



SOCIETY FOR MINING, METALLURGY, AND EXPLORATION, INC.

P. O. BOX 625002 • LITTLETON, COLORADO • 80162-5002

PREPRINT
NUMBER

93-45

ALTERNATIVE REDUCTIVE BLEACHING PROCESS FOR KAOLIN

LETTERMAN HALL LIBRARY
609 CHERRY STREET
KANSAS CITY, MO. 64110
U. S. A.

E. S. Forbus

R. H. Young

M. J. Willis

Engelhard Corporation
Gordon, Georgia

For presentation at the SME Annual Meeting
Reno, Nevada — February 15-18, 1993

Permission is hereby given to publish with appropriate acknowledgments, excerpts or summaries not to exceed one-fourth of the entire text of the paper. Permission to print in more extended form subsequent to publication by the Society for Mining, Metallurgy, and Exploration (SME), Inc. must be obtained from the Executive Director of the Society.

If and when this paper is published by the SME, it may embody certain changes made by agreement between the Technical Publications Committee and the author so that the form in which it appears is not necessarily that in which it may be published later.

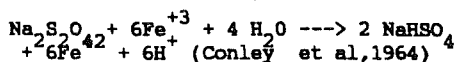
Current year preprints are available for sale from the SME, Preprints, P.O. Box 625002, Littleton, CO 80162-5002 (303-973-9550). Prior year preprints may be obtained from the Engineering Societies Library, 345 East 47th Street, New York, NY 10017 (212-705-7611).

PREPRINT AVAILABILITY LIST IS PUBLISHED PERIODICALLY IN
MINING ENGINEERING

Abstract. A process for producing reductive bleach in-situ in kaolin slurries has been developed. The bleach is formed by mixing an iron sponge powder (-325M) with slurry treated with SO₂. The process has been successfully demonstrated in production, and applied to several grades. The color, brightness, and viscosity of the bleached product is equivalent to or better than that of product bleached with commercial sodium hydrosulfite. The tested products can be bleached at a cost, which is 38-54% of those associated with the use of commercial bleach.

Introduction

Reduction bleaching is used to improve the brightness and color of the kaolin pigments sold to the paper and speciality industries. The bleach reduces the iron oxide associated with kaolin deposits to a colorless form by the following reaction.



At present, sodium hydrosulfite is used by the kaolin industry as the reductive bleach. It is often purchased commercially as a liquid solution and added into an acidified slurry. Prior to the use of commercial sodium hydrosulfite, kaolin plants manufactured zinc hydrosulfite on site by adding zinc dust to sulfuric acid made by passing SO₂ gas into water. This process was abandoned in the 70's due to environmental concerns about zinc in waste waters.

In the 1980's two new bleach processes were patented by Engelhard (Tiethof 1978, Tiethof 1979). The first process made sodium hydrosulfite from an iron hydrosulfite. Difficulties with separating the iron hydroxide byproduct from the bleach and a decrease in the cost of commercial bleach caused the project to be abandoned. The second process made aluminum hydrosulfite by mixing aluminum powder with SO₂, similar to the method used to manufacture zinc hydrosulfite. The process was never scaled up because of the highly exothermic nature of the reaction and the potential of hydrogen gas under certain process conditions.

A process has recently been developed by Engelhard which produces a reductive bleach in-situ. A fine mesh iron powder is mixed into a kaolin slurry along with SO₂ to form iron hydrosulfite in the slurry itself by the following reaction:



The in-situ bleach reaction overcomes several of the disadvantages of the previously patented method of producing sodium hydrosulfite from iron hydrosulfite. The in-situ produced hydrosulfite ion quickly reduces the iron oxides in the kaolin. Therefore, the in-situ process does not require the formation of a sodium salt to overcome any stability problems that might be present with the iron hydrosulfite. The elimination of the need to form the sodium salt also removes the need to filter and wash the product in order to remove

iron hydroxide from the sodium hydrosulfite. Because of the lower concentration of the reactants in an in-situ reaction, no refrigeration is needed to counteract the deleterious effects of the heat generated in the reaction. The in-situ process can be easily installed as part of the present bleaching process and does not require the construction and operation of a separate chemical plant to supply the needs of the kaolin plant.

The process has been successfully scaled up. In production trials, the products bleached by the in-situ process had similar brightnesses, color, and viscosities to those of products bleached with the commercial sodium hydrosulfite. Improvements in viscosity have been with some types of clay. The production costs are 39%-64% lower than the commercial bleach.

Material and Methods

Laboratory Experiments

Unbleached kaolin slurries (20-30% solids) were bleached in the laboratory by adding iron powder and a source of sulfite ions. The average particle size of the iron powders tested ranged from 44 microns to 1500 microns. The sources of sulfite ions included either sodium sulfite, sodium bisulfite, sodium metabisulfite, or sulfur dioxide. When necessary, the slurry was adjusted to a pH value of 3 with sulfuric acid. In some experiments alum was added as the commercially available solution. Samples were allowed to react for times varying from 30 min to 16 hours. Samples were then filtered, dried, and pulverized for brightness and color analyses. Brightnesses of samples bleached by the experimental process were compared to samples bleached with a commercial dry sodium hydrosulfite at a pH near 3.

Production Trials

During production trials, control samples were taken from the production bleach line in which liquid sodium hydrosulfite bleach, acid, and alum were mixed in the slurry with static mixers. In the demonstration unit, SO₂ gas, and alum were mixed in the slurry by the vacuum induction unit placed in a 50 gallon in-line reaction (Diagram #1). The 44 micron Fe powder was pumped to the reactor as a 100x concentrate made from iron powder and a side stream of bleached product. The iron powder was fed into the side stream of slurry with a volumetric dry feeder. The SO₂ was fed as a liquid from one ton cylinders to a vaporizer. The SO₂ gas levels were controlled with a sulfonator. Samples were collected from a sample port on the bleach reactor.

Results and Discussion

Determination of the Optimum Reactants

Iron

The bleach reaction rate is affected by the particle size of the iron powder. A sample treated with a 1500 micron iron powder was

bleached from a brightness of 82.6 to a brightness of 84.5 after one hour of reaction time. The maximum brightness potential of 86.8 was measured after 16 hours. In contrast the sample treated with 44 micron iron powder reached the same maximum brightness potential in the first hour of bleaching. After the initial screening experiments, the 44 micron powder was routinely found to react in less than half an hour. This is the same time frame as that of commercial sodium hydrosulfite.

The optimum concentration of iron varied with the type of kaolin being processed. Products made from Tertiary crudes had demands of about 0.2 Kg/t (0.5 lb/t) whereas products made from Cretaceous crudes had demands between 0.5 and 0.75 Kg/t (1 -1.5 #/t).

If the iron concentrations exceeded the demand of the product, brightness was repressed and the slurry developed a dark grey color unless excessive amounts of SO₂ were added (Graph #1). When these products were spray dried the yellowness index was directly proportional to the amount of iron in excess of the demand (Graph #2).

When products were bleached with the pre-determined optimum iron and SO₂ levels all added iron was converted to the soluble ferrous state. During filtration 90%-100% of the added iron could be found in the water removed by filtration. No unreacted iron powder could be isolated from a slurry of the redispersed filter cake by exposing the slurry to a magnet for an hour.

Sulfur

Although some bleaching was seen with sodium bisulfite and sodium sulfite, the maximum bleached brightnesses were seen using acidified sodium metabisulfite or sulfur dioxide. Sulfur dioxide was found to be superior in performance and cost to the other reagents.

The optimum levels of SO₂ were determined for samples by measuring the brightness of the product at different levels of SO₂ at a given iron addition rate (Graph #2). The majority of the products obtained maximum brightnesses with 9-12 #/t SO₂ at the iron levels determined previously to give the maximum brightness.

The pH of the slurry decreased rapidly with the addition of SO₂. This eliminated the need to flocculate the slurry with sulfuric acid as with conventional bleaching. The pH of the typical in-situ bleached product ranged from 2.5 to 3.0.

Effect of Flocculants

Flocculation of the unbleached feed with alum or sulfuric acid was tested as a method of decreasing the levels of SO₂ required by the in-situ process. Alum addition was found to decrease the level of SO₂ required to obtain maximum brightness (Graph #3). In contrast, when sulfuric acid was at concentrations which resulted in pH changes in the range of 6.2 down to 2.2, the brightness was repressed by the presence of the acid (Graph #4).

When tested in production, 4 to 6#/T of alum were routinely added to the in-situ bleach process. Brightnesses were enhanced by the addition of alum in all grades tested (Table #1). Alum was often required to obtain brightness equivalent to sodium hydrosulfite on a routine basis. When tested at a 95% confidence level, a #1 Coating Clay was found to have a 0.3 point lower brightness when bleached with no alum than with 4#/T of alum. The latter product had a brightness equal to that of a product bleached by the conventional method with sodium hydrosulfite.

Summary of Plant Evaluations

Product Physical Properties

Five different product streams were successfully bleached in plant trials by the in-situ process using the demonstration unit. The products varied in brightness potential from 84.4 to 91.0 (Table #2). When tested at the 95% confidence limit, there were no statistically significant differences between the products bleached by the normal production method using sodium hydrosulfite and those bleached by the in-situ unit. The Brookfield and Hercules viscosities of the in-situ bleached products were found to be equal or better than the conventionally bleached product (Table #3).

Production Rates and Costs

A #2 (80%-2 micron) coating clay was found to filter at an equal or slightly faster rate than the conventionally bleached product. Rates for the in-situ and conventionally bleached product were 9.9T/Hr and 8.9T/Hr, respectively. The specific resistance of the acid filter cakes (at 10% solids) was higher for the in-situ product (3400 ohms) than the conventionally bleached material (2700 ohms). This is indicative of a lower soluble salt content in the in-situ product.

The production chemical costs were significantly lower than the conventional method using commercial sodium hydrosulfite, acid, and alum (Table #2).

Environmental Impact

The in-situ bleaching process described here using the vacuum induction unit did not have a significant impact on the air or water quality in the plant. During filtration trials, the ACGIH (American Council of Governmental Industrial Hygienist) time weighted average (TWA) of 2 ppm SO₂ or 15 min exposure limit of 5 ppm of SO₂ were not exceeded in the air over the storage tanks containing filter feed or around the filters. Generally the level of SO₂ never exceeded 1 ppm over the storage tank of filter feed except when pumping slurry over into an empty tank. Levels of 3 ppm were measured during the initial 15 min of filter slurry addition, but quickly fell to 1 ppm or less as the tank filled. The levels of SO₂ over tanks containing conventionally bleached material were usually less than 0.5 ppm.

When bleached kaolin is filtered it forms a cake which is usually rinsed with water to remove soluble salts. Under these conditions less than 1 ppm of SO₂ was found in building when in-situ bleached material was filtered. Levels were often equal to that of the conventionally bleached material when filter cakes were rinsed. In contrast when filter cakes were not rinsed, the TWA of the in-situ bleached material rose to 1.4 ppm, whereas the TWA of the conventionally bleached material remained near the detection limits of 0.5 ppm.

In-situ bleaching was not expected to have any significant impact on the plant waste waters leaving the impound. The impound is used to settle particulates in plant waste water over a 30-60 day residence time. The concentration of iron in the filtrate of in-situ bleached and conventionally bleached product were 10 ppm and 90 ppm respectively. After a week of storage 100% and 95.6% of the iron in filtrate of the in-situ and conventionally bleached samples was removed with neutralization by sodium hydroxide. The turbidity of filtrate from in-situ and conventionally bleached products were 20 NTU (Nephelometric Turbidity Unit) and 40 NTU, respectively. The NTU limit in Georgia is 50 NTU.

Conclusion

An in-situ reductive bleaching process using iron powder and SO₂ gas has been successfully applied to the kaolin industry. Product brightness, color, and viscosity were equal or better than the product bleached with sodium hydrosulfite. Production rates were better or equal to that of the conventional process, and the environmental impact on the plant was minimal. The chemical costs of in-situ bleaching were significantly lower than for the conventional bleach process. The process is patented under U. S. Patent No. 5,145,814.

REFERENCES

1. Conley, R.F., Golding, H.J., and Taranto, M.W. 1964, "Improvement of Iron Bleaching in Clays through Potentiometric Control of Sodium Dithionite Addition," I & EC Process Design and Development, Vol 3, No. 2, pp. 183-188.
2. Tiethof, J.A., 1978, "Hydrosulfite Production," Patent No. 4,076,795.
3. Tiethof, J.A., 1979, "Hydrosulfite Preparation," Patent No. 4,157,980.

Table 1. Effects of Alum Addition on Brt

#/T Alum	Brt. in Grade of Kaolin ^a				
	#3	#2	#1	#P ^a	#P ^b
0	83.1	82.3	86.3		88.3
2	83.4	83.1	86.5	89.5	88.4
4	83.5	85.8	86.8	89.9	88.7
6	83.8	85.8	86.4	90.2	88.2

^aAll grades contained 7-9#/T SO₂ and
1.5#/T Fe

^b#1 Premium

^cDelaminated

Table 2. Comparison of Brt & Savings
of Two Bleach Processes

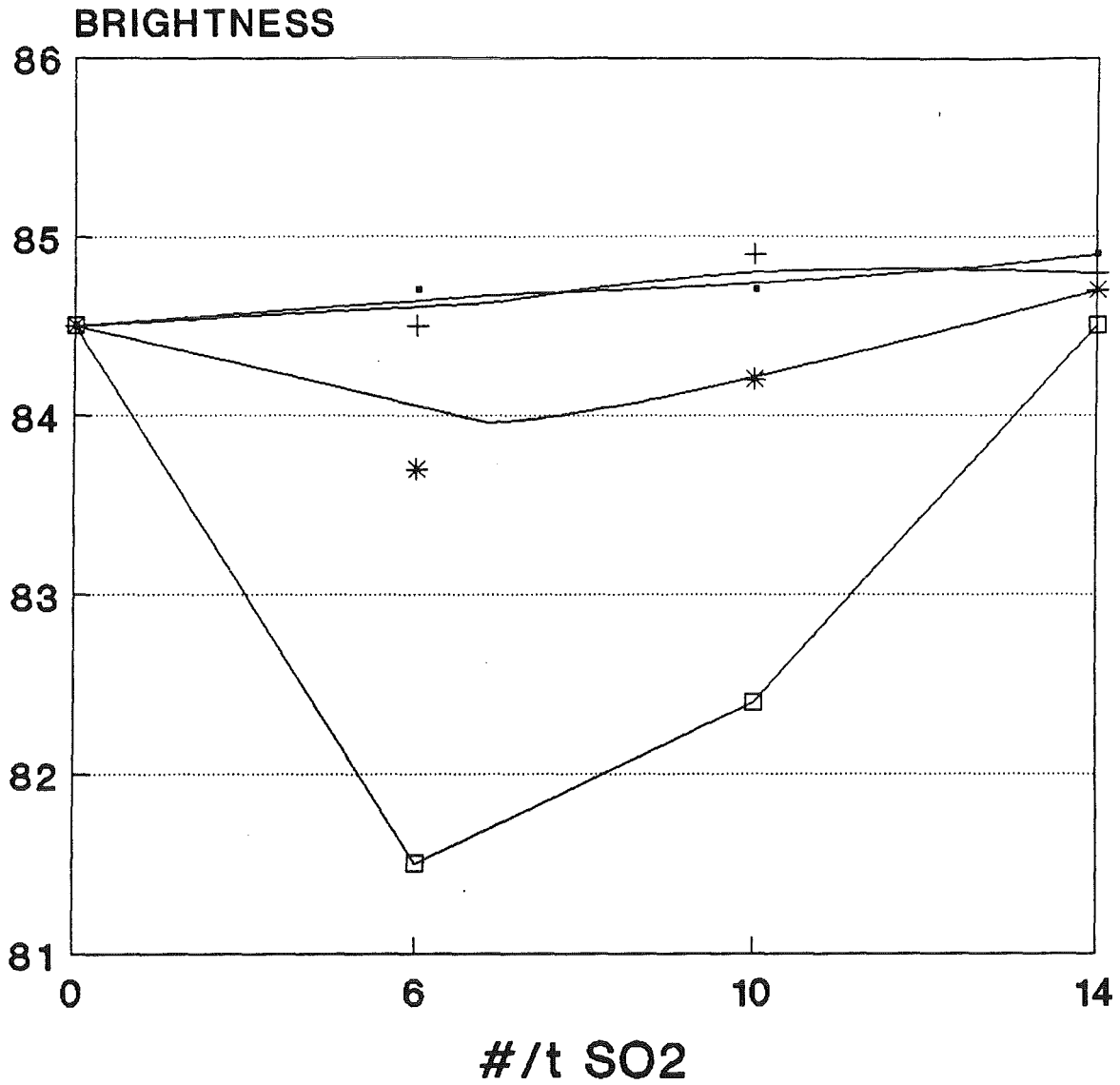
Product	# of Samples	Brightness		% Savings
		In-Situ	Control	
#1 Coating	16	86.20	86.22	49.0
#2 Coating	36	86.13	86.26	37.9
#3 Coating	18	84.25	84.12	39.9
#1 Premium	3	90.36	90.38	62.0
Delaminated	31	88.27	88.29	49.4

Table 3. Comparison of Product Viscosities

Product	Brookfield (cps)		Hercules (dynes @ 1100 rpm)	
	In-Situ	Conventional	In-Situ	Conventional
#1 Coating	193	203	4.5	4.6
#2 Coating	340	390	16.0	15.0
#3 Coating	132	121	10.7	9.0
#1 Premium	220	220	7.2	4.3
Delaminated	90	94	9.5	13.1

GRAPH # 1

Effects of Fe and SO2 on Brightness



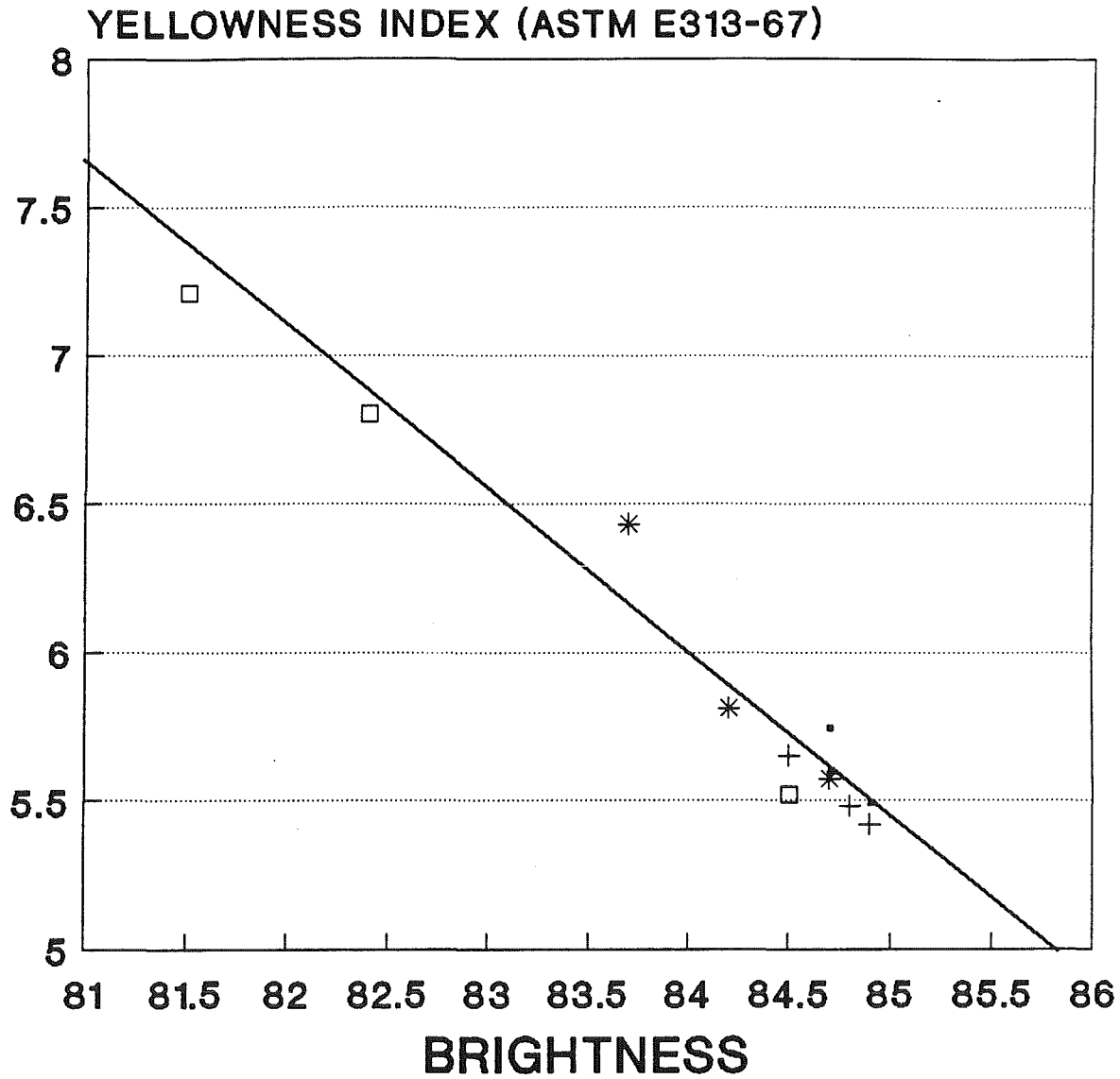
—+— 0.25 #/t Fe

—+— 0.5 #/t Fe

—*— 1.0 #/t Fe

—□— 1.5 #/t Fe

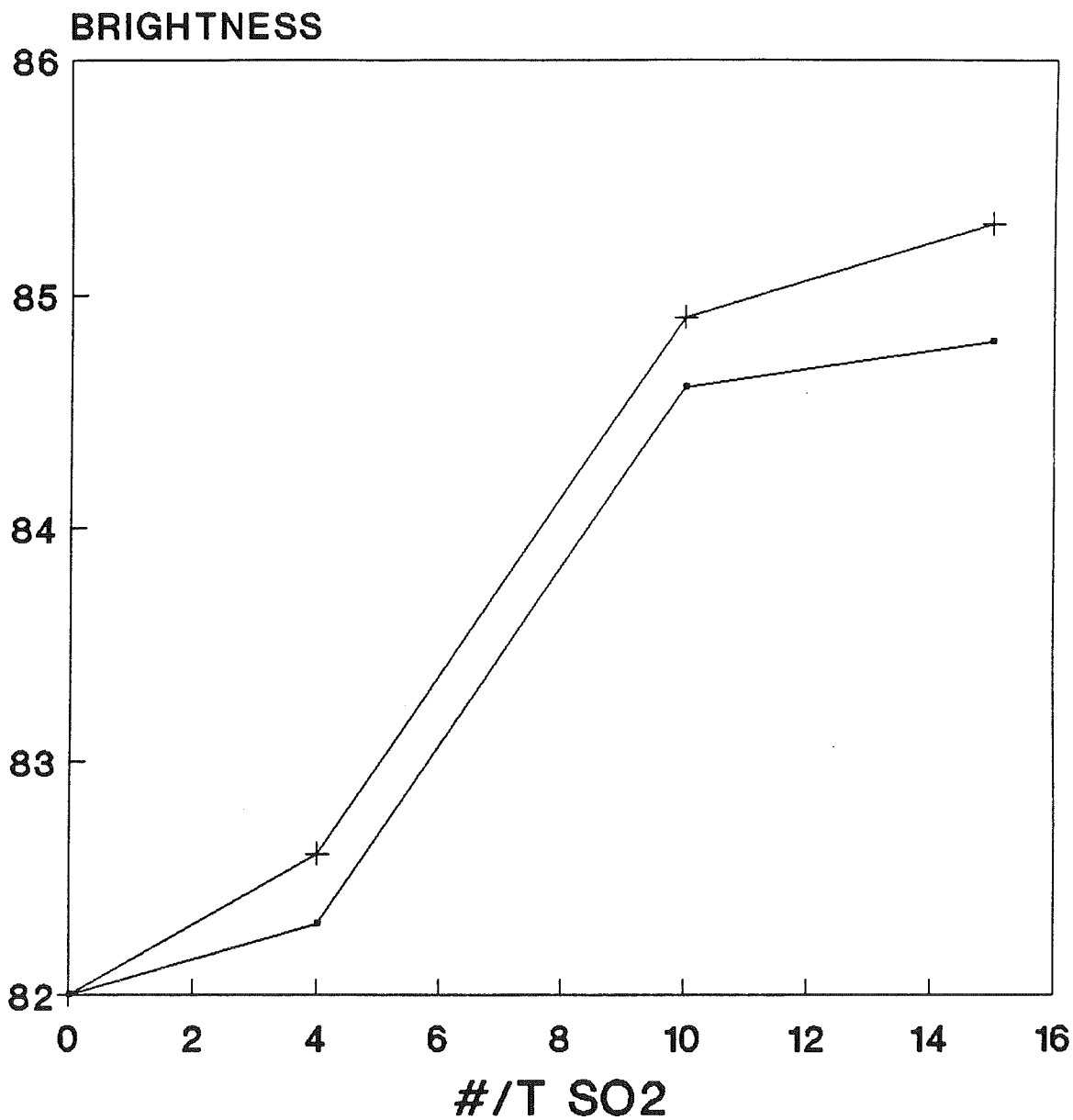
GRAPH # 2
Effect of Fe on Yellowness Index



• 0.25 #/t Fe + 0.5 #/t Fe
* 1.0 #/t Fe □ 1.5 #/t Fe

$$YI = 50.6 - (0.53 \cdot BRT) \quad r = 0.98$$

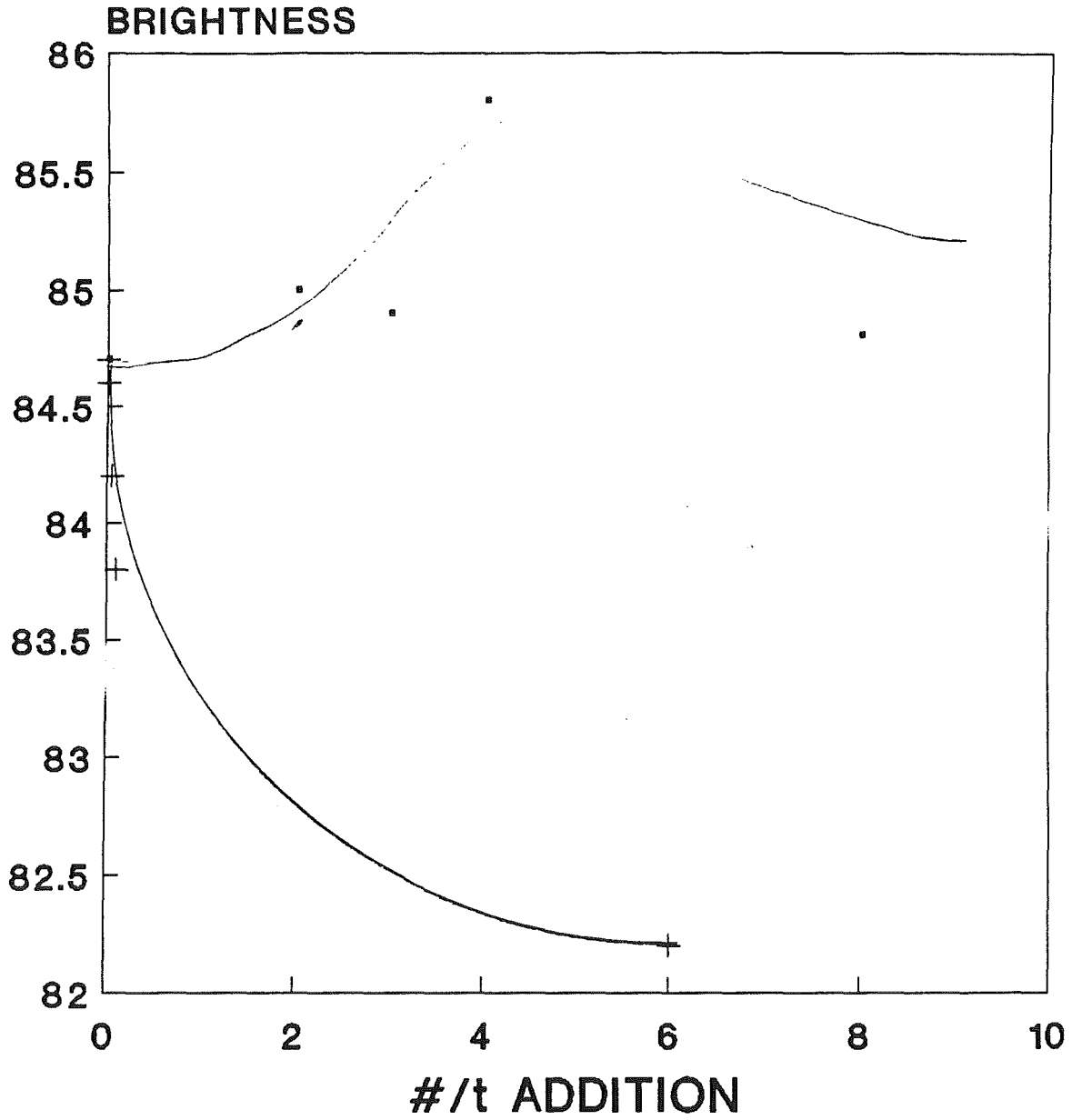
GRAPH # 3 Effects of Alum Addition on Brightness



—•— NO ALUM —+— 4 #/t ALUM

Samples contained 1.5#/t Fe

GRAPH # 4
Effect of Flocculants on Brightness



• ALUM + H2SO4

SAMPLES TREATED W/ 1.6#/T FE & 8#/T SO2

SCHEMATIC
DIAGRAM # 1
BLEACH REACTOR

