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Homogeneity characterization of binary grain mixtures using a variance analysis of two-dimensional numerical fractions

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Abstract. A theoretical approach to homogeneity characterization by means of composition variance analysis is presented. A multiscale sampling image analysis is proposed to determine, using the model, both the intensity and the scale of segregation in a binary particle mixture. The method is applied to characterize the homogeneity evolution of a WO_3 -NiO grain mixture with mixing time. The results show that the homogenization is controlled by a kind of diffusion process.

1. Introduction

Many fabrication processes of materials involve a powder-mixing step. Composite materials need prior mixing of the different phases. Some single-phase materials, which are obtained by solid–solid reaction, also require powder mixing. The quality of the resulting material is often highly related to the homogeneity of the initial mixture. Moreover, in the case of multiphase materials, the physical properties are intimately dependent on the homogeneity of the phase distribution in the final product.

The classical mechanisms which are commonly invoked to describe powder homogenization in a shaking mixer are (Lacey 1954, Perry 1963)

- (1) convection of particle assemblies from one point to another of the mixer,
- (2) diffusion of individual particles from regions where they are in excess to regions where they are lacking and
- (3) shearing which breaks down the particle clumps appearing when cohesion forces between particles are important.

In simple rotating drum mixers, the predominant mixing mechanism is diffusion (Fan *et al* 1970, Schofield 1970), and any convection must take place at the very beginning of the process. Such mixers exhibit good performance, as long as the differences in density and particle size of the two components are not too large (Ashton and Valentin 1966, Fan *et al* 1970).

Quantitative characterization of the mixing mechanisms can be made by analysing the composition distribution of samples taken uniformly in the mixture, and using the two parameters defined by Danckwerts (1953):

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(1) the *intensity of segregation* which characterizes the amplitude of the composition differences in the mixture;

(2) the *scale of segregation* which defines a mean correlation distance of the composition.

Convection and shearing tend to reduce the scale of segregation, while diffusion tends to reduce the intensity of segregation.

If the sampling interval of the composition measurements is sufficiently small, and the total length of the analysis sufficiently large, the intensity and scale of segregation can be obtained from the autocorrelation function of the composition (Danckwerts 1953, Schofield 1970). However, analysis is very often performed on samples which are scattered over all the mixture, and only the composition variance is used to follow the mixing process (Lacey 1943, Poole *et al* 1964, Ashton and Valentin 1966, Cartilier and Moës 1986, Herbig 1986). Different expressions are used to derive an intensity of segregation, or rather a mixing index from the variance of the mixture composition (see Fan *et al* (1970) for a review). These parameters are generally dependent on the size of the samples used for the analysis. We shall now discuss this point and show that a multiscale variance analysis can be used to characterize both the intensity and the scale of segregation in a binary mixture of particles.

2. Theoretical approach

Lacey (1954) proposed a theoretical definition of the intensity of segregation, based on an analysis of the variance of the numerical fraction in a binary mixture of particles 1 and 2, with mean numerical fraction p of particles 1. His theory can be summarized as follows.

Let us first consider samples uniformly taken out of the mixture, the samples consisting of one particle. The expectation value E_1 and the variance σ_1^2 of the number N_1 of particle 1 in a sample are given by

$$E_1(N_1) = p \quad (1)$$

$$\sigma_1^2(N_1) = (1-p)^2 p + p^2(1-p) = p(1-p). \quad (2)$$

Let us now consider samples consisting of N adjacent particles. If the mixture is homogeneous, they are equivalent to N independent samples of one particle, and the expectation value and variance of N_1 are deduced:

$$E_N^*(N_1) = Np \quad (3)$$

$$\sigma_N^{*2}(N_1) = Np(1-p) \quad (4)$$

where the superscript asterisk refers to the ideal homogeneous mixture.

In fact, the distribution of N_1 -values is binomial with the first moment given by (3) and the second moment by (Udny Yule and Kendall 1964)

$$E_N^*(N_1^2) = Np + N(N-1)p^2. \quad (5)$$

Lacey also expressed the variance of the unmixed material, i.e. samples are uniformly taken out of the pure phases before mixing, and the N particles are all exclusively of one phase 1 or 2:

$$\sigma_N^{\text{oz}} = (N - Np)^2 p + (Np)^2(1-p) = N^2 p(1-p) \quad (6)$$

where the superscript zero refers to the unmixed material. He deduced a mixing index, which is in fact an intensity of segregation from the comparison of the variance σ_N^2 of the actual mixture with the two limits σ_N^{*2} and σ_N^{o2} :

$$I = \frac{\sigma_N^2 - \sigma_N^{*2}}{\sigma_N^{o2} - \sigma_N^{*2}}. \quad (7)$$

The intensity of segregation is then zero for the homogeneous mixture, and unity for the unmixed material.

For such a parameter to be an intrinsic characteristic of actual mixtures, it should be independent of the sample size N , whatever the degree of mixture, and not only for the homogeneous and unmixed limits. In order to discuss this point, a relationship between the variance and sample size of an inhomogeneous mixture is necessary. In the following, we shall consider a mixture with one characteristic scale S of segregation: for sample sizes much smaller than S , the composition variations inside the samples are small compared with the composition variation between the samples while, for sample sizes much larger than S , the composition variations between the samples are small compared with the composition variations inside the samples. The first case will be referred to as 'large-scale segregation', and the second as 'small-scale segregation', but it should be remembered that 'small scale' and 'large scale' are relative to an experimental reference, i.e. to the sample size.

Lacey (1954) stated, without demonstration, that the intensity of segregation is independent of the sample size for 'diffusive mixing'. By diffusive mixing, he means in fact that samples do not contain particle clumps characteristic of a convection mechanism. This is equivalent to the case of large-scale segregation. Carley-Macaulay and Donald (1962) affirm that 'it can be shown statistically' that the residual variance $\sigma_N^2 - \sigma_N^{*2}$ varies as $N(N-1)$ provided that the composition variations inside the samples can be neglected, which corresponds again to large-scale segregation. With such a variation, the intensity of segregation would be independent of the sample size, as σ_N^{*2} and σ_N^{o2} are given by (4) and (6).

On the other hand, the composition variance has been calculated when the sample size is larger than any scale of segregation in the mixture (Dukes 1951, Lacey 1954, De Chazal and Hung 1968).

However, a more general relationship between the variance and sample size can be derived from a calculation of Bosanquet (a discussion in Rose 1959), for a mixture containing randomly distributed clumps of N_p particles. The composition variation between clumps is characterized by the variance $\sigma^2(p_c)$ of the numerical fraction p_c of particles 1 in the clumps. The calculation assumes that the composition variance between samples can be decomposed into a sum of two independent contributions: the first is due to statistical variations and corresponds to the variance of a homogeneous mixture of identical composition; the second is related to the variance $\sigma^2(p_c)$ and is valid only in the two limiting cases of small-scale and large-scale segregation ($N \ll N_p$ or $N \gg N_p$):

$$\sigma_N^2 = \sigma_N^{*2} + N^2 \frac{\sigma^2(p_c)}{1 + N/N_p}. \quad (8)$$

With such an expression, the intensity of segregation, as defined by (7), would be a function of the sample size N . In fact, we would like the intensity of segregation to be characteristic of the amplitude of the composition differences in the mixture, whatever the scale of segregation. Therefore, the variance of the mixture should be compared not with that

of the unmixed material, but with that of a mixture with the same clump repartition (same scale of segregation), and with complete segregation between the clumps (i.e. clumps are exclusively of one phase 1 or 2). The variance of such a mixture can be obtained by developing $\sigma^2(p_c)$ as in (2):

$$\sigma_N^{o2} = \sigma_N^{*2} + N^2 \frac{p(1-p)}{1+N/N_P} \quad (9)$$

It is worth noting that equation (4) for the homogeneous mixture and equation (6) for the unmixed material should be able to be obtained from equation (9) as N_P tends respectively to unity and to infinity. This is not exactly the case, which shows some limits of Bosanquet's model.

With the general expression (9) for σ_N^{o2} , the intensity of segregation can be calculated using (7):

$$I = \frac{\sigma^2(p_c)}{p(1-p)} \quad (10)$$

It is independent of the sample size in both large-scale and small-scale segregation, and it is characteristic of the amplitude of the composition differences in the mixture ($I = 0$ for the homogeneous mixture, and $I = 1$ for the mixture with complete segregation on any scale).

Hence, an estimate of the intensity of segregation can be obtained from a variance analysis of the numerical fraction in samples of size N , using equation (7), σ_N^{*2} and σ_N^{o2} being determined from (4) and (9), respectively. The difficulty is that the reference σ_N^{o2} is a function of the scale of segregation, characterized by N_P , which is *a priori* unknown. In order to determine both the intensity and the scale of segregation, a multiscale variance analysis must be performed. The parameter $M = \sigma_N^{o2}/\sigma_N^{*2}$, often used in the literature as a mixing index, can be plotted versus N . Referring to Bosanquet's model (equations (8) and (9)) M should vary as follows:

$$N \ll N_P \text{ (large-scale segregation): } M = 1 + NI \quad (11)$$

$$N \gg N_P \text{ (small-scale segregation): } M = 1 + N_P I \quad (12)$$

Hence, the intensity I of segregation may be estimated from the slope of the linear variation at small N -values (11), and then the scale of segregation N_P from the abscissa at which a deviation from the linear variation is obtained. N_P can also be determined from the asymptotic limit of M (12), using the value of I calculated at small N -values.

The calculation of Bosanquet is based on the assumption that the two contributions to the composition variance between samples (statistical variations in the composition, and dispersion of the clump compositions) can be separated. In the following, another model of the mixture will be considered. Under more restrictive conditions, this model allows a more rigorous calculation of the composition variance. The model of the mixture consists of a random arrangement of two domains D_i and D_s , having different compositions, lower (i) or greater (s) than the mean value, each domain being homogeneous (figures 1 and 2). This can be regarded as limited for real inhomogeneous mixtures, which may present continuous fluctuations of the composition. The influence of an ordered arrangement of the domains will also be examined. It will be seen that the results obtained are very similar to those derived from Bosanquet's theory, which gives more weight to the analysis of the scale and intensity of segregation from the variance-sample size relationship, as proposed above.

The parameters p (the average numerical fraction of particles 1 in the mixture), p_α (the average numerical fraction of particles 1 in the domain D_α ($\alpha \equiv i$ or s)) and x_α (the fraction of the total number of particles in the domain D_α ($\alpha \equiv i$ or s)) are related by the expression

$$x_i p_i + x_s p_s = p \quad (13)$$

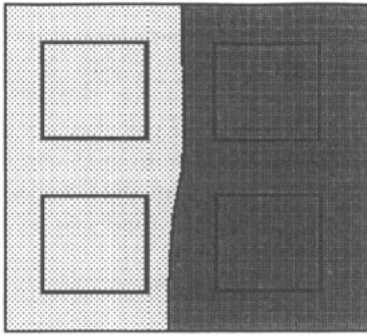


Figure 1. Samples in a mixture with large-scale segregation.

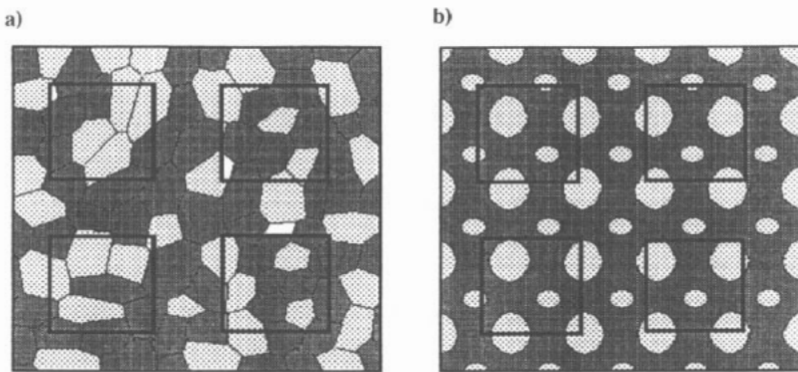


Figure 2. Samples in a mixture with small-scale segregation: (a) domains as a random packing of cells; (b) ordered domains.

2.1. Large-scale segregation

Let us first consider that the size of the domains is large with respect to the sample size (figure 1). The variance of the number of particles 1 per sample has the general expression

$$\sigma_N^2(N_1) = E(N_1^2) - E^2(N_1) = E(N_1^2) - N^2 p^2. \quad (14)$$

If the samples are uniformly distributed in the mixture, this becomes

$$\sigma_N^2(N_1) = x_i E_i(N_1^2) + x_s E_s(N_1^2) - N^2 p^2 \quad (15)$$

where $E_i(N_1^2)$ (or $E_s(N_1^2)$) represents the expectation value of N_1 in the domain D_i (or D_s) and is deduced from (5) by replacing p by p_i (or p_s):

$$\sigma_N^2(N_1) = Np(1-p) + N(N-1)x_i x_s \Delta p^2 = \sigma_N^{*2}(N_1) + N(N-1)x_i x_s \Delta p^2 \quad (16)$$

where $\Delta p = p_s - p_i$ represents the composition difference between the two domains. The case of complete segregation is obtained as $p_i = 0$ and $p_s = 1$ and leads to equation (6) corresponding to the unmixed material, as expected. The intensity of segregation, as defined by (7), can be derived:

$$I = x_i x_s \frac{\Delta p^2}{p(1-p)}. \quad (17)$$

This is the exact analogue of (10), as $\sigma^2(p_c)$ is simply equal to $x_i x_s \Delta p^2$ in our model.

2.2. Small-scale segregation

Let us now assume that the size of the domains is small with respect to the sample size (figure 2).

2.2.1. Random arrangement of the domains. An approximate calculation will be given here by assuming that the mixture is a random arrangement of cells from D_i and D_s (figure 2(a)), each cell containing the same number N_P of particles, and applying the analysis of Lacey to the cells. The variance of N_1 when samples are constituted of one cell ($N = N_P$ particles) can be expressed by

$$\sigma_{N_P}^2(N_1) = x_i E_i(N_1^2) + x_s E_s(N_1^2) - N_P^2 p^2 \quad (18)$$

where $E_i(N_1^2)$ (or $E_s(N_1^2)$) represents the expectation value of N_1^2 for a cell of N_P particles in the domain D_i (or D_s) and is deduced from (5) by replacing p by p_i (or p_s) and N by N_P . Equation (18) can then be rewritten

$$\sigma_{N_P}^2(N_1) = N_P p(1-p) + N_P(N_P - 1)x_i x_s \Delta p^2. \quad (19)$$

If the cell arrangement is disordered, the variance for samples containing N_c cells ($N_c = N/N_P$) can be deduced:

$$\sigma_N^2(N_1) = N_c \sigma_{N_P}^2(N_1) = N/N_P \sigma_{N_P}^2(N_1). \quad (20)$$

Then, by using (19), σ_N^2 can be rewritten

$$\sigma_N^2(N_1) = Np(1-p) + N(N_P - 1)x_i x_s \Delta p^2 = \sigma_N^{*2}(N_1) + N(N_P - 1)x_i x_s \Delta p^2. \quad (21)$$

As before, the case of complete segregation is obtained with $p_i = 0$ and $p_s = 1$, and the intensity of segregation again given by (17). The case of homogeneous mixture (equation (4)) is obtained as N_P equals unity, as expected.

2.2.2. Ordered arrangement of the domains. Let us now suppose that the arrangement of the domains is ordered, with a period (representing the scale of segregation here) which is lower than the sampling size (figure 2(b)). Each sample will then contain the same numbers $N_i = Nx_i$ of particles in the domain D_i and $N_s = Nx_s$ of the particles in the domain D_s .

The number of N_1 of particles 1 in a sample is the sum of the number of particles 1 in D_i and in D_s :

$$N_1 = N_1^i + N_1^s. \quad (22)$$

The distribution of particles 1 in D_i and D_s can be considered as independent, and hence

$$\sigma_N^2(N_1) = \sigma_{N_i}^2(N_1^i) + \sigma_{N_s}^2(N_1^s). \quad (23)$$

As N_i and N_s are constant, equation (4) can be used for $\sigma_{N_i}^2(N_1)$ and $\sigma_{N_s}^2(N_1)$ by replacing N by N_i (or N_s) and p by p_i (or p_s), which yields

$$\sigma_N^2(N_1) = Np(1-p) - Nx_i x_s \Delta p^2 = \sigma_N^{*2}(N_1) - Nx_i x_s \Delta p^2 \quad (24)$$

$\sigma_N^2(N_1)$ is then smaller than the value $\sigma_N^{*2}(N_1)$ of the homogeneous mixture, and the intensity of segregation is always given by (17).

2.3. Variation in σ^2/σ^{*2} with sampling size N

Complete analysis of the intensity and scale of segregation can be made by analysing the variance σ_N^2 at different sampling sizes N .

The ratio $M = \sigma_N^2/\sigma_N^{*2}$ can be calculated using the previous models. For sampling sizes much smaller than the segregation scale, equations (16) and (4) give

$$M = 1 + (N - 1)I. \quad (25)$$

For sampling sizes much larger than the segregation scale, equations (21) and (24) are used for random and ordered arrangements, respectively, of the domains:

$$\text{random domains : } M = 1 + (N_P - 1)I \quad (26)$$

$$\text{ordered domains : } M = 1 - I. \quad (27)$$

Equations (25) and (26) are very similar to (11) and (12) derived from Bosanquet's theory and merge into one another as $N \gg 1$ and $N_P \gg 1$. The expected variation in M with $N - 1$ is shown figure 3 in the case where the mixture presents a typical scale N_P of segregation. For N -values much smaller than N_P , the variation is linear with slope I ; for N -values much higher than N_P , M is constant.

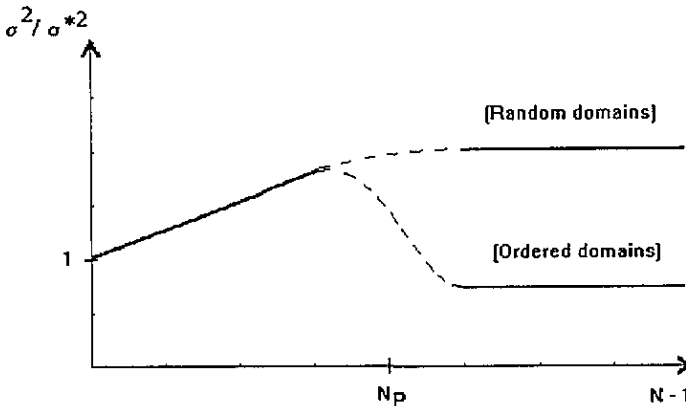


Figure 3. Expected variation in the ratio $M = \sigma_N^2/\sigma_N^{*2}$ with the sampling size $N - 1$ (only the full lines are representations of the models).

The intensity of segregation can then be estimated from the slope of the first part of the curve. The N -values at which a deviation from the linear variation is observed gives a range of values for the scale of segregation. This estimation process, which does not use the asymptotic value of M (small-scale segregation), avoids any specification about the nature (random or ordered; continuous or discontinuous) of the domain arrangement.

Extension of the method to the case of several scales of segregation is outside the scope of this paper. However, it could be shown that, if the scales are independent, and sufficiently different, the plot of M versus $N - 1$ would exhibit several linear parts, from which the different scales of segregation, associated with their intensity, could be determined (see Missiaen and Chaix (1994) for a similar analysis with the variance of the volume fraction).

3. Experimental procedure

Homogeneity characterization was carried out on WO_3 (phase 1)–NiO(phase 2) mixtures. The purpose was to follow the evolution of inhomogeneities of the mixture versus mixing time for a given mixer. No attempt was made to improve homogeneity by testing different mixing apparatus. Powders were sieved in the 63–100 μm size class. The value $v_1 = 0.75$ of the WO_3 volume fraction was calculated to ensure a stoichiometric composition (the mean numerical fraction n_1 of WO_3 grains equals 0.75, if the size distributions of NiO and WO_3 grains are assumed identical). The densities of NiO and WO_3 are 6.7 g cm^{-3} and 7.1 g cm^{-3} , respectively. All the powders are free flowing. The grain shapes are polyhedral for both oxides.

3.1. Mixture preparation

Powders were mixed in an epoxy-resin cylindrical crucible ($h = 15 \text{ mm}$; $d = 6 \text{ mm}$) placed in a plastic bottle which was shaken with a Turbula rotating mixer during times from 1 s to several hours. A liquid epoxy resin was then slowly poured into the crucible with a microsyringe. After solidification for a few hours, the cylinder was cut perpendicular to its axis, and the section was polished. Figure 4 shows a typical section of a mixture. The analysed sections contained several thousand particles.

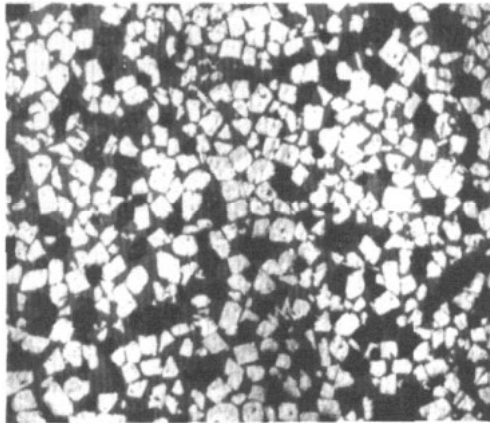


Figure 4. Typical section of a mixture.

It can be assumed that the coating process does not modify the particle packing, since the liquid resin is light with respect to the solids and solidifies without any volume variation. This has been checked on a loose packing of glass beads, which was characterized by image analysis after such preparation. The estimated packing fraction and 3D mean coordination number were 0.60 and 5.9, respectively (Missiaen 1989), values which are close to those which are generally admitted in literature for such packings (see, e.g., Scott (1960) and Bennett (1972)). Therefore, it can be concluded that the preparation process does not alter the packing characteristics.

3.2. Image analysis of the sections

The sections were studied with a Nacet NS1500 image analyser. 20 video views were made from each sample. Two images were thresholded from each view: one for the NiO grains, and one for the WO₃ grains. The grains at the edge of a field were erased, whereas the grains inside the field were reduced to a point by homotopic marking (Coster and Chermant 1985) so that edge effects could be avoided during further cutting out of the fields. An external strip, the width of which exceeded the maximum particle radius, was removed from each field, in order to avoid the contribution of grains at the edge (figure 5).

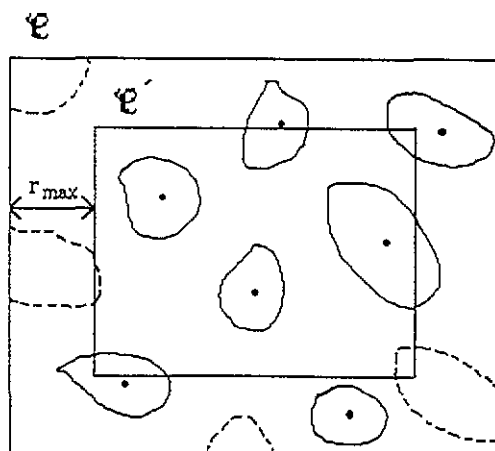


Figure 5. Principle of field analysis: the grains which hit the edges are removed while the others are indicated by a point.

Identical square fields were then cut out in every initial field, large enough to contain a number of grains higher than a fixed value N . By a series of erosions, keeping the square shape of the field unchanged, the number of grains was brought back to N in every field. The number of point markers of each phase could then be evaluated, and therefore the variance $\sigma_N^2(N_1)$ of the number of WO₃ grains per field. Different sampling scales were examined this way, and the function $\sigma_N^2/\sigma_N^{*2} = f(N - 1)$ plotted for each mixture.

In order to characterize any scale of segregation in the mixture, the sampling scale variation must be as large as possible. The choice is that of the magnification; a compromise must be made to include as many grains as possible in every field, while keeping the resolution sufficient to be able to separate these grains easily. In our case, samples containing 2–48 grains could be cut out from every field. The need to separate the individual grains means that we cannot deal with a large number of grains on the same image. So it is not easy to quantify a large scale of segregation (more than 50 grains) by this method. A variance or covariance analysis of the volume fraction can be used to increase the sampling size limit (Missiaen and Chaix 1994).

4. Results

Figure 6 presents the results obtained for different mixing times. Although fluctuations may be observed on the curves, a general trend can be drawn as the mixing time increases. For

short mixing times (less than 1 min), the ratio σ^2/σ_N^{*2} rapidly tends to values lower than unity. Consistently with our models, this result is a testimony of the very small scale of segregation, with an ordered arrangement of the domains having a short period of a few grains. For intermediate mixing times (1 min–1 h), a curve with a maximum is observed, indicating that the scale of segregation is in the interval of analysis, i.e. between two and 48 grains. For longer mixing times (1–5 h), the curve is globally increasing, indicating a scale of segregation larger than the maximum analysed sampling size (48 grains).

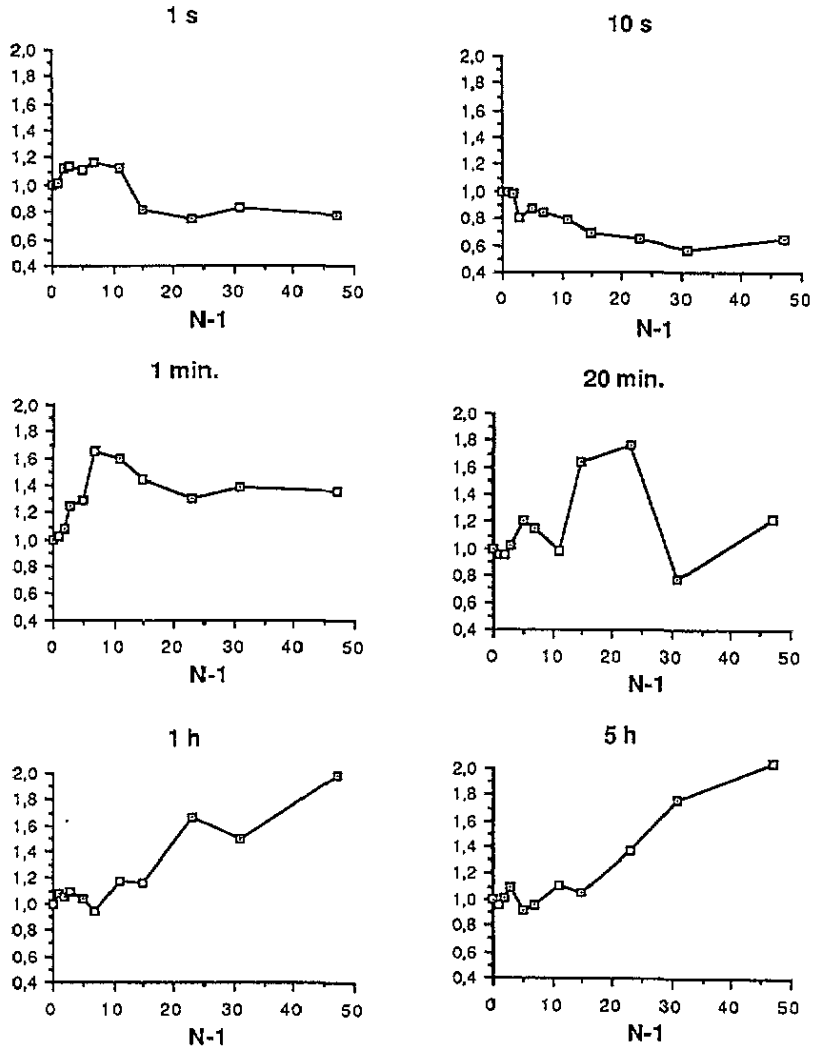


Figure 6. Experimental variation in the mixing index σ_N^2/σ_N^{*2} with $N - 1$ for different mixing times.

An increase in the segregation scale with increasing mixing time is then observed. For mixing times longer than 1 min, the intensity of segregation can be estimated from equation (25) by linear regression on the increasing part of the variation. The composition

Table 1. The intensities of segregation and the composition differences versus mixing time.

t_M	I (%)	Δp
1 s	—	>0.39
10 s	—	>0.53
1 min	9	0.26
10 min	3.9	0.17
20 min	3.6	0.16
1 h	2.1	0.13
5 h	2.4	0.13

difference Δp is deduced with the assumption $x_i = x_s = 0.5$ (domain of equal size). For mixing times shorter than 1 min, the intensity of large-scale segregation cannot be computed because the increasing part of the curve is too limited, but Δp can be estimated from the height of the asymptotic level by using (27), assuming perfect order, and hence a lower bound for Δp is obtained. The values given in table 1 show a global decrease in the intensity of segregation, i.e. a decrease in composition differences, with increasing mixing time.

5. Discussion

First, the importance of the multiscale sampling analysis of homogeneity must be emphasized. Let us imagine, for instance, that analysis has been performed only on a scale of 48 grains. An increase in the mixing index σ_N^2/σ_N^{*2} with increasing mixing time would have been observed (figure 6). It would then have been concluded that a demixing of the mixture has occurred, which signifies that the mixing efficiency would become worse as the mixing time increases. Global analysis yields a completely different interpretation, as seen below.

Indeed, an increase in the scale of segregation associated with a decrease in the intensity of segregation with increasing mixing time has been observed. Convection and shearing tend to reduce the scale of segregation. This is not evidenced in our case. If convection plays a role, it must be at the very beginning of the mixing, because a scale of segregation of about a few grains is observed after mixing for only a few seconds.

In our case, at least for mixing times longer than 1 min, homogenization seems to be controlled by a kind of diffusion process, which agrees with the literature data. Indeed, the evolution of the concentration profile in the case of atomic diffusion is qualitatively comparable with that deduced from our results; it yields a decrease in the intensity of segregation, associated with an increase in the scale of segregation. The first effect is due to a decrease in the amplitude of composition differences in the mixture. The second effect is attributed to the progressive elimination of particle clumps by diffusion, which becomes more rapid as their size decreases, in this way increasing the mean scale of segregation. This description is of course qualitative, and estimation of the average intensity of segregation in a random packing of inhomogeneous clusters, by assuming that 'diffusion' obeys Fick's law on a microscopic scale, is far more problematic.

It can be seen that the decrease in the intensity of segregation is slow after mixing for 1 h. The residual intensity of segregation (2.4%) is still important; it corresponds to a composition deviation $\Delta p = 0.13$, i.e. 18% of the mean value.

6. Conclusions

This work presents a method which gives estimates of both the intensity and the scale of segregation in a binary mixture of particles. The method is based on a multiscale sampling analysis of the 2D numerical fraction variance. It uses a variance-sample size relationship, which is calculated from a simple model of the mixture. This relationship looks like that derived by Bosanquet (a discussion in Rose 1959) with a slightly different model. The method was applied to the characterization of homogeneity evolution during mixing of a binary WO_3 -NiO powder mixture. After mixing for 1 min, the homogenization is controlled by a kind of diffusion process. The composition differences in the mixture are still important even after mixing for several hours.

References

- Ashton M D and Valentin F H H 1966 *Trans. Inst. Chem. Eng.* **44** 166-88
Bennett C H 1972 *J. Appl. Phys.* **43** 2727
Carley-Macaulay K W and Donald M B 1962 *Chem. Eng. Sci.* **17** 493-506
Cartililier L H and Moës A J 1986 *Drug Dev. Ind. Pharmac.* **12** 1203-18
Coster M and Chermant J L 1985 *Précis d'Analyse d'Images* (Paris: CNRS) p 202
Danckwerts P V 1953 *Appl. Sci. Res. A* **3** 279-96
De Chazal L E M and Hung Y C 1968 *Am. Inst. Chem. Eng.* **14** 169-73
Dukes J A 1951 *Int. Chem. Eng.* **32** 521
Fan L T, Chen S J and Watson C A 1970 *Ind. Eng. Chem.* **62** 53-69
Herbig R 1986 *J. Powder Bulk Solids Technol.* **10** 7-12
Lacey P M C 1943 *Trans. Inst. Chem. Eng.* **21** 53-9
Lacey P M C 1954 *J. Appl. Chem.* **4** 257-68
Missiaen J M 1989 *Thèse Institut National Polytechnique de Grenoble, Ecole Nationale Supérieure de Mécanique (Saint-Étienne)* p 137
Missiaen J M and Chaix J M 1994 *J. Microsc.* **175** 195-204
Perry J H 1963 *Chemical Engineers Handbook* 4th edn (New York: McGraw-Hill) pp 21-35
Poole K R, Taylor R F and Wall G P 1964 *Trans. Inst. Chem. Eng.* **42** 305-15
Rose H E 1959 *Trans. Inst. Chem. Eng.* **37** 47-64
Schofield C 1970 *Trans. Inst. Chem. Eng.* **48** 28-34
Scott G D 1960 *Nature* **188** 908
Udny Yule G and Kendall M G 1964 *An Introduction to the Theory of Statistics* (London: Griffin)