K_2 = interfacial rate constant, cm./sec.
k_1 = interfacial rate constant, (cm.)(g.-mole)/(cc.)(atm.)(sec.)
k_2 = interfacial rate constant, sec.$^{-1}$
m = function defined by Equation (12)
n = function defined by Equation (13)
P = pressure, atm.
S_o' = observed value of $d\,\theta/d\sqrt{\omega}$ at $\omega = 0$
S_o'' = observed value of $d^2\theta/d\sqrt{\omega}^2$ at $\omega = 0$
T = temperature, K.
t = time, sec.
x = distance, cm.

Greek Letters

ω = frequency, sec.$^{-1}$
ω^* = value of ω at which the observed value of $\theta = \pi/2$
θ = phase angle, rad.

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Continuous Ion Flotation of Dichromate

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An experimental investigation is presented of the continuous ion flotation of dichromate, with the use of a cationic surfactant, ethylhexadecyldimethylammonium bromide. The feed streams contain concentrations of dichromate ($Cr_2O_7^{2-}$) ranging from 10 to 100 mg./liter, and feed ratios of surfactant to dichromate from 2.5 to 6.0 (on a weight basis) are employed. The effects of feed concentration of dichromate, of feed concentration of surfactant, of liquid detention time, of air rate, and of feed into and above the foam phase are established. Results are presented in terms of the effluent concentrations of dichromate and surfactant, the ratios of effluent flow rate to feed flow rate, removal ratios, and enrichment ratios. For three-column series operation, predictions show that a feed stream containing 100 mg./liter dichromate may be separated (with approximately 400 mg./liter of surfactant) into an effluent stream containing 8 mg./liter of dichromate and a collapsed foam stream containing 468 mg./liter of dichromate.

Ion flotation involves the addition to aqueous solution of a surface-active agent that has a hydrophobic part (generally containing a long hydrocarbon chain) of opposite charge to the inorganic ion that is to be separated. An insoluble compound is formed between the hydrophobic cation or anion and the inorganic anion or cation of interest; the compound, which is surface-active, may then be floated to the surface of the solution and carried into a foam phase by aeration of the solution. The compound is preferentially adsorbed at the air-aqueous solution interfaces associated with the foam-generating bubbles. An extensive discussion of ion flotation has been presented by Sebba (8), and Rubin and Gaden have reviewed a number of applications (7).

The ion flotation of dichromate has been studied previously (3 to 5), but virtually all of the experiments were conducted on a batch basis, foaming a given volume of feed solution with the dependent variables changing as functions of time. The batch studies were carried out with feed solutions containing from 5 to 99 mg./liter of dichromate ion and from 202 to 396 mg./liter (added in several doses) of a cationic surfactant, ethylhexadecyldimethylammonium bromide (EHDA-Br). Most efficient operation was achieved with a molar feed ratio of EHDA ion to dichromate ion from 2.1 to 3.0, and removal ratios (defined as the quantity of dichromate floated per unit quantity of dichromate in the feed) ranging from 80 to 95% were obtained. For the ion flotation of dichromate to be a feasible technique for the treatment of industrial wastes, the process would have to be conducted with continuous flow ion flotation units. The results of the batch experiments were sufficiently promising to merit an experimental investigation of the continuous ion flotation of dichromate.

In the present study, continuous flow experiments include the effects of the dichromate concentration in the feed stream, of the surfactant concentration in the feed stream, of liquid detention time, and of air rate. Dependent variables include effluent concentrations of dichromate and of surfactant, the effluent rate, the enrichment ratio, and the removal ratio. Multicolumn operation is discussed and the influence of feed into the foam phase is established.

EXPERIMENTAL

A schematic diagram of the experimental apparatus used in these studies is presented as Figure 1. The compressed air was filtered, saturated to approximately 95% humidity, metered with a calibrated rotameter, and diffused through a 20-μ, porous metal aerator, 5.6 cm. in diameter. The solutions of dichromate (reagent grade potassium dichromate) and of surfactant (EHDA-Br) were pumped into the column at combined rates of from 0.025 to 0.10 liter/min. The ratio of the dichromate flow rate to the EHDA-Br flow rate was always maintained at 4:1. The concentrations in the feed tanks were adjusted to provide concentrations (in mg./liter of *combined* feed) of dichromate ranging from 10 to 100 mg./liter (as $Cr_2O_7^{2-}$) and of EHDA-Br ranging from 30 to 400 mg./liter. The *p*H of the combined feeds was 5.2. All of the results are discussed considering a combined feed stream entering the column and all feed concentrations are given on the basis of a single feed stream. Due to complete mixing in the liquid phase in the flotation column, such an approach was validated. Also, all weight concentrations are given in terms of weight of the surfactant compound, EHDA-Br, and weight of the dichromate ion, $Cr_2O_7^{2-}$; this is done because most weight analyses are given in terms of hexavalent chromium (Cr^{6+}) or dichromate and not in terms of any specific compound of dichromate.

The flotation column was cylindrical, 10 cm. in diameter, 105 cm. in height, and was made of Lucite. The steady state liquid volume was varied from 2.0 to 6.0 liters, which, together with the range of flow rates employed, gave detention times of from 40 to 240 min. In the first and second series of experiments, both feeds entered the column at the midpoint of the liquid phase and the height of foam removal above the foam-liquid interface was maintained at 15.2 cm. In the final series of experiments foam heights of 15.2 and 41.9 cm. were employed, and the feeds entered the column 20.0 and 29.2 cm. above the foam-liquid interface. Temperature was held within the range 26° to 28°C.

With time measured from start-up, approximately 2.5 hr. were required to achieve steady state operation. After steady state was reached, three to four effluent (bottoms) samples were taken in 0.5-hr. intervals and analyzed for dichromate (*9*) and for surfactant (*1*). The effluent and collapsed foam flow rates were measured volumetrically. Generally, excellent agreement in the sample analyses and in the flow rates was obtained. Random analyses of the collapsed foam stream were made for material balance verification and to eliminate any possibility of the chemical reduction of the dichromate. The analysis for dichromate was accurate to within ±0.8 mg./liter and for EHDA-Br to within ±5%.

The characteristics of the colloidal particulates formed upon reaction between dichromate and EHDA have been discussed previously (*5*). However the size of the particulates was reported erroneously. More careful observation has shown them to be approximately 2μ in diameter, with aggregates as large as 10μ in diameter. In the experiments reported herein, dichromate was floated in particulate form, as evidenced by minute orange crystals in the foam and some turbidity (cloudiness) in the liquid phase in the flotation column.

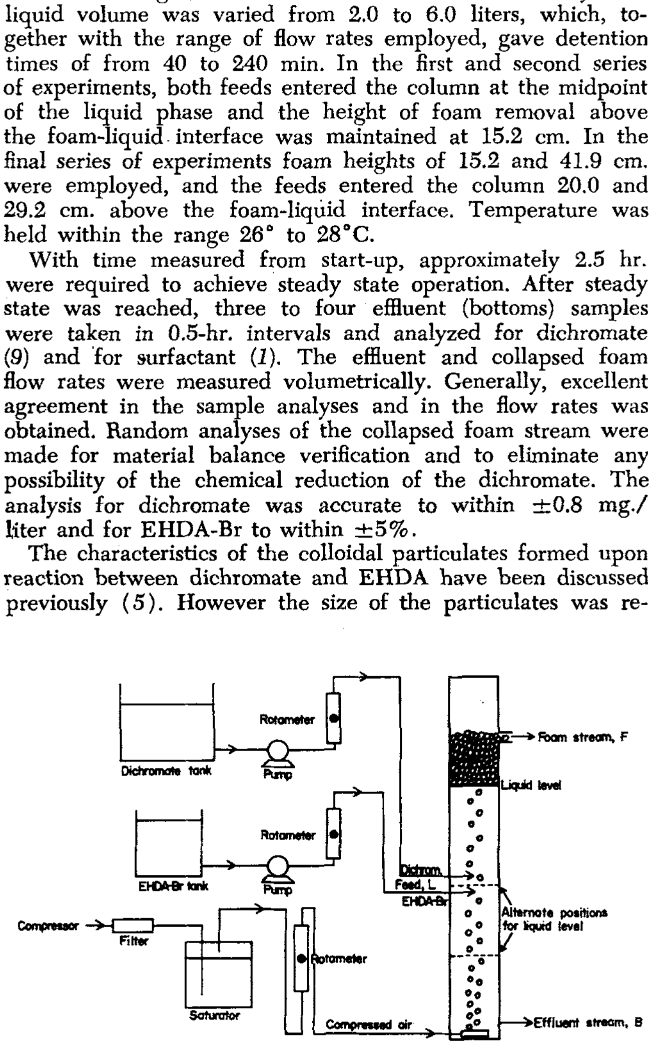

Fig. 1. Schematic diagram of experimental apparatus.

EFFECT OF FEED STREAM CONCENTRATIONS OF DICHROMATE AND SURFACTANT

The first series of experiments was conducted to investigate the continuous ion flotation of feed streams containing a rather wide range of dichromate concentrations (10 to 100 mg./liter as $Cr_2O_7^{2-}$) and with EHDA-Br to dichromate ratios in the feed ranging from 3.0 to 6.0 on a weight basis (from 1.7 to 3.4 on a gram ion basis). In each experiment, the air rate was 1,500 ml./min. (at 25°C. and 1 atm.), the combined liquid feed rate entering the column at the midpoint of the liquid phase was 0.05 liter/min., the steady state liquid volume in the flotation column was 2 liters giving a 40-min. detention time, and the height of foam removal above the foam-liquid interface was 15.2 cm. For each experiment the following material balances can be written and used to calculate the concentrations of dichromate z_f and EHDA-Br x_f in the collapsed foam stream:

$$L = B + F \tag{1}$$

$$z_1 L = z_b B + z_f F \tag{2}$$

$$x_1 L = x_b B + x_f F \tag{3}$$

For eleven experiments with z_1 ranging from 10 to 100 mg./liter and x_1 ranging from 30 to 400 mg./liter, with weight feed ratios x_1/z_1 of 3.0, 3.5, and 4.0, the following relation between the effluent dichromate and feed dichromate concentrations was obtained:

$$z_b = 0.63\, z_1^{0.90} \tag{4}$$

The average deviation of values calculated with Equation (4) from experimental values was 11%. [Average deviation $= \frac{|\text{experimental} - \text{calculated}|}{\text{experimental}}$ (100).] For all of the experiments z_b/z_1 ranged from 0.30 to 0.53. The effluent surfactant concentrations did not correlate well with feed dichromate concentrations: at z_1 = 10 mg./liter $x_b \doteq 5$ mg./liter, at $z_1 = 25$, $x_b \doteq 9$, at $z_1 = 50$, $x_b \doteq 39$, at $z_1 = 75$, $x_b \doteq 50$, and at $z_1 = 100$, $x_b \doteq 95$. x_b/x_1 ranged from 0.10 to 0.25. For approximate values, the following relation was obtained:

$$x_b = 0.19\, z_1^{1.3} \tag{5}$$

The average deviation of values calculated with Equation (5) from experimental values was 25%.

For the feed stream concentrations of dichromate investigated, the feed stream concentrations of EHDA-Br and the x_1/z_1 ratios which could be used were limited by the flow rate of the effluent stream and by the controlling values of the effluent flow to feed flow ratio B/L, which were 0.0 and 1.0, each corresponding to no separation. For a total of fourteen experiments, including two with x_1/z_1 ratios of 6.0, data for B/L are presented in Figure 2. The sensitivity of B/L, and thus of the steady state flow of foam, to x_1/z_1 is clearly evidenced: at z_1 = 50 mg./liter and $x_1/z_1 = 6.0$, all of the feed would be driven into the foam; at z_1 = 100 mg./liter and $x_1/z_1 = 3.0$, no foam was produced and no separation was obtained. A few experiments were carried out with $x_1/z_1 = 2.5$; no foam stream was produced ($B/L = 1.0$) at z_1 = 75 mg./liter, but at $z_1 = 50$, it was possible to operate. From a consideration of Figure 2 and from the fact that z_b was almost not dependent on x_1

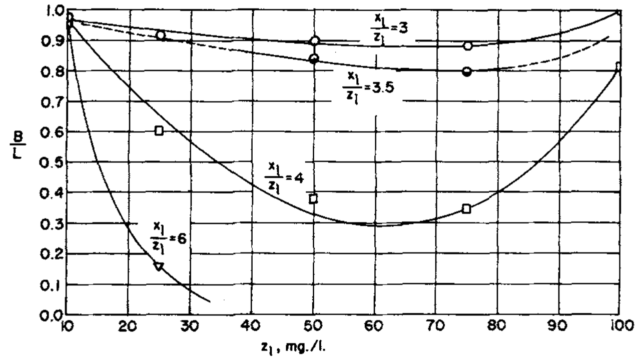

Fig. 2. Relations between B/L and z_1 for various feed ratios.

for the x_1/z_1 ratios employed, it is best to operate with a feed ratio of 3.0 (or in certain cases, 2.5). Increasing x_1/z_1 from 3.0 to 4.0 generated a larger, more dilute foam stream and had practically no effect on z_b. For $z_1 = 10$ mg./liter, increasing x_1/z_1 from 4.0 to 6.0 had no effect on z_b, while for $z_1 = 25$ mg./liter, a similar increase reduced z_b from 11 to 7 mg./liter, but clearly at the expense of an extreme decrease in B/L.

The minima in the curves of Figure 2 were brought about by two effects. First, an increase in z_1 at constant x_1/z_1 tended to provide a greater quantity of excess EHDA-Br (over the quantity necessary to react with the dichromate) and more foam (lower B/L). The contacting of dichromate and EHDA in approximately stoichiometric quantities would not provide excess EHDA and thus a very small quantity of foam would be formed; as the effective ratio of EHDA to dichromate for a run (a function of both x_1/z_1 and x_b/z_b) was increased (by increasing x_1/z_1), the excess quantity of EHDA was increased and more foam was produced. Second, it appears that the EHDA-dichromate particulates, although being preferentially adsorbed at the air-solution bubble interfaces, had a negative effect on foam stability. At constant x_1/z_1, increasing z_1 caused the production of more particulates which were adsorbed at the bubble interfaces and carried from solution, but thereby tending to produce an increase in B/L. These two opposing effects, which have been discussed in detail for batch operation (*4*), could have produced the minima.

Two useful parameters in the evaluation of any foam separation process are the removal ratio, defined as the rate of dichromate flotation into the collapsed foam stream per unit rate of dichromate fed to the flotation column, z_fF/z_1L, and the enrichment ratio, defined as the concentration of dichromate in the collapsed foam (overhead) divided by that in the effluent (bottoms), z_f/z_b. For most efficient operation, both are to be maximized. Both parameters are related to z_1 for $x_1/z_1 = 3.0$ and 4.0 in Figure 3. The maxima in both curves for the removal ratios were produced by the same two effects that caused the minima in B/L in Figure 2. An increase in z_1 at constant x_1/z_1 produced more foam breaking dichromate-EHDA particulates and poorer removal, while the greater excess of EHDA-Br provided more foam and a larger carrying medium for the particulates and better removal. The improvements in the removal ratio by raising x_1/z_1 from 3.0 to 4.0 are clear, but the poorer enrichment ratios at $x_1/z_1 = 4.0$ show that the increase simply carried more entrained liquid into the foam stream. The variation in the removal ratios and enrichment ratios for EHDA-Br was somewhat similar to that for dichromate. For $x_1/z_1 = 3.0$ and 4.0, x_fF/x_1L ranged from 0.79 to 0.97 and x_f/x_b ranged from 7.1 to 180. For a given experiment, the value of each parameter for the surfactant was always greater than the value of the corresponding parameter for dichromate. The relative quantities of EHDA-Br and dichromate in the collapsed foam stream x_f/z_f ranged from 3.8 to 7.1 mg./mg. or from 2.2 to 4.1 mg. ion EHDA/mg. ion $Cr_2O_7^{2-}$. The stoichiometric value is, of course, 2.0 mg. ion/mg. ion. The fact that the experimental values were always greater than 2.0 indicates that surfactant was removed both by a foam fractionation mechanism as a soluble ionic species and by an ion flotation mechanism as a particulate compound with dichromate.

Multicolumn Operation

Although the experimental data were obtained from a single ion flotation column, they may be utilized to establish the performance obtainable from a multicolumn series ion flotation unit. In such a unit, the effluent or bottoms stream from the first column would serve as the feed stream to the second column, the effluent stream from the second column would serve as the feed stream to the third, etc. Of course, additional surfactant would have to be added to the feed to each column. The collapsed foam streams from the series of columns could be combined or subjected to further treatment individually. The typical performance of a three-column unit was calculated for a feed stream containing 100 mg./liter dichromate and entering the first column at 0.05 liter/min. The operating conditions were assumed to be the same as those used in the procurement of the experimental data, and the separation achieved in each column is based on Equation (4), Figure 2, and a smooth curve through the data for x_b vs. z_1. The effluent from the third column would contain 8 mg./liter dichromate and 8 mg./liter surfactant, and the flow rate of the effluent stream would be 80% of that of the feed stream. The combined collapsed foam stream consisting of the three collapsed foam streams from the individual columns would contain 468 mg./liter dichromate and 2,000 mg./liter surfactant. In the three columns a total of 403 mg./liter surfactant would have to be added. For the same operation a feed stream containing 50 mg./liter dichromate would be split into an effluent stream containing 8 mg./liter dichromate and a combined collapsed foam stream containing 230 mg./liter dichromate. The feed, effluent, and foam concentrations of EHDA-Br would be 190, 5, and 940 mg./liter, respectively, and the effluent flow rate would be 80% of that of the feed.

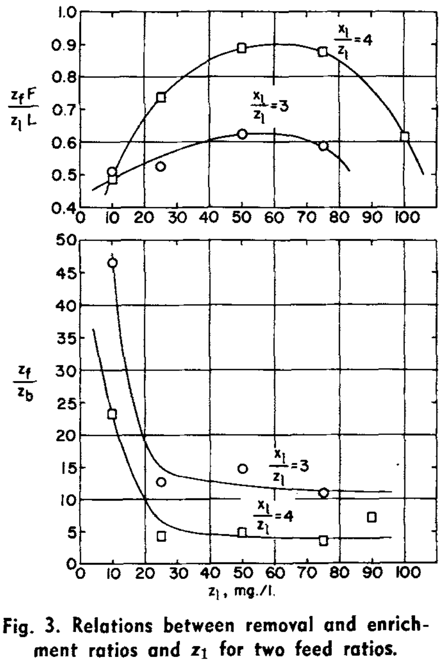

Fig. 3. Relations between removal and enrichment ratios and z_1 for two feed ratios.

EFFECT OF DETENTION TIME AND AIR RATE

A second series of experiments was conducted to establish the influences of liquid detention time, which is defined as the steady state volume of liquid in the column divided by the feed rate, and of air rate. The feed streams contained 10, 25, 50, and 75 mg./liter of dichromate, and for each experiment the feed EHDA-Br to dichromate ratio x_1/z_1 was 3.0. The foam height was maintained at 15.2 cm. above the foam-liquid interface.

Detention Time

Data for the residual concentrations of dichromate and of EHDA-Br and detention time for four values of z_1 (and x_1) are presented in Figure 4. The lines and curves were drawn to give the best fit to the data. The range of detention times was covered by varying the liquid volume from 2.0 to 6.0 liters and the feed rate from 0.025 to 0.10 liter/min. The air rate was maintained at 1,500 ml./min. The effect of detention time on x_b and z_b was approximately the same at $z_1 = 10$ and 25 mg./liter and was much more pronounced on x_b than on z_b at $z_1 = 50$ and 75 mg./liter. The effluent concentration of dichromate z_b could be readily related to detention time:

$$z_b = 1.3\, z_1^{0.90}\, \theta^{-0.18} \tag{6}$$

Above a detention time of 30 min. the B/L ratio was virtually independent of θ, varying from 0.87 to 0.99 in a random manner. At constant θ, B/L decreased slightly with increasing z_1. At $\theta = 20$ min., B/L ranged from 0.76 to 0.89.

Variation in liquid volume at constant feed rate had a measurable effect on both the effluent concentration of dichromate and the effluent concentration of EHDA-Br. This behavior was opposite to that noted for the continuous foam fractionation of EHDA-Br solutions (*6*) for which a variation in liquid volume in a similar column from 0.9 to 10.0 liters had no effect on the separation. It appears that in the latter case equilibrium was readily established, while in the present study, due to the reaction between dichromate and EHDA, equilibrium was not established but was only approached as the liquid volume was increased.

For three-column series operation, an increase in detention times in the first two columns would produce an improved separation, while an increase in detention time in the third column would have a negligible effect, due to the low concentration of dichromate in the feed to the third column. The insensitivity of operation in the third column would tend to mask any improvement obtained in the first two columns.

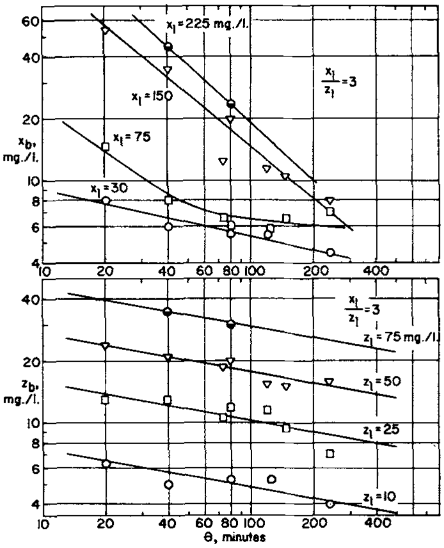

Fig. 4. Effect of detention time upon effluent dichromate and EHDA-Br concentrations.

Air Rate

For experiments conducted with a feed rate of 0.05 liter/min., detention time of 40 min., and feed concentration of dichromate of 50 mg./liter, air rate had a very limited effect on the ion flotation process. With a feed concentration of EHDA-Br of 150 mg./liter, elevation of the air rate from 1,500 to 3,000 ml./min. produced no change in z_b and B/L and reduced x_b from 35 to 30 mg./liter. With a feed concentration of EHDA-Br of 125 mg./liter, elevation of the air rate from 1,500 to 7,500 ml./min. again produced no change in z_b and B/L and reduced x_b from 14 to 7 mg./liter. In contrast, for $L = 0.05$ liter/min., $\theta = 40$ min., $z_1 = 100$ mg./liter, and $x_1 = 400$ mg./liter, elevation of the air rate from 1,500 to 2,000 ml./min. decreased z_b from 47 to 33 mg./liter and x_b from 100 to 60 mg./liter. However, this was accomplished at the expense of an extreme increase in collapsed foam rate, decreasing B/L from 0.82 to 0.35. This provided a more dilute foam and lower enrichment ratios. It appears that the high effluent concentrations of dichromate and EHDA-Br caused the sensitivity to air rate.

In an evaluation of the factors controlling the continuous foam fractionation of solutions of pure surfactants (*2*), it was concluded that a parameter defined as the air flow rate divided by the feed flow rate was a significant variable. For three surfactants the effluent concentration was correlated with the ratio of air to feed flow. In the ion flotation of dichromate, with feed streams containing approximately 60 mg./liter or less of dichromate, the air-to-feed flow ratio appears to be of no significance. For higher values of z_1, it may have a significant effect, but air rate elevation tends to worsen column performance.

EFFECT OF VARIABLE FEED POSITION

A final series of experiments was conducted to determine the influence of inserting the feed stream into and above the foam phase in an ion flotation unit. The values of the significant independent variables and the results obtained are shown in Table 1. The first set of data compares feed into the liquid with both feeds sprayed through small glass nozzles above the foam. The dichromate nozzle was located 29.2 cm. above the foam-liquid interface, 14.0 cm. above the foam removal port; the EHDA-Br nozzle was located 20.0 cm. above the interface and 4.8 cm. above the port. In all three cases, better stripping of the dichromate was obtained with the spray feeds, and in two of the three better stripping of the EHDA-Br was obtained. However, this was accomplished at the expense of lower B/L ratios and poorer enrichment. The latter disadvantage could possibly be overcome by reflux of a fraction of the collapsed foam.

In the second set of data, the feed streams (of dichromate and of EHDA-Br) entered the column through twin glass tubes positioned at heights of 13 cm. below or 20 cm. above the foam-liquid interface. The elevated air rate was necessitated by the low foam rate obtained with feed at 20 cm. and a foam height of 41.9 cm. Comparison of the second and third runs shows that elevation of the foam height at constant feed position not only provided more adequate drainage of the foam stream, but also better stripping of dichromate from the effluent. This serves to indicate that separation is occurring in the rising foam stream, in contrast to the behavior noted for pure surfactant feed streams (*2*). The improved separation must be weighed against the higher air flow which was required.

TABLE 1. EFFECT OF VARIABLE FEED POSITION ON THE ION FLOTATION OF DICHROMATE

$L = 0.025$ liter/min., $\theta = 80$ min., air rate = 1,500 ml./min., foam height = 15.2 cm.

z_1, mg./liter	x_1, mg./liter	Feed position	z_b, mg./liter	x_b, mg./liter	B/L	z_f/z_b	x_f/x_b
25	75	Into liquid	11	6	0.97	36	360
25	75	Sprayed above foam	5	9	0.82	20	42
50	150	Into liquid	20	20	0.96	39	160
50	150	Sprayed above foam	12	12	0.76	14	49
100	400	Into liquid	37	40	0.77	21	53
100	400	Sprayed above foam	10	16	0.47	19	46

$z_1 = 50$ mg./liter, $x_1 = 150$ mg./liter, $L = 0.025$ liter/min., $\theta = 80$ min., air rate = 3,000 ml./min.

Feed position	Foam height, cm.	z_b, mg./liter	x_b, mg./liter	B/L	z_f/z_b	x_f/x_b
Into liquid, 13 cm. below interface	15.2	20	17	0.96	39	200
Above foam, 20 cm. above interface	15.2	22	11	0.93	13	120
Into foam, 20 cm. above interface	41.9	14	16	0.99	210	700

CONCLUSIONS

An experimental investigation has been made of the continuous ion flotation of dichromate using a cationic surface-active agent, ethylhexadecyldimethylammonium bromide. The feed streams contained from 10 to 100 mg./liter of dichromate ion.

1. For single-column flotation with a fixed set of operating conditions, the optimum feed ratio, from this study, of surfactant to dichromate is between 2.5 and 3, depending on the flow rate of collapsed foam that is obtained. With feed ratios in this range, the ratio of the effluent to the feed concentration of dichromate varies from 0.42 to 0.51 and the flow rate of the effluent (bottoms) stream varies from 89 to 98% of the feed flow rate. For feed concentrations of dichromate 25 mg./liter and greater, removal ratios of about 0.6 and enrichment ratios of about 12 are obtained.

2. Based upon calculations for three ion flotation columns operated in series, a feed stream containing 100 mg./liter of dichromate may be split into an effluent stream containing 8 mg./liter and a collapsed foam stream containing 468 mg./liter. Approximately 400 mg./liter of the surfactant must be added in the three columns, and the effluent flow rate is 20% of that of the feed, providing a foam rich in both dichromate and surfactant.

3. Increasing the liquid detention time above 40 min. in single columns produces further reductions in the residual concentrations of dichromate and of surfactant, but would have little effect on the performance of a multicolumn unit. Liquid volume affects the separation, and for feed dichromate concentrations less than 60 mg./liter the air flow rate to feed flow rate ratio has little influence on the separation, both in contrast to the foam fractionation of pure surfactants. Inserting the feed above the foam phase reduces the effluent concentrations, but at the expense of larger and more dilute collapsed foam streams.

4. The continuous ion flotation of dichromate shows sufficient promise for future study, including multicolumn operation with foam reflux, more concentrated feed streams, and the use of other surface-active agents. The process appears to have some merit for the removal and recovery of dichromate from industrial wastes. Relation of the continuous data presented in this study to the batch data presented previously (4) is difficult, since in the batch studies multiple additions of surfactant were employed and time was not a controlled variable.

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NOTATION

B = effluent (bottoms) flow rate, liter/min.
F = collapsed foam flow rate, liter/min.
L = flow rate of combined feed stream, liter/min.
x_b = concentration of EHDA-Br in effluent stream, mg./liter
x_f = concentration of EHDA-Br in collapsed foam stream, mg./liter
x_1 = concentration of EHDA-Br in combined feed stream, mg./liter
z_b = concentration of dichromate (as $Cr_2O_7^{2-}$) in effluent stream, mg./liter
z_f = concentration of dichromate in collapsed foam stream, mg./liter
z_1 = concentration of dichromate in combined feed stream, mg./liter
θ = liquid detention time in flotation column, min.

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