Extraction of Uranyl nitrate in Perforated-plate Towers of Alternative Flow Type

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Uranyl nitrate was extracted with T. B. P. (tri-butyl phosphate)–kerosene as a mixed solvent from its nitric acid solution, in alternative flow type perforated-plate extraction towers. The effects of the operating conditions on the tower performance were studied and then the results obtained here were compared with those of other experiments undertaken using pulse columns. It was found that these towers of alternative flow type might probably be used successfully for the industrial purpose.

1. Introduction

The most important problems in developing the atomic energy industry are the production of uranium as the fuel and the reprocessing of irradiated fuels. Up to now, in order to solve these problems, many production methods and treating operations have been developed, and the solvent extraction mothod is now appriciated as one of the most useful operations. In early days, packed tower, ordinary perforated-plate tower, mixer- and settler-type extractor and pulse column were emyloyed in this operation, and though nowadays the latter two[6)9)7)2)] have been preferably used, the developments of more effective equipment are strongly desired.

In this point of view, one of the authors contrived and designed the perforated-plate tower of alternative flow type[8)], and found it to have some excellent points, by the extracting experiments for benzene (HOAc)-water and methylisobutyl ketone (HOAc)-water systems. Accordingly, this experiment was carried out to make sure whether the tower was suited for the solvent extraction of uranium or not.

2. Experimental

a) **Apparatus:—** The towers used in this study were circular in cross section and the essential dimensions are shown in Fig. 1 and Table 1. The walls were made of glass and the plates were of stainless steel (SUS 27) of 1 mm. thick with resin lining on one side in order to prevent from being wetted by the dispersed phase. The flow sheet of this apparatus is identical with that of the previous werk[8)] and it is not shown here. Of course, in alternative flow type tower, the light phase and heavy phase flow through the column alternatively. i. e., during one phase is flowing, another phase cesses to flow. For the most runs in this study, the time flowing in one cycle for each phase, were 4 seconds and the rest time at each flow reverse was taken as 1 second. Therefore one cycle required 10 seconds ($=4+1+4+1$). Here, we call the phase "continuous" with which the tower is filled before the start of the run.

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Table 1. Plates used.

	plate 1	plate 2
d_0 (cm)	0.10	0.18
n	180	55
% of free area	7.9	7.9

The flow rate was determined by mess-cylinder and stop-wtch. Flow rates were between $4.3 \sim 57.3$ m³/m²hr. Sampling was made 3 or 6 minutes after the run started, but in the case where the flow was very slow, it was made 10 minutes after the start.

b) Materials used:— The uranyl nitrate used was a commercial product of E. P. grade. Uranyl nitrate was dissolved into 2N nitric acid aqueous solution. The concentration of uranyl nitrate solution used here as the feed to the tower, was 0.5 g nitrate in one litre of solution at 25°C. As the solvent, 20 parts of T.B.P. was mixed with 80 parts of commercial kerosene by volume.

c) Determination of equilibria:— Several reports[1)4)5)] on the distribution coefficients of uranyl nitrate between water phase and T.B.P. phase, have been published. But materials or conditions employed by them are somewhat different from those used in the present work. Therefore, we determined these coefficients for ourselves.

The analysis of uranium was made by the Acid Poroxide Method[3)] using E.P.U. Type 2. photoelectric spectrometer made by Hitachi Co..

Namely, the uranium in aqueous solution was diluted with water to a suitable concentration and pH. of which was arranged to be 4.5 with buffer solution (mixture acetic acid 1 mole and sodium acetate 1 mole, pH.=4.5). Prepared aqueous solution thus was analysed by the above mentioned method. The uranium in organic solvent was extracted with water. Then uranium that was taken into water, was
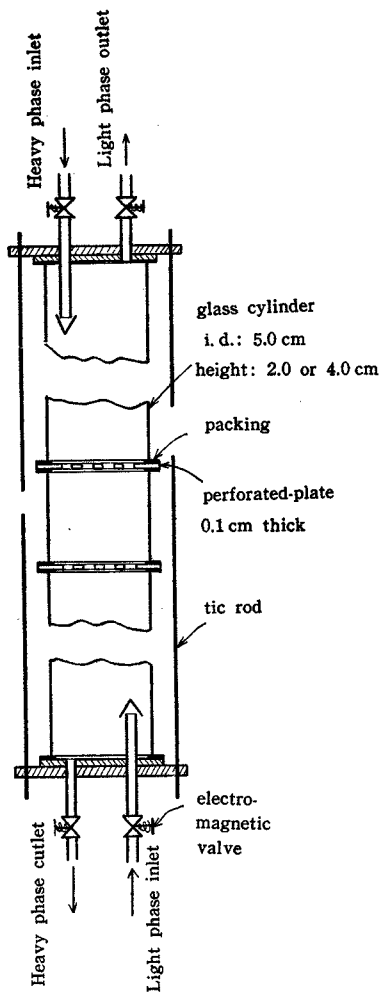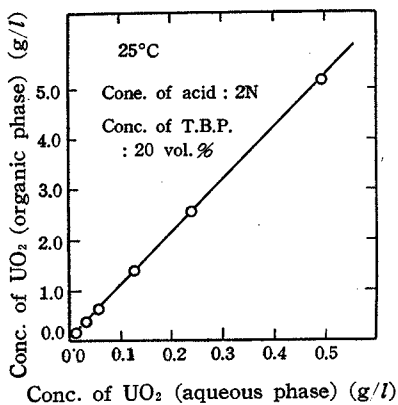

Fig. 1. Tower

glass cylinder
i. d.: 5.0 cm
height: 2.0 or 4.0 cm

packing

perforated-plate
0.1 cm thick

tic rod

electro-
magnetic
valve

Fig. 2. Equilibrium data

25°C
Conc. of acid : 2N
Conc. of T.B.P.
: 20 vol.%

Conc. of UO₂ (aqueous phase) (g/l)

analysed quite as same the method as employed in the case of water phase analysis. Fig. 2 shows the solubility equilibrium, and Fig. 3~5 shows the effect of nitric acid
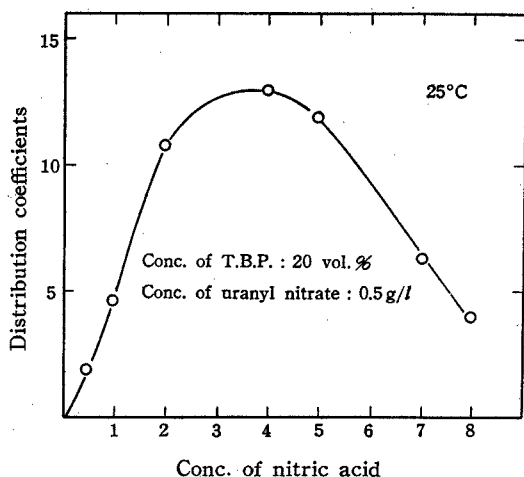

Fig. 3. Variation of distribution coefficient
with acid concentration

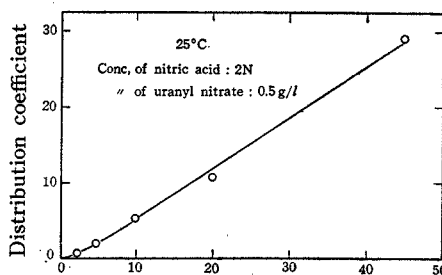Conc. of T.B.P. in kerosene solution (vol. %)

Fig. 4. Variation of distribution coefficient
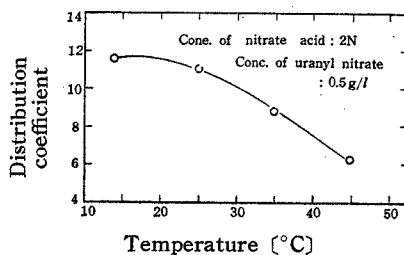with T.B.P. concentration

Fig. 5. Variation of distribution coefficient
with temperature.

concentration, kerosene concentration and temperature on the distribution coefficient, respectively. Judging from these diagrams, we carried out this study with 2N nitric acid and with mixed solvent (20 vol. % of T.B.P. and 80 vol. % of kerosene) at 25°C.

d) **Recovery of the solvent:—** Sato[4] says that uranium dissolved in organic solvent can be recovered completely by being washed with 5~10 wt. % aqueous solution of oxalic acid, ammonium carbonate or sodium carbonate. But it is not clear whether the orgrnic solvent treated with these solutions may be used repeatedly or not. The authors examined it by treating the spent solvent with 10 wt. % sodium carbonate aqueous solution and found that the properties of the solvent had hardly changed even after seven times' washing.

e) **Calculation of results:—** Material balances were calculated for each run from the concentrations and flow-rates of the entering and outgoing liquids. Employing data for which errors in material balance were within 5%, mean overall $(H.T.U.)$ values on the basis of aqueous layer were calculated from the following equation.

$$(H.T.U)_{mow} = \frac{h(\Delta c_w)_{lm}}{c_{w1} - c_{w2}}$$

(1)

Here C_{w1} and C_{w2} is the concentration of uranyl nitrate, g/l, in acid phase at its inlet and outlet respectively, and $(\Delta c_w)_{lm}$ g/l, is logarithmic mean of driving forces at the

top and bottom of the column. h is the effective height of the tower, cm.

3. Interpretation of results

a) **Observations:**— While the flow rate through the perforations was small, bubbles were formed separately near the plate, but as the velocity through the holes became high. bubble layer formed at the principal interface began to grow. At even higher velocity bubbles became smaller except the case where the interface was close to the plate. In latter case dispersed phase formed a rod flow and the plate efficiency was depressed. In this experiment, the bubbles of light phase were more stable than those of heavy phase. Fig. 6 and 7, shows representative data. In the former, where acid phase
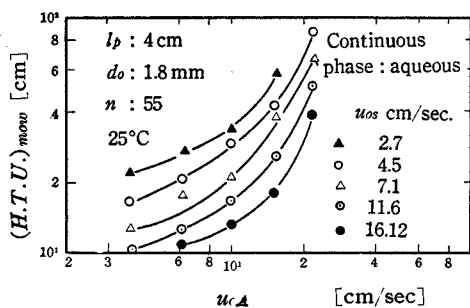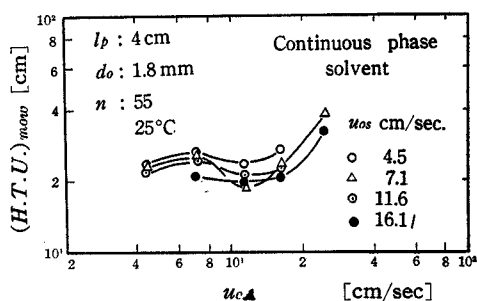

Fig. 6. $(H.T.U.)_{mow}$ vs $u_{c\Delta}$

Fig. 7. $(H.T.U.)_{mow}$ vs $u_{c\Delta}$

is continuous. The effect of the flow rates on the values of $(H.T.U.)_{mow}$ is more evident than in the latter, where solvent phas is continuous. Quite the same inclination had been observed in the previous study for benzene (HOAc)-water and methylysobutyl ketone (HOAc)-water systems.

For the perforated-plate alternative flow type extraction tower, a lot of operational variables may be considered. However, we have carried out most of all experiments, keeping the ratio of flow rates of acid phase to solvent phase as unity.

b) **Effects of flow rate:**— Fig. 8 shows how the values of $(H.T.U.)_{mow}$ are affected by the flow rates, where the ratio of flow rates is unity. In the case, acid phase is continuous, $(H.T.U.)_{mow}$
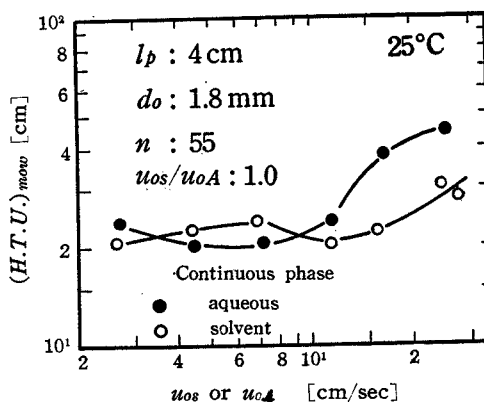

Fig. 8. $(H.T.U.)_{mow}$ vs. $u_{os} = u_{o\Delta}$

has minimum value at the velocity of about 5 cm/sec. This is considered to come from the following facts. As the velocity became higher, turbulence in the liquid became violent, the number of effective perforations increased and the principal interface on the stage went down, increasing the length of movement of droplets and forming the

drop layer. If the velocity became higher moreover, the flow of acid phase became rod like and drop layer disappeared. On the other hand, when the organic phase was taken as continuous, increase in the acid phase flow rate had little effects on the state of flow in the tower, except a little rise in the position of the princial interface.

c) **Effects of plate spacing:—** As supposed from the previous experiments, it was better to construct the plate spacing shorter. (Fig. 9). From this figure it seems better to operate with organic phase as continuous than with acid phase as continuous.

d) **Effects of hole size:—** We used two kinds of perforated plate having the same free area (see Table 1), one had perforations of 1.8 mm in diameter and the other had those of 1.0 mm. The values of $(H.T.U.)_{mow}$ obtained are shown in Fig. 10.

The velocity to make the value of $(H.T.U.)_{mow}$ minimum, is a little higher for the plate of 1.0 mm perforation than that of 1.8 mm perforation. As the free areas of both plates are the same, the throughput is proportional to u_0.

It is interesting that for plates with smaller holes, the throughput is greater than for plates with larger holes, at their optimum velocities. Then, it seems better to use shorter plate spacings and smaller perforations. In accordance with this Fig. 11 shows very good performance, where 1_p is 2.0 cm and d_0 is 1.0 mm.

e) **Effects of flowing period:—** The time of duration of flow, under the condition where u_{os}/u_{oA} equals to unity, had little effects on $(H.T.U.)_{mow}$ in this experiments.

f) **Effects of the velocity ratio** (u_{0s}/u_{0A}):—

As a characteristic of the tower employed here, the solvent ratio is determined by controlling either the follow-
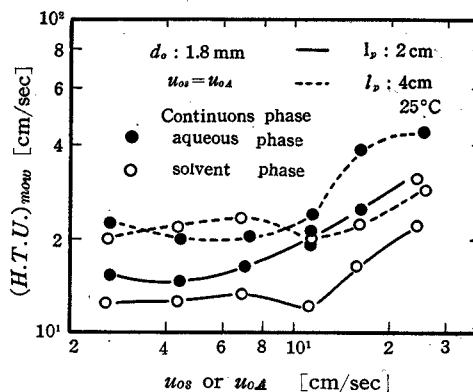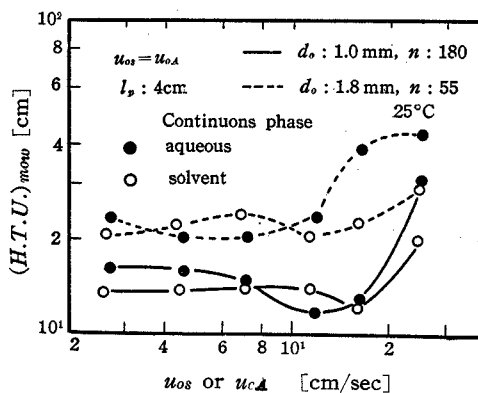
Fig. 9. Effects of l_p

Fig. 10. Effects of d_o
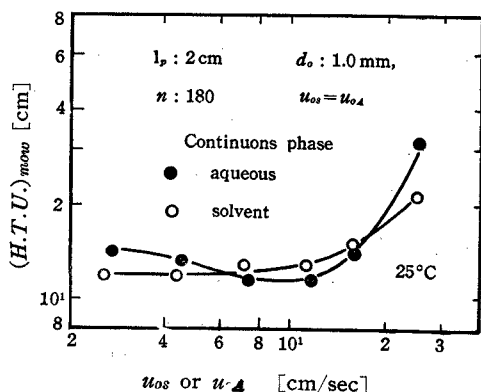
Fig. 11. $(H.T.U.)_{mow}$ vs $u_{os}(=u_{cA})$

duration time in one cycle for the each phase, or the velocities of each phase though the perforations.

The results obtained for the plate spacing of 2 cm by varring the velocities or the flowing duration times of each phase, keeping the flow rates of both phases constant as identical as 23.7 1/hr.

In this case, as shown in Fig. 12, the value of $(H.T.U.)_{mow}$ was minimum at the
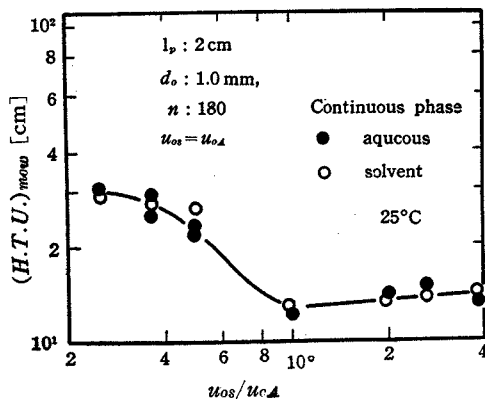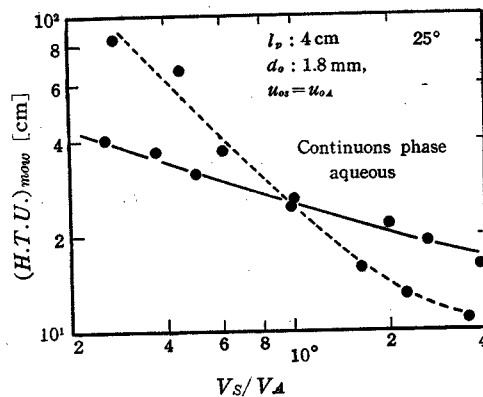

Fig. 12. $(H.T.U.)_{mow}$ vs (u_{os}/u_{oA})

Fig. 13 $(H.T.U.)_{mow}$ vs (V_S/V_A)

velocity ratio, u_{0s}/u_{0A}, of 1.0. On the left hand in this diagram, u_{0s} is small whereas u_{0w} is large.

No difference is found by selection of continuous phase. This is perhaps because of the short spacing of the plates.

g) **Effects of the ratio of flow rate** (the duration times of flow for each phase were changed, the value of u_{0s}/u_{0A} was kept constant):— The solid line in Fig. 13 shows the variation of $(H.T.U.)_{mow}$'s values under the condition, indicated in Table 2, $(u_{0s}/u_{0A}=11.6$ cm/sec.) And the dotted line represents the case when the value of u_{0s} or u_{0A} was varried keeping the total flow rate of the both phases constant $(41\sim46$ 1/hr) as the same value as in Table 2.
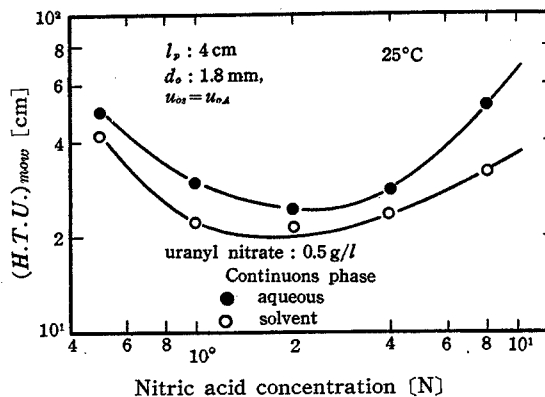
It should be recognized that

Fig. 14. $(H.T.U.)_{mow}$ vs acid concentration

Table 2. Operating conditions in Fig. 13

run number	duration of flow per one cycle (sec)		total throughput (1/hr)
	aqueous phase	solvent phase	
1	3.0	1.5	41
2	4.0	1.5	43
3	5.8	1.5	46
4	1.5	3.0	4.1
5	1.5	4.0	43
6	1.5	5.8	46
$d_0=1.8$mm $l_p=4$cm $u_{os}=u_A=11.6$ cm/sec			

those two curves cross each other at $u_{0s}/u_{0A}=1$, and on left hand and right hand, the comparative situation of these curves is reversed.

h) Effects of concentrations:—

① of acid. As is seen from Fig. 14, values of $(H.T.U.)_{mow}$ varied with the acid concentration, showing preferable values over the concentration range from 1.0 to 4.0 N.

② of uranyl nitrate. For the case of acid phase (2N nitric acid) was continuous, data are indicated in Fig. 15. In this case $(H.T.U.)_{mow}$ was constant.

③ of T.B.P. (Fig. 16) For higher T.B.P. concentration, the values of $(H.T.U.)_{mow}$ became smaller, especially when the organic phase was taken to be continuons.

i) Effects of temperature:— The higher the temperature was, the lower the values of $(H.T.U.)_{mow}$ became (Fig. 17).

In practical, however, we must take account of corrosion and temperature should not be taken so high.
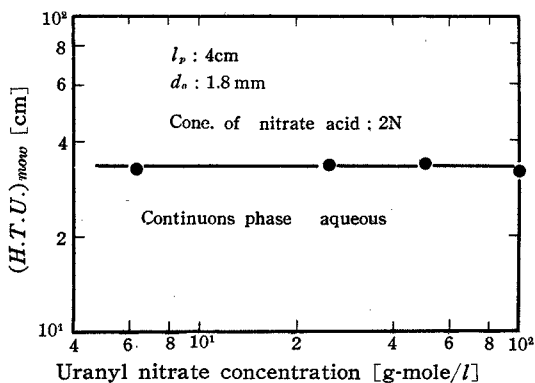

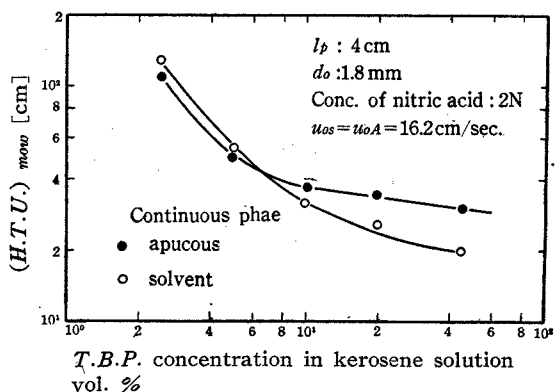Fig. 15. $(H.T.U.)_{mow}$ vs uranyl nitrate concentration.

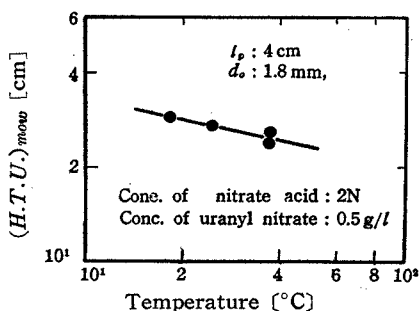Fig. 16. $(H.T.U.)_{mow}$ vs T.B.P. concentration

Fig. 17. $(H.T.U.)_{mow}$ vs temperature

4. Comparison of present results with those of other's

Several investigations[2)6)9)] have been carried out on the extraction of uranyl nitrate, employing pulsed columns. The apparatus used by them are not identical to each other, and of course is different from our present work. Cmparable data are presented in Fig. 18. Factors, such as concentrations of acid and uranyl nitrate, frequency and amplitude of pulsation, corresponding to each curve in this figure, are as shown in Table 3.

Judging from this figure, the perforated-plate tower of alternative flow type, em-

Table 3. Operating factor of the experiments in Fig. 18

Author	amplitude × frequency $a \times f$	continuos phase	direction of extraction	d_0 (cm)	l_p (cm)	h (cm)	% of free area	V_0/V_A	aqueous phase		organic phase		conc. of nitric acid in aqueous phase (N)
									specific gravity	conc. of $UO_2\left(\dfrac{mole}{l}\right)$	specific gravity	T.B.P. vol % in organic phase	
Sege[6]	125 (2.5×5.0)	aqueous phase	organic phase aqueous phase	0.31	5.0	—	23	1.25	1.0	—	0.85	30	0.01
	138~175 2.5×(55~70)	//	aqueous phase organic poase	0.31	5.0	—	23	1.67	1.3	0.18	0.60	30	2.6
Yagi[9]	150	//	//	0.3	5.0	25	19	0.33	—	0.025	—	30	0.5~0.6
Oyama[2]	106 1.0×106)	—	//	1.0×1.0 Raschig ring	—	93	—	1.00	—	0.005 ~0.3	—	20	—
Ueyama	—	aqueous phase and orgonic phase	//	0.1	2.0	24	8	1.00	—	0.0013	0.83	20	2.0

ployed here, has appreciably good performance. The right hand ends of these curves except authors', are restricted by flooding. Because of the different flow mechanism, in the alternative flow type tower, no flooding were observed, within the range of our experiment.
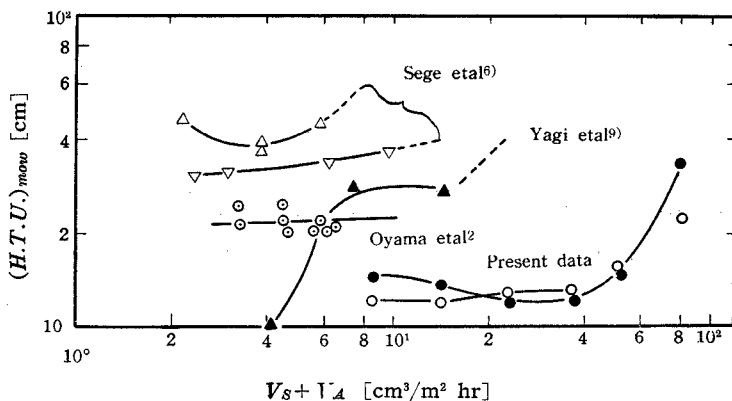

Fig. 18. Comparison of the results with other's

5. Conclusion

The effects of various operation factors on the performance of alterative flow type perforated-plate towers, were studied. The most suitable operating conditions in this work were found to be as follows.

1. Using solvent as the continuous phase.
2. Taking plate spacing as 2.0 cm. and perforation diameter as 1.0 mm..
3. Using nitric acid of 2-N. and 20. vol. % T.B.P. solution (diluent: kerosene).
4. Employing u_{0s}/u_{0A} of 1.0, if the flow rates ratio of both phases is kept unity.

Furthermore, the duration time of the flow in one cycle and uranyl nitrate concentration had no effects on the tower performance in our experiment. Emyloying the most suitable operating conditions above mentioned, we observed the values of $(H.T.U.)_{mow}$ between 12 and 16 cm.. All values of $(H.T.U.)_{mow}$ were between 10 and 90 cm. and most of all were 20~30 cm..

Comparison of $(H.T.U.)$s' value or of throughput in present work with those of other investigators, shows the possibility of this type extraction tower to be utilized in uranium industry.

Notation

a	:	amplitude of pulsation	(cm)
d_o	:	diameter of perforation	(cm)
f	:	frequency of pulsation	(c.p.m.)
l_p	:	plate spacing	(cm)
n	:	number of perforations in one plate	(—)
u_{os}	:	velocity of solvent phase or organic phase through the perforation	(cm/sec)

u_{oA} : velocity of acid phase or aqueous phase through the perforation (cm/sec)

$(H.T.U.)_{mow}$: mean overall $(T.H.U.)$ value on the basis of aqueous phase (cm)

V_o, V_s: flow rate of organic phase or solvent phase (m^3/m^2hr)

V_A : flow rate of acid phase or aqueous phase $(m^3/^2hr)$

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