CLARIFICATION OF NATAL JUICES WITHOUT THE AID OF SULPHUR

SOME FACTORY AND LABORATORY TRIALS

By M. VIGER.

INTRODUCTION.

In general, it is the consensus of opinion that simple defecation of Natal juices, without the aid of sulphur, has never been successful.

Many chemists in this country have spent a considerable amount of time on research, and the latest ideas from overseas have been tried out in the laboratory. The efforts of these investigators have not been crowned with success. In most countries simple defecation is the usual routine treatment for raw sugar manufacture. The treated juices settle completely in an hour, or at the most in an hour and ten minutes. The juices are bright and clear, the mud volume is even lower than our highly sulphited juices, and the insoluble solids content of the settlings is fairly high. The question naturally arises: Why does the floc produced by only liming the juices in other countries, settle rapidly and yield a low mud volume? The writer has, for many years, carried out a certain amount of laboratory work on the purification of juices without sulphur, and considering that the proportion of variety canes has reached the high figure of 80 per cent., it was thought that the time would be most opportune to put these laboratory experiments to the acid test. The process was tried out for a week in the factory—it failed utterly.

LABORATORY AND FACTORY PROCEDURE.

In these tests the mixed juice was first heated to 185°F., then pumped to the correcting tanks, where it was limed to pH 8.4. The liming of the juice was conducted in such a way so that the bulk of the milk of lime (about 95 per cent.) was first introduced into the empty tank before filling it with the hot juice. When the tank was filled, it was adjusted to pH 8.4 and then corrected with phosphoric acid paste solution to pH 7.8. The juice was then reheated to boiling point and settled. The clarified juice was at a pH of 7.4.

The chemicals used per ton of cane were approximately as follows:—

Lime 3.5 lbs.

Phosphoric acid paste 1.1 lbs.

OBSERVATIONS OF LABORATORY EXPERIMENTS.

It was quite evident, from laboratory tests, that the settling rate of these juices was slower and gave a larger mud volume than the juices treated with sulphur. The insoluble solids content of the muds was also low. The quality of the clarified juice was fair and compared favourably with juices obtained by our standard method of clarification.

OBSERVATIONS OF FACTORY TRIAL.

During the trial it was observed that the settling rate of the clarified juice was slower than with sulphitation, the capacity of the subsiders had to be increased by 33 per cent. There was also a larger volume of settlings to be filtered. The Oliver Campbell filters could hardly cope with the muds, they were strained to the utmost.

The purity rise from mixed to clarified juice was slightly inferior, being 1.3 as against 1.6 for hot sulpho-defecation. The clarity of the juice was not at all times satisfactory, it was rather erratic. The sulphated ash per cent. brix for the mixed and clarified juices did not show any appreciable differences in comparison with juices treated with sulphur, the figures were 3.49 per cent. for the mixed juice and 3.52 per cent. for the clarified juice. Sucrose in filter cake rose from 0.7 per cent. to 1.6 per cent.; this was probably due to the very much lower insoluble solids content of the settlings, which varied from 2.2 per cent. to 3.1 per cent. as against 6 per cent. to 7 per cent. for sulphitation. Under these conditions a larger amount of cush-cush must necessarily be added to the settlings previous to filtering. There was no appreciable change in the yield of sugar per cubic foot of massecuite cured. The amount of final molasses per cent. cane and its purity compared favourably with figures obtained from sulpho-defecation. The sugar produced was very good, it polarized 99.24 with a safety factor of 0.151. The filtration rate (Elliot test) gave a figure of 116.

Another good feature was the fact that the factory output was not reduced. The massecuites were free and cured easily and there was no apparent increase in viscosity. From a recovery point of view, the results were most disappointing. The recovery of sucrose from the mixed juice dropped to the extent of 3 per cent. Undetermined losses were exceedingly high. The process was abandoned.

For comparison the figures obtained for the laboratory experiments and those obtained for the factory trial are tabulated. It will be seen that a fairly close agreement was obtained between the two sets of figures.

Table 1.—**Average Figures showing Results of Laboratory Tests.**

	MIXED JUICE.				CLARIFIED JUICE.								
No. of Tests.	Brix.	Purity.	Reducing Sugar Ratio.	Ash per cent. Brix.	Brix.	Purity.	Reducing Sugar Ratio.	Ash per cent. Brix.	Purity Rise.	Clarity Kopke.	pH.	Mud per cent. by Volume.	Insoluble Solids per cent.
12	13.52	84.62	3.53	3.58	13.89	86.12	3.10	3.60	1.50	32	7.54	25.92	2.15
Average Figures of Factory Trial.													
Week ...	13.87	84.74	3.41	3.49	14.17	86.04	2.99	3.52	1.30	28	7.40	—	2.34

Some fifteen years ago a similar run was conducted in the factory. The process used was that of Charles Muller.[1] The mixed juice was superheated to a temperature of 241°F., then cooled to 175°F. through a heat exchanger, limed to pH 8.6 and corrected with phosphoric acid paste solution to pH 7.8 and then heated to boiling point.

The process was tried over a period of three weeks. It was observed that the factory output was reduced by 25 per cent. through the slower boiling of the massecuites and greater difficulty was experienced at the centrifugals due to the viscosity of the products. The quality of sugar produced was fair, it polarized 98.5. In this case also the sucrose recovery dropped to the extent of 3 per cent.

CARTER'S CLAY PROCESS.

A patented process of simple defecation using clay as a clarifying agent has recently been evolved by Mr. R. A. Carter, acting chemist to the Umfolozi Co-operative Sugar Planters, Ltd.

It must be said at the outset, of all the various simple defecation processes tested in the laboratory, this new method of clarification, without the aid of sulphur, has given the best and most promising results.

A series of laboratory experiments were undertaken; in this way a procedure was found which best suited our juices at Darnall.

The clay used in these trials had a yellow ochre colour. The material is found near the mill.

Results obtained by this new method of clarification were compared with the figures obtained by hot sulpho-defecation, which, so far, has given excellent results in this country.

The *modus operandi* with clay is as follows:—

A clay suspension in water equivalent to 3½ grams of clay is first added per litre of cold mixed juice. This is followed by liming with milk of lime at 10°Be. to pH7.6, then 0.250 grams of phosphoric acid paste (about 41 per cent. soluble P_2O_5) dissolved in water is added. The mixture is again corrected with milk of lime to pH 7.5, heated to boiling point and decanted during 1½ hours. This time of settling represents usual factory practice. The amount of chemicals used as above, clarified all types of juices at Darnall. The colour and clarity compared favourably with juices defecated by hot sulpho-defecation. The chemicals used per ton of cane are approximately as follows:—

Clay 7 lbs. per ton cane.

Lime 2.5 lbs. per ton cane.

Phosphoric acid paste 0.5 lb. per ton cane.

The following analyses were made:—

Mixed juice: Brix, purity, reducing sugars, sulphated ash, and calcium.

Clarified juice: Brix, purity, reducing sugars, clarity kopke, pH, sulphated ash, and calcium.

At the same time the settling rate was plotted during 1½ hours at intervals of fifteen minutes, the final mud volume was noted and the amount of insoluble solids therein was determined.

It was also thought that some quality index of the juices could be obtained by filtering the defecated hot juice under standard conditions of temperature, filter cloth, time and vacuum.

It will probably be argued that this test is arbitrary. This may be so, but it does give an idea of the quality of juices treated by various methods of clarification.

In these tests an Elliot filter leaf was used.

The analyses are as follows:—

Table 2.—**Results of Analyses, Carter's Process.**

	MIXED JUICE.			CLARIFIED JUICE.							
Test No.	Brix.	Purity.	Reducing Sugar Ratio.	Brix.	Purity.	Reducing Sugar Ratio.	Purity Rise.	Clarity Kopke.	pH.	Mud per cent. by Volume.	Insoluble Solids per cent.
1	14.95	87.10	1.69	15.00	87.90	1.52	0.80	40	7.00	20.50	2.60
2	13.90	84.30	2.05	14.00	86.30	2.05	2.00	70	7.00	30.00	2.30
3	12.50	83.20	3.75	12.50	86.00	3.44	2.80	25	6.90	29.80	2.20
4	14.60	88.40	1.70	14.35	91.40	1.52	3.00	69	7.20	28.50	2.40
5	14.00	85.50	2.33	14.10	86.40	2.22	0.90	21	7.00	24.50	2.80
6	13.50	83.50	3.46	13.50	85.50	3.19	2.00	21	7.00	28.70	2.30
7	13.80	88.40	1.48	14.05	89.40	1.31	1.00	20	7.00	20.40	2.60
8	15.00	86.70	1.92	15.00	87.90	1.90	1.20	38	7.00	26.40	2.40
9	12.20	85.50	2.02	12.10	88.50	1.77	3.00	26	7.00	29.20	2.10
10	15.00	87.90	1.52	15.10	89.60	1.33	1.70	49	7.20	25.30	2.70
11	14.45	86.00	1.93	14.30	88.60	1.74	2.60	31	7.30	27.30	2.30
12	14.70	88.80	2.07	14.80	90.30	2.02	1.50	35	7.00	30.30	2.20
13	13.80	89.00	1.54	13.90	90.60	1.35	1.60	33	7.10	27.20	2.60
14	14.00	86.10	1.58	14.20	87.20	1.45	1.10	39	7.30	25.30	3.00
15	13.70	86.70	2.72	13.80	88.50	2.46	1.80	32	7.00	28.50	2.40
Average...	14.01	86.47	2.12	14.05	88.27	1.95	1.80	37	7.07	26.79	2.46
Average figures of 15 analyses for hot liming with sulphitation 2.5 gms. per litre:—											
Average...	14.41	86.26	2.68	14.82	87.88	2.29	1.62	29	7.03	17.10	6.76

Method of Clarification.	SULPHATED ASH.			CALCIUM.		
	Sulphated Ash per cent. Brix.		Ash Decrease per cent.	CaO per cent. Brix.		CaO Increase per cent.
	Mixed Juice.	Clarified Juice.		Mixed Juice.	Clarified Juice.	
Clay	3.64	3.44	5.50	0.346	0.420	21.38
Sulphitation	3.44	3.42	0.58	0.306	0.407	33.01

Table 3.—**Quality Index Obtained by Filtration.**

Time in minutes.	CLAY PROCESS. Millilitres of filtrate at each minute.	CLAY PROCESS. Total millilitres of filtrate after each minute.	HOT SULPHITATION PROCESS. Millilitres of filtrate at each minute.	HOT SULPHITATION PROCESS. Total millilitres of filtrate after each minute.
1	458	458	533	533
2	210	668	283	816
3	142	810	242	1,058
4	125	935	184	1,242
5	121	1,056	167	1,409
6	104	1,160	167	1,576
7	99	1,259	125	1,701
8	88	1,347	123	1,824
9	85	1,432	100	1,924
10	81	1,513	84	2,008
11	67	1,580	84	2,092
12	64	1,644	75	2,167
13	56	1,700	59	2,226
14	52	1,752	50	2,276
15	45	1,797	50	2,326

The juices treated with clay gave a total volume of 1,797 ml. and those treated by sulphitation gave a total volume of 2,326 ml.

In these tests the juices treated by the hot sulphitation method are of a better quality.

EXPERIMENTS ON SETTLING RATE WITH MODIFIED MILK OF LIME.

Experiments have been done with a view to improving the settling rate and also the insoluble solids of the muds. Some success has been achieved in this direction. Although the procedure used may be interesting from a laboratory point of view, its practical application remains to be proved.

It was found that by passing carbon dioxide through the milk of lime used for tempering the juice, a much faster settling rate is obtained. The figures run very close to sulphitation. The insoluble solids content of the settlings were somewhat improved—an average figure of 3.98 per cent. was found. The milk of lime used in these experiments had a calcium carbonate content of about 55 per cent.

The settling rate figures are as follows :—

Table 4.—**Settling Rate.**

Time in minutes...	15	30	45	60	75	90
Process.	Mud per cent. by Volume.					
Clay	54.7	35.8	31.9	29.3	27.9	26.8
Sulphitation	30.4	23.4	20.5	18.9	18.1	17.1
Clay + modified milk of lime	32.4	25.0	22.0	20.2	18.6	17.8

SUMMARY OF RESULTS.

The clarification of Natal juices without the aid of sulphur was tried both in the laboratory and the factory. Of all the methods tried, the Carter clay process has proved the most promising.

The purity rise from mixed to clarified juice in this process is good. It compares favourably with sulpho-defecation.

The loss of reducing sugars is negligible. This is to be expected, as the juices were limed in the cold, whereas hot liming followed by sulphitation, as a rule, shows a larger destruction of reducing sugars.

The clarified juice from the clay treatment shows a better reduction of ash, although the lime salts have increased in the clear juice, the proportion is smaller than with sulphitation.

The settling rate is slower and the settlings have a larger volume than juices treated by sulphitation. This would probably necessitate an increase in the settling capacity and a larger filtering area.

Insoluble solids content of the settlings is low for juices treated with clay. This is a disadvantage for the filters.

The quality index, although arbitrary, is inferior to juices treated by sulphitation.

The simple defecation of juices with clay has great possibilities. It also has many advantages over sulpho-defecation. This is especially true in war-time, when sulphur is not only expensive but at a premium. On the other hand, further studies are required to improve the settling rate. An increase in the amount of insoluble solids of the muds is also desirable.

Experiments to improve the rate of settling by passing carbon dioxide through the milk of lime used for tempering the juices gave encouraging results.

Reference.

[1] Muller, Charles (1921): Cause and Remedy of Difficult Defecation of Cane Juice. I.S.J., **23**, 597.

The PRESIDENT said that one of the problems arising out of the war was the shortage of materials. The Sugar Industry especially felt the shortage of chemicals for processing. Attention had recently been drawn in the local press to the possibilities of clarifying Natal juices without the aid of sulphur. Mr. Viger's paper was therefore of particular interest at the present moment.

Mr. BOOTH said he had tried to cut down the use of sulphur without eliminating it entirely, but his experience was that with insufficient sulphur, although a fair defecation might still be obtained, the work of the boiling house was slowed down and it made a big difference to the massecuites.

Although the Muller process was not commented on very favourably in this paper, his own investigations and communications with various authorities led him to believe that the process might still find application in this country.

In Mr. Viger's factory trials in clarification without sulphur there was a loss of 3 per cent. in recovery, but the ash, the yield and purity of massecuites and molasses, as well as the viscosity, remained the same. Under these circumstances he could not see to what the loss of recovery could be attributed.

He found the process very interesting and had received samples for experimentation, but had not had the time as yet to carry out experiments with it. Canes after rains were often dirty with adhering mud and clay, which gave a lot of trouble in the factory. The speaker would like to know what the difference was between such clay and that used by Mr. Viger. Was it a special type of clay found by Mr. Carter, with properties suitable for clarification ?

Mr. VIGER, in reply, stated that the losses were undetermined losses and it appeared to be bound up with the process, as both before and after the factory trial they did not occur. He gave the following sucrose profit and loss account as a percentage of sucrose in juice :—

	Average of two weeks before test.	Test week.	Average of two weeks after test.
In juice	100.00	100.00	100.00
In filter cake	0.27	0.65	0.59
In final molasses	11.19	10.92	10.31
Undetermined	0.43	3.46	0.92
Recovered	88.11	84.97	88.18
Total loss	11.89	15.03	11.82
B.H. efficiency	102.8	99.11	101.3
Molasses in cane	3.53	3.41	3.36
Lbs. sugar per cubic ft. massecuites	41.6	41.3	42.2

The Muller process was also tried with sulphitation and there, unlike the trial without sulphur, no trouble was experienced.

The clay used at Darnall was not the same as used by Mr. Carter at Umfolozi. Its composition was as follows : 29.5 per cent. silicate, 39.5 aluminium oxide, and 34 per cent. moisture, with small quantities of iron and magnesium.

It was interesting to note that the literature had for some years mentioned bentonite as a clarifying agent in sugar manufacture.

Mr. CARTER said that he had tried many different types of clay, and nearly all of them were quite satisfactory. In the factory, however, entrainment was encountered as a result of the juices boiling so exceptionally freely in the evaporators. It was also noticed that the juice from the evaporators, though clear, was almost jet black for the first couple of hours. It was found afterwards that most of the scale from the evaporators and syrup tanks had been removed.

Mr. WOUTERS said that sodium carbonate was made in this country, but also imported from East Africa at a much lower cost. He suggested that it be used instead of lime in pre-liming and also for the removal of scale.

Mr. VIGER said that Smith in Australia was working on a method of clarification using sodium carbonate. He had not seen the results yet, but thought that sodium carbonate would be found a rather expensive chemical.

Mr. CARTER stated that working with an acid instead of an alkaline clay the juices settled much quicker. In reply to certain questions by Mr. du Toit, Mr. Carter said he had tried the clay process with and without phosphoric acid, and also with a small quantity of sulphur dioxide. For Umfolozi juices, which are comparatively rich in phosphates, the addition of phosphoric acid was in his opinion unnecessary, and had the disadvantage of giving a light precipitate of larger volume. Clay with lime and carbon dioxide gave the same result as that obtained without the carbon dioxide. The addition of 0.5 gram of sulphur per litre gave a very nice juice, but did not improve the volume of precipitate.

Mr. BIJOUX said that as a result of recent investigations the MacMar process was patented in America. In this process carbon dioxide from flue gases was dissolved and later regenerated from alkali carbonate lye in the presence of ammonia. A very high efficiency of carbon dioxide recovery was claimed.

About 2.2 tons of carbon dioxide were required per 100 tons of cane in the double carbonatation process, allowing for 40 per cent. unavoidable wastage. The average bagasse per cent. cane in South Africa was about 35 per cent. of 52 per cent. moisture, which on combustion, according to Nöel Deerr, would give rise to 28 tons of carbon dioxide per 100 tons cane. Only part of the carbon dioxide from the flue gases need therefore be recovered for double carbonatation, and even less for a single carbonatation.

The concentration of the carbon dioxide from the lye would probably be at least double that of the original in the flue.

If ammonium phosphate were used in treating the partially tempered juices there would be a liberation of ammonia at the higher pH, and this could again be used in the process of recovering the carbon dioxide.

The lye solution for absorbing the carbon dioxide was found best when made from potassium carbonate, or failing that sodium carbonate, but calcium carbonate might also be found sufficiently effective.

The speaker thought that the necessary plant might be erected largely from material already in the factory. If this could be done the cost should not be prohibitive, and a change to a semi-carbonatation process, using largely waste products, ought to be both more economical and efficient than sulphitation.

Dr. HEDLEY thought that, with the present acute shortage of sulphur, this was certainly a question which deserved consideration. Germany had shown that it was practical to recover carbon dioxide from flue gases and utilize it industrially. Carbon dioxide from bagasse furnaces was not only purer, but should be at a higher concentration than that in the flue gases from coal. He had often thought that experiments should be carried out to see whether the carbon dioxide in our flue gases could not be used in clarification. Its concentration was practically the same as that of sulphur dioxide required for sulphitation. Natal Estates, with double carbonatation, used about double, 30 per cent., the concentration of carbon dioxide in the flue.

Mr. RAULT said that they found the speed of gassing and neutralising in their process dropped very rapidly if the concentration in carbon dioxide dropped below the normal 28 to 30 per cent. Even with a comparatively small quantity of lime and carbon dioxide a quick settlement was obtained with the muddy carbonated liquors, and it was not necessary to use the large volumes of lime as practised in Natal Estates Limited in refining juices by the double carbonatation in order to substitute carbon dioxide for sulphur dioxide. All that would be necessary to work a simplified carbonatation process at any factory would be the erection of a small kiln and gas pump. This ought not to cost much and would be easy to work. The large lime consumption was only necessary for easy filtration but not so much for quick settling.