EFFECT OF CULLET LEVEL ON AMBER GLASS QUALITY, WORKABILITY AND COMMERCIAL VIABILITY

By

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ABSTRACT

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The effect of high cullet levels on amber container glass was studied. A statistical approach was taken in assessing glass quality, glass workability and commercial viability. Cullet levels were increased from 40% to 70%. Glass quality was assessed in terms of stone, seed and blister levels, as well as composition and colour stability. Glass workability was assessed in terms of bottle faults due to checks, thin walls and cavity related defects. Commercial viability was assessed in terms of production efficiency and bottle breaking pressure. The results show that there was an overall improvement in glass quality, glass workability and commercial viability after the batch sulphate levels were increased at 60% cullet. It was found that the glass viscosity characteristics had an overriding effect on glass workability and commercial viability. These results are of primary importance because of increasing glass recycling, environmental issues and the trend toward lighter weight containers. It is recommended that cullet levels be increased as needed up to 70%, provided batch excess sulphate levels are kept constant. Further work at cullet levels up to 100% should be initiated to assess the possibility of full recyclability of glass in the future.

TO MY WIFE, TARNIA.

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LIST OF SYMBOLS, ABBREVIATIONS AND ACRONYMS

41m/c	Forming machine 41
42m/c	Forming machine 42
ACI	Australian Consolidated Industries
AGM	Australian Glass Manufacturers
ART	Automatic Random pressure Tester
bpm	Bottles per minute
C/O	Change over
CID	Cavity Identification Device
CUR	Check Under Ring
CVI	Commercial Viability Index
DC	Distribution Channel
F	F statistic
k	Number of data samples
MB1	Glass furnace Melbourne 1
MB4	Glass furnace Melbourne 4
MIN	Minute
n	Number of moles
N	Total number of observations in all samples
n_i	Number of observation in each sample
NNPB	Narrow Neck Press & Blow forming process
O-B	Owens - brockway
PIC	Production Information Computer
ROA	Recyclers of Australia
S.D.	Standard deviation
SID	Sidewall Inspection Device
SK	Pearsonian coefficient of skewness
SS(E)	Error sum of squares
SS(Tr)	Treatment sum of squares
SST	Total sum of squares
T..	Grand sum of all data
T550%	Light transmission at 550nm wavelength
T_i	Sum of data of the i^{th} treatment
tpd	Tonnes per Day
TW	Thin Wall
x_{ij}	The j^{th} observation of the i^{th} sample
XRF	X-Ray Fluorescence machine

1.0 INTRODUCTION

Using high cullet levels (greater than 50%) is not new. As early as 1968 Manring and Conroy[1] conducted classic experiments with cullet and batch. They showed that as the cullet percentage increased, interference occurred between the cullet and the soda ash, causing prolonging of melting times. Part of their work involved plant scale melts of 100% cullet. A relatively quiet period prevailed after this, until the early to mid eighties when the subject assumed importance again.

Both the environmental movements and the glass manufacturers' push toward light weight containers around the world, were responsible for this trend. The environmental push was led by Canada and California in the U.S.A. where legislation demands up to 60% cullet reuse[2]. Laws have been no less stringent in the state of Victoria, where in 1985 the government introduced the Beverage and Container bill requiring 60% cullet recycling by 1991. A further bill, Environmental Protection (Resource Recovery) Act, was introduced in 1991 specifying a 50% reduction in waste by the year 2000. This bill has placed the onus on local councils and industry by introducing a $2 levy on each tonne of waste going to land fill. In 1991 recycling rates in Victoria were 57% of manufactured container glass and if current trends continue they will grow at between 5% to 10% per annum. In terms of manufacturing, the Narrow Neck Press and Blow (NNPB) Process led to the introduction of more convenience orientated, single trip containers throughout the 1980's and hence to an increase in available cullet. The growth in tonnes of recycled glass over the past eight years in Victoria is shown in Figure 1.

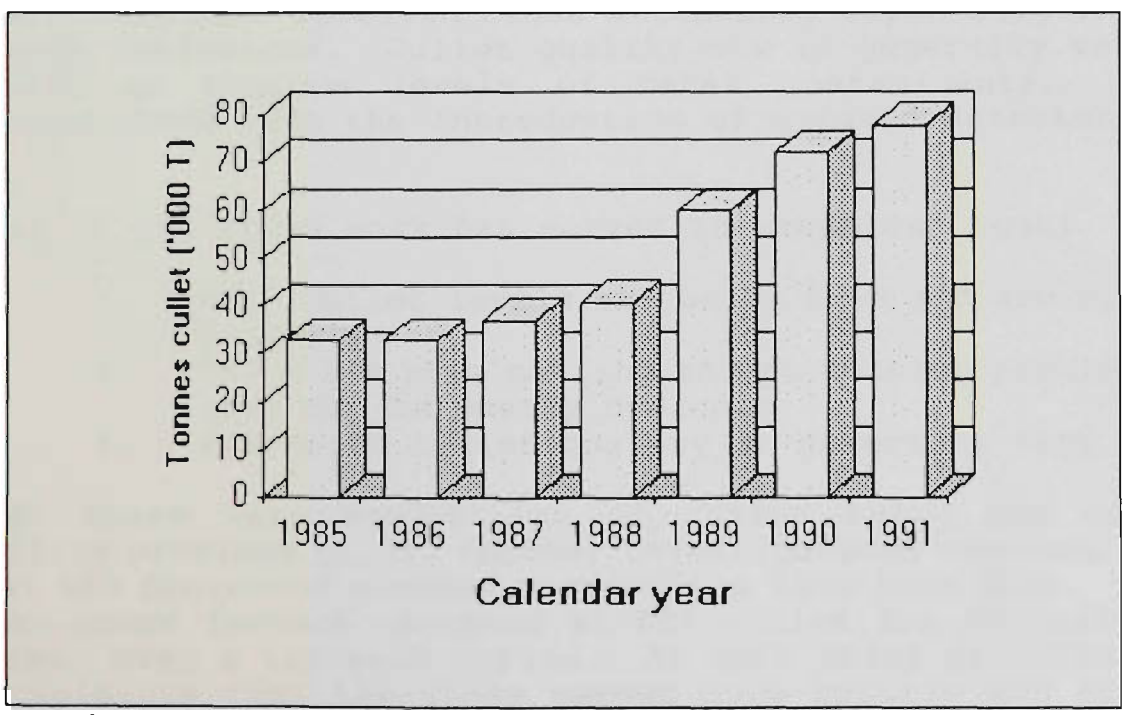

Figure 1. Tonnes of cullet recycled in Victoria

With the change from the 30% cullet domain to 60%, came both associated benefits and processing problems. Werner [3] recorded fundamental batch-cullet segregation problems leading to uneven batch pattern and in the extreme, unstable forming conditions. Hilson [4] reported that a flattening of the furnace optical profile was required at high cullet levels resulting in a fuel consumption higher than expected. Other articles report reduced raw material usage [5], savings in fuel usage and reduced furnace superstructure temperatures [6], as cullet levels are increased. Appropriate solutions were found to most operating problems.

Glass quality problems were also reported especially in amber glass. Weiser [7] reported that as the cullet percentage was increased, the effect of carbon additions on the transmission of light at 550 nm was significantly reduced. Hilson [4] reported that carbonaceous material in ecology cullet can dramatically offset normal colour control practices. On the matter of seed levels, Hilson [4] reports high seed levels being encountered after running at 100% amber cullet for some months. Significantly, both quality problems were overcome through the implementation of appropriate batch adjustments. Again, Hilson [4] recorded variation in ecology cullet composition. He concluded that although there was a drift over a number of months, the daily variation was minor and did not significantly alter the final glass composition.

Other areas of interest have been the method of collecting recycled glass and the quality of the resultant cullet. Throughout the world there are two common collection programs, the curbside and the dropoff collection. Both methods can be economically sustained according to an American study [8], with the curbside method generally more costly but having better participation rates. The curbside method has been adopted in Victoria. The quality of the cullet has also received close attention, especially in regard to foreign inclusions. Cullet quality now is generally very good with zero or minimum levels of metal contaminants. Recent innovations have seen the introduction of ceramic detectors [9].

All of the above work has served to establish that:

1. High cullet levels are being used and are likely to increase;
2. There are some melting and processing problems, but they can be mostly overcome;
3. Processed cullet quality is generally very good.

Although there were suggestions of cullet being the cause of workability problems [1,2], further investigations were not carried out. At AGM Spotswood similar suggestions have been made. At this plant an amber furnace operated at 60% cullet for several months at a time, over a two year period. At this level of cullet there were complaints that the glass seemed more brittle and difficult to form than at lower cullet percentages.

The purpose of this work was to investigate the production of commercial amber glass and the effect that different levels of cullet have on the formability and quality of the final product. Cullet levels range from 40% to 70% of the batch weight. The effect on final product was measured in terms of glass quality, glass workability and commercial viability. In particular, this study determines whether these glass attributes can be related to variation in cullet level or whether the overall glass chemistry is the dominating factor. Within reasonable commercial constraints, only the cullet level of the batch was altered.

The furnace used in this work is known as MB4. It services two bottle forming machines making light weight amber containers at high production rates. A general layout of the glass manufacturing operation is shown in Figure 2. The furnace was totally rebuilt three months before this study commenced. As one of the machines does not change jobs, this setup was ideal for carrying out this investigation.

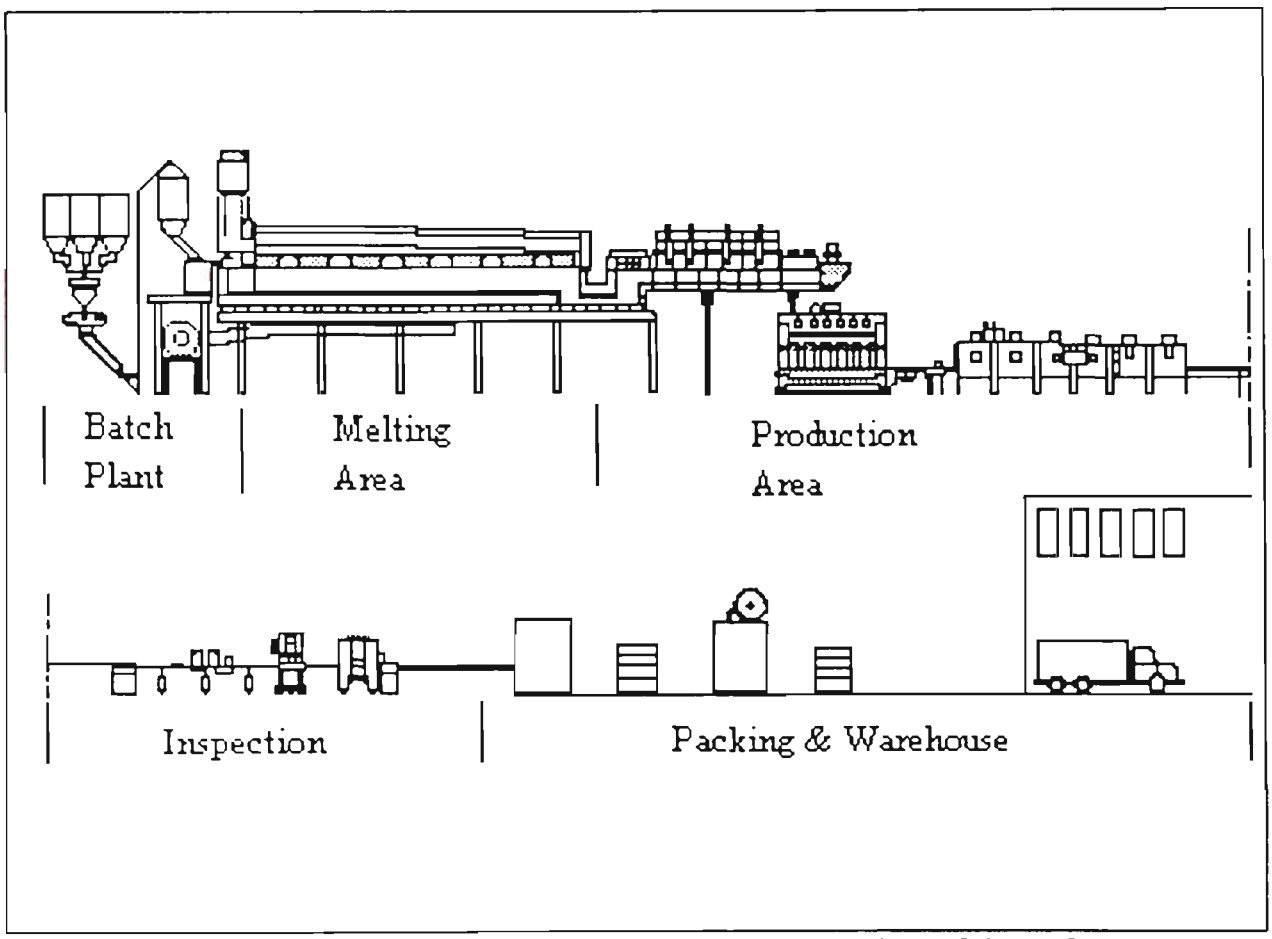

Figure 2. Typical glass plant production line layout

2.0 BACKGROUND

2.1 ANALYTICAL BASIS

To investigate the effect of batch cullet changes on the final product quality and forming performance, measurements were made in three major areas. They were:

1. glass quality;
2. glass workability;
3. commercial viability.

These areas were chosen because they are important elements in successful bottle manufacture and because several authors [1][3][5][6], have expressed concern that higher levels of cullet may adversely effect them. The specific measurements made for each area are discussed in the following section.

2.1.1 GLASS QUALITY is the fundamental building block for successful bottle manufacture. The quality of the glass is determined by the batching and melting process and is determined before the forming process begins. It was assessed by investigating the following specific attributes:

GLASS COMPOSITION STABILITY - is critical in maintaining all other quality factors steady. The glass composition determines the glass viscosity characteristics which have a large bearing on bottle forming characteristics. The target composition of the glass in this study is shown in Table 1. Glass composition stability is also referred to as glass density stability. The density can be measured easily and is sensitive to composition change.

SEED LEVELS - are an indication of how well the glass is being melted and refined. Seeds are gas bubbles trapped in the glass which are less than 3mm in diameter.

BLISTER LEVELS - are inherently a quality problem in amber glass. They are formed in the refiner or forehearth and can be attributed to poor forehearth firing, unstable glass sulphur chemistry or mixing of inhomogenious layers of glass [11]. Blisters are gas bubbles trapped in the glass that are larger than 3mm in diameter.

STONE LEVELS - are a measure of foreign inclusions found in the formed container. Certain inclusions, especially those from cullet (clay, metallic silicon), are highly stressed and can result in bottle failure. The electronic device used to detect these inclusions was able to detect particles down to 0.8mm in diameter.

LIGHT TRANSMISSION STABILITY at 550nm WAVELENGTH(T550%) - is a major customer requirement for amber glass. The T550% is monitored because it represents the amber colour of the container in the visible region. The amber transmission spectra in Figure 3, has a light transmission of approximately 25% at 550nm. The light transmission is controlled in amber glass by adjusting the glass redox balance using addition and removal of small amounts of carbon.

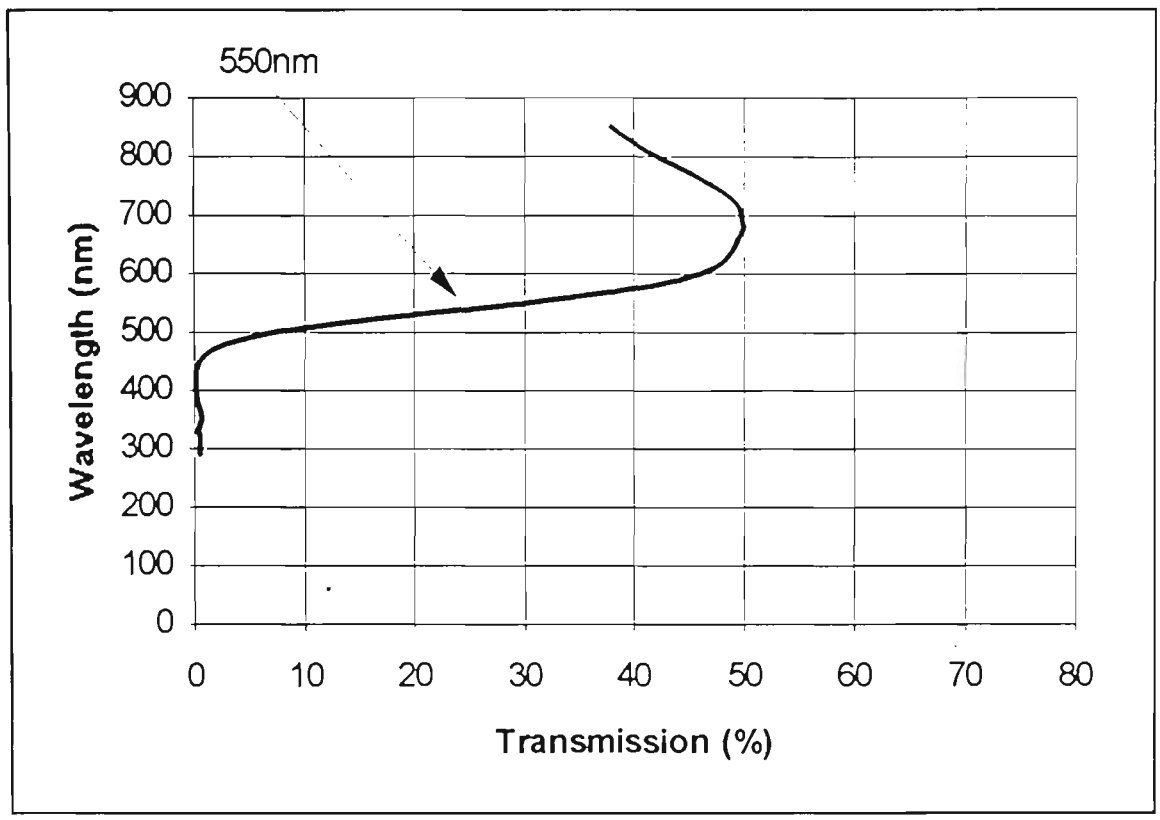

Figure 3. Chromaticity diagram of amber glass

Table 1. MB4 amber glass target composition

Oxide	Percent
SiO_2	71.7
NaKO	14.3
CaO	11.5
MgO	0.5
AlTiO	1.4
Fe_2O_3	0.3
SO_3	0.08

OWENS-BROCKWAY(O-B) AMBER STABILITY CRITERIA - are a set of five factors relating to the amber glass chemistry, developed through experience, relating to the stability of the glass. Their importance in amber glass is due to the delicate nature of the iron/sulphur balance required to form the amber chromophore [12]. It is this attribute alone that is the most crucial aspect of the amber glass quality.

2.1.2 GLASS WORKABILITY is a measure of how well the glass viscosity characteristics suit the bottle forming operation. The viscosity characteristics determine at what temperature the forming range will occur and how quickly the glass will cool (Appendix I).

The forming operation takes place in the glass visco-elastic region [13]. The viscous properties are dominant in the early stages of the parison formation and stresses that are set up can be dissipatated quickly. Toward the end of the process the elastic properties start to dominate and it is possible that the container although still being viscous, can be brittle as well. Tooley [13] reports that it is common to take one bottle from a forming machine and when squeezed with a pair of tongs it will shatter, another could as well collapse without breaking. This occurs in the viscosity region of log 6 to log 7 (Appendix I). It is possible to envisage that this would occur if there were inconsistencies in temperature or composition throughout the container. In extreme cases the elastic properties of the glass may result in checks (closed cracks) being formed during the parison formation.

Three major forming faults were measured in this study to assess glass workability. These faults were chosen because they were the main losses occurring on these production lines and could be related to the glass viscosity characteristics. The specific faults measured are as follows:

CHECK UNDER RING (CUR) - (or horizontal and vertical checks) can be related to the healing or reheat characteristic of the glass. There are several mechanical and machine operating causes for this fault [14], however there are times when the glass appears "hard" or "brittle" and the CUR losses increase. This is the most significant bottle fault related to glass workability.

THIN WALLS (TW) - are an indication of the glass flow characteristics or homogeneity. It is critical that the glass flows evenly throughout the container to achieve design wall thickness. The viscosity of the glass at a particular forming temperature is determined by the glass composition (Appendix I), however if the glass is not homogeneous, then uneven distribution may occur. This bottle fault is also a factor of the container design and machine settings, although for forming machine 42 (42m/c), the container design remained unchanged throughout the study.

CAVITY IDENTIFIED DEFECTS (CID) - are bottle defects that are identified as critical by an experienced operator, on-line, and are rejected by cavity. Generally, CID faults can be attributed to the forming machine operation, because the bottle defect is occurring on a particular cavity of the machine. Some examples of CID faults are, internal stuck glass, crizzled seam, a glass spike and split bottom. By comparing CID faults to TW and CUR losses, an indication is gained as to whether the glass or the machine is the major cause of the losses.

2.1.3 **COMMERCIAL VIABILITY** is a measure of the commercial success of the final container. This is measured as a check against the workability and glass quality results. It is possible to have excellent glass quality and poor commercial success of a container. The two parameters measured to assess commercial viability were chosen because they are excellent indicators of how a container will perform on filling lines. The parameters measured were:

EFFICIENCY - is an indication of the overall success of the job. It is the number of containers packed divided by the total number inspected.

BREAKING PRESSURE - is measured on bottles from every cavity of the machine at regular intervals throughout each shift. The measurements are made after the containers have been electronically checked for faults, so is an excellent indication of the final resilience of the container and the strength of the glass.

2.2 EQUIPMENT

2.2.1 CULLET PROCESSING

The cullet was processed at a plant run by Recyclers of Australia (ROA). The plant receives colour sorted glass from curb side pick-ups. Figure 4 shows a layout of the plant. The beneficiation begins via an air conditioned picking station where the incoming material is hand picked from three separate conveyors. The contaminants targeted at this point are ceramics and lead. A single conveyor takes the glass to a pre-screen, passing under a magnetic overband before being crushed in a Hazemag™ crusher. The crushed glass passes over a #(20mm) screen with a vacuum nozzle above to remove aluminium paper and plastics. The over-size material is returned to the main in-feed belt and passes through a separate air conditioned picking station where remaining ceramic contaminates are removed. The under-size glass falls onto the out-feed conveyor where it passes under a metal detector before being dumped onto an open processed cullet pile out-side. If metal is detected, it is removed from the main stream of material via a flap gate arrangement. The rejected glass and metal passes under another metal detector where the metal is again deflected onto a belt and into a waste container, while the glass is returned to the outward conveyor. The processed cullet is transported to AGM by 25 tonne semi trailers.

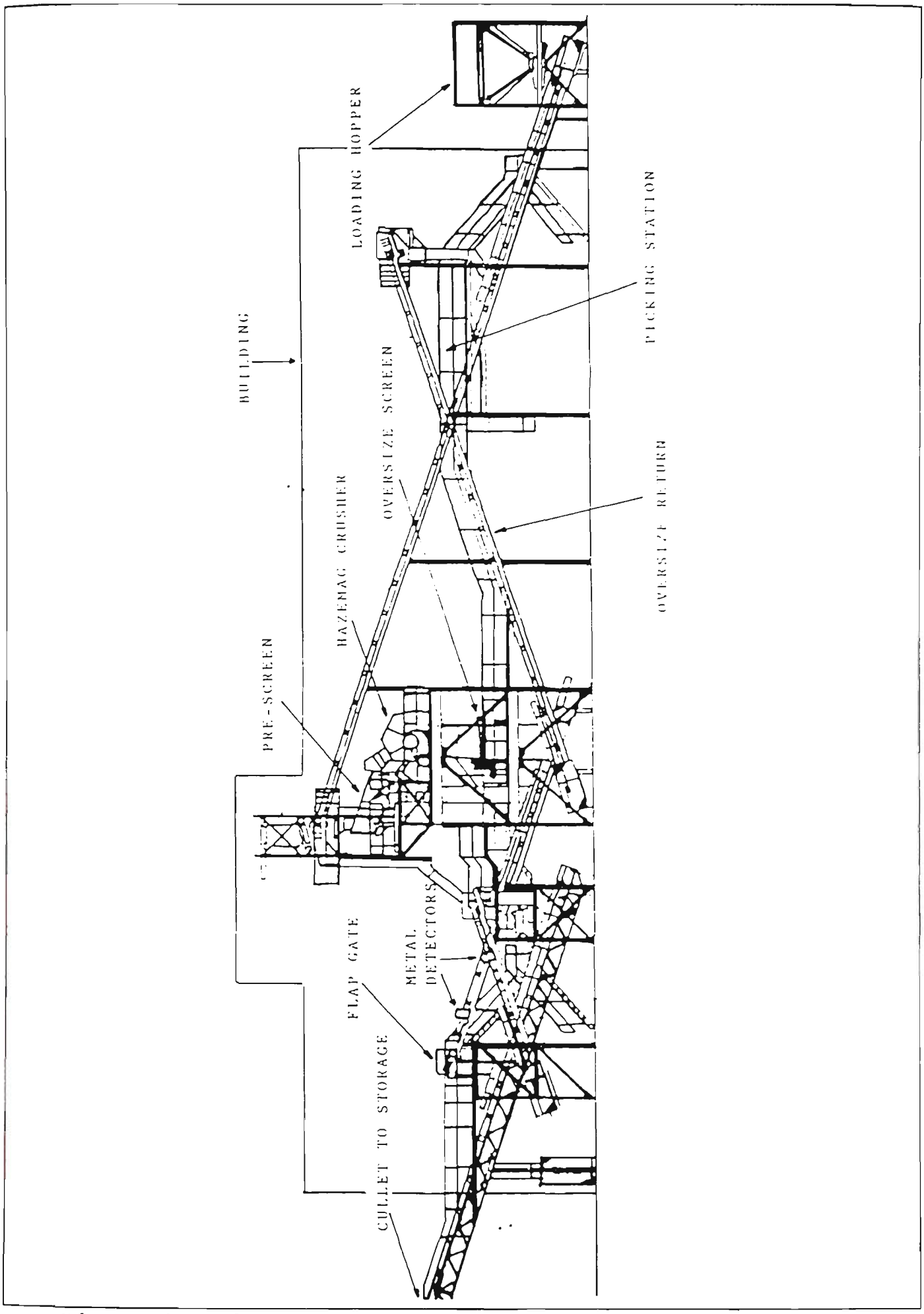

Figure 4. Cullet plant layout (ACI Engineering Services)

2.2.2 BATCH HOUSE

The batch house at AGM Spotswood is an in-line batch house using 13 weigh scales (Figure 5). The cullet is weighed out with the other raw materials (in a separate weigh scale for each colour), and then is mixed in a rotating drum mixer. The total melted weight of a batch is 1.8 tonnes. The batch house services four furnaces, producing an average of 840 tonnes per day (tpd). Flint, dark green and amber glass batch is mixed from the single batch house. The storage facilities allow for only 24 hours storage of cullet.

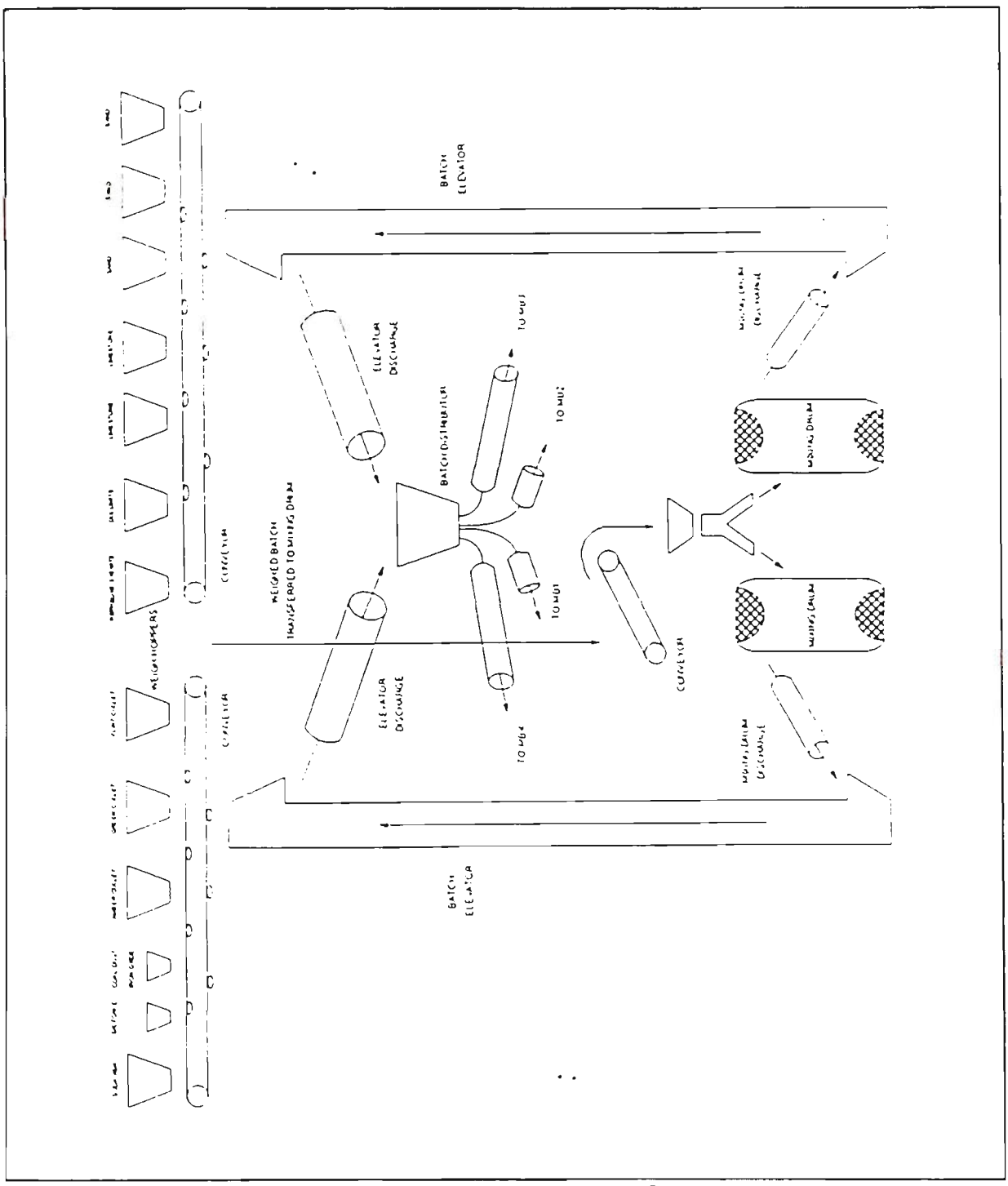

Figure 5. Batch house layout

2.2.3 FURNACE

The furnace (MB4), has two 106 tonne mass flow batch storage silos and the batch is fed into the furnace via two Hartford™ style chargers. It is a six port, regenerative, cross fired furnace running on natural gas alone (no electric boosting) and has a melting area of 112m^2 with a depth of 1350mm (Figure 6). The furnace was built in 1980 and the first campaign lasted just short of eleven years. A total rebuild of the furnace took place in 1991, and recommissioning was in September of that year.

The furnace is controlled by a Bailey distributed control system. The glass temperature is controlled automatically via a cascaded control loop to the crown temperature and gas flow. Glass temperature is measured via thermocouples placed in the furnace floor refractories. Glass level measurement is carried out using a dipping probe situated in the low profile refiner. Control of the level is done through the Bailey system.

2.2.4 REFINER/FOREHEARTH

A low profile refiner is used to distribute the glass to two forehearths set at either side of the furnace (Figure 7). On the 41m/c side, the refiner goes through a right angle turn into an Emhart™ forehearth with three cooling zones. On the 42m/c side the right angle turn is performed through a distribution channel (DC) with chamfered corners, leading into an Owens-Brockway™ (O-B) high performance forehearth with two cooling zones. The refiner and both forehearths are fired by natural gas and each has a form of centre-line cooling. The refiner, DC and the forehearths, have glass depths of 15, 8 and 6 inches respectively. Both forehearths use side wall electrode heating in the conditioning section to help produce even gob temperatures. Tri-level thermocouples are used to measure and control forehearth glass temperature. A direct digital control system is used to automatically control the refiner and forehearth operating temperatures.

2.2.5 FORMING MACHINES

The main bottle forming machine studied is referred to as forming machine 42 (42m/c). It is an O-B™ ten section blow and blow quad machine producing 520 bottle per minute (bpm) on average. A typical timing cycle and machine layout for a blow and blow operation are shown in Figure 8. 42 machine has an auto swab rejection cycle that rejects containers after mould swabbing has occurred. The containers produced on 42m/c are 375ml beer containers, referred to as stubbies. Forming machine 41 (41m/c) is an Emhart™ ten section triple gob blow and blow machine. A general diagram of the forming machine operation is shown in Figure 9.

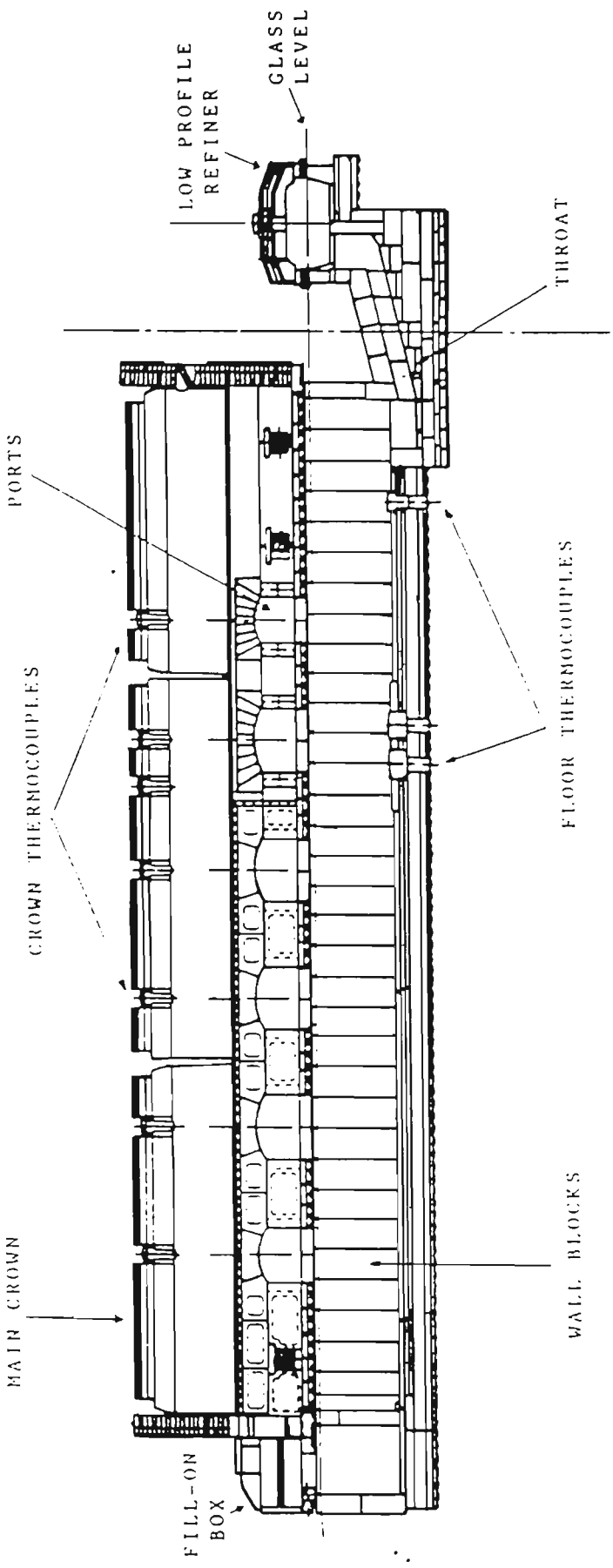

Figure 6. MB4 furnace overview (ACI Engineering Services)

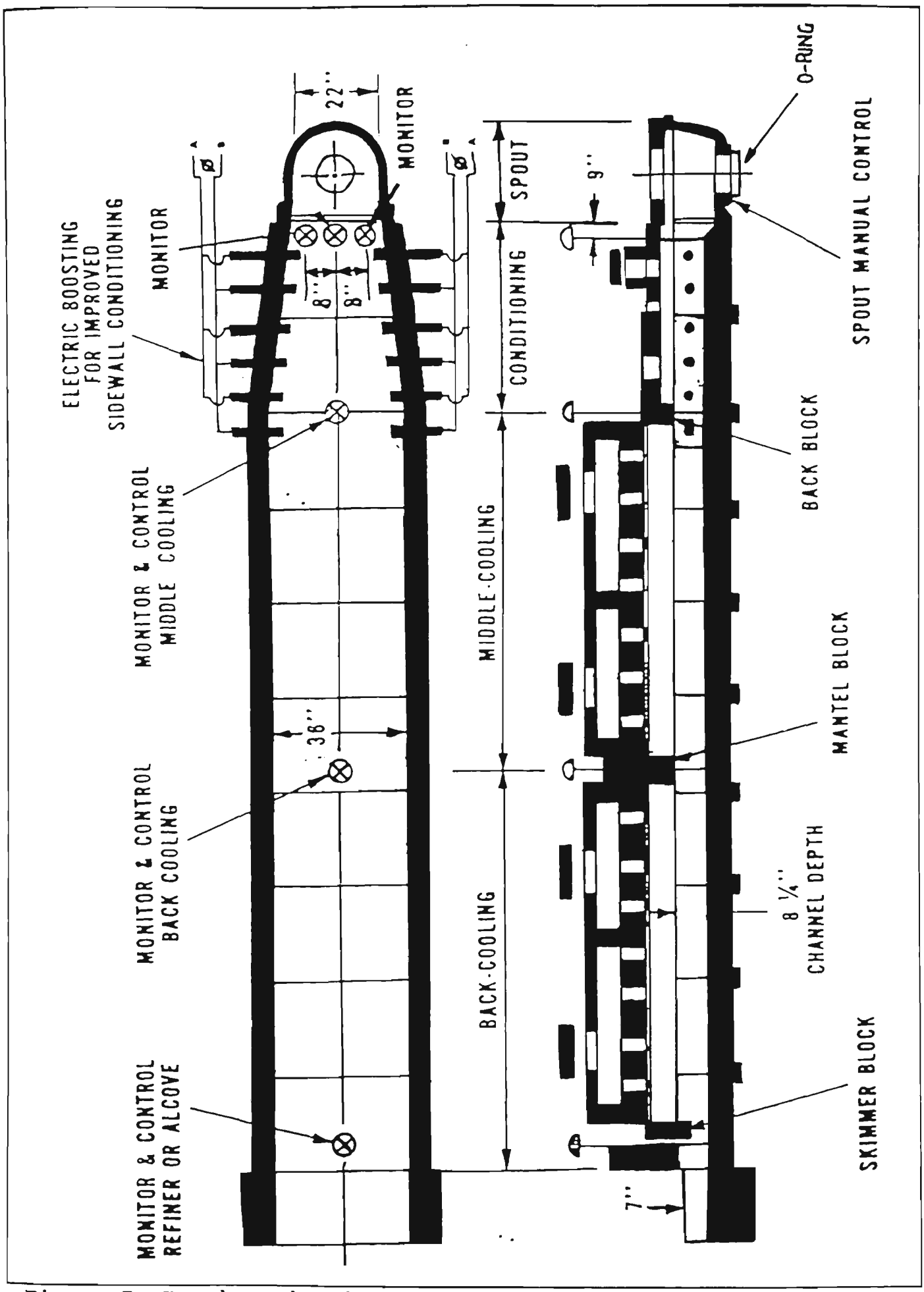

Figure 7. Forehearth schematic diagram (O-B Foreheath training manual)

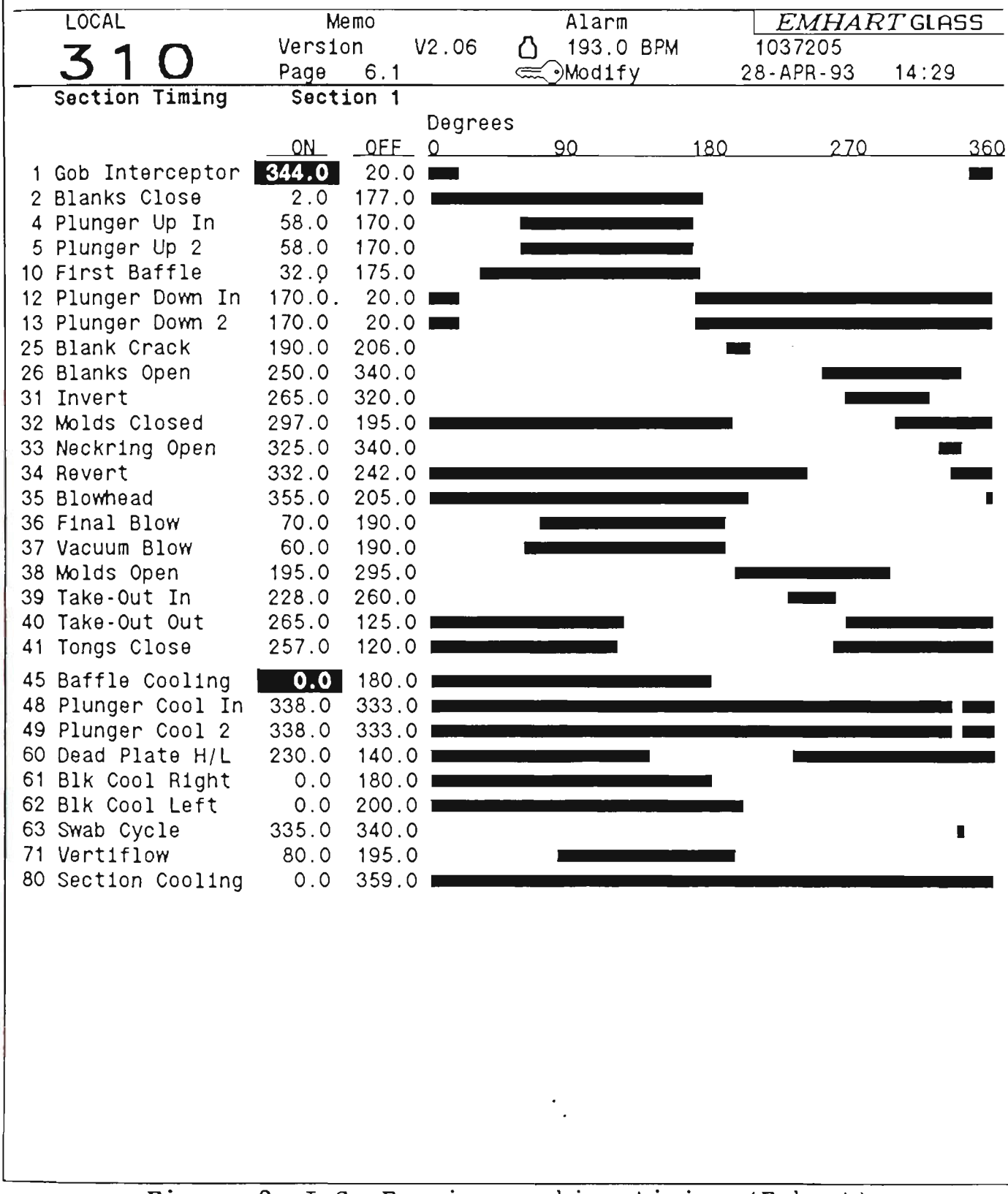

Figure 8. I.S. Forming machine timing (Emhart)

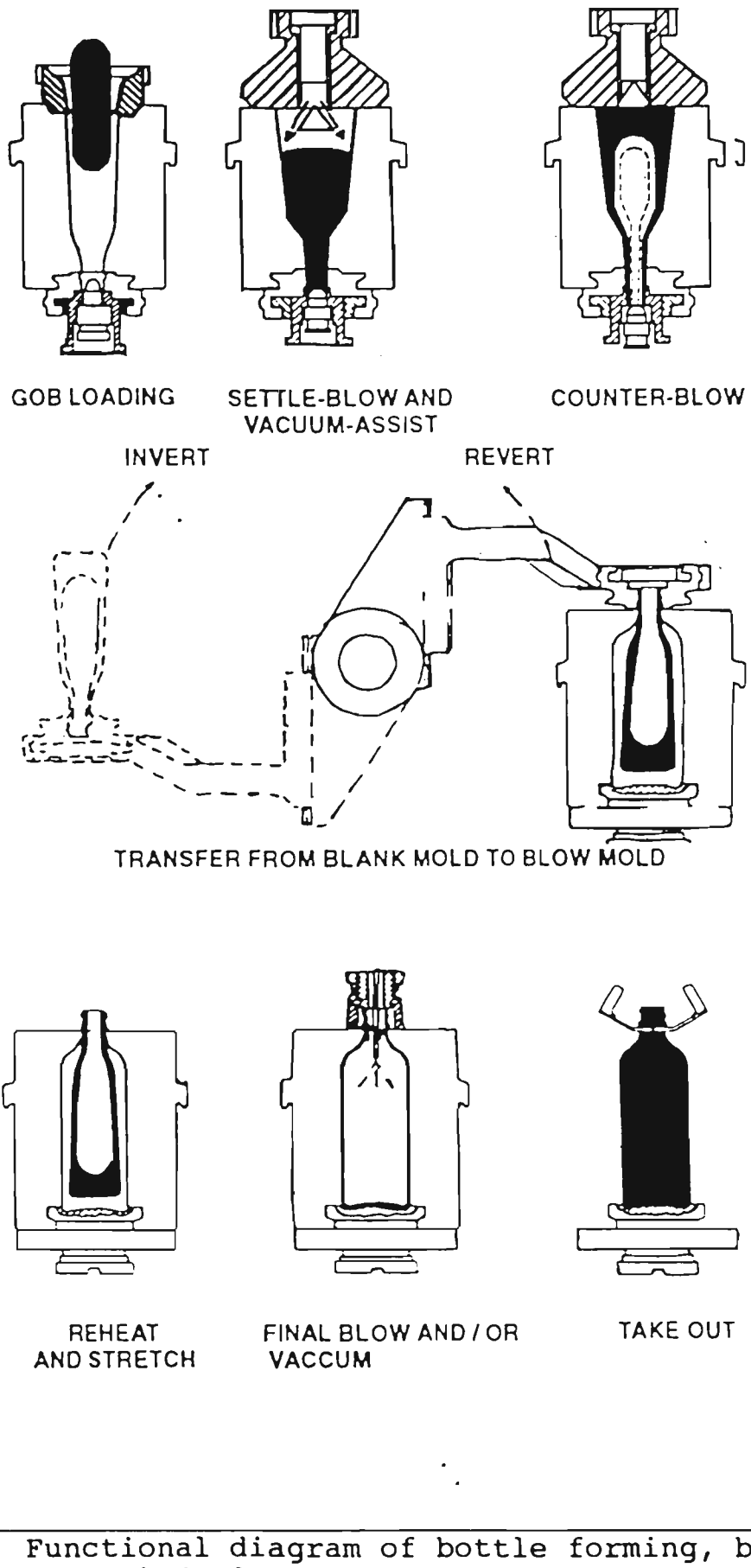

Figure 9. Functional diagram of bottle forming, blow & blow process (Emhart technical training manual)

2.2.6 BOTTLE INSPECTION

The bottle checking equipment used to check bottle faults in the inspect and pack area are O-B designed, called Triple Check Inspectors (Figure 10). They are multi functional devices that inspect every container for bottom checks, horizontal and vertical checks in the finish (CUR), side wall defects (SID), thin walls (TW), out of round, container height and bore diameter. There are five of these devices servicing the 42m/c production line and the same for the 41m/c production line. The faults analysed using this equipment were, SID, CUR and TW.

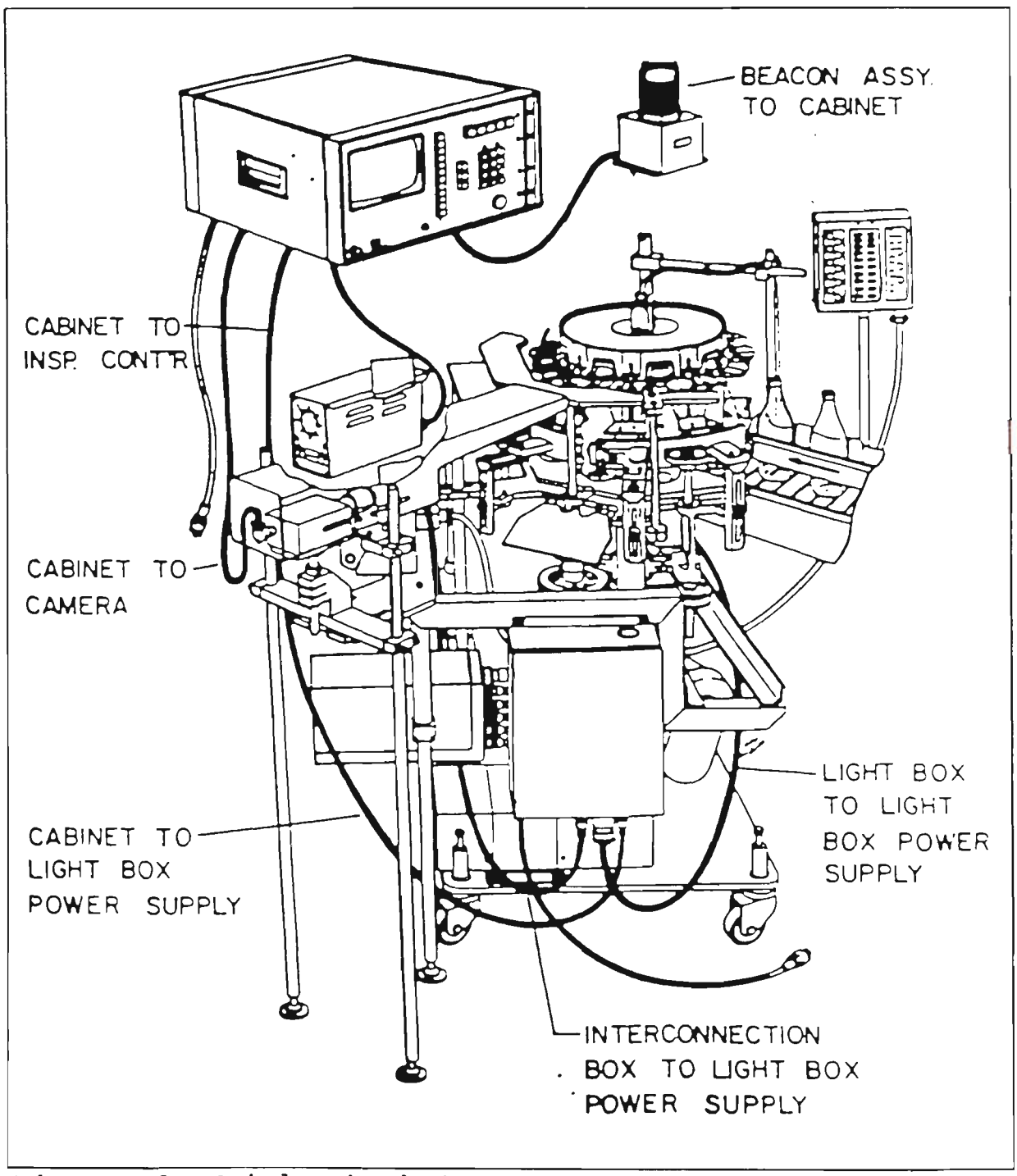

Figure 10. Triple check inspector (O-B technical manual)

Thin wall defects are determined using a radio frequency gauge (RFG) in conjunction with a probe roller (Figure 11). This device inspects a 15mm width of glass in the straight vertical side of the 375ml beer as it is rotated 360°. The RFG uses the dielectric properties of glass (the dielectric constant of air being the reference) to create a useable signal that is proportional to the glass thickness. The control circuitry discards all but the lowest signal recorded and compares this with the reject set-point.

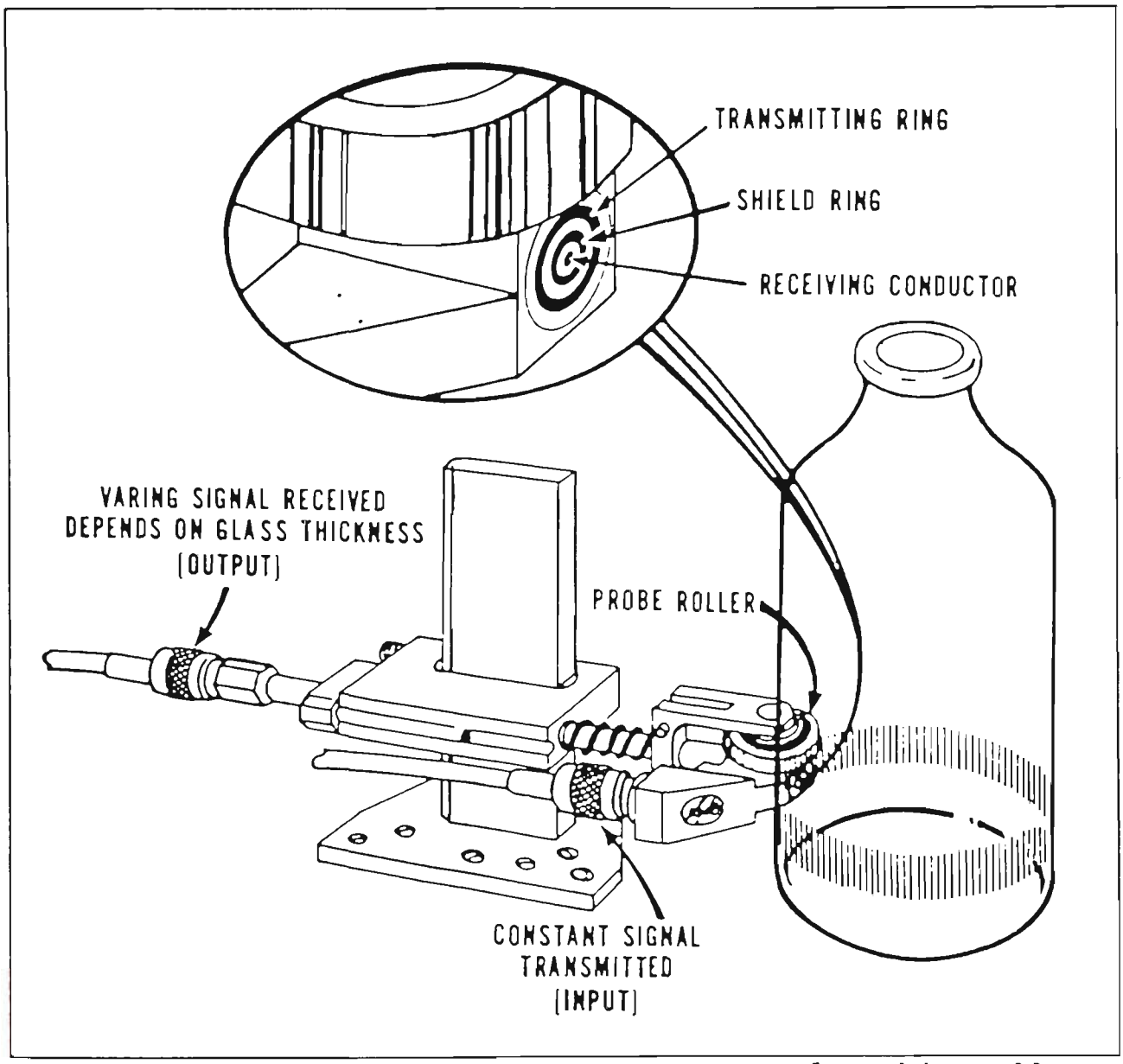

Figure 11. Radio frequency gauge (RF), for thin wall defects (O-B technical manual)

The check detectors used to measure CUR defects are an electro-optical device that detect both vertical and horizontal checks in the finish (Figure 12). They consist of a light source projecting a small line of light into the container finish and two photocells that pick up reflected light from a defect and convert it into an electrical signal. This signal then causes the container to be rejected.

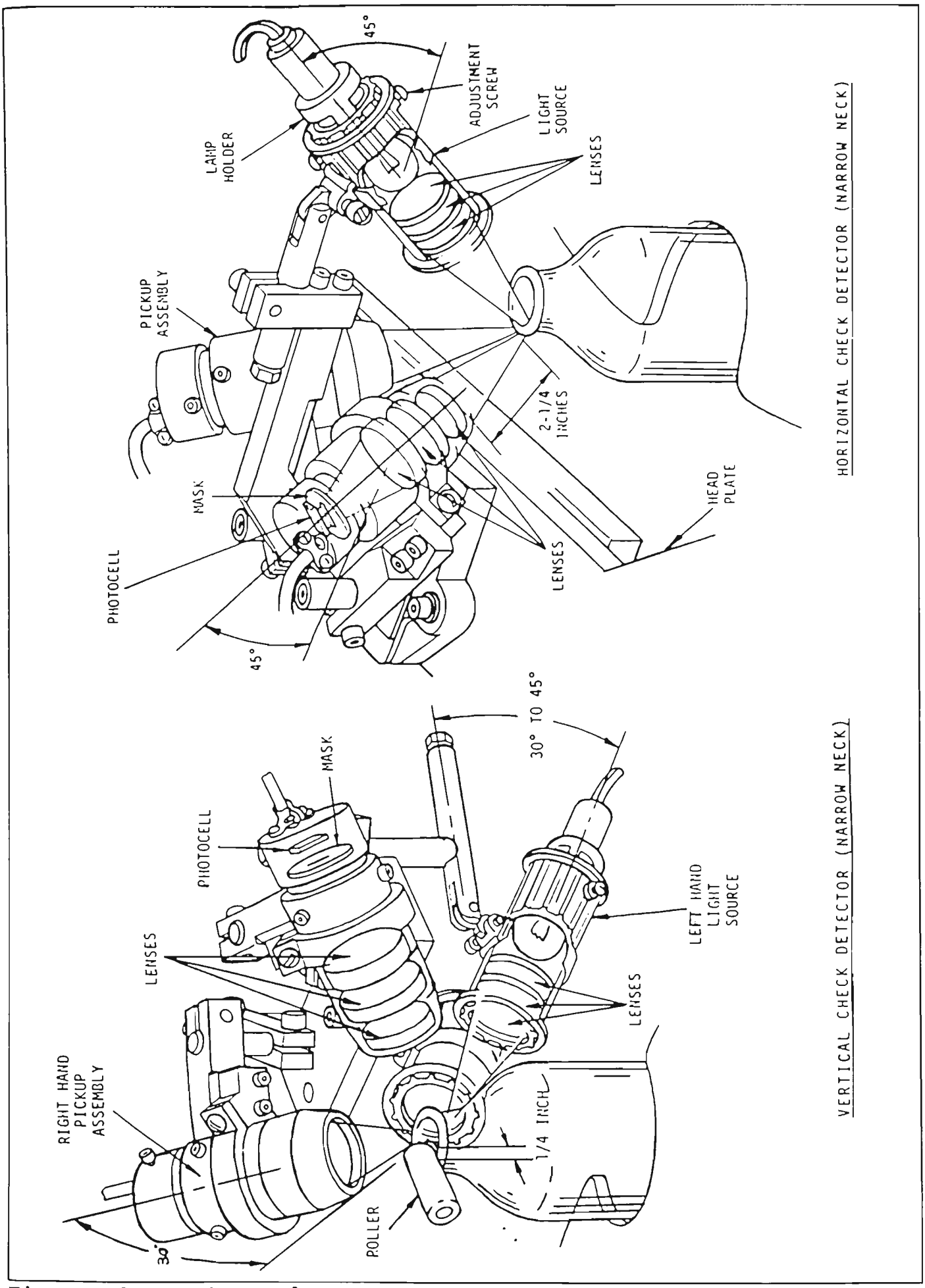

Figure 12. Horizontal & vertical check detectors for CUR faults (O-B technical manual)

The sidewall inspection device (SID) uses a special camera and light box setup to detect defects that block light in the container (Figure 13). If a defect blocks out light as the container is rotated 360°, this is picked up by one or more of the cameras sensing diodes and transferred back to the electronic processing device that determines whether the image is dark enough to be a defect. This equipment can detect stones with diameter greater than 0.8mm. One limitation is that the area of the logogram on the stubby cannot be checked. Other defects are also detected such as birdswings, blisters and stuck glass.

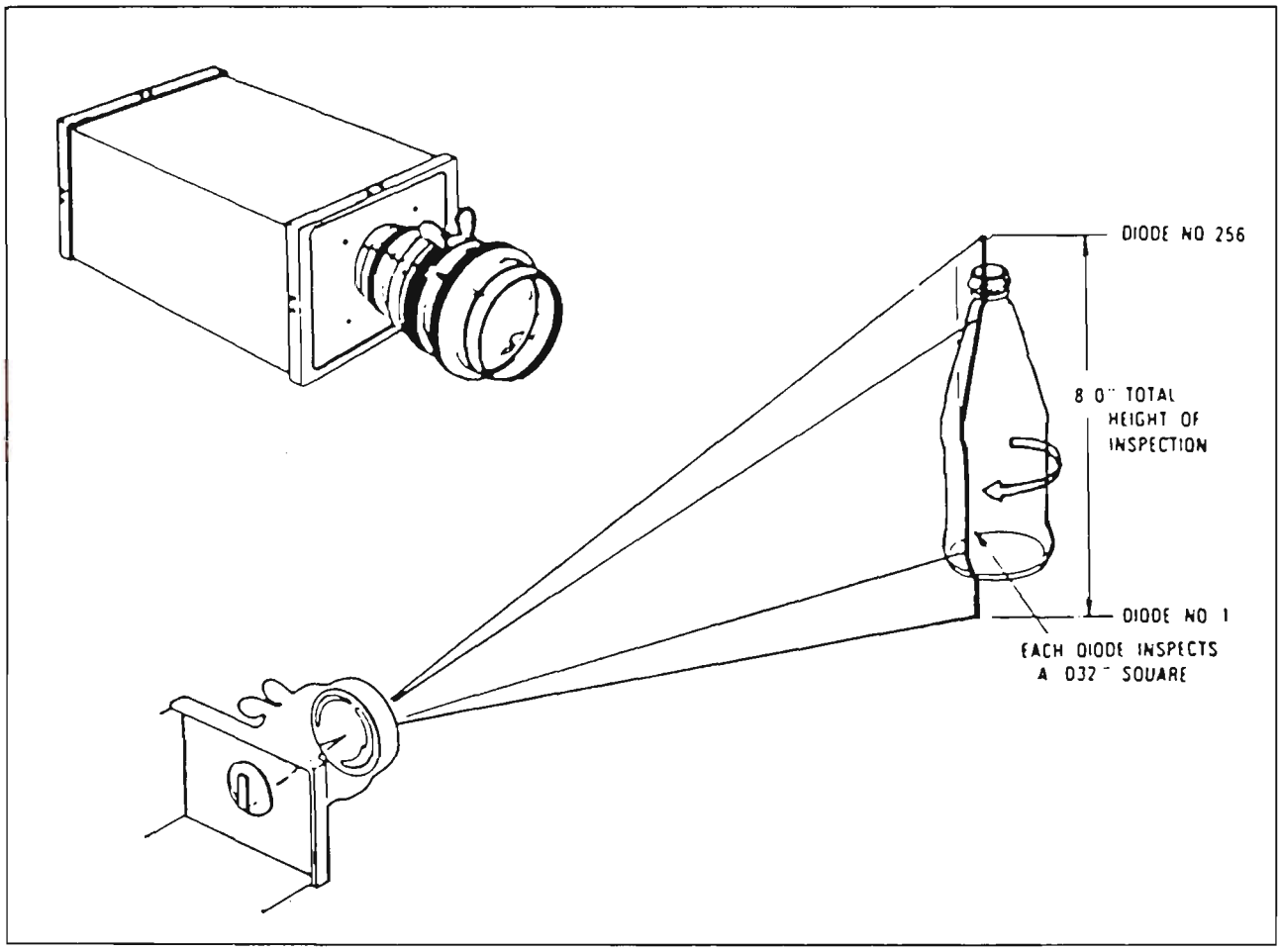

Figure 13. Side wall inspector, for SID faults (O-B technical manual)

The other major piece of equipment used in the inspect and pack area is the Cavity Identification Device (CID). It is able to read the cavity identification rings moulded into the base of each container (Figure 14). The rings create a reflection onto silicon solar cells that produce an electrical signal. This signal is analysed and decoded by the electronic circuitry. Each cavity on the forming machine has a unique number that is registered on the bottle by the CID rings. If a critical fault occurs on a particular cavity, then that mould number is keyed into the device by an operator and it is rejected. The mould is rejected until the fault is rectified.

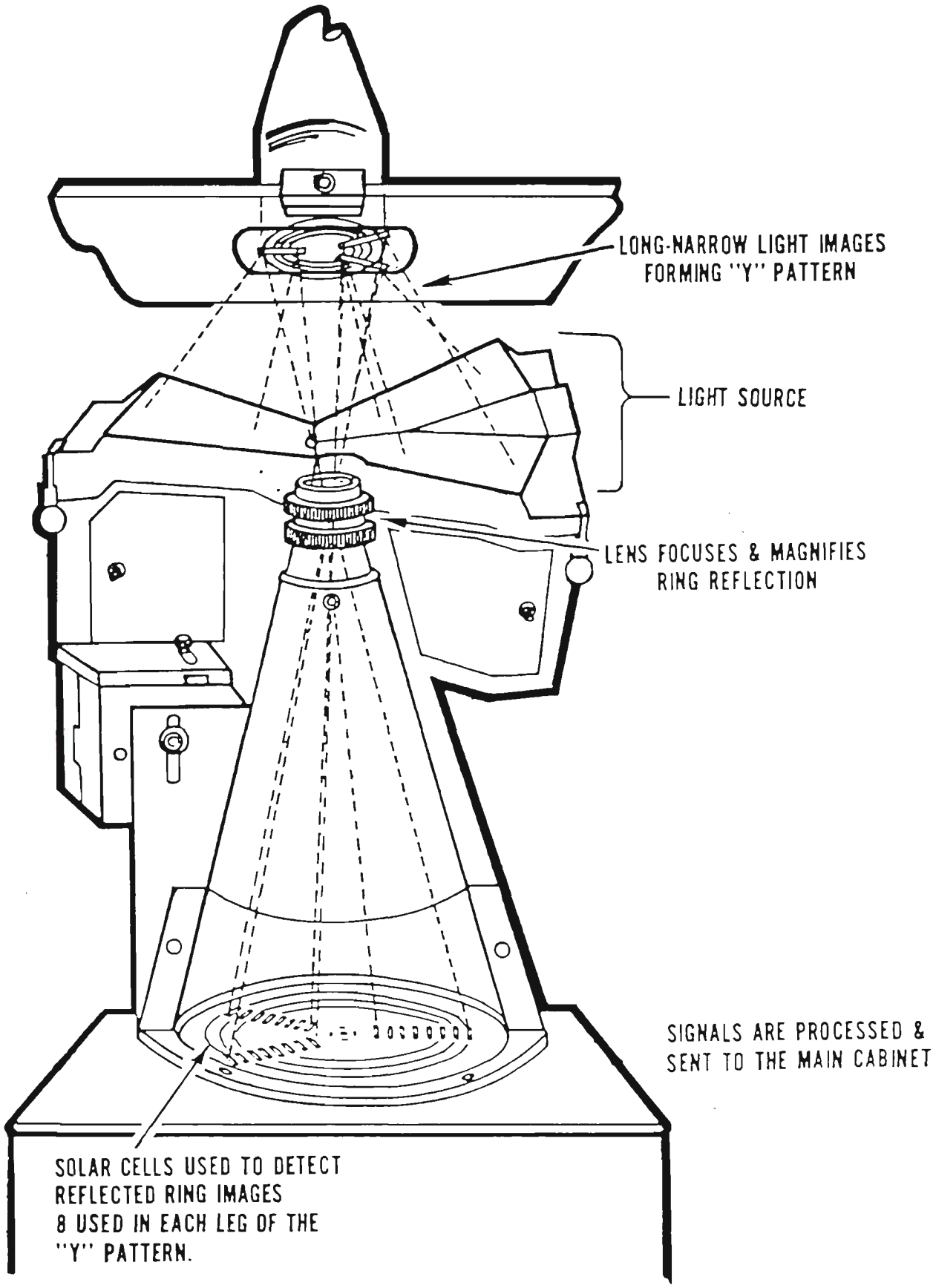

Figure 14. Cavity identification device for CID rejects (O-B technical manual)

The CID is also used to select containers for on-line automatic random pressure testing (ART). The containers selected for pressure testing are filled with water prior to testing to prevent explosion. Once filled with water, compressed air is used to pressurise the container to failure, or to a maximum pressure of 40 Kg/cm^2. A minimum breaking pressure is preset into the device for alarm purposes.

The on-line data from the CID, ART and Triple Check Inspectors is collected into one common production information computer (PIC). This computer performs calculations on the raw data to display and store information as percentages of the total production. From this data it also produces an overall production efficiency based on number of article rejected to those produced. A number of reports are available for a range of time periods. The data used in this study was based on the shift averages calculated by the PIC. A typical summary report is shown in Appendix 2.

2.2.7 LABORATORY EQUIPMENT

There are a number of different apparatus used in the laboratory area to determine glass quality measurements. The particular instruments used for this project include a spectrophotometer, an X-ray fluorescence (XRF) machine, a density comparator and a microscope. Both the XRF and density comparator are used as a measure of the glass composition, the spectrophotometer for light transmission measurements and the microscope for determining seed levels. A light station was also used for blister counting.

The spectrophotometer used in the plant laboratory has a wavelength range varying from 250nm to 1000nm, with manual selection of the desired wavelength. Quartz sample cells are used and are filled with a "refractive index liquid" mixture of benzol alcohol and methanol to reduce light reflectance as the incident beam passes through the glass sample. Radiation transmitted through the test sample is measured and digitally displayed.

Glass density was measured using the sink/float dense liquid method. The apparatus consisted of a water bath containing a test tube filled with "heavy liquid" for glass samples, another test tube filled with "heavy liquid" housing a thermocouple, a water heater and a stirrer (Figure 15). A standard glass sample of known density is used to correlate the density of the glass samples as the pieces sink due to the dense liquid's becoming less dense when the water bath is heated. This measurement of glass density is a way of monitoring composition changes quickly on a daily basis. If a significant change in density occurred and the source of the change could not be identified, then further analysis was carried out using X-Ray Fluorescence to determine precisely the compositional change responsible.

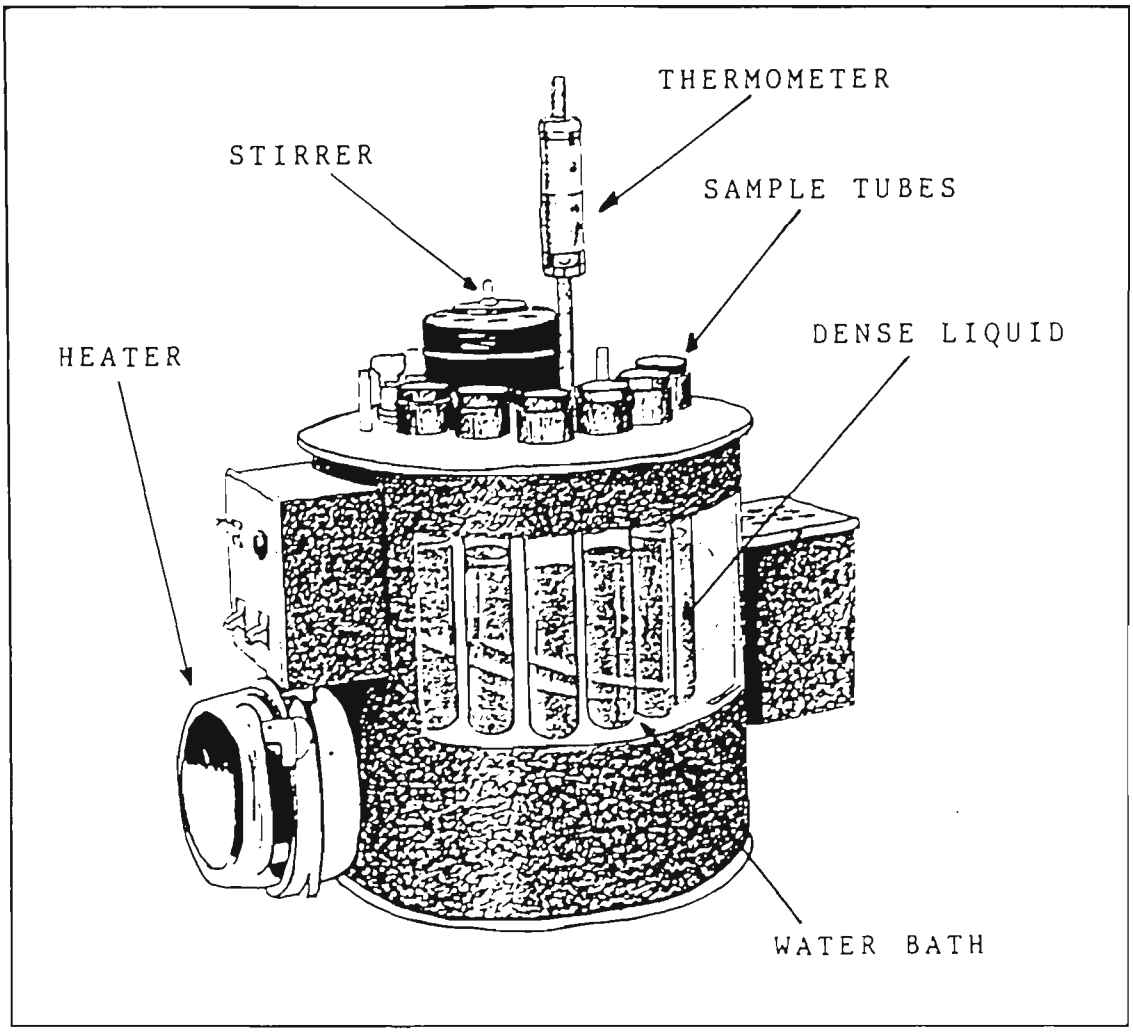

Figure 15. Sink/float glass density comparator (American Glass Research International Inc.)

The principles behind x-ray fluorescence(XRF) are that by directing an energetic x-ray beam at a sample, the sample is excited and emits characteristic fluorescent x-rays. For the analysis of a glass sample, a wave dispersive instrument was employed. A computer attached to the XRF machine automatically calculated the glass oxide results as percentages. The machine was calibrated each day by running a monitor sample - a solid glass disc - which internally corrects for any slight drift inherent in the system.

When an analysis was required (generally the analysis were carried out weekly throughout this work) the glass in question was sampled from a number of containers. A sample weight of approximately 100g was crushed to produce a powder that has 99% minus 200 mesh. Boric acid was used to overcome matrix effects associated with using x-rays on a composite sample. The computer attached to the XRF calculated theoretical physical properties as well as the oxide level in the glass.

3.0 EXPERIMENTAL DESIGN

3.1 BATCH & FURNACE OPERATION

Commercial batch adjustments, furnace and machine operating changes were made throughout this experiment. The types of changes were:

1. Carbon changes to maintain T550% specifications;

2. Furnace operating temperature changes that might be expected due to increased cullet[6]; and

3. Forming machine timing.

Changes of this nature and significant glass chemistry changes made were documented. A general description of the method was recorded and is shown, followed by a tabular layout of action taken and appropriate comments. A schematic diagram of the MB4 facility, including the furnace, refiner, forehearths, forming machines, annealing lehrs, bottle inspection equipment and palletisers are shown in Figure 16.

3.1.1 BATCH HOUSE

The furnace MB4 used for this study began a new campaign in September 1991. The initial batch cullet percentage was 40%. The project results were collected from the 4th December of that year. Unless stated, only amber cullet was added to the batch (ie no mixed or green cullet was included). Amber factory return cullet was blended with the ecology cullet by adding it into the storage receival hopper. The factory return cullet was passed through a metal detector and bottle breaking bar before being dumped into a holding bay. Regardless of the efficiency of the forming machines on MB4, approximately 30 tpd of factory return cullet was added to the total amount of cullet used each day. The composition of the return cullet was well known from the regular XRF results of MB4 glass, and this composition was used in the batch calculation. The composition used for the ecology cullet was based on the long term target composition of the amber glass production.

Essentially, the target composition for the batch remained the same throughout the experiment. The only significant change was a reduction in iron target from 0.325% to 0.3%. From time to time adjustments were made to the ecology amber cullet composition to correct glass density and composition drift. Glass density variation as a whole was looked at for all furnaces. A number of changes were made to the batch house operation to reduce the variation. In particular, the issues tackled were moisture variation in sand and limestone, weighing accuracy, batch moisture consistency and minimisation of material losses throughout the batch delivery system. A particular historical problem existed with the soda ash weighing hopper where a 7Kg reduction on the recipe weight was incorporated to achieve target composition. Following several modifications, this factor was removed.

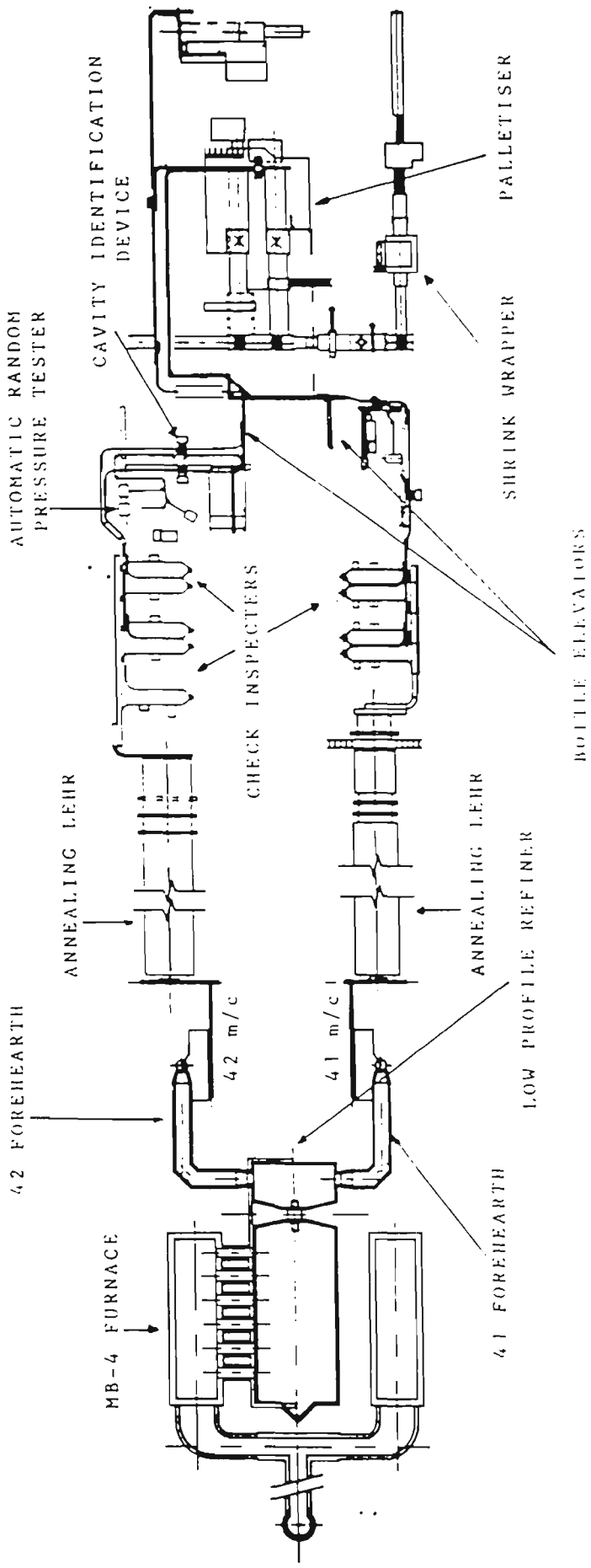

Figure 16. Schematic Diagram of MB4 facility (ACI Engineering Services)

3.1.2 MB4 FURNACE

Furnace operation at AGM Spotswood and in particular MB4 is directed to producing glass to ACI divisional quality requirements, and delivering the glass to the refiner within a required temperature range for the forming operation, with optimum fuel economy. The temperature range for glass entering the refiner was on average + and - 5°C. The absolute value was reduced on several occasions to improve fuel performance. (That is, the glass temperature was reduced in the furnace.) Dual stoking - where both batch stokers work together - was used for batch entry into the furnace. A crown temperature gradient was maintained and checked on a weekly basis. The only operational change departing from normal practice, was when a bubbler was installed in the throat of the furnace. This was installed arising from a separate study relating to a light streak that appears in the container. (This is not a new phenomenon and was part of an on-going program - it is not related to cullet level). Glass level control was maintained within + and - 0.3mm. Departure from this norm when the level moved outside + and - 1.0mm was considered abnormal. Weight variation was usually experienced on the machines if glass level changed by 2.0mm.

3.2 41 & 42 FORMING MACHINES

3.2.1 42 MACHINE(42m/c)

This forming machine was dedicated to producing the 375ml beer container referred to as a stubby. The bottle speed remained close to 520 bpm throughout the study and a single blank design was used. Blank sets were changed every six weeks and programmed machine down time of two days for maintenance was carried out twice. Abnormal occurrences were considered to be those where all sections on the machine were down for a period longer than 20 minutes. During such periods the blanks and moulds lost temperature, resulting in poor performance after restarting the machine. Problems causing abnormal occurrences of this nature include:

1. Failure of the shear mechanism;
2. Stopping to change an orifice ring or plunger;
3. Gob loading difficulties; and
4. Failure of ancillary machine conveyors required for bottle off-take.

All machine down-time was recorded on shift supervisors reports and on forming machine operator sheets.

3.2.2 41 MACHINE(41m/c)

This forming machine produced four different products during the study. They were:

1. 375ml stubby;

2. 375ml Crown Lager; and

3,4. Two similar 375ml mid neck beers.

The three container profiles and the dates that they were produced are shown (Figure 17).

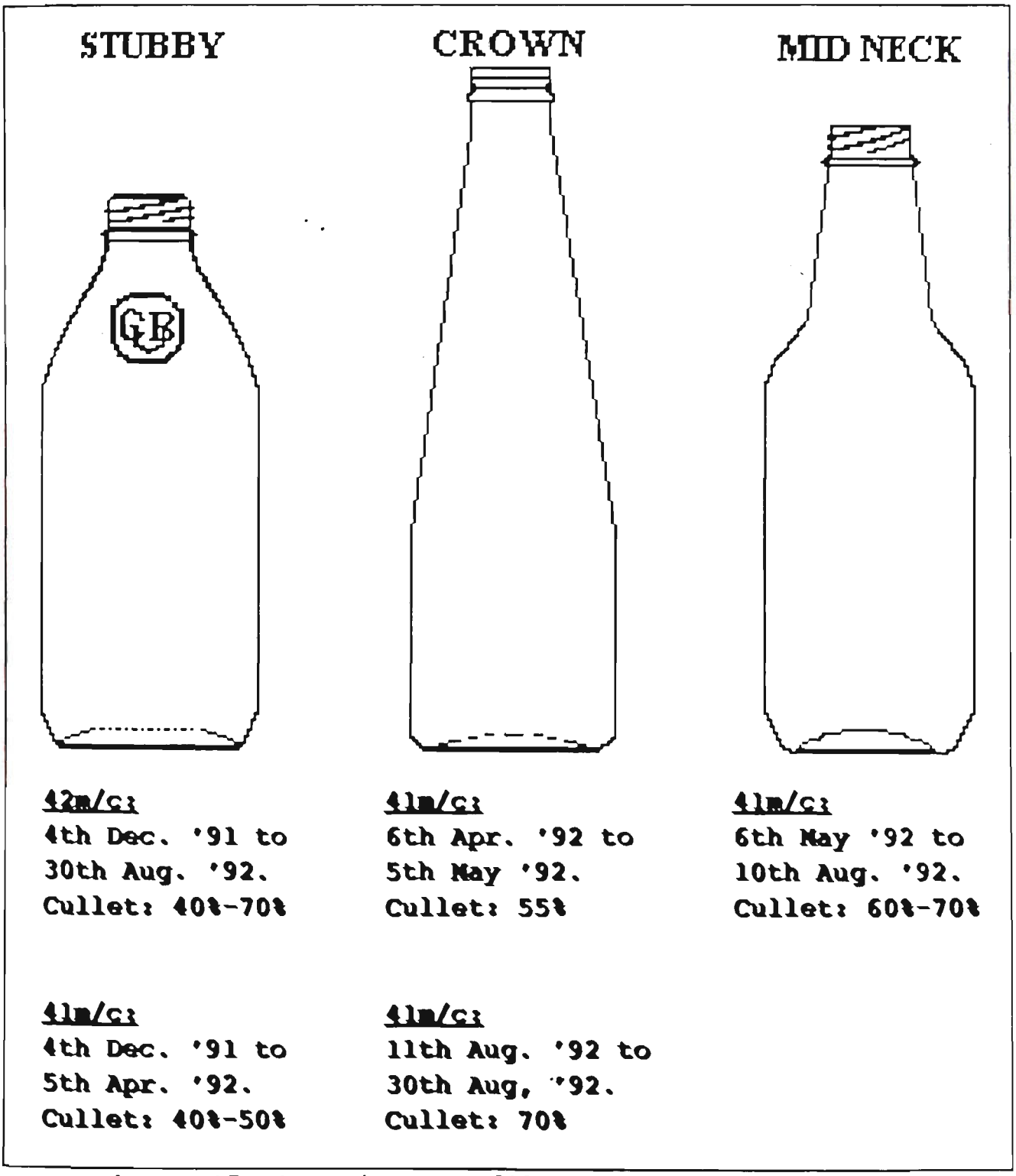

Figure 17. Container profiles and production dates

3.3 ASSESSMENT TECHNIQUES

3.3.1 GLASS QUALITY was assessed in the following way:

1. Glass composition stability was monitored by measuring glass density daily and also by X-ray fluorescence (XRF) analysis, carried out weekly. ACI divisional targets [10] were used to assess glass density and glass oxide variation. A constant target composition was used throughout the study. The main concern was the compositional stability of the major glass oxides, silica (SiO_2), sodium oxide (Na_2O) and calcium oxide (CaO).

2. Seed counts were carried out daily and ACI divisional methods and targets [10] were used to grade seed levels. The seed count results are reported as seeds per 100g of glass. Results are shown graphically.

3. Blister levels were checked daily during this work. Assessment was based on ACI divisional quality guidelines [10]. Blister levels are reported as blisters per 10Kg of glass. The results are graphed.

4. Stone levels were monitored via the electronic checking equipment (SID) and recorded on the production information computer (PIC). ACI divisional stone level guidelines [10] were used for assessment. The stone losses are reported as a percentage and the results are graphed.

5. Light transmission stability at 550nm wavelength (T550%) was monitored daily and the standard deviation was used to assess the variation according to ACI divisional guidelines [10]. The results are reported as the percent of light transmission at a wavelength of 550nm.

6. Owens-Brockway (O-B) amber stability criteria were determined from the glass XRF results. The glass stability was assessed according to these guidelines.

3.3.2 GLASS WORKABILITY was assessed in the following way:

1. Checks under ring (CUR) were monitored via the electronic check inspectors and recorded on the PIC. Statistical analysis was carried out to check both the total percentage losses and the variation.

2. Thin walls (TW) were monitored electronically and recorded on the PIC. The data was analysed statistically to check both the total percentage losses and the variation.

3. Cavity identified defects (CID) were monitored electronically and recorded on the PIC. Statistical analysis was carried out to check both the total percentage losses and the variation.

3.3.3 COMMERCIAL VIABILITY was assessed in the following way:

1. Efficiency information was gathered from the PIC. Statistical analysis was carried out to check both the total efficiency and the variation.

2. Breaking pressure information was obtained from the Automatic Random Pressure Tester (ART) and was analysed statistically for the total value and variation.

3.4 SUMMARY OF ACTIVITIES

3.4.1 40% CULLET

The period that 40% cullet was used started on 4 December 91 and finished on 14 january 92, a total of 41 days. A raw material change from magnesite to dolomite was undertaken in three steps during this time. The change was based on economics and the glass composition was kept constant. There was also a short time where 10% mixed cullet made up the total of 40% due to cullet storage constraints. Two carbon number adjustments were made to maintain the T550%. The o-ring was changed twice during this period and one set of reconditioned blanks were added to the system (Table 2).

Table 2. Summary of breakdowns affecting 42m/c at 40% cullet.

DATE	ACTION	COMMENT
4 DEC 91	DATA COLLECTION COMMENCED	40% CULLET
10 DEC 91	42 ELECTRICAL FAILURE	DOWN 60 MIN.
25 DEC 91	42 PALLETISER DOWN	LOST 25 MIN.
28 DEC 91	42 O-RING CHANGED	DOWN 45 MIN.
29 DEC 91	42 PUSHER STACKER	DOWN 20 MIN.
31 DEC 91	42 O-RING CHANGED	DOWN 105 MIN.
2 JAN 92	10% MIXED CULLET ADDED 42 LOADING TROUBLE 42 FULL SET RECON BLANKS	HOPPER AVAILABILITY DOWN 30 MIN. DOWN 60 MIN.
3 JAN 92	42 LOADING TROUBLE	DOWN 165 MIN.
9 JAN 92	42 CROSS CONVEYOR DOWN	DOWN SEVERAL HOURS
13 JAN 92	42 COLD END CONVEYOR DOWN	DOWN 105 MIN.
14 JAN 92	C/O MAGNESITE - DOLOMITE 10% MIXED CULLET REMOVED	CHEAPER RAW MATERIAL HOPPER AVAILABILITY

3.4.2 45% CULLET

Forty five percent(45%) cullet was used for the period between 15 January 92, 27 January 92. This 13 day time span had a carbon number range of 2 with no other batch changes (Table 3).

Table 3. Summary of breakdowns affecting 42m/c at 45% cullet.

DATE	ACTION	COMMENT
15 JAN 92	CULLET INCREASED 5%	45% CULLET
17 JAN 92	42 BLOCKED FUNNEL	DOWN 45 MIN

3.4.3 50% CULLET

The period involving 50% cullet was a reasonably active time including several operational changes. For this reason it resulted in a lengthy time period of 70 days at this percentage, from 28 January 92 to 6 April 92. Early in the program, a two day period of machine maintenance occurred when the machine was shut down. A mix of machine related problems occurred after this, with persistent invert arm troubles, loading difficulties, shear replacement and o-ring replacement(twice). A furnace operating change was instigated when a bubbler was installed in the throat. The purpose of this was in regard to a separate investigation regarding a light streak that is often evident in amber glass. It was thought that if the streak was being formed in the furnace, then installing the bubbler in the throat would homogenise it with the bulk glass. On the batch side, the iron target was reduced from 0.325% to 0.3%. This change was made after information was received regarding a set of amber glass stability criteria. A reduction in the weight of soda ash being weighed out was also made, in an attempt to overcome an historical over-target percentage of NaKO being produced in the glass. A range of 2 carbon numbers was required to maintain the T550% (Table 4).

Table 4. Summary of breakdowns affecting 42m/c at 50% cullet.

DATE	ACTION	COMMENT
28 JAN 92	CULLET INCREASED 5%	50% CULLET
2 FEB 92	42 (GENERAL) POWER FAILURE	DOWN 180 MIN.
17 FEB 92	42 MAINTENANCE 42 CONVEYOR DOWN IRON LEVEL REDUCED 0.325% TO 0.3%	DOWN 240 MIN. DOWN 180 MIN. TO HELP REDUCE LIGHT STREAK
25 FEB 92	42 LOSS OF M/C AIR	DOWN 60 MIN.
2 MAR 92	42 SHUT DOWN MAINTENANCE	PLANNED
4 MAR 92	42 START UP 42 FULL SET NEW BLANKS	PLANNED
10 MAR 92 11 MAR 92 12 MAR 92	42 INVERT ARM PROBLEM	HE SHEETS RELATE THIS PROBLEM TO INCREASE IN CUR'S
13 MAR 92	42 CHANGED SHEARS	DOWN 30 MIN.
14 MAR 92	42 BAD LOADING B GOB	DOWN 30 MIN.
15 MAR 92	JAMMED TROUGH IN GOB DISTR	DOWN 60 MIN.
17 MAR 92	42 BAD LOADING A,B	DOWN 45 MIN.
18 MAR 92	42 O-RING CHANGED	DOWN 150 MIN.
19 MAR 92	BUBBLER OPERATING IN THROAT	RELATED TO LIGHT STREAK
23 MAR 92 24 MAR 92	BUBBLER BLOCKED & RESTARTED	REFINER TEMP. INCREASED 10°C
3 APR 92	42 ELEVATOR STOPPED	LOST 20 MIN.
6 APR 92	42 BLISTER/SEEDY GLASS	DOWN 40 MIN.

3.4.4 55% CULLET

For 21 days between 7 April 92 and 26 April 92, 55% cullet was used in the batch. The throat bubbler was turned off at the beginning of this period after trials indicated that its effect was negligible. This period of machine operation was characterised by loading problems and the o-ring was changed once. A full set of reconditioned blanks was put into operation part way through this period. A modification was made to the soda ash weigh hopper in response to the soda over target problem. No carbon number changes were made (Table 5).

Table 5. Summary of breakdowns affecting 42m/c at 55% cullet.

DATE	ACTION	COMMENT
6 APR 92	CULLET INCREASED 5%	55% CULLET
7 APR 92	42 LOADING PROBLEMS	DOWN
8 APR 92	42 LOADING PROBLEMS	DOWN 30 MIN.
9 APR 92	BUBBLER IN THROAT OFF	HAD NO EFFECT ON LIGHT STREAK
10 APR 92	42 OFF CONVEYOR DOWN	DOWN 55 MIN.
15 APR 92	42 LOADING PROBLEMS 42 FULL SET RECON BLANKS	DOWN 20 MIN.
16 APR 92	42 ELEVATOR TROUBLE	DOWN 20 MIN.
18 APR 92	42 STONE IN O-RING	DOWN 45 MIN.
20 APR 92	42 GOB DISTRIBUTOR PROBLEMS	DOWN 270 MIN.
21 APR 92	42 LOADING TROUBLE	DOWN 190 MIN.
22 APR 92	SODA ASH FLAP GATE INSTALLED	4Kg SODA ADDED TO RECIPE
24 APR 92	42 LOADING TROUBLE	DOWN 4 Kg SODA ADDED

3.4.5 60% CULLET

The 43 day period involving 60% cullet was a time of significant change in the amount of refining additive (sodium sulphate) in the batch. The amount of saltcake added to the batch was increased over an eighteen day period from a traditional 6/1000 (6 parts saltcake / 1000 parts sand) to 13/1000. This was undertaken due to a production problem that occurred on another amber facility, the furnace MB1. This furnace had recently undergone a colour change from green to amber and was running at 70% cullet. The glass was extremely seedy, blistery and contained an intense dark amber streak. It was not until the saltcake ratio was increased to 10/1000 (from 6/1000), that the glass quality improved rapidly (Table 6).

Shortly after this experience, advice was received from Owens-Brockway resulting in the saltcake calculation being changed. The method suggested, considers all the sulphur containing batch ingredients as sulphur trioxide (SO_3), including the retained sulphur added through the cullet. Sulphur trioxide was also

Table 6. Summary of breakdowns affecting 42m/c at 60% cullet.

DATE	ACTION	COMMENT
27 APR 92	CULLET INCREASED 5% SALTCAKE RATIO CHANGED FROM 6 TO 8/1000	60% CULLET CHANGED DUE TO MB1 GLASS QUALITY EXPERIENCE
29 APR 92	42 REMOVE STONE FROM O-RING 42 SHEARS STOPPED	DOWN 30 MIN. DOWN 270 MIN.
30 APR 92	42 SHEARS STOPPED -4Kg SODA FROM RECIPE	DOWN 20 MIN. DENSITIES HIGH
1 MAY 92	SALTCAKE RATIO CHANGED FROM 8 TO 10/1000	
3 MAY 92	42 BROKEN PLUNGER	DOWN 180 MIN.
4 MAY 92	42 BROKEN PLUNGER	DOWN 120 MIN.
6 MAY 92	42 BLOCKED FUNNEL SALTCAKE 10 TO 12/1000	DOWN 20 MIN.
10 MAY 92	42 BROKEN PLUNGER 42 REPLACED O-RING, PLUNGER	DOWN 60 MIN. DOWN 130 MIN.
11 MAY 92	42 CHANGED BLANK HOLDERS	
13 MAY 92	42 SHEARS CHANGED	DOWN 25 MIN.
14 MAY 92	SALTCAKE CHANGED FROM 12/1000 TO 13/1000	
16 MAY 92	42 No.3 HEAD PROBLEMS	HIGH CUR'S
18 MAY 92	42 PLANNED MAINTENANCE & BOOT CHANGE	
21 MAY 92	42 START UP	
28 MAY 92	42 PROBLEM WITH SHEARS	DOWN 75 MIN.
29 MAY 92	42 REPLACEMENT BLANKS	0.5 NEW, 0.5 RECON.
30 MAY 92	42 LOSS OF GAS TO REFINER	DOWN 150 MIN.
01 JUN 92	42 PALLETISER PROBLEMS	LOSS 140 MIN.
03 JUN 92	42 COMPLAINTS ABOUT SHEARS & O-RING	
04 JUN 92	42 O-RING CHANGED	DOWN 60 MIN.
05 JUN 92	42 COLD END CONVEYOR DOWN	LOSS 20 MIN.
06 JUN 92	42 COLD END CONVEYOR DOWN	LOSS 50 MIN.
08 JUN 92	42 SHEARS NOT CUTTING .	DOWN 80 MIN.
09 JUN 92	42 LATE LOADING	UNEVEN WEIGHT

removed from the system as retained sulphur in the molten glass. An excess amount of SO_3 was targeted, to ensure adequate mixing action occured via the sulphate reactions. (The calculation is shown in Appendix III.) In this way the saltcake ratio did not remain static with cullet percentage changes. These changes on MB4 resulted in an unstable T550% measurement for a time, as the carbon/sulphur balance equilibrated, affecting the amber chromophore. This resulted in a carbon number range of 13 being required to correct the T550% movement.

On the machine side it was a busy time with the o-ring being changed four times. Persistent problems with the shears continued throughout the 60% period. Broken plungers and loading difficulties were also prevalent. The machine had a two day stop for planned maintenance and a full set of new and reconditioned blanks was put into the system. The furnace floor temperature was systematically reduced from 1210°C to 1180°C. The 60% cullet period started on 28 April 92 and ended on 9 June 92.

3.4.6 65% CULLET

The 22 day period at 65% cullet extended from 10 June 92 to 30 June 92. It was a very quiet period with no carbon changes. The machine activity was low, apart from some loading and plunger problems (Table 7).

Table 7. Summary of breakdowns affecting 42m/c at 65% cullet.

DATE	ACTION	COMMENT
10 JUN 92	CULLET INCREASED 5%	65 % CULLET
21 JUN 92	PROBLEMS WITH SHEARS & LOADING	DOWN 70 MIN.
22 JUN 92	BROKEN NEEDLES & BAD LOADING	DOWN 85 MIN.

3.4.7 70% CULLET

The 70% cullet period started on 1 July 92 and ended on 30 August 92, taking 61 days. The period included a range of six carbon numbers. The ecology cullet composition was altered to bring the silica target for the cullet into line with the glass

batch. A new source of nepheline syenite was introduced, but the target alumina content remained the same. The machine received a set of new blanks and the o-ring was changed once. There were more problems with loading and shears (Table 8).

Table 8. Summary of breakdowns affecting 42m/c at 70% cullet.

DATE	ACTION	COMMENT
11 JUL 92	42 LOADING TROUBLE	DOWN 35 MIN.
12 JUL 92	42 SHEARS CHANGED	DOWN 75 MIN.
24 JUL 92	42 COLD END ELECTRONICS	LOSS 60 MIN.
30 JUL 92	42 ALL BLANKS CHANGED	NEW BLANKS
08 AUG 92	42 PROBLEM WITH SHEARS	DOWN 30 MIN.
09 AUG 92	42 PROBLEM WITH SHEARS	DOWN 135 MIN.
10 AUG 92	42 PALLETISER TROUBLE	LOSS 35 MIN.
11 AUG 92	42 CHANGED O-RING	DOWN 90 MIN.
14 AUG 92	42 CONVEYOR DOWN, PROBLEMS WITH SCOOP	DOWN 340 MIN.

4.0 RESULTS - GLASS QUALITY

4.1 GLASS QUALITY

Glass quality is a fundamental consideration in producing container glass. From a glass technology view point this includes glass composition, seed levels, blister levels, stone levels, transmission stability at 550nm and amber stability criteria. The results obtained for each of these aspects of glass quality are shown as follows.

4.1.1 GLASS COMPOSITION

Glass density measurement is an excellent indicator of a change in composition. The ACI divisional glass quality standard requires that the density does not change by more than 0.0011 Tonnes/m^3 ("11 points") within 24 hours. The stipulation in regard to the long term variation of the glass density is also not more than + and - 11 points. At all cullet levels the 24 hour density variation was less than ACI divisional quality standard. The long term variation was also within divisional guidelines and following an increase between 45% and 55% cullet, it remained steady(Figure 18).

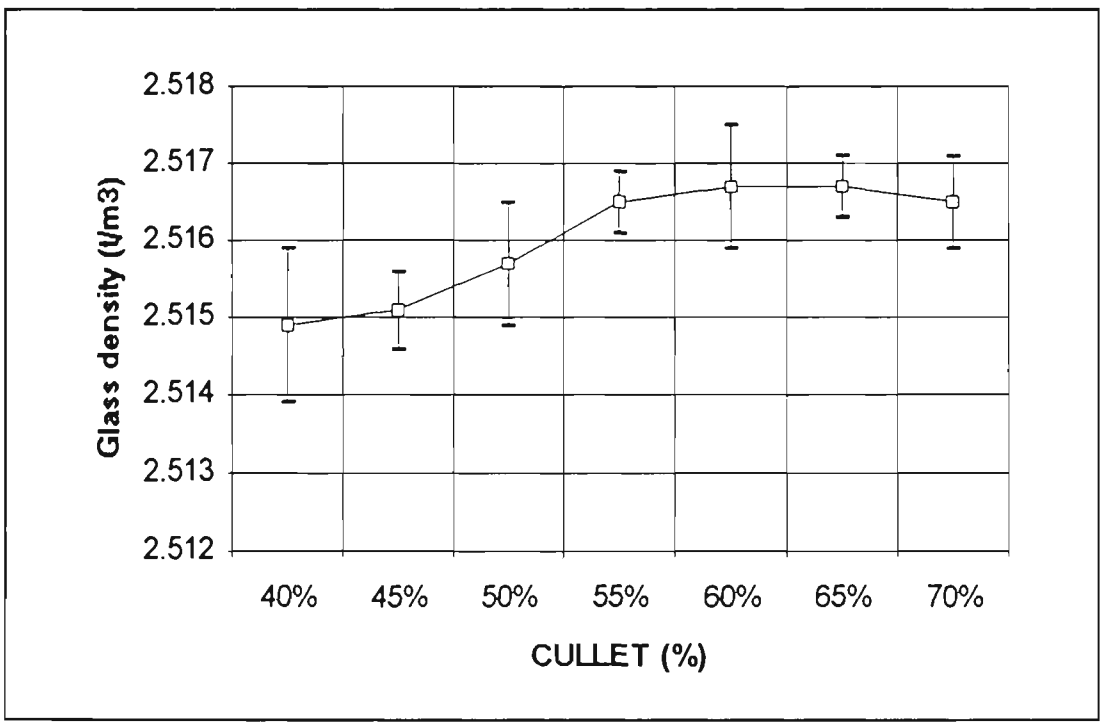

Figure 18. MB4 glass density & S.D. Vs cullet

Major glass oxide analyses are reflected in glass density measurements. These explain why the glass density has changed. Calcium oxide (CaO) has the largest effect, as a 0.1% increase in this oxide will cause a 10 point increase in density. Sodium oxide (NaO) has approximately half the effect while an increase in silica oxide (SiO_2) reduces the density slightly. The major glass oxide results are shown in Figures 19,20 and 21. The major contributor to the overall rise in glass density, in this study, was the

calcium oxide. This value peaked at 55% cullet and had a slight decrease afterwards. The effects of NaO, SiO_2 and CaO on the density were minor, as the rise of one was attenuated by the drop of another. The relationship between these oxides and the glass density are shown in detail in Table 12 and Figure 58 in Appendix I.

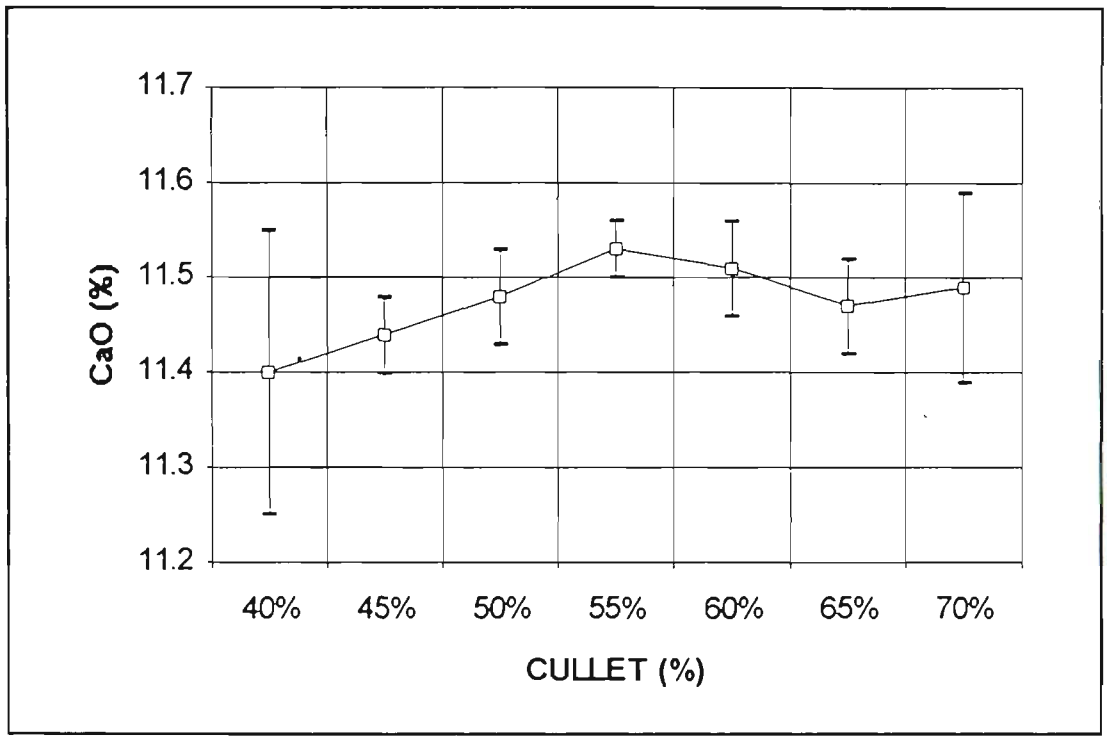

Figure 19. CaO & S.D. Vs cullet, (target = 11.5%)

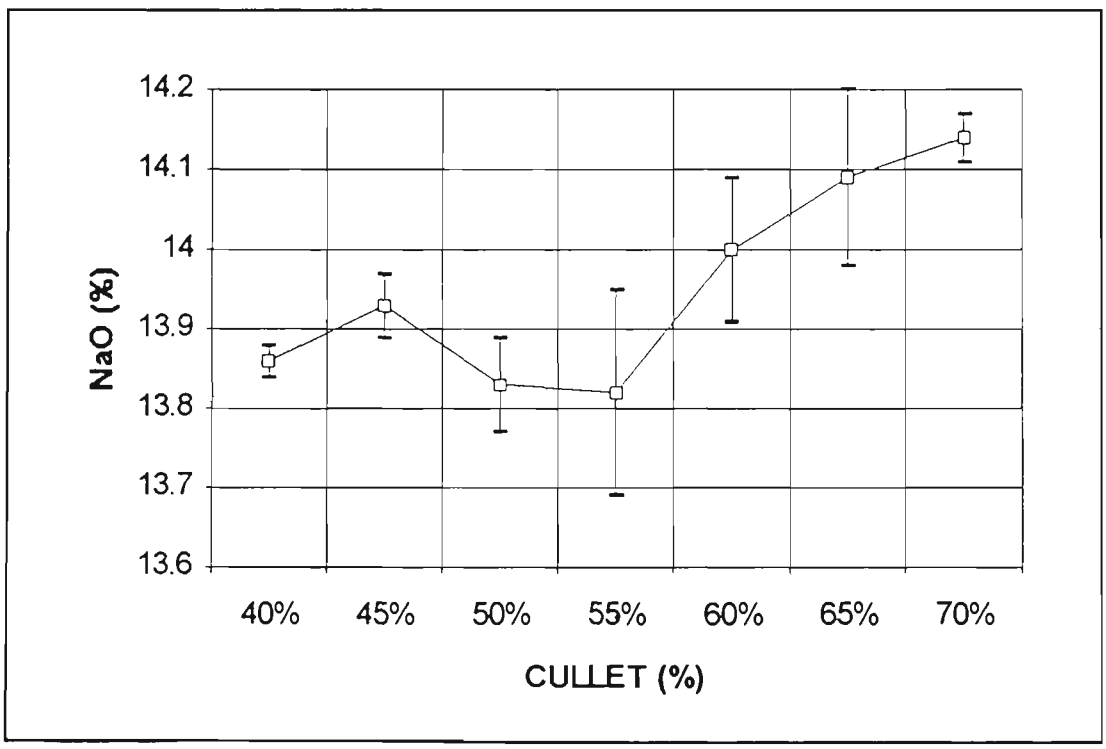

Figure 20. NaO & S.D. Vs cullet, (target = 13.9%)

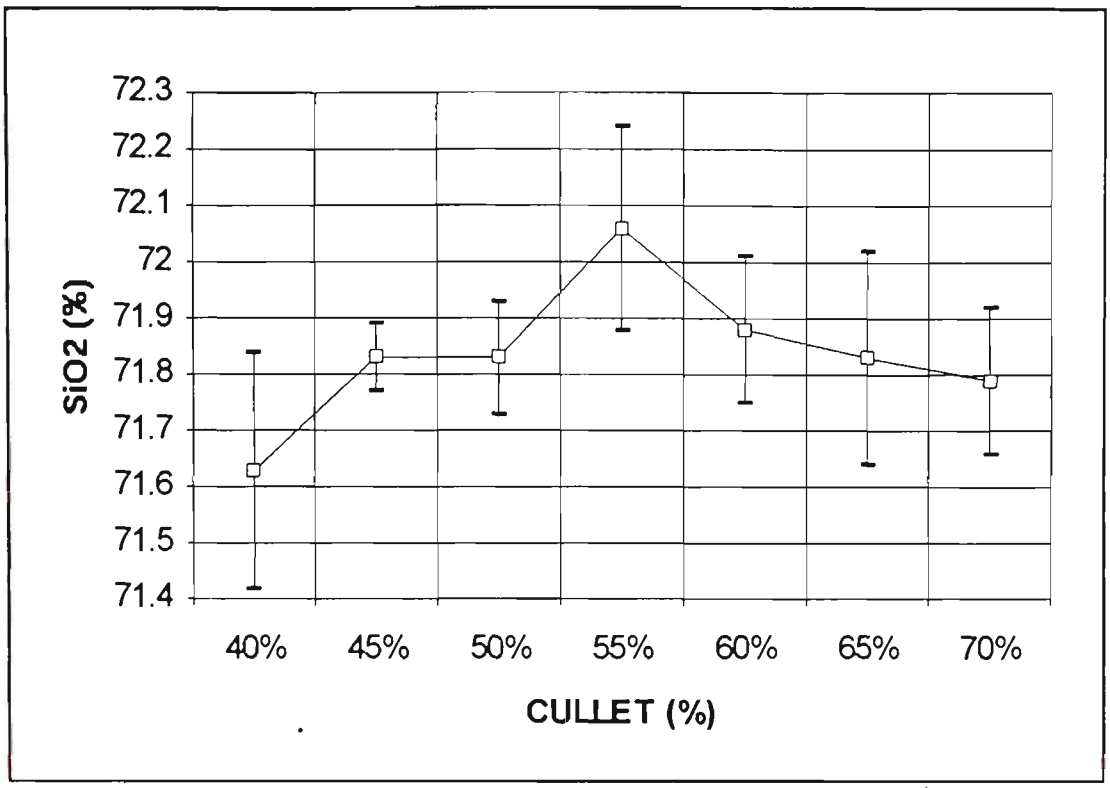

Figure 21. SiO_2 & S.D. Vs cullet, (target = 71.9)

4.1.2 SEED LEVELS

Divisional quality assurance standards for glass seed levels are based on the number of seeds per 100g of glass and are set out as follows:

Excellent	≤ 50
Acceptable	50 - 150
Borderline	150 - 250
Unacceptable	≥ 250

From Figure 22, it is seen that at all cullet levels (except at 40%) the seed levels were excellent. There was also significant improvement from 40% to 70% cullet. An increase in glass temperature (furnace floor temperature) or a decrease in furnace tonnage will reduce seed levels. However, in this study the glass temperature was reduced by 25°C with a 10 tonne range in furnace tonnage, and yet the seed level decreased (Figure 23). The major improvement was due to changes made to the saltcake refining and this is discussed in the glass quality analysis section.

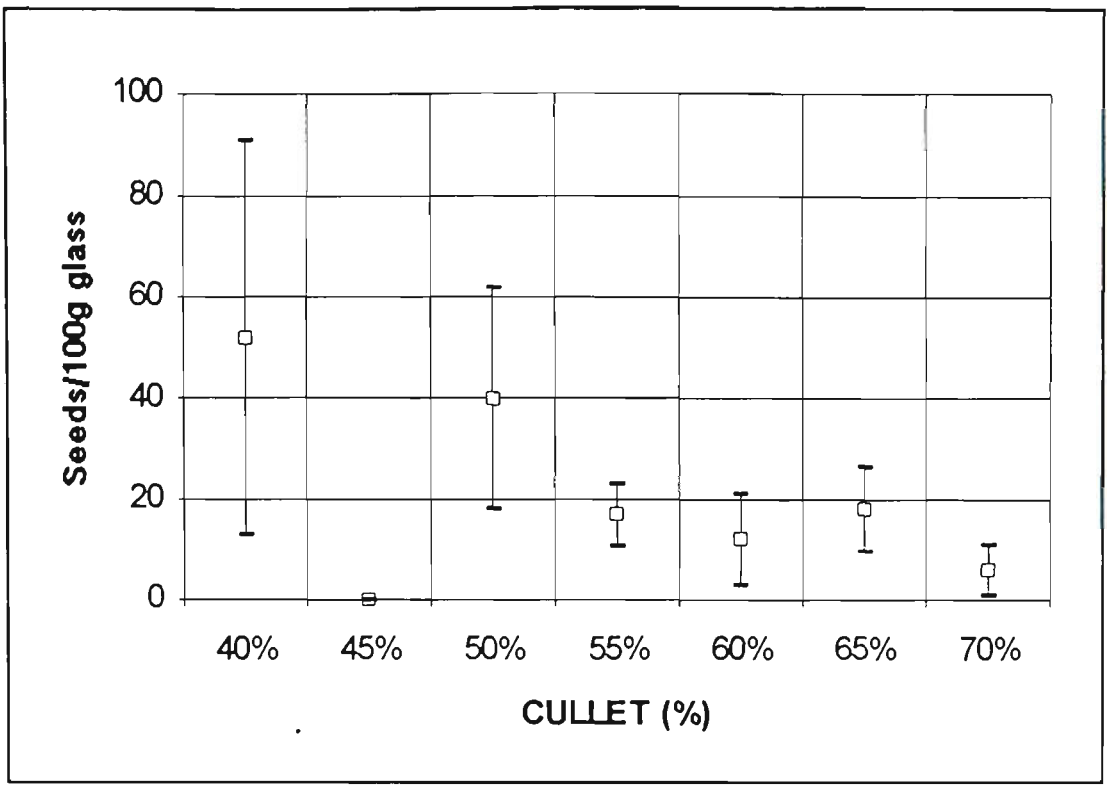

Figure 22. MB4 seeds/100g & S.D. Vs cullet

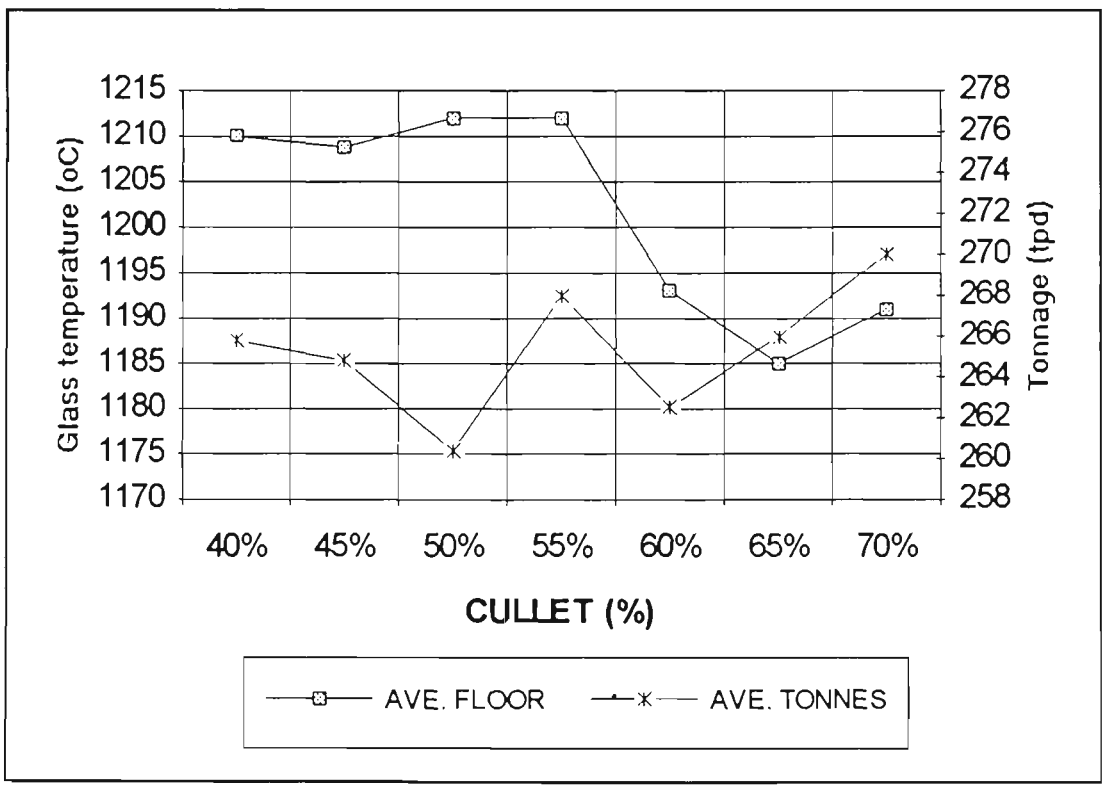

Figure 23. MB4 glass temperature & tonnage Vs cullet

4.1.3 BLISTER LEVELS

ACI divisional quality targets for blister levels in container glass are given as the number of blisters per 10Kg of glass. They are set out as follows:

good	≤ 60
acceptable	60 - 200
poor	≥ 200

Figure 24 shows the average blister level for both machine lines, while Figures 25 & 26 show the individual results for 42m/c and 41m/c respectively. Unacceptable blister levels were experienced at 50% cullet on 42m/c and 55% cullet on 41m/c. An increase in tonnage on 41m/c occured during the 55% cullet period which may in part explain the blister level increase for that machine line. However, at both cullet percentages(50% & 55%), large variance in blister levels were experienced on both machines, indicating that the glass was unstable during this time. In all cases, (individual machine results and the average), there was an improvement in blister levels from 50% to 70% cullet with the average improving dramatically after 60% cullet. Blister levels at 65% and 70% cullet were generally excellent. The major improvement was due to changes made to the saltcake refining, which resulted in increased levels of sulphide and free sulphate in the glass. These changes were implemented during the 60% cullet period and are discussed in the glass quality analysis section.

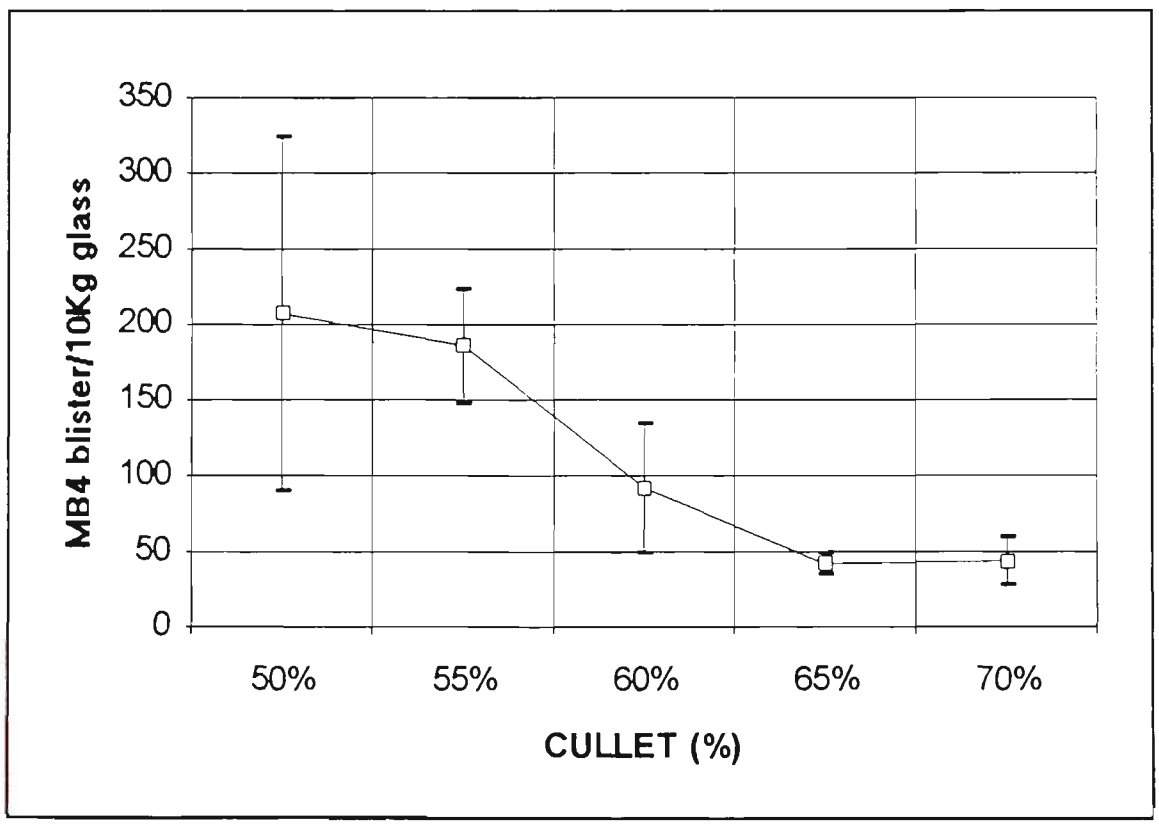

Figure 24. MB4 blister/10Kg & S.D. Vs cullet

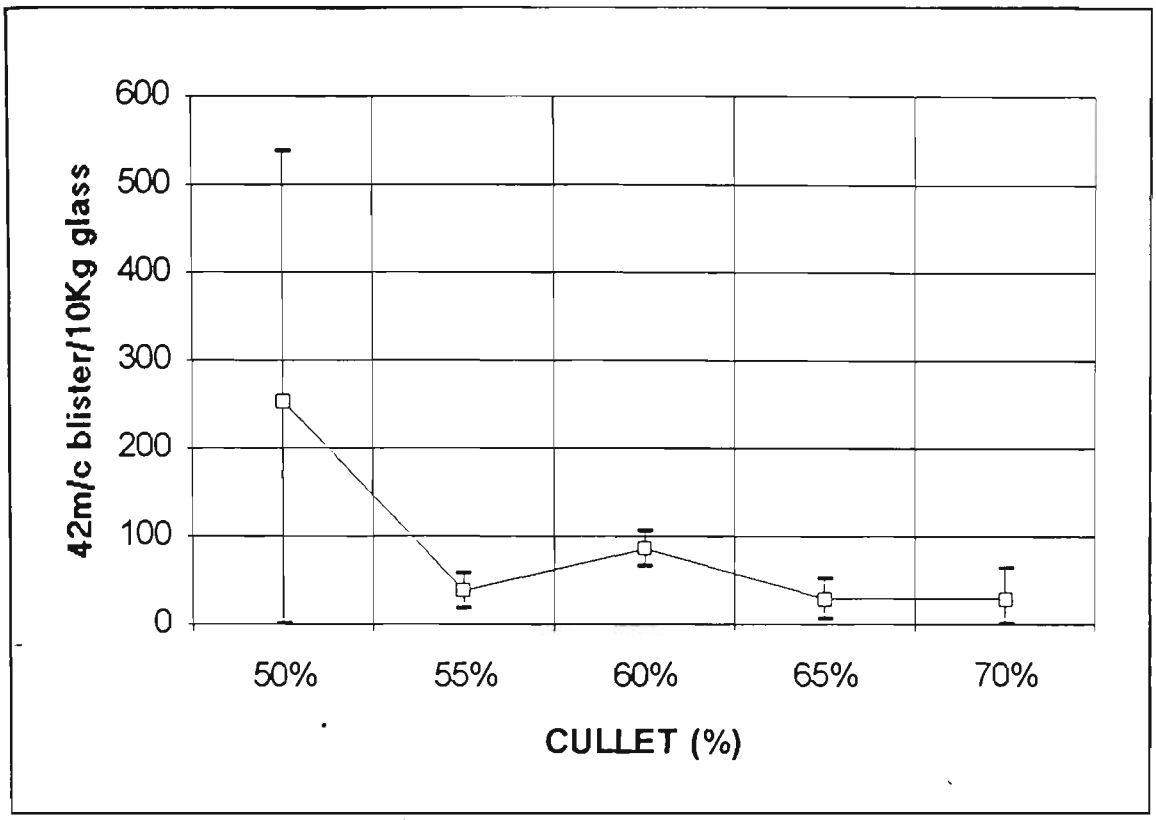

Figure 25. 42m/c blister/10Kg & S.D. Vs cullet

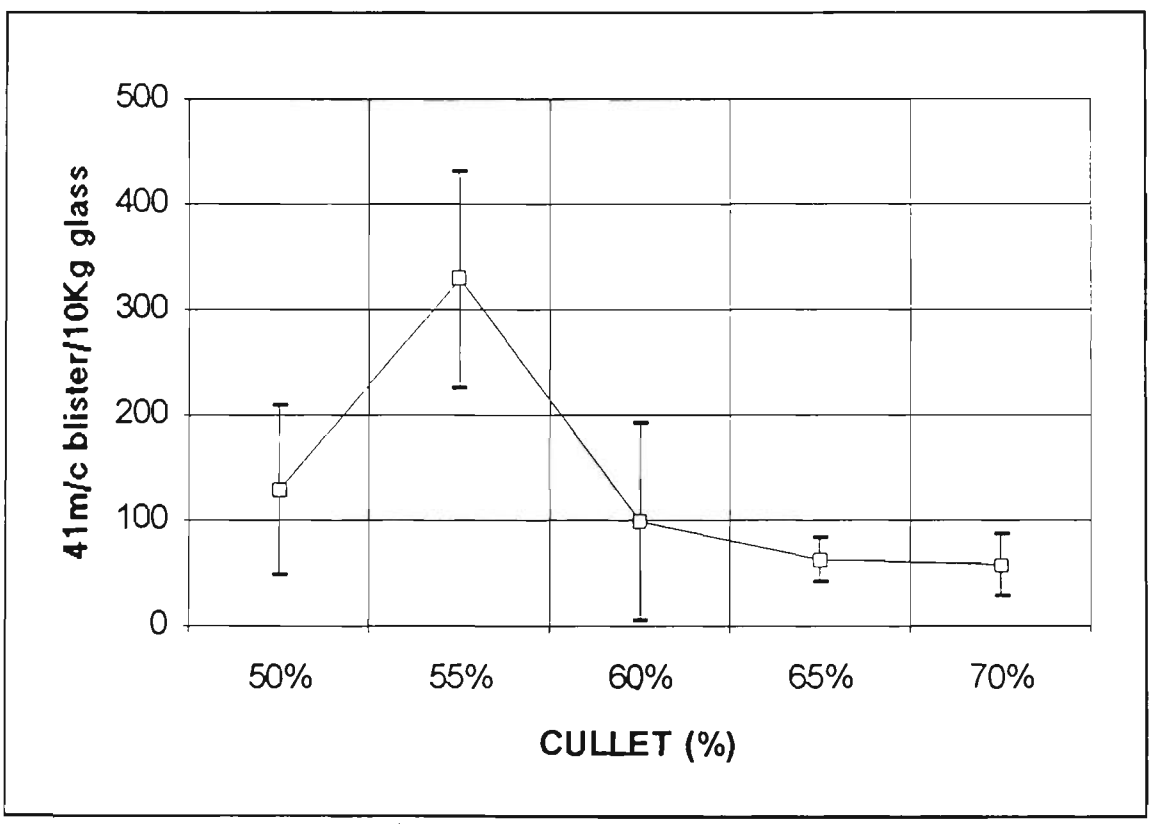

Figure 26. 41m/c blister/10Kg & S.D. Vs cullet

4.1.4 STONE LEVELS

Divisional quality standards require that there are less than 0.8% stones per day. That is, less than 0.8% of bottles produced should be rejected for stone inclusions. For the 375ml beer container this equates to 20 stones/tonne of glass.

The following stone count results are based on SID rejects. These results reflect 42m/c only, as the job changing on 41m/c resulted in quantum changes in the SID reading on that machine due to the different shape of the container and different setting on the check inspectors. Figure 27 shows that for all cullet levels the percentage of bottles rejected because of stones was within the quality target.

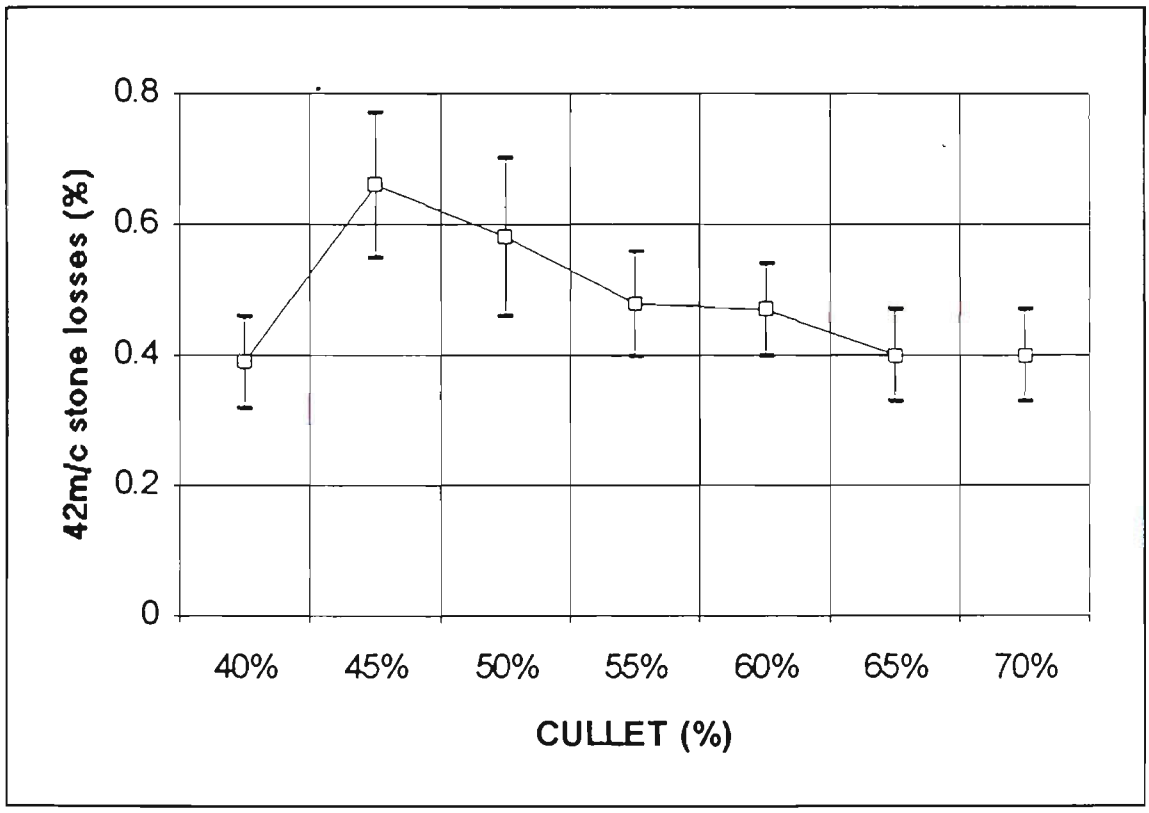

Figure 27. 42m/c stone losses & S.D. Vs cullet

4.1.5 LIGHT TRANSMISSION AT WAVELENGTH OF 550nm (T550%)

The target T550% for the amber glass during this work was 19%, except during the 40% cullet period where the target was 18% for commercial reasons. The working range for this variable to meet customer requirements was + and - 2% transmission. If the transmission readings remain in this range, the visual aspect of the container is considered to remain unaltered. From Figure 28, it is seen that the average T550% value was within + and - 1% of the target. However, over the range of cullet levels there was a trend toward a larger standard deviation, indicating that there was a tendency for the colour stability to be more variable at higher

cullet levels.

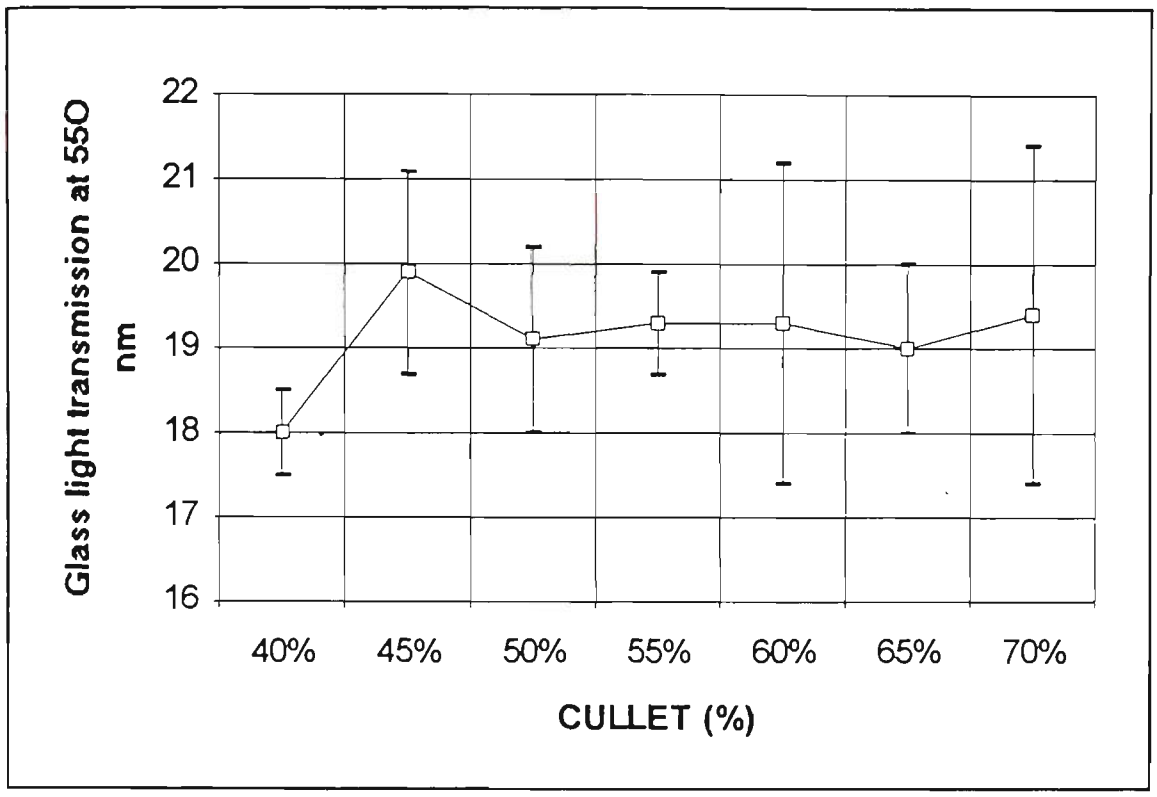

Figure 28. MB4 T550% & S.D. Vs cullet

4.1.6 OWENS-BROCKWAY STABILITY CRITERIA

Amber glass is classed traditionally as an unstable glass. During the refining and conditioning stages, there is a tendency for the sulphide to become oxidised to produce sulphate blisters. Any major changes in the production operation, such as tonnage or temperature, are likely to increase the level of blister or seed. The O-B stability criteria are a set of parameters calculated from the weight and mole percent values of iron and sulphide ions in the amber chromophore. The amber chromophore is produced by ferric ions surrounded by oxygen and sulphide ions. The balance of iron to sulphide ions is critical for both glass refining and colour stability. The results of the stability parameters compared to O-B recommended values are shown in Table 9.

There was a general trend toward the targeted stability parameter range. This was initially due to the reduction in the iron target and then the increase in the saltcake level, starting from the 60% cullet period.

Table 9. O-B Amber stability values & targeted range

Cullet (%)	Range				
	Fe^{3+}(%)	$\frac{Fe^{3+}(\%)}{S^{2-}(\%)}$	$\frac{S^{2-}(n)}{Fe^{3+}(n)}$	$\frac{Fe^{2+}(\%)}{Fe(\%)}$	Residual SO_3(%)
	0.03 - 0.05	1.0 - 1.5	1.0 - 1.25	81 - 85(%)	0.003 - 0.008
50	0.068	2.96	0.87	77.5	0.015
55	0.060	2.74	0.96	80.3	0.017
60	0.063	1.85	1.37	79.1	0
65	0.062	1.92	1.33	77.9	0
70	0.05	1.30	1.91	82.4	0

5.0 ANALYSIS - GLASS QUALITY

The glass quality results indicate that, at a level of 70% cullet in amber glass, the process can be controlled well within acceptable tolerances. However, at this amber cullet percentage (70%), it was found that a major change in the way batch sulphate levels were determined was necessary.

One major area of concern before this study commenced, was the possibility of large variation in the composition of the cullet. This study shows that this was of little concern. There was a drift in density by 18 points from 40% cullet in December 1991 to 70% cullet in August 1992, however 90% of that change occurred between 40% and 55% cullet. From this time on, the drift was not significant. Firstly, the drift in density was due to an increase in calcium oxide shown in Figure 19. This was due to corrective action that was being taken within the batch house weighing operation, aiming at reducing density variation for all four furnaces at AGM Spotswood. The work carried out in regard to CaO involved improving both the moisture control and the on-line moisture compensation for the limestone. With increased confidence in the repeatability of the weighing system, it was possible to make adjustments to the cullet composition used in the batch formulation. This was only deemed necessary on one occasion for ecology cullet, however the factory return cullet composition determined from XRF analysis of the product glass was updated after each analysis (usually every one or two weeks).

It could be argued that in Australia there is a unique situation, because being the only supplier of container glass, ACI has reasonable control over the cullet composition. However Hilson [4] showed in his work based in Canada (where there are many different suppliers), that the daily composition variation of a large stock pile of cullet was negligible, although over a larger time span some drift in composition did occur. The density and major oxide results for this work show that the composition drift at higher cullet levels is negligible.

Seed and stone levels are two fundamental glass quality measures that can be related to all glass types. At all cullet percentages monitored in this work, these two parameters were well within acceptable ACI quality guidelines. It was expected that seed levels would be good for a furnace that was pulling recommended loads, however there was a downward trend in seed levels throughout the increase in cullet level, despite a 25°C reduction in furnace floor temperature. This indicates, that with an increase in cullet level, the melting and refining ability of the glass improved. Stone levels measured by SID rejects remained static throughout the various cullet levels. The level was acceptable and indicated that under steady furnace operating conditions there was a background level of stones that did not deteriorate as the cullet percentage increased. Hence, cullet stone contamination was not a major problem at higher cullet

levels. Stone levels were much more sensitive to changes in furnace operation. This was evident on one occasion when the furnace floor (glass) temperature fell below 1180°C and the SID losses increased significantly. This example is shown in Figure 29.

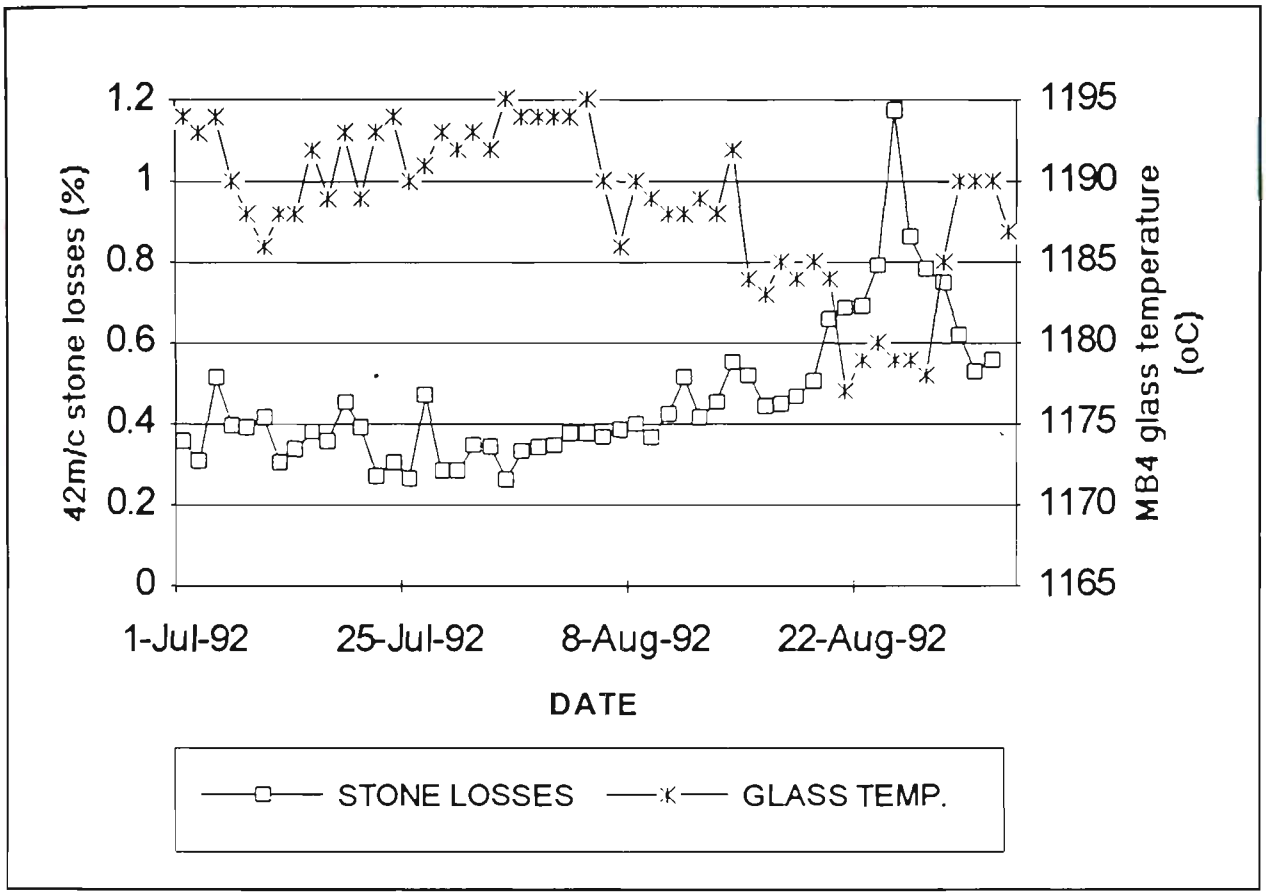

Figure 29. MB4 glass temperature & 42m/c stone losses at 70% cullet

The three other glass quality aspects (blister levels, T550% and O-B amber stability criteria) relate more specifically to amber glass. Amber being a reduced glass is less stable than an oxidised glass and is sensitive to gas evolution [11]. Blisters, unlike seed, are formed in the refiner and forehearth where reduction and oxidation reactions take place. In particular, the oxidising effect of the cooling wind in the refiner will produce typical sulphate blisters according to Equation 1.

$$S^{2-} + 2O_2 \rightarrow SO_4^{2-} \qquad (1)$$

A reduction can take place according to Equation 2.

$$2SO_3 \rightarrow 2SO_2 + O_2 \qquad (2)$$

The mixing of reduced and oxidised portions of glass can also produce blister according to Equation 3.

$$3SO_3 + Na_2S \rightarrow Na_2O + 4SO_2 \qquad (3)$$

To avoid the occurrence of blister, it is necessary to have stable operating conditions and the correct balance between sulphide and sulphate. This criteria applies to the three remaining glass quality aspects (blister, T550% & O-B stability parameters) and will be discussed in the following. The role of sulphate in amber glass is also discussed in chapter 10.

The data obtained for blister levels at 50% and 55% cullet for each machine and the average of both, were unacceptable. Although for both cullet periods one machine showed an acceptable result, the fact that there was no consistency between machines indicated that in general the glass was unstable and sensitive to changes in forehearth operation on either machine. The significant improvement in blister levels at 60% cullet (and subsequently at higher cullet levels) was due to a change in the sulphate level employed in the batch formulation. This result is seen in Figure 30 where a steady improvement in blister levels occurred as the batch saltcake levels were increased. The main benefit of the extra sulphate was to enhance the mixing and refining effect in the melting process and improve the homogeneity of the final glass. This resulted in fewer streams of glass having different oxidation states, and hence less of reaction 2 (Equation 2) taking place.

The glass on MB4 at 60% cullet prior to the addition of extra saltcake, required a higher concentration of sulphide. This was evident by the fact that as the saltcake level was increased and a constant glass carbon number was maintained, the T550% decreased. Ryder [15] indicated that as the sulphate level was increased, the transmission at 550nm should also increase. Therefore, the MB4 glass was sulphate limiting: As the saltcake was increased, there was abundant carbon available to reduce it further and to form more sulphide, hence the reduction in T550%. It is also possible that as the glass was "over reduced" prior to the saltcake change, this was another cause of blisters occurring via Equation 2. The saltcake was increased to 13/1000 sand at which stage the glass T550% no longer continued to decrease. This indicated that the sulphate was no longer limiting the amber chromophore formation. The reduction in blister levels indicated that there was also sufficient sulphate for glass refining.

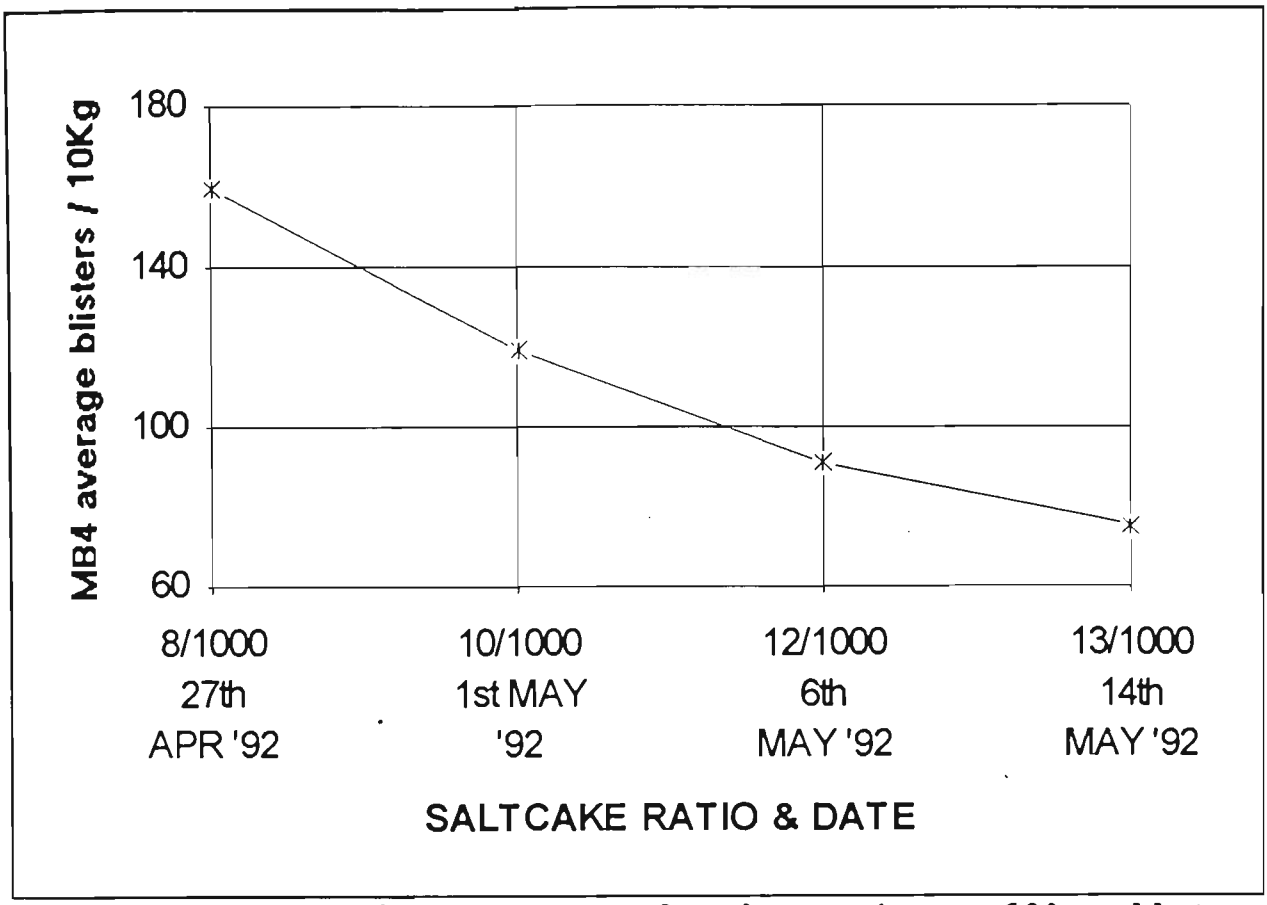

Figure 30. MB4 blister Vs saltcake ratio at 60% cullet

The introduction of extra saltcake to aid the refining of the glass was a significant factor in successfully running at higher cullet levels. Several authors have indicated problems with refining and colour control at higher levels of cullet. Hilson [4] related the experience of producing glass at 100% cullet for several months and then running into a serious seed and blister problem. In his study, this was only alleviated by reducing the cullet level to 85% and increasing the saltcake ratio from 10/1000 sand to 15/1000 sand. A similar experience occurred at AGM Spotswood on another amber furnace at 70% cullet (prior to running 60% on MB4), where by coming out of a colour change, the glass remained seedy and blistery for several weeks. This problem was only overcome by increasing the saltcake ratio from 6/1000 sand to 12/1000 sand. Weiser [7] shows experimental results in amber glass produced from 0% to 50% cullet where the retained SO_3 level in the glass was reduced with the cullet increase. He relates this to a reduction in retained sulphide sulphur, possibly due to oxidation and volatilisation of the sulphide in the cullet during melting. The retained sulphide sulphur results for MB4 however, show a 50% increase in sulphide level from 55% cullet to 60% cullet, after the saltcake increases were made. As the depleted sulphide supply was replaced, the ferric to sulphide balance approached the optimum ratio for producing a stable amber chromophore ion (Table 9), reducing the tendency for the sulphide to become oxidised. The overall increase in retained sulphide and the resulting improvement

in blister levels are shown in Figure 31.

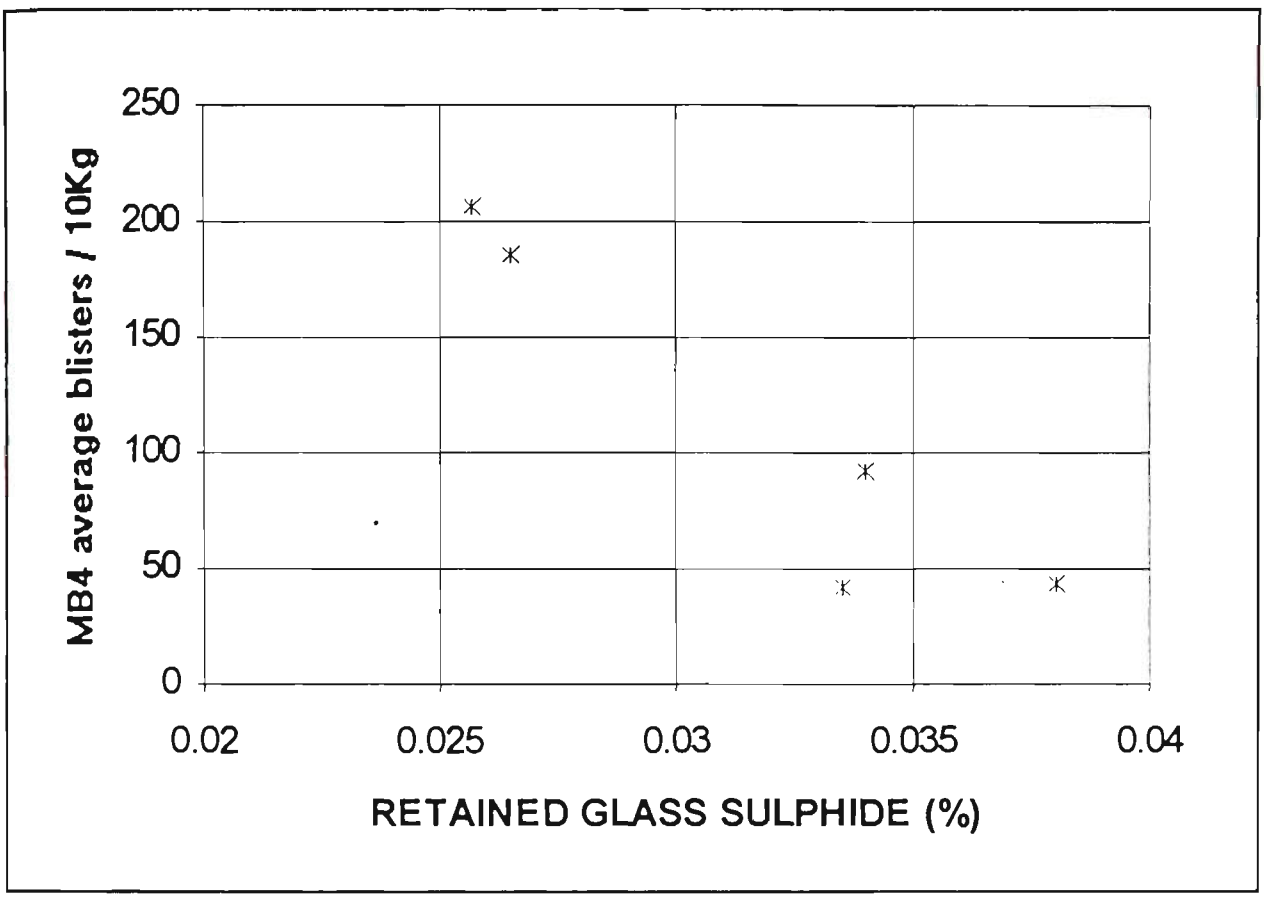

Figure 31. MB4 blister Vs retained sulphide

Information received from Owens-Brockway [16] suggested that, at higher cullet levels, a more appropriate method of determining batch saltcake requirements was to maintain a constant excess amount of sulphate based on an SO_3 balance on the glass. A 1Kg excess of SO_3 per 1000Kg glass was suggested as a minimum amount for all cullet levels. The procedure and the calculation to arrive at this suggested value is shown in Appendix III. The excess sulphate value of 1Kg is based on practical experience and has proved successful, as evidenced by the improved blister levels achieved during this work. Further discussion on the saltcake additions are found in chapter 8. Figure 32 shows the theoretical relation between excess SO_3, cullet level and the traditional ratio method of saltcake determination. It can be seen that if the saltcake ratio remained at 6/1000 sand, for MB4 amber glass above 40% cullet, there would be an excess SO_3 value of less than 1Kg. At a saltcake ratio of 12/1000 sand, there is adequate excess SO_3 up to 70% cullet. In the past, cullet levels have remained relatively low, (less than 40%) and a saltcake ratio of 6/1000 sand would have provided sufficient excess sulphate to ensure adequate

refining and sulphide formation.

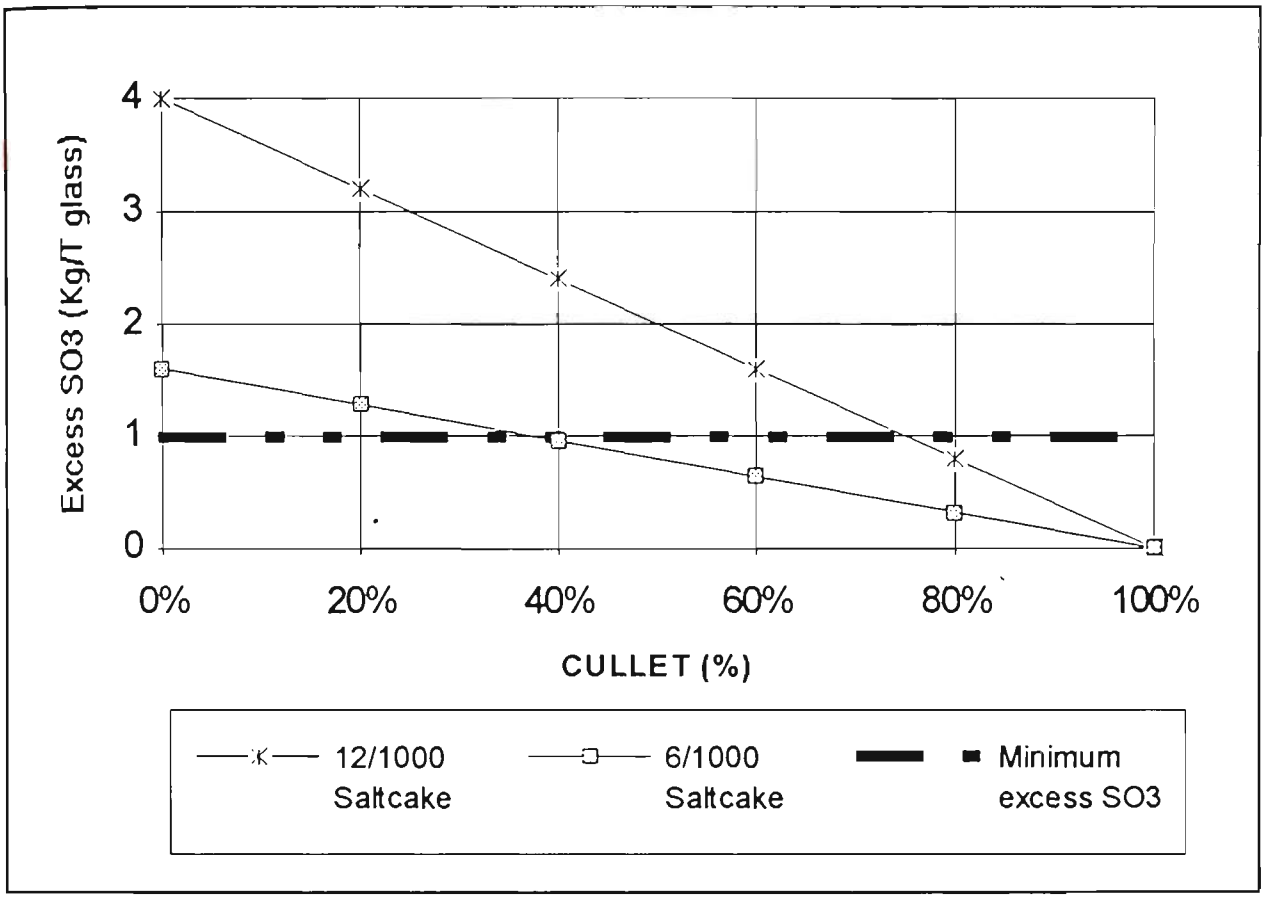

Figure 32. Theoretical glass excess SO_3 % Vs cullet

At all levels of cullet, Figure 28 indicates that the average target T550% value was achieved. (At 40% cullet the target value was 18%.) However, the standard deviation of the value at 70% cullet is four times larger than at 40% cullet. This result is in line with Hilson [4] who indicated that large variations in colour can occur due to different amounts of carbonaceous material being left in the cullet after processing. It does appear that, as the cullet level increases, the possibility of T550% variation goes up. However, for the 70% cullet period the carbon source was changed during the early period in July '92 and then changed again toward the end of the month. If the period of August is considered, the standard deviation is reduced to 0.8% transmission. Although not as good as at 40% cullet, the colour control is commercially acceptable.

The Owens-Brockway stability criteria were monitored as a final consideration of amber glass quality at higher cullet levels. These parameters are based on practical experience in producing

stable amber glass having low seed and blister counts and minimum amounts of "light streak", that is often associated with amber glass. The basis for the parameters are that, for the glass to be stable, the amber chromophore must be stable and that an iron level of 0.28% to 0.3% is required to minimise the amount of sulphur needed to produce the colour [11]. By having less sulphide retained in the glass (comparative to an iron level of 0.16%), there is reduced tendency for blister formation due to oxidation. There is a limit to how high the iron level can go (not more than 0.325% Fe_2O_3 by weight), as the glass takes on a greenish tinge.

The percent reduction reported as Fe^{2+}/Fe with a range of 81% to 85% is supported by Volf [17] in that only around 80% of the bivalent iron can be formed under reducing conditions. This is because the FeO-silicates decompose at high temperature. Once the total level of iron and the percent reduction have been established, the range of ferric iron required is also set. The amber chromophore is well established as being a complex species containing ferric and sulphide ions and the proportions of each, according to Volf [18], are 12-15% Fe^{3+} and 5-7% S^{2-} by weight. This gives an operating ratio Fe^{3+}/S^{2-} of around 2, which is in reasonable agreement with the target O-B parameter. The residual SO_3 operating range is to ensure that the glass is not sulphate limited.

There were two significant changes made to the glass chemistry in an effort to approach these stability criteria. The first resulted in the glass iron target being reduced from 0.325% to 0.3% midway during the 50% cullet period. This caused a slight drift of the parameters toward the target during the 55% cullet period. The other, was the doubling of the saltcake ratio during the 60% cullet period, which saw a definite trend toward the required operating range even with the cullet level increased. Although these parameters can only be considered as a guide to achieving a stable amber chemistry, the fact that blister levels and seed levels improved as the target parameter range was approached strongly supports these guidelines.

This study has shown that, to a level of 70% cullet, amber glass quality can achieve and surpass the requirements of commercial quality standards. It was shown that to achieve these standards a new approach to sulphate batch calculations was required. One area of quality, namely the variability of the transmission at 550nm, was borderline at 70% cullet. This area could benefit from further detailed analysis. A further question to be answered: Can the excess sulphate calculation and stability criteria based parameters be extrapolated to a cullet level of 100%?

6.0 RESULTS - GLASS WORKABILITY

6.1 GLASS WORKABILITY

Glass workability is related to the glass viscosity-temperature curve and the forming machine setup. A particular glass composition determines the viscosity of the glass at different temperatures and the rate at which the glass will cool (Appendix I). The three criteria used in this study to determine glass workability at different cullet levels were checks under the ring (CUR), container thin walls (TW) and the percent losses due to critical faults determined by experienced operators and rejected by the cavity identification device (CID). The categorised results are shown below. In all cases the main objective was to study the results of forming machine 42(42m/c), however forming machine 41(41m/c) was used as a check against whether faults could be regarded as mostly machine related or glass related. Major machine breakdowns that adversely effected bottle fault losses and were outside the normal variation were removed from the data set. This Analysis is shown in Appendix II.

The total average losses of the three categories studied for 41m/c and 42m/c are shown in Figure 33. These trends best reflect the workability rating of the glass at each cullet level. 42 machine, having a single job running for the entire time, shows that the effect of cullet increases on workability was detrimental until 60% cullet. The improvement on 41m/c starts at 55% cullet. This was more related to the heavy weight job on the machine at that stage.

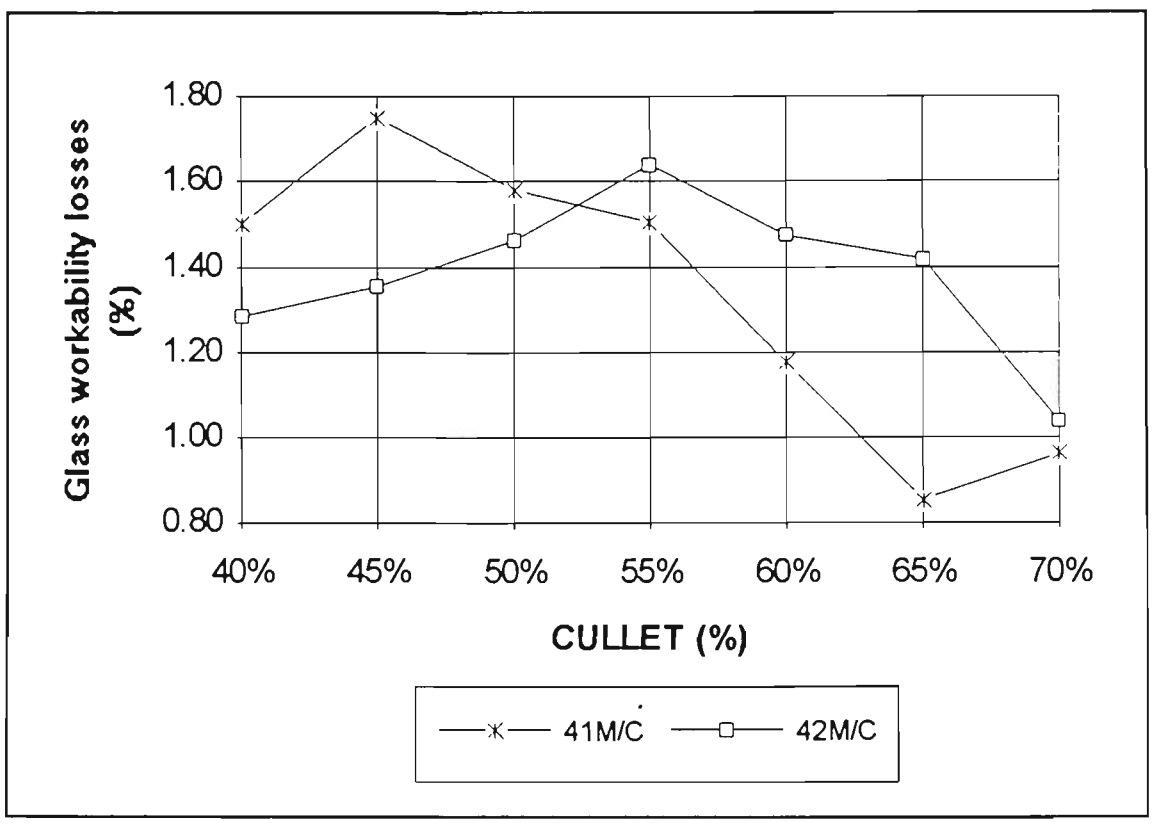

Figure 33. Average workability losses Vs cullet

6.1.1 CHECK UNDER RING

Figure 34 shows the CUR losses for both 41m/c and 42m/c at increasing cullet levels. Losses on both machines follow each other closely, indicating that the effect of the glass was the over-riding factor in these results. There are two exceptions. Firstly, at 55% cullet, when a heavier weight job was put onto 41m/c: the moulds for this job did not have the usual Vertiflow™ cooling facility and this created more CUR faults. (This job also run toward the end of the 70% cullet period with Vertiflow™ moulds and the CUR fault rates were improved). Secondly, at 60% cullet 42m/c results showed a significant shift in mean. This drop in CUR losses followed a period of maintenance on the machine and a change in the glass sulphate levels.

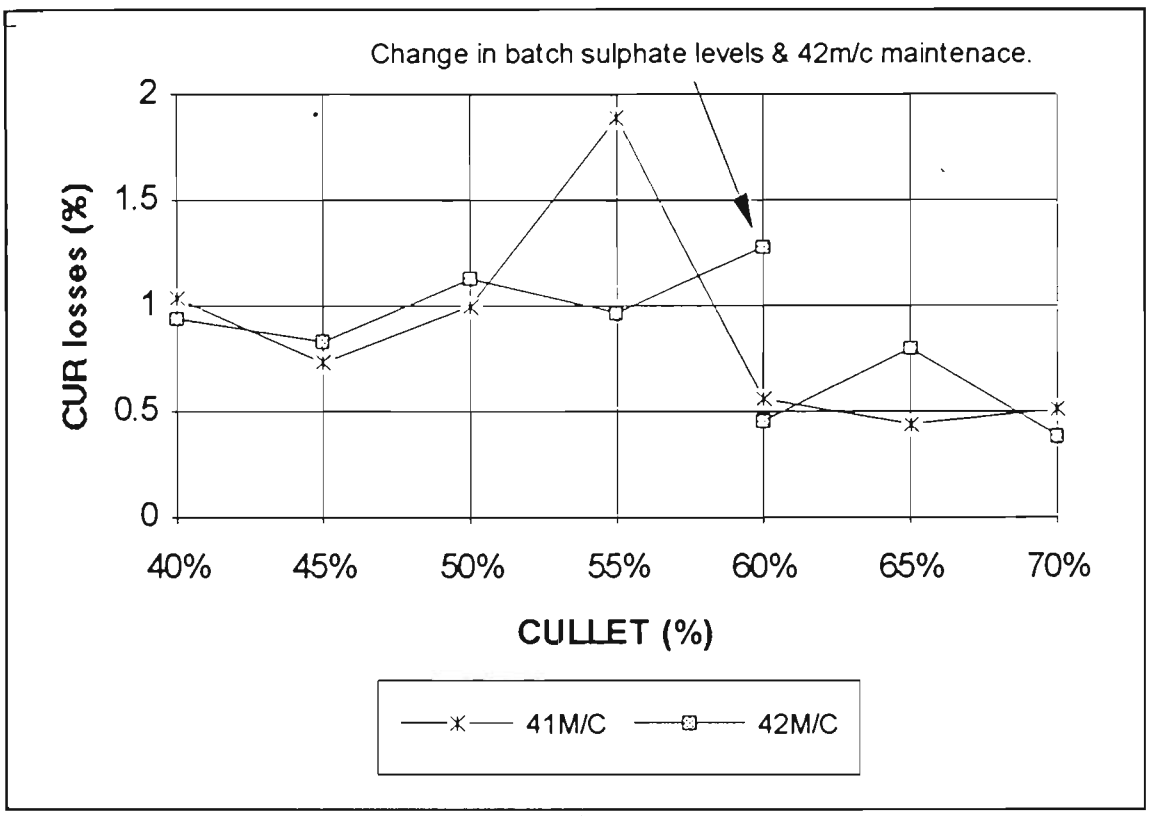

Figure 34. 41m/c & 42m/c CUR losses Vs cullet

Figures 35 and 36 show the individual machine CUR performance. In both cases the average CUR losses and variability improved after the 60% cullet level as compared to levels below 60%. Statistical analysis was carried out to compare the mean CUR losses at 40%,45%,50% & 55% with the losses at 60%, 65% & 70% cullet. Only 42m/c was analysed because it had the same job running for the entire time of the study. The critical F-value was 3.92 at 0.05 significance level and statistical analysis revealed 69.9, indicating that there was a significant reduction in mean CUR losses for cullet levels at 60% and above. The statistical test procedure is explained in Appendix II.

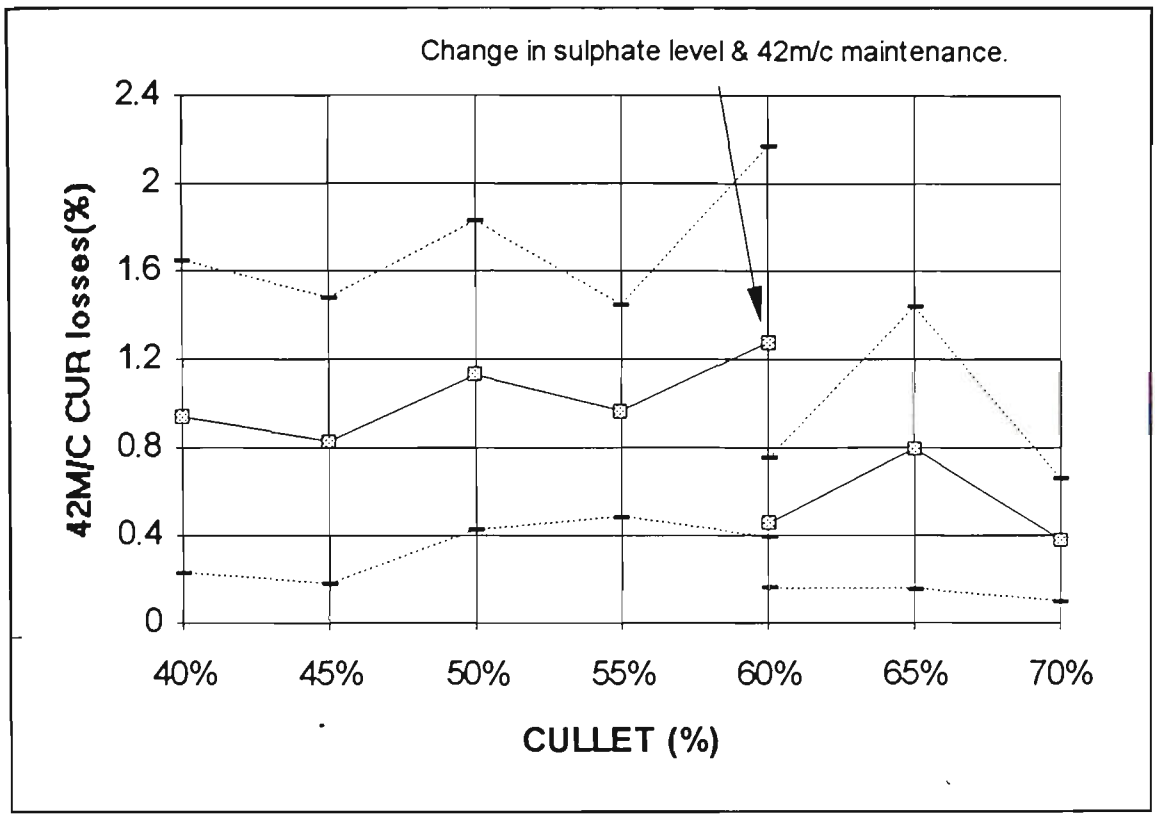

Figure 35. 42m/c CUR losses & variance Vs cullet

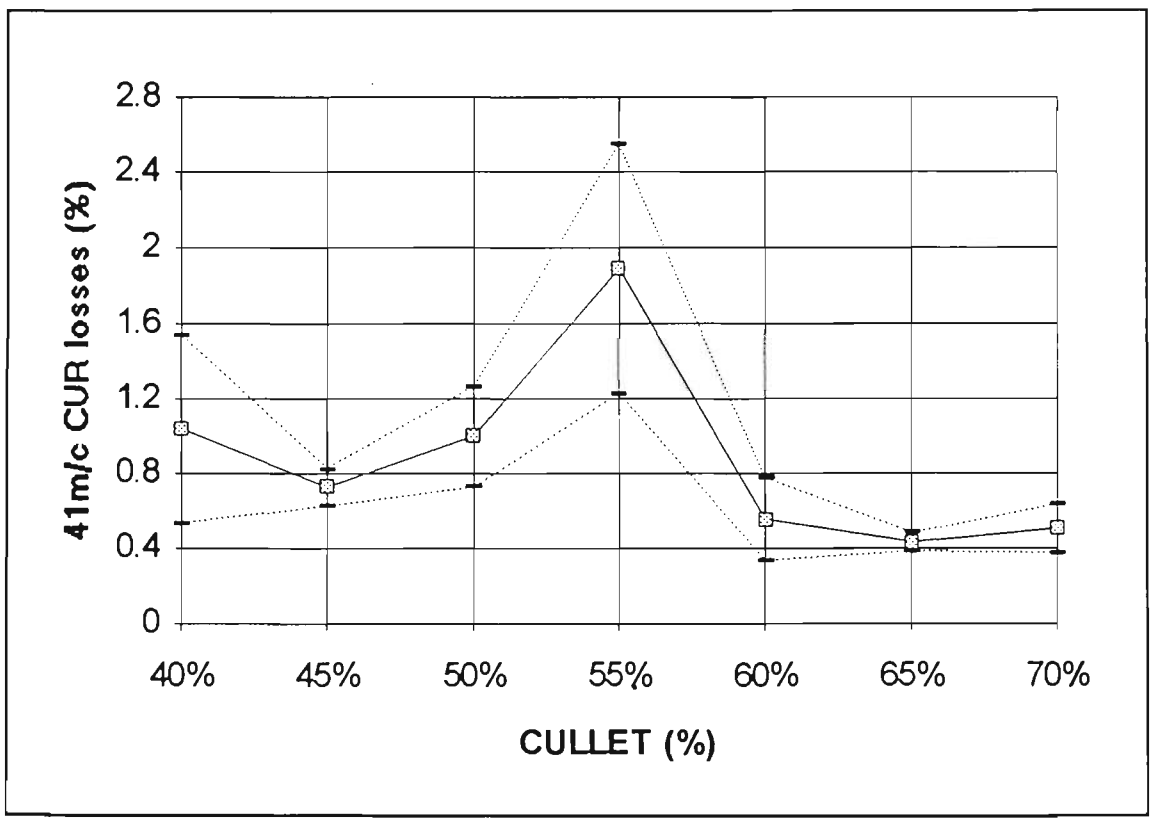

Figure 36. 41m/c CUR losses & variance Vs cullet

6.1.2 THIN WALL LOSSES

The thin wall losses for both machines are shown in Figure 37. At 40%, 45% and 50% cullet, both 41m/c and 42m/c were making the same container and showed similar thin wall loss trends. Also, at 60%, 65% and 70% cullet 41m/c was making a container of similar capacity and weight, but with a different neck and wall profile. (Figure 17 shows the three container profiles and the dates they were running on 41m/c). The losses for 41m/c had a similar trend to 42m/c at these cullet levels. At 55% the heavier job on 41m/c showed an improvement in thin wall defects, as it would be expected.

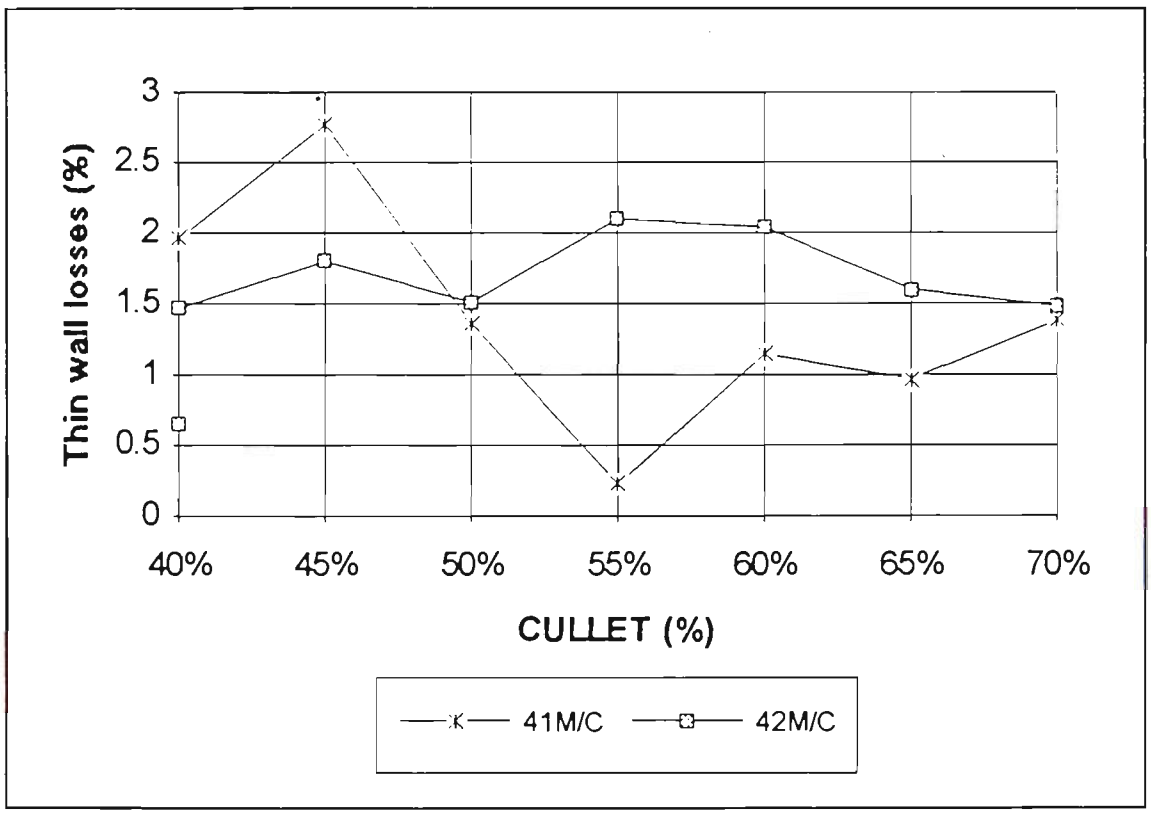

Figure 37. 41m/c & 42m/c thin wall losses Vs cullet

Figures 38 and 39 show the individual machine thin wall losses and variance. 41 machine shows an overall reduction in average losses for 55%, 60%,65% & 70% cullet, however this was mainly due to the change in job type. 42 machine showed an increase in losses at 55% and 60% cullet, but better results for 40%,45%,50%, 65% and 70%.

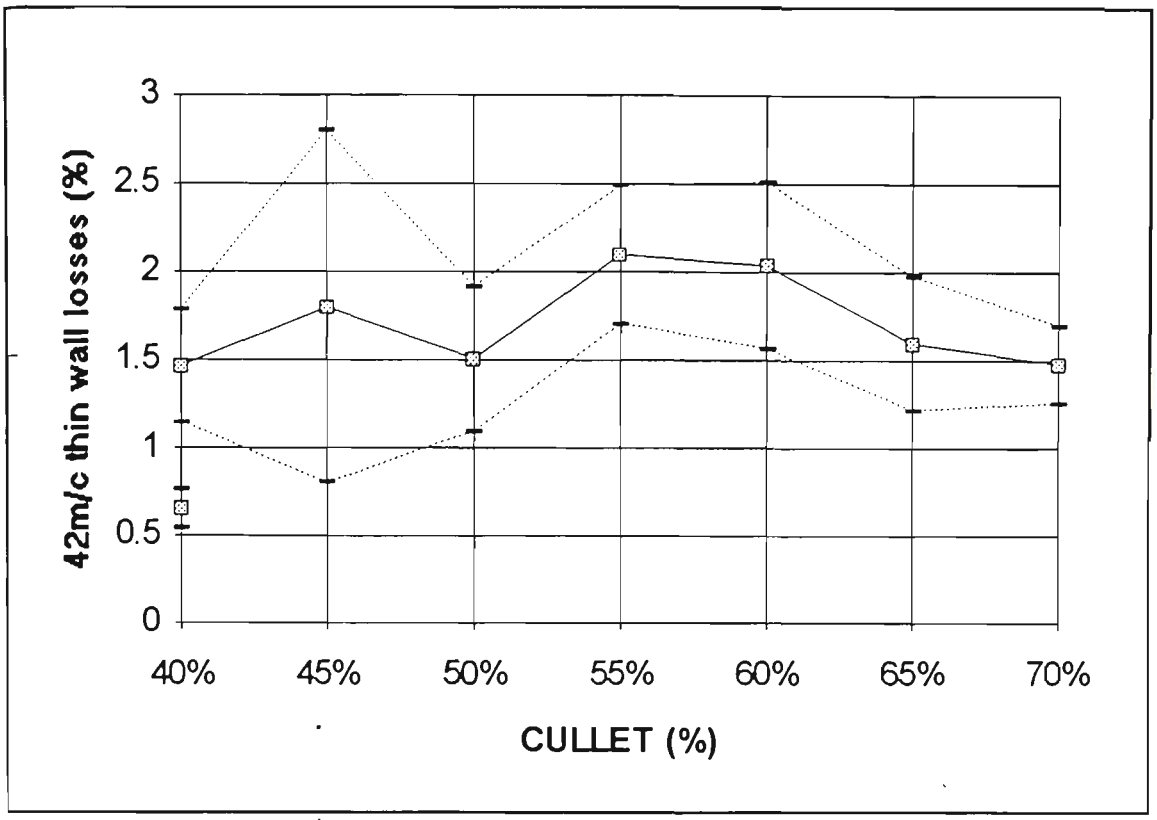

Figure 38. 42m/c thin wall losses & variance Vs cullet

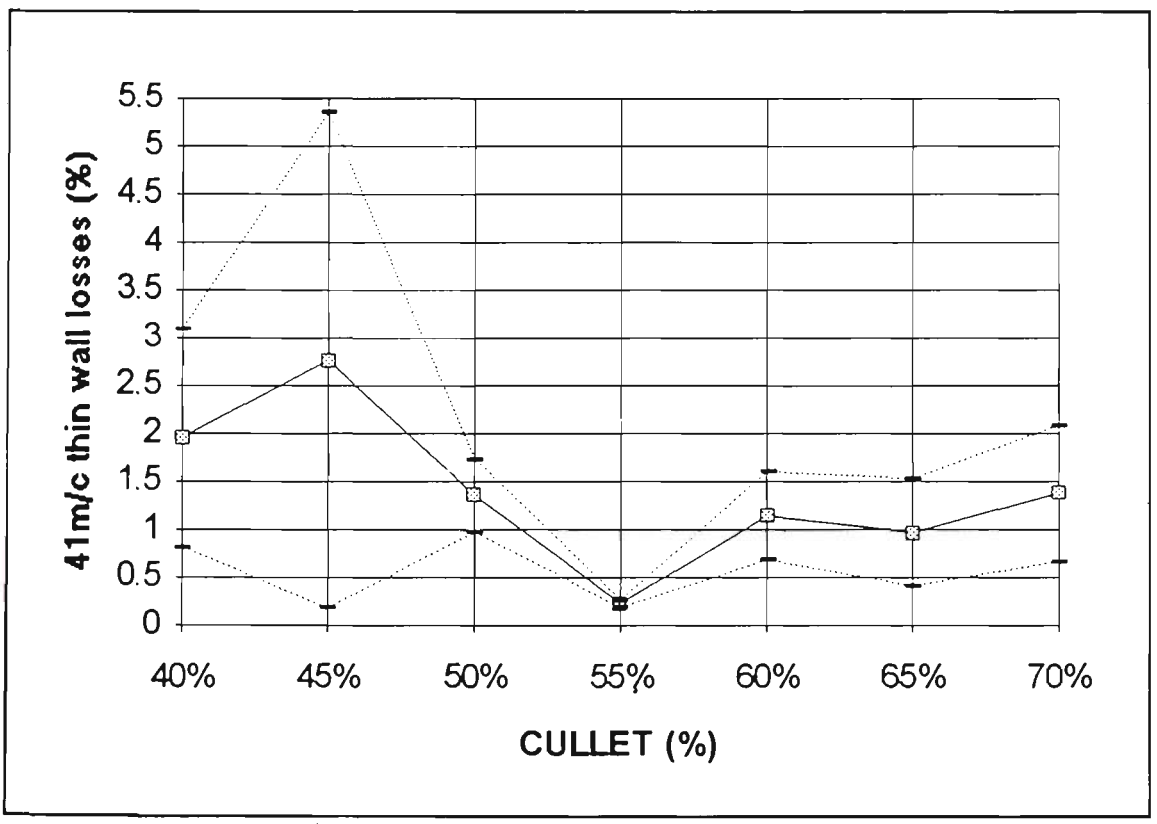

Figure 39. 41m/c thin wall losses & variance Vs cullet

6.1.3 CAVITY IDENTIFICATION LOSSES

Figure 40 shows the CID losses for both 41m/c and 42m/c although data was not available for 41m/c at 40% and 45% cullet. For the data available, both machines show an improving trend for cullet levels above 60%.

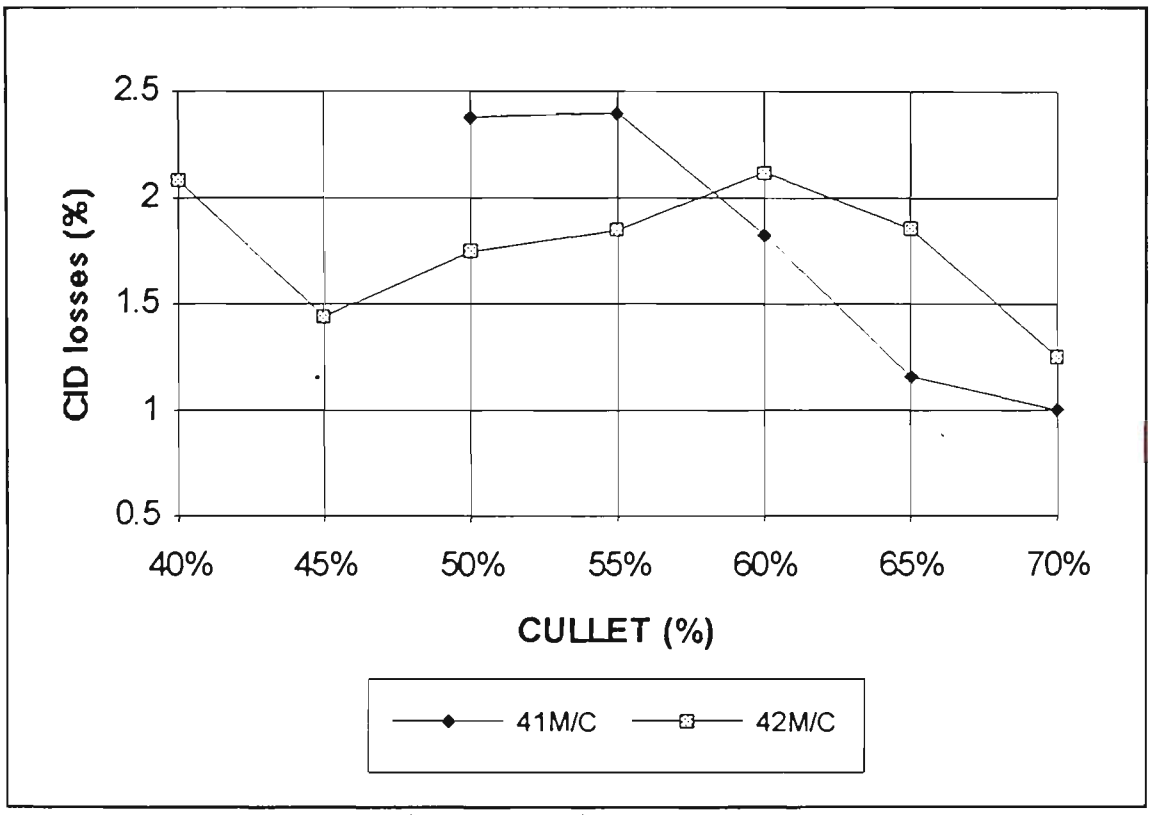

Figure 40. 41m/c & 42m/c CID losses Vs cullet

Individual machine loss charts are shown in Figures 41 & 42. 42 machine CID losses at 70% cullet were not too dissimilar than those at 45% cullet.

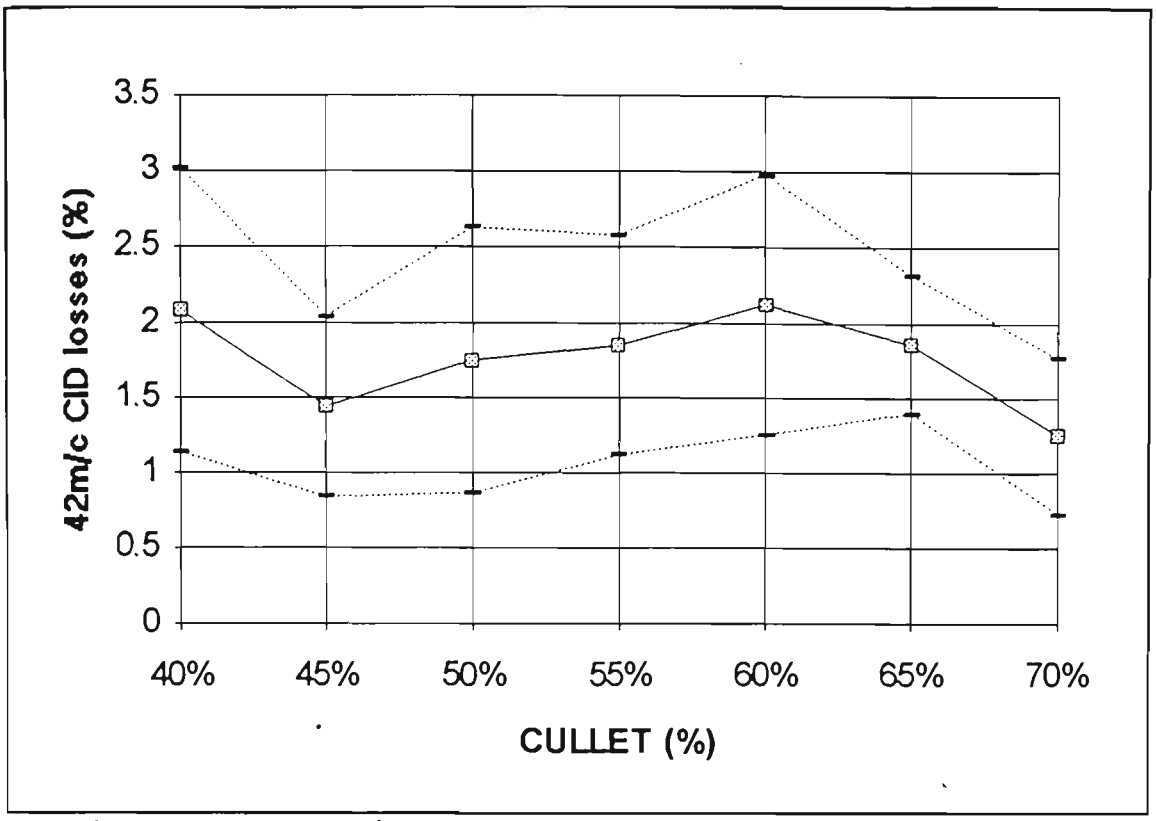

Figure 41. 42m/c CID losses & variance Vs cullet

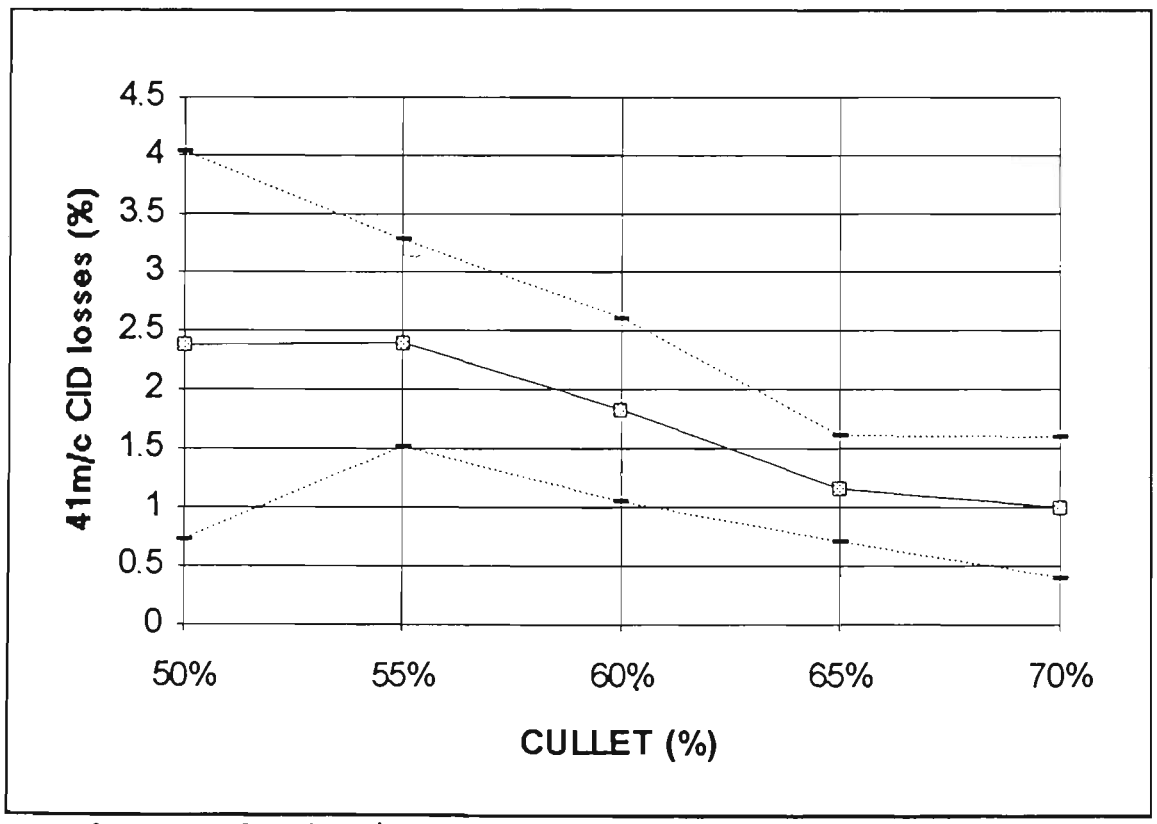

Figure 42. 41m/c CID losses & variance Vs cullet

7.0 ANALYSIS - GLASS WORKABILITY

The results obtained from the glass workability study indicated that, at 70% cullet in amber glass, the forming process could be expected to perform to the optimum capacity. The result trend shown in Figure 33 suggests however, that the batch sulphate changes made at the 60% cullet level were significant in improving workability. This was most likely due to the increased mixing effect the sulphate reactions have on the glass, hence ensuring that the glass is more homogenous as it enters the refiner and forehearth. This becomes more important as the cullet level increases, and it tends to even out any composition differences between the batch and cullet.

Thin wall losses on 42m/c at 40% cullet are shown in Figure 43. There was an increase in the mean losses at around the 27th of December. The low thin wall losses that occurred prior to this time were never achieved again during this study. There were no significant changes on the machine or in its operation. The only action in the area at the time that may have contributed to the increase was the changing of the orifice ring on the 28th December. This may have resulted in some cold glass forming in the bowl, causing uneven glass distribution to occur. From a glass composition point of view the increase in thin wall losses may be due to an increase in CaO that occurred during that period and is shown in Table 10. Prior to the change, the CaO concentration had

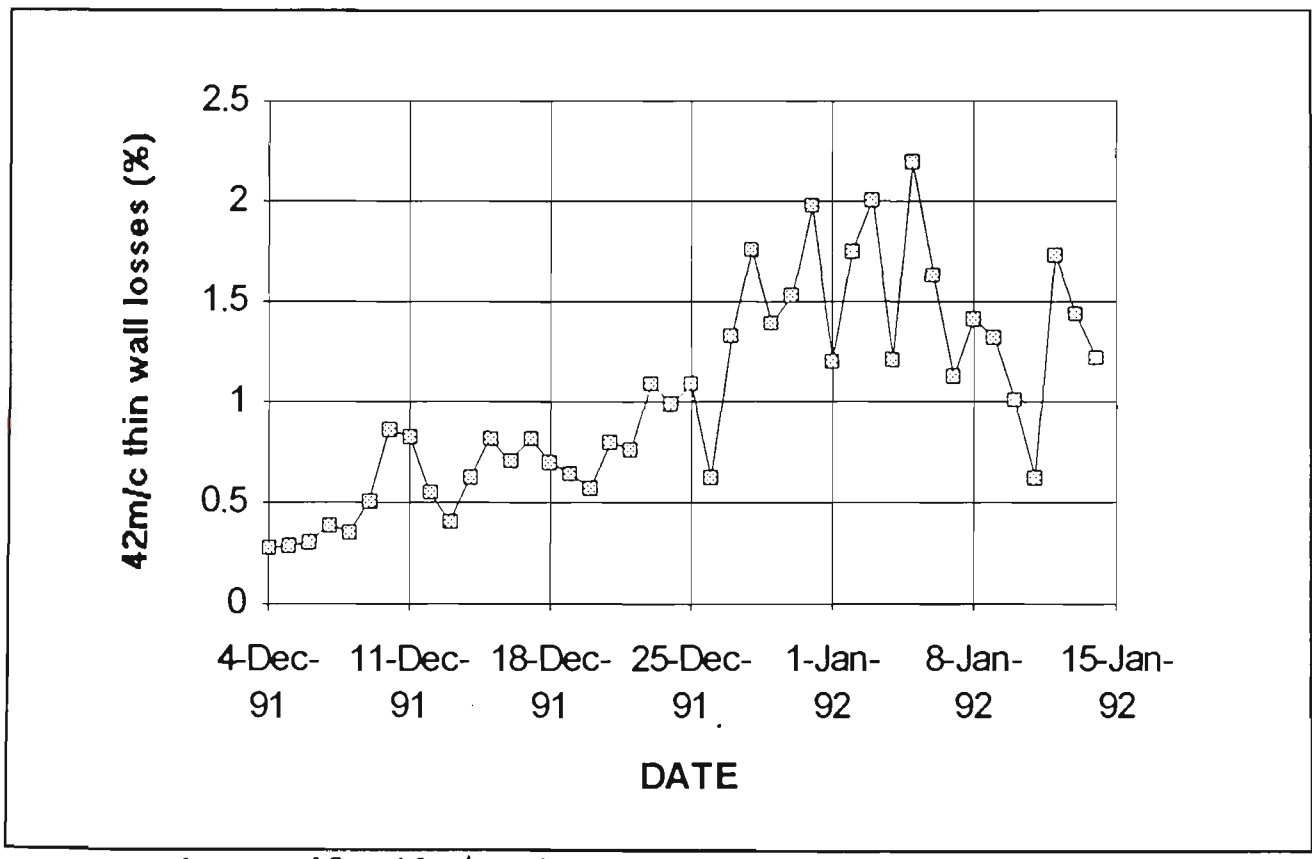

Figure 43. 42m/c thin wall losses at 40% cullet

been below target by 0.2%, but after that time it was generally closer to target. Also during December, a raw material change was made from magnesite to dolomite as the MgO source. Theoretically this change should not have affected the glass forming characteristics as the composition remained unchanged. However, the fact that there is a second source of CaO with dolomite may have had some bearing on the final glass physical properties.

Table 10. Glass CaO content at 40% cullet

Date	CaO (%)
10/12/91	11.29
24/12/91	11.50

Figure 44 shows that 41m/c did not follow the same trend as 42m/c and for this reason one would have to favour a machine related cause. However, the change in the mean requires further investigation.

Disregarding the earlier results from December, the thin wall losses show little change at the higher cullet levels. This indicates that there was no loss in homogeneity or glass distribution characteristics at 70% cullet. The earlier low level losses in December were most likely due to machine or forehearth changes, but possible composition effects require further investigation.

Check under the ring losses improved significantly at 60% cullet and above. 42 machine showed a definite downward shift in mean part way through the 60% cullet period. This followed a two day period of maintenance on the machine and a change in the fundamental operation of the forming process, when a period of vacuum on the blank cycle was removed. However, it is possible that this result is due primarily to the increased sulphate

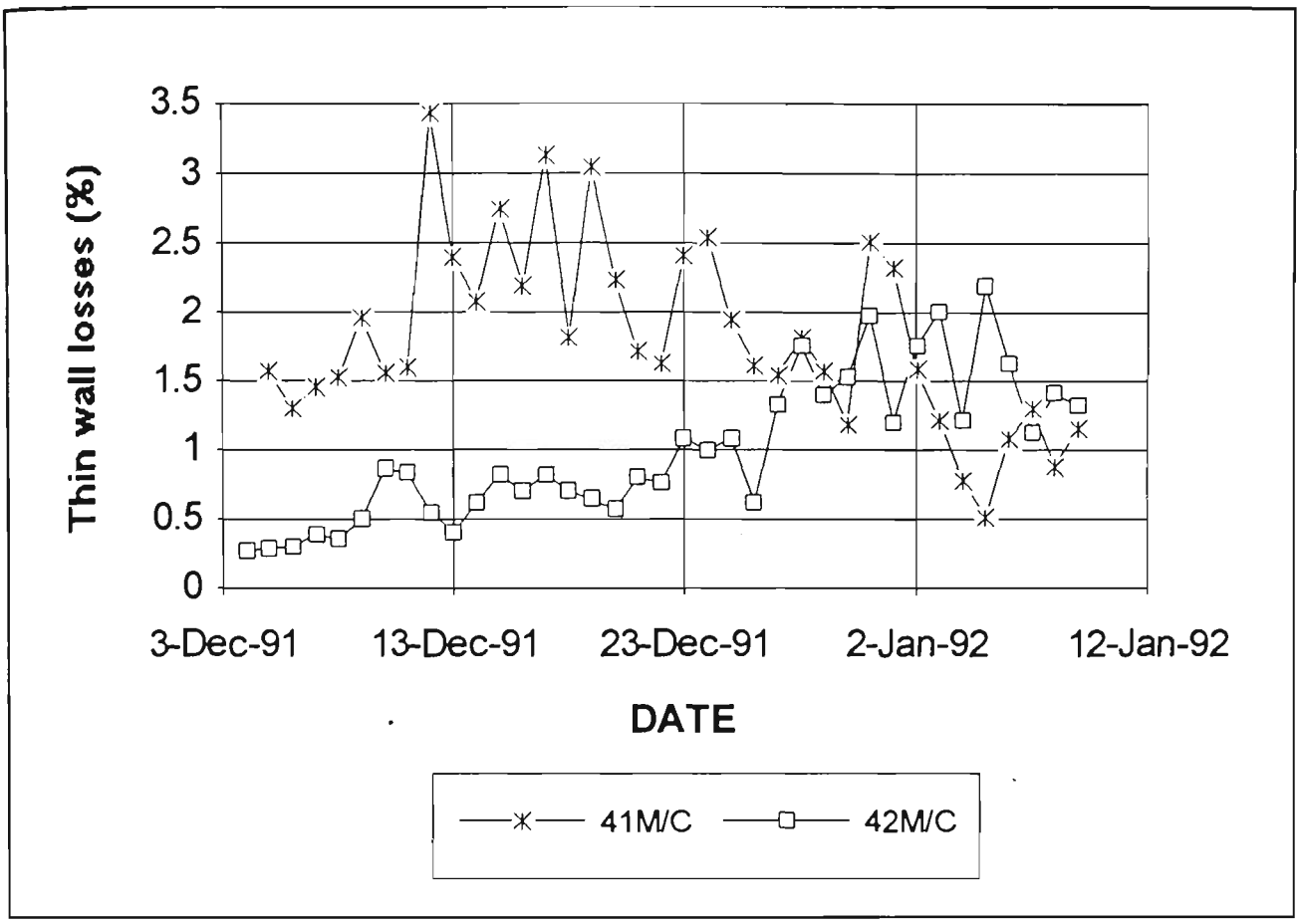

Figure 44. 41m/c & 42m/c thin wall losses at 40% cullet

addition to the glass. Figure 45 shows that both 41m/c and 42m/c followed the same trend for CUR losses during the 60% cullet period. No forming machine alteration was made on 41m/c. The lower CUR losses continued to the end of the study including the two month period at 70% cullet. By maintaining a set excess amount of saltcake per tonne of glass, the resultant mixing produced a more durable glass and reduced the tendency for separate composition streams to occur.

The overall CID loss trend is shown in Figure 40. The level of critical forming faults were reduced on both machines at cullet levels above 60%. One could argue that the improvement was due to an increased quality awareness in both the forming area and the inspecting area and continual improvements to the forming process and machine operation. This argument suggests that simply, the CID loss improvement reflects a general machine performance improvement and this was why the CUR losses improved also. However it cannot be denied that at worst, higher cullet levels have not affected the forming process and quite feasibly, the process has been improved due to changes made to the glass refining to accommodate the cullet.

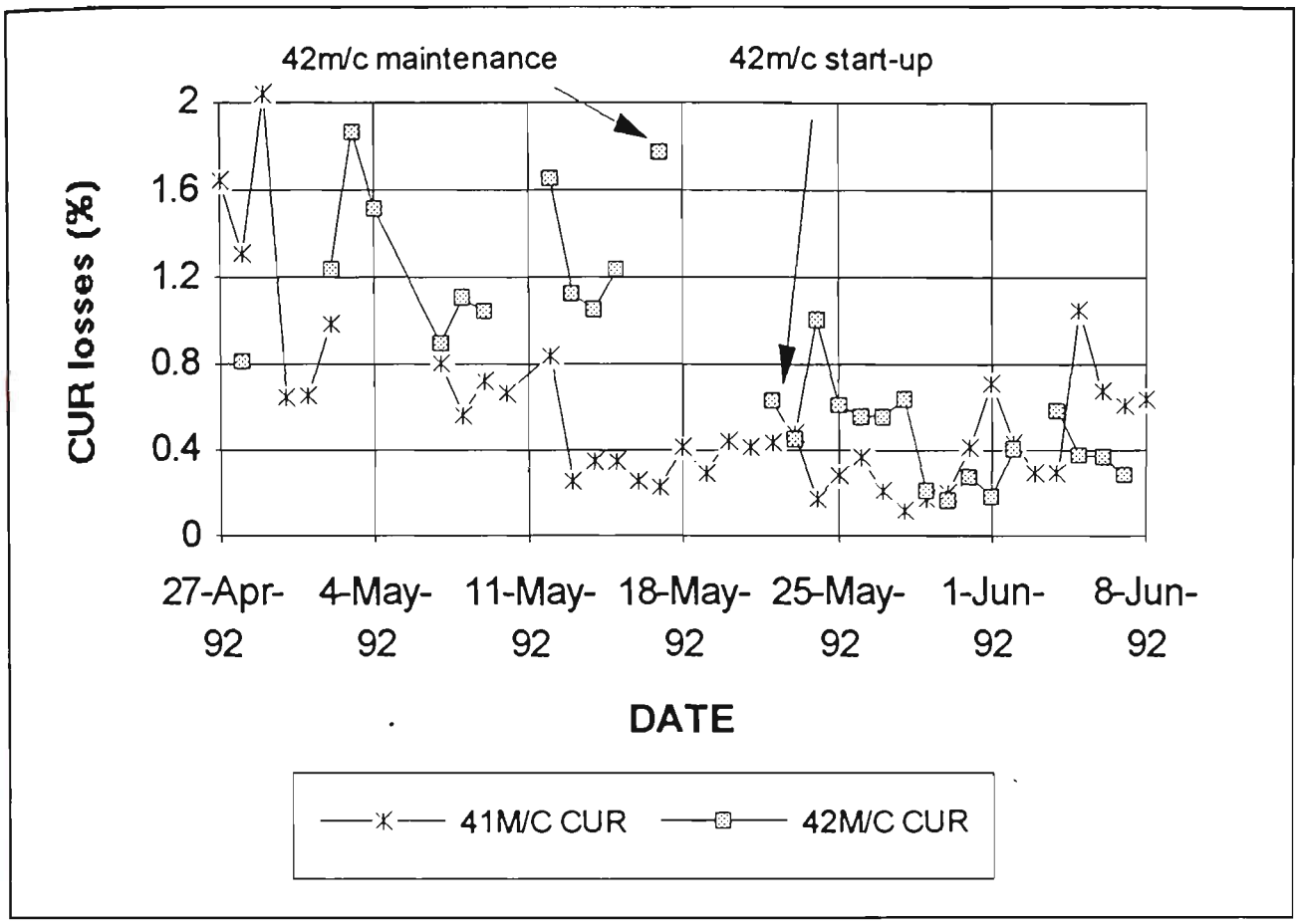

Figure 45. 41m/c & 42m/c CUR losses at 60% cullet

In conclusion on glass workability it follows that:

1. Glass workability improved at cullet levels above 60% after changes were made to the batch refining process;

2. Machine or forehearth changes were the most likely cause of the lower thin wall losses at 40% cullet, however certain aspects of the glass composition require further investigation;

3. The sulphate changes made to the batch at 60% cullet and above improved the mixing ability of the glass and produced a homogenous and stable amber glass, resulting in more predictable forming characteristics.

8.0 RESULTS - COMMERCIAL VIABILITY

8.1 COMMERCIAL VIABILITY

It is essential to have satisfactory glass quality and workability. If the product does not perform in a commercial sense then improvements are required. In this study commercial viability was investigated in terms of two parameters, job efficiency and container breaking pressure. These two parameters are good indicators of product performance for two reasons. Firstly, while container breaking pressures are high, there is little risk of producing containers that may fail on a filling line and secondly, high efficiencies mean increased profitability. The results of these two parameters in respect to increases in cullet level are discussed in this section.

Figure 46 shows the combined average values for efficiency and breaking pressure for 41m/c and 42m/c, as a percentage of their theoretical value. (The values shown are the sum of the bottle breaking pressure and efficiency divided by the sum of the theoretical breaking pressure and efficiency). In this study this value was known as the Commercial Viability Index (CVI). The trend shown reflects the commercial viability rating of the glass at each cullet level. The effect of the cullet increases was detrimental on commercial viability until a turning point at 55% cullet, where a gain in values occurred to 65% followed by a slight decrease to 70% cullet.

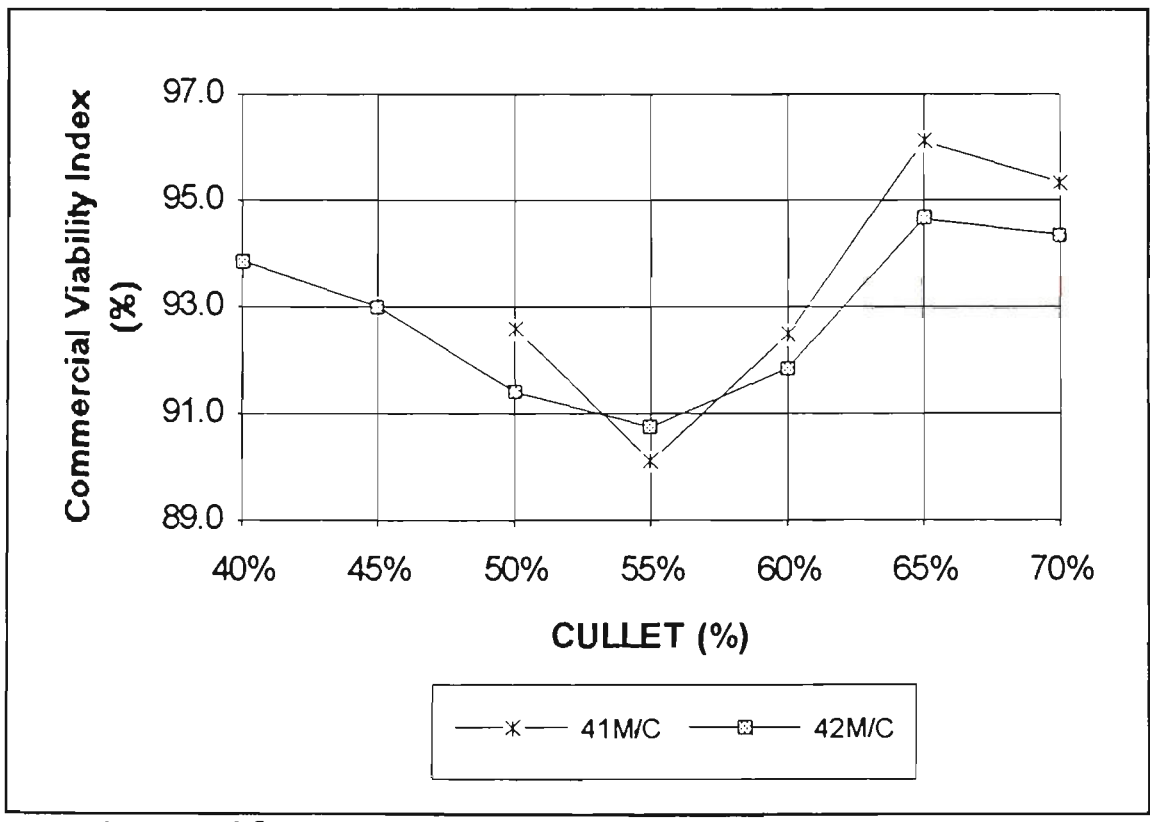

Figure 46. Commercial Viability Index Vs cullet

8.1.1 JOB EFFICIENCY

Figure 47 shows the efficiency losses for both 41m/c and 42m/c although data was not available for 41m/c below 50% cullet. For the data available both machines show an improving trend to 70% cullet level after the lowest efficiency at 55%. Despite 41m/c having five job changes during the period shown, the two machines show very similar trends. This shows that since there were differences in machine set-ups and maintenance periods, the glass had an overriding effect on commercial performance.

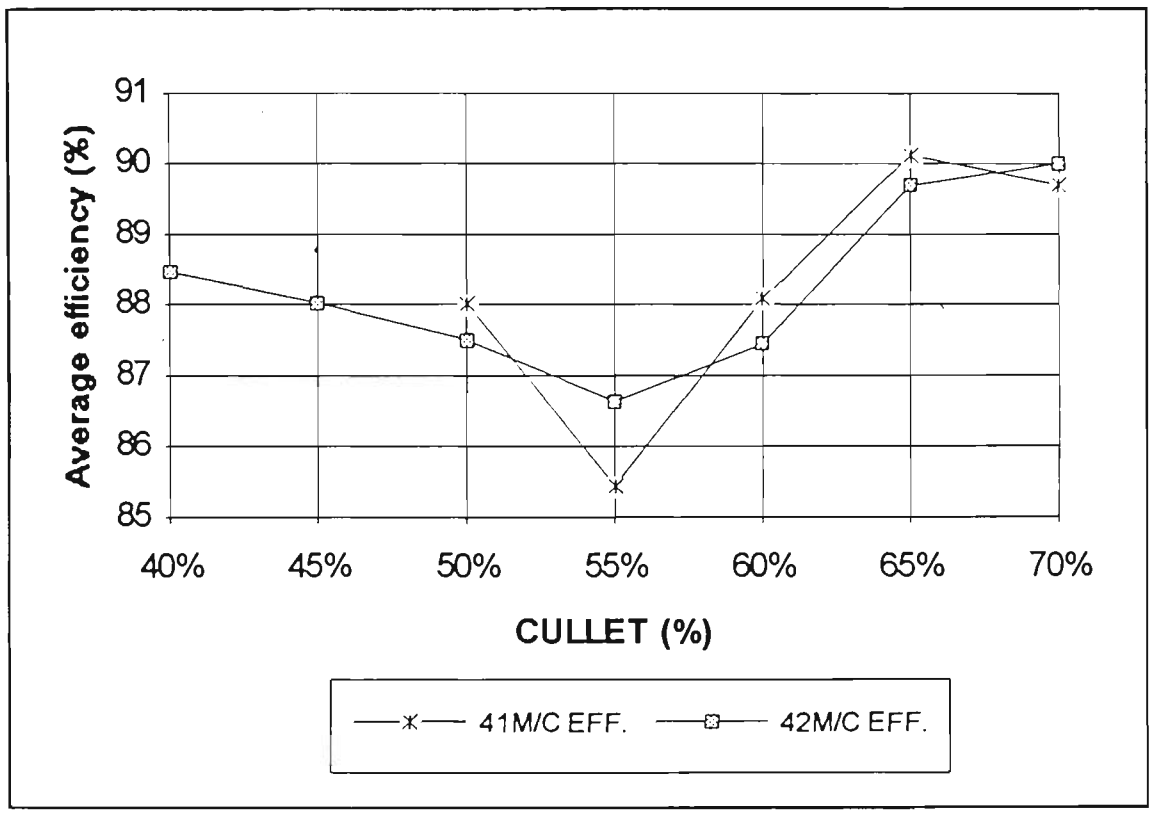

Figure 47. 41m/c & 42m/c efficiency Vs cullet

Similar results were reflected in the individual efficiency charts shown in Figure 48 & 49. The downward trend in efficiency for 42m/c was turned around in the latter part of the 60% cullet period following two days of machine maintenance and changes to the batch saltcake levels. Statistical analysis was carried out to compare the mean efficiency at 40%,45%,50% & 55% cullet compared to 60%, 65% & 70% cullet. Only 42m/c was analysed because it had the same job running for the entire time of the study. The critical F-value was 3.92 at 0.05 significance level and statistical analysis revealed 22.1, indicating that there was a significant improvement in mean efficiency for cullet levels at 60% and above. The statistical test procedure is explained in Appendix II.

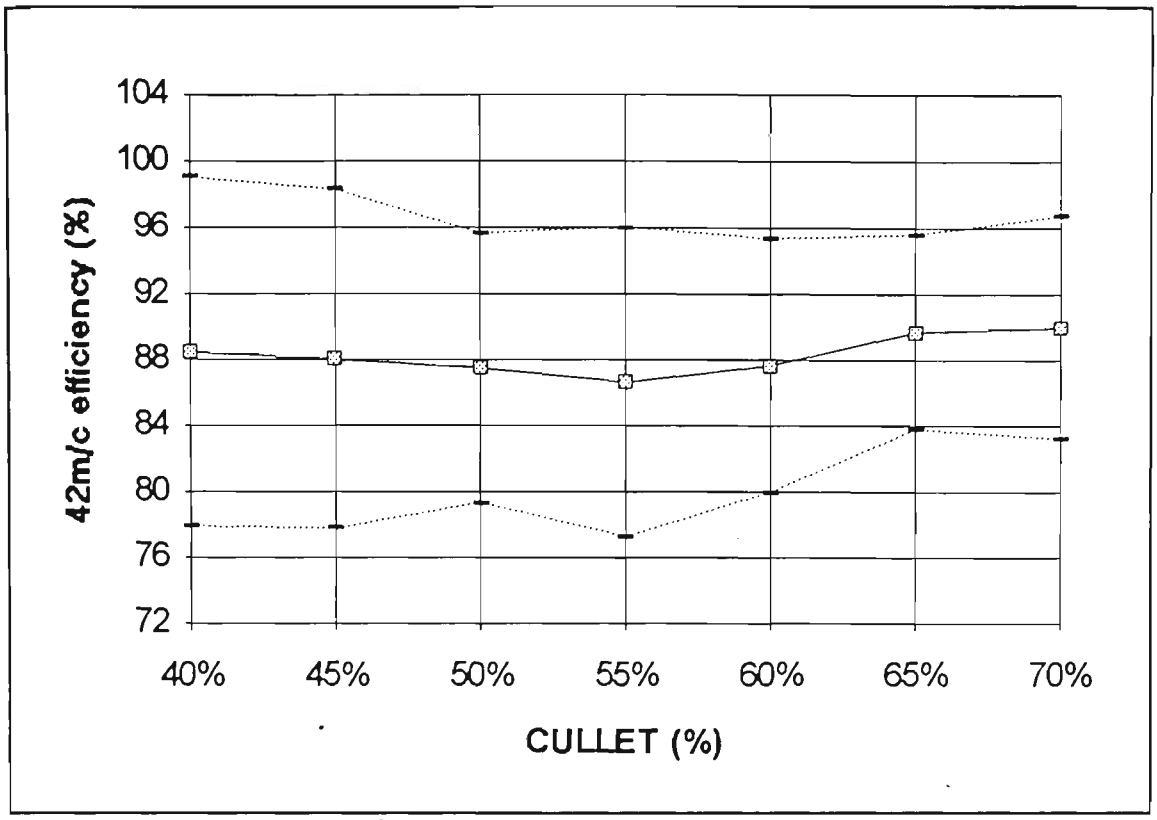

Figure 48. 42m/c efficiency & variance Vs cullet

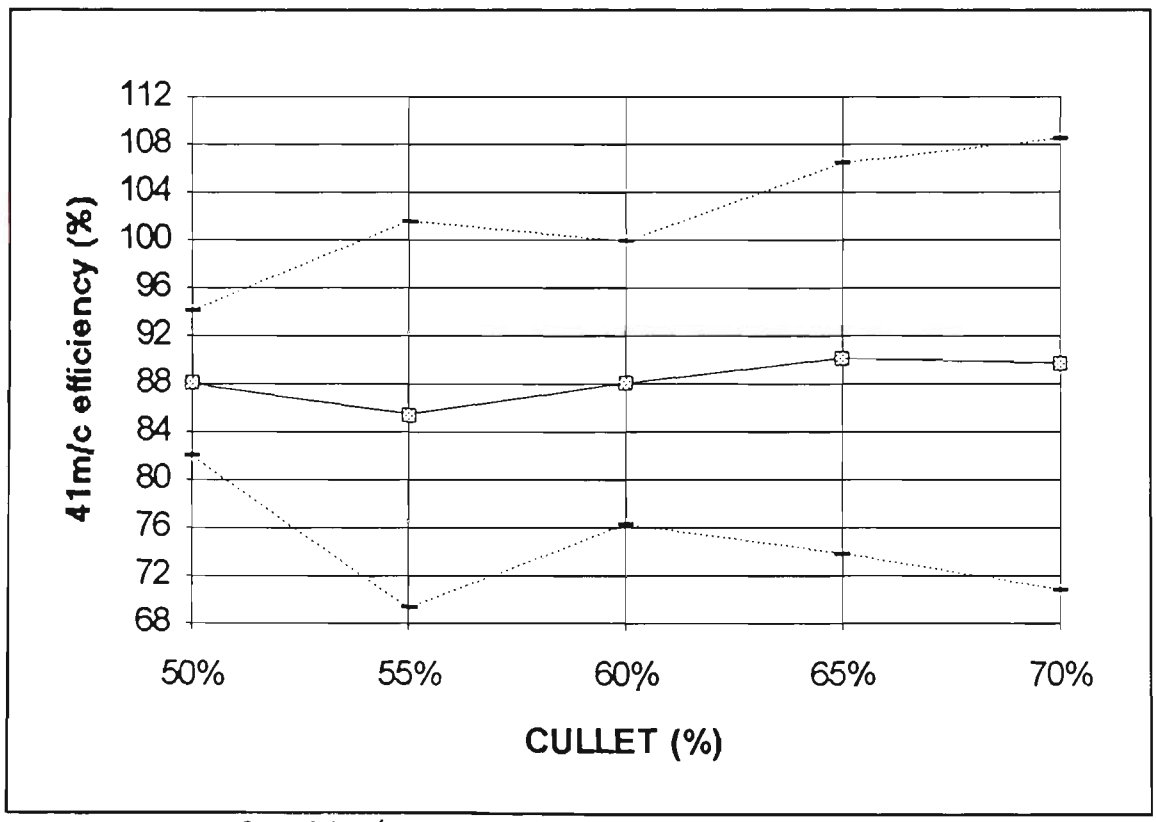

Figure 49. 41m/c efficiency & variance Vs cullet

8.1.2 BREAKING PRESSURE

The breaking pressure values for product from both machines are shown in Figure 50. The general trend for both machines was very similar, however the emphasised changes on 41m/c are due to different jobs running. This is demonstrated best by considering the 40%, 45% and 50% cullet levels when both machines were running the same job and the breaking pressure values were similar. As the job types changed at 55% cullet, the same trend remained but the overall values changed. At 55% cullet the heavier weight bottle on 41m/c showed an improvement in breaking pressure compared with 42m/c as it would be expected.

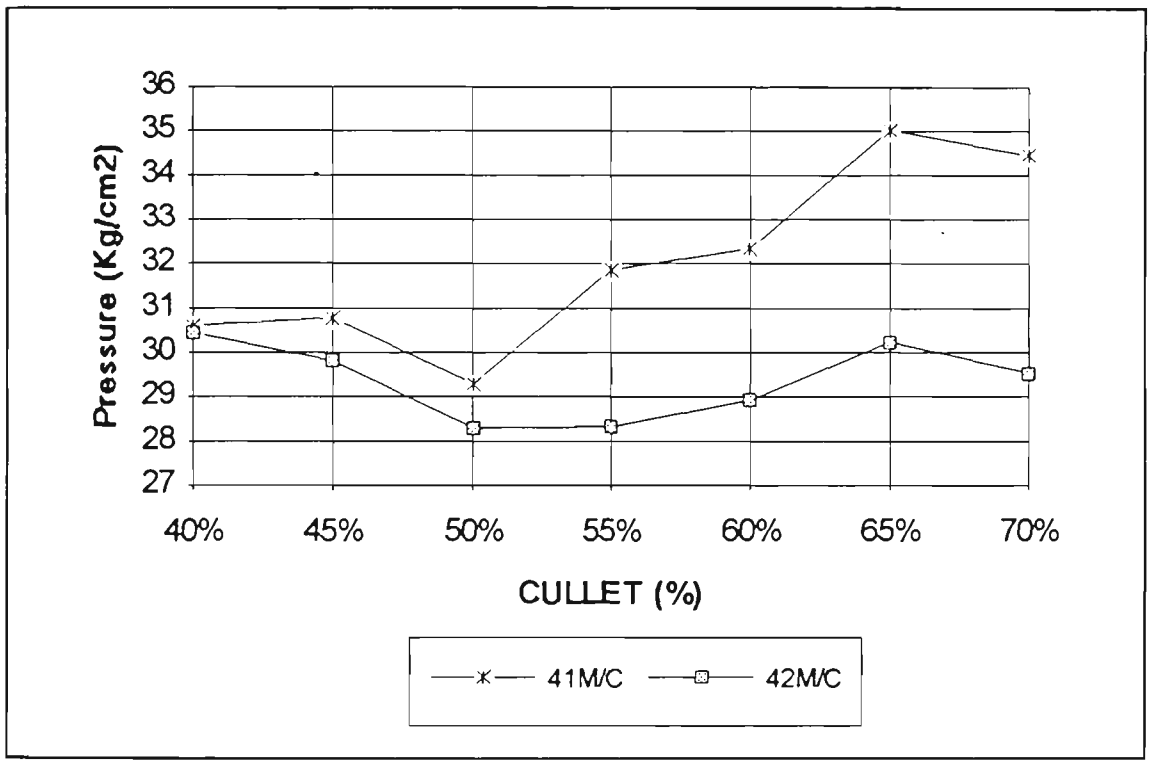

Figure 50. 41m/c & 42m/c breaking pressure Vs cullet

Figures 51 and 52 show the individual machine breaking pressure values and variance. 41 machine shows an overall increase in average pressures for 60%, 65% & 70% cullet over 40%, 45% & 50% cullet, however this was mainly due to the change in job type. 42 machine showed reduced pressures at 50%, 55% and 60% cullet, with a slight improving trend being evident at 60% cullet. Statistical analysis was carried out to compare the mean breaking pressure at 40%, & 45% cullet compared to 65% & 70% cullet. Only 42m/c was analysed because it had the same job running for the entire time of the study. The critical F-value was 3.92 at 0.05 significance level and statistical analysis revealed 2.2, indicating that there was no significant difference in mean breaking pressure between these cullet levels. The statistical test procedure is explained in Appendix II.

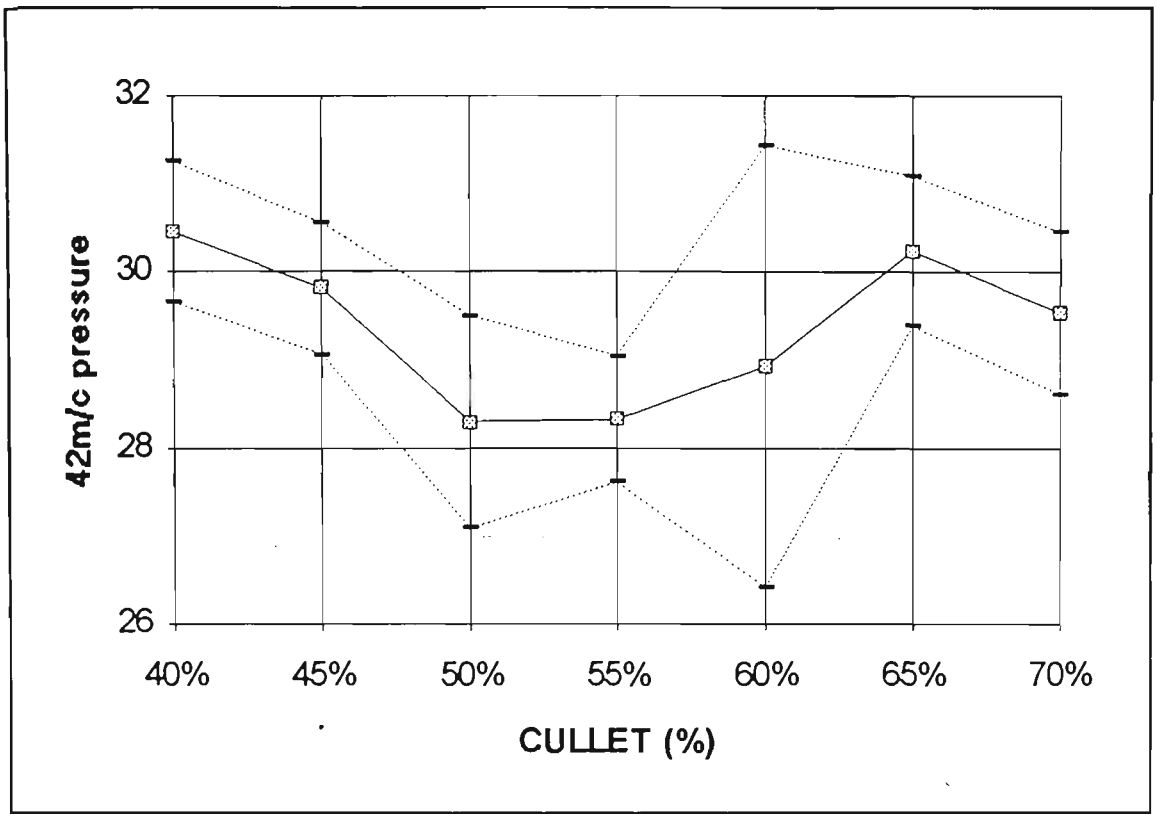

Figure 52. 42m/c breaking pressure & variance Vs cullet

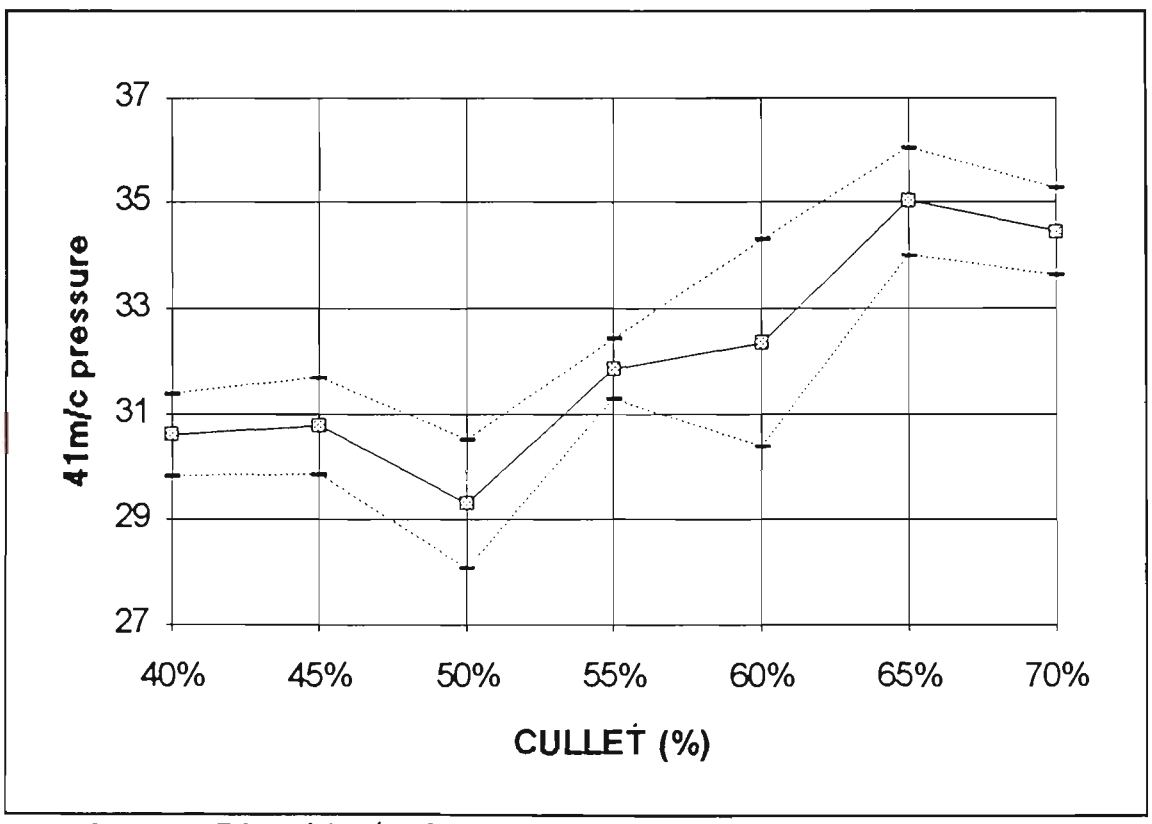

Figure 51. 41m/c breaking pressure & variance Vs cullet

9.0 ANALYSIS - COMMERCIAL VIABILITY

The results from the previous section show that at 70% cullet there was no loss in the commercial viability of the amber product compared with 40% cullet. The results were very much a mirror image of the workability data. As workability losses went up efficiency and pressures came down, as indicated in Figures 33 & 46. This was to be expected as efficiency and breaking pressure depend on consistent operation of the forming machines. Despite there being two machines involved in the study and several job changes on 41m/c, the resultant data trend for commercial viability on both machines was remarkably similar. This leads to the conclusion, that the common denominator between the two operations was the glass. In particular with the glass, it was the sulphate levels, decreasing with every increase in cullet percent, that brought about reduced performance. After the sulphate levels were increased at 60% cullet, the performance parameters also improved (Figure 53).

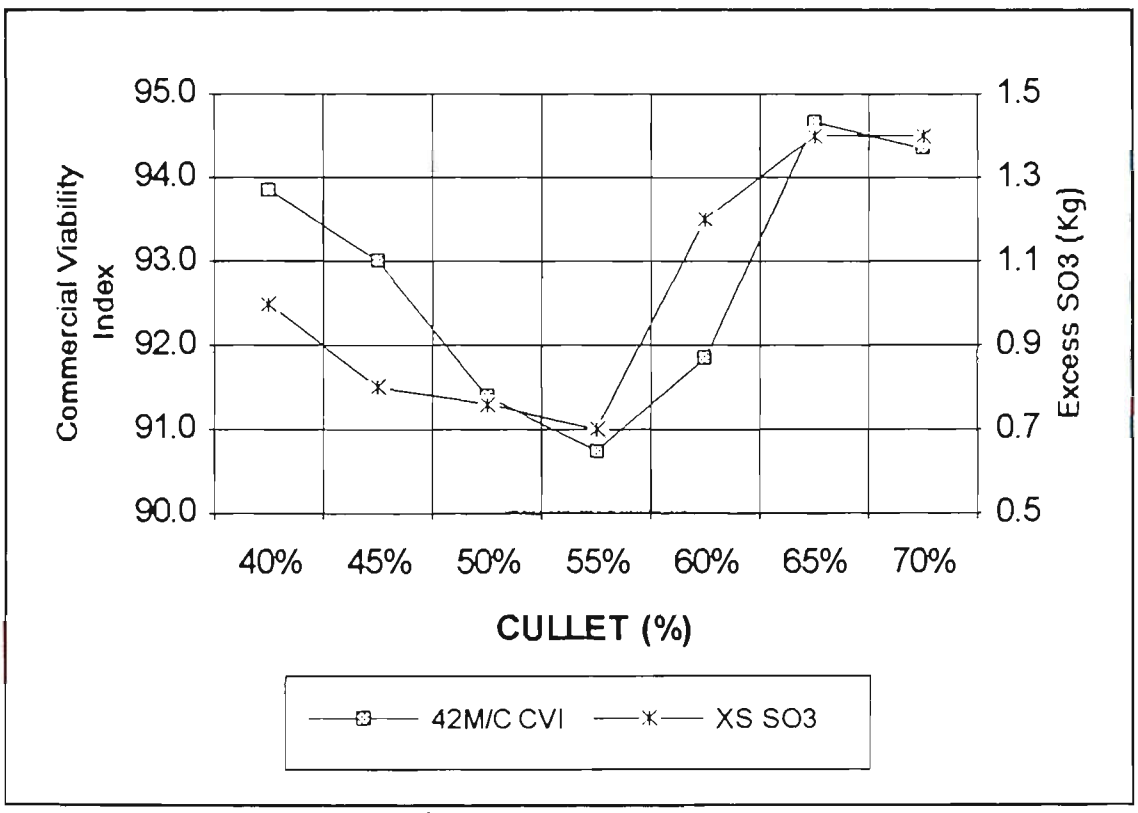

Figure 53. 42m/c CVI & excess SO_3 Vs cullet

Another result that ties in with the workability results was the breaking pressure on 42m/c at 40% cullet. These showed an inverse relation to thin wall defects. High pressures were recorded during the first half of the 40% cullet period, but dropped away significantly as thin wall defects increased (Figure 54).

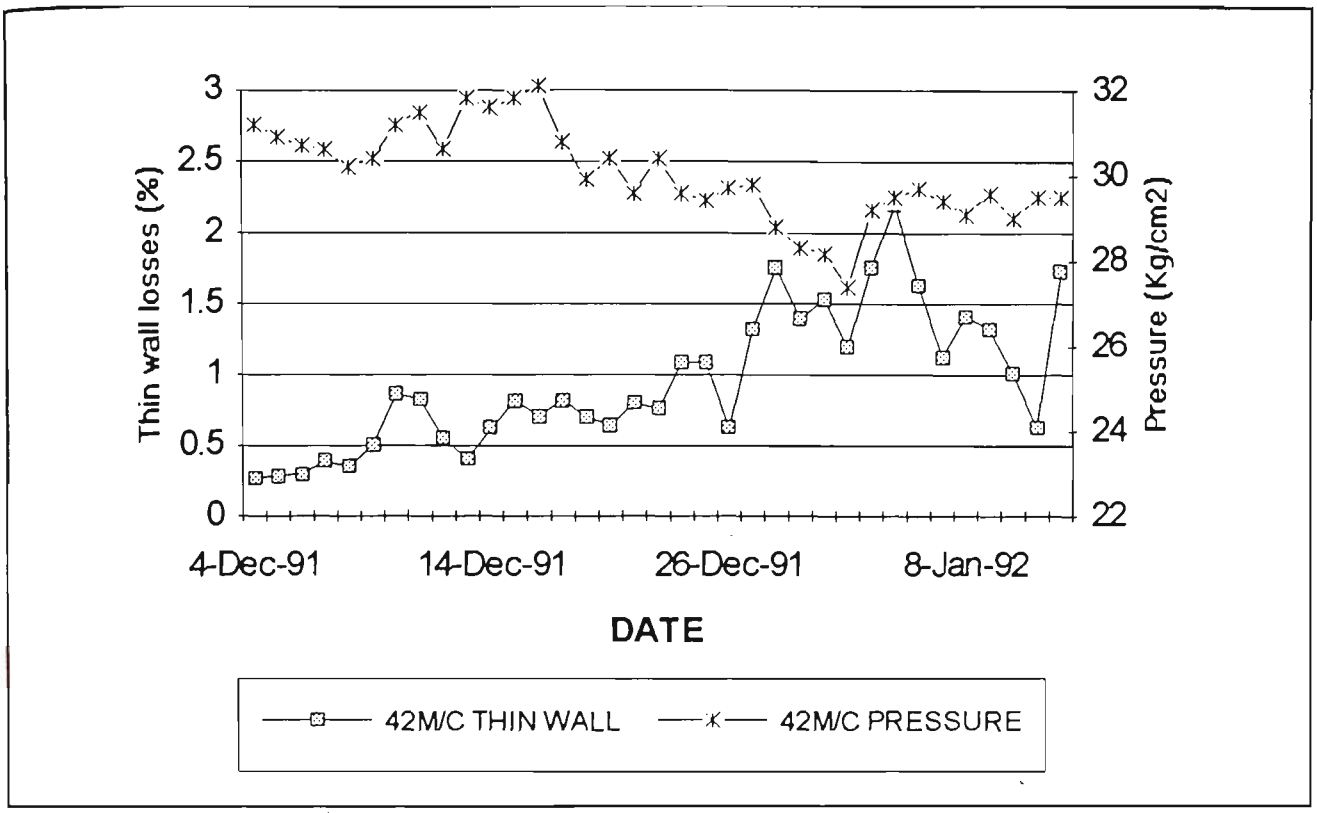

Figure 54. 42m/c thin wall losses & breaking pressure at 40% cullet

The breaking pressure values on 41m/c remained steady throughout the 40% cullet period, indicating that the 42m/c experience was not glass related (Figure 55).

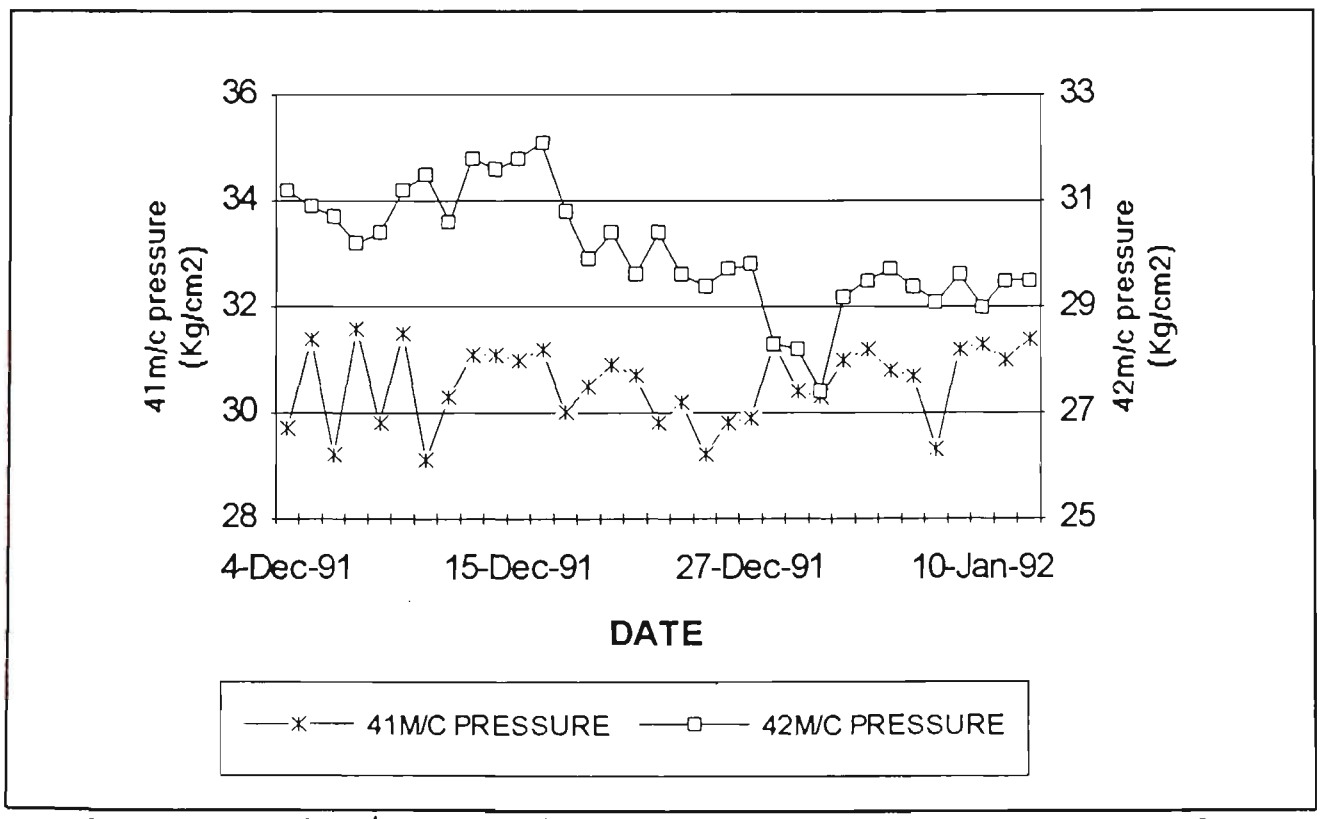

Figure 55. 41m/c & 42m/c breaking pressure at 40% cullet

Breaking pressure values remained stagnant when comparing the values at 40% & 45% cullet with 65% & 70% cullet for 42m/c, but dropped off at cullet levels in between. This was a reflection of the reduced sulphate levels that occurred during the 50%, 55% and 60% cullet levels. Hence, for a specific glass composition, job design and forming machine setup, there is no significant difference in breaking pressure performance at cullet levels to 70%, so long as adequate batch sulphate levels are used to maintain glass homogeneity. The higher breaking pressure values recorded for 41m/c show how job design affects these values.

Job efficiency was good throughout the whole study, however 42m/c showed a significant 2% improvement from the latter half of the 60% cullet period and through 65% and 70% cullet. As was discussed in the workability analysis, the improvement on 42m/c followed a two day maintenance period. However, the author maintains that the improvement was due significantly, to increased sulphate levels that were instigated during the first half of the 60% cullet period. This is because 41m/c also exhibited improved efficiency exhibiting a similar trend to 42m/c. Figure 56 shows the efficiency of both machines during a period where 41m/c was running a mid neck beer, the batch sulphate levels were being increased and 42m/c maintenance was carried out. From this graph it appears that both machines were showing signs of improved efficiencies before the maintenance period occurred on 42m/c.

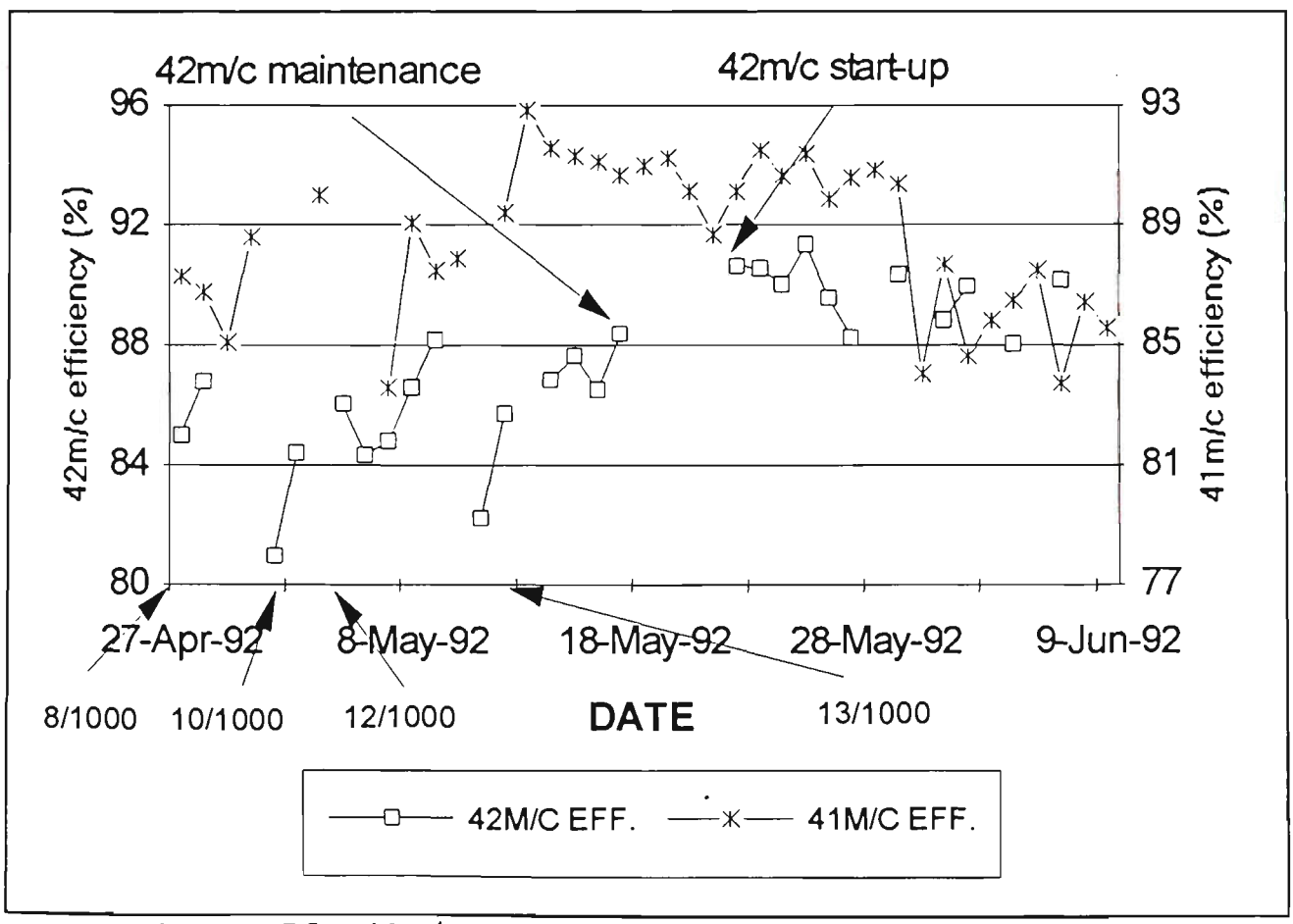

Figure 56. 41m/c & 42m/c efficiency at 60% cullet

In conclusion on commercial viability, it follows that:

1. Commercial viability of the job was not affected by cullet level when adequate batch sulphate levels were maintained;

2. Container breaking pressure was effected more by bottle design than cullet level;

3. Commercial viability of the job improved at 65% and 70% cullet after sulphate levels had been increased in the batch, at 60% cullet.

10. DISCUSSION ON SULPHATE REACTIONS

Throughout the previous analysis it has become evident that the change in sulphate levels at 60% cullet had a significant benefit on the final product quality. The basic function of sulphate in the batch and possible reasons for the change in performance are discussed in this section.

Sodium sulphate is one of the most common refining agents used in soda-lime glasses and is used commonly throughout ACI. Its aid to the glass melting process has three stages [21]:

1. At approximately 1000°C, sodium sulphate is a liquid and is almost completely insoluble in the glass. It collects at the melt-solid or melt-gas interface and acts as a surfactant. This allows the dissolution of solid batch particles to proceed at an increased rate.

2. At approximately 1300°C, thermal decomposition occurs, breaking down the interfacial barriers. Transfer of the reaction products into the glass melt occurs (Equation 4).

$$Na_2SO_4(l) + nSiO_2(l) \rightharpoonup Na_2O.nSiO_2(l) + SO_2(g) + \frac{1}{2}O_2(g) \qquad (4)$$

The transfer of materials upsets the interfacial tension between the two liquid phases, causing release of energy that results in vigorous mixing.

3. At approximately 1450°C, the gaseous reaction products of Equation (4) reach atmospheric pressure, resulting in the vigorous development of bubbles. These bubbles serve a homogenising function as they transfer soda from a high concentration area to the melt surface, where a silica rich layer exists.

Sodium sulphate is also dissolved into the melt according to Equation 5:

$$Na_2SO_4(l) + 2C(s) \rightharpoonup Na_2S(l) + 2CO_2(g) \qquad (5)$$

A proportion of the sulphide formed is retained in amber glass and combines with ferric iron to form an amber chromophore. The main function of the sodium sulphate however, is to aid the dissolution of silica and create mixing between the batch components.

After the melting reactions have taken place, there is an amount of retained sulphur in the form of SO_3 and S^{2-}. In amber glass, this is generally around 0.08% of the glass weight. It is possible that during the conditioning period, as the glass flows

to the machines, the reactions according to Equations (1), (2) and (3) will take place and cause blister. According to Volf [18], the "internal reaction" (Equation (3)), is a particular phenomenon of amber glasses at the point of contact of glass streams that are not homogenous. This supports the argument that the glass was poorly mixed (prior to the sulphate being increased at 60% cullet) and this internal reaction was occurring to form blisters.

Another phenomenon that can occur when sulphate refining is employed is sulphate foam. Sodium sulphate has limited solubility in the glass melt and under the right conditions it will separate and flow onto the glass surface. There are two mechanisms available for foam formation:

1. The foam formation can occur when the equilibrium of Equation (4) is forced to the left by decreasing temperature, decreasing SiO_2 content or increasing SO_2 or O_2 content in the furnace atmosphere[18].

2. Na_2SO_4 and $CaCO_3$ form an eutectic at 780°C and this forms a strong bond preventing separation of Na_2SO_4 at higher temperatures. However, if the CaO content is low, the likelihood of foam occurring will also increase.

The occurrence of foam is a problem as it creates crystallisation centres in the glass, through the absorption of sodium silicate fluxes, CaO and MgO. Crystallisation centres occur in the area of contact between streams of various composition, according to, for example, Equation (6).

$$(CaO.nSiO_2) + Na_2SO_4 \rightharpoonup CaSO_4 + (Na_2O.nSiO_2) \qquad (6)$$

This results in a glass exhibiting increased "fragility and breakability", which is of significant concern in container production [18].

This raises two questions:

1. Firstly, concerning the formation of foam. Was it possible that during the pre 60% cullet period there were a set of conditions that created excessive sulphate foam? Manring and Conroy's [1] classical experiments with cullet show that melting times did not continue to decrease as the cullet percent was increased because the soda ash was preferentially reacting with the cullet rather than the silica. Despite the fact that sodium sulphate is mostly insoluble in the glass melt, it does seem feasible that the cullet is interfering with the sulphate reaction. One scenario is that at high cullet levels, the cullet melts before the sulphate decomposition temperature is reached and surrounds much of the silica, separating it from the sodium sulphate and

preventing the vigorous mixing reaction. The sulphate, in contact with the cullet, forms a sulphate foam.

2. Secondly, assuming that the formation of excessive foam was taking place, consider the formation of crystalline centres. When the raw material change was made from magnesite to dolomite (during the 40% cullet period), did the composition of the dolomite allow it to be preferentially absorbed into the sulphate foam, thus creating a further crystalline centre and hence the increase in thin wall defects and reduction in breaking pressure after that time? By increasing the sulphate level at 60% cullet, sufficient excess sulphate was added to provide adequate mixing and to improve the homogeneity of the glass, but perhaps a degree of sulphate foam is still occurring, limiting the improvement in thin wall defects. This requires further investigation.

Whatever the particular mechanism that results in additional saltcake being required, this study shows that a practical solution to the problem can be found. The decomposition reaction (Equation (4)), supports the traditional batch sulphate addition method, of "x" Kg of sulphate per 1000 Kg of sand ("x" varying from 4 to 12 depending on the type of glass). However, it was found that adequate refining was only achieved by maintaining a minimum of 1.2 Kg of excess SO_3 per 1000 Kg of glass.

11.0 SUMMARY & CONCLUSION

This study was conducted to observe the effects that higher cullet levels have on the final amber glass product. Cullet levels from 40% to 70% were investigated at 5% intervals. It stemmed from two reasons, the first that glass recycling rates are currently around 60% and likely to increase, and secondly that on previous occasions when 60% cullet had been run in amber glass at AGM Spotswood, there was a feeling amongst the forming specialists that the glass became brittle and hard to form. This investigation took into account three variables: glass quality, glass workability and commercial viability.

Glass quality is the essential building block for consistent forming characteristics. The five aspects of glass quality investigated were, composition stability, seed levels, stone counts, blister levels, colour measurement stability at 550nm and O-B amber stability criteria. This study found that in all areas except colour stability at 550nm, there was an improvement at 70% cullet relative to 40% cullet. All facets of glass quality could be maintained within ACI divisional quality specifications at 70% cullet. Two findings in particular were important.

1. The target glass composition could be maintained to + and - 0.13% of all major oxides at 70% cullet, and

2. A change in the batch sulphate determination was required when higher cullet percentages were used to maintain a minimum amount of excess SO_3 per tonne of glass.

Glass workability was assessed using three sub-variables: The percent of ware lost to checks(glass hardness), thin walls(glass homogeneity) and cavity related faults. For checks and cavity related faults, the percent losses were less at 70% cullet compared to 40% cullet for both 41m/c and 42m/c. Thin wall losses on 42m/c were unchanged at 70% cullet compared to 40% cullet. Two major findings resulted:

1. As the cullet level was increased from 40% to 60%, the forming losses increased. At 60% cullet the batch sulphate levels were increased significantly to maintain a minimum excess amount of SO_3 and following this, workability losses were reduced on both forming machines as the cullet was further increased to 70%. The increased sulphate in the batch served to better refine the glass, to provide more mixing between the cullet and batch ingredients and to reduce the sulphate foam formation. Hence, one concludes that the glass "hardness and brittleness" referred to by the forming specialists was related to excessive sulphate foam formation and a slightly inhomogenious glass. Furnaces containing boost or bubblers may not experience this to the same degree.

2. In this study, 42m/c - a ten section quad -, ran the same job all the time. 41 machine - a ten section triple -,had five job changes with three different types of jobs. Despite the differences between machines and jobs, the overall trend of the workability losses were similar on both machines. This leads to the conclusion that the glass viscosity characteristics have an overriding effect on the forming operation.

Commercial viability of the job was assessed by considering job efficiency and breaking pressure of the container. 42 machine showed a 2% improvement in job efficiency at 70% cullet compared to 40% cullet. 41 machine showed a similar trend despite running five different jobs during this time. Breaking pressure on 42m/c was unchanged at 70% cullet compared to 40% cullet. Breaking pressure was related to the percent of thin wall losses and the job design. Overall, the commercial viability of the job on both machines was better at 70% cullet compared to 40% cullet.

Under plant conditions there are many changes that take place to the forming operation in a nine-month period. They include daily machine timing changes, mechanical parts upgrades, job changes, blank and mould changes and alterations in refiner and forehearth operation. There are also changes in the batch and furnace area. Different raw materials are used and operating parameters are altered in the furnace. Despite the number of variables, it was shown in this study that glass forming characteristics had an overriding effect on the workability and commercial viability of the container produced. In this study an improvement in glass quality, workability and commercial viability was achieved using 70% cullet relative to 40% cullet, after a minimum glass excess SO_3 level was introduced to the batch formulation.

12.0 RECOMMENDATIONS

There are three major recommendations for further study:

1. On a commercial scale similar to the situation in this study, continue to increase the cullet level in amber glass to 100%. The three areas of investigation should be continued. The purpose of this recommendation is to check that by maintaining adequate sulphate levels, the final glass product quality, workability and commercial viability do not suffer.

2. To investigate an optimum sulphate level for amber glass running high cullet levels. A similar assessment of glass quality, workability and commercial viability (as in this study) could be used.

3. The statistical method should be refined to develop a standard glass industry procedure. This would be useful to determine optimum glass compositions for particular ware and forming machine combinations.

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APPENDIX I

GLASS VISCOSITY-TEMPERATURE RELATIONSHIP

All commercial soda-lime glasses exhibit the same type of viscosity temperature relationship. Only the rate of change of viscosity and the particular temperature at which a given viscosity occurs, differs. It is this "cooling rate" and the "working" viscosity range of the glass that affect the glass container forming operation. Figure 57 shows a typical temperature-viscosity curve for soda lime glass. The working range of the glass for container glass is:

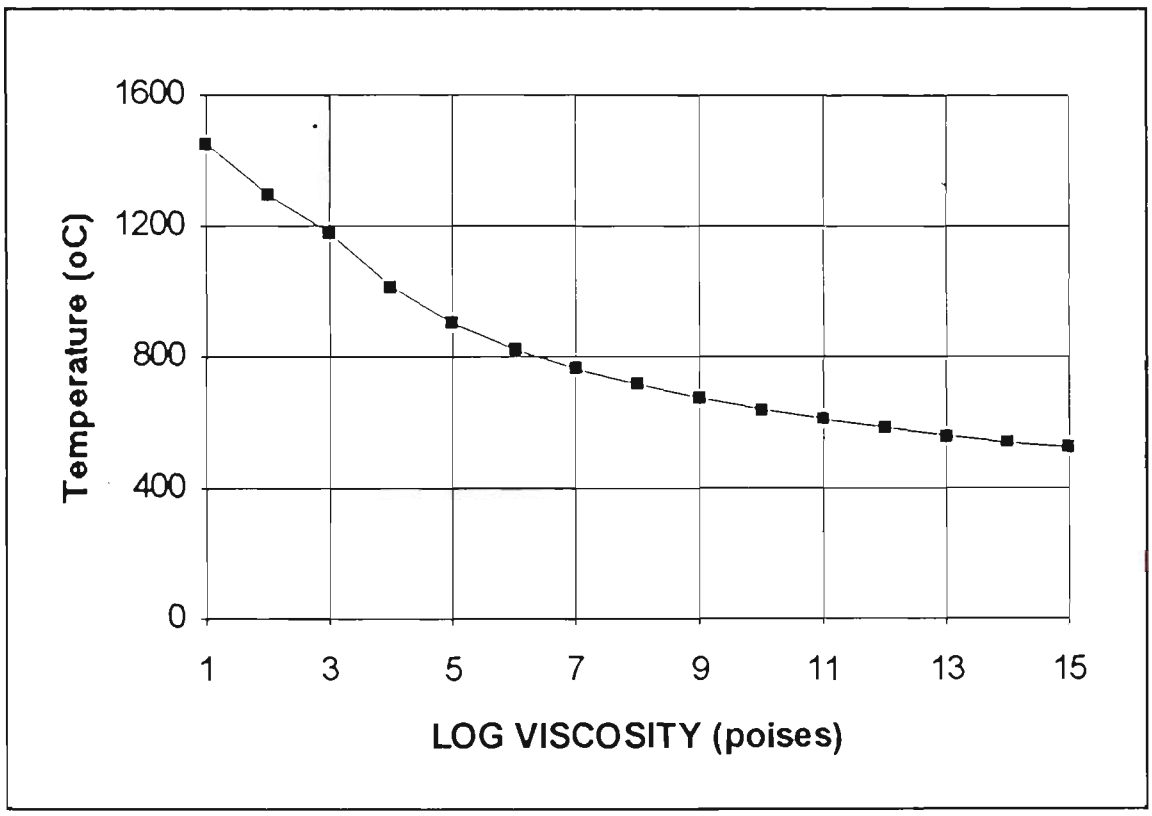


Figure 57. Temperature Vs Log viscosity for commercial soda-lime-silica glass

log viscosity = 3 (beginning of the forming range) and
log viscosity = 7 (end of forming operation).

For a given glass composition there is a different rate of cooling between these two viscosity limits, referred to as the cooling time. Although other factors such as container wall thickness, bottle design and mould cooling wind affect machine production rate, the cooling time data represents the potential ability of the glass to "set-up" during the forming operation.

In the forming process, non-equilibrium temperature conditions exist. Hence the viscosity values given in any data are only one part of a sample of glass. However, viscosity data used as a comparison between glass of different compositions is quite useful. The general operating points and corresponding viscosities are shown in Table 11. By comparing glass viscosity characteristics it is possible to designate fast setting and slow setting glasses. The rate at which the glass sets is very much dependant on the glass composition and not necessarily on the temperature difference between log viscosity 3 to log viscosity 7. The change in glass density, viscosity temperatures and cooling times are compared at different compositions in Table 12. Also the predicted glass density at each cullet level, using the actual glass compositions from this study are shown in Figure 58. It is seen that in all but one case the predicted density falls within the standard deviation of the actual density.

Table 11. General glass viscosity and operational ranges.

Manufacturing Process	Log Viscosity Range(ç)	Log viscosity points (ç)
Melting & Refining	1.7-2.0	2.0
Glass flow in furnace	2.0-2.5	2.5
Forming & after-working	2.5-8.0	forming 3.0
		working 4.0
		softening 7.6
Annealing & Tempering	12-15	Annealing 13
		Strain point 14.5

Another important parameter in the glass viscosity characteristics is the liquidus temperature. This is the temperature at which glass will devitrify (form a crystal structure)if cooled slowly enough: It is important that the forming temperature be sufficiently above the liquidus temperature to ensure devitrification does not occur. Devitrification may occur in cooler areas of a refiner or forehearth.

In summary, the following points relate to forming and viscosity:

1. The difference between the log3 and log7 temperatures,
2. The rate of heat removal between log3 and log7,
3. The difference between the log3 and liquidus temperature.

Table 12. Glass physical properties

Oxide	Composition change			
	Target	+0.1% CaO	+0.1% NaO	+0.1% SiO2
	Percent			
Na2O	13.9	13.9	14	13.85
CaO	11.5	11.6	11.5	11.45
Al2O3	1.4	1.4	1.4	1.4
Fe2O3	0.3	0.3	0.3	0.3
TiO2	0	0	0	0
Cr2O3	0	0	0	0
MgO	0.5	0.5	0.5	0.5
K2O	0.4	0.4	0.4	0.4
Li20	0	0	0	0
SiO2+Gas	72	71.9	71.9	72.1
Total %	100	100	100	100
	degrees celcius			
LOG 2	1424.6	1422.4	1421.9	1427.0
LOG 3	1171.1	1169.8	1169.1	1172.8
LOG 3.6	1067.5	1066.4	1065.6	1068.9
LOG 7	758.9	758.7	757.7	759.6
LOG 7.65	726.3	726.3	725.3	726.8
LOG 13.4	553.7	553.9	553.0	553.8
	seconds			
Cooling time	98.5	98.3	98.7	98.5
	tonnes/m3			
Density	2.5116	2.5126	2.5122	2.5107
	tonnes/m3			
Density diff.	0.0000	0.0011	0.0006	-0.0008
Note: When SiO2 was increased by 0.1%, both CaO & NaO decreased by 0.05%				

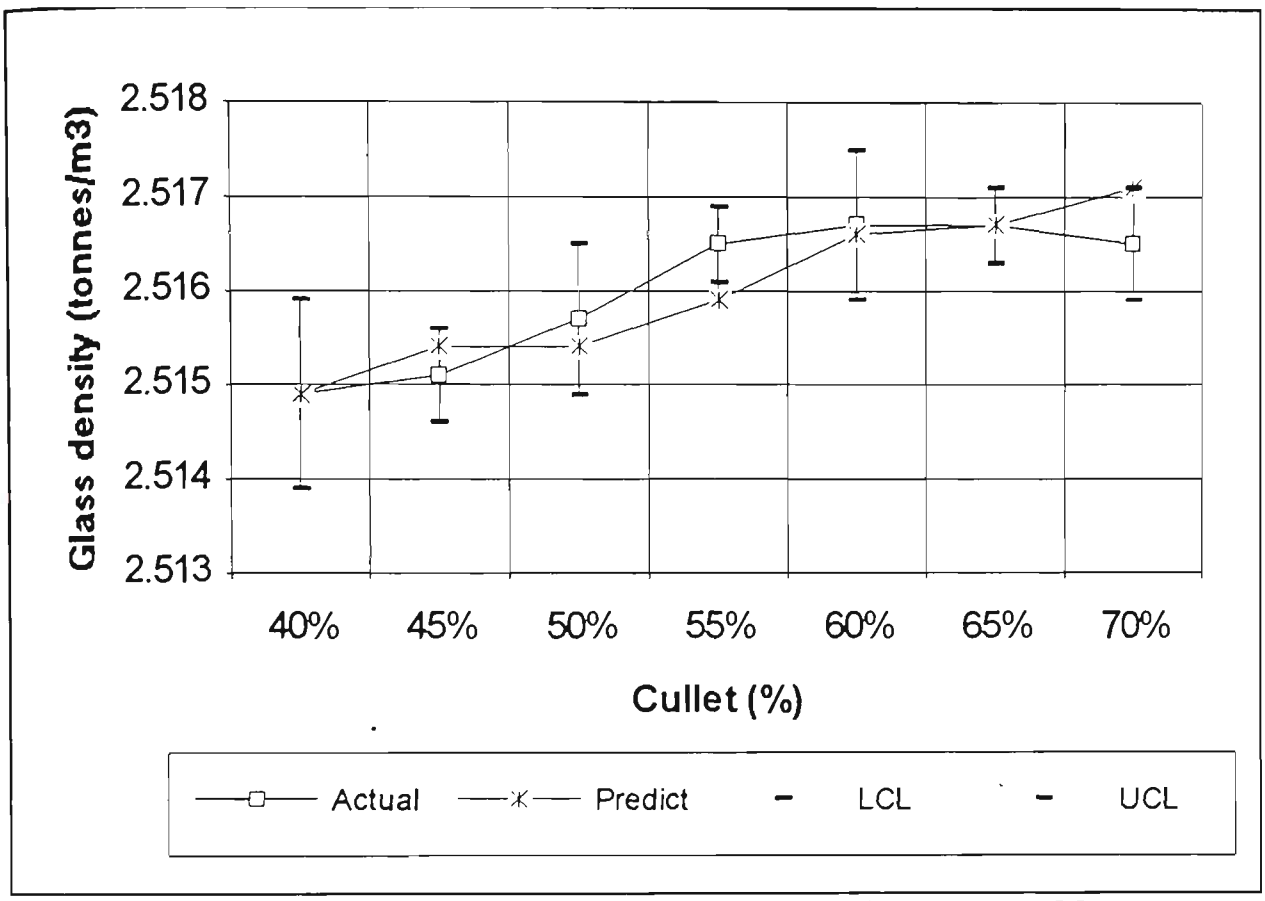


Figure 58. Predicted & actual density Vs cullet

APPENDIX II

STATISTICAL ANALYSIS

The statistical analysis used to analyse the data of this study was based on the assumption that the data followed a normal distribution. This is supported by the central limit theorem [20], which states that for large samples, the sampling distribution of the mean can be approximated closely with a normal distribution. Freund [20] also states that unless the distribution has a very unusual shape a sample size of 30 is considered large. The continuous distribution function is shown below for the data gathered on 42m/c. The charts show the frequency distribution and cumulative distribution. All the data exhibits a reasonable approximation to the characteristic bell shaped distribution with differing amounts of skewness. The skewed "tail" of the distribution is due to the presence of some relatively high or low value data. A measure of this is the Pearsonian coefficient of skewness (SK).

$$SK = \frac{3\,(mean - median)}{standard\ deviation} \qquad (7)$$

For the normal distribution assumption to be valid the value of SK should lie within + and - 3 [20]. The value of SK for each set of data from 42m/c is shown on the corresponding distribution chart. For all the analysed data in this study, the above criteria were met to assume a close approximation to the normal distribution. The data graphed in Figures 59 to 65 represents values at all cullet percentages.

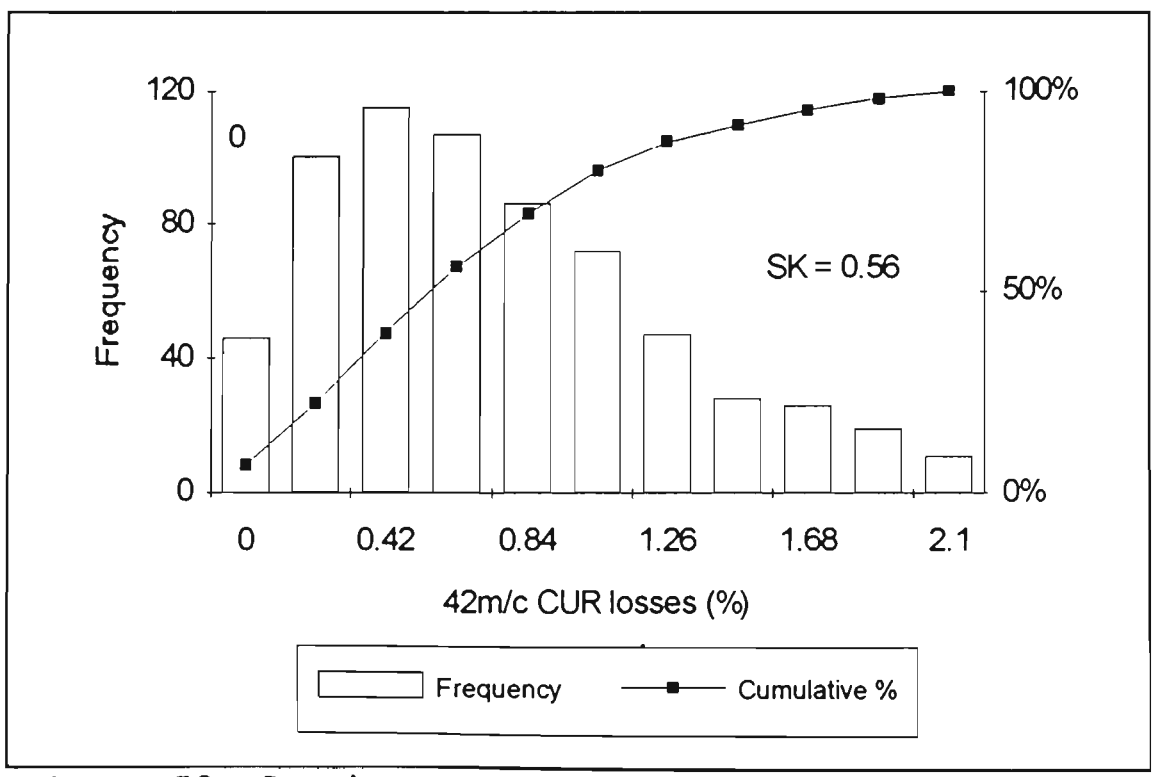


Figure 59. Continuous distribution, 42m/c CUR losses

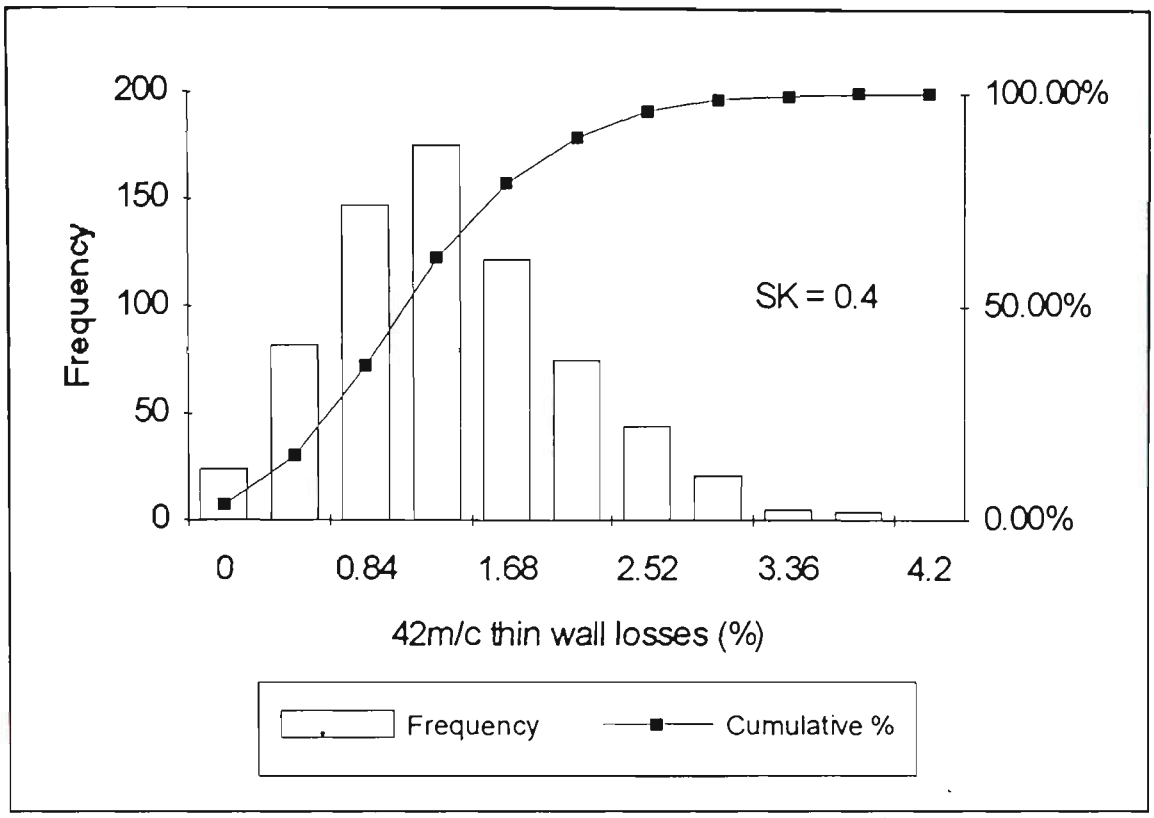


Figure 60. Continuous distribution, 42m/c thin wall losses

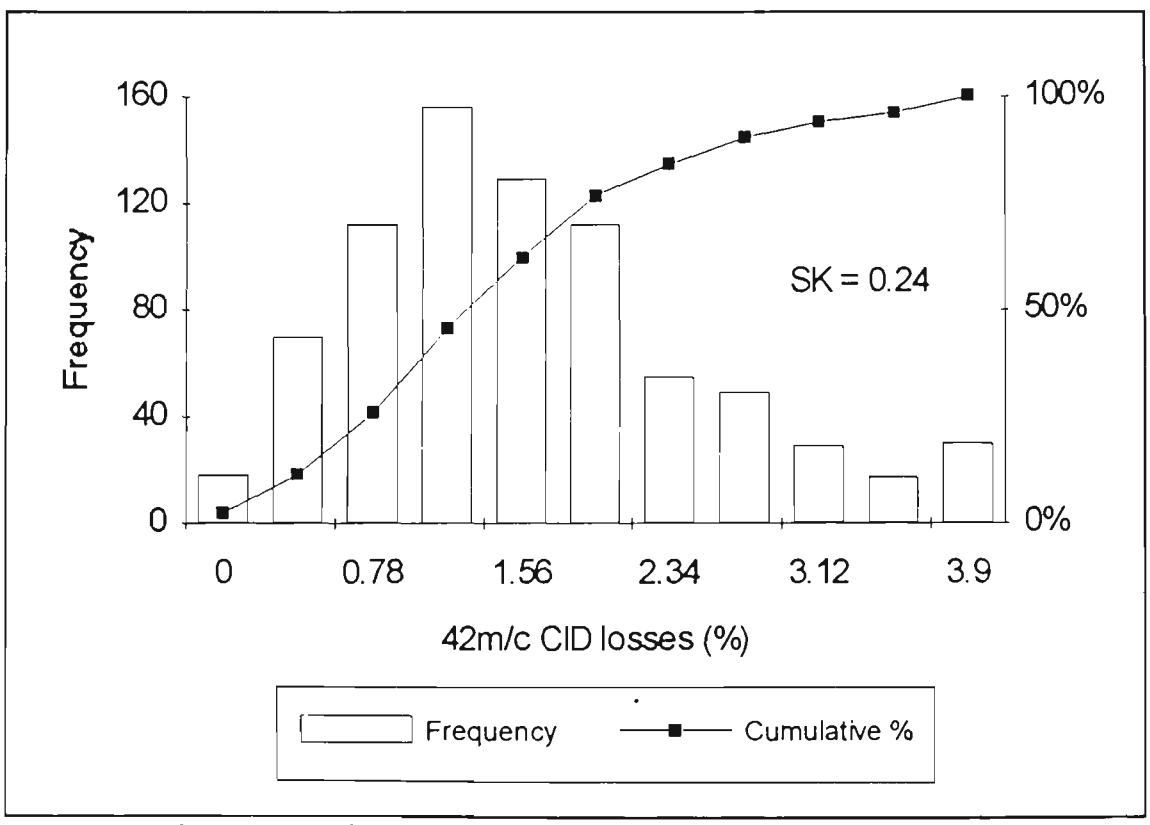


Figure 61. Continuous distribution, 42m/c CID losses

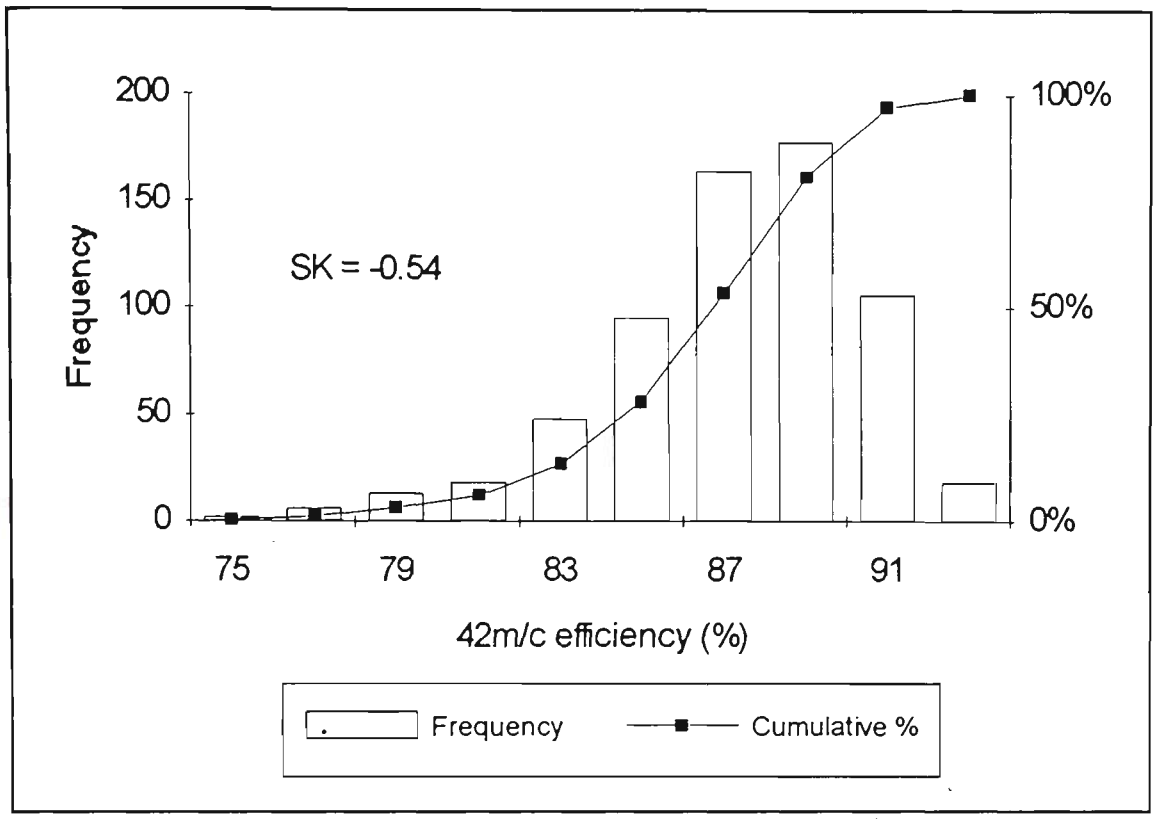


Figure 62. Continuous distribution, 42m/c efficiency

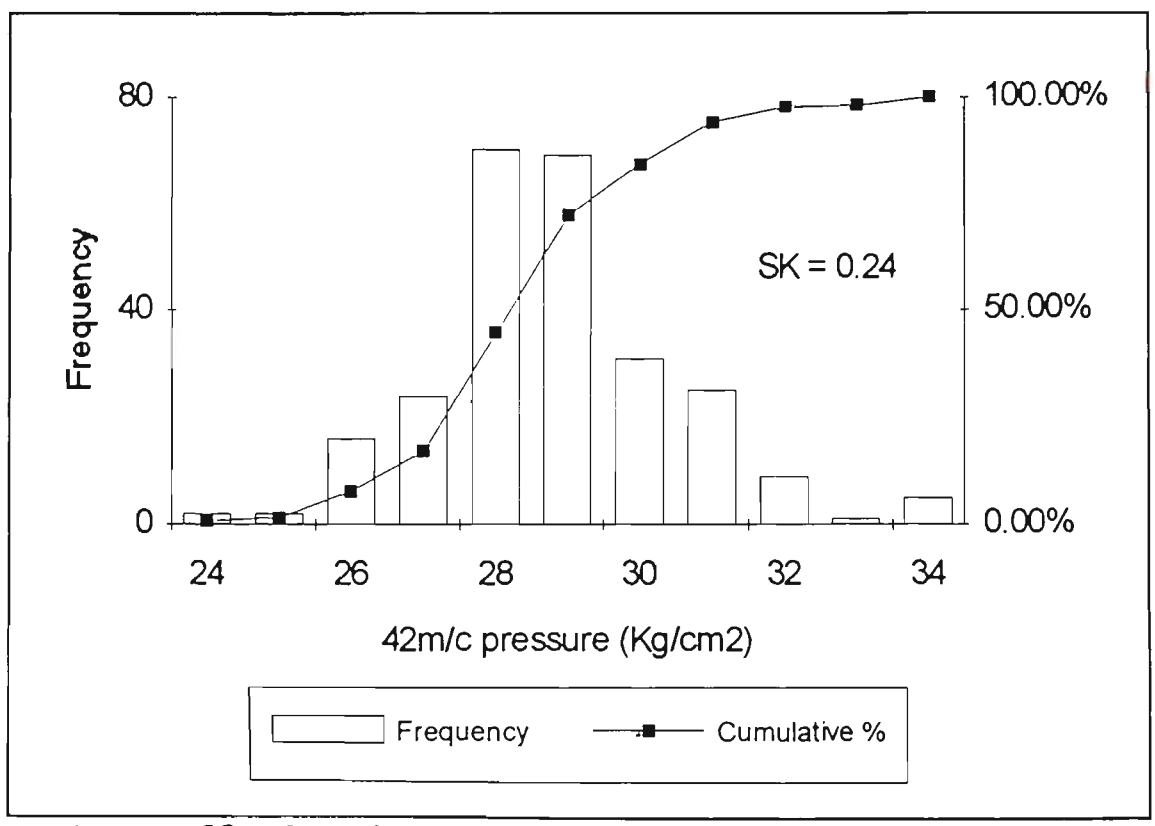


Figure 63. Continuous distribution, 42m/c breaking pressure

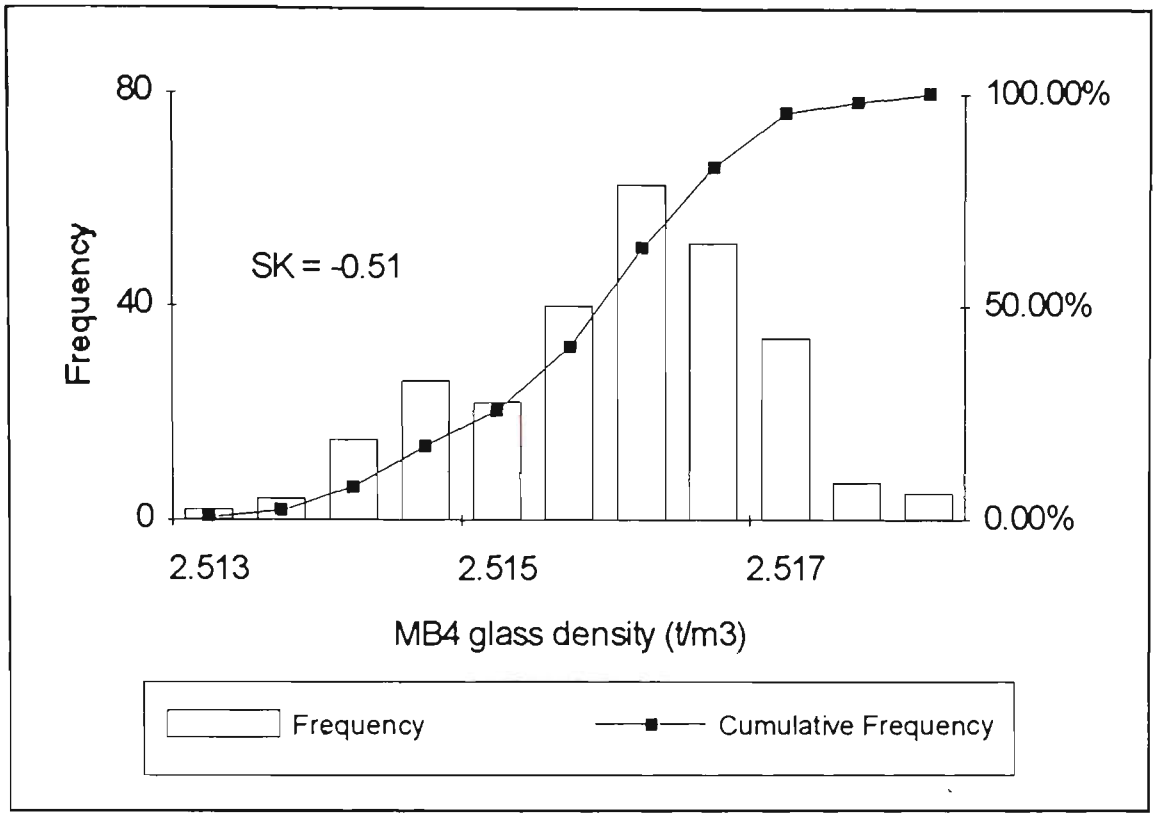


Figure 64. Continuous distribution, MB4 density

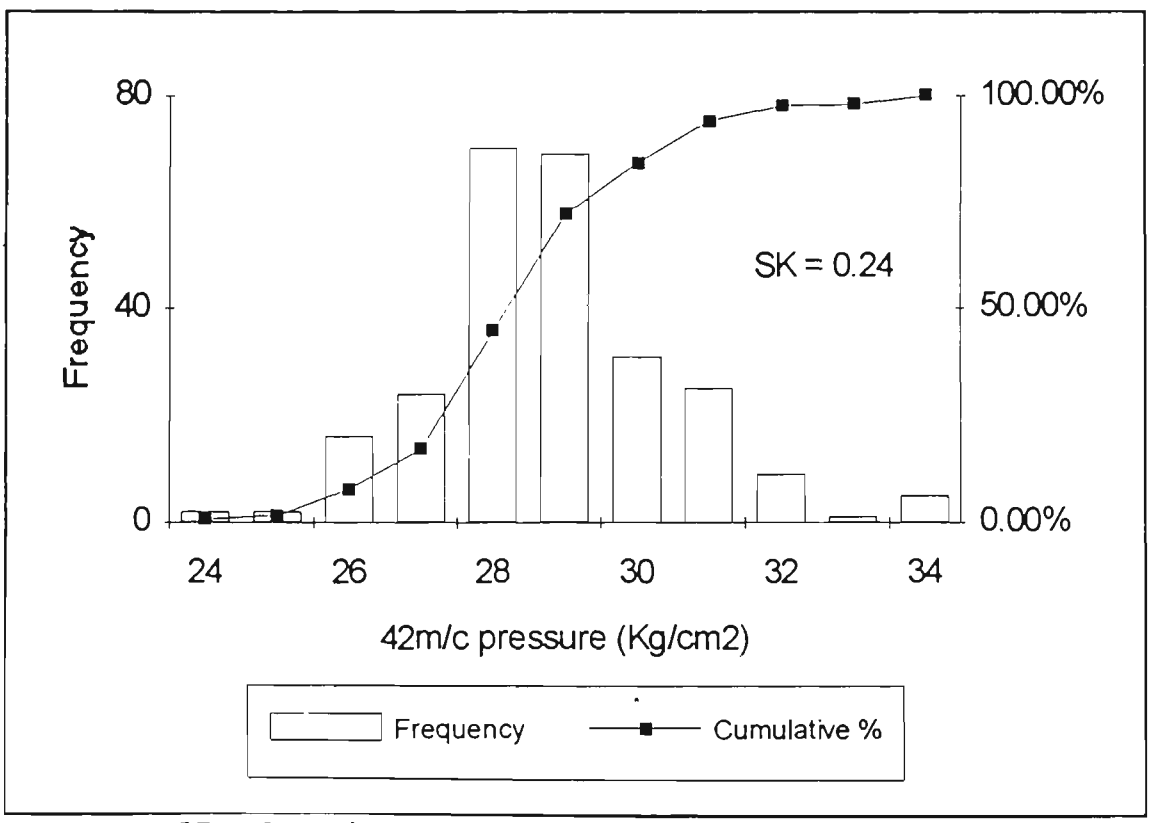


Figure 65. Continuous distribution, 42m/c SID losses

DATA ANALYSIS - CONTROL CHARTS

The experimental work carried out was controlled in the following way. It was assumed that furnace operating parameters, forehearth operating parameters and daily forming machine adjustments would be randomised [23]. In other words, these operating parameters would fall within the "normal" bounds of operation. In that way cullet adjustments would be the major factor effecting bottle quality, workability and commercial viability. However there was another significant effect on bottle quality and that was the breakdowns of forming machine.

These effects were removed in the following way:

1. The raw data for a particular bottle fault was plotted out in a control chart format for each cullet percentage. The data was an average of 8 hours production (eight hours = one shift). The data was taken from the daily production information computer (PIC) sheets. An example of the PIC data format is shown in Table 13.

2. The control lines were setup using standard control chart theory [23]. The upper control limit (UCL) and the lower control limit (LCL) were given by:

$$UCL = \mu + A3 * \mathfrak{C} \quad (8)$$

$$LCL = \mu - A3 * \mathfrak{C} \quad (9)$$

UCL = upper control limit
LCL = lower control limit
A3 = factor from standard control chart tables
ç = mean value for set of data
$\mathfrak{C}$ = standard deviation of set of data

The raw data set up in control chart format for 42m/c is displayed in Appendix IV.

3. Once the control chart was set-up any data points that were outside the control limits were investigated to determine whether the cause was machine related. The machine related causes for 42m/c are shown in chapter 3. An example of 42m/c CUR losses at 40% cullet in control chart format with machine related faults labelled is shown in Figure 66. Data that was outside the control limits and shown to be machine related was removed from the data set. A new control chart was then plotted with the adjusted data set (Figure 67). This procedure was followed with all parameters monitored.

4. An average and variance value was then taken from the adjusted data set for each cullet level. These values were plotted out, (chapter 4, 6 and 8) and used for further statistical analysis.

Table 13. Example of Production Information Computer print

MB.PIC.42 24 HOUR LINE SUMMARY REPORT 3-JUL-92

42 LINE 2-JUL-92 7:00 AM - 3-JUL-92 7:00 AM

JOB: 15507 375ML.N.R.BEER.CUB.
FINISH: 26-540 COLOR: AMBER

	7:00- 3:00	3:00-11:00	11:00- 7:00	24 HOUR
PRODUCTION PERFORMANCE				
SPEED (BPM)	522.7	522.7	522.7	522.7
EFFCY (%)	90.4	90.5	90.8	90.5
PACKED (BTL)	226712	226979	227755	681446
LOSS (BTL)	24172	23901	23129	71202
LINE RATINGS				
MANUAL INSP.	0	0	0	0
WORST DEFECTS (%)				
THIN WALL	1.16	1.55	0.98	1.23
CIDI REJECTS	0.77	0.74	0.59	0.70
SPLIT FINISH	0.38	0.47	0.47	0.44
CHECKED FINISH	0.48	0.32	0.21	0.34
SID	0.30	0.36	0.27	0.31
QQC SAMPLES	0.31	0.30	0.31	0.30
LINE OVER FINISH	0.12	0.51	0.13	0.25
CRIZZLED BOTTOM	0.01	0.02	0.35	0.13
NOT MADE UP FINISH	0.07	0.05	0.04	0.05
CHOKED NECK	0.01	0.01	0.02	0.01
CRIZZLED FINGER	0.00	0.00	0.00	0.00
CHECKED BODY	0.00	0.00	0.00	0.00
WORST SECTIONS (%)				
4B	0.10	0.37	0.19	0.22
THIN WALL	0.08	0.29	0.18	0.18
7A	0.07	0.48	0.05	0.20
LINE OVER FINISH	0.00	0.32	0.01	0.11
1A	0.28	0.24	0.08	0.20
THIN WALL	0.28	0.23	0.07	0.19
3B	0.05	0.18	0.29	0.17
THIN WALL	0.04	0.11	0.14	0.10

Figure 66. 42m/c CUR losses at 40% cullet

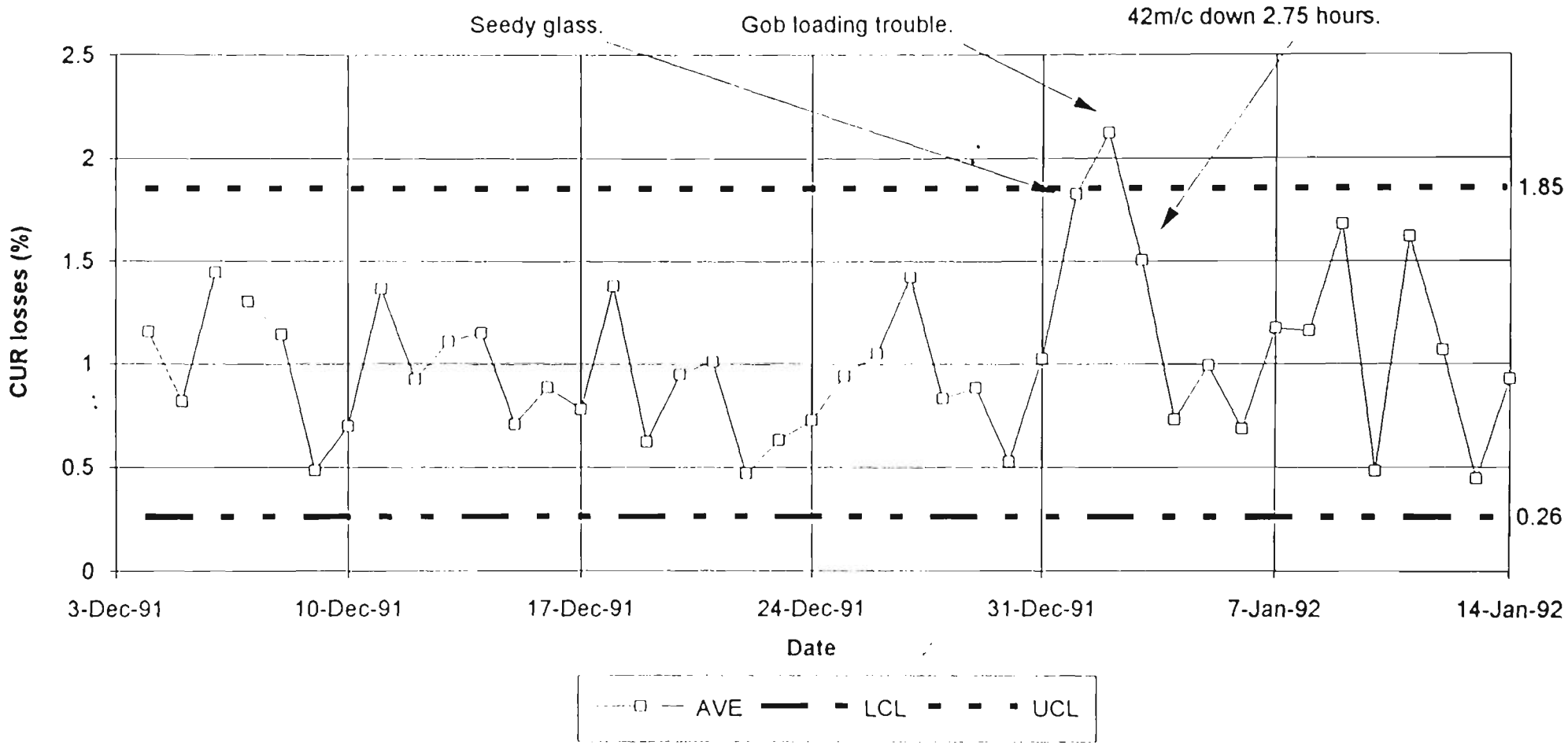
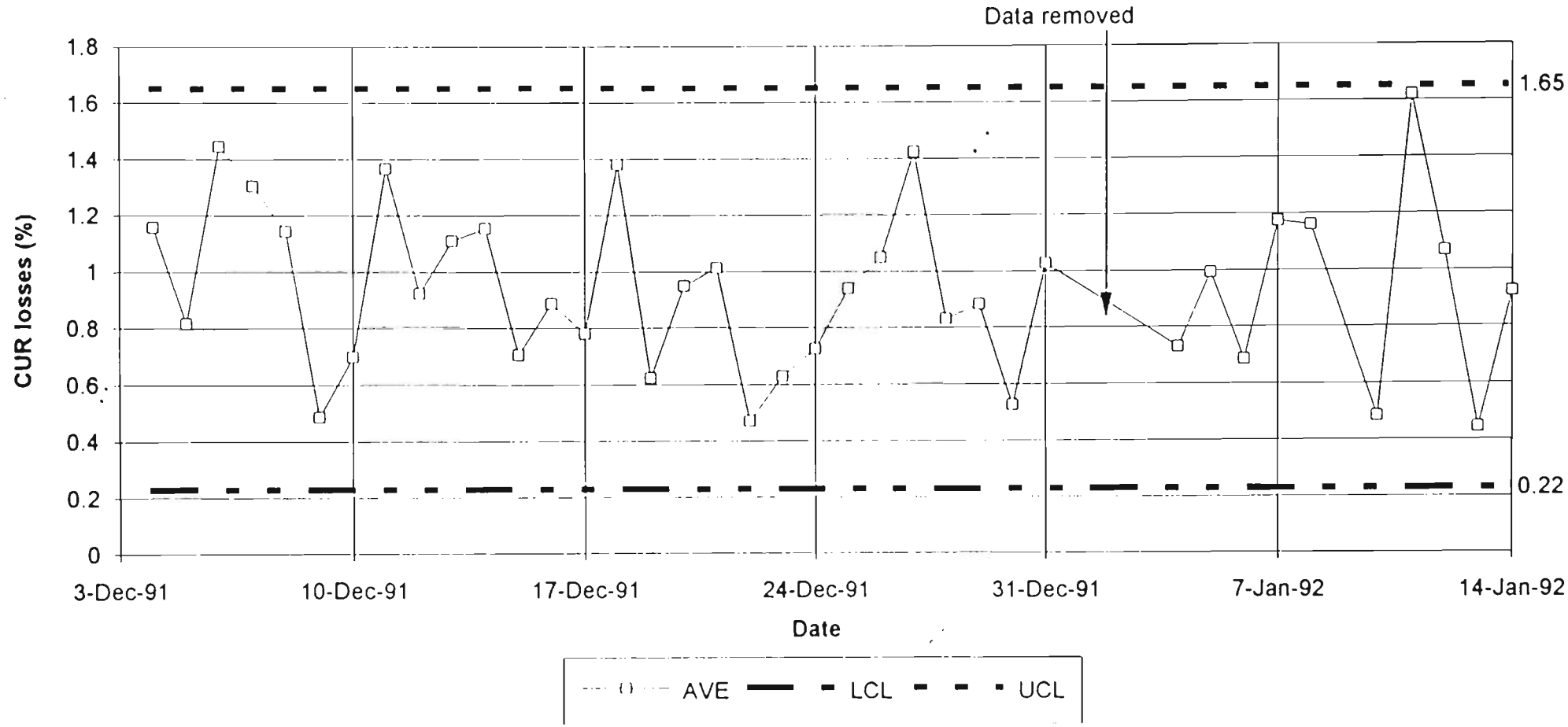


Figure 67. 42m/c (adj.) CUR losses at 40% cullet



ONE WAY ANALYSIS OF VARIANCE

Once the machine related faults had been removed from the data, the main effect on bottle faults was the glass viscosity characteristics and cullet level changes. To determine whether mean loss values at certain cullet levels were significant in comparison to others, the F statistic or variance ratio was used [23]. The F statistic is defined as:

$$F = \frac{(\textit{estimate } \mathfrak{C} \textit{ based on variation among } \mu's)}{(\textit{estimate } \mathfrak{C} \textit{ based on the variation within sample})} \quad (10)$$

If F is large, it can be said that the variation among means is too great to be attributed solely to chance. The critical value of F is based on the criterion of Figure 68. For this work $F_{0.01}$ was used as the critical value and these values are tabulated by Freund [23].

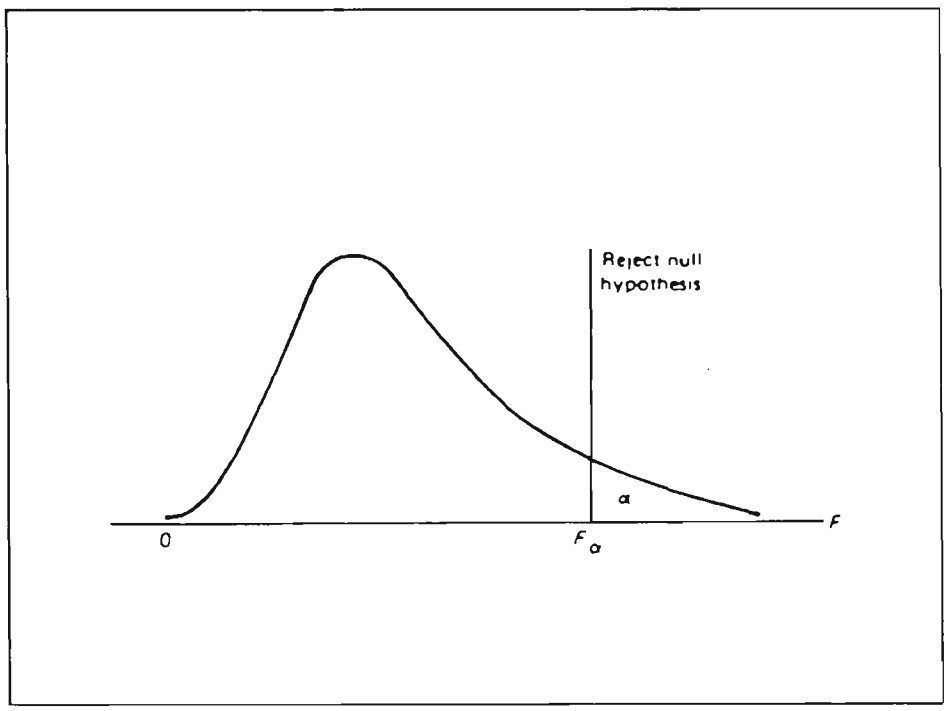


Figure 68. Test criterion for F statistic (Freund [23])

In an analysis of variance the method is to measure the total variation of a set of data as a sum of terms, which can be attributed to specific causes of variation. In this work there were two sources of variation, (1) the difference caused by cullet levels and (2) chance, or experimental error. Hence the total sum

of squares can be expressed as a sum of these two terms as shown below.

$$SST = SS(Tr) + SS(E) \tag{11}$$

SST = total sum of squares
SS(Tr) = treatment sum of squares
SS(E) = error sum of squares

Now the individual terms are calculated as follows: (Freund [20])

$$SST = \sum_{i=1}^{k} \sum_{j=1}^{n_i} x_{ij}^2 - \frac{1}{N} * T_{..}^2 \tag{12}$$

$$SS(Tr) = \sum_{i=1}^{k} \frac{T_i^2}{n_i} - \frac{1}{N} * T_{..}^2 \tag{13}$$

$$SS(E) = SST - SS(Tr) \tag{14}$$

k = the number of data samples
n_i = the number of observations in each sample
x_{ij} = the jth observation of the ith sample,
(i = 1,2,...k and j = 1,2,...n)
T_i = sum of values of the ith treatment
T.. = grand sum of all data
$N = n_1 + n_2 + ... n_k$

If the total sum of squares is divided by the total number of degrees of freedom (N-1), the variance is obtained. Also, the treatment mean square and error mean square are given by:

$$MS(Tr) = \frac{SS(Tr)}{k - 1} \tag{15}$$

MS(Tr) = treatment mean square

$$MS(E) = \frac{SSE}{(N - 1)} \quad (16)$$

MS(E) = error mean square

It follows on from Equation 15 and 16 and the definition of the F statistic, that:

$$F = \frac{MS(Tr)}{MS(E)} \quad (17)$$

Hence the data for the determination of F is displayed in an analysis of variance table similar to Table 14.

A sample calculation follows, showing the calculation comparing the CUR losses on 42m/c at 40%, 45%, 50% and 55% cullet

Table 14. Typical analysis of variance table.

Source of variation	Degrees of freedom	Sum of squares	Mean square	F
Treatment	k-1	SS(Tr)	MS(Tr)	$\frac{MS(Tr)}{MS(E)}$
Error	N-k	SS(E)	MSE	
Total	N-1	SST		

with 60%, 65% and 70% cullet. Included is the raw data values for the shift average CUR losses, the daily average CUR losses and the average CUR losses squared. The data and results are presented in Tables 15 and 16.

Table 15. Raw data and calculated values for 42m/c CUR losses

DATE	DAY SHIFT	AFTERNOON SHIFT	NIGHT SHIFT	AVERAGE	X2ij
		40% cullet			
4-Dec-91	1.25	1.35	0.87	1.16	1.34
5-Dec-91	0.6	1.22	0.63	0.82	0.67
6-Dec-91	1.33	1.49	1.52	1.45	2.09
7-Dec-91	1.76	0.68	1.47	1.30	1.70
8-Dec-91	0.75	1.79	0.89	1.14	1.31
9-Dec-91	0.42	0.63	0.41	0.49	0.24
10-Dec-91	0.43	0.71	0.96	0.70	0.49
11-Dec-91	1.86	0.96	1.28	1.37	1.87
12-Dec-91	1.38	0.93	0.46	0.92	0.85
13-Dec-91	1.73	0.72	0.88	1.11	1.23
14-Dec-91	1.47	1.11	0.88	1.15	1.33
15-Dec-91	1.08	0.34	0.7	0.71	0.50
16-Dec-91	0.47	0.29	1.9	0.89	0.79
17-Dec-91	0.69	0.93	0.72	0.78	0.61
18-Dec-91	1.25	0.85	2.04	1.38	1.90
19-Dec-91	0.8	0.66	0.41	0.62	0.39
20-Dec-91	0.53	1.3	1.02	0.95	0.90
21-Dec-91	0.97	0.87	1.2	1.01	1.03
22-Dec-91	0.6	0.51	0.3	0.47	0.22
23-Dec-91	0.56	0.81	0.52	0.63	0.40
24-Dec-91	0.93	0.69	0.56	0.73	0.53
25-Dec-91	0.52	1.17	1.13	0.94	0.88
26-Dec-91	1.12	1.08	0.95	1.05	1.10
27-Dec-91	1.59	1.71	0.97	1.42	2.03
28-Dec-91	1.28	0.82	0.39	0.83	0.69
29-Dec-91	0.95	0.88	0.82	0.88	0.78
30-Dec-91	0.5	0.73	0.35	0.53	0.28
4-Jan-92	0.85	0.61	0.73	0.73	0.53
5-Jan-92	1.2	1.08	0.7	0.99	0.99
6-Jan-92	1.21	0.56	0.29	0.69	0.47
7-Jan-92	1.91	1.33	0.28	1.17	1.38
8-Jan-92	0.49	1	1.99	1.16	1.35
10-Jan-92	0.45	0.8	0.2	0.48	0.23
11-Jan-92	1.49	1.63	1.74	1.62	2.62
12-Jan-92	2.15	0.41	0.64	1.07	1.14
13-Jan-92	0.58	0.38	0.37	0.44	0.20
14-Jan-92	1.17	0.76	0.84	0.92	0.85
		45% cullet			
15-Jan-92	1.26	0.71	0.67	0.88	0.77
16-Jan-92	0.78	1.49	0.77	1.01	1.03
17-Jan-92	1.11	1.16	0.9	1.06	1.12
18-Jan-92	0.49	0.54	0.84	0.62	0.39
19-Jan-92	0.31	0.44	1.09	0.61	0.38
20-Jan-92	0.69	0.47	1.37	0.84	0.71
21-Jan-92	1.75	1.27	0.91	1.31	1.72
22-Jan-92	1.13	1.18	0.73	1.01	1.03
24-Jan-92	1.86	0.82	0.73	1.14	1.29
25-Jan-92	0.54	0.32	0.45	0.44	0.19
26-Jan-92	0.46	0.49	0.29	0.41	0.17
27-Jan-92	0.2	0.53	1.22	0.65	0.42

DATE	DAY SHIFT	AFTERNOON SHIFT	NIGHT SHIFT	AVERAGE	X2ij
		50% cullet			
28-Jan-92	0.85	0.61	0.73	0.73	0.53
29-Jan-92	0.78	0.57	1.37	0.91	0.82
30-Jan-92	1.91	0.63	0.58	1.04	1.08
31-Jan-92	1.22	0.44	0.78	0.81	0.66
1-Feb-92	0.86	1.31	0.77	0.98	0.96
3-Feb-92	1.67	0.95	0.72	1.11	1.24
4-Feb-92	0.71	0.71	1.05	0.82	0.68
5-Feb-92	2.03	1.34	0.84	1.40	1.97
6-Feb-92	1.28	0.59	1.46	1.11	1.23
7-Feb-92	0.72	0.51	0.72	0.65	0.42
8-Feb-92	0.43	0.85	0.63	0.64	0.41
9-Feb-92	0.73	0.96	1.58	1.09	1.19
10-Feb-92	0.6	0.86	1.01	0.82	0.68
11-Feb-92	0.87	0.83	0.84	0.85	0.72
12-Feb-92	0.9	1.42	1.13	1.15	1.32
13-Feb-92	2.16	1.17	0.88	1.40	1.97
14-Feb-92	0.61	1.64	0.51	0.92	0.85
15-Feb-92	1.2	0.5	0.56	0.75	0.57
16-Feb-92	0.27	0.54	0.54	0.45	0.20
18-Feb-92	0.9	0.58	1.6	1.03	1.05
20-Feb-92	0.83	1.41	0.79	1.01	1.02
21-Feb-92	1	1.18	0.92	1.03	1.07
22-Feb-92	1.23	0.94	0.81	0.99	0.99
23-Feb-92	0.86	0.67	1.83	1.12	1.25
24-Feb-92	0.71	0.98	1.01	0.90	0.81
25-Feb-92	0.69	1.17	1.92	1.26	1.59
26-Feb-92	1.62	1.13	0.89	1.21	1.47
27-Feb-92	1.58	1.2	0.57	1.12	1.25
28-Feb-92	1.05	1.75	1.11	1.30	1.70
29-Feb-92	1.16	1.57	0.94	1.22	1.50
1-Mar-92	0.89	1.35	1.24	1.16	1.35
2-Mar-92	0.82	0.83	0	0.55	0.30
5-Mar-92	1.3	1.38	0.82	1.17	1.36
6-Mar-92	1.34	1.09	2.05	1.49	2.23
7-Mar-92	2.17	2.43	1.71	2.10	4.42
8-Mar-92	1.75	1.35	1.65	1.58	2.51
9-Mar-92	0.75	1.17	1.41	1.11	1.23
14-Mar-92	2.01	1.08	1.32	1.47	2.16
15-Mar-92	1.19	1.97	0.94	1.37	1.87
16-Mar-92	0.86	0.39	1.18	0.81	0.66
17-Mar-92	1.85	1.2	1.24	1.43	2.04
19-Mar-92	1.3	1.42	1.41	1.38	1.90
20-Mar-92	0.41	0.94	0.88	0.74	0.55
21-Mar-92	0.68	0.44	0.64	0.59	0.34
22-Mar-92	0.62	1.33	1.99	1.31	1.72
23-Mar-92	1.17	1.07	1.07	1.10	1.22
24-Mar-92	1.31	1.52	1.78	1.54	2.36
25-Mar-92	1.8	2.27	1.94	2.00	4.01
26-Mar-92	2.65	2.67	1.35	2.22	4.94
27-Mar-92	0.99	0.94	0.47	0.80	0.64
28-Mar-92	0.76	1.23	1.28	1.09	1.19
29-Mar-92	0.85	0.9	0.63	0.79	0.63

DATE	DAY SHIFT	AFTERNOON SHIFT	NIGHT SHIFT	AVERAGE	X2ij
30-Mar-92	0.97	1.99	2.26	1.74	3.03
31-Mar-92	1.96	1.18	0.73	1.29	1.66
1-Apr-92	1.21	1	0.79	1.00	1.00
2-Apr-92	0.98	1	1.09	1.02	1.05
3-Apr-92	1.49	2.05	1.6	1.71	2.94
4-Apr-92	1.72	1.23	0.64	1.20	1.43
5-Apr-92	1.26	1.33	1.19	1.26	1.59
		55% cullet			
6-Apr-92	0.74	0.97	1.46	1.06	1.12
8-Apr-92	0.91	1.15	1.26	1.11	1.22
9-Apr-92	1.17	0.77	0.47	0.80	0.65
10-Apr-92	0.67	0.66	0.96	0.76	0.58
11-Apr-92	1.05	1.1	1.2	1.12	1.25
12-Apr-92	1.33	1.56	0.8	1.23	1.51
13-Apr-92	1.03	1.02	0.87	0.97	0.95
14-Apr-92	1.06	1.06	0.51	0.88	0.77
15-Apr-92	0.92	0.82	1.12	0.95	0.91
16-Apr-92	1.29	1.79	1.79	1.62	2.64
17-Apr-92	1.63	0.77	0.83	1.08	1.16
18-Apr-92	1.04	1.05	0.96	1.02	1.03
19-Apr-92	2.07	1.52	0.82	1.47	2.16
20-Apr-92	0.64	0.68	0.54	0.62	0.38
21-Apr-92	1.32	1.28	0.98	1.19	1.42
22-Apr-92	0.9	0.93	0.85	0.89	0.80
25-Apr-92	0.62	0.5	0.12	0.41	0.17
26-Apr-92	0.31	0.3	0.44	0.35	0.12
		60% cullet			
27-Apr-92	0.3	1.55	0.91	0.92	0.85
28-Apr-92	0.65	1.18	0.61	0.81	0.66
2-May-92	1.34	1.11	1.25	1.23	1.52
5-May-92	2.65	1.31	1.65	1.87	3.50
6-May-92	1.95	2.16	0.44	1.52	2.30
7-May-92	1.2	0.83	0.65	0.89	0.80
8-May-92	1.21	0.83	1.27	1.10	1.22
9-May-92	0.98	0.91	1.24	1.04	1.09
12-May-92	1.49	1.7	1.76	1.65	2.72
13-May-92	1.07	0.81	1.51	1.13	1.28
14-May-92	1.53	0.89	0.73	1.05	1.10
15-May-92	1.75	0.35	1.6	1.23	1.52
17-May-92	2.95	1.12	1.25	1.77	3.14
22-May-92	0.93	0.62	0.34	0.63	0.40
23-May-92	0.62	0.38	0.35	0.45	0.20
24-May-92	0.97	1.27	0.78	1.01	1.01
25-May-92	0.85	0.49	0.49	0.61	0.37
26-May-92	0.73	0.55	0.38	0.55	0.31
27-May-92	0.6	0.6	0.47	0.56	0.31
28-May-92	0.5	0.58	0.83	0.64	0.41
29-May-92	0.42	0.1	0.12	0.21	0.05
30-May-92	0.08	0.2	0.22	0.17	0.03
31-May-92	0.22	0.27	0.34	0.28	0.08
1-Jun-92	0.17	0.13	0.26	0.19	0.03
2-Jun-92	0.47	0.45	0.29	0.40	0.16
4-Jun-92	0.42	0.76	0.56	0.58	0.34

DATE	DAY SHIFT	AFTERNOON SHIFT	NIGHT SHIFT	AVERAGE	X2ij
5-Jun-92	0.41	0.16	0.56	0.38	0.14
6-Jun-92	0.21	0.4	0.5	0.37	0.14
7-Jun-92	0.29	0.39	0.18	0.29	0.08
		65% cullet			
10-Jun-92	0.19	0.39	0.18	0.25	0.06
11-Jun-92	0.5	0.36	0.28	0.38	0.14
12-Jun-92	0.73	0.31	0.31	0.45	0.20
13-Jun-92	0.51	0.32	0.42	0.42	0.17
14-Jun-92	0.92	0.69	1.05	0.89	0.79
15-Jun-92	0.64	0.28	0.52	0.48	0.23
17-Jun-92	0.7	0.42	0.85	0.66	0.43
18-Jun-92	0.49	0.39	0.44	0.44	0.19
19-Jun-92	0.75	0.64	0.35	0.58	0.34
20-Jun-92	0.7	0.82	0.31	0.61	0.37
23-Jun-92	0.7	1.36	0.83	0.96	0.93
24-Jun-92	0.87	0.93	1.68	1.16	1.35
25-Jun-92	1.43	2.09	1.68	1.73	3.00
26-Jun-92	1.81	1.69	1.78	1.76	3.10
27-Jun-92	1.18	1.43	0.57	1.06	1.12
28-Jun-92	0.91	1.21	1.4	1.17	1.38
29-Jun-92	0.86	0.24	0.73	0.61	0.37
30-Jun-92	0.72	0.98	0.54	0.75	0.56
		70% cullet			
1-Jul-92	0.36	0.45	0.89	0.57	0.32
2-Jul-92	0.48	0.32	0.21	0.34	0.11
3-Jul-92	0.26	0.33	0.62	0.40	0.16
4-Jul-92	0.42	0.16	0.45	0.34	0.12
5-Jul-92	0.43	0.32	0.43	0.39	0.15
7-Jul-92	0.54	0.3	0.6	0.48	0.23
8-Jul-92	0.45	0.54	0.53	0.51	0.26
9-Jul-92	0.32	0.47	0.81	0.53	0.28
10-Jul-92	0.39	0.63	0.31	0.44	0.20
11-Jul-92	0.6	0.62	0.52	0.58	0.34
12-Jul-92	0.41	0.42	0.16	0.33	0.11
23-Jul-92	0.72	0.66	0.74	0.71	0.50
25-Jul-92	0.39	0.16	0.4	0.32	0.10
26-Jul-92	0.67	0.7	0.26	0.54	0.30
27-Jul-92	0.11	0.55	0.71	0.46	0.21
28-Jul-92	0.33	0.38	0.25	0.32	0.10
29-Jul-92	0.25	0.85	0.57	0.56	0.31
30-Jul-92	0.33	0.19	0.18	0.23	0.05
31-Jul-92	0.22	0.18	0.17	0.19	0.04
1-Aug-92	0.46	0.18	0.15	0.26	0.07
2-Aug-92	0.62	0.19	0.11	0.31	0.09
3-Aug-92	0.37	0.27	0.25	0.30	0.09
4-Aug-92	0.39	0.29	0.22	0.30	0.09
5-Aug-92	0.4	0.19	0.19	0.26	0.07
6-Aug-92	1.19	0.72	0.39	0.77	0.59
7-Aug-92	0.32	0.23	0.36	0.30	0.09
11-Aug-92	0.37	0.24	0.35	0.32	0.10
12-Aug-92	0.47	0.33	0.26	0.35	0.12
15-Aug-92	0.31	0.63	0.16	0.37	0.13
16-Aug-92	0.15	0.17	0.23	0.18	0.03

DATE	DAY SHIFT	AFTERNOON SHIFT	NIGHT SHIFT	AVERAGE	X2ij
17-Aug-92	0.32	0.54	0.56	0.47	0.22
18-Aug-92	0.77	0.61	0.51	0.63	0.40
19-Aug-92	0.68	0.59	0.3	0.52	0.27
20-Aug-92	0.46	0.22	0.19	0.29	0.08
21-Aug-92	0.26	0.3	0.18	0.25	0.06
22-Aug-92	0.36	0.57	0.51	0.48	0.23
23-Aug-92	0.79	0.08	0.06	0.31	0.10
24-Aug-92	0.09	0.08	0.11	0.09	0.01
25-Aug-92	0.27	0.12	0.44	0.28	0.08
26-Aug-92	0.33	0.24	0.19	0.25	0.06
27-Aug-92	0.48	0.12	0.12	0.24	0.06
28-Aug-92	0.14	0.1	0.2	0.15	0.02
29-Aug-92	0.25	0.16	0.21	0.21	0.04
30-Aug-92	0.37	0.4	0.57	0.45	0.20

Table 16. Significance between 42m/c CUR losses @ (40-55)% & (60-70)% cullet

N	k				
218	2				
T..^2/N	Xij^2	SST	SSTr	SSE	F
156	195.48	39.94	9.77	30.17	69.94
N1	N2		MS(Tr)	MS(E)	
127	91		9.77	0.14	
T1^2/N1	T2^2/N2	(SUM Ti^20)/N	DoF	DoF	F CHART
133.14	32.17	165.31	1	216.00	6.63
F calculated is much larger than F from critical value chart, hence the difference between cullet levels is significant.					

APPENDIX III

CALCULATION OF REQUIRED SULPHATE ADDITION TO GIVE AN EXCESS SO_3 LEVEL OF 1.25 Kg PER TONNE OF GLASS MELTED

METHOD

Step 1. Calculate batch on a sulphate free basis.

Step 2. Convert to 1 tonne total melted weight.

Step 3. Calculate the weight of sulphur as SO_3 being added from all sources other than sodium sulphate.

Step 4. Calculate the weight of sulphur retained as SO_3 in the glass after melting.

Step 5. After subtracting the result of Step (4) from Step (3), calculate the additional weight of sodium sulphate to be added to increase the result of subtracting Step (4) from Step (3) to give 1.25 Kg.

SAMPLE CALCULATION

Step 1, 2 & 3.
Batch weights calculated for one tonne melted weight of glass on a sulphate free basis at 70% cullet.

Material	Weight (Kg)	Sulphur as %SO3	Weight SO_3(Kg)
Sand	209.0	0	0
Soda Ash	67.8	0	0
Limestone	64.5	0	0
Nepheline Syenite	12.5	0	0
Iron Oxide	0.9	0	0
Amber Cullet	700.0	0.08	0.56

Total weight of sulphur being added (excluding sodium sulphate) 0.56 Kg

Step 4.
The percent of sulphur retained in the glass, expressed as SO_3 (determined by XRF) is 0.08%.

Hence the weight of SO_3 retained in one tonne of glass is:

$$1000 * 0.0008 = \underline{0.8 \text{ Kg}}$$

Step 5.
The excess SO_3 from the sulphate free batch is:

SO_3 IN - SO_3 OUT = EXCESS SO3

0.56 - 0.8 = -0.24 Kg

Hence the weight of SO_3 required from sodium sulphate is:

1.25 - (-0.24) = 1.49 Kg

Sodium sulphate decomposes according to the following equation:

$$Na_2SO_4 \rightarrow Na_2O + SO_3 \qquad (18)$$

So for each kilogram of sodium sulphate added to the batch, only (80/142) or 0.56 Kg of SO_3 is added.

The weight of sodium sulphate required to give 1.25 Kg of excess SO_3 is:

1.49/0.56 = 2.66 Kg

This result can be expressed as parts of sodium sulphate per 1000 parts of sand:

(1000/209) * 2.66 = 12.7

APPENDIX IV

RAW DATA SHOWN IN CONTROL CHART FORMAT.

CONTROL CHARTS FOR 42m/c.

Figure 69. 42m/c DAILY AVERAGE CUR LOSSES AT 40% CULLET

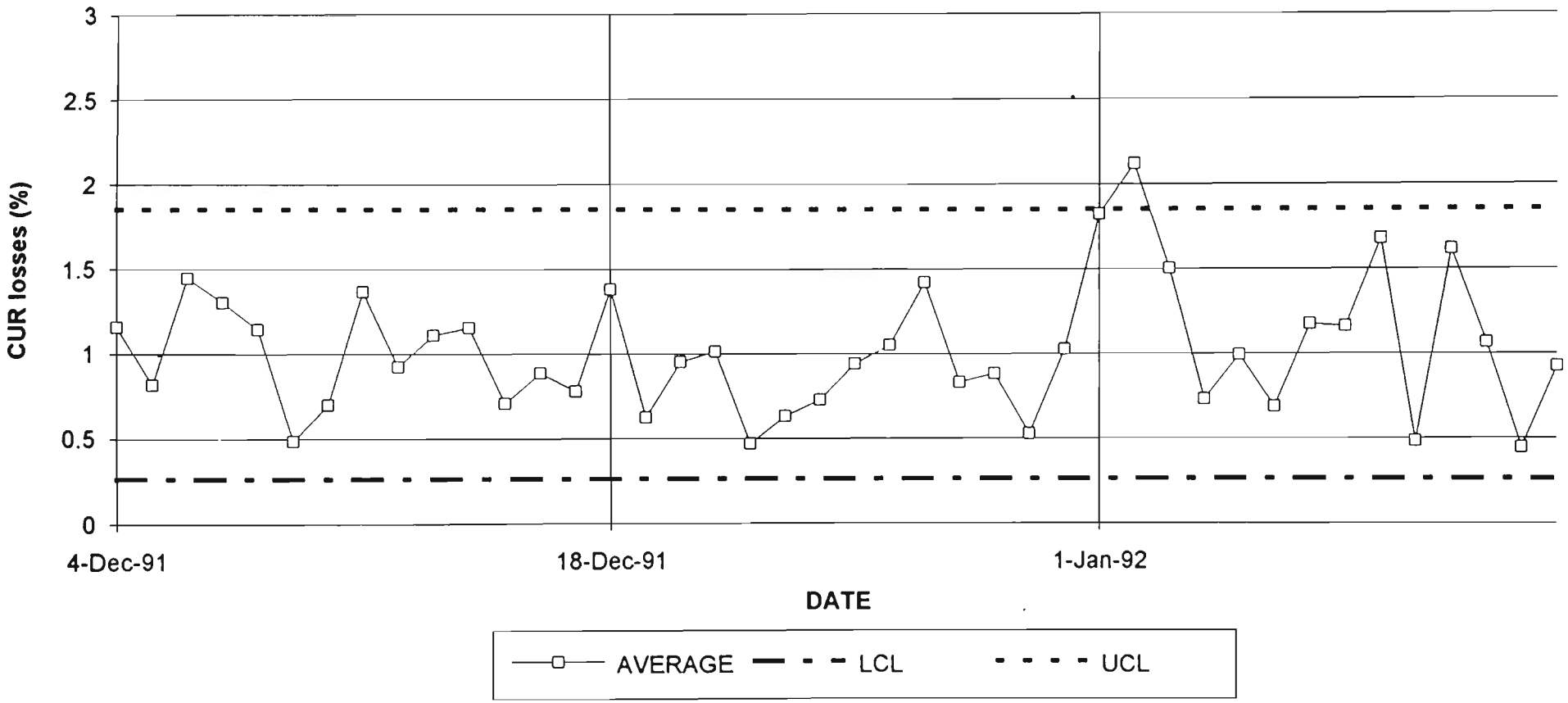


Figure 70. 42m/c DAILY AVERAGE CUR LOSSES AT 45% CULLET

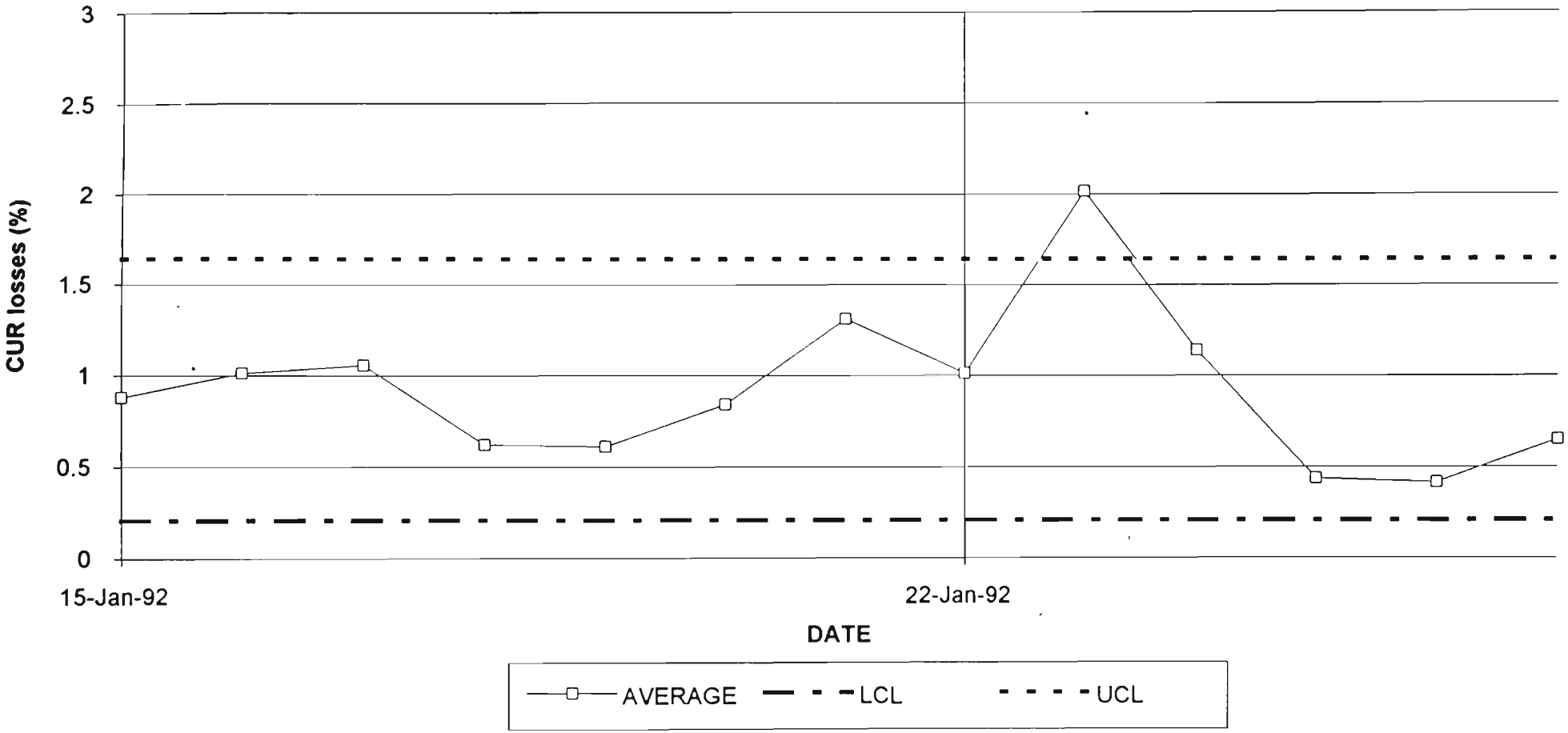


Figure 71. 42m/c DAILY AVERAGE CUR LOSSES AT 50% CULLET

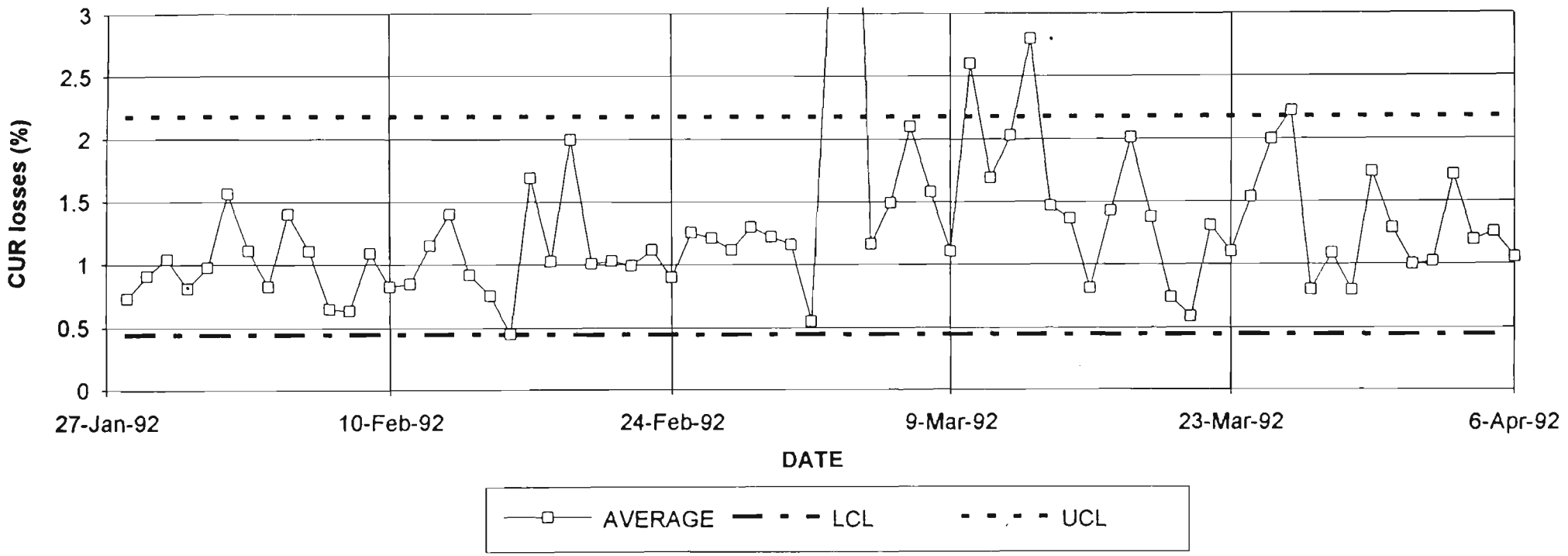


Figure 72. 42m/c DAILY AVERAGE CUR LOSSES AT 55% CULLET

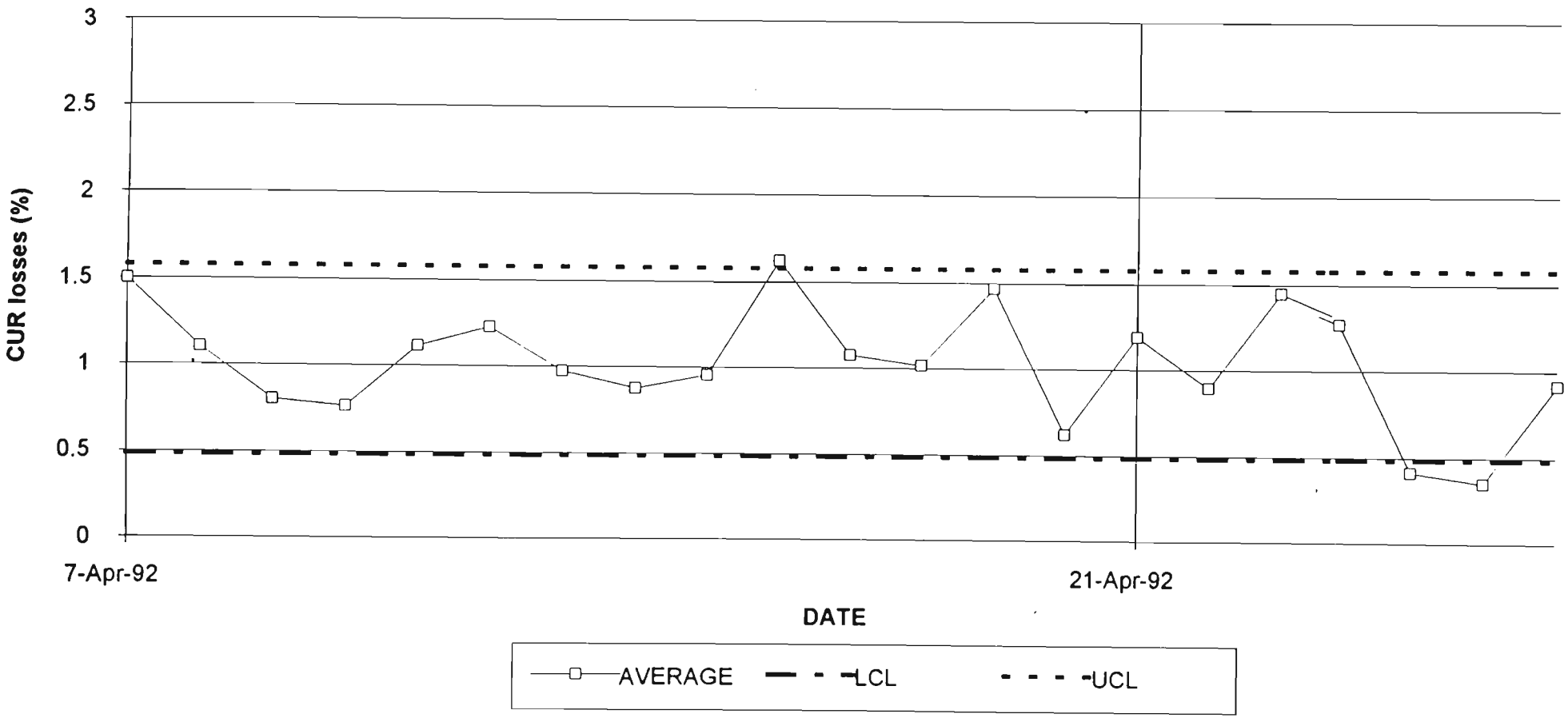


Figure 73. 42m/c DAILY AVERAGE CUR LOSSES AT 60% CULLET

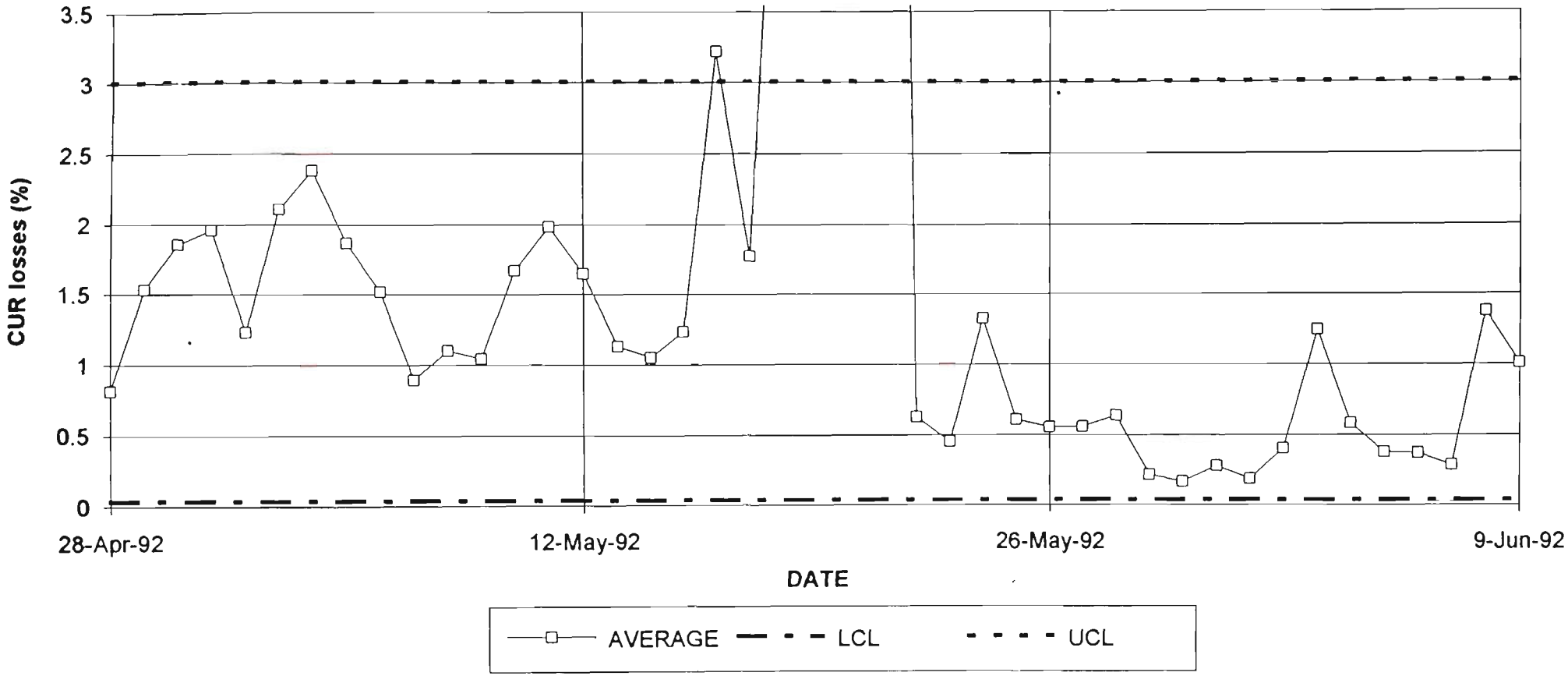


Figure 74. 42m/c DAILY AVERAGE CUR LOSSES AT 65% CULLET

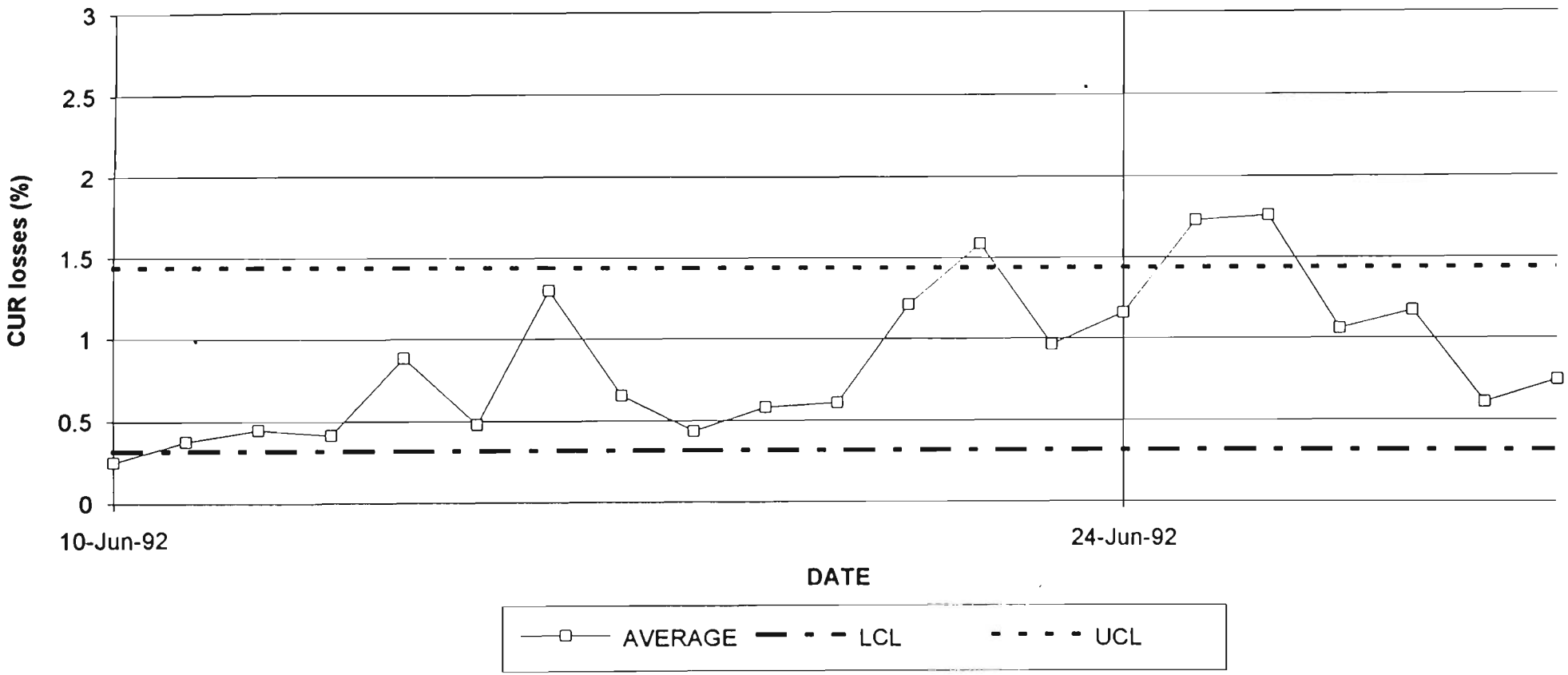


Figure 75. 42m/c DAILY AVERAGE CUR LOSSES AT 70% CULLET

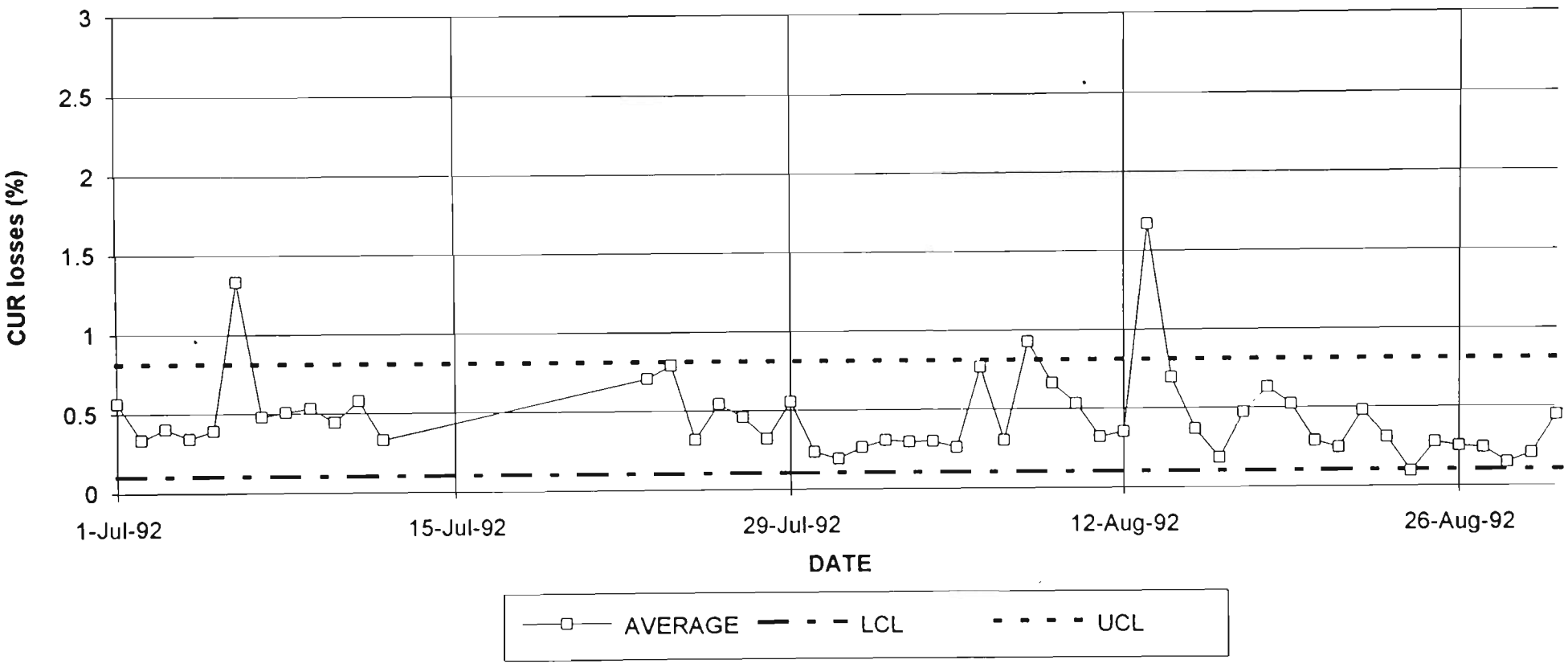


Figure 76. 42m/c DAILY AVERAGE THIN WALL LOSSES AT 40% CULLET

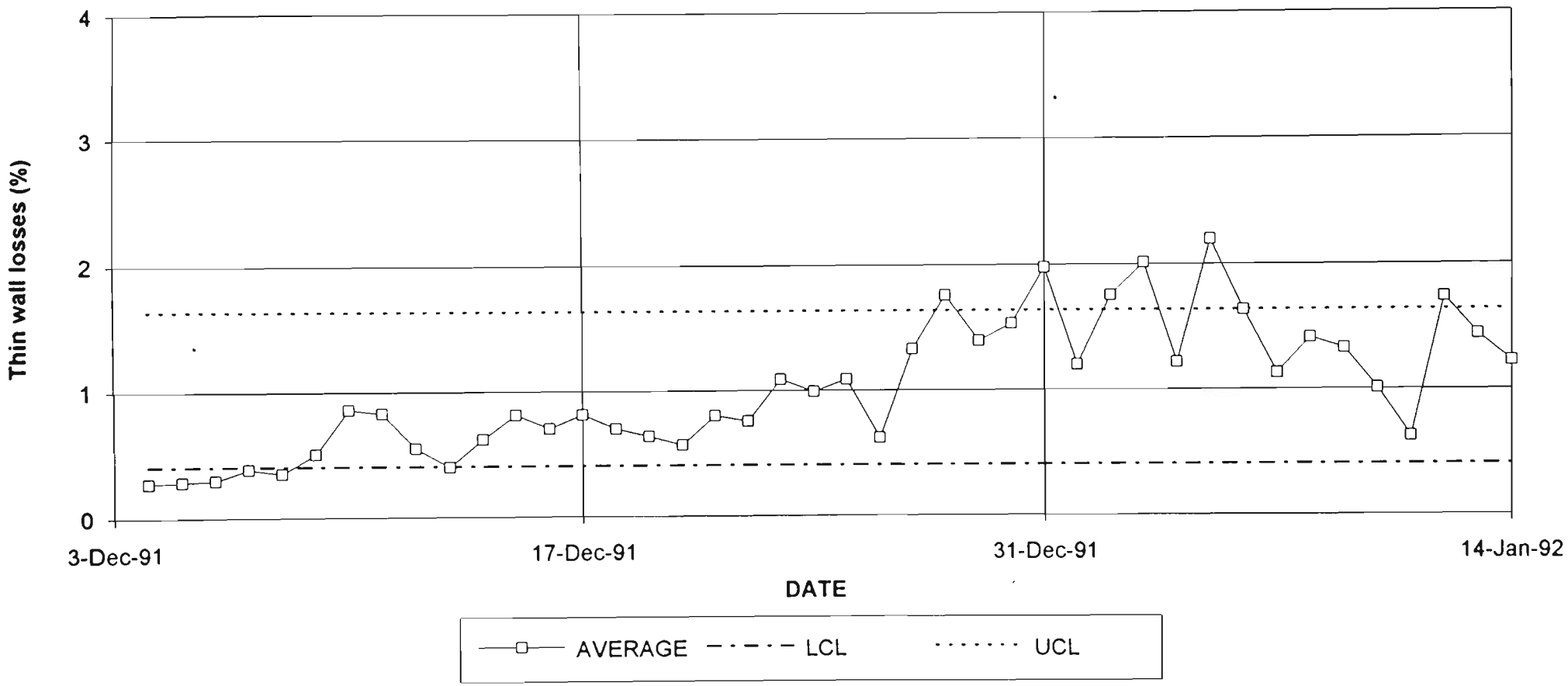


Figure 77. 42m/c DAILY AVERAGE THIN WALL LOSSES AT 45% CULLET

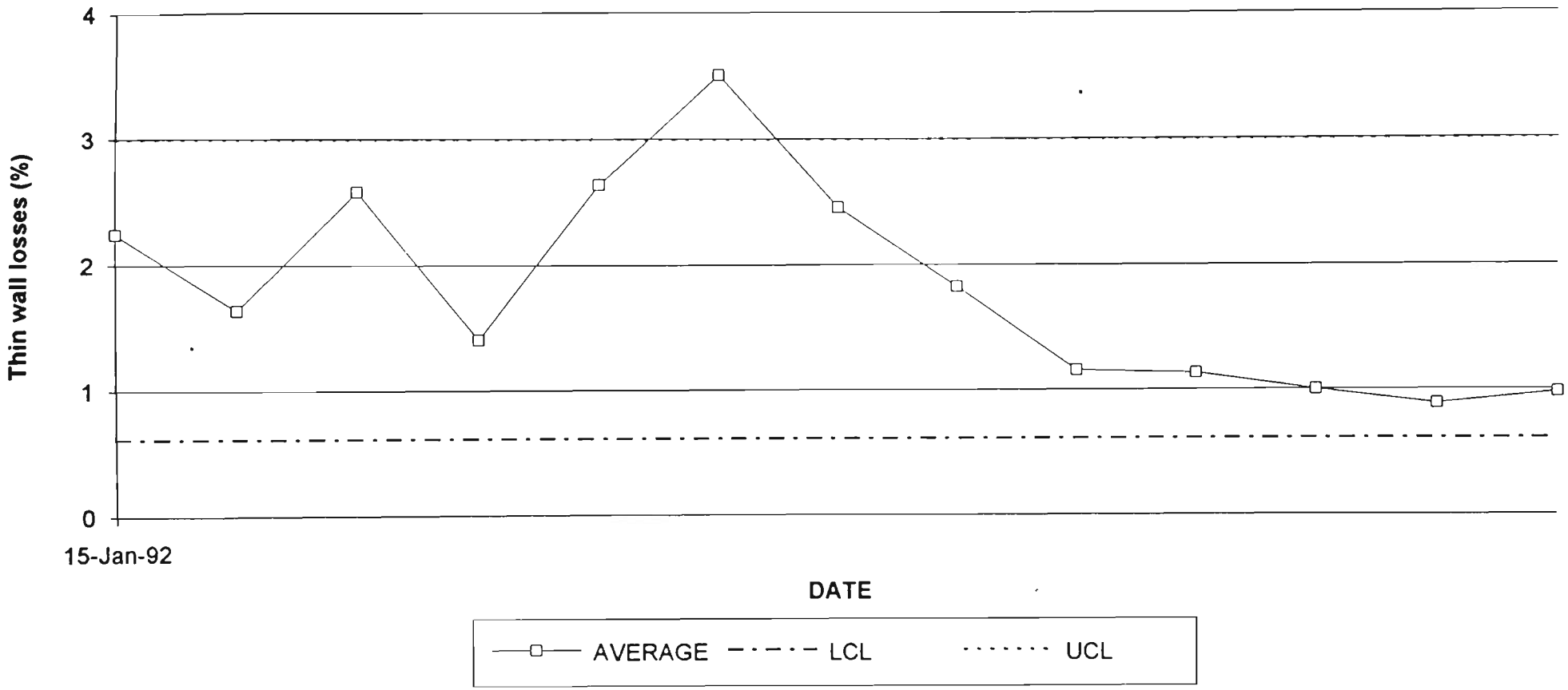


Figure 78. 42m/c DAILY AVERAGE THIN WALL LOSSES AT 50% CULLET

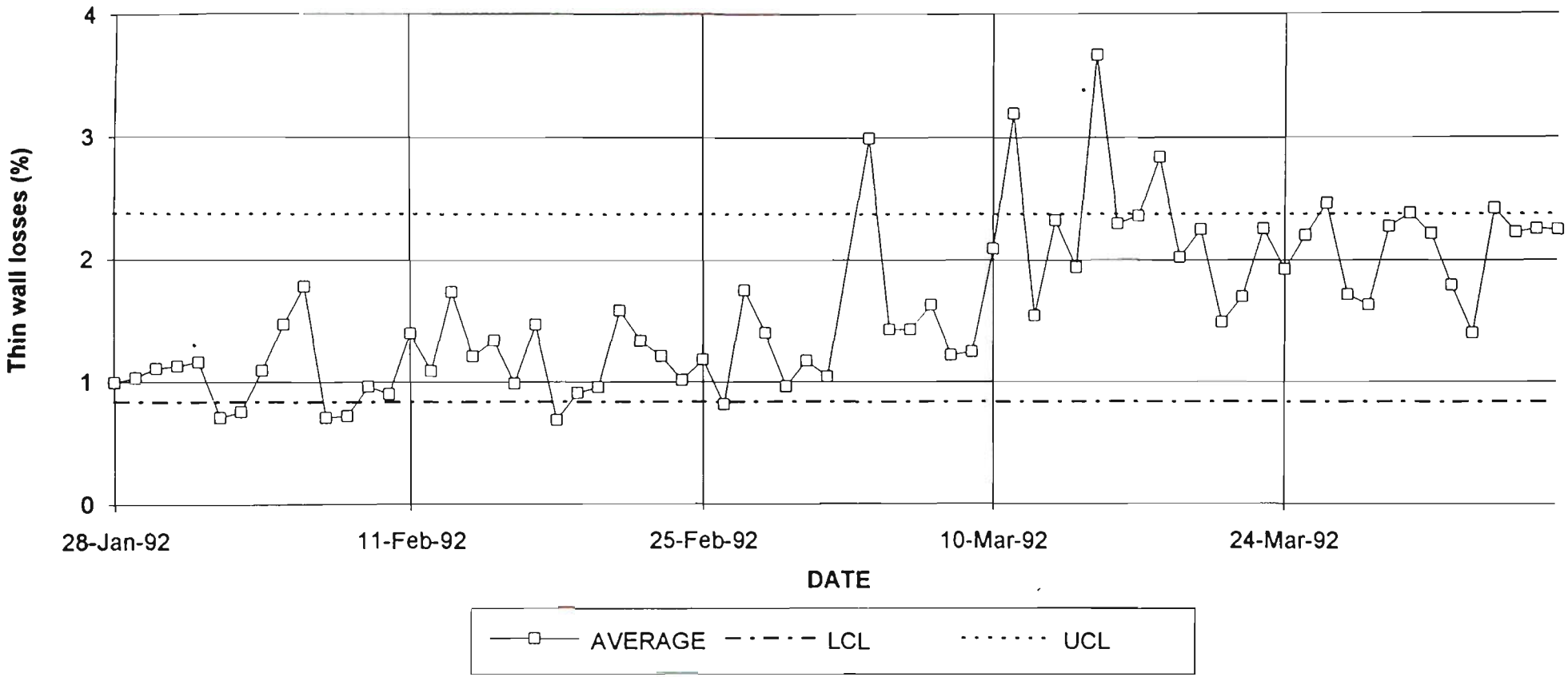


Figure 79. 42m/c DAILY AVERAGE THIN WALL LOSSES AT 55% CULLET

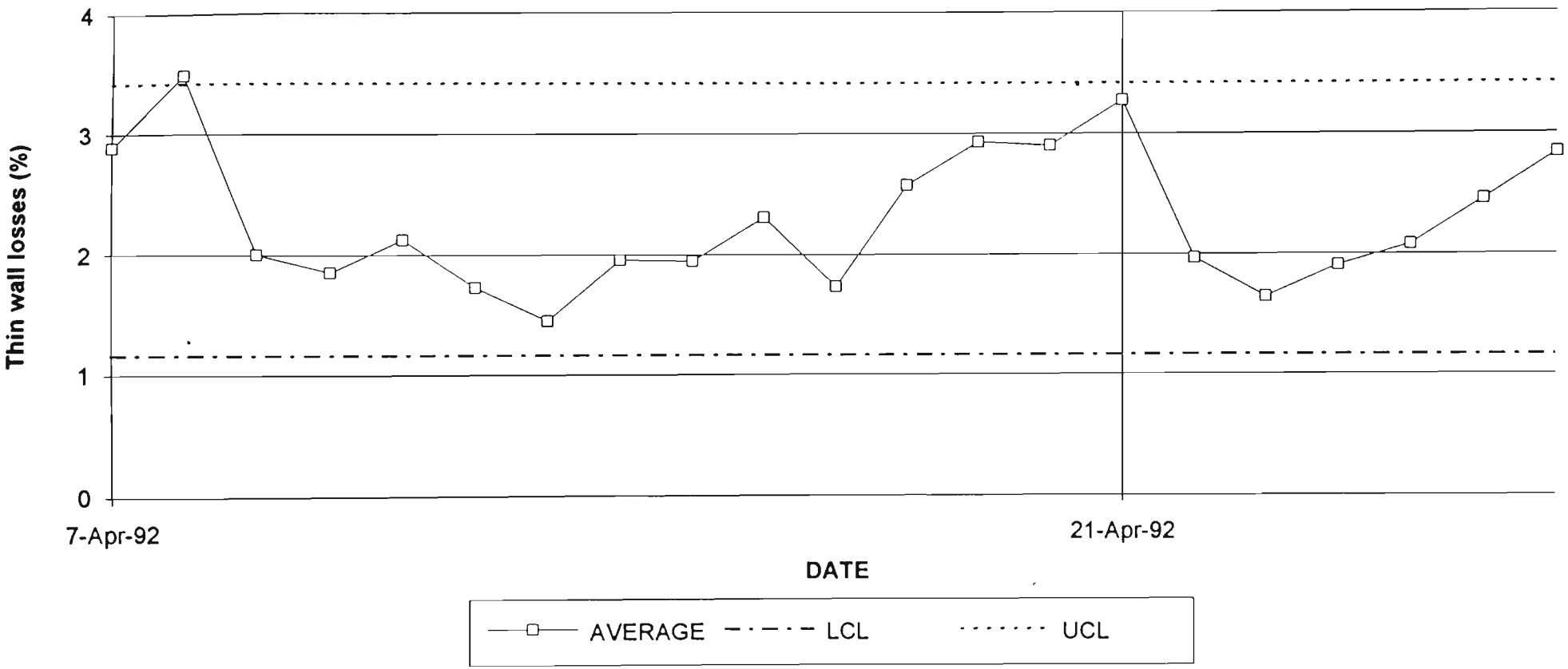


Figure 80. 42m/c DAILY AVERAGE THIN WALL LOSSES AT 60% CULLET

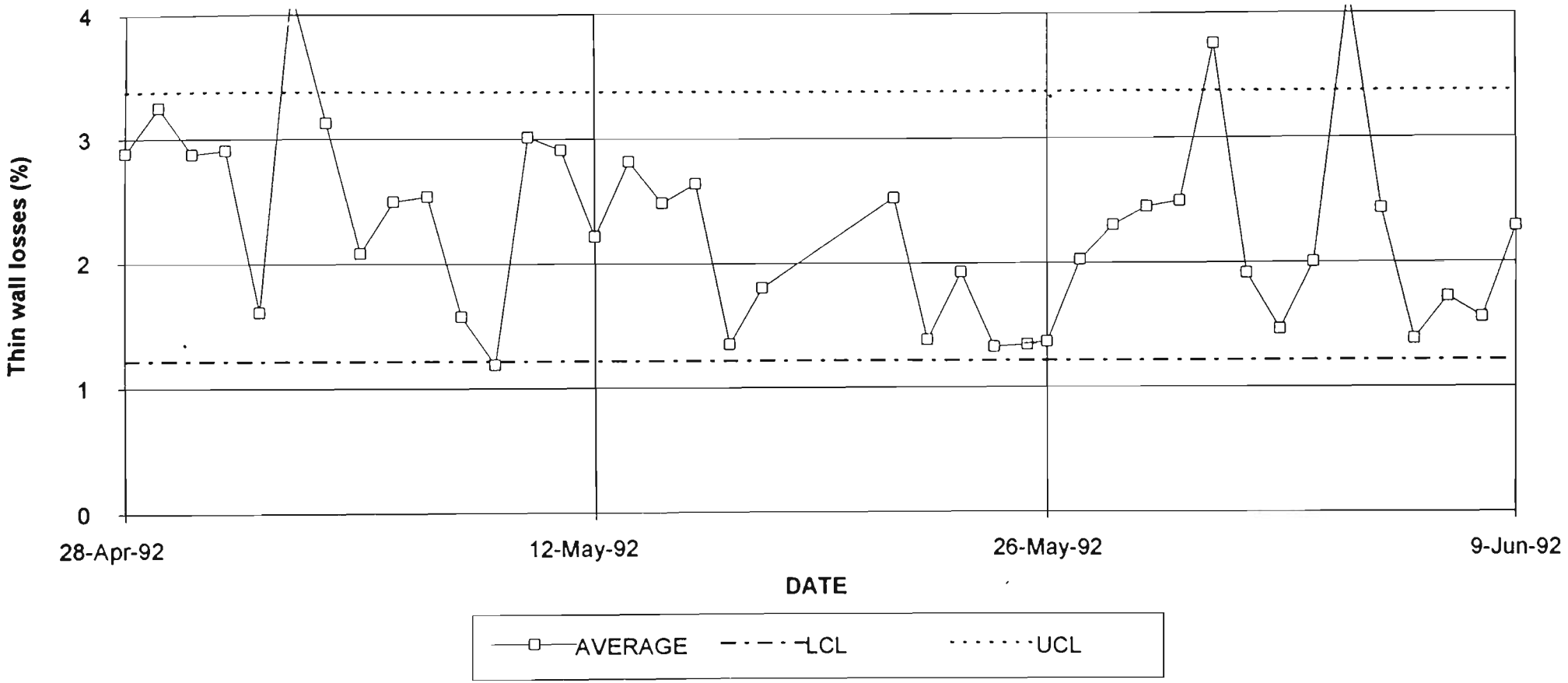


Figure 81. 42m/c DAILY AVERAGE THIN WALL LOSSES AT 65% CULLET

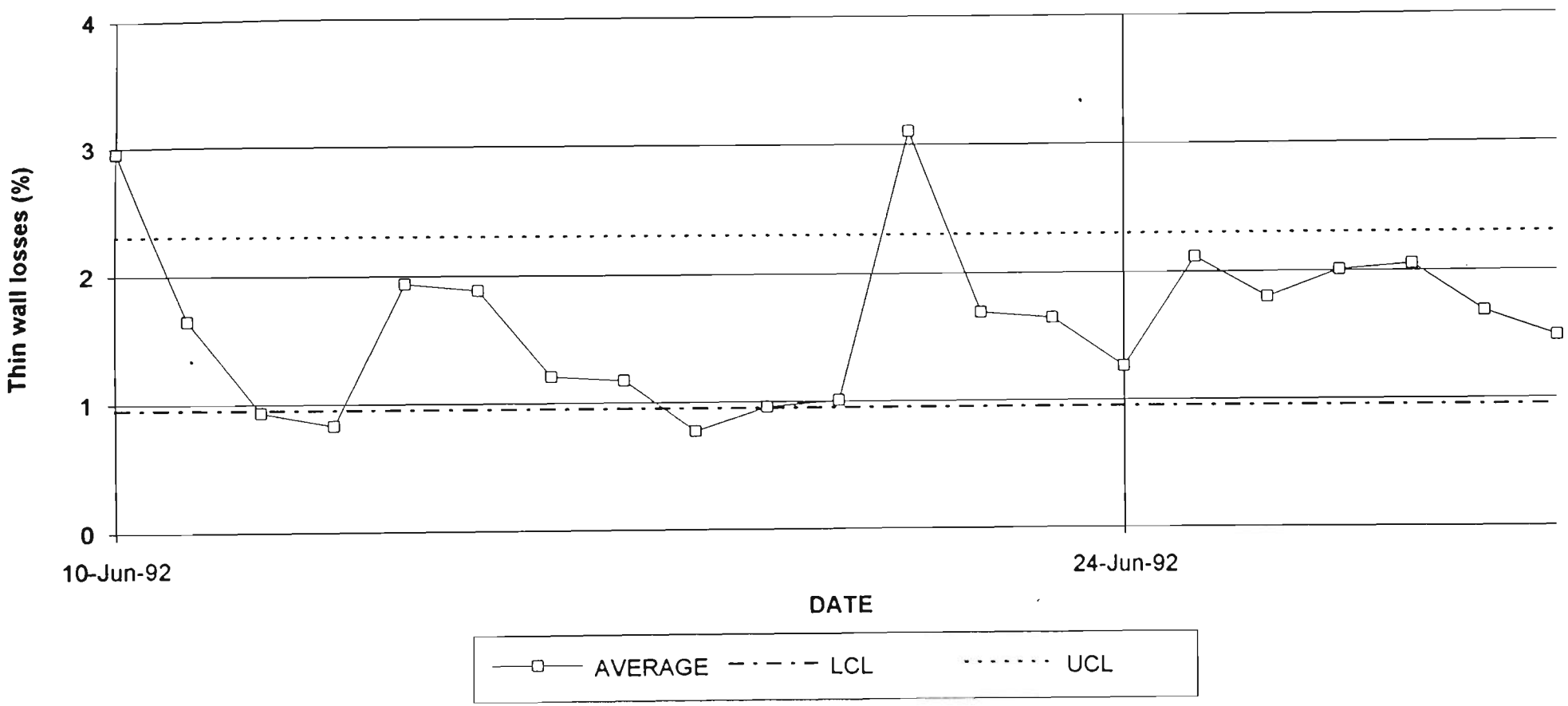


Figure 82. 42m/c DAILY AVERAGE THIN WALL LOSSES AT 70% CULLET

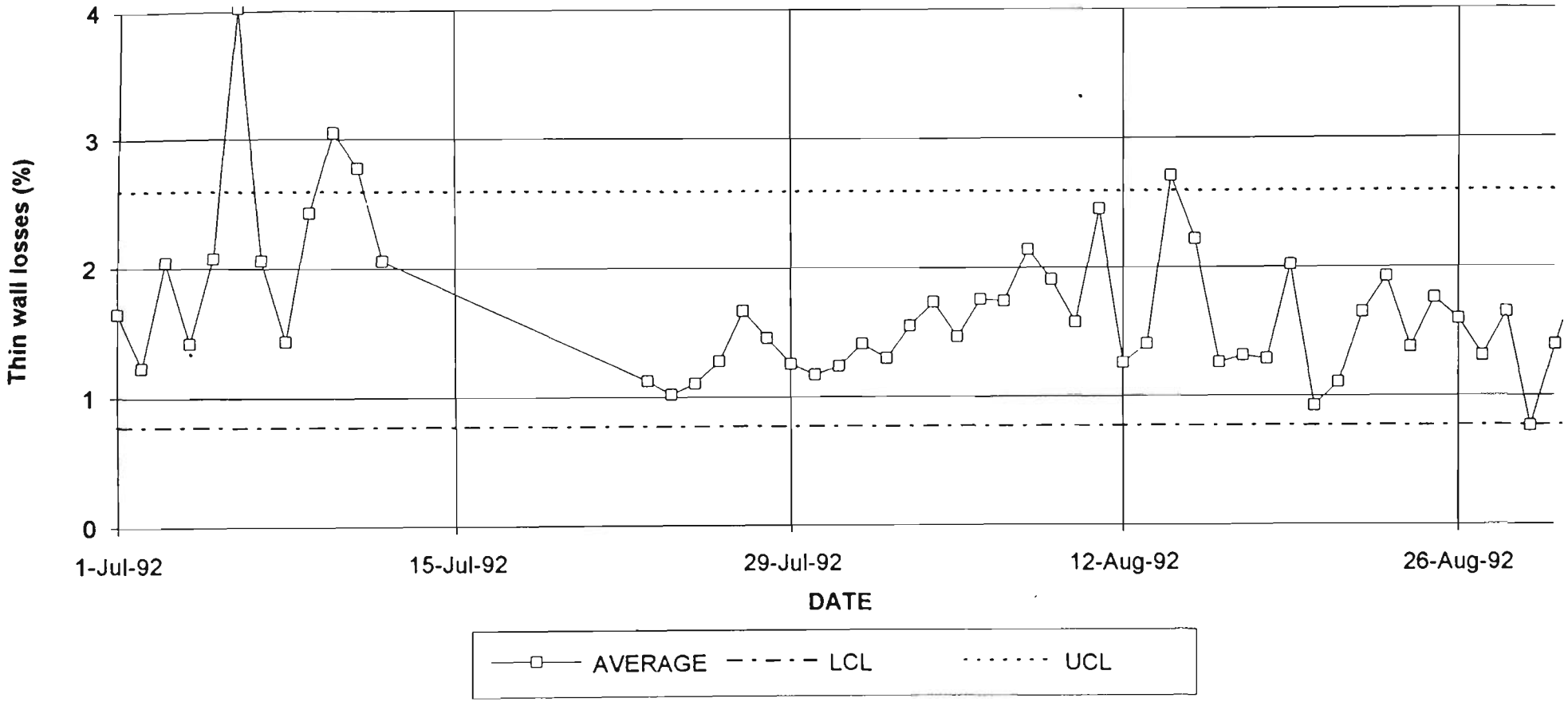


Figure 83. 42m/c DAILY AVERAGE CID LOSSES AT 40% CULLET

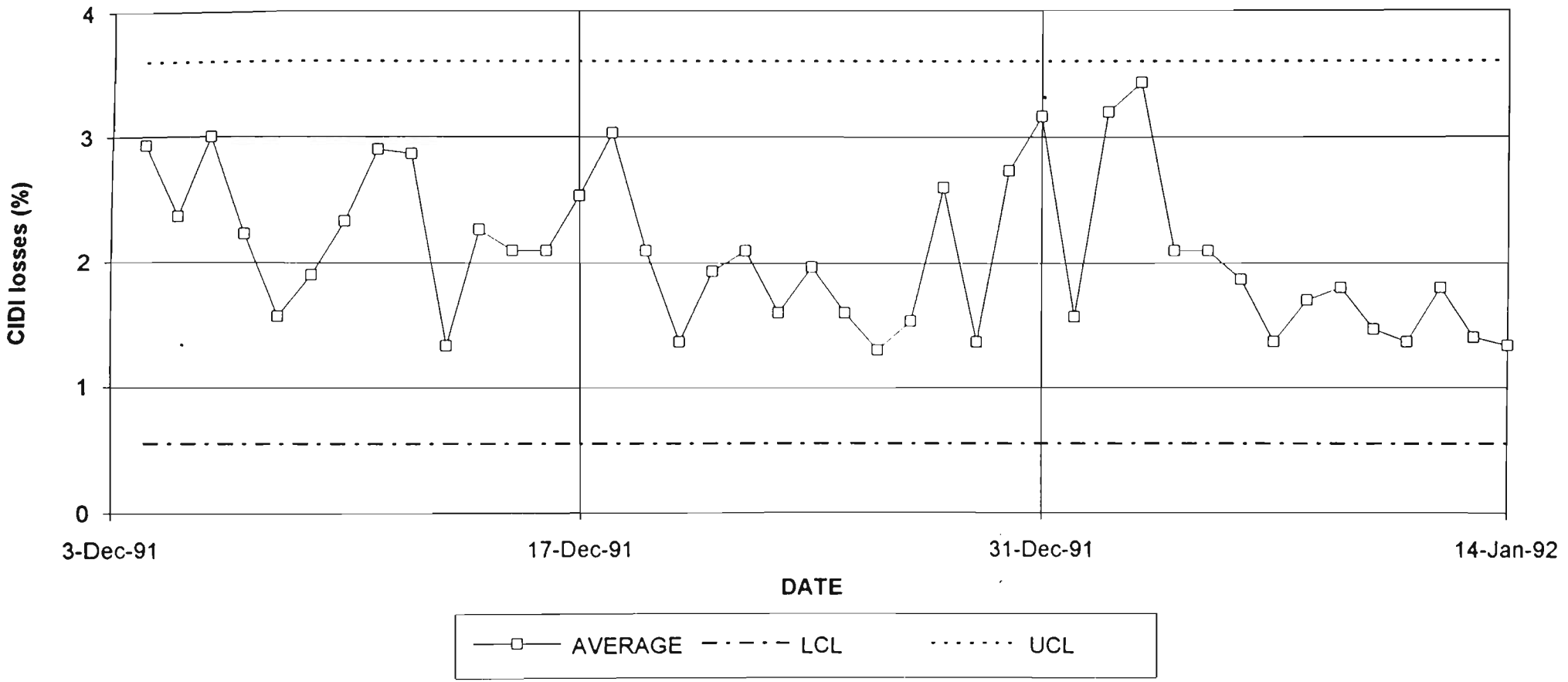


Figure 84. 42m/c DAILY AVERAGE CID LOSSES AT 45% CULLET

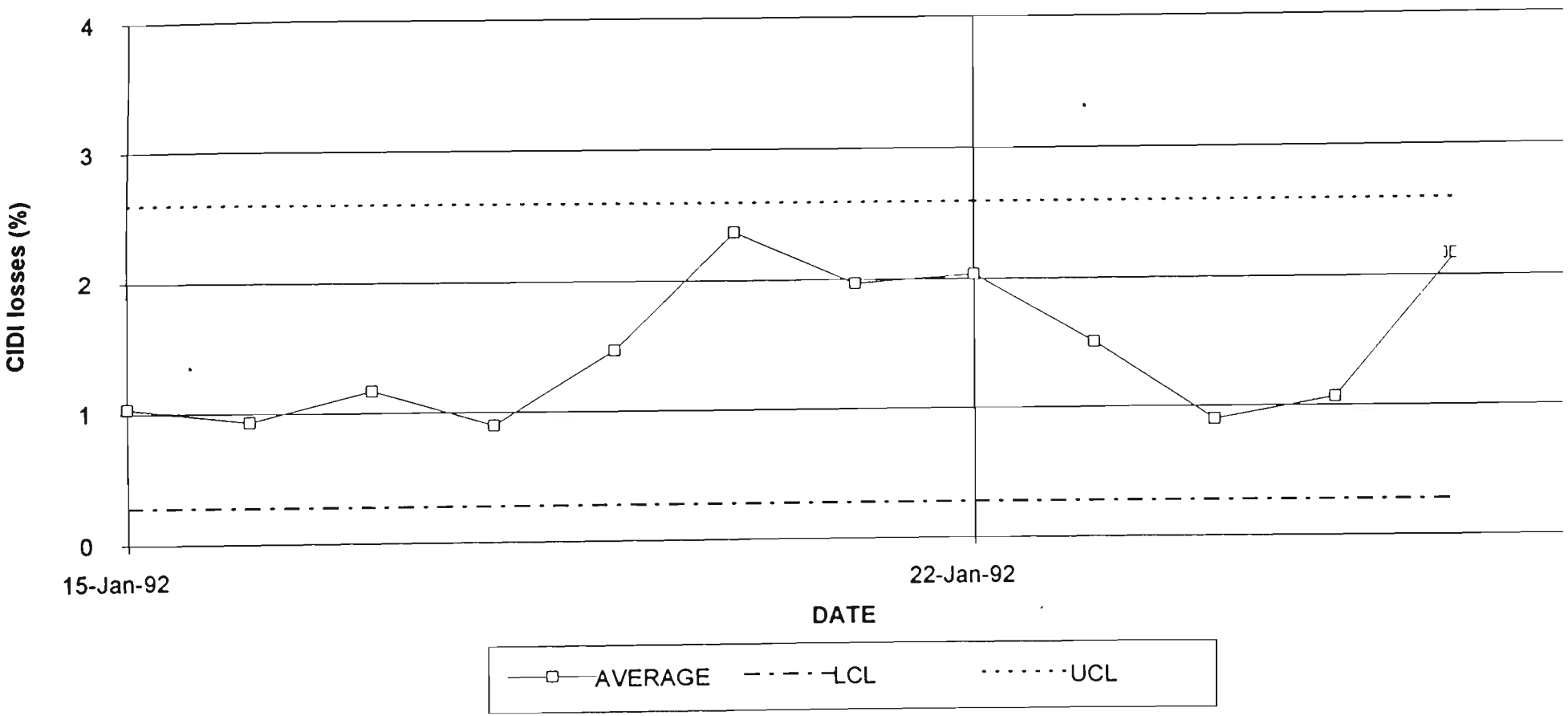


Figure 85. 42m/c DAILY AVERAGE CID LOSSES AT 50% CULLET

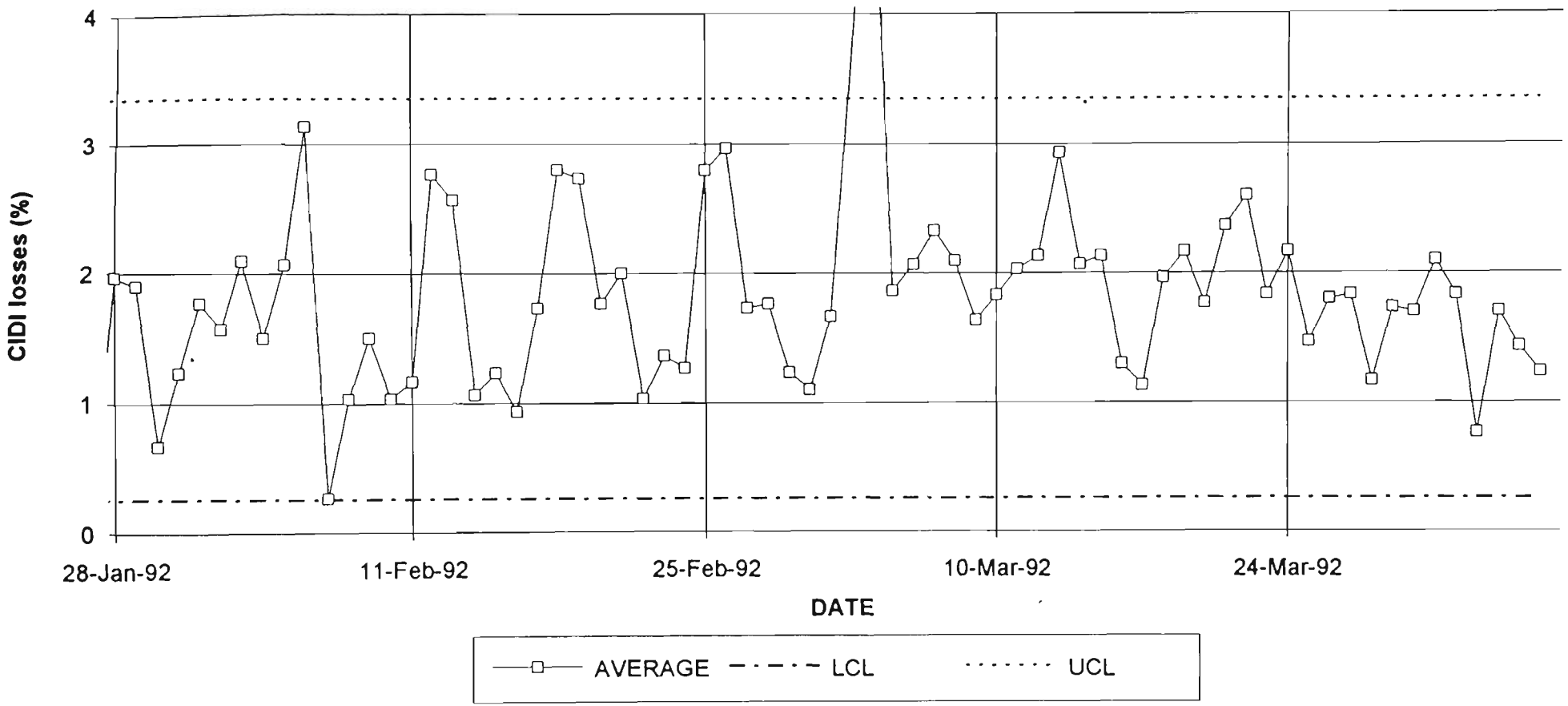


Figure 86. 42m/c DAILY AVERAGE CID LOSSES AT 55% CULLET

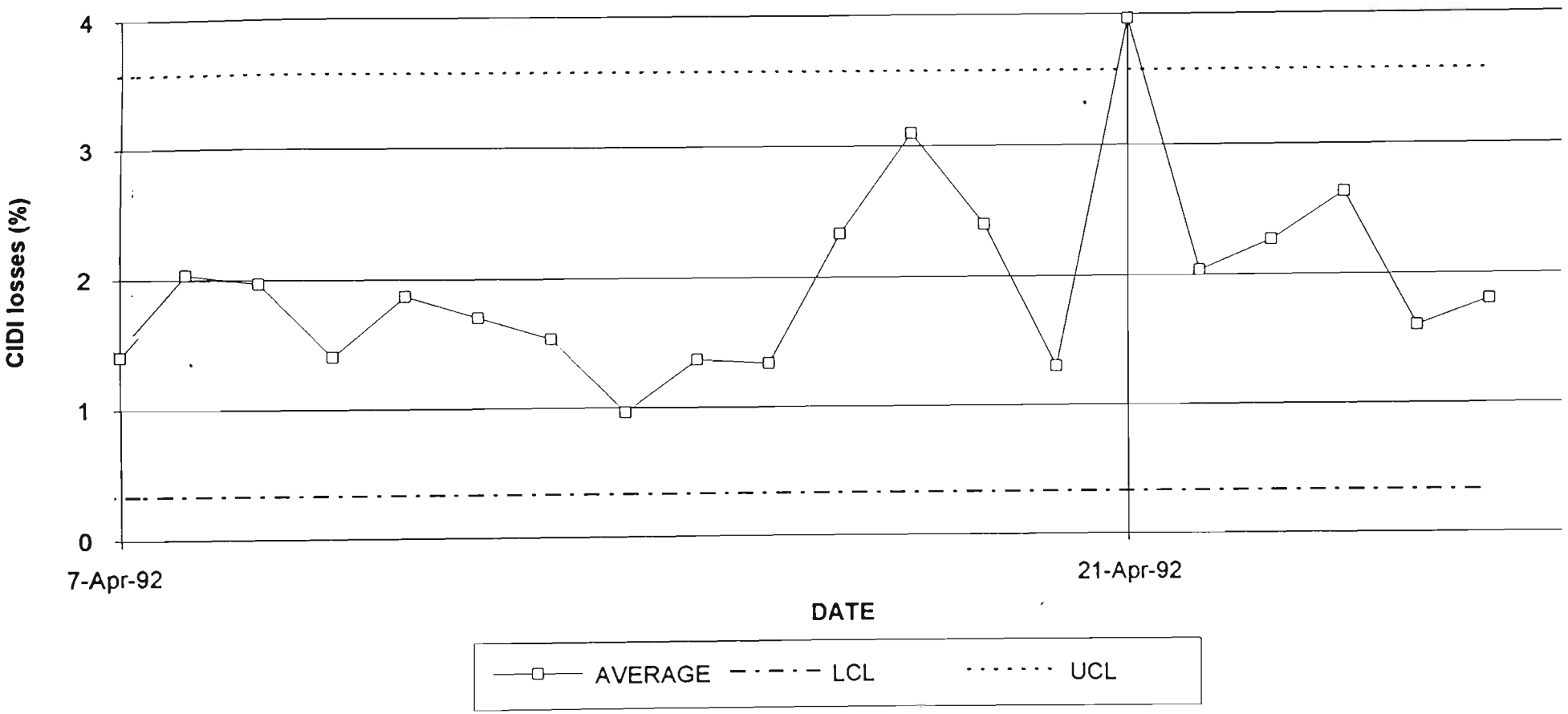


Figure 87. 42m/c DAILY AVERAGE CID LOSSES AT 60% CULLET

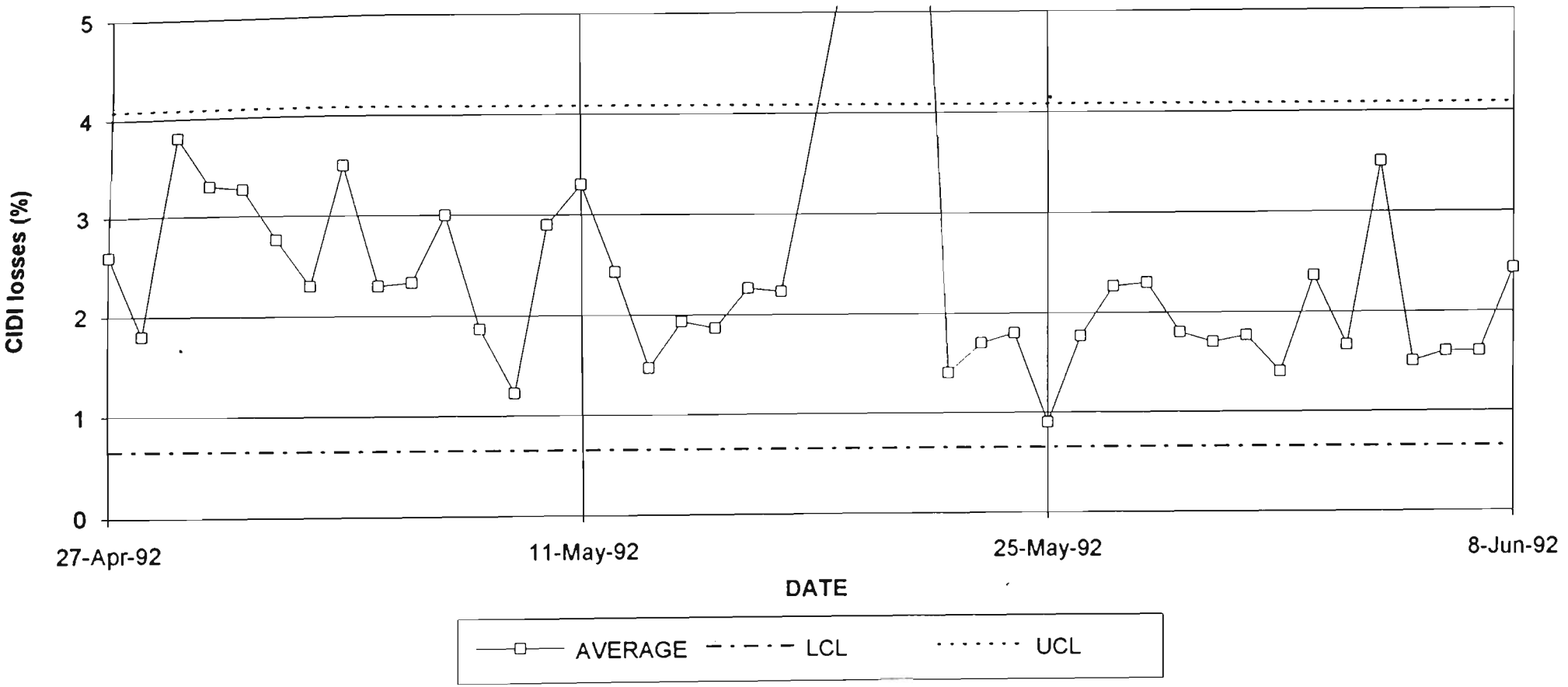


Figure 88. 42m/c DAILY AVERAGE CID LOSSES AT 65% CULLET

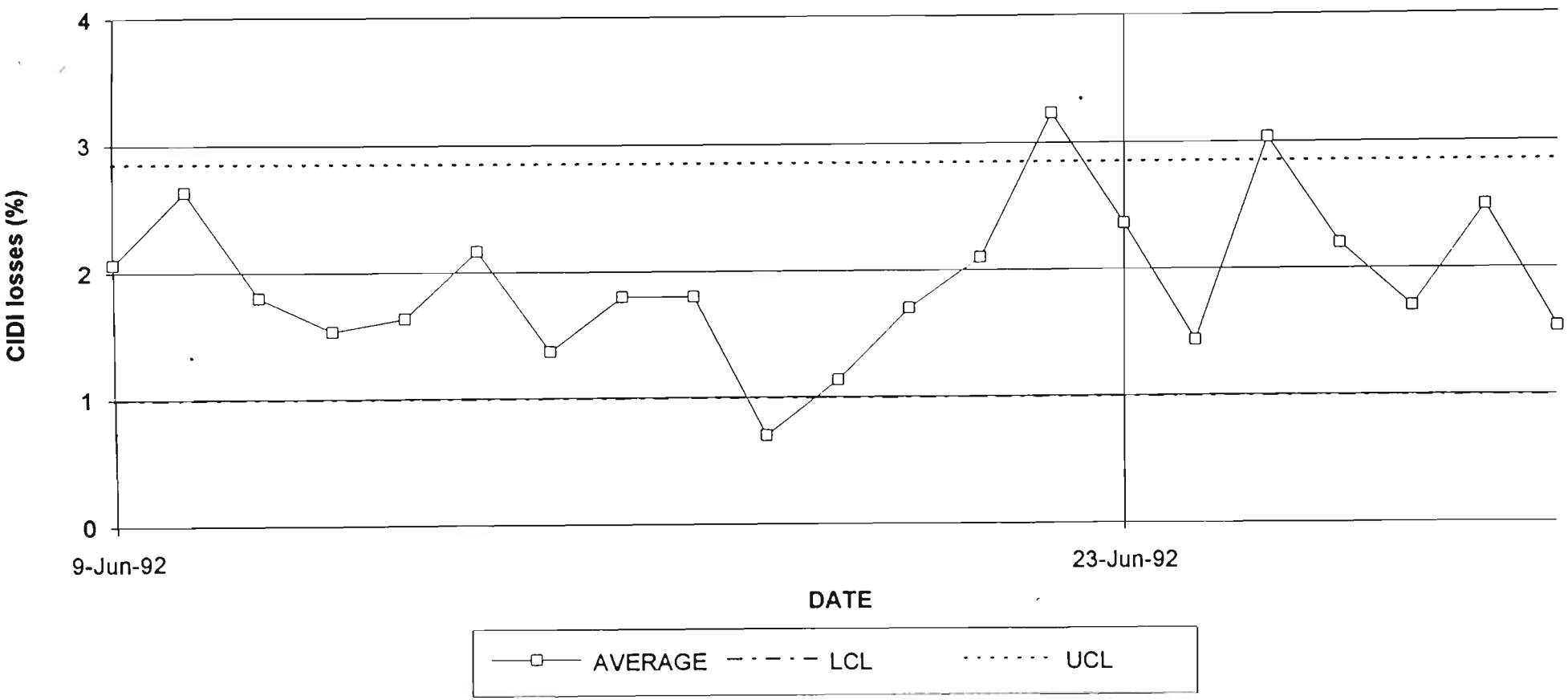


Figure 89. 42m/c DAILY AVERAGE CID LOSSES AT 70% CULLET

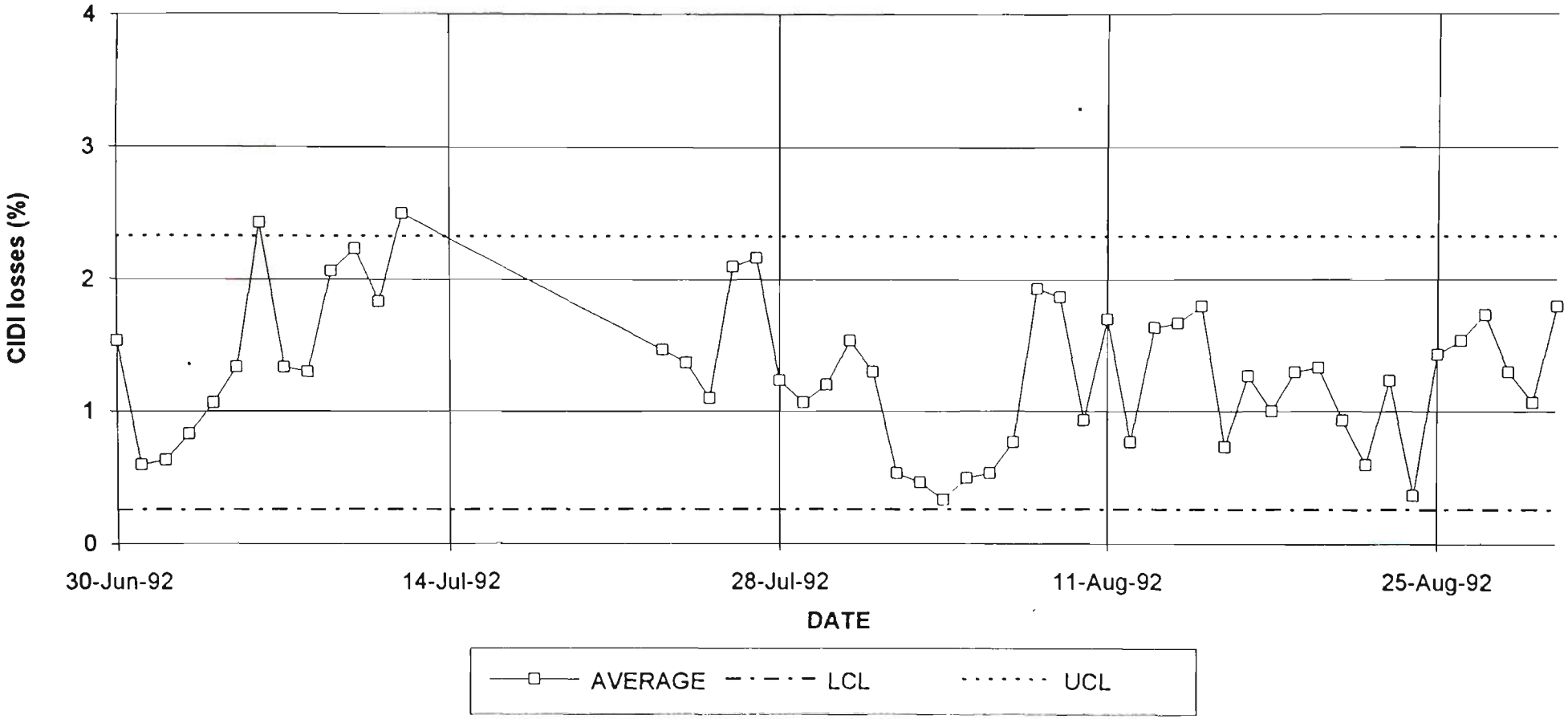


Figure 90. 42m/c DAILY AVERAGE EFFICIENCY AT 40% CULLET

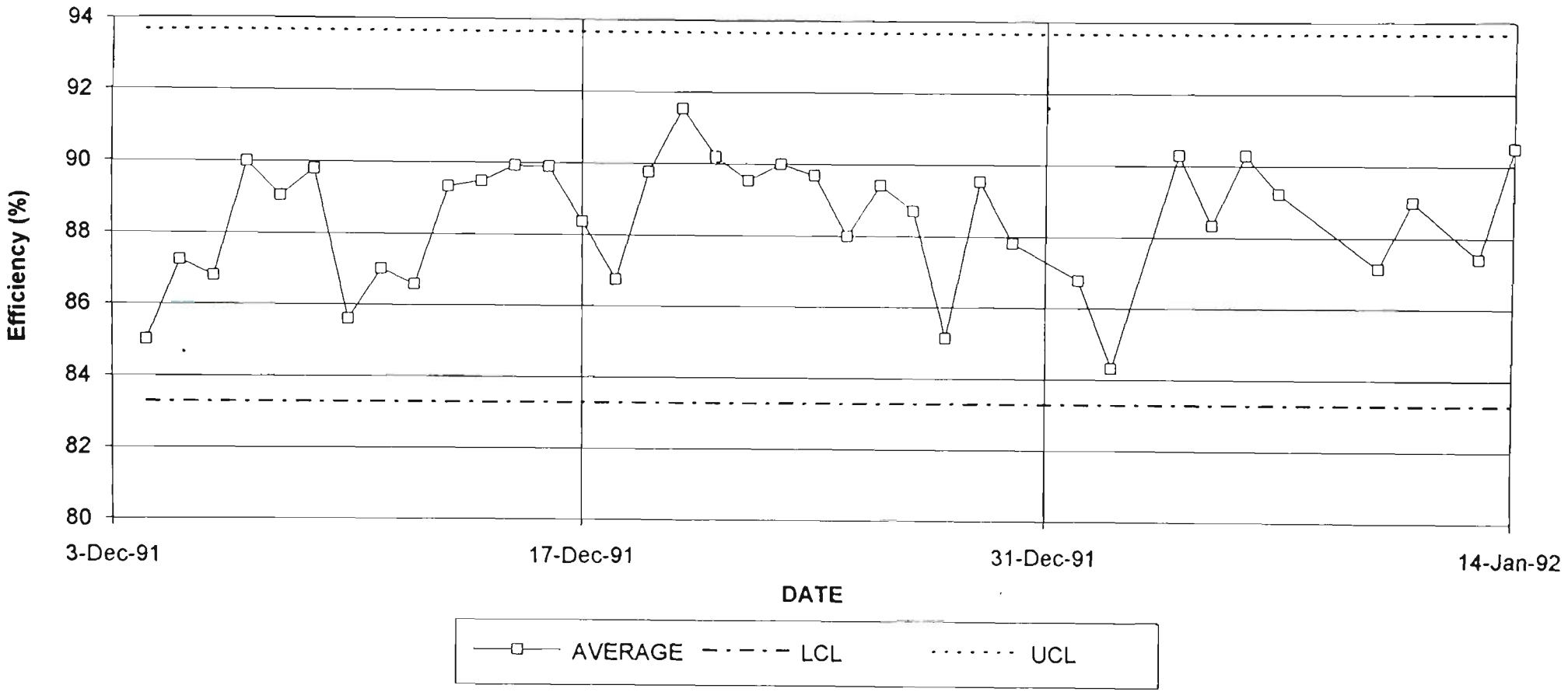


Figure 91. 42m/c DAILY AVERAGE EFFICIENCY AT 45% CULLET

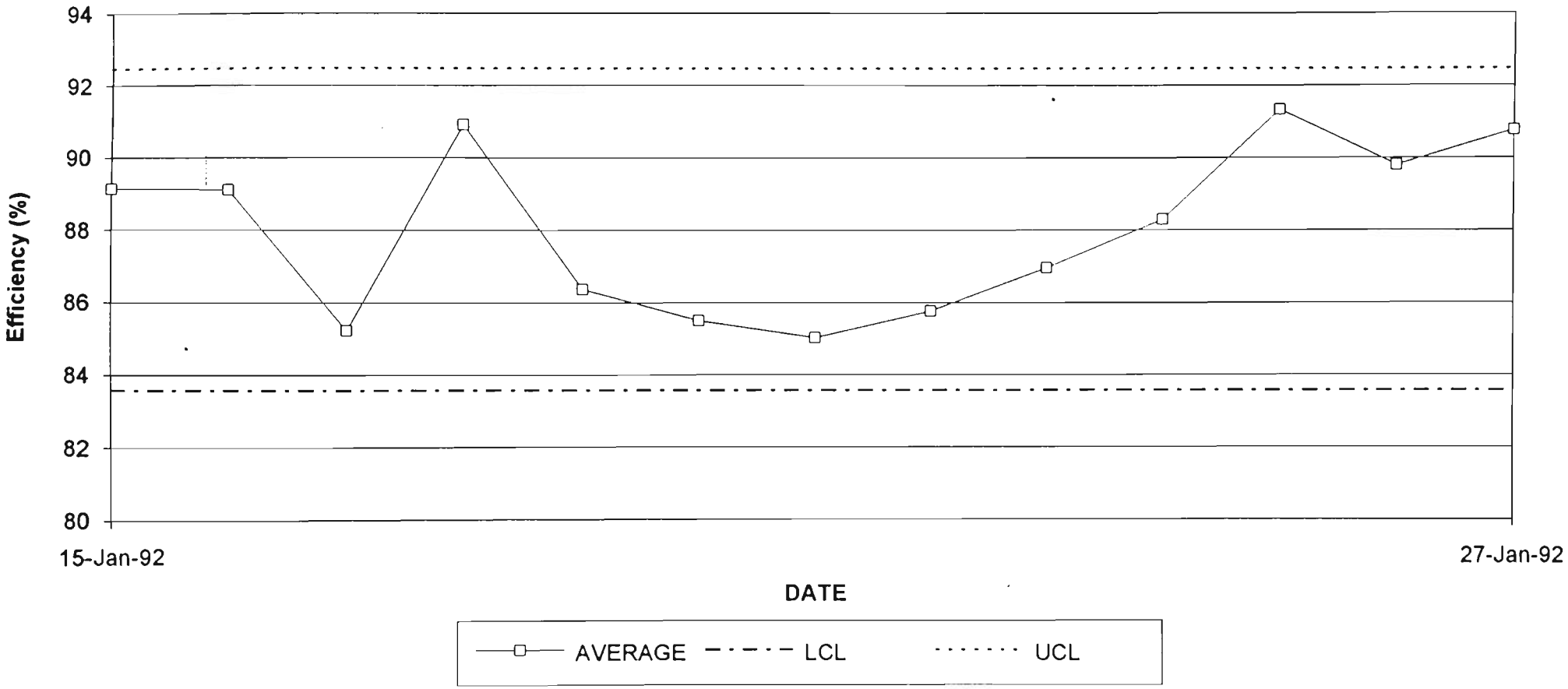


Figure 92. 42m/c DAILY AVERAGE EFFICIENCY AT 50% CULLET

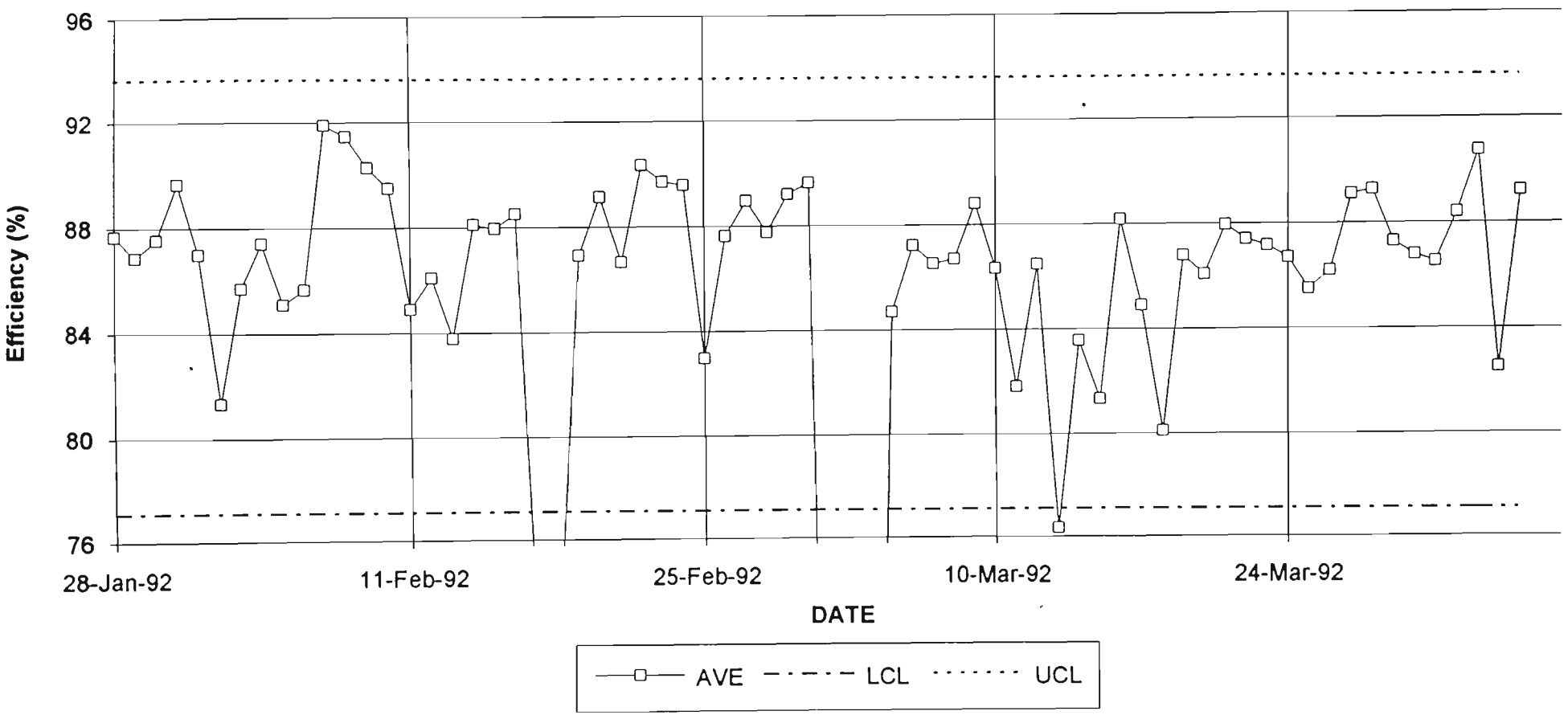


Figure 93. 42m/c DAILY AVERAGE EFFICIENCY AT 55% CULLET

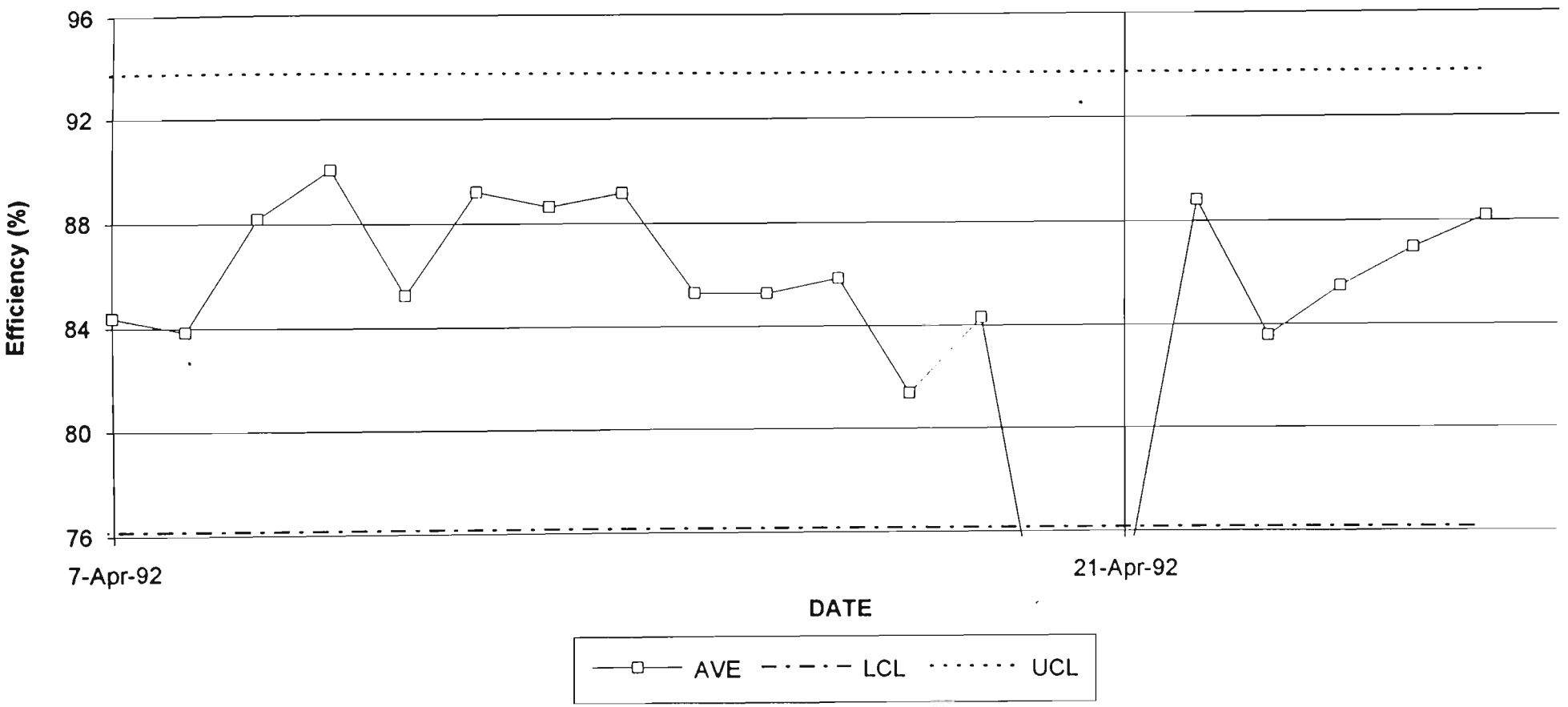


Figure 94.42m/c DAILY AVERAGE EFFICIENCY AT 60% CULLET

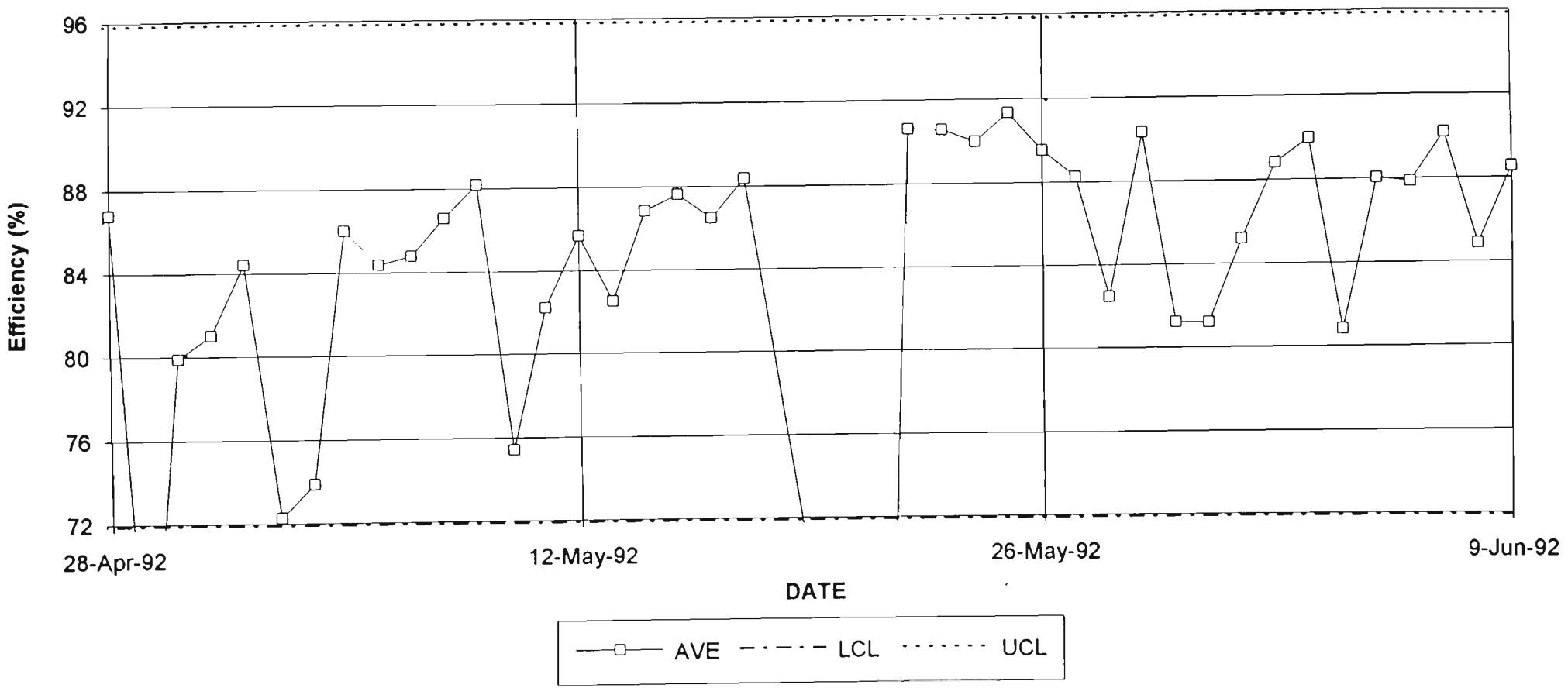


Figure 95. 42m/c DAILY AVERAGE EFFICIENCY AT 65% CULLET

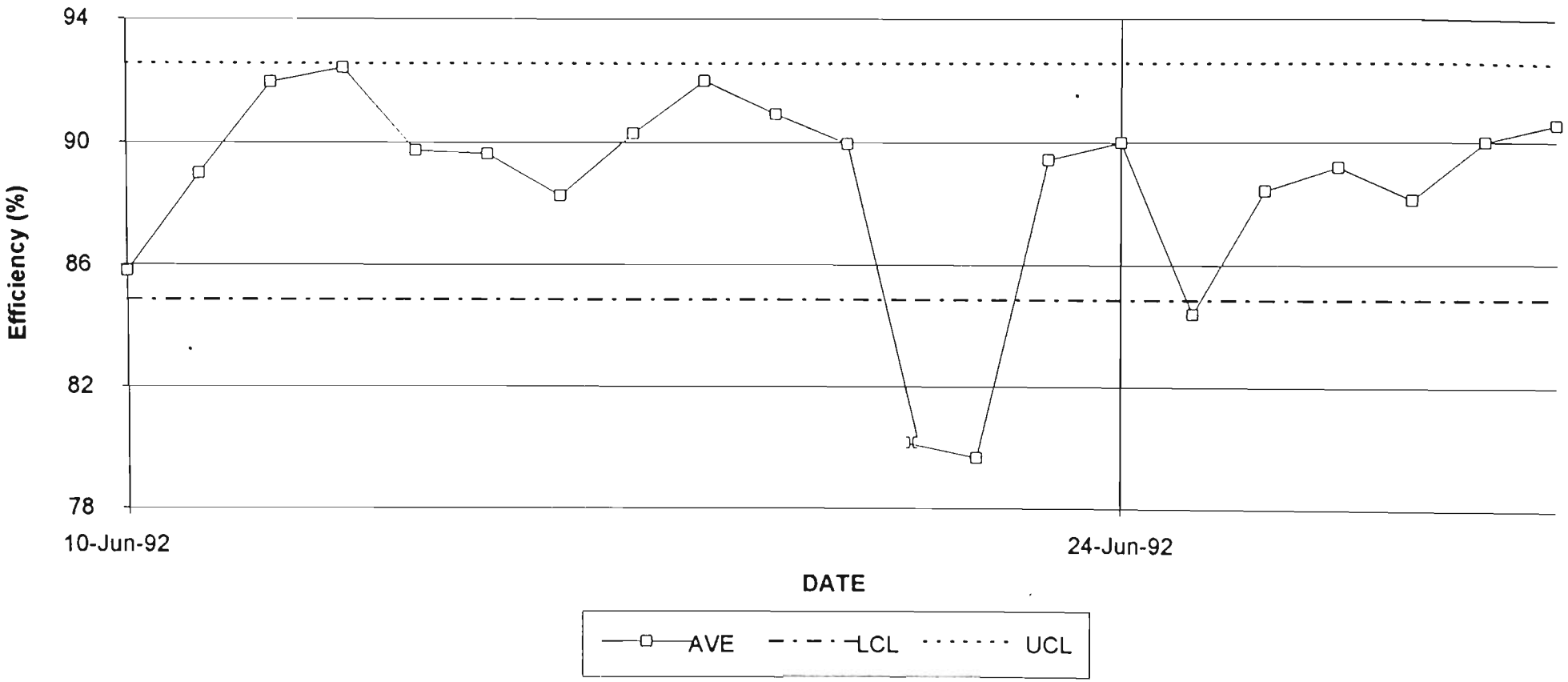


Figure 96. 42m/c DAILY AVERAGE EFFICIENCY AT 70% CULLET

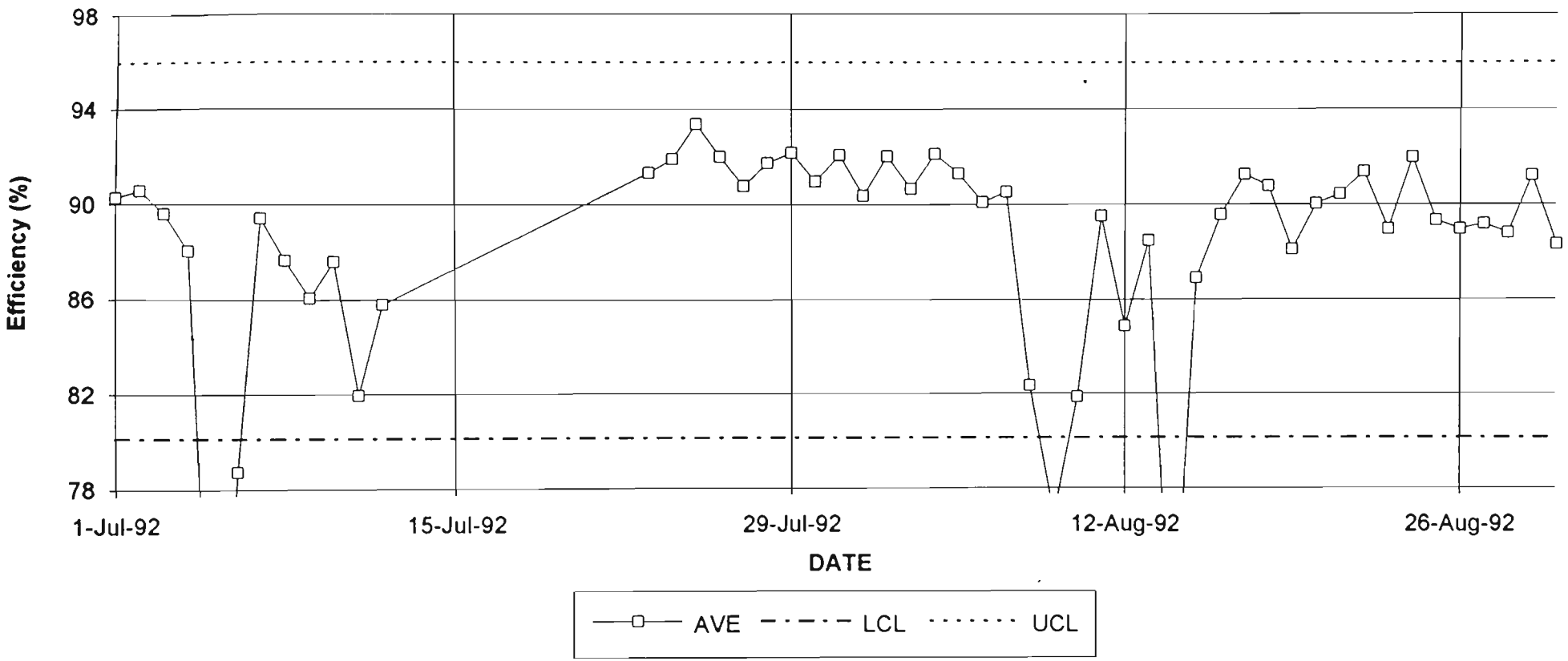


Figure 97. 42m/c DAILY AVERAGE BREAKING PRESURE AT 40% CULLET

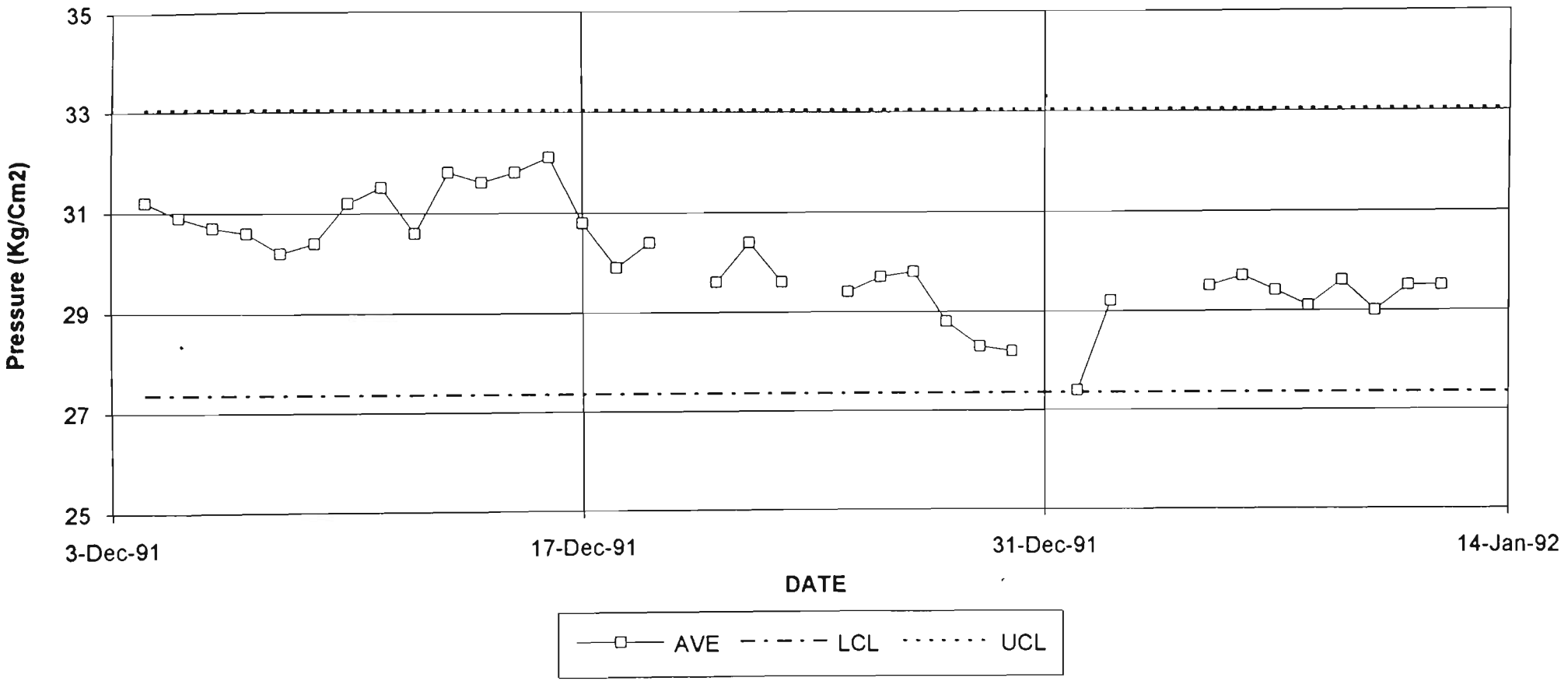


Figure 98. 42m/c DAILY AVERAGE BREAKING PRESURE AT 50% CULLET

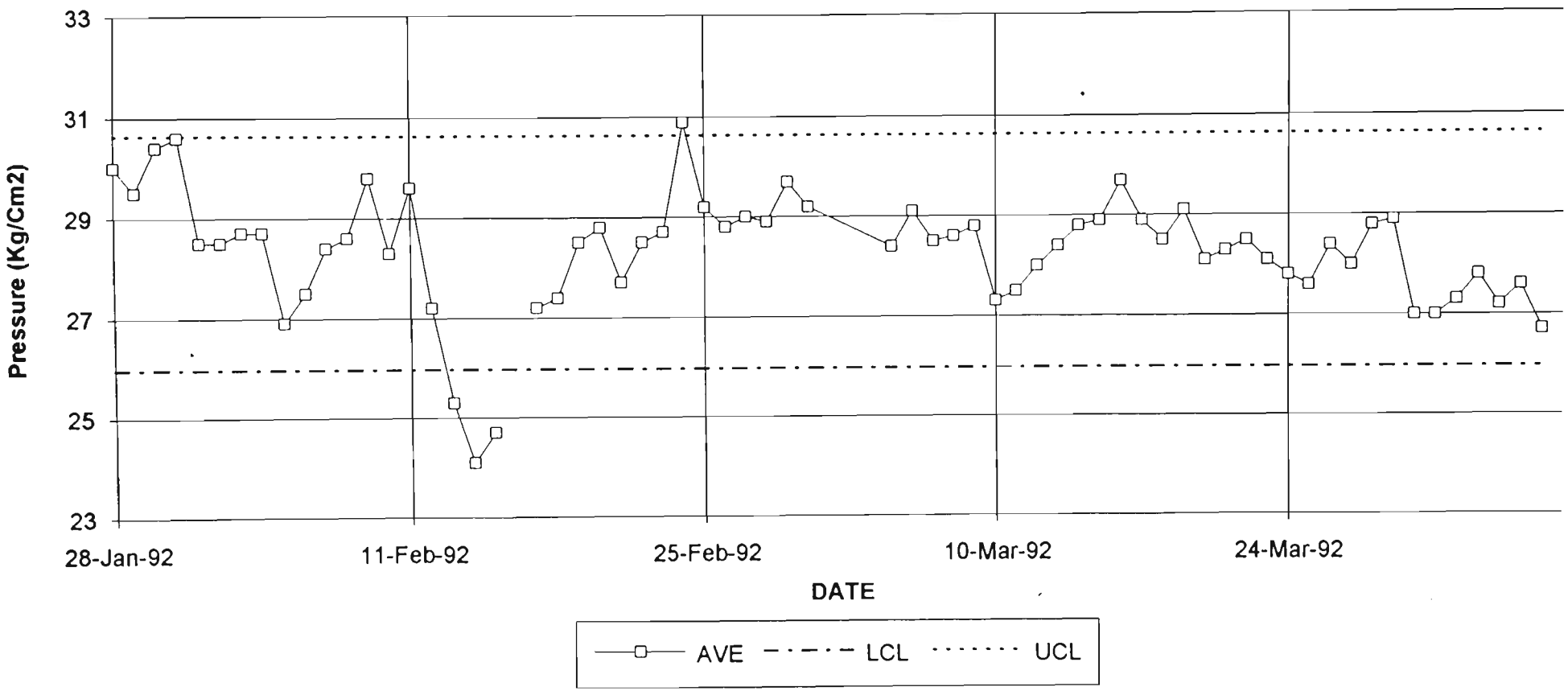


Figure 99. 42m/c DAILY AVERAGE BREAKING PRESURE AT 55% CULLET

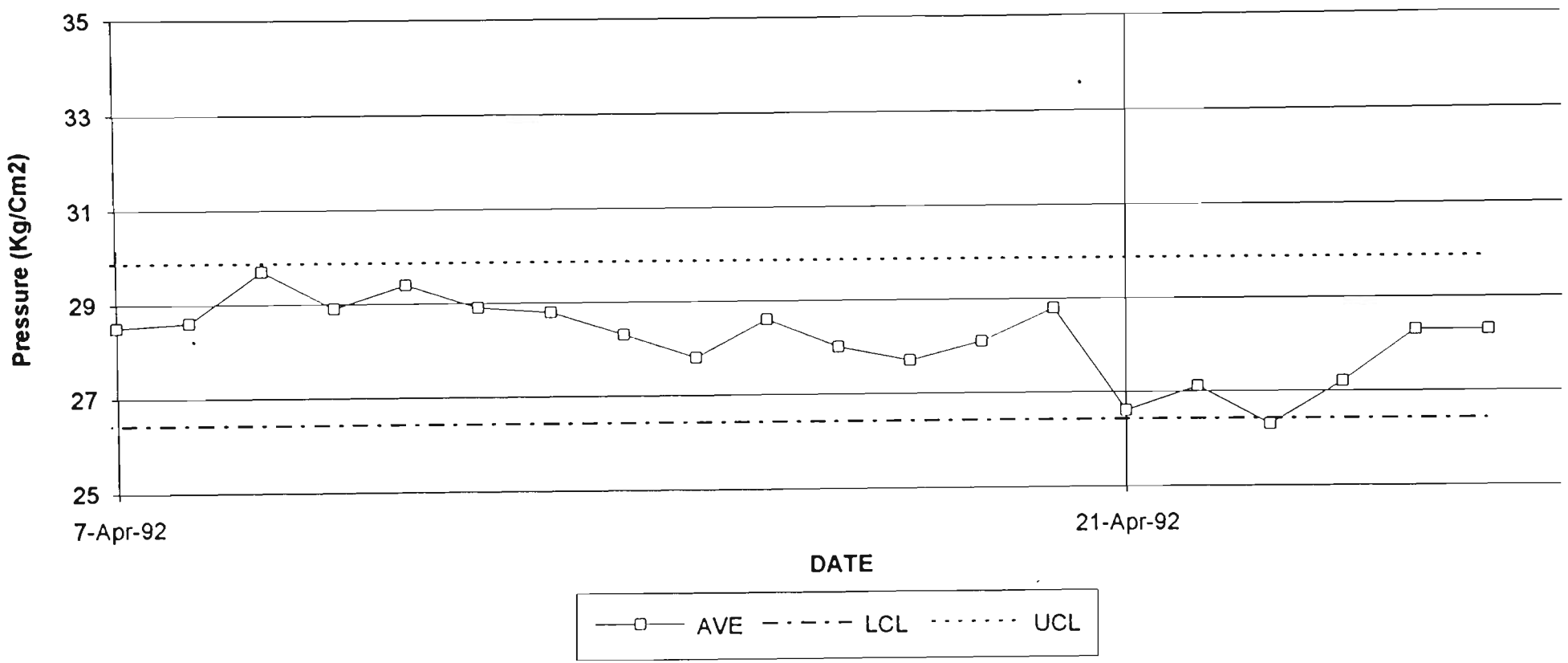


Figure 100. 42m/c DAILY AVERAGE BREAKING PRESURE AT 60% CULLET

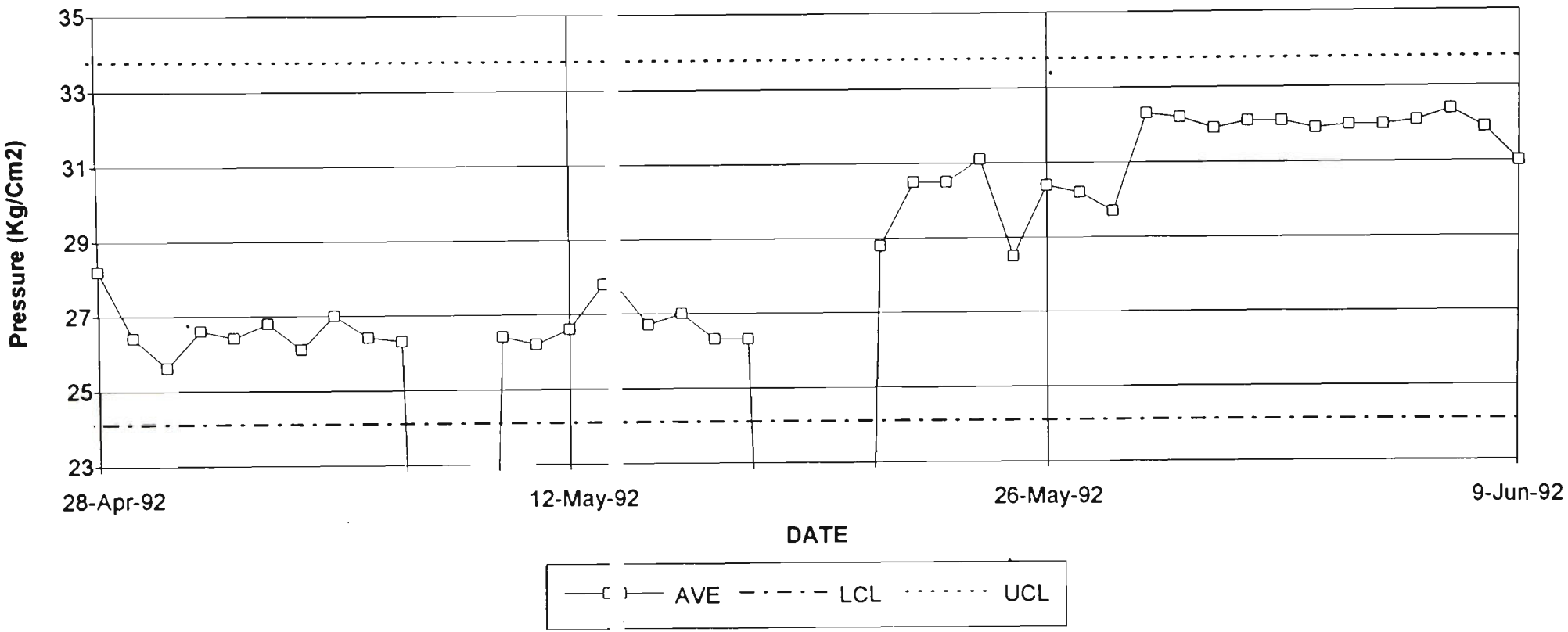


Figure 101. 42m/c DAILY AVERAGE BREAKING PRESURE AT 65% CULLET

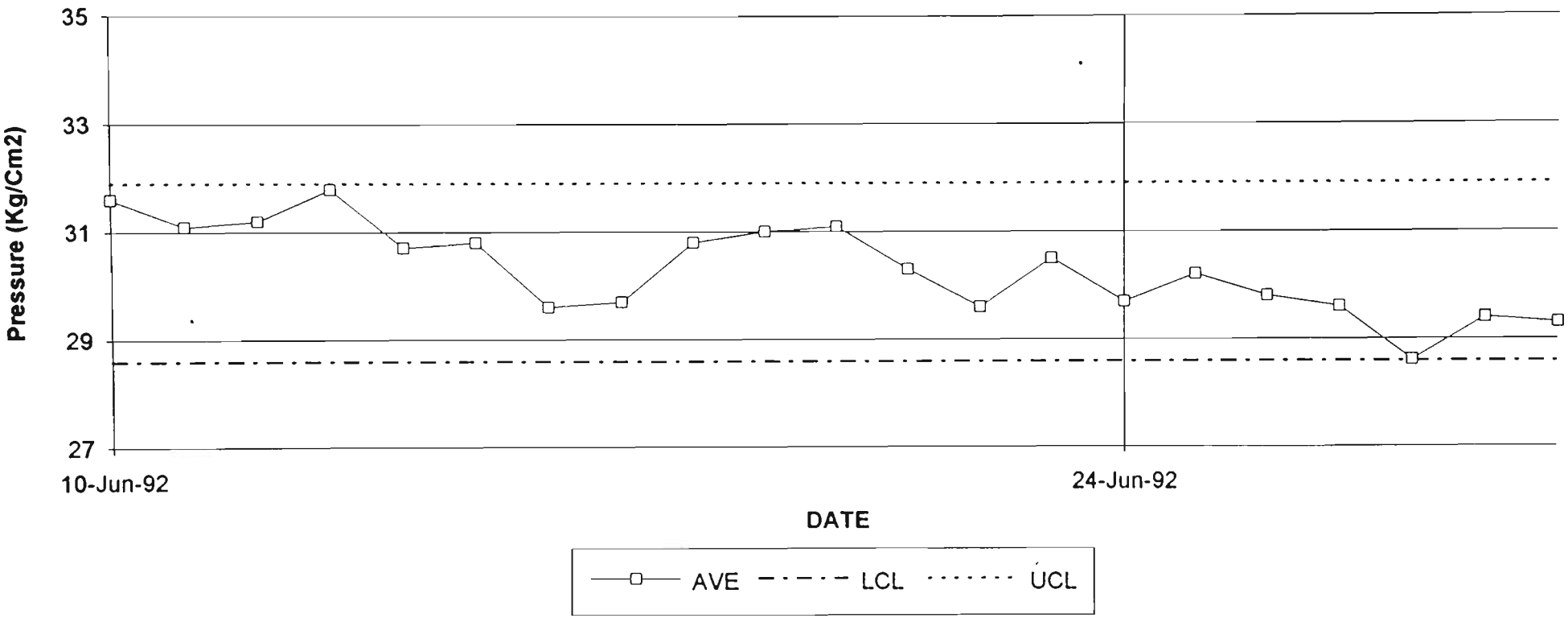


Figure 102. 42m/c DAILY AVERAGE BREAKING PRESURE AT 70% CULLET