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COMBINED CARBONATATION AND SULPHITATION IN CANE SUGAR REFINING

by

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DISSertation
submitted in compliance with the requirements for the
MASTERS DIPLOMA IN TECHNOLOGY
in the department of
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at the
TECHNIKON WITWATERSRAND

Supervisor : Dr K Richter
Co-supervisor : Mr MGS Cox

November 1992
I hereby declare that the dissertation which I submit herewith for the Master's Diploma in Technology to the Technikon Witwatersrand, apart from recognized assistance, is my own work and has not previously been submitted by me to another institution to obtain a degree or higher degree.

Bryan Peter Lavarack
ACKNOWLEDGMENTS

I wish to place on record my sincere thanks to:

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Messrs Jaap Besijn, Fred Cronje and Paul Kirkirides and staff in the Process Department.

My parents for boarding me during my sojourns from Johannesburg and for being such exemplary parents.

My dearest wife, Mandy, without whose love and support this would not have been possible.
SYNOPSIS

Laboratory and pilot plant trials were carried out on a modified carbonatation process to reduce overall refining costs. Sulphur dioxide dosages of less than 250ppm on brix were added to carbonatated liquors. The resultant filtered liquor had an additional 4.6% colour removal and a 10% ash gain relative to factory liquors. Reducing sugars and filterability were not affected. Additional colour removal of 14% was noted in the affinated crystal colour of crystals grown from the resultant brown liquors in the SMRI pilot pan. The failure of the combined carbonatation - sulphitation process to remove the ash that the carbonatation process does, negates the cost benefits of the additional colour removals. The reason for the ash "gain" is that the sulphur dioxide partially dissolves the calcium carbonate, releasing the adsorbed ash and colour. The colour is then adsorbed onto the calcium sulphite.
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1. INTRODUCTION

1.1 THE ROSSBURGH REFINERY

Hulett Refineries at Rossburgh in Durban presently processes 650 000 tons of raw sugar per year. The raw sugar is termed very high Pol (abbreviated VHP). The Pol is the percentage ratio of sucrose to total soluble solids and the specification for VHP is 99.3 degree Z minimum.

The raw sugars are melted (dissolved) and refined in three processes - carbonatation, resin decolourisation and crystallisation.

In the first process, milk of lime (calcium hydroxide) is added to the melted liquors and is saturated with scrubbed flue gases to form a calcium carbonate precipitate. The saturation takes place in three stages. The precipitate, or mud, is filtered off and the filtered liquor is called brown liquor. The carbonatation process removes both ash and colour impurities.

In the second process, the brown liquor is passed through two sets of resin beds. The resin absorbs colour bodies onto the surface and is regenerated once a day with brine and caustic soda. After twenty such regenerations, or cycles, the beds are acid washed. The liquor is called primary liquor after
passing through the first set of resin vessels and secondary liquor after the second set. The secondary liquor is concentrated via double effect evaporators. The concentrated liquor is called fine liquor.

The last refining stage is the crystallisation process wherein sugar crystals are grown from the mother liquor to the correct size, in what is known as a first boiling. The sugar crystals are separated from the syrup in centrifuges, dried in rotary driers and sent for packaging. More refined sugar can be crystallised from the centrifuged syrups in further boilings. Normally four boilings can be achieved before the refined sugar colour specification is exceeded.

The remaining syrup, or molasses, is sent to the recovery house, where the crystallisable sugar is recovered in further boilings. When no more crystallisable sugar can be economically extracted, the molasses is called exhaust molasses. Some of the lower grade sugars are dried and sold depending on market requirements. The rest is remelted (redissolved) and recycled to the main melter.

1.2 PROJECT BACKGROUND

Hulett Refineries is continuously looking into reducing the costs of refining sugar. The second refining stage, namely resin decolourisation has high refining costs. The raw
material costs for resin decolourisation amounts to RO.84 per ton raw sugar for 100 units colour removal, while that for carbonatation is RO.38 per ton raw sugar for 100 units colour removal. (Refer Appendix F)

From the recent work of the Sugar Milling Research Institute, Lionnet\(^{10}\) has suggested that the need for decolourisation by resin could be reduced by 50% if the liquor is sulphited. The sulphitation level recommended is that currently used in industry, namely approximately 150 parts per million of sulphur dioxide.

The costs involved in designing, erecting, commissioning and operating a new sulphitation station have ruled out this possibility\(^{14}\). However by combining the sulphitation process with the carbonatation process, duplication of plant and equipment could be avoided. That is, additional lime can be added via the lime wheel and sulphur dioxide introduced in the saturator vessels and the resultant calcium sulphite precipitate removed via the existing filters.

1.3 PROJECT OBJECTIVE

The primary objective of the project is to develop a combined carbonatation-sulphitation process to reduce overall refining costs.
Savings in costs could be effected through reduced loadings on the resin plant or through fewer reject refined sugar boilings. Also, modifications to existing plant and equipment should be minimal to save on costs.

Arising from the primary objective are various factors that require investigation.

Firstly, the effect of carbonatation - sulphitation be determined on colour removal, pH, ash removal, filterability and reducing sugars. This should be compared to carbonatated liquors. The sulphitation dosages should be less than 250 parts per million on brix.

Secondly, the colour transfers, as reported by Lionnet\(^9\), be verified. That is to show that the colour of the crystals grown from the carbonatated-sulphited liquors is less than those grown from carbonatated liquors.

Thirdly, that the cost benefits of the carbonatation - sulphitation are calculated.

The sulphitation can take place at various stages in the carbonatation process. Since the dosage is light, it would be desirable to dose at the end of the process when most of the refining work has been done by carbonatation. That is the sulphitation will remove colour bodies difficult to remove in
carbonatation. If sulphitation were done before the main carbonatation, it would be less effective.

The project was undertaken in three stages, namely a literature survey, laboratory tests and pilot plant trials.
2. LITERATURE SURVEY

Thirty years of Tate and Lyle's sugar industry abstracts were reviewed at the Sugar Technology Department's library of Tongaat Hulett Sugar. The only traceable paper linking sulphitation and carbonatation is Reference 4, namely, the Sulphi-Carbonation process by Dubey and Mavi. The paper presents laboratory results in which cane juice is limed and sulphited before liming and first carbonatation. The objective being to cut down lime consumption in the carbonatation process. The paper has no direct relevance to the project.

The carbonatation and sulphitation processes are well documented in the literature.
3. EXPERIMENTAL

3.1 INITIAL LABORATORY TESTS

Initial tests involved the laboratory carbonatation and sulphitation of raw sugar solutions and of factory main melt samples. The laboratory procedure is described in Appendix A.

The repeatability of the laboratory scale carbonatation was open to question, in that the lime preparation and addition procedure are subject to error.

3.2 LABORATORY TESTS ON FACTORY CARBONATATED LIQUORS

By using partially carbonatated liquors, it is possible to eliminate potential sources of error made in the laboratory carbonatation.

B saturator liquor (the feed to C saturator) was selected. Catch samples were split into three subsamples. The first subsample was gassed out with 10 percent carbon dioxide and filtered. That is, the carbonatation was completed on the saturator liquor and a laboratory brown liquor prepared. The second subsample was reacted with 200 parts per million sulphur dioxide on brix and filtered to yield a sulphited brown liquor. The third subsample was subjected to 500 parts per million sulphur dioxide on brix and filtered. A similiar
experimental trial was done on A saturator liquor with dosages up to 2 000 parts per million sulphur dioxide on brix. The method is outlined in Appendix A.

3.3 CSTR PILOT PLANT TRIALS ON CARBONATATED LIQUORS

In order to simulate process conditions, the pilot plant saturator was designed as a continuously stirred tank reactor (CSTR). Lines from A saturator and B saturator fed a tun dish which continuously discharged into the 30 litre volume saturator. The excess flows to the tun dish were returned to the process. The 30 litre volume was maintained by a goose neck on the drain pipe from the bottom of the vessel. The residence time was 10 minutes to simulate conditions in C saturator.

Figure 1 Pilot Plant Saturator configured as a CSTR
Although the pilot plant saturator ran for periods up to an hour, difficulty was found with the blocking of lines on the extended runs. The main problem was the drain line, although the feed lines were troublesome.

The sulphur dioxide was added via a rotameter which initially worked well. However the gas rapidly absorbs water, with the result that when the system was off line, the stainless steel ball in the rotameter fouled. This made the results totally unreliable.

A more dependable dosage method was sought. A small weighable stainless steel bomb was procured. The bomb was filled with sulphur dioxide and the dosage determined by weighing. A trial was done using the saturator as a batch reactor rather than as a continuous one. The advantages were namely: no blockages, better sampling and the sulphur dioxide dosage rate would not be as critical.

3.4 BATCH PILOT PLANT TRIALS ON CARBONATATED LIQUORS

Samples from the B saturators were taken at five minute intervals over a period of ninety minutes and placed in the pilot saturator. The composited sample was tested for pH and brix before sulphitation.

C saturator was similarly sampled, except the sampling was
delayed by 10 minutes to allow for the C saturator residence time.

Both the C saturator sample and the sulphited B saturator sample were filtered on a Macsalab filter. The resultant brown liquors were termed non-sulphited brown liquor and sulphited brown liquor respectively.

The experimental method is detailed in Appendix D.

Filterability tests were done on the C saturator and sulphited B saturator liquors.

ICUMSA colours, conductivity ash, pH and later sulphated ash and reducing sugars were analysed on the brown liquors.

Boiling tests were performed at the SMRI wherein sugar crystals were grown from the brown liquors. The sugar crystals were centrifuged, mingled with low colour syrup (affinated) and centrifuged again. The ICUMSA colours of the brown liquor feed and the affinated sugar crystals were determined.
4. RESULTS AND DISCUSSION OF LABORATORY TESTS

4.1 LABORATORY TEST RESULTS

The initial laboratory results are tabulated in Appendix B and the results of the laboratory tests on factory carbonated liquors appears in Appendix C.

4.2 DISCUSSION OF INITIAL LABORATORY TESTS

The initial tests investigated the colour and ash removal effects of pure carbonation, pure sulphitation and a combination of the two. The tests were done on laboratory prepared raw sugar solutions and later on factory main melt samples. The initial results should only be used as a guide, since the lime preparation and addition procedure is subject to error.

Table 1  Colour removal for laboratory carbonation tests on raw sugar and main melt catch samples

<table>
<thead>
<tr>
<th>Catch Sample</th>
<th>% CaO on brix</th>
<th>Sample colour</th>
<th>Brown liquor colour</th>
<th>% Colour Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Sugar</td>
<td>0.6%</td>
<td>1337</td>
<td>720</td>
<td>46.1%</td>
</tr>
<tr>
<td>Raw Sugar</td>
<td>0.6%</td>
<td>1363</td>
<td>727</td>
<td>46.7%</td>
</tr>
<tr>
<td>Raw Sugar</td>
<td>0.6%</td>
<td>1502</td>
<td>803</td>
<td>46.5%</td>
</tr>
<tr>
<td>Main Melt</td>
<td>0.6%</td>
<td>1255</td>
<td>644</td>
<td>48.7%</td>
</tr>
</tbody>
</table>
Table 2  Colour removal for Hulett Refineries’ carbonatation station during 91/92 season

<table>
<thead>
<tr>
<th>Process Stream</th>
<th>% CaO on brix</th>
<th>Stream colour</th>
<th>Brown liquor colour</th>
<th>% Colour removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Sugar</td>
<td>0.6%</td>
<td>1315</td>
<td>763</td>
<td>42.0%</td>
</tr>
<tr>
<td>Main Melt</td>
<td>0.6%</td>
<td>1294</td>
<td>763</td>
<td>41.0%</td>
</tr>
</tbody>
</table>

* % CaO on melt was 0.68% for 91/92 season. Assuming a remelt of 10%, % CaO on brix is (0.68/1.1) or 0.6%

The colour removals for the laboratory scale carbonatation were better than the plant figures; approximately 46% versus approximately 41% respectively. Several factors could explain this. Firstly, analytical error in colour analysis. Secondly, errors in the lime preparation procedure. Thirdly, longer residence times (2 hours for laboratory versus 1 hour for factory). Lastly, the factory figures could be misleading.

There were significant recycles to the main melter of A saturator liquor via the oversized sampling lines and of cloudy brown liquor from the filters. This is shown by the colour removal on melting (91/92 season averages of 1315 and 1294 ICUMSA units for raw sugar and main melt respectively).

The colour removals for the laboratory scale sulphitation were ambivalent. A 4.3% removal and a 12.8% gain were reported. Refer tables 10 and 13 in Appendix B.
The combined laboratory carbonatation-sulphitation showed an approximate 2% extra colour removal than pure carbonatation. See tables 11 and 14 in Appendix B.

The conductivity ash removals varied widely in these laboratory tests. One sulphitation test showed a slight ash removal, three had no change while the rest exhibited ash gains. Refer to tables 10, 11, 13 and 14 in Appendix B.

During the laboratory carbonatation it was found necessary to maintain the pH below 9.6 to avoid excessive foaming. Frankland has observed the foaming of carbonatated liquors at high pH. The reason for the foaming is unclear.

4.3 DISCUSSION OF LABORATORY SULPHITATIONS OF CARBONATATED LIQUORS

In order to eliminate the laboratory carbonatation step and simulate plant conditions, factory carbonatated samples were subjected to low sulphitations. The test results are in Table 15, Appendix C.

The extra colour removed, through low sulphitation, is higher than the previous tests indicated. There would appear to be a relationship between pH and colour removal. The B sat 91/09/05 run indicates that sulphitation of liquor at pH 8.2 gives no extra colour removal.
Excessive sulphitation (2 000ppm on an A saturator liquor) can be detrimental to colour removal, in that the 2 000ppm sulphur dioxide had an additional 0.2% colour removal, yet the 1 000ppm had the highest additional colour removal of 8.7% for the respective trial. The reason for this is discussed in 5.10 below.

The picture as regards ash removals for the combined technique is not clear. One run exhibited a removal of 4%, another three showed no change and the rest had ash gains relative to pure carbonatation. Analytical error can in part explain the discrepancies. For example, a 4% ash removal is equivalent to a difference in ash content of 0.01%.
5. RESULTS AND DISCUSSION OF PILOT PLANT TRIALS

5.1 BATCH VERSUS CONTINUOUS SATURATOR

Ideally the continuous saturator would have been the better of the two types as it closely simulates the plant. The design proved impractical in that the drain line blocked, resulting in the saturator overflowing. The feed lines also blocked on several occasions. Sulphur dioxide dosage rates had to be strictly controlled to the continuous saturator in order to prevent under- or overdosing.

5.2 REJECTION OF PRELIMINARY RUN RESULT

A preliminary test run was done on the batch reactor during which the stirrer kept tripping. There was a gain in the colour of the sulphited brown liquor of over 7% (886 versus 823). The filterability of the carbonatated-sulphited liquor was noticeably less than the C saturator liquor (33 versus 38). The pH's of the liquors were all above 9.

The most likely explanation for this is that during the periods of no mixing, highly localised sulphur dioxide concentrations of low pH caused the destruction of calcium carbonate and release of adsorbed colour molecules. The loss of calcium carbonate filter aid and the released colour bodies negatively influenced filterability. See 5.10 below.
5.3 COLOUR REMOVAL

Pure sulphitation in the order of 4 000ppm yields colour removals of approximately 40 percent\(^1\). Assuming a linear relationship, 200ppm should yield approximately 2% colour removal. Noodsberg refinery has shown colour removals of 10% to 15% for low sulphur dioxide dosages\(^3\). The test average of 4.6% falls between the Noodsberg and linear relation figures.

Table 3  Additional ICUMSA colour removed for low sulphur dioxide dosages on saturator liquor samples

<table>
<thead>
<tr>
<th>Trial run &amp; sulphur dioxide dosage</th>
<th>Non-sulphited brown liquor colour</th>
<th>Sulphited brown liquor colour</th>
<th>Additional colour removed</th>
<th>% Additional colour removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 170ppm</td>
<td>762</td>
<td>729</td>
<td>33</td>
<td>4.3%</td>
</tr>
<tr>
<td>2 230ppm</td>
<td>953</td>
<td>884</td>
<td>69</td>
<td>7.2%</td>
</tr>
<tr>
<td>3 210ppm</td>
<td>851</td>
<td>803</td>
<td>48</td>
<td>5.6%</td>
</tr>
<tr>
<td>4 240ppm</td>
<td>834</td>
<td>826</td>
<td>8</td>
<td>1.0%</td>
</tr>
<tr>
<td>5 210ppm</td>
<td>870</td>
<td>814</td>
<td>56</td>
<td>6.4%</td>
</tr>
<tr>
<td>6 120ppm</td>
<td>944</td>
<td>925</td>
<td>19</td>
<td>2.0%</td>
</tr>
<tr>
<td>7 140ppm</td>
<td>1032</td>
<td>969</td>
<td>63</td>
<td>6.1%</td>
</tr>
<tr>
<td>8 150ppm</td>
<td>885</td>
<td>852</td>
<td>33</td>
<td>3.7%</td>
</tr>
<tr>
<td>Av.180ppm</td>
<td>891</td>
<td>850</td>
<td>41</td>
<td>4.6%</td>
</tr>
</tbody>
</table>

Average additional colour removed = 891-850 = 41 ICUMSA units or \((41/891) \times 100 = 4.6\%\)
5.4 COLOUR REMOVAL VERSUS SULPHUR DIOXIDE DOSAGE

For the limited number of trials, there is no correlation between colour removal and sulphur dioxide dosage. The correlation coefficient $r$ is 0.183.

Run 4 has the highest dosage, yet the lowest colour removal, and Run 7 has a low dosage and a high colour removal. If these data points are excluded the correlation coefficient $r$ is 0.987! Further experimental work would be necessary to confirm a correlation between colour removal and dosage. Refer to graph in Appendix E.

5.5 COLOUR TRANSFERS

Colour transfer is the ratio of the affinated sugar crystal colour to the feed liquor colour. The concept is more complex than simple ratios since the ratio implies that the linear plot of affinated crystal colour to liquor colour should pass through the origin. This rarely happens$^{10}$ (equations 1, 2 and 3). Since eight data points are insufficient for a plot, the simple ratios will have to suffice.

The correlation coefficient is 0.661 for the non-sulphited brown liquor transfer plots and 0.434 for the sulphited brown liquor transfer plots. Lionnet$^9$ recommends a minimum of twenty points for a plot.
Table 4  Colour comparisons of non - sulphited and sulphited brown liquor samples and their affinated crystals

<table>
<thead>
<tr>
<th>Trial run &amp; sulphur dioxide dosage</th>
<th>Non-sulphited</th>
<th></th>
<th></th>
<th></th>
<th>Sulphited</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brown liquor colour</td>
<td>Affi- nated crystal</td>
<td>Colour transfer</td>
<td>Brown liquor colour</td>
<td>Affi- nated crystal</td>
<td>Colour transfer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 170ppm</td>
<td>762</td>
<td>25</td>
<td>0,033</td>
<td>729</td>
<td>25</td>
<td>0,034</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 230ppm</td>
<td>953</td>
<td>27</td>
<td>0,028</td>
<td>884</td>
<td>24</td>
<td>0,027</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 210ppm</td>
<td>851</td>
<td>24</td>
<td>0,028</td>
<td>803</td>
<td>19</td>
<td>0,024</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 240ppm</td>
<td>834</td>
<td>23</td>
<td>0,028</td>
<td>826</td>
<td>20</td>
<td>0,024</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 210ppm</td>
<td>870</td>
<td>28</td>
<td>0,032</td>
<td>814</td>
<td>24</td>
<td>0,029</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 120ppm</td>
<td>944</td>
<td>31</td>
<td>0,033</td>
<td>925</td>
<td>26</td>
<td>0,028</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 140ppm</td>
<td>1032</td>
<td>32</td>
<td>0,031</td>
<td>969</td>
<td>26</td>
<td>0,027</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 150ppm</td>
<td>885</td>
<td>33</td>
<td>0,037</td>
<td>852</td>
<td>24</td>
<td>0,028</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Av.180ppm</td>
<td>891</td>
<td>28</td>
<td>0,031</td>
<td>850</td>
<td>24</td>
<td>0,028</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sulphitation dosages of less than 250ppm combined with carbonatation have a noted effect in reducing colour transfer from the mother liquor to the crystal. The average colour transfer is 0.028 for the sulphited compared with 0.031 for the non - sulphited. That is the average colour of the affinated crystal grown from the sulphited liquor is 4 colour units less or 14% less than that of the non - sulphited.

Honig states "There is a favourable influence of the
sulphurous acid on the coloured matters and the action of the acid prevents or slows down colour formation in later stages viz. evaporation and crystallisation. This action is attributed to the reducing properties of sulphurous acid."

Zerblan\(^7\) explains that "The sulphur dioxide combines with the reducing sugars and blocks carbonyl function, which is essential for caramel and melanoidin formation. Bleached juices, exposed to air, darken at the contact surface."

Clearly the combined carbonatation-sulphitation has an effect due to the sulphur dioxide which is greater than the additional colour removal of 4.6% of the colour of the brown liquor.

In order to obtain a preliminary cost estimate a figure of 14% additional colour removal is suggested in place of 4.6%, as the figure accounts for the improvement in refining during crystallisation. (The figure is only preliminary as it would require more data points and tests with resin to yield an accurate one. As stated above the concept is more complex than simple ratios). Refer to 5.9 below.

Caution should be exercised when comparing colour transfers since it is known that these values vary throughout the season\(^9\) and the plots need not pass through the origin.
Consequently incorrect conclusions may be drawn. Lionnet\textsuperscript{10} notes that "The real transfer for the sulphitation treatment is about 15\% lower than that found for the original liquor boilings". The preliminary figure of 14\% calculated above verifies Lionnet's findings. Although these figures tie in closely there are significant rounding errors in the preliminary figure.

5.6 FILTERABILITY OF CARBONATATED - SULPHITED LIQUORS

Table 5 Filterability indices of C saturator liquor and corresponding sulphited saturator liquor samples

<table>
<thead>
<tr>
<th>Trial run and sulphur dioxide dosage</th>
<th>C saturator liquor filterability</th>
<th>Sulphited saturator liquor filterability</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 170ppm</td>
<td>80</td>
<td>77</td>
</tr>
<tr>
<td>2 230ppm</td>
<td>46</td>
<td>47</td>
</tr>
<tr>
<td>3 210ppm</td>
<td>97</td>
<td>98</td>
</tr>
<tr>
<td>4 240ppm</td>
<td>71</td>
<td>74</td>
</tr>
<tr>
<td>5 210ppm</td>
<td>81</td>
<td>74</td>
</tr>
<tr>
<td>6 120ppm</td>
<td>80</td>
<td>75</td>
</tr>
<tr>
<td>7 140ppm</td>
<td>63</td>
<td>60</td>
</tr>
<tr>
<td>8 150ppm</td>
<td>86</td>
<td>82</td>
</tr>
<tr>
<td>Av. 180ppm</td>
<td>76</td>
<td>74</td>
</tr>
</tbody>
</table>
Composite samples of C saturator liquor and sulphited saturator liquor were tested for filterability with the method outlined in Reference 8.

On average, the filterability index falls by 3% for sulphitation less than 250ppm on brix.

The low dosage sulphitation neither aids nor hinders filtration significantly.

5.7 ASH

Conductivity ash gains are observed for the low level sulphitations. On the last four runs, sulphated ash analyses were done in addition to the conductivity ash measurements. The results are presented in Table 6 overleaf.

All runs, without exception, noted an inability of the carbonatation-sulphitation process to remove the same quantity of ash that carbonatation does. This means in effect an ash "gain".

The sulphated ash determination confirmed the conductivity ash results. There was a possibility that the conductivity measurement would yield incorrect results because of the influence of the unreacted sulphur dioxide or pH effects.
Ash "gains" are not acceptable for production, as ash is regarded as molasses creating or melassigenic and would lower the overall refinery yield. Refer 5.9 below.

The reasons for the ash gains are discussed in 5.10 below.

Table 6  Ash gains for low sulphur dioxide dosages on saturator liquor samples

<table>
<thead>
<tr>
<th>Trial run and sulphur dioxide dosage</th>
<th>Non-sulphited brown liquor conductivity ash</th>
<th>Sulphited brown liquor conductivity ash</th>
<th>Non-sulphited brown liquor sulphated ash</th>
<th>Sulphited brown liquor sulphated ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 170 ppm</td>
<td>0.18</td>
<td>0.19</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2 230 ppm</td>
<td>0.24</td>
<td>0.27</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3 210 ppm</td>
<td>0.20</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4 240 ppm</td>
<td>0.21</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5 210 ppm</td>
<td>0.19</td>
<td>0.21</td>
<td>0.15</td>
<td>0.16</td>
</tr>
<tr>
<td>6 120 ppm</td>
<td>0.20</td>
<td>0.22</td>
<td>0.18</td>
<td>0.21</td>
</tr>
<tr>
<td>7 140 ppm</td>
<td>0.24</td>
<td>0.25</td>
<td>0.19</td>
<td>0.21</td>
</tr>
<tr>
<td>8 150 ppm</td>
<td>0.19</td>
<td>0.21</td>
<td>0.18</td>
<td>0.20</td>
</tr>
<tr>
<td>Av. 180 ppm</td>
<td>0.21</td>
<td>0.23</td>
<td>0.18**</td>
<td>0.20**</td>
</tr>
</tbody>
</table>

Average conductivity ash gain = 0.02 or 10% gain
Average** sulphated ash gain = 0.02 or 11% gain

** Average of runs 5, 6, 7 and 8.
5.8 REDUCING SUGARS

The reducing sugars were determined on the sulphited and non-sulphited brown liquors for four runs. There was no increase in the reducing sugar content for sulphur dioxide dosages less than 250ppm.

Table 7 Reducing sugar gains or losses for low sulphur dioxide dosages on saturator liquor samples

<table>
<thead>
<tr>
<th>Trial run and sulphur dioxide dosage</th>
<th>Non-sulphited brown liquor reducing sugars</th>
<th>Sulphited brown liquor reducing sugars</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 210ppm</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>6 120ppm</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>7 140ppm</td>
<td>0.24</td>
<td>0.25</td>
</tr>
<tr>
<td>8 150ppm</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td>Av. 160ppm</td>
<td>0.23</td>
<td>0.23</td>
</tr>
</tbody>
</table>

5.9 THE BOTTOM LINE

The aim of the project is to reduce overall refining costs. The costs are calculated in Appendix F and tabulated below:
Table 8  Raw material costs per ton raw sugar for 100 ICUMSA units colour removal for various refining processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Raw material cost per ton raw sugar for 100 units colour removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonatation during 91/92 season (not including carbon dioxide costs)</td>
<td>R 0.38 / t</td>
</tr>
<tr>
<td>Resin decolourisation during 91/92 season</td>
<td>R 0.84 / t</td>
</tr>
<tr>
<td>Carbonatation - sulphitation pilot plant trials (allowing for additional benefits in crystallisation)</td>
<td>R 0.79 / t</td>
</tr>
</tbody>
</table>

Possible savings in raw material refining costs for 47 units colour*** removed per ton raw sugar in a year is:

\[
= \{\text{Resin + Resin regeneration costs}\} - \{\text{Sulphitation costs}\}
\]

\[
= \{R \ 0.84/t \times (47/100) \times 650 \ 000t/yr\} - \{R \ 0.79/t \times (47/100) \times 650 \ 000t/yr\}
\]

\[
= R \ 257 \ 000/yr - R \ 241 \ 000/yr
\]

\[
= R \ 16 \ 000/yr
\]

*** 47 colour allows for 14% additional colour removal in crystallisation stage and is calculated in Appendix F.
However against this saving is the possible losses in yield through the ash gain. This yield is given by the Rendement formula:

\[ \text{Yield} = \text{Pol} - (4.5 \times \text{ash} - 1 \times \text{reducing sugars}) \]

Since there is an ash gain of 0.02%, the yield will decrease by 0.09%. In terms of production this is a loss of 585 t/yr (0.09% of 650 000 t/yr). In monetary terms, assuming a price of raw sugar of R1 200 /yr this amounts to a loss of R700 000 /yr.

Clearly the project is not feasible due to the inability of the carbonatation - sulphitation method to remove the ash the present carbonatation process does.

5.10 REASON FOR ASH GAIN

Ash as well as colour is adsorbed onto the surface of the calcium carbonate in the carbonatation process. The optimum filterability for carbonatation is known to occur at pH 8.2. For sulphitation a lower final pH is recommended. Honig and Thumann have noted plant figures of 6.8 to 7.0.

Mellor quotes the work of Rohrig in which calcium sulphite is prepared by passing sulphur dioxide into water containing suspended calcium carbonate. This suggests that any free sulphur dioxide will react with either calcium carbonate or
calcium hydroxide to form calcium sulphite.

At pH 8.2 most of the hydroxide has been converted to the carbonate and dosing with sulphur dioxide at such a level would result in the destruction of carbonate and release of colour and ash impurities. Above pH 8.2 dissolution of the carbonate is likely, but will be reduced by the reaction with the hydroxide. Sulfitation of any carbonatated liquor will result in the partial destruction of carbonate and release of impurities. The colour molecules are then adsorbed onto the calcium sulphite to a greater or lesser extent.

![Figure 2 Optimum pH for calcium carbonate and calcium sulphite precipitation](image)

Clearly, localised high concentrations of sulphur dioxide and sulfiting low pH saturator feed are detrimental to refining.

5.11 ALTERNATIVE PROCESS ROUTES

To avoid the destruction of calcium carbonate and its negative consequences of ash formation, four alternative
process routes are suggested for evaluation.

**FIRST ALTERNATIVE : DOSE SULPHUR DIOXIDE BEFORE CARBONATATION**

![Diagram](image)

**Figure 3** First alternative: sulphite before carbonation

Sulphur dioxide could be introduced into the line linking the lime wheel and A saturators. In-line mixers could ensure a fair degree of sulphitation before carbonation in the A saturators. This alternative was not considered in the project, since it would be more cost effective to lightly sulphitate once most of the carbonation refining work had been effected. That is, costly sulphur dioxide would be wasted removing colour which could be more cheaply removed by carbonation.
SECOND ALTERNATIVE: ADD LIME AND SULPHITATE IN B SATURATOR

This process would involve a lime take-off line to two dosing pumps which would supply lime to the B saturators. This should elevate the pH sufficiently to minimise the dissolution of the carbonate in the B saturators by the sulphur dioxide. The excess lime would be gassed out with carbon dioxide. This system would be relatively costly and may impose processing difficulties, since good pH control would be essential to prevent under- or overdosing of lime or sulphur dioxide. No automatic pH control system has been found to work reliably in the saturators at the refinery. The
dosing of small quantities of lime could be problematic due to blockages in the small diameter lines or at the point of introduction in the saturator vessels.

THIRD ALTERNATIVE: BY-PASS PART OF THE A SATURATOR FEED TO B SATURATOR AND SULPHITATE

\[ \text{MAIN MELTER} \rightarrow \text{LIME WHEEL} \]

\[ \text{A SATURATORS} \rightarrow \text{BY-PASS LINE} \]

\[ \text{SO}_2 \rightarrow \text{B SATURATORS} \]

\[ \rightarrow \text{C SATURATOR} \]

\[ \rightarrow \text{AUTOFILTERS} \]

Figure 5 Third alternative: By-pass part of the A saturator feed to B saturator and sulphitate

This is a modification of the second alternative, the difference being that the lime dosing is replaced by A saturator feed, which has by-passed the A saturators. The pH in B saturator would be raised by the unreacted lime. A
drawback would be the introduction of additional colour bodies directly into B saturator via the by-pass. Automatic pH control and by-pass flow control would be essential to ensure correct dosing. This alternative is costly and may pose operational difficulties.

FOURTH ALTERNATIVE: SEPARATE SULPHITATION STATION AFTER CARBONATATION

Figure 6 Fourth alternative: Separate sulphitation or Sulflotation station
This is the most costly alternative. The main advantages are that it incorporates known technology and could be used with good effect during periods when the raw sugar quality is poor or when manufacturing export sugar.

None of the four alternatives were evaluated as they were outside the scope of the project.
6. CONCLUSIONS

Colour removal for the combined carbonatation-sulphitation is pH dependant. Dosing below pH 8.2 is not recommended as it leads to colour formation. Other laboratory scale tests indicate that if the pH of the saturator liquor exceeds 9.6, serious foaming problems can arise in the saturator vessels.

On average, 180ppm sulphur dioxide dosage on brix removed an additional 40 ICUMSA units colour or 4.6% of the brown liquor colour. The average colours of the affinated sugar crystals boiled from the sulphited and non-sulphited brown liquors were 24 and 28 respectively. This is a reduction in colour of 4 ICUMSA units or 14% of the affinated crystal colour.

These observations corroborate the findings of other workers; that is the action of sulphur dioxide prevents or slows down colour formation during evaporation and crystallisation. Further experimental work would be necessary to confirm a correlation between sulphur dioxide dosage and additional colour removals.

Low dosage sulphitation has no significant effect on filtration.

Reducing sugars, on average, showed no gain for the carbonatation-sulphitation procedure.
All the pilot plant trials noted an inability of the carbonatation - sulphitation method to remove all the ash carbonatation does. The 10% relative higher ash contents would lower the refinery yield. Through the Rendement formula, a higher ash content of 0.02% results in a sugar loss of 587 tons per year. This loss outweighs any possible savings effected by the combined carbonatation - sulphitation procedure. The conductivity ash results were confirmed by sulphated ash analysis.

The ash "gain" occurs because the sulphur dioxide partially dissolves the calcium carbonate on which the ash was adsorbed. Colour bodies are similarly liberated from the carbonate, but are adsorbed onto the calcium sulphite.

Four alternative carbonatation - sulphitation processes are suggested.
7. REFERENCES

1. Bervoets A, Hulett Refineries 91/92 season statistics
3. Cox M, Private communication
8. Lavarack B, The determination of the filterability of carbonatated liquor, Tongaat Hulett Sugar Ltd R&D report 11/82
9. Lionnet G, Private communication
11. Mellor J, A comprehensive treatise on inorganic and theoretical chemistry Vol X S,Se, p282, Longmans
13. SASTA, Laboratory manual for SA sugar factories
14. Tayfield D, Private communication
16. Winterburn M, Private communication, AECI sales office New Germany
A. LABORATORY CARBONATATION AND SULPHITATION PROCEDURE

Apparatus:
- Carbon dioxide cylinder, regulator and flowmeter
- Air cylinder, regulator and flowmeter
- Sulphur dioxide cylinder, regulator and flowmeter
- Two Dreschel bottles, 1 litre volume and 3 porosity sintered glass bubbler
- Water bath at 80 degree C
- 50ml glass burette
- Soap solution
- Tubing
- pH meter and buffer solutions for calibration
- Filter bomb with water jacket
- Stop watch

Method:
1. Calibrate flow of air and carbon dioxide through Dreschel bottle containing 350g of liquor at 80 deg C. Use stop watch and time soap bubble moving up burette. Air and carbon dioxide flow rates should be set at 6.5ml/sec and 0.80ml/sec respectively.

2. Prepare a lime solution by measuring out the correct quantity of dried lime. Add a few ml water to hydrate lime.
(3) Measure the brix of the liquor and weigh off 350g liquor
(4) Add a few drops of lime to the Dreschel bottle and stir.
Immerse in water bath at 80 deg C and gas out with carbon dioxide/air. Continue adding lime.
(5) Periodically check pH of mixture to ensure it does not rise above 9.6 when foaming becomes noticeable.
(6) Start sulphitation when most of the lime has been consumed.
(7) Set flow of sulphur dioxide through the second Dreschel bottle containing water at 0.20ml / sec on rotameter.
(8) Transfer bubbler to first Dreschel bottle containing 350g liquor. Time sulphur dioxide addition. Remove bubbler and shut off sulphur dioxide.
(9) Gas out with carbon dioxide/air to approx pH 8.
(10) Filter the mixture in a heated filter bomb.

(Steps 6, 7 and 8 pertain to sulphitation and are ignored for pure carbonatation. Likewise the carbonatation steps should not be followed for pure sulphitation).

Calculations:

\[
\text{Mass of lime} = \frac{\text{lime dosage} \times \text{brix} \times \text{mass of liquor}}{\text{CaO content}} \times 100
\]

Lime dosage = 0.6% CaO on brix
CaO content in lime = 88%
Brix = 66.0°
Mass of liquor = 350g
Mass of lime = \( \frac{0.6 \times 100 \times 66.0 \times 350}{100 \ 88 \ 100} \) = 1.58g lime

Time for sulphur dioxide addition for required sulphur dioxide dosage.

Mass of sulphur dioxide =

= sulphur dioxide dosage \times \text{brix} \times \text{mass of liquor \over 100}

Volume of sulphur dioxide =

= \frac{\text{mass of sulphur dioxide}}{\text{mol mass sulphur dioxide}} \times 8.314J \times \text{temperature} \over \text{mol K} \times \text{pressure}

Time of sulphur dioxide addition = \frac{\text{volume of sulphur dioxide}}{\text{volumetric flow rate}}

Sulphur dioxide dosage = 200ppm
Temperature = 300K
Pressure = 101325 Pa
Vol. flow of sulphur dioxide = 0.20 ml/sec

Mass of sulphur dioxide required = \( \frac{200}{1000000} \times 66.0 \times 350 \) = 0.046g

Volume of sulphur dioxide = \( \frac{0.046g \times 8.314J \times 300K}{64g/mol \times \text{mol K} \times 101325 \text{ Pa}} \) = 17.7 ml

Time of sulphur dioxide addition = \( \frac{17.7 \text{ ml}}{0.20 \text{ ml/s}} \) = 89 second
### Table 9  Effect of laboratory carbonatation on colour and conductivity ash removal on raw sugar samples

<table>
<thead>
<tr>
<th>% CaO on brix</th>
<th>Raw sugar colour</th>
<th>Brown sugar liquor colour</th>
<th>% colour removal</th>
<th>Raw sugar ash</th>
<th>Brown sugar liquor ash</th>
<th>% ash removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6%</td>
<td>1337</td>
<td>720</td>
<td>46.1%</td>
<td>0.13</td>
<td>0.12</td>
<td>8%</td>
</tr>
<tr>
<td>0.5%</td>
<td>1354</td>
<td>787</td>
<td>41.9%</td>
<td>0.13</td>
<td>0.13</td>
<td>0%</td>
</tr>
<tr>
<td>0.4%</td>
<td>1427</td>
<td>842</td>
<td>41.0%</td>
<td>0.13</td>
<td>0.12</td>
<td>8%</td>
</tr>
</tbody>
</table>

### Table 10  Effect of laboratory sulphitation on colour and conductivity ash removal on raw sugar samples

<table>
<thead>
<tr>
<th>% CaO on brix</th>
<th>Raw sugar colour</th>
<th>Brown sugar liquor colour</th>
<th>% colour removal (gain)</th>
<th>Raw sugar ash</th>
<th>Brown sugar liquor ash</th>
<th>% ash removal (gain)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02%</td>
<td>1363</td>
<td>1538</td>
<td>(12.8%)</td>
<td>0.13</td>
<td>0.20</td>
<td>(54%)</td>
</tr>
<tr>
<td>0.02%</td>
<td>1363</td>
<td>1450</td>
<td>(6.4%)</td>
<td>0.12</td>
<td>0.17</td>
<td>(42%)</td>
</tr>
<tr>
<td>0.02%</td>
<td>1439</td>
<td>1539</td>
<td>(6.9%)</td>
<td>0.13</td>
<td>0.16</td>
<td>(23%)</td>
</tr>
</tbody>
</table>
### Table 11: Effect of laboratory sulphitation combined with laboratory carbonatation on colour and conductivity ash removal on raw sugar samples

<table>
<thead>
<tr>
<th>% CaO on brix</th>
<th>Raw sugar liquor color</th>
<th>Brown sugar liquor color</th>
<th>% color removal</th>
<th>Raw sugar ash</th>
<th>Brown sugar ash</th>
<th>% ash removal (gain)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Trial 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6%</td>
<td>1363</td>
<td>727</td>
<td>46.7%</td>
<td>0.13</td>
<td>0.13</td>
<td>0</td>
</tr>
<tr>
<td>0.6% + 200ppm SO₂</td>
<td>1439</td>
<td>741</td>
<td>48.5%</td>
<td>0.13</td>
<td>0.18</td>
<td>(38%)</td>
</tr>
<tr>
<td><strong>Trial 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6%</td>
<td>1502</td>
<td>803</td>
<td>46.5%</td>
<td>0.13</td>
<td>0.13</td>
<td>0</td>
</tr>
<tr>
<td>0.6% + 200ppm SO₂</td>
<td>1502</td>
<td>756</td>
<td>49.7%</td>
<td>0.13</td>
<td>0.12</td>
<td>8%</td>
</tr>
</tbody>
</table>

Increase in percent colour removal for combined carbonatation sulphitation of raw sugar samples:

- for Trial 1 = 48.5% - 46.7% = 1.8%
- for Trial 2 = 49.7% - 46.5% = 3.2%

Increase in percent ash removal for combined carbonatation sulphitation of raw sugar samples:

- for Trial 1 = (38%) - 0 = (38% gain)
- for Trial 2 = 8% - 0 = 8%
Table 12  Effect of laboratory carbonatation on colour and conductivity ash removal on main melt samples

<table>
<thead>
<tr>
<th>% CaO on brix</th>
<th>Main melt colour</th>
<th>Brown liquor colour</th>
<th>% colour removal</th>
<th>Main melt ash</th>
<th>Brown liquor ash</th>
<th>% ash removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6%</td>
<td>1255</td>
<td>644</td>
<td>48.7%</td>
<td>0.28</td>
<td>0.19</td>
<td>32%</td>
</tr>
<tr>
<td>0.4%</td>
<td>1194</td>
<td>714</td>
<td>40.2%</td>
<td>0.29</td>
<td>0.20</td>
<td>31%</td>
</tr>
<tr>
<td>0.1%</td>
<td>1194</td>
<td>961</td>
<td>19.5%</td>
<td>0.29</td>
<td>0.28</td>
<td>3%</td>
</tr>
</tbody>
</table>

Table 13  Effect of laboratory sulphitation on colour and conductivity ash removal on a main melt sample

<table>
<thead>
<tr>
<th>% CaO on brix</th>
<th>Main melt colour</th>
<th>Brown liquor colour</th>
<th>% colour removal</th>
<th>Main melt ash</th>
<th>Brown liquor ash</th>
<th>% ash (gain)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200ppm SO₂</td>
<td>1255</td>
<td>1193</td>
<td>4.3%</td>
<td>0.28</td>
<td>0.34</td>
<td>(21%)</td>
</tr>
</tbody>
</table>
Table 14: Effect of laboratory sulphitation combined with laboratory carbonatation on a main melt sample

<table>
<thead>
<tr>
<th>% CaO on brix</th>
<th>Main melt colour</th>
<th>Brown liquor colour</th>
<th>% colour removal</th>
<th>Main melt ash</th>
<th>Brown liquor ash</th>
<th>% ash removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6%</td>
<td>1255</td>
<td>644</td>
<td>48.7%</td>
<td>0.28</td>
<td>0.19</td>
<td>32%</td>
</tr>
<tr>
<td>0.6% + 200ppm SO₂</td>
<td>1255</td>
<td>620</td>
<td>50.6%</td>
<td>0.28</td>
<td>0.19</td>
<td>32%</td>
</tr>
</tbody>
</table>

Increase in percent colour removal for combined carbonatation sulphitation of a main melt sample

\[ = 50.6\% - 48.7\% = 1.9\% \]

Increase in percent ash removal for combined carbonatation sulphitation of a main melt sample

\[ = 32\% - 32\% = 0\% \]
C. LABORATORY TEST RESULTS ON THE SULPHITATION OF FACTORY CARBONATATED LIQUORS

Table 15  Laboratory test results on the sulphitation of catch samples of factory carbonatated liquors

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Colour</th>
<th>Increase in % colour removal</th>
<th>Conductivity ash</th>
<th>Increase in % ash removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1 Sat</td>
<td>8.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>91/07/05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+carb'n</td>
<td>7.9</td>
<td>1122</td>
<td>-</td>
<td>0.28</td>
<td>-</td>
</tr>
<tr>
<td>+200ppm</td>
<td>8.0</td>
<td>1109</td>
<td>1.1%</td>
<td>0.28</td>
<td>0</td>
</tr>
<tr>
<td>+500ppm</td>
<td>8.4</td>
<td>1011</td>
<td>9.9%</td>
<td>0.29</td>
<td>(4% gain)</td>
</tr>
<tr>
<td>B1 Sat</td>
<td>8.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>91/09/02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+carb'n</td>
<td>7.8</td>
<td>933</td>
<td>-</td>
<td>0.23</td>
<td>-</td>
</tr>
<tr>
<td>+200ppm</td>
<td>7.9</td>
<td>892</td>
<td>4.4%</td>
<td>0.23</td>
<td>0</td>
</tr>
<tr>
<td>+500ppm</td>
<td>8.3</td>
<td>823</td>
<td>11.8%</td>
<td>0.22</td>
<td>4%</td>
</tr>
<tr>
<td>B Sat</td>
<td>8.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>91/09/05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+carb'n</td>
<td>7.6</td>
<td>772</td>
<td>-</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>+200ppm</td>
<td>7.5</td>
<td>775</td>
<td>(0.4% gain)</td>
<td>0.20</td>
<td>0</td>
</tr>
<tr>
<td>+500ppm</td>
<td>7.6</td>
<td>769</td>
<td>0.4%</td>
<td>0.20</td>
<td>0</td>
</tr>
<tr>
<td>A Sat</td>
<td>9.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>91/09/05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+carb'n</td>
<td>7.4</td>
<td>969</td>
<td>-</td>
<td>0.23</td>
<td>(4% gain)</td>
</tr>
<tr>
<td>+100ppm</td>
<td>7.6</td>
<td>939</td>
<td>3.1%</td>
<td>0.24</td>
<td>(4% gain)</td>
</tr>
<tr>
<td>+200ppm</td>
<td>7.9</td>
<td>947</td>
<td>2.3%</td>
<td>0.24</td>
<td>(4% gain)</td>
</tr>
<tr>
<td>+500ppm</td>
<td>7.9</td>
<td>908</td>
<td>6.3%</td>
<td>0.24</td>
<td>(4% gain)</td>
</tr>
<tr>
<td>+1000ppm</td>
<td>7.5</td>
<td>885</td>
<td>8.7%</td>
<td>0.26</td>
<td>(13% gain)</td>
</tr>
<tr>
<td>+2000ppm</td>
<td>6.2</td>
<td>967</td>
<td>0.2%</td>
<td>0.29</td>
<td>(26% gain)</td>
</tr>
</tbody>
</table>
D. PILOT PLANT PROCEDURE

Apparatus:
Sulphur dioxide cylinder, regulator
250ml stainless steel sample bomb
Tubing and pipe fittings
Balance
Two litre beaker
Five litre sample container, two of
Stirrer
Macsalab filter press, 16 litre capacity
25 litre drums
Stainless steel saturator, 40 litre, flanged at bottom.
Flanged plate contains gas inlet, drain and temperature controlled kettle element. Refer Figure 1 page 8.

Method:

(1) Sample 1.0 litre of B Sat and 1.0 litre of B1 Sat at 5 minute intervals over an hour and a half. Collect 36 litres of sample in the stainless steel saturator. Take 200ml sample for pH and brix.

(2) Sample 2.0 litres of C Sat at 5 minute intervals starting 10 minutes after the first B Sat sample. 200ml of the 2.0 litre is composited in a 5 litre sample container. Determine filterability, brix and pH of composite.

(3) Filter 8 litre batches of liquor in the Macsalab filter.
Precoat filter with 250ml Hyflo. Stir in 3 x 250ml Hyflo into liquor before filtration. Filter at pressures up to 100kPa(g), filter to dryness.

(4) Heat reactor containing 36 litres of liquor to 80 deg C.

(5) Weigh sample bomb containing sulphur dioxide before dosing.

(6) Add sulphur dioxide over a period of 1 hour, stirring constantly.

(7) Reweigh bomb after dosing.

(8) Take sample of carbonated/sulphited liquor for filterability, brix and pH.

(9) Filter C Sat liquor to produce non-sulphited brown liquor. Obtain 32 litres for boiling test.

(10) Filter sulphited saturator liquor to produce sulphited brown liquor. Obtain 32 litres for boiling test.

Calculations:

Sulphur dioxide dosage = \( \frac{\text{mass of sulphur dioxide} \times 1,000,000}{\text{sat. liquor volume \times Sugar conc.}} \)

Mass of sulphur dioxide = 1063.5 - 1058.4 = 5.1g
Saturator liquor volume = 36.0 litres
Brix = 67.8
Sugar concentration\(^1\) (Table 8) = 904 g/l

Sulphur dioxide dosage = \( \frac{5.1g \times 1,000,000}{36.0 \times 904 \text{ g/l}} \)
= 160ppm (rounded to 2 significant figures)
E. PLOT OF SULPHUR DIOXIDE DOSAGE VERSUS COLOUR REMOVAL

![Graph showing the relationship between ppm sulphur dioxide and additional percentage colour removal.]

**Figure 7** Plot of sulphur dioxide dosage versus additional percent colour removal for carbonatation - sulphitation pilot plant runs
F. COSTING CALCULATION

Data:

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantity/Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw sugar melt</td>
<td>650 000 t/yr</td>
</tr>
<tr>
<td>Lime costs</td>
<td>R1 290 000 /yr</td>
</tr>
<tr>
<td>Resin costs</td>
<td>R1 840 000 /yr</td>
</tr>
<tr>
<td>Resin regeneration costs</td>
<td>R1 054 000 /yr</td>
</tr>
<tr>
<td>Sulphur dioxide costs</td>
<td>R1 230 /t + R73 /t (Transport) + R37 000 /yr (Tanker hire)</td>
</tr>
</tbody>
</table>

Season averages (91/92)¹ :

- Raw sugar colour: 1315
- Main melt colour: 1294
- Brown liquor colour: 763
- Primary liquor colour: 477
- Secondary liquor colour: 239
- Refined sugar colour: 42
- Lime usage: 0.68% /melt
- Available CaO in lime: 88.9%

Assumed:

- 10% remelt to melt
- Mol mass calcium oxide: 56 g/mol
- Mol mass sulphur dioxide: 64 g/mol

Calculations:

Colour removal across carbonatation = 1294 - 763 = 531
Colour removal across resin = 763 - 239 = 524
Colour removed for 180ppm sulphur dioxide (Table 3) = 41
Colour removed for 180ppm sulphur dioxide assuming 14% additional colour removal = 1.14 x 41 = 47

Lime cost per ton raw sugar = \( \frac{R1 290 000 /yr}{650 000 \text{ t/yr}} \)

= R1.99/t for 531 colour removal

or R0.38/t for 100 colour removal

Resin + Resin regeneration costs per ton raw sugar =

\[ \frac{(R1 840 000 + R1 054 000) /yr}{650 000 \text{ t/yr}} \]

= R4.54/t for 524 colour removal

or R0.84/t for 100 colour removal
Sulphur dioxide cost per year =
\[
= \frac{180}{1000} \times 1.1 \times 650 \, 000 \times (R1 \, 230 + R73) + R37 \, 000
\]
\[
= 128.7 \, t/yr \times R1 \, 303 \, /t + R37 \, 000 \, /yr
\]
\[
= R205 \, 000 \, /yr
\]

Lime costs of sulphitation per year =
\[
= 128.7 \, t/yr \times \frac{56}{64} \times \frac{100 \, t \, lime}{88.9 \, t \, CaO} \times R1 \, 290 \, 000
\]
\[
= 0.68 \times 650 \, 000 \, t \, lime
\]
\[
= R37 \, 000 \, /yr
\]

(Stoichiometry: 56t CaO reacts with 64t sulphur dioxide)

Sulphur dioxide cost per ton raw sugar =
\[
= \frac{(R205 \, 000 + R37 \, 000)}{650 \, 000 \, t/yr}
\]
\[
= R0.37 \, /t \, for \, 41 \, colour \, removal
\]
\[
or \, R0.90 \, /t \, for \, 100 \, colour \, removal
\]

Assuming there is a 14% additional colour removal effected by sulphitation in crystallisation, the sulphur dioxide cost per ton raw sugar =
\[
= R0.37 \, /t \, for \, 47 \, colour \, removal
\]
\[
or \, R0.79 \, /t \, for \, 100 \, colour \, removal
\]