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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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° 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_2O_5	Fe_2O_3	Al_2O_3	CaO	F	SiO_2	V_2O_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

	Silica:Soda Ratio	Per Cent Silicate	Ml. of Silicate Added
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 mμ, 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 ($-\log I/Io$) by the equation,

$$-\log I/Io = (\tau+\alpha)d/2.303$$

in which Io 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 abcissa 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

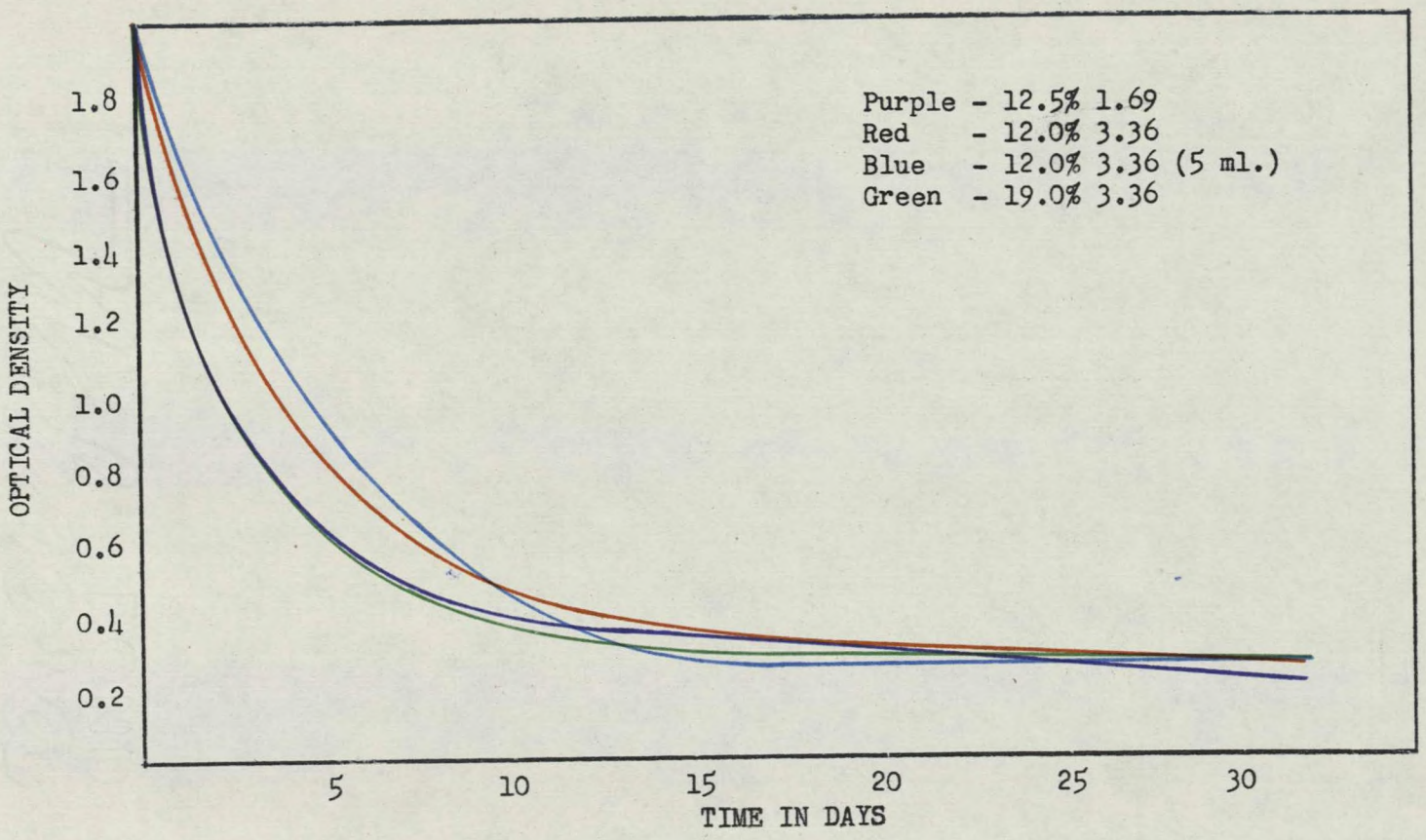

Figure 1
Change in Turbidity with Time
Normal Acid

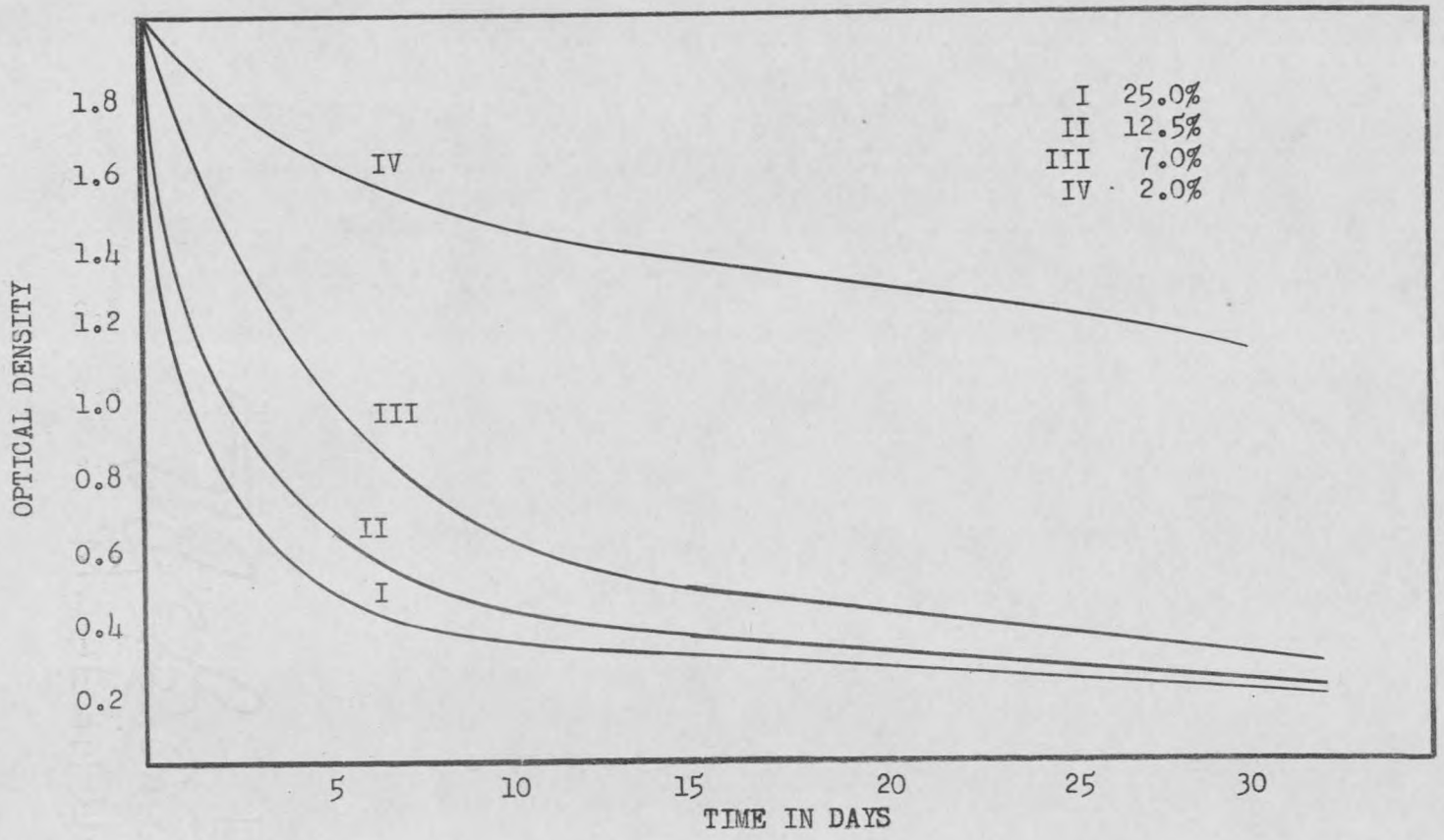

Figure 2
Change in Turbidity with Time
Various Levels of Silicate (1.69) with Normal Acid

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

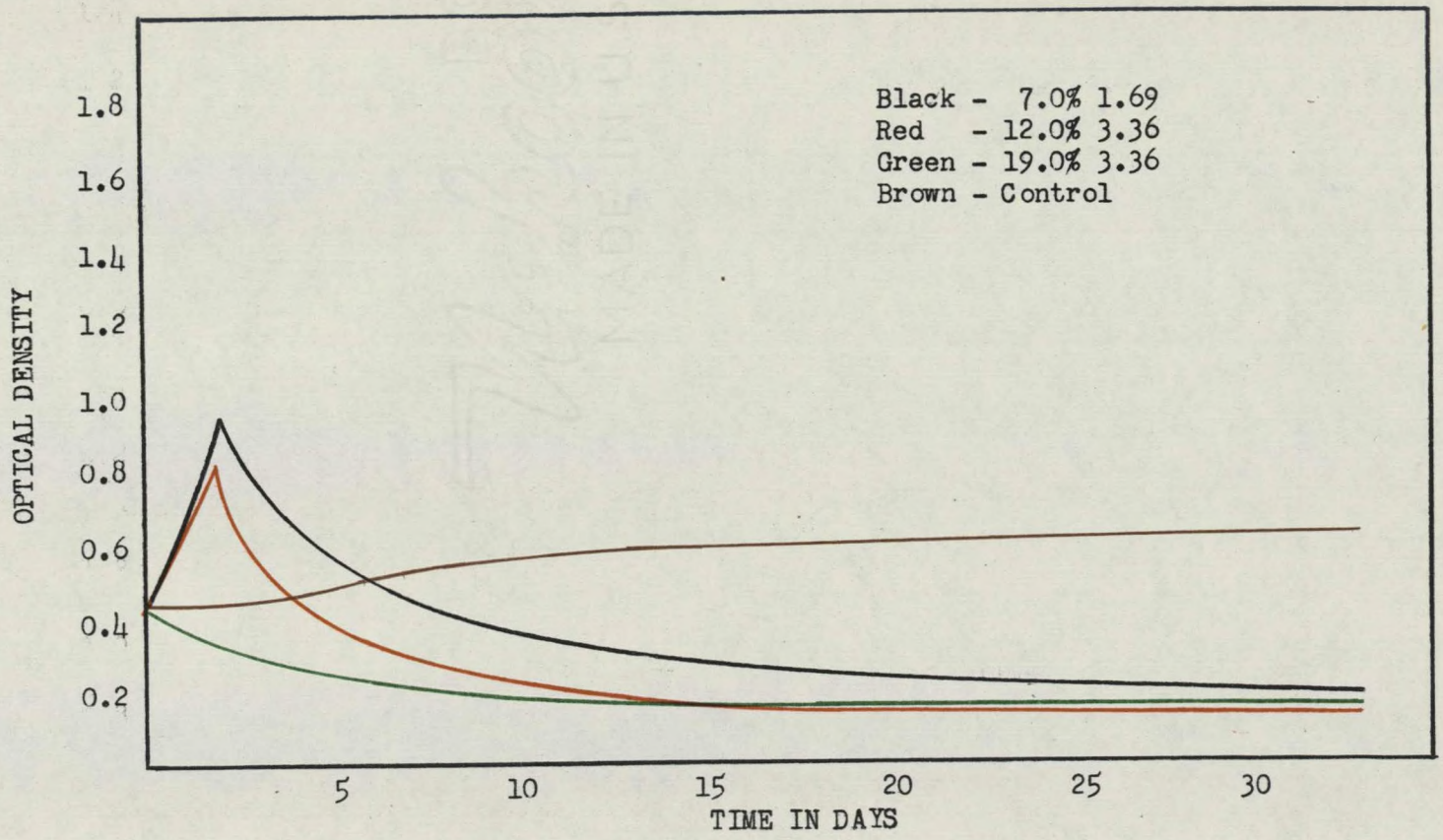

Figure 3
Change in Turbidity with Time
Treated Acid

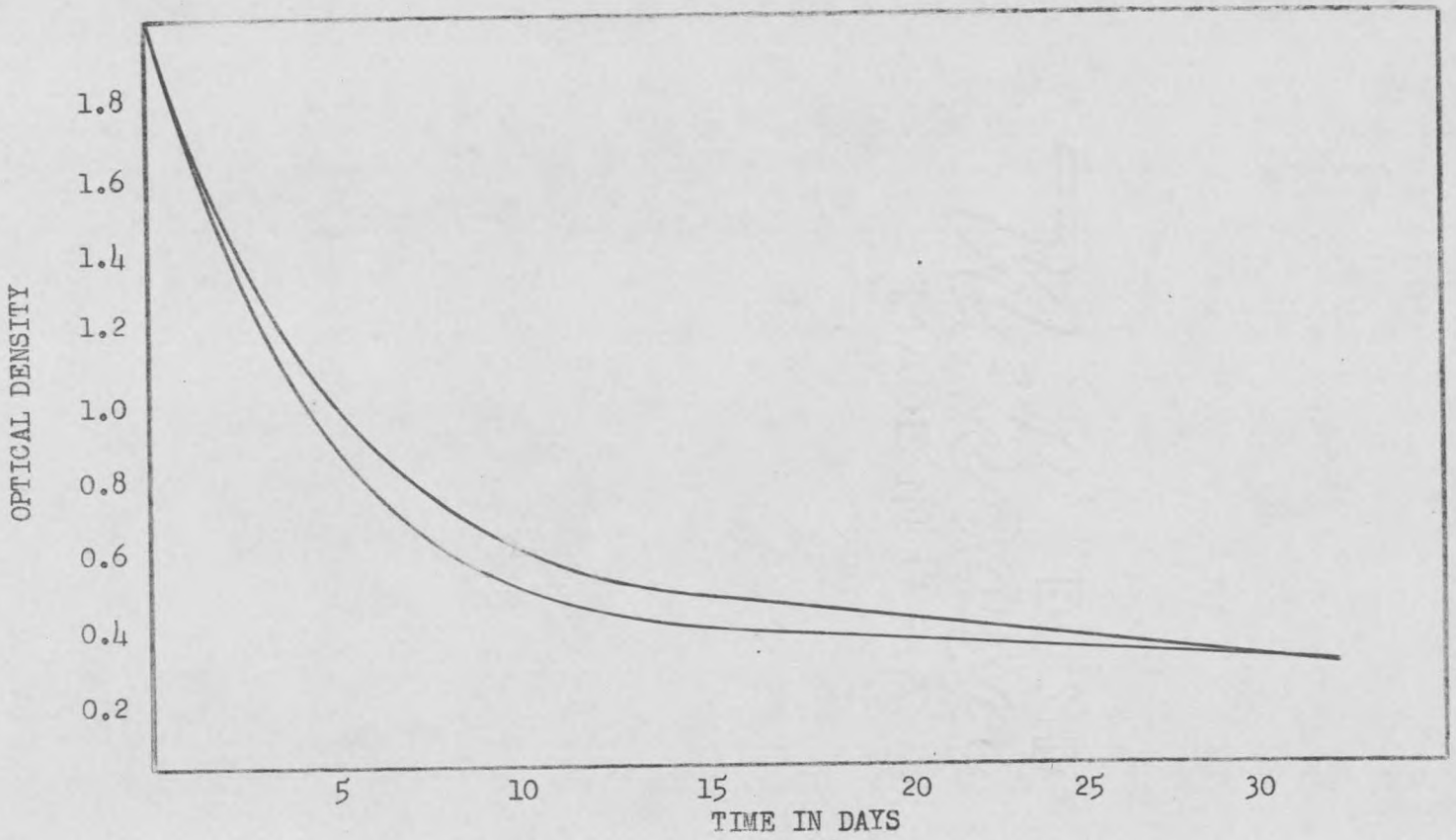

Figure 4
Change in Turbidity with Time
Duplicate Treatments on Normal Acid
7% (1.69)

is the amount of acid immediately available after treatment and the length of time he must wait before shipping the product. Figure 5 shows sedimentation rates for the same tests as those appearing in the previous graphs. The gel mass containing the sludge settled rapidly; in one week the settling was nearly complete except for very small particles settling more slowly. Thus, the acid could be decanted and shipped after two weeks of settling. On reaching its destination in two to three weeks, it would have a high degree of clarity and only a little sludge would be on the bottom of the tank car.

Figure 6 is a chart showing the amounts of acid available from various treatments. Lower percentages of silicate in the treatment result in more acid available; but, as seen previously, are not as good in removing turbidity. The ratio 3.36 is generally the best; 12 per cent (3.36) being nearly as good as 7 per cent (1.69) with equal treatments (10 ml.) and, surprisingly enough, with only one-half as much silicate is just as good. Unfortunately, a percentage less than 12 per cent of the 3.36 was not tested. It is possible that a lower percentage of this ratio might be better than any tested. Another possibility is that ratios higher than 3.36 might be better.

The experiment with electrolysis was set up to follow indications that a small amount of current hastened deposition of the fine sediment remaining in normal acid after the initial drop of larger particles. Using electrolysis alone, it was found that approximately 4,000 coulombs, when passed through the sample of 400 to 1,300 grams, were sufficient to produce an increased rate of settling. Quantities less than 4,000

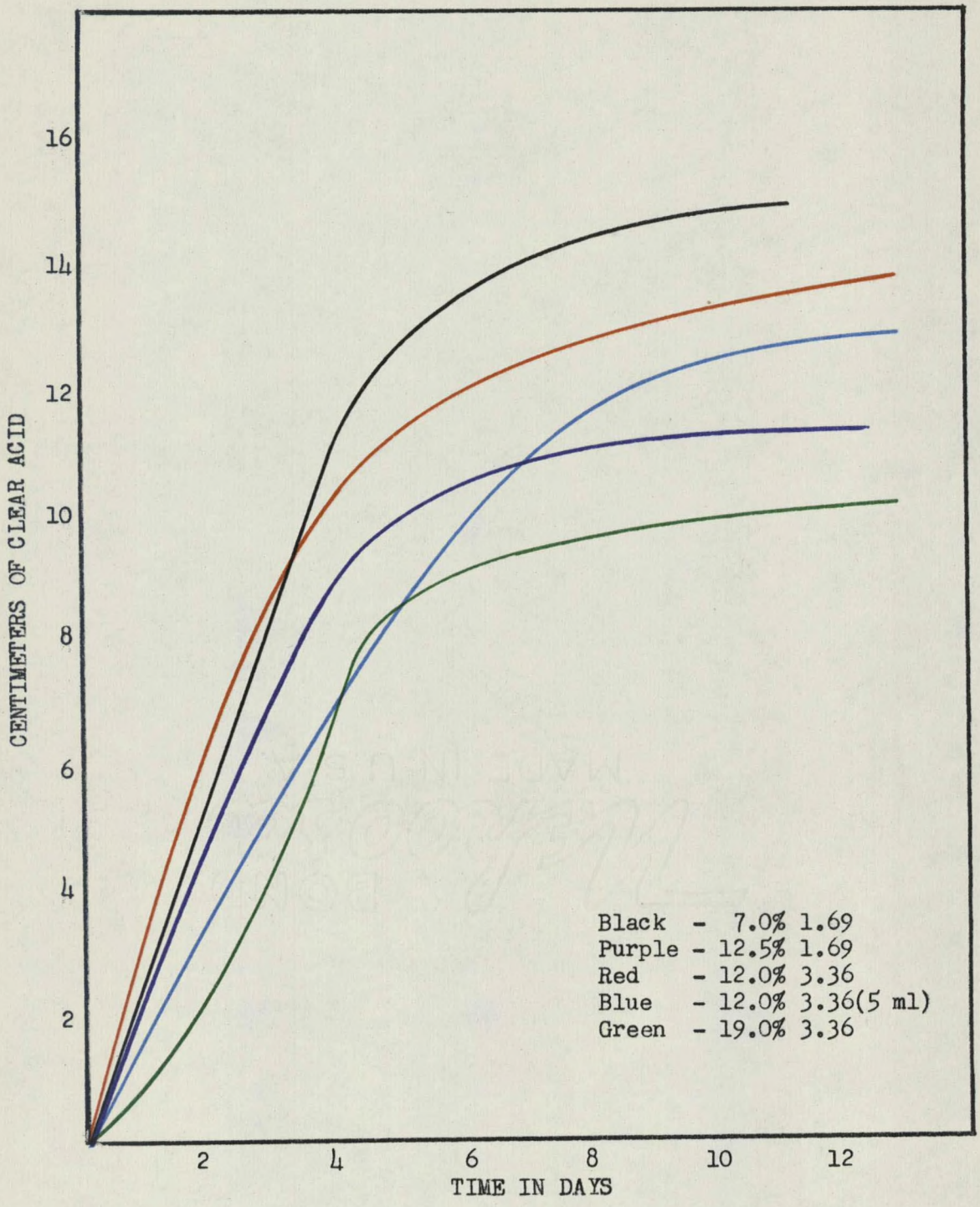

Figure 5
Sedimentation Rates for Normal Acid

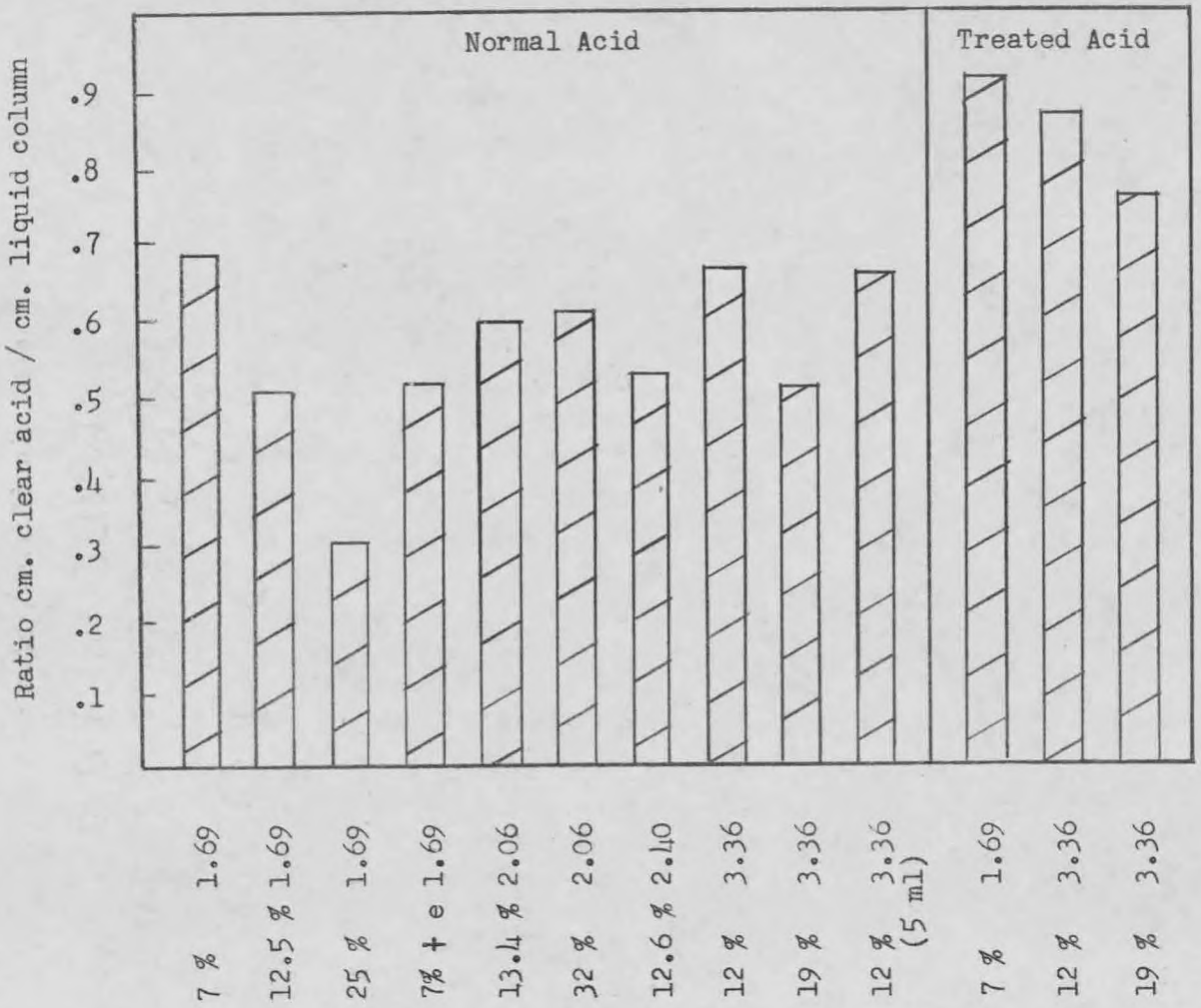

Figure 6
Quantities of Available Acid from Various Treatments

coulombs had no effect. The only immediate change obvious was a yellowing of the acid's blue-green color which probably was due to oxidation of the vanadium. It was nearly one month after electrolysis before any increased settling rate could be observed; but after the rate did increase, sedimentation proceeded quite constantly and was accompanied by a yellow-green deposition on the sides of the tube. Two months after electrolysis the sample was slightly more clear than treated acid will get; five and a half months after electrolysis it was extremely clear and comparable to the samples of silicate-treated normal acid after six or seven weeks of standing.

When silicate was added to the electrolytic experiment, the same general effects were obtained as in the other silicate tests. The decrease in turbidity was more rapid, but there was more sediment. The effect of electrolysis was to make the test with 7 per cent (1.69) nearly identical with the test using 12.5 per cent silicate.

Table III gives the results of the analyses for P_2O_5, Fe_2O_3, and fluorine. The percentages given are for the tested samples not corrected for the dilution occurring during treatment. The control for the normal acid series was a sample of the same acid as the tested samples which had been allowed to stand 12 weeks. At this time it had dropped all of the larger particles and was roughly equivalent to the treated acid control shown in Figure 4. The treated acid control was from the same acid from which the samples for testing were obtained and had become quite turbid again.

A large reduction of the two impurities, iron and fluorine, was

Table III

Results of Analyses

	P_2O_5%	Fe_2O_3%	F%
Normal Acid			
No silicate	54.3	2.70	0.86
7% (1.69) 10 ml	51.6	1.47	0.39
12% (3.36) 10 ml	51.7	1.15	0.30
12% (3.36) 5 ml	50.7	1.21	0.41
19% (3.36) 10 ml	51.0	1.28	0.16
32% (2.06) 5 ml	49.9	1.02	0.20
7% (1.69) 10 ml + e	51.0	0.99	0.25
Treated Acid			
No silicate	51.8	1.33	0.86
7% (1.69) 5 ml	51.0	1.17	0.54
12% (3.36) 5 ml	51.1	0.98	0.35
19% (3.36) 5 ml	50.5	1.10	0.35

observed. The low amount of fluorine in the normal acid control, equal to that in the treated acid control, was because it was very well settled. The proportionate reduction in the amount of iron was greater with normal acid than with treated acid although in this experiment the treated acid control was more turbid than the normal acid control. The important indication from this table is that the P_2O_5 content is not greatly reduced by sodium silicate treatment. The acid is weakened by only about 1/2-1/3 the amount one would weaken it by dilution with the volumes used for treatment. Because of this, it is assumed that concentration following treatment with sodium silicate would not be necessary. The variations in values among the different tests, especially with regard to P_2O_5, are again probably not significant; the average of these assays could be expected when using this treatment.

These results may be briefly summarized as follows:

1. There was a marked improvement in the quality of the acids from nearly all tests.

2. Little significance may be held for the differences in various treatments, except in the amounts of acid available from the treatments.

3. Low percentages of silicate are best because the amount of acid available is greater.

4. The best silica:soda ratio investigated was 3.36. The next best was 1.69.

5. There are two suggested treatments for normal acid. First and preferably, the addition of about 8 per cent by weight of a 10 per cent solution of 3.36 sodium silicate which will exhibit both a good sedimen-

tation rate and low amounts of sediment while producing an acid of fair clarity. Second, the addition of about 8 per cent by weight of a 10 per cent solution of 1.69 sodium silicate which will exhibit an acid of good clarity with a fair sedimentation rate and slightly higher amounts of sediment.

6. It is not probable that any advantage would be gained by a combination of soda ash and sodium silicate treatments or by including electrolysis in the treatment.

Table IV

Data for Results Shown in Figure 1

Test	Day	Optical Density	Test	Day	Optical Density
10 ml.12.5% (1.69)	0	2.0	10 ml.12% (3.36)	0	2.0
	4	.720		3	1.25
	8	.600		4	.940
	12	.387		5	.700
	14	.356		8	.556
	20	.288		13	.393
	32	.215		17	.328
	37	.208		22	.284
				35	.240

Test	Day	Optical Density	Test	Day	Optical Density
5 ml.12% (3.36)	0	2.0	10 ml.19% (3.36)	0	2.0
	3	1.21		3	.955
	4	1.01		4	.700
	5	.795		5	.593
	8	.604		8	.469
	13	.318		13	.320
	17	.378		17	.284
	22	.256		22	.256
	35	.250		35	.233

Table V

Data for Results Shown in Figure 2

Test	Day	Optical Density	Test	Day	Optical Density
10 ml.25% (1.69)	0	2.0	10 ml.12.5% (1.69)	0	2.0
	5	.437		4	.720
	8	.386		8	.600
	12	.305		12	.387
	14	.294		14	.356
	16	.282		20	.288
	20	.238		32	.215
	32	.177		37	.208
	37	.177			

Test	Day	Optical Density	Test	Day	Optical Density
10 ml.7% (1.69)	0	2.0	10 ml.2% (1.69)	0	2.0
	4	1.10		10	1.42
	10	.583		14	1.30
	14	.481		18	1.19
	18	.432		22	1.09
	22	.382		30	1.05
	30	.253			
	43	.232			

Table VI

Data for Results Shown in Figure 3

Test	Day	Optical Density	Test	Day	Optical Density
Control	0	.432	5 ml. 7% (1.69)	0	.432
	2	.420		2	.940
	3	.437		3	.720
	4	.475		4	.668
	7	.500		7	.488
	12	.552		12	.347
	16	.545		16	.266
	21	.565		21	.229
	33	.585		33	.181
Test	Day	Optical Density	Test	Day	Optical Density
5 ml. 12% (3.36)	0	.432	5 ml. 19% (3.36)	0	.432
	2	.797		2	.312
	3	.530		3	.275
	4	.482		4	.272
	7	.300		7	.219
	12	.188		12	.163
	16	.154		16	.158
	21	.128		21	.152
	33	.111		33	.143

Table VII

Data for Results Shown in Figure 4
10 ml. 7% (1.69)

Day	Optical Density	Day	Optical Density
0	2.0	0	2.0
4	1.10	4	1.12
10	.583	8	.622
14	.481	15	.375
18	.432	18	.348
22	.382	24	.310
30	.253	29	.288
43	.232	48	.244

Table VIII

Data for Results Shown in Figure 5

Test	Day	Cm. clear acid
12.5% (1.69)	2	4.7
	4	9.0
	5	10.0
	8	11.0
	12	11.2
	32	11.2

Test	Day	Cm. clear acid
7% (1.69)	1	2.5
	2	5.8
	4	11.0
	6	13.4
	8	14.0
	17	14.8

Test	Day	Cm. clear acid
12% (3.36)	1	5.0
	2	7.5
	3	9.5
	4	11.0
	5	11.4
	8	12.8
	13	13.6
	17	14.0

Test	Day	Cm. clear acid
12% (3.36) 5 ml.	1	2.2
	2	3.4
	3	4.6
	4	7.0
	5	8.5
	8	11.8
	13	12.8
	17	13.2

Test	Day	Cm. clear acid
19% (3.36)	1	1.5
	2	3.4
	3	5.4
	4	7.9
	5	8.6
	8	9.5
	13	10.0
	17	10.0

V. DISCUSSION

Those sodium silicates having silica:soda (Na_2O) molecular ratios lying between 1:1 (metasilicate) and 4:1 (orthosilicate) are known collectively as water glasses or soluble silicates. Since the ability of the silicate to produce a particular effect often is a function of the above molecular ratio, it was desirable to investigate the effects in this case over a range of ratios. The particular ratios were chosen because specific gravity-concentration tables are available for these ratios.

When a solution of sodium silicate is added to a concentrated acid, silica is precipitated as a gelatinous hydrate, silicic acid. According to Hurd (1938), simple molecules of silicic acid are usually formed by the reaction of the sodium silicate with an acid and these simple molecules slowly condense to form a more complex structure. Water is split out between simpler silicic acid molecules to form a heavily hydrated polysilicic acid structure. When enough of these large structures have accumulated, the system "sets" into a semisolid, elastic mass.

If 10 ml. of sodium silicate are added to 85 ml. of technical phosphoric acid (53 per cent P_2O_5), 30 minutes will elapse before the system sets into an elastic mass which will not pour from the tube. Nothing resembling this process occurs when sodium silicate is added to crude phosphoric acid. Instead, there is an immediate formation of a gelatinous mass which will not set and is not elastic. This is due to the presence of silicofluoride. When hydrofluosilicic acid is mixed with the technical phosphoric acid and sodium silicate added, there is

an immediate formation of a gelatinous mass just as with crude acid. The sodium ion from dissociation of the sodium silicate immediately precipitates the silicofluoride and thus interferes, somehow, in the formation of the polymeric structure. Most metallic salts react with sodium silicate solutions to produce a colloidal metal silicate accompanied by a thickening of the whole mass, e.g., aluminum phosphate gives a tenacious mass (Mellor, 1925). This suggested that aluminum and other metal ions might be removed with sodium silicate; however, no significant amount of aluminum seemed to be removed from solutions of $AlPO_4$ in technical phosphoric acid. Iron was shown to be removed from the crude acid (Table III), but this was probably just the removal of suspended iron phosphates.

Aside from this possibility that metallic ions might be removed by the treatment, another effect which definitely has a role in the treatment is the mechanical dragging down of particles by the gelatinous mass as it settles. Although this is undoubtedly a very important effect, it is not the entire mechanism of purification for when a sample of acid was treated with sodium silicate and immediately centrifuged, an acid was obtained which had relatively little turbidity. However, its turbidity then increased for two or three days after which it again began to decrease. The same thing occurred when a sample was centrifuged on the second day after treatment, but by the fifth day there was no increase in turbidity detected following centrifugation. This suggests that a slow reaction, possibly a polymerization of silicic acid, was occurring. If it were a

polymerization reaction, it could conceivably entrap colloidal particles of the impurities inside the polymeric structure and thus carry them down as the polymer or aggregate settled.

If this process is to be economically feasible, an important consideration is the cost. The method of purification with sodium carbonate, which is now in use at the Anaconda plant, requires a large excess of alkali metal ion to effectively remove the fluosilicates. At the present, 35 pounds of soda ash (presumably 58 per cent Na_2CO_3) are added to each ton of No. 1 overflow that is processed. This is equivalent to 74 pounds per ton of concentrated acid. Based on the April 16, 1951 quotation for dense soda ash in the "Oil, Paint, and Drug Reporter," this treatment costs 96.5 cents per ton of shipping acid. In contrast, assuming that concentrating from 51 per cent P_2O_5 is not required and that 8 per cent by weight of a 10 per cent sodium silicate solution is added to concentrated acid, the proposed treatment requires 47.2 pounds of sodium silicate per ton of acid and costs 44.8 cents per ton based on the quotation for 40° Baumé sodium silicate.

VI. SUMMARY

Producers of phosphoric acid that use the sulfuric acid process have a problem with sludges coming out of solution when the acid is concentrated. These sludges, consisting principally of iron and aluminum phosphates with some silicofluorides, settle very slowly. Furthermore, they continue to form and settle for months following manufacture of the acid. The continuous formation and settling of solids is especially troublesome when the acid is used as liquid fertilizer and is distributed through small nozzles into irrigation waters.

Precipitation of the silicofluorides as sodium silicofluoride by adding sodium carbonate improves the acid by shortening the settling time to about four weeks. However, the acid so treated will not remain clear but gradually becomes increasingly turbid again, at least if it is permitted to stand in contact with its sediment.

A more desirable method of purification was sought which would produce a better acid within the same length of time as required by the soda ash method.

It was found that treating the turbid acid coming from the evaporator with about 8 per cent by weight of a 10 per cent sodium silicate solution is a satisfactory method of purification.

Analyses showed that the acid was only slightly weakened by this treatment while large amounts of the impurities were removed.

The mechanism of the process is partly the mechanical dragging down of solids by the gelatinous mass of silicic acid formed in the reaction of the sodium silicate with the crude acid, partly the

precipitation of sodium silicofluorides and possibly the removal of very fine particles through settling of slow-forming, polymeric structures of silicic acid which have entrapped the particles.

Some advantages of treating with sodium silicate may be listed as follows:

1. A superior product is produced.

2. The settling time required is shorter, thereby increasing the production capacity.

3. The cost of purification is lower.

Likewise, some disadvantages are:

1. Less acid is available from each ton evaporated due to the large amounts trapped in the gel mass and sludge. However, these solids are such that they may be easily flushed from tanks and passed over a filter. The dilute acid recovered could be used in much the same way as the No. 2 and No. 3 overflows are now used.

2. An engineering problem is involved in that there must be a way of rapidly and thoroughly mixing the sodium silicate into the acid; otherwise the silicate coagulates in large lumps and is less effective.

3. The acid is diluted to some extent, but this may partially be overcome by using higher silica ratios in lesser quantities as indicated in the experiment with 5 ml. of 12 per cent (3.36) instead of the usual 10 ml.

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