

**LABORATORY OPTIMISATION OF THE
CARBONATATION PROCESS WITH REGARD TO
COLOUR REMOVAL AT THE MALELANE REFINERY**

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Submitted in fulfilment of the academic requirements for the degree of

M-Tech

In the Department of Chemical Engineering

M L Sultan Technikon, Durban

April 2001

Abstract

The purpose of this investigation was to identify and then optimise the factors that affect the decolourisation during the carbonatation process. Batch carbonatation tests, carried out in a pilot plant in the laboratory, were performed to establish the effect of selected factors on the decolourisation of melt.

Of the selected factors namely, method of lime addition, colour of melt, amount of lime added and value of final pH during carbonatation it has been shown that only the amount of lime, melt colour and the value of the final pH during carbonatation influence the decolourisation during carbonatation.

Generally at the Malelane refinery the maximum decolourisation achieved is 45% with the addition of 0,85 to 0,90% CaO (on brix). This work has shown that up to 63% decolourisation can be achieved with the addition of 3,0% CaO (on brix). Adding more lime has a number of disadvantages namely more carbon dioxide would be required, chemical costs would increase and the extra calcium carbonate formed may require additional filter capacity, therefore it is recommended that this option (more lime) only be used during periods of high colour loading in the refinery.

The results have also shown that lower colour carbonated liquor will be achieved if the carbonatation reaction is stopped at a final pH value of about 10 rather than the typical pH of 8,5. Generally during carbonatation (final pH 8,5) about 40 to 45% of the colour

present in the melt is removed. It has been found that up to 65% decolourisation can be achieved if the carbonatation reaction is stopped at a final pH of about 10. The advantages of terminating the carbonatation reaction at the final pH of 10 at Malelane are twofold. Firstly a higher liquor decolourisation would be achieved and secondly less carbon dioxide (about 30%) would be required.

It has also been shown that at pH 10 most of the lime added to melt was removed (measured as calcium and conductivity ash) from the carbonated liquor.

Terminating the carbonatation reaction at the final pH of 10 could reduce the filterability of the carbonated liquor. The experimental results have shown that terminating the carbonatation reaction at a pH value of 10,0 decreases the index of carbonatation filterability by about 20%. This difference however, was not considered to be significant for the Malelane refinery.

It is therefore recommended that full scale tests be done at the Malelane refinery evaluating the effect of the high final pH of 10,0 on decolourisation, and on the filterability of the carbonated liquor.

Preface

I hereby declare that this entire dissertation is my own work, unless stated otherwise in the text, and that it has not been submitted, in whole or in part, for a degree to any other Technikon or Institution.

Manogran Moodley

April 2001

Acknowledgements

I wish to place on record my sincere appreciation to the following persons and organisations that contributed greatly to this project.

- Mr PM Schorn who supported and motivated this project to the management of the Malelane mill.
- Mr GH Jones and Mr JV Coetzee who supported this investigation and made funds available for the project.
- Mr S Sibiya (Malelane laboratory) who performed the numerous colour analysis.
- Mr P Gouws, Mr S Pretorius and Mr H van Deventer from the Malelane factory for their help.
- Mrs H Potgieter who did most of my typing.
- My colleagues in the Malelane production department for their support.
- Mrs M Ronaldson and Mr T Rungasamy of the SMRI who carried out the calcium analysis.
- Mr D Joseph (SMRI) for constructing the pilot plant.
- Dr GRE Lionnet, my external supervisor, for assistance, guidance and friendship.
- Dr VL Pillay, my internal supervisor, for assistance and guidance.
- The Sugar Milling Research Institute for the loan of the filtration apparatus.
- My wife and my family for their love and support.

TABLE OF CONTENTS

Chapter	Description	Page
Chapter 1	Introduction and objective	25
1.1	Introduction	25
1.2	Objectives of carbonatation	26
1.2.1	Filterability of the carbonated liquor	28
1.2.1.1	Main factors that have been optimised to improve liquor filterability	28
1.2.1.2	Main factors that affect the filterability of the carbonated liquor	30
1.3	Motivation to optimise the carbonatation process at Malelane	31
1.4	Approach	32
Chapter 2	Description of the current process at Malelane	33
2.1	Melting system	34
2.2	Liming system	35
2.3	Gassing system	35

2.4	A and B-saturators system	35
2.5	Filtration system	36
2.6	Decolourisation at the Malelane carbonatation station	36
Chapter 3	Literature Review	37
3.1	Introduction	37
3.2	Chemistry	38
3.2.1	CO ₂ and water	38
3.2.2	CO ₂ and OH ⁻	39
3.3	Impurities	40
3.3.1	The effect of impurities	41
3.3.1.1	Carbonatation and filtration processes	41
3.3.1.2	Crystallisation process	42
3.3.1.3	Sugar quality	43
3.3.2	Removal of impurities by carbonatation	44
3.3.2.1	Colour	44
3.3.2.2	Turbidity	45

3.3.2.3	Starch	45
3.3.2.4	Dextran	46
3.3.2.5	Gums	46
3.3.2.6	Silica	46
3.3.2.7	Sulphates (SO ₄) ²⁻	46
3.4	Factors that influence carbonatation	46
3.4.1	Carbon dioxide gas absorption	47
3.4.2	Temperature	49
3.4.3	Reaction time	49
3.4.4	Brix	49
3.4.5	Quality of lime	50
3.4.6	Method of lime addition	50
3.4.7	The effect of feed colour	50
3.4.8	Quantity of lime	50
3.4.9	The effect of final pH	52
3.5	Aims of this work	54
3.5.1	Factors that were kept constant during the batch carbonatation	55

Chapter 4	Experimental	59
4.1	Comparison of batch versus continuous carbonatation	59
4.1.1	Impurity removal	59
4.1.2	Filterability of carbonated liquor	60
4.1.3	Gassing efficiency	60

4.2	Experimental equipment	60
4.2.1	Carbonatation equipment	60
4.2.1.1	Gas supply	61
4.2.1.2	Reaction vessel	62
4.2.1.3	Stirrer	62
4.2.1.4	Gas sparger	62
4.2.1.5	Water bath	63
4.2.1.6	pH meter	63
4.2.2	Filtration equipment	63
4.2.3	Sundry analytical equipment	64
4.2.3.1	Spectrophotometer	64
4.2.3.2	Digital refractometer	64
4.2.3.3	Atomic absorption spectrophotometer	64
4.2.3.4	Conductivity meter	65
4.3	Analytical procedure	65
4.3.1	Colour	65
4.3.2	Calcium	66
4.3.3	Conductivity ash	66

4.4	Experimental procedure	66
4.4.1	Carbonatation	66
4.4.2	Filtration	67
4.5	Influence of equipment parameters on colour removal	68
4.5.1	Carbonatation process	68
4.5.1.1	Repeatability of the analytical method for colour	69
4.5.1.2	Repeatability of the carbonatation experimental procedure	69
4.5.1.3	The effect of stirrer speed on the colour of the carbonated liquor	71
4.6	Conclusions	72
Chapter 5	The effect of the method of lime addition on the decolourisation of melt	73
5.1	Evaluation of different methods of milk of lime addition	73
5.2	Conclusion	74
Chapter 6	The effect of feed colour and lime	75

quantity on the decolourisation of melt

6.1	Tests on different melt colours	75
6.2	Mechanism of colour removal by carbonatation	85
6.3	Conclusions	86

Chapter 7 The effect of final pH on colour and on calcium removals from melt

7.1	The effect of final pH on decolourisation of melt	88
7.1.1	The effect of final pH on decolourisation of melt of 1170 colour	89
7.1.2	The effect of the final pH on decolourisation of melt of 1326 colour	92
7.1.3	The effect of the final pH on decolourisation of melt of 1000 colour	94
7.1.4	The effect of the final pH on	95

decolourisation of melt of 1906
colour

7.2	The effect of final pH on calcium removal from melt	100
7.2.1	The effect of final pH on calcium removal from melt of 1170 colour	100
7.2.2	The effect of final pH on calcium removal from melt of 1326 colour	102
7.2.3	The effect of final pH on calcium removal from melt of 1000 colour	103
7.2.4	The effect of final pH on calcium removal from melt of 1906 colour	104
7.3	The effect of final pH on conductivity ash removal from melt	105
7.4	The effect of final carbonated liquor pH on colour, calcium and conductivity ash removals from melt	107
7.5	Conclusions	111

Chapter 8	The effect of final pH on the filterability of carbonated liquor	112
8.1	The effect of final pH on the filterability of carbonated liquor	112
8.1.1	The theory of filtration	112
8.1.2	Determination of the index of carbonatation filterability	114
8.1.3	Filterability tests done on liquor carbonated from melt of 938 colour	116
8.1.4	Filterability tests done on liquor carbonated from melt of 1641 colour	119
8.2	Conclusions	120
Chapter 9	Conclusions and recommendations	121
Chapter 10	References	128

List of Tables

Table Number	Table Description	Page
Table 3.1	The effect of carbonated liquor pH on gassing efficiency at two South African refineries (Frankland, 1981).	48
Table 4.1	Colour results for melt and carbonated liquor replicates.	69
Table 4.2	Repeatability carbonatation tests on melt of 1753 colour.	70
Table 4.3	Repeatability carbonatation tests on melt of 620 colour.	71
Table 4.4	The effect of stirrer speed on the colour of the carbonated liquor.	72
Table 5.1	Different methods of milk of lime addition on melt of 1099 colour.	74
Table 6.1	Colour results of tests done on melt of 510 colour.	76
Table 6.2	Colour results of tests done on melt of 1109 colour.	78
Table 6.3	Colour results of tests done on melt of 1763 colour.	81
Table 6.4	Comparison of colour and turbidity removal by physical and chemical methods (Bennet, 1972).	85
Table 6.5	Colour of carbonated liquor and number of colour units removed from melts of different colours by similar	87

amounts of lime.

Table 7.1	The lowest carbonated liquor colours achieved and their respective pH values for the tests done on the four melt samples.	98
Table 8.1	Results from one filtration test.	115
Table 8.2	Results of the filtration tests done on liquor carbonated from melt of 938 colour.	117
Table 8.3	The effect of suspended matter on carbonated liquor filterability (Murray, 1972).	118
Table 8.4	Results of the filtration tests done on liquor carbonated from melt of 1641 colour.	119
Table 9.1	Results for the three melt samples.	123
Table 9.2	Calcium removal from the four melt samples at similar final carbonated liquor pH values.	125

List of Figures

Figure Number	Figure Description	Page
Figure 1.1	Simplified flow diagram for the manufacture of refined sugar at Malelane.	27
Figure 2.1	Schematic diagram of the carbonatation station at Malelane.	34
Figure 3.1	The effect of the quantity of CaO on melt decolourisation, Moodley (1992).	52
Figure 3.2	The effect of final liquor pH on decolourisation during carbonatation and at different lime addition rates, Kelly <i>et al.</i> , (1973).	54
Figure 4.1	Carbonatation experimental equipment.	61
Figure 6.1	The effect of the quantity of CaO added to melt of 510 colour on the colour of the carbonated liquor.	77
Figure 6.2	The effect of the quantity of CaO added to melt of 510 colour on the number of colour units removed and the % decolourisation.	77
Figure 6.3	The effect of the quantity of CaO added to melt of 1109 colour on the colour of the carbonated liquor.	80
Figure 6.4	The effect of the quantity of CaO added to melt of 1109 colour on the number of colour units removed and the % decolourisation.	80

Figure 6.5	The effect of the quantity of CaO added to melt of 1763 colour on the colour of carbonated liquor.	82
Figure 6.6	The effect of the quantity of CaO added to melt of 1763 colour on the number of colour units removed and the % decolourisation.	82
Figure 6.7	Melt colour versus the maximum number of colour units removed.	83
Figure 6.8	Melt colour versus the number of colour units removed at similar lime dosage levels.	84
Figure 7.1	The effect of final pH on the colour of the liquor carbonated from melt of 1170.	90
Figure 7.2	The effect of final pH on the number of colour units removed and the % decolourisation for the melt of 1170 colour.	91
Figure 7.3	The effect of final pH on the colour of the liquor carbonated from melt of 1326.	92
Figure 7.4	The effect of final pH on the number of colour units removed and the % decolourisation for the melt of 1326 colour.	93
Figure 7.5	The effect of final pH on the colour of the liquor carbonated from melt of 1000	94
Figure 7.6	The effect of final pH on the number of colour units	95

removed and the % decolourisation for the melt of 1000 colour.

Figure 7.7	The effect of final pH on the colour of the liquor carbonated from melt of 1906.	96
Figure 7.8	The effect of final pH on the number of colour units removed and the % decolourisation for the melt of 1906 colour.	98
Figure 7.9	The effect of final pH on the calcium concentration of the liquor carbonated from the melt of 1170 colour.	101
Figure 7.10	The effect of final pH on the calcium concentration of the liquor carbonated from the melt of 1326 colour.	102
Figure 7.11	The effect of final pH on the calcium concentration of the liquor carbonated from the melt of 1000 colour.	103
Figure 7.12	The effect of final pH on the calcium concentration of the liquor carbonated from the melt of 1906 colour.	104
Figure 7.13	The effect of final pH on the conductivity ash concentration of the liquor carbonated from the melt of 1000 colour.	105
Figure 7.14	The effect of final pH on the conductivity ash concentration of the liquor carbonated from the melt of 1906 colour.	106
Figure 7.15	The effect of final pH on the calcium content and on	108

the colour of the liquor carbonated from melt of 1170
colour.

Figure 7.16	The effect of final pH on the calcium content and on the colour of the liquor carbonated from melt of 1326 colour.	109
Figure 8.1	Plot of $\frac{d\theta}{dV}$ versus V for a sample of carbonated liquor.	116
Figure 9.1	Melt and carbonated liquor colours.	122

Glossary

<u>Word</u>	<u>Description</u>
Affination	The washing of sugar crystals to remove the molasses film.
Ash	The residue remaining after incineration at 650°C of a sample which was pre treated with sulphuric acid.
Brix	The percentage by mass of the total soluble solids of aqueous sucrose solution.
Carbonated liquor	Melt that has been limed and gassed with carbon dioxide and then filtered.
Colour	<p>The absorbance measured with a spectrophotometer at 420 nm, using a 0,45 micron membrane for filtration and at pH 7. In the text the term decolourisation is used and is defined as follows :-</p> $\text{Decolourisation (\%)} = \frac{\text{Melt colour} - \text{carbonated liquor colour}}{\text{Melt colour}} \times 100$
Conductivity ash	Is a measure of the concentration of ionised soluble salts present in the liquor sample.
Crystallisation pan	A vessel in which sugar crystallisation takes place under vacuum.
Dextran	A polysaccharide consisting of glucose units linked predominantly in a α 1-6 mode. Two methods are used to analyse for dextran viz. the Haze (Anon, 1994) and Roberts (Anon, 1990) methods.

Filterability	This is a measure of the filtering characteristics of a sample of carbonated liquor and is expressed as follows :- $\text{Filterability (\%)} = \frac{\text{volume of filtrate from sample}}{\text{Volume of filtrate from standard.}} \times 100$
Gums	Polysaccharides that are soluble in water and precipitable in alcohol.
Masseccuite	The mixture of crystals and mother liquor discharged from a vacuum pan. In a refinery four masseccuites (1 st , 2 nd , 3 rd and 4 th) are normally boiled.
Melt	A solution of raw sugar in water.
Milk of lime	A solution of calcium hydroxide in water. The concentration of lime in melt is generally expressed as % CaO (on brix).
Non – pol	Brix minus pol.
Oligosaccharides	Are polymers of simple carbohydrates containing two to nine monomer units.
Pol	The apparent sucrose content of any solution expressed as a percentage by mass and determined by the single or direct polarisation method.
Reducing sugars	These are chemically reducing sugars found in sugar solutions, the main ones being glucose and fructose.
Starch	A polysaccharide consisting of amylose and amylopectin.
Sweetwater	A dilute sucrose containing stream not actually part of the refining process.

Turbidity

The difference in absorbance measured with a spectrophotometer at 420 nm and at pH 7, between an unfiltered and filtered sample using a 0,45 micron membrane for filtration.

LISTS OF ABBREVIATIONS

<u>ABBREVIATION</u>	<u>DESCRIPTION</u>
ICUMSA	International Commission for Uniform Methods of Sugar Analysis
ICU	ICUMSA Units
MAU	Milli Absorbance Units
ML	Malelane
SASTA	South African Sugar Technologists Association
SMRI	Sugar Milling Research Institute
VHP	Very high pol

CHAPTER 1

Introduction and objective

1.1 Introduction

The purpose of a refinery is to remove impurities from the incoming raw sugar and to produce refined sugar of an acceptable quality. This is achieved through a number of unit processes at the Malelane Refinery.

Unit processes in a classical refinery, consist of affination, clarification, decolourisation and crystallisation (Clark,1983). Classically, clarification has been regarded as pre-treatment for the decolourising stage (Bennet,1990). The most commonly used clarification processes are carbonatation and phosphatation, with liquor clarification being an essential pre-treatment for the decolourisation stage that may include either ion - exchange resin, activated carbon or any other solid adsorbent. The efficiency of the decolourisation stage is dependent to a critical degree, on how well the clarification has been carried out, and for this reason, these two processes are closely inter-related.

In South Africa a number of local conditions have caused a departure from this classical arrangement of unit processes in refining. Firstly, since very high pol (VHP) sugar, which is of very good quality, is an industry standard, affination is not required and is thus not practised in any of the local refineries. Secondly, the distinction between clarification and decolourisation is not as apparent. In South Africa most of the decolourisation takes place in conjunction with clarification at five of the seven local

refineries. In other words only two of the local refineries have classical decolourising unit processes and both use ion - exchange with acrylic, strong base, resins. The clarification stage at the one refinery is phosphatation while at the other it is carbonatation.

At the Malelane refinery most of the impurity removal takes place during the clarification process, which consists of carbonatation and sulphitation. A simplified sketch of the refining processes at Malelane is given in Figure 1. Basically, the carbonatation process consists of adding a slurry of calcium hydroxide in water to the raw melt solution, to a desired pH. Then carbon dioxide gas is bubbled into the sugar solution, in saturators, under controlled conditions of alkalinity and temperature. Generally the carbon dioxide is added to the saturators in two stages, with the major part of the gassing carried out in the first saturator. The impurities are both absorbed by, and enmeshed in, the conglomerated particles of the calcium carbonate precipitated by the reaction of the carbon dioxide and calcium hydroxide. Separation of the clear liquor and the calcium carbonate is done by filtration.

1.2 Objectives of carbonatation

Refinery carbonatation has two main objectives, the first being the production of calcium carbonate that filters well and secondly, the production of a voluminous precipitate of calcium carbonate with a surface area as large as possible on which the impurities can be adsorbed.

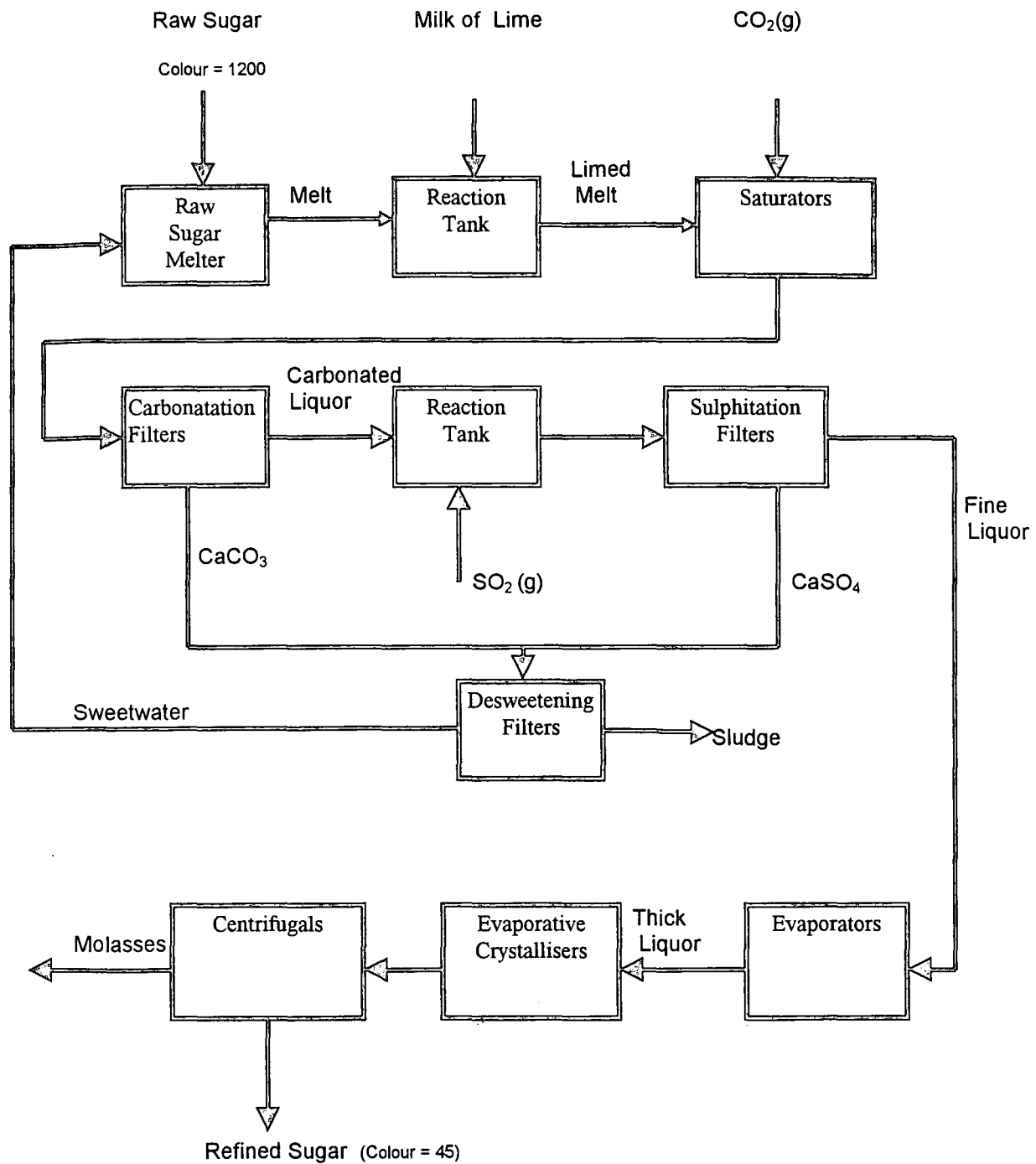


FIGURE 1.1. Simplified flow diagram for the manufacture of refined sugar at Malelane.

1.2.1 Filterability of the carbonated liquor

These two objectives (section 1.2) may be conflicting. Generally, in full scale carbonatation, filterability is improved at the expense of impurity removal. This is done because filtration problems in a refinery can adversely affect the performance and throughput of the refinery. Generally, when the carbonated liquor is difficult to filter, the melt brix or the melt rate is reduced. This is expensive in terms of extra steam and lost production. Some of the main factors that have been optimised with the objective of producing a liquor that filters well will be briefly discussed.

1.2.1.1 Main factors that have been optimised to improve liquor filterability

- **Final liquor pH**

In a classical refinery (Clark, 1983), carbonatation is basically a pre-treatment for the decolourisation process. Most of the earlier carbonatation work was therefore done with the objective of forming a calcium carbonate that filters well. In two saturator systems, for maximum filterability, Bennet (1974) recommends a pH of 9,5 in the first saturator and a pH of 8,0 to 8,5 in the second saturator.

The carbonatation process has also been extensively studied in South Africa by Murray (1972), Murray and Runggas (1975) and Runggas (1978a),. Here again, most of the carbonatation work was done with the objective of optimising the filterability of the liquor. It is recommended (Runggas, 1978a) that in multiple saturator stations, a drop down to a pH value of 9,3 should be achieved in the first vessel(s) and the pH of the carbonated liquor leaving the final saturator vessel should be 8,0 to 8,5. In South Africa

most carbonatation refineries have implemented the recommendation made by Bennet (1974) and Runggas (1978a).

• **Quantity of lime**

The filterability of any carbonated liquor will depend largely on the amount and nature of the impurities present in the original melt, therefore, for every carbonated liquor there is a particular lime dosage, (Bennet, 1974) at which the filterability will be the optimum. Tests done by Bennet (1990) on raw sugar of two different qualities have shown that the maximum liquor filterability on one liquor occurred at a lime dosage of 0,6% CaO (on brix) and on the other liquor at 1,2 % CaO (on brix). It is therefore important that the optimum amount of lime be added in a refinery, as the addition of excess lime will have a number of disadvantages which are listed in the literature review (section 3.5.2.3).

Chapman (1967) therefore recommends that the refinery should have the capability of gassing limed melt which has 0,8% CaO (on brix), but cautions that during normal operation the % CaO added to melt should be well below 0,8%. For most of the carbonatation tests done by Chapman (1967) a CaO of 0,5 % was used.

The effect of the amount of lime added on the filterability of the carbonated liquor was also studied by Murray and Runggas (1975). They used a final pH of 9,0, a temperature of 80°C and retention time of one hour with a 60 brix melt. The quantity of lime added varied from 0,25 to 1,25 % CaO (on brix). The results showed that the optimum filterability occurred at a lime addition rate of 0,75%. Generally in South

African refineries the lime added varies from 0,5 to 1,2% CaO (Lamusse, 1988 and Wiehe *et al.*, 1986).

- **Temperature**

Temperature has an effect on liquor viscosity and also on the quality of the precipitated calcium carbonate particle. The degree of calcium carbonate conglomeration increases with temperature up to about 82°C (Bennet, 1974). Work done by Murray and Runggas (1975) has shown that the maximum filterability of the carbonated liquor occurred at a temperature of 86°C. Bennet (1990) recommends a temperature of 82°C for the carbonatation reaction.

- **Retention time**

The retention time of the liquor in the saturator would have an influence on the filterability of the carbonated liquor. Bennet (1990) recommends a 45 minute retention in the first saturator while Murray and Runggas (1975) used a 1 hour retention time for laboratory carbonatation tests. The retention time in most saturators in South African refineries vary from 40 minutes to 1 hour (Getaz *et al.*, 1990).

1.2.1.2 Main factors that affect the filterability of the carbonated liquor

It has been shown (section 1.2.1) that the carbonatation process has been optimised mainly with regard to the filterability of the carbonated liquor. Many workers have studied filtration and have found that suspended solids (Donovan and Lee, 1994) and starch (Alexander, 1957; Bennet, 1967; Bennet and Gardner, 1967; and Murray, 1972)

were the two main causes of filtration problems in a refinery. Levels of suspended solids greater than 300 mg/kg brix caused filtration problems at a United Kingdom refinery (Lee and Donovan, 1995). In South Africa (Simpson and Davis, 1998) the levels of suspended solids is generally low with an average value of 157 (minimum of 51 and maximum of 623) mg/kg brix. In South Africa starch is not generally considered a problem in the refinery (Simpson and Davis, 1998) and low (average 103 mg/kg brix) values were reported.

1.3 Motivation to optimise the carbonation process at Malelane

The refinery at Malelane is currently optimised for maximum filterability and no filtration problems are generally experienced. This can be attributed to a number of reasons. Firstly very high pol (VHP) sugar, which is of very good quality, is produced by the raw sugar factory. Secondly the levels of the main filtration impeding substances (starch and suspended solids) are low in South Africa (Simpson and Davis, 1998) when compared to overseas refineries. The results of measurements done on raw sugar from Malelane have shown that the levels of both suspended solids (average 68 mg/kg brix) and starch (average 90 mg/kg brix) were low when compared to overseas refineries. Thirdly with Malelane being a back-end refinery (refinery attached to raw sugar factory) the quality of the sugar from the raw sugar factory can be controlled to a certain extent.

In view of these advantages it would therefore be worthwhile to the optimise the carbonatation process at Malelane with regard to impurity removal. Any improvement in

decolourisation during carbonatation at Malelane would have major benefits in terms of costs and sugar quality

1.4 Approach

The information in section 1.3 helped to select the overall objective of the project which was to optimise the carbonatation process at the Malelane refinery with regard to impurity (mainly colour) removal. The project was investigated in the following manner:

- A literature survey on refinery carbonatation was carried out.
- The factors that influence the carbonatation process were identified.
- A pilot plant was constructed to carry out laboratory carbonatation.
- The effectiveness of the carbonatation process on the removal of impurity, mainly colour, was assessed by optimising the most important factors that influence the carbonatation process identified in the literature.

Chapter 2

Description of the current process at Malelane

This chapter describes the carbonatation process used by the Malelane refinery.

Introduction

The carbonatation process carried out at the Malelane refinery is a continuous one where limed melt and flue gas are continuously added to the two parallel A-saturators while the pH is maintained at 9,5. In the B-saturator the carbonated melt from the A-saturators and flue gas flow continuously into the saturators while the pH leaving the B-saturator is maintained around 8,5. Good pH control at the saturators is important in terms of filterability of melt. The pH control system installed at Malelane is a cascade control loop which incorporates the flue gas flow and the melt pH. A schematic diagram for the carbonatation system is given in Figure 2.1.

2.1 Melting system

The sugar from the raw sugar factory is sent to the melter, where steam and water are added to produce a melt of 65 brix at a temperature of 70°C. The melt then flows to a storage tank before being pumped to a melt heater which heats the melt from 70°C to 85°C. The heated melt then flows to the milk of lime and melt wheels.

2.2 Liming system

The liming system consists of the milk of lime and melt wheels, which are proportioning devices consisting of two revolving bucket wheels, one for melt and the other for the milk of lime. The speed of either wheel can be independently varied so that the required amount of milk of lime (0,85 to 0,90% CaO on brix) can be achieved. The melt wheel speed can be varied and is used to control the refinery throughput. Under normal operations the melt wheel is maintained at a speed of 6,5 rpm. Surplus melt from the melt wheel overflows back to the melt buffer tank. The melt and milk of lime flow into a short retention tank, with a stirrer, where mixing of the two streams takes place. The limed melt flows by gravity into two parallel A-Saturators.

2.3 Gassing system

The Malelane refinery generally uses flue gas extracted from a bagasse fired boiler. Burning bagasse yields higher carbon dioxide contents and lower levels of sulphur dioxide as compared to a coal fired boiler (Lamusse, 1988). The flue gas is cooled to 50°C, scrubbed with water and then pumped to the refinery. The average carbon dioxide content of the flue gas is about 10 to 12% (volume/volume).

2.4 A and B-Saturators system

The two A-saturators which are in parallel, have an effective volume of 24 m³ each. Both saturators are fitted with conventional calandrias and are fed with steam to keep the temperature at about 85°C. The flue gas is introduced through perforated pipes beneath the calandria. The carbon dioxide reacts with the milk of lime to form calcium

carbonate as it bubbles through the melt solution. The excess flue gas escapes to the atmosphere through a chimney. The pH in the A-saturators is automatically controlled at a value of 9,5.

The carbonated melt is at a pH value of 9,5 and overflows to the B-saturator, which has no calandria and has an effective volume of 30 m³. In this vessel more flue gas is added until the carbonated melt pH is at 8,5. The carbonated liquor then flows into the filter supply tank.

2.5 Filtration system

The calcium carbonate precipitate is removed in a pressure filter using polypropylene needle felt filter cloths. Filter cycles of about 4 hours are achieved. The initial liquor, which is cloudy, is sent to the B-saturator while the concentrated sludge is desweetened using plate and frame filters. The clear liquor is pumped to the next unit operation in the refinery, which is the sulphitation station.

2.6 Decolourisation at the Malelane carbonatation station

A colour survey carried out by the SMRI (Moodley and Hastie, 1994) has shown that decolourisation at the carbonatation station varied from 8 to 45%, the average being 30%. A further survey (Moodley, 1994) showed results of about 50%. Currently at the Malelane refinery, the decolourisation achieved at the carbonatation station is about 40 to 45%.

Chapter 3

Literature review

This chapter contains the findings of a review of the literature on refinery carbonatation.

3.1 Introduction

The carbonatation process has been used in refineries for more than 85 years (Chapman, 1967). It is a robust process and the reagents used are cheap. The process has remained practically unchanged for many decades.

Basically, the process consists of adding a slurry of calcium hydroxide in water to the melt solution to a desired pH. Then carbon dioxide gas is bubbled into the solution in saturators under controlled conditions of alkalinity and temperature. The process involves two stages, the first (first saturator) involves the formation of a voluminous precipitate of calcium carbonate with a very large surface area on which can be adsorbed colour bodies and less soluble salts. The second stage (second saturator) involves the conditioning of the precipitate in order to improve its filterability (Chapman, 1982). The impurities are both absorbed by, and enmeshed in, the conglomerated particles of the calcium carbonate precipitated by the reaction of the carbon dioxide and calcium hydroxide (Bennet, 1974). Separation of the carbonated liquor from the calcium carbonate is done by filtration.

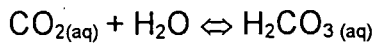
3.2 Chemistry

This section is summarised from unpublished notes prepared by Lionnet (personal communication).

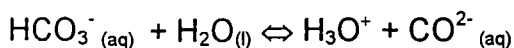
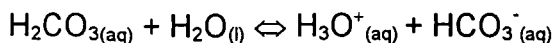
3.2.1 CO₂ and water

The chemistry of carbon dioxide is well described in many text books, but as is often the case, the conditions which apply are ideal; thus the systems consist of pure water, pure calcium hydroxide, etc., at 25°C, which simplify the discussion and make the results more exact, but less practical. It is however useful to consider some of the basic points.

CO₂ in aqueous solution exists only partly as H₂CO₃, being largely present as CO_{2(aq)}, the ratio of CO₂/H₂CO_{3(aq)} being 600:1.

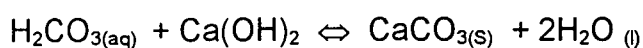
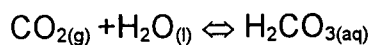


H₂CO₃ is a weak acid, ionising in two steps, and thus a solution of CO₂ in water is slightly acidic, with a pH of 5,7:

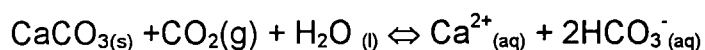


3.2.2 CO₂ and OH⁻

As a weak acid, a solution of carbon dioxide in water will react with bases. Of particular interest here is its reaction with lime or calcium hydroxide :

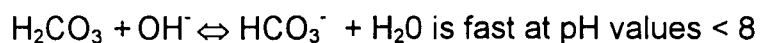
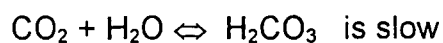


The calcium carbonate precipitates and removes calcium from solutions, but with more carbon dioxide :



And now the bicarbonate is soluble. This reintroduces calcium into the solution.

As with most weak acids, reactions and equilibria are controlled by pH. In this system it is established that :



At pH >11 however:

$\text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^-$ is slow and

$\text{HCO}_3^- + \text{OH}^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O}$ is fast

In the pH range 8 to 10 both sets of reaction occur. Interpretations of acid/base behaviour of this type of system are therefore complicated since reaction rates vary and there are pH dependencies.

The situation in impure sugar solutions of high brix, and high temperatures when carbon dioxide reacts with an impure milk of lime, can only be much more complex. The solubilities and equilibria cannot be established with any certainty. The measurement of pH under these conditions is difficult. For these reasons laboratory or pilot plant investigations dealing with carbonatation in the sugar industry are very system specific.

3.3 Impurities

VHP sugar as produced by a raw sugar mill, has a pol of about 99,3% (mass/mass) and moisture level of 0,10% (mass/mass) (Pillay, 1990). The brix of the sugar is therefore 99,9% (100-0,10) and its non-pol content 0,60% (99,9-99,3). This non-pol represents the impurities in the sugar and these impurities will have a negative effect on some of the unit operations in the refinery. Firstly certain impurities will have a profound effect upon the nucleation and growth or flocculation process (Alexander 1957; Murray *et al.*, 1974) involved in the formation of the calcium carbonate conglomerate. Secondly some

impurities will impact upon the filtration processes (Lee and Donovan, 1995) in the refinery. Thirdly the presence of certain impurities will adversely affect the sugar crystallisation process (Morel du Boil, 1995) and lastly refined sugar quality (Clark and Legendre, 1996) will be influenced by some impurities.

3.3.1 The effect of impurities

Impurities impact on a number of areas, as mentioned above (section 3.3). Each of the major areas is considered in turn.

9

3.3.1.1 Carbonatation and filtration processes

◦ Starch

The starch molecule consists of a straight chain amylose fraction and a branched chain amylopectin fraction (Murray, 1972). Studies done by Murray *et al.*, (1974) suggest that the amylose fraction coats the surface of the growing calcium carbonate crystals suppressing agglomerate formation, which leads to poor filtration. Alexander (1957) pointed out that starch would cause problems in a carbonatation refinery by affecting the particle size of the calcium carbonate crystal. It has also been shown that starch interferes with the growth of the calcium carbonate crystal and subsequently causes filtration problems (Murray, 1972). With carbonated liquors starch was found to be the most detrimental impurity for filtration (Kaga *et al.*, 1966). Starch is considered as one of the more serious impurities in carbonatation refineries.

- **Gums**

Laboratory carbonatation tests done by Hidi and McCowage (1984) have shown that the presence of gums had an adverse effect on filtration.

- **Dextran**

High molecular weight dextran (1×10^7) at 1000 mg/kg brix, reduced the filterability from 63 to 7%, but dextrans with molecular weight of $0,1 \times 10^6$ and 2×10^6 , at the same concentration, had no effect (Hidi *et al.*, 1984). High levels of dextran (> 1000 mau as measured by the Haze method) in the liquor did not cause any filtration problems at the Thames refinery (Donovan, 1993).

- **Silica (silica is normally expressed as Na_2SiO_3)**

The addition of silica to melt decreased the filtration (Hidi *et al.*, 1984). Yamane *et al.* (1965) have shown that silica is one of the filtration impeding impurities in raw sugar.

3.3.1.2 Crystallisation process.

- **Oligosaccharides**

Certain oligosaccharides tend to transfer preferentially to the crystal so that the raw sugar entering the refinery is enriched with compounds that will prevent efficient crystallisation of the refined sugar crystal (Morel du Boil, 1995). The oligosaccharides adversely affect crystallisation by selective adsorption on different crystal faces thus causing crystal elongation and retarding crystal growth rates (Morel du Boil, 1995).

- **Starch**

Starch can increase viscosity of the liquor and hence lower the yield of sugar (Clark and Legendre, 1996).

3.3.1.3 Sugar quality

- **Colour**

One of the main refined sugar quality specifications is colour. Colour in cane juice and in the sugar is of several types. ^aThe different types of colourants and their sources (Clark and Legendre, 1996) are given below.

- ***Cane Plant*** : flavonoids, phenolics, some colour precursors, metabolic and defence compounds.
- ***Factory*** : melanoidins (reaction products of reducing sugars and amino nitrogen), caramels and melanins (heat derived compounds).
- ***Refinery*** : alkaline degradation products of fructose.

Work done by Lionnet and Moodley (1995) has shown that under South African conditions the colour of the affinated crystal is totally controlled by the feed liquor colour and crystal size. The crystal size cannot be changed due to market constraints. Therefore to produce acceptable sugar colour, the colour of the liquor before crystallisation should be as low as possible.

- **Ash**

The processes that remove ash in the refinery at Malelane are carbonatation and sulphitation. Ineffective pH control and carryover of suspended matter at the filter station will influence the ash levels in refined sugar.

- **Turbidity**

Turbidity is the cause of "sediment" a common refined sugar specification (Clark and Legendre, 1996). Turbidity in liquor is due to a suspension of impurity particles of diameter greater than 0,1 μm (Bennet, 1974). The composition of these particles covers a wide range of inorganic and organic material and includes some colloidal impurities (Bennet, 1990).

3.3.2 Removal of impurities by carbonatation

The objective of the carbonatation station is therefore to remove as much of the above impurities as possible. Carbonatation shows a remarkable specificity in the removal of any impurity capable of forming a sparingly soluble calcium salt (Bennet, 1974). This accounts for the outstanding feature of the process in the removal of sulphates, phosphates and colour. The removal of some specific impurities is reviewed below.

3.3.2.1 Colour

The carbonatation process is very efficient in removing colour. The decolourisation will depend on the incoming melt colour, the lower the melt colour the less the

decolourisation (Chapman, 1967). The decolourisation over carbonatation can vary from 10% to 90% (Chapman, 1967). A decolourisation of about 65% is obtained in the Thames refinery (Donovan, 1993). Bennet (1990) has shown that carbonatation removes over 50% of the colour in the melt stream. Colour surveys carried out by the Sugar Milling Research Institute (Moodley, 1993) have shown that in South African refineries the decolourisation over carbonatation varied from 26 to 46%. The results of batch laboratory carbonatation tests carried out by Bennet (1974) have shown that 70 to 80% of the melt colour was removed during carbonatation. At the Malelane refinery the average decolourisation is between 40 and 45% (Moodley and Schorn, 1997).

3.3.2.2 Turbidity

Carbonatation is very effective in the removal of turbidity. Carbonatation can remove between 29% (Runggas (1978b), 1978) and 99% (Bennet, 1974) of the turbidity in raw melt.

3.3.2.3 Starch

Laboratory tests carried out by Bennet (1974) showed that carbonatation removed about 40% of the starch present in the melt sample. At a starch concentration of 120 mg/kg brix in the raw sugar solution, the carbonatation process removed about 50% of the starch present. But at the 500 mg/kg brix level, the amount of starch removed was about 80% (Murray, 1972). Laboratory carbonatation tests done by Runggas (1978b) have shown that carbonatation removed between 40 and 45% of the starch present in the melt sample.

3.3.2.4 Dextran

Carbonatation is the only refining process found to achieve significant dextran removal (Fowler,1981).

3.3.2.5 Gums

Work done by Runggas (1978b) shows that carbonatation removed 37% of the gums present in melt.

3.3.2.6 Silica

The results of laboratory tests indicate that carbonatation can remove about 60% of the silica present in melt (Bennet,1974).

3.3.2.7 Sulphates (SO_4^{2-})

Approximately 80% of the sulphates present in melt are removed during carbonatation (Bennet,1974).

3.4 Factors that influence carbonatation

In a carbonatation/sulphitation refinery, the major clarification process is the carbonatation process. Therefore it is important that the carbonatation station is optimised in terms of gas absorption and impurity removal. Some of the factors that influence the performance of the carbonatation station will be discussed.

3.4.1 Carbon dioxide gas absorption

The carbon dioxide gas absorption will be affected by the design of the saturators, the brix, temperature and pH of the melt. In conventional saturators the gas absorption is about 35% (Chapman, 1967). Efficiencies of 100% have been achieved with the use of in line mixers (Hulpiau *et al.*, 1978). The effect of temperature on gas absorption is well known. The absorption of carbon dioxide by calcium hydroxide in a refinery is greater at higher temperatures. Although gases are less soluble at higher temperatures, the increase in absorption with higher temperatures is due to the higher rate of reaction. Frankland (1980,1981) investigated the effect of carbonated liquor pH on the efficiency of carbon dioxide absorption during both laboratory and full-scale carbonatation at two South African refineries. The results from the two refineries are given in Table 3.1.

As expected, pH has a marked effect on the gassing efficiency. In the highly alkaline region high efficiencies were achieved and as the pH values were lowered, the efficiencies decreased.

Table 3.1

The effect of carbonated liquor pH on gassing efficiency at two South African refineries (Frankland, 1981).

pH	Gassing Efficiency [#]	
	Refinery 1	Refinery 2
10,5	100	100
10	40	70
9,5	30	30
9	25	20
8,5	22	26

$$\text{\# \% gassing efficiency} = \frac{\text{CO}_2\% \text{ gas feed} - \text{CO}_2\% \text{ gas outlet}}{\text{CO}_2\% \text{ gas feed}} \times 100$$

At the Malelane refinery the flue gas having a carbon dioxide concentration of between 7 to 14% (volume/volume), is extracted from the boiler (Wiehe and Pillay, 1986). Lamusse (1988) reported on the use of boiler flue gas for carbonatation. At Malelane the gas is cooled to 50°C, scrubbed with water and then pumped to the refinery where it is piped directly into the saturators. The gas is introduced through perforated holes in the pipe beneath the calandria of the saturator. This method of introducing the gas into the vessel is very inefficient (Chapman, 1967).

3.4.2 Temperature

Temperature has an effect on liquor viscosity and also on the quality of the precipitated calcium carbonate particle. The degree of calcium carbonate conglomeration increases with temperature up to about 82°C (Bennet, 1974). Work done by Murray and Runggas (1975) has shown that the optimum temperature for laboratory carbonatation was 86°C. Bennet (1990) recommends a temperature of 82°C for the carbonatation reaction. One of the factors that influences the alkaline degradation of reducing sugars to lactic acid is temperature. To minimise the formation of lactic acid at the Hulett's Refinery the temperature of liming has been reduced from 80 °C to less than 75 °C (Cox *et al.*, 1990).

3.4.3 Reaction time

The retention time of the liquor in the saturator would have an influence on the impurity removal; Bennet (1990) recommends a 45 minute retention in the first saturator while Murray and Runggas (1975) used a 1 hour retention time for laboratory carbonatation tests.

3.4.4 Brix

The higher the brix of the liquor, the higher the viscosity. This would have an adverse effect on the performance of the filters and thus influence the impurity removal. On the other hand, if the brix is too low then the energy consumption at the refinery evaporators would increase. Experience at the Malelane refinery (Wiehe and Pillay, 1986) shows that the optimum brix of the liquor should be between 60 and 67.

3.4.5 Quality of lime

The quality of the lime used in the carbonatation has an influence on the filterability of the carbonated liquor (Bennet, 1990). The "ageing" (storage time of milk of lime between slaking and use in the refinery) of milk of lime is also considered to be important by some workers. Murray and Runggas (1975) recommend an "ageing" time of two hours.

3.4.6 Method of lime addition

Generally, the required amount of milk of lime is added in one stage to the melt (Chapman, 1967; Wiehe and Pillay, 1986).

3.4.7 The effect of feed colour

The performance of the carbonatation station will depend to a large extent on the amount and nature of the impurities present in the original raw sugar. According to Chapman (1967) the amount of colour removed during carbonatation depends on the colour of the feed stream. The lower the original colour the less is the percentage removal.

3.4.8 Quantity of Lime

Lime (added as a slurry of calcium hydroxide in water), usually expressed as % CaO on brix, has an effect on decolourisation and on the filterability of the calcium carbonate

precipitate formed. The degree of decolourisation will depend on the incoming sugar colour and on the amount of lime added. More lime will remove more colour until the optimum level is reached. The addition of 0,6% (mass/mass) CaO to melt removed between 61 and 74% of the colour in the melt stream (Bennet,1974). A graph of lime addition versus liquor decolourisation is given in figure 3.1. The results indicate that there is an optimum dosage of lime. Work done on carbonated liquor at the Sugar Milling Research Institute (Lionnet and Moodley, 1995) has shown that the alkaline degradation of the reducing sugars caused the colour of the liquor to increase from 971 to 2031. A refinery in South Africa (Cox *et al.*, 1990) had experienced higher than normal ash gains. An investigation carried out showed that calcium was solubilised when it reacted with lactic acid to form calcium lactate, which was not removed during carbonatation. The major source of lactic acid in the refinery was found to be the result of the chemical destruction of reducing sugars under alkaline conditions during liming. Laboratory trials done by Cox *et al.* (1990), showed that one of the factors that influenced the alkaline degradation of reducing sugars to lactic acid was the amount of lime added. To minimise the formation of lactic acid in the refinery, the lime addition was reduced from 0,7% to 0,6% CaO on brix.

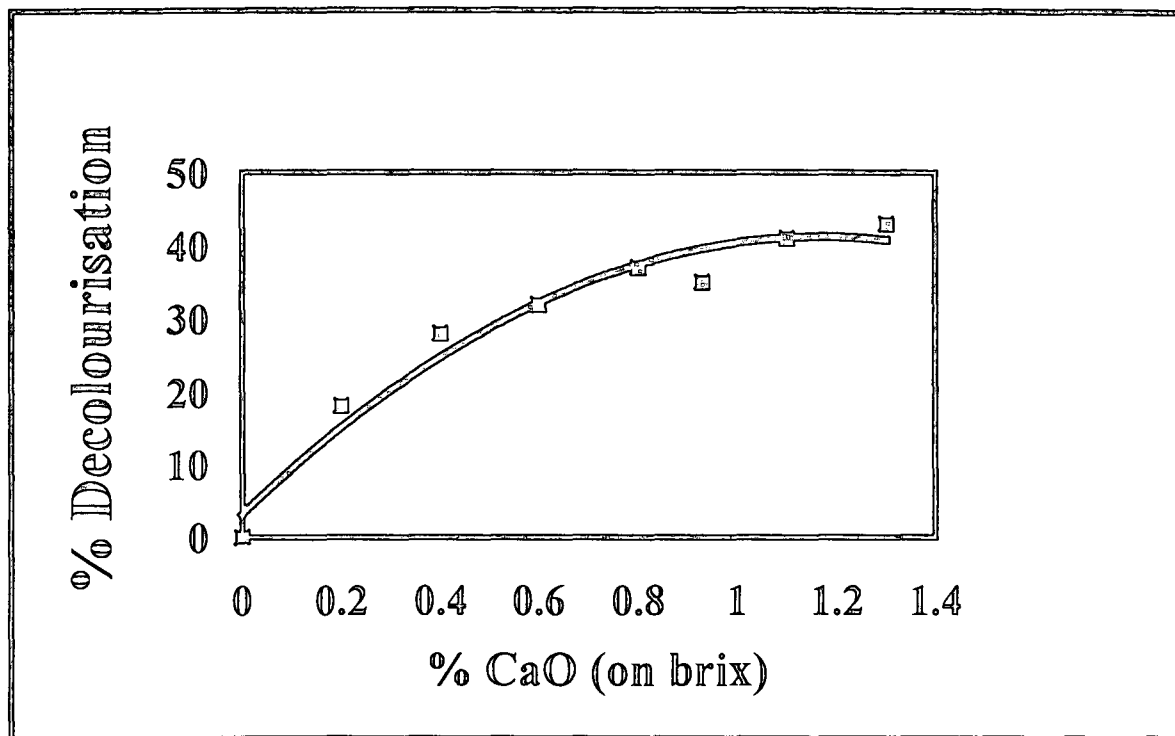


FIGURE 3.1. The effect of the quantity of CaO on melt decolourisation, Moodley (1992).

3.4.9 The effect of final pH

The efficiency of the carbonatation process on the removal of impurities depends on pH control. Incomplete precipitation of the calcium in the liquor would result in poor filtration and high ash in refined sugar. When excess carbon dioxide is added soluble calcium bicarbonate would be produced which would result in the impurities being freed. To produce calcium carbonate of good filtering characteristics, the pH in the first saturator should be 9,5 and in the second saturator should be 8,5 (Murray and Runggas, 1975). On the negative side at high pH values, destruction of reducing

sugars occurs. The rate of destruction of the reducing sugars would depend on the temperature and on the contact time.

Batch carbonatation tests, with different lime addition rates, were done by Kelly *et al.* (1973) and the effect of final pH on the decolourisation of the melt during carbonatation was evaluated. The required amount of milk of lime was added to the melt and the carbonatation reaction was initiated by bubbling carbon dioxide gas through the sample. As the reaction proceeded sub samples of the carbonatated liquor were withdrawn at various pH values. The samples were then analysed for colour. According to Kelly *et al.* (1973) the maximum decolourisation during carbonatation occurred at pH values between 9,2 to 9,4. The results are given in Figure 3.2.

Similar tests were done by Yamane (1954), where during the carbonatation process sub samples were withdrawn at various pH values and the colour measured. The results (Yamane, 1954) showed that the higher the final pH after carbonatation, the better was the decolourisation.

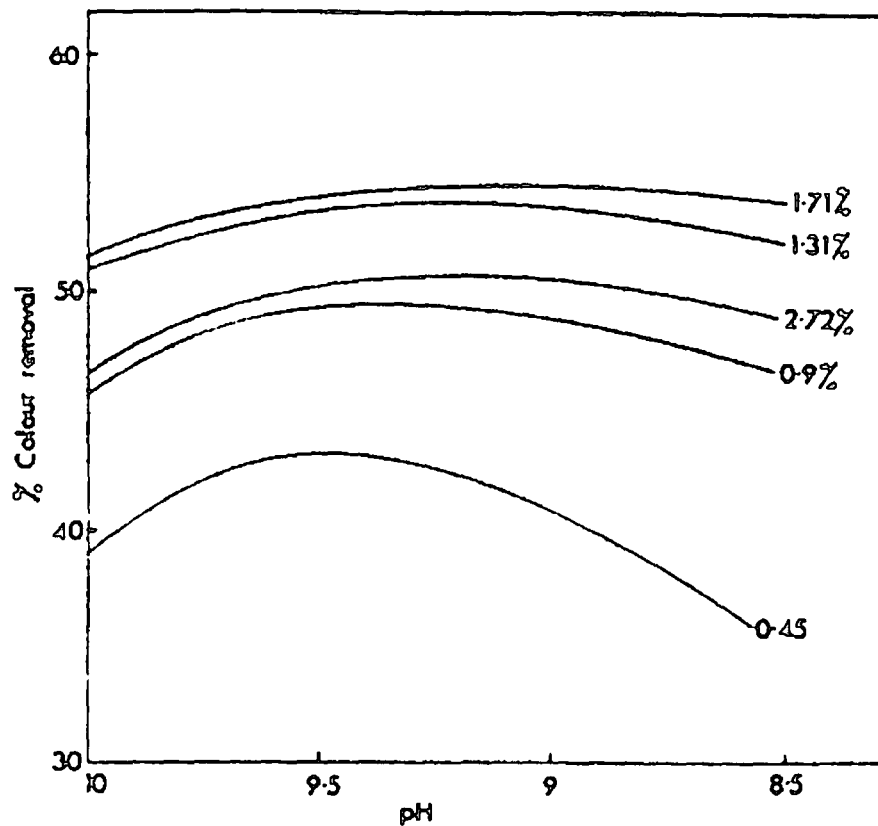


FIGURE 3.2. The effect of final liquor pH on decolourisation during carbonatation at different lime addition rates, from Kelly *et al.*, 1973.

3.5 Aims of this work

The literature survey helped to identify all possible factors, which are discussed in section 3.4 that affect the decolourisation during the carbonatation process.

The aims of this work was therefore to optimise some of the factors, which have been selected according to their influence on the operation of the refinery as identified in the literature (section 3.4). Batch, pilot plant carbonatation tests were used and some of the cost effective findings will be implemented industrially.

3.5.1 Factors that were kept constant during the batch laboratory

carbonatation tests

Some of the factors given in section 3.4 such as temperature (section 3.4.2), reaction time (section 3.4.3), and brix (section 3.4.4), cannot be easily changed in the plant due to the effect they will have on the throughput and on the energy usage in the refinery. The values recommended in literature and which are currently being used at the Malelane refinery, were therefore be kept constant during the laboratory tests. The values that were used are listed below.

- Temperature of melt (section 3.4.2) = 80°C.
- Reaction time (section 3.4.3) = 60 minutes
- Brix of melt (section 3.4.4) = 65

The quality of lime (section 3.4.5) at Malelane is generally regarded as good with an average CaO content around 90%. The effect of lime quality on the carbonatation process was therefore not evaluated.

3.5.2 Optimisation of the selected factors that affect the decolourisation during the carbonatation process.

It is important in terms of cost and of sugar quality that the maximum amount of impurities be removed during the carbonatation process. The selected factors that influence the removal of impurities from melt during carbonatation will be discussed.

3.5.2.1 The effect of the method of lime addition (section 3.4.6)

At the Malelane refinery the required amount of milk of lime is added in one stage to melt. The limed melt is then gassed in two stages to the final pH of 8,2. The effect of varying the method of lime addition will be evaluated.

3.5.2.2 The effect of feed colour (section 3.4.7)

According to Chapman (1967) the amount of colour removed during carbonatation depends on the colour of the feed stream. The lower the original colour the less is the percentage removal. Tests will be done to evaluate the effect of melt colour on the decolourisation during carbonatation.

3.5.2.3 The effect of quantity of lime (section 3.4.8)

One of the main factors which affect the level of impurity removal, is the amount of lime added. There is a point at which the impurity removal is maximised and the addition of any more lime will not remove more impurities.

- **Addition of excess lime**

The addition of excess lime will have the following disadvantages:

- More lime requires more carbon dioxide gas for neutralisation. This would require additional power and energy.
- Additional calcium carbonate is formed which increases filter resistance.
- Due to the additional filter cake formed, more sweetwater is generated.
- The mass of filter cake to be disposed off will increase.
- The loss of sugar in the filter cake will increase.
- There will be an increase in refinery chemical costs (cost of excess lime).

- **Addition of insufficient lime**

If the quantity of lime is inadequate then the impurity removal will not be optimised.

This will have adverse effects on the filtration of the liquor, on the crystallisation and on the refined sugar quality. These points have been covered in detail in section 3.3.

3.5.2.4 The effect of final pH (Section 3.4.9)

- **On colour removal**

Kelly *et al.* (1973) have shown that the maximum decolourisation during carbonatation occurred at a final pH value of 9.2 to 9.4. Work done by Yamane (1954) also showed that the higher the final pH during carbonatation, the better was the decolourisation.

In view of these observations namely, that the maximum decolourisation during carbonatation occurred at higher final pH values (i.e. final pH > 9), batch carbonatation

tests will be done where the final pH during carbonatation will be varied and the effect that this has on the colour removal will be evaluated.

Kelly *et al.* (1973) did not evaluate the effect that pH has on the filterability of the carbonated liquor.

- **On the filterability of the carbonated liquor**

Laboratory carbonatation tests done by Murray and Runggas (1975) have shown that the maximum filterability of the carbonated liquor occurs at a pH value of 8,2. Kelly *et al.* (1973) on the other hand have shown that the maximum decolourisation during carbonatation occurred at a final pH of 9,2 to 9,4. As noted above this effect was not evaluated by Kelly *et al.* (1973) . Laboratory filtration tests will therefore be done to compare the filterability of carbonated liquors that have been gassed with carbon dioxide to final pH values of 8,2 and 10,0.

CHAPTER 4

Experimental

This chapter describes the experimental apparatus used to carry out the tests.

Introduction

The refinery at Malelane has a continuous carbonatation process. It is not practical, due to the complexity of the process, to carry out continuous carbonatation in the laboratory and for this study batch carbonatation was done. Most pilot plant work described in the literature also used batch carbonatation. The advantages and disadvantages of batch carbonatation when compared to continuous carbonatation will be discussed.

Batch carbonatation of 65 brix melt was practised in a refinery in England for about sixty years. Milk of lime was added and the limed melt was gassed to a final pH of 9,1 (Chapman, 1967) in one tank.

4.1 Comparison of batch versus continuous carbonatation

4.1.1 Impurity removal

Batch carbonatation tests were carried out by Bennet (1974). The results achieved were then compared to those obtained by continuous carbonatation. No significant differences between the two processes were found.

4.1.2 Filterability of carbonated melt

Work done by Bennet and Gardiner (1967) has shown that calcium carbonate crystals grown in a batch process were more difficult to filter when compared to calcium carbonate crystals grown in a continuous process. The replacement of the batch system with a continuous one led to improved filtration (Chapman, 1967). According to Chapman (1967) this was due to better pH and temperature control during continuous carbonatation.

4.1.3 Gassing efficiency

Frankland (1981) found no difference in gassing efficiency between batch carbonatation tests done in the laboratory and full scale continuous carbonatation tests done in two South African refineries.

As the objective of the investigation is to optimise the impurity removal at the Malelane refinery the results obtained from tests done by batch carbonatation should be comparable to results obtained from continuous carbonatation.

4.2 Experimental Equipment

4.2.1 Carbonatation equipment

A sketch of the experimental equipment used to carry out the carbonatation tests is given in Figure 4.1.

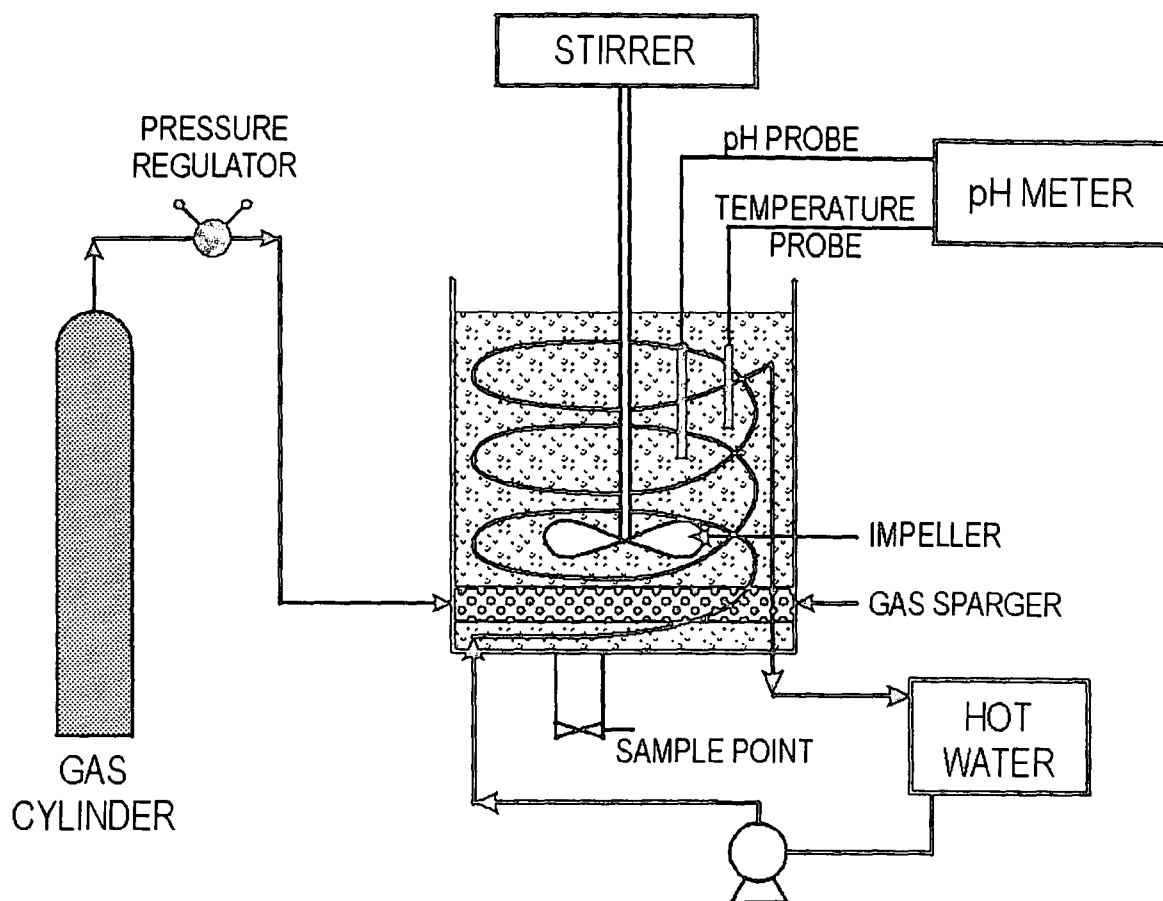


FIGURE 4.1. Carbonation experimental equipment.

4.2.1.1 Gas supply

Although the refinery at Malelane uses flue gas which has a carbon dioxide content of 10 to 12% (volume/volume), it was decided to carry out the laboratory tests using pure carbon dioxide gas. Previous carbonation work done (Frankland, 1981) using pure carbon dioxide gas has shown that there was a slight increase in gassing efficiency and that a shorter reaction time was achieved with the pure carbon dioxide gas when compared to flue gas containing 12% of carbon dioxide. These differences are not seen as being critical.

4.2.1.2 Reaction Vessel

The five-litre reaction vessel is constructed of perspex. Water heated to 82°C in a water bath is circulated through a copper coil, placed in the reaction vessel. This maintains the temperature of the melt at the chosen value of 80°C (section 3.4.2). The gas enters the reaction vessel through a gas sparger which disperses it into tiny bubbles. The impeller then disperses the gas into the melt solution. At the bottom of the vessel is the sample valve.

4.2.1.3 Stirrer

The stirrer is made by Heidolph and can be operated at five different speeds (40, 80, 125, 190 and 300 rpm). The impeller fitted to the stirrer is an axial flow one that has been designed for gas/liquid applications. The impeller (Anon, 1996) is capable of dispersing gas and controlling flow patterns at significantly higher gas rates than other axial flow impellers. When compared to conventional Rushton type radial flow turbines, the impeller can provide up to 30% greater mass transfer (Anon, 1996) at equal torque and power.

4.2.1.4 Gas sparger

The sparger has been purchased from Mott International (USA). The sparger is made of stainless steel and introduces the carbon dioxide into the melt through thousands of tiny pores, thus creating bubbles far smaller and numerous than with a drilled pipe or other sparging methods. This will increase the absorption of the gas.

4.2.1.5 Water bath

The ten litre water bath is fitted with a Julabo EM heater which has a pump. The water in the bath is maintained at 80°C. The hot water is pumped through the coil in the reaction vessel thus heating the melt to 80°C.

4.2.1.6 pH meter

The pH meter used is a Crison microPH 2001. The electrode is made of glass and is filled with potassium chloride solution. The pH meter was calibrated on a daily basis with pH 4 and 7 buffers, as recommended by the operating manual. The pH values reported in this paper were measured at 25°C unless otherwise stated. It has also been observed that there was approximately a one unit difference between the pH value of the melt recorded at 80°C and at 25°C, with the latter being higher.

4.2.2 Filtration equipment

This equipment was used to carryout the filterability tests as described in section 4.3.2. The apparatus consists of a 2 litre cylindrical pressure vessel, fitted with an enclosed water jacket. The vessel was maintained at 80 °C, by circulating hot water through the jacket. Compressed air from the factory was used to maintain the required pressure of 300 kpa. The filtration vessel has a Whatman No. 42 filter paper fitted at the bottom.

4.2.3 Sundry analytical equipment

4.2.3.1 Spectrophotometer

A spectrophotometer was used for the colour analysis and details of the instrument used at Malelane are given below: -

Make : Spectronic

Model : Geneys 5

Serial number : 3V19263001

4.2.3.2 Digital refractometer

A refractometer was used to measure brix and details of the instrument used at Malelane is given below: -

Make : Bellingham and Stanley Ltd

Model : RFM 500

Serial number : Y94008

4.2.3.3 Atomic absorption spectrophotometer

An atomic absorption spectrophotometer was used to measure calcium and details of the instrument used by the SMRI is given below :-

Make: Varian

Model : Spectra AA 20

4.2.3.4 Conductivity meter

A conductivity meter used to measure conductivity ash and details of the instrument used by the SMRI is given below: -

Make: Metrohm

Model: E527

4.3 Analytical procedure

4.3.1 Colour

ICUMSA colour (Anon,1994) is a measure of the amount of colour contained in a sugar solution. It was determined according to the method specified by the International Commission for Uniform Methods of Sugar Analysis (ICUMSA). The procedure for the colour analysis is as follows :-

- For the melt colour determination, the melt sample was added to de-ionised water to form a sugar solution of concentration between 30 and 50 °brix. This solution was then filtered through a 0,45 micron membrane.
- The solution was transferred to a 50 ml beaker and the pH value measured.
- The solution pH was then adjusted to a value pH of 7,0 at room temperature using hydrochloric acid or sodium hydroxide, depending on the original pH.
- The refractometer brix was measured and the corresponding concentration of total solids (g/cm^3) was looked up in tables in SASTA Laboratory Manual (Anon, 1985).
The refractometer was described in Section 4.1.3.2.

- The absorbance of the solution was measured, using the spectrophotometer, at a wavelength of 420 nm. The spectrophotometer was described in section 4.1.3.1
- The ICUMSA colour of the solution was then calculated according to equation 5.2.1 -

$$\text{ICUMSA Colour} = \frac{\text{Absorbance (420nm)} \times 10\,000}{\text{Concentration Total Solids (g/cm}^3\text{)} \times \text{Cell Length (mm)}} \quad 5.2.1$$

4.3.2 Calcium

Calcium ions were analysed by atomic absorption and the method used by the SMRI has been described in detail by Lionnet (1998).

4.3.3 Conductivity ash

Conductivity ash has been measured by the SMRI using a conductivity method and has been described in detail by van Staden *et al.*, (1999).

4.4 Experimental procedure

4.4.1 Carbonatation

- 2200 grams of melt at 65 brix was added to the reaction vessel.
- The melt was stirred at 300 rpm and hot water at 80°C was circulated through the coil in the reaction vessel, until the temperature of the melt reached a value of 80°C. This took approximately ten minutes.

- The required CaO as milk of lime (10% solution) was added to the melt and the limed melt was allowed to mix for a period of 5 minutes.
- A 50 gram sample of the limed melt was taken for calcium analysis.
- The carbonatation reaction was initiated by opening the gas supply valve. The gas flow meter was adjusted to deliver 5 litres of carbon dioxide per minute.
- The pH value of the melt was monitored.
- When the pH reached the required value the reaction was stopped by shutting off the gas supply.
- The carbonatated melt was stirred (300 rpm) for a period of one minute.
- The sample was then extracted by opening the sample valve. The sample was cooled and stored in a freezer for analysis.

4.4.2 Filtration

- 2200 grams of melt at 60 brix was carbonatated as described in 4.3.1.
- To 500 grams of the carbonatated sample, 0,05% (mass/mass) filter aid (celite 577) was added.
- The sample was stirred manually for 2 minutes.
- The sample was transferred to the filtration vessel which was fitted with a Whatman No. 42 filter paper.
- The sample was allowed to stabilise for 10 minutes to allow the temperature of the sample to reach 80°C.
- The air line (factory compressed air) was connected to the vessel.

- The pressure regulator on the air line was set at 300 kPa.
- As soon as the pressure valve was opened, the liquor outlet was opened.
- The time taken to collect 20,40 60.....220 mls of filtered liquor was recorded.
- The information was used to calculate the filtration rate. This is described in detail in section 8.1.2

4.5 Influence of equipment parameters on colour removal

Introduction

The term sugar colour is defined as the complex collection of molecules which contribute to the increased light absorbance of sugar solutions at a particular wavelength. In sugar refining, colour is conveniently used as a measure of the level of non-sugars of a sugar solution due to the fact that most non-sugars are coloured (Hubbard, 1993). Therefore colour will be the main impurity that will be measured in this study.

4.5.1 Carbonatation process

As the objective of this investigation is to optimise the colour removal during carbonatation, it is important therefore that the method used to analyse for colour and the carbonatation procedure used yield repeatable colour values. To investigate this further sub-samples of the melt and carbonated liquor were analysed for colour by the same analyst. Also a number of carbonatation test were done on the same melt sample under identical conditions.

4.5.1.1 Repeatability of the analytical method for colour

Three different samples of melt and a sample of carbonated liquor were divided into four sub samples and analysed for colour by the same analyst. The results are given in Table 4.1.

Table 4.1

Colour results for melt and carbonated liquor replicates

	Replicates				
Sample	1	2	3	4	Confidence level (95%)
Melt 1	1015	1027	1030	1018	11 units
Melt 2	959	971	965	973	10 units
Melt 3	1768	1771	1741	1731	32 units
Carbonated Liquor	519	520	508	522	10 units

The maximum absolute differences in the colour values of melts 1, 2, 3 and carbonated liquor are 15, 14, 40 and 14 units respectively. From the results in table 4.1, it can be concluded that for colours between 500 and 1000 the confidence level for the colour analysis is 10 units and for colours around 1700 the confidence level is 32 units.

4.5.1.2 Repeatability of the carbonatation experimental procedure

For the carbonatation tests one percent CaO (on brix) as 10% solution (mass/mass) milk of lime was added to the melt sample, with stirring (300 rpm), at 80°C. The mixture

was allowed to mix for five minutes. Thereafter the carbon dioxide was introduced into the melt sample at a flow rate of 5 l/min. The reaction was allowed to proceed until the desired final pH value was reached. The reaction was then stopped. The sample was then analysed for colour. This procedure was repeated five times on the same melt. The results are given in Table 4.2.

Table 4.2

Repeatability carbonatation tests on melt of 1753 colour.

Replicate	Colour of carbonated liquor	% Decolourisation
1	1338	24
2	1352	23
3	1330	24
4	1327	24
5	1320	25
Average	1333	24

The confidence level (95%) for the five carbonated liquor colours is 15 units. The maximum absolute difference between the 5 samples is 30 units. These results are acceptable (section 4.4.1.1). The procedure used to carry out the carbonatation test is therefore acceptable.

The decolourisation achieved for these tests (24%) is low (typical 45%) and is due to the fact that the melt colour is high and more lime should have been added.

A further series of test were done on a melt colour of 620. The results are given in Table 4.3.

Table 4.3

Repeatability carbonatation tests on melt of 620 colour.

Replicate	Colour of carbonated liquor	% Decolourisation
1	320	48
2	330	47
3	320	48
Average	323	48

The results indicate that the maximum absolute difference is 10 units. This is acceptable (section 4.4.1.1).

4.5.1.3 The effect of stirrer speed on the colour of the carbonated liquor

The melt was limed with 0,64% CaO (on brix) as a 10% solution of milk of lime (mass/mass) and the normal carbonatation procedure (described in section 4.3.1) was carried out except that the stirrer speed was varied. The first test was carried out at 125 rpm and the second test was carried out at 300 rpm. The results are given in Table 4.4.

Table 4.4

The effect of stirrer speed on the colour of the carbonatated liquor.

Stirrer speed (rpm)	Colour of carbonatated liquor
125	1006
300	994

The difference (12 units) in colour between the two liquors is within experimental error (section 4.4.1.1). There is no significant difference between the two liquor colours and it can therefore be concluded that the stirrer speeds evaluated have no effect on the decolourisation of the melt.

4.6 Conclusions

The following conclusions can be made with regard to the validation of the carbonatation equipment:-

- The procedure used to carry out the carbonatation tests yields repeatable colour results.
- The stirrer speeds (125 and 300 rpm) have no significant effect on the decolourisation during carbonatation.

CHAPTER 5

The effect of the method of lime addition on the decolourisation of melt

Introduction

At the Malelane refinery the required amount of milk of lime is added to melt in one stage. Experiments were done to evaluate whether varying the method by which the milk of lime is added, has an effect on the amount of colour removed (section 3.4.6)

5.1 Evaluation of different methods of milk of lime addition

For these tests 1,2% CaO (on brix) was added as a 10% milk of lime solution (mass/mass). The following methods of lime addition were evaluated on the same melt sample.

- Test 1 – Normal carbonatation – described in section 4.3.1
- Test 2 – The sample was limed to a pH of 9,5 , gassed to a final pH of 8,5 and the balance of the milk of lime was added and the sample re-gassed to a final pH of 8,5.
- Test 3 - Half the milk of lime was added and the sample was gassed to a final pH of 8,5 .The balance of the milk of lime was added and the sample re –gassed to the final pH of 8,5.

The results are given in Table 5.1.

Table 5.1**Different methods of milk of lime addition on melt of 1099 colour.**

Test	Colour of carbonated liquor	% Decolourisation
1	585	47
2	578	47
3	569	48

There is a 7 unit difference in colour between the carbonated liquor from test 1 (normal carbonatation) and the liquor from test 2, which indicates that the liming procedure used in test 2 does not significantly effect the carbonated liquor colour. Between the carbonated liquors from test 1 and test 3 there is 16 unit difference in the colour values, this may indicate that the liming method used for test 3 could have had an effect on the carbonated liquor colour. This difference in colour is however small (3%).

5.2 Conclusion

When compared to test 1 (normal carbonatation, described in section 5.3.1), the liming method used in test 2 (described in section 5.1) produced a carbonated liquor which was similar, while the method used for test 3 (described in section 5.1) produced a carbonated liquor which was 3 % higher in colour. This difference however is not considered to be significant. The two methods of liming (test 2 and 3) described in section 5.1, did not therefore have a significant effect on the decolourisation of melt when compared to the normal method of lime addition (test 1).

CHAPTER 6

The effect of feed colour and lime quantity on the decolourisation of melt

Introduction

At the Malelane refinery the same amount of lime is added to melt irrespective of the colour. Experiments will be carried out with varying melt colours. The amount of lime added to melt at the Malelane refinery is about 0,85 to 0,90% CaO (on brix). Experiments will be carried out to establish whether this is the optimum amount of lime. The justifications for the work done here are discussed in sections 3.4.7 and 3.4.8.

6.1 Tests on different melt colours

Three series of carbonatation tests (procedure described in section 4.3.1) were carried out using various amounts of lime added, as a 10% milk of lime solution (mass/mass). Each series was done on a melt of a different colour.

The first series of tests was done on melt of 510 colour. The amount of lime added varied from 0,4 to 3,0% CaO (on brix). All the results are given in Table 6.1.

The carbonated liquor colour results are plotted in Figure 6.1. The results indicate that as the amount of CaO was increased from 0,4% (on brix), the colour of the carbonated

liquor decreased until a CaO level of 2,4% (on brix) was reached. At this point the lowest liquor colour was achieved.

The number of colour units removed and the % decolourisation at the various CaO levels are given in Figure 6.2. The maximum colour removed (333 units) and decolourisation (65%) occurred at the lime dosage of 2,4%.

Table 6.1

Colour results of tests done on melt of 510 colour

Sample	% CaO (on brix))	Colour
Melt	0	510
Carbonated Liquor	0,4	475
Carbonated Liquor	0,8	375
Carbonated Liquor	1,2	291
Carbonated Liquor	1,6	252
Carbonated Liquor	2,4	177
Carbonated Liquor	3,0	218

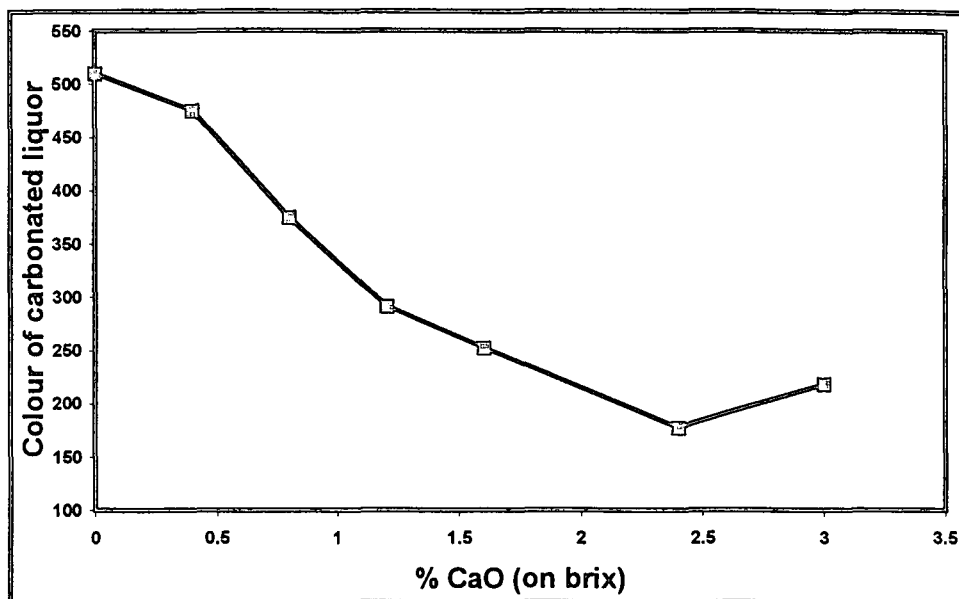


FIGURE 6.1. The effect of the quantity of CaO added to melt of 510 colour on the colour of carbonated liquor.

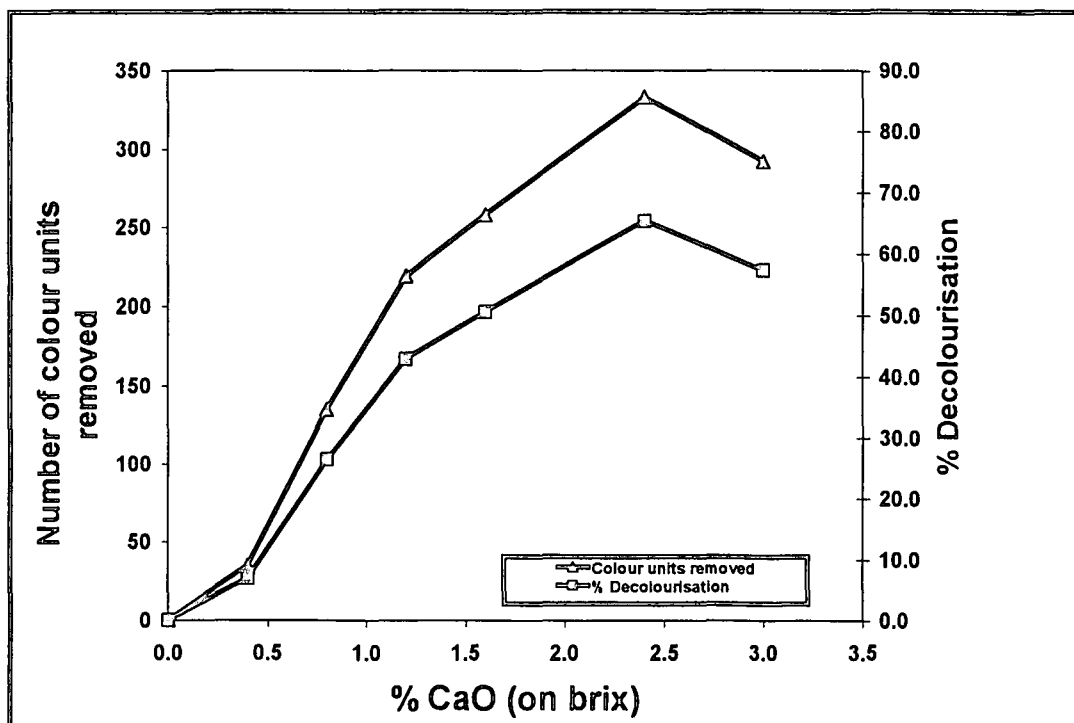


FIGURE 6.2. The effect of the quantity of CaO added to melt of 510 colour on the number of colour units removed and the % decolourisation.

The second series of tests were done on melt of 1109 colour. The amount of lime added varied from 0,5 to 2,5% CaO (on brix). The colour results are given in Table 6,2.

Table 6.2

Colour results of tests done on melt of 1109 colour

Sample	% CaO (on brix))	Colour
Melt	0	1109
Carbonated Liquor	0,5	922
Carbonated Liquor	1,0	645
Carbonated Liquor	1,5	501
Carbonated Liquor	2,0	425
Carbonated Liquor	2,5	377

The carbonated liquor colour results are plotted in figure 6.3.

The results (Figure 6.3) indicate that as the amount of CaO was increased from 0,5% (on brix) the colour of the liquor began to decrease from an initial melt colour of 1106 to a value of 377 at the CaO value of 2,5% (on brix). It would appear that the colour of the carbonated liquor was beginning to level off at the lime dosage of 2,5% but more lime (3,0%) should have been added to confirm this.

The number of colour units removed and the % decolourisation at the various CaO levels are given in Figure 6.4. As the lime addition was increased the number of colour

units increased and the maximum colour units removed (732 units) occurred at the lime dosage of 2,5% CaO (on brix). The maximum decolourisation (figure 6.4) for this test was 66%.

The third series of tests were done on melt of 1763 colour. The amount of lime added varied from 1,0% to 3,5% CaO (on brix). The results are given in Table 6,3.

The carbonated liquor colour results at the various lime dosages are plotted in Figure 6.5. The lowest carbonated liquor colour was achieved with a lime dosage of 3,0%. The number of colour units removed and the % decolourisation at the various CaO levels are given in Figure 6.6. The maximum colour units removed (924 units) and decolourisation (52%) occurred at the lime dosage of 3,0%.

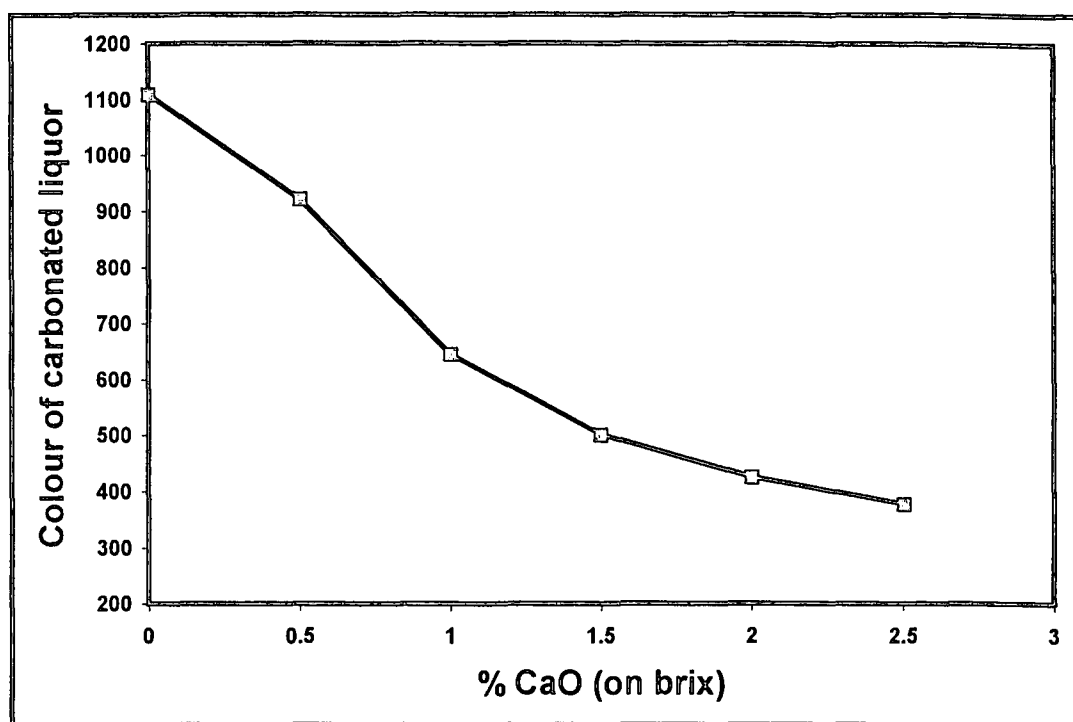


FIGURE 6.3. The effect of the quantity of CaO added to melt of 1109 colour on the colour of carbonated liquor.

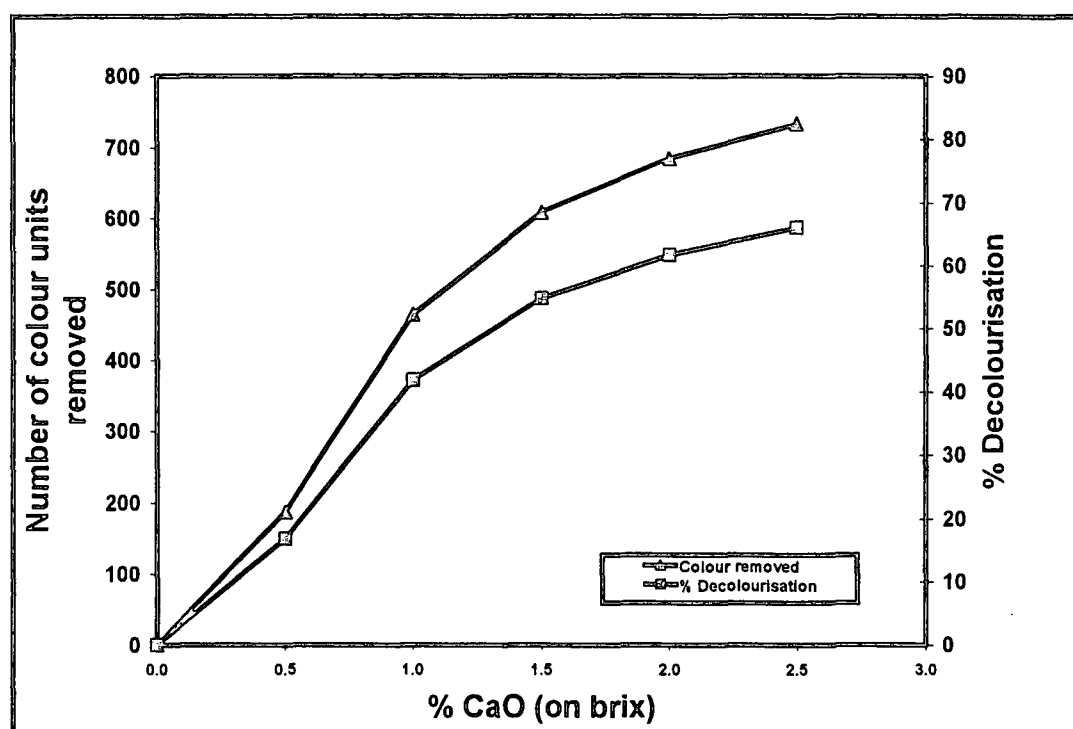


FIGURE 6.4. The effect of the quantity of CaO added to melt of 1109 colour on the number of colour units removed and the % decolourisation.

Table 6.3**Colour results of tests done on melt of 1763 colour**

Sample	% CaO (on brix))	Colour
Melt	0	1763
Carbonated Liquor	1,0	1645
Carbonated Liquor	1,5	1431
Carbonated Liquor	2,0	1107
Carbonated Liquor	2,5	896
Carbonated Liquor	3,0	839
Carbonated Liquor	3,5	889

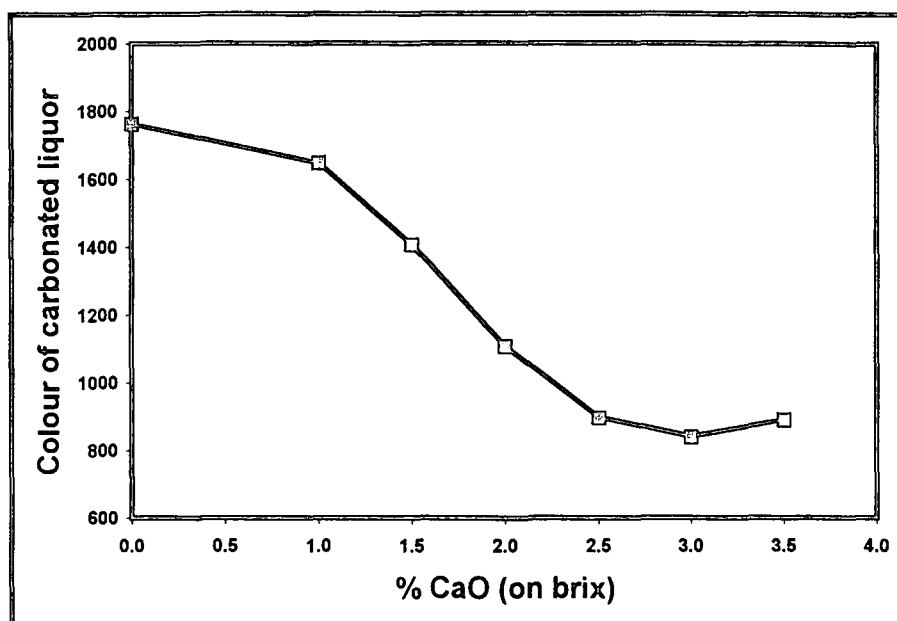


FIGURE 6.5. The effect of the quantity of CaO added to melt of 1763 colour on the colour of carbonated liquor.

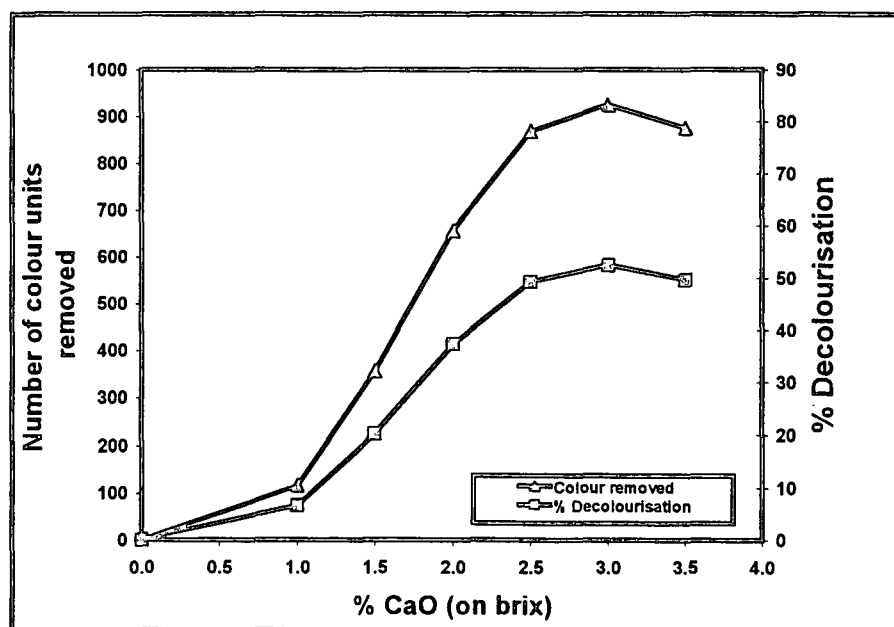


FIGURE 6.6. The effect of the quantity of CaO added to melt of 1763 colour on the number of colour units removed and the % decolourisation.

The maximum number of colour units removed for each of the three tests and the corresponding melt colours have been plotted in Figure 6.7.

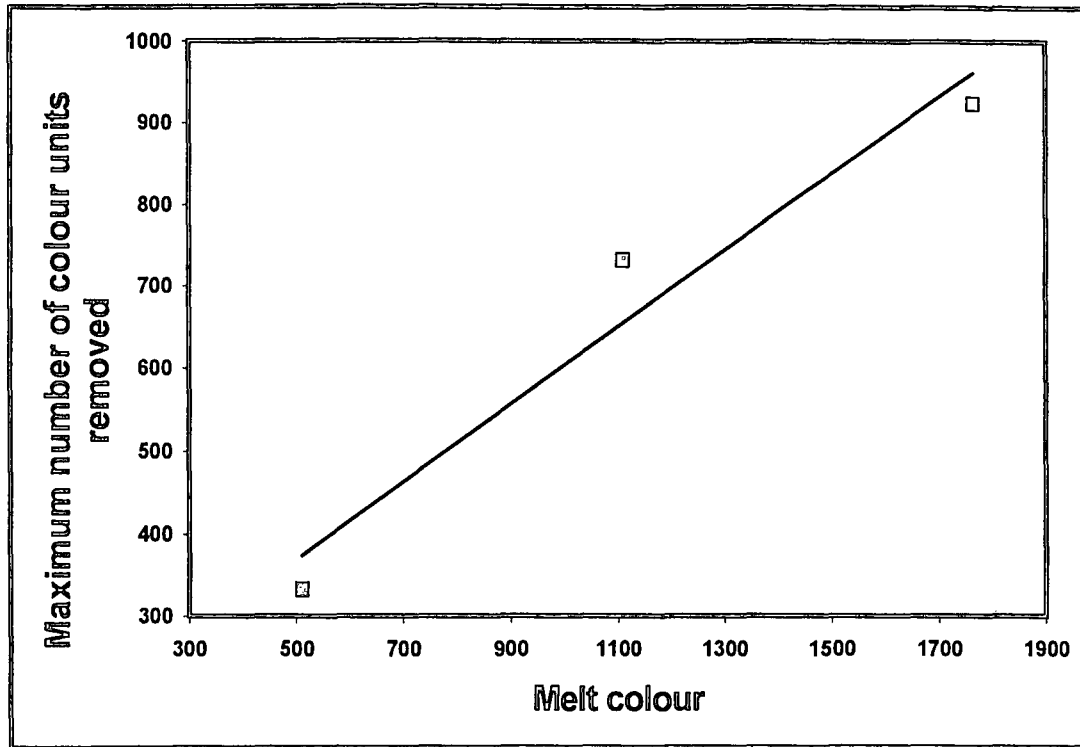


FIGURE 6.7. Melt colour versus the maximum number of colour units removed.

It can be seen (figure 6.7) that there is a strong correlation between the colour of the melt and the maximum number of colour units removed during carbonatation.

The number of colour units removed by similar amounts of lime (2,5%) for the three tests has been plotted against the melt colours in Figure 6.8. There is a good correlation between the melt colour and the number of colour units removed.

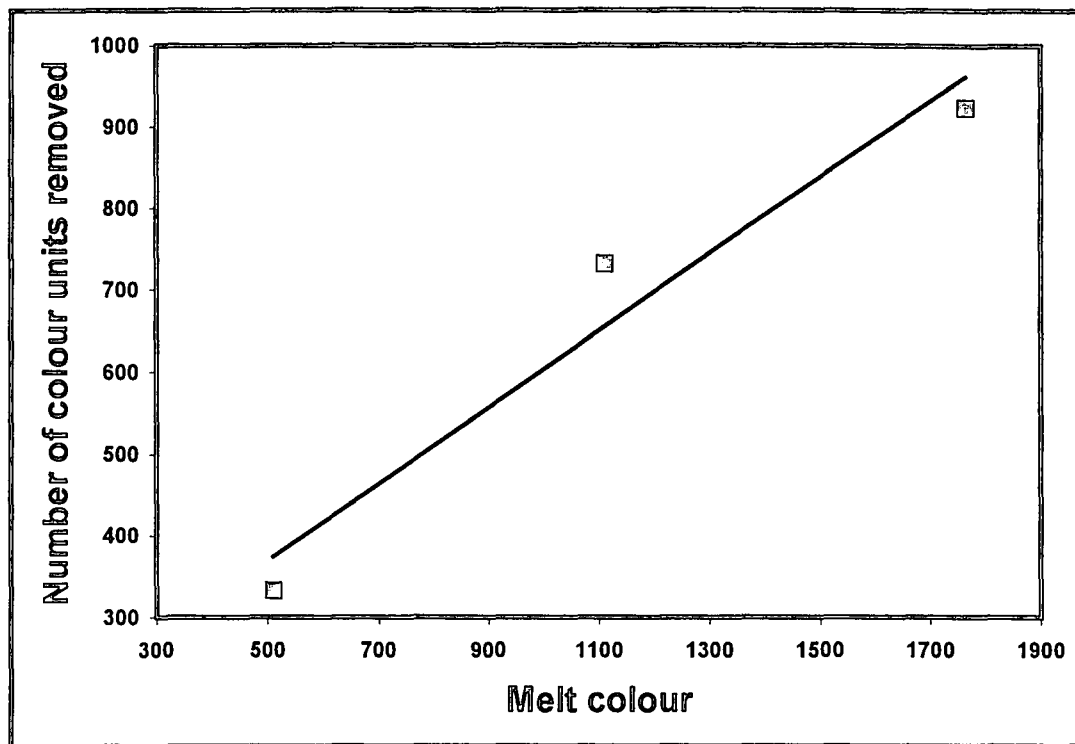


FIGURE 6.8. Melt colour versus the number of colour units removed at similar lime dosage levels.

The results of the decolourisation test done on the three different melt colours have shown that the number of colour units removed during carbonatation is dependent on the initial melt colour and the amount of lime added. The mechanism by which colour is removed by carbonatation will be discussed.

6.2 Mechanism of colour removal by carbonatation

Bennet (1972) showed that during carbonatation the impurities were incorporated into the growing crystal carbonate mainly by chemical co-precipitation. In the experiments done by Bennet a comparison was done between the physical removal of selected impurities and that obtained by the traditional carbonatation (chemical removal) process. For the physical removal tests, inert calcium carbonate was added to the liquor and the liquor was filtered and analysed. The results were then compared to those obtained by normal carbonatation tests done on the same melt sample. Some of the results mainly, colour and turbidity, are given in Table 6.4.

Table 6.4

Comparison of colour and turbidity removal by physical and chemical methods
(Bennet, 1972)

Impurity	Original	Physical	Chemical
Colour	2480	1270	630
Turbidity	312	4	1

Bennet noted that the chemical, that is the conventional formation of calcium carbonate crystal in situ, produced a much higher removal of the impurities. Yet, the inert calcium carbonate added had about ten times the crystal surface area than the chemically precipitated calcium carbonate.

Bennet (1972) used two analytical methods, namely X-ray diffraction (XRD), and X-ray fluorescence (XRF), to study the composition and nature of the carbonatation precipitates. The results showed that the crystalline pattern of the precipitated calcium carbonate was distorted by the incorporation of the impurities. Thus the impurities are chemically included inside the growing calcium carbonate crystal, and this results in efficient removal.

The findings in this chapter, namely that the number of colour units removed during carbonatation is dependent on the initial melt colour and the mass of lime added can be explained by the above mentioned mechanism of impurity removal as proposed by Bennet (1972) in that the colour bodies are incorporated into the growing calcium carbonate crystal. Therefore, the higher the melt colour and the more lime added, the better would be the colour removal. There is however a point at which the colour removal would be optimised.

6.3 Conclusions

The results of the tests done in this chapter have shown that the decolourisation during carbonatation depends on the amount of lime added and also on the colour of the melt.

At the Malelane refinery the lime added is about 0,85 to 0,90% CaO (on brix) and at this lime addition level about 45% decolourisation is achieved. The results of the laboratory batch tests done have shown that higher levels of decolourisation (up to 63%) can be achieved with the addition of more lime (3,0% CaO on brix).

The laboratory batch carbonatation tests have also shown that with higher melt colours, the same amount of lime added removes more colour units as shown in Table 6.5.

Table 6.5

Colour of carbonated liquor and the number of colour units removed from melt of different colours by similar amounts of lime

CaO% (on brix)	Melt colour	Carbonated liquor colour	Number of colour units removed
2,4	510	179	333
2,5	1109	377	732
2,5	1763	896	867

Although a larger number of colour units is removed from the melt with a highest colour (1763) by the same amount of lime, the carbonated liquor colour is too high (896) for Malelane . To produce refined sugar of an acceptable quality at Malelane the colour of the carbonated liquor should be less than 550 colour.

CHAPTER 7

The effect of final pH on colour and on calcium removals from melt

Introduction

In refinery carbonatation there are two factors that are inter – related namely impurity removal and filterability of the carbonated liquor. In this chapter the effect of final pH on colour, calcium and conductivity ash removals will be discussed. The justification for the work done here is discussed in section 3.4.9

7.1 The effect of final pH on decolourisation of melt

Batch carbonatation tests, with different lime addition rates, were done by Kelly *et al.* (1973) and the effect of final pH on the decolourisation of the melt during carbonatation was evaluated. The required amount of milk of lime was added to the melt and the carbonatation reaction initiated by bubbling carbon dioxide gas through the sample. As the reaction proceeded, sub samples of the carbonatated liquor were withdrawn at various pH values. The sample was then analysed for colour. According to Kelly *et al.* (1973), the maximum decolourisation during carbonatation occurred at pH values between 9,2 to 9,4.

Similar tests were done by Yamane (1954), in which sub samples were withdrawn at various pH values and the colour measured during the carbonatation process. The

results (Yamane, 1954) showed that the higher the final pH during carbonatation, the better the decolourisation.

Tests were therefore done to evaluate the effect of final pH on the colour of the carbonatated liquor at Malelane.

Generally at the Malelane refinery the lime added is about 0,85 to 0,90 % CaO (on brix) and at this lime addition level about 45% decolourisation is achieved. The results in chapter 6 have shown that high levels of decolourisation (up to 63%) can be achieved with the addition of more lime (3,0% CaO on brix). The possibility of increasing the lime addition at Malelane cannot currently be implemented for two reasons. Firstly, the refinery does not have the capacity to produce enough carbon dioxide gas to react with high amounts of lime (>1% CaO on brix) and secondly, the filter capacity is limited. In view of these factors most tests in this chapter have been done with the lime addition rate of approximately 1% CaO (on brix).

7.1.1 The effect of the final pH on decolourisation of melt of 1170 colour

One percent CaO (on brix) as a 10% milk of lime solution (mass/mass) was added to the melt sample, with stirring at 80°C. The limed melt was allowed to mix for a period of ten minutes. Carbon dioxide gas was then introduced into the reaction vessel and as the carbonatation reaction proceeded, 100 ml sub samples of the carbonatated liquor were taken at various pH values. The samples were filtered and analysed for colour, calcium, and conductivity ash. The colour results are plotted in Figure 7.1.

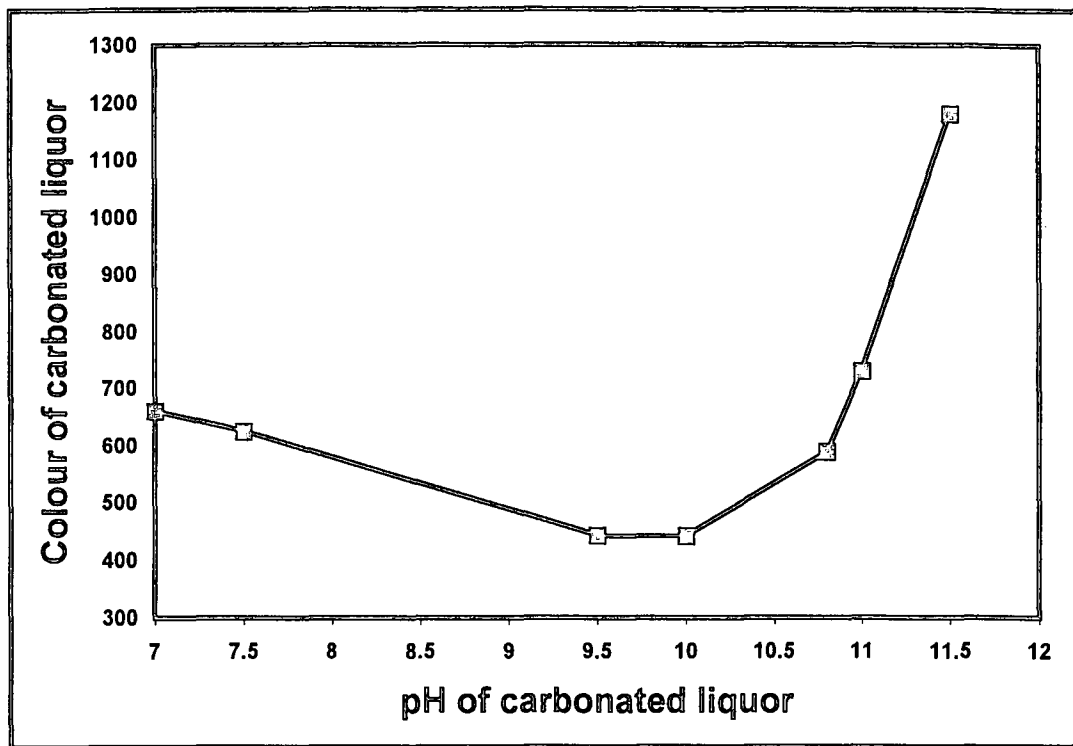


FIGURE 7.1. The effect of final pH on the colour of liquor carbonated from melt of 1170 colour.

The results indicate that the colour of the carbonated liquor decreased progressively as the pH value decreased until a pH value of about 10,0 where the colour of the liquor seemed to level off and then as the pH value decreased below 9,5, the colour seemed to increase. In this experiment the lowest colour value (441) measured occurred at a pH value of 10.

The number of colour units removed and the % decolourisation at the various pH values are given in Figure 7.2

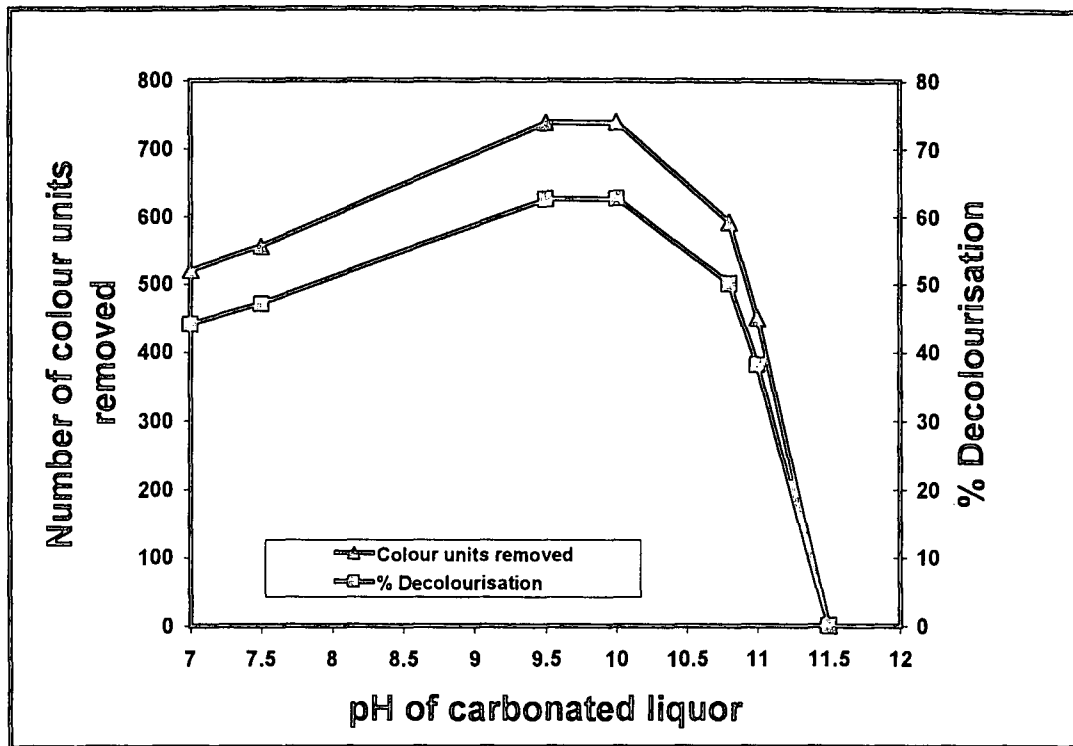


FIGURE 7.2. The effect of final pH on the number of colour units removed and the % decolourisation from melt of 1170 colour.

The maximum number of colour units removed (733) and decolourisation (62%) occurred at the pH value of 10,0. As the pH values decreased below 9,5 the decolourisation and the number of colour units removed decreased.

It was decided to repeat the experiments to confirm the results obtained in 7.1.1. The tests were done on melts of different colours.

7.1.2 The effect of the final pH on decolourisation of melt of 1326 colour.

The same experimental procedure as described in section 7.1.1 was carried out for this test. The carbonated liquor colour results are plotted in Figure 7.3.

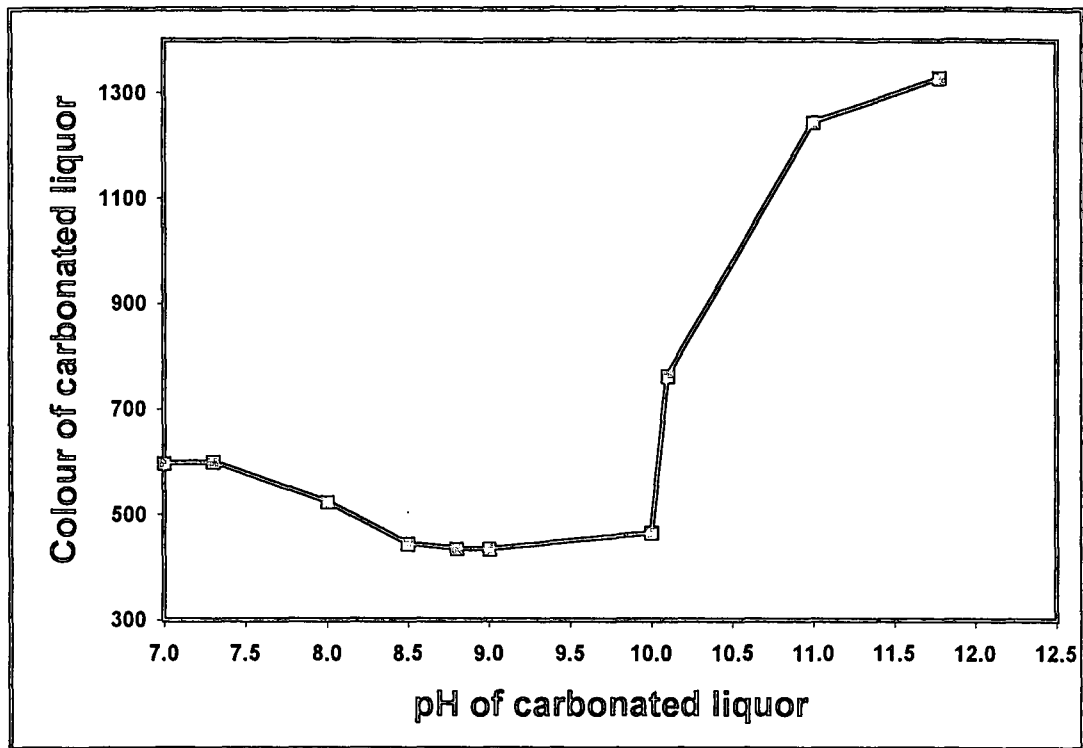


Figure 7.3. The effect of final pH on the colour of liquor carbonated from melt of 1326 colour.

Here again the results indicate that the colour of the liquor decreased progressively as the pH value decreased until a pH value of about 10,0 where the colour of the liquor seemed to level off. As the pH value decreased below 8,5 the colour increased. In this experiment, the lowest colour occurred at pH values between 9,0 and 10.

The number of colour units removed and the % decolourisation at the various pH values are given in Figure 7.4

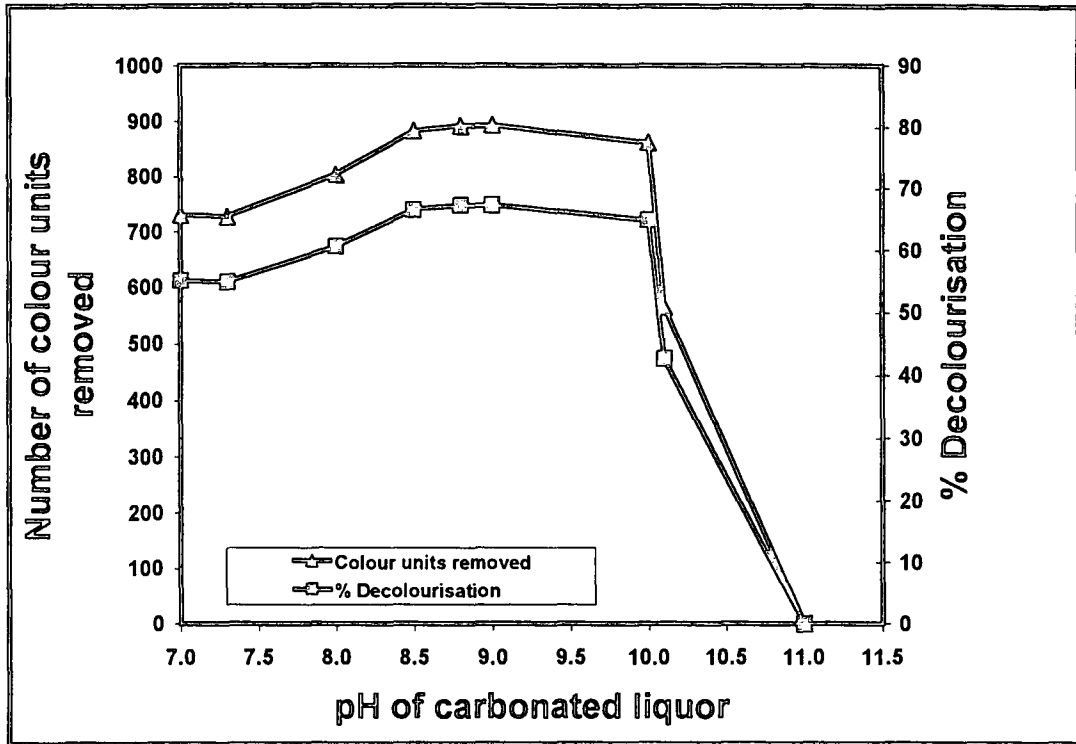


FIGURE 7.4. The effect of final pH on the number of colour units removed and the % decolourisation from melt of 1326 colour.

The maximum number of colour units removed and decolourisation occurred at the pH values between 9,0 and 10,0 and as the pH value decreased below 8,5 the decolourisation and the number of colour units removed decreased.

7.1.3 The effect of the final pH on decolourisation of melt of 1000 colour.

The same experimental procedure as described in section 7.1.1 was carried out for this test. The carbonated liquor colour results are plotted in Figure 7.5.

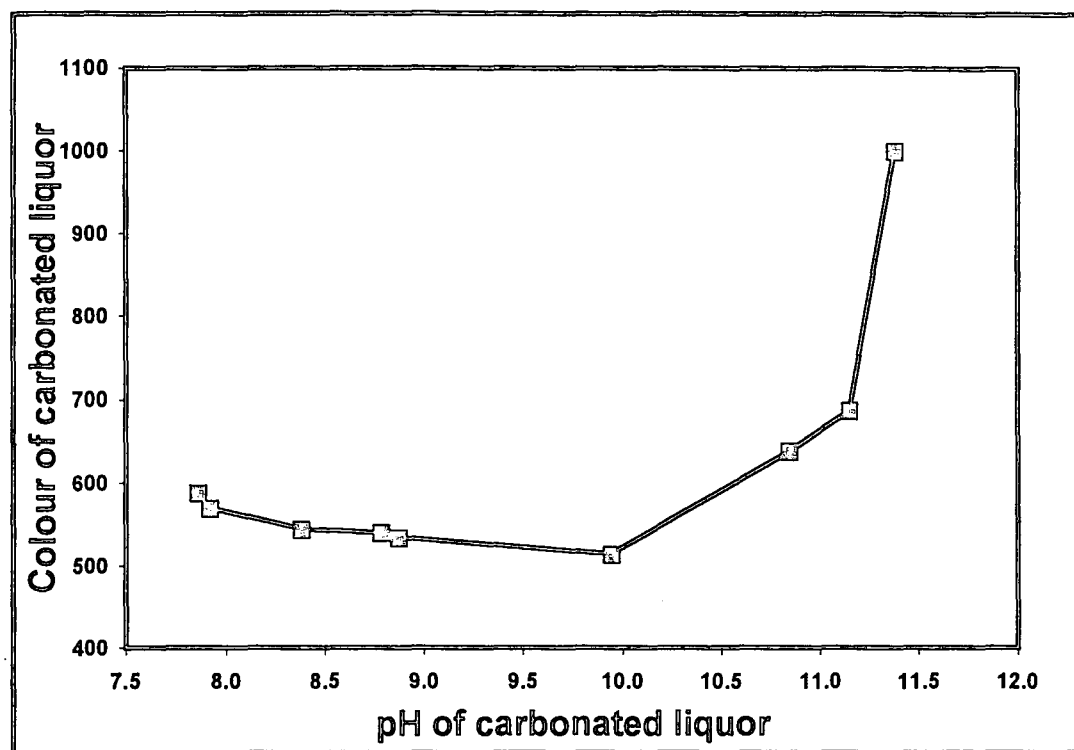


Figure 7.5. The effect of final pH on the colour of liquor carbonated from melt of 1000 colour.

The colour of the carbonated liquor decreased progressively as the pH value decreased and the lowest value was obtained at pH 9.9. Thereafter the colour of the liquor seemed to increase slightly.

The number of colour units removed and the % decolourisation at the various pH values are given in Figure 7.6. The maximum number of colour units removed and decolourisation occurred at the pH value of 9,9.

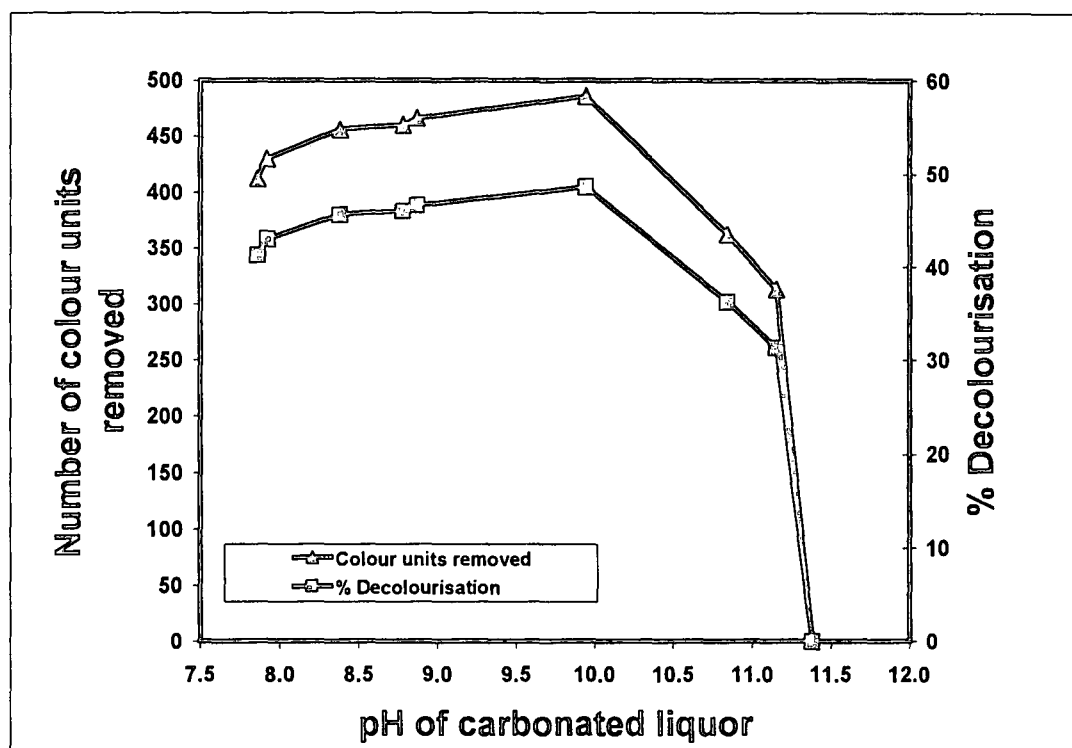


FIGURE 7.6. The effect of final pH on the number of colour units removed and the % decolourisation from melt of 1000 colour.

7.1.4 The effect of the final pH on decolourisation of melt of 1906 colour.

The same experimental procedure as described in section 7.1.1 was carried out for this test. The colour results are plotted in Figure 7.7.

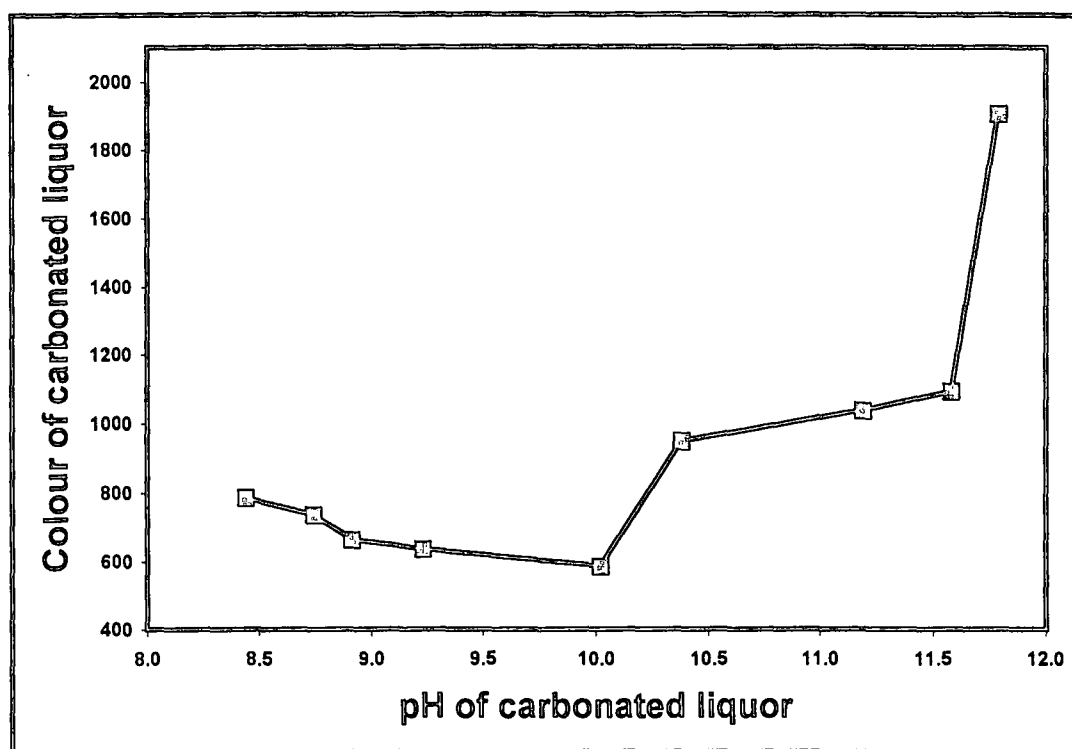


Figure 7.7. The effect of final pH on the colour of liquor carbonated from melt of 1906 colour.

The results indicate that the colour of the liquor decreased progressively as the pH value decreased until a pH value of about 10,0 where the lowest liquor colour was obtained.

The number of colour units removed and the % decolourisation at the various pH values are given in Figure 7.8 The maximum number of colour units removed and decolourisation occurred at the pH value of 10,0.

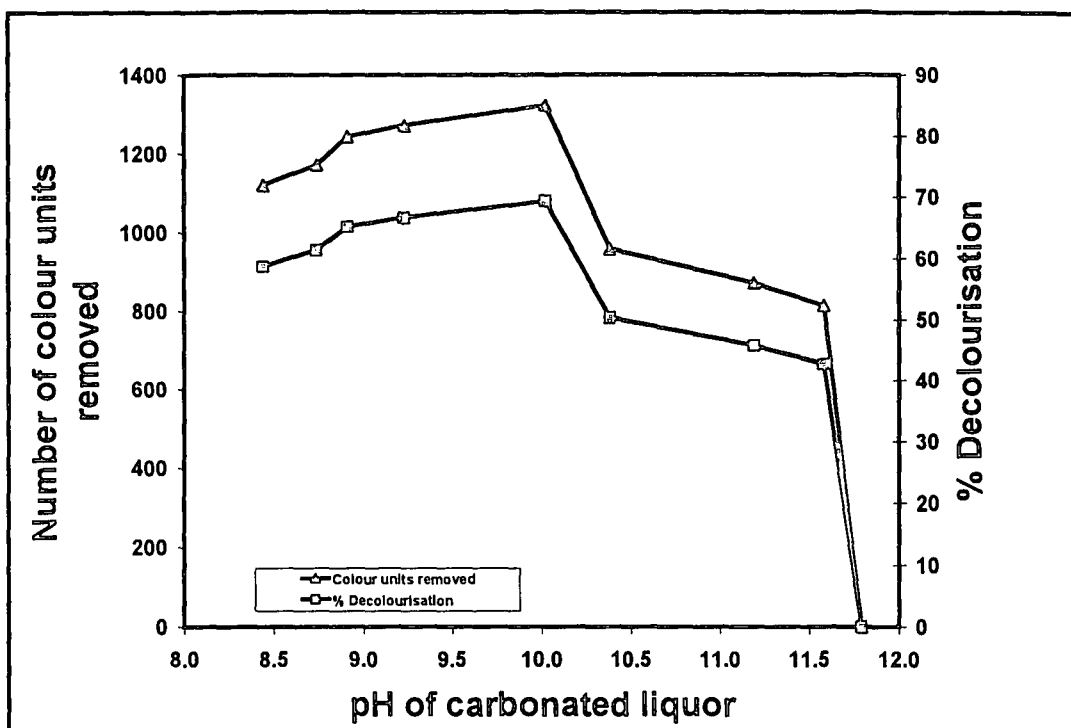


FIGURE 7.8. The effect of final pH on the number of colour units removed and the % decolourisation from melt of 1906 colour.

The lowest carbonated liquor colours and their respective pH values obtained for the tests done on the four melt colours are given in Table 7.1.

Table 7.1

**The lowest carbonated liquor colour and their respective pH values for the tests
done on the four melt samples**

Melt colour	pH value	Carbonated liquor colour	Number of colour units removed
1000	9,9	514	486
1170	10,0	441	739
1326	9,0	465	891
1906	10,0	584	1322

The results (Table 7.1) show that for three of the melt samples, the lowest carbonated liquor colour was obtained at the pH value of approximately 10 while for the fourth melt the pH value was 9. For this particular melt (1326 colour) at pH 10,0, 861 colour units were removed and when the pH was reduced to 9,0 only 31 additional colour units were removed. It can therefore be assumed that for the melt of 1326 colour, most of the colour was removed at the pH value of 10,0. These results (Table 7.1) have therefore shown that for the batch carbonatation tests performed on Malelane melt of four different colours, the lowest carbonated liquor was obtained at the final pH value of around 10.

Similar observations were made by Kelly *et al.* (1973). In their work the optimum pH was found to be 9,2 to 9,4.

Yamane (1954) working on cane juices also found that there was an optimum pH at which most of the colour is removed and when the juice was carbonated below this pH value, some of the colour bodies were desorbed.

The results of the experimental work done in section 7.1 have highlighted two points about carbonatation. Firstly, that the maximum colour is removed at the pH value of about 10 and secondly, as the liquor is gassed further, the colour of the liquor seems to increase.

An attempt will be made to try and explain these findings by using the chemistry of carbonatation.

Bennet and Gardiner (1967) studied the flocculation of calcium carbonate on a laboratory scale. In their tests, 0,5% CaO was added to melt of 65 brix and carbon dioxide was bubbled into the solution which was maintained at 75°C. As the carbonatation reaction proceeded, sub samples of liquor were withdrawn at various pH values and analysed for calcium carbonate. The results showed that the precipitation of calcium carbonate occurred (critical flocculation pH) at a pH value of 10,1 and as the pH decreased to 9,0 most of the calcium carbonate had precipitated. Thereafter, as the pH decreased, small additional amounts of calcium carbonate precipitated and the precipitation was complete at pH 8,5. Bennet (1967) also noted that the critical flocculation pH can be affected by impurities present in the melt.

Bennet (1972) has also shown that during carbonatation the impurities were incorporated into the growing crystal carbonate mainly by chemical co-precipitation. The results obtained in section 7.1 can be explained by the findings of Bennet and Gardner (1967) and Bennet (1972), in that most of the colour is removed during the chemical precipitation of the calcium carbonate crystal and this occurs mainly between pH values of 9,0 to 10,1.

The results of the tests done on the four different melt colours also seem to indicate that there is an optimum pH where most of the colour is removed during carbonatation and further addition of carbon dioxide seems to increase the colour of the liquor. This observation may be due to the bicarbonate – carbonate equilibrium where some of the colour bodies are being desorbed due to the formation of soluble calcium bicarbonate. This will be discussed further in section 7.3.

7.2 The effect of final pH on calcium removal from melt

The experimental procedure for these tests has been described in section 7.1.1.

7.2.1 The effect of final pH on calcium removal from melt of 1170 colour

The pH values and the calcium concentration of limed melt and the carbonated liquors are plotted in Figure 7.9.

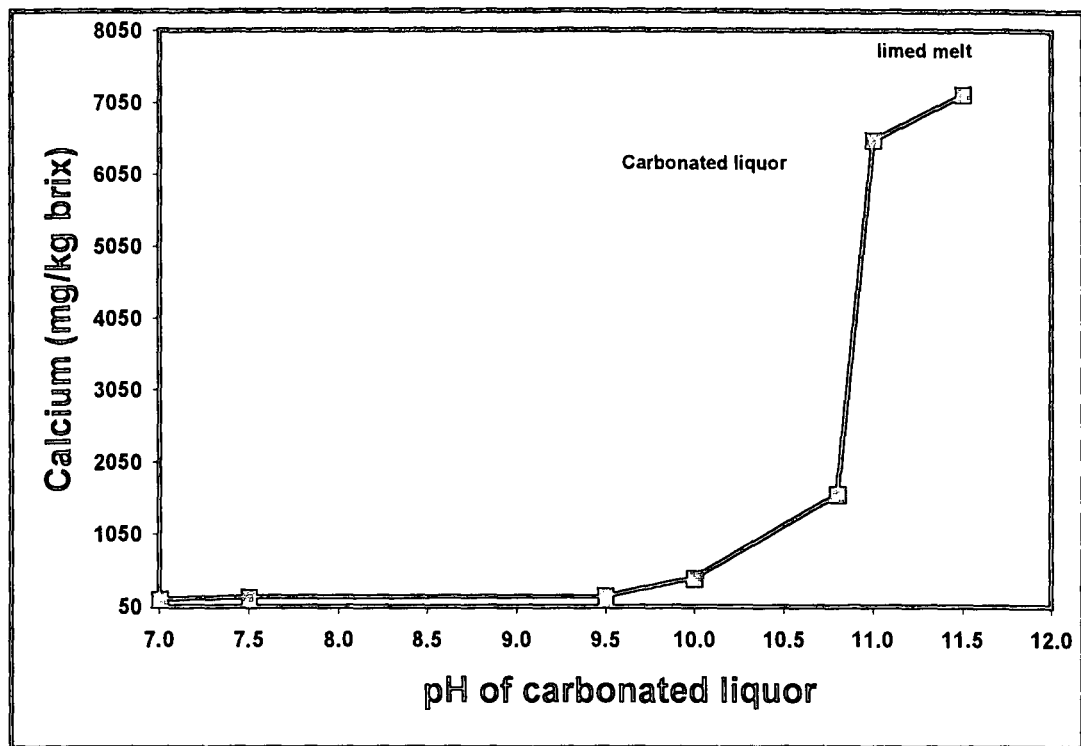


FIGURE 7.9. The effect of final pH on the calcium concentration of liquor carbonated from melt of 1170 colour.

The results indicate that most (94 to 97%) of the calcium added as milk of lime has been removed from the carbonated liquor between the pH values of 9,5 and 10,0 and small additional amounts of calcium were removed as the pH was decreased from 9,5 to 7,0.

7.2.2 The effect of final pH on calcium removal from melt of 1326 colour

The pH values and the calcium concentration of limed melt and the carbonated liquors are plotted in Figure 7.10.

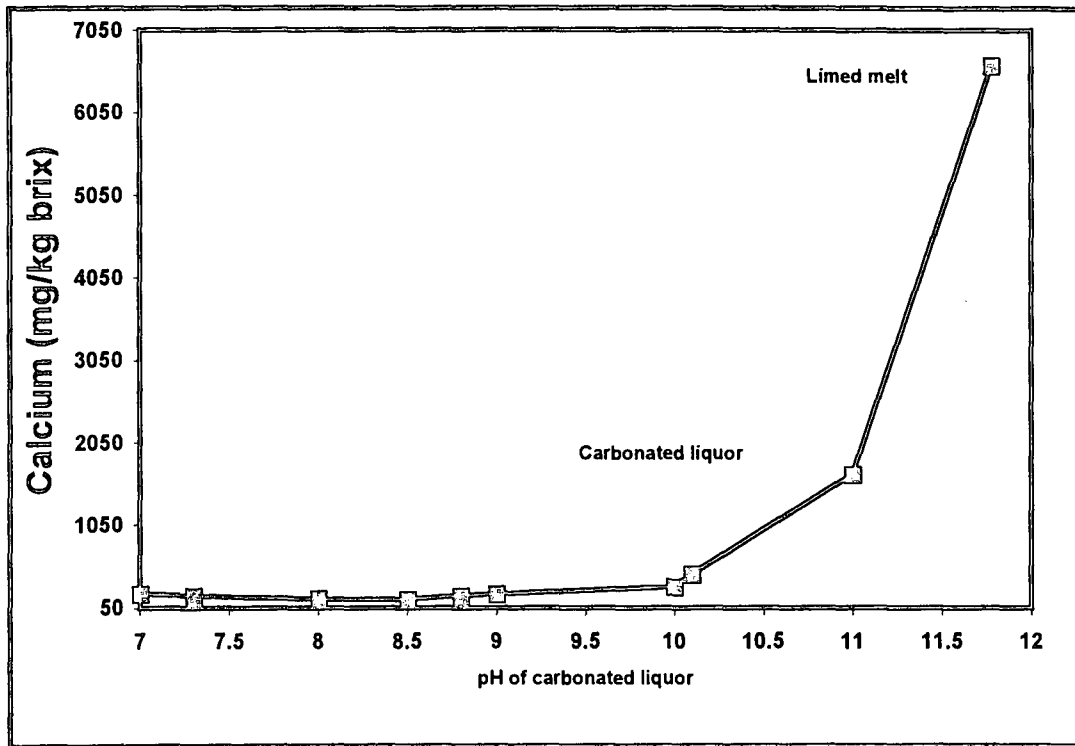


FIGURE 7.10. The effect of final pH on the calcium concentration of liquor carbonated from melt of 1326 colour.

The results also indicate that most (95 to 97%) of the calcium added has been removed from the carbonated liquor at pH values between 9 and 10 and small additional amounts of calcium were removed as the pH was decreased from 9,0 to 7,0.

7.2.3 The effect of final pH on calcium removal from melt of 1000 colour

The pH values and the calcium concentration of limed melt and the carbonated liquors are plotted in Figure 7.11.

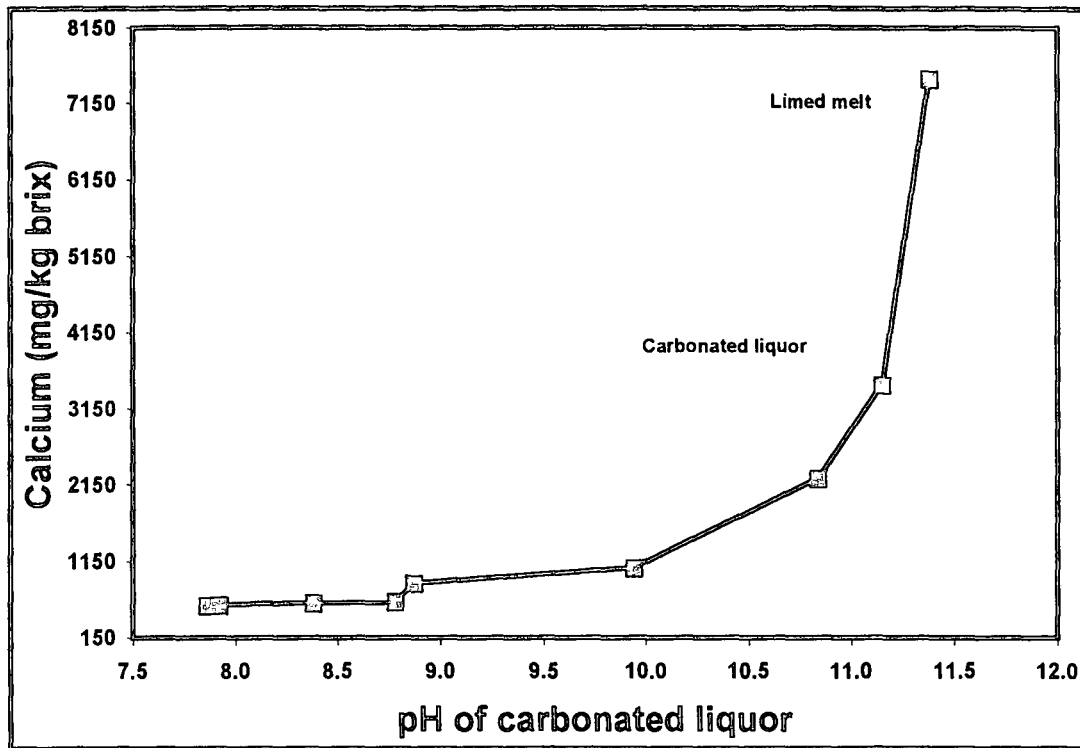


FIGURE 7.11. The effect of final pH on the calcium concentration of liquor carbonated from melt of 1000 colour.

The results indicate that most (88 to 91%) of the calcium added was removed from the carbonated liquor at pH value of 9,9 and small additional amounts of calcium were removed as the pH was decreased from 9,9 to 7,9.

7.2.4 The effect of final pH on calcium removal from melt of 1906 colour

The pH values and the calcium concentration of limed melt and the carbonated liquors are plotted in Figure 7.12.

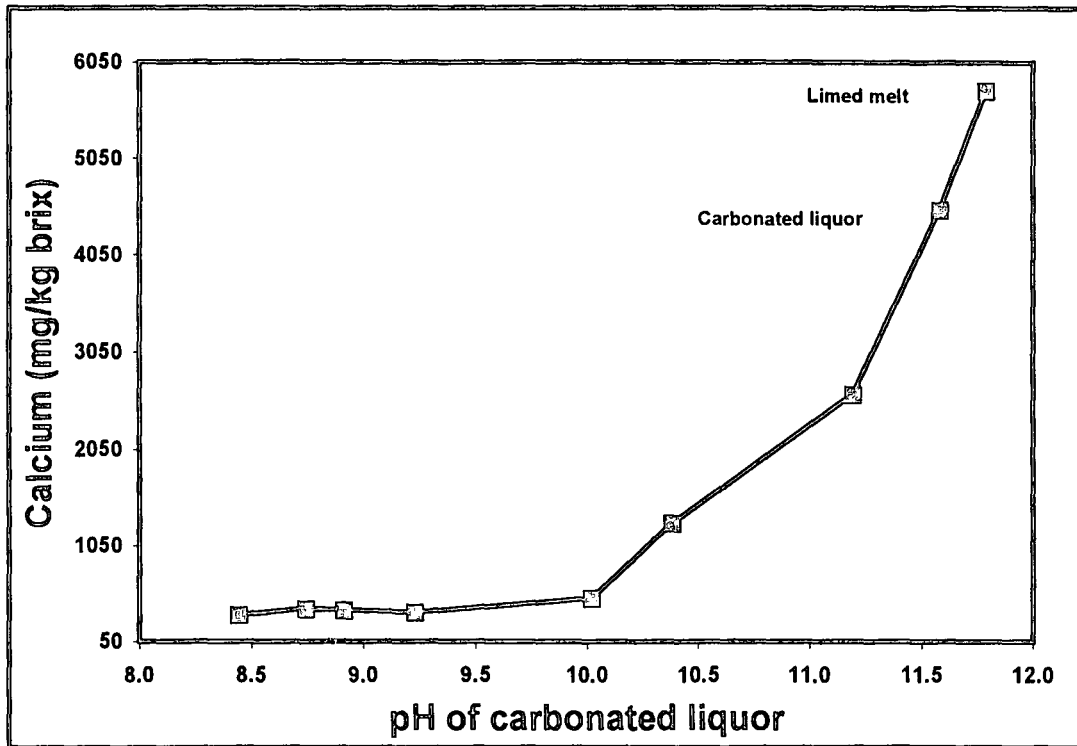


FIGURE 7.12. The effect of final pH on the calcium concentration of liquor carbonated from melt of 1906 colour.

The results indicate that most (91%) of the calcium added has been removed from the carbonated liquor at pH value of 10,0 and small additional amounts of calcium were removed as the pH was decreased from 10,0 to 8,4.

The results of the batch carbonatation tests done on the four melt samples have shown that most of the calcium added as milk of lime was removed from the liquor, between the pH values of 9 and 10 and the further reduction of the liquor pH with the addition of gas removes only small additional amounts of calcium.

7.3 The effect of final pH on conductivity ash removal from melt

The experimental procedure for these tests has been described in section 7.1.1.

The conductivity ash results obtained for the tests done on two of the melt samples (1000 and 1906 colour) have been plotted in figures 7.13 and 7.14 respectively.

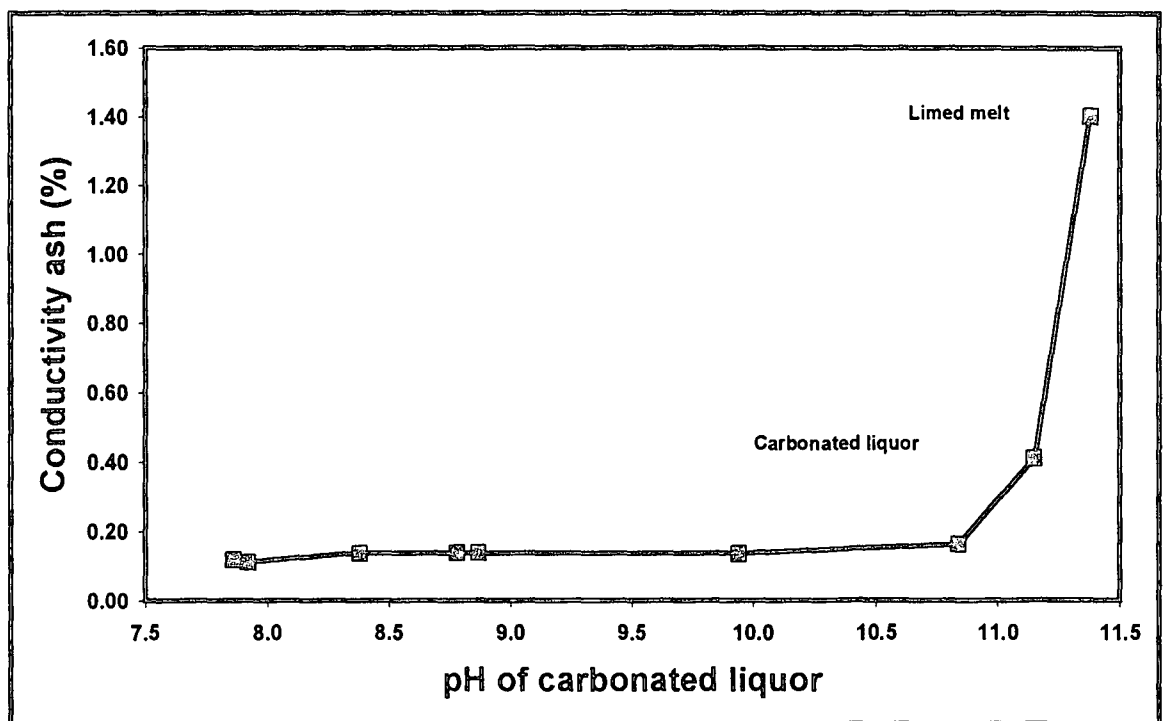


FIGURE 7.13. The effect of final pH on the conductivity ash concentration of liquor carbonated from melt of 1000 colour.

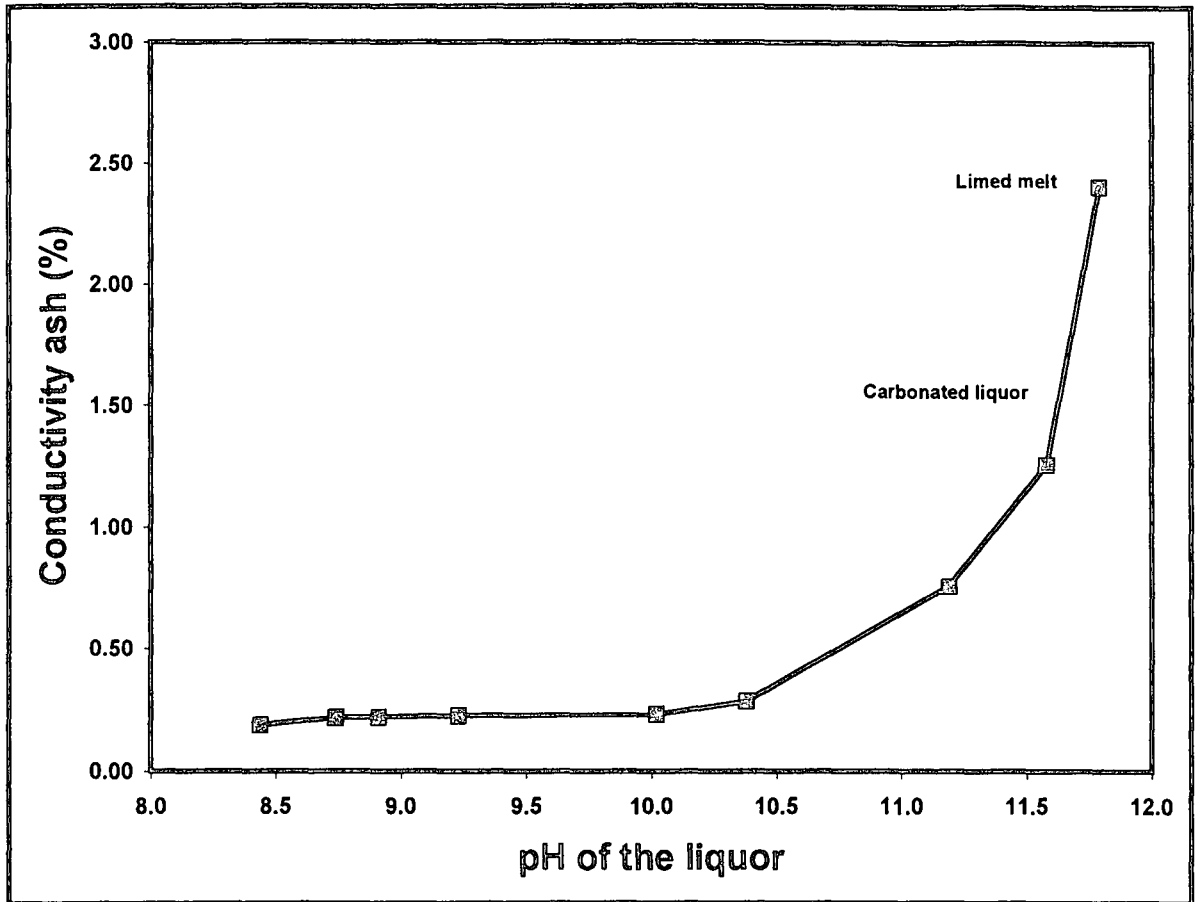


FIGURE 7.14. The effect of final pH on the conductivity ash concentration of liquor carbonated from melt of 1906 colour.

The results in Figures 7.13 and 7.14 both show that at the pH value of 10 most of the conductivity ash has been removed and that as the pH was decreased further the conductivity ash levelled off.

7.4 The effect of final carbonated liquor pH on colour, calcium and conductivity ash removals from melt

It has been observed (section 7.1) that there is an optimum pH where most of the colour is removed during carbonatation and further addition of carbon dioxide seems to increase the colour of the liquor. The relationship between pH and calcium ion concentration of any carbonated liquor according to Bennet (1974) is determined by the bicarbonate–carbonate equilibrium. The occurrence of the calcium bicarbonate reaction during the carbonatation process would be signified by an increase in the calcium content of the liquor.

The final liquor pH values and the calcium and colour results for the tests done on melts of 1170 and 1354 colour have been plotted in Figures 7.15 and 7.16 respectively. The results for these melts have been chosen because they were gassed to a lower final pH (7.0) when compared to the other melt samples (1000 and 1906 colour).

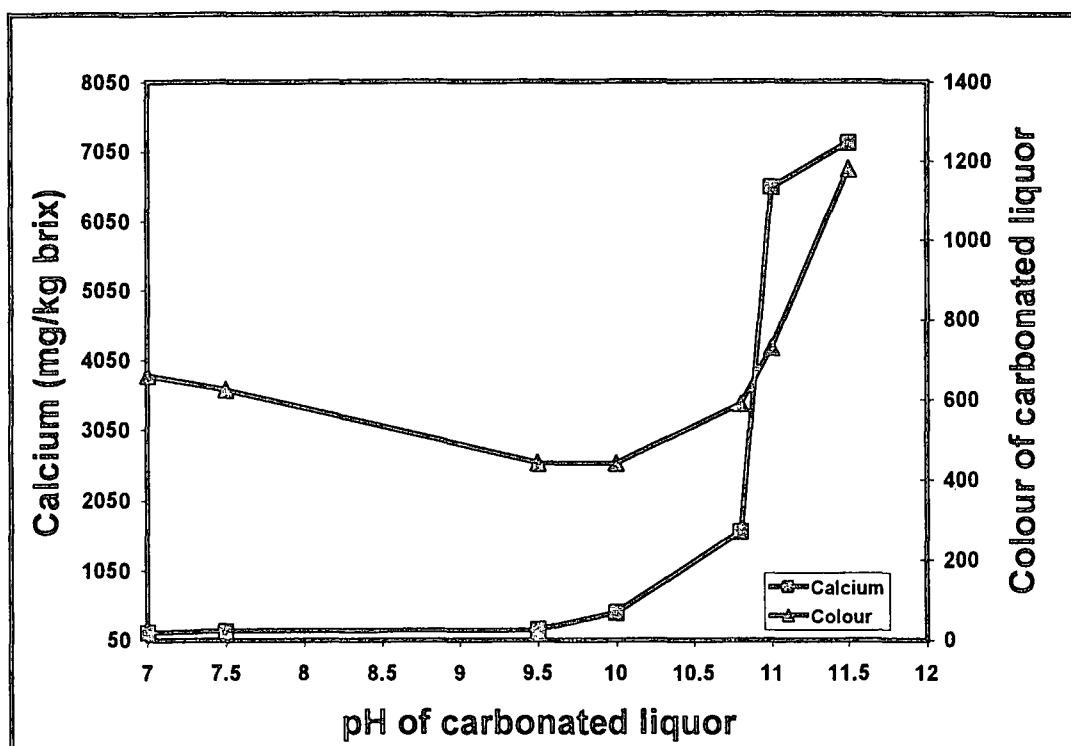


FIGURE 7.15. The effect of final pH on the calcium content and on the colour of the liquor carbonated from melt of 1170 colour.

The calcium content of the liquor (Figure 7.15) continued to decrease as the pH was lowered but the colour of the liquor began to increase as the pH value was decreased below 9,5.

The results of the tests done on the melt of 1326 colour have been plotted in Figure 7.16.

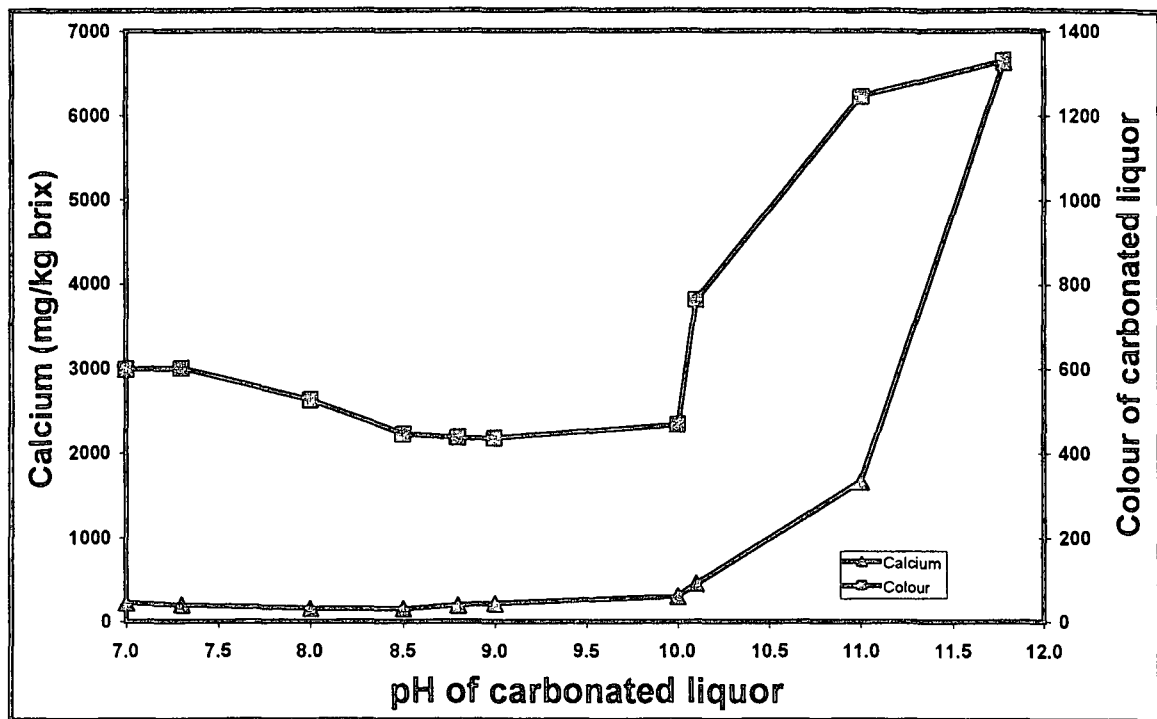


FIGURE 7.16. The effect of final pH on the calcium content and on the colour of the liquor carbonated from melt of 1326 colour.

Here again it can be seen that the calcium content of the liquor (Figure 7.16) continued to decrease as the pH was lowered but the colour of the liquor began to increase as the pH was decreased below pH 8,5.

The results (Figures 7.15 and 7.16) show no evidence of the occurrence of the calcium bicarbonate reaction.

In the literature there is no data on the effect of final carbonated liquor pH on the concentration of calcium ions in the liquor. But measurements have been done for conductivity ash.

Murray and Runggas (1975) evaluated the influence of the carbonatation reaction pH on the conductivity ash of the filtered carbonated liquor. In their tests 0,8% CaO was added to melt of 60 brix and carbon dioxide was bubbled into the solution which was maintained at 80°C. As the carbonatation reaction proceeded, sub samples of liquor were withdrawn at various pH values, filtered and analysed for conductivity ash. The results showed that the majority of the conductivity ash was removed when pH 9,3 was reached. When the pH was reduced from 9,3 to 8,7 a small amount of additional conductivity ash was removed. Thereafter the amount of conductivity ash in the liquor levelled off when the pH was reduced from 8,7 to 7,2.

At the SMRI, (Lionnet, personal communication) melt from a refinery was carbonated in the laboratory and sub-samples were removed at various pH values. The sub samples were centrifuged and the supernatant analysed for conductivity ash. The results show that most of the conductivity ash was removed at the pH value of 10. As the pH was decreased below 10, small additional amounts of conductivity ash were removed. The lowest conductivity ash value was obtained at the pH value of 7,1.

The results of work done by both Murray and Runggas (1975) and Lionnet (personal communication) showed that as the pH was reduced during the carbonatation reaction,

the amount of conductivity ash in the liquor continued to decrease until a point was reached where the amounts levelled off. There is therefore no indications of the calcium bicarbonate reaction occurring.

The present results regarding the removal of conductivity ash during the carbonatation process, shown in section 7.3, are similar to the observations made by Murray and Runggas (1975) and Lionnet (personal communication).

No reason could be found for the increase in the liquor colour when the pH was in general reduced from 9,5 to 7,0. This should be investigated further but is beyond the scope of this work.

7.5 Conclusions

The results of the tests done in this chapter have shown that the maximum decolourisation during carbonatation occurred at a final pH value of about 10. At this pH value most of the lime added to melt was removed (measured as calcium and conductivity ash) from the carbonated liquor.

CHAPTER 8

The effect of final pH on the filterability of carbonated liquor

Introduction

The results in chapter 7 indicate that the maximum decolourisation, during the laboratory carbonatation tests, occurred at the pH value of about 10. When the pH value was decreased further with carbon dioxide the colour of the liquor increased. At the Malelane refinery the final carbonated liquor pH is around 8,0 to 8,5. At these pH values according to the literature (section 1.2.1.1) the maximum liquor filterability was obtained.

Tests were therefore done to investigate the effect of final pH on the filterability of the carbonated liquor. The justification for the work done here is discussed in section 3.4.9.

8.1 The effect of final pH on the filterability of carbonated liquor

8.1.1 The theory of filtration

The equation (Murray,1972) describing filtration of an incompressible filter cake is as follows:

$$\frac{d\theta}{dV} = \frac{(\alpha_c \eta M)}{A^2 P} V + \frac{\alpha_s \eta}{AP} \quad \dots(1)$$

Where $\frac{d\theta}{dV}$ is the reciprocal of the instantaneous filtration rate $[s \ m^{-3}]$

α_c is the average specific cake resistance $[m \ Kg^{-1}]$

α_s	is the average specific septum resistance	$[m^{-1}]$
η	is the filtrate viscosity (assumed equal to the viscosity of a pure sucrose solution of the same concentration and at the same temperature)	$[Pa.s]$
M	is the mass of cake forming solids /unit volume of filtrate	$[kg\ m^{-3}]$
V	is the cumulative volume of filtrate	$[m^3]$
P	is the pressure applied	$[Pa]$
A	is the filtration area	$[m^2]$

A plot of $\frac{d\theta}{dV}$ against V , should give a straight line with the slope s ($s\ m^{-6}$) and

$$s = \frac{\alpha_c \eta M}{A^2 P} \quad \dots(2)$$

Now Bennet (1967) has defined $F(m^2)$, the filterability, as

$$F = \frac{1}{\alpha_c M} \quad \dots(3)$$

Substituting equation (3) into (2) and re-arranging

$$F = \frac{\eta}{s A^2 P}$$

$$\text{or } \sqrt{F} = \sqrt{\frac{\eta}{s A^2 P}}$$

where \sqrt{F} is the index of carbonatation filterability.

In the present work, the filtration tests were done at a constant pressure (300 kPa) and with a melt brix of 60.

Now for the filtration apparatus used here	A	$=$	$0,00353\ m^2$
	P	$=$	$300\ 000\ Pa$
	η (at 60 brix and 80°C)	$=$	$0,0052\ Pa.s$

$$\therefore \sqrt{F} = \sqrt{\frac{0,0052}{s \times (0,00353)^2 \times (300\,000)}}$$

$$\sqrt{F} = \sqrt{\frac{0.00139}{s}} \quad [m] \quad (4)$$

Where s is the slope expressed in sm^{-6}

We note that the higher the \sqrt{F} the better the filtration performance

8.1.2 Determination of the index of carbonatation filterability

The procedure that was used to carry out the filtration test has been described in detail in section 4.3.2. The method used to determine the index of carbonatation filterability will now be described, using the results (time and volume) of the first filtration test as given in Table 8.1.

Table 8.1

Results from one filtration test.

Time (θ) (s)	Volume (V) (m ³)	d θ (s)	dV (m ³)	$\frac{d\theta}{dV}$ (s m ⁻³)
22	0,00004			
54	0,00006	32	0,000020	1600000
86	0,00008	32	0,000020	1600000
128	0,0001	42	0,000020	21000000
179	0,00012	51	0,000020	2550000
236	0,00014	57	0,000020	2850000
303	0,00016	67	0,000020	3350000
380	0,00018	77	0,000020	3850000
458	0,0002	78	0,000020	3900000
545	0,00022	87	0,000020	4350000
644	0,00024	99	0,000020	4950000

A plot of $\frac{d\theta}{dV}$ against V, should give a straight line with the slope s (s m⁻⁶) and substitution of s into equation 4 will give the index of carbonatation filterability. The plot of $\frac{d\theta}{dV}$ against V, is given in Figure 8.1

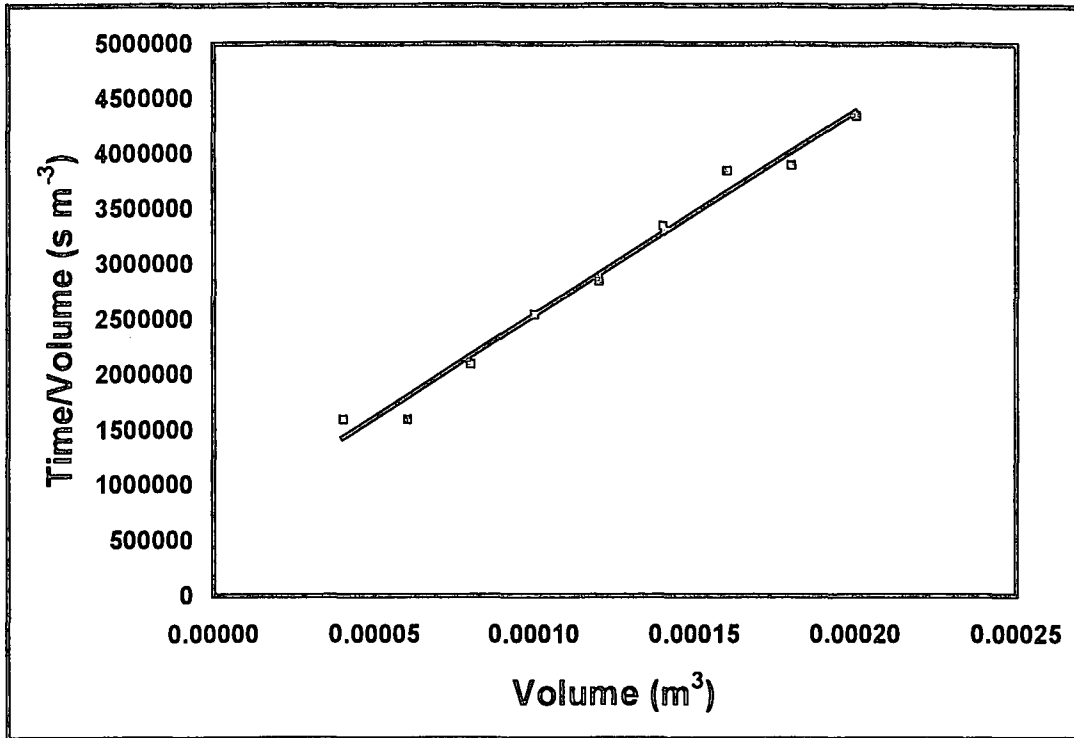


FIGURE 8.1. Plot of $\frac{d\theta}{dV}$ versus V for a sample of carbonated liquor.

The slope of the curve in Figure 8.1 is $18,5 \times 10^9 \text{ s m}^{-6}$ ($r = 0,98$) and substitution of the slope into equation 4 yields an index of carbonatation filterability of $27 \times 10^{-8} \text{ m}$.

8.1.3 Filterability tests done on liquor carbonated from melt of 938 colour

For these tests 1% CaO (on brix) was added to melt. In the first test the sample was gassed with carbon dioxide to a final pH of 9,8 and in the second test the sample was gassed to a final pH of 8,2. Filtration tests were then carried out on the samples. The

results were used to calculate the index of carbonatation filterability (\sqrt{F}). The filtered sample were also analysed for colour. The results are given in Table 8.2.

Table 8.2

Results of the filtration tests done on liquor carbonated from melt of 938 colour.

Determinand	Final pH of 8,2	Final pH of 9,8
Colour of carbonated liquor	604	483
$\sqrt{F} \text{ (x } 10^{-8}\text{m)}$	37	27

The results indicate that the carbonated liquor with the higher final pH had a lower colour (20%) than the liquor with the lower final pH. On the negative side the index of carbonatation filterability of the liquor with the higher final pH (9,8) has decreased from $37 \times 10^{-8}\text{m}$ to $27 \times 10^{-8}\text{m}$.

Filterability measurements on carbonated liquor have been done previously and some of the values obtained will be discussed and also compared with the results in Table 8.2.

Murray (1972) investigated the effects of suspended matter on the filterability of the carbonated liquor and his results are in Table 8.3.

Table 8.3

The effect of suspended matter on carbonated liquor filterability (Murray,1972).

Particles removed by ultrafiltration	$\sqrt{F} \text{ (x } 10^{-8} \text{m)}$
Unfiltered sample	32
All particles > 40 μm removed	39
All particles > 20 μm removed	40
All particles > 3 μm removed	45
All particles > 0,8 μm removed	47
All particles > 0,45 μm removed	54
All particles > 0,20 μm removed	58

The index of carbonatation filterability ($32 \times 10^{-8} \text{m}$) obtained on carbonated liquor by Murray (1972) is within the values listed in Table 8.2. The results (Table 8.3) also show that the filterability of the ultrafiltered liquor improved when compared to the unfiltered sample.

Filtration tests done on catch samples of carbonated liquor from a refinery by Lavarack (1982) have shown that for the forty two tests done, the average index of carbonatation filterability was $41 \times 10^{-8} \text{m}$ with the minimum being $26 \times 10^{-8} \text{m}$ and the maximum being $60 \times 10^{-8} \text{m}$. Values measured at Tate and Lyle refineries (Bennet, 1967) varied from 25 to 75 ($\times 10^{-8} \text{m}$).

The filterability of the liquors in Table 8.2 were therefore within the normal acceptable range. Some further tests were done on a melt of different colour to confirm the results obtained in Table 8.2 .

8.1.4 Filterability tests done on liquor carbonated from melt of 1641 colour

For these tests 1% CaO (on brix) was added to melt. The first sub-sample was gassed with carbon dioxide to a final pH of 10,0 while the second test was gassed to a final pH of 8,3. Filtration tests were then carried out on the liquors and the index of carbonation filterability (\sqrt{F}) was calculated. The results of the four series of test carried out are given in Table 8.4.

Table 8.4

Results of filtration tests done on liquor carbonated from a melt of 1641 colour.

Sample	$\sqrt{F} \text{ (x } 10^{-8}\text{m)}$	
	Final pH of 8,3	Final pH of 10,0
Test 1	37	25
Test 2	41	25
Test 3	26	29
Test 4	27	25
Average	33	26

The average results are similar to those obtained in section 8.1.2 (Table 8.2). The filterability of the carbonated liquor with the higher final pH (10,0) is lower than the

carbonated liquor with the lower final pH (8,3). The average difference in the filterability of the carbonated liquors is about 20%.

8.2 Conclusions

The results of the filtration tests (Table 8.4) have shown that there is a decrease in the index of carbonatation filterability of the carbonated liquor with the higher final pH (10,0) as compared with the carbonated liquor with the lower final pH (8,3).

CHAPTER 9

Conclusions and recommendations

The main objective of this work is given in section 3.5.1.2 and it is now possible to establish how well it has been met.

Of the factors evaluated it has now been established that the decolourisation during carbonatation is determined by the feed melt colour (section 3.5.1.2.2) amount of lime added to melt (section 3.5.1.2.3), and by the final pH of the carbonatation reaction (section 3.5.1.2.4).

- **Effect of feed colour** (section 3.5.1.2.2)

It has also been shown (section 6.1) that the colour of the melt has an effect on the number of colour units removed during carbonatation with similar lime addition rates. The addition of 2,4% CaO (on brix) of lime to melt of 510 colour removed 333 units of colour while the addition of 2,5% CaO (brix) to melt of colours 1109 and 1763 removed 732 and 867 units of colour respectively.

At the Malelane refinery to produce refined sugar of acceptable colour (< 45) the carbonated liquor colour should be less than 600 colour. It can be seen from the results in Figure 6.6, that although a large number of colour units (924) was removed from the melt of 1763 colour, the carbonated liquor colour (839) was too high for Malelane. The

melt and lowest carbonated liquor colours achieved for the tests done in section 6.1 have been plotted in Figure 9.1. It can be seen from the graph that a carbonated liquor of acceptable colour (< 600) can only be produced when the melt colour is less than 1400 colour.

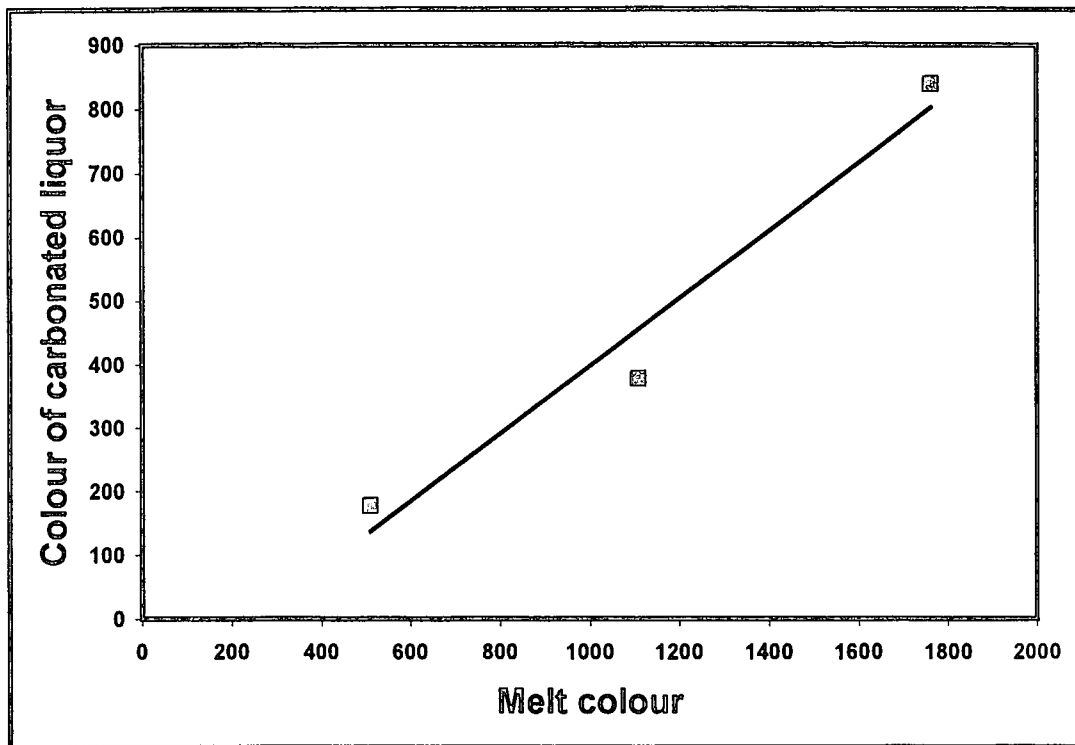


Figure 9.1. Melt and carbonated liquor colours.

- Amount of lime added

It has been shown (section 6.1) that higher levels of decolourisation can be achieved with the addition of more lime to melt. Generally at the Malelane refinery the maximum decolourisation achieved is 45% with the addition of 0,85 to 0,90% CaO (on brix). This

work has shown that up to 63% decolourisation can be achieved with the addition of 3,0% CaO (on brix). The maximum number of colour units removed and the lowest carbonated liquor colours achieved for the three melt samples at the respective lime addition rates are given in Table 9.1.

Table 9.1

Results for the three melt samples

Melt colour	% CaO (on brix)	Carbonated liquor colour	Number of colour units removed
510	2,4	177	333
1109	2,5	377	732
1763	3,0	839	924

The results in table 9.1 indicates that as the melt colour increased, more lime needs to be added to achieve the maximum colour removal.

The addition of more lime offers the benefit of more decolourisation but has the following disadvantages: -

- More carbon dioxide would be required.
- More lime required – chemical cost would increase
- Large quantities of carbonate may require additional filter capacity.
- The extra sludge formed – will increase the sugar loss.

The option of adding extra lime can be utilised during periods when the input melt colour to the refinery is high. This happens when operational problems in the raw sugar factory occur or when cane quality is poor (rainy season). Execution of this option would depend on the availability of carbon dioxide gas and on the filter capacity of the refinery.

The basic mechanism by which colour is removed during carbonatation is (section 6.2) that the colour bodies are incorporated into the calcium carbonate crystal by chemical co-precipitation. In view of this, therefore more lime would remove more colour until an optimum is reached. With higher melt colours colour removal would also be higher.

- **Final pH of carbonatation reaction** (section 3.5.1.2.4)

The results have also shown (section 7.1) that a lower colour liquor will be achieved if the carbonatation reaction is stopped at a final pH of about 10 rather than the typical pH of 8,5. Generally during carbonatation (final pH 8,5) about 40 to 45% of the colour present in the melt is removed. In this work it has been shown that up to 65% decolourisation can be achieved if the carbonatation reaction is stopped at a final pH of 10,0.

At this pH it has also been shown (7.2) that most of the calcium added as milk of lime has been removed during the carbonatation process. The four different melt colours and the percent calcium removals at similar pH values are given in Table 9.2.

Table 9.2

Calcium removal from the four melt samples at similar final carbonated liquor pH values

Melt colour	pH of carbonated liquor	% Calcium removal
1000	10,0	85
1170	10,0	94
1326	9,9	95
1906	10,0	91

The results in Table 9.2 show that between 85 and 95% of the calcium added as milk of lime has been removed at the pH value of around 10.

The results (section 7.3) have also shown that at about pH 10 most of the conductivity ash has been removed from the carbonated liquor.

The mechanism for the removal of colour, calcium and the conductivity ash at a pH around 10 has been described in section 7.1.4 and has mainly to do with the flocculation of the calcium carbonate precipitate. It was shown that the impurities are incorporated into the calcium carbonate crystal during the flocculation process, which occurs around the pH value of 10.

It was also observed (section 7.1) that when the pH was reduced to values below 9,5 carbonated liquor colour increased. Attempts have been made to find an explanation

for this phenomenon by investigating the possible conversion of the calcium carbonate to calcium bicarbonate. This conversion would release some of the occluded colour and also increase the calcium and conductivity ash of the liquor. It was shown (section 7.3) that there was no evidence of the calcium bicarbonate reaction occurring even when the liquor was carbonated to a final pH value of 7,0. Further work should be done to investigate this further.

No reason for the increase in the liquor colour when the pH was reduced from 9,5 to 7,0 could be found and no explanation is offered at this stage. This should be investigated further. It was regarded as beyond the scope of this work.

The advantages of terminating the carbonatation reaction at the final pH of 10,0 are twofold. Firstly higher decolourisation would be achieved and secondly less carbon dioxide (about 30%) would be required.

The only possible disadvantage of terminating the carbonatation reaction at the final pH of about 10 has to do with the filterability of the carbonated liquor.

The index (\sqrt{F}) of carbonatation filterability has been measured (section 8.1.2) and values of between 25 to 75 ($\times 10^{-8}$ m) have been reported in the literature. In this work the filterability measurements were done on liquors carbonated to a final pH of 8,3 and 10. The values obtained varied from 25 to 41 ($\times 10^{-8}$ m) and were within the normal acceptable range. There was a 20% difference between the value measured at pH 8,3

and pH 10. This difference however, was not considered to be significant for the Malelane refinery.

It is therefore recommended that full scale tests be done in the refinery to evaluate the effect of the high final pH (10,0), on decolourisation and the on the filterability of the liquor.

CHAPTER 10

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