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# RELIABILITY OF SCANNING ELECTRON MICROSCOPY INFORMATION

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ABSTRACT

The reliability of information obtained with the scanning electron microscope is influenced by human and instrumental factors. The human factor enters, for example, when a microstructure is described as being typical of the material when in fact it is only a minor component. Some instrumental factors include charging of the specimen, problems differentiating between positive and negative relief and distortion of the shape of the sample in micrographs. The determination of the amount of a phase present in a composite is a complex problem involving both preparation of representative surfaces and appropriate methods of evaluation. A number of experimental results are provided. Where smearing of surfaces is not a problem, point counting evaluation on sawn surfaces is shown to provide reliable results.

La véracité des renseignements obtenus à l'aide du microscope électronique à balayage est influencée par les facteurs humains et instrumentaux. Le facteur humain entre en jeu, par exemple, lorsqu'une microstructure est décrite comme étant typique du matériau lorsqu'elle n'est en réalité qu'une composante secondaire. Certains facteurs instrumentaux comprennent le chargement du spécimen, les problèmes de différenciation entre le relief négatif et le positif et la distorsion de la forme de l'échantillon dans les microphotographies. La détermination de la quantité d'une phase présente dans un composé, occasionne un problème complexe de préparation des surfaces représentatives et de mise au point de méthodes d'évaluation appropriées. Un nombre de résultats expérimentaux est fourni. Lorsque les taches en surfaces ne constituent pas un problème, l'évaluation en comptant les points aux surfaces sciées fournit des résultats fiables.

## Introduction

Understanding of the mechanism of hydration of cement has been greatly advanced by the use of the scanning electron microscope (SEM) during the past decade. However, a certain amount of confusion may have also been generated by the publication of non-representative micrographs or the misinterpretation of them. In this paper some problems that may lead to the misinterpretation of results obtained with the SEM are discussed. The major problems affecting the reliability of the data can be divided into human and instrumental factors.

## Human Factors

A problem commonly affecting the visual interpretation of SEM data is the selection of non-representative micrographs that are subsequently described as showing the typical morphology of the sample. Sometimes micrographs are selected for inclusion in a paper primarily because they show a well-defined morphology, but the author has failed to note that the observed feature may have comprised only a very small percentage of the sample. The incidence of this sort of problem is perhaps on the wane, as researchers gain more experience in scanning electron microscopy.

Another problem that sometimes arises is the misinterpretation of the observed morphology. This problem is especially serious when, in the absence of energy-dispersive x-ray facilities, morphology is used exclusively to identify the phases observed. There are cases on record where a cubic phase was described but examination of the micrographs showed no clearly defined cubic material to be present.

## Instrumental Factors

In this section, some examples of results that are misleading due to instumental factors associated with the coating apparatus or the SEM are discussed.

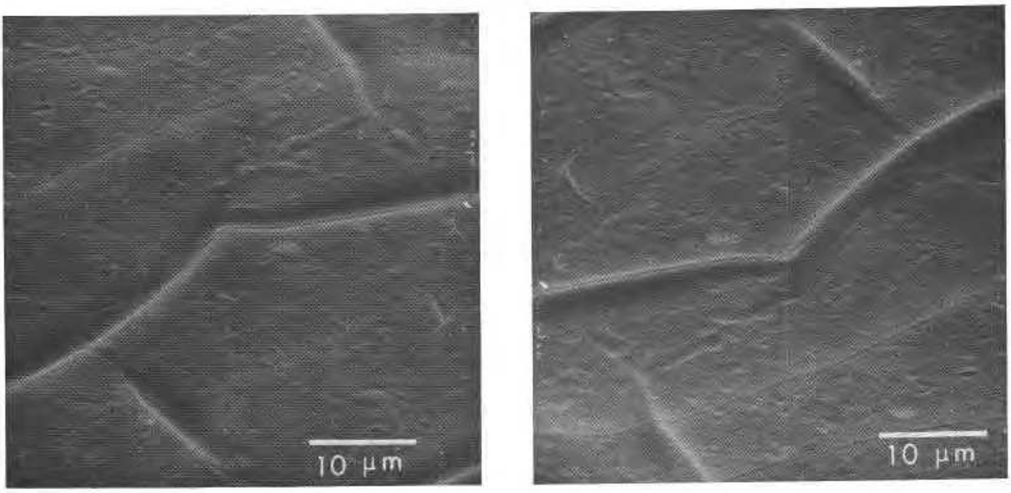
The thickness of the coating frequently varies considerably and small areas where it is virtually absent may occur. At higher magnifications regions that are poorly coated give rise to charging artifacts that may be mistaken for features of the sample. However, with the coating techniques currently being employed and in the magnification range commonly used in cement research this is not usually a serious problem.

Holland (1) has reported the occurrence of artifacts when a sputter coating unit was used with gold and palladium. Incorrect operation of the unit may cause deposition of fine globules of gold which at high magnification impart an artificial surface texture.

One of the SEM-related factors that sometimes causes difficulty is the possibility of incorrectly differentiating between positive and negative relief, especially when examining micrographs. If the micrographs are inverted by mistake, cracks appear as ridges, as can be seen in Fig. 1. This is less of a problem in the microscope itself, especially if a y-modulation unit is available to differentiate between the two.

Purchase of a 3-D viewing system such as that of Chatfield*(2), may be warranted when correct identification of positive and negative relief of three-deminsional effects are important. The system produces two images, one red and one green, superimposed on a color television screen. The combined image is viewed with a pair of red and green filter stero glasses. Alternatively, stereoscopic pairs of micrographs can be made with the conventional SEM by tilting the sample between exposures, but this method is somewhat tedious and is not regularly used.

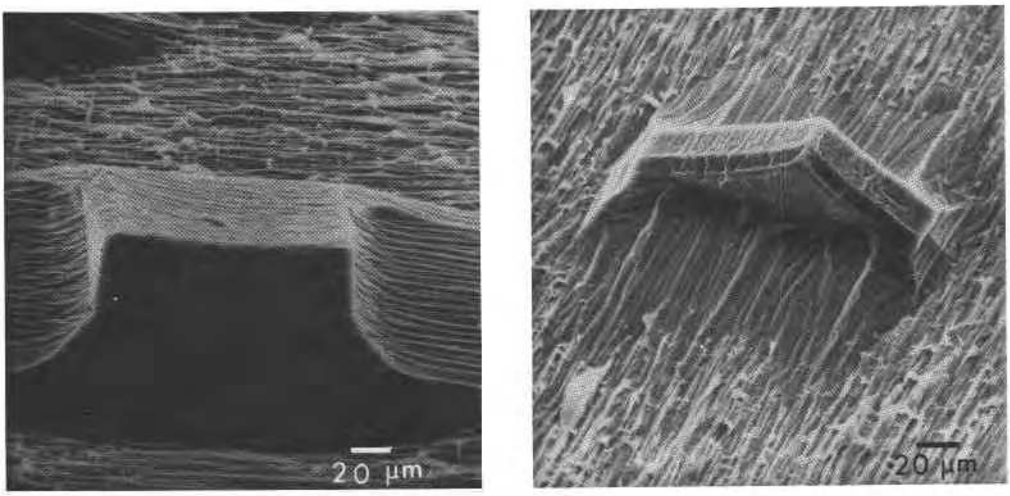
* Manufactured by the Ontario Research Foundation




(a) (b)

FIG. 1

Effect of inversion of a micrograph on topographic features:
(a) micrograph in correct orientation showing cracks in the surface of a fiber reinforced plastic;
(b) same micrograph inverted, cracks appearing as ridges.

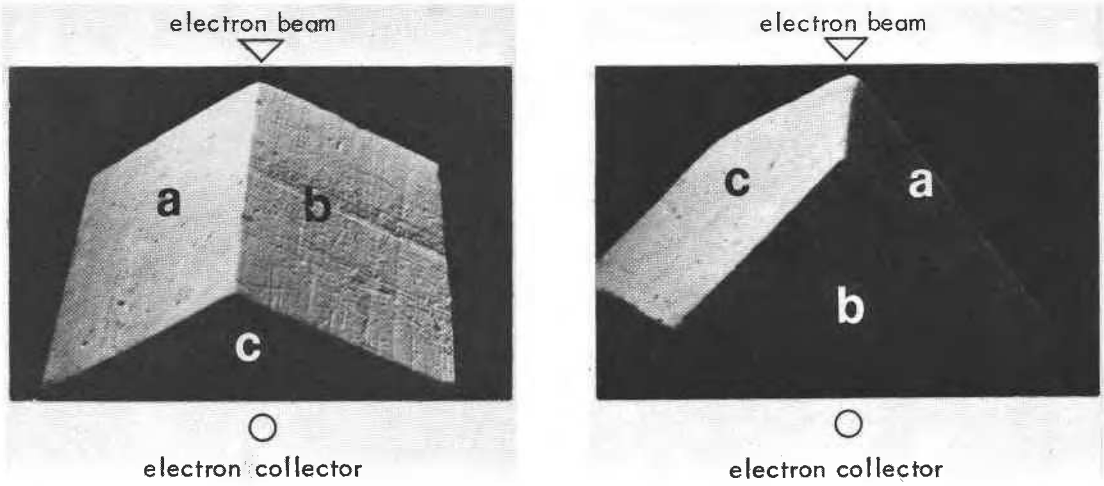



(a) (b)

FIG. 2

Micrographs of replicas of etch pits in ice viewed from different directions: (a) apparent cubic morphology; (b) true hexagonal morphology.

Artifacts affecting the apparent shape of features observed in the SEM may be generated by the geometry of the incident electron beam and the takeoff angle of the secondary electron detector relative to the sample. This is illustrated in Fig. 2, which is a micrograph of a replica of etch pits in a surface of ice. In Fig. 2(a), the etch pits appear cubic in shape but Fig. 2(b), which was obtained by rotating the sample, shows the true hexagonal morphology. Figure 3 shows the reason for the apparent cubic form of the etch pits in Fig. 2(a). In




(a) (b)

FIG. 3

Model showing how some ice crystals may appear to have cubic morphology when viewed in the SEM:
(a) apparent cubic morphology when face 'c' is in electron shadow and not visible;
(b) model viewed from another angle; face 'c' is now illuminated by electron beam and true hexagonal morphology is seen.

Fig. 3(a), the hexagonal face 'c' is invisible because the electron beam does not strike it and no electrons are reflected from this face to the collector. As a result, the observer sees an apparent cubic form. In Fig. 3(b) the hexagonal face is tilted towards the collector and the observer sees the true hexagonal morphology of the etch pit. Shape distortion of the image may also be caused by tilt of the specimen in the microscope if the image is not corrected electronically. This distortion is evident with spheres that appear elliptical in outline as seen in Fig. 4.

## Percentage Estimation

Two factors strongly influence the estimation of the percentage of a component, especially a minor one, in a composite material: (i) the representativeness of the surface being examined, and (ii) the accuracy of the method used. When a composite material is fractured, the fracture will pass preferentially through the weaker phase; hence more of that phase will be visible on the fractured surface than is present in the material. It is therefore evident that estimates of the percentages of materials present in composites derived from information obtained on fractured surfaces may not always be correct, even when an accurate method of estimation is used. However, when the purpose of the examination is to determine the cause of failure of the composite, examination of a fractured surface is essential.

Even when a surface is representative of a sample, the determination of the percentage of a component is not an easy task. Various statistical methods for determining volume percentages from areal measurements are available; unfortunately, in cement and concrete research, visual estimation, a most unreliable method, is generally used. Fig. 5 illustrates this problem. In a trial carried out in this laboratory on "dummy" samples containing 5% of a white phase as shown in Figs. 5a and 5b, estimates of the amount thought to be present varied

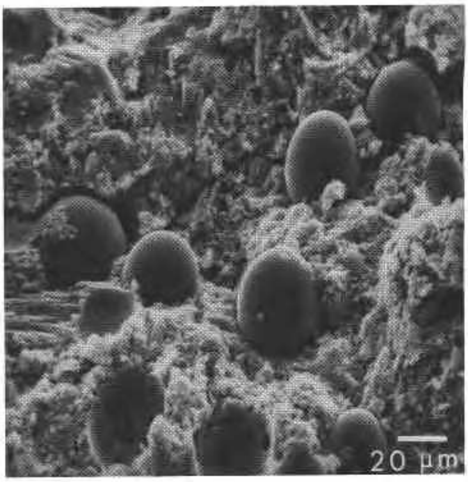



FIG. 4

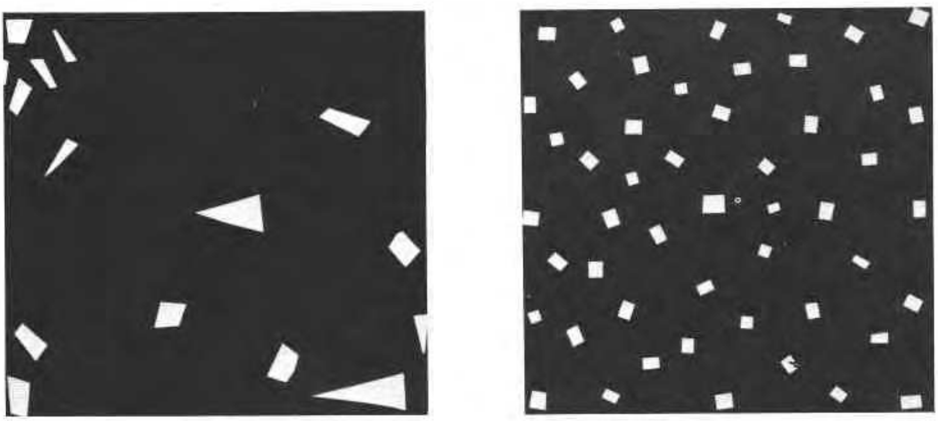
Micrograph showing latex spheres in portland cement paste; sample contained 12% latex. Latex spheres appear elliptical in outline because tilt correction not applied to image.

from 2% for Fig. 5a to 40% for Fig. 5b. In a second trial carried out at the annual Transportation Research Board Meeting in Washington, in January 1988, a group of experienced cement chemists and microscopists estimated more accurately the percentages in the two figures, suggesting that accuracy of estimation improves with experience.

## Quantitative Determination of Proportions Present

As early as 1848, the French petrographer Delesse (3) showed mathematically that in a random cross-section of a uniform aggregate the area occupied by each constituent is proportional to its volume in the sample. This concept led to the development of quantitative microscopy. Different methods of determining the areal amount and hence volume of a constituent on a plane surface are described in various handbooks on petrographic procedures, e.g., Quantitative Microscopy (4).

The simplest method is probably the point count. The advantage of this method is that at each point the only decision that has to be made is if the point is on or off the selected feature. In this study, known amounts of different phases in specimens were determined by the point count method using the Cambridge Mark IIA scanning electron microscope. The procedure was as follows:



(a) (b)

FIG. 5

Diagrams in which percentages of white phase in black matrix are to be estimated visually:
(a) white particles of variable shape and size;
(b) white particles of more uniform shape and size.

The sample was step scanned in the x direction by rotating the x-axis control by 180° for each step. After each rotation it was noted if a point at the centre of the screen was on or off the desired phase. When the edge of the sample was reached, the sample was moved one or more steps at right angles to the traverse direction and the procedure repeated until the desired number of frames had been counted. A point at the centre of the screen was used because, when necessary, the magnification could be increased to aid in identification without moving the sample.

In order to estimate the percentage of a phase in the sample it was necessary to determine the number of frames to be counted, using the following equation:

$$P = \frac{1}{\sigma^2(V_v)} [V_v(1 - V_v)] \qquad (1)$$

where P is the number of frames required to give the desired accuracy, $\sigma^2$ is the variance and $V_v$ is the estimated volume fraction of the phase to be determined. An estimate of the volume fraction $V_v$ was first made by counting until about 10 points fell on the phase to be determined and was substituted in Eq. (1). P was then calculated.

Table 1 shows the number of frames that have to be counted, in hypothetical samples containing varying amounts of the phase being investigated, in order to obtain an accuracy of 10%. If an accuracy of 5% rather than 10% is required, the number of frames counted must be increased from 1900 to 7490 in a sample containing 5% of the phase under investigation; if, for the same sample, an accuracy of 20% is acceptable, the number of frames counted can be reduced to 475. Comparatively few investigations in cement and concrete research warrant the expenditure of effort necessary to count manually the large number of frames necessary to obtain a reasonable level of accuracy. In favorable cases, however, when a polished surface can be prepared without undue smearing of the phase of interest, an image analyser could be used to determine, automatically, the percentage of that phase. The Quantimet Image Analyser* is a typical apparatus, consisting of a plumbicon scanner, a T.V. display, a system control module, a 2-D detector and a computation module. The image on the T.V. monitor is line scanned. There are 800 picture points per line and hence the system can be compared to a very accurate point system. The analyser can be programmed to give grain size distribution, percentages of the different phases that are distinguishable, and areas occupied by those phases; the results are obtained in a matter of seconds. An accuracy of about ± 2% has been reported (5). Some type of image analysis apparatus is undoubtedly the best method for obtaining quantitative data from micrographs. For satisfactory results, however, it is essential that representative samples be used and that distortion of shape does not occur because of instrumental factors.

Table 1

Ratio of Number of Frames Counted to Percentage of Phase in Sample, for an Accuracy of 10%.

| Percentage of Phase in Sample | Number of Frames |
|---|---|
| 5 | 1900 |
| 10 | 900 |
| 15 | 700 |
| 20 | 400 |

An image analysis system can be obtained for about $18,000 but its capabilities are very limited. A useful system will cost between $50,000 and $100,000, a price that is difficult to justify unless the machine is in almost constant use.

Alternatively, there are methods by which the percentage of a component can be estimated more expeditiously, though with lesser accuracy, than the point

* Manufactured by Image Analysis Corporation

count procedure. One of these, the grid count method, was tested in this laboratory. Ten micrographs were taken, uniformly distributed in a cross-pattern on the sample. A grid 1 x 1 cm in size with 120 squares was laid over each micrograph and the area occupied by the desired phase was estimated. The results were generally unsatisfactory but were probably more accurate than those that could be obtained by visual estimation. Details of these experiments will be described later.

## Procedures for Sample Preparation and Evaluation of Methods of Determining Percentages of Phases Present

### Preparation of Sample Surfaces

The experimental results presented in this paper show that fractured surfaces of some composite materials can provide incorrect data when the average composition of the sample is required. Surfaces prepared by cutting with a diamond saw eliminate the problem encountered with some fractured surfaces, but with soft composites, smearing at the surface may prevent indentification of phases.

There are other, more sophisticated, possible methods that could be applied to the problem. Possibilities include the free-abrasive wire slicing system supplied by Geos Corporation* and the water-jet cutting apparatus supplied by Flow Research Inc.** Another possibility would be to begin with a sawn surface and machine a fresh surface with an ion milling apparatus. One problem with this apparatus is that if the sample is heat sensitive (as is cement paste) it is essential to use a cold stage. This adds considerably to the cost. In fact the main problem with these alternative methods suggested is cost. The ion milling apparatus with a cold stage attachment costs about $20,000; the other equipment is even more expensive. It is difficult to justify such an expenditure unless the apparatus is in almost daily use.

### Representativeness of Surfaces and Methods of Evaluation

In the quantitative analysis of a composite containing a small percentage of a weak phase in a strong matrix a surface prepared by cutting, e.g., with a diamond saw, should not be influenced by the differences in strength between the two components as would a fracture surface. A number of samples were prepared to demonstrate this effect.

In the first system, latex spheres about 25 μm in diameter were mixed with portland cement, which was then hydrated. A micrograph of the sample is shown in Fig. 4. The results of the percentages obtained by point counting on sawn and fractured surfaces are shown in Table 2.

Table 2

Comparison of Results of Point and Grid Counts on Sawn and Fractured Surfaces of Samples Containing 12 and 5% Latex Spheres in Portland Cement (p.c.)

| Sample | Surface Preparation | Point Count | Grid Count |
|---|---|---|---|
| 12% latex in p.c. | fractured | 19.7 | 13.9 |
| 12% latex in p.c. | sawn | 11.4 | 7.9 |
| 5% latex in p.c. | fractured | 10.8 | 5.1 |
| 5% latex in p.c. | sawn | 5.0 | 3.3 |

* Geos Corporation, 420 Fairvield Ave., Stanford, Connecticut 06902, U.S.A.

** Flow Research Inc., P.O. Box 5040, Kent, Washington 98031, U.S.A.

In Table 2 it is clear that the point count results for sawn surfaces are satisfactory and unbiased, but that the point count results for fractured surfaces for both 5% and 12% specimens are much too high. Although some of the errors can be attributed to surface roughness of the fractured surfaces, this would not account for the large errors that were found. The bond between cement paste and latex was evidently weaker than that between crystals in cement and therefore a fracture would tend to run round one latex sphere and on to an adjacent one rather than cut directly through the sample. As a result, an excessive amount of latex was observed on fractured surfaces.

The results obtained by the grid count method involving 10 uniformly distributed micrographs were reasonably accurate for the fracture surfaces but quite low for the sawn surfaces.

A second system consisted of strong silicon carbide whiskers in (relatively) weak portland cement paste. The results are shown in Table 3 and a micrograph of a sample is provided as Fig. 6. Here sawn surfaces were too smeared for the SiC to be observed. Fractured surfaces, as expected, yielded values that were lower than the true values. These were slightly lower for the point count method, and considerably lower for the grid count method.

Table 3

Comparison of Results of Point and Grid Counts on Sawn and Fractured Surfaces of Samples Containing 5 and 10% Silicon Carbide in Portland Cement(p.c.)

| Sample | Surface Preparation | Point Count | Grid Count |
|---|---|---|---|
| 10% SiC in p.c. | fractured | 8.6 | 4.5 |
| 10% SiC in p.c. | sawn | - * | - |
| 5% SiC in p.c. | fractured | 3.6 | 2.3 |
| 5% SiC in p.c. | sawn | - | - |

* The surface was too smeared for the SiC to be observed.

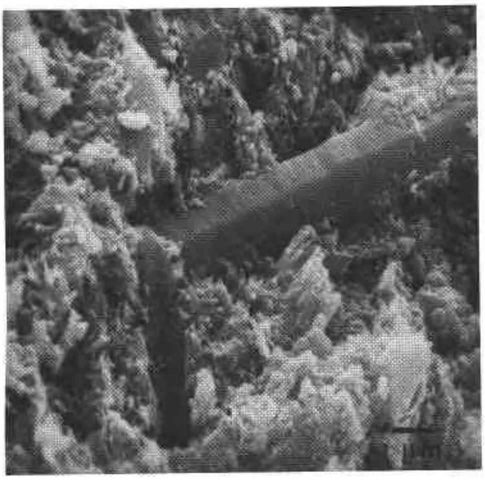


FIG. 6

Micrograph showing SiC whiskers in portland cement paste; sample contained 10% SiC.

Both preceding systems involved reasonably strong (cement paste) matrices. To study the effect of a weak matrix a number of samples of gypsum were prepared with various inclusions. Micrographs of two of these are shown in Figs. 7 and 8.

In the first set, 19.8% latex was added to hemihydrate which was then hydrated and prepared for examination. The results are given in Table 4.

In Table 4, where both the inclusion (latex spheres) and the matrix (gypsum) are soft, the point count results are reasonably good for both sawn and fractured surfaces. The grid count results seriously underestimate the amount of latex present for either type of surface.

Another set of specimens was made, consisting of mica in gypsum; the results obtained from examination of them are shown in Table 5. Here, as expected, the fract-

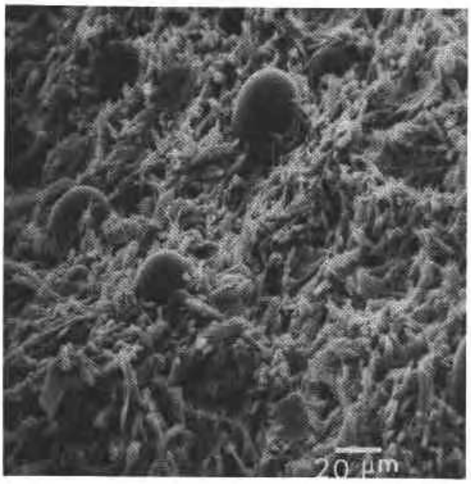



FIG. 7

Latex spheres in gypsum.

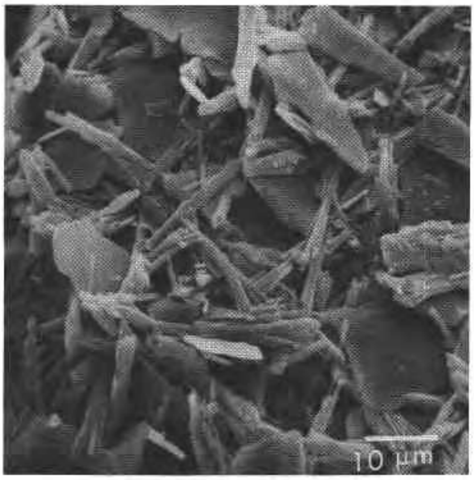



FIG. 8

Large, flat, mica flakes in gypsum; sample contained 20% mica.

Table 4

Comparison of Results of Point and Grid Counts on Sawn and Fractured Surfaces of Samples Containing Latex Spheres in Gypsum

| Sample | Surface Preparation | Point Count | Grid Count |
|---|---|---|---|
| 19.8% latex in gypsum | fractured | 19.5% | 9.0% |
| 19.8% latex in gypsum | sawn | 17.5% | 11.1% |

ure surfaces yielded point count evaluations that were too high, indicating that the fracture had passed preferentially through the mica flakes. Again the sawn surfaces provided good point count estimations. In this particular series the grid count estimations were reasonably satisfactory.

Table 5

Comparison of Results of Point and Grid Counts on Sawn and Fractured Surfaces of Samples Containing 5 and 20% Mica in Gypsum

| Sample | Surface Preparation | Point Count | Grid Count |
|---|---|---|---|
| 20% mica in gypsum | fractured | 25.8 | 17.2 |
| 20% mica in gypsum | sawn | 20.2 | 21.5 |
| 5% mica in gypsum | fractured | 8.8 | 5.4 |
| 5% mica in gypsum | sawn | 6.6 | 5.9 |

## Conclusions

During the past 12 years, invaluable information has been obtained by the examination of samples in the SEM. However, incorrect interpretation of the morphology of various features can arise owing to a number of causes.

1. The surface texture of the sample may be affected by improper use of a sputter coating unit.

2. If the micrographs are inverted by mistake, negative relief can appear positive and vice versa.

3. The sample geometry and its relationship to the incident angle of the electron beam and the takeoff angle of the detector can result in misinterpretation of the morphology. In the sample cited in this paper, hexagonal etch pits appeared to be cubic.

4. Distortion of the shape of the image of the sample will occur if the sample is tilted and electronic tilt correction is not applied to the image.

Quantitative estimates of phases present in composites are difficult to obtain and the problem may be compounded if the phases are not easily identified. When fractured surfaces of composites containing phases of different strengths were examined, it was shown that the fractures passed preferentially through the weaker phase causing the amount of that phase to be overestimated. This observation may be used to advantage, however, when a sample is examined to determine the cause of its failure. Examination of sawn surfaces overcomes the problem of overestimating the amount of the weaker phase but sawing smears the surface of many samples.

For quantitative estimates of the proportions present it is clear that point count estimates are much superior to grid count results, the latter yielding only very rough estimates particularly when only small proportions of the phase of interest are present. For some samples, however, this may be better than a visual estimate, and comparatively little extra effort would be needed to take the required 10 uniformly distributed micrographs. Visual estimates tend to be highly unreliable unless made under favorable circumstances by experienced investigators.

## Acknowledgements

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