An investigation into the novel application of high power ultrasound on the deinking of mixed office waste paper

Thesis

An Investigation into the Novel Application of High Power Ultrasound on the Deinking of Mixed Office Waste Paper

Jonathan Lane

A thesis submitted in partial fulfilment of the requirements of the Open University for the degree of Doctor of Philosophy

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Abstract

The current paper recycling processes are surveyed pointing out the major stages and the variety of chemical/mechanical treatments the fibres undergo. The reduction or replacement of chemical/mechanical treatments presents possible advantages in prolonging fibre life.

The results from recycled office waste which has been treated with ultrasound show a change in the particle size distribution of toner particles - making these particles easier to remove using established flotation techniques. Particle size distributions were measured using image analysis on thin (20gsm) paper handsheets. To establish the affect of sonication on fibres, a variety of virgin fibres were obtained from UK Paper, Sittingbourne.

Results from virgin fibres which have been treated using ultrasound indicate an absence of cutting compared to conventional techniques. Fibres were found to have the same average length (0.6mm) after ultrasound treatment as the control sample, refined fibres were reduced to approximately 0.3 mm in length. Freeness decreased in both virgin sonicated and refined sonicated samples. The decrease in freeness was accompanied by an increase in the strength properties of both categories of fibres.

Experiments with a prepared office waste furnish showed that ultrasonic treatment could decrease the size distribution of fused toner particles. The control sample had an average size of 80.9 μm, after 1 minute sonication this was decreased to 54.9μm, decreasing further to 46.8μm after 2 minutes sonication.

After demonstrating that ultrasound could decrease the particle distribution of the prepared office waste a more realistic and variable furnish was used. The experiments were conducted at room temperature, 50°C and 75°C. These temperatures were chosen to study the behaviour of fused toners as it approaches and exceeds its glass transition point, essentially the melting point of an amorphous polymer. It was found that the toner is easier to remove as the glass transition temperature is approached. Ultrasound is effective in breaking up large toner particles and detaching particles smaller than 25 microns in diameter.

Associated Studies.

1 Attendance of relevant international conferences and seminars.

- 11th Fundamental Research Symposium, "Fundamentals of Papermaking Materials", 21-26 September 1997, Robinson College, Cambridge.
- "Paper Recycling 96", International Conference organised by PPI, 6-10 December 1996, Lancaster Gate Hotel, London.
- Recycling 95, 40th EUCEPA Symposium, organised by PITA, 16-18 October 1995, Northern College of Music, Manchester.
- DTI Conference on Clean Technology, 22 May 1996, Willowby Hotel, Leicester.
- Fluidsonics Conference, organised by FFR Ultrasonics, 21 April 1995, Willowby Hotel, Leicester.

2 Attendance at meetings of

- Papermaking, Printing and Packaging Group of the Institute of Physics.
- Institute of Printing
- Polymer Group Symposium at University of Birmingham.

3 Visits to related exhibitions

- Papex 95, Exhibition of papermaking, 17-19 October 1995, Manchester G-Mex..
- DRUPA 95, International exhibition of printing, 1-10 May 95, Dusseldorf

4 Papers presented at

- 3P's Group of the Institute of Physics, 20 November 1997, Aylesford Newsprint, "Deinking of Mixed office Waste using Ultrasound"
- Poster presented at Flexo 97, 17-18 April 1997, NEC Birmingham.
- DTI Conference on Clean Technology, 22 May 1996, Willowby Hotel, Leicester, "High Power Ultrasound in Paper Making".
- Paper and demonstration during British Print Week, 21 November 1995, LCPDT, "Novel Deinking Techniques in the World of Paper Recycling"

5 Visits to Related Companies

- Aylesford Newsprint,
- UK Paper Sittingborne,
- UK Paper, Kemsley Recycling Facility,
- James Cropper Mills, Cumbria.
- Coates Inks, St Marys Cray.

Aims

The aim of this study is to investigate the interaction of high power ultrasound with toner particles and chemically treated paper fibres in a mixed office waste furnish to study the removal of toner particles by ultrasound action. In order to conduct a detailed study, a literature survey of the recycling of paper and previous applications of ultrasound to deinking was undertaken.

- To investigate the deinking of toner printed office waste in the absence of chemicals by the application of ultrasound.
- To investigate the effect of ultrasound on virgin fibre characteristics.

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1.0 Introduction

A result of the demand for fast, high quality office printing has been an increase in the amount of mixed office waste paper.

Mixed office waste is a source of high quality waste paper.[1] It consists of coated or uncoated wood free paper that has been printed using non-impact printing method.

The inks used in the printing process contain thermoplastic resins. These resins produce tough, rub-proof films when fixed to the paper by a combination of heat and pressure.[2] The ink forms large (>40 microns) particles during pulping which are difficult to remove by conventional ink removal techniques..

Within the last 5-10 years the need for quality waste paper has meant the pressure to reuse and recycle quality grades such as mixed office waste has increased. Research into different techniques of removing the toners from the fibres has produced agglomeration chemicals, magnetic deinking, and enzyme deinking.[4,5] Ultrasound offers a method of breaking down the large plate-like particles and detaching them from the fibres.

The first use of ultrasound in paper deinking was in 1979.[111,112] These experiments demonstrated that using ultrasound produced using a whistle generator could detach toner particles without the addition of chemicals. Unfortunately the action of the whistle generator cut the fibres resulting in unacceptable loss of fibres during deinking.

In this investigation high power ultrasound has been used without addition of chemicals to break down and detach fused toner particles into sizes that can be readily removed in the commercial deinking systems.

In the introductory chapters the pressures to recycle mixed office waste are debated. In chapter 2 commercial deinking systems are examined and the particular problems that non-impact printed waste presents to the deinking process are discussed. A review of the nature of ultrasound and where ultrasonics are commercially employed has been presented.

2.0 Background to Recycled Paper Production

In this chapter the background to the recycling of paper will be examined. Recycling and reuse of resources within the paper industry is not a new development but has been practised since the beginning of modern papermaking. The reasons behind the recent increase in paper recycling and some statistics to demonstrate the increase in paper use and re-use will be explained.

2.1 Legislation and the Pressure to Recycle Paper.

In the eighteenth century paper was made from linen rags collected from refuse and pounded to separate the fibres, then formed into sheets of paper. A popular but anonymous rhyme survives to this day.[6]

Rags make paper
Paper makes money
Money make banks
Banks make loans
Loans make beggars
Beggars make rags

Woodfibre was used to make paper for the first time in the nineteenth century, mainly because the supply of cotton rags could not keep pace with rising demand. Recycling of woodfibre rapidly became important to countries without large forest reserves but with a high demand for paper, such as in the UK. Initially, the recycling of paper was primarily due to economic reasons rather than environmental issues.

The main source of fibre in the UK is now in fact waste paper, and not virgin fibre.[7,8] During the second World War severe restrictions were imposed on the use of paper, waste paper was collected and recycled. This recycling involved simply the repulping of paper and reforming it into new sheets. As no ink removal was attempted, the result was a very dark sheet of paper. During World War II approximately 50% of all paper was recycled.[9]

The recycling of paper and board has continued since the war, with the added impetus of public concern over environmental issues. The shortage of landfill and use of fossil fuels forced many industries to become more "environmentally aware." The paper industry was more established than other industries in its recycling activities but did not publicise them.

As a result the public image of paper with regard to environmental issues suffered. Environmental concern grew amongst consumers, partly because paper recycling was seen as something that everyone could become involved in.[14] This concern transformed itself into a political response, with many different legislative initiatives.[147] There are mandatory recycling limits set in many USA states, the German packaging ordinance,[148] Belgian eco-tax,[148] and recently the UK landfill tax. Politicians managed to appear both environmentally conscious, and raise money for their treasuries. The UK landfill tax is expected to raise around £450 million each year.[10]

Other taxes were ostensibly environmental in their aim, but were in fact, directed at the protection of local interests, the Belgian eco-tax being the most obvious of these.[11] In America, the Federal Government has directed that all federal purchases of paper should have a significant recycled fibre content.[12] This executive order, which came into force in October 1993, specifies that printing and writing grades that are purchased by federal agencies must contain at least 20% post consumer waste from December 31st 1994, with an increase to 30% on December 31st 1998.[13] The printing and writing grades specified include high speed copier paper, offset paper, computer printout paper, file folders, carbonless and white envelopes. The executive order gives the American Environmental Protection Agency (EPA) power to set guidelines. The EPA defined three types of recycled materials. The first type is 'recovered materials', which includes mill broke, in-plant scrap as well as all post consumer materials.[14] The second type is 'post consumer recovered waste', which includes paper products that have served their purpose and would otherwise be destined for landfill. The final type defined by the EPA is 'wastepaper', which includes a combination of mill broke products, finished paper products from obsolete inventories and post consumer recovered material.

2.2 Paper Recycling Statistics

Statistics on secondary fibre are only available after a time lag of around 3 to 6 months. The terms recycled paper, recovered paper, waste paper, are all used to describe the collection and re-use of paper. In this thesis the term secondary fibre will be used to distinguish between virgin (fibre which has never been reused) and recovered (recycled within the manufacturing process) or recycled (fibre that has been printed and reused).

The global consumption of paper and board products was 210 million tons in 1995, and is forecast to grow to 418 million tons by the year 2010. Globally the market for paper and board can be divided into three major regions, North America, Western Europe and Asia. These three areas consume around 90% of all paper and paperboard. Asia can be further broken down into Japan and other Asia. North America and Western Europe consume 57% of the global production of all paper.

Printing and writing (P&W) grade consumption closely follows economic growth. Correspondingly most of these papers are consumed in the First World. Table 2.1 below gives some indication of the changes that can be expected in the future of P&W grades.[15]

Country	Demand 1995 %	Projected Demand 2000 %
North America	32	32
W Europe	29	28
Japan	13	13
Asia	18	19
Other Europe	3	3
Latin America	4	4
Africa	1	1

Table 2.1 Printing and Writing Grades Forecast

Emge & Co. have revised their forecast figures for the world consumption of printing and writing grades in the light of the SE Asia economic problems. P&W consumption was forecast to increase globally by 4%, with Asia increasing its share of these grades by 7.5%. Forecasts now predict P&W will grow by 1.3% during 1998, and 1.6% in 1999. A dramatic slowdown on previous figures but the world demand for P&W grades is still forecast to increase from 88 million tonnes to 90.4 million tonnes during the period 1998-2000.

When discussing secondary fibre production and associated statistics, the terms recovery rate and utilisation rate are frequently used. Recovery rate defines the amount of paper that is collected and reused. It is usually given as a percentage for a particular country and represents the amount of paper collected against the amount of paper consumed in that country. Utilisation rate is the amount of recovered paper that is used to produce paper against the amount of paper consumed. It is possible to have a higher utilisation rate than

recovery rate, that is to use more secondary fibre than is collected in the country. If this occurs then the country is a net importer of wastepaper.

The recovered paper business has suffered in the past from wild fluctuations in the price of wastepaper.[16] Wastepaper prices are affected by its supply and demand. The availability of secondary fibre differs from virgin fibre production. Trees can be left standing during periods of low demand but secondary fibre cannot be stored indefinitely and if not collected it is usually sent to landfill or incineration. Waste paper which is not collected today is unlikely to be available for collection tomorrow.[17]

Grading of wastepaper will be discussed later in this chapter. The different grades of wastepaper have different recovery and utilisation rates. Table 2.2 below gives the information for the global paper industry in 1994.

	Paper Production 10^6tons	Recovery 10^6tons	Utilisation rate %
Newsprint	33.9	12.5	36.7
Printing and Writing	82.6	7.3	8.9
Tissue	16.3	6.6	59.0
Corrugated	76.1	48.5	63.8
Cartonboards	28.1	17.6	62.5
Other paper and boards	34.5	13.0	37.8

Table 2.2 Utilisation Rates for Grades of Paper 1994

The average global recovery of all paper grades was 117 million tons, with a recovery rate of 42% in 1995. Newsprint and corrugated grades are well recovered globally. These figures show how effectively these sectors of the paper industry reuses its waste. Newsprint is collected from printers and consists of over-issues. Corrugated grades provide bulk. As the main strength of corrugated grades comes from other components the corrugation can be of poor quality fibre. Tissue collection rates are the amount recovered from converters and producers, this material is not post consumer, but would otherwise be lost to landfill or incineration. Printing and writing grades currently have a low recovery rate.[26] Most of this paper is recovered from printing houses and paper converters. This paper would be in the form of shavings and cut-offs of control strips. To increase the amount of paper recycled in the printing and writing grades more collections would have to be made from offices. Unfortunately this recovered paper could include non-impact

printed waste, as well as contraries, such as food, toner cartridges, and plastics.

Paper mills in America increased their use of recovered paper by more than nine percent in 1996, helping raise the U.S. paper recovery rate to an estimated 44.8 percent in that year. U.S. mills increased their utilisation of recovered paper from 31.4 to 34.3 million tons from 1995 to 1996 (according to preliminary estimates by American Forest And Paper Association (AF&PA)). The AF&PA has set a target of 50% recovery rate by the year 2000.[18] Achieving this goal will depend on several factors, including expanding office paper recovery programs as well as tapping into new sources.

It is important to note that not all paper is able to be recycled or is worth recycling, for example wallpapers. Some paper is always lost to the recycling process for a variety of reasons, e.g. cigarette papers, hygiene papers, papers used as electrical insulators.

In conclusion the amount of paper that is produced seems set to increase into the year 2000 and beyond. The amount of paper that will be recycled also seems set to increase as paper mills seek to safeguard a valuable raw material, and as more governments set mandatory recycling targets. The increases in the amount of paper recycled will not be evenly spread across all types of paper. Newsprint is a sector that already collects and recycles a significant quantity of paper. Forecasts express the opinion that printing and writing grades will increase their use of recycled fibre. The printing and writing sector of the paper industry currently uses less than 10% of recycled fibre. This percentage will increase and the extra paper for this increase will be mixed office waste - currently a poorly collected resource.

2.3 Introduction to Recycling -Categorisation of Waste Paper

Waste paper is sorted and categorised into various grades.[19,20,21] The sorting can be done at source or by a wastepaper merchant. Sorting of paper increases its value by removing any unwanted papers, plastic and other non-cellulosic materials. The drawback is that sorting is expensive. Sorting of paper at source is cheaper than sorting at the merchants. However, sorting paper at source cannot guarantee that it will not include unwanted material, as sorting is not supervised by trained personnel. Most mills, irrespective of the

type of paper produced obtain their waste paper from a merchant. Merchants obtain the paper from four sources, industrial, commercial waste, office waste, and household waste.

Grading of wastepaper assists mills in identifying their raw materials. Wastepaper cannot be sorted into differently printed types, for example, lithographic or xerographic printed, but is sorted into grades. Wastepaper cannot be sorted into printed types because the post press stages add material that is difficult to classify. For example, a glossy magazine will have a coated art paper as the cover, printed with quality four colour lithographic printing, the rest of the magazine will consist of a part mechanical grade which can be coated also printed by the lithographic process. Inserts in the magazine will include adhesives to stick gifts, samples, etc. Other inserts may include plastic coverings, laminates, and papers printed using other processes.

Wastepaper grades tend to be country specific. The UK structure is given in table 2.3.

Group 1	Best white shavings, fine shavings, white and cream shavings, and white coated shavings
Group 2	White unprinted, white duplex and other mechanical wood pulp cuttings, slightly printed white card cuttings, best one-cuts, printed woody one-cuts, white and light tone shavings, white and coloured shavings
Group 3	White and lightly printed scanboard
Group 4	Ledgers, white and coloured heavy letter, white and coloured continuous stationary waste, white and coloured carbonless copy paper, quire, best white pams
Group 5	Over-issue news, once read news, over-issue white and coloured woody pams, news and pams, telephone directories. and soft covers, once read woody pams.
Group 6	Buff envelope cuttings buff tabulating card, coloured tabulating cards, light brown and buffs
Group 7	Double lined Kraft and new KLS cuttings
Group 8	Container waste (old KLS)
Group 9	Mixed papers
Group 10	Coloured card
Group 11	Contaminated grades

pams = Pamphlets and Magazines
KLS = Kraft LinerS

Table 2.3 UK Wastepaper Grade Structure

The higher quality grades are at the top of the table and the poorer quality, cheaper grades at the lower end. Groups 1 to 4 would be used in printing and writing grades. Groups 7 to

11 would be used in packaging as corrugating materials. As can be seen the structure of the grades is fairly disorganised, demonstrating the difficulty in separating different types of printing. Grades 1 to 4 are generally unprinted or printers waste, this segment of the market is well collected and recycled.

Group A - Ordinary qualities	
A0	Unsorted mixed wastepaper
A1	Mixed papers and boards(unsorted)
A2	Mixed papers and boards(sorted)
A3	Board cuttings
A4	Supermarket waste
A5	Corrugated container waste
A6	New shavings of corrugated board
A7	Over issue pamphlets and magazines
A8	As above (free from adhesive)
A9	Mixed news and pamphlets
A10	As above, free from adhesive
A11	Mixed pams and magazines

Group C - High qualities	
C1	Mixed light coloured printers
C2	Light coloured woodfree shavings
C3	Coloured tabulating cards
C5	Buff tabulating cards
C6	Mixed white letters
C7	White woodfree letters
C8	White woodfree continuous letters
C9	As above free from colouring
C10	Printed white multiply board
C11	Unprinted white multiply board
C12	White newsprint
C13	White magazine paper
C14	White woody coated paper
C15	White woodfree coated paper
C16	White woody shavings
C17	Mixed white shavings
C18	White woodfree shavings
C19	White woodfree shavings uncoated

Group B - Medium qualities	
B1	Once read news
B2	Over issue news
B3	White lined board cuttings
B4	Mixed coloured shavings
B5	Bookbinding shavings
B6	As above without adhesive
B7	Coloured letters
B8	White wood free books
B9	Bookquire
B10	Best coloured pams
B11	White carbonless copy papers
B12	Coloured carbonless copy papers
B13	Coated board

Group D - Kraft qualities	
D0	Brown corrugated
D1	Corrugated Kraft I
D2	Corrugated Kraft II
D3	Used Kraft sacks
D4	Clean used Kraft sacks
D5	Used Kraft
D6	New Kraft

Table 2.4 European Wastepaper Grading Structure

The European grading system, shown in table 2.4, divides the waste into four distinct categories, with chemical pulps in Group C (high qualities) and mechanical pulps in group B (medium qualities). Kraft and liner board is found in Group D. Each of the groupings is graded. This structure is more organised than the UK gradings, but still does not allow mills to buy just post consumer photocopier paper, for example.

A mixed office waste mill would work with the grades found in group C, these grades are capable of being deinked, and are wood free.

2.4.0 Secondary Fibre Preparation

Virgin fibre is not intended to be reused because the raw materials that go into the construction of paper and board products are not chosen for their ability to be recycled.[22,23,24] The recycling of paper brings problems because chemicals and other additives used in its manufacture can interfere with any subsequent reuse. Products made from recycled fibre must compete with those made from virgin fibre, and must meet technical specifications, such as those defined by burst, tear, and smoothness tests.

Papermakers do not normally make recycled paper just to be environmentally friendly, but rather because there is a significant difference in the cost of the raw materials. Recycled paper will not sell just because it is recycled but must compete with other products on quality and price. Mixed office waste is in demand as a raw material for paper making as the fibres have already been bleached, and so have high brightness.

Paper recycling is basically a laundering process.[25,29] The adhesion of ink to paper is due to chemical, mechanical, electrostatic and Van der Waals forces. Deinking is a two stage process, where the ink is first detached from the fibres and then removed from the pulp.

To produce high quality deinked pulp, mills must use specialist equipment.[27,28] There are four ink removal processes involved in the recycling of fibres. These processes are washing,[30] flotation,[31,32,33] cleaning,[34,35] and screening.[36,37]

Paper and board are a complex amalgam of cellulose fibres, inorganic components such as fillers, and organic chemical additives. Secondary fibre treatment involves the selective removal of contaminants.[28] The removal of objects such as wire bindings, stones, plastic bags and inks is obvious. These contaminants are detrimental to the quality. However some of these "contaminants" are beneficial, such as the mineral clays used in loading, and would ideally be retained for reuse in the finished sheet.

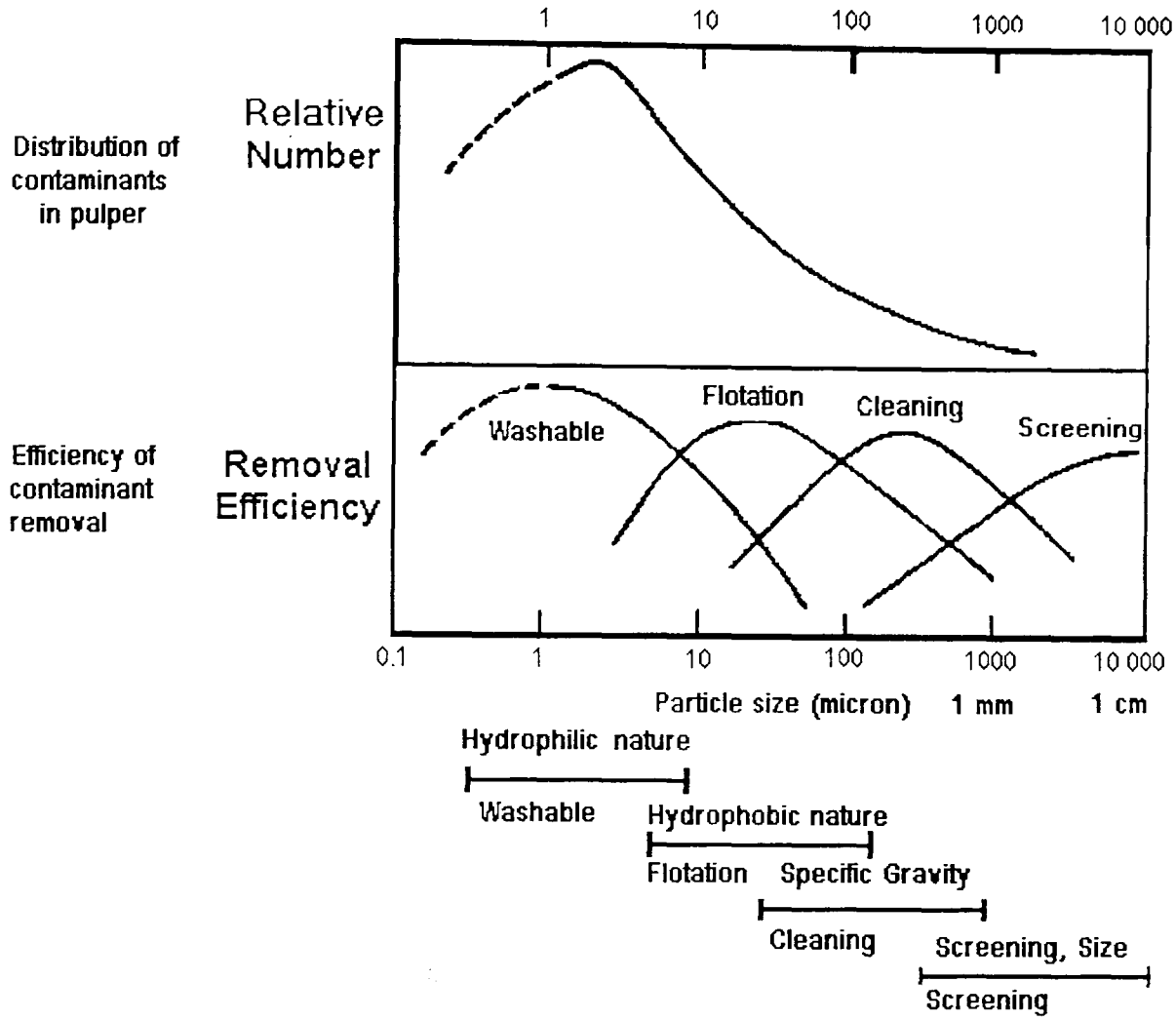


Figure 2.1 Ink Particle Size Removal Chart

Due to the variable size, shape and density of the contaminants each process removes different components.[38] It should be noted that particles of approximately 50μm size are visible to the average person's unaided eye; below this size magnification is required to observe their presence. Optical microscopy allows objects to be identified to approximately 1μm. Below this limit light waves are longer than the objects under observation, and special techniques such as electron microscopy must be used.

Washing removes the smallest contaminants, well below the visual level. Flotation removes particles that are larger, just entering the visual level. Particles below the size of optical recognition do not contribute to the "speckiness" of a sheet but do contribute detrimentally to its overall brightness. Speckiness is quantifiable as the number of visible particles; these particles detract from the overall brightness and make the sheet of paper look soiled. The speckiness of the paper can also contribute to the poor printability. Certain particles, particularly toner particles can soften on heating and attach to rolls and press blankets. If the particle is large enough or sticky enough it can cause the paper web

to break. Rethreading a paper machine after a paper web break is time consuming and costly. Screening and cleaning remove particles larger than the visual limit. Screening is incorporated in all mills to remove large contaminants that would cause abrasive wear to machinery.

2.4.1 Pulper[21]

Before the recycling of paper can begin the sheets of collected paper must be broken down into individual fibres. The first step in the recycling of paper involves a pulper, (see figure 2.2). There are many different types of pulper design, including circular tanks, D style, and vertical pulpers. The pulper, of whatever design, is a large vessel where the secondary fibre to be recycled is added to water. At the base of the vessel are large rotors, these rotors circulate the water/paper mix and cause the fibre web to break down into discrete fibres; this is known as defibring. The water added to the pulper can contain chemicals, usually a pH control agent, a bleaching agent and a surfactant. The exact mix of chemicals will vary from mill to mill depending on the papers being recycled. Pulpers can be operated as a batch or continuous process. They are usually characterised as being either high or low consistency pulpers. Consistency is measured as the ratio of the mass of oven dry fibre to pulp expressed as a percentage of the volume of stock sampled. Low consistency is usually held up to 8%, high consistency above 10%. High consistency pulping holds some advantages which include more effective use of bleaching chemicals, saving in energy costs and decreased fibre cutting.

The mechanical forces in the pulper also promote the detachment of the ink from the fibre by fibre-fibre abrasion. The extent of pulping is important as it is the main factor in determining the particle size distribution of the pulp. On completion of the pulping the separated ink particles are then removed by a combination of size dependent removal processes.

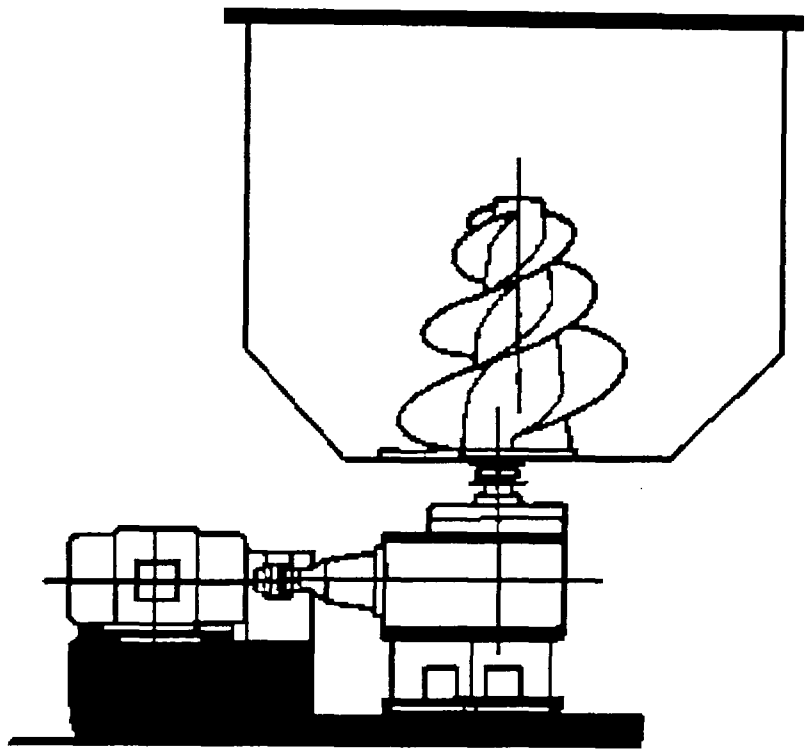


Figure 2.2 Pulper

2.4.2 Screening

In the screening and cleaning processes contaminants are removed from the fibre suspension by purely mechanical means.[36] Screens are generally designed to remove contaminants greater than 150μm in diameter, see figure 2.3. Screening relies on passing the fibre suspension through meshes of varying sizes and shapes allowing the contaminants through while retaining the fibres. The perforated area is known as the basket. The coarsest screening removes the largest contaminants, in the size range of millimetres, and may consist of a drilled plate positioned after the pulper. Baskets with holes are generally used in coarse screening to remove flat contaminants such as un-defibred paper or ink flakes. Hole sizes are typically 1.0 to 2.0mm diameter. To remove smaller contaminants slotted baskets are used.

Two forms of screening can be employed, high consistency and low consistency screening. Coarse screening is performed at a consistency of around 4 to 5 %. Intermediate size screening is performed using slotted baskets with the stock at high consistency.

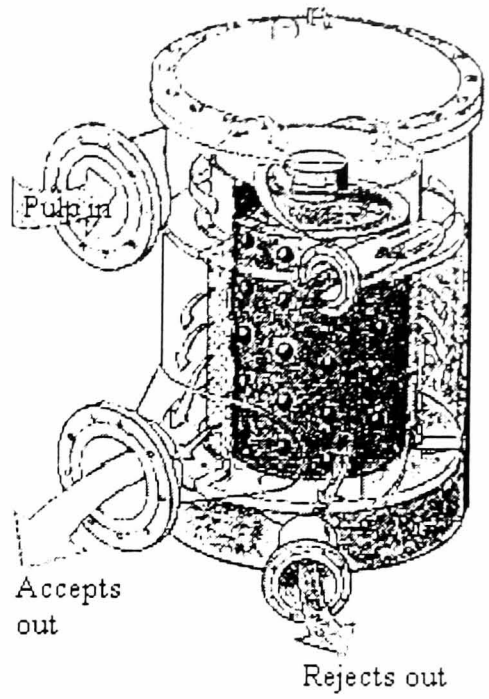


Figure 2.3 Cut-away view of a screen

Fine screening is normally carried out after deinking by forcing the pulp through the screens under pressure. It is carried out at a lower consistency, normally between 1.0 to 1.5%. The slots employed have widths of between 0.20 to 0.50mm.

2.4.3 Cleaning

Cleaning is more properly known as centrifugal cleaning. Cleaning separates contaminants whose densities are significantly different from those of fibre and water.[34] Two types of cleaning can be employed, high consistency cleaners or low consistency cleaners.

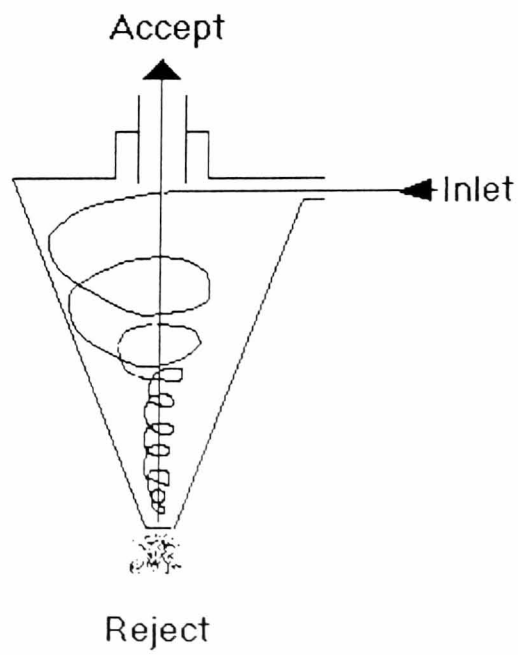


Figure 2.4 Diagram of Hydrocyclone

Centrifugal cleaners rely on the flow of pulp into a chamber, (see figure 2.4). The hydrocyclone, patented in 1891, causes a vortex to develop within the chamber. This vortex results in the dense particles migrating to the outside of the vortex, while the lighter particles move to the inside of the vortex. At the bottom of the cleaner the flow of pulp is reversed and the stock flows up the centre of the cleaner towards the exit. The dense material that is thrown outwards is rejected. Particle settling velocity is proportional to particle size. Smaller particles with slower settling velocities are more difficult to remove. Rejects are controlled by altering the size of the orifice at the base of the cleaner and hence the pressure within the chamber. Cleaners are usually mounted in banks to maximise the flow of pulp through the cleaners.

High consistency cleaners remove dense contaminants such as stones and metal objects that have a significantly higher density than that of water. High consistency cleaners are included even when the mill uses a virgin furnish, to remove particles that may cause abrasive wear to pumps etc. They are installed near to the pulping stage to minimise the damage to other machinery. These cleaners operate using a low pressure drop, and typically reject material with a size of 2 mm or larger.

Low consistency centrifugal cleaners are used to remove contaminants that are less dense than water such as ink and adhesive particles. Removal of these contaminants can only occur if the particles to be removed have a density of less than $800kgm^{-3}$.

Low consistency cleaners are arranged in banks so that the accepted stock cascades from one into another. The rejects from the first stage are fed to the second stage, acceptable fibre from the second stage is fed back to the primary stage. This system can involve three or four stages. This cascading allows fibre to be recovered and ensures that it is cleaned adequately. Rejects from the final stage are usually discharged to effluent.

Problems caused by stickies and pressure sensitive adhesives have prompted research into improved cleaner design to maximise their efficiency. One advance is the asymmetrical cleaner, which removes particles whose densities are very close to $1000kgm^{-3}$, and which have proved to be difficult to remove.[34] These particles are too small to be screened, too large to be washed, too heavy to be subject to flotation and too light to be reverse cleaned. They are known as 'swimmer stickies' and their removal represents a major problem for

the recycling industry.

2.4.4 Flotation[31,32,33]

Flotation is a technique that removes the separated ink particles from a suspension by attracting them to air bubbles.[39] This produces contaminants in a form that are highly concentrated with respect to the pulp suspension. Flotation relies on the surface chemistry of bubbles and ink to selectively remove particles. Effective flotation begins at the pulper where the degree of pulping determines the particle size distribution. The paper is pulped, usually under alkaline conditions, to release the ink from the fibre. The ink is released as a result of the fibre swelling in the alkali. Other chemicals can be added depending on fibre furnish, such as hydrogen peroxide to bleach the pulp, chelating agents to sequester any heavy metal ions present which would otherwise degrade the peroxide, and sodium silicate, which also helps stabilise the peroxide. Flotation is most efficient in removing ink particles in the range 10-100μm with maximum effectiveness for particles in the range 30-80μm.

Flotation cells differ in design and construction, but all work on the same principles. Pulp, at a consistency of around 1%, is mixed with air bubbles. The separated ink particles attach themselves to the surface of the bubbles. The bubbles rise to the surface of the flotation cell where they are removed as a froth. The froth can be removed by scraping, flowing over a weir or by air pressure.

The efficiency of the flotation process is affected by the size of the bubbles, the volume of air passing through the system, and the foam removal system. To improve the efficiency the number of collisions between bubbles and ink particles must be maximised. It is also important that the bubbles are stable because if they collapse the ink particles would be returned to the pulp slurry.

Chemicals used in the flotation cell are fatty acid soaps. These are blends of 16-18 carbon atom chains such as steric, oleic and linoleic acids.[40] Fatty acid soaps are supplied as sodium salts, in solid or liquid form. The sodium salt is converted to a calcium salt by displacement of the sodium ion by calcium. The calcium ions present in the water may be

sufficient otherwise calcium salts must be added. The calcium salts of the fatty acid form microprecipitates in the flotation cell as they are insoluble in water. Synthetic surfactants are specialised non-ionic surfactants that eliminate the need for the addition of calcium salts.[41]

The major losses of fibres in the recycling process occur at the flotation stage. The fibres are coated with fillers, such as calcium carbonate and these fillers present a hydrophobic area to the flotation bubble. Fibres attach to the hydrophobic bubble and are removed from the furnish.[41]

2.4.5 Surfactant Action

Surfactants or surface active agents are species that are active at the interface of two phases.[42] A surfactant accumulates between the phases and modifies the surface tension. In the recycling process, surfactant is a general term used to describe dispersants, collectors, and anti-deposition agents.

Surfactant molecules are composed of a hydrophilic component and a hydrophobic component. The hydrophilic portion of the molecule has an affinity for water, while the hydrophobic portion has an affinity for non polar materials. In deinking, the hydrophobic area will associate with the ink and dirt present whilst the hydrophilic portion will remain associated with the water. The classic theory of surfactant action is based on the formation of micelles, shown in figure 2.5.

The four major classifications of surfactants are: anionic, cationic, non-ionic, and amphoteric. Anionic surfactants are water soluble and develop negative ions. Cationic surfactants yield positive ions and are considered to be poor cleaners. Non-ionic surfactants are the most widely used for surface cleaning and are uncharged. Amphoteric surfactants develop a negative or positive charge depending on whether the solution is alkaline or acidic.

Anionic surfactants are good detergents, however, if they contain weak acid groups they can be made insoluble by hard water metal ions, such as calcium and magnesium.

Non-ionic surfactants, a separate class of synthetic surfactants, are prepared by attaching ethylene oxide molecules to a water-insoluble molecule. Depending on the number of ethylene oxides and the number of carbon atoms, the synthetic surfactants can be classified as a wetting agent, a detergent, or an emulsifier.

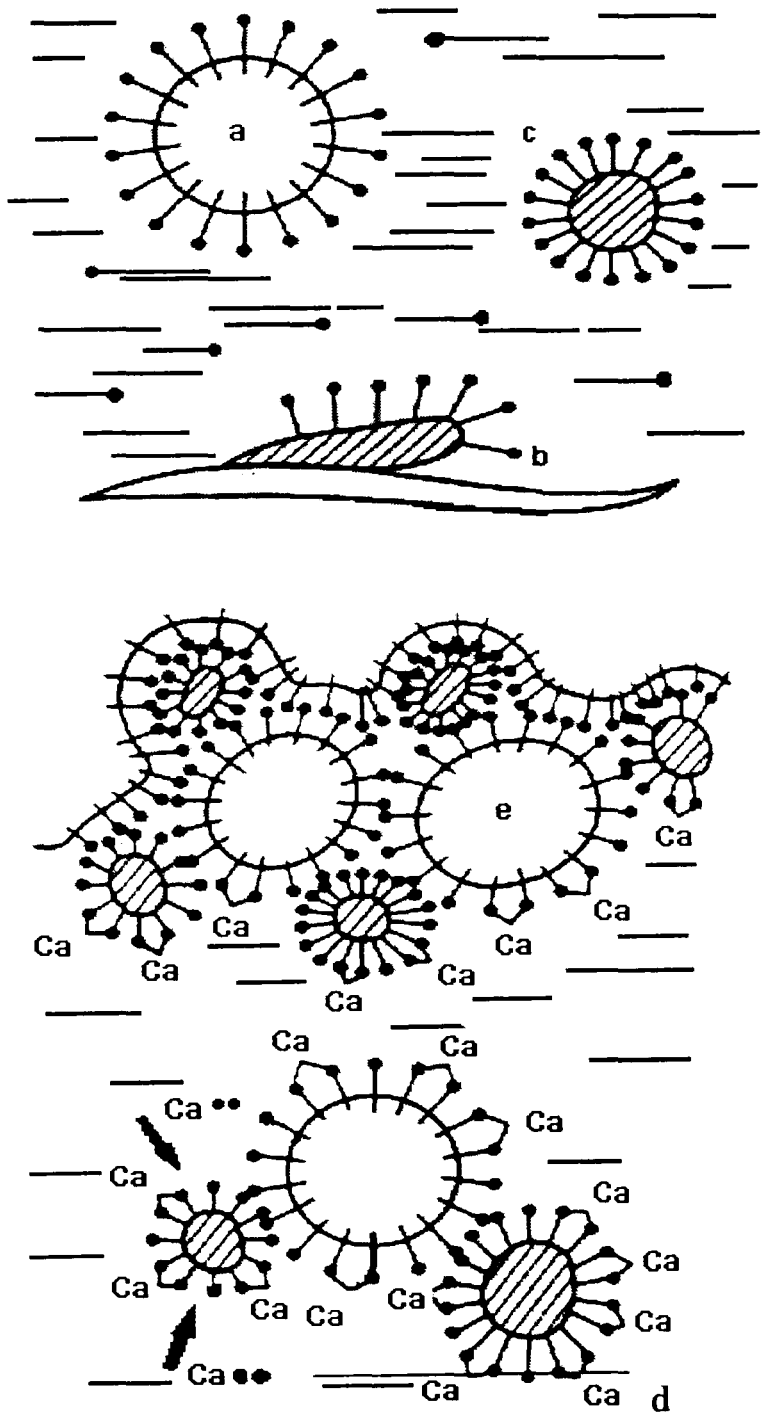


Figure 2.5 Surfactant action [43]

a Foam laden with ink particles
b Ink particles detaching from fibres
c Dispersed Ink particles
d Ink particles whose surface active agent (soap) has reacted with hardening constituents and can now deposit on air bubbles.
e Foam particles laden with ink particles

The hydrophobic tail of a surfactant can be straight chained, branched, long or short, double or single bonded. Each of these surfactants will have different properties and will react differently to prevailing conditions in a paper mill. A commonly used method of characterising surfactants is the Hydrophilic-lipophilic balance or HLB test. This is the value or percentages of hydrophilic to hydrophobic groups in the structure.[44]

2.4.6 Washing

Washing removes only small particles of separated ink. The particles most efficiently removed by washing are less than 10 μm in size.[45] To remove particles larger than this is possible but requires large amounts of water. Washing was traditionally used in the USA for deinking newsprint furnishes, where the ink consists of an easily dispersed oil-based vehicle. The technique was not adopted in Europe due to a difference in furnishes and more stringent restrictions on the use of water. Most mills operating today use a combination of washing and flotation, removing the larger particles by flotation and the smaller particles by washing.

Washing relies more on mechanics rather than on chemistry to remove particles from the furnish. The aim of the process is to trap fibres against a mesh or wire while allowing the contaminants to pass through. Washing removes all particles below a certain size, regardless of their chemical nature. The size of the particles removed is dependent on the size of the mesh and the washing device used.[46] The efficiency of washing is greatest for particles sized between 5 and 15μm, however removal of particles up to 25μm is possible. Particles smaller than 5μm are not removed as they tend to enter the lumen of the fibre, or adhere strongly to the fibre surface.

The chemistry of washing is much simpler than that of flotation. A surfactant is used to lower the surface tension, this allows the ink and loading to be more easily suspended in water. The most common surfactants employed are nonylphenol ethoxylate and linear ethoxylated alcohols.[47] The requirement for wash deinking is to keep the ink particles small and hydrophilic. The hydrophilicity of the contaminants is important otherwise the particles can redeposit on the fibres. Other chemicals are added prevent the re-deposition and agglomeration of the ink.

2.4.7 Dispersion[48,49]

Some mills incorporate a dispersion stage midway through the deinking phase. This allows particle sizes to be reduced, to promote removal by flotation or washing. Other mills use dispersion as a final 'polishing' stage to decrease the size distribution of the largest particles.

Dispersion subjects the pulp to high shear conditions at elevated temperatures. The shear is produced by forcing the pulp between interlocking teeth, that grind up the particles. A combination of high consistency, (20-40%), and high temperature (70-120°C) reduces the particle size distribution. Dispersion allows the presence of contaminants to be masked by reducing the ink particle size distribution to below the optical recognition limit. Dispersion decreases the particle size distribution by crushing the particles thus reducing the size but increasing the number of particles. Dispersion can also have a negative effect on the pulp quality, by shortening fibres, leading to greater fibre losses in any subsequent ink removal process.

2.5 Recycled Paper Formation

After deinking, the recycled pulp is reformed into paper. The formation of recycled pulp into paper is exactly the same as the formation of virgin fibre. A short description of the paper making process can be found in appendix 5.

2.6 Conclusions

There will be an increase in the amount of fibre collected for recycling with many countries setting higher targets for the recovery of paper. Established sources of waste paper are already well collected, and so waste paper merchants are looking to new sources. The much heralded 'paperless office' has failed to materialise and waste office paper looks set to be a main resource for increased collection. However, office papers do present some problems to recycling mills. Most office papers consist of xerox or laser printed waste known generically as non-impact printed (NIP) waste. The problems in recycling office waste are a result of the type of inks that are employed. These inks contain a strongly binding plastic that forms large flakes when recycled. These are discussed more fully in section 4.0.

3.0 Non-Impact Printing - An Introduction

Impact printing incorporates traditional printing equipment from typewriter mechanisms, producing a few pages an hour, to large web fed newsprint presses that produce thousands of copies per hour.[65] All of these processes involve the contact of an ink bearing image area, typewriter hammer or lithographic roll,[50] with the paper in order to transfer the ink to the paper. In *non-impact* printing as the name suggest there is no contact between the part of the press forming the image and the paper. Examples of non-impact printing include ink-jet, laser, photocopiers, digital presses, and dye sublimation printers. The term non-impact printing has become associated with the class of printers where the images and text are stored electronically, and this electronically stored data is used to direct the print engine.

3.1 Printing Inks

The conventional processes include lithography, letterpress, flexography and intaglio printing.[51] Conventional printing relies on the transfer of ink to paper via an image roll. The image roll may impact on the paper, as in direct printing or transfer the image to an intermediate roll, and thence to the paper; this is known as offset printing.

The pigments used in printing inks can be either organic or inorganic. The particle size distribution of the pigment is important. Pigments must be produced to a certain size distribution for each particular ink. Large particles should be avoided as they will appear as lumps on the final printed sheet thus reducing print quality.[66]

Non-impact inks differ from conventional inks in that in the majority of cases they are solid and not liquid. Toner compositions vary with machine manufacturer, but they generally consist of pigment, base resin, and charge control agent.[54] In non-impact xerographic printing the pigment is carbon black or iron oxide and the conventional vehicle is replaced with a polymer. The vehicle in non-impact inks is a solid, usually a polystyrene or styrene-acrylate resin in which the pigment is dispersed.[53] The resin is then formed into a powder with the correct properties for the toner. The toner must have a small enough particle size to be able to flow into the structure of the paper sheet, and have a suitable softening point for the printing process. The softening point of the toner is governed by the glass transition

point of the polymer resin. The glass transition temperature is an important factor in the recycling of these toners as the temperatures used in the recycling process can be close to it. Above the glass transition point the toner is more pliable and deformable. A more deformable toner can be removed from one fibre but can then re-adhere to others. The deinking efficiency is affected by the surface energy relationships between the toner, deinking surfactant and paper.

Removal of toner from paper fibres is inefficient when using conventional deinking. The detached toner forms large flat plate-like particles that range in size from 40 to several hundred microns.[52] In addition the detachment process is inefficient, leading to the production of toner-fibre aggregates. To remove the toner from the pulp two approaches have been taken:-

reduction of the particle size so that they can be removed by flotation or

increase particle size to enable the particles to be removed by screening.

Reduction of the particle size may be accomplished by using dispersion, as described in section 2.4.7. Increasing the particle size is more difficult but is usually achieved with a gentle pulping process and agglomeration chemicals to make the toner particles stick together.

Ink jet inks are liquid, often water or alcohol based.[55] The ink is fixed to the paper by evaporation and absorption into the surface. As the inks are water or alcohol based they present no problem with regards to removal in deinking. However the pigments or dyes can colour the paper fibres.

3.2 Recent Developments in Printing

'Computer to press' is used to describe the advances in digital printing.[55] 'Computer to press' signifies the production of an image plate or equivalent by digital means. The method is usually xerographic or its variant. Digital printing can produce high quality colour images where information can be changed at every impression. In addition there is virtually no 'make ready' time.

Conventional printing processes are capable of transferring huge amounts of data from a set of printing plates. The main problem in speeding up non-impact printing is in the

processing of data to get it into a form appropriate for printing. A secondary problem is fixing the ink to the sheet of paper. This is in contrast to the conventional process where the rate determining step is the speed at which the paper can be fed into the press. As toner is fixed using a heated roller, heat must be transferred over a wide area and the temperature must be raised to around 100°C - above the softening point of the polystyrene vehicle. Much of the applied heat is lost in heating the water present in the paper and not in fixing the toner to the paper.

3.3 Ink Jet printing

Ink jet printers are an important part of the non-impact printed market.[56] The method is reliable, quiet and able to print colour. The disadvantage is that it is relatively slow with regard to conventional laser printing, which is in turn much slower than the conventional printing processes. Ink jet printers rely on a water or alcohol based liquid ink which is propelled as small droplets toward the sheet of paper to be printed. Control of the ink droplets is important in defining the resolution of the printer. The production of the droplets is controlled by either an acoustical or a thermal process; delivery of the droplets is controlled by electrostatic or droplet on-off methods.

The three basic elements in an ink jet system are shown in Figure 3.1.[57] The main elements are the nozzle, the charging system, and the deflector. Liquid ink from a reservoir, is forced into the rear of the nozzle under a controlled pressure. The ink is broken into droplets by the expansions and contractions of a piezoelectric element. The expansions and contractions occur at around one hundred thousand times each second. Exit of the droplets is controlled by electrostatic means. Each droplet is charged to the desired level. From the charging stage the droplet flies between two charged plates. The charged plates, which are kept at a constant voltage, influence the droplet according to the amount of charge placed on it. The result is a vertical displacement pattern. A droplet with no charge is unaffected by the charged plates and passes through to be intercepted by a gutter. The gutter recirculates the ink back to the reservoir.

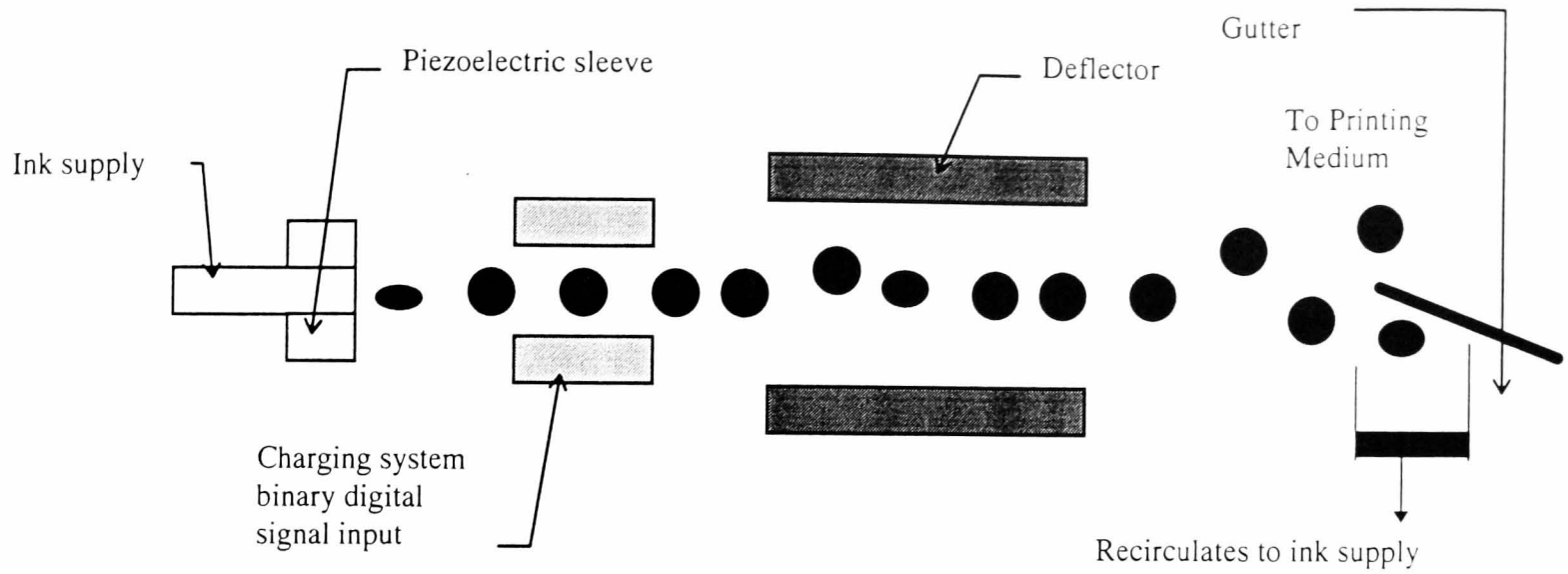


Fig 3.1 Schematic Diagram of Ink-jet system

3.4 Xerography

Xerography is a well established printing method. The first copy by xerography was produced by Chester Carlson in 1938. Xerography[58] is more generally known as electrophotography. Dry or liquid ink, known as toner, forms an image directly onto the printed paper copy. In the original process paper used in the copier had to be coated with a photoconductive layer. This layer was given an electrical charge, exposed to the original document using optics, developed in the image areas and then fused using high temperatures.

Current non-impact printing differs from earlier copier systems in that the image is transferred to the paper via an intermediate carrier roll. This makes coating the paper unnecessary, allowing a greater range of substrates to be printed. The indirect electrophotographic printing is known as xerography. The process is shown diagrammatically in figure 3.2.

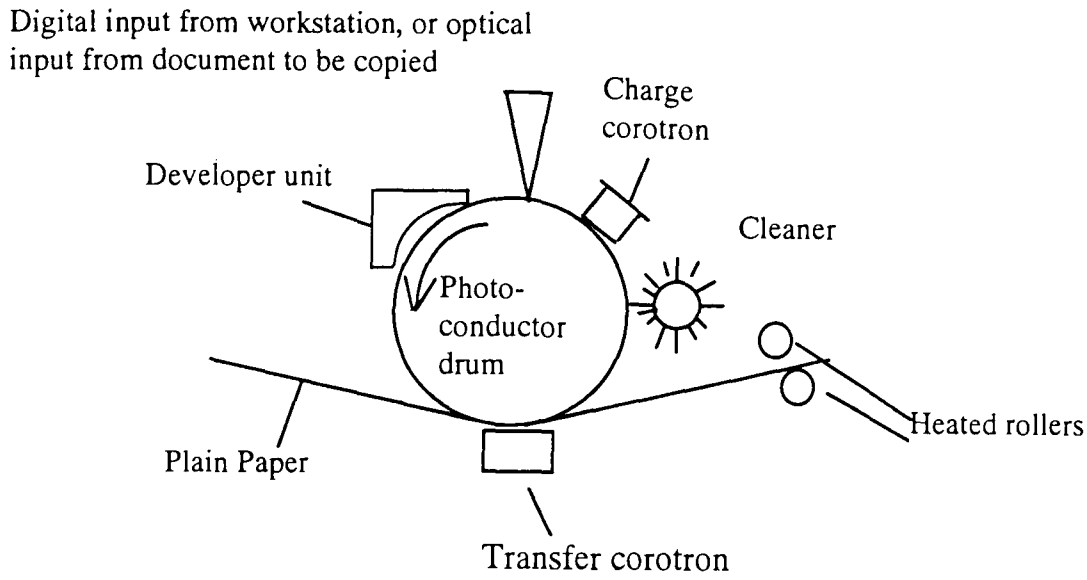


Fig 3.2 Process steps in xerography[58]

Xerography operates in two stages; transfer and cleaning. The use of an indirect image carrier requires that the image is transferred from the surface of the carrier to the printed substrate. Mechanical pressure is not used to transfer the image as in a conventional printing process but instead electrostatic forces are used. The image is not transferred completely, as is true with conventional printing, and the intermediate transfer roll must be cleaned of toner before the next printing cycle.

The next step of the electrophotographic process, once the drum has been cleaned, is to charge it electrostatically. The material of the photoconductor accepts and retains an electric charge when brought into proximity to a corona discharge produced by a charge corotron. The corotron electrodes have different designs depending on the manufacturer. The charge that is placed on the surface of the photoconductor is either positive or negative, dependent on the type of photoconductor used. One property of the imaging drum that is essential to xerography is photoconductivity.[59] The photoconductive substance is an insulator in the dark and retains charge. The absorption of a photon excites an electron into the conduction band of the material and charge flows away to earth from these areas. Originally the photoconductor was selenium alloyed with various additives, more recently cadmium sulphide and various organic materials have been used.

Light reflected from the image strikes the charged photoconductor as it moves past the exposure station. In most non-impact printers the light used is a laser beam which is modulated as it moves across the image. The modulation of the beam is achieved by

interrupting the beam according to the digital information supplied by the computer. The modulator can be either an acousto-optic or an electro-optic device. The laser produces a constant light output but the beam is interrupted several million times a second. The modulator acts as a light valve, only permitting light to pass at certain times. Usually the ON condition of the light valve allows light to pass, represents the background areas of the image. The OFF condition relates to the image areas. The photoconductor belt now has a latent image on its surface, this latent image must be developed.

In developing the image a stream of triboelectrically charged toner particles is placed on the surface of the photoconductor. Particles are attracted to the charged image areas but not to the discharged non-image areas. The photoconductor is never fully discharged and retains a small amount of charge. To avoid attracting toner to this small charge a bias voltage is applied to the toner delivery system. This reverse charge is sufficient to counteract the charge on the non image areas and so prevent the deposition of toner.

Toners can be broadly divided into two types; dry and liquid.[60] Dry toners are powders composed of a pigment and a polymer material. The pigment is usually carbon black or iron oxide. The pigment and polymer are combined in beads or carrier particles. These beads exist to transport the toner through the printer. The beads are between 8 and 100μm in diameter. Smaller toner beads have been in development by printer manufacturers, with Hewlett-Packard claiming a 0.3μm diameter toner bead.

Liquid toners comprise a charged particle carried in a bath of insulating liquid, usually a hydrocarbon vehicle. The size distribution of the toner particles suspended in the fluid is smaller than that found in the dry toner systems, with a typical diameter of around 0.1-2μm.[60] This particle size distribution is comparable to those found in lithographic inks.

After leaving the development zone the toned image is ready for transfer to the printing substrate. The printing substrate is usually presented above the development zone to prevent stray toner particles dropping onto it. The toner is held to the photoconductor by electrostatic forces. The printing substrate is brought into close proximity to the photoconductor. Transfer to the printing substrate is achieved by electrostatically charging it. The charge is placed on the substrate by using a similar device to the one that charges the drum, this is known as the transfer corotron. The transfer corotron is located on the

opposite side of the substrate to the photoconductor. Its purpose is to produce a charge on the substrate so that the toners experience a greater attraction towards the printing substrate than to the photoconductor drum. This produces a migration of toner from the drum to the printing substrate.

After transfer the photoconductor drum is cleaned to remove any residual toner. Cleaning would not, in theory, be needed if identical images were to be transferred on every cycle. However, the advantage of non-impact printing is that the image can be changed on every cycle.

After transfer the printed image is fixed to the substrate, usually by a combination of heat and pressure. The fixing occurs at a temperature of around 90 to 150°C. At this temperature the polymer material in the toner bead melts and fuses to the substrate. Dry toners are fused by the application of heated rolls or infra-red heaters. Liquid toners are fused to the substrate by evaporating the liquid carrier, this occurs at higher temperatures than the fusion of dry toner systems typically 150-200°C.

Liquid toners have much more in common with conventional printing inks than do dry toners. The evaporation of the hydrocarbon carrier is comparable to the evaporation drying of a gravure ink. The size distribution of the particles contained in the hydrocarbon carrier is also comparable to the sizes found in conventional printing inks.

3.5 Recent Developments in Non-Impact Printing

In the last ten years non-impact printing has seen developments in the introduction of colour and increased speed. These increases in speed have lead to certain digital printing systems being almost as fast as the conventional processes. The Indigo E-print[61] can print 800 impressions per hour, and the latest machine manufactured by Xeikon,[62] the DCP/32D produces 4200 full colour A4 pages per hour. These systems have the advantage that each copy can be unique. Monochrome printers too have advanced and are capable of printing 420 pages a minute, 25200 impressions an hour. Nipson recently announced a new version of their Nipson 7000, which has a resolution of 480 dots per inch (dpi) capable of 420 pages per minute.[63]

From its introduction in 1993 until mid 1995 Indigo had supplied 275 presses and more are being installed weekly. Xeicon announced in September 1997 that it had shipped its thousandth digital printing press. It is estimated that 1 billion sheets of A4 paper will be printed by Xeicon printers in 1998.[62]

The inks used by the digital presses are with one exception no different from conventional toners, they have the same characteristics as the toners used in laser printers only the colour of the pigment varies. The one exception to these toners is the ink used in the Indigo digital press. This ink is liquid and is a polymerising ink, which cures over a period of hours to form a tough rub-proof coating.[64]

3.6 Conclusions

Non-impact printed waste is increasing in quantity. Digital printing as a whole is set to increase its market share. The inks used in digital printing cause problems when deinked in a conventional recycling process. They are not removed efficiently by screens or cleaners and lead to large unsightly specks in the finished recycled paper. The flotation process can also be inefficient as toner particles adsorb surfactant molecules and become hydrophilic. All these problems associated with the recycling of mixed office waste are more fully discussed in section 4 and 7. These problems will only increase as the sector of mixed office waste is exploited as a source of high quality white fibre. There is a need for research into new methods of deinking or removing toners from fibres.

4.0 Ultrasonics[67,68,70]

Ultrasound is a series of high intensity vibrations. These vibrations cause changes within fluids through which they are radiated. This chapter presents the background to the theory of ultrasound and some of the physical and chemical effects it can produce.

4.1 Introduction

The only distinction between audible sound and ultrasound is that the latter cannot be detected by the human ear. Sound energy is transmitted as a longitudinal wave, as opposed to a transverse wave such as light and requires an elastic medium in which to travel. The theory of propagation of ultrasound is exactly the same as that for audible sound.

Sound is generated in a material as a result of some mechanical disturbance taking place within that material. Sound waves travel through a series of compressions and expansions.

These compressions and expansions can come about as a result of a shock, such as an explosion or sudden impact. Alternatively the sound may be generated as a result of a continuous vibration, for example speech, or the motion of a machine.

Vibrations are characterised by their frequencies, that is the number of complete periodic cycles undergone in unit time. The unit of frequency is the Hertz (Hz). One Hertz is one cycle per second. Higher frequencies are expressed as kilohertz, megahertz or gigahertz. The range of human hearing is between 20 Hz and 18 KHz. Sounds below the range of human hearing are called infrasound.[71] The ultrasound used in this project had vibrations of around 20 KHz.

This frequency of 20 KHz is just beyond the range of human hearing, at the beginning of the ultrasonic range. The range at which cavitation occurs extends from the audible range to around 500 kHz. Above 1 Mhz, sound is used for imaging, for example in sonar or medical ultrasound scans. Figure 4.1 shows a representation of the sound spectrum. The upper range of hearing decreases with age as the skin of the typanic membrane becomes less flexible.

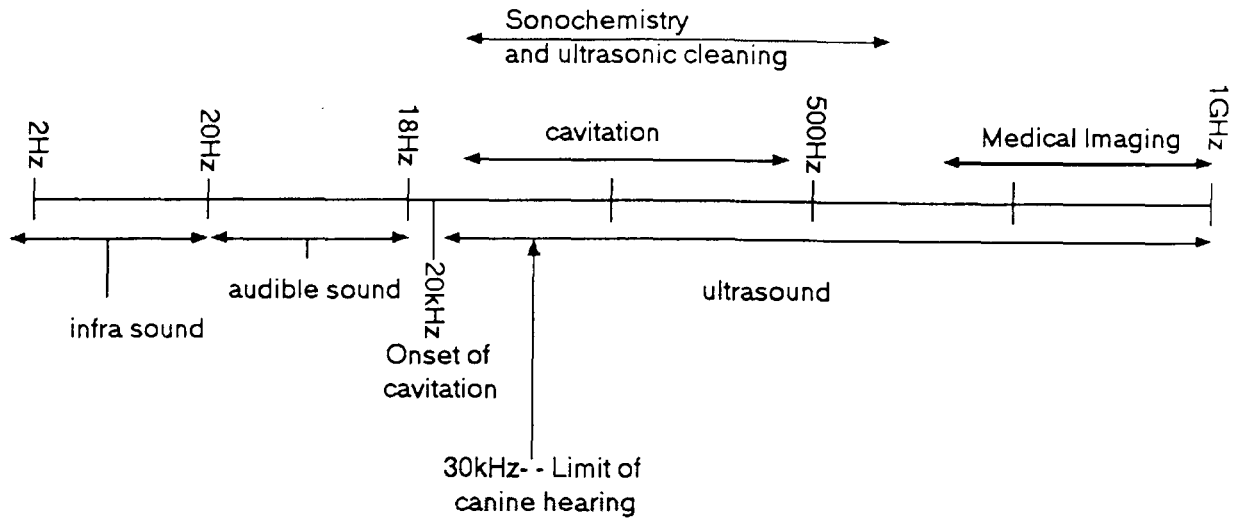


Figure 4.1 Acoustic Spectrum

4.2 Production of Ultrasound

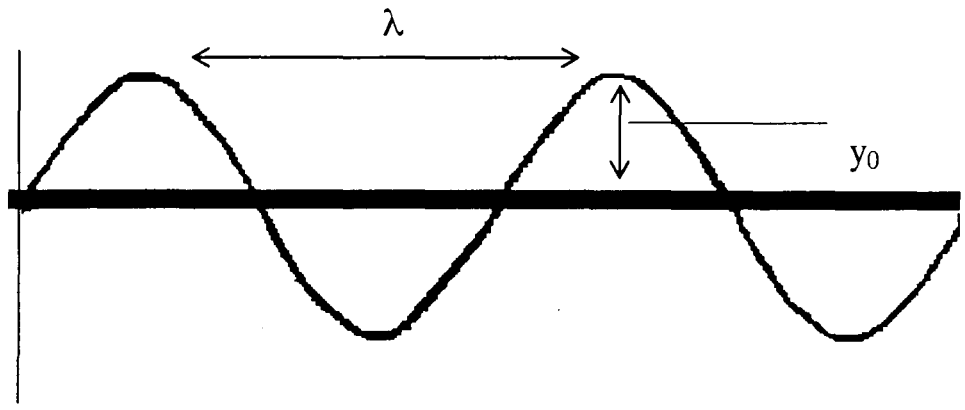
Piezoelectric materials can be used to produce or detect sound.[72] The piezoelectric effect is displayed by certain materials in response to an applied mechanical stress. Piezoelectric materials are usually crystalline in structure. When the crystal is subjected to stress the deformation of the crystal causes an electrical field to develop on its faces; positive and negative charges appear on opposite faces. If such a crystal is placed in an applied electric field the reverse process occurs and a stress is induced causing the material to undergo a deformation. The size of the deformation is dependent on the nature of the material, the symmetry of the crystal and the orientation of the crystal relative to the external field.[72,73,74]

Many crystalline materials exhibit piezoelectric behaviour to some degree. Few, however, have the mechanical and electrical properties that allow their use in the detection or generation of sound waves. Quartz is one such material. A single crystal of quartz is the most common commercially available transducer material. A transducer is a piezoelectric crystal with electrodes embedded within the crystal to enable the introduction of an electric field and so produce deformations in the crystal. The best use of a quartz transducer is at one of its resonance frequencies, non-resonant frequencies are less efficient. Most other piezoelectric materials are either ceramics or polymers, for example, polycrystalline ferroelectric materials such as lead zirconate titanate and barium titanate.[74]

4.3 Propagation of Ultrasound [72]

It was noted earlier that sound moves as a longitudinal wave. The vibrations of the particles take place in the direction of motion of the sound. Sound waves require a medium to allow transmission. For most applications the ultrasound is generated from a plane surface oscillating with a simple harmonic motion. Figure 4.2 shows the variation in displacement against time.

Figure 4.2 Displacement of Particles Against Time



y_0=amplitude
λ=wavelength

The time taken to execute one complete vibration is period T. The reciprocal of the time period T measured in seconds is equal to the frequency in hertz.

$$T = \frac{1}{f} \qquad \text{eqn 4.1}$$

The shape of the curve is sinusoidal and is represented as equation 4.2.

$$y = y_0 \sin \frac{2\pi t}{T} = y_0 \sin 2\pi f t = y_0 \sin \omega t \qquad \text{eqn 4.2}$$

where y = displacement at any time t and
$\omega = 2\pi f$ (known as the angular frequency)

The vibrating source transmits energy to the particles, atoms or molecules, which are in immediate contact with it. The energy is transmitted progressively through the material. Figure 4.3 below illustrates two parallel plates separated by the material of propagation. The left hand plate is the source of the vibration, which is vibrating with a simple harmonic motion, the right hand plate acts as the receiver. The intervening material can be divided

into a number of very thin layers, each of equal thickness. If the left hand plate was to be displaced to the right by a given amount then the first layer closest to the plate, layer A, will be displaced. Layer B is also displaced in turn, and the displacement is progressively transmitted from one layer to the next until the final layer is reached and then the receiver is displaced by a similar amount. If a layer at a distance x is considered, the time for the sound to reach this layer is equal to x/c, where c is the speed of sound. The phase of the vibration in this layer at any time t is identical to that of the source $t-\frac{x}{c}$ and the value y of that displacement is obtained by substituting into the sinusoidal curve of equation 4.2.

$$y=y_0 \sin \omega \left(t - \frac{x}{c} \right) \qquad \text{eqn 4.3}$$

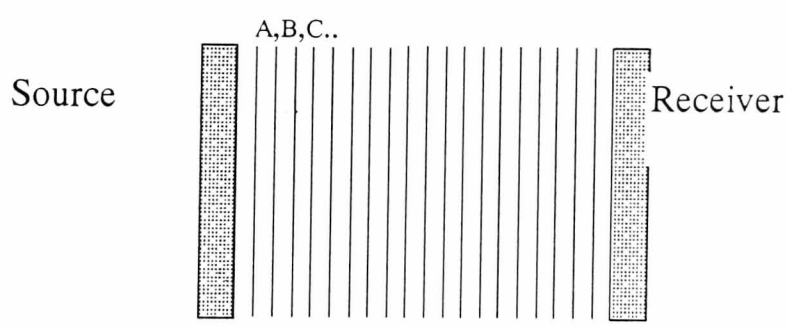


Figure 4.3 **Displacement of Layers in a Medium**

It takes a small but finite time for the energy to pass from one layer to the next and so sound waves take a certain time to pass from the source to the receiver. The velocity of the waves has a constant value for a given material under given physical conditions. The velocity constant is dependent on the elastic modulus and the density of the material. Some values for the speed of sound in common materials are given in table 4.1. Only sound waves that do not lose energy during propagation have been considered. Any loss of energy in the process is known as attenuation.

Material	**Density kgm^{-3}**	**Speed of sound ms^{-1}**
Water	1000	1435 (@25°C)
Air	1.2	344 (@25°C)
Steel	7800	6000
Titanium	4500	5160
Quartz	2600	5700
Beech(along fibre)*		3340
Oak(along fibre)*		3850
Ash(along fibre)*		4670

(* From Handbook of Chemistry and Physics 1981-2, GRC Press Inc)[75]

Table 4.1 **Speed of Sound through some Common Materials**

The longitudinal waves relevant in ultrasound are compression waves. At any given time the layers take on the appearance shown in Figure 4.4, below where the centres of neighbouring compressed or expanded regions are separated by distances of one wavelength, λ.

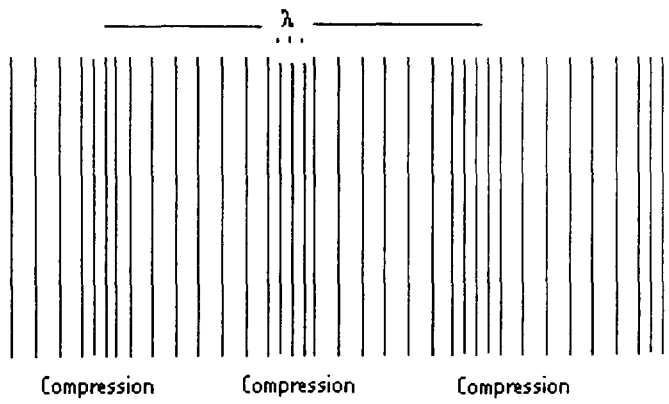


Figure 4.4 Sound Waves Travelling through a Medium

The three main characteristics of acoustic waves are particle displacement, particle velocity and acoustic pressure.

The particle displacement is the displacement of a body at a distance x from the transmitter. If the propagating material is assumed not to absorb the sound then the displacement will be the same for all particles along the path of the sound wave.

Particle velocity is defined as the velocity of a vibrating particle in the medium, *not* the velocity of the waves, at a given time and location. It is given by the equation 4.4:

$$u = u_0 \sin \omega (t - x/c) \qquad \text{eqn 4.4}$$

where u = particle velocity
u_o = the particle velocity amplitude

The material carrying the sound waves is subjected to an alternating pressure called the acoustic pressure, p, which is given by the equation 4.5:

$$p = p_0 \sin \omega (t - x/c) \qquad \text{eqn 4.5}$$

Where p_0 is the acoustic pressure (or stress) amplitude.

All of the above effects are important for ultrasonic cleaning. Cleaning using ultrasound relies on the removal of dirt by acoustic pressure acting on the surface of articles to be cleaned. The dirt is simply pushed off the surface by the pressure waves.

So far only the movement of sound waves through a medium has been considered. There is another effect that is caused by ultrasound that contributes, in some cases, significantly to the effects of ultrasound. This effect is known as cavitation.

4.4 Cavitation[76,77,78]

Acoustic cavitation can be described as the creation of new surfaces within a liquid, this is a very broad definition which would include boiling. Acoustic cavitation can be applied to the case of a liquid subjected to a varying pressure, superimposed upon an ambient pressure. Sound energy of a certain intensity travelling through a liquid can cause bubbles to develop in that liquid. During the expansion phase of the wave the pressure can be sufficient to evaporate the liquid to form bubbles of vapour; the bubbles can then either collapse at the next compression cycle or grow and shrink over several compression and expansion cycles. These are known as cavitation bubbles. Acoustic cavitation can be defined as the case where expansion and contraction of bubbles occurs. There are two types of cavitation bubbles, transient and stable.[81]

Stable cavitation bubbles oscillate about an equilibrium size.[78] They are relatively permanent and may exist for many cycles of compression and expansion. Transient cavitation bubbles are much less permanent and exist for only one pressure cycle. In their short lifetime they expand to at least double their original size and often more than this. They then collapse violently, sometimes disintegrating into a multitude of much smaller bubbles.

Cavitation was first observed as a phenomenon as long ago as 1850.[79] Cavitation was observed when the Royal Navy's battleship 'Dreadnought' made only half of its planned speed and was plagued with vibration. It was discovered that the propeller blades were set at too harsh an angle and this was forming cavitation bubbles on the surface of the blades which created the vibration, and resulted in the lack of speed. Erosion of the propeller

blades was accelerated as a result of the cavitation. The pioneering work was performed by Lord Rayleigh who wrote of a spherical cavity collapsing.[80]

This type of cavitation was caused by transient cavitation bubbles, and the study of this form of cavitation dominated the early research in this area. Transient cavitation bubbles cause effects such as erosion[82], sono-luminescence,[83,84,85,86] emulsification,[87] molecular degradation,[88,89] sonochemistry,[68,90,91,92] and biological disruption.[93] These effects are all related to the very high pressures and temperatures developed in the transient implosion.

Stable cavitation is also important, being involved with initiating surface oscillation and microstreaming effects. In an observed cavitation field there will always be more stable cavitation bubbles than transient bubbles. Stable bubbles are far longer lived than transients and their overall effect is far greater. Stable bubbles can eventually degenerate into transient bubbles.

Having described how transient and stable bubbles are produced it is important to understand what is happening inside the bubbles. There are two possibilities for a cavity existing within a liquid. The cavity can be created from either a liquid's vapour or from permanent gas, usually air. Thus four types of bubbles can be defined; gas or vapour-filled transient or stable cavitation bubble.

In a transient bubble it is safe to assume that there is no time for any mass flow, by diffusion of gas into or out of the bubble. However, evaporation and condensation may occur from the walls of the bubble. It can be assumed that a collapsing gaseous transient cavitation bubble contains a constant amount of permanent gas and a collapsing vaporous bubble will contain only vapour. The vapour will remain at or near the equilibrium vapour pressure. The collapse of a vaporous cavitation bubble will be much more violent as there will be less gas to cushion the implosion.

If the liquid in which cavitation is occurring is entirely gas free then the cavitation bubbles must be all vaporous in nature. Intuition might dictate that stable cavitation events may not occur. This is true, but there is also a thermal mechanism whereby vaporous cavities can exist in a sound field.

Thus far single bubbles have been considered. In practice a very complex situation exists where bubble *fields* are the main form in which cavitation bubbles are found. In this situation there are many bubbles; each collapsing and undergoing transitions between stable and transient cavitation. The transition between stable and transient is not always obvious. The transition from stable to transient may occur with the simple passage of time or there may be changes in the acoustic or other environmental conditions which precipitate change. The demarcation area between stable and transient states, is known as the Transient Cavitation Threshold. There is another region lying below the transient region where stable cavities can increase in size to become transient bubbles. This is termed the Stable Cavitation Threshold.

There are changes that occur in a fluid when the cavitation threshold is reached. As soon as the cavities are formed within the liquid the acoustic properties of the fluid change and the liquid becomes more compressible. The acoustic scattering potential of a bubble is greater than that of either a solid or liquid particle. Oscillating bubbles are very good at redistributing the acoustic energy. Once a liquid reaches the threshold of cavitation it changes its acoustic properties. The liquid also becomes acoustically lossier, this means part of the energy put into the system is re-radiated as sound energy by collapsing cavitation bubbles. With transient bubbles, energy is extracted from the sound beam and rapidly concentrated into small volumes. A great deal of energy is given up by the bubble as it finally collapses. Part of this energy goes into producing sound.

The factors that affect the extent of cavitation are:-

a Ultrasound intensity; frequency, amplitude

b Medium of liquid; viscosity, vapour pressure, surface tension

c Dissolved gases, or suspended solids

d Temperature

a The intensity of the ultrasound is an important factor in the production of cavitation because there is a limit below which cavitation will not occur. The intensity, I, is the power (W) transferred per unit area(A), and is given by equation 4.6. [94] This is referred to as the cavitation threshold. Below this limit the sound passes through a liquid with the normal compressions and expansions. The amplitude of the sound is important to the

cavitation threshold. The larger the amplitude the more likely it is that cavitation bubbles will form. The amplitude of the sound wave is dependent on the acoustic pressure.

$$I = W/A = \frac{P^2}{2\rho c}$$

eqn 4.6

Where P = acoustic pressure,
ρ = density of the material being sonicated, and
c = speed of sound in the medium

Cavitation is most prevalent at the lower end of the ultrasound spectrum. As the frequency increases the size of the bubbles decreases. Cavitation activity declines as the compressions and expansions become closer together. At the higher end of the ultrasound spectrum there is very little cavitation activity.

b The liquid in which ultrasound is travelling will affect whether cavitation occurs. The more viscous the fluid the less likely it is that cavitation will occur. It is difficult to get cavitation to occur in oils and waxes as these fluids are too viscous.

The vapour pressure of the liquid being sonicated is important; if the liquid is saturated with a gas then the gas will affect the cavitation (see below). Liquids with a high vapour pressure tend to cavitate with a greater intensity.

The surface tension of the liquid is an important factor. Surface tension is a force that tends to decrease the size of bubbles within a liquid.[95,96] Bubbles decay by surface tension effects if not driven by sound waves.

c Dissolved gases and suspended solids provide seeding points at which cavitation can occur. The presence of suspended solids causes a localised decrease in the surface tension of a liquid. This change in surface tension allows cavitation bubbles to be initiated more easily. Dissolved gases can lead to the development of stable cavitation bubbles by forming gas bubbles within the liquid. These bubbles grow when irradiated with sound and can form either transient or stable cavitation bubbles, depending upon the local conditions.

d The extent of cavitation in water decreases as the temperature increases. In most other solvents the intensity is greater at higher temperatures. The reason for this is that the vapour pressure of the liquid inside the cavitation bubble decreases, leading to a less stable bubble. Above a certain temperature cavitation will not occur. In a study of cavitation intensities of different fluids, water was the fluid that was found to cavitate with the greatest intensity.[97] Water and methylene chloride were found to be the only solvents in which cavitation intensity is greater when the liquids are cooled than when heated.

4.5 Effects of Cavitation

Cavitation can cause a number of different effects, some of which have been mentioned previously. Sonochemistry is a term given to chemistry that is affected by sound energy. A wide range of chemical reactions are affected by sound energy. Sono-luminescence is the production of light from the collapse of a cavitation bubble. High power ultrasound has also been used in water treatment,[98,99] in food processing, and for particle size reduction.[100]

Cavitation bubbles generate other effects when they collapse. As well as the erosion of metal surfaces, cavitation bubbles can also create radicals and a jet stream as they collapse.

Reactions that are influenced by cavitation bubbles began to be studied at about the same time as reactions initiated by ionising radiation. Cavitation bubbles create free radicals as the bubbles collapse. Each collapsing bubble can form 10^5-10^6 radical pairs,[101] (see equation 4.7).

$$H_2O \longrightarrow H^{\bullet} + OH^{\bullet} \qquad \text{eqn 4.7}$$

The radicals formed are very reactive species. The $OH^{\bullet}$ radical is responsible for all the oxidation in the lower atmosphere.[102] The $OH^{\bullet}$ radical can attack other species to form secondary radicals, or react with another $OH^{\bullet}$ radical to form hydrogen peroxide, (see equation 4.8).

$$OH^{\bullet} + OH^{\bullet} \longrightarrow H_2O_2 \qquad \text{eqn 4.8}$$

Hydrogen peroxide is used in the bleaching of virgin paper fibre and during the recycling of mixed office waste.[103,108] However, the levels of hydrogen peroxide produced by ultrasound are too low for any significant bleaching effect to be observed.

Another effect of cavitation bubbles is the micro jet stream. This is not to be confused with the streaming pressure of the sound waves, which is caused by the movement of the compressions and expansions across a solid surface.

The micro jet stream is created by the implosion of a cavitation bubble close to a solid surface. A bubble that is initiated near to a surface can collapse directionally and project a jet of liquid onto it. Figure 4.5 below shows diagrammatically the collapse of two bubbles, one resting on a solid surface and the other half a bubble radius distance from the surface.

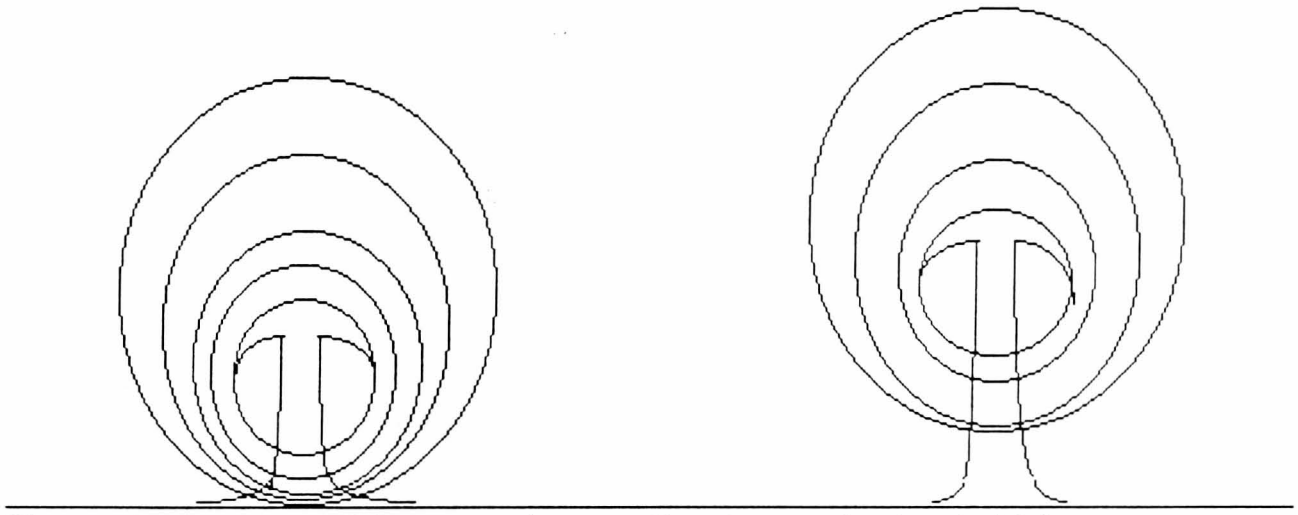


Figure 4.5 **Diagram of two collapsing cavitation bubbles**

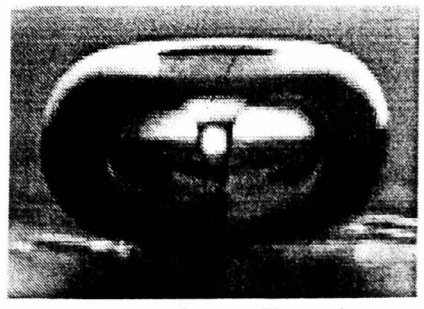


Figure 4.6 **Photomicrograph of a collapsing cavitation bubble**

The cavitation bubble collapses asymmetrically and projects a jet towards the surface. The bubble does not have to be in contact with the surface to jet stream. These diagrams are solutions of a theoretical problem calculated by Plesset and Chapman.[104] Photographic studies of the asymmetric collapse of cavitation bubbles have also been undertaken by several groups.

Single bubble collapse has been studied by several research groups. An example of the collapse of a single is bubble is shown in figure 4.6.[104,118] Other groups have studied the collapse of bubbles using high speed movie cameras.[105,106,107] An example of this work is shown in Figure 4.7. The bubble was initiated at a distance of 2.3mm from the surface. The collapse of the bubble was photographed at a speed of 305,000 frames per second. Speeds calculated for the collapse of the bubble range between 128 and 170 ms^{-1}.

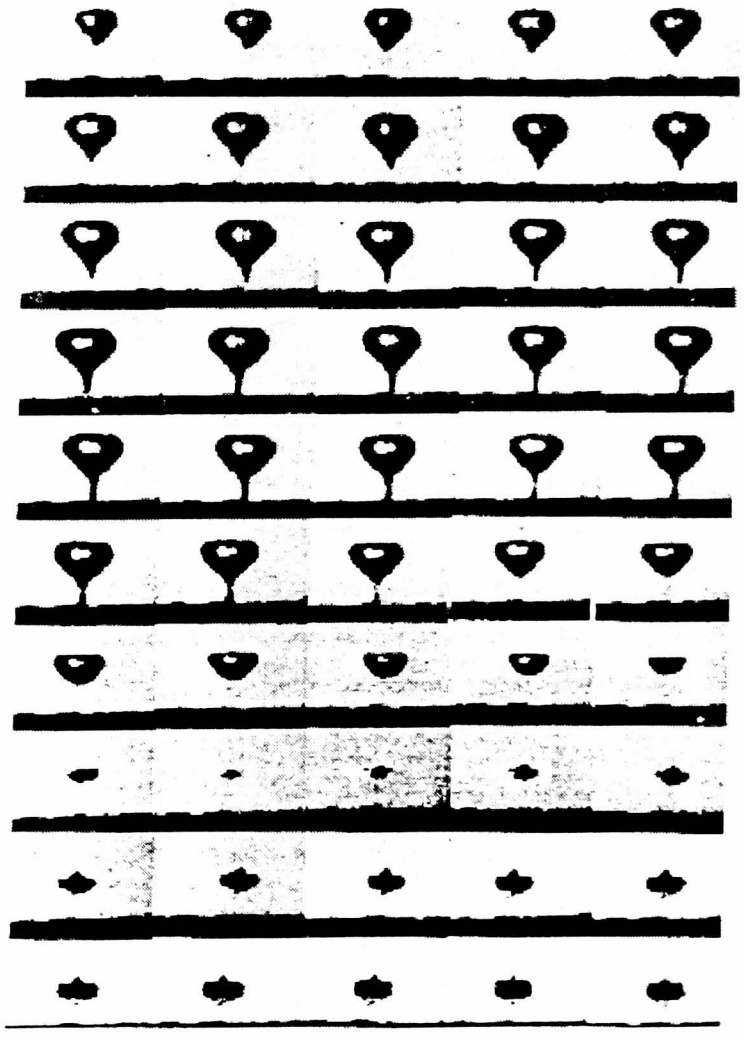


Figure 4.7 **Photomicrographs of Single Bubble Collapse**

Pressures created under the liquid jet are of the order of thousands of Nm^{-2}. These can be calculated from equation 4.9

$$P \approx (\rho c)_L V \qquad \text{eqn 4.9}$$

Where P = pressure developed on impact
ρc = acoustic impedance of liquid
V = velocity of collapse

If the speed of sound is taken to be 1500 ms^{-1} in water, and V is 130 ms^{-1}, we obtain the pressure as 1930 Bar. However the time taken for the jet to propagate is very short, around 10^{-7} sec, and so this pressure will act on the surface for only a very short time.

This pressure is enough to cause erosion in resistant metals, however their transitory nature makes it unlikely that erosion will occur over a short period of time, the effects of cavitation erosion would only be experienced over longer periods. Less resistant materials, of course, can be eroded in much shorter periods.

4.6 Ultrasound and the Paper Making Process

Ultrasound is widely used for monitoring and control in the paper making process;[119,120] for instance to determine the tensile strength of paper. Ultrasonics are also used as a non destructive testing (NDT) technique. Ultrasound was investigated with regard to its effects on wood fibres as far back as the 1930's.[109] The effect of ultrasound on paper fibres was first investigated in 1950.[110] This early paper noted the effects of ultrasound on various fibres, unbleached sulphite pulp and bleach Kraft pulp. The experiments were carried out using a quartz oscillator at a frequency of 500 KHz. The authors found there was a beating effect indicated on the Canadian Standard Freeness index, but the fibres were not shortened by the effects of the treatment. Fibres from the experiments were subjected to microscopic examination. It was found that the fibres had fibrillated, or increased their surface area, and that the effect was not simply due to thermal interactions.

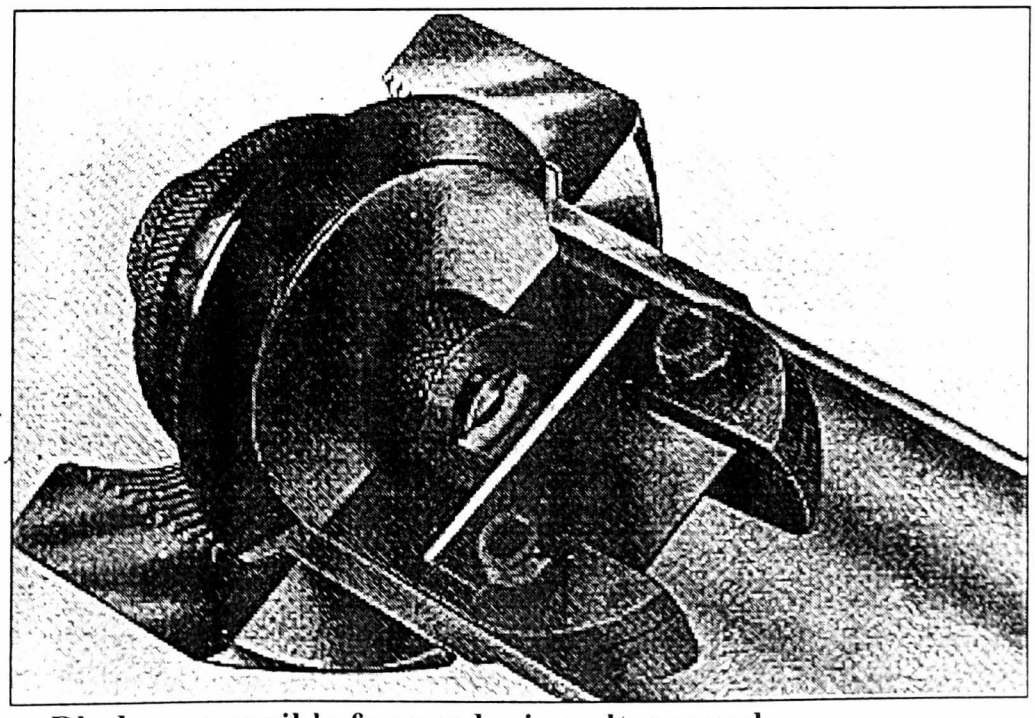


Figure 4.8 Blade responsible for producing ultrasound

The effects of ultrasound on the recycling of paper was first investigated at Syracuse University by Turai and Teng[111] using a whistle jet device. The whistle jet or liquid jet is a

means of creating ultrasound by vibrations. The vibrations are produced by the oscillation of a blade inside a chamber. The blade oscillates due to a thin stream of pulp impinging on the surface. The blade and chamber are shown in figure 4.8. This work eventually reached pilot plant stage, reported in the following year.[112] The pilot plant stage was capable of sonicating 110 litres of pulp per minute at a maximum consistency of 8%. It was possible to deink the paper without the use of chemicals. The waste used in the trial was a heavily printed polymeric ink or paper coated with overprinted varnish. This was chosen as it was difficult to deink using conventional methods. The ultrasound whistle jet was compared with conventional hydrapulping. Hydrapulping produced a sheet of paper that had a large number of ink particles attached to paper fibres. Whistle jet treatment of the sample reduced the particle size of the ink.

A probable reason for not continuing the work was that the blade was cutting fibres as efficiently as a refiner, leading to a loss in yield. However, the amount of power put into the system was lower per litre for the pilot plant than the laboratory set-up suggesting that there were possible economies of scale.

A study of ultrasound and paper fibres in 1981,[113] was reported as a 'Note on Ultrasonics for Deinking Waste Paper'. This work also used a whistle jet device.

In 1990 evaluation work was started on a deinking surfactant by two workers at London College of Printing.[114] The surfactant was ineffective until the work was repeated in a low power ultrasound cleaning bath. The resulting papers showed an increase in brightness and a reduction in the ink particle sizes.

No further work on ultrasound and paper fibres was reported until 1993 when workers at the University of Wisconsin-Green Bay investigated the use of ultrasound in the deinking of laser printed waste.[115] The ultrasonics was delivered to the pulp slurry in an ultrasound cleaning bath, with power of 180 watts radiating into a container of 1.2 litres. To evaluate the effect of frequency, piezoelectric transducers were glued to the base of stainless steel beakers. This work used low power ultrasound at three different frequencies, 22, 34 and 54 KHz. Power in these experiments was limited to 25 watts.

The pulp produced was washed, subjected to flotation and formed into handsheets before being examined using a camera based ink particle size analyser. It was found that ultrasound could reduce the size of the ink particles, particularly the particles above 400μm in size. The group found that ultrasound with a frequency of 22 KHz was effective in breaking up large particles to a size where they could be removed by washing or flotation.

It was suggested that ultrasonics could be used as a standalone treatment for laser printed waste or as a polishing step for mixed office waste grades. The low power used in these experiments (25 watts) was applied over 120 minutes. The higher frequency resulted in smaller particles. No mention of temperature rise was made in the experiments. However, this is an important parameter when dealing with the toners described in this paper. The glass transition temperature governs the point at which the toner softens and flows. If the heating effect of ultrasound increases the temperature to the glass transition temperature then the toner may undergo changes which facilitate removal.

In these experiments the ink particles were removed by flotation but without using chemicals. The particle distribution was reported as the ratio of particles below 260μm to those above 260μm. According to this data the ultrasound increased the number of particles present. After sonication and washing there were still more particles present on the handsheets than in the original material, however, the size of these particles was decreased. No indication of the mechanism for the breakdown of toner particles was given. The report noted that ultrasound of 22 KHz was effective in reducing particles greater than 260μm in diameter to a size where they could be removed by flotation and washing. The report considered that the inability of ultrasound to break down large particles after 10 minutes treatment could be due to the relative probability of collision of a cavitation bubble and an ink particle.

Further research[116] compared the effect of an ultrasound whistle with the effect of a piezoelectric horn system. The horn system operated at a nominal 500 watts. After ultrasound treatment it was found that 100% of the particles were less than or equal to 0.04 mm^2, before ultrasound 54% of the particles were in this size category. The ultrasound energy supplied to the pulp varied between 100 and 300 watts. It was found that ultrasound could reduce the particle size distribution of toner particles. These experiments did not state the time of sonication. The rationale behind the paper by Scott and Gerber

was a comparison of the efficiencies of ultrasound and a whistle jet system with regard to cost. These workers suggested that the piezoelectric transducer would be too costly to operate in a commercial environment.

The final research paper that has utilised ultrasound to change the particle size distribution of toner has been by Offill and Vendetti, working at North Carolina State University.[117] This work used piezoelectric transducers, working at a maximum power of 1200 watts. The work was carried out in a cleaning bath, with the pulp slurry being stirred constantly.

All the research papers indicated that application of ultrasonics could reduce the ink particle size distribution of toner but without giving precise details of the distribution as it related to the deinking processes. No workers attempted to present a theory of the action of ultrasound on the toner. The investigations carried out on paper fibres used low power or inefficient transducers. Such research would only yield information on the streaming effects of ultrasound, and not the more efficient effects induced by cavitation activity.

The aims of this research were to assess the effects of high intensity ultrasound on toner printed papers with a view to exploring both the effect on paper fibres and the mechanisms whereby the toner detaches and breaks up under the influences of ultrasound fields. The lower end of the ultrasound spectrum was chosen for this project as the findings of Norman, Sell and Danelski showed that frequencies around 22 KHz were particularly effective in breaking up large toner particles.

In conclusion it can be seen that ultrasound can reduce the ink particle size distribution of toner particles. Ultrasound can also affect paper fibres by decreasing their freeness and increasing strength properties. No theory exists for the interaction of fibres or toner particles with ultrasonic energy. To apply a low energy ultrasonic field to a pulp sample and expect results to translate to high energy, large throughput systems is unrealistic. Low power systems will only provide information on low power systems.

4.7 Conclusions

This chapter has been an introduction to the physics of ultrasound, the physical effects produced by cavitation bubbles, and the pressures and velocities of their collapse. The chemical effects of ultrasound are many and most applications of sonochemistry are aimed at accelerating reactions through the mixing of components, however, sonochemistry is not limited to this and can influence reactions through the production of radicals.

5.0 Description of Apparatus Used

The equipment and associated principles used to produce and analyse the samples are described below.

5.1.0 Production of Paper Pulp

Ideally the treatments that the fibres and inks receive should not differ between the industrial and laboratory processes. A brief description of the papermaking process can be found in appendix 5. The stages in making paper, be it in a laboratory or an industrial setting, are the same. These are reducing the fibre mat to individual fibres, separating ink from fibres, removing ink from the slurry and finally forming the fibres into new sheets. The laboratory papermaking process is performed on a batch system and handsheets of paper are made.

5.1.1 Laboratory Disintegrator

Disintegration is a mechanical treatment to separate interlaced fibres with minimal change to their structural properties. The disintegrator used was a British Standard Disintegrator, shown in figure 5.1.1. This conformed to International Standard ISO 5263 and Tappi T205.

Disintegration of pulp is controlled by the number of revolutions of the propeller blades in the disintegrator. The disintegration of pulp was carried out to Tappi standard T205, except with regard to the temperature control. The temperatures employed are recorded in the experimental notes.

A mass of 60 grammes of dry paper (maximum load) was first soaked for 3 hours, at the desired temperature and then disintegrated.

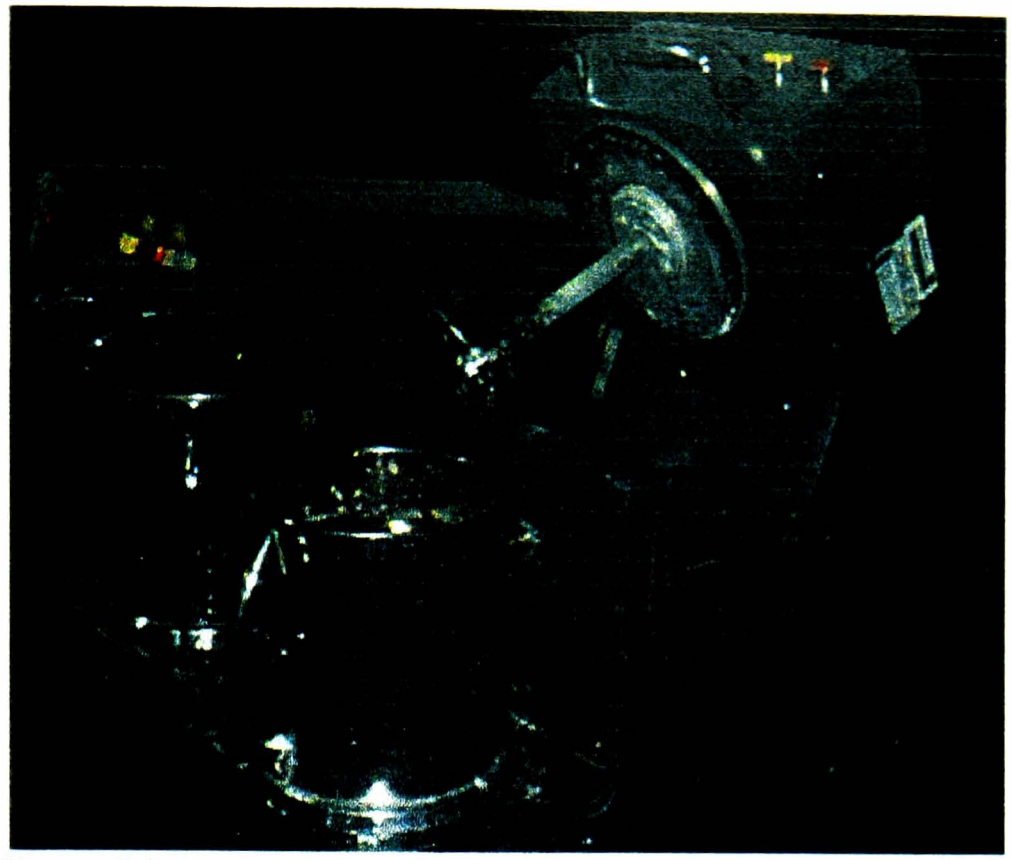


Figure 5.1.1 Standard Disintegrator

5.1.2 Laboratory Hand Sheet Former

Hand sheet formation is an essential parameter for the measurement of pulp and paper physical properties.[121] The handsheet former used for this project was designed and built within the School of Printing Technology as part of this project. It can produce handsheets of consistent weight, and has the same drainage time (4±1 seconds) as a standard handsheet former.

Approved machines are constructed to high accuracy according to the tolerances laid out in T205 (1980). The original former designed for this project consisted of a length of 20cm diameter plastic pipe with a filter, and a drainage plug. This former went through several evolutions, to reduce the amount of water used, produce lower leakage from the seals, and improve the discharge mechanism.

A new version (Mark II) figure 5.1.2, was constructed from 15cm diameter commercially available pipe. The same filter mechanism was used, but an improved external discharge mechanism was employed. The Mark II version also enabled easier access to the handsheet, thus reducing the number of damaged sheets. A synthetic 'wire' was used for the formation of the fibre network as this permitted easier removal of the fibre web than a

conventional copper wire. The aperture size of the mesh used was 65 microns, compared to the size of the mesh used in the standard laboratory handsheet former which is 80 microns.

This laboratory handsheet former was able to form accurately reproducible handsheets at 20gsm.

Figure 5.1.2 Custom made Laboratory Handsheet former

5.1.3 Ultrasonics Equipment

The ultrasound equipment used was supplied by FFR Ultrasonics Ltd and is shown in figure 5.1.3. The transducer is a quartz piezoelectric element (A) which feeds an aluminium amplifier (B), which in turn drives a rectangular horn section (C). The horn is made from 2.5Al/3V titanium alloy. Two slots are cut into the horn and these allow the base of the horn to vibrate evenly across its section. Without them the horn would crack under the acoustic pressure developed.

The transducer produces vibrations at around 20KHz, providing a peak amplitude of 30μm which the amplifier increases to 45μm at the tip of the horn. Power output is registered on the digital readout of the generator and is proportional to the depth of horn immersion. Maximum power output is 2000 watts, corresponding to complete submergence of the horn. The transducer is cooled by an external fan, forcing air over the outer parts of the horn and amplifier. An air pump cools the internal parts of the transducer

The energy produced by the horn was radiated into a stainless steel reaction vessel (D). The temperature of the pulp in the reaction vessel is kept constant by circulating the stock during sonication. The reaction vessel itself was immersed in water to control the temperature of the stock contained within it.

The horn produces sound energy beyond the range of human hearing. However, there are associated secondary harmonics and cavitation bubbles bursting which are audible as a high pitched noise; this necessitates ear protection.[128] To minimise the noise produced the ultrasound apparatus was enclosed in a sound proofed box. The box was constructed of particle board lined with polystyrene. The box incorporated a door to allow experiments to be monitored. The sound proofing extends to wrapping the box with thick cloth to ensure that any sound that escapes the box is muffled.

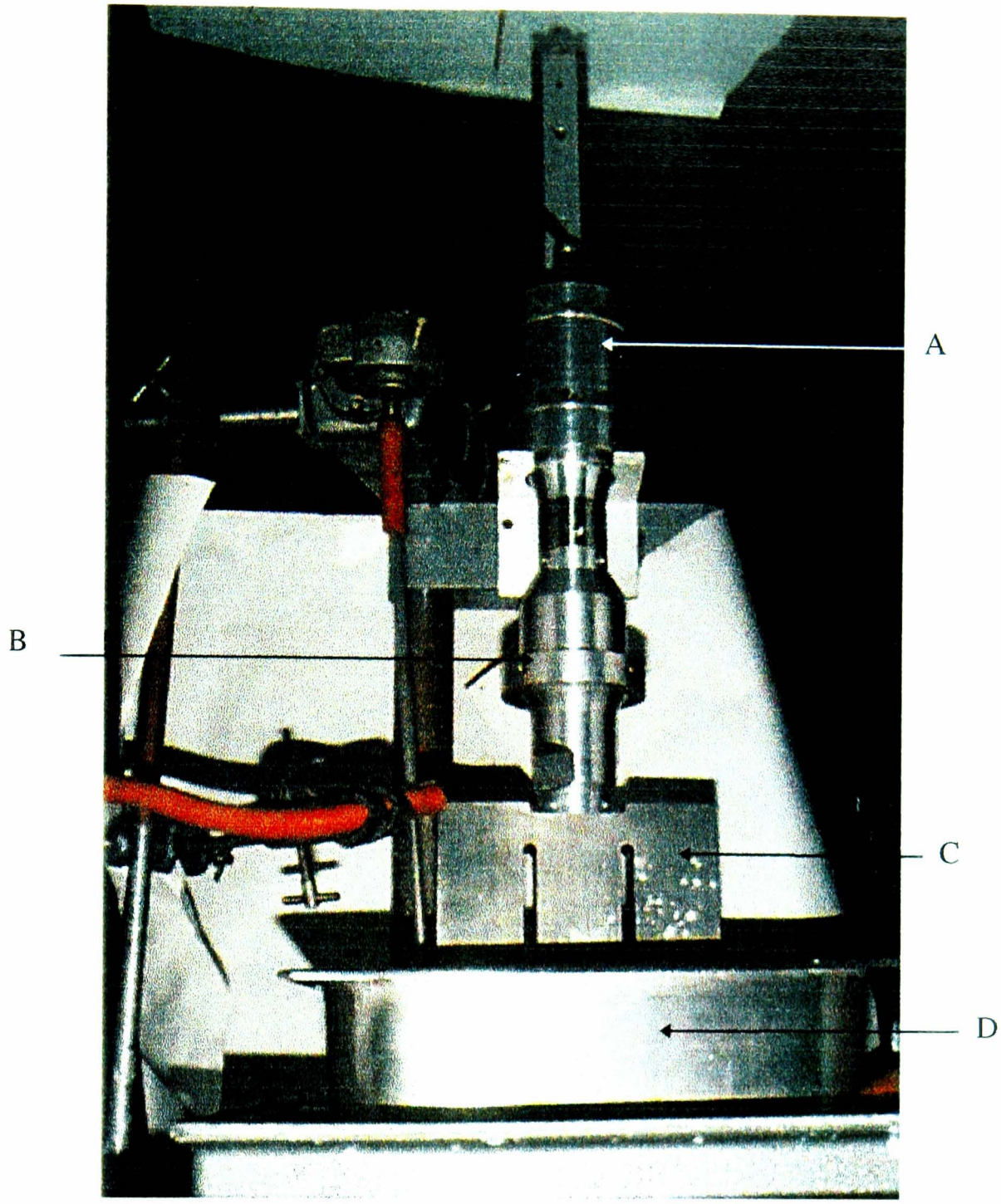


Figure 5.1.3 Ultrasonic generator and Horn

5.1.4 Laboratory Froth Flotation Cell[122]

The laboratory flotation cell employed was manufactured by Voith International. The cell consisted of a square tank of Plexiglas open at the top with a motor driven propeller. Beneath the top of the box was a lip that served as a collection point for the flotated stock. The stock to be flotated was drawn into a spiral case by the propeller, and air drawn through a separate pipe and mixed with the suspension. The turbulence produced in the pulp as it passed through the perforations of the case created a fine dispersion of bubbles in the suspension. The pulp (100 grammes oven dry at a consistency of 1%) was placed into the cell and further diluted to 0.5% consistency. The pH of the stock was adjusted to 8.5 but the level of alkalinity was dependent on the surfactant system used. The surfactant

used in these experiments was Surfax MT90 and was supplied by the Stevenson Chemical Company. It is a fatty acid soap that requires heating to achieve complete dissolution in distilled water. It was added at a ratio of 0.1% on oven dry fibre. The stock was continuously agitated by a stirrer. The rate of air flow was adjusted to 10 litres per minute. The froth that formed on the surface of the pulp was scraped off and collected in an overflow tray. The rejects from the flotation were concentrated and retained for further examination. Losses from the flotation cell due to particle removal were replaced by the addition of water throughout the process. After 15 minutes of flotation the air flow was stopped and the pulp drained from the flotation cell. This pulp was then made into handsheets to permit analysis of the remaining ink particles.

5.1.5 Hyperwashing Apparatus[123,124]

The hyperwashing apparatus consisted of a sieve mounted in a holder. The sieve had a size 100 mesh, equivalent to 150 microns.[125] The pulp was poured into the sieve and water at a constant reproducible pressure was applied for two minutes. The jet of water was moved around the pulp in a fixed spiral pattern. This pattern was maintained for two minutes, to ensure that all the pulp has been subjected to the same treatment.

The jet of water traps the fibres and particles against the mesh of the sieve, unattached particles are forced though the gaps in the mesh and are removed; larger and fibre attached particles are retained by the mesh. The gaps in the mesh were 150 x 150 μm. This aperture was too small to allow fibres to pass through. The largest disk like particle that would pass though would be approximately 220μm in diameter.

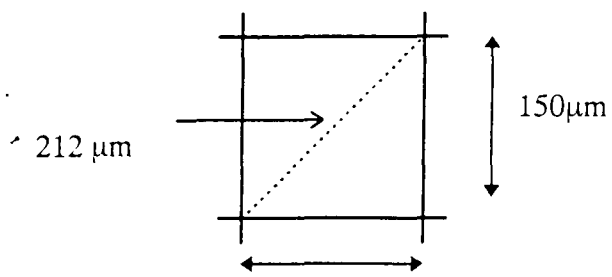


Figure 5.1.4 Diagrammatic Representation of Hyperwashing Apparatus Aperture

5.2.0 Analysis of Paper and Ink Particle Size Distributions

As stated previously the deinking processes remove particles of different sizes. Washing removes the smallest particles, up to 10μm in diameter, flotation removes particles of 10 to 100μm, screening and cleaning remove particles from 250 to 400μm. To allow a comparison of the relative efficiencies of the removal process the numbers and sizes of particles must be quantified.

Particle size analysis of irregularly shaped particles is only meaningful when closely defined; the length, area, diameter or volume may be measured. The only absolute method of measuring particles is by microscopy. Traditional methods of particle size distribution determination include sieving, gravitational and centrifugal sedimentation.[130]

Sieving[131,132] has been used for dry samples for many years and can identify particles down to about 100μm but it is a slow technique. Gravitational sedimentation [133] is used for wet samples down to a diameter of 1μm but is also slow, often taking hours or days. Centrifugal sedimentation[134] was introduced to speed up the process, but it can be hours before a result is obtained. The Coulter method[135] relies on the sample being suspended in an electrolyte. The resulting suspension flows through a small orifice in a glass tube. As each particle passes through the tube it displaces an equal volume of electrolyte, thus changing the electrical resistance across the orifice. The change in resistance is measured by electrodes.

Newer techniques have become available to speed up particle size analysis. Laser scattering is a technique that uses laser light to quantify the size of particles present in aerosols and liquids. Image analysis is a computer based recognition system, which can be applied to a wide range of systems.

In this work image analysis will be employed to determine the toner particles present on handsheets. The laser diffraction technique was used to establish the particle size distributions of particles in suspension, that is particles which are detached from fibres.

5.2.1 Image Analysis - Introduction

Image analysis allows quantification of an image with great accuracy. The use of image analysis is widespread and includes applications in the pulp,[136] paper,[137] printing,[138] steel, packaging industries as well as the medical and research fields. It can quantify many different parameters such as size, circumference, area, shape, and position.[139] The image analysis of handsheets produced from recycled pulp allows qualitative and quantitative assessment of ink particle distributions.

Many of these applications of image analysis involve the identification of particles or inclusion bodies within a field of view. To ensure proper and full identification of the target bodies from the background it is helpful to have maximum possible contrast between the two opposing media. For example identifying black toner on white paper, or white stains on a dark piece of cloth.

The image analyser detects toner particles that are present on thin paper handsheets. These particles are either attached to or detached from fibres. The image analyser cannot distinguish without information on the history of the pulp, for example, if the sample has undergone a hyperwashing or flotation treatment.

5.2.1a Use of Image Analysis to Investigate Pulp and Paper

Image analysis has been used in the pulp and paper industry for some time and has been applied to the identification of ink particles in recycled fibre. Toner particles in a pulp are easily identified using image analysis as they provide a good contrast to the paper fibres. However, image analysis on its own cannot identify whether a particle is attached to a fibre.

Another of the major uses of image analysis within the pulp and paper industry is the identification of stickies.[140] These are contraries, that is, unwanted materials that have become incorporated into the pulp during the recycling process. They derive from self adhesive labels and glues from other binders used in the printing process. These glues are not removed by flotation or cleaning. They cause problems as the adhesives may stick to

parts of the paper machine or printing press. The number of stickies in a sample can be determined by performing image analysis under ultra violet light.[145] The chemical structure of the adhesives enables them to fluoresce under UV, making them stand out against the fibres which do not fluoresce. Image analysis can also identify wire marks,[141] mottle,[142] sharpness, and fluffing.[143]

5.2.1b Principles of Image Analysis

There are five main steps involved in analysing samples using image analysis: image capture, segmentation, object detection, measurement, and analysis.

Image Capture Image capture entails the conversion of the image into an electronic signal suitable for processing. An image can be considered as a distribution of energy, this energy can be part of the electromagnetic spectrum, electrons, or acoustic waves. The image capture system quantises the image into spatial and tonal differences. Spatially the image is divided into an array of picture elements, or pixels. The pixels are usually arranged into a square or rectangular pattern, for example 512 by 512 pixels, giving a total of 262,144 pixels. The tone of an image is determined by the relative intensity of the energy. Tonally, the image is usually divided into either 64 or 256 intensity levels. These levels are often referred to as grey levels.

Segmentation Segmentation is the separation of the regions of interest within an image from the background. Thresholding is the simplest method of achieving this end because it can be applied where the overall illumination of the sample can be carefully controlled. The selection of the threshold level is performed, by the user, to isolate objects of interest within the sample. All intensities below the selected level are then treated as black and all levels above as white. The result of this segmentation is that the image is transformed into a binary format, where the pixels are either of interest or background, according to their intensity level.

Object Detection An object is a region of interest within the image. Data is reduced by not describing each pixel and its intensity level, but rather by a description of the size and position of the regions of interest within the image. Object detection is a data reduction step.

Measurement Correct measurement of the regions of interest is dependent on the correct segmentation of the image. The boundary between a region of interest and the background is important, as the image analyser will only count between defined boundaries.

Analysis Once the measurements have been made the results can be analysed to classify the sample. A list of thousands of numbers does not lend itself to easy classification. For this reason a graphical output of the results is usually used, though sometimes a statement such as "10 percent of the object in this sample are greater than x mm" may be used. The simpler the final data, the easier it is to make a judgement about the sample.

5.2.1.c Requirements for Image Analysis Testing[144]

To accomplish the accurate image analysis of ink particles on handsheets suitable optics to identify the particles of interest must be available. A method of forming uniform and consistent handsheets is the second requirement.

5.2.1d Optics

The optics must be able to identify the various particle size ranges of interest. In this project a Hitachi KP-141 monochrome camera was mounted on a GS stereo microscope. The magnification was x3. This level of magnification gave a field of view of around 2.5mm by 2.5mm which was adequate to accommodate the largest particles without sacrificing the resolution of the smallest. It is recommended by PIRA[144] that 'magnifications capable of detecting a minimum particle of 4 square microns for one pixel' should be used. The microscope used for the image analysis was fitted with reflected and transmitted light sources both capable of variable intensities.

The image analysis system consists of a camera, a stable platform from which to capture images, followed by an image digitising facility and a way of displaying the captured images. The image analysis system was driven by a Pentium 133 MHz microcomputer. The camera and microscope system is shown in figure 5.2.1.

The camera used was mounted on a GS stereo microscope, figure 5.2.2. Calibration of the microscope and camera was achieved using a graticle. Calibration enabled a typical minimum particle size of 55μm^2, (8.2 microns in diameter) to be detected by the system. However, the software uses a 2x2 matrix to identify a particle from the background signal. this means that whilst the smallest particle that the optics can detect is approximately 8 microns in diameter, in order to be recognised by the software as a particle the smallest size object will be 16 microns by 16 microns.

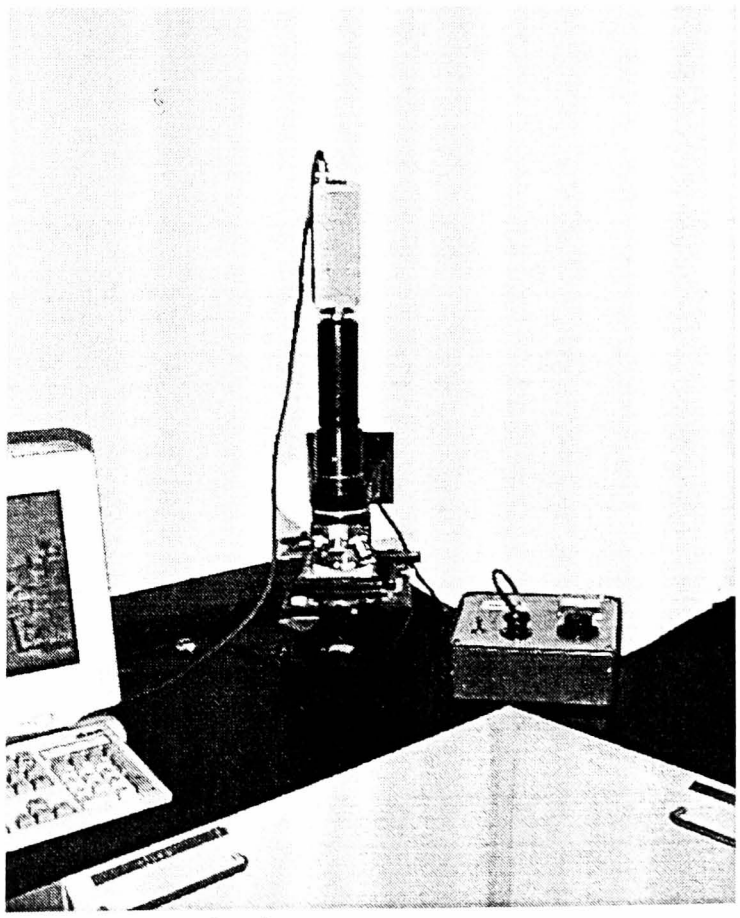


Figure 5.2.1 Camera and microscope

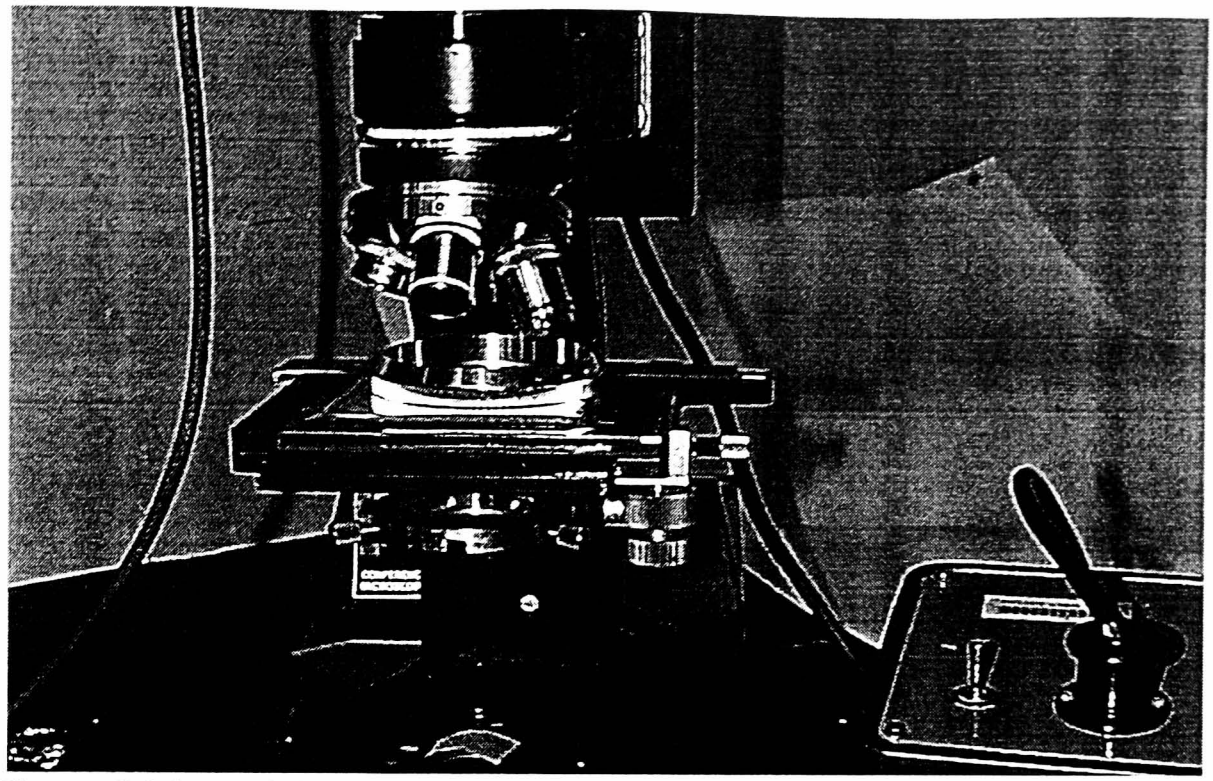


Figure 5.2.2 Microscope stage

5.3.0 Laser Diffraction - Introduction

Laser diffraction is a recently developed technique[129] to establish the particle size distributions of suspended particles. The popularity of laser diffraction is due to its accuracy and reproducibility. The technique can be used across a large particle size range, from 0.1μm to greater than 8000μm.[129]

The laser scattering apparatus used in this project, the LS130, was supplied by Coulter International and is capable of resolving particles in suspension from 0.1 to 900μm.

5.3.1 Theory of Laser Diffraction

When a particle is placed in the path of a light beam, the light is scattered. There are three elements to the scattering: reflection, refraction and diffraction. The light is scattered in all directions but the scattered light is not uniformly distributed. The greatest intensity is in the forward direction and is due mostly to diffraction, (see Figure 5.3.1.) The diffracted light displays a series of concentric rings known as Fraunhofer patterns. They consist of a bright central disk, known as an Airey disk, surrounded by circles of decreasing intensity. The pattern is symmetrical about its central axis, and decreases in intensity with increasing angle of scatter.

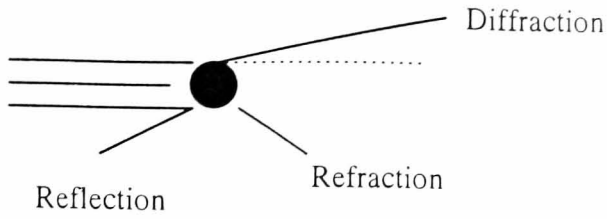


Figure 5.3.1 **Scattering of Light from a Particle**

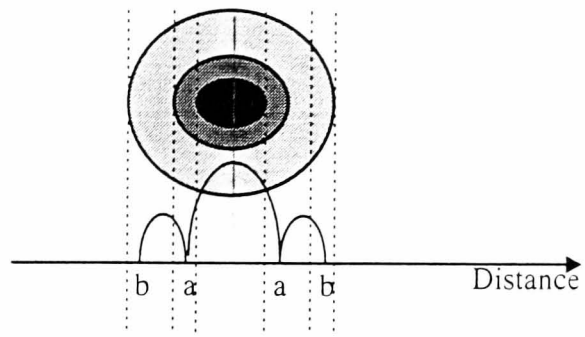
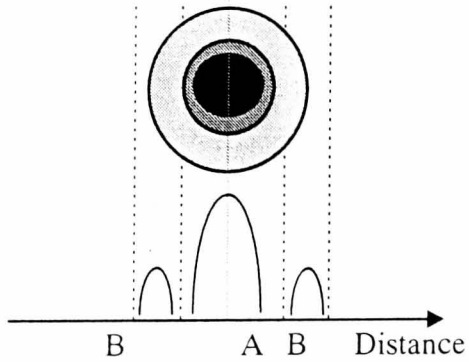
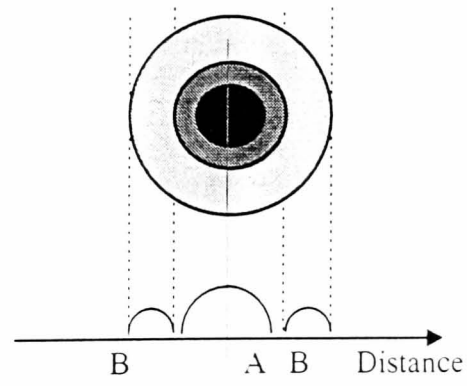


Figure 5.3.2 **Intensity of Light Scattered from a Particle**

Figure 5.3.2 is representative of the light intensity falling on the detectors. The darker the area the more intense the light falling on it, and the stronger the signal. The central area is the Airey disk. The secondary peaks are characteristic of the size of particle. The first minimum is lower for a large particle.



Large particle diffraction pattern



Small particle diffraction pattern

Figure 5.3.3 **Difference in light scattering from two particles**

Large particles diffract light at low angles whilst small particles diffract light at higher angles, (see Figure 5.3.1.) Large particles diffract light more intensely, small particles with much less intensity. The diffraction patterns produced by a single large particle and a single small particle can therefore be differentiated, this can be seen in Figure 5.3.3. A single particle is not introduced into the laser beam but rather a distribution of particles of different sizes passes through. Each size of particle would have a slightly different angular spacing. It is possible to analyse the data from such a graph and establish the distribution

of particle sizes required. Figure 5.3.4 shows the distribution obtained by measuring five classes of particles. The important points are the maximum intensity and the angle of first minimum of the light falling on the detectors, as these two pieces of information are used to calculate the particle size.

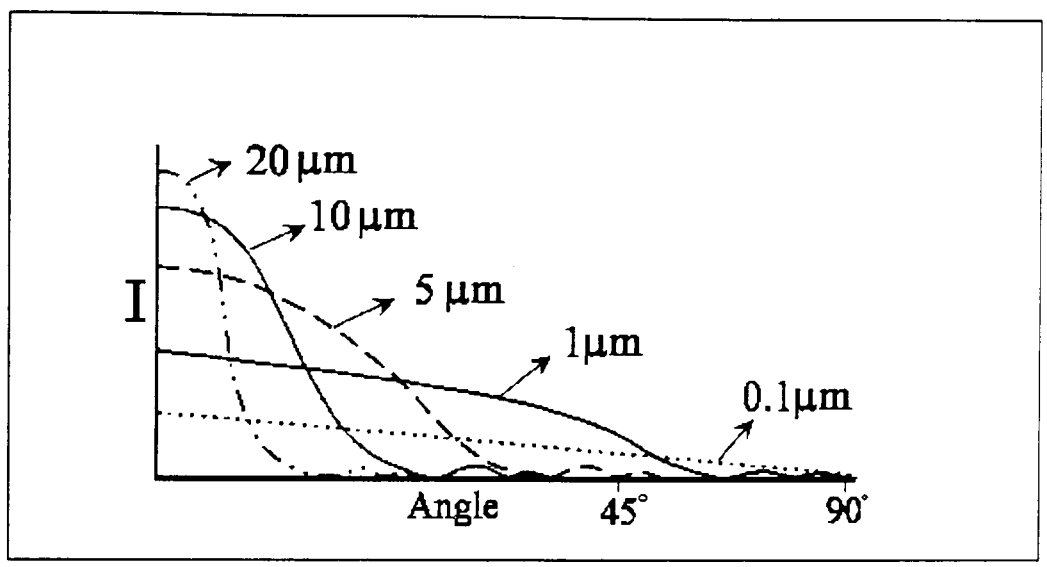


Figure 5.3.4 Intensities of different size particles

The large particles diffract high intensities at low angles and small particles diffract at lower intensities but over much larger range of angles. The true measurements taken by the laser scattering machine would be an 'ensemble' of particles. The information from each particle that passes through the analyser is presented in the graph.

Data from the LS130 is available in a wide range of formats. Most common is the cumulative volume distribution. This gives the equivalent size distribution of spherical particles from 0.1 to 900µm. Data can be obtained directly from the detectors and processed off-line.

Data from the LS130 can be compared with that from other techniques, for example sieving, by approximating the size of particles which would fit though a set of sieves. It is important to remember that laser scattering measures equivalent spherical diameters of particles, and not those particles directly whereas other techniques measure the amounts of particles directly.

The volume of sample required varies with sample concentration. The instrument determines the extent of attenuation to the laser beam to give an estimate of the amount of sample required.

Reference materials of known spherical diameter are used to check that the readings are within acceptable error limits. The standard reference materials provided are glass beads, latex solution, and garnet particles in suspension.

5.4 Nikon Reflection and Transmitted Light Microscope

The Nikon Optiphot microscope is fitted with objectives of x10, x20, x50, and x100. This provides magnifications of x100, to x1000, allowing identification of objects down to approximately 5μm. Transmitted and reflected light options are available on the instrument, both transmitted and reflected light can be polarised. Bright field and dark field illuminations are available.

The microscope shown in figure 5.4.1 was used to identify fibres, to classify any damage done to them during sonication and to determine the status of any particles present; for example, whether they are attached or detached from fibres.

Fibres can be identified from their general appearance. For example silk and cotton fibres are very long, 20-30 mm in length, while a groundwood pine fibre may be only 2-3 mm in length. Markings on the fibre are also important, for example wood fibres have pits found on their sides.

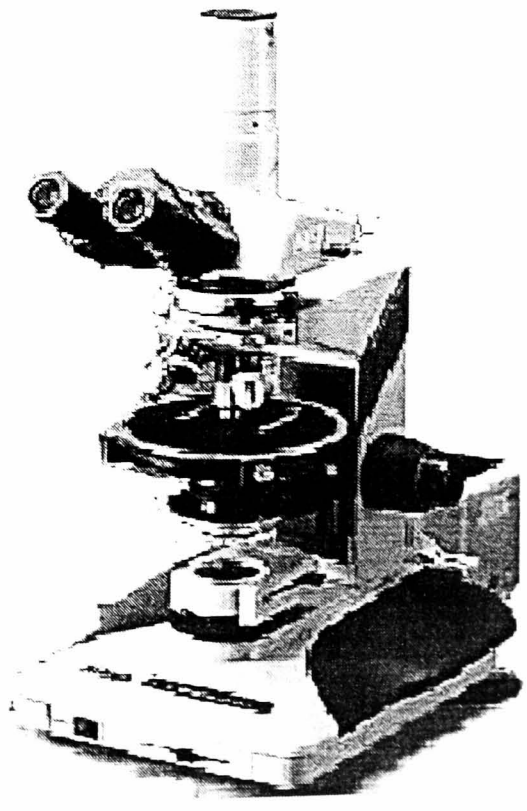


Figure 5.4.1 **Nikon Optiphot Microscope**

Images were captured using a JVC 1270, colour CCD camera, mounted on a C mount, and printed via a Fargo colour dye sublimation printer.

5.5 Kajaani Fibre Length Analyser

The Kajaani fibre length analyser allows the quantitative and statistical evaluation of the lengths of paper fibres. A representative sample of fibres is taken from the pulp and diluted in water to a low consistency. The fibres are then added through a wide bodied pipette to the bowl of the analyser which is filled with water. The fibre suspension is agitated to prevent the fibres from flocculating. Flocculation of the fibres would prevent correct measurement of the sample, as the fibres would not enter the analyser one at a time. The very dilute fibre suspension is drawn through a capillary tube under vacuum. The fibres are drawn into the tube individually presenting their longitudinal axis. The fibres pass through a light beam and the time that the beam is occluded by the fibre is used to determine the length of the fibre.

To obtain a representative sample of fibres a minimum 4000 fibres for each sample are analysed. Each pass through the machine was repeated three times.

5.6 Burst Tester and Tear Testers

Both the burst and the tear tester are standard pieces of equipment used in the testing of paper and board products. The burst tester works by inflating a rubber diaphragm onto which the sample is clamped. The expansion of the diaphragm stresses the paper and eventually causes it to rupture. The oil pressure required to break the sample is indicated on the dial of the machine. Details of the Standard method of burst testing can be found in BSI 4459.

The tear tester works by swinging a calibrated weight through a partially cut known length of paper. The paper is clamped in the path of the swinging weight. Full details on the tear testing of paper can be found in BSI 4459.

5.7 Canadian Standard Freeness Tester

The Canadian Standard Freeness (CSF) Tester is used to determine the rate of drainage of a dilute pulp suspension. The rate of drainage of a pulp is a measure of the amount of work done on the fibres during stock preparation. The work done on fibres changes their morphology. These changes are fibrillation of the secondary walls of the fibre, fibre shortening, and the formation of fines; the latter two occur mainly during beating or refining.

Changes to individual fibres affect the properties of the pulp as a whole. Fibrillation and fibre shortening result in increased fibre flexibility. This results in the compacting of the pulp when formed into a pad, and an increase in the overall surface area of the fibres. The increase in the surface area leads to a larger amount of water being retained by the fibres. The inhibition of drainage from the fibres is measured to give a reading of freeness. This is therefore a physical measurement of a property that would otherwise best be observed under a microscope.

The Canadian Standard Freeness test was originally designed for groundwood testing. It can be applied to chemical pulps, but does not give an absolute value. Comparison between chemical and groundwood pulps should not be attempted, however comparison between chemical pulps is acceptable.

This apparatus consists of a drainage chamber and a rate measuring funnel. The drainage chamber is fitted with a calibrated screenplate through which the water drains at a fixed rate. A known amount of pulp, (1 litre), at a known consistency, (0.3%), is placed in the drainage chamber. The base of the drainage chamber is sealed, and a quick release lid is then lowered onto the upper part of the chamber. The lower half of the drainage chamber is swung away, and a pet-cock on the lid released. This releases the vacuum inside the drainage chamber, and the water drains through the screenplate. Water that is discharged with laminar flow through the funnel is collected in a graduated container. The volume collected is measured, and corrections for temperature and pulp concentration are applied to obtain the measure of freeness. Any excess water is drained through an opening into a second container.

The apparatus of the CSF is shown in figure 5.7.1. The pulp is placed into the container G. and drains through the mesh at the base of G. The filtrate from the mesh is channelled by the funnel at H, where the fluid with laminar flow is split into the measuring cylinder from which the measurement is taken.

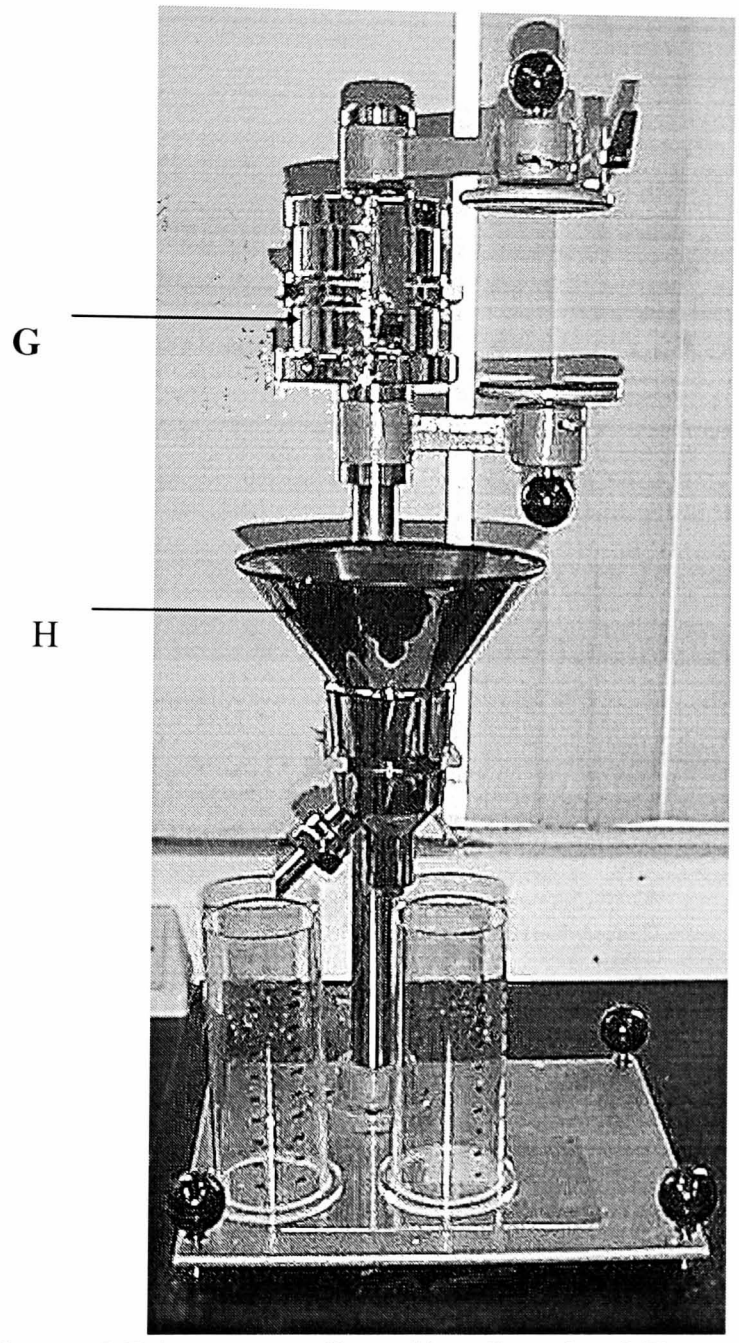


Figure 5.7.1 Canadian Standard Freeness Tester

6.0 Investigations into Fibre Damage

Chemically pulped fibres from wood presented themselves as the sector of the papermaking industry most likely to increase in the amounts recycled. Before concentrating on the problem of mixed office waste an investigation into the interaction of ultrasound and paper fibres was undertaken. A simple system was initially studied for the effects of fibre damage before moving on to more complex fibre and toner systems.

Virgin fibres were obtained from UK Paper at Sittingbourne. A variety of fibres was used in the study, corresponding to the tree species used in UK Paper's printing and writing grades. Kotlas (a short fibred hardwood) and Arracruz (Eucalyptus) fibres were examined for their response to ultrasound treatment. Fibres were supplied in lap form, which had not undergone refining treatment, or addition of size or fillers. The lap was soaked in distilled water and disintegrated using a British Standard disintegrator for 2000 counts.

Fibres were treated with ultrasound for different time intervals. Slides were made and examined under a microscope to determine the extent of damage to the fibres. The fibres were also investigated using a Kajaani fibre length analyser to evaluate the degree of cutting occurring.

Untreated Arracruz fibres were also measured to establish the fibre length distribution of the sample. The Kajaani equipment requires a minimum of 4000 fibres in the sample to ensure statistical integrity. Shown in figure 6.0.1 is the distribution obtained from disintegrating unrefined Arracruz fibre samples. The graph shows two samples from different batches. The distribution shows a peak at 0.6 mm, the most common length of fibre. The two distributions are very similar giving good agreement between the samples.

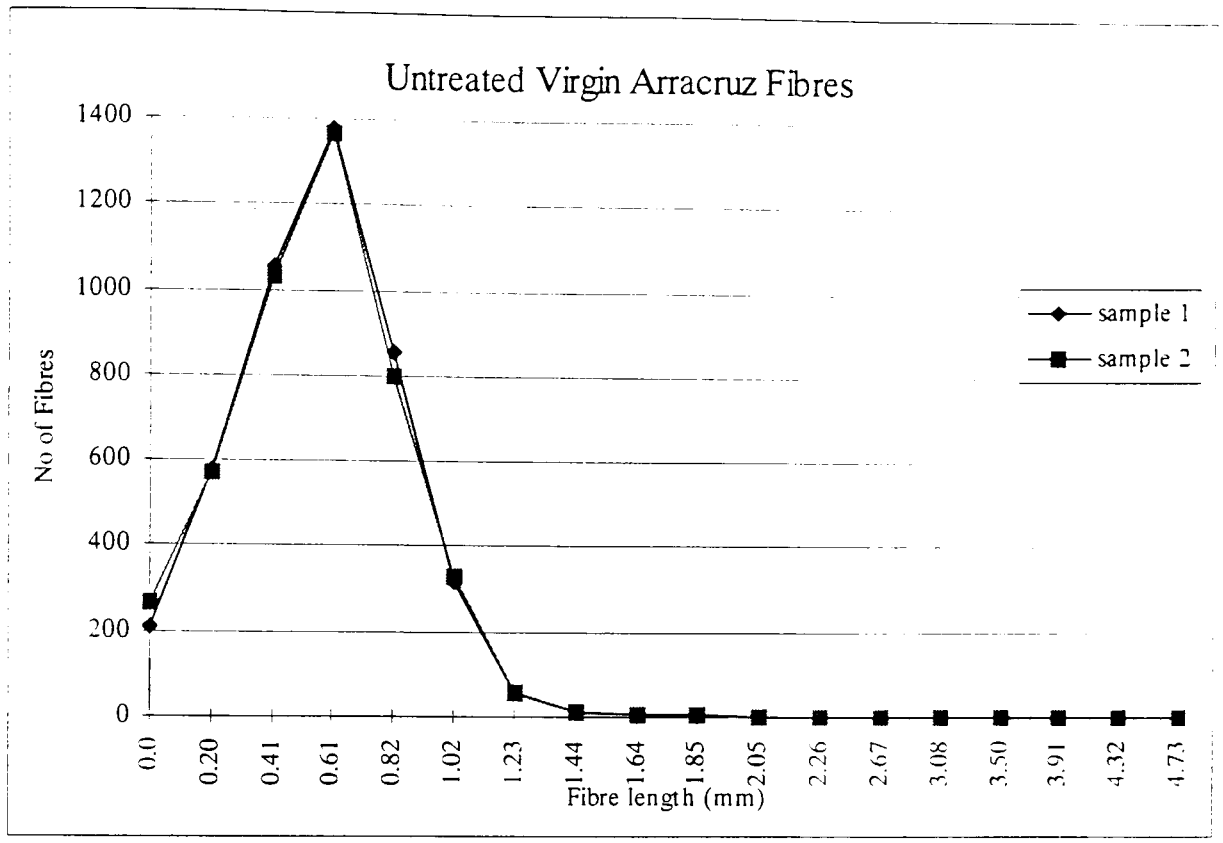


Figure 6.0.1 Untreated Arracruz Fibres

Fibre length (mm)	Number sample 1	Number sample 2	% Distribution Sample 1	% Distribution Sample 2
0.0	207	269	4.63	6.05
0.20	577	571	12.90	12.85
0.41	1052	1029	23.51	23.15
0.61	1380	1364	30.84	30.69
0.82	857	797	19.15	17.93
1.02	319	329	7.13	7.40
1.23	58	58	1.30	1.30
1.44	10	11	0.22	0.24
1.64	6	6	0.13	0.13
1.85	4	4	0.90	0.09
2.05	2	2	0.04	0.04
2.26	1	1	0.02	0.02
2.67	1	2	0.02	0.04
3.08	0	1	0	0.02
3.50	0	0	0	0
3.91	0	0	0	0
4.32	0	0	0	0
4.73	0	0	0	0
Total	4474	4444	100%	100%

Table 6.0.1 Fibre lengths of Arracruz fibres

Fibres with lengths less than 0.2 mm are usually disregarded, as they are considered to be fines, however they are included in table 6.0.1 for completeness. A relatively small number of fibres are longer than 1.2 mm, fibres longer than 2 mm are rare. The fibre number distribution is shown for information and other distributions will be shown as a percentage. The distribution shown above in table 6.0.1 is represented in figure 6.0.2.

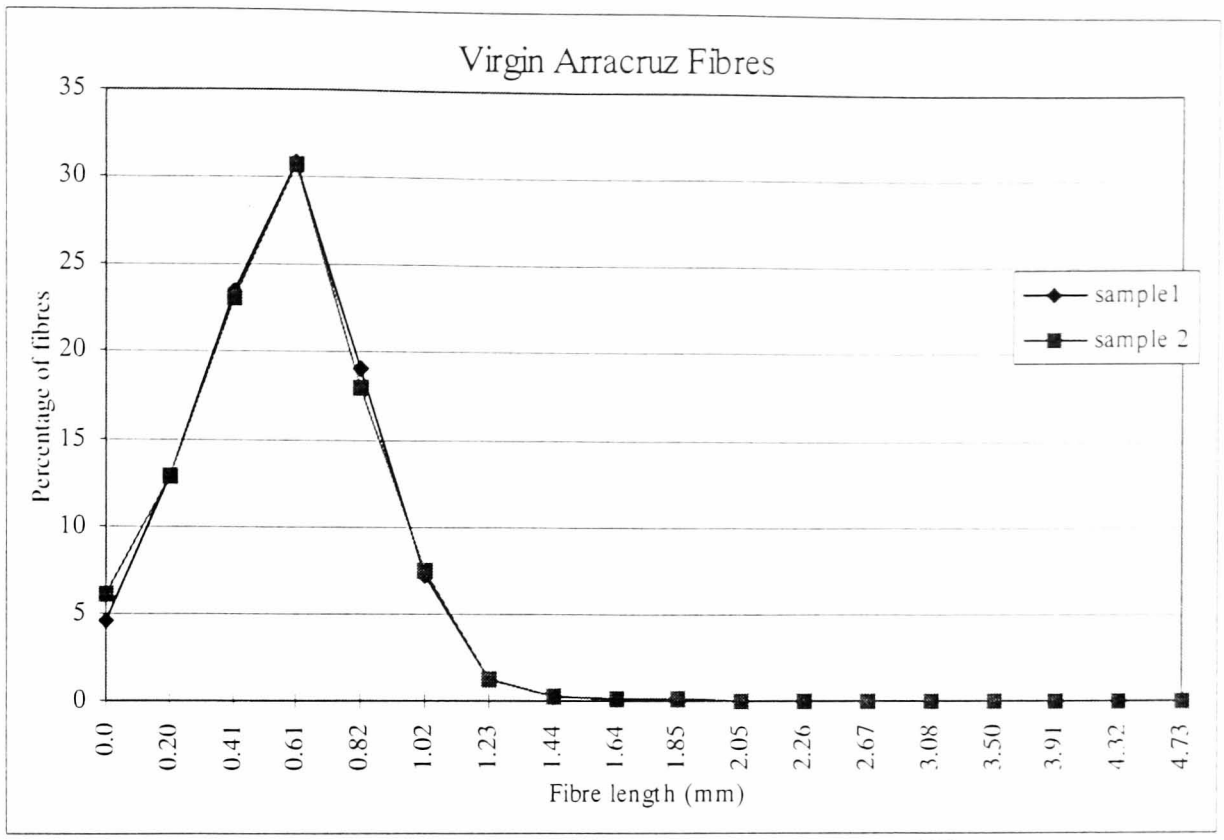


Figure 6.0.2 Percentage Distribution of Untreated Arracruz Fibres

The use of percentage distributions allows comparisons of distributions between samples and between different treatments to be made.

The Arracruz sample was treated with ultrasound for a total of 20 minutes at a consistency of 1%. The temperature was controlled in this sample by immersing the reaction vessel in a cold water bath and by cyclically sonicating for 5 minutes, followed by 5 minutes cooling. Figure 6.0.3 shows the percentage distribution obtained from two samples.

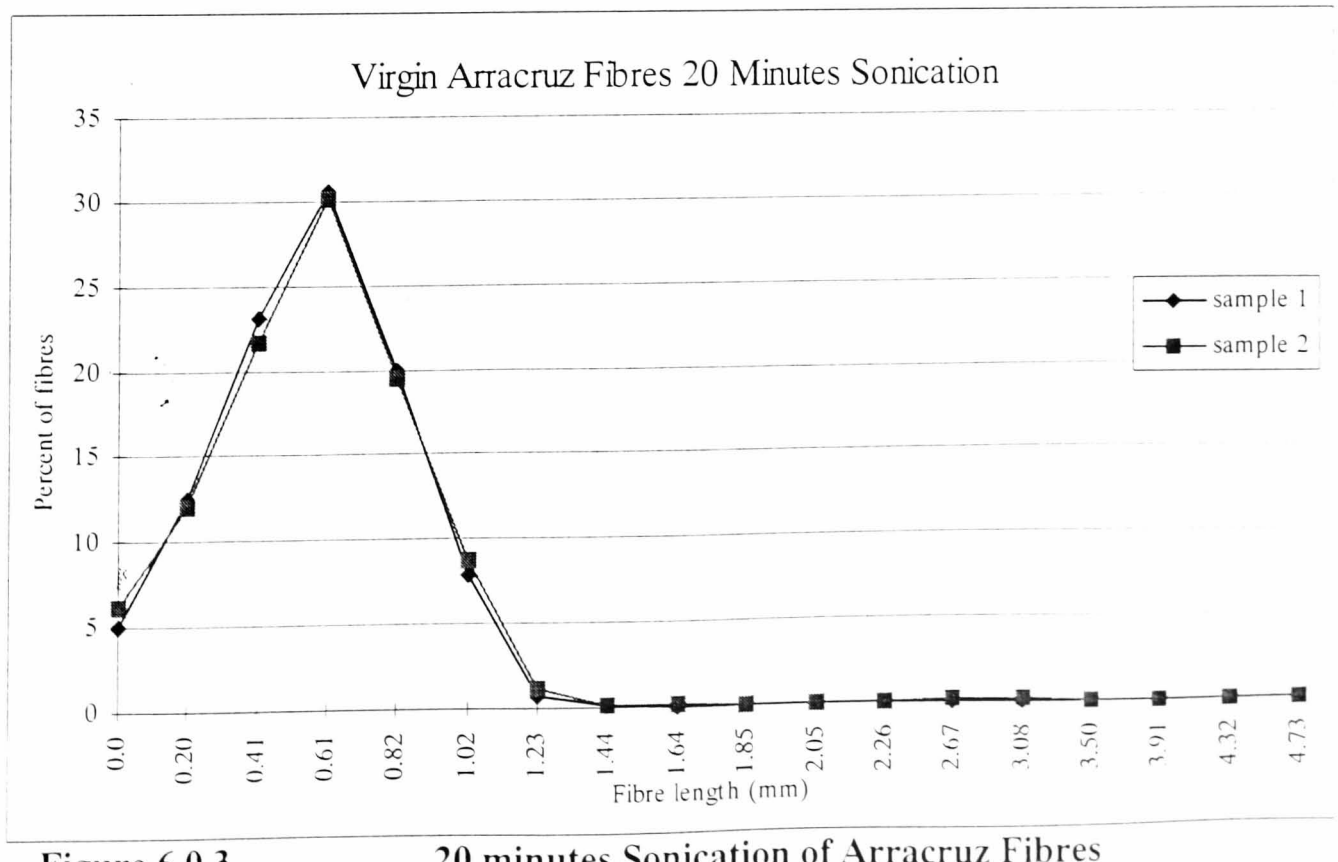


Figure 6.0.3 20 minutes Sonication of Arracruz Fibres

Comparison of the two treatments as shown in figure 6.0.4 is an average of both samples for each treatment.

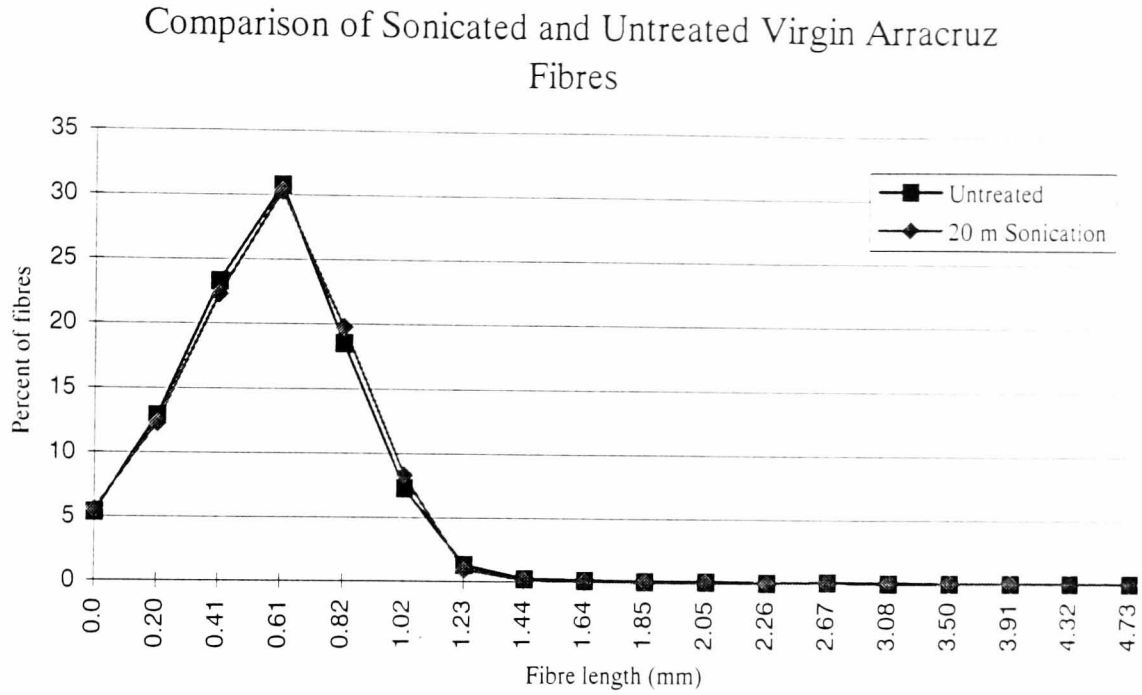


Figure 6.0.4 **Comparison of Sonication and Control Samples**

There is no significant difference between the two sets of data, the most common fibre length remains at 0.6 mm, with a few fibres longer than 2.0 mm. The results therefore show that there is no cutting effect from the ultrasound. Unrefined Arracruz fibres were then treated with a PFI mill for 3000 counts.[149] The PFI mill is a laboratory beater, designed to mimic the commercial refining process. It consists of a small disc type refiner, with a toothed rotating cylinder turning within a stationary complementary housing. The comparison of untreated with refined Arracruz samples is shown in figure 6.0.5.

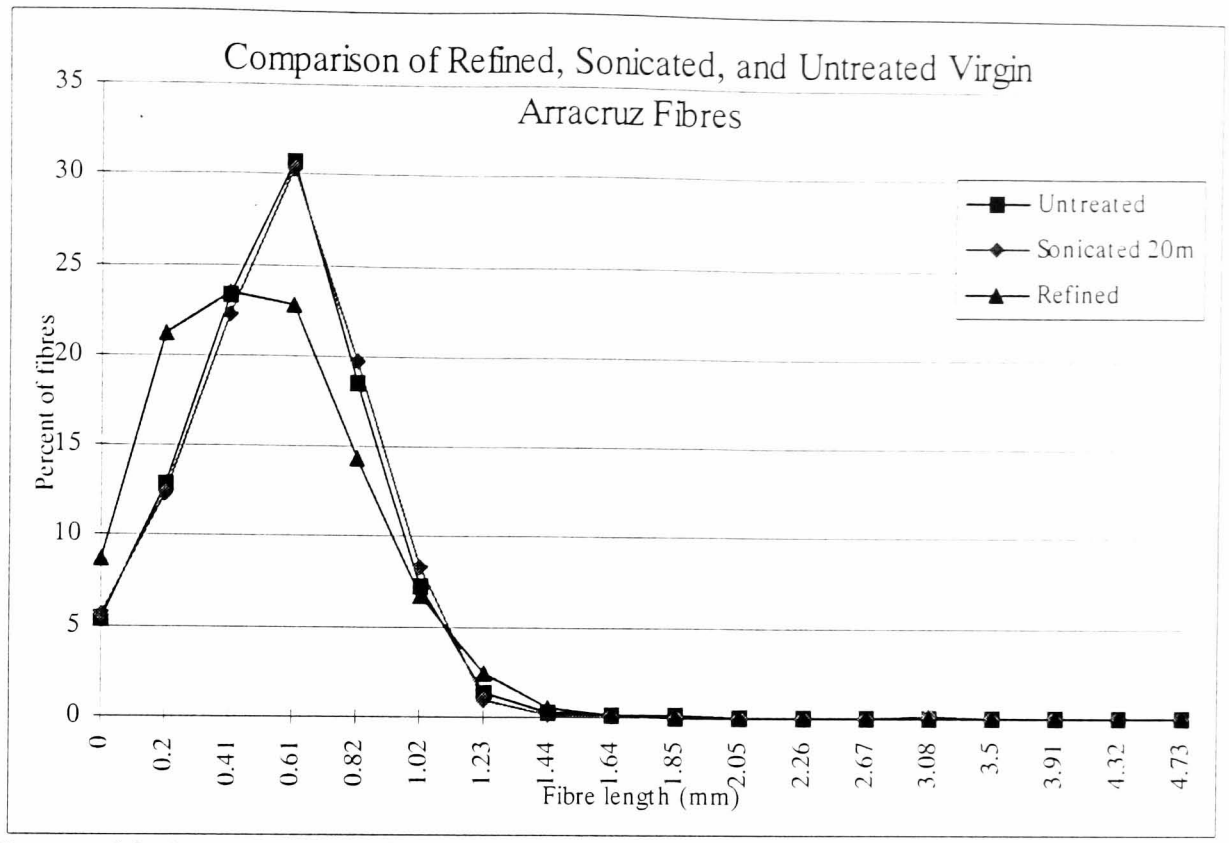


Figure 6.0.5 **Comparison of Treatments for Arracruz Fibres**

Refining shortened the fibres considerably, with the most common fibre length being between 0.3 and 0.4mm. The untreated fibres were much longer than the refined fibres.

Fibre length(mm)	Untreated sample 1	Untreated sample 2	Sonicated 20min (1)	Sonicated 20min (2)	Refined sample 1	Refined sample 2
0.0	207	269	211	260	1600	1084
0.20	577	571	526	505	4025	2586
0.41	1052	1029	969	903	4112	2888
0.61	1380	1364	1286	1258	4361	2764
0.82	857	797	839	818	2504	1600
1.02	319	329	331	367	1142	667
1.23	58	58	33	46	246	135
1.44	10	11	4	6	56	23
1.64	6	6	2	4	25	8
1.85	4	4	1	0	7	5
2.05	2	2	1	1	6	6
2.26	1	1	0	2	6	0
2.67	1	2	0	3	6	1
3.08	0	1	0	7	0	0
3.50	0	0	0	2	3	0
3.91	0	0	0	0	2	1
4.32	0	0	0	0	0	0
4.73	0	0	0	0	0	0

Table 6.0.2 **Comparison of Arracruz Fibre Lengths**

Shown in table 6.0.2 are the numbers of fibres detected in each category for each sonication and refining treatment. The numbers of fibres in the refined samples are larger due to the demands of the apparatus. Shorter fibres demand greater numbers to ensure statistical

integrity. After testing Arracruz fibres other fibre types were examined. Kotlas, a hardwood, was tested, with a more detailed ultrasound treatment. Kotlas fibres were treated for 5 minutes, 10 minutes, 15 minutes and 20 minutes. The results of this experiment are shown in figure 6.0.6. Each data point is the average of 2 samples.

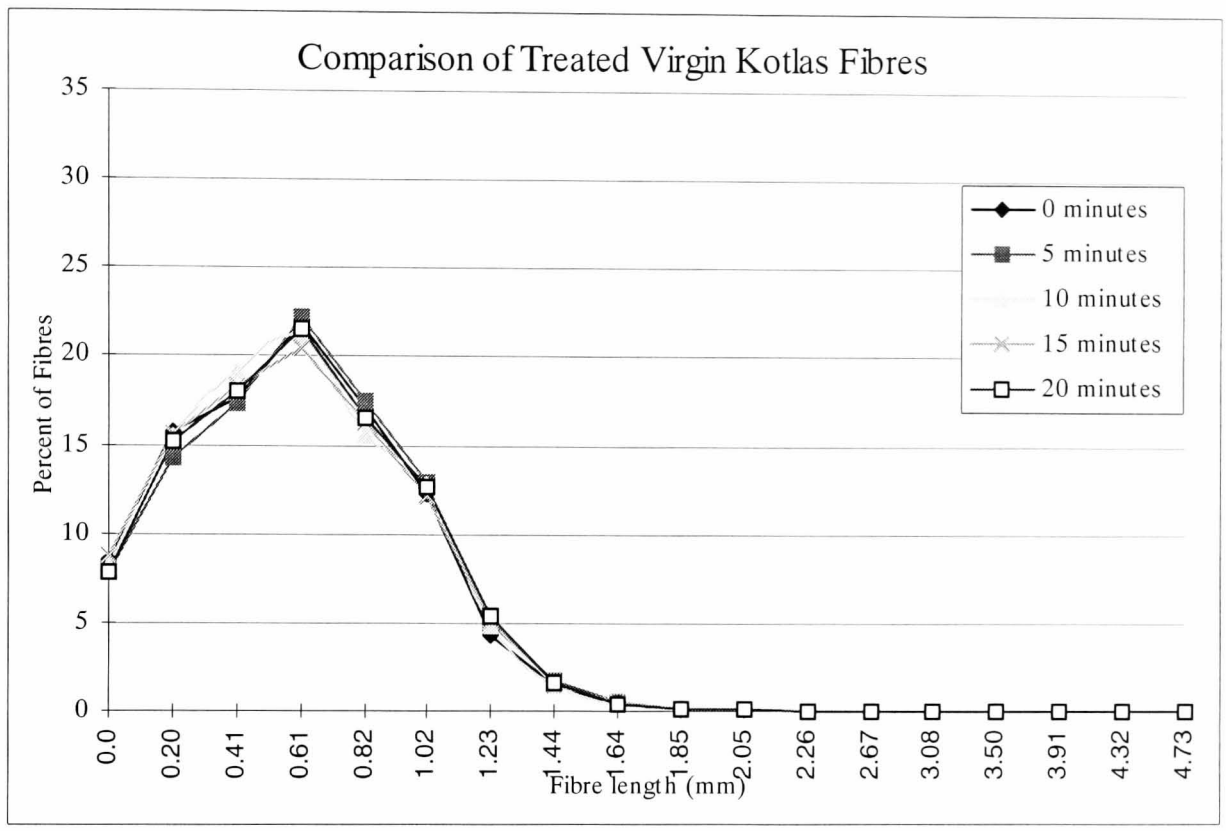


Figure 6.0.6 Comparison of Sonication of Kotlas Fibres

All the distributions display the same trend in that all treatments had the same affect on the average fibre length. The results show that there was no cutting associated with ultrasound treatment. The samples that were untreated in this case were also subjected to a mechanical refining treatment in the PFI mill. The results of this experiment are shown in figure 6.0.7 overlaid with figure 6.0.6. The refined fibres exhibited a much shorter average length than those which were sonicated.

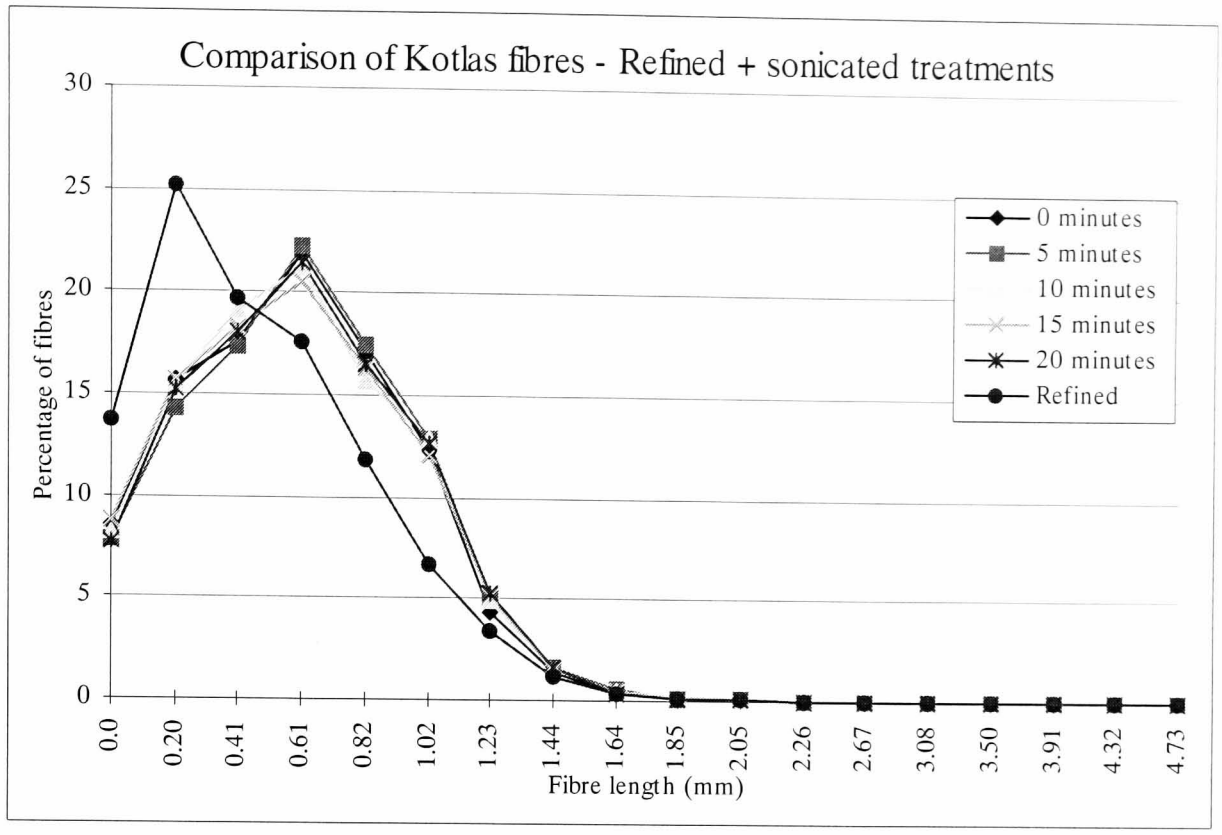


Figure 6.0.7 **Comparison of Treatments for Kotlas Fibres**

The refined fibres had an average length of around 0.2mm, the untreated and sonicated samples had retained their original length. Shown in figure 6.0.8 is a photomicrograph of Arracruz fibres after refining in a PFI mill. The result shows that the fibres are fibrillated and cut by the action of the refining treatment.

Fibre length (mm)	0m1	0m2	5m1	5m2	10m1	10m2	15m	15m2	20m1	20m2	PFI-1	PFI-2
0.0	387	356	462	436	337	400	461	351	460	370	1484	1834
0.20	724	643	889	766	648	729	857	665	894	724	2773	3333
0.41	746	783	1096	908	823	881	1013	805	1094	835	2211	2544
0.61	1019	887	1392	1180	897	991	1123	904	1271	1021	1966	2295
0.82	754	732	1110	915	672	725	889	666	978	789	1129	1434
1.02	563	508	797	691	568	574	633	521	736	617	790	934
1.23	192	187	333	252	206	231	279	212	317	251	267	343
1.44	62	62	103	92	49	85	82	54	97	77	71	84
1.64	19	14	31	31	16	21	19	19	18	21	32	33
1.85	6	5	9	11	11	10	1	4	11	5	11	11
2.05	7	4	9	8	3	5	6	3	8	9	7	11
2.26	0	3	4	5	3	4	3	2	5	5	2	7
2.67	2	4	8	10	7	2	4	6	11	10	4	5
3.08	1	3	7	3	3	2	4	8	3	6	0	2
3.50	5	1	3	1	6	2	5	5	5	4	2	1
3.91	2	1	4	1	1	1	4	5	5	4	1	0
4.32	1	1	4	1	0	0	3	3	1	2	0	0
4.73	0	20	0	0	1	0	2	1	1	1	0	0

Table 6.0.2 **Fibre Length Data for Kotlas Fibres**

Examination of the sonicated fibres revealed that whilst they underwent fibrillation there were few, if any, partial fibres. This indicates that there was no cutting of the fibres by ultrasound action. This was to be expected as there were no blades or associated mechanical crushing actions present in the sonication of fibres. The implication was therefore that the mechanism by which ultrasonic energy couples to the fibres does not induce cutting or breaking of the fibre.

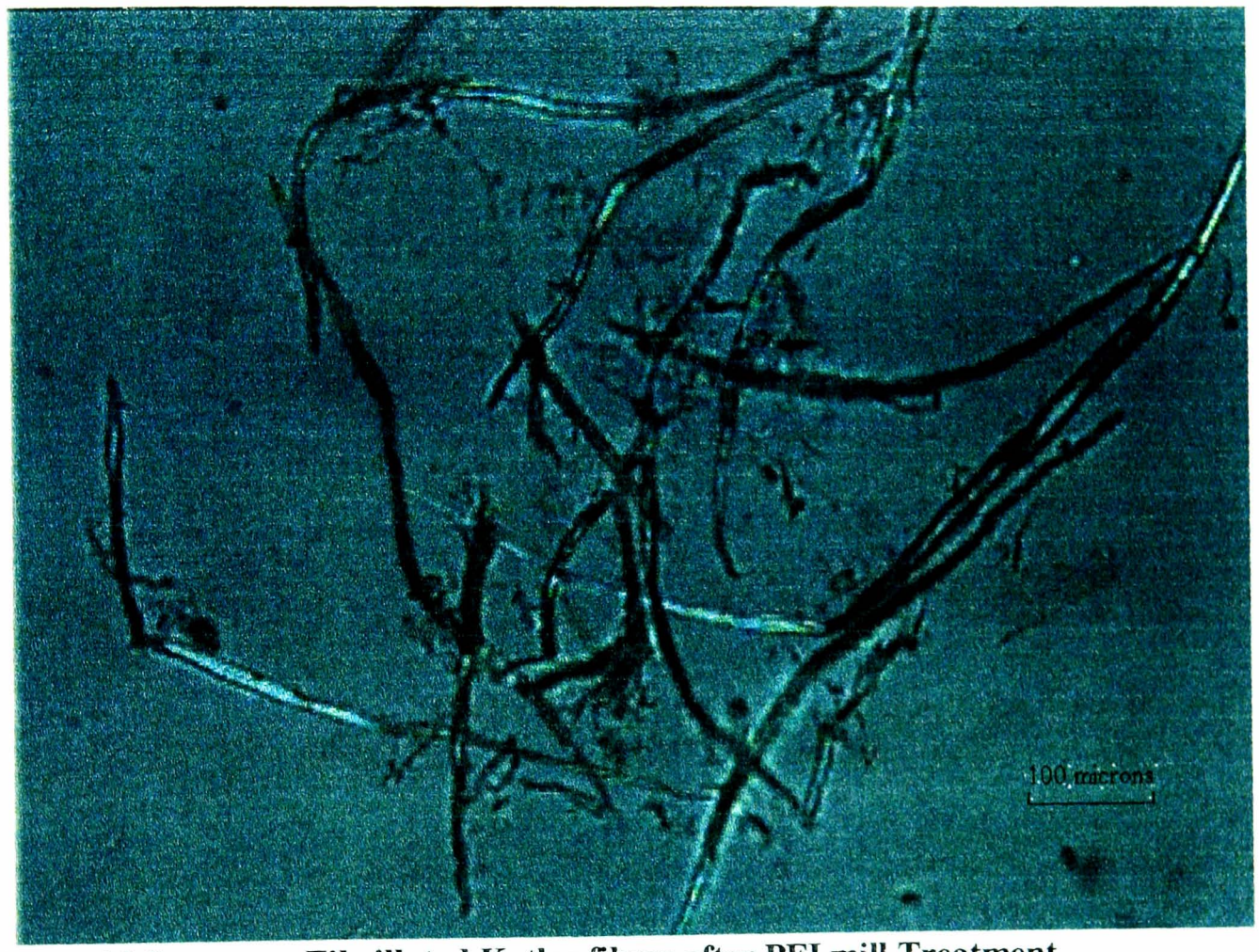


Figure 6.0.8 Fibrillated Kotlas fibres after PFI mill Treatment

The fibres were also examined using a Canadian Standard Freeness (CSF) tester, see section 5.7. Fibrillated fibres have increased surface area and retain more water, leading to an decrease in freeness. The table below shows the CSF values for control, sonication and PFI refined samples. The treatments were repeated and the results averaged.

Sample	CSF 1	CSF 2	Average
control (0 min)	620	616	618
5 minute	563	562	562
10 minute	556	555	555
15 minute	564	555	559
20 minute	554	545	549
PFI mill	103	129	116

Table 6.0.2 **CSF values for Refined Fibres**

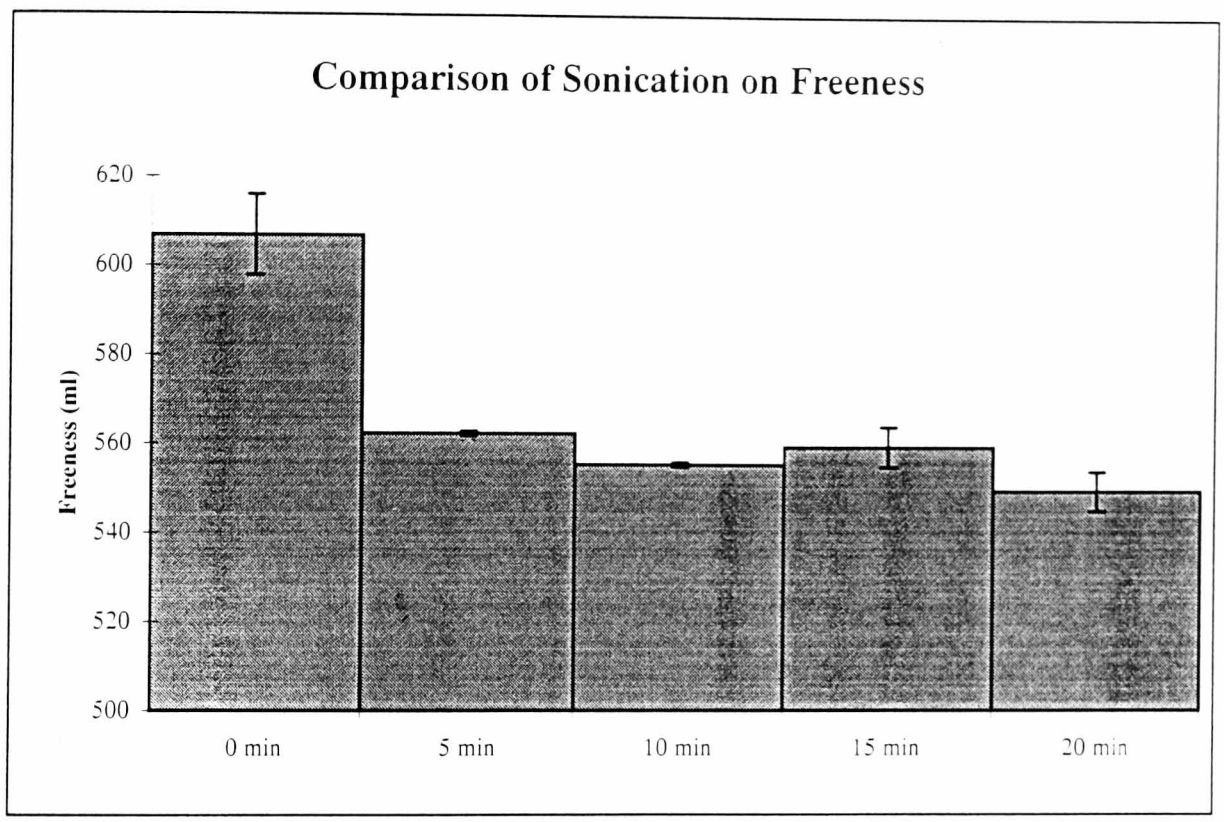


Figure 6.0.9 **Effect of Sonication on CSF**

6.1 Discussion of Fibre Experiments

The fibres selected for examination to treatment with ultrasound were chosen from UK Paper's furnish for their Ecoprint series of paper as they are used as copier papers. Kotlas and Arracruz fibres are chemically treated to remove lignin from the fibres during the pulp production process. The chemical digestion of lignin can damage fibres leading to a weaker, less durable fibre. The fibres were evaluated using a Kajaani fibre length analyser and microscopic analysis. The ultrasound treated fibres retained the same average fibre length distribution as untreated fibres, thus demonstrating that no cutting had taken place. The fibrillation of the fibres within the ultrasound reaction vessel must be due to the interaction of the fibres with ultrasound as there were no crushing or cutting blades present in the reaction vessel in which the fibres were treated. The fibres are too long to come into resonance with the ultrasound. The wavelength of sound at 20kHz in water is around 74

mm, the fibres used in this series of experiments were much shorter. 0.6 mm for Arracruz and 0.8 mm for Kotlas fibres.

With knowledge of the effects of ultrasound it can be seen that the interaction of paper fibres with ultrasound will be complex. The energy stored in the cavitation bubble will be given out when the bubble collapses. It is the nature and the way that this energy interacts with the fibre that is of importance.

Cavitation bubbles are initiated on any defect within the liquid structure. Dust, or other solutes present in a liquid can provide a seed point for cavitation bubble formation. The cavitation bubble grows and shrinks over several acoustic cycles before collapsing. The growing and shrinking of the bubble can cause erosion of resistant materials. The collapsing cavitation bubble produces a force of approximately 1900 bar, (section 4.4). In addition the imploding cavitation bubble can propel a jet of liquid towards any solid surface. The jet can move with a velocity of 400km per hour, further increasing the damage and washing away debris to leave a surface fresh for further attack.

A collapsing cavitation bubble may impart its stored energy to the fibres as kinetic energy. The fibres may be accelerated into the walls of the reaction vessel or into other fibres. The interaction of fibres with each other and the walls of the vessel would then cause the fibrillation. A parallel to this theory was first proposed for the interaction of polymer particles in solution.[76] The particles tended to aggregate into larger entities due to particle fusion under cavitation. The high velocity collision of the particles lead to the formation of 'dumbbell' shaped particles. This theory however, would only be applicable if the fibres were of a comparable size to the cavitation bubbles. The fibres are however larger than the bubbles by a factor of approximately 100. Cavitation bubbles at 20 KHz are approximately 23 μm in size,[94] the paper fibres used in these experiments are around 0.6 mm long, however, the fibres are similar in width to a cavitation bubble, 20-30 μm.

The most likely explanation for the fibrillation of the fibres is that a cavitation bubble is initiated on a paper fibre, possibly where there is prior damage to the fibre and where bleaching or delignifing chemicals remain. These chemicals would tend to decrease the local surface tension of the water making it easier for the cavitation bubble to be initiated.

The collapsing bubble then increases the damage to these fibre. The collapsing bubble and resultant jet stream exaggerates existing damage. Ultrasound treatment is unlikely to initiate new damage to the fibres.

The fibrillation on the fibres could be increased by using another effect of ultrasound, that of streaming. The streaming effect, not that of jet streaming, tends to push the liquid and fibres to the base of the reaction vessel. The fibres could be trapped at the base of the vessel, with cavitation activity occurring around and on them. The trapped fibre would be held where the cavitation bubbles, possibly several, could produce fibrillation. The vessel would be acting as an anvil, and the cavitation bubbles as a hammer, to crush and batter the fibres.

The most likely explanation is that the two effects of ultrasound work in harmony, the streaming effect trapping fibres where they can be crushed by the collapsing cavitation bubbles.

The pressure developed in the collapsing cavitation bubble, 1900 bar, is sufficient to cause erosion of metals and so could be expected to cause the fibrillation effects seen in the photomicrograph, figure 6.0.8. Little evidence exists of shear rates developed in a refiner or beater. However, the power required to produce the CSF value of 116 ml in the fibres refined in the PFI mill has been estimated at 200 kWh/tonne.[149]

The damage caused to the fibres in the PFI mill is greater than would be expected from paper fibres used in a fibre furnish. In a further experiment, fibres were prepared from a commercially available product (White Swan Paper). The paper was soaked at room temperature for 3 hours before disintegration in a British Standard Laboratory Disintegrator. After disintegration the pulp was washed to remove fillers. Pulp was sonicated for 5, 10 and 15 minutes; a control sample was also prepared. The fibres were examined using the CSF, and the results shown in figure 6.1.1. The vertical axis of the graph is the freeness reading as corrected using the supplied table, the horizontal axis is the time of sonication: The refined fibres in this figure are the commercially available fibres. The control sample is labelled 0m in both the unrefined and refined samples, also included in figure 6.1.1 is a trend line for both unrefined and refined fibres.

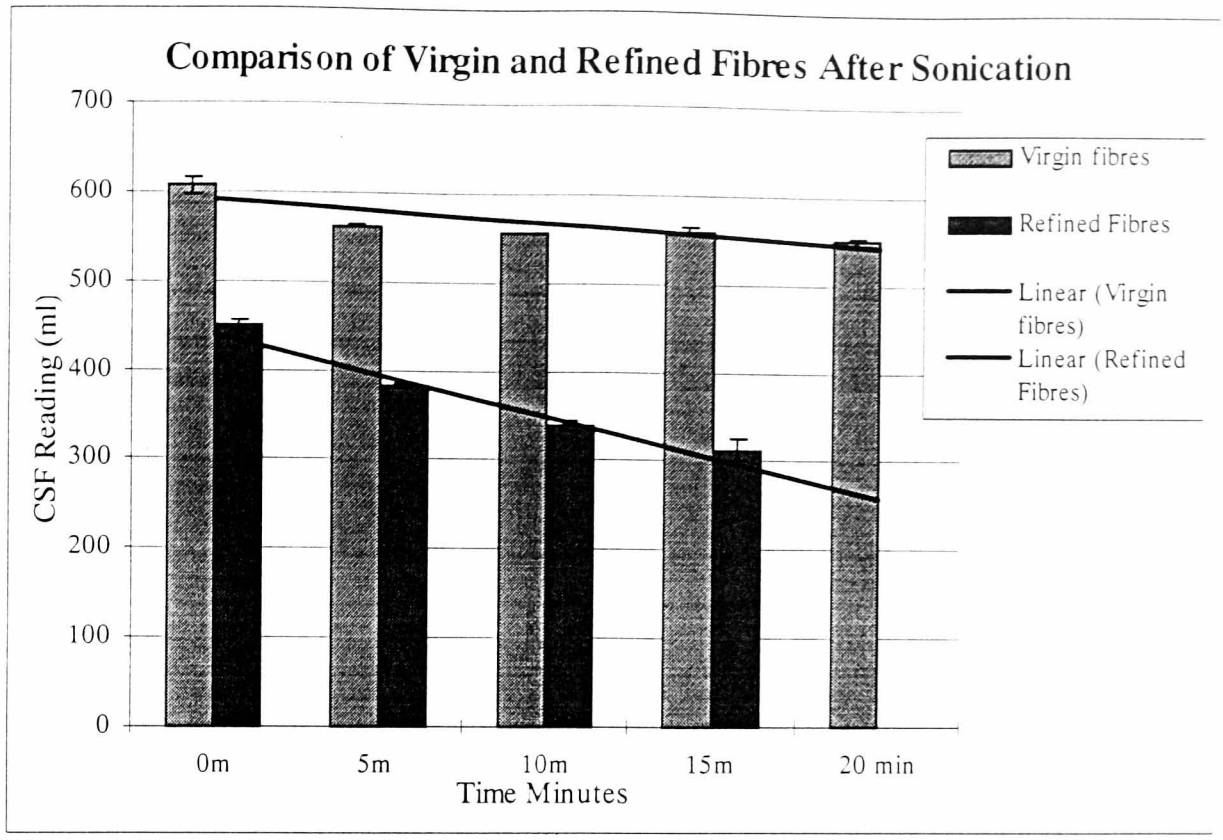


Figure 6.1.1 Comparison of Sonication on Untreated and Refined Fibres

The action of ultrasound decreased the freeness of the fibres for both the refined and unrefined fibres. The decrease in freeness was *greater* for the refined samples than for the unrefined fibres. The freeness of the unrefined fibres decreased after 5 minutes sonication; additional sonication treatment did not decrease the freeness further. Sonication of the refined samples lead to decreased freeness after 5 minutes this decrease continued as sonication times increased.

The refined fibres were examined under the microscope, the fibres in the photomicrograph, figure 6.1.2 were treated with ultrasound for 15 minutes.

The fibres surrounding the area K, in the photograph have edges which are hazy and indistinct. This is caused by fibrillation of the fibres coupled with material being forced out of the fibre. The force developed by ultrasound was sufficient to increase the fibrillation of the fibres, but not sufficient to initiate damage to the fibres.

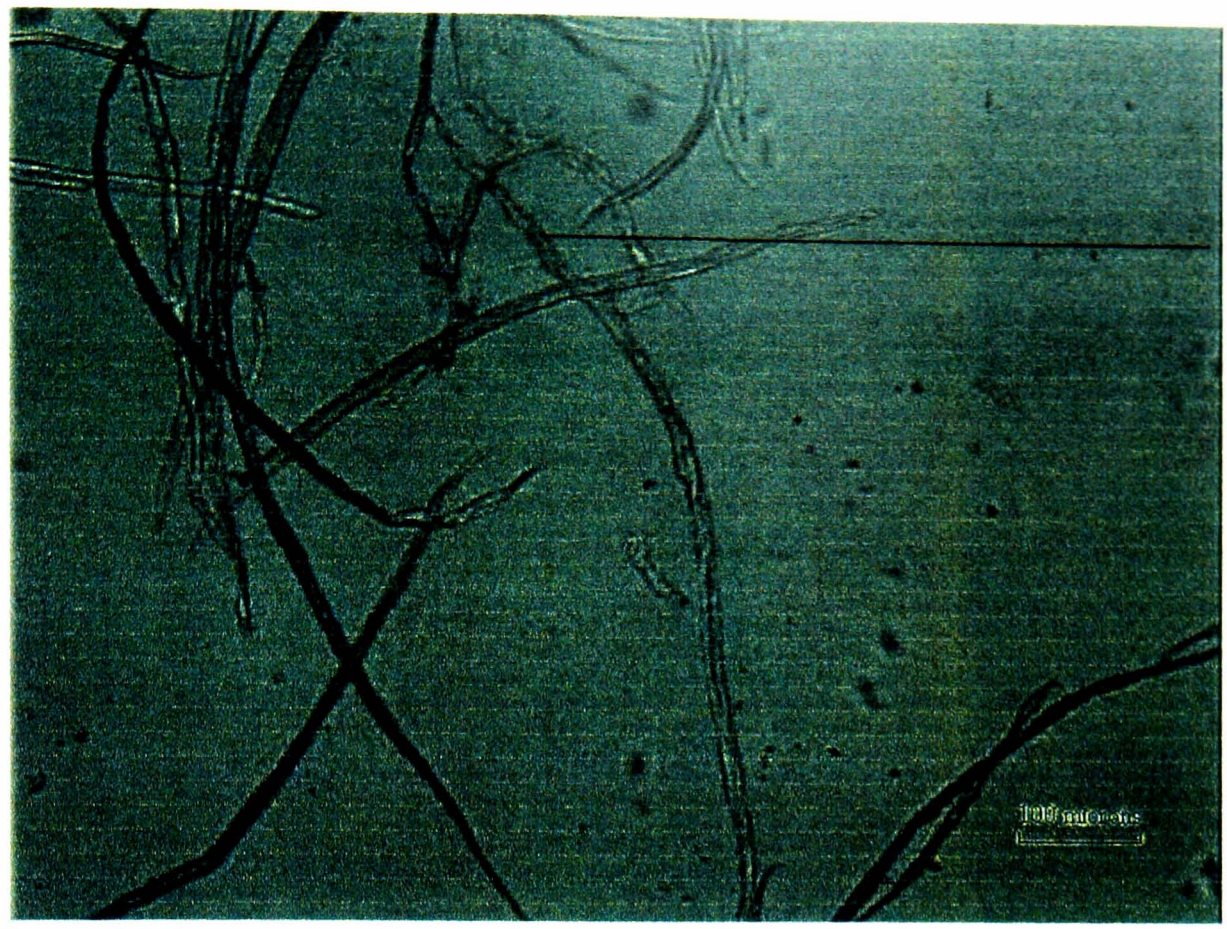


Figure 6.1.2 **Photomicrograph of Refined and Sonicated fibres**

The sites available for cavitation bubbles to exploit are limited on unrefined fibres and had all been exploited after 5 minutes sonication. There were more sites available on the refined fibres which resulted in the decrease in freeness as sonication times increased.

In conclusion the treatment of fibres with ultrasound did not cut the fibres, but did enhance fibrillation, leading to an increase in surface area and inter-fibre bonding of the fibres. Conventional refining on the other hand shortens fibres considerably after a short period of time and introduces a large number of damage sites which lend themselves to further, progressive fibrillation in the presence of ultrasound.

This supports the observation that ultrasound can influence the morphology of paper fibres, exploiting existing damage, increasing the surface area of the fibres and subsequently increasing bonding strength of the finished paper.

Having characterised the effects of ultrasound on a simple fibre system the same treatment was applied to an idealised mixed office waste furnish to establish whether the ultrasound would deink the printed toner from the fibres. The next section deals with this.

7.0 Toners and Adhesion

Mixed office waste comprises a complex mix of paper fibres and toner particles when re-pulped. The pulp slurry contains a mixture of organic paper fibres, inorganic clays, pigments, and synthetic toner resins.

The xerographic process described in section 3.4 produces a printed image that is stable, resistant to abrasion and has good contrast with the paper. These qualities, which are desirable in the printed sheet, cause problems when recycling office waste.

The components of four toners[150] are shown in table 7.1. The toner particles are thermoplastic resins, which soften and flow when heated above a certain temperature. Other components include pigments, and additives to control charge and allow the toner to flow. Once cooled they form a hard film. The temperature at which a thermoplastic resin undergoes a second order thermodynamic transition is known as the glass transition temperature (Tg) which which marks the transition from glass-like to rubber-like behaviour. When a polymer exceeds its glass transition point it becomes deformable and can be more readily pressed around surface fibres.

The toner is not readily removed from the fibres as it is so intimately associated with them due to the strong forces of adhesion. Toner particles are also difficult to remove from the pulp once detached from the fibres. Fused toner particles form a film on the paper surface approximately 20 to 50 microns thick, depending on the toner system used. After repulping, the resulting particle size distribution will include a percentage of particles that are too large to be removed by flotation and washing. Removal by screening can also be ineffective as the flexible cross section of the particles may permit them to be accepted when presented to the screening slots. Centrifugal cleaning of toner particles is not efficient as their density difference with water is not sufficient for their effective removal.

Toner	dichloromethane extractable %	Organic components	Inorganic components
A	68.9	Acrylate polymer.* Aromatic hydrocarbons (related to styrene copolymers)	Silicon* Iron Sulphur Calcium
B	24.0	Hydrocarbon related to epoxy-type material.* Organic ester	Silicon* Titanium Sulphur Iron
C	21.6	Acrylate polymer.* Aromatic hydrocarbons (related to styrene copolymers)	Iron* Manganese Silicon Chromium
D	81.4	Acrylate polymer.* Aromatic hydrocarbons (related to styrene copolymers) Organic Acids	Iron * Silicon Aluminium

* Predominant component

Table 7.1 Analysis of components contained in various toners

With these problems in mind, and with the growing importance of mixed office waste as a fibre source, several different approaches have been taken to improve the removal of toner particles from pulps. These approaches have included adsorbing the toner particles onto a polystyrene substrate,[151] agglomeration of the particles using chemicals,[47,152] steam explosion,[153] ultrasonic deinking,[109-117] making the particles denser,[155] and removal of certain types of toners using magnetic deinking.[154]

7.1 Theory of Particle Aggregation and Break-up[156]

Particle aggregation is the process by which small particles collide and adhere to one another. In the pulping and disintegration of recycled paper, the break-up of particles is important because the removal processes can only remove particles in certain size distributions. If a particle falls between the size removal categories it will not be removed and will affect the final sheet quality, either as a large speck of ink or as a more general greyness of the sheet of paper.

Generally the rate of particle aggregation and break-up depends on the motion of the particles in the suspension. The nature of the forces acting on the particles are dependent

on their size. With smaller particles, in the size range 10μm and below, under conditions of low turbulence, Brownian motion controls the rate of aggregation. Larger particles are influenced by gravity. With an increase in particle size and high turbulent intensity, break-up and aggregation can occur by different mechanisms, but these are largely governed by the frequency and energy of collisions between particles.

Particles will be broken up by stress as a result of turbulence. Shear stress (τ_s) is measured in Nm^{-2} and is defined by the equation 7.1:

$$\tau_s = \mu(\varepsilon/\nu)^{1/2} \qquad \text{eqn 7.1}$$

where μ=liquid viscosity ($kg\ m^{-1}s^{-1}$)
ε=aggregate porosity (m^2s^{-3})
ν=kinematic viscosity of liquid (m^2s^{-1})

Shear rates above τ_s=2.6 Nm^{-2} begin to disrupt aggregates. High shear rates above τ_s=5.3 Nm^{-2} can lead to the disruption of strong aggregates,[157] deformable aggregates will be stretched before breaking; rigid aggregates will suffer surface erosion. Turbulent stress levels are generally considered to be mild below 0.75Nm^{-2}. Stress levels below this value are more likely to promote particle-particle attachment, that is, aggregation rather than the reverse.

7.2 Surface Energy Considerations in Deinking

The particle size distribution of toner particles during repulping has been studied in several research publications. Researchers have examined the toners using optical microscopy and scanning electron microscopy.[158] They identified four key steps in the deinking process: detachment of ink from fibres, adjustment of particle size and geometry, separation of the dispersed ink particles, and finally clarification and recycling of the process water. The detachment and adjustment of particle size may occur simultaneously.

Other researchers have examined the rôle of the substrate in the deinking process.[159] A commercially available paper was treated with four different starches to produce papers

with different surface properties. The papers were then printed with different laser printers prior to deinking. The work of adhesion (W_a), was calculated for each toner and paper. The work of adhesion between two solids *i* and *j* immersed in a liquid is given in equation 7.2

$$W_{ij} = \gamma_{iL} + \gamma_{jL} - \gamma_{ij} \qquad \text{eqn 7.2}$$

where γ_{iL}= interfacial free energy between solid *i* and liquid L

γ_{jL}= interfacial free energy between solid *j* and liquid L

γ_{ij}= interfacial free energy between solid *i* and solid *j*

The work of adhesion is the work required to separate solids *i* and *j*. Shown in table 7.2 is some experimental data for the toners listed in table 7.1.[150]

Toner		Work of Adhesion mJ/M^2
B	B	-31.72
B	A	-13.81
B	C	-11.68
B	D	-3.2
A	A	3.16
A	C	5.59
A	D	12.14
C	C	9.01
C	D	15.36
D	D	20.35

Table 7.2 Work of Adhesion between Toners

From this data it can be seen that toner B has no tendency to associate with any other toner particles, as shown by the high negative values for the work of adhesion. Toner D shows a high affinity for other toners, as shown by the high positive values for the work of adhesion. Toners A and C show a moderate tendency to aggregate together. In a real mixed office waste furnish it would be difficult if not impossible to precisely identify all the toners present, so any or all of these combinations may exist.

Other researchers have exploited contact angle measurements.[150] Here four toners were evaluated for their constituents and their hydrophobicity. All toners examined produced hydrophobic surfaces as indicated by high contact angles (>90°), but showed lower contact

angles after their surfaces had been wetted. The interaction between a toner particle and a flotation bubble is a function of the surface tension of the liquid and the surface energy of the toner. Fibre surfaces usually present a polar surface for contact angle measurements. A toner particle can adsorb surfactants, changing the surface energy of the particle and making a previously hydrophobic particle hydrophilic. The change in surface energy due to adsorption of surfactant can affect the deinkability of the toner particles as they will not interact with the flotation bubbles after adsorption. Ling[150] suggested that adsorption also changes the glass transition temperature, making the toner more pliable at lower temperatures.

The adhesion of the toners to the substrate is also important.[159] In this publication, the work of adhesion was calculated for different base-papers. Shown in table 7.3 is the affect of base-paper on the work of adhesion for three different toner formulations.

All values are in mJ/m^2.

Base-paper	Texas	Kyocera	HP LaserJet
Uncoated	61.27	60.96	62.42
Anionic Starch	50.98	55.30	55.42
Cationic Starch	42.72	46.68	44.68
Neutral Starch	41.2	45.36	42.76

Table 7.3 Work of adhesion between paper and toner

It can be seen that the work of adhesion between the paper and the toner is greater than the interaction between toners (table 7.2) by a factor of three for uncoated paper. Toner is three times more difficult to detach from uncoated paper than it is to detach from other toner particles. This publication went on to assess the deinking of the treated papers and the toners. It was found that the cationic starch paper had the lowest number of particles remaining after flotation for all printer types. The work of adhesion values were similar for the cationic and neutral starch treated papers.

7.3 Prepared Office Waste Experiments

It was found in work with virgin fibres, see section 6, that ultrasound did not appreciably cut the fibres, even at long (≥20 minute) exposure intervals. Further work was conducted to establish the amount of ultrasound required to change the particle size distribution of toners so that they could be readily removed by flotation or washing. To quantify the changes in the distribution of ink particles the Ink Measurement Program (IMP) program and equipment at Pira International was used.

Initially low levels of exposure to ultrasound were made, to minimise the effect of ultrasound heating on the samples. The times chosen were selected to investigate the effect of short term sonication on toner particles, namely 1 and 2 minutes.

The office waste stock was prepared from A3 (298 x 420mm) sheets printed with a black solid covering 50% of the total area. The stock was prepared using equipment previously described in section 5.1. The paper (60 g) was ripped into 2x2 cm squares and soaked at room temperature for 3 hours. The pulp was disintegrated for 2000 counts in a British Standard Laboratory Disintegrator, then sonicated for 1 and 2 minutes at a consistency of 1.5%. A control sample which had been disintegrated but not sonicated was retained. Four handsheets at $20gm^{-2}$ were formed using a standard handsheet former. The handsheets were then examined using the IMP image analysis program.

The data below is shown in categories that originally related to bin categories assigned by the IMP program. The bin categories have been translated into particle diameters. The graphs shown below in figures 7.3.1 and 7.3.2 show the averages plus the standard deviation for each particle count. Each experiment was performed twice.

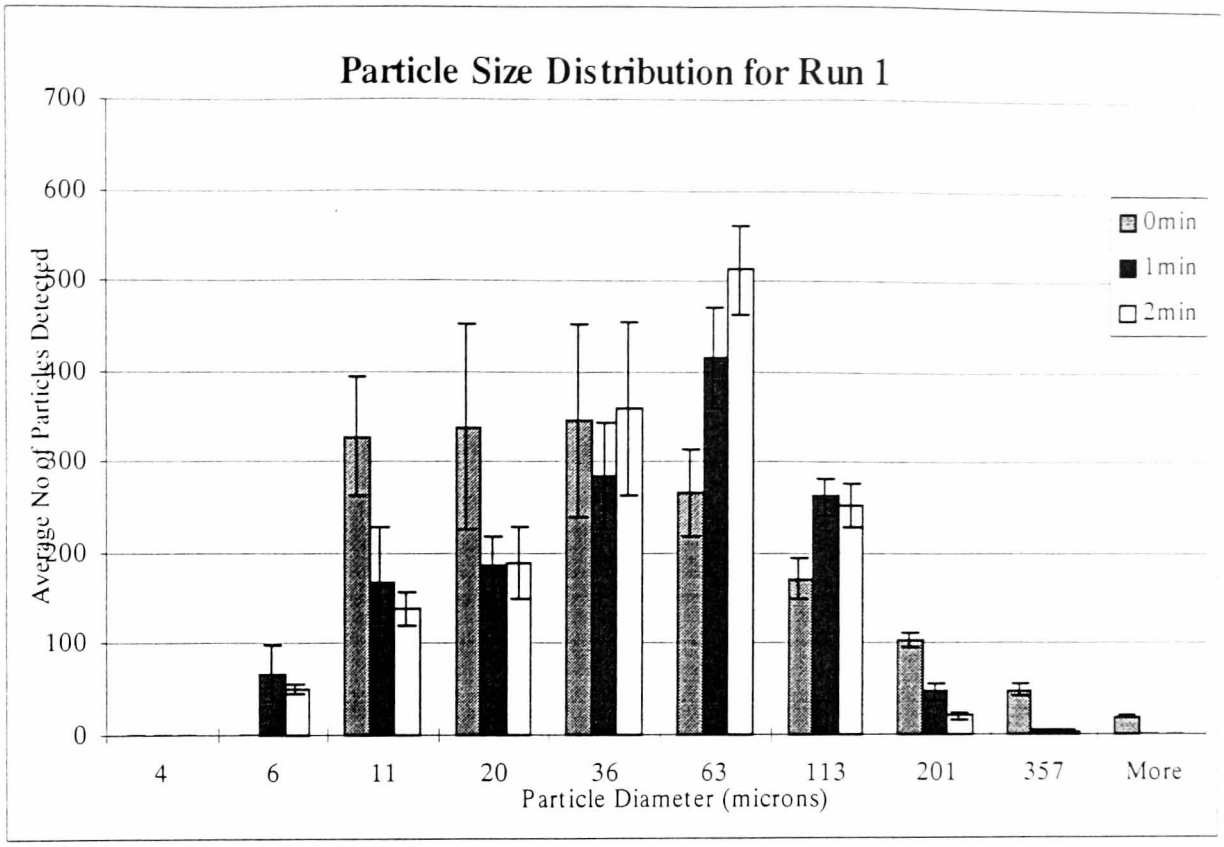


Figure 7.3.1 **Particle distribution for Run 1**

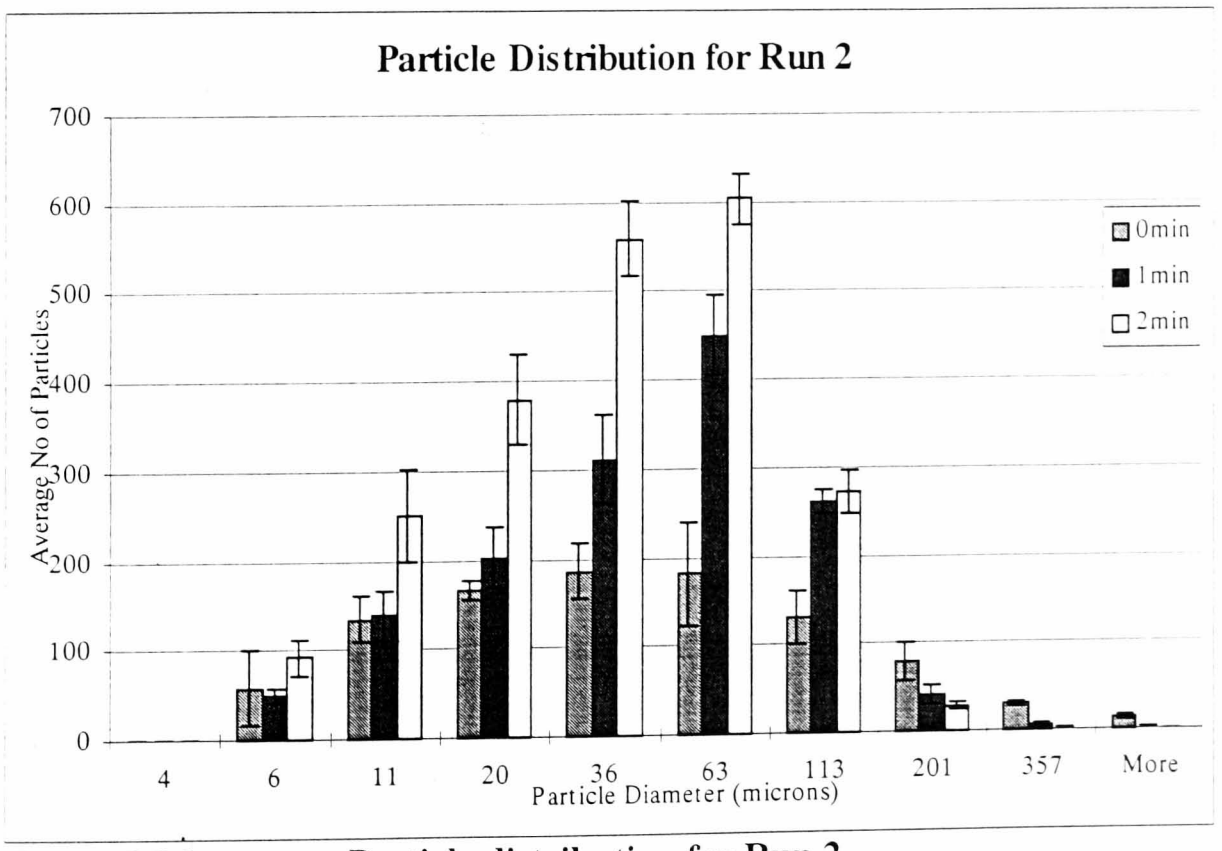


Figure 7.3.2 **Particle distribution for Run 2**

7.4 Discussion of Prepared Office Waste Experiments

These experiments yielded distributions with a large number of detected particles. The particles in the control samples occupied all size categories. The handsheets obtained were very dark, making detection and counting of the particles slow using the IMP program. After sonication, although the number of particles increased, the handsheets became lighter

in tone. Shown in table 7.4 is the average particle diameter of each experiment and the total average. These averages were calculated from the areas of the particles detected on the handsheets.

	Control (μm)	1 minute (μm)	2 minutes (μm)
Mean - run 1	72.9	54.5	49.2
Mean - run 2	88.9	54.8	44.4
Mean - Total	80.9	54.6	46.8

Table 7.4 Particle Diameters Before and After Sonication

The average particle size distribution decreased from 80.9 microns diameter to 54.6 microns after 1 minute ultrasound, and decreased further to 46.8 microns after 2 minutes sonication. The average particle size distribution in run 1 decreased from 72.9 microns diameter to 49.2 microns after 2 minutes sonication, and from 88.9 to 44.4 microns in run 2. The sonicated samples were found to have more particles present on the handsheets, an increase from 1216 per handsheet after disintegration in run 1 to 1434 after 1 minute sonication. The particle number increased further to 1526 after 2 minutes sonication. The numbers of particles produced in run 2 were 982 after disintegration, 1461 particles after 1 minute and 2187 particles after 2 minutes sonication.

The distribution of the particles is important to the removal of toner in the deinking process. However, the largest particles present in the sample would not have been removed by screening if they presented their narrow aspect to the screen. Furthermore, cleaning would be ineffective due to the relative density of the toner particles. The most effective removal technique would be flotation, as the flotation process removes particles most efficiently in the range 30-80μm. However, if some of these particles were attached to fibres, thus increasing their effective size, they too would not be removed from the pulp.

The major question to be answered is:- What is the nature of the breakdown of the particles? The toner particles are large films of polymeric material. (see section 7.0). The films are between 20 and 50 microns thick and are bound together by chemical and physical bonds. The hypothesis proposed is that break-up of the toner particles which are attached could occur in one or other of two ways:

i) the large toner particles could be detached from the fibre as an intact entity and then broken down

ii) the toner particle could remain attached to the fibre whilst ultrasonic effects break down the particle until a certain critical size is reached, when it is finally detached from the fibre.

However whilst the preceding experiments confirmed that ultrasound does break up toner particles, no information on the nature of the mechanism involved was obtained.

To further explore the hypothesis, further experiments were undertaken on the prepared office waste using flotation and washing experiments to remove detached particles from the pulp.

7.5 Flotation Washing Experiments

To elucidate the toner/fibre interaction, experiments were performed at Pira International using their flotation deinking cell. The samples used in this case were prepared as described in section 7.3. The samples were treated in the same manner, at the same consistency and for sonication times previously described.

After sonication the samples were given four different treatments. The four treatments were disintegration, washing, flotation, and finally a combination of flotation and washing.

After this processing, the pulps were formed into handsheets at $20gm^{-2}$ as previously described and the number of particles counted using the IMP software program. Four handsheets were produced from each of the treatments. The data is presented graphically with 10 size categories. These original categories are presented below, and have been translated into the equivalent particle diameter from the particle area.

The control sample (0 min), in figure 7.5.1, showed a broad distribution of particle sizes present on the handsheets with no well defined maximum but with a peak at 36 microns. Sonication of this pulp lead to a decrease in the number present in largest size categories. After 1 minute sonication there were no particles present in the largest (more) size category, and the numbers of particles detected in the smaller categories increased. The

distribution also showed a more clearly defined maximum of between 36 and 63 microns. After sonication for 2 minutes the category in which the maximum number of particles occurs did not change, however, no particles in the largest two categories were detected. No attempt was made to remove particles when forming the handsheets. It can be seen that sonication broke up the large particles into smaller pieces.

Ultrasound treatment increased the average number of particles present from 1534 to 2110 after 1 minute and then to 2281 after 2 minutes, this represented an increase of 48% in the number of particles present.

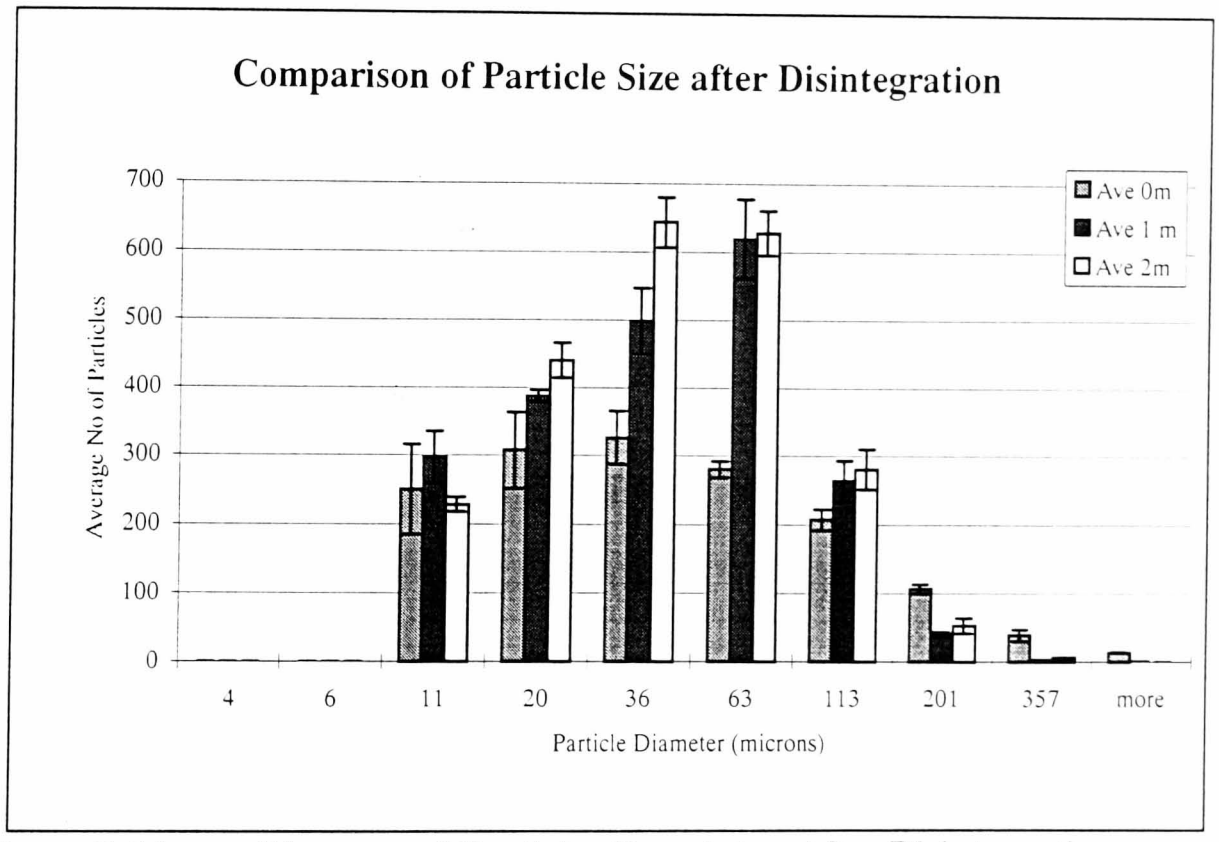


Figure 7.5.1 Diameter of Particles Remaining After Disintegration

The simplest ink particle removal technique is that of washing, it is also the least efficient. In the technique employed 10 litres of pulp at 1% were drained through a 100 mesh sieve followed by an additional washing with a further 10 litres of water. It should be noted that this washing treatment was not the same as the hyperwashing technique used in later experiments and described in section 5.1.5. Handsheets were formed from the remaining pulp. Shown in figure 7.5.2 is the averaged data from handsheets made after this treatment.

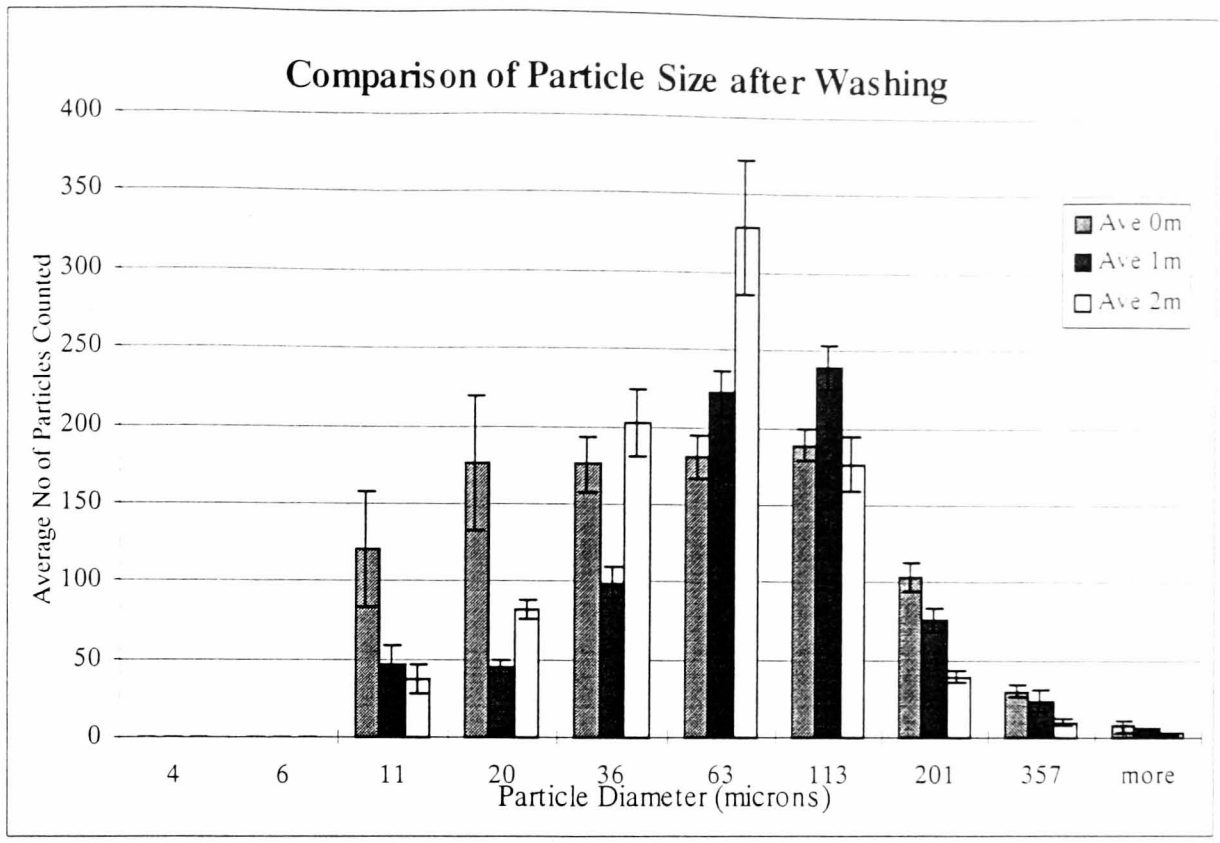


Figure 7.5.2 Diameter of Particles Remaining After Washing

The washing process can only remove from the distribution, particles that had been detached and that were smaller than the size of the mesh against which the fibres were trapped. The distribution above is therefore a measure of the numbers of particles that were attached to fibres; the higher the number the fewer particles detached. At the smaller end of the distribution, below 36 microns, the control category had the greatest number of particles suggesting low detachment of unsonicated particles. The lower counts for sonicated particles indicated a greater degree of detachment. Thus, for 2 minutes, the greatest number of particles was produced by the breakdown of larger ones but the lower number of particles at 11 microns suggests that more particles had been detached. Above 63 microns there were more particles in the sonicated sample than the control samples, suggesting low detachment of sonicated samples in this category.

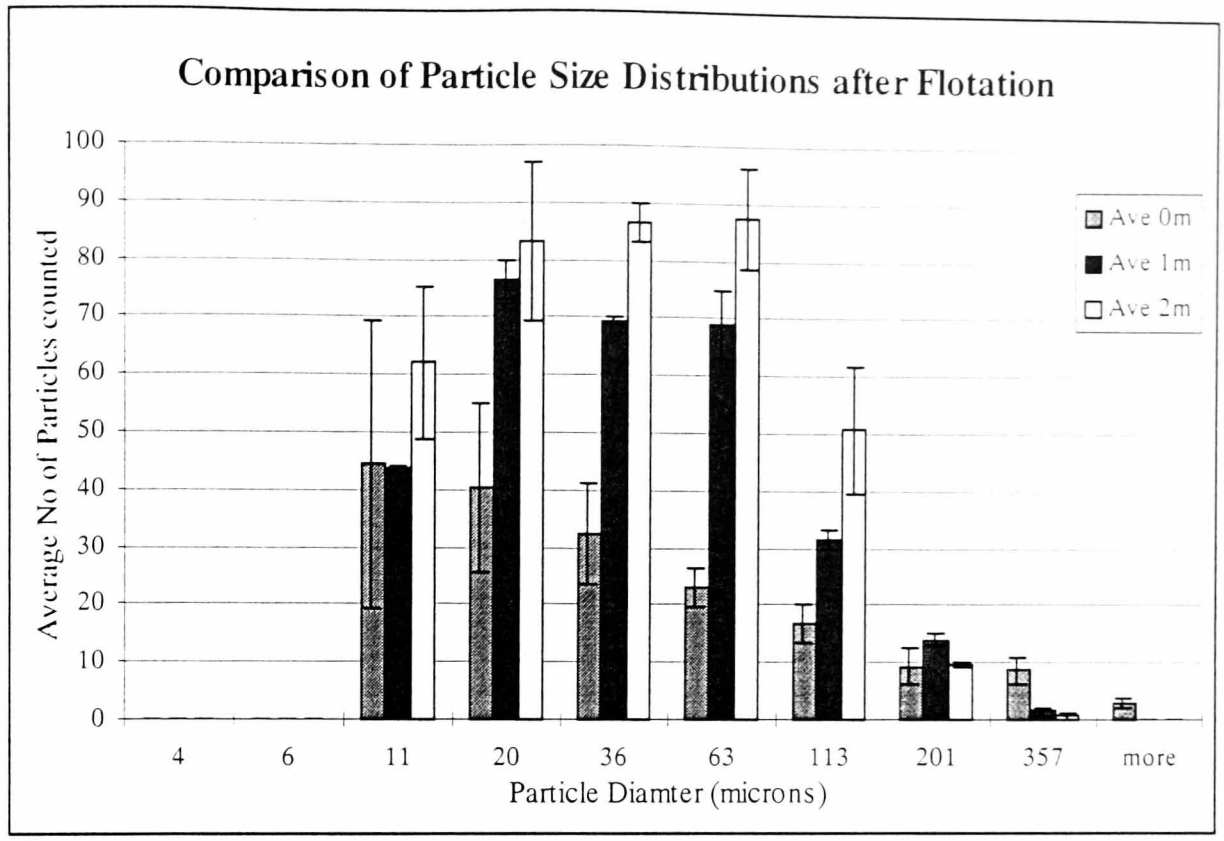


Figure 7.5.3 Diameter of Particles Remaining After Flotation

The particle size distribution after flotation is shown in figure 7.5.3. It indicates a narrower distribution than that produced by washing. The category with the largest number of particles detected was that for 63 microns. The control sample had large particles, greater than 200 microns, present, however it was the 2 minute ultrasound treatment sample that had the greatest number of particles present. These particles were reduced in size by ultrasound but were not removed from the pulp by flotation because they were still attached to fibres. Large particles were reduced in size, but small particles were still present in the handsheets after ultrasound treatment.

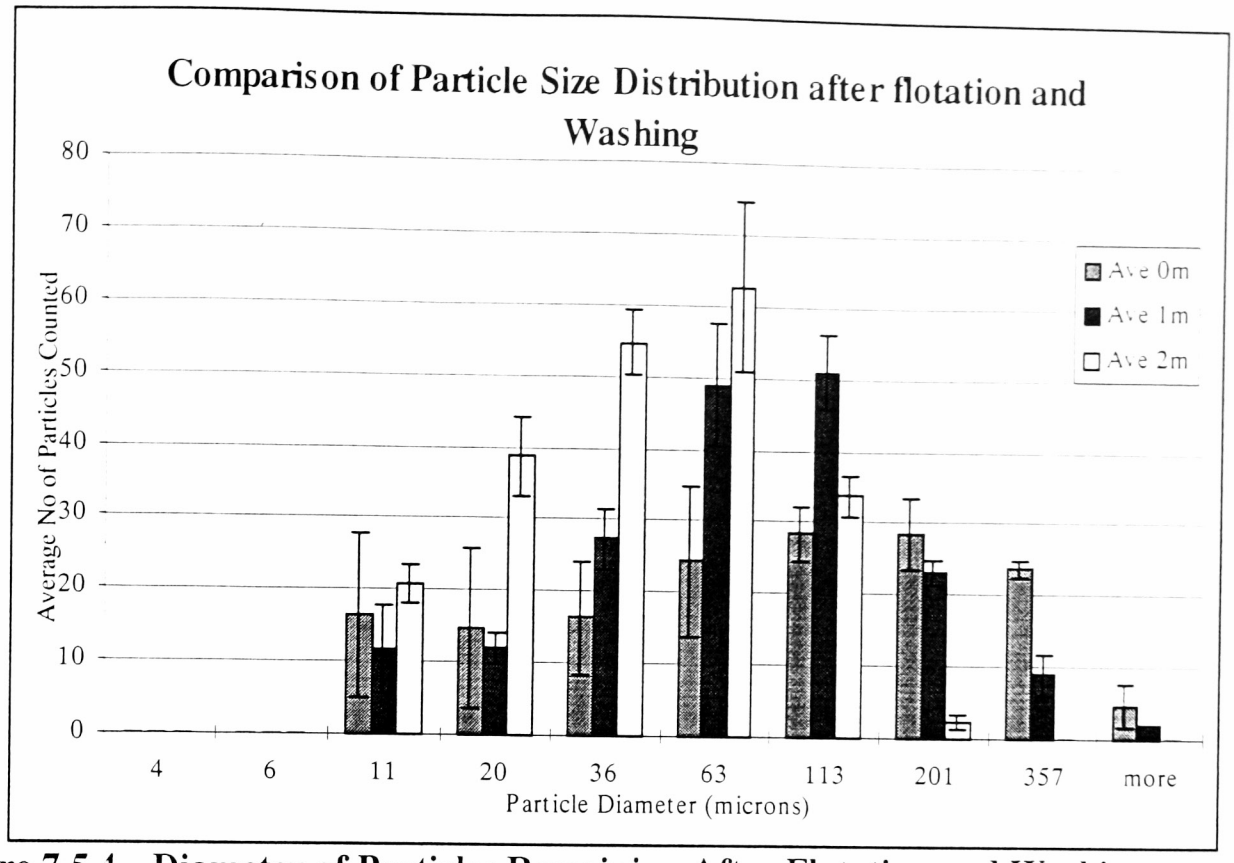


Figure 7.5.4 Diameter of Particles Remaining After Flotation and Washing

A similar trend was observed for the combined washing and flotation experiment represented in figure 7.5.4. The total numbers of particles were lower for all categories. The control sample again had large particles present on the handsheet, 1 and 2 minutes ultrasound had shifted the distribution towards the smaller size categories.

7.6 Discussion of Flotation and Washing Experiments

The number of particles detected on the handsheets increased and the distribution moved to smaller sizes, as sonication time increased. After 2 minutes sonication the 36 and 63 micron size categories showed an increase in the number of particles detected from 281±12 to 619±57. The control sample had the largest particles present in the distribution with 52±8 particles in the category of 357 microns and above. After 1 minute sonication only 3 particles were detected in the same category.

The flotation experiment yielded a different distribution (see figure 7.5.3). The particles in the largest size categories had disappeared. However, the number of particles present in the smaller ranges were greater after sonication than before treatment.

Flotation removes particles in the distribution range approximately 10-100 microns with a peak removal of 30-80 microns. It was in this range that the sonicated samples had the greater number of particles compared to the control sample. The reason for the increase must be that smaller particles are formed during sonication but *not* removed during flotation. The particles were still be attached to fibres which prevented them being removed by flotation. Particles with fibres attached have been termed 'hairy' particles by Berg *et al.*[160] These workers studied the particle distributions found after repulping mixed office waste under various conventional pulping conditions: between 6-19% consistency, at various temperatures, under the influence of surfactant and at various pH values. They found that the great majority of the largest particles have fibres either attached or incorporated into the structure of the toner particle. The smallest particles, 100-200 microns diameter, were found to have fewer 'hairy' particles present. The pulping consistency was found to affect the breakdown of toner particles but not the extent of detachment. Higher pulping consistency was found to be more effective in breaking down particles but that there was no effect on the degree of detachment of toner particles by any of the applied treatments.

The break-up of the toner particles was easier to accomplish than was their detachment from the fibres. This is due to their relative values for the work of adhesion between the toner and paper fibres, which is three times higher than the work of cohesion within fused toner particles. Toner particles require shear stresses or impact to break them down and detach them from fibres. It is possible that the only significant increases in the detachment of toner from fibre arise when the temperature is increased. At elevated temperatures, above the glass transition temperature of the polymeric resin, the toner may become more pliable and easier to detach.

In the present study it has been demonstrated that ultrasound breaks up the toner particles but detachment of the particles is restricted. The particles appear to remain attached to the fibres until a critical size is reached, when they may be detached by interaction with ultrasound. Cavitation bubbles at 20kHz are approximately 23 microns in diameter.[94] Furthermore the effects of jet streaming have been used to explain the agglomeration of polystyrene beads in suspension. The beads formed a dumbbell shape, by jet streaming induced fusion of the beads. However, they had to be of a size similar to that of the cavitation bubbles, in this case 23 microns. If this is so, it is reasonable to assume that

optimum interaction of detached toner particles with ultrasound should occur in the same size region. The maximum effect would cause particle detachment from fibres.

In summary the process that may be occurring when the fibre/toner agglomerates interact with ultrasound energy is one in which the large toner particles are broken down whilst still attached to the fibres. The particles attached to fibres are not eliminated by the removal processes and remain attached until they reach a size where jet streaming can interact with them, that is around 20 microns.

It was therefore decided to perform the sonication experiments at three different temperatures in order to explore the affects of temperature on the ease of toner/fibre release.

8.0 Investigations using Text Based Mixed Office Waste

The investigation into prepared office waste in section 7 produced distributions with large numbers of ink particles which made counting slow. In order to speed up the process and to investigate a furnish similar to commercial waste, the following procedure was adopted.

The paper used in this series of experiments consisted of roughly equal amounts of laser printed waste and photocopier waste. Staples, paper clips and dirty paper were excluded as were mechanical and Kraft papers. The paper was collected from within the college and included laser printed waste from several HP laser jet printers, plus photocopier waste from Sharp 2022 and 2035 photocopiers. The paper was collected in one episode, torn into squares approximately 2x2cm and stored. The torn paper provided a reservoir of evenly mixed waste paper for all the following experiments.

Experiments were performed over four different temperature ranges. Each range consisted of three batches and each batch had five ultrasound treatments namely 0, 1, 2, 5 and 10 minutes sonication which took place under neutral conditions. From each treatment eight handsheets were formed - four from pulp that was unwashed and four from hyperwashed pulp. A total of 120 handsheets were examined for each temperature range.

As previously described, the paper was soaked for 3 hours before disintegration. Temperatures at which the soaking took place were as follows: room temperature for ranges 1 and 2, 50°C for temperature range 3 and 75°C for temperature range 4.

During each experiment attempts were made to maintain the sample at the same temperature at which soaking took place.

8.1 Transformation of Bin Categories

The image analysis program, IMP, measures the area of particles detected. The particle data was stored as a simple list of all particles in the order of detection, however, this is not conducive to visualisation. To enable comparison of different treatments the areas of the particles were transformed into their diameters.

The size categories used in the subsequent graphs are based on the sizes of particles that can be removed using commercial deinking and recycling processes. The size categories were designated by the following terms: washing, flotation, cleaning, screening and larger. The sizes of each category are shown below.

Larger particles	>450μm
Screening	250-450μm
Cleaning	100-250μm
Flotation	25-100μm
Washing	<25 μm

The raw distribution was collated into the size categories listed above by processing according to the area of the particle against the area of an equivalent circular particle (ECP). The results of the ECP is calculations are shown in table 8.1.0.

Size Categories	Range of Diameters (micron)	Area (micron^2)
Larger	above 450μm	>159000
Screening	250 to 450 μm	159000
Cleaners	100 to 250 μm	70680
Flotation	25 to 100 μm	7850
Washing	<25 μm	491

Table 8.1.0 Particle Diameters calculated from Areas

The areas were inputted into Microsoft Excel 5.0 and the numbers of particles with areas corresponding to the bin categories were calculated. These were then expressed as both the numbers of particles, and as a cumulative percentage.

The data from this file was saved and formed the basis for other calculations including the averages for each batch. Information presented directly from the program had a different set of bin categories. Each category is in square microns:- 10 to 32, 32 to 100, 100 to 316, 316 to 1000, 1000 to 3162, 3162 to 10000, 10000 to 31623, 31623 to 100000, larger than 100000.

The operation of the image analysis system imposed a lower limit on the size of the particles that could be detected. This limit is dependent on the magnification of the images. If the smallest particle that could be detected was around 55 square microns, then

the image processing software would only count a region of interest as a particle if it is larger than a two by two matrix. This effectively meant that the smallest particle that could be detected would be approximately 8 microns in diameter. The overlaying of a two by two matrix decreased the amount of 'noise' or false readings, arising from the presence of dark areas on paper fibres. The lower limit of the image analysis system could be extended but only by increasing the magnification. However, an increase in magnification leads to a decrease in the field of view and so the largest particles present on the handsheets would not be detected as they extended beyond the field of view.

8.2.0 Temperature Range 1

Samples of mixed office waste (150 grammes) were soaked as previously described, followed by disintegration for 2000 counts in a British Standard Disintegrator. Each sample was then made up to 10 litres at a consistency of 1.5%. Two litre aliquots were taken and sonicated at a power of 1kW ± 20 watts, at a frequency of 20kHz under neutral conditions. The temperature was allowed to rise within the reaction vessel, see table 8.2.1. An untreated sample was retained to act as a control. After treatment the samples were equally divided to study the effects of hyperwashing on the samples.

	Batch 1		Batch 2		Batch 3	
	initial	final	initial	final	initial	final
1 minute	20	24	22	26	18	23
2 minute	20	28	22	32	18	26
5 minute	20	39	22	36	19	36
10 minute	20	46	22	48	19	45

Table 8.2.1 Temperature Data for Range 1 (°C)

After treatment the resultant pulp samples were formed into handsheets of 20 gsm using the laboratory handsheet former. Four handsheets were formed from each of the treatments, i.e. 0, 1, 2, 5 and 10 minutes, hyperwashed and unwashed, a total of 40 handsheets per batch. The experiment was repeated 3 times. Tables 8.2.2 to 8.2.7 show the statistics for the sizes and numbers of particles in each batch of handsheets. The 0 minutes data or the control sample had not been treated with ultrasound. Figures 8.2.1 to 8.2.5 give the results of the particle size distributions for each of the simple sonication treatments.

The data presented in tables 8.2.2 to 8.2.7 was obtained from each batch and shows the distribution of toner particles found on the handsheets. The standard deviation figure indicates the range of sizes of particles detected. For example batch 1 unwashed sample produced a mean of 182 microns with a standard deviation of 280. The standard deviation figure was larger than the mean, seeming to make the mean figure trivial. It should be noted that the smallest particle detected was 8 microns, a characteristic of the IMP program, and the largest particle detected was 858 microns, thus the mean is an attempt to portray the entire distribution in a single figure

The data for the unwashed samples is given in figures 8.2.1 to 8.2.5.

	Time of sonication				
	0m	**1m**	**2m**	**5m**	**10m**
Mean (μm)	182.5	118.1	70.1	56.2	43.2
Standard Error	55.2	40.3	19.5	14.3	9.7
Median	51.1	46.1	37.2	37.4	28.1
Mode	8.4	11.1	8.4	8.4	8.4
Standard Deviation	280.1	205.5	117.9	88.1	68.5
Minimum (μm)	8.4	8.4	8.4	8.4	8.4
Maximum (μm)	858.3	668.6	484.0	351.3	293.7
Count	663	678	1349	1460	2477
Confidence Level (95.0%)	77.3	56.4	27.2	20.0	13.6

Table 8.2.2 Batch 1 Statistics Unwashed

	Time of sonication				
	0m	**1m**	**2m**	**5m**	**10m**
Mean (μm)	202.7	202.3	93.7	76.3	61.9
Standard Error	68.0	63.9	30.0	30.4	25.5
Median	56.1	92.4	54.3	41.5	34.9
Mode	8.4	11.9	8.4	13.9	10.3
Standard Deviation	306.0	264.5	135.2	126.2	105.6
Minimum (μm)	8.4	8.4	8.4	8.4	8.4
Maximum (μm)	901.7	615.5	405.1	385.4	328.8
Count	411	294	411	296	295
Confidence Level (95.0%)	95.30	89.61	42.69	42.10	35.74

Table 8.2.3 Batch 1 Statistics After Hyperwashing

	Time of sonication				
	0m	1m	2m	5m	10m
Mean (μm)	190.5	77.9	68.4	48.6	44.2
Standard Error	61.2	25.4	23.8	12.0	8.8
Median	28.7	33.5	33.9	33.6	33.9
Mode	8.4	8.4	8.4	8.4	8.4
Standard Deviation	318.2	139.9	142.6	73.4	55.7
Minimum (μm)	8.4	8.4	7.8	7.8	7.8
Maximum (μm)	989.2	551.9	628.9	317.1	289.0
Count	730	924	1287	1392	1647
Confidence Level (95.0%)	85.8	35.5	33.3	16.8	12.3

Table 8.2.4 Batch 2 Statistics Unwashed

	Time of sonication				
	0m	1m	2m	5m	10m
Mean (μm)	225.9	156.5	131.9	86.1	94.0
Standard Error	62.4	54.1	48.7	35.7	40.8
Median	131.4	59.3	35.5	41.9	41.2
Mode	8.4	8.4	8.4	8.4	10.3
Standard Deviation	281.8	251.2	245.0	164.4	165.6
Minimum (μm)	8.4	8.4	8.4	8.4	8.4
Maximum (μm)	712.2	843.8	812.6	560.0	456.6
Count	417	465	642	448	270
Confidence Level (95.0%)	87.4	75.8	68.2	50.1	57.3

Table 8.2.5 Batch 2 Statistics After Hyperwashing

	Time of sonication				
	0m	1m	2m	5m	10m
Mean (μm)	176.7	100.8	69.3	52.7	43.3
Standard Error	52.8	44.2	23.6	10.8	12.0
Median	54.7	46.9	43.8	39.2	33.4
Mode	8.4	8.4	8.4	8.4	8.4
Standard Deviation	276.9	251.3	129.5	69.1	75.0
Minimum (μm)	8.4	8.4	8.4	8.4	8.4
Maximum (μm)	937.1	1376.3	627.3	280.4	455.3
Count	759	1042	901	1691	1512
Confidence Level (95.0%)	73.9	62.0	33.1	15.1	16.9

Table 8.2.6 Batch 3 Statistics Unwashed

	Time of sonication				
	0m	1m	2m	5m	10m
Mean (μm)	217.0	145.0	105.8	65.8	38.5
Standard Error	61.4	47.0	37.4	21.1	11.5
Median	116.9	67.0	54.3	47.8	16.3
Mode	8.4	8.4	8.4	10.3	8.4
Standard Deviation	278.2	226.4	171.5	83.6	61.4
Minimum (μm)	8.4	8.4	8.4	8.4	8.4
Maximum (μm)	758.6	662.7	528.2	223.3	232.0
Count	422	539	442	246	811
Confidence Level (95.0%)	86.1	65.9	52.4	29.6	16.1

Table 8.2.7 Batch 3 Statistics After Hyperwashing

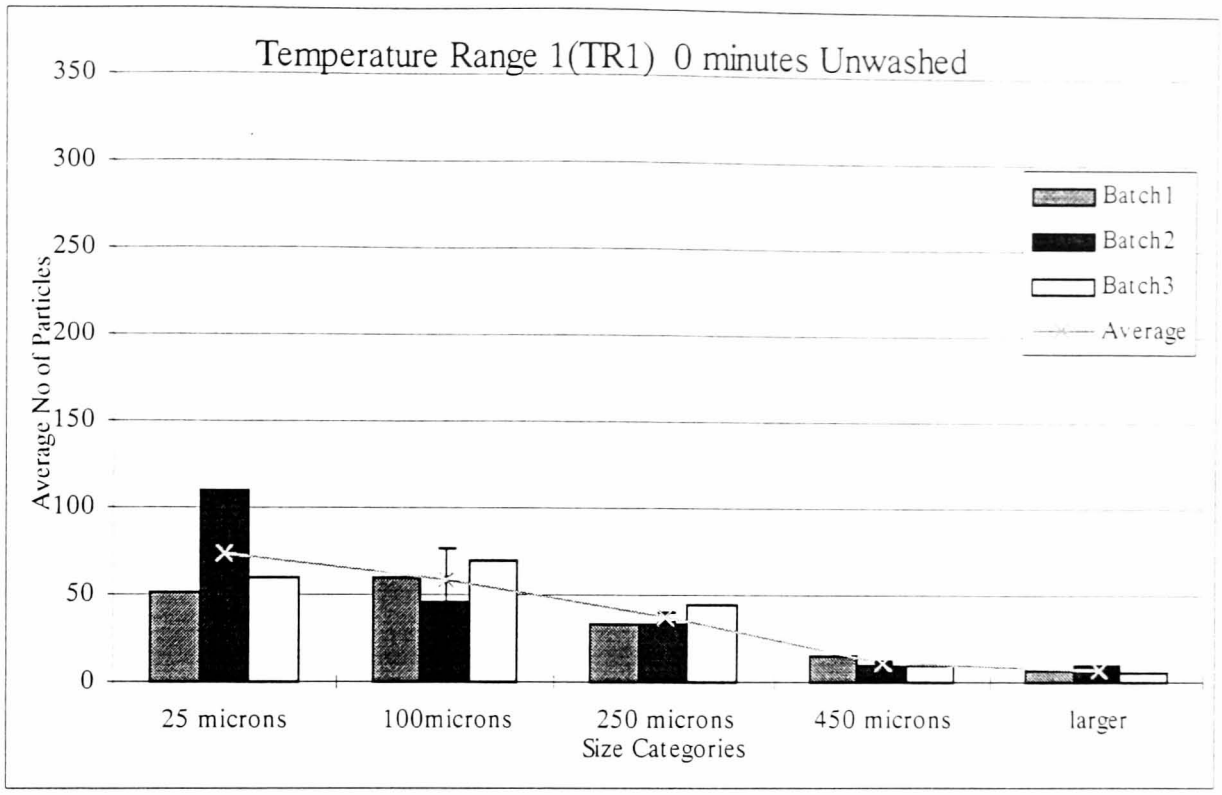


Figure 8.2.1 Toner Particle Count for Range 1 Unwashed 0 minute Sonication

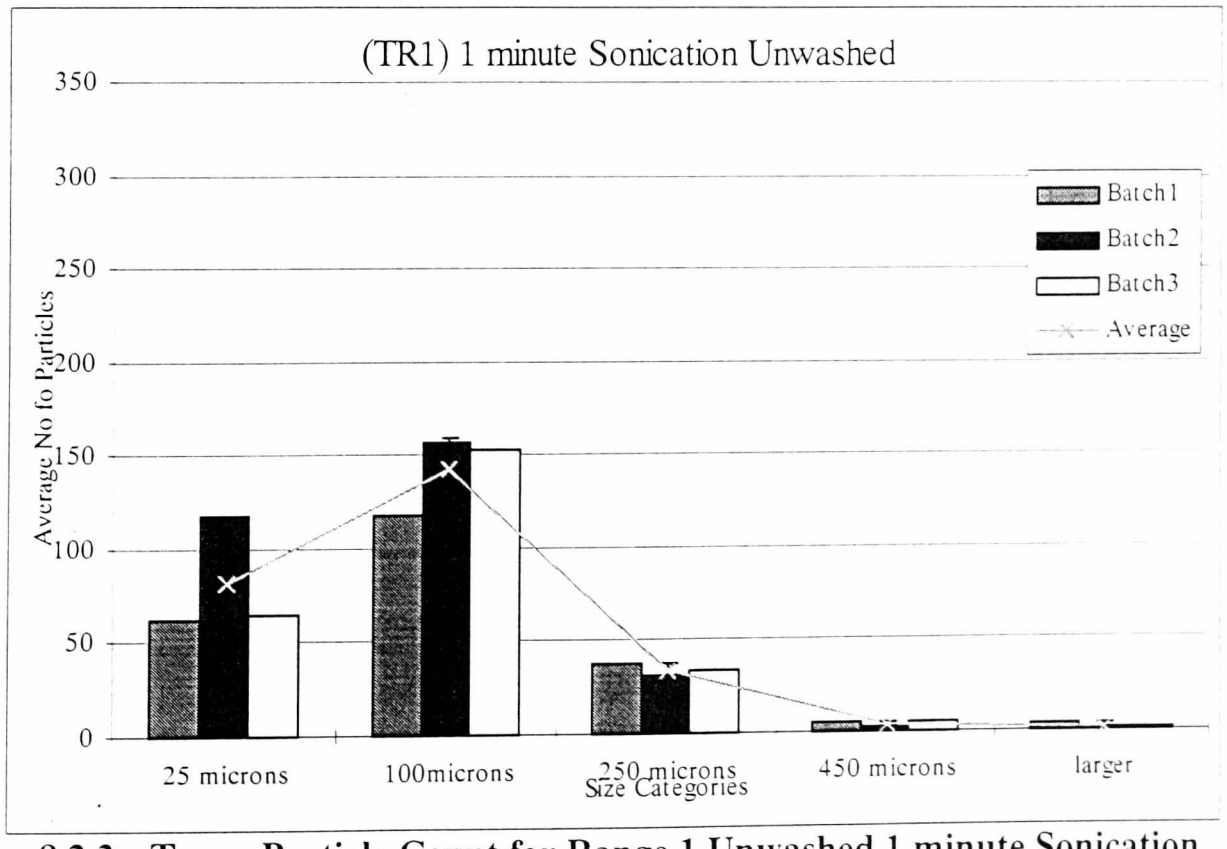


Figure 8.2.2 Toner Particle Count for Range 1 Unwashed 1 minute Sonication

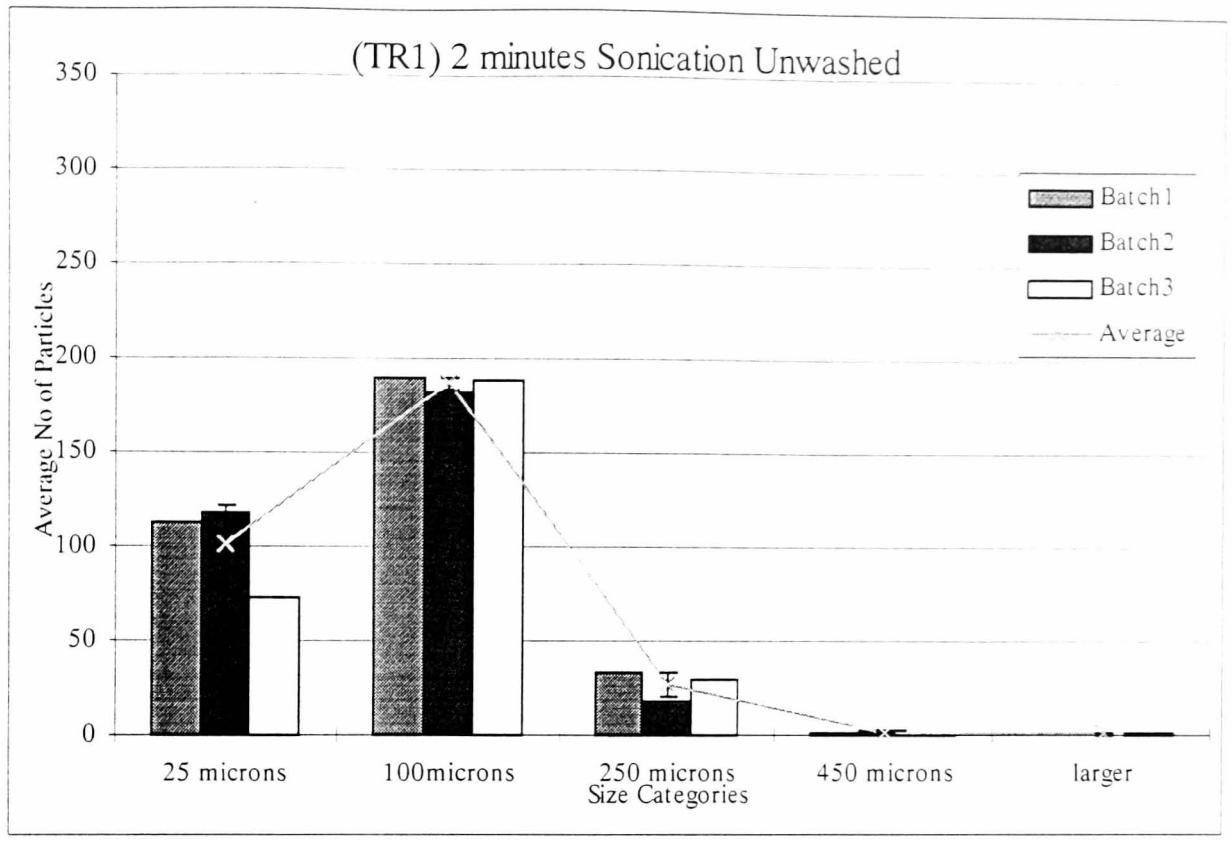


Figure 8.2.3 Toner Particle Count for Range 1 Unwashed 2 minutes Sonication

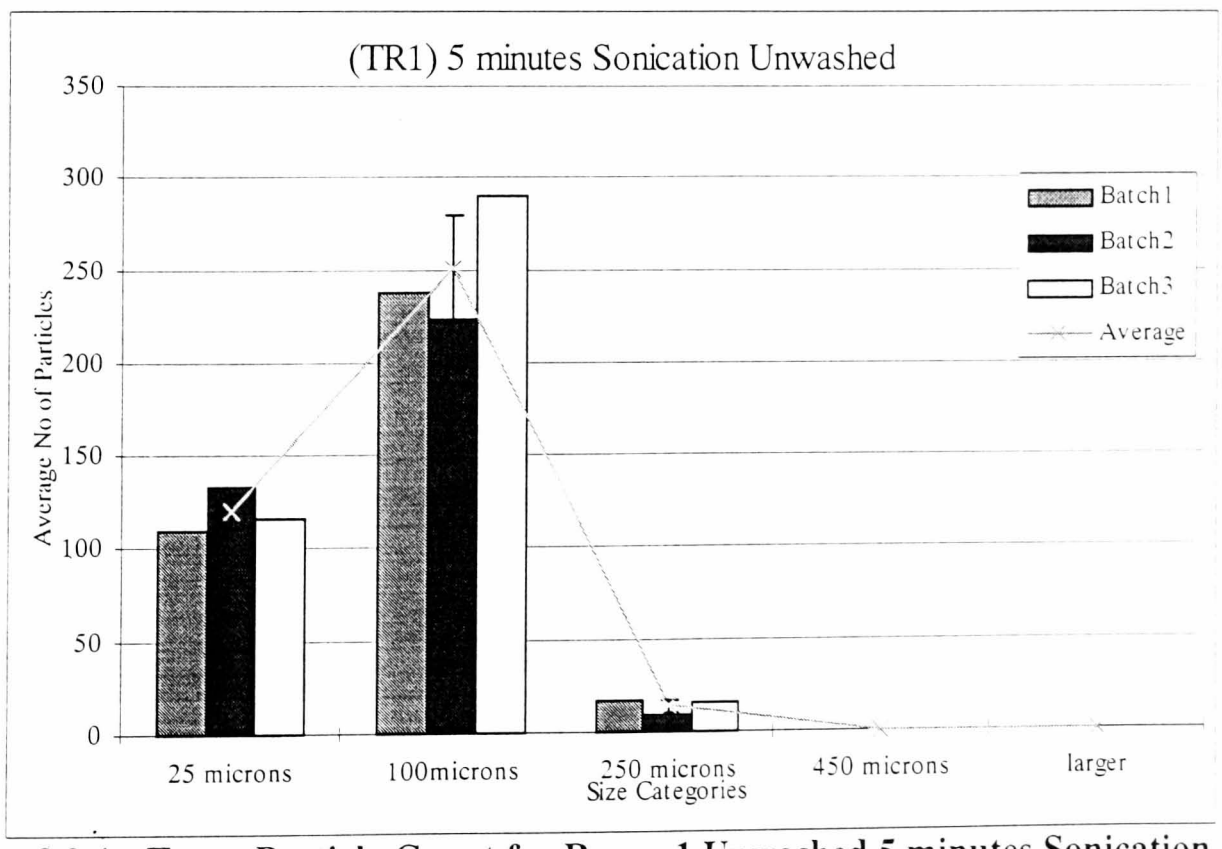


Figure 8.2.4 Toner Particle Count for Range 1 Unwashed 5 minutes Sonication

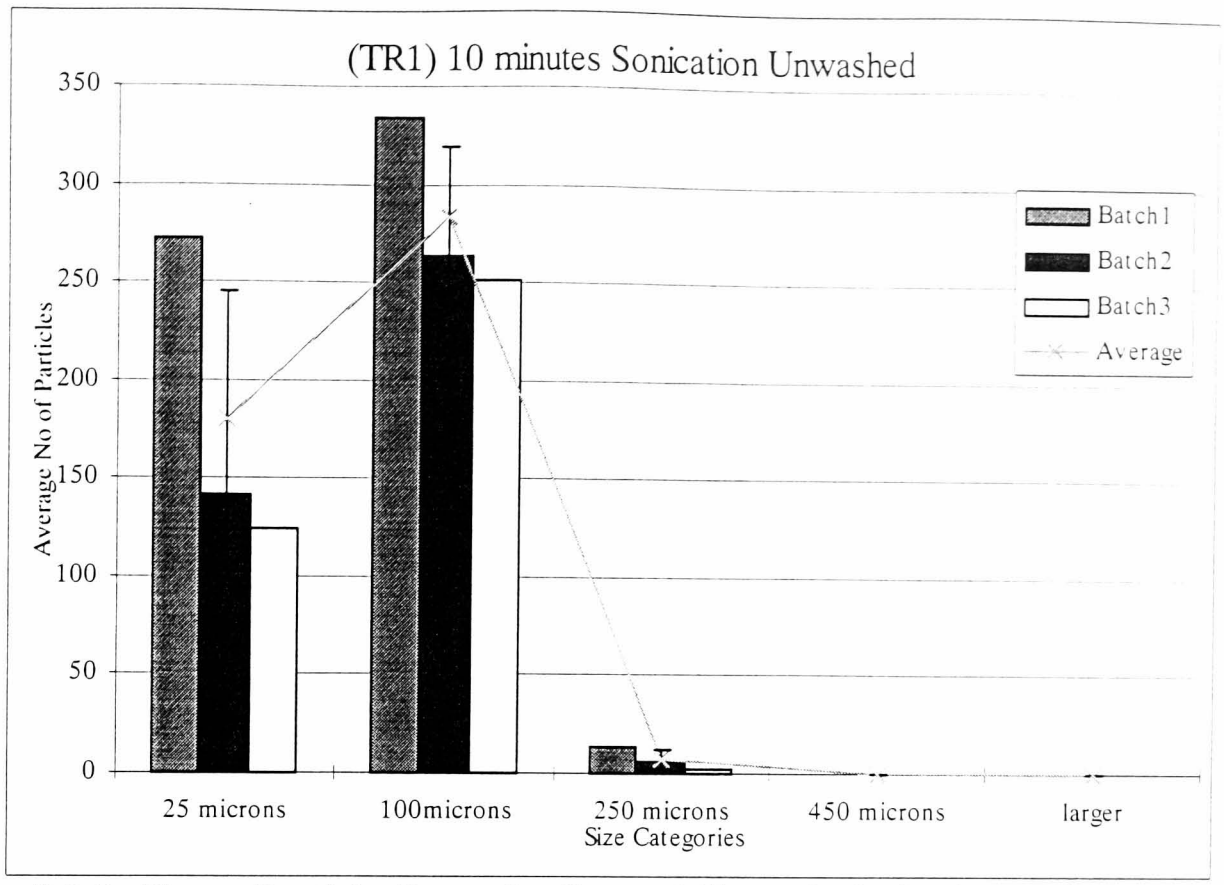


Figure 8.2.5 Toner Particle Count for Range 1 Unwashed 10 minutes Sonication

The control sample (figure 8.2.1) shows the particle distribution of toner particles after disintegration. A broad distribution was obtained with particles detected in all size categories. Sonication for 1 minute lead to the break-up of the particles in the largest size categories (>450 microns) and an increase in the number of particles detected in the smaller size categories. As sonication was increased to 2 minutes there were very few particles detected that were larger than 250 microns. Sonication for 5 and 10 minutes produced similar results with the break-up of particles larger than 250 microns, and an increase in numbers for the smaller size categories. The actions of ultrasound on the pulps caused the break up of large toner particles into smaller particles.

The most effective sonication time was found to be 5 minutes. The percentage of particles above 100 microns in diameter after 10 minutes sonication was 1.6%, compared to 29.7% in the control sample. This meant that provided the toner particles were detached, over 98% of the toner could be removed by a combination of flotation and washing.

The data for the hyperwashed samples is presented below, see figures 8.2.6 to 8.2.10. The hyperwashing treatment of the samples has been described in section 5.1.5, and is a modification of the technique used in the experiments described in section 7.5. The hyperwashing technique was used in the following experiments as it was simple to perform

and resulted in the removal of a large range of particle sizes. Hyperwashing removes detached particles below 220μm but does not have to rely on the toner particles having particular surface characteristics or the addition of chemicals to the pulp. It is an effective technique in the laboratory processing of pulps but in an industrial setting would require a prohibitive amount of water.

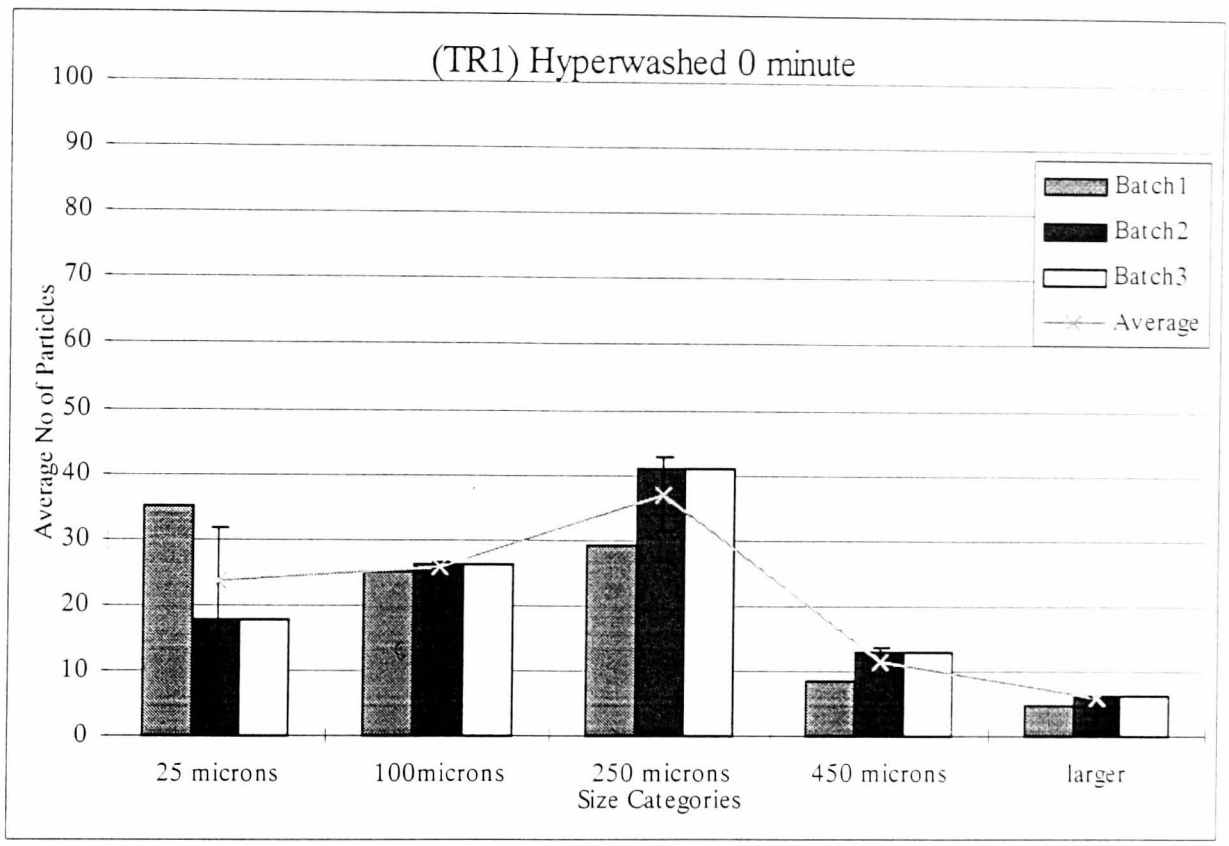


Figure 8.2.6 Toner Particle Count for Range 1 Hyperwashed 0 minute Sonication

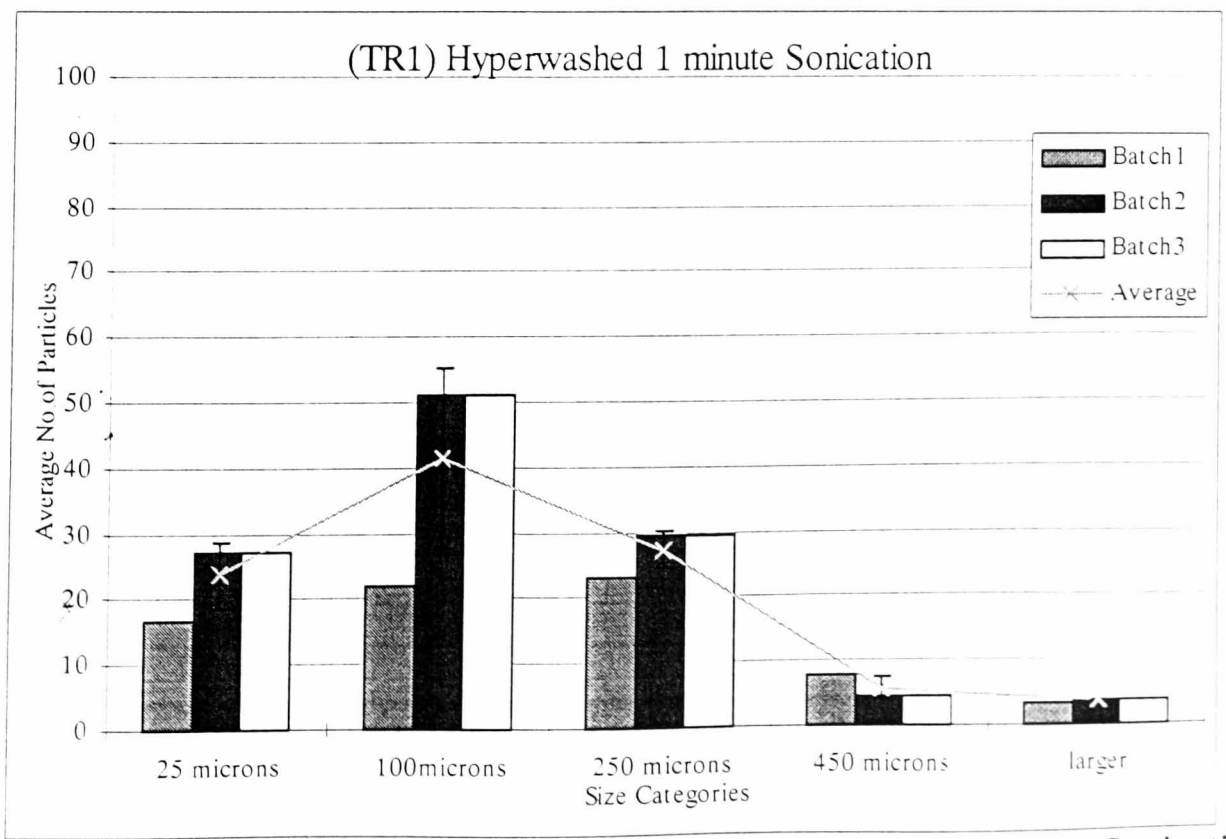


Figure 8.2.7 Toner Particle Count for Range 1 Hyperwashed 1 minute Sonication

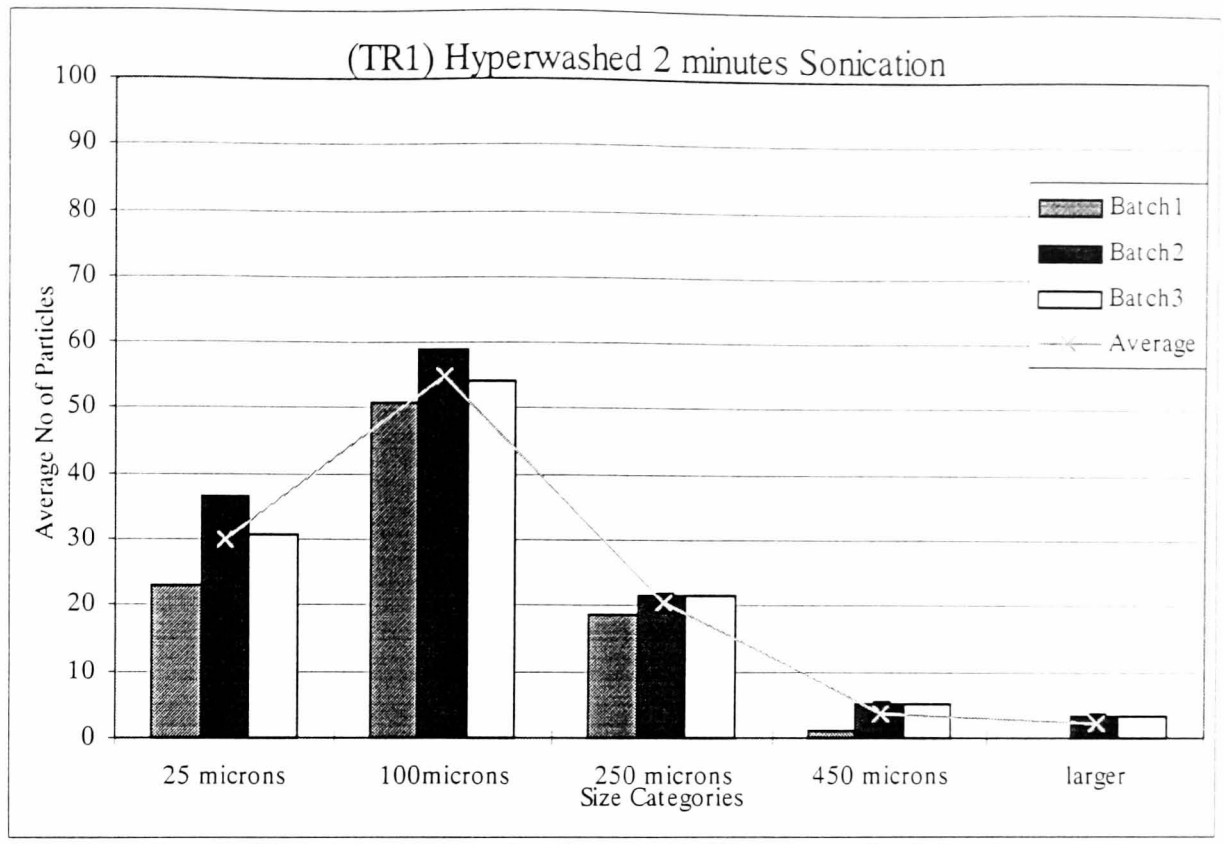


Figure 8.2.8 Toner Particle Count for Range 1 Hyperwashed 2 minutes Sonication

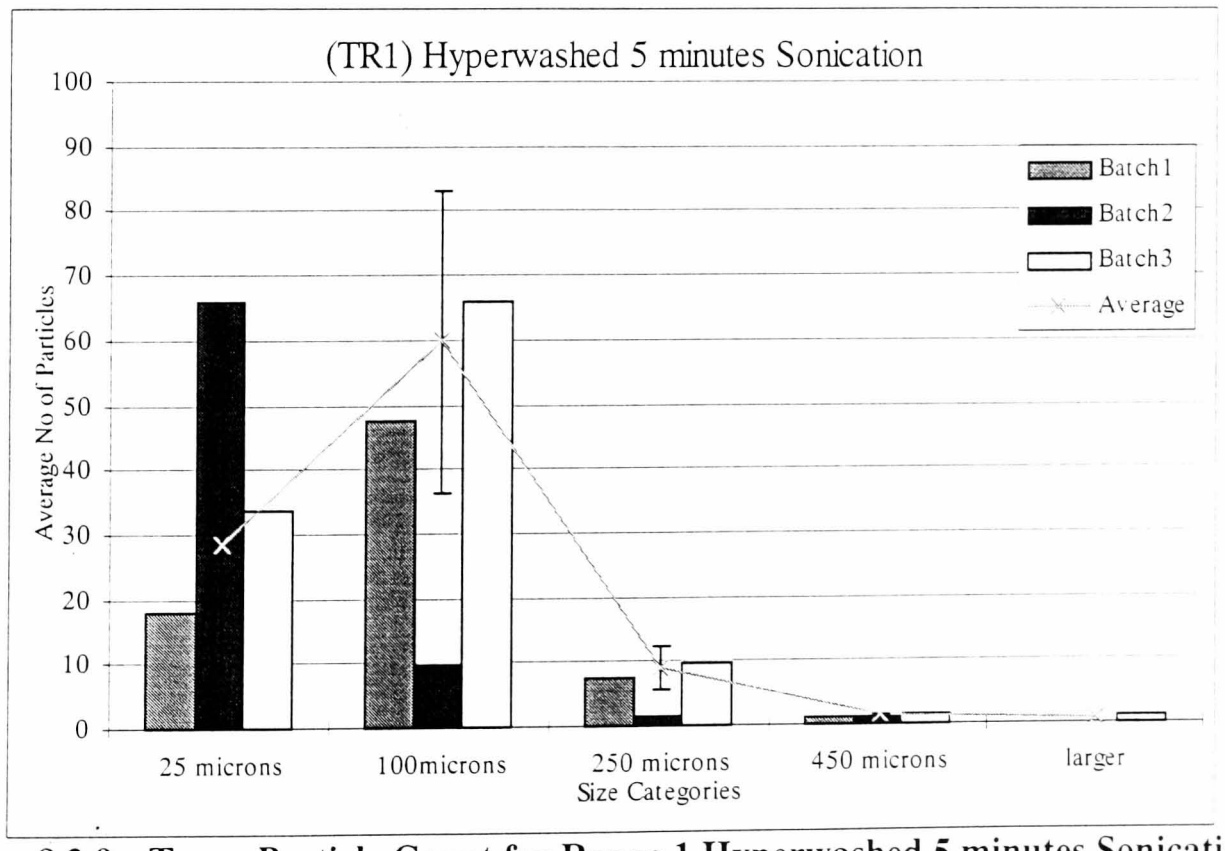


Figure 8.2.9 Toner Particle Count for Range 1 Hyperwashed 5 minutes Sonication

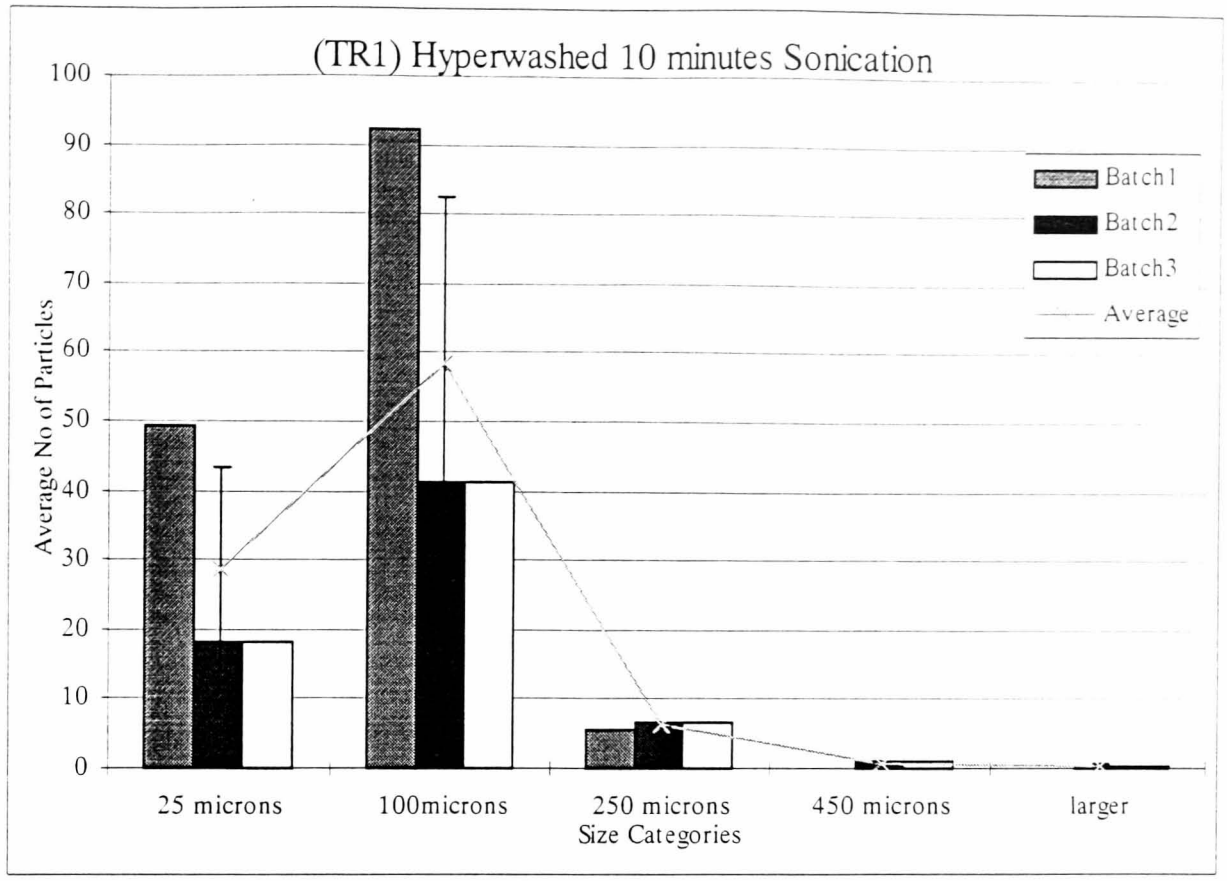


Figure 8.2.10 Toner Particle Count for Range 1 Hyperwashed 10 minutes Sonication

It was found that the numbers of particles detected after pulps had been hyperwashed were much reduced in the smallest two categories. The percentage removal was established by comparing the numbers of particles detected before and after hyperwashing. In the control sample the extent of particle removal was 45%, after 1 minute sonication this increased to 63% and after 10 minutes was further increased to 80%. The ultrasound action broke up the largest toner particles into smaller detached particles. These detached particles were removed from the pulp by hyperwashing, however not all the toner particles were detached.

The handsheets and pulp samples were both examined microscopically. Figure 8.2.11 was obtained under transmitted polarised light at 100x magnification. This image is of a diluted sample of pulp that was not treated with ultrasound. The only treatment these fibres have undergone is the disintegration process. Fibrillation can be detected as hazy edges to some of the fibres. The dark central object (A) shows a toner particle, still attached to a number of fibres.

In contrast, the second image (figure 8.2.12) shows the same pulp after 10 minutes ultrasound treatment when viewed under the same conditions. The particles have been reduced in size to around 25 microns, and are no longer attached to the fibres. The largest

toner particle shown in figure 8.2.12, labelled B, was found to be approximately 100 microns in diameter.

Figure 8.2.11 **Photomicrograph of Disintegrated Fibres and Toners**

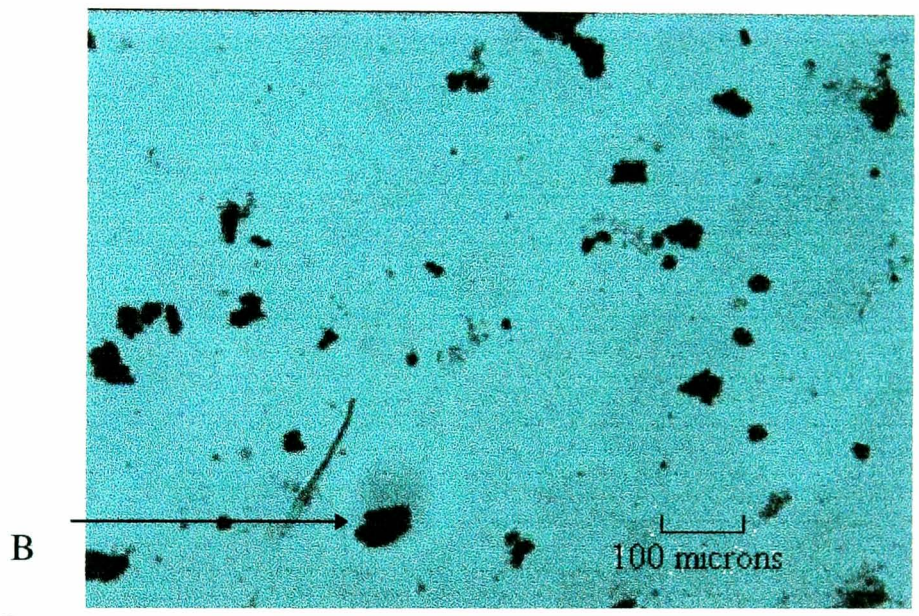


Figure 8.2.12 **Photomicrograph of Fibres and Toners after 10 minutes Sonication**

In conclusion, the ultrasound treatment effected the size distribution of toner particles, and caused detachment of toner particles from fibres. A more detailed discussion of the results follows in section 8.2.1.

8.2.1 Discussion of Results for Temperature Range 1

The mean particle size of particles detected on the handsheets, along with their standard deviations, is shown in Figure 8.2.8.

	0 minute	1 minute	2minute	5minutes	10 minutes
Batch 1	182.51 ± 280	118.05 ± 205	70.07 ± 117	56.15 ± 88	43.20 ± 66
Batch 2	190.49 ± 318	77.94 ± 139	68.38 ± 142	48.63 ± 72	44.18 ± 55
Batch 3	176.67 ± 276	100.82 ± 251	69.32 ± 129	52.70 ± 69	43.32 ± 75

Table 8.2.8 Average Particles size before hyperwashing (μm)

Overall the particle diameter decreased from 183 microns in the control sample, to 99 microns after 1 minute sonication. The decrease in particle diameter continued, with a diameter of 69 microns being obtained after 2 minutes. However the decrease did not continue at this rate, with a diameter of 43 microns being attained after 10 minutes sonication. The particles detected on the handsheet produced from sonicated pulp were more regular in size, this was confirmed by the decrease in the standard deviation of the detected particles. The standard deviation of the control sample was found to be 293 microns this decreased to 68 microns after 10 minutes sonication. The ultrasound treatment broke the fused toner down into smaller particles resulting in a narrower size distribution.

	0 minutes	1 minutes	2 minutes	5 minutes	10 minutes
Batch 1	202.70 ± 306	202.29 ± 264	93.67 ± 135	76.29 ± 126	61.89 ± 105
Batch 2	225.86 ± 281	156.46 ± 251	131.91 ± 244	86.06 ± 164	93.96 ± 165
Batch 3	216.98 ± 278	145.01 ± 226	105.78 ± 171	65.8 ± 83	38.48 ± 61

Table 8.2.9 Average Particle Size after Hyperwashing (μm)

There were fewer particles present on the hyperwashed handsheets. The average particle number decreased from 717 particles in the unwashed control sample to 438 particles after hyperwashing. After 10 minutes sonication treatment 1878 particles per batch were detected before hyperwashing and only 458 particles after hyperwashing.

With the unwashed samples although the *distribution* of particles remained essentially unchanged, the total number of particles increased as sonication time increased. After hyperwashing the distribution was again unchanged, but the numbers of particles detected was significantly decreased.

Estimation of the critical size for toner reduction

Quantification of the removed particles was obtained by examining the laser scattering data for the filtrates of the samples. The data for all batches is given in figures 8.2.13, 8.2.14, and 8.2.15, below. In the control sample the volume of particles found at 25 microns was around 1.8%. This volume distribution increased after 10 minutes sonication to 2.5%. These particles are too large to be filler particles which have a typical size of less than 5 microns, and too small to be fibres with an average length of around 0.6 mm. It was assumed that they were detached toner particles. Sonication lead to an increase in the volume of particles present in the filtrates. The maximum sized particles that could pass through the hyperwashing filter was 220 microns. However from the data obtained from the filtrates the significant increase in detected particles occurred at a size of 25 microns. The increase in the volume of this fraction of the filtrate lead to the assumption that the largest toner particles were being broken up by the ultrasound treatment to form smaller particles but only when they reached a size of around 20-25 microns did they become detached from the fibres.

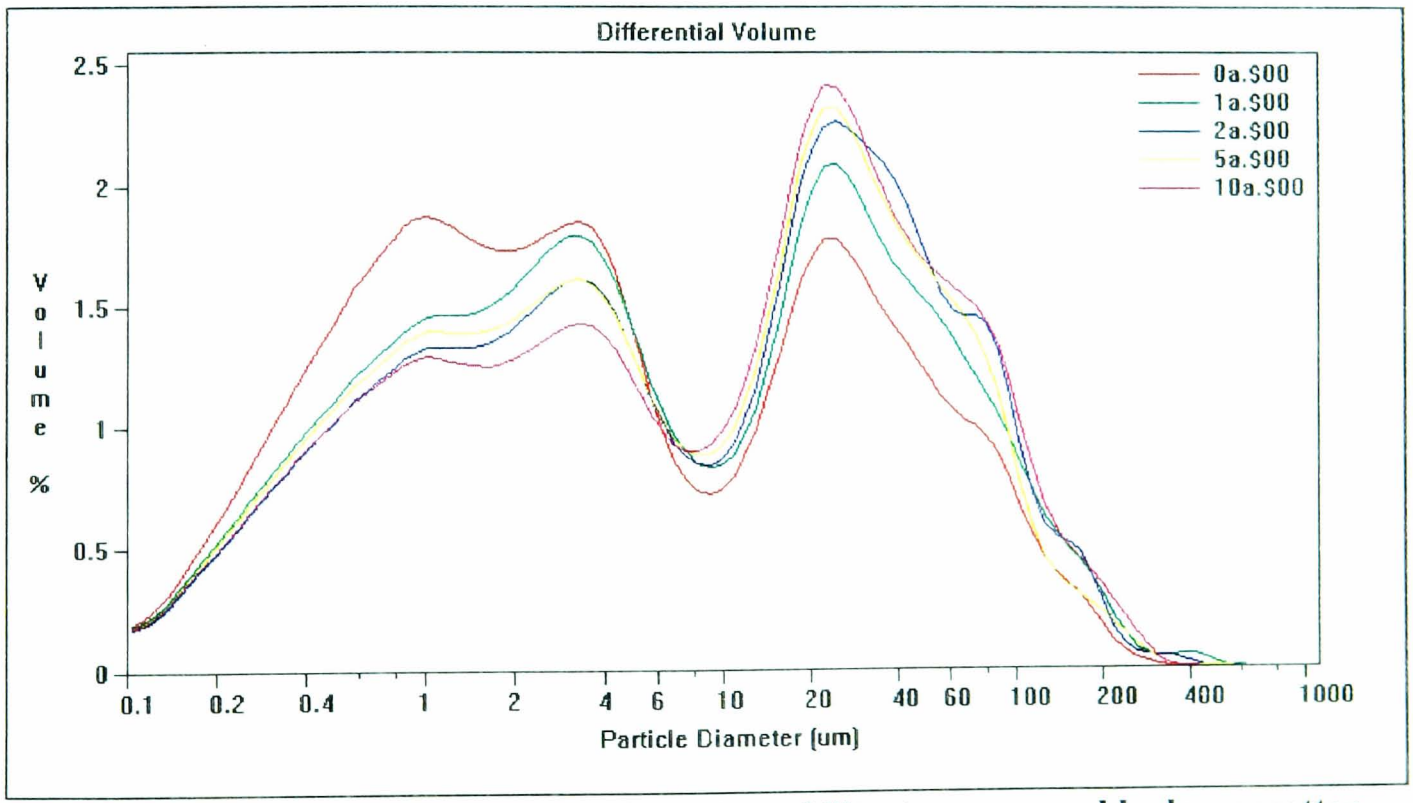


Figure 8.2.13 TR1 Particle Size Distribution of filtrates measured by laser scatter- Batch 1

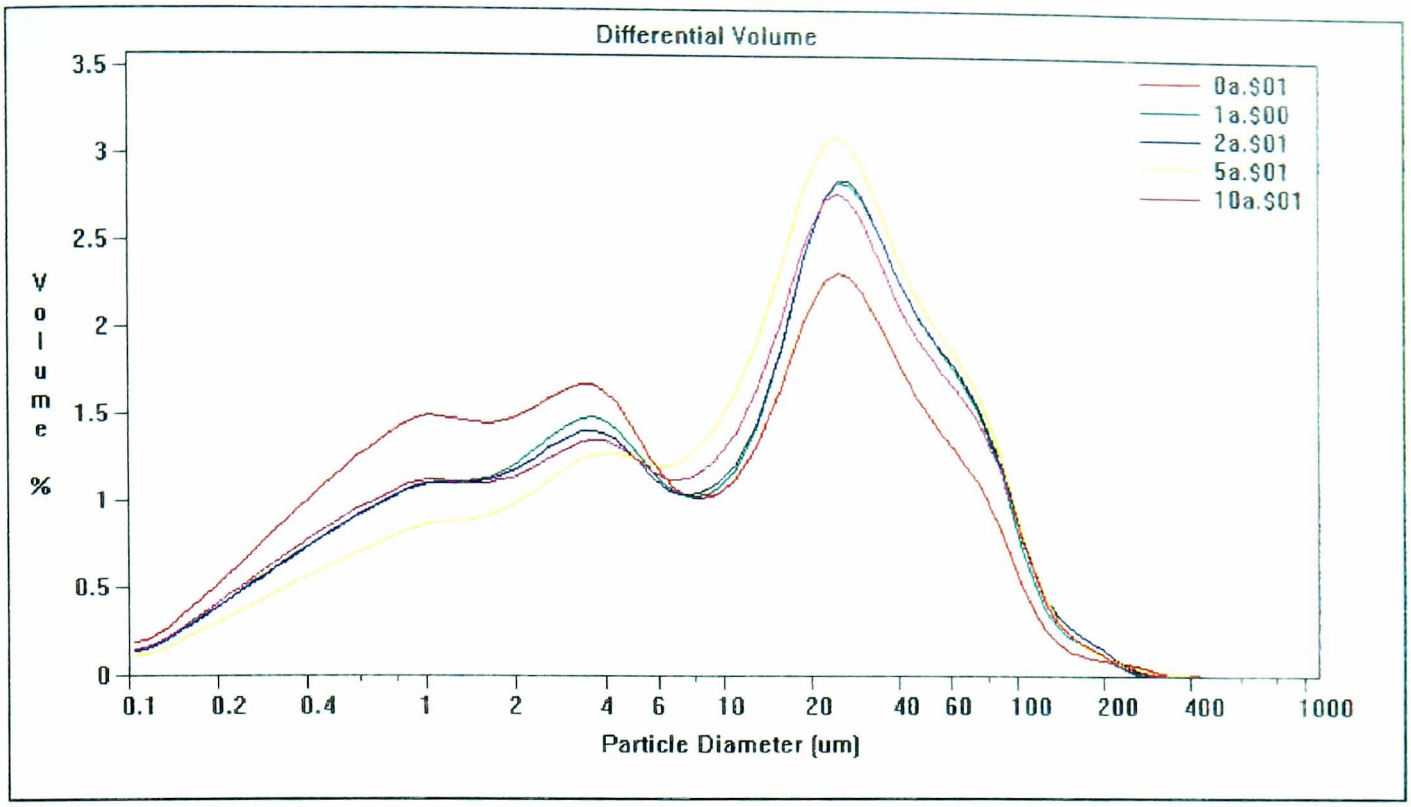


Figure 8.2.14 TR1 Particle Size Distribution of filtrates measured by laser scatter- Batch 2

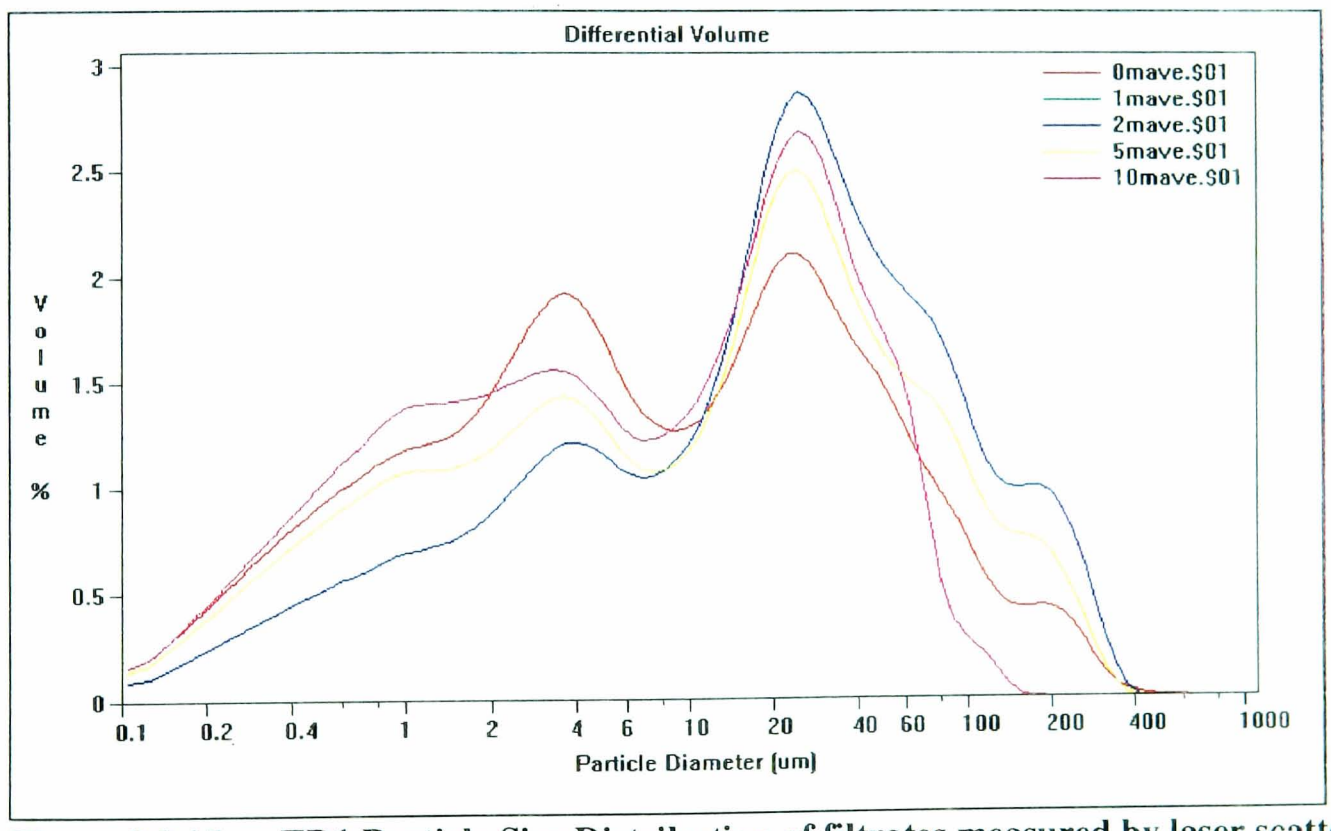


Figure 8.2.15 TR1 Particle Size Distribution of filtrates measured by laser scatter- Batch 3

Toners are manufactured by different methods, the pigment is dispersed through the polymeric material, prior to the polymeric resin being reduced to the required size. Examples of typical pigments used in toners are shown in table 7.1. There are two sizes of particle to consider, firstly the particle size of the pigment itself, typically very small - less than 0.1 micron, secondly the particle size of the toner beads. Shown in figure 8.2.16 is the

the volume distribution of a toner used in Sharp photocopiers. This toner was examined by dispersing it in water using a small amount of detergent to form a paste. The distribution was found to be bimodal, with a peak at 20 microns and another peak at 90 microns. This toner contained two sizes of bead. The purpose of the two sizes of beads was probably to ensure that the toner flowed efficiently into the paper with the larger toner beads moving into the larger voids within the paper.

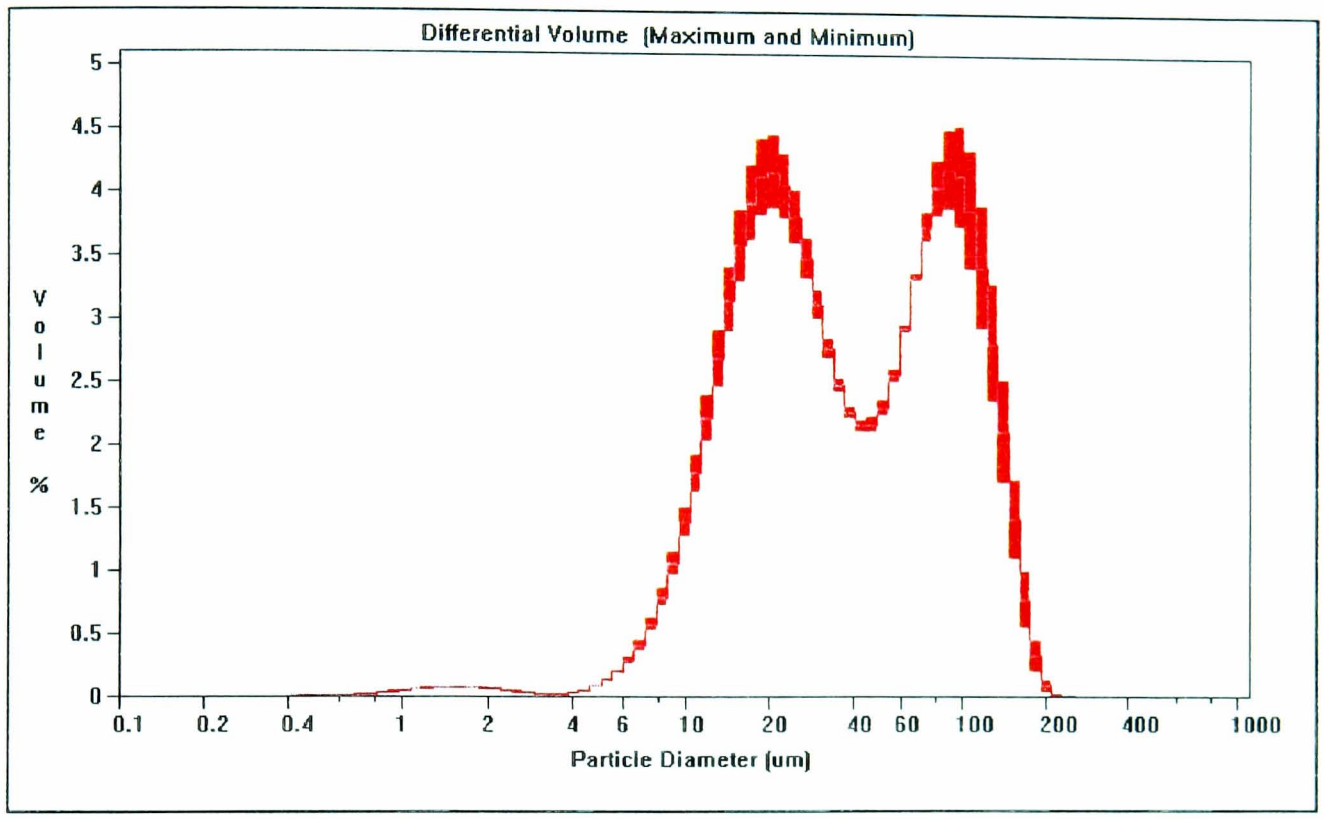


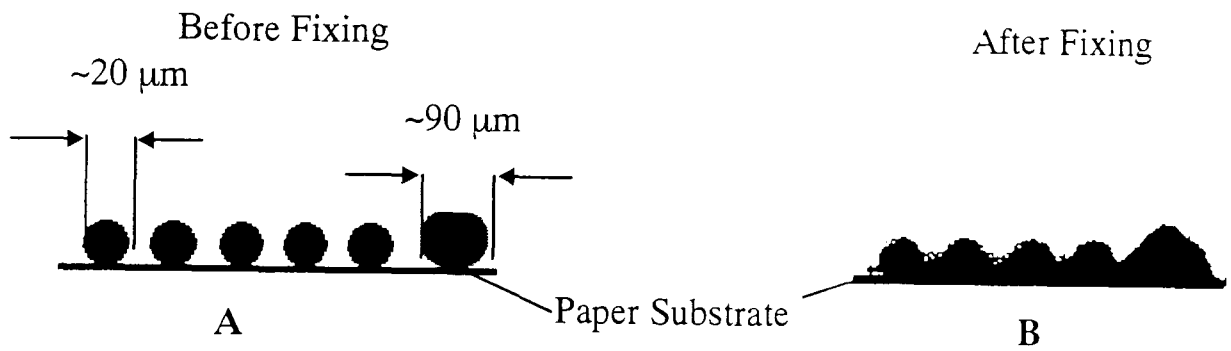
Figure 8.2.16 Particle Distribution of Sharp Toner

The distribution contained very few particles that were less than 2 μm in size. The important sizes were those of the polymer beads and not the pigment particles.

The smaller toner bead was similar in size to the particle size which showed greatest increase in the filtrate data. It appeared that the toner was being broken down by ultrasound treatment to its 'native' state. In figure 8.2.16 the distribution presented is a volume distribution, indicating there were approximately 4 times as many 20 micron beads as 90 micron beads. Thus, the relative volumes detected in the filtrate samples were lower, with no peak, but a shoulder at 90 microns, see figure 8.2.15.

The laser scattering data of the sonicated pulps also indicated an increase in the number of particles detected with a size of 90μm.

Before the toner is formed into an image on the paper it is given a charge. The charge on the toner enables it to be attracted to the paper and form the image. The toner particles sit a certain distance apart from each other on the surface of the paper due to the repulsion between similarly charged particles (see figure 8.2.12(A) & (C)). To fix the toner to the paper it is heated until the beads flow together to form a solid area as shown in figure 8.2.12(B) & (D).



Plan of Toner Particles Before Fixing and, after fixing

Figure 8.2.12 **Fixing of Toner Beads to Paper Surface**

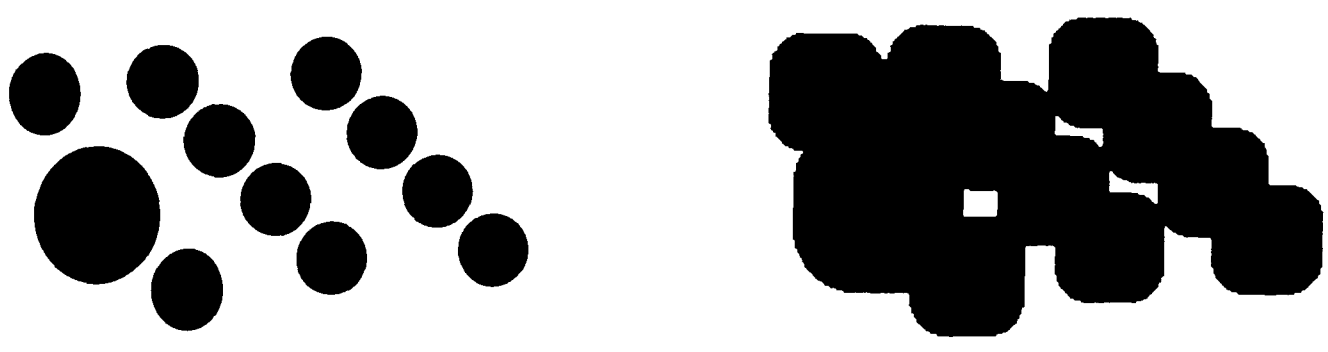


Figure 8.2.12 **Fixing of Toner Beads to Paper Surface**

Microscopic examination of printed toners has shown that the fixed image has a clinkered appearance.[170] The hypothesis is that the fixing of the toner to the substrate leads to the formation of areas where the toner is not as thick as were the original beads. The work of cohesion between the toners is not as great as the work of adhesion between the toner and the paper surface. In the areas between the original beads the fused toner is thinner and these thinner areas may act as 'perforations' for the break-up of the fixed toner into smaller particles. The fibre may well act as an anvil to the ultrasound hammer, anchoring the particle so that it can be broken down. Toner particles are lightweight, with a density very similar to water, and unattached toner particles would be jetted away from a cavitation bubble. By providing a base the fibres prevent the particles being pushed away thus assisting in their breakdown.

Once the fixed toner has been reduced to its native size it will be small enough to interact with a cavitation bubble which results in detachment from the fibre. The collapsing bubble develops pressures of 1900 bar, enough to detach the toner from the fibre.

The percentage of toner particles detached by ultrasound and removed by hyperwashing are given in figure 8.2.17. The final two sonication treatments, 5 and 10 minutes, removed similar amounts of toner suggesting an optimum exposure to ultrasound, close to 5 minutes.

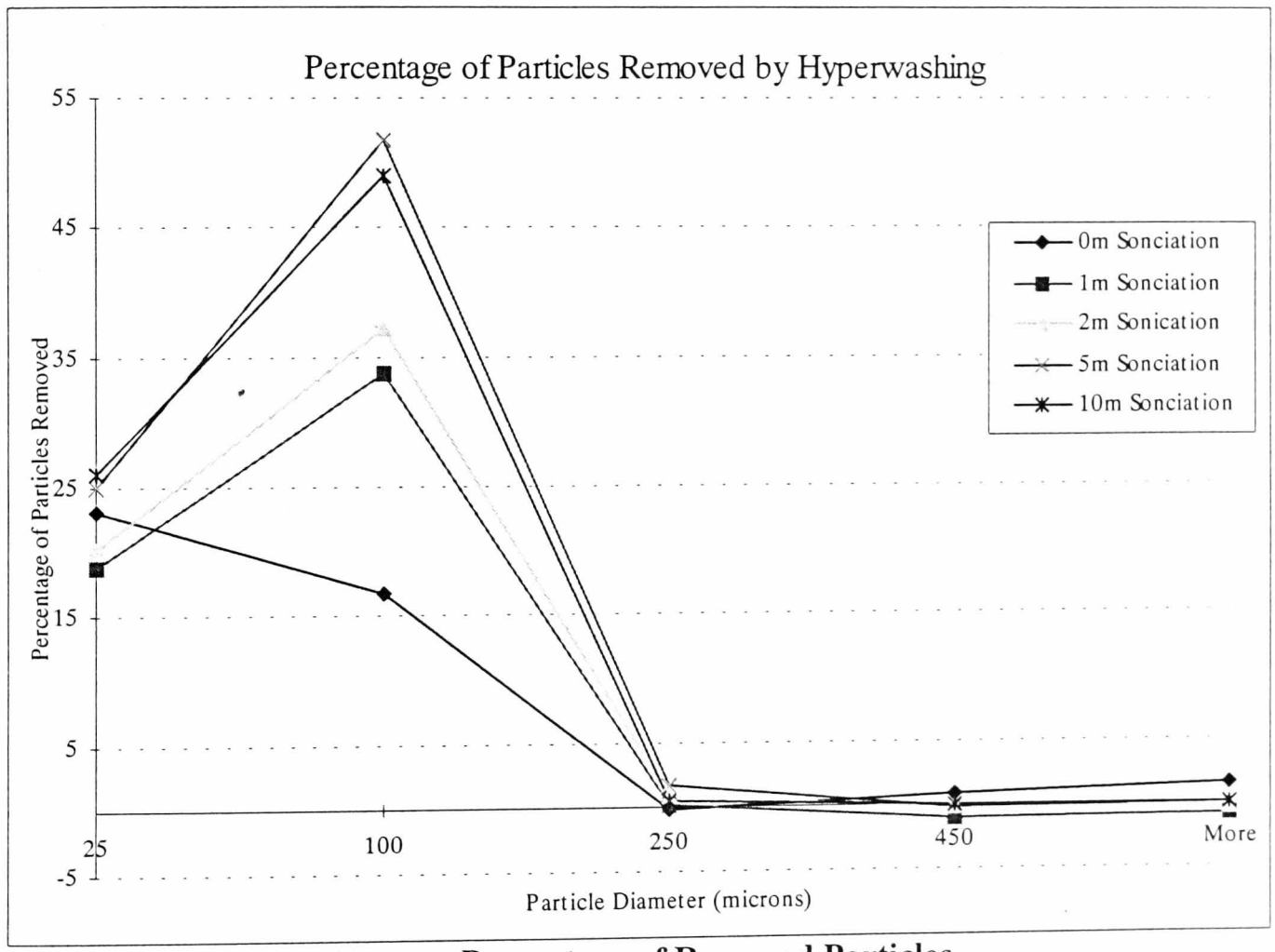


Figure 8.2.17 Average Percentage of Removed Particles

Summarising the results obtained

- Fixed toner particles are broken up by ultrasound treatment into their native sizes of around 25 and 90 microns.
- Once the native size has been reached significant detachment of toner from fibres takes place.
- The native sized toner particles could be removed by conventional washing and/or flotation techniques.

In an attempt to minimise the effects of temperature variation it was decided to repeat the experiments at a controlled temperature. The temperature chosen was below the glass transition temperature of the toner, to permit the study of the ultrasound interaction with hard brittle toners. In the literature it was suggested that cavitation bubbles were more commonplace and more efficient at lower temperatures. Thus it was decided to carry out experiments at lower temperatures than were used for temperature range 1. These experiments are detailed in section 8.3.0.

8.3.0 Temperature Range 2

Samples of mixed office waste were prepared from laser and photocopier waste using the procedure described in Section 8.2.0. The samples were again treated with ultrasound for 1, 2, 5, and 10 minutes at a power of 1 kW ± 20 watts, at a frequency of 20 kHz under neutral conditions. However, in this experiment the temperature was controlled within the reaction vessel by packing ice around it; the temperature was kept as low and stable as possible during sonication. Temperature stabilisation was difficult and variations in temperature during the experiments are shown in Table 8.3.1. An untreated sample was retained to act as a control.

	Batch 1		Batch 2		Batch 3	
	initial	final	initial	final	initial	final
1 minute	18.5	24	18	23	14	22
2 minute	16	28	18	25	12	23
5 minute	17	35	14	33	10	28
10 minute	16	34	11	40	10	30

Table 8.3.1 Temperature Data for Range 2 (ºC)

Shown in tables 8.3.2 to 8.3.7 are the statistics from the three batches. of both unwashed and hyperwashed samples.

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	152.3	89.4	70.0	47.7	35.9
Standard Error	49.8	32.7	22.6	13.3	6.5
Median	52.0	32.5	34.6	29.6	26.1
Mode	8.5	8.5	8.5	8.5	8.5
Standard Deviation	247.5	177.5	130.5	80.0	43.0
Minimum (μm)	8.5	8.5	8.5	8.5	8.5
Maximum (μm)	747.3	703.4	586.2	329.2	171.7
Count	612	874	1121	1326	1893
Confidence Level (95.0%)	152.3	89.4	70.0	47.7	35.9

Table 8.3.2 Batch 1 Statistics Unwashed

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	171.7	121.7	75.3	51.4	41.7
Standard Error	54.9	41.3	24.2	12.5	9.7
Median	67.2	53.6	43.9	37.7	33.3
Mode	8.5	8.4	8.4	9.4	8.4
Standard Deviation	267.4	208.0	123.0	63.6	45.8
Minimum (μm)	8.5	8.4	8.4	8.4	8.4
Maximum (μm)	830.0	690.1	430.1	205.5	119.7
Count	564	645	669	665	490
Confidence Level (95.0%)	830.0	690.1	430.1	205.5	13.6

Table 8.3.3 Batch 1 Statistics After Hyperwashing

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	152.8	102.3	67.1	46.6	35.6
Standard Error	50.2	33.8	21.1	12.3	7.9
Median	46.7	33.8	33.7	32.2	26.8
Mode	8.5	8.5	8.5	8.5	9.5
Standard Deviation	259.4	190.2	121.8	72.2	44.2
Minimum (μm)	8.5	8.5	8.5	8.5	8.5
Maximum (μm)	782.5	680.1	486.8	366.2	159.2
Count	716	1005	1120	1182	978
Confidence Level (95.0%)	70.3	47.3	29.5	17.2	11.1

Table 8.3.4 **Batch 2 Statistics Unwashed**

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	169.5	120.3	92.3	49.9	40.1
Standard Error	58.2	39.5	35.2	14.5	10.2
Median	59.3	51.6	46.3	34.4	30.8
Mode	8.5	8.5	8.5	8.5	8.5
Standard Deviation	276.3	200.2	170.5	65.9	44.8
Minimum (μm)	8.5	8.5	8.5	8.5	8.5
Maximum (μm)	748.2	621.9	647.2	241.3	131.5
Count	508	658	552	430	371
Confidence Level (95.0%)	81.6	55.4	49.3	20.3	14.3

Table 8.3.5 **Batch 2 Statistics After Hyperwashing**

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	159.4	103.8	70.2	43.9	44.9
Standard Error	55.1	36.4	22.9	11.8	12.5
Median	46.6	38.9	36.0	28.0	33.9
Mode	8.4	8.4	9.4	8.4	8.5
Standard Deviation	267.6	191.2	122.8	70.1	62.1
Minimum (μm)	8.4	8.4	8.4	8.4	8.4
Maximum (μm)	805.8	558.6	430.8	306.9	260.1
Count	558	763	823	1252	616
Confidence Level (95.0%)	77.2	51.0	32.1	16.5	17.5

Table 8.3.6 **Batch 3 Statistics Unwashed**

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	165.7	113.4	78.0	53.2	39.0
Standard Error	57.2	39.9	27.3	19.3	8.8
Median	81.3	51.5	40.2	31.3	28.1
Mode	11.2	8.4	8.4	8.4	8.5
Standard Deviation	253.2	192.9	127.9	97.1	51.6
Minimum (μm)	8.4	8.4	8.4	8.4	8.4
Maximum (μm)	725.4	621.7	408.6	459.4	219.1
Count	385	549	482	635	1213
Confidence Level (95.0%)	80.2	55.9	38.3	27.1	12.3

Table 8.3.7 **Batch 3 Statistics After Hyperwashing**

The control samples contained the largest particles, these particles were not present in the sonicated samples. The largest particles detected in the control sample were 778 microns in diameter, the maximum sized particles detected after sonication were much smaller, for example 656 microns after 1 minute sonication.

The tables above show data as number distributions, the same data is presented below in figure 8.3.1 to 8.3.10. Each batch result is the average of four handsheets, the average of all 12 handsheets is also included in the graph along with error bars displaying the amount of variation between the handsheets.

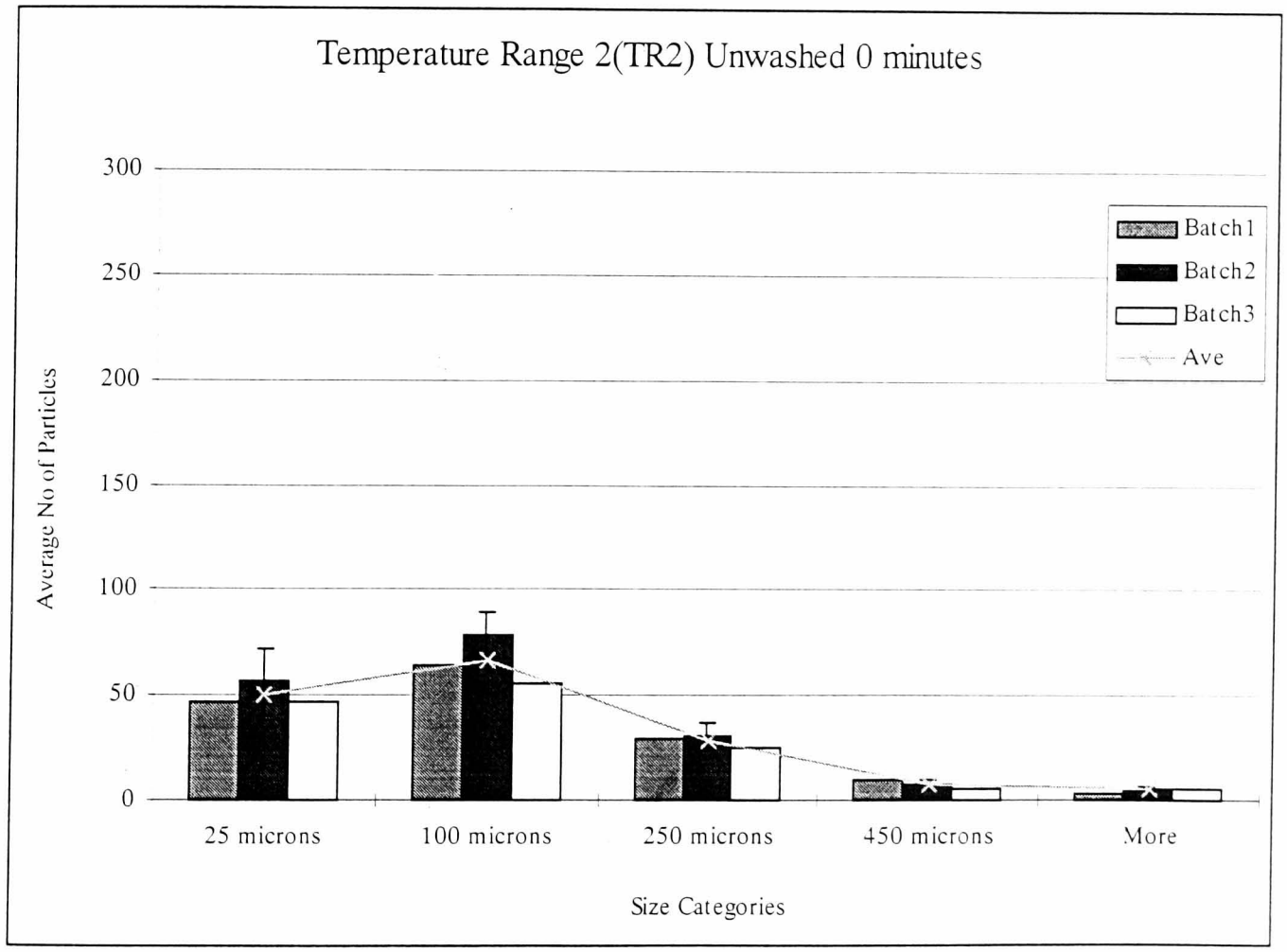


Figure 8.3.1 Toner Particle Count for Range 2 Unwashed 0 minute Sonication

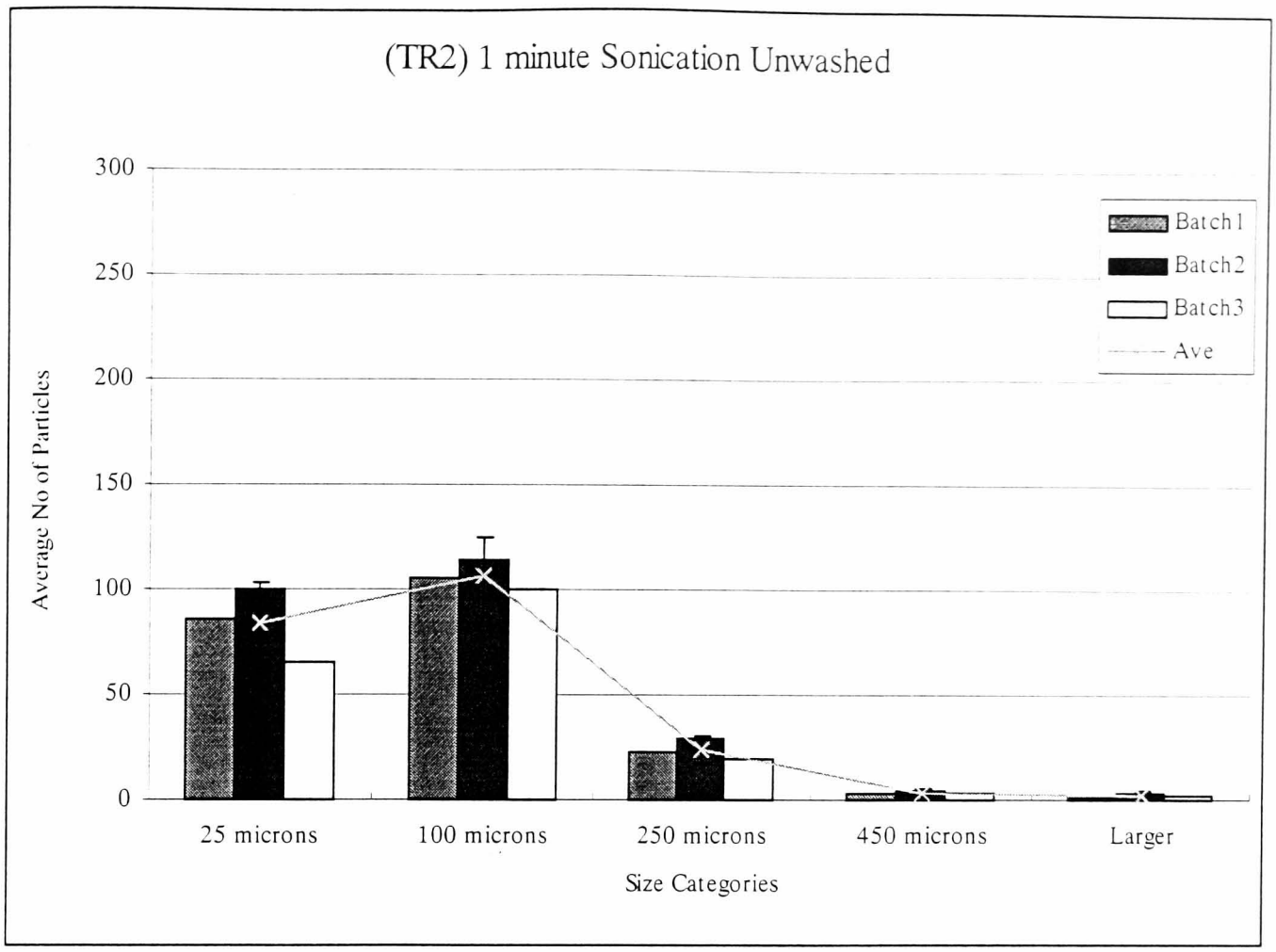


Figure 8.3.2 Toner Particle Count for Range 2 Unwashed 1 minute Sonication

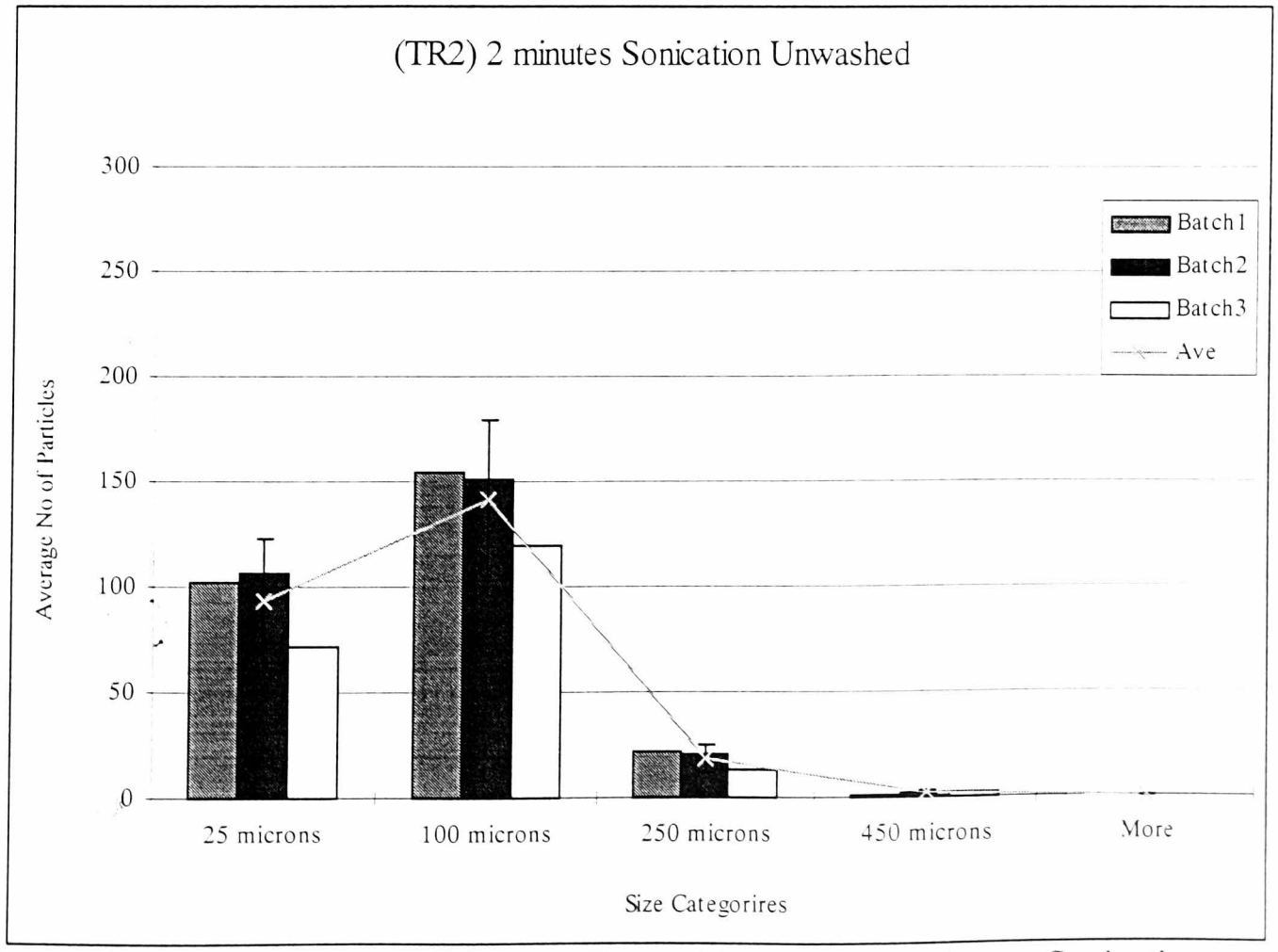


Figure 8.3.3 Toner Particle Count for Range 2 Unwashed 2 minutes Sonication

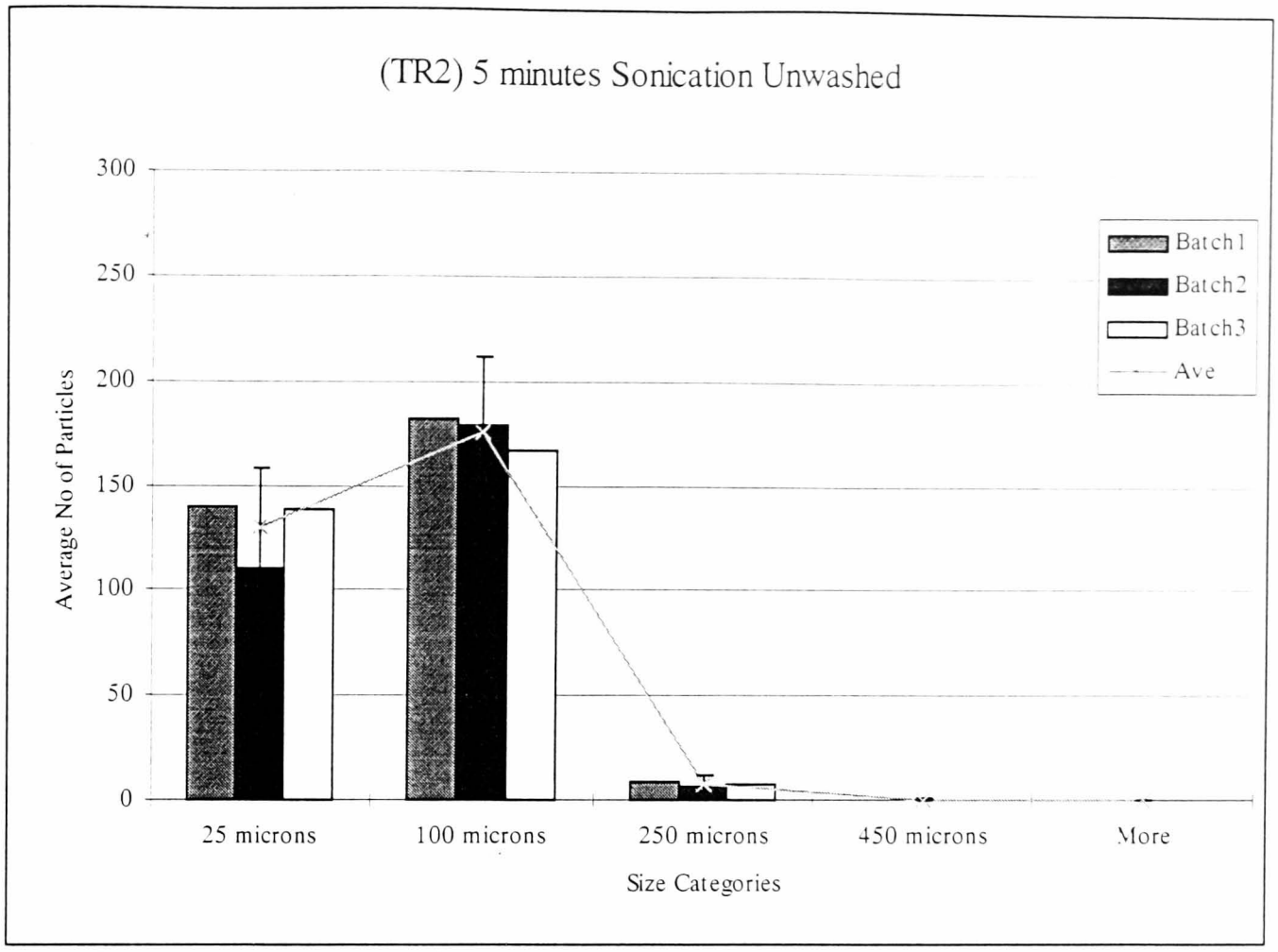


Figure 8.3.4 Toner Particle Count for Range 2 Unwashed 5 minutes Sonication

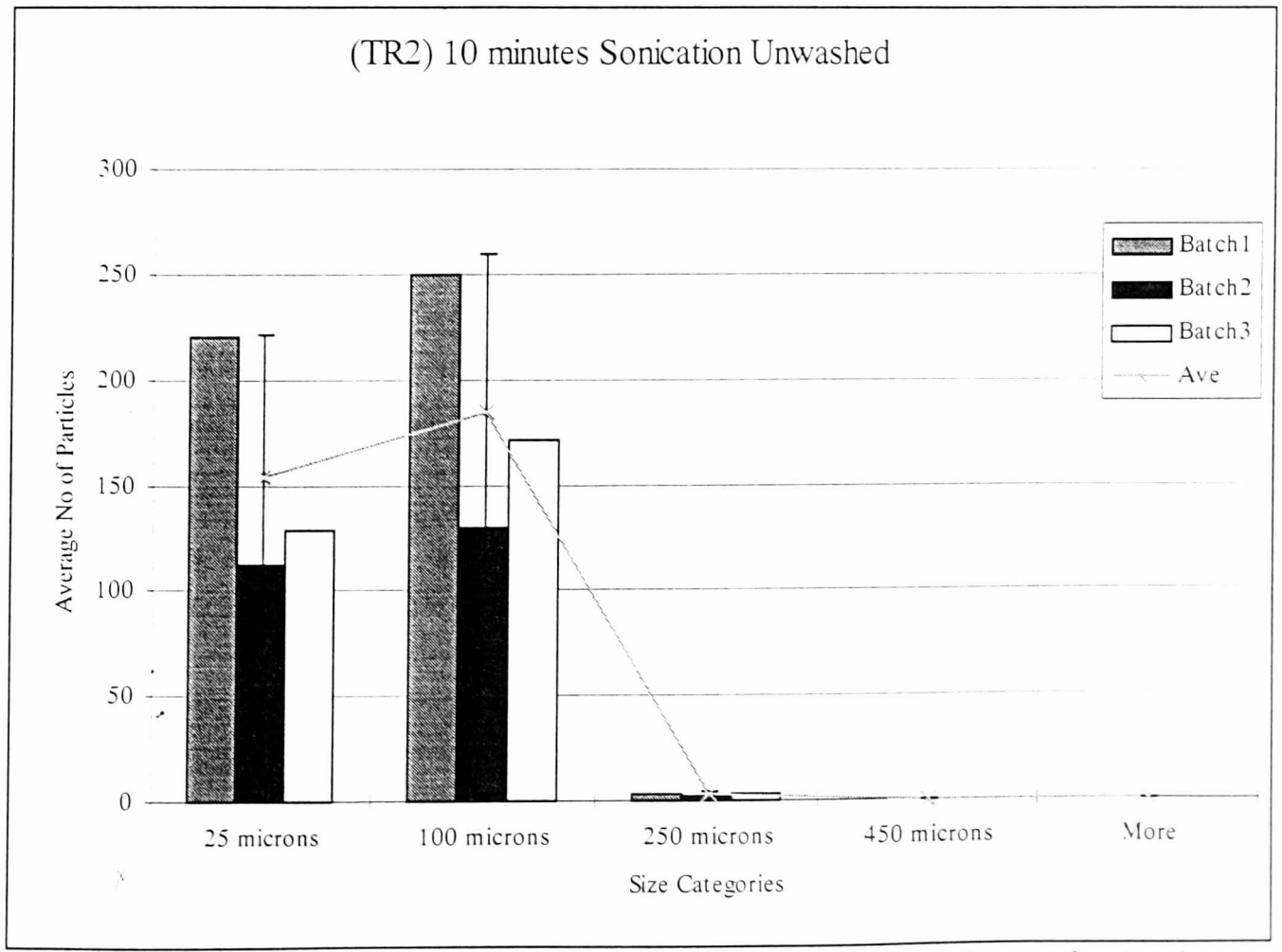


Figure 8.3.5 Toner Particle Count for Range 2 Unwashed 10 minutes Sonication

The largest particles detected in temperature range 2 were found in the control sample. In this temperature range the percentage of particles equal to or less than 100 microns in the

control sample was 74%, this was increased to 86% after 1 minute sonication, 92% after 2 minutes, until 10 minutes where 99% were less than 100 microns in diameter. The percentage of particles in the 100 micron category increased from 42% in the control sample to 48% after 1 minute sonication, however for 2, 5 and 10 minutes sonication the percentage remained constant at 55% of the particles. The data from the hyperwashed pulps is shown in figure 8.3.6 to 8.3.10.

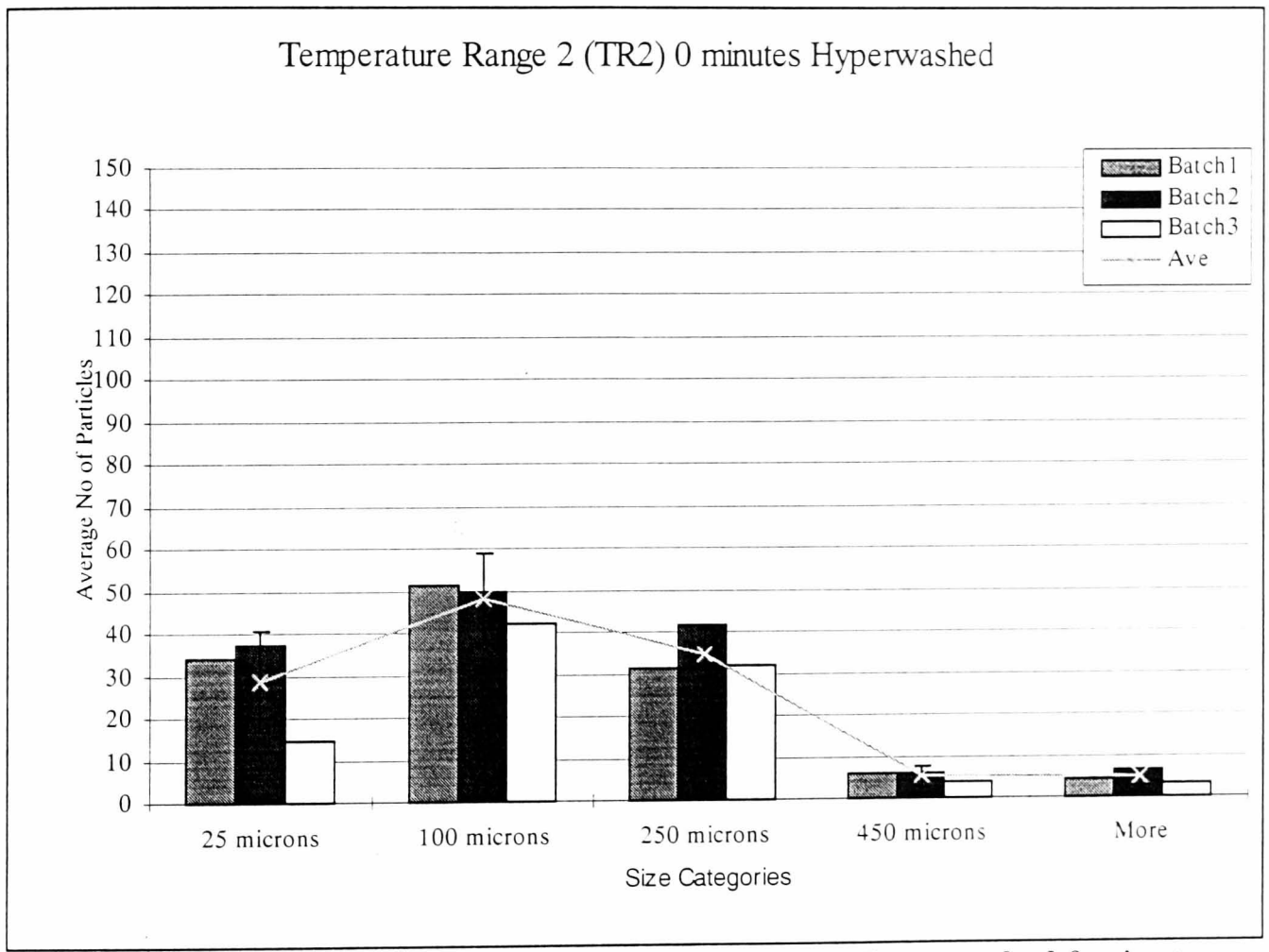


Figure 8.3.6 **Toner Particle Count for Range 2 Hyperwashed 0 minute Sonication**

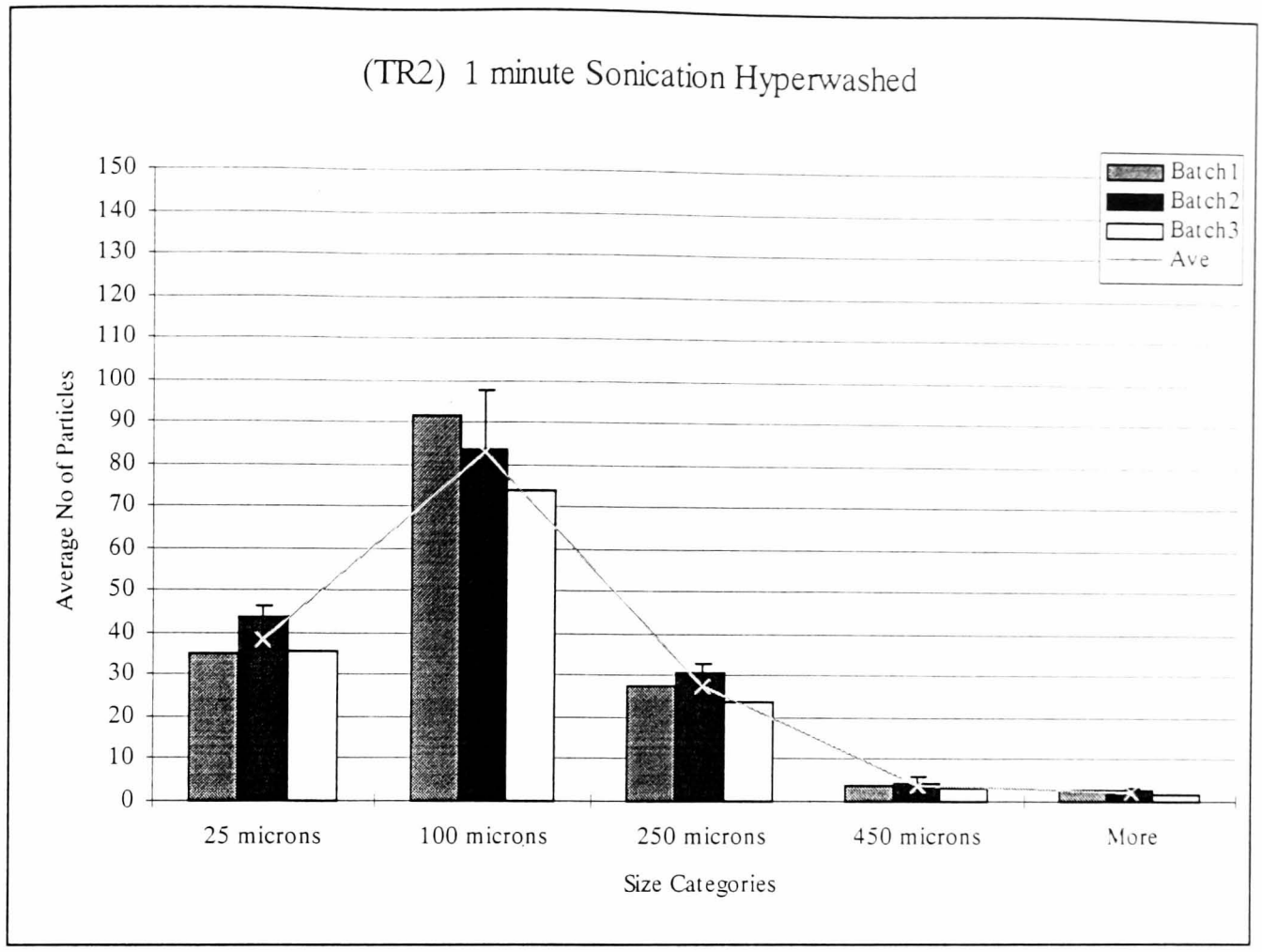


Figure 8.3.7 **Toner Particle Count for Range 2 Hyperwashed 1 minute Sonication**

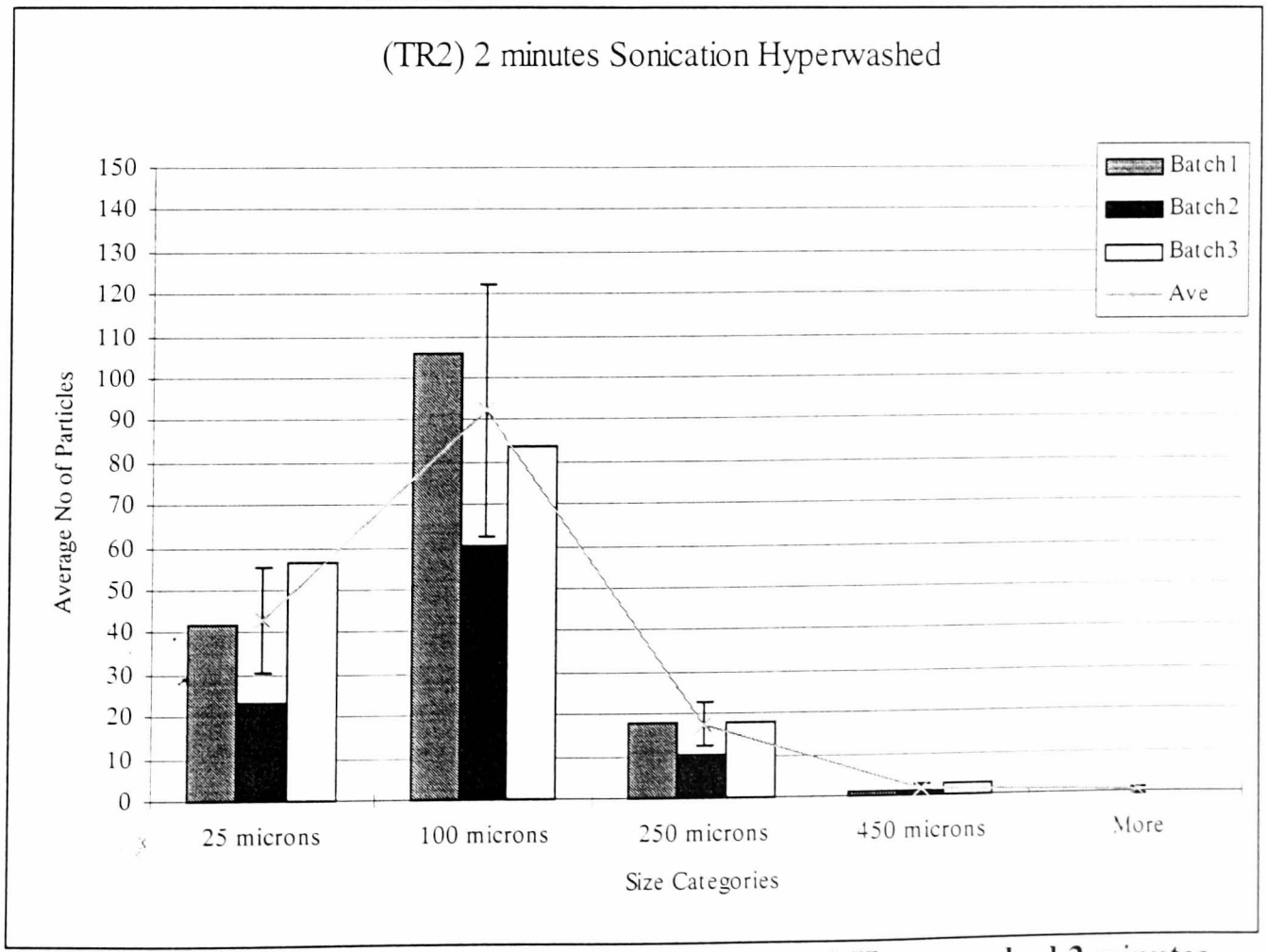


Figure 8.3.8 **Toner Particle Count for Range 2 Hyperwashed 2 minutes Sonication**

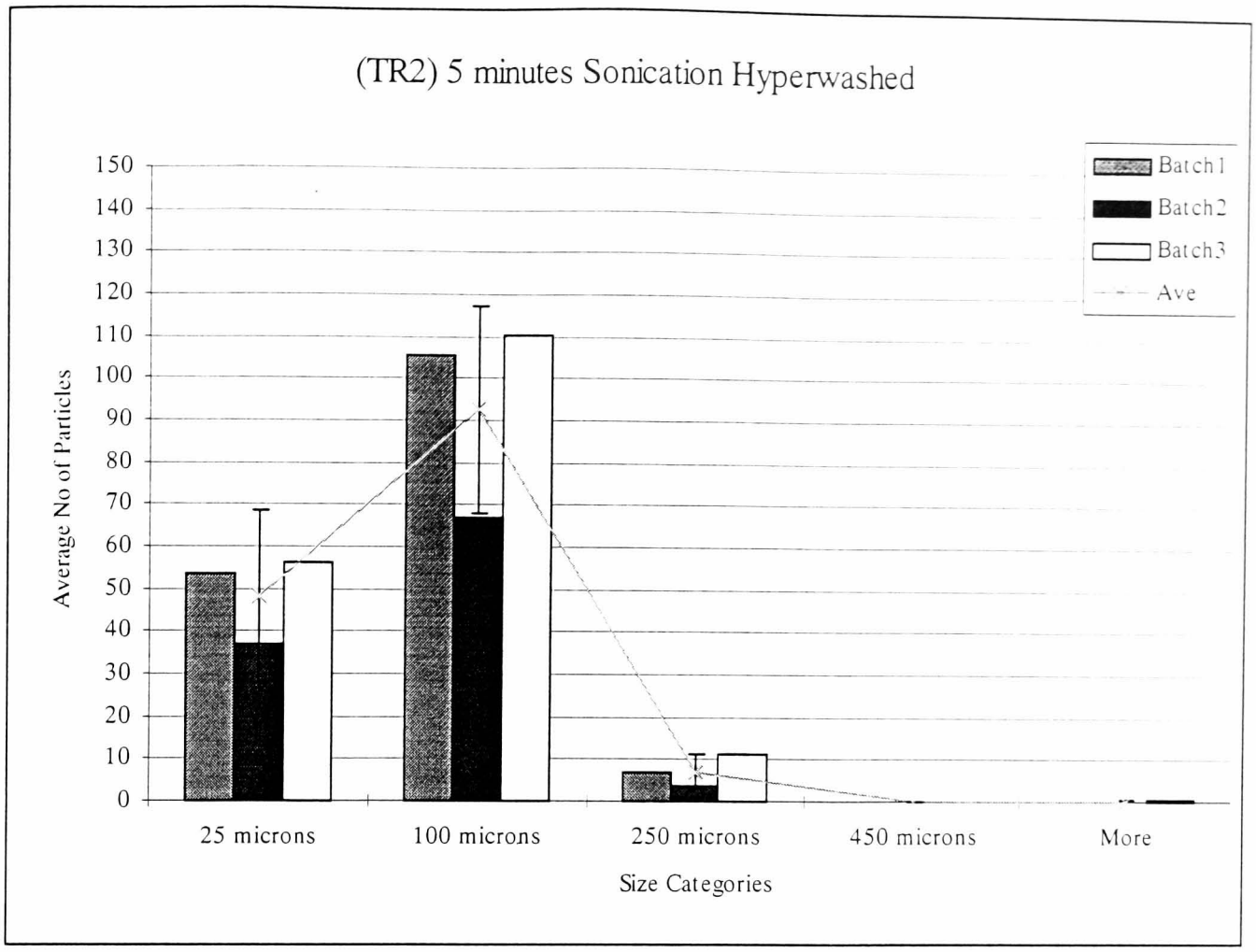


Figure 8.3.9 **Toner Particle Count for Range 2 Hyperwashed 5 minutes Sonication**

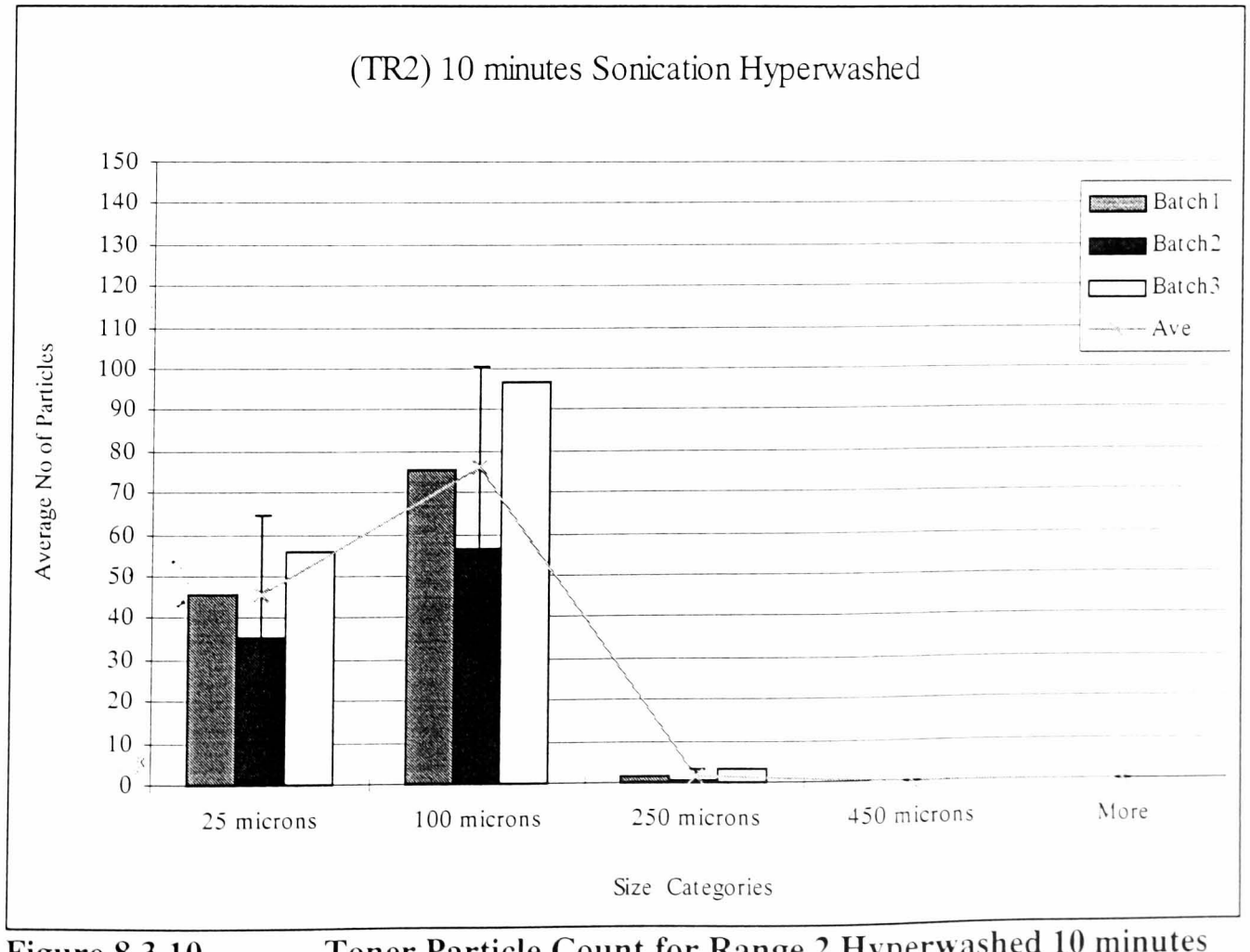


Figure 8.3.10 **Toner Particle Count for Range 2 Hyperwashed 10 minutes Sonication**

After hyperwashing the percentage of particles detected that were equal to or less than 100 microns in the control sample was 63%, after sonication and hyperwashing this percentage increased to 78% after 1 minute, 87% after 2 minutes, 95% after 5 minutes and 98% after 10 minutes.

The pulps were examined with a Canadian Standard Freeness (CSF) tester to establish the amount of damage caused to the fibres by the ultrasound treatment. The CSF was discussed in section 5.7.0. The standard procedure was followed and the raw data corrected for temperature and consistency differences by using the tables supplied with the instrument. The data obtained is shown in table 8.3.8.

	Batch 1				Batch 2				Batch 3				average	SD
0 min	449	457	481	467	430	446	440	450	500	479	475	436	459.2	20.4
1 min	417	424	454	450	440	440	422	422	421	439	449	469	437.3	15.6
2 min	450	447	428	424	430	447	427	430	457	432	459	456	440.6	12.7
5 min	448	440	423	409	430	426	415	411	435	442	457	466	433.5	17.2
10min	397	415	402	406	413	399	399	396	413	406	424	428	408.2	10.1

Table 8.3.8 CSF values for Temperature Range 2 (ml)

The CSF measures the amount of damage caused to the fibres. The CSF value decreased as the ultrasound treatment proceeded. The water associated with the fibres was slower to drain after sonication. The trend was the same for all the batches measured: the greatest value was found in the control sample and the values decreased as the ultrasound treatment was increased.

During the process of measuring the CSF values the pulp passed though a screen. The filtrates were collected and passed through a Coulter LS130 to analyse the population of particles separated from the fibres. The statistics from each of the filtrates are shown in table 8.3.9.

Particle Size in µm	Ultrasound Treatment 0 min % >	1 min % >	2 min % >	5 min % >	10 min % >
2.000	74.69	66.97	68.51	73.48	74.79
25.00	43.33	25.36	30.18	32.33	36.87
100.0	11.04	0.49	6.84	3.94	11.56
250.0	3.00	0.00	0.02	0.00	0.83
450.0	1.76	0.00	0.00	0.00	0.00
600.0	1.04	0.00	0.00	0.00	0.00

Table 8.3.9 Filtrate Particle Statistics for TR2 samples

The size distributions of filtrates from temperature range 2 pulps are given in figure 8.3.11. The results are the average of 4 samples per ultrasound treatment. As sonication proceeded the particles detected in the filtrates decreased in size. Again a bimodal distribution was detected. As found in the previous experiment most toner particles were detached from the fibres after being reduced to their native size.

The result also showed significant differences in the number of particles detected in the range 0.1-10 μm. Most fillers used in paper manufacture are found in this size range. These fillers are mineral clays, such as kaolin, are brittle powders. When sonicated the fillers break up into smaller particles as a result of inter particle collisions. This breakup increases their total surface area. Experiments performed on suspensions of fillers supplied by English China Clay,[161] indicated that exposure to ultrasound resulted in suspensions that took longer to settle out.

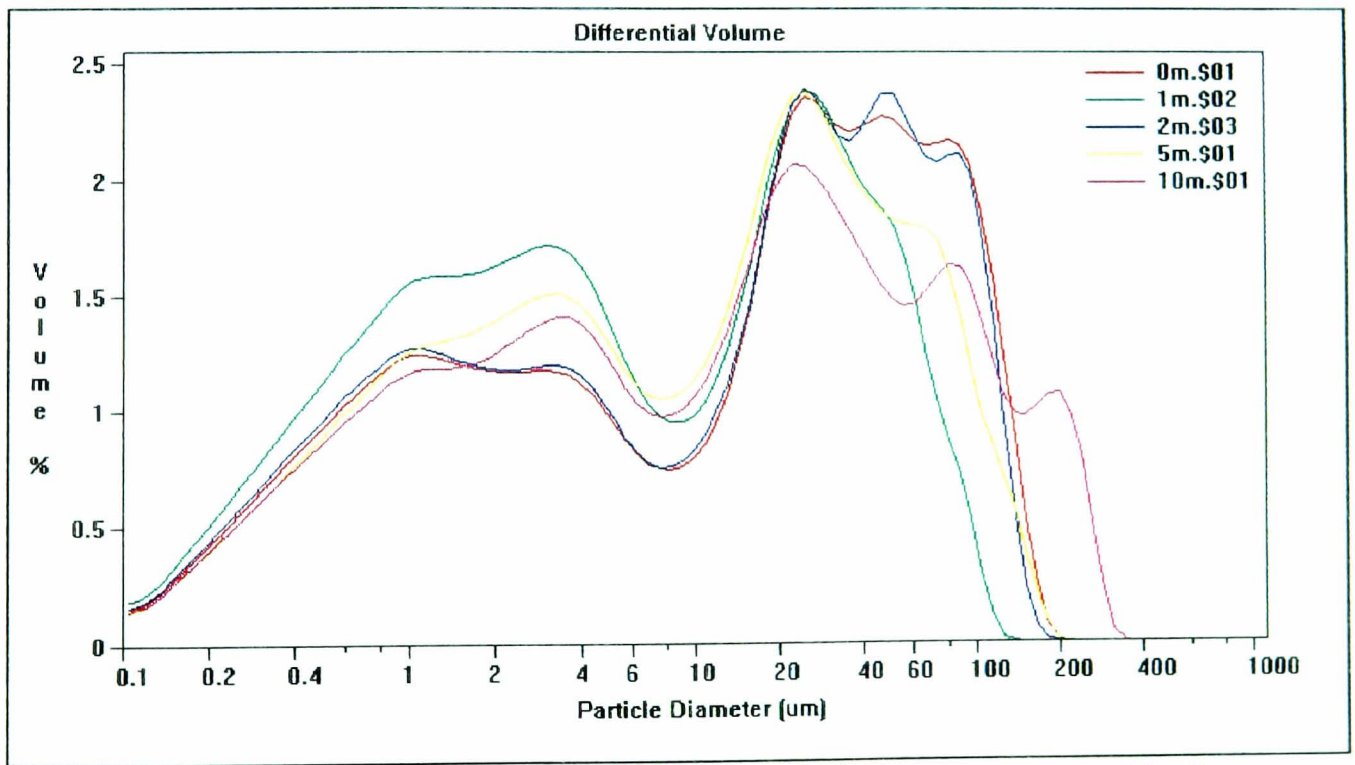


Figure 8.3.11 TR2 Filtrate Particle Size Distribution measured by laser scatter-Batch 1

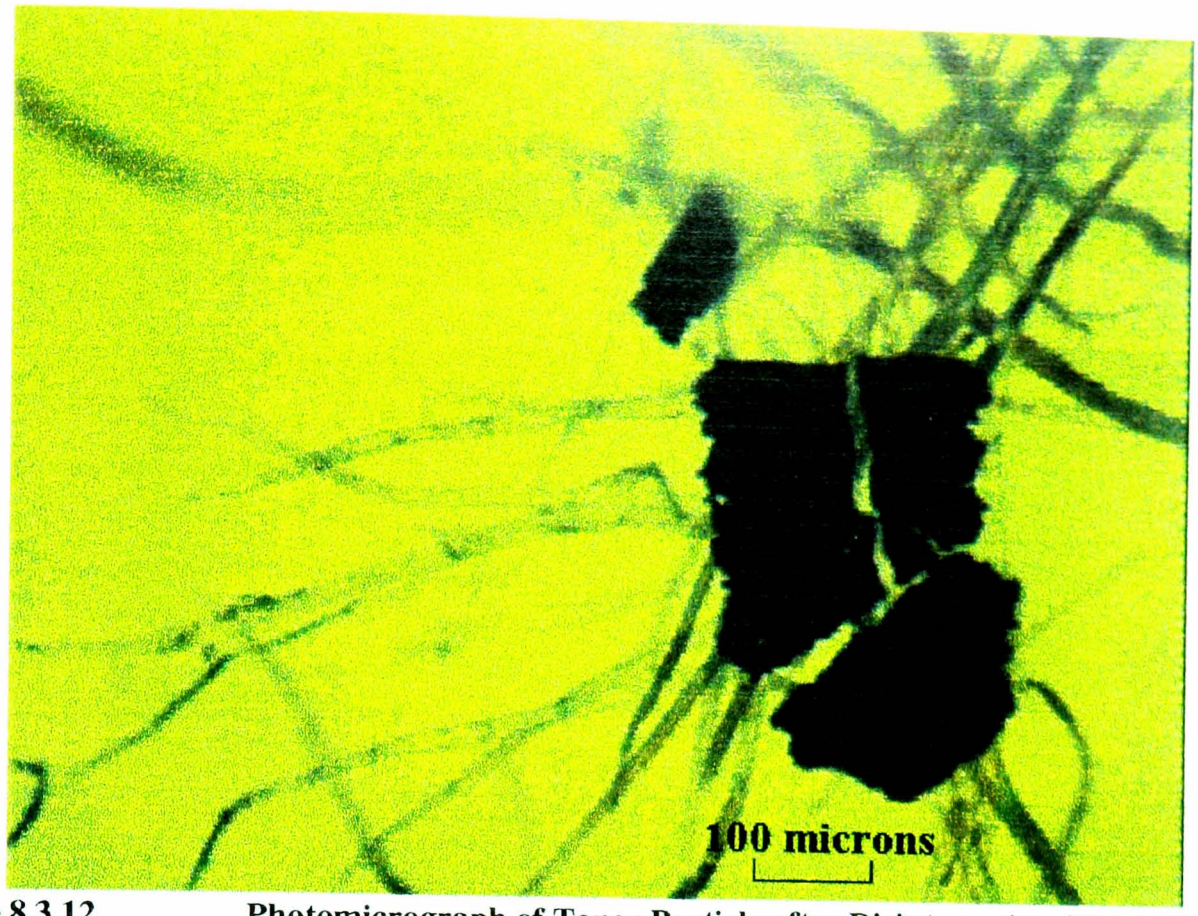


Figure 8.3.12 **Photomicrograph of Toner Particle after Disintegration (TR2)**

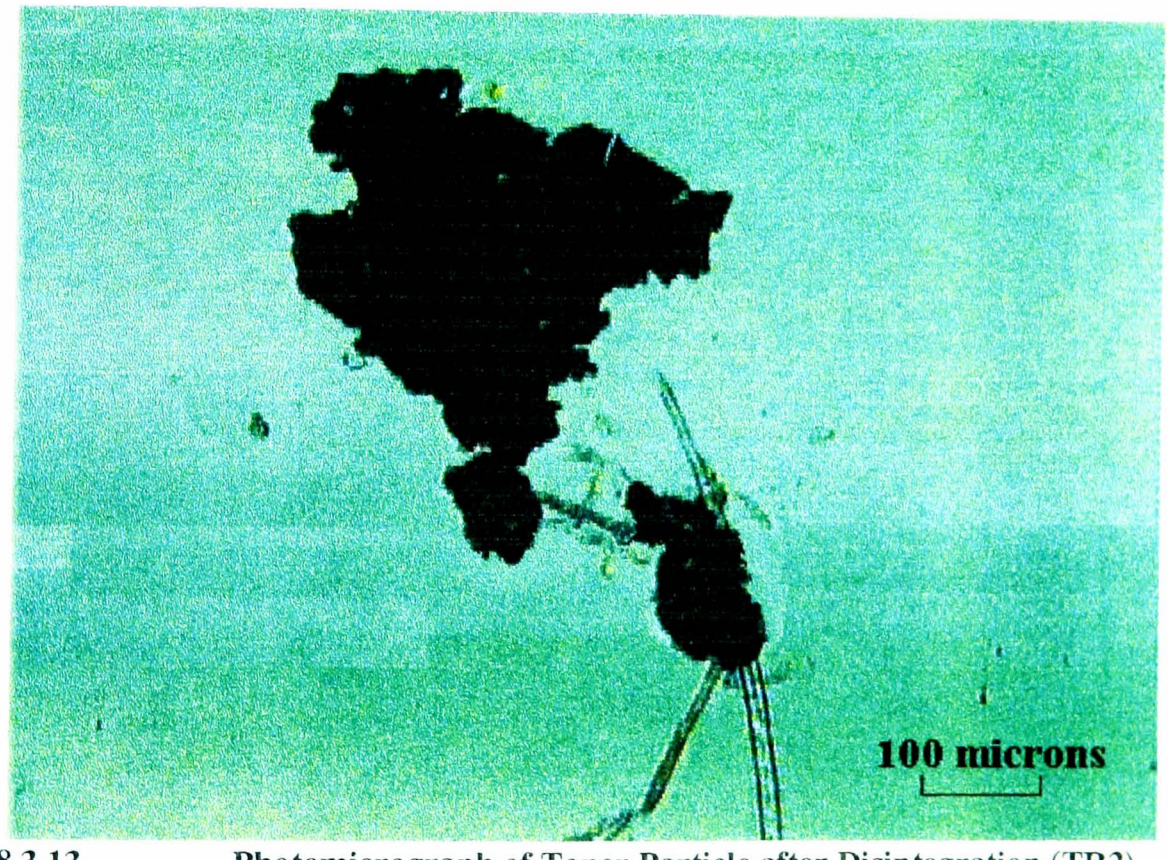


Figure 8.3.13 **Photomicrograph of Toner Particle after Disintegration (TR2)**

Figures 8.3.12 and 8.3.13 are of photomicrographs of pulped samples from temperature range 2 that have not been subjected to sonication. Figure 8.3.12 was obtained using polarised reflected light whilst polarised transmitted light was used to produce figure 8.3.13. The samples had been subjected to disintegration and indicated that cracks had formed or are forming within the structure of the fused toner agglomerates. In figure

8.3.12 large cracks can be seen running laterally down and across the particle, essentially splitting it into three parts each with a diameter of approximately 200 microns. All three parts are still attached to the fibres.

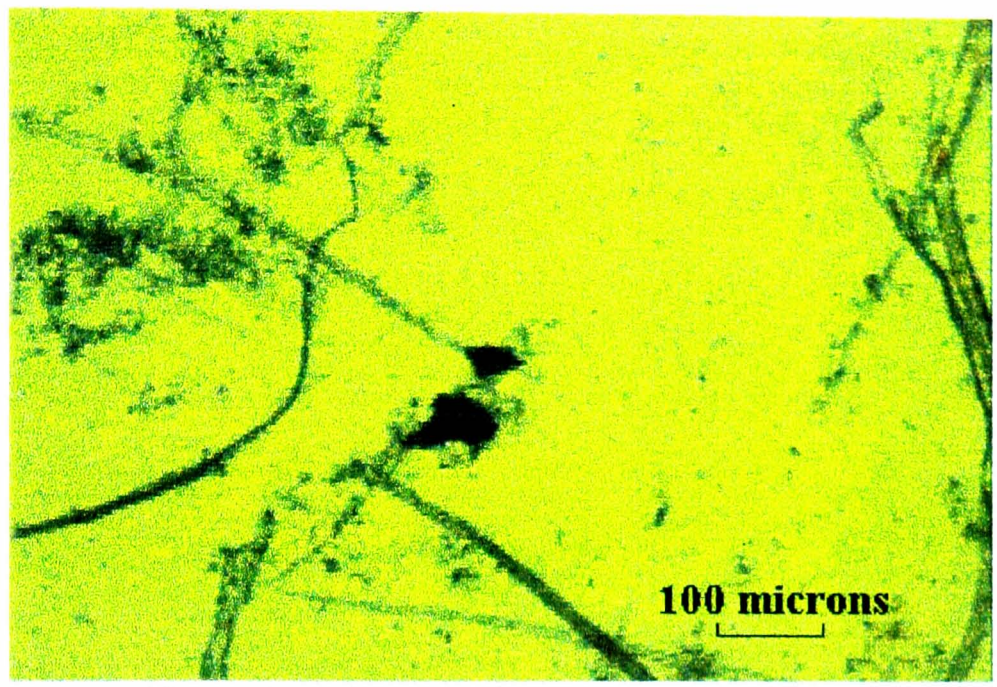


Figure 8.3.14 **Photomicrograph of Toner Particle after 10 minutes Sonication (TR2)**

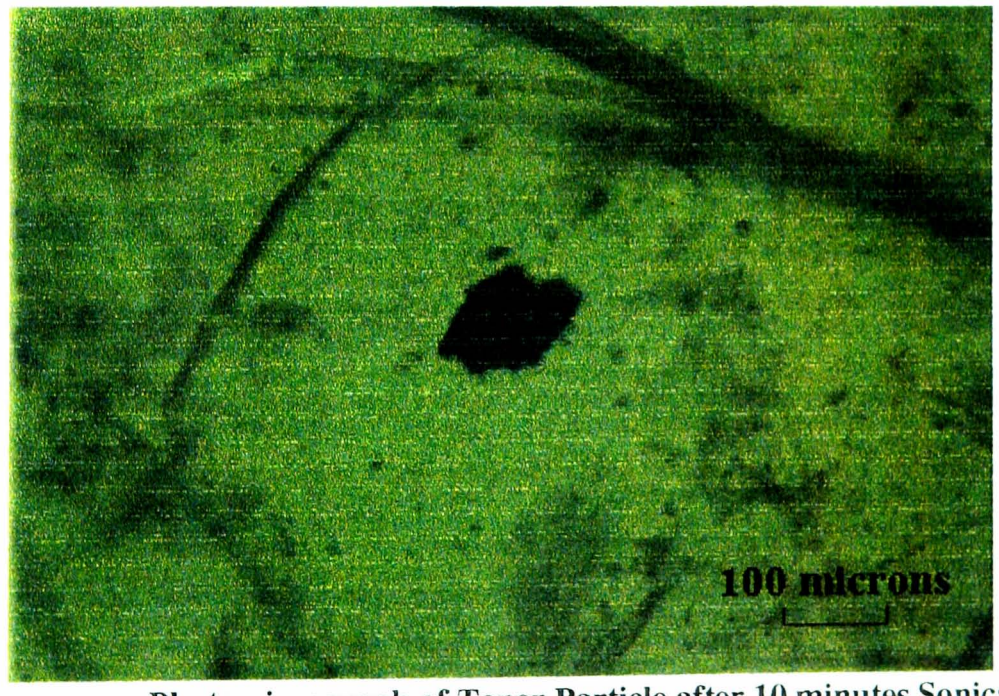


Figure 8.3.14 **Photomicrograph of Toner Particle after 10 minutes Sonication (TR2)**

Figures 8.3.14 and 8.3.15 are from the same batch of pulp that had been subjected to the disintegration process and 10 minutes sonication, these images were taken using reflected polarised light.

In figure 8.3.14 the particles appear to be still attached to the fibres, or at least to the fibrils surrounding the fibre, however in figure 8.3.15 the particle is detached. As a result of the treatment particles have been reduced in size to around a diameter of 100 microns or less.

8.3.1 Discussion of Results for Temperature Range 2

Shown in Table 8.3.11 are the average particle sizes detected on the handsheets for the unwashed samples of temperature range 2.

	0 minute	1 minute	2 minutes	5 minutes	10 minutes
Batch 1	152.3 ± 247	89.6 ± 177	70.0 ± 130	47.7 ± 80	35.9 ± 43
Batch 2	158.2 ± 284	102.3 ± 190	67.1± 121	46.6 ± 72	35.6 ± 44
Batch 3	159.4 ± 267	103.8 ± 191	70.2 ± 122	43.9 ± 70	44.9 ± 62

Table 8.3.11 Average Particle Diameter before Hyperwashing (μm)

As with previous treatments the average particle size decreased as the sonication time increased. The average particle size had been decreased by half after 2 minutes ultrasound and after 10 minutes sonication the average particle size had again decreased by a half - from 156 microns in the control sample to 69 microns and was halved again to 39 microns after 10 minutes sonication.

	0 minute	1 minute	2 minutes	5 minutes	10 minutes
Batch 1	171.7± 285	121.6 ± 190	75.3 ± 121	51.4 ± 72	41.7 ± 44
Batch 2	169.5± 276	120.3 ± 200	92.3 ± 170	49.9 ± 66	40.1 ± 45
Batch 3	165.7 ± 253	113.4 ± 193	77.9 ± 128	53.2 ± 97	39.0 ±52

Table 8.3.12 Average Particle Diameter after Hyperwashing (μm)

The numbers of particles detected on the handsheets after hyperwashing was found to be lower when compared to the unwashed samples. When the categories that contain particles removable by hyperwashing, that is less than 250 microns in diameter are compared, it can be seen that sonication produced more particles that were removable by hyperwashing, see figure 8.3.16.

Inspection of data in 250 microns category showed the numbers of particles present decreased as sonication increased. This was as a result of particles being broken down by

ultrasound action whilst still attached to fibres. As work of adhesion between toner particles and fibres is greater at lower temperatures more toner would be expected to remain adhered to the fibres.

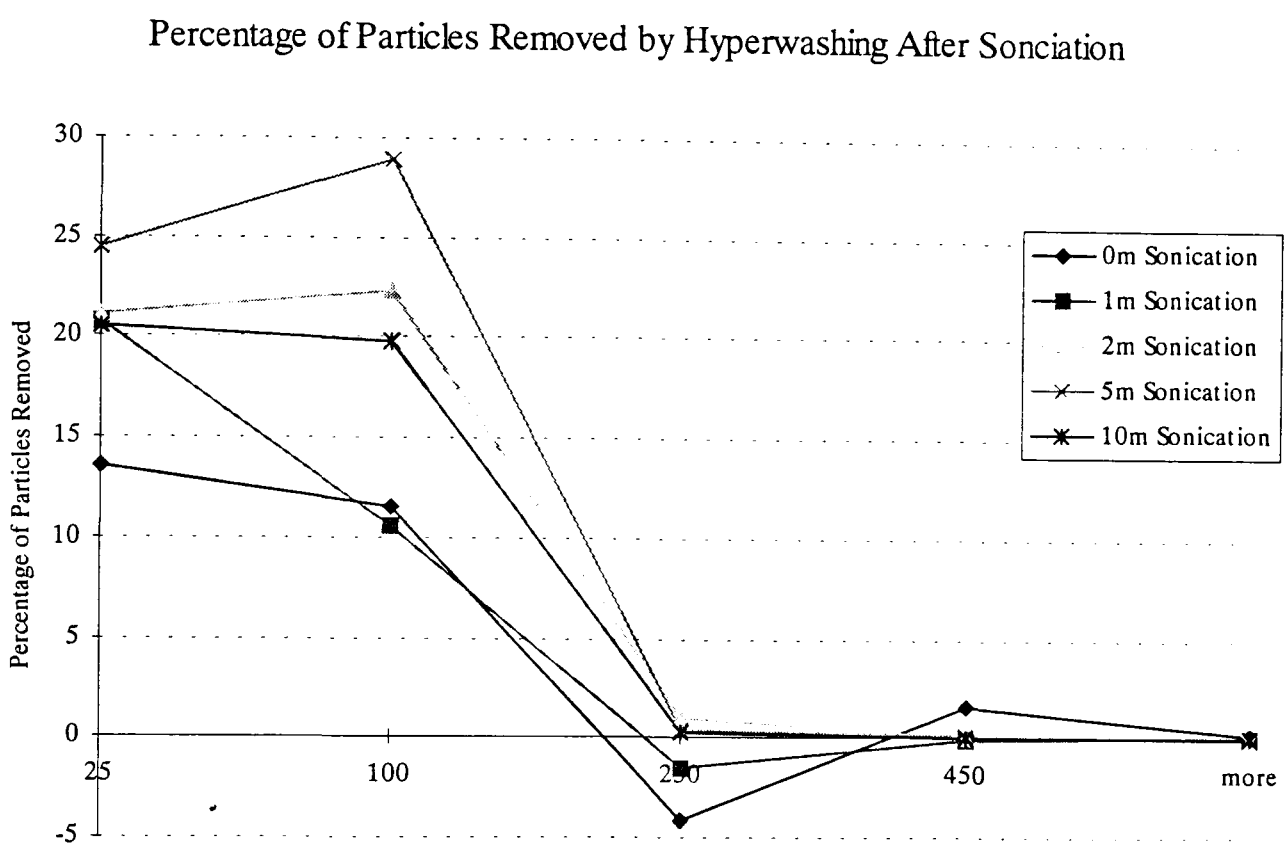


Table 8.3.15 Percentage of Particles Removed after Hyperwashing

The temperatures in range 1 experiments rose to approximately 45°C after 10 minutes sonication, while with range 2 it rose to only 25°C for the same period of sonication. At the temperatures used in temperature range 2 the toner was well below its glass transition temperature and was rigid and brittle. The rigid fixed toner was broken into small shards as the fibres flexed under ultrasound action. This shattering action left much of the toner still attached to the fibres, but created a large number of smaller sized particles. This was confirmed by the laser scattering data. The 1 minute treatment produced more small particles in the range less than 5 microns, than other sonication treatments.

Ultrasound shattered the toners, especially at low exposure times where sonication was applied prior to any heating taking place. Sonication for 1 minute lead to an increased number of detached particles (figure 8.3.16) in the 100 micron category, but not an increase in the percentage detached in the 250 micron category. Prolonged sonication increased the percentage of 100 micron toner removed from the pulp. Temperature control was difficult

to achieve during the longer sonication times, the smaller toner particles produced in the first period of sonication when the pulp is cool, were not so prevalent after longer sonication times. Larger, 100 micron particles were produced as the temperature rose mirroring the results found in the temperature range 1 experiments.

The 25 micron particles were produced by stresses induced by ultrasound in the largest particles. These stresses resulted in a large number of very small particles being produced. For the first minute of sonication this was the predominant action.

After longer sonication times (greater than 2 minutes) the larger particles were broken up as the ultrasound exploited the 'perforations' in the large toner particles. Figure 8.3.16 shows the percentage of 100 micron particles removed by hyperwashing for temperature ranges 1 and 2.

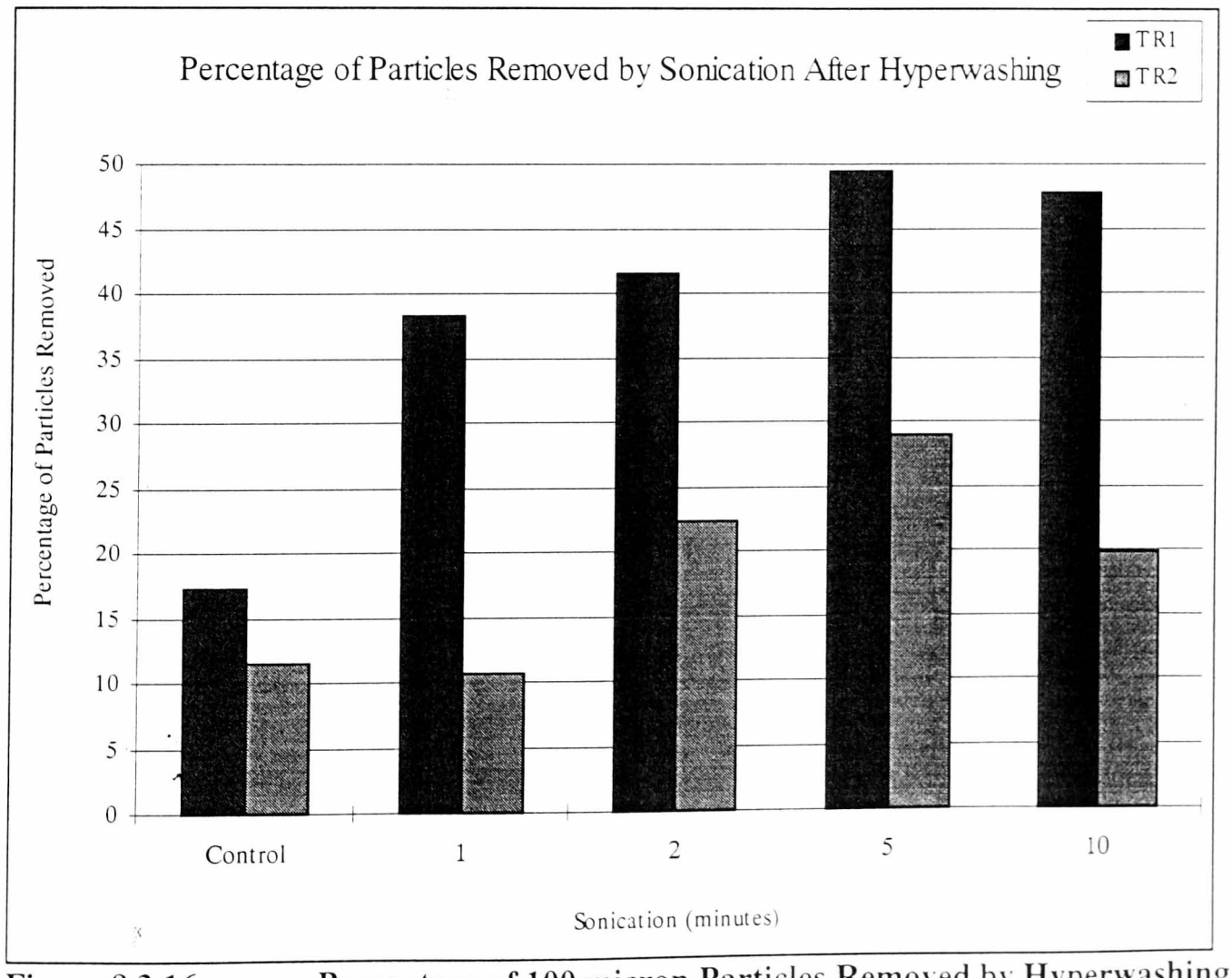


Figure 8.3.16 **Percentage of 100 micron Particles Removed by Hyperwashing after Sonication**

The percentage of particles removed is greater for temperature range 1. This could be a result of the higher work of cohesion between toner particles, and the higher work of

adhesion between toner and paper fibres at lower temperatures. At higher temperatures the work both of cohesion and adhesion are lowered and particles would be easier both to break-up and to detach.

Concluding from the results of temperature range 2:

- Confirmed that ultrasound broke up toner particles and then detached them, once the particles are reduced in size close to their native size.
- Disintegration at low temperatures lead to distributions containing large particles.
- Particles produced under low temperature conditions were difficult to detach from the fibres because of the higher work of adhesion between the particle and the paper fibres.
- Sonication was less effective at removing toner particles at lower temperatures. In temperature range 2 the 100 micron category, disintegration removed 12% of particles, this increased to 26% after 5 minutes sonication. The removal rates for temperature range 1 are 17% for disintegration and 50% for 5 minutes sonication.

Temperature range 2 was not successful in confirming that cavitation effects were more efficient at lower temperatures. The higher work of adhesion between toners and fibres resulted in more toner remaining attached to the fibres.

In order to investigate a system where the works of cohesion and adhesion were lowered it was decided to study a higher temperature system, closer to the glass transition temperature of the toners. In this system it was hoped that, though cavitation effects would be reduced the higher temperature would permit greater toner removal due to the lower work of adhesion. These experiments are detailed in section 8.4.0.

8.4.0 Temperature Range 3

Samples of mixed office waste were prepared using the technique described in section 8.2.0. Temperature range 3 experiments were conducted by soaking 150g fibre in water at 50°C for 3 hours. The resulting pulp was disintegrated and sonicated as previously outlined. The temperatures at the start and finish of the sonication were noted and are shown in table 8.4.1.

	batch 1		batch 2		batch 3	
	initial	final	initial	final	initial	final
1 minute	46	50	40	44	40	45
2 minute	46	52.5	45.5	54	41	50
5 minute	46	56	43.5	57	41	56
10 minute	50	68.5	43	60	43	63

Table 8.4.1 Temperature Data for Range 3 (ºC)

After ultrasonic treatment each sample was divided equally to study the effects of hyperwashing on the samples. Handsheets were made from the pulp and examined using the IMP program. Four handsheets were formed for each of the treatments, representing 0, 1, 2, 5 and 10 minutes sonication, for unwashed and hyperwashed samples giving a total of 40 handsheets per batch. The experiment was repeated 3 times. The data presented in tables 8.4.2 to 8.4.7 are the numerical values calculated from the areas of the particles.

	Time of Sonication				
	0m	**1m**	**2m**	**5m**	**10m**
Mean (μm)	202.3	88.2	60.3	42.2	39.4
Standard Error	65.3	29.8	18.9	9.6	12.3
Median	80.6	39.4	35.5	30.7	18.6
Mode	9.4	8.4	8.4	8.4	8.7
Standard Deviation	280.9	157.1	104.1	53.8	48.6
Minimum (μm)	8.4	8.4	8.4	8.4	8.4
Maximum (μm)	727.8	562.4	412.4	217.3	187.2
Count	343	778	913	987	610
Confidence Level (95.0%)	91.5	41.7	26.5	13.5	21.2

Table 8.4.2 Batch 1 Statistics Unwashed

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	188.6	119.2	74.0	51.7	49.8
Standard Error	58.0	41.0	26.6	15.8	15.2
Median	82.0	60.9	49.2	39.7	44.0
Mode	8.4	8.4	8.4	9.4	8.4
Standard Deviation	258.0	187.0	118.9	64.8	48.8
Minimum (μm)	8.4	8.4	8.4	8.4	8.4
Maximum (μm)	651.0	566.2	443.8	221.0	121.5
Count	392	434	400	281	107
Confidence Level (95.0%)	81.3	57.4	37.3	22.2	21.4

Table 8.4.3 Batch 1 Statistics After Hyperwashing

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	211.8	113.7	71.8	50.5	41.3
Standard Error	63.4	38.2	23.0	10.2	8.0
Median	84.7	52.8	46.7	40.8	34.0
Mode	8.4	8.4	9.4	8.4	11.9
Standard Deviation	279.7	188.9	120.1	55.6	42.0
Minimum (μm)	8.4	8.4	8.4	8.4	8.4
Maximum (μm)	776.5	611.6	482.1	184.8	129.6
Count	380	600	749	900	744
Confidence Level (95.0%)	88.8	53.5	32.2	14.2	11.3

Table 8.4.4 Batch 2 Statistics Unwashed

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	215.4	131.7	96.5	62.1	41.9
Standard Error	70.1	48.0	31.8	29.7	13.8
Median	111.1	60.1	53.6	42.7	29.5
Mode	8.4	8.4	10.3	9.4	8.4
Standard Deviation	294.3	215.2	156.6	116.7	48.4
Minimum (μm)	8.4	8.4	8.4	8.4	8.4
Maximum (μm)	908.6	757.8	562.1	449.5	124.4
Count	311	405	588	240	150
Confidence Level (95.0%)	98.3	67.3	44.6	41.6	19.5

Table 8.4.5 Batch 2 Statistics After Hyperwashing

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	234.5	87.5	58.2	47.2	38.4
Standard Error	75.3	25.4	17.7	9.1	8.4
Median	80.3	46.1	35.3	35.8	30.9
Mode	8.4	8.5	8.5	8.5	11.2
Standard Deviation	338.4	134.3	102.1	52.8	41.2
Minimum (μm)	8.4	8.5	8.5	8.5	8.4
Maximum (μm)	1008.7	432.4	555.6	172.8	133.7
Count	409	784	1121	1130	582
Confidence Level (95.0%)	105.5	35.6	24.7	12.8	11.8

Table 8.4.6 Batch 3 Statistics Unwashed

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	209.5	137.6	127.6	71.0	49.8
Standard Error	64.9	48.1	48.2	32.0	26.4
Median	104.2	54.9	39.1	34.7	29.5
Mode	8.4	8.4	8.4	9.4	8.4
Standard Deviation	280.4	216.9	216.0	127.8	85.4
Minimum (μm)	8.4	8.4	8.4	8.4	8.4
Maximum (μm)	764.4	583.0	625.2	445.3	269.3
Count	348	412	403	253	109
Confidence Level (95.0%)	91.0	67.5	67.6	45.0	37.2

Table 8.4.7 Batch 3 Statistics After Hyperwashing

The trend in this data was recorded in previous experiments, the largest particles found in the control sample were not present in the samples which had been sonicated for more than 2 minutes. The largest particles detected on the handsheets are detailed in the maximum category. The largest particles detected in the unwashed control sample had an average diameter of 837 microns, compared to 535 microns after 1 minute and 150 microns after 10 minutes sonication.

The results of the image analysis of the handsheets is presented graphically in figures 8.4.1 to 8.4.5.

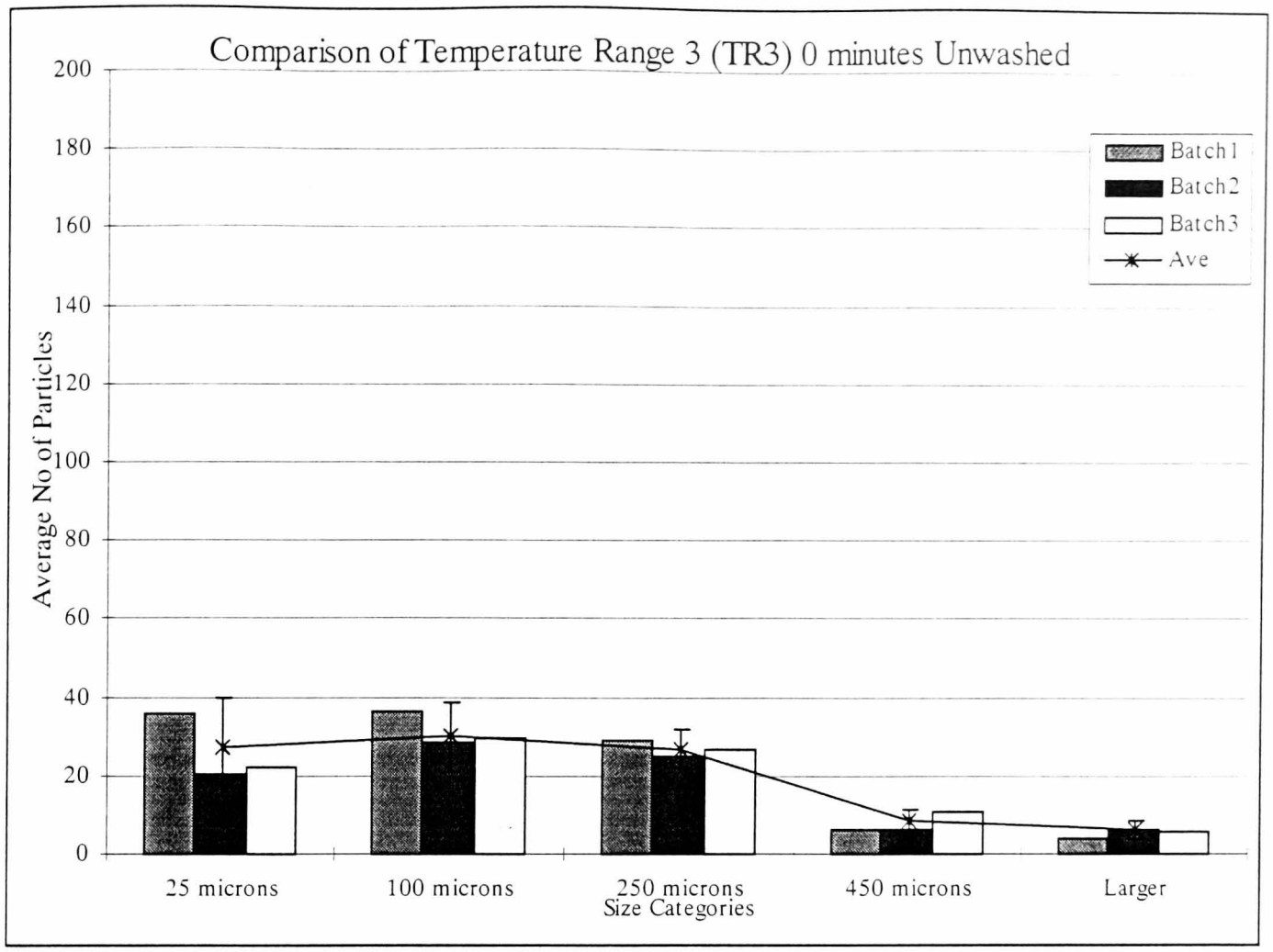


Figure 8.4.1 Toner Particle Count for Range 3 Unwashed 0 minute Sonication

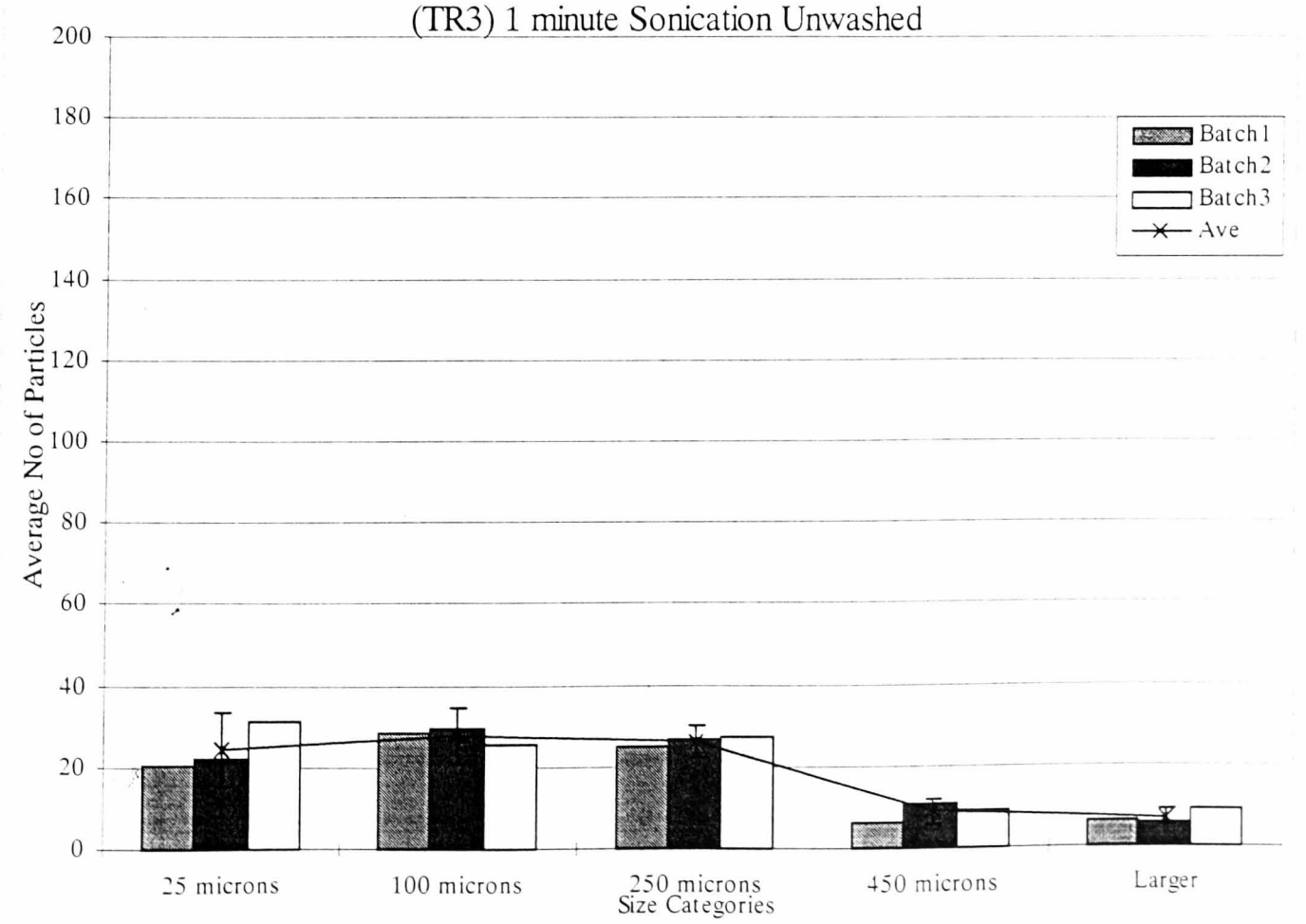


Figure 8.4.2 Toner Particle Count for Range 3 Unwashed 1 minute Sonication

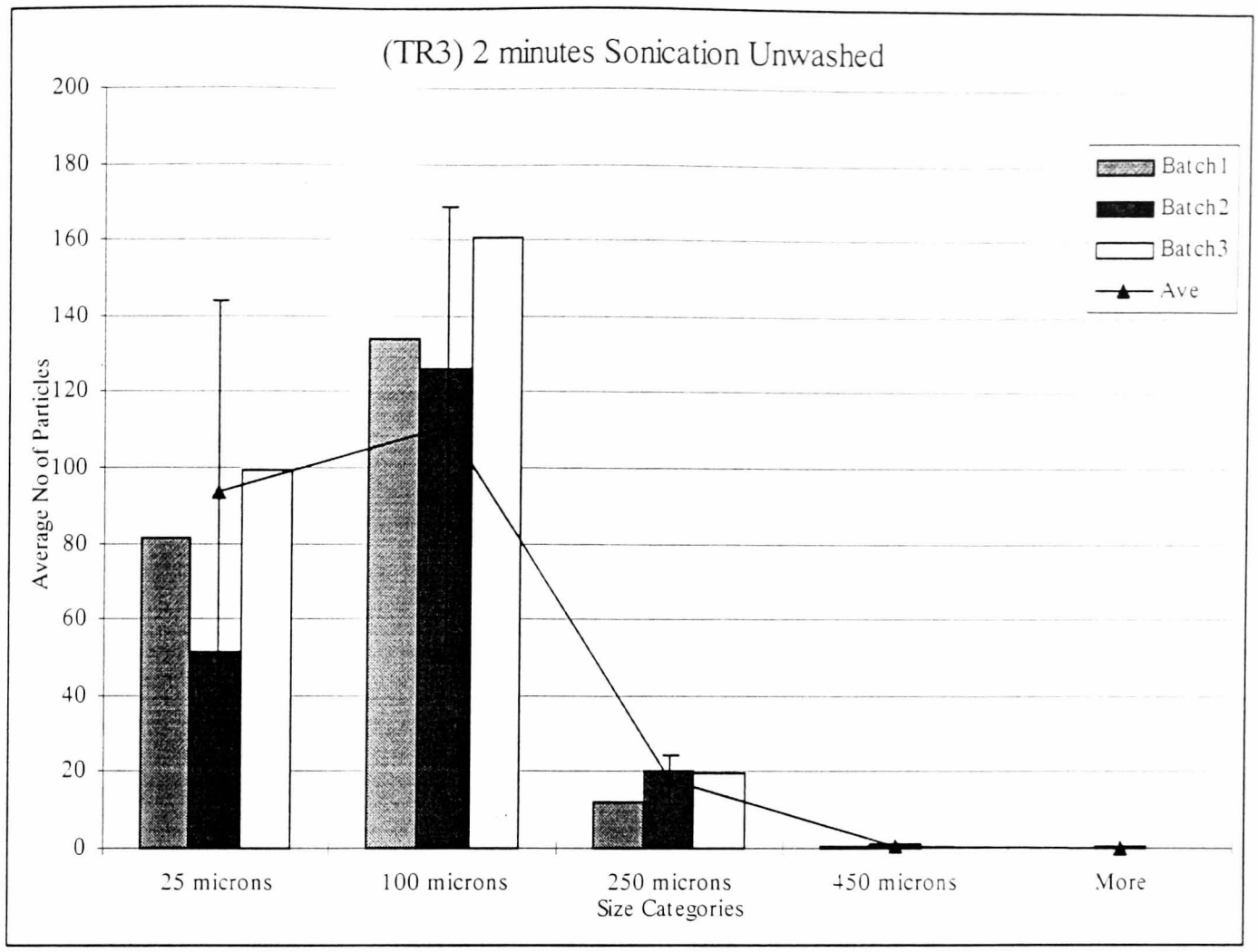


Figure 8.4.3 Toner Particle Count for Range 3 Unwashed 2 minutes Sonication

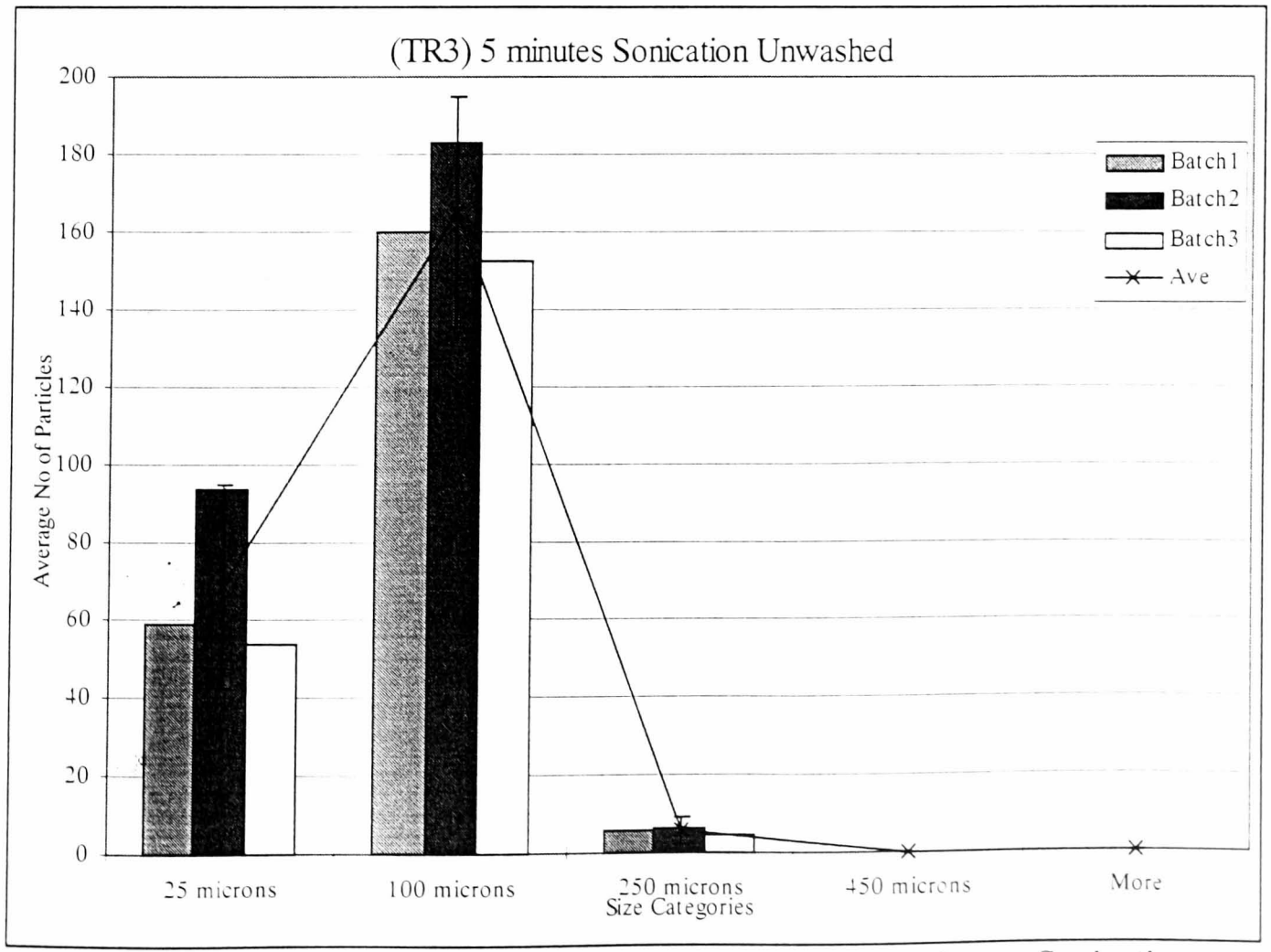


Figure 8.4.4 Toner Particle Count for Range 3 Unwashed 5 minutes Sonication

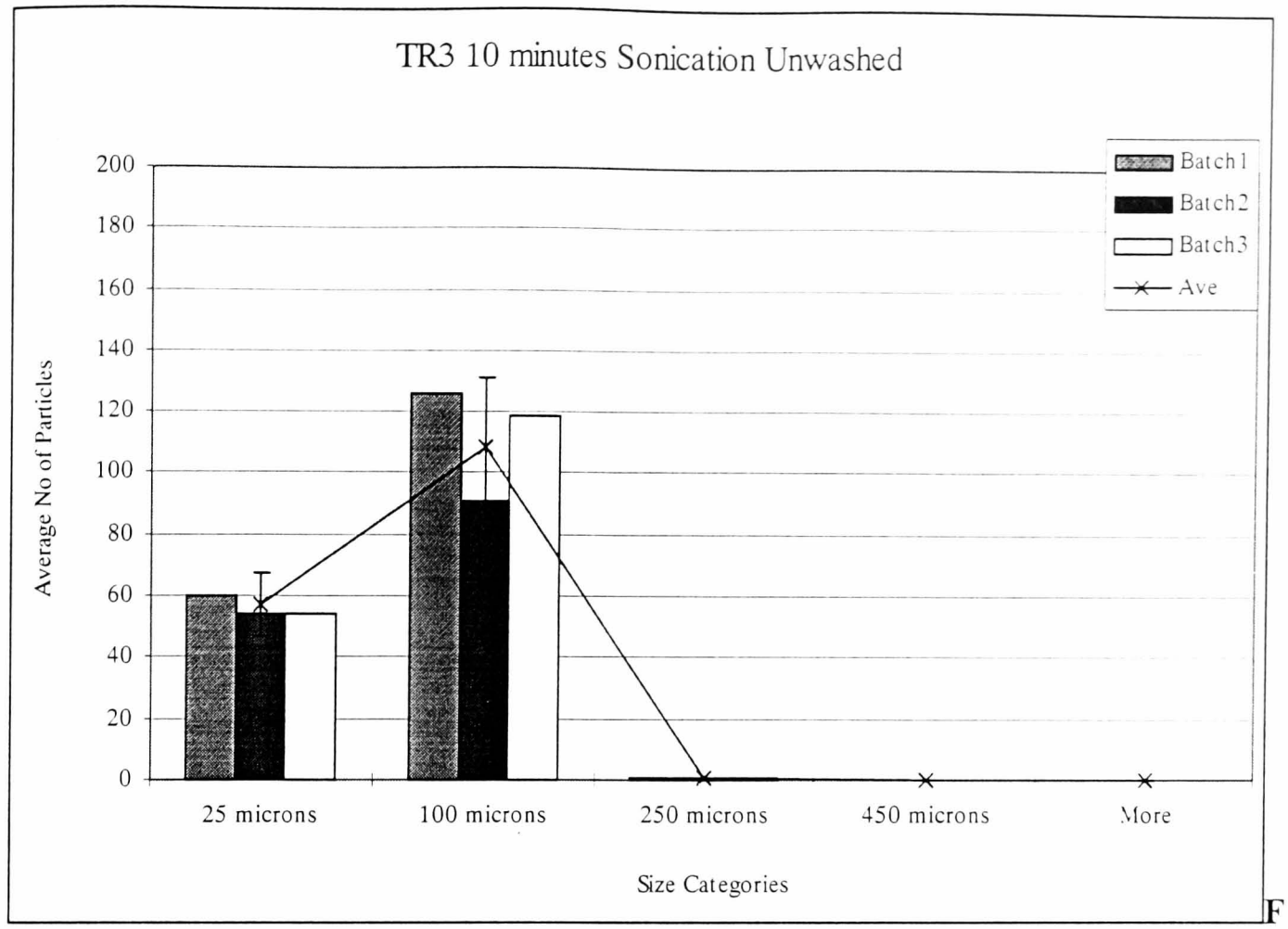


Figure 8.4.5 Toner Particle Count for Range 3 Unwashed 10 minutes Sonication

Again the control sample produced a broad distribution with particles present in all categories. As sonication time increased, the numbers of particles in the smaller size categories increased. The number of toner particles equal to or less than 100 microns in diameter found in the control sample was 55%, after 10 minutes sonication the percentage was of the order of 100% (99.6%).

The figures 8.4.6 to 8.4.10 give the numbers of particles counted on the handsheets after hyperwashing the pulps.

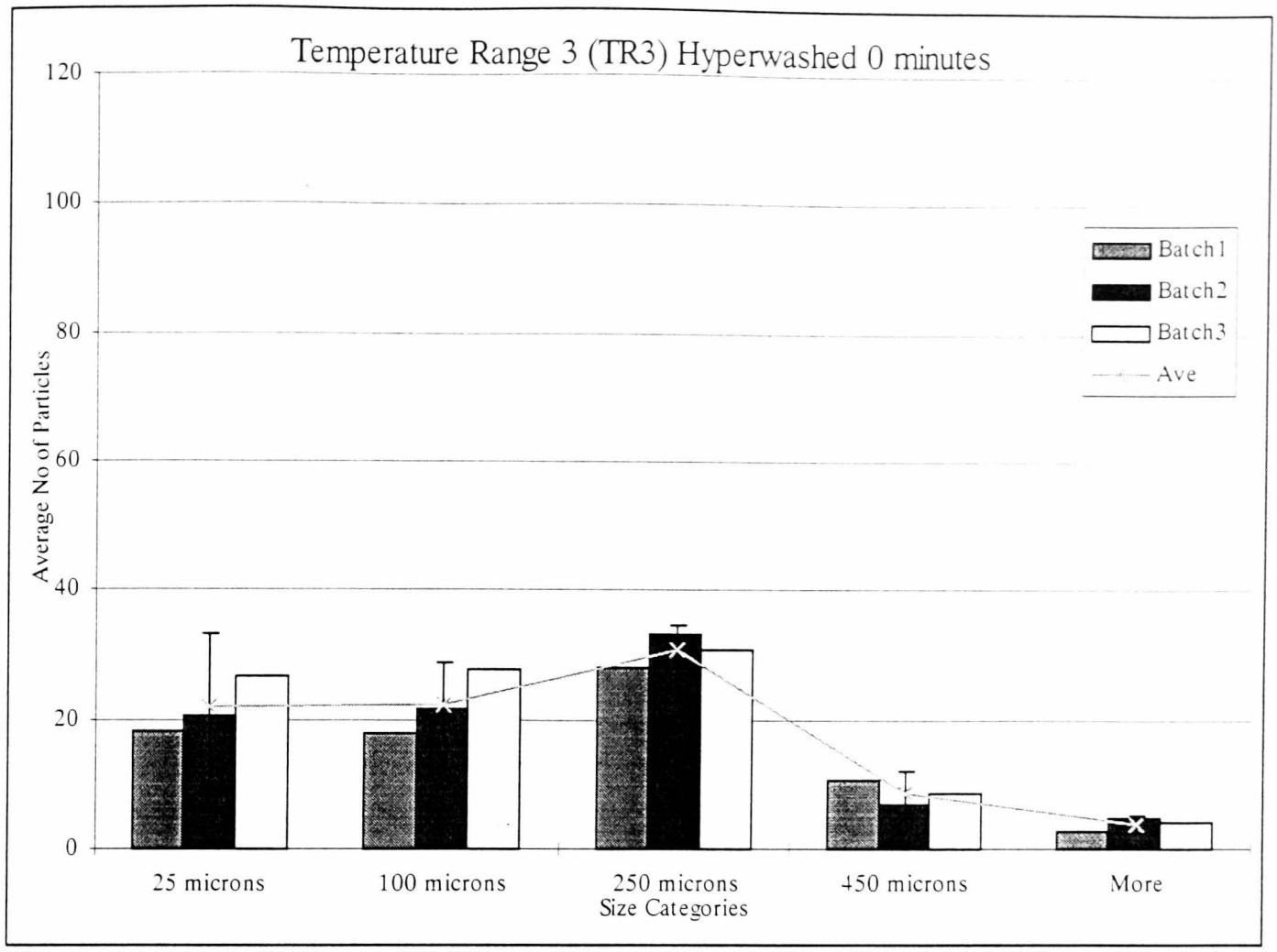


Figure 8.4.6 **Toner Particle Count for Range 3 Hyperwashed 0 minute Sonication**

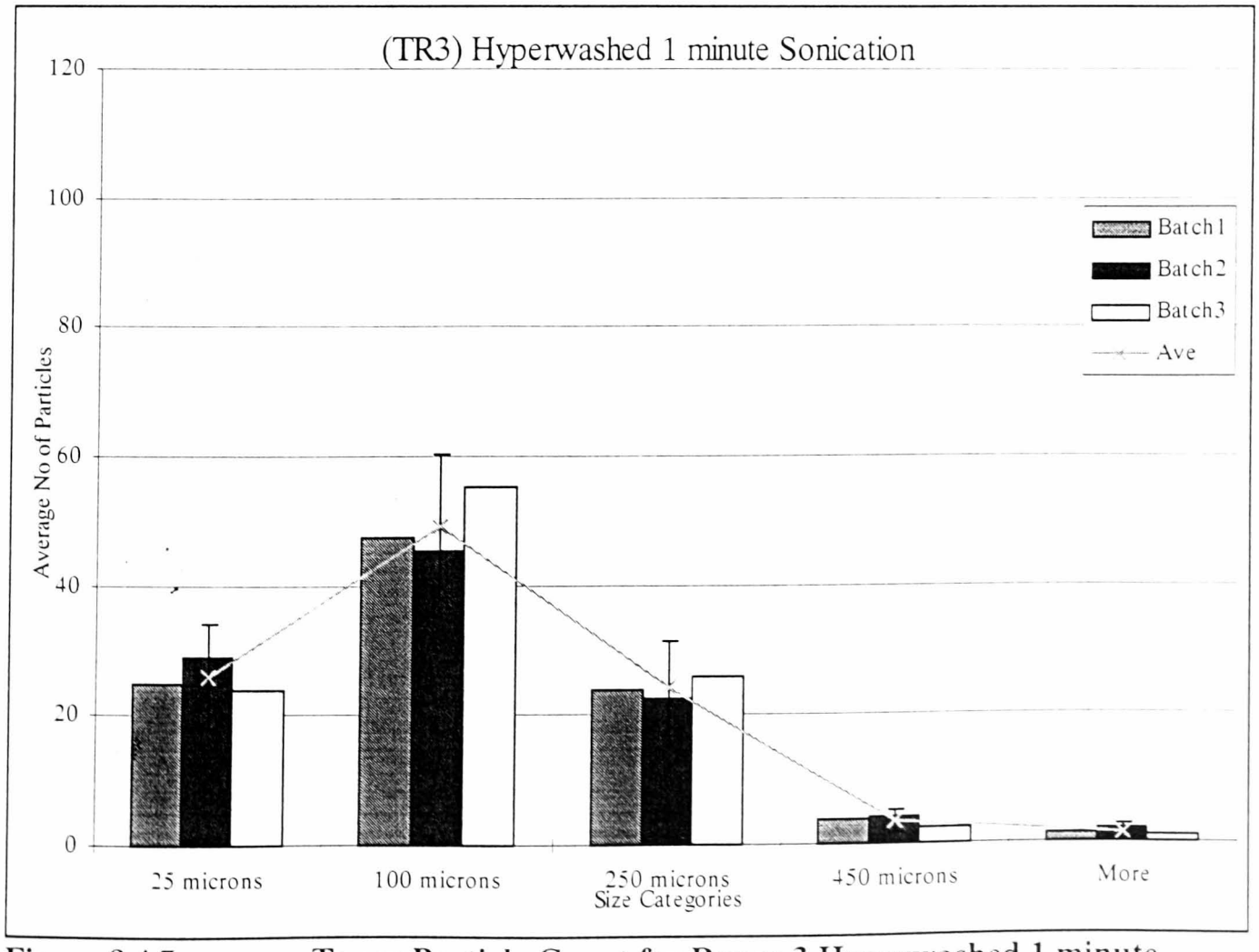


Figure 8.4.7 **Toner Particle Count for Range 3 Hyperwashed 1 minute Sonication**

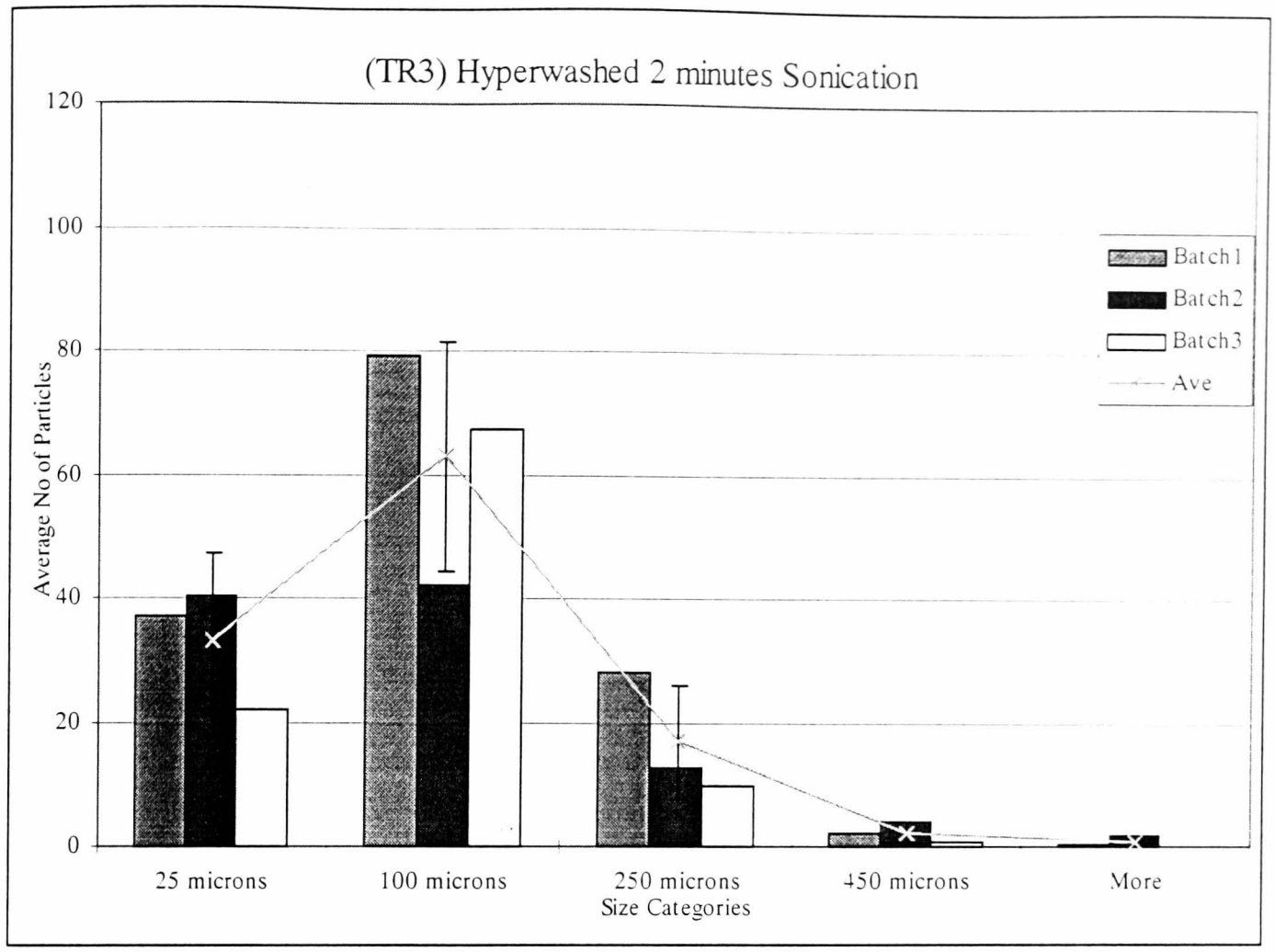


Figure 8.4.8 **Toner Particle Count for Range 3 Hyperwashed 2 minute Sonication**

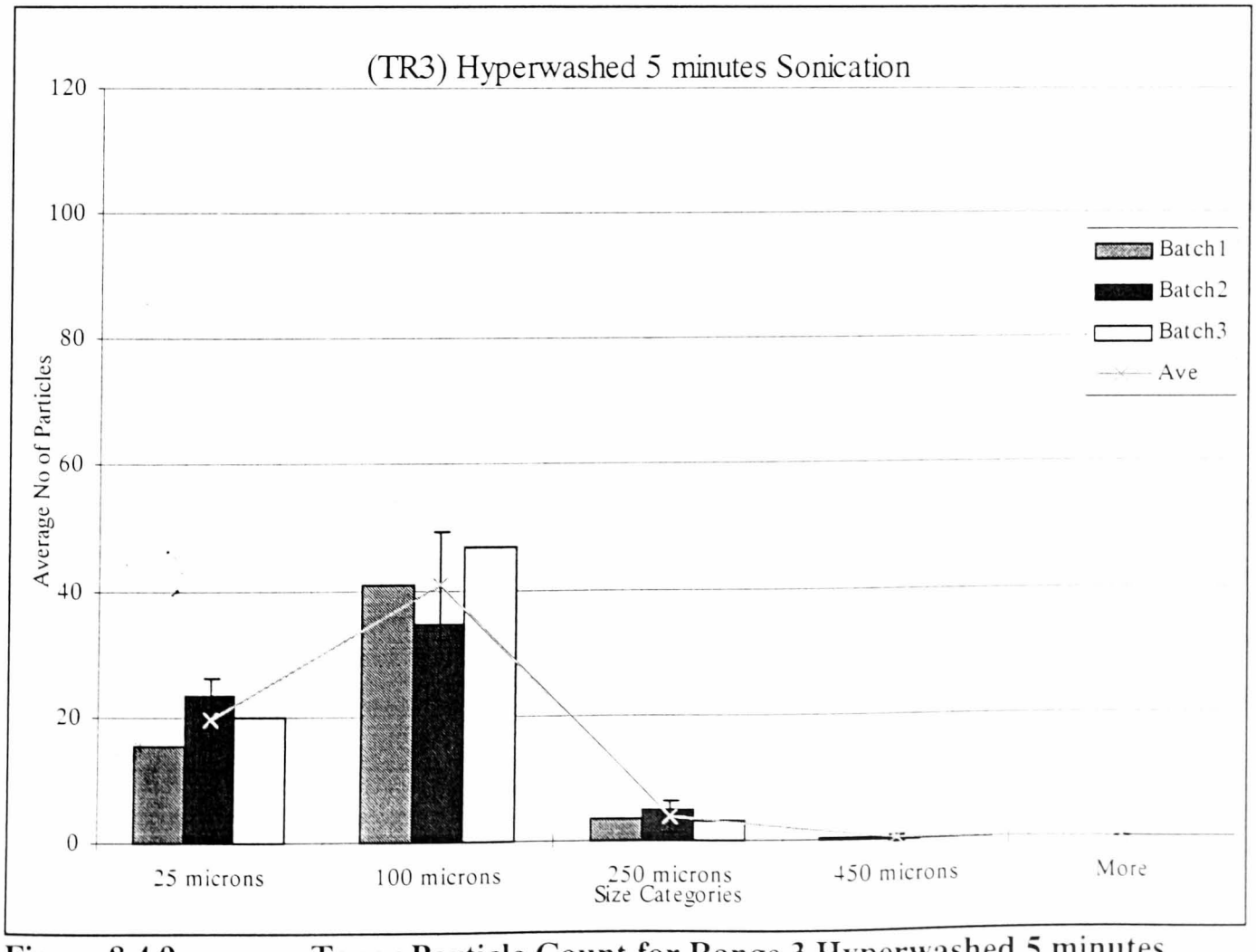


Figure 8.4.9 **Toner Particle Count for Range 3 Hyperwashed 5 minutes Sonication**

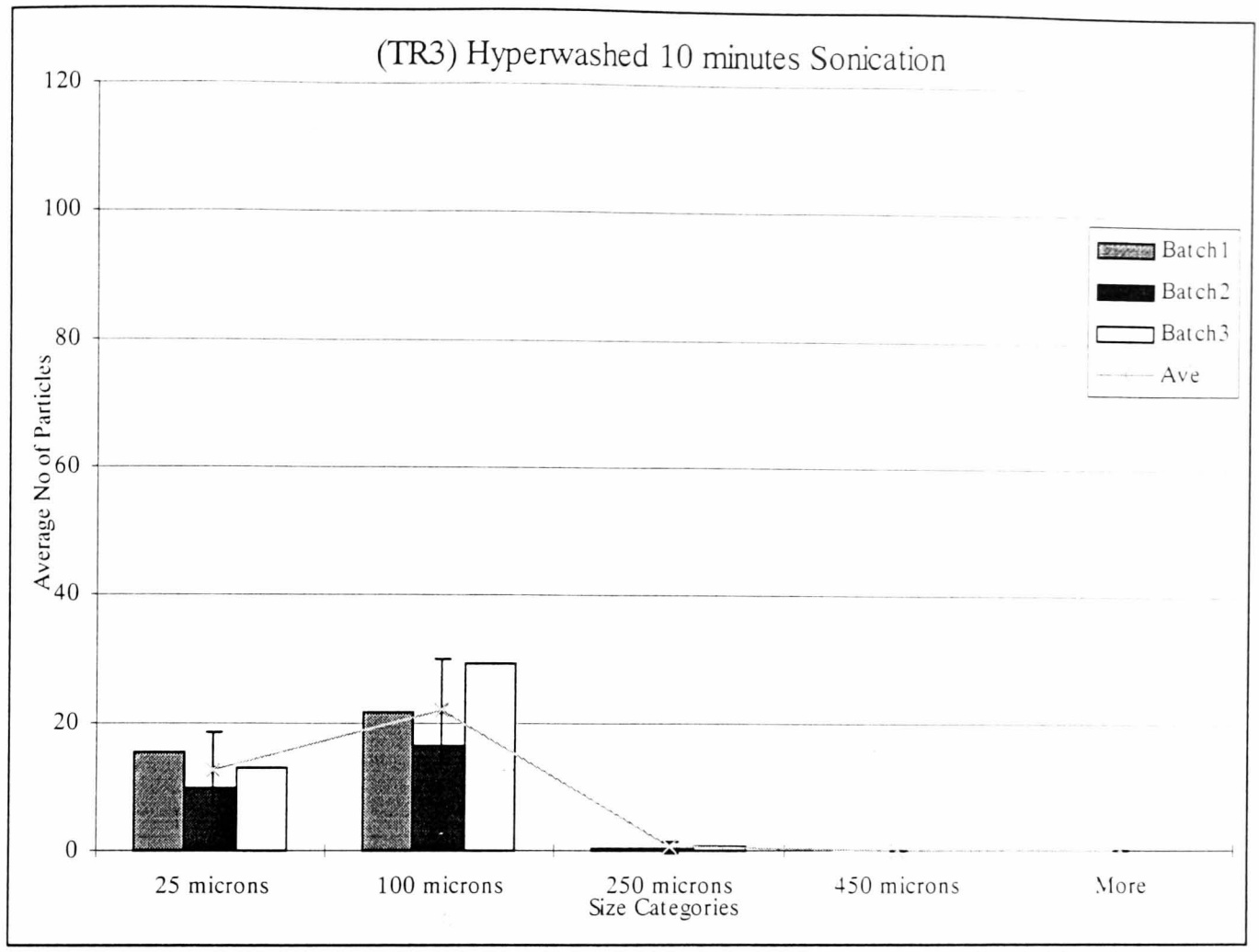


Figure 8.4.10 **Toner Particle Count for Range 3 Hyperwashed 10 minutes Sonication**

The amount of toner removed by hyperwashing the control sample was 7%. After 2 minutes sonication 50% of the particles were removed, increasing to 74% after 5 minutes sonication and 77% after 10 minutes sonication. The percentage of particles present in the hyperwashed samples in the 25 and 100 micron categories increased from 30% in the control sample to 54% after 1 minute sonication, rising further to 60% after 2 minutes treatment and 67% after 10 minutes sonication.

The sonicated pulp samples were examined using the Canadian Standard freeness (CSF) tester (section 5.7.0) to assess any change in fibre damage. The CSF results were corrected using the table supplied. The corrected results are shown below in table 8.4.8. The freeness readings decreased with increasing exposure to ultrasound indicating a progressive increase in fibrillation

	Batch 1				Batch 2				Batch 3				Average	Sd
0 minute	425	449	431	456	467	443	458	449	440	428	428	450	443.67	12.9
1 minute	427	416	434	418	422	450	461	437	427	433	440	440	433.75	12.5
2 minutes	408	421	425	-	389	422	432	437	417	432	412	422	419.73	12.8
5 minutes	390	383	397	377	418	395	395	416	411	419	429	427	404.75	16.7
10 minute	375	393	377	362	414	386	411	396	413	395	409	415	395.5	16.1

Table 8.4.8 **CSF values for Temperature Range 3 (ml)**

The filtrates from the CSF were examined in the Coulter LS 130. The standard operating procedure was followed for all measurements made on the LS130. The results are given in figures 8.4.11 to 8.4.13 and are discussed in section 8.4.1.

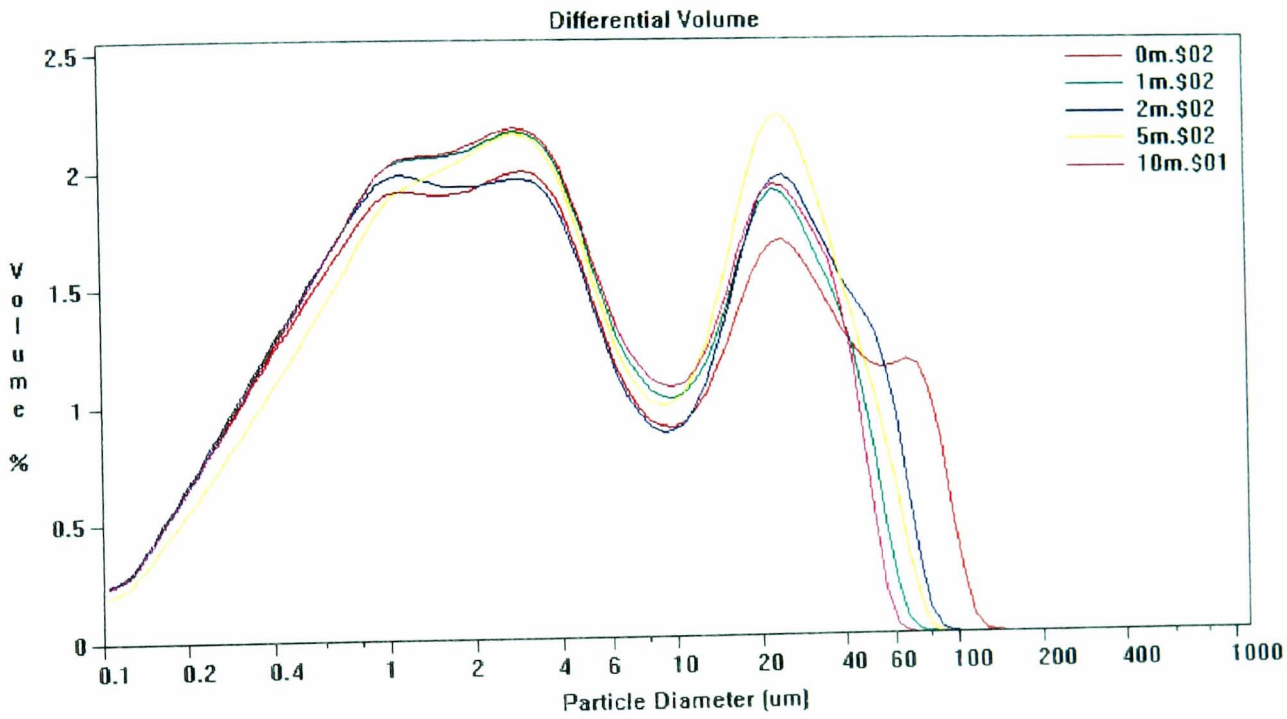


Figure 8.4.11 **TR3 Filtrate Particle Size Distribution measured by Laser Scatter, Batch 1**

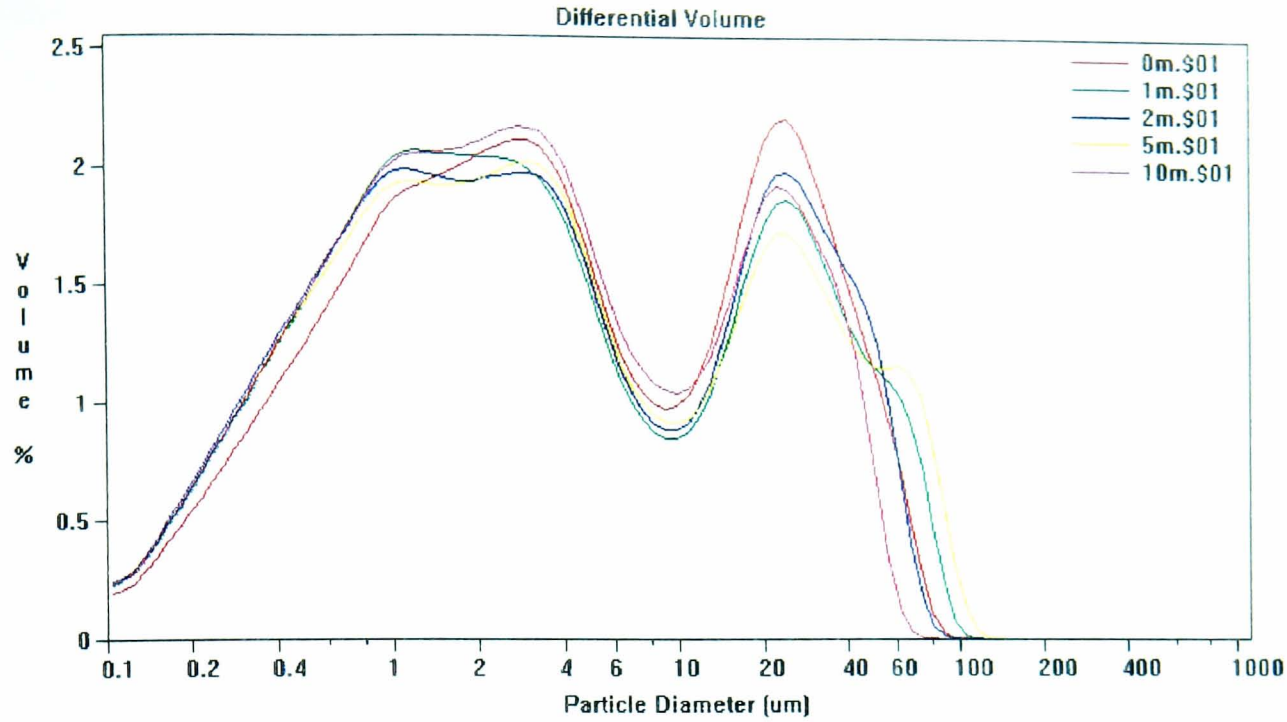


Figure 8.4.12 **TR3 Filtrate Particle Size Distribution measured by Laser Scatter, Batch 2**

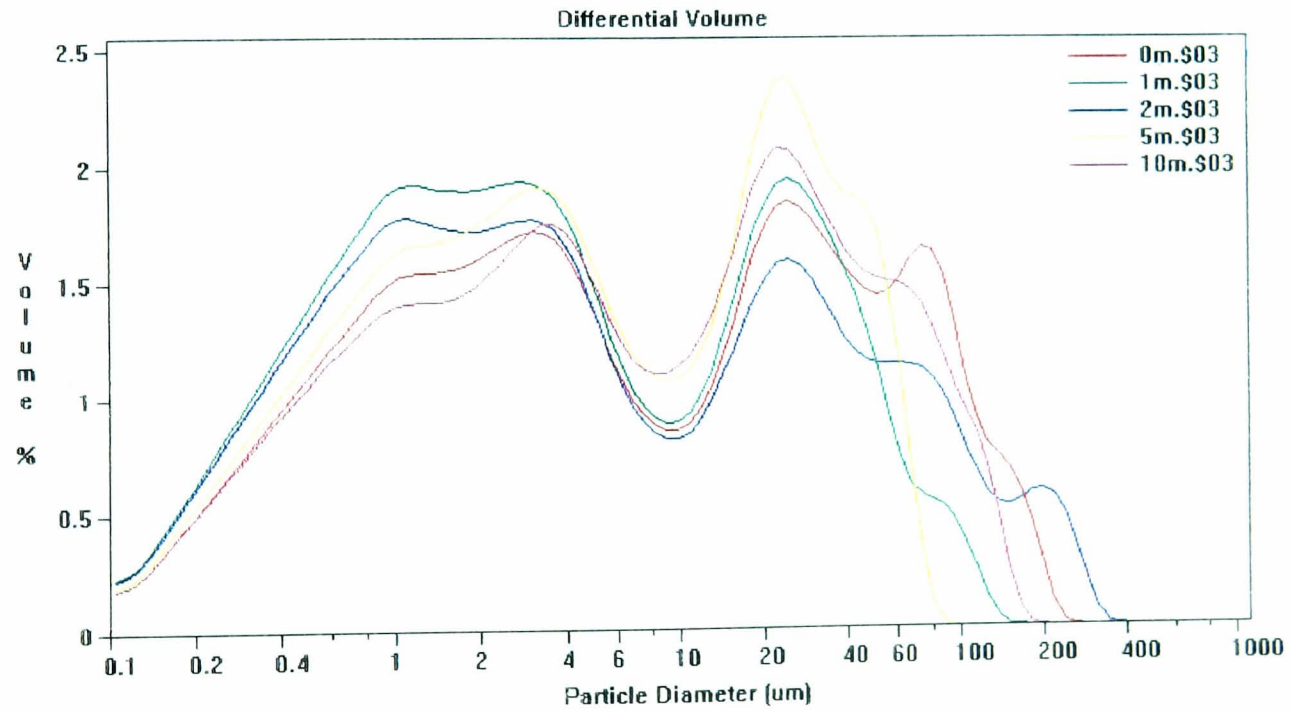


Figure 8.4.13 **TR3 Filtrate Particle Size Distribution measured by Laser Scatter, Batch 3**

8.4.1 Discussion of Results for Temperature Range 3

These experiments were conducted at or around 50°C. The average particle diameters measured on the handsheet produced are shown in figure 8.4.13 for the unwashed pulp samples.

	0 minutes	1 minute	2 minutes	5 minutes	10 minutes
Batch 1	202.3 ± 281	88.2 ± 157	60.3 ± 104	42.2 ± 54	39.4 ±49
Batch 2	211.8 ± 280	113.6 ± 189	71.8 ± 120	50.5 ± 56	41.3 ± 42
Batch 3	234.5 ± 338	87.5 ± 134	58.2 ± 102	47.2 ± 53	38.4 ± 41

Table 8.4.9 Average Particle Diameter before Hyperwashing (μm)

The average particle diameter again decreased with sonication. The average of all unwashed data shows that the mean particle diameter decreased from 217 microns in the control sample to 95 microns after 1 minute of sonication. After 10 minutes sonication the average particle diameter was reduced to 43 microns. Average particle diameters found on handsheets formed from hyperwashed pulps are given in figure 8.4.2.

	0 minutes	1 minute	2 minutes	5 minutes	10 minutes
Batch 1	188.6 ± 258	119.2 ± 187	74.0 ± 119	51.7 ± 65	49.8 ± 49
Batch 2	215.4 ± 294	131.7 ± 215	96.5 ± 157	62.1 ± 117	41.9 ± 48
Batch 3	209.5 ± 280	137.6 ± 217	127.6 ± 216	71.0 ± 128	49.8 ± 85

Table 8.4.10 Average Particle Diameter after Hyperwashing (μm)

The percentage of particles removed in the temperature range 3 experiments are shown in figure 8.4.14. Extended ultrasound treatment increased the number of particles removed at a rate which decreased exponentially with time.

As previously noted the majority of particles are only detached when they have been reduced to a size below 100 microns in diameter. The efficiency of removal of the particles was greater at the elevated temperatures employed in temperature range 3. Temperature range 3 was less efficient than both temperature ranges 1 and 2 at detaching particles after simple disintegration, with only 8% of particles removed in the 100 micron category, sonication was more efficient, after 1 minute 23% of particles were removed in this category, and after 5 minutes 52% were removed.

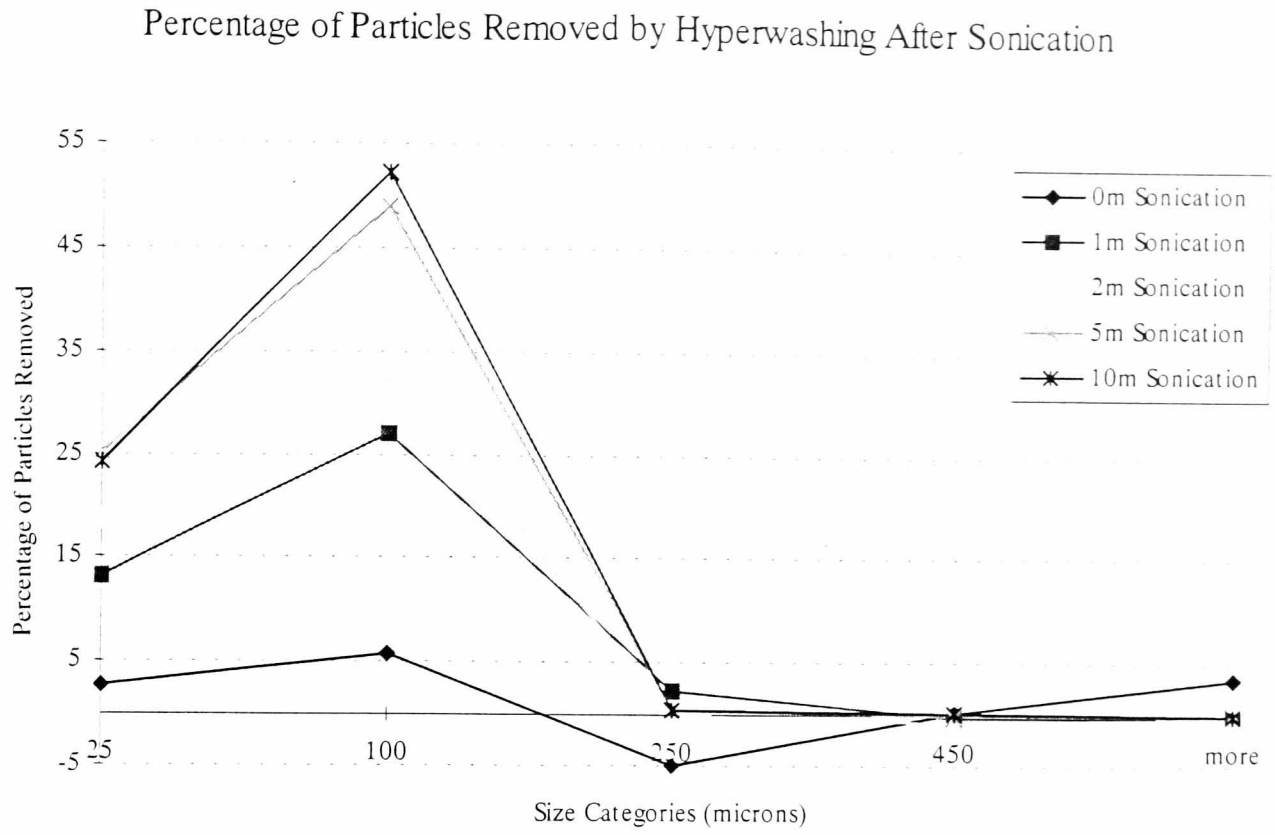


Figure 8.4.14 Percentage of Particles Removed after Hyperwashing

At higher temperatures the work of adhesion between toners and paper and the work of cohesion between toners is lowered. The lower work of cohesion between toner particles makes these toner particles easier to break down at higher temperatures. The lower cohesion between toners can be seen by comparing the rate of break down of particles in temperature range 2 and 3.

Examination of the filtrates (see figures 8.4.11, 8.4.12 and 8.4.13), for these samples pulped at higher temperature showed that the particles most commonly detected had diameters of around 25 and 90 microns. This confirmed that the fused toner was being broken into particles similar in size to their native size prior to being detached from the fibres.

The percentage of removed particles was greater for temperature range 3 samples than was found in the previous experiments. Figure 8.4.15 shows the relative efficiency of removal by hyperwashing of the particles in the 100 micron category for temperature ranges 1, 2 and 3.

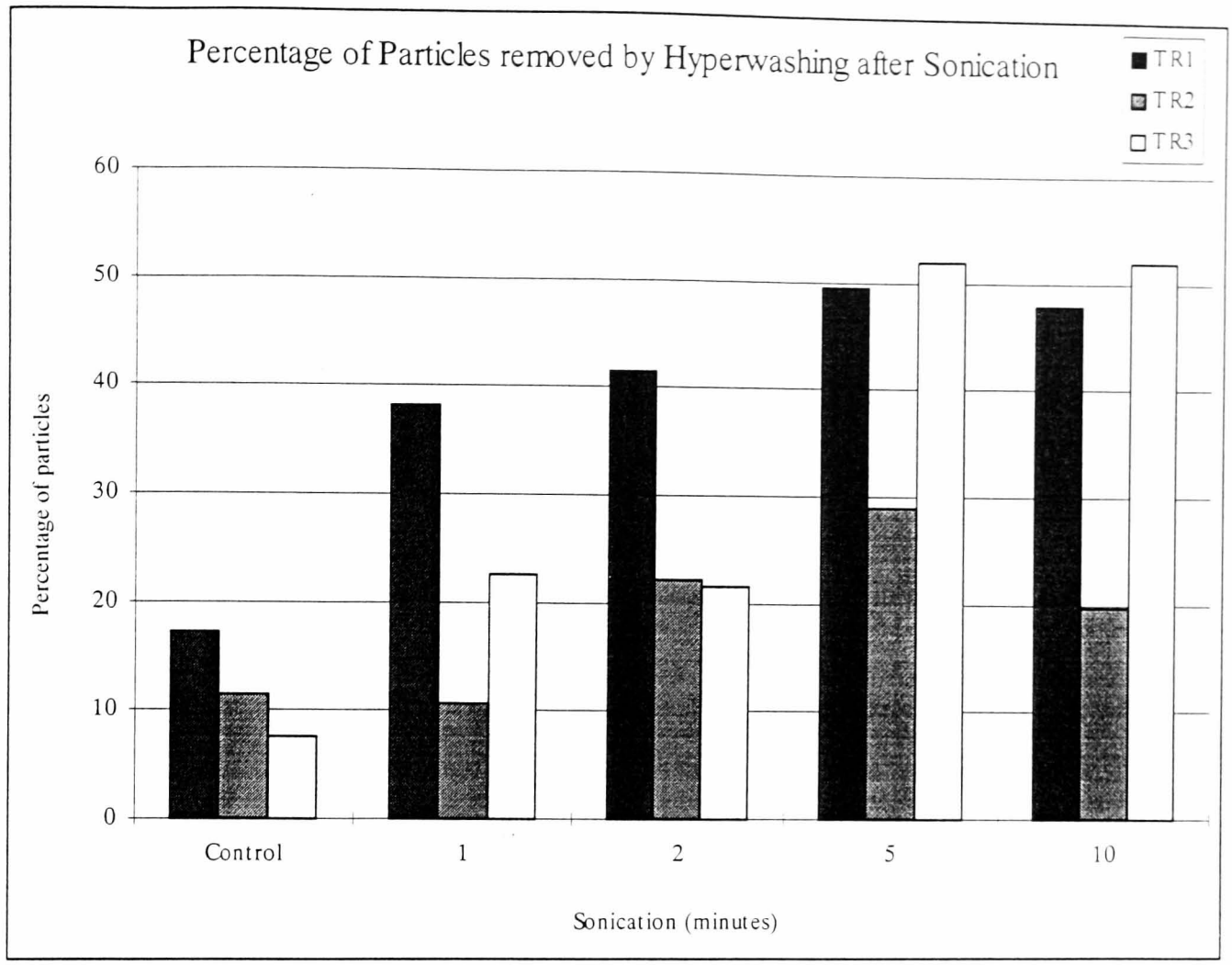


Figure 8.4.15 **Percentage of 100 micron Particles Removed by Hyperwashing after Sonication**

The removal of toner efficiency increased at higher sonication times. In all experiments the greater the sonication time the greater the removal of toner. The affect of temperature indicated a more effective removal of toner as the glass transition temperature is approached.

As noted in section 7.0 the toner's glass transition temperature is an important parameter in the deinking of mixed office waste. The pulps in temperature range 3 were soaked at a temperature of 50°C. The heating effect caused by ultrasound treatment increased the temperature of the pulps by 4°C after 1 minute; 5°C after 2 minutes; 12°C after 5 minutes and 18°C after 10 minutes, (Table 8.4.1).

The temperatures used in range 3, especially at the end of sonication, were close to the glass transition temperature of the toner. Glass transition temperatures of Sharp toners were measured at between 67 and 72°C. The higher temperatures employed in this third set of experiments makes the toner softer and more pliable, as a result of this its removal by ultrasound is enhanced.

Summarising the results obtained

- Disintegration at high temperature lead to poor detachment of the toner from fibres, with only 8% of toner particles detached in the control sample.
- Sonication at higher temperatures results in increased detachment of toner particles.

To investigate the effects of sonication above the glass transition temperature it was decided to perform a series of experiments close to or above the glass transition temperature, at around 75°C. These experiments are detailed in section 8.5.0.

8.5.0 Temperature Range 4

Temperature range 4 experiments were conducted by soaking 150g fibre in water at 75°C for 3 hours. The resulting pulp was disintegrated and sonicated as previously outlined. The temperatures at the start and finish of the sonication were noted and are shown in table 8.5.1.

	batch 1		batch 2		batch 3	
	initial	final	initial	final	initial	final
1 minute	62	65	58	61	55	59
2 minutes	62	69	64	69	64	70
5 minutes	60	73	58	74	72	86
10 minutes	58	77	57	78	70	88

Table 8.5.1 Temperature Data for Range 4 (ºC)

The measured glass transition temperature of the toners used in these experiments were between 67 and 72°C. The results of these three experiments are given in Tables 8.5.2.to 8.5.7.

To compare the trends graphs of the averaged data from the handsheets are given in Figures 8.5.1 to 8.5.5.

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	160.6	81.7	61.9	54.9	52.6
Standard Error	45.9	23.5	13.3	11.5	9.2
Median	34.7	40.8	37.1	40.1	36.6
Mode	8.4	9.4	8.4	8.4	8.4
Standard Deviation	236.4	134.2	88.3	71.2	62.8
Minimum (μm)	8.4	8.4	8.4	8.4	8.4
Maximum (μm)	621.6	529.4	343.0	360.5	244.1
Count	703	1061	1955	1482	2136
Confidence Level (95.0%)	64.3	32.9	18.6	16.1	12.9

Table 8.5.2 Batch 1 Statistics Unwashed

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	222.1	113.0	92.8	70.8	67.4
Standard Error	54.7	27.6	22.1	15.5	20.8
Median	158.6	85.0	71.5	62.7	51.9
Mode	8.4	10.4	9.5	10.4	9.4
Standard Deviation	252.0	132.7	105.0	69.8	78.3
Minimum (μm)	8.4	8.5	8.5	8.5	8.4
Maximum (μm)	604.8	434.7	350.7	192.6	251.3
Count	450	536	508	413	201
Confidence Level (95.0%)	76.7	38.7	31.0	21.7	29.2

Table 8.5.3 Batch 1 Statistics After Hyperwashing

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	212.7	100.7	76.7	62.4	52.0
Standard Error	56.6	26.0	20.7	10.5	8.8
Median	68.5	54.3	39.5	45.3	38.4
Mode	8.4	8.4	8.4	8.4	9.4
Standard Deviation	283.1	152.0	135.5	70.8	57.3
Minimum (μm)	8.4	8.4	8.4	8.4	8.4
Maximum (μm)	814.6	490.3	606.8	196.5	164.1
Count	626	1169	1839	2062	1813
Confidence Level (95.0%)	79.3	36.4	29.0	14.7	12.3

Table 8.5.4 **Batch 2 Statistics Unwashed**

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	229.1	127.2	117.1	74.1	62.8
Standard Error	58.7	34.9	37.7	17.6	15.3
Median	140.2	83.7	69.1	60.6	53.8
Mode	8.5	9.4	8.5	8.4	10.3
Standard Deviation	273.5	173.9	177.8	76.9	62.5
Minimum (μm)	8.4	8.4	8.5	8.4	8.4
Maximum (μm)	715.6	605.3	533.6	175.0	145.9
Count	473	620	493	366	278
Confidence Level (95.0%)	82.2	48.8	52.9	24.6	21.5

Table 8.5.5 **Batch 2 Statistics After Hyperwashing**

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	127.9	69.0	58.0	49.5	42.9
Standard Error	32.9	17.7	9.9	8.7	6.9
Median	34.0	35.7	41.7	36.2	32.0
Mode	8.5	9.5	8.5	8.5	8.5
Standard Deviation	199.2	117.9	67.5	57.3	48.0
Minimum (μm)	8.5	8.5	8.5	8.5	8.5
Maximum (μm)	672.5	543.0	222.6	223.6	201.6
Count	1348	1968	2181	1879	2356
Confidence Level (95.0%)	46.0	24.8	13.8	12.2	9.7

Table 8.5.6 **Batch 3 Statistics Unwashed**

	Time of Sonication				
	0m	1m	2m	5m	10m
Mean (μm)	200.7	94.6	59.6	59.0	47.3
Standard Error	50.7	29.7	13.8	16.1	13.5
Median	134.3	58.5	41.1	45.9	40.0
Mode	8.5	8.5	8.5	8.5	8.5
Standard Deviation	238.3	141.9	68.2	68.2	49.2
Minimum (μm)	8.5	8.5	8.5	8.5	8.5
Maximum (μm)	626.8	493.6	170.2	231.4	109.6
Count	488	522	604	320	176
Confidence Level (95.0%)	71.1	41.6	19.3	22.6	19.0

Table 8.5.7 **Batch 3 Statistics After Hyperwashing**

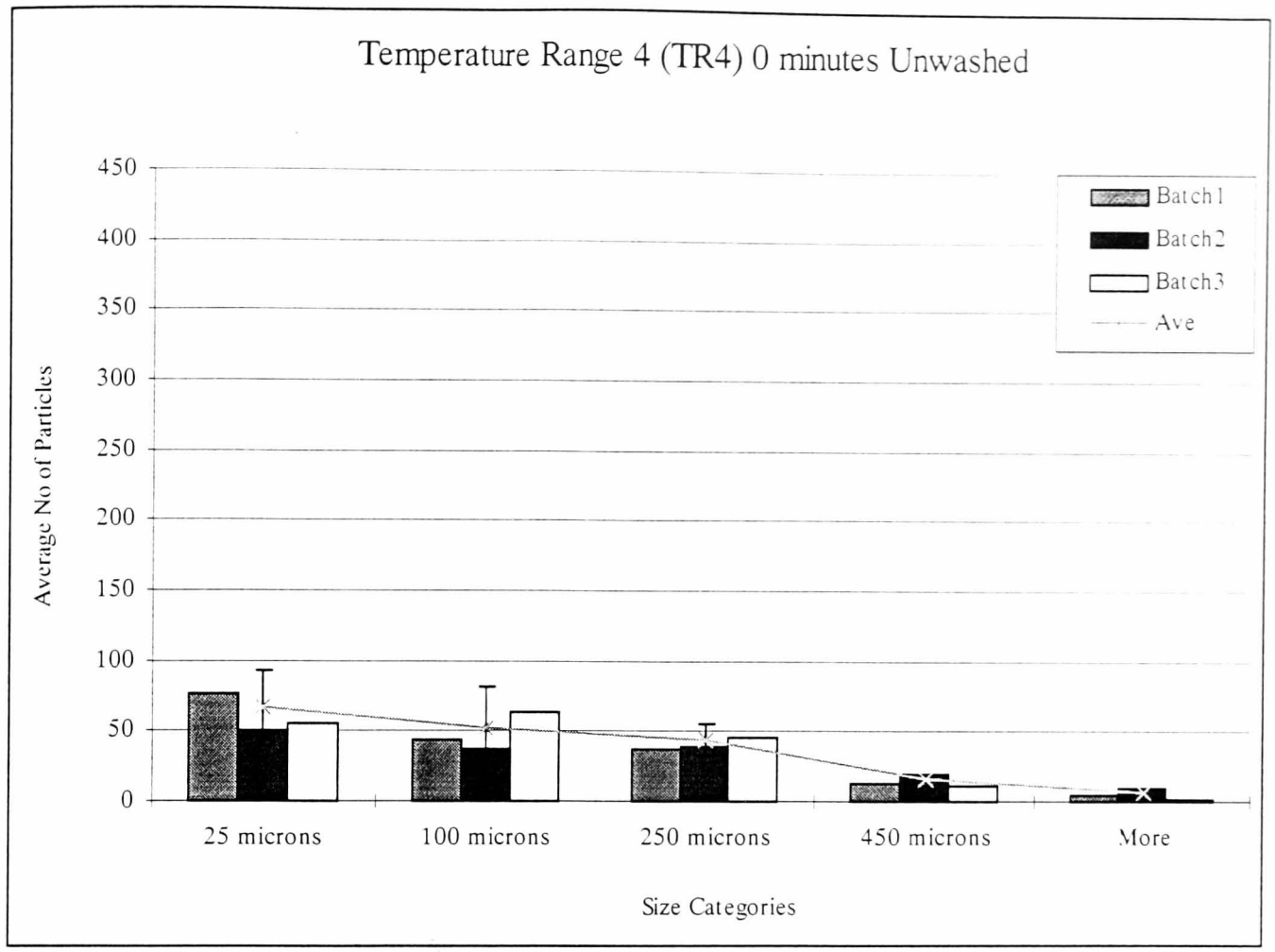


Figure 8.5.1 Toner Particle Count for Range 4 Unwashed 0 minute Sonication

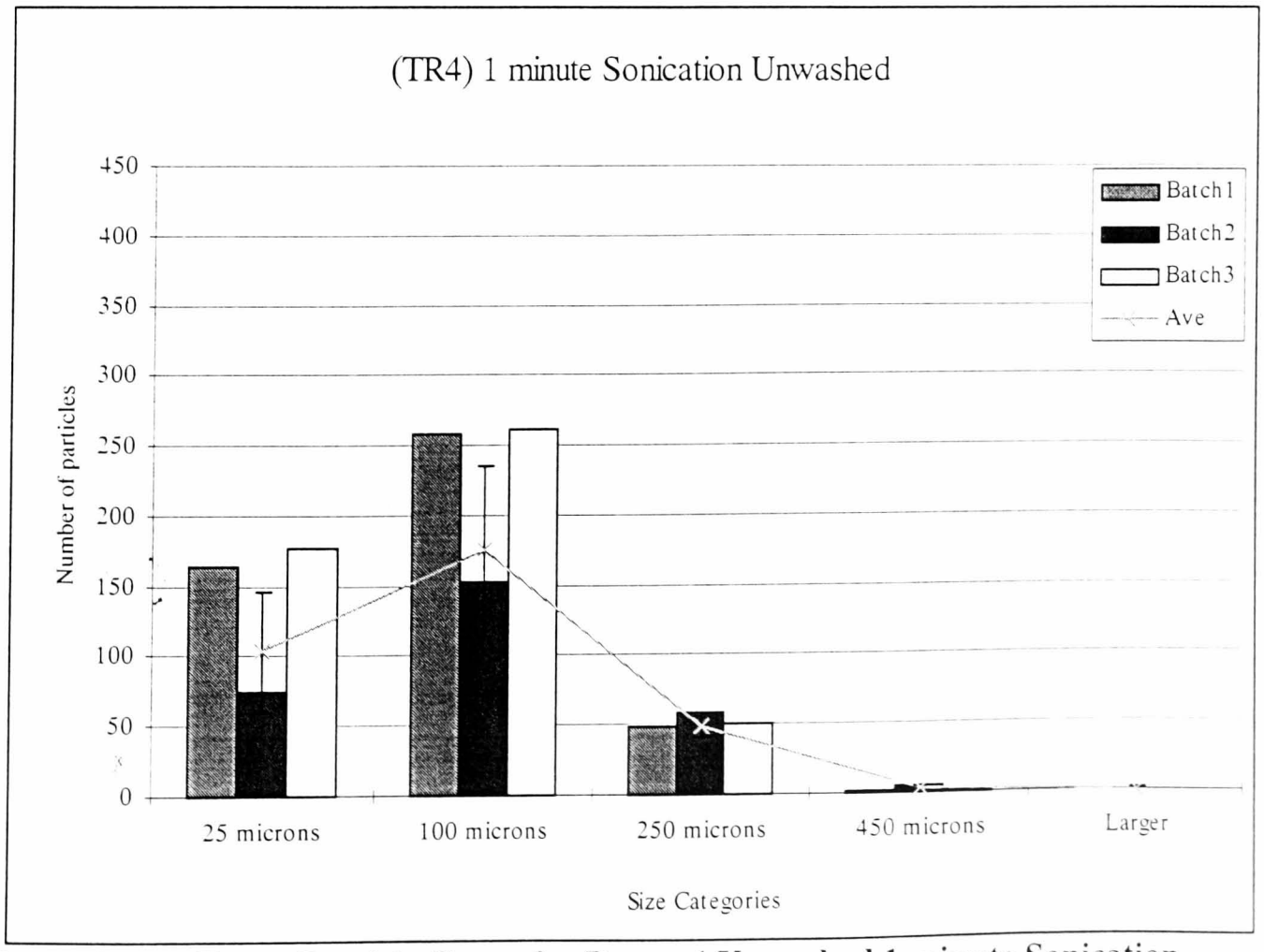


Figure 8.5.2 Toner Particle Count for Range 4 Unwashed 1 minute Sonication

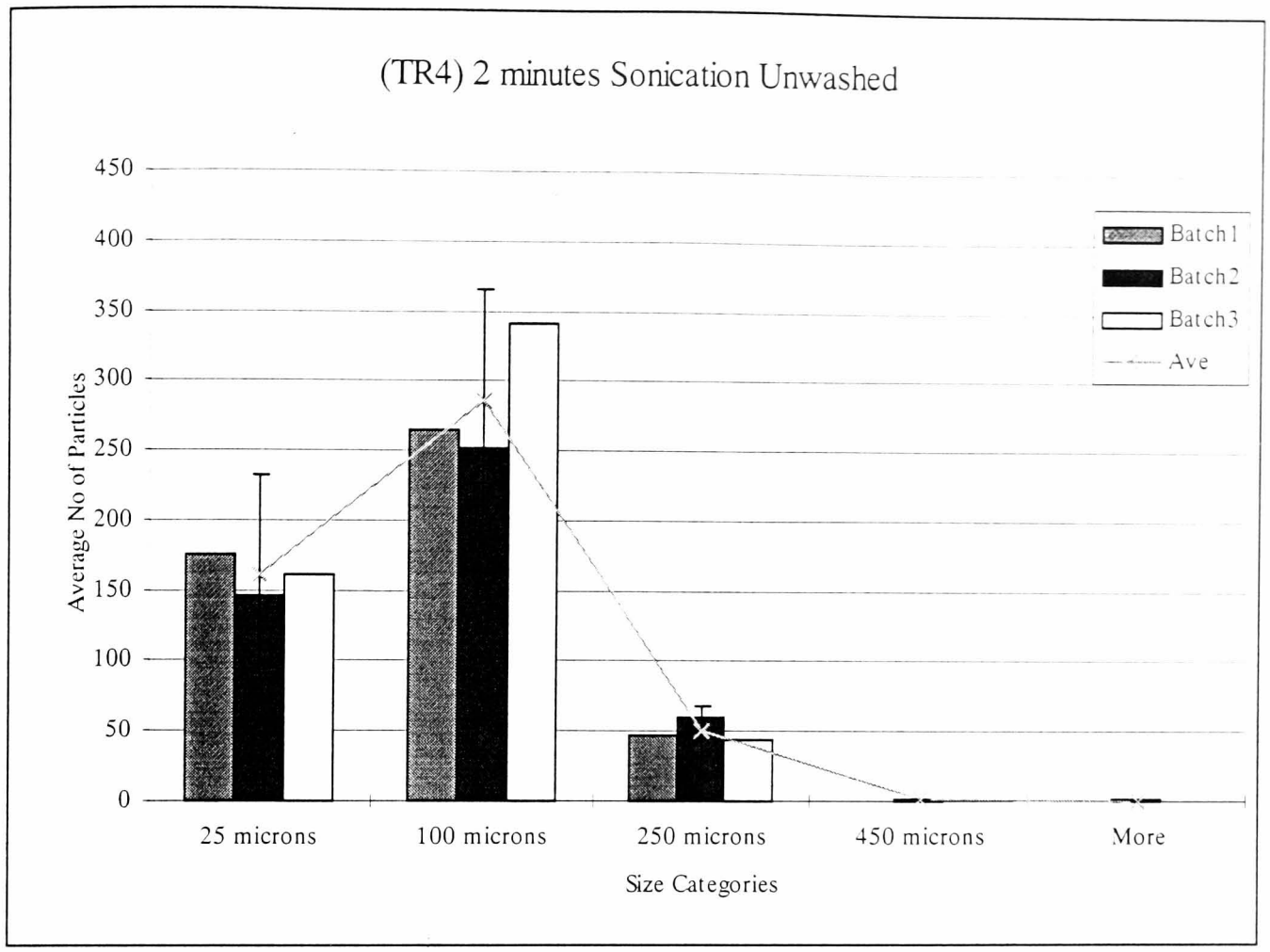


Figure 8.5.3 Toner Particle Count for Range 4 Unwashed 2 minutes Sonication

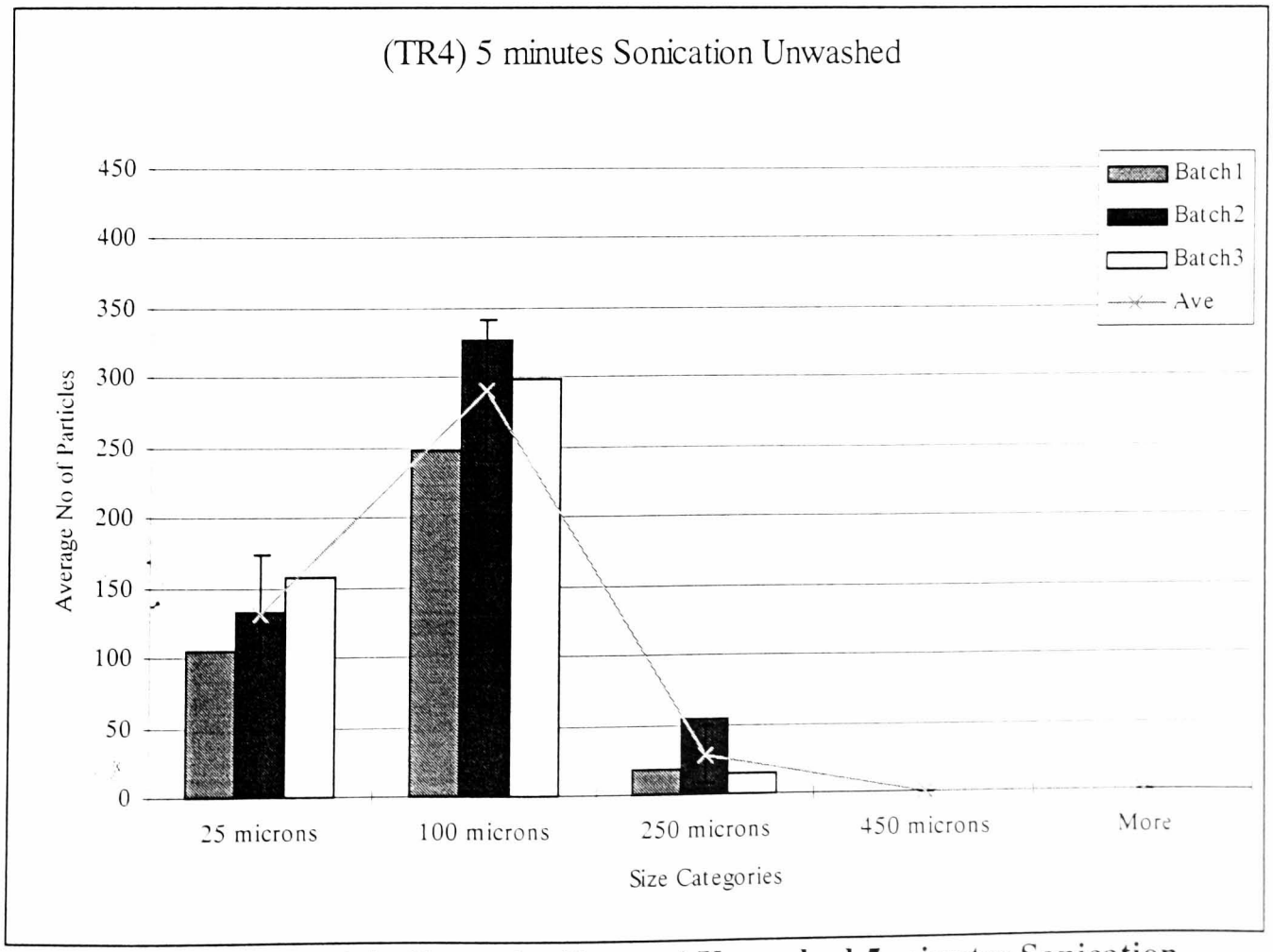


Figure 8.5.4 Toner Particle Count for Range 4 Unwashed 5 minutes Sonication

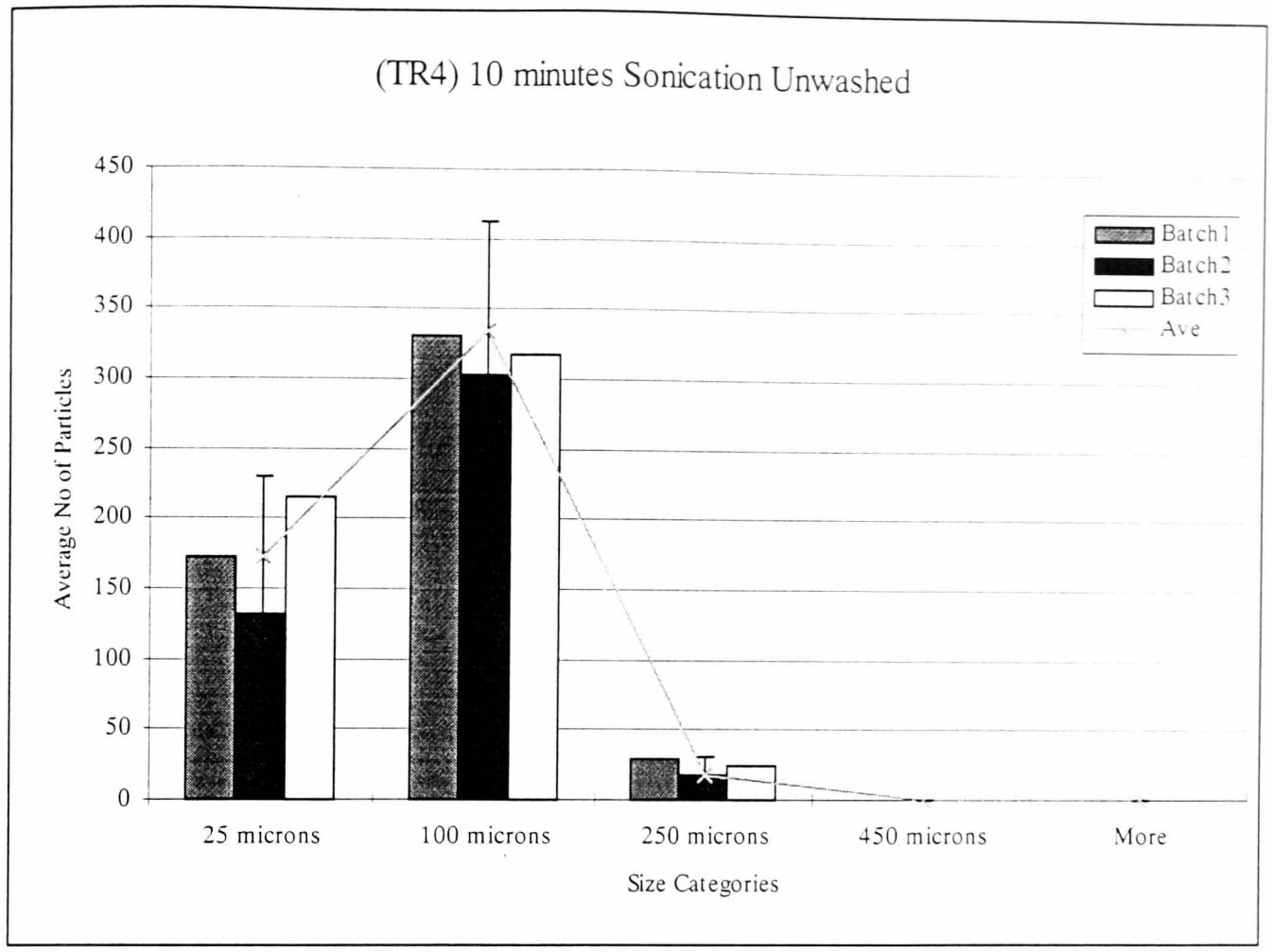


Figure 8.5.5 Toner Particle Count for Range 4 Unwashed 10 minutes Sonication

Disintegration of these samples yielded a very broad distribution of particle sizes. Very large particles, greater than 450μm were present in the distribution. The percentage of particles equal to or less than 100 microns in the control sample was 69%.

After 1 minute of ultrasound treatment the percentage of particles with diameters equal to or less than 100 microns was 85% and this rose to 96% after 10 minutes sonication. After 10 minutes sonication 64% of all particles were detected in the 100 micron category.

Figures 8.5.6 to 8.5.10 shows the results obtained from analysis of handsheets produced from hyperwashed pulps prepared for temperature range 4.

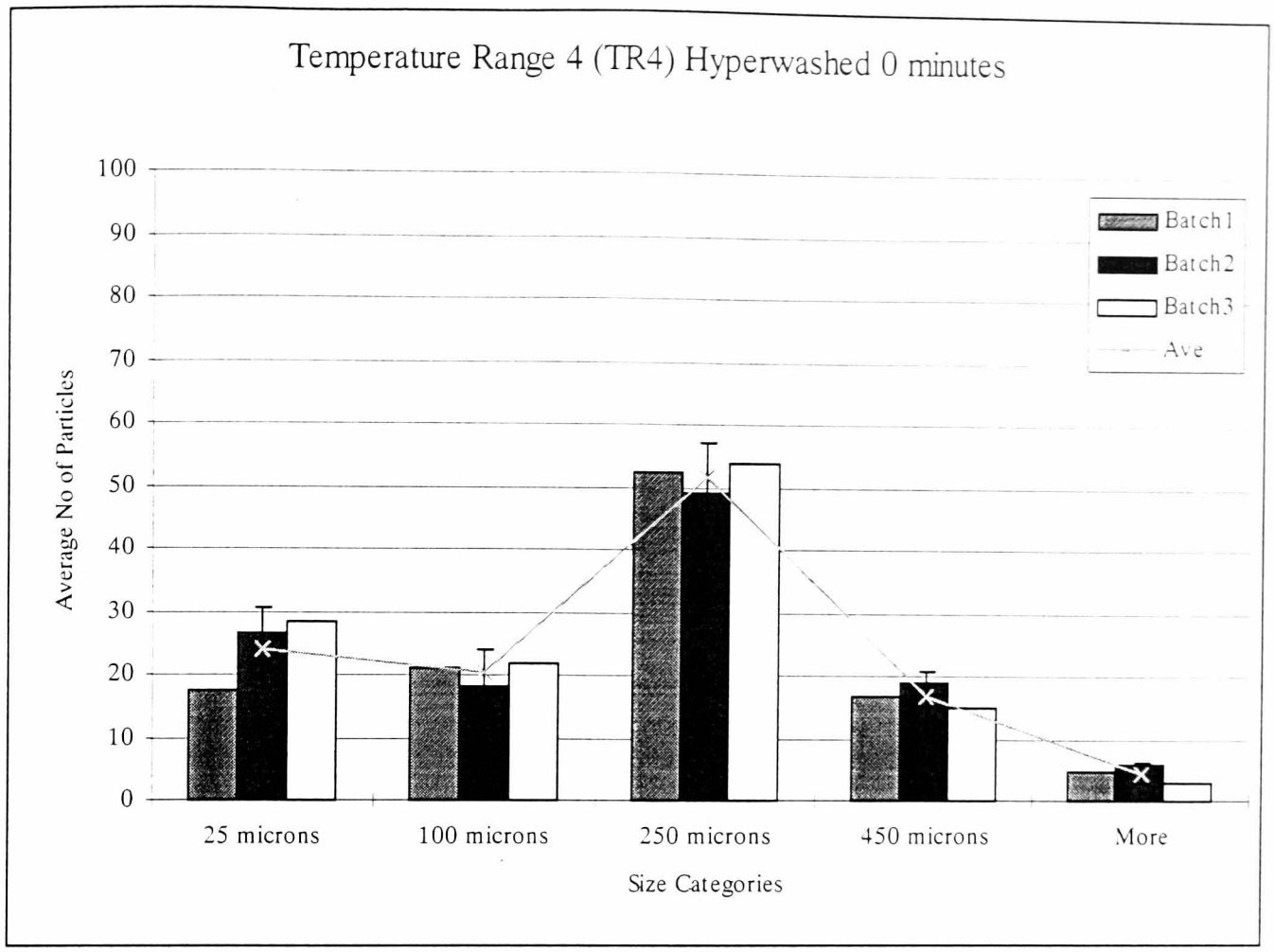


Figure 8.5.6 Toner Particle Count for Range 4 Hyperwashed 0 minute Sonication

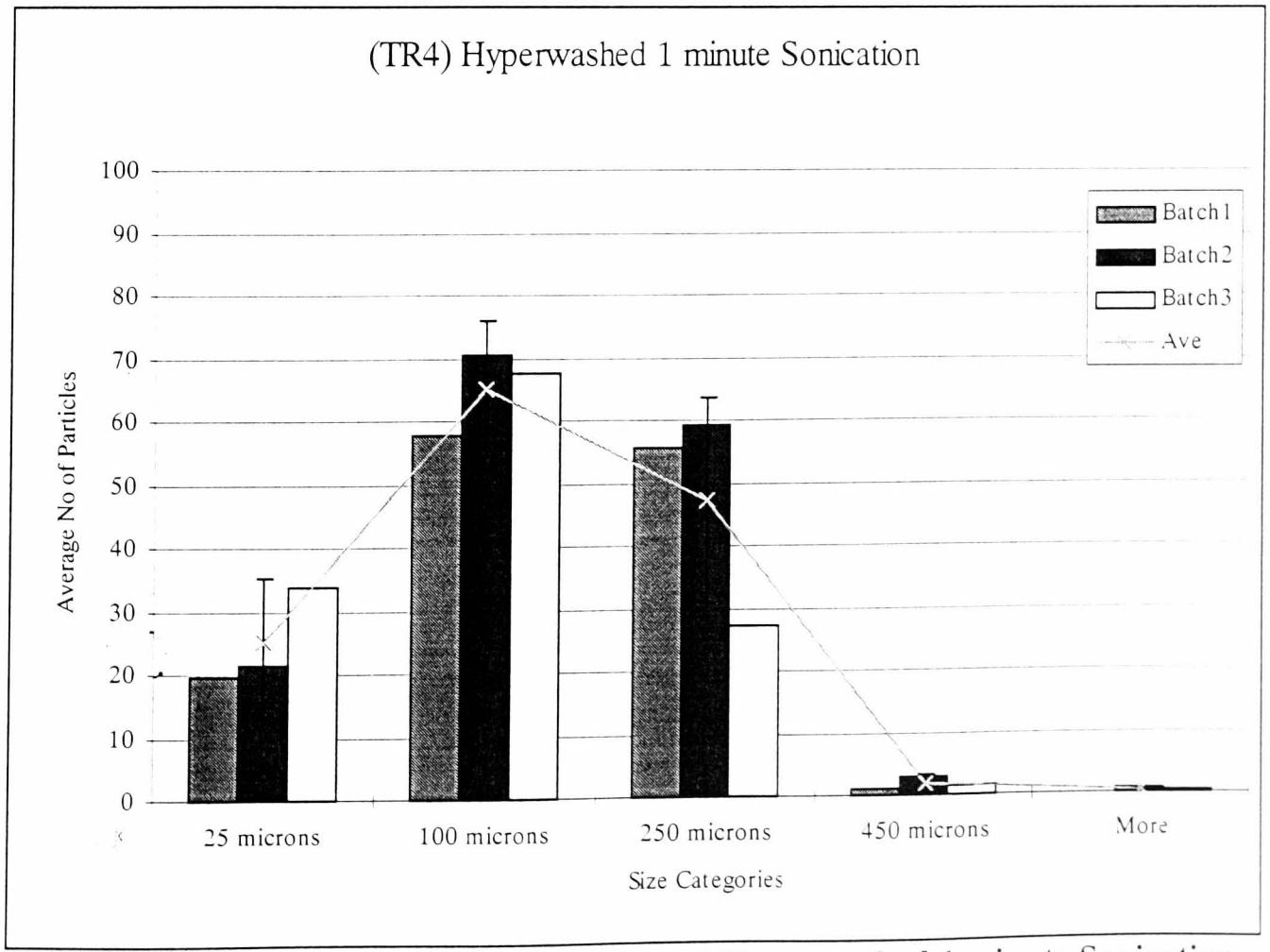


Figure 8.5.7 Toner Particle Count for Range 4 Hyperwashed 1 minute Sonication

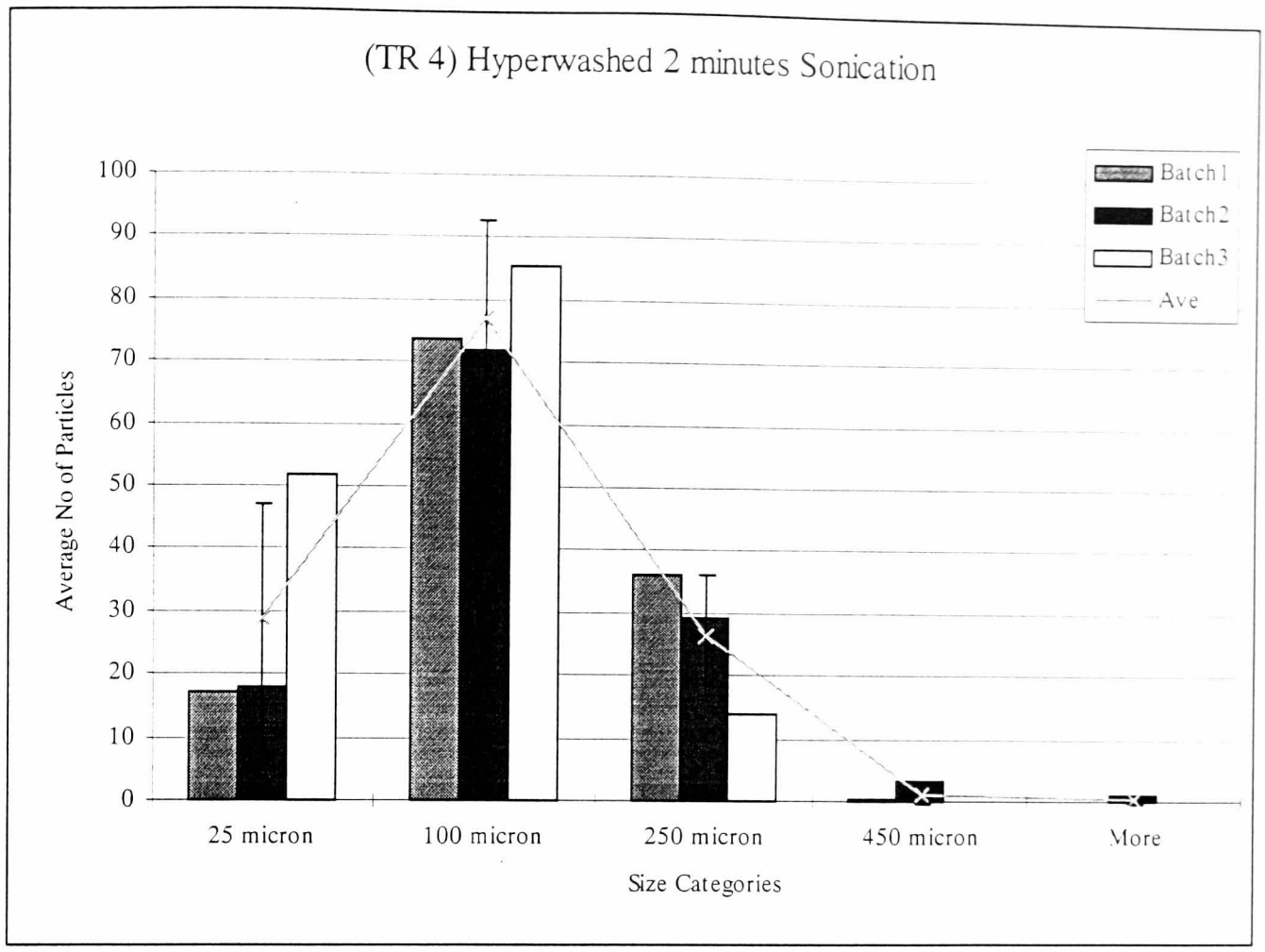


Figure 8.5.8 Toner Particle Count for Range 4 Hyperwashed 2 minutes Sonication

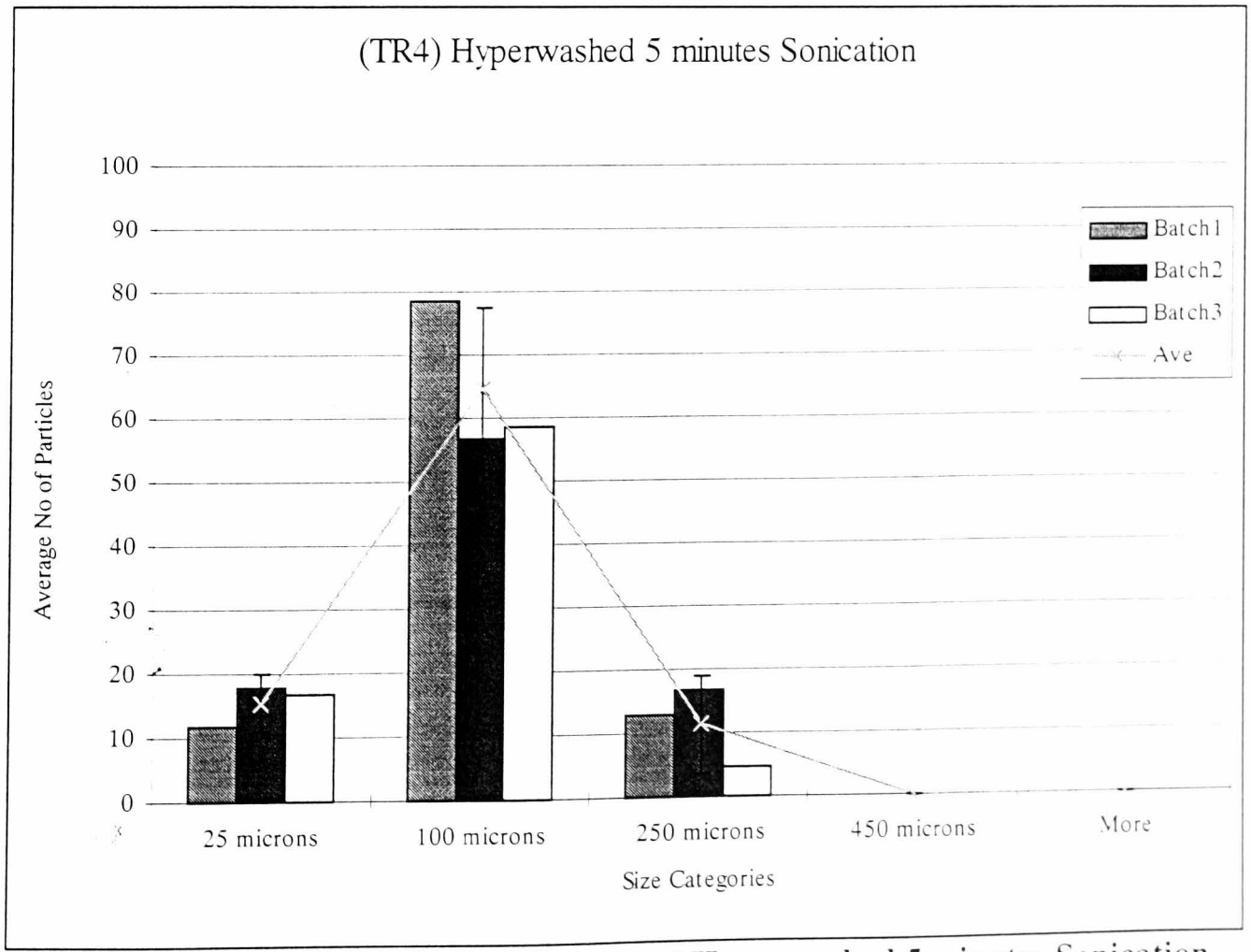


Figure 8.5.9 Toner Particle Count for Range 4 Hyperwashed 5 minutes Sonication

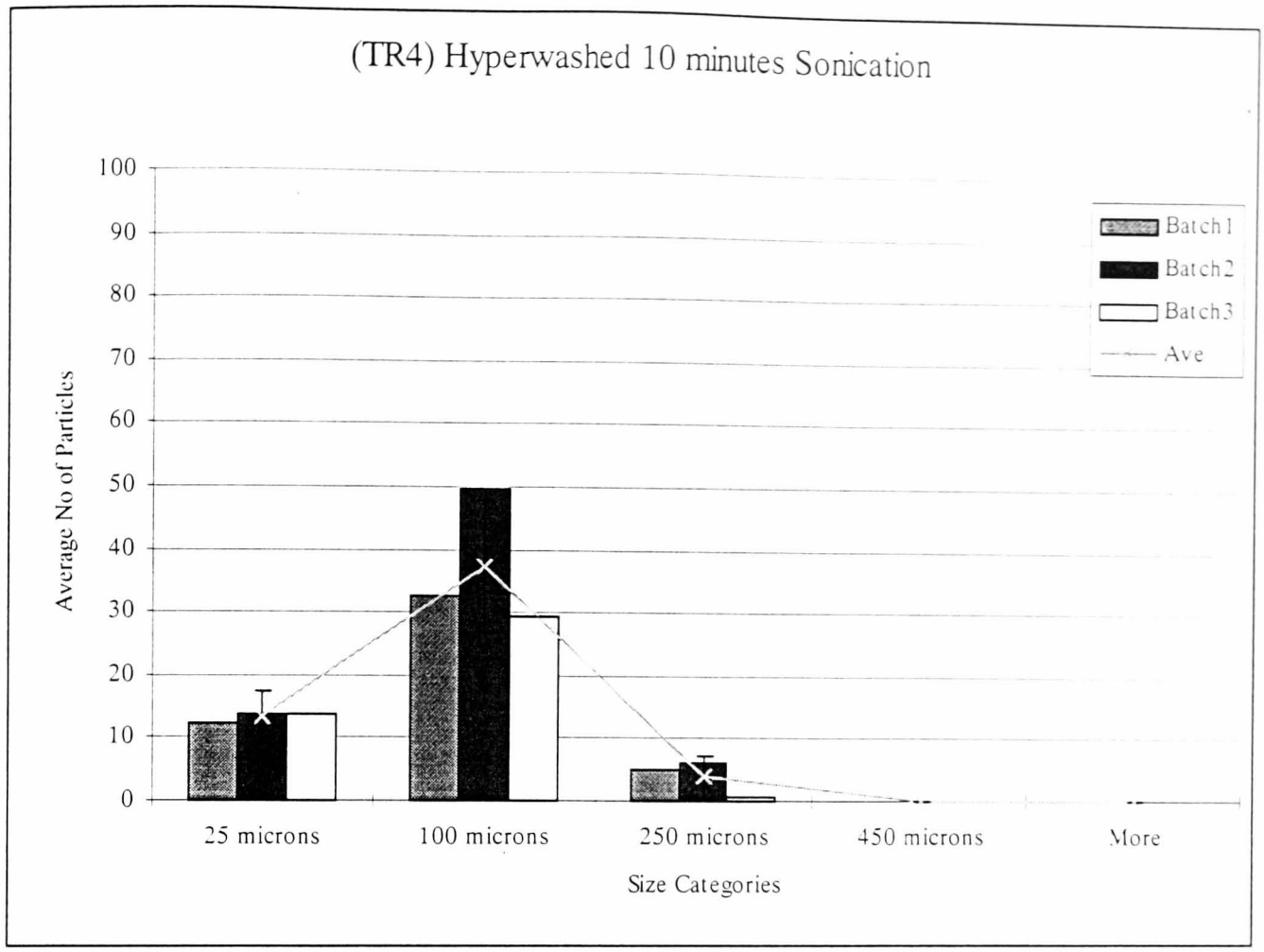


Figure 8.5.10 **Toner Particle Count for Range 4 Hyperwashed 10 minutes Sonication**

Comparison of the unwashed and hyperwashed results showed that this high temperature treatment, temperature range 4, had a distinct effect on detachment of toner particles. Simple disintegration at this temperature released 20% of 100 micron sized particles and 29% of 25 micron sized particles.

Sonication for 1 minute produced a slightly increased amount of detachment with 34% of particles in the 100 micron category and 25% in the 25 microns category. This extent of release was achieved with an increased number of particles, 2677 in the control sample against 4198 after 1 minute sonication.

As sonication times were extended the numbers and extent of toner release continued to increase. After 10 minutes sonication only a few particles (0.8%) remained that were larger than 100 microns.

After treatment with ultrasound the fibres were examined using a Canadian standard freeness tester. The corrected CSF data is shown in table 8.5.8.

Time	CSF
0m	389
1 min	362
2 min	356
5 min	318
10 min	282

Table 8.5.8 **CSF values for Temperature Range 4 (ml)**

From the filtrates obtained from the CSF apparatus the population of particles in suspension were determined using laser scattering techniques. The results are shown in figure 8.5.11.

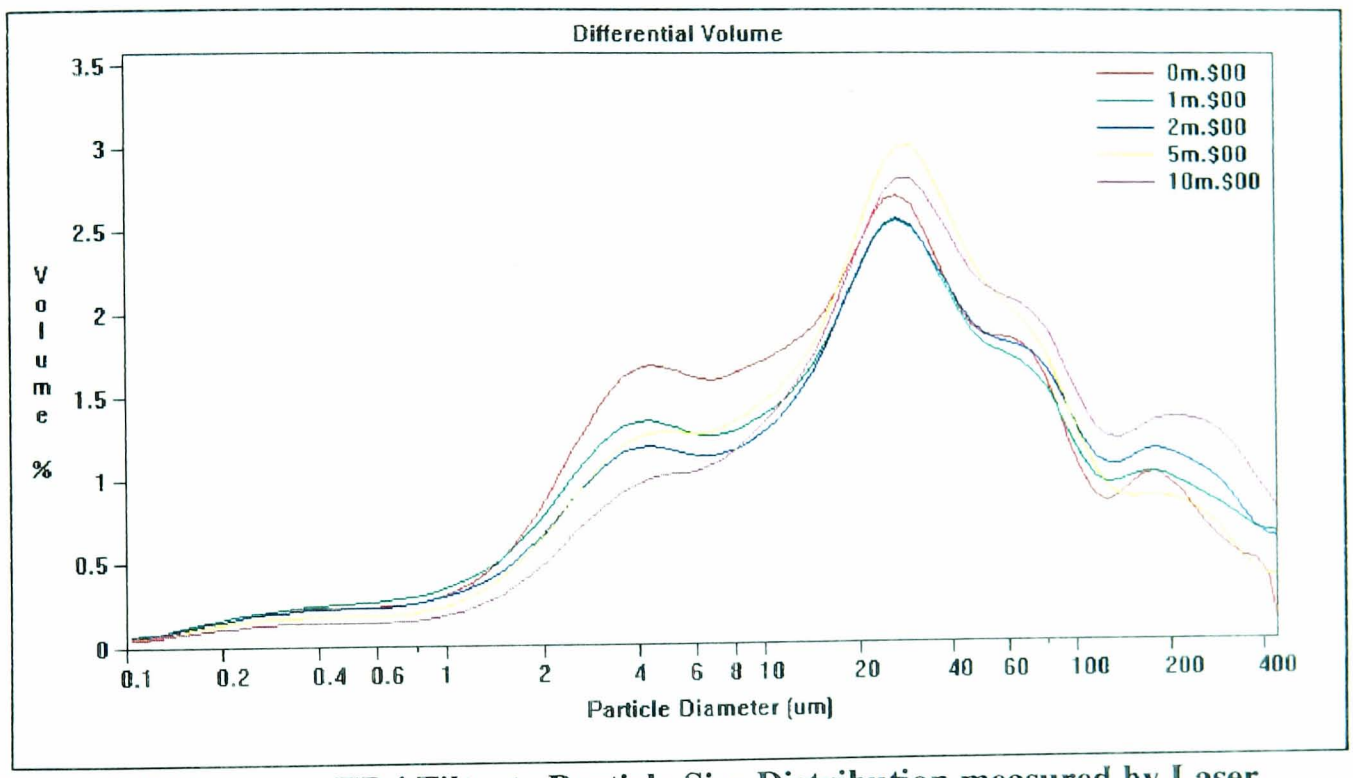


Figure 8.5.11 **TR4 Filtrate Particle Size Distribution measured by Laser Scatter, Batch 1**

These results obtained for temperature range 4, are fully discussed in the following section, 8.5.1.

8.5.1 Discussion of Results for Temperature Range 4

Temperature range 4 experiments were performed at 75°C, to ensure that the toners were above their glass transition temperatures. The average particle diameters found on handsheets produced from unwashed pulps are shown in table 8.5.9, and from the hyperwashed pulps in table 8.5.10.

	0 minutes	1 minute	2 minutes	5 minutes	10 minutes
Batch1	160.6 ± 236	81.7 ± 134	61.9 ± 88	54.9 ± 71	52.6 ± 63
Batch2	212.7 ± 283	100.7 ± 152	76.7 ± 135	62.4 ± 71	52.0 ± 57
Batch3	127.9 ± 199	69.0 ± 118	58.0 ± 67	49.5 ± 57	42.9 ± 48

Table 8.5.9 Average Particle Diameter Before Hyperwashing (μm)

The average particle diameter in the control sample before hyperwashing was 160 microns, after hyperwashing the diameter increased to 217 microns.

	0 minutes	1 minute	2 minutes	5 minutes	10 minutes
Batch1	222.1 ± 252	113.0 ± 133	92.8 ± 105	70.8 ± 70	67.4 ± 78
Batch2	229.1 ± 273	127.2± 174	117.1 ± 178	74.1 ± 77	62.8 ± 62
Batch3	200.7 ± 238	94.6 ± 142	59.6 ± 68	59.0 ± 68	47.3 ± 49

Table 8.5.10 Average Particle Diameter After Hyperwashing (μm)

The percentage of particles removed in the hyperwashing process are given in Figure 8.5.12. Again, the sonicated samples displayed the greatest removal rate. The control sample for the 100 micron category had the least number of particles removed from the pulp, and the 10 minutes sonication the greatest number.

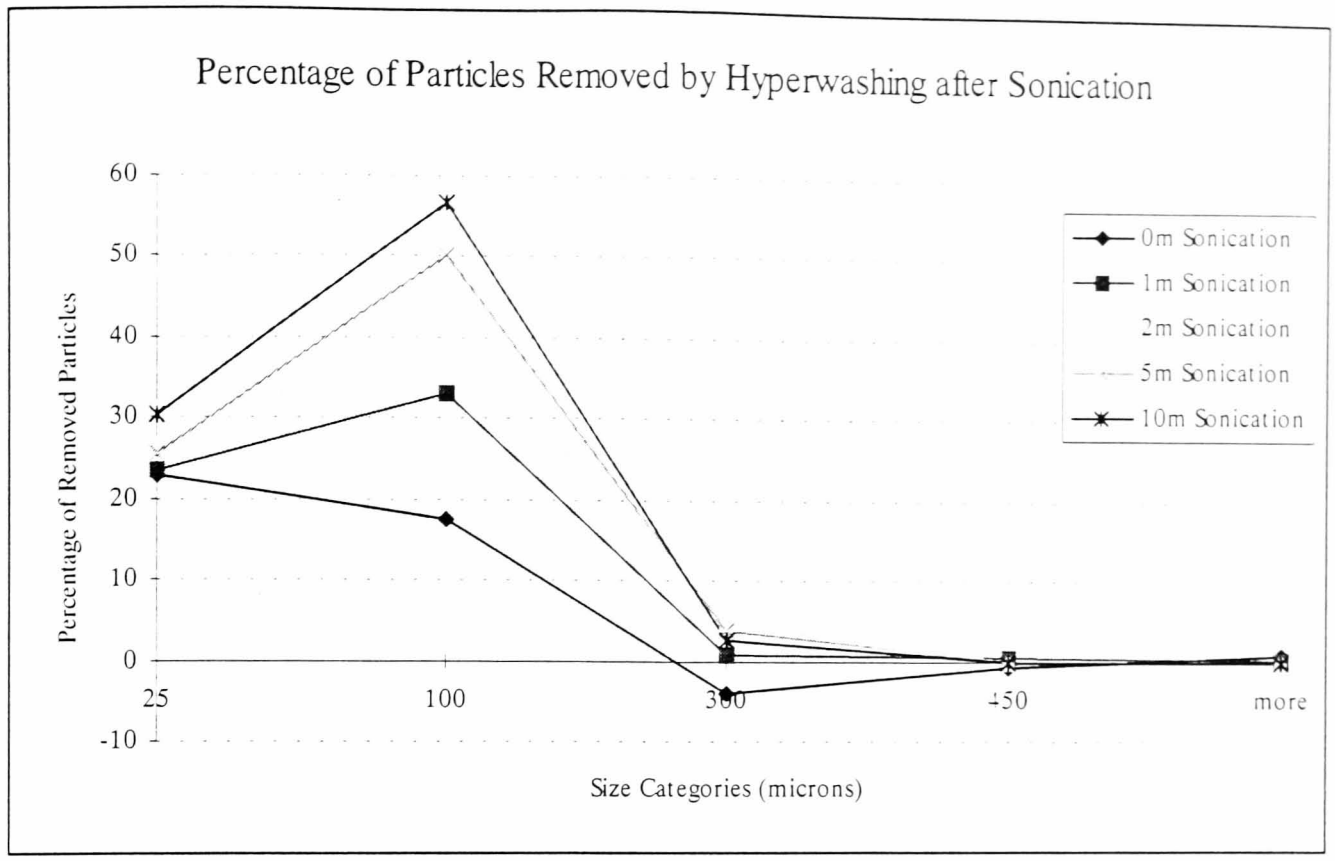


Figure 8.5.12 **Percentage of Particles Removed by Hyperwashing after Sonication**

Figure 8.3.13 shows the percentage of 100 microns particles removed for the four temperature ranges investigated.

Although increasing the temperature increased the rate of break down of particles it did not significantly affect the extent of detachment. Once the toner particles had reached a temperature of approximately 45°C they became easier to detach from the fibres.

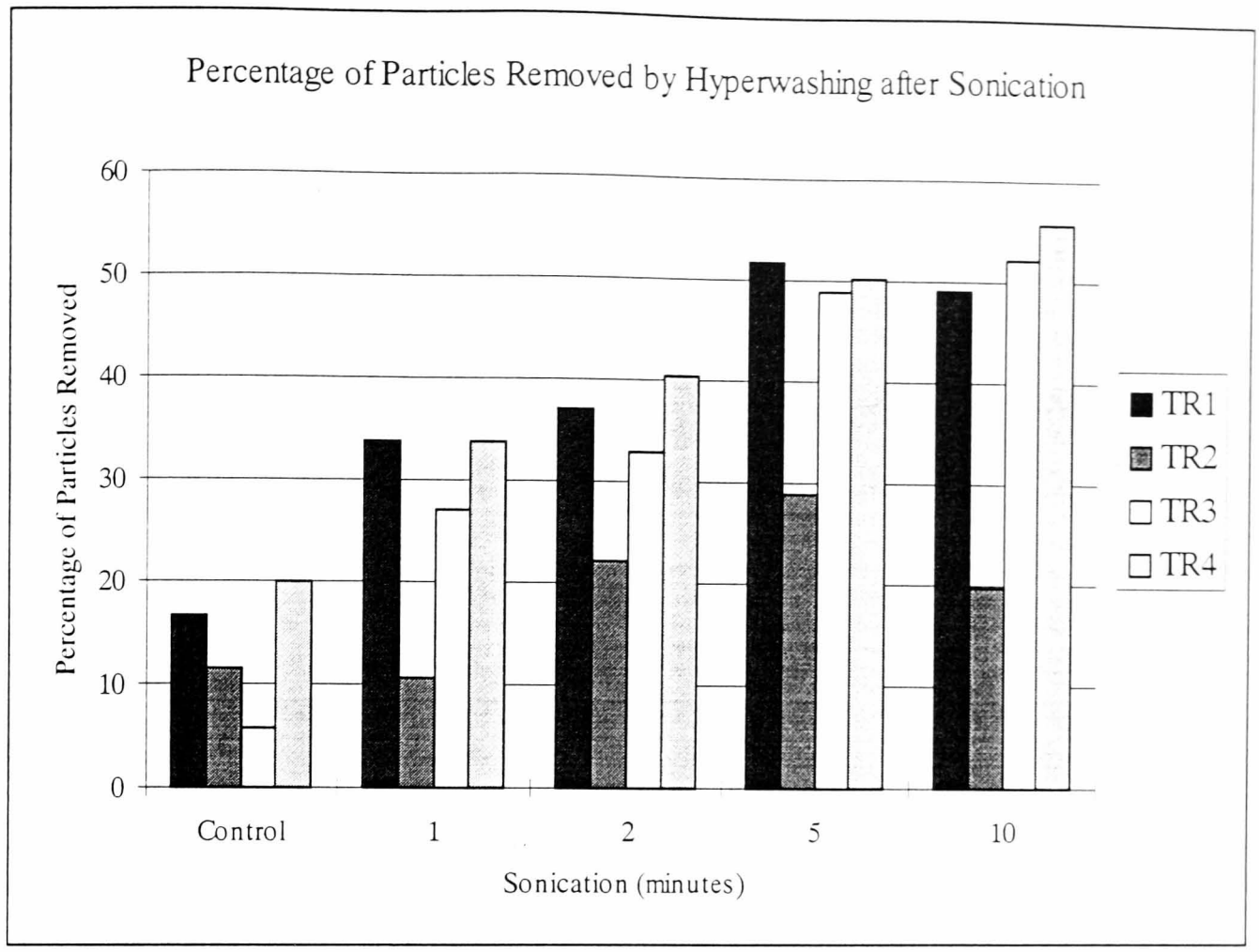


Figure 8.5.13

In conclusion:

- At higher temperatures the toner particles were rapidly broken down in size.

The overall conclusions of the experiments performed in section 8 are more fully discussed in section 9.2.

9.0 Final Conclusions

In section 6 a simple system was designed to investigate whether ultrasound caused damage to fibres, specifically to virgin fibres. The *conventional* papermaking process leads to damage of fibres and recycling can exacerbate this damage. This damage shortens fibres with subsequent loss during flotation or cleaning operations resulting in a reduced fibre yield.

Having established that exposure to ultrasound does not cut fibres, a determination of the exposure required to break-up or detach toner particles from fibres was undertaken. Previous work had not put forward a hypothesis for the interaction of ultrasound with fused toner particles.

9.1 Estimating Ultrasound Power used in Experiments

The power supplied to the horn is important during these experiments. Ultrasound induces a heating effect and this affects the extent of cavitation in water. It was therefore necessary to compare the amount of energy the horn delivered at different temperatures in order to correlate this with the available cavitation intensity.

	TR 2		TR3		TR4	
	°C	PD	°C	PD	°C	PD
1 minute	5.7	9.3	4.3	30.7	4.3	30.7
2 minute	8.7	12	8.3	38.7	8.3	38.7
5 minute	18.7	9.7	12.8	84.3	12.8	84.3
10 minute	25.3	48.3	18.5	141.3	18.5	141.3

Table 9.1.1 Average Temperature Rise and Power Demand

Shown in table 9.1.1 is the average increase in temperature during sonication, for each temperature range. The column labelled 'PD' is the decrease in power demand of the horn as indicated by the LED power indicator of the ultrasonic generator unit. This figure is obtained by subtracting the initial power reading when the horn is first lowered into the pulp suspension, from that reading at the end of the experiment. These figures are in watts and represents the amount of power supplied to the piezoelectric element, but *not* the power that was radiated from the horn tip. There are energy losses involved in the production of ultrasound, though it is difficult to quantify the amount and nature of these

losses for a particular system. The relationship between input and output powers is therefore tenuous at best.

Time minutes	TR2 Starting Temperatures (18°C)	TR3 Starting Temperatures (50°C)	TR4 Starting Temperatures (75°C)
1 minute	47,600	36,000	36,000
2 minutes	73,000	70,000	70,000
5 minutes	157,000	108,000	108,000
10 minutes	213,000	155,000	155,000

Table 9.1.2 Energy in Joules Required to Heat Pulp

Table 9.1.2 shows the calculated energies required to heat the pulp samples to the temperatures shown in table 9.1, assuming that only water is present in the reaction vessel and that the heating is carried out under adiabatic conditions. The thermal mass of the pulp content has been ignored since it was only 1.5% of the bulk. The amount of energy was greater at lower temperatures because of the greater temperature increase.

Shown in table 9.1.1 is the fall in demand against increase in temperature for the three different temperature ranges. As can be seen the temperatures of ranges 3 and 4 increased at the same rate. The rate of increase of range 2 was slower as in this experiment the temperature was controlled using an ice bath.

The amount of electrical energy demanded by the horn is dependent on the temperature of the liquid being sonicated. The most efficient use of ultrasound in water has been found to been around 60°C.[97] This corresponds most closely to the temperatures used in temperature range 3 experiments.

Measurement of the effects of ultrasound can be undertaken using different techniques, including chemical dosimetry to measure the concentration of radicals present in the fluid after sonication. Dosimetry can be extended to the use of Electron Spin Resonance (ESR) and Nuclear Magnetic Resonance (NMR) to determine the effects of ultrasound in real time. Both NMR and ESR measure the changes in the chemical environment of hydrogen atoms and electrons respectively, to give an indication of the concentration of radicals present in the fluid.

In an attempt to indicate the extent of radical formation infra red spectroscopy was used. Cellulose, which comprises paper fibres, contains hydroxyl moieties. By measuring the hydroxyl signal before and after sonication it was thought possible to establish the amounts added to the fibre. This experiment was performed using a Breuker FTIR Spectroscope. The fibres were extensively dried, but interfering signals were larger than any additional radical activity and no useful information was obtained.

Another method employed to determine the extent of cavitation activity was the estimation of damage to aluminium foil. The method entailed placing a thin metal foil holder in the ultrasound bath where it was irradiated with ultrasound for a known time. The foil was examined after sonication to determine the number and distribution of the holes produced, each hole being the result of a cavitation bubble collapsing. This method provided a visual record of the pattern of cavitation in a particular vessel. Visual inspection of the foil gave information about the overall activity but image analysis provided a more accurate method of counting the holes. The data from these experiments is given in appendix 7.

In a variation of this technique, the foil was substituted by exposed photographic film. The film used was Agfa duplicating D7M film developed using Agfafix chemicals.

A holder suspended the film 7 cm from the base of the reaction vessel. The reaction vessel was filled with 2 litres of distilled water and the holder placed in the water. The horn was lowered into a reproducible position, the tip of the horn 7 mm above the film.

The films were sonicated for 30, 60 and 90 seconds. The temperature of the water was noted before and after sonication; the power supplied to the horn was noted. After sonication the films were removed from the holder, washed in distilled water, before being dried

Figure 9.1.1 represents the average numbers of holes detected on the films for each sonication time. The numbers of holes detected increased linearly as sonication time

increased. Included on the graph are error bars for the standard deviation of the number of holes detected.

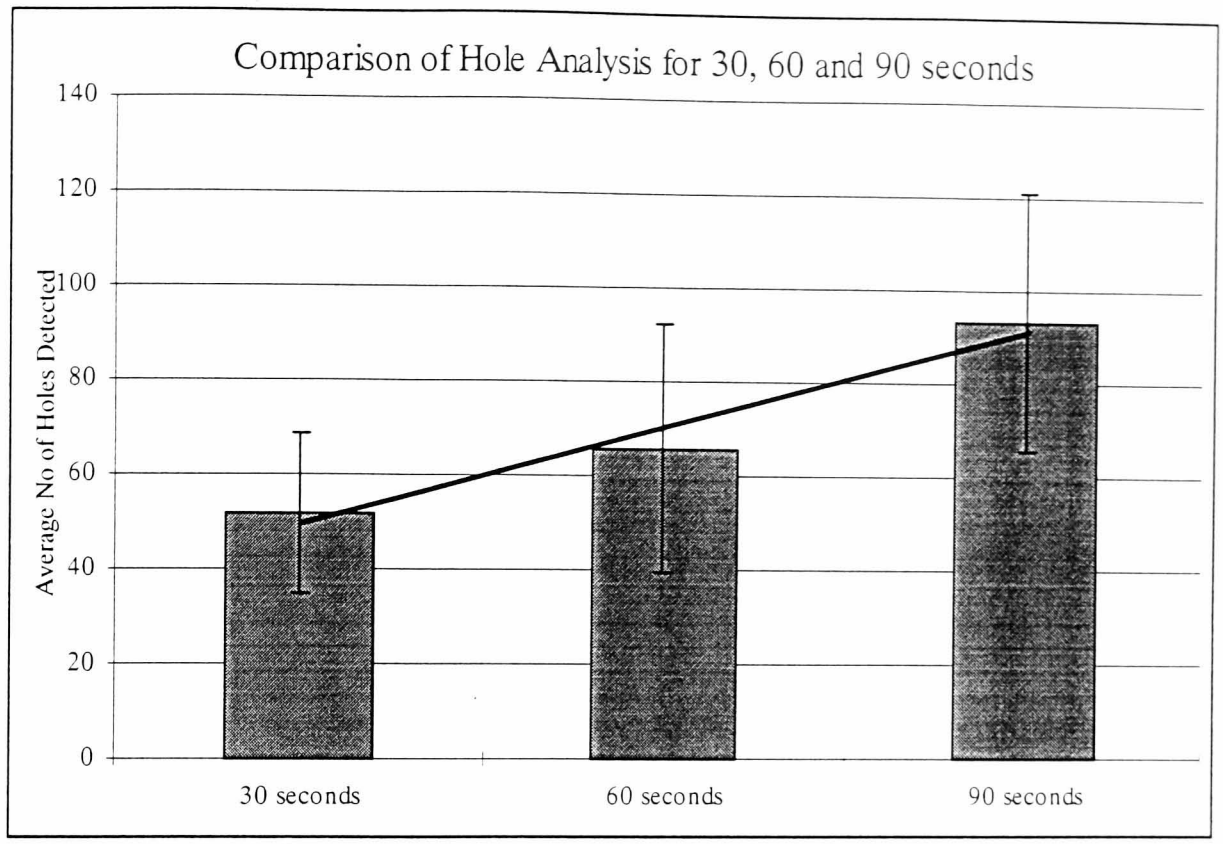


Figure 9.1.1 Number of Holes Detected on films after Sonication

If each detected hole is assumed to be a single cavitation event then the total number of cavitation bubbles imploding on the films can be estimated at a distance of 8 mm from the horn. However, at close proximity, cavitation activity is so intense that the erosion of the developed silver surface is excessive. The film emulsion was stripped off its backing and no estimate other than a visual examination of the area of the holes could be made.

As the number of holes increases linearly with sonication time it seems reasonable to assume that the probability of cavitation events will remain constant. The graph obtained in figure 9.1.1 could be extrapolated to longer time intervals, perhaps up to 10 minutes used as the longest sonication treatment.

It has been shown then that the use of exposed film in conjunction with transmitted light image analysis can quickly and accurately determine the nature of cavitation in a reaction vessel. The technique does have its limitations, in that very close to the horn cavitation activity tends to damage the film extensively, however a measure of the distance that cavitation extends can be made. The furthest extent of cavitation activity from the horn has been made; it is approximately 10 mm within the reaction vessel used. Thus the area of

cavitation extends to a depth of approximately 10 mm, across the entire area of the horn, giving a total volume subjected to cavitation of approximately 51 cm^3.

The total volume of the reaction vessel is 2000 cm^3, so while sonication occurs, only 50cm^3 of the pulp is subject to cavitation activity, around 2.5% of the reaction vessel. Sonication for 10 minutes may at first seem an excessive treatment, however as the pulp is constantly stirred during this treatment each fibre will receive only 600/40=15 seconds sonication. For 1 minute sonication the time under the horn is 1.5 seconds. Thus, ultrasound can alter the particle size distributions of the fused toners after very short exposure levels per cubic centimetre.

9.2 Ultrasound Action on Fibres - Conclusions

To investigate the extent of damage to fibres, pulped samples were sonicated for various times and then compared to untreated pulp. The average lengths of the fibres after both treatments were found to be the same; there was no cutting of the fibres during sonication. An unsonicated sample of pulp was refined in a laboratory refiner, (a PFI mill), and the fibre length distribution measured. The refiner was found to have decreased the average fibre length from 0.6 mm to around 0.3 mm. These shortened fibres are more likely to be lost in any subsequent recycling process. Retaining the length of the fibres is an important feature in both papermaking and recycling processes.

To measure the damage caused by sonication to the fibres the CSF apparatus was used. Figure 9.2.1 shows the CSF values for the sonicated virgin pulp samples described in section 6.0. However, the freeness of the refined sample was found to be 116 ml, approximately a quarter of the value for the sonicated samples. For comparison, the freeness value for the untreated (0 minutes) pulp was 607 ml, after 5 minutes treatment this decreased to 562 ml, decreasing slowly until 20 minutes where the value was 550 ml. This comparison confirms the greater extent of damage and fibrillation during mechanical refining.

The sonicated samples had lower values due to the greater amount of water retained within the fibre. This water is associated with increased fibrillation or greater surface area of fibres. As can be seen in figure 9.2.1 the CSF value of the fibres decreased significantly

after 5 minutes sonication, but thereafter decreased more slowly. The damage caused by sonication only affects certain parts of the fibre. These areas had been attacked by ultrasound after 5 minutes, after which there were no more sites present. The damage was caused after a relatively short exposure and greater exposure did not further affect the fibres. The freeness of the sonicated pulp samples described in section 8 were also measured, figure 9.2.2 details the effect of sonication on these samples.

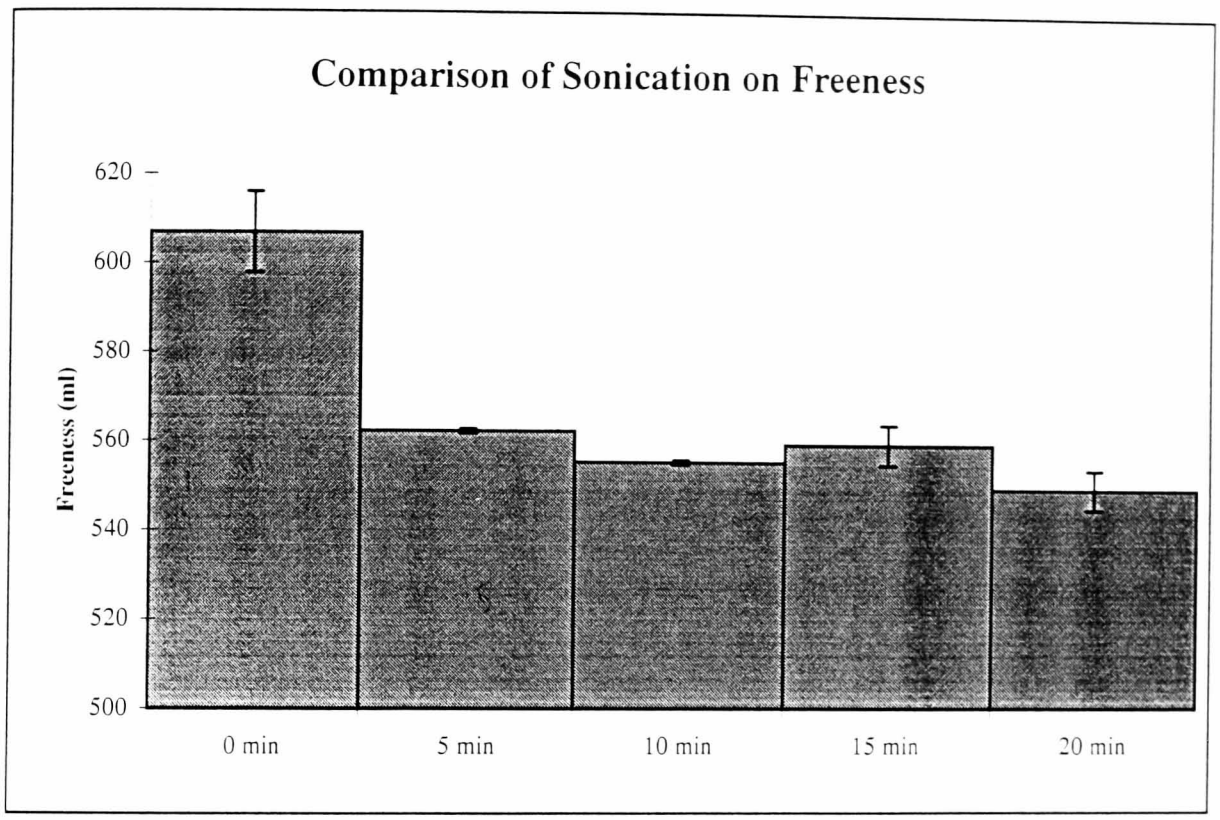


Figure 9.2.1 Effect of Sonication on CSF value for Virgin Fibres

The freeness values for samples taken from temperature ranges 2-4 were lower than the freeness values for virgin fibres. The fibres discussed in section 8 had been refined; the control samples (0 minutes) received no sonication. Sonication of the samples lead to a decrease in the value of freeness which was due mainly to increased fibrillation of the fibres.

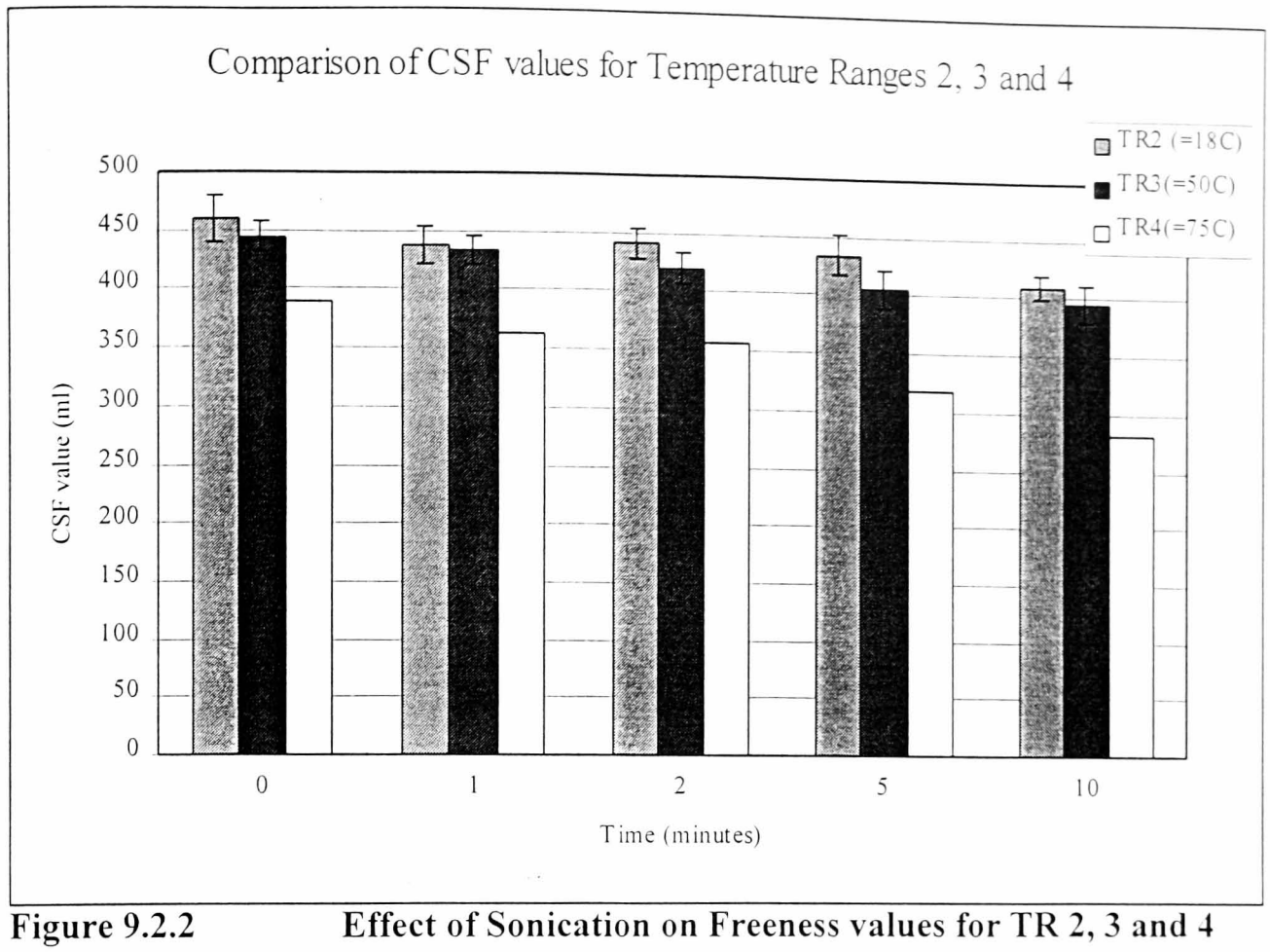


Figure 9.2.2 Effect of Sonication on Freeness values for TR 2, 3 and 4

Paper fibres consist of microfibrils containing cellulose molecules which are hydrophilic polysaccharides of repeating β-D-glucopyranose monomer units. These polysaccharide chains have a strong tendency to associate with each other by forming inter and intra molecular hydrogen bonds. The hydrogen bonds between cellulose chains allow the microfibril to bend and provide increased strength. The cellulose chains contain regions of crystalline and amorphous cellulose, amorphous regions give the fibre flexibility, while the crystalline regions provide tensile strength. The overall strength of the fibres comes from the chains of polysaccharides. A collection of polysaccharide chains can be thought of a thread known as a microfibril, hundreds or thousands of threads are bound up to form a strand known as a fibril, and many strands form a rope or paper fibre. There can be thousands of microfibrils in a paper fibre, the overall tensile strength is a result of their collective cohesion.

The hydrogen bonding characteristics of the cell wall of the fibre contributes to inter-fibre bonding. As a cell wall swells it will have a higher specific surface area and more sites available for bonding to other fibres. A poorly swollen cell wall will offer fewer sites for bonding and leads to a weaker sheet of paper being formed.

Fibrillation of the fibre wall occurs when a swollen fibre is subjected to mechanical action.[170] The flexibility of the fibres is increased during refining as the outer cell wall is stripped away.[171] If refining is too energetic or proceeds for too long a period of time then the fibres will eventually be cut.[169] The stripping away of the fibre wall is known as external fibrillation. The external fibrillation of the fibres can be thought of as the fraying of a rope. As one thread begins to unwind then the strength of the rope is decreased.

The decrease in the freeness values is mainly due to fibrillation of the fibres. as seen in the photomicrographs 6.1.2, 8.3.14, 8.3.15. It was hypothesised in section 6.1 that the damage to fibres was due to the effect of cavitation bubbles. Whilst cavitation activity is a significant part of the overall effect produced by ultrasound its importance decreases at higher temperatures.

The gradual, continuous reduction in CSF values found for temperature range 4 and to a lesser degree range 3 cannot be due to cavitation activity as the temperatures involved are at or beyond the upper limit of cavitation. The question arises as to what other ultrasound effect could cause a decrease in freeness?

The acoustic pressure produced by an ultrasound wave may be the answer. The acoustic pressure alternates at the frequency of the ultrasound and results in rapid local accelerations as the particles or liquid experience changes in compression and expansion. The local acceleration experienced by a particle is given by the equation 9.1.

$$g = 2\pi f(2I/\rho_0 c)^{1/2} \qquad \text{eqn 9.1}$$

where f = frequency
I = power density of horn (Wcm^{-2})
ρ_0= density of water, ($1000kg\ m^{3}$)
c = speed of sound, ($1480\ ms^{-1}$)

Under the conditions used in this study ($I=20\ Wcm^{-2}$), the amplitude of the variable acceleration will be $4.2 \times 10^{6}\ ms^{-2}$. This acceleration is of the same order as that achieved in modern ultracentrifuges. As paper fibres are subjected to this force approximately 40.000 times a second the local acceleration due to ultrasound is very large.

The fibres are subjected to alternate compression and decompression cycles: this will contract and restore the fibre across its narrow aspect, as shown in figure 9.2.3.

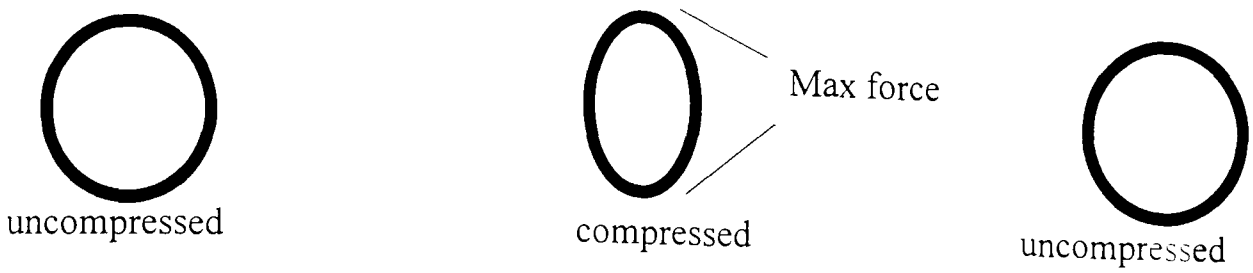


Figure 9.2.3 **Changes in diameter of fibre during sonication**

The interaction with ultrasound changes the effective diameter of the fibre. The diameter of the fibre does change during its lifetime, but these changes are very much slower than the changes undergone during sonication.. The fibre wall can undergo changes during drying but these changes take minutes or hours to accomplish.

In addition the fibre is also subject to the acoustic pressure. Using the same conditions as described above, the acoustic pressure developed by the ultrasonic horn in this study is 7.6 bar. (section 7).

This pressure also acts on the wall of the fibre, placing stresses on it which are transmitted to the component polysaccharide chains.

The acoustic pressure acting upon the fibres stresses them, and exerts maximum force at their edges as shown in figure 9.2.3. The alternating pressure leads to a change in the wall structure. The force exerted at the outer edges of the fibre is repeated with such rapidity that it is sufficient to cause the fibrils of the fibre to begin to unravel. The unravelling fibrils lead to an increase in the surface area of the fibre which is indicated by decreasing freeness values. The wall of the fibre may also contribute to the increase in surface area as voids are formed its surface due to the stresses placed on it. The increase in surface area should lead to an increase in hydrogen bonding between the fibres. Figure 9.2.4 shows the burst index for 60gsm handsheets made with the virgin Arracruz fibres used in section 6. The burst index takes into account variations in grammage. Sonication increased the burst strength of the fibres but in parallel with measured CSF values, the effect levelled off with sonication time.

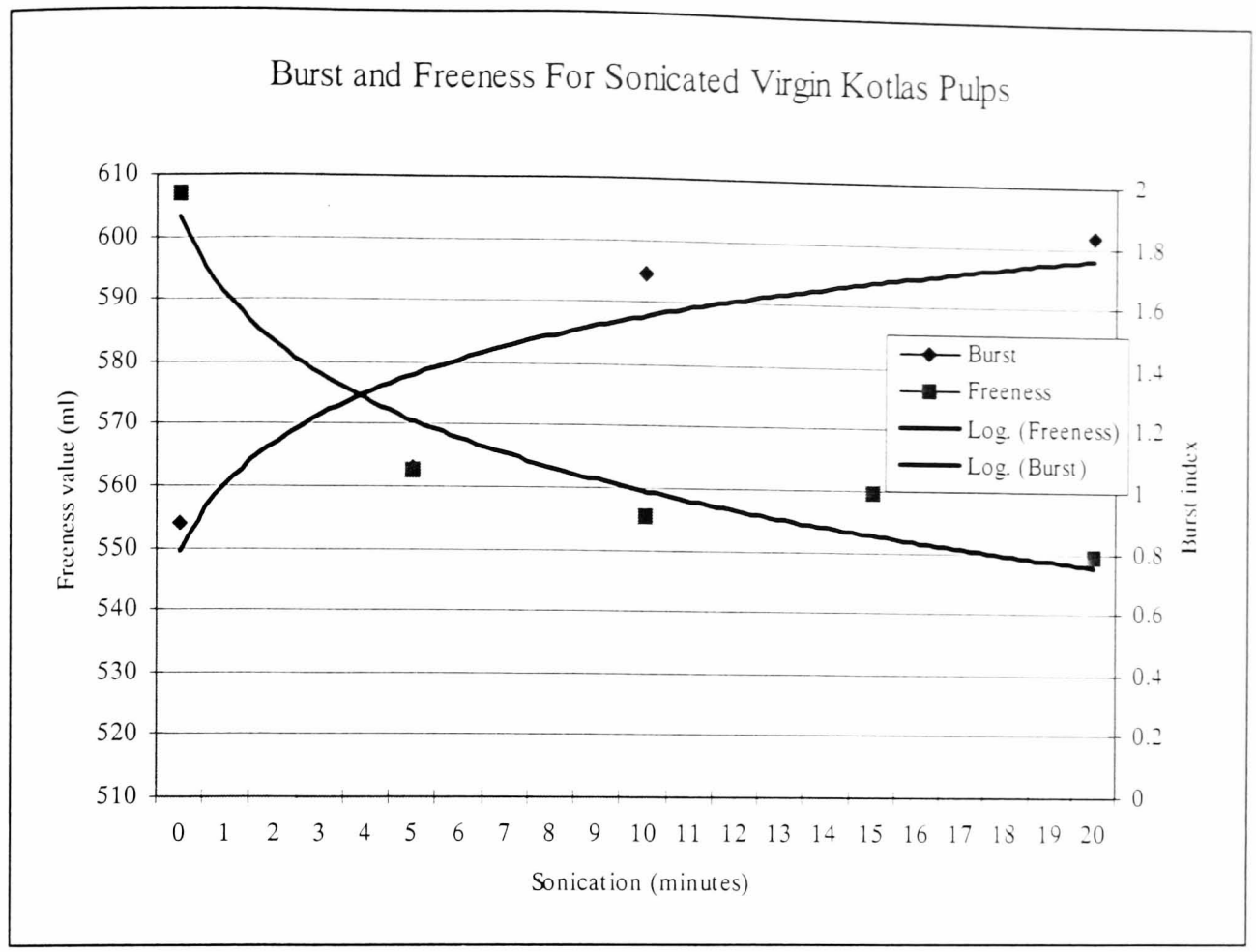


Figure 9.2.4 Burst index and Freeness for Sonicated Virgin Arracruz Fibres

Additionally the burst index increased at the same rate that the freeness decreased. Both burst and freeness values reached a plateau at 20 minutes sonication. The trend-lines included within figure 9.2.4 are both exponential. The freeness decreased rapidly at first then slowed down as sonication proceeded.

Shown in figure 9.2.5 is the burst index for 60 gsm handsheets prepared from pulp described in section 7. The burst index also increased for these samples, however, the increases came about after shorter exposure to ultrasound.

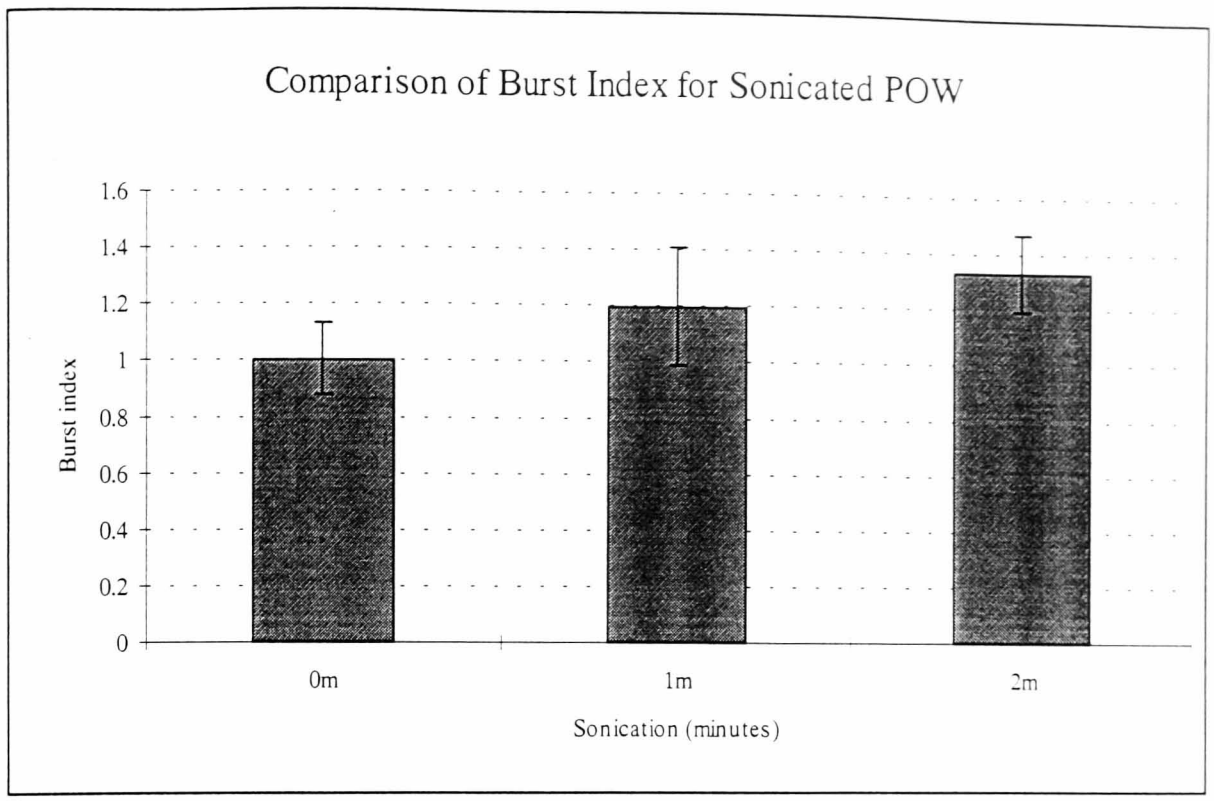


Figure 9.2.5 Burst index for Sonicated Prepared Office Waste

These fibres had been previously refined, which begins the process of fibrillation, and the additional treatment with ultrasound has exacerbated the fibrillation and caused the increase in burst strength.

In conclusion,

Sonication of the virgin fibres did not cut them, but the deformation of the fibre wall leads to an increase in fibrillation, a decrease in freeness, and a related increase in bonding between the fibres.

The fibrillation of the fibres came about by the action of ultrasonic waves on the cell wall, disrupting cellulose chains and partially unravelling them. Ultrasound did not cause cutting of the fibres, which retained their length, thus decreasing the probability of loss during recycling.

There was damage caused to the fibres during sonication, but this appeared to be limited to fibrillation, which actually lead to an increase in the strength properties of papers made from these fibres.

9.3.0 Ultrasound action on Fused Toner Particles - Conclusions

It was seen in early work that ultrasound could change the particle size distribution of toner particles. The early systems used, described in section 7.3 to 7.6, attempted to quantify the exposure to ultrasound required to change the distribution. These experiments simplified the problem of mixed office waste by using a single toner system and one type of paper in order to reduce some of the errors produced by repulping a variable mix of paper and toner. Unfortunately the toner chosen broke down into small particles that made detection and counting of the particles very slow. Attempts were made to reduce the number of particles present (section 7.5) but the techniques used were either inefficient at toner removal or else removed fibres.

Subsequent experiments were carried out using a mix of paper that included different toner formulations, all printed on uncoated paper. To investigate the detachment of toner particles using ultrasound a washing technique was adapted. This provided a simple, quick and effective method of removing detached particles on a laboratory scale but was impractical on a larger scale as too much water was required. The questions that were asked at the beginning of the discussion were:-

i) Are the toners broken down by ultrasound in a similar way at all temperatures or do the physical properties of the toner have any bearing on the nature of their break-up?

ii) Are the toner particles detached from the fibres by ultrasound or do they remain attached until the particle is small enough to interact with the cavitation bubble directly?

9.3.1 Break-up of Toner Particles

In response to the first question it would appear that the particles are acted upon by ultrasound while still attached to the fibres. At all temperatures investigated particles were still detected after sonication and hyperwashing. Since they were not removed the particles must have been strongly attached to fibres. It is likely that the particles shield the fibres from the affects of ultrasound, and so the fibre is not subjected to the local

accelerations discussed in section 9.1. If these local accelerations did affect the fibre it would be expected that the toner would be released as the fibre vibrated.

This did not occur as attached particles were detected after hyperwashing for all ultrasound treatments investigated. Shown in figure 9.3.1 is a comparison of particles in the 100 micron category removed by hyperwashing after sonication. The plots have a trendline fitted, which is logarithmic. The numbers of particles removed increased after sonication but up to a limiting number. This limiting number decreased as the temperature of the pulp decreased.

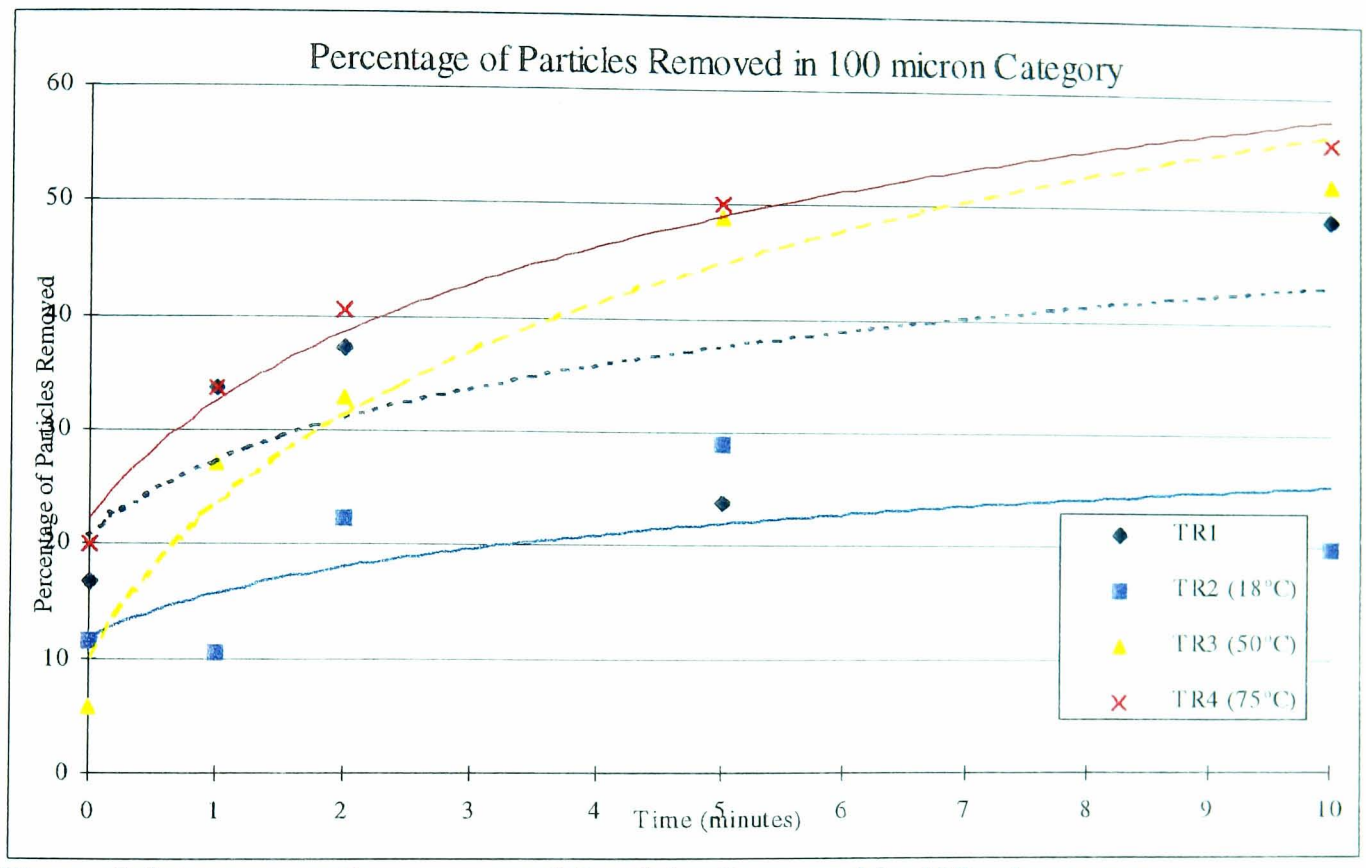


Figure 9.3.1 Percentage of Particles Removed in 100 micron range

Thus, the breakdown of the toner did not occur at the same rate for all temperatures. Examining the two extremes of temperature, namely temperature ranges 2 and 4, which were performed at approximately 18°C and 75°C respectively, a difference could be seen in the distributions after hyperwashing. The percentage of particles removed from the pulps was lowest for temperature range 2, the lowest temperature. The higher temperature ranges gave consecutively higher removal percentages. The curves for temperature ranges 1, 3, and 4 all follow similar paths. This indicated that the temperature is not important once the glass transition temperature of the toner had been approached. The same data was plotted on a log scale, see figure 9.3.2.

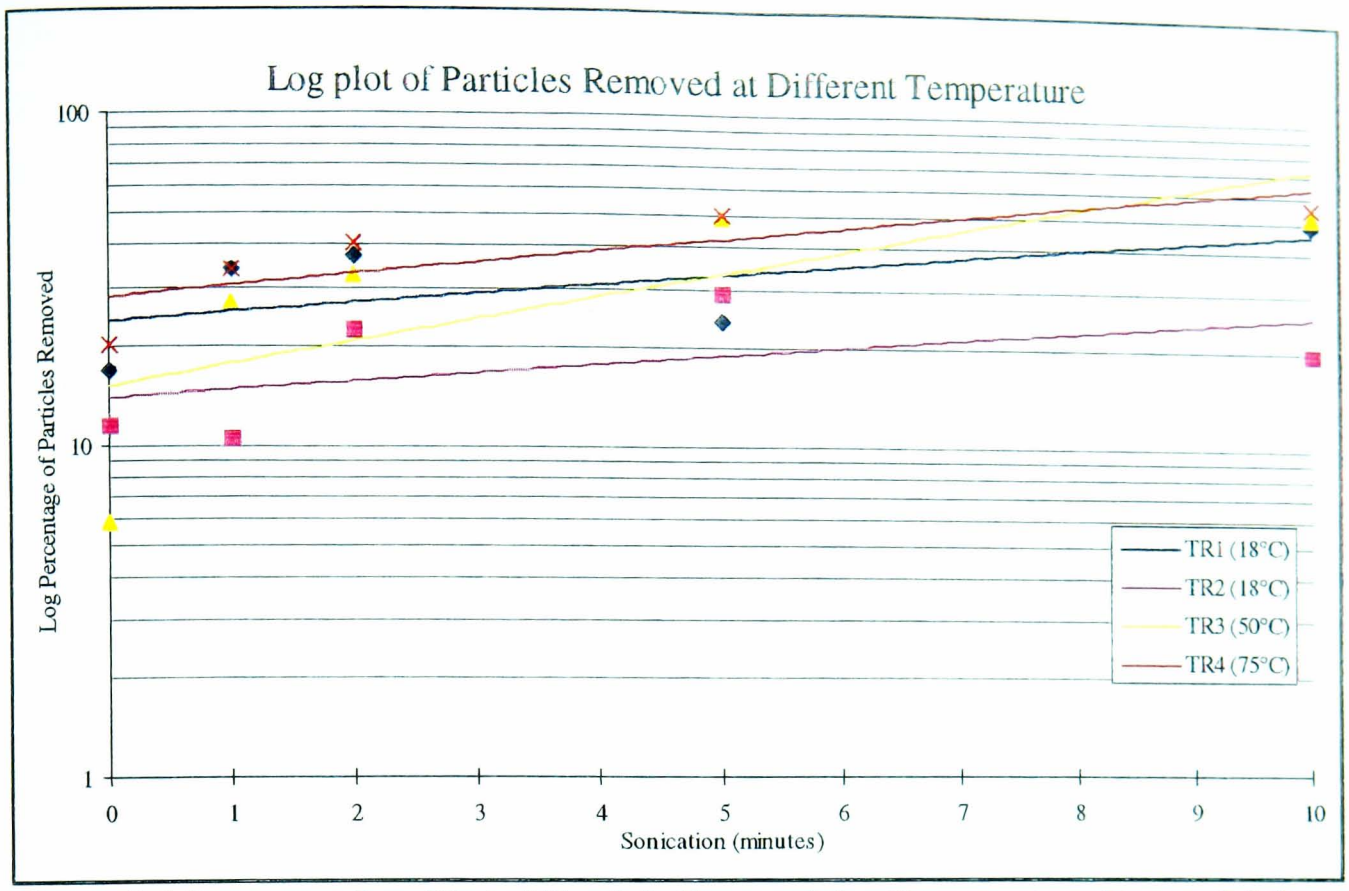


Figure 9.3.2 **Log Plot of Particle Removal for Temperature Ranges1,2,3, and 4 for 100 micron Category**

The gradient of each line varied with the temperature. Range 2 was performed at the lowest temperature, and had the shallowest slope. Ranges 3 and 4 were performed at higher temperatures and had steeper gradients. Examining the 25 micron category, which included particles from 0 to 25 microns figure 9.3.3 was produced.

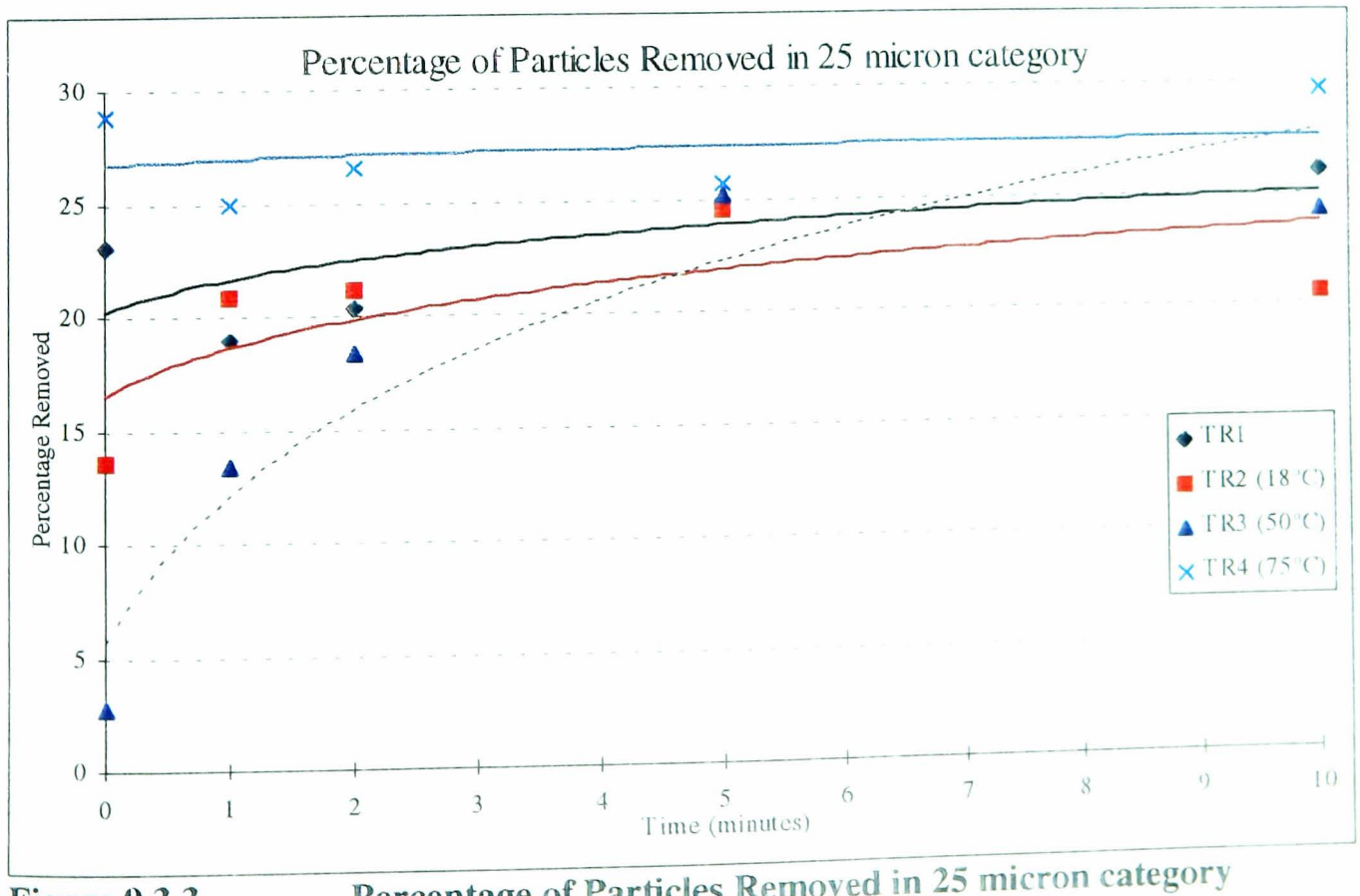


Figure 9.3.3 **Percentage of Particles Removed in 25 micron category**

The glass transition temperature of the toner is between 66 and 72°C. The numbers of toner particles removed was greatest in the highest temperature range, range 4 and the lowest removal rate was in temperature range 2 (low temperature). Clearly, the temperature of the pulp did have an effect on the effectiveness of deinking of toners from fibres. Temperature ranges 1, 2 and 4 all have similar gradients in figure 9.3.4, the exception being range 3 which has a steeper gradient.

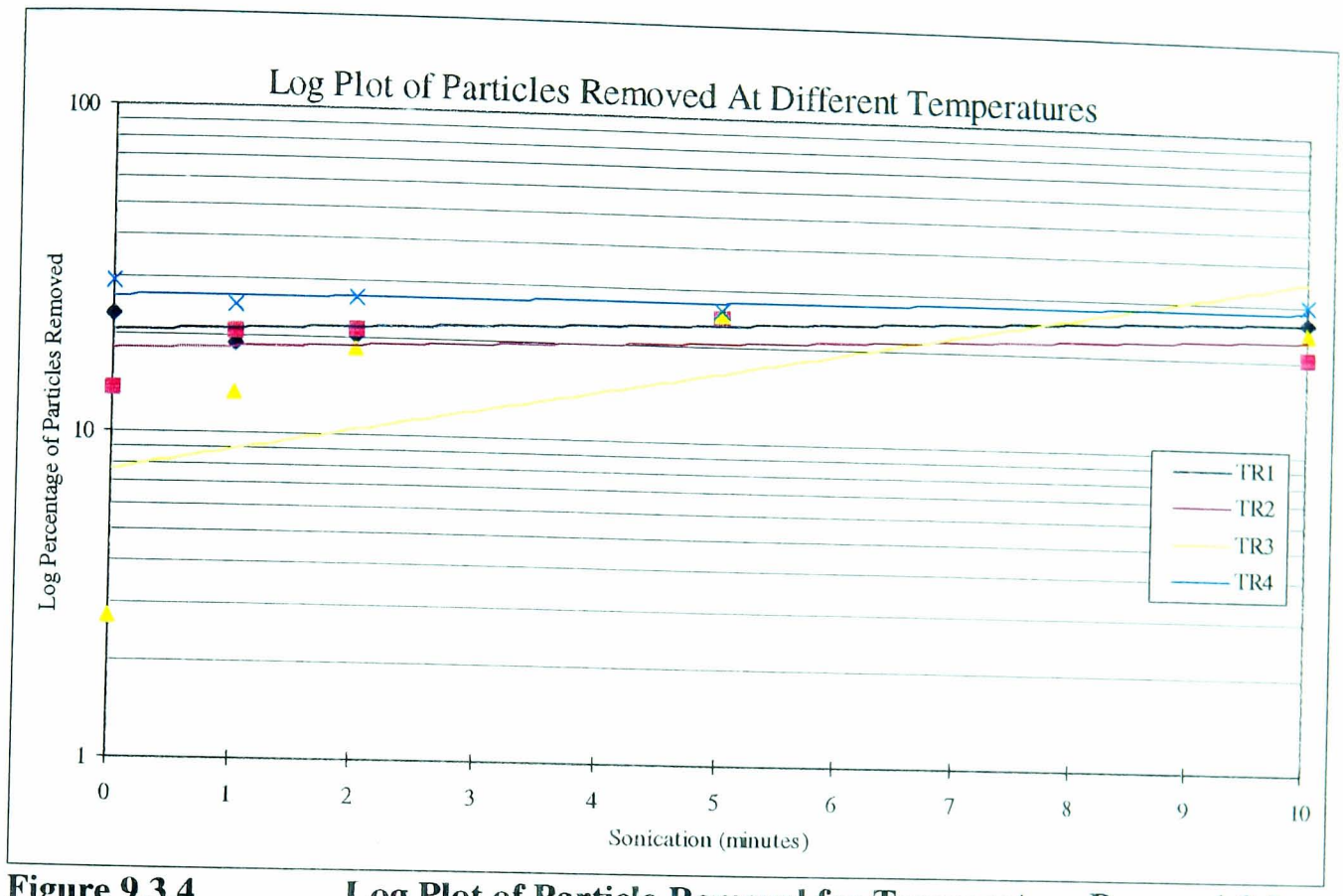


Figure 9.3.4 **Log Plot of Particle Removal for Temperature Ranges 1,2,3, and 4 for 25 micron Category**

At lower temperatures the toner particle is relatively hard and brittle. On interacting with rigid particles the acoustic pressure displacement will cause the toner particle to crack and shatter as it is below its glass transition temperature. An analogy is that of toffee, another polymeric material, which cracks and splits when struck with a hammer. The cracking will not necessarily lead to removal of the large toner particles and these will still be attached to fibres. It may however lead to the release of small shard-like pieces.

More efficient removal of toner at higher temperature must be due to the changed physical characteristics of the toner. The toner becomes more pliable and less brittle as the temperature increases. Forces applied to the toner particle by the acoustic pressure wave would be more likely to shear than to crack or resonate it. This is because the toner is softer and more pliable at the higher temperatures. Ultrasound interaction with soft,

pliable particles would be more likely to break them up than the interaction with hard, rigid particle.

9.3.2 Toner Particle Detachment

To answer the second question, concerning the removal of toner particles after break down, the particles could be removed by the interaction of a cavitation bubble with the toner particle. Cavitation bubbles have been discussed in greater detail in section 2.4.4. A cavitation bubble can be formed on any surface present in the liquid. Collapsing cavitation bubbles produce radicals and collapse occurs near a solid surface. An asymmetric jet of liquid can be propelled at high speed, (~400 km/hr), toward the surface. (jet streaming)

9.4 Further Work

The work undertaken was performed in a batch-wise process. To facilitate the application of the method to an industrial situation it would have to be done in a continuous process. To investigate a continuous flow sonication would require the use of an annular ultrasound horn. This type of horn has an aperture in the centre of a titanium ring. This design focuses the ultrasound energy into a small area, leading to very intense ultrasound energy being released into the centre of the horn. Several of these horns employed in series, possibly operating at different frequencies would improve the breakdown of different sizes of ink and toner particles before their removal using conventional processes.

Higher power transducers could be used to investigate the deinking of mixed office waste. New transducer materials for example, Terfenol, a mix of lanthanide materials work on the magnostrictive principle. These materials can produce large deformations and greater cavitation activity. Their use was restricted due to problems in crystal growth. but they are now becoming larger and more powerful.

With sufficient power, sonication of the fibre suspension could be used to refine, allowing the pulp suspension to flow though a pipe, where it is sonicated, and then onto the paper machine. The drainage of the pulp on the wire is monitored using the point where the wet line disappears. Sonication power could be increased or decreased to bring this line into

the correct position, in combination with reduction in refining power. Such a method would maximise fibrillation necessary for good papermaking whilst minimising fibre damage during refining.

Regarding the fibrillation and decrease in freeness of the fibres, further investigations of the effect of ultrasound on the cell wall of papermaking fibres could be undertaken. The surface modification of the fibres should be explored in greater detail. Size exclusion chromatography is a technique used to determine the size of voids in the fibres wall. The structure and chemistry of the cell wall is a vital part of the bleaching process. Use of this technique to see if voids in the fibres get larger after sonication or if sonication produces a new fibre surface would be a next step.

In addition a study could be made into the use of ultrasound to assist in the bleaching process, by driving bleaching chemicals into the fibres wall where they will be more effectively used. The cell wall of the fibre is the point where bleaching of the fibre occurs, and sonication appears to affect this area. By forcing the bleaching chemicals into areas where they will be best used, a greater bleaching effect could be seen or at least the same brightness achieved with less chemical usage.

Ultrasound can alter the zeta potential of fibres. Changing the surface charge may improve the adhesion of fillers to fibres, thus increasing their opacity. Fillers can stick to fibres by simple attraction between the polar surface of the clay and the surface of the fibre. Increasing the charge on the fibre may attract more filler particles, and lead to a greater retention rate of the filler, and a more effective use of this expensive additive.

Overall, it has been shown that ultrasound has the ability to implement many changes to fibres and particles without the addition of chemicals. It has been demonstrated that the time spent by each fibre or cubic centimetre of pulp, under the horn and subject to cavitation is very short ~2 seconds for 1 minute sonication. Fibres are not cut but are fibrillated, leading to an increase in strength properties, fused toner particles are broken down to smaller size distributions.

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Appendices

Appendix 1 Temperature Range 1 Data

In this data zero (0) indicates that there were no particles detected, a dash (-) indicates that the handsheet data was unreadable or the handsheet was not measured due to damage.

Number of Particles counted for batch 1

	Particle size ranges in microns																			
Ultrasound	0 to 25				25 to 100				100 to 250				50 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	43	32	63	67	60	57	63	61	27	38	35	31	12	14	16	17	12	6	5	4
1 minute	66	54	65	-	123	115	115	-	38	45	31	-	5	5	4	-	5	4	3	-
2 minute	112	132	134	73	153	222	233	151	21	34	43	33	0	2	1	3	1	1	0	0
5 minute	99	90	133	119	236	222	246	246	13	17	19	18	0	1	1	0	0	0	0	0
10 minutes	225	199	376	288	288	296	428	324	13	15	14	11	0	0	0	0	0	0	0	0

Number of Particles counted for Hyperwashed batch 1

	Particle size ranges in microns (Hyperwashed)																		
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450		
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3
0 minutes	30	19	49	42	31	19	28	23	34	28	30	25	11	7	9	7	10	3	5
1 minute	9	11	37	10	19	22	35	12	21	31	24	17	3	10	8	11	3	6	2
2 minute	28	19	27	19	60	41	48	55	18	19	19	18	2	1	1	1	0	0	0
5 minute	14	15	18	25	40	58	50	42	7	17	2	4	0	3	0	1	0	0	0
10 minutes	56	42	50	-	85	98	94	-	5	8	4	-	0	0	0	-	0	0	0

Appendix 1 Temperature Range 1 Data

Number of Particles counted for batch 2

	Particle size ranges in microns																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	131	146	54	-	53	53	31	-	36	39	27	-	9	13	9	-	11	11	9	-
1 minute	109	134	109	-	133	177	159	-	28	28	37	-	2	3	3	-	2	0	0	-
2 minute	91	153	130	99	195	202	169	162	17	22	17	17	3	1	4	2	0	0	2	0
5 minute	96	194	108	-	216	261	194	-	8	11	9	-	0	0	1	-	0	0	0	-
10 minutes	197	128	175	68	266	257	302	228	5	8	9	4	0	0	0	0	0	0	0	0

Number of Particles counted for Hyperwashed batch 2

	Particle size ranges in microns																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minute	25	15	18	13	23	13	40	29	39	44	51	30	9	19	12	12	7	3	8	7
1 minute	41	21	27	20	60	50	44	51	31	33	29	25	3	4	4	7	3	3	5	4
2 minute	18	19	73	-	44	54	79	-	16	18	31	-	5	3	7	-	3	3	4	-
5 minute	41	40	31	23	48	75	75	66	12	6	11	10	1	2	2	1	0	2	0	2
10 minutes	21	12	15	25	24	46	33	62	6	12	2	6	1	0	1	2	0	0	1	1

Appendix 1 Temperature Range 1 Data

Number of Particles counted for batch 3

	Particle size ranges in microns																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	63	49	66	-	75	73	59	-	42	46	45	-	12	8	8	-	6	5	4	-
1 minute	79	54	61	-	150	136	172	-	23	41	36	-	7	7	1	-	0	1	1	-
2 minute	83	88	74	48	204	185	189	175	25	26	23	45	2	0	0	3	1	1	0	2
5 minute	147	128	92	99	317	280	273	290	16	21	13	15	0	0	0	0	0	0	0	0
10 minutes	101	144	111	141	234	257	243	272	4	3	1	1	0	0	0	0	0	0	0	0

Number of Particles counted for Hyperwashed batch 3

	Particle size ranges in microns (Hyperwashed)																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	25	15	18	13	23	13	40	29	39	44	51	30	9	19	12	12	7	3	8	7
1 minute	41	21	27	20	60	50	44	51	31	33	29	25	3	4	4	7	3	3	5	4
2 minute	18	19	55	-	44	54	65	-	16	18	31	-	5	3	7	-	3	3	4	-
5 minute	41	40	31	23	48	75	75	66	12	6	11	10	1	2	2	1	0	2	0	2
10 minutes	21	12	15	25	24	46	33	62	6	12	2	6	1	0	1	2	0	0	1	1

Appendix 2 Temperature Range 2 Data

In this data zero (0) indicates that there were no particles detected, a dash (-) indicates that the handsheet data was unreadable or the handsheet was not measured.

Number of Particles counted for batch 1

	Particle size ranges in microns																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	45	39	48	56	64	68	65	59	34	40	19	24	14	5	9	11	2	3	3	4
1 minute	83	76	90	96	110	72	133	106	20	27	17	28	2	4	2	3	2	0	2	1
2 minute	109	74	104	123	168	121	119	209	26	16	16	30	3	0	1	1	1	0	0	0
5 minute	119	150	120	169	146	224	182	177	4	13	13	7	0	1	0	1	0	0	0	0
10 minutes	296	189	136	261	334	204	169	293	5	3	2	1	0	0	0	0	0	0	0	0

Number of Particles counted for Hyperwashed batch 1

	Particle size ranges in microns (Hyperwashed)																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	45	41	34	29	47	55	55	43	42	41	41	42	7	3	6	8	9	6	5	5
1 minute	33	26	44	38	93	97	95	81	26	26	27	32	1	3	7	5	3	4	1	2
2 minute	35	43	48	42	104	125	111	84	18	21	15	18	3	1	1	0	0	0	0	0
5 minute	44	36	57	78	109	109	134	70	11	5	7	5	0	0	0	0	0	0	0	0
10 minutes	39	45	65	33	93	79	77	53	3	2	1	0	0	0	0	0	0	0	0	0

Appendix 2 Temperature Range 2 Data
Number of Particles counted for batch 2

	Particle size ranges in microns																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	47	45	50	83	66	69	83	95	28	28	27	41	7	7	11	6	6	4	7	6
1 minute	75	108	109	108	139	91	129	97	34	22	37	26	3	5	4	6	6	1	4	1
2 minute	155	117	74	79	192	169	89	153	25	14	20	25	2	2	3	0	0	0	1	0
5 minute	117	106	98	121	211	194	160	149	10	6	7	2	1	0	0	0	0	0	0	0
10 minutes	169	94	98	87	206	87	144	84	4	1	1	3	0	0	0	0	0	0	0	0

Number of Particles counted for Hyperwashed batch 2

	Particle size ranges in microns (Hyperwashed)																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	22	30	47	37	35	40	69	62	31	28	34	32	10	4	3	6	3	4	6	5
1 minute	41	57	45	31	53	110	90	81	21	34	40	27	5	7	2	4	1	3	4	2
2 minute	45	47	20	23	134	109	37	59	25	19	5	19	3	0	1	2	2	2	0	0
5 minute	41	32	36	38	80	56	66	65	6	3	1	6	0	0	0	0	0	0	0	0
10 minutes	32	44	34	32	83	63	36	45	1	1	0	0	0	0	0	0	0	0	0	0

Appendix 2 Temperature Range 2 Data
Number of Particles counted for batch 3

	Particle size ranges in microns																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	42	42	49	55	63	52	63	46	32	27	11	29	3	7	8	5	5	7	9	3
1 minute	66	62	87	47	91	91	102	114	11	21	21	25	3	2	3	7	1	1	3	5
2 minute	73	104	50	59	92	114	105	166	12	14	8	17	2	2	2	3	0	0	0	0
5 minute	172	122	175	84	162	157	242	105	4	11	12	4	1	1	0	0	0	0	0	0
10 minutes	140	94	194	86	170	125	264	126	3	3	7	1	0	0	0	0	0	0	0	0

Number of Particles counted for Hyperwashed batch 3

	Particle size ranges in microns (Hyperwashed)																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	14	13	19	13	30	50	51	39	32	39	29	28	4	2	5	4	2	3	4	4
1 minute	34	40	28	40	67	79	75	74	28	23	22	21	6	1	2	3	2	2	1	1
2 minute	53	49	67	-	110	90	51	-	25	15	14	-	4	2	2	-	0	0	0	-
5 minute	35	98	36	-	107	115	109	-	8	10	16	-	0	0	0	-	1	0	0	-
10 minutes	100	32	40	53	132	82	84	88	6	1	2	3	0	0	0	0	0	0	0	0

Appendix 3 Temperature Range 3 Data

In this data zero (0) indicates that there were no particles detected, a dash (-) indicates that the handsheet data was unreadable or the handsheet was no measured.

Number of Particles counted for Batch 1

No of particles counted	Particle size ranges in microns																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	22	25	20	14	22	31	37	23	25	30	22	22	8	6	9	3	6	6	5	7
1 minute	69	72	41	64	108	128	91	94	26	25	29	17	2	4	1	3	2	1	0	1
2 minute	86	105	101	33	121	176	112	128	7	11	12	18	0	2	1	0	0	0	0	0
5 minute	67	57	51	39	155	189	134	133	6	3	4	6	0	0	0	0	0	0	0	0
10 minutes	-	48	50	65	-	90	98	168	-	53	25	13	-	0	0	0	-	0	0	0

Number of Particles counted for Hyperwashed Batch 1

No of particles counted	Particle size ranges in microns (Hyperwashed)																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	25	16	13	53	23	20	35	33	28	32	36	28	9	6	8	11	6	3	3	4
1 minute	18	27	17	34	51	65	52	53	37	28	14	25	-	4	2	0	0	0	1	3
2 minute	15	24	22	27	71	67	81	51	10	15	9	5	1	1	1	0	0	0	0	0
5 minute	18	16	29	17	35	42	54	57	3	3	7	0	0	0	0	0	0	0	0	0
10 minutes	15	13	11	-	20	39	29	-	1	1	0	-	0	0	0	-	0	0	0	-

Appendix 3 Temperature Range 3 Data
Number of Particles counted for Batch 2

No of particles counted	Particle size ranges in microns																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	17	29	28	14	39	35	24	21	28	22	32	24	12	8	11	13	8	6	5	4
1 minute	56	39	21	37	84	77	54	89	24	25	37	35	3	3	2	6	5	1	1	1
2 minute	35	67	53	-	122	115	141	-	16	26	19	-	2	1	1	-	0	0	1	-
5 minute	78	47	56	55	170	170	148	152	11	4	4	5	0	0	0	0	0	0	0	0
10 minutes	71	55	55	58	106	120	139	138	1	1	0	0	0	0	0	0	0	0	0	0

Number of Particles counted for Hyperwashed Batch 2

No of particles counted	Particle size ranges in microns (Hyperwashed)																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	31	8	15	19	25	15	17	14	30	29	31	23	14	10	6	13	4	2	2	3
1 minute	36	23	21	20	61	44	59	25	32	22	30	12	5	5	3	2	3	2	0	0
2 minute	29	20	32	68	98	74	83	62	36	21	22	33	2	1	1	4	1	1	0	0
5 minute	12	15	22	12	37	41	49	37	2	4	6	2	0	1	0	0	0	0	0	0
10 minutes	9	13	29	11	11	24	29	22	0	0	2	0	0	0	0	0	0	0	0	0

Appendix 3 Temperature Range 3 Data
Number of Particles counted for Batch 3

No of particles counted	Particle size ranges in microns																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	16	48	33	27	22	36	19	26	23	34	23	29	8	9	13	6	11	7	9	10
1 minute	61	63	45	32	136	121	90	103	28	37	20	37	4	1	4	2	0	0	0	0
2 minute	45	60	65	227	123	129	170	221	9	19	20	30	0	0	0	0	0	1	0	0
5 minute	68	145	83	78	128	171	238	194	2	14	4	5	0	0	0	0	0	0	0	0
10 minutes	51	68	62	37	90	107	99	66	0	1	0	1	0	0	0	0	0	0	0	0

Number of Particles counted for Hyperwashed Batch3

No of particles counted	Particle size ranges in microns (Hyperwashed)																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	29	12	24	17	26	19	18	24	29	34	37	33	11	4	9	3	4	4	5	6
1 minute	30	44	19	23	52	51	31	47	22	31	18	19	3	6	4	4	3	1	2	2
2 minute	44	47	33	37	44	36	46	42	9	17	10	15	5	4	3	4	2	1	4	0
5 minute	14	19	34	27	44	30	29	35	10	2	4	3	1	1	0	0	0	0	0	0
10 minutes	6	9	13	11	10	13	19	24	0	0	0	2	0	0	0	0	0	0	0	0

Appendix 4 Temperature Range 4 Data

In this data zero (0) indicates that there were no particles detected, a dash (-) indicates that the handsheet data was unreadable or the handsheet was not measured.

Number of Particles counted for Batch 1

	Particle size ranges in microns																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	115	52	75	65	55	36	42	43	38	33	38	40	18	14	9	11	2	4	3	10
1 minute	70	100	106	69	119	143	170	110	43	41	51	31	3	0	0	3	0	1	1	0
2 minute	261	102	275	66	345	196	372	146	69	29	74	17	1	1	0	1	0	0	0	0
5 minute	66	147	91	115	233	285	237	237	19	12	23	16	1	0	0	0	0	0	0	0
10 minutes	244	155	162	130	465	297	314	250	52	25	21	21	0	0	0	0	0	0	0	0

Number of Particles counted for Hyperwashed Batch 1

	Particle size ranges in microns (Hyperwashed)																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	17	17	12	24	23	22	24	16	61	52	45	51	12	15	25	15	6	7	3	3
1 minute	16	19	18	26	45	50	69	67	48	56	56	62	0	1	1	2	0	0	0	0
2 minute	15	18	16	19	69	56	79	91	35	40	30	39	0	0	0	1	0	0	0	0
5 minute	10	12	11	14	77	74	81	83	9	9	8	25	0	0	0	0	0	0	0	0
10 minutes	6	14	12	18	43	32	30	26	9	2	2	7	0	0	0	0	0	0	0	0

Appendix 4 Temperature Range 4 Data
Number of Particles counted for Batch 2

	Particle size ranges in microns																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	68	39	46	50	29	35	39	50	34	47	31	42	23	15	23	15	6	13	9	12
1 minute	97	59	71	70	195	120	158	140	65	57	56	57	4	6	8	3	1	2	0	0
2 minute	56	176	238	115	187	307	307	203	52	59	76	51	5	0	1	2	0	4	0	0
5 minute	92	160	96	186	282	301	325	402	37	71	52	58	0	0	0	0	0	0	0	0
10 minutes	178	100	96	152	329	279	267	341	19	14	22	16	0	0	0	0	0	0	0	0

Number of Particles counted for Hyperwashed Batch 2

	Particle size ranges in microns (Hyperwashed)																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	33	27	23	23	16	15	21	21	45	45	47	59	22	14	19	20	6	5	6	6
1 minute	17	26	22	21	63	84	66	69	42	62	61	72	2	2	2	6	1	0	1	1
2 minute	14	18	20	19	60	92	70	66	29	32	28	28	5	2	4	2	0	1	1	2
5 minute	12	16	27	17	54	49	71	53	18	6	22	21	0	0	0	0	0	0	0	0
10 minutes	10	22	13	10	49	53	41	56	2	11	5	6	0	0	0	0	0	0	0	0

Appendix 4 Temperature Range 4 Data
Number of Particles counted for Batch 3

	Particle size ranges in microns																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	125	-	45	50	138	-	55	60	66	-	59	58	13	-	14	17	4	-	1	3
1 minute	208	-	143	142	324	-	208	241	58	-	41	45	2	-	2	2	0	-	0	2
2 minute	116	142	172	215	267	334	377	385	32	47	38	56	0	0	0	0	0	0	0	0
5 minute	206	169	103	150	348	300	227	320	18	15	10	13	0	0	0	0	0	0	0	0
10 minutes	312	159	191	197	518	298	285	374	5	7	5	5	0	0	0	0	0	0	0	0

Number of Particles counted for Hyperwashed Batch 3

	Particle size ranges in microns (Hyperwashed)																			
Ultrasound	0 to 25				25 to 100				100 to 250				250 to 450				Larger than 450			
	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
0 minutes	35	23	27	28	20	17	26	25	55	58	52	51	14	12	17	16	4	3	2	3
1 minute	45	23	49	19	79	66	70	55	31	30	32	16	1	1	2	2	1	0	0	0
2 minute	67	65	39	37	86	113	78	64	12	16	16	11	0	0	0	0	0	0	0	0
5 minute	20	14	15	18	64	71	58	42	7	4	1	6	0	0	0	0	0	0	0	0
10 minutes	17	11	16	11	28	27	36	27	0	0	1	2	0	0	0	0	0	0	0	0

Appendix 5

A.5.0 Paper production

During paper manufacture virgin and recycled fibres are formed into a web mat.[1,2,3] The manufacturing processes for both fibres are the same, only the original source differs. A brief description of the paper production process is included in this appendix.

A.5.1 Preparation of virgin fibre.

The main raw material used in paper manufacturer is pulp and the majority of the world's pulp is produced from wood fibre.[4] Only a small percentage, approximately 5%, is produced from annual crops.[5] Fibres from these annual crops are known as non-wood fibres, examples include bagasse and esparto grass whilst bamboo fibres are used in tropical countries. Cotton and manila fibres have been traditionally used to make banknotes,[5] papers made with these fibres are exceptionally strong and durable.

The trees used for paper production are managed like any other crop, with a longer period before the return on capital invested is realised. Many more trees are planted than harvested, they are tended and managed throughout their life cycle from seedlings to harvesting.

Trees that are used in the manufacture of paper are usually harvested soon after they reach their maximum size. Once the bark is removed from the tree it is reduced to small pieces known as chips. The chips are screened to remove oversized pieces and knotty material. Other woody material such as wood shavings and sawdust may be added. At this point the wood chips comprise cellulose, hemicellulose and lignin.

Cellulose is a naturally occurring polymer, the structure of which was elucidated in 1923[6] by Purves shown in figure A.5.1.

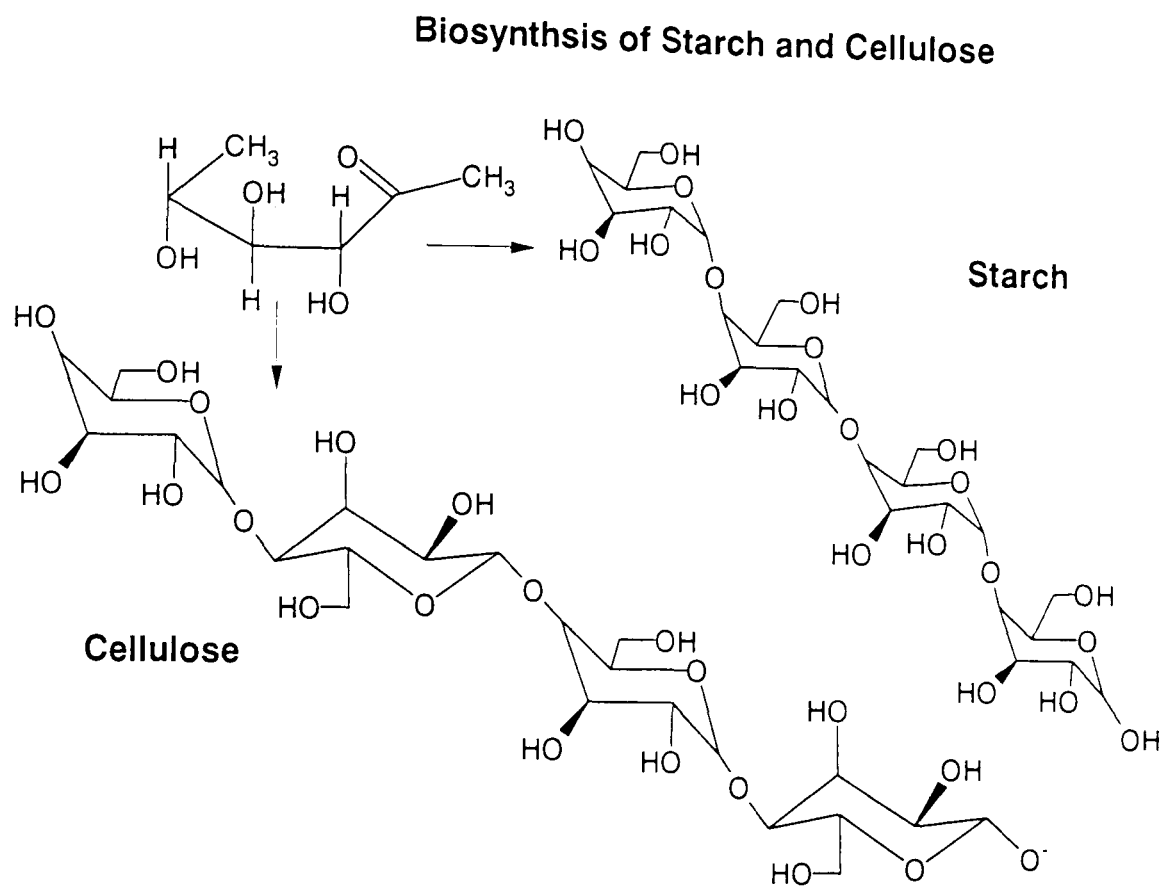
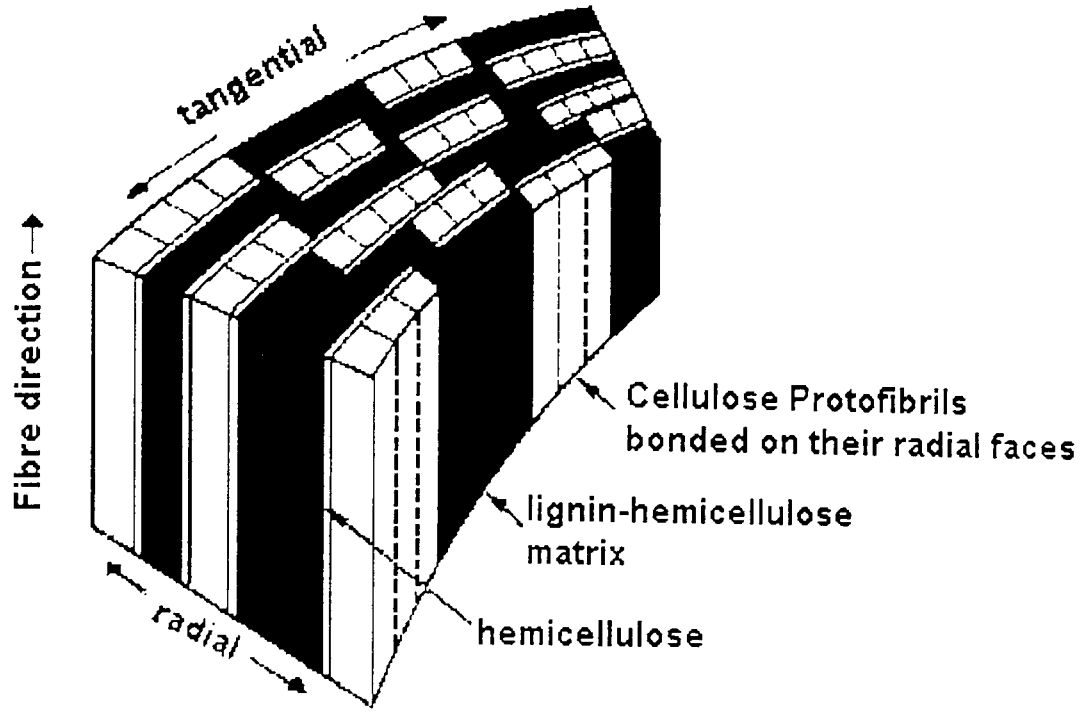


Figure A.5.1 Structure of Cellulose and Starch[7]

The empirical formula of cellulose is $C_6H_{10}O_5$.[8] Cellulose exists as fibres in woody plants, it is these fibres that are used in paper making. Hemicelluloses are branched polymers of the carbohydrate sugars xylose, arabinose, galactose, mannose and glucose. Hemicelluloses bind bundles of cellulose fibrils to form microfibrils, which enhance the stability of the cell wall. They also cross-link with lignin, creating a complex web of bonds which provide structural strength. Cellulose molecules can form hydrogen bonds between fibres giving the strength to the finished paper. Cellulose provides the tensile strength of the fibre, and hemicellulose can be thought of as a 'cement' binding the fibres together.



Schematic representation of the ultrastructural arrangement of Cellulose, lignin and hemicellulose in the fibre wall of black spruce tracheids.

Figure A.5.2 Structure of Cellulose Hemicellulose and Lignin in Cell wall[9]

Lignin is a very complex natural polymer with many random couplings, the exact chemical structure is not known. The physical and chemical properties of lignin vary depending on the extraction technology employed. For example, lignosulfonates are hydrophilic whilst Kraft lignins are hydrophobic.[10] Lignin is photochemically unstable and discolours on exposure to UV radiation and heat, turning a yellow colour. Paper made with fibres containing residual lignin will discolour on exposure to UV light.

Pulp can be made from fibres either where the lignin has been removed or where it is still present. Pulps that are manufactured from fibres containing lignin are known as 'mechanical pulps'; those made with fibres free from lignin are known as 'chemical pulps'.

Pulp fibres are obtained from trees - the tree species are divided into two groups, hardwoods and softwoods. In softwoods there is virtually one type of fibre with one length, hardwoods contain many different types of fibre with long, short and thick fibres being present. Fibres extracted from hardwoods are normally shorter than those extracted from softwoods.

Mechanical pulps are created by grinding fibres together in order to separate them. The major mechanical pulping processes are Stone Groundwood (SGW), Refiner Mechanical

(RMP), Thermomechanical (TMP), and Chemithermomechanical (CTMP). The various production conditions employed in each process results in different pulps being produced. These pulps will each be used to produce specific products. Generally, mechanical pulps are used for lower grade papers where permanence is not required. Mechanical pulps have low brightness, low strength, and contain relatively large amounts of shives, or fibre bundles. The shives are visible in the final sheet and detract from the overall quality by appearing as blotches. To address some of these issues of poor quality and in response to the increased demand for papers suited to four colour printing of newspapers, the improved grades mentioned above were introduced. Chemithermomechanical pulp undergoes treatment to remove part of the lignin and is bleached to produce a brighter final sheet. This produces a paper that is brighter and less prone to yellowing than traditional TMP but the brightness falls short of a chemical pulp. Introduction of these grades has widened the range of mechanical pulps allowing them into markets that were not previously open to them.

In chemical pulps the lignin has been removed from the pulp by using a combination of heat, pressure and chemical action. The wood chips are digested at elevated pressures and temperatures to dissolve the lignin from the wood chips. The resulting fibre contains the maximum amount of cellulose. The lignin that is removed is known as black liquor and has a significant calorific value. This black liquor is burned to generate energy which partially offsets the costs of heating the digestion vessel.

The major chemical pulping processes are the Kraft and sulphite process.[11] The sulphite process is carried out under acid, alkali, or neutral conditions. In the Kraft process the chips are chemically digested using a pulping liquor containing alkali and sulphur containing salts. This liquid dissolves the lignin and allows the fibres to be separated. After digestion the pulp is washed to remove the chemicals and the dissolved lignin related materials. Kraft digestion produces a pulp that is dark brown in colour which is unsuitable for printing and writing (PW) grades but is used in board and packaging grades. For use in printing and writing grades the Kraft pulp must be bleached, this is accomplished with oxidative chemicals. Traditionally chlorine based chemicals were used but recently these are being replaced by other bleaching techniques to decrease the effluent load and comply with legislation. Globally 80% of all pulp manufactured is from the Kraft (sulphate) process.[11]

The active reagents in the Kraft process are Sodium hydroxide (NaOH) and Sodium Suphide (Na_2S) that produce the hydroxide ion and hydrosulphide ion, respectively. The chemistry of the Kraft pulping liquor can be described as follows:-[9]

$$S^{2-} + HOH \rightleftharpoons SH^- + OH^- \qquad \text{eqn A.5.1}$$

$$SH^- + HOH \rightleftharpoons H_2S + OH^- \qquad \text{eqn A.5.2}$$

Since most of the inter-unit connections within lignin are ethers, their cleavage is a major part of the depolymerization reaction. Carbon-carbon bonds are quite stable and are not attacked in the reaction.

The Sodium Sulphite process, often known as the Sulphite process, is not as widely used as the Kraft process for economic reasons. The pulp produced is chemically purer than that from the Kraft process and is easier to bleach. The process is accelerated greatly by the addition of expensive anthraquinone. The reactions that occur during sulphite pulping are sulphonation, hydrolysis and condensation.

A.5.2 Paper manufacture

Once the fibres have been prepared they must be formed into paper or board. Paper is a web of fibres held together by hydrogen bonds.[12] The making of paper begins with the suspension of fibres in water, and papermaking can be thought of as the controlled removal of that water from the fibres. Sheets of finished paper typically contain between 5 and 10% water, depending on the relative humidity of the atmosphere.

Paper machines vary considerably in their size and design, the largest machine in the UK is at Aylesford Newsprint, where the machine is around 200m long, four storeys high, and produces paper on a reel 9.2 metres wide.[13]

An integrated paper mill produces paper from pulp that is produced on the same plant. Paper can also be produced from dried pulp that is brought into the mill, as laths. This type of mill is known as a non-integrated paper mill. Pulp that is brought into a non integrated mill is known as market pulp.

A.5.3 Fibre modification

Cellulose paper fibres have to be modified before use in the papermaking process. This modification is accomplished by swelling the fibres and increasing their surface area.[15] The swelling and increase in surface area of the fibre is achieved by refining. Refining increases the ability of fibres to form bonds. Without refining, paper formed on a machine would not be strong enough to progress though the machine. Refining fibrillates the fibres, this is the partial unravelling of the cellulose fibres. The unravelling of the fibres has the effect of increasing their surface area and hence its ability to bond together. In addition to the formation of these fibrils, hemicelluloses present in the fibre are exposed to water and assist in the bonding. A refined fibre has a large surface area with hemicelluloses available for bonding. Fibres of this type are hydrated and are slow to release water. This is known as 'wet' fibre. A wet furnish is much slower to drain than one that is 'free'. The freeness of paper is an important characteristic in paper making. An example of a paper made with a heavily refined fibre is greaseproof paper. This paper is stiff, translucent, and heavy. This is due to the characteristics of the fibres, which have been refined excessively, and results in short fibres with extensive fibrillation. The result is a dense paper with few pores or voids in it. In contrast an example of a paper which is made from a very free pulp is blotting paper. Blotting paper has very little strength, is bulky and has an open porous structure.

Refining paper fibres invariably shortens them and leads to the formation of fines. Fines are partial fibres or fragments of fibres which have an influence on the freeness of the paper.[14] Fines can be lost in the virgin paper making process in the white water. Short fibres and fines can also be lost in the paper recycling process, where they are removed in the flotation or cleaning processes. The short fibres and fillers attach themselves to flotation bubbles and are removed from the furnish.[16] It is important to keep the fibres as long as possible in both the virgin and recycled papermaking process so as to retain their strength characteristics.

There are two main types of refiners: conical and disc. The main element of the conical refiner is a tapering roll mounted on a shaft drive, see figure A.5.3. This roll rotates in a complimentary stationary housing. The inner cone can be adjusted horizontally to vary the distance between the bars of the rotating cone and the stationary blades. The clearance

between the two sets of bars allows the refining treatment to be varied. Stock is fed into the narrow end of the cone and passes through the cone to the larger end where the stock is and then pumped to the paper machine.

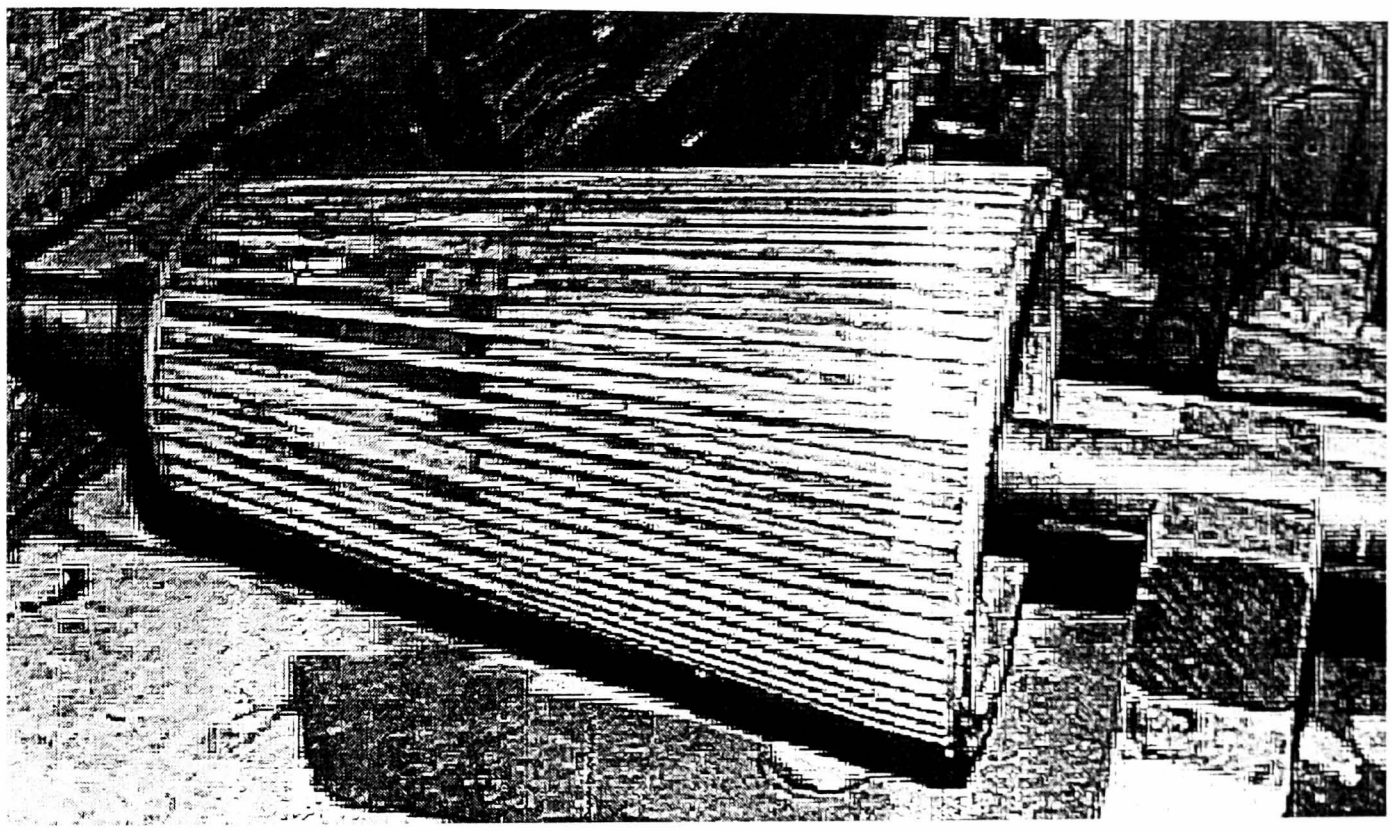


Fig A.5.3 Conical Refiner Blade

Disc refiners have two heavy discs as the moving parts. Again one of the discs is driven, the other disc is stationary. Stock is fed into the centre of the disc where it is thrown radially outwards, refining occurs when the bars of the rotating and stationary discs interact. The extent of refining treatment can be varied by changing the clearance between the discs.

An important feature of recycled fibre is that it has already been through the refining process and requires less subsequent treatment. Recycled fibres can be formed into paper after the removal of ink with minimal refining. Usually only a separation of the fibres is required, with possibly control of fibre length.

A.5.4 Additives

Mineral fillers and non fibrous materials are added to the fibre suspension to modify the properties of the paper. These non fibrous materials are known as loading. The mineral fillers are clays, such as kaolin, or finely divided calcium carbonate. Another possible

loading is titanium dioxide, which brightens the paper by absorbing ultra violet radiation then re-emitting the energy as blue light. The addition of fillers coats the fibres with insoluble mineral pigments. This adds opacity to the fibres as well as increasing their brightness and softness.

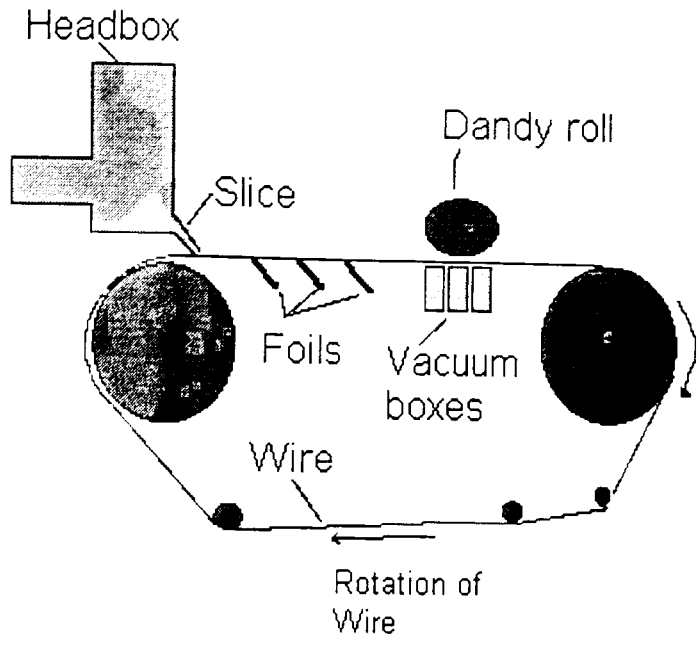
Another class of chemical that can be added is size. Sizing allows the paper to take ink without smearing. Without the addition of size water based inks would spread through the paper and cause feathering. The most common size employed used to be rosin plus aluminium sulphate as a mordant. However, this size was discontinued as the acidity of the of the aluminium salts made it impractical to use calcium carbonate as a filler. Neutral sizing is carried out today using a variety of hydrophobic chemicals, the most widely used are Alkyl Ketene Dimer (AKD) and Alkenyl Succinic Anhydride (ASA). AKD and ASA react with the surface of the cellulose fibres and bind to it, making the fibre surface hydrophobic.[18] These chemicals react under neutral conditions which allow the use of calcium carbonate fillers.

A.5.5 Paper formation (Wet end)

After the loading has been added to the fibres, the suspension which is known as the furnish is directed onto the paper machine wire shown in figure A.5.4. The water is removed first by gravity and the application of a vacuum, before passing to the drying section.

To reduce the tendency of fibres to flocculate the furnish is diluted to around 1 part fibre to 99 parts water. This lower consistency improves formation of the sheet.[1] The diluted furnish is held in the machine chest, while other additives, such as dyestuffs, are incorporated into the furnish. The chest is kept agitated to maintain the fibres in suspension. When required the stock is pumped out of the machine chest to the paper machine. The furnish is delivered to the paper machine by a flow box or headbox.

Figure A.5.4 **Diagram of Wet end**



The headbox ensures an even formation of the paper across the web by keeping fibres dispersed until they are formed on the wire. The design of the headbox usually takes the form of a tapering box. Small diameter pipes deliver the stock to the base of the headbox. The delivery pipes vary in diameter, this prevents the fibres from flocculating by varying the velocity of the flow of the stock. The flow of the stock onto the wire is controlled by an orifice at the base of the headbox known as the slice opening. The slice is wedge shaped with a horizontal opening at the base, and a sloping plate hinged at the top. At the top of the sloping plate is an adjustable stainless steel strip, known as the slice lip, whose function is to control the amount of stock passing onto the wire. The level of stock in the headbox is constantly monitored and controlled to maintain the grammage of the paper within accurate limits.

The orientation of individual fibres as they leave the headbox is important to the finished sheet of paper. Fibres have a tendency to align themselves with the flow of stock from the headbox. This alignment of the fibres creates a machine direction (MD). A paper with a pronounced machine direction fibre orientation will have a low resistance to tearing in the machine direction, but a higher tearing resistance across it. The jet of stock from the headbox is dependent on the pressure in the headbox. The jet wire velocity ratio is used to measure the MD. A jet velocity lower than the wire velocity will lead to a fibres being aligned in the machine direction, a jet velocity greater that the wire leads to a more random fibre orientation, and thus a more even sheet of paper free from MD and cross direction stress.

The stock is placed on the wire as a very dilute suspension. to prevent the stock from flowing over the sides of the paper machine deckle boards are used. The wire used on modern paper machines is not made of metal, but plastic, woven into an endless belt. The perforations in this belt are governed by the type of stock being formed on the machine. A pulp that is wet will require more perforations to allow the water to flow away faster. Water drains spontaneously from the underside of the wire at first, but as the consistency of the stock increases then the removal of water must be assisted. The water is removed from the bottom of the wire by foils. The foils support the wire and remove water from the base of the wire by breaking through the surface of the water. This water runs down to be reused, and is known as white water as it is rich in the loading and fines. There is a limit to the amount of water that can be removed by gravity and foils. The drainage of the web is assisted by the application of vacuum. Foils encased in boxes and connected to vacuum pumps are used. The web, which contains around 80% water, then passes onto rolls which apply a partial vacuum removing the water from the web. These rolls are known as couch rolls, they are hollow perforated rolls that draw water from the fibre mat by vacuum.

The paper web then moves into the press section. The purpose of the press section is to remove as much water as possible by the application of pressure, before the paper is heated to dry it. The web may be pressed against one or more felts to remove water. The felt is an endless band of fabric, originally knitted wool, but today synthetic fibres are used. Water is pressed out of the web and into the felts. The felt is washed and dried on its journey back to the paper web. At the end of the press section the web of paper contains around 35-40% fibre, i.e. 60-65% water.

A.5.6 Paper formation (Dry end)

Finally the web runs against a series of steam heated rollers to remove more water by evaporation. Before the final drying begins the paper is run through two plain rolls to remove any impression that the felts may have left. The drying section is usually arranged in two tiers so that the web of paper can be fed around the section in a figure of eight arrangement. The temperature of the rolls is graded to have maximum temperature in the centre of the drying section, with minima at the start and finish. This temperature gradient ensures that the web is not damaged by sudden heating or cooling.

The web of paper is then reeled up on steel spindles, before being cut to size for the customer. Paper is supplied as reels to large customers, for example a newspaper press, or can be sheeted for use in a copier.

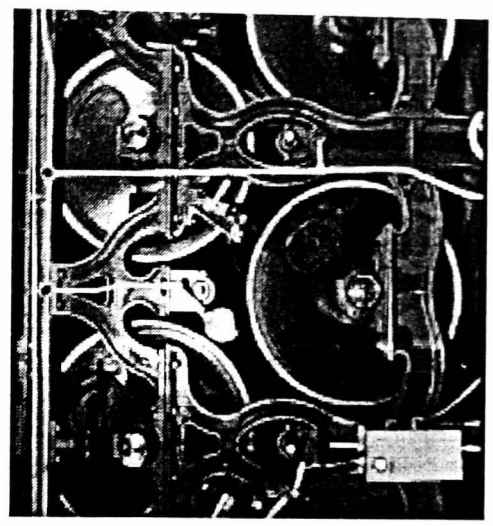


Figure A.5.5 **Section of Dryers on Paper Machine**

Appendix 6

A.6.0 Secondary Optical Particle Detection

There are two theories of particle sizing, the Mie and Fraunhofer. Each is applicable for different sizes of particles. The Mie theory applies for submicron particle sizing and requires knowledge of the complete refractive index of the particle. The complete refractive index comprises of the refractive index combined with the adsorption coefficient. Mie theory is only applicable to spherical mondisperse particles. Fraunhofer particle sizing is only applicable to particles of around 2μm, though it can be extended to a lower value than this. To extend the range of measurement an additional optical system to the laser scattering component is used. The system known as Polarisation Intensity Differential Scatter (PIDS), uses light of different wavelengths to obtain information about the particles.

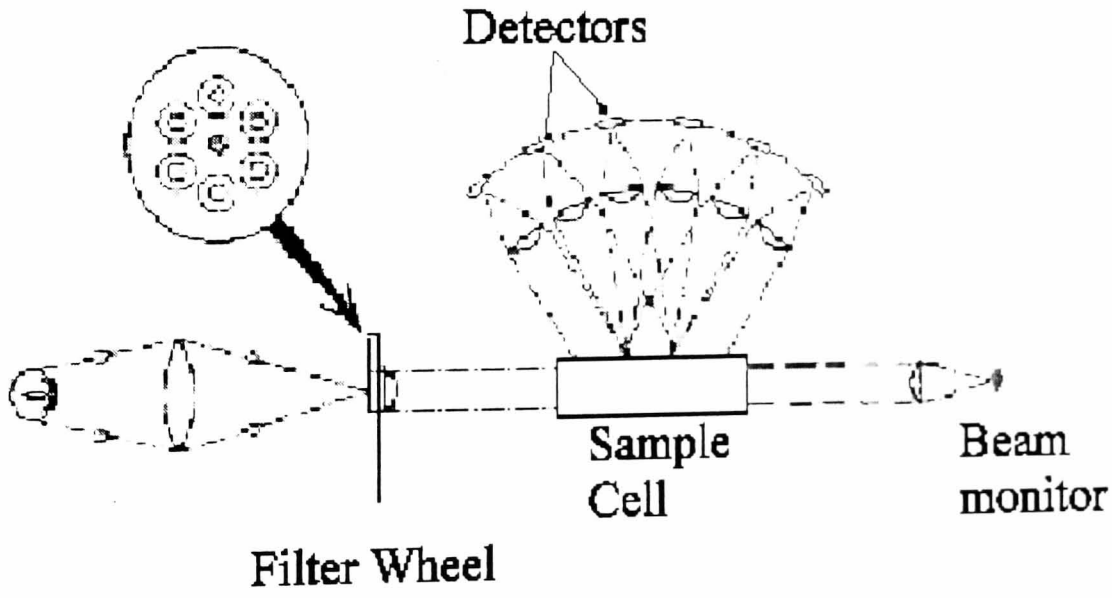


Figure A.6.1

Figure A.6.1 shows a typical arrangement of the light source, detectors and sample cell. The filter wheel is a diffraction grating used to obtain the different wavelengths. The sample is pumped through the sample cell and is irradiated.

A.6.1 Coulter ™ LS130 Particle sizer

The theory of laser scattering was discussed in section 5.3.0. Laser scattering is used to study micron and submicron sized particles when suspended. In this study the particles are obtained from the filtrates of the washing process. Controlling the LS130 is a Pentium 133 MHz computer whilst the electronics on board the LS130 in turn control the large fluid module (LFM). This circulates the fluid around the laser diffraction and PIDS systems of the instrument (Figure A.6.2). The large fluid module is shown in figure A.6 (A), the main body of the machine is labelled B. An internal view of the machine is given in figure A.6.3. The main lens can be seen at A.6.(Z), the internal graticle for calibration purposes in seen at A.6.(Y). The sample cell is labelled A.6.(W), fluid is pumped from the LFM into the diffraction module at X and passes up through the cell. The laser beam shines from left to right across the sample cell, and then on to the main lens.

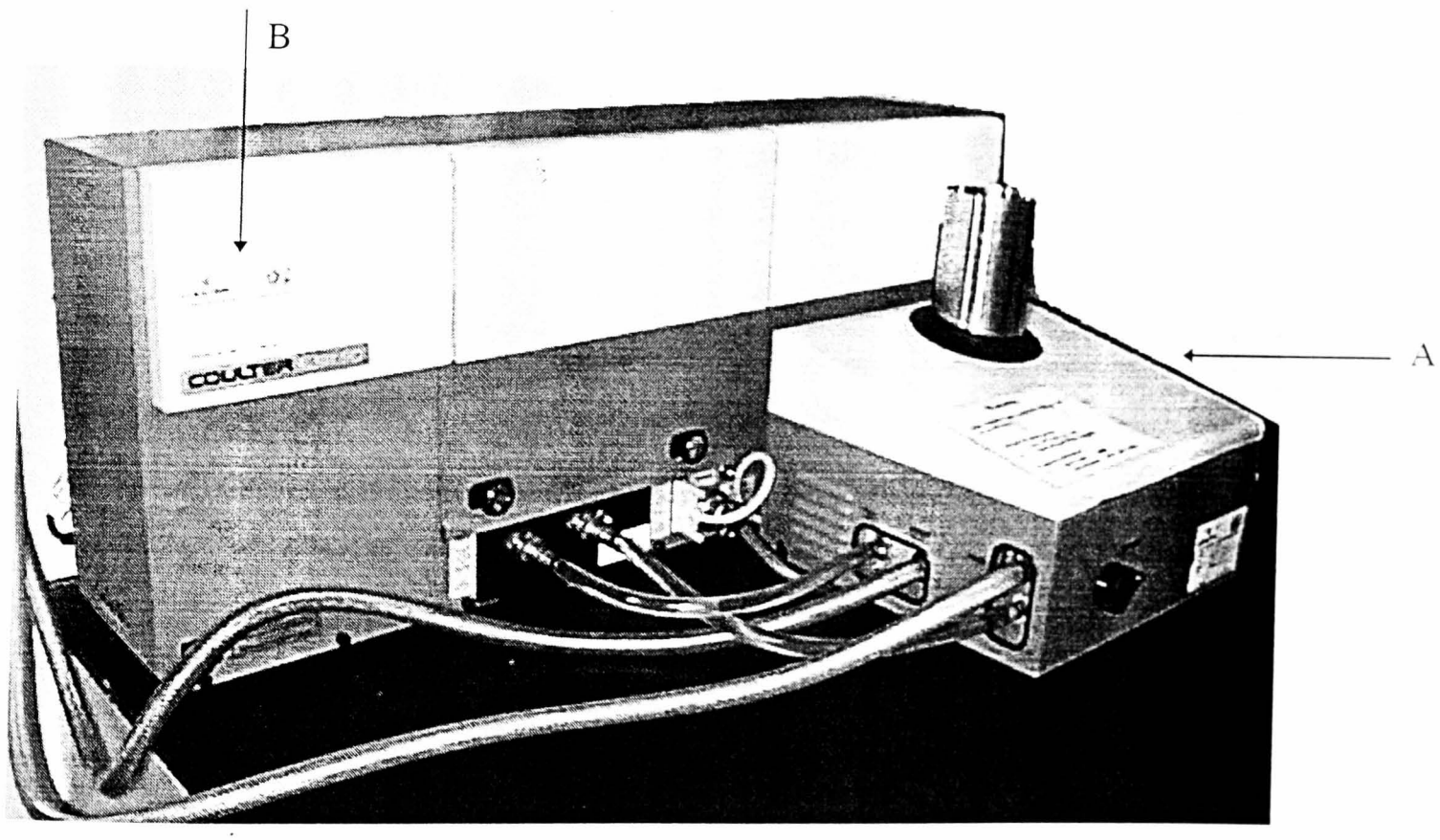


Figure A.6.2 Laser Scattering Module

The LFM has an ultrasound facility, to sonicate any samples that are difficult to disperse. The sonication also assists in the removal of air bubbles from the system. Air bubbles can be introduced as a result of the pouring or shaking liquid samples. These air bubbles appear as particles with a narrow distribution centred around 100μm. This population will change over a period of time as the bubbles gradually disappear. Bubbles can be avoided

by allowing a longer circulation time or by switching the pump on and off momentarily in order to allow the bubbles to move to the surface and burst.

The secondary particle sizing section of the apparatus can be seen in the figure A.6.(Q). The sample is pumped from the bottom to the top where it is irradiated by a tungsten lamp. The filter wheel produces wavelengths of 450nm (blue), 600nm (red/orange), and 900nm (near infra red). Particles are illuminated for a specific time and in a set sequence:- 450nm-vertical, 450nm-horizontal, 600nm-vertical, 600nm-horizontal, 900nm-vertical, 900nm-horizontal.

The different wavelengths are used because submicron sized particles interact differently with the shorter wavelengths. For example a 0.1μm particle will interact strongly with light of 450nm wavelength and less strongly with light of 900nm wavelength. The reverse applies for a 0.4μm particle. The PIDS effect only occurs when a particle diameter is between 10-60% of the incident wavelength; light of 450nm provides information about particles with diameters of between 45-270nm. The two theories, Fraunhofer and Mie, work in unison to give the distribution of submicron particles. An analogy for the PIDS effect is a ball floating on water. A wave travelling across the water will cause the ball to move up and down when viewed from the side. Viewed from a directly above it is difficult to resolve the vertical motion. The electrons in the particles cause polarised light to be scattered, observation of this scattering is made at 90º.

The scatter pattern is measured by the detectors which measures the vertical and horizontal components of the polarisation. When subtracted from each other the net result is the PIDS signal. This information is combined with the scattering data to give the full particle size distribution of the sample.

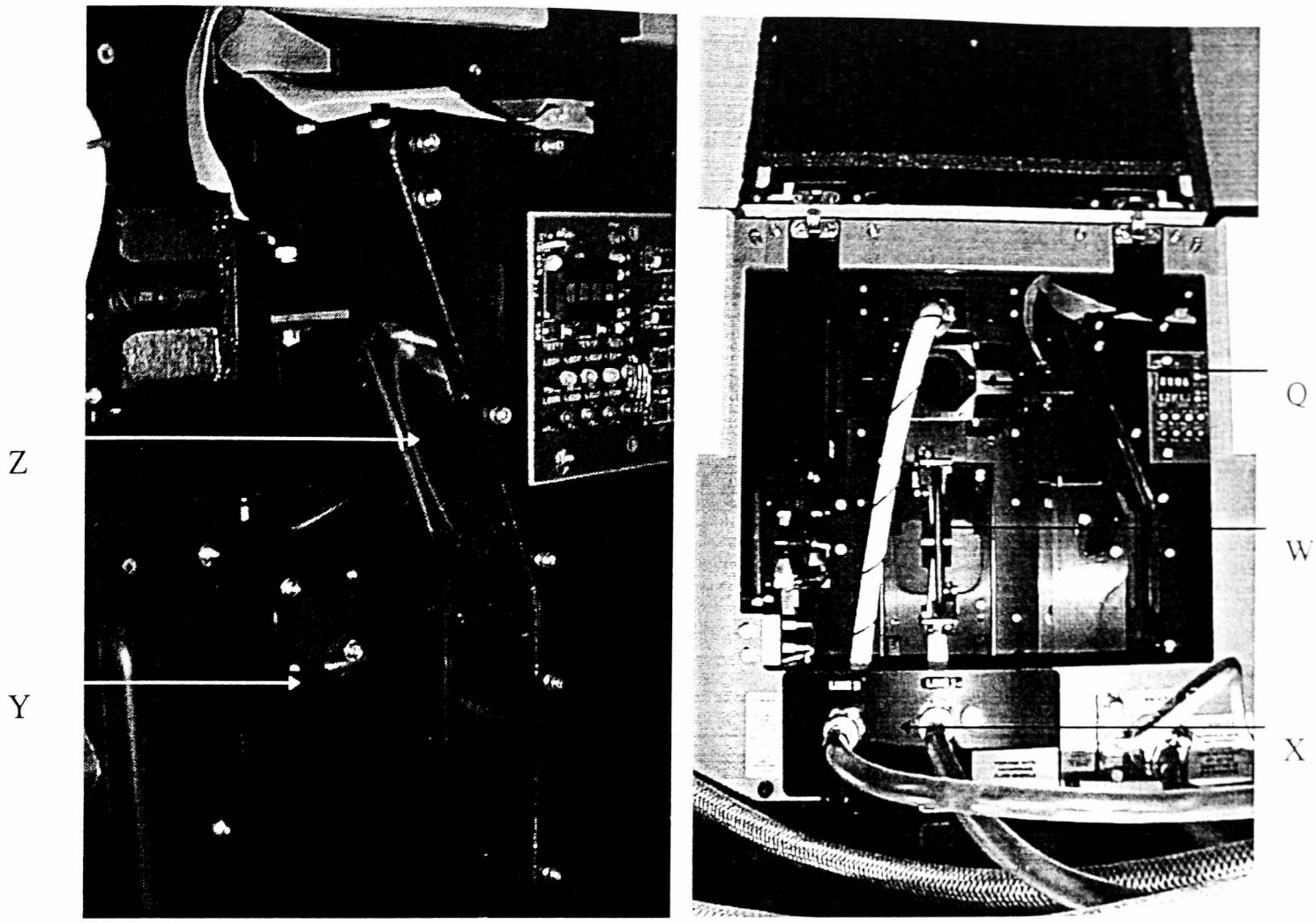


Figure A.6.3 **Internal views of Laser Scattering Module**

Appendix 7 - Data from Analysis of Cavitation Activity on Exposed Films

	30s1	30s2	30s3	30s4	30s5	30s6	30s7	30s8	30s9	30s10	30s11	average
Total part.	0.317631	0.230397	0.467229	0.605575	0.164938	0.309502	0.307038	0.556627	0.183634	0.199644	0.175759	0.319816
Total part.	66	46	93	160	33	62	42	39	43	53	40	61.54545
Part Count	605010.9	438850.1	889958.7	1153474	313333.2	587961	583279	1057410	348848.6	379258.8	333889.3	608297.7
Part Area/I	4812.597	5008.626	5023.971	3784.846	4998.132	4991.971	7310.419	14272.49	4270.549	3766.871	4393.976	5694.041
Sd sample	6967.49	7737.126	7051.732	5856.663	8141.849	8538.017	18992.27	50443.3	12460.32	11131.15	3348.971	12788.08
Sd pop	6914.505	7652.565	7013.717	5838.332	8017.538	8468.882	18764.81	49792.39	12314.58	11025.64	3306.844	12646.35

	1m1	1m2	1m3	1m4	1m5	1m6	1m7	1m8	1m9	average
Total part.	0.447256	0.223772	0.529922	0.586904	2.524455	0.72965	0.720184	0.80726	0.524998	0.830893
Total part.	401	23	41	53	138	69	100	97	78	74.875
Part Count	849354.2	424951.4	1006462	1114686	4794220	1385686	1367710	1533075	997028.3	1577977
Part Area/I	1115.352	9729.236	12924.93	11073.66	18293.16	10574.64	7201.843	8322.266	6730.738	10606.31
Sd sample	4179.094	6451.614	13358.33	11731.54	59899.05	12048.99	6456.082	14850.65	8426.298	16652.82
Sd pop	4173.88	6309.803	13194.41	11620.34	59681.63	11961.36	6423.721	14773.9	8372.109	16542.16

	90sr1	90sr2	90sr4	90sr5	90sr6	90sr7	90sr8	90sr9	ave
Total part.	0.762598	0.560054	0.697746	0.665009	1.015225	1.648581	1.467624	2.04901	1.108231
Total part.	61	60	86	75	101	119	98	146	93.25
Part Count	1435478	1054218	1313403	1251781	1933743	3140122	2795446	3902837	2103378
Part Area/I	12501.6	9334.227	8113.32	8866.781	10051.74	13853.62	14975.75	14034.32	11466.42
Sd sample	28950.62	7508.573	9160.52	10888.54	13769.47	22699.64	18105.71	14981.09	
Sd pop	28712.34	7445.739	9107.105	10815.71	13701.14	22604.06	18013.09	14929.7	

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