

# MULTIPLE EFFECT EVAPORATOR SCALE IN NATAL

By G. C. DYMOND.

The question of scaling of evaporator tubes is one that has exercised the minds of sugar operatives in varying degrees the world over. These degrees vary with the nature of the juice, the efficiency of clarification and the concentration of the syrup.

The literature on the ash components of sugarcane is enormous, and shows that here are raw material variables over which the sugar manufacturer has no control. His only hope has been by improved methods of clarification, whereby the more obnoxious substances such as silica are reduced, with no increase in lime salts.

In recent years the advent of the ion-exchange process, whereby a high percentage of ash is removed, shows the way to eventual removal of this bugbear of sugar manufacture.

The manner in which incrustations result in lost evaporating capacity is indicated by the composition of Natal evaporator scales.

The following are the analyses of four weekly average samples of scale taken from a quadruple effect evaporator during the 1950-51 season.

	Vessels.			
	1.	2.	3.	4.
Ash per cent. dry substance :	79.60	85.90	82.00	91.30
	77.16	77.96	84.16	90.16
	90.60	89.04	84.40	90.16
	79.46	86.76	81.82	88.66
Average :	81.70	84.92	83.10	90.07

	Vessels.			
	1.	2.	3.	4.
Organic matter per cent. dry substance :	20.40	14.10	18.00	8.70
	22.84	22.04	15.84	9.84
	9.40	10.96	15.60	9.84
	20.54	13.24	18.18	11.34
Average :	18.30	15.08	16.90	9.93

Prinsen Geerligs in his 1909 edition of "Cane Sugar and its Manufacture," gives the following figures for loss in ignition :—

	Vessels.			
	1.	2.	3.	4.
Defecation:	22.28	25.97	31.62	39.91
	29.10	23.97	33.15	35.50
Defecation and sulphitation :	24.35	30.63	33.58	—
	19.80	20.40	21.36	20.11
Average :	23.88	25.24	29.93	31.84

Spencer-Meade, 1945 edition, quotes much lower figures (Archief, 1900) :—

	Vessels.			
	1.	2.	3.	4.
Combustible matter	20.37	13.41	11.04	5.08

From these comparisons, it would appear that our scale is harder than those quoted by Prinsen Geerligs, but somewhat softer than the figures given by Spencer-Meade.

## Composition.

**Silica.** Silica may be present in the raw juice as calcium silicate or as gelatinous silica. This obnoxious scaling material may also be introduced by the lime and phosphoric paste used in clarification.

	Vessels.			
	1.	2.	3.	4.
Silica per cent. ash, 1950-51 scale :	8.53	31.39	46.73	59.48
	6.74	9.30	49.76	56.23
	36.03	41.95	25.02	47.97
	4.53	15.37	14.92	43.32
Average :	13.96	24.50	34.11	51.75

Comparative figures from Prinsen Geerligs and Spencer-Meade are :—

	Vessels.			
	1.	2.	3.	4.
Prinsen Geerligs	4.01	9.76	28.59	33.51
Spencer-Meade	7.79	7.43	39.26	54.39

From these comparisons it appears that more silica is deposited in the first two vessels of our evaporators than in other countries.

The introduction of silica from external sources such as lime and phosphoric paste should be avoided by strict standards.

Recent analyses of lime and phosphoric paste show :—

	Lime	Phosphoric Paste
Silica... ..	1.3- 1.6	0.4- 0.5
Iron and alumina per cent. ...	1.9- 2.6	1.0- 1.5
Lime (CaO) per cent. ...	77.0-90.5	37.0
Sulphates per cent....	trace	2.0- 2.5
Moisture per cent. ...	—	14.0-19.0
Phosphate P <sub>2</sub> O <sub>5</sub> ...	—	45.0-50.0

These introduced impurities may well account for irregularities when assessing the ash values of various clarification processes.

**Iron and alumina.** The amounts found were as follows:—

	Vessels.			
	1.	2.	3.	4.
Iron and alumina	52.85	27.77	5.88	2.08
per cent. ash :	59.62	46.53	6.70	3.23
	8.13	7.70	10.59	3.19
	65.44	36.77	13.51	1.61
Average :	46.51	29.69	9.17	2.53
Average (including abnormal third series) ...	59.30	37.02	8.70	2.31

These figures vary considerably from those stated by the aforementioned authorities. This may be partly due to the high alumina content of the phosphoric paste.

	Vessels.			
	1.	2.	3.	4.
Prinsen Geerligs	8.12	4.82	3.98	3.73
Spencer-Meade	2.03	1.53	2.31	2.58

The use of non-corrosive paints throughout the clarification process, in order to reduce these large amounts of iron in our scale, may be well worth while.

**Lime salts.** According to Prinsen Geerligs, the solubility of calcium sulphite is low in alkaline juices, especially at high temperatures, so that calcium sulphite can only occur in scale when present in the juice as bisulphite and after being decomposed into normal sulphite and sulphurous acid. This condition existed in all the scales tested. The actual percentage was not determined. Calcium phosphate is usually found in predominance in the first vessel, as calcium oxalate and silica are in the last.

#### Lime as CaO.

	Vessels.			
	1.	2.	3.	4.
CaO per cent.	22.22	24.03	24.69	15.07
scale :	19.44	22.63	23.43	18.30
	24.34	23.12	29.67	20.70
	11.95	20.80	34.66	24.70
Average :	19.49	22.64	28.11	19.69

Prinsen Geerligs gives the following figures:—

	Vessels.			
	1.	2.	3.	4.
Defecation ...	39.13	31.96	13.97	23.42
	30.17	31.83	30.00	18.79
Defecation and sulphitation ...	31.90	29.35	13.09	—
	29.33	32.63	21.70	15.12
Single carbonatation	12.81	4.31	21.47	—
Double carbonatation	38.52	16.27	12.30	—

Double carbonatation and sulphitation—

Good ...	13.67	17.21	22.90	—
Bad ...	30.91	29.06	34.60	30.91

These figures give no true comparisons. It is of more importance to see in what form our lime salts occur.

**Sulphates.** The percentage of sulphur trioxide found was extraordinarily high compared with that given in the literature. Thus:—

	Vessels.			
	1.	2.	3.	4.
SO <sub>3</sub> per cent. ash	14.01	14.65	20.77	21.03
	12.88	19.84	17.98	20.30
	30.25	26.42	33.73	25.86
	15.76	25.22	35.27	29.48
Average :	18.22	21.53	26.94	24.17

Comparisons:—

Prinsen Geerligs	4.17	3.74	1.19	0.54
Spencer-Meade	2.02	1.92	0.54	1.65

From these figures it appears that our evaporator scales contain more silica and iron compounds, while the lime, though not in itself excessively high, is present mainly in the form of sulphites and sulphates.

#### Analysis of Normal and Abnormal Pan Scale, the Latter Occurring when Crushing Old Fire Cane.

	Ash per cent.	Organic matter per cent.	SiO <sub>2</sub> per cent. ash.	Iron and alumina per cent. ash.	CaO per cent. ash.	SO <sub>3</sub> per cent. ash.
Normal scale	85.5	14.50	54.01	2.67	18.93	22.92
Fire scale	82.90	17.10	39.40	8.30	22.78	29.50

These analyses in themselves do not indicate any serious abnormality in the composition of the scale. It was noticeable, however, that the quantity when crushing fire cane perceptibly increased. This in itself would cause less heat transference and slower boiling.

The foregoing data is scanty and has been given as a basis for discussion, in order to stimulate a wider study of an important subject.

**Mr. Dymond** said the paper in itself demonstrated no new facts and was merely a record of a few analyses of evaporator scale in Natal. The subject was, however, of great economic importance and the object in presenting the paper was to stimulate discussion and formulate a plan of co-operative work for the future. Such a plan could be based on the collection of samples at the various mills throughout the crop. The S.M.R.I. had a very full programme of work, but there appeared no reason why much of this type of work could not be done at the mill laboratories during the off crops. In this way a system of co-operative work could be built up in the industry.

**Mr. Barnes** said the subject was of deep interest to every sugar factory, not only in Natal. It raised annually a good deal of attention and numerous devices had been tried with the object of preventing scale formation in the various vessels. Once this scale-forming material was present in the juice and entered the first vessel of the evaporator it had to come out in that or one of the subsequent vessels or in the ultimate products—the sugar or the molasses.

Another approach to the subject might be to make a mineral analysis of the juice and of the molasses and compare the results with scale analysis taken about the same time. An important point was the lack of knowledge of the amount of scale formed. The analysis he had suggested might give some indication of the probable quantity of scale which would be deposited in the vessels. Figures of the actual quantity could perhaps be obtained by occasionally withdrawing a calandria tube and weighing it before and after the removal of scale.

The question of loss of heating capacity in evaporator vessels had recently been the subject of discussion in Trinidad from a different aspect. There an unexpected loss of efficiency had been found in the second vessel of a quadruple effect. Upon examination it was found that on the steam side of the tubes there was a heavy deposit of dark green waxy material. This was reported to a regional meeting and the subject thoroughly discussed. It was suggested that the material was carried over by steam distillation of material in the juice which had not been removed in the clarification process. In short, they were distilling the waxy matter from the juice in the first vessel and the material was being carried over and deposited in the second. There were negligible traces in the third. It seemed that as far as the second vessel was concerned one had to look on both sides of the tubes. He suggested that the comparisons given by Prinsen Geerligs in 1909 should be cautiously used; the canes in those days were entirely different from those grown to-day and the use of artificial fertilizers had increased during the forty odd years between Geerlig's work and Mr. Dymond's work.

**Dr. Douwes Dekker** said that Mr. Dymond's reference to data published by Prinsen Geerligs might occasion the impression that in later years little work was done in Java in connection with scaling. Such impression would, however, be far from correct. In the twelve years preceding World War II, the Experiment Station analysed about 550 incrustations. The weight of incrustations and the influence of scaling on the heat transfer coefficient were also frequently determined. A summary of the knowledge obtained by these investigations had been

given by Honig in a paper read at the I.S.S.C.T. Brisbane Congress in 1950.

A classification of scales in raw sugar mills, depending on the chief constituents as shown in the following table, proved to be useful in discussions about the cleaning and behaviour of evaporator scales:

Class of scale	Characteristic components	Analytical criterion
phosphate scale	phosphates of lime and magnesium	$P_2O_5$ percentage $> 25$
sulphate scale	sulphate of calcium	$SO_4$ percentage $> 25$
silicic acid scale	silicic acid usually combined with sesquioxides	$SiO_2$ percentage $> 30$
sesquioxide scale	$Fe_2O_3$ and $Al_2O_3$ , usually combined with $SiO_2$ and phosphates	$Fe_2O_3$ $Al_2O_3$ percentage $> 15$
organic acid scale	the only organic acids actually determined and analysed are oxalic acid and aconitic acid	oxalic acid — or aconitic acid — percentage $> 10$

It had further been found that the rate of scaling was related in a complex way to the composition of the juice to be concentrated. On this point, Honig said:

“It should be noted that the suspended matter in juice has no direct effect upon the scaling. It is the author's experience that if limed mixed juice without settling is passed through the evaporator the rate of scaling is reduced. When preheated limed raw juice was concentrated without settling in a pre-evaporator, acting as a flash tank and giving complete removal of included air and at the same time improving the steam economy, scaling in the pre-evaporator was insignificant. In the same way it has been observed that there is no direct relation between the clarity of the clarified juice and the scaling of evaporators. Only the dissolved non-sugars or those that are present in a colloidal state can enter into the formation of scale.

“The following rules may be stated as to the composition of scales:

“(1) If the sulphate content of clarified juice is over 800 mg  $SO_4$  per litre, a typical sulphate scale in the third and fourth body of the evaporator is usually found.

“(2) If the phosphate content of the juice is high and the pH of the clarified juice is over 8, or below 6.5, a typical phosphate scale is formed in the first two bodies of the evaporator set.

“(3) The lime and magnesium contents of the clarified juice are of the greatest significance in relation to the rate of deposition and also the composition of scale. If the total hardness of the clarified juice exceeds 700 mg CaO per litre it is found that the scales are high in calcium in the last three bodies of the evaporator and that a substantial percentage of magnesia is found in the first body of the evaporator.

"(4) If the effluent supply juice is a mixture of clarified juice, coming from the clarifiers, and filtrate together with sweet juices from the press station, there is great risk of the formation of scales high in silicic acid in the last bodies of the evaporator and high in sesquioxides in the first bodies of the evaporator. The available data gives the impression that it is specifically the difference in the pH values of these two juices which gives an after-effect in the evaporators, resulting in the precipitation of these non-sugars, where this precipitation *in statu nascendi* is the cause of this typical scaling.

"Further it has been found that the *sweet* water from a press station is one of the undesirable components of mixed clarified juice, usually causing an exceptionally high degree of scaling, especially scales high in sesquioxides and silicic acid. This degree of scaling cannot be correlated with the concentrations of these non-sugars; it is caused more by their physical-chemical nature. Clarified juices have been made either acid by  $\text{SO}_2$  or slightly alkaline by the addition of milk of lime to settlings before filtration, as a corrective method to prevent either discoloration in the evaporator process or to prevent the formation of acid condensate that can sometimes be observed in factories where acid juices are concentrated, or to improve the rate of filtration. This practice is always responsible for an increase in the rate of scaling. Once again a precipitation reaction must occur on concentration and heating after mixing and the precipitate of organic non-sugar is deposited on a heating surface."

The degree of scaling might be expressed in terms of the amounts of scaling non-sugar adhering to the evaporator surface in mg per litre of evaporated water as follows:

low	...	...	...	18 mg per litre
medium	...	...	...	18-20 mg per litre
high	...	...	...	20 mg per litre

In evaporators a scale weighing less than 0.1 kg per  $\text{m}^2$  ( $\frac{1}{3}$  oz. per sq. ft.) was regarded as a thin scale, a medium scale weighed 0.1-0.5 kg per  $\text{m}^2$ , and a heavy scale more than 1 kg per  $\text{m}^2$ . Scaling was considered extremely heavy if, after 250 hours operation, more than 1 kg scale per  $\text{m}^2$  was formed. The main significance of scaling in the sugar factory was the effect in reducing the coefficient of heat transfer, and the only way to come to a good understanding of the significance of scaling was to determine the actual value of the overall heat transfer. This must be done simply by measuring with recording instruments the amount of condensate formed in the last body in a given period, and noting the temperature of the steam, juice and condensate.

The effect of incrustation on the heat transfer was different for different classes of scales. Hard sulphate scales, for example, usually reduced the heat transfer less than soft phosphates or organic scales.

It had been found that the  $\text{P}_2\text{O}_5$  content of clarified juice was in some way related to the rate of incrustation of other constituents. High  $\text{P}_2\text{O}_5$  percentages tended to decrease silica and sulphate incrustation and to a certain limit CaO incrustation, which later on increased with higher  $\text{P}_2\text{O}_5$  content.

This might have a bearing on the use of phosphates in chemical compounds which were recommended for the prevention of scaling. On the other hand the amount of  $\text{P}_2\text{O}_5$  in the quantities of anti-scaling compounds which were recommended as efficient was sometimes so small that the effect was difficult to understand. In this connection attention should be drawn to the small percentages of incrustating non-sugars in clarified juice which were actually deposited during the evaporation process, which phenomenon was also difficult to explain.

Dr. Douwes Dekker said further that he welcomed Mr. Dymond's suggestion of investigations to be done by the mills' technologists and would like to stress the importance of measuring the amount of scale, in addition to the chemical analysis. The investigation would, of course, be more complete if it were also possible to determine the effect of the incrustation on the overall heat transfer. Although the S.M.R.I. would probably not be in a position to undertake this type of work next season, advice and assistance would gladly be given to mills contemplating investigation.

**Mr. Dymond** said he felt the paper had achieved its object, firstly in causing Dr. Douwes Dekker to give the Congress his valuable experiences of evaporator scales in Java and secondly the general opinions expressed on the possibilities of co-operative work at the mills on such subject. He would certainly bring the matter up for discussion in Council.

**Mr. du Toit** said he was not happy about the analysis of the phosphoric paste. It was shown to contain 26 per cent. alumina but he was quite sure it was not alumina and he asked whether it might not be calcium phosphate that had been precipitated. This would also explain why the CaO content was so low. He was glad Mr. Dymond had advocated the analysis of scale being done at the mills. He hoped this would be possible, but if it were not and the S.M.R.I. could not help owing to pressure of work, he believed that African Explosives & Chemical Industries, who had opened a special department for this type of work, would assist.

Another point of interest was the high organic matter in the scales and he thought it would be advisable to have aconitic acid determined as well. It was known that calcium aconitate, like calcium sulphate, had a negative solubility coefficient and did occur in Natal scale but the extent would be interesting to know. He asked Dr. Douwes Dekker about the occurrence of oxalates in scales and juices. Prinsen Geerligs said that oxalate did occur in cane juice but in a later publication he had denied this and said that he had assumed its presence in juice

from its presence in scale and molasses, but he had been unable to detect it in juice.

**The President** at this stage expressed the view that as the discussion was following the lines that might be expected on the paper which was to follow, it had been decided to cut into the discussion on Mr. Dymond's paper and ask Mr. Schleiss to read his paper, "The Use of Sodium Hexametaphosphate for Preventing the Formation of Calcium Oxalate Scale in Evaporators During the Manufacture of Solid Wattle Bark Extract."