

# A STUDY OF FACTORS INFLUENCING REFINERY CARBONATATION

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## Abstract

Some parameters associated with optimising carbonatation refinery control have been investigated in the laboratory and the results interpreted with reference to the continuous two-saturator stage refinery process. Included in the present study are the influence of the A-saturators and B-saturator pH values on the filterability and conductivity ash content; the relationship between A-saturator temperature and filterability; the influence of % CaO on solids' value on filterability together with an examination of the so-called "ageing" phenomenon of milk of lime and its influence on filterability.

## Introduction

Towards the end of 1974 a redesigned carbonatation saturator system was introduced at Hulets Refinery (HR). Based on twin A-saturators followed by one B-saturator, the new concept has shown distinct advantages over the former A-, B-, C-saturator process, for example considerably improved filterability of the slurry resulting in an increased refinery throughput. Thus interest has been generated within the sugar industry by the success of this system particularly in view of the proposed rationalisation and development of some back end refining operations in Southern Africa.

This paper summarises part of an SMRI laboratory investigation into the factors controlling the efficiency of the carbonatation process. The results listed refer specifically to the carbonatation of raw sugar composite samples obtained from HR during 1974 i.e. prior to the introduction of the new system. The influence of temperature and pH of operation were examined with reference to filtering quality and conductivity ash content of the carbonatated liquor produced. Other factors such as the influence of lime quality were also investigated. The experimental laboratory techniques employed in this project are generally applicable to the determination of optimum conditions of processing raw sugar by carbonatation.

## Experimental

The experimental work was carried out at the SMRI on a laboratory carbonatation apparatus which has been described in detail elsewhere<sup>3</sup>.

The filtration data provided by this unit has shown adequately that a high correlation ( $r = 0,94$ ) exists between slurries produced at HR and in the SMRI laboratory from the same source of raw sugar<sup>1</sup>. For the present study, two composite samples of raw sugar — sugars X and Y were collected from HR during the months of June and October 1974 respectively. Rock lime samples were similarly obtained from HR over a corresponding period of time and used in the laboratory carbonatation reaction. Analytical data on raw materials used were supplied by the analytical laboratory of the SMRI and appear in the appendix.

The laboratory filtration rates, designated as  $f_{c-lab}$ , are a measure of the filtering quality of the carbonatation slurry. The mode of filtration and apparatus are described elsewhere.<sup>4</sup>

## Results and discussion

The advantages of the continuous twin A-, B-saturator system have been debated for some time. Bennett<sup>2</sup> proposed

that the reaction conditions within the first saturators i.e. A-saturators, largely determine the filterability of the final carbonatated liquor while the conditions of the second i.e. B-saturator govern the ash constituents of the liquor.

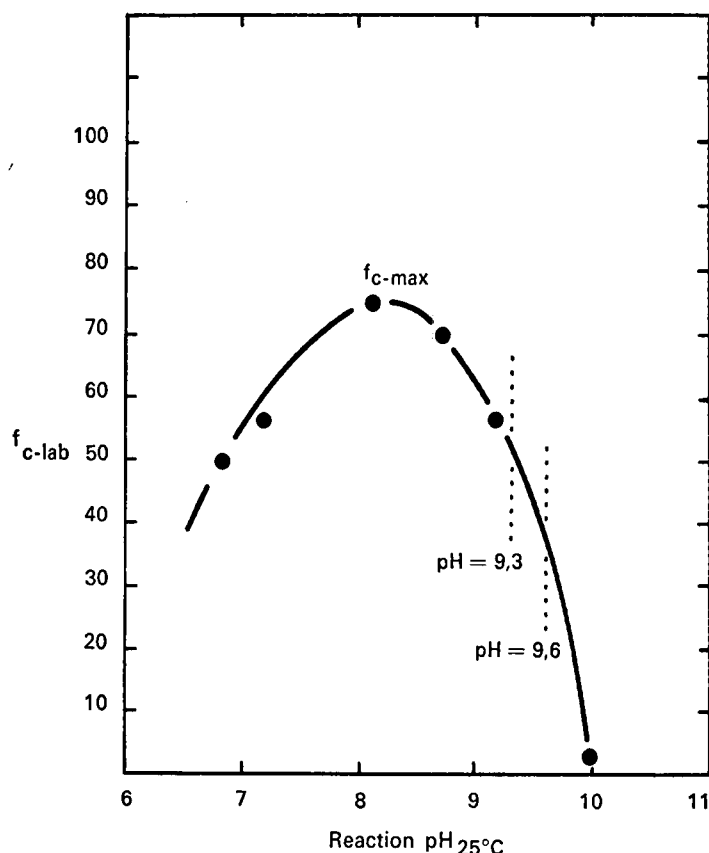
The above parameters, viz. filterability and ash, as well as others directly associated with the carbonatation process were investigated under steady-state laboratory conditions. The results were interpreted with reference to the continuous 2-stage refinery process.

### (a) pH-filterability relationship\*

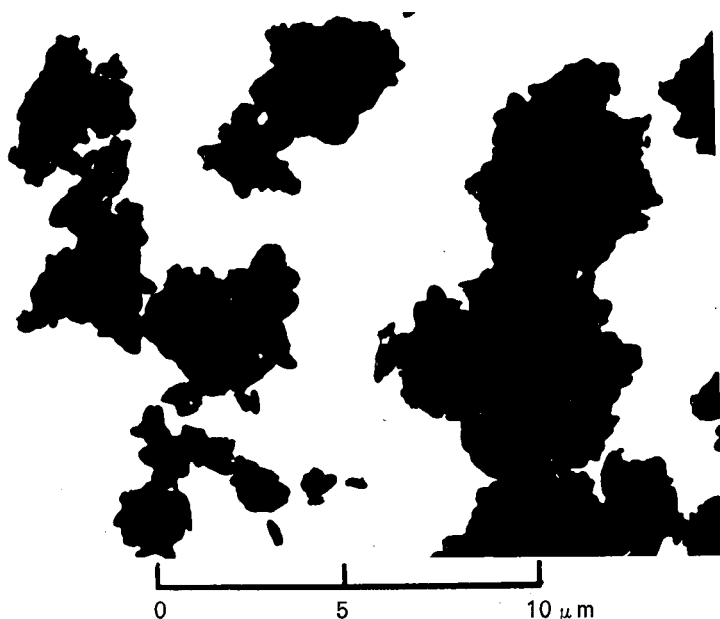
The influence of reaction pH on the laboratory carbonatation filterability,  $f_{c-lab}$ , at constant temperature and constant brix is shown in Fig. 1.

The results indicate that the maximum filterability of Sugar X occurs at the reaction pH = 8,2. Thus ideally, a single saturator operating at this pH level with an average retention

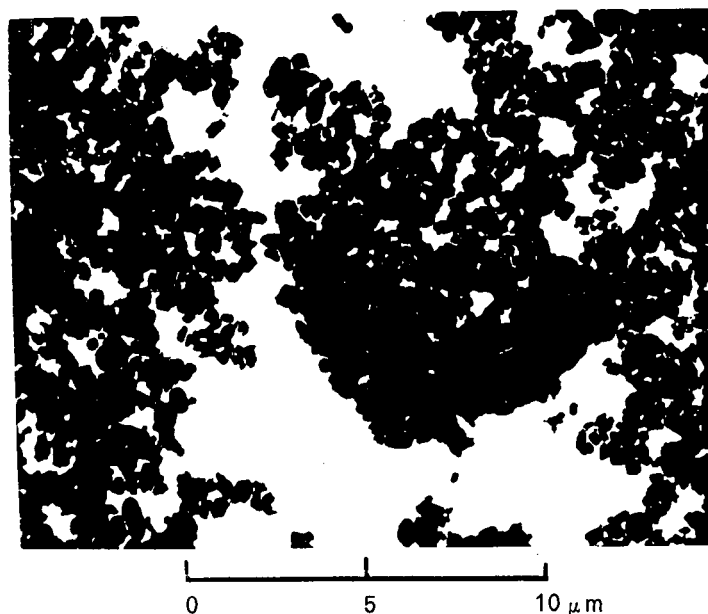
\* Sugar X was used in this study.



**FIGURE 1** Influence of pH of reaction on laboratory carbonatation filterability,  $f_{c-lab}$   
Reaction Conditions:  
retention time . . . 1 hr.  
temperature . . . 80°C  
milk of lime . . . 0,8% CaO on solids  
°brix . . . 60,0°  
Raw Sugar . . . Sugar X (HR Composite Sample)



**FIGURE 2a** CaCO<sub>3</sub> crystals grown at pH=9,0  
 Good conglomeration  
 Good filtration characteristics,  $f_{c-lab}=63,0$   
 Original mag.  $\times 700$  on 35 mm film



**FIGURE 2b** CaCO<sub>3</sub> crystals grown at pH = 9,8  
 Poor conglomeration  
 Extremely poor filtration characteristics,  $f_{c-lab} = 15,0$   
 Original mag.  $\times 700$  on 35 mm film

time of 1 hour will produce a carbonatation slurry with optimum filtering performance. However a major practical difficulty precludes working at such low pH conditions on a refinery scale: gassing efficiency is so poor as to require an inordinate amount of gas, — composition approx. 10% CO<sub>2</sub> in air—to reach and maintain a pH of 8,2. (This problem is solved simply in the laboratory by using a glass sinter disc.)

The refinery solution to this problem clearly demands the compromise of operating the A-saturator at a minimal pH for a maximal period. But even within the confines of practicability improvements can be achieved: for example under laboratory conditions it was found that a lowering of pH from 9,6 to 9,3 resulted in an increase in  $f_{c-lab}$ , from 39,0 to 51,0 representing a >20% overall improvement in filter throughput (see Fig. 1). Last-mentioned pH values are within the potential range of operation of most A-saturators.

The observed increase in filterability with drop in reaction pH is attributable to the propensity of calcium carbonate to form better and larger conglomerates at lower pH values. An examination of calcium carbonate precipitates under the electronmicroscope readily illustrates this.

Figure 2a shows a calcium carbonate precipitate grown at pH 9,0. Large conglomerates provide for very good filterability, while sparse conglomeration and small particle size account for the extremely poor filterability of the sample shown in Fig. 2b, which was grown at pH 9,8. The drop in filterability with pH values of below 8,2 as shown in Fig. 1 is probably likewise due to a decrease in the degree of conglomeration formed. The latter observation is, however, only of theoretical interest, as it is unlikely that an A-saturator will operate at such low pH values.

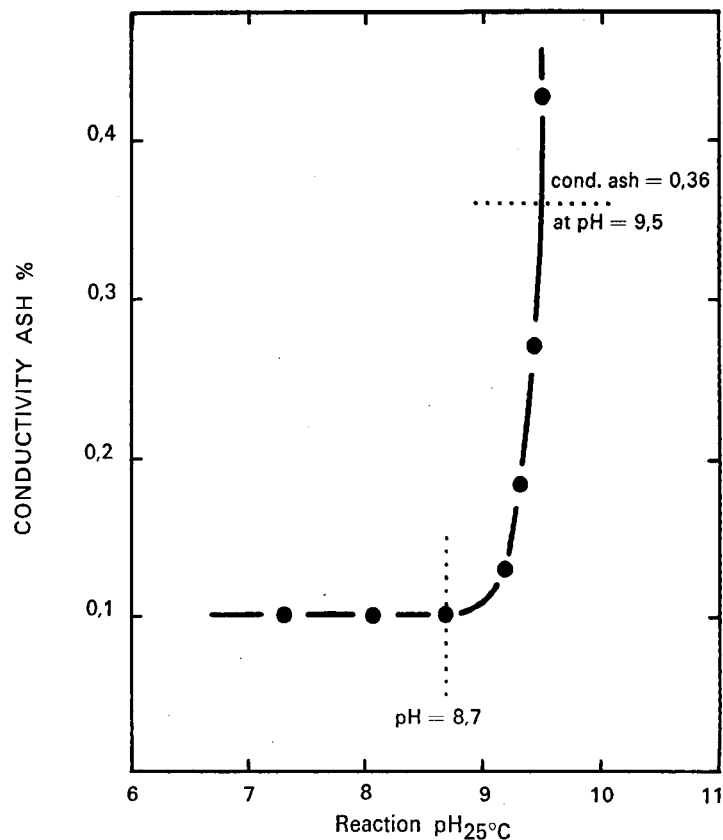
**(b) pH-conductivity ash % relationship\***

The ash content of filtered carbonatated liquor may be considered as originating from two major sources. Firstly, from the raw sugar itself, i.e. any ionic material which is incapable of being either physically adsorbed by, or chemically incorporated into, the growing CaCO<sub>3</sub> solid phase during the carbonatation process, e.g. K<sup>+</sup>, Cl<sup>-</sup>.

Secondly, and more importantly, the contribution of calcium to the ash content. This is a function of the calcium

bicarbonate-carbonate equilibrium and is controlled by the reaction conditions i.e. most significantly by pH, with temperature and brix as additional variables.

The influence of reaction pH on the conductivity ash of the filtered carbonatated liquor from Sugar X is shown in Fig. 3.



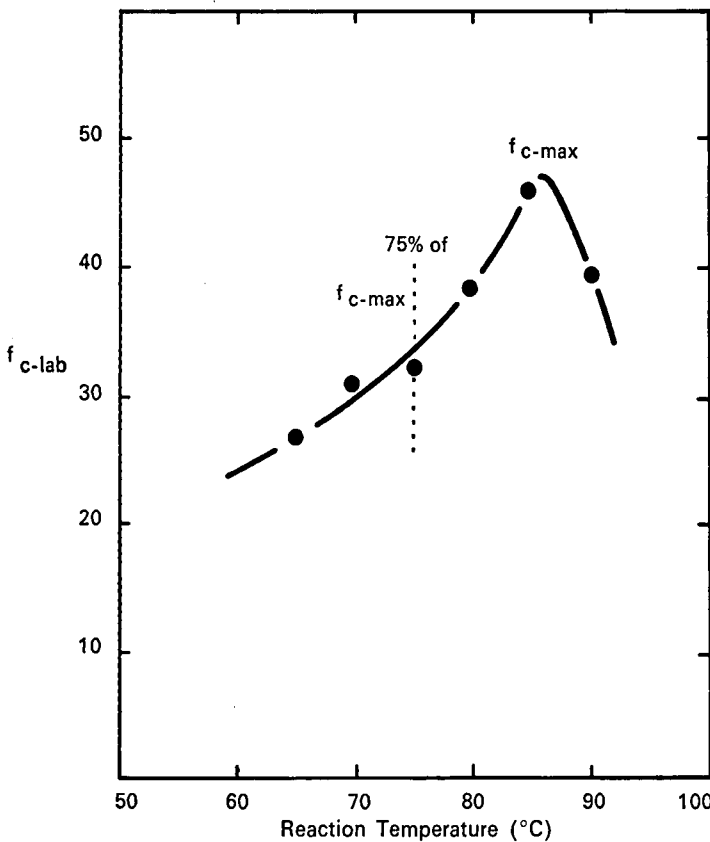
**FIGURE 3** Influence of pH of reaction on conductivity ash % of filtered carbonatated liquor.  
 Reaction Conditions:  
 retention time . . . 1 hr.  
 temperature . . . 80°C  
 milk of lime . . . 0,8% CaO on solids  
 °brix . . . 60,0°  
 Raw Sugar . . . Sugar X (HR Composite Sample)

\* Sugar X was used in this study.

As can be seen the conductivity ash % drops with decrease in reaction pH until a constant minimum value at pH 8,7 or below is reached. The maximum pH permissible is 8,7 if minimum ash content is to be achieved. For example, for a refinery processing Sugar X (at laboratory conditions of temperature and brix) the pH of B-saturator should never exceed pH = 8,7. Further, if A-saturator were to have been operated at around pH 9,5, the conductivity ash of the liquor from A-saturator would be 0,36% (see Fig. 3) — being due predominantly to the calcium contribution to conductivity ash. The function of B-saturator is therefore, to reduce this excessive ash to a value approximating the equilibrium minimum value of 0,10%.

(c) Reaction temperature – filterability relationship†

The operational temperatures for A- and B-saturators are recognised as being important factors in achieving optimal performance. The temperature of B-saturator is usually maintained as high as is practicable to facilitate filtration by reducing the liquor viscosity. Laboratory results have shown that the variation in conductivity ash % is not significant within the normal B-saturator temperature range of 78° – 88°C. However, the influence of A-saturator temperatures on the filterability was less well understood. In order to investigate this relationship, samples of Sugar Y were processed at various temperatures. The results are shown in Fig. 4.



**FIGURE 4** Influence of reaction temperature on laboratory carbonation filterability,  $f_{c-lab}$   
 Reaction Conditions:  
 retention time . . . 1 hr.  
 milk of lime . . . 0,6% CaO on solids  
 °brix . . . 60,0°  
 pH . . . 9,0  
 Raw Sugar . . . Sugar Y (HR Composite Sample)

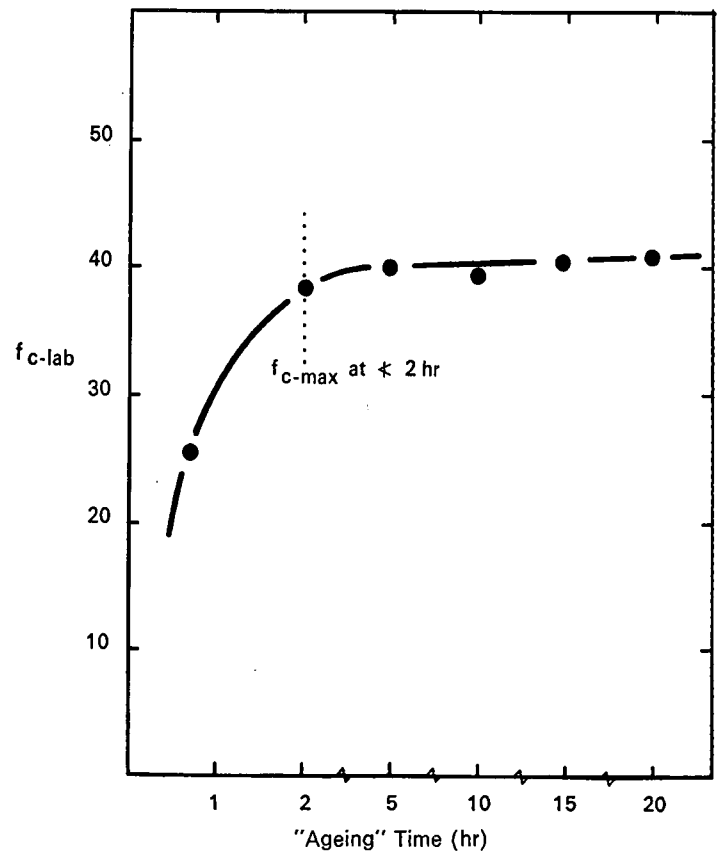
As is evident from the graph, maximum filterability ( $f_{c-max}$ ) is achieved when operating at 86°C. However, practical

† Sugar Y was used in this study.

difficulties arose in the laboratory when operating at this temperature e.g. production of excessive foam, increase in brix due to evaporation. As these are not easy to control on a laboratory scale yet are likely to occur also at the refinery level a satisfactory filterability i.e. 75% of  $f_{c-max}$  (see Fig. 4) for Sugar Y was achieved by maintaining an A-saturator reaction temperature of 75°C.

(d) Lime: “ageing” effect on filterability†

Conditioning of lime by “ageing” is a process whereby slaked lime is retained at an elevated temperature for a given period of time between slaking and use in the saturator. Some authorities have recommended “ageing” times of up to 16 hours in order to achieve maximum liming efficiency. An investigation to establish whether this phenomenon has a significant influence on the carbonation experiments was carried out in the laboratory and HR lime samples were used for this purpose. The milk of lime was conditioned at 80°C for up to 20 hours retention time in a sealed vessel equipped with a magnetic stirrer. Samples were withdrawn and used for carbonation in the normal way. Results are shown in Fig. 5.

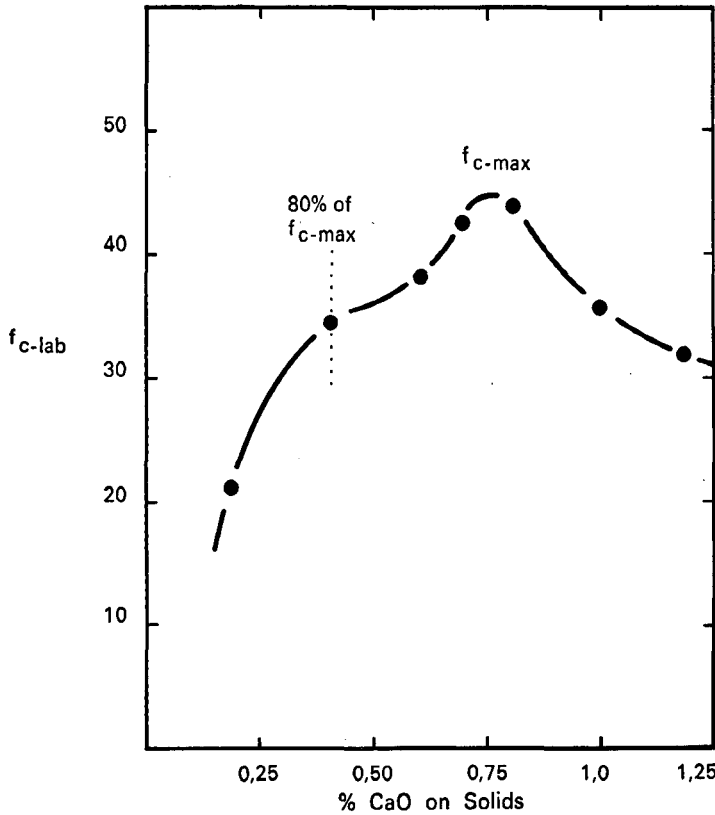


**FIGURE 5** Influence of “ageing” of milk of lime on laboratory carbonation filterability,  $f_{c-lab}$   
 Reaction Conditions:  
 retention time . . . 1 hr.  
 temperature . . . 80°C  
 milk of lime . . . 0,6% CaO on solids  
 °brix . . . 60,0°  
 pH . . . 9,0  
 Raw Sugar . . . Sugar Y (HR Composite Sample)

As can be seen from Fig. 5, freshly slaked lime is considerably inferior to milk of lime “aged” for a period greater than 2 hours. However, no further significant increase in filterability was found for retention times in excess of 2 hours. The concentration of milk of lime used in these experiments was lower than that used at HR ( $SG_{lab}=1,04$  compared with  $SG_{ref}=1,09$ ) and it is not yet known whether “ageing” varies with lime concentration.

(e) Lime: % CaO on solids effect on filterability†

The quantity of milk of lime (expressed as %CaO on solids) used in carbonatation refinery processes in South Africa varies widely viz. from 0,5% to >1,2% CaO on solids. Yet it is desirable to minimise the amount of CaCO<sub>3</sub> precipitate produced, because this results both in a concomitant improvement in filter cycle performance and a decrease in the amount of sweet water produced. The influence of % CaO on solids on filterability of Sugar Y was studied under standardised conditions and the results are shown in Fig. 6 below.



**FIGURE 6** Influence of amount of lime added as “% CaO on solids” on the laboratory carbonatation filterability,  $f_{c-lab}$   
 Reaction Conditions:  
 retention time . . . 1 hr  
 temperature . . . 80°C  
 °brix . . . 60,0°  
 pH . . . 9,0  
 Raw Sugar . . . Sugar Y (HR Composite Sample)

The results show that an optimum filterability follows a lime dosage of 0,7—0,8% CaO on solids. A drop in lime dosage to 0,4% CaO on solids reduces filtering quality by approximately 20% while analytical data suggests that the removal of ash and suspended matter is not greatly affected by this decrease in level of lime dosage.

**Concluding remarks**

It must be noted that the optimum values of saturator pH, temperature, % CaO on solids etc. which have been discussed

† Sugar Y was used in this study.

in this investigation refer exclusively to the processing of the raw sugar on which the study was performed i.e. either Sugar X or Sugar Y. Raw sugars of other quality may require a different set of processing conditions for optimum performance.

The results have shown that it is possible to derive from the laboratory valuable information on carbonatation reaction conditions of raw sugar with respect of pH of A- and B-saturators, A-saturator temperature and %CaO on solids values.

A detailed analysis can further serve to indicate the magnitude in loss of performance which may be expected when operating at conditions other than the recommended optima. More rigorous attention paid to factors such as the pH—conductivity ash% relationship may discourage such refinery malpractices as addition of slaked lime to carbonatated liquor as a “filter aid” when filterability is poor thus resulting in high ash values.

Other factors which are to be incorporated into this continuing investigation include colour removal, influence of brix and effect of starch content as well as suspended matter content of raw sugar on the carbonatation process.

**REFERENCES**

- Alexander, J. B. and Matic, M. (1974). Starch—its occurrence, importance and removal in sugar manufacture. Proc Tech Session on Cane Sugar Refining Research.
- Bennett, M. C. (1974). Physical chemistry of phosphatation and carbonatation (Parts I, II) Int Sug J 76: 40–44; *ibid.* 76: 68–73.
- Murray, J. P. and Runggas, F. M. (1973). Filtering quality of raw sugar: influence of “ageing” during storage. Revue Agricole et Sucrière de Lîle Maurice, 52 (No. 4) 256–262.
- Murray, J. P. (1972). Filtering quality of raw sugar: influence of starch and insoluble suspended matter. S Afr Sug J, 56 585–598.

**Appendix**

Analytical data on raw sugars used in study.

	Starch (ppm ± 10)	(a*c) 420 nm	(a*c) 560 nm	Cond. Ash %	Red. Sugars %
Sugar X . . . .	70	0,93	0,19	0,14	0,11
Sugar Y . . . .	90	0,84	0,19	0,12	0,09

	CaO%	MgO%	(Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> )%
Milk of lime for Sugar X	82	2,1	1,8
Milk of lime for Sugar Y	80	1,3	2,3

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