



The purification of crude phosphoric acid with sodium silicate
by Joseph C Street

A thesis submitted in partial fulfillment of the requirements of the degree Masters of Science
Montana State University

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Abstract:

Phosphoric acid that is made by the- sulfuric acid process contains most of the impurities originally present in the starting materials. A considerable quantity of the impurities begins to come out of solution when the acid is being concentrated and slowly continues to come out for months following the concentration. - Treatment of the phosphoric acid with sodium silicate in solution is presented as a method for removal of these impurities. When this treatment is used, the acid requires only a short settling time to attain a high degree of clarity.

The treatment has the advantages of low Cost, avoidance of reconcentration, and production of a product superior to that obtained by other methods.

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**A thesis submitted in partial fulfillment
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**MONTANA STATE UNIVERSITY
Bozeman, Montana**

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I. ABSTRACT

Phosphoric acid that is made by the sulfuric acid process contains most of the impurities originally present in the starting materials. A considerable quantity of the impurities begins to come out of solution when the acid is being concentrated and slowly continues to come out for months following the concentration.

Treatment of the phosphoric acid with sodium silicate in solution is presented as a method for removal of these impurities. When this treatment is used, the acid requires only a short settling time to attain a high degree of clarity.

The treatment has the advantages of low cost, avoidance of reconcentration, and production of a product superior to that obtained by other methods.

II. INTRODUCTION

Currently, there are two general methods for phosphoric acid manufacture, the sulfuric acid process and the thermal process. The thermal process involves the volatilization of phosphorus from tricalcium phosphate under reducing conditions. The phosphorus is oxidized to P_2O_5 and subsequently dissolved. This process is used in the production of technical grade acid since it yields acid of relatively high purity. In contrast, the phosphoric acid produced by the action of sulfuric acid on phosphate rock contains the greater portion of the impurities originally present in the starting materials. Consequently, such acid is used principally in the manufacture of fertilizer salts where, in most cases, the presence of such impurities has little effect on the value of the product.

The Anaconda Copper Mining Company at Anaconda, Montana manufactures phosphoric acid from Idaho phosphate rock and sulfuric acid which is made from by-product gases from the reduction of sulfide ores. The phosphoric acid is used in the company's phosphate fertilizer plant. Finely ground rock, calcined at about $900^{\circ} C.$ to drive off moisture and oxidize the organic matter, is treated with sulfuric acid to form calcium sulfate and orthophosphoric acid. The sulfuric acid is added at the rate of approximately one part of 50° Baumé acid to one part of rock assaying about 30-32 per cent P_2O_5 . The sulfuric acid is diluted to approximately 30° Baumé with weak phosphoric acid, while in the agitators, in order to secure a more favorable reaction rate. The phosphoric acid from this reaction has a concentration of approximately

20 per cent P_2O_5 . The acid is separated from the calcium sulfate by filtration with a belt-type vacuum filter. Three acid solutions are obtained from the filter. The No. 1 overflow is that acid passing through the filter with no rinsing. This fraction is further processed. The No. 2 overflow is obtained by rinsing the filter cake with a weak acid known as the No. 3 overflow. The No. 3 overflow is the weak acid from the final rinsing of the cake with water. The No. 2 overflow is used to dilute the sulfuric acid in the agitators and assays about 12 per cent P_2O_5 . The No. 3 overflow assays only 1 to 2 per cent P_2O_5 .

The No. 1 overflow is allowed to stand a few days so that any sediment passing through the filter may settle out. This dilute acid must be concentrated to 45 per cent P_2O_5 for use in the manufacture of Treble Superphosphate, and frequently acid is prepared for shipping purposes that has a concentration of 53 per cent P_2O_5 . This is accomplished by evaporation in steam-heated, single-stage, vacuum evaporators.

During the evaporation when the acid concentration has reached about 40 per cent P_2O_5 , a large quantity of solids begins to come out of solution. The settling is very slow due to the high viscosity of the concentrated acid. Moreover, after the initial deposition of sediment in the evaporators, a slower process continues in which particles of colloidal dimensions gradually clump together until an aggregate is formed of sufficient size to settle out. In this way, sludge may still be settling months after the acid was manufactured. It has been shown that this sludge has fertilizer value so that sediment in the acid going to

the fertilizer plant is tolerated. However, when acid is prepared for shipping purposes a higher degree of purity is required. The principal use for Anaconda "shipping acid" is as liquid phosphate fertilizer applied through small nozzles into irrigation water. Solids obstruct the nozzle openings causing slow, erratic flow and high maintenance costs.

The purification of such acid is quite costly. It usually requires nearly complete neutralization of the acid with a base which precipitates the impurities as insoluble salts while the phosphate salt formed remains soluble. As an example, treatment with finely ground limestone produces a solution of monocalcium phosphate, a certain amount of dicalcium phosphate and precipitates iron and aluminum phosphates, calcium fluoride, and calcium fluosilicates. These precipitates can readily be removed by filtration (Waggaman, 1927). The calcium phosphate solution must again be mixed with sulfuric acid to restore the phosphoric acid and precipitate calcium sulfate. Likewise, the acid must again be concentrated following such a procedure.

Table I gives typical analyses of Anaconda phosphoric acid, phosphate rock, and acid sludges. The acid analyzed was a well-settled sample. A more complete analysis shows calcium, magnesium, arsenic, sodium, potassium, chromium, manganese, titanium and zinc in amounts varying from 1/10 to 1/2 per cent (as the oxide) and traces of copper, lead, nickel, barium, boron, and strontium. The acid is colored blue-green by the relatively large amounts of vanadium present. A large part of the total fluorine is present as silicofluoride (Hill, Marshall and

Table I

Typical Analyses of Anaconda Phosphoric Acid, Phosphate Rock,
and Acid Sludges*

	P ₂ O ₅	Fe ₂ O ₃	Al ₂ O ₃	CaO	F	SiO ₂	V ₂ O ₅
Acid	53.5%	1.00%	0.99%	0.25%	0.77%	0.14%	0.42%
Rock	30.5	0.49	1.49	45.0	3.40	5.90	0.29
Normal Acid Sludge	47.0	7.0	3.0	0.05	1.30	0.2	
Treated Acid Sludge	51.7	9.2	4.9	0.01	1.60	0.43	

*Data furnished by the Anaconda Copper Mining Company.

Jacob, 1932). The silicofluoride is slightly soluble in phosphoric acid up to 10 per cent P_2O_5 becoming less so as the acid is concentrated (Hampel, 1949).

The sludges are alcohol-washed solids from the settling tanks. The chemical nature of these solids is not entirely clear, but they are evidently phosphates of iron and aluminum together with insoluble fluosilicates. The phosphates of iron and aluminum may be hydrated. The bulk of the sludge is a gelatinous mass containing the crystalline fluosilicates. Removal of the crystalline particles eliminates much of the difficulties with plugged nozzles.

The present procedure for purification at the Anaconda plant removes the silicofluorides by precipitation with sodium carbonate. Treatment of the dilute No. 1 overflow with sodium carbonate in quantities in excess of the theoretical required to precipitate the silicofluorides produces an acid from which the solids settle out much faster than from normal acid. Henceforth in this paper, "treated acid" will refer to acid treated in this way in contrast with the untreated "normal acid". Treated acid even after standing four to five weeks is still quite turbid although much clearer than normal acid which has stood for the same length of time. Two different samples of treated acid were observed to increase in turbidity on standing for long periods. Since these acids were stored in wax-lined bottles, the increased turbidity could not have been due to dissolved silicates from the glass.

Because of this effect it was still desirable to obtain an acid which contained no sediment, which required only a short settling time

to attain this purity, and which would remain clear for a long period of time. The present work was undertaken in an effort to find a process which would meet this objective. As a result of this work, treatment of the crude acid with aqueous solutions of sodium silicate is being presented as a feasible process.

III. GENERAL EXPERIMENTAL PROCEDURE

Samples of sodium silicate having the ratios silica:soda of 1.69, 2.06, 2.40 and 3.36 were prepared by fusing washed sea sand with sodium carbonate. The glasses formed were extracted with water in the autoclave at 20 pounds steam pressure for one hour. The extracts were then about 25-30 per cent sodium silicate, i.e., 25 per cent Na_2O plus SiO_2 . By evaporation or dilution, solutions of the desired concentrations were obtained.

All tests were performed in 10-inch test tubes paraffined to protect them from the corrosive hydrogen fluoride present in the acid. Eighty-five ml. of the crude phosphoric acid (approximately 140 g.) and 10 ml. of silicate solution were mixed rapidly in a beaker using a high-speed stirrer. The silicate solution was added to the agitating acid in a thin stream from a pipette. Ten ml. of solution were added in the case of normal acid, 5 ml. in the case of treated acid. The sodium silicate immediately formed a gelatinous mass and stirring was continued until this mass was broken up into an even consistency throughout. The mixture was then poured into a test tube.

One sample was electrolysed, in addition to the sodium silicate treatment, as an exploratory experiment. This sample of 85 ml. of normal acid received 10 ml. of 7 per cent silicate (ratio 1.69) and was electrolysed at 0.1 ampere and 4.0 volts for 17 hours (about 6,000 coulombs) using carbon electrodes and constant stirring. The sample was then poured into a test tube for observations.

A complete list of tests is presented in Table II with the exception

Table II

Complete List of Tests Performed

	<u>Silica:Soda</u> <u>Ratio</u>	<u>Per Cent</u> <u>Silicate</u>	<u>Ml. of Silicate</u> <u>Added</u>	
Normal Acid	1.69	1.0	10	
	1.69	2.0	10	
	1.69	7.0	10	
	1.69	12.5	10	
	1.69	25.0	10	
	2.06	9.5	10	
	2.06	13.4	10	
	2.06	32.0	10	
	2.06	32.0	5	
	2.40	9.0	10	
	2.40	12.6	10	
	3.36	12.0	10	
	3.36	19.0	10	
	3.36	12.0	5	
	3.36	19.0	5	
	Treated Acid	1.69	7.0	5
		1.69	7.0	10
		2.06	9.5	5
		2.06	19.0	5
		2.40	9.0	5
2.40		18.0	5	
3.36		12.0	5	
3.36		19.0	5	

of the one test using electrolysis. Suitable controls were also observed for each case, both acid with no silicate added and acid with no silicate but diluted with water to the same extent as the tests.

Record was kept of the settling rate by measuring the centimeters of clear acid at intervals of one to four days. This was possible because the gelatinous mass settled as a unit and there was a well-defined line separating this from the clear acid. After settling was complete, the ratio of the height of sediment in the tube to the total height of liquid in the tube was recorded. The diameters of the tubes varied making a ratio comparison necessary rather than simply a height comparison.

After two or three days, there was sufficient relatively clear acid to decant and measure its turbidity. Turbidity was measured as optical density with a Coleman spectrophotometer, Model 11, using matched, square cuvettes. Samples were compared at 560 μ , the wavelength of minimum absorption, against an arbitrary standard. This standard was prepared by dissolving ammonium vanadate in technical phosphoric acid (53 per cent P_2O_5) and reducing the vanadate to a blue-green color approximating that of the sample acid. Following the comparison, the sample decanted was carefully replaced in its tube.

Turbidity (τ) is related to optical density ($-\log I/I_0$) by the equation,

$$-\log I/I_0 = (\tau_{\text{red}})d/2.303$$

in which I_0 is the intensity of the incident light, I is the intensity of the transmitted light, α is the absorption coefficient, and d is the

distance the light travels through the medium (cell thickness). In order for this method to give accurate comparisons of turbidity, α must neither vary in each sample as sedimentation proceeds nor vary appreciably between samples. This was not strictly the case and because of differences in refractive indices, differences in size of particles, and polydispersity of particles, exact comparisons could not be made.

After the samples had reached their maximum clarity, certain of them were selected as representing superior treatments and were assayed for P_2O_5 , Fe_2O_3 , and fluorine for comparison with the corresponding values for non-treated acid. P_2O_5 was assayed by the method of the Association of Official Agricultural Chemists (1945). The sample is dissolved in nitric acid and ammonium phosphomolybdate is precipitated from the dilute acid solution with an excess of ammonium molybdate. The precipitate is filtered, washed, and dissolved in an excess of standard sodium hydroxide. Back-titration of the excess base with standard hydrochloric acid gives an indirect measure of the P_2O_5 .

The fluorine was assayed by the method of Hoffman and Lundell (1938) and is given here in some detail since it is not ordinarily encountered. A 6-8 gram sample of acid is washed into a 125 ml. Claisson flask which is fitted with rubber stoppers, a delivery tube for admitting sulfuric acid and water, a thermometer, and a condenser which delivers the distillate into a 400 ml. beaker through a curved adapter. The end of the adapter is immersed in 20 ml. of a 20 per cent solution of sodium hydroxide contained in the beaker. The flask rests in a 4 cm. hole in an asbestos gauze and is heated with a hot flame such as that of

a Tirril burner. Thirty ml. of dilute sulfuric acid (1+1) are admitted through the delivery tube, the flask is heated to vigorous boiling and heating is continued until the temperature of the liquid in the flask reaches 160° C. Then, without removing the source of heat, water is admitted through the delivery tube at such a rate that the temperature of the liquid in the flask remains between 160° and 170° C.; 300 ml. of distillate is collected between these temperatures. The alkaline distillate is evaporated to a volume of 250 ml., 3 ml. of 10 per cent sodium chloride are added, and the pH is adjusted to just basic to bromphenol blue. Two ml. of diluted hydrochloric acid and 5.0 g. of solid lead nitrate are added and the mixture is heated on the steam bath until the lead nitrate is dissolved; then 5.0 g. of sodium acetate are added and the mixture stirred vigorously while digesting on the steam bath. After standing overnight at room temperature, the precipitated lead chlorofluoride is filtered and washed with a saturated solution of lead chlorofluoride. The precipitate and filter paper are transferred to the original beaker and 100 ml. of dilute nitric acid are added to dissolve the precipitate. The chloride is determined in this solution by the Volhard method and is equal to the fluoride concentration.

Iron was also determined by the method of Hoffman and Lundell (1939) in which ferric iron is reduced with stannous chloride and titrated with potassium permanganate.

IV. EXPERIMENTAL RESULTS

In each of the tests performed there was observed a marked improvement in the acid; within 30-40 days a clear acid was obtained. Figures 1 and 2 show the rapid decrease in turbidity as indicated by the large drop of optical density when normal acid is treated with silicate. Figure 1 shows four of the results of better treatments. Curve II, Figure 2, represents the same sample as is represented by the purple curve of Figure 1. There was only one better curve than those shown; the treatment was 5 ml. of 19 per cent (3.36). The balance of the treatments fell between 7 per cent (1.69), line III, Figure 2, and 12.5 per cent (1.69), line II, Figure 2. It is odd to find that the 12.5 per cent (1.69) and the 12 per cent (3.36) were both superior to corresponding percentages of silica:soda ratios of 2.06 and 2.40. It was not expected that both the extreme ratios of silica:soda would be superior. Curves for the controls are not given but they just barely leave the abscissa in 30 days.

These curves show that there was an early, rapid decrease in turbidity which gradually leveled out and approached the same approximate value. There was no indication that the turbidity ever increased again, at least within three months. Instead there was a continued, but very slow, decrease.

Figure 2 shows the results of treating with one ratio (1.69) in increasing concentrations. It is seen in treatments I, II, and III that again a common point was approached. Treatment IV (2 per cent) was evidently too low a concentration. Treatment I (25 per cent) had too

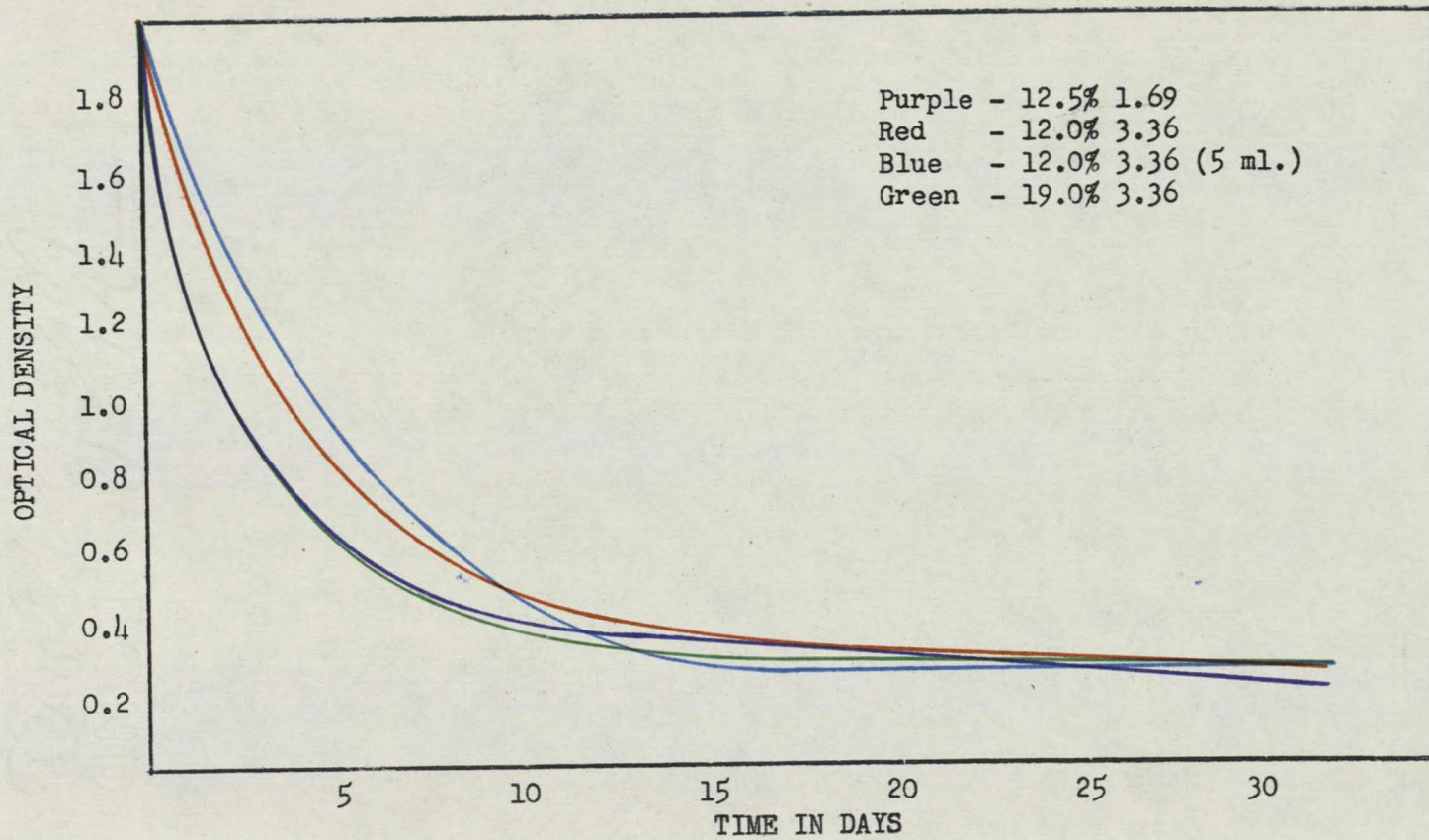


Figure 1
Change in Turbidity with Time
Normal Acid

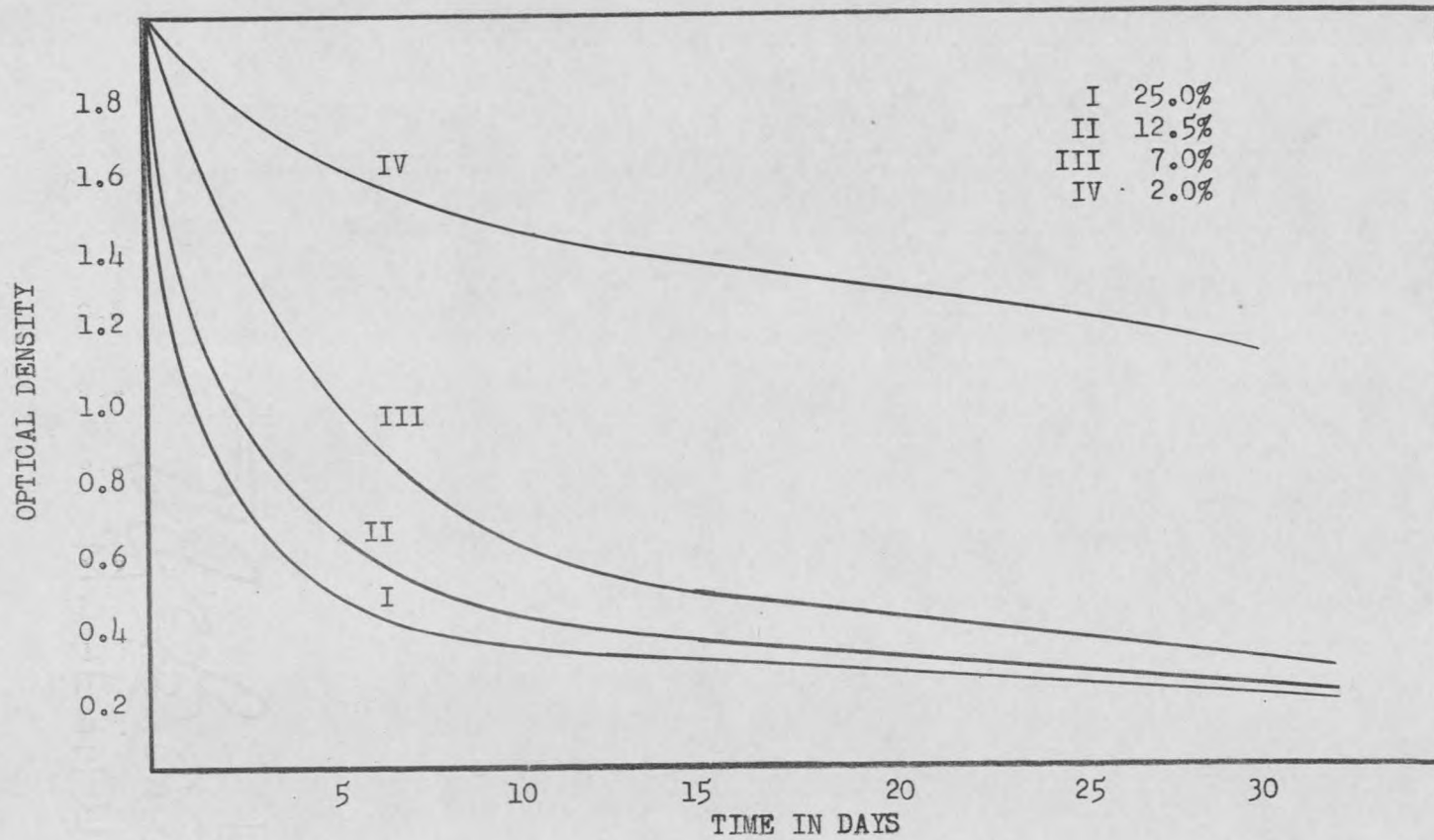


Figure 2
 Change in Turbidity with Time
 Various Levels of Silicate (1.69) with Normal Acid

much sediment and was, consequently, not as desirable as II and III.

Figure 3 shows the results of some treatments with treated acid and a control. The tests with treated acid were made in order to investigate the possibility of a combination of the soda ash treatment with the sodium silicate treatment. The control was 85 ml. of acid diluted with 5 ml. of water. The undiluted control had an even greater positive slope, i.e., a greater increase in turbidity. The initial increases in turbidity were due to the gel mass, which settled enough in two days to leave clear acid. Nineteen per cent (3.36) settled so much faster that no increase in turbidity was measured on the second day. The tests with treated acid reached a higher clarity as indicated by the optical density than corresponding treatments of normal acid but exhibited about the same amount of light scattering. It is assumed that a different absorption coefficient makes readings higher.

Thus, in every case, for both normal and treated acids except possibly the 2 per cent (1.69), a particular clarity was approached by all and in nearly the same length of time. When this point was reached one could detect scarcely any light scattering when visually comparing the sample with the standard. Variations in turbidity during the first few days after treatment are apparently without any particular significance since the same clarity in the solution is achieved in the same length of time with all of the better treatments. This is demonstrated in Figure 4 which shows the results of a pair of duplicate treatments.

Of far more importance to the producer than the relatively insignificant variations in the turbidity curves during the first few days

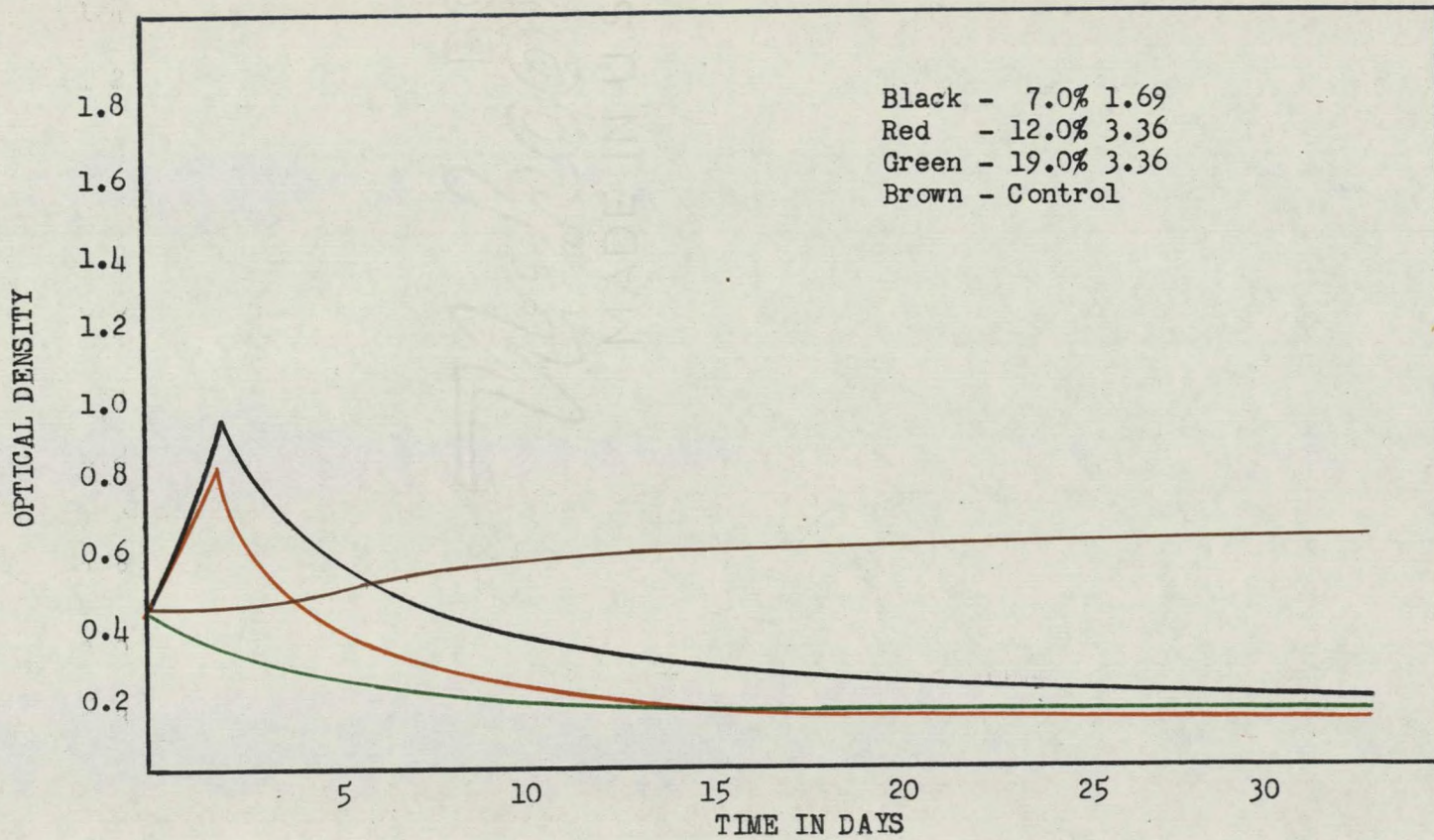


Figure 3
 Change in Turbidity with Time
 Treated Acid

