The 6th International Symposium on East Asian Resources Recycling Technology
October 23 - 25, 2001, Gyeongju (慶州), Korea
ISBN: 89-952527-0-7 93530

Preparation of Macroporous Pellet from Industrial Waste Flyash by Foaming Method

Jai-Koo Park, Hyun-Jung Kim

Dept. of Geosystem and Environment Engineering, Hanyang University, Seoul, Korea

jkpark@hanyang.ac.kr

ABSTRACT

Macroporous pellets were prepared from industrial waste flyash by foaming method. The surface and inside of flyash pellets, the shape was almost spherical and the average size was about 3 mm, were composed of the spherical pores interconnected through windows. The controlling of pellet size was conducted with solid loading. The flyash pellets with different relative density were characterized for porosity, average pore size, and specific surface area. As results, most physical properties had a tendency to increase as relative density decreased - extension ratio increased. The correlation between relative density and other properties was inspected through microstructural features evaluated by SEM. As a result, high porosity and high specific surface area were estimated to result from the superior connectivity between pores.

Key words : Flyash pellets, Foaming method, Physical properties

1. Introduction

Now, about 200 million tones of flyash is annually generated in Korea and it is expected that about 550 million tones will be generated in 2006.[1)] But, it is a present situation that about 15% of which is being only recycled.[1)] On the other hand, flyash recycling operations in case of advanced countries has reached the high stage from 40 to 60%. It is thought that such a low recycling is caused by unburned-carbons contained in flyash and non-uniformity of components. Therefore, recycling of solid waste like flyash is above all important in the field of environmental industry. Such being the case, this work was directed to recycle flyash as environmental material for purifying pollutants.

Generally, porous material means a matter that many pores on surface and in inside exists. Because of high porosity resulted from many pores, porous materials were known to hold high permeability, high specific surface area, good insulating characteristics, high refractoriness, chemical resistance and long life in severe environments.[2)] Usually, porous materials are prepared by two types of methods - polymeric sponge method and foaming method.[3,4)] Preparation of porous materials using foaming method forms 3-dimensional network structure.[4)] In addition to, we can control physical properties of porous materials because foams are generated by artificial operation.[5,6)] By reason of that, porous materials are applied widely in the fields of environmental industries. Many applications for porous materials run as follows: filters for high temperature gas purification, membranes for separation processes, catalyst carriers, refractories, thermal insulation, and biomedical developments that can be used for restitution of skeletal and dental functions.[2)]

But, the shape of porous materials produced up to date is almost cubic. This type of porous materials is not so efficient as pellets in view of operations such as fluidity, abrasion and packing and so on. Also, pellets prepared by conventional methods such as spray-drying have low porosity as well as the problem that surface pores of them clogged. However, recently our laboratory have prepared the sizable porous pellets to have high porosity by pseudo double emulsion method(PDEM).[7] Therefore, this study was focused on preparation of porous pellets used flyash as starting material and evaluation of their physical properties.

2. Experiment

2.1 The Preparation Process

Fig. 1 shows the overall process to prepare porous pellets. The process is composed of slurry preparation, foaming, pelletizing, drying, and sintering.[7] The starting material was a flyash (Poryung thermoelectric power plant, mean particle size 21μm) containing about 6 to 8%(w/w) unburned-carbon. The chemical analysis for flyash is given in Table 1. The stable slurry made up of particles under 3μm was prepared by Attrition Mill(Korea Material Development Co. LTD). The optimum milling was conducted during 3hrs at 800rpm as wet milling. As Fig. 2 shows the variation of mean particle size of flyash slurry according to milling time, line A represents optimum milling time. The measurement was conducted using particle size analyzer(Model No. SALD-2001, Shimadzu). The concentration of prepared slurries was 40 and 50%(v/v) respectively.

The prepared slurries were extended to different extension ratio(E_R) by foaming method. Ammonium Lauryl Sulfate($C_{12}H_{29}NO_4S$, Fluka Chemical Corp.) was added to maximize the stabilization of foams. The foamed slurries were used to prepare porous pellets by PDEM. After the prepared greenbodies were dried at room temperature, they were Sintered at 1200℃ for 1hr.

2.2 property measurements

The prepared pellets for evaluating physical properties were three kinds of sample that the extension ratio was different respectively.

The total porosity(ε_T) of pellets was determined using the following equation:

$$\varepsilon_T = \frac{(\rho_r - \rho_b)}{\rho_r} \quad (1)$$

where ρ_r and ρ_b means the real and bulk densities respectively. The average pore size(d_{ave}) and the microstructure of pellets were evaluated using image analysis system[8](Model No. KH-2200, Media Cybernetics) and scanning electron microscopy(SEM ; Model No. JSM-6300, JEOL). The specific surface area(S_W) of pellets was measured through the multipoint Brunauer-Emmett-Teller(BET) technique by adsorption of nitrogen(Model No. NOVA-1000, Quantachrome Corp.).

3. Results and Discussion

3.1 The Preparation of macroporous pellets

Fig. 3(a) shows the shape of pellets prepared using 50%(v/v) slurry. The average pellet size was about 3mm and the shape was very similar to sphere. As Fig. 3(b) and 3(c) shows the pore structure on surface and in inside of a pellet, it was observed through image analysis system. From Fig. 3(b) and 3(c) we could know that the pellets prepared by foaming method and PDEM had the circular-shaped pores and was porous materials formed by a lot of open pores.

The recovery of pellets was calculated as W_2 / W_1. Where, W_1 and W_2 is defined as the amount of solids contained in injected slurry and sintered pellets respectively. As a result of that, the recovery was over about 90%.

The mechanism that porous pellets are prepared by PDEM is very complicated. Recently, Park, Jai-Koo et al.[7] has demonstrated that pellet size could be controled with revolution rate of impeller. But, the parameters influencing pellet size are very diverse. In this work, the controlling of pellet size was conducted as changing solid loading. At Fig. 4, A and B curves indicate pellet size distribution that the concentration of injected slurry is 40 and 50%(v/v) respectively. The average pellet size was about 2.5mm and 3mm respectively. From this result, we could induce that the pellet size increases in proportion to solid loading. As Fig. 5(a) and Fig. 5(b) show the flow behavior of flyash slurries, they respectively presents the variation of shear stress and viscosity according to shear rate. The two results indicate that the viscosity of 50% slurry was higher than that of 40% slurry at the same shear rate. That implies that the adhesion between particles, the resistance for external force, is much stronger in case of 50% slurry. In consequence, the pellet size could be controlled on the basis of this facts.

3.2 The physical properties

Three kinds of samples taking different relative density were prepared for evaluating the physical properties of flyash pellets. The evaluated properties were porosity, average pore size, specific surface area. The values of those were presented in Table 2.

The true density of flyash measured by water immersion method[9] based on Archimedean principle was 2.185 g/cc. The bulk densities of pellets were evaluated to be 0.620, 0.798 and 1.424 g/cc depending on extension ratio. The relative densities of pellets calculated from two results ranged from 0.284 to 0.524.

The total porosity of pellet calculated with Eq. (1) varied from 47.63 to 71.57%. In comparison with theoretical values, the results calculated above were not as high as those. The result implies that the difference between two values resulted from the shrinkage generated in the course of drying and sintering.

For measuring average pore size, about 50 images were taken a sample in a kind of pellet. The data presented in Table 2. shows that the average pore size was not sensitive to relative density. However, The average pore size had a tendency to increase slightly as relative density was decreased. In the light of the results reported by Selpulveda[10] in 1997, it is clear that these results is correct.

The specific surface area results obtained through multipoint BET technique is depicted in Table 2. The values increased highly from 3.53 to 11.98 m^2/g with the relative density. The specific surface area data is supplemented with the microstructural features illustrated in Fig. 6. As Fig. 6 was observed by SEM, the results shows that the inner structure of pellet was composed of spherical pores and circular windows interconnecting pores varying in connectivity depending on relative density. Though specific surface area varies with starting material, the value of flyash pellet will be classified into much higher value than that of other porous materials prepared by gelcasting.[10] Consequently, this result is thought to result from the considerable interconnection between inner pores.

4. Conclusion

On the basis of the results described above, the followings could be derived.

1. The porous flyash pellet was prepared by both foaming method and pseudo double emulsion method and the recovery of that came to over 90%. The shape of prepared pellet was closely similar to a sphere and the size of that was about 3 mm. Also, the surface and inside of pellet was composed of the considerable amount of spherical pores.
2. In this work, the solid loading of slurry was applicable as the controlling parameter of pellet size. As a result, pellet size, too, had a tendency to increase as solid loading increased.
3. The physical properties of flyash pellet, which relative density ranged from 0.28 to 0.52 g/cc, were evaluated in the present work. Although the variation of average pore size depending on relative density was slight, the majority of properties was considerably influenced on relative density. In consequence, the result above was due to the improvement of interconnection between inner pores, which resulted from the increment of extension ratio.

Acknowledgements

The authors wish to thanks the Ceramic Processing Research Center(CPRC) of KOSEF for financial support of this work.

References

1. 한국전력공사, 석탄회 - 이용가치와 재활용기술, (1994)
2. P. Sepulveda, "Gelcasting Foams for Porous Ceramics", J. Am. Ceram. Soc. Bul., **76**(10), 61-65 (1997).
3. T. Fujiu, "Processing and Properties of Cellular Silica Synthesized by Foaming Sol-Gels," J. Am. Ceram. Soc., **73**(1), 85-90 (1990).
4. J. S. Woyansky and C. E. Scott, "Processing of Porous Ceramics," J. Am. Ceram. Soc. Bul., **71**(11), 1674-1682 (1992).
5. P. Selpulveda and J. G. P. Binner, J. Euro. Ceram. Soc. **19**, 2059- (1999).
6. H. X. Peng, Z. Fan, J. R. G. Evans and J. J. C. Busfield, J. Euro. Ceram. Soc. **20** 807- (2000).
7. J. S. Lee and J. K. Park, "Preparation of Porous Ceramic Pellets by Pseudo Double-Emulsion Method from 4-phase Foamed slurry", Journal of Material Science Letters, **20**(3), (2001).
8. J. K. Park and S. H. Lee, "Observation and Segmentation of Gray Images of Surface Cells in Open Cellular Foams", Journal of Ceramic Society of Japan, **109**(7), 580-586 (2001).
9. W. J. Chao and K. S. Chou, "Studies on the Control of Porous Properties in the Fabrication of Porous Supports", Key Engineering Materials, **115**, 93-108 (1996).
10. P. Sepulveda, F. S. Ortega, M. D. M. Innocentini, and V. C. Pandolfelli, " Properties of High Porous Hydroxyapatite Obtained by the Gelcasting of Foams", J. Am. Ceram. Soc., **83**(12), 3021-24 (2000).

Table 1. Chemical analysis of flyash used in this work. (wt.%)

component / material	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O	Na_2O	TiO_2	Ig. loss
flyash	71.90	17.50	2.42	-	1.77	0.48	0.69	0.64	1.01	3.59

Table 2. The physical properties of pellets according to relative density.

Relative density (ρ_b / ρ_r, -)	Total porosity (ε_T, %)	Average pore size (d_{ave}, μm)	Specific surface area (Sw, m^2/g)
0.52	47.63	66	3.53
0.37	63.41	70	6.09
0.28	71.57	73	11.98

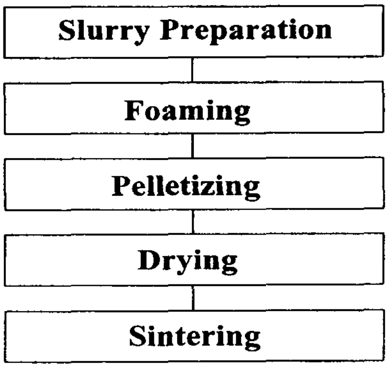

Fig. 1. The flowchart for total process preparing macro-porous flyash pellets.

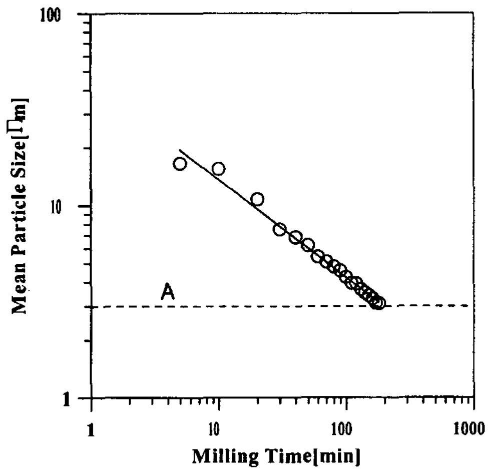

Fig. 2. Mean particle size of flyash slurry according to milling time.

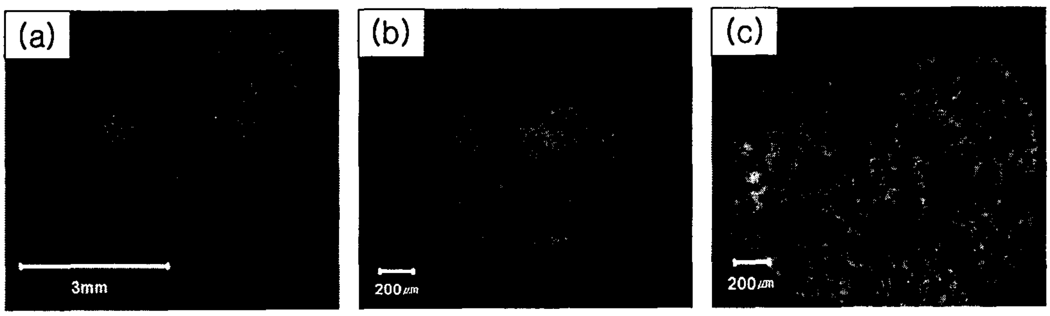

Fig. 3. (a) Macroporous flyash pellets and pores (b) on the surface and (c) in inner part of them.

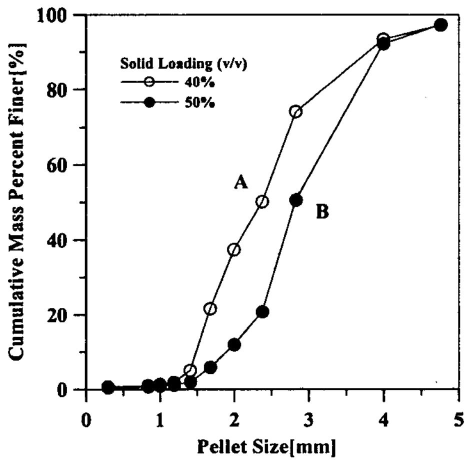

Fig. 4. The variation of pellet size according to solid loading.

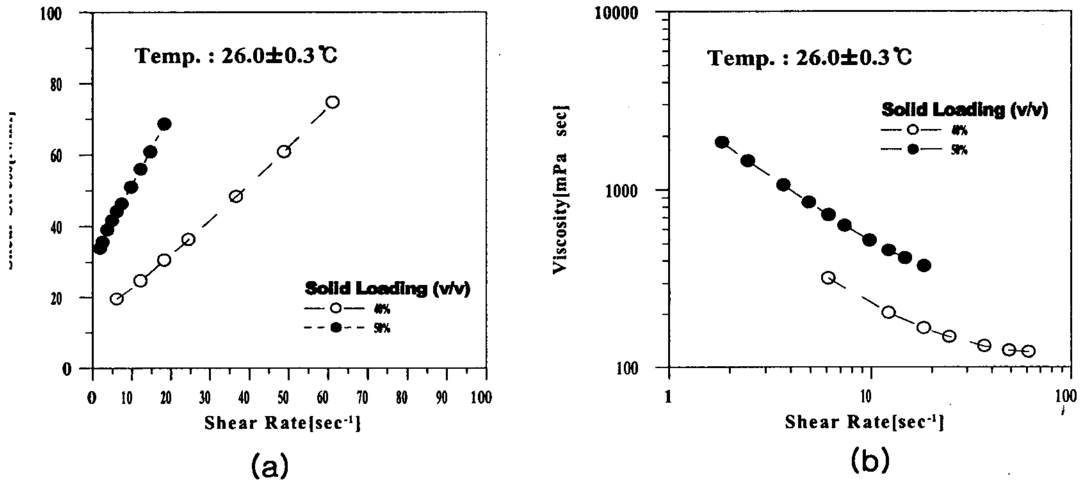

Fig. 5. The variation of (a) shear stress and (b) viscosity according to shear rate. (parameter : solid loading(v/v))

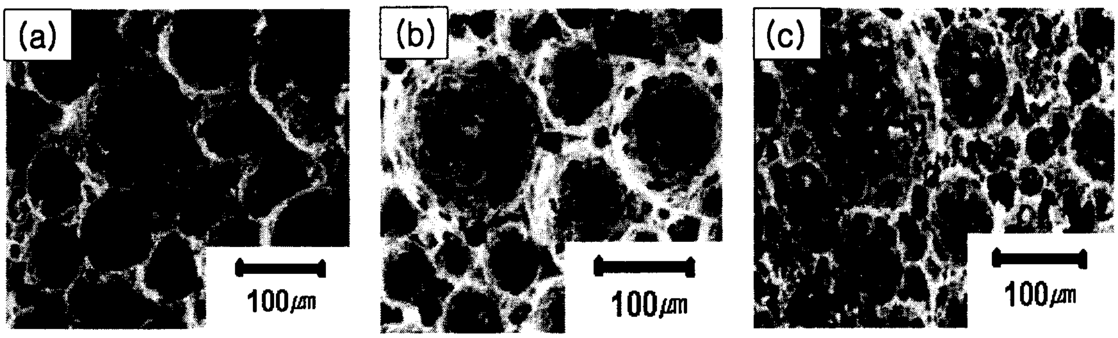

Fig. 6. Microstructures of macroporous flyash pellets with various relative density : (a) 0.52 g/cc, (b) 0.37 g/cc, and (c) 0.28 g/cc.