$\infty$ = boundary $\infty$

**Superscripts**

$*$ = constant value at fog boundary
$'$ = $d/dT$
$''$ = $d^2/dT^2$

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# Behavior of Countercurrent Liquid-Liquid Columns with a Liquid Metal

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**Packed columns are being considered for contacting liquid metals with molten salts to extract fission products from spent nuclear fuel. Extraction rates between a liquid cadmium alloy and a liquid chloride salt were measured at 530°C. in a prototype column. With a system of water and a low melting metal alloy, measurements of the pressure drop, limiting flow rates, and hold-up were made and compared with the predictions of existing correlations. These data indicate that packed columns might be effective contacting devices for pyrochemical processes.**

Countercurrent extraction columns are being studied as a means of contacting liquid metals and liquid salts in pyrochemical processes (*1*) to recover spent nuclear fuel from fast breeder reactors. Metals and salts in the range of 500 to 800°C. are used as the solvents for uranium and plutonium. The metals used are alloys of magnesium with zinc, copper, or cadmium, and the usual salts are mixtures of the chlorides of magnesium, calcium, and alkali metals. The rare earth fission product elements can be separated from uranium and plutonium by oxidation-reduction reactions with magnesium between the salt and metal phases, as the rare earths distribute more strongly to the salt phase than uranium and plutonium (*2*).

TABLE 1. SELECTED LIQUID METAL AND SALT PROPERTIES

(at 600°C.)

| Liquid metals | Density, g./cc. | Viscosity, cp. | Surface tension, dynes/cm. |
|---|---|---|---|
| Bi | 9.66 | 1.5 | 350 |
| Cd | 7.72 | 1.5 | 590 |
| Mg (660°C.) | 1.57 | 1.2 | 570 |
| Zn | 6.80 | 2.2 | 770 |
| Cd-6 wt. % Mg-2 Zn | 6.3* | 1.5* | 590* |
| Cu-33 wt. % Mg | 4.0 (*6*) | 3 (*6*) | 800* |
| Wood's metal (100°C.) (Bi-25 wt. % Pb-13 Cd-12 Sn) | 9.66 (*6*) | 3.4 (*6*) | 500* |
| Liquid salt | | | |
| $MgCl_2$–20 wt. % NaCl-20 KCl | 1.76 | 1.7 | 87 |

* Estimated

Future fuel recovery processes for fast breeder reactors will be required to recover at least 99% of the plutonium and more than 90% of the uranium with an overall decontamination factor from 100 to 10,000 for fission products. Larger fission product decontamination factors will not significantly reduce the radioactivity of the recovered fuel because of the buildup of short-lived uranium and plutonium isotopes in recycled fuel.

A conceptual pyrochemical reprocessing plant serving several power reactors with a total thermal power of the order of 20,000 MW would receive about 200 kg./day of core fuel having an average burnup of 100,000 MW-days/tonne and containing 20 wt. % plutonium and about 500 kg./day of blanket fuel (*3*). The plutonium-rare earth partition column would have four to eight theoretical stages and would be roughly 2 to 5 in. in diameter.

## PREVIOUS STUDIES

The technology (*4*, *5*) of liquid-liquid extractions columns is based primarily on investigations with aqueous-organic

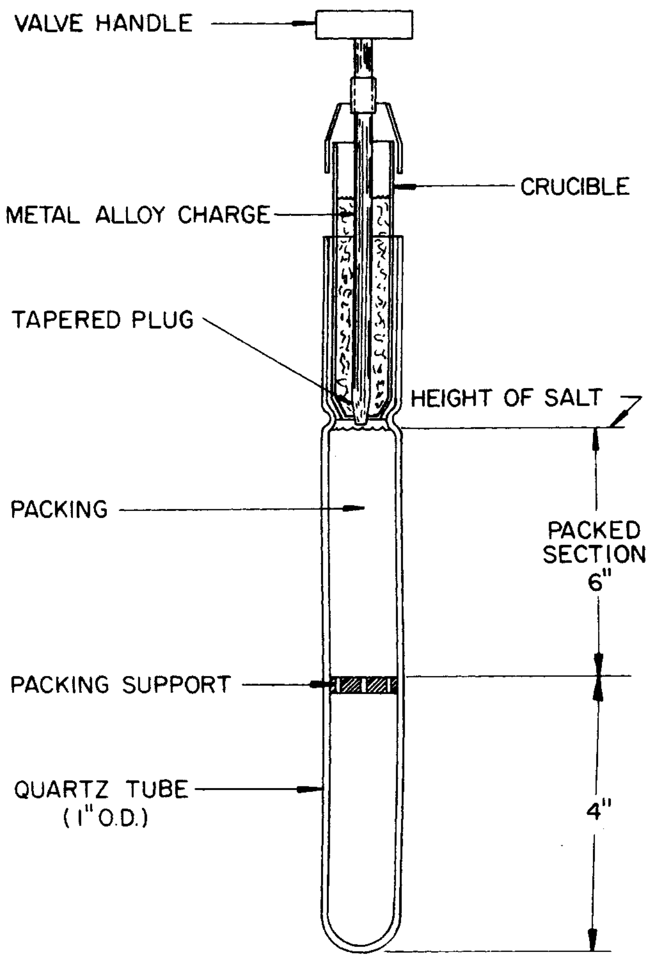

**Fig. 1. Apparatus for transient extraction experiments.**

systems having densities from 0.7 to 1.6 g./cc., viscosities from 0.5 to 40 cp., and interfacial tensions from 7 to 50 dynes/cm. These physical properties do not include those of all the metal-salt systems (Table 1) that are of interest to pyrochemical processes.

There are a few published studies of extraction kinetics between liquid metals and liquid salts. Katz, Hill, and Speirs (*7*) measured the kinetics of samarium extraction from a single drop of bismuth falling through a static column of chloride salt. They concluded that the extraction rate was controlled by mass transfer within the metal drop. With the bismuth metal-chloride salt system in a countercurrent column, Hill and Kukacka (*8*) found overall mass transfer coefficients based on the salt phase of 0.0003 to 0.003 sec.$^{-1}$ in a 3-in. I.D. disk-and-doughnut column and about 0.0047 sec.$^{-1}$ in a 2-in. I.D. column packed with spheres. Olander (*9*) concluded that the extraction rate of zinc from single metal drops falling through chloride salt mixtures was controlled by the salt phase. Burkhart and his students (*10, 11*) at Iowa State University studied extraction rates between bismuth-lead alloys and low melting chloride salts in mechanically agitated columns. Extraction rates in simple packed columns were thought to be low because large metal drops would be stable and would fall rapidly through unagitated columns.

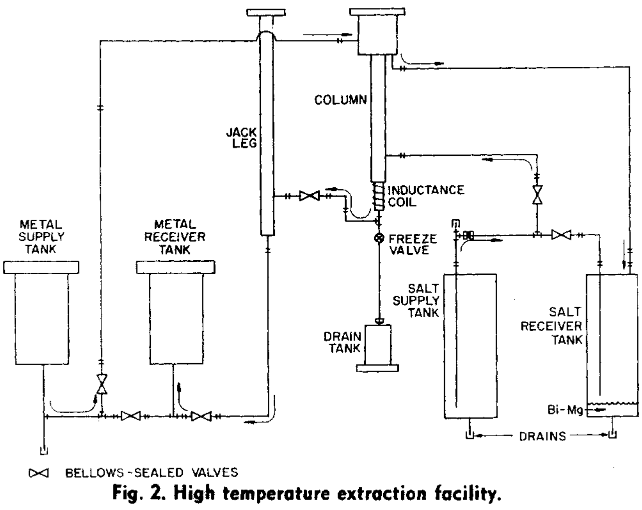

**Fig. 2. High temperature extraction facility.**

## MASS TRANSFER RATES

An estimate of the mass transfer coefficient in a metal-salt system was obtained by dropping liquid metal into a static column of salt contained in a quartz tube (Figure 1). The central 6 in. of tube was packed with ¼-in. tantalum Raschig rings and the tube filled to the top of the packing with molten salt ($MgCl_2$-20 wt. % NaCl-20 KCl). A crucible placed over the packing was filled with a cadmium-magnesium alloy in which the distributing solute (uranium or cerium) was dissolved. The flow of metal was controlled by a valve in the bottom of the crucible. The dispersed metal phase did not appear to wet the packing. When the supply of metal was exhausted, the fluids were frozen rapidly by plunging the tube into a bath of low-melting liquid metal. The phases were separated and analyzed for the solute element. Equilibrium concentrations of the distributing solute were determined in separate experiments.

Estimates of the mass transfer coefficient shown in Table 2 were obtained by assuming that the change of solute concentration in the metal phase was negligible, that the salt phase did not move up the column significantly, that the equilibrium metal holdup in the packing was reached in a time that was short compared to the total time of metal flow, and that transfer took place only in the packed section. With these assumptions, the mass transfer coefficients based on the salt phase are given by

$$(k_s a) = \left(\frac{1}{T}\right) \ln \frac{1}{\left[1 - \frac{y(T)}{y^*}\right]} \qquad (1)$$

### High-Temperature Apparatus

A high temperature facility was built and operated to obtain extraction rate data with columns operating at steady state. The equipment, shown schematically in Figure 2, was made of 304 stainless steel and was resistance heated. The column was a 3-ft.-long, 1-in. pipe that was packed with ¼-in. Raschig rings except for the bottom 3 in. The column had a 3 in. I.D. top disengaging section that contained weirs to

TABLE 2. TRANSIENT EXTRACTION RATES FROM CADMIUM ALLOY TO A CHLORIDE SALT

Nominal compositions:
Metal: Cd-4 wt. % Mg
Salt: $MgCl_2$-20 wt. % NaCl-20 KCl

| Distrib. solute | Initial conc. wt. % | Temp., °C. | Column height, in. | Contact time, sec. | % Equilib. | Mass transfer coefficient $k_s a$, sec.$^{-1}$ |
|---|---|---|---|---|---|---|
| U | 0.240 | 490 | 6 | <300 | 76 | >0.005 |
| U | 0.244 | 610 | 6 | 60 | 36 | 0.0074 |
| U | 0.206 | 560 | 6 | 110 | 58 | 0.0079 |
| Ce | 0.45 | 620 | 6 | 40 | 30 | 0.008 |

Table 3. Operating Conditions and Results for High Temperature Counter-Current Extraction Experiments

Column length: 33 in.
Column temperature: 520°-530°C.
Cerium distribution coefficient: 1.13 wt. % Ce in salt/wt. % Ce in metal

| | Run numbers 3 | 4 | 6 |
|---|---|---|---|
| Inlet compositions (wt. %) | | | |
| Metal: Ce (Cd-6.9% Mg-2.6 Zn) | 0.65 | 0.595 | 0.818 |
| Salt: Ce ($MgCl_2$-19% NaCl-19 KCl) | <0.001 | 0.002 | 0.006 |
| Flow rates (g./min.) | | | |
| Metal | 220 | 1080 | 788 |
| Salt | 693 | 181 | 672 |
| Results | | | |
| Operating time (min.) | 45 | 32 | 20 |
| Extraction rate (Ce g./min.) | 0.76 | 1.2 | 2.7 |
| *HETS* (in.) | 47 | 15 | 41 |
| *HTU* (in.) | 27 | 38 | 44 |

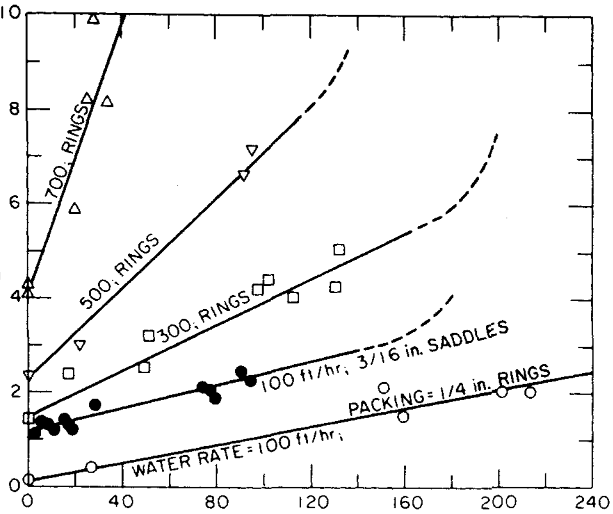

**Fig. 3. Pressure drop in metal-water column (1 in. I.D., 26 in. long); packings: 1/4-in. Raschig rings (open symbols); 3/16-in. saddles (closed symbols).**

maintain the salt level in the column and to separate the metal feed from the effluent salt. The temperatures of the metal entering and of the salt leaving the column were measured by thermocouples immersed in these phases. The temperature of the packed section of the column was measured by thermocouples in contact with the outside of the column.

## EXPERIMENTAL TECHNIQUES

To begin an experiment, liquid metal (the discontinuous phase) was sprayed into the column above the packing by applying gas pressure to the metal supply tank. The metal flowed by gravity through the column and jack leg and into the metal receiver tank. When the metal interface had been established at the bottom of the column, salt was pushed by gas pressure from the salt supply tank, through the column, and into the salt receiver tank. The salt-metal interface was maintained below the column in a section of ½-in. O.D. tubing. The position of the interface was determined by a mutual inductance coil (*12*) and controlled by gas pressure in the adjacent jack leg. The amount of solute (cerium) transferred into the salt was determined by taking filtered samples (*13*) of the liquids entering and leaving the column. Liquid flow rates were calculated from the rate of change of the liquid levels in the supply and receiver tanks. Liquid levels in the metal tanks were determined by mutual-inductance (*12*) and resistance probes and in the salt tanks by time-delay reflectometer and resistance probes.

To prepare for the next experiment, the cerium that had been extracted into the salt was removed by contacting the salt with Bi-6 wt. % Mg alloy in the salt receiver tank. Additional cerium was dissolved in the liquid metal, and the solutions were pushed by gas pressure from the receiver tanks into their supply tanks.

The extraction rates from three experiments are summarized in Table 3. The calculation of the number of transfer units was based on metal phase concentrations. In each experiment, the overall cerium material balance was better than ± 5% and was within the precision of the chemical analyses. The accuracy of the cerium extraction rates was 10%, but the accuracy of determining the number of transfer units was only 30%, with the largest error being in the cerium distribution coefficient in the column. After two runs, the total entrainment of the cadmium metal solvent with the effluent salt was less than .01 g. Cd/kg. salt.

The measured mass transfer rates were in a range that would make packed columns practical for contacting liquid metals and salts, but larger rates are expected in process columns with improved designs. In run 6, the flow rates were very near the estimated limiting flow condition. The data were insufficient to make any conclusions about the effect of flow rates. As only one column length and type of packing were tested, effects of the entrance regions, column length, and packing could not be determined.

### Low-Temperature Apparatus

To supplement the high temperature work, the hydraulic behavior of a packed column was studied using Wood's metal (Bi-25 w/o Pb-13 Cd-12 Sn) as the dispersed phase and water as the continuous phase. The liquid metal did not wet the column packing. The low temperature column resembled the high temperature facility and was operated in a similar manner. The glass column was contained in a glass enclosure maintained between 85° and 90°C. The top and bottom disengaging sections were of a larger diameter than the column, and the packing extended into these sections.

## PRESSURE DROP

The pressure drop in the low temperature column was determined with a manometer of which one leg was the column and the other leg a small glass tube in which the aqueous phase was static. The pressure drop through the column was the pressure required to equalize the liquid levels in both legs of the manometer. Kinetic energy effects were negligible, and a correction was made for the pressure drop in the expanded disengaging sections and across the packing restrainers.

Typical data from columns packed with ¼-in. Raschig rings or 3/16-in. saddles are shown in Figure 3. These data were correlated by modifying Ergun's (*14*) equation for the flow of a single fluid through porous beds. The form, similar to one suggested by Fan (*15*), is:

$$\frac{\Delta P g_c}{L} = \alpha\, \mu_c\, A \left(\frac{A}{\epsilon^3}\right) u_c + \beta\, \rho_c \left(\frac{A}{\epsilon^3}\right) (u_c)^2 \quad (2)$$

The pressure drop data were fitted with Equation (2) by setting $\alpha$ and $\beta$ equal to 4.16 and 0.292, respectively (i.e., the values determined by Ergun) and by using $A$ and $A/\epsilon^3$ as the adjustable parameters. The effect of the dis-

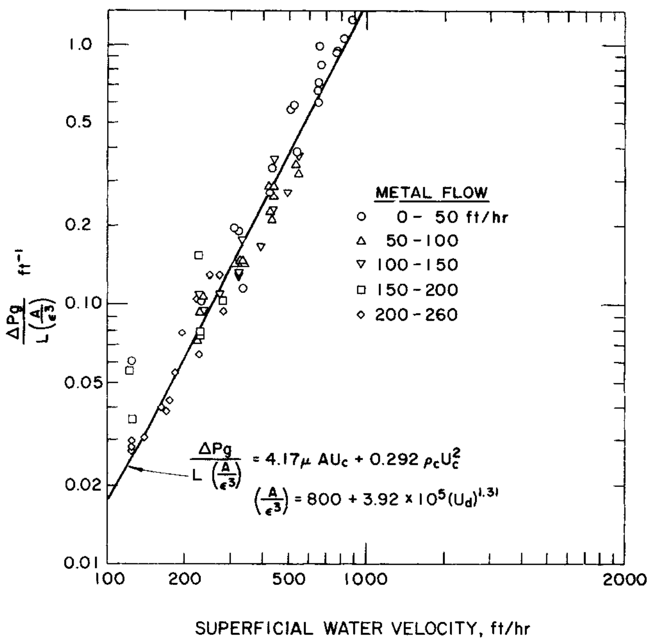

**Fig. 4. Pressure drop correlation for metal-water column; packing: 1/4-in. Raschig rings.**

continuous phase could be accounted for by assuming that the column void fraction decreased while the specific surface area of the packing remained constant. Over the stable operating range, $A/\epsilon^3$ was independent of water rate and could be expressed as a function of metal rate by

$$(A/\epsilon^3) = (A/\epsilon_0{}^3) + \gamma(u_d)^{1.3} \tag{3}$$

The constant $\gamma$ was a function of the packing and presumably of the properties of the fluids although this was not determined. At the higher water rates near the flooding point, $(A/\epsilon^3)$ increased rapidly.

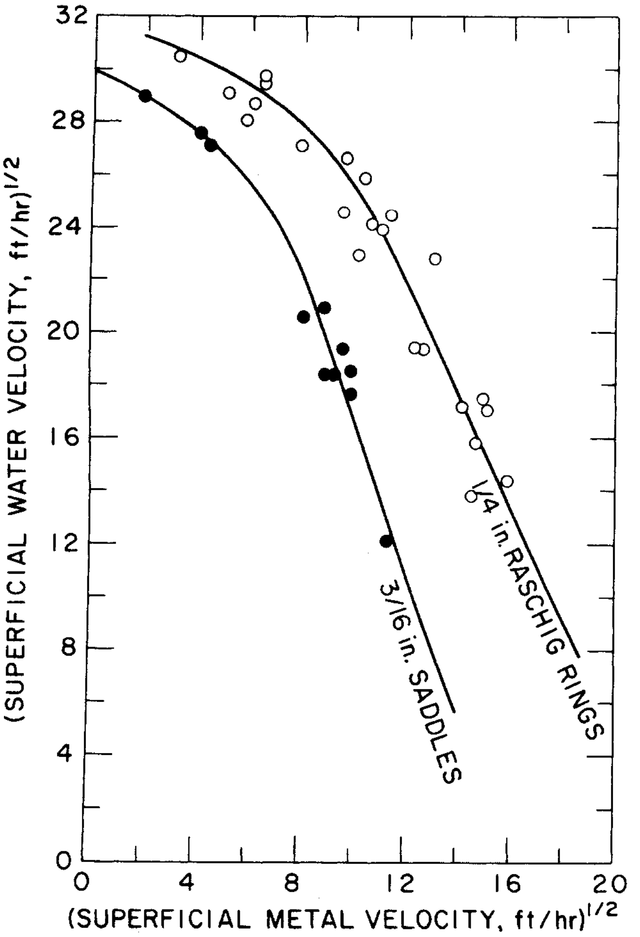

**Fig. 5. Limiting flows in metal-water column (1 in. I.D., 26 in. long)**

The correlation of data for ¼-in. Raschig rings is shown in Figure 4 where $A = 160$ ft$^{-1}$ and $\epsilon_0 = 0.558$. This experimentally determined void fraction at zero metal flow was lower than the actual total void fraction (0.94) of the packed column because the internal voids of the packing did not carry the full fluid flow. The specific surface was approximately equal to the surface area of solid cylinders with the same overall dimensions as the Raschig rings.

## FLOODING

Limiting flows were determined in the low temperature column by observing the metal holdup in the column and the pressure drop across the column as the water rate was increased incrementally and the metal rate was fixed. The flooding point was defined as the point when the metal holdup began to increase and the pressure drop tended to become unstable. The data for two types of packing are shown in Figure 5, and in Figure 6 the data for the ¼-in. rings are compared with predictions of published flooding correlations (*16–20*). None represented the data adequately, although the expressions of Dell and Pratt (*16*) and of Sakiadis and Johnson (*20*) predicted the slope at the lower water rates. Values of the surface area and void fraction of the packing determined from the column pressure drop were used to calculate the four predicted lines in Figure 6. Dell's correlation was modified by deleting the interfacial tension effect, as its statistical significance seemed low. This modification and the use of his recommended value of $A/\epsilon^3$ for the metal Raschig rings gave an improvement in the fit, as shown in Figure 6.

It was thought that at high water rates, the limiting flows deviated from the usual straight line relationship because of turbulence in the discontinuous phase. In a study of single liquid drops falling through a stationary water column, Hu and Kintner (*21*) found that, above a critical Reynolds number (3,000 for Wood's metal drops), the drag coefficient of a fluid drop increased above that for a solid sphere, and distortion caused by motion within the drops became evident. The local Reynolds number of a metal drop in the column was estimated to be 2,500 in the region of curvature of the flooding lines. This value is ap-

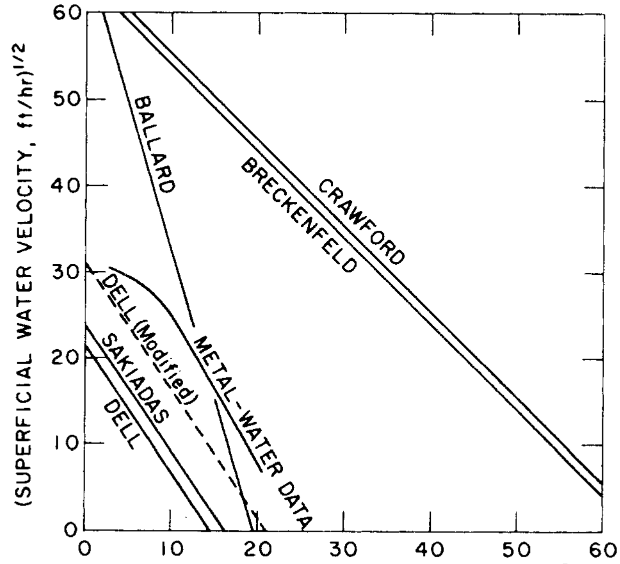

**Fig. 6. Predictions of limiting flows for metal-water column.**

proximately equal to the critical Reynolds number for a single drop considering the uncertainties involved in the calculation.

## HOLDUP

The amount of metal in the column at any given time was determined by simultaneously stopping the flow of metal to the column and passing cold instead of hot water through the column. The column was then disassembled and the frozen metal separated from the column and the packing. Although the metal droplets tended to coalesce after the cold water flow was started, this method gave an accurate (within ± 5%) value of the total discontinuous phase holdup at steady state.

The amount of metal in the column packed with 3/16-in. saddles ranged from 15 to 35% of the total void fraction; packed with ¼-in. Raschig rings, it was 10 to 25%. This range is above that predicted by published correlations (*22, 23*). After an initial increase in metal content at very low metal flow rates, the holdup increased slowly with metal flow rate. It was nearly independent of water flow rate until the limiting flows were approached.

Motion pictures taken of the column showed that the metal collected at specific locations (usually at the larger voids) and formed pools. When the pools reached a critical size, small droplets were expelled and fell rapidly to pools below. The pools vibrated when struck by a falling droplet, ultimately causing the pool to break up. A residual amount of metal usually remained after the pool had dispersed. The falling droplets did not pass through the column more than a few inches. In ordinary systems, coalescence and degradation of drops are rather slow processes once the drops have reached a size corresponding to the open passages in the packing. The high frequency of the coalescence and degradation of metal drops and the vibration of the metal pools may enhance the mass transfer rate in a metal-salt contactor.

## CONCLUSIONS

For packed columns with a liquid metal flowing countercurrent to a lighter continuous phase, pressure drops can be estimated by an Ergun-type equation and limiting flows by a modified Dell and Pratt's correlation. The holdup of the discontinuous phase appeared to be higher than predicted, and coalescence and degradation of the dispersed phase seemed to be relatively more important than in ordinary systems. The flow patterns within the dispersed phase may be influenced by vibrations induced by the energetic coalescence process and, at some flow conditions, by turbulence. Although additional data are necessary, studies to date show that packed columns can be used in pyrochemical processes for nuclear fuel recovery. Presumably packed columns will be useful for liquid metal contacting in other processes, such as metal purification.

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## NOTATION

$A$ = surface area of packing per unit superficial column volume (sq.ft./cu.ft.)
$g_c$ = 32.2 $(\text{lb.}_m)(\text{ft.})/(\text{lb.}_f)(\text{sec.})^2$
$HETS$ = height equivalent to a theoretical stage (in.)
$HTU$ = height of a transfer unit (in.)
$k_s a$ = overall mass transfer coefficient based on salt phase $(\text{sec.}^{-1})$
$L$ = length of packed column
$\Delta P$ = pressure drop in aqueous phase $(\text{lb.}_f/\text{sq.ft.})$
$T$ = total time of metal flow in transient column (sec.)
$u$ = superficial velocity in packed section (ft./sec.)
$y$ = solute concentration in salt phase (wt. frac.)
$y^*$ = solute concentration in salt in equilibrium with metal phase

### Greek Letters

$\alpha$, $\beta$, $\gamma$ = constants
$\epsilon$ = void fraction of packing
$\mu$ = viscosity $(\text{lb.}_m)/(\text{ft.})(\text{sec.})$
$\rho$ = density (lb./cu.ft.)

### Subscripts

$c$ = continuous phase
$d$ = discontinuous phase
0 = zero metal flow rate

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