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Foam Separation of Phenolate, Orthophosphate, and Dichromate; Batch and Continuous, Multicolumn Operation

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Summary

Results in terms of residual ratios are compared for the batch foam separation from aqueous solution of phenolate, orthophosphate, and dichromate, using a cationic surface-active agent. Effects of pH and of initial surfactant concentration are considered and dichromate is most readily separated.

For the single-column foam separation of dichromate in a continuous flow unit, residual ratios are minimized at a feed dichromate concentration of 60 mg/liter, for feed surfactant/dichromate ratios ranging from 3 to 4 g/g. The performances of series, multicolumn units have been calculated in terms of various parameters for feed dichromate concentrations of 25, 50, and 100 mg/liter. Better results for single (and multiple) columns could be achieved by using a greater foam height, with the feeds entering at the midpoint of the column of foam.

The foam separation of anions from aqueous solution holds promise for the treatment of industrial wastes, not only enabling the removal of objectionable materials from the effluent but also permitting the recovery of specific anions in a concentrated, collapsed foam stream. The concentration of anions from extremely dilute solutions may allow accurate analyses for objectionable or toxic materials. Phenol (*1,2*), orthophosphate (*3*), and dichromate (*4–6*) have been foam-separated with a cationic surfactant, employing batch operation. Dichromate (*6,7*) has been foam-separated using a continuous flow unit. In these studies, independent variables have included feed anion concentration, feed surfactant concentration, pH, the presence of interfering anions, gas flow

rate, detention time, and feed position. Upon contacting phenol or phosphate with the cationic surfactant, all species remained dissolved in solution; the mechanism of the foam-separation process involved either the formation of a soluble, surfactant-anion complex which was adsorbed at the air–aqueous solution interfaces of the foam-producing bubbles or the adsorption of the surfactant at the interfaces followed by the electrostatic attraction between the surfactant and the oppositely charged anions. Upon contacting dichromate with the cationic surfactant, a second phase was formed consisting of colloidal-size particulates; the surface-active particulates were then absorbed at the bubble interfaces and floated from solution.

The objective of this study is, first, a comparison of the residual ratios obtained from the batch foam separation of phenolate, orthophosphate, and dichromate, including the effects of pH and of the initial surfactant concentration; and, second, the establishment for the first time of the feasibility of multicolumn, continuous-ion flotation of dichromate for the removal and recovery of hexavalent chromium.

BATCH FOAM SEPARATION OF PHENOLATE, ORTHOPHOSPHATE, AND DICHROMATE

Experimental

A schematic diagram of the experimental apparatus used is presented as Fig. 1. Details of the apparatus and procedure have been reported previously (*1–6*). The filtered nitrogen gas was saturated with water, metered with a calibrated rotameter, and passed through diffusers of approximately 50 μ porosity. For phenolate and orthophosphate, the nitrogen rate was about 400 ml/min at 25°C and 1 atm; for dichromate a nitrogen rate of 4250 ml/min was required, owing to decreased foam volumes produced by dichromate and to the multiple surfactant-addition method that was employed. For each experiment 2 liters of initial solution were prepared containing phenol, monobasic potassium phosphate, or potassium dichromate, and the pH was adjusted with potassium hydroxide, sodium hydroxide, or hydrochloric acid. The initial solution was placed in the column, varying concentrations of ethylhexadecyldimethylammonium bromide (EHDA-Br), a cationic surfactant, were added, and the nitrogen flow was begun. Foam was

collected continuously and each experiment was terminated after all foaming had ceased; in the case of dichromate, additional quantities of EHDA-Br (which are included in the initial concentrations presented below) were added during the experiment. After completion, the volume of the residual solution was measured, and the residual concentrations of EHDA-Br and of phenol, orthophosphate, or dichromate were determined.

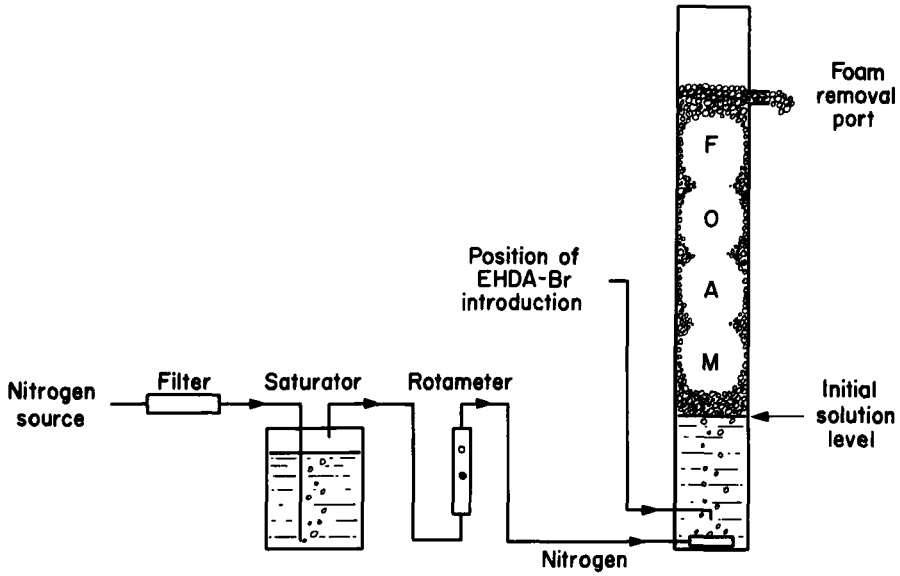

FIG. 1. Diagram of experimental apparatus for batch studies.

A Comparison

The effect of pH on the foam separation of the three anions is given in Fig. 2, in terms of the residual ratios. The concentration of the anion in the residual solution is given by z_r and that in the initial solution by z_i; the volume of the residual solution is V_r and that of the feed solution, V_i, always 2 liters. The residual ratio represents the weight of anion (phenolate, orthophosphate, or dichromate) *not* removed by foam separation (left in the residual solution) to that initially present; a value of 1.0 indicates no separation, a value of 0.0 indicates complete separation. The separate ordinate scale is needed for the dichromate because of the considerably better separations which were obtained. (The initial phosphate concentration is as PO_4, phenol as C_6H_5OH, and dichro-

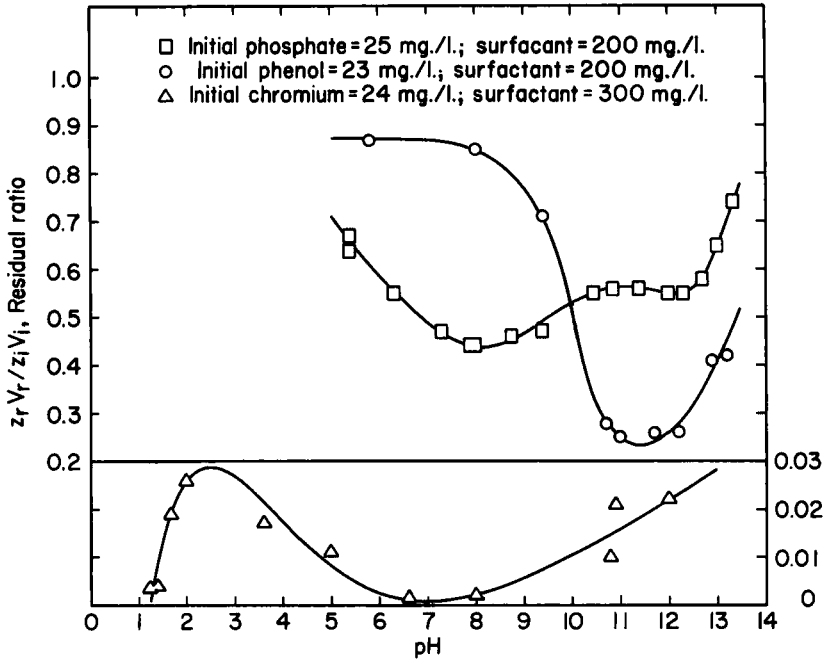

FIG. 2. Relations between residual ratios and pH for three anions.

mate as Cr.) Considering the magnitudes of the scales, pH had a much smaller effect on the foam separation of dichromate than it did on the foam separation of phenolate and orthophosphate. Probable reasons for the minima and maximum in the curves for phenolate and orthophosphate have been reported (*1,3*); they involve the interconversion of species and interferences from hydroxide. For phenol, the pH must be elevated to approximately 11 before the ionized phenolate form predominates.

The effect of variations in the initial surfactant concentration is presented in Fig. 3 for 3.5×10^{-4} *M* solutions of the three anions, each at constant pH. The residual ratio for each anion decreases exponentially with increasing EHDA-Br concentration. At a given EHDA-Br concentration the residual ratio for dichromate is lower than that for phenolate, which in turn is lower than that for orthophosphate. The differences clearly become considerably greater, particularly for dichromate, as the initial EHDA-Br is increased. It appears that if the initial EHDA-Br were decreased to about 150 mg/liter the residual ratio for dichromate would be greater than that for the others; this would be brought about by the ex-

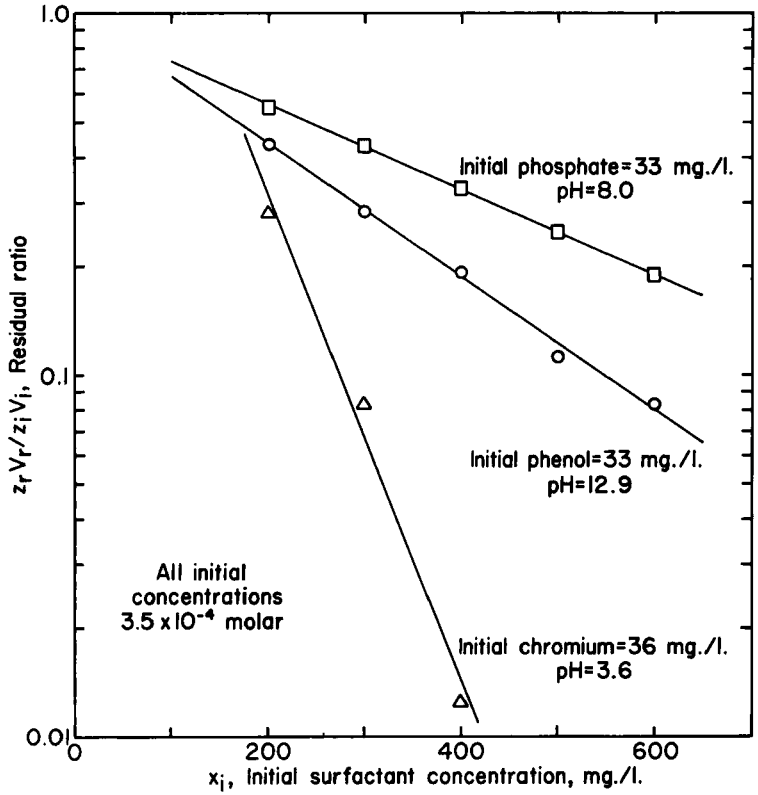

Fig. 3. Relations between residual ratios and initial surfactant concentrations for three anions

tremely small foam volume that would be produced with dichromate which decreases foamability at the low EHDA-Br concentration.

Comparing the three anions, the foam separation of dichromate appears to be, by far, the most promising process. As a result, further studies of dichromate have been conducted on a continuous-flow basis, which would be the only feasible mode of operation for industrial waste treatment.

CONTINUOUS FOAM SEPARATION OF DICHROMATE; MULTICOLUMN OPERATION

Experimental

A schematic diagram of the apparatus used in studies of the continuous foam separation of dichromate is presented as Fig. 4.

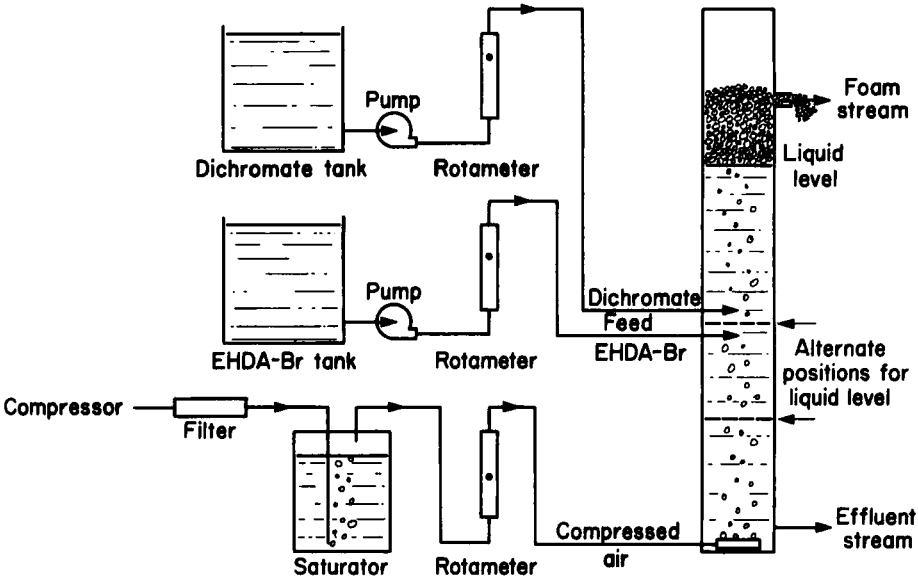

FIG. 4. Diagram of experimental apparatus for continuous dichromate studies.

The solutions of dichromate and 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) and of EHDA-Br ranging from 30 to 400 mg/liter. All the results are discussed considering a combined feed stream entering the column, and all feed concentrations are given on the basis of one combined feed stream. The pH of the combined feeds was 5.2. 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. The combined feeds entered the solution at approximately the midpoint and the foam stream was continuously removed from a port located 15.2 cm above the liquid level (foam-solution interface). In some later experiments, the feed position and foam height were varied. Compressed air was diffused through the solution by means of a 20-μ, porous metal aerator. After start-up, approximately 2.5 hr was required to reach steady state; then the effluent and collapsed foam flow rates were meas-

ured volumetrically, and effluent samples were taken and analyzed for dichromate and for EHDA-Br.

Single-Column Operation

Results have been reported (6,7) for the effect of the feed concentration of dichromate (z_1), the ratio of EHDA-Br to dichromate in the feed (x_1/z_1), detention time, feed rate (L), air rate, and foam height and feed position upon the dichromate concentration in the stripped effluent stream (z_b), upon the EHDA-Br concentration in the stripped effluent stream (x_b), and upon the flow rate of the stripped effluent stream (B).

A useful parameter for a description of the efficiency of a continuous foam-separation process is the residual ratio, z_bB/z_1L, the weight of dichromate in the effluent stream divided by that in the feed stream. For an air rate of 1500 ml/min and a detention time of 40 min, results are presented in Fig. 5. The weight-feed ratios,

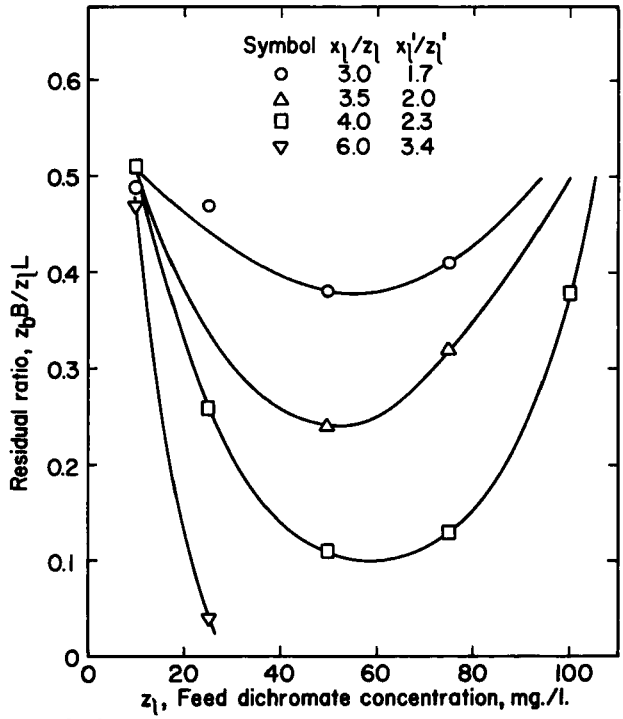

FIG. 5. Residual ratios obtained with various surfactant/dichromate feed ratios, continuous operation.

x_1/z_1, are varied from 3.0 to 6.0 (from 1.7 to 3.4 on a mole basis). Theoretically 2 g moles of the monovalent EHDA cation are required to react with each gram mole of the divalent dichromate anion. Minima in the curves are obtained at about 55 to 60 mg/liter of dichromate in the feed. The selection of the proper feed ratio would depend on the effluent concentration of dichromate required and on the magnitude of the effluent stream required. For these experiments z_b/z_1 ranged from 0.28 to 0.53, x_b/x_1 from 0.10 to 0.25, and B/L from 0.16 to 0.98. The residual ratios for EHDA-Br, x_bB/x_1L varied from 0.03 to 0.21, consistently being less than those for dichromate.

Multicolumn Operation

Although the experimental data were obtained from a single foam-separation column (*6,7*), they may be utilized readily to establish the performance obtainable from a multicolumn, series unit. In such a unit, the effluent 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

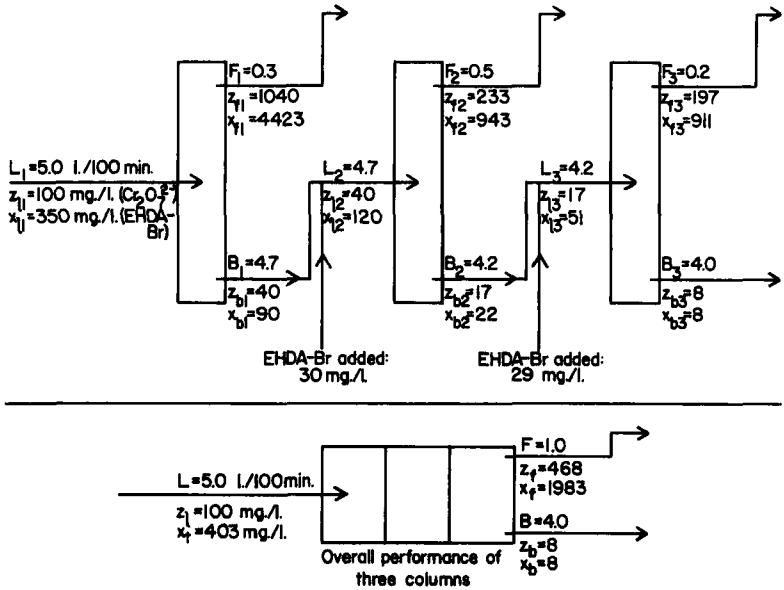

FIG. 6. Multicolumn performance for a 100 mg/liter dichromate feed.

third, etc. Of course, additional surfactant would have to be added to the feed to each column, because the concentration of surfactant in the effluent from the first column would not be sufficient for foam separation in the second column, etc. The collapsed foam streams from the series of columns could be combined or subjected to further treatment individually. A typical performance for a three-column unit is shown in schematic diagram as Fig. 6. The concentration of dichromate in the foam is designated z_f, the concentration of EHDA-Br in the foam, x_f, and the flow rate of the foam stream (liquid), F. The feed stream contains 100 mg/liter of dichro-

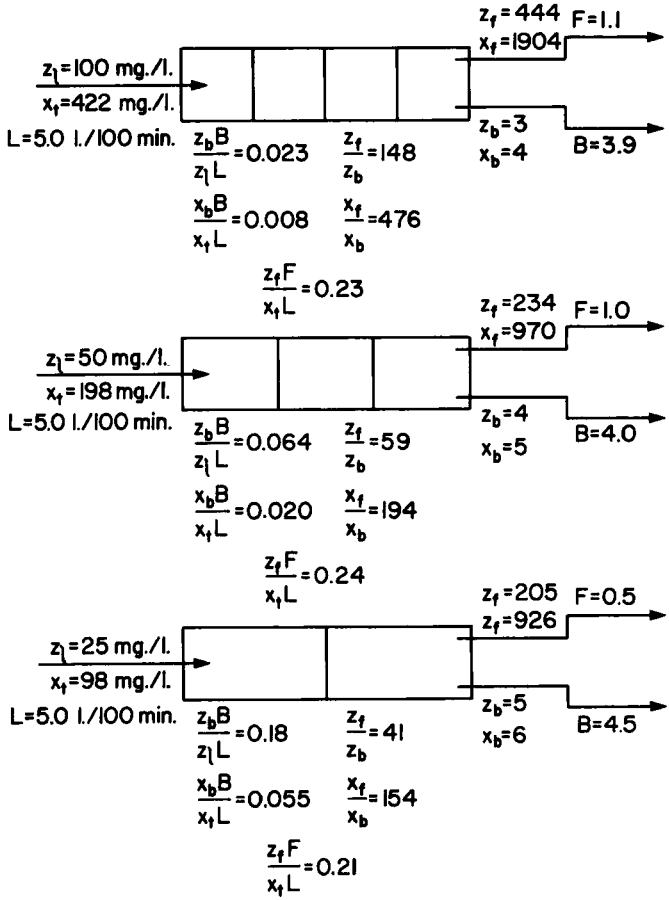

FIG. 7. Over-all multicolumn performances.

mate, to which are added 350 mg/liter EHDA-Br, and enters the first column at a rate of 5.0 liters per 100 min. The air rate is 1500 ml/min and the detention time is 40 min. To the effluent from the first column are added an additional 30 mg/liter EHDA-Br to obtain an EHDA-Br: dichromate ratio in the feed to the second column of 3.0. In the second column operation is again at an air rate of 1500 ml/min and detention time of 40 min. At the bottom of Fig. 6, the over-all performance of the three-column unit is given, assuming that the three collapsed foam streams are combined and that the total EHDA-Br added in the feed streams to the three columns is given on the basis of a single addition to the feed to the first column (x_t). The dichromate residual ratio for this over-all unit would be $z_bB/z_1L = 0.064$. For a single column with $z_1 = 100$ mg/liter and $x_1/z_1 = 4.0$ (Fig. 5), the residual ratio would be 0.39.

Over-all, multicolumn performances for four columns and a dichromate feed concentration of 100 mg/liter, for theee columns at $z_1 = 50$ mg/liter and for two columns at $z_1 = 25$ mg/liter, are given in Fig. 7. The objective in each foam separation process is the reduction of the effluent dichromate concentration to 5 mg/liter or less. For each operation there are given the dichromate residual ratio, the EHDA-Br residual ratio, the dichromate enrichment ratio (z_f/z_b), the EHDA-Br enrichment ratio (x_f/x_b), and the weight of dichromate recovered per unit weight of EHDA-Br fed (z_fF/x_tL). In each case, about $\frac{1}{4}$ g dichromate is recovered per gram of EHDA-Br fed. Of course, different numbers of columns could be utilized, depending upon the objective of the foam-separation process.

Effect of Foam Height and Feed Position

It is quite likely that further improvements in the multicolumn performances could be obtained by modifications in the operational conditions employed in the individual columns. It has been shown that variations in detention time and air rate (6,7) have a small effect on the separation that would be achieved. In Fig. 8 the effects on single-column operation of changing the foam height and feed position are indicated. In each experiment the air rate was 3000 ml/min and the detention time was 80 min; the feed concentration of dichromate was 50 mg/liter and the two feeds entered at a combined rate of 0.025 liter/min. With the column at the left, the foam height was maintained at 42 cm above the liquid level and the feeds entered the column through glass tubes 52 cm above the

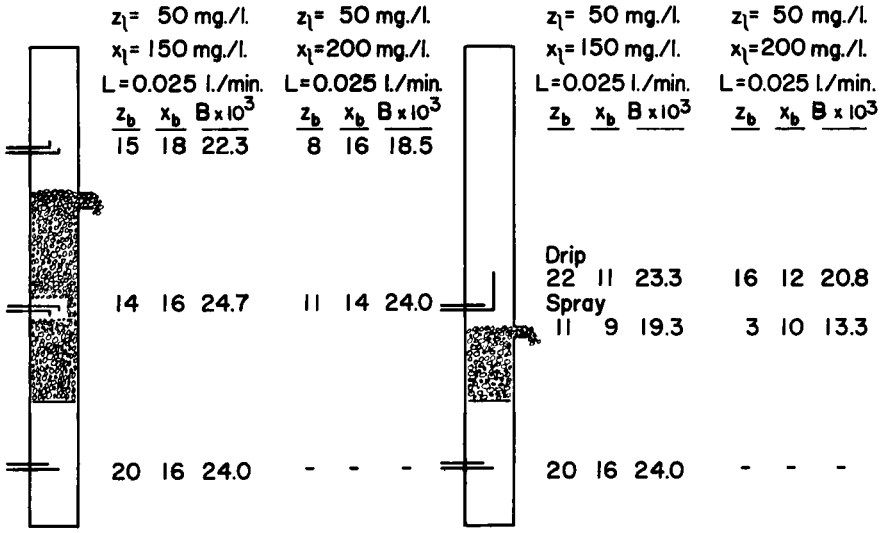

FIG. 8. Effect of variable feed position and foam height.

level (10 cm above the foam-removal port), 20 cm above the level, or in the middle of the solution (about 15 cm below the level). The best results are achieved at the midpoint; the effluent dichromate concentration is comparable to feed at the top, but what is more important, a higher effluent rate is achieved than with feed at the top. A much richer foam stream would result with feed at the midpoint.

With the column at the right, the foam height was maintained at 15 cm above the interface, and the feeds were either sprayed through glass nozzles or fed through ordinary glass tubes (dripped) 20 to 30 cm above the interface (5 to 15 cm above the foam port), or fed at the middle of the solution. Spraying of the feed produces lower effluent concentrations of dichromate, but at the expense of considerably higher foam rates and more dilute foam streams. Going from the left column to the right column (drip) at constant feed position (midpoint), better results, in terms of lower effluent dichromate concentrations and higher effluent flow rates, are achieved with the high column of foam. Operation with the right column with feed into the solution is that considered in the above sections on single and multicolumn operation, but at a higher air rate and longer detention time. Owing to the high effluent rate and reasonable values for the effluent concentrations of both dichromate

and EHDA-Br, it appears that the left column (high foam) with feed at the midpoint provides the best performance.

CONCLUSIONS

A comparison is presented of the batch foam separation of phenolate, orthophosphate, and dichromate, including the effects of pH and of initial surfactant concentration. Dichromate is least influenced by pH, and for a given surfactant concentration, considerably better results are achieved than for phenolate or phosphate.

For the single-column foam separation of dichromate in a continuous-flow unit, residual ratios go through minima at a feed dichromate concentration of about 60 mg/liter, for surfactant: dichromate feed ratios ranging from 3 to 4 g/g. Combining several columns in series, multicolumn performances have been calculated. With a four-column unit, a 100 mg/liter dichromate feed can be reduced to 3 mg/liter, using 422 mg/liter of surfactant. The combined, collapsed foam stream contains 444 mg/liter of dichromate and 1904 mg/liter of surfactant. It appears that even better results could be achieved by using a greater foam height, with the feeds entering at the midpoint of the column of rising foam.

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Nomenclature

Batch studies

V_i	volume of initial solution, liters
V_r	volume of residual solution (after foaming), liters
x_i	concentration of surfactant, EHDA-Br in initial solution, mg/liter
z_i	concentration of phenolate, orthophosphate (PO_4), or dichromate (Cr) in initial solution, mg/liter
z_r	concentration of phenolate, orthophosphate (PO_4), or dichromate (Cr) in residual solution, mg/liter

Continuous studies

B flow rate of effluent stream, liters/min or liters/100 min
F flow rate of collapsed foam stream, liters/min or liters/100 min
L flow rate of combined feed stream, liters/min or liters/100 min
x_b concentration of surfactant, EHDA-Br in effluent stream, mg/liter
x_f concentration of surfactant, EHDA-Br in collapsed foam stream, mg/liter
x_1 concentration of surfactant, EHDA-Br in combined feed stream, mg/liter
x_1' concentration of surfactant, EHDA-Br in combined feed stream, moles/liter
x_t concentration of surfactant, EHDA-Br fed to multicolumn system based on all surfactant added in feed to first column, mg/liter
z_b concentration of dichromate (Cr_2O_7) in effluent stream, mg/liter
z_f concentration of dichromate (Cr_2O_7) in collapsed foam stream, mg/liter
z_1 concentration of dichromate (Cr_2O_7) in combined feed stream, mg/liter
z_1' concentration of dichromate (Cr_2O_7) in combined feed stream, moles/liter

REFERENCES

1. R. B. Grieves and R. C. Aronica, *Intern. J. Air Water Pollution*, **10**, 31 (1966).
2. R. B. Grieves and R. C. Aronica, *Nature*, **210**, 901 (1966).
3. R. B. Grieves and D. Bhattacharyya, *Separation Sci.* **1**, 81 (1966).
4. R. B. Grieves and T. E. Wilson, *Nature*, **205**, 1066 (1965).
5. R. B. Grieves, T. E. Wilson, and K. Y. Shih, *A.I.Ch.E.J.*, **11**, 820 (1965).
6. R. B. Grieves, K. Y. Shih, T. E. Wilson, and S. M. Schwartz, *Proceedings of the 20th Purdue Industrial Waste Conference, Eng. Extension Ser. 118*, p. 197, July 1965.
7. R. B. Grieves and S. M. Schwartz, *A.I.Ch.E.J.*, **12**, 746 (1966).

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