

# ASH GAIN DUE TO LACTIC ACID FORMATION DURING CARBONATATION

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## Abstract

Hulett Refinery had been experiencing problems with higher than normal ash gains since the 1987/88 season. Investigations into the composition of the ash showed the major cause of the ash gain to be an increase in calcium. It was proposed that the calcium was solubilised by reaction with lactic acid to form calcium lactate which was not removed during carbonatation. This proposal was later confirmed by laboratory carbonatations with controlled additions of lactic acid. A programme of lactic acid analysis was started and the results showed that the major cause of lactic acid formation was chemical destruction of reducing sugars under alkaline conditions during liming and not as a byproduct of microbial action as originally surmised. Laboratory simulations of the process were done under a range of conditions with temperature, time, lime addition and reducing sugars as the variables, and a model equation was developed from the laboratory results. This enabled predictions to be made of the extent of lactic acid formation under various conditions. Modifications of the process conditions based on this equation led to a reduction in lactic acid formation and a consequent reduction in the ash gain across the refining process.

## Introduction

Hulett Refinery processes approximately 2 000 tons of VHP sugar per day using carbonatation, ion-exchange and crystallisation as the main refining tools. The products of the refinery are basically white sugar and molasses plus a small quantity of speciality products which may be considered as blends of sugar and molasses. Soluble ash introduced into the refinery has the undesirable effect of increasing the solubility of sucrose in molasses, rendering an additional amount of sucrose unrecoverable and causing a considerable financial loss. The quantity of sucrose lost due to ash in a Refinery may be estimated from the Rendement or Commercial Yield (Honig,<sup>2</sup> Lyle,<sup>3</sup> Meade and Chen<sup>4</sup>):

$$\text{Yield} = \text{Pol} - (4,5 \times \text{Ash} + \text{RS})$$

The references given have the ash factor ranging between 3 and 5 and the reducing sugar factor between 1 and 7. The particular values in the above formula have been found to be reliable in predicting the yield from raw sugar at Hulett Refinery and show that the unrecoverable sucrose due to ash is 4,5 times the weight of ash. A conservative calculation shows that for every 10% of ash gained approximately R350 000 is lost per year. It was thus a cause for concern when Hulett Refinery began experiencing unacceptably high ash gains between the ash "in" in raw sugar and the ash "out" in sugar and molasses.

Initially no positive link could be made with any likely cause except for the possibility that it was tied in to either the commissioning of the new ion-exchange plant or to low pH levels in remelting. Measures that were taken on these assumptions had no effect and so it was decided to form a project team to study the problem in a more systematic way. The team initially consisted of members from the refinery

and the Sugar Milling Research Institute (SMRI) who instituted an extensive sampling and analysis programme to identify the main constituents of the soluble ash and perform mass balances on these components. Later Tongaat-Hulett STD staff joined the project team, and using the data from the earlier work put the emphasis onto establishing why the ash gain was occurring and finding solutions.

This paper gives an outline of the investigation programme and highlights the important findings that were crucial to the success of the project. Data from laboratory experiments are presented which confirm the results from the factory survey and enable a model to be derived to predict performance under various conditions. Finally a considerable reduction in the ash gain at Hulett Refinery is shown from the time the recommendations from the project findings were implemented.

## Factory Investigations

### Ash Balance and Constituents

It was necessary to establish which ash constituents were the major contributors towards the ash gain. The two most likely components were calcium and sodium, because calcium is added directly as Ca(OH)<sub>2</sub> during carbonatation and sodium as NaCl is used in large amounts during the regeneration of decolourising resin. A programme of analysing weekly composite samples of the major refinery streams for calcium, sodium and potassium was started. Potassium was included as it constitutes a large portion of the incoming ash. The average results covering an eight week period are given in Table 1 and a diagrammatic representation of the total ash and its composition change through the process is shown in Figure 1.

Table 1  
Refinery ash balance

		Raw Sugar	Brown Liquor	Fine Liquor	Molasses
Tons Solids		2040	2183	2087	86
Sulph. Ash	% Brix kg	0,13 2652	0,18 3929	0,17 3548	4,09 3517
Ca <sup>++</sup>	ppm on Brix	149	293	267	5860
CaSO <sub>4</sub>	ppm on Brix	507	996	908	19924
CaSO <sub>4</sub>	% total ash	39	55	53	49
CaSO <sub>4</sub>	kg	1034	2174	1895	1713
Na <sup>+</sup>	ppm on Brix	23	47	46	1337
Na <sub>2</sub> SO <sub>4</sub>	ppm on Brix	71	145	142	4118
Na <sub>2</sub> SO <sub>4</sub>	% total ash	6	8	8	11
Na <sub>2</sub> SO <sub>4</sub>	kg	145	317	296	354
K <sup>+</sup>	ppm on Brix	182	269	206	4793
K <sub>2</sub> SO <sub>4</sub>	ppm on Brix	406	600	459	10688
K <sub>2</sub> SO <sub>4</sub>	% total ash	31	33	27	26
K <sub>2</sub> SO <sub>4</sub>	kg	828	1310	958	919
Balance of ash	kg	645	128	399	531

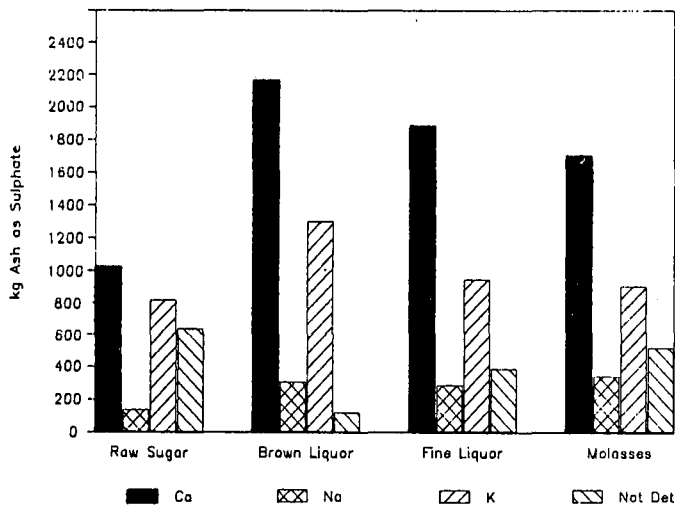


FIGURE 1 Composition of refinery ash.

Normally more than 95% of the ash leaves the process in molasses, thus the ash in refined sugar was ignored in the balances. Table 1 and Figure 1 show that the calcium added to the process over carbonatation is responsible for nearly all of the ash gain. Therefore factors affecting and means of controlling soluble calcium during carbonatation required investigation.

**Lactic Acid Survey**

Lactic acid levels across melting and carbonatation were monitored on a weekly basis and these data were used in a mass balance to identify areas of concern.

It became apparent early in the programme that there were two major sources of lactic acid in the refinery. Firstly there was a large increase between the raw sugar melt and the

saturator supply, due to high levels of lactic acid in the Sweetwater Tank. Secondly an even larger increase was found between the saturator supply and brown liquor. These points can be seen in Figure 2. The data used were averaged values from 8/4/89 to 22/4/89. The tonnages in the mass balance are tons/day.

The lactic acid contribution from sweetwater could be ascribed to microbial action, but the increase across carbonatation was clearly due to a chemical reaction as microbiological activity is minimal at the high temperatures, brixes and pH values found there.

The residence time between saturator supply and brown liquor is approximately 1,5 hours. Thus, it was necessary to establish if the lactic acid was being formed at a steady rate across the whole carbonatation process, or at any one particular stage. This was done by monitoring saturator supply liquor, A B and C saturators and brown liquor for three weeks. The results are given in Figure 3.

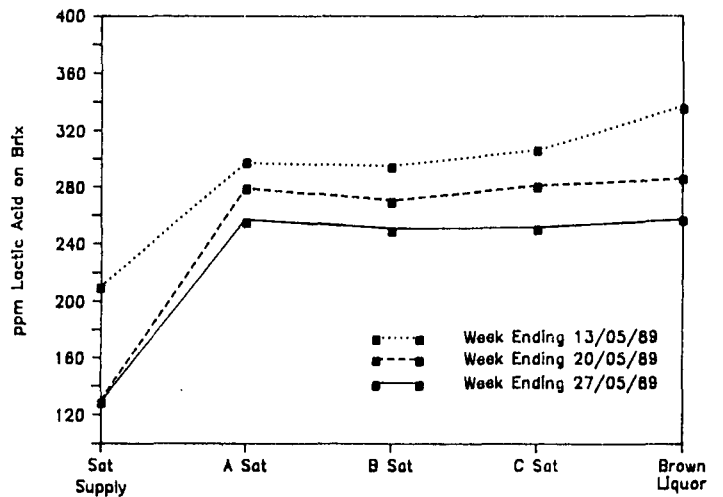


FIGURE 3 Lactic acid levels across carbonatation.

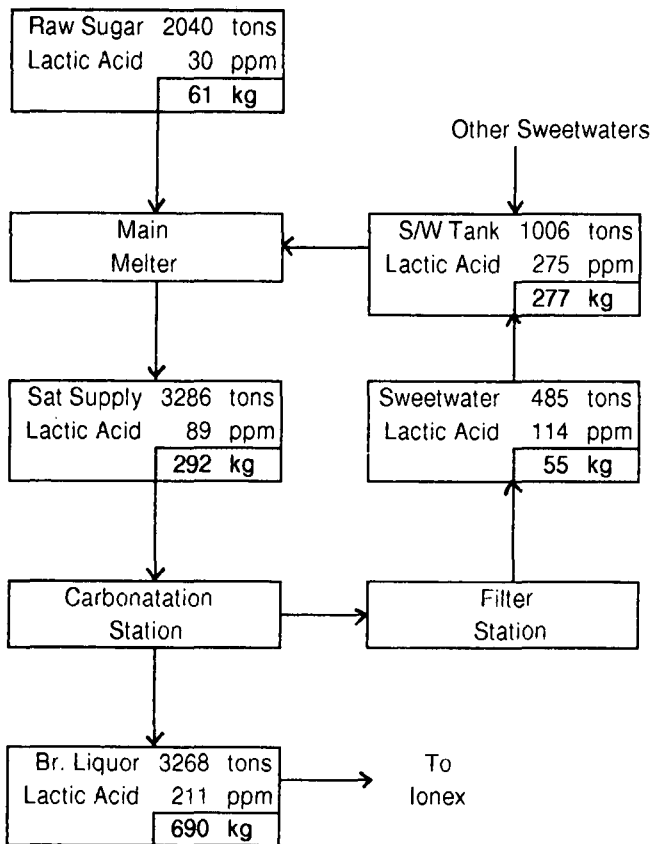


FIGURE 2 Lactic acid mass balance across carbonatation.

The results showed effectively that all the lactic acid was being formed between the saturator supply liquor and A saturator. This narrowed the search down to a small area of the process with the liming tank (high temperatures and pHs) being the main suspect. Further detailed monitoring of lactic acid levels over a 5 week period gave the following results (Table 2).

These results confirmed that the lactic acid was being formed during the pre-carbonatation liming and led to the laboratory investigations designed to establish the conditions that caused this formation and its effect on calcium levels.

Table 2  
Lactic acid formation during liming

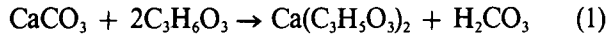
Week Ending	ppm Lactic Acid		
	Sat. Sup.	Limed Liq.	A Sat.
15/07	62	170	134
22/07	98	217	185
29/07	91	225	235
05/08	95	204	169
12/08	101	256	221
Ave	89	214	189

**Laboratory Investigations**

**Calcium Solubility**

The effect that lactic acid has on the solubility of calcium was tested by laboratory scale carbonatation experiments. A number of saturator liquor samples (pH ± 9,5) with lactic acid added (150 to 1 500 ppm on brix) were carbonatated with flue gas at 65°C to a pH of 8,0. The carbonatated liquor was filtered and the calcium content of the filtrate measured.

The stoichiometric relationship between calcium carbonate and lactic acid is:



$\text{C}_3\text{H}_5\text{O}_3$  mol. wt. = 90,1 and Ca mol. wt. = 40,1

Thus if the reaction is stoichiometric 100 parts of lactic acid will prevent 22,2 parts of calcium from precipitating during carbonatation.

**Table 3**  
Calcium held in solution as lactate

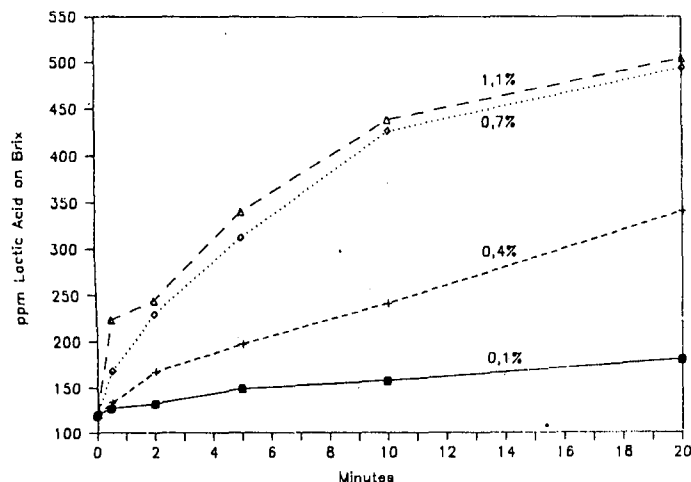
	ppm on Brix				
	150	300	452	741	1481
Lactic Acid added	150	300	452	741	1481
Base Calcium level	220	220	220	219	219
Calcium level after carb.	260	297	335	385	537
Measured Calcium increase	40	77	115	166	318
Predicted Calcium increase	34	68	102	164	329

The results in Table 3 show that the additional amount of calcium over the base level held in solution corresponds stoichiometrically to the added lactic acid. Thus the quantity of calcium kept in solution can be estimated using equation (1) as can the ash gain due to the presence of lactic acid.

**Lactic Acid Formation**

The laboratory trials involved heating saturator supply liquor to the required temperature in a water bath, adding lime slurry and withdrawing and rapidly cooling samples at various time intervals. Lactic acid content, using the gas chromatographic technique was determined on all samples. Reducing sugars using the Luff School method were determined on some of the samples. Standard conditions were taken to be those currently in use at Hulett Refinery i.e. temperature : 80°C, lime % brix : 0,7. Trials were conducted to determine the effect of the following variables:

- Retention time
- Lime % brix range 0,1% to 1,1%

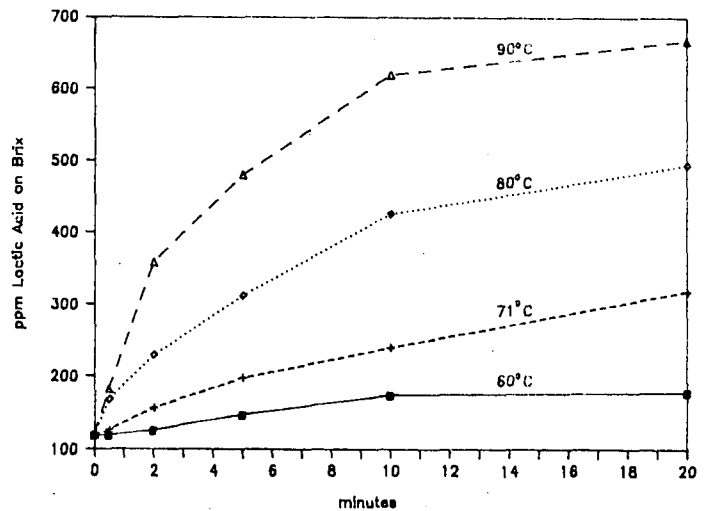


**FIGURE 4** The effect of lime % brix on lactic acid formation.

- Temperature range 60°C to 90°C
- Initial reducing sugar concentration range 0,1% to 0,5% on brix (solutions were prepared using VHP sugar to which a mixture of equal amounts of glucose and fructose was added).

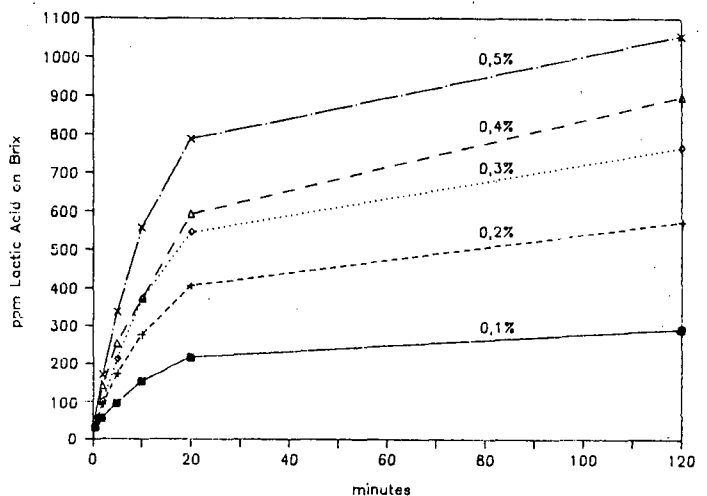
The effect of the quantity of lime added to the saturator supply liquor at 80°C and 0,1% RS on brix is shown in Figure 4. Formation of lactic acid increases with increasing lime % brix. A sharp increase is noted between 0,4 and 0,7% lime on brix but above 0,7% lactic acid formation appears to increase only slightly.

Figure 5 shows the effect of temperature on lactic acid formation at 0,7% lime on brix and 0,1% RS on brix. Lactic acid formation is very temperature dependent and the rate of formation increases rapidly above 70°C.



**FIGURE 5** The effect of temperature on lactic acid formation.

The final variable to be evaluated for its effect on lactic acid formation was the initial reducing sugars concentration at standard conditions (Figure 6).



**FIGURE 6** The effect of reducing sugars level on lactic acid formation.

**Kinetic Evaluation**

For kinetic evaluation, the degradation of reducing sugars in alkaline medium to form lactic acid was assumed to follow first order reaction kinetics. The rate equation for first order reaction is:

$$x = A_0 (1 - e^{-kt}) \quad (2)$$

which can be written as

$$\ln(A_0 - x) = -kt + \ln(A_0) \quad (3)$$

where k = rate constant

A<sub>0</sub> = initial concentration of reactant (assumed to be equivalent to the maximum concentration of lactic acid formed)

x = the concentration of lactic acid formed in time t

Therefore a plot of ln (A<sub>0</sub> - x) versus t should be linear with a slope equal to -k.

The results of the first three runs to determine the effect of temperature on k are shown in Table 4, and the four runs to determine the pH effect of lime % brix on k in Table 5. (Data obtained at 60°C were excluded since a correlation coefficient of only 0,77 was obtained).

**Table 4**  
Kinetic data for the effect of temperature

Temp °C	k/(min)	Intercept	Corr. coeff.
71	0,0281	6,0450	0,998
80	0,0906	5,9312	0,984
90	0,3262	6,7346	0,982

**Table 5**  
Kinetic data for the effect of lime % brix

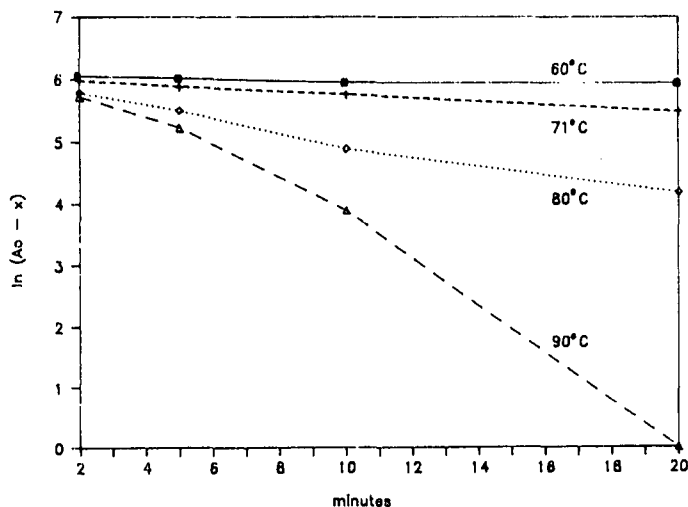
lime % brix	k/(min)	Intercept	Corr. coeff.
0,1	0,0063	6,0591	0,968
0,4	0,0325	6,0545	0,991
0,7	0,0906	5,9312	0,984
1,1	0,0960	5,8745	0,987

Correlation coefficients obtained in Tables 4 and 5 suggest that the formation of lactic acid does follow first order kinetics. These correlations are shown graphically in Figures 7 and 8.

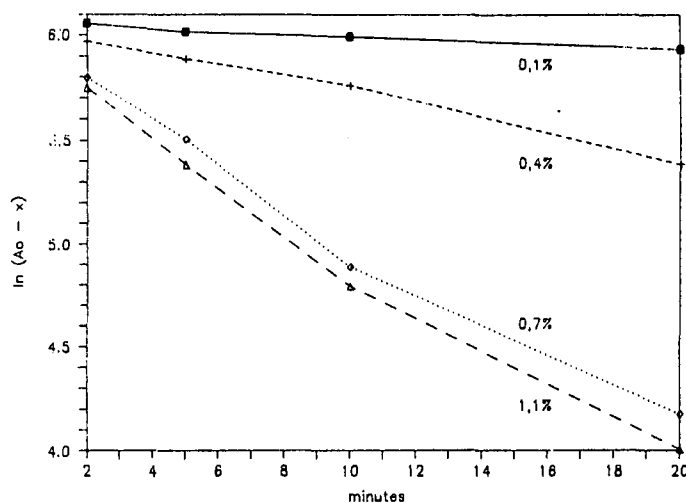
The combined effects of temperature and lime % brix on k were determined using the 1st order rate equation and the Arrhenius equation and subjecting the data in Tables 4 and 5 to multilinear regression analysis. The following equation was obtained.

$$\log k = 15,15 + 0,479 \log (\text{lime \% brix}) - \frac{5655}{T+273} \quad (4)$$

with a correlation coefficient of 0,956.



**FIGURE 7** The effect of temperature on the rate constant.



**FIGURE 8** The effect of lime % brix on the rate constant.

The above equation is similar to the equation obtained for the decomposition rate constant of hexoses by De Bruijn *et al.*<sup>1</sup>.

$$\log k = 16,9 - \text{pOH} - \frac{5620}{T+273} \quad (5)$$

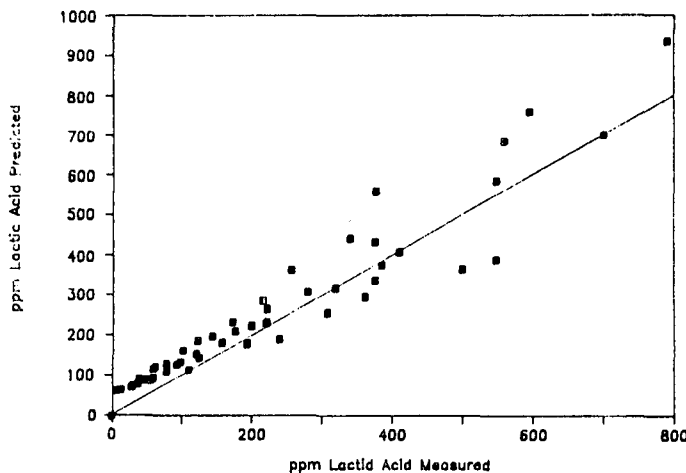
The results of the final five runs to determine the effect of initial reducing sugars concentration on amount of lactic acid formed are shown in Table 6.

**Table 6**  
Kinetic data for the effect of initial reducing sugars level

Initial % R/S	k/(min)	Intercept	Corr. coeff.
0,1	0,0642	5,5928	0,999
0,2	0,0604	6,3043	0,999
0,3	0,0619	6,6171	0,999
0,4	0,0516	6,7553	0,995
0,5	0,0672	6,9208	0,998

The results in Table 6 show that the rate constant k for the reaction of lactic acid formation is not dependent on the initial reducing sugar concentration. The amount of lactic acid formed however, increases with increasing initial reducing sugar concentration.

To obtain a model equation to predict the amount of lactic acid formed the original form of the 1st order rate reaction was used.



**FIGURE 9** Measured versus predicted lactic acid formation.

$$x = A_o (1 - e^{-kx}) \quad (6)$$

The initial reducing sugar concentration was incorporated into the equation as follows:

$$A_o = a * (\% RS) \text{ where } a \text{ is a constant} \quad (7)$$

$$x = a * (\% RS)(1 - e^{-kx})$$

Linear regression analysis was conducted on experimental data obtained for x and % RS (1-e<sup>-kx</sup>). The following equation was obtained.

$$x = 57,75 + 2090(\% RS)(1 - e^{-kx}) \quad r = 0,984$$

Figure 9 shows a correlation between measured values obtained for all laboratory trials and predicted values using derived equations.

### Operating Results

#### Discussion

Having established that lactic acid was being formed during liming and after implementing the recommended plant operating conditions for improvement, routine weekly analysis of lactic acid in saturator supply and A saturator was started. The concentration of lactic acid formed during liming was calculated and this is shown as weekly averages in Figure 10.

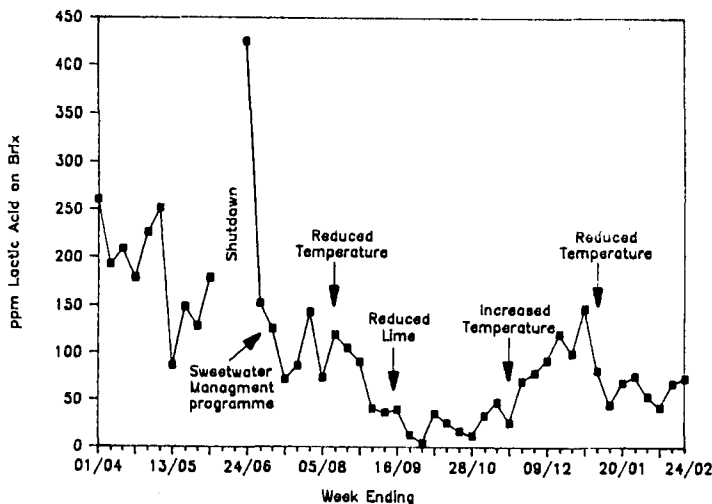


FIGURE 10 Lactic acid increase from sat supply to A saturator.

Figure 10 shows the high levels of lactic acid formation early in the season, followed by a steady decline as the various measures to reduce formation were put into force. The effect of microbial action can be seen in the very high levels for the first week after the two week shutdown. It was necessary to increase temperatures in December to overcome filtration problems, which was a retrograde step in terms of lowering lactic acid levels. This was corrected in January by

Table 7  
Period average data for the 1989/90 season

Period	Ash gain %	Lactic acid gain ppm.bx	Lactic acid A Sat ppm.bx	Brown Liquor pH
Wks 52-04	39,8	214	378	8,14
Wks 05-09	39,3	160	375	8,00
Wks 12-18	28,5	155	278	8,39
Wks 19-22	30,1	90	170	8,18
Wks 23-26	17,2	24	127	8,23
Wks 27-30	20,9	23	149	8,25
Wks 31-39	15,5	80	232	8,51
Wks 40-43	13,4	68	177	8,38
Wks 44-47	19,8	60	151	8,23

reducing the liming temperature again and introducing heating in A saturator by means of steam injection.

#### Statistical Analysis

The ash gain figures determined by the refinery after every stocktake (usually each month but sometimes longer) were compared with the lactic acid formation during liming and total lactic acid in A Sat for the same periods. The brown liquor pH was also included as it is well known that it can have a considerable effect on the solubility of calcium salts. These data are set out in Table 7.

Linear regressions were done between all the variables in Table 7 (9 data points) and a correlation matrix drawn up.

	Ash Gain	LA Gain	A Sat LA	Br Liq pH
Ash Gain	1	0,84	0,81	-0,72
LA Gain		1	0,96	-0,31
A Sat LA			1	-0,37
Br Liq pH				1

The ash gain is well correlated (99% confidence) with the lactic acid gain across carbonatation and the lactic acid level in A Sat and correlated (95% confidence) with the brown liquor pH. There is strong intercorrelation between the lactic acid gain and the lactic acid in A Sat as expected, whereas the brown liquor pH is independent of the other variables.

Although the lactic acid gain gives slightly better correlations with the ash gain, in theory, the A saturator lactic acid level should be the better variable to use. A multilinear regression using both the A saturator lactic acid concentration and the Brown Liquor pH gave the following predictive formula.

$$\% \text{ Ash Gain} = 0,0653(\text{A Sat LA}) - 32,3(\text{BL pH}) + 276 \quad r = 0,93 \quad (8)$$

$$\text{A Sat LA coefficient } t \text{ value} = 4,0$$

$$\text{BL pH coefficient } t \text{ value} = 3,1$$

i.e. both terms are significant at 99% confidence level.

The result of plotting the predicted ash gains derived by using the relationship above and the measured refinery ash gains from Table 7 is shown in Figure 11.

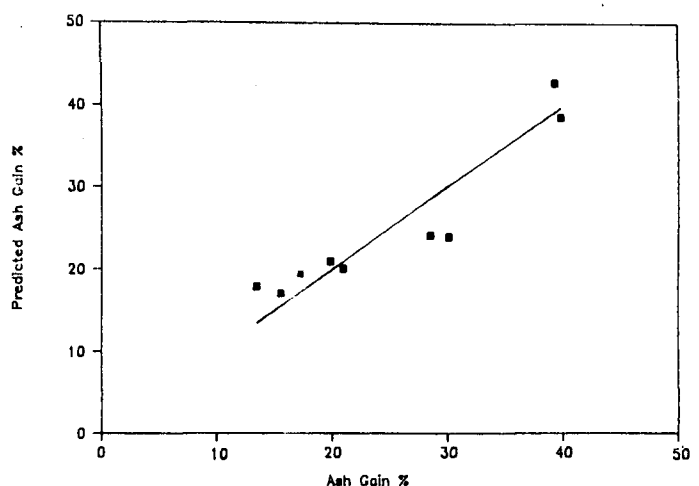


FIGURE 11 Actual versus predicted ash gain.

### Conclusions

Two areas have been identified as major sources of lactic acid in the refining process. Firstly a large increase occurs between the raw sugar melt and the saturator supply liquor, which is due to high levels of lactic acid of microbial origin in the sweetwater tank. Secondly an even larger increase occurs between the saturator supply liquor and brown liquor which is due to chemical degradation of reducing sugars in the liming tank.

Laboratory trials showed that the alkaline degradation of reducing sugars to form lactic acid appears to follow first order reaction kinetics. The amount of lactic acid formed is dependent on retention time, temperature, lime % brix and initial reducing sugar concentration. An increase in one or more of the above variables causes an increase in lactic acid content or formation rate of lactic acid.

A model equation has been derived from the kinetic evaluation of the results. This model can be used to relate retention time, temperature, lime % brix and initial reducing sugar concentration to the amount of lactic acid formed. Although some scatter is noted in Figure 9 there is still good agreement between measured and predicted lactic acid values.

Bench scale carbonatation trials have demonstrated that lactic acid and calcium ions react stoichiometrically and that every 100 parts of lactic acid present allow 22 parts of calcium to pass through carbonatation and ultimately end up in the molasses.

The temperature of liming has been reduced from  $> 80^{\circ}\text{C}$  to  $\pm 75^{\circ}\text{C}$  and the lime addition from  $> 0,7\%$  to between  $0,5$  and  $0,6\%$  on brix. Implementation of these modifications

to the process indicated by the model have resulted in a considerable reduction in the amount of lactic acid being formed by chemical degradation. A corresponding reduction in the refinery ash gain from average figures of  $+40\%$  down to  $+15\%$  has been measured over the same period.

Further improvements still remain to be made in the area of microbiological destruction of sugars and consequent formation of lactic acid. This is giving a base level of 100 ppm lactic acid on brix and has been unaffected by the process modifications made to liming.

### Acknowledgements

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### REFERENCES

1. De Bruijn, JM, Kieboom, APG and van Bekkum, H (1986). *Sugar Technology Reviews* No 13: 21-52.
2. Honig, P (1963). *Principles of Sugar Technology* Volume III: Elsevier, Amsterdam, 472-477.
3. Lyle, O (1957). *Technology for Sugar Refinery Workers* 3rd Edition: Chapman & Hall, London, 346-349.
4. Meade, G and Chen, J (1977). *Cane Sugar Handbook* 10th Edition: John Wiley & Sons, New York, 402.