Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Particle Chromatographic Separation of Coal Fly Ash

Robert P. Kane[a]; William R. Wilcox[a]
[a] DEPARTMENT OF CHEMICAL, ENGINEERING CLARKSON COLLEGE OF TECHNOLOGY, POTSDAM, NEW YORK

To cite this Article Kane, Robert P. and Wilcox, William R.(1978) 'Particle Chromatographic Separation of Coal Fly Ash', Separation Science and Technology, 13: 7, 565 — 572
To link to this Article: DOI: 10.1080/01496397808057111
URL: http://dx.doi.org/10.1080/01496397808057111

SEPARATION SCIENCE AND TECHNOLOGY, 13(7), pp. 565–572, 1978

Particle Chromatographic Separation of Coal Fly Ash

ROBERT P. KANE and WILLIAM R. WILCOX

DEPARTMENT OF CHEMICAL ENGINEERING
CLARKSON COLLEGE OF TECHNOLOGY
POTSDAM, NEW YORK 13676

Abstract

Attempts were made to totally separate the 13 types of particles in a coal fly ash. While a considerable separation was obtained, it was far from complete even with optimal operating conditions. The best results were obtained with camphor as the host material in the tilt rotating zone melting technique with a tube rotation rate of 25 rpm and a tube tilt angle of 30° to the horizontal. Additional zone passes improved the separation only slightly. The zone travel rate at which each particle type was trapped, and the length over which each type was trapped, both increased as the tube rotation rate was increased and as the tilt angle was decreased. If a bubble contacted the interface during horizontal operation, the trapping occurred at significantly lower freezing rates and the separation was considerably worse. The smaller particles were trapped at lower freezing rates than larger particles. Naphthalene and biphenyl proved to be poor hosts because of extensive bubble formation at the interface during zoning. Particles were trapped at impractically low freezing rates with Salol.

INTRODUCTION

In particle chromatography, mixtures of particles are separated by controlled solidification of a melt in which the particle mixture is suspended (*1–5*). Separation of artificial mixtures was studied in prior work. In the present research we applied the technique to a real mixture—coal fly ash. The hope was that the different types of particles would be completely separated from one another to aid in characterization.

EXPERIMENTAL

As with previous work (*4*, *5*), the technique of tilt rotating zone melting was employed for the experiments. Details are given elsewhere (*6*). The organic hosts, in which the ash was suspended, were first zone refined to reduce the content of impurities and dissolved gases. This required three to four upward passes at 1 cm/hr.

In the experiments the ash mixed with an organic host was placed near one end of a 1.2-cm o.d. Pyrex tube. The mass of fly ash was varied from 0.005 to 0.1 g with no apparent influence on the separation obtained. A Teflon plug was inserted between the organic and the end of the tube to allow for expansion upon melting. The zone-refined organic was placed between the portion containing particles and the other end of the 30-cm long tube.

In the particle chromatography experiments a molten zone was generated at the end containing the particles. In order to produce the desired concave interface shape (*7*), it was necessary to make the zone about 8 cm long in this particular apparatus. The tube was rotated at 10 to 75 rpm and tilted up to 60° to the horizontal (so that the zone moved upward along an incline). The initial zone travel rate was 1 mm/hr, with the rate increased by 2 mm/hr each hour. Most of the experiments were done with the rate increased constantly, but a few were done by increasing the rate incrementally by 1 mm/hr each 30 min. In the latter operating mode the zone was moved only during the day and was turned off each night. It was remelted and repositioned each morning. The separation was not detectably less with this manual model of operation than with the automatic method of continuously increasing the zone travel rate.

The fly ash was from the electrostatic precipitator at a coal-fired power plant operated by the Niagara Mohawk Power Co. at Tonawanda, New York. The bulk analysis furnished by Niagara Mohawk showed 3.82 wt% CaO, 40.67 wt% SiO_2, 24.66 wt% Al_2O_3, 14.76 wt% other inorganics, and 20.07% weight loss in combustion. We observed 13 different types of particles, as summarized in Table 1. Some agglomerates were also present. It was found that these could be dispersed without fracturing individual particles by application of an ultrasonic field to a suspension in acetone or methanol. This was done except for the early runs, and was followed by drying in an oven at 60°C before use in the particle chromatography runs.

After a run, the tubes were cut into sections. The organic was evaporated off in a vacuum at 60 to 120°C. The particles were examined in optical microscopes at 70× and 500×.

TABLE 1

Classification of Fly Ash Particles

Appearance	Size (μm)	Approx. no. %
1. Transparent spheres	<10	40
2. Transparent spheres with other particles within	30–120	5
3. Transparent spheres with gas bubbles within	30–120	5
4. Transparent irregular (appear to be fragments of spheres)	25–90	3
5. Milky white spheres	35–70	5
6. Dark black spheres	<10	20
7. Glossy black spheres	10–40	5
8. Carbonaceous appearing spheres	30–90	5
9. Irregularly shaped carbonaceous	30–120	10
10. Red spheres	20–140	<2
11. Irregularly shaped, red-orange	10–25	
12. Rectangular or oblong, orange	30–50	
13. Brown spheres	30–50	

NAPHTHALENE RESULTS

Because most prior work had been done with naphthalene as a host material, it was also used here initially. Five runs were made at rotation rates of 15 to 30 rpm and tilt angles up to 60°. At 60° and 15 rpm the particles did not tumble along the interface and were all trapped without separation above zone travel rates of 5 mm/hr. At lower tilt angles the particles did tumble along the interface. The principle problem with naphthalene was the formation and trapping of gas bubbles near the interface soon after the ash contacted the interface. This suggests that the ash aided nucleation of bubbles from the dissolved gas rejected by the growing interface, as had been observed previously for carbon particles in freezing naphthalene (*1*, *8*). In the present experiments these bubbles moved with the interface up to a zone travel rate of about 9 mm/hr. Some particles came out in bands, but without any separation being evident. At zone travel rates of 9 to 20 mm/hr, many gas worms formed, with particles along their sides and no evidence of separation. Above 20 mm/hr, discrete bubbles were trapped as formed. In the horizontal run a large gas bubble formed at the top of the zone. This large bubble intermittently touched the interface, with trapping of clusters of particles each time it did so.

Thus it soon became apparent that a different host material was required. Salol (phenyl salicylate) pushed ash particles only at low rates, and was discarded. Many bubbles formed when biphenyl was tried. Finally, reasonable results were obtained with camphor, and so all effort was concentrated on optimizing the separation using it.

CAMPHOR RESULTS

With camphor as host, 37 runs were performed at rotation rates from 2 to 75 rpm and tilt angles of 0 to 45°. Unlike the naphthalene experiments, the majority of the particles were suspended and did not settle on the interface during tube rotation. Particles were trapped individually and not in clusters, as was common with naphthalene. Distinct bands, each about 5 mm long, were formed with scattered particles in between. Typical particle distributions are summarized in Fig. 1 and Table 2. While a separation was obtained, it was not perfect, as had been hoped. At no single

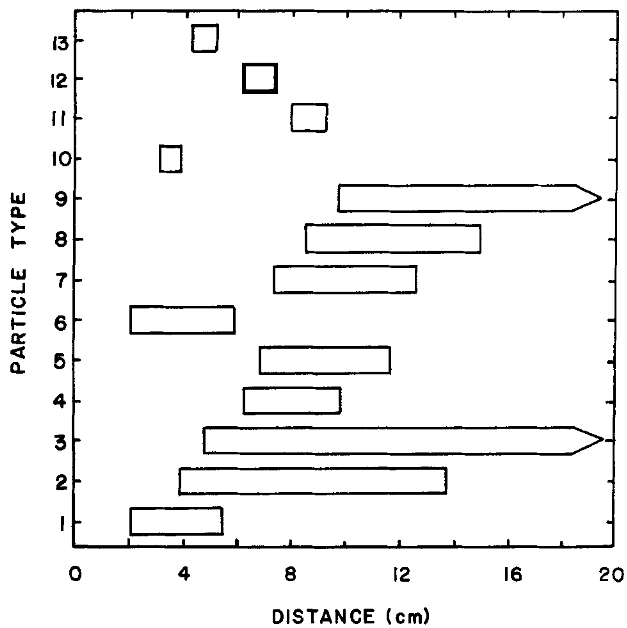

FIG. 1. Positions in camphor rod over which each particle type was found in Experiment 019C. 30° tilt angle, 25 rpm tube rotation. Arrow on end of bar indicates that some of that particle type pushed to the end of the tube (i.e., not trapped).

TABLE 2

Number Percent of the Particle Types Trapped at Several Positions in the Camphor Rod Experiment 019C

Position (cm)	Particle type[a]												
	1	2	3	4	5	6	7	8	9	10	11	12	13
2	80	*	*	*	*	20	*	*	*	*	*	*	*
4	75	2	2	*	*	17	*	*	*	2	*	*	2
6	T	25	25	15	15	T	15	*	*	*	2	3	*
8	T	10	15	10	15	T	15	30	*	*	5	*	*
10	T	15	20	*	20	T	10	30	5	*	*	*	*
12	T	10	20	*	T	T	5	40	25	*	*	*	*
14	T	T	10	*	T	T	T	20	70	*	*	*	*
16	T	*	15	*	*	T	*	T	85	*	*	*	*

[a] T denotes that a trace number of that particle type was present. * denotes that none of that particle type was observed in that position.

point in any tube was there only a single type of particle present. As an aid to future particle chromatography studies, we now discuss the factors which influenced the separation.

Seven runs were performed with rotation rates ranging from 10 to 75 rpm and tilt angles from 15 to 45°. Data of the sort displayed in Fig. 1 were taken. The zone travel rate V_c^i at which trapping first began for the ith particle type was correlated by an equation of the form

$$V_c^i = A_0^i + A_1^i R + A_2^i T \tag{1}$$

where the A's are constants, R is the rotation rate in rpm, and T is the tilt angle in degrees. The values of A_0 ranged from 2.39 to 6.22×10^{-6} m/sec, A_1 from 0.0134 to 0.0227 m/sec (rpm), and A_2 from -0.105 to -0.0125 m/sec (degrees). The values of A_1 and A_2 did not appear to depend on A_0, so the deviations from the mean for each particle type were correlated to give overall values of $A_1 = 0.019$ and $A_2 = -0.026$. In other words, the freezing rate required to trap each given type of particle increased as the tube rotation rate increased and as the tilt angle decreased, with the dependence on rotation rate and tilt angle being relatively independent of the type of particle. While our data were fit to a linear equation, it is known that the dependence on rotation rate is nonlinear (*1*, *7*) and that V_c becomes very large as the tube becomes horizontal ($T \rightarrow 0$), unless a gas bubble touches the interface (*4*, *5*). In one horizontal experiment containing such a bubble, the values for V_c for the 13 particles were reduced an average of 23% from an equivalent run with a 30° tilt angle.

The values for V_c with 25 rpm rotation and 30° tilt were increased by only about 2% by making two additional zone passes (i.e., three passes vs one). However, in the second and third zone passes, particle types 1 and 6 were trapped in an annular ring when the zone travel rate exceeded 10 mm/hr. (With a single zone pass, particles were trapped predominantly near the center of the tube.) All particles trapped in this annulus were under 10 μm in size, and were of both the black and the white particle types. At a zone travel rate of 13 mm/hr, some particles were also trapped in a disk in the center. As the freezing rate increased, this inner disk contained more particles and expanded, while the outer annulus gradually disappeared. The particles trapped in the disk were different from those in the annulus. We have no explanation for this phenomenon.

Another parameter of importance to particle chromatography is the distance L^i over which a given type of particle is trapped. (With the constant acceleration of 2 mm/hr^2 experiments, zone travel rate V and distance down the tube L are related by $V = \sqrt{4L + 1}$. Distances over which a given particle type was trapped could only be measured to within 5 mm.) There was no correlation ($r^2 = 0.0018$) of this distance L^i with the distance $L_c{}^i$ at which the ith type of particle was first trapped. However, L^i varied with rotation R and tilt T according to

$$L^i = B^i + 0.03R - 0.04T$$

with L^i in cm, R in rpm, and T in degrees. In other words, increasing the rotation rate increased the length over which a particle was trapped, while increasing the tilt had the opposite effect. (Recall that rotation and tilt had the same effects on V_c, and hence on L_c.) At 25 rpm and 30° tilt, two additional zone passes decreased the average trapping length for all types of particles by only 8%. Operating horizontally with a bubble increased the average L by 62%.

The most important parameter for particle chromatography is the overlap between trapping bands of different types of particles. The overlap was calculated for several fly ash particle types, with overlap defined as the length of overlap divided either by the total length of the two bands together, or the length of the earliest band if the particles in the second band were not all trapped by the end of the tube. For particle types 1 and 2, and 3 and 6, the minimum overlap occurred with 20 rpm and 45° tilt. However, the overlap of most bands was a minimum for 25 rpm and 30° tilt. The separation was significantly worse for horizontal operation with a gas bubble contacting the interface.

It was noticed that for a given particle type the smaller particles were trapped first at a lower zone travel rate. That is, some separation by size was occurring, which tended to reduce the separation by particle type.

Consequently, rough size separations were performed using an ATM Sonic Sifter with 200, 270, and 400 mesh screens. Those particles larger than 270 mesh were similar to those that had been pushed the full length of the tube (i.e., not trapped at maximum freezing rate employed). They were mostly the irregular carbonaceous-appearing particles and the larger glass beads. These were not trapped by the end of the tube at 30° and 20 rpm. At 10 rpm they were separated somewhat, but still not completely. The 270 to 400 mesh particles were only trapped in bands when the rotation rate was under 20 rpm. This fraction contained most of the odd-shaped and colored particles, which were trapped in very narrow regions. The separation was still not complete, however. The smallest particles (under 270 mesh) were trapped in bands, but the separation was not markedly improved.

Finally, Shih and Donaghey's (*3*) operating method was tried. Ten zone passes were made in the horizontal mode at 35 mm/hr (i.e., constant V, no acceleration). A bubble contacted the interface in only the first zone pass. The separation was very poor; worse than that achieved with three zone passes with acceleration and a tilted tube.

DISCUSSION

While separations *were* obtained, they were inadequate for analytical purposes. Part, but only part, of our difficulties may be attributed to variations in size and shape of each given particle type. A more fundamental problem seems to be simply that the interactions of the particles with the freezing interface were not sufficiently different. This may be understood from the viewpoint that disjoining pressure provides the repulsive force tending to prevent a particle from being trapped (*4*, *9*). One really would not expect the disjoining pressure to differ markedly for the different types of coal fly ash particles, since they are predominately inorganic oxides, probably with adsorbed water on their surfaces. This suggests that particle chromatography should be considered as a separation technique only if the particles differ markedly from one another, e.g., separation of metal particles from organic particles, separation of large particles from small particles, etc.

Acknowledgments

This research was supported by the Electric Power Research Association under Contract RP854–1 and by the National Science Foundation under Grant ENG76–00701.

REFERENCES

1. V. H. S. Kuo, "Removal and Separation of Particles by Crystallization," Ph.D. Dissertation, University of Southern California, Los Angeles, 1972.
2. V. H. S. Kuo and W. R. Wilcox, *Sep. Sci.*, *8*, 375 (1973).
3. T. T. Shih and L. F. Donaghey, *Application of Velocity-Selective Freeze-Pushing to the Separation and Characterization of Air-Borne Solid Particulate Matter in Air Pollution Samples*, University of California, Berkeley, 1973.
4. K. H. Chen, "Particle Pushing and Separation of Particulate Mixtures by Solidification," Ph.D. Dissertation, University of Southern California, Los Angeles, 1976.
5. K. H. Chen and W. R. Wilcox, *Sep. Sci. Technol.*, *13*, 387 (1978).
6. R. P. Kane, "Particle Chromatographic Separation of Fly Ash," M.S. Thesis, Clarkson College of Technology, Potsdam, New York, 1977.
7. V. H. S. Kuo and W. R. Wilcox, *Ind. Eng. Chem., Process Des. Dev.*, *12*, 376 (1973).
8. W. R. Wilcox and V. H. S. Kuo, *J. Cryst. Growth*, *19*, 221 (1973).
9. A. A. Chernov, D. E. Temkin, and A. M. Mel'nikova, *Sov. Phys.-Crystallogr.*, *21*, 369 (1976).

Received by editor November 14, 1977