Quantifying morphology of nickel crystals

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Synopsis

Particle morphology is a term that is used to describe the overall external shape and appearance of particulate solids. From the physical point of view, a precipitated solid is characterized primarily by the size and morphology of the particles (Sohnel and Garside, 1992).

If the morphology of the crystal structures is to be related to the processing conditions, then the morphologies need to be quantified in some way. This can be achieved by using surface area measurements as well as fractal dimensions.

The key idea is that rugged and indeterminate systems can be described by using a fractional number that describes the ruggedness of the system (Kaye, 1989). In other words, when the complexity of a structure, such as an agglomerate, increases with increasing magnification, it is useful to employ fractal dimensions to describe the structure. Fractal geometry proposes that, instead of attempting to measure the length of an irregular boundary, the rate at which the length of the boundary approaches infinity with increasing resolution should be calculated.

Cross-sectional profiles of rugged particles can thus be quantified using the fractal dimension, and a measurement of the ruggedness of the morphology obtained.

One of the additional uses of measuring the fractal dimension is that the measured value can be related to the physical properties and formation characteristics of the particle (Kaye and Trottier, 1995).

The morphology of nickel crystals was quantified with fractal dimension calculations of particle cross-sections. Particle cross-sections were obtained by mounting the particles in resin and polishing back. These were then photographed using Scanning Electron Microscopy and the resulting profiles analysed using the structured walk technique.

Introduction

Particle morphology is a term that is used to describe the overall external shape and appearance of particulate solids. From the physical point of view, a precipitated solid is characterized primarily by the size and morphology of the particles (Sohnel and Garside, 1992).

Morphology of nickel crystals is important for a number of reasons. Firstly, the morphology of the powder determines its ability to be formed into a stable, robust briquette. The briquette characteristics determine their ease of handling and transport. Secondly, the morphology is related to the uptake and retention of impurities in the crystal. The undesirable morphology tends to develop inclusions of impurities from the mother liquor, and thus the purity of the final product is compromised.

The morphology of nickel powders produced by precipitation ranges from 'cauliflower' (see Figure 1) to 'bally' (see Figure 2), the cauliflower shape being a more open, dendritic and less dense type of structure, the bally shape being a more dense, closed structure. It is not yet clearly understood what the relationship is between processing conditions and the morphology of the crystal product.

If the morphology of the crystal structures is to be related to the processing conditions, then the morphologies need to be quantified in some way. This can be achieved by using surface area measurements as well as fractal dimensions.

Surface area measurements can be time consuming and costly, and part of the motivation for exploring the concept of using fractal dimensions is that it is possibly a cheaper method of achieving a similar measurement. In addition, the fractal dimension measurement can potentially provide more information about the crystal history and formation mechanisms. This would be useful in tracing back the different morphologies to particular reaction parameters. In addition, in many fields, researchers are coming up with ways to link the measured dimension of the fractals to their physical properties (Kaye and Trottier, 1995). For

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 SA ISSN 0038–223X/3.00 + 0.00. First presented at SAIMM, Copper Cobalt Nickel and Zinc Recovery Conference, *Jul. 2001.*

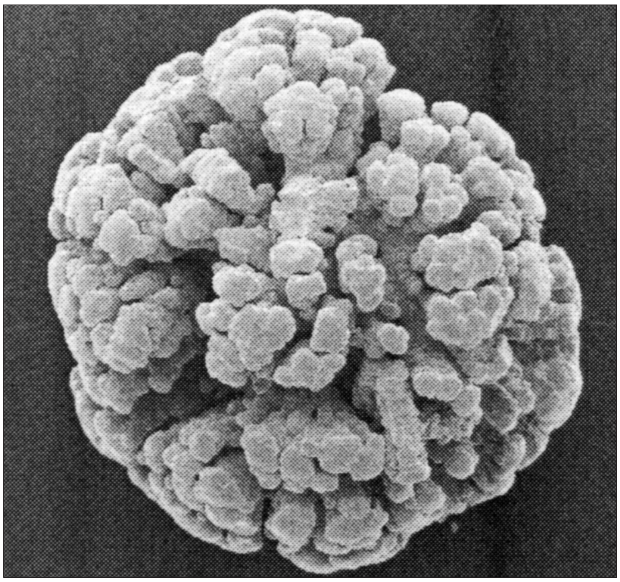

Figure 1—'Cauliflower' morphology

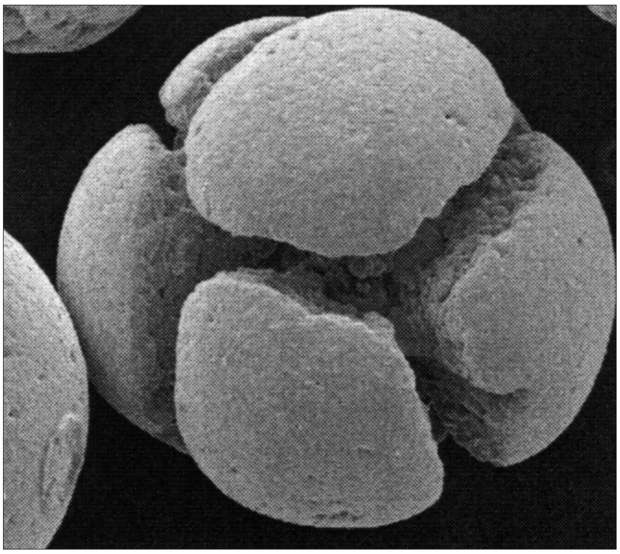

Figure 2—'Bally' morphology

example, fractal characterization procedures have been shown to have potential application in tracking the physical changes in abrasive fine particles as they deteriorate in performance during use as a polishing powder.

The key idea is that rugged and indeterminate systems can be described by using a fractional number that describes the ruggedness of the system (Kaye, 1989). In other words, when the complexity of a structure, such as an agglomerate, increases with increasing magnification, it is useful to employ fractal dimensions to describe the structure. Fractal geometry proposes that, instead of attempting to measure the length of an irregular boundary, the rate at which the length of the boundary approaches infinity with increasing resolution should be calculated.

Measuring fractal dimensions

Cross-sectional profiles of rugged particles can thus be quantified using the fractal dimension, and a measurement of the ruggedness of the morphology obtained. The boundary fractal dimension of a two-dimensional particle profile can be deduced from data generated by a scale variant exploration of the profile (Kaye and Trottier, 1995). The exploration of a profile and various scales is achieved by constructing polygons with sides of decreasing length around the structure. These polygons produce a series of increasing perimeter estimates (Figure 3).

The normalized perimeter estimate of each polygon is plotted on a logarithmic plot against the resolution parameter, λ, which is also normalized. This type of data plot is known as a Richardson plot (Kaye *et al.*, 1992).

The slope (m) of the best-fit line can be used to calculate the fractal dimension of the structure as follows:

$$\delta = 1 + |m|$$

On a purely visual level, the magnitude of the fractal dimension appears to match the rugged appearance of the profile. However, the fractal dimension does not give information about the overall gross shape of a particle. Two particles might well exhibit the same fractal dimension, but have a very different overall shape.

Structural and textural fractals

One of the additional uses of measuring the fractal dimension is that the measured value can be related to the physical properties and formation characteristics of the particle (Kaye and Trottier, 1995).

The overall fractal dimension can give a measure of the ruggedness of a particle, but there is more information to be gained by making experimental measurements at very small stride lengths and by looking more closely at the Richardson plot. For rugged particles, the difference between the structure and the texture can also be identified on the Richardson plot.

For example, in Figure 4, (Kaye, 1989), the Richardson plot generated from the carbon-black profile illustrated yields two fractal slopes. The portion of the line with slope $\delta = 1.39$ is related to the topography i.e. the overall structure of the agglomerate, and this is defined as the structural fractal, δ_S. The portion of the line with slope $\delta = 1.39$ is defined as the textural fractal, and describes the texture of the particle i.e. the nature of the profile at much higher resolutions. For the carbon-black example, the fractal dimensions can provide information on the combustion processes and formation dynamics of the fume particles (Kaye and Trottier, 1995).

Experimental method

Fourteen grab samples of various nickel powders ranging from 'very cauliflower' through to 'very bally', were tested. See Table I.

Table I shows the apparent density measurement of 14 of the samples, as this is currently one of the routine plant measurements used to assess the morphology and thus the ability of the powder to be formed into a stable, robust briquette. The apparent density of each sample was calculated by weighing 5 ml of powder as measured in a measuring cylinder. It was not possible to measure the

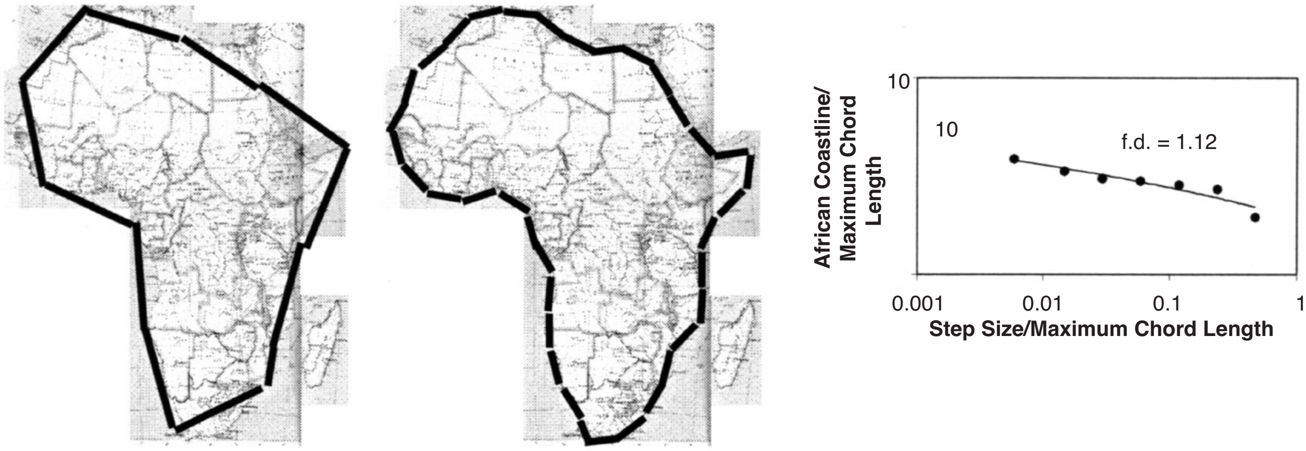

Figure 3—Perimeter estimates obtained by constructing polygons around a two-dimensional profile

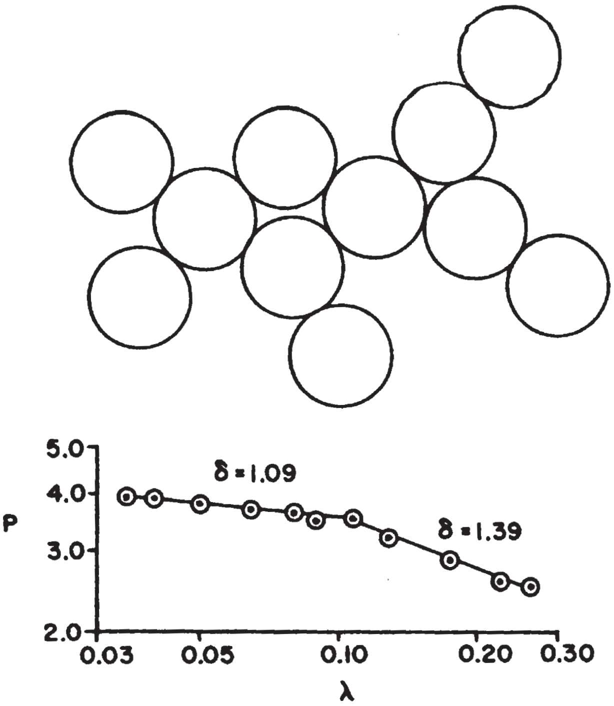

Figure 4—Richardson plot showing structural and textural fractals

apparent density of samples B2 and VB7, due to the extreme inhomogeneity of the samples, some of the powder balls being up to 0.5 cm in diameter.

Plant personnel classified the samples into the various descriptive categories on the basis of experience and visual judgement.

All the samples were mounted in resin, back polished and photographed using Scanning Electron Microscopy. The polishing allowed the perimeter of the crystal surface to be measured using the alternate structured walk technique (Kaye *et al.*, 1993). The magnitude of the various perimeter estimates, normalized with respect to the Feret diameter of the profile, were plotted against the resolution parameter, λ, which was also normalized with respect to the Feret diameter. The slopes of the different data lines were used to estimate the fractal dimension (Kaye *et al.*, 1993). Sample B2 was highly inhomogeneous, and thus two measurements were generated for this sample: B2(a) and B2(b).

Results

It was not possible to measure the fractal dimension of the two samples identified as very cauliflower, due to the presence of deep fissures within the particles that created 'islands' separated from the core of the particle. See Figure 5.

Table I shows the results of the fractal dimension measurements of the remaining samples. Figure 6, and Figure 8 show the Scanning Electron Microscope profiles and the Richardson plots for sample C4, B1 and VB3, from which the fractal dimensions for those samples were obtained.

Figure 9 shows a numerical relationship between apparent density and morphology once the morphological descriptors have been transformed into numerical values. Each category of sample ('very cauliflower', 'cauliflower', 'bally' and 'very bally') was arbitrarily assigned an equidistant number for the purposes of linear regression.

Table I

Summary of classification, apparent density and fractal dimension of sixteen powder samples

Label	Classification	Apparent density [g/cm³]	Fractal dimension
VC1	Very cauliflower	2.94	-
VC2	Very cauliflower	3.52	-
C1	Cauliflower	3.60	1.1647
C2	Cauliflower	2.85	1.3600
C3	Cauliflower	3.88	1.1003
C4	Cauliflower	4.30	1.2547
B1	Bally	4.42	1.1842
B2(a)	Bally	Bally powder	1.1068
B2(b)	Bally	Bally powder	1.1135
VB1	Very bally	4.60	1.0385
VB2	Very bally	4.63	1.0093
VB3	Very bally	3.11	1.0785
VB4	Very bally	4.34	1.0210
VB5	Very bally	3.68	1.0803
VB6	Very bally	4.90	1.0235
VB7	Very bally	Bally powder	1.0356
VB8	Very bally	4.12	1.0238

From Figure 9 it is apparent that the 'very bally' samples show a far greater variation in the apparent density than do the 'very cauliflower' samples. This could be due to the fact that the more 'bally' samples tend to have a narrower particle size distribution (Butler and Lewis, 2000) than the 'cauliflower' samples, and thus are more difficult to pack in a consistent manner in a measuring cylinder.

There is an extremely weak trend of increasing apparent density with increasing 'bally-ness' of the sample. The best-fit least squares linear regression line through the points yields a linear regression coefficient of 0.3115, indicating that 31% of the variability in the data can be accounted for by the linear relationship.

Figure 10 shows a plot of the fractal dimension of the sample against its descriptor transformed into a numerical form. Once again, each category of sample ('very cauliflower', 'cauliflower', 'bally' and 'very bally') was arbitrarily assigned an equidistant number for the purposes of linear regression. Since it was not possible to carry out the structured walk technique for the 'very cauliflower' samples, there are no data points for this category. There is more variation in the fractal dimension of the 'cauliflower' samples than in the 'bally' samples, probably due to the fact that the ruggedness of the profile introduces more possibilities for discrepancies and error in the results.

There is a weak trend of decreasing fractal dimension

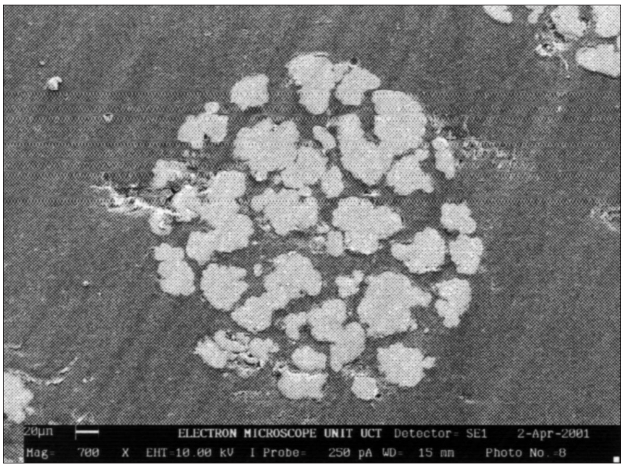

Figure 5—Extremely rugged particle characterized by deep fissures and 'islands' in the profile

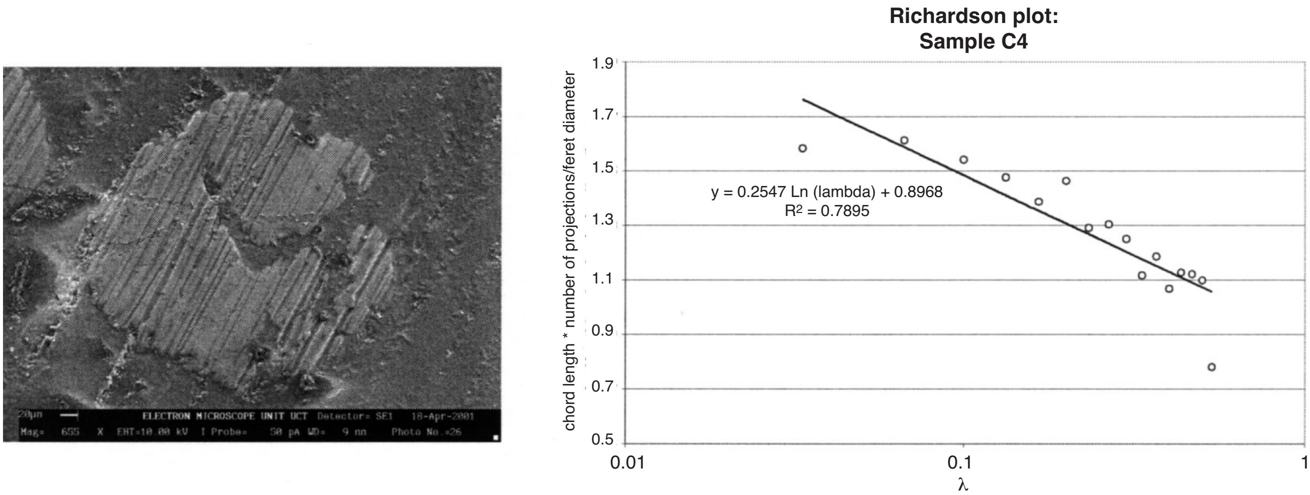

Figure 6—Scanning Electron Microscope profile and Richardson plot for sample C4 (δ =1.25)

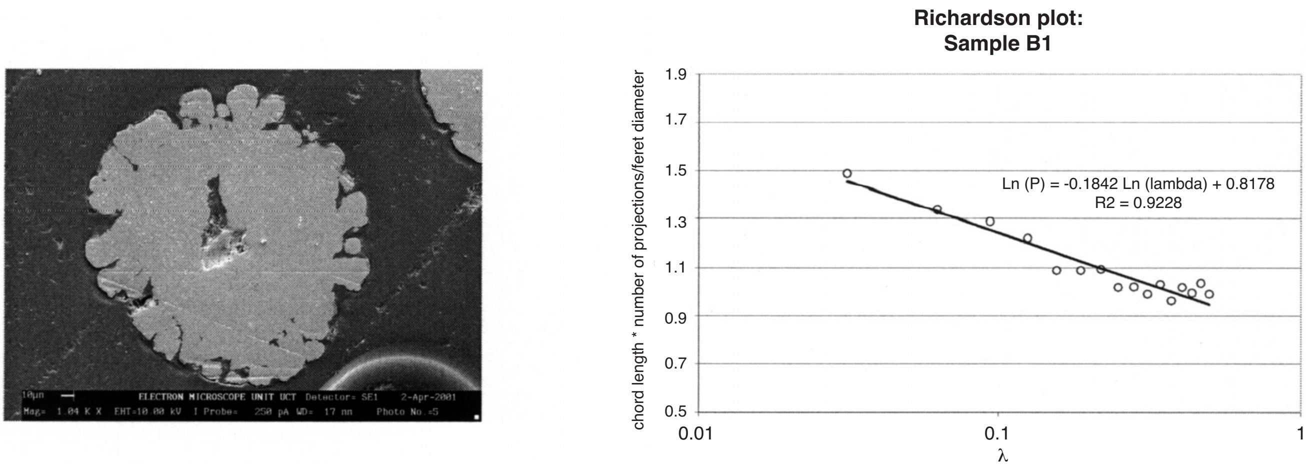

Figure 7—Scanning Electron Microscope profile and Richardson plot for sample B1 (δ = 1.1842)

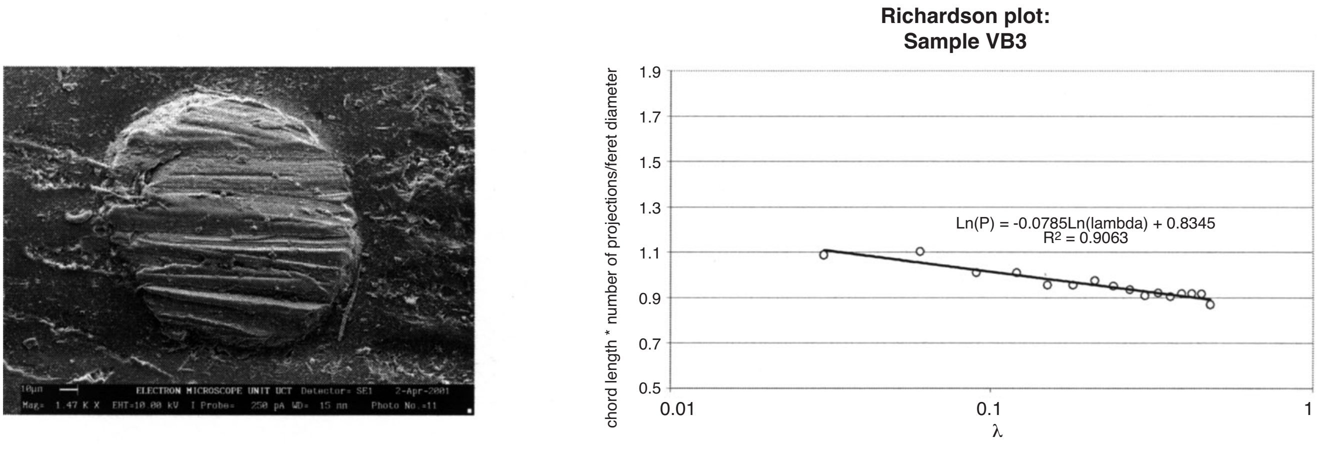

Figure 8—Scanning Electron Microscope profile and Richardson plot for sample VB3 (δ = 1.0785)

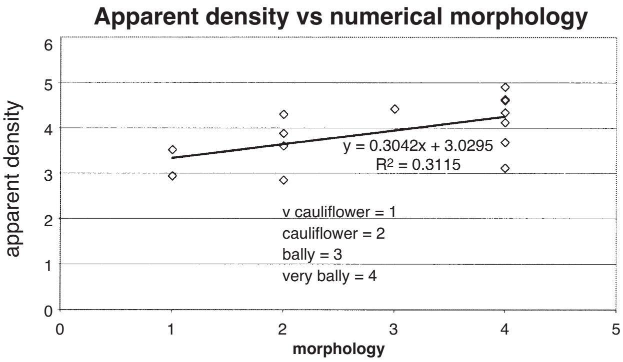

Figure 9—Apparent density vs morphology

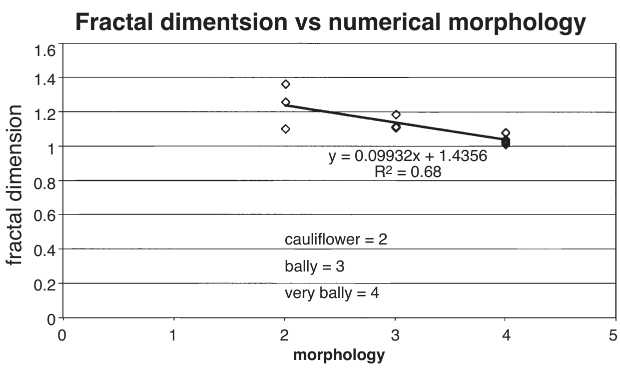

Figure 10—Fractal dimension vs morphology

with increasing 'bally-ness' of the samples. The best-fit least squares linear regression line through the points yields a linear regression coefficient of 0.68, indicating that 68% of the variability in the data can be accounted for by the linear relationship.

Discussion

In general, the numerical analysis indicates that a more rugged surface is characterized by a steeper slope on the Richardson plot, although the relationship between morphology and fractal dimension is relatively weak. However, the data also shows that fractal dimension is a better predictor of morphology than apparent density, which is the measurement currently used on the plant.

One of the objectives of this work, the calculation of structural and textural fractals for the nickel powders, has not been achieved. This is partly due to the limitations of the manual method used for the perimeter estimates and partly due to the insufficiently high resolution of the measurements.

There is clearly much uncertainty in this work and scope for development and improvement on a number of levels.

Structured walk technique

Problems with this measurement method include the fact that it is not possible to measure the fractal dimension of one of the categories of sample ('very cauliflower'), due to its extremely rugged profile with 'islands' developing due to the deep fissures in the cross-section. This highlights a shortcoming of the structured walk technique and indicates the need to develop a technique that will be able to encompass the full range of samples. Although it is low-tech, manual and easy to implement, the structured walk technique can also be problematic in that it is subject to the error inherent in any manual technique.

Descriptors

One of the problems with this work is its reliance on a subjective, qualitative assessment of the descriptive category into which the sample falls. For this work, the samples were classified as 'very cauliflower', 'cauliflower', 'bally' or 'very bally' on the basis of past experience and visual judgement. Another problem with using these categories is that they are discrete, and the spectrum of morphologies is not. The relationship between fractal dimension and morphology might well be stronger if the full spectrum of morphologies were able to be represented in the data. A more robust variable to describe the effect of the morphology of the particle would be its ability to be formed into a stable, robust briquette. This is a quantity that could easily be measured using a briquette mould and a pressure test. This is the subject of current work. This will allow the direct comparison of fractal dimension with 'briquettability', without having to go through the intermediate of a qualitative assessment of morphology.

Sampling

The error introduced by sampling in this work is significant. When the grab samples are mounted into the resin and back polished, each sample will be exposed at a different depth of its cross-section. The crystals selected for measurement were not only those that presented maximum cross-sectional areas, but also those that appeared to be representative of the descriptive category. This was a subjective assessment. In addition, only one (and in one case, two) profiles were measured for each sample. In other words, the data collected was based on the measurement of a single crystal. Ongoing data collection will improve the accuracy of the results.

Alternative techniques

Some promise lies in a technique to characterize surfaces called 'molecular tiling'. The technique was proposed originally by Avnir and Pfeiffer (1983) to quantify surface fractal dimension and consists of adsorbing a series of gases on a surface and determining the mono layer coverage using an appropriate physisorption model. Smaller molecules have more access to finer surface structure than do larger molecules and a larger surface area is measured. It is possible to relate this difference in measured surface coverage to the fractal dimension of the surface. The technique has been used to study catalytic fabric filters, carbon fibres and fly ash. The intention is that the technique could lead to a routine measurement of surface fractal dimension, which in turn could be used to correlate mesoscale properties from the microscale properties provided by the fractal dimension. These correlations are still in development (Ludlow, 2001).

Mosaic transformation has been shown to estimate fractal dimensions that compare well with the structural fractal dimensions estimated by other procedures (Kaye *et al*., 1994). The technique involves transforming the profile to be evaluated into a mosaic of varying tile size. To estimate the perimeter, one counts the number of tiles and multiplies by the side length of the tile. One advantage of this is that it can be implemented by an investigator without access to sophisticated instrumentation.

Computer-aided image analysis also offers potential for evaluating boundary fractal dimensions (Kaye *et al*., 1994).

It has also been shown that the fractal structure of powder grains affects the flow of metal powders (Chan and Paige, 1997). This work was carried out using a shear cell, but it is also possible to carry it out using an avalanching disc (Personal Communication, Kaye 2000), that has potential to separate out the differences in the different types of nickel powder.

Conclusions

It has been shown that a relationship between fractal dimension and morphology exists, and that the fractal dimension is a better predictor of morphology than apparent density, which is the measurement currently used on the plant.

The inability of the structured walk technique to discern the structural and textural fractals and to measure the fractal dimension of the 'very cauliflower' samples highlight the need to select or develop a more sophisticated technique.

Quantifying 'briquettability'

The qualitative descriptors used for the data analysis should be replaced by a quantitative variable that describes the ability of the sample to be formed into a briquette.

Sampling

Ongoing data collection should minimize the errors associated with sampling and measurement of single particles.

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