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*A computer program has been set up in Fortran language to calculate pore size distribution using the Cranston-Inkley method of calculation. Nitrogen adsorption isotherms were determined on amosite and chrysotile asbestos at −195°C. Size reduction had a major effect on increasing pore volumes of both asbestos materials.*

# The porosity of amosite and chrysotile asbestos

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## Introduction

In a recent study,[1] two of the authors made a series of 56 adsorption-desorption isotherms of argon and nitrogen on amosite and chrysotile asbestos in three states of subdivision. This work showed the chrysotile to have a larger surface area and greater porosity than the amosite, and more hysteresis on desorption. A limited number of Cranston-Inkley[2] calculations and Sing[3] plots confirmed this. In the present work, Cranston-Inkley calculations were made from nitrogen isotherms obtained at −195°C to determine the effects of preconditioning temperature and size reduction on pore size distribution and total porosity.

Asbestos is a generic term applied to certain fibrous, inorganic minerals. Chrysotile is a serpentine mineral with an idealized empirical formula of $3\,MgO.2SiO_2{\cdot}2H_2O$. Chrysotile fibers are currently considered to be tubular with material of lower electron density than the fiber walls filling the tubes.[4] Amosite is a member of the amphibole group of minerals and is monoclinic in shape. Chemically, it is a magnesium iron silicate ($Fe^{2+}{}_{5.5}Mg_{1.5}Si_8O_{22}(OH)_2$. Amosite fibers are made of laths which appear



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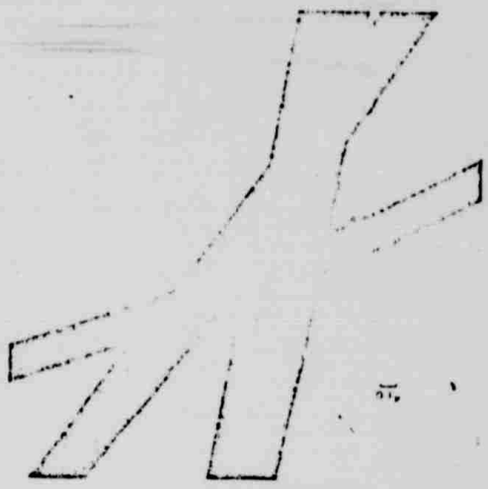


Figure 1 – Electron micrograph of amosite.

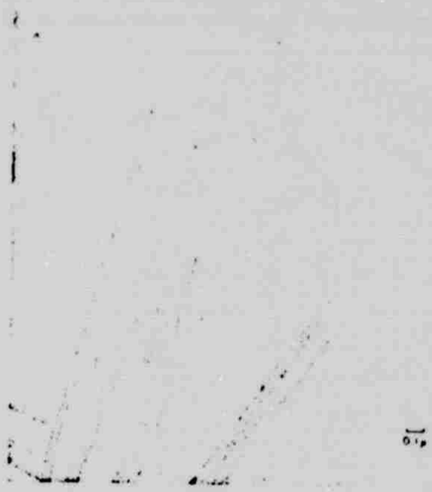


Figure 2 – Electron micrograph of chrysotile.

to be made of layer upon layer of thin, sheet-like material.[3]

Electron micrographs were made of the individual fibers of both materials at total magnifications of approximately 65,000X. These are shown in Figures 1 and 2. They confirm the tubular structure of chrysotile and show the amosite fibers to be solid and considerably greater in diameter than the chrysotile.

## Materials and methods

The amosite used was from the H. K. Porter Company* operation in South Africa and was designated 202-901. The chrysotile consisted of loose fibers obtained from the Bell mines in Canada and was marked Grade 3T.

Adsorption-desorption isotherms were made using the surface properties equipment described by Scheel, *et. al.*[4] This system consists of a Cahn RH electrobalance for measuring weight change of the sample during adsorption, a Wallace and Tiernan Model FA 145 Bourdon gauge for measuring pressures from 1 to 800 torr, and a Bendix GE-340 thermistor gauge for measuring pressures from 0 to 1 torr.

Experiments were made with both asbestos samples in three states of subdivision, namely, as received, mechanically dispersed, and impact milled at liquid nitrogen temperature. The mechanically dispersed asbestos was prepared by mixing 5 grams of sample and 1,000 grams of distilled water in a Ver-Tis mixer for 20 minutes at 20,000 RPM, using a tantalum impeller. This method has been used in the National Institute for Occupational Safety and Health laboratory for preparing asbestos samples for animal exposure tests. The impact milled material was prepared by grinding in a Spex mill cooled with a liquid nitrogen bath. This effectively broke up the fibers so that their geometric mean sizes were 0.8 $\mu$ in length and 0.31 $\mu$ in diameter for amosite, and 0.61 $\mu$ in length and 0.15 $\mu$ in diameter for chrysotile.

Nitrogen was obtained from the Air Reduction Company. It contained 5.3 ppm argon, 0.5 ppm hydrocarbons, and it had a dewpoint of −105°C.

A series of preconditioning experiments was made at 25, 150, 250, and 400°C to determine the effect of temperature on surface area. Since there was no difference in surface area at 25 and 150°C, no further tests were made at 150°C. Preconditioning was thus done at 25, 250, and 400°C for a minimum time of 16 hours while pumping to a final pressure of $0.4\text{-}1.5 \times 10^{-7}$ torr.

*Mention of commercial names or concerns does not constitute endorsement by the Department of Health, Education, and Welfare.

TABLE I

Program for Determining Porosity at Various Pore Sizes

```
      DIMENSION L(37),T(37),R(36),C(36),F(35,35),D(36),V(35),S(36),      PSD1  10
     1DESC(12),VNTP(37)                                                  PSD1  20
      DATA L/300,290,280,270,260,250,240,230,220,210,200,190,180,170,160PSD1  30
     1,150,140,130,120,110,100,90,80,70,60,50,45,40,35,30,25,20,14,10,14PSD1  40
     2,12,10/                                                            PSD1  50
      DATA T/13.52,13.52,13.43,13.32,13.17,13.05,12.89,12.74,12.59,12.45PSD1  60
     1,12.29,12.12,11.93,11.71,11.50,11.26,11.03,10.79,10.51,10.20,9.889PSD1  70
     2,9.530,9.150,8.705,8.215,7.838,7.243,6.858,6.427,5.962,5.443,4.819PSD1  80
     3,4.333,3.808,3.530,3.116,2.672/                                    PSD1  90
      DATA C/0.,.5,.52,.54,.56,.58,.60,.62,.65,.68,.71,.75,.79,.84,.89, PSD1 100
     1.95,1.02,1.1,1.19,1.3,1.44,1.6,1.8,2.04,2.44,1.4,1.56,1.76,2.,2.34PSD1 110
     2,2.86,1.34,1.49,1.68,1.93,2.26/                                    PSD1 120
      DO 30 I=1,36                                                       PSD1 130
      J= I+1                                                             PSD1 140
      IF (I.EQ.1)GO TO 20                                                PSD1 150
      TIJ= T(I)+T(J)                                                     PSD1 160
      K= I-1                                                             PSD1 170
      DO 10 N=1,K                                                        PSD1 180
   10 F(K,N)= (D(N)-TIJ)/D(N)**2                                         PSD1 190
   20 D(I)= (L(I)+L(J))/2.                                               PSD1 200
   30 R(I)= (D(I)/(D(I)-2.*T(J)))**2                                     PSD1 210
C *** READ NUMBER OF ADSORPTION ISOTHERM DATA SETS ********************PSD1 220
      READ 1,NRUN                                                        PSD1 230
      DO 90 ISET=1,NRUN                                                  PSD1 240
C *** READ SAMPLE # :DESCRIPTION, STEP VOLUMES & B.E.T. SPECIFIC SURFACEPSD1 250
      READ 1,NSET,DESC,(VNTP(I),I=1,37),SBET                             PSD1 260
    1 FORMAT(2X,I3,2X,12A4/10F8.3/10F8.3/10F8.3/7F8.3/F8.3)              PSD1 270
      CUMV= 0.                                                           PSD1 280
      CUMS= 0.                                                           PSD1 290
      DO 60 I=1,36                                                       PSD1 300
      SUM= 0.                                                            PSD1 310
      IF (I.EQ.1)GO TO 50                                                PSD1 320
      K= I-1                                                             PSD1 330
      DO 40 N=1,K                                                        PSD1 340
   40 SUM= SUM+F(K,N)*V(N)                                               PSD1 350
   50 V(I)= R(I)*(VNTP(I)-VNTP(I+1)-C(I)*SUM)                           PSD1 360
      IF (V(I).LT.0.)GO TO 70                                            PSD1 370
      CUMV= CUMV+V(I)                                                    PSD1 380
      S(I)= 63.36*V(I)/D(I)                                              PSD1 390
   60 CUMS= CUMS+S(I)                                                    PSD1 400
      K= I                                                               PSD1 410
   70 PRINT 2,NSET,DESC                                                  PSD1 420
    2 FORMAT(1H1/25H PORE SIZE DISTRIBUTION--/9H SAMPLE #,I3,2H :,12A4//PSD1 430
     15X,59H LAYER    EST. PORE   MEAN      SURFACE  PERCENT  CUMULATIVE//PSD1 440
     25X,57HDIAMETER    VOLUME    DIAMETER    AREA    OF TOTAL  PERCENT//62PSD1 450
     3H  N     (A)     (ML-NTP/G)   (A)      (M**M/G)  AREA(%)  AREA(%)//62PSD1 460
     4H --  -------    ------     -----     -------   ------    ------)   PSD1 470
      CPCT= 0.                                                           PSD1 480
      DO 80 N=1,K                                                        PSD1 490
      PCT= 100.*S(N)/CUMS                                                PSD1 500
      CPCT= CPCT+PCT                                                     PSD1 510
   80 PRINT 3,N,L(N),L(N+1),V(N),D(N),S(N),PCT,CPCT                      PSD1 520
    3 FORMAT(I3,2X,I3,1H-,I3,F10.3,F10.1,F10.3,2F10.2)                   PSD1 530
      PRINT 4,I,L(I),L(I+1),V(I)                                         PSD1 540
    4 FORMAT(22H LAST VALUE----------/I3,2X,I3,1H-,I3,F10.3/1X,51(1H-))PSD1 550
      PCTV= 100.*(CUMV-VNTP(1))/VNTP(1)                                  PSD1 560
      PCTS= 100.*(CUMS-SBET)/SBET                                        PSD1 570
      AVGD= 63.36*VNTP(1)/SBET                                           PSD1 580
   90 PRINT 5,CUMV,CUMS,VNTP(1),SBET,PCTV,PCTS,AVGD                      PSD1 590
    5 FORMAT(15H TOTALS      V'=,F7.3,  13H          S'=,F7.3//         PSD1 600
     1       15H PORES<100A: V=,F7.3,  13H   B.E.T.: S=,F7.3//         PSD1 610
     2       16H     100(V'-V)/V=,F5.1,15H%  100(S'-S)/S=,F5.1,1H%//    PSD1 620
     3       44H AVERAGE PORE DIAMETER= 4(.001594V/S)*10000=,F6.2,3H A.)PSD1 630
      END                                                                PSD1 640
```



*The Porosity of Amosite and Chrysotile Asbestos (1976)*
ACL Doc 25435 · Page 3 of 6
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TABLE II
Summary of Results from Cranston-Inkley Calculations

| SAMPLE | PRECONDITIONING TEMPERATURE, °C. | BET SURFACE AREA SQ. M./G. | AVG. PORE DIAM., A | TOTAL PORE VOLUME ML./G. |
|---|---|---|---|---|
| Amosite, As Received | 25 | 1.3 | 58.5 | 0.0019 |
| | 250 | 2.2 | 63.6 | 0.0035 |
| | 400 | 2.8 | 55.1 | 0.0039 |
| Amosite, Mech. Dispersed | 25 | 5.9 | 68.0 | 0.0100 |
| | 250 | 6.9 | 61.0 | 0.0105 |
| | 400 | 7.0 | 54.4 | 0.0095 |
| Amosite, Impact Milled | 250 | 11.9 | 85.7 | 0.0255 |
| Chrysotile, As Received | 25 | 15.3 | 56.4 | .0216 |
| | 250 | 19.3 | 62.9 | .0296 |
| | 400 | 22.1 | 61.9 | .0342 |
| Chrysotile, Mech. Dispersed | 25 | 30.6 | 78.1 | .0598 |
| | 250 | 35.1 | 64.1 | .0578 |
| | 400 | 36.3 | 66.4 | .0602 |
| Chrysotile, Impact Milled | 250 | 48.4 | 80.6 | .0975 |

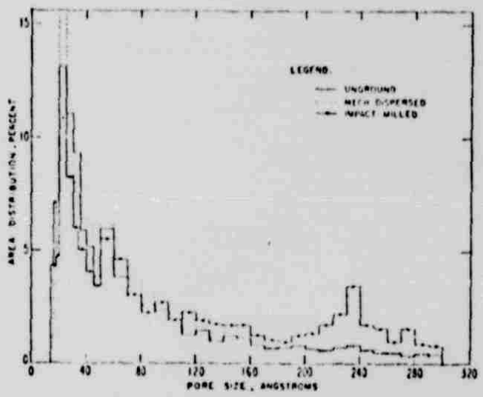



Figure 3 - Effect of grinding on amosite pore size.

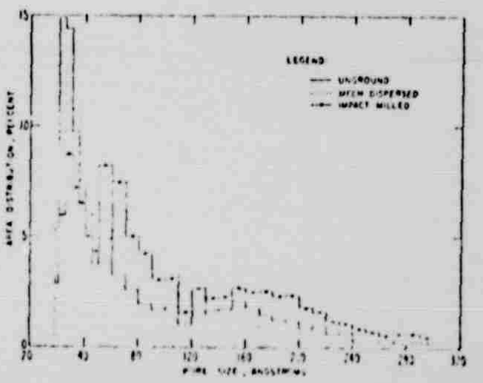



Figure 4 - Effect of grinding on chrysotile pore size.

Pore size distribution was calculated using the method of Cranston and Inkley.[2] This method makes three principal assumptions:[4]

1. The pressure at which a pore of a given radius empties follows the Kelvin equation $\ln(P/Po) = 2\gamma V/RTr$ where P = pressure above an interface with radius of curvature, r, Po = vapor pressure for temperature, T, $\gamma$ = surface tension, V = molar volume, R = gas constant.
2. As a pore empties, the wall of the pore retains an adsorbed layer whose thickness varies like that of a flat surface.
3. Pores larger than 300A in diameter contribute little to the total surface area of the specimen.

The method of calculation is given in considerable detail by Cranston and Inkley.[2] Essentially, the volume of nitrogen in each pore size increment is calculated. This type of calculation is readily performed with a computer. A program has been developed using an IBM 370 computer with Fortran language. The program in a form suitable for keypunching is shown in Table I.

## Results

The data are tabulated in Table II. Figures 3-6 are bar graphs showing the effect of grinding on the pore size distribution of amosite and chrysotile, and the effect of preconditioning temperature on the pore size distribution of mechanically dispersed amosite and chrysotile.



The Porosity of Amosite and Chrysotile Asbestos (1976)
ACL Doc 25435 · Page 4 of 6
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As may be seen, chrysotile is much more porous than amosite. However, in most cases similarly processed samples of amosite and chrysotile have similar average pore diameters.

As expected, size reduction has a major effect on the pore volumes of both asbestos materials. Mechanical dispersion increases the total pore volume of untreated amosite by a factor of three and impact milling increases this value approximately seven times. With chrysotile, which is considerably more porous, the increases in total pore volumes, are approximately two times and 3½ times, respectively. Figures 3 and 4 show that mechanical dispersion has very little effect on the pore size distributions of both asbestos samples. Impact milling, in which the samples are subjected to collision with 440C stainless steel rods, gives pore size distributions that contain larger amounts of pores greater than 100A in diameter for amosite and 150A for crystotile than the unground and mechanically dispersed samples.

For years, investigators at NIOSH and other laboratories have noted that finely ground asbestos fibers lost much of their fibrogenicity.[7] This has been attributed to shorter fiber length and loss of crystallinity on grinding.[8] There is a considerable difference of opinion as to the effective median fiber length with values of 2 to 20 $\mu$ being reported.[9-11]

It would appear that the change in pore size distribution caused by impact milling may have some effect on the lack of toxicity of these fibers. Any material adsorbed in larger pores (>100A) would be more readily desorbed while the smaller pores would tend to retain adsorbate. We doubt that the crystallinity of the impact milled material has been affected since grinding occurred at −195°C, thus preventing local overheating of the fibers.

Increasing the preconditioning temperature from 25 to 400 °C, has little effect on the total pore volume of mechanically dispersed amosite and chrysotile. However, the samples preconditioned at 250 and 400 °C had smaller average pore diameters than the sample preconditioned at 25°C. The data are plotted in Figures 5 and 6 showing the percent area distribution in the various pore size fractions. Evidently, mechanical dispersion broke up many of the fiber bundles, thus creating more

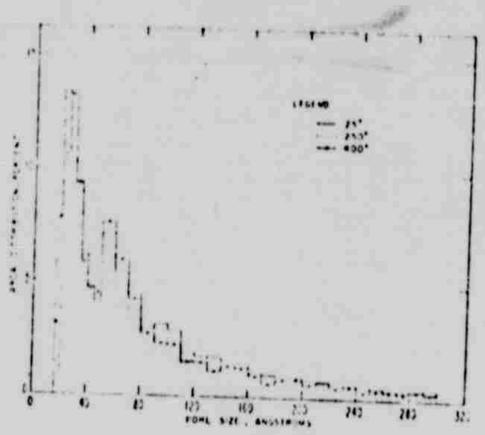


*Figure 5. Effect of preconditioning temperature of mechanically dispersed amosite.*

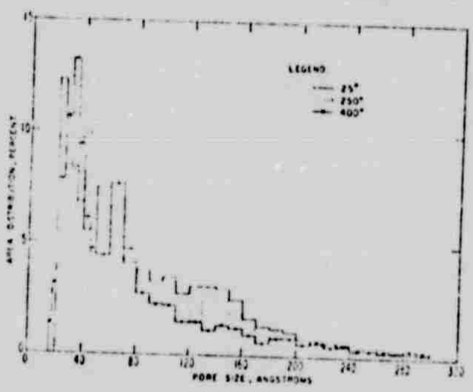


*Figure 6. Effect of preconditioning temperature on mechanically dispersed chrysotile.*

surface area. Although more water was volatilized at higher preconditioning temperatures as determined by weight loss, there was little effect on the total pore volume, thus indicating that the water was held on the surface or in pores smaller than 10A in diameter which were unavailable to nitrogen.

In the case of unground amosite and chrysotile, increasing the preconditioning temperature increases the total pore volume, thus indicating that volatilizing water must create more pores. The effect on average pore diameter was minor. Examination of the material heated to 400 °C, showed no physical difference




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between it and the original sample except for a slight darkening in color. Comparison of electron micrographs of the original and preconditioned samples showed the materials to be essentially the same.

More surface area was contained in pores between 20 and 30 Å diameter than in any of the other fractions. This is similar to the results obtained by Naumann and Dresher,[4] who found a maximum in the pore size distribution at 25 Å using chrysotile from Cassiar, B.C.

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*The Porosity of Amosite and Chrysotile Asbestos (1976)*
ACL Doc 25435 · Page 6 of 6
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