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Precipitate Coflotation of Orthophosphate and Fluoride

Orthophosphate and fluoride are simultaneously precipitated from aqueous solution, 5.26 $\times$ 10^{-3} M. in each, by La (III). The precipitates are cofloated by the anionic surfactant sodium laurylsulfate, with optimum flotation at pH 4.0 and a stoichiometric lanthanum concentration based on $LaPO_4$ and LaF_3. Over pH 3.5 to 6.0, better than 95% flotation of the total orthophosphate and precipitated fluoride that are present can be floated at a molar sodium laurylsulfate to orthophosphate plus fluoride ratio of 0.023. At lower sodium laurylsulfate concentrations, the flotation decreases at pH 3.5 and 6.0 compared to pH 4.0-5.0; at pH 4.0, an increase in the La(III) concentration decreases the flotation.

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SCOPE

The removal of a soluble ionic species from aqueous solution followed by concentration in a foam or froth can be accomplished by precipitating the ion, then by adding a surface-active agent to act as a collector-frother, and then by aerating the suspension and floating the precipitate-surfactant particulates to the surface of the suspension. The initial charge of the precipitate has a significant effect on the adsorption (or exchange) of the surfactant on the particles, with the change established either by desorption of one of the ionic species of the solid or by adsorption of ions from solution onto the surface of the crystal. The constituent ions of the precipitate present in solution are preferentially adsorbed over other ions. The surfactant, added as a collector-frother in a flotation process, serves three or more functions: the adsorption (or exchange) of the surfactant on the surfaces of the particles makes the precipitate suitable for gas bubble attachment (the surfactant may also promote aggregation of the precipitate, becoming incorporated in the precipitate structure); interaction between surfactant adsorbed on the particles and "free" surfactant adsorbed at the gas-liquid, bubble interfaces produces bubble attachment to the particles; and "free" surfactant acts as a frother, producing a stable foam, which may be further stabilized by the presence of particulates.

The objective of this work is to investigate experimentally the simultaneous precipitation of orthophosphate and fluoride by lanthanum (La (III)) over an acidic pH range (pH 3.5 to 6.0), followed by coflotation of $LaPO_4$ plus LaF_3 (plus crystals containing both orthophosphate and fluoride) with a single surfactant. The effects of pH, lanthanum concentration, and surfactant concentration are discussed in terms of flotation results, in terms of calculated and experimentally-measured solution concentrations of the ionic species of significance, and in terms of the characteristics of the precipitate particles. Lanthanum has been reported as an orthophosphate precipitant superior to Al (III), Fe (III), and Ca (II) salts (Recht et al., 1971; Leckie and Stumm, 1970; Yuan and Hsu, 1970). In particular, at the same cation to orthophosphate ratios, La (III) has yielded lower soluble orthophosphate concentrations (by as much as three orders of magnitude) over a broader pH range compared to Al (III) (Recht et al., 1971). Precipitation with Ca (II) necessitates an alkaline pH. La (III) also yields a small solubility product with fluoride (Eriksson and Johansson, 1970), although the soluble fluoride concentrations are higher than those of orthophosphate. The precipitation of orthophosphate by Al (III) is influenced by the presence of fluoride (Leckie and Stumm, 1970; Yuan and Hsu, 1971).

Possible applicability of this work is to the treatment of aqueous wastes produced by wet scrubbers used by the phosphoric acid manufacturing industry (Barber and Farr, 1970; Anon., 1970). Both orthophosphate and fluoride can be scrubbed simultaneously from stack emissions by a variety of wet air pollution control devices. However, the under-flow stream from the scrubbers must be treated for phosphate and fluoride removal and possible recovery before discharge to a receiving stream. The 5.26 $\times$ 10^{-3}M. concentrations each of orthophosphate and fluoride used in

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the experiments detailed below, are representative of a phosphoric acid manufacture scrubbing waste (Anon., 1970).

Precipitate flotation has been studied by several investigators, beginning with Skrylev and Mokrushin (1961) and Baarson and Ray (1964). The most recent investigations include the flotation of magnesium hydroxide (Kalman and Ratcliff, 1971), of chromium hydroxide (Bhattacharyya et al., 1971; Grieves and Lee, 1971), of silver, uranium, gold, nickel, and zinc precipitated by a hydrophilic organic reagent (Mahne and Pinfold, 1969; Pinfold and Mahne, 1969), of zinc and lead hydroxides (Rubin and Lapp, 1969, 1971) and of cyanide complexed with Fe (II) Grieves and Bhattacharyya, 1969). Practically all of these studies have involved the precipitation and flotation of a single ionic species, including ionic strength effects and the competition of other species; different species have been progressively precipitated and floated (stage-wise) by pH variation, etc. No investigations have been carried out of the simultaneous precipitation of two ions by a single precipitant, followed by the coflotation of the precipitates with a single surfactant at constant pH.

CONCLUSIONS AND SIGNIFICANCE

Equimolar concentrations of orthophosphate and of fluoride, precipitated by La (III) in the stoichiometric concentration, can be floated readily at acidic pH with the strongly basic, anionic surfactant sodium laurylsulfate. Better than 95% flotation is achieved over pH 3.5 to 6.0, using 0.023 mole SLS per mole orthophosphate plus fluoride. Maximum flotation of $98^+\%$ is obtained at pH $= 4.0^+$, with the collapsed foam volume about 10% of the initial suspension volume and yielding about a 10-fold concentration increase, comparing the orthophosphate and fluoride in the initial suspension and the foam. At lower SLS concentrations, the flotation at pH 5.0–6.0 falls off due to reduction of the surface charge of the precipitate and insufficient surfactant adsorption for efficient collection and flotation; the flotation at pH 3.5 falls off due to increased solution concentrations of La^{3+} and LaF^{2+}, interacting with the SLS and stabilizing a fine colloidal precipitate which requires additional SLS for aggregation. At pH 4.0, an increase in the La (III) concentration to 2% greater than the stoichiometric decreases the flotation due essentially to the same effects as a pH reduction from 4.0 to 3.5.

The feasibility of the precipitate co-flotation process for the treatment of phosphoric acid manufacture scrubbing wastes, which may also contain pyrophosphate and polyphosphates, will depend on lanthanum recovery, either by precipitation of $La(OH)_3$ or by extraction of a La (III) chelate at low pH. La (III) will also precipitate pyrophosphate and polyphosphates readily (Recht et al., 1971). This study has shown that two initially soluble anions can be simultaneously precipitated with a single precipitant, and the precipitates can be co-floated efficiently with a single surfactant. Future work should include variation in the initial orthophosphate and fluoride concentrations, particularly including nonequimolar solutions to see if a stoichiometric lanthanum concentration is again optimum.

EXPERIMENT

The precipitation of orthophosphate ($NaH_2PO_4 \cdot H_2O$) and fluoride (NaF) ions present in distilled water solution was carried out by adding lanthanum ($LaCl_3 \cdot 6H_2O$) in an approximately stoichiometric ratio. Reagent Grade chemicals were used throughout. The concentrations of orthophosphate and of fluoride were each held constant at 5.26×10^{-3}M. (5.26 mM.). The La(III) concentration was varied from 6.88 to 7.37 mM. After La(III) addition, the precipitating suspension was allowed to mix for 10 min., and the *p*H was elevated from 2.2 ($LaPO_4$ formation had released H^+) to a fixed value between 3.5 and 6.0 with NaOH. The suspension was mixed for an additional 15 min. after *p*H adjustment. The anionic surfactant, sodium laurylsulfate (SLS), was added and was mixed with the precipitate suspension for 15 min. The initial SLS concentration was varied between 0.069 mM. and 0.243 mM.

Two series of preliminary experiments showed that the cationic ethylhexadecyldimethylammonium bromide (a strong base collector) and the anionic sodium oleate (a weak acid collector) were essentially ineffective at *p*H 4.0 to co-float orthophosphate and fluoride as La(III) precipitate. Sodium oleate was suggested by its use as a collector in the commercial flotation of fluorite and phosphorite. In contrast, the anionic, strongly acidic, sodium laurylsulfate provided almost complete flotation.

The flotation experiments were carried out by placing 2.0 liters of the initial NaH_2PO_4-NaF-$LaCl_3$-SLS suspension in a Pyrex foam separation column, 82 cm in height and 9.7 cm in diameter. Air was saturated with water, metered with a calibrated rotameter, and diffused through a sintered glass diffuser of 50 micron porosity at a rate of 600 ml/min. (at 1.0 atm and 25°C). The average bubble size was determined by a technique described previously (Grieves and Bhattacharyya, 1969) to be in the range 500-700 microns. The initial suspension was then aerated until all foam formation ceased (with the foaming time varying from 5 to 40 min. depending on *p*H and concentrations). The foam was removed continuously from a port located 7.0 cm above the initial suspension level. At the termination of each experiment, the volume was measured of the residual suspension left in the foam separation column, and the optical density (OD $=$ $\log_{10}$ distilled water transmittance/suspension transmittance) was determined with a Beckman DB-G spectrophotometer at 400 $m\mu$ (path length $=$ 10 mm.). The optical densities were also measured of the initial suspension before and after surfactant addition.

The soluble lanthanum (La^{3+}) concentration in the residual suspension was measured by the standard hardness technique (Anon., 1965), using EDTA as the titrant and Eriochrome Black T as the indicator. Total fluoride was determined by digestion for 30 min. of a 50 ml sample of the residual suspension with 50 ml of 20% KOH (Woyski and Harris, 1963). The digested suspension was then cooled, neutralized to *p*H 11.5 with H_2SO_4, and filtered to remove precipitated $La(OH)_3$. The filtrate was then neutralized to *p*H 11.2, the ionic strength was adjusted with $NaNO_3$, and total fluoride (as F^-) was determined with a Beckman fluoride selective electrode (Anon., 1968). Since the fluoride selective electrode is sensitive to OH^- ions, it was necessary to prepare a calibration curve at *p*H 11.2.

Total orthophosphate was measured by a modification of the ammonium molybdate method, using stannous chloride as the reducing agent (Anon., 1965b). No interference due to lanthanum or fluoride was observed. In all experiments, the suspension containing orthophosphate in both precipitated and soluble forms was diluted to bring the concentration of total orthophosphate in the range of 2.1×10^{-7}M. to 1.1×10^{-5}M. The only modification required was the length of the shaking time after the addition of benzene-isobutanol solvent and the molybdate reagent. A minimum of 2 min. shaking time was required. This resulted in the breakdown of orthophosphate from $LaPO_4$ and the subsequent reaction with ammonium molybdate. Several analyses with known feed orthophosphate concentrations, and containing $LaPO_4$, gave very reproducible results within ± 1%.

SOLUBILITY OF LANTHANUM PHOSPHATE AND FLUORIDE

The various equilibria involved in the NaH_2PO_4-NaF-$LaCl_3$ aqueous system are

$$LaPO_4(s) \rightleftarrows La^{3+} + PO_4^{3-} \qquad K_s = 3.75 \times 10^{-23} \quad (1)$$

$$PO_4^{3-} + H^+ \rightleftarrows HPO_4^{2-} \qquad K = 2.00 \times 10^{12} \quad (2)$$

$$HPO_4^{2-} + H^+ \rightleftarrows H_2PO_4^- \qquad K = 1.59 \times 10^{7} \quad (3)$$

$$H_2PO_4^- + H^+ \rightleftarrows H_3PO_4 \qquad K = 1.59 \times 10^{2} \quad (4)$$

$$LaF_3(s) \rightleftarrows La^{3+} + 3F^- \qquad K_s = 8.13 \times 10^{-18} \quad (5)$$

$$La^{3+} + F^- \rightleftarrows LaF^{2+} \qquad K = 1.41 \times 10^{5} \quad (6)$$

$$F^- + H^+ \rightleftarrows HF \qquad K = 1.90 \times 10^{3} \quad (7)$$

The solubility product for Equation (1) was obtained from Tananaev and Vasiléva (1963), the association constants for Equations (2), (3), and (4) from Leckie and Stumm (1970), and the solubility product for Equation (5) and the association constants for Equations (6) and (7) were obtained from Eriksson and Johansson (1970). Three additional material balance equations are required to give ten equations in the ten unknown equilibrium concentrations:

$[LaPO_4]_s$
$[PO_4^{3-}]$
$[HPO_4^{2-}]$
$[H_2PO_4^-]$
$[H_3PO_4]$
$[LaF_3]_s$
$[LaF^{2+}]$
$[F^-]$
$[HF]$
$[La^{3+}]$

$$[La]_i = [LaPO_4]_s + [LaF_3]_s + [LaF^{2+}] + [La^{3+}] \quad (8)$$

$$[P]_i = [LaPO_4]_s + [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4] \quad (9)$$

$$[F]_i = 3[LaF_3]_s + [LaF^{2+}] + [F^-] + [HF] \quad (10)$$

in which $[La]_i$, $[P]_i$, and $[F]_i$ are the initial concentrations of lanthanum, orthophosphate, and fluoride, molar. Equations (1) through (10) were solved to yield the ten equilibrium concentrations as a function of pH and of the initial ratio of lanthanum to orthophosphate and fluoride, defined as $[La]_i/([P]_i + [F]_i/3)$, at constant initial concentrations of $[P]_i = 5.26 \times 10^{-3}$M. and $[F]_i = 5.26 \times 10^{-3}$M. (5.26 mM.). The digital computation method used to solve the equations was a compromise between the Newton-Raphson algorithm and the method of steepest descent. It should be noted that the formation of a mixed lanthanum-orthophosphate-fluoride precipitate could not be included in the predictive solubilities.

Results are presented in Figures 1 and 2. Figure 1, at a constant $[La]_i/([P]_i + [F]_i/3)$ of 1.00 (the stoichiometric ratio and with $[P]_i = [F]_i$) indicates an exponential decrease in the soluble orthophosphate concentration with pH elevation: at pH 4.0, the total soluble orthophosphate (virtually all present as $H_2PO_4^-$) is only 0.07% of the initial orthophosphate. The total soluble fluoride ($HF + F^- + LaF^{2+}$) is 4.2% of the initial fluoride. The species $HF + F^-$, LaF^{2+}, and La^{3+} also decrease almost exponentially with pH over pH 2.0 to 3.5, but from pH 4.0 and above, there is little further decrease.

Figure 2, at a constant pH of 4.0, indicates that orthophosphate and fluoride as F^- can be decreased substan-

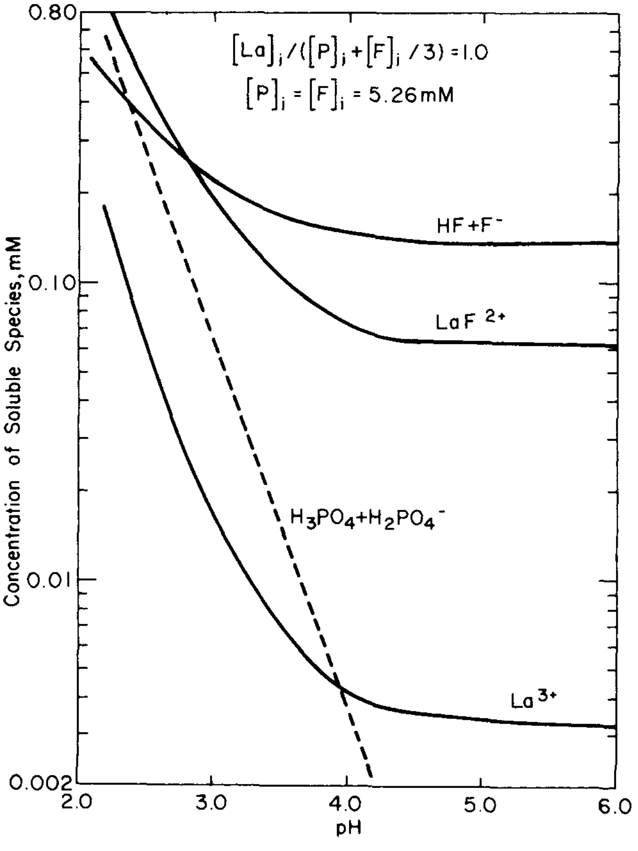

Fig. 1. Calculated concentrations of soluble species versus pH.

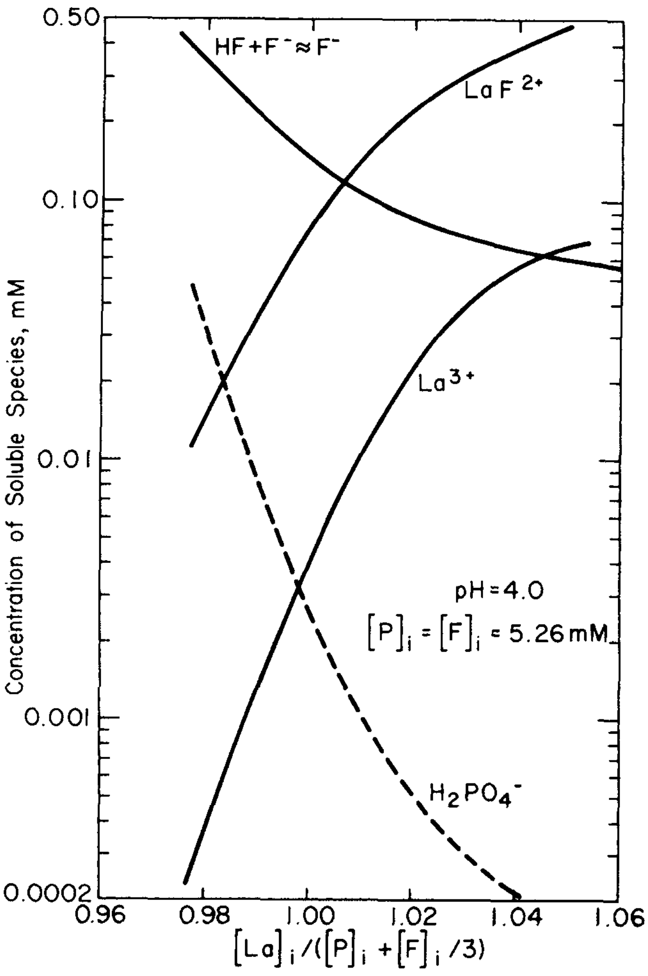

Fig. 2. Calculated concentrations of soluble species versus initial ratio of lanthanum to orthophosphate and fluoride.

TABLE 1. COLLAPSED FOAM VOLUME BEHAVIOR FOR EXPERIMENTS DETAILED IN FIGURE 4

pH	$[SLS]_i$, mM.	V_f/V_i
3.5	0.104	0.18
3.5	0.174	0.08
3.5	0.243	0.09
4.0	0.104	0.06
4.0	0.174	0.10
4.0	0.243	0.12
5.0	0.104	0.28
5.0	0.174	0.31
5.0	0.243	0.38
6.0	0.104	0.32
6.0	0.174	0.43
6.0	0.243	0.60

tially ($H_2PO_4^-$ by an order of magnitude or more) by elevation of $[La]_i/([P]_i + [F]_i/3)$ above 1.00. However, it should be stressed that both LaF^{2+} and La^{3+} increase with the initial ratio. From Figure 2, an optimum $[La]_i/([P]_i + [F]_i/3)$ should exist, to provide acceptably low concentrations of all soluble species of significance. However, that optimum should depend not only on the predicted solubility of the precipitates, but on the precipitate flotation efficiency.

PRECIPITATE COFLOTATION RESULTS

A series of batch, precipitate flotation experiments was conducted at the following conditions:

$$[P]_i = 5.26 \text{ mM.}$$
$$[F]_i = 5.26 \text{ mM.}$$
$$[La]_i/([P]_i + [F]_i/3) = 0.98 \text{ to } 1.02$$
$$[SLS]_i = 0.069 \text{ to } 0.243 \text{ mM.}$$
$$pH = 3.5 \text{ to } 6.0$$

in which $[SLS]_i$ is the initial surfactant concentration. Flotation results were determined in terms of total orthophosphate in the residual suspension, $[P]_r$, in terms of total fluoride in the residual suspension, $[F]_r$, and in terms of the optical density of the residual suspension $[OD]_r$. A comparison of percent flotations in terms of optical density versus total orthophosphate and versus fluoride is given in Figure 3. The closeness of the points to the 45° line shows that little soluble orthophosphate and soluble fluoride were floated by the anionic surfactant and that the optical density of the suspension being floated changed only due to the removal of precipitate particles which were carried from the suspension into the foam. A similar agreement between turbidity and total phosphate was observed in precipitation and sedimentation studies with $LaPO_4$ (Recht *et al.*, 1971). All flotation results described below are given in terms of optical density. According to Figure 3, the results would be somewhat conservative for total orthophosphate at percent flotations <50 and somewhat liberal for total fluoride at percent flotations >90, with the latter produced by the greater concentrations of F^- and LaF^{2+}.

Based on the predicted concentrations from Figure 2 of soluble $H_2PO_4^-$, F^-, LaF^{2+}, and La^{3+}, a series of flotation experiments was conducted at $[La]_i/([P]_i + [F]_i/3) = 1.00$, varying the pH and the initial SLS concentration. Results are presented in Figure 4. At all three SLS concentrations, a maximum percent flotation occurred at a pH between 4.0 and 5.0, but somewhat closer to 4.0. At pH 3.5 and 6.0, the effect of a decrease in SLS concentration was much more pronounced than at pH 4.0-5.0. At $[SLS]_i = 0.243$ mM., better than 95% flotation of total orthophosphate plus precipitated fluoride was achieved over pH 3.5 to 5.5.

For these same experiments, the collapsed foam volumes are given in Table 1, *in terms of* V_f/V_i, *the total volume* of foam (collapsed, as liquid) accumulated at the termination of each flotation experiment divided by the initial suspension volume of 2.0 liters. With the exception of the lowest surfactant concentration at pH 3.5, V_f/V_i increased with $[SLS]_i$ at constant pH (to be expected, with more surfactant present to act as a frother) and increased with pH at constant $[SLS]_i$. The foam volume should be minimized to optimize the flotation operation: hence the desirability of operation at pH 4.0 in contrast to 5.0 (with both equally desirable according to Figure 4). The foam volume behavior can give some insight into the roles of the surfactant in the flotation process, as discussed below.

A final series of flotation experiments was conducted at pH 4.0 and $[SLS]_i = 0.174$ mM., varying the ratio $[La]_i/([P]_i + [F]_i/3)$ but at constant $[P]_i = [F]_i$. Table 2 shows that a slight improvement in the flotation of total orthophosphate and fluoride was achieved by decreasing

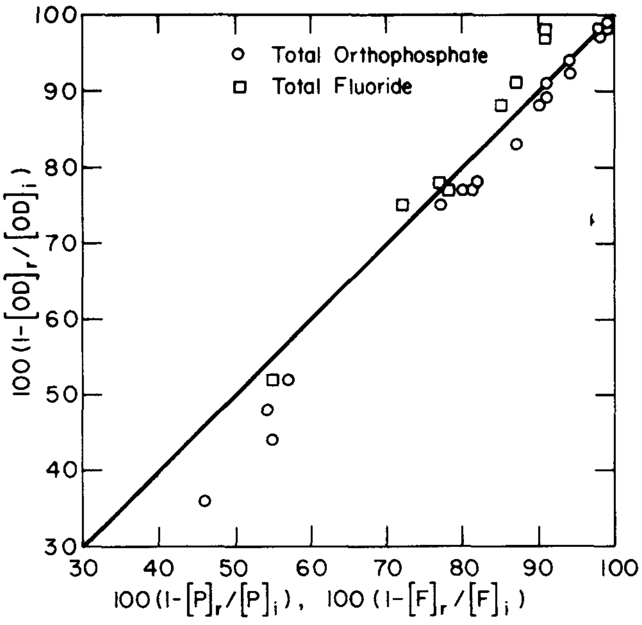

Fig. 3. Flotation results in terms of optical density and orthophosphate and fluoride concentrations.

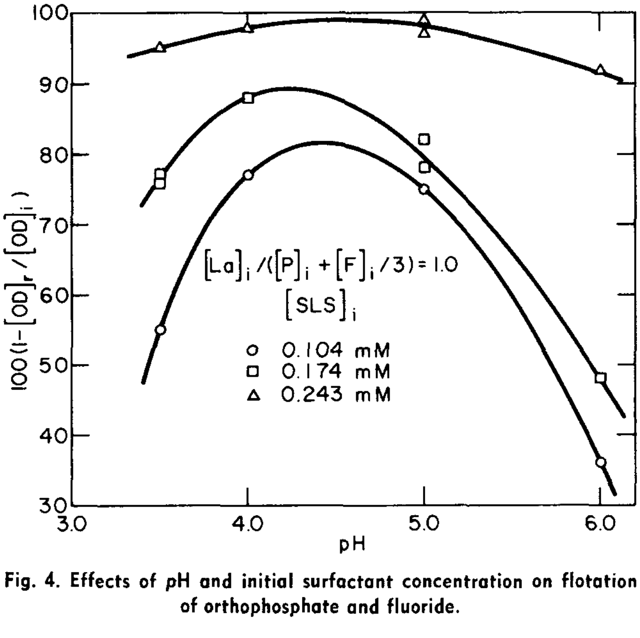

Fig. 4. Effects of pH and initial surfactant concentration on flotation of orthophosphate and fluoride.

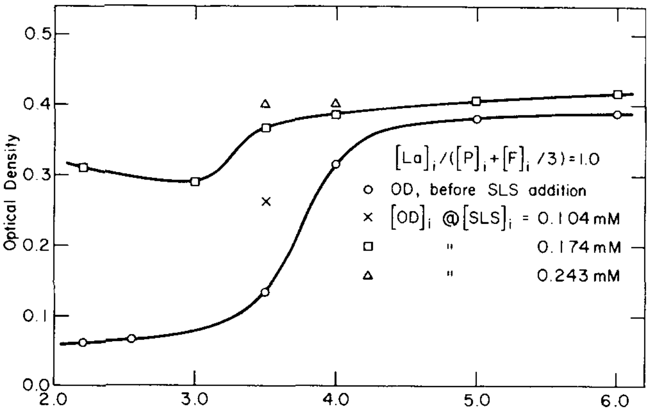

Fig. 5. Optical densities of initial suspensions versus pH, before and after surfactant addition.

the lanthanum ratio from 1.00 to 0.98, but at the expense of a substantial increase in the collapsed foam volume. Operation at a lanthanum ratio greater than 1.00 is clearly not desirable, at the initial concentrations that were employed.

DISCUSSION OF FLOTATION RESULTS

Figure 4 shows that essentially complete flotation of the $LaPO_4$ and LaF_3 (and perhaps some mixed precipitate crystals) occurred at *p*H 4.0^+ with flotation conducted until foaming completely ceased; and that the flotation fell off as the *p*H was elevated, with the effect most pronounced at the lowest surfactant concentration. Also from Table 1, the foam volume increased substantially with *p*H. This behavior is indicative of decreasing surfactant adsorption on the surfaces of the particles with elevation in *p*H, producing incomplete particle attachment to the rising air bubbles; this effect was most evident at *p*H 6.0 and the lowest surfactant concentration, but was largely overcome at the highest surfactant concentration. The decrease in surfactant adsorption was validated by filtering the initial suspensions and analyzing the filtrate for SLS. Table 3 presents the filtration results vs. *p*H at the intermediate surfactant concentration: at *p*H 6.1, the total quantity of SLS adsorbed on the precipitate was not detectable. Figure 5, at $[La]_i/([P]_i + [F]_i/3) = 1.0$ and $[P]_i = [F]_i$, indicates that at *p*H 5.0-6.0, there was virtually no change in the optical density of the initial suspensions upon adding surfactant, again indicating reduced adsorption. In this *p*H region, the precipitate particles were coarser than at *p*H 4.0, at which the precipitate was more finely divided.

The effectiveness of SLS as a collector, in contrast to the ineffectiveness of the cationic ethylhexadecyldimethylammonium bromide (see Experiment section), indicates a positively-charged precipitate, although the sign of the charge could not be measured as with chromium hydroxide (Bhattacharyya et al., 1971) because the $LaPO_4$ and LaF_3 was too finely-dispersed. The charge was produced undoubtedly by adsorption of La^{3+}, and/or LaF^{2+} on the particle surfaces. The decreased surfactant adsorption from *p*H 4.0-6.0 was probably produced by the decreased positive charge on the precipitate as La^{3+} and LaF^{2+} (Figure 1) were reduced. Studies by Buyers and Andrieth (1950) showed that H^+ adsorption was probably not significant at *p*H ≤ 4.5, but H^+ adsorption might have influenced the charge above *p*H 4.5.

As the *p*H was decreased from 4.0 to 3.5, the nature of the precipitate before surfactant addition changed, according to Figure 5, with an abrupt decrease in the optical density. At *p*H 3.5 before surfactant addition, the particles were relatively unaggregated (compared to *p*H 4.0 and above); the colloidal particles were undoubtedly stabilized by the adsorption of La^{3+} and LaF^{2+}, whose concentrations increased abruptly as the *p*H was decreased (Figure 1). To check the predicted behavior of the concentration of La^{3+}, initial suspensions, before surfactant addition, were filtered and analyzed for La^{3+}: results are presented in Table 4. Agreement between experimental and predicted values is not poor, considering the co-precipitate system that was involved.

The decrease in flotation in going from *p*H 4.0 to 3.5, again which was very slight at the highest surfactant concentration (Figure 4), appears to have been caused by insufficient surfactant adsorbed on the particle surfaces. Instead, the surfactant may have been incorporated in the structure of the aggregating $LaPO_4$ and LaF_3: note from Figure 5 at *p*H 3.5 the large change in optical density upon surfactant addition; or the surfactant may have been tied up as an insoluble complex or ion pair with La^{3+} and LaF^{2+}. At *p*H 3.5, La^{3+} (Table 4) and LaF^{2+} (Figure 1) could theoretically have interacted with 0.225 mM. SLS. An additional flotation experiment was conducted, contacting a 0.070 mM. La^{3+} ($LaCl_3$) distilled water solution with 0.220 mM. SLS which resulted in a slightly turbid solution. Upon aeration until foam cessation, the residual

TABLE 2. EFFECT OF THE INITIAL LANTHANUM RATIO AT *p*H 4.0 AND $[SLS]_i = 0.174$ mM.

$\frac{[La]_i}{[P]_i + [F]_i/3}$	$100\,(1 - [OD]_r/[OD]_i)$	V_f/V_i
0.98	91	0.28
1.00	88	0.10
1.02	52	0.04

TABLE 3. SURFACTANT ADSORPTION MEASUREMENTS

$[La]_i/([P]_i + [F]_i/3) = 1.0$
$[SLS]_i = 0.174$ mM.

*p*H	$[SLS]_{\text{adsorbed}}/[SLS]_i$
2.2	0.43
3.5	0.23
4.0	0.10
6.1	$\simeq 0$ (not detectable)

TABLE 4. MEASURED AND PREDICTED VALUES OF La^{3+}

*p*H	$[La^{3+}]$, mM., measured	$[La^{3+}]$, mM., Figure 1
2.2	0.11	0.16
3.0	0.023	0.018
3.5	0.014	0.0069
4.0	0.0043	0.0041
6.0	0.0014[*]	0.0033
@ *p*H 4.0		
$\frac{[La]_i}{[P]_i + [F]_i/3}$		
0.98	0.0029	0.00040
1.00	0.0043	0.0041
1.02	0.0122	0.0229

[*] Lowest detectable concentration by analytical technique that was employed.

La^{3+} concentration was 0.019 mM. and residual SLS concentration was 0.076 mM., indicating the approximately stoichiometric ion flotation of La (laurylsulfate)$_3$, but more important, indicating a clearcut interaction between SLS and La^{3+}. There was no way to observe experimentally the possible interaction between LaF^{2+} and SLS, due to the presence of LaF_3. The possible insufficiency of surfactant could also be ascertained from Table 3, with the decrease in free surfactant in going from pH 4.0 to 3.5.

In summary, from pH 4.0 to 3.5, the nature of the precipitate changed, being stabilized as a fine, positively-charged colloid by La^{3+} and/or LaF^{2+}. The colloid could be aggregated by surfactant, but at the lower surfactant concentrations too much surfactant was tied up in the structure of the aggregated $LaPO_4$ and LaF_3, together with the surfactant which interacted with La^{3+} and LaF^{2+}; not enough was available for surface adsorption to promote collection of the particles and flotation. If the pH were reduced below 3.5, the flotation undoubtedly would have dropped off further: La^{3+} and LaF^{2+} would have continued to increase, interacting with more SLS, and nonprecipitated $H_2PO_4^-$ and H_3PO_4 would have become appreciable (Figure 1).

The objective of increasing the ratio $[La]_i/([P]_i + [F]_i/3)$ at pH 4.0 (Table 2) was to decrease the F^- concentration; however, the improvement in the total fluoride that was precipitated would be expected to be slight due to the increase in LaF^{2+} (Figure 2). The explanation of the flotation behavior in going from $[La]_i/([P]_i + [F]_i/3) = 1.00$ to 1.02 appears practically identical to that in going from pH 4.0 to 3.5. The increased La^{3+} (Table 4, bottom, again indicating reasonable agreement between experimental and predicted values) and LaF^{2+} stabilized finely-divided $LaPO_4$ and LaF_3 particles, requiring increased SLS for aggregation (compared to larger particles), and themselves interacted with the surfactant. The optical density before SLS addition at a 0.98 ratio was 0.29, at 1.00 was 0.32 (Figure 5), and then at 1.02 dropped abruptly to 0.14.

The significance of the parameter $[La]_i/([P]_i + [F]_i/3)$ should not be over-emphasized, because throughout this study $[P]_i = [F]_i$: at nonequimolar initial concentrations, the stoichiometric value of 1.0 might not be optimum. However, the fact that 1.0 (in contrast to 0.8 or 1.2, for example) did turn out to be optimum at $[P]_i = [F]_i$, does lend some validity to speculation that a stoichiometric lanthanum concentration might also yield excellent flotation for nonequimolar solutions.

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NOTATION

[F] = fluoride concentration, molar or millimolar
i = subscript designating initial suspension, before precipitate flotation
[La] = lanthanum concentration, molar or millimolar
[OD] = optical density of suspension at 400 millimicrons, measured by spectrophotometer
[P] = orthophosphate concentration, molar or millimolar
r = subscript designating residual suspension, after precipitate flotation
[SLS] = sodium laurylsulfate concentration, molar or millimolar
V_f/V_i = ratio of collapsed foam volume to initial suspension volume

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