Simultaneous Removal and Recovery of Cadmium and Cyanide Ions in Synthetic Wastewater by Ion Exchange

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Abstract—Simultaneous removal and recovery of cyanide and cadmium ions using a strong-base anion exchange resin was studied on the basis of formation of Cd-CN complexes at high pH in synthetic wastewater containing cyanide and cadmium ions. Strong-base anion exchange resin particles, of Dowex1X8-50, were contacted with synthetic aqueous solutions. For different molar ratios between cyanide and cadmium, ion exchange characteristics of cadmium-cyanide complexes were studied experimentally in a batch reactor. Treatment efficiencies of packed and fluidized beds were compared under various conditions. Several regenerants, NaSCN, NaCN, and NaOH, were used to regenerate the exhausted resin. The rates of regeneration and recovery for the various regenerants were estimated and discussed. The resin used in this work, Dowex1X8-50, can exchange about 6.6 CN⁻ meq./g resin and 3.2 Cd²⁺ meq./g resin of cyanide and cadmium ions as complexes, respectively. Free cyanide ion has a lower selectivity than Cd-CN complexes on the anion exchange resin. The degree of treatment efficiency applied in this study was greater in the fluidized bed than packed bed. NaSCN was the best regenerant among regenerants used for regeneration of resin saturated with Cd-CN complexes.

Key words: Ion Exchange, Simultaneous Removal, Cadmium and Cyanide, Recovery

INTRODUCTION

Cyanide has been used to enhance the electroplating of metals [Horner, 1995; Lee and Hong, 1995], and to leach precious metals from ores [Herzorg, 1990]. In general, heavy metal-cyanide complexes can be formed under the high pH of wastewater. Since the presence of Cu-CN and Cd-CN complexes in water has presented a serious problem in several operations [Hsu et al., 1991], the removal and recovery of metal-cyanide complexes is very important not only for environmental protection but also because they are valuable materials.

The conventional method for eliminating cyanide ions from water is alkaline chlorination where cyanide can be totally oxidized to cyanate and then to CO_2 and N_2. But such oxidative processes using chloride, hydrogen peroxide and ozone can possibly create toxic gases (ClCN, CNO) and other chemicals (cyanate, chlorinated phenol) as by-products. Furthermore, these methods are ineffective for complexed cyanide because they cannot destroy metal complexes [Avery and Fries, 1975; Hassan et al., 1991; Bhakta et al., 1992]. The electrochemical process is another treatment method in which cyanide is destroyed while recovering metal [Zhou and Chin, 1993]. This method also requires relatively high energy costs to operate and large amount of chemicals. Cho et al. recently studied the treatment method using polysulfide at alkaline pH. Cyanide is transformed to thiocyanate by polysulfide and is precipitated. This method still presents a disposal problem of sludge waste containing toxic cyanide [Cho and Jeong, 1999]. Several other methods have been suggested in the literature for treating water containing cyanide ions. These include evaporation, reverse osmosis, electro dialysis, activated carbon adsorption, and ion exchange [Gupta, 1985; Goncalves et al., 1998; Park and Hahn, 1999; Yu and Kaewsam, 1999; Lee and Suh, 2000].

Ion exchange has been applied in heavy metal treatment because of the following advantages: 1) no secondary pollutant, 2) very compact facility, 3) easy recovery of metals, and 4) more versatile than other methods. One problem often cited, the disposal of regeneration solution, has been solved by combination with other methods [Goto and Goto, 1987; Short et al., 1997]. In particular, regeneration of the resin exhausted with metal-cyanide complexes requires vigorous conditions which destroy the complexes within the resin matrix before regeneration can take place [Avery and Fries, 1975]. Most studies on regeneration of this resin have been shown by a combination with the following processes: acidification, cation ion exchange, electrowinning, and gas permeable membrane [Goldblatt, 1956; Ritcey, 1989; Short et al., 1997; Kim et al., 1998; Lee et al., 1999; Noh et al., 1999].

In this work, simultaneous removal and recovery of cyanide cadmium ions using strong-base anion exchange resin was studied on the basis of formation of Cd-CN complexes at high pH in synthetic wastewater containing cyanide and cadmium ions [Horikawa and Hirasawa, 2000]. Ion exchange characteristics of Cd-CN complexes were studied experimentally in a batch reactor. Treatment efficiencies for packed and fluidized beds were compared in terms of the volume of the liquid treated per unit pressure drop. In addition, the rates of regeneration and recovery for the various regenerants, NaSCN, NaCN, and NaOH were estimated and discussed.

EXPERIMENTAL

1. Experiment and Analysis

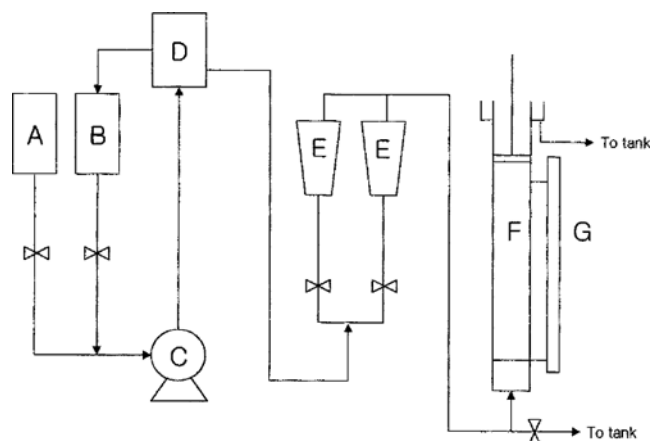Synthetic wastewater solutions were prepared by dissolving re-

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Table 1. Physical properties of Dowex1X8-50

Mean diameter [m]	3.64×10^{-4}
Density of resin [kg/m²]	1108.30
Moisture content [%]	43.00
Cross-linkage* [%]	8.00
Total capacity* [meq./g]	3.50
Capacity** [meq./g]	1.23-1.27
Distance of two functional group* [Å]	11.20

*given data.
**determined by experiment.

Fig. 1. Schematic diagram of the experimental apparatus.
A: Water tank, B: Solution tank, C: Pump, D: Head tank, E: Flow meter, F: Reactor, G: Piezometer tube

agent grade sodium cyanide and cadmium (II) nitrate in distilled water. The solution pH was adjusted to 12 to form optimum Cd-CN complexes using sodium hydroxide and an ionic strength adjustor (ISA). The ion exchange resin used in this work was a strong-base, gel type, Dowex1X8-50 (Dow Chem. Co.). The physical properties of Dowex1X8-50 are shown in Table 1.

Fig. 1 shows a schematic diagram of the experimental apparatus for the study of ion exchange in a liquid-solid semi-fluidized bed to remove simultaneously Cd^{2+} and CN^- from synthetic solution.

The ion exchange column for this study is made of an acrylic tube 20 mm in diameter and 600 mm in height. The column has a mobile upper retaining grid, which is made of a 60 mesh stainless steel net, and is also fixed in the column to adjust it as a fixed bed or a semi-fluidized bed.

2. Procedure of Exchange Experiment

A batch test was carried out at 25±0.5 °C using 1,000 mL conical flasks. Synthetic solutions, with molar ratios between cyanide and cadmium ions of 3, 4 and 5, were contacted with 1 g of resin. Samples were taken periodically and analyzed to obtain the concentration of ions in the solid and liquid phases.

For column tests, synthetic solutions were passed through the column, packed with about 20 g of the ion exchange resin. The effluent concentrations were monitored to obtain the breakthrough curve. In this work, the breakthrough time is defined as the time at $C_i/C_0=0.1$. The axial pressure profile along the column was measured by using pressure taps attached on the column wall. The tem-

perature of solutions was kept at 16±0.5 °C during experiments.

Regeneration tests were performed in a batch reactor which was kept in a thermostat at 25±0.5 °C. Resin particles, weighing 0.5 g, were contacted with synthetic solution to exhaust them in a shaking bath over 24 hours and rinsed with distilled water to prepare for regeneration experiments. The concentration of cadmium in the liquid phase was measured to obtain regeneration rate.
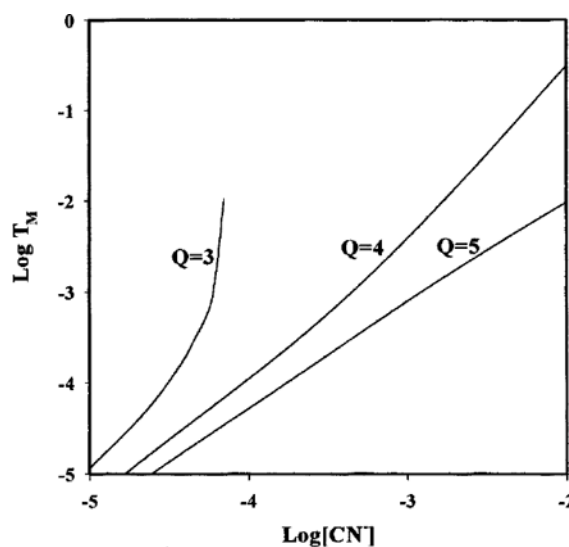
3. Analysis

A cyanide ion selective electrode (Orion 9606) was used for analysis of cyanide. The cyanide electrode did not respond to the total cyanide ions in the presence of cadmium ions because of stable Cd-CN complexes. Therefore, decomplexation was conducted using ethylene-diamine-tetra-acetic acid (EDTA). The concentration of cadmium ion was measured by ICP (Inductively Coupled Plasma Spectroscopy, Leeman 010-2106, U.S.A.).

RESULTS AND DISCUSSION

1. Speciation in Solution

Fig. 2 is cadmium-cyanide distribution diagram calculated by the formation constants. The relative amounts of various complexes were calculated by Gupta [1985]. Gupta studied the relative amounts of Cd-CN complexes formed in the aqueous solution for various molar ratio (Q) between cyanide and cadmium ions [Gupta, 1985].

Table 2 shows the compositions of cyanide for different Q values. In the case of a molar ratio of 4 (T_{CN}=7.69 mM, T_{Cd}=1.92 mM),

Fig. 2. Cadmium-cyanide distribution diagram.

Table 2. Theoretical composition of cyanide for different Q values in aqueous solution (Q=molar ratio between cyanide and cadmium ions)

Composition [%]	Free cyanide	$CdCN^+$	$Cd(CN)_2$	$Cd(CN)_3^-$	$Cd(CN)_4^{-2}$
Q=3	1.02	0.44	9.53	70.38	18.63
Q=4	8.44	0.01	0.01	27.84	63.70
Q=5	22.71	0.00	0.03	7.86	69.40

*$Cd(CN)_2$: Solid state.

about 92% of total cyanide is present in the form of $Cd(CN)_3^-$ and $Cd(CN)_4^{-2}$, and about 8% of total cyanide is present as free cyanide at pH 12. On the other hand, in the case of a molar ratio of 5 (T_{CN}= 9.60 mM, T_{Cd}=1.92 mM), the cadmium is present predominantly as $Cd(CN)_4^{-2}$, $Cd(CN)_3^-$ and about 23% of the total cyanide is present as free cyanide in solution. In the case of a molar ratio of 3 (T_{CN}= 5.76 mM, T_{Cd}=1.92 mM), because the stability constant of OH^- is greater than that of CN^- at pH 12, cadmium ion is precipitated as $Cd(OH)_2$ [Kim et al., 1986].

2. Ion Exchange Characteristics of Cd-CN Complexes

Figs. 3, 4 and 5 are the decay curves for cyanide and cadmium ions in a batch reactor for molar ratios of 3, 4 and 5. These figures show that the decay curves are similar in shape in all cases even though the equilibrium values are different. In the case of molar ratio of 4, cyanide and cadmium ions are removed as Cd-CN complexes. For a molar ratio of 3, cyanide and cadmium ions are re-
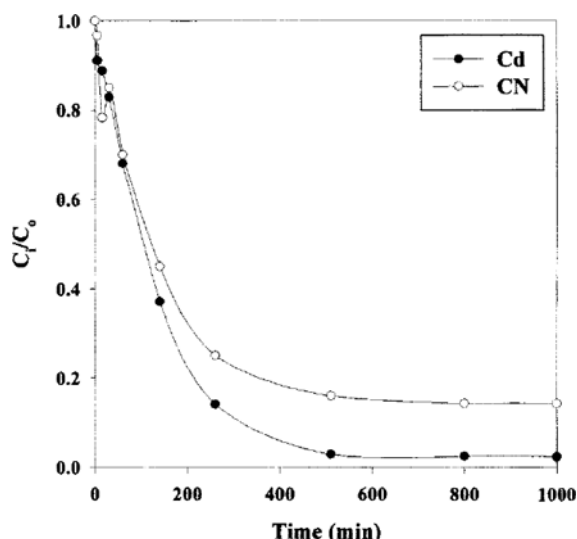

Fig. 3. Decay curves of cyanide and cadmium ions in a batch reactor (Q=3, T_{CN}=5.76 mM, T_{Cd}=1.92 mM).
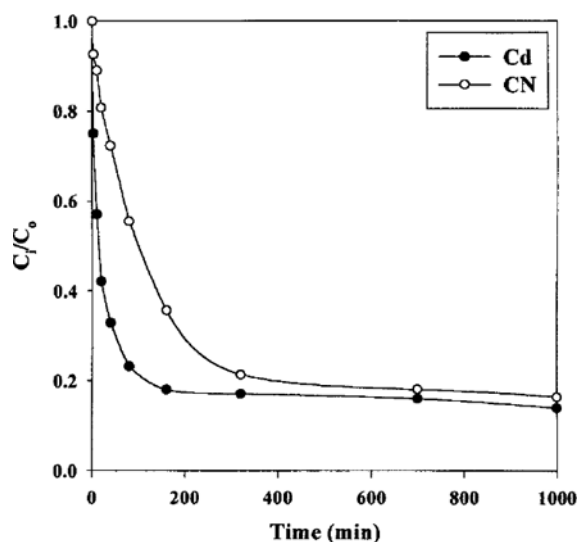

Fig. 4. Decay curves of cyanide and cadmium ions in a batch reactor (Q=4, T_{CN}=7.69 mM, T_{Cd}=1.92 mM).
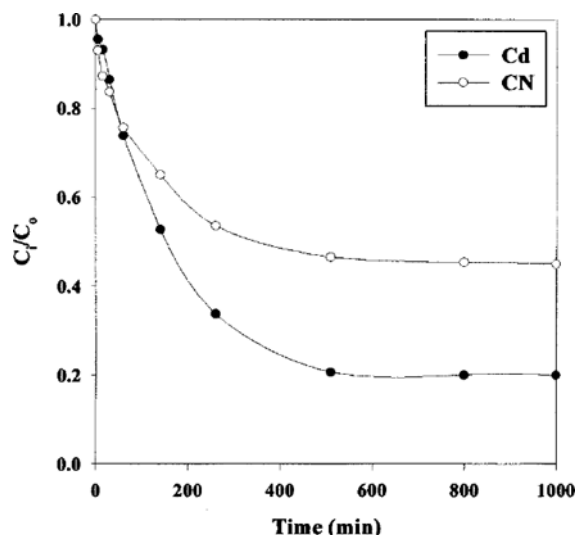
Fig. 5. Decay curves of cyanide and cadmium ions in a batch reactor (Q=5, T_{CN}=9.60 mM, T_{Cd}=1.92 mM).

moved by ion exchange and precipitation, $Cd(OH)_2$. In this case, it is observed that the removed amount of cadmium is much greater than the equilibrium amount of cadmium, even though the removed amount of cyanide is the same as the molar ratio of 4. The decay curves of cyanide at molar ratio of 5 reach equilibrium at 50 percent of inlet concentration, even though the decay curves of cadmium are similar to decay curves of other molar ratios. This could be explained by the fact that free cyanide ion, 23% of total cyanide, is not totally removed by resin at molar ratio of 5. An ion-exchanged Cd-CN molecule on a site will interfere with the ion exchange reaction of other comparable size ions on the neighboring sites. Thus, one molecule of a Cd-CN species may occupy other nearby protonated sites. In turn, free cyanide ion has a lower selectivity on the anion resin than Cd-CN complexes.

Resin used in this experiment, Dowex1X8-50, can exchange about 1.98 CN^- meq./g resin 0 meq./g resin of free cyanide and cadmium in free cyanide ions or cadmium ions solutions, respectively. On the other hand, the resin can exchange approximately 6.6 CN^- meq./g resin and 3.2 Cd^{2+} meq./g resin of cyanide and cadmium ion as complexes, respectively. The Cd-CN complexes enhanced to the ion exchange capacities of free cyanide and cadmium ion.

3. Breakthrough Curves for Various Beds

Fig. 6 shows the breakthrough curves of cyanide that is removed as Cd-CN complexes for the respective beds.

The static height of resin charged in each operating column is 137±1 mm. In the case of the fluidized bed operation, the total bed height is about 260 mm when the fluidization reaches steady state. For the semi-fluidized bed operations, a retaining grid was positioned at 226 mm height in the column. The minimum fluidizing velocity (U_{mf}), determined experimentally, for resin particles of 0.36 mm mean diameter in swollen state, was 0.71 mm/sec. For semi-fluidized bed experiments, liquid velocity of 7.77 U_{mf} was used to obtain typical upper packed and lower fluidized sections. At steady state, the height of the upper packed bed section in the semi-fluidized bed was about 33% of total bed height, and the lower section was in a fluidized state.
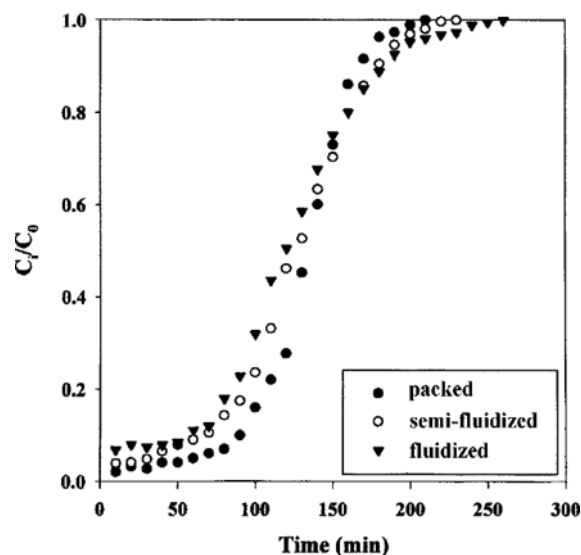
Fig. 6. Breakthrough curves of cyanide in the packed, semi-fluidized, and fluidized beds (U=1.71 ml/s, Q=4, T_{CN}=7.69 mM, T_{Cd}=1.92 mM).

Fig. 7. Breakthrough curves of cyanide in cadmium ions in a semi-fluidized bed (U=1.22 ml/s, Q=4, T_{CN}=7.69 mM, T_{Cd}=1.92 mM).

It is seen that the breakthrough curve obtained from the semi-fluidized bed lies between those obtained from the packed and fluidized bed, since the semi-fluidized bed possesses the features of both the fluidized and packed beds. Fig. 6 also shows that the shape of the breakthrough curve for the packed bed is steeper than for the fluidized bed, since mass transfer in axial direction in a packed bed has more predominant effect than that of radial direction. On the other hand, since the fluidized bed has a wider adsorption zone than that of packed bed and mass transfer in radial direction is substantial, the breakthrough curve in the fluidized bed is smoother than the other curves.

Fig. 7 shows the breakthrough curves of cyanide and cadmium ions in a semi-fluidized bed for molar ratio of 4. The synthetic solution used in this experiment has 8.44% of free cyanide and 91.5% as $Cd(CN)_3^-$ and $Cd(CN)_4^{2-}$. It is shown that the exit concentration of cyanide was higher than that of cadmium during the ion exchange operation due to the free cyanide ion which has lower selectivity on anion exchange resin of this work.

Treatment efficiencies in terms of the volume of the liquid treated (ΔV) per unit pressure drop for various conditions are compared in Table 3.
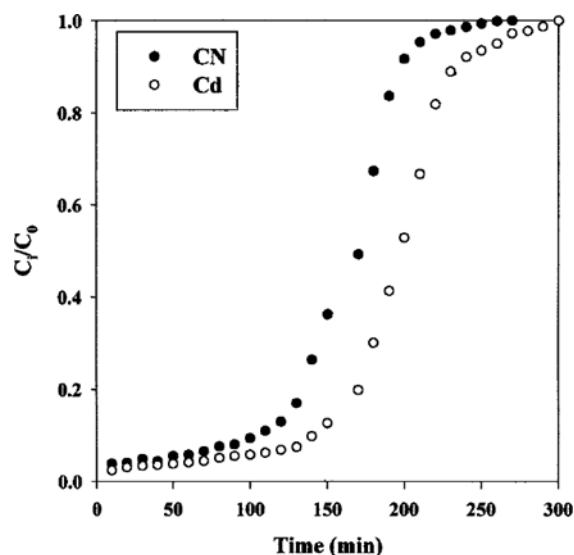
The liquid volume treated is calculated by (breakthrough time)× (liquid volumetric flow rate). In Table 3, the breakthrough time decreases as the bed type is changed from packed to fluidized beds, but the treatment efficiency increases. This result is natural, since the packed bed operation has the highest pressure drop among the three reactor types. For a semi-fluidized bed, we indicate that the lower the height of the packed bed section, the faster the breakthrough time is and the higher the efficiency for the same liquid velocity. This could be explained from the fact that the features of the fluidized bed increase as the packed bed section is decreased. At high velocity, the effluent concentration in the fluidized bed rapidly exceeds the breakthrough concentration due to back mixing of liquid.

4. Results of Regeneration Test

Table 4 shows the result of batch tests for various regenerants.

Regeneration of resin saturated as Cd-CN complexes with NaOH is found to be poor among the three regenerants, although NaOH is commonly used as regenerant for anion exchange resin. These results indicate that Cd-CN complexes have very strong affinity to the strong base resin. Table 4 also shows NaSCN and NaCN are good regenerants. It is reasoned that the resin saturated as Cd-CN complexes has a much higher affinity for the thiocyanate ion as com-

Table 3. Comparison of the treatment efficiency for various conditions

Run	H_s (m)	H_t (m)	U $(m^3/s)\times10^6$	Packed bed section (%)	T_b (min)	ΔV $(m^3)\times10^3$	$-\Delta P/L$	$\eta\times10^3$ (m^3)
PB	0.137	0.137	1.71	100	85	8.72	1.51	5.78
PB	0.136	0.136	2.28	100	43	5.88	1.87	3.15
SFB	0.136	0.226	1.71	33.24	72	7.39	1.25	5.91
SFB	0.136	0.226	2.28	41.79	40	5.47	1.30	4.21
SFB	0.136	0.184	1.71	56.10	85	8.72	1.40	6.23
FB	0.136	0.260	1.71	0.00	55	5.64	0.04	148.50
FB	0.136	0.329	2.28	0.00	30	4.10	0.03	164.16

PB: Packed bed, SFB: Semi-fluidized bed, FB: Fluidized bed, H_s: Height of initial static bed, H_t: Height of overall bed, T_b: Breakthrough time, ΔP: Bed pressure drop [m H_2O], $-\Delta P/L$: Pressure drop per unit depth [-], η: Treatment efficiency [=ΔV/(−ΔP/L)]

Table 4. Regeneration rate in batch reactors for various regenerants

Regenerants	Cadmium loaded [mg]	Cadmium regenerated [mg]	Regeneration rate [%]
NaOH	176.0	107	60.79
NaCN	174.3	127	72.86
NaSCN	171.9	152	88.42

pared with the chloride and hydroxide ions. In other words, thiocyanate has the largest polarizability. We also regenerate the resin, which was saturated as SCN^- (CN^-) or with NaSCN (NaCN) using high concentration of NaCl.

CONCLUSIONS

The basic ion exchange characteristics of Cd-CN complexes were studied experimentally in batch and column reactors. Free cyanide ion has a lower selectivity than Cd-CN complexes on the anion exchange resin. This could be explained by the size, ion pairing and site competition of complexes. The resin used in this work, Dowex1X8-50, can exchange about 6.6 CN^- meq./g resin and 3.2 Cd^{2+} meq./g resin of cyanide and cadmium ions as complexes, respectively. The degree of treatment efficiency applied in this study was greater in fluidized bed than that of packed bed. NaSCN showed the best regeneration rate for the regeneration of resin saturated with Cd-CN complexes.

ACKNOWLEDGMENT

NOMENCLATURE

C_0	: inlet concentration of reactant [mg/l]
C_i	: effluent concentration of reactant [mg/l]
H_t	: height of initial static bed [m]
mM	: molar concentration [mg-mole/l]
T_b	: breakthrough time [min]
T_{Cd}	: total cadmium concentration [mg-mole/l]
T_{CN}	: total cyanide concentration [mg-mole/l]
U	: superstitial fluid velocity in axial direction [mm/s]
U_{mf}	: minimum fluidizing velocity [mm/s]

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