

NOTES ON JUICE CLARIFICATION AT UMFOLOZI

(A Modified Sulphitation Process for White Sugar Manufacture)

By J. O. DUCHENNE.

The question has often been asked at recent congresses of the South African Sugar Technologists as to the origin of the large rises in purity obtained on clarification at Umfolozi, and whether these rises of 3° to 3½° were the cause of the enhanced recovery observed. The writer hopes to answer these queries best by giving a full description of his modification of the sulphitation process, and its partial application on our Umfolozi cane juices.

The old St. Lucia Sugar Company's mill on the south bank, under the direction of Francis Maxwell,¹ employed his sulphitation tank process from 1916 to 1924. The rebuilt factory at Riverview, under the technical direction of Desplaces, and later Haddon, also employed the cold sulphitation method from the start in 1927; a sulphitation tower operated with the stationary burners then in vogue; the sulphured juice was then limed and heated. In 1934 the "hot liming" process,² sometimes referred to as "Harloff's Process, Modified," was adopted by O'Connor. It afforded easier filtration of the settlings with filter presses; low purity Uba juices being the raw material as a rule. Muddy canes from flooded areas also made filtration difficult. The writer witnessed this throughout the whole of the 1930 season; but the worst difficulty was the presence of starch complexes in the Uba juices.³ Clarification improved with the crushing of the new P.O.J. varieties, and later the Co. responded well to the hot liming process. The process was as follows:—

After screening cold, and later hot, the juice at 170°F. was limed, in 2,000-gallon tanks fitted with revolving paddles, with six to seven buckets of milk of lime at 15° Beaumé (12-15 gallons). After liming each tank was discharged to be pumped to the sulphur tower. SO₂ dosage was to slight acidity, the juice then filling each 2,000-gallon "correcting" tank in turn. There it was "tempered" by piped lime-milk (flue gases being pumped in at this stage to effect a blow-up with CO₂ in the "sulphi-carbonation" method installed by Haddon). Paddles on cross-arms were installed in the correcting tanks in 1935, and phosphoric acid at 15° Bé added. The tempering aimed at securing a pH (colorimetric) of 7.6-7.8 with Bromthymol blue paper, before heating to 215°F. and pumping to settling tanks.

The control then centred on the first heating, the SO₂ control, which was about 2 grams per litre, and the tempering. This was observed by the juice-preparer, in a series of glass phials, the rate of settling, clarity and colour of the settled juice giving him the indications for further adjustments. Improvements

consisted in the change over to a continuous flow of juice from tank to tank whilst liming continuously to the same extent, in the first tank; the adoption of freshly prepared milk of lime in 1937, and the use of a rotary sulphur burner—necessary with the rising tonnage. Certain clarification tests had been carried out by the writer in 1937 which, continued later with better equipment (electrometric pH meter), aimed at finding the effects of additions of lime to hot mixed juices, and the best dosage. Little was certain apart from the formation of a precipitate, the destruction of some reducing sugars and other deleterious results about which we are warned in the textbooks when overliming. On the other hand, there was much discussion on "using less lime and other chemicals" amongst the factory staffs, who were as much in the dark as the technologist as to "what was a correct dosage for sulphitation of cane juices."

In doing these tests on incremental liming with calcium saccharate and milk of lime, on a series of juices in 300 ml. cylinders, it was found that with increasing dosage of lime the flocculation became bulkier and the juice more transparent and lighter in colour, until a transition occurred above a certain dosage: the precipitates decreased in volume and the juice became slightly darker in colour with little loss in clarity. (See examples 1 and 2.) This point was established as the start of re-resolution in excess lime hydrate of the precipitated (reversible) colloids, as evidenced by their part re-precipitation on addition of a mineral acid (HCl).

The following are typical examples of the method of determining the point of maximum effective lime clarification.

Example 1.

Co.301 cane mixed juice from mills, heated to 60°C. and 100 mls. portions, limed in nine glass cylinders, with the results below, after settling half hour:—

Lime per 100 ml. added.	CaO grams per litre.	pH Elec.	Volume of precipitate.	CaO in clear juice.	Colour of clear juice.
0.5 m.	.714	9.60	18%	.224	Dark, as molasses.
1.0	1.428	10.50	29%	.280	Dirty yellow brown.
1.5	2.142	11.10	55%	.900	Clear yellowish brown.
1.6	2.284	11.12	60%	.960	Clear yellowish, cloudy.
1.65	2.35	11.15	62%	.980	Clear amber.
1.7	2.43	11.20	65%	1.40	Clear light amber.
1.8	2.57	11.23	75%	1.46	Clear light amber.
1.9	2.71	11.29	85%	1.56	Light amber, clearest.
2.0	2.86	11.30	73%	1.68	Light amber, slight cloudiness.

The juice in the eighth cylinder at 11.29 pH is taken as the point of maximum precipitation and clarification.

Example 2.

Mixed juice from P.O.J.2725 canes, at 140°F. testing, 5.10 pH limed and settled half hour:—

Lime per 100 ml. added.	CaO grams per litre.	pH Elec.	Volume of precipitate.	Colour of clear juice.
0.2	0.33	7.75	18.2%	Dark.
0.4	0.67	8.30	21.9%	Dark.
0.8	1.34	9.70	36.4%	Reddish brown.
1.0	1.674	10.10	43.7%	Yellow, cloudy.
1.2	2.01	10.47	47.3%	Light yellow.
1.4	2.34	10.65	50.9%	Clear yellow.
1.5	2.51	10.80	54.5%	Clear yellow.
1.6	2.68	10.88	56.4%	As No. 7 above (clearest).
1.7	2.84	11.00	60.0%	As above, slightly cloudy.
1.8	3.01	11.04	56.4%	As above, slightly cloudy.
1.9	3.18	11.13	54.6%	As above, slightly cloudy.
2.0	3.35	11.20	54.0%	As above, slightly cloudy.

For this juice 11.00 pH shows the maximum precipitation with peptisation of the precipitate when excess lime addition occurs, as in cylinders 10, 11 and 12.

Moreover, this point of "most precipitation and clearest juice" or, more correctly, effective liming point, was found to be the same for the four varieties of cane juices tested; it was characterised by a pH of 10.85-10.90. This point was found to be independent of the quantities of added lime, or combined lime. This is well illustrated on Curve I; and Curve II shows the increase in volume of the precipitate and further decrease after a culminating point. Thus the pH of liming was proved to be a better guide than alkalinity in grams per litre, of CaO, and better still than volumetric dosage of lime. On further treatment to remove soluble lime from the best clear juices as calcium sulphite, a juice of known purity was found to have had its purity increased 4.60°. The writer inferred that if SO₂ is made to react in a settled or filtered, limed juice (after liming to near 11 pH), a purification was possible equally as good as with carbonatation processes.⁵

The pH of liming at the factory was studied, and found to be 8.7-9.5 and 2 to 2.2 grams CaO/litre. An application on the factory scale was not possible, owing to the extra filtration or settling capacity required, the necessity of economy, etc.

On resuming the laboratory tests during a drought-affected season (1946), most of the cane juices showed an effective liming point of 11.25. The next season, with canes unaffected by droughts, this was again lower, viz. 10.9-11.05. On the average the variations are 0.2 pH ± than 11.05, confirmed many times over six years' tests. It has also been evidenced in the writer's experiments that sulphitation provides a clearer and purer juice if the sulphitation is energetic enough to obtain a reduction (bleaching point) around 5.8-6.0 pH before the second liming. This corresponds to a rH₂ drop of about 35 to 7.

The soluble alkalinity of the juices tested after liming and settling lie between 0.65 to 1.4 grams CaO/litre, requiring 0.8 to 1.7 grs. SO₂/litre. The second liming can be to 8-8.5, with subsequent addition of phosphoric acid to pH 7.2-7.6, and this gives the best juices with higher purity increases after bringing to boiling point and settling. This is illustrated in examples 3 to 7.

Example 3.

Showing actual results of the process.

Raw mixed juices from Co.301 cane, taken before and after liming in the factory at 145° and 10.8 pH (12/11/1947).

Raw juice analysis.	Limed juice.	Clarified juice.	
Brix 15.96	—	15.20	} After heating treated juice to 95° C. and settling, second precipitate = 15 per volume.
Pol 53.3	—	54.75	
Sucrose % ... 13.08	—	13.49	
Purity... .. 81.96	—	88.75	
pH 5.0	10.80	7.50	

Lime added = 1.500 grs./litre.
After filtration, lime in clear juice = 0.644 grs./litre.

- (1) SO₂ gas added 1.05 grs./litre.
- (2) pH after sulphitation 6.0 pH.
- (3) Corrected with milk of lime to ... 7.7 pH.
- (4) Phosphoric acid added, to ... 7.54.

- (a) Degrees Lovibond colour (1 cm. cell) } 1. 0.8 red + 4.0 yellow after liming and filtering at 7.5 pH.
= 1.5 red + 9 yellow, for the clear } 2. 0.1 red + 0.7 yellow limed juice... .. at 7.0 pH.
- (b) Colour reduction, compared to limed } 1. 46.7% of red + 56 juice = % of yellow, and } 2. 94% of red, 92.2% of yellow at 7 pH.
Nett rise in apparent purity = 6.79

Non-sugar elimination = ±48 per cent.

Example 4.

Cold raw juice from factory scales, heated to 60°C. and limed to 11.30 pH. Settled for one hour, clear juice treated as below (10/12/1947):

Cold raw juice.	Clear settled juice.	Clarified juice.
Brix ... 13.62	Residual CaO content, 1.2888 grs./litre.	Brix... 13.15
Pol. ... 44.85	SO ₂ added, to 1.50 grs./litre.	Pol. ... 46.3
Suc. % 11.125	Fresh lime added to 8.5 pH.	Suc. % 11.50
Purity 81.65	then phosphoric acid to 7.4 pH. Juice heated to 95° and settled.	Purity 87.46

The rise in purity was 5.81° or 32 per cent. elimination of non-sugars. Juice colour pale straw, sparkling.

Example 5.

Juice from first heaters, 12/12/1947, from various canes taken. Analysed 84.53 purity, on cooling a portion.

Juice at 65°C., limed to 9.2 pH and settled, giving 34 per cent. precipitate or settlings. After adding extra lime to 10.87 pH at 66°C. to clear juice, one-half filtered and treated as below, "A." The other was not filtered, but sulphured direct as in "B."

"A," Filtered, pH 10.87.

Lime as CaO in clear juice = 1.232 grs.
 SO₂ gas added to 1.85 grs./litre.
 pH of sulphured juice = 6.0.
 Corrected acidity to 8.0 pH with lime.
 Lime, then phosphoric acid solution commercial to 7.2.
 Heated to 99° C. and settled 10 minutes, giving brilliant lemon yellow juice.

Brix	14.47
Pol.	53.0
Sucrose per cent.	13.12
Apparent purity	90.67
Raw juice	84.53

Rise = 6.14°

"B," Unfiltered, pH 10.87.

Sulphured to 1.65 grs./litre.
 pH of sulphured juice 6.5.
 Correction to 8.3 pH with lime.
 Tempered with H₃PO₄ to 7.3.
 Heated from 54° C. to 99° C. and settled 10 minutes. Juice clear, lemon yellow colour.

Brix	14.05
Pol.	51.25
Sucrose per cent.	12.685
Apparent purity (ash per cent. = .50)	90.28
Raw juice (ash per cent. = .80)	84.53

Rise = 5.75°

Result: Non-sugar elimination = 40 per cent.
 Ash reduction = 37 per cent. Juice "A" gives a higher rise in purity of 0.4°, due to previous filtration.

Example 6.

Uba cane juice (August, 1948). Canes of 11.8 per cent. sucrose.

Raw mixed juice.	Limed juice.	Clarified juice.
Brix ... 14.16	Brought to 70° C.	Brix... 14.02
Pol. ... 46.6	Limed to 11.55 pH.	Pol. ... 49.6
Suc. % 11.50	Filtered, sulphured to 1.7 grs./litre.	Suc. % 12.25
Purity 81.23	Lime added to 8.2 pH + phosphoric acid to pH of 7.4. Heated to 95° C. and settled.	Purity 87.38

Rise in purity 6.15°. Non-sugar elimination 32.8 per cent.

Example 7.

Variety N:Co:310 juice, first large scale crushing.

Mixed juice, 26/6/1948.		Clarified juice.
Brix... .. 16.00	Juice was limed at	Brix... .. 16.08
Pol. 58.1	factory to 10.86 pH,	Pol. 60.4
Sucrose % 14.24	filtered and sulphur-	Sucrose % 14.84
Purity ... 89.00	ed to 6.0 pH. Tem-	Purity ... 92.30
Glucose ... 0.21	pered as usual to 7.4	Glucose ... 0.18
Ratio ... 1.48	pH.	Ratio ... 1.21

Purity rise = 3.30°. Non-sugar elimination 31.6 per cent.

Lovibond colour 0.2 red + 1.0 yellow (pale green). Evaporated two hours to syrup of 58.7° brix, colour now 0.9 red + 4.0 yellow; that is, equal to light honey or olive oil colour. Excellent clarity and excellent flavour. The ash was 1.60 per cent. Viscosity = 180 Redwood seconds at 20° C.

Factory Scale Application.

It is thought that the process of liming to high alkalinities in the sulphitation process, in its partial application as adopted at Umfolozi since October, 1947, has at least solved the question of quantity of chemicals debated years ago. Thus in Table 1, the rise in lime and sulphur consumption since 1947 is due to application of hot liming at 10.8-10.9 pH for the latter half of the season.

The effect of this is illustrated on Curve III, showing rise in purity, and increase of recovery over theoretical recovery by "S.J.M." formula. These results were obtained using a "Micromax" pH meter-recorder, and later a Beckman pH meter-recorder using immersed electrodes (glass and calomel).⁴ In Table 1 it will be seen that the increased purity coincided with gains of 1,200 to 1,500 tons of sugar per season, caused, it is thought, by the ease of crystallisation of syrups and molasses. Improved clarity of syrups, less scaling, higher brix of syrups, decreased foaming and brilliant sugar crystals, were the definite advances gained in 1948-49 seasons. These properties also resulted in a 10 per cent. increase in capacity after treatment. The writer thinks that, owing to the large increase in tonnage of juice, it was unfortunately not possible to achieve the degree of sulphitation required in seasons 1950 and 1951, and only a small gain resulted. Another interesting fact is the decrease in lime used since the relegation of filter presses, in 1942.

It is concluded that the application of the first part of the modified sulphitation process described⁵ has resulted in a gain of 2 per cent. recovery for a 3° purity rise in 1947-48-49.

For the second part, i.e. separation of the settlings and sulphitation of the clear limed juice, large-scale trials were occasionally possible during 1949 and 1950; after provision of extra clarifiers and pumps, as minimum requirements for a double settling process. During the tests, an increased weight of "mud" was noticed, due to elimination of more non-sugars, the increase being 20-25 per cent., and the increased decolorisation and fluidity of the syrup, with the expected purity rises, confirmed our previous notions.

Much work has been done in studying the settling characteristics, susceptibility to spoilage (Thermophilic), and effect of high alkalinities. As a result of the earlier test runs, certain improvements were brought in the final runs which will be made use of, when steam and capacity are more abundant.

REFERENCES.

- ¹ Maxwell, W. F.: Sulphitation in White Sugar Manufacture. 1st ed., 1916, p. 10.
- ² Latham: Proc. 5th Congress S.A.S.T.A., 1931, p. 109; also Haddon, I.S.J., June, 1933, p. 244.
- ³ Fauilhrade: The Presence of Starch in Uba Juices. Proc. Congress S.A.S.T.A.
- ⁴ Laubscher: Notes on the Functioning of Sulphur Towers. 24th Congress, S.A.S.T.A., 1950, p. 43.
- ⁵ S.A. Patent No. 544 of 1948: An Improved Process for the Purification of Sugar Juices.

USE OF CHEMICALS AND PURIFICATION OF CANE JUICES

COMPARISON OF CLARIFICATION RESULTS AT UMFOLOZI

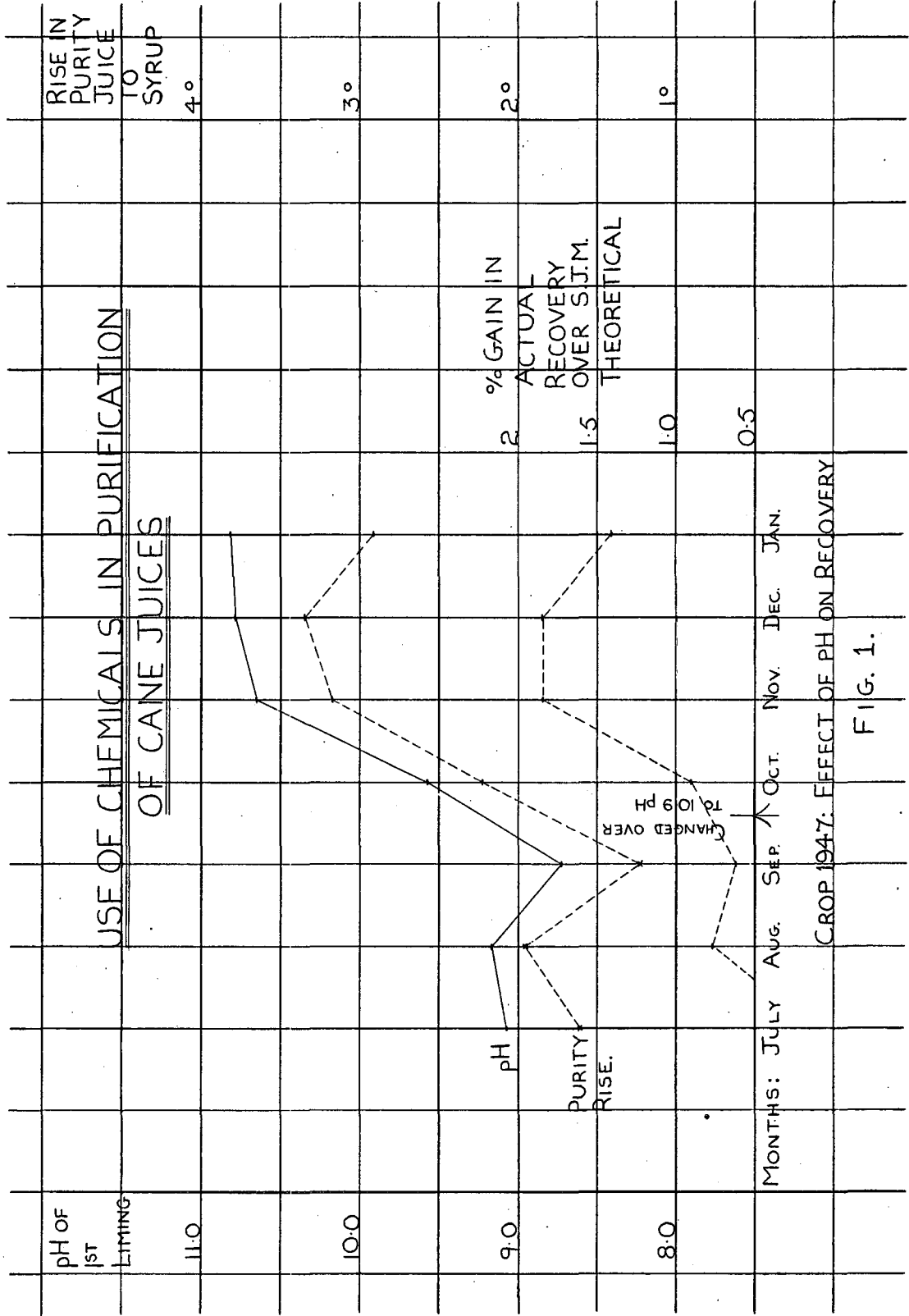
Chemicals used for clarification for seasons 1939-49 and subsequent change over to liming at high pH's (10.8—11.1) from October, 1947.

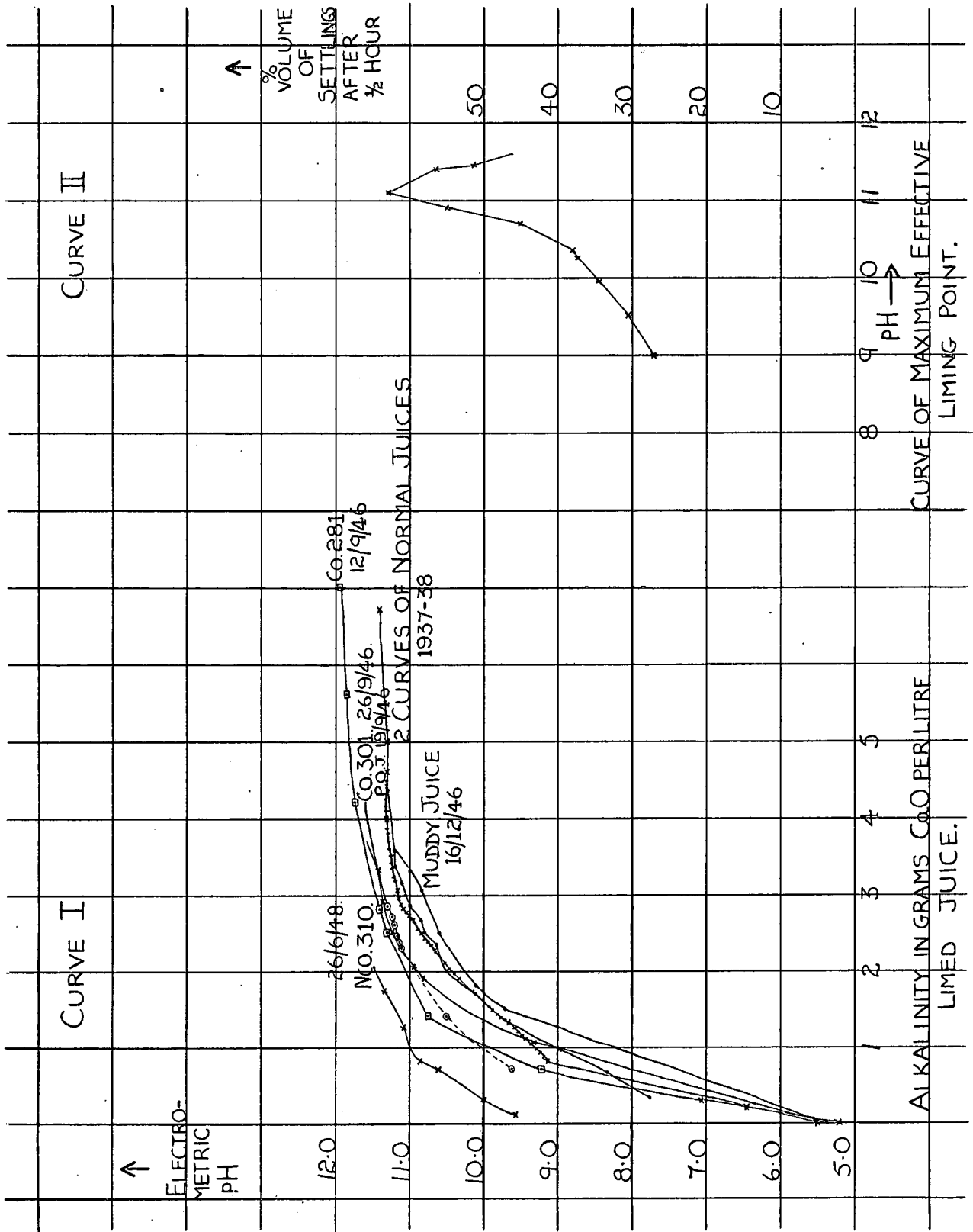
Per ton cane of—	1941.	1942.	1943.	1944.	1945.	1946.	1947.	1948.	1949.	1950.
Lime	7.350	6.021	4.027	3.280	2.913	4.043	4.162	5.826	6.242	5.718
Sulphur... ..	2.034	1.354	1.727	1.119	1.102	1.337	1.469	2.338	2.421	2.357
Phosphoric acid	0.234	0.291	0.358	0.027	0.200	0.239	0.088	0.093	0.035	0.044
pH of limed juice	—	—	—	—	—	—	9.80	10.77	10.86	10.84
(a) Mixed juice purity	84.90	83.78	84.45	84.75	85.31	85.27	83.42	83.08	82.36	83.74
(b) Syrup purity... ..	86.68	85.31	85.81	85.82	86.39	85.00	85.87	86.17	85.91	85.18
(b)—(a) Rise in purity	+1.98°	+1.53°	+1.36°	+1.07°	+1.08°	-0.27°	+2.45°	+3.09°	+3.55°	+1.44°
Factory recovery per cent.	87.15	86.94	88.71	88.35	89.54	88.16	88.34	89.81	89.77	88.59
Theoretical S.J.M. recovery per cent.	87.96	86.89	88.49	88.93	89.688	89.20	87.45	87.044	86.373	87.633
Pol. of sugar	97.892°	97.614°	98.02°	98.98°	98.19°	98.086°	98.110°	98.2390°	98.1863°	98.3794°
S.J.M. tons sugar available	31,686.84	32,561.82	32,925.07	32,950.82	35,619.87	34,608.98	37,421.69	37,585.29	38,058.12	50,390.48
Actual tons sugar made... ..	31,393.47	32,582.23	33,006.04	32,737.04	35,757.87	34,196.12	37,804.19	38,780.19	39,554.76	50,942.92
Difference from available	-293.37	+20.41	+81.02	-213.77	+138.80	-412.85	+382.498	+1194.90	+1496.64	+552.44
Molasses purity	44.49°	42.81°	39.91°	39.67°	41.10°	41.89°	42.24°	42.23°	40.20°	40.27°
Sucrose per cent. scums... ..	4.06	0.62	0.66	0.87	0.44	0.466	0.39	0.59	0.76	0.88
Difference of recovery	-0.81	+0.05	+0.22	-0.58	+0.35	-0.04	+0.89	+2.77	+3.41	+0.96

REMARKS.

1. Lower gain in recovery over theoretical in 1950 due to low rise in purity, has been calculated to be -1.54 per cent. = 1,299.331 tons sugar. This was due to lack of sulphitation (capacity increase). Total recovery gain should have been +2.50 per cent. and, excluding effect of white sugar, higher polys., etc., +0.83 = 3.33 per cent. over and above theoretical S.J.M. recovery per cent.

2. Using only the first part of the process, i.e. due to correct liming at optimum pH, therefore, since October 1947, we have gained an extra 2 per cent. factory recovery at least, equivalent to about 1,200 tons sugar per crop (or 200 tons per month).





Mr. Dymond thanked Mr. Duchenne for his paper and said it was of great interest to him. He referred to the increasing quantities of lime and thereafter sulphating to neutrality. Mr. Dymond said he had observed, as Mr. Duchenne showed, that increasing quantities of lime gave rise to increases in purity. He said that two years ago he went to Umfolozi, where Mr. Duchenne explained the details of the process which had been tried out at Darnall laboratory, but which were found impracticable. The mud quantity obtained was too high. He asked what extra equipment had had to be used and what were the normal maximum and minimum precipitates found in his process.

Mr. Duchenne said that the precipitates indicated in the table, where tall narrow cylinders were used, were not the same as those which would be found on a factory scale. The capacity required would be approximately double the normal settling equipment required because two settlings were needed.

Dr. Douwes Dekker then said that Mr. Duchenne's paper was most important and was complementary to Mr. Dymond's paper presented earlier in the morning. He asked whether apparent purities were given throughout. Dr. Dekker said there was a recent publication in India about a similar process which he thought had been patented, but he did not know whether the Indian process had developed simultaneously with Mr. Duchenne's. He said he thought that filtration under both processes seemed to be made considerably easier. He asked whether Mr. Duchenne had read the Indian paper and, if so, what his reactions to it were. He also asked whether the two figures on page 3, example B, referring to ash per cent., were a misprint.

Mr. Duchenne replied that these figures should read .50 and .80 per cent. He stated that the purities in his paper were all apparent purities. Mr. Duchenne indicated that he had read in the *Sugar Journal* of 1951 of an Indian process which was similar in many respects to his; however, the process he had invented was granted a patent early in 1948.

Dr. Douwes Dekker said he thought Dr. Saha might wish to patent his process in South Africa so that dates were important. He asked if Mr. Duchenne had any information about glucose deterioration.

Mr. Duchenne said he had not referred to glucose destruction, but from his figures it was about 16 per cent.

Mr. Phipson asked if Mr. Duchenne could say how he proposed dealing with the two types of muds produced in his process. He asked if they would be mixed or filtered separately.

Mr. Duchenne replied that the muds were mixed and filtered together. The filtration, he said, was excellent at the high pH using the Oliver-Campbell filters.

Mr. Steyn asked if there would be the same high purity rise if a start was made with a high purity mixture.

Mr. Duchenne replied that as a general principle the lower the purity of the juice the higher would be the rise. He stated that this had been well confirmed by the tests at Umfolozi.

Mr. du Toit asked if Mr. Duchenne would explain why the sugar recovery in 1948-49 was so much higher than the S.J.M. sugar available.

Mr. Duchenne said that this was due to the higher purity as a result of the higher pH. The rise in purity corresponded to the rise in recovery. He stated that there were other factors in the factory which also contributed to the higher sugar recovery, but these all derived from, or were dependent on, a good purification at the start.

Mr. Dymond asked members to accord Mr. Duchenne a vote of thanks for this most important paper on another aspect of juice clarification. A lot of research in this country had to a certain extent been given to juice clarification because it was appreciated that our juices differed from those in other countries. He said Mr. Duchenne had contributed greatly to our knowledge of juice clarification.