

PHOSPHORIC ACID AS AN AID TO CLARIFICATION, AND OBSERVATIONS ON LIMING TECHNIQUES AND MUD VOLUMES

By G. G. CARTER

The contents of this paper are based on experimental and practical observations collected over the past years.

(1) An Investigation into the Application of Laboratory Clarification Tests and a Comparison of the Different Liming Techniques

Following along the lines of work done by C. W. Davis of the C.S.R. Co., Australia, a series of experiments were carried out to determine the effects of different liming techniques using a laboratory settling apparatus.

This apparatus consisted of two tubes of 1.5 in. I.D. by 36 in. suspended in individual water jackets through which hot water was circulated. The maximum temperature of the circulating water was 80° C., which caused initial convection currents when the hot juice was poured into the settling tubes.

The criteria used in the settling tests were settling rate and clarity, i.e., the percentage transmission through a 1 cm. cell at a wavelength of 0.615 microns.

Sampling of mixed juice was done at the scales and the juice was found to yield a higher clarity on standing. Davis feels that this is due to enzymatic break down of Starch and the release of bound Phosphate. The maximum time lag allowed was six minutes from the scales to processing in the Laboratory.

The Test Procedure for processing of the Juice was as follows:

- (i) Juice was sampled at the scales and used within 6 mins.
- (ii) Approximately 375 mls was treated to varying lime sequences.
- (iii) The lime was added in the vortex of a stirrer and addition controlled by pH meter.
- (iv) The sample was boiled for 3 mins. to ensure complete degasification.
- (v) The boiling slurry was poured into a preheated settling tube and allowed to settle. The time of settling was recorded and the final mud vol. percentage calculated.
- (vi) After a certain time (depending on whether a coagulant was used or not) the juice was sampled and tested for clarity and impurities present.

Davis' observation on the mixing of lime and juice was found to be true and the addition of lime to the surface yielded juice clarities which averaged 4, whilst when added in the vortex of a stirrer this improved to an average of 11.

The most important part of the procedure was to establish whether the settling apparatus gave comparable results to the factory or not, and whether there was a correlation between the two laboratory settling tubes. Initially this latter point was markedly different until the tubes were fed in parallel rather than in series by the circulating pump.

The test revealed that there was no difference between the settling rates in the two tubes. See Table I.

Table I

TUBE A		TUBE B	
Time (Mins.)	Mud Ht. in cm. Av.	Time (Mins.)	Mud Ht. in cm. Av.
0	59.5	0	59.0
10	45.5	10	45.8
15	39.3	15	39.5
20	34.0	20	33.5
25	30.1	25	29.7
30	27.3	30	26.7
35	25.0	35	24.5
40	23.5	40	23.0
45	22.2	45	21.9
50	21.0	50	20.8
55	20.1	55	20.0
60	19.3	60	19.0
65	18.5	65	18.3
70	17.8	70	17.7
75	17.2	75	17.0
80	16.8	80	16.5
85	16.5	85	16.2
90	16.0	90	15.7

The comparison between tubes and factory using the same process techniques, showed that the clarity obtained in the tubes was always slightly inferior due to the thermal difference between settling tube and jacket.

The tubes yielded a clarity of 9, whereas the comparable Factory performance was on average 12, at the time when comparison was made.

Once the initial procedure had been established a series of tests were begun to establish what liming technique gave the best results as far as settling rate and clarity were concerned.

In order to obtain the bulk of data required to substantiate whether one liming technique was better than another, use was made of coagulants to cut the settling time from 3 hrs. to 30 mins. Having established the best method the coagulant was omitted when final comparisons were made to ensure no bias.

From over 100 tests conducted the best sequence of liming was found to be heating to 160° F., allowing

to stand for 10 mins. to emulate the starch tanks then liming to 7.6 pH and heating to boiling. The clarity of juice so obtained was superior to any other technique used. In settling rate it was not the fastest, the addition of lime after heating (such as we do here at Tongaat) having the benefit of reforming the flocs and resulted in the most rapid settling of the tried liming techniques.

This reformation of flocs and the consequent increase in settling rate does tend to give evidence to the theory of floc break up.

The difference in clarity between a straight heat lime heat sequence and the method here at Tongaat lay in the haze which the latter juice had and the darkness of the juice it produced. The CaO content of mill juices averaged 414 ppm., whereas those in the laboratory were only 337 ppm. The author feels that this could in part explain the dark juice colour since an excess of lime (in our case not properly reacted) can cause mellonoid darkening. The average clarity's for clarified juices of different techniques are given in Table II.

Table II

Sequence	H.L.	L.H.	H.L.H.	L.H.L.	H.L.H.L.
Clarity	2	16	21	5	11
	1	14	12	5	9
	3	12	15	4	8
	4	9	22	7	12
	—	7	21	—	—
	0	11	29	9	13
	0	0	18	5	7
	0	0	19	6	4
	0	0	18	8	15
	Clarity Av.	2.5	11.5	19.4	6.1

The addition of Phosphoric acid was tried and improved the clarity of the Juice so that clarities of 28 were common, whilst figures as high as 41 were recorded. This opened a new line of investigation on the use of Phosphoric acid as a clarifying agent.

(2) The Significance of Mixed and Clarified Juice Phosphate Contents in Clarification

At Tongaat the Phosphate contents of the Mixed and Clarified Juices are recorded daily. The analysis is done on a twenty-four hour composite by the Official Method. The average monthly results for the preceding five years are recorded in Table III.

From the table it may be seen that there has been a gradual decrease in P_2O_5 in Mixed Juice over the past four years. This decrease in Phosphate content is possibly due to the fact that cane is now cut earlier than in previous years. The lowering of P_2O_5 level has resulted in increased difficulty in clarification.

This age-old problem of mud settlement prompted the investigation of Phosphoric Acid as an aid to settling—both to improve the settling rate and to help thicken muds.

From laboratory tests the addition of progressive increments of Phosphoric Acid to Mixed Juice prior to clarification showed gains in the rate of mud settling. However, increases in mud volume above a limit of 350 ppm. resulted. These facts are shown in Table IV.

From the results the best P_2O_5 limit appeared to be at 330 ppm. of P_2O_5 in Mixed Juice.

Another point that arose from the tests, was that the colour and clarity of the acid treated juices was excellent, and according to Honig¹ the Phosphoric Acid is beneficial to the removal of silicic acid, iron salts and nitrogen-containing non-sugars.

It was decided on the results of experimental work that a plant scale trial should be carried out. This trial period was given for 42 hours. The dose of H_3PO_4 added was set at 100 ppm., since this would increase the P_2O_5 level in Mixed Juice to the desired 330 ppm. mark.

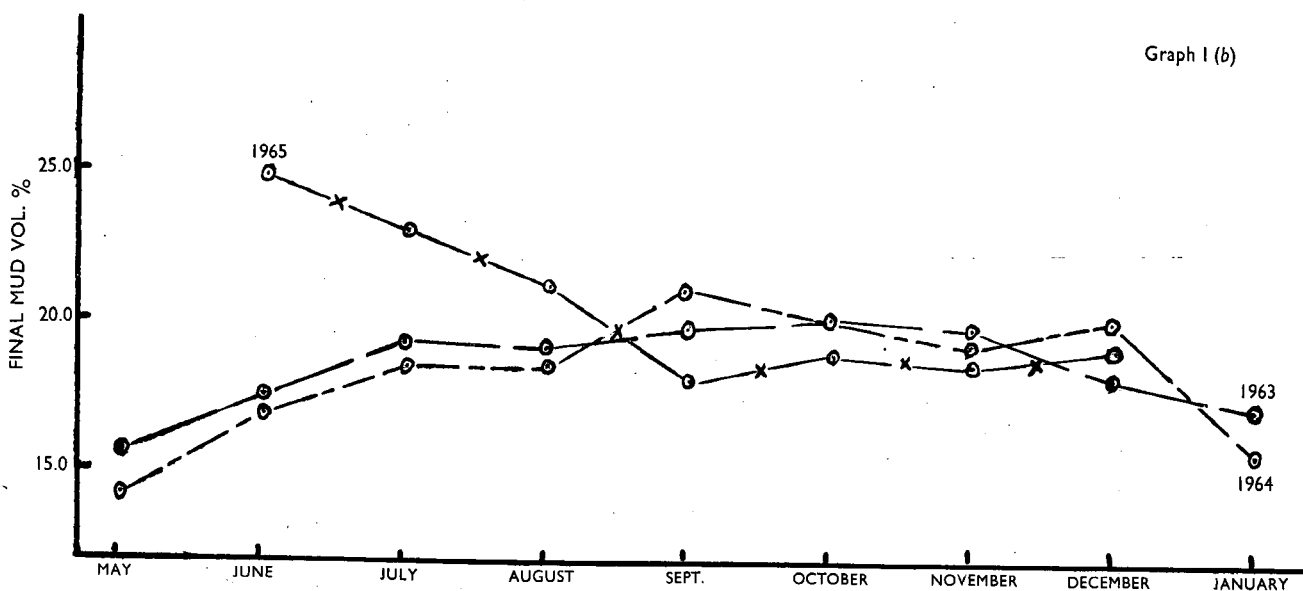
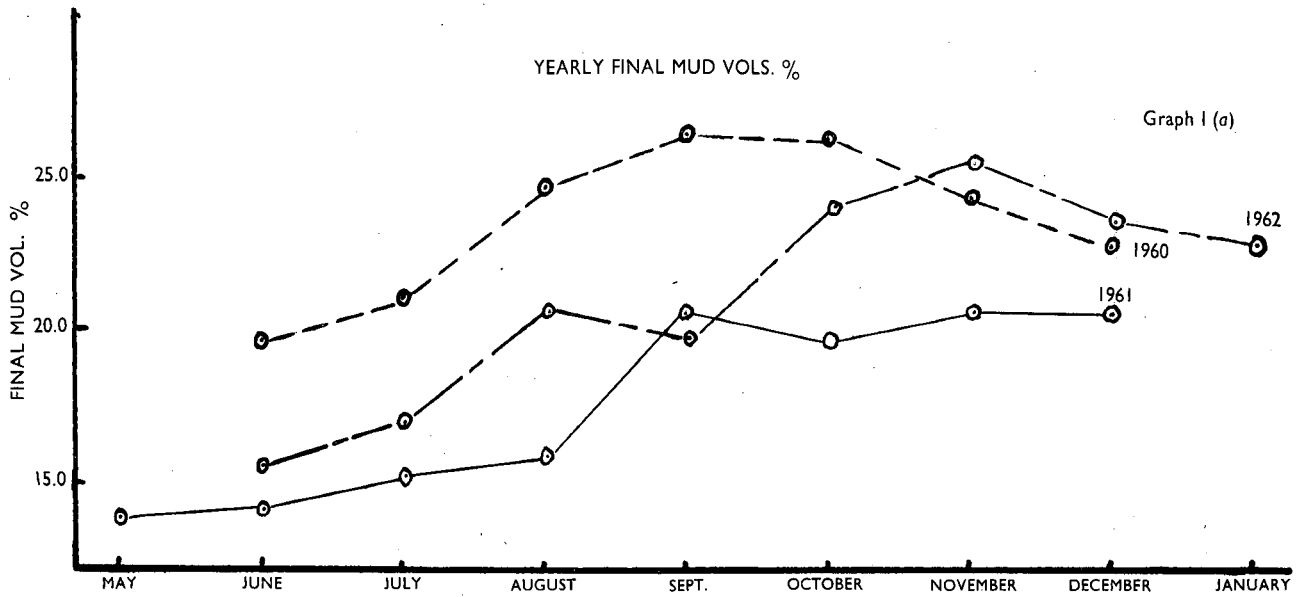
Table III

Average Monthly Phosphate contents of Mixed and Clarified Juices in ppm.

Date	January	May	June	July	August	September	October	November	December
1961	Mixed Juice	—	328	306	274	294	298	306	320
	Clarified Juice	—	27	25	40	32	35	35	52
1962	Mixed Juice	—	341	318	334	326	312	318	295
	Clarified Juice	—	42	42	43	44	50	50	22
1963	Mixed Juice	286	237	293	303	284	303	308	311
	Clarified Juice	25	41	27	36	24	36	21	28
1964	Mixed Juice	272	266	269	294	302	297	303	281
	Clarified Juice	27	27	20	21	25	31	21	27
1965	Mixed Juice	266	232	257	272	280	253	258	241
	Clarified Juice	41	43	39	43	43	31	46	42
Av.	Mixed Juice	275	295	289	295	297	293	298	290
	Clarified Juice	29	34	31	37	33	37	35	32

Table IV

Increments of H ₃ PO ₄	Standard Juice	25 ppm.	50 ppm.	75 ppm.	100 ppm.
Average Total P ₂ O ₅ Content	270 ppm.	295 ppm.	332 ppm.	350 ppm.	405 ppm.
Increase in Settling Rate %	100%	+7.5%	+8.7%	+9.3%	+11.2%
Mud Volume %	100%	78%	91%	103%	109%



The Factory Trial

On 25th November 1965 at 11.30 a.m. the Phosphoric Acid treatment was started by adding 100 ppm. of acid to the heated juice prior to secondary heating. The process conditions at the time were cold liming to 6.5 pH heating to 160° F. followed by the addition of Phosphoric Acid and then heating to boiling before adding the final dose of lime to bring the pH of clarified Juice to 7.3. This addition ended at 9 p.m. on 26th November, 1965.

The results of the test are given below together with all analyses thereon:

Table V
Analysis of Mixed Juice Prior to Test

P_2O_5 ppm.	Starch ppm.	Gum %	Silica ppm.	CaO ppm.
243	378	2.41	84	238
245	327	3.81	73	149
230	353	3.10	87	143
270	279	1.04	79	176
237	298	2.63	58	156
255	307	2.97	71	158
Av. 247	323	2.67%	76	170

Table VI
Analysis of Clarified Juice Prior to the Test

Clarity	P_2O_5 ppm.	Starch ppm.	Gum ppm.	Silica ppm.	CaO ppm.
4	49	297	4,875	151	437
7	42	248	5,400	148	417
8	44	220	5,265	137	425
5	56	200	4,735	161	421
7	69	217	4,870	163	397
3	50	263	4,130	159	263
Av. 5.7	52.0	241	4,546	154	393

Removal of Impurities as % of original in Mixed Juice:
79% 25% — Increase of 203% Increase of 230%

Table VII
Analysis of Mixed Juice during the 1st Stage of the Test

P_2O_5 ppm.	Starch ppm.	Gum %	Silica ppm.	CaO ppm.
259	320	2.41	84	176
273	373	3.17	77	149
260	385	1.96	78	176
212	346	2.63	65	168
251	356	2.58	76	167

Table VIII
Analysis of Clarified Juice during the 1st Stage of the Test.

Clarity	P_2O_5 ppm.	Starch	Gum	Silica ppm.	CaO ppm.
6	52	—	4,732	157	437
9	76	—	4,253	154	412
13	59	—	4,979	163	316
16	41	—	3,875	147	373
17	61	—	4,873	137	398
16	71	—	4,350	121	321
13.0	69.3	—	4,510	147	376

Impurity Removal as % of original in Mixed Juice:
72.5% — — Increase of 194% Increase of 225%

From the results the tests clearly indicated no substantial improvement in the removal of impurities known to cause a decrease in filterability. The author felt that this was due to the fact that the acid addition was ineffectual in producing a good floc when cold liming was being done, resulting in excess P_2O_5 in the clarified juice, i.e., 69 as against 52.

Thus a run was made for 9 hours on Juice which was run through the starch tanks and then had 100 ppm. of phosphoric acid added prior to hot liming. The method found to be so successful in the laboratory.

The phosphate addition was started at 9 a.m. on 1st December 1965 and run until 6 p.m. of the same day.

The results are as given below in Tables IX and X.

Table IX
Analysis of Mixed Juice during the 2nd Part of the Trial

P_2O_5 ppm.	Starch ppm.	Gums %	Silica ppm.	CaO ppm.
	342	2.80	67	175
	367	3.90	74	152
260	320	2.63	83	195
24 hr. sample	335	—	86	160
260	341	3.11	78	170

Table X
Analysis of Clear Juice during the 2nd Part of the Trial

Clarity	P_2O_5 ppm.	Starch ppm.	Gums ppm.	Silica ppm.	CaO ppm.
8	50	246	5,435	132	359
8	48	203	6,300	127	360
14	44	197	4,000	129	326
15	39	156	4,760	136	340
19	40	159	4,830	129	317
17	38	163	5,975	146	320
14	43	187	5,295	134	333

Removal of Impurities, as % of original in Mixed Juice:
83.5% 45% — +172% +196%

Discussion of Results

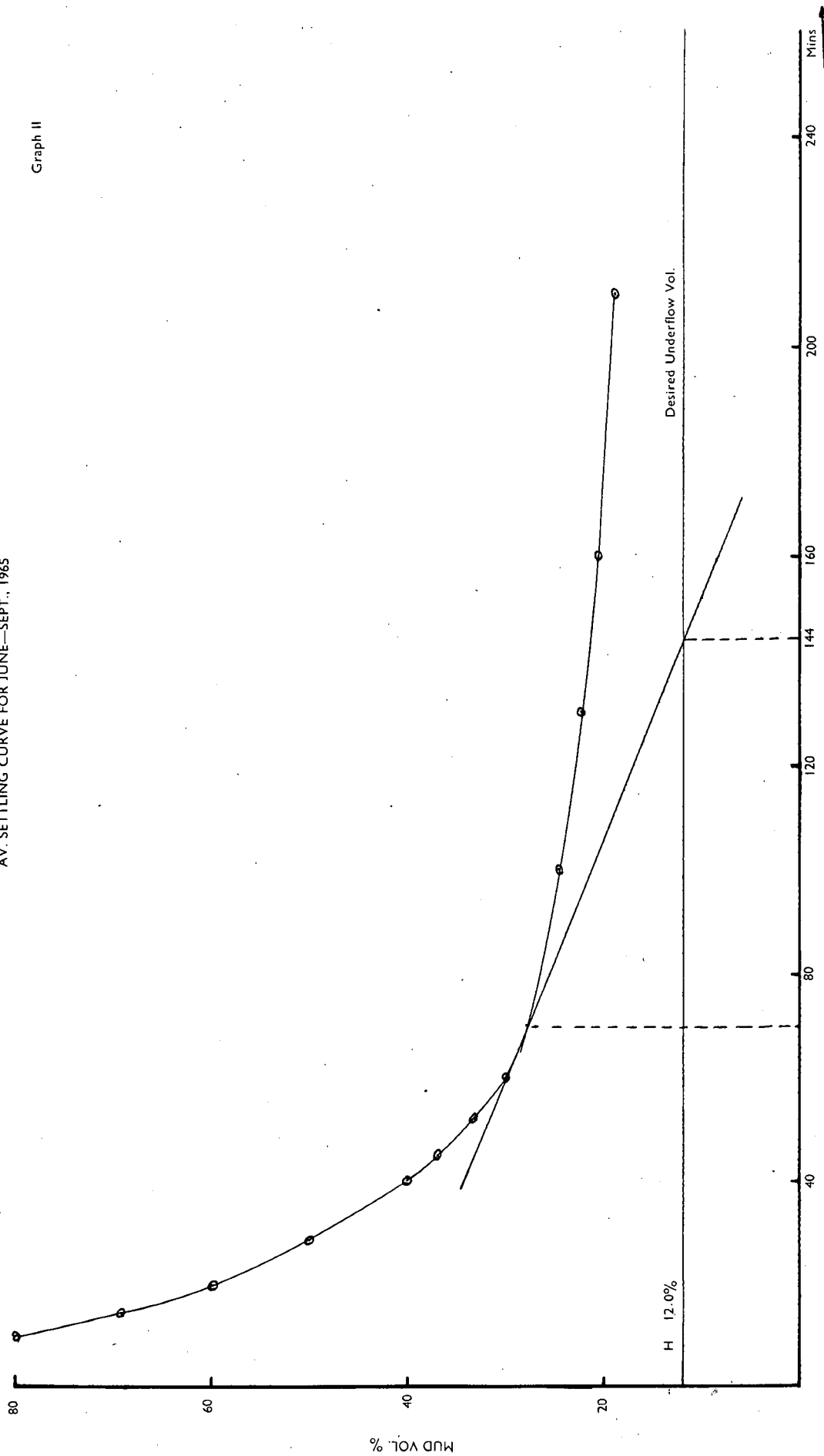
From the figures shown in Table IV it may be seen that the addition of Phosphoric Acid is beneficial to the mud-settling rate and to the compaction of mud volume. The results of the factory trial show that there is an improvement in phosphate removal of 4.5 per cent, silica removal 30 per cent and calcium oxide removal 36 per cent. This removal of inorganic matter no doubt accounted for the better clarity figures recorded and must result in better sugar quality. It therefore seems likely that phosphoric acid can prove an effective aid to the defecation process employed in Natal. However, it is desirable for more data to be obtained, preferably on the factory scale, before great significance can be attached to these results.

(3) Final Mud Volumes and their Significance in Clarifier Operation

Using the apparatus for settling described in this paper, daily mud settling tests have been recorded at Tongaat for the last five years, the significant figure

AV. SETTLING CURVE FOR JUNE—SEPT., 1965

Graph II



at the end of 3½ hrs. being the final mud volume percentage of original volume.

From the daily mud settling tests the monthly final Mud Volume percentages have been plotted on Graph I.

Here it is seen that all the curves with the exception of 1965 follow the same general trend with a gradual increase in mud volume over the winter months and then a decrease as the summer months arrive. This is in contrast to the general practical difficulties which are experienced when the rainy months come.

It will be seen that 1965 in contrast to the preceding years started differently, and then as the season progressed, became more normal in its characteristics. This resulted in conditions being such that, whereas all clarifiers were operating prior to October after this month, times came when two Bachs were shut down.

What is the purpose of these mud volume figures? The answer is that from them clarifier capacity can be calculated using the Kynch construction as illustrated by C. W. Davis.²

See Appendices I and II and Graphs I, II, III and IV where actual cases are taken for conditions at Tongaat.

It will show the estimated clarifier capacity in September and November, which bears out the statement on conditions mentioned in a preceding paragraph.

This is thus a very good method for checking on whether settler capacity is great enough for existing conditions.

Discussions and Conclusions

From the information presented in this paper the following points are made:

- (i) It has been found that the method advocated by Davis for the estimation of clarifier capacity in a raw sugar factory applies well at Tongaat.
- (ii) The liming technique which may be expected to yield the clarified juice with the highest clarity is a straight heat lime heat sequence with proper process lime mixing.
- (iii) Addition of phosphoric acid in increments up to a total P₂O₅ content of 330 ppm. in mixed juice increased the mud settling rate, the clarity of the clarified juice and decreased the final percentage mud volume.

Acknowledgments

I should like to thank Mr. Boyes for the help he has given me and wish also to thank the Tongaat Sugar Company for permission to publish this Report.

References

1. Honig, P., Vol. I, Inorganic Non-Sugars, Chapter 9, 341.
2. Davis, C. W. (1958) Development and Application of a Laboratory Clarification Test. 18 I.S.S.C.T.

APPENDIX I

Estimation of Required Capacity of Clarifier

A common method for predicting area requirements is based on the mathematical analysis by Kynch. Using this, Talmage and Fitch have derived the following procedure for estimating industrial requirements from laboratory tests:

- (a) Plot the height of the settling interface against time, and draw a horizontal line at a height (H_u) corresponding to the desired solids concentration of the underflow. Graph II and III.
- (b) Draw the tangent to the curve at the critical point to intersect the underflow line at time T_u (in hours). (The critical point is defined as the point at which the settling interface goes into compression and the flocs at the surface receive mechanical support from the neighbouring solids.)

The unit settling area required is then given by the relationship:

$$\text{Area} = T_u/H_o \text{ (sq. ft./cu. ft. of feed/h.)}$$

where H_o = Initial height, in ft., in the settling tube.

The determination of the critical point, by observation of the settling curve, limits the accuracy of this

method. In this region the slope of the curve changes rapidly and any slight mislocation can result in major discrepancies in T_u.

Further expansion of Kynch's mathematical approach indicated that a plot of settling height against time on logarithmic co-ordinates should show a discontinuity at the critical point. Graph IV. The critical point so defined by this discontinuity was then employed in the conventional Kynch construction as shown in Graph II and III.

For Tongaat for the months of June, July, August and September, the critical point was 70 minutes and T_u was ± 140 minutes. The Initial Height of the tube was 60 cms., thus the settling area required was:

$$\frac{140}{60} \times \frac{2.54 \times 12}{60} = 1.18 \text{ sq. ft./cu. ft.}$$

Thus for 250 tons per hour plus 20 per cent recycling of Oliver filtrates this would be:

$$250 + 50 = 300$$

$$\therefore \frac{300 \times 2,000}{62.4 \times 1.06} = \frac{600,000}{66.2} = \underline{\underline{9,080 \text{ cu. ft.}}}$$

$$\begin{aligned} \therefore \text{sq. ft. reqd.} &= 9,080 \times 1.18 \\ &= \underline{10,700 \text{ sq. ft.}} \end{aligned}$$

Available capacity is 2 Dorrs of 3,620 sq. ft.
 Plus 4 Bachs of $5 \times 4 \times \pi/4D^2$
 = 6,268 sq. ft.

Total area available was thus 9,880 sq. ft., which shows that under these conditions the plant was at full capacity theoretically during the four months.

APPENDIX II

Clarifier capacity required in November.

Here ratio of sq. ft./cu. ft. of feed required is cut to

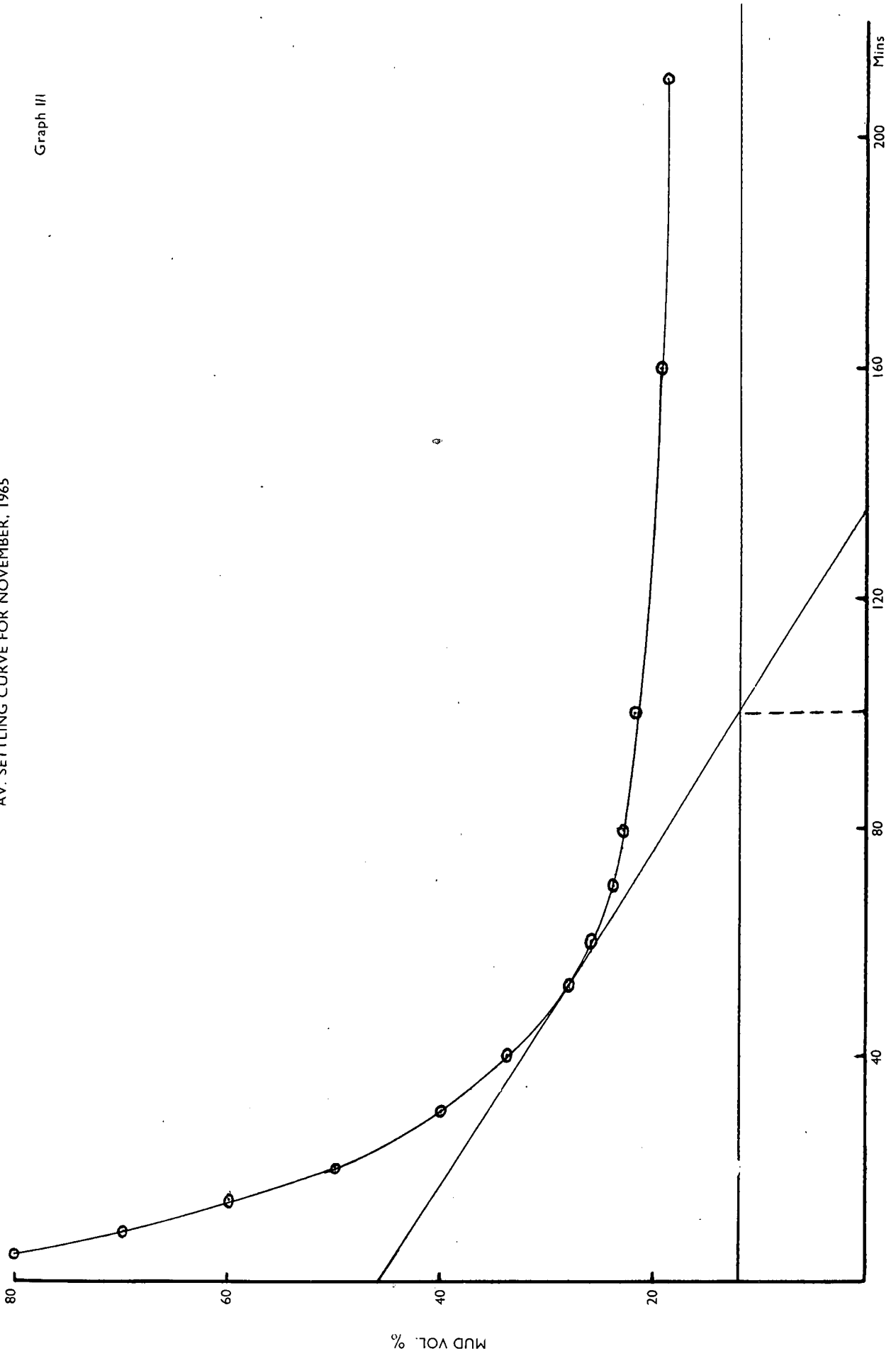
$$\frac{100}{60} \times \frac{2.54 \times 12}{60} = 0.85$$

$$\therefore 9,080 \times 0.85 = 7,718 \text{ sq. ft.}$$

This then is 2 Dorrs and 2½ Bachs.

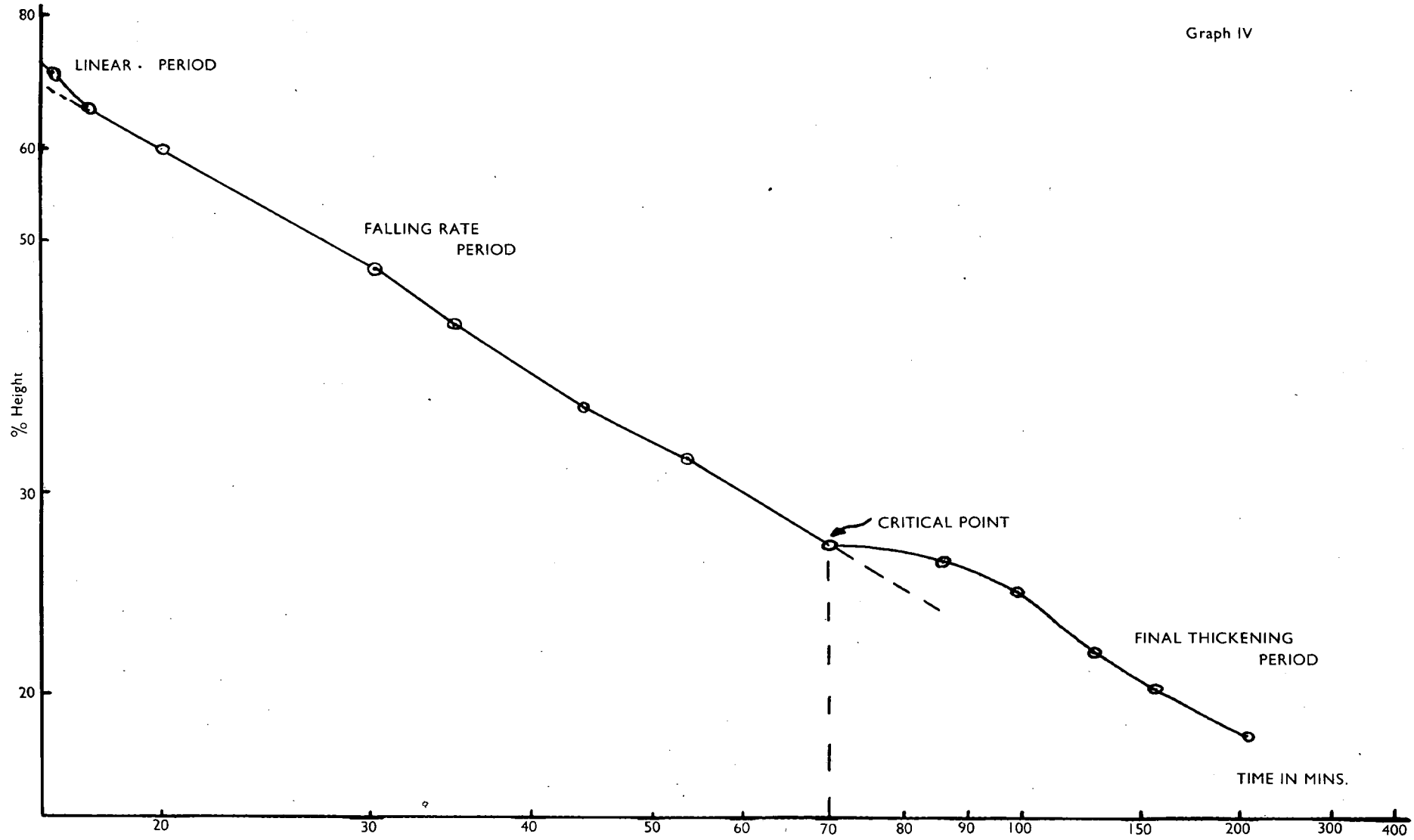
Graph III

AV. SETTLING CURVE FOR NOVEMBER, 1965



LOG—LOG. GRAPH TO CALCULATE CRITICAL

Graph IV



Dr. Graham: With the heat lime heat sequence advocated in the paper, retention of the juice at 160° for ten minutes would probably result in appreciable loss of sucrose. If this were modified so that the first liming took the pH up to say 6.0 before holding in the retention tank would the clarification be as efficient as was found with the conditions used in the tests? Nicholson said in 1959 that the CSR Co. was not using this method for starch removal only because at the time they did not have adequate pH control of mixed juice.

Mr. Carter: I do not have sufficient evidence to answer that question. I fail to see why it should make any difference to the clarity of the juice but it will certainly mean a saving in inversion losses.

Mr. Boyes: Tongaat lost very little sucrose in the starch removal process because returned filtrate was added to the mixed juice increasing the pH to 6. With a retention time of ten minutes the percentage loss of sucrose entering the removal process was approximately 0.12%.

Mr. Buchanan: The inclusion of 20% recycled filtrate in the feed to the clarifier (as in the appendix)

is incorrect for sizing purposes since the recycled filtrate contains only a small amount of solids.

Mr. Angus: On page 1 of the paper it states "the tubes yielded a clarity of 9 whereas the comparable factory performance was 12".

The reason for this was probably that in the laboratory testing was in batch as against the continuous clarification that applies in factory clarifiers.

I wonder also about the effect of seeding old sludge on to new sludge that is forming. Is this relied on for mixed juice clarification? I think a pilot plant should be used to carry out tests from jars up to factory clarifiers.

Mr. Carter: I must stress that *on average* the clarity in the laboratory tubes was worse than in the factory.

Mr. Boyes: When Tongaat and Umfolozi tried to clarify filtrate from the Oliver filters separately it was found that the clarity of the raw juice dropped. On stopping filtrate clarification and returning the filtrate to the raw juice the clarity returned to normal. I think the reason is that the filtrate contains tiny granular particles of precipitate which assist in the formation of floc by seeding the precipitate formed.