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ELECTRON-MICROSCOPIC DETERMINATION OF CHRYSOTILE CONTENT OF HEDMAN CATIONIC FIBRE

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I Introduction

The purpose of this study has been to analyze samples of a mineral powder, described as being predominantly lizardite, which is called "Hedman Cationic Fibre" to determine the quantity and distribution of the chrysotile asbestos fibre content. Two lots of material, identified as 2811B and 2910A by Hedman Mines Limited, were examined.

Samples for electron microscopy were prepared by using a new technique which provides a uniform and representative dispersion of particles on a specimen support. Ultrasonic agitation was not used.

Samples of the material were examined in a JEM 100U transmission electron microscope (TEM) in which selected area diffraction was used to differentiate between chrysotile and non-chrysotile matter. A Cambridge Stereoscan scanning electron microscope (SEM) was then used to obtain photographs of a number of dispersed samples.

To assist with particle measurement and counting, automatic data logging was employed. Thus it was possible from SEM photographs

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2167

to size over 9000 particles with two dimensions measured on each particle. Five separate powder samples were taken from the material provided. From these, 11 pairs of photographs were made, each pair comprising a high (4000X) and low (1000X) magnification picture of the same general area of specimen.

The data was analysed using a special computer program and the following information derived from each photograph:

- a) content by weight of chrysotile;
- b) content by volume of chrysotile;
- c) number percent of all chrysotile fibres, which are longer than 5 micrometers;
- d) weight percent of all particles, which consist of chrysotile fibres longer than 5 micrometers;
- e) number of fibres longer than 5 micrometers per milligram of Hedman material;
- f) average fibre length.

Inspection of the results indicated that the dispersions were indeed sufficiently uniform and that enough data was obtained to provide a representative analysis of the material supplied.

II Sample Preparation

In order to provide a suitable sample for purposes of particle counting it was necessary to disperse the material so as to be suitable for electron microscopic examination. In all cases distilled water which had been filtered through a 0.1µm filter was used as the dispersing medium.

In an initial attempt to solve the dispersion problem, samples were added to 500ml of water and then vigorously shaken by hand before dilution to 1 part in 200. They were then centrifuged onto cover glasses at 7000G for thirty minutes. A TEM examination of the sample revealed widely dispersed chrysotile, plate-like and clay-like matter. Further samples exhibited a distribution consisting of widely dispersed clumps of particles which were generally not suitable for quantitative evaluation.

The next method attempted involved dilution as before with 0.01718gms of material (randomly selected from various areas of one of the Hedman lots) into 110ml distilled and filtered water, of which 10ml was further diluted in 90ml of water so that the final concentration was 15.61 micrograms per ml of solution. 50ml of this solution was then deposited onto a filter (0.1µm Millipore) by vacuum filtration so that

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the sample deposited was 7.81×10^{-4} gm of Hedman material.

The filter material was dissolved on a mesh support in acetone over TEM grids with previously prepared carbon grids.¹ These specimens proved to be satisfactory for TEM examination.

The final method of sample dilution settled upon used the concentrations, manual shaking method, and vacuum filtration as described above. However, Nuclepore filters (0.1 μ m pore size) were substituted for the Millipore filters. These filters were then cut into pieces which were mounted directly in the SEM for examination. In this way, the time-consuming and possibly clump-causing filter dissolution step was eliminated and the background picture was less confusing than the paper filter, which is fibrous, or carbon film which can break and sag.

The adopted method consisted then, of simple dispersion, hand agitation and vacuum filtration only. Violent mechanical methods, such as ultrasonic agitation or centrifuging, are not involved and total sample collection provides an easy check of uniformity of distribution over large sample areas.

Five filters were prepared by this method, three from lot

2170

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#2910A and two from lot #2811B and two areas were cut from each of these filters for SEM examination.

III Microscopic Examination and Identification

Observation of dispersed samples using an optical microscope revealed a large number of particles below 5 microns. For this reason optical methods could not be used for analysis due to the limited resolving power of the optical microscope.

A mixture of fibrous and non-fibrous particles was observed when the samples were examined in a TEM at magnifications up to 20,000X. The particles that appeared to be fibrous were found to have an electron diffraction pattern identical to that of chrysotile. The particles that appeared amorphous seldom exhibited any diffraction pattern at all, and those that appeared flaky were found to have diffraction patterns similar to mica which does not resemble that of chrysotile (Figures 1 and 2).

The samples prepared for TEM examination were not as well dispersed as those prepared for the SEM. Furthermore, the larger particles or fibres were often opaque or too long for proper identification and sizing in the TEM.

FOS-00-0000022847

2171

It was therefore decided to do all of the work using the SEM. This meant that identification was purely visual since the SEM does not permit electron diffraction. Further TEM examination confirmed, however, that the visual identification criteria were satisfactory.

IV Counting Method

Examination in the SEM indicated that the non-chrysotile particles could be approximated by spheres and therefore a single measurement of diameter is sufficient; chrysotile on the other hand is tubular and requires measurements of both length and diameter. Results showed that it was possible to assume that the chrysotile fibres were approximately circular in cross section, or that, where they were obviously oval, an equivalent circular cross section could be estimated with a reasonable degree of accuracy. The stereo pairs shown in Figure 3 lend further support to this assumption.

The volume of non-chrysotile matter is calculated as $\frac{4}{3}\pi D^3/8$ where D is the diameter of the equivalent sphere. The chrysotile volume is $L\pi D^2/4$ where L is the fibre length and D is the diameter of the equivalent cylinder.

2172

FOS-00-0000002848

After a sample had been prepared by the technique described above, SEM pictures were taken from randomly chosen areas of the filter and photographs were taken at two nominal magnifications. Enlargements of nominal size 8" x 8" were made from these SEM pictures such that the final magnifications were of the order of 1000X and 4000X. In practice the specific magnifications were measured for each enlargement by comparison to the original SEM photograph, of which the magnification was known. Typical pictures are shown in Figures 4 to 7.

The pictures were measured using semi-automatic data acquisition equipment and analyzed by means of a computer program for this purpose. The data acquisition system consisted of a Carl Zeiss TG23 size counter, a Fluke 8300A digital meter and a Hewlett Packard 3489A data punch. The Zeiss instrument contains a variable diameter lightspot which is projected through the photograph from the back. The operator turns a wheel to adjust the lightspot diameter to match one dimension of a particle and a precision potentiometer mounted coaxially with the shaft of the wheel is automatically turned in the same proportion. The potentiometer has a linearity of 0.15% and varies from approximately 1000 to 9000 ohms. Its resistance value is read by the digital meter to four figures precision when a foot switch is depressed. At the same time, the footswitch causes a needle to punch a hole in the

FOS-00-0000002849

photograph at the centre of the measured particle, so that it will not be counted twice. The digital resistance measurement is transmitted to the datapunch where it is translated into ASCII code and punched onto a paper tape. Thus a record of all measurements is made automatically at the rate of about 20 measurements per minute.

The operators have been trained to recognize chrysotile by its fibrous or cylindrical form and make two readings, the first being length, the second diameter. All other material is read twice at the same wheel setting.

The computer program (Appendix III) has been designed to distinguish non-chrysotile records by recognizing those pairs of adjacent readings which are within 4 ohms of each other. Chrysotile is recognized by the sequence of a higher and a lower number. If extraneous readings have been introduced by the operator, they are recognized by the fact that they cause the readings to get out of step such that some low-high number combinations occur. When this happens, these data and the adjacent data are printed out by the computer and may be corrected by the operator at the computer terminal. Measurements which exceed the size of the lightspot (typically less than 1% of the total number) are measured by means of a vernier caliper and entered into the program from the terminal keyboard.

Once the data has been read and corrected by the computer,, the magnification and range factors are fed into it along with the sample number. A calibration of the lightspot size has been made using size standards and this is included in the computer program. The computer sorts the data, makes the required calculations and prints out the final data in the form shown in Appendix II.

It is possible to estimate the total particle mass of any observed area by calculating that area (from the photograph and the magnification factor), dividing by the effective filter area (908mm^2) and multiplying by the sample mass. This also is done by computer and is printed out with the final results as a check of accuracy as will be discussed below.

Examination of the literature revealed no clear cut value for the density of lizardite except for one reference² which gave a value of approximately 2.55gm/cm^3 . The tabulated³ value for chrysotile of 2.56gm/cm^3 falls near this value; therefore, it was decided to use the chrysotile density for all material. Consequently, the mass and volume distributions are identical. The validity of this assumption is supported by the agreement which was subsequently found between mass calculated on this basis for all particles in the sample area and mass interpolated from the total weighed mass distributed over the whole

sample area.

The data collected follows in Appendix II. The chrysotile particles are sorted into categories by length, these categories separated logarithmically. The lengths are listed in the first column and the accumulated numbers of fibres below each length are listed in the second. The number percents calculated with respect to the total number of fibres counted are listed in the third and the mass percent with respect to total fibre mass are listed in the fourth column. The amount above any particular length may be found by subtracting the given figures from 100%. This is how the "number percent longer than 5 microns" is determined.

The mass of the sample is computed by totalling the particle weights (estimated volumes x density). The value obtained is compared with that estimated from the gross sample weight as described above (1 nanogram = 10^{-9} grams or 10^{-6} milligrams). The comparison shows that deviation between the two values is typically less than 45% with a few values in excess of 70% these latter all being positive. Inspection of the related photographs showed that major discrepancies could often be explained by an unusually large particle in the field of view upsetting the distribution. Generally the agreement between the two mass estimates can be regarded as evidence that the sampling

methods are adequate.

The percent mass of chrysotile is calculated with respect to the total sample mass, which is then subdivided into the mass percent of fibres longer than 5 microns. Finally the number of fibres longer than 5 microns per milligram of material is calculated.

The values obtained are summarized in Appendix I. The second figure attached to each mean value consists of twice the standard error. That is, the probability of finding the true mean, i.e. that which is calculated from an extremely large number of samples, lies between the limits set by this figure is 95%. The standard error of the mean has been calculated by dividing the standard deviation of the mean by the square root of 11, the number of samples over which each mean value is calculated.

The average percent of fibres found per photograph was about 22% and the counts at high and low magnification agreed within experimental accuracy. The fibre mass computed at 1000X magnification as a percent of total mass was felt to give a more significant value as it included larger (and therefore higher mass) fibres. Its value was found to be $19.7 \pm 5.5\%$.

Although the total number percents of fibres are within experimental accuracy of each other at the two magnifications, figures for number percent greater than a given length are functions of the magnifications, as the latter determines the range of measurable sizes. The effective range is $1\mu\text{m}$ to $200\mu\text{m}$ at 1000X and $.25\mu\text{m}$ to $50\mu\text{m}$ at 4000X. The lower limit is determined by the minimum lightspot size and the upper limit is estimated as the length of one side of the photographic enlargements used for measurement. Since the higher magnification range brackets the $5\mu\text{m}$ length more symmetrically than the low magnification range, the figures at 4000X for number percents are considered to give a more suitable interpretation of the results.

Thus the values obtained were as follows:

$8.1 \pm 3.0\%$ of all chrysotile fibres observed in the $.25$ to $50\mu\text{m}$ range were longer than $5\mu\text{m}$.

$1.7 \pm 0.6\%$ of all particles in the $.25$ to $50\mu\text{m}$ range consisted of chrysotile fibres longer than $5\mu\text{m}$.

$9.6 \pm 6.1\%$ of the mass of particles in the $.25$ to $50\mu\text{m}$ range consisted of chrysotile fibres longer than $5\mu\text{m}$.

Hedman Cationic Fibre

AVERAGE FIBRE LENGTH

Magnification: 4000X

Sample Number	Number of Fibres Counted	Average Length (um)
B13	76	1.88
B19	48	2.51
A28	69	2.92
A211	84	2.29
A33	60	1.81
A39	67	2.50
A42	114	2.66
A415	82	1.78
A416	71	3.71
B52	73	2.03
B513	74	3.62
Mean of figures for average length of fibres	-	2.5

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Hedman Cationic Fibre

FIBRES LONGER THAN 5 MICRONS

Magnification: 4000X

Sample Number	Number of Particles Counted	Number Percent of all Particles which are Fibres Longer than 5µm
B13	410	0.24
B19	302	1.32
A28	291	3.09
A211	469	0.85
A33	397	0.25
A39	281	2.49
A42	439	2.05
A415	376	1.33
A416	394	2.79
B52	319	0.94
B513	414	2.90
Mean value		1.7
2X standard error		± 0.6

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2180

Hedman Cationic Fibre

MASS OF CHRYSOTILE

AS A PERCENT OF TOTAL MASS

Magnification: 4000X

Sample Number	Number of Particles Counted	Number of Fibres Counted	Mass of Chrysotile as a Percent of Total Mass
B13	410	76	2.90
B19	302	48	3.75
A28	291	69	38.11
A211	469	84	7.69
A33	397	60	16.64
A39	281	67	9.43
A42	439	114	26.69
A415	376	82	4.38
A416	394	71	14.45
B52	319	73	6.36
B513	414	74	23.90
Mean Value			14.0
2X standard error			6.5

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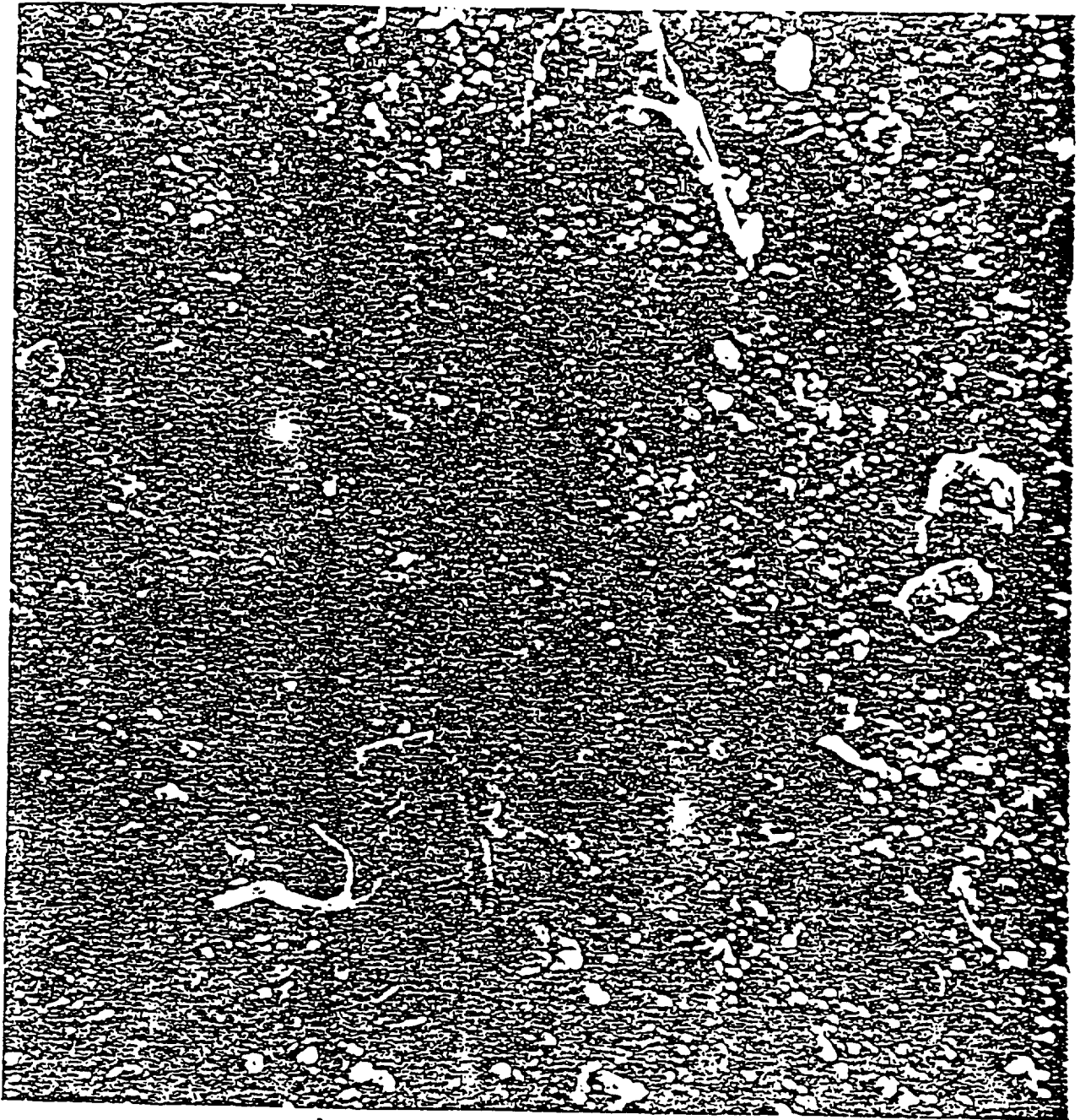


Figure 4: Test of the proposed algorithm.