DEVELOPMENT OF NEW BAYER PROCESS FLOCCULANTS

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New Bayer process flocculants which contain hydroxamate functional groups have been evaluated in laboratory settling tests in Bayer plants processing a wide variety of bauxites. Such tests have given consistently very low overflow solids, generally less than 20% of the solids obtained with conventional polyacrylates. Pilot settler tests have given similar results. Plant settler tests have now also achieved overflow solids reductions of up to 80%. Floc structure and optimum mixing conditions are different from those for polyacrylates, and work is continuing to optimize compositions and application conditions.

Introduction

A new class of hydroxamated flocculants for the Bayer process has been previously described (1, 2). The chemistry of these materials is distinctly different from that of conventional synthetic red mud flocculants, which are polyacrylates or acrylic acid/ acrylamide copolymers. These new polymers contain hydroxamate functional groups in addition to both carboxylic and amide groups, and the inclusion of hydroxamate groups provides for very strong attachment of polymer to mud particles, leading to characteristics which are quite different from those exhibited by the conventional flocculants.

Laboratory Settling Tests

"Overflow" Clarity

Since the discovery of these flocculants, the major benefit has been exceptionally good overflow clarities. As reported earlier, laboratory settling tests consistently give overflow suspended solids only 10-40% of those obtained with conventional polyacrylates, for a wide variety of bauxite ores. Typical results of lab settling tests are given in Figures 1 and 2 for feeds derived from Boke ores. For the new settling agents, these tests show the characteristic decrease in suspended solids with increasing dosage, down to extremely low clarities; the suspended solids from the polyacrylate are typically nearly independent of dosage or increase somewhat with dosage. Clarities obtained with the new settling agents in such lab tests are several times better than those from the polyacrylate. (Clarities obtained with polyacrylates in lab tests are typically considerably poorer than they actually are in the plant, by factors of two or more. This is thought to be primarily due to the longer retention time in the plant settler-several hours, vs. usually only 30 minutes in the lab tests-which favors the relatively slow acting polyacrylate.)

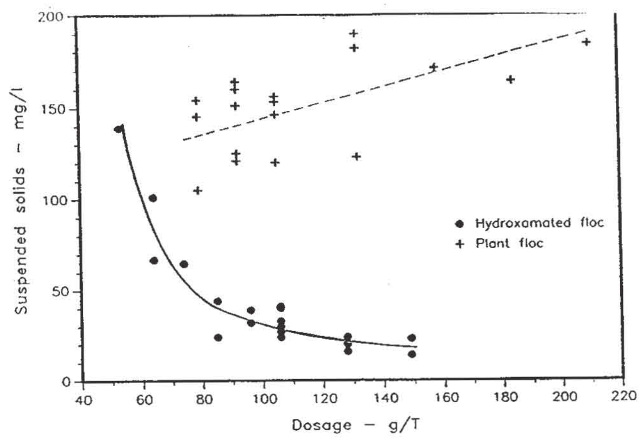

Figure 1. Suspended solids vs. dosage, lab tests.

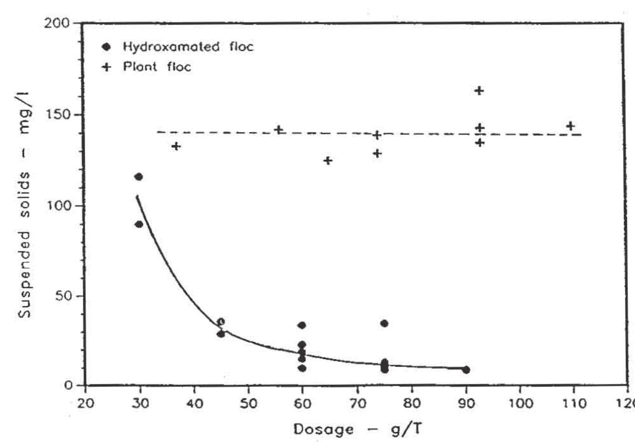

Figure 2. Suspended solids vs. dosage, lab tests.

The extremely good clarities possible with the hydroxamated flocculants were noted quite early. Since then, major improvements have been made in increasing molecular weight and hence reducing the required dosages, without losing the clarity benefits.

Excellent clarities have always been possible in lab settling tests. As discussed below, however, the floc formation and consequently the optimum mixing conditions are different for the hydroxamated flocculants compared to polyacrylates. In lab tests, a very wide range of results can be obtained just by varying the mixing conditions, so it should not be surprising that the new reagents cannot be added into the Bayer process streams in the plant in the same manner now used for polyacrylates. In addition, clarities and settling rates are naturally dependent on the composition of the hydroxamated flocculant. Through experience with effects of polymer composition and of mixing, the excellent clarities observed in the lab have now been obtained in plant tests also.

Floc Stability

There are clearly significant differences between the new settling agents and polyacrylates in their mechanism of floc formation. The hydroxamate group is known to be strongly bonded to transition metal species, particularly iron, which is prevalent in the surface of most of the mineral particles constituting red muds. The improved clarities appear to be a direct consequence of this strong attachment. Experience with these reagents has shown that strong, stable flocs are formed. This is demonstrated, e.g., by the results illustrated in Figures 3 and 4. In these experiments, the red muds were first flocculated with either a polyacrylate or an hydroxamated flocculant. The settled muds were then remixed to various degrees, using from 10 to 100 strokes of a perforated plunger, and sampled for "overflow" clarity thirty minutes later. With a moderate amount of mixing, up to 20 strokes, both types of flocculated mud showed considerably reduced rates of resettling and increased overflow solids.

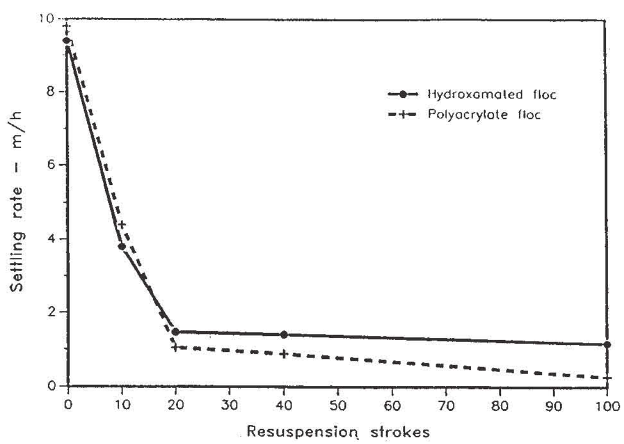

Figure 3. Effect of shear, after initial settling, on settling rate.

With still more severe remixing, the flocs in the polyacrylate-treated sample further deteriorated greatly; flocs were extensively broken up and hardly resettled at all after 100 strokes, with an extremely low settling rate and overflow "clarity" (after 30 minutes) of 3.7 grams/liter! In contrast, the sample treated with hydroxamated flocculant showed relatively small further decreases in settling rate and clarity with the severe mixing, indicating that the small flocs formed after the initial remixing were unusually shear resistant.

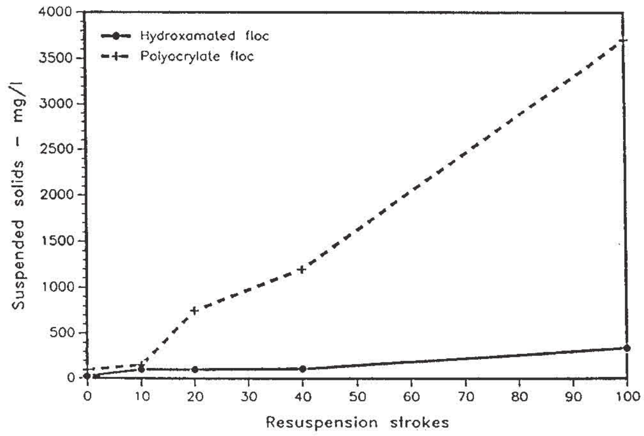

Figure 4. Effect of shear, after initial settling, on clarity.

Such observations are consistent with the stronger bonding produced by the hydroxamated flocculants compared to polyacrylate. Because of the strong interaction, it is expected that an hydroxamated molecule will be attached at multiple points on each particle, with consequently a relatively small number of particles being contacted by each molecule. The result is a small, but quite strong aggregate. If most of the functional groups are used up in forming these small aggregates, however, formation of larger aggregates may be rather weak. Strong, small aggregates, but relatively weak large aggregates are in accord with observations. The problem of weak large aggregates can be readily overcome by adding more hydroxamated flocculant after the small, strong flocs are formed, to collect the small flocs into large ones with high settling rates.

Mixing Effects

The formation of flocs and stability of flocs to shear are quite dependent on mixing conditions. In laboratory settling tests, it is obviously possible to use any desired amount of mixing and consequently obtain a rather wide range of results. Each laboratory at a Bayer plant generally has a method of mixing which establishes dosages and settling rates which correspond to stable plant operation. These lab tests, however, have in the past been used only for polyacrylates, and it is now clear that they do not apply well to our hydroxamated flocculants. More importantly, the mixing conditions in the plant settlers, i.e., the points of addition, have been optimized for polyacrylates and are not necessarily optimum for hydroxamated flocculants.

Dependence of polyacrylate and hydroxamated flocculants on mixing conditions is illustrated by lab settling tests where addition of the polymer is done in two quite different ways: 1) the polymer is added all at once, with a moderate amount of mixing (this approximates what is usually done for polyacrylate testing), or 2) the polymer is added in two stages; a first portion followed by quite thorough mixing, then a second portion, followed by moderate mixing as above. Results of such testing using a plant polyacrylate are shown in Figures 5 and 6 (West Australian ore).

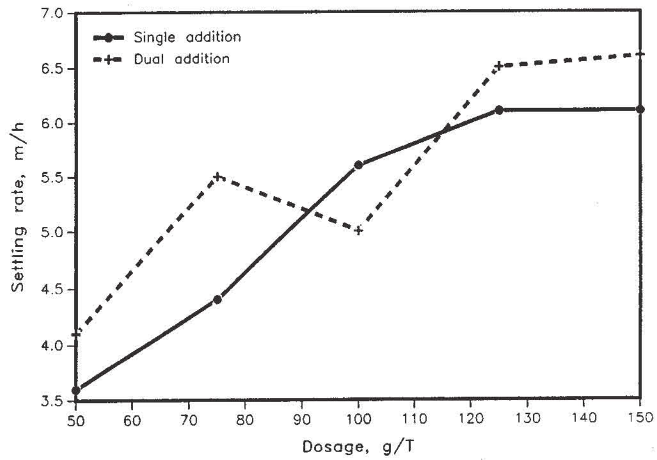

Figure 5. Lab settling rates using polyacrylate. Comparison of single and dual addition of floc.

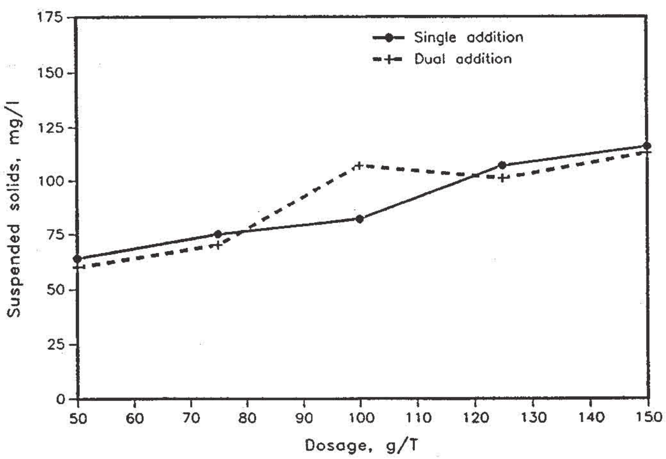

Figure 6. Lab clarities using polyacrylate. Comparison of single and dual addition of floc.

The two sets of data for the polyacrylate, based on quite different addition methods, agree well with one another. Settling rates increase only slowly with increasing dosage and clarities get worse with increasing dosage. For other ores, it is sometimes found that the dual addition gives somewhat higher settling rates, but clarities do not improve when using polyacrylates.

An hydroxamated flocculant shows a much different comparison between the single and dual addition methods (Figures 7 and 8). Both clarities and settling rates are improved substantially by using the dual addition. Clarities are already good even with the single addition, but are still better with the dual addition. The effect on settling rate is even more striking, with nearly a factor of two improvement in rate when using the dual addition (except at the lowest dosage). Much higher settling rates are attained with the hydroxamated flocculant than with the polyacrylate.

The differences in dependence of settling rates and clarities on polymer addition and mixing for polyacrylates vs. hydroxamated flocculants certainly reflect differences in floc structures, as already indicated above.

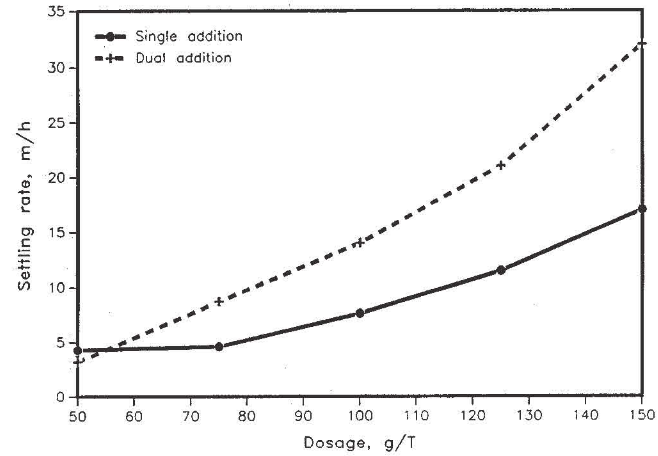

Figure 7. Lab settling rates using hydroxamated flocculant. Comparison of single and dual addition of floc.

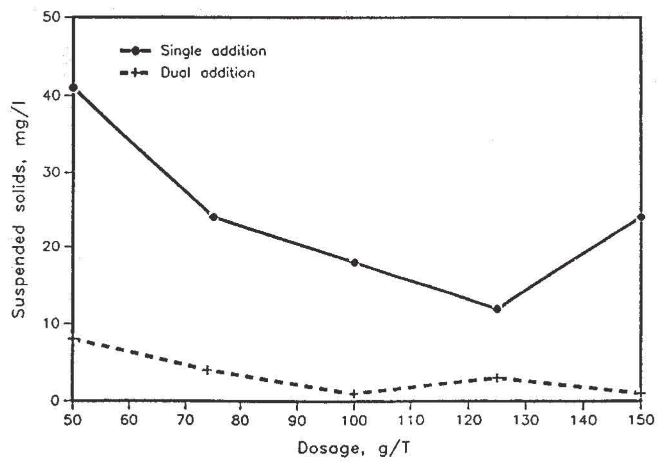

Figure 8. Lab clarities using hydroxamated flocculant. Comparison of single and dual addition of floc.

It is also noted that attachment of polyacrylate to mud particles is relatively slow; there is an apparent induction time (30-60 seconds in the above experiments) and settling is very uneven in the early stages, with no clear mud interface. This relatively slow attachment is at least partly responsible for the fact that the polyacrylate molecules end up rather uniformly distributed amongst the suspended mud particles, so it makes no significant difference whether the polymer is added in one or two stages. This slow attachment is also consistent with the increasing overflow solids with increasing settling rate; with faster settling rates, more small particles are left behind before they have had a chance to become part of a large floc.

Hydroxamated flocculants are adsorbed much more quickly and strongly than polyacrylates, and are consequently less uniformly adsorbed and more dependent on the addition and mixing conditions. In contrast to the poorly defined initial settling with polyacrylates, the hydroxamated flocculants give no induction time and a very sharp mud interface essentially from the very beginning of settling, with very clear liquor above the interface, all indicative of rapid attachment to the mud particles. If the hydroxamated flocculant is added all at once and quickly mixed in, it is expected to be reasonably uniformly adsorbed on the mud particles, and because of the rapid attachment will be fairly effective in collecting most of the suspended particles. If, however, only part of the polymer is added followed by vigorous mixing, the individual particles can be more effectively collected into the small, but stable flocs mentioned earlier. A second addition of polymer then needs only to attach to the outside surfaces of the small flocs and bond them together to give large flocs with high settling rates.

To a large extent, clarity is determined primarily by the first addition of hydroxamated flocculant to form the small, stable flocs, while the second addition is most important in controlling settling rate. Therefore, at a given total dosage, it is possible to enhance either settling rate or clarity by varying the ratio of hydroxamated flocculant in the first and second additions.

Pilot Settler Tests

In a one meter diameter pilot settler with a flow of approximately ten liters per minute, excellent relative results were again obtained. Here the results with the polyacrylate were considerably poorer than they were in the plant settlers, with overflow suspended solids approximately twice as high as in the plant. Such higher results were attributed primarily to the short distance between the feed well and the overflow, so that there was significant short-circuiting. This would be less important for the new reagents with their faster initial floc formation and settling.

Some of the better results for two of the new reagents used in the pilot unit are summarized in Figure 9, where it is seen that clarities could be maintained at suspended solids levels of only 10-15 mg/l, equal to about 10% of the suspended solids obtained with the polyacrylate. As indicated above, results for the polyacrylate in the plant settlers are better than seen here, so we could not expect the same relative improvement in the plant. Nevertheless, there appeared to be no reason why we should not see the same good absolute numbers, namely 10-15 mg/l overflow clarities, when using our new reagents in the plant.

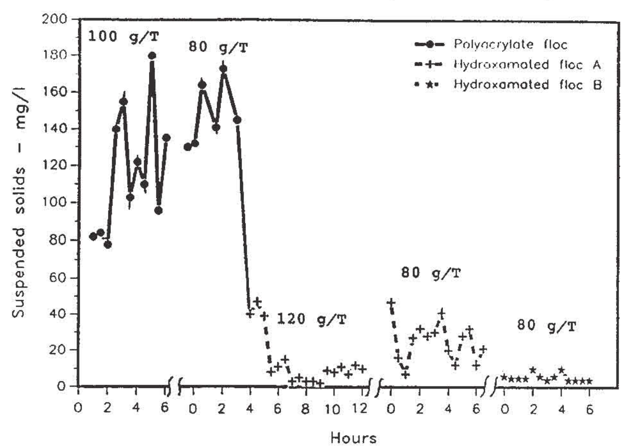

Figure 9. Pilot settler overflow clarities vs. operating time.

Plant Tests

The first plant tests with the hydroxamated flocculants gave overflow clarities that were not nearly as good as predicted from the lab and pilot testing. In one of the earlier tests (Figure 10, using a Boke ore), however, one of the new settling agents gave an average overflow clarity of only 25 mg/l on one settler, compared to about 60 mg/l on another identical settler running at the same time with polyacrylate. In addition, the overflow clarity from the settler using the new reagent is clearly more consistent.

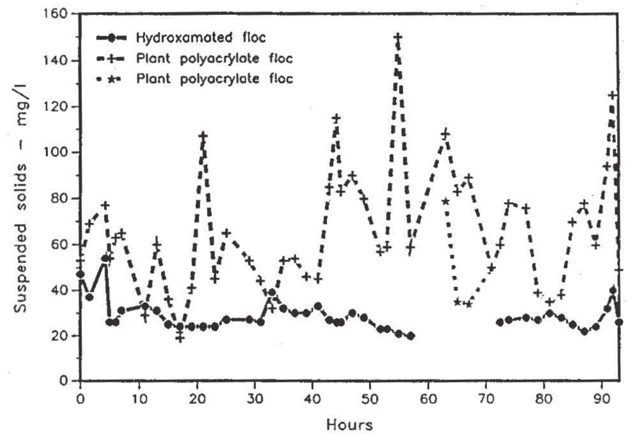

Figure 10. Comparison of overflow clarities from two plant settlers running at the same time, on polyacrylate or on hydroxamated flocculant.

Although some fair clarity improvements were seen in the early plant tests, underflow mud densities tended to be low. This appeared to be due to the much more dynamic conditions in the plant settlers, compared to the rather static lab testing, or even the small pilot settler. High feed flow rates gave mixing which seemed to be considerably more vigorous than any used on the small scale. In addition, the mud bed is subject to disturbances by the rake, possibly by the high velocity of the incoming feed, and there is a net upflow velocity of approximately 0.5 m/h associated with the overflow. These more dynamic conditions appeared to lead to some breakup of the large flocs formed with the hydroxamated flocculant, with consequently poorer compaction and possibly some fragments carried up with the overflow.

Through changes in polymer composition, together with the manner in which the polymer is mixed in, this problem of floc breakup has been eliminated. Recent plant tests have produced clarity improvements close to those seen in lab settling tests. Figure 11 shows the dramatic effect observed when switching from the usual plant polyacrylate (plus starch) to an hydroxamated flocculant. Starting from an average clarity of 38 mg/l, the average was reduced to only 10 mg/l. Operation was again quite consistently good with the new reagent.

At the same time, underflow mud densities are quite comparable to those obtained with polyacrylate, with stable operation as shown in Figure 12. Actually, it may be possible to get higher usable mud densities than with polyacrylates. Unlike polyacrylates at high dosages, which lead to very dense, sticky muds, densities with hydroxamated flocculants are much less likely to become excessive, and at the same mud densities, the hydroxamated muds are less viscous than those obtained with polyacrylates. Such differences in mud characteristics are directly related to the differences in floc structure mentioned above.

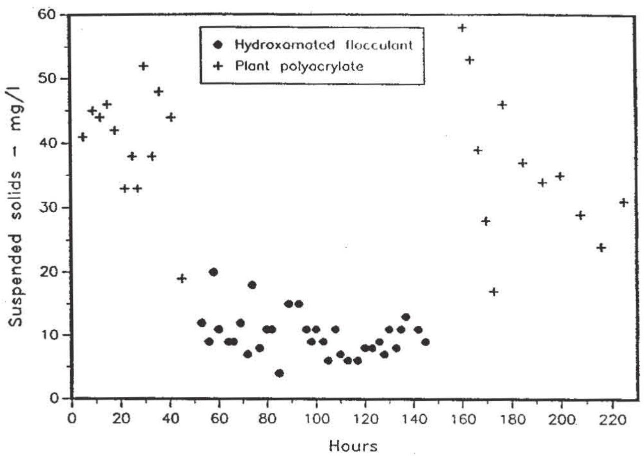

Figure 11. Overflow clarities for plant settler switched to hydroxamated flocculant and back to polyacrylate.

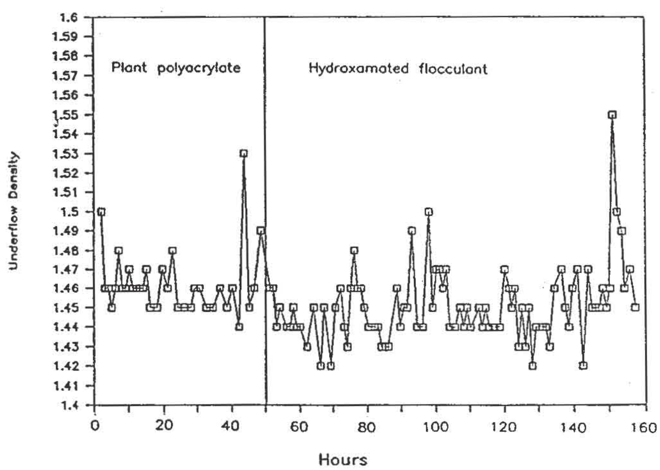

Figure 12. Underflow densities corresponding to the clarities of Figure 11.

Summary

The mechanism of flocculation with the new hydroxamated flocculants is found to be distinctly different from that for the conventional polyacrylates. The hydroxamated flocculants are more rapidly and more tightly bound to the mud particles, resulting in small but very stable flocs. These small flocs can be readily aggregated together with additional flocculant to give high settling rates and exceptionally good overflow clarities.

This difference in mechanism leads to a unique property for the hydroxamated flocculants, namely that clarities improve substantially with increasing dosage. At the same time, settling rates and underflow densities also naturally increase, but there do not appear to be any adverse effects of overdosing. Again because of differences in the floc structure, muds formed with the hydroxamated flocculants do not readily become too dense and sticky as happens with polyacrylate overdosing. This may well provide other substantial benefits in addition to the clarity improvements.

Through optimization of composition and mixing conditions, extremely good and consistent overflow clarities averaging only 10 mg/l have been demonstrated in one plant. There now appears to be no reason why similar results cannot be obtained in any Bayer plant.

References

(1) A. S. Rothenberg, D. P. Spitzer, M. E. Lewellyn, and H. I. Heitner, "New Reagents for Alumina Processing," Light Metals (1989) 91-96.

(2) D. P. Spitzer and W. S. Yen, U. S. Patent 4,767,540, 1988.