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Precipitate Coflotation of Calcium Sulfite and Calcium Carbonate: Application to Solids Removal from SO_2 Wet-Scrubbing Slurries

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Abstract

An experimental study was conducted of the precipitate flotation of calcium sulfite, calcium carbonate, and of mixtures of both particulate species from suspensions of the order 0.1 *M*, with application to particle separation from the purge stream from a SO_2–limestone wet scrubber. The strongly acidic, anionic surfactant, sodium dodecylbenzenesulfonate (NaDBS) provided excellent flotation of both calcium sulfite and calcium carbonate at neutral pH. For concentrations of calcium sulfite plus calcium carbonate of 3.7, 7.8, and 12.0×10^{-2} *M*, 95% flotation of precipitated sulfite and 97% flotation of carbonate can be accomplished at molar surfactant to sulfite plus carbonate ratios of 0.0035, 0.0023, and 0.0015, respectively.

INTRODUCTION

Precipitate flotation enables the removal of an initially-soluble ion from aqueous solution and its concentration in a foam stream by first precipitating the ion, then by adding a surface-active agent to act as a collector-frother, and finally by aerating the suspension and floating the precipitate particulates (with adsorbed surfactant) to the surface of the suspension. Three reviews (*1–3*) have summarized all pertinent precipitate flotations that have been reported in the world literature. Four studies have recently been conducted with systems containing two precipitates: La(III) phosphate and fluoride (*4*), and Cu(II) and Fe(III) hydroxide or Cu(II) and Fe(III) sulfide (*5*, *6*). Calcium sulfite has been successfully floated from dilute suspension with an anionic surfactant (*7*).

A major problem of the limestone scrubbing process for SO_2 absorption and precipitation from steam-electric power plant stack gases is the removal of the reaction products, calcium sulfite, and to a lesser extent, calcium sulfate, that build up in the closed loop (*8–11*). This is accomplished by permitting a certain percentage of the slurry exiting from the scrubber to pass through a separation device; the solids are removed from the slurry and the clarified water is returned to the feed flow to the scrubber. The percentage of the slurry that must be purged is related to the quantity of the reaction product that is produced in the limestone scrubber: for an inlet stack gas stream containing 0.32 mole-% SO_2 (for 4% sulfur coal under typical combustion conditions), approximately 3.3 wt-% of the slurry exiting the scrubber must be continuously purged. The slurry typically contains about 10 wt-% particulates: 5% calcium carbonate, 4% calcium sulfite, and 1% calcium sulfate. The rather high particle concentrations are produced by the use of seed crystals in the scrubber feed, and the relative concentrations of sulfite and sulfate are determined by the quantity of excess air used in the combustion process. A purge-stream separation process that would separate the calcium carbonate from the other two particulate species would be quite desirable.

Separation processes that have been investigated include sedimentation and filtration (*9*). Sedimentation does not produce good results for calcium sulfite due to the small size of the particles (5 to 50 μm) and their flat shape. Filtration runs are generally short with intermittent operation resulting from the necessity of the frequent cleaning of the filter medium.

An initial study (*7*) has indicated the feasibility of floating calcium sulfite from rather dilute, 0.3 to 1.1 $\times 10^{-2}$ *M*, aqueous solutions over pH 6.5 to 10.0, in the presence of calcium sulfate. Flotation was accomplished with the strongly acidic, anionic surfactant, sodium dodecylbenzenesulfonate (NaDBS) at a feed NaDBS to sulfite ratio of 0.011 mole/mole, which resulted in 71% removal of total sulfite and 93% flotation of precipitated sulfite. An increase in the feed calcium to sulfite ratio from 1.0 to 2.0 did not affect the flotation as long as sufficient surfactant was present, but substantially improved the removal of total sulfite due to enhanced precipitation. The foams were about 20 times more concentrated in sulfite than the feed suspensions.

The objective of this investigation is to establish the feasibility of floating calcium sulfite and/or calcium carbonate from suspensions containing both precipitates at feed concentrations in the range 1.6×10^{-2} to 4.9×10^{-2} M in total sulfite, 0.4×10^{-2} to 1.2×10^{-2} M in sulfate, and 4.6×10^{-2} to 13.7×10^{-2} M in carbonate. These concentrations are approximately 10% of those encountered in a purge stream from a limestone wet scrubber. However, they would simulate the overflow from a first-stage sedimentation unit, with precipitate flotation considered as a second, polishing stage. Other than the work of Aplan (*5*, *6*), these concentrations are at least an order of magnitude greater than those employed in other precipitate flotation studies (*1*–*3*). Specific objectives include the determination of the coflotability of both precipitates, the success of the flotation process in the separation of calcium sulfite from calcium carbonate, and any influence of the presence of the anionic surfactant NaDBS (which would be present in the clarified stream recycled to the scrubber) on the precipitation of calcium sulfite.

EXPERIMENTAL

The batch, precipitate flotation experiments were carried out in a 9.5-cm in diameter by 81.9 cm in height Pyrex column. A small magnetic stirrer was placed in the base of the flotation column in order to prevent the solids in the feed suspension from settling prior to the start-up of each run. Nitrogen gas was saturated with water, was metered with a calibrated rotameter, and was diffused through a 3.0 cm diameter, sintered glass frit of 50 μm nominal porosity at a rate of 0.4 liter/min (at 25°C and 1 atm). In each experiment, 2.0 liters of the initial suspension were floated until all foam formation ceased, which generally required from 5 to 15 min. The foam was removed continuously from a port located 7.0 cm above the initial suspension level, 34 cm above the base of the column.

Three series of experiments were conducted. The first involved calcium sulfite precipitate. Sodium sulfite and calcium chloride solutions in double distilled water (all salts, acids, and bases were Analytical Reagent Grade) of proper concentrations (molar Ca^{2+}/SO_3^{2-} ratio of 1.0) were contacted, brought approximately to the 2-liter feed suspension volume, and were gently mixed for 15 min with a magnetic stirrer to bring the precipitation reaction to equilibrium. Approximately 19 mole-% of the sulfite was converted to sulfate by dissolved oxygen oxidation; experimental conditions were controlled to maintain that conversion at an approximately constant value. A known volume of 1.0×10^{-2} M sodium dodecylbenzenesulfonate (NaDBS, Pilot Chemical Co., 90% active) was then added, the mixture was brought to the final 2.0 liter volume and was mixed for an additional 10 min, and then the feed suspension was placed in the flotation column.

The second series of experiments involved powdered calcium carbonate. Ten (10.00) grams of 200 mesh calcium carbonate were added to approximately 2 liters of water, the suspension was mixed for 10 min, and the pH was adjusted with 1.0 *M* HCl, followed by 10 additional minutes of stirring. Then NaDBS was added, as above.

The third series of experiments involved mixed suspensions of calcium sulfite and calcium carbonate. The pH of a calcium carbonate suspension was adjusted to 5.5 with 1.0 *M* HCl (with 10 min of mixing), to provide approximately 1 mole of Ca^{2+} for each mole of $SO_3{}^{2-}$ (including any sulfite oxidized to sulfate). A sodium sulfite solution was added, the mixture was stirred for 20 min, 1.0 *M* NaOH was added, and after 15 min of additional stirring the pH was 6.9. That pH value would be typical of a scrubber purge stream. Then NaDBS was added, as above.

Analyses were conducted on the feed suspensions prior to NaDBS addition and on the residual suspensions remaining in the column after flotation. For total calcium, the suspension was acidified with H_2SO_4 to dissolve all particles, and the pH was then elevated to above 10 with NaOH (with no reprecipitation observed); the solution was titrated with EDTA, using murexide as the indicator (*12*). The analysis of soluble calcium followed the same procedure except for the initial acidification; the precipitate was removed from solution prior to analysis via vacuum filtration of the sample through a 0.45-μm Millipore filter. Total sulfite was determined in the acidified solution by a potassium iodide–potassium iodate–thyodene titration procedure (*12*), and soluble sulfite with a vacuum-filtered sample. In both the calcium and sulfite analyses, the presence of NaDBS did not provide any appreciable interference.

The surfactant, NaDBS, that was present in the vacuum-filtered samples of the residual suspensions was determined with a Beckman Carbon Analyzer, subtracting the inorganic carbon measurement from the total carbon measurement to yield the DBS^- concentration as carbon.

The concentration of precipitated carbonate in the residual suspensions could not be determined directly, due to the problem of the degassing of carbon dioxide upon solution acidification. Instead, it was assumed to be equal to the difference between the concentration of precipitated calcium and the concentration of precipitated sulfite, also taking calcium sulfate into account. Some calcium sulfate was probably present in the residual suspensions, but its flotation was likely to be proportional to that of calcium sulfite, and the sulfate concentrations were low compared to carbonate.

RESULTS AND DISCUSSION

Flotation of Calcium Sulfite

The feed suspensions contained the following concentrations: 3.3 × 10^{-2} *M* total sulfite, 0.8 × 10^{-2} *M* total sulfate, 4.1 × 10^{-2} total calcium, 3.3 × 10^{-2} *M* precipitated sulfite (only about 1% of the sulfite remained in solution), and 3.6 × 10^{-2} *M* precipitated calcium. The pH was the unadjusted value of 7.6: a previous study with more dilute suspensions indicated that calcium sulfite precipitate flotation was relatively independent of pH over the range 6.5 to 10.0 (*7*). The flotation results are given in Fig. 1 in terms of the percent flotation of precipitated sulfite, based on concentrations in the feed and residual suspensions. The flotation of precipitated calcium closely paralleled that of the sulfite. The optimum NaDBS concentration was 3.0 × 10^{-4} *M*, or 0.009 mole DBS^- per mole of precipitated SO_3^{2-}. This latter figure compares favorably with the optimum ratio of 0.011 mole/mole established for calcium sulfite suspen-

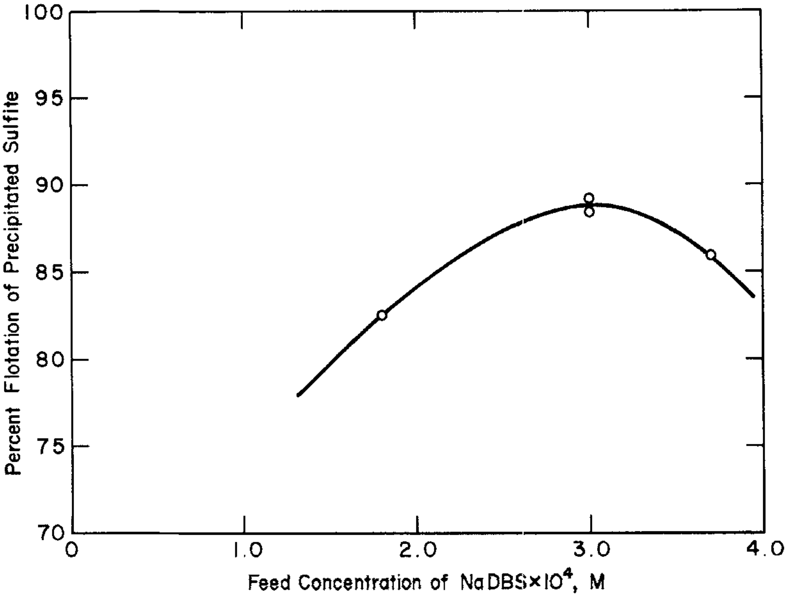

FIG. 1. Effect of surfactant (NaDBS) concentration on precipitate flotation of calcium sulfite.

sions that were five times more dilute (7). In the case of the dilute suspensions, the precipitation reaction (at a comparable molar $Ca^{2+}/SO_3{}^{2-}$ ratio of 1.0) was less efficient, with 69% precipitation of the total sulfite, compared to 99% for the suspensions in Fig. 1. For the concentrated suspensions at 3.0×10^{-4} *M* NaDBS, the ratio of precipitated sulfite in the foam to that in the residual suspension was 32.

Flotation of Calcium Carbonate

The feed suspensions contained the following concentrations: 5.0×10^{-2} *M* total calcium and total carbonate; at pH 7.2, 4.9×10^{-2} *M* particulate calcium carbonate; at pH 8.7, 5.0×10^{-2} *M* particulate calcium carbonate. The flotation results are given in Fig. 2, utilizing the same scales for comparison with Fig. 1. Excellent flotation of the calcium carbonate particles was achieved at both pH 7.2 and 8.7, with an optimum NaDBS concentration of 0.6×10^{-4} or 0.0012 mole DBS^- per mole $CO_3{}^{2-}$ (or Ca^{2+}). Fuerstenau and Miller (*13*) reported 100% flotation of

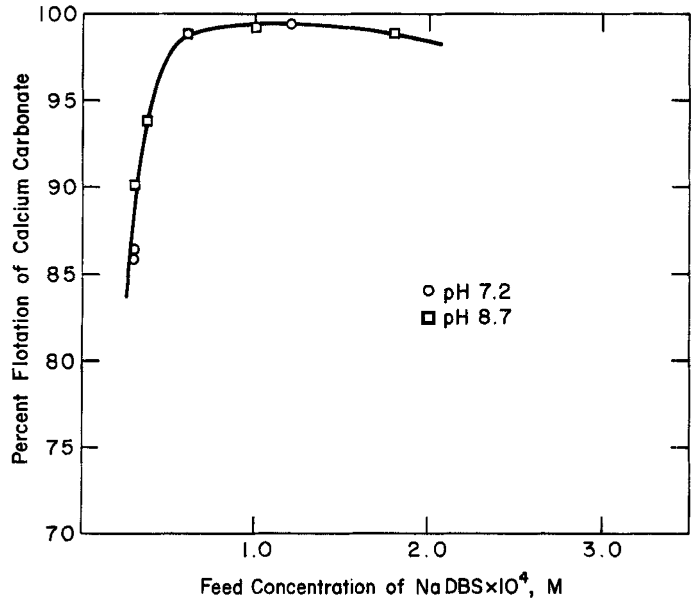

FIG. 2. Effect of surfactant (NaDBS) concentration on flotation of calcium carbonate.

finely-ground calcite with sodium dodecylsulfonate at a molar surfactant to calcium ratio of 0.0005. For the suspensions in Fig. 2 at the NaDBS concentration of 0.6×10^{-4} *M*, the ratio of precipitated calcium carbonate in the foam to that in the residual suspension was 3300.

Flotation of Calcium Sulfite–Calcium Carbonate Mixed Suspensions

Three concentrations of calcium sulfite and calcium carbonate in the feed suspensions were utilized. The molar ratio of Ca^{2+} to total $SO_3{}^{2-}$ plus particulate $CO_3{}^{2-}$ was maintained at 1.0. Also, the ratio of calcium sulfite precipitate to calcium carbonate was held at approximately 0.68 mole/mole, a typical value in the purge stream from a SO_2 wet scrubber. Data for the feed suspensions are given in Table 1. Flotation results are presented in Figs. 3 and 4, utilizing the same scales for comparison with Figs. 1 and 2. For calcium sulfite, 95% flotation was achieved with 1.3×10^{-4} *M* NaDBS, 1.8×10^{-4} *M* NaDBS, and 1.8×10^{-4} *M* NaDBS for feed suspensions A, B, and C, respectively. The presence of calcium carbonate, and perhaps the different mode of precipitation of calcium sulfite, clearly enhanced the flotation of calcium sulfite, comparing curve B of Fig. 3 with Fig. 1.

For calcium carbonate, from Fig. 4, 1.3×10^{-4} *M* NaDBS, 1.8×10^{-4} *M*, and 1.8×10^{-4} *M* concentrations, which produced 95% flotation of calcium sulfite, produced 97% flotation of calcium carbonate, for feed suspensions A, B, and C, respectively. A comparison of curve B of Fig. 4 with Fig. 2 shows that the presence of calcium sulfite retarded the flotation of calcium carbonate at a constant NaDBS concentration. This was probably due to the higher total particle concentration in the mixed suspension.

TABLE 1

Feed Suspension Concentrations

Suspension	A	B	C
pH	6.9	6.9	6.9
Total sulfite $\times 10^2$, *M*	1.6	3.3	4.9
Total sulfate $\times 10^2$, *M*	0.4	0.8	1.2
Total calcium $\times 10^2$, *M*	4.6	9.1	13.7
Precipitated sulfite $\times 10^2$, *M*	1.5	3.2	4.8
Precipitated carbonate $\times 10^2$, *M*	2.2	4.6	7.2
Precipitated calcium $\times 10^2$, *M*	3.8	8.3	12.9

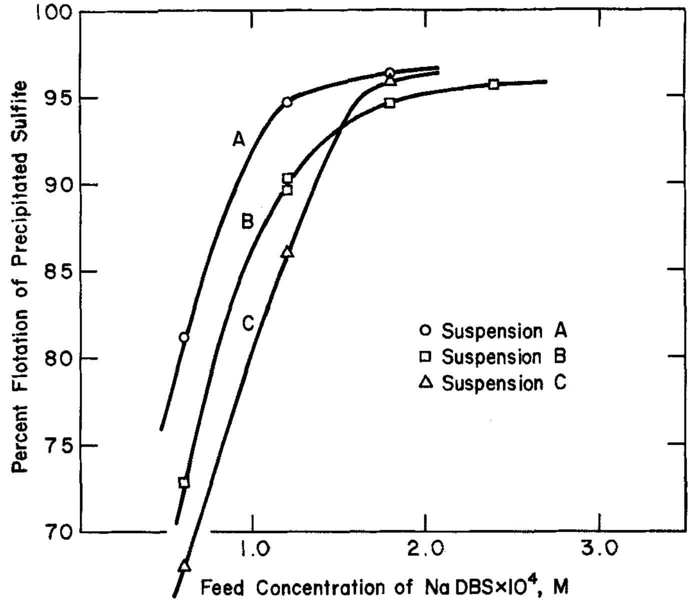

FIG. 3. Effect of surfactant (NaDBS) concentration on precipitate flotation of calcium sulfite from mixed suspensions of calcium sulfite and calcium carbonate at three concentration levels (see Table 1).

From Figs. 3 and 4 it is obvious that the separation of calcium sulfite from calcium carbonate via flotation with NaDBS is not possible, unless a selective flotation depressant could be found. On the other hand, excellent flotation of both species (95% for calcium sulfite and 97% for calcium carbonate) can be achieved at molar DBS^- to precipitated SO_3^{2-} plus CO_3^{2-} ratios of 0.0035, 0.0023, and 0.0015 for feed suspensions A, B, and C, respectively. At these NaDBS concentrations the ratios of precipitated sulfite plus carbonate in the foam to those in the residual suspensions were 256, 219, and 168, respectively.

One final experimental run was conducted that did not involve flotation. The purpose of this experiment was to see if a residual concentration of NaDBS would affect the precipitation of sulfite. Some NaDBS would be recycled with the clarified (by sedimentation followed by precipitate flotation) effluent from the purge stream and thus would be present in the wet scrubber. For the experiments with the mixed suspensions of calcium sulfite and calcium carbonate, the percent flotation or removal of NaDBS

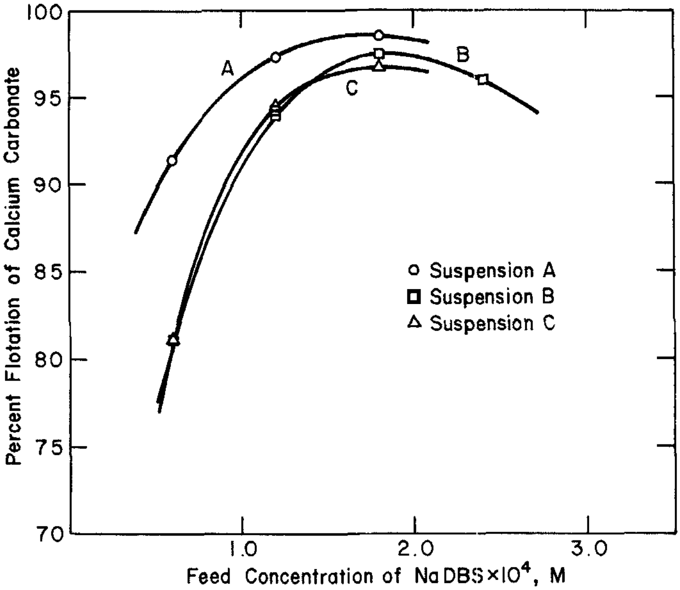

FIG. 4. Effect of surfactant (NaDBS) concentration on flotation of calcium carbonate from mixed suspensions of calcium sulfite and calcium carbonate at three concentration levels (see Table 1).

averaged 73% for the 11 experiments shown in Figs. 3 and 4, ranging from 65 to 82%. For an NaDBS dosage of 2.0×10^{-4} *M*, that would mean a NaDBS concentration of 0.54×10^{-4} *M* in the clarified effluent. This concentration would be diluted by about a factor of 20 to 1 in the wet scrubber. The precipitation reaction of Suspension B (see Table 1) was repeated, except in the presence of 0.4×10^{-4} *M* NaDBS. The precipitation results were virtually identical to those in the absence of NaDBS.

CONCLUSIONS

Mixed suspensions of calcium sulfite and calcium carbonate, at concentrations about 10% of those in the purge stream of a limestone wet scrubber, can be clarified readily by flotation with the strongly acidic, anionic surfactant, sodium dodecylbenzenesulfonate (NaDBS). For concentrations of calcium sulfite plus calcium carbonate of 3.7, 7.8, and 12.0×10^{-2} *M*, 95% flotation of precipitated sulfite and 97% flotation of carbonate can be achieved at molar surfactant to sulfite plus carbonate ratios of 0.0035, 0.0023, and 0.0015, respectively. At the molar calcium to sulfite plus carbonate ratio of 1.0, rather complete precipitation of sulfite is achieved, ranging from 92 to 98% for the three feed suspensions. About 20% of the total sulfite is oxidized to sulfate, and it is likely that the calcium sulfate is floated along with the calcium sulfite. For the three feed suspensions, the ratios of precipitated sulfite plus carbonate in the foam to that in the residual suspension are 256, 219, and 168, respectively. The presence of NaDBS in the recycle to the SO_2 wet scrubber appears to have no effect on the precipitation of calcium sulfite in the scrubber. The surfactant demand for typical combustion and scrubbing conditions is 0.002 lb NaDBS/lb limestone.

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