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Studies on the Low Gas Flow Rate Foam Separation of U(VI) from Sulfate Media

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Abstract

The two low gas flow rate foam separation processes, "ion and precipitate flotation," were investigated for the separation of hexavalent uranium from dilute sulfate solutions at different conditions of pH, gas flow rate, and concentration of uranyl, collector, and sulfate ions using the anionic collector sodium lauryl sulfate and the two cationic collectors cetyl trimethyl ammonium bromide and lauryl amine hydrochloride. No significant removal could be achieved with sodium lauryl sulfate, whereas cetyl trimethyl ammonium bromide and lauryl amine hydrochloride gave high uranium recoveries. Precipitate flotation was generally less sensitive than ion flotation to all the factors tested, and both the rate and ultimate removal were much greater. Lauryl amine hydrochloride causes a shift of the initial pH at which precipitate flotation begins to lower values, and the extent of shifting depends on the collector concentration. The reasons for this shift as well as the effects of the different factors on the flotation results are discussed.

INTRODUCTION

The term "low gas flow rate foam separation" implies two flotation techniques (ion flotation and precipitate flotation) which, in contrast to foam fractionation and froth flotation, utilize low rates of gas flow (*1*). In these low gas flow rate processes the separation occurs only at the gas–liquid interface and not in the foam phase. Ion flotation was introduced by Sebba in 1959 (*2*). Sebba's technique was partly based on the earlier work of Langmuir and Schaefer (*3*) concerning the adsorption of metallic ions on monolayers of stearic acid. In the ion flotation technique a surfactant ion of a charge opposite to that of the ion to be floated is added to the solution in a stoichiometric amount and well mixed so that an insoluble soap is formed between the surfactant ion and the ion to be separated. The insoluble soap is then levitated to the surface in the form of a scum by means of a gentle stream of gas bubbles. According to Sebba (*4*), the collector must be introduced in the form of ions and not as micelles, and the final collector-ion product must be insoluble in water. This technique, as originally described by Sebba, is a true flotation process since it involves the foam separation of a heterogeneous system. However, it is sometimes possible to float a soluble ion-collector product, and the technique in this case can be called homogeneous ion flotation (*1*).

Precipitate flotation was introduced in 1963 by Baarson and Ray (*5*). In this technique the metal ion to be removed is precipitated prior to the addition of the collector. Precipitation may be accomplished by either pH adjustment or by adding a suitable chemical. The precipitate flotation process involves the foam separation of purely heterogeneous systems.

The fact that uranyl ion can form anionic complexes of the type $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$ with dilute sulfuric acid solutions (*6*) makes it probable that uranium(VI) can be floated at low pH values in the form of anionic complexes using cationic collectors. By the addition of alkali to the uranyl solution, the insoluble hydroxide $UO_2(OH)_2 \cdot H_2O$ (*7, 8*) is produced via soluble hydrolysis intermediates, and it is expected that the hydroxide can be floated by the precipitation technique. On further addition of alkali to the uranyl solution the pH passes into the basic region and the diuranate is obtained when the ratio of NaOH to the uranium present is 3.0 or greater (*9*). The hydrolysis intermediates have been extensively studied by many investigators (*8, 10–15*) and a variety of formulas have been proposed. Since ion flotation depends on the electrostatic attraction between the unlike charges of the ion to be floated and that of the collector, the success or failure of a certain group of collectors to float uranium at the different pH values may throw some light on the nature of the hydrolysis species present in solution.

However, although Sebba (*4*) has demonstrated the ion flotation of uranium from sulfuric acid solutions with cationic collectors, Skrylev and Mokrushin (*16*) removed small amounts of uranium from waste waters by precipitating with potassium ferrocyanide and floating the uranyl ferrocyanide precipitate, and Rabrenović (*17*) used an ordinary flotation cell and a combination of cationic collector and liquid ion exchanger and succeeded in recovering it from leach liquors, the literature still lacks a thorough and systematic study of both ion and precipitate flotation of uranium. The aim of this work is, therefore, to investigate the low gas flow rate foam separation of hexavalent uranium from sulfate solutions and to find the effects of the different factors on the process.

EXPERIMENTAL

Apparatus and Reagents

The flotation system used consisted of a pure nitrogen cylinder connected to a flotation cell through a fine pressure reduction unit, filter flasks containing baryta solution and distilled water, and an oil manometer. The flotation cell itself was supported over a filter flask and was made of a No. 4 sintered glass disk of 7.0 cm diameter fused to a Pyrex glass column of about 27 cm height, drawn at the bottom into the form of a funnel.

For the experimental work described, a stock solution of 0.1 *M* uranyl sulfate was prepared from an Analar sample. The exact concentration of uranyl ion in this stock solution was determined gravimetrically by the 8-hydroxyquinoline method (*18*). From this stock, more dilute solutions were prepared by appropriate dilutions. Solutions of known concentration of A.R. sulfuric acid, sodium sulfate, and CO_2-free sodium hydroxide were used to provide the sulfate ions or to adjust the pH. Since hexavalent uranium can form anionic carbonate complexes (*19*) in the presence of carbonate ion, freshly boiled distilled water was used for the solution preparation throughout the whole work. For the same reason the N_2 gas was passed through baryta solution before being introduced into the flotation cell.

The collectors sodium lauryl sulfate (NaLS) and lauryl amine (LA) were provided by Fluka, whereas cetyl trimethylammonium bromide (CTAB) was a BDH product. The lauryl amine was converted to the hydrochloride (LACl) by dissolution in dry ethyl ether and passing dry HCl gas. The salt was then filtered, washed with dry ether, and the excess ether evaporated under vacuum. The collector solutions were freshly prepared daily and the collectors themselves were evaporated twice with absolute ethyl alcohol before dissolution to convert any micelles to the ionic form as recommended by Sebba (*4*). Absolute ethanol was used as solvent for the dissolution of the collectors as well as frother. One milliliter of alcohol per 450 ml uranyl solution was used except for collector concentrations higher than 6×10^{-4} M where 3 ml were used to ensure complete dissolution of the collector. Since NaLS is not soluble in absolute ethanol, a 50% by volume solution of ethanol and freshly boiled distilled water was used as the solvent to allow the simultaneous addition of collector and frother.

General Procedure of Flotation

A known aliquot of the standard uranyl sulfate solution was quantitatively transferred to a 500-ml volumetric flask and diluted to about 450 ml with distilled freshly boiled water. The calculated amount of Na_2SO_4 and H_2SO_4 or NaOH that would give the desired sulfate strength and pH were then added, and the solution made to volume with freshly boiled distilled water, the pH measured and adjusted if necessary, and the solution left for about 10 min before transferring to the flotation cell. The flotation procedure adopted was similar to that described by Rubin et al. (*1*) and consists in transferring 450 ml of the uranyl solution to the flotation cell and passing N_2 gas at a rate (R) of 27 cm^3/min except when specified. The pH of the solution in the cell was measured using a Dr. Langé model VI pH-meter and a combined glass electrode. An aliquot was then withdrawn for uranium analysis. The solution of collector in ethyl alcohol was injected with a syringe in one injection while vigororously stirring the solution. That instant was recorded as the zero time. The foam was left in the cell except when it was too excessive, in which case the uppermost layer was skimmed at regular time periods to prevent flooding. Samples of the bulk solution were withdrawn at predetermined intervals for uranium determination and pH measurement. The percent uranium was determined either polarographically or fluorimetrically according to its concentration, after destroying the organic matter. For the polarographic determination, the catalytic nitrate wave method (*20*) was applied using a pen recording Radiometer polarograph type PO3m. The fluorimetric analyses were carried out by the aid of a Caratom fluorimeter.

After each experiment the flotation cell and all glassware were washed with ethyl alcohol, concentrated nitric acid, and distilled water.

RESULTS AND DISCUSSIONS

Effect of pH

The study of the effect of pH on the flotation system under investigation is important from three viewpoints. First, the initial pH will determine whether the uranium is present in the soluble form or as a precipitate. This in turn will determine whether the process will be an ion flotation or a precipitate one. Second, the pH will determine the nature of the soluble uranyl species present and consequently it will determine whether ion flotation can take place by the concerned collector or not. Third, since the solutions were unbuffered to prevent complex formation of the uranyl ions and the buffering anions, changes in pH by the collector would be expected and an increase or a decrease in the pH would depend on the basicity or acidity of the collector used. This pH variation can lead to changes in the nature of the uranyl species already present in the solution. These changes would, or course, be remarkable at high collector additions.

To study the effect of pH on the low gas flow rate foam separation of uranium, different molar concentrations (*C*) of uranyl sulfate solutions ranging from 10^{-5} to 10^{-3} in sulfate media of 0.039 ionic strength were subjected to flotation at different pH values using a constant molar ratio (Cc/C) of collector:uranium. Since sodium lauryl sulfate did not show any appreciable removal of U(VI) from sulfate media, additional tests were carried out in a nitrate medium of the same ionic strength and under the same conditions as that of sulfate for comparison. Results obtained after 15 min bubbling at a rate of 27 cm^3/min using NaLS, CTAB, or LACl are shown in Figs. 1, 2 (Curves I and III), and 3, respectively.

As shown from the results, on using NaLS for the separation of uranium from nitrate media (Fig. 1) almost no removal is observed until a pH slightly higher than 2 is reached. At that point flotation begins and increases with the pH, rapidly at first and then slowly up to a pH of about 5.3. Removals at this pH range can be attributed to the ion flotation of some hydrolyzed polymeric cationic uranyl species. At pH 5.3 the percent removal starts to increase again with a sharp slope until recoveries approaching 90% are reached, and then the percent removal becomes rather constant up to the maximum pH studied (pH 9.0). The high recoveries obtained in this pH range can be related to the flotation of the hydroxide and uranate precipitates. The nonflotation of U(VI) ions from sulfate media with anionic collectors and its simultaneous removal from nitrate media probably indicate that the sulfate anion can complex all the uranyl species, which is in accordance with the literature (*15*). Since precipitate flotation also depends on charge difference between the collector and the ion to be separated, it can be concluded that in the presence of SO_4^- even the uranyl hydroxide and the uranate precipitates can acquire a negative charge.

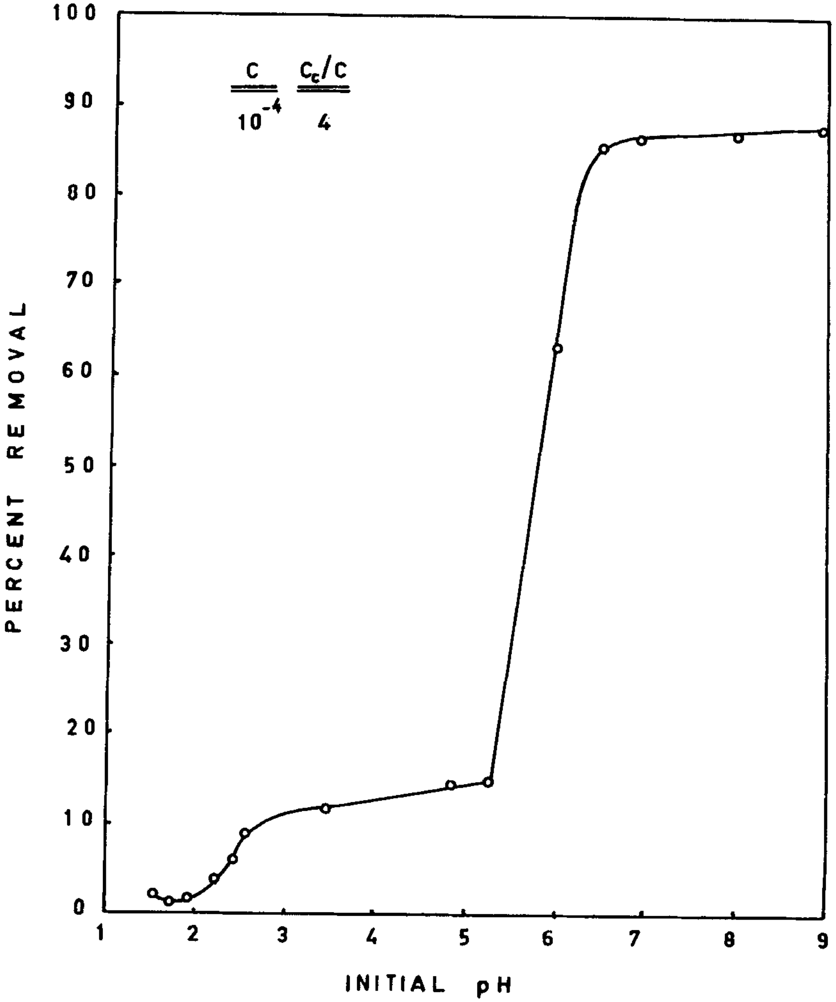

FIG. 1. Foam separation of U(VI) with NaLS from nitrate media.

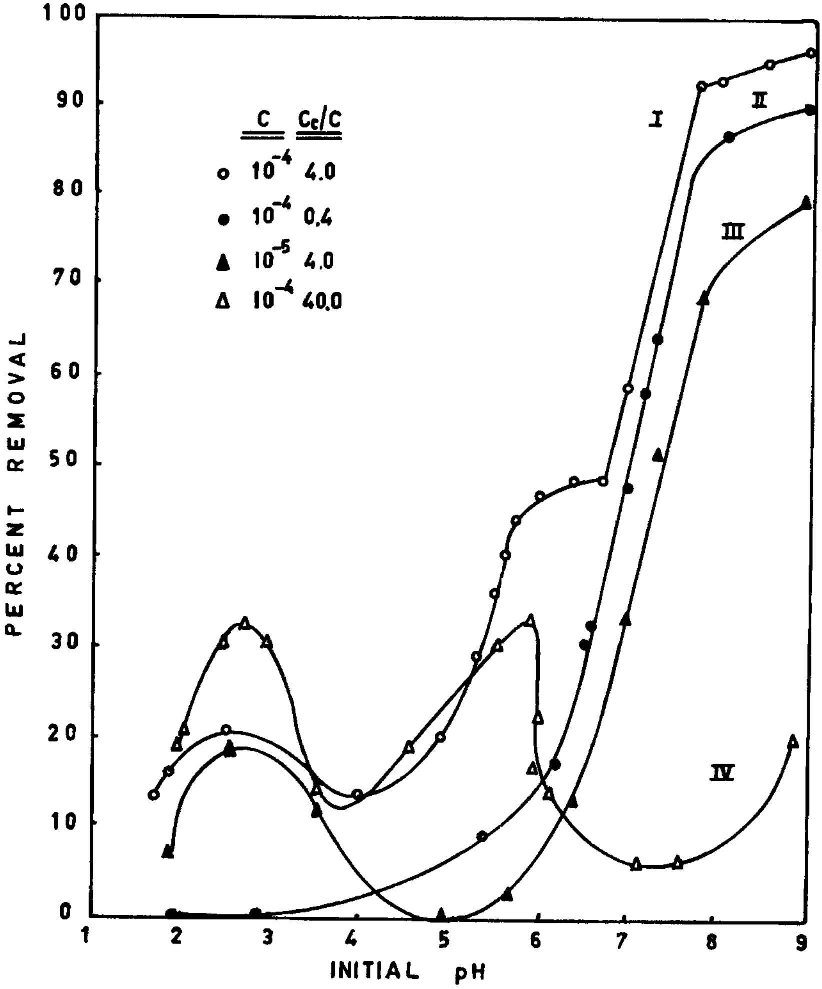

FIG. 2. Foam separation of U(VI) with CTAB from sulfate media.

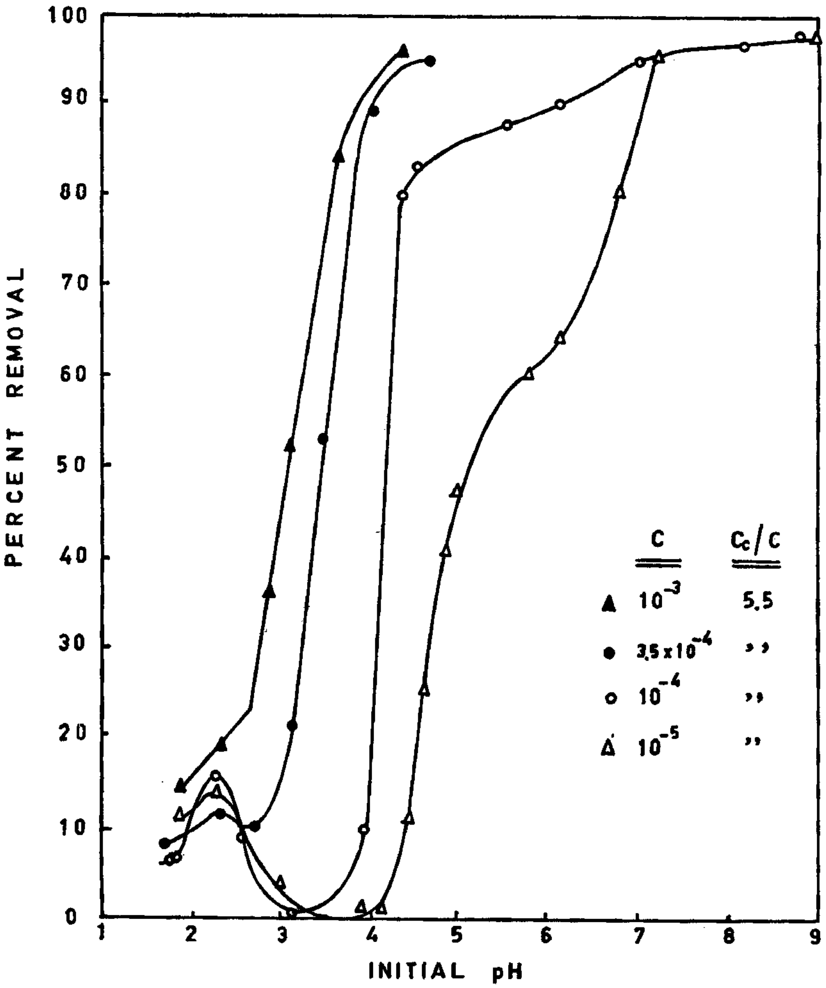

FIG. 3. Foam separation of U(VI) with LACl from sulfate media.

The percent removal–pH curves obtained for the two uranium concentrations studied using CTAB as collector show the same general trend to some extent (Fig. 2, Curves I and III). Thus for both uranyl concentrations some uranium removals were obtained at pH values $\leqslant 2$. This may be attributed to the fact that at these pH values and in presence of sulfate anions, hexavalent uranium can exist in the form of the anionic complexes $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$ (*6*) which can compete well, especially the latter one, with the SO_4^{2-} anion for the positively charged collector cation and then levitate to the surface, i.e., ion flotation takes place. The percent uranium removal increases on increasing the pH, reaching an optimum at around pH 2.5. The high removals obtained in this case may be due to the existence of $U_2O_5(SO_4)_3^{4-}$ complex (*21*). The comparatively lower percent removal obtained in the lower pH region may be due to the fact that the anionic uranyl complexes exist only in very low concentrations (*21*). On increasing the basicity of the solution the percent removal decreases to a minimum, perhaps due to changes in the uranyl species present. At still higher pH values some variations are obtained for the different uranium concentrations. In the case of the higher concentration studied (10^{-4} *M*) the percent removal increases again with an increase of pH until an optimum removal of about 50% is reached when a short plateau is formed. Removals in this pH region may be due to the flotation of the uranate. A further increase in the pH results in a sharp jump in the percent removal, probably due to the precipitate flotation of the uranyl hydroxide, and recoveries approaching 100% can be obtained. This high recovery continues up to pH 9.0 and perhaps higher, indicating the flotation of the diuranates as well. At low uranium concentrations (10^{-5} *M*) negligible recoveries are obtained from pH ~3.5 up to about 6.0 where the percent removal steadily increases with increasing pH until a maximum is attained when the uranium is completely precipitated. The short plateau previously observed in the case of the high uranium concentration tested is not formed when low uranium concentrations are floated, probably because of the nonprecipitation of the uranate. In general, the overall results further confirm the possibility that in the presence of sulfate anion the different species can acquire a negative charge.

On comparing the results obtained by CTAB with those obtained by LACl (Fig. 3), it is generally noticed that for the same uranium concentration the precipitation flotation curves obtained on using the LACl collector are noticeably shifted to lower pH regions. In addition, the precipitation curves for the different uranium concentrations with the amine collector

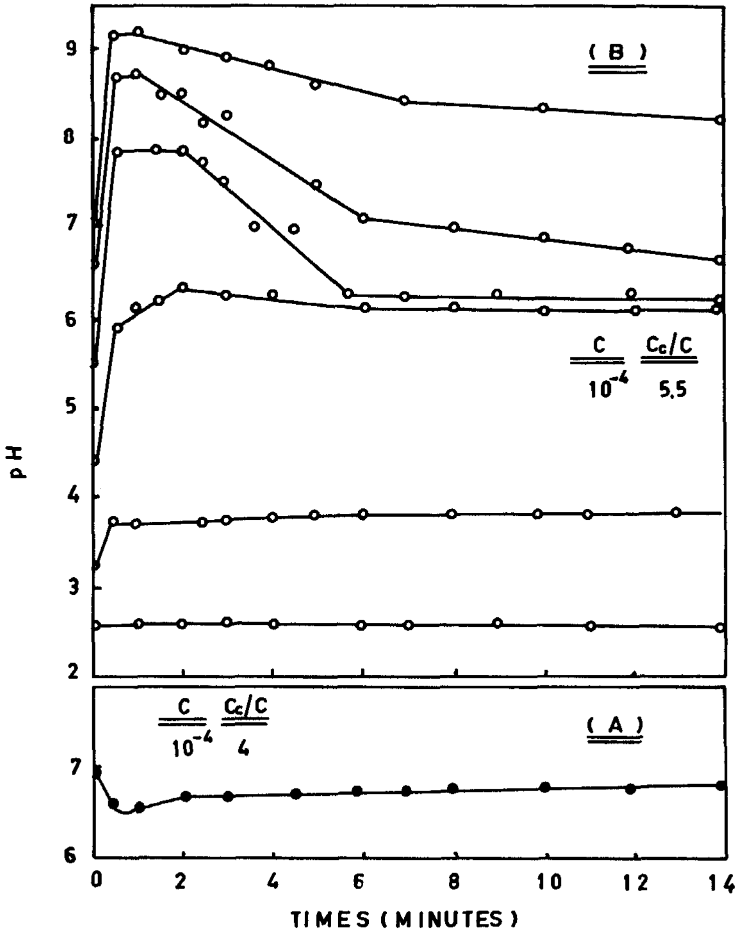

FIG. 4. pH changes of flotation systems of different initial pH values with time.

are displaced more toward the acidic regions as the uranium concentration is increased. These differences are thought to be mostly due to the pH variations which occur on adding the collector. As shown in Fig. 4, when CTAB is used the pH changes are very slight and the collector tends to lower the pH of the system just after its addition, whereas the amine causes a considerable rise of the solution pH, which can cause the precipitation of uranium, and consequently the precipitation curves are obtained

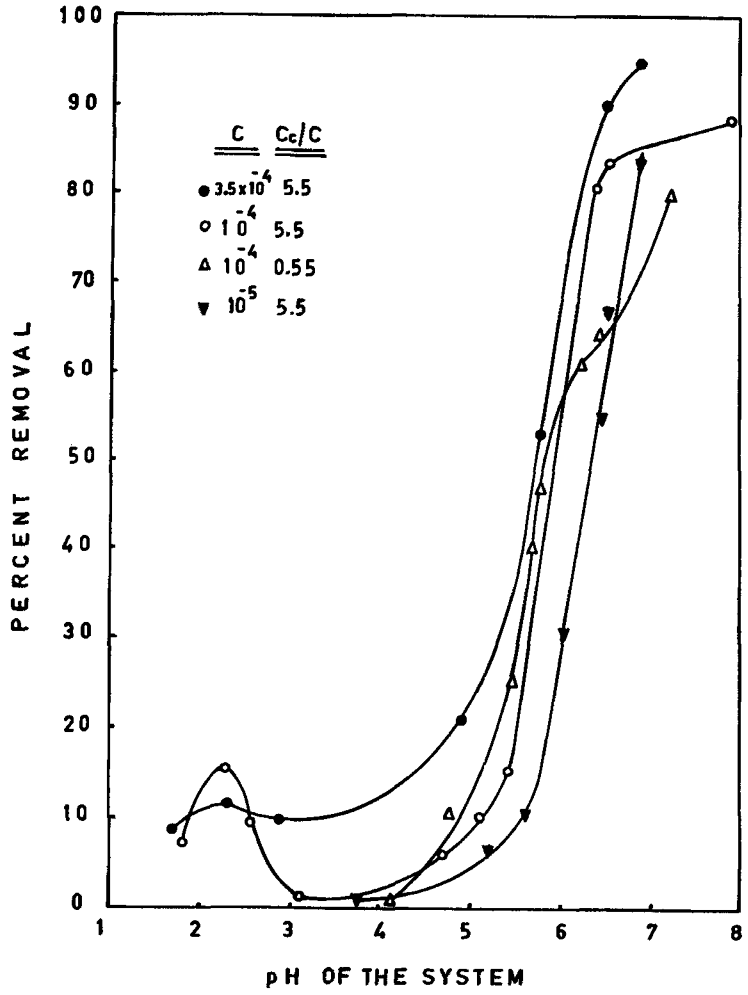

FIG. 5. Percent removal vs the pH reached just after the addition of the collector (LACl).

at initial pH regions lower than those for CTAB. However, it seems very probable that the parts of these curves obtained at initial pH values lower than that of the complete precipitation of uranium are not totally due to precipitation flotation but are rather obtained by mixed flotation, i.e., flotation of soluble and insoluble uranyl species which are formed by reason of the pH changes that take place during the flotation. Again, since a constant collector: uranium ratio was used throughout this set of experiments, then high uranium concentrations require higher quantities of the collector, and as a result the pH values are more shifted toward the alkaline side and the precipitate flotation curves are apparently displaced toward lower initial pH values. However, if the pH of the system just after the addition of the collector is considered (Fig. 5), almost no displacement is observed and the curves obtained are gathered in a pH region near to that occupied by the precipitation curves obtained by CTAB.

Since the extent of change in the solution pH depends upon the initial pH, being more pronounced as the initial pH approaches neutrality and rather negligible in the acidic region (Fig. 4), then the ion flotation curves which are only obtained in acidic media are unaffected except at very high collector concentrations.

Effect of Collector Concentration

For sulfate media of 0.039 ionic strength, the results obtained at constant uranium concentration of 10^{-4} *M* and various concentrations of the collector are presented in Fig. 2 (Curves I, II, and IV) and Fig. 6 for CTAB and LACl, respectively. Figure 7 shows the effect of different molar ratios of uranium to a constant concentration of LACl. From the figures it is observed that in case of LACl the precipitate flotation curves obtained for the same uranium concentration are more and more shifted toward the acidic side as the collector: uranium ratio is increased, i.e., better removals are obtained at the same pH as the collector: uranium ratio is increased. This again can be related to the remarkable pH rise which occurs on the addition of this collector, which is not the case with CTAB. The maximum percent removal obtained by precipitate flotation seems to be independent of collector concentration, assuming that enough collector is added and that the collector: uranium ratio is not very high. Too high collector: uranium ratios cause incomplete flotation or even negligible separations, as in case of CTAB. Ion flotation, on the other hand, is very dependent on the collector concentration, so that at low ratios of collector: uranium no removals could be obtained.

Effect of Sulfate Concentration

Results obtained for the percent removal of U(VI) from 0.0006, 0.013, 0.056, and 0.13 *M* sulfate solutions at different pH values using LACl

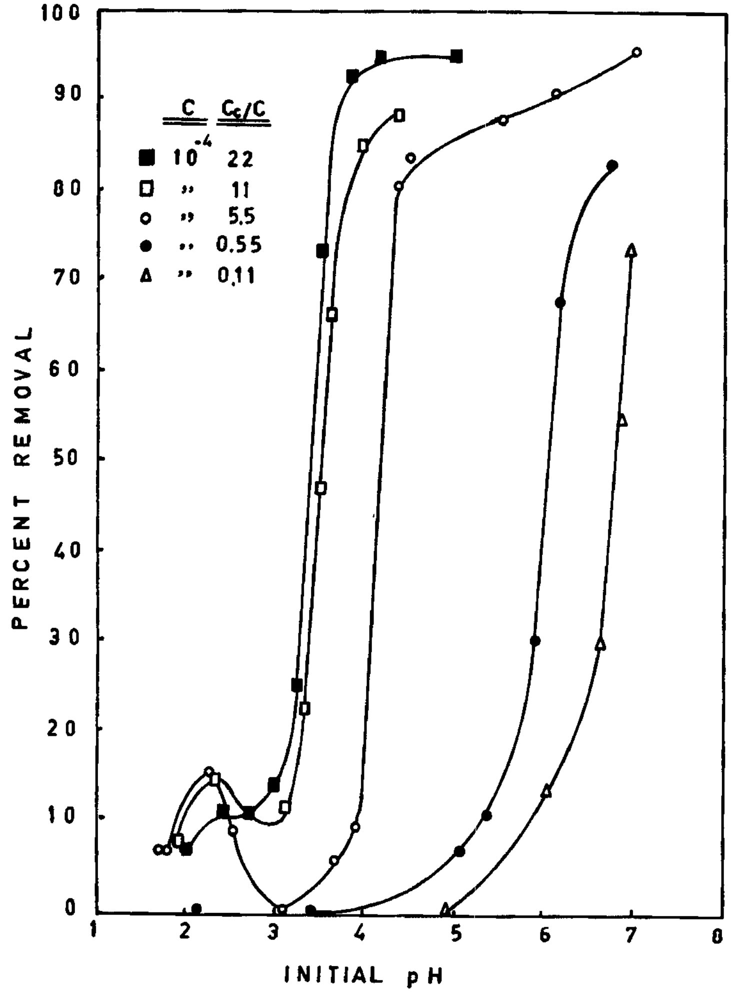

FIG. 6. Flotation of 10^{-4} *M* solution of U(VI) at different collector (LACl) ratios.

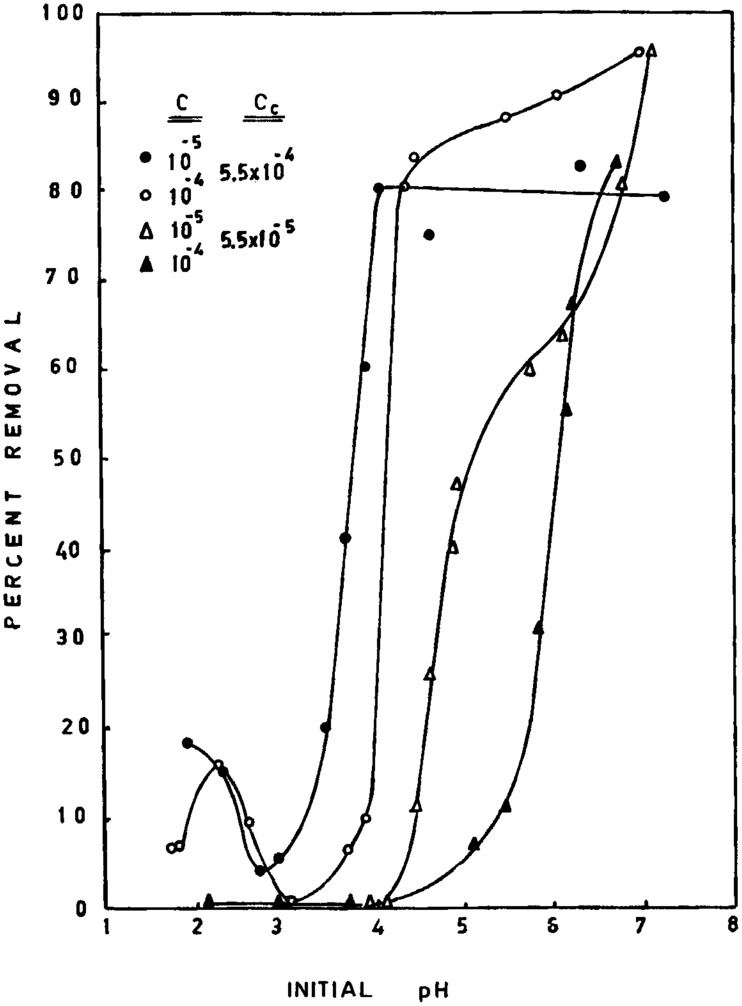

FIG. 7. Effect of U(VI) concentration at constant concentration of LACl (6×10^{-4} *M*).

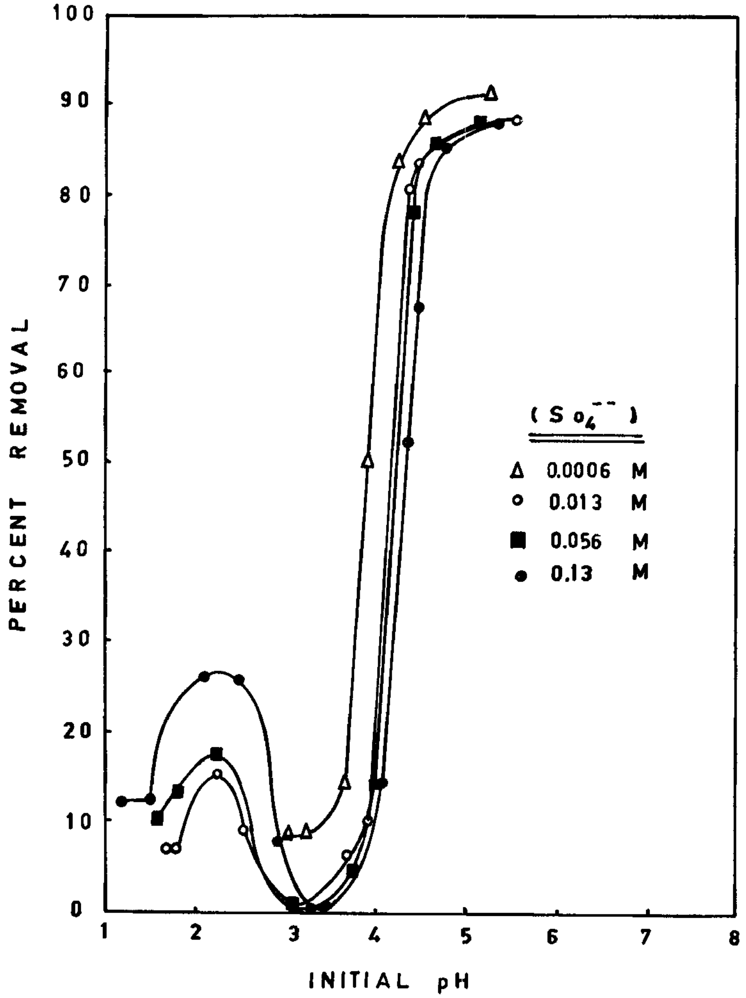

FIG. 8. Effect of sulfate concentration on the flotation of 10^{-4} *M* solution of U(VI) with LACl.

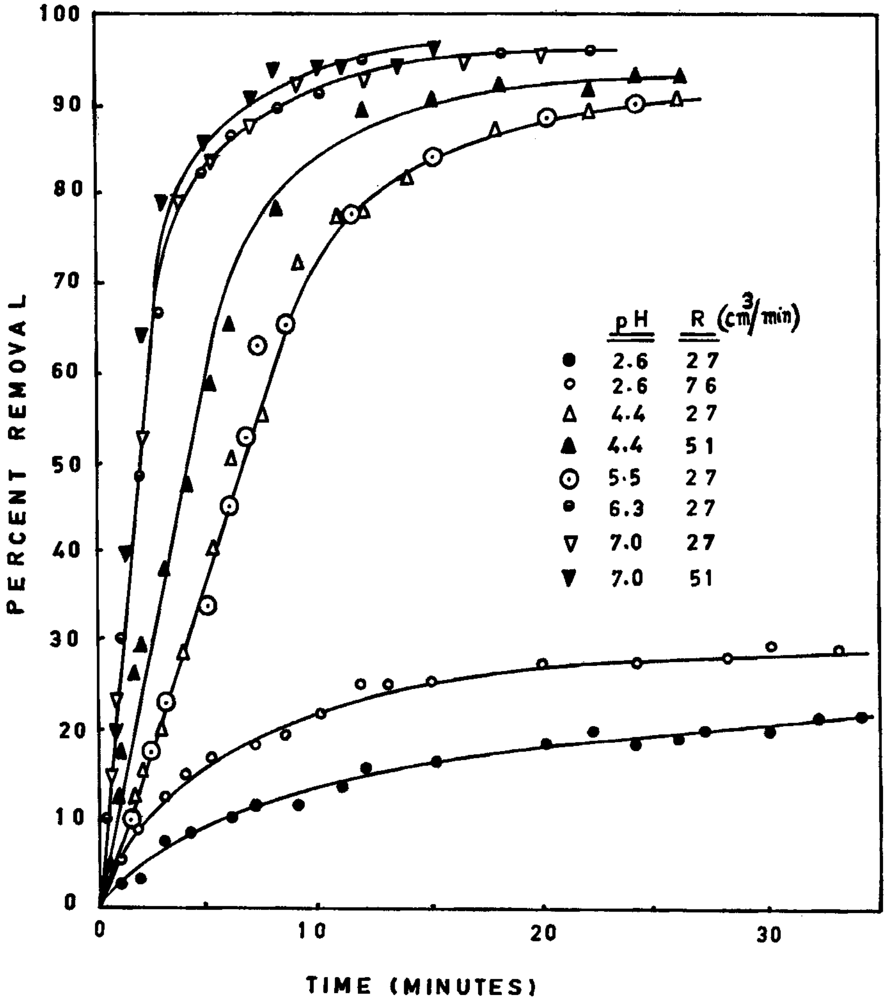

Fig. 9. Foam separation of U(VI) with LACl at different initial pH values and gas flow rates.

collector are presented in Fig. 8 and show that at high sulfate concentrations the precipitate flotation curves are slightly shifted toward the alkaline side with little decrease in the ultimate removal. This is perhaps due to the strong complex formation between uranyl ion and sulfate ions in the more concentrated sulfate solutions. In the case of ion flotation, better removals are obtained at the higher sulfate concentrations tested, probably because the $UO_2(SO_4)_2^{2-}$ complex prevails at high sulfate concentrations and UO_2SO_4 at lower ones (*22*).

Effect of Gas Flow Rate and Time Period of Bubbling

The rate of removal curves obtained at different values of initial pH and gas flow rate (*R*) for U(VI) from 0.013 *M* sulfate solutions using LACl as collector are shown in Fig. 9. From the results it is observed that at low pH values (pH 2.6) where ion flotation takes place, the initial rate of removal increases as the rate of gas flow increases, but the maximum removal percent tends to have a certain limiting value. At suitably high pH values (e.g., at pH 6.3 and 7.0 in Fig. 9) where precipitate flotation can take place, the initial rate of flotation is comparatively very high and the percent removal is not affected by the gas flow rate in the range studied. At intermediate pH values (4.4 and 5) where uranium is liable to be precipitated only after the addition of the collector increases the pH value, the rate of uranium flotation is obviously affected by the rate of gas flow as is the case at pH 2.6 where there is no opportunity for precipitate flotation. This suggests that flotation at the intermediate pH values is due to the flotation of soluble hydrolyzed polymeric species and the colloidal material which is formed just before the precipitation of the hydroxide (*8*), together with the flotation of some precipitated uranate and uranyl hydroxide, i.e., mixed flotation takes place.

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