Structural Ratio for Predicting the Voidage of Binary Particle Mixtures

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Knowledge of the voidage of mixtures of particles is important for predicting the packing properties of particulate products and the rheology of concentrated particle suspensions and fluidized particles, which again determines handling properties. Powders containing more than one type of particle are used extensively in industry, for example, for the coatings, food, pharmaceutical, cosmetics, and cement industries. In this article an improved method for predicting the voidage of binary particle mixtures, applicable to both spherical and nonspherical particles will be presented.

Westman (1936) developed an empirical model for predicting the voidage of binary particle mixtures. He devised a simple conical expression containing one fit parameter G (the relation is given below). Various workers have since given empirical relations for G as a function of the ratio of particle diameters $r \equiv d_{p,s}/d_{p,l}$ where the subscripts s and l refer to the small and large particle fractions, respectively. Relations for $G(r)$ fitted to data for spherical particles do not work for nonspherical ones. Yu et al. (1993) suggested using a packing equivalent particle diameter for nonspherical particles, and showed that the relation given $G(r)$ for spherical particles could then also be used for nonspherical ones. A number of other workers have addressed the problem of packing of binary mixtures, but none appear to carry as much promise as the Westman equation for modeling both spherical and nonspherical particles. The Westman equation accounts correctly for both of the extremes $r = 1$ and $r \to 0$, which can both be calculated analytically as mentioned below.

Westman's (1936) equation for the total bed volume occupied by unit volume of solid material (called the specific volume) V (equal to $1/(1-\epsilon)$, where ϵ is the fractional voidage of the particle bed), is in the notation of Yu et al. (1993)

$$\left(\frac{V - V_l X_l}{V_s}\right)^2 + 2G\left(\frac{V - V_l X_l}{V_s}\right)\left(\frac{V - X_l - V_s X_s}{V_l - 1}\right) + \left(\frac{V - X_l - V_s X_s}{V_l - 1}\right)^2 = 1 \quad (1)$$

where X is the volume fraction. The fit parameter G is related to the particle size ratio, but is independent of the composition of the mixture. Yu et al. (1993) give the following expression for $G(r)$

$$\frac{1}{G} = \begin{cases} 1.355\, r^{1.566} & (r \le 0.824) \\ 1 & (r > 0.824) \end{cases} \quad (2)$$

In the limiting case where the two particle fractions are identical $r = 1$; the packed bed voidage will not change when they are mixed. It is reasonable that in the case where the particle sizes of the two fractions are the same (while V_l may differ from V_s), V will be lying approximately on the straight line connecting V_l and V_s as indicated in the diagram shown in Figure 1. The other limiting case is where $r \to 0$. The lowest possible voidage in that case is obtained if a bed of large particles is poured, and the voids subsequently are filled with small particles. The bed properties then become

$$\epsilon = \epsilon_s \epsilon_l$$

or

$$V = \frac{V_l V_s}{V_l + V_s - 1} \quad (3)$$

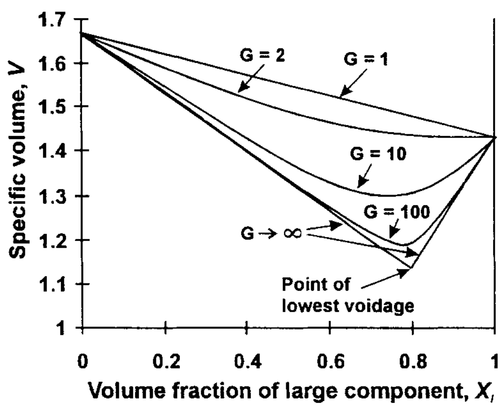

Figure 1. Effect of value of G on the calculated value of V as a function of the mixture composition.

where ϵ_s and ϵ_l are the fractional void volumes of beds of the pure particle fractions. The corresponding volume fraction of large particles is, in terms of the voidage fraction

$$X_l = \frac{1 - \epsilon_l}{1 - \epsilon_l \epsilon_s} \tag{4}$$

This point is also indicated in Figure 1. Westman and Hugill (1930) showed (and this is easily verified) that for other compositions of such mixtures, V lies on the straight line segments (also shown in the figure) connecting this point with those corresponding to the pure particle fractions.

The Westman equation (Eq. 1) caters for both of these two extreme conditions with the values 1 and ∞, respectively, for the parameter G.

In order to evaluate the predictive power of Eqs. 1 and 2 and investigate the potential for further improvement, a considerable number of experimental data of the voidage of binary particle mixtures were extracted from the literature. These data include 331 measurements of spherical particle mixtures (extracted from McGeary, 1961; Yerazunis et al., 1962; Epstein and Young, 1962; Yerazunis et al., 1965; Ridgway and Tarbuck, 1968; Aïm et al., 1967, 1968; Eastwood et al., 1969; Formisani, 1991; Yu et al., 1992) and 148 measurements of nonspherical particle mixtures (extracted from Yerazunis et al., 1962; Yu et al., 1992, 1993). The data are for powder beds consisting of diverse materials and varying in state from tapped over loosely packed to fluidized and settled beds in liquids. Sample preparation is an important part of measuring packed-bed voidage and standard procedures for this have been published. In the Westman method, the packing of the mixtures is expressed in terms of the packing of the pure constituents. When using this method, therefore, the only requirement on sample preparation is that the procedure should be the same for all the samples.

Prediction of Voidages for Spherical and Nonspherical Particles

The predictive power of Eqs. 1 and 2 is good, the correlation coefficient r^2 between calculated and experimental voidages is 0.957 for spherical particles.

The voidages of mixtures of nonspherical particles cannot be predicted directly from Eqs. 1 and 2. Yu et al. (1993) propose using Wadell's sphericity ψ (the ratio of surface areas of a volume equivalent sphere and the actual particle), and to modify the value of r empirically by substituting the volume equivalent particle diameter d_v (equal to d_p for spherical particles) with a packing equivalent particle diameter d_{pa} calculated from

$$d_{pa} = \left(3.1781 - 3.6821\frac{1}{\psi} + 1.5040\frac{1}{\psi^2}\right)d_v \tag{5}$$

Equation 5 contains three empirical constants. The predictions of Eqs. 1, 2 and 5 are very good; the correlation coefficient r^2 is 0.984. The voidages of these nonspherical particles span a wider range than those of spherical ones, giving rise to a higher correlation coefficient.

An advantage of using this method is that the equivalent particle diameter can be estimated directly on the basis of the particle properties. There is also a theoretical advantage in having defined a particle diameter, which is equivalent in terms of packing behavior. A disadvantage in the practical use of this method is that d_{pa} is difficult to determine, either directly from packing behavior or indirectly through determination of the Wadell shape factor and the use of Eq. 5. Also, nonsphericity has to be dealt with using a separate method and a total of five empirical constants are involved for this.

We propose an alternative and supplemental approach to the prediction of the voidage of binary mixtures, which will work directly in the same form for both spherical and nonspherical particles, and which involves only one empirical constant in total. The new method also requires less experimental data (data which is, moreover, more easily obtained in practice) as input. Instead of using a ratio of linear particle dimensions, we propose using a structural ratio, which is the size ratio relevant to the packing of binary mixtures of particles: the ratio of the volume of a small particle with its associated interstitial region to the volume of the interstitial region associated with a large particle.

Structural Ratio

Consider the sketch of a binary mixture of spherical particles shown in Figure 2a. The voidage of the entire bed depends on the ability of the smaller particles to fill the interstitial space between the larger particles. In such an interstitial space, the surfaces of the larger particles constitute walls for the bed of smaller particles. The voidage fraction of packed beds is higher at solid walls, causing the voidage to be higher than ϵ_s. The thickness of the near-wall region of increased voidage is about 0.5 of the particle diameter (Ben Aïm and le Goff, 1967, 1968). How significant this is in increasing the mean voidage of the bed of small particles in the interstitial space. Thus, this depends on the dimensions of the smaller particles relative to that of the interstitial space. A limiting case is when the particles are relatively very small ($r \to 0$); the void fraction then approaches ϵ_s.

If the small particles are nonspherical, however, each particle with its associated void occupies a larger volume than a volume-equivalent spherical particle (Figure 2b). r, the ratio of volume-equivalent particle diameters, can therefore, not be used directly in the same predictive relations as for spherical particles. A similar argument shows that r is not the appropriate size ratio if the large particles are nonspherical. We introduce the structural ratio which is the ratio directly relevant for the packing of the smaller particles in the interstices of the larger ones, whether either fraction is spherical or not.

The total number of particles in the unit volume of the bed can be calculated from the voidage and the volume equivalent diameter [for nonmonosized particles, the number-volume mean diameter should be used (Allen, 1990)]

$$\frac{(1-\epsilon)}{[(\pi/6)d_v^3]} \tag{6}$$

In a bed of large particles the volume of interstitial space per particle is

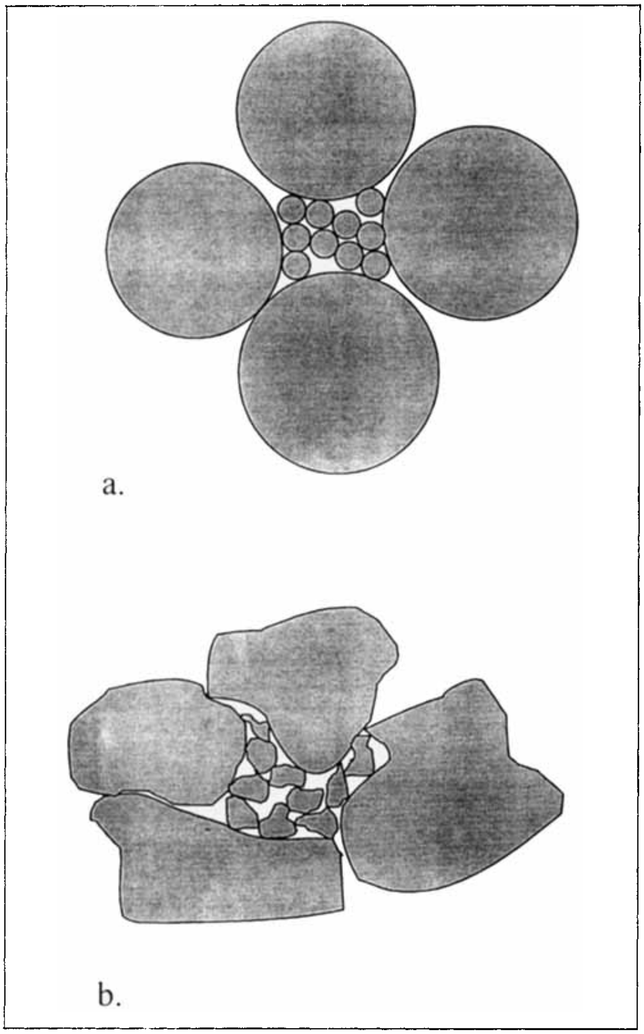

Figure 2. Binary mixtures: (a) spherical; (b) nonspherical particles.

$$\frac{\epsilon_l}{\left[\frac{1-\epsilon_l}{(\pi/6)d_{v,l}^3}\right]} \qquad (7)$$

In a bed of small particles, the volume of a particle with its associated interstitial space is

$$\frac{1}{\left[\frac{1-\epsilon_s}{(\pi/6)d_{v,s}^3}\right]} \qquad (8)$$

Dividing Eq. 8 by 7 and rearranging gives the structural ratio

$$r_{str} = \frac{[(1/\epsilon_l)-1]r^3}{(1-\epsilon_s)} \qquad (9)$$

This ratio is not symmetric in the small and large particles, and does not become unity if the two particle fractions are the same. It does, however, reflect the size ratio directly relevant for the packing of binary mixtures of particles. The arguments used above are only valid for smaller volume ratios, where the concept of small particles filling the interstices between large ones. It will turn out, however, that using r_{str} also in the gray area of comparable particle sizes leads to excellent predictive power.

As with the conventional size ratio, we need to relate r_{str} to G empirically. The following functional form has been chosen

$$G = r_{str}^k + (1-\epsilon_l^{-k}) \qquad (10)$$

The functional form of the first term is the same as that of Yu et al. (1993), except that including a multiplying constant does not improve the fit. The term in parenthesis is mostly small, but is added to ensure that the value of G becomes unity for identical particle fractions. This avoids having to split up the expression for G as done in previous work. An optimization gives the value of -0.63 for the value of k. Equations 9 and 10 can easily be written in terms of Vs by using the fact that $\epsilon = (1-1/V)$.

Figure 3a shows a parity plot for spherical particles; the correlation coefficient, r^2 is 0.954. Since the ratio r_{str} reflects

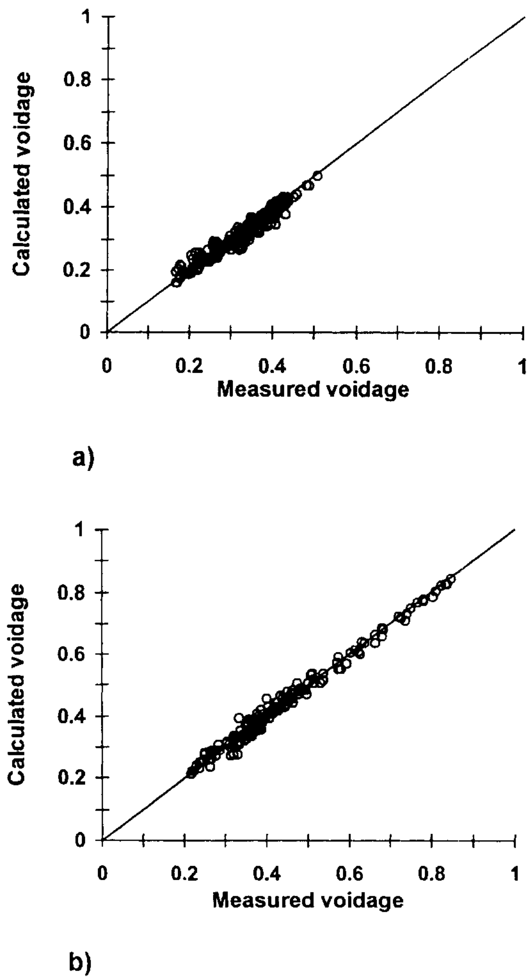

Figure 3. Parity plots: (a) spherical and (b) nonspherical particles.

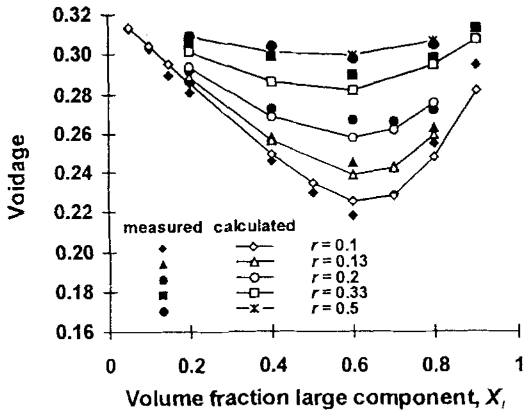

Figure 4. Calculated and measured voidage as a function of the composition of a binary mixture.
From Sohn and Moreland (1968).

the ratio directly relevant for the packing of particles, Eq. 9 can be used in the same form and with the same value for k for nonspherical particles. Figure 3b shows a parity plot, the correlation coefficient is 0.986.

Mixture Size Distribution

In what went before, only cases in which both the particle fractions are monosized or have a narrow size distribution have been considered. If one or both of the fractions has a wider size distribution, it is to be expected that the relations predicting the mixture packing behavior from the packing of the pure fractions will be different. The packing of each of the two fractions separately is then more efficient (see, for instance, Hoffmann and Finkers, 1995), and one would expect that the effect of mixing them in reducing the voidage will be less significant.

Sohn and Moreland (1968) have published experimental data for such binary mixtures. Equations 1 with 9 do not give a good fit to their results with the same value for k as for monosized particles. However, if the constant is changed to -0.345, the fit with the data becomes excellent. Figure 4 shows the data of Sohn and Moreland with the predictions of Eqs. 1 and 9 using this value for k.

This suggests the possibility that the exponent k can be related to the spread of the size distributions of the two fractions to obtain an even more generally applicable prediction based on the use of structural ratio.

Concluding Remarks

The relation of Westman, Eq. 1 with the relation for $G(r)$ suggested by Yu et al. (1993), Eq. 2 describes the voidage of binary mixtures of spherical particles adequately well. The modification of the particle diameter suggested by Yu et al. (1993), Eq. 5, has a theoretical merit, and predicts the packing behavior of nonspherical particles well.

The structural ratio, r_{str}, is the ratio which is directly relevant for the packing of binary particle mixtures. Using r_{str} has the advantage that less empirical parameters (in fact, only one) need be used for fitting the predictive relations to the data. Moreover, the same relations with the same constant can be used for nonspherical as for spherical particles. Another advantage in using r_{str} for the practical prediction of the voidage of binary mixtures of nonspherical particles is that the use of Eqs. 9 and 10 requires no value for the particle sphericity or packing data other than those required by the Westman Equation itself.

Notation

r = ratio of linear particle dimensions
r^2 = correlation coefficient, the square of Pearson's r

Subscripts

l = large fraction
s = small fraction
v = volume equivalent

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