Title	The degree of mixing for completely randomized mixture of particulate solids
Sub Title	
Author	Sakano, Hiroshi
Publisher	慶応義塾大学工学部
Publication year	1974
Jtitle	Keio engineering reports Vol.27, No.2 (1974.) ,p.43- 61
JaLC DOI	
Abstract	The purpose of the present paper is to characterize statistically completely randomized mixture of equisized solid particles which are classified into less than two types according to their densities or compositions. To measure the degree of mixing, the author defines the mean square deviation about the weight concentrations of key component between the partitions of mix, and calculates its expectations for completely randomized mixture based on hypergeometric distribution. It is essential improvement that the void fraction is taken into consideration and the method of ratio estimate is used. Finally, the author describes the mixing process by using one- and two-dimensional mixing Markov chains and shows the expectation of mean square deviation for completely randomized mixture can be achieved as a limit of the process.
Notes	
Genre	Departmental Bulletin Paper
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=KO50001004-00270002-0043

KEIO ENGINEERING REPORTS
VOL. 27 NO. 2

THE DEGREE OF MIXING FOR COMPLETELY RANDOMIZED MIXTURE OF PARTICULATE SOLIDS

By

HIROSHI SAKANO

FACULTY OF ENGINEERING
KEIO UNIVERSITY
YOKOHAMA 1974

KEIO ENGINEERING REPORTS
VOL. 27, NO. 2, pp. 43-61, 1974

THE DEGREE OF MIXING FOR COMPLETELY RANDOMIZED MIXTURE OF PARTICULATE SOLIDS

HIROSHI SAKANO

Dept. of Administration Engineering, Keio University, Yokohama 223, Japan

(*Received Sep. 17, 1973*)

ABSTRACT

The purpose of the present paper is to characterize statistically completely randomized mixture of equisized solid particles which are classified into less than two types according to their densities or compositions.

To measure the degree of mixing, the author defines the mean square deviation about the weight concentrations of key component between the partitions of mix, and calculates its expectations for completely randomized mixture based on hypergeometric distribution. It is essential improvement that the void fraction is taken into consideration and the method of ratio estimate is used.

Finally, the author describes the mixing process by using one- and two-dimensional mixing Markov chains and shows the expectation of mean square deviation for completely randomized mixture can be achieved as a limit of the process.

1. Introduction

The two-component mixing system of equisized particulate solids has been discussed by a lot of authors. Above all, the completely random mixture has been often treated by their research works since P. M. C. Lacy showed the theoritical variance of sample content based on binomial distribution (1943).

The number of specific type of particles in a spot sample drawn from completely randomized mix with various types of equisized finite particles is a random variable with hypergeometric distribution, which was stated by S.S. Weidenbaum (1953), but the author could find no reporters who make a theory of the mixing with hypergeometric distribution. This fact is out of the question for practical application such as large mixture in industry or under the assumption of particles' movements being independent to others, while it can not be set at naught when we study theoretically the complete mixing state as a realized state of stochastic process. Therefore, most results caluculated in this paper are based on hypergeometric distribution.

Though we image many kinds of material as composition of particles, only two components—the key component and the rest- are essentially treated. While all particles are classified into not less than two types according to their compositions or densities.

To measure the degree of mixing and to describe the mixing processes, we divide the space of mixture into some cells and defines the mean square deviation about the weight concentrations of the key constituent between these cells. For completely randomized mixture, the author calculates the expectation of the mean square deviation and then, using this value, derives the expected values of the mixing indexes.

If the densities of particles are different, it is to be noted that the total weight of particles in each cell is also a random variable (K. STANGE, 1954). And only a few reporters (Y. ŌYAMA, 1939, 1940) have discussed on the influences of void fraction to solid mixing. Not only the changes of apparent volume of mixture, but also the variation of the total number of particles in a spot sample (R. BLUMBERG & J. S. MARITY 1953) is considered to be caused by void fraction. In view of these facts, the author introduces the method of ratio estimate and the model of void particle which was proposed by him.

Y. ŌYAMA, & K. AYAKI, (1956), I. INOUE, & K. YAMAGUCHI, (1969) studied the mixing process described by Markov chain, but their reports were not necessarily clear with respect to following three points. 1; They did not give the sufficient conditions for the movement of particle to be a Markov chain. 2; They neglected the changes of void fractions in whole mixture and in each cell. 3; They did not derive the expected value of mean square deviation.

The author improves these points, and then shows the expectation of the mean square deviation for completely randomized mixture is equal to one of the limits of mixing process described by Markov chain under the assumptions of local randomization and ergodicty of two dimensional Markov chain.

2. Definition of Mean Square Deviation

The author wants to study the mixing process for an aggregate of heterogeneous equisized solid particles. In order to describe the state of such aggregate, let us consider a space in which the aggregate of particles is located. At first, we consider the size of this space to be measured by N unit spaces whose volumes are u (equivolume). Let us assume the size of each unit space is enough to contain at most one particle. Next, we divide this space into K cells so that the i-th cell has m_i unit spaces ($\sum_{i=1}^{i=K} m_i = N$).

We classify the components of particles into key material and the rest, and then name the key material "A". Besides, "q_j", $j=1\sim L$ are used to distinguish the L types of particles according to their composition or densities. Let us introduce the following symbols;

- f_j is the weight of component A contained in q_j-particle.
- w_j is the weight of q_j-particle.
- N_j is the number of q_j-particle in whole mixture.
- N_s is the total number of particles in whole mixture, where $N_s=\sum_{j=1}^{j=L}N_j$.
- v is the volume of each particle (equisized).
- V is the true volume of mixture, where $V=N_s \cdot v$.
- W is the weight of mixture, where $W=\sum_{j=1}^{j=L}w_jN_j$.
- u_a is the apparent volume of whole mixture ($u_a \geqslant V$).
- m_{ji} is the number of q_j-particles in the i-th cell.
- h_i is the total number of particles in the i-th cell, where $h_i=\sum_{j=1}^{j=L}m_{ji}$.
- g_i is the total weight of particles in the i-th cell, where $g_i=\sum_{j=1}^{j=L}w_jm_{ji}$.
- Y_i is the wall effect in the i-th cell.
- m_{iT} is defined as $m_{iT}=m_i-Y_i$.
- N_T is defined as $N_T=N-\sum_{i=1}^{i=K}Y_i$, where $N_S \leqslant N_T$.
- e_i is the void fraction of the i-th cell. $\left(\text{The void fraction of whole mixture is } \dfrac{u_a-V}{u_a}.\right)$

Now we define the concentration of the key constituent A in the i-th cell as follows:

(2.1) $$c_i^A=\left(\sum_{j=1}^{i=L}f_jm_{ij}\right)/g_i$$

which is the ratio of the weight of component A to the total particle weight in the i-th cell.

The concentration of key constituent A in whole mixture, c_0^A, is written as

(2.2) $$c_0^A=\frac{1}{W}\sum_{j=1}^{j=L}f_jN_j\ .$$

If we suppose not only $N_S=N$, $L=2$ (only two types of particles), $f_1/w_1=1$, $f_2/w_2=0$, but also $w_1=w_2$ (equal density), then we have

(2.3) $$c_i^A=m_{1i}/m_i, \quad c_0^A=N_1/N_S\ .$$

We shall treat this case in the following section III. Most writers have adopted the volume (number) fractions (2.3) as concentration which are the special cases of (2.1) (2.2).

Using above definitions, the author defines "mean square deviation from c_0^A", by $(\sigma_b^A)^2$, which is;

(2.4) $$(\sigma_b^A)^2=\sum_{i=1}^{i=K}\frac{g_i}{W}(c_i^A-c_0^A)^2\ .$$

Be it noted; $c_0^A=\sum_{i=1}^{i=K}\frac{g_i}{W}c_i^A$, hence

$$(\sigma_b^A)^2=\frac{1}{W}\sum_{i=1}^{i=K}\frac{(\sum_{j=1}^{j=L}f_jm_{ji})^2}{g_i}-(c_0^A)^2 .$$

For a completely unmixed system where each cell is composed of the same type of particle, the value of c_i^A is any one of f_j/w_j, $j=1\sim L$. Therefore it is easily verified that $(\sigma_b^A)^2$ is given by:

(2.5)
$$\frac{1}{W}\sum_{j=1}^{j=L}N_jf_j\left(\frac{f_j}{w_j}\right)-(c_0^A)^2 ,$$

we denote this by $(\sigma_0^A)^2$.

If $f_i=0$ $j\geq 2$, then $(\sigma_0^A)^2=c_0^A\left(\frac{f_1}{w_1}-c_0^A\right)$. As is well known, $(\sigma_0^A)^2=c_0^A(1-c_0^A)$ when $L=2$, $f_1/w_1=1$, $f_2/w_2=0$.

For a perfect mixing, which can be hardly achieved by the ordinary mixing, we put $c_i^A=c_0^A$, $i=1\sim K$, by distributing L-types of particles in the same proportion to each cells. Then we have

(2.6)
$$(\sigma_b^A)^2=0 .$$

If we introduce such $(\sigma_w^A)^2$ as $c_0^A(1-c_0^A)=(\sigma_w^A)^2+(\sigma_b^A)^2$, then we may think $(\sigma_b^A)^2$ is between cells variance and $(\sigma_w^A)^2$ is within cells variance. For a completely unmixed system, $(\sigma_w^A)^2=\frac{1}{W}\sum_{j=1}^{j=L}(f_jN_j)\left(1-\frac{f_j}{w_j}\right)$, for a perfect mixing, $(\sigma_w^A)^2=c_0^A(1-c_0^A)$. (For a perfect mixture, $(\sigma_w^A)^2=0$.)

In the following, the superscripts of c_i^A, c_0^A, σ_b^A, σ_0^A are omitted for simplicity.

The concentration at each cell varies from time to time as the mixing proceeds, but the mixing process is not always a stochastic process. Hence, for clear distinction, we use the random variables $M_{ji}(t)$, $H_i(t)$, $G_i(t)$, $C_i(t)$ and $D_b^2(t)$, corresponding to m_{ji}, h_i, g_i, c_i, σ_b^2 respectively, when we regard the value of concentration at any fixed mixing time t as a realized value of a stochastic process.

By the same reason, we use $U_a(t)$, $\varepsilon_i(t)$ as the random variables which describe u_a, e_i at mixing time t ($V\leq U_a(t)\leq uN$).

Let us represent the intial condition prior to mixing at mixing time $t=0$ by S_0: the number of q_j-particles in the i-th cell is represented by $m_{ji}(0)$. We shall use this symbol in the last section.

We define completely randomized mixture as randomly mixed batch in which every combination of the locations of particles (not always countable) is realized with an equal chance. Let M_{ji}, H_i, G_i, C_i, D_b^2, U_a, ε_i be random variables for completely randomized mixture, which are independent of time parameter t. We distinguish randomized mixture from random mixture in which any pair of particles has no correlation. On the other hand, we do not distinguish randomly mixed state from complete mixing state as mentioned in section IV. The complete mixing state is usually attained as a limit of a mixing operation. It should be noted that the complete mixing we treat here must satisfy the mixture property, which is a stronger condition than ergodicity (E. HOPF, 1934).

3. Degree of Mixing for Completely Randomized Mixture

A number of formulas to measure the degree of mixing have been devised. In this paper, they are restricted to statistical formulations based on concentration. T. YANO & Y. SANO (1964) classified the statistical formulas for the degree of mixing of binary solid mixture. In order to evaluate the state of mixture at the end of mixing, they assert the following index is suitable;

$$I_e=1-\sqrt{\sigma_b^2/\sigma_0^2}$$

And, they say, for the purpose of describing the state of mixture on the way of mixing, the following index is reasonable;

$$1-I_d=1-\frac{\sigma_0^2-\sigma_b^2}{\sigma_0^2-\sigma_R^2}$$

where $\sigma_R^2=E(D_b^2)$, is the expected value of mean square deviation from c_0.

In this paper, let us consider $1-I_d$ and the following index I_e^* instead of I_e;

$$I_e^*=1-\sigma_b^2/\sigma_0^2$$

For a completely unmixed system (see 2.2),

$$I_e^*=I_d=0$$

For a perfect mixing, from (2.6)

$$I_e^*=1,\quad 1-I_d=1-\frac{\sigma_0^2}{\sigma_0^2-\sigma_R^2}.$$

In the following discussion in this section, we are to treat only the simplest case that $N_s=N$, $L=2$, $f_1/w_1=1$, $f_2/w_2=0$, $w_1=w_2$, but the arguments about mixing index and volume sampling can be extended to the general case by applying the results in the succeeding sections.

For completely randomized mix, every one of the $\binom{N_S}{m_i}$ combinations of state as to the i-th cell is achieved with equal probability $\binom{N_S}{m_i}^{-1}$, where $m_i=M_{1i}+M_{2i}$. Therefore we may consider that, for any i, the random variable M_{1i} has hypergeometric distribution whose mean and the second moment are

$$E(M_{1i})=m_i\frac{N_1}{N_S} \tag{3.1}$$

and

$$E(M_{1i}^2)=m_i\frac{N_1}{N_S}\left\{(N_1-1)\frac{m_i-1}{N_S-1}+1\right\}.$$

From (2.3) and (3.1),

(3.2) $$E(C_i)=E\left(\frac{M_{1i}}{m_i}\right)=\frac{N_1}{N_S}=c_0 \ .$$

Hence, the variances of C_i, $i=1\sim k$, are

(3.3) $$V(C_i)=\frac{c_0(1-c_0)}{m_i}\frac{N_S-m_i}{N_S-1}, \ i=1\sim k.$$

By definition of σ_b^2 and (3.3), we obtain the expected value of mean square deviation from c_0, σ_R^2, as follows;

(3.4) $$\sigma_R^2=E(D_b^2)=E\left(\sum_{i=1}^{i=K}\frac{m_i}{N_S}(C_i-c_0)^2\right)=\sum_{i=1}^{i=K}\frac{m_i}{N_S}V(C_i)=c_0(1-c_0)\frac{K-1}{N_S-1} \ .$$

Thus σ_R^2 depends on K, c_0 and is in inverse proportion of N_S-1. But it is independent of the way of division of mixture into cells. Here we note that the formula (3.3) can be easily seemed in the usual simple random sampling theorem.

By the way, the covariance of C_i and C_j is:

(3.5) $$\text{Cov }(C_iC_j)=\frac{N_1}{N_S^2}\left(\frac{-N_S+N_1}{N_S-1}\right)<0 \ ,$$

since $$E(M_{1i}M_{1j})=\frac{N_1(N_1-1)}{N_S(N_S-1)}m_im_j \ .$$

From (3.4), the expected values of $1-I_d$ and I_e^* are:

$$E\left(1-\frac{\sigma_0^2-D_b^2}{\sigma_0^2-\sigma_R^2}\right)=0 \ ,$$

and

(3.6) $$E(1-D_b^2/\sigma_0^2)=\frac{N_S-K}{N_S-1}=1-\frac{K-1}{V/v-1} \ .$$

Formula (3.6) implies that, if $K<1$, and the other conditions are unchanged, the smaller the size of particles becomes, the better the degree of mixing does. This coincides with the result given by T. FUJIMORI, & H. ISHIKAWA in their experiment (1972).

In a similar way, we can give the expected value of mixing index which is to be estimated by the spot sampling. Note that each realized state of completely randomized mixture is not only a sample drawn from the stochastic processes, but also a population by itself for spot sampling. We may consider each lot has one-to-one correspondence to an aggregate of particles in a cell.

Let $\bar{c}$ and s^2 be the sample mean and the sample variance from completely randomized mixture such as the sample size is n and increment sizes are $m_{(i)}$, $i=1\sim n$. That is;

$$\bar{c}=\sum_{i=1}^{i=n}\frac{m_{(i)}}{N_n}C_{(i)} \ , \quad s^2=\sum_{i=1}^{i=n}\frac{m_{(i)}}{N_n}(C_{(i)}-c_0) \ ,$$

where $N_n=\sum_{i=1}^{i=n}m_{(i)}$.

Then, from (3.2), (3.3) and (3.5)

$$E(\bar{c})=c_0,\quad V(\bar{c})=\frac{c_0(1-c_0)}{(N_S-1)}\left(\frac{N_S}{N_n}-1\right),$$

$$E(s^2)=\frac{c_0(1-c_0)}{N_n/n}\,\frac{N_S-N_n/n}{N_S-1}.$$

Comparing above formula with (3.4), we have

$$E(s^2)=\frac{(nN_S/N_n)-1}{K-1}\sigma_R^2.$$

In particular, increment sizes are all m and $N_S/\mathrm{m}=K$, then

$$\sigma_R^2=E(s^2)=\frac{c_0(1-c_0)}{m}\,\frac{N_S-m}{N_S-1}=\frac{c_0(1-c_0)}{m}+0\left(\frac{1}{N_S}\right).$$

In this case, s^2 is coincident with an estimator of D_b^2.

Most of the works so far adopted this estimator to measure the degree of mixing. The expectations of $1-I_d$ and I_e^* are

$$E\left(1-\frac{\sigma_0^2-s^2}{\sigma_0^2-\sigma_R^2}\right)=0$$

$$E\left(1-\frac{s^2}{\sigma_0^2}\right)=\frac{N_S}{N_S-1}\left(1-\frac{1}{m}\right)=\left(1-\frac{1}{m}\right)+0\left(\frac{1}{N_S}\right):\ N_S\geq 1,$$

which depend on the increment sizes.

(To measure the quality of mixture, we had better use $c_0(1-c_0)$ instead of σ_0^2 in I_d and I_e^*.)

4. Ratio Estimate

In this section, we shall examine the general case the the density of particles is not homogeneous and the number of particles in a cell is varing. We can no longer call $E(C_i(t)-c_0)^2$ "variance" because $C_i(t)$ is usually a biased estimator of c_0.

From (2.5), $\sigma_R^2(t)$, the expected value of mean square deviation from c_0 at mixing time t, is

$$\sigma_R^2(t)=E(D_b^2(t))=\frac{1}{W}\sum_{i=1}^{i=K}E\frac{(\sum_{j=1}^{j=L}f_jM_{ji}(t))^2}{G_i(t)}-c_0^2. \tag{4.1}$$

The value of $\sigma_R^2(t)$ increases as the differences of weights, compositions, among L kinds of particles become large.

For example in case of $L=2$, (4.1) is expanded as; if $w_2>w_1$,

$$\frac{1}{W}\sum_{i=1}^{i=K}E((f_1-f_2)M_{1i}(t)+f_2m_i)^2\left(\sum_{r=0}^{r=\infty}\frac{(w_2-w_1)^r}{(w_2m_i)^{r+1}}M_{1i}^r(t)\right)-c_0^2 \ ,$$

and if $w_1>w_2$,

$$\frac{1}{W}\sum_{i=1}^{i=K}E((f_2-f_1)M_{2i}(t)+f_1m_i)^2\left(\sum_{r=0}^{r=\infty}\frac{(w_1-w_2)^r}{(w_1m_i)^{r+1}}M_{2i}^r(t)\right)-c_0^2 \ .$$

Therfore $\sigma_R^2(t)$ decreases as $f_2\to f_1$ or $w_2\to w_1$.

$E(C_i(t))$ and (4.1) can be calculated approximately on replacing $G_i(t)$ in the denominators of themselves by $E(G_i(t))$. Then,

$$E(C_i(t))\doteqdot\sum_{j=1}^{j=L}f_jE(M_{ji}(t))/\sum_{j=1}^{j=L}w_jE(M_{ji}(t)) \tag{4.2}$$

$$\sigma_R^2(t)\doteqdot\frac{1}{W}\sum_{i=1}^{i=K}\{\sum_{j=1}^{j=L}f_j^2E(M_{ji}^2(t))+2\sum_{r<j}f_rf_jE(M_{ri}(t)M_{ji}(t))\}/ (E_{j=1}^{j=L}w_jE(M_{ji}(t))-c_0^2 \ . \tag{4.3}$$

For an aggregate of particles with different densities, no completely randomized mix can be attained practically because the segregation occures by gravity or acceleration (Y. OYAMA, 1939; M. B. DONALD & B. ROSEMAN, 1962; etc.). However, the influence of such phenomena may be reduced as small as possible by using some special kind of mixers. In the following discussion, we deal with such an ideal critical mixing that the differences of particle weights do not cause the segregation.

Now, let us investigate completely randomized mix. To begin with, we introduce the frequency function (density) of H_i, which is expected to be obtained from experiment, and denote it by $f_i(y)$. (As for the definition of H_i, see section II.)

Using the hypergeometric distribution, we get

$$E(M_{ji})=EE(M_{ji}|H_i)=\frac{N_j}{N_S}E(H_i) \ , \tag{4.4}$$

$$E(M_{ji}^2)=EE(M_{ji}^2|H_i)=\frac{N_j(N_j-1)}{N_S(N_S-1)}E(H_i^2)+\frac{N_j(N_S-N_j)}{N_S(N_S-1)}E(H_i) \ , \tag{4.5}$$

$$\begin{aligned}E(M_{ji}M_{ri})&=\frac{1}{2}\{E(M_{ji}+M_{ri})^2-E(M_{ij}^2)-E(M_{ri}^2)\}\\&=\frac{N_jN_r}{N_S(N_S-1)}(E(H_i^2)-E(H_i)) \ .\end{aligned} \tag{4.6}$$

Let substitute (4.4) (4.5) (4.6) into (4.2) and (4.3), we have

$$E(C_i)\doteqdot c_0 \ ,$$

$$\sigma_R^2\doteqdot\frac{1}{W^2}\{(\sum_{j=1}^{j=L}f_jN_j)^2(d_r-K-N_S+1)+\sum_{j=1}^{j=L}f_j^2N_j(N_SK-d_r)\}\frac{1}{(N_S-1)} \tag{4.7}$$

where $$d_r=\sum_{i=1}^{i=K}\frac{E(H_i^2)}{E(H_i)} \ .$$

Here, for the sake of convenience, let $Q(N_S)$ be

$$\sum_{j=1}^{j=L} f_j^2 N_j(N_S-N_j)-2\sum_{r>j} f_r N_r N_j \ .$$

If $w_i \neq w_j$ for some $i \neq j$ and yet $N_S=N$, then from (4.7),

$$\sigma_R^2 \doteqdot \frac{1}{W^2} Q(N_S)\frac{K-1}{N_S-1} \ , \quad \text{since } E(H_i^2)=m_i^2 \ , \quad E(H_i)=m_i \ .$$

If $N_S \leq N$ and yet $w_j=w$ for any j, then it should be noted that C_i is an unbiased estimator of c_0. Namely,

$$E(C_i)=\sum_{j=1}^{j=L}\frac{f_j}{w}E\left(\frac{M_{ji}}{H_i}\right)=\sum_{j=1}^{j=L}\frac{f_j}{w}\sum_c c\sum_{y=0}^{y=m_i}P(M_{ji}=cy \mid H_i=y)f_i(y)$$

$$=\sum_{j=1}^{j=L}\frac{f_j}{w}\sum_{y=0}^{y=m_i}f_i(y)\sum_{x=0}^{x=y}\frac{x}{y}\binom{N_j}{x}\binom{N_s-N_j}{y-x}\Big/\binom{N_s}{y}=c_0 \ .$$

Moreover, in this case,

$$\sum_{i=1}^{i=K}E\left(\frac{M_{ji}^2}{H_i}\right)=\sum_{i=1}^{i=K}\sum_{y=0}^{y=m_i}f_i(y)\sum_{x=0}^{x=y}\frac{x^2}{y}P(M_{ji}=x \mid H_i=y)$$

$$=\frac{N_j}{N_S}\left\{(N_j-1)\frac{N_S-K}{N_S-1}+K\right\} \ ,$$

$$\sum_{i=1}^{i=K}E\left(\frac{M_{ji}M_{ri}}{H_i}\right)=\frac{N_S-K}{N_S(N_S-1)}N_jN_r \ .$$

Therefore, we get

$$\sigma_R^2=\frac{1}{W^2}Q(N_S)\frac{K-1}{N_S-1} \ , \tag{4.8}$$

where $w_j=w$ for all j.

It is important (4.8) gives a exact value. In other words, the expected value of mean square deviation for completely randomized mix does not depend on the void fraction or the number of particles in each cell.

In the next section, we shall construct a model such that the distribution of H_i is provided by the following distribution,

$$f_i(y)=\binom{N_S}{y}\binom{N_T-N_S}{m_{iT}-y}\Big/\binom{N_T}{m_{iT}} \ . \tag{4.9}$$

Then the bias of ratio estimate in (4.7) is, from (4.8),

$$E(D_b^2-\hat{D}_b)=\frac{c_0(c_0W-1)(N_S-N_T)(K-1)}{(N_T-1)(N_S-1)} \ ,$$

where
$$\hat{D}_b=\frac{1}{W}\sum_{i=1}^{i=K}\frac{(\sum_{j=1}^{j=L}f_jM_{ji})^2}{E(G_i)}-c_0^2 \ .$$

5. Void Fraction of Completely Randomized Mix

Both the number of particles in the i-th cell, h_i, and the apparent volume of mix, u_a, change every moment on account of porous in the mix. In particular, the void fraction of the i-th cell, e_i, should vary even if u_a were constant.

For instance, AKAO, Y. and NODA, T. (1968) showed by their experiment that the apparent volume of mix which contains a large number of equisized spherical particles increases at the beginning of mixing and then approaches a constant value as the mixing proceeds, while the void fraction of equivolume spot samples, i. e., local voidge variation from the mix, always fluctuates. Also this kind of phenomena was mentioned by D. P. HAUGHEY & G. S. G. BEVERIDGE (1966) and H. KUNO (1972) in a random packing,

Let us denote by " $e_{\min}$ " the minimum value of void fraction of the mixture obtained by the closest packing.

In the practical application, $e_{\min}$ is given, and yet the capacity of unit space, u, is unknown. Then, u must be set as follows;

$$u=v/(1-e_{\min}) \tag{5.1}$$

We further define by " $e_{\max}$ " the maximum value of void fraction. Here, $\max\, u_a=uN=V/(1-e_{\max})$.

U. ŌISHI (1956), T. UEMATSU (1951), H. E. WHITE & S. H. WALTON (1937) showed $e_{\min}$ is about 0.26 for spherical or elliptical particles. D. P. HAUGHEY and G. S. G. BEVERIDCE (1969) stated in their review that the bulk mean value of 0.40 to 0.41 are obtained by the loose random packing of identical spheres. It may be natural that the void fraction in the loose random packing corresponds to the upper bound of void fraction for completely randomized mix, which we write by e_r.

The difference between $e_{\max}$ and e_r is mainly due to the wall effect (in a wide sence). The wall effects, Y_i, $i=1\sim K$, are the ones of a mixer's wall, floor and opening (i. e., boundary of mix) upon the mixing in thier vinical cells. In this paper, we assume Y_i, $i=1\sim K$, are all constant. Then, e_r is constant and modelled as follows;

$$e_r=\frac{uN_T-V}{uN_T} \quad . \quad (N_T=N-\textstyle\sum_{i=1}^{i=K} Y_i) \tag{5.2}$$

The determination of Y_i depends on not only the type of mixer but also the shape of particles.

Note that, if we suppose all particles are able to occupy only N_T-fixed-locations, then our model is a kind of " imaginary particle model ". In this case, as there is no distinction between imaginary particles (i. e., the locations with only void), the density $f_i(y)$ is given by

$$P(H_i=y)=\frac{(m_{iT})_y\cdot(N_T-m_{iT})_{N_S-y}}{\sum_{y=0}^{y=m_{iT}}(m_{iT})_y\cdot(N_T-m_{iT})_{N_S-y}} \quad , \tag{5.3}$$

where $\qquad (x)_y$ means $\dfrac{x\,!}{(x-y)\,!}$.

When the capacity of the i-th cell, m_i, is sufficiently large relatively to particle size, we can neglect wall effect Y_i (see P. F. BENENATI & C. B. BROSILOW (1962), etc).

If the effect of gravity is completely neglected such as mixing in an artificial satellite, we need not consider wall effect: in this case, (5.3) is formally true if N_T and m_{iT} are replaced by N and m_i.

Let us denote by α the cells on the border plane of mix intersecting its covering space. It must be cared that we do not recognize the void included in α as mix. We assume the void fraction in α is $e_{\min}$. Then,

$$U_a(t)=(N-\sum_{i\in\alpha}(m_{iT}-H_i(t)))u, \quad U_a(0)=(N-\sum_{i\in\alpha}(m_{iT}-\sum_{j=1}^{j=L}m_{ji}(0)))u.$$

From (5.1) and from the definitions of $U_a(t)$, $\varepsilon_i(t)$, we have

$$E(U_a(t))=\frac{V}{1-e_{\max}}-\sum_{i\in\alpha}(m_{iT}-E(H_i(t)))\frac{V}{1-e_{\min}}\ , \tag{5.4}$$

$$E(\varepsilon_i(t))=E\left(\frac{m_iu-H_i(t)v}{m_iu}\right)=1-\frac{1-e_{\min}}{m_i}E(H_i(t))\,, \tag{5.5}$$

$$V(\varepsilon_i(t))=\frac{(1-e_{\min})^2}{m_i^2}V(H_i(t))\ . \tag{5.6}$$

To show the change of void fraction in the i-th cell, we make the following definition;

$$m_i^v=m_i-h_i-Y_i\ , \qquad 0\leq m_i^v\leq \max(m_i,\ N-N_T)\ .$$

Let M_i^v be the random variable corresponding to m_i^v for completely randomized mix. Since $M_i^v=m_i-H_i-Y_i$, $P(M_i^v=y)=f_i(y-Y_i-m_i)$. In general, there are too many physical conditions to study the theoretical background of m_i^v in mixing (many-body problem), so we construct a model: the void in the i-th cell whose volume is m_i^vu behaves as if it were an aggregate of particles and the rest containing Y_i were settled in some fixed point in the i-th cell. We call this new kind of particle, the $(L+1)$-th type particle, the "void particle".

In this thesis, we treat the typical case that the volumes of void particles are all v (hypothesis). Then M_i^v shows the number of void particles in the i-th cell. Under this hypothesis, to introduce the void particle is equivalent to replacing the probability (5.3) in imaginary particle model by the hypergeometric distribution (4.9). On the other hand, Y. AKAO and T. NODA approximated the probability (5.3) by binomial distribution (1968). (For practical sake, both distributions are almost equal since $N_T\leqslant 10\,m_i$.)

For completely randomized mix on the void particle model,

$$E(H_i)=m_{iT}\frac{N_S}{N_T}, \qquad E(H_i^2)=m_{iT}\frac{N_S}{N_T}\left((N_S-1)\frac{m_{iT}-1}{N_T-1}+1\right)\ .$$

While, from (5.1) and (5.2), $N_T=\dfrac{1-e_{\min}}{1-e_r}N_S$.

Using above formuras and (5.4), (5.5), (5.6) and (4.7), we have

$$E(U_a)=\frac{V}{1-e_{\max}}-\frac{(e_r-e_{\min})v}{(1-e_{\min})}\sum_{i\in a}m_{iT},$$

$$E(\varepsilon_i)=e_r-\frac{Y_i}{m_i}(1-e_r)\ ,$$

$$V(\varepsilon_i)=\frac{m_{iT}(1-e_r)(e_r-e_{\min})(N_S-m_{iT}-N_Se_{\min}-m_{iT}e_r)}{m_i^2(N_S-1-N_Se_{\min}-e_r)}\ ,$$

$$\sigma_R^2=\frac{1}{W^2}Q\left(\frac{1-e_{\min}}{1-e_r}N_S\right)\frac{(K-1)(1-e_r)}{N_S(1-e_{\min})-(1-e_r)}\ .$$

6. Local Randomization and Markov Chain

The wall effects are not to play any essencial part through this section, hence we put $Y_i=0$ for all i and use N, m_i instead of N_T, m_{iT} with generality. While, the following discussion is based upon the hypothesis of the void particle model. Consequently, the total number of locations which are occupied by particles is at most N. Therefore the locations of all particles at mixing time t can be represented by N-tuple valued random variable $\boldsymbol{X}(t)$. We can number $N!$ permutations as the state space of $\boldsymbol{X}(t)$.

The mixing process $\{\boldsymbol{X}(t)\}$ is induced by Markov process if the mixing operations are mutually independent as to mixing time and have a common distribution (J. K. DOOB, 1953, p. p. 187-190.). (Whenever the hypothesis of the void particle is rejected, the results of this section may be applied by putting $N=N_S$.)

The three problems pointed in section I are improved by introducing the concept of " independent mixing operator ", " local randomization " and " two dimensional transition probability ".

Now, we think the mixer where mixing time parameter t is considered to be discrete, and suppose the following two assumptions for every cell in addition to uniformity of physical properties of particles.

The first assumption is the existence of independent mixing operator. That is; the particles in the k-th cell ($k=1\sim K$) are always distributed to the i-th cell ($i=1\sim K$) at the rate, $p_{ki}^{(d)}$, with probability P_d ($d=1\sim I$) such that for every mixing time

(6.1) $$\sum_{k=1}^{k=K}m_k p_{ki}^{(d)}=m_i\ .$$

This is a natural assumption if the operating conditions of the mixer are stationary and independent of mixing time.
We put $P_{ki}=\sum_{d=1}^{d=I}p_{ki}^{(d)}P_d$. Then, from (6.1) and $\sum_{d=1}^{d=I}P_d=1$,

(6.2) $$\sum_{k=1}^{k=K}m_kP_{ki}=m_i\ .$$

The second assumption is the local randomization. Namely, at least any one of next two cases has to hold for any k-th cell such that there exists no i-th cell satisfies $p_{ki}^{(d)}=1$ for all d.

The one; the particles coming into the k-th cell input randomly to every part of it. The other; the particles being distributed from the k-th cell to other cells output randomly from every point they locate.

The mechanism of mixing is considered as whole and local mixing, the former concerns with connective mixing and the latter concerns with diffusive mixing. The distribution of particles from a cell to another depends on whole mixing and uniformity of a cell (local randomization) depends on local mixing. The concept of local randomization has been applied by H. SAKAMOTO (1960).

Let us give a number to all particles by $l=1\sim N_T$, and further define the random variable $X^l(t)$, such that $X^l(t)=i$, if the l-th particle visits the i-th cell at mixing time t.

From (6.2) and $\sum_{i=1}^{i=K} m_i=N$, for all i

$$\sum_{i=1}^{i=K} P_{ki}=1, \quad 1\geq P_{ki}\geq 0, \quad k=1\sim K.$$

In view of the first and the second assumptions, for any given d, the probability that the l-th particle moves from the k-th cell to the i-th cell is equal to the chance that a specific particle is involved in the sample selecting randomly $m_k p_{ki}^{(d)}$ particles out of m_k particles.

Therefore,

$$P(X^l(t+1)=i|X^l(t)=k)=\sum_{d=1}^{d=I} P_d\cdot\binom{m_k-1}{m_k p_{ki}^{(d)}-1}\bigg/\binom{m_k}{m_k p_{ki}^{(d)}}=P_{ki}\ .$$

Giving the initial condition $P(X^l(0)=s_0)=1$, $P(X^l(0)\neq s_0)=0$, it is easy to show that discrete random variables $\{X^l(t),\ t\geq 0\}$ possess the Markov property (Markov property; K. L. CHUNG 1960.). Consequently, $\{X(t),\ t\geq 0\}$ is a Markov chain with stationary transition probabilities P_{ki}, k, $i=1\sim K$.

Let F be $\{(ij);\ i,\ j=1\sim K\}\cap\{(\text{ii});\ m_i=1\}^c$. The two dimensional conditional probabilities are defined by $P_{(kr)(ij)}=P(X^l(t+1)=i\quad X^{l'}(t+1)=j|X^l(t)=k\quad X^{l'}(t)=r)$ for any mixing time t, any pair of particles $(l,\ l')$, $l\neq l'$, and any $(kr)\in F$.

In view of the first and the second assumptions, we define $p_{(kr)(ij)}^{(d)}$ such as;

$$p_{(kr)(ij)}^{(d)}=p_{ki}^{(d)}p_{rj}^{(d)} \qquad ;\ k\neq r,$$

$$p_{(kk)(ij)}^{(d)}=\frac{(m_k-2)!}{(m_kp_{ki}^{(d)}-1)!\,(m_kp_{kj}^{(d)}-1)!\,(m_k-m_kp_{ki}^{(d)}-m_kp_{kj}^{(d)})!}\bigg/\frac{m_k!}{(m_kp_{ki}^{(d)})!\,(m_kp_{kj}^{(d)})!\,(m_k-m_kp_{ki}^{(d)}-m_kp_{kj}^{(d)})!}$$

$$=\frac{m_k}{m_k-1}p_{ki}^{(d)}p_{kj}^{(d)}\ ;\ i\neq j\ ,$$

$$p_{(kk)(ii)}^{(d)}=\binom{m_k-2}{m_k p_{ki}^{(d)}-2}\bigg/\binom{m_k}{m_k p_{ki}^{(d)}}=\frac{p_{ki}^{(d)}(m_kp_{ki}^{(d)}-1)}{m_k-1}\ .$$

It can be verified that

$$P_{(kr)(ij)}=\sum_{d=1}^{d=I} p_{(kr)(ij)}^{(d)}P_d\ . \tag{6.3}$$

From (6.3), for any $(kr)\in F$

$$\sum_{(ij)\in F} P_{(kr)(ij)}=1, \quad 1\geq P_{(kr)(ij)}\geq 0, \quad i,\, j=1\sim K.$$

Giving the initial condition $P(X^l(0)=s_0 \ \ X^{l'}(0)=s_0')=1$, it is proved that $\{(X^l(t), X^{l'}(t)),\ t\geq 0\}$ is two dimensional Markov chain whose state space is F and transition probabilities are $P_{(kr)(ij)}$, (kr), $(ij)\in F$.

Let $P_{ki}(t)$, k, $i=1\sim K$ be t-step transition probabilities and $P_{(kr)(ij)}(t)$, (kr), $(ij)\in F$ be t-step two dimensional transition probability. As is well known,

$$(6.4) \qquad (P_{ki}(t))=(B_{\mathrm{I}})^t, \quad (P_{(kr)(ij)}(t))=(B_{\mathrm{II}})^t,$$

where B_{I} is a stochastic matrix, (P_{ki}), and B_{II} is a two dimensional transition matrix, $(P_{(ks)(ij)})$.

We note that if $m_i=m_k$ for all (ik), then from (6.2), $\sum_{k=1}^{k=K} P_{ki}=1$, namely B_{I} and B_{II} are double stochastic matrices.

Now, by using the method of indicator function, we can derive:

$$(6.5) \quad \begin{cases} E(M_{ji}(t)|S_0)=\sum_{k=1}^{k=K} m_{jk}(0)P_{ki}(t), \\ E(M_{ji}^2(t)|S_0)=\sum_{k=1}^{k=K} m_{jk}(0)P_{ki}(t)+\sum_{s=1}^{s=K}\sum_{k\neq s} m_{js}(0)m_{jk}(0)P_{(sk)(ii)}(t) \\ \qquad +\sum_{s=1}^{s=K} m_{js}(0)(m_{js}(0)-1)P_{(ss)(ii)}(t), \\ E(M_{ji}(t)M_{ri}(t)|S_0)=\sum_{s=1}^{s=K}\sum_{k=1}^{k=K} m_{js}(0)m_{rk}(0)P_{(sk)(ii)}(t), \\ E(M_{ji}(t)M_{jk}(t)|S_0)=\sum_{s=1}^{s=K}\sum_{r\neq s} m_{js}(0)m_{jr}(0)P_{(sr)(ik)}(t) \\ \qquad +\sum_{s=1}^{s=K} m_{js}(0)(m_{js}(0)-1)P_{(ss)(ik)}(t), \\ E(M_{ji}(t)M_{r\tau}(t)|S_0)=\sum_{s=1}^{s=K}\sum_{k=1}^{k=K} m_{js}(0)m_{r\tau}(0)P_{(sk)(i\tau)}(t). \end{cases}$$

When the initial condition S_0 is given and B_{I}, B_{II} are provided by experiment, we can approximately calculate $E(C_i(t))$, $\sigma_R(t)$, $V(C_i(t))$ and $Cov(C_i(t)C_j(t))$ by (4.2), (4.3) and (6.5). (Then, we utilize the eigenvalues of B_{I}, B_{II} or the relation (6.4).) Besides, $E(H_i(t)|S_0)=\sum_{j=1}^{j=L} E(M_{ji}(t)|S_0)$, $E(H_i^2(t)|S_0)=\sum_{j=1}^{j=L} E(M_{ji}^2(t)|S_0)+2\sum_{r<j} E(M_{ji}(t)M_{ri}(t))$, so that we can derive $E(U_a(t))$, $E(\varepsilon_i(t))$ and $V(\varepsilon_i(t))$ from (5.4), (5.5) and (5.6).

We remark, if the mixing operator is deterministic, the foregoing arguments can be applied by putting $P_i=1$, $P_{ki}=p_{ki}^{(1)}$. Then, using (6.3), i. e., $P_{(kr)(ij)}=p_{(kr)(ij)}^{(1)}$, the formulas (6.5) are transferred into the formulas written with only B_{I}.

By the way, from (6.2),

$$\frac{m_i}{N}=\sum_{k=1}^{k=K} P_{ki}\frac{m_k}{N}.$$

Here, we set $m_i/N=\pi_i$, so that

$$(6.6) \qquad \pi_i=\sum_{k=1}^{k=K} P_{ki}\pi_k, \quad \sum_{i=1}^{i=K}\pi_i=1, \quad \pi_i\geq 0:\ i=1\sim K.$$

If the Markov chain $\{X^l(t),\ t\geq 0\}$ consisted of finite states is ergodic (i. e., irreducible and aperiodic, or irreducible and regular, or strongly mixing; P. BILLING-

SLEY, 1965), $\{\pi_i, i=1\sim K\}$ is the unique solution of the system of equation (6.6) and is the limit distribution of $\{P_{ki}(t), i=1\sim K\}$. Namely π_i is independent of the initial condition S_0 and $\pi_i=\lim_{t\to\infty} P_{ki}(t),\ k=1\sim K$.

Let two dimensional Markov chain with state space F be ergodic. Then, it can be proved as follows that the original Markov chain $\{X^l(t), t\geq 0\}$ is also ergodic.

Proof. It is obvious, since all possible states of two dimensional chain communicate, that the states of the original chain consist of one communicating class. Here we assume the original chain is periodic. As is well known (W. FELLER, 1957), all states of the original chain have the same period, which we denote by $d>0$. Now if $P(X^l(t)=s_t,\ X^{l'}(t)=s_t')>0$, then there exists $\{r\}$ such that $P(X^l(t+r)=s_t\ X^{l'}(t+r)=s_t'|X^l(t)=s_t,\ X^{l'}(t)=s_t')>0$. From the uniformity of period, $r=nd$, where n is an integer, therefore there exists G. C. M. of $\{r\}$. This contradicts to aperiodicity of two dimentional chain. Q. E. D.

And then there exists unique stationary distribution $\{\pi_{ij};\ (ij)\in F\}$ which satisfies $\pi_{ij}=\lim_{t\to\infty} P_{(kr)(ij)}(t)$, and $\sum_{(ij)\in F}\pi_{ij}=1$, $\pi_{ij}=\sum_{(kr)\in F}P_{(kr)(ij)}\pi_{ij}$, $\pi_{ij}\geq 0$. By these relations and (6.3), it can be verified that

$$\pi_{ii}=\frac{m_i(m_i-1)}{N(N-1)} \qquad \pi_{ij}=\frac{m_im_j}{N(N-1)} .$$

Therefore, from (6.5)

$$\lim_{t\to\infty} E(M_{ji}(t)|S_0)=m_i\frac{N_j}{N} ,$$

$$\lim_{t\to\infty} E(M_{ji}^2(t)|S_0)=m_i\frac{N_j}{N}\left\{(N_j-1)\frac{m_i-1}{N-1}+1\right\} ,$$

$$\lim_{t\to\infty} E(M_{ji}(t)M_{ri}(t)|S_0)=\frac{m_i(m_i-1)}{N(N-1)}N_jN_s ,$$

$$\lim_{t\to\infty} E(M_{ji}(t)M_{jk}(t)|S_0)=\frac{N_j(N_j-1)}{N(N-1)}m_im_k ,$$

$$\lim_{t\to\infty} E(M_{ji}(t)M_{rk}(t)|S_0)=\frac{N_jN_r}{N(N-1)}m_im_k .$$

Consequently, if B_{II} satisfies ergodic conditions, we get

$$\lim_{t\to\infty}\sigma_R^2(t)\doteqdot\frac{1}{W}\sum_{i=1}^{i=K}\{\sum_{j=1}^{j=L}f_j^2E(M_{ji}^2|S_0)-2\sum_{r>j}f_rf_jE(M_{ri}M_{ji}|S_0)\}/$$

$$\{\sum_{j=1}^{j=L}w_jE(M_{ji}|S_0)\}-c_0^2\doteqdot\sigma_R^2 ,$$

and also $\lim_{t\to\infty} E(\varepsilon_i(t)|S_0)=E(\varepsilon_i)$, $\lim_{t\to\infty} V(\varepsilon_i(t)|S_0)=V(\varepsilon_i)$, $\lim_{t\to\infty} E(U_a(t)|S_0)=E(U_a)$.

In particular, when $w_j=w$ for all j and $N=N_S$,

$$\lim_{t\to\infty} E(C_i(t)|S_0)=c_0,\quad \lim_{t\to\infty} V(C_i(t)|S_0)=\frac{Q(N_s)(N_s-m_i)}{m_iW^2(N_s-1)}=V(C_i) ,$$

$$\lim_{t\to\infty} Cov(C_i(t)C_j(t)|S_0) = -Q(N_s)/N_s(N_s-1) = Cov(C_iC_j).$$

I. INOUE, & K. YAMAGUCHI (1969) showed the value of $\sum_{i=1}^{i=K}\frac{m_i}{N_s}(E(C_i(t)|S_0)-c_0)^2$ in the simplest case ($L=2$, $f_1/w_1=1$, $f_2/w_2=0$, $N=N_s$), which takes 0 for completely randomized mix, but, of course, it is not $\sigma_R^2(t)$, which takes the value represented by (3.4) for completely randomized mix.

Finally, we refer to the relation among $\boldsymbol{X}(t)$ and $X^l(t)$, $l=1\sim N$. ($\boldsymbol{X}(t)$ is defined at the beginning of this section.)
Let $\tilde{X}^l(t)$ be random variable such that

$\tilde{X}^l(t)=i$, if the l-th particle occupies the i-th location at time t.

By the assumption of independent mixing operator, it is clear that $\{\boldsymbol{X}(t),\ t\geq 0\}$, $\boldsymbol{X}(t)=(\tilde{X}^l(t),\ l=1\sim N)$, is a Markov chain, so that $\{\tilde{X}^l(t),\ t\geq 0\}$ is a Markov chain with state space $(1, 2, \ldots, N)$. From the identity of all particles

$$\sum \tilde{x}^1_{(t)},\cdots,\tilde{x}^{l-1}_{(t)},\ \tilde{x}^{l+1}_{(t)},\cdots,\ \tilde{x}^N_{(t)} P(\boldsymbol{X}(t)|\boldsymbol{X}(t-1))$$
$$= P(\tilde{X}^l(t)|\boldsymbol{X}(t-1)) = P(\tilde{X}^l(t)|\tilde{X}^l(t-1))\ .$$

Note that, $X^l(t)$ is a lumped process combining the states of $\tilde{X}^l(t)$ with respect to each cell. A Markov chain $\{\tilde{X}^l(t),\ t\geq 0\}$ is lumpable if and only if the transition probabilities have the same values as to each state of $\{X^l(t),\ t\geq 0\}$ (KEMENY & SNELL 1960). This equality of transition probabilities corresponds to the assumption of local randomization. The completely randomized mix is provided as a limit of N-tuple Markov chain $\{\boldsymbol{X}(\mathrm{t}),\ t\geq 0\}$ if it is mixing, hence the ergodicity of B_{II} is not a sufficient but a necessary condition for completely randomized mix in the strict sence. But it is the time we conclude the degree of mixing of complete mixing state is evaluated well by $\lim_{t\to\infty}\sigma_R^2(t)$, and described one- and two-dimentional transition probabilities.

Acknowledgement

The author would like to express his sincere appreciation to Professor Heihachi SAKAMOTO for his valuable suggestion, Professor Yoshio HAYASHI for his support and Professor Yasutoshi WASHIO for his advice.

REFERENCES

AKAO, Y.: "Mixing Statistics by Sampling Methods—Introduction to Mixing Index", Funtai-Kōgaku Kenkyū-kai-Shi, Vol. 5, pp. 1018-1034 (1968).

AKAO, Y. and NODA, T.: "Study on the Mixing Index by the Imaginary Particle Model", *Chem. Eng. Japan*, Vol. 33, 6, pp. 582-587, (1969).

BENENATI, R. F. and BROILOW, C. B.: "Void Fraction Distribution in Beds of Spheres", *A. I. Ch. E. Journal*, Vol. 8, 3, pp. 359-361, (1962).

BERG. T. G. O., MCEONALD, R. L. and TRAINOR, R. J.: "The Packing of Spheres", *Powder Techn.*, Vol. 4, 4, pp. 183-188, (1970).

BERTHOLF, W. M.: "The Analysis of Variance in a Sampling Experiment", Symposium on Bulk Sumpling (A.S.T.M), pp. 36-45, (1950).

BILLINGSLEY, P.: "Ergodic theory and Information", *John Wiley & Sons*, (Sec. 1, 3, 11), (1965).

BLUMBERG, R. and MARITY, J. S.: "Mixing of Solid Particles", *Chem. Eng. Sci.*, Vol. 2, pp. 240-246, (1953).

BOURNE, J. R.: "Some Statistical Relationships for powder Mixtures", *Chem. Engr. Lond.*, Vol. 198, pp. 198-200, (1965).

"Variance-sample Size Relationships for Incomplete Mixtures", *Chem. Eng. Sci.*, Vol. 22, pp. 693-700, (1967).

BROTHMAN, A., WOLLEN, G. N. and FELDMAN, S. M.: "New Analysis Provides Formula To Solve Mixing Problems", *Chem. & Metal Engr.*, April, pp. 102-106, (1945).

BUSLIK, D.: "Mixing and Sampling with Special Reference to Multi-sized Granular Material", *Bull. Am. Soc. Test. Mater.*, Vol. 165, pp. 66-92, (1950).

CARLEY-MACAULEY, K. W. and DONALD, M. B.: "The Mixing of Solid in Tumbling mixers", *Chem. Eng. Sci.*, "I", Vol. 17, pp. 493-506, (1962), "II", Vol. 19, pp. 191-199, (1964).

CHUDZIKIEWICY, R.: "Factors Affecting the Degree of Granular Materials", Vol. 1, 1, pp. 124-129, (1961).

CHUNG, K. L.: "Markov Chains with Stationary Transition Probabilities", *Springer*, pp. 1-41, (1960).

COCHRON, W. G.: "Sampling Techniques" *John Wiley & Sons*, pp. 29-33, 158-188, (1963).

COULSON, J. M. and MAITRA, N. K.: "The Mixing of Solid Particles", *Ind. Chemist.*, Febr. pp. 55-60, (1950).

DANCKWERTS, P. V.: "The Definition and Measurement of Some Characteristics of Mixtures", *Appl. Sci. Res.*, Vol. 3, Sec. A, pp. 280-296, (1952).

DOOB, J. L.: "Stochastic Processes", *John Wiley & Sons*, pp. 172-190, (1953).

DONALD, M. B. and ROSEMAN, B.: "Mechanisms in a Horizontal Drum Mixer", *Brit. Chem. Eng.*, Vol. 7, 10, pp. 749-753, (1962).

DUNCAN, A. J.: "Bulk Sampling: Problems and Lines of Attack", *Technometrics*, Vol. 4, 2, pp. 319-344, (1962).

FELLER, W.: "An Introduction to Probability Theory and its Apprications", *John Wiley & Sons*, Vol. "I", pp. 338-377, (1957), Vol. "II", pp. 47-63, 157-164, (1966).

FUJIMORI, T. and ISHIKAWA, H.: "Sampling Error or Taking Analysis Sample of Coal After the Last State of Reduction Process", JUSE, (1972).

GAYLE, J. B. and LACEY, O. L. and GARY, J. H.: "Mixing of Solids: Chi Square as a Criterion", *Ind. Eng. Chem.*, Vol. 50, 9, pp. 1279-1282, (1958).

GIBILARO, L. G., KROPHOLLER, H. W. and SPIKINS, D. J.: "Solution of a Mixing Model due to Van de Vusse by a Simple Probability Method", *Chem. Eng. Sci.*, Vol. 22, pp. 517-523, (1967).

HAUGHEY, D. P. and BEVERIDGE, G. S. G.: "Local Voidage Variation in a Randomly Packed Bed of Equal Size Spheres", *Chem. Eng. Sci.*, Vol. 21, pp. 905-916, (1966).

"Structural Properties of Packed Beds—A Review", *Can. J. Chem. Eng.*, Vol. 47, 2, pp. 130-140, (1969).

HIGUTI, I.: "A Statistical Study of Random Packing of Unequal Spheres", *Ann. Inst. Statist. Math.*, Vol. 12, pp. 257-265, (1961).

HOGG, R., Cahn, D. S., HEALY, T. W. and FUERTENAU, D. W.: "Diffusional Mixing in an Ideal Spstem", *Chem. Eng. Sci.*, Vol. 21, pp. 1025-1038, (1966).

HOPF, E.: "On Causality, Statistics and Probability", *J. Math. Physics*, Bd. Vol. 13, pp. 51-102, (1934).

INOUE, I. and YAMAGUCHI, K.: "Analysis of Solid Mixing and Stochastic Process", Funtai-Kōgaku Kenkyū-kai Shi, Vol. 5, pp. 1010-1018, (1968).

" Particle Motion in Mixer and Mixing Process-Mixing in a Two-Dimentional V-type Mixer ", *Chem. Eng. Japan*, Vol. 33, 3, pp. 286–292, (1969).

INOUE, I., YAMAGUCHI, K. and SATO, K.: " Motion of Particle and Mixing process in a Horizontal Drum Mixer ", *Chem. Eng. Japan*, Vol. 34, 12, pp. 1323–1329, (1970).

JAECH, J. L.: " Estimation of Particle Size Distribution Based on Observed Weights of Group of Particles ", *Technometrics*, Vol. 7, 4, pp. 505–515, (1965).

KEMENY, J.G. and SNELL, J.L.: " Finite Markov Chains ", van Nostrand, pp. 123–140, (1960).

KNOTT, M.: " Sampling Mixtures of Particles ", *Technometrics*, Vol. 9, 3, pp. 365–371, (1967).

KUNO, H.: " Numerical Calculation of Two Dimensional Random Packing of Circles ", *J. Jap. Soci. Powder and Power Metallurgy.* Vol. 19, pp. 85–89, (1972).

LACY, P. M. C.: " The Mixing of Solid Particles ", *Trans. Inston. Chem. Engrs.*, Vol. 21, pp. 53–59, (1943).

" Developments in the Theory of Particle Mixing ", *Joappl. Chem.*, Vol. 4, pp. 257–268, (1954).

LIN, M.: " Mixing for Markov Operators ", *Z. Wharscheinlichkeitstheorie verw. Geb.*, Vol. 19, pp. 231–242, (1971).

MACRAE, J. C. and GRAY, W. A.: " Significance of the Properties of Materials in the Packing of Real Spherical Particles ", *Brit. J. Apple. Phys.*, Vol. 12, pp. 164–172, (1961).

MANNING, A. B.: " The Theory of Sampling Granular Material for the Determination of Size Distribution ", *Inst. Fuel.*, Decem., pp. 153–155, (1937).

MIYAGI, S.: " Statistical Consideration on the Mixing of Powdery Materials ", *J. Cream. Assoc. Japan*, Vol. 58, pp. 417–420, (1950).

MORAN, P. A. P.: " A Note on Recent Research in Geometrical Probability ", *J. Appl, Prob.*, Vol. 3, pp. 453–463, (1966).

MORI, Y., JIMBO, G. and YAMAZAKI, M.: " On the Residence Time Distribution and Mixing Characteristics of Powder in Open-Circuit Ball Mill ", *Chem. Eng. Japan*, Vol. 28, 3, pp. 204–214, (1968).

ŌISHI, I.: " Tōdai-kyutai no Juten-jōtai to Kikōritsu ", *Kōgyō Kagaku Zasshi*, Vol. 59, 3, pp. 310–315, (1956).

ORNING, A. A.: " Coal Sampling Problems ", Symposium on Bulk Sampling (A. S. T. M.), pp. 29–35, (1950).

ŌYAMA, Y. and AYAKI, K.: " Studies on the Mixing of Particulate Solids ", *Chem. Eng. Japan.* Vol. 20, 4, pp. 148–155, (1956).

ŌYAMA, Y.: " Suihei-kaiten-entō nai no Ryutai no Undō ", *Bull. Inst. Plys. Chem. Research* (Tokyo), " Rept. 1 ", Vol. 12, pp. 953, (1933), " Rept. 2 ", Vol. 14, pp. 570–583, (1935), " Rept. 3 ", Vol. 14, pp. 770, (1935), " Rept. 4 ", Vol. 15, pp. 320, (1936), " Rept. 5 ". Vol. 18, pp. 600–639, (1939). " Rept. 6 ", Vol. 19, pp. 1070–1087, (1940), " Rept. 7 ", Vol. 19, pp. 1088–1102, (1940). " Suihei-shindo ni yoru Ryutai no Juten to Kongō-sōsa ", " Rept. 1 ", *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), Vol. 34, pp. 1262, (1938), " Rept. 2 ", *Bull. Inst. Phys. Chem. Research* (Tokyo), Vol. 19, pp. 1103–1122, (1940).

PAWLOWSKI, J.: " Zur Statistik der Homogenisierprozesse ", *Chem. Eng. Techn.*, Vol. 36, 11, pp. 1089–1099, (1964).

POULE, K. R., TAYLOR, R. F. and WALL, G. P.: " Mixing Powders to Fine-scale Homogeneity: Studies of Batch Mixing ", *Trans. Instin. Chem. Engers.*, Vol. 42, pp. 305–315, (1964).

RIDGWAY, K. and TARBUCK, K. J.: " The Random Packing of Spheres ", *Brit. Chem. Eng.*, Vol. 12, 3, pp. 384–388, (1967).

ROSEMAN, B.: " Mixing of Solids ", *Industrial Chemist*, Feb., pp. 84–89, (1963).

ROSE, H. E.: " A Suggested Equation Relating to the Mixing of Powders and its Application to the Study of the Performance of Certain Types of Machine ", *Trans, Instn, Chem. Engers.* Vol. 37, pp. 47–64, (1959).

ROSE, H. E. and ROBINSON, D. J.: " The Application of the Digital Computer to the Study of Some Problems in the Mixing of Powders ", A. I. Ch. E.-I. Chem. E. Symposium Series

(London: Instn. Chem. Engrs), No. 10, pp. 52-70, (1965).

SAKAMOTO, H.: "Contribution to the Theory of Systematic Sampling and Beding Methods in Quality Control", *Proceeding of Fanc. Eng. Keio, Univ.*, Vol. 13, 51, pp. 1-46.

SAWAHATA, Y.: "On the Circulation of Particles in a 2-Dimensional V-Type Mixer", *Chem. Eng. Japan*, Vol. 30, pp. 1140-1146, (1966).

SCOTT, G. D.: "Packing of Spheres", *Nature* Vol. 188, pp. 908-909, (1960), "Radial Distribution of the Random Close Packing of Equal Spheres", *Nature* Vol. 194, pp. 956-957, (1962).

SHINNER, R. and NAOR, P.: "A Test of Randomness for Solid-solid Mixture", *Chem. Eng. Sci.*, Vol. 15, pp. 220-229, (1961).

STANGE, K.: "Ein Verfahren zur Beurteilung des Gütegrades von Mifchungen", *Ingenicur. Archiv.*, Vol. 20, pp. 398-417, (1952).

"Beurreilung von Mischgeräten mit Hilfe statistischer Verfahren", *Chem. Ing. Tech.*, Vol. 26, pp. 150-155, (1954).

"Die Mishgüte einer Zufallsmischung als Grundlage zur Beurteilung von Mischversuchen", *Chem. Eng. Tech*, Vol. 26, pp. 331-337, (1954).

SUGIMOTO, M., ENDOH, K. and TANAKA, T.: "Behavior of Granular Materials Flowing through a Rotating Cylinder—Mechanism of Segregation and Fluctuation in the Rate of Binary Mixtures", *Chem. Eng. Japan*, Vol. 30, 5, pp. 427-432, (1966).

TOYAMA, S.: "The Slide between Solid Bed and the Wall in the Rotary Drum", *Chem. Eng. Japan*, Vol. 31, 3, pp. 282-286, (1967).

UEMATSU, T., TSUCHIYA, K. and OKAMURA, O.: "Ryutai no Jūten oyobi Masatsu", Nihon Kikai Gakkai Ronbunshū, Vol. 17, 56, pp 72-77, (1951).

VISMAN, J.: "Test on the Binomial Sampling Theory for Heterogeneous coals", Symposium on Coal Sampling (A. S. T. M.), pp. 141-152, (1954).

"Further Discussion: A General Theory of Sampling", *Materials Research and Standards MTRSA*, Vol. 11, pp. 32-37, (1971).

WEIDENBAUM, S. S.: "A Fundamental Study of the Mixing of Particulate Solids", *PhD. Thesis in Che . Eng., Columbia University*, New York, June, (1953).

"Mixing of Solids", *Advances in Chem. Eng.*, Vol. 2, Academic Press, pp. 209-324, (1958).

WEIDENBAUM, S. S. and BONILLA, G. F.: "A Fundamental Study of the Mixing of Particulate Solids", *Chem. Eng. Progress*, Vol. 51, 1, pp. 27-38, (1955).

WHITE, H. E. and WALTON, S. F.: "Particle Packing and Particle Shape", *J. Am. Ceram. Soc.*, Vol. 20, pp. 155-166, (1937).

WISE, M. E.: "On the Radii of Five Packed Spheres in Mutual Contact", *Philips Research Reports*, Vol. 15, 2, pp. 101-106, (1960).

YANO, T., KANISE, I., TANAKA, K. and KURAHASHI, S.: "Influences of the Physical Properties of Powders upon the Mixing Degree and Mixing Speed of Several Types of Mixers", *Chem. Eng. Japan*, Vol. 22, 12, pp. 759-763, (1958).

YANO, T., KANISE, I., SANO, Y., OKAMOTO, Y. and TSUTSUMI, M.: "Influence of Particle Size Powder on Mixing Degree and Mixing Speed in Several Types of Mixers", *Chem. Eng. Japan*, Vol. 23, 9, pp. 539-594, (1959).

YANO, T. and SANO, Y.: "Some Considerations on Expressions for the Degree of Solid Mixing", *Chem. Eng. Japan*, Vol. 29, 4, pp. 214-223, (1965).