[Chem. Pharm. Bull. 30(12)4457—4463(1982)]

Computer Simulation of Agglomeration by a Two-dimensional Random Addition Model. III.[1] ——Agglomeration Kinetics and Micromeritic Properties of Closely-packed Agglomerates of Heterogeneous Binary Circles——

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(Received March 20, 1982)

Computer simulation of closely packed agglomeration of heterogeneous binary circles on a two-dimensional plane was conducted by the use of a random addition model to investigate the mechanism of agglomeration of dispersed particles in a liquid suspension. Under centripetal force, a new coarse or fine circle approached a coarse circle placed on the origin from a random direction. The production of approaching circles was regulated by the probability coefficient of collision (P_c), defined as n_f/n_{f0}. The diameter of agglomerate (D_m) was defined as the square root of the area of the 360-gon inscribed in the periphery of the agglomerate. The growth rate of agglomerate was described by equation (3) in the text.

$$\log D_m = C_3 \log t + C_4(\lambda) \tag{3}$$

The constant C_3 reached a maximum at 50 to 60% coarse circle fraction in the agglomerate. The value of D_m ($=10^{C_4(\lambda)}$ at $t=1$) increased with increasing coarse circle fraction and the diameter ratio of circles in the agglomerate. The kinetics of agglomeration simulated by the present model followed the first-order rate equation (5) in the text.

$$\ln \frac{n_f}{n_{f0}} = -kt \tag{5}$$

The porosity of the agglomerate reached a maximum at 50—60% coarse circle fraction in the agglomerate. The coordination number of the agglomerate increased with increasing coarse circle fraction in the agglomerate. This finding was explained by the fact that the coordination number of coarse circles was larger than that of fine circles in the agglomerate.

Keywords——computer simulation of agglomeration; two-dimensional random addition model; agglomeration kinetics; layering agglomeration; coordination number; porosity

Introduction

The present authors have been studying the mechanism of agglomeration of dispersed particles in liquid suspension, so-called wet spherical agglomeration,[2-4] by Monte Carlo simulation on a digital computer. The simulations were conducted by using a random walk model[5,6] and a random addition model.[1,7] The former model is advantageous for describing the change in size of individual agglomerates and the agglomeration kinetics of poly-dispersed particles. The latter model is useful to simulate the shape and the internal structure of an agglomerate in relation to the adhesion behavior of particles.

In the previous paper, the authors simulated the agglomeration of mono-sized circles on a two-dimensional plane by the use of the random addition model. By that simulation, the parameters affecting the internal packing structure of the agglomerate were clarified. By introducing the probability coefficient of collision, the kinetics of layering agglomeration was explained successfully. The present study deals with the simulation of the closely packed

agglomeration of a binary mixture of circles with different diameters. The aim of the study was to elucidate the effect of the diameter difference on the agglomeration process and the micromeritic properties of the resultant agglomerate, as well as to test the kinetic equation derived in the previous paper[1] to describe the heterogeneous agglomeration.

Method

Closely Packed Agglomeration of a Binary Mixture of Different-sized Circles——The agglomeration process was basically the same as described in the previous study.[1] At the starting point, a coarse circle was placed on the origin of a two-dimensional plane. The n-th ($n=2,\ldots.199$) circle approached the center circle from a random direction, which was determined by a pseudo random number, between 0 and 2π, produced by the computer. The type of approaching circle, *i.e.* coarse or fine, was determined by comparing the fine circle fraction ($0<F_f<1$) set in advance with a pseudo random number ($0<R_n\leqq 1$) produced by the computer. When $R_n\geqq F_f$, the circle was defined as a coarse circle, and otherwise it was defined as a fine circle. At the same time, the composition of agglomerate produced by this simulation was determined automatically by setting F_f. The diameter ratio of coarse circle to fine one was set to 2, 3, 5, 6 or 7. The diameter of fine circles was taken as a unit with arbitrary dimension. The approaching circle followed a straight line passing through the origin until it encountered the first circle on the trajectory. Upon contact, the approaching circle rolled around the circle already deposited, to approach more closely to the origin. When the circle contacted another one during this rolling action, it was decided whether the circle would stop or roll further by examining whether the position contacted was stable or not. If the position was unstable, the circle rolled again around the closer circle to the origin. This procedure was repeated until it reached a stable position. When the circle settled at a stable position, it was decided whether or not the circle remained there by comparing the probability coefficient of adhesion, P_a ($P_a=0.5$, in this study) with R_n produced by the computer. When $R_n\leqq P_a$, the circle remained, otherwise it was released from that position. At this point, unit agglomeration time was supposed to have elapsed. By this means, the agglomeration time was counted. Thereafter a new $(n+1)$-th circle approached the origin and followed the above procedure. The frequency of production of approaching circles was controlled by introducing the probability coefficient of collision, P_c. When $R_n\leqq P_c$, a new circle was produced. When $R_n>P_c$, no circle was produced, but unit agglomeration time elapsed. In this study, P_c was defined as n_f/n_{f0}, where n_{f0} ($=240$, in this study) and n_f are the numbers of circles in the system at agglomeration times $t=0$ and $t=t$, respectively. Therefore, the growth rate of the agglomerate decreased with elapsing agglomeration time.

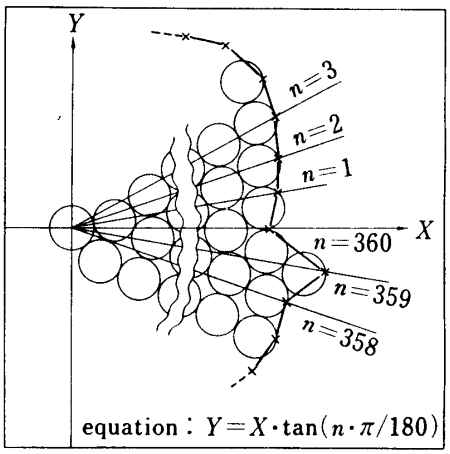

Fig. 1. Definition of Agglomerate Size

Definition of Diameter and Porosity of Agglomerate——The diameter of the agglomerate was defined as the square root of agglomerated circle area. The area of the agglomerate, S_a was defined as the area of a 360-gon inscribed in the periphery of the agglomerate, and was calculated by summing the areas of 360 triangles as shown in Fig. 1. The porosity of the agglomerate (ε) was defined according to equation (1):

$$\varepsilon = 1 - \frac{\pi r_f^2 n_f + \pi r_c^2 n_c}{S_a} \qquad (1)$$

where n_f and n_c are the numbers of fine and coarse circles, respectively, and r_f and r_c are the radii of the fine and coarse circles, respectively.

Results and Discussion

Analyses of the Agglomeration Process

Representative simulation results are shown in Fig. 2, which illustrates the growth of the agglomerate. At the initial stage, drastic changes in the micromeritic properties of the agglomerate, such as shape, size and porosity, were observed, as seen in a random coalescence agglomeration. At the later stage, the agglomerate shape gradually approached a circle and the change in the micromeritic properties became small. This behavior is characteristic of layering agglomeration.

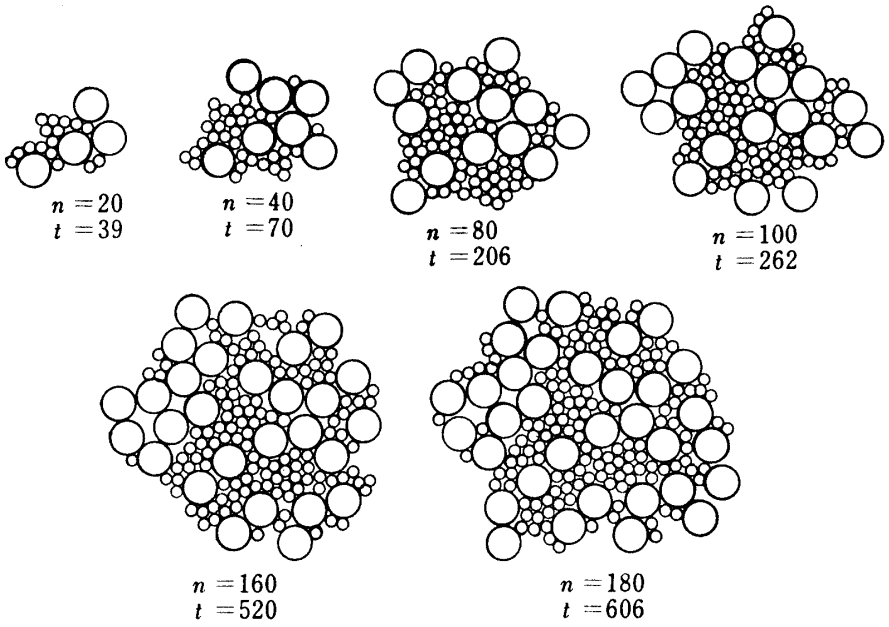

Fig. 2. Simulation Result for the Growth of Agglomerates

Diameter ratio of circles: 1: 3.
t: agglomeration time, n: number of circles composing the agglomerate.

The agglomeration process described above was quantitatively described by plotting the diameter and the porosity of the agglomerate against agglomeration time as shown in Figs. 3 and 4, respectively. As expected, at the initial stage, the agglomerate grew rapidly. The growth rate increased with increasing coarse circle fraction in the agglomerate (Fig. 3). The porosity of the agglomerate also increased with agglomeration time as shown in Fig. 4. Compared with the growth process of the agglomerate, the porosity of the agglomerate rapidly reached an equilibrium state. Furthermore, a smaller variation of the porosity with the coarse particle fraction in the agglomerate was found. However, the variation increased

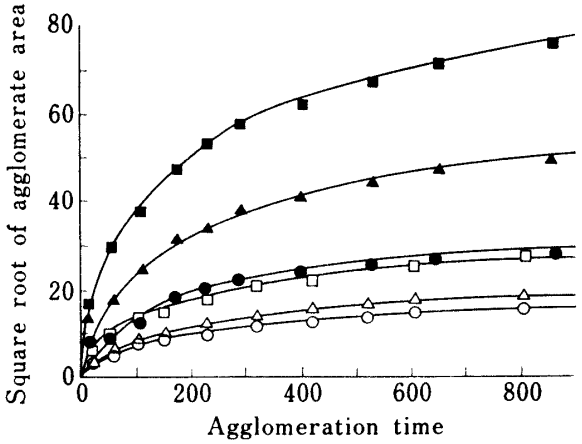

Fig. 3. Agglomerate Diameter as a Function of Agglomeration Time

Diameter ratio of circles: open symbols, 1: 2; solid symbols, 1: 6.
Coarse circle fraction in agglomerate (%): ○, 9.5; ●, 10; △, 28.5; ▲, 37; ■, 90.5; □, 93.

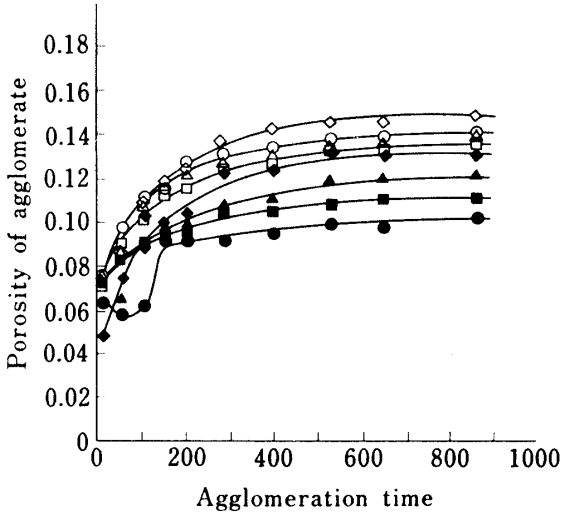

Fig. 4. Porosity of the Agglomerates as a Function of Agglomeration Time

Diameter ratio of circles: open symbols, 1: 2; solid symbols, 1 : 6.
Coarse circle fraction in agglomerate (%): ○, ●, 10; △, ▲, 37; ◇, ◆, 53.5; □, ■, 90.5.

with increasing difference in the diameters of two circles in the agglomerate. The porosity of the agglomerate with 50 to 60% coarse circle fraction was significantly higher than that of the other agglomerates. This phenomenon might be interpreted by considering that when the coarse circle fraction was extremely low or high, the agglomerate could essentially be regarded as a mono-sized circle agglomerate having the closest packing structure. It was found that the agglomerate became denser when the difference in the diameters of the approaching circles was great.

Kapur[8] classified the agglomeration process into two processes, *i.e.*, random coalescence and non-random coalescence agglomeration, based on the cohesion mechanism of particles. The random coalescence agglomeration occurs by random cohesion of particles, while the non-random coalescence agglomeration is caused by the restricted cohesion of particles depending on particle size, particle shape, surface properties, *etc.* The kinetic equations for random and non-random coalescence agglomeration are given by equations (2) and (3), respectively,

$$\log D_m = C_1(\lambda)t + C_2 \tag{2}$$

$$\log D_m = C_3 \log t + C_4(\lambda) \tag{3}$$

where C_2 and C_3 are constants, $C_1(\lambda)$ and $C_4(\lambda)$ are functions of the coalescence rate λ, D_m is the median diameter of agglomerates, defined as the square root of agglomerate area in the present system because the dimension of the system can be selected arbitrarily, and t is the agglomeration time. When the diameter of agglomerates was plotted against the agglomeration time on a log-log graph, a linear relationship was obtained except at the initial stages, as shown in Fig. 5, but this was not the case on a semi-log graph. The results indicate that the agglomeration process in the present study occurs by non-random coalescence. This finding was also supported by the present simulation results illustrated in Fig. 1, showing that the agglomeration at the later stage was promoted by a preferential cohesion of fine circles to the agglomerated core circle, so-called layering agglomeration, which is a representative non-random coalescence agglomeration mechanism.

The slope of the straight line (C_3) in Fig. 5 is a measure of the growth rate of the agglomerate, given by equation (4):

$$C_3 = \frac{\log D_1/D_2}{\log t_1/t_2} \tag{4}$$

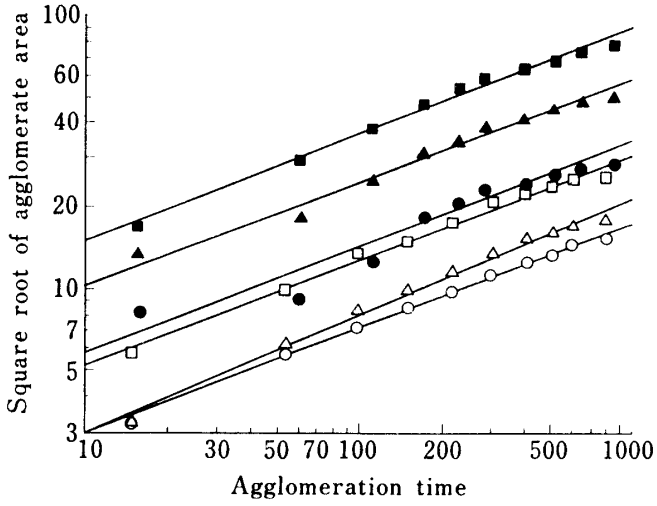

Fig. 5. Agglomerate Diameter as a Function of Agglomeration Time

Diameter ratio of circles: open symbols, 1: 2; solid symbols, 1 : 6. Coarse circle fraction in agglomerates (%): ○, 9.5; ●, 10; △, 28.5; ▲, 37; ■, 90.5; □, 93.

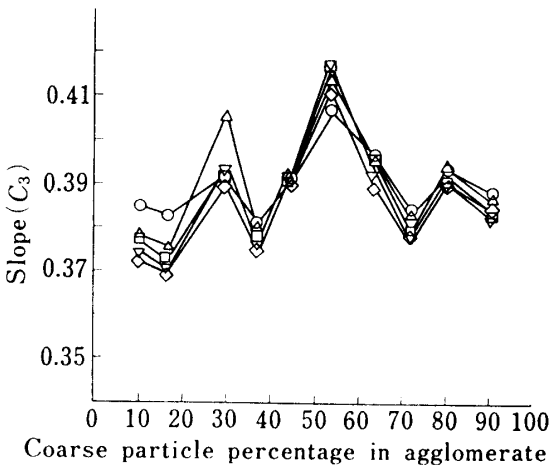

Fig. 6. Relationship between C_3 and Coarse Circle Fraction in the Agglomerates

Diameter ratio of circles: ○, 1: 2; △, 1: 3; □, 1 : 5; ▽, 1: 6; ◇, 1 : 7.

where D_1 and D_2 are the diameters of agglomerate at agglomeration times t_1 and t_2, respectively. The slope is plotted as a function of the coarse circle fraction in the agglomerate (Fig. 6). The slope was almost independent of the diameter ratio of approaching circles, although a slight variation was found. At 50 to 60% coarse circle fraction in the agglomerate the slope reached the maximum. The results in Fig. 6 are in good accord with the fact that the porosity change of the agglomerate with 50 to 60% coarse circle fraction with agglomeration time was the highest, as found in Fig. 4.

$C_4(\lambda)$ in equation (3) is defined as log D_m at agglomeration time, $t=1$. In Fig. 7, D_m ($=10^{c_4(\lambda)}$ at $t=1$) calculated from the intercept of the straight line with the ordinate, at $t=1$, in Fig. 5 is plotted against the coarse circle fraction of the agglomerate. As expected, D_m ($t=1$) increased with increasing coarse circle fraction of increasing ratio of the coarse circle diameter to the fine circle diameter. D_m ($t=1$) was assumed to be an approximation of the diameter of an imaginary core circle for layering agglomeration in the present system.

In the previous study,[1] the authors showed that the agglomeration kinetics for layering agglomeration could be described theoretically by a first-order equation (5) derived from a population balance of particles in the system:[9,10]

$$\ln\left(\frac{n_f}{n_{f0}}\right) = -Kt \tag{5}$$

where K is the agglomeration rate constant. It was found in the previous study[1] that the kinetics of mono-sized circle agglomeration obeyed equation (5) only when the probability coefficient of collision was defined as n_f/n_{f0}. To test whether this equation is adaptable to the present simulation or not, log (n_f/n_{f0}) was plotted against agglomeration time. All data fell on a straight line, as shown in Fig. 8, which indicates that equation (5) can be applied generally as a layering agglomeration model irrespective of the diameter ratio of circles and the circle composition in the agglomerate.

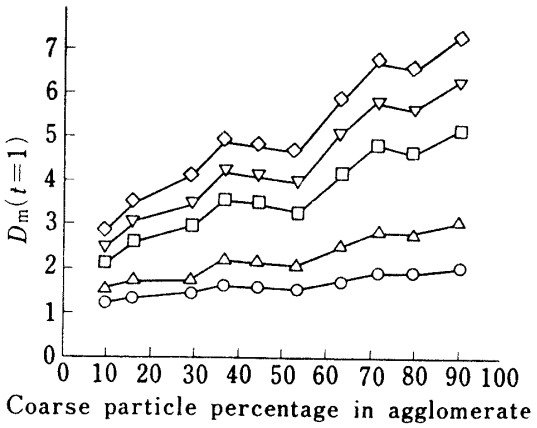

Fig. 7. Relationship between D_m ($t=1$) and Coarse Circle Fraction in the Agglomerates

Diameter ratio of circle: ○, 1:2; △, 1:3; □, 1:5; ▽, 1:6; ◇, 1:7.

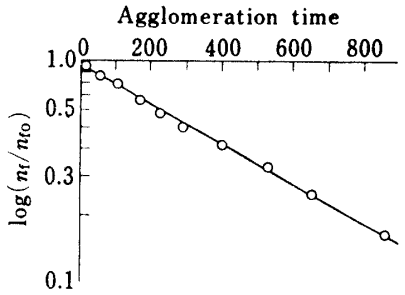

Fig. 8. First Order Kinetic Plot of Agglomeration

Micromeritic Properties of the Resultant Agglomerate

Representative internal packing structures of circles composing the agglomerate produced by the present simulation are shown in Fig. 9. It was found that the internal packing structure was determined by the coarse circle fraction and the diameter ratio of circles in the agglomerate, whereas the agglomerate shape was little affected by these factors. A larger interstitial void was formed around the coarse circles than around the fine circles, irrespective of the coarse circle fraction and the circle diameter ratio in the agglomerate.

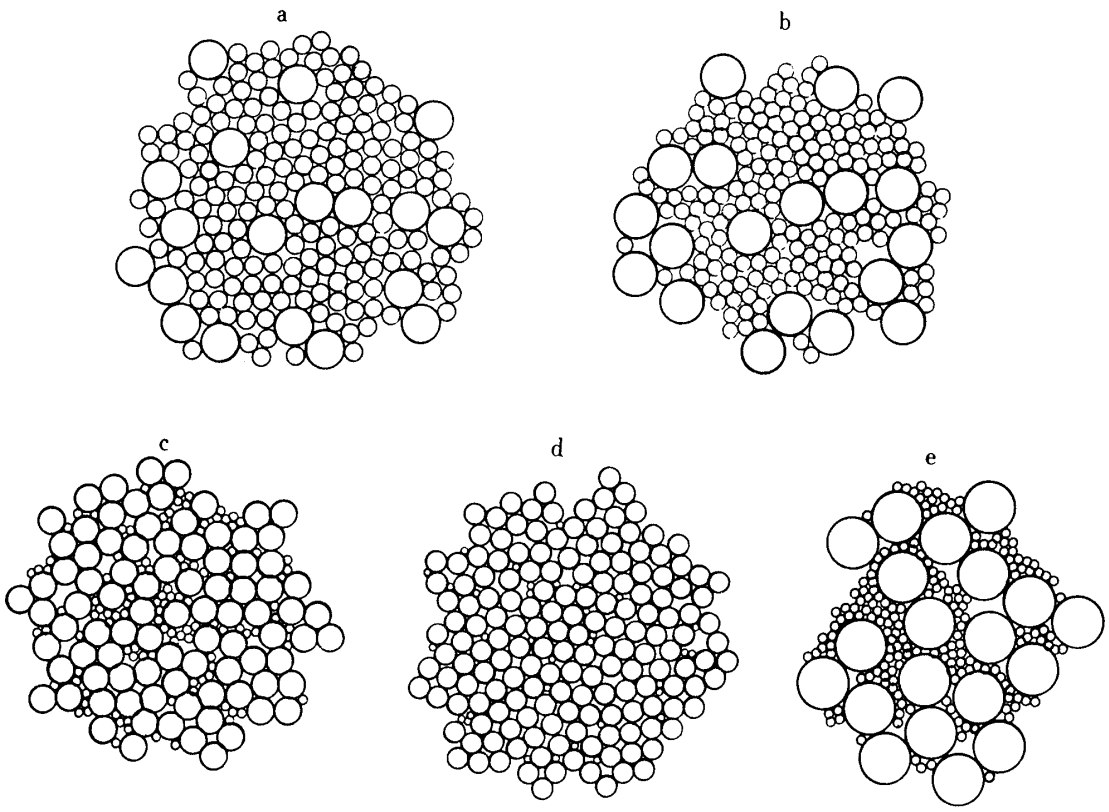

Fig. 9. Internal Packing Structures of Agglomerates as a Function of Diameter Ratio of the Circles

a, diameter ratio 1:2, coarse circle fraction 9.5%;
b, diameter ratio 1:3, coarse circle fraction 9.5%;
c, diameter ratio 1:3, coarse circle fraction 45%;
d, diameter ratio 1:3, coarse circle fraction 83.5%;
e, diameter ratio 1:6, coarse circle fraction 10%.

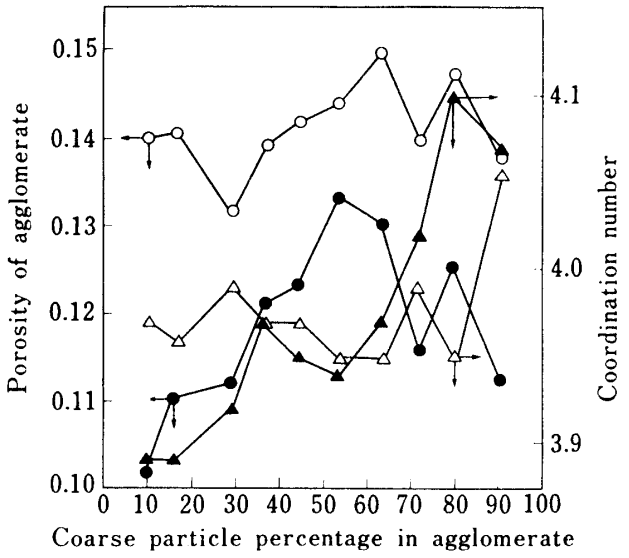

Fig. 10. Porosity and Average Coordination Number of Agglomerates as a Function of Coarse Circle Fraction

Diameter ratio of circles: open symbols, 1: 2; solid symbols, 1 : 6.

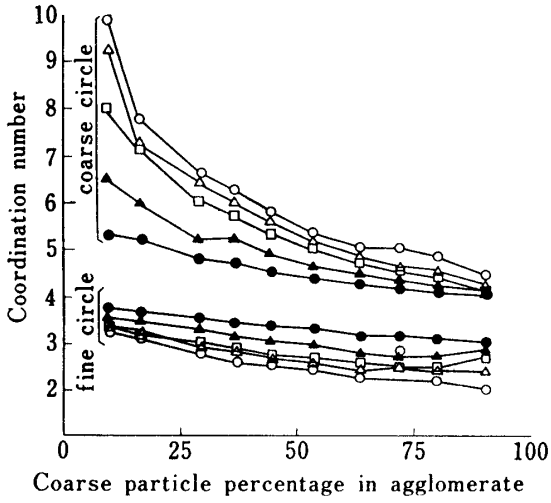

Fig. 11. Coordination Numbers of Coarse and Fine Circle in the Agglomerates

Diameter ratio of circles: ●, 1 : 2; ▲, 1: 3; □, 1: 5; △, 1 : 6; ○, 1: 7.

The porosity and the average coordination number of the agglomerate are plotted as a function of the coarse circle fraction in the agglomerate and the circle diameter ratio in Fig. 10. The porosity of the agglomerate with 50 to 60% coarse circle fraction was the maximum, in accord with the finding in Fig. 4. This trend was marked when the diameter ratio of the two circles in the agglomerate was large. The average coordination number increased with increasing coarse circle fraction of the agglomerate, although it fell a little at 50 to 60% coarse circle fraction.

This finding is explained by the fact that the coordination number of coarse circles was larger than that of fine circles, and the difference in coordination number between coarse and fine circles increased with increasing diameter ratio of the two circles, as shown in Fig. 11. When the diameter difference between the two circles was great, the coordination number of the coarse circles increased greatly at lower coarse circle fraction, whereas it fell at higher coarse circle fraction. However, this effect on the average coordination number of the agglomerate was only apparent, since the average coordination number of the agglomerate (CN_A) is determined by equation (6).

$$CN_A = CN_c F_c + CN_f F_f \tag{6}$$

where CN_c and CN_f are the coordination numbers of coarse circles and fine circles, respectively. F_c and F_f are the coarse and fine circle fractions, respectively.

Acknowledgement The computer used in this study was a FACOM 230-28 of the Gifu City Office. The valuable advice of Mr. J. Kariya (Gifu City Government) is acknowledged.

References and Notes

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