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SOME OBSERVATIONS ON THE DISTRIBUTION OF TRACE METALS IN CHRYSOTILE ASBESTOS

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Abstract—The distribution of iron, chromium, nickel, cobalt and scandium in a number of samples of chrysotile asbestos, including the standard reference samples prepared under the auspices of the International Union Against Cancer (UICC) was investigated. The composition of material separated magnetically from chrysotile was examined, using radioactive tracer methods. The solubility of these elements was measured by leaching samples of chrysotile in N hydrochloric acid at 25°C and compared with the solubility of the structural magnesium. These investigations show that all the metals considered can replace magnesium in the brucite layer of chrysotile. In addition, however, with the possible exception of scandium, they are also present in accessory minerals associated with the fibre.

INTRODUCTION

CHRYSOTILE is the most abundant member of the serpentine class of asbestiform minerals and accounts for over 90 per cent of the asbestos produced today. It is a magnesium silicate with composition $Mg_3Si_2O_5(OH)_4$. The basis of its structure is a sheet of silica tetrahedra. To one side of this is attached a sheet of brucite ($Mg(OH)_2$) 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 which is relieved by curvature, resulting in the hollow cylindrical morphology of the chrysotile fibril. Fibril diameters vary between 0.01 and 0.08 μm , but the mean values are generally in the range 0.03–0.04 μm (ATKINSON *et al.*, 1971). Chrysotile fibres consist of bundles of fibrils and it has been suggested that the voids between bundles are filled with a non-crystalline solid.

In addition to the major structural elements, chrysotile invariably contains trace metal impurities which may be present as (a) isomorphous substitutes for structural elements, (b) fragments of host rock or accessory minerals or (c) fine particles of alloy produced by the abrasive action of asbestos on processing equipment (CRALLEY *et al.*, 1967). The minerals most commonly found in association with chrysotile are magnetite (Fe_3O_4) and brucite, which may be intergrown with the fibre. Other minerals associated with chrysotile have been reported by a number of authors (FAESSLER and BADOLLET, 1947; SPEIL and LEINWEBER, 1969; GIBBS, 1971) and include actinolite, antigorite, awaruite, chlorite, chromite, magnesite and talc.

The role of trace metals in the aetiology of asbestos-induced cancers has been reviewed recently by HARINGTON (1973). HARINGTON and ROE (1965) considered the presence of chromium and nickel in chrysotile to be of possible significance, as these metals are known to be carcinogenic under certain circumstances. DIXON *et al.* (1970) have suggested that trace metals associated with inhaled asbestos could

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. Recently, CRALLEY (1971) has indicated that particles of metallic alloys, associated with asbestos fibres, could give rise to high concentrations of biologically active cations at localized tissue sites and that these could be responsible for asbestos carcinogenesis.

Because of the possible significance of trace metals in this context, it is important to establish their levels in various types of asbestos and particularly the standard reference samples, prepared under the auspices of the International Union Against Cancer (UICC) (TIMBRELL *et al.*, 1968). In fact, measurements of iron, chromium, cobalt, nickel, manganese and scandium in a range of samples, including the UICC materials, have been reported by CRALLEY *et al.* (1968) and HOLMES *et al.* (1971) using atomic absorption spectrophotometry (AAS) and neutron activation analysis (NAA) respectively. In addition to the concentrations of trace metals, however, information on their chemical form and solubility is also required and up to the present, little information on this aspect has been published. In the investigations described in this report, the leaching of trace metals in mineral acid has been used, together with other techniques, to obtain information on their distribution between the fibre and associated minerals.

MATERIALS

The samples of chrysotile asbestos used in this study included the following:

- The standard reference samples of Rhodesian and Canadian chrysotile (UICC A and B) and the rough milled samples (UICC AR and BR) from which the reference samples were prepared by milling.
- The eight samples of Canadian chrysotile from different mines which were blended to produce the standard reference sample of Canadian chrysotile. These are referred to as Canadian A-H.
- A sample of chrysotile from the Cassiar Mine in British Columbia used in an OECD project on non-metallic minerals. This is referred to as Cassiar AAA.

The UICC standard reference samples were milled to give a high proportion of fibres in the respirable range so that they could be administered to experimental animals by inhalation, without further treatment. The samples from the individual Canadian mines were ground in a different type of mill and are reported (TIMBRELL, 1971) to have a slightly shorter fibre length distribution than the UICC standard reference materials. The Cassiar AAA sample is rough milled and has a much coarser texture than the UICC reference samples. Measurements of iron, chromium, cobalt, manganese, nickel and scandium in these samples are listed in Table 1. In general there is satisfactory agreement between measurements made by different laboratories.

METHODS

Neutron activation of chrysotile

When chrysotile asbestos is irradiated with thermal neutrons, some of the constituents become radioactive. After two weeks, when the short-lived activation products have decayed, the γ -ray spectra of all samples of chrysotile examined have a

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characteristic appearance with major photopeaks due to ^{46}Sc , ^{51}Cr , ^{59}Fe and ^{60}Co . These radionuclides are all produced in (n, γ) reactions on the corresponding stable elements which are invariably present as impurities in, or associated with, chrysotile asbestos fibres. These activation products provide convenient tracers for the parent elements. To minimize radiation damage to the chrysotile structure, irradiations were generally restricted to 3 days in a flux of about $6 \times 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$.

TABLE 1. LEVELS OF TRACE METALS IN SAMPLES OF CHRYSOTILE FROM VARIOUS REGIONS

Source	Lab.	Fe (%)	Cr	Co	Mn (ppm)	Ni	Sc
Rhodesia (UICC A)	AERE	1.7	1390	55	450	1360	6
Rhodesia (UICC A)	DHEW	0.6	1378	54	393	1482	—
Canada (UICC B)	AERE	2.6	490	50	480	820	5
Canada (UICC B)	DHEW	1.2	317	45	444	802	—
Canada (Mine A)	AERE	4.8	520	63	540	720	5
Canada (Mine B)	AERE	3.5	780	110	580	1820	4
Canada (Mine C)	AERE	2.0	1200	60	420	1510	12
Canada (Mine D)	AERE	4.1	930	78	600	840	7
Canada (Mine E)	AERE	3.2	440	57	610	540	5
Canada (Mine F)	AERE	2.9	730	78	450	1790	8
Canada (Mine G)	AERE	1.9	480	44	420	1520	8
Canada (Mine H)	AERE	3.2	380	53	530	330	6
Cassiar AAA	AERE	1.5	590	47	—	1320	10
Cassiar AAA	TNAFL	1.35	350	60	400	1400	—
Cassiar AAA	UB	1.20	545	50	630	1400	11

AERE Atomic Energy Research Establishment, Harwell.

DHEW Dept. of Health Education and Welfare, Cincinnati.

TNAFL Asbestos Fibre Laboratory, Turner and Newall Ltd.

UB Postgraduate School of Studies, University of Bradford.

Separation of magnetic material from chrysotile

Magnetic fractions were separated from suspensions of neutron irradiated samples of chrysotile, which had been fully opened by both mechanical treatment with a Silverson mixer and ultrasonics. The separated magnetic material was dissolved following fusion with sodium peroxide and the associated activation products measured by γ -ray spectrometry. The fraction of the total iron, chromium, cobalt and scandium separated magnetically was determined by comparing the activity of separated activation products with that obtained by dissolving a weighed amount of the intact material, using the same fusion method.

Leaching in hydrochloric acid

Accurately weighed samples of neutron irradiated chrysotile (about 20 mg) were washed into glass tubes with 25 ml of N hydrochloric acid.* The tubes were stoppered and the chrysotile dispersed by brief hand shaking. The stoppered tubes were placed in a constant temperature bath at 25°C and the contents mixed by inversion once each day. After leaching for a predetermined time, the chrysotile was removed by centrifuging and 20 ml of the supernate taken for analysis by γ -ray spectrometry. The fraction of the total scandium, chromium, iron and cobalt leached was deter-

*Prepared from ARISTAR grade hydrochloric acid. BDH Chemicals Ltd., Poole, Dorset.

mined from measurements of ^{46}Sc , ^{51}Cr , ^{59}Fe and ^{60}Co in these supernates and in standards prepared by dissolving accurately weighed amounts of irradiated chrysotile following fusion with sodium peroxide. Measurements of magnesium, iron and nickel were also made on the supernates by atomic absorption spectrophotometry. The standards used in this case were prepared by dissolving chrysotile in a mixture of sulphuric and hydrofluoric acids (TRENT and SLAVIN, 1964). Although this treatment does not dissolve all the chromium in certain samples, it appears to be satisfactory for measurements of magnesium, iron and nickel.

Measurements of radionuclides by γ -ray spectrometry

The γ -ray scintillation spectrometer used for the detection of activation products consisted of a 48 cm³ coaxial lithium drifted germanium detector with a cooled FET input stage and low noise preamplifier. This was connected to an on-line computer system using 2048 channels for the accumulation of spectra. The numerical analysis of spectra was performed on an IBM 370/175 computer using an appropriate version of a general computer programme (SALMON, 1965).

Atomic absorption spectrophotometry

The measurements of iron, nickel and magnesium were made on a Perkin-Elmer Model 290B atomic absorption spectrophotometer. All analyses were carried out using a three slot Belling burner with an air/acetylene flame. The hydrochloric acid solutions were aspirated directly into the flame without any pretreatment. The concentrations of the elements in each solution were determined by direct comparison with standards prepared in N hydrochloric acid. It is well known that when nickel is determined in the presence of iron, some interference can be expected. This possibility was checked using the method of standard additions on a range of sample solutions. However, it was found that the concentration of iron in these samples was insufficient to affect the measurement of nickel.

RESULTS AND DISCUSSION

Separation of magnetic material

The fractions of the total iron, chromium, cobalt and scandium separated magnetically from various samples of chrysotile are shown in Table 2. The fraction of the total iron removed by this treatment varied from 19 to 53 per cent. Some of the

TABLE 2. PERCENTAGE OF THE TOTAL IRON, CHROMIUM, COBALT AND SCANDIUM ASSOCIATED WITH MAGNETIC FRACTIONS SEPARATED FROM CHRYSOTILE ASBESTOS

Source	Fe	Cr	Co	Sc
Rhodesia (UICC A)	26	6	10	<1
Canada (Mine A)	54	10	20	<1
Canada (Mine B)	58	4	22	<1
Canada (Mine C)	19	3	7	<1
Canada (Mine D)	41	10	13	<1
Canada (Mine E)	43	13	15	<1
Canada (Mine F)	55	12	23	<1
Canada (Mine G)	40	9	13	<1
Canada (Mine H)	36	6	23	<1

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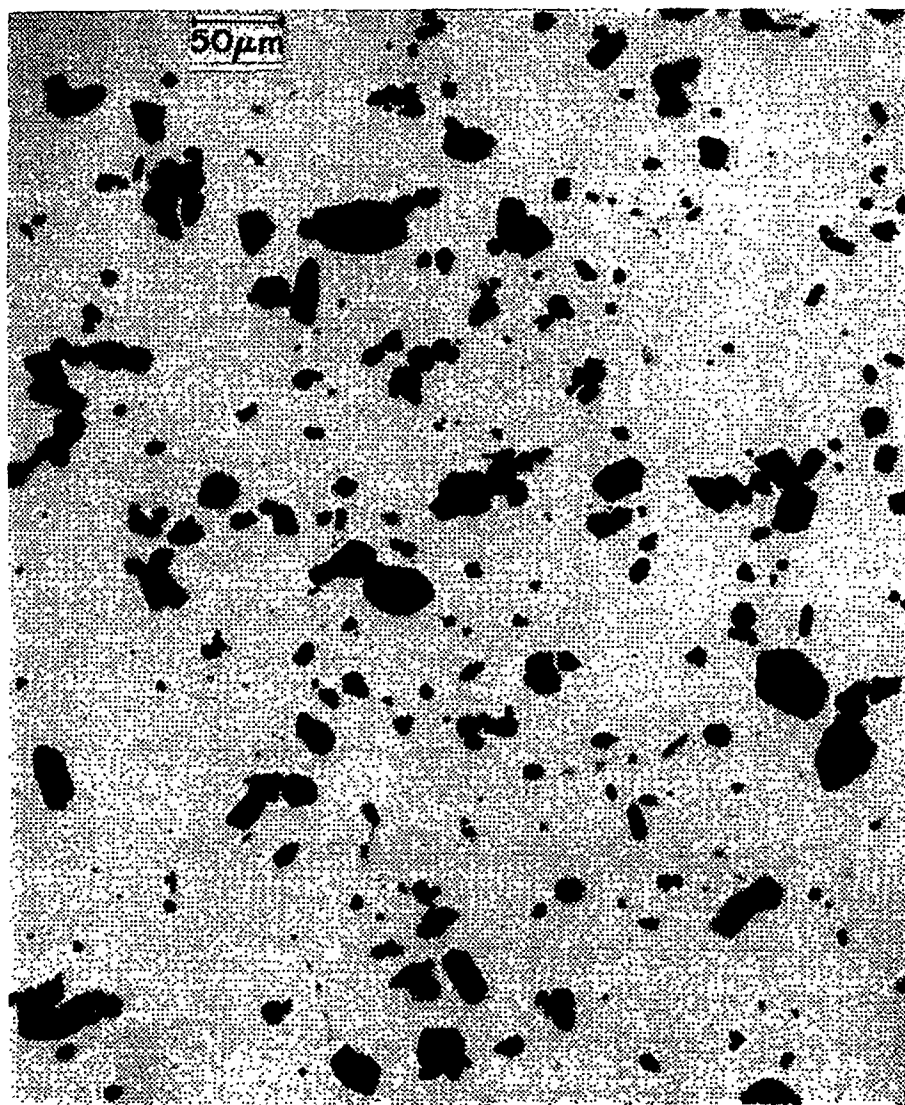


FIG. 1. Optical micrograph of particles of magnetite separated from a sample of Canadian chrysotile.

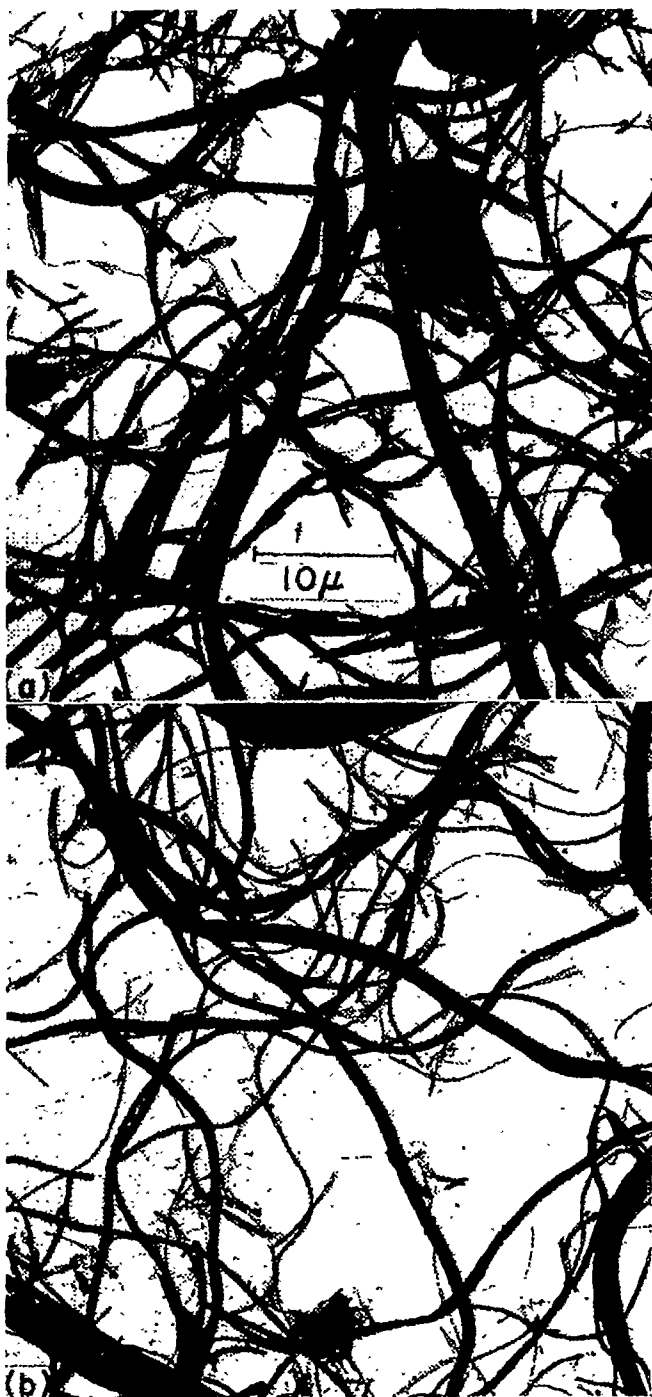


FIG. 2. Electron micrographs of the Rhodesian standard reference sample (UICC A). (a) Unleached (b) All magnesium removed by leaching in N hydrochloric acid.

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chromium (3–13 per cent) and cobalt (7–23 per cent) were also separated by this procedure, but in no case was any of the scandium removed. The material isolated by this technique consists mainly of irregular particles of magnetite generally less than 50 μm dia (Fig. 1). Treatment of the material, separated magnetically, with N hydrochloric acid at room temperature indicated that the cobalt was somewhat more soluble, and the chromium less soluble, than the iron. This implies that the chromium and cobalt are not homogeneously distributed in the separated magnetic fraction.

Solubility of magnesium in N hydrochloric acid

The solubility of chrysotile magnesium in mineral acids has been studied by a number of authors. Acids attack chrysotile by reaction with the hydroxyl groups and the magnesium is then free to diffuse out leaving a siliceous residue in place of the original lattice. Eventually all the magnesium can be removed by this treatment. The siliceous residue retains the fibrous morphology of the original chrysotile, but has little mechanical strength. Electron micrographs of intact and fully depleted chrysotile fibres (UICC A) are shown in Fig. 2.

The acid decomposition of fibrillar chrysotile has been studied by ATKINSON and RICKARDS (1971) who showed that the rate of reaction is directly proportional to acid concentration in the range 1–12 N. At concentrations lower than this, the rate of reaction decreases more slowly. A possible explanation is that at lower concentrations, the diffusion of magnesium ions out of the fibrils becomes the rate controlling process. The reaction proceeds from the outside of the fibril and a boundary can be seen in electron micrographs of partially leached fibrils which defines the extent of the reaction. No change in the chrysotile lattice can be detected in advance of the reaction boundary, either by X-ray or electron diffraction. In our own work, chrysotile fibres were used so that the rate of reaction was affected by interfibrillar as well as intrafibrillar diffusion.

The loss of magnesium from the UICC standard reference samples of chrysotile on leaching in N hydrochloric acid at 25°C is shown in Fig. 3 plotted against the square root of the leaching time. Also included are corresponding values for the loss

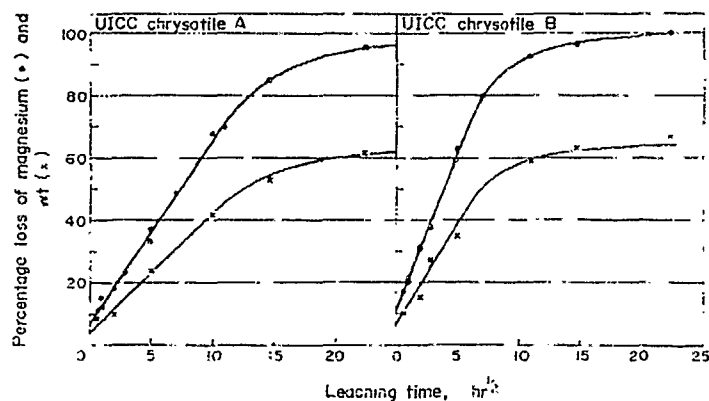


FIG. 3. Loss of magnesium (•) and weight (x) from UICC standard reference samples A and B on leaching in N hydrochloric acid at 25°C.

C A). (a) Unleached acid.

in weight, which appears to be somewhat greater than the theoretical value of 57 per cent when all the magnesium has been removed. This discrepancy is almost certainly due to the production, during leaching, of colloidal silica which is not separated by centrifugation. The loss of magnesium can be represented by a straight line, when correlated in this manner, until about 70 per cent has dissolved after which there is a departure from linearity.

It is apparent from Fig. 3, that the magnesium of chrysotile B dissolves more rapidly than that of A under these conditions. To compare the rate at which magnesium is dissolved, similar measurements were made on a number of samples of chrysotile and the slopes of the linear portions of the leaching curves obtained by linear regression. The results of these measurements are illustrated Fig. 4 which shows that magnesium in chrysotile obtained from mines in Quebec (Canadian A,

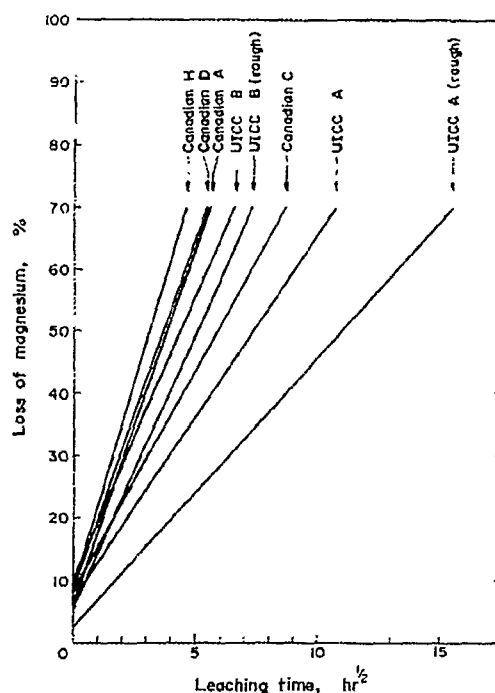


FIG. 4. Loss of magnesium from various samples of chrysotile on leaching in N hydrochloric acid at 25°C.

D and H) is most soluble. The solubility of magnesium in the UICC standard reference samples is greater than in the rough milled samples from which they were prepared. Clearly, milling increases magnesium solubility and this can be attributed to fibre shortening, fibre opening and lattice distortion. However, the fact that the magnesium of rough milled B dissolves more rapidly than that of the fine milled A indicates that other factors are as important as mechanical processing in determining magnesium solubility. Intrinsic variations in solubility are probably attributable to

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Canadian B dissolves more rapidly than the rate at which magnesium is dissolved in the other samples of chrysotile. The number of samples of chrysotile obtained by milling is indicated in Fig. 4 which shows that the intercept (Canadian A, Quebec)

differences in the porosity of fibre bundles and this in turn may reflect differences in the solubility of interfibrillar material.

It has been suggested that the intercept of leaching curves of this type gives an indication of the surface magnesium of a sample and, as shown in Fig. 4, milling has the effect of increasing the intercept as well as the slope of the leaching curve. However, the presence of free brucite in a sample also enhances the value of this intercept, so that some of the variation observed may be due to the presence of small amounts of this mineral. The Canadian sample B has been reported by WAGNER *et al.* (1970) to contain 20 per cent of brucite and as shown in Fig. 5 (B) this has the effect of increasing the intercept to about 35 per cent of the total magnesium.

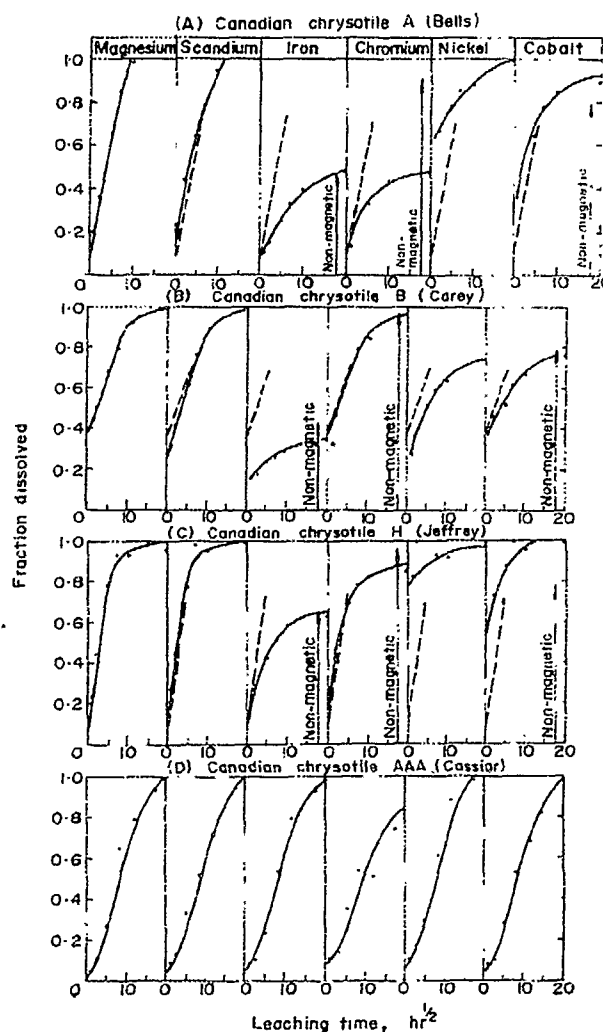


FIG. 5. Dissolution of magnesium and trace metals from various samples of chrysotile in N hydrochloric acid at 25°C.

in N hydrochloric acid

the UICC standard from which they were obtained. It can be attributed to the fact that the sample of the fine milled A was used in determining the leaching rate attributable to

Solubility of trace metals in N hydrochloric acid

In Fig. 5, leaching curves for magnesium, scandium, iron, chromium, nickel and cobalt are compared for different samples of chrysotile. The magnesium leaching curve (broken line) is superimposed on those of the trace elements. If a trace element is incorporated in the octahedral layer of chrysotile as an isomorphous substitute for magnesium then it will dissolve at the same rate in acid and if its ionic radius is similar to that of magnesium, it will diffuse out of the fibre at the same rate. If the trace element is only present in this form, then its leaching curve should superimpose on that of the magnesium. If, on the other hand, a fraction of the trace element is present as a relatively insoluble mineral then it will dissolve more slowly than the magnesium. By comparing the leaching rates of a trace element with that of the structural magnesium, it is possible to obtain information on its distribution.

In all samples examined, the rate of dissolution of the scandium matches that of the magnesium very closely. This indicates that scandium occurs in chrysotile almost exclusively as an isomorphous substitute for magnesium. It has been reported by WHITTAKER and MUNTUS (1970), that the ionic radii of these elements are similar and that it is likely that a charge balancing substitution of Sc, Al for Mg, Si may account for a substantial proportion of the scandium in ferro-magnesian minerals. It would appear therefore, that ^{46}Sc provides a useful long-lived radioactive tracer for magnesium, but its complex metabolism limits its usefulness in studies *in vivo*.

The leaching curves for iron show that in general, when all the magnesium has dissolved, only a fraction of the iron has passed into solution. The soluble component corresponds quite closely in most cases with the fraction of iron that cannot be separated magnetically. This component is indicated by the vertical line in Figs. 5(A)–(C). It appears therefore that some of the iron in these samples is present in the brucite layer and dissolves with the magnesium, while most of the remainder is accounted for by magnetite, which is relatively insoluble under these conditions.

In about half the samples examined, the chromium remaining undissolved when all the magnesium has been leached corresponds to that which can be separated magnetically. In the Canadian samples A, D, E and F however, it is apparent that only part of the insoluble chromium can be accounted for by that separated with the magnetite (see Fig. 5A). Unpublished work on the analysis of chrysotile shows that when measurements of chromium are based on solutions obtained by dissolving the fibre in boiling hydrofluoric acid, low values are obtained for the same four samples. Following treatment with hydrofluoric acid, relatively large, chromium rich particles can be observed when all the fibre has dissolved. Although these have not been identified, they probably represent chromite and their presence accounts for the observed discrepancies in the analysis of chromium.

It is clear that some of the cobalt in all samples examined is present in the octahedral layer and dissolves out of the fibre with the magnesium. In the Rhodesian standard reference sample, Cassiar AAA and Canadian samples C, D and G, most of the cobalt is present in this form. In practically all samples, a small fraction of the cobalt remains undissolved when all the magnesium has been removed and this appears to be accounted for in most cases by the cobalt which accompanies magnetite. In the Canadian samples A, D, E and especially H, part of the cobalt is present as a relatively soluble impurity, so that initially, the fraction of cobalt leached exceeded that of the magnesium (see Figs. 5A and C).

In general, the behaviour of nickel parallels that of cobalt. In cases where there is a relatively soluble cobalt component, rather more of the nickel appears to be in this form, so that there is a greater initial disparity in the nickel and magnesium leaching curves.

CONCLUSIONS

These investigations show that the distribution of trace metals in commercial chrysotile asbestos samples is complex. The metals examined can all be present as isomorphous substitutes for magnesium in the octahedral layer of the chrysotile fibril and scandium appears to be almost uniquely present in this form. In samples which contain little associated mineral impurity (e.g. Cassiar AAA) most of the other trace metals are contained in the brucite layer so that they dissolve at the same rate as the structural magnesium in mineral acids (see Fig. 5D). In most samples however, trace metals are also present in associated minerals and alloys, some of which are relatively insoluble (magnetite and chromite) and others relatively soluble with reference to structural magnesium.

In general, it is true to say that the concentration of most trace metals is very much greater in the mineral and alloy impurities associated with chrysotile than in the fibre itself. This accounts for the observations of KUPPEL *et al.* (1968) who showed that the concentration of trace metals in 10 μ m sieve fractions of asbestos frequently differed considerably from that in the bulk material. GRUBBS (1971) has pointed out that trace metals tend to be concentrated in the respirable fraction of airborne dust encountered in Canadian chrysotile mills.

It has been shown by HOLMES and MORGAN (1967) that trace metals associated with chrysotile dissolve at a significant rate following its administration to rats by intrapleural injection. More recently, MORGAN *et al.* (1971) using chrysotile in which most of the cobalt is present in the brucite layer, showed how the excretion of ^{60}Co can be used as an index of magnesium solubility *in vivo*. In the same paper it was shown how the distribution of trace metals between fibre and associated mineral affects their solubility *in vivo*.

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