ROLES OF ADDITIVES AND SURFACE CONTROL IN SLURRY ATOMIZATION

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FINAL PROJECT REPORT

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to

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Pittsburgh Energy Technology Center
Department of Energy

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SUMMARY

This project studies the rheology and airblast atomization of micronized coal slurries. Its major objectives are (1) to promote further understanding of the mechanisms and the roles of additives in airblast atomization of coal water slurry (CWS), and (2) to investigate the impacts of coal particle surface properties and interparticle forces on CWS rheology.

We have found that the flow behavior index (n) of a suspension (or slurry) is determined by the relative importance of the interparticle van der Waals attraction and the interparticle electrostatic repulsion. The interparticle attraction, measured by the Hamaker constant scaled to the thermal energy at 25°C (A/kT), causes particle aggregation, which breaks down at high shear rates, and thus leads to slurry pseudoplastic behavior ($n<1$). At a constant particle volume fraction and surface charge density (qualitatively measured by the zeta potential in deionized water), n decreases linearly as A/kT increases. The relative viscosity of the pseudoplastic suspension with respect to that of the suspending liquid is found to be independent of particle density and correlate well with the particle Peclet number which equals the particle diffusional relaxation time multiplied by shear rate. Specifically, the relative viscosities of the pseudoplastic glycerol/water coal slurry and the ethylene glycol/glycerol sand slurry, at same volume fractions as well as similar particle size distributions and liquid viscosities, as functions of the particle Peclet number fall along the

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same line. Since particle diffusional relaxation time increases with particle radius cubed, larger particles in an aggregated system diffuse to a lesser extent than smaller particles within the same time scale of shear, and less energy is dissipated as a result.

We have developed a three-parameter model in terms of liquid-to-air mass ratio, the Weber number, and the Ohnersorge number for primary atomization based on the classical wave mechanism, momentum balance and energy considerations. The mass median diameters (MMDs) of atomized CWSs can be described by these models with correlation coefficients of 0.95 to 0.97. We have also established that the effects of coal particle surface properties and additives on atomized drop sizes can be accounted for by their effects on slurry rheology.

Anionic dispersant concentration dictates the CWS rheology. As the concentration exceeds a threshold value, the interparticle electrostatic repulsion counter-balances the interparticle van der Waals attraction and, thus, the CWS becomes Newtonian at moderate to high shear rates. For example, as the anionic dispersant (Coal Master) increases in quantity from 0.15 to 1.35 wt% polymer on coal basis, the CWS of Upper Freeport coal at 0.55 volume fraction (62 wt%) changes from a pseudoplastic behavior with a flow behavior index of 0.76 and a flow consistancy index of 20 (cgs units) to a Newtonian behavior with a viscosity of 2 P. The CWS of 0.15 wt% polymer has high shear viscosities (at prevailing atomization conditions) of 2.1 to 2.5 P. These two slurries have been atomized using a twin-fluid jet atomizer to drops with MMDs of 76 and 43 μm at air-to-slurry mass ratios of 0.35 and 0.33, respectively. Sedimentation testings show that the former slurry is stable with no settling for up to three weeks, but a soft packing forms at the bottom at the end of the fourth week. In contrast, the latter slurry settles easily.

LIST OF MAJOR PUBLICATIONS (copies of reprints attached)

1. S.C. Tsai and K. Ghazimorad, "Correlation Between the Hamaker Constant and the Flow Behavior Index of a Concentrated Suspension," J. of Rheology, 34, 1327-1332, 1990.

2. S.C. Tsai and B. Viers, "Airblast Atomization of Viscous Liquids, "Fuel, 69, 1412-1419, 1990.

3. S.C. Tsai, K. Ghazimorad, and B. Viers, "Airblast Atomization of Micronized Coal Slurries Using a Twin-fluid Jet Atomizer," Fuel, 70, 483-440, 1991.

4. S.C. Tsai, K. Ghazimorad, B. Viers, and N. Widjaja, "Rheology and Atomization of Micronized Coal Water Slurries," Proc. of ASME 4th International Symposium on Solid Liquid Flow, FED 118, 123-130, 1991.

5. Q.Y. Song and S. C. Tsai, "Magnetic Seeding Flocculation of Weakly Magnetic Iron

Minerals," Int. J. of Mineral Processing, 34, 219-229, 1992.

6. Tsai and Viers, "Airblast Atomization of Viscous Newtonian Liquids Using Twin-fluid Jet Atomizers of Various Designs," J. of Fluid Eng., 114, 113-118, 1992.

7. S.C. Tsai, D. Botts, and J. Plouff, "Effects of Particle Properties on the Rheology of Concentrated non-Colloidal Suspensions," J. of Rheology, 36, 1291-1305, 1992.

STUDENT PARTICIPATION AND OUTCOME

Three undergraduate students (Dale Botts, Brian Viers, and Khashayar Ghazimorad) who completed senior projects under my supervision with partial support by the DOE have entered our MS in Engineering program, and continue research under my supervision. Botts completed his thesis and obtained a Master Degree in Engineering in October, 1992, and plans to obtain a Ph.D.. My other undergraduate students involved in this project are Nuragung Widjaja, Jon Peters, Paul Childs, and John Hecht. Widjaja has entered the graduate program in the University of Southern California. Paul Childs plans to enroll in our MS program. Jon Peters is working in an energy company and John Hecht is seriously considering graduate study.

MAJOR NEW FINDINGS AND CONCLUSIONS

A wide variety of particles ranging from monodispersed polystyrene spheres P_2 and Upper Freeport Coal (Up1 and Up4) particles of irregular shape to polydispersed glass beads #5000 and Pittsburgh Seam #8 coal (Pgh) are used. The densities, volume mean diameter (VMD) and the mass median diameter (MMD) of the partilces used are listed in Tables I and II, and the coal analyses are given in Table II. Both nonaqueous and aqueous liquids and nonaqueous liquid mixtures with viscosities ranging from 1 cP (water) to 10 P (glycerol) are used as the suspending liquids. An anionic dispersant, Coal Master A23M from Henkel Corporation containing 44 wt% ammonium naphthalene sulfonate formaldehyde polymer, is used in the CWS preparation. While the detailed experimental methods and results are given in the attached copies of reprints, the major new findings and conclusions obtained in this project are given as follows:

Slurry Rheology

(1) The flow behavior index of a suspension is determined by the relative importance of the interparticle van der Waals attraction and the interparticle electrostatic repulsion. The interparticle attraction causes particle aggregation which breaks down at high shear rates and thus leads to slurry pseudoplastic behavior ($n<1$). At a constant particle volume fraction and surface charge density (qualitatively measured by the zeta potential in deionized water), n decreases linearly as the nondimensional Hamaker constant (A/kT) increases as shown in

Fig. 1. In this figure, the non- aqueous suspensions include polystyrene spheres, glass beads, and irregularly shaped sand particles suspended in silicone oils, ethylene glycol, glycerol, and mixtures of ethylene glycol and glycerol. The aqueous suspensions include coal particles suspended in mixtures of water and glycerol or ethylene glycol or i-propanol. Note that the Hamaker constant is calculated by the Lifshitz equation:

$$A = \frac{3}{4} kT \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right)^2 + \frac{3h\nu_e \left(n_1^2 - n_3^2\right)^2}{16\sqrt{2}\left(n_1^2 + n_3^2\right)^{\frac{3}{2}}}$$

where h and k are the Planck and Boltzman constants, respectively; ϵ_1 and ϵ_3 are, respectively, the dielectric constants of particle and the suspending liquid; n_1 and n_3 are the corresponding refractive indices; ν_e is the absorption frequency. The Hamaker constant of solid suspended in a liquid mixture is assumed to be the sum of those of solid in pure liquids multiplied by the liquid volume fractions [Tsai and Ghazimorad, 1990].

(2) Both Fig. 2 and Fig. 3 show that the relative viscosity (η_r) of the pseudoplastic suspension with respect to that of the suspending liquid (η_o) correlates well with the particle Peclet number which equals the time required for a particle to diffuse a distance comparable to its average radius ($\bar{a}$) multiplied by shear rate ($\dot{\gamma}$). The relative suspension viscosity is also shown in these figures to be independent of particle density [Tsai, Botts and Plouff, 1992]. Specifically, the relative viscosities as functions of particle Peclet number for the 0.45 volume fraction slurries of Upper Freeport (Up1 and Up4) coal in 74/26 wt/wt of glycerol/water and sand in 80/20 wt/wt of ethylene glycol/glycerol fall along the same curve. The corresponding curves for Illinois #6 coal (ILL) and for Pittsburgh Seam #8 (Pgh) coal lie slightly above and far below as shown in Fig. 3, respectively. This finding may be attributed to the slightly narrower size distribution of the ILL coal and much broader size distribution of the Pgh coal as compared to the Upper Freeport Up1 and Up4 coals as shown in Fig. 4.

(3) While the flow behavior index of a concentrated suspension is independent of the shape of particles with aspect ratios close to unity, its relative viscosity is strongly influenced by the particle shape. Presence of irregularly shaped particles results in reduction in the maximum particle packing fraction. Therefore, a suspension of irregulary shaped particles has a higher relative viscosity than one of spherical particles of the same volume fraction. Using the maximum packing fraction (φ_M) as the sole parameter which accounts for the effects of particle shape and size distribution, the Krieger-Dougherty rigid sphere model of colloidal suspensions satisfactorily depicts the relative viscosity of a Newtonian noncolloidal suspension as a function of particle volume fraction (φ) as shown in Fig. 5. This maximum packing fraction (φ_M) is in very good agreement with the maximum volume fraction obtained by sedimentation. Note that the intrinsic viscosity [η] is taken as 2.67 in the rigid sphere model:

$$\eta_r = (1 - \varphi/\varphi_M)^{-[\eta]\varphi_M}$$

[Tsai, Botts and Plouff, 1992].

(4) Coal dispersant concentration predominates the CWS rheology. Less quantity is required for the lower ranking Pgh and ILL coals than the higher ranking Upper Freeport coal to form Newtonian slurries at moderate rates (above 100 s^{-1}). Nevertheless, as shown in Table III, the relative viscosities of Newtonian CWSs using both Upper Freeport and Pittsburgh Seam coals and anionic dispersant A23M are an order of magnitude higher than those predicted by the Krieger-Dougherty rigid sphere model with the intrinsic viscosity $[\eta]$ equaling 2.67 and the maximum packing fraction determined from sedimentation.

Airblast Atomization of Viscous Liquids and Micronized Coal Slurries

(1) The twin-fluid jet atomizer whose dimensions are given in Table IV is designed to minimize errosion of the nozzle tip. As shown in Fig. 6, the slurry passes axially through the center of the distributor. The atomizing air passes through the 15°-angled slits drilled in the 45° taper of the distributor and, thus, swirls around the slurry jet. The nozzle has a single discharge port of diameter larger than the diameter of the distributor for slurry passage. As shown in Table V, atomized drops obtained by 15° swirl (distributor #1) are significantly smaller than those by 5° swirl (distributor #3) [Tsai and Viers, 1992].

Also shown in Table V, the atomized drop sizes substantially decrease as the atomizing air pressure exceeds a threshold value which varies from less than 170 to 220 kPa depending on the nozzle diameters [Tsai and Viers, 1990; Tsai and Viers, 1992].

(2) While pseudoplasticity plays a significant role in atomization, the high shear viscosity dictates the atomized drop sizes. The atomized drop sizes, represented by the mass median diameter scaled to an atomizer characteristic length (MMD/L_c), can be described in terms of three nondimensional groups, namely, slurry-to-air mass ratio ($\dot{M}_S/\dot{M}_A$), the Weber number (We), and the Ohnesorge number (Z):

$$MMD/L_c = (1+\dot{M}_S/\dot{M}_A)\left\{x2 \cdot We^{-x1} + x3 \cdot Z^{j \cdot x1}\right\}$$

where j = 1 or 2, We equals the ratio of aerodynamic force to surface tension and Z represents the viscous effect. This model is based on the classical wave mechanism, momentum balance, and energy considerations. The three parameters (xi, i= 1 to 3) are determined by the best least square fit of the model to the experimental results using the iterative generalized inverse method. As shown in Table VI, the exponents of the We^{-1}- and Z- dependencies fall between the values, 2/3 and 1/3, predicted by the acceleration and the capillary wave mechanisms, respectively. Very good agreement (see Fig. 7) has been

obtained between the model and the experimental drop MMDs [Tsai and Viers, 1990; Tsai and Viers, 1992].

(3) Both Newtonian and pseudoplastic CWSs of Upper Freeport coal (Up3 with 12.5 μm MMD and 17.8 μm VMD) at 0.55 volume fraction (62 wt%) have been prepared through use of an anionic dispersant (Coal Master) alone in quantities ranging from 0.15 to 1.35 wt% polymer on coal basis. The CWS of 0.15 wt% polymer has a flow behavior index of 0.76 and high shear viscosities (at prevailing atomization conditions) of 2.1 to 2.5 P. The CWS of 1.35 wt% polymer is Newtonian with a viscosity of 2 P. These two slurries have been atomized using a twin-fluid jet atomizer to drops with MMDs of 76 and 43 μm at air-to-slurry mass ratios of 0.35 and 0.33, respectively. Sedimentation testings show that the former slurry is stable for one month.

TABLE I. Particles Sizes and Densities

Particle	VMD, μm	MMD, μm	Density, g/cc
Polystyrene P_1	77.8	72	1.05
Polystyrene P_2	6.0	5.5	1.05
Glass bead #4000 GL1	30.5	29	2.39
Glass bead #5000 GL4	22.6	20.9	2.39
Glass bead 20-40 μm* GL5	24.2	15.8	2.39
Sand 20-40 μm*	--	--	2.50
Sand, <63 μm, unsieved	--	--	2.50
Upper Freeport coal	4.4	4.4	1.33
Illinois #6 coal	7.8	3.7	1.37

*Sieved to 20-40 μm using the Alpine Air-jet Siever

Table II. COAL ANALYSES

Analysis Dry basis	Upper Up2	Freeport Up3	Coal Up1 & Up4	Pittsburgh Seam, Pgh	Illinois #6 ILL
Volatile, %	23.1	25.2	28.4	42.4	40.6
Ash, %	16.7	9.1	5.4	3.9	4.2
Carbon, %	72.1	81.1	82.8	78.4	75.2
Hydrogen, %	4.5	5.1	5.1	5.4	5.2
Nitrogen, %	1.3	1.4	0.7	1.4	1.4
Oxygen, %	5.5	3.3	4.8	7.9	11.5
Sulfur, %	0.7	0.6	1.2	3.1	2.5
Particle size					
MMD, μm	10	12.5	4.0	9.2	7.8
VMD, μm	15.8	17.8	4.9	12.9	9.9

TABLE III. Newtonian CWSs Using Anionic Dispersant A23M

A23M Concentration wt% of Coal	Volume	Coal Loading Fraction	wt%	Shear Rate s^{-1}	Relative Viscosity Measured	Predicted[a)]	w/φ_M[b)]
1.15	0.48	UP1	54	250-1500	1150	162	0.49
1.15	0.45	UP1	52	250-5000	450	27	0.49
1.15	0.45	UP1	52	100-750[c)]	450	27	0.49
1.20	0.43	UP1	50	500-5000	300	16	0.49
1.73	0.50	UP2	57	700-6000	160	17.6	0.60
0.75	0.55	UP3	62	500-6000	200	32	0.63
0.36	0.55	UP3	62	500-8000	205	32	0.63
1.35	0.55	UP3	62	500-8000	215	32	0.63
0.38	0.40	Pgh	48	150-440[d)]	43	6	0.59
0.36	0.45	Pgh	53	4000-8000	145	9.7	0.59
0.61	0.45	Pgh	53	25-440[d)]	165	9.7	0.59
0.38	0.49	Pgh	57	200-1300	520	16.5	0.59
0.37	0.52	Pgh	60	1000-4500	1520	29	0.59

a) Predicted by the Krieger-Dougherty Equation with intrinsic viscosity $[\eta]$ equaling 2.67.
b) Determined from sedimentation except 0.59 estimated for Pittsburgh #8 coal (Pgh).
c) The aqueous solution contains 35 wt% glycerol.
d) Measured with Haake rotational rheometer RV2.

TABLE IV. Atomizer Dimensions

Nozzle tip No.	Discharge Diameter cm	Cross Section cm^2
1	0.249	4.866×10^{-2}
2	0.178	2.483×10^{-2}
3	0.305	7.306×10^{-2}

Distributor* No.	Dia. cm	Slit Design No.-cm x cm -deg.	Cross Section, cm^2 Liquid	Air
1	0.152	6-0.16 x 0.097 - 15	1.815×10^{-2}	9.312×10^{-2}
2	0.152	4-0.24 x 0.076 - 15	1.815×10^{-2}	7.354×10^{-2}
3	0.152	6-0.16 x 0.097 - 5	1.815×10^{-2}	9.312×10^{-2}
4#	0.244	6-0.086x 0.114 - 15	4.676×10^{-2}	5.925×10^{-2}

*Diameter of the central opening for liquid flow
#Variflo atomizer by Delavan Corp., South Carlorina

TABLE V. Effect of Slit Angle on Glycerol Atomization Using Nozzle #1

Dtr. No.	Slit Angle deg.	$1+\dot{M}_L/\dot{M}_A$	P_A kPa	We	MMD μm
1	15	1.76	211	263	40 (79)*
1	15	1.72	177	278	85
3	5	1.93	177	241	131 (89)*
3	5	1.76	177	249	121 (81)*
1	15	2.09	218	278	54 (94)*
1	15	2.28	170	197	93
3	5	2.33	149	202	174 (109)*

* Values calculated using the following equation for atomization at inlet air pressures below the threshold pressure:

$$MMD/L_c = (1+\dot{M}_L/\dot{M}_A)\{8.5 \cdot We^{-0.47} + 1.4\, Z^{0.47}\} \cdot 10^{-2}$$

where L_c equals 0.152 cm.

TABLE VI. Semi-empirical Model for Airblast Atomization of Micronized Coal Slurries and Viscous Liquids with viscosities up to 10 P

$$MMD/L_c = (1+\dot{M}_S/\dot{M}_A)\{x2 \cdot We^{-x1} + x3 \cdot Z^{x1}\} \cdot 10^{-2} \quad (1)$$

$$MMD/L_c = (1+\dot{M}_S/\dot{M}_A)\{x2 \cdot We^{-x1} + x3 \cdot Z^{2\,x1}\} \cdot 10^{-2} \quad (2)$$

Sample	xl	x2	x3	c.o.c.*	95% confi. Interval	Eq.
Glycerol	0.47±0.04	7.9±0.8	1.38±0.14	0.94 (a)	0.88-0.97	(1)
	0.60±0.04	12.0±1.0	1.10±0.04	0.93 (b)	0.87-0.97	(1)
	0.30±0.02	5.0±0.5	1.0±0.1	0.94 (a)	0.88-0.97	(2)
	0.38±0.03	6.0±0.6	0.80±0.03	0.93 (b)	0.87-0.97	(2)
CWS	0.39±0.02	13.5±0.9	1.90±0.06	0.96 (a)	0.90-0.98	(1)
	0.36±0.01	12.0±0.4	0.23±0.02	0.97 (b)	0.94-0.99	(1)
	0.30±0.02	11.5±0.9	1.26±0.02	0.95 (a)	0.87-0.98	(2)
	0.37±0.01	13.3±0.6	0.17±0.02	0.97 (b)	0.94-0.99	(2)

* Coefficient of correlation

(a) Atomization at air pressures below a threshold value

(b) Atomizing air pressure above the threshold value, MMD is replaced by VMD in the case of glycerol atomization

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Fig. 7 Correlation between the wave mechanism based-models and the measured nondimensional drop MMDs of atomized micronized coal slurries at atomizing air pressures a) below and b) above the threshold pressure (diagonal lines represent perfect correlation)

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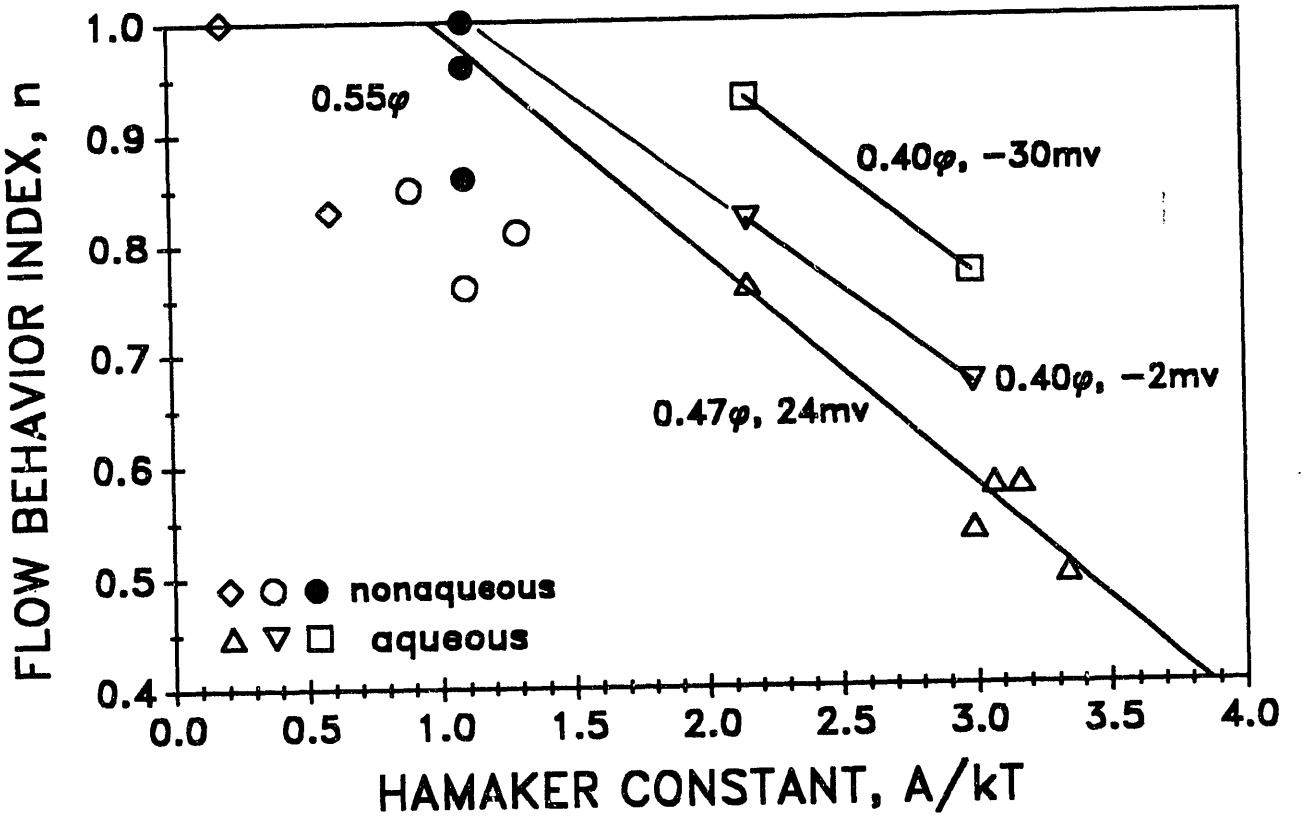

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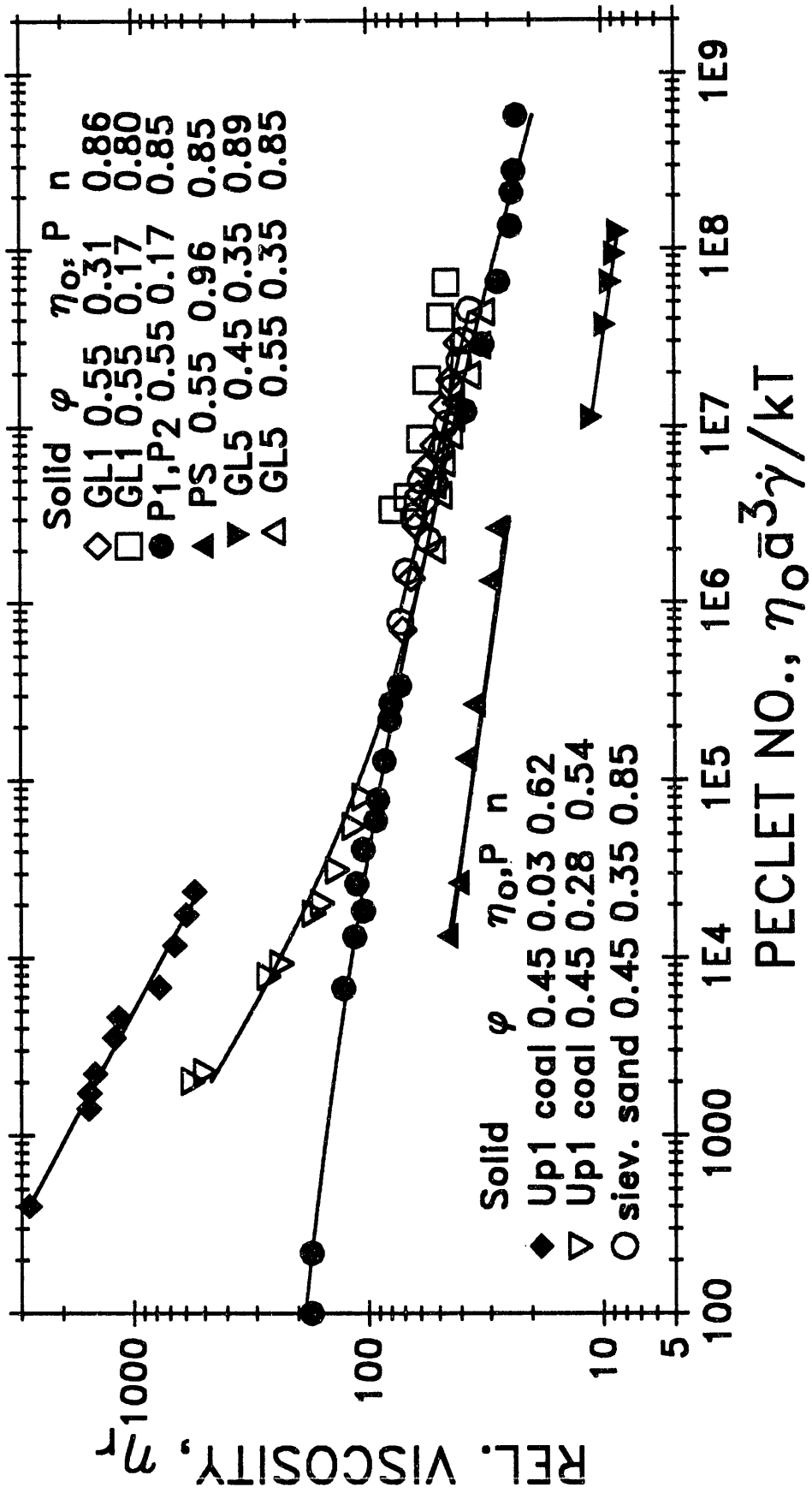

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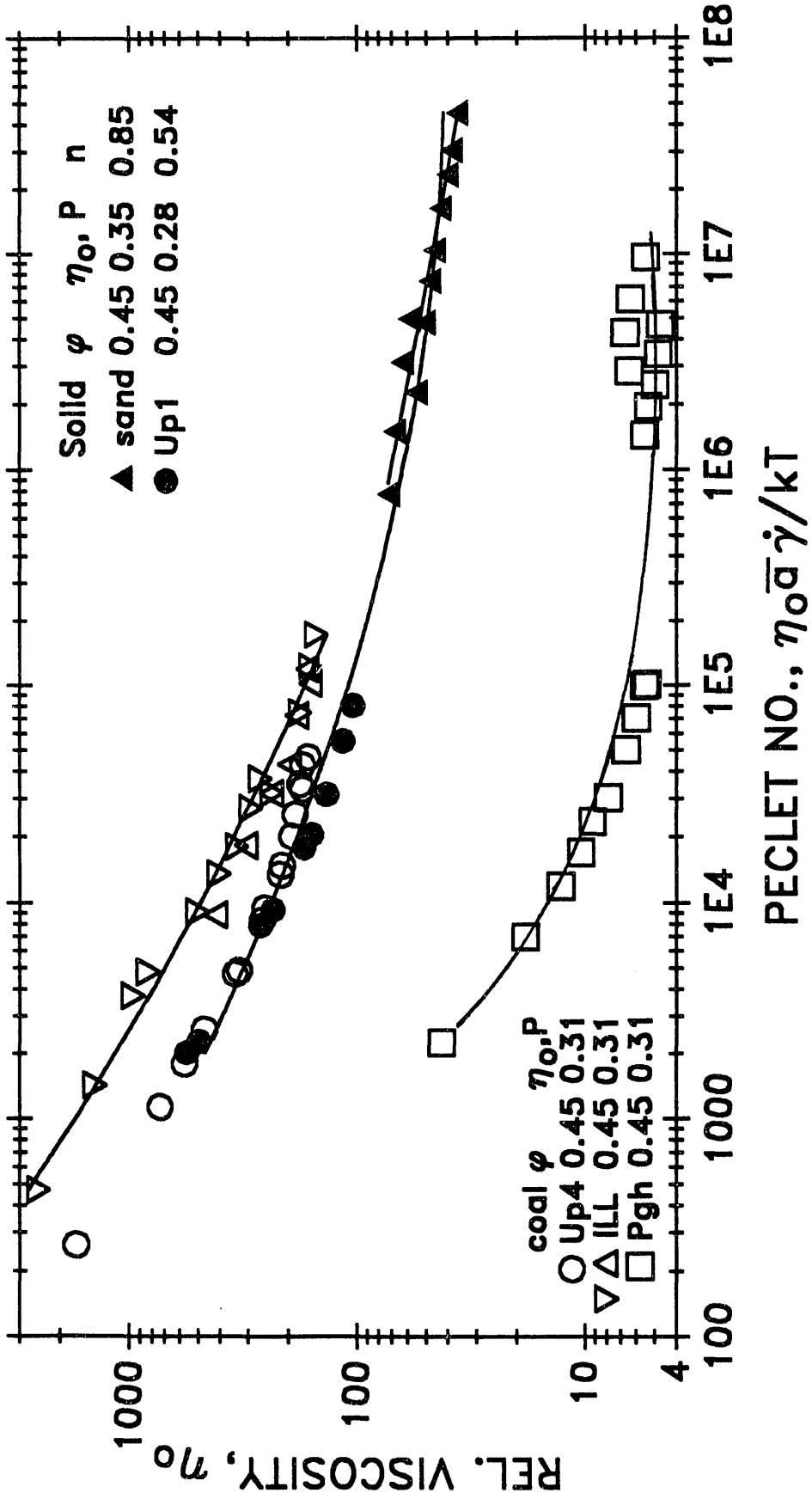

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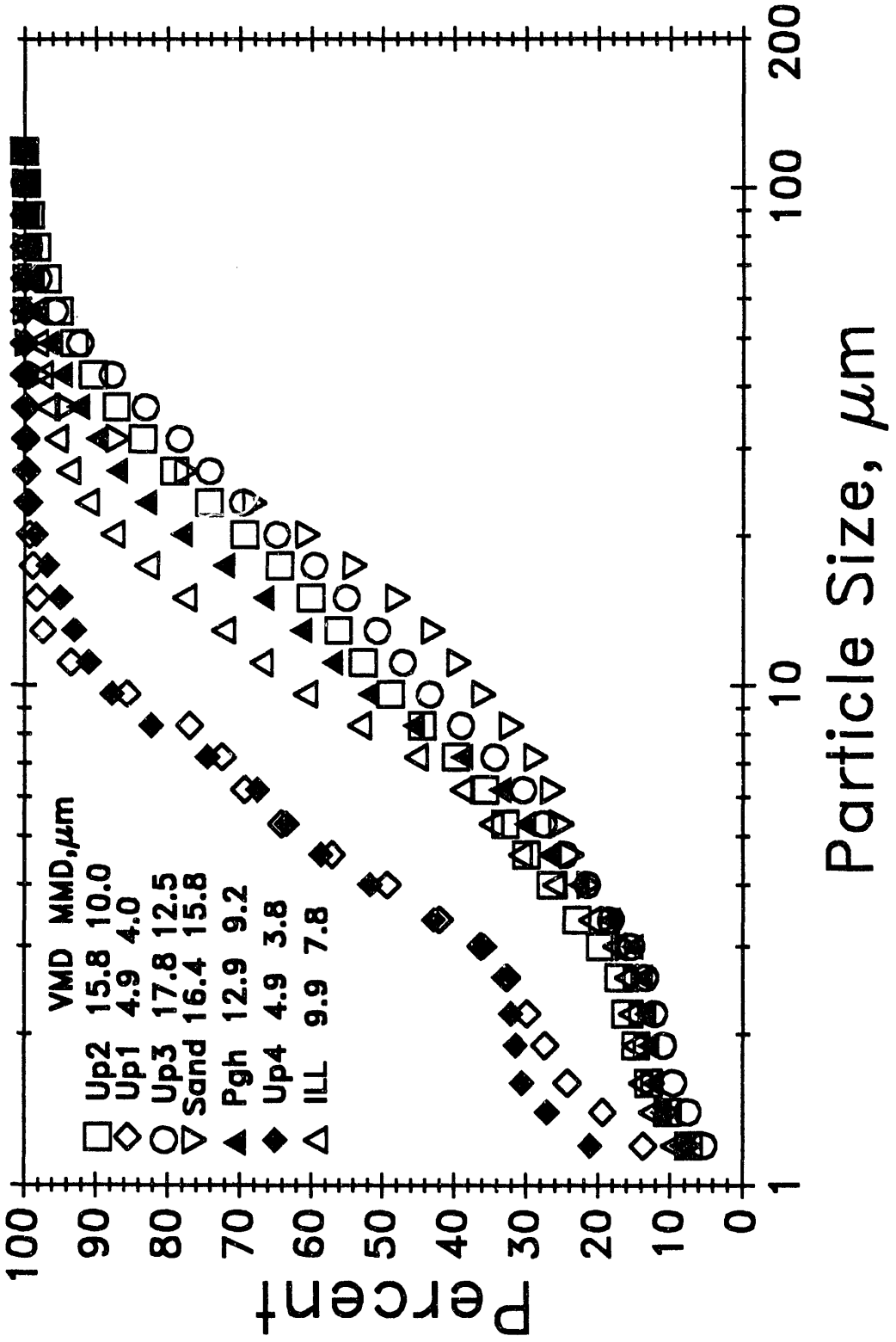

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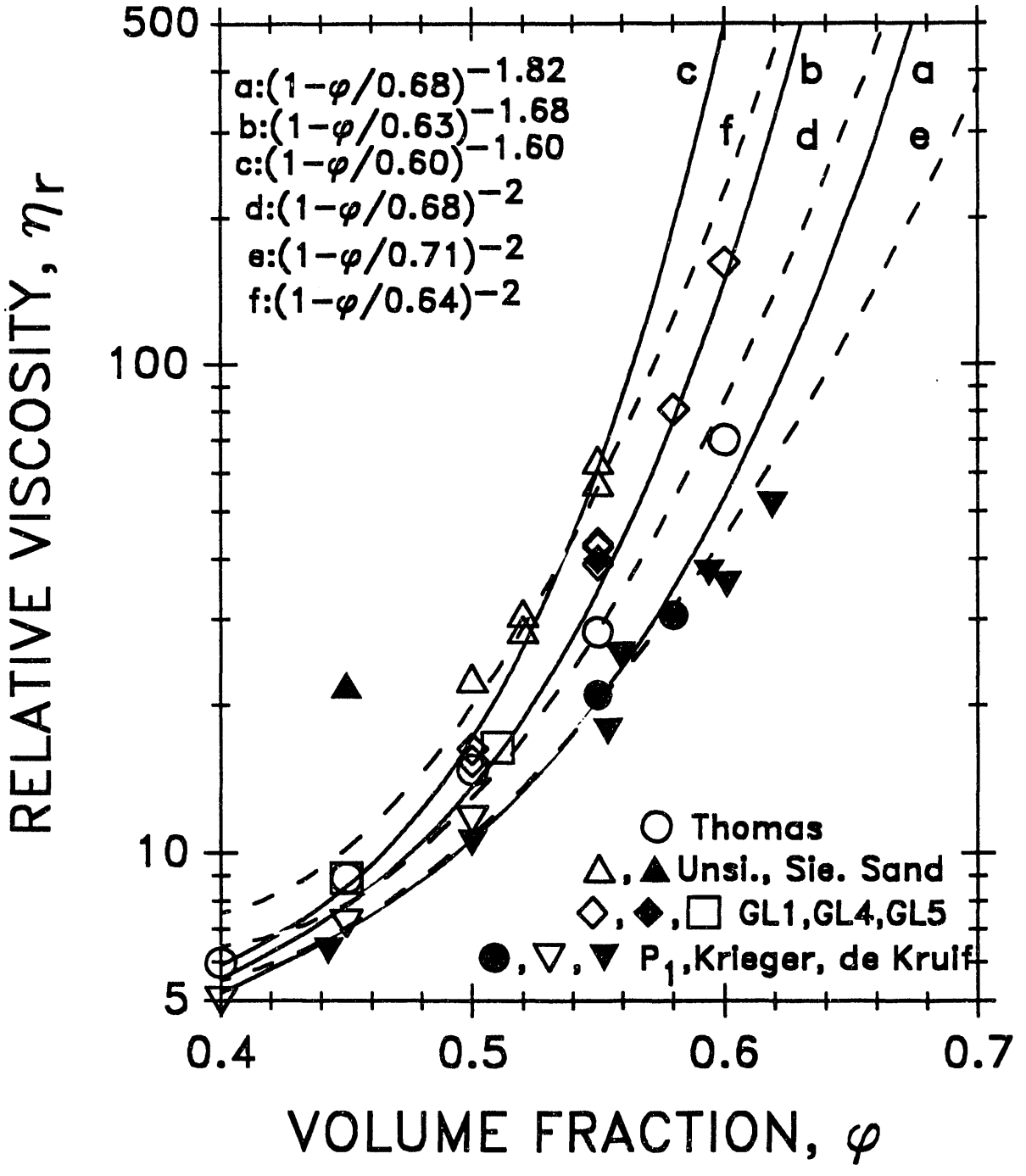
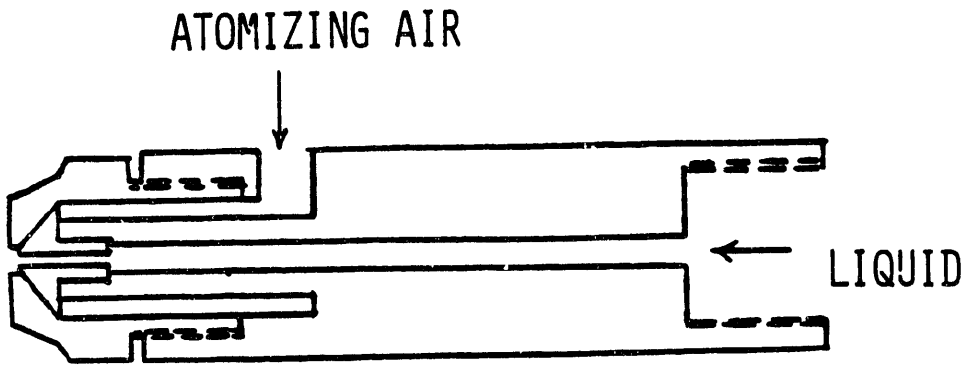


Fig. 6 Design of a twin-fluid jet atomizer



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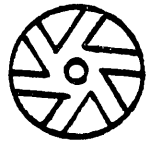

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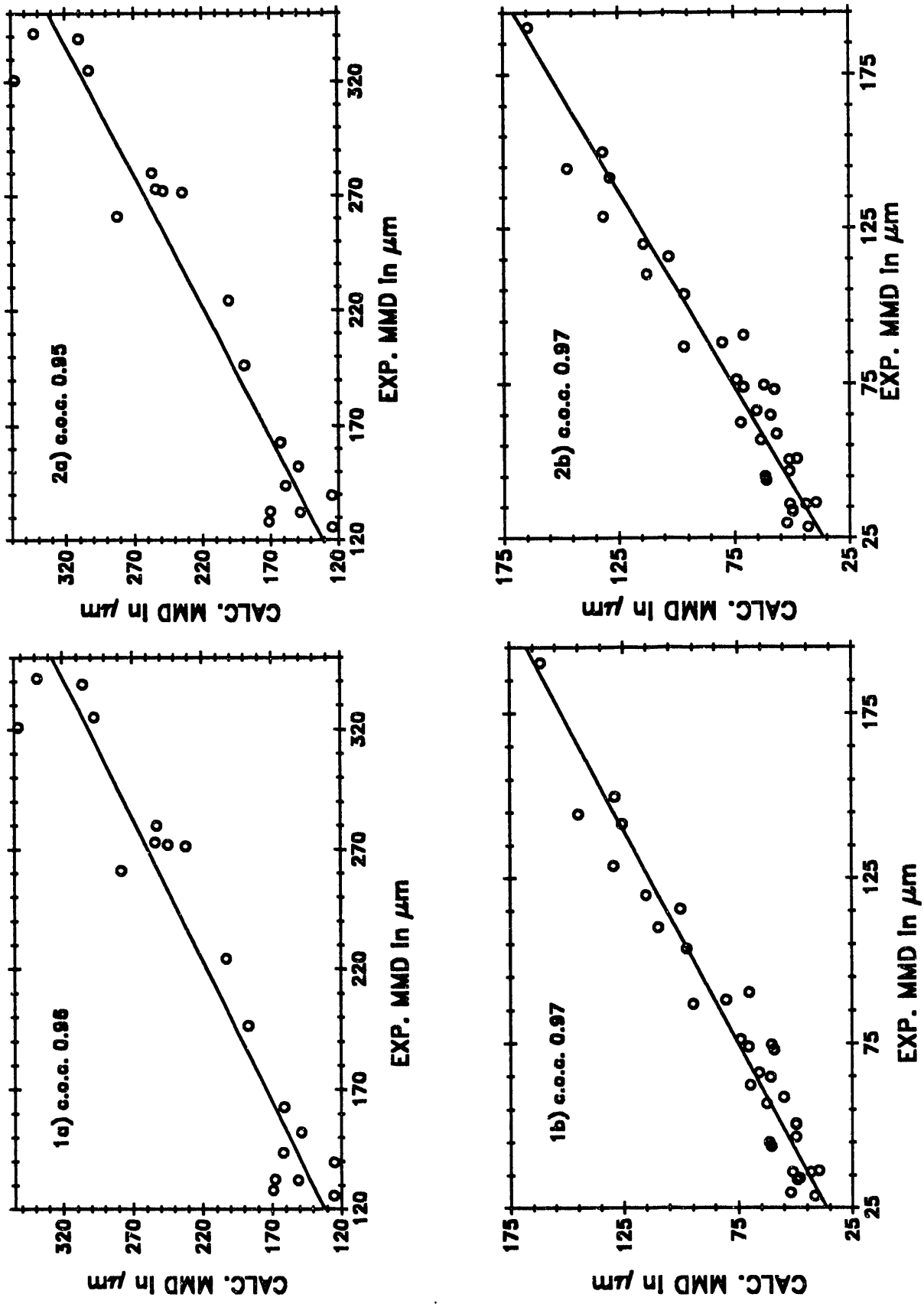

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