Chemical characteristics of asbestos and associated trace elements

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The known varieties of asbestiform minerals can be classified either as serpentine or amphibole according to their crystal structure. Chrysotile is the sole commercial representative of the serpentine class and is by far the most common of the asbestiform minerals, accounting for over 90% of the asbestos produced today. The five amphibole varieties used commerically are amosite, anthophyllite, crocidolite, actinolite and tremolite. The asbestiform minerals have been the subject of a number of reviews in recent years (Hodgson, 1965; Speil & Leineweber, 1969). Their physical and chemical properties can be related directly to their crystal structures, which have been well established.

In addition to its major structural elements, asbestos invariably contains trace metal impurities. These may be present as isomorphous substitutes for structural elements, as fragments of host rock and accessory minerals; or as fine particles of alloy produced by the abrasive action of the asbestos on processing equipment (Cralley *et al.*, 1967). This paper will review current information concerning the levels of designated trace metals in asbestos with particular reference to the UICC standard reference samples.

CHRYSOTILE

Composition

Chrysotile ($Mg_3Si_2O_5(OH)_4$) has a layered structure, the basis of which is a sheet of silica tetrahedra. Attached to one side of this is a brucite ($Mg(OH)_2$) layer, in which two out of every three hydroxyls are replaced by the apical oxygens of the silica tetrahedra. A mismatch in the dimensions of the two sheets introduces a strain into the structure; this is relieved by curvature, resulting in the hollow cylindrical morphology of the chrysotile fibril. Fibril diameters vary between about 10 and 80 nm, but the mean values are generally in the range of 30–40 nm (Atkinson *et al.*, 1971). Chrysotile fibres consist of bundles of fibrils, and it has been suggested that the voids between the bundles are filled with a non-crystalline solid.

Associated trace elements

The minerals most commonly found in association with chrysotile are magnetite (Fe_3O_4) and brucite, which may be intergrown with the fibre. Gibbs (1971) has reported that other minerals associated with chrysotile from the asbestos mining areas in Quebec include actinolite, antigorite, awaruite, chlorite, chromite, magnesite, nemalite and talc.

Magnetite can be separated magnetically from fully opened fibre. Using neutron-activated samples, Morgan *et al.* (1971b) separated magnetic fractions from a number of samples of chrysotile, and they found that the fraction of iron present as magnetite varied from 19–58%. Small amounts of chromium (3–13%) and cobalt (7–23%) were separated with the magnetic phase, but in no case was any of the scandium removed by this method.

Neutron activation analysis (NAA) has been used by Holmes *et al.* (1971) to measure the levels of chromium, cobalt, iron, manganese and scandium in a number of samples of asbestos, including the UICC standard reference samples. These values, together with measurements of nickel by atomic absorption spectrophotometry (AAS) are sum-

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marised in Table 1. Also included in Table 1 are measurements made on the eight samples of Canadian chrysotile which were blended to produce the UICC sample of Canadian chrysotile (Chrysotile B). Cralley *et al.* (1968) used AAS to measure a similar range of elements in the UICC samples and their values are also included in Table 1. With the exception of iron, agreement between the two laboratories is satisfactory.

In general, nickel is best determined by AAS and is homogeneous at the 10 mg level, using the reproducibility of replicate determinations of a number of trace metals as an index of homogeneity. Another advantage of NAA is that it can be used non-destructively. To achieve accurate results with AAS, it is essential to ensure that both fibre and accessory minerals are completely dissolved before the solution is aspirated. Some minerals are insoluble in boiling hydrofluoric acid, and it is necessary to use fusion to dissolve all the contaminating minerals.

Table 1. Levels of trace metals in samples of asbestos from various regions

Source	Lab	Fe (%)	Cr (ppm)	Co (ppm)	Mn (ppm)	Ni (ppm)	Sc (ppm)
Chrysotile							
Rhodesia (UICC A)	AERE [a]	1.7	1390	55	450	1360	8
" "	DHEW [b]	0.6	1378	54	393	1482	—
" (UICC AR)	DHEW	0.91	1170	43	231	1284	—
Canada (UICC) B	AERE	2.6	490	50	480	820	5
"	DHEW	1.24	317	45	444	802	—
Canada (UICC BR)	DHEW	1.08	317	46	419	873	—
Canada (Mine A)	AERE	4.8	515	63	540	720	5
" (Mine B)	AERE	3.5	780	110	580	1820	4
" (Mine C)	AERE	2.0	1200	60	420	1510	12
" (Mine D)	AERE	4.1	930	78	600	840	7
" (Mine E)	AERE	3.2	435	57	610	540	5
" (Mine F)	AERE	2.9	730	78	450	1790	8
" (Mine G)	AERE	1.9	480	44	420	1520	8
" (Mine H)	AERE	3.2	380	53	530	330	6
Cyprus	AERE	3.1	340	54	720	870	2
Amosite							
South Africa (UICC)	AERE	M [c]	35	7	11800	< 100	5
" "	DHEW	M	31	11	13350	33	—
Crocidolite							
South Africa (UICC)	AERE	M	18	2	880	< 100	0.5
" "	DHEW	M	20	10	833	8	—
NW Cape (Mine A)	AERE	M	< 20	0.6	240	< 100	< 0.1
" " (Mine B)	AERE	M	< 20	0.4	170	< 100	0.3
Transvaal (Mine A)	AERE	M	20	0.8	140	< 100	0.6
" (Mine B)	AERE	M	< 20	0.6	220	< 100	0.3
Anthophyllite							
Finland (UICC)	AERE	4.4	870	50	1060	1360	5
"	DHEW	2.0	584	24	986	414	—

[a] Atomic Energy Research Establishment, Harwell, UK.
[b] Department of Health Education and Welfare, Cincinnati, USA.
[c] Massive.

scandium by NAA, but the other elements can be determined with adequate sensitivity by either technique. NAA is more sensitive than AAS for evaluating the levels of the majority of elements, and this is an advantage when small samples are to be analysed. For example, Morgan & Timbrell (1971) used NAA to determine the amounts of chrysotile and crocidolite in 10 mg samples of blended asbestos and also to show that the UICC sample of Canadian chrysotile

Emission spectrography has also been used for the analysis of a wide range of elements in the UICC samples (Timbrell, 1970). The accuracy of this method is, however, inferior to that which can be achieved with either AAS or NAA.

As shown in Table 1, the levels of trace metals in all the chrysotile samples fall within well-defined ranges; thus it does not appear that the source of a sample can be identified by its trace element comple-

tion. After 2 months, about 30% of the magnesium had dissolved; but after this period, further leaching occurred only very slowly.

AMPHIBOLE ASBESTOS

Composition

Idealised chemical formulae for the three main types of amphibole asbestos are given below. Where cations are written in parentheses without subscripts a variable composition is indicated, with the most abundant species first.

Crocidolite	$Na_2Fe_3^{+3}Fe_2^{+2}Si_8O_{22}(OH)_2$	
Amosite	$(Fe^{+2}Mg)_7$	$Si_8O_{22}(OH)_2$
Anthophyllite	$(MgFe^{+2})_7$	$Si_8O_{22}(OH)_2$

The variability in composition is due to the fact that the crystal structure can accommodate many ions in the spaces between the silica ribbons, and it is the variable nature of host rocks which contributes different ions to this structure.

Associated trace elements

As shown in Table 1 the levels of chromium, nickel and cobalt in amosite and crocidolite are generally one or two orders of magnitude lower than in chrysotile. The levels of these elements in anthophyllite are, however, very similar to those in chrysotile. Manganese is found in rather similar concentrations in all the UICC samples, with the exception of the amosite which contains 1.4% of this element.

Solubility of amphiboles

The amphiboles are much more resistant to attack by acids than is chrysotile. From unpublished work referred to by Hodgson (1965) it appears that the weight loss in refluxing 4N hydrochloric acid is in the order:

amosite ≫ crocidolite > anthophyllite.

More recent leaching studies (Morgan *et al.*[1]) with the UICC reference samples show that in 0.1 N hydrochloric acid at 25°C the structural iron of amosite is slightly more soluble than is that of crocidolite, 9 and 7%, respectively, being dissolved in 28 days. In neutral phosphate/citrate buffer at the same temperature, about 3% of the iron dissolved in the same period. The iron of the anthophyllite was considerably more soluble than was the magnesium, which indicates that these elements may be located at different sites in the crystal structure of this amphibole.

Excretion of ^{59}Fe by rats which had been injected intrapleurally with neutron-irradiated amosite and crocidolite (Holmes & Morgan, 1968) showed that the structural iron dissolves *in vivo*, but at a much slower rate than does the magnesium of chrysotile. Langer *et al.* (1972) measured the Mg:Si ratios in amphibole fibres isolated from lungs of asbestos workers and compared them with the corresponding ratio in the appropriate UICC reference sample. The magnesium loss from amphiboles in the lung appeared to follow the sequence:

anthophyllite > amosite > crocidolite.

DISCUSSION

Harington & Roe (1965) suggested that asbestos carcinogenesis could be due to the presence of trace metals such as chromium or nickel, which are known to be carcinogenic under certain circumstances. An alternative hypothesis has been put forward by Dixon *et al.* (1970), who suggested that trace metals associated with asbestos inhibit the metabolism of benzpyrene, thus increasing the residence time of this carcinogen in the lung. They found that nickel, chromium and beryllium were the most effective inhibitors of benzpyrene hydroxylase. If this theory is correct, then the role of asbestos is purely that of a passive carrier of trace metals. Recently, Cralley (1971) has indicated that alloy metal particulates associated with asbestos fibres could give rise to high concentrations of biologically active cations at localised tissue sites, and that these could be responsible for asbestos carcinogenesis. Metals such as manganese, which are high in the electromotive series, could have the effect of precipitating metals lower in the series when they dissolve.

If the role of trace metals in asbestos carcinogenesis is to be elucidated, more information is required on their distribution between fibre and contaminating minerals and alloys. Attempts to correlate carcinogenicity with trace metal concentration *per se* are pointless, since it is clear that they can be present

[1] Unpublished data.

ment. With the possible exception of the manganese of Chrysotile A, it appears that the UICC standard reference samples were not significantly contaminated during the milling process which was required to produce a high proportion of respirable material from the rough-milled samples (AR and BR in Table 1).

In addition to making measurements of trace metals in bulk samples of asbestos, Cralley *et al.* (1968) also determined the same metals in < 10 μm fractions, prepared by the sieving method of Kupel *et al.* (1968). They showed that, in some cases, the composition of the < 10 μm fractions differed considerably from that of the bulk material. As this sieving process must have the effect of concentrating the non-fibrous material in the < 10 μm fraction, a change in composition relative to the bulk material would be expected. Gibbs (1971) measured levels of cobalt, iron, manganese and nickel in different grades of chrysotile fibre from a number of mines in Quebec and found that the shorter grades invariably contained the highest concentration of all four metals.

Solubility of chrysotile asbestos

The solubility of chrysotile in mineral acids has been studied by a number of workers. Acids attack chrysotile by reacting with the hydroxyl groups on the surface of the fibrils. Electron micrographs of partially decomposed fibrils show that they consist of an inner layer of intact chrysotile and an outer layer of silicaceous residue. As decomposition proceeds, the electron diffraction pattern becomes weaker, although the fibre morphology is retained. Atkinson & Rickards (1971) showed that at room temperature, the rate of attack is directly proportional to acid concentration provided this is greater than 1 N; at lower concentrations, however, the rate of attack decreased more slowly, possibly because the diffusion of magnesium becomes the rate-controlling process. The reaction rate with fibrillar chrysotile is independent of acid type, provided the acid is fully ionised. Morgan *et al.* (1971b) studied the rate at which magnesium was leached from chrysotile fibres in N hydrochloric acid at 25°C. Leaching curves were obtained which showed that milling increases the magnesium solubility, but that the origin of the fibre is also an important factor. Intrinsic differences in solubility are attributed mainly to variations in the porosity of fibre bundles, but fibril diameter and the nature of the interfibrillar material may also play a part.

Using neutron-activated chrysotile, the same workers compared the leaching curves of the associated chromium, cobalt, iron and scandium with that of the magnesium; they were thus able to determine the fractions of these elements which were present as isomorphous substitutes for the magnesium. Virtually all the scandium appears to be present in this form in all the samples examined, presumably because its ionic radius is close to that of magnesium (Whittaker & Muntus, 1970). Generally, most of the non-magnetic iron, chromium and cobalt could be accounted for in the octahedral (brucite) layer of the fibre. In some samples from Quebec, however, a considerable fraction of the chromium is present in an insoluble non-magnetic phase (probably chromite).

Cralley *et al.* (1968) showed that trace metals associated with asbestos have a finite solubility in bovine serum; and Holmes & Morgan (1967), using neutron-activated chrysotile, found that the associated chromium and cobalt dissolved at a significant rate after its administration to rats by intrapleural injection.

Evidence is accumulating that chrysotile magnesium dissolves fairly readily *in vivo*. Langer *et al.* (1970) used the electron microprobe to analyse the Mg:Si ratio in fibres isolated from the lungs of animals and of workers occupationally exposed to asbestos. In both series they found ratios consistent with magnesium-depleted chrysotile. Recently, Pooley (1972) has examined chrysotile fibres, isolated from human lung, by electron diffraction and has been able to obtain characteristic diffraction patterns. Work with magnesium-depleted chrysotile, obtained by acid leaching *in vitro*, showed that such patterns could be obtained from fibres with up to half their magnesium removed; the fibres isolated from lung could therefore have lost up to half their magnesium *in vivo*.

Morgan *et al.* (1971a) have used a radioactive tracer technique to obtain information on the rate of magnesium dissolution *in vivo*. They selected samples of chrysotile in which most of the cobalt is present in the octahedral layer as an isomorphous substitute for magnesium and, after neutron irradiation, injected them intrapleurally into rats. As leached cobalt is excreted quite rapidly, the excretion of ^{60}Co was used as an index of magnesium solubility. The results indicate that the magnesium on the surface of the fibre (which accounts for 5–10% of the total) dissolves within a few days of administra-

in a variety of chemical and physical forms with varying solubility. As evidence accumulates that chrysotile magnesium dissolves at a finite rate *in vivo*, the effect of magnesium removal on the cytotoxicity and carcinogenicity of chrysotile should be investigated.

SUMMARY

The chemical characteristics of asbestiform minerals are described, with particular reference to the UICC standard reference samples. Measurements of the levels of chromium, cobalt, iron, manganese, nickel and scandium in a range of samples are reported, together with information on their distribution between fibre and accessory minerals. The solubility of structural and trace constituents of asbestos, both *in vitro* and *in vivo*, is discussed.

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