Ordered Mixing: A New Concept in Powder Mixing Practice

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SUMMARY

A randomization concept of powder mixing has largely been explored in the past. Non-cohesive, non-interacting particulate systems are primarily mixed by this process. Cohesive, interacting particulate systems may also be mixed to a high degree of homogeneity. Many of the requirements of this type of mixing are different from those required for randomization. The process of mixing cohesive, interacting particulate systems follows a "disorder to order" concept and has been termed ordered mixing.

Ordered mixing probably occurs widely in actual systems. Although the requirements for ordered mixing are different from those for random mixing, the rate of mixing follows the same laws. Ordered mixtures are frequently more homogenous than random mixtures and, in certain cases, may offer a better approach to practical mixing problems.

INTRODUCTION

Powder mixing has been the subject of numerous investigations over the past decade [1,2]. For simplicity, most of the systems examined have consisted of comparatively coarse, free-flowing particles and have led to the concept of randomization or "shuffling" of the particles as the mixing process. The randomization may be brought about by a variety of mechanisms, including diffusion and convection, according to the variety of mixer employed. Randomization requires equally sized and weighted particles, with little or no surface effects, showing no cohesion or interparticle interaction, to achieve the best results. Undoubtedly, this is an important process in powder technology today and has served a useful purpose in enabling mixing theories to be quantified. However, it cannot be applied to all practical mixing situations, especially for cohesive or interacting particulate systems and may, therefore, not be unique amongst explanations of powder mixing phenomena.

A concept of ordered mixing may be useful in explaining powder mixing of cohesive or interacting fine particles. There is no theoretical reason why fine particles cannot be mixed by a randomizing process. However, cohesive properties and other surface phenomena usually develop with increasing fineness and these will tend to order rather than to randomize the mixing operation. Where there are large differences in particle size, fine and coarse particles would tend to segregate at a faster rate than they would mix together, unless some interacting forces were utilized to mix the system. Ordered mixing may be considered to be different from random mixing since it does not require equally sized or weighted particles; it requires particle interaction, *i.e.* adsorption, chemisorption, surface tension, frictional, electrostatic or any other form of adhesion. It results in an ordered mixing arrangement of the particles, which is best shown diagrammatically in Fig. 1(a) for an equal mixture of black and white particles, although ordered mixtures are more likely to occur where there are a few large black particles and many small white particles. Figure 1(b) shows the same mixture in a randomized pattern.
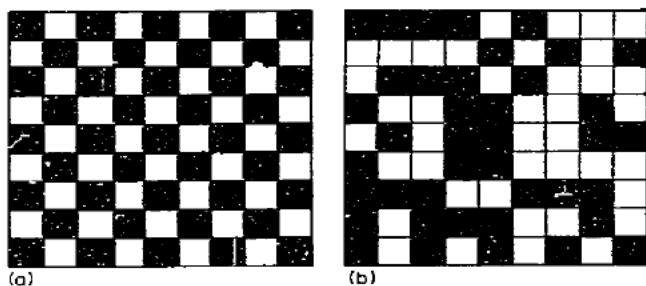
Indications that ordered mixing may occur

Fig. 1.(a). Ordered mixture of equal proportions of black and white particles.

Fig. 1(b). Randomized mixture of equal proportions of black and white particles.

are available in the literature from mixing observations [3,4] and from angle of repose date [5 - 7], which show that adhesion of fine particles considerably affects the properties of the particulate system.

Studies of homogeneity of powder mixtures have frequently been based on the heterogeneity of the completely randomized mixture [8 - 10]. Such a basis would be unsatisfactory for ordered mixtures. However, other concepts of homogeneity, such as those using as a basis the required degree of homogeneity [11] or of a standard degree of heterogeneity [12], should provide a useful solution for the examination of homogeneity of ordered mixtures.

The rate of mixing is generally described by a logarithmic relationship [13] as would be required by the first-order kinetics suggested for ordered mixing. It is the purpose of this paper to consider the possibilities of ordered mixing and to examine if such a concept would be useful in explaining homogeneity and rate of mixing in certain applications and, as such, provide a useful addition to the theory and practice of powder mixing operations.

THEORY

Consider spheres of diameter D and diameter d, where $D >> d$. Surface area of a large particle = πD^2. The area occupied by each small particle adhering to a larger one will be the projected area $\pi d^2/4$. Therefore the number of small particles adhering to each larger one in a monolayer = $4D^2/d^2$.

Allowing for the fact that the small particles will not pack regularly or that there will be some areas of the larger particles devoid of bin-

ding sites, only a fraction, f, of this number, n, will actually adhere in a monolayer:

$$n = 4fD^2/d^2 \tag{1}$$

A more exact solution [7] for small particles close-packed in an hexagonal arrangement is given by

$$n = \frac{2\pi \ (D + d)^2 \ f}{\sqrt{3} \ d^2} \tag{2}$$

If the mixture contains 1% by weight of particles of diameter, d, 5×10^{-4} cm in particles of diameter, D, 5×10^{-2} cm, then the number of small, N_d, and large N_D, particles in a 1-g sample is given by (the density for each is taken as 1.2 g cm^{-3}):

$$N_d \pi \frac{d^3}{6} 1.2 = 0.01; N_d = 1.27 \times 10^8$$

$$N_D \pi \frac{D^3}{6} 1.2 = 0.99; N_D = 1.26 \times 10^4$$

Thus the number of small balls adhering to each large one is given by $n = N_d/N_D = 1.0 \times 10^4$, and substituting this value in eqn. (1) gives $f = 0.25$.

The equilibrium situation

There are a definite number of small particles that may adhere to a single large particle for any given system. Consider this to be the equilibrium situation. Thus, in the example given above there are 10^4 small particles associated with each large particle. Each unit of the system is identical and it may be considered to consist of a single material.

If a lower percentage of fine particles had been used then the total number of adherence sites in the larger particles would not have been filled. Under these conditions it is probable that some large particles would have a larger number of small particles associated with them than others. In such a case each unit may be different and the system could be considered to consist of many components. Alternatively, an equilibrium situation could be established by some sites on the larger particles being more active than others. These sites would be saturated more rapidly, resulting in a single component system in which the fraction f of fine particles adhering to large ones is reduced compared with the maximum possible value.

If an excess of fines had been used, then the

equilibrium situation will be attained by adherence at all available sites and the excess fines may attempt to mix with this material in a random manner. Thus, a binary mixture could theoretically exist, but its composition would be different from that considered by the ingredient concentrations present. In the above example, if 10% fines had been used the concentration of coarse particles would be 90%. The coarse particles would come to equilibrium with 0.9% of fine material giving concentrations of 90.9 and 9.1 adhered units and excess fines respectively.

Homogeneity

Buslik [12] defined homogeneity, H, as the reciprocal of (W_1), that weight of sample necessary to give a standard deviation of 1%:

$$H = 1/W_1$$

or using a logarithmic scale, where H_i is an index of homogeneity,

$$H_i = -\log W_1 \tag{3}$$

For a randomized mixture, the standard deviation, σ, is given by

$$\sigma^2 = G(100 - G)w/W \tag{4}$$

where G is the percentage of ingredient in the mixture, w is the effective mean particle weight and W is the sample weight. This equation applies where all particles are of the same weight; corrections must be applied in calculating the effective mean weight of multisized systems.

If $\sigma = 1\%$ as required by the definition of homogeneity, then

$$W_1 = G(100 - G)w \tag{5}$$

Substituting in eqn. (3),

$$H_i = -\log [G(100 - G)w] \tag{6}$$

For a single component, the value of H_i can be calculated from the minimum sample size that may be considered. For example, Buslik, in considering pure hydrogen gas, took the minimum sample size as a single hydrogen molecule, thus giving the limiting value which H_i can attain as 23.5. Sodium chloride was treated similarly, excepting that the minimum sample size could be either a sodium ion or a chloride ion giving rise to a discontinuity in the evaluation of H_i, which lies between 22.0 and 22.2.

In a completely ordered system, the components are mixed so that they may be considered as a single material. Thus, the evaluation of H_i

for such a system would follow exactly the same arguments as for sodium chloride. The sample size would necessarily have to be smaller than one complete ordered unit and the homogeneity would lie between the respective values for the weights of a large (W_D) and a small (W_d) particle adhering to it.

$$W_D = 1.2\pi \frac{D^3}{6} \text{ and } W_d = 1.2\pi \frac{d^3}{6}$$

giving $4.11 < H_i < 10.11$.

Where only 0.5% of fines has been used, H_i still lies within the above limits providing an equilibrium situation can be attained. Where an excess of fines is used (*i.e.* 10%), then the problem is complicated since both ordered mixing will occur and randomized mixing can, in theory, also occur.

If the same system of 1% by weight of fine particles is considered to be randomly dispersed in large particles at a sample weight of 1 g, two mathematical treatments are possible. Firstly, the samples could consist of clumps of weight equivalent to a single particle, and being randomly distributed then $H_i = -\log G(100 - G)W = -\log (99 \times 1 \times 1) = -2.00$.

Or, alternatively, if the individual samples were considered as pharmaceutical tablets requiring the range of contents to be ± 15% of the mean, then

$$3\sigma = 0.15 \times 1, \text{ and } \sigma = 0.05.$$

If this system is randomized, substitution of eqn. (4) in eqn. (6) gives

$$H_i = -\log \sigma^2 W \tag{7}$$

Since $W = 1$ g, then $H_i = +2.60$; either index of homogeneity being considerably less than the homogeneity that could be obtained for the completely ordered system.

RATE OF MIXING

The rate of ordered mixing follows first-order kinetics, since the rate of mixing will be proportional to the number of fine particles remaining to adhere onto the larger particles. For a given particulate system, the rate of mixing will be proportional to the concentration of unmixed fine particles. Such a mixing rate is also applicable to random mixing [13], and thus both mixing phenomena could not be separated by a simple examination of the kine-

tics of the mixing process. However, whereas coarse, equally sized and weighted particles randomize relatively quickly, a mixture of large and small particles would randomize very slowly and segregate very rapidly. This latter system, however, could mix extremely rapidly by an ordered process. Thus, examination of the actual rates of mixing might provide a useful clue as to the type of mixing taking place.

APPLICATION OF ORDERED MIXING

The literature on powder mixing theory is unanimous in the requirement that only equally sized, equally dense particles can be mixed to fine-scale homogeneity. Such a situation is not true in practice, where small concentrations of fine powders are often incorporated into more coarse materials with a high degree of homogeneity. One example is the incorporation of tablet lubricants into tablet granules. Applications already exist and ordered mixing provides a means of understanding how such processes are possible. Undoubtedly, other applications can be considered as soon as the mechanisms of ordered mixing are fully recognized and understood.

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