Continuous, Dissolved-Air Ion Flotation of Hexavalent Chromium

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An experimental investigation is presented of the ion flotation of dichromate from aqueous solution with a cationic surfactant and using a non-ionic polymer as a flocculant aid. A dissolved-air, continuous flow unit is used (with a surfactant-dichromate premix period of 1 hr.) with a feed rate of 120 liters/hr. of a stream containing from 25 to 100 mg./liter of dichromate. Within the ranges of the variables studied, optimum results are obtained with a molar surfactant to dichromate feed ratio of about 2, a feed polymer dosage of about 3% of the dichromate feed concentration, a recycle rate 200% of the feed rate, and a column detention time of 35 min. With an air requirement of 0.043 liters of air (at STP)/liter of feed delivered at 40 lb./sq. in. gauge, feed streams containing from 25 to 100 mg./liter of dichromate can be readily reduced to 10 mg./liter of dichromate and 30 mg./liter of surfactant. The primary advantage of the process lies in the concentration of dichromate, surfactant, and polymer in a small liquid volume of collapsed foam, less than 1% of the total feed throughput. Foam concentrations are of the order of 10,000 to 20,000 mg./liter of dichromate.

Inorganic and organic ions may be removed and concentrated from aqueous solution by the addition of a surface-active agent that has a hydrophobic part (containing the long hydrocarbon chain) of opposite charge to the ion to be separated. A finely divided, insoluble compound is formed which is surface active and which may be floated to the surface of the solution and carried into a foam or froth above the solution by attachment to rising air bubbles. An extensive discussion has been presented by Sebba (*14*), and many recent studies have been reported (*2*, *10* to *12*), including some modifications.

Hexavalent chromium in the form of chromate and/or dichromate is found in a multiplicity of industrial wastes, being produced mostly from those metal finishing industries involved with the cleaning of metals or with chromeplating. Treatment of spent baths and rinses for chromate recovery and of plant effluents to meet state requirements involves solutions containing from 5 to 10 to several thousand milligrams per liter of hexavalent chromium. Chemical reduction followed by precipitation and ion exchange is at present the most commonly used treatment technique.

Dispersed-air (diffused) ion flotation of dichromate has been studied previously, both in a batch unit (*6*, *8*, *9*) and in a continuous-flow unit (*5*, *7*). In the batch investigations, 2-liter feed solutions containing from 5 to 99 mg./liter of dichromate were treated with a cationic surfactant, ethylhexadecyldimethylammonium bromide (EHDA-Br). The dichromate-surfactant particulates that were floated were stoichiometric and had an approximate formula $[C_{16}H_{33}C_2H_5(CH_3)_2N]_2\,Cr_2O_7$. Most efficient operation was achieved with a molar feed ratio of EHDA ion to dichromate ion from 2.1 to 3.0, obtaining removal ratios (defined as the quantity of dichromate floated per unit quantity of dichromate in the feed) from 80 to 95%, but often at the expense of large quantities (liquid) of foam. The effect of interfering anions was established. The continuous-flow study utilized a virtually identical unit, with a 4-in. diameter flotation column containing sintered glass air diffusers of 50-micron porosity. Similar dichromate feed concentrations and molar feed ratios were employed, except that feed was continuously pumped to the column at rates from 1.5 to 6.0 liters/hr. and a continuous effluent (bottoms) and a continuous collapsed foam stream were removed. The effects of feed dichromate concentration, of molar feed ratio, of detention time, of air rate, and of variable feed position were established.

Dissolved-air flotation, based on the release of a pressurized flow in which air is dissolved, has been shown to be effective in particulate removal where dispersed air failed (*4*). Success was attributed to the fine air bubbles which adhered more readily to the insoluble matter. Vrablik (*15*) reported a mean bubble diameter of 80 microns released from a 50 lb./sq. in. gauge solution, compared with a typical diameter of 1,000 microns in dispersed-air flotation. In other flotation applications, larger bubbles may be more beneficial.

The objective of this study was to evaluate, for the first time, the efficiency of a dissolved-air ion flotation process, operated on a continuous-flow basis. A flotation unit was designed, built, and tested for feed rates of 30 to 120 liters/hr. The effects on the removal of dichromate and surfactant are established of the utilization of a nonionic polymer as a flocculant aid, of the percent recycle, of detention time, of the dichromate feed concentration, and of the molar surfactant to dichromate feed ratio. Relative optima are determined and a comparison is made with a laboratory-scale, dispersed-air unit.

EXPERIMENTAL APPARATUS AND PROCEDURE

A schematic diagram of the experimental apparatus is presented as Figure 1. Equipment included a Lucite column 11 in. in diameter and 12 ft. in height; dichromate-surfactant-feed supply tank with polyethylene liner; polymer supply bottle; polyester-lined pressure tank for air dissolution, 1 ft. in diameter and 2 ft. long; plastic overflow tank, rotameters, pumps, and other control fittings. All liquid carrying conduits were Schedule 80 PVC plastic pipe, except for Tygon tubing used for feed and polymer transport. The extensive employment of plastic was to retard surface adsorption rather than to control corrosion.

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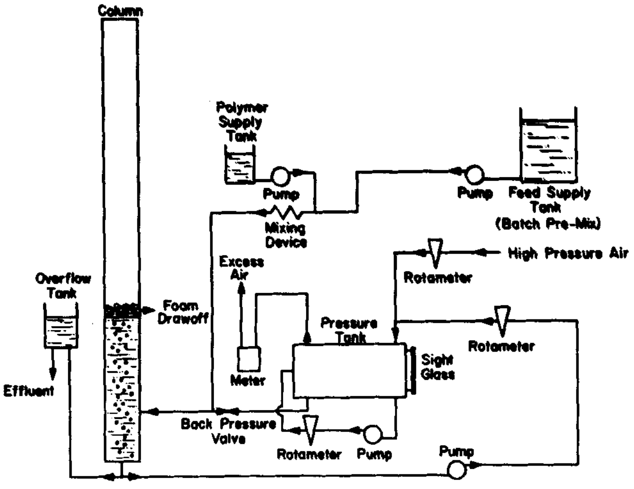

Fig. 1. Schematic diagram of experimental apparatus.

The feed supply tank stored sufficient dichromate-surfactant solution for a complete run; the capacity was 190 liters (50 gal.). Because of the time delay in precipitate formation, particularly at high surfactant to dichromate feed ratios, the feed was held 1 hr. after preparation before a run. The feed solution consisted of distilled water, potassium dichromate (C.P.), and EHDA-Br (technical). Dow N12 was the non-ionic, organic polymer used as a flocculant aid. Polymer and feed streams were blended in a mixing device to enhance contact before continuing to the column. The mixing device comprised a series of four constricted fittings, each diverting the flow 90 to 120 deg.

The liquid level in the column was maintained at 4 ft. above the base by the overflow tank. Detention times ranging from 36 to 131 min. were obtained by varying the feed rate from 121.8 to 31.2 liters/hr. Both the recycle and effluent streams were removed at the bottom of the column. In the recycle portion of the underflow, air was dissolved at 40 lb./sq. in. gauge and the stream was returned to the column. At the column inlet, located 1.5 ft. above the base, the pressurized recycle expanded against the liquid head with the formation of bubbles from the precipitated air. The dichromate-surfactant-polymer feed, consisting of particulates which had been flocculated, was introduced to the column at this point.

Air was dissolved in the recycle liquid in the pressure tank. The liquid level was regulated at approximately one-half the capacity of the tank. Recirculation of the tank contents at a rate of 4 liters/min. facilitated the dissolving of air. This is one of the many methods used currently in dissolved air flotation processes and approximates the approach employed by the Komline-Sanderson Engineering Corporation. The effective air flow rates to the column ranged from 1.32 to 7.50 liters/hr.; the concentration of dissolved air attained, as percent of saturation (*15*) varied from 40 to 57%, with an average of 49%.

Accumulated foam at the liquid surface was removed through a 1-in. port. This foam would not flow by gravity and had to be drawn off with a vacuum trap. Generally, one-half of the foam in the column was collected for analysis at the termination of each experiment. Effluent was sampled from the overflow tank at intervals corresponding to the displacement time. Displacement time is the calculated ratio of liquid volume in the column divided by the sum of the feed plus the recycle flow rates, and thus is indicative of the volumetric displacement rate in the column. Generally steady state was achieved within 1 to 3 hr. after start-up. Each sample was analyzed for dichromate content; the sample when steady state was first found to exist and the subsequent samples were averaged for the steady state concentration for that run. The sample which yielded a value of dichromate concentration closest to the average was analyzed for surfactant content. All runs were made at approximately 25°C.

Dichromate was analyzed as chromium by atomic absorption spectrophotometry with a Perkin-Elmer Spectrophotometer Model 303 (*1*). Foam samples were diluted 500 to 1 to bring their concentration within the range of the instrument. All results are presented as milligrams per liter of dichromate (Cr_2O_7). The concentration of EHDA-Br was determined in the effluent and foam stream by the procedure of Cross (*3*). A maximum aliquot of the sample was taken without exceeding a surfactant concentration of 30 mg./liter upon dilution to 50 ml. Flocculated surfactant-dichromate particulates produced erratic results in both the dichromate and surfactant determinations unless they were first dissolved. Solution was effected by the addition of concentrated nitric acid at 1% by volume of sample; the nitric acid provided no interference to the analysis. A specific analytic method for the non-ionic polymer, Dow N12, has not been developed thus far.

RESULTS AND DISCUSSION

Generally, results are considered in terms of the removal ratios $(z_1 - z_b)/z_1$ and $(x_1 - x_b)/x_1$. The concentrations of dichromate and of EHDA-Br in the feed stream are represented by z_1 and by x_1, respectively, and the concentrations in the effluent or bottoms stream are given by z_b and x_b, respectively. Actually the removal ratios should indicate the weight of dichromate or surfactant floated per weight in the feed, and therefore should include the feed and foam flow rates. However, for virtually every experiment the effluent flow rate was greater than 99.0% of the feed flow rate, and these ratios are adequate measures of the removals which were achieved by dissolved-air flotation.

Utilization of Polymer

The first series of runs was made to establish the effects of the additions of varying concentrations of the non-ionic polymer, Dow N12, to the feed stream. Results are given in Figure 2 for a feed dichromate concentration of 100 mg./liter, a molar surfactant to dichromate ratio of 2.7, a detention time of 36 to 37 min., and a recycle ratio of 200%. The polymer had little effect until its feed concentration was raised to about 3% of the feed dichromate concentration; then a sharp increase in both dichromate and surfactant removals could be noted, with the effect more pronounced for the dichromate. Considering two other experiments with all conditions held constant, except at a lower molar feed ratio of 2.0, flocculating with polymer at a dosage of 3.3% increased the dichromate removal from 0.80 to 0.89.

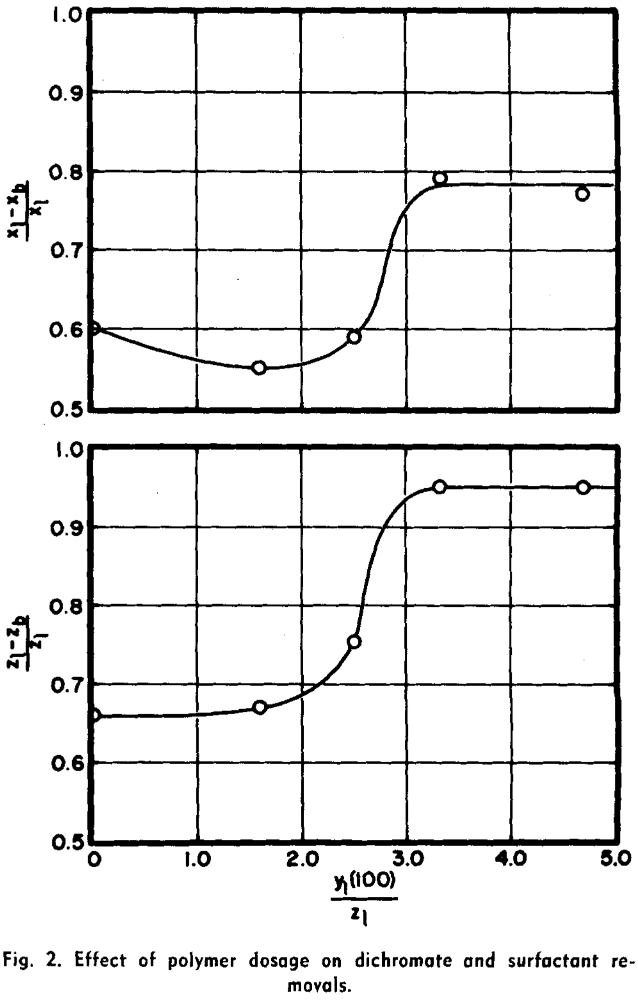

Fig. 2. Effect of polymer dosage on dichromate and surfactant removals.

A comparison can be made with a previous study (7) in which dispersed-air flotation with no polymer, a 4-in. column, a 40-min. detention time, and a molar feed ratio of 2.3 were employed. Dichromate and surfactant removals of 0.62 and 0.82 were achieved but at the expense of a foam stream 18% of the feed stream. The effluent dichromate concentration was 40 mg./liter, compared with values of 20 and 34 mg./liter obtained in this study.

In our dissolved-air study, addition of polymer brought about a marked flocculation of the dichromate-surfactant particulates into aggregates which were readily susceptible to air bubble attachment. Without polymer at a molar feed ratio of 2.7 the visual discernment of discrete particles was difficult. Apparently the "stringy" nature of the particulates was inefficient for air bubble adhesion. Colloid formation at a molar feed ratio of 2.0, but also without polymer, must differ somewhat because discrete particles were observable; this is probably the cause for greater dichromate removal than at a molar feed ratio of 2.7 (also without polymer).

For all additional experiments, the non-ionic polymer was added to the feed in a concentration of 3.25% of the dichromate concentration in the feed. Other polymers were not investigated.

Effect of Operating Variables

A second series of experiments was conducted to determine the effects of polymer blending, of surfactant-dichromate feed contact, of percent recycle, and of detention time. The feed concentration of dichromate was 100 mg./liter, the molar feed ratio was 2.7, except where indicated at 2.0, and the polymer dosage was 3.25% of the feed dichromate concentration.

Several runs were made, which are not reported, that produced inconsistent results; this occurred because of inadequate blending of the polymer with the preformed dichromate-surfactant particulates. Incorporation of the mixing device described previously rectified this condition. Two runs were made with all conditions held constant, except one was made without the device; an increase in dichromate removal from 0.89 to 0.97 was achieved by ensuring adequate contact with the polymer.

Each run was commenced 1 hr. after the surfactant and dichromate were first contacted. Two pairs of experiments at two sets of conditions were carried out with the 1-hr. contact compared with a 19-hr. contact and a 1-hr. contact compared with a 43-hr. contact. The longer contact periods produced increases in dichromate removals from 0.61 to 0.72 for one pair and from 0.89 to 0.92 for the other pair. Thus if they could be designed for, longer contact periods would produce better flotation results.

In a full scale unit, the premix period could be eliminated and completely continuous operation could be achieved with a feed supply tank of capacity several times that of the column.

The influence of percent recycle was determined by three experiments shown in the first part of Table 1. A slight improvement in dichromate and surfactant removals was achieved by increasing the recycle rate from 100 to 200% of the feed rate. However, there was a marked drop upon an increase to 275%. At the high value the displacement time of 10 min. was too short for satisfactory operation; the zone of formed air bubbles could be seen to extend down to the underflow and short circuiting of particles to the effluent probably resulted. At the longer detention time of 130 min. the increase from 140 to 200% again produced a slight improvement.

Removals were determined at detention times of 37, 77, and 131 min., at 200% recycle, as shown in the second half of Table 1. Maximum dichromate removal was achieved at about 77 min. with no further benefit at 131 min. Operation at 37 min. produced a decreased removal of both dichromate and surfactant compared with 77 min., but the decrease was not significant compared with the doubled column capacity at the short detention time. Two experiments at a lower molar feed ratio of 2.0 indicated no effect in shortening the detention time from 73 to 37 min. Similar behavior had been indicated with dispersed-air ion flotation in a 4 in. column (7); an increase in detention time beyond 40 min. did not affect the removals significantly.

TABLE 1. EFFECTS OF PERCENT RECYCLE AND OF DETENTION TIME

Feed dichromate, $z_1 = 100$ mg./liter
Molar feed ratio, $x_1'/z_1' = 2.7$
Detention time = 36 to 39 min.

Percent recycle	$\frac{z_1 - z_b}{z_1}$	$\frac{x_1 - x_b}{x_1}$
100	0.94	0.80
200	0.95	0.79
275	0.81	0.70
Detention time = 130 min.		
140	0.96	0.81
200	0.97	0.86

Feed dichromate, $z_1 = 100$ mg./liter
Molar feed ratio, $x_1'/z_1' = 2.7$
Percent recycle = 200

Detention time, min.	$\frac{z_1 - z_b}{z_1}$	$\frac{x_1 - x_b}{x_1}$
37	0.95	0.79
77	0.97	0.81
131	0.97	0.86

Effect of Feed Concentrations of Dichromate and Surfactant

A third series of runs was carried out to determine the effects of the molar feed ratio and of the feed concentration of dichromate on dissolved-air ion flotation. In each experiment the polymer dosage was 3.25% of the feed dichromate concentration, the recycle rate was 200% of the feed rate, and the detention time was 36 to 37 min.

The influence of 1.4, 2.0, 2.7, and 4.1 molar feed ratios on dichromate and surfactant removals is given in Figure 3. The maximum dichromate removal was 0.95 at a feed ratio of about 2.7. As it would be expected, the maximum surfactant removal was achieved at the lowest feed ratio.

For these experiments the molar ratio of surfactant in the foam to dichromate in the foam was 2.3, 2.5, 2.3, and 2.2 at the above feed ratios. All foam values were greater than the stoichometric 2.0 ratio that was determined previously (*8*) upon analysis of dichromate-surfactant particulates. However the quantity of excess surfactant (noncomplexed with the dichromate) was not large, particularly compared with that indicated in dispersed-air ion flotation (*7*). The feed ratios of 4.1 and 2.7 were 86 and 17% in excess of the corresponding foam ratios, while the feed ratios of 1.4 and 2.0 gave deficiencies of 39 and 20%. As expected, in the latter cases there was a deficiency of surfactant in the feed to effect reaction with the dichromate. However, a feed ratio closer to 2.0 than to 2.7 would be recommended, since the increased dichromate removal at 2.7 was not proportionate to the greater utilization of surfactant at 2.0. The diminished removal of dichromate at a feed ratio of 4.1 can be attributed to the presence of surfactant in too large an excess. The particulates may have been peptized into a stable colloid, as hypothesized by Sebba (*13*), or the excess surfactant may have competed with the surfactant-dichromate particulates for the air bubble interfaces.

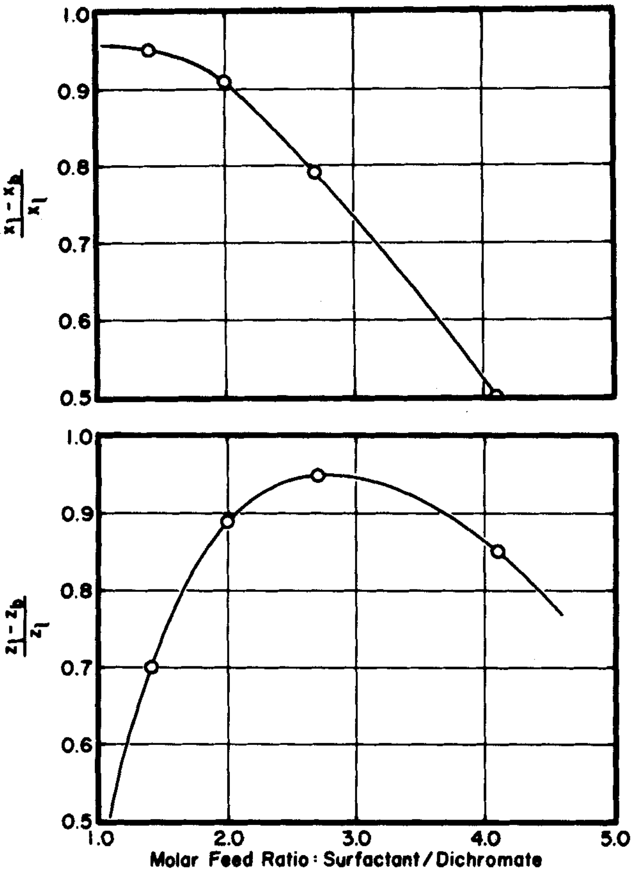

Fig. 3. Effect of molar feed ratio on dichromate and surfactant removals.

In additional experiments the feed concentration of dichromate was varied from 100 to 50 to 25 mg./liter, at the two feed ratios of 2.0 and 2.7. The effluent concentrations of dichromate were virtually independent of the feed concentrations, ranging from 4.9 to 5.7 mg./liter at the feed ratio of 2.7, and ranging from 9.8 to 11.2 mg./liter at the feed ratio of 2.0. The effluent surfactant concentrations increased with increased feed dichromate at the feed ratio of 2.7 but remained constant, ranging only from 28 to 31 mg./liter at the feed ratio of 2.0. These results may be contrasted directly to those reported for dispersed-air ion flotation without a polymer (7). The effluent dichromate concentration and surfactant concentration were both power functions of the feed dichromate concentration and were virtually independent of the feed ratio. The constant effluent dichromate concentrations achieved in this study indicate a limiting concentration that could be effected by the dissolved-air unit at the constant operating conditions investigated. The removal of both dichromate and of surfactant decreased as the feed concentration of dichromate was decreased.

The Foam

All the results reported have involved the effluent stream. A foam stream did not really exist, since it was taken from the column intermittently, and then only by the use of a vacuum trap. The total quantity of foam (collapsed, as liquid) formed during an experiment never exceeded 1.0% of the total feed throughput of 180 to 190 liters. An enrichment ratio can be calculated, defined as the concentration of dichromate in the total quantity of foam formed, z_f divided by the steady state concentration of dichromate in the effluent stream, z_b. The enrichment ratio is not as significant a variable as it would be in a dispersed-air ion flotation process in which a steady state foam stream would be removed; however it does provide a good measure of the total separation achieved.

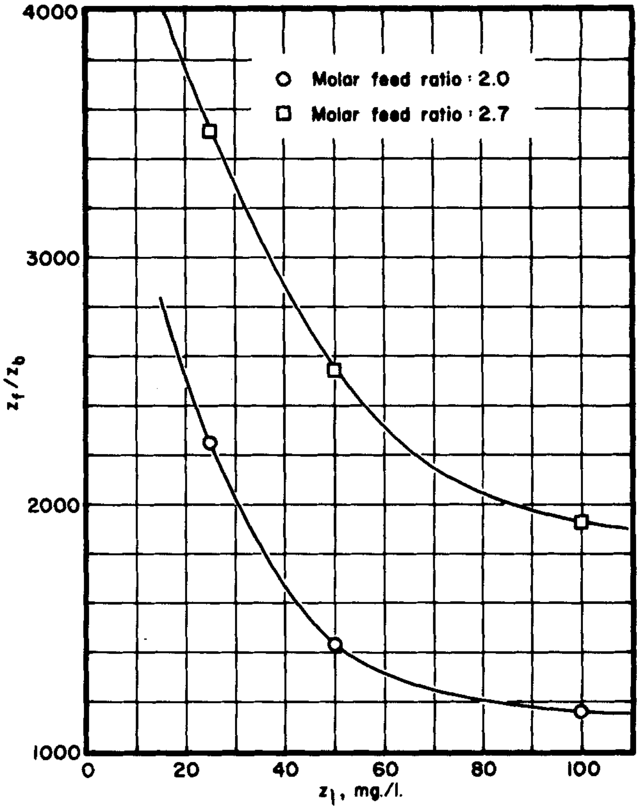

Fig. 4. Dichromate enrichment ratios.

At a feed dichromate concentration of 100 mg./liter, molar feed ratio of 2.7, polymer dosage of 3.25%, and percent recycle of 200, an increase of the detention time from 37 to 77 to 131 min. increased the dichromate enrichment ratio from 1,930 to 3,810 to 9,100. The greater detention times permitted the particles to be held longer before removal, producing more efficient drainage.

At feed ratios of 2.0 and 2.7, with a polymer dosage of 3.25%, percent recycle of 200, and detention time of 37 min., enrichment ratios are related to the feed dichromate concentrations in Figure 4. At a constant feed ratio, the enrichment ratio increased as the feed dichromate concentration was decreased, since the lower the quantity of total foam solids (dichromate-surfactant particulates), the greater the benefits of concentration factors such as drainage of water and compaction due to the rising air bubbles. Since the effluent dichromate concentration was independent of the feed dichromate concentration, the richer foam yielded a greater enrichment ratio. At a constant feed concentration of dichromate, an increase of the molar feed ratio from 2.0 to 2.7 produced an increased enrichment ratio. Foam concentrations were somewhat lower at the higher feed ratio, but this was more than offset by the lower effluent dichromate concentration to provide a greater enrichment ratio. Analogous to that stated above, the smaller quantity of dichromate in the foam at the lower feed ratio afforded the more concentrated foam.

CONCLUSIONS

The dissolved-air ion flotation of dichromate has been investigated in an 11-in. diameter flotation column with a continuous feed rate of 120 liters/hr. A surfactant-dichromate premix period of 1 hr. was used. A cationic surfactant, EHDA-Br, and a non-ionic polymer, Dow N12, were employed as flotation agent and flocculant aid, respectively. Within the ranges of the variables studied, optimum results were achieved with a molar surfactant to dichromate feed ratio of approximately 2, a feed polymer dosage of about 3% of the dichromate feed concentration, a recycle rate 200% of the feed rate, a detention time of about 35 min., the provision of adequate contact time between the dichromate and surfactant, and the provision of adequate mixing of the polymer with the dichromate-surfactant particulates. A typical air requirement was 5.1 liters (at STP)/hr., delivered at 40 lb./sq. in. gauge, or 0.043 liters air (at STP)/liter of feed. With these conditions, feed streams containing from 25 to 100 mg./liter of dichromate could be treated effectively, producing effluent streams containing 10 mg./liter of dichromate and 30 mg./liter of surfactant (or containing 5 mg./liter of dichromate with a feed ratio of 2.7). For the 100 mg./liter of feed, for example, the total of 10,800 mg. of dichromate could be concentrated in a liquid volume (collapsed foam) of 0.9 liters, producing a foam concentration of 12,000 mg./liter and an enrichment ratio of 1,200.

Compared with diffused-air ion flotation in a 4-in. column, also at a 40-min. detention time and molar feed ratio of 2, but with no polymer and a feed rate of 3 liters/hr., the air requirement would be 27 liters of air (at STP)/liter feed, delivered at 3 lb./sq. in. gauge. A 100 mg./liter dichromate feed could be reduced to 40 mg./liter and a 25 mg./liter feed to 11 mg./liter, but at the expense of foam stream rates from 3 to 16% of the feed rate.

The dissolved-air ion flotation of dichromate, with a polymer flocculant aid, appears to be particularly promising for dichromate removal and recovery. The dichromate (and surfactant and probably the polymer) can be concentrated in a very small volume of liquid; this volume leads to further steps for the economical recovery of dichromate and of surfactant.

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NOTATION

x_b = concentration of surfactant (EHDA-Br) in effluent stream, mg./liter
x_1 = concentration of surfactant in feed stream, mg./liter
x_1' = concentration of surfactant in feed stream, mole/liter
y_1 = concentration of polymer in feed stream, mg./liter
z_b = concentration of dichromate, as Cr_2O_7, in effluent stream, mg./liter
z_f = concentration of dichromate in foam, mg./liter
z_1 = concentration of dichromate in feed stream, mg./liter
z_1' = concentration of dichromate in feed stream, mole/liter

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A Predictive Theory for Diffusion in Mixed Solvents

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A relationship for the diffusion coefficient of a dilute species in a mixture of two solvents is developed. The result, based on the linear additivity of the frictional activation energy which is valid for completely miscible, nonassociated systems, predicts the diffusion coefficient of the solute in terms of the limiting values of the diffusion coefficient of the solute in each of the solvents, the limiting values of the solvent pair diffusion coefficient, and two thermodynamic factors. The equation is confirmed for some recent experimental data.

In systems consisting of more than two components, the characterization of the diffusion process is considerably more complex than that of the simple binary case in which only one properly defined diffusion coefficient is required. This, of course, is due to the appearance of interactions between the several flows, and, in general these effects are more pronounced the more nonideal the system.

In order to describe adequately the diffusional behavior of such systems, one must adopt more general linear relations in which the flux of any species depends on all of the independent concentration gradients. In certain regions of the composition field of multicomponent systems, a simpler description is possible. A trivial example is the case in which all species are dilute in a single solvent. In this case the matrix of multicomponent diffusion coefficients reduces to diagonal form, the flux of each dilute