

THE ROLE OF SODIUM SILICATE IN NEWSPRINT DEINKING

by

W. J. Pauck

Submitted in fulfilment of the academic
requirements for the degree of
Master of Science in the
School of Pure &
Applied Chemistry,
University of Natal,
Durban.

April 2003

ABSTRACT

Mondi Ltd. operates a deinking plant at its Merebank mill. The plant recycles 85 000 tons per annum of flat news and magazine to produce a furnish for its newsprint papermachines. A review of the relevant pulping and flotation chemistry literature revealed that the role played by sodium silicate appears to be multi-faceted and in some dispute. Sodium silicate has an undisputed role in pH buffering, hydrogen peroxide stabilisation and the prevention of fibre yellowing. However, its role in deinking is said to be that of an ink collector or alternatively an ink dispersant. The mill's own experience has shown that the sodium silicate plays a vital role in the deinking process.

Sodium silicate's ability to disperse ink, both alone and in the presence of calcium ions and fatty acid soaps, was investigated using a model ink system. A representative newsprint ink base was dispersed in the laboratory under conditions similar to those encountered in a deinking pulper. The resultant dispersions were studied using turbidity and particle size analysis. The morphology of the ink particles was determined using a scanning electron microscope. Sodium silicate proved to be a poor disperser of ink particles, but nevertheless appeared to greatly influence the dispersing properties of the soap in the presence of calcium ions.

The nature of the interactions between sodium silicate, calcium ions and the collector soap were studied in an attempt to elucidate the role of sodium silicate. A model system consisting of the sodium salt of collector soap, calcium ions and sodium silicate was studied under the conditions that prevail in a typical newsprint deinking pulper. It was found that the soap and the sodium silicate compete for the calcium ions, and sodium silicate showed a measurable chelating effect on calcium ions. Thus, increasing levels of sodium silicate lead to an increase in the concentration of sodium soap in solution. It was hypothesised that this effect would lead to better dispersion of ink particles and improved deinking performance.

This chelating effect was evaluated in laboratory deinking studies. Samples of newsprint were pulped in a 25l Lamort laboratory pulper under a variety of conditions, viz. with fresh water, with an excess of soap, with an excess of calcium, with and without sodium silicate. The pulps were floated in a 20l flotation cell. The brightness

and colour of the unfloated and floated pulps were measured. The level of the final brightness after flotation was taken as a measure of deinking efficiency.

The highest final brightness was achieved when there was an excess of sodium soap and a low Ca hardness in the pulper. Softening the water used in pulping without adding excess sodium soap did not significantly improve pulp brightness. The lowest final brightness occurred in the presence of an excess of calcium in the pulper. Calcium in the pulper in the presence of sodium silicate did not result in a significantly lower final brightness.

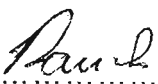
The results support the hypothesis that sodium silicate sequesters the soluble calcium in a pulping system, thereby increasing the sodium soap concentration and the resultant deinking performance. Apart from sodium silicate's chief role as a peroxide stabiliser, the sequestering action on calcium appears to be its main mechanism of action in a deinking system.

An appreciation of this role will facilitate the optimisation of deinking systems with respect to calcium hardness and silicate concentration. To this end it was recommended that the Merebank deinking plant should evaluate the use of water with a low calcium ion concentration and the addition of some soap into the pulper to improve their deinking plant performance.

PREFACE

The experimental work described in this dissertation was carried out in the laboratories of the Mondi Ltd. Merebank mill and in the Department of Applied Chemistry, University of Natal, Durban, from January 1999 to December 2001, under the supervision of Professor J Marsh.

These studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others it is duly acknowledged in the text.

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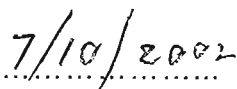
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ACKNOWLEDGEMENTS

I would like to thank Professor Jeremy Marsh for his guidance and supervision of this dissertation.

In addition, I am indebted to the following people for their invaluable assistance in the various analyses that were required in the course of this work:

Dr. F Graham for her assistance in the preparation of samples and the carrying out of the SEM and EDS analysis of ink particles.

Dr. A Spark for the GC and FTIR analyses.

Dr. A Kindness for the ICP analysis.

I would also like to express my gratitude to the laboratory staff in the main laboratory at the Merebank mill, for putting up with me and assisting in many ways, especially Mr. S Ramkellawan, Mr. S Reddy and Miss N Magwaza.

A big thank you to Mr. P Watson, for his assistance in procuring the samples of ink base and for listening to my theories.

Lastly, I would like to thank the management of the Mondi Ltd. Merebank mill, for their financial support of this project. In particular, I would like to thank Mr. J Ratcliff and Mr J Hunt, for their on-going support during this work.

GLOSSARY OF TERMS AND ABBREVIATIONS

Consistency	Mass percent of fibre in a pulp.
EDS	Electron dispersive spectroscopy.
Filler	Minerals such as clay (kaolin) or calcium carbonate, which are added to a sheet of paper during manufacture to enhance the optical properties of the paper and to reduce the raw material cost.
Fines	Very small fragments of fibre and colloidal material, which occur in paper and pulp mill process water circuits.
Furnish	The fibre and fillers that constitute the raw materials of a sheet of paper.
Lignin	Lignin is the substance that binds the fibre cells together in wood. It is an amorphous, glassy polymer of uncertain structure, comprising phenolic monomeric units.
nm	Nanometers, or 10^{-9} meter.
ppm	Parts per million.
Pulp	An aqueous suspension of wood fibres.
rpm	Revolutions per minute.
SEM	Scanning electron microscope.
Shives	Small bundles of unseparated fibres, usually arising when wood is incompletely separated into fibres during pulping.
Stickies	Stickies arise when waste paper is recycled, and are formed from the resins and lattices that are used in the manufacture of printed materials.

1: GENERAL INTRODUCTION

1.1 An Overview of Deinking

In 2000 the global paper industry used an estimated 145 million tons of recycled fibre. This was only slightly less than the estimated 185 million tons of wood and non-wood pulp produced. These figures are expected to grow to 195 million and 225 million tons per annum respectively (World trade in waste paper 2001). This means that recycled fibre constitutes a significant proportion of the fibre used in today's paper industry. In many parts of the world, such as Central, Western and Southern Europe and the Far East the paper industry would not exist without this valuable fibre resource. Even in areas which have abundant natural forests, such as Scandinavia and North America, recycled fibres are used as blends with virgin pulps in the production of many grades of paper. In the last decade, the consumption of recovered paper has grown at an annual rate of 6%, compared to the 3% annual growth in paper production and the 2% growth in the production of chemical pulp and mechanical pulp. (Goettsching & Pakarinen 2000: 12-22) This growth in the usage of recycled fibres has been encouraged by the growth in environmental awareness in the industrialised nations, coupled with stringent environmental legislation. The use of recycled fibre has been most successful in the densely populated developed countries, where recycling and collection efficiencies make the use of recycled fibre a cost effective alternative to virgin fibre.

Environmental awareness by the general public has driven the promulgation of environmental legislation in developed countries. This legislation aims to limit the amount of waste produced by domestic households and industrial operations, and has been necessary because of the growing mountains of waste material and limited landfill capacity, coupled with the increasing costs of waste disposal.

The first flotation deinking plant was installed in the United States in the late 1950's. Since then the production capacity has grown dramatically. By 1980 the worldwide production capacity was about 3,5 million tons and has since grown exponentially to 25 million tons in 1997. The deinking capacity was expected to exceed 30 million tons per annum in the year 2000. The majority of this capacity is in Europe (44%), with 25% each in the United States and Asia, with the remaining 6% in South America, Africa and Oceania (Goettsching & Pakarinen 2000: 12-22).

The utilisation rate, or the amount of recovered paper used as a raw material, varies widely according the grade of paper manufactured. In addition, the yields of the deinking processes also vary depending on the grade of paper produced. This yield loss is a result of the differing quality requirements in the ultimate end products. Based on statistics and estimates given by Goettsching & Pakarinen (2000: 12-22), the amount of recycled fibre in the different grades of paper has been estimated in Table 1.1 below.

Table 1.1 Utilisation rates, process yields and amount of recycled fibre in different grades of paper.

Paper Grade	Utilisation rate, (Germany, 1998) %	Estimated yield of deinking process %	Estimated recovered fibre in final product %
Packaging and cardboard	96	90-95	86-91
Hygiene papers	70	60-75	42-52
Specialty papers	48	70-95	34-46
Graphic papers (including newsprint)	37	65-85	24-31
Newsprint	115	65-85	75-98

As can be seen from Table 1.1, packaging papers and cardboard contain the highest levels of recycled fibre, because the dark or brown colours of the final product do not require high levels of ink removal. The level of recycled fibre in the hygiene papers is only moderate, due to high yield losses in the flotation and washing stages of the recycling process. The average recycled fibre content of the graphic papers is not very high. This is due to the high brightness requirements of many of the grades, particularly the Xerographic photocopy papers and other high quality grades, which do not allow high levels of recycled fibre addition. Newsprint, which also falls under the classification of graphic papers, is an exception. The utilisation rates of newsprint have reached a very high level. This has been driven by economic considerations and the development of deinking processes that produce a fibre of such a quality that can be re-used at high levels.

In South Africa the situation is a little different to the rest of the world. There is currently no legislation governing the re-use of recycled paper. Nevertheless the recovery rate has grown from 29% in 1984 to 42% in the year 2000. This corresponds to about 770

000 tons per annum (Hunter 2000). This is expected to grow to over 800 000 tons per annum by 2002 (Hunter 2001). In the absence of legislation, the increasing collections have been driven by the major paper manufacturers, mainly by aggressive promotion of the recycling ethic and the paying of good prices for waste paper.

The average global waste paper utilisation rate is expected to grow further, but at a lower rate than at present. It is expected that a balanced utilisation rate of about 50% will be achieved by the year 2010 (Goettsching & Pakarinen 2000 7: 12-22). This means that the average recycled fibre content of a paper or board product will be about 42.5% after recycling losses have been taken into account. The utilisation rates are expected to stabilise at these levels, due to decreasing availability of suitable raw materials and ever increasing quality demands on the finished products.

1.2 Newsprint deinking at the Mondi Ltd. Merebank mill

The sponsor of this study, Mondi Paper Company Ltd., operates a recycling plant at its Merebank mill in Durban, South Africa. This plant was built in 1990 and has a capacity to recycle 85 000 tons per annum of waste paper. It can produce about 70 000 tons per annum of deinked newsprint pulp, which constitutes about 25% of the newsprint furnish of the two newsprint machines at the Merebank mill. The waste paper is collected and sorted off-site by Mondi Paper Waste and delivered to the mill, baled as "flat news" and "magazine".

The process is depicted in Figure 1 below (p. 6). The process is essentially a single stage alkaline flotation process, followed by a washing stage, dispersion and hydrosulphite bleaching. A 70/30 blend of newsprint and magazine paper is fed into the pulper, together with 10.0 kg/ton (kg active chemical per ton of dry pulp) of sodium silicate, 4.8 kg/ton hydrogen peroxide, a trace of enzyme scavenger and enough caustic soda to bring the pH into the range 9.8 - 10.2. The waste is pulped at a consistency of 10-15% and at a temperature of 45 °C for about 15 minutes. After pulping, the stock is diluted to a consistency of approximately 7% before the heavy media separator, 4% before the high density cleaners and 3% before the coarse screens. After screening further dilution to about 1% takes place, and 4 kg/ton of collector soap and 2.0-3.5 kg/ton of calcium chloride are added just before the flotation cell. The target calcium hardness in the flotation cell is 250 ppm as calcium carbonate. The ink is floated off in a two-stage Voith flotation cell, at a pH of 8.2 - 8.5. Thereafter

the pulp is again cleaned, screened, thickened and washed. After washing on the wire press, any remaining ink particles are dispersed, before it is bleached at medium consistency with sodium hydrosulphite, to a brightness of over 62. At the washing stage sulphuric acid is used to adjust the pH of the pulp to 6 - 6.5. The water recovered in the disc filter thickener is split into two streams, designated cloudy and clear. The cloudy water is heated to 50 °C with steam and used for dilution in the pulper and up to the flotation cell. From the flotation cell forward clear water is used for dilution. The water and fibre flows are clearly indicated on Figure 1 (p. 6). Excess soap and calcium hardness is circulated back into the pulper from the disc filter. After the disc filter, white water from the paper machine is used for washing and dilution of the pulp.

The conditions described above will form the basis for all experimental investigations.

It is common practice in the industry to express chemical additions as anhydrous chemical as a fraction of dry fibre in the pulp. In these instances, units such as kg/ton or percent (%) are used. However, as most chemical additives used in paper recycling are soluble in water, the concentration in aqueous solution is of interest when investigating their chemistry. In order to determine the aqueous concentration when chemical additions are made on the basis of dry fibre, the consistency must be taken into account. Accordingly, in this work the following conventions will apply:

1. Units such as kg/ton or percent will denote chemical additions expressed as anhydrous chemical per dry mass of fibre.
2. The unit of parts per million (ppm) will refer specifically to the aqueous solution concentration of a particular chemical.

Thus, if 10 kg/ton of sodium silicate is added to a pulp of 10% consistency, the concentration of sodium silicate in solution will be ca. 1100 ppm.

1.3 Objectives of the study

The role of sodium silicate in a newsprint deinking system is understood to be multifaceted (See Section 2.2). In addition to experimental work in the industry, this understanding seems to be drawn from the application of sodium silicate in other areas of industry, especially its application in the detergent industry. A number of workers

have experimentally studied the effects of sodium silicate in a deinking system (Ali *et al.* 1994, Liphard *et al.* 1991, Mak & Stevens 1993), but most quote the work of Ali *et al.* (1994) or refer to the application of sodium silicate in the detergent industry.

In the opinion of Crosby (1999), sodium silicate is an essential component of the deinking process at Mondi Merebank. Attempts to eliminate sodium silicate from the deinking recipe resulted in an immediate deterioration in deinking efficiency.

It was felt that the current understanding of the role of sodium silicate is still sufficiently broad and uncertain as to merit further study. The objective of this work will be to study the role of sodium silicate in a newsprint deinking pulping system, with a view to clarifying which of the many mechanisms discussed in Section 2.2 actually operate in a deinking pulping system. The mechanism most often referred to by authors in the field is the dispersing action of sodium silicate.

1.4 Scope and delimitation

The scope of this study will be limited to that of a newsprint deinking pulping system, as defined by the commercial process of the sponsor of the study, and as outlined in Section 1.2 above.

The plant processes a mixture of recovered newsprint and magazines, but in the interests of simplicity, only the deinking of newsprint will be studied. This eliminates the influences that high levels of filler, paper coatings and a greater variety of inks could have on the experimental results.

1.5 Anticipated Benefits

A better understanding of the role of sodium silicate in a deinking system will allow the commercial process described above to be optimised, thereby improving the quality of the pulp produced. Alternately, optimising the use of process chemicals could lead to monetary savings or improved operating efficiencies.

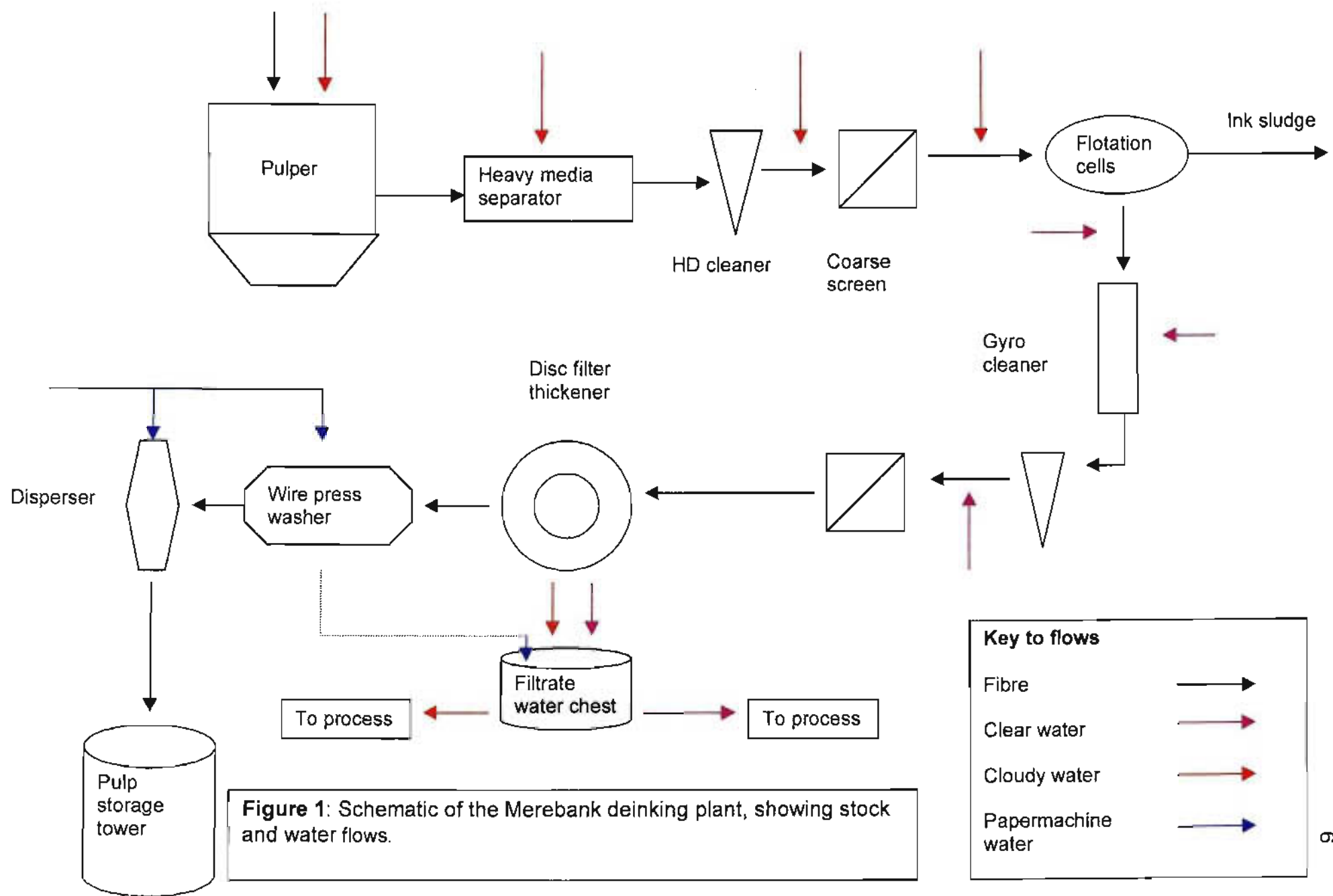


Figure 1: Schematic of the Merebank deinking plant, showing stock and water flows.

2. BACKGROUND

2.1 The unit operations of newsprint deinking

2.1.1 Introduction

Recycled paper as a raw material for a deinking process consists of a wide variety of components in addition to the fibres that will be used again to manufacture paper. These components originate from the products into which paper is made, and are typically substances such as:

- Additives used in the production of paper, for example mineral fillers, coating components, dyes, sizing agents and process chemicals.
- Printing inks, adhesives, binders, foils and coatings.
- Foreign materials such as wire, stones, paper clips, staples and string.

It is very important in the collection and storage processes to eliminate the contamination of waste paper by such materials. In addition, it is important not to allow the recycled paper to age for too long in storage. The thermal ageing of inks, particularly under conditions of high temperature, impact on the ink detachment, fragmentation and subsequent removal by deinking (Haynes 2000).

Table 2.1: Efficiency ranges for the main separation processes after pulping.

Contaminant size, mm	Unit operation	Separation mechanism
> 1	Centrifugal cleaning	Density, size, shape
0.1 – 1.0	Screening	Size, shape, deformability
0.001 – 1.0	Flotation	Size, surface properties
0.0001 – 0.01	Washing	Particle size, shape

The complex mixture of materials described above must be separated into high quality usable fibres and into numerous waste streams that must be eliminated from the system. This is achieved by a variety of separation processes, which classify and eliminate contrary materials based on their particle size and other particle properties. The main separation processes perform best in particular particle size ranges, as summarised in Table 2.1 above (Goettsching & Pakarinen 2000: 91-209, Dash & Patel 1997).

From the table it can be seen that there is some overlap in the separation efficiency ranges of the various separating processes. They also make use of different particle properties to achieve separation. The flotation process relies heavily on the surface properties of the particles, which are influenced by the chemistry of the system. All of the other processes are essentially physical separation process, although chemistry does play some role in the washing process. In addition to the primary separation processes, a number of other unit operations, such as pulping, dispersing, dewatering and bleaching are necessary to achieve separation.

A more detailed description of the unit processes in newspaper recycling will now be given. They will be discussed in the order in which they occur in the Merebank recycling plant, although other combinations are possible. The ideal combination of unit operations is strongly dependant on the quality of the raw material and the desired properties of the final deinked product.

2.1.2 Pulping

The purpose of the pulper is to break down the waste paper into a pulp, which renders the stock pumpable and facilitates the addition of processing and bleaching agents. Chemistry plays an important role in this process, as many chemicals are added at this stage. Also, the important processes of ink separation and stabilisation have their beginnings in the pulping process.

In the Merebank plant a batch pulper is used. The batch pulper is a large cylindrical stainless steel vessel with a large impellor and a perforated plate to allow for the extraction of the pulp. The pulper is charged with water, waste paper and process chemicals and under the action of the rotating impellor the paper is broken down into individual fibres. It is necessary for the paper fibres to be wetted and the hydrogen bonding forces that bond the fibres together in the dry state to be overcome. Pulping occurs under alkaline conditions and in the consistency (% fibre solids) range of 10 to 15%. The pulping time is 15 minutes at 45°C. The addition of chemicals will be discussed under the section on pulper chemistry.

2.1.3 Centrifugal Cleaning

Centrifugal cleaning is normally used in combination with screening to effect removal of contrary materials in a recycling system. Cleaners are essentially hydrocyclones and make use of centrifugal force to separate undesirable particles on the basis of differences in density relative to water. Accordingly, heavy particles such as sand and metal, and light particles such as shives and plastic material are effectively removed by a cleaner system. Cleaners are most efficient at removing fairly large, dense particles, as detailed in Table 2.1 above.

In the Merebank plant, two sets of cleaners are in operation, before and after the flotation cell (see Figure 1, p. 6).

2.1.4 Screening and Fractionation

Screening consists of passing the recycled fibre pulp through a screen plate perforated with small holes or slots. Debris and unwanted material such as shives, coarse fibre, stickies and small fragments of plastic are removed on the basis of size exclusion and to a lesser extent on shape and flexibility. Highly conformable particles will force themselves through even fine perforations. Slotted screens with slot widths of down to 0.1 mm are in common use. Again, screen geometry and design factors play a large role in the performance and efficiency of the screens. It is not possible to avoid fibre losses or to remove all the debris in one screening stage. In order to optimise the screening efficiencies, multistage screening is commonplace. In the Merebank operation, the screening system uses a combination of 1.6 mm holes and 0.25 mm slots, and is carried out in two separate stages (see Figure 1, p. 6).

2.1.5 Flotation

The flotation process is the heart of any deinking operation and is one of two main methods for removing ink from a waste paper pulp. The process involves the removal of ink particles from a fibre suspension by injecting fine air bubbles into the pulp. The bubbles move to the surface, and in the process pick up hydrophobic ink particles. Once on the surface, the bubbles form a stable foam layer, which incorporates the ink and other floated material. This foam bed is removed

mechanically from the fibre suspension below. The physical flotation processes have been described using hydrodynamic and probability processes by various authors (Heindel 1999; McCool 1993; Schulze 1991). In its simplest terms, the flotation process has been described as a combination of three main steps (McCool 1993):

- a. The probability of collision, dependent on the number and size of the air bubbles and ink particles.
- b. The probability of attachment of air bubbles and ink particles, dependent on the surface chemistry of the various particles.
- c. The probability of removal of the air bubble-particle complex from the system.

Steps a. and c. above are determined mainly by process equipment and conditions, such as consistency, temperature, agitation, retention time and flotation cell design. On the other hand step b. is determined by the surface chemistry of the system. The detailed chemical mechanisms and process conditions will be discussed in more detail in Section 2.2.3 below. Deinking flotation had its origins in mineral flotation and early flotation cells were borrowed from that industry. In the early 1950's the Denver cell, originally designed for mineral flotation, was first used in deinking flotation (McCool 1993). Since then a large amount of effort has gone into the design of equipment specifically for deinking, and many manufacturers have developed their own unique design features. Shapes of flotation cells vary from square, rectangular, cylindrical (horizontal or vertical) to elliptical and even pressurised. Most have some form of internal agitation and fine air bubbles are introduced by high-speed impellers or fine nozzles. (McCool 1993, Goettsching & Pakarinen 2000: 91-209.) Many commercial processes consist of multiple flotation stages, necessary to achieve the desired pulp quality. The flotation cells at the Merebank mill were made by Voith, and consist of multi-stage elliptical units.

2.1.6 Washing

In contrast to flotation, washing is a process of removing contaminants by high dilution and filtration. In this process very finely dispersed particles (less than 30 microns), colloidal particles and dissolved entities are removed in the filtrate. Such particles include fillers, fibre fines, stickies and fine ink particles. The washing process is less selective than the flotation process, but removes a wide variety of materials. It is however not able to remove larger particles, which tend to become

entrained in the fibre mat during the filtration process. Washing and flotation are often used in combination in many commercial deinking plants (McCool 1993). Washing is more often used to remove fillers and fines from recycled fibres, whilst flotation is used to selectively remove inks. However, in the case of flexographic inks, which are very finely dispersed, washing is used as a means of separation. Washing is normally carried out in some sort of dewatering machine such as a disc filter, belt filter or drum filter. (Goettsching & Pakarinen 2000:176-181.) At Merebank, washing is carried out after dewatering by means of a wire press. White water from the paper machines is used as washing water (see Figure 1, p. 6).

2.1.7 Dewatering

In addition to the washing of recycled fibre suspensions, dewatering is a unit operation in its own right in the processing of recycled fibres. Dewatering is the process of removing the liquid components of a fibre pulp from the solid (usually fibre) components. Aside from the washing processes described above, dewatering is usually done to make subsequent processes more efficient or cost effective. For example bleaching processes are more effective and use fewer chemicals at higher consistencies, and smaller storage volumes are required for high consistency pulp. Dewatering also allows the recycling of process water back into earlier stages of the process in order to conserve process chemicals or process heat. This has important consequences, in that contaminants and process chemicals are cycled up and concentrated, which can have a significant effect on the process.

Dewatering is also a means of separating water systems, as would be the case in an alkaline process followed by an acidic one, thereby obviating the need to carry out expensive neutralisation steps.

Dewatering is typically a filtration process, and is carried out on an industrial scale using belt, drum or disc filters. These machines are often vacuum or pressure assisted. The pulp feed is normally at a consistency of 2-3.5% and they typically deliver a fibre cake with a consistency ranging from 5% for disc filters up to about 25% for wire presses. The filtrate resulting from this process is not clean, and normally contains small quantities of fibre fines, colloidal material and soluble entities. A filtrate consistency of 100 – 1000 parts per million is typical. (Goettsching & Pakarinen 2000: 168-175.)

In the Merebank deinking plant, the dewatering function is performed by means of a disc filter. The disc filter in the Merebank plant separates the paper machine water circuit (pH 6-6.5) from the recycled fibre plant water system (pH >8). The filtrate from the disc filter is divided into cloudy and clear streams. The cloudy stream is richer in fine fibrous and colloidal matter. In the Merebank process, the cloudy water is recycled back to the process, heated up with steam and is used to repulp the recovered paper (at 10-15% consistency). This water is then further used to dilute the pulp down to the final flotation consistency of ca. 1%.

The cloudy filtrate was analysed for calcium hardness and residual soap concentration.

The filtrate was found to have a hardness in the range of 66 to 96 ppm Ca^{2+} and a residual soap concentration of 150 to 234 ppm. The methodology of this determination is detailed in Section 3.2.

2.1.8 Dispersing

Dispersing breaks up remaining ink and dirt specks into particles that are too small to be detected visually. In addition it detaches ink particles still attached to the fibres and conditions the fibre for papermaking. In the Merebank process, dispersing is carried out in a machine called a disperger, and takes place just before the pulp is pumped to the storage silo.

2.1.9 Bleaching

Bleaching in the context of deinking refers to the removal of yellowness or other undesirable colour from the fibres. This is achieved by the addition of bleaching chemicals at various stages of the process. The first bleaching stage is the addition of hydrogen peroxide into the pulper. The hydrogen peroxide counteracts the tendency of fibres to yellow in an alkaline environment. The final bleaching stage usually takes place at the end of the process, where reductive bleaching with sodium hydrosulphite is carried out, usually in the pulp storage chests. If a higher final brightness is desired, then a multistage peroxide/hydrosulphite bleaching sequence is necessary. This is not normally required for newsprint. In the Merebank plant, hydrogen peroxide is added into the pulper, and sodium hydrosulphite is used

as a final bleaching stage to increase the pulp brightness to over 62 brightness units.

2.2 Chemistry of Deinking

The main components of a typical newsprint deinking system are the fibres, the aqueous carrier phase, the printing inks, the mineral fillers and the many process chemicals that are necessary to achieve deinking. Every one of these components can interact with each other, and a commercial deinking system is a very complex system. It is appropriate to consider each individual component in turn, in order to develop a complete picture of what occurs in a deinking system.

2.2.1 The Printing Inks

The main printing processes in use today are the letterpress, offset lithography, rotogravure and flexographic processes. The rotogravure inks are mainly used in the printing of illustrated magazines and other high quality work, usually on coated paper. Letterpress is used mainly for printing of newspapers, but its use is declining and is no longer a significant process (Goettsching & Pakarinen 2000: 283, Aspler 1991). Flexographic printing of newsprint is used to some extent in the United States of America and Italy, but not elsewhere, and certainly not in South Africa. Flexographic printing is the dominant process for the printing of packaging papers (Aspler 1991).

Offset lithography is by far the most commonly used printing process for mass circulation newspapers, due to the quality of print achieved and the good economics of the process. (Goettsching & Pakarinen 2000: 293). It is foreseen that the market share of the offset printing process, which was at 65% of circulation in North America in 1991, will grow into the future (Aspler 1991).

In general a printing ink comprises a vehicle or carrier, a binder, a colourant (pigment or dyestuff) and a variety of additives. The vehicle is a solvent that dissolves the binder and carries the pigment in a fluid state. The binder is a material that envelopes the pigments and forms a film on the surface of the paper, thereby adhering the pigments to the paper. The colourants are materials that impart colour to the ink. In the case of black inks, the pigment is almost exclusively carbon black.

The compositions of the printing ink vary depending on the printing process used (Dobias *et al.* 1992).

A black web-fed offset printing ink can be expected to have a typical composition as summarised in Table 2.2. (Dobias *et al.* 1992, Goettsching & Pakarinen 2000: 270.)

Table 2.2: Typical composition of black printing inks.

Component	Offset – Coldset	Offset- Heatset	Type of material
Pigment	15-25%	20-25%	Carbon black
Carrier	ca. 60%	25-40%	Mineral oil, 200°C-400°C boiling range
Binder	10-20%	25-35%	Hydrocarbon resins Vegetable drying oils Alkyd resins Phenol-modified colophony resins
Additives	1-5%	5-10%	Drying oils, dispersants, plasticizers, waxes.

In the printing press the ink is applied to the surface of the paper. The carrier, depending on its nature, either evaporates or penetrates into the web of paper, allowing the binder to form a film on the paper surface. This is a purely physical drying process, and is typical of binders such as hydrocarbon or colophony resins. Such high-boiling hydrocarbon resins never truly harden or dry, but remain on the paper surface. However, binders such as alkyd resins and drying oils undergo a further chemical drying process. This can be either an oxidative drying or a heat, UV or electron beam initiated curing process. The nature of the physical drying processes and the chemical nature of the printing ink binders and pigments play a large role in determining the deinkability of the resultant printing ink. It has been found that binders and solvents that are covalently bonded; uncrosslinked; alkaline insoluble and wet pigments are easy to deink. In contrast, solvents and binders that are polar; crosslinked; alkaline soluble and wet pigments poorly are difficult to deink (Goettsching & Pakarinen 2000: 274). These inks typically form large coherent ink particles on repulping and can't be easily emulsified (Read 1986). It has been found that as the recovered paper ages, the deinkability deteriorates. This is particularly the case with inks that contain crosslinking binders (Goettsching & Pakarinen 2000: 293).

When reference is made to ink particles in a deinking system, the particles are, in fact, agglomerates of pigment and the binder system used in the ink. It is actually

the binder that determines the surface chemistry of the ink particle (Read 1991), the ease with which it can be removed and the ultimate particle size distribution (Read 1986).

Once the ink has been applied to the web of paper in the printing process, it dries by loss of solvent and by cross-linking reactions, and the pigment in its binder matrix sits on the surface of the paper. In order to be recycled, the recovered paper must be re-pulped and the ink must be separated from the fibre substrate. This is accomplished in the first stage of the deinking process, the pulper.

In South Africa, all newspapers are printed by offset lithography, using cold-set or heat-set inks. The pigment in black inks is carbon black, and hydrocarbon resins are used as binders. No drying oils or alkyd resins are used (Watson 2001). The typical composition of South African newsprint inks is discussed in more detail in Section 3.3 below.

2.2.2 The Chemistry in the Pulper

Water, recovered paper and a variety of chemicals are charged to the pulper and mixed together for a period ranging from 4 to 60 minutes, at a temperature of 45 to 60 °C and a pH of 9.5 to 10.5. However, conditions of 12% consistency, 60 °C and 20 minutes pulping time are considered to be optimum (Ali *et al.* 1994).

At Merebank, the specific pulping conditions are 15% consistency at 45°C for 15 minutes. The water used to repulp the paper is recycled filtrate from the disc filter, as detailed in Sections 1.2 and 2.1.7 above. The elevated temperatures ensure faster kinetics and increased solubilities of the process chemicals (McCormick 1990). The function of the pulper is to convert the recovered paper into a pulp, which can be pumped and processed. In addition it has to perform the first critical step in the recycling sequence: the separation of ink from the fibre and the stabilisation of the ink particles to prevent their re-deposition onto the fibres. Three mechanisms of ink re-deposition have been identified. These are lumen loading, chemical re-deposition onto the fibre surface and mechanical re-deposition onto the fibre surface. In lumen loading small ink particles migrate through the pits in the fibre wall into the hollow centre of the wood fibre, called the lumen. Through a process of physio-chemical adsorption ink particles can adhere to the surface of the fibres. Ink particles can also be mechanically snagged by irregularities on the fibre surface. In order for this

redeposition not to occur, both the fibres and the ink particles must be stabilised and hydrophilic in nature. Any hydrophobic character will lead to immediate re-deposition (Goettsching & Pakarinen 2000: 244). The separation of the ink from the fibres is facilitated by the fibre-to-fibre friction and mechanical action in the pulper (Schriver 1990, Borchardt 1993, 1997). Chemically, the ink removal mechanism has been compared to a laundering process, which is facilitated by the high alkalinity and the presence of surfactants and complexing agents (Borchardt 1993, Larsson 1987). The removal of ink is considered to be essential for the successful deinking of recovered paper. If the ink is not separated from the fibre or re-deposits onto the fibre, its subsequent removal by flotation will not be possible.

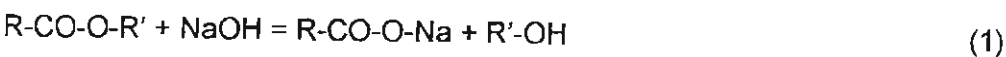
The chemicals that are commonly added to a newsprint deinking system are: sodium hydroxide (NaOH), hydrogen peroxide (H₂O₂), chelating agents, sodium silicate, surfactants and collectors. Typical (Ferguson 1991) and Merebank specific levels of addition are listed in Table 2.3 below.

Table 2.3: Addition levels of principal pulping chemicals.

Chemical	Merebank addition, % on fibre	Typical addition level, % on fibre
Sodium hydroxide	As required by pH	0.8 – 1.5
Hydrogen peroxide	0.48	0.5 – 2.0
Chelant	nil	0.15 – 0.4
Sodium silicate	1.0	1.0 – 3.0
Surfactant/collector	nil	0.25 – 1.5

Every deinking plant needs to carefully optimise the addition rates of each individual chemical to ensure optimum performance.

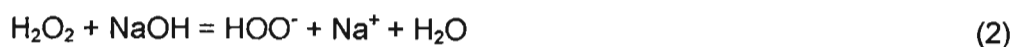
Sodium hydroxide is used to adjust the pH of the pulping system into the alkaline region of 9.5 to 10.5. In the case of the Merebank plant, pulping is carried out at pH 9.8 to 10.2. At this pH the fibres take up water, are softened and are said to swell and become more flexible. Printing ink binders that consist of drying oils or alkyd resins would be partially saponified (Ferguson 1992a, McCormick 1990) according to the following general reaction:



These saponified ink resins would have enhanced solubility in alkaline medium and would carry a negative charge in solution. However, based on work carried out by Ben & Dorris (1999) and Johansson & Ström (1999), very little saponification of the ester group was found to occur. Only minor oxidation and limited polymerisation of the fatty acid chains took place. In any event, because the printing inks used in South Africa do not contain drying oils, the saponification mechanism of ink removal is not expected to play a role.

An undesirable side effect of adding caustic soda to a fibre pulp is that the fibres yellow or darken in a process known as "alkali darkening" (Ferguson 1991, 1992a). Alkali darkening is caused by the formation of chromophores in the lignin molecules. If too much caustic soda is added, excessive yellowing can occur. In addition contrary materials such as stickies can be softened, which makes their removal by mechanical screening difficult. It has been shown that at a pH in excess of 10.2 the pulper brightness of a 70:30 newsprint/magazine furnish starts to deteriorate (Ferguson 1991).

Hydrogen peroxide is added to the pulper to overcome the effects of alkali darkening. The reaction with caustic soda at pH 10.0-11.5 and 40-80 °C is:



The perhydroxyl anion (HOO^-) is the active species in the bleaching reaction (Ferguson 1992a). From reaction (2) it can be seen that the concentration of NaOH can influence the bleaching reaction in addition to raising the pH. The concentrations of both species need to be taken into account in arriving at the optimum bleaching performance (Ferguson 1992a). A number of side reactions can occur, as a result of the many contaminants present in the system. Heavy metal ions such as Fe^{2+} , Mn^{2+} and Cu^{2+} can catalyse the decomposition of hydrogen peroxide according to reaction (3) below:

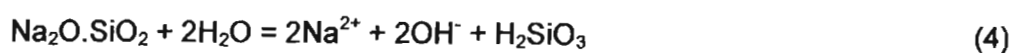


In order to prevent this decomposition, chelating agents such as the sodium salts of DTPA (diethylenetriaminepentaacetic acid) or EDTA (ethylenediaminetetraacetic acid) are commonly added to the pulper. The chelants preferentially complex with

the offending metal ions and thus prevent the decomposition of hydrogen peroxide. It has been shown that certain printing inks can be a significant source of heavy metals (Ferguson 1991). The addition of chelant has been discontinued in the Merebank process, as it has been found to be unnecessary.

Bacteria that occur in the process water can produce an enzyme called catalase that can also decompose the hydrogen peroxide (Goettsching & Pakarinen 2000: 243, Sundblad & Mattila 2001). Counter measures such as shock dosing with peroxide or the addition of enzyme inhibitors are necessary to combat the problem. A propriety enzyme scavenger of the type described by Sundblad & Mattila (2001) is added in the Merebank process.

Sodium silicate is added to the pulper, most usually in the form of a 41.6 °Be solution. (°Be or degrees Baume' = $145(1-1/SG)$). In this form it is a viscous liquid containing approximately 8.9% Na₂O and 29% SiO₂. Sodium silicate has a number of functions in the deinking system. Firstly, it confers alkalinity on the system and acts as a pH buffer, according to reaction (4) below, which is a simplification of the complex reactions that actually occur:



This reaction buffers out at pH 11.3 (McCormick 1990). From reaction (4) it is clear that sodium silicate will interact with the sodium hydroxide and hydrogen peroxide present in the system. Secondly, it is known that sodium silicate improves the peroxide brightening response by stabilising the environment in which the hydrogen peroxide carries out its bleaching function (Ali *et al.* 1988). In their work, they report that an extra 2 to 7 brightness points can be achieved by the use of sodium silicate in the bleaching process. The actual mechanism is unclear, but is thought to involve the formation of a colloidal structure with heavy metal ions (Ferguson 1991, 1992a). In addition, Ali *et al.* (1988) report that sodium silicate reduces the rate of alkali darkening by reducing the extent of peroxide decomposition. Thirdly, it is known that the addition of sodium silicate improves the performance of a deinking system, yielding higher brightness after pulping and flotation (Ali *et al.* 1994). Again, the mechanism of this action is unclear, but has been attributed to the dispersing action of sodium silicate (Ferguson 1991). This mechanism forms the subject of this investigation, and will be addressed in more detail later. The use of sodium silicate leads to a build up of silicates in solution. The silicates can be carried forward to the

paper machine systems, where they can interfere with retention aid systems (McCormick 1990) and where deposits and scale formation can occur. It is therefore important not to overdose the system with silicate.

It should be noted that the Merebank plant is not using a conventional sodium silicate, but is using a proprietary formulated product that has been designed to optimise the stabilisation of hydrogen peroxide.

The mechanical action of the pulper impellor alone is not sufficient to completely remove all ink attached to the fibres (Rao & Stenius 1998). To this end surfactants are sometimes added to a pulping system in order to assist with the wetting of the recovered paper, the dispersion of ink or the stabilisation of ink particles to prevent re-deposition onto the fibres (Schrivver 1990). The surfactants are usually non-ionic molecules based on ethylene oxide/propylene oxide block copolymers (Ferguson 1991, Rao *et al.* 1999), whose efficiency depends on their hydrophilicity. These surfactants tend to reduce the flotation efficiency, as the calcium-soap particles and ink particles are stabilised by the surfactants (Johansson & Ström 1999).

Collector chemicals, whilst most frequently added at the flotation stage, are sometimes added into the pulper. The most commonly used collectors are the sodium salts of fatty acids. The fatty acids would have a similar action to the dispersants discussed above, in particular the dispersion of ink in the pulper (McCormick 1990, Borchardt 1997, Rao & Stenius 1998). The fatty acid soap will only act as a dispersant if there is an excess for free soap anions, which will depend in turn on the concentration of calcium in the pulper (Rao & Stenius 1998). If there is a high hardness in the pulper, the calcium ions will precipitate the free fatty acid, rendering it inert and ineffective as a dispersant (Weigl *et al.* 1987).

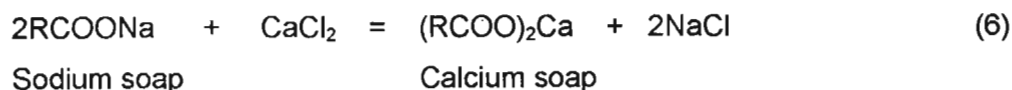
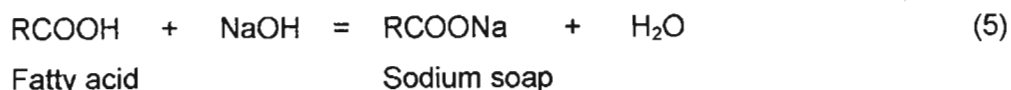
No fatty acids or surfactants are added into the pulper at Merebank. However, 150 to 234 ppm of residual soap and 66 to 96 ppm calcium hardness is recycled back to the pulper in the disc filter filtrate, as described in Section 2.1.7.

At the conclusion of the pulping process, the fibres should be well separated from each other and well dispersed in the process solution. The yellowing that was induced by the high pH environment has been counteracted by the hydrogen peroxide, and only a small residual concentration of hydrogen peroxide should exist. The residual peroxide after pulping is monitored in the Merebank process, and a

small residual is maintained by adjusting the amount of hydrogen peroxide added. Most importantly, the ink particles should be separated from the fibre, well dispersed and sufficiently stabilised to ensure that no re-deposition onto the fibres occurs. The chemical nature of the ink and the chemical and hydrodynamic processes in the pulper will have determined the ink's particle size distribution. This pulp is passed through various physical separation processes (as described in Section 2.1 above) before it is pumped to the flotation cell. Just before the flotation cell the fibre suspension from the pulper is diluted with recycled process water to a consistency of 1% and the pH is adjusted to 8.5 with sulphuric acid. Collector soap at 4 kg/ton dry fibre and sufficient calcium chloride (2.0 – 3.5 kg/ton dry fibre) to obtain a calcium hardness in solution of 250 ppm as CaCO_3 is added. In the flotation cell air is bubbled through the fibre pulp. The air rises to the surface and forms a head of foam on the surface of the pulp. This head of foam, now laden with ink particles together with some fibres, fines and filler, flows over a weir and is thereby removed from the system.

2.2.3 Chemistry in the Flotation Cell

The chemistry in the flotation cell is essentially the opposite of what happens in the pulper. The pulping process is a dispersion process, whereas the flotation process is an agglomeration process. In order for flotation to be successful, the ink particles must be hydrophobic and must agglomerate to an ideal particle size range of 10 to 100 microns (Ferguson 1992b). Goettsching & Pakarinen (2000: 245) state that a size range of 20-40 microns is ideal, and Borchardt (1997) quotes a range of 30-80 microns. Once in the particle size range, the ink particle is able to attach itself to an air bubble that is rising through the flotation pulp. To achieve this objective, it is necessary to add chemicals called collectors. The collectors most widely used in newsprint deinking systems are commercial fatty acids, which are usually blends of C16 to C18 saturated and unsaturated carboxylic acids such as stearic (C18:0), oleic (C18:1), palmitic (C16:0), linoleic (C18:2), linolenic (C18:3) and palmitoleic acids (C16:1). The fatty acid can be introduced into the system in a number forms: solid soap pellets, liquid soap, or the free fatty acid itself, which must be converted to the soap *in situ*. Regardless of the method of addition, the soap must be converted to the calcium salt of the fatty acid according to reactions (5) and (6) below, before it can function as a collector. (Ferguson 1992b, Johansson *et al.* 1996, Johansson & Ström 1999.)



Whilst the sodium soap is sparingly soluble in water at low concentrations, the calcium soap is insoluble, and precipitates out of solution as a fine white precipitate. The calcium level required for effective collector activity is widely accepted to be about 200 ppm of calcium, as CaCO_3 (Ferguson 1992b). This equates to 80 ppm of Ca^{2+} . The calcium is added to the system in the form of a calcium chloride solution. However, in areas where the water is naturally hard, or recovered paper that contains large amounts of calcium carbonate filler is used, the addition of extra calcium might not be necessary.

There are two main schools of thought as to the mechanism of ink removal by flotation. Many workers (Goettsching & Pakerinin 2000, Linck 1990, McCool 1993, Schriver 1990) refer to the work of Larsson *et al.* (Larsson, A., Stenius, P., Odberg, L. Sv. Papperstidning 88(3),R2(1985) and 87(18),R165(1984)). This theory suggests that, in the presence of calcium ions, the soap precipitates according to equation (6) as very small particles, or micro-precipitates (Ferguson 1992b) onto the surface of the ink particles. This renders the ink more hydrophobic and agglomerates the ink into larger particles. These soap-coated particles enhance the adhesion of the ink to the air bubbles and facilitate their removal from solution. Figure 2.1 below depicts this process:

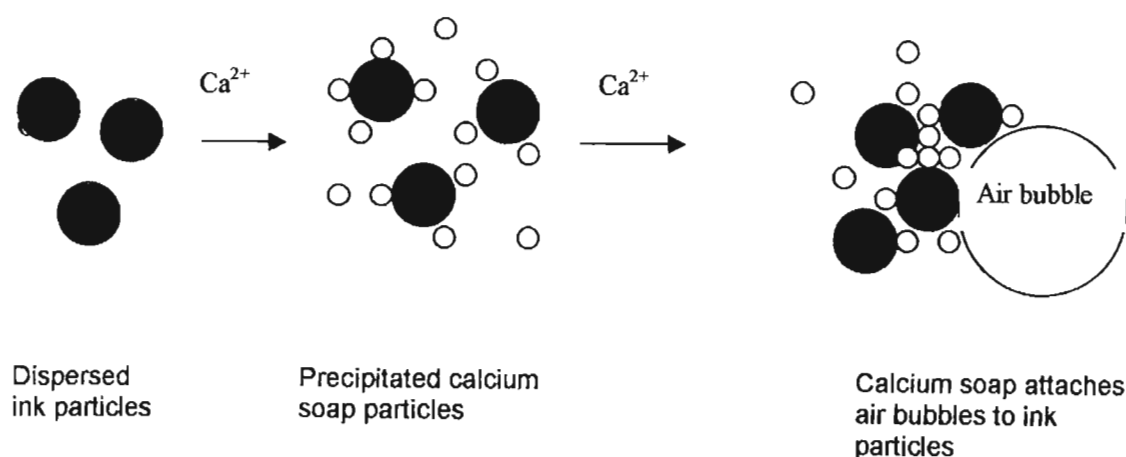


Figure 2.1: Collecting mechanism of calcium soap, according to Larsson *et al.*

According to Larsson (1987), this layer of sub-micron calcium soap particles was visible under a scanning electron microscope.

McCormick (1991) has proposed another theory for the flotation of ink particles. An ink particle that has been lifted from the fibres in the pulping process is dispersed by the soap molecules. The soap molecules are adsorbed onto the surface of the ink particle. When the calcium ions are added, they react with the soap molecules according to reaction (6) (p. 21). However, instead of the normally linear soap/calcium salt, a strained configuration is assumed, because the soap molecules are adsorbed onto the surface of the ink particle. Nevertheless, the positive charge on the soap particle has now been neutralised and the ink particle is more hydrophobic. When two ink particles collide, a re-arrangement of the adsorbed calcium soap molecule takes place, and the calcium ion now acts as a bridge between two ink particles. This process can repeat itself and larger ink agglomerates can be built up. In a similar way, the calcium soap adsorbs at the air/water interface, producing stable air bubbles. When such a stabilised air bubble collides with an ink particle, a similar calcium soap re-arrangement takes place and the ink particle is attached to an air bubble, *via* the calcium link. This mechanism is shown in pictorial form in Figure 2.2 below.

Putz, Schaffrath & Goettsching (1993) have proposed a model in which the surfactants adsorb onto the surface of the ink particle and facilitate the breakdown of the "hydrate cover" that acts as a barrier between the ink particles and the air bubbles. Once this hydrate cover is disrupted, attachment to the air bubble occurs and ink removal by flotation can take place.

In reviewing the abovementioned mechanisms of ink collection, Johansson *et al.* (1996) indicate that a co-agglomeration of ink and soap particles occurs, which is induced by the excess of calcium and other cations in a deinking system.

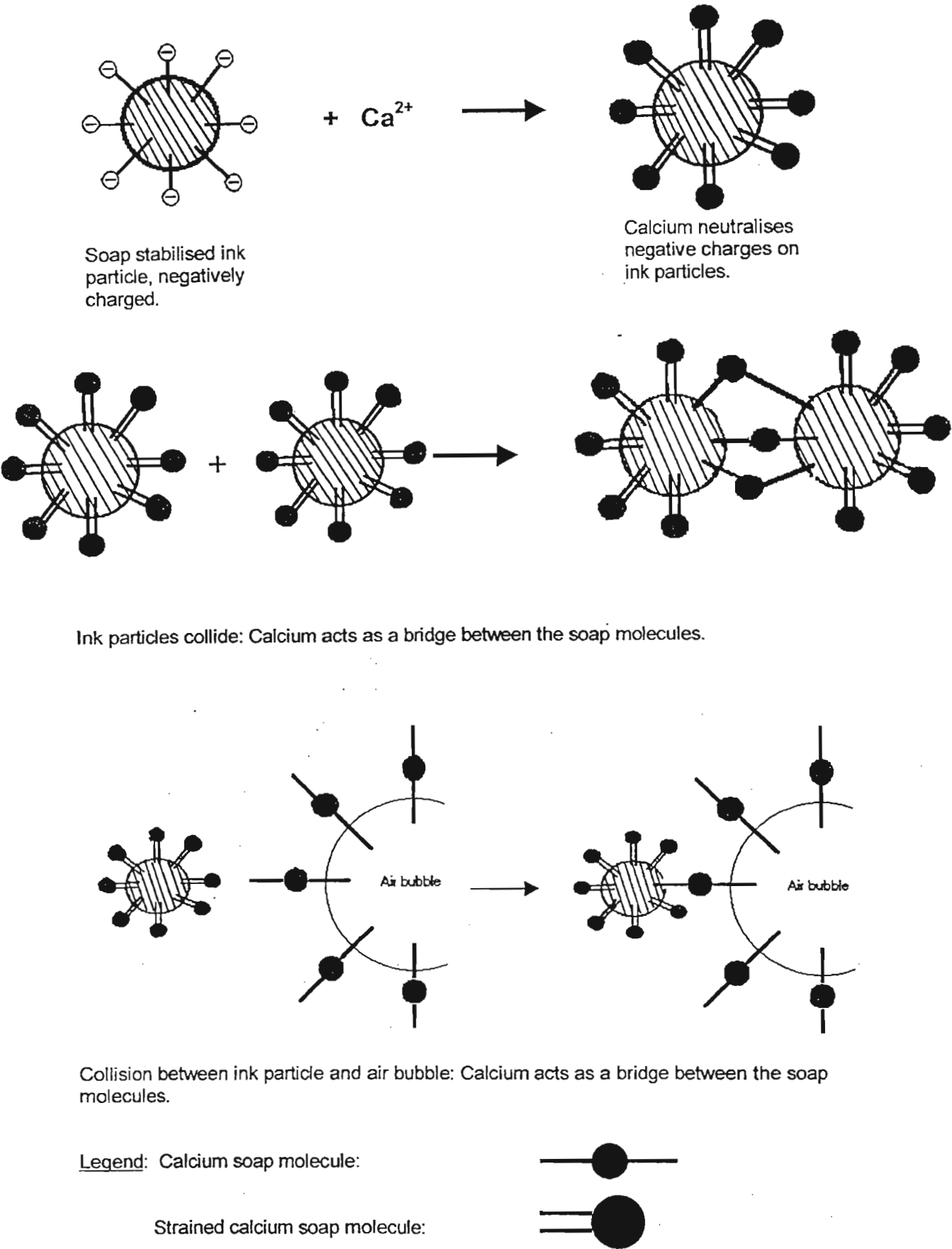


Figure 2.2: Mechanism of ink agglomeration and flotation, according to McCormick (1991).

2.2.4 The Soap and Surfactants

The fatty acids are the most commonly used surfactants in the deinking of newsprint. Commercial blends of predominantly stearic, oleic and palmitic acid are usually used. These fatty acids have good dispersing and foaming properties and exhibit rapid biodegradability (Goettsching & Pakarinen 2000: 254), which is an important factor in the event that residues of soap find their way into effluent systems. A potential disadvantage of the fatty acid soaps is their sensitivity to water hardness, according to equation (6) (p. 21) above. However, as outlined in Section 2.2.3 above, the reaction with calcium is an integral part of the collecting mechanism, and ensures that the ink particles are in the correct particle size range for efficient flotation. The optimum fatty acid chain length for newsprint flotation is reported to be C16 (Mak & Stevens 1993). The ideal degree of unsaturation, as measured by the Iodine Value, depends on the water hardness. Collectors with higher iodine values need higher water hardness to perform well (Mak & Stevens 1993).

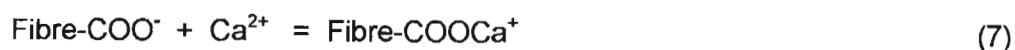
The handling and dosing of fatty acid soaps can be problematic in a practical plant situation, due to their solid waxy form at ambient temperature. These soaps need special preparation and storage measures to effectively dose them into a system. Liquid solutions need to be kept hot and spills can solidify, blocking drains and making floors slippery (Turvey 1990). In order to avoid these difficulties, a number of synthetic surfactants have been developed, which allow easy handling and are not sensitive to water hardness. However, in a wide-ranging study of a number of different surfactants, it was found that fatty acid based systems out-performed all other types (Mak & Stevens 1993). Nevertheless, the final choice of surfactant for deinking is determined by a host of practical factors, which might outweigh the considerations of deinking efficiency alone.

In the Merebank plant, a commercial soap, consisting of a blend of 85% tallow oil/ 15% palm oil and supplied in the form of noodles, is used as the fatty acid collector. The soap noodles are converted on-site into a ca. 5% solution for addition into the process. A detailed analysis is contained in Appendix A.

2.2.5 The Role of the Calcium Ion

The important role that the calcium ion plays in the mechanism of ink removal by flotation has been discussed in Section 2.2.3 above. In addition to this collecting role, the calcium ion exhibits numerous interactions with other components of a deinking system.

It has been established that the hardness of a flotation system influences the amount of fibre that is lost during the flotation process (Turvey 1987, 1990, 1991). This fibre loss is undesirable and constitutes a loss of yield in the process. In a case study reported by Turvey (1990), a fibre loss of 7 -10% was observed at a hardness of ca. 280 ppm calcium. The calcium ions can interact with the fibres present in a deinking system. Schwinger & Dobias (1991) report that the calcium cation adsorbs onto the surface of the fibre, which results in a reduction of the normally negative surface charge to almost neutral. It is this neutralisation of surface charge that renders the fibres hydrophobic and thus floatable. Turvey (1991) claims that the calcium cations are held onto the fibre surface via the numerous carboxylic acid groups that occur on a fibre surface in an alkaline environment, as per equation (7) below.



In addition, under the alkaline conditions encountered in a deinking system, the calcium ions could precipitate as calcium hydroxide as per equation (8).



However, according to Oliveira & Torem (1996) and Froass *et al.* 1997, this reaction does not become significant below pH 12.

Calcium will also react rapidly with sodium silicate to form insoluble calcium silicate.



Froass *et al.* 1997 have shown that the critical precipitation concentration for calcium in a silicate solution is about 1.4 mmol/l (ca. 56 ppm of calcium) at pH 9.2,

60°C and 39 mmol/l SiO₂ (ca. 2340 ppm SiO₂). These calcium silicates are known to form deposits on stainless steel process equipment.

If any bicarbonates are present in solution, calcium will also react with these as in equation (10) below.



Turvey (1991) reports that the adsorption of calcium onto the fibre predominates the above reactions under alkaline conditions, and is responsible for the flotation of fibres. Turvey (1991) reports that small ink particles are capable of interacting with calcium ions, and will deposit onto a fibre *via* the calcium half-salt reaction (7) above.

If a deinking system contains mineral fillers such as kaolin (aluminium silicates), these filler particles will usually carry a negative surface charge. Calcium ions adsorb onto the surface of the mineral filler, partially neutralising the negative charge (Liphard *et al.* 1991).

2.2.6 Fillers

One of the major components in a deinking system is the mineral filler. The filler most commonly occurring is clay, or kaolin, although fillers such as talc or calcium carbonate can also occur (McCormick 1991). The fillers usually originate from the magazine component of the recovered paper mix. Newsprint is usually deinked in combination with recovered magazine papers, as it has been found that it is difficult to deink newsprint on its own by flotation (Schrivier *et al.* 1990, Zabala & McCool 1988). The blending ratio is typically 70% newsprint: 30% magazine, although this can vary depending on availability and final pulp properties desired. Some deinking operations that do not use a magazine/newsprint blend will actually add fillers to the deinking cell, as it is believed that the filler improves the deinking efficiency (Schrivier 1990, Zabala & McCool 1988). It is hypothesised that the ink particles adsorb onto the surface of the filler, thereby producing larger, more easily floatable particles (Zabala & McCool 1988). A theory proposed by McCormick (1991) suggests that the negatively charged clay particles will neutralise the weak positive surface charge of the calcium on the ink surface, thereby forming a protective filler layer around an air

bubble carrying ink to the surface. Clay particles normally exhibit a plate-like structure with a negative surface charge.

Grant & Blain (1995) have shown that filler clays or talc absorb ink mineral oils and in the process form ink-coated mineral particles, which are stable to mechanical shear and adhere well to air bubbles in flotation.

Shen *et al.* (1995) report that the addition of clay to a laboratory flotation cell significantly reduced the fibre losses from the cell, without negatively affecting the flotation deinking performance.

Work done by Schriver *et al.* (1990) has shown that with fatty acid flotation chemistry, the best deinking performance was obtained from a calcined filler clay, followed by talc and a low surface area zeolite. Calcium carbonate did not appear to assist the deinking process. In this work a scavenging action was proposed as the mechanism of deinking.

However, workers are not unanimous on the benefits of fillers in the deinking process. Letcher & Sutman (1991) have reported work that demonstrates that fillers have no effect on deinking performance.

It is sometimes desired, in addition to removing ink, to remove the filler as well. Fatty acid collectors do remove a small quantity of filler, but special collectors are usually required to remove the fillers efficiently. This is normally accomplished in a dedicated second flotation stage, using proprietary flotation collectors (Liphard *et al.* 1991).

In the Merebank plant, no additional filler is added to enhance flotation. However, fillers such as clay and calcium carbonate are introduced via the magazine component of the recovered paper feedstock. The newsprint and magazine is blended in the proportion of 70:30.

2.2.7 Sodium Silicate

The final major chemical component of a newsprint deinking system is the sodium silicate. The use of sodium silicate in the deinking process derives from its use in

other fields of application. In order to investigate the role of sodium silicate in deinking, it is necessary to understand the general chemistry of the soluble silicates.

2.2.7.1 The general chemistry and properties of soluble silicates

The soluble silicates are a combination of silica and an alkali metal oxide, usually in the presence of water. The general formula can be written: $x \text{SiO}_2 : \text{M}_2\text{O}$, where M is Na, K or Li, and x is the molar ratio. Molar ratios of 2:1 are termed "alkaline" and ratios of 3.3:1 are referred to as "neutral".

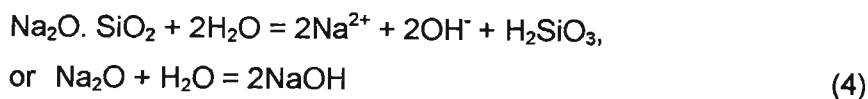
The sodium silicates are available as solid powders or as viscous solutions. The use of solutions is the norm in the paper industry. The density of such solutions is usually expressed as degrees Baume' ($^{\circ}\text{Be}'$) or degrees Twaddle ($^{\circ}\text{Tw}$) at 20 $^{\circ}\text{C}$. The units are defined in terms of the specific gravity (SG) as follows:

$$^{\circ}\text{Be}' = 145(1 - 1/\text{SG}) \text{ and } ^{\circ}\text{Tw} = 200(\text{SG} - 1)$$

The specific gravity and viscosity depend on the molar ratio and the concentration in solution. (Crosfield 1993)

The sodium silicate used in the Merebank process is a proprietary formulated product designed to optimise the stability of hydrogen peroxide. However, in this investigation, a conventional 3.3:1 molar ratio, 38% solids, 79 $^{\circ}\text{Tw}$ sodium silicate was used. A comprehensive data sheet is contained in Appendix A.

As already mentioned, solutions of sodium silicate are strongly alkaline, by virtue of reaction (4):



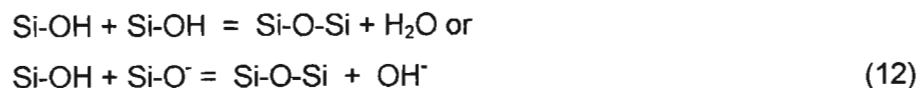
The buffering ability of sodium silicate is similar to that of sodium hydroxide, but occurs at a lower pH.

The silicate glasses consist of SiO_4 tetrahedra, either as monomers or as polymers of up to four tetrahedral units, each sharing an atom of oxygen to form Si - O - Si linkages. The SiO_4 units form random arrangements, with the cations located in the interstices.

Silicates in solution are governed by a number of chemical equilibria, depending on concentration and pH. Firstly an acid base equilibrium as in equation (11),



and secondly a polymerisation/depolymerisation equilibrium as in equation (12):



In dilute or very alkaline solutions the silicate is present mainly as monomeric species of the form H_4SiO_4 to HSiO_4^{3-} . As an alkaline solution of silicate is neutralised, rapid formation of a solid silica gel occurs at around pH 5-6 and lower (Anderson *et al.* 1982).

According to Crosfield (1993), the silicate forms the silicate anion (SiO_4^{4-}) in solution. Depending on the molar ratio and solution concentration, these SiO_4^{4-} anions can occur as monomeric (SiO_4^{4-}), dimeric ($\text{Si}_2\text{O}_5^{2-}$) or even higher molecular weight polymeric units. The polymers are not only linear, but can also be cage-like in structure. For a given concentration and pH, an equilibrium distribution of polymeric units is established, which rapidly re-arranges if the conditions are changed.

The SiO_4^{4-} anion has a strong negative charge and will adsorb onto selected sites on mineral and mineral oxide surfaces. This will confer a strong surface charge to the mineral particle, resulting in its improved wettability, de-flocculation and suspension (Crosfield 1993, Falcone 1982).

The SiO_4^{4-} anion reacts with multivalent metal ions to form insoluble silicate complexes. At high metal ion concentrations the soluble silicates react with calcium, aluminium or magnesium to form insoluble precipitates. At lower concentrations the silicates can sequester iron and manganese ions in water treatment applications. This sequestering action is utilised in the detergent industry, where silicate reacts with the water hardness ions to reduce their activity and thereby enhance surfactant performance. This is termed "building" in the industry (Crosfield 1993, Falcone 1982).

The soluble silicates, by virtue of their high alkalinity, tend to saponify organic oils and fats. The soluble soaps thus formed improve the overall detergent action. The silicates are more efficient emulsifiers than straight alkalis such as sodium hydroxide (Crosfield 1993).

The stability of silicate solutions is highly dependent on the pH. When the pH of a silicate solution is forced below about 9, an insoluble silica gel is formed. This occurs almost instantaneously in a concentrated solution, but can take many hours in dilute (less than 1% SiO₂) solutions. (Crosfield 1993)

2.2.7.2 The experimental work on the effects of sodium silicate in deinking

The effects of including sodium silicate in a deinking formulation have been investigated by a number of workers, each of whom have drawn their own conclusions as to sodium silicate's function and mechanism in deinking. In this section the results and conclusions of the various workers are presented.

The most comprehensive study is reported by Ali *et al.* (1994), who have found that:

- As the dosage of sodium silicate increases from 0% to 5% on dry fibre (or 0 to 5000 ppm in solution for a 10% consistency pulp), the brightness of the final pulp increased.
- Silicate enhances the removal of ink by forming larger particles, which are more easily removed by air flotation.
- It is postulated that the sodium silicate prevents suspended ink particles from re-depositing on the fibre surface.
- Sodium silicate had a stabilising function on hydrogen peroxide.
- Sodium silicate removes more ink than caustic soda alone.
- Brightness losses and yellowing increase as the alkalinity of a deinking system increases. This is reduced in the presence of sodium silicate.

This laboratory study involved the repulping of a 70/30 blend of newsprint and magazine, deinking by washing, deinking by flotation and measurement of brightness, lightness (L*), yellowness (b*) and particle size distribution by image analysis.

Mahagaonkar *et al.* (1997) report on experimental work that demonstrates that sodium silicate leads to higher brightness and reduced ink speck counts when used in the deinking of newsprint. They too suggest that the reason for this is that sodium silicate contributes to wetting, peptization, ink dispersion, alkalinity, buffering and peroxide stabilisation. In a second study by Mahagaonkar *et al.* (1996), sodium silicate again was found to have beneficial effects in deinking. This was attributed to its surface active properties. This study found that the nature of the alkali (calcium, magnesium and ammonium oxides and hydroxides) used in combination with sodium silicate did have an influence on the outcome.

An opposing view is offered by Mathur (1991), who reports that the surface active properties of sodium silicate do not play a role in ink removal. Instead, the chelation of metal ions such as Fe^{2+} , Mg^{2+} , and Cu^{2+} , which tend to decompose hydrogen peroxide, is the main reason behind the higher brightness observed when sodium silicate is used. In his study a constant alkalinity was maintained and the addition of chelant (DTPA) was optimised by determination of the amount of heavy metals in the system.

Read (1991) lists, without presenting any work, the functions of sodium silicate as being a dispersant, pH buffer and peroxide stabiliser. Ferguson (1992a) quotes the work of Ali *et al.* (1994). McCormick (1990) attributes pH buffering, detergency, particle lubrication and water softening (sequestering of calcium and magnesium ions) properties to sodium silicate. Again, no experimental work was presented. Borchardt (1995) states that sodium silicate is added to the pulper to act as a dispersant and to reduce ink re-deposition.

Santos *et al.* (1996) report on work that demonstrates that sodium silicate, together with all the standard deinking chemicals reduces the fragmentation of ink, which leads to improved flotation. In their study, sodium silicate was attributed the role of collector.

Renders *et al.* (1996) present evidence on the basis of image analysis that sodium silicate agglomerates small ink particles to form larger ones. Renders (1993) postulates that calcium and magnesium silicate complexes agglomerate small ink particles, on the basis of image analysis measurements on pulped samples. Dionne (1994) draws the same conclusions based on similar work.

However, not all workers are convinced that sodium silicate plays a positive role in deinking. Mak & Stevens (1993), in their study of the characteristics of fatty acids in deinking, found that sodium silicate was not a significant determinant of deinking performance. Zabala & McCool (1988) reported that they were able to eliminate sodium silicate from a commercial deinking system and replace it with a metal chelant with no negative effects on brightness.

In the Merebank deinking plant, attempts to eliminate sodium silicate from the process resulted in an immediate fall-off in deinking efficiency and loss of brightness. Crosby (1999) observed that " ...the collecting efficiency of ink particles by fatty acid soaps would appear to be greatly enhanced by the presence of sodium silicate."

In addition to the effects that sodium silicate has on ink removal, other effects have also been reported. Sodium silicate has been shown to reduce the fibre losses during deinking (Liphard *et al.* 1991, Ackermann *et al.* 1999).

Also, sodium silicate has been found to suppress the flotation of fillers (Ackermann *et al.* 1999, Mathur 1994). The action of sodium silicate in this case is related to its use in mineral flotation processes, where it functions by selectively adsorbing onto the surface of unwanted gangue minerals such as silica or iron oxide, thereby rendering them hydrophilic and depressing their flotation. Minerals such as chromium, copper, tin, fluorspar and phosphates are processed in this manner (Crosfield 1993).

2.2.7.3 A summary of the chemistry of sodium silicate in deinking

The previous section has reported on a lot of experimental work in the field. A number of opposing views are presented, all backed up by experimental evidence. In order to clarify the various roles of sodium silicate in deinking, the findings of the experimental work reported in Section 2.2.7.2 are consolidated in this section under a number of functional headings.

pH Buffering action and saponification

Solutions of sodium silicate are strongly alkaline, by virtue of reaction (4) (p. 18) above. The buffering ability of sodium silicate is similar to that of sodium hydroxide, but occurs at a lower pH.

Sodium silicate is a possible contributor to the saponification of ink binders, by virtue of reaction (1) (p. 16) above. However, this action has been refuted (see Section 2.2.2) and South African printing inks do not contain saponifiable binders. (Refer to Section 3.3 below).

Peroxide stabilisation

As discussed in Section 2.2.2, the silicates are known to perform an important role in the stabilisation of hydrogen peroxide in the bleaching of paper pulp. In this application it is reported to perform the roles of metal ion chelator, metal surface passivator, pH buffer, coating agent and detergent. The formation of the peroxysilicate ion is said to play a role in the bleaching chemistry (Ali *et al.* 1988). Transition metal ions such as iron, copper and manganese catalyse the decomposition of hydrogen peroxide, and the inclusion of sodium silicate chelates these ions and enhances bleaching efficiency (Crosfield 1993). This role is ascribed to by Mathur (1991) and Zabala & McCool (1988).

Prevention of yellowing

It has been established that sodium silicate reduces the yellowing of pulps in an alkaline environment (Ali *et al.* 1994, Renders *et al.* 1996).

Ink agglomerator or collector

This is the role of sodium silicate put forward by Renders *et al.* (1996), Renders (1993) and Dionne (1994), who postulate that the calcium and magnesium silicate complexes are actively involved in ink agglomeration. Ali *et al.* (1994) and Santos *et al.* (1996) also claim that sodium silicate acts as an ink agglomerator. Crosby (1999), in his observations on the effects of removing sodium silicate from the Merebank deinking process, alludes to the collecting effect of sodium silicate. It must

be pointed out that collecting behaviour is, as the name suggests, an agglomeration process. This is the opposite of a dispersing process.

Ink dispersant

This view is supported by Mahagoankar *et al.* (1996) and (1997), Read (1991), Ferguson (1992), McCormick (1990) and Borchardt (1995). In most instances, when this view is presented, it is in the absence of any direct experimental evidence. One of the origins of this view must be the use of sodium silicate to achieve enhanced oil recovery from mature oil fields. A solution of sodium silicate is pumped into the oil well, where it reacts with the free fatty acids in the oil to form soaps. These soaps reduce the surface tension and enhance the recovery of the oil (Crosfield 1993, Krumrine 1982). Also, soluble silicates are added into detergent formulations, where they are reputed to be more efficient emulsifiers than alkalis such as caustic soda. In the presence of the silicate anion, oil and grease is broken down into fine droplets which can be more completely saponified (Crosfield 1993, Schreiber 1982).

Sequestering action

The sequestering action of sodium silicate is well known in the detergent field, where it complexes water hardness salts and protects the surfactants. This is known as "building" in the detergent industry. McCormick (1990) makes mention of this function in deinking, but does not elaborate or present any experimental evidence. From the application of silicates in oil recovery, Krumrine (1982) reports that sodium silicates yield enhanced oil recoveries relative to sodium hydroxide, and attributes this to the interaction of the silica moiety with hardness ions. Weigl (1987) reports that the precipitation of calcium soaps in a pulper leads to higher surface tensions and reduced emulsification of inks, leading to increased redeposition of ink onto the fibres.

2.3 Assessment of deinking efficiency

The efficiency of the deinking process can be measured in two ways. Firstly, the efficiency of the process is determined by measuring the yield, which is defined as the pulp mass remaining after the deinking process as a percentage of the mass of recovered paper fed to the process. The deinking process typically removes ink,

some fibres, and mineral fillers such as clay or calcium carbonate. A single flotation deinking stage normally has a yield of about 85-90% (Goettsching & Pakarinen 2000: 295). A lower yield generally means a higher quality final product due to better deinking, but with negative economic implications. The yield is therefore a compromise between quality and cost. Flotation deinking plants are designed to optimise both these factors. Another way of looking at the efficiency of the deinking process is to consider the reject rate. The reject rate is the amount of material rejected by the deinking process relative to the amount of feed, and is really the converse of the yield as discussed above. The yield of the Merebank deinking plant is estimated to be about 82% (Cerff 2002).

The other main criteria of deinking efficiency are the optical properties of the pulp. There are three aspects to the optical properties; the brightness; the colour and the dirt content, which together determine the appearance of the final pulp to the human eye.

2.3.1 The Brightness

The brightness of the pulp is defined as the spectral reflectance at 457 nanometers (R_{457}) as measured by a spectrophotometer. The main methods are TAPPI T452 om-92, "Brightness of pulp, paper and paperboard (directional reflectance at 457 nm)" and the ISO standards ISO 2469, "Paper, board and pulps – measurement of diffuse blue reflectance factor (ISO brightness)" and ISO 2470, "Paper, board and pulps – measurement of diffuse reflectance factor (ISO brightness)". All of these methods measure the percentage reflectance of a pulp or paper sample at 457 nanometers, relative to a magnesium oxide standard. The geometry of the incident light differs between the TAPPI and ISO methods. In the TAPPI method the incident beam is at 45° , whereas in the ISO methods a diffuse incident light is used. The methods give similar results (Goettsching & Pakarinen 2000: 296).

The brightness is often used to measure the efficiency of deinking systems, but it has some major drawbacks. The removal of ink from a system will result in an increase in brightness, because the ink has a lower brightness than the pulp. However, the removal of other, naturally bright components such as filler clay may result in a decrease in final brightness, even though ink has been removed as well. Thus there is no direct correlation between brightness and ink content, and small ink particles have a greater influence on the brightness than larger ink particles (McCool

1993). Nevertheless, brightness is widely used as a measure of the quality of deinked pulp.

2.3.2 The Colour

Unfortunately, the R_{457} value alone will not describe the optical appearance of a coloured sample. With the aid of colourimetry, the response of the human eye to colour can be simulated and quantified. The system used to achieve this is called the CIELAB colour system, which makes use of a set of three colour co-ordinates in a colour space to describe a colour. The co-ordinates are L^* which denotes the lightness, a^* denotes the red-green axis and b^* represents the yellow-blue axis. (Goettsching & Pakarinen 2000: 296)

2.3.3 Dirt Content

The human eye cannot detect particles less than 50 microns in diameter (Goettsching & Pakarinen 2000: 269). Particles greater than this are detected as individual specks and particles below the visibility limit produce a grey appearance. With the help of image analysis techniques, the number of ink specks can be analysed quantitatively and the efficiency of deinking can be measured more directly (Anderson 1993, McCool 1993).

2.3.4 Effective residual ink concentration

This technique involves the measurement of the reflectance of a sample pad of pulp in the infrared region (950 nanometers) of the spectrum. At this wavelength only the black printing inks absorb light (Goettsching & Pakarinen 2000:268). The attenuation of the incident beam therefore gives a direct measure of the amount of printing ink on the surface of the pulp pad.

Depending on the requirements of the deinked pulp, the above methods can be used alone or in combination to evaluate the final appearance of the deinked pulp. Therefore, the brightness could be used as an overall measure of deinking efficiency, and image analysis could be used to determine more specifically the amount of ink removed, bearing in mind that each image analysis system has a

lower size limit below which it can't detect ink particles. This is usually about 2 microns (McCool 1993).

The efficiency of the deinking process and the reject rate of the process are dependant on each other. In general, the higher the reject rate the greater the removal of ink and other contaminants, but the lower the yield of the process. The ultimate efficiency of a deinking process can be determined by a process called "infinite flotation" (McCool 1993). This is determined by floating a sample of pulp in a laboratory flotation unit for an extended period of time. This results in complete removal of the ink, but at the cost of a high yield loss. One way of determining the ultimate deinking efficiency that could be achieved is by measuring the edge brightness. This is the brightness of the unprinted edge of the waste paper, and the deinked pulp can come to within 1-2 points of this figure, before final bleaching (McCool 1993).

In the Merebank deinking operation, brightness and pulp strength are the only quantitative criteria used for assessing deinked pulp quality. A visual determination of dirt, or visible ink spots, is also carried out.

3. DISPERSING PROPERTIES OF SODIUM SILICATE

3.1 Introduction

In the review of the literature in the previous section it emerged that a number of workers in the deinking industry consider the main function of sodium silicate in deinking, aside from its role as a stabiliser of hydrogen peroxide bleaching, to be its ink dispersing properties. However, sodium silicate in alkaline solution exists mainly as the SiO_4^{4-} anion, either singly or as a low molecular weight polymer (Crosfield 1993). This anion is an ionic, polar, hydrophilic chemical entity. It does not contain the hydrophilic/lipophilic character that is typical of a normal surfactant molecule. On the other hand, an offset ink particle of the type used in newsprint in South Africa is a highly hydrophobic entity, consisting of carbon black pigment and hydrocarbon resin binders. Notwithstanding the fact that the soluble silicates are used in detergent formulations and as oil dispersants, it is difficult to understand how the SiO_4^{4-} anion would have any affinity for an ink particle, such as would be necessary if the SiO_4^{4-} anion were to function as a dispersant for the ink. In view of this, as well as the prevalent view in the industry that sodium silicate acts as a dispersant, it was decided to investigate the ink dispersion properties of sodium silicate, to determine if they indeed played a role in the deinking mechanism.

3.2 Conditions in the pulper

In order to establish conditions for the experimental work, it was necessary to determine the conditions that prevail in the pulper of the Merebank deinking plant. To this end, the amount of excess calcium after pulping was determined, and also the amount of calcium and soap being returned to the pulper in the filtrate from the dewatering disc filter after the flotation stage. These process flows have been described in Sections 1.2 and 2.1 above.

3.2.1 Hardness in the pulper

Samples of pulp were drawn from the pulper (on completion of pulping) and filtered on a Buchner filter under vacuum. The resulting filtrate was analysed for free calcium by

EDTA titration according to a standard Mondi method, detailed in Appendix B. The results are shown in Table 3.1 below.

Table 3.1 Calcium hardness and residual soap in the pulper, in ppm.

Sample	Ca hardness, ppm Ca^{2+}	Residual soap ppm
1. Addis and Khathi (1992)	21	-
2. Pulper (12/1999)	39	-
3. Pulper (1/2000)	44	-
4. Cloudy filtrate (3/2000)	96	188
5. Cloudy filtrate (4/2000)	66	150
6. Cloudy filtrate (4/2000)	-	234

The hardness in the pulper has varied somewhat over time, and is currently at ca. 40 ppm. In a company internal report, Addis and Khathi (1992) report a plant pulper hardness which varied around 53 ppm CaCO_3 or 21 ppm Ca^{2+} .

3.2.2 Residual soap in solution

The amount of residual soap in solution in the disc filter cloudy filtrate was determined by a partition-gravimetric method. This method, entitled "Determination of soap, oil and grease" is a standard Mondi Merebank method, and is described in detail in Appendix B. The results for a period of time are also shown in Table 3.1 above.

The nature of the petroleum ether extract residue from the above mentioned method was determined by Fourier Transform Infrared Spectroscopy (FTIR), as detailed in Appendix C. The spectrum of the filtrate residue was compared to that of the known collector soap, and was confirmed to be a fatty acid.

The nature of the residue was further confirmed to be a fatty acid by gas chromatography, again by comparison against the known collector soap. The details of this comparison are given in Appendix D.

It must be remembered that the disc filter filtrate sample is the filtrate after flotation. It therefore contains excess soap (150 - 234 ppm) and excess calcium (66 - 96 ppm) that

were not consumed fully in the flotation cell. This water is fed back to the pulper, where it is used to re-pulp the incoming waste paper.

3.3 Choice of a model ink system as a method of investigation

A typical commercial deinking system is a complex mixture of many components, all of which can interact with each other. These interactions have been comprehensively discussed in the preceding chapter. In order to investigate the dispersing properties of sodium silicate in more detail, it was decided to use a model ink system. This consists of dispersing an ink in water, without components such as fibre, fillers and other substances that are normally found in a deinking system. The dispersing properties of such a simple system can then be studied in the absence of disturbing substances. This method of study has been successfully used by other workers to study deinking phenomena (Dorris & Nguyen 1993, Milanova & Dorris 1993, Oliveira & Torem 1996, Magda & Lee 1999).

Oliveira & Torem (1996) reported on the use of sodium stearate, oleic acid and sodium dodecyl sulphate as dispersants for a typical offset ink. Milanova & Doris (1993) made aqueous dispersions of flexographic inks, but reported great difficulty in making dispersions of offset inks. They found that it was necessary to use dispersants and high pH to successfully disperse oil-based offset inks. Dorris & Nguyen (1993) report that it is easy to make a stable aqueous dispersion of flexographic ink. A feature of all of these dispersion experiments was the use of a complete ink, consisting of vehicle (solvent and binder) and pigment (carbon black). However, as explained in Section 2.2.1, when a printing ink is applied to the surface of the paper, the carrier either evaporates or penetrates into the web of paper, leaving the binder and pigment to form a film on the paper surface. Thus, the ink particle that is removed from the paper surface in the deinking process differs somewhat from the fluid ink that is applied in the printing process, in that the solvent has disappeared. This problem was recognised by Johansson *et al.* (1996), who tried to study ink dispersions based on dry ink that had been redispersed.

In this work it was decided to try to work with a substance that is as similar as possible to the ink particles that would be removed in flotation, but that is still liquid enough to allow for easy dispersion. Accordingly, a local supplier of newsprint printing inks was

requested to supply a printing ink base, consisting of binder and pigment, but no solvent. The approximate composition of the ink base was as follows:

Carbon black	30%	
Crude mineral oil	50%	(Boiling point over 300 °C)
Hydrocarbon resin	5%	(Gilsonite resin)
Petroleum distillate	15%	(Boiling point 280-310 °C)

It is evident from the composition of the ink base that it contains very little saponifiable material that could be expected to saponify in alkaline medium and contribute to the dispersion of the material. The Gilsonite resin itself has an acid value of 2.3 and a saponification value of 5.6. (See Appendix A). The dispersion trials were carried out using this ink base.

3.4 Experimental Method

Great difficulty was experienced in producing a dispersion of the ink base. The ink base was very viscous and extremely hydrophobic. The ink tended to adhere to the stirrer shaft and to the sides of the beaker, and very small quantities of ink actually went into the dispersed state. Similar problems were also reported by Milanova & Dorris (1993). The ink base was very viscous, and the dispersion had to be prepared at over 95 °C in order for the ink base to be of low enough viscosity to disperse in the water.

The dispersion trials were carried out with the commercial grades of caustic soda lye (45%), sodium silicate (38% solids, $\text{SiO}_2\text{:Na}_2\text{O}$ ratio 3.3:1), calcium chloride (32%) and collector soap (97% purity, 80/20 blend of Tall oil and Palm oil). Typical analyses of these materials are given in Appendix A. All of these chemicals, with the exception of the sodium silicate, are in use at the Mondi Merebank deinking plant.

After some trial and error the following method was found to produce a stable ink dispersion:

1. Five hundred and fifty millilitres of deionised water was heated to over 95 degrees Centigrade in a 1 litre beaker.

2. Caustic soda, sodium silicate, calcium chloride and soap were added in various combinations and amounts to the hot water.
3. An excess of ink base (ca. 2 g) was added to the hot solution under vigorous agitation. The solution was agitated at 1500 rpm with a 25mm radius impellor type stirrer for 1 minute. The ink base was very viscous and a high temperature was required to soften the ink base sufficiently to allow dispersion to take place.
4. The pre-dispersed ink was then placed under an ultrasonic disperser for 15 minutes to complete the dispersion. A Sonics & Materials Inc. high intensity ultrasonic processor model VCX400 was used in combination with a standard 13mm model CV26 high intensity probe. The ultrasonic dispersion was performed at 20kHz with a maximum power input of 400W. The probe was tuned at an amplitude of 30% in a solution of hot water (98 °C) prior to dispersing.
5. The dispersion was allowed to cool, the excess undispersed ink was skimmed off, and the dispersion was decanted into another container.
6. An incident beam of light, of intensity I_0 , is scattered as it passes through a dispersion. The intensity I , of the beam of light is given by the relation $I = I_0 e^{-t}$, where t is the turbidity, or decrease in light intensity per unit length, and l is the path length. According to the familiar Beer's Law, the turbidity is proportional to the concentration of particles in suspension (Barrow 1973: 750.) Accordingly, the absorbance ($\log_{10}(I_0/I)$) of the solution was measured in a 1 cm optical cell at 555 nm. The absorbance, or optical extinction, was taken as a measure of the turbidity of the solution, which is proportional to the amount of dispersed ink. The absorbance measurements were performed on a Philips PU8625 UV/visible spectrophotometer.
7. A 5 ml. sample aliquot of ink dispersion was filtered on a 0.8 micron Millipore filter of 47mm diameter. The quantity of sample was chosen to ensure that discrete, un-agglomerated ink particles were formed on the surface of the filter. Image analysis was performed on the resultant pattern of ink specks to determine the particle count and size distribution. The measurement field was about one square centimetre, and four measurements per filter disk were made. Milanova & Dorris (1993) reported a similar technique, but used reflectance measurements instead of image analysis to determine the amount of carbon black dispersed. Nguyen *et al.* (1991) have reported a successful image analysis method for residual ink particles size in a pulp slurry. However, in this work a simplified method has been used, in the light of the fact that no fibres are present and the ink particles are generally quite large. The area of the ink particle on the Millipore filter is proportional to the particle size of the original ink particle in suspension, and the particle count is obviously directly

related to the number of ink particles in suspension. The details of the image analysis system are as follows:

Image analyser: Quantimet 520 VO5 by Cambridge Instruments Ltd.

CCD Camera: Philips type LDH0701/10

Camera lens: Tamron SP, 35-80mm macro zoom lens.

The samples were placed on a Haiser light stage and illuminated with 4 x 25W white incandescent lights.

The system had a minimum resolution of 20.8 microns per pixel. The system analysed the particle size distribution and produced a mean and median particle size and a particle count.

8. Individual ink particles were isolated from the Millipore filter by excising a small area of filter and mounted on a stub with double-sided tape. The sample was sputter coated with gold and examined under a Hitachi S520 scanning electron microscope (SEM). An energy level of 10kV was used for imaging. Photographs were taken of typical particles and the complete surface of the particle was scanned by energy dispersive spectroscopy (EDS) at 20kV, using a Link Isis EDS system, to determine the concentrations of calcium and silicon on the surface of the ink particles.
9. The following combinations of NaOH, CaCl₂ and soap were compared at addition levels of 0, 1000, 2000 and 4000 ppm of sodium silicate. This range corresponds to and exceeds the practical range of addition of sodium silicate in commercial systems. At 0 ppm of sodium silicate, caustic soda was used to adjust the pH of the solution to 10. No caustic soda addition was necessary when sodium silicate was added, as the pH was always in the range of 10 to 11.
 - Experiment 3.1: Sodium silicate at a SiO₂:Na₂O ratio of 3.3 to 1
 - Experiment 3.2: Sodium silicate at a SiO₂:Na₂O ratio of 2.0 to 1. This was achieved by adding NaOH to the 3.3 silicate solution in the appropriate ratio.
 - Experiment 3.3: Sodium silicate in the presence of 80 ppm Ca²⁺ ion. The level of 80 ppm was chosen towards the upper limit of the levels of calcium found occurring in the pulper make up water (cloudy filtrate), as listed in Table 3.1 (p. 39) above. The silicate and the calcium produced a white milky solution, due to the formation of insoluble calcium silicate. The turbidity of this milky solution was determined before the ink was dispersed, and subtracted from the final turbidity in order to obtain the incremental turbidity due to the dispersed ink.

- Experiment 3.4: Sodium silicate in the presence of 50 ppm sodium soap. The level of 50 ppm was much lower than actually found in the filtrate water (see Table 3.1, p. 39), but was considered enough to produce a stable ink dispersion for the purposes of comparison.
- Experiment 3.5: Sodium silicate in the presence of 50 ppm calcium soap. The calcium soap was generated by adding the stoichiometric quantity of calcium chloride to the soap solution.

This method was successful in producing stable ink dispersions. Upon standing for a few days some settling of ink particles was observed. However, these were easily re-suspended with agitation. Because of the low dispersing power of the caustic soda and the sodium silicate, the amount of mechanical energy put into the process played a large role in the final result. Although every care was taken to reproduce the amount of dispersing energy that was put into the dispersions, the repeatability of the results was not all that good. Nevertheless, the differences were sufficiently large to draw some conclusions about the dispersing behaviour of the different systems.

3.5 Results and discussion

3.5.1 Turbidity Measurements

The results of the turbidity measurements on the five experiments described above are depicted in Figure 3.1 (p. 46) below. The dispersion trials were carried out at least in triplicate, and the averages for each series are displayed as a bar graph. The raw data is displayed in Appendix E. The variability is shown as plus/minus one standard error displayed on each bar.

As can be seen from Figure 3.1 (p. 46), the variability of some of the results was quite high. Nevertheless, the following general trends in the turbidity are evident.

- There is a small difference between the 3.3:1 $\text{SiO}_2\text{:Na}_2\text{O}$ ratio silicate (turbidity 0.176-0.216) and 2.0:1 ratio silicate (turbidity 0.176-0.283) with respect to ink dispersing power. An increasing concentration of silicate (from 0 ppm to 4000 ppm) shows a slight positive trend, which is greater with the 2.0:1 silicate. This is consistent with the knowledge that silicates disperse better than caustic soda alone (*i.e.* 0 ppm silicate).

- By comparing the experiments with and without soap, it is clear that the dispersing ability of the silicates is inferior to that of soap, whether in the form of the sodium soap or the calcium soap. The 3.3:1 silicate produced turbidities in the range 0.176-0.216, whereas the sodium soap produced turbidities of 0.510-0.636 and the calcium soap turbidities of 0.375-0.512.
- The presence of calcium seems to reduce the dispersing ability of the silicates and the soap. This can be seen by comparing the turbidities of Experiment 3.3 (0.094-0.198) to those of the 3.3:1 silicate (0.176-0.216), and the sodium soap (0.510-0.636) to the calcium soap (0.375-0.512)
- The amount of sodium silicate present influences the dispersing action of the soap. This trend is positive for calcium soap and negative for sodium soap. This can be seen by referring to Figure 3.1 below, where the sodium silicate concentration varies from 0 ppm up to 4000 ppm.

3.5.2 Ink Particle Size Measurements

The particle size of the ink is important for successful removal by flotation, as discussed in Sections 2.1.1 and 2.2.3. In addition, good dispersants will produce dispersions with fine particles (Blain *et al.* 1995, Goettsching & Pakarinnen 1999: 244) and poor dispersants will produce dispersions with larger particles. Thus, particle size is an important indicator of dispersing ability.

The median particle sizes of the various experiments are depicted in Figure 3.2. The median particle area was chosen in preference to the mean particle area as the median as a measure of central tendency is less sensitive to outliers. Again, the variability of particle size was quite large in some instances, but it can be seen that the experiments in which calcium was present, generally produced the largest particles. Experiment 3.3 (silicate/calcium) and Experiment 3.5 (silicate/calcium soap) produced dispersions with median particle areas in excess of 5000 microns². All the other experiments produced particles smaller than 5000 microns². This seems to be consistent with the general observation that calcium has an agglomerating effect in a deinking system, as discussed in Section 2.2.3, Larsson (1987) and Nguyen *et al.* (1991).

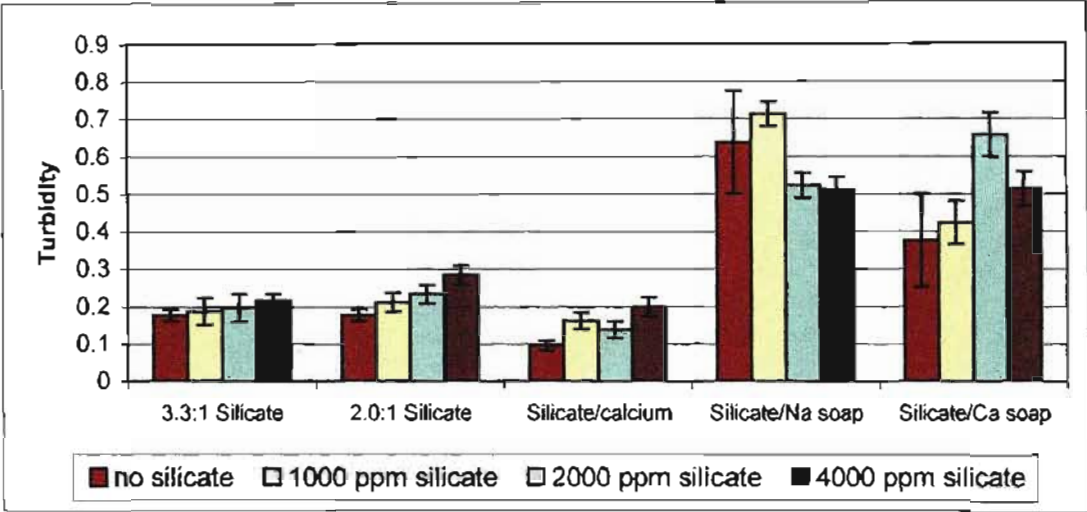


Figure 3.1: Turbidity of ink dispersions as a function of silicate concentration (0 to 4000 ppm) for Exp. 3.1 (3.3:1 silicate), Exp. 3.2 (2.0:1 silicate), Exp. 3.3 (silicate/calcium), Exp. 3.4 (silicate/Na soap) and Exp.3.5 (silicate/Ca soap). See p. 43 for quantities.

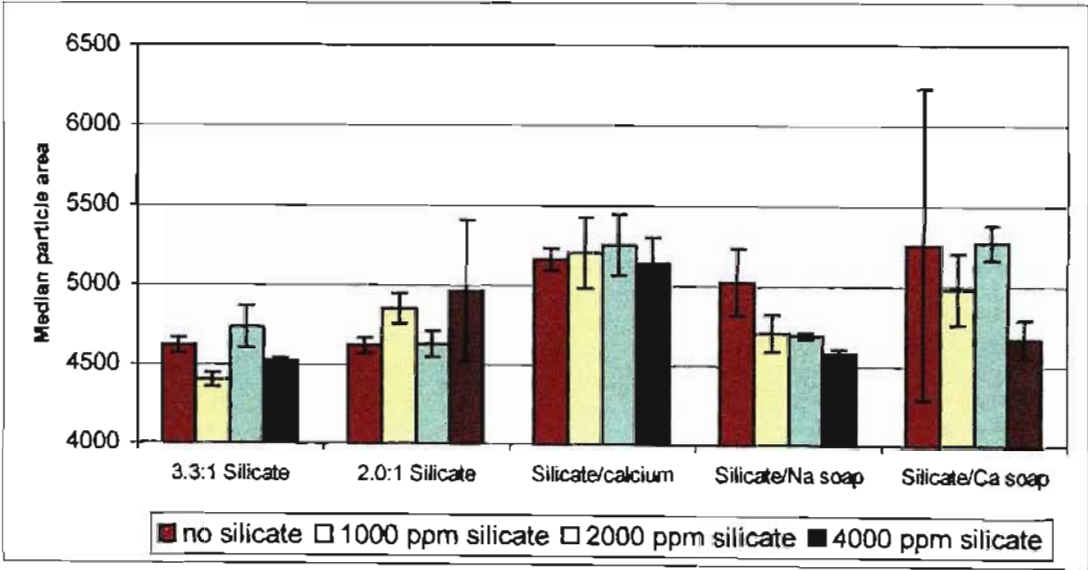


Figure 3.2: Median particle area in microns², of ink dispersions as a function of silicate concentration (0 to 4000 ppm) for Exp. 3.1 (3.3:1 silicate), Exp. 3.2 (2.0:1 silicate), Exp. 3.3 (silicate/calcium), Exp. 3.4 (silicate/Na soap) and Exp.3.5 (silicate/Ca soap). See p. 43 for quantities.

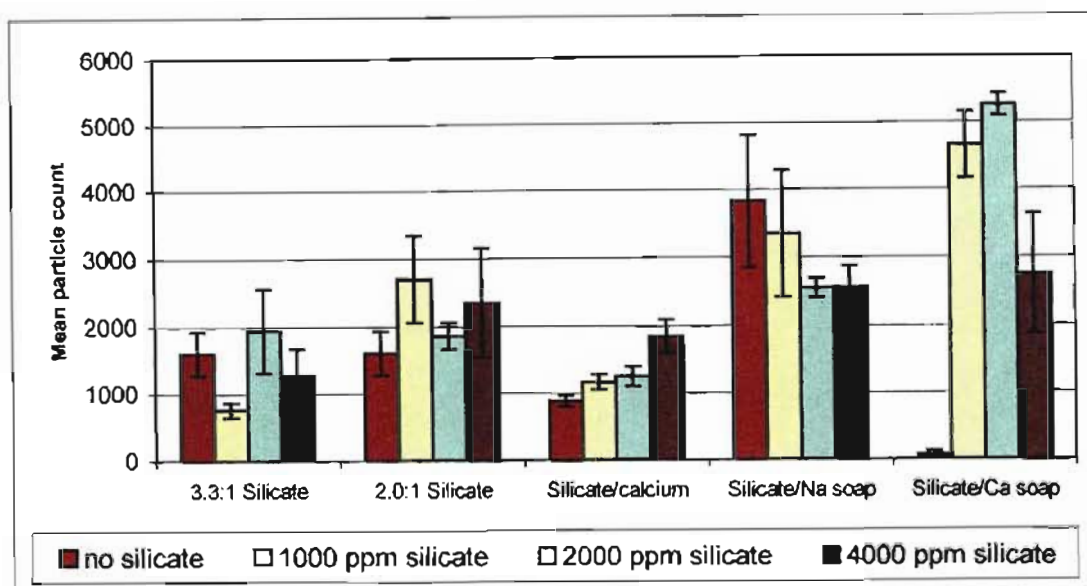


Figure 3.3: Mean ink particle counts of ink dispersions as a function of silicate concentration (0 to 4000 ppm) for Exp. 3.1 (3.3:1 silicate), Exp. 3.2 (2.0:1 silicate), Exp. 3.3 (silicate/calcium), Exp. 3.4 (silicate/Na soap) and Exp.3.5 (silicate/Ca soap). See p. 43 for quantities.

3.5.3 Ink Particle Counts

A good dispersing agent can be expected to produce many more particles than a poor dispersing agent, as it is able to stabilise a larger interfacial area. Therefore, the number of particles in a dispersion is another indication of dispersing ability.

The mean ink particle counts as measured by the image analyser are shown in Figure 3.3 above. The raw data is contained in Appendix E.

The experiments which contained soap generally produced dispersions with the most particles. Experiment 3.4 (silicate/Na soap) showed particle counts of 2554-3830 and Experiment 3.5 (silicate/Ca soap) showed a count of 67-5225. All other experiments had particle counts below 2741. The calcium containing dispersions at zero addition of sodium silicate contained the least number of particles. Again it was evident that the amount of sodium silicate present greatly modified this behaviour.

3.5.4 Dispersing Ability

It is difficult to interpret the particle size and particle count results in the preceding sections in isolation. However, if a good dispersant produces a dispersion with a large number of small particles, and poor dispersant produces a dispersion with a smaller

number of larger particles, the dispersing ability of a substance should correlate with the following model:

$$\text{Dispersing power} = f(\text{Number of particles/Particle size})$$

A plot of the quotient particle count/particle size against the turbidity of the dispersions is shown in Figure 3.4.

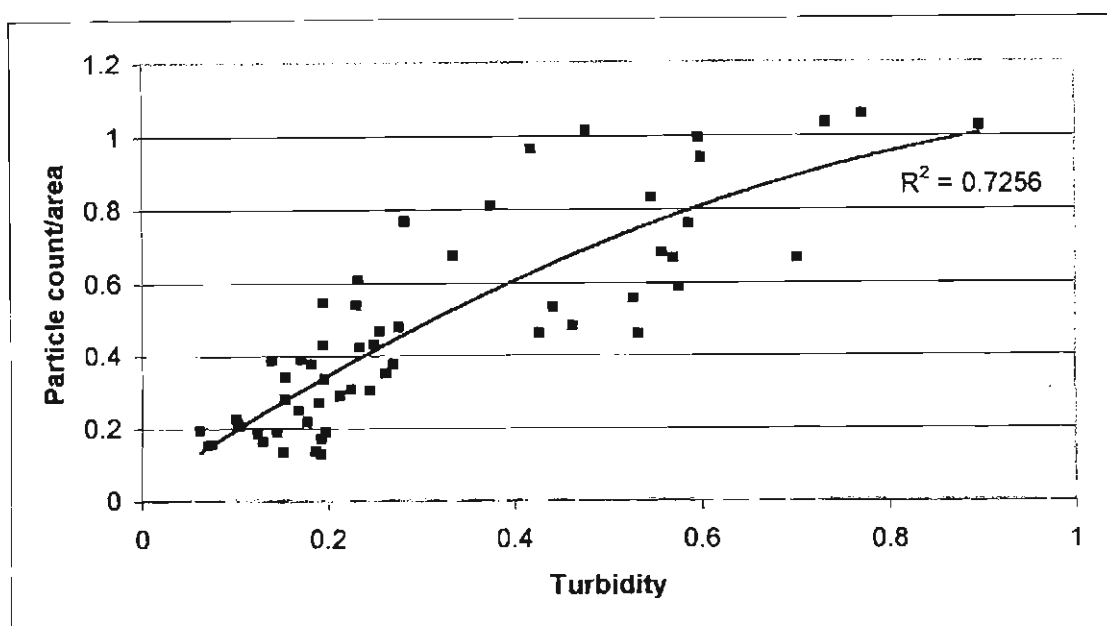


Figure 3.4: Dispersing power vs. Turbidity

Figure 3.4 demonstrates that a reasonably positive correlation ($R^2 = 0.72$) exists between the turbidity and the model proposed above. Therefore, despite the variability of the results obtained, and the difficulty of interpreting the particle size and particle count data in isolation, a reasonable amount of agreement exists between the three measures of dispersing ability employed. It should also be remembered that the image analysis has not detected particles below about 20 microns in diameter, whereas the optical turbidity measurement would take into account all the ink particles present. This factor would contribute to the scatter of results observed in Figure 3.4.

3.5.5 Particle Morphology and Surface Analysis

Typical ink particles from each series of experiments were examined under a scanning electron microscope (SEM) for morphology and surface characteristics, and an

elemental surface scan by EDS was performed. Borchardt & Rask (1994) report on the use of electron microscopy to qualitatively determine the effect of process variables on laser ink particle size and geometry. Blain *et al.* (1995) and Grant & Blain (1995) used the same technique, and reported micrographs of larger agglomerated ink particles of about 30 microns in diameter, as well as smaller individual ink specks. Oliveira & Torem (1996) also used SEM to study the effect of metallic cations on particle agglomeration. They reported on the effects of solution chemistry on floated ink particle morphology. The agglomerated ink particles tended to have rough surfaces, with either spheroidal (Blain *et al.* 1995) or irregular (Oliveira & Torem 1996) shape. In contrast, a dispersed particle tends to form a spherical shape with as small an interfacial area as possible (Barrow 1973).

3.5.5.1 Ink dispersed in caustic only

The particles were typically large and irregular in shape, as shown in Figure 3.5 (p. 51) below. This particle is similar in appearance to the agglomerated particles reported by Blain *et al.* (1995), and suggests that they were formed by agglomeration, rather than by a dispersing action. This can be attributed to the poor dispersing ability of caustic soda alone. The EDS spectrum of the surface of this particle is shown in Figure 3.6 (p. 51). The surface of the particle is essentially devoid of any metallic elements.

3.5.5.2 Ink dispersed in sodium silicate

The ink particles in this experiment ranged in size from small to large, of regular spherical shape. Figure 3.7 (p. 52) shows a SEM picture of a large particle of ca. 250 microns diameter surrounded by a number of smaller particles of 10 to 20 microns diameter. The smooth regular surfaces and spherical shape suggest a dispersing action rather than an agglomeration action as was the case with caustic soda above. The EDS silicon map in Figure 3.7 (p. 52) shows the distribution of silicon. The concentration of silicon is proportional to the density of the white areas in the map. It can be seen that the area occupied by the large particle corresponds to a lower concentration of silicon. Although the surface of the large particles did not contain any traces of silicon, the small particles did show traces of silicon on the surface or perhaps incorporated into the particle itself. Figure 3.8 (p. 52) is an EDS spectrum of the surface of such a small particle. The small size, smooth spherical shape and the presence of

silicon suggests that the sodium silicate has dispersed the small particle. The larger particle is associated with a lack of silicon.

3.5.5.3 Ink dispersed in caustic soda, in the presence of 80 ppm calcium

With reference to Figure 3.9 (p. 53), it can be seen that the ink particles were large (ca. 100 microns) and spheroidal, also with rough surfaces. The EDS spectrum in Figure 3.10 (p. 53) confirms that there were traces of calcium on the surface of the particle. The appearance of the particle in Figure 3.9 (p. 53) is similar to that in Figure 3.5 (p. 51), and so one could conclude that agglomeration rather than dispersion has taken place.

3.5.5.4 Ink dispersed in sodium silicate, in the presence of 80 ppm calcium

With reference to Figure 3.11 (p. 54), it can be seen that the particles were variable in size, (35 – 200 microns), of regular spherical shape with smooth surfaces. Figure 3.11 (p. 54) shows a large and a small particle. The small particles contained traces of silicon, but no calcium, as shown by the EDS spectrum in Figure 3.12 (p. 54). The intense white areas in the element maps in Figure 3.11 (p. 54) show the occurrence of silicon and calcium. It can be seen that the area occupied by the ink particles shows low concentrations of silicon and calcium. This would seem to imply that there are no surface associations between ink and calcium silicate. The range of particle sizes suggests a variable dispersing power, but nevertheless shows no signs of an agglomerated structure. It seems as if the silicate has "neutralised" the agglomerating effect of the calcium observed earlier.

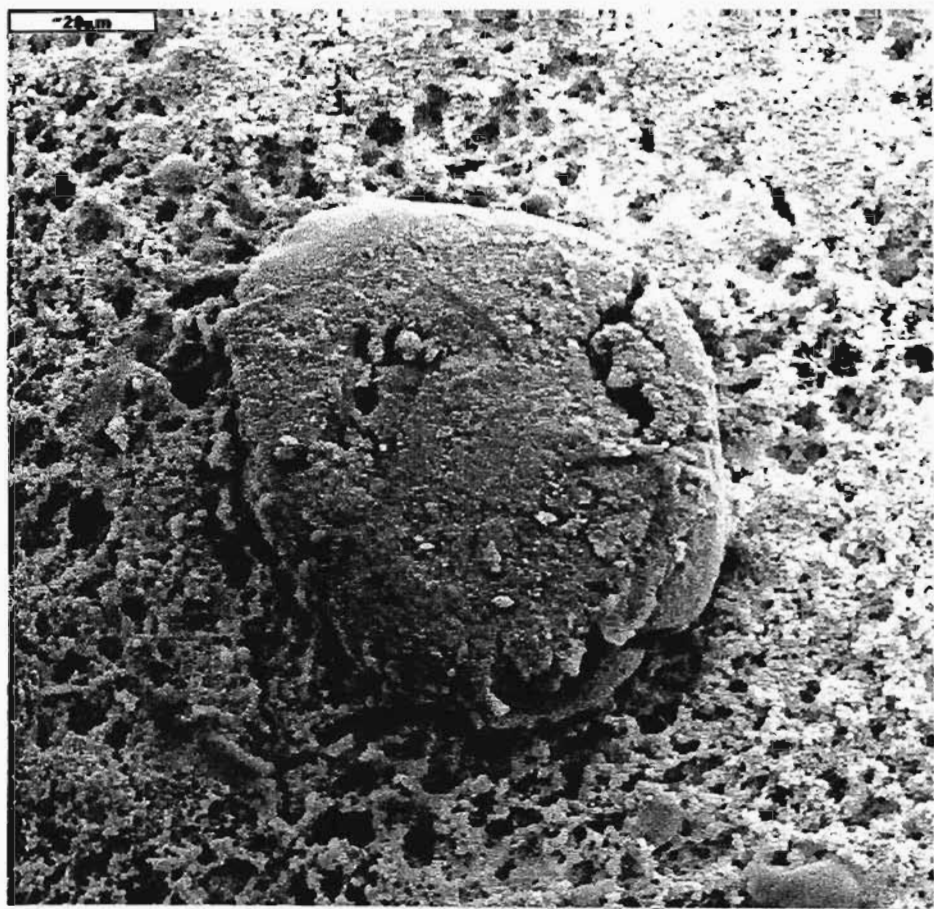


Figure 3.5: Ink particle dispersed in caustic soda only. The appearance suggests formation by agglomeration.

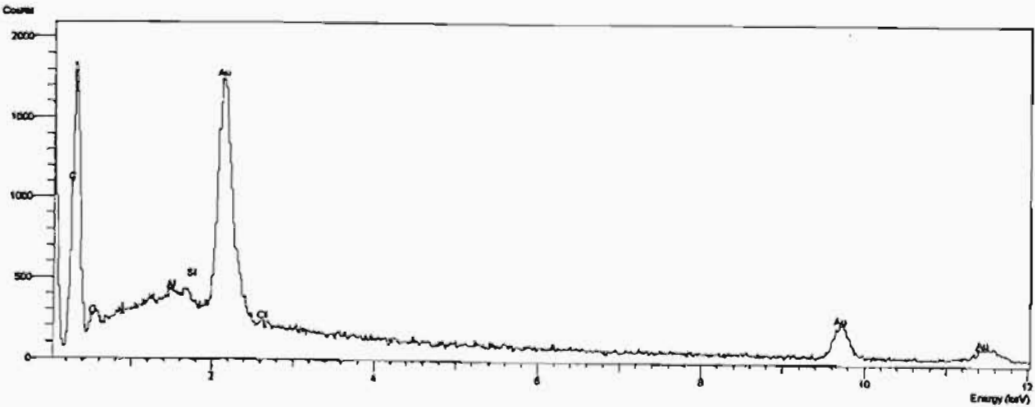


Figure 3.6: EDS spectrum of the ink particle depicted in figure 3.5. The surface is free of any metallic ions.

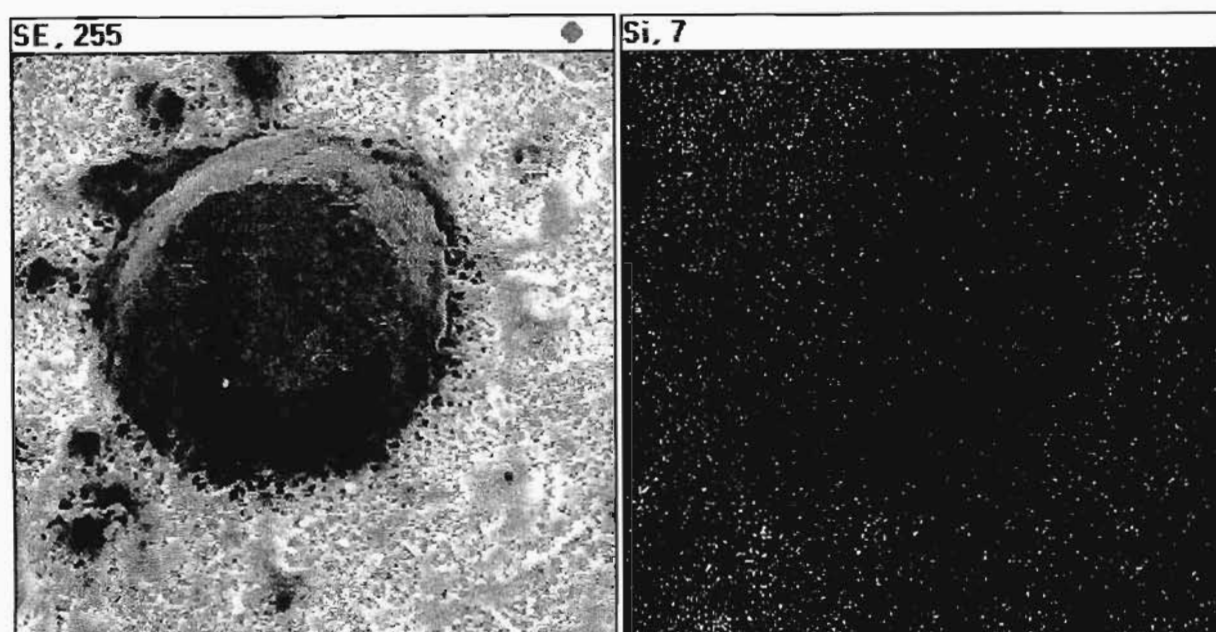


Figure 3.7: Ink dispersed in sodium silicate. The large particle is 250 microns in diameter. The small particles are 10 to 20 microns in diameter. The distribution of silicon is shown in the Si map on the right. The dense white areas correspond to higher concentrations of silicon.

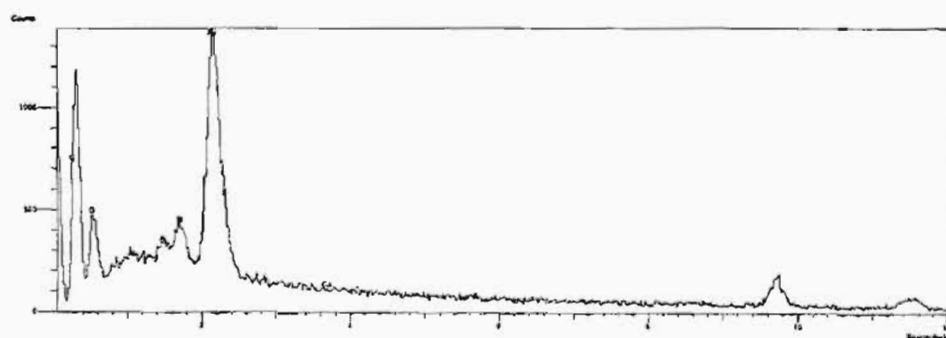


Figure 3.8: EDS spectrum of a smaller ink particle dispersed in sodium silicate solution, showing traces of silicon at 1.8keV.

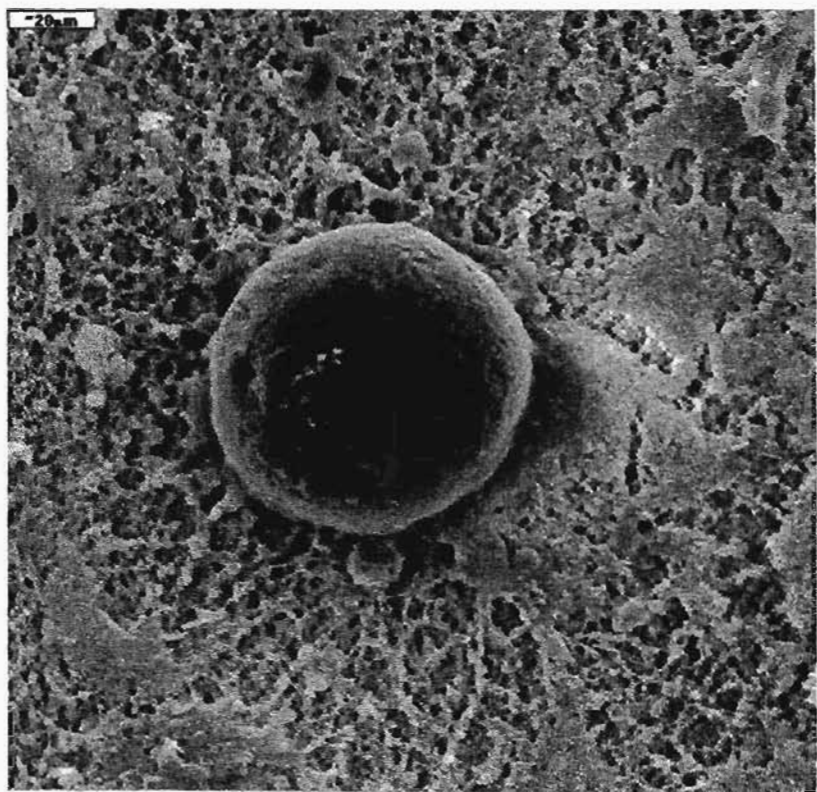


Figure 3.9: Ink particle dispersed in NaOH, in the presence of 80 ppm calcium

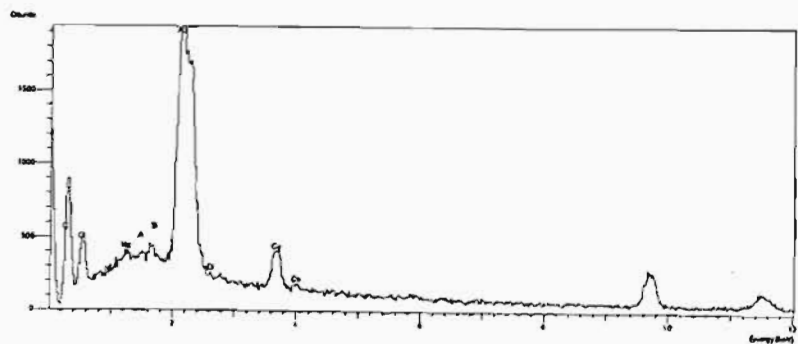


Figure 3.10: EDS spectrum of ink particle dispersed in NaOH and 80ppm Calcium. The presence of calcium on the surface is indicated at 3.7 keV.

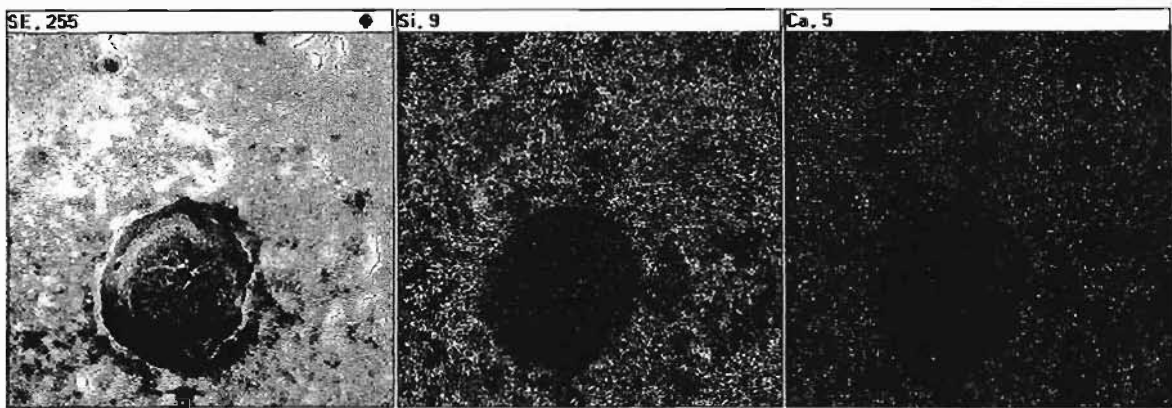


Figure 3.11: Ink dispersed in sodium silicate and 80ppm calcium. The large particles are 200 microns in diameter, the smaller particle is 35 microns in diameter. The Si and Ca element maps are shown centre and right respectively.

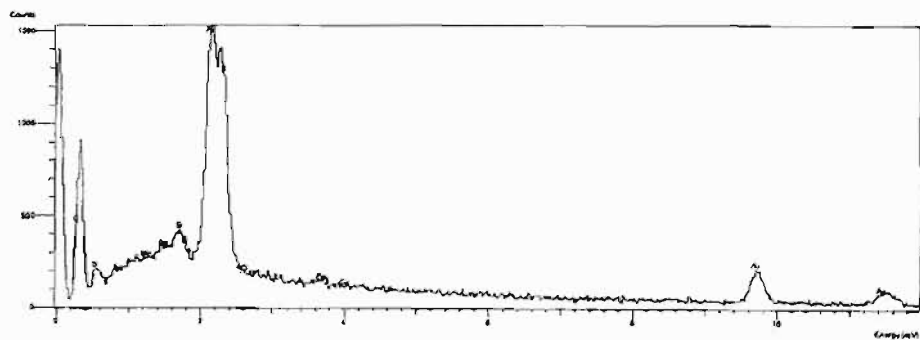


Figure 3.12: EDS spectrum of a small particle dispersed in sodium silicate/80 ppm calcium. The presence of silicon is indicated by the peak at 1.7 keV.

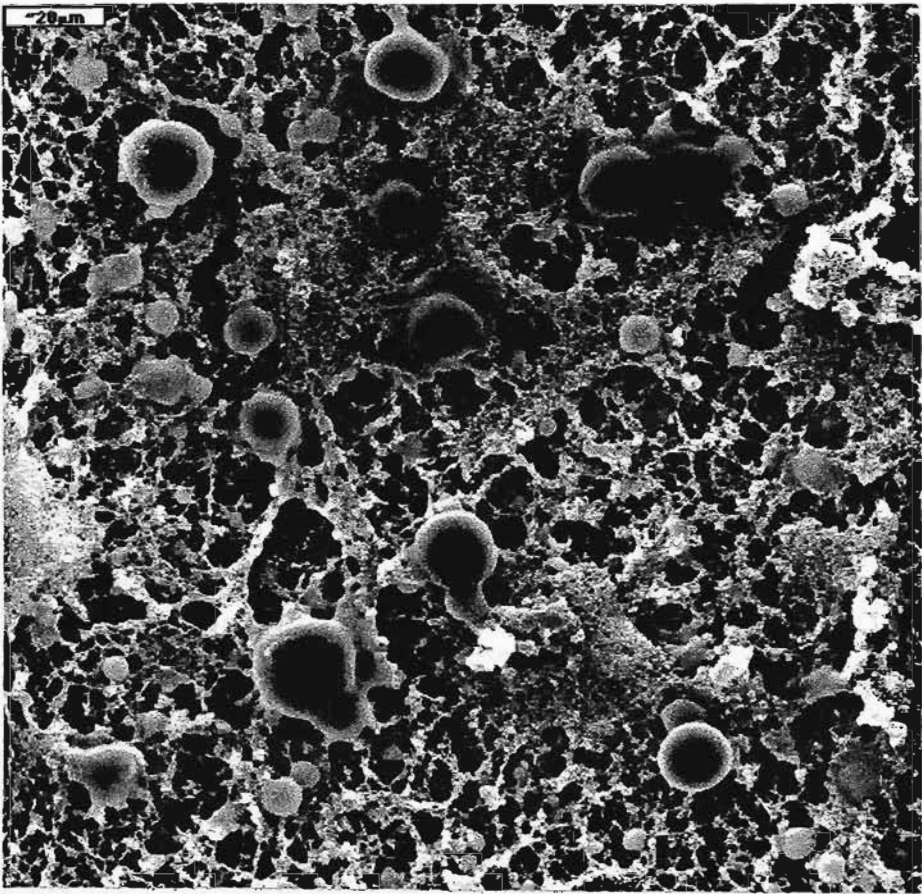


Figure 3.13: Ink dispersed in sodium soap/ sodium silicate.

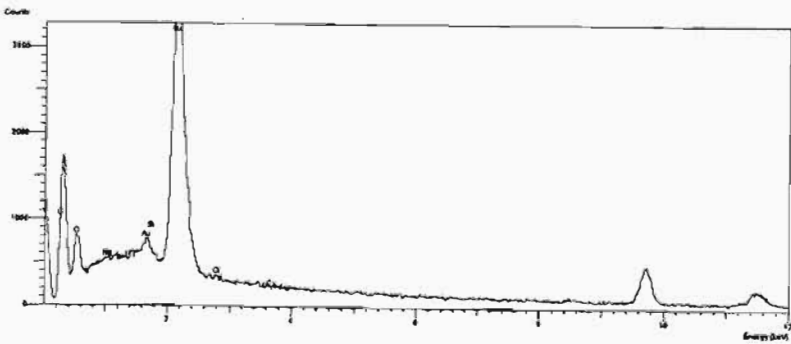


Figure 3.14: EDS spectrum of ink particles dispersed in sodium soap/silicate.

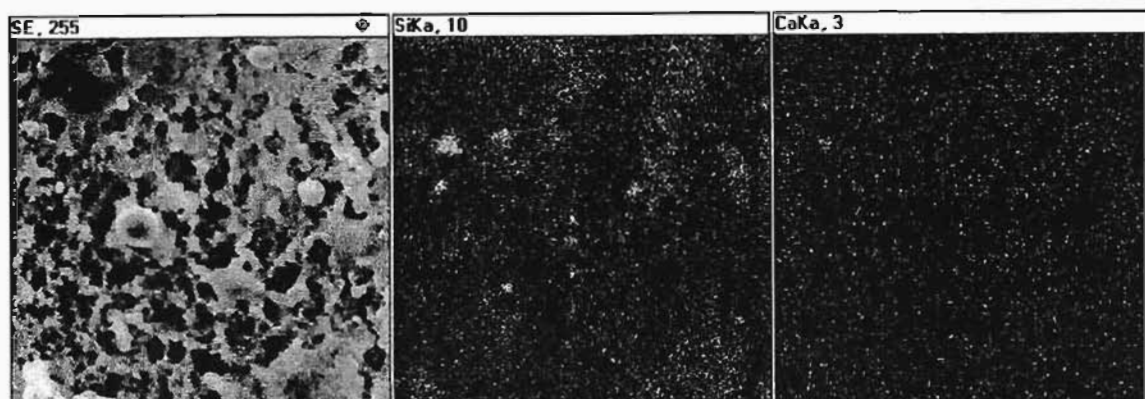


Figure 3.15:- Ink dispersed in calcium soap/sodium silicate. The Si and Ca element maps are shown centre and right respectively. This is a carbon coated image, which results in an inferior image, but superior element mapping.

3.5.5.5 Ink dispersed in the sodium soap, in the presence of sodium silicate.

As Figure 3.13 (p. 55) indicates, numerous smaller smooth spherical particles were noted, which suggested good dispersion and no significant agglomeration, although a number of particles had adhered together to form doublets or triplets. There was no evidence of silicon associated with the particle, as the EDS spectrum in Figure 3.14 (p. 55) confirms. It is as though the soap, as a superior dispersant, has displaced the silicate.

3.5.5.6 Ink dispersed in the calcium soap, in the presence of sodium silicate.

This dispersing system also produced large numbers of small spherical particles (Figure 3.15 above). It can only be assumed that there was sufficient free, unprecipitated fatty acid soap to ensure dispersion of the ink.

The calcium or silicon again did not appear to be associated with the particles (Figure 3.15). Larsson (1987) has reported that submicron size calcium soap particles form layers on ink particles, and that these are observable under SEM. There was no evidence of such associations in this work, either visually (SEM) or as calcium ion (EDS).

3.6 Conclusions and further work

The turbidity measurements of the ink dispersions showed that the sodium and calcium soaps at 50 ppm were better dispersants of ink than sodium silicate at 4000 ppm or caustic soda at pH 10. This was reinforced by the particle count and particle size measurements. The SEM micrographs also supported this, by showing many small spherical particles, with insignificant signs of agglomeration. There was no evidence of silicon on the surface of the ink particles, which presumably had been displaced by soap molecules.

The general understanding that sodium silicate is a better dispersant than caustic soda alone was confirmed by the turbidity measurements, which showed increasing trends as the amount of sodium silicate was increased. The SEM micrographs of ink dispersed in caustic soda indicated evidence of agglomeration, whereas the ink dispersed in sodium silicate showed no agglomerated structure. The EDS spectra showed evidence of silicon on finely dispersed ink particles, suggesting that silicate was involved in the dispersion process.

The widely held view that calcium has an agglomerating role in deinking was confirmed by the dispersion experiments. Dispersing in the presence of calcium gave dispersions with the lowest turbidity and particle counts and largest particle size. The SEM micrographs confirmed the presence of large agglomerated particles, with traces of calcium on the surface.

In the experiments in which the ink was dispersed in a combination of sodium silicate and calcium, there was no evidence, either visual (SEM) or from EDS to suggest that calcium silicate associates with ink particles. This has been suggested as a collecting mechanism for sodium silicate by Renders (1993) and Dionne (1994).

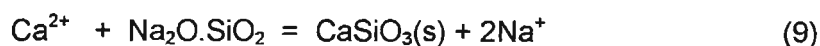
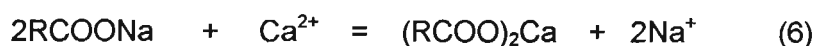
In the light of the above discussion, it seems that although sodium silicate itself has some limited dispersing action on the types of ink that occur in the Merebank deinking pulping process, it can't be regarded as an efficient dispersant when compared to a fatty acid soap. Therefore, any soap present in a system is likely to dominate any dispersing actions that might occur. Nevertheless, the dispersing experiments clearly demonstrated that the amount of sodium silicate present in the solution does influence

the particle size and dispersing behaviour of the other main components on the pulping process, namely the calcium ion and the soap. The nature of these interactions needs to be investigated more fully. This investigation forms the next part of the experimental work reported in this dissertation.

4: SEQUESTERING PROPERTIES OF SODIUM SILICATE

4.1 Introduction

The dispersing work in Chapter 3 has shown that sodium silicate is not as good an ink dispersant as a fatty acid soap. On the other hand, the amount of sodium silicate present in the dispersing systems did appear to influence the dispersing result in some way. It was therefore necessary to investigate the interactions between sodium silicate, calcium and soap under the conditions that pertain to a typical newsprint deinking pulper. As discussed in Sections 2.2.3 to 2.2.5, a number of reactions can take place between sodium silicate, soap and calcium at high pH. These are:



It is known that the concentration of soap influences the removal of ink from the fibres (Borchardt 1993). In addition, equation (6) has been studied extensively with respect to ink agglomeration (Section 2.2.3), but also occurs in the pulper (Weigl 1987), where it is likely to negatively influence ink removal from the fibres. Equation (9) also occurs in the pulper, but has mainly been studied for its effect on deposit formation in bleaching systems (Froass *et al* 1997). Equation (8) is not expected to have any effect in a deinking system, as it only occurs at pH's greater than 13 (Oliveira & Torem 1995, Froass *et al.* 1997). Free fatty acid (Equation (5)) ionises to the carboxylic acid soap above pH 6 (Johansson *et al.* 1996).

It is apparent from the above reactions that there is considerable competition for the calcium ions in a deinking system. The conditions of water hardness, pH, silicate concentration and soap concentration that prevail in the pulper will determine which species are present, which will in turn have a profound effect on the performance of the deinking system. The above reactions are well known, but it would be of interest to know which reaction would predominate under typical pulping conditions, with a view to understanding how the total system would behave.

4.2 Independant competition for calcium ions by soap and sodium silicate.

The chemical reactions as defined by equations (6) and (9) above were studied as a first step to determine how sodium silicate could influence the soap concentration in pulping, and thence the deinking system performance.

4.2.1 Experimental

1. All solutions were made up in deionised water using the commercial grade chemicals in use in the Merebank deinking plant. The specifications for these chemicals are detailed in Appendix A. The calcium chloride contains about 1% magnesium, which was disregarded for the purposes of this investigation. The chemistries of calcium and magnesium under the alkaline conditions in this study are very similar (Falcone 1982).
2. Calcium solutions containing 20, 50 and 150 ppm of Ca^{2+} were made up. These concentrations correspond to low, medium and very high hardness levels, and were chosen to encompass the concentration ranges found in practice in the Merebank deinking pulper, as detailed in Table 3.1 (p. 39).
3. Sodium silicate and sodium soap solutions were added to the calcium solution in increasing concentrations and the pH was adjusted into the range 9.95 – 10.05 with sodium hydroxide or hydrochloric acid. The solutions were allowed to stand overnight to allow the precipitates that formed to settle out. The solutions were filtered and the clear supernatant solution or filtrate was analysed for residual calcium. The calcium was determined by EDTA titration, according to the method described in Appendix B. The titrations were done in duplicate, and the average is reported.
4. The effect of pH was investigated by making up solutions as described above and adjusting the pH to various values between 7.5 and 11.
5. The influence of temperature was investigated by making up solutions as described above, at various elevated temperatures. The solutions were maintained at the elevated temperatures by immersing in a thermostatically controlled water bath for four hours. After four hours, the clear supernatant

solution was withdrawn with a pipette and titrated as described in Section 4.2.1.3 above.

4.2.2 Results and discussion

The residual calcium concentrations in ppm were plotted against the ppm of sodium silicate or soap added. The following results were obtained:

4.2.2.1 The Influence of Concentration

The residual concentrations of calcium remaining in solution after addition of varying amounts of sodium silicate or sodium soap are shown in Figure 4.1 to 4.3 below.

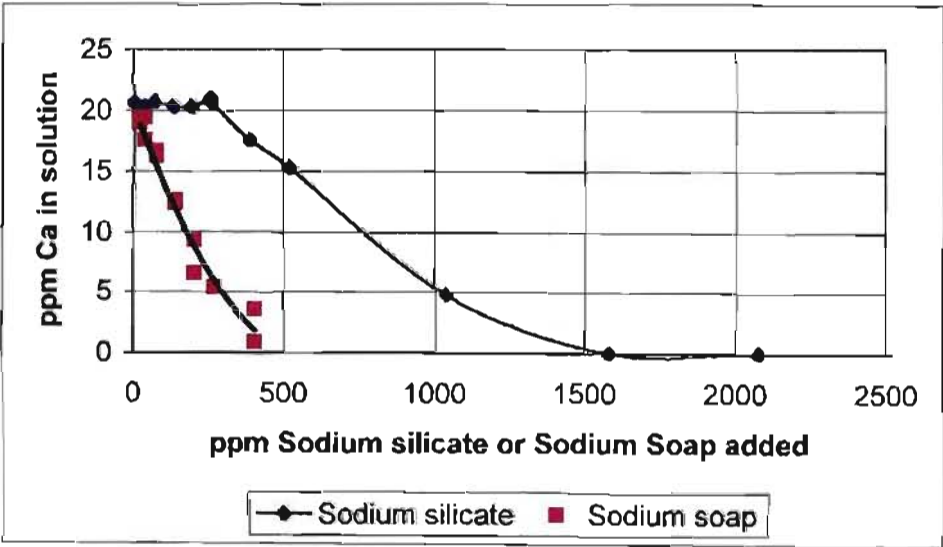


Figure 4.1: Residual Ca^{2+} concentration in solution at a 20 ppm initial calcium concentration

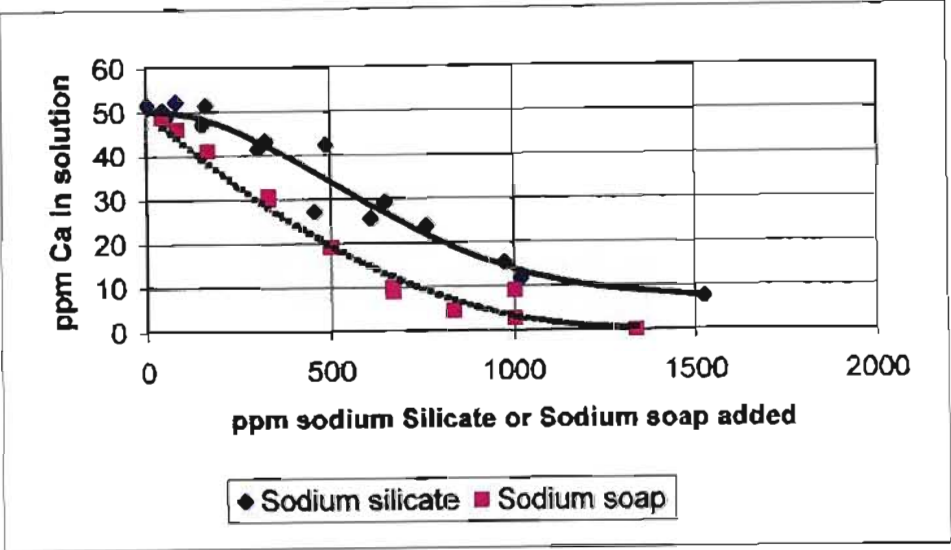


Figure 4.2: Residual Ca^{2+} concentration in solution at a 50 ppm initial calcium concentration

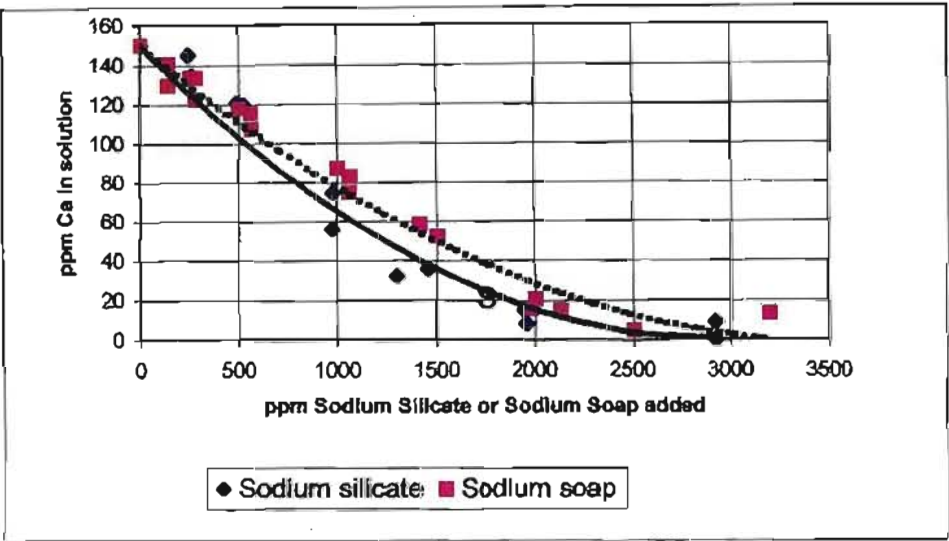


Figure 4.3: Residual Ca^{2+} concentration in solution at a 150 ppm initial calcium concentration

At low concentrations of calcium (Figure 4.1), the soap removes more calcium from solution than sodium silicate, per mass of material added. However, as the concentration of calcium increases, the difference in calcium removal decreases, so that at 150 ppm (Figure 4.3), the sodium silicate becomes marginally more effective than soap in removing calcium from solution.

4.2.2.2 The Influence of pH

As discussed in Section 2.2.2, the pulping stage of the de-inking process normally takes place at about pH 10. The calcium-silicate and calcium-soap interactions were studied over a broad pH range. The initial calcium concentrations were set at 50 and 150 ppm. The calcium concentration level of 20 ppm was not studied in these experiments, as it was considered to be too low to be of relevance to the current Merebank process conditions. A 1:1 molar ratio of calcium to silicate/soap was chosen for these experiments, because this corresponded to a point about one third of the way down the curves in Figures 4.2 and 4.3, where the concentration was changing quite rapidly. The pH was adjusted using hydrochloric acid or sodium hydroxide. Figures 4.4 and 4.5 depict the calcium removal by sodium silicate and sodium soap at two levels of initial calcium concentration.

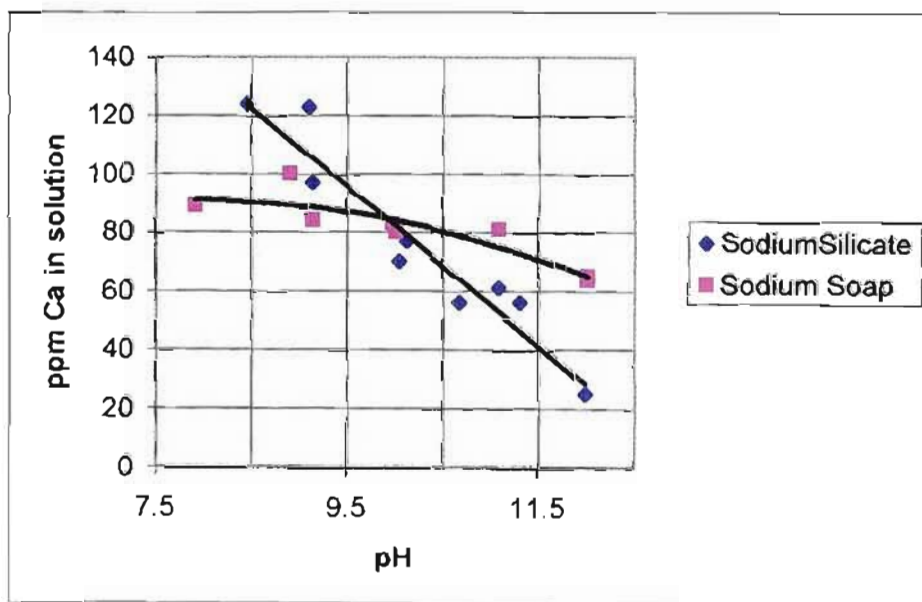


Figure 4.4: Calcium removal by sodium silicate and soap as a function of pH. Initial calcium concentration 150 ppm. Calcium to silicate/soap molar ratio is 1:1.

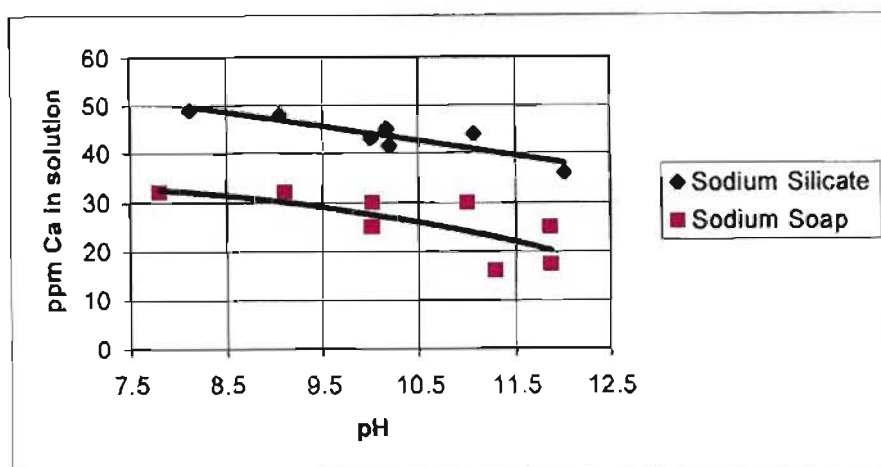


Figure 4.5: Calcium removal by sodium silicate and sodium soap at an initial calcium concentration of 50 ppm. Calcium to silicate/soap molar ratio is 1:1.

At lower calcium concentrations (figure 4.5), soap is more effective in removing calcium, throughout the alkaline pH range. However, at higher hardness (figure 4.4), the soap is more effective at lower pH, but as the pH increases the silicate becomes more effective at calcium removal.

In order to determine whether the removal of calcium from solution was in fact due to the addition of soap or sodium silicate and not due the effect of pH (reaction (8) above), the calcium concentration of a 150 ppm calcium solution was studied over a wide pH range. Figure 4.6 indicates that calcium would not be precipitated from solution under these conditions below pH 11. This result agrees with the work of Froass et. al. (1997), who report an inflection point for this reaction at a pH of 12.5. This is way above the pH normally encountered in newsprint deinking pulpers.

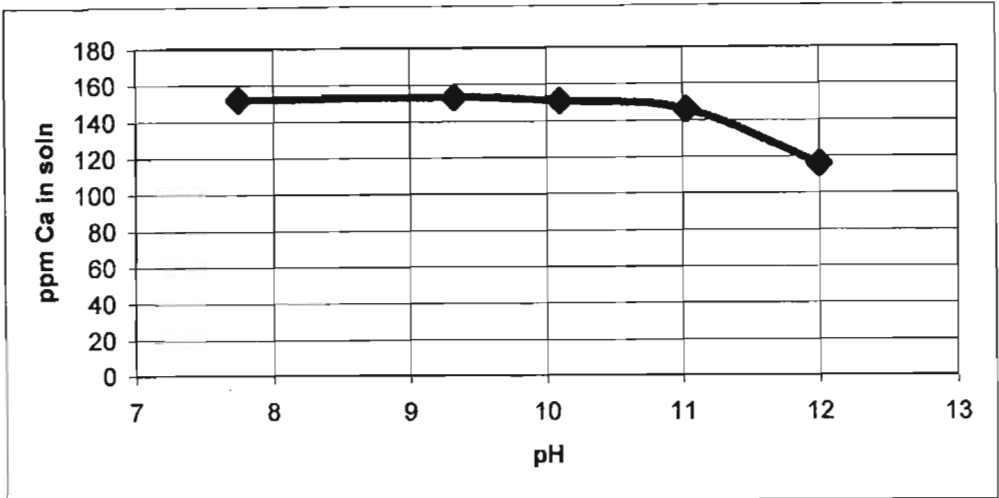


Figure 4.6: The effect of pH on Ca^{2+} concentration, at an initial Ca^{2+} concentration of 150 ppm.

4.2.2.3 The influence of temperature

All of the experimental work was carried out at room temperature, about 23 °C. However, pulping is normally carried out at about 45 °C. The effect of temperature was determined at pH 10 and at 1:1 molar ratios of calcium to sodium silicate and soap, at the initial calcium concentration levels of 50 ppm and 150 ppm. The rationale for choosing these conditions is explained in Section 4.2.2.2 above. Figures 4.7 and 4.8 below depict the calcium removal from solution by sodium silicate and sodium soap as a function of temperature, at initial calcium concentrations of 50 ppm and 150 ppm respectively.

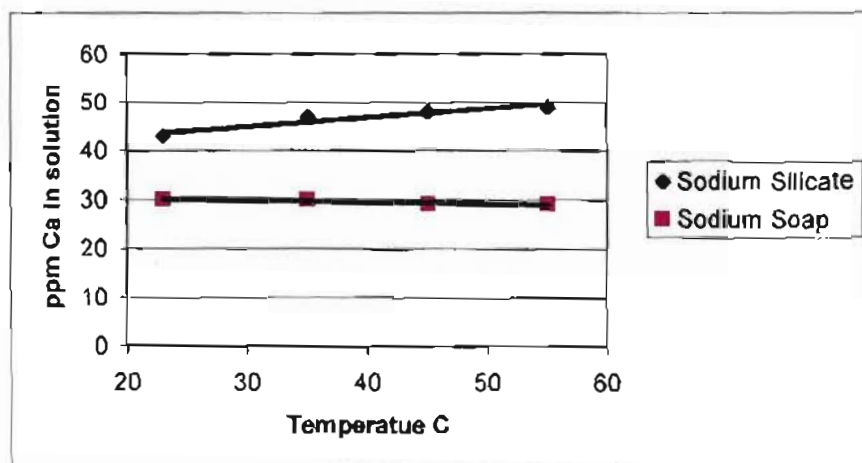


Figure 4.7: Calcium removal by sodium silicate and soap as a function of temperature, at an initial calcium concentration of 50 ppm. Calcium to silicate/soap molar ratio is 1:1.

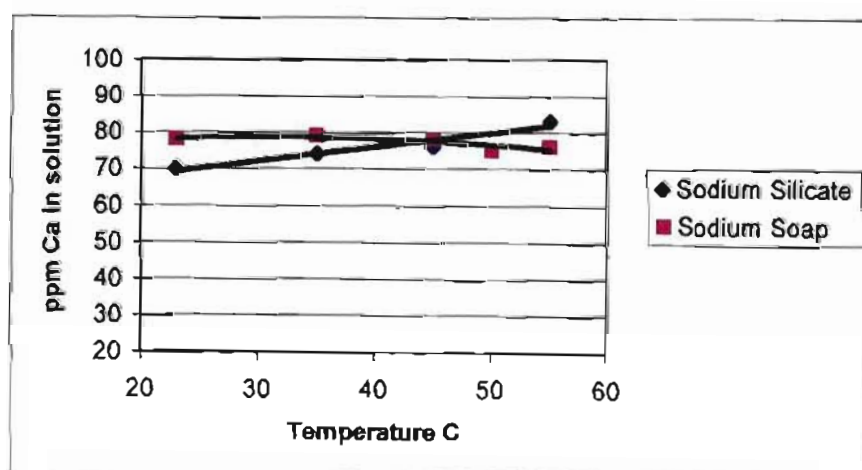


Figure 4.8: Calcium removal as a function of temperature, at an initial calcium concentration of 150 ppm. Calcium to silicate/soap molar ratio is 1:1.

The very small slope of the curves in Figures 4.7 and 4.8 indicate that overall, temperature does not play a significant role in calcium removal.

4.2.3 Conclusions

Both sodium silicate and soap react with calcium to form insoluble precipitates, as per equations (6) and (9) above. At low calcium concentrations the soap tends to react preferentially with the calcium (Figure 4.1), but as the calcium concentration increases

(Figure 4.2) the sodium silicate exerts increasing competition for the calcium ion, until the reaction with silicate eventually predominates (Figure 4.3).

Whereas the ability of sodium silicate to remove calcium ions from solution increases with increasing pH, as shown in Figures 4.4 and 4.5, this is more pronounced at higher concentrations (Figure 4.5). The ability of soap to remove calcium ions from solution is also not greatly influenced by pH. (Figures 4.4 and 4.5)

In addition $\text{Ca}(\text{OH})_2$ only starts to precipitate out at pH values above 11 (Figure 4.6). Therefore, the insolubility of calcium hydroxide is not a contributing factor to calcium removal under normal pulping conditions.

The influence of temperature on the calcium ion removal by either soap or silicate is not great. All the experimental work was carried out at room temperature, whereas the pulping reaction occurs at about 45 °C. The temperature profiles shown in Figures 4.7 and 4.8 indicate that any conclusions drawn from working at room temperature should apply equally well at the higher temperatures.

In the Merebank deinking plant pulper, the hardness introduced by the disc filter filtrate is in the region of 66 to 96 ppm Ca^{2+} . This hardness would be augmented by a certain amount of hardness from the recovered paper, and reduced by the sodium silicate added into the pulper. The net effect of this is that the hardness reduces by 60 ppm down to about 40 ppm after pulping, as shown in Table 3.1 (p. 39). With reference to Figure 4.3, this amount of calcium would consume either ca. 850 ppm of sodium silicate or ca. 1000 ppm of soap. Therefore, in the absence of sodium silicate, some of the soap returning to the pulper in the disc filter filtrate (150 to 230 ppm, as per Table 3.1) would be precipitated. In addition, in excess of 850 ppm of sodium silicate would be required to reduce the hardness down to a low level. In practice, however, additional calcium will be introduced into the pulper by the recovered paper. This level would depend on the type of paper and nature of fillers, but is not likely to aggravate the situation described above, because calcium will not dissolve significantly in the high pH environment of the pulper. Ten kg/ton dry fibre (equivalent to ca. 1000 ppm in solution) of sodium silicate is added into the Merebank pulper, which might seem to be a little too low, in the light of the above discussion.

In the subsequent flotation stage in the Merebank process, the pulp is diluted down to 1% consistency with filtrate water, and additional calcium is added to achieve flotation

at about 100 ppm calcium hardness. This additional calcium would “mop up” excess sodium silicate and precipitate the excess soap, according to the collecting mechanisms discussed in Section 2.2.3. Too much excess silicate could hinder the collecting action of the calcium.

4.3 Competition between sodium soap and silicate for Ca^{2+} ions, when all three species are present.

The preceding section demonstrated that there was competition for the calcium ion by the silicate anion and the soap anion. However, the competition for the calcium was fairly even, and it appears as if an equilibrium situation exists, with all three components i.e. the silicate anion, the soap and the calcium ion, likely to be present in the solution at one time. It is important to establish whether, under the conditions operating in a deinking pulper, the sodium silicate will be able to significantly influence the concentration of the soap, which will, in turn, determine the extent of ink removal and ink particle stabilisation. Therefore, in this section the behaviour of the three species silicate/soap/calcium system will be investigated.

4.3.1 Experimental

4.3.1.1 Experimental conditions

The experimental conditions for this section were derived from the analysis of disc filter filtrate water as given in Table 3.1 (p. 39). This information is repeated again for convenience as Table 4.1 below. It must be remembered that the concentrations listed in Table 4.1 are equilibrium concentrations after filtration.

Table 4.1 Residual calcium hardness and residual soap in the pulper, in ppm.

Sample	Ca hardness, ppm Ca^{2+}	Residual soap extract, ppm
1. Addis and Khathi (1992)	21	-
2. Pulper (12/1999)	39	-
3. Pulper (1/2000)	44	-
4. Cloudy filtrate (3/2000)	96	188
5. Cloudy filtrate (4/2000)	66	150
6. Cloudy filtrate (4/2000)	-	234

With reference to Table 4.1 above, a series of experiments was designed to determine the influence of sodium silicate on the concentration of residual soap in solution. The starting conditions for these experiments are detailed in Table 4.2 below. These starting concentrations are higher than those listed in Table 4.1, but after reaction yielded similar residual concentrations of calcium and silicate.

An attempt was made to simulate a number of practical scenarios that could occur in a deinking pulper: a low hardness/high soap situation, a high hardness/low soap situation and a high hardness/high soap situation. These are summarised in Table 4.2 below.

Table 4.2: Initial addition rates of calcium and soap.

Experi- ment	Ca conc., ppm	Soap conc., ppm	Comments
4.1	50	380	This corresponds to a low hardness/high soap situation (1:1 molar ratio).
4.2	100	380	Simulates a high hardness/high soap situation.
4.3	100	200	Simulates a high hardness/low residual soap situation.

4.3.1.2 Experimental methods

Solutions of soap and calcium chloride, using the commercial products as specified in Appendix A were made up and mixed in the above ratios with solutions of sodium silicate, at room temperature. The sodium silicate concentration was varied from 0 ppm up to about 4000 ppm. This range corresponds to the range used in practice, as well as the range of concentrations employed in the dispersing work of Chapter 2. The pH was adjusted with hydrochloric acid into the range 9.95 – 10.05, to fall within the practical range of 9.5 to 10.5. The mixtures were allowed to stand for about 1 hour to allow the precipitates to equilibrate and settle out. The precipitates were filtered off and the residual soap in the filtrate was determined as per the method "Determination of soap, oil and grease" in Appendix B. This method involves acidification of a soap solution, and extraction with petroleum ether. The petroleum ether is evaporated to yield a fatty acid residue, which is weighed. This residue is referred to as the "petroleum ether extract" in this work.

4.3.1.3 Calibration curves

A calibration curve for this system was also established. Standard soap solutions were made up in the range of 5 ppm up to 180 ppm anhydrous soap, in the absence of calcium and sodium silicate. The standards were subjected to the same extraction procedures as the test series (Appendix B).

4.3.1.4 Analysis of residual calcium and silica

The clear filtrates were also analysed for residual calcium and silica using the technique of inductively coupled plasma spectrophotometry (ICP). Argon gas was used as a carrier on a Jobin Yvon JY24 spectrophotometer, with J-YESS version 4 software. The instrument was calibrated with solutions made up using the commercial grades of sodium silicate and calcium chloride as detailed in Appendix A, using the assay values as given by the suppliers. It was not considered necessary to calibrate the instrument with exact standards, because in these experiments absolute values were not required, but rather changes and trends. The same set of standards was used for all analyses.

The calcium and silica were determined at wavelengths of 393.366 nm and 251.432 nm respectively. The instrument's software constructed the calibration curve and calculated the results automatically. The method of analysis and a sample copy of an analysis are displayed in Appendix G. The results of the ICP analysis are displayed in Appendix F, alongside the residual soap concentration data.

4.3.2 Results and discussion

4.3.2.1 Calibration curve and repeatability

A standard calibration curve of petroleum ether extract (*i.e.* fatty acid) as a function of the amount of standard anhydrous soap in solution yielded the curve in Figure 4.9 below. The method yielded a strong correlation between the petroleum ether extract (fatty acid) and the amount of soap in solution. The best-fit curve to these points, with a correlation coefficient of 0.947 (Figure 4.9), was used to convert the ppm petroleum ether extract results into ppm residual soap in solution.

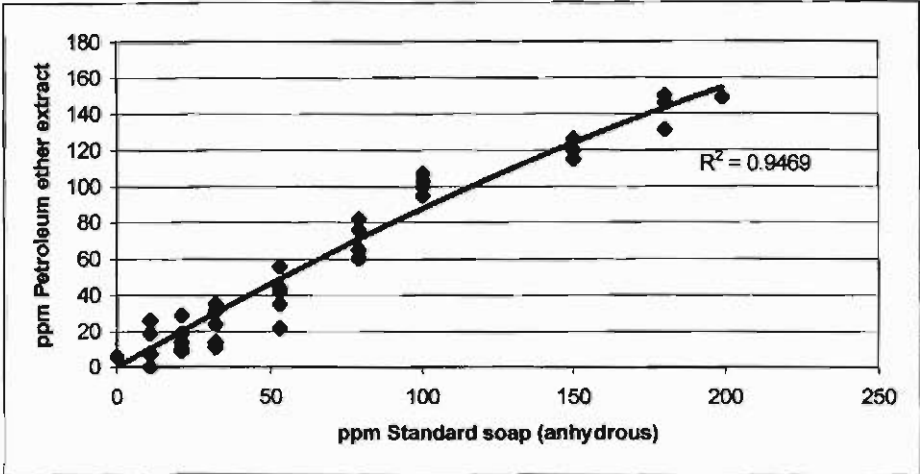


Figure 4.9: Calibration curve for partition gravimetric method, showing ppm petroleum ether extract (fatty acid) vs. ppm standard soap (anhydrous).

In order to determine the repeatability of this method, five extracts of a standard 100 ppm soap solution were performed. This yielded the following ppm petroleum ether extracts, listed in Table 4.3.

Table 4.3: Repeatability of the method: "Determination of soap, oil and grease".

Sample	ppm petroleum ether extract
1	100.5
2	93.5
3	96.5
4	88.5
5	96.5
Mean	95.1
Standard deviation	4.45
Standard error	1.99
95% confidence interval	5.26

4.3.2.2 Experiment 4.1: Low calcium, high soap system

The petroleum ether extract as a function of increasing concentrations of sodium silicate for this experiment is shown in Figure 4.10 below. The error bars indicate the standard error of the experimental results.

The ppm petroleum ether extract results (as displayed in Figure 4.10) were converted to ppm residual soap in solution using the calibration curve in Figure 4.9 above, and plotted on the same graph as the residual calcium and residual silicate results from the ICP analysis (Figure 4.11). The raw data is displayed in Appendix F.

The residual soap in solution varied from 89 to 227 ppm (Figure 4.11) and the calcium decreased from 20 to 16 ppm. The concentration of residual soap in solution showed an increasing trend with respect to sodium silicate addition.

4.3.2.3 Experiment 4.2: High calcium, high soap system

The data for this experiment (Appendix F and G) was manipulated as described in Section 4.3.2.2 above and the results are shown in Figures 4.12 and 4.13 below. A similar trend of increasing residual soap concentration with increasing sodium silicate is evident. The residual soap concentration increased from 86 ppm to 168 ppm, whilst the residual calcium concentration decreased from 75 ppm down to 27 ppm.

4.3.2.4 Experiment 4.3: High calcium, low soap system

As described above, the results for this experiment are shown below in Figures 4.14 and 4.15 respectively. In this case, the residual soap is much lower, in the range 26 to 99 ppm, with calcium falling from 96 ppm to 39 ppm. The same trends as noted above were observed.

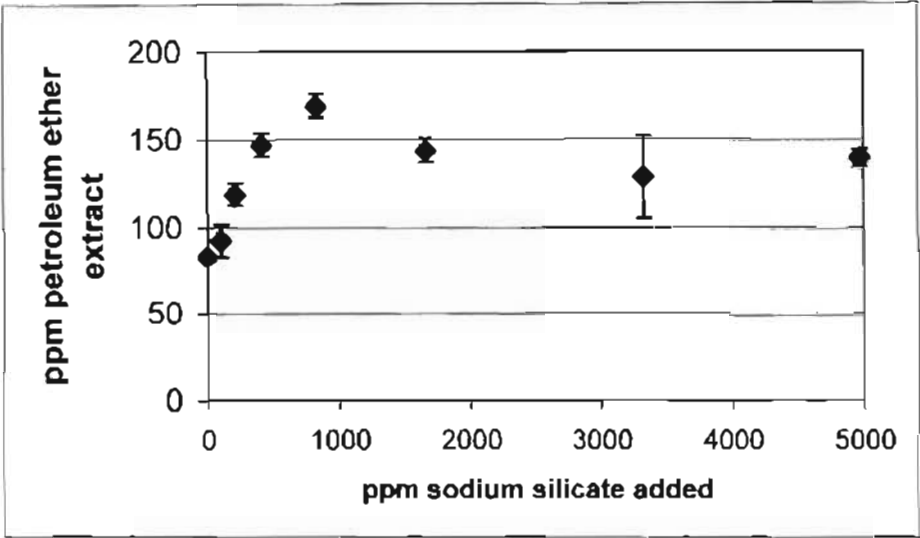


Figure 4.10 Petroleum ether extract as a function of sodium silicate addition, in the presence of 50 ppm calcium and 380 ppm soap

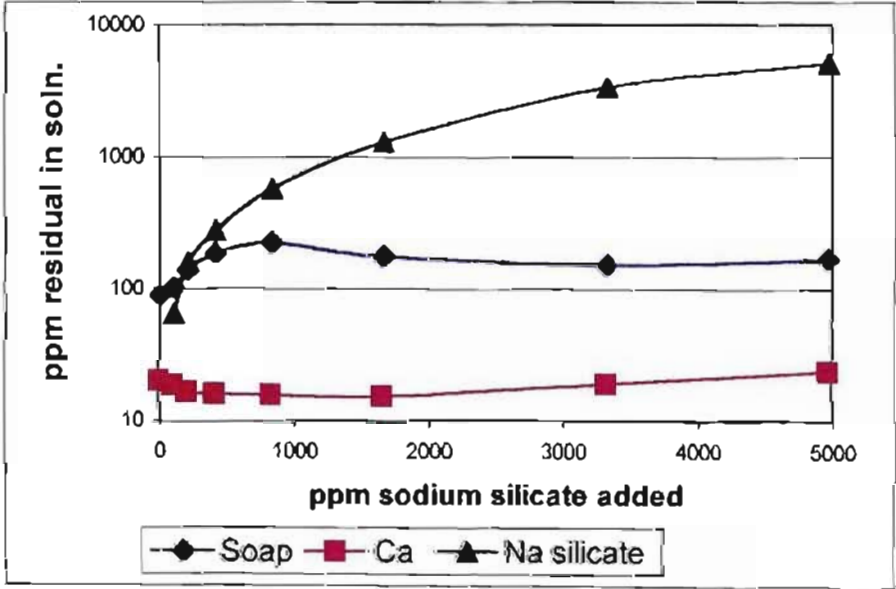


Figure 4.11: Residual soap, calcium and silicate in solution as a function of sodium silicate addition, in the presence of 50 ppm calcium and 380 ppm soap.

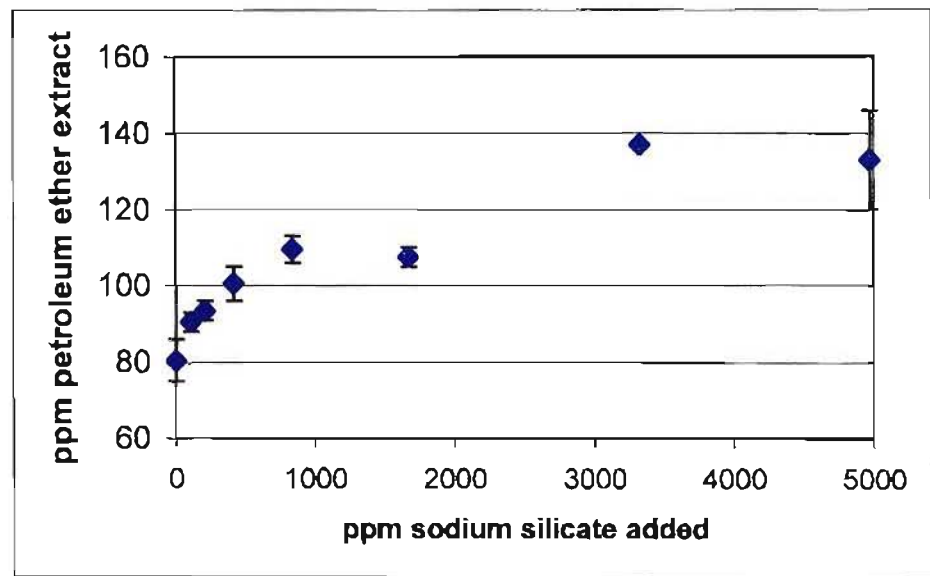


Figure 4.12: Petroleum ether extract as a function of sodium silicate addition, in the presence of 100 ppm calcium and 380 ppm soap.

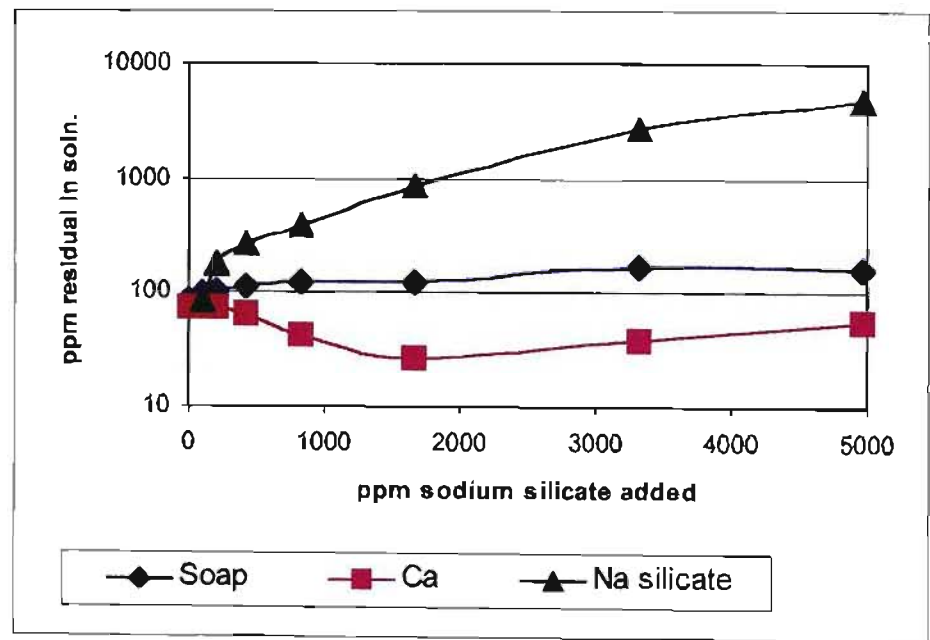


Figure 4.13: Residual soap, calcium and silicate in solution as a function of sodium silicate addition, in the presence of 100 ppm calcium and 380 ppm soap.

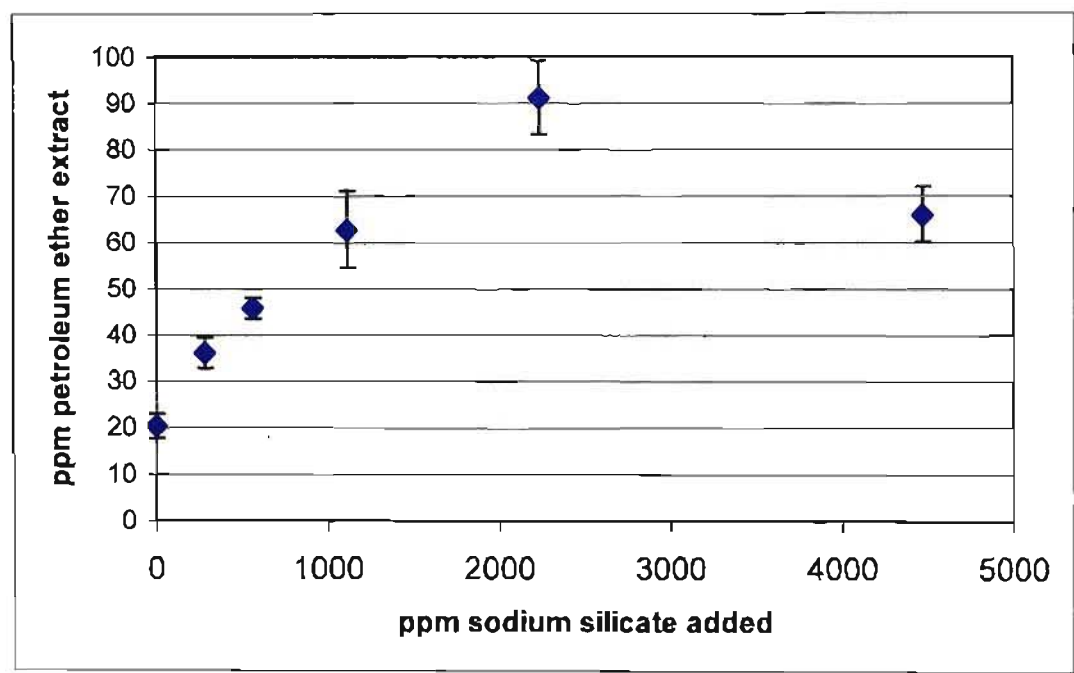


Figure 4.14: Petroleum ether extract as a function of sodium silicate addition, in the presence of 100 ppm calcium and 200 ppm soap

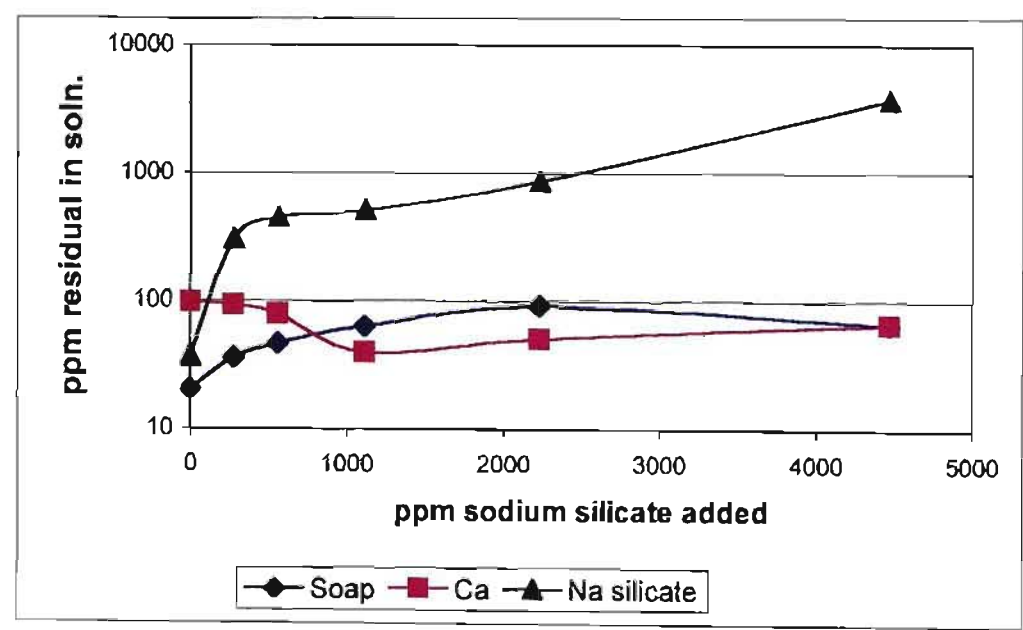


Figure 4.15: Residual soap, calcium and silicate in solution as a function of sodium silicate addition, in the presence of 100 ppm calcium and 200 ppm soap.

4.3.3 Conclusions

In general, as the concentration of sodium silicate increased, there was an upward trend in the concentration of residual soap in solution. In some experiments (Figures 4.10 and 4.14) there was an indication that a maximum was reached, and that further increases in sodium silicate concentration resulted in a decrease in soap concentration. This phenomenon was not investigated further, and is subject to confirmation, but indicates that an optimum level of sodium silicate addition might exist; with negative consequences if too much is added.

The residual sodium silicate concentration, not unsurprisingly, showed a steady increase to very high levels in all experiments. On the other hand, the calcium concentrations tended to stabilise at low levels, and even showed a minimum, which corresponds approximately with the maximum in residual soap concentration, as shown in Figures 4.11, 4.13 and 4.15. It is interesting to note that the calcium levels were not reduced to zero, even in the presence of large over-concentrations of sodium silicate.

Although the residual concentrations of soap and calcium in the experimental work were slightly lower than the actual Merebank plant values listed in Table 4.1 (p. 68), they were generally in the same range.

In the Merebank deinking pulper, the recovered paper, together with 10 kg/ton dry fibre (ca. 1000 ppm in solution) of sodium silicate and other deinking chemicals (see Section 1.2) are pulped with disc filter filtrate. The sodium silicate will complex the excess calcium and, in the manner described above, will result in an increased soap concentration in solution. This can be seen in the fact that the filtrate water hardness is about 60 to 100 ppm before pulping and about 40 ppm after pulping (Table 4.1, p. 64). The soap in solution helps to remove the ink from the fibres and stabilises the dispersed ink particles.

This pulp is further diluted down to 1% consistency with filtrate water just before flotation. Extra soap (4 kg/ton dry fibre or 40 ppm in solution) is added and calcium chloride is added to bring the hardness up to ca. 100 ppm. It is likely that all the soap now exists as the calcium soap, because of the high excess hardness. At this stage of the process sodium silicate's work is done. The literature contains no references to sodium silicate playing a role in ink flotation, other than to suppress the flotation of

fillers and fibres (see Section 2.2.7.2). The flotation of fibres (Section 2.2.5) has been ascribed to the adsorption of calcium onto the surface of the fibre, which renders it hydrophobic and thus floatable. If sodium silicate complexes calcium as suggested above, one could speculate that this would result in less adsorption of calcium onto the fibres and thus less fibre loss during flotation.

This work confirms that, under the conditions prevailing in a deinking pulper, sodium silicate has a chelating effect on calcium ions, which "protects" the soap and leads to higher soap activities in the pulper.

5: LABORATORY DEINKING STUDIES

5.1 Introduction

The work in the previous chapter showed that sodium silicate had a measurable chelating effect with calcium ions under the conditions found in a deinking pulper. This resulted in an increase of soap concentration in solution, which would be available to remove the ink from the fibres, thereby producing a better deinking effect. An improvement in deinking performance could be achieved by adding increasing quantities of sodium silicate to the pulper. However, the indiscriminate use of sodium silicate in the pulper is not the preferred route to improved deinking, because of the added costs of adding more chemicals as well as the effects of the deposition of silicate scales in the downstream processes. Therefore, some other method needs to be found to reduce the amount of calcium in the pulper, whilst simultaneously increasing the amount of soap in the pulper, without adding additional chemicals.

As described in Section 1.2, the floated pulp is dewatered on a disc filter. The filtrate is heated with steam and returned to the pulper for re-use as pulping water. This water has a hardness of 66 to 96 ppm calcium and contains about 200 ppm of soap in solution (refer to Table 3.2, p. 39). It would be of interest to know if the use of cleaner, softer water would improve the overall deinking result, thereby obviating the addition of more sodium silicate.

A series of experiments was devised to simulate the effect of various qualities of water in the pulping system.

5.2 Experimental method

In order to determine the effect of different calcium and soap levels in the pulper on the final deinking result, a number of experiments were devised. These are detailed in Table 5.1 below. The concentrations of calcium and soap used in these experiments were solution concentrations, and not based on the amount of fibre. This was done to relate the experiments in this section to those carried out in Chapter 4. In the deinking experiments, potable or tap water was used in all cases. The local potable water is very soft, with an average calcium concentration of ca. 7 mg/l (ppm) and a magnesium

concentration of ca. 3 mg/l (ppm). (Umgeni Water Report 2000). Thus, the hardness introduced by the potable water can be regarded as negligible. Although the Mondi Merebank deinking plant recycles a blend of newsprint and magazine, only newsprint was used in this series of experiments. This was done to simplify the experimental conditions and remove some possible interfering factors that could be introduced by the magazine paper, such as fillers like clay or calcium carbonate, different inks and coating latexes.

Table 5.1: Experimental conditions for pulping – concentration in parts per million parts of water.

Experi- ment	Composition of pulper water	Objective
5.1	Water + 100 ppm calcium + 200 ppm sodium soap	This simulates a normal pulper water. Refer to Table 3.1 (p. 39)
5.2	Water (potable)	To simulate the use of "fresh" process water i.e. to not recycle the disc filter filtrate.
5.3	Water + 200 ppm soap	To simulate the addition of extra soap in the pulper.
5.4	Water + 100 ppm calcium	To simulate pulping in a high hardness environment.
5.5	Water + 100 ppm calcium, no sodium silicate	To simulate pulping in a high hardness environment in the absence of sodium silicate.

A standard laboratory method for pulping and flotation has been developed and used at the Mondi Merebank mill for flotation investigations (Addis and Kathi 1992). This laboratory method produces comparable results to that produced by the recycling plant, although slightly different amounts of chemical reagents are used. These methods are detailed below. The experiments in each series were repeated at least five times in order to obtain statistically significant results.

5.2.1 Laboratory pulping method

Based on the work of Addis and Kathi (1992), the following laboratory pulping method was used.

1. Newspaper samples were drawn from the deinking plant warehouse at regular intervals. Due to practical constraints, it was not possible to use exactly the same types of newspaper for each pulping and flotation experiment. Nevertheless, no newsprint older than 3 months was used. It is well known that ageing deteriorates the newsprint and adversely affects the deinking result (Haynes 2000). The

samples generally contained editions of some or all of the following South African newspapers: The Cape Times, Die Burger, The Daily News, The Tribune, Ilanga, Rapport, The Citizen, The Sowetan and The Cape Argus. This inconsistent sample produced some variability in the results, but represents a good cross section of the papers and printing inks used in South Africa. The conclusions drawn from this work would thus be applicable to the local industry.

2. A Lamort 25 litre laboratory pulper was used to pulp the newsprint. This pulper has a working volume of 15 litres and contains a helical rotor. A photograph of the pulper is depicted in Appendix H.
3. The following chemicals were added in order into the pulper:

Water at 55 °C	13.5 litres
Caustic soda lye 45%	36g (or 12.9 kg anhydrous /ton dry fibre)
Sodium silicate 38%(Na ₂ O:SiO ₂ 3.3:1)	34g (or 10 kg anhydrous/ton dry fibre)
Enzyme scavenger	0.5 ml

In addition to these chemicals, calcium (as calcium chloride) and sodium soap were added as outlined in Table 5.1 above. With the exception of sodium silicate, the commercial chemicals in use in the Merebank deinking plant were used in these experiments. The specifications are given in Appendix A. No chelating agent has been in use in the deinking plant for many years, and so none was added in the laboratory work. However, an enzyme scavenger is being used in the plant, and was added in the laboratory work. The enzyme scavenger is used to deactivate catalase enzymes, which can rapidly decompose hydrogen peroxide. (Sundblad & Mattila 2001). A water temperature of 55°C ensured a final pulping temperature of 50°C.

4. The chemicals were mixed briefly. Thereafter 1.4 kg of air-dry newsprint (ca. 10% moisture) was torn into strips and introduced into the pulper. Unprinted edges from each newspaper used were torn off and retained. The brightness of the unprinted edges was measured according to Tappi T452 om 92: Brightness of pulp, paper and paperboard (Directional reflectance at 457 nm.), to determine the unprinted, or edge brightness. Newspapers were sampled at random from the deinking plant warehouse. It was not possible to use exactly the same type of newspaper for each experiment, but no newspapers older than three months were used. The paper, water and chemicals were mixed until the paper had started to disintegrate (about 30 seconds) and then 22 g of hydrogen peroxide 30% (equivalent to ca. 5 kg/ton dry fibre) was added and the paper was pulped for 15 minutes at 50°C.
5. A sample was drawn and the temperature, consistency, pH, hardness and residual peroxide were determined according to standard Mondi Merebank methods, as

detailed in Appendix B. The addition of hydrogen peroxide was such that a small residual peroxide concentration at least 0.35 kg/ton dry fibre was maintained, to ensure complete bleaching.

6. Handsheets were made on a Standard British Sheet Machine according to Tappi method T205 om-88: Forming handsheets for physical tests of pulp. A minimum of six handsheets were made, and the brightness and colour were determined on an Elrepho 3000 machine, according to Tappi T452: Brightness of pulp, paper and paperboard (Directional reflectance at 457 nm.). The average brightness of the six handsheets is reported.

5.2.2 Laboratory flotation method

Immediately after the paper had been pulped and tested, the flotation was commenced, according to the method below. A laboratory flotation cell with a working volume of 20 litres was used, and is depicted in Appendix H.

1. The equivalent of 0.200 kg of dry fibre (calculated as $0.2/\text{pulper consistency} \times 100$) was weighed out for flotation.
2. The pulp and most of the flotation water were mixed in the flotation cell and a 250 ml. sample was taken for a hardness test. The hardness was determined as per Appendix B.
3. Collector soap was pre-mixed with some hot water and added at a rate of 7.2 g/kg (kg/ton) of dry fibre. The current addition rate in the Merebank deinking plant was 4 kg/ton dry fibre, but it was necessary to add more soap in the laboratory flotation cell to achieve a good head of foam and comparable flotation results to the plant (Addis & Kathi 1992). In experiments 5.1 and 5.3 (see Table 5.1 p. 79), where 200 ppm of soap was added into the pulper water, the amount of soap added at the flotation stage was decreased accordingly, so that the total soap addition rate of 7.2 g/kg dry fibre was maintained.
4. Based on the result of the hardness test, calcium chloride was added to achieve a hardness of 250 ppm as CaCO_3 , according to the following calculation:

$$\text{ml of calcium chloride} = \frac{(250 - \text{ppm calcium hardness}) \times 18}{\text{Calcium chloride conc (mg/ml)}}$$
 250 ppm of calcium hardness as CaCO_3 corresponds to 100 ppm of calcium hardness as Ca.
5. The flotation cell was topped up with water. The temperature of the water was such that the final flotation temperature was 40°C.

6. Air was introduced into the flotation cell, and the pulp was floated for 20 minutes. The ink and foam were scooped off manually. The flotation period of 20 minutes was excessively long, but the objective was to achieve “infinite” or “hyperflotation” (McCool 1993), to ensure complete removal of all ink by flotation. The objective of this experiment was to determine the effect of various pulping conditions on deinking efficiency. Incomplete flotation would interfere with the interpretation of the results. Addis & Kathi (1992) used a flotation time of 15 minutes, and some preliminary flotation work (Figure 5.1) indicated that a flotation time of only 10 minutes was enough to remove virtually all the ink.

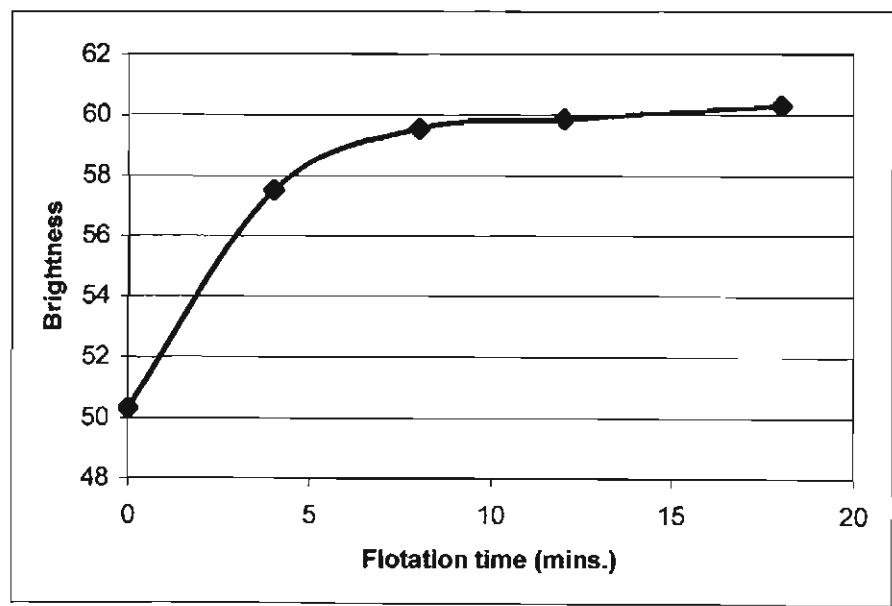


Figure 5.1: Final brightness as a function of flotation time.

7. After flotation, a 10-litre sample of floated pulp was taken and tested for temperature, pH and hardness (Appendix B). Six handsheets were made up according to Tappi T205 and the brightness and colour were determined according to Tappi T452. The detailed results are listed in Appendix I. The average brightness of the six handsheets is reported.
8. For each pulper batch, the flotation was done in duplicate. The average of the duplicate results was taken.

5.2.3 Assessment of deinking efficiency

This experimental work was intended to investigate the effect of various pulping conditions on the overall deinking result. Unfortunately, it is not possible to determine the efficiency of ink removal from the paper fibres immediately after pulping. It is necessary to first remove all the ink by flotation and then measure the final brightness. As a result, in order to achieve complete removal of all floatable ink by "hyperflotation", soap addition levels were high and flotation times were long. It is only the un-floatable ink that was still adhering to the fibres that would remain behind and be determined in the final brightness measurement.

As discussed earlier in Section 2.3, there are a number of techniques to determine the amount of ink in a pulp: brightness measurement, colour measurement, image analysis and ERIK measurements. Of these, only the brightness and colour measurement techniques were available to measure deinking efficiency.

It was found that the top side of the handsheets generally yielded a higher brightness, by about 2 points for the floated pulps and 3-4 points for the unfloated pulps. The higher brightness is a result of ink washout during the formation of the sheet in the sheet maker. The method of preparation of the handsheet prior to the brightness measurement, and the side that is measured, have a large influence on the final result (Dorris 1999a & 1999b). Dorris (1999a & 1999b) found that handsheets formed on a Standard British Sheet Machine according to Tappi T205 showed the greatest loss of ink by washout. This normally distorts the results in an assessment of flotation efficiency, but in this investigation it was desirable to measure only the non-removable ink. Hence the method employed to make the handsheets is appropriate to the final objectives of this work.

5.3 Results and Discussion

5.3.1 Brightness measurements

The flotation results are tabulated in Appendix I, and are summarised pictorially in Figure 5.2 to 5.4 below. As a result of the considerations in Section 5.2.3 above, only the topside sheet brightness was used in the deinking assessment, and is reported in

Appendix I. Figure 5.2 depicts the results of the brightness measurements in the course of the pulping and flotation experiments.

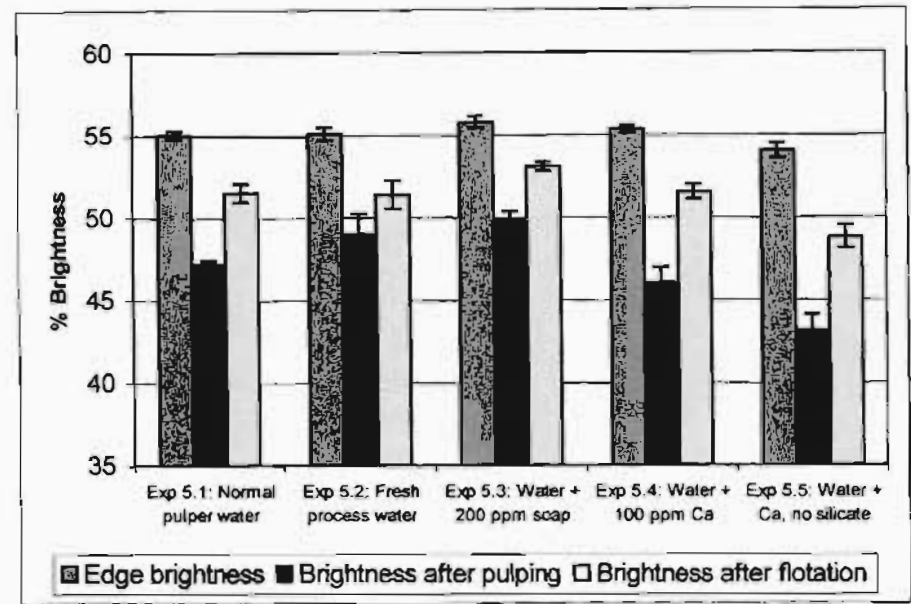


Figure 5.2 – Brightness results in deinking. The error bars indicate the standard error.

The edge brightness, or brightness of the unprinted paper, represents the starting point for each series of experiments. An ANOVA test applied to the edge brightness demonstrates that there was no significant difference between the series at the 95% level of confidence. The ANOVA test is detailed in Appendix I.

The significance of the brightness before flotation, or after pulping, is difficult to interpret, but has been related to the amount of ink fragmentation in the pulper. (Pirttinen & Stenius 2000). The more the ink fragments, the finer the particle size and the lower the brightness. If the ink fragmentation is too great, the efficiency of flotation could be affected. In this series of experiments, the presence of calcium in the pulper (experiments 5.1, 5.4 and 5.5) seems to coincide with lower pulper brightness and by implication greater ink fragmentation. This appears to contradict the earlier findings in this and other work, where larger particles were associated with the presence of calcium. It is likely that the complex physical interactions that take place in the pulper probably could change the final ink particle size distribution.

The efficiency of deinking is often assessed by quoting the brightness increase achieved in flotation. Whilst this method might be valid for comparison of flotation results where the same pulp is floated, in this work this can be misleading. Therefore, the final brightness after flotation was taken as the measure of deinking efficiency. There was no significant difference between the final brightness of the normal pulping conditions (experiment 5.1), pulping with fresh water (experiment 5.2) and pulping with hard water (experiment 5.4). However, when pulping was carried out in the presence of an excess of free and available fatty acid soap (experiment 5.3), a statistically significant (at 95% confidence) improvement in final brightness was achieved. The statistical analysis is shown in Appendix I.

5.3.2 L* measurements

The greyness or lightness of a piece of paper is measured by the L* value. In this work the L* value was found to correlate closely with the brightness. This correlation for the initial edge brightness and the final floated brightness is shown in Figure 5.3. Because of this close correlation, the L* values for the pulping and flotation experiments were not analysed further.

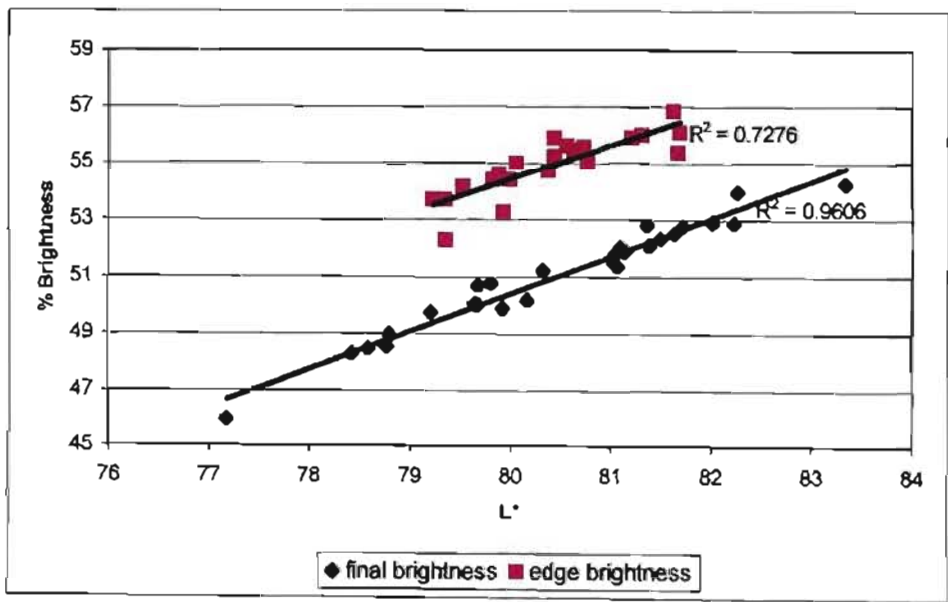


Figure 5.3 - Correlation between brightness and L* (Lightness). The raw data is displayed in Appendix I.

The difference between the two lines is due to the yellowing of the fibres during pulping and flotation, which is discussed below.

5.3.3 The yellowness, or b^* value

Figure 5.4 depicts an analysis of the b^* value, or yellowness of the fibre before and after pulping and flotation.

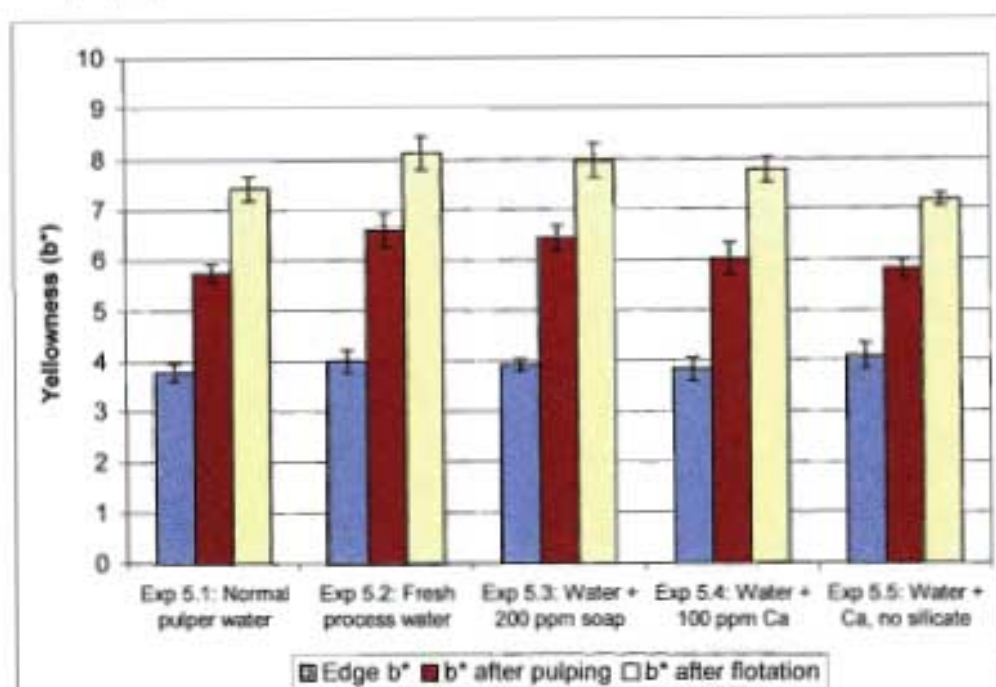


Figure 5.4 - Changes in yellowness during pulping and flotation. The error bars indicate the standard error. Raw data in Appendix I.

It is apparent that the greatest yellowing has occurred in experiments 5.2 and 5.3, and the least in experiment 5.5. The yellowing is a result of exposure of the fibres to alkaline conditions, and is the reason for the inclusion of hydrogen peroxide in the deinking pulper. Yellowing also results in a decrease in brightness, and offsets the brightness gains made by removing the ink from the paper. Notwithstanding the yellowing in experiment 5.3, the highest brightness was also achieved in this experiment, which suggests that the ink removal was even greater than indicated by the final brightness alone.

5.4 Conclusions

The highest final brightness of 53.1% was achieved in experiment 5.3, in which an excess of soap was present in the pulper. The lowest final brightness of 48.8% was attained in experiment 5.5, which contained no silicate and an excess of hardness in the pulper. The presence of calcium in the pulper, as long as sodium silicate was present, did not negatively affect the final brightness. This can be seen in the

brightness' of 51.5%, 51.4% and 51.5% obtained in experiments 5.1, 5.2 and 5.4 respectively. This can be understood by the fact that the calcium is being sequestered by the silicate, rendering it inert in the form of calcium silicate. However, once the sodium silicate is removed (experiment 5.5), a lower brightness (48.8%) is achieved. It could be argued that the absence of sodium silicate from the pulper in experiment 5.5 negatively affected the bleaching and resulted in a lower brightness. However, the yellowing results (see Figure 5.4 p. 86) suggest that the bleaching was not impaired by the absence of silicate. The b^* value obtained in experiment 5.5 was 7.17, as opposed to a b^* value of 7.96 for experiment 5.3. Another factor in support of this is that an excess of hydrogen peroxide after bleaching was maintained. This suggests that, as long as sodium silicate is present in a pulper, the calcium will be sequestered and the soap would be "protected", enabling it to launder the ink off the fibre. In the absence of silicate, the calcium precipitates the soap and renders it ineffective.

From the point of view of optimising the Mondi Merebank deinking process, this would suggest that the use of fresh water alone in the repulping stage would not be enough to achieve a significant improvement in deinking. However, if a portion of the collector soap is added into the pulper, a significant improvement in deinking performance could be gained.

6: CONCLUSIONS AND RECOMMENDATIONS

6.1 General conclusions

The original objective of this work was to investigate the ink dispersing behaviour of sodium silicate. This was based on many literature references in the deinking field that alluded to the ability of sodium silicate to disperse oils and fats.

6.1.1 The dispersing properties of sodium silicate

The experiments to evaluate the dispersing properties of sodium silicate suggested that its dispersing properties were only slightly superior to those of caustic soda, but inferior to the ink dispersing ability of fatty acid soaps. It was however apparent that the amount of sodium silicate present when used in combination with calcium and soap did influence the dispersing result in some way. It appeared as if there were interactions between the calcium, sodium silicate and soap.

On the evidence of SEM and EDS analysis, there was some indication of interactions between calcium and ink and silicate and ink. These interactions appeared to be disrupted in the presence of stronger dispersing agents such as soaps. There was no evidence of colloidal calcium silicate on the surface of the ink particles.

6.1.2 The sequestering properties of sodium silicate

The interactions between sodium silicate, calcium and collector soap were investigated. As a first step, the silicate-calcium system and the soap calcium-system were examined.

6.1.2.1 The silicate-calcium and soap-calcium systems

Both collector soap and sodium silicate react with calcium to form insoluble precipitates of calcium silicate and calcium soap respectively. The dispersing work suggested that these entities did not associate in any way with the ink particles. The soap precipitated relatively more calcium at low hardness, with sodium silicate's precipitating effect becoming more pronounced at higher hardness.

These effects were not greatly influenced by temperatures in the normal range of the deinking process and the precipitation of calcium as calcium hydroxide was not significant below pH 11.

The pH of the solution did exert some influence. As the pH was increased the precipitating effect increased, with sodium silicate showing greater sensitivity to pH. However, pulping is normally carried out at pH's closely controlled in the region of 10, so pH does not afford many possibilities to influence the pulping process.

6.1.2.2 The soap-silicate-calcium system

In the deinking literature, the calcium-soap system has received a lot of research attention, mainly in the context of the flotation process and the agglomeration of soap stabilised particles. In addition, the calcium-silicate system has been the subject of some work in the context of pulp bleaching and deposit formation. However, the three-species system of calcium-soap-silicate, which exists in most newsprint deinking systems, had not been studied. A study of this system revealed that both soap and the silicate anion compete for the calcium ion. Although the soap seems to have a greater affinity for the calcium, the sodium silicate, when present in excess amounts also precipitates a significant amount of calcium, and actually results in an increase in the soap concentration in solution. This effect however seems to plateau, depending on conditions, at about 2000 ppm of sodium silicate in solution. This is reflected in the fact that the normal addition rate of sodium silicate is about 2.5% as anhydrous chemical per ton of fibre (or ca. 2500 ppm in solution for a 10% consistency pulp). In addition, the calcium is not completely removed from solution, and a residual concentration of calcium remains.

6.1.2.3 Implications for a deinking system

It is known that a certain amount of soap in the pulper is essential for the successful removal of ink from the fibres. The presence of sodium silicate results in decreased hardness and increased soap concentration. It is suggested that it is by this mechanism the sodium silicate has a positive effect on deinking performance, rather than due to any strong intrinsic dispersing effect of its own.

6.1.3 The effect on deinking

A series of laboratory scale deinking experiments were conducted to confirm this proposed mechanism. These experiments confirmed that pulping with an excess of soap in solution produced the highest final brightness of deinked pulp.

It is reported in the literature that calcium present in the pulper has a negative effect on ink removal. However, in this work, pulping in the absence of calcium did not produce any improvement in final deinked brightness. In addition, pulping in the presence of calcium also did not show any deleterious effect on overall deinking performance. This can be understood by the fact that the calcium is chelated by the sodium silicate, effectively removing it from the deinking system. This would also tend to add further weight to the suggestion that colloidal calcium silicate plays no role in the deinking mechanism, as has been suggested by some workers.

Pulping in hard environment in the absence of sodium silicate resulted in the lowest final brightness. This can be explained by the fact that now, with no sodium silicate to "protect" any soap that might be in solution, the soap is precipitated by the calcium to form the ineffective calcium soap. This results in poor removal of ink from the fibres and low final brightness.

6.2 Final conclusion as to the role of sodium silicate in newsprint deinking

On the basis of the evidence that has emerged in this work, it is proposed that sodium silicate operates via a sequestering mechanism. This consists of chelating the calcium hardness and protecting any soap that might be present in the pulper, enabling it to perform its function of laundering the ink off the fibres. This will also result in an ink particle that is better stabilised and less likely to redeposit onto the fibres during the pulping operation. Once these soap-stabilised ink particles proceed to the flotation operation, they can be agglomerated more effectively by the calcium collector, and thereby removed more effectively from the pulp mass. This sequestering mechanism operates over and above sodium silicate's prime role of chelating metal ions and stabilising hydrogen peroxide.

6.3 Recommendations

1. The study of the interaction of sodium silicate, soap and calcium ions under various conditions of concentration and pH has suggested that it is undesirable to have calcium ions present during pulping. This is because any calcium present will precipitate free soap in solution as well as react with sodium silicate to affect its ability to act as a peroxide bleach stabiliser.
2. Laboratory scale pulping and flotation experiments failed to show a significant improvement when soft water rather than recirculated water was used for pulping. This should, however, be tested on a plant scale, as it may be possible to marginally reduce the amount of sodium silicate used without adversely affecting pulp brightness. It will still be necessary to add calcium chloride before flotation because it is needed to convert all soap present from the sodium soap to the calcium soap, which is the required ink collector.
3. Laboratory pulping and flotation experiments have conclusively shown that a significantly improved brightness can be achieved when fresh water instead of recirculated water is used for pulping, with some soap added. It is recommended that a plant trial be carried out to confirm this and to ascertain the optimum dosage of soap and sodium silicate required. The level of soap added during pulping should be compensated by an equivalent reduction in the amount of soap added before flotation, to avoid increased reagent costs.

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APPENDIX A

Raw material specifications

Raw material specifications are presented for the following:

1. Collector soap – Silacross collector P.
2. Calcium chloride.
3. Sodium silicate 3.3:1, 38% - Silchem 3379.
4. Offset ink binder – Gilsonite resin.

National Starch and Chemical

Fax

To: Jimmy Pauck**From:** Vinodh Singh**Fax:** 031- 4612115**Pages:** 01 (inclusive)**Phone:** 082 809 1572**Date:** 01/12/00**Re:** Silacross Collector P**CC:**

☒ **Urgent** ☐ **For Review** ☐ **Please Comment** ☐ **Please Reply** ☐ **Please Recycle**

• Below is the information as requested. The information below is however **confidential** and is to be used only as a reference. I also apologize for not supplying this information sooner. Please advise should you request any further assistance.

Regards, Vinodh.

Blend: 80% AEE Toilet Tallow / 20% Palm Kernel Oil bleached to 1.0 red units (max.) when measured in a lovibond 130mm cell

Colour: Good creamy white – free of any contamination, discoloration of foreign objects. Reading not to exceed 80° when measured at dR460 using barium standard. (Using Elrepho Mat Reflectance Meter D65/10)

Odour: Typical – free of any evidence of rancidity or unsaponified oil odour

Grit: Any evidence of grit when tables are washed down in cold running water must be Between : & +. Values > 4 are rejectable

ANALYSIS	NOMINAL %	UPPER LIMIT %	LOWER LIMIT %	RESULTS
Moisture	10.00	12.00	9.00	
Total Fatty Content	82.00	83.00	80.00	
Free Alkalinity as NaOH	Nil	0.05	Nil	
Free Fatty Acid as Oleic Acid	0.300	1.000	Nil	
Salt as NaCl	0.600	0.800	Nil	
*Alcohol Insolubles	1.000	1.100	Nil	
*EHDP as Acid	0.030	0.033	0.027	
* EDTA as Acid	0.065	0.070	0.060	
* Phosphoric Acid as 80%	0.267	0.285	0.252	
* Unsaponified + Unsaponifiables	0.600	1.000	Nil	
* Fine Passing 3350 Micron Mesh	0.100	0.200	Nil	
*Size Analysis: Diameter Length	8mm 20mm	10mm 30mm	6mm 10mm	

* Analysis not required – for information only

QC APPROVED / REJECTED: _____

DATE: _____

APPENDIX A-1

Further information on collector soap: Silacross Collector P.

The collector soap is a blend of 85% Tallow fatty acid and 15% Palm oil fatty acid. These fatty acids have the following approximate % composition:

Carbon chain	Tallow	Palm oil	Approx. composition
C8 –C10		5.5	0.8
C12:0		48	7.2
C14:0	3	16	5.0
C16:0	23	8	20.8
C16:1	2.5		2.1
C18:0	22	3	19.2
C18:1	34	17	31.5
C18:2		2.5	0.4
Other	15.5		13.2
Saponification value mgKOH/g	197	245-255	205

This information was obtained from the supplier.

POLIFINCHEMICALS DIVISION
PRODUCT SPECIFICATION

PS-013

INDUSTRIAL CALCIUM CHLORIDE SOLUTION

Old Spec No: 230

DESCRIPTION, PROPERTIES AND HAZARDS

Refer to the Material Safety Data Sheet

SAMPLING AND TESTING

As per current sampling and testing schedule

SPECIFICATION

Appearance	The material shall be clear to slightly cloudy, off-white to yellowish liquid, containing not more than 0,1% m/m sediment.
Strength	Min 32,0 m/m as CaCl_2
pH	4,0 to 6,0

METHOD

According to latest analytical method.

REASON FOR REVISION

1.	Annual Revision	Process changes to plant	30/08/91
2.	Change format	Delete density, lead, zinc, fluorine. Change pH	16/06/93
3.	Change format	Change in Company Name and allocate new spec number	07/07/94
4.	Revision	Issuing authority changed and procedure revised.	24/02/97
5.	Revision	Method numbers removed	31/07/97

ISSUED BY: SYSTEMS ADMINISTRATOR: CHEMICALS

APPROVED BY: PRODUCT MANAGER: CYANIDE AND DERIVATIVES

OPERATIONS MANAGER: CYANIDE AND DERIVATIVES

MAIN LABORATORY MANAGER: MIDLAND

DATE ISSUED: 31/07/97
REVISION 5

WILL BE REVISED ON REQUEST


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Calcium Chloride Solution
1. General Information
1.5 Main Properties



Material is at Normal Conditions:	Liquid.
Appearance & Color:	Clear to slightly turbid liquid
Odor Threshold:	Odorless.
Boiling Point:	116°C
Freezing Point:	- 7°C
Specific Gravity: g/cc (H2O = 1)	20% CaCl2 1.19 @ 27°C 34% CaCl2 1.34 45% CaCl2 1.47
Vapor Density: (Air = 1)	Not applicable.
Solubility in Water:	Complete.
pH:	Neutral to slightly Alkaline.
Vapor Pressure (mm Hg @ 20°C) (PSIG):	1.1 kPa
35% CaCl2:	
Evaporation Rate: (Ether = 1.0)	Not applicable.
% Volatiles by Volume: (at 20%)	Not applicable.
Molecular Weight:	110.99 as anhydrous CaCl2



	POLIFIN RAW MATERIAL SPECIFICATION This specification cancels and replaces Raw Material Specification No. 837 B	NO. 837
		REVISION 3
		DATE OF ISSUE: November 1998
		PAGE 1 OF 2
Tariff No.: GRADED LIMESTONE (CALCIUM CARBONATE)		Commodity No.:

1. GENERAL

1.1 Description

Limestone, the naturally occurring form of calcium carbonate, CaCO_3 , is in the form of light grey/white stones.

1.2 Properties of pure calcium carbonate

Molecular mass : 100,09
 Density : 2,83
 Melting point : 825°C
 Angle of repose : 37 - 43°C

See Material Safety Data Sheet No:

2. SPECIFICATION

2.1 Appearance

The material shall be a light grey stone, free from visible impurities and foreign matter.

2.2 Calcium carbonate content

Not less than 95,5 % (m/m) as CaCO_3 .

2.3 Silica

To lie within the range 0,9 to 1,1 % (m/m) as SiO_2 .

2.4 Magnesium carbonate

To lie within the range 1,9 to 2,1 % (m/m) as MgCO_3 .

2.5 Loss on ignition

Not more than 43,3 % (m/m)

2.6 Bulk density

To lie within the range 1380 to 1520 kg/m^3

2.7 Particle size range

Greater than 9,5 mm sieve : between 0 and 20 %
 Greater than 6,3 mm sieve : between 80 and 100 %
 Smaller than 6,3 mm sieve : between 0 and 20 %

3. DESIRABLE PROPERTIES

3.1 Product test

The product prepared using this raw material must conform to the relevant Polifin Ltd Product Specification.

3.2 Packaging

MAIN LABORATORY
 AUTHORISED COPY

Number 8 Date 13 NOV 1998

13-11-1998

1 - GENERAL INFORMATION

Hydrochloric Acid

1.4 Specifications

Note: Refer to latest specification sheets.

Hydrochloric Acid -
Industrial : 30/33% m/m HCl

Specification

Appearance	The material shall be a colourless to yellowish fuming liquid, free from any visible impurities
Strength	30,0 to 33,0% m/m as HCl
Organics (total)	Not more than 5 ppm m/m
Iron	Not more than 15 ppm m/m as Fe
Flouride	Not more than 5 ppm m/m as F
Dissolved Chlorine	Not more than 5 ppm m/m as Cl

Hydrochloric Acid -
Chemically Pure (CP Grade)

Specification

Appearance	The material shall be a colourless fuming liquid, free from any visible impurities
Colour	Not more than 0,4 yellow Lovibond units
Strength	Strength within the range 30,0 to 33,0% m/m as HCl
Free Chlorine	Not more than 2 ppm m/m as Cl ₂
Iron	Not more than 1 ppm m/m as Fe
Sulphated ash	Not more than 100 ppm m/m
Sulphates	Not more than 20 ppm as SO ₄
Lead	Not more than 2 ppm m/m as Pb
Arsenic	Not more than 1 ppm m/m as As
Sodium	Not more than 5 ppm m/m as Na
Total Hardness	Not more than 5 ppm m/m as Ca
Mercury	Not more than 0,4 ppm m/m as Hg

APPENDIX A-3

National

ORIGINAL

NUMBER :	A 14010
DATE ISSUED :	22/01/1997
REPLACES :	12/94

PRODUCT SPECIFICATION

PRODUCT	:	Silchem 3379			
DESCRIPTION	:	Clear to hazy grey viscous liquid which may contain black specks.			
PACKAGING	:	Bulk tanker			
SPECIFICATION		LIMITS		TEST METHOD	
		<u>% m/m Dry Basis</u>			
Chemical		Maximum	Minimum		
Ratio SiO ₂ : Na ₂ O		3,35	3,20	Molar ratio 3,35 - 3,46	TM W101
Density ° Twaddell		81	77	@ 20°C	TM W100
% Na ₂ O		9,16	8,45	Subject to density	TM W101
% SiO ₂		29,80	28,30	Subject to density	TM W101

APPENDIX A-3


National Starch & Chemical (Pty) Ltd.

SILCHEM SODIUM SILICATE SOLUTIONS - TYPICAL VALUES

Grade Silchem	Pack Size (kg)	Major Applications	Mean Density at 20°C			Mean Weight Ratio SiO ₂ : Na ₂ O	Mean Na ₂ O %	Mean SiO ₂ %	Mean Total Solids %	Viscosity @ 20°C CP *
			*Tw	*Be	SG					
3008	308	Spray dried detergents, deflocculation	108	50,8	1,54	2,0	14,87	28,78	44,65	500
3036	326	Foundry - CO ₂ process	126	56,0	1,63	2,0	16,68	33,42	50,10	4000
3035	335	Soap manufacture, deflocculation of clay slips	135	58,7	1,68	2,0	17,58	35,22	52,80	25000
2080	280	Welding rod manufacture	80	41,4	1,40	2,0	11,75	23,50	35,25	200
2314	314	Foundry - CO ₂ process	114	52,6	1,57	2,3	14,36	33,04	47,40	1700
2410	310	Tube winding adhesive, cardboard laminating	110	51,5	1,55	2,4	13,68	32,87	46,55	1150
2692	292	Foundry - self set process	92	45,	1,46	2,6	11,42	29,73	41,15	100-300
2992	292	Adhesion	92	45,7	1,46	2,9	10,75	31,20	41,95	300-500
3379	279	Soil consolidation, refractory linings, furnace cement, briquetting, agglomeration, pelletising, adhesives	79	41,1	1,395	3,3	8,81	29,04	37,85	200-400

* Unless a range is stated, the viscosities given are average values

SILCHEM SODIUM SILICATE GLASS - TYPICAL VALUES

Grade	Pack Size (kg)	Applications	Mean Weight Ratio SiO ₂ : Na ₂ O	Mean Na ₂ O	Mean SiO ₂	Physical Form
Silchem G20	50	Mining and detergents	2,0 : 1,0	33,3	66,7	Lump
Silchem G33	50	Mining and detergents	3,3 : 1,0	23,26	76,74	Lump

SILTK12



Ziegler Chemical & Mineral Corporation

What is Gilsonite?

Gilsonite, or North American Asphaltum is a natural, resinous hydrocarbon found in the Uintah Basin in northeastern Utah. This natural asphalt is similar to a hard petroleum asphalt and is often called a natural asphalt, asphaltite, uintaite, or asphaltum. Gilsonite is soluble in aromatic and aliphatic solvents, as well as petroleum asphalt. Due to its unique compatibility, gilsonite is frequently used to harden softer petroleum products. Gilsonite in mass is a shiny, black substance similar in appearance to the mineral obsidian. It is brittle and can be easily crushed into a dark brown powder.

Gilsonite is found below the earth's surface in vertical veins or seams that are generally between two and six feet in width, but can be as wide as 28 feet. The veins are nearly parallel to each other and are oriented in a northwest to southeast direction. They extend many miles in length and as deep as 1500 feet. The vein will show up on the surface as a thin outcropping and gradually widen as it goes deeper. Due to the narrow mining face, Gilsonite is mined today, much like it was 50 or 100 years ago. The primary difference is that modern miners use pneumatic chipping hammers and mechanical hoists.

History

The mineral now known as Gilsonite or North American Asphaltum was discovered in the early 1860's, but it was not until the mid-1880's that Samuel H. Gilson began to promote it as a waterproof coating for wooden pilings, as an insulation for wire cable, and as a unique varnish. Gilson's promotion of the ore was so successful that, in 1888, he and a partner formed the first company to mine and market gilsonite on a commercial scale.

Originally, Gilsonite was sold as "Selects" and "Fines"; the low softening point ore with conchoidal fracture was known as "Selects". The higher softening point ore with a pencillated structure was known as "Fines". Selects commanded a higher price than Fines because of its better purity, good solubility, and usefulness in the paint, stain, and varnish industries.

Time and technology have changed this classification system. Processing of Gilsonite now removes most of the inert contaminants and newer, more powerful, solvents make the higher softening point grades more interesting to the user. Today, Gilsonite is graded by softening point (a rough measure of solubility) and particle size. All grades carry a degree of quality far superior to those first small amounts of crude Gilsonite marketed in the 1880's.

Technical Information

The information in these pages is based on laboratory evaluation and field experience. It is correct to the best of our knowledge. Since use and application of our products are beyond our control, Ziegler Chemical & Mineral Corporation cannot be responsible for obtained results whether used alone or in combination with other products. Recommendations are made without warranty or guarantee and buyer assumes all risk and liability.

[How is Gilsonite packaged?](#)

[Where is Gilsonite Sold?](#)

[Physical Properties of Gilsonite](#)

[Chemical Properties of Gilsonite](#)

[Gilsonite's Compatibility with other products](#)

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Physical Properties of Gilsonite

Color in Mass	Black
Color in Streak or Powder	Brown
Softening Point	265-400 °F
Moisture Content	0.5 %
Ash Content	0.5 %
Specific Gravity @ 77°F	1.04-1.06
Hardness (Moh's Scale)	2
Penetration	0
Volatility, Weight %, 5 Hours @ 325°F	< 2%
5 Hours @ 400°F	< 4%
5 Hours @ 500°F	< 5%
Flash Point, C.O.C.	600 °F
Acid Value	2.3
Saponification Value	5.6
Iodine Number	0

Iodine Number	0
Heat of Combustion	17,900 Btu / lb.
Heat of Fusion	9990 Btu / lb.
Specific Heat of Solid Phase	0.52 Btu / lb. / °F
Specific Heat of Liquid Phase	0.61 Btu / lb. / °F
Glass Transition Temperature, T _g	185-225 °F
Bulk Density, Lump	40 lbs. / ft ³
Electrical Resistivity	4.0 x 10 ¹² ohm-cm
Viscosity, Brookfield	
@ 375°F	55,000 cps
@ 400°F	22,800 cps
@ 425°F	6,600 cps
@ 450°F	2,800 cps

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Chemical Properties of Gilsonite

Gilsonite is included in a class of solid bitumens known as asphaltites. Gilsonite deposits are located in eastern Utah in the United States. They are different from other asphaltites because of their:

- high asphaltene content
- high solubility in organic solvents
- high purity and consistent properties
- high molecular weight
- high nitrogen content

Gilsonite is available in different grades categorized by softening point. Softening point is used as an approximate guide to melt viscosity and behavior in solution. The chemical differences are small between Gilsonite grades, with only subtle variations in average molecular weight and asphaltene/resin-oil ratios.

The precursor of Gilsonite is believed to be kerogen from the Green River formation deep below the Uintah Basin in eastern Utah. Mild thermal reductive degradation of this kerogen and subsequent fractionation as it was geologically squeezed to the surface are believed to be responsible for the formation of the unique deposits we mine today.

Elemental Analysis:

	Weight %
Carbon	84.9
Hydrogen	10.0
Nitrogen	3.3
Sulfur	0.3
Oxygen	1.4
Trace elements	0.1
	<hr/>
	100.0
Aliphatic carbon	68.3
Aromatic carbon	31.7
H/C atomic ratio	1.42

Proximate Analysis:

	Weight %
Volatile matter	84.5
Fixed carbon	15.0
Ash	0.5
	<hr/>
	100.0

Molecular Structure:

A variety of sophisticated analytical tests have been run on Gilsonite from the Uintah Basin to characterize its unique properties. For reference, the test methods include vacuum thermal gravimetric analysis (TGA), nuclear magnetic resonance (NMR), Fourier transform infrared spectrometry (FTIR), vapor pressure osometry (VPO), high performance liquid chromatography (HPLC), rapid capillary gas chromatography (RCAP), and several fractionation techniques. H/C ratios and NMR analysis indicate the presence of a significant aromatic fraction. Most of the aromatics exist in stable, conjugated systems, probably porphyrin-like structures that relate to the geologic source of the product. The remainder of the product consists of long, paraffinic

chains.

Typical Component Analysis	Softening Point, °F			
	<u>290</u>	<u>320</u>	<u>350</u>	<u>375</u>
Asphaltenes	57	66	71	76
Resins (Maltenes)	37	30	27	21
Oils	<u>6</u>	<u>4</u>	<u>2</u>	<u>3</u>
	100	100	100	100

A very unique feature of Gilsonite is its high nitrogen content, which is present mainly as pyrrole, pyridine, and amide functional groups. Phenolic and carbonyl groups are also present. The low oxygen content relative to nitrogen suggests that much of the nitrogen has basic functionality. This probably accounts for Gilsonite's special surface wetting properties and resistance to free radical oxidation.

The average molecular weight of Gilsonite is about 3000. This is very high relative to other asphalt products and to most synthetic resins. This may relate to Gilsonite's "semi-polymeric" behavior when used as a modifying resin in polymeric and elastomeric systems. There is some reactive potential in Gilsonite. Crosslinking and addition type reactions have been observed. Gilsonite is known to react with formaldehyde compounds under certain conditions.

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Gilsonite Solutions

Gilsonite is an important component of today's printing inks, paints & industrial coatings. Gilsonite is used as a hard resin and carbon black dispersant in a variety of coatings. Solutions of Gilsonite (sometimes called cutbacks or varnishes) are an excellent starting point for blending Gilsonite with other components of a final product formulation. Some formulators convert dry Gilsonite into liquid solution in their own facilities. Others will request a pre-made solution. Both are available from Ziegler Chemical & Mineral Corp.

Converting dry, granular Gilsonite to a liquid solution also provides the opportunity to remove the small amount of abrasive grit that occurs in natural asphaltums. Stabilizing additives can also be added if a poor solvent is used or if high concentrations of Gilsonite are desired.

Solubility:

Gilsonite is soluble in aliphatic, aromatic and chlorinated hydrocarbon solvents. It has limited solubility in most ketones, but is soluble in mixed aromatic solvents that contain a ketone component. Gilsonite is not soluble in water, alcohols, or acetone.

Solution Preparation:

Three basic procedures are used to dissolve Gilsonite. In each case, precautions for flammable materials should be used.

Cold-cutting: Gilsonite is generally soluble in aliphatic and aromatic solvents at ambient temperatures. Some agitation should be used. The rate of solution will depend on the type of solvent, the type and severity of mixing, and the grade of Gilsonite. The solution rate can be increased by using a high shear mixer, such as a Cowles disperser. When a ball mill or a paddle mixer is used, lump grade Gilsonite is recommended. When high energy mixing is available, either lump or pulverized grades may be used. Care must be taken to avoid "dry balls" of undissolved solid when using pulverized grades.

Hot-cutting: The rate of solution can be increased by heating. Steam coils or hot oil is preferred. Direct-fired heating can be hazardous. Care must be taken to avoid or make up for vaporized solvent. Facilities for solvent containment are often necessary. The maximum processing temperature will depend on the boiling range of the solvent.

Hot fluxing: Gilsonite can be hot fluxed into asphalts and high boiling oils. Once blended, the combination can then be let down with a solvent to reach the desired viscosity. This hot fluxing with another product can help overcome limitations of solubility. Selecting the correct blend or co-solvent can

yield compatibility with a solvent that is normally of limited solubility.

Hot Fluxing Procedure:

Heat the oil to 200°F or more. Most of the high boiling, low aromatic ink oils in use today will require a temperature of at least 300-330°F. With good agitation, add dry Gilsonite at a rate that maintains constant dispersion of the particles until they dissolve. Be alert for foaming that can be caused by traces of moisture in the Gilsonite. Continue to agitate for 15 to 30 minutes beyond the point when the last of the Gilsonite particles is detected. The Gilsonite should now be completely dissolved and the solution ready for discharge.

Filtration:

The varnish must be filtered to remove the grit that is a natural component of Gilsonite. There are two common filtration methods. Each provides a different degree of cleanliness. Both methods are normally preceded by passing the hot varnish through a course wire screen (approx. 1/4") to remove any large stones.

For a normal degree of cleanliness, the prescreened, hot varnish is passed through wire screen baskets of about 200 mesh (74 microns). Cloth bag filters can also be used, at a higher cost, when the company doesn't have the personnel to clean the wire baskets. Disposal of the bags is also a consideration. Be careful to use bags that can tolerate elevated temperatures if hot cutting is performed.

For extra cleanliness, the prescreened, hot varnish is passed through cartridge filters of about 5 to 25 microns. These filters are also disposable.

Viscosity Modification:

Some Gilsonite solutions can be quite viscous at ambient temperature. Also, some solutions can steadily increase in viscosity over time. These characteristics are usually observed when using low aromatic oils with poor solvent power or when high percentages of Gilsonite are used. In these cases, small amounts of viscosity modifiers are often added to (1) keep the hot varnish sufficiently fluid for easy filtration and (2) to reduce and stabilize the ambient viscosity so the solution remains fluid until it is used.

The following is a partial list of modifiers that are effective at stabilizing the viscosity of Gilsonite solutions.

1. Soft asphalt flux. This is often substituted for 15 to 20 % of the Gilsonite in the varnish. At this level, it reduces the softening point of the Gilsonite by about 30°F. It should not be used when maximum hardness and rub resistance is desired, or when fast solvent release is required, or when restrictive health safety regulations are in effect.
2. Tridecyl alcohol (TDA). More volatile than some modifiers (a flash point of 180°F), but effective. Generally used at 3-10%, based on the Gilsonite content.
3. Low molecular weight alcohols. Examples are n-propanol and n-butanol. These are effective, but their high volatility usually restricts their use to fast drying systems or products that are stored and used at ambient temperature.
4. Tall oil fatty acids. These are mainly oleic and linoleic acids with small amounts of rosin acids present. They are used for their high flash point and low

volatility. In some cases, stearic or oleic acid, or vegetable oils such as linseed or soya bean oil, can be substituted for tall oil fatty acids with comparable performance.

5. Surfactants. A wide variety of commercial surfactants are also effective. Care must be taken to avoid any undesirable side effects on the performance of the final product.

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APPENDIX B

Mondi Merebank standard test methods

The following standard test methods are presented:

1. Determination of calcium hardness.
2. Determinations of soap, oil and grease.
3. Determination of residual peroxide.
4. Determination of consistency.
5. Determination of pH.

QUALITY MANAGEMENT SYSTEM

Prepared by : P.N.P. *PNP*

DEPARTMENT TECHNICAL DEVELOPMENT

Sect Head : T.H. *TDH*

Subject : WATER ANALYSIS

Dept Man : J.C.R. *JCR*

Issued on : MAY 1992

Revised on : NOVEMBER 1998

Pg 1 of 1

DETERMINATION OF CALCIUM HARDNESS

Reagents:

1. Standard Sodium Versanate solution (EDTA).
2. Potassium Hydroxides, 10% Solution.
3. Calcon indicator solution.

Method:

1. Pipette 100ml of the sample into a 250ml beaker.
2. Add 4ml of the Potassium Hydroxide 10% solution and 5 drops of the indicator.
3. Titrate with the Sodium Versanate standard solution until the colour changes from red – wine to blue.

Calculation:

ml of Sodium Versanate used x f x 10 = ppm CaCO₃

APPENDIX B-2

MONDI PAPER COMPANY LIMITED –PAPER DIVISION

Reference: IT300/01/0018

QUALITY MANAGEMENT SYSTEM

Prepared by: PT.....

DEPARTMENT TECHNICAL DEVELOPMENT

Sect Head: TH.....

Subject: WATER ANALYSIS

Dept Man: TvR.....

Issued On: MAY 1992

Revised on: NOVEMBER 1998

Pg 1 of 2

DETERMINATION OF SOAL, OIL & GREASE

Sampling

Care should be taken that the sample is representative. Samples should be taken in clean, glass stoppered bottles, previously washed with solvent and air-dried before use. The bottle should not be completely filled, as a loss of floating oil may occur in stopping. It is advisable to collect the desired quantity of sample in an oversized bottle that has previously been marked on the outside at the desired volume.

Storage

Samples should be analyzed as soon as possible after sampling, since many oils and hydrocarbons are utilized by bacteria.

If storage is unavoidable, use 5ml 1:1 Sulphuric acid per litre, to inhibit bacterial action.

Reagents:

1. Sulphuric Acid (H_2SO_4) 1:1
2. Petroleum ether, boiling point 35° to 60°C . Distilled at least twice in an all-glass apparatus, discarding the last 10 percent remaining in the flask at each distillation. The residue on evaporation should be less than should be less than 0.1mg per 100ml.

Method:

1. Transfer the sample to a two litre separating funnel, and acidify with 5ml Sulphuric acid per litre.
2. Rinse the flask carefully with 15ml of petroleum ether and add washing to the separating funnel.
3. Add an additional 25ml petroleum ether to the separating funnel, shaking vigorously for 2 minutes.

APPENDIX B-2

MONDI PAPER COMPANY LIMITED –PAPER DIVISION

Reference: IT300/01/0018

QUALITY MANAGEMENT SYSTEM

Prepared by: PT.....

DEPARTMENT TECHNICAL DEVELOPMENT

Sect Head: TH.....

Subject: **WATER ANALYSIS**

Dept Man: TvR.....

Issued On: MAY 1992

Revised on: NOVEMBER 1998

Pg 2 of 2

DETERMINATION OF SOAL, OIL & GREASE

4. Allow the ether layer to separate, withdraw the aqueous portion of the sample into a clean container and transfer the solvent layer into 2 clean weighed distilling flasks capable of holding at least three volumes of solvent. If a clear ether layer cannot be obtained, filter the solvent layer into the weighed distilling flask through a funnel containing an ether-moistened Whitman 40 (or equivalent) filter paper. Use a small funnel and filter paper twice with fresh 5ml increments of petroleum ether.
5. Return the sample to the separating funnel, rinsing the container with 15ml ether.
6. Add the ether washing and add an additional 15ml ether to the separating funnel, and agitate for another two minutes.
7. Allow the solvent layer to separate, and discard the aqueous phase.
8. Add the ether extraction to the weighed distilling flask, and rinse the separating funnel with 20ml ether.
9. Add the ether washing the weighed distilling flask.
10. Distill off all but approximately 10ml of the ether extract, keeping the source of heat at about 70°C. Then the disconnect the condenser, and boil off the remaining solvent at the same temperature.
11. Dry the flask on a water-bath.
12. Cool in a dessicator and weigh.

Calculation:

The total gain in weight of flask less the calculated residue from the solvent, as determined by the distillation or evaporation of a measured quantity, indicates the amount of extracted soap, oil or grease in the water sample.

Soap, grease of oil in mg/l – $\frac{(\text{g wt gain} - \text{mg residue}) \times 1.000}{\text{ml sample}}$

TECHNICAL DEPT.



mondi paper company

HYDROGEN

PEROXIDE

BLEACHING

MANUAL

APPENDIX B-3

- 37 -

RESIDUAL PEROXIDE DETERMINATION

Object: To determine residual peroxide concentration in pulp slurries.

Apparatus: 1 - Buchner funnel
1 - 400 ml beaker
1 - 250 ml Erlenmeyer flask
1 - 25 ml graduated cylinder
1 - 25 ml pipette
1 - 50 ml burette

Reagents: 0.10 N $\text{Na}_2\text{S}_2\text{O}_3$
25% H_2SO_4
10% KI solution
Saturated Ammonium Molybdate solution
Soluble starch

Procedure: 1. Obtain a sample of pulp from the Bleach Tower prior to the dilution and neutralisation with sulphuric acid.
2. Place sufficient pulp in a clean Buchner funnel to collect approximately 100 ml of effluent.
3. Pipette 25 ml of the effluent into the 250 ml Erlenmeyer flask.
4. Add 25 ml of 25% H_2SO_4 , 10 ml KI solution, 3 drops of molybdate solution.
5. Titrate with 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ to a pale yellow colour, add 10 ml of starch and continue titration until the blue colour disappears.

Calculation: (a) Residual Peroxide = $\frac{\text{Titration} \times \text{N} \times 17.01}{\text{mls sample}} \text{ (g/l)}$
= Titration \times N \times 0.68

(b) % Residual Peroxide on B.D. Pulp =

$$\frac{100 - \% \text{ Cons}}{\% \text{ Cons}} \times \frac{\text{Res. in g/l}}{10}$$

APPENDIX B-3

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or Apply the relevant data to the NOMOGRAPH as indicated.

If the normality of the Sodium Thiosulphate is not exactly $N/10$ calculate the equivalent mls. of exactly $N/10$ $Na_2S_2O_3$

$$(c) \quad \% \text{ Peroxide Consumption} = \frac{\% H_2O_2 \text{ Added} - \% \text{ Residual}}{\% H_2O_2 \text{ Added}} \times 100$$

$$(d) \quad \% \text{ Residual peroxide} = \frac{\text{Residual peroxide}}{10}$$

APPENDIX B-4

QUALITY MANAGEMENT SYSTEM

Reference: IT/300/04.0001

DEPARTMENT: STOCK PREP LABORATORY

Prepared by: PNP

SUBJECT: CONSISTENCY

Section Head: TH

Issued On: March 2000

Dept Man: JCR

Revised On: March 2000

PG 1 OF 2

DEFINITION

Consistency is the percentage of bone dry (B.D.) fibre in suspension in a given slurry or "wet" sample of pulp and water.

DETERMINATION OF CONSISTENCY

Consistency is determined by filtering the fibres out of a weighed or measured quantity of stock and then weighing the B.D. fibres obtained. The percentage is calculated against the total mass or volume of the stock taken. There are two basic types of consistency determinations.

1. Volumetric Method

This method is used for pulps with a consistency below 2,0% eg. Headbox, white waters wire tray, etc.

1.1 Procedure

This method is used for pulps with a consistency below 2,0% eg. Headbox, white waters, wire tray, etc.

1.1 Procedure

- a) Measure out a 250ml of sample in a measuring cylinder.
- b) Place a dried and weighed No. 4 filter paper in the consistency apparatus and form a sheet.
- c) Ensure that the weight of the filter paper is recorded on the side of the paper that is facing the wire.
- d) Press the sheet between two blotters.
- e) Dry the sheet on a hot plate or dryer.
- f) Weigh the B.D. sheet on a toppan balance.
- g) Subtract the weight of the filter paper before calculation.
- h) Calculate: $\% \text{ consistency} = \frac{\text{wt of B.D. sheet} \times 100}{250}$

APPENDIX B-4

QUALITY MANAGEMENT SYSTEM

Reference: IT/300/04.0001

DEPARTMENT: STOCK PREP LABORATORY

Prepared by: PNP

SUBJECT: CONSISTENCY

Section Head: TH

Issued On: March 2000

Dept Man: JCR

Revised On: March 2000

PG 2 OF 2

2. Gravimetric Method

This method is used for pulps with a consistency of 2,0% and above, eg. Chemical pulp, TMP, GWD, RCF, Broke, Stock-ex-blend and RCF.

2.1 Procedure

- a) Tare a cup or breaker of suitable size on the toppan balance.
- b) Weigh out 50g of pulp sample.
- c) Dilute the sample with water and transfer to the consistency apparatus to form a sheet.
- d) Refilter the filtrate.
- e) Press the sheet between two blotters
- f) Dry on the hot plate.
- g) Weigh B.D. sheet on the toppan balance.
- h) Calculate: %cons = wt. Of B.D. sheet x 2.

NOTE:

1. These methods are used when freeness (CSF) determination is not required.
2. When a CSF as well as a consistency is required for the volumetric method, measure out 1000ml of sample for the test.
3. When a CSF as well as a consistency is required for the Gravimetric method, a table is provided with suggested "weights" for different consistencies to give an acceptable B.D. sheet that will dry rapidly (See Table 1).
4. All results are to be logged down in the log sheets (see Appendix 1 & 2).
5. Results are to be reported in writing to the machineman and to the Stock Prep Operator (See Appendix 3).

APPENDIX B-4

TABLE 1

Testing of samples with a consistency of 2,0% and above.

- 1. Visually estimate consistency
- 2. Weigh required stock to be taken
- 3. Table 1 below - grams of sample to make 2 litres.

ESTIMATE CONSISTENCY	APPROXIMATE STOCK TO BE TAKEN
2,00	300g
2,20	270g
2,40	250g
2,60	230g
2,80	210g
3,00	200g
3,20	185g
3,40	175g
3,60	165g
3,80	155g
4,00	150g
4,25	140g
4,50	135g
4,75	125g
5,00	120g
5,20	115g
5,40	110g
5,60	105g
6,00	100g
6,20	97g
6,40	94g
6,60	91g
6,80	88g
7,00	85g

APPENDIX B-5

QUALITY MANAGEMENT SYSTEM

Reference: IT/300/04.0003

DEPARTMENT: STOCK PREP LABORATORY

Prepared by: PT

SUBJECT: pH Measurement

Section Head: TH

Issued On: March 2000

Dept Man: JCR

Revised On: March 2000

PG 1 OF 2

DEFINITION

pH is a measure of the hydrogen ion concentration of a solution. A pH of 7 is neutral, below 7 is acid, above 7 is alkaline.

i) Standardize pH Meter (Crison 2001)

- a) Press the temperature symbol key to select the temp. Press the upper half of the key to increase the temp or the lower half of the key to decrease the temp.
- b) Press the calibration key and the 'pH' key.
- c) Immerse the electrode into the 7.02 buffer solution.
- d) Press the calibration key and wait 5 seconds for the readout to stabilise.
- e) Remove the electrode from the solution and rinse with distilled water.
- f) The instrument will then automatically request the use of the 4.00 buffer solution.
- g) Immerse the electrode into the 4.00 buffer solution.
- h) Press the calibration key and wait 5 seconds for a stable readout.
- i) Remove the electrode from the solution and rinse with distilled water.
- j) The instrument is ready to measure pH.

ii) pH Measurement (Crison 2001)

- a) Press the temperature key according to the sample.
- b) Immerse the electrode in the sample and shake slightly.
- c) Press the pH key, and wait for the readout to stabilise.
- d) The display will freeze on the last and correct pH value

iii) Standardize pH METER (Mettler)

- a) Press the "ON/OFF" key to turn the display off.
- b) Press and hold the "MODE" key and press the "ON/OFF" key again.
- c) The display will show b=1.
- d) Release the "MODE" key.
- e) Press the "READ" key to select the required buffer solution.
- f) Place the electrode into the buffer solution and press the "CAL" key.
- g) The pH meter automatically end points when calibrating.
- h) Remove the electrode from the buffer solution and press the "CAL" key.
- i) To return to sample measurement press the "READ" key.
- j) To return to the sample measurement press the "READ" key.

APPENDIX B-5

QUALITY MANAGEMENT SYSTEM

Reference: IT/300/04.0003

DEPARTMENT: STOCK PREP LABORATORY

Prepared by: PT

SUBJECT: pH Measurement

Section Head: TH

Issued On: March 2000

Dept Man: JCR

Revised On: March 2000

PG 2 OF 2

iv) pH Measurement (Mettler)

- a) Place the electrode into the sample and press the **"READ"** key to start the measurement.
- b) The readout will stabilize but will not freeze at the endpoint.
- c) To freeze the display at endpoint press the **'READ'** key.

v) Standardize pH meter (Beckman P310)

- a) Rinse the electrode with deionised water; blot excess water.
- b) Immerse electrode into **4.00** buffer solution. Stir briefly with electrode to remove bubbles from the electrodes surface.
- c) Press **STD**.
- d) After the eye stops flashing the display will read **4.00**.
- e) Rinse the electrode and blot the excess water.
- f) Immerse electrode into **7.00** buffer solution. Stir briefly.
- g) Press **STD**.
- h) After the eye stops flashing the display will read **pH 7.00**.
- i) The standardization is complete.

vi) pH Measurement (Beckman)

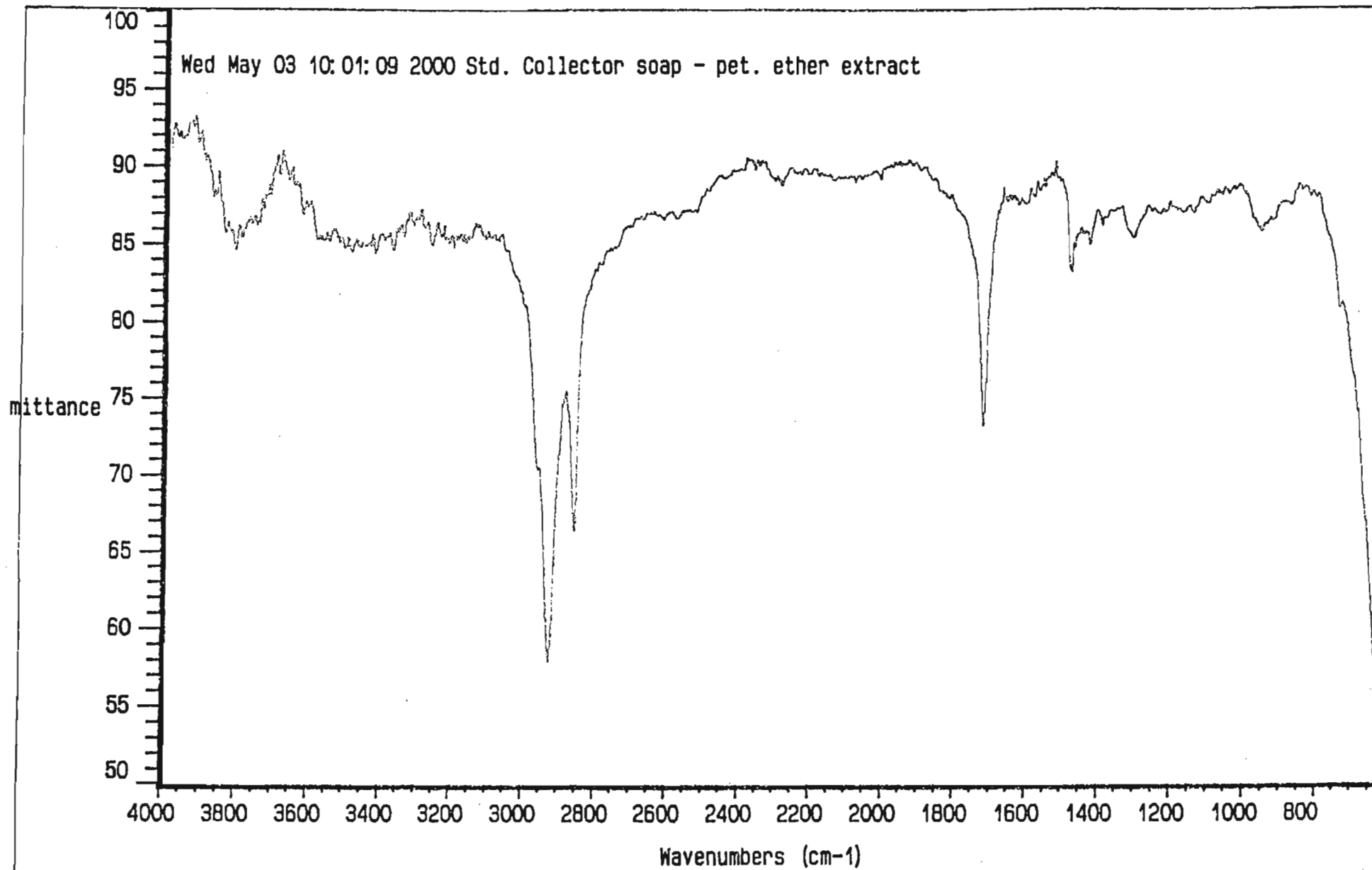
- a) Rinse electrode and blot excess water.
- b) Immerse electrode into sample: stir briefly.
- c) Press **pH**.
- d) After the **eye** stops flashing the display will read the **pH** of the sample.

APPENDIX C

Identification of the dry residue of the petroleum ether extract, as generated by test method: Determination of soap, oil and grease.

The following FTIR spectra are presented:

1. FTIR of petroleum ether extract of a standard collector soap. Identified as "Standard collector soap".
2. FTIR of petroleum ether extract residue of a disc filter filtrate sample dated 3/2000. Identified as "RFP cloudy water sample #1".
3. FTIR of petroleum ether extract residue of a disc filter filtrate sample dated 4/2000. Identified as "RFP cloudy water sample #2".

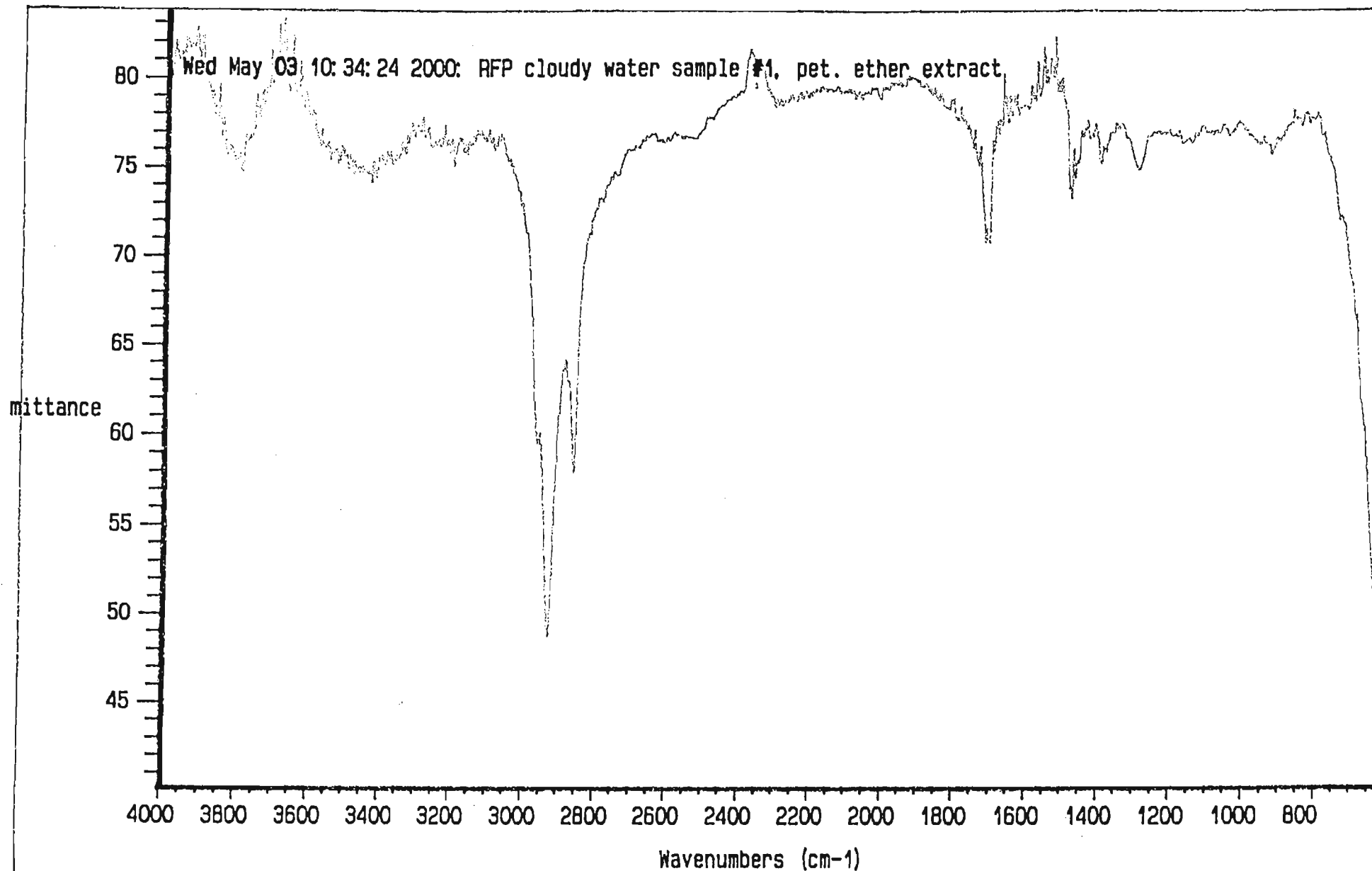


Date: Wed May 03 10:01:17 2000

Wed May 03 10:01:09 2000 Std. Collector soap - pet. ether extract

Scans: 6

Resolution: 4.000

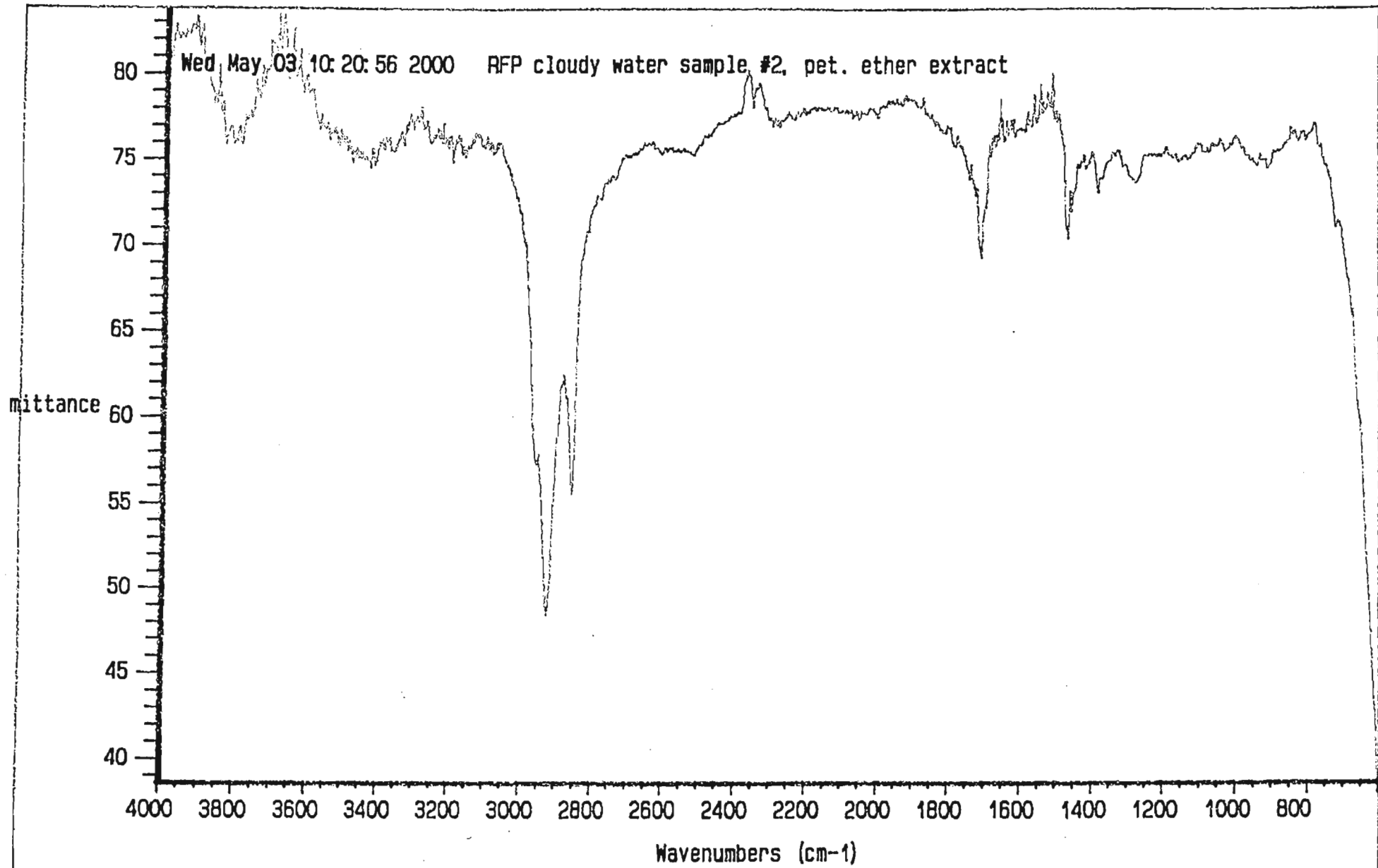


Date: Wed May 03 10:34:31 2000

Wed May 03 10:34:24 2000: RFP cloudy water sample #1, pet. ether extract

Scans: 6

Resolution: 4.000



Date: Wed May 03 10:21:02 2000

Wed May 03 10:20:56 2000 RFP cloudy water sample #2, pet. ether extract

Scans: 6

Resolution: 4.000

APPENDIX D

Identification of the dry residue of the petroleum ether extract, as generated by test method: Determination of soap, oil and grease.

The following method and gas chromatograms are presented:

1. Conditions for fatty acid analyses.
2. GC of petroleum ether extract of standard collector soap. Identified as "Standard collector soap".
3. GC of petroleum ether extract of a disc filter filtrate sample dated 3/2000. Identified as "RFP cloudy water sample #1".
4. GC of petroleum ether extract of a disc filter filtrate sample dated 4/2000. Identified as "RFP cloudy water sample #2".

APPENDIX D-1

Conditions for fatty acid analysis

The following method and conditions were used to perform the gas chromatographic analysis of the fatty acid collector soap extracts:

1. The concentrated extract was reacted with an excess of chlorotrimethylsilane, to form a volatile TMS derivative.
2. The derivatised fatty acid was injected into a Fisons GC 8000 gas chromatograph, under the following conditions:
 - Temperatures: injector 230 °C, detector 230 °C.
 - Carrier gas: N₂ at 60 kPa. Detector: air at 110 kPa and H₂ at 40 kPa.
 - Temperature program: 140° for 3 mins, increase to 210° at 10 °/min, hold at 210° for 20 mins.
 - Column: Perkin Elmer N931-6402 PE wax, 30 m, 0.25 mm I.D., 0.15 micron film thickness.

Software Version : 6.1.0.2:G07
Operator : manager
Sample Number :
AutoSampler : NONE
Instrument Name : Fisons
Interface Serial # : 9209280002
Delay Time : 0.00 min
Sampling Rate : 3.1250 pts/s
Volume Injected : 1.000000 µL
Sample Amount : 1.0000
Data Acquisition Time : 05/03/00 12:28:16 PM PM

Date : 05/03/00 12:58:28 PM PM
Sample Name :
Study :
Rack/vial : 0/0
Channel : A
A/D mV Range : 1000
End Time : 30.00 min

Area Reject : 0.000000
Dilution Factor : 1.00
Cycle :

Raw Data File : C:\PenExe\Tcws\Ver6.1.0\Examples\Collector soap std001.raw
Result File : C:\PenExe\Tcws\Ver6.1.0\Examples\Collector soap std.002.rst
Inst Method : C:\Fame\fame from C:\PenExe\Tcws\Ver6.1.0\Examples\Collector
soap std.002.rst
Proc Method : C:\Fame\fame
Calib Method : C:\Fame\fame
Sequence File : C:\PenExe\Tcws\Ver6.1.0\Examples\Collector soap std.seq

DEFAULT REPORT

Peak #	Time [min]	Area [µV•s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
-	0.271	0.00	0.00	0.00	0.00		-----
1	3.797	8649509.28	993913.36	97.00	97.00	BE	8.7025
2	4.225	56987.84	8252.27	0.64	0.64	EV	6.9057
3	4.436	74922.30	13754.17	0.84	0.84	VV	5.4472
4	4.589	7474.66	1800.91	0.08	0.08	VB	4.1505
5	5.385	6883.68	2354.15	0.08	0.08	BB	2.9241
6	7.039	12852.16	4241.35	0.14	0.14	BB	3.0302
-	8.208	0.00	0.00	0.00	0.00		-----
-	8.296	0.00	0.00	0.00	0.00		-----
-	8.670	0.00	0.00	0.00	0.00		-----
-	8.774	0.00	0.00	0.00	0.00		-----
-	8.893	0.00	0.00	0.00	0.00		-----
-	9.180	0.00	0.00	0.00	0.00		-----
7	9.350	30527.04	8488.49	0.34	0.34	BB	3.5963
8	9.895	1444.48	557.33	0.02	0.02	BB	2.5918
-	10.174	0.00	0.00	0.00	0.00		-----
-	10.306	0.00	0.00	0.00	0.00		-----
-	10.455	0.00	0.00	0.00	0.00		-----

APPENDIX D-2

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05/03/00 12:58:28 PM PM Result:

C:\PenExe\TcWS\Ver6.1.0\Examples\Collector soap
std.002.rst

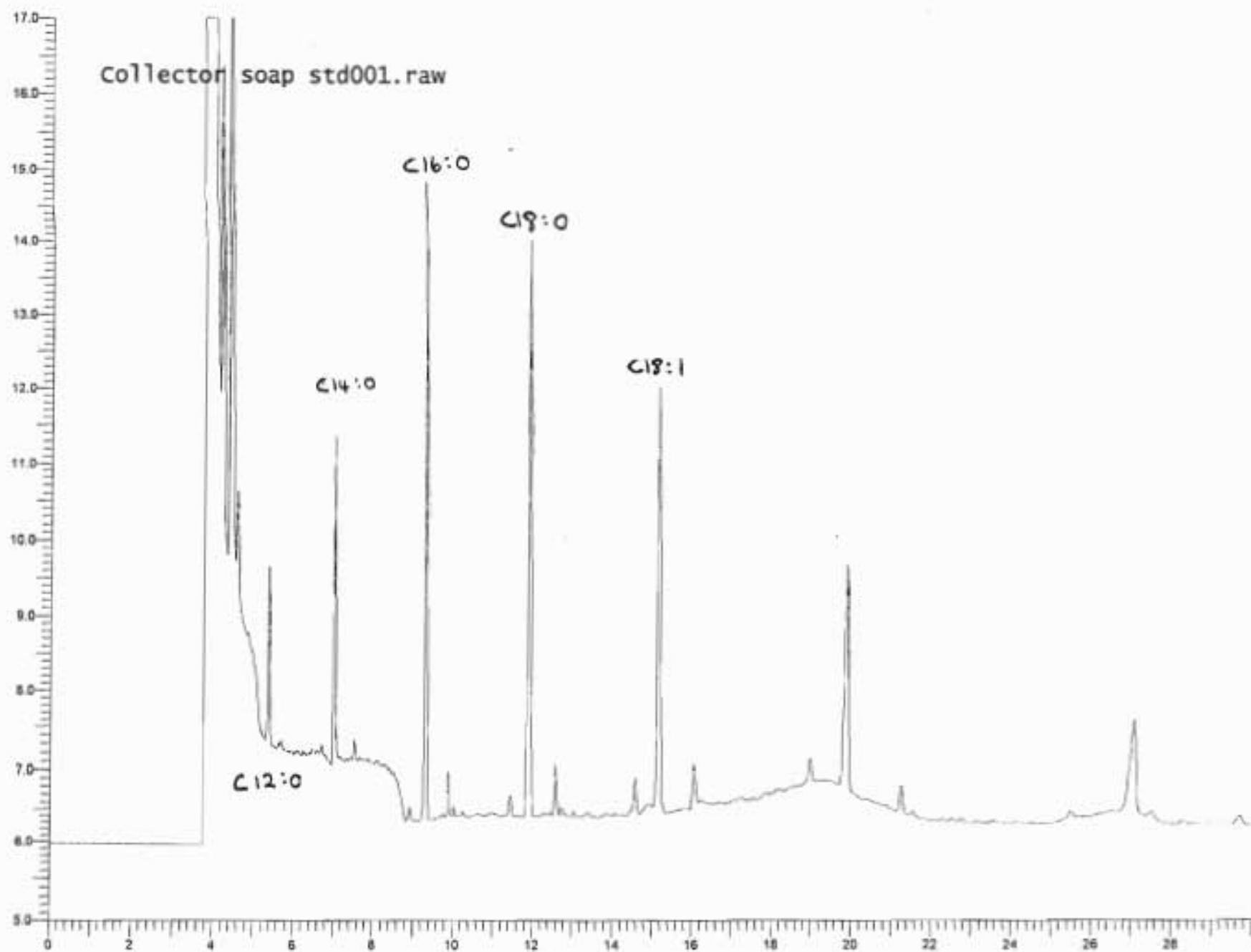
Peak #	Time [min]	Area [$\mu\text{V}\cdot\text{s}$]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
-	10.600	0.00	0.00	0.00	0.00		-----
-	10.959	0.00	0.00	0.00	0.00		-----
-	11.660	0.00	0.00	0.00	0.00		-----
9	11.949	35396.80	7699.88	0.40	0.40	BB	4.5971
-	12.244	0.00	0.00	0.00	0.00		-----
-	12.663	0.00	0.00	0.00	0.00		-----
-	13.607	0.00	0.00	0.00	0.00		-----
10	15.205	25684.80	5486.78	0.29	0.29	BB	4.6812
11	19.939	15126.56	2779.68	0.17	0.17	BB	5.4418
		8916809.60	1.05e+06	100.00	100.00		

Warning -- Signal level out-of-range in peak

Missing Component Report

Component Expected Retention (Calibration File)

peak1	0.271
pcb1	8.208
pcb2	8.296
pcb3	8.670
peak38	8.774
peak39	8.893
pcb4	9.180
peak50	10.174
pcb7	10.306
peak52	10.455
peak53	10.600
pcb8	10.959
pcb9	11.660
peak63	12.244
peak65	12.663
peak66	13.607



Software Version : 6.1.0.2:G07
Operator : manager
Sample Number :
AutoSampler : NONE
Instrument Name : Fisons
Interface Serial # : 9209280002
Delay Time : 0.00 min
Sampling Rate : 3.1250 pts/s
Volume Injected : 1.000000 µL 30 µl.
Sample Amount : 1.0000
Data Acquisition Time : 05/03/00 01:43:36 PM PM

Date : 05/03/00 02:13:44 PM PM
Sample Name :
Study :
Rack/Vial : 0/0
Channel : A
A/D mV Range : 1000
End Time : 30.00 min

Area Reject : 0.000000
Dilution Factor : 1.00
Cycle :

Raw Data File : C:\PenExe\Tcws\Ver6.1.0\Examples\RFP #2002.raw
Result File : C:\PenExe\Tcws\Ver6.1.0\Examples\RFP #2002.rst
Inst Method : C:\Fame\ fame from C:\PenExe\Tcws\Ver6.1.0\Examples\RFP
#2002.rst
Proc Method : C:\Fame\ fame
Calib Method : C:\Fame\ fame
Sequence File : C:\PenExe\Tcws\Ver6.1.0\Examples\RFP #2.seq

DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
-	0.271	0.00	0.00	0.00	0.00		-----
1	3.808	9277887.29	993940.03	89.31	89.31	BV	9.3345
2	4.239	77525.97	14103.59	0.75	0.75	VV	5.4969
3	4.452	327524.66	65379.81	3.15	3.15	VE	5.0096
4	4.610	32041.28	7861.53	0.31	0.31	EB	4.0757
5	5.443	28700.48	8995.98	0.28	0.28	BB	3.1904
6	7.175	81410.56	20457.86	0.78	0.78	BB	3.9794
7	7.631	4916.96	1714.14	0.05	0.05	BB	2.8685
-	8.208	0.00	0.00	0.00	0.00		-----
-	8.296	0.00	0.00	0.00	0.00		-----
-	8.670	0.00	0.00	0.00	0.00		-----
-	8.774	0.00	0.00	0.00	0.00		-----
-	8.893	0.00	0.00	0.00	0.00		-----
-	9.180	0.00	0.00	0.00	0.00		-----
-	9.373	0.00	0.00	0.00	0.00		-----
8	9.560	157950.08	24653.91	1.52	1.52	BB	6.4067
-	9.866	0.00	0.00	0.00	0.00		-----
9	10.049	15536.96	5105.01	0.15	0.15	BB	3.0435

APPENDIX D-3

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05/03/00 02:13:44 PM PM Result:

C:\PenExe\TcWS\Ver6.1.0\Examples\RFP #2002.rst

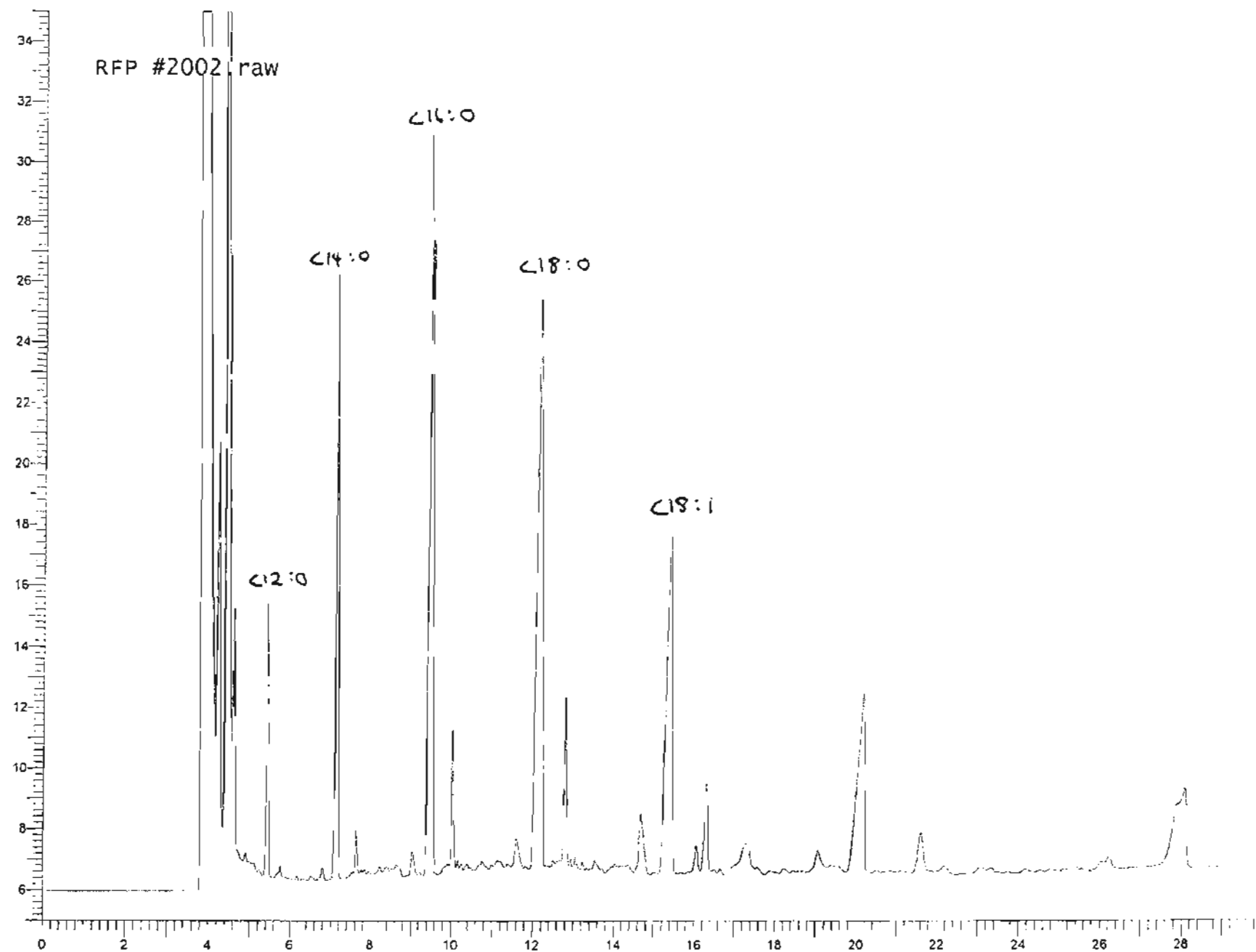
Peak #	Time [min]	Area [$\mu\text{V}\cdot\text{s}$]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
-	10.174	0.00	0.00	0.00	0.00		-----
-	10.306	0.00	0.00	0.00	0.00		-----
-	10.455	0.00	0.00	0.00	0.00		-----
-	10.600	0.00	0.00	0.00	0.00		-----
-	10.959	0.00	0.00	0.00	0.00		-----
-	11.660	0.00	0.00	0.00	0.00		-----
10	12.223	160169.76	19170.98	1.54	1.54	BB	8.3548
-	12.663	0.00	0.00	0.00	0.00		-----
11	12.819	20457.92	5420.47	0.20	0.20	BB	3.7742
-	13.607	0.00	0.00	0.00	0.00		-----
12	14.683	12874.56	1803.45	0.12	0.12	BB	7.1388
13	15.453	113080.32	11396.17	1.09	1.09	BB	9.9227
14	16.316	16560.00	2933.02	0.16	0.16	BB	5.6461
15	20.204	62143.84	5773.78	0.60	0.60	BB	10.7631
		10388780.64	1.19e+06	100.00	100.00		

Warning -- Signal level out-of-range in peak

Missing Component Report

Component Expected Retention (Calibration File)

peak1	0.271
pcb1	8.208
pcb2	8.296
pcb3	8.670
peak38	8.774
peak39	8.893
pcb4	9.180
pcb5	9.373
pcb6	9.866
peak50	10.174
pcb7	10.306
peak52	10.455
peak53	10.600
pcb8	10.959
pcb9	11.660
peak65	12.663
peak66	13.607



RFP cloudy water sample #2

Software Version : 6.1.0.2:G07
 Operator : manager
 Sample Number :
 AutoSampler : NONE
 Instrument Name : Fisons
 Interface Serial # : 9209280002
 Delay Time : 0.00 min
 Sampling Rate : 3.1250 pts/s
 Volume Injected : 1.000000 µL
 Sample Amount : 1.0000
 Data Acquisition Time : 05/03/00 01:05:14 PM PM

Date : 05/03/00 01:35:26 PM PM
 Sample Name :
 Study :
 Rack/vial : 0/0
 Channel : A
 A/D mV Range : 1000
 End Time : 30.00 min

Area Reject : 0.000000
 Dilution Factor : 1.00
 Cycle : 1

Raw Data File : C:\PenExe\TcWS\Ver6.1.0\Examples\RFP #2001.raw
 Result File : C:\PenExe\TcWS\Ver6.1.0\Examples\RFP #2001.rst
 Inst Method : C:\Fame\ fame from C:\PenExe\TcWS\Ver6.1.0\Examples\RFP #2001.rst
 Proc Method : C:\Fame\ fame
 Calib Method : C:\Fame\ fame
 Sequence File : C:\PenExe\TcWS\Ver6.1.0\Examples\RFP #2.seq

DEFAULT REPORT

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
-	0.271	0.00	0.00	0.00	0.00		-----
1	3.707	9164488.24	993825.47	94.09	94.09	BV	9.2214
2	4.138	95742.93	18191.85	0.98	0.98	VV	5.2630
3	4.351	222835.71	43396.50	2.29	2.29	VE	5.1349
4	4.508	19307.52	4898.12	0.20	0.20	EB	3.9418
5	5.334	28986.88	9785.48	0.30	0.30	BB	2.9622
6	7.044	33832.96	10540.14	0.35	0.35	BB	3.2099
7	7.529	2155.04	815.49	0.02	0.02	BB	2.6426
-	8.208	0.00	0.00	0.00	0.00		-----
-	8.296	0.00	0.00	0.00	0.00		-----
-	8.670	0.00	0.00	0.00	0.00		-----
-	8.774	0.00	0.00	0.00	0.00		-----
-	8.893	0.00	0.00	0.00	0.00		-----
-	9.180	0.00	0.00	0.00	0.00		-----
8	9.381	35692.80	9432.57	0.37	0.37	BB	3.7840
9	9.932	3152.00	1248.10	0.03	0.03	BB	2.5254
-	10.174	0.00	0.00	0.00	0.00		-----
-	10.306	0.00	0.00	0.00	0.00		-----

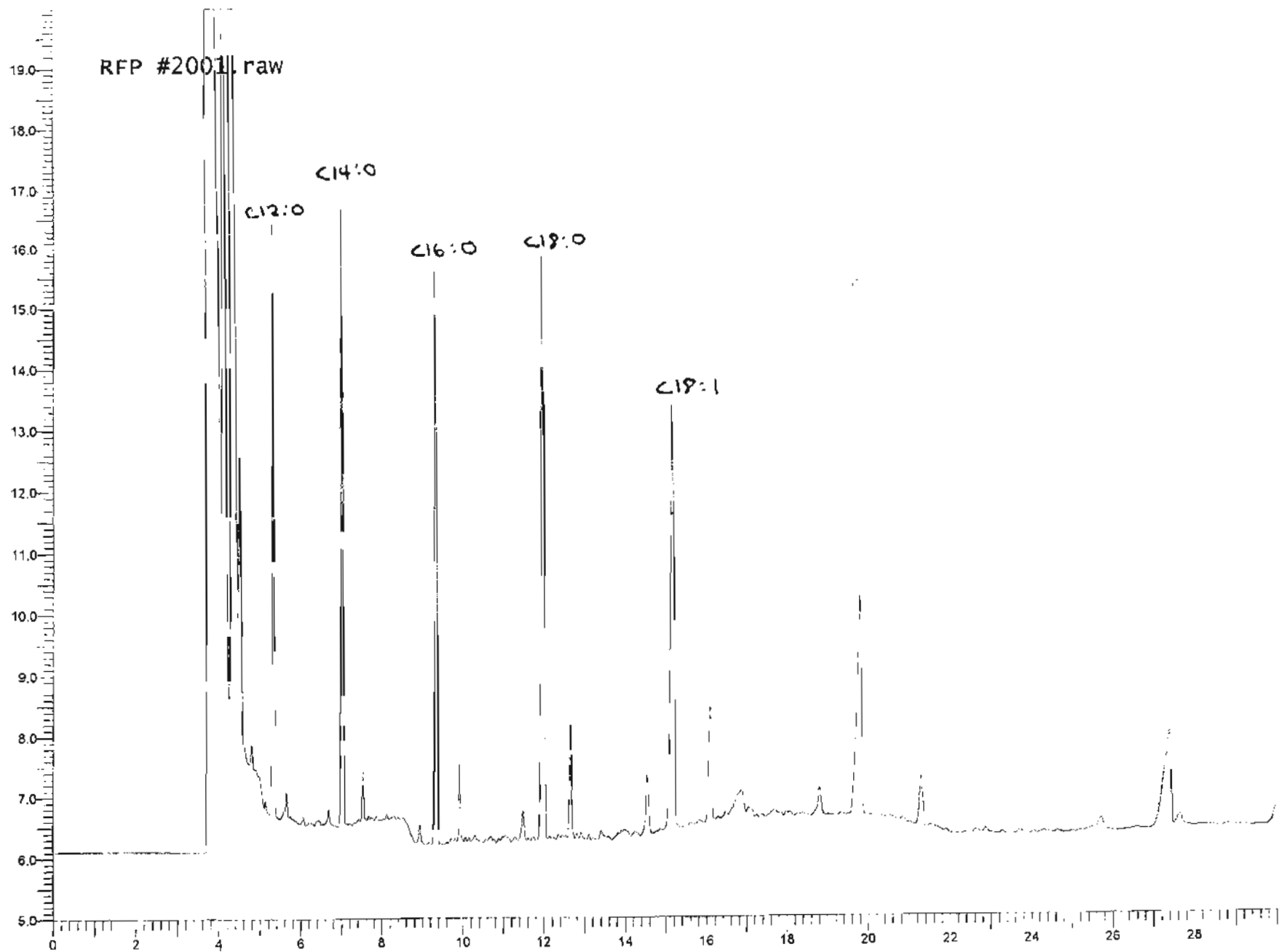
APPENDIX D-4

05/03/00 01:35:26 PM PM Result:
C:\PenExe\TcWS\Ver6.1.0\Examples\RFP #2001.rst

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
-	10.455	0.00	0.00	0.00	0.00		-----
-	10.600	0.00	0.00	0.00	0.00		-----
-	10.959	0.00	0.00	0.00	0.00		-----
-	11.660	0.00	0.00	0.00	0.00		-----
10	12.023	47652.48	9740.21	0.49	0.49	BB	4.8923
-	12.244	0.00	0.00	0.00	0.00		-----
11	12.666	5689.76	1826.10	0.06	0.06	BB	3.1158
-	13.607	0.00	0.00	0.00	0.00		-----
12	14.556	3485.60	850.82	0.04	0.04	BB	4.0968
13	15.217	43064.00	7046.39	0.44	0.44	BB	6.1115
14	16.107	8994.24	1839.37	0.09	0.09	BB	4.8898
15	19.844	24690.08	3445.60	0.25	0.25	BB	7.1657
		9739770.24	1.12e+06	100.00	100.00		

Warning -- Signal level out-of-range in peak
Missing Component Report
Component Expected Retention (Calibration File)

peak1	0.271
pcb1	8.208
pcb2	8.296
pcb3	8.670
peak38	8.774
peak39	8.893
pcb4	9.180
peak50	10.174
pcb7	10.306
peak52	10.455
peak53	10.600
pcb8	10.959
pcb9	11.660
peak63	12.244
peak66	13.607



APPENDIX E

Dispersing properties of sodium silicate

The raw data for the dispersing experiments are presented:

APPENDIX E: Dispersing properties of sodium silicate

Components	Exp 3.1: 3.3:1 Sodium silicate				Exp 3.2: 2.0:1 Sodium silicate				Exp 3.3: Sodium silicate/calcium				Exp 3.4: Sodium silicate/Na soap				Exp 3.5: Sodium silicate/Ca soap			
Sodium silicate (ppm)	0	1010	2020	4050	0	1010	2020	4050	0	1010	2020	4050	0	1010	2020	4050	0	1010	2020	4050
Calcium as Ca(ppm)	0	0	0	0	0	0	0	0	80	80	80	80	0	0	0	0	3.52	3.52	3.52	3.52
Na Soap(ppm)	0	0	0	0	0	0	0	0	0	0	0	0	50	50	50	50	50	50	50	50
Turbidity at 555 nm																				
	0.139	0.192	0.234	0.213	0.139	0.195	0.182	0.270	0.075	0.225	0.196	0.195	0.897	0.733	0.576	0.557	0.625	0.375	0.772	0.570
	0.230	0.178	0.232	0.249	0.230	0.282	0.255	0.245	0.103	0.062	0.105	0.275	0.586	0.703	0.527	0.441	0.245	0.477	0.599	0.546
	0.152	0.192	0.124	0.186	0.152	0.154	0.262	0.334	0.070	0.198	0.145	0.168	0.426	0.702	0.462	0.532	0.255	0.418	0.597	0.419
	0.19				0.19				0.130		0.101	0.154								
	0.171				0.171															
average	0.176	0.187	0.197	0.216	0.176	0.211	0.233	0.283	0.094	0.162	0.137	0.198	0.636	0.713	0.522	0.510	0.375	0.423	0.656	0.512
standard error	0.016	0.005	0.036	0.018	0.016	0.038	0.025	0.027	0.014	0.051	0.022	0.027	0.138	0.010	0.033	0.035	0.125	0.030	0.058	0.047
Median particle area (square microns)																				
	4700	4424	4529	4545	4700	4716	4508	4597	5043	4754	4936	5103	5422	4876	4647	4612	4289	4637	5285	4656
	4705	4317	4981	4532	4705	5039	4788	4448	5328	4918	4912	4815	4948	4481	4716	4521	6229	5396	5456	4889
	4437	4462	4692	4493	4437	4798	4590	5643	5226	5473	5559	5073	4708	4751	4897	4605		4912	5079	4470
	4611				4611				5059	5678	5617	5580								
	4653				4653															
average	4621	4401	4734	4523	4621	4851	4629	4963	5164	5206	5256	5143	5028	4703	4687	4579	5259	4982	5273	4672
standard error	49	43	132	16	49	97	83	442	69	220	192	159	210	117	21	29	970	222	109	121
Particle count (particles)																				
	1822	572	1914	1264	1822	2581	1703	1730	782	1013	1665	2192	5559	5047	2727	3145	0	3755	5595	3100
	2539	946	3031	1959	2539	3968	2248	1358	1143	1518	1010	2306	3761	1816	2629	2408	189	5475	5126	4067
	593	765	879	621	593	1643	1818	3945	789	1057	1048	1268	2171	3164	2262	2108	12	4733	5044	1057
	1249				1249				832	1076	1270	1560								
	1823				1823															
average	1605	761	1941	1281	1605	2697	1858	2344	887	1166	1248	1832	3830	3342	2539	2554	67	4654	5255	2741
standard error	325	108	621	386	325	645	197	808	86	118	150	249	979	937	142	308	61	498	172	887

APPENDIX F

Sequestering properties of sodium silicate

The following raw data are presented:

1. Independent competition for calcium ions by soap and sodium silicate.
2. Independent competition for calcium ions by soap and sodium silicate under different temperature and pH conditions.
3. Competition for calcium between sodium silicate and soap, when all three species are present.

APPENDIX F-1

SEQUESTERING PROPERTIES OF SODIUM SILICATE

Raw data: Independent competition for calcium ions by soap and sodium silicate at various initial calcium concentrations.

Initial calcium conc. 20 ppm		Initial calcium conc. 50 ppm		Initial calcium conc. 150 ppm	
ppm sodium silicate added	ppm Ca remaining in soln	ppm sodium silicate added	ppm Ca remaining in soln	ppm sodium silicate added	ppm Ca remaining in soln
0	21	0	52	130	141
0	21	42	50	244	145
17	19	51	49	260	135
35	20	80	52	487	121
69	21	153	47	520	120
130	20	163	51	975	75
195	20	305	42	975	56
260	21	325	43	1300	32
261	21	458	27	1462	36
390	18	489	42	1950	15
520	15	610	25	1955	8
1040	5	650	29	2924	9
1582	0	763	24	2927	0
2079	0	974	15		
2938	0	1017	12		
		1526	8		
ppm sodium soap added	ppm Ca remaining in soln	ppm sodium soap added	ppm Ca remaining in soln	ppm sodium soap added	ppm Ca remaining in soln
43	49	43	49	141	141
83	46	83	46	142	130
167	41	167	41	256	133
334	31	334	31	281	133
334	30	334	30	283	123
501	19	501	19	502	118
502	19	502	19	563	115
668	10	668	10	567	107
669	9	669	9	1002	87
835	5	835	5	1062	75
1001	9	1001	9	1065	83
1002	3	1002	3	1417	59
1334	0	1334	0	1504	52
				1980	16
				2003	21
				2131	15
				2502	5
				3193	14

APPENDIX F-2

SEQUESTERING PROPERTIES OF SODIUM SILICATE

Raw data: Independent competition for calcium ions by soap and sodium silicate under different temperatures and pH conditions.

	Initial calcium conc. 50 ppm		Initial calcium conc. 150 ppm	
Temperature	Temperature	ppm calcium remaining in solution	Temperature	ppm calcium remaining in solution
Calcium silicate	23.0	43.0	23.0	70.0
	35.0	47.0	35.0	74.0
	45.0	48.0	45.0	76.0
	55.0	49.0	55.0	83.0
Calcium soap	23.0	30.0	23.0	78.0
	35.0	30.0	35.0	79.0
	45.0	29.0	45.0	78.0
	55.0	29.0	50.0	75.0
			55.0	76.0
pH		ppm calcium remaining in solution		ppm calcium remaining in solution
	pH		pH	
Calcium silicate	8.1	49.0	8.5	124.0
	9.1	48.0	9.1	123.0
	10.0	43.0	9.1	97.0
	10.2	45.0	10.0	70.0
	10.2	41.5	10.1	77.0
	11.1	44.0	10.7	55.9
	12.0	36.0	11.1	61.0
			11.3	56.0
			12.0	25.0
Calcium soap	7.8	32.0	7.9	89.0
	9.1	32.0	8.9	100.0
	10.0	25.0	9.1	84.0
	10.0	25.0	10.0	83.0
	10.0	30.0	10.0	80.0
	11.0	30.0	10.0	82.0
	11.3	16.0	11.1	81.0
	11.9	25.0	12.0	63.6
	11.9	17.4	12.0	65.0

APPENDIX F-3

SEQUESTERING PROPERTIES OF SODIUM SILICATE

Competition for calcium by sodium silicate and soap, when all three species are present

	Experiment 4.1: 380 ppm Soap, 50 ppm Ca								Experiment 4.2: 380 ppm Soap, 100 ppm Ca								Exp 4.3: 200 ppm Soap, 100 ppm Ca					
Initial concentrations																						
Sodium soap (ppm)	378	378	378	378	378	378	378	378	378	378	378	378	378	378	378	378	200	200	200	200	200	200
Sod. Silicate (ppm)	0	104	208	416	832	1663	3327	4972	0	104	208	416	832	1663	3327	4972	0	280	560	1114	2233	4472
Ca (ppm)	50	50	50	50	50	50	50	50	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Results																						
Pet. ether extract (ppm)	80	85	130	159	183	139	152	134	86	93	91	105	113	110	137	120	17	31	44	81	71	89
	83	81	118	146	161	158	105	144	75	88	96	96	106	105	137	146	26	38	40	51	103	61
	86	111	108	135	164	134											24	47	52	62	94	64
																	15	37	43	81	113	56
																	28	50	39	75	60	
mean pet. ether extract	83	92	119	147	169	144	129	139	81	91	94	101	110	108	137	133	21	36	46	63	91	66
standard error	1.7	9.4	6.4	6.9	6.9	7.3	23.5	5.0	5.5	2.5	2.5	4.5	3.5	2.5		13.0	2.7	3.3	2.2	8.3	8.0	5.9
Residual soap (1)	89	101	139	185	227	180	154	172	86	98	102	112	125	122	168	162	26	39	48	65	99	69
Ca, ppm (2)	20	19	17	16	16	16	19	24	75	74	75	64	42	27	38	56	96	92	78	39	50	66
Na silicate, ppm (2)	0	64	159	278	574	1300	3337	5122	0	86	179	270	393	854	2686	4841	37	305	447	514	862	3771

Notes:

- (1) The residual soap was calculated from the mean petroleum ether extract using the calibration curve, Figure 4.9.
 - (2) The residual calcium and sodium silicate was determined by ICP analysis, as detailed in Appendix G.
- All quantities are expressed as parts per million (ppm).

APPENDIX G

Analysis of residual calcium and silica by inductively coupled plasma spectroscopy (ICP)

The following raw data are presented:

1. Method of analysis.
2. Sample copy of analysis printout.

APPENDIX G-1

Method of analysis – ICP determination of Ca and Si.

1. The analysis was performed on a Jobin Yvon JY24 spectrophotometer, using J-YES version 4 software to analyse and display the results.
2. Calibration solutions were made up using the commercial products as specified in appendix A. The assay figure as supplied was used to calculate the concentrations. The following standard concentrations were made up:

Name	Si conc. ppm	Ca conc. ppm
STDLOW	0	0
STD1	4.8	1
STD2	9.6	2
STDHIGH	24	5

3. The calibration curve was constructed by the machine's software, and was used to calculate the concentration of calcium and silicon in solution.
4. Using the appropriate dilution and molecular weight factors, the final concentrations in ppm of calcium [Ca] and sodium silicate [$\text{Na}_2\text{O}:(\text{SiO}_2)_{3.3}$] were calculated. These are reported in appendix F.

APPENDIX G-2

Zero Order has been found at step number :

16361.0

24/8/2000.

-----11:20:54 1/ 4/80 -----

Results for STDLOW # Measures :5 (R)

EL SIGNAL/sigma EL SIGNAL/sigma

Si 2313.0/ 1.4% Ca 2703.1/ 13%

-----11:24:25 1/ 4/80 -----

Results for STD1 # Measures :5 (R)

EL SIGNAL/sigma EL SIGNAL/sigma

Si 3841.2/ 2.0% Ca 27002/ 4.6%

-----11:28:03 1/ 4/80 -----

Results for STD2 # Measures :5 (R)

EL SIGNAL/sigma EL SIGNAL/sigma

Si 5392.9/ 2.2% Ca 54597/ 2.2%

-----11:31:32 1/ 4/80 -----

Results for STDHIGH # Measures :5 (R)

EL SIGNAL/sigma EL SIGNAL/sigma

Si 9807.1/ 2.8% Ca 143490/ 2.7%

	Standard	Intensity	Concentration	Calc.Conc.	% Error	Validity
Si 251.432						
0	STDLOW	2313.0	0.00000	-0.02390	0.0	1
1	STD1	3841.2	4.6000	4.6262	0.55	1
2	STD2	5392.9	9.6000	9.7507	1.6	1
3	STDHIGH	9807.1	24.000	23.760	-1.0	1

Intercept Slope 2nd Order SD Correl.
-7.36491 0.003174 0.000000 0.164742 0.999929

	Standard	Intensity	Concentration	Calc.Conc.	% Error	Validity
Ca 393.366						
0	STDLOW	2703.1	0.00000	0.00061	0.0	1
1	STD1	27002	1.0000	0.92954	-7.0	1
2	STD2	54597	2.0000	1.9845	-0.78	1
3	STDHIGH	143490	5.0000	3.3629	7.7	1

Intercept Slope 2nd Order SD Correl.
-0.102728 0.000038 0.000000 0.224978 0.999293

----- 11:40:40 1/ 4/80 ----- Method: JPAUCK

Sample III A- 1

EL	Wave	Concentration	SD	RSD
Si	251.432	0.539 PPM	0.051	9.4
Ca	393.366	3.82 PPM	0.127	3.3

APPENDIX G-2

Intercept	Slope	2nd Order	SD	Correl.
-0.102728	0.000038	0.000000	0.224978	0.999283

----- 11:40:40 1/ 4/80 ----- Method: JPAUCK

Sample III A- - 1

EL	Wave	Concentration	SD	RSD
Si	251.432	0.539 PPM	0.051	9.4
Ca	393.366	3.82 PPM	0.127	3.3

----- 11:44:04 1/ 4/80 ----- Method: JPAUCK

Sample III B- - 1

EL	Wave	Concentration	SD	RSD
Si	251.432	2.18 PPM	0.105	4.8
Ca	393.366	1.83 PPM	0.069	3.8

----- 11:47:39 1/ 4/80 ----- Method: JPAUCK

Sample III C - - 1

EL	Wave	Concentration	SD	RSD
Si	251.432	3.20 PPM	0.288	9.0
Ca	393.366	1.55 PPM	0.026	1.7

----- 11:51:12 1/ 4/80 ----- Method: JPAUCK

Sample III D- - 1

EL	Wave	Concentration	SD	RSD
Si	251.432	3.68 PPM	0.399	11
Ca	393.366	0.787 PPM	0.028	3.5

----- 11:54:37 1/ 4/80 ----- Method: JPAUCK

Sample III E- - 1

EL	Wave	Concentration	SD	RSD
Si	251.432	10.8 PPM	0.392	3.6
Ca	393.366	0.524 PPM	0.022	4.1

----- 11:57:38 1/ 4/80 ----- Method: JPAUCK

Sample III G- - 1

EL	Wave	Concentration	SD	RSD
Si	251.432	18.0 PPM	0.872	4.8
Ca	393.366	0.604 PPM	0.043	7.1

APPENDIX G-2

Zero Order has been found at step number :
-----11:20:54 1/ 4/80 -----

16361.0

24/8/2000.

Results for STDLOW # Measures :5 (R)

EL SIGNAL/sigma EL SIGNAL/sigma

Si 2313.0/ 1.4% Ca 2703.1/ 13%

-----11:24:25 1/ 4/80 -----

Results for STD1 # Measures :5 (R)

EL SIGNAL/sigma EL SIGNAL/sigma

Si 3841.2/ 2.0% Ca 27002/ 4.6%

-----11:28:03 1/ 4/80 -----

Results for STD2 # Measures :5 (R)

EL SIGNAL/sigma EL SIGNAL/sigma

Si 5392.9/ 2.2% Ca 54597/ 2.2%

-----11:31:32 1/ 4/80 -----

Results for STDHIGH # Measures :5 (R)

EL SIGNAL/sigma EL SIGNAL/sigma

Si 9807.1/ 2.8% Ca 143490/ 2.7%

	Standard	Intensity	Concentration	Calc.Conc.	% Error	Validity
Si 251.432						
0	STDLOW	2313.0	0.00000	-0.02390	0.0	1
1	STD1	3841.2	4.8000	4.8262	0.55	1
2	STD2	5392.9	9.6000	9.7507	1.6	1
3	STDHIGH	9807.1	24.000	23.760	-1.0	1

Intercept Slope 2nd Order SD Correl.
-7.36491 0.003174 0.000000 0.164742 0.999929

	Standard	Intensity	Concentration	Calc.Conc.	% Error	Validity
Ca 393.366						
0	STDLOW	2703.1	0.00000	0.00061	0.0	1
1	STD1	27002	1.0000	0.92954	-7.0	1
2	STD2	54597	2.0000	1.9845	-0.78	1
3	STDHIGH	143490	5.0000	5.3829	7.7	1

Intercept Slope 2nd Order SD Correl.
-0.102728 0.000038 0.000000 0.224978 0.999283

----- 11:40:40 1/ 4/80 ----- Method: JPAUCK

Sample III A- - 1

EL	Wave	Concentration	SD	RSD
Si	251.432	0.539 PPM	0.051	9.4
Ca	393.366	3.82 PPM	0.127	3.3

APPENDIX G-2

Intercept	Slope	2nd Order	SD	Correl.
-0.102728	0.000038	0.000000	0.224978	0.999283

----- 11:40:40 1/ 4/80 ----- Method: JPAUCK

Sample III A- - 1

EL	Wave	Concentration	SD	RSD
Si	251.432	0.539 PPM	0.051	9.4
Ca	393.366	3.82 PPM	0.127	3.3

----- 11:44:04 1/ 4/80 ----- Method: JPAUCK

Sample III B- - 1

EL	Wave	Concentration	SD	RSD
Si	251.432	2.18 PPM	0.105	4.8
Ca	393.366	1.83 PPM	0.069	3.8

----- 11:47:39 1/ 4/80 ----- Method: JPAUCK

Sample III C - - 1

EL	Wave	Concentration	SD	RSD
Si	251.432	3.20 PPM	0.288	9.0
Ca	393.366	1.55 PPM	0.026	1.7

----- 11:51:12 1/ 4/80 ----- Method: JPAUCK

Sample III D- - 1

EL	Wave	Concentration	SD	RSD
Si	251.432	3.68 PPM	0.399	11
Ca	393.366	0.787 PPM	0.028	3.5

----- 11:54:37 1/ 4/80 ----- Method: JPAUCK

Sample III E- - 1

EL	Wave	Concentration	SD	RSD
Si	251.432	10.8 PPM	0.392	3.6
Ca	393.366	0.524 PPM	0.022	4.1

----- 11:57:38 1/ 4/80 ----- Method: JPAUCK

Sample III G- - 1

EL	Wave	Concentration	SD	RSD
Si	251.432	18.0 PPM	0.872	4.8
Ca	393.366	0.604 PPM	0.043	7.1

APPENDIX G-2

Zero Order has been found at step number :
-----11:20:54 1/ 4/80 -----

16361.0 24/8/2000.

Results for STDLOW # Measures :5 (R)

EL SIGNAL/sigma EL SIGNAL/sigma
Si 2313.0/ 1.4% Ca 2703.1/ 13%

-----11:24:25 1/ 4/80 -----

Results for STD1 # Measures :5 (R)

EL SIGNAL/sigma EL SIGNAL/sigma
Si 3841.2/ 2.0% Ca 27002/ 4.6%

-----11:28:03 1/ 4/80 -----

Results for STD2 # Measures :5 (R)

EL SIGNAL/sigma EL SIGNAL/sigma
Si 5392.9/ 2.2% Ca 54597/ 2.2%

-----11:31:32 1/ 4/80 -----

Results for STDHIGH # Measures :5 (R)

EL SIGNAL/sigma EL SIGNAL/sigma
Si 9807.1/ 2.8% Ca 143490/ 2.7%

	Standard	Intensity	Concentration	Calc.Conc.	% Error	Validity
Si 251.432						
0	STDLOW	2313.0	0.00000	-0.02390	0.0	1
1	STD1	3841.2	4.8000	4.8262	0.55	1
2	STD2	5392.9	9.6000	9.7507	1.6	1
3	STDHIGH	9807.1	24.000	23.760	-1.0	1

Intercept Slope 2nd Order SD Correl.
-7.36491 0.003174 0.000000 0.164742 0.999929

	Standard	Intensity	Concentration	Calc.Conc.	% Error	Validity
Ca 393.366						
0	STDLOW	2703.1	0.00000	0.00061	0.0	1
1	STD1	27002	1.0000	0.92954	-7.0	1
2	STD2	54597	2.0000	1.9845	-0.78	1
3	STDHIGH	143490	5.0000	5.3829	7.7	1

Intercept Slope 2nd Order SD Correl.
-0.102728 0.000038 0.000000 0.224978 0.999283

----- 11:40:40 1/ 4/80 ----- Method: JPAUCK

Sample III A- - 1

EL	Wave	Concentration	SD	RSD
Si	251.432	0.539 PPM	0.051	9.4
Ca	393.366	3.82 PPM	0.127	3.3

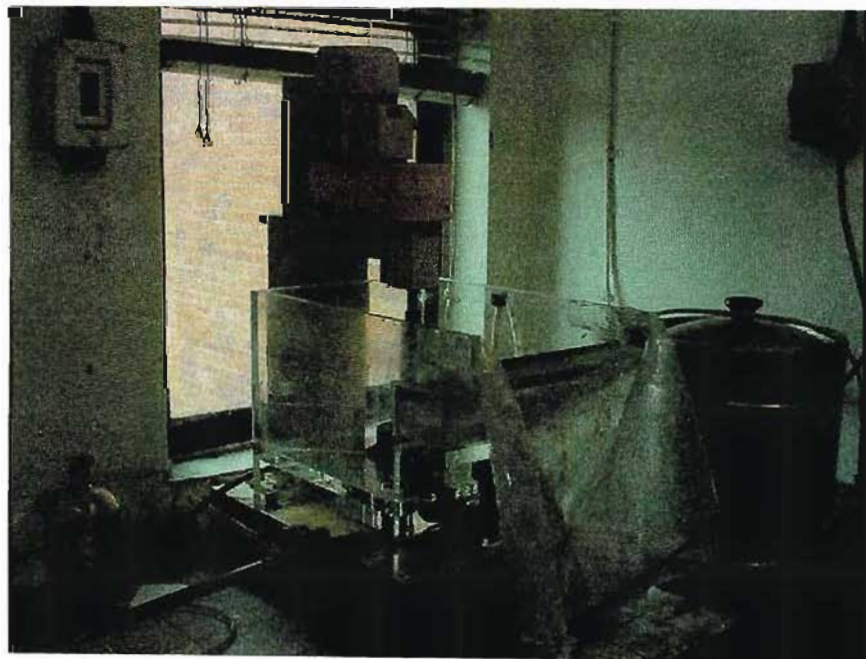
APPENDIX G-2

Intercept	Slope	2nd Order	SD	Correl.
-0.102728	0.000038	0.000000	0.224978	0.999283
----- 11:40:40 1/ 4/80 ----- Method: JPAUCK				
Sample III A-	-			1
EL	Wave	Concentration	SD	RSD
Si	251.432	0.539 PPM	0.051	9.4
Ca	393.366	3.82 PPM	0.127	3.3
----- 11:44:04 1/ 4/80 ----- Method: JPAUCK				
Sample III B-	-			1
EL	Wave	Concentration	SD	RSD
Si	251.432	2.18 PPM	0.105	4.8
Ca	393.366	1.83 PPM	0.069	3.8
----- 11:47:39 1/ 4/80 ----- Method: JPAUCK				
Sample III C	-			1
EL	Wave	Concentration	SD	RSD
Si	251.432	3.20 PPM	0.288	9.0
Ca	393.366	1.55 PPM	0.026	1.7
----- 11:51:12 1/ 4/80 ----- Method: JPAUCK				
Sample III D-	-			1
EL	Wave	Concentration	SD	RSD
Si	251.432	3.68 PPM	0.399	11
Ca	393.366	0.787 PPM	0.028	3.5
----- 11:54:37 1/ 4/80 ----- Method: JPAUCK				
Sample III E-	-			1
EL	Wave	Concentration	SD	RSD
Si	251.432	10.8 PPM	0.392	3.6
Ca	393.366	0.524 PPM	0.022	4.1
----- 11:57:38 1/ 4/80 ----- Method: JPAUCK				
Sample III G-	-			1
EL	Wave	Concentration	SD	RSD
Si	251.432	18.0 PPM	0.872	4.8
Ca	393.366	0.604 PPM	0.043	7.1

APPENDIX H



Photograph of 25 litre Lamort laboratory pulper.



Photograph of a 20 litre laboratory flotation cell.

APPENDIX I

Laboratory deinking experiments

The raw data of the following deinking experiments are presented:

1. Brightness of unprinted paper, after pulping and after flotation.
2. Statistical analysis (ANOVA and T-test) of the above data. This analysis was performed using a Microsoft Excel® spreadsheet function.
3. Lightness and brightness of unprinted paper and pulp after flotation.
4. Yellowness of unprinted paper, after pulping and after flotation.

APPENDIX I-1

RESULTS OF LABORATORY DEINKING EXPERIMENTS

Raw data: Brightness of unprinted paper (edge brightness), brightness after pulping and after flotation, under various pulping conditions.

Experiment:	Exp 5.1: Normal pulper water			Exp 5.2: Fresh process water			Exp 5.3: Water+200 ppm soap			Exp 5.4: Water+100 ppm calcium			Exp 5.5: Water+calcium, no silicate		
Measurement	Edge bright-ness	Bright-ness after pulping	Bright-ness after flotation	Edge bright-ness	Bright-ness after pulping	Bright-ness after flotation	Edge bright-ness	Bright-ness after pulping	Bright-ness after flotation	Edge bright-ness	Bright-ness after pulping	Bright-ness after flotation	Edge bright-ness	Bright-ness after pulping	Bright-ness after flotation
Top side brightness	55.0	47.5	52.8	53.7	47.0	48.3	56.7	48.0	52.3	55.9	42.4	49.8	55.0	40.5	48.5
	54.6	47.8	52.8	55.2	53.7	54.2	55.4	49.1	52.9	55.3	47.1	51.9	53.3	40.4	46.0
	55.6	47.2	51.2	56.0	48.4	51.4	54.4	50.9	52.5	54.7	46.3	52.0	52.3	43.9	50.0
	54.4	46.5	50.0	56.1	45.1	50.1	56.9	51.1	53.7	55.9	46.9	52.1	54.9	46.1	50.8
	55.6	47.1	50.7	55.4	47.0	49.9	55.9	49.3	52.9	55.0	47.6	51.8	54.4	43.4	48.5
				55.8	53.2	54.3	55.5	51.0	54.0				54.2	44.7	49.0
				53.7	48.7	51.5									
Mean brightness	55.0	47.2	51.5	55.1	49.0	51.4	55.8	49.9	53.1	55.4	46.1	51.5	54.0	43.2	48.8
Standard deviation	0.55	0.52	1.26	1.02	3.22	2.23	0.91	1.26	0.64	0.52	2.09	0.99	1.06	2.30	1.66
Standard error	0.25	0.23	0.56	0.39	1.22	0.84	0.37	0.52	0.26	0.23	0.93	0.44	0.43	0.94	0.68

APPENDIX I-2

ANALYSIS OF VARIANCE

ANOVA: edge brightness

5.1	5.2	5.3	5.4	5.5
55.0	53.7	56.7	55.9	55.0
54.6	55.2	55.4	55.3	53.3
55.6	56.0	54.4	54.7	52.3
54.4	56.1	56.9	55.9	54.9
55.6	55.4	55.9	55.0	54.4
	55.8	55.5		54.2
	53.7			

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
5.1	5	275.197	55.0394	0.30341
5.2	7	385.86	55.1229	1.04366
5.3	6	334.72	55.7867	0.83183
5.4	5	276.789	55.3578	0.27273
5.5	6	324.048	54.008	1.12868

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	10.2811	4	2.57029	3.3582	0.0256	4.21846
Within Groups	18.3691	24	0.76538			
Total	28.6502	28				

ANOVA: final brightness of 5.1, 5.2 and 5.4

5.1	5.2	5.4
52.8	48.3	49.8
52.8	54.2	51.9
51.2	51.4	52.0
50.0	50.1	52.1
50.7	49.9	51.8
	54.3	
	51.5	

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance
5.1	5	257.5	51.5	1.58105
5.2	7	359.66	51.38	4.95377
5.4	5	257.55	51.51	0.98375

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.06459	2	0.03229	0.01131	0.98876	3.73889
Within Groups	39.9818	14	2.85584			
Total	40.0464	16				

- Conclusions:** 1) There is no significant difference between the edge brightnesses of the differene experiments.
 2) The final brightness of experiments 5.1, 5.2 and 5.4 do not differ significantly.

Notes: This statistical analysis was performed using Microsoft Exel statistics functions.

APPENDIX I-2

T- tests on final brightness

5.1	5.2	5.3	5.4	5.5
52.8	48.3	52.3	49.8	48.5
52.8	54.2	52.9	51.9	48.0
51.2	51.4	52.5	52.0	50.0
50.0	50.1	53.7	52.1	50.8
50.7	49.9	52.9	51.8	48.5
	54.3	54.0		49.0
	51.5			

t-Test: Two-Sample Assuming Unequal Variances t-Test: Two-Sample Assuming Unequal Variances t-Test: Two-Sample Assuming Unequal Variances

	5.1	5.3
Mean	51.5	53.0583
Variance	1.58105	0.41362
Observations	5	6
Hypothesized Mean Difference	0	
df	6	
t Stat	-2.511	
P(T<=t) one-tail	0.02292	
t Critical one-tail	1.94318	
P(T<=t) two-tail	0.04584	
t Critical two-tail	2.44691	

	5.2	5.3
Mean	51.38	53.0583
Variance	4.95377	0.41362
Observations	7	6
Hypothesized Mean Difference	0	
df	7	
t Stat	-1.9045	
P(T<=t) one-tail	0.04928	
t Critical one-tail	1.89458	
P(T<=t) two-tail	0.09856	
t Critical two-tail	2.36462	

	5.4	5.3
Mean	51.51	53.0583
Variance	0.98375	0.41362
Observations	5	6
Hypothesized Mean Difference	0	
df	7	
t Stat	-3.0039	
P(T<=t) one-tail	0.00992	
t Critical one-tail	1.89458	
P(T<=t) two-tail	0.01983	
t Critical two-tail	2.36462	

t-Test: Two-Sample Assuming Unequal Variances

	5.1	5.5
Mean	51.5	48.7933
Variance	1.58105	2.75251
Observations	5	6
Hypothesized Mean Difference	0	
df	9	
t Stat	3.07464	
P(T<=t) one-tail	0.00863	
t Critical one-tail	1.83311	
P(T<=t) two-tail	0.01325	
t Critical two-tail	2.26216	

- Conclusions:** 1) The final brightness of experiment 5.3 is significantly higher than that of experiments 5.1, 5.2 and 5.4., with 95% confidence.
2) The final brightness of experiment 5.5 is significantly lower than experiment 5.1.

Notes: This statistical analysis was performed using Microsoft Excel statistics functions.

APPENDIX I-3

Results of laboratory deinking experiments

Raw data: Lightness (L*) and brightness of unprinted paper and after flotation.

Experiment	Unprinted edge		Final, after flotation	
	L*	Brightness	L*	Brightness
5.1	80.0	55.0	81.7	52.8
	79.9	54.6	81.4	52.8
	80.7	55.6	80.3	51.2
	79.8	54.4	79.7	50.0
	80.5	55.6	79.7	50.7
5.2	81.3	56.0	81.1	51.4
	81.7	56.1	80.2	50.1
	81.7	55.4	79.9	49.9
	79.2	53.7	78.4	48.3
	79.3	53.7	81.0	51.5
5.3			81.5	52.3
	80.6	55.4	82.0	52.9
			81.6	52.5
	81.6	56.9		
	81.2	55.9	82.2	52.9
5.4	80.7	55.5	82.3	54.0
	80.4	55.3	81.1	51.9
	80.4	54.7	81.1	52.0
			81.4	52.1
	80.7	55.0	81.0	51.8
5.5			78.6	48.5
	79.9	53.3	77.2	45.9
	79.3	52.3	79.6	50.0
			79.8	50.8
	80.0	54.4	78.8	48.5
	79.5	54.2	78.8	49.0

APPENDIX I-4

RESULTS OF LABORATORY DEINKING EXPERIMENTS

Raw data: Yellowness (b^* value) of unprinted paper (edge b^*), after pulping and after flotation, under various pulping conditions.

Experiment	Exp 5.1: Normal pulper water			Exp 5.2: Fresh process water			Exp 5.3: Water+200 ppm soap			Exp 5.4: Water+100 ppm calcium			Exp 5.5: Water+calcium, no silicate		
Measurements	Edge b^*	b^* before flotation	b^* after flotation	Edge b^*	b^* before flotation	b^* after flotation	Edge b^*	b^* before flotation	b^* after flotation	Edge b^*	b^* before flotation	b^* after flotation	Edge b^*	b^* before flotation	b^* after flotation
Top side b^*	4.43	5.92	8.20	4.14	6.19	8.34	4.15	6.64	8.09	3.41	4.79	6.81	4.56	5.41	7.12
	3.61	5.77	7.42	4.72	6.19	8.02	3.67	6.26	8.45	3.86	6.45	8.08	4.45	6.46	7.46
	3.84	5.97	7.42	4.15	6.49	7.84	3.89	6.98	8.17	4.23	6.31	7.74	3.56	5.52	7.32
	3.64	6.02	7.40	3.56	8.15	9.40	4.24	5.41	6.46		6.07	8.23	3.79	5.46	6.85
	3.41	5.07	6.65	3.46	5.82	6.91	3.65	7.01	8.83		6.42	7.98		6.17	7.48
					6.67	8.21		6.23	7.74					5.86	6.77
Mean	3.79	5.75	7.42	4.00	6.59	8.12	3.92	6.42	7.96	3.83	6.01	7.77	4.09	5.81	7.17
Standard deviation	0.39	0.39	0.55	0.51	0.82	0.80	0.27	0.60	0.82	0.41	0.70	0.57	0.49	0.43	0.30
Standard error	0.17	0.17	0.25	0.23	0.33	0.33	0.12	0.24	0.33	0.24	0.31	0.25	0.25	0.18	0.12

APPENDIX J

The EDS spectra displayed in the text are depicted again, in larger format for extra clarity.

APPENDIX J

EDS spectra of ink particles:

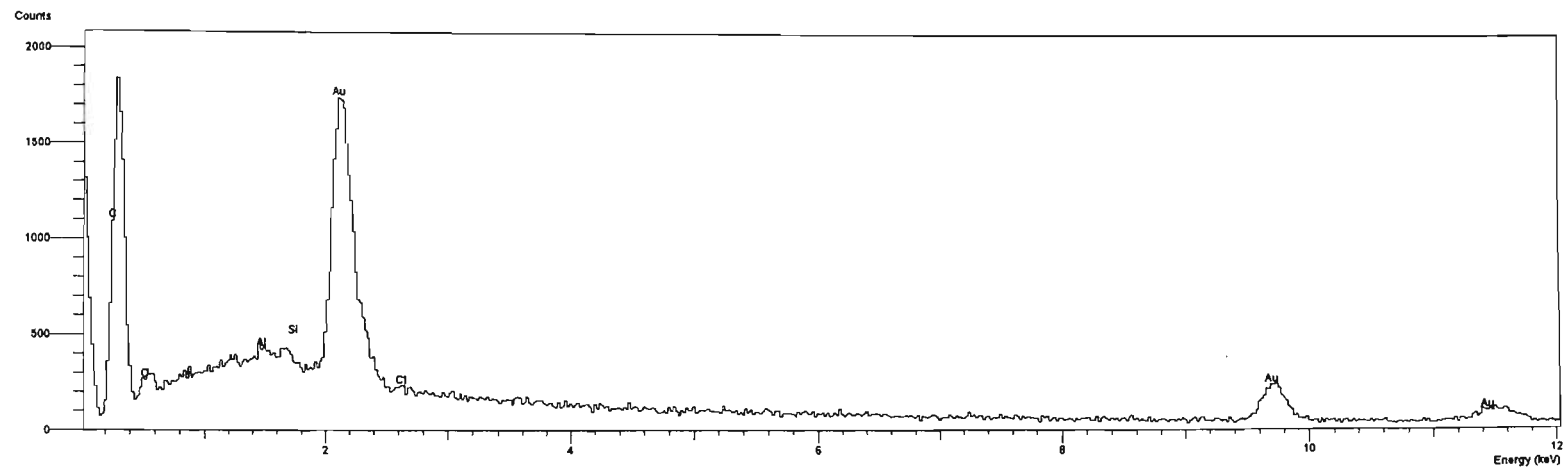


Figure 3.6: EDS spectrum of the ink particle depicted in figure 3.5. The surface is free of any metallic ions.

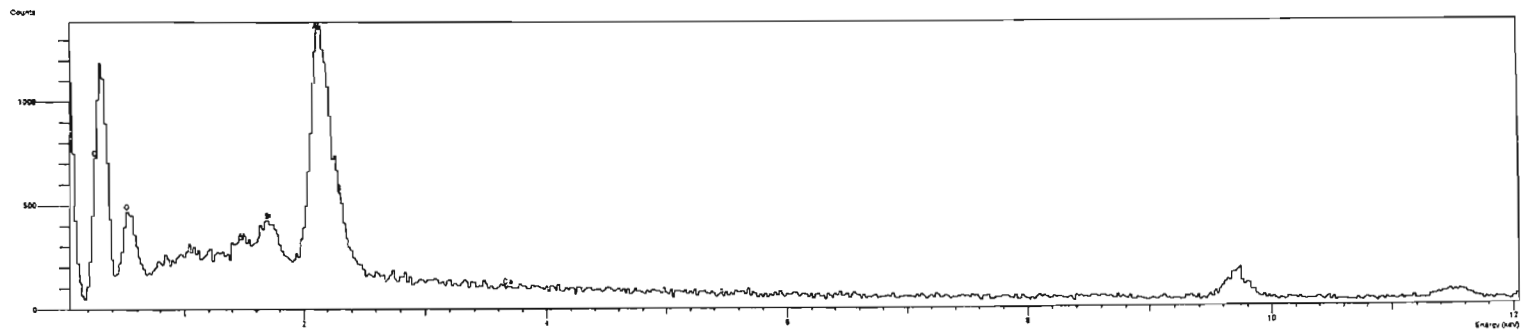


Figure 3.8: EDS spectrum of a smaller ink particle dispersed in sodium silicate solution, showing traces of silicon at 1.8keV.

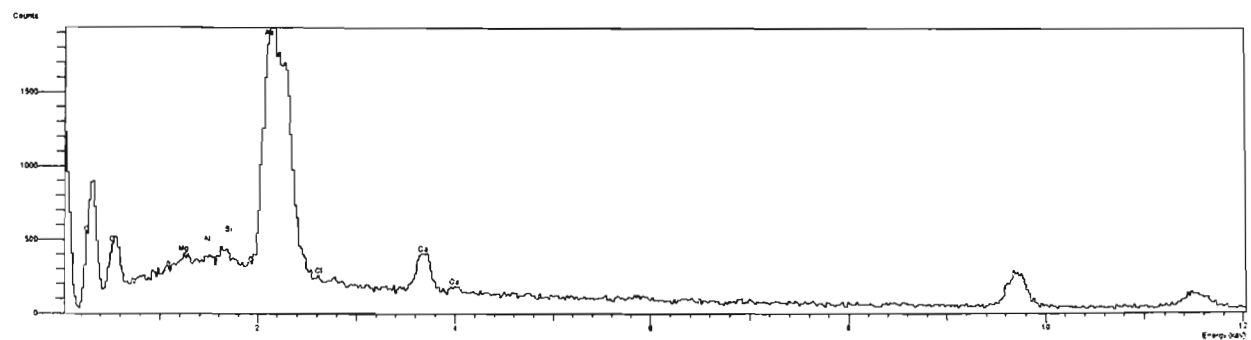


Figure 3.10: EDS spectrum of ink particle dispersed in NaOH and 80ppm Calcium. The presence of calcium on the surface is indicated at 3.7 keV.

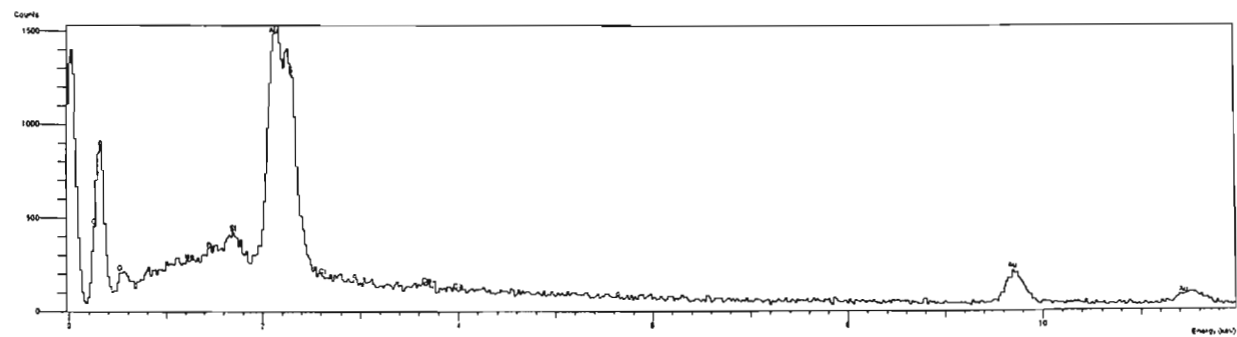


Figure 3.12: EDS spectrum of a small particle dispersed in sodium silicate/80 ppm calcium. The presence of silicon is indicated by the peak at 1.7 keV.

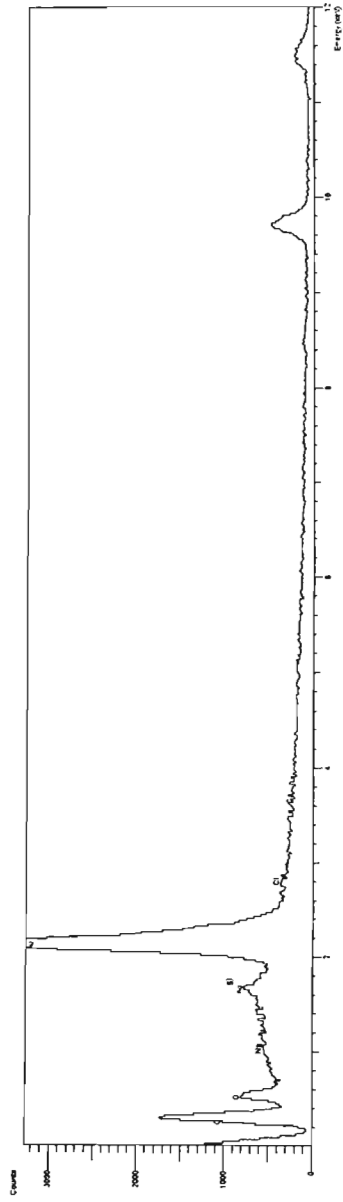


Figure 3.14: EDS spectrum of ink particles dispersed in sodium soap/silicate.

APPENDIX K

The SEM micrographs displayed in the text are depicted again, in larger format for extra clarity.

APPENDIX K

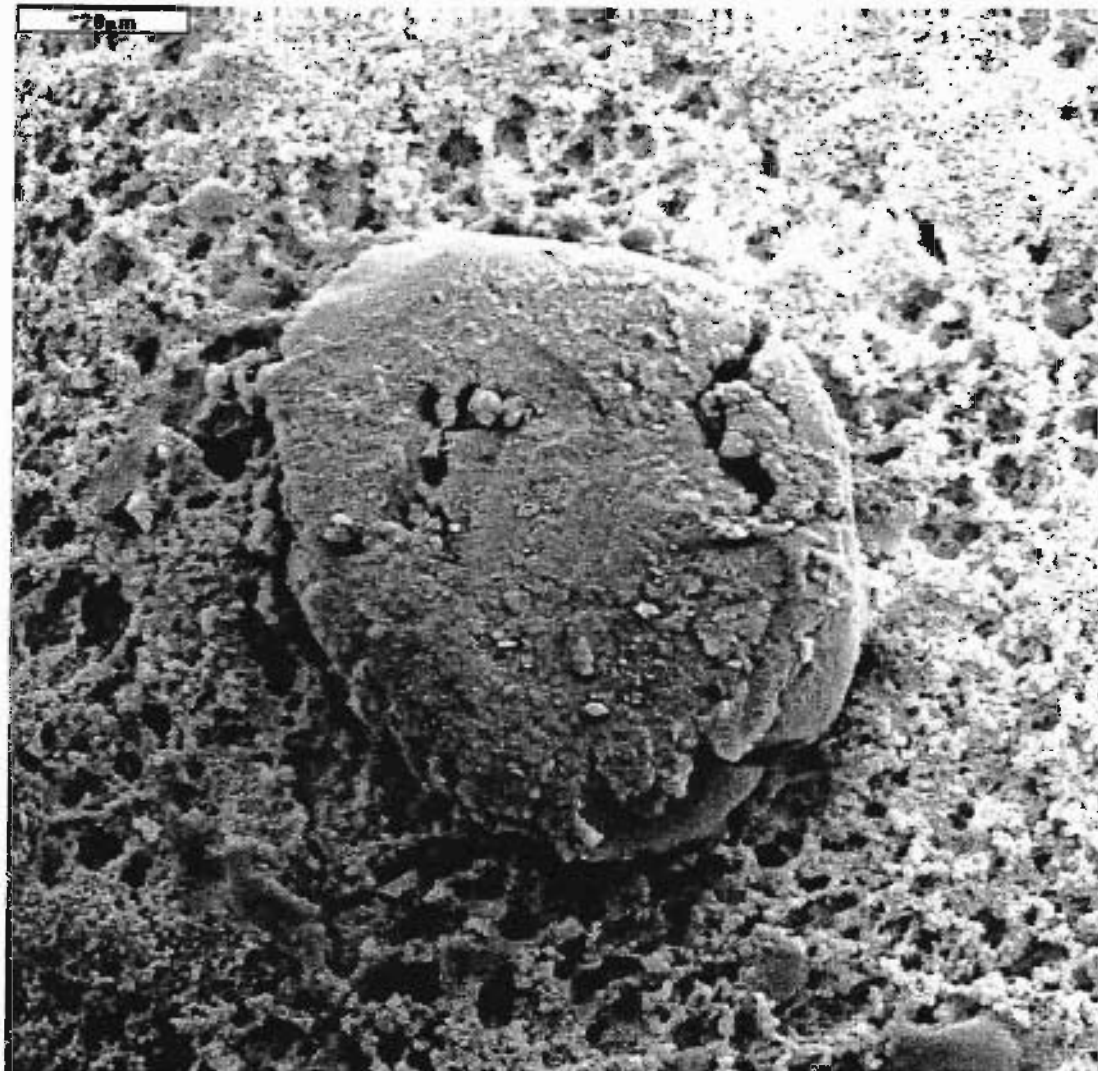


Figure 3.5: Ink particle dispersed in caustic soda only. The appearance suggests formation by agglomeration.

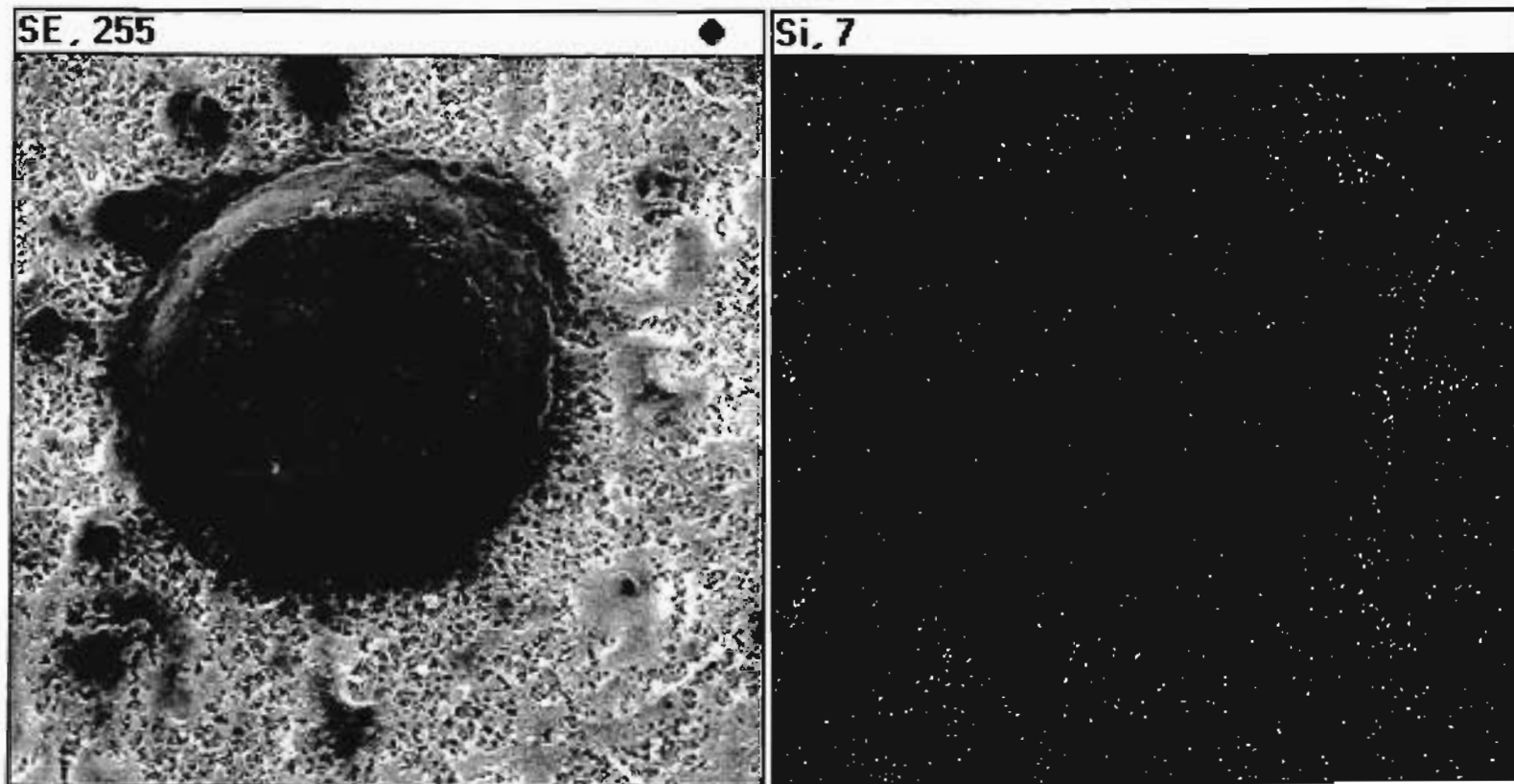


Figure 3.7: Ink dispersed in sodium silicate. The large particle is 250 microns in diameter. The small particles are 10 to 20 microns in diameter. The distribution of silicon is shown in the Si map on the right. The dense white areas correspond to higher concentrations of silicon.

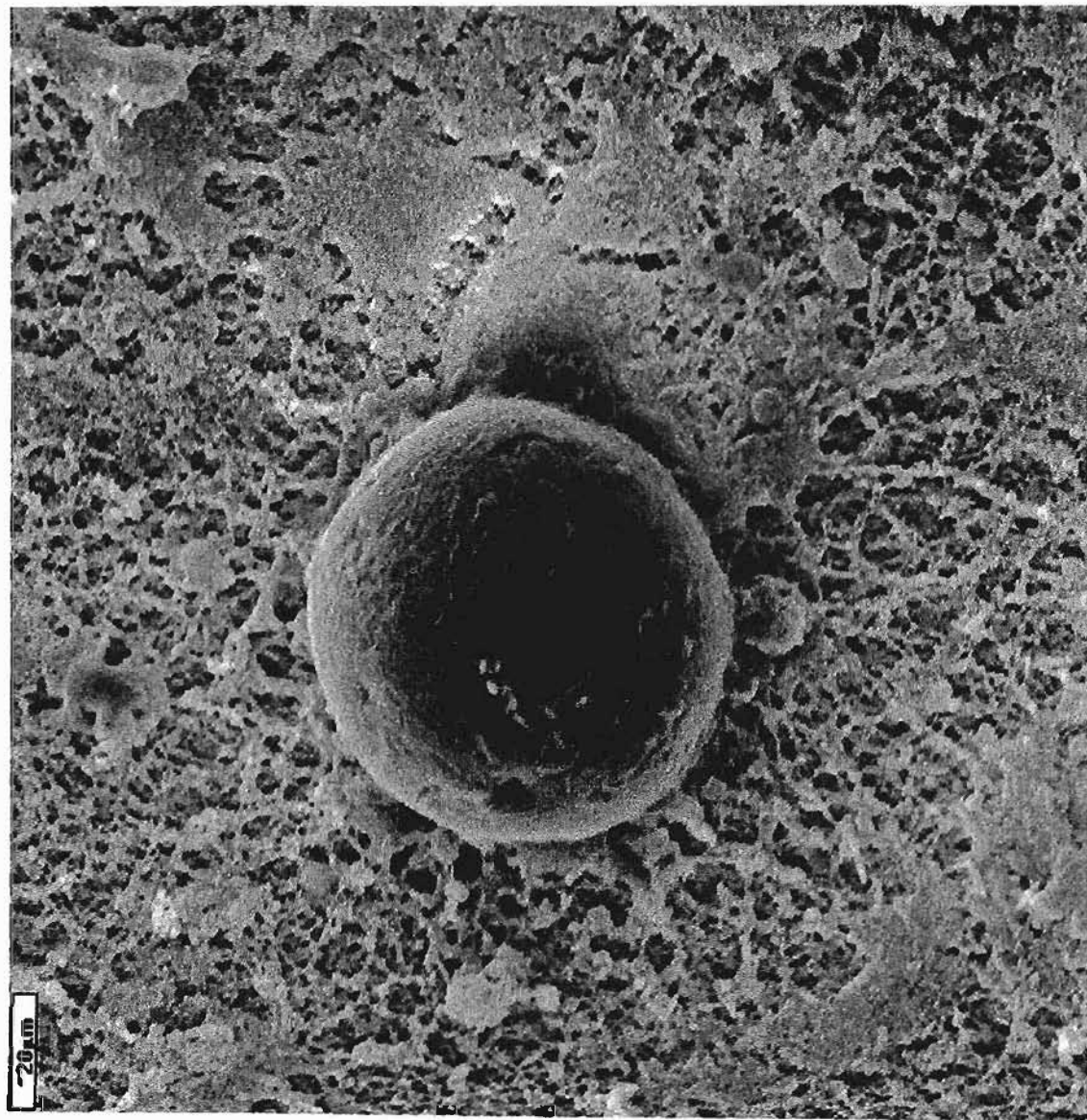


Figure 3.9: Ink particle dispersed in NaOH, in the presence of 80 ppm calcium

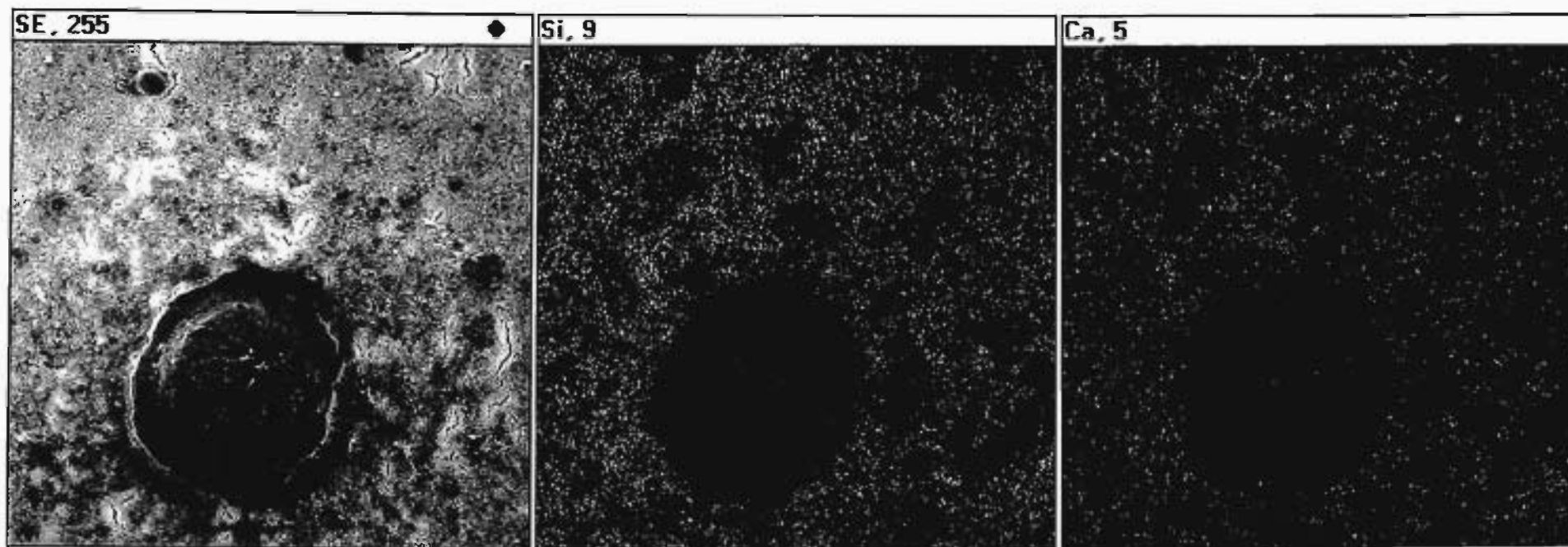


Figure 3.11: Ink dispersed in sodium silicate and 80ppm calcium. The large particles are 200 microns in diameter, the smaller particle is 35 microns in diameter. The Si and Ca element maps are shown centre and right respectively.

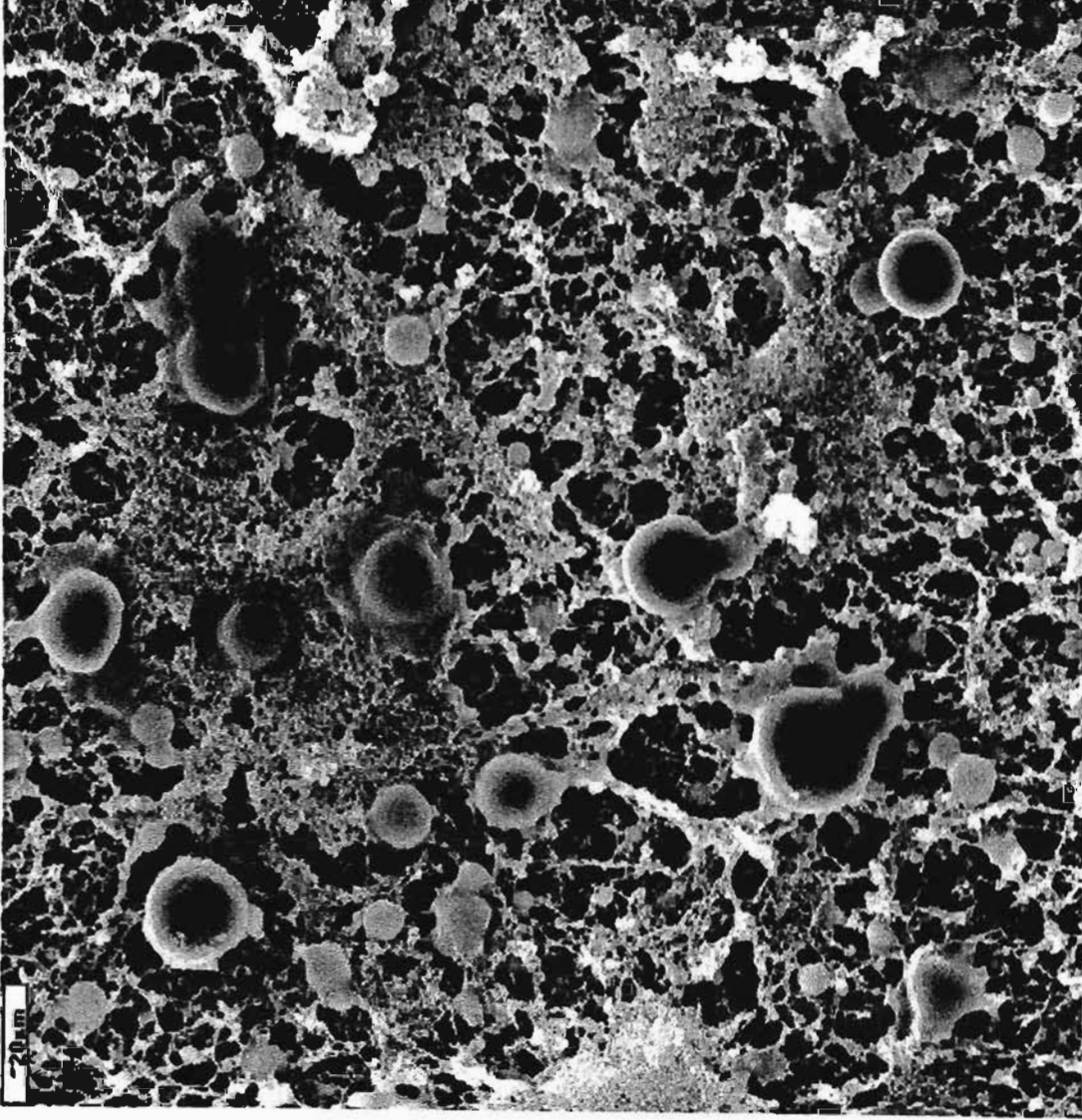


Figure 3.13: Ink dispersed in sodium soap/ sodium silicate.

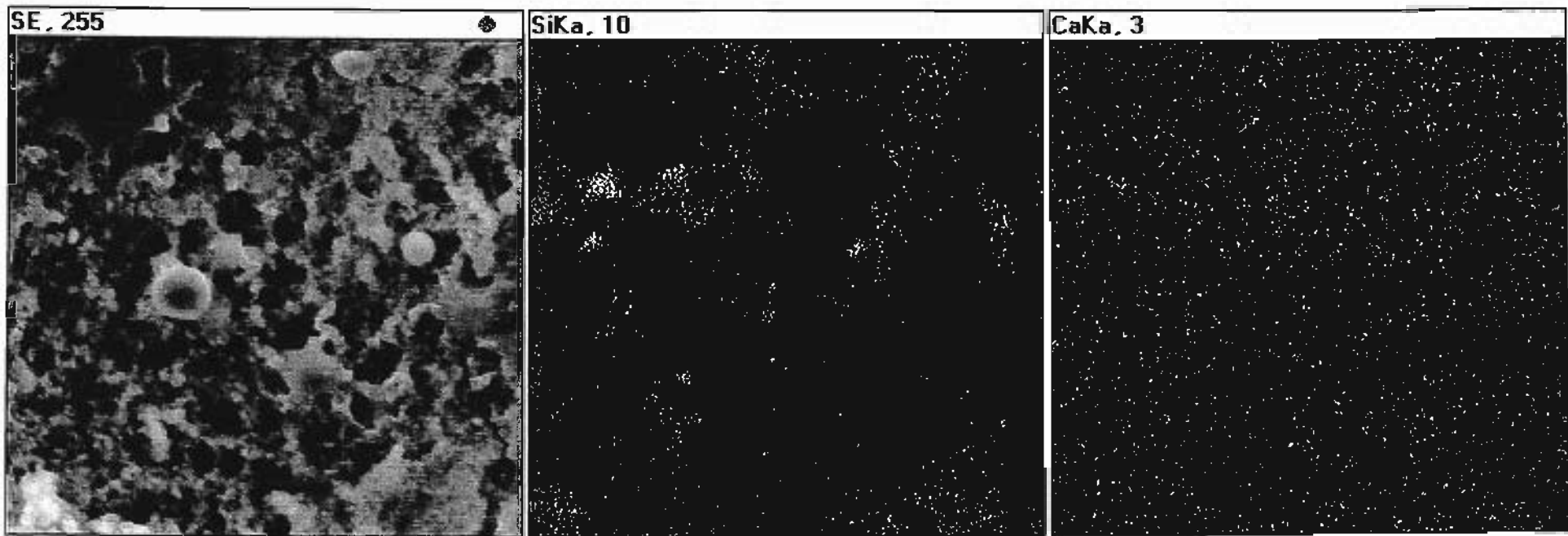


Figure 3.15:- Ink dispersed in calcium soap/sodium silicate. The Si and Ca element maps are shown centre and right respectively. This is a carbon coated image, which results in an inferior image, but superior element mapping.