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R D REPORT NO. 119

HARDENING OF RAW SUGAR

SRDC PROJECT NO. CSR8S

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FOREWORD

Australia has a long term contract to supply the Soviet Union with raw sugar. While the contract seeks to avoid delivery in the coldest months, the long transport from Black Sea ports and possible delays can lead to hardening in rail cars. The consequence would be slow unloading of rail cars, extra demurrage, and extra labour cost. The buyers claim that sugar from other sources such as Cuba does not harden to the same extent.

The work covered by this report aimed to investigate the fundamental mechanism of hardening. This has been done by examining the effect of various physical factors such as chemical analysis of sugar, crystal size and shape and the physical properties of the syrup layer on the crystal.

The result is a set of optimum quality parameters for sugar to be sold to the Soviet Union.

W.B. Clarke

for

M R Player
Chief Technologist

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The Sugar Research and Development Corporation

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ABSTRACT

The hardening or "caking" of raw sugar exported to countries with colder climates such as the Soviet Union presents a problem in the marketing of Australian raw sugar. Moisture migration, as a result of temperature differentials in raw sugar exposed to sub zero temperatures, has been recognised as the driving mechanism of this caking phenomena.

Factories in the Soviet Union do not exclusively process Australian raw sugars and it is claimed that sugars received from their major supplier, Cuba, do not present them with the same handling difficulties.

This investigation aimed to elucidate the fundamental mechanisms of raw sugar hardening, in the hope that appropriate measures can be taken to ensure acceptable handling characteristics of Australian raw sugars.

Results indicate that the solution to this problem lies in using sugar manufactured to certain specifications, in some ways mirroring the qualitative characteristics of Cuban sugar. The main areas most likely to provide some basis for improvement appear to be ;

- (i) a higher RS/Ash ratio, greater than 1. Currently Australian raw sugar RS/Ash ratios range 0.6-0.8 units;
- (ii) higher DI than currently used, greater than 40 units. Australian sugar currently averaging mid 30's to low 40's;
- (iii) larger crystal mean aperture around 1.0 mm, currently 0.6-0.8mm;
- (iv) reduced variation of crystal size i.e. lower coefficient of variation;
- (v) pol in 98.0-98.8 range, especially avoiding higher pol sugars.

Results also allow us to identify sugars possibly already manufactured to these specifications, or will allow us to ensure suitable sugars for export are produced.

Consequently, the solution relies on optimising several characteristics in order to provide some synergistic improvement to raw sugar handling characteristics.

SUMMARY

The aim of the investigation was to collect data relating to raw sugar hardening i.e. physicochemical data. The approach taken involved sampling various types of sugar from various mill regions and subjecting these samples to conditions not unlike those experienced at Soviet factories which process Australian raw sugar i.e. compacted sugar in sub-zero climates. Having done so, measurements were then taken to assess which quantifiable sugar properties have some bearing on the hardening process. Syrup centrifugally stripped from Br JA raw sugar was analysed to assess the contribution of syrup quality to raw sugar hardening. Normal raw sugar samples were also analysed including (i) Australian raws; (ii) Cuban raws and (iii) Lab manufactured raws.

The use of shear strength as a measure of hardening propensity allowed all sugars to be assessed for hardening characteristics when subjected to the same storage conditions. Karl Fischer (KF) moisture determinations allowed the investigation to assess the moisture content of raw sugar and syrup removed from that sugar.

Shear strength

A proportional relationship was found to exist between moisture in both sugar syrup and the gross sample and shear strength i.e. higher strength achieved with increased total and syrup moisture content.

DI data followed a second order polynomial function indicating sugar DI's below 25 and above 40 would be best for reduced hardening in colder climates.

The % syrup removed from the gross sugar indicated to some degree the viscosity of the syrup removed i.e. lower viscosity proportional to increased quantity of syrup removed. Results indicated sugar coated by more viscous syrups attained higher shear strength.

Larger crystal size i.e. mean aperture produces a less-efficient packed bed which attains a lower shear strength. Cuban sugars examined tended to be of large mean aperture 0.9-1.0mm. In addition, increased % fines in the samples tested resulted in increased propensity to harden. Greater variety of crystal size led to the development of greater shear strength. This was shown in sugars of certain segregated size (i.e. sieved) achieving a lower shear strength than normally distributed sugar samples.

Measurement of the quantity of material precipitated in 50% v/v aqueous alcohol from syrup removed from the gross crystal indicated a proportional relationship between the alcohol insoluble material in syrup and shear strength i.e. greater quantity of material in syrup led to increased degree of caking.

Karl Fischer Moisture determinations

Typically, KF moisture results were 0.01-0.02 units higher than conventional oven dried results, reflecting the degree of bound or trapped moisture freed during the KF determination.

Invert coated sugars

The coating of sugars with invert syrup yielded sugars which caked to a lesser extent than normal Australian raws. Cuban sugars consistently have a higher RS/Ash ratio in comparison to Australian made sugars.

Syrup purity

HPLC determinations of syrups allowed purity data to be generated for the samples examined. Results indicated a reduction in syrup purity as a function of time i.e. the exhaustion of syrup over time.

Glass transition (T_g) temperature

Glass transitions measured for 90/91, 91/92 season, invert coated sugars and their syrups indicated that sugar samples had a broader range than the syrups, but generally no major differences were noted. Invert coated sugar yielded the lowest range, reflecting the effect of a higher RS/Ash content on suppressing ice formation in the crystal syrup layer.

Moisture migration

Moisture migration trials conducted by Sydney University for inclusion in this investigation provided factual data supporting the theory that the driving force behind this migration is the result of partial pressure differentials arising from temperature and moisture differentials present in the sugar pile. The investigation highlighted that the nature of caking experienced i.e. hard/brittle or soft/sticky depended upon the magnitude of the temperature differential, the time period for which the differential existed and the initial moisture content of the sugar examined.

Ideally, sugars manufactured for the purpose of export to countries such as the Soviet union, where it is anticipated that the cargo will be subjected to sub-zero temperatures for any length of time, should address some or all of the characteristics outlined above.

The main areas in sugar quality likely to provide some improvement were found to be;

- (i) RS/Ash ratio : higher than currently available, greater than 1 desirable;
- (ii) Dilution indicator (DI) : greater than 40 units. Currently, Australian sugar DI's range mid 30's to low 40's;
- (iii) Mean aperture (MA) : larger MA required, around 1.0 mm, currently 0.6-0.8 mm;
- (iv) Coefficient of variation (CV) : reduce the present variation in crystal size;
- (v) Pol : manufacture in the 98.0-98.8 range, avoiding higher pol sugars.

TABLE OF CONTENTS

		<u>Page No.</u>
A.	Introduction	1
B.	Literature Review	2
C.	Approach to the problem	3
D.	Theory	4
E.	Experimental	5
1.0	Shear strength analyses	5
1.1	Shear strength methodology	6
1.2	Jenike Shear tester	6
1.3	Results	7
1.3.1	Time and temperature	7
1.3.2	Moisture - total sugar and syrup	8
1.3.3	Sugar dilution indicator (DI)	8
1.3.4	% Molasses removed from the sugar crystal	8
2.0	Other syrup characteristics affecting shear strength	9
2.1	Precipitate from crystal syrup in 50% v/v aqueous alcoholic solution	9
2.2	Inorganic ions in syrup coating - Ca, K, Mg	9
3.0	Karl Fischer moisture determinations	10
3.1	Experimental conditions	10
3.2	Syrup layer	10
3.3	Whole samples	10
3.4	Mettler automated Karl Fischer moisture titrator	11
3.5	Results	12
4.0	Invert coated sugars	13
4.1	Production of invert	13
4.2	Coating of Br 1 sugar with invert syrup	13
4.3	Results	14
4.3.1	Analysis of cane invert	14
4.3.2	Analysis of coated/non-coated sugars	14
4.3.3	Shear strength reduction	15
4.3.4	Pol reduction as a function of RS/Ash in syrup	15
5.0	DI Modified sugars	16
5.1	Syrup characteristics over time	16
5.2	Shear strength	17
6.0	Glass transition temperature	17
6.1	Differential scanning calorimeter	17
6.2	Results	17

TABLE OF CONTENTS (cont)

	<u>Page No.</u>	
7.0	Contribution of crystal geometry/shape to hardening propensity	19
7.1	Sugars manufactured from the same molasses	19
7.2	Crystal fraction taken from the same gross sample	20
7.3	Results	20
8.0	Humidity of storage environment	22
8.1	Adopted method	23
8.2	Humidity cabinet	23
8.3	Results	24
9.0	Moisture migration	25
9.1	Experimental conditions	26
9.2	Moisture migration	27
9.3	Results	28
10.0	Surface tension analyses	29
10.1	Adopted method	29
10.2	Results	30
11.0	Cuban Sugar & The Cuban Story	30
11.1	Shear strength	30
11.2	Syrup characteristics	31
11.3	Crystal geometry	31
11.4	The Cuban story	32
11.4.1	The USSR incident	32
11.4.2	Cuban manufacturing techniques	32
11.4.3	Quality of Cuban raw sugar	33
11.4.3.1	Consequences of a higher RS/Ash ratio	33
11.4.3.2	Crystal mean aperture (MA) and coefficient of variation (CV)	33
F.	Conclusions	34
G.	Recommendations	37
H.	Acknowledgments	38
I.	Bibliography	38
J.	Appendices	41
a.	Plot of shear strength as a function DI	

A. Introduction

Raw sugar has the ability to harden if subjected to varying temperatures and humidities, and unlike refined sugar, is encapsulated in a viscous syrup layer. The composition and physical characteristics of this syrup layer are of prime interest as it is thought to provide a means by which raw sugar can harden.

Handling problems experienced with raw sugar shipped to the Soviet Union during 1983 indicated that the sale of sugar to countries experiencing sub-zero climates may pose a problem. Raw sugar sent in 1983, the first Australian\Soviet trade of this product, became extremely hard and difficult to remove from rail wagons in which the sugar is generally transported 500 km to Kupyiansk, but is also transported some 3000 km to distant destinations in the Kazakhstan and Kirgiz regions (see Fig 1), and to Vladivostok in the east (not shown).

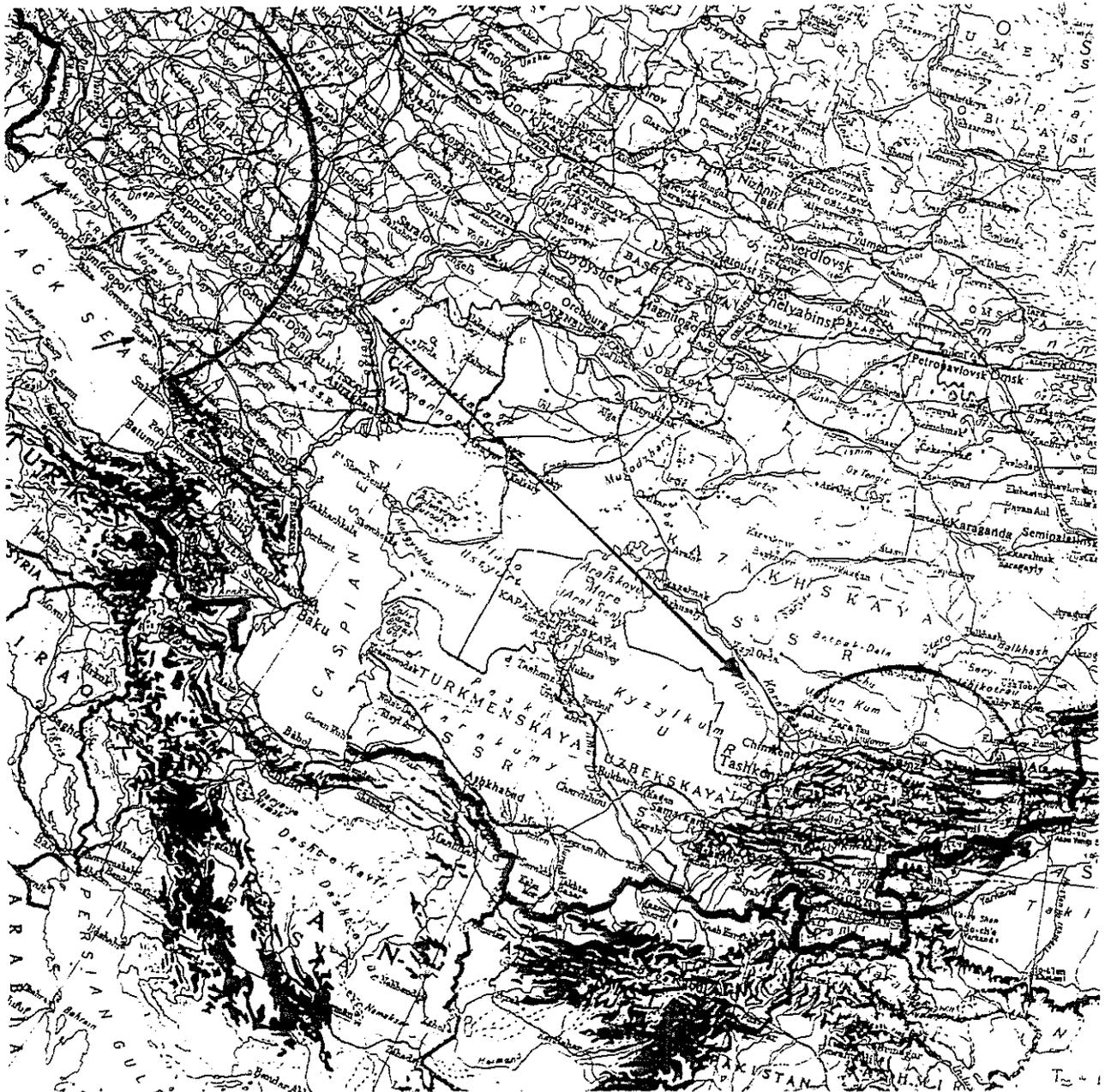


Figure 1 - Map indicating the location of commonly used ports and raw sugar destinations in the Soviet union :

0 800 km

Not only is Australian raw sugar targeted as having unfavourable handling characteristics in cold climates, it is also claimed that Cuban raw sugar does not present the Soviet's with the same handling problems.

The solution therefore lies in :-

- i) selecting suitable sugars which have acceptable handling characteristics in sub zero climates or;
- ii) manufacturing such sugars.

In order to do this, it is necessary to qualify what makes a "good" sugar in terms of ease of handling in sub-zero climates, and to assess how these characteristics contribute to the overall hardening process. Currently, raw sugar sent to the Soviet union is selected on information gained from previous investigations.

B. Literature Review

As early as 1923 (Duker), hardening or 'caking' of raw sugar has been observed and its causes sought. Although investigations into the hardening of raw sugar continued for another five decades, the 1983 Soviet hardening issue highlighted the need to refocus efforts in this field.

Initially, small sample compaction/shear strength testing (Anon, 1984) was conducted to determine whether some sugars were more susceptible to hardening than others. Results seemed to indicate that higher pol sugars had a lower strength than Br JA sugars. Full scale refrigerated rail car tests then revealed this to be false as a result of moisture migration from the bulk of the sugar to the walls of the transport containers. Following research then recognised the role of moisture migration as being the reason for sugar at the centre of a transported bulk sample becoming hard, dry and dusty. Vender (1984-85), simulating Soviet steel grain wagon conditions, in which one tonne sugar samples could be vibrated, compacted and cooled down to -10°C , reproduced the hardening effect.

As high pol varieties became solid and brittle during transportation in cold environments as a result of moisture migration, and low pol sugars also suffered from handling difficulties in the colder climates, it was believed that some optimum pol could be used to overcome the effect achieved by both extremes. However, a range of sugars tested with polys falling between Br 1 and Br JA (Vender, 1984-85) could not continually produce the required performance to accommodate the demanding Soviet conditions.

Cuban sugars, considered to be superior to Australian raws in terms of ease of flowability in cold climates, were analysed and small scale laboratory results reflected this. It is notable that the brix, purity and reducing sugars (RS) percent impurity were generally higher for Cuban sugars than Australian sugars. Crystal size and size distribution also differed for Cuban sugars which may influence their behaviour. Saito et al (1963) found that Cuban raw sugars had a higher calcium content, while Australian raw sugars had higher potassium and magnesium levels.

Wright et al (1987) investigated the possibility of coating raw sugar with invert sugar in order to alleviate the hardening propensity of Australian raws. Results indicated that partial invert coating may provide some solace in providing a solution to the hardening problem. As results were obtained under small scale conditions, it is thought that confirmation should be obtained on a full scale basis.

Other attempts using anti-caking agents to alter hardening propensity of sugars were made. A series of surface active agents applied at low dosages were tried but with little success (Dibella, 1984). The only additive considered to be of any use was the addition of reducing sugar. It is thought that the solubility of sucrose in the sucrose\RS\water system is reduced, thus reducing the tendency of sucrose crystallisation from that system.

Noble (1986) examined the surface appearance and structure of sugar crystals via electron microscopy. Australian, Cuban and Brazilian sugars were examined under varying compression and freezing conditions. Although the crystal bridging was noted in Australian but not Cuban sugar, contradictions with previous pol vs strength data in addition to the scale of the testing, led some members of the Raw Sugar Quality Technical Committee (RSQTC) to believe the test gave misleading results.

Neskovski (1988) in his investigation prepared suitable containers to be used in conjunction with a high speed, temperature controlled centrifuge allowing the removal of the syrup coating from raw sugar.

C. Approach to the problem

The aim of this investigation was to examine the fundamental mechanism(s) of raw sugar hardening. To do so, several physico-chemical characteristics of raw sugar were measured as a function of (i) time; (ii) storage conditions; (iii) sugar syrup and crystal physical and chemical characteristics.

Raw sugar samples were taken from both 90/91 and 91/92 seasons, as well as Cuban samples and samples manufactured in a small scale pan.

Raw sugar characteristics were quantified using the following analytical techniques;

- (i) shear strength - providing a measure of the hardening propensity of raw sugar under various climatic conditions i.e. temperature, humidity;
- (ii) general sugar analyses - both physical and chemical properties;
- (iii) Karl Fischer moisture determinations - allowed moisture determinations of syrup removed from raw sugar and total sugar moisture;
- (iv) Glass Transition temperature - to establish whether the test provided an indication for sugars with low propensity to harden;
- (v) HPLC determinations - to assess syrup purity information as a function of time;
- (vi) AAS determinations - to assess contribution of selected inorganic ions to raw sugar hardening.

Therefore, the investigation concentrated on specific, quantifiable parameters of the sugars examined and assessed these parameters in terms of their effect upon raw sugar hardening. Having determined which characteristics could be cost-effectively modified to achieve the desired result, specifications for such sugars were formulated.

D. Theory

The mechanism by which raw sugar hardens is moisture migration through a mass of sugar. Raw sugar is a medium through which heat is conducted and moisture migrates via molecular diffusion. Heat conduction has been expressed by Fourier law (Vender, 1989, c) as;

$$J_T = J_{T,x} + J_{T,y} + J_{T,z} = -\left(\frac{\partial kT}{\partial x} + \frac{\partial kT}{\partial y} + \frac{\partial kT}{\partial z}\right) \quad (1)$$

$$= - \text{grad} (kT) \quad (2)$$

and moisture migration in the form;

$$J_m = J_{m,x} + J_{m,y} + J_{m,z} = -\left(\frac{\partial DC_V}{\partial x} + \frac{\partial DC_V}{\partial y} + \frac{\partial DC_V}{\partial z}\right) \quad (3)$$

$$= - \text{grad} (DC_V) \quad (4)$$

where ;

- C_V = concentration of water vapour, kg m^{-3} ,
- D = diffusivity, m^2s^{-1} ,
- J_m = flux of diffusing vapour, $\text{kg m}^{-2}\text{s}^{-1}$,
- $J_{m,r}$ = components of vector J_m , $r=x,y,z$, $\text{kg m}^{-2}\text{s}^{-1}$,
- J_T = flux of heat, kW m^{-2} ,
- $J_{T,r}$ = components of flux J_T , $r=x,y,z$, kW m^{-2} ,
- k = thermal conductivity of bulk sugar, $\text{kW m}^{-1} \text{K}^{-1}$,
- T = absolute temperature, K ,
- x,y,z = coordinates of a point in the sugar body, m .

It is generally accepted that the driving force of a rate process is given by a difference of activities, and in the case of water vapour in bulk sugar, this can be replaced by (say) partial pressures of the gaseous phase. As the concentration of water vapour (C_V) in the bed has been shown to be dependent upon bed porosity (Vender, 1989, c), water diffusion through the bed will also be dependent upon bed porosity, which in turn is a function of crystal geometry.

$$C_V = \epsilon \frac{M_W}{RT} P_W \quad (5)$$

where;

- M_W = molecular weight of water = $18.015 \text{ kg mol}^{-1}$
- P_W = partial pressure vapour, kPa
- R = gas constant = $8.31439 \text{ kJ kmol}^{-1} \text{K}^{-1}$
- ϵ = porosity (void fraction) of sugar bed, dimensionless.

As water concentration differences may occur throughout the bed as a result of partial pressure differences, it is necessary to refer to a single point in the bulk, using x, y, z coordinates of that point as in the equations above.

If for example, a container of sugar subjected to adverse temperature changes will aim to attain equilibrium by redistributing the moisture within the bulk. If for example the container is subjected to sub-zero temperatures, moisture will migrate from the warmer regions closer to the centre of the bulk to colder regions near the walls of the container. History has shown (Player, 1985) that in doing so, the warmer region, now deficient in water, becomes hard and brittle whilst the colder regions become wet and sticky (see Fig 2).

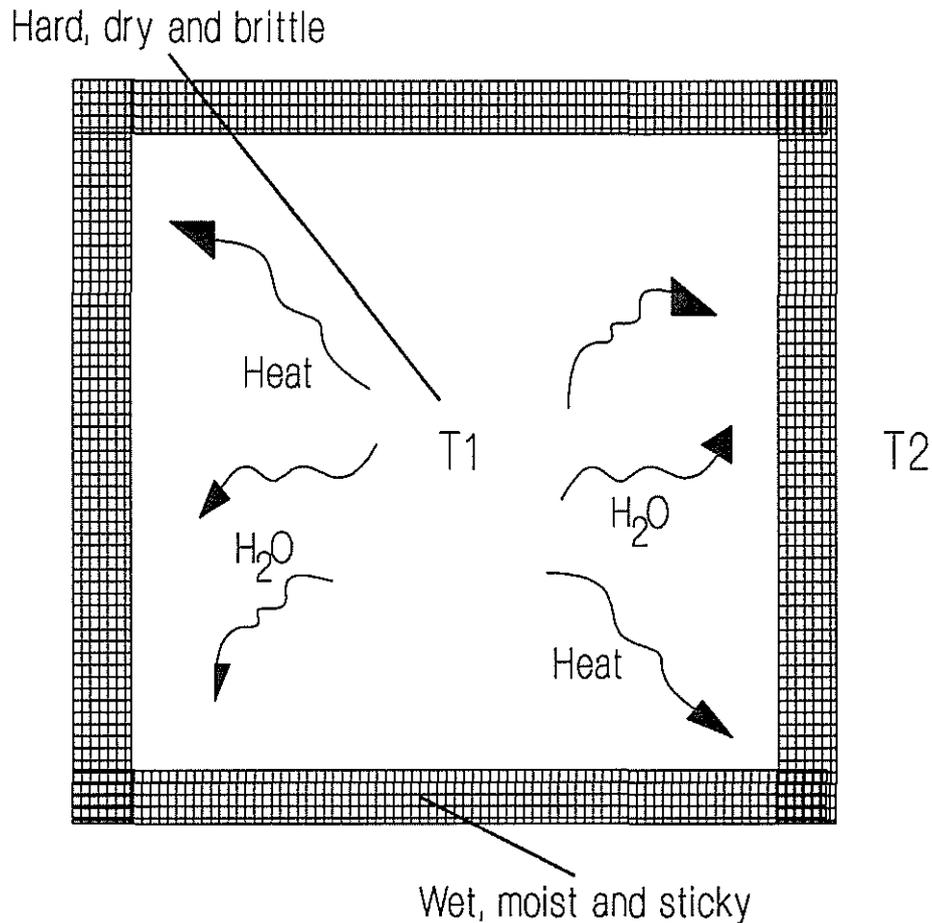


Figure 2 - Schematic representation of moisture migration in a gross sample of raw sugar subjected to sub-zero temperatures, $T_1 > T_2$.

As a consequence, the sugar is difficult to handle, expending energy and man hours to start the sugar flowing again if at all.

Migrating moisture therefore has the task of moving from one region to another in the bed, relying on the properties of the sugar in the packed bed to enable such transfer, and depends upon such factors as (i) concentration of water vapour; (ii) thermal conductivity; (iii) temperature differentials of the bulk sugar.

E. Experimental

1.0 Shear strength analyses

The measurement of shear strength involves applying a horizontal load across the sample and recording the maximum shear force achieved in the process. Determinations were conducted as per documentation recommendations (Wiche, 1989), with samples maintained at both $+5^{\circ}\text{C}$ and -10°C in order to assess the effect of varied climatic conditions on the hardening of raw sugar, similar to those conditions experienced at Soviet union factories.

In order to assess raw sugar hardening characteristics of aging sugar, six sugars were sampled from the 1990/91 season and analysed over a 45 week period. Initially, analyses were performed weekly to ascertain whether the sugars underwent any changes in composition and/or physical characteristics. This was then followed by fortnightly then monthly analyses as the sugar aged over the duration of the investigation. In addition, 91/92 season sugar was sampled and analysed as per 90/91 season sugars over the remainder of 1991.

1.1 Shear strength methodology

Each sample was analysed as outlined below, weights and equivalent loads placed on the cells appear in Table I.

TABLE I - Shear cell preconsolidation, consolidation and shear loads (in kg)

Condition	Small cell $\text{Ø} = 6.5\text{cm}$	Large cell $\text{Ø} = 9.5\text{cm}$
Preconsolidation	4.5	9.1
Major Consolidation	6.4	12.8
Shear	5.0	9.5

NOTE : Small cells were used for -10°C work, large cells for $+5^{\circ}\text{C}$ work.

Preconsolidation - a procedure whereby each sample cell is subjected to the same vertical force in order to prepare uniform samples for testing.

Consolidation - having preconsolidated the sample cell, each cell is sheared causing the material to flow under consolidating stresses until a steady-state condition is reached i.e. constant stress as function of time.

Major consolidation load - a desired load is placed on the cell for a desired period of time. This step endeavours to simulate the sample as if it were under loaded conditions e.g. sugar at the bottom of a large pile. In this investigation, the major consolidation load was applied for 24 hours prior to shearing.

Shearing - the final stage which involves applying a horizontal load across the sample until a maximum shear force is reached.

1.2 Jenike Shear tester

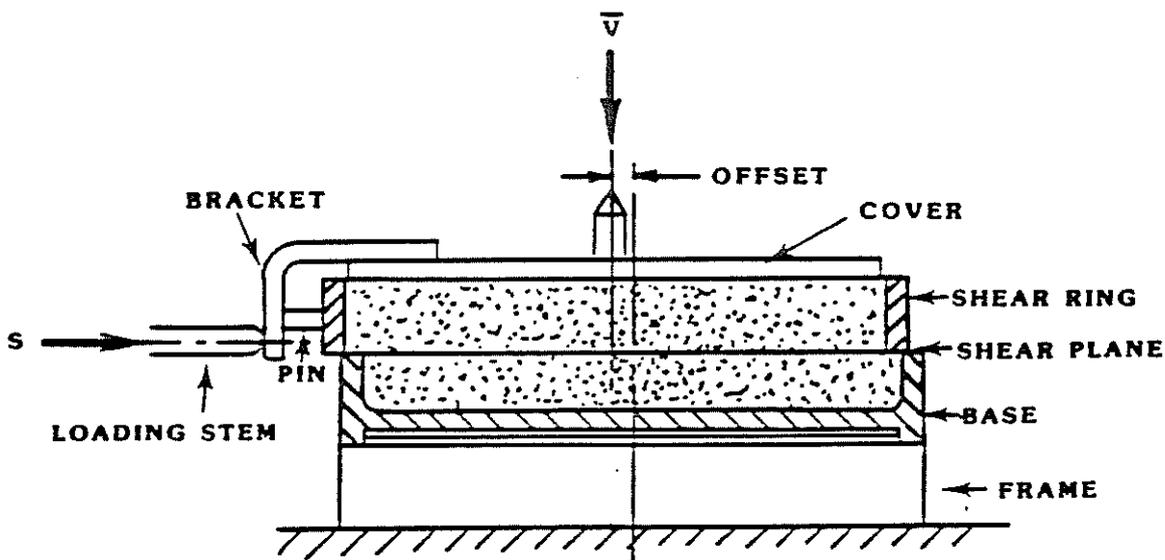


Figure 3 - Jenike Shear Tester cell indicating direction of applied loads

The Jenike shear testing (JST) machine delivers a load across a sample cell, containing the material under investigation, by means of an electro-mechanically driven stem moving horizontally at a constant rate (see Fig 3). The shear force is measured by a strain gauge load cell incorporated in the instrument, and allows for output to a chart recorder or similar voltage recording device.

1.3 Results

The chief method of analysis chosen for the investigation was shear strength, as the technique provided the best indicator for the hardening propensity of raw sugar. Note, a higher value for shear strength obtained equates to greater degree of hardness.

1.3.1 Time and Temperature

For 90/91 season sugar, fluctuations occurred in shear strength as a function of time suggesting that after some 30 weeks storage at a bulk sugar terminal, raw sugar strength reaches some stable strength relative to each sugar (see Fig 4).

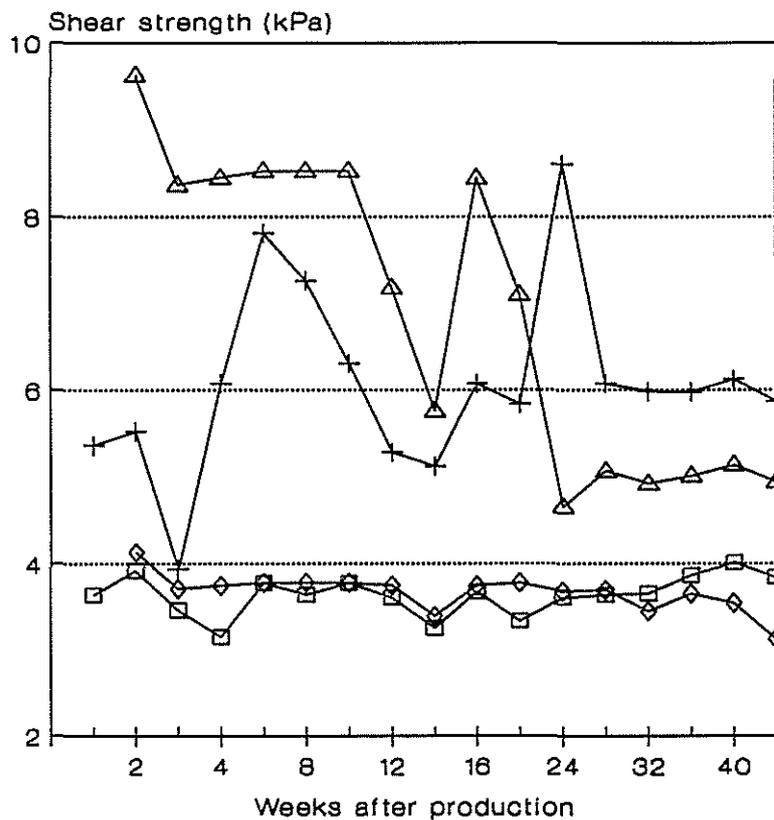


Figure 4 - Shear strength as a function of time, Sample 1 : □ +5°C, -10°C;
Sample 2 : ◇ +5°C, △ -10°C.

Similar fluctuations were noted for 91/92 season sugars, the only difference being that the new season sugars attained a greater degree of hardness i.e. greater shear strength. Similar differences between "aged" and fresh sugars was observed by Bagster (1985) who noted that fresh sugar attained a greater shear strength than 8 month old sugar.

1.3.2 Moisture - total sugar and syrup

As obtained previously (Vender, 1984/85), Br JA and Br 1 sugars exhibited increased strength with increased total moisture content, characterised by the following relationship.

$$S = 4.5048 + 4.7862 \times \text{WTR} \quad (6)$$

where $r = 0.59$, $n = 92$, S = shear strength at -10°C

1.3.3 Sugar Dilution Indicator

The Dilution Indicator (DI) of sugar is a measure of the dilution by water of impurities in the syrup layer surrounding each crystal, and is calculated viz -

$$\text{DI} = \frac{\% \text{ Water} \times 100}{\% \text{ Impurities}} \quad (7)$$

DI results indicated that the following relationship exists between DI and shear strength, as per the following equation.

$$S = -14.495 + 1.771(\text{DI}) - 0.047(\text{DI}^2) \quad (8)$$

where S = shear strength at -10°C .

This relationship indicates that the majority of sugar currently exported to colder climates (i.e. $28 < \text{DI} < 38$) will experience handling difficulties due to DI characteristics. Dilution indicators in the ranges $24 > \text{DI} > 40$ would provide one characteristic favouring handling \ transportation of raw sugar in cold climates, the emphasis being on the higher DI sugars (see Appendix A for plot).

1.3.4 % Molasses Removed From The Sugar Crystal

The % molasses (or syrup) removed from centrifuged raw sugar samples was calculated and its relationship to shear strength was found to be;

$$S = 7.7819 - 1.3518 \times \% \text{ Molasses} \quad (9)$$

where $r = -0.47$, $n = 24$, S = shear strength at -10°C

Assuming that the % syrup removed is inversely proportional to syrup viscosity, results obtained correlate well with previous data from Bagster (1982), who observed a decrease in shear strength for a Br JA sugar with a decrease in molasses viscosity (see Fig 5).

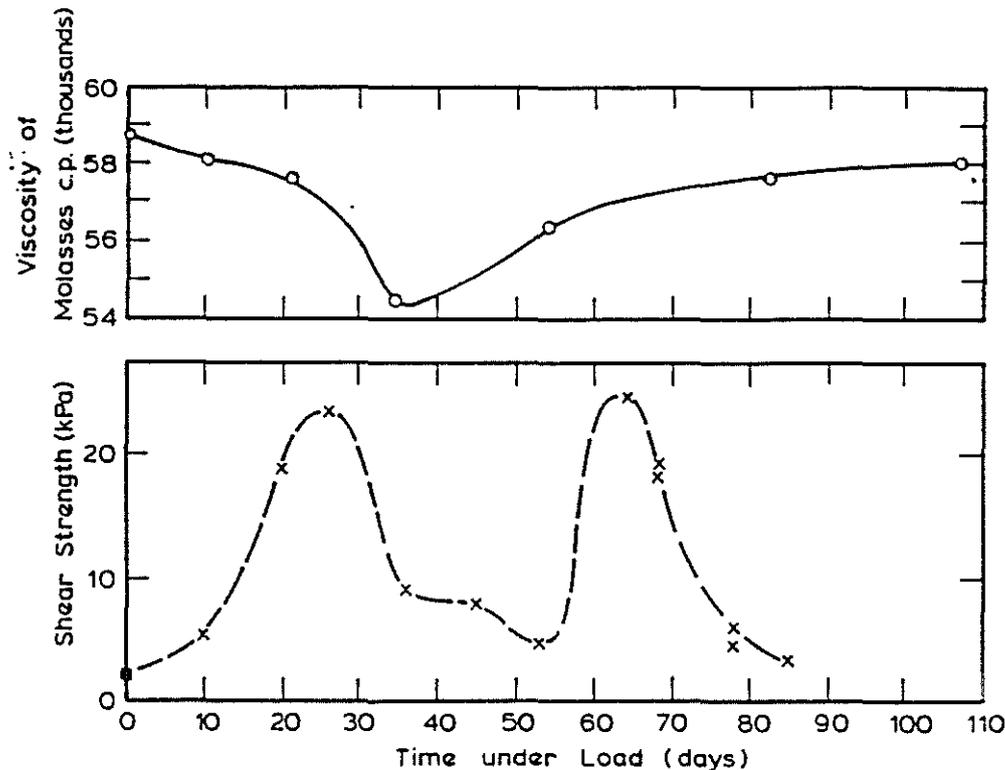


Figure 5 - Viscosity and sugar shear strength over time. (Bagster, 1986).

2.0 Other Syrup Characteristics affecting shear strength

2.1 Precipitate from Crystal Syrup in 50% v/v aqueous alcoholic solution

Having observed varying quantities of colloidal precipitate in syrup/alcoholic solvent mixtures, an attempt was made to quantify the significance of this precipitated material to raw sugar hardening.

Results indicated that a higher proportion of precipitated material was accompanied by an increase in sugar shear strength. For 90/91 season Br JA sugars examined, the following relationship exists;

$$S = 1.9668 + 18.1026 \times \% \text{ ppte} \quad (10)$$

Correlation $r = 0.88$, $n = 23$, $S =$ shear strength at -10°C

Hence a strong relationship exists between the precipitated material in the syrup coating the crystal and shear strength for the samples tested.

2.2 Inorganic ions in Syrup coating - Ca, K, Mg

Saito et al (1976), studying South African, Cuban and Australian raw sugar refining quality, found that Cuban raw sugars had higher levels of calcium (Ca) in comparison to Australian sugars, whilst Australian sugars possessed higher potassium (K) and magnesium (Mg) levels.

As it is the syrup constituents which are of prime importance in the hardening mechanism, K, Ca and Mg levels were measured in Br JA sugars.

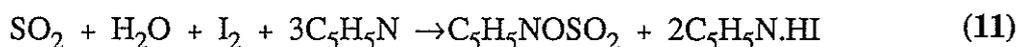
Due to the fact that the Cuban sugars received needed to have their DI's altered to obtain syrup for analysis, figures in Table II represent ratios of ions in each syrup only.

TABLE II - Ratio's of K, Ca and Mg derived from centrifugation.

Sugar Origin and number	Inorganic ion ratio		
	K/Ca	K/Mg	Ca/Mg
Australian			
Hambleton - 32/33	6.0	8.1	1.3
Inkerman - 92	5.6	8.9	1.6
Cuban			
ex mv "Peony Islands"	4.8	7.2	1.5
ex mv "Varadero"	3.9	7.1	1.5

3.0 Karl Fischer moisture determination

The Karl Fischer (KF) titration, utilising the iodometric reaction in Equation 11, provides the ideal analysis for moisture levels in raw sugar and their syrups.



End point detection is achieved electronically by a double platinum electrode immersed in the reacting solution. On converting all water in the system, any additional KF reagent supplies excess iodine to the system which depolarises the previously polarised electrodes, resulting in a rapid increase in the measured current i.e. the endpoint.

3.1 Experiment conditions

The following experimental parameters were used throughout all KF moisture determinations;

- Solvent - 50:50 formamide\hydranal solvent mixture;
- Temperature - reaction cell temperature thermostatically maintained to 50 ± 1 °C

NOTE : Drift, the rate at which external moisture enters the reaction cell, and titrant concentration determinations were conducted in accordance with documentation supplied with the instrument, in order to insure the integrity of sample results.

3.2 Syrup layer

A quantity of molasses is first removed from the sugar sample via centrifuge at 18000 rpm for 2 hours at 25°C in specially prepared centrifuge tubes. The resulting molasses is removed from the centrifuge tube and treated as per whole samples prior to introduction into the KF environment.

3.3 Whole samples

Raw sugar samples were dissolved in formamide in a 1:7 sugar:formamide ratio . Following dissolution the resulting solution was injected in to the reaction cell and titrated after a 2 minute stir period. The percent moisture in the original sample was calculated using the exact ratio of sugar to formamide, the mass of sample used and the moisture content of formamide.

3.4 Mettler Automated Karl Fischer moisture Titrator

The Mettler DL18 titrator is a complete analysis system for determining sample water content utilising the Karl Fischer method.

The stoichiometric conversion of water in the cell is traced using a two-pin platinum electrode which has a current source applied to its poles. Voltage measures at the polarised electrode allows the unit to detect when the last traces of water are titrated out, signalled by a voltage drop to virtually zero.

At the completion of the titration, microprocessor controls display the moisture content present in the sample and the unit readies itself for the next determination. Drift, the rate at which external moisture enters the reaction cell, is determined by the instrument and ideally should range between 25 and 50 μg water per minute.

Used in conjunction with a Mettler DL18 KF titration unit (see Fig 6), the KF titration provides an efficient, rapid and accurate method for analysing solids, liquids or syrups.

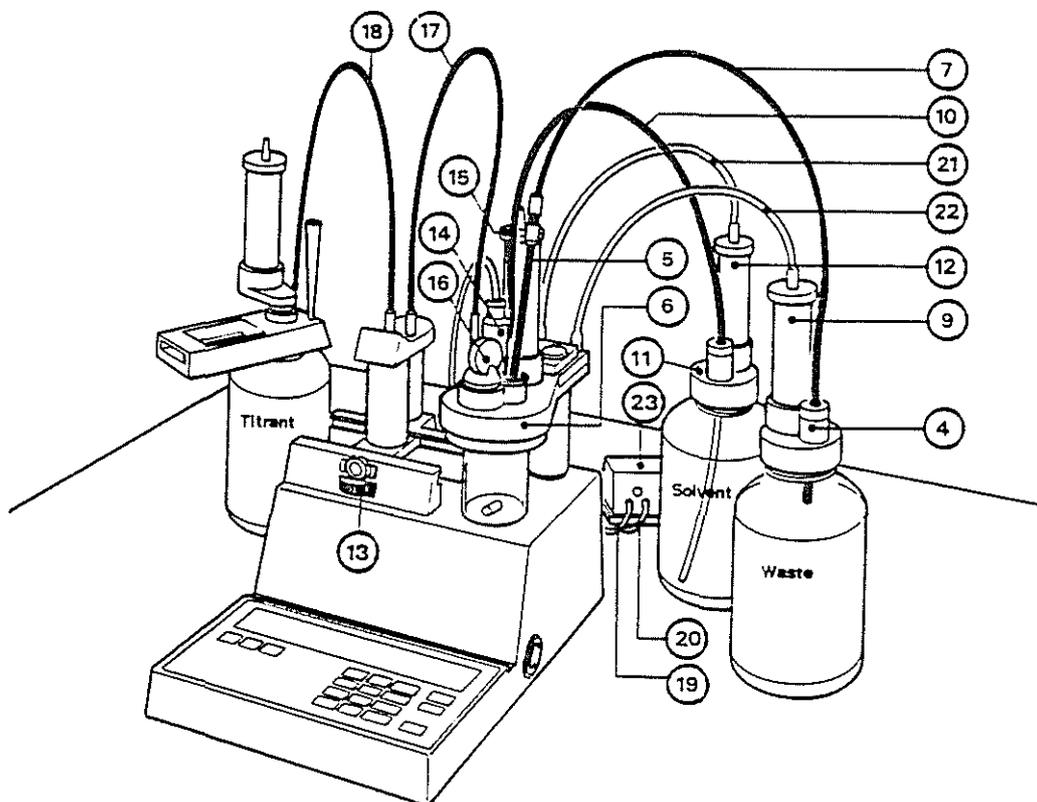


Figure 6 - Mettler DL 18 Karl Fischer Titration Unit

3.5 Results - Karl Fischer moisture determinations

Karl Fischer moisture determinations of syrup centrifugally stripped from Br JA samples allowed the investigation of the syrup's role in hardening to be assessed. Results at both -10°C and $+5^{\circ}\text{C}$ indicate that shear strength is proportional to syrup moisture i.e. at higher syrup moistures, a higher strength is achieved.

$$S = 1.9176 + 0.238 \times \text{Syrup Moisture} \quad (12)$$

where $r = 0.45$, $n = 48$, S = shear strength at -10°C

Comparison of conventional loss-on-drying moisture results and Karl Fischer generated results yielded the following relationship.

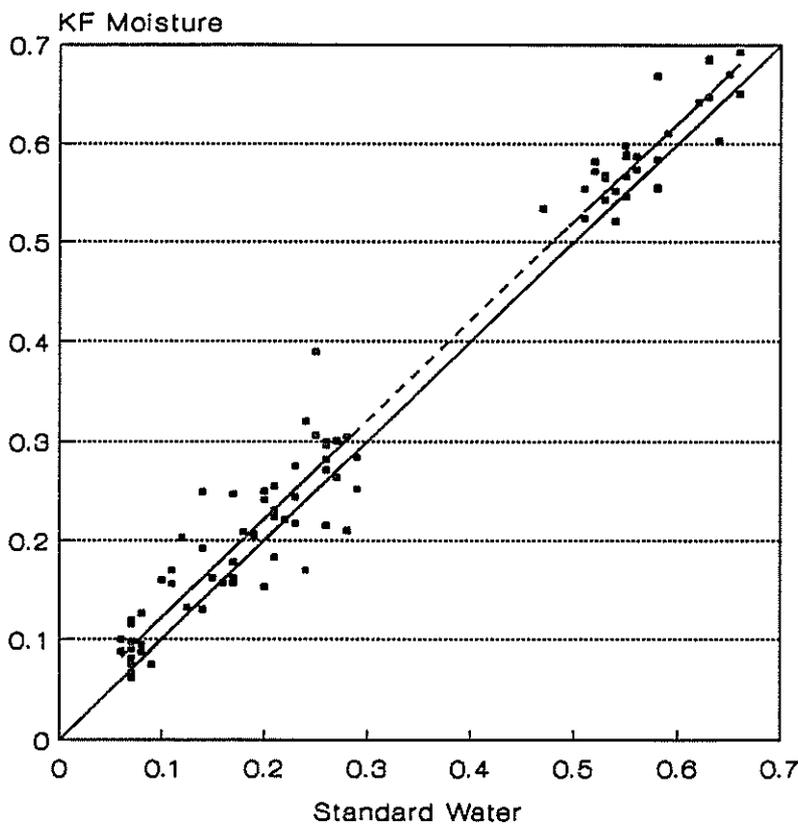


Figure 7 - Relationship between results derived from conventional moisture determinations and Karl Fischer determinations.

Standard moisture determinations rely on loss-on-drying i.e. outermost moisture driven off followed by internal moisture migrating to the syrup/air interface. On the other hand, the KF method involves dissolving up the sample thus releasing all moisture into the reaction cell for quantitative assessment. The displacement achieved between parity (lower line extending to origin) and the linear regressed line for KF data reflects the level of physically bound water in the gross crystal released as a result of the KF method.

4.0 Invert coated sugars

The effects of coating raw sugar with invert syrup has been investigated previously by Ames et al (1980), Dibella (1984) and Wright et al (1987) for various purposes. The reduced caking propensity realised as a result of the increased quantities of reducing sugar in the gross sugar sample is further quantified in this section of the investigation. In addition, the quality of the altered syrup as a function of time is also appraised.

The coating process was designed to produce Br JA sugar conforming to Ministers Standards, from the combination of Br 1 sugar and cane invert.

4.1 Production of invert

A sufficient quantity of fresh cane invert was received from Racecourse mill 1991 production run to accommodate all the coating work carried out in this investigation. The invert syrup was diluted to 70 °Bx in order to provide a syrup of suitable viscosity to facilitate the application of this syrup onto conventional Br 1 sugar.

4.2 Coating of Br 1 sugar with invert

The following method was employed to combine the diluted invert syrup and Br 1 sugar. The aim was to investigate the effect of the addition of known quantities of invert syrup on the hardening propensity, and not to achieve some specific pol.

4.2.1 Add a known quantity of Br 1 sugar to the mixing device, which in this case consisted of a small scale ribbon mixer (see Figure 8).

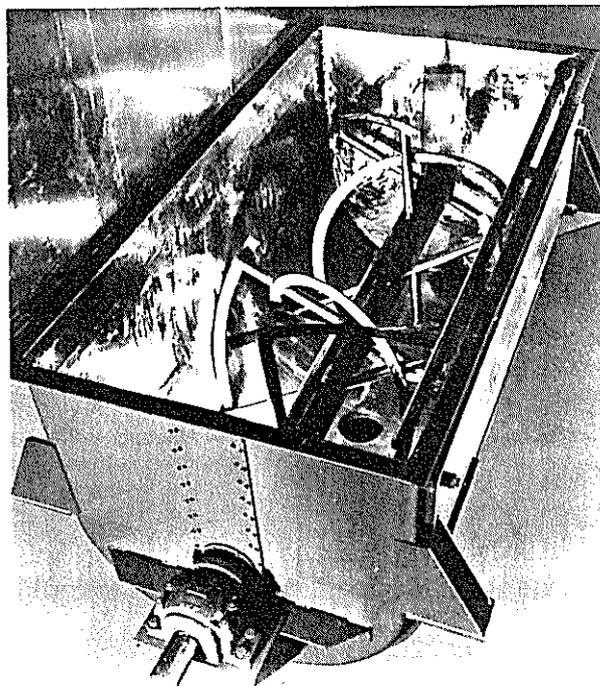


Figure 8 - Conventional ribbon mixer, (Kirk-Othmer, 1980).

4.2.2 Using the following calculation, the appropriate quantity of 70 °Bx invert syrup was taken and heated to 30-35 °C.

$$M_I = \frac{I \times M_s}{B_I \times 100} \quad (13)$$

where: M_I = mass of invert required for desired dosage;
 I = invert dosage required, % invert solids on sugar;
 M_s = mass of sugar to be coated (grams);
 B_I = brix of invert (°Bx).

4.2.3 Begin mixing the sugar in the mixing device and add a fine stream of heated 70°Bx invert syrup to the centre of the mixer.

4.2.4 Continue mixing the sugar/syrup for a total period of 10 minutes, alternating the direction of the blades at one minute intervals.

4.2.5 Sub-sample the coated sugar in 2 kilogram quantities via a sampling port at the base of the mixing device for subsequent analysis.

4.3 Results - Invert coated Sugar

4.3.1 Analysis of cane invert

The following table comprises the results obtained for Racecourse mill 1991 production run cane invert used in the investigation.

TABLE III - Analysis of Racecourse mill cane invert - 1991 production run.

Analysis	Result
Sucrose (%)	14.0
Reducing sugars (%)	65.2
Total sugars (% by inversion)	80.5
Dextran (mg/kg)	186
Brix (° by spindle)	86.8

4.3.2 Analysis of coated/non-coated sugars

Having coated the source sugar with two different quantities of invert syrup, samples were analysed to assess the chemical/physical property changes that had occurred as a consequence.

TABLE IV - Initial analysis results for invert coated and source sugar.

Analysis	Source sugar	1% Invert coated* sugar	1.2% Invert coated sugar
Polarisation	98.95	98.04	97.30
Reducing Sugars	0.21	0.94	1.37
Ash	0.24	0.27	0.28
Water	0.15	0.29	0.52
Colour (ph 7)	2039	2075	2073

* % invert coating = % invert solids on sugar

4.3.3 Shear strength reduction

Results indicate that the presence of greater amounts of reducing sugars in the syrup coating effectively reduces the shear strength of the source sugar by 15-20%.

TABLE V - Average data for invert coated sugars

Sample	Pol (%)	RS/Ash	DI	Shear Strength +5°C (kPa)	Shear Strength -10°C (kPa)
Source	99.06	0.90	29	3.34	5.25
1% Invert coated	97.60	4.33	33	2.69	4.61
1.2% Invert coated	97.29	5.04	32	2.64	4.67

4.3.4 Pol reduction as a function of RS/Ash in syrup

As expected, the presence of reducing sugars in the syrup reduced the Pol of the source sugar by an amount proportional to the quantity of invert syrup added. By calculating the % syrup surrounding the crystal viz (White and Guo, 1984; Vender, 1989, a), one can reflect the change (or drop) in Pol as a consequence of the RS/Ash ratio present in the syrup. Fig 9 reveals this relationship for RS/Ash ratios of 0.6 and 1.0.

$$\% \text{ Syrup} = \frac{W}{W_s} \times 100 \quad (14)$$

where W = sugar total moisture (%); W_s = syrup total moisture (%).

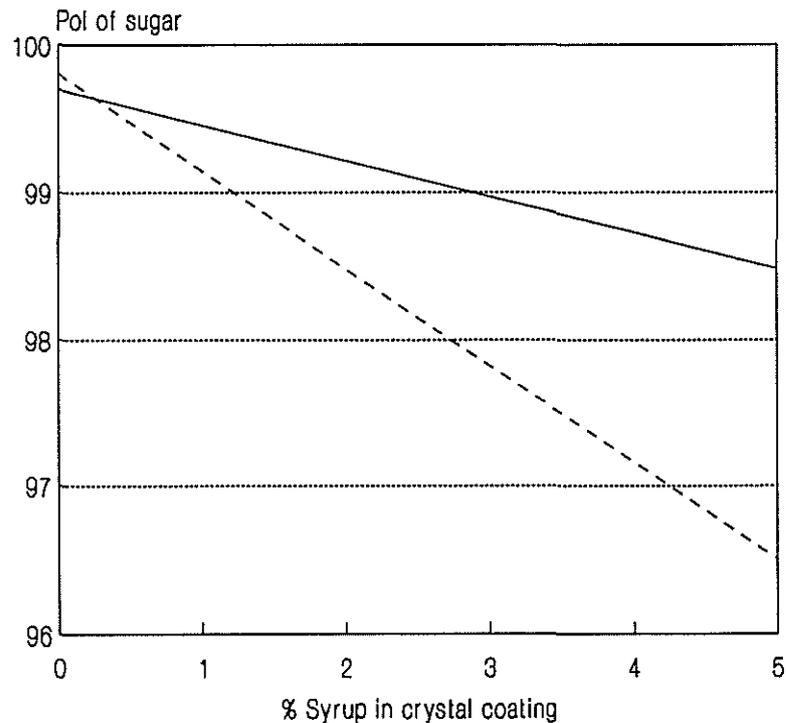


Figure 9 - Plot of relationship between RS/Ash ratio of syrup surrounding crystal and its effect on pol. - - - RS/Ash=1.0, ——— RS/Ash=0.6

Theoretically, if the sugar crystal comprised 100% sucrose, both lines in Fig 9 would cut the y-axis at Pol = 100. Realistically, the following reasons suggest why this y-intercept varies depending on the RS/Ash ratio present.

- The crystal is impure hence the assumption that 0% syrup = 100% sucrose is invalid. This argument is supported by previous investigations into the liquid inclusions (Mackintosh, 1970) and mother liquor entrapment (Mantovani et al, 1986) in the gross crystal, reducing the purity of that crystal.
- The calculation for the quantity of syrup surrounding the gross crystal is merely an estimation relating to total and syrup moisture. Inherent errors in both these measurements are also reflected in this figure.
- Other optically active constituents present in the syrup will alter the pol to an extent making it virtually impossible to correct for these varied constituents in a wide variety of syrups, and to account for the effect they have on pol.

5.0 Dilution Indicator (DI) modified sugars

In order to assess hardening characteristics of freshly prepared sugar, one sample of sugar was modified by adding water and drying to produce a desired DI. Two sugars, one low DI and one high DI, were produced from the same source, each having different DI's to the original sugar.

5.1 Syrup Characteristics over time

As a consequence of fluctuations in syrup moisture and syrup sucrose over time, both low and high DI sugars exhibited decreasing syrup purity over time (see Fig 10). It is thought that the continual migration of sucrose molecules in the syrup towards the bulk crystal, coupled with the migration of syrup moisture towards the syrup/air interface, is responsible for the stepwise reduction in syrup purity over time.

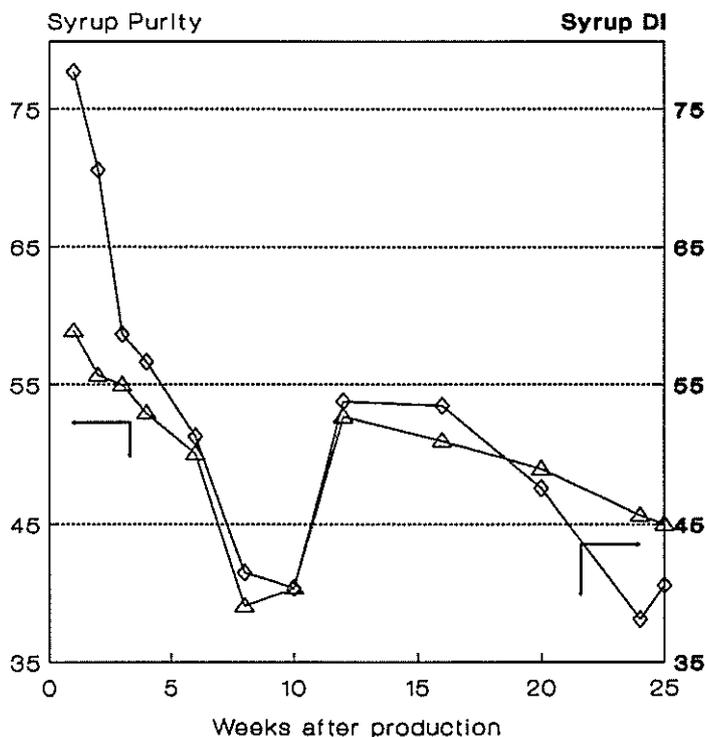


Figure 10 - Plot of syrup characteristics as a function of time for high DI sugar : ◇ DI, △ Purity.

5.2 Shear Strength

Although the DI achieved artificially goes beyond the range for average sugars, the exercise of modifying DI has a profound effect on shear strength. As reported by Vender (1984/85), the high DI sugar produced the lowest shear strength. As the shear strength of the lower DI sugar at -10°C constantly exceeded instrument limits, no data was generated for correlations between shear strength and other parameters for this sugar.

6.0 Glass transition temperature

The point at which a material undergoes a transition from liquid-like to solid-like state denotes a glass-transition at a particular temperature i.e. the glass transition temperature T_g (Noel et al, 1990). Honig (1953) reported the freezing point depression of aqueous sucrose solutions, stating that a 58° brix solution has a freezing point of -3.7°C .

Noel et al (1990) considered the freezing behaviour of a 50° brix aqueous sucrose solution. "The presence of sucrose will depress the freezing point of water. On cooling to below this temperature, ice can form on heterogeneous nuclei....On cooling at a relatively modest rate (e.g. 1°C per minute) to -50°C , the ice growth will lead to an increase in sucrose concentration in the water that is still liquid. This depresses the freezing point further and also increases the viscosity. This slows ice crystallisation by slowing the diffusion of water to the growing crystal surface....Eventually, ice crystallisation becomes so slow....The liquid sucrose-water mixture is maximally freeze-concentrated and has become glassy."

Whether the same occurs in the syrup layer surrounding each raw sugar crystal is not known. However it is believed that if the measurement of such a phase change can be made of various sugars, it may indicate, as a consequence of syrup characteristics, sugars which will possess suitable handling characteristics in colder climates.

6.1 Differential Scanning Calorimeter

Differential scanning calorimetry (DSC) involves a process whereby both sample and reference materials are subjected to a continually increasing temperature at a constant rate. Heat is added to either the sample or reference material in order to maintain the two at identical temperatures. The added heat therefore compensates for endothermic or exothermic processes occurring in the sample (see Figs 11, 12).

6.2 Results

Work conducted by the University of Technology, Sydney indicates a suppression of the sugar and syrup ice points in the -5 to -10°C range, an endothermic trough in the spectra (see Table VI Fig 13).

TABLE VI - Ice-point suppression regions for selected sugars and syrups

Sample Type (Sample Number)	Ice-point suppression range ($^{\circ}\text{C}$)
Invert coated sugar (940043)	-7.0 to -10.2
Invert syrup	-7.0 to -10.5
90/91 season sugar (940017)	-6.5 to -10.2
90/91 sugar syrup	-5.5 to -9.5
91/92 season sugar (940044)	-5.5 to -10.4
91/92 sugar syrup	-6.0 to -10.0

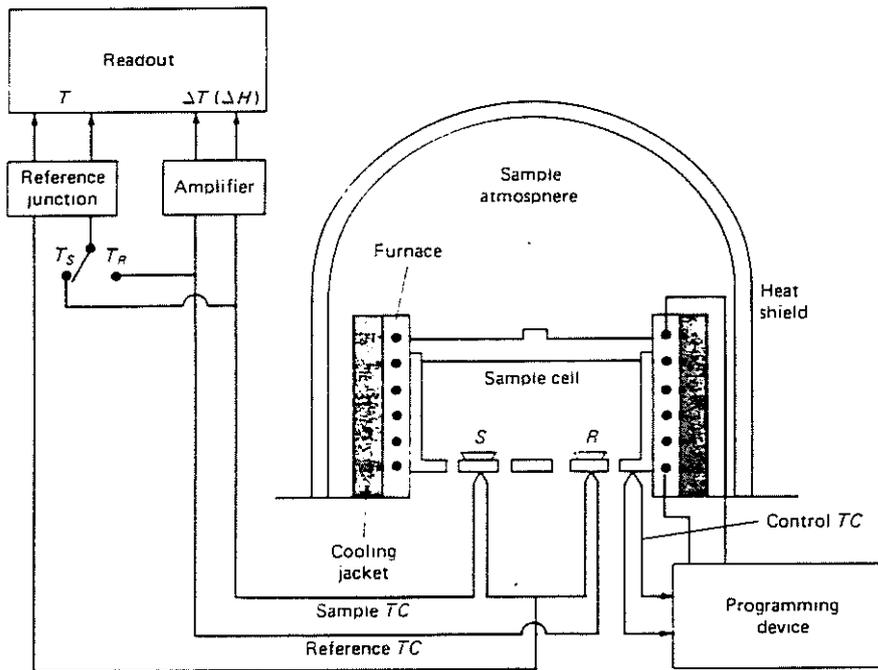


Figure 11 - Schematic representation of differential scanning calorimetry (DSC) apparatus, (Skoog, 1985).

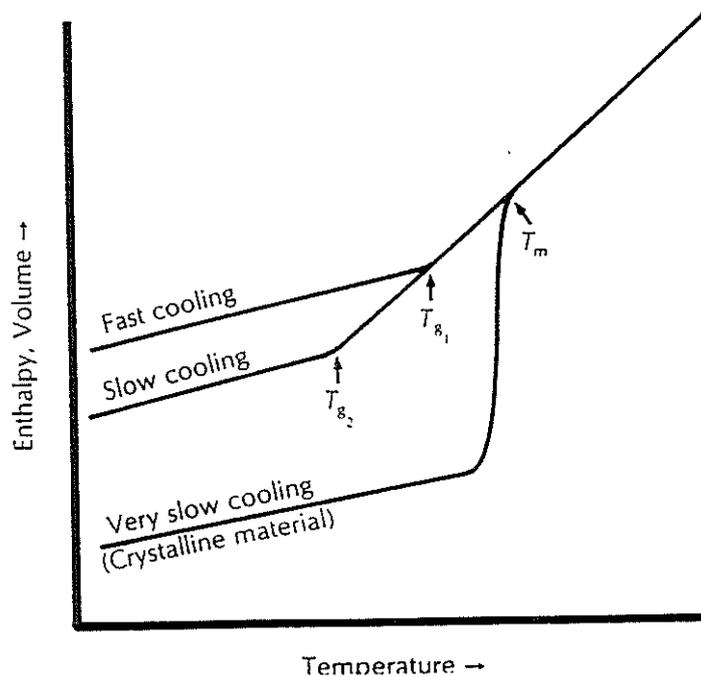


Figure 12 - Typical DSC output, enthalpic measurement as function of temperature, showing glass transitions T_{g1} and T_{g2} and the melting temperature T_m , (Noel et al, 1990).

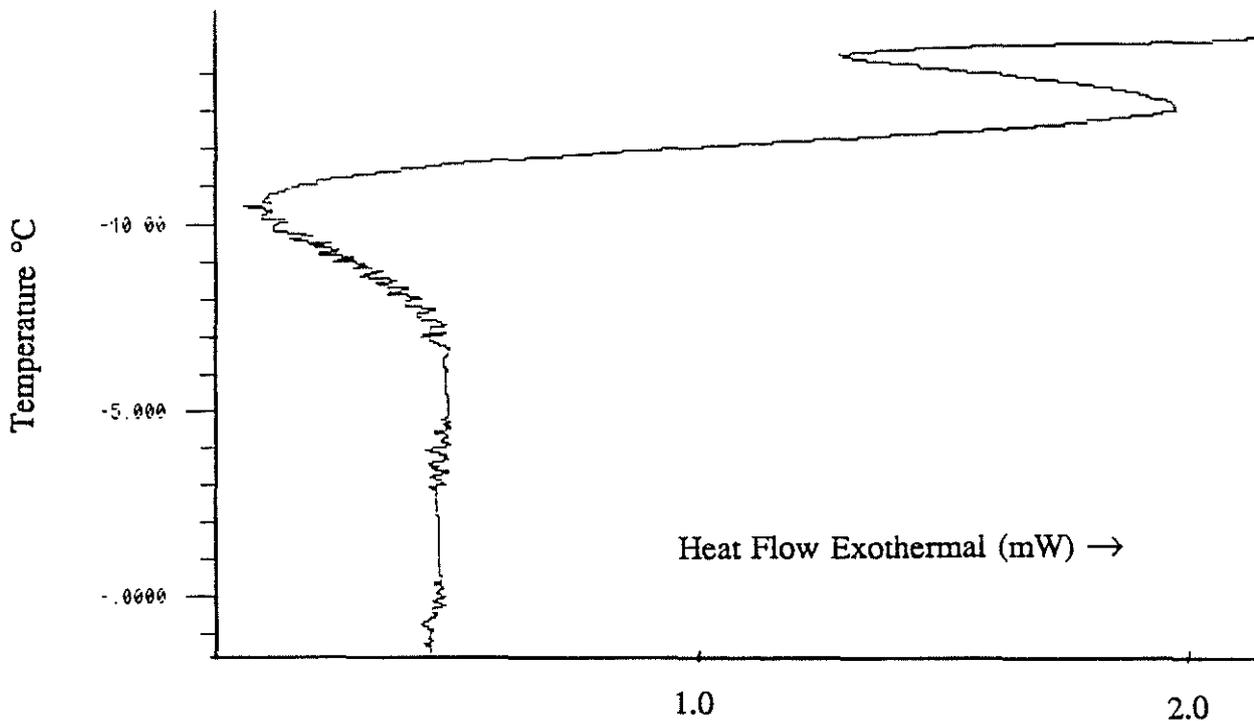


Figure 13 - Typical output from thermal analysis equipment for samples investigated in this report.

The sugar samples tend to have a broader range in comparison to the isolated syrup. This condition may have resulted from the fact that isolated syrup has a fixed quantity of sugars whilst the syrup in contact with the crystal has access to additional sugars from the crystal/syrup boundary. Having additional sugars to draw on may allow crystal syrup to suppress ice-point to a lower temperature.

7.0 Contribution of crystal geometry/shape to hardening propensity

7.1 Sugars manufactured from the same molasses

Modelling of mass transfer within sugar beds (Vender, 1989, b) suggests that moisture migration in bulk sugar is a function of sugar bed permeability, relating to the geometry of crystals in the packed bed. Sugar beds produced from larger, inefficiently packing crystals would therefore tend to exhibit less hardening or caking than say a well packed bed.

In this portion of the investigation, several sugars of varying crystal size were manufactured from the same molasses in order to assess crystal physical characteristics on hardening. By using the same starting material, it was hoped that the effect of other variables on hardening e.g. impurities, syrup quality etcetera would be minimised.

7.2 Sieved sugars - fractions collected from the same gross sample

A simpler way of obtaining sugar of essentially the same qualitative parameters bar crystal size, shape and distribution, was achieved by merely separating certain crystal fractions from a gross, mixed sample and analysing each fraction collected. The following fractions were collected;

- a. crystals greater than 850μ ($c > 850\mu$)
- b. crystals smaller than 850μ and larger than 600μ ($850\mu > c > 600\mu$)
- c. crystal smaller than 600μ ($c < 600\mu$).

7.3 Results

Quantities of three different molasses samples were collected for this portion of the investigation, the analysis for which appears in Table VII.

TABLE VII - Analysis of molasses used for small scale raw sugar manufacture.

Molasses	Source	Pol ^a	RS	Water	Total Sugars ^b	Ash	°Brix
A	Unknown	59.3	2.8	28.9	67.3	4.2	74.3
B	Victoria Mill						
	1. A Molasses	52.1	6.3	27.4	62.3	6.3	76.6
	2. B Molasses	47.3	7.9	27.9	58.1	8.0	77.2
C	Hambledon Mill liquor	61.7	2.0	30.7	69.3	2.3	71.2

^a - Double polarisation, CSR A&MS Method N^o35

^b - Total sugars after inversion, CSR A&MS Method N^o23.

7.3.1 Sugars manufactured from the same molasses

Due to the difficulty involved in obtaining sufficient quantities of sugar for analysis from molasses samples A and B, no analyses were performed on the sugar produced from this molasses. Fortunately, adequate quantities of sugar from molasses C - Hambledon Mill liquor was made, the analysis for which appears in Table VIII.

TABLE VIII - Analysis results for effect syrup sugar manufactured to produce varying crystal size.

Date sugar manufactured	Analysis			
	Pol	Water	DI	MA
12/8/91	98.03	0.47	31	0.61
13/8/91	97.84	0.83	62	0.73
14/8/91	97.93	0.50	32	0.85
15/8/91	98.57	0.34	31	0.82

Analysis of these sugars all manufactured from the same effect syrup indicated an inversely proportional relationship between crystal size i.e. mean aperture (MA) and shear strength (see Fig 14).

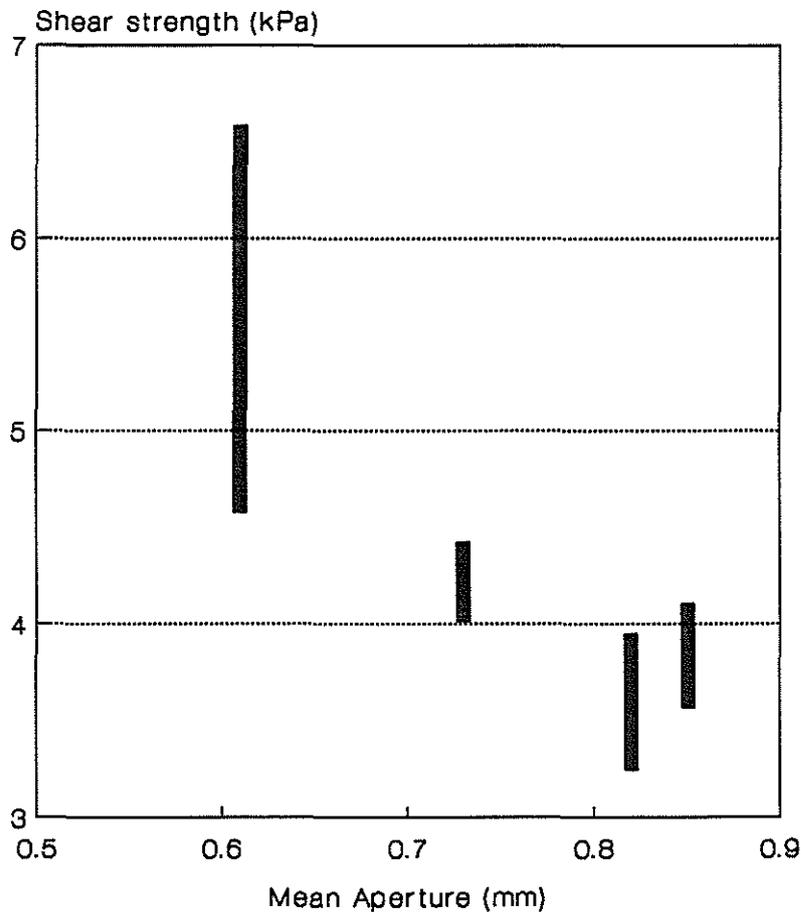


Figure 14 - Shear strength as a function of mean aperture for sugars manufactured from the same liquor.

7.3.2 Crystal fractions taken from the same gross sample

Although the process of separating certain crystal fractions from a gross sample produces sugar samples which no longer have a normal distribution of crystal sizes within them, the exercise suggests that sugars containing less moisture, even though they have good packing efficiency, required a greater amount of time to equilibrate than similar crystal sized sugars of higher moisture content (see Table IX).

TABLE IX - Shear strength as a function of sieved crystal size and moisture

Sugar Water	Low (0.17%)			High (0.32%)		
	1	2	3	1	2	3
N° Days at -10°C						
Sieve Size (μ)						
<600	1.61	2.31	2.41	3.01	2.94	2.97
600-850	2.45	2.38	2.38	3.15	2.80	2.87
>850	1.96	1.89	1.92	2.45	2.45	2.45

Graphical representation of the <600 μ data is shown in Fig 15

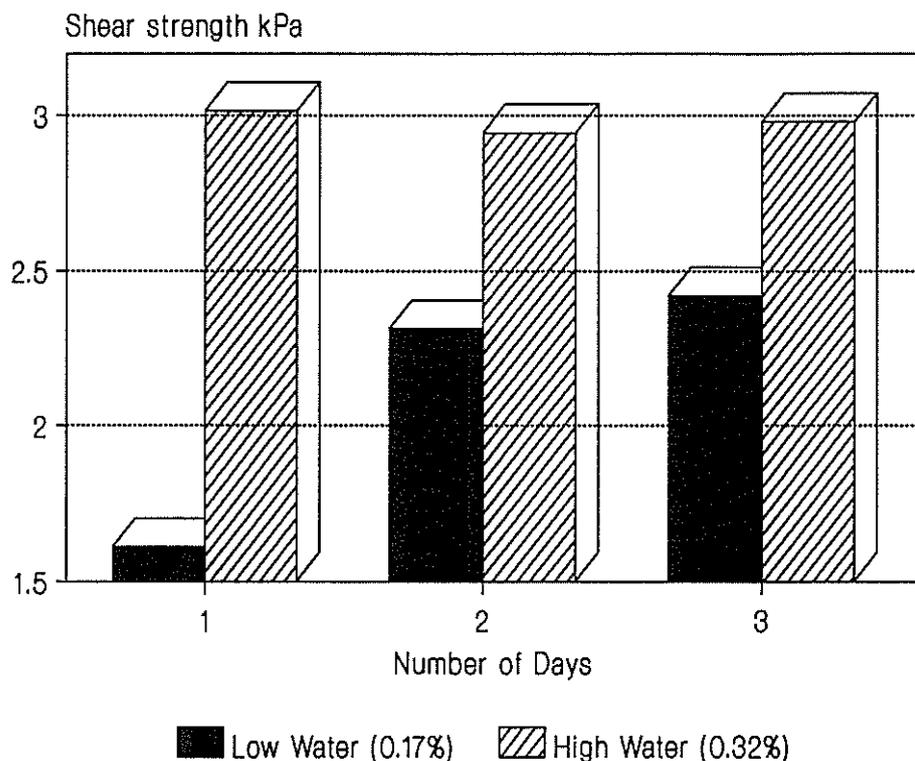


Figure 15 - Graphical representation of <600 μ data, plot of changes in shear strength of sieved sugar as a function of time.

Note that the low moisture sugar required 3 days to attain a stable shear strength whilst the higher moisture sugar reached "constant" strength relatively quickly, even though a similar degree of packing would have been achieved by both sugars.

Other observations that can be made is that;

a. The higher moisture sieved sugar attained a higher shear strength when subjected to the same conditions as the low moisture sugar;

b. The shear strength achieved by sieved sugars overall is much lower than that achieved by all other non-sieved sugars analysed. This suggests that by reducing the distribution of crystals in the bulk sample, reduction in caking propensity may be realised.

8.0 Humidity of storage environment

The relationship between equilibrium relative humidity (ERH) and raw sugar characteristics has been researched previously; Miller & Wright (1971), Korbonits & Vukov (1973), Lu et al (1977), Petri & Carpenter (1979), Bagster (1985), Bagster & Rizzo (1987), Russell (1988).

Raw sugar exposed to atmospheres of varying relative humidity (RH) will in turn vary qualitatively to the imposed change. If the ambient RH is higher than the ERH of the sugar, the syrup layer enveloping the crystal will absorb moisture to attain equilibrium and vice-versa. The magnitude of this change ultimately affects the composition of the syrup layer. Therefore, by subjecting raw sugar to environments of varying RH, the investigation sought to obtain data in relation to syrup quality, sugar characteristics etc.

A simple way of obtaining an environment of appropriate RH is achieved by enclosing a saturated solution of a particular salt in a sealed container. Table X indicates the relative humidity over various saturated salt solutions.

TABLE X - Relative humidity of air over saturated salt solutions*

Saturated Salt	% RH	
	5°C	20°C
Sodium Chloride	76	76
Sodium Dichromate	59	55
Magnesium Chloride	34	33

* Australian Std AS1113 - 1971. Laboratory humidity cabinets (Non-injection type). Standards Association Australia.

8.1 Adopted method

The following method was used to expose raw sugar to environments of varying %RH.

8.1.1 The desired saturated salt solution was placed in the humidity cabinet (see Fig 16) with stirrers and circulating fan running. When the %RH within the cabinet had come within 5% of its expected value, loaded shear cells and containers filled with sugar were placed in the cabinet.

8.1.2 Following 72 hours, the %RH of the environment was measured and recorded.

8.1.3 Samples were then removed from the cabinet and analysed.

8.2 Humidity Cabinet

Previous investigations assessing shear strength as a function of % RH (Bagster et al, 1987) had exposed the shear cells to humidities for chosen periods of time without maintaining a load on the cell. The ideal system maintains a load on the shear cells so as to mimic the real life situation in which compacted sugar is subjected to environments of varying humidities. The investigation sought to remedy this by conducting experiments whereby the shear cells were subjected to varying relative humidities whilst still under load. Figure 16 gives a schematic representation of the cabinet constructed in order to achieve the desired conditions.

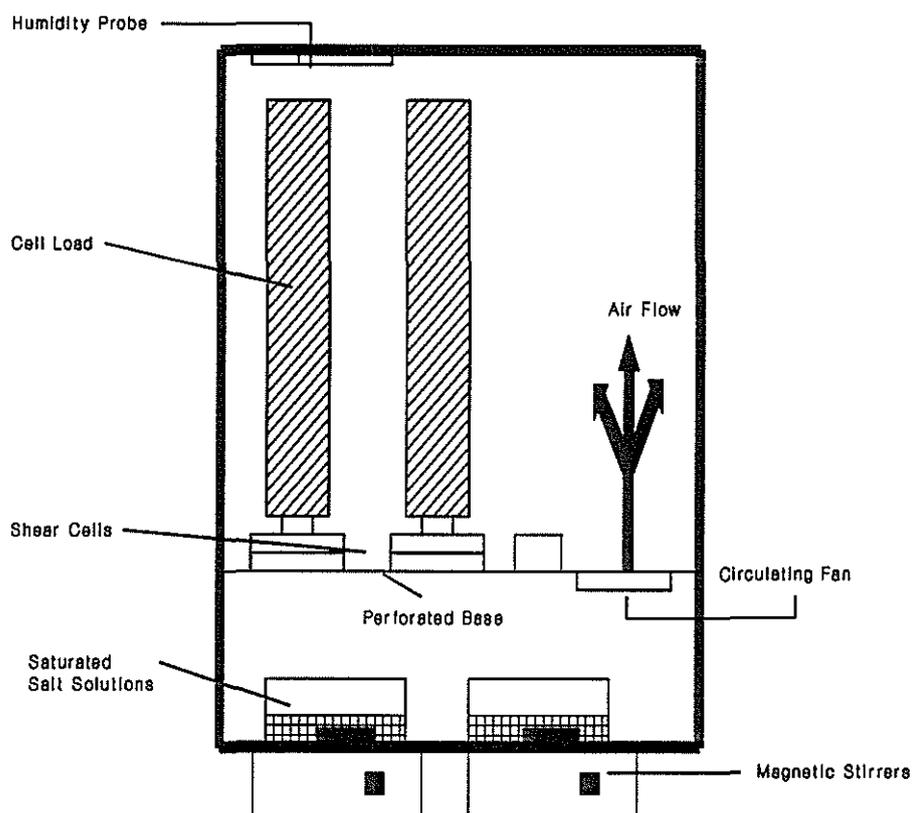


Figure 16 - Schematic representation of humidity cabinet constructed for the investigation.

In order to maintain appropriate temperature stability, the cabinet was placed in a thermostatically controlled cool room to $4 \pm 1^\circ\text{C}$. The cabinet also had sufficient room to store containers of raw sugar so that qualitative parameters of these sugars could be assessed.

8.3 Results

Miller and Wright (1971) demonstrated a close empirical relationship exists between ERH and DI. Russell (1988) investigated this relationship and found a lower ERH existed as a function of DI. Results generated in this investigation reinforce the ERH/DI relationship established previously, as can be seen in Fig 17.

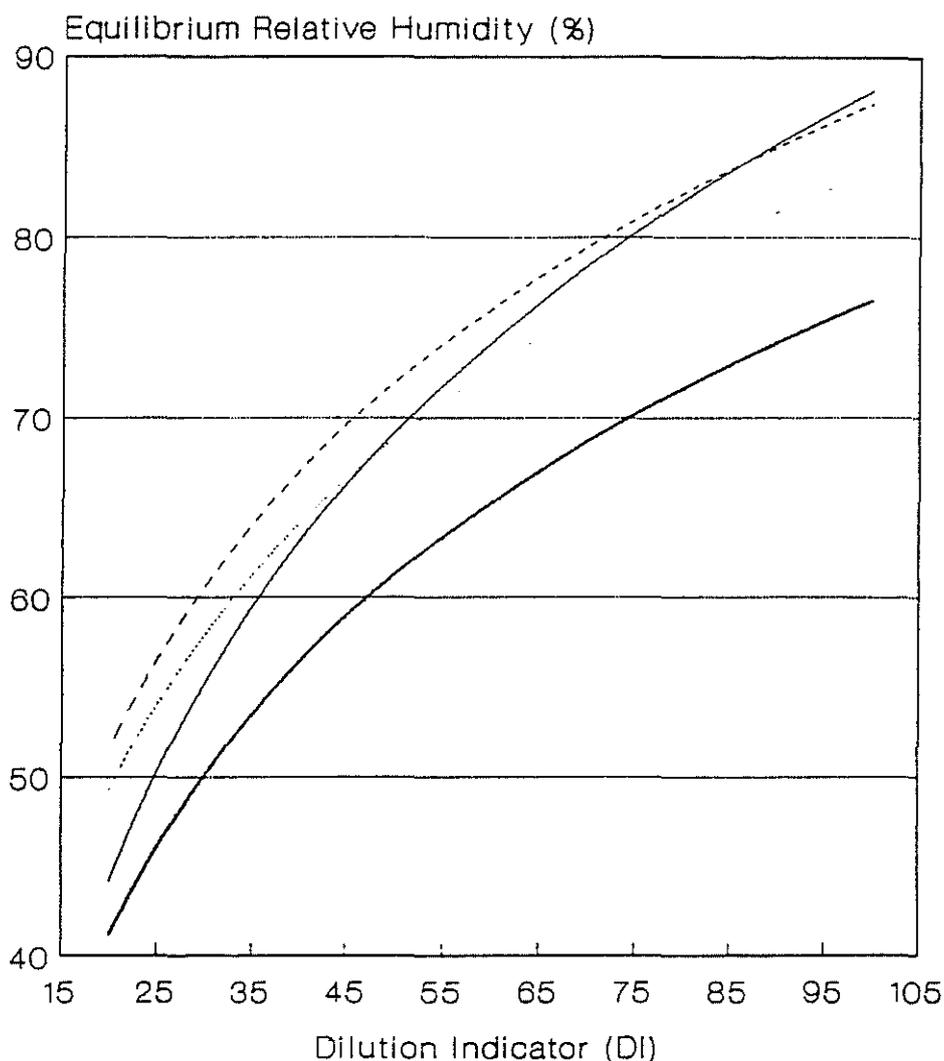


Figure 17 - Equilibrium relative humidity (ERH) v DI relationship as reported by Miller and Wright 20°C - - -; 30°C - - - -; Russell ———; and this report ———.

9.0 Moisture migration

Investigation into the migration or movement of moisture in bulk sugar came to the fore as a result of the large scale compaction testing (Vender, 1984-85), which highlighted the significance of such a phenomena to the hardening propensity of raw sugar. The driving force behind this migration is the difference of the partial pressures of the water vapour, a function of the temperature and moisture content of the sugar.

Vender (1989, b) states that diffusivity through a packed bed involves several processes between the air/syrup and syrup/crystal boundaries (see Fig 18).

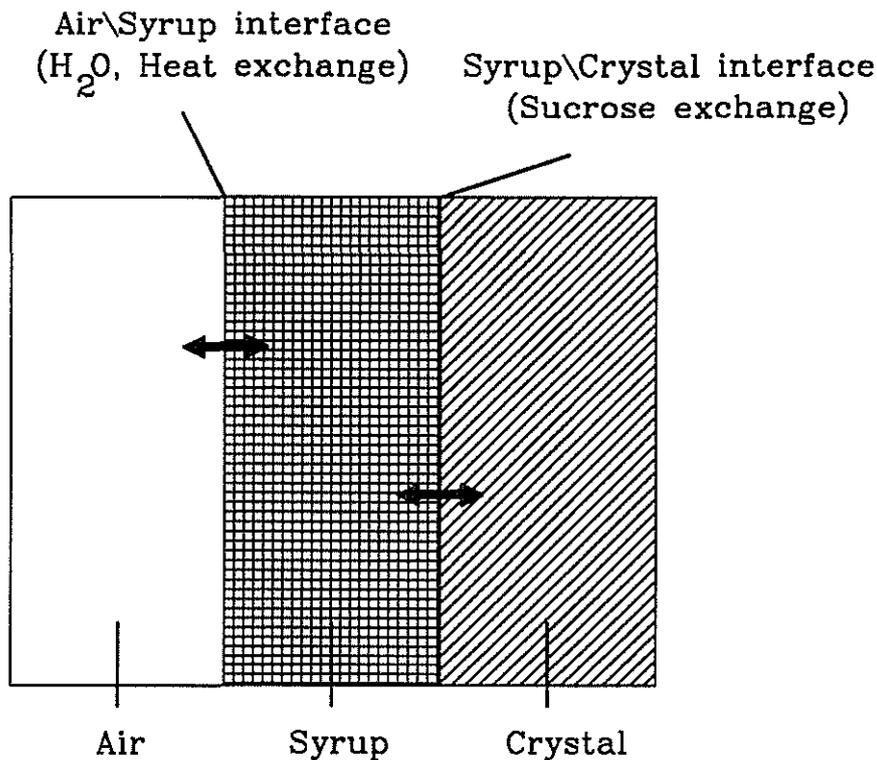


Figure 18 - Schematic representation of air\syrup\crystal boundaries present in each raw sugar crystal.

Vender (1989, b) found the rate of moisture migration (flux) in air to be many times greater than that in syrup i.e. the ratio of flux of moisture in air over flux in syrup yielded the value of 2.64×10^4 . Although this result indicated that moisture diffusivity in the syrup layer is relatively small in comparison to air moisture diffusivity, it suggests that the flux perpendicular to the syrup surface may have a controlling role in the transfer of moisture across the air\syrup boundary.

Other observations made by Vender (1989, b) are that;

- Heat conduction leads to the redistribution of moisture even if no external moisture changes are involved,
- Moisture concentration increases in zones of lower than average temperatures and decreases in zones of above average temperature.

9.1 Experimental Conditions

The following represents the method adopted (Bisley, 1991) for the investigation of moisture migration in sugar. It consisted of using a device which provided the desired temperature differential across a sugar bed of a specified thickness.

Preliminary trials were conducted using wet sand as the bed material. This medium was chosen as it provided a system where only external water surrounding the sand grains was susceptible to migration through the bed. Plate temperatures of 30, 50 and 70°C were used to heat one plate whilst the other plate remained at ambient temperature (ambient temperature was reported to fluctuate 17-25°C) for both sand and sugar runs.

Experimental parameters used for this portion of the investigation appear in Table XI below.

TABLE XI - Experimental parameters used for the investigation of moisture migration in raw sugar

Material	Sand			Sugar					
	1	2	3	1	2	3	4	5	6
Parameter									
Block height (cm)	6.0	4.0	3.0	3.0	3.0	4.0	3.0	6.0	6.0
Bottom water temp (°C)	60	60	60	50	70	70	30	31	31
Top water temp (°C)	22	24	25	18	20	25	18.5	16	16.5
Voidage fraction	0.36	0.36	0.36	0.36	0.32	0.25	0.22	0.12	0.18
Duration (minutes)	44	25	28	40	19	98	350	250	250

Of the sugar beds exposed to various temperature differentials, sugar was sampled from Run 6 in order to assess any moisture changes in the bed material.

Plots of relative humidity and water partial pressure versus temperature were generated to reflect qualitative changes in the bed as a result of the induced moisture migration.

9.2 Moisture migration rig

In order to expose a bed of sugar to a specific temperature differential, a rig was designed to enable variable bed depths, temperature gradients etc. Figure 19 gives a schematic representation of the constructed rig. The bed height was fixed using wooden blocks to separate the two plates. Changes in relative humidity and temperature were taken at the centre of the rig to eliminate side wall effects.

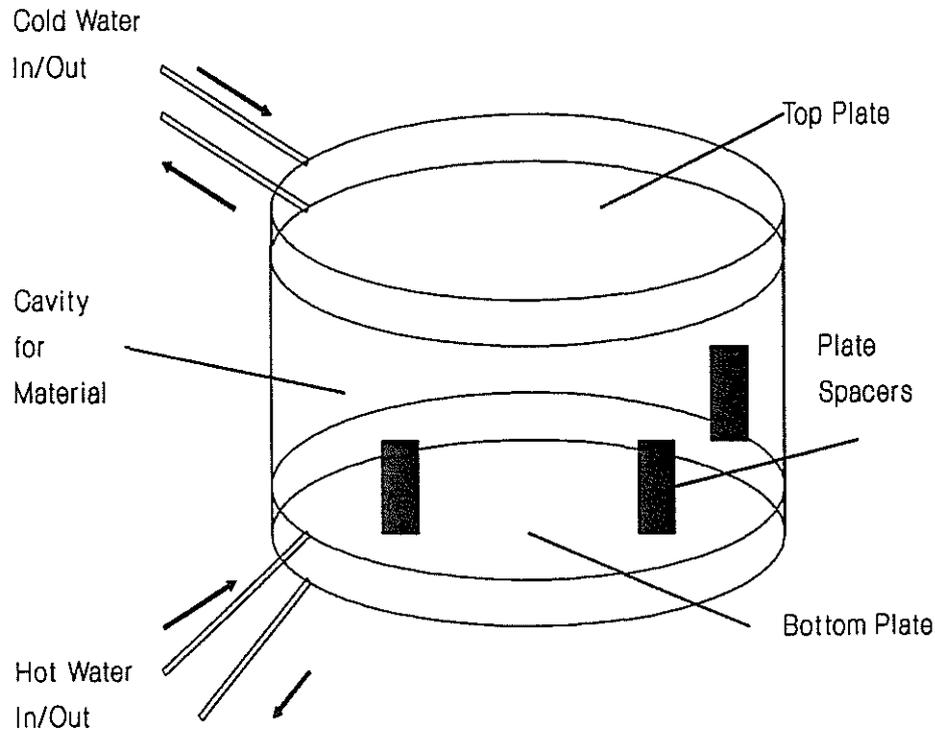


Figure 19 - Schematic representation of the moisture migration rig constructed for the investigation.

9.3 Results

The following summarises work conducted by Bisley (1991) for the purpose of providing the investigation with factual data on moisture migration in raw sugar.

Imposing a temperature differential on a packed bed of sugar results in moisture migration in the bed from an area of high temperature\partial partial pressure to an area of low temperature\partial partial pressure. Changes in relative humidity as a result of moisture movement in the bed was also apparent. Figures 20 and 21 reflect the degree of change experienced in the investigation for Run 6.

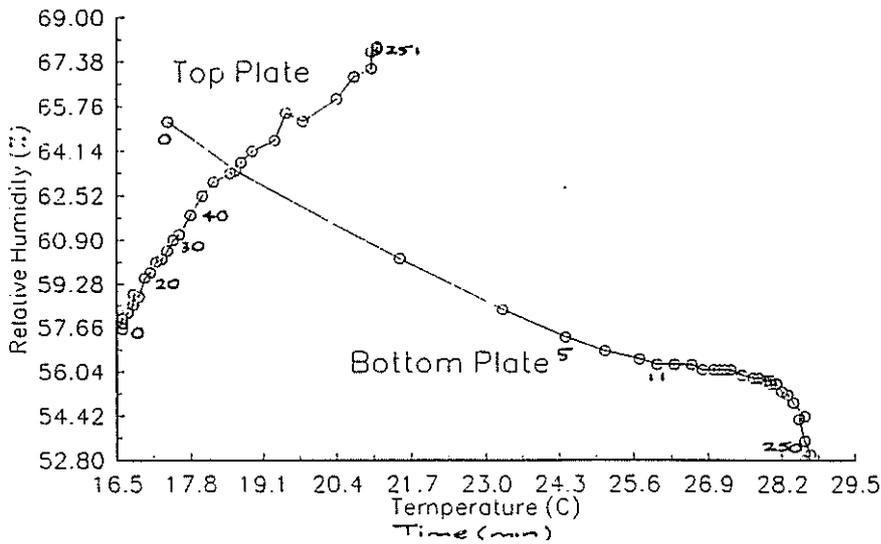


Figure 20 - Relative humidity versus temperature : sugar Run No 6

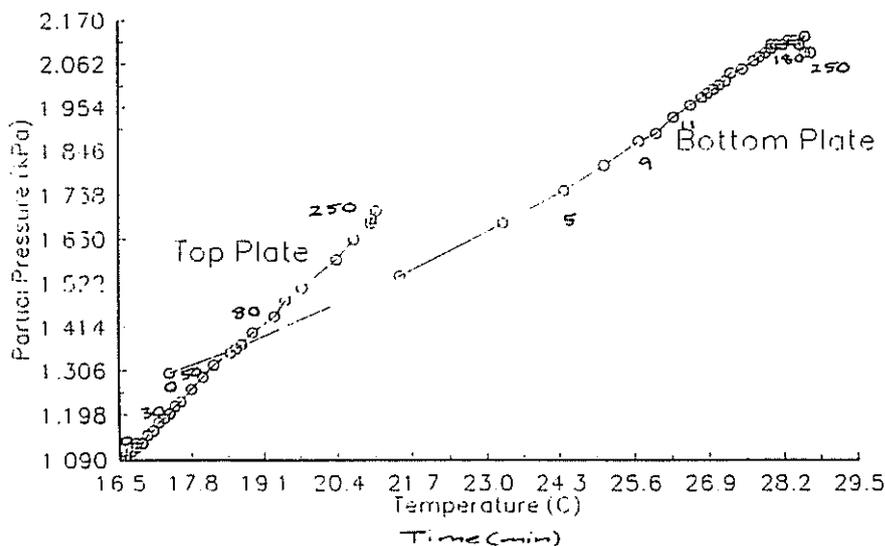


Figure 21 - Partial pressure of water vapour versus temperature : sugar Run No 6.

Bisley (1991) states in her observations that "the sugar appears harder on the base of the apparatus (near the warm plate).....no visual observation of water droplets" i.e. no condensation had occurred for Run 6. However, other observations, particularly sugar runs 1, 2, 3 and 5 showed signs of condensation, mimicking the Soviet experience (Player, 1985) in that sugar at the cold end of a gradient underwent some form of condensation and became "sticky" whilst the drier, warmer end tended to be hard and brittle. These results confirmed the decrease in water content of sugar near the warmer plate with water migrating towards the colder plate (see Table XII).

TABLE XII - Moisture results for migration runs No 5 and 6

Run No \ Sample location	Initial Moisture (%)	Final Moisture (%)
Run No 5		
Prior to experiment	0.28	0.31
Near top (cold) probe	0.28	0.35
Near bottom (hot) probe	0.28	0.19
Clump of moist sugar	0.28	2.0
Run No 6		
Prior to experiment	0.58	0.68
Near top probe	0.58	0.59
Near bottom probe	0.58	0.56

Clumps of moist sugar observed in Run 5 result from the excess moisture condition experienced as a result of moisture migration. The degree of water diffusivity in the syrup layer will vary throughout the bed, hence some regions within the bulk may experience high moisture conditions (i.e. forming clumps) whilst other regions remain clump free.

The work by Bisley (1991) re-enforces the theory proposed earlier by Vender (1984-85) in that the driving mechanism for moisture migration occurs as a result of partial pressure gradients in the bulk sugar generated by temperature gradients.

10.0 Surface tension analyses

As shown in previous investigations by Horiki (1965), Powers (1982), Mikus and Budicek (1986), Vender (1984-85) and Wright et al (1987), the quality of syrup surrounding the sugar crystal is of prime importance when examining hardening characteristics.

As only a small amount of syrup is removed from raw sugar following centrifugation (typically 0.05-0.1 g), any measurement of physical or chemical properties is hindered. Fortunately, the surface tension of the syrup may be measured using the drop weight method. Requiring a capillary, micrometer-driven syringe and an analytical balance, the method as outlined below is fast and inexpensive.

10.1 Adopted method

10.1.1 Following centrifugation, the derived syrup is drawn through a fine capillary of known radius (r).

10.1.2 Once sufficient syrup is drawn into the capillary, a micrometer device is attached to the vertically suspended syringe and wound until one drop of syrup is expelled from the capillary.

10.1.3 From the mass of the drop (m), the surface tension (γ) is calculated using Eq 15.

$$\gamma = \frac{\phi mg}{2\pi r} \quad (15)$$

where

g = acceleration due to gravity

ϕ = calculation correction factor.

The correction factor (ϕ), as stated by Shaw (1980), is required because on detachment (a) the drop does not completely leave the capillary tip; (b) the surface tension forces are seldom exactly vertical and (c) there is a pressure difference across the curved liquid surface.

10.2 Results - Syrup surface tension

Surface tension analyses of syrup removed from several raw sugars failed to yield any sensible, reproducible data. Consequently, no data for this analysis is reported.

11.0 Cuban Sugars & The Cuban Story

Quantities of two cuban sugars were received with analysis figures shown in Table XIII.

TABLE XIII - Analysis of Cuban sugars received for Sugar Hardening investigation.

Sugar Origin	Analysis					
	Pol	RS	Ash	RS/Ash	Water	DI
ex mv "Varadero"	98.23	0.48	0.40	1.2	0.35	25
ex mv "Peony Islands"	98.11	0.48	0.39	1.2	0.43	30

11.1 Shear Strength

As reported previously by Vender (1984/85), Cuban sugars yielded lower shear strengths in comparison to all other Australian sugars tested, especially at -10°C as shown in Table XIV.

TABLE XIV - Mean shear strength of Cuban and Australian sugars used in the investigation.

Sugar Origin	Shear Strength (kPa)	
	+5°C	-10°C
Cuban		
ex mv "Peony Islands"	2.63	4.26
ex mv "Varadero"	2.87	4.10
Australian		
Moreton - 15 ^a	3.02	5.59
Moreton - 16 ^a	3.00	4.67
Bingera - 48 ^b	3.39	5.53
Bingera - 62 ^b	3.26	5.64
Hambledon - 32/33 ^c	3.64	6.08
Inkerman - 92 ^c	3.70	5.07

Sugar Type: a - Very High Pol (VHP), b - Br 1, c Br JA.

11.2 Syrup characteristics

Centrifugation of "as received" Cuban sugar failed to yield any syrup for analysis. Consequently, the DI of each sugar was increased to accommodate the removal of syrup. As with Australian sugars, Cuban sugar syrup purity decreased with time, however the small quantities of sample obtained allowed only a small amount of data to be generated.

11.3 Crystal Geometry

Cuban sugars, noted for their handling superiority in cold climates, tended to consist of larger crystals in comparison to Australian sugars tested (see Fig 22).

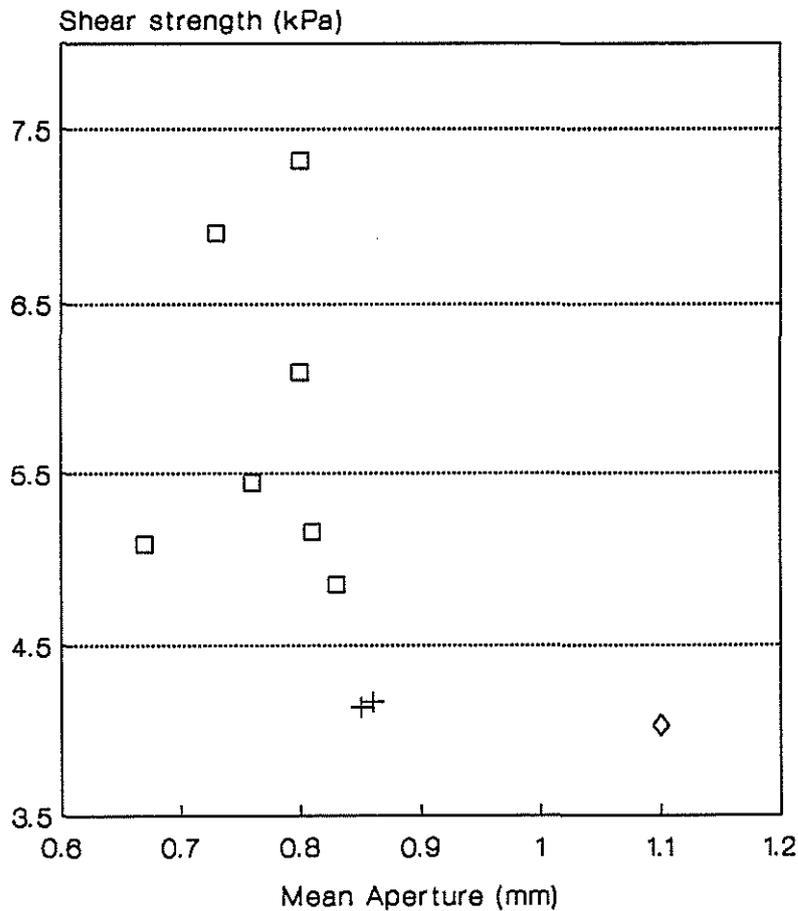


Figure 22 - Plot of mean aperture versus shear strength for various sugars; \square Australian sugars; $+$ Cuban sugars; \diamond Lab manufactured.

A plot of % fines i.e. % crystal passing through 600 μ sieve versus shear strength also gives some understanding of the role of crystal geometry in the caking process (see Fig 23).

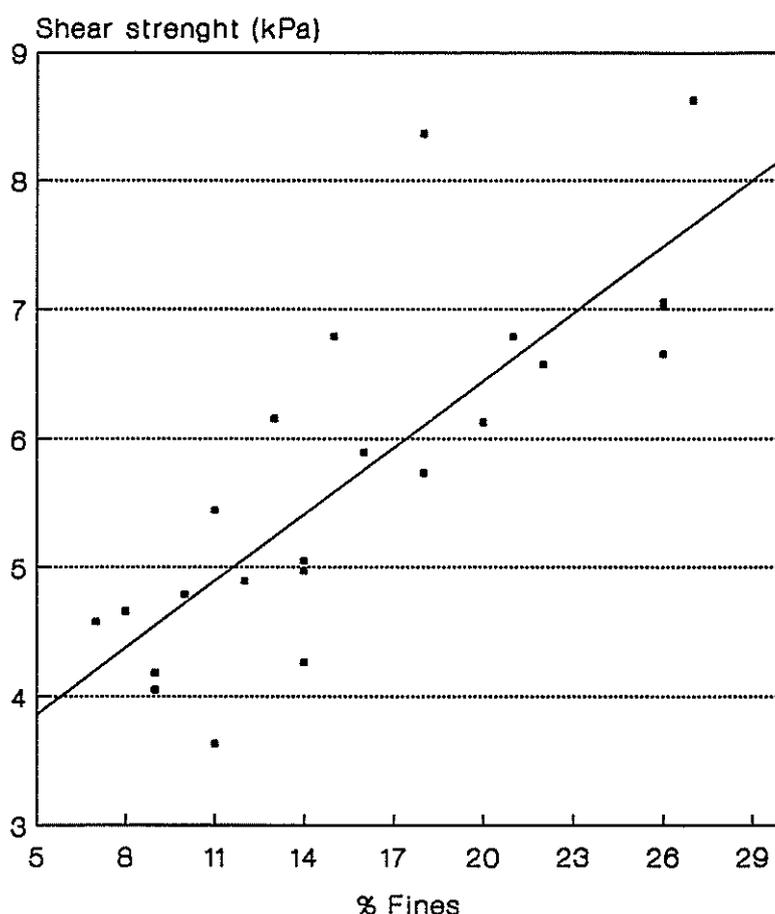


Figure 23 - Plot of % fines versus shear strength for various sugars.

11.4 The Cuban Story

Cuban sugar has for a long time held the distinction of having superior handling characteristics in cold climates in comparison to its Australian counterpart, a claim made at Soviet factories where such sugars are refined. The following aims to illustrate why this perception is held, and how Australian raw sugar may be manufactured to overcome the handling difficulties currently experienced in cold climates.

11.4.1 The USSR incident

Handling difficulties experienced with Australian raw sugar in the USSR in 1982 and 1983 resulted in a research program which investigated the hardening or "caking" phenomena. From this research an "optimum Pol" theory evolved which claimed to overcome the handling difficulties experienced with both high and low Pol sugars i.e. at some specific pol, caking would be minimised. Unfortunately, full-scale testing of sugars made to tight specifications did not fulfil these expectations as a result of moisture migration in the bulk sample. This observation merely fuelled more research into moisture migration and hardening in raw sugar.

11.4.2 Cuban manufacturing techniques

The quality of raw sugar produced at Cuban mills reflects the milling\storage techniques utilised. As the Cuban process does not involve a drier stage (Palaez, 1991), the raw sugar relies on evaporative cooling\drying whilst being transported to the pile via sugar thrower. Storage

environmental conditions during stockpiling will therefore directly affect the quality of the stored sugars. An indication of the variability of quality of raw sugar exported from Cuba is realised in the following data (see Table XV).

TABLE XV - Quality of Cuban raw sugar 1980-1990*

Quality Parameter	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990
Pol (%)	98.00	97.96	97.96	97.84	97.55	95.98	96.97	97.64	97.64	97.22	97.30
RS	0.40	0.38	0.49	0.36	0.44	0.75	0.74	0.64	0.62	0.50	0.35
Ash	0.39	0.44	0.38	0.40	0.36	0.38	0.38	0.41	0.42	0.37	0.43
RS/Ash	1.03	0.86	1.29	0.90	1.22	1.97	1.95	1.56	1.48	1.35	0.81
Water	0.72	0.71	0.66	0.92	1.28	1.28	1.14	0.89	0.63	1.08	0.54
DI	56	53	48	74	36	47	60	61	36	64	25
Colour	1538	1544	1473	1813	1249	3078	Ω	Ω	1463	1380	1140

* - (Gutknecht, 1991)

Ω - Values not kept in records

11.4.3 Quality of Cuban Sugar

11.4.3.1 Consequences of a higher RS/Ash ratio

As can be seen in Table XII, Cuban sugar generally exhibits a higher RS/Ash ratio than most Australian sugars (typically RS/Ash=0.8). As a result, several characteristics of the gross sample are changed.

a. The presence of a greater proportion of reducing sugars in the syrup layer results in an increased hygroscopic nature of the syrup layer (Lu et al, 1977). Therefore, a higher RS content reduces the ERH of the sugar, reducing the hardening propensity by inhibiting migration of moisture away from the syrup.

b. As a result of a higher RS content in the surrounding syrup, less syrup of high RS/Ash would be required to achieve the same pol. This relationship was borne out in data generated in this investigation, as seen in Fig 9.

As a consequence, Cuban sugar consisting of higher RS/Ash syrup will tend to have less syrup coating the crystal. The reduced % syrup therefore inhibits moisture migration further as the network of water carrying material is reduced, reducing the hardening propensity of that sugar.

c. Cuban sugar is generally of larger mean aperture in comparison to Australian sugars. Larger crystals equate to a smaller crystal surface area per unit mass, effectively increasing the thickness of the syrup layer. In doing so, the effective area of the syrup/air boundary is reduced, thus possibly altering the diffusion flux in the exchange of moisture across this boundary (Vender, 1989), possibly altering the degree or magnitude of caking.

Results tabled in this report indicate an inverse relationship between crystal mean aperture and shear strength (see Figs 14, 22).

11.4.3.2 Crystal Mean Aperture (MA) and Coefficient of variation (CV)

Specifications for Cuban raw sugar (Palaez, 1991) indicate a 75% caught #20 (840 μ) sieve criteria i.e. a minimum 75% of the crystal should be >840μ. Comparatively, Australian sugar achieves specifications limits by attaining % fines (% crystal passing through 600μ sieve) less than 15%. This equates to minimum 85% crystal >600μ. It is therefore the nature of this criteria

that leads to an increased MA for Cuban sugar, as one requires a certain MA i.e approximately 1.0 to achieve this criteria (see Fig 22). Assuming MA/CV data for two hypothetical sugars to be 1.0/30 and 0.9/30 respectively, arithmetic probability plots indicate that the % fines for the former sugar would be half that of the latter (see Figure 24, Table XVI).

TABLE XVI - Figures taken from arithmetic probability plot for two hypothetical sugars.

Sugar	MA	CV	% Fines
Sugar 1	1.0	30	7
Sugar 2	0.9	30	14

As indicated in Fig 23, reducing the % fines effectively reduces the propensity of raw sugar hardening.

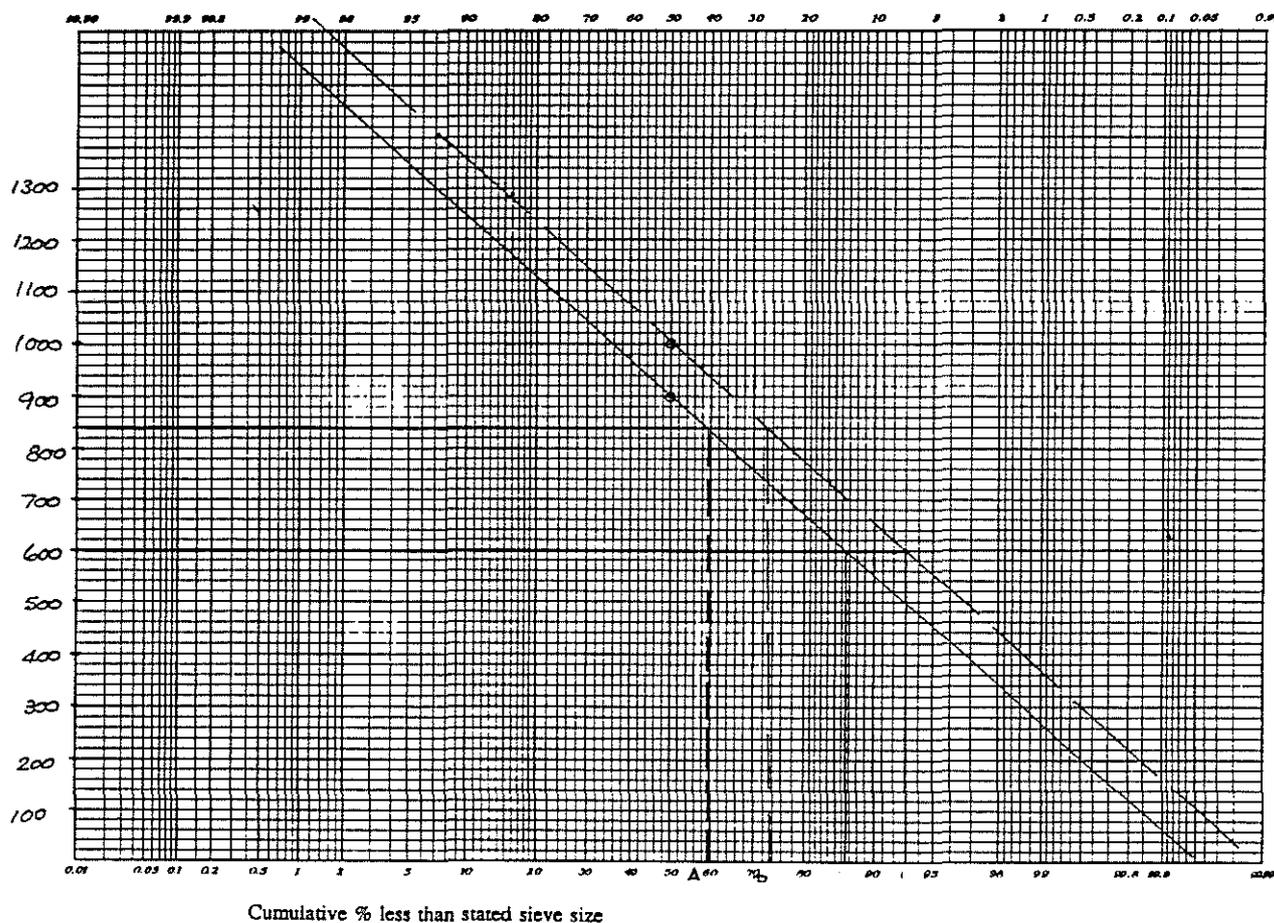


Figure 24 - Arithmetic probability plot of sieve size (μm) v cumulative % caught for stated sieve for two hypothetical sugar samples.

F. Conclusions

Although this investigation has assessed the significance of several raw sugar qualitative characteristics in relation to hardening on a case-per-case basis, the solution to the problem lies in combining these individual findings into one optimum solution.

Sugar and Syrup Quality

The moisture content of both raw sugar and syrup centrifugally removed from the crystal indicated that higher moisture sugars (approx 0.5%) tended to harden to a greater extent than the lower moisture sugars. It could be argued that the moisture matrix present in a pile of sugar contributes to the degree with which moisture will migrate within that pile. Consequently, a matrix that provides a good medium for moisture migration i.e. higher % moisture sugars will tend to harden to a greater extent. This effect was illustrated in the shear strength data generated for sieved sugar crystals. It was noted that the <600u crystals of comparatively high moisture (0.32%) attained higher shear strength over a shorter period of time (1 day), in contrast to the lower moisture sugar (0.17%) which required three days to attain some equilibrated strength. This suggests that although the physical component of the sugar bed was essentially the same for both sugars, the underlying factor is that the period each sugar required to harden is a function of the moisture present. Higher pol sugars would therefore mitigate the degree of hardening as a result of the lower moisture, although very high pol sugars (ca. 99.00 pol) should be avoided.

As a consequence of pol and water, the derived quantity DI is another quality parameter that can be addressed to minimise the likelihood of caking. Results indicated that DI's <25 and >40 units provide a sugar with reduced propensity to harden. This again is a reflection of the contribution sugar moisture makes, but also takes into consideration sugar impurities. It suggests that higher purity sugars would reduce the hardening propensity of raw sugar.

The measurement of syrup purity as a function of time indicated that a degree of "exhaustion" is achieved some 25 weeks after production. Both DI and purity of syrup removed from freshly prepared sugars levelled-off after approximately 25 weeks. It was also noted that some 25 weeks after production, shear strength of sugars examined attained some form of equilibrium and maintained a somewhat constant strength. This may reflect the contribution of syrup purity to raw sugar hardening propensity as a function of time.

The quantity of reducing sugars (RS) in the syrup layer was found to have a significant effect upon the shear strength achieved by some sugars. Br 1 sugars coated with invert syrup attained a lower strength than all other normally manufactured sugars examined. The presence of reducing sugars in the syrup has the effect of;

- i) increasing the hygroscopic nature of the syrup layer via reducing the partial pressure of the water in that syrup (Lu et al, 1977). Therefore the tendency for moisture to migrate in the sugar is reduced, reducing the inclination for that sugar to cake;
- ii) reducing the available sucrose in the syrup layer thus reducing the tendency for crystallisation of sucrose from that syrup (Bates, 1942);
- iii) reducing the purity of the syrup layer by replacing sucrose/ash species with RS/ash species, allowing a greater quantity of the sucrose in the syrup layer to crystallise onto the bulk crystal thus reducing the likelihood of further crystallisation due to the reduced purity (Gupta et al, 1968).

One other contribution made by RS in the syrup layer is that the higher the RS content of the syrup, assuming the gross crystal comprises 100% sucrose, less syrup is needed to attain the same pol. Therefore, by further reducing the quantity of syrup surrounding the crystal, one reduces the medium through which hardening can occur i.e. moisture migration as a function of the air\syryp\crystal boundary relationship.

Alcohol insoluble material in crystal syrup

The strong proportional relationship exhibited between the quantity of alcohol insolubles in the syrup layer and shear strength introduces another factor into the hardening mechanism arena. It is possible that the presence of this material in the syrup layer increases the viscosity of the syrup, thus promoting syrup thickening and consequently caking.

Physical characteristics

A claim made by Soviet officials during the hardening experience in 1984 (Player, 1985) was that Australian sugar tended to contain a higher proportion of fine grained sugar, and that it was this fine grain that produced the handling difficulties. Although the increased level of fine grain does yield higher shear strengths, it is more likely to be the distribution of crystals in the bulk which relates more closely to the hardening propensity. Results of sieved sugars versus normal sugars reflect a lower shear strength for the sieved group (see Table XVII).

TABLE XVII - Comparison of shear strength data for sieved, non-sieved sugars.

Sugar Type	Shear Strength (kPa)
Sieved	
< 600 μ	1.61 - 3.01
600-850 μ	2.38 - 3.15
> 850 μ	1.89 - 2.45
Non Sieved	
Cuban	4.10 - 4.26
Australian	4.67 - 6.08

Cuban sugar examined consisted of larger average sized crystal in comparison to all other Australian sugar tested. Results indicated an inverse relationship between crystal mean aperture and shear strength, suggesting a larger crystal is preferable in reducing the caking propensity.

Humidity of storage environment

Sugars subjected to varying relative humidities indicated an increase in DI as a function of % relative humidity (%RH). In environments of increased %RH, the equilibrium relative humidity (ERH) of the sugar is lower than that of the environment, resulting in the migration of moisture to the syrup layer until equilibrium is attained. The humidity differential therefore provides another mechanism for moisture migration in bulk sugar, independent of temperature.

Moisture migration

The moisture migration work conducted at Sydney University (Bisley, 1991) for inclusion into this report verifies the theory that the driving mechanism behind moisture migration is indeed the differential of partial pressure of water vapour present in the system. Moisture migrates from areas of high water vapour pressure (hot region) to an area of low water vapour pressure (cold region), resulting in dry\brittle sugar in the warmer regions and moist\sticky sugar in cooler regions. This experimentation mimics that experiences realised in bulk sugar sent to the U.S.S.R. during 1984 i.e. varying degrees of hardness in sugars subjected to temperature differentials of 10-15 °C.

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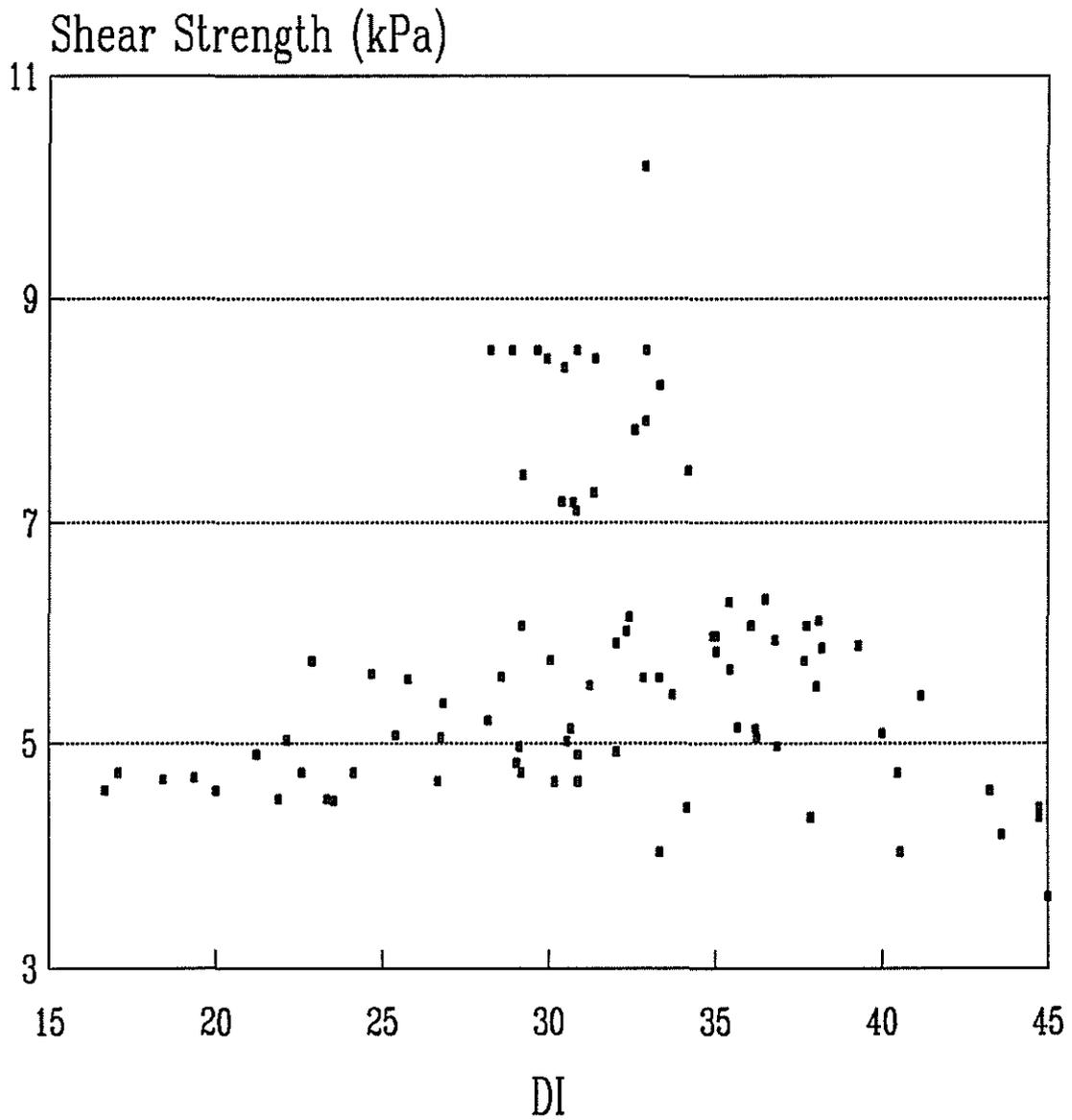
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Appendix A
Plot of Shear strength (kPa) as a function of DI



Data may be represented by the following 2nd order relationship;
Shear strength (at -10°C) = $-14.495 + 1.771(\text{DI}) - 0.47(\text{DI}^2)$.

