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A STUDY OF SURFACE CHARACTERISTICS OF SELECTED ASBESTOS FIBRE BY ELECTROPHORESIS

by

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MINERAL PROCESSING DIVISION

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A. A. Winer*, L. L. Sirois** & A. Page***

SUMMARY

Presently certain chrysotile fibre from Coalinga, California, is being promoted as a desirable additive in paper products. Samples of chrysotile fibre were received from Carey-Canadian Mines Ltd., consisting of asbestos from East Broughton, P. Q., and from Coalinga, California. A study of these samples was undertaken, by electrophoresis, to determine the suitability of the Carey fibre as a paper additive.

The results of this investigation indicate that brucite and other associated minerals can affect the fibre characteristics. Processing the fibre appears to alter its zeta potential, possibly because of the removal of some or all of the associated minerals. The Coalinga and East Broughton fibre appeared to become more similar after processing as evidenced by their zeta potential or electrophoretic mobility.

It is possible that zeta potential measurements can be used to predict fibre behaviour at any processing stage or in the final product. Further study is required.

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INTRODUCTION

Chrysotile, one of Canada's most important industrial minerals, has many end uses e. g. in asbestos-cement products, as reinforcing agents in resins etc.. The overall desirable properties of chrysotile asbestos have not yet been duplicated by any single material.

The remarkable nature of chrysotile is in large part due to its surface characteristics. Although some knowledge of the surface characteristics exists, much remains to be learned. It is unlikely that chrysotile asbestos can be fully exploited unless detailed studies of such characteristics as surface properties are undertaken.

This report discusses the application of a commercial instrument for determining the electrophoretic mobility of selected chrysotile fibre samples; the mobility can be translated into zeta potential. The asbestos samples received from Carey-Canadian Mines Ltd. were from the plant at East Broughton, P. Q., and from Coalinga, California. The zeta potential was also determined for a sample of fibrous brucite which was associated with chrysotile from East Broughton.

PREVIOUS WORK

The external surface layer of chrysotile is composed of hydroxyl ions adjacent to magnesium ions and therefore, according to Pundsack (1), would be expected to have basic properties and strong surface activity. A schematic structure of chrysotile is shown in Figure 1 (2).

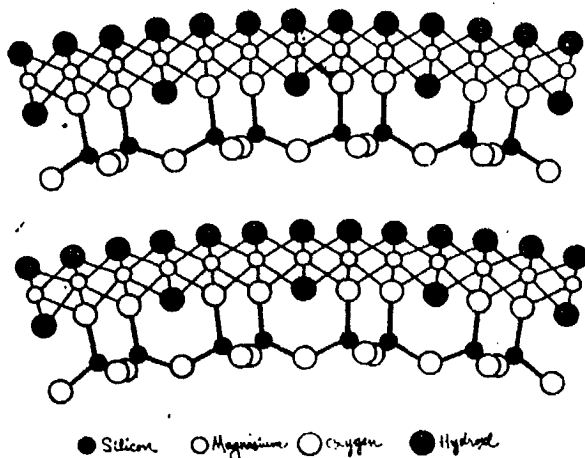


FIGURE 1. Schematic Representation of the Structure of Chrysotile Asbestos.

Badollet (3) summarized the reaction of chrysotile and other asbestiform minerals with a number of compounds, particularly acids and bases. The reaction with hydrochloric acid is said to proceed in three steps, according to Pundsack (1).

- (a) the reaction with free brucite ($Mg(OH)_2$)
- (b) the reaction with hydroxyl groups in the structure
- (c) the reaction of the hydroxyl groups associated with the silica

The surface behaviour of chrysotile asbestos enables it to be used in many important practical applications. Drainage rates, reactions in asbestos-cement systems, its behaviour as a paper additive, etc., are all highly influenced by the surface properties and the electrical charge on the surface of the fibre.

Martinez (5) reversed the charge polarity of chrysotile with sodium silicate. This occurred at a pH of 10.9, which is below that of the normal zero-point of charge of 11.8 found by Martinez and Zucker (4). Martinez increased the rate of filtration by the deposition of sodium silicate on chrysotile. Sodium phosphate and sodium carbonate solutions were also used to decrease the positive charge on chrysotile but they did not reverse the polarity. Pundsack (6) removed the constitutional water from chrysotile by thermal dehydroxylation to increase the drainage rate by giving it the properties of a harsh fibre.

Various methods have been used for measuring the surface charge or zeta potential of chrysotile. Its zero-point-of-charge was determined by Pundsack (6), by titrating until a floc formed at a pH of about 10.1. Martinez and Zucker (4), using a streaming potential method, found that its zero-point-of-charge occurred at pH 11.8. The maximum positive zeta potential occurred at a pH of 3.0. Robinson (7), using a streaming potential method, obtained for MgO a zero-point-of-charge at pH 12.5 ± 0.5 .

OUTLINE OF ZETA POTENTIAL THEORY

The interaction between a charged solid surface and an aqueous solution leads to the development of an electrical double layer. A simple illustration of this phenomenon occurs, for example, with silica in water, where negative charges are fixed on the mineral surface and the solution phase has an increased positive charge density in the immediate vicinity of the surface. This excess charge will degrade with distance from the surface, and at the same time it will give rise to diffusion currents in the solution that will attempt to minimize this ionic concentration near the solid surface.

When a surface acquires its charge by obtaining ions from the solution, the process is mainly controlled by the activity, in the solution, of the species in question. Consequently, there must be a concentration at which all forces are in equilibrium and the total net transfer of ions becomes zero. When this situation occurs, there will be no excess charge on the surface and consequently no cause for the existence of an electrical double layer.

The zero point of charge will occur when this electrical double layer is absent and the surface of the solid shows no excess positive or negative charge due to the presence of excess anions or cations. It is thus determined by the critical concentration or the activity of the potential-determining ions in the solution.

The zeta potential is the potential at the surface separating the immobile part of the double layer from the diffuse part. It is a simultaneous measure of the charge of the diffuse double layer, and of its distance from this surface. When a liquid containing, for example, negatively charged particles is placed in an electric field, the negative particles are attracted to the anode and counter ions to the cathode. This attraction increases with the charge on the particle. The velocity of the particle in a given field increases with the charge density of the double layer.

Therefore, the velocity of a colloidal particle in an electric field is proportional to that field and to the zeta potential of the particle.

There are two methods for evaluating the electrophoretic mobility of particles in liquids: they involve the measurement of particle velocity either individually, by observing the particles directly with a microscope, or collectively, by measuring the velocity of a mass of particles by following the movement of a sharp concentration gradient.

The measurement of the velocity of individual particles in a potential gradient is carried out in an apparatus shown in Figures 2 to 4. This apparatus consists essentially of a microscope with a calibrated reticule for the observation of the individual particles, and a transparent cell, equipped with platinum measuring electrodes, that contains the colloidal suspension under study connected with a source of constant voltage.

The cell itself is transparent, long, and cylindrical. The electrical double layer at the cell wall itself imparts a motion to the whole suspension in the cell. The suspension moves rapidly in one direction near the wall, more slowly further from the wall, and in the opposite direction at the center of the cell. At some region in the cell there is no net motion applied to the suspension as the result of the zeta potential of the cell wall-liquid interface. It is in this region that the observed velocity of the particles in the system is equal to their electrophoretic velocity. Calculations have shown that this

stationary level is located at a distance equal to 14.8% of the diameter from the wall of a cylindrical cell.

In use, the cell is filled with the suspension under study, and a known potential is applied. With an objective lens that gives a small depth of focus, the microscope is focused at the stationary level and the time for a particle to move a known distance is measured with a stopwatch. The results are reported as mobility, in cm/sec (v/cm) or converted to zeta potential by Equation 1.

$$V_E = DE\zeta/4\pi\eta \quad (\text{Eq 1})$$

where

- V_E = electrophoretic mobility
- D = dielectric constant of the medium
- E = externally applied potential
- ζ = zeta potential
- η = viscosity of the medium

EQUIPMENT

Photographs of the Zeta-Meter and details are shown in Figures 2, 3 and 4.

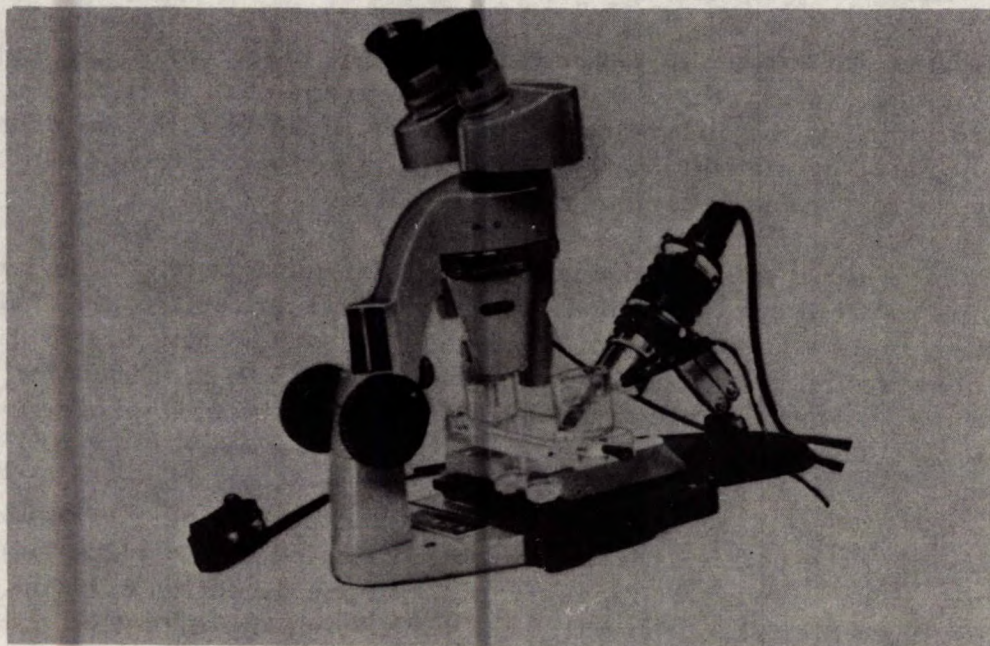


FIGURE 2. The Zeta-Meter Stereoscopic Microscope with Illuminator, Cell and Cell Holder, and Mechanical Stage.

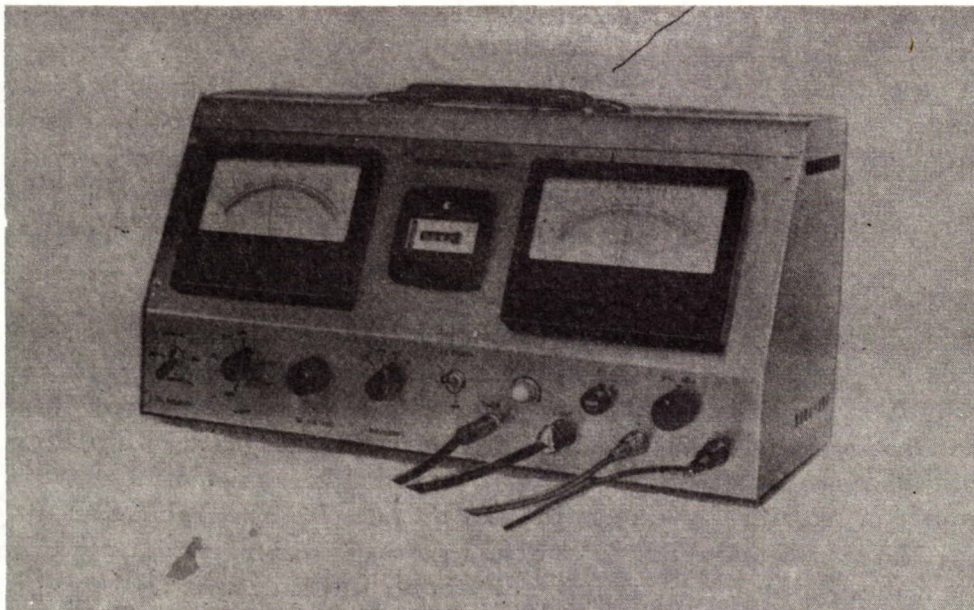


FIGURE 3. The Zeta-Meter Power Unit.

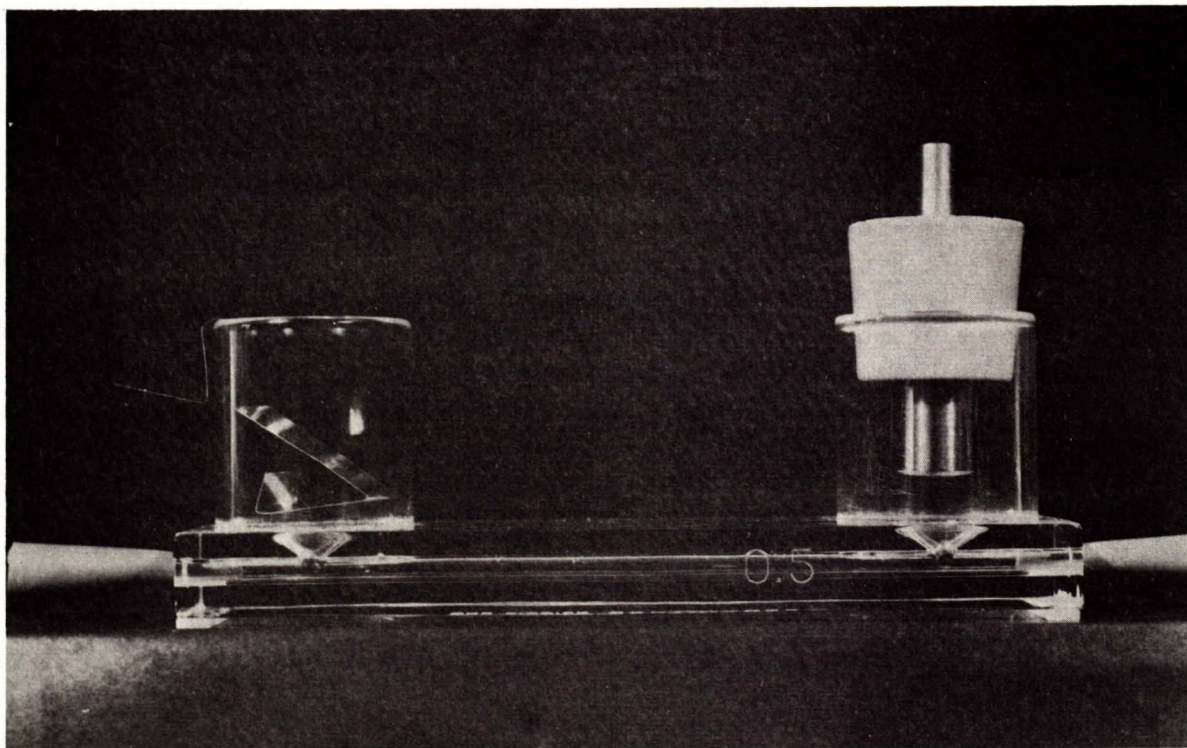


FIGURE 4. Details of Cell.

EXPERIMENTAL TECHNIQUE

The electrophoretic mobility was measured using the apparatus shown in Figures 2, 3 and 4. Solutions containing approximately 50 ppm of asbestos were placed in the cell (Figure 4) and the mobility was determined using an applied d-c voltage of 67V. In each determination a supporting electrolyte of 10^{-3} N potassium chloride was used. All readings were taken at a temperature of $25 \pm 1^{\circ}\text{C}$.

Curves of electrophoretic mobility were obtained by varying the pH of a 10^{-3} N solution of potassium chloride with hydrochloric acid and potassium hydroxide. The latter two compounds were used since they did not add different ions to the system. The above solution containing 50 ppm of asbestos was agitated in a Waring Blendor for 3 to 4 minutes. The large asbestos particles were removed by passing the asbestos suspension through a 325 mesh screen. Dissolved gases were removed by placing the suspension under high vacuum for about one minute. Following this, the temperature was decreased to $25 \pm 1^{\circ}\text{C}$ in a constant-temperature bath, and the electrophoretic mobility of the asbestos particles was measured.

Precautions, and Limitation of Measurement

The pH of distilled water will decrease to 5.8 because of CO_2 absorption from the atmosphere. In the neutral range very accurate pH measurements are required, therefore these were done in a nitrogen atmosphere. The electrophoretic mobility cannot be measured accurately with the Zeta Meter outside the limits of pH 2 and 11.5, since the conductivity becomes very large, essentially creating a short circuit. The electrical current in the electrophoretic cell (measured in microamperes) also changes markedly beyond these limits. For example, at pH 2, the current may be increased by nearly 15 percent within a few minutes.

Heat generated by the illuminator produces convection currents causing the particle to move in an erratic path. This causes difficulty in measuring the time and distance the particle has travelled.

All fibre samples were carefully examined under the microscope to insure that no adulterants, such as magnetite or brucite, adhered to the fibres. These adulterants would modify the velocity of the asbestos fibre, leading to erroneous results.

RESULTS AND DISCUSSION

The data obtained by electrophoretic measurements are presented in Table 1. Also included are the specific-surface areas of the processed samples, previously determined by nitrogen gas adsorption.

TABLE 1

Electrophoretic and Surface Area Measurements
of Asbestos Samples

Fibre Sample	Origin	Specific-Surface Area in m^2/g	pH at which Zero-Point-of Charge occurs
Raw	Vein fibre; Carey-Canadian East Broughton, P. Q.	—	11.2±0.2
OS-2231	Processed; Carey-Canadian East Broughton, P. Q.	19.94	Estimated above pH 11.5
OS-2299	Processed; Carey-Canadian East Broughton, P. Q.	23.21	Estimated above pH 11.5
Raw	Vein fibre; Coalinga, Calif.	—	11.5±0.2
VS-1903	Processed; Coalinga, Calif.	53.68	Estimated above pH 11.5
Brucite	Vein fibre; Carey-Canadian East Broughton, P. Q.	—	7.2±0.2

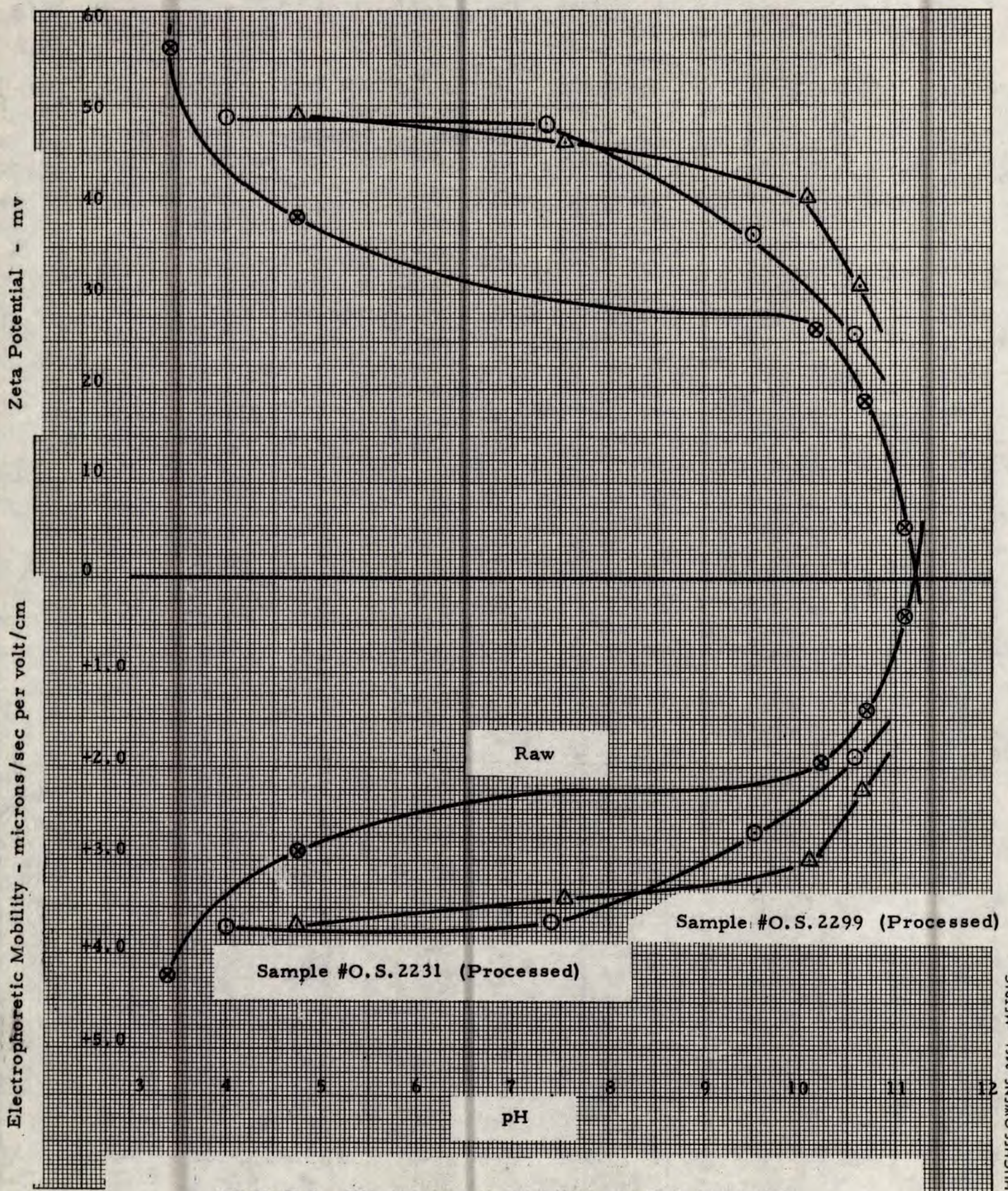


FIGURE 5. Electrophoretic Mobility and Zeta Potential of Chrysotile Fibre from Carey-Canadian Mines, East Broughton, P.Q.

Curves showing the variation of electrophoretic mobilities and zeta potentials at different pH values are included in Figures 5 to 8.

Figure 5 shows the variation of mobilities and zeta potentials with pH, of the Carey-Canadian fibre both in its raw and processed form. The zero-point-of-charge of the raw fibre occurs at $\text{pH } 11.2 \pm 0.2$; at this point the surface charge of the mineral changes from positive to negative. This reversal in surface charge does not occur for the two processed samples, within the range of pH values studied. The surface characteristics of the two processed samples appear to be similar. This could be because of the similarity of treatment or because the treatment removed constituents leaving the fibre surfaces electrically similar

A marked difference exists between the raw and processed samples as shown in Figure 5; the surface is less positively charged on the raw sample. The treatment used by Carey-Canadian Mines for the two processed samples has had a marked influence on the character of the fibres, but no definite explanation can be given since the type of treatment is not known. It is possible that certain constituents associated with the fibre were removed during processing, which would be detectable by means of the Zeta Meter.

Figure 6 shows the variation of mobilities and zeta potentials with pH of the Coalinga fibre in raw and processed form. There is also a marked difference between the raw and processed samples from Coalinga. In general the raw sample again appears less positively charged than the processed fibres. The zero-point-of-charge for the raw sample occurs at $\text{pH } 11.5 \pm 0.2$, whereas there is no charge reversal for the processed material within the pH values studied.

Raw samples shown in both Figures 5 and 6 have characteristic curves, indicating that electrophoresis is a useful technique for characterizing certain surface properties of asbestos. A raw sample of fibrous brucite from Carey-Canadian Mines was also examined and a graph of its electrophoretic mobility versus pH is shown in Figure 7. The zero-point-of-charge occurred at a pH of 7.2 ± 0.2 , which is markedly different when compared with the two samples of chrysotile asbestos fibre. Brucite can be found as an adulterant in Carey-Canadian chrysotile fibre and would be expected to affect its characteristics and mobilities if the brucite is not removed. The zeta potential of brucite would be expected to be different from that of chrysotile because of their different crystal structures.

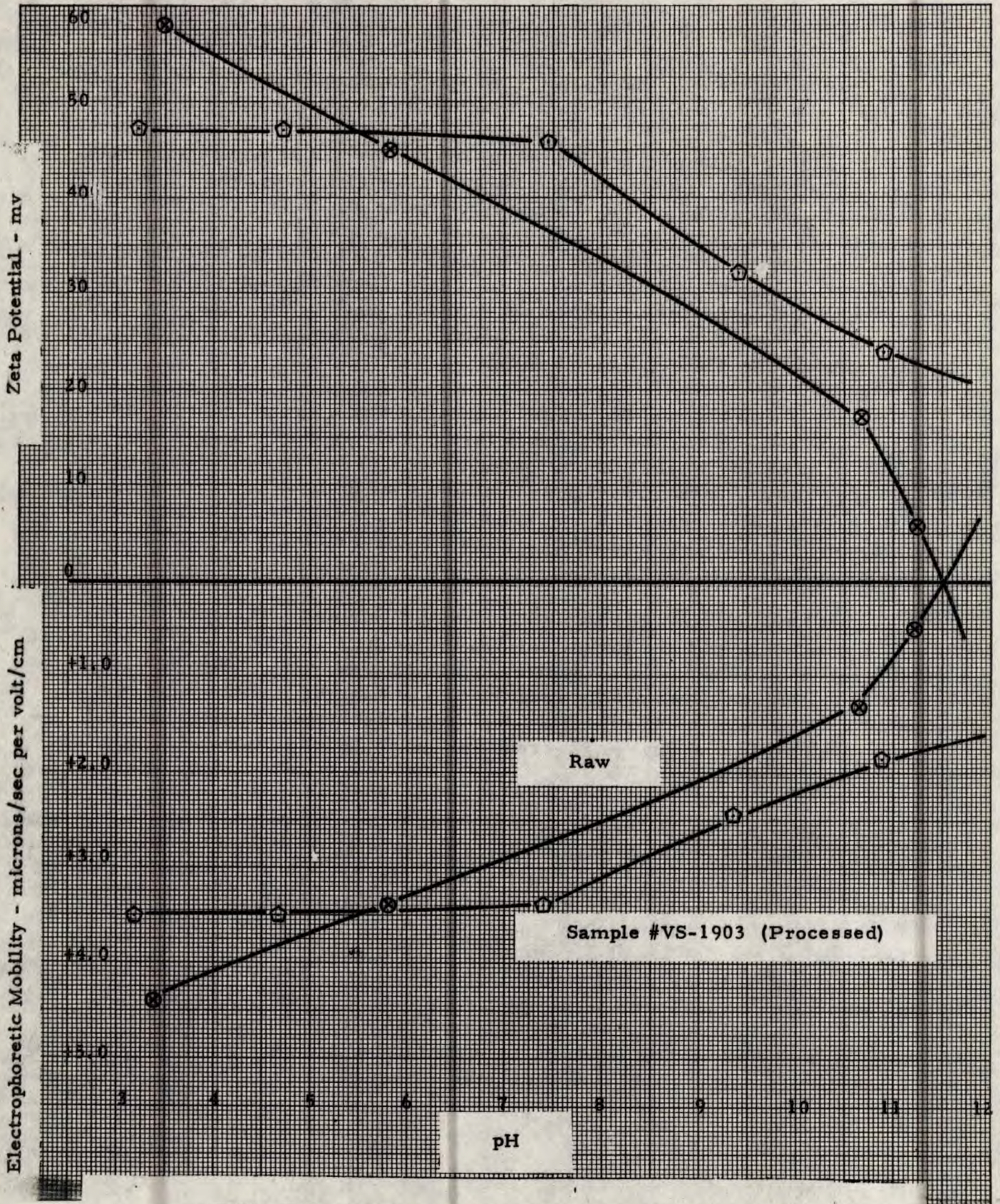


FIGURE 6. Electrophoretic Mobility and Zeta Potential of Chrysotile Fibre from Coalinga, Calif.

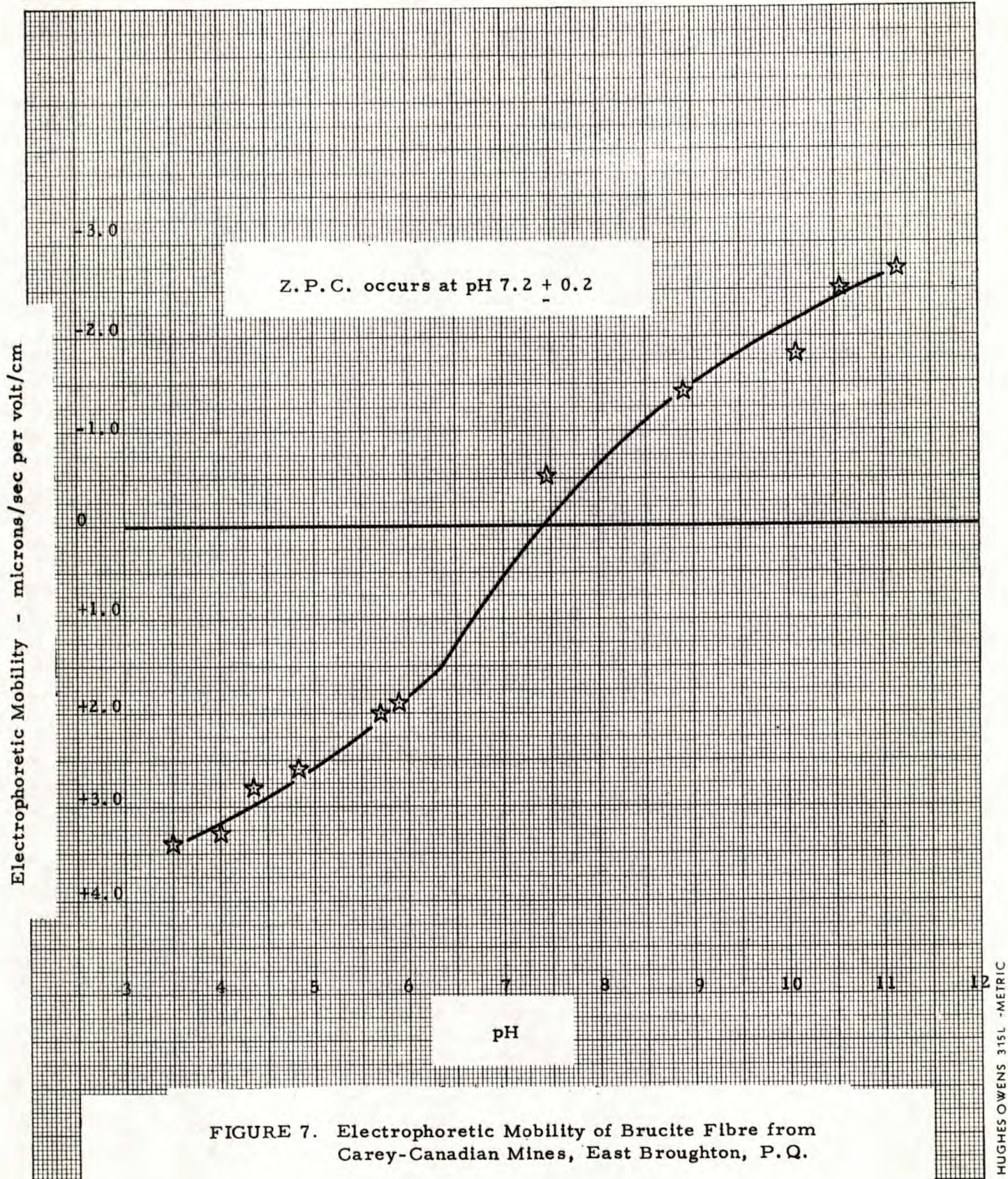


FIGURE 7. Electrophoretic Mobility of Brucite Fibre from Carey-Canadian Mines, East Broughton, P.Q.

Figure 8 illustrates the close similarity of the three processed samples of chrysotile. A spectroscopic analysis of these samples, shown in Table 2, demonstrates the ability of the electrophoretic method to indicate surface characteristics of asbestiform minerals. This analysis illustrates the close similarity between the three chrysotile samples, as does the Zeta Meter. The surface area measurements listed in Table 1 do not appear to correlate with the other data and do not appear to affect surface characteristics, as determined by zeta potential measurements. However, during blending all the samples were reduced to very small particle size, perhaps to a similar size distribution, by the special polytron cutting blade used in the Waring Blendor. Naumann and Drescher (8) have found, in certain cases, that intensive dispersion of chrysotile asbestos has increased the surface area of nearly all chrysotile asbestos.

TABLE 2

Chemical Analysis

Sample No.	Si	Mg	Mn	Fe	Cr	Al	V	Ca	Ti	Ni
OS-2299	PC	PC	0.05	0.79	0.18	0.10	0.005	0.06	0.01	0.09
OS-2231	PC	PC	0.04	0.88	0.20	0.13	0.003	0.14	0.02	0.09
VS-1903	PC	PC	0.05	0.57	0.16	0.16	0.005	0.14	0.04	0.07

CONCLUSIONS

The results of this investigation indicate that brucite and other associated minerals can affect the fibre characteristics. Processing of the fibre appears to alter its zeta potential, possibly because of removal of some or all of the associated minerals. The Coalinga and East Broughton fibres appear to have become more similar after processing, as evidenced by their zeta potentials or electrophoretic mobilities.

It is possible that zeta potential measurements can be used to predict fibre behaviour at any processing stage or in the final product. Further study is required.

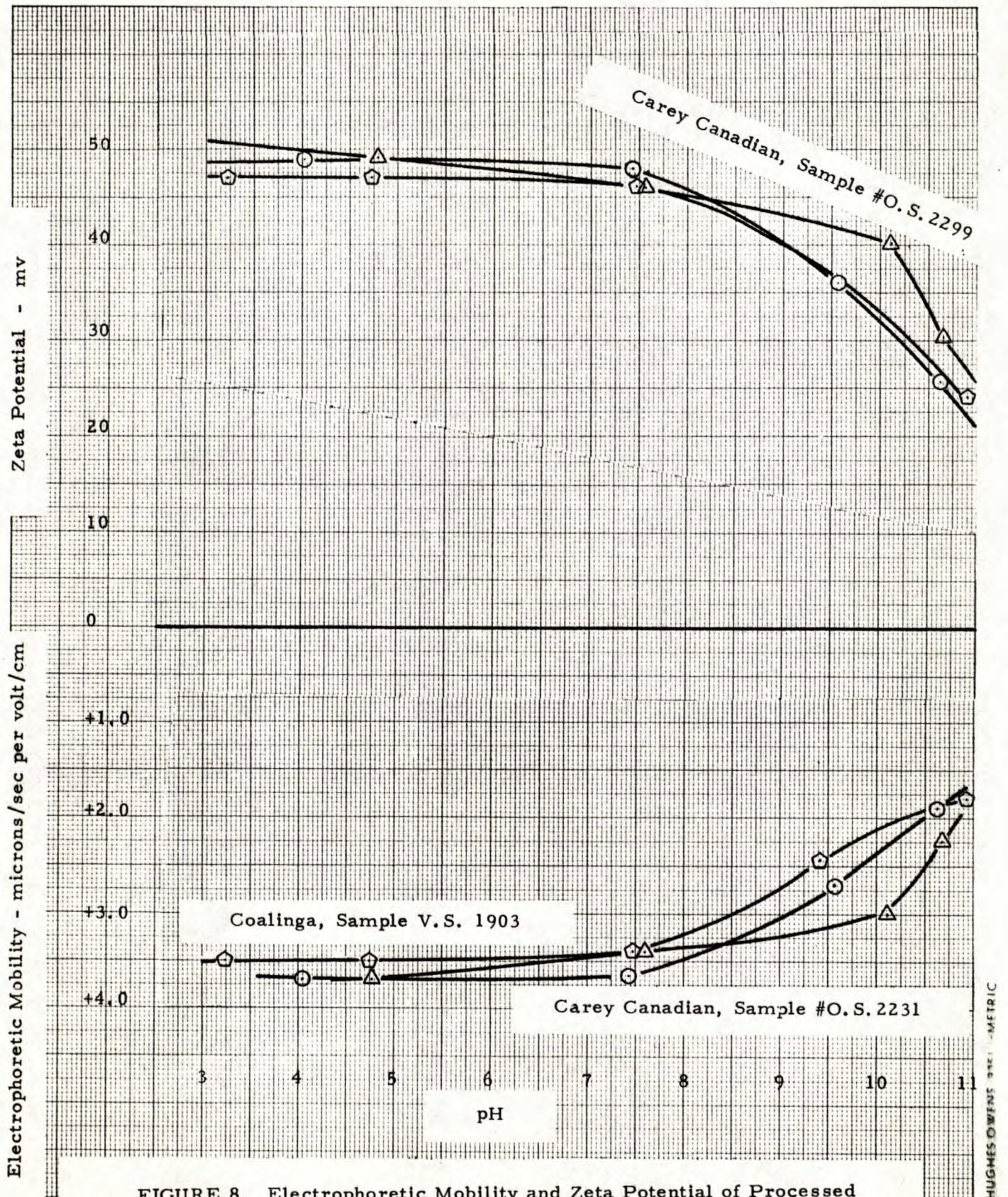


FIGURE 8. Electrophoretic Mobility and Zeta Potential of Processed Chrysotile Fibre from Carey-Canadian Mines, P.Q. and Coalinga, Calif.

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