2, Validation 117) was analysed for this report. Other samples of asbestos cement have previously been analysed with similar results.

The sample was broken with a hammer and small particles and fibres bundles were picked out and suspended in ultra pure water in a sealable bottle. The contents were both shaken and subject to low powered ultrasonic treatment for about 1 minute to disperse the fibres. A single drop was then pipetted onto a carbon film supported on an EM grid and allowed to dry. The prepared grids were examined in a FEI CM12 scanning transmission electron microscope (TEM) fitted with an EDAX DX Prime energy dispersive analysis system. In addition, selective area electron diffraction (SAED) was carried out to examine the structure of the fibres and in some cases to index the diffraction pattern from the fibre. Polarised light microscopy analysis with dispersion staining was also used to identify the fibres present. HSL has accreditation under ISO 17025 for all the analyses carried out (United Kingdom Accreditation Service (UKAS)).

During the breaking up of the sample, an air sample was also collected in the close vicinity, as the piece of asbestos cement was struck 3 or 4 times with a small hammer. A 0.4 μm pore size polycarbonate filter in a conductive-cowled holder was used to collect the airborne particles released. The filter was prepared for TEM analysis using the procedure in international standard method ISO 10312:95.

Fibres, from a sample of the reference chrysotile asbestos (UICC A) were also prepared by suspending them in water and forming drop mounts as described above.

A different sample of asbestos cement was later prepared using acetone instead of water to investigate assertions that the coatings on fibres were dissolved during the time that the fibres were in water.

4 ANALYSIS

4.1 TEM analysis

The procedures which were followed to make the observations and identification of the chrysotile fibres are set out in the international standard methods ISO10312:95 and ISO 13794:99.

These standards describe an identification procedure that uses a number of observations to unambiguously identify the type of asbestos present. For asbestos this includes:

1. Morphology (shape of the crystals)
2. High magnification structure of the individual fibres (fibrils)
3. Energy dispersive x-ray analysis (EDXA) of the fibre chemistry by comparison to a standard.
4. Examination of the characteristic selective area electron diffraction pattern.
5. Measurement of the atomic spacing of the crystal lattice.

In nearly all situations, compliance with 1,2 & 3 or 1,2 & 4 would be regarded as giving an unambiguous identification of chrysotile asbestos.

4.2 PLM analysis

The method used for polarised light microscopy (PLM) analysis of asbestos was published by HSE in its methods for determining hazardous substances series (MDHS 77) and subsequently as Annex 2 in HSG 248. The material is first observed under low powered stereo microscopy to look for fibres and fibre bundles and if seen, representative fibres are picked out and mounted in a suitable refractive index oil, to observe a range of optical properties and the dispersion colours (and hence measure the refractive index of the fibre).

5 RESULTS OF THE TEM ANALYSIS OF THE BULK SAMPLE

5.1 Fibre morphology and structure

The appearances of the fibres from the asbestos cement are shown in figures 2 a-e at various magnifications. Although particles were sometimes either overlying or attached to the fibres hardly any fibres were seen to have any surface changes or any indication of a surface coating.

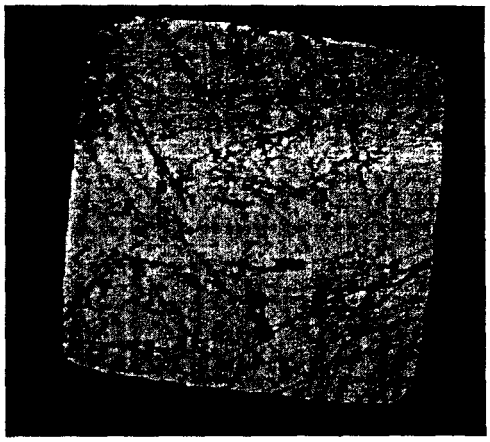


Figure 2a: Cement particles and chrysotile asbestos fibres extracted from sample at low magnification. The fibres show the characteristic long thin fibres and fibre bundles associated with a typical asbestos morphology.

0 50 μm

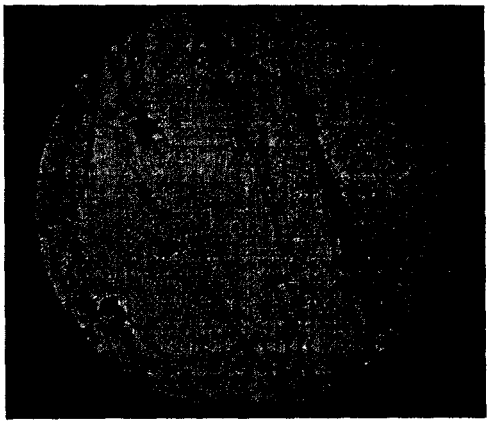


Figure 2b: A number of small cement particles can be seen to be attached to the chrysotile fibres.

0 20 μm

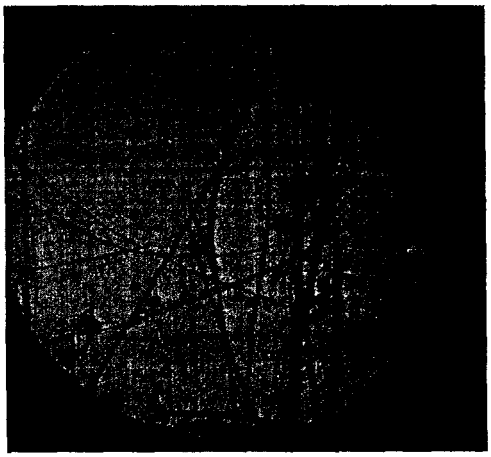


Figure 2c: Part of the same field of view as figure 1Aand 1B.

0 5 μm

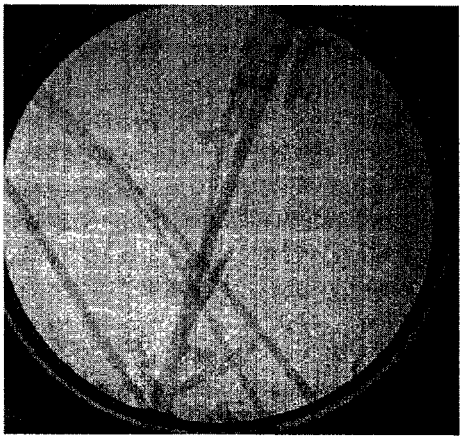


Figure 2d: Fibres at high magnification showing no evidence of coating or many attached particles.

0 0.5 μm

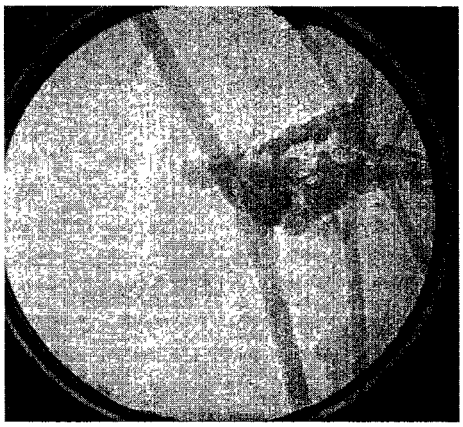


Fig 2e: Example of particle attached to chrysotile fibres. An example of the characteristic tubular structure of chrysotile can be seen. Any significant change to the chemistry is likely to be reflected by the tubular structure being broken down.

0 0.5 μm

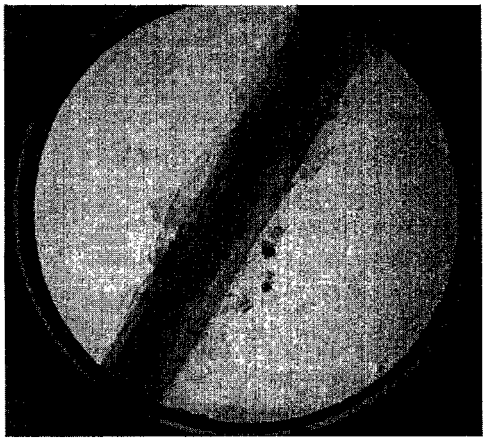


Figure 3: Example of an anthophylite fibre from a cement matrix, which appears to be coated with a calcium and aluminium material and small particles.

0 0.5 μm

Although coated asbestos fibres can be present in asbestos cement, it was not easy to find one in the sample prepared and an example from another asbestos cement sample (see figure 3) shows that a low electron density coating is visible along some of the fibre along with some discreet particles. However, this still appears to be particles and material attached to the external surface of the fibre, the fibre outline is still easily distinguishable and there is no evidence of any surface reaction between the fibre and the cement. The sample in figure 3 was shown to have increased amounts of aluminium and calcium when analysed by EDXA.

5.2 Energy dispersive X ray analysis results

EDXA procedures work by focussing the electrons into a small area (or probe) on a small area of the fibre. Ideally the electrons in the beam react only with the material targeted in the probe to give rise to x-ray emissions. Some of the x-ray emissions are due to the disruption of the electrons in the atomic shells of an atom, which produce a quantum of x-ray energy that is characteristic of the element and the electron transitions taking place. The EDXA technique collects and measures the energy of x-rays produced and displays a graph of x- ray energy (in KeV) along the bottom axis versus frequency of occurrence. An EDXA spectrum will usually show a number of characteristic x-ray peaks, associated with the elements present. A typical spectrum from the chrysotile fibres in the sample of asbestos cement tested is shown in figure 4. Using standards to calibrate the detector it is possible to carry out a quantitative analysis, expressed in terms of the oxide weight % for each element giving a peak above the background of continuous x-rays that also reach the detector; this is listed in figure 4.

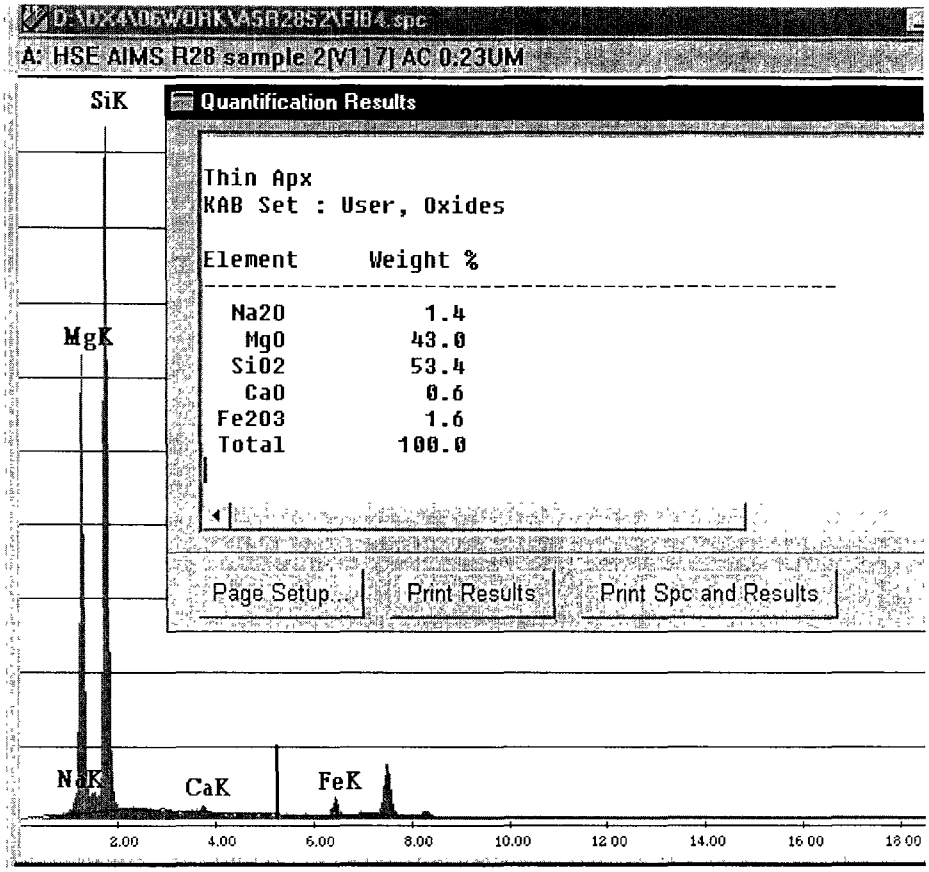


Figure 4: Energy dispersive x-ray spectrum collected from the fibre.
The quantitative values for each element have to be assessed from the spectrum by subtracting the area under the peaks of characteristic x-rays from the background (see the continuous line plot near bottom of the spectrum).

The relative peak: background intensity will affect the accuracy of the analysis. The sodium (Na) peak is essentially buried in the background so has a poor peak:background ratio.The ability to model and accurately remove the background from the smaller intensity peaks will also affect the precision and accuracy of the measured values and these around 0 - 2% are due to the poor peak to background ratio rather than a sodium peak.

In contrast, the Silicon (Si) and Magnesium (Mg) peaks have very good peak : background ratios. It can be seen that the spectrum contains small peaks of iron (Fe), calcium (Ca) and Aluminium (Al). The Al is not marked on this display but is between the Si and Mg peaks (directly under the K of NaK in figure 4). The unmarked peaks after the iron (Fe) peak is from the metal (nickel) grid used to support the carbon film.

As mentioned above, the ideal situation is one where the peaks in the spectrum derive only from the part of the fibre under the electron probe. However, the presence of peaks from the support grid, which is usually 50 or more probe diameters away, shows that this is not the case. X-rays are very energetic and if produced in significant numbers and of sufficient energy can travel in a wide variety of directions, for some

distances, and may strike other objects nearby giving rise to secondary X-ray peaks with characteristic energies associated with the elements present in the object.

Therefore if the fibres are surrounded by other particles they may contribute small peaks to the spectrum, as will the support film, EM grid and other instrumental factors. It is therefore necessary to look at the composition of surrounding particles and the background from an area of the carbon film near the fibre to see what peaks are present. As the carbon film is thin and made up of a light element, it has low electron density and it will not produce X-rays of a high energy or cause them to scatter, so it will generally contribute little secondary x-rays and underestimate the contribution from other particles compared to when the probe is placed on a more electron dense crystalline fibre. An example of a typical background is given in figure 5.

It can be seen that relatively small amounts of silicon and calcium are present in the spectrum. The unmarked peak by the silicon is sulphur and it is possible some calcium sulphate is present – this is added to cement. Calcium sulphate is soluble in water, and when a drop mount is prepared, it may possibly be deposited in a small amount over the grid and fibres. The weight percentages give the relative peak intensities of the background in relation to the silicon peak and only a small contribution from the background will be expected in fibres of diameters >0.1 μm.

Typical compositions of the particles of cement (see figure 6) show that they have high levels of calcium so it is not surprising that some calcium will appear in the fibre spectra from secondary x-ray emissions from the surrounding nearby or attached particles. The results of the quantitative x-ray analyses carried out on a number of fibres on two samples are given in tables 1 & 2. Fibres were primarily chosen, based on decreasing size and without any obvious attached particles in the region of the electron probe. These can be compared to results from fibres prepared in the same way from the UICC chrysotile standard (table 3) and published information from analysis of fibres from different mines (table 4).

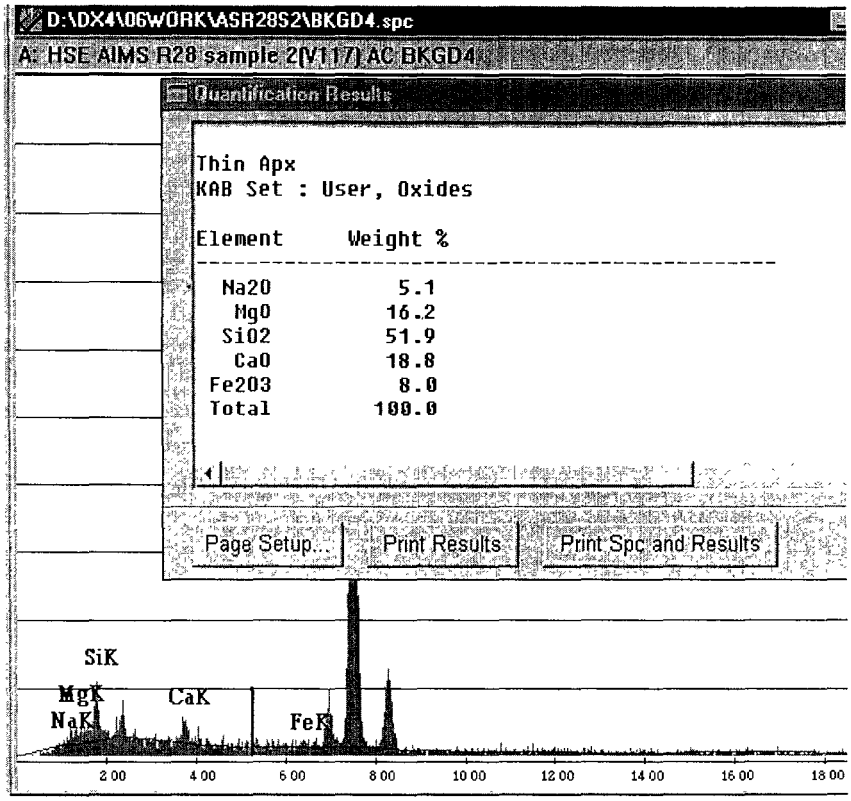


Figure 5: Example of background from the blank carbon support film near to fibre 4. (Note the weight % is relative to the height of the silicon peak which is very small compared to the EM grid peaks either side of the 8 Kev marker and only a small addition to a chrysotile spectrum will result, where the Si peak is many times greater than the EM support gird peaks).

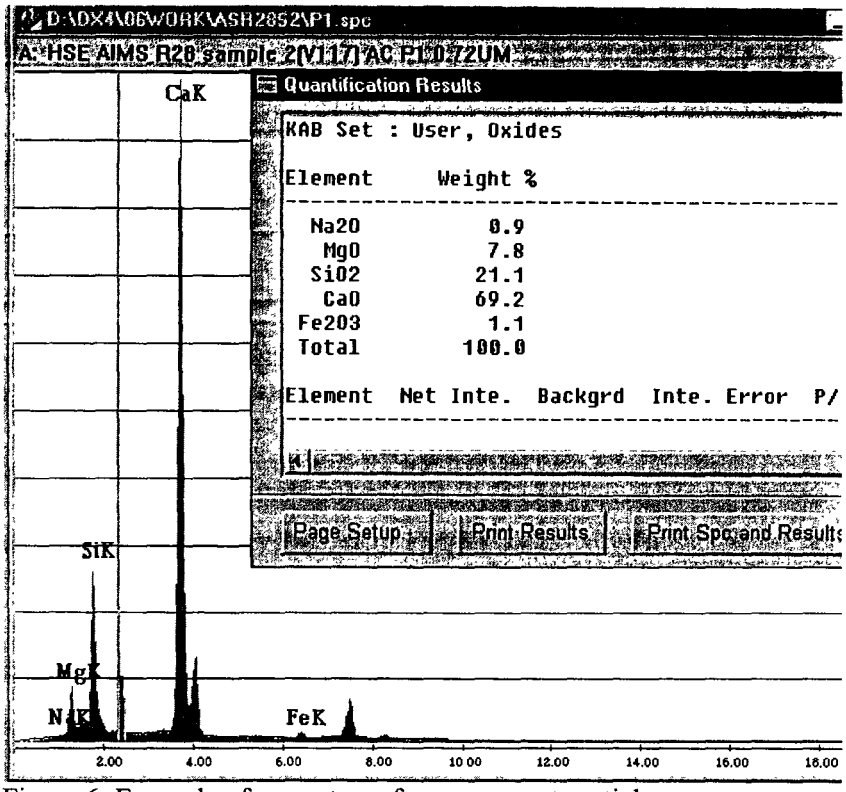


Figure 6: Example of a spectrum from a cement particle

Table 1: Table of results from quantitative EDX analysis of chrysotile asbestos fibres from asbestos cement sample (not corrected for water content). Background results are given at the end of the table.

Fibre Name	Fibre Diameter (μm)	Na_2O (%)	MgO (%)	SiO_2 (%)	CaO (%)	Fe_2O_3 (%)
FIB1	0.41	1.5	40.7	54.8	1.2	1.8
FIB2	0.21	1.4	36.5	59.5	0.4	2.2
FIB3	0.55	1.4	45.3	50.5	0.8	2.0
FIB4	0.23	1.4	43.0	53.4	0.6	1.6
FIB5	0.14	1.7	44.4	51.8	0.6	1.6
FIB6	0.05	2.8	45.9	47.5	1.8	2.0
FIB7	0.05	2.9	43.2	50.2	2.2	1.5
FIB8	0.03	2.1	45.2	48.5	2.7	1.5
FIB9	0.02	2.5	45.8	48.7	1.5	1.6
Average all		**2.0**	**43.3**	**51.7**	**1.3**	**1.8**
Average >0.1 um		1.5	42.0	54	0.7	1.8
Published	Shabanti*	-	**45.2**	**44.5**	**1.2**	**1.1**
BKGD3	-	1.4	9.9	61.8	18.9	8.1
BKGD4	-	5.1	16.2	51.9	18.8	8.0
BKGD7	-	2.6	12.5	60.0	18.8	6.0
BKGR8	-	1.8	9.8	61.5	18.8	8.0

*Adjusted for water content by x1.12, only a selection of oxides are shown

Table 2: Summary of main elements in oxide weight percent from typical EDX analysis of fibres from the UICC A chrysotile standard (not corrected for water content).

Fibre diameter (µm)	Al_2O_3 (%)	MgO (%)	$Si0_2$ (%)	Ca0 (%)	Fe_2O_3 (%)
0.78	1.7	47.3	49.3	0	1.7
0.333	1.6	46.6	50.5	0.2	1.1
0.21	1.6	47.1	48.4	0.2	2.2
0.197	1.6	47.4	49.4	0.2	1.5
0.091	2	45.9	49.7	0.7	1.8
0.05	3	42.4	51.7	1.1	1.8
Average	1.9	46.1	49.8	0.4	1.7

Table 3: Published composition of chrysotile from different mines (A.Hodgson)

Composition of chrysotile from different mines						
Oxide Weight %	Thetford	Cassiar	Asbestos	Shabani	Average	Adjusted without H_2O
MgO	39.78	41.28	38.22	40.3	39.9	**45.44**
SiO_2	38.75	40.75	39	39.7	39.55	**45.05**
CaO	0.89	0.35	2.03	1.08	1.09	**1.24**
Al_2O_3	3.09	3.37	4.66	3.17	3.57	**4.07**
Fe_2O_3	3.62	0.72	2.07	0.97	1.85	**2.1**
H_2O	12.22	12.86	11.37	12.17	12.15	-
Total without H_2O	86.13	86.47	85.98	85.22	85.95	**97.9**

It can be seen that the chrysotile fibres in the bulk sample (table 1) and UICC A chrysotile standard (table 2) showed that there was a general trend to increasing amounts of calcium with decreasing fibre diameter. As discussed above it appears that there is a small amount of calcium in the background of the support film and varying amounts from the surrounding cement particles. The amount of calcium appears relatively higher as the peak heights of the magnesium and silicon decrease with reduced fibre diameter. Therefore the fibre diameter appears to be an important factor in determining the percentage of calcium found and a simple average value without taking into account the fibre diameters will give a biased result. This suggests that the results from larger diameter fibres (>0.1 um) will provide a more accurate estimate of the calcium content than from the finer fibrils, assuming no cement particles are close to the electron beam.

The average amount of calcium reported from typical composition from mines was, 1.24%. This was higher than the average calcium oxide weight percentage found for the chrysotile standard and from the asbestos cement sample for <0.1 µm fibres. Therefore it does not appear that there is a significant uptake of calcium in the chrysotile fibres that were separated from the cement matrix, especially when taking into account that a large number of calcium rich cement particles are present in the

asbestos cement samples and the poor precision of the EDX method for weight percentage evaluations of <1%.

The much larger peaks of silicon and magnesium show variations between individual fibres of several percent. The average percent by weight value for MgO was 45.4 for the mine data, 46.1 for the standard and 43.3 for the asbestos cement sample, although the latter was biased by one very low result. Again given the variation in individual fibres in the same sample there is relatively little difference in the Mg content.

As it has been claimed that the coating on fibres is rapidly removed in water a different sample of asbestos cement sample was prepared in acetone (table 4). When examined a high proportion of the fibres were again uncoated and without any surface alteration but there were many small individual cement particles present, some of which were overlaying or attached to the fibres.

Typical results from the EDX analysis of randomly chosen fibres are given in table 4. There appeared to be no significant differences between the water and acetone prepared fibres and it was apparent that the calcium content was again related to the number and closeness of fine cement particles to the area being analysed.

Table 4: **Results from quantitative EDX analysis of randomly chosen chrysotile asbestos fibres from a sample of asbestos cement prepared in acetone (not corrected for water content and ranked by increasing fibre diameter).**

Fibre diameter (μm)	MgO (%)	Al_2O_3 (%)	SiO_2 (%)	CaO (%)	Fe_2O_3 (%)
0.05	42.4	3.2	47	2	5.6
0.07	37.7	4.5	49.2	2	6.6
0.095	43.7	2.5	49.2	1.6	2.9
0.11	40.7	3.1	45.9	1.3	9
0.155	44.3	1.8	50.7	0.7	2.5
0.17	46.8	1.9	47.6	1.1	2.6
0.21	40.2	3.4	46.7	1.1	8.7
0.287	47.1	1.9	47.1	1.5	2.4
0.452	46.3	1.8	48.8	0.4	2.8
1.41	43.7	1.5	46.7	1.3	6.8
Av all	43.29	2.56	47.89	1.3	4.99
Av >0.1	44.16	2.20	47.64	1.06	4.97

Again the average calcium content for >0.1 μm diameter fibres are lower than the published values from various commercial chrysotile mines (table 3). Taking into account the contribution from the many nearby calcium rich particles, there appears to be no strong evidence from this additional sample prepared in acetone that the chrysotile fibres obtained from the asbestos cement sample have undergone substantial changes in the calcium, silicon and magnesium content.

Obviously, where small particles are visibly attached or overlying the fibre and are included in or close to the focussed electron beam (probe), the calcium and other elements in these particles will be added into the EDX spectrum of the chrysotile fibre.

5.3 Selective area electron diffraction

Chrysotile has a unique structure, which means that the same characteristic electron diffraction pattern is usually obtained from most fibres regardless of fibre orientation. Following the ISO standards, observation of the characteristic chrysotile pattern alone is sufficient to identify a fibre as chrysotile. Nearly all of the fibres that were observed using selective area electron diffraction (SAED) gave the characteristic diffraction pattern of chrysotile.

Although not required by the international standard, several of the SAED patterns from the chrysotile fibres were indexed against the accepted standard (JPCDS) values for the atomic lattice spacing (d-spacing). Several d-spacings of the main reflections were measured using a gold d_{111} diffraction ring to calibrate the measurements. Table 4 compares the measured values with the published values. As small distances are being measured between diffraction spots (some of which are blurred) an exact match is normally accepted from the atomic lattice spacing if several measurements are within $\pm$5% of the published values. A check against the gold calibration standard showed that measurements were calibrated to within $\pm$2% of the correct value. Given the above, all three patterns from fibres from the cement samples gave a good match for the d-spacing values for the accepted standard of chrysotile asbestos. Any change to the internal structure or chemistry would have affected the atomic lattice dimensions and the d-spacings of the fibres.

Table 4: Examples of the measured d-spacings from the electron diffraction patterns of selected fibres from AIMS sample R28s2v117s grid G1.

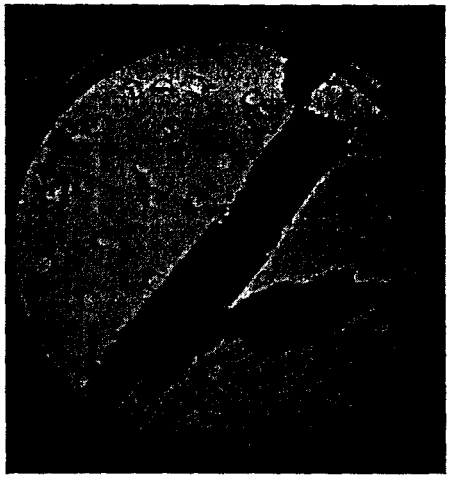
		Fibre 1		Fibre 2		Fibre 3	
Miller indices of plane	Standard value (nm)	Measured Distance (nm)	Percent error (%)	Measured Distance (nm)	Percent error (%)	Measured Distance (nm)	Percent error (%)
002	0.728	0.709	-2.6	0.76	4.4	0.722	-0.8
004	0.364	0.359	-1.4	0.366	0.5	0.359	-1.4
020	0.454	Diff	-	0.451	-0.7	0.451	-0.7
110	0.455	0.456	0.2	0.469	3.1	0.464	2.0
130	0.266	0.261	-1.9	0.268	0.8	0.256	-3.8
200	0.266	0.258	-3.0	0.255	-4.1	0.263	-1.1
Diff = spot too blurred to measure accurately							

6 RESULTS OF THE TEM ANALYSIS OF THE AIR SAMPLES

Due to the short sampling time (a few minutes) and the limited amount of material disturbed the air filter was relatively lightly loaded with particulate and fibre. Grid H4 was scanned for particles and fibres and examples of the types of fibres and particles seen are give below, along with examples of the EDXA spectra obtained.

Figure 7 - 11: Examples of particles, fibres and fibre bundles found on air sample grid H4 of Aims sample R28S2 V117s. All pictures are approximately the same magnification. (0_____5μm)

Figure 7: Spectrum from fibres along one edge of encapsulated chrysotile bundle.



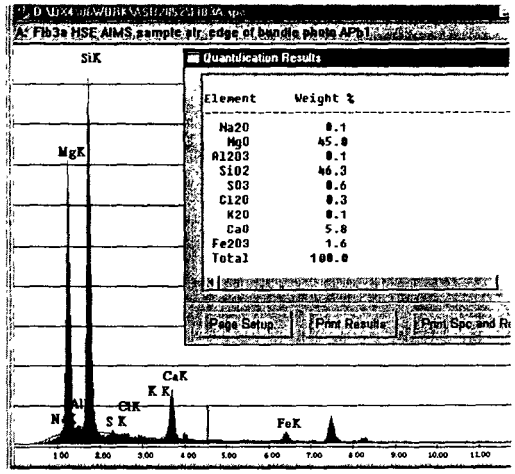
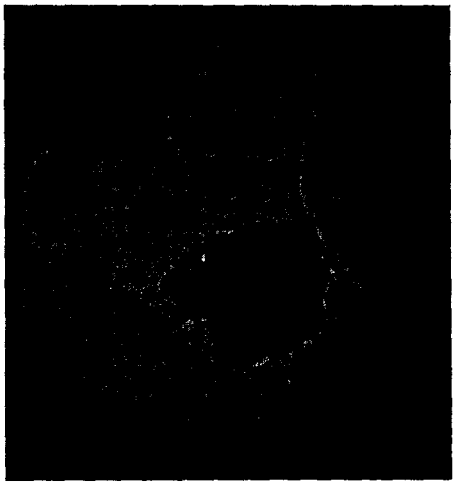
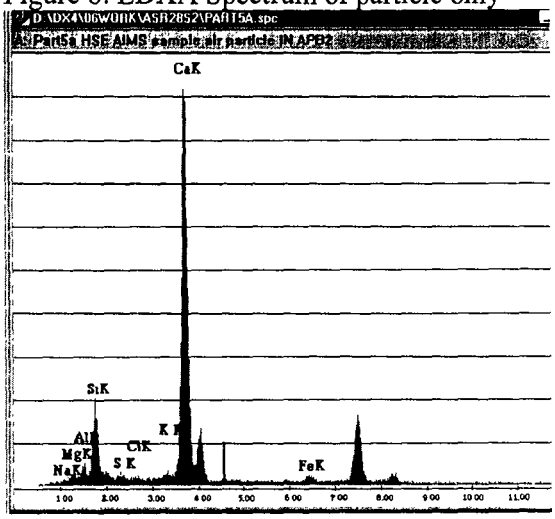


Figure 8: EDXA Spectrum of particle only





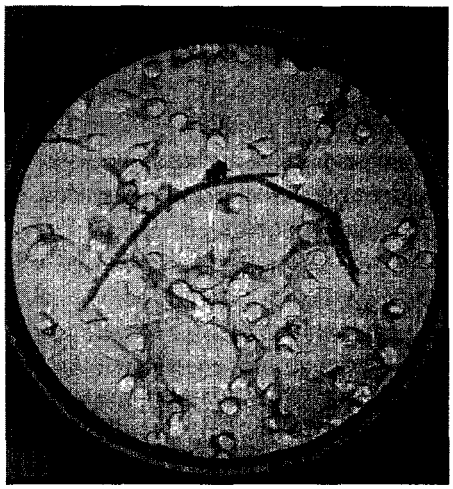


Figure 9: EDXA Spectrum from fibre

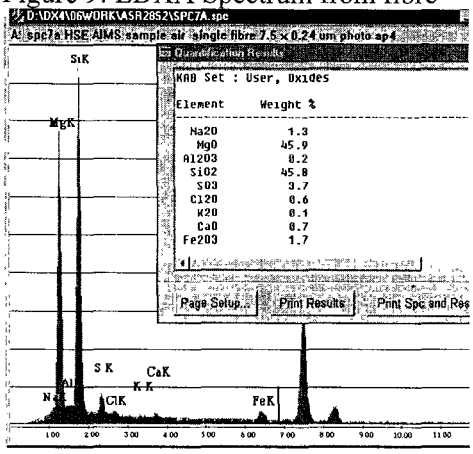
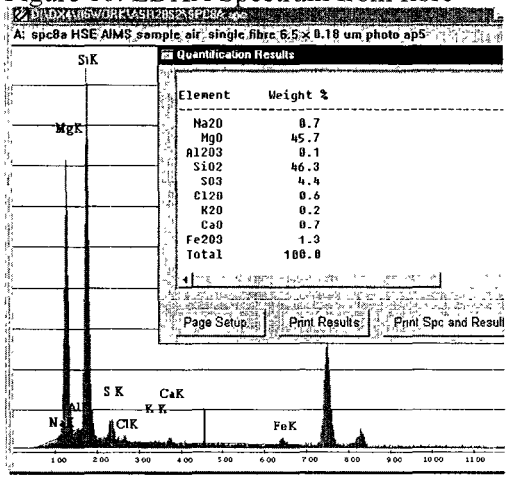




Figure 10: EDXA Spectrum from fibre



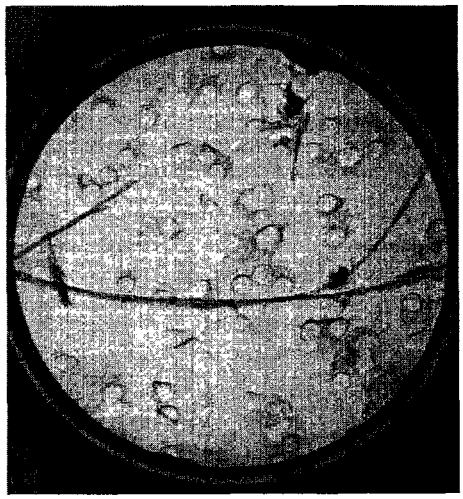
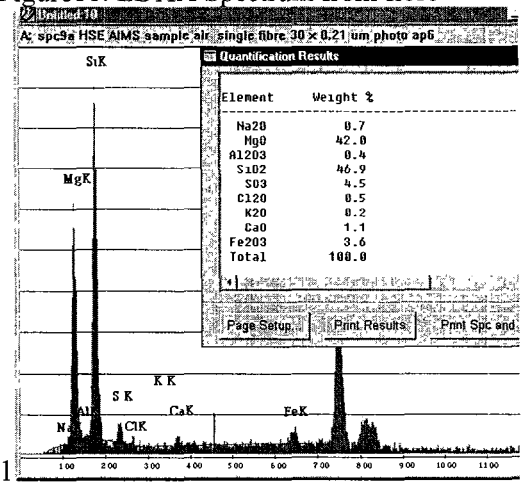


Figure11: EDXA Spectrum from fibre



It can be seen that the fine airborne fibres released usually had only a few small particles attached or overlying the fibres and the fibres found were essentially free of any coating (see figures 9 –11). Figure 7 showed a large fibre agglomerate, where most of the fibre is encapsulated in the cement matrix giving a higher Ca peak from the exposed end. Figure 8 gives the spectrum from the cement particle attached to the fibre. Examples of the energy dispersive x-ray spectra from the fibres (see figures 9 – 11) away from the vicinity of any attached particles gave chrysotile spectra similar to that from the standard and published information in tables 2 &3. The main change is a slight increase in the sulphur content.

The fibres in figures 7 – 11 were also analysed by electron diffraction and all gave the characteristic chrysotile SAED pattern.

7 RESULTS OF THE PLM ANALYSIS

Although PLM analysis was not carried out again on this sample of asbestos cement, the samples used are from the AIMS proficiency testing scheme and all 246 laboratories that analysed the samples reported the presence of chrysotile asbestos in the sample. It is therefore clear that the optical properties of the fibres in the sample were not significantly changed. If calcium had been adsorbed into the structure of the fibre the refractive index and hence dispersion staining colours used to measure the refractive index would also have been changed. That all 246 laboratories reported chrysotile asbestos, suggests that it was still present in this sample.

8 DISCUSSION

8.1 Evidence for changes to the chrysotile fibres

The fibres found in the bulk analysis and on the airborne filters were unambiguously chrysotile asbestos fibres, which showed no significant alteration. Often the dispersed fibres would have a few small particles attached or overlying the fibre but this was not extensive and cannot be viewed as anything other than attached particles of the cement matrix. The chemistry of the fibre was consistent with the chrysotile standard and published information from the main commercial chrysotile mines worldwide.

The tubular structure seen in many of the fibrils and the characteristic chrysotile asbestos diffraction patterns obtained are strong evidence against the adsorption of calcium into the chrysotile structure. If calcium were being adsorbed to form an altered mineral the d-spacings would also change. It is highly unlikely that the tubular structure would be able to accommodate the larger Ca atoms without some change in the structural and physical appearance of the fibres.

Chrysotile is well known to have poor resistance to acids and is capable of chemical change due to the loss of magnesium and hydroxide ions from the outer layers of the scroll structure. Acid attacked chrysotile shows clear damage to the fibril structure in the TEM and the EDX analysis shows a large reduction in the magnesium peak. This

was not observed for this sample but has been found in chrysotile fibres from water samples and from the weathered surface of AC sheets exposed to acid rain. When working with asbestos cement and breaking the material it was shown that unaltered chrysotile fibres were released.

Even when cement coated fibres occur it will be subject to weathering and will dissolve. This may also occur in the lung where fibres that reach the deep lung will be bathed in a constant flow of fluid and surfactants that coat the lung's surface. However, it was clear that the large majority of the chrysotile fibres in the asbestos cement sample analysed were unchanged and that unaltered chrysotile fibres were released to air.

This analysis and observation is consistent with other analyses of asbestos cement samples from other sources carried out by HSL.

8.2 Evidence for coating of fibres

The fibres inspected in the asbestos cement sample examined, appeared to be uncoated except that some cement particles from the matrix were present (see figure 2). These could not be described as a coating but were calcium-rich small particles and agglomerates , which were sometimes attached to the chrysotile fibres. The presence of the calcium-rich particles in the sample would also contribute to the presence of calcium in the EDX spectra.

Examples of coated fibres have been seen in other samples. Although some discreet particles were visible (see figure 3) it can also be seen that there is a more diffuse low electron density gel like coating on parts of the fibre, rather than discreet particles. In the particular fibre found, both calcium and aluminium were present in the spectrum. Pooley (2004) reported that the coated fibres had additional calcium and silicon but this could also be an artefact of the EDX analysis or due to magnesium depletion of the chrysotile fibre due to weathering. A calcium hydroxide gel is formed during the hydration process of Portland cement and could coat some of the individual fibres. Calcium hydroxide is the most water-soluble component of cement and is easily removed by normal weathering processes and presumably by immersion in water or lung fluids. If the coating on fibres is readily removed by water it is clear evidence that there is no overall change to the chemistry of the fibres.

In weathered samples of asbestos cement the chrysotile fibres are more resistant than the cement matrix so a surface layer of predominantly chrysotile fibres may form. PAH's have been reported to collect and concentrate on the exposed chrysotile fibres on the weathered surface of asbestos cement. Although the presence of moisture reduces this process it would also seem possible for exposed chrysotile fibres on the surface of weathered asbestos cement to be coated with PAH's.

Overall, it appears that the vast majority of fibres are uncoated and there is no evidence to support the claim that all the chrysotile has been chemically or structurally altered.

8.3 Evidence for airborne fibre release

The claim that respirable airborne chrysotile fibres are not able to be released from asbestos cement products was refuted by the individual airborne fibres sampled during the breaking of the test sample with a hammer. There are also a number of papers in the published peer reviewed scientific literature that have measured the airborne release of asbestos fibres from asbestos cement sheet as well as HSL's own database of measurements (see annex 1).

The measurements have been carried out by the regulatory method based on phase contrast microscopy (PCM) fibre counts (e.g. annex 1 to 83/477/EEC and HSG 248). This method counts all fibres of countable dimensions but does not identify individual fibres. The counting rules used for PCM analyses (prior to November 2006) do not allow the fibre to be counted if attached or overlain by a particle of >3 μm in width. Therefore the published data would not have counted any asbestos fibres attached to a cement particle >3 μm width, as it would be unlikely to reach the pulmonary region of the lung.

8.4 Evidence for loss of carcinogenic potency due to use of the asbestos in asbestos cement.

Although outside the scope of the current paper, it is worthwhile to note that there is substantial evidence from animal experiments that inhaled chrysotile fibres are carcinogenic. However, some authors have argued that the carcinogenic response from chrysotile is solely due to the "overload effect" on the lung and not the chrysotile fibre itself or is due solely (or in part) to the amphibole asbestos impurities in the chrysotile. Others accept that chrysotile is a cause of lung cancer but not mesothelioma, or that while chrysotile may be carcinogenic there is no evidence from animal experiments that the chrysotile fibres from asbestos cement are carcinogenic. It is not easy to unravel the claims and counter claims about the carcinogenic nature of chrysotile and it is noted that from the number of reviews on these issues over the last 2-3 years (e.g. Lemen, 2004; Le et al., 2004 and Yarborough, C. M. 2006) that the debate continues.

The claims that chrysotile in asbestos cement had reduced carcinogenic potency were particularly in vogue in the 1980's when prohibition on asbestos cement was being considered. These claims were specifically tested using sensitive interperitoneal injection into rats. No observed differences in the carcinogenic potencies were found between 20 year-old weathered chrysotile asbestos fibres from the surface of asbestos cement sheets and UICC chrysotile asbestos (Spurny, 1988). These results were supported by work carried out by Tiles and Beck (1990) who also reported that the carcinogenicity of the weathered asbestos-cement chrysotile fibres is comparable to that of standard chrysotile fibres following intraperitoneal (i.p.) application and even greater than the unaltered asbestos cement fibres taken from the core of the weathered sheets. The reason for these difference was attributed to the lower amount of chrysotile in the core sample (10%) as compared with the weathered surface sample (30%). However, the ability of the free chrysotile fibres on the weathered surface to

collect PAH's could even mean that the weathered chrysotile may be of more concern. Experimental evidence showed that chrysotile asbestos is a particularly good absorber of PAH's and can absorb about 10,000 times more than glass wool but this difference is substantially reduced at normal atmospheric humidity (Gerde and Scholander, 1990). Results from interperitoneal injection of rats (Minardi and Maltoni, 1988) reported that acid leaching reduced the carcinogenicity of weathered chrysotile (52%) compared to unaltered UICC chrysotile standards (~80%) and had longer latency times, but it was unclear whether the reduction was also due to the lower numbers and concentration of fibres present in the asbestos cement sample.

This research was accepted as reasonable proof that asbestos cement was a carcinogenic hazard and has remained relatively unchallenged until the work in the 1990's on man-made vitreous fibres (MMVF'S) led to an extensive debate on the merits of different animal models and test procedures. The crux of the debate was whether intraperitoneal or intrapleural injection testing of the lung lining was too sensitive and instillation and inhalation into the lung itself gave a better estimate of carcinogenicity. Again the influence of lung overload was central to some of the arguments. Application of the protocols developed for MMVF's to chrysotile asbestos in recent years have been funded by the asbestos industry to demonstrate that risk from chrysotile inhalation is more similar to MMMF's than other types of asbestos and have led to renewed calls that chrysotile should be treated differently from other asbestos types. However, no further work has been carried out to show whether fibres from asbestos cement have a different level of carcinogenicity than standards of chrysotile asbestos.

Human epidemiology has shown that chrysotile asbestos cement manufacture is low risk compared to other asbestos products. The low risk is largely due to the lower levels of fibre emissions in the manufacturing industry, as much of the asbestos production is carried out using wet processes and when dry the asbestos is locked into a resilient cement matrix. There was also increasing use of dust controls in western production plants. Emerging evidence from China suggests that the higher airborne levels of chrysotile do give rise to lung cancer and mesothelioma (Li, 2004).
The risk from asbestos will depend upon dose, however the lower levels of airborne chrysotile fibre released from asbestos cement manufacture cannot be used to infer that there is no carcinogenic hazard.

8.5 Current EU and UK regulatory position on asbestos

The UK regulatory position is in line with the European Union (e.g. 83/477/EEC and 2003/ 87/EC) and the vast majority of regulatory agencies worldwide in accepting the findings of the World Health Organisation (WHO), International Programme for Chemical Safety (IPC), International Agency for Research on Cancer (IARC) etc. that chrysotile asbestos along with the other regulated forms of amphibole asbestos are category 1 human carcinogens.

The marketing, use and importation of chrysotile asbestos have been prohibited in the UK from 1999 and throughout the EU from 2005. EU directives (83/477/EEC and 2003/ 87/EC) control the risk and have set an upper exposure limit to which people cannot be legally exposed.

The UK has distinguished between the higher risk asbestos containing products for many years (e.g. ASLIC 1983, and the Asbestos Regulations 2006) by using a system of licensed contractors to remove higher risk asbestos products. Asbestos cement is regarded as a lower risk product and does not need a licensed removal company when work is carried out on it. However, all work with asbestos comes under the Asbestos Regulations 2006 (which recently replaced by CAWR 2002) and exposure should be reduced to as low as reasonably practicable.

Most of the reviews carried out by HSE on the toxicology (Meldrum, 1997) and on human epidemiology from asbestos production and manufacturing (Hodgson and Darnton, 2000) have concluded that chrysotile is a carcinogen but has a lower risk than the two other main types of commercially used asbestos (crocidolite and amosite). Hodgson and Darnton thought the risk from mesothelioma from crocidolite and amosite asbestos were of the order of 500 and 100 times greater than for chrysotile asbestos. The risk from lung cancer was thought to be some 10-50 times higher for crocidolite and amosite than chrysotile alone. The HSE review by Meldrum, 1987, to an extent, agreed with the asbestos industry assertion that there is a dose threshold for chrysotile induced lung cancers as these are related to fibrosis. This is still disputed by some.

HSE recognises that there is substantial evidence for chrysotile being a carcinogen but acknowledges that it has a lower risk than the other commercial types of asbestos. It is not assumed or accepted that there is no risk and chrysotile is regulated using the same legislation and procedures as used for other types of asbestos. However a lower exposure / control limit had been applied for many years and current guidance and risk estimates take into account the lower level of risk between the types of asbestos (e.g. MDHS 100, CD 205).

9 CONCLUSIONS

The fibres found from a well-characterised asbestos cement sample showed that both the bulk and air samples had the same morphology as a reference standard of chrysotile asbestos.

Many fibrils in the sample, when viewed at higher magnification, showed the characteristic tubular structure associated with chrysotile fibrils.

Individual fibres analysed by energy dispersive X-ray (EDX) analysis showed chemistry is similar to a reference standard of chrysotile and to published compositions for chrysotile from various source mines around the world (when adjusted for water content).

For fibres above 0.1 μm diameter the calcium content was generally less than 1% by weight and the precision of the EDXA technique is limited at these levels.

Different sections of the same fibres, also gave the characteristic selective area electron diffraction patterns associated with the chrysotile structure. Three electron diffraction patterns were indexed and gave a close match to the published d-spacings for chrysotile.

The analysis carried out showed that the samples contained fibres of chrysotile asbestos and released chrysotile asbestos fibres to air when substantially disturbed.

There is no evidence that any chemical or structural alteration changes have occurred to the majority of the chrysotile fibres since they were added to the cement.

The above conclusions also have been reached when examining other samples of asbestos cement.

The claims being made to HSE and in internet articles and in some sections of the newspaper industry could not be reproduced and the majority of the chrysotile fibres in asbestos cement are unchanged and retain their hazard.

Only a small percentage of "coated" fibres have been observed. This does not appear to be made up of fine particles but may be due in part to the calcium hydroxide gel that is formed during the hydration process of Portland cement. Calcium hydroxide is the most water-soluble component of cement and is easily removed by normal weathering processes.

The EU's position on asbestos cement, is that it is a hazardous material as it contains ~10% of a category 1 human carcinogen (predominantly chrysotile but crocidolite and amosite are present in a few percent of sheet material). All materials or preparations containing more than 0.1 % of a carcinogen come under the marketing and use directive and should be labeled as carcinogenic hazard and alternative substitutes used if possible. The importation and use of the six regulated forms of asbestos was prohibited in the EU in 2005.

HSE considers that the risk of exposure to airborne asbestos fibres is lower in asbestos cement products compared with some other asbestos containing products due to:

- The relatively lower amount of asbestos used in this product compared to others;

- the hard resistant nature of the cement matrix which makes it more difficult to release airborne fibres;

- the high use of chrysotile asbestos compared to amosite and crocidolite asbestos.

This low risk factor is why the asbestos cement products can be removed without the need to notify HSE, or the mandatory use of a licensed asbestos removal contractor. However all asbestos containing materials are subject to the Asbestos Regulations 2006.

The external surface of an asbestos cement sheet is subject to weathering of both the cement and the asbestos. The surface weathers at a rate largely dependent on the cement, which may corrode at a rate of 0.02 – 0.1 mm/year in most environments depending on the acidity of the rain and other factors. The chrysotile is more resistant and these fibres will be preferentially exposed on the surface in some environments.

PAH's have been reported to collect and concentrate on the exposed chrysotile fibres on the weathered surface of asbestos cement. Although the presence of moisture reduces this process it would also seem possible for exposed chrysotile fibres on the surface of weathered asbestos cement to be coated with PAH's.

Weathering of the exposed surface of asbestos cement will produce a number of chemical reactions and changes to the cement and chrysotile fibres, depending on the local environment. In acidic environments the exposed chrysotile will lose Mg OH_2 from the structure and as this progresses some loss of structural order will occur. This does not seem to occur to fibres still inside the cement matrix, which has an alkaline pH.

Sensitive animal tests based on intraperitoneal injection in rats have shown that there was no reduction in the carcinogenic potency of magnesium depleted weathered chrysotile compared to UICC chrysotile asbestos standards.

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11 ANNEX 1: MEASURED AIRBORNE FIBRE CONCENTRATIONS FROM WORK WITH ASBESTOS CEMENT.

Table A1: Work on asbestos cement roofs personal exposure to asbestos

Range	Reference	
All work on ac roofing and sheets	Not detected/<0.01 - 1.1 f/ml (from data below)	
Roof Repair "Representative"	Not detected - 0.3 f/ml	(CONSAD, 1990)
Roof Removal "Representative"	Not detected - 0.2 f/ml	(CONSAD, 1990)
Dry - replacing corrugated asbestos cement	0.01, <0.01 f/ml	(Roberts, 1985)
Collecting sheets and cleaning	0.24 f/ml	(Roberts, 1985)
Removal of corrugated sheets (detachment and sliding to gutter)	0.047 f/ml	(Preat, 1993)
Throwing sheets into lorry	0.161 f/ml	(Preat, 1993)
Removal of corrugated sheets (detachment, stacking on elevator, placing in pallets)	0.028, 0.038 f/ml	(Preat, 1993)
Removal of corrugated sheets (detachment)	0.018 f/ml	(Preat, 1993)
Stacking of sheets of pallets	0.032 f/ml	(Preat, 1993)
Removal of slates (detached with hammer)	0.064 f/ml	(Preat, 1993)
Sliding slates to gutter; throwing to ground	0.195 f/ml	(Preat, 1993)
Removal of slates (detachment and stacking)	0.037, 0.044 f/ml	(Preat, 1993)
Removal of slates (detachment and placing in container on roof)	0.050, 0.176 f/ml	(Preat, 1993)
Removal of slates (pulling off, stacking on elevator, broken slates thrown to ground)	0.100, 0.122 f/ml	(Preat, 1993)
Removal of slates (detachment with hammer, sliding to gutter)	0.068 f/ml	(Preat, 1993)
Bringing slates down and throwing into container	0.056 f/ml	(Preat, 1993)
Wet (but not effective)	Mean 0.020 f/ml	(Lange & Thomulka, 2000)
Roof Replacement		
Dry replacement (severely weathered) - unfastening, removal, stacking, disposal, installation of new roofing	0.03 - 0.24 f/ml	(Brown, 1987)
Dry unfastening, removal, disposal, installation of new roofing (no stacking)	0.03, 0.03 f/ml	(Brown, 1987)
Dry replacement (severely weathered)	0.04 - 0.27 f/ml	(Brown, 1987)
Dry removal (painted)	0.07 - 0.32 f/ml	(Brown, 1987)
Wet removal (painted) and replacement (careful handling and wetting as stacked)	Not detected - 0.07 f/ml	(Brown, 1987)
Replacement (severely weathered) after lignin sulphonate treatment	0.23 f/ml	(Brown, 1987)
Replacement (severely weathered) after sealing with acrylic resin	0.03 - 0.08 f/ml	(Brown, 1987)
Replacement (severely weathered) after sealing with acrylic resin	0.04 - 0.26 f/ml	(Brown, 1987)
Roof Removal - Demolition		
Dry (building collapsed)	0.10 - 0.47 f/ml	(Brown, 1987)
Dry (from scissors lift)	0.04 - 0.12 f/ml	(Brown, 1987)
Sheets stacked in confined space	0.30 - 0.53 f/ml	(Brown, 1987)

Sheets stacked in confined space (accumulated dust under laps and ridges)
0.34 - 1.1 f/ml (Brown, 1987)

Wet 0.05 - 0.06 f/ml (Brown, 1987)
Wet (sheets staked in confined space) 0.10 - 0.13 f/ml (Brown, 1987)
Wet (sheets staked in confined space; accumulated dust under laps and ridges)
0.29 - 0.68 f/ml (Brown, 1987)

Sealed with acrylic resin 0.11 - 0.32 f/ml (Brown, 1987)
Sealed with acrylic resin (sheets stacked in confined space; accumulated dust under laps and ridges)
0.41 - 0.76 f/ml (Brown, 1987)

Table A2: Summary of all results in HSL database for asbestos cement work.

	Type of sample	No of data /site entries	Mean (f/ml)	SD	Minimum of means	Maximum of means	No of samples	Sum (mean * number)	Weighted mean (f/ml)
All	All	51	0.189	0.757	0	5.45	245	48.184	0.197
	Personal	36			0.0015	0.23	94	7.665	0.082
	Static	8			0	0.4	103	24.486	0.238
	Unspecified	7			0.008	5.45	48	16.033	0.334
Dry	All				0				
	Personal	7	0.124	0.076	0.03	0.23	39	4.450	0.114
	Static								
	Unspecified								
Not Known	All	43	0.203	0.825	0	5.45	198	43.494	0.220
	Personal	28	0.057	0.052	0.0015	0.195	47	2.975	0.063
	Static	8	0.120	0.149	0	0.4	103	24.486	0.238
	Unspecified	7	0.881	2.019	0.008	5.45	48	16.033	0.334
Wet	All								
	Personal	1	0.03		0.03	0.03	8	0.240	0.030
	Static								
	Unspecified								