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ROOM-TEMPERATURE MAGNETIZATION MEASUREMENTS OF SOME CANADIAN CHRYSOTILE AND UICC* ASBESTOS SAMPLES

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ABSTRACT

The room-temperature magnetic properties of several Canadian chrysotiles, as well as UICC standard reference samples of chrysotile and amphibole asbestos, have been investigated. For the Canadian chrysotile, the paramagnetic susceptibility χ was measured to be in the range 1.9 to 3.5 x 10^{-6} emu/gOe. This is in good agreement with the corresponding calculated values. The values of χ for the UICC amphibole sample range from 7.8 to 71.5 x 10^{-6} emu/gOe, also in good agreement with the Curie–Weiss values. For the UICC chrysotile samples, however, the measured values, 3.8 to 9.2 x 10^{-6} emu/gOe, are two to four times the corresponding calculated values. This discrepancy can be attributed to the presence of superparamagnetic magnetite impurities in the UICC chrysotiles. The UICC amosite and anthophyllite samples show high values of the coercive force H_C, 183 Oe and 428 Oe, respectively, and of the reversal field H_{CR}, 731 Oe and 829 Oe, respectively. This, together with the spectrographic analysis of the samples, suggests the presence of titanomagnetite impurities. The coercive force and reversal field of the other samples can be explained in terms of the magnetic properties of magnetite impurities. On the basis of the measurements of H_C and H_{CR}, as well as the remanent and saturation magnetizations, we conclude that all of the asbestos samples, with the exception of crocidolite, show the presence of a range of particle sizes for the magnetic impurities. The magnetic properties of the crocidolite sample show evidence of pseudo-single domain, equidimensional magnetite with grain sizes between 3.8 and 6.4 μm.

Keywords: magnetization, chrysotile, anthophyllite, amosite, crocidolite, asbestos, magnetite.

SOMMAIRE

On a étudié les propriétés magnétiques à température ambiante de plusieurs échantillons de chrysotile canadien, ainsi que celles d'étalons UICC de chrysotile et d'amphibole asbestiforme. Les chrysotiles canadiens possèdent une susceptibilité paramagnétique χ dont les valeurs mesurées s'étalent entre 1.9 et 3.5 x 10^{-6} emu/gOe, ce qui concorde bien avec les valeurs calculées. Pour l'amphibole asbestiforme UICC, χ va de 7.8 à 71.5 x 10^{-6} emu/gOe, valeurs qui concordent aussi avec les prédictions Curie–Weiss. Pour les étalons UICC de chrysotile, cependant, les mesures, qui se situent entre 3.8 et 9.2 x 10^{-6} emu/gOe, surpassent les valeurs calculées par un facteur de 2 à 4. Ce décalage serait dû à la présence d'impuretés de magnétite superparamagnétique. Les échantillons UICC d'amosite et d'anthophyllite montrent des valeurs élevées de la force coercitive H_C (183 et 428 Oe, respectivement) et du champ d'inversion H_{CR} (731 et 829 Oe, respectivement). Ces observations, ainsi que les données analytiques obtenues par spectrographie, font supposer la présence d'impuretés de titanomagnétite dans ces deux étalons. La force coercitive et le champ d'inversion des autres échantillons peuvent s'expliquer par les propriétés magnétiques des impuretés de magnétite. Les mesures de H_C, de H_{CR}, ainsi que des magnétisations rémanente et de saturation, indiquent dans tous les échantillons asbestiformes, sauf la crocidolite, un domaine de variation granulométrique des impuretés magnétiques. On attribue les propriétés magnétiques de la crocidolite à des domaines de magnétite, pseudo-monocristallins et équidimensionnels, dont la taille oscille entre 3.8 et 6.4 μm.

(Traduit par la Rédaction)

Mots-clés: magnétisation, chrysotile, anthophyllite, amosite, crocidolite, amphibole asbestiforme, magnétite.

INTRODUCTION

Recently, the magnetic properties of asbestos and the impurities associated with it have been used in a variety of applications. For example, the remanent field of magnetite impurities in asbestos has been used by Cohen (1978), Stroink (1980) and Stroink *et al.* (1981) to estimate the amount of respirable asbestos dust in the lungs of miners. The magnetic properties of asbestos also serve to align the fibres, suspended in a fluid, in an external magnetic field; they allow one, using the degree of

*Union Internationale Contre le Cancer.

alignment, to identify different types of asbestos fibre (Timbrell 1975) and to estimate fibre quantities (Timbrell 1975, Riss & Chatfield 1981). However, despite the value of such research and the necessity for a good understanding of the magnetic properties of the asbestos itself, little work has been done on the actual magnetic characteristics of different types of asbestos. Here we present the results of magnetization measurements of chrysotile asbestos from four distinct Canadian mining regions, as well as measurements on the UICC standard reference samples of chrysotile and amphibole asbestos. These measurements complement our previous Mössbauer measurements of the Canadian chrysotiles (Blaauw *et al.* 1979) and the UICC samples (Stroink *et al.* 1980).

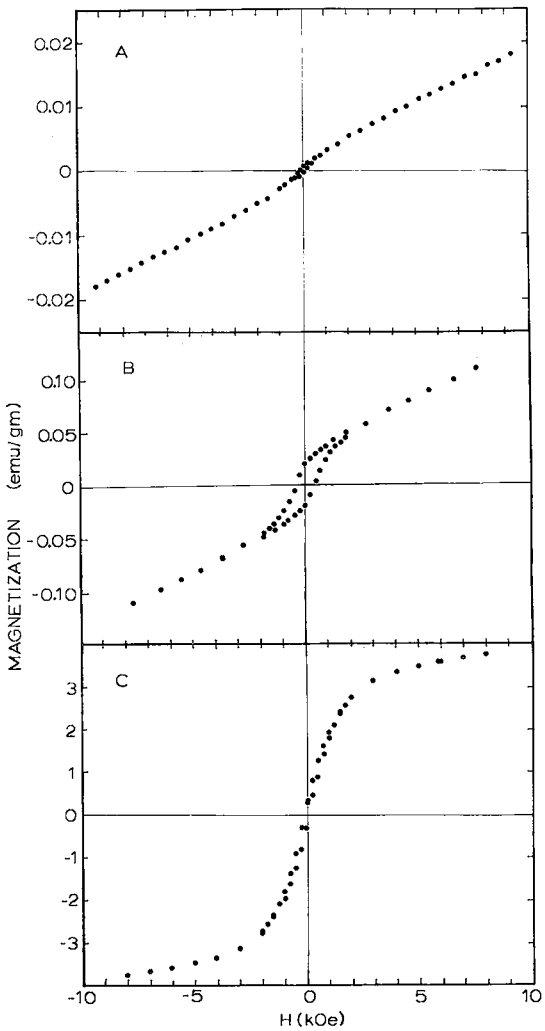

FIG. 1. Magnetization curve for three asbestos samples for applied fields up to 10 kOe: A chrysotile from Cassiar, B.C., B UICC anthophyllite and C UICC crocidolite.

SAMPLE MATERIALS AND EXPERIMENTAL METHODS

The Canadian chrysotile samples were obtained from four different mining regions: (a) Cassiar Asbestos Corp. Ltd., Clinton Creek, Yukon Territory, (b) Cassiar Asbestos Corp. Ltd., Cassiar Mine, Cassiar, B.C., (c) Asbestos Corp. Ltd., British-Canadian and King Beaver Mines, Thetford, Quebec, and (d) Canadian Johns-Manville Co. Ltd., Advocate Mine, Baie Verte, Newfoundland. These samples were prepared by separating the fibres by hand from the different ore samples. Care was taken that no observable impurities were present in the resulting materials, which were then crushed to prevent any preferential orientation of the fibres. Powder X-ray-diffraction measurements showed small traces of impurities of the type found by Badolett & McGourty (1958). We do not expect these small quantities to influence the interpretation of the magnetic measurements.

The magnetic properties of five UICC samples, Canadian chrysotile, Rhodesian (Zimbabwean) chrysotile, Finnish anthophyllite, South African amosite and South African crocidolite, were also measured. These samples consist primarily of respirable fibres as defined by the Johannesburg Conference on Pneumoconiosis. This type of particle-size distribution has been discussed by Trudeau (1979). The actual fibre-length distribution of the UICC samples has been compared with the Johannesburg distribution by Timbrell (1970).

Room-temperature magnetization measurements were made using a PAR–155 vibrating sample magnetometer. Samples were prepared by compressing approximately 100 mg (approximately 0.05 cm^3) of the asbestos dust in a teflon holder by means of a threaded rod. Previous Mössbauer measurements on UICC asbestos samples (Stroink *et al.* 1980) have indicated that samples prepared in this way have randomly oriented fibres. The magnetization of the samples was obtained from our measurements after subtracting the diamagnetic contribution due to the empty sample holder.

EXPERIMENTAL RESULTS

The magnetization curves of all the samples

show some hysteresis at low fields ($H \lesssim 1$ kOe) and a constant positive slope for large fields ($5 \lesssim H \lesssim 10$ kOe). Typical magnetization curves for the asbestos minerals are shown in Figure 1. The paramagnetic susceptibility χ is given as the slope of this curve in the high-field region. It was assumed that the magnetization of any magnetic impurities in the samples was saturated for large applied fields and did not contribute to the susceptibility. The saturation magnetization M_s is the intercept with the $H = 0$ axis of the high-field part of the curve extrapolated back to the magnetization axis. Values of χ and M_s were obtained from a least-squares fit of the high-field data and are given in Tables 1 and 2, respectively.

From the details of the hysteresis loop in the magnetization curve, we obtained the remanent magnetization M_r as the intercept on the $H = 0$ axis, and the coercive force H_c as the intercept on the $M = 0$ axis. We also measured the low-field susceptibility χ_0 and the coercivity of remanence (reversal field) H_{CR}, that is, the reverse field necessary to leave the sample with zero magnetic moment after saturation. The results of these measurements are given in Table 2. Because of the small values of the low-field susceptibility in two of the Canadian chrysotiles (a and b), we are unable to obtain reliable values of H_{CR} but estimate that they would be less than 100 Oe.

TABLE 1. CALCULATED AND MEASURED VALUES OF THE HIGH FIELD SUSCEPTIBILITY

Sample	% iron	χ_{calc} ($\times 10^{-6}$	χ_{meas} emu/g0e)
Canadian chrysotile a	1.12	2.6	2.3
Canadian chrysotile b	1.04	2.4	2.2
Canadian chrysotile c	0.91	2.1	1.9
Canadian chrysotile d	1.28	2.9	3.5
UICC Canadian chrysotile	1.04	2.4	9.2
UICC Rhodesian (Zimbabwean) chrysotile	0.85	1.9	3.8
UICC Finnish anthophyllite	4.4	10.1	7.8
UICC South African amosite	28.0	64.0	69.9
UICC South African crocidolite	27.0	62.0	71.5

Discussion

Susceptibility of asbestos

The Curie–Weiss law gives the paramagnetic susceptibility of a material in terms of the concentration of the magnetic ions n, its atomic weight M and effective magnetic moment μ:

$$\chi = \frac{n\mu^2 N_o}{3kM(T-T_c)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

N_o is Avagadro's number, k the Boltzmann constant and T_c the Curie temperature. In the asbestos samples considered, the presence of iron is responsible for the magnetic behavior. The value of the effective magnetic moment of the Fe ions is obtained from the ionic state of the iron. Previous Mössbauer measurements on the Canadian chrysotiles (Blaauw *et al.* 1979) and the UICC samples (Stroink *et al.* 1980) have shown that the iron in these materials occurs in the high-spin Fe^{2+} and Fe^{3+} states. For the susceptibility calculations, an average value for high-spin iron of 5.5 μ_B was used (Earnshaw 1968). For the samples studied here, the Curie temperatures have been found to be small or zero (Thornton *et al.* 1974); thus, we have used $T_c = 0$ K.

TABLE 2. HYSTERETIC PROPERTIES OF THE ASBESTOS SAMPLES

Sample	M_s ($\times 10^{-3}$	M_r emu/gm)	H_c (Oe)	H_{CR} (Oe)	M_r/M_s	H_{CR}/H_c	χ_0 ($\times 10^{-6}$emu/g0e)
Canadian chrysotile a	12	0.3	21	-	0.025	-	0.12
Canadian chrysotile b	1.7	0.2	44	-	0.12	-	0.04
Canadian chrysotile c	73	3.2	13	76	0.044	5.8	2.7
Canadian chrysotile d	620	8.0	12	84	0.013	7.0	6.1
UICC Canadian chrysotile	1560	80	61	286	0.051	4.7	9.3
UICC Rhodesian (Zimbabwean) chrysotile	601	40	78	301	0.067	3.9	3.8
UICC Finnish anthophyllite	36	15	428	829	0.42	1.9	0.42
UICC South African amosite	68	21	183	731	0.31	4.0	0.88
UICC South African crocidolite	3170	220	103	368	0.069	3.6	13.8

Calculated values of the susceptibility are given in Table 1. The values of the iron concentration in the asbestos fibres were obtained from previous neutron-activation, electron-microprobe and Mössbauer-effect measurements (Timbrell 1970, Blaauw *et al.* 1979, Stroink *et al.* 1980).

Table 1 shows that the measured values of the susceptibility are close to the predicted ones in all cases except for the UICC Canadian chrysotile and the UICC Rhodesian (Zimbabwean) chrysotile. For these samples, the measured susceptibilities are considerably larger than the predicted values based on their iron content. We suspect that ferrimagnetic magnetite impurities are not saturated in these materials at fields of $5 < H < 10$ kOe and, consequently, contribute to the measured high-field susceptibilities. This is discussed further in the next section.

Magnetite

At room temperature, magnetite is ferrimagnetic; however, its magnetic properties are dependent upon the size and shape of the particles. Where the size of the particles is much smaller than the size of a single domain (SD), magnetite is superparamagnetic (SPM). Where the particles are single domain or pseudosingle domain (PSD), they have large M_r and H_{CR} values (Stacey & Banerjee 1974, Dunlop & Bina 1977).

The total amount of magnetite in each sample can be estimated from the saturation magnetization M_s. This quantity is divided by the saturation magnetization of pure magnetite at room temperature, 92 emu/g, to yield the magnetite concentration. The resulting values are given in column (a) of Table 3. The values are consistent with the values obtained from our previous Mössbauer work.

TABLE 3. CONCENTRATION OF MAGNETITE IN ASBESTOS MINERALS*

Sample	Weight % Magnetite a	b
Canadian chrysotile a	0.0013	0.0075
Canadian chrysotile b	0.0018	0.0143
Canadian chrysotile c	0.079	0.23
Canadian chrysotile d	0.67	0.57
UICC Canadian chrysotile	1.7	5.7
UICC Rhodesian (Zimbabwean) Chrysotile	0.65	2.9
UICC Finnish anthophyllite	0.039	1.1
UICC South African amosite	0.074	1.5
UICC South African crocidolite	3.4	15.7

*Obtained as follows: (a) $100 \times M_s/92$, (b) $100 \times M_r/1.4$.

Column (b) of Table 3 contains a similar estimate based on the remanent magnetization. The remanent magnetization of each sample is divided by the remanent magnetization of multidomain (MD) magnetite, 1.4 emu/g (Parry 1965). In all cases except for the Baie Verte chrysotile (sample d), the estimate based on the remanent magnetization is larger than that based on the saturation magnetization, suggesting the presence of SD or PSD magnetite particles in the samples. We are not aware of other techniques that have been used to estimate the magnetite concentration in the UICC samples.

The magnetic properties of SD and PSD magnetite particles have been the subject of a number of recent investigations (Dunlop & Hale 1976, Day 1977, Dunlop & Bina 1977, Day *et al.* 1977, Moskowitz & Banerjee 1979). These studies have shown that the values of H_C and M_r for equidimensional magnetite grains increase as the particle size decreases below about 15 μm. For particles of less than about 250 Å, magnetite becomes superparamagnetic. On the basis of these studies, a rough classification of the magnetic properties of equidimensional magnetite grains can be made on the basis of particle size (Table 4).

Comparing the measured values of M_r/M_s and H_{CR}/H_C in Table 2 with the values given in Table 4, we see that all three UICC amphiboles contain PSD particles. However, as might be expected with natural samples, with the exception of crocidolite, the values cannot be attributed to particles of only a single size. Comparing the parameters given in Table 2 with similar data obtained for different grain-sizes of magnetite (Day *et al.* 1977), we find that the grain-size distribution of the magnetite particles in crocidolite is relatively narrow, between approximately 3.8 and 6.4 μm. For the other amphibole sample, however, the values of H_{CR}/H_C and M_r/M_s are larger than those expected for equidimensional magnetite. Either the values that we have measured are more common for titanomagnetites (Day *et al.* 1977),

TABLE 4. CLASSIFICATION OF THE MAGNETIC PROPERTIES OF MAGNETITE GRAINS BASED ON PARTICLE SIZE

Size (μm)	Classification	Magnetic Parameters
<.025	SPM	$H_C \simeq 0$, $M_r \simeq 0$
.025 < d < .05	SD	$H_R/H_C < 1.5$, $M_r/M_s \simeq 0.5$
.05 < d < 15	PSD	$1.5 < H_R/H_C < 4$, $0.02 < M_r/M_s < 0.5$
>15	MD	$H_R/H_C > 4$, $M_r/M_s \simeq 0.017$

or they could indicate needle-shaped magnetite particles (Evans 1977).

The presence of titanomagnetite in UICC anthophyllite and amosite is consistent with the spectrographic analysis of the UICC samples (Timbrell 1970); these results show that the amount of Ti in these samples is similar to the amount of Fe_3O_4 estimated by us in the samples (Table 3, column a), but that the Ti quantities in the other UICC samples are small in comparison with their magnetite content.

The presence of needle-shaped SD magnetite inclusions could explain, at least in part, the alignment of some amphibole fibres perpendicular to an applied magnetic field when suspended in a fluid. However, only very rarely have needle-shaped magnetite or titanomagnetite particles been observed, by means of electron microscopy, near or attached to amphibole asbestos fibres (N. Rowland, priv. comm. 1980, Cressey & Whittaker *in prep.*).

Evidence for the presence of magnetite in the Mössbauer spectra obtained on specimens of chrysotile indicates that magnetite is indeed responsible for the magnetic behavior of the samples. The small quantities of magnetite present in Canadian chrysotiles a and b, and consequently the small value of χ_0 in these samples, together with the relatively small values of H_C, show how no reliable values for H_{CR} could be measured in these samples.

A comparison between the magnetic data of the chrysotile samples and those of Table 4 shows that, with the exception of sample d (Baie Verte) and possibly sample a (Clinton Creek), the samples contain some PSD particles. The larger values for H_C and H_{CR} in the UICC chrysotile samples suggest that those specimens, ground from bulk commercial samples (Timbrell *et al.* 1968), contain a larger fraction of PSD particles than the "clean", hand-picked fibres. In addition, the high-field susceptibility suggests that a certain fraction of the magnetite particles in the UICC chrysotile samples is superparamagnetic; measurements at low temperatures might confirm this.

It is difficult to draw any definite conclusions concerning the low-field susceptibility χ_0. As pointed out previously (Dunlop 1977), the initial susceptibility of PSD particles depends on H_{CR}, but in our samples this dependence is obscured by our poor knowledge of the distribution of MD, PSD and SPM particles. Only in the case of the crocidolite, containing magnetite of a fairly well-defined particle-size, can we confidently compare our values with literature values on PSD particles of magnetite. By assuming that χ_0 is a result of magnetite only, we divide the observed value of χ_0 in crocidolite by the magnetite content (Table 3, column a) and obtain a value of 0.21 G/Oe, in good agreement with the measurements on magnetite of similar particle sizes by Day *et al.* (1977) and Parry (1965).

Finally, we would like to comment on the use of the remanent field of asbestos to estimate the magnetite content in asbestos and, from this, the total amount of asbestos dust in the lungs of asbestos miners (Cohen 1973, Stroink *et al.* 1981). Columns (a) and (b) in Table 3 show that the use of the remanent field of multidomain magnetite to estimate the magnetite content in asbestos is unreliable because of the presence of SD and PSD particles of magnetite in most asbestos samples. However, if the remanent magnetic field *per* unit mass of respirable dust samples from a particular mine or mill are fairly constant in time, then this remanent field can be used for this estimate. Preliminary results of isothermal remanent magnetization (IRM) measurements on respirable asbestos dust (Stroink 1980) show that IRM_{max} of this dust at two locations in the mill did not change significantly during a one-year period. Additional investigations to settle this point are necessary. The measurements here show, however, that the complete M–H curve of the sample is necessary to obtain a better understanding of the nature of magnetism in asbestos.

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