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# Alizarin Red S as a Flotation Modifying Agent in Calcite-Apatite Systems

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## ABSTRACT

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Alizarin red S, a dye that stains calcite, was tested for its preferential adsorption and selective flotation effects in calcite and apatite mineral systems. Interestingly, alizarin red S was found to adsorb more on apatite than on calcite, and to depress its flotation with oleate more than that of calcite. Reagent dosage and conditioning time had major effects, and when these variables were optimized, selective depression of apatite could be obtained from mixtures with calcite. Extended premixing of calcite and apatite reduced selectivity. However, selectivity was restored when an acid wash stage was introduced prior to conditioning with alizarin red S. Tests conducted with reagents related in structure with alizarin red S, suggest adsorption to be controlled more by the -OH groups rather than the -$SO_3$ group of the molecule.

## INTRODUCTION

The beneficiation of phosphate ores containing carbonaceous gangues is complicated by similarities in the chemical composition of the minerals present (Somasundaran, 1975; Hanna and Somasundaran, 1976; Lawver et al., 1982). The objective of this research has been to develop reagents that interact selectively with minerals on the basis of specific differences in their surface chemical composition. In this paper, results obtained for oleate flotation of apatite and calcite using a dye, alizarin red S, as a modifying agent are presented. Alizarin red S was selected for this study because of its use as a selective staining agent for calcite (Friedman, 1959). The mechanism involves the reaction of $Ca^{2+}$ ions with the reagent which yields a purple-red calcium salt (Feigl and Anger, 1972). The structure of alizarin red S is shown in Fig. 1.

Initially, adsorption tests were conducted, and flotation experiments were performed on calcite and apatite separately, to determine reagent concentrations, conditioning times and pH values where differences in flotation behavior

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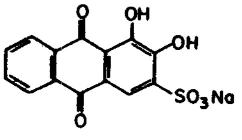

Fig. 1. Alizarin red S.

were maximal. Flotation on mixed mineral systems were then done to determine the reagent's effectiveness as a modifier.

## EXPERIMENTAL

### *Minerals*

For flotation experiments, $-17+35$ mesh Icelandic spar calcite and $-17+35$ mesh Canadian fluorapatite were used. Both samples were deslimed, cleaned with dilute nitric acid, and stored in triple-distilled water. For adsorption experiments, synthetic precipitated calcite and hydroxyapatite (Fisher Scientific Co.) with specific surface areas, as measured by the Quantasorb apparatus, of 0.85 $m^2/g$ and 26.1 $m^2/g$, respectively, were used. These high-surface-area samples were necessary to facilitate adsorption measurements.

### *Reagents*

Reagent-grade oleic acid was obtained from Fisher Scientific Company. Stock solutions were prepared by neutralizing oleic acid with 10% excess KOH, and dissolving in deaerated triple-distilled water. Certified-grade alizarin red S was obtained from Aldrich Chemical Company. All inorganic salts and pH buffers were reagent grade or better. Triple-distilled water was used for all experiments.

### *Methods*

#### *Adsorption*

The mineral sample was first conditioned in electrolyte solution at the required pH for three hours on a wrist shaker (pH measurements as a function of time indicated that three hours were needed to obtain a stable pH). The suspension was then conditioned for the length of time required for equilibrium, as determined from adsorption kinetics experiments; four hours were found to be sufficient for each system. Finally, the sample was centrifuged for 15 min at 4500 rpm, and the supernatant separated from the mineral bed. Reagent concentrations were determined using a UV spectrophotometer.

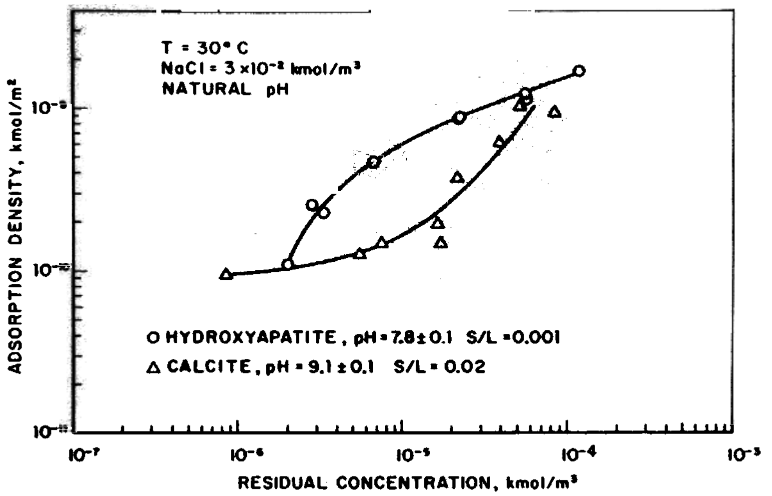

Fig. 2. Adsorption isotherms of alizarin red S on calcite and hydroxyapatite in $3\times10^{-2}$ kmol/m$^3$ NaCl.

### *Flotation*

An amount of mineral (1–2 g) was added to a 100-ml cylinder containing collector solution, electrolyte and pH buffer. The suspension was tumbled for 10 min at 17 rpm. Flotation was then carried out in a modified Hallimond cell for 10 s, using purified nitrogen at a rate of 20 ml/min. In the case of tests with binary mixtures, calcite and apatite were separated after flotation by gravity in tetrabromoethane. In experiments with alizarin red S, the mineral was first added to alizarin red S and electrolyte solution at natural pH, and conditioned for the desired length of time. Concentrated collector solution and pH buffer were then added, and the suspension conditioned for 10 min. In all cases, an aliquot was taken just prior to flotation for pH measurements.

## RESULTS AND DISCUSSION

### *Adsorption of alizarin red S*

The adsorption kinetics of alizarin red S on calcite and hydroxyapatite were found to be similar for the two minerals, and adsorption was complete after about two hours. Adsorption isotherms obtained for alizarin red S on calcite and hydroxyapatite are given in Fig. 2. Interestingly, hydroxyapatite is seen to adsorb alizarin red S more strongly than calcite, and in addition, was found to have been stained by the reagent. These results appear contrary to what would have been expected on the basis of the reagent's ability to stain coarse calcite mineral selectively over coarse apatite. Importantly, some possibility for selectivity was indicated in these tests, since at a concentration of $10^{-5}$ kmol/m$^3$ adsorption on hydroxyapatite is about four times greater than that on calcite.

Adsorption densities of alizarin red S on hydroxyapatite and calcite as a function of pH are given in Fig. 3. The shapes of the curves are almost identical for both minerals. A moderate dependence on pH exists, with maximum adsorption between pH 11 and 11.5. The shape of the pH dependence suggests that adsorption is not controlled primarily by electrostatic forces involving the sulfonate group, since such a dependence would result in higher adsorption at lower pH. Adsorption experiments with benzenesulfonate and catechol tend to support the view that the -OH groups control the adsorption of alizarin red S. Table 1 lists the adsorption kinetics results of benzenesulfonate on calcite. Clearly, the adsorption is negligible. On the other hand, catechol adsorbs on calcite at levels twice as high as alizarin red S (see Fig. 4).

Since alizarin red S adsorbs on calcite and apatite, its presence could modify the flotation behavior of these minerals. If alizarin red S and the collector compete for the same adsorption sites, then alizarin red S would depress flotation response.

### *Flotation of calcite and apatite*

Flotation results obtained for calcite and apatite with oleate are given in Figs. 5 and 6. Calcite shows a sharp drop in flotation between pH 8 and 10; while elsewhere in the tested pH range, flotation is more than 95%. The flotation of apatite, on the other hand, is nearly 100% between pH 6 and 12, with recovery dropping sharply when the pH is lowered below 6.

When the mineral is first conditioned for 10 min with alizarin red S prior to the addition of oleate, flotation is severely affected at pH levels above 8 (see Figs. 5 and 6). The minimum in calcite flotation is also lower, with flotation remaining at the 50% level at higher pH values. The effect on apatite flotation is even more marked; the plateau that existed between pH 6 and 12 has been reduced to a peak at pH 7. There is essentially no flotation above pH 9. The observation that the flotation of apatite is depressed to a greater extent than that of calcite, indicates some correlation between the adsorption and flotation tests despite the differences in mineral samples employed.

The flotation results showed that alizarin red S could significantly alter flotation behavior of salt-type minerals, and suggested possibilities for selective flotation above pH 10 with alizarin red S pretreatment. In this pH range, calcite floats moderately while apatite does not float. By optimizing key variables such as alizarin red S concentration and conditioning time, it was possible to make use of this difference in floatability to obtain separation.

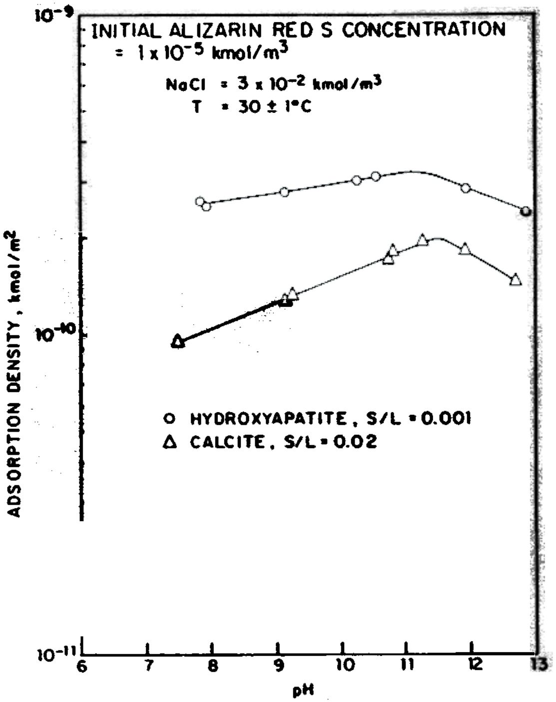

Fig. 3. Adsorption of alizarin red S on calcite and hydroxyapatite as a function of pH in $3\times10^{-2}$ kmol/m$^3$ NaCl.

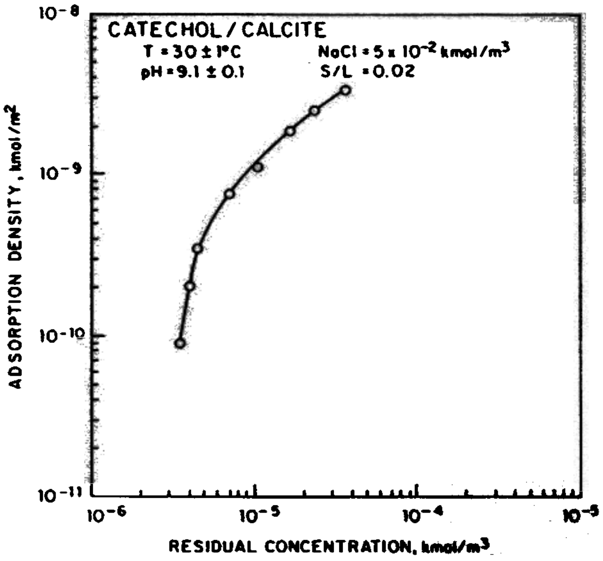

Fig. 4. Adsorption isotherm of catechol on calcite in $5\times10^{-2}$ kmol/m$^3$ NaCl.

TABLE 1

Adsorption kinetics of benzenesulfonate on calcite in $5 \times 10^{-2}$ kmol/m$^3$ NaCl

| Conditioning time (min) | Adsorption density ($10^{10} \times$ kmol/m$^2$) |
|---|---|
| 1 | 0 |
| 10 | 0.7 |
| 60 | 0.7 |
| 150 | 0 |
| 250 | 0 |

### *Flotation of calcite/apatite mixtures*

Results obtained for the flotation of calcite/apatite mixtures as a function of alizarin red S concentration are given in Fig. 7. In the absence of alizarin red S modifier, oleate floats both minerals at close to 100% levels. As alizarin red S concentration is increased to $5 \times 10^{-6}$ kmol/m$^3$, the flotation of calcite remains high, near 90%, while apatite flotation is depressed to 5–10%. Only at

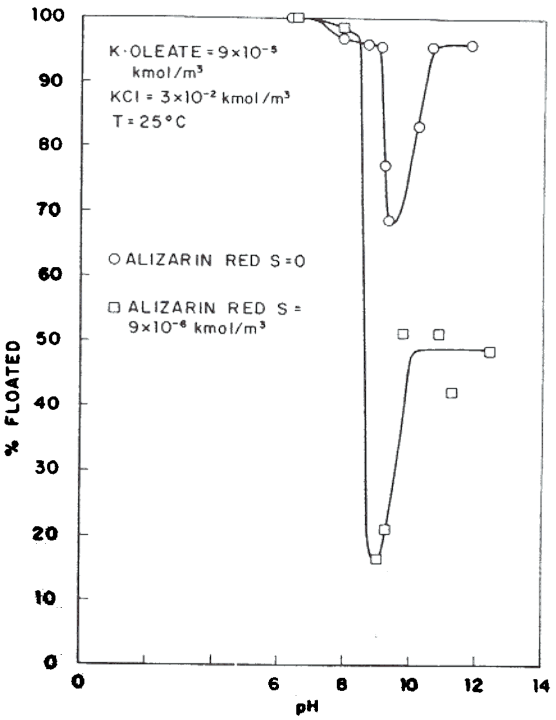

Fig. 5. The effect of alizarin red S on calcite flotation in $9 \times 10^{-5}$ kmol/m$^3$ K-oleate.

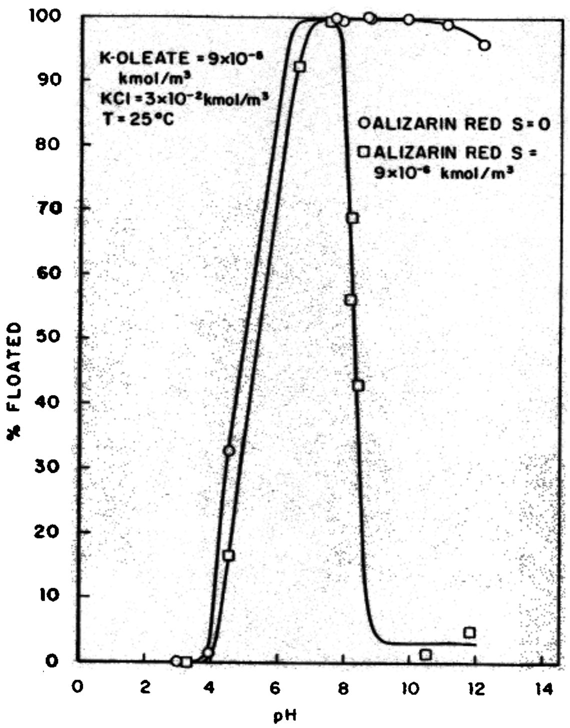

Fig. 6. The effect of alizarin red S on apatite flotation in $9\times10^{-5}$ kmol/m$^3$ K-oleate.

concentrations above $5\times10^{-6}$ kmol/m$^3$, is calcite flotation affected significantly.

The flotation dependence on conditioning time is given in Table 2. The data show that with the longer conditioning time, separation of the minerals is reduced due to the greater depression of calcite. Consequently, the effect of the reagent dosage is less significant in this case than when shorter conditioning times are used. Clearly, the duration of conditioning has a controlling influence on selectivity, and this may be attributed to surface chemical alterations induced

TABLE 2

Flotation (%) of calcite and apatite from binary mixtures at pH 10.5 as a function of conditioning time in the presence of alizarin red S

| Alizarin red concentration:<br>Conditioning time (min) | $9\times10^{-6}$ kmol/m$^3$ | | $9\times10^{-7}$ kmol/m$^3$ | |
|---|---|---|---|---|
| | Apatite(%) | Calcite(%) | Apatite(%) | Calcite(%) |
| 1 | | | | |
| 10 | | | | |

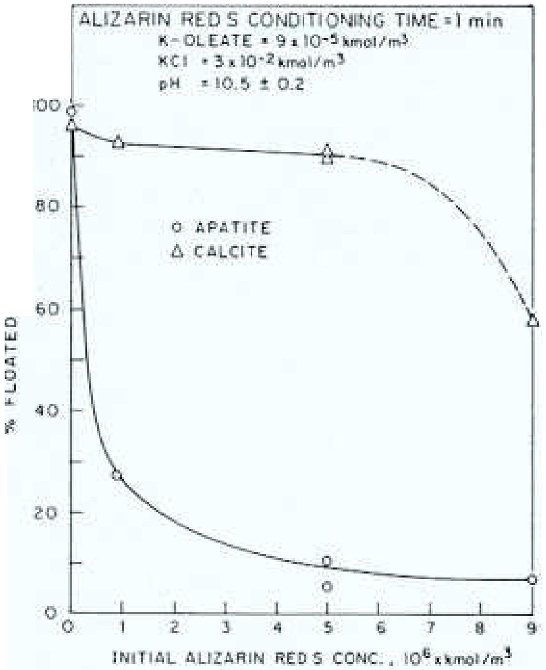

Fig. 7. Flotation of calcite and apatite from binary mixtures at pH 10.5 as a function of alizarin red S concentration.

by dissolved mineral species (Griffin and Jurinak, 1973; Amankonah et al., 1985a; Ananthapadmanabhan and Somasundaran, 1985).

In order to more fully investigate the above effect, experiments were conducted by first conditioning the calcite/apatite mixture in electrolyte solution for one hour prior to reagent addition. This mixture, when conditioned in alizarin red S solution for one minute, yielded a much lower calcite recovery, an average of 52% (see Table 1) compared to 90% without the premixing (see Fig. 7). Also, apatite flotation is increased. The result, as expected, is a convergence in the flotation properties of the two minerals.

Considering the tendency for calcite and apatite to produce surfaces with similar properties in solution (Bilsing and Gruner, 1973; Ananthapadmanabhan and Somasundaran, 1984; Amankonah et al., 1985b), it was thought useful to attempt a preliminary step, acid wash, for enhancing separation. Acid treatment can cause dissolution of any surface precipitate, and thus, promote the generation of fresh mineral surfaces.

In a typical experiment, following one hour of calcite/apatite conditioning in electrolyte solution, HCl was added to reduce pH to 2.8. The suspension was conditioned for 3 min, after which the supernatant was decanted, and alizarin red S solution added. The suspension was then conditioned for one minute,

TABLE 3

Effect of pretreatment on the flotation of calcite and apatite from binary mixtures in $9 \times 10^{-5}$ kmol/m$^3$ K-oleate

| Pretreatment | Alizarin red S concentration | pH | % Calcite floated | % Apatite floated |
|---|---|---|---|---|
| 1 hour in $3 \times 10^{-2}$ kmol/m$^3$ KCl | $2 \times 10^{-6}$ kmol/m$^3$ | 10.5 | 49<br>56 | 32<br>37 |
| 1 hour in $3 \times 10^{-2}$ kmol/m$^3$ KCl + 3 min acid wash | $5 \times 10^{-6}$ kmol/m$^3$ | 10.7 | 84 | 24 |

followed by the regular flotation procedure. Results in Table 3 show increased selectivity with acid wash. Calcite flotation, reduced to 52% by the premixing procedure, approaches levels attained with fresh mineral when washed in acid solution. Thus, the acid wash procedure appears to restore the floatability of calcite, and lead to improved separation.

## SUMMARY AND CONCLUSIONS

Alizarin red S has been seen to depress the flotation behavior of both calcite and apatite, but the latter more markedly than the former. Thus, staining behavior is not necessarily a reliable indicator for choosing effective flotation modifying agents. For obtaining selectivity with alizarin red S, the key variables are its concentration and conditioning time. Experiments have shown that by controlling these variables, separation of calcite from apatite is possible. The best results were obtained by conditioning the minerals for one minute in alizarin red S solutions between $2 \times 10^{-6}$ and $5 \times 10^{-6}$ kmol/m$^3$, and floating with oleate at pH 10.5. For a 50:50 mixture of calcite and apatite under these conditions, 90% of the calcite was found to float, compared to only 10% for apatite. Thus, alizarin red S appears to be a promising reagent for the beneficiation of phosphatic minerals. The results also clearly show the feasibility of developing reagent schemes for flotation based upon those used in mineralogical and analytical chemistry tests.

## ACKNOWLEDGEMENTS

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