INVESTIGATIONS ON ECO-FRIENDLY DE-INKING AGENTS FOR PAPER RECYCLING

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By

RADHAKRISHNAN P.V.

SCHOOL OF ENVIRONMENTAL STUDIES
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY

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DECLARATION

I here by declare that the work presented in this thesis is a bonafide record of original research work done by me under the supervision and guidance of Dr.A.Mohandas, Director, School of Environmental Studies, Cochin University of Science and Technology, Cochin and that it has not previously formed the basis for the award of any other Degree, Diploma, Associateship, Fellowship or other similar title or recognition.

Cochin

October,1999

Radhakrishnan, P.V.

CERTIFICATE

This is to certify that the Ph.D. thesis entitled **"Investigations on eco-friendly de-inking agents for paper recycling"** is an authentic record of original research work carried out by Mr. Radhakrishnan, P.V. under my supervision and guidance. I further certify that no part of this thesis has previously formed the basis for the award to the candidate of any Degree, Diploma, Associateship, Fellowship or other similar title of this or any other University or Society.

Dr. A. Mohandas,

Director,
School of Environmental Studies,
Cochin University of Science and Technology,
Cochin

Cochin
October, 1999

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CONTENTS

List of Tables.

Chapter: 2

Chapter: 3

Chapter: 4.

Chapter: 5.

List of figures

Chapter: 2

Chapter: 3

Chapter: 4

CHAPTER 1

INTRODUCTION

Paper is more than an industrial and commercial commodity. It is easily the cultural barometer of a nation, and effective growth and rising welfare of a nation cannot be achieved without a rise in the consumption of all kinds of cultural and industrial qualities of paper. Besides, paper being essential for liquidation of illiteracy, it is the most essential means of communicating thoughts of the peoples of the world and of developing better understanding between them. Process of modern democracy itself will be seriously hampered if paper is not available in sufficient quantities or without paper what would be there to safeguard human rights, the right to education, the right to culture, and the right of information. Paper has yet another important function, namely, as a packaging material par excellence. Packaging and wrapping are an index of standard of living. It is an established fact that for any increase in national income, there is more than proportionate increase in paper consumption (Shukla and Pandey, 1979).

Paper industry has had a chequrered career in the past two decades with shortage of raw materials and power, rising cost, control over prices, and pattern of production and increasing cost of chemicals, thus affecting the profitability of operation. When paper industry is faced with acute shortage of conventional fibrous raw materials, rising costs of imported pulp, and even the judiciary taking very serious view of environmental considerations the importance of recycling of waste paper to the maximum extent can not be undervalued (Kapoor *et al.*,1995). The future demand of raw materials can be met by proper recycling of waste paper. The waste paper is a cheap material having higher yield. Properly processed waste paper can be used for most of the paper grades including writing or printing and light shade grades.

Additionally, the use of waste paper is a better utilization of the waste product and can provide source of income to the poor (Kaul, 1998). Recycled fiber has been an important source of paper making fiber in the last 100 years (Barassi and Welsford, 1992). About 30% of global fiber consumption is derived from waste paper (Mc Kinney, 1988).

The use of the recovered paper in the manufacturing has increased during the last 10 years. In 1991, 37% recovered paper was used worldwide as a raw material in paper production (Stork, *et al.*, 1995). Recycled fiber has been used in the manufacture of various paper and board grades for many years. The use of recycled fiber worldwide is expected to reach 130 million tones by 2001. This means a rise from 33% recycled fiber used in 1988 to 41% in 2001 (Bhardwaj *et al.*, 1997). The growing importance of de-inking grades will be one of the key trends in the future waste paper industries. Even Japan, whose efforts to recycle paper have been strenuous, has been unable to get its national recovery rate of waste paper above 52% (Andersen,1997). As reported by Thomson (1999) recently, while Sweden has a recovery rate of 62% in 1997 India has achieved only 16.5%. Recycling will be the implicit fate of all paper produced in the future. Paper makers are focusing on recycling as an economic necessity (Heise *et al.*,1996).

Pulp and paper manufacture is one of the most important industries in India categorized as a 'Core Sector Industry' (Bajpai *et al.*,1993). The first paper mill was setup in India more than 100 years ago. Presently, about 380 paper mills are in existence in India with an installed capacity of about 4 million tons per annum as registered with the Government of India and this includes 340 units producing paper and paper board in private sector (Datt and Sundaram, 1997). Raw materials wise classification of 380 paper mills reveals that 28 mills are forest-based and 111 agro-based. The remaining 241 mills use rags, waste paper etc. as raw material. These mills constitute about 30% of the total installed capacity. Out of the 380 mills 135 numbers of large, medium and small paper mills are lying closed. (Rao, *et al.*, 1998).

Raw material availability at affordable cost is the prime concern and constraint for Indian Pulp and Paper Industry. It is predicted that per capita consumption of paper in India will rise from 3 Kgs to 6 Kgs before 2005 A. D. To meet the demand in the coming years Indian industry will be forced to use more and more waste paper by recycling as well as by imports, as practiced today (Rangan, 1997).

The paper mills who are not using waste paper presently will be forced to go in for this. Those who use small amounts will be required to increase the use of recycled fibers.

Any paper fiber used for a second time in the production of useful paper is defined as secondary fiber. Paper made from secondary fiber pulp has special properties desirable in the converting process. These include greater dimensional stability, less tendency to curl, better retention of size and fillers, increased opacity, more uniform formation, and better reproduction of imprint and colors for the production of tissue paper. It is reported that greater bulk and softness is realized when substantial amounts of secondary fibers are used. The disadvantages of secondary fibers include low strength (because the waste material has been previously processed in to paper and consequently has had considerable amount of refining treatments), low brightness, short fiber length, non uniformity of color and low freeness (Felton, 1970).

Efficient removal of ink is necessary to recycle used paper in to high value products. The removal process involves detaching the ink from paper's cellulose fibers and then separating the dispersed ink particle from the pulp slurry. This process is known as "de-inking" (Borchardt, 1993).

The first successful de-inking experiments were carried out and patented by Matthias Koops in England in 1800. The first recorded de-inking of printed waste paper was around 1900. Around 1960 a new process using flotation cells was borrowed from the mining industry and used to float the ink from the fiber (Barassi and Welsford, 1992). Conventional de-inking is necessary for large-scale secondary fiber utilization. It involves flotation and washing. These systems require mechanical and chemical treatments following re-pulping to separate the ink and contaminants from the pulp slurry.

The recycle potentiality of waste paper is mainly dependent on the type of ink, printing process used, and the paper to be recycled. Efficient recovery of secondary paper fiber also requires thorough and cost effective methods of de-inking (Bassemir, 1979).

A typical de-inking process

The de-inking process involves ten basic steps (Douglas and Secor, 1987). They are:

1. Pulping,
2. Pre-washing heat and chemical loop,
3. Screening,
4. Thorough flow cleaning or reverse cleaning,
5. Forward cleaning,
6. Washing,
7. Flotation,
8. Dispersion,
9. Bleaching, and
10. Water re-circulation and make up.

Among these the major steps selected for the present study were the following:

1. **Pulping:**

This process includes slushing of secondary fiber in the pulper and addition of chemicals. The pulper is filled with a batch of waste paper, water and chemicals, and then pulped for about an hour at 55 to 70°C at a pH of 9-11. The ink is stripped from the waste paper in the pulper which is operated at a consistency ranging from 8-16%. The high consistency, hot temperature, and brisk agitation make this a good location for addition of chemicals. The stock is then diluted to 4-5% consistency. In short, during pulping the paper is dispersed into a fibrous slurry using chemical, mechanical, and thermal energy to detach the ink form the fibers. Sodium hydroxide, sodium silicate, hydrogen peroxide and detergents are commonly used to saponify the ink binders.

2. **Flotation:**

Developed almost entirely by the metallurgy industry, flotation technology involves in the bubbling of air through suspensions to remove certain components. Although cells differ in design, a common principle is the introduction of air bubbles into the stock. By chemically modifying the surfaces of the ink particles and bubbles, the ink is made to adhere more readily to the air bubbles and float to the surface of the cell, where the foam can be skimmed off. De-inking efficiency is controlled by manipulating factors such as water hardness, pH, consistency, particle size, bubble size, quantity of air, dwell time in the cell, temperature, and the type and the amount of chemicals added etc. But many of the variables are inter related and a change in one may cause dramatic changes in one or more of the others (Forester, 1987).

3.Bleaching:

High quality de-inked pulp can be obtained by bleaching. Bleaching chemicals, that can produce paper containing de-inked pulp with equivalent brightness to that produced from virgin pulp, are in search for. The move towards more environmentally favoured bleaching agents rejected the chlorine based bleaching agents. Recently, formamidine sulfinic acid (FAS), sodium hydrosulphite, hydrogen peroxide etc., are commonly used. A simple approach to post bleaching of de-inked pulp is reductive treatment with sodium hydrosulphite, or FAS, or an oxidative step with hydrogen peroxide. Paper dyes or remaining color shades can be bleached only with reductive bleaching agents. The average paper dyes are very stable against oxygen based bleaching chemicals like H_2O_2 (Eul *et al.*, 1989).

Since molecular or morphological structure of the recycled fiber is not the same as that of virgin fiber, the bleaching methods utilized conventionally may be injurious to the former. Therefore, attention should be paid to identification of various chromophores responsible for color development in waste papers. The bleaching methods selected should be such that only chromophores are attacked leaving cellulose fibers unharmed. More over, this bleaching methods should be environmentally friendly (Kaul, 1998).

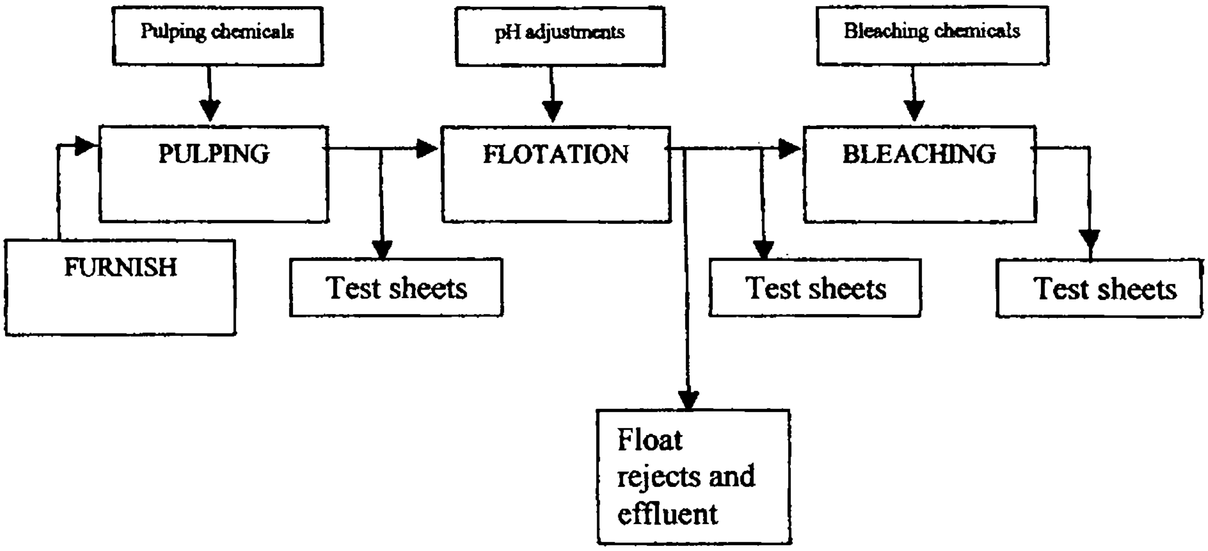
Environmental impact

A fundamental change in society's attitudes to the use of our natural resources, and to the production of excessive amounts of waste through careless use and consumption is observed. Our society now sees the waste stream produced by our modern life styles as a high cost problem that must be solved and as a long term threat to the viability of the environment and our present lifestyle (Kerr, 1991).

Utilization of waste paper is bound to have an impact on environmental cleaning in a big way as this, in turn, will reduce deforestation and help in preserving the ecology of the forest.

The pressure to conserve natural resources and reduce solid waste from the community has lead to an increased trend toward recycling of old news papers, periodicals and magazines, and office wastes (Richardson *et al.*, 1992). Recycling reduces the requirement for virgin fiber and energy and can lower the environmental impact of paper manufacture (Frederick *et al.*, 1996).

The flow chart of the present investigation



The present investigation focuses on three main areas of de-inking: i.e., pulping, floatation and bleaching. This work is an attempt to:

(1) Compare different types of floatation cells,

(2) Evaluate the role of different chemicals in de-inking and identification of more environmentally favourable substitutes,

(3) Bleach the de-inked pulp for improving the brightness, and

(4) Generate data regarding environmental effects of de-inking.

These objectives were analyzed separately, detailed studies conducted, and described in the next chapters.

CHAPTER 2

COMPARISON OF FLOTATION UNITS

Flotation de-inking is a common practice for the removal of ink from waste paper in many recycling paper mills. This was introduced to paper industry in 1980's. Existing technologies and process designs of flotation de-inking are based on experience obtained from mineral flotation processes (Zhu *et al.*, 1998).

A lot of research and development is continuing into the equipment for ink removal in order to improve ink removal efficiency, improve yields and reduce costs. The fact that so many different types of flotation equipment are offered suggests that equipment design is still maturing, no one design has yet proved significantly superior at ink removal (Barassi and Welsford, 1992).

The two major colorants found in printing inks are pigments and dyes. Flotation can remove effectively an ink that contains pigment as the colorant, because pigments, such as carbon black, are insoluble powders that are trapped among pulp fibers and can be removed by the chemical and mechanical actions employed by the process (Hache and Joachimides, 1992). The ink particles removed are relatively large and little or no washing is employed to remove smaller ink particles (Borchardt, 1993).

The de-inking chemistry and the physicochemical interactions among air bubbles, fibers, fines, fillers and ink particles are very complex. Many problems such as high fiber and water losses (Ajersch *et al.*, 1992., Turvey, 1993., Ajersch and Pelton, 1996), fiber contamination by de-inking chemicals (Ferguson, 1992a., Epple *et al.*, 1994), low efficiency in the removal of small ink particles etc., (Dorris and Nguyen, 1995) remained unsolved. Therefore, new technologies based on the mechanistic understanding of flotation processes are needed to solve or alleviate the above problems.

The ultra-fine ink particles present in the pulp can be removed by a special froth flotation technique (reverse shear floc-flotation). Detailed literature survey showed that there are only a few references for removal of the ultra-fine particles from de-inked pulp. A similar example of shear floc flotation of ultra-fine scheelite ore (Koh and Warren, 1979, 1980) is characterized by selective flocculation of the desired mineral with high shear agitation conditions under suitable reagent combinations. These floccules can then be floated using the principles of froth flotation.

MATERIALS AND METHODS

Flotation cells

Two types of flotation cells were used in this investigation in order to compare their efficiency, a single chamber unit with five litre capacity cell (Fig. I), and a double chamber unit with the same capacity having a main agitation chamber and a turbulence-free frontal chamber (TFFC), fabricated in our laboratory (Fig. II). A modified version of the second one with bristles attached to the side walls was also tried (Fig.III). The emphasis in the study is more on comparative results rather than the mechanism by which the test flotation cells function in de-inking.

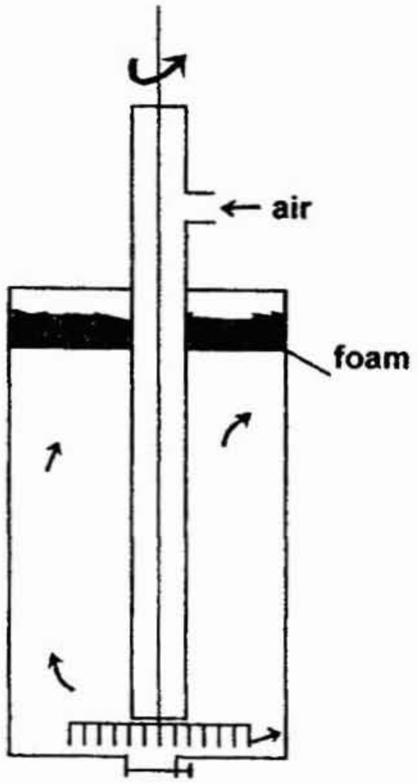


Fig. I. Single chamber flotation cell

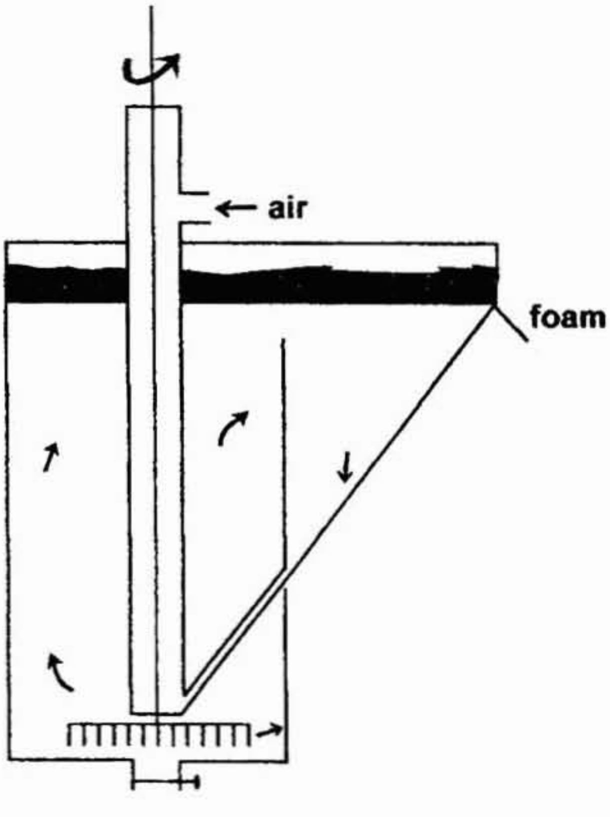


Fig. II. Double chamber flotation cell

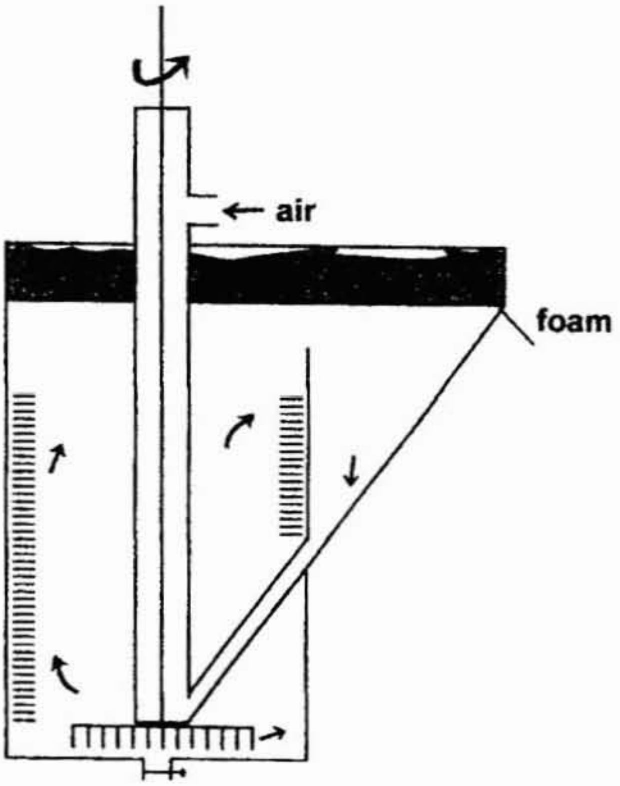


Fig.III. Double chamber flotation cell with bristles

Furnish

The furnish used in this study was a 70:30 mixture of news papers and magazines. Old news papers (ONP) of recently offset printed dailies and old magazines (OMG) were used for the various tests.

The news papers and magazines of about 3 months old were separately torn into pieces of one inch square and stored in opaque plastic bags as stock. A 120gm oven-dried (105°C) sample from this stock was used for each trial.

Pulping

The percentages of chemicals used are for the oven-dried fiber and represent a typical formula. The chemicals were added to 870ml de-ionised water at 50°C to 55°C in the following order: 0.4% DTPA, 1.2% sodium hydroxide (10% solution), 2.5% sodium silicate, 0.25% surfactant, and 1.0% hydrogen peroxide (10% solution).

Immediately after adding the peroxide the pulping liquor was poured over the waste paper in the pulper. Total pulping time was 30 minutes. When the pulping was completed, the exit pH was noted. The exit pH was controlled by adjusting the level of caustic soda to give a pH of 9.5 to 10.2. The pulp was then ready for flotation.

In another study, pulping was carried out with 120gm each of ONP and OMG independently, at 12% consistency to evaluate the relative merit of pulping ONP and OMG together. After independently pulping, they were mixed in the ratio of 70:30 and 80:20, respectively, before flotation.

Flotation

From the pulp (prepared above) a sample was taken and diluted with de-ionised water to 1.0% consistency. This was then placed in a blender and blended for one minute. The pH was adjusted to 8.5 using dilute H_2SO_4. The stock was poured into the flotation cell. The flotation time was 10 minutes. The foam generated was continuously skimmed off into a catch pan. This lost fiber and ink mixture (float reject) was filtered over a pre-weighed filter paper. It was dried in an oven and weighed to determine yield loss. Experiments were conducted to evaluate the performance of the flotation cell at different consistencies of the pulp suspension. The pulp solution remaining in the flotation cell was poured over a 63 micron sieve and pressed out to increase pulp consistency to about 10%.

Sheet formation

Buchner funnel pulp pads and hand sheets were prepared to evaluate the de-inked pulp brightness. The pad was formed using a vacuum--assisted Buchner funnel with a Whatman No. 41 filter paper. The brightness sheet was prepared as described in TAPPI T 218 om- 91. Standard handsheets of 1.2gm were formed in accordance with TAPPI method T 205 om -88 for physical tests of pulp.

Testing

The most common measurement for performance of de-inking process is pulp brightness. It was measured according to TAPPI method T 452 om-87. Physical testing of pulp handsheet was carried out according to

TAPPI method T 220 om-88. Freeness of pulps was measured following the TAPPI method T 227 om-92. The ash content of all samples was determined according to TAPPI method T 413 om-85. ISO brightness, light scattering coefficient and light absorption coefficient were measured with Technidyne color touch instrument.

Few standard methods are available for the preparation of different recycled pulp specimens. One of the major constraints in this direction is the variable nature of the wastepaper. A large number of physical and chemical variables affect the preparation of de-inked pulp specimens. Consequently, it is very difficult to obtain reproducible and comparable results from one laboratory to another (Levesque *et al.*,1998).

RESULTS AND DISCUSSION

A comparative study of the efficiency of three different flotation cells employing the same principle in de-inking was made. The post flotation brightness against different pH, on each of the flotation cells, is presented in Table 2:1 and illustrated in Fig. 2:1. The initial pulper brightness i.e., the pre-flotation brightness was only 53.3%. The increase in brightness noted after flotation, definitely proves the importance of flotation in de-inking process. Among the three types of flotation cells tried, double chamber cell with bristles gave maximum brightness (63.5%) at pH 4.5. From the figure it is clear that the double chamber cell with bristles was more efficient than the other two cells at all pH levels tested. The figure also explains the effect of pH on the brightness. The brightness percentage was found to be higher in single chamber cell when compared to the double chamber cell with out bristles. Among the three cells tested the highest brightness was recorded by double chamber cell with bristles. The double chamber cell provides a means for a type of re-circulation and also help the retention of the fiber in the turbulence-free frontal chamber for a longer duration.

A very large number of variables, both chemical and physical, affect the rate of flotation. The hydrophobicity of particles, a thermodynamic criterion, is a pre-requisite for their surface attachments to bubbles and their rise to form a froth layer (Dorris and Nguyen, 1995). Schulze (1984) clearly indicated the importance of hydro dynamic conditions with in a flotation cell on its flotation efficiency. Ink-removal efficiency depends on several factors such as the ability to separate the ink particles from the fibers, the collision probability between ink particles and air bubbles, the interfacial energy between ink particles and air bubble surfaces, the specific contact surface area between ink particles and air bubbles, the stability of the froth for final ink removal etc. (Zhu *et al.*, 1998).

The modified version with bristles produced small sized bubbles which enhance the separation of ink thereby increasing the brightness. The air bubbles are stabilized by the foaming chemicals through a decrease in the surface tension of the water (Felton, 1980). A part of the surface of fibers, fines and fillers becomes hydrophobic and they stick to air bubbles and get floated (Turvey,1993). As explained by Takahashi and Hiromichi

(1994) the ink particles are absorbed on the air bubble and removed. They also explained that there are three particles i.e., cellulose, ink, and bubble and four main interactions between them in the flotation cell that controls the effective removal of ink particles. They are ink-ink, ink-bubble, ink-cellulose and cellulose-bubble. Smaller ink particles are responsible for brightness reduction (McKinney, 1988) and which are removed by the flotation cell with bristles attachment. The particles of ink that negatively affects the brightness fall below 40µm. (Marchildon, *et al.,* 1989). The flotation cell removes most of the small particles to eliminate their influence and hence the increase in brightness. As stated by Forester (1987) the air bubble should be as small as possible so that the greatest possible active surface is obtained. Too large or too many bubbles cause coalescing and hence a corresponding reduction in available bubble surface in reaction. Micrometer sized particles show very high degree of hydrophobicity and flocculating characteristics, and thereby enhance the removal of ink particles. The findings of Raghavan *et al.*, (1993) and Epple *et al.*,(1994) also support the present results.

Fiber carry over loss, consistency and brightness

The understanding of fiber loss in flotation is very limited. Turvey (1987 and 1993) indicated that fiber loss was due to fiber adhesion to air bubbles which was then removed with the froth. Ajersch and Pelton (1996) disagreed with this observation, and recently Dorris and Page (1997) also. They found that the hydrophobicity of a fiber surface does not contribute to fiber loss and fiber loss is due to mechanical entrainment of fibers in the froth. Deng and Abazeri, (1998), in a recent study, found that both physical entrainment of fibers in an air bubble net work and adhesion of hydrophobic part of fiber surfaces on air bubble surfaces contribute to the total fiber loss. The minimum loss practical in flotation de-inking is probably around 2.0 % (Turvey,1993).

In order to find out the fiber carry over loss (float rejects) with these flotation cells mean percentage loss was estimated and the results are presented in Table 2:2, and illustrated in Fig 2:2. The single chamber cell showed a mean fiber loss of 7.5%. The double chamber cell without bristles produced a mean yield loss of 5.6%. The lowest mean fiber loss 4.2% was observed in the double chamber cell with bristles. In the double chamber unit the turbulence-free frontal zone keeps the fibers for a longer time in the cell and keeps to have a form of re-circulation. In the case of the third unit the bristles will reduce the bubble size and hence the bulk removal of fiber was prevented. The smaller bubble size, and the presence of re-circulation, both present in the case of double chamber cell with bristles, may have contributed to the variation in fiber loss when compared to the other two cells. Yield losses were significantly greater in the experiments using the different types of flotation cells. Lower yield loss was obtained in the cell attached with bristles.

Consistency (concentration) of pulp suspension is another factor related to fiber loss and brightness. Usually the consistency used for pulp flotation is 1.0 %. The result of an increased consistency on brightness and fiber loss is presented in Table 2:3 and Fig. 2:3. The relationship between consistency, brightness and fiber loss was found to be directly proportional upto 1.5% consistency. At 2.0% consistency the fiber loss was found to be higher. If the consistency was increased further, i.e., upto 2.5 or 3.0%, the fiber loss becomes low due to lack of proper agitation and air flow. At 2.0% consistency it was observed that the ink particles were poorly separated from the thick slurry and even visible in de-inked pulp. Thus, the brightness is decreased. If the duration of flotation was increased at 2.0% consistency the brightness becomes higher because of the lowering of consistency in the cell due to high fiber loss. That yield suffers was already reported by Forester (1987) when the consistency is allowed to increase. According to him the floatation cell consistency must be kept below 1.2%. At higher consistencies fiber entrapment causes losses of fibers being carried to surface and discharged in the effluent stream. It can be seen that increased brightness was accompanied by increased yield loss. These results agrees with those obtained by Borchardt and Matalamuki, (1994).

From this study it was observed that the double chamber cell with bristles produced the highest brightness and lowest yield loss. Even though the single chamber cell produced more brighter pulp than the double chamber one without bristles it was on the expense of high yield loss. Of the three, double chamber cell with bristles was superior to the other two cells.

The present study allows operating consistency to be increased with out sacrificing ink removal efficiency and also not much yield loss. The optimum consistency was found to be 1.5%. Operating the system at higher consistency has the advantage of reducing the capital investment, power and water handling requirements. A quantitative study of the relationship among fiber loss and froth structure and fluid dynamics with in the froth is needed.

Physical and optical characteristics of the de-inked pulp

A combination of 70% (ONP) and 30% (OMG) was used initially as feed stock for pulping. Colored ink specks were visible on the post flotation brightness pads due to insufficient de-inking. This is a very undesirable property for any paper making application. Hence the pulping of the ONP and OMG was done separately. The OMG is predominantly of chemical pulp and also had high ink content, pulping separately is more desirable. The two pulps were mixed then in the ratio 70:30 and 80:20 ONP/OMG prior to flotation.

Microscopic examination of the pulp samples revealed a composition of 71.6% mechanical fiber and 28.4% chemical fiber in the 70:30 ONP/OMG blend. The 80:20 ONP/OMG mix contained 77.7% mechanical fiber and 22.3% chemical fiber.

The results of the pulp evaluation is given in Table 2:4. Properties of pulp such as freeness, strength, optical properties etc. were measured. The recycled pulp sample with 30% OMG contained 9.4% ash whereas the 20% OMG sample contained 7.8% ash which denotes that the filler and coating contents were high in the original paper samples and may contribute to the loss of strength properties. The ash content of the two samples were nearly the same denotes that there was only a small variation in filler content between the two pulp samples. The de-inked pulp contains filler originating from clay, calcium carbonate and titanium dioxide. Major filler loss from the pulp is caused by drainage during filtering. (Letscher and Sutman,1992). As the OMG percentage was high in 30%OMG sample the ash content was also high. It was observed that a reduction of 5.4 and 4.6 percentage of ash occurred with 30% OMG and 20% OMG furnish respectively after the sheet making procedure. This reduction may be due to a loss of fillers and fines during the sheet making process. Addition of filler reduces strength. The strength of paper is mainly due to fiber to fiber bonds. Pigments or filler particles occupy space between fibers and interfere with fiber bonding to give a significant reduction in strength (Lane,1981, Parsons,1981).

In the present study the freeness of the pulp was found to be 150 and 145 ml CSF (Canadian Standard Freeness) for 70:30 and 80:20 ONP:OMG mixtures, respectively (Table 2.4). Howard and Bichard, (1992) reported that all pulps recycled with fines retained showed a drop in freeness, and fines have long been regarded as the main factor influencing freeness. The obvious implication is that fines accumulation in a closed system causes the drop in freeness.

Opacity was found to be 94.1% for 70:30 ONP/OMG and 93.9% for 80:20 ONP/OMG samples. As suggested by Hipple, (1991) opacity is a virtue of recycled fiber and has been attributed to an increased number of short fibers and contaminants in the recycled pulp. In the paper making process, optical properties of paper are improved by the addition of fillers. The pigment particles occupy voids between the fibers leading to more fiber to air and pigment to air interfaces, thus increasing opacity (Lane,1981., Parsons,1981).

According to the Kubelka-Munk theory, the light scattering coefficient and the light absorption coefficient determine opacity. Opacity increases with an increase in either factor. Even though the light scattering coefficient and light absorption coefficient were slightly higher for the 30% OMG sample that did not seem to influence opacity.

Bauer Mc Nett fiber classification result of the two pulp samples are given in Table 2:4. The fraction retained in different meshes were comparable. The long fiber fraction was around 25% in both the samples. Fractionation on a laboratory scale with a Bauer Mc Nett fiber classifier proved successful at separating office recovered paper into two stream of different fiber length. The long fiber component resulting from fractionation was significantly upgraded compared to the short fiber fraction (Abubakr *et al.*,1995). Duncan (1979) reported that de-inked pulp acts as an excellent filler fiber in combination with long-fibered pulps and generally improves paper formation. It is also reported by Ortner (1980) that secondary fiber mixture can produce pulp with good brightness and excellent strength properties.

The short fiber fraction was higher and this may be due to the presence of fillers originating from the OMG. This is also evidenced by the higher percentage of fines in the 70 : 30 sample. It is reported that during re-pulping reduction of fiber length and some fragmentation of the fibers occurs (Robinson, 1980).

The wet web strength of the two pulp samples was also nearly the same. Howard and Bichard (1992) reported that there is no significant change in strength during recycling. The decrease in strength with the use of secondary fiber is partly due to fiber length and partly to the de-inking process itself (Hipple, 1991). The factors responsible for inferior wet tensile strength are fiber deformation, quality and quantity of fines, fiber length distribution, and the presence of additives, such as adhesives, surfactants and electrolytes (Robinson, 1980). Chemical pulps usually have higher tear, tensile and burst indices compared with mechanical pulps (Howard and Bichard 1992).This explains the use of magazine and news papers together in the de-inking process.

Mechanical pulp is widely used in printing paper for its good printability and low raw material cost. Incorporation of magazines has the benefits of introducing chemical fiber into the furnish which can offset the reduction of strength properties reported to occur during recycling of mechanical pulps. Retulainen (1992) reported that addition of chemical pulp causes an increase in strength, since chemical pulp is inherently stronger than mechanical pulp. According to him this is primarily due to increased bonding and increase in load bearing capacity of the fibrous component. Desirable strength properties of paper can be achieved using optimal mixtures of long fibers and fine particles, the quality of the fine particles also being essential (Corson, 1980., Karenlampi, 1995).The desired combinations of optical and strength properties may be reached by manipulating the proportions of different types of fines (Retulainen *et al.*,1993).

Tensile index, tear index and burst index of the two samples are presented along with the tensile strength, tear strength and burst in Table 2:4.The addition of 10% excess of OMG did not greatly enhance strength properties. The observed enhancement in the 30% OMG is due to the beneficial effect of the increased percentage of chemical fiber present.

The presence of significant amount of ash or filler contributes to the brightness of the de-inked pulp. The brightness of the pad was 65.6 and 64.1 percent. Brightness also depends on the initial brightness of the fiber and on the degree of removal of dyes and inks. Retention of the brighter chemical pulp originating from the magazines account for the higher brightness of pulp containing 30 percent OMG sample.

The light absorption coefficient of the two samples are given in Table 2:4. The furnish with 20 percent OMG and 30 percent OMG showed very slight difference in light absorption coefficient. The presence of white fillers often increases the brightness of paper due to light absorption coefficient decrease (Mahagaonkar *et al.*,1998).

Porosity was less as more fines were present in the 70:30 sample. The filler portion coming from the magazine accounts for the higher percentage of fines.

Folding endurance was less for the 30%OMG furnish. Increased amount of chemical fiber could have increased folding endurance. The combined effect exerted by mechanical fiber, chemical fiber, and fillers and fines retained in the de-inked pulp offers a complex system. Hence, it is not easy to quantify, many of the properties.

The CIE L*a*b* color values of the pulp samples were also similar. This shows that a change of 10% OMG fraction did not have any appreciable effect on color coordinates. The 70:30 ONP/OMG sample had L*- 87.4, a*- 0.7 and b*- 6.3 while the 80:20 ONP/OMG sample had L*- 86.2, a*-0.6 and b*6.3, respectively.

Table 2:1 Comparison of flotation cells

(Pre-flotation brightness 53.3%ISO)

pH	Brightness %ISO		
	Single chamber flotation cell	Double chamber flotation cell	
		without bristles	with bristles
4.5	63.0	61.4	63.5
5.5	62.7	61.0	63.0
6.5	62.2	60.7	62.6
7.5	61.5	60.2	61.7
8.5	60.7	59.4	61.3

Pulper condition

Furnish – 70:30 ONP/OMG

DTPA – 0.4%

NaOH – 1.2% (exit pH 10.2)

Na_2SiO_3 – 2.5%

Surfactant – 0.25%

H_2O_2 – 1.0%

Consistency – 12.0%

Temperature – 55° C

Duration – 30 minutes

Flotation condition

Consistency – 1.0%

pH – 8.5

Duration – 10 minutes

Fig. 2:1. Comparison of flotation cells

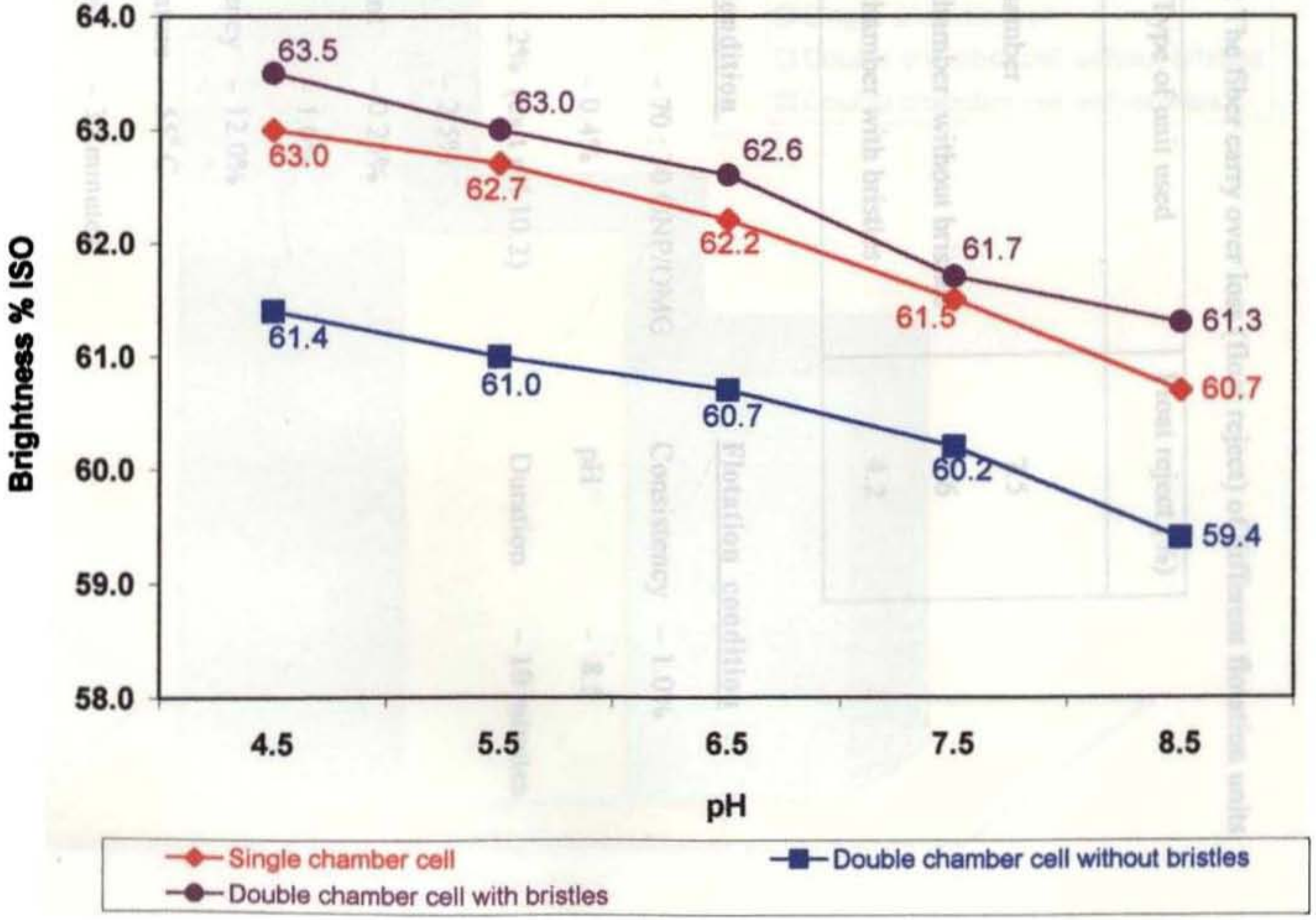


Table 2:2 The fiber carry over loss (float reject) of different flotation units

Type of unit used	Float reject (%)
Single chamber	7.5
Double chamber without bristles	5.6
Double chamber with bristles	4.2

Pulper condition

Furnish – 70 : 30 ONP/OMG

DTPA – 0.4%

NaOH – 1.2% (exit pH 10.2)

Na_2SiO_3 – 2.5%

Surfactant – 0.25%

H_2O_2 – 1.0%

Consistency – 12.0%

Temperature – 55° C

Duration – 30 minutes

Flotation condition

Consistency – 1.0%

pH – 8.5

Duration – 10 minutes

Fig. 2:2. Fiber carry over loss of flotation cells

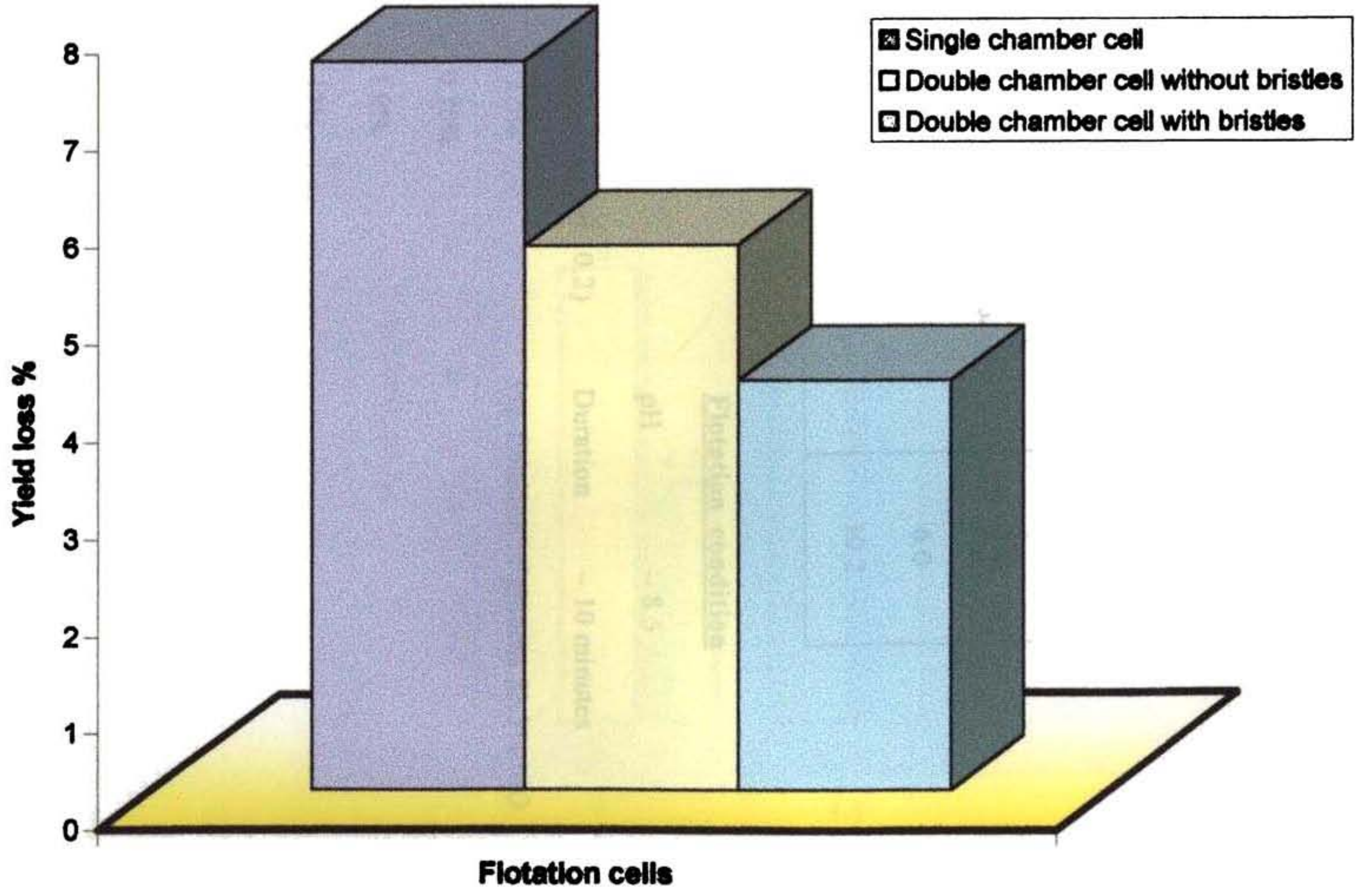


Table 2:3 Relationship among consistency, brightness and fiber carry over loss (float reject)

Consistency (%)	Brightness increase (% ISO)	Float reject (%)
1.0	8.0	4.2
1.5	9.7	6.0
2.0	8.9	10.2

Pulper condition		**Flotation condition**	
DTPA	- 0.4%	pH	- 8.5
NaOH	- 1.2%(exit pH 10.2)	Duration	- 10 minutes
Na_2SiO_3	- 2.5%	Pre-flotation brightness 53.3% ISO	
Surfactant	- 0.25%		
H_2O_2	- 1.0%		
Consistency	- 12%		
Temperature	- 55° C		
Duration	- 30 minutes.		

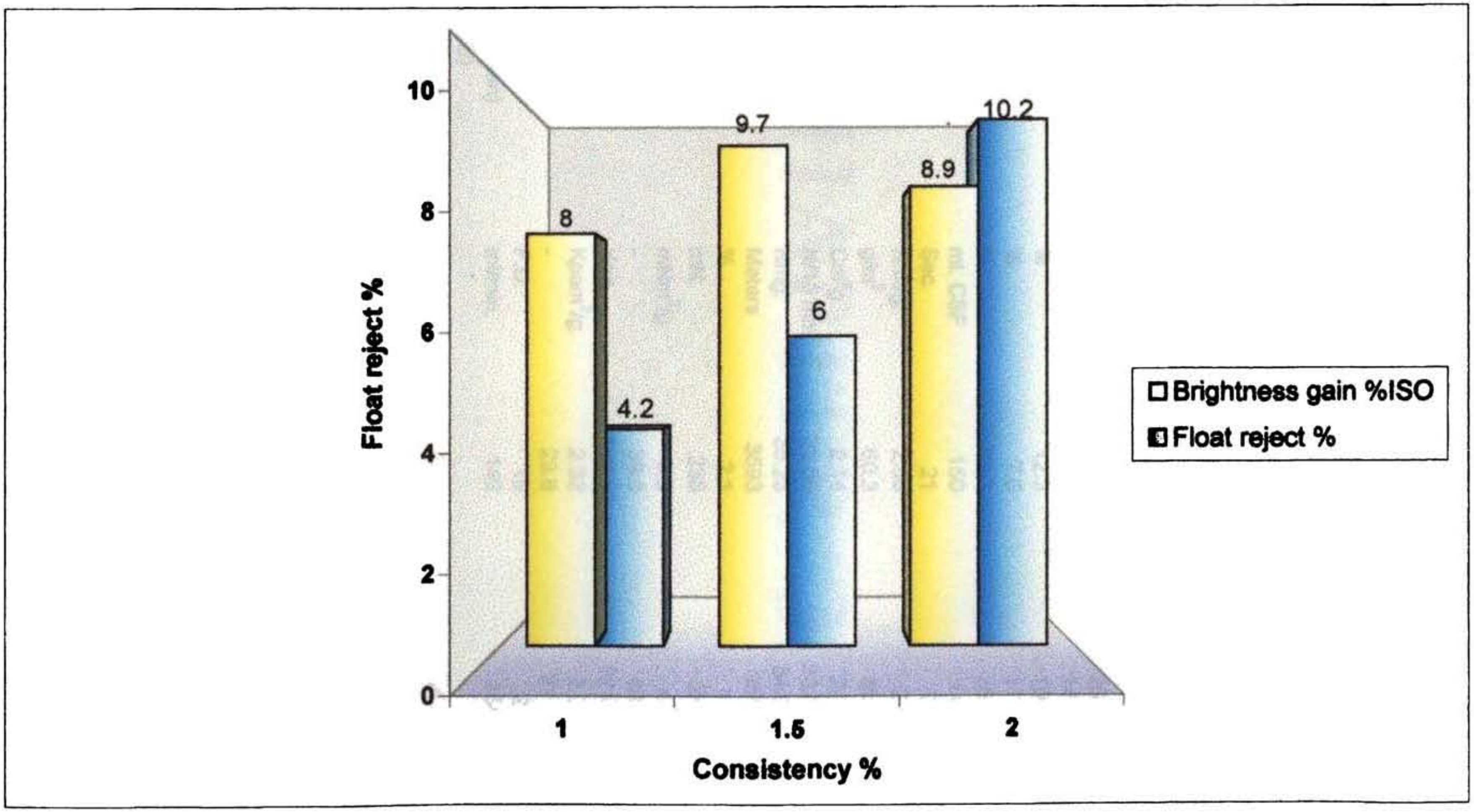


Fig.2:3. Relationship among consistency, brightness and float reject

Table.2:4. Physical and optical characteristics of the de-inked pulp

Particulars	Units	Sample	
		70:30 ONP/OMG	80:20 ONP/OMG
Consistency	%	10	10
Moisture	%	8.26	9.66
Ash			
(a) De-inked pulp	%	9.4	7.8
(b) Handsheet	%	4	3.2
Thickness	Microns	128.75	124.4
Fiber classification(Bauer-Mcnett)			
+ 30	%	24.6	26.7
- 30+50	%	17.2	14.8
-50+100	%	12.3	10.3
-100+200	%	7.6	11.5
- 200	%	38.3	36.8
Freeness	ml. CSF	150	145
Drainage time	Sec.	21	26
Wet Tensile index	N.m/g.	2.59	2.4
Basis weight	g/m^2	60.3	58.7
Bulk	Cm^{3}g.	2.14	2.12
Tensile strength	N/15 mm.	31.86	30.66
Tensile index	Nmg.	35.23	34.82
Breaking length	Meters	3593	3552
Stretch	%	2.1	1.7
Tearing strength	mN.	235	280
Tear index	mNm^2/g.	3.9	4.8
Tear factor	-	39.8	48.7
Bursting strength	Kpa.	139.8	121.8
Burst index	Kpam^2/g.	2.32	2.07
Burst factor	-	23.6	21.2
Folding endurance	F.D.	19	25
Porosity (Bendtsen)	ml/min.	142	156
Brightness(ISO)			
(a) Brightness pad	%	65.6	64.1
(b) Handsheet	%	63.6	62.2
Opacity(printing)	%	94.1	93.9
Yellowness	%	17	17
Light scattering coefficient	m^2/Kg.	58	53.69
Light absorption coefficient	m^2/Kg.	2.93	2.84

CHAPTER 3

THE ROLE OF
DIFFERENT CHEMICALS IN DE-INKING

The de-inking process involves detaching the ink from the cellulose fibers and then separating the dispersed ink particles from the pulp slurry by flotation. The principal chemicals involved in this process are sodium hydroxide, hydrogen peroxide, sodium silicate, chelating agents, surfactants, and collector chemicals. Not all furnishes require all of these chemicals invariably. Every furnish will require careful optimization. The amount of each chemicals to be added is dependent on the furnish, the water and the presence of other chemicals. Each chemical should be custom optimized for maximum performance. (Ferguson, 1992b). The objective of the present study is to examine the effects of different chemicals in flotation de-inking and to search for more environmentally favoured substitutes. The de-inking chemistry and the physicochemical interactions among air bubbles, fibers, fines, fillers and ink particles are very complex (Zhu *et al.*, 1998).

MATERIALS AND METHODS

The Furnish

A 70:30 mixture of ONP : OMG blend as furnish was used for all the tests. The recently printed newspapers (ONP), and magazines (OMG) (3months old) were separately torn into pieces of one inch square and stored in opaque plastic bags as stock. From this 120 gm oven-dried (105°C) sample was used for each trial.

Extraction of surfactants from natural sources

In the present investigation, natural products showing surfactant properties were extracted from three plants, *Acacia intsia, Sapindus trifoliatus* and *Sida rhombifolia*. The extraction procedure was common for all the three plants. Weighed out 100 gm. each of dried bark powder of *Acacia intsia,* powdered fruit wall of *Sapindus trifoliatus* and dried aerial parts of *Sida rhombifolia*. They were extracted separately with methanol in Soxhlet apparatus, cooled, filtered and then fractionated with water:butanol mixture. The butanol fraction was collected and evaporated in a water bath, and finally oven dried at 40°C (Hostettmann, 1989).

Pulping

Chemicals were added to 870ml de-ionised water at 50- 55^0 C in the following order; 0.4% DTPA, 1.5 % NaOH (10% solution), 2.5 % sodium silicate, 0.25% surfactant and 1.0% H_2O_2 (10% solution). Immediately after adding the peroxide the pulping liquor was poured over the waste paper in the pulper. The contents were then pulped for 30 minutes. The exit pH was controlled by adjusting the level of NaOH to give a pH of 9.5 to 10.2. The percentages given for the chemicals are on oven-dried (O.D) fiber and represent a typical formula.

Flotation

During flotation the re-pulped stock was diluted to 1.0% pulp consistency, and a constant pH of 8.5 was maintained using 1N H_2SO_4 Flotation was carried out for 10 minutes in the 5 lit. capacity froth flotation unit with bristles attachment. The inky foam was constantly removed and collected in a catch pan by manual skimming.

Buchner funnel pulp pads and hand sheets were prepared to evaluate the brightness of the pulp at the pulper and the de-inked stocks. From each sample handsheets were made according to TAPPI standard method T218 om- 91. The most common measurement for performance of de-inking is pulp pad brightness. The ISO brightness of all samples was determined according to TAPPI method T 452 OM - 87 using Technidyne.

RESULTS AND DISCUSSION

De-inking chemicals

Sodium hydroxide

Sodium hydroxide was used to adjust the pH of the pulp to the alkaline region and to saponify or hydrolyse the ink resins. At pH 9.5-11.0, the pH conventionally used for re-pulping, the fibers would take up some water and become more flexible. The primary effect of caustic is to increase the swelling of cellulose fibers. During saponification ink pigment is released by the breakdown of ink binder. Sodium hydroxide addition during re-pulping of thermo mechanical pulp (TMP) increases the level of fiber swelling (Gurnagul,1995). The addition rate of sodium hydroxide during pulping is usually presented as a percentage on O.D. fiber. It is to be noted that the amount of NaOH added is the amount required to reach a given pH, and not a given dose on fiber.

The effect of alkalinity on the brightness after pulping and flotation de-inking is given in Table 3:1 and illustrated in Fig. 3.1. The brightness of the pulper was found to increase with the pH up to 10.2. Above a pH of 10.2, the brightness decreased. The increase in brightness at the pulping stage without ink removal is due to the bleaching effect. This agrees with an earlier report of Ferguson (1992a). With increasing pH at the pulping stage an improvement in final brightness was observed after flotation. As alkali concentration increases, an increase in de-inking effectiveness is also observed (Carmichael, 1990). The absorption of hydroxide ions increases the electrostatic repulsion between fibers and ink particles (Forester, 1987). The same trend was observed in the brightness achieved after flotation de-inking also. The pHs indicated for post-flotation, (8.5 and 5.5) are the pHs at which the handsheets were prepared. The highest post floatation brightness was obtained when the pulping was carried out at pH 10.2. The highest brightness of 60.8 was obtained for the hand sheet prepared at pH 5.5. Addition of sodium hydroxide to wood–containing furnish (ONP) will cause the pulp to yellow and darken (Mahagaonkar, *et al.*, 1996). The pulps darken upon reaction with alkali. This loss in brightness is known in the pulp and paper industry as "alkali darkening"(Giust *et al.*,1991). The decrease in brightness is attributed to the alkali darkening the lignin suffers at high pH. Contradictory results are also reported by Borchardt (1993) that an increase in pulping pH from 9.0 to 12.0 in the presence of 1.0 per cent hydrogen peroxide does not decrease handsheet brightness.

Table 3:2 and Fig. 3.2 demonstrate the effects of pH reduction on the brightness of post-flotation pulp. A significant gain in brightness was observed (3.3% ISO). A three point increase of brightness with a decrease in flotation pH from 9.0 to 5.5 was reported earlier by Borchardt (1993). This may be due to precipitation or agglomeration of colloidal ink and stickies due to the change in pH, and a reduction in the number of chromophores as explained by Ferguson(1992a).

Hydrogen peroxide

Hydrogen peroxide is used in the de-inking system in the pulper to protect the brightness of the fiber and to enhance ink removal, and in a bleaching stage to increase fiber brightness (Carmichael,1990). Hydrogen peroxide is used to decolorize the chromophores generated by the alkaline pH in wood containing pulps. It is increasingly being used to replace the traditional chlorine based chemicals because it is more environmentally acceptable. Peroxide bleaches with very little yield loss (Johnson and Allison, 1992). Peroxide helps to minimize alkaline darkening and yellowing in de-inking stage (Carmichael,1990). The peroxide decomposition products and conditions have been identified as contributing to loss of brightness in virgin pulps (Liden and Ohman,1998). It is reasonable to expect a similar effect with recycled fiber also. Table 3:3 and Fig.3.3 show the inter-relationship between peroxide and sodium hydroxide on brightness. In the absence of hydrogen peroxide in the pulping stage excess sodium hydroxide causes alkali darkening and thus results in low brightness. In all other cases residual hydrogen peroxide minimises the alkali darkening. Every dose of hydrogen peroxide at 1.5% sodium hydroxide gave maximum brightness. With additional doses of NaOH the brightness was found to decrease due to the high pH. The optimum dose is not a fixed ratio between the caustic and the peroxide. This increase in brightness agrees with the explanation of Carmichael (1990) that in addition to brightening the fiber, peroxide helps in ink removal by oxidising the varnish or oily substances in the ink, and penetrating and through decomposing help separation of ink particles from fibers. The pulp then begins to lose brightness due to alkali darkening. Table 3:4 and Fig. 3:4 demonstrate the rapid consumption of peroxide at high caustic levels. As caustic additions were increased, the brightness of the pulp reached a maximum point. The brightness increased from 58.2% ISO to 60.5% ISO and decreased to 57% ISO as the percentage of NaOH was increased from 0.5% through 1.5% to 3%. High pHs favour peroxide decomposition. Thus at high caustic levels both rapid decomposition of peroxide and reduction in brightness was observed. It is to be noted that the NaOH should be optimum for maximum hydrogen peroxide performance.

Table 3:5 and Fig. 3:5 illustrate the increase in brightness with respect to the peroxide concentration. When the peroxide charge increases from 0 to 3.0% an increase in brightness was observed (52.8 to 64% ISO) i.e., a gain of around 11% ISO unit. When peroxide is increased from 0 to 1% a gain of 7.4 % ISO was observed. When concentration was increased further from 1 to 1.5% the brightness gain was 1.3% only. A further increase of upto 3.0% gave a brightness upto 64.0% ISO unit. Thus, the optimum peroxide dose is around 1.0%. Such a trend of a drastic increase in brightness upto 1.0% peroxide followed by a lesser increase after 1.0% peroxide was also reported by Pettit (1992).

Chelating agents

DTPA (Diethylene triamine penta acetic acid) is the most commonly used chelant, although EDTA (Ethylene diamine tetra acetic acid) is also used. Table 3.6 and Fig. 3.6 show the results obtained from increasing doses of DTPA. A gain of 1.1% brightness was achieved with 0.4% DTPA at the pulping stage. With the same dose the brightness increased by 7.7% and 9.7%ISO at pHs 8.5 and 5.5 respectively after flotation. Addition of more than 0.4% DTPA did not enhance the brightness. Both the pre-flotation brightness and post-flotation were enhanced by the addition of DTPA at the pulping stage. The figure already indicates the requirements for DTPA assisting in the enhancement of brightness. The behavior of any metal present would be affected by DTPA, (It prevents the catalytic decomposition of hydrogen peroxide used in the re-pulping of waste paper). The role of the chelant is to form soluble complexes with the heavy metal ions. The complexes thus formed prevent these ions from decomposing the hydrogen peroxide. The amount of heavy metal ions present in the furnish determine the amount of chelant that is to be added at the pulping stage.

A chelation step to remove metal ions (Dick and Andrews,1965) is commonplace when brightening mechanical pulps with hydrogen peroxide. Transition metal ions such as iron, manganese and copper greatly accelerate the catalytic decomposition of the active perhydroxyl ion, presumably through a free-radical mechanism (Bambrick,1985). The perhydroxyl ion is considered to be the active component responsible for the brightening reaction, and any unwanted side reactions which favour its decomposition waste peroxide and distract from the brightening process. Metals occurring naturally in wood are the primary source of metal ions in pulp, with secondary contamination arising from the process water and equipment (Dick and Andrews,1965).

Degradation

Chelating agents such as DTPA and EDTA have been banned in some countries, where the effluent stream discharges into a water system because of the disruptive effects of the chemicals in aquatic life. Its presence in the process therefore required that its effect on metal transport both with in the process and in the environment be determined along with possible removal mechanisms such as bio-degradation.

Sodium silicate

When the amount of sodium hydroxide is increased the rate of ink removal also increased, but the fiber undergoes alkali darkening. To moderate alkali darkening sodium hydroxide can be partly replaced with sodium silicate. As sodium silicate is a source of alkalinity and will affect the pH, increasing the silicate will increase the pH, and this may call for a reduction in the NaOH addition rate.

Table 3:7 and Fig. 3:7 show the role of sodium silicate on a 70 : 30 ONP/OMG furnish. Here the pH of the pulper is held at 10.2 constant by adjusting the level of caustic soda and no chelant is used. The brightness at the pulping stage of the furnish increased as the amount of silicate is increased. The curves also depict the dispersant effect of silicate. The lines representing the pulper and post flotation brightness were found to show a similar increasing trend as the silicate helps to disperse the ink. The higher the dose of the silicate, the higher the post flotation brightness.

The process was repeated with the addition of 0.4% DTPA at the pulping stage. Table 3:8 and Fig. 3:8 depict the same trend. The presence of the chelant increased the pulper brightness and therefore the post flotation brightness. The dispersant effect of the silicate is still obvious. Silicate aids in ink removal through an ink dispersant action or by preventing the ink from re-depositing on the fiber surface(Ferguson, 1992b). Ali *et al.*,(1994) attributed this increase in brightness to two distinct functional characteristics of soluble silicates: pH buffering and detergency. The buffering capacity is more important at high alkalinities compared to low alkalinities. The detergency i.e., ability to wet, disperse, emulsify, and suspend soils in aqueous system also improves the brightness significantly. It also prevents the re-deposition of ink onto the fibers. This reason may be attributed to the increased brightness in the present investigation also.

Sodium alginate

Silicates creates problems such as scaling and fouling equipment, wires and belts and high temperature break down to silica causing fouling. Replacement of sodium silicate with a polymeric stabilizer is one of the several alternatives to reduce the ill effects of silica (Ferguson, 1992a). The result of sodium alginate treatment in place of sodium silicate is depicted in Table 3:9 and Fig. 3:9. The curves are very similar to those obtained with sodium silicate (Table.3:8 and Fig.3:8). Alginate gave comparable brightness to that of silicate. At 2.5% each of sodium silicate and sodium alginate the brightness values were not much different. The pulper brightness was 50.3 (Table.3:8 and Fig.3:8) and 48.5 (Table.3:9 and Fig.3:9) percentages, respectively. Similarly at pH 5.5 the brightness were 60.0% ISO(Table.3:8 and Fig.3:8) and 58.2% ISO(Table.3:9 and Fig.3:9), respectively. The dispersant effect is also evident as in the case of silicate.

On an environmental standpoint sodium alginate can be considered as a good silicate replacement. But there is little published data available on the performance of silicate replacements in a de-inking plant.

Surfactants

This study was intended to provide comparable results, demonstrating de-inking surfactant effectiveness in flotation but no effort was made to optimize pulper chemistry and process conditions for each product. The performance of a series of synthetic de-inking surfactants (SDS) was compared with a series of natural products having surfactants properties, denoted here as natural de-inking surfactants (NDS), in flotation de-inking. The extracts isolated from *Sapindus trifoliatus, Acacia intsia and Sida rhombifolia* are designated here as NDS 1, NDS 2, and NDS 3 respectively.

Four surfactants having different HLB value have been chosen for de-inking a 70:30 ONP/OMG blend. A comparison of de-inking efficiency of the surfactants were made. The results are presented in Table 3:10 and Fig 3:10. The brightness gain is measured relative to the pulper pad brightness. All the tested surfactants gave almost similar brightness at the pulping stage except SDS 4. In the case of SDS 1 the pulper brightness was slightly high, 53.3% ISO unit. Surfactant SDS 1 with HLB value of 11.5 was found to be the most efficient in de-inking, and SDS 4 having an HLB value of 17.2 the least efficient. The highest post flotation brightness was observed for SDS 1 (63.5 % ISO unit) at pH 4.5. The other surfactants lagged behind. The same effect was evident at other pH values tested.

The increase in brightness at pH 4.5 for post flotation was 10.2% ISO units in the case of SDS 1 where as only 5.2% ISO increase was found in the case of SDS 4 when compared to the pulper brightness. Surface active agents play a major role in the detachment of ink particles from fibers. Surfactants play many roles in flotation de-inking as a dispersant to separate the ink particles from the fiber surface and prevent the re-deposition of separated particles on fibers, as a collector to agglomerate small particles to large ones, change the surface of particles from hydrophobic and as a frother to generate a foam layer at the top of the flotation cell for ink removal

(Ferguson, 1992a). These materials disperse the colors and form the foam needed for flotation. Non ionic detergents have proved to be the most effective in de-inking (Forester, 1987). All surfactants contain both hydrophilic and hydrophobic groups. One method of characterising surfactants is by using the Hydrophilic Lipophilic Balance. The size and strength of the hydrophilic group in relation to the hydrophobic group dictate the function of the surfactant. The ratio between the two groups is expressed as a numerical value called Hydrophilic Lipophilic Balance or HLB (Olson and Letscher,1992). Surfactants with a lower HLB value, i.e., the more hydrophobic surfactants proved to be the most efficient (Rao,*et al.*,1999). In the case of non ionic surfactants the more hydrophilic the surfactant the more inefficient is the release of ink (Rao and Stenius,1998). The structure of surfactants influenced the de-inking of xerographic paper (Marchildon, *et al.*, 1989). Surfactants are added during the pulping to promote ink particle detachment from fibers and dispersion of detached ink in the process water. Mechanism of ink removal is similar to those proposed for liquid soil removal from fabrics (Borchardt, 1993). Surfactants also can provide some control over the particle size of detached inks. The ink detachment mechanism of surfactants, as suggested by Rao and Stenius, (1998) may be a two step process: ink softening followed by ink release. Depending on surfactant concentration, release of ink, therefore may occur either by lifting of ink aggregates or by removal of layers that disperse as small particles. A possible explanation for the differences in de-inking efficiency is the different migration rates of the surfactants to the ink water interface (Rao *et al.*,1999).

Surfactants provide effective de-inking and ink dispersion, but it causes unacceptable foam problems in effluent. As the effluent subsequently goes into streams, the presence of foam has to be controlled and kept to a minimum (Mah,1983).

The search to identify less foamy and environmental friendly surfactants lead to the identification and isolation of products of plant origin with surfactant properties. In the study of naturally occurring substances having surfactant properties, surfactants were isolated from three plants as detailed earlier in this chapter, a comparative study of the three was made and the results are presented in Table 3:11 and Fig 3:11. With increasing pH brightness was found to decrease even though NDS 1 showed better de-inking capability. At pH 4.5 it produced an increase of 4.1% ISO brightness units compared to NDS 3 and with regard to NDS 2 an increase of 2% ISO unit. This trend was evident at all pH values selected. All the three surfactants gave almost similar brightness values at the pulping pH. It is observed that NDS 1 produced small sized bubbles than the other two and better foaming characteristics. Better foaming capability combined with better ink removal efficiency enhanced the brightness when NDS 1 was used as the surfactant. The overall behavior of the various synthetic and natural surfactants were similar (Table 3:10 & Fig.3:10 and Table 3:11 & Fig. 3:11). The highest brightness gain observed for SDS 1 (63.5%ISO at pH

4.5), was slightly greater than NDS 1(62.5%ISO at pH4.5). These two surfactants do not differ greatly in their efficiency in removing ink particles.

The yield loss caused by the surfactants along with brightness values are presented in Table 3:12 and Fig. 3:12. With the exception of SDS 4 yield losses were some what greater for the other surfactants. The brightness values in the de-inking test showed dependence on yield loss. Increased brightness was accompanied by increased yield loss. NDS 1 produced a brightness of 60.1%ISO with 5.0% yield loss at pH 8.5. At same pH, NDS 2 and NDS 3 produced brightness of 58.2% ISO and 55.1% ISO with 4.0% and 2.8% yield loss, respectively. SDS 1 with 4.2% and SDS 4 with 1.8% yield loss produced brightness of 61.3% ISO and 51.7% ISO respectively at pH 8.5. The overall trend showed an increasing brightness with yield loss, even though SDS 1 with 4.2% yield loss recorded the highest brightness gain of 8.0% ISO. This behavior is consistent with that observed in several series of laboratory de-inking experiments done under different conditions and using different surfactants (Borchardt, 1993). Brightness increase across the flotation cell had a strong inverse correlation with process yield (Letscher and Sutman, 1992). The surfactant type is one among the major factors affecting pulp losses (Ajersh and Pelton,1996). At pH 8.5 NDS 1 produced affordable yield loss (5.0%) and good brightness (60.1%ISO) hence it is possible to improve ink removal efficiency with out increasing floatation yield loss.

All process parameters i.e., de-inking effectiveness, yield loss, surfactant foaming properties in all process steps should be considered when evaluating de-inking surfactants.

The natural surfactants can provide excellent de-inking results, low yield loss and acceptable foaming levels. Each potential surfactant should be evaluated for their performance in the de-inking process. The effectiveness of naturally obtained surfactants may become an eco-friendly and economical ingredient in paper recycling processes. Its use in other branches of science which employ flotation and generate froth will be the future scope of this work and extraction on large scale will also require further attention.

Table 3:1 Effect of pulping alkalinity on brightness

pH	Brightness % ISO		
	Pulper	Post floatation pH 8.5	Post floatation pH 5.5
8.6	47.0	56.5	58.4
9.0	47.1	57.0	58.7
9.4	48.0	58.1	59.2
9.8	49.0	59.0	60.0
10.2	49.2	59.6	60.8
10.6	44.5	58.8	59.6

Pulper condition

DTPA	- 0.4%
Na_2SiO_3	- 2.5%
Surfactant	- 0.25%
H_2O_2	- 1.0%
Consistency	-12.0 %
Temperature	- 55°C
Duration	- 30 minutes

Flotation condition

Consistency	- 1.0%
pH	- 8.5
Duration	- 10 minutes

Fig. 3:1. EFFECT OF PULPING ALKALINITY ON BRIGHTNESS

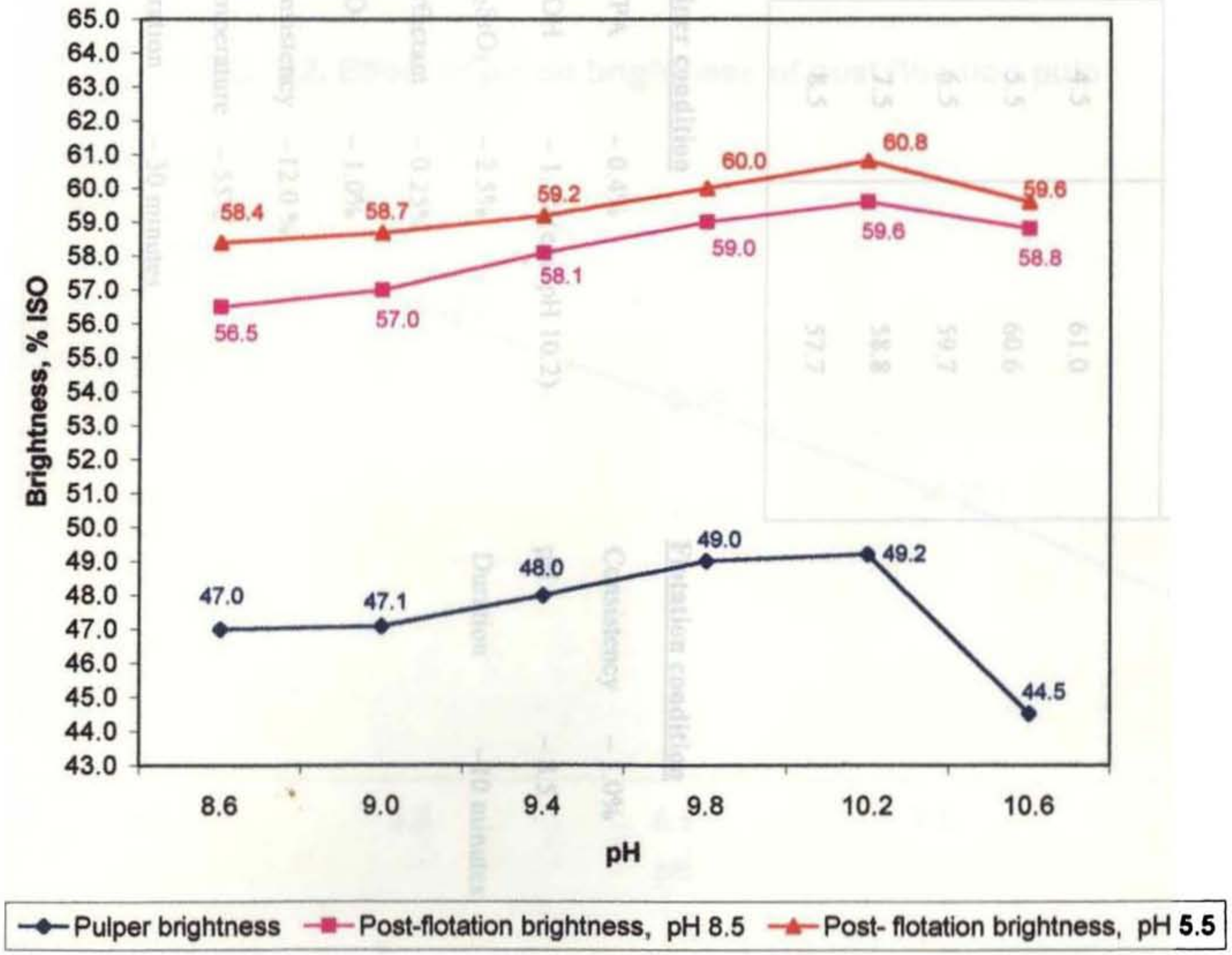


Table 3:2 Effect of pH on brightness of post flotation pulp

pH	Brightness % ISO
4.5	61.0
5.5	60.6
6.5	59.7
7.5	58.8
8.5	57.7

Pulper condition

DTPA - 0.4%

NaOH - 1.5%(exit pH 10.2)

Na_2SiO_3 - 2.5%

Surfactant - 0.25%

H_2O_2 - 1.0%

Consistency -12.0 %

Temperature - 55°C

Duration - 30 minutes

Flotation condition

Consistency - 1.0%

pH - 8.5

Duration -10 minutes

Fig. 3:2. Effect of pH on brightness of post flotation pulp

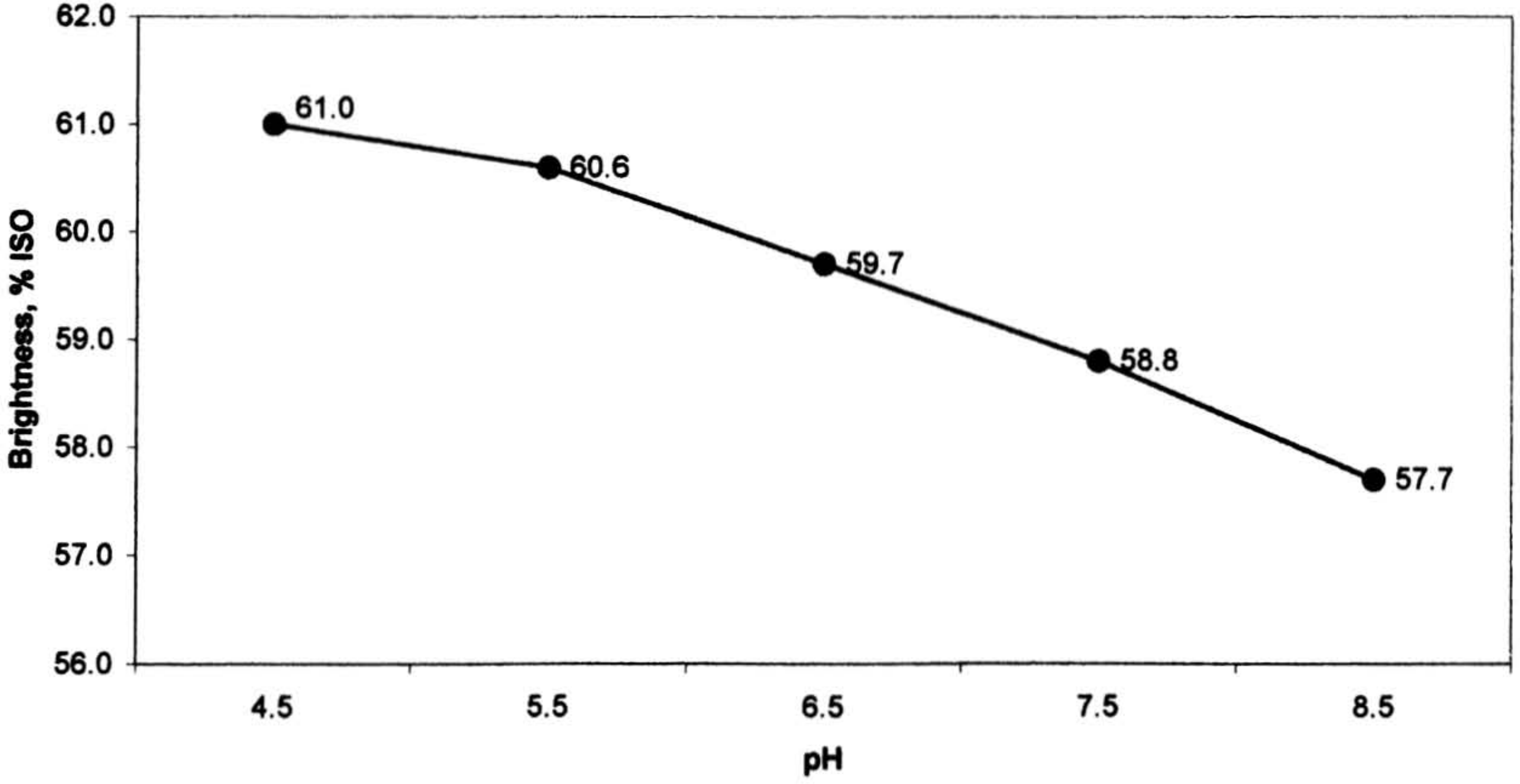


Table 3:3 Variation of brightness with NaOH and H_2O_2

NaOH %	Brightness % ISO				
	H_2O_2 %				
	0.0	0.5	1.0	1.5	3.0
0.5	56.0	57.5	58.0	58.2	59.0
1.0	55.0	57.4	60.0	60.5	62.0
1.5	52.8	58.0	60.2	61.5	64.0
2.0	52.0	56.3	58.0	60.0	62.5
2.5	51.8	55.2	56.5	58.0	61.0
3.0	51.0	54.8	56.0	57.0	59.8

Pulper condition

Furnish - 70:30 ONP/OMG

DTPA - 0.4%

Na_2SiO_3 - 2.5%

Surfactant - 0.25%

Consistency -12.0%

Temperature - 55°C

Duration - 30 min.

Flotation condition

Consistency - 1.0%

pH - 8.5

Duration - 10 min.

Fig. 3:3 Variation of brightness with NaOH and H_2O_2

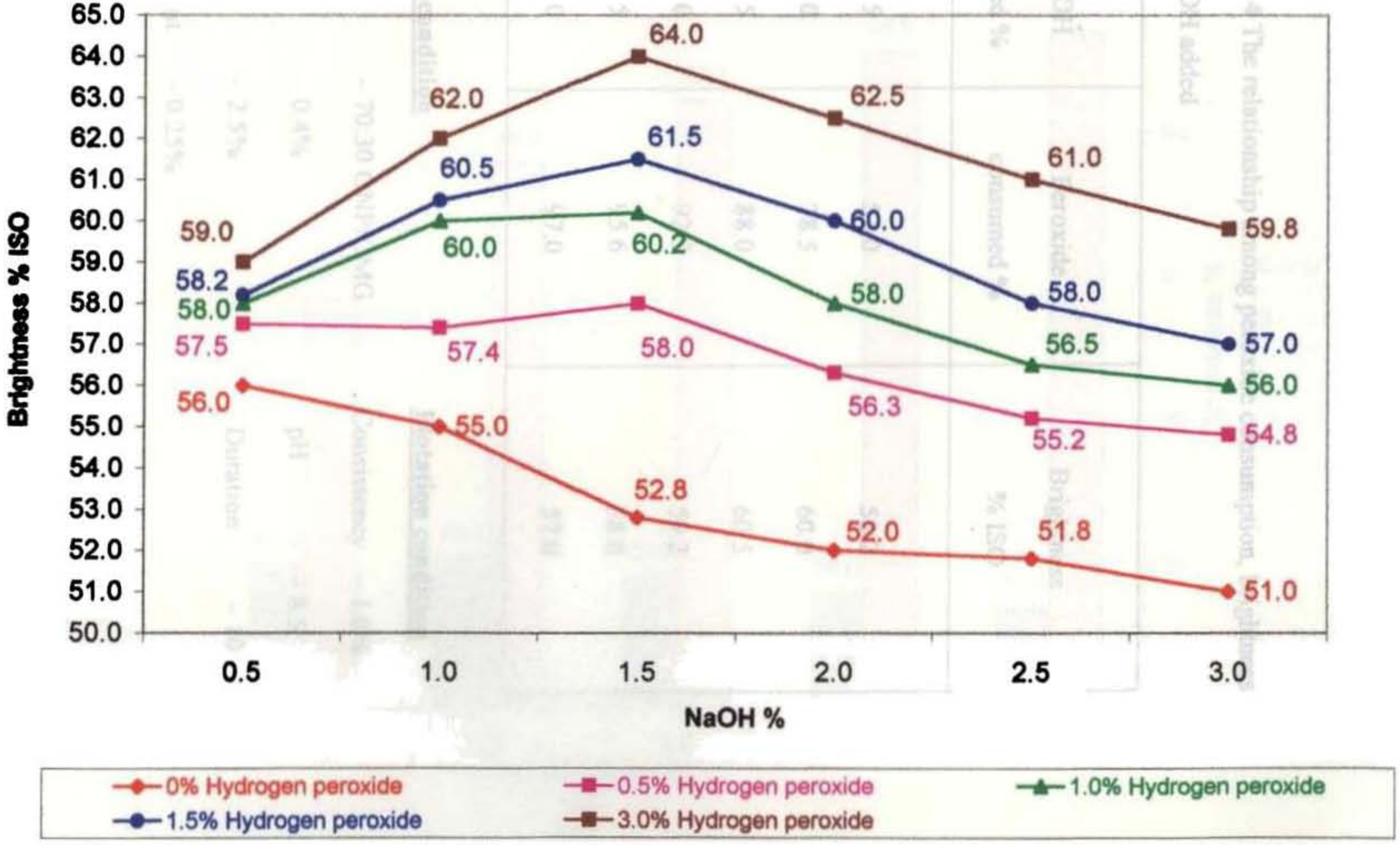


Table 3:4 The relationship among peroxide consumption, brightness and NaOH added

NaOH added %	Peroxide consumed %	Brightness % ISO
0.5	53.0	58.2
1.0	78.5	60.0
1.5	88.0	60.5
2.0	92.3	59.2
2.5	95.6	58.0
3.0	97.0	57.0

Pulper condition

Furnish - 70:30 ONP/OMG

DTPA - 0.4%

Na_2SiO_3 - 2.5%

Surfactant - 0.25%

H_2O_2 -1.0%

Consistency - 12.0%

Duration - 30 minutes

Flotation condition

Consistency - 1.0%

pH - 8.5

Duration - 10 minutes

Fig. 3:4. The relationship among peroxide consumption, brightness and NaOH added

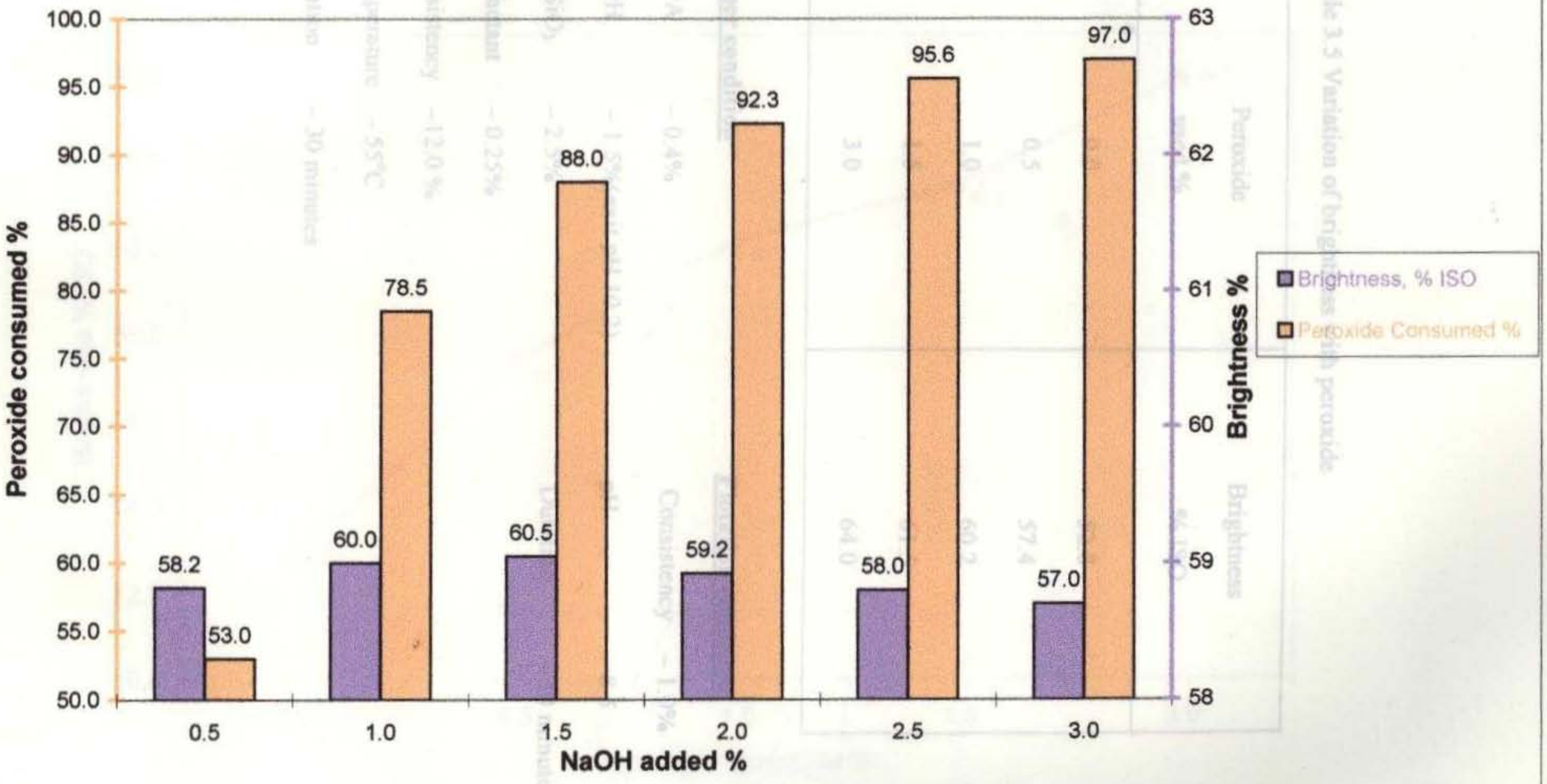


Table 3.5 Variation of brightness with peroxide

Peroxide used %	Brightness % ISO
0.0	52.8
0.5	57.4
1.0	60.2
1.5	61.5
3.0	64.0

Pulper condition

DTPA - 0.4%

NaOH - 1.5%(exit pH 10.2)

Na_2SiO_3 - 2.5%

Surfactant - 0.25%

Consistency -12.0 %

Temperature - 55°C

Duration - 30 minutes

Flotation condition

Consistency - 1.0%

pH - 8.5

Duration -10 minutes

Fig. 3:5 Variation of brightness with peroxide

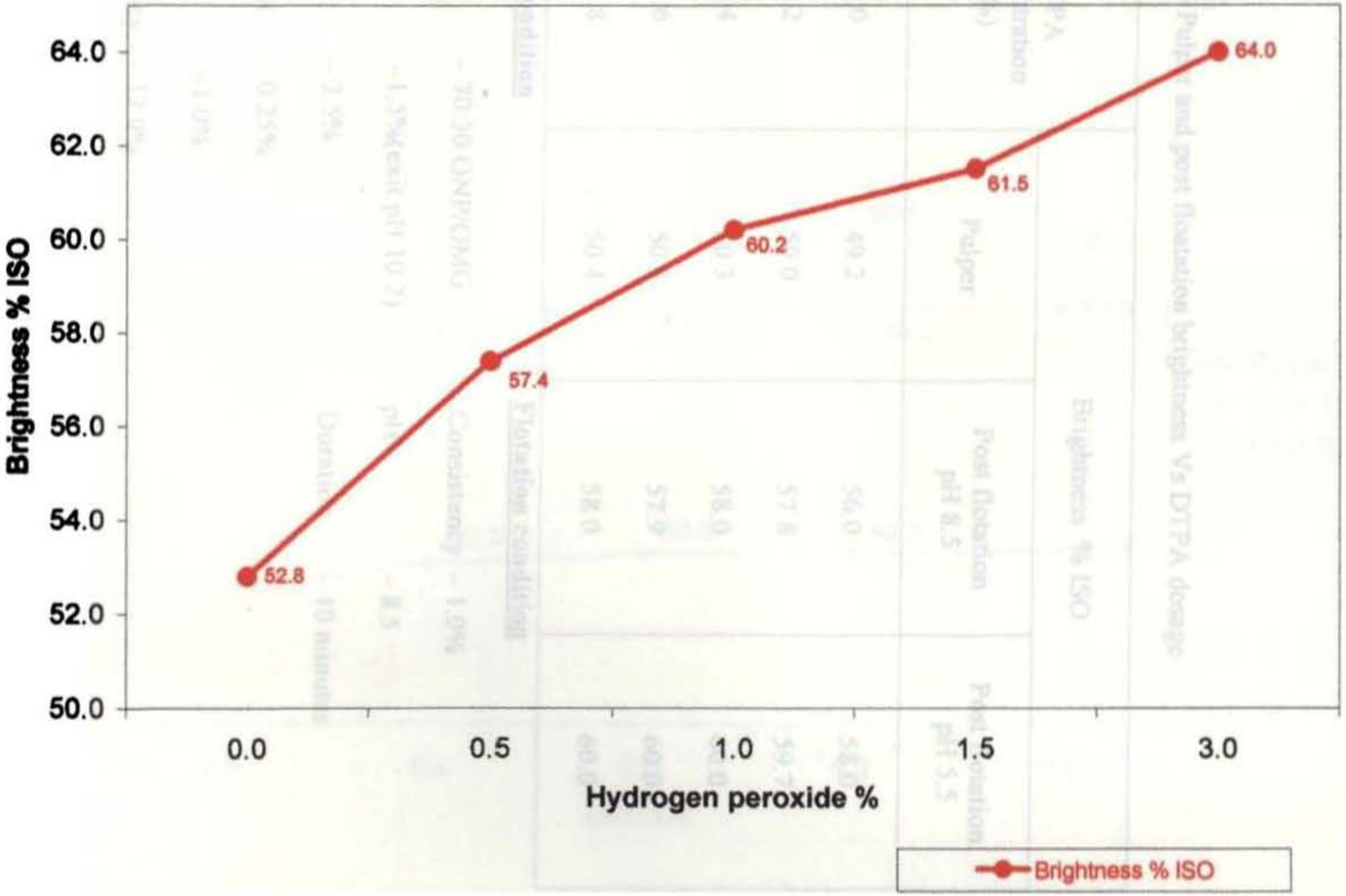


Table 3.6 Pulper and post floatation brightness Vs DTPA dosage

DTPA concentration (%)	Brightness % ISO		
	Pulper	Post flotation pH 8.5	Post flotation pH 5.5
0.0	49.2	56.0	58.0
0.2	50.0	57.8	59.7
0.4	50.3	58.0	60.0
0.6	50.3	57.9	60.0
0.8	50.4	58.0	60.0

Pulper condition

Furnish - 70:30 ONP/OMG

NaOH -1.5%(exit pH 10.2)

Na_2SiO_3 - 2.5%

Surfactant - 0.25%

H_2O_2 -1.0%

Consistency - 12.0%

Temperature -55°C

Duration - 30 minutes

Flotation condition

Consistency - 1.0%

pH - 8.5

Duration - 10 minutes

Fig.3:6. Pulper and post flotation brightness Vs DTPA dosage

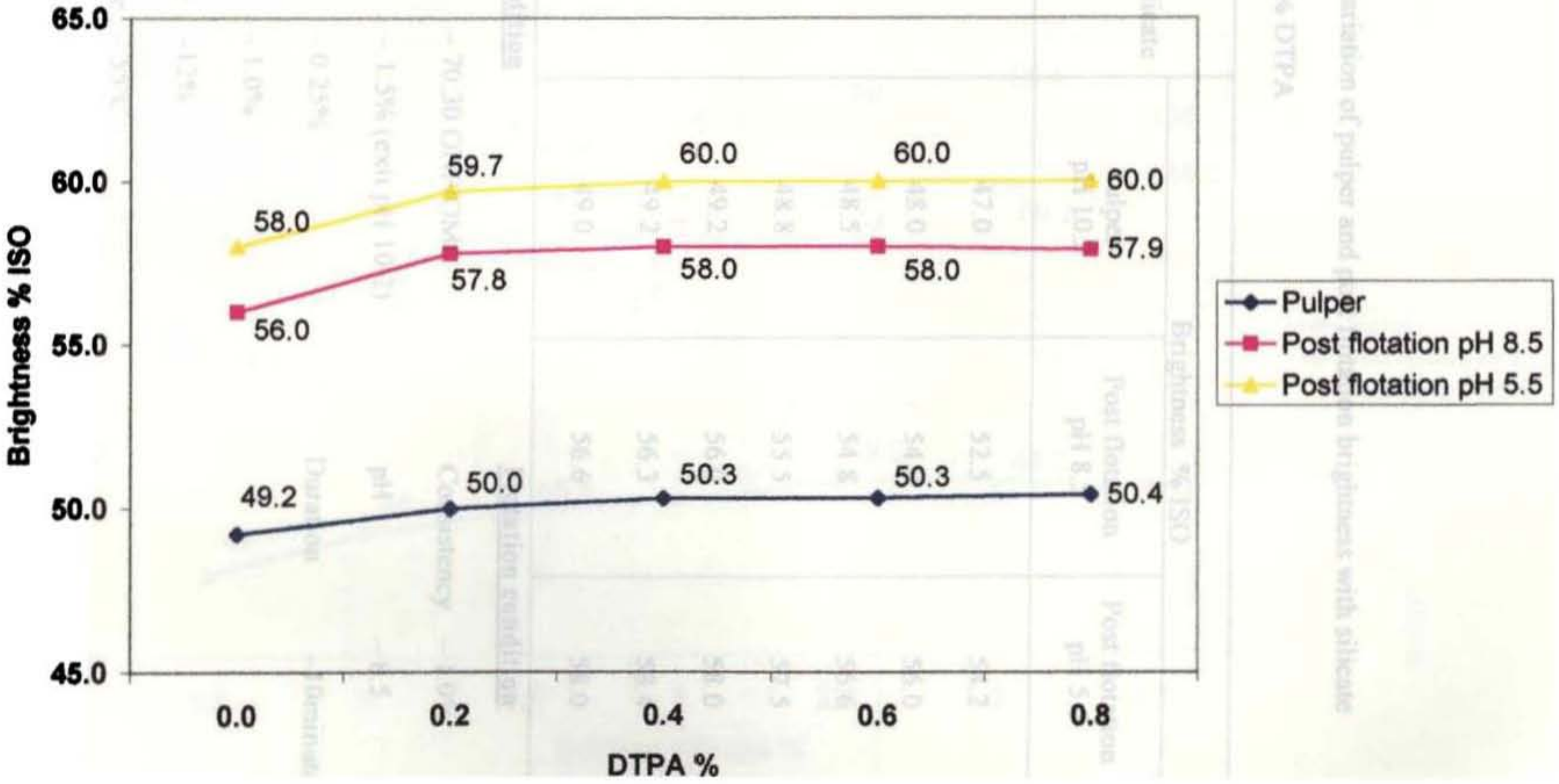


Table 3:7 Variation of pulper and post flotation brightness with silicate dosage at 0% DTPA

Sodium silicate %	Brightness % ISO		
	Pulper pH 10.2	Post flotation pH 8.5	Post flotation pH 5.5
0.5	47.0	52.5	54.2
1.0	48.0	54.0	56.0
1.5	48.5	54.8	56.6
2.0	48.8	55.5	57.5
2.5	49.2	56.0	58.0
3.0	49.2	56.3	58.4
3.5	49.0	56.6	58.0

Pulper condition

Furnish - 70:30 ONP/OMG

NaOH - 1.5% (exit pH 10.2)

Surfactant - 0.25%

H_2O_2 - 1.0%

Consistency - 12%

Temperature - 55°C

Duration - 30 minutes

Flotation condition

Consistency - 1.0%

pH - 8.5

Duration - 10minutes

Fig. 3:7. Variation of pulper and post flotation brightness with silicate dosage at 0% DTPA

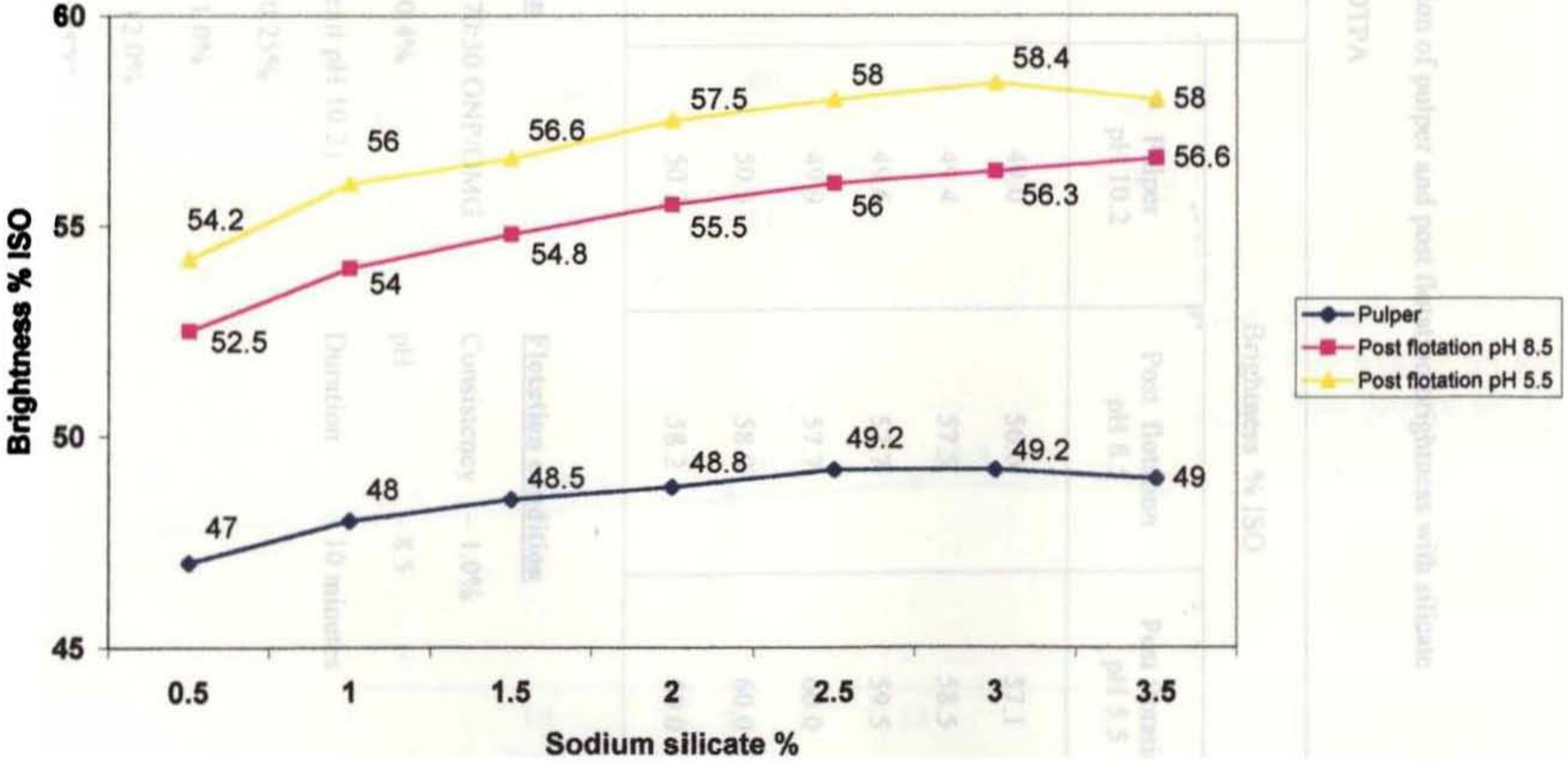


Table 3:8 Variation of pulper and post flotation brightness with silicate dosage at 0.4% DTPA

Sodium silicate %	Brightness % ISO		
	Pulper pH 10.2	Post flotation pH 8.5	Post flotation pH 5.5
0.5	49.0	56.0	57.1
1.0	49.4	57.5	58.5
1.5	49.6	57.7	59.5
2.0	49.9	57.7	60.0
2.5	50.3	58.0	60.0
3.0	50.2	58.2	60.0

Pulper condition

Furnish - 70:30 ONP/OMG

DTPA - 0.4%

NaOH - 1.5% (exit pH 10.2)

Surfactant - 0.25%

H_2O_2 - 1.0%

Consistency - 12.0%

Temperature - 55°C

Duration 30 minutes

Flotation condition

Consistency - 1.0%

pH - 8.5

Duration - 10 minutes

Fig. 3:8. Variation of pulper and post flotation brightness with silicate dosage at 0.4% DTPA

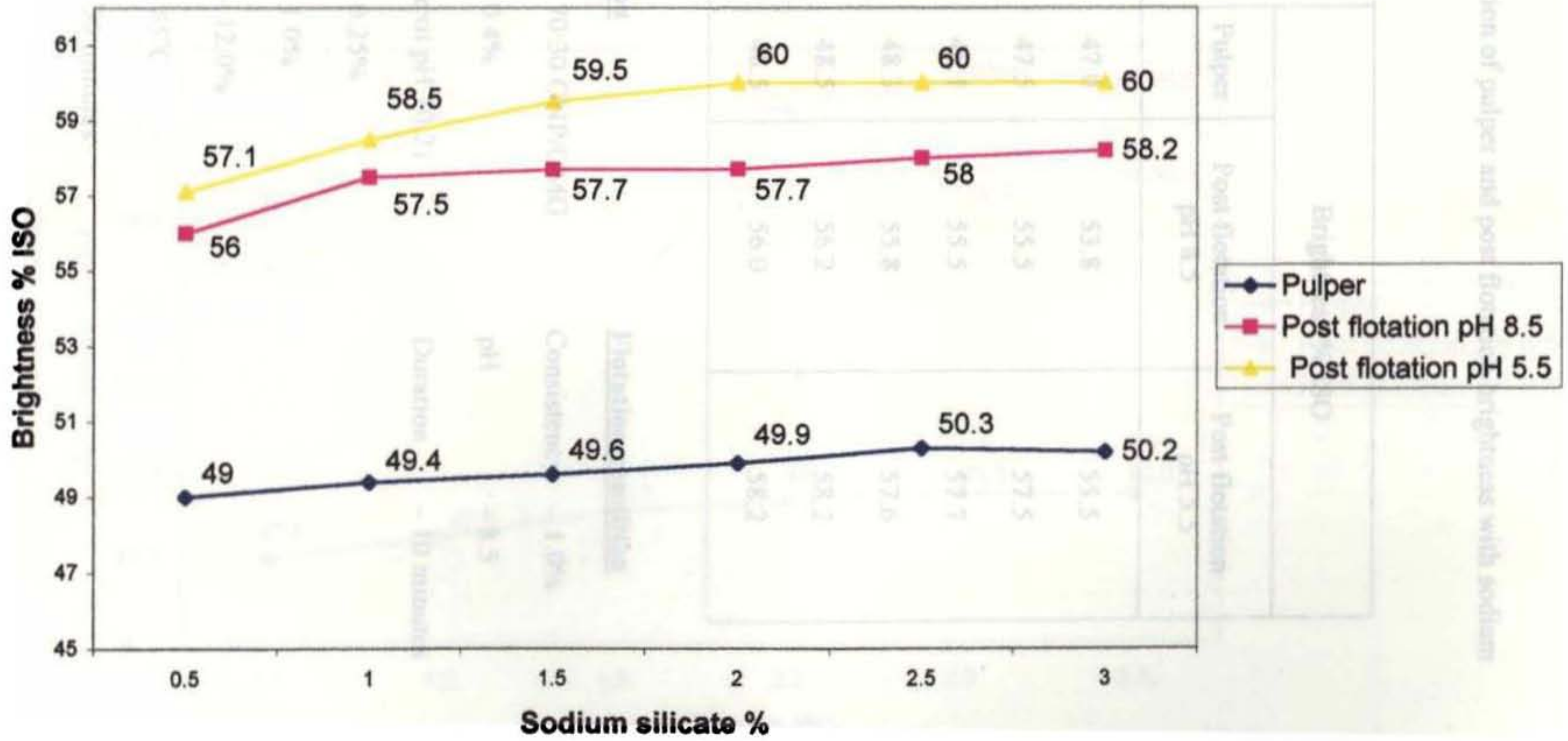


Table 3:9 Variation of pulper and post flotation brightness with sodium alginate dosage

Sodium alginate %	Brightness % ISO		
	Pulper	Post flotation pH 8.5	Post flotation pH 5.5
0.5	47.0	53.8	55.5
1.0	47.5	55.5	57.5
1.5	48.1	55.5	57.7
2.0	48.3	55.8	57.6
2.5	48.5	56.2	58.2
3.0	48.5	56.0	58.2

Pulper condition

Furnish - 70:30 ONP/OMG

DTPA - 0.4%

NaOH - 1.5% (exit pH 10.2)

Surfactant - 0.25%

H_2O_2 - 1.0%

Consistency - 12.0%

Temperature - 55°C

Duration - 30 minutes

Flotation condition

Consistency - 1.0%

pH - 8.5

Duration - 10 minutes

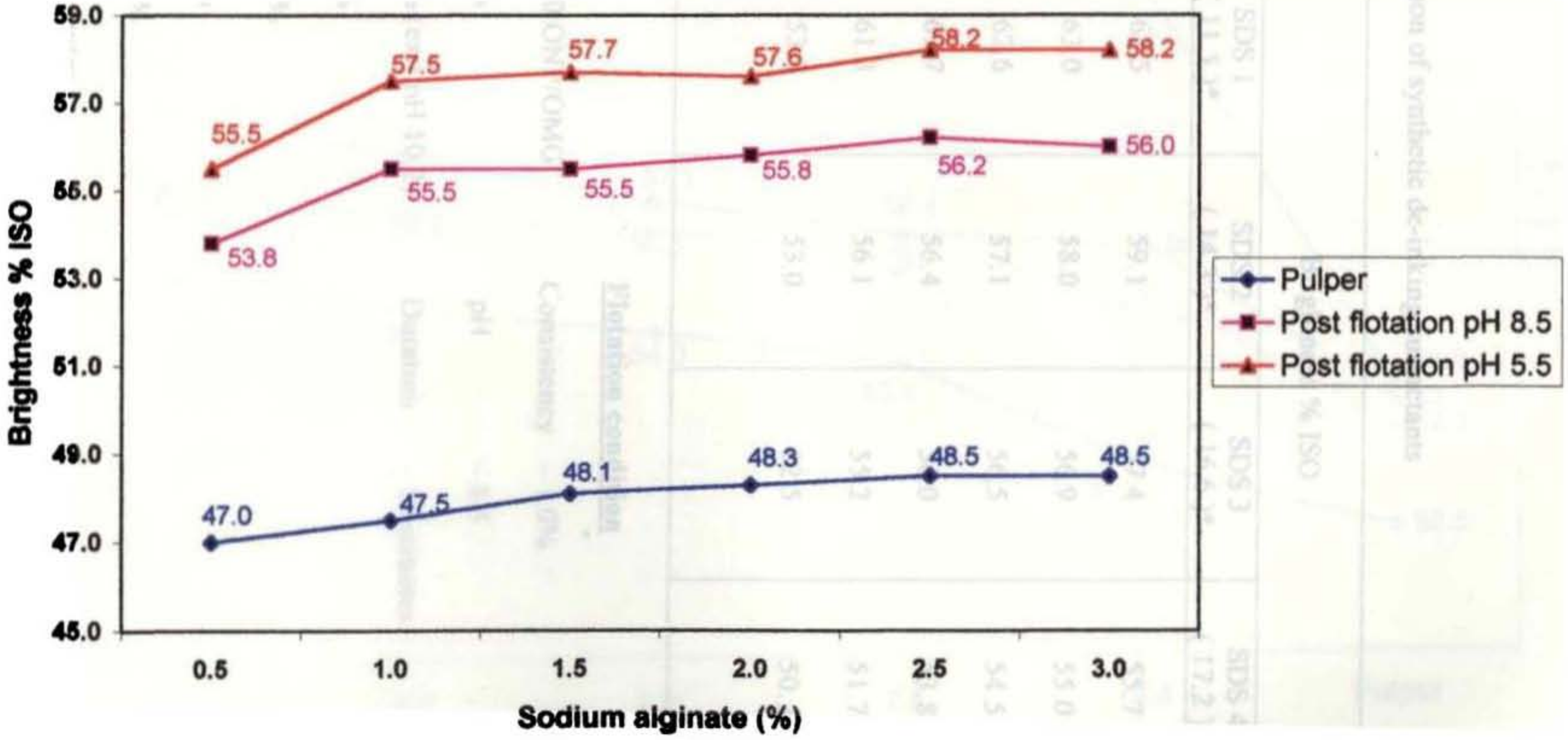


Fig. 3:9 Variation of pulper and post flotation brightness with sodium alginate dosage

Table 3.10 Comparison of synthetic de-inking surfactants

pH	Brightness % ISO			
	SDS 1 (11.5)*	SDS 2 (14.3)*	SDS 3 (16.6)*.	SDS 4 (17.2)*
4.5	63.5	59.1	57.4	55.7
5.5	63.0	58.0	56.9	55.0
6.5	62.6	57.1	56.5	54.5
7.5	61.7	56.4	56.0	53.8
8.5	61.3	56.1	55.2	51.7
Pulper	53.3	53.0	52.5	50.5
*HLB Value				

Pulper condition

Furnish	– 70:30 ONP/OMG
DTPA	– 0.4%
NaOH	– 1.5% (exit pH 10.2)
Na_2SiO_3	2.5%
Surfactant	– 0.25%
H_2O_2	– 1.0%
Consistency	– 12.0%
Duration	– 30 minutes

Flotation condition

Consistency	– 1.0%
pH	– 8.5
Duration	– 10 minutes

Fig.3:10.Comparison of synthetic de-inking surfactants

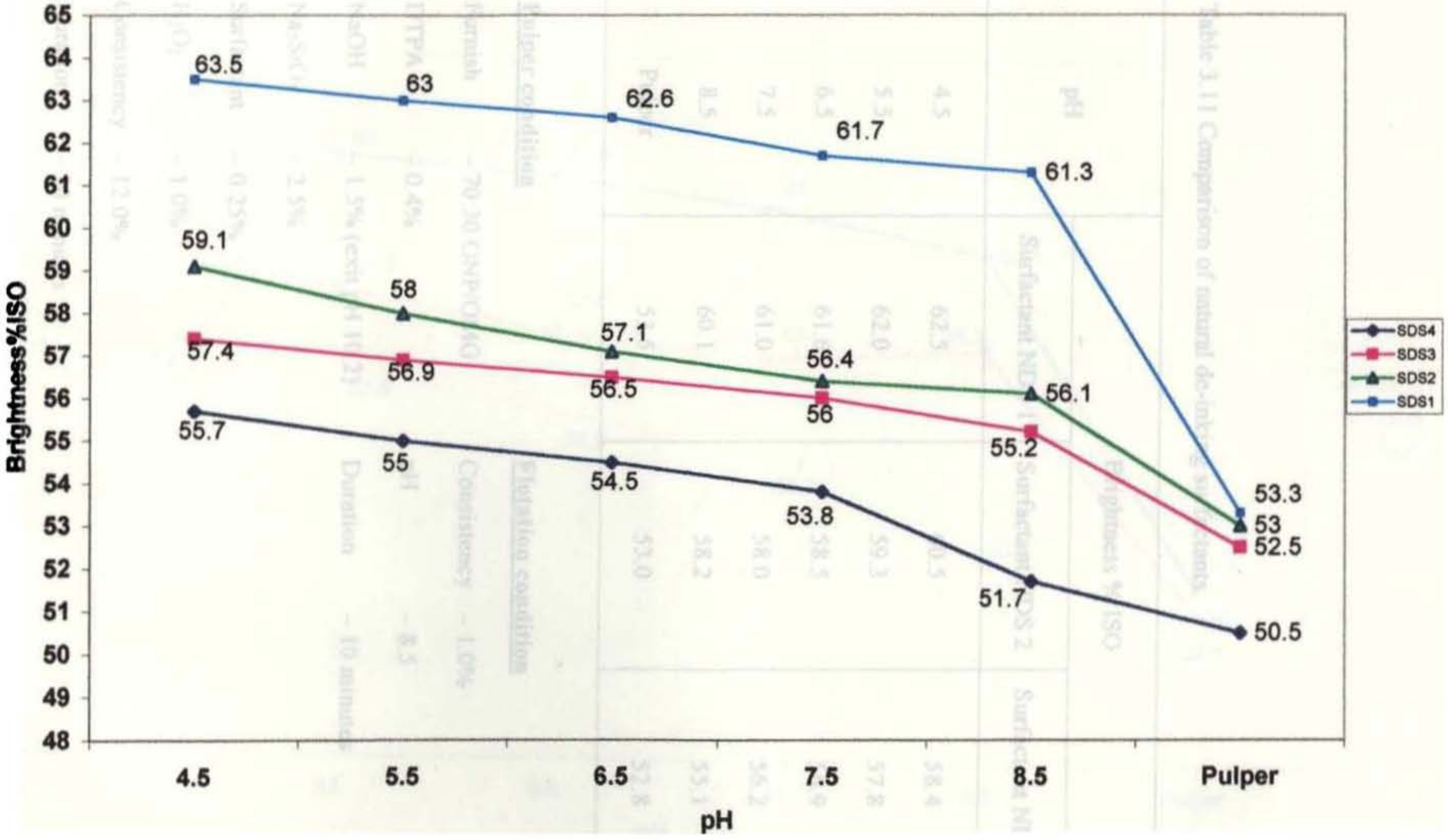


Table 3.11 Comparison of natural de-inking surfactants

pH	Brightness % ISO		
	Surfactant NDS 1	Surfactant NDS 2	Surfactant NDS 3
4.5	62.5	60.5	58.4
5.5	62.0	59.3	57.8
6.5	61.6	58.5	56.9
7.5	61.0	58.0	56.2
8.5	60.1	58.2	55.1
Pulper	53.5	53.0	52.8

Pulper condition

Furnish	- 70:30 ONP/OMG
DTPA	- 0.4%
NaOH	- 1.5% (exit pH 10.2)
Na_2SiO_3	- 2.5%
Surfactant	- 0.25%
H_2O_2	- 1.0%
Consistency	- 12.0%
Duration	- 30 minutes

Flotation condition

Consistency	- 1.0%
pH	- 8.5
Duration	- 10 minutes

Fig. 3:11. Comparison of natural de-inking surfactants

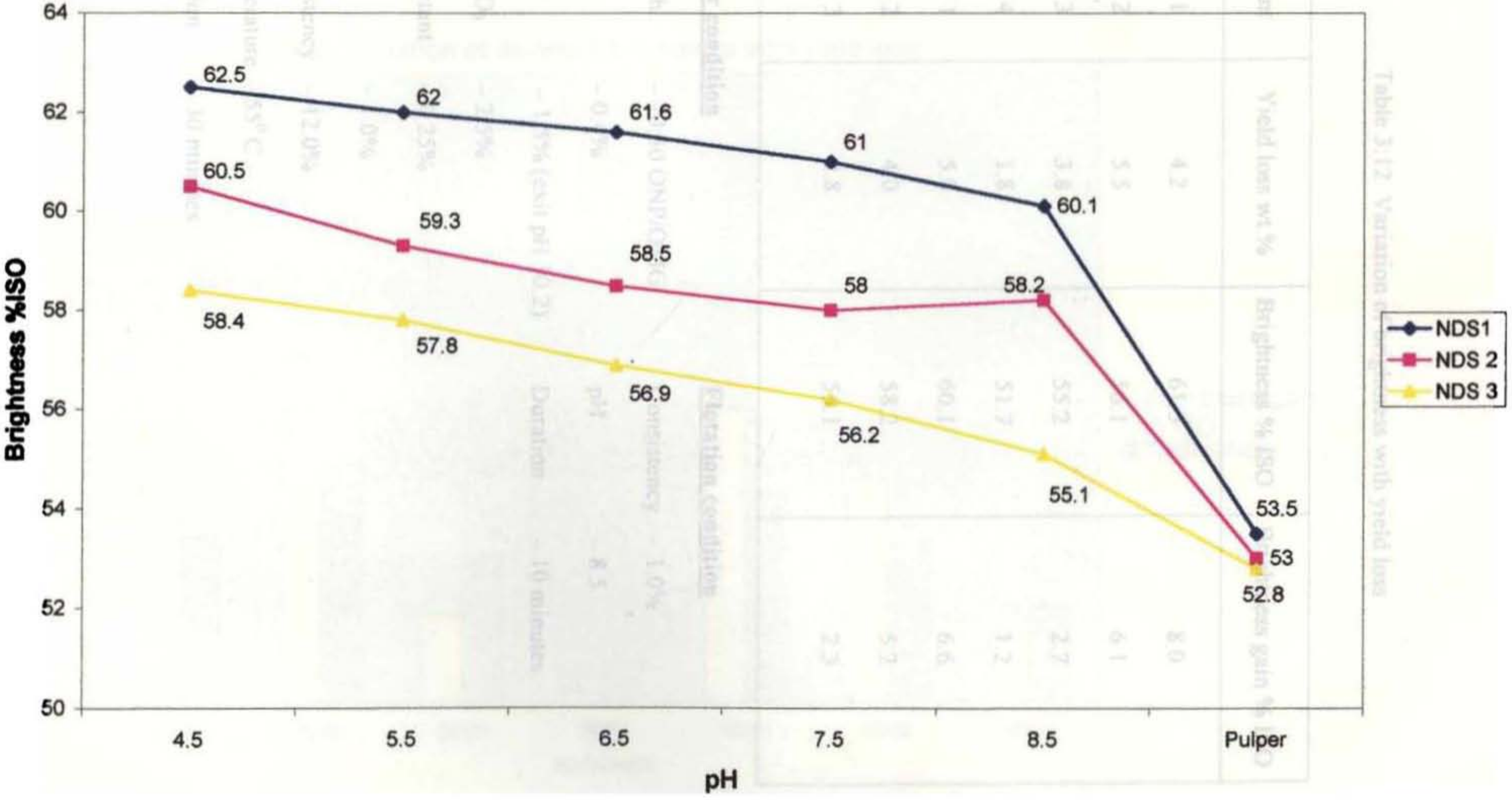


Table 3:12 Variation of brightness with yield loss

Surfactant	Yield loss wt %	Brightness % ISO	Brightness gain % ISO
SDS 1	4.2	61.3	8.0
SDS 2	5.5	56.1	6.1
SDS 3	3.8	55.2	2.7
SDS 4	1.8	51.7	1.2
NDS 1	5.0	60.1	6.6
NDS 2	4.0	58.2	5.2
NDS 3	2.8	55.1	2.3

Pulper condition

Furnish – 70:30 ONP/OMG

DTPA – 0.4%

NaOH – 1.5% (exit pH 10.2)

Na_2SiO_3 – 2.5%

Surfactant – 0.25%

H_2O_2 – 1.0%

Consistency 12.0%

Temperature – 55^0 C

Duration – 30 minutes

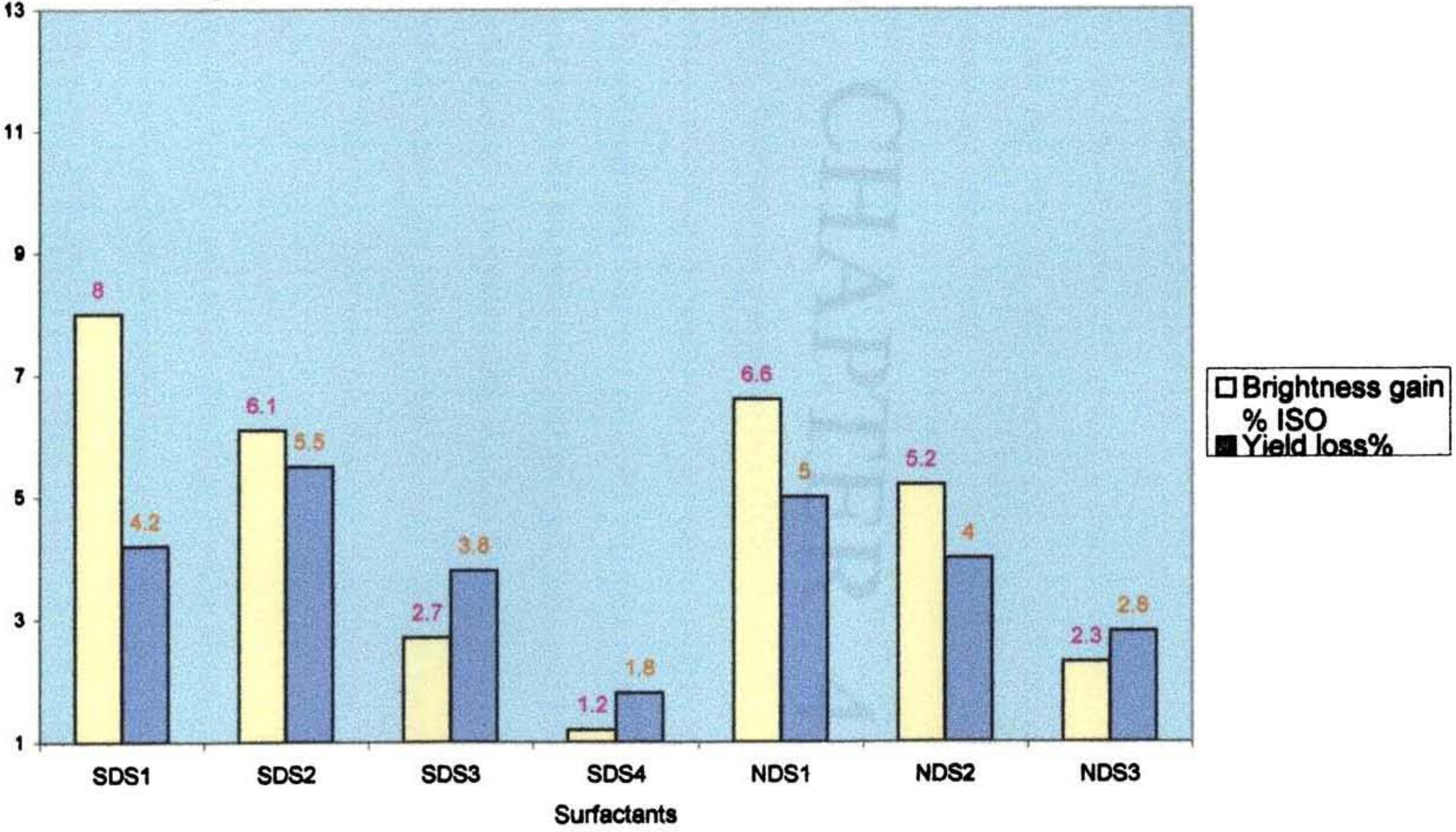
Flotation condition

Consistency – 1.0%

pH – 8.5

Duration – 10 minutes

Fig. 3:12. Variation of de-inked brightness with yield loss



CHAPTER 4

BLEACHING OF DE-INKED PULP

With the growing urge to reuse recycled fiber as a raw material source for making high quality papers, the role of bleaching chemicals is more and more critical. The aim of bleaching is to increase brightness without yellowing. Other aims of bleaching are to avoid color shades, to improve cleanliness, and to minimise yield loss.

There are three broad classes of bleaching chemicals, chlorine based chemicals, chlorine free oxidising, and chlorine free reductive bleaching chemicals (Johnson and Allison, 1992).

Environmental pressure coupled with legislation is driving the replacement of several existing chemicals used in the de-inked pulp bleaching industry. Total chlorine compound-free (TCF) bleaching is now becoming a common technology for bleaching of mechanical pulp (Sain and Daneault, 1997), and kraft pulp (Lierop *et al.*,1994). Hydrogen peroxide is increasingly used to replace the traditional chlorine based chemicals because it is more environmentally acceptable (Johnson and Allison, 1992). The other preferred chemicals are sodium hydrosulphite and formamidine sulfinic acid (FAS). This is in tune with moving away from chlorine based bleaching agents.

Pigments and dyes are two major colourants found in printing inks. Dyes, which are soluble organic molecules fixed to the fibers, are largely unaffected by flotation and washing (Hache and Joachimides, 1992). Dyes are also largely unaffected by oxidative bleaching but some can be declourised by reductive bleaching (Helmiling *et al.*, 1989; Hanchett, 1994).

A recycled fiber furnish may contain a variety of pulps, for example, from high quality bleached kraft to unbleached ground woods. Added to the heterogeneity of the fiber composition are the presence of contaminants, paper additives and dyes in the original waste paper, and the discoloration of the fiber as a result of the handling process. Thus, no single bleaching sequence is suitable for bleaching all secondary fiber pulps.

Case studies in which H_2O_2, sodium hydrosulphite, FAS and sodium bisulphite are used for bleaching de-inked pulp are discussed. The study focuses on the optimum conditions for the bleaching of recycled fiber (RCF) with the above chemicals. The search is for bleaching chemicals that can produce paper containing RCF with equivalent brightness to that produced from virgin pulp. Bleaching is performed after de-inking. Ideally all ink and paper chemicals should be removed from the furnish before any bleaching is attempted. For post bleaching, the other parts of the process must be at optimum, otherwise the contaminants present will make it uneconomic to upgrade low quality pulp (Eul *et al.*, 1989., Helmling *et al.*, 1986). It should be noted that the mechanical pulp present in recycled newsprint and magazines has been bleached at least once as virgin pulp, with hydrosulphite, chlorine based bleaching agents, or hydrogen peroxide. Again, the waste paper has got bleached in a pulper during re-pulping with hydrogen peroxide before reaching the post bleaching stage. It is reasonable to assume that recycled fibers that have been exposed to bleach reagents will be less responsive to additional bleaching compared to virgin fibers (Joachimides and Hache, 1991).

The role of hydrogen peroxide in the post bleaching is to improve the brightness of the pulp by modifying color-causing groups within the fibre such as those contained in lignin. The role of sodium hydrosulphite, FAS and sodium bisulphite is to act primarily on the dye component of the pulp. Dyes are largely unaffected by peroxide bleaching but many can be de-colorised by reductive bleaching (Hanchett, 1994).Reductive processes utilizing chemicals such as sodium hydrosulphite or FAS tend to strip the unwanted color tints from recycled pulps more effectively than do the oxidative processes (Lierop and Liebergott,1994). Consequently, recycled fiber bleaching will depend firstly on the type of furnish (i.e., the amount of lignin containing fiber and content of dye), and secondly on the brightness requirement. (Adam *et al.*, 1997). The purpose of this work is to compare the bleaching action of sodium hydrosuphite, hydrogen peroxide, FAS and sodium bisulhite on de-inked pulp produced in the laboratory.

MATERIALS AND METHODS

A 70:30 mixture of ONP/ OMG blend was pulped using a typical procedure. The pulp was then diluted to 1.0% consistency and de-inked by flotation. It was then concentrated to a consistency of 15.0% and stored.

Furnish

A 70:30 mixture of ONP:OMG blend as furnish was used for all the tests. The recently printed newspapers (ONP) and magazines (OMG) (3months old) were separately torn into pieces of one inch square and stored in opaque plastic bags as stock. From this 120gm oven-dried (105°C) sample was used for each trial.

Pulping

Chemicals were added to 870ml de-ionised water at 50- 55^0 C in the following order of: 0.4% DTPA, 1.5% NaOH (10% solution), 2.5% sodium silicate, 0.25% surfactant , and 1.0% H_2O_2 (10% solution). Immediately after adding the peroxide the pulping liquor was poured over the waste paper in the pulper.

The contents were then pulped for 30 minutes. The exit pH was controlled by adjusting the level of NaOH to give a pH of 9.5 to 10.2. The percentages given for the chemicals are on oven-dried (O.D) fiber and represent a typical formula.

Flotation

For flotation the re-pulped stock was diluted to 1.0 % consistency. Flotation was carried out for 10 minutes at pH 8.5 in the 5 litre capacity double chamber froth flotation unit with bristles. The inky foam was constantly removed by manual skimming.

Bleaching

The thickened pulp was crumbled in a laboratory blender. Chemicals were added and bleached in a controlled water bath. Buchner funnel pulp pads and hand sheets were prepared to evaluate pulp brightness. Standard test hand sheets were formed in accordance with TAPPI test method T 218 om-91and brightness measurement performed as per TAPPI test method T 452 om-87. Brightness was measured with an Elrepho Reflectance Photometer. The optimum bleaching conditions reported earlier were followed in the present investigations also.

Hydrogen peroxide bleaching

The de-inked pulp was crumbled in a commercial blender. H_2O_2 was used for post bleaching at 1.0,2.0 and 3.0 percent on O.D. fiber. The pulp was diluted with distilled water, DTPA, sodium hydroxide and H_2O_2 solution (in the same order) to 10 percent consistency. The peroxide bleaching period was 2h. at 60^0C.

Hydrosulphite and bisulphite bleaching

Sodium hydrosulphite was used at 0.5, 1.0 and 1.5% on O.D. fiber. Bisulphite concentration used was from 2% to 8%. Sealed plastic bags were used for bleaching with various dosages of hydrosulphite and sodium bisulphite. Atmospheric oxygen was excluded from the bleaching bag by removal under vacuum suction and replacement with nitrogen. The pH was adjusted as required, and the hydrosuphite solution added. Bleaching time was 90-120 minutes at 65^0 C. Pulping consistency was 5 %. The change in brightness with time was determined by the periodic withdrawal of samples of pulp. Initial pulp brightness was 60.0%.

FAS bleaching

FAS was used at 0.5, 1.0 and 1.5% on O.D. fiber. The pulp was diluted with water, NaOH and FAS solution to 10% consistency. Bleaching was continued at 60°C for 45 minutes. FAS : NaOH ratio was 2:1.

RESULTS AND DISCUSSION

Hydrogen peroxide

For several reasons, hydrogen peroxide has become a versatile bleaching agent. It can be used for bleaching mechanical and chemical pulps and also for the reinforcement of alkaline extraction stages (Liden and Ohman, 1998). The effect of sodium hydroxide addition in peroxide post bleaching is shown in Table 4:1 and Fig. 4:1.As NaOH dose was increased upto 0.75% the brightness gain reached a maximum of 3.2% ISO and then declined to 3.1% ISO at 1.0% of NaOH. The sodium hydroxide dosage is optimum between 0.75 and 1%. DTPA dosage was held at 0.15 percent. On peroxide bleaching, maintaining the proper alkalinity assures that there is sufficient per hydroxyl anion (HOO^-), the active bleaching agent (Joachimides and Hache, 1991). A ratio of 0.75 to 1 is typical.

Table 4:2 and Fig. 4:2 illustrate the effect of H_2O_2 on brightness. This study used an NaOH/H_2O_2 ratio of 0.85. The brightness gains were low (4.2% ISO unit) in relation to the high levels of peroxide applied (3%). Fig. 4:2 illustrates the increase of brightness versus peroxide and shows that very little brightness gain is achieved in going from 1 to 2% hydrogen peroxide.

Addition beyond 2% results in small incremental brightness gains. In other words the brightness tends to level out and higher brightness would not be possible. Some printing dyes are not very reactive to peroxide and it is likely that post peroxide treatment primarily bleached the fiber. It is already reported by Lierop and Liebergott (1994), that application of peroxide improved the brightness but imparted a yellow tint to the pulp. The yellowing of pulp during peroxide bleaching was probably caused by the alkaline conditions in the peroxide stage.

During alkaline hydrogen peroxide bleaching of both chemical and chemi-mechanical pulps there is a positive correlation between minimum hydrogen peroxide decomposition and an optimum bleaching result (Colodette,*et al.*,1990).

Sodium hydrosulphite (dithionite)

In de-inked pulps, chromophores may be associated with lignin and printing ink. The recycled pulp has already undergone some brightness reversion and reverted pulp is difficult to bleach again. On the other hand many printing inks (colorants) are reducible to colorless compounds. Thus, the principle action of hydrosulphite and FAS is probably on the dye component rather than the lignin component (Joachimides and Hache, 1991). Sodium hydrosulphite (sodium dithionite) is widely used in the reductive bleaching of mechanical pulps. This reagent is used under acidic conditions to produce brightness gains of upto 12 % ISO. The curves for brightness gain against pH are shown in Table 4:3 and Fig. 4:3. The figure also depicts the relationship between pH and hydrosulphite concentration on brightness gain. A low gain at low pH is found to increase to the maximum around pH 7. The optimum initial pH for hydrosulphite bleaching varies between 6 and 8. This was in agreement with earlier results reported (Pettit, 1992).

The ISO brightness for 0.5, 1 and 1.5% hydrosulphite are 62.5, 64.5 and 64.8%ISO units. Under optimum conditions the brightness increases with increasing amounts of hydrosulphite. Table 4:4 and Fig. 4:4 are used to depict the above results. The time/temperature/chemical charge relationship is important and must be optimised for each case (Johnson and Allison, 1992). A hydrosulphite stage after a peroxide stage improves the final brightness of de-inked pulp as reported by Lierop and Liebergott (1994).

Table 4:5 and Fig. 4:5 indicate the bleaching effect of FAS and hydrosulphite, under conditions optimum for both the chemicals. The bleaching performance of FAS was slightly better than hydrosulphite. At1.5% of each of the chemicals FAS produced a brightness gain of 1.5% ISO compared to hydrosulphite. It was found that the optimum condition for bleaching is not changed too much from those used to bleach virgin mechanical pulps. (Hache and Joachimides, 1992).

Sodium bisulphite

Aqueous solution of sodium hydrosulphite decomposes during storage and during bleaching process to form sodium bisulphite as one of the decomposition product.

$Na_2S_2O_4 + O_2 + H_2O \rightarrow NaHSO_3 + NaHSO_4$

If oxygen is limited it decomposes as

$2Na_2S_2O_4 + O_2 + 2H_2O \rightarrow 4NaHSO_3$

and in the absence of oxygen

$2Na_2S_2O_4 + H_2O \rightarrow 2NaHSO_3 + Na_2S_2O_3$

The sodium bisulphite formed thus has some reductive bleaching capacity(Kuys and Abbot,1996). Hence, it could be used as a substitute for hydrosulphite in the bleaching of de-inked pulps.

The trials were conducted initially to optimise the bleaching response of the bisulphite and compare it to dithionite bleaching. By determining the brightness after different reaction times the optimum conditions were determined using 8% sodium bisulphite (on O.D. pulp) at pH 7 and temperature at 65°C. The bleaching responses of the ONP/OMG blend with 8.0% bisulphite at pH 7 were compared to those produced by 1.0% hydrosulphite at pH 7 at 65°C (Table 4:6 and Fig. 4:6) and it can be seen that significant brightness gain can be made using bisulphite. Although favourable brightness gains can be made using bisulphite bleaching it can only be achieved using a high concentration of bisulphite. At the optimum conditions hydrosulhite bleached pulp gave a brightness of 64.5%ISO and bisulphite bleached pulp produced a brightness of 65.6%ISO unit. Again the bisulphite bleached pulp reached a brightness plateau around 2hrs., while the brightness of hydrosulhite bleached pulp peaks after about 1hr., and then declines.

The experiments in this study have revealed that a brightness gain of around 4.0% ISO can be obtained by the bleaching of the de-inked pulp. The pH and chemicals applied must be carefully controlled to get maximum brightness. Sodium sulphite is an unlikely replacement for sodium hydrosulphite.

Table 4:1. Variation of brightness gain with NaOH at 1.0% H_2O_2

(Initial brightness 60.0% ISO)

NaOH %	Brightness gain % ISO
0.50	2.5
0.75	3.2
1.00	3.1

Table 4:2 Effect of H_2O_2 on brightness gain

(Initial brightness 60.0% ISO) NaOH –0.85%

H_2O_2 %	Brightness gain % ISO
1.0	3.5
2.0	4.0
3.0	4.2

Fig.4:1. The relationship between bleaching chemicals on brightness gain

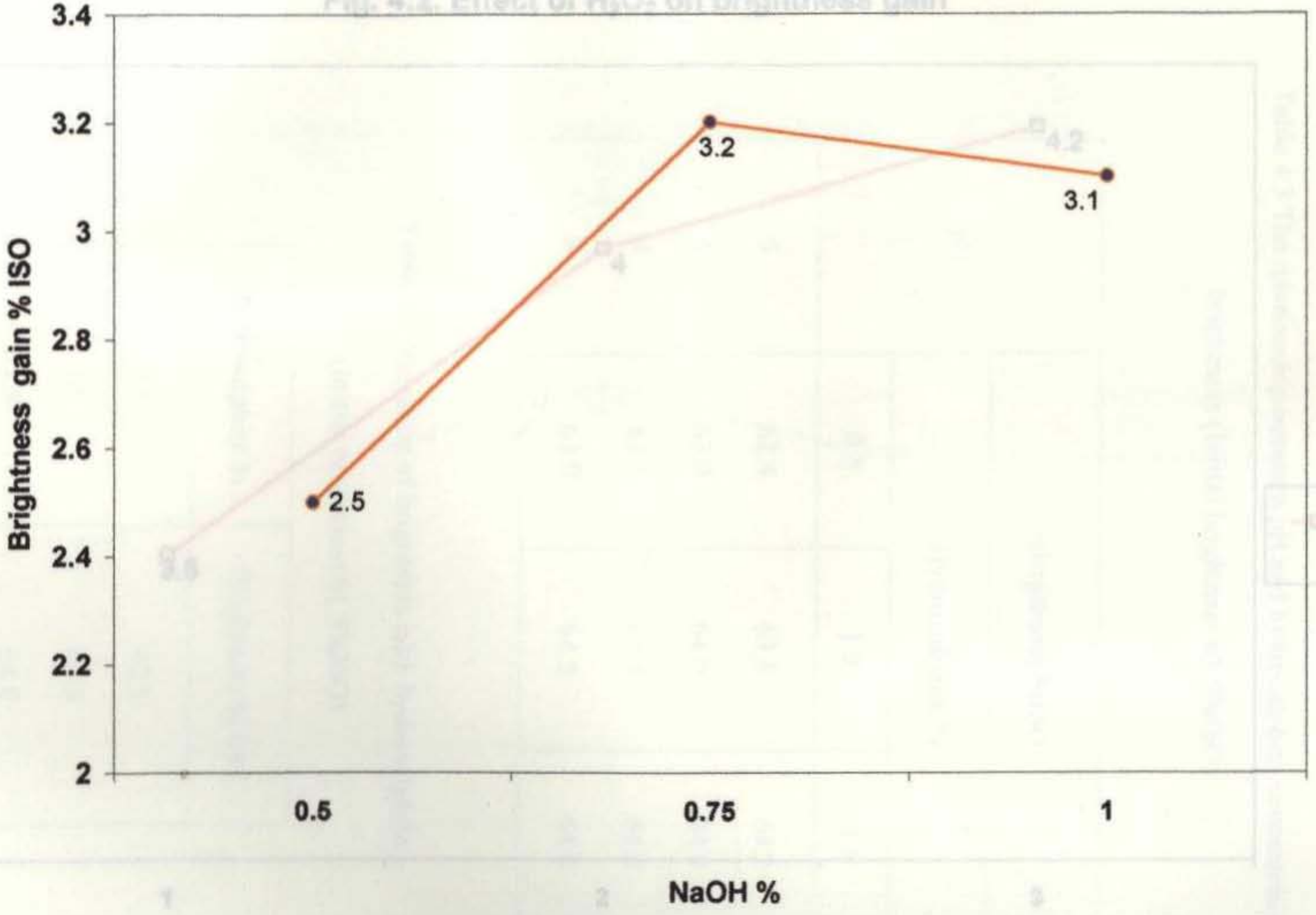


Fig. 4:2. Effect of H_2O_2 on brightness gain

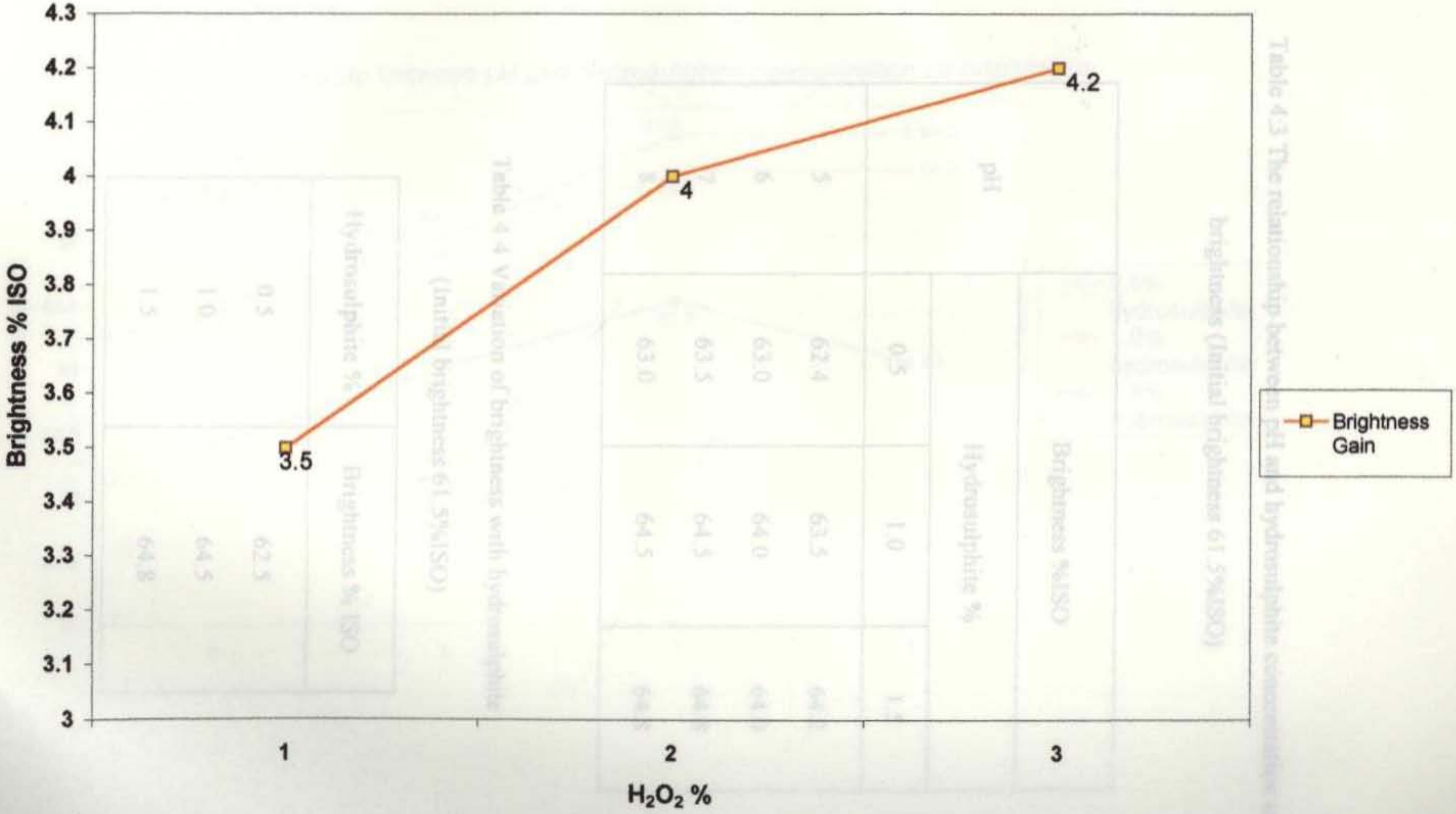


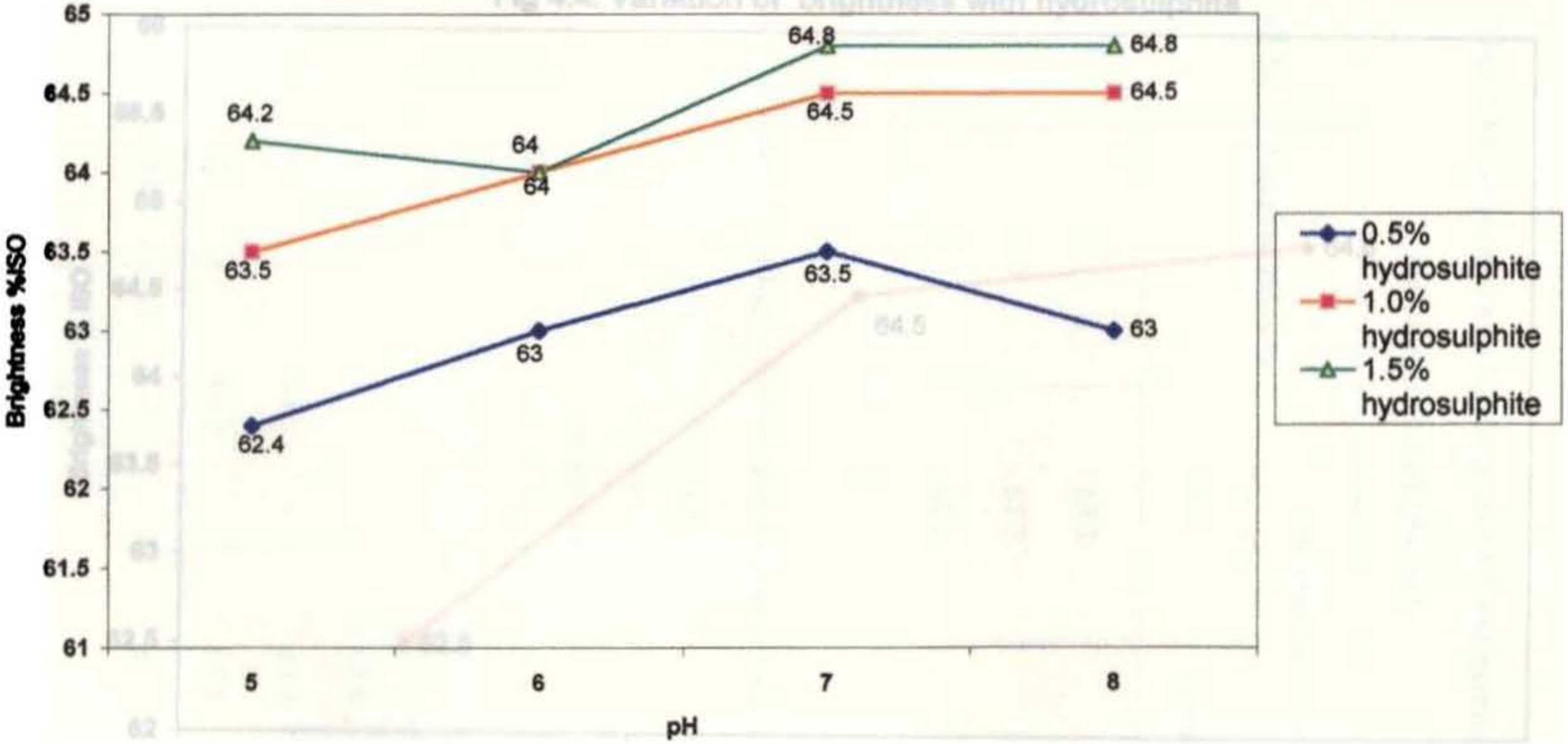
Table 4:3 The relationship between pH and hydrosulphite concentration on brightness (Initial brightness 61.5%ISO)

pH	Brightness %ISO		
	Hydrosulphite %		
	0.5	1.0	1.5
5	62.4	63.5	64.2
6	63.0	64.0	64.0
7	63.5	64.5	64.8
8	63.0	64.5	64.8

Table 4.4 Variation of brightness with hydrosulphite (Initial brightness 61.5%ISO)

Hydrosulphite %	Brightness % ISO
0.5	62.5
1.0	64.5
1.5	64.8

Fig.4:3. Relationship between pH and hydrosulphite concentration on brightness



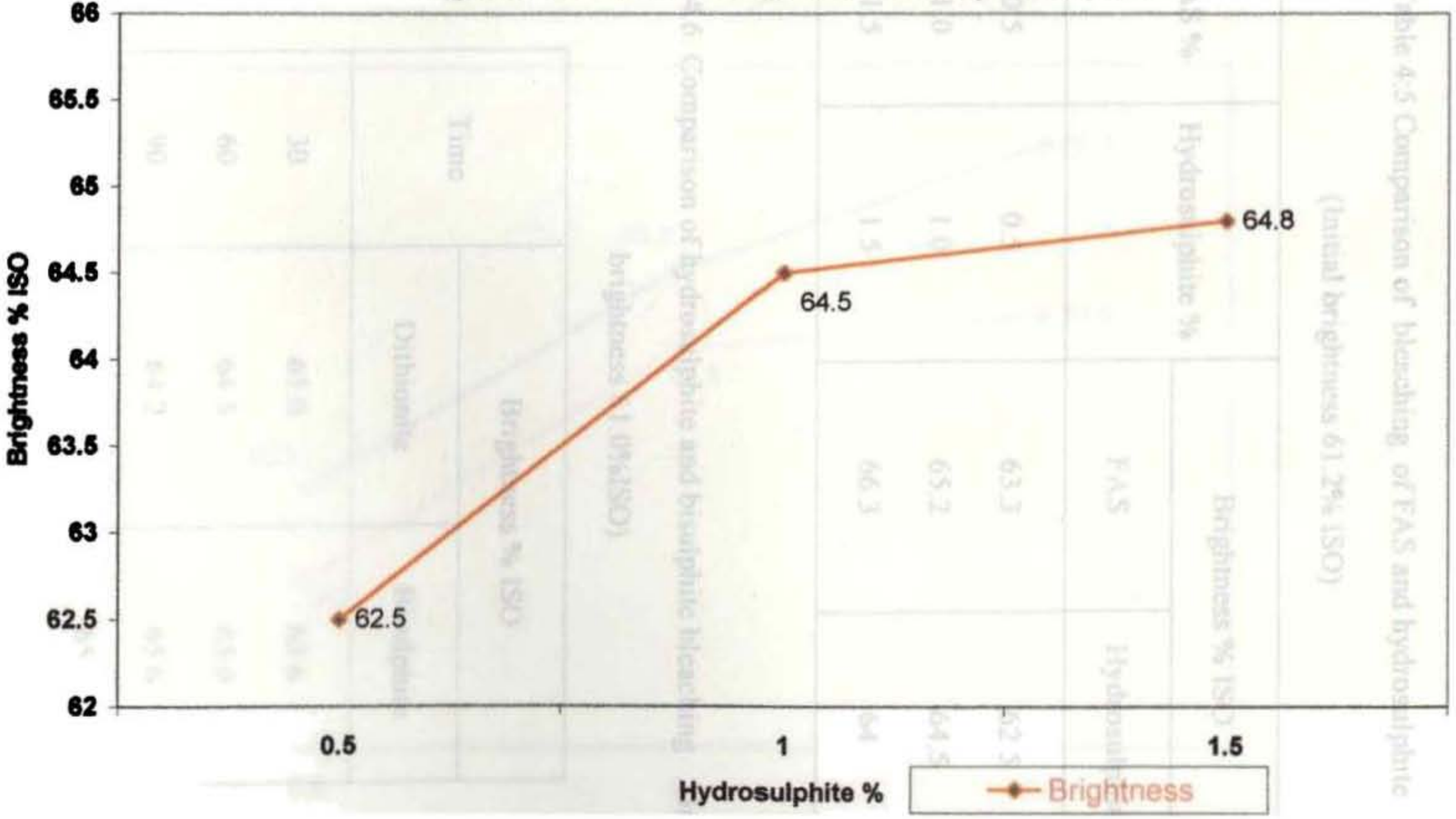


Fig 4:4. Variation of brightness with hydrosulphite

Table 4:5 Comparison of bleaching of FAS and hydrosulphite

(Initial brightness 61.2% ISO)

FAS %	Hydrosulphite %	Brightness % ISO	
		FAS	Hydrosulphite
0.5	0.5	63.3	62.5
1.0	1.0	65.2	64.5
1.5	1.5	66.3	64.8

Table 4.6. Comparison of hydrosulphite and bisulphite bleaching (Initial brightness 61.0%ISO)

Time	Brightness % ISO	
	Dithionite	Bisulphite
30	63.0	63.6
60	64.5	65.0
90	64.2	65.6
120	--	65.6

Fig. 4:5.Effect of FAS and hydrosulphite on brightness

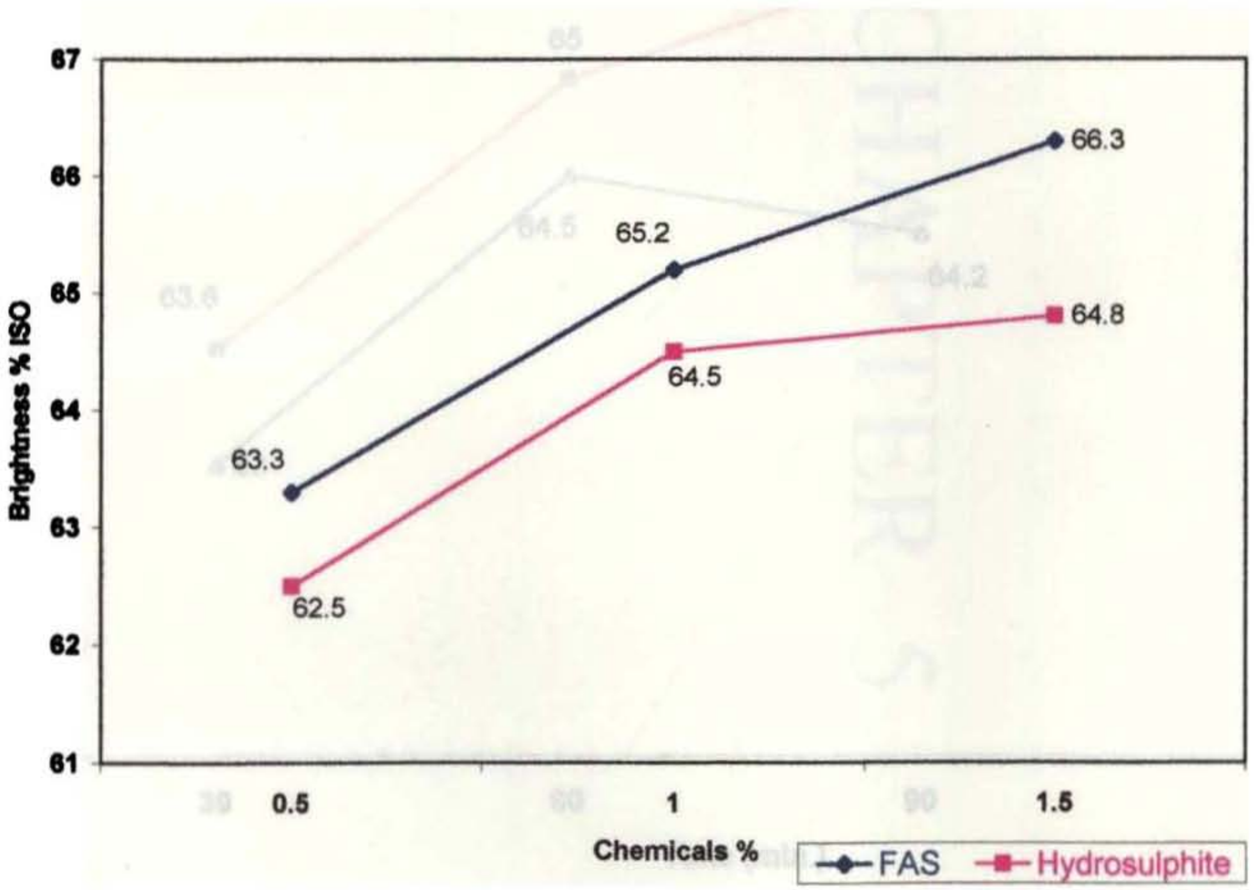
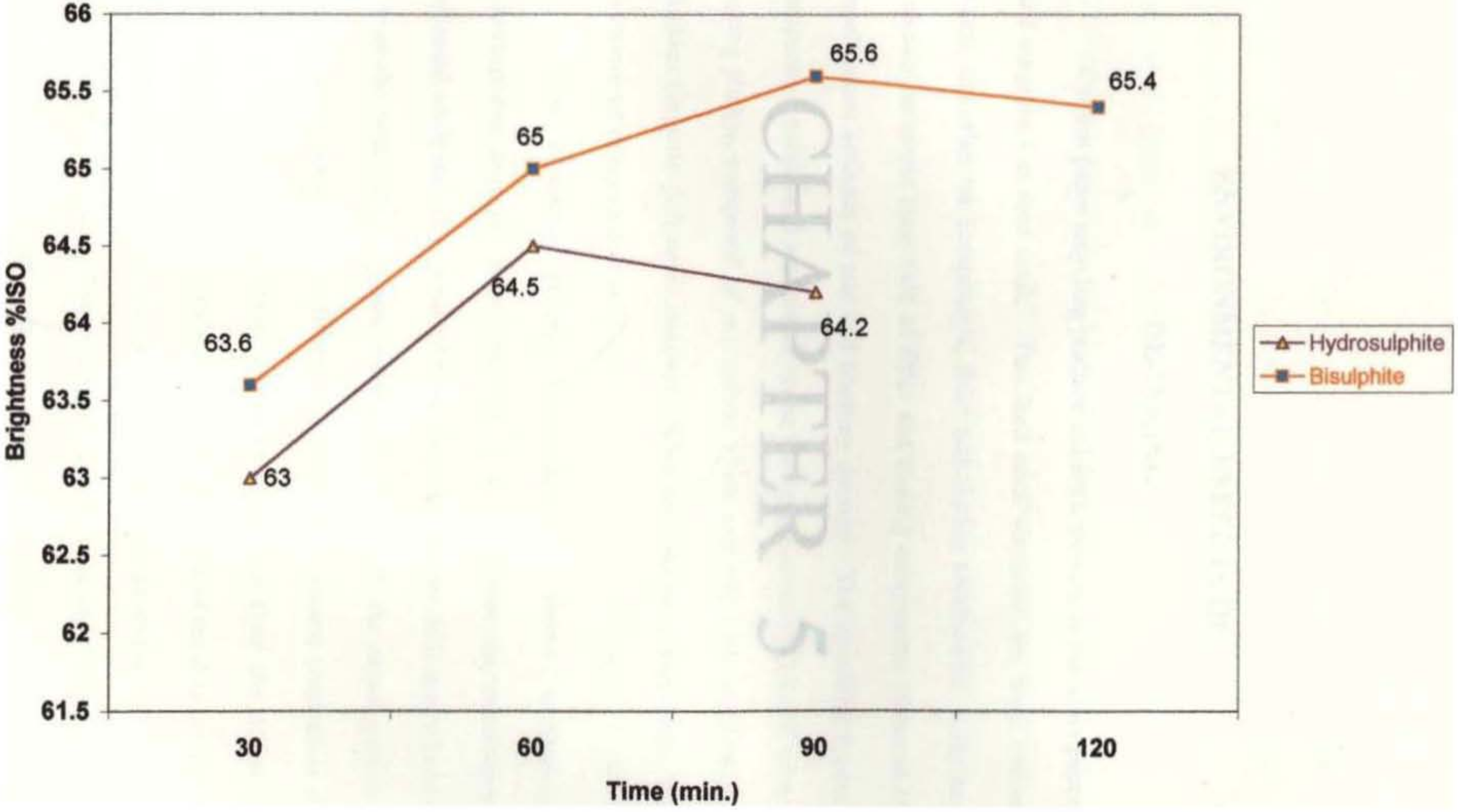


Fig. 4:6. Comparison of hydrosulphite and bisulphite bleaching



CHAPTER 5

ENVIRONMENTAL EFFECTS OF DE-INKING

Current paper recycling practice utilises a mixture of old news papers and magazines as feed stock. This feed stock comprises the fibre, carbon black, and other ink components, filler and coating components. Clay and calcium carbonate form bulk of filler and coating components followed by much lesser amounts of talc and titanium dioxide. The de-inking process produces a substantial amount of waste material commonly known as de-inking sludge, composed of the carbon black and other ink components, stickies (organic polymeric material), filler and coating components, and unrecovered or rejected fiber.

The de-inking process technology has shown tremendous development over the years, but less is known about the components released while the ink is removed from the printed paper. Still less is known about the route where by the components leave and, the extent they are degraded or removed by effluent treatment. The present attempt is to monitor the key environmental pollutants originating from the de-inking process. This information would provide at least some of the data needed to assess the impact on both river and land disposal of de-inking effluent and solid residues. Because of the increasing cost of land fill disposal and the decreasing availability of sites, it is important to find alternate disposal means for the sludge from the recycled paper plants. The amount and composition of sludge vary significantly with the type of waste paper recycled and the efficiency of the de-inking process employed (Latva-Somppi *et al.*, 1994). A typical flotation de-inking plant produces about 80-150Kg of dry sludge per ton of recycled pulp (Raitio, 1992) or 160-500Kg wet sludge per ton depending on the moisture content. This means that a recycle plant has to dispose of a substantial quantity of waste sludge which has a considerable negative impact on the environment.

Heavy metals are one such class of pollutants that must be evaluated. This is because various metal containing compounds are added to inks to achieve particular properties. For eg., blue inks contain copper phthalocyanine as one component (Richardson *et al.*,1992). The presence of such components necessitates their quantification with respect to concentration, speciation and destination.

The disposal options for solid residues produced could include incineration and land application. Another option is recovery of clay and other useful substances from solid residues. To assess these potentials the solid residue be analysed for relevant parameters (Johnston and Wiseman, 1996).

Recovery of energy, useful materials, or both from the sludge could provide an economical alternative to landfill disposal. The fly ash produced was not a hazardous material (Fredrick *et al.*, 1996). Some work has already been done on sludge composition, heavy metal content and heating value

(Kraft and Orender, 1993., Latva-Somppi *et al.*, 1994., Tran, *et al.*, 1997 and Douglas *et al.*, 1998). The combustion behavior of the sludge and the chemical and thermal properties of the resulting ashes have not been systematically studied. The objective of the present research is to study the sludge chemistry, thermal behavior and ash properties.

MATERIALS AND METHODS

The heavy metals and alkaline earth metals are measured from the process water discharge(post flotation), effluent and the sludge obtained from laboratory studies. The liquid portion passing through 63 micron sieve was collected, filtered through 0.45micrometer membrane filter and analysed as process water discharge. The inky foam was filtered through Whatman No. 40 filter paper and the filterate was again filtered through a 0.45 micrometer membrane filter and analysed as effluent for parameters such as pH, TDS, COD, and heavy and alkaline earth metals. The heavy metals Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Pb, and alkaline earth metals Mg, Ca, Sr, and Ba respectively. The filtrate was analyzed by Atomic Absorption Spectrophotometer (AAS) and Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES).

The portion collected on Whatman No.40 was termed de-inked sludge. Weighed de-inked sludge samples were dried for 24 hours at 105°C and determined the moisture content. The ash samples were prepared as follows: dried sludge samples were burned in fume hood, the residue was then heated in a muffle furnace for one hour at various temperatures from 500°C to 1200°C.

The bulk chemical composition of the ash was determined by means of AAS and ICP-AES. X- ray diffraction analysis were used for mineralogical examination of the ash.

Heating value of the sludge was measured by bomb calorimeter on oven dried samples.

RESULTS AND DISCUSSION

Table. 5.1 provides an analysis of the concentration of metals in process water discharge from flotation de-inking and in the effluent produced.

The results of analysis show the need for sequestering agent in the pulping stage since the paper contains many metals as shown in the Table 5.1. Coloured inorganic pigments, white pigments and extenders used in the printing inks are the source of the metals (Young, 1973). These metals are of some concern although the majority of them are retained in the pulp (Barassi and Welsford, 1992). Metals present in inks, clay fillers, coatings and fiber also may be released into either solid or liquid effluents form the process. The result showed that the de-inking process did not contribute significantly any Fe, Al, Mn or Zn. The concentrations of the other metals were also hardly significant in terms of their environmental impact. The behavior of any metal present would be affected by the presence of the sequestering agent. The sequestering agent can solubilise metals previously present in the particulate form which would have either precipitated or been absorbed on to other particulate material and removed through effluent treatment sludge (Richardson *et al.*, 1992). The metals thus mobilised will transport the sequesterant into the environment where, depending upon the respective formation constants of the metal complexes present in sediments of the receiving water and those in the effluent, the metal complex present in the effluent can exchange with metals form the sediments as a metal–DTPA complex (Richardson *et al.*, 1992). Sequestering agents may or may not degrade in a biological treatment process. Their behavior in the de-inking effluent water has not been thoroughly investigated.

The study of effluents showed high COD values (720mg/lit.). At high alkaline pH, de-polymerisation of cellulose occurs, as a result, an increase in COD was observed (Mahagoankar *et al.*, 1996). The effluent also showed high content of dissolved solids (712mg/lit.).

The process water discharge contained very small amounts of certain heavy metals and alkaline earth metals. The total dissolved solids content was 622 mg/lit. (Table 5:1). As these concentrations are not very high this water can be re-circulated for flotation.

De-inking sludge

Sludge samples from laboratory de-inking operation employing a flotation de-inking process was analysed and presented in Table 5:2. The sludge characteristics such as moisture content, volatile content,combustible organic material, heating value and ash contents were estimated.

Moisture content and heating value

The moisture content was found to be about 45 wt percentage. The heating value of de-inked sludge varied between 8.2-14.5 MJ / Kg. on a dry basis. This value is similar to those for black liquor, dry solids and municipal solid wastes (Latva-Sömpi *et al.*, 1994). This low value and the difficulty in de-watering fibrous materials to less than 45% moisture content (wet basis) made it a low quality fuel (Frederick *et al.*, 1996). It was also proved by Dorraiswamy *et al.* (1996) that the major limiting factor in burning the secondary fiber rejects as fuel is their high moisture content.

Ash analysis

The ash content of the de-inking sludge samples averaged about 45-50 weight percent. This showed a composition of about equal amounts of mineral and fiber. The substantial amount of ash shows that a large amount of filler and coating material with a significant potential value is being wasted currently. The chemical analysis of ash showed that it consists mostly of SiO_2, Al_2O_3, CaO and a small amount of MgO, TiO_2, Fe_2O_3, Na_2O and K_2O (Table 5:3). The main components SiO_2, Al_2O_3 and CaO are derived from coating materials primarily kaolinite clay ($Al_2O_3 . 2SiO_2 . 2H_2O$) and calcite ($CaCO_3$) (Smook, 1982) while MgO and TiO_2 are derived respectively from talc and rutile/anatase. Since SiO_2 and Al_2O_3 account for major portion of the ash it can be concluded that the ash is mainly dehydrated clay.

Table 5:4 shows the minerals identified by XRD in ash prepared at 600°C, 800°C, 1140°C and 1200°C for 1 hour. All major coating materials were found to be present i.e., clay, CaO_3, TiO_2 and talc. At 600^{0}C the presence of metakaolinite (and complementary absence of kaolinite) shows that burning off the fibre at this temperature is sufficient to dehydrate kaolinite. Conversely, the carbonate appears to be largely unaffected. This 600^{0}C temperature is insufficient to burn the ink particles and hence the material is still black in colour. At 1140^{0}C the material is essentially fully dehydrated and the carbon is removed (Johnston and Wiseman,1996).

On heating to 970-1000^{0}C, the metakaolinite begins to break down and transforms into amorphous silica and an alumina-silica spinel phase. Also, the carbonate is reduced and a calcium silicate phase with a woolastonite type structure begins to form. This reaction sequence progresses with increased heating through 1000 to 1100^{0}C. At this stage the formation of refractory mullite and cristobalite from metakaolinite have commenced. At 1200^{0}C calcium silicate is the major phase (Latva-somppi *et al.*,1994).

Visual observation and increased difficulty in grinding the samples showed clearly that with increased heating and the progressive formation of calcium silicate, mullite and cristobalite phases, the material became more fused and abrasive in nature. This is a very undesirable characteristic for any potential paper filling or coating application as such abrasive materials will cause unacceptable wear on the paper making and coating machinery.

These observations obtained with XRD results suggest that it is not possible to produce an ash which has the required properties for its subsequent use in paper filling and coating applications.

The initial de-inking sludge was black or grey in colour due to the ink particles present. With incineration the brightness progressively increased. At high temperatures the material has developed a significant yellow undertone, which is not a suitable condition for any paper coating application.

In a conventional incineration process the fiber and organic matter are converted to carbon dioxide and to water by burning. The mineral matter around 50% of the initial de-inking sludge is converted to ash and has to be disposed of by land filling. To achieve a white product after fully oxidising the carbon and colourants in the ink requires about 1100^0C. At this high temperature the carbonate and clay components react to form a product composed of calcium silicate, mullite, and cristobalite phases fused together as agglomerates, which are irregular and abrasive. Due to combustion other impurities are also oxidised and a yellow undertone is imparted to the product. At $600\text{-}800^0$C the clay component is dehydrated but the ink particles are not oxidised effectively. It is hence very clear that thermal incineration alone is unable to yield a product with properties suited for use in paper filling and coating application. It thus seems that continued disposal by land filling is the option now available for the de-inked sludge or its ashed residue.

Table 5:1. Results of analysis of process water discharge and liquid effluent

Parameters	Concentration μg/L.	
	Process water discharge	Effluent
*TDS	622.00	712.00
*COD	--	720.00
Al	1015.30	1496.40
V	12.17	3.74
Cr	172.53	28.78
Mn	214.55	169.70
Fe	256.33	543.30
Ni	8.22	5.76
Cu	42.14	182.52
Zn	299.06	619.20
Cd	2.41	3.71
Pb	55.00	62.80
Mg	421.25	444.32
*Ca	13.05	5.17
Sr	22.48	11.97
Ba	673.40	9.73
*mg/L.		

Table 5:2 Composition of sludge

Moisture, wt %	-	56.46
Dry solids, wt %	-	43.54
Dried at 105°C, Proximate, wt %		
Ash	-	45.20
Volatiles	-	47.54
Fixed carbon	-	7.25
Calorific value (MJ/Kg.)	-	10.7

Table 5:3. Chemical composition of ash and clay

Element oxide	Heating at 600°C	Heating at 1140°C	Clay
SiO_2	33.45	37.80	46.00
Al_2O_3.	20.27	22.02	39.00
Fe_2O_3	0.72	0.76	0.40
MnO	0.07	0.08	--
CaO	29.57	32.37	0.05
MgO	2.45	2.74	0.05
TiO_2	0.53	0.60	0.45
Na_2O	2.01	1.99	0.07
K_2O	0.16	0.11	0.03
P_2O_5	0.92	1.03	--
Loss on ignition	9.49	0.30	14.00

Table 5:4. Mineral components in the de-inking sludge

Sample	Major phases	Minor phases
Initial de-inking sludge	Calcium carbonate Kaolinite clay	Talc
TC 600°C	Meta Kaolinite Calcium carbonate	Talc
TC 800°C	Meta Kaolinite Amorphous silica	Talc Calcium silicate
TC 1140°C	Calcium silicate	Mullite Cristobalite
TC 1200°C	Calcium silicate	Mullite Cristobalite
TC - Thermal combustion		

CHAPTER 6

SUMMARY AND CONCLUSION

The present investigation as detailed in the previous chapters definitely meets its primary objectives. The objectives were analyzed in each chapter in the following way. The results were briefly discussed.

Chapter 1.**Introduction**, deals with the need for recycling waste paper, the history of de-inking, present day status and problems of de-inking and an overlook of the main objectives with the program followed for present study.

Chapter II. **Comparison of floatation cells** deals different types of flotation cells, their ink removal efficiency and fiber carry over loss. Three types of flotation cells were employed in the study, they are single chamber cell, double chamber cell without bristles, and double chamber cell with bristle lined inner walls. Among these the double chamber with bristles was found to have better ink removal efficiency and less fiber carry over loss.

In addition to this, de-inked pulp evaluation was also done. For this physical properties of the pulp such as tensile, tear, burst, freeness and ash content etc. of the de-inked pulp were analysed. Optical properties like brightness, opacity, light scattering coefficient and light absorption coefficient etc. were also analysed. The pulp evaluation results of two blends of ONP/OMG in the ratio 70:30 and 80:20 were compared. It was found that the laboratory de-inked pulp from the present study had comparable properties and that a 10% OMG difference in the furnish did not affect the strength and optical properties appreciably.

The role played by sodium hydroxide, DTPA, sodium silicate, hydrogen peroxide and surfactants were described under the title **"The role of different chemicals in de-inking"** in chapter III. The de-inking response of newsprint and magazine furnish, pulping conditions and floatation were evaluated and presented in this chapter. The importance of these chemicals in de-inking was established. Sodium alginate was found to be a suitable replacement for sodium silicate. The evaluation of the effectiveness of commercially available surfactants in de-inking by flotation were compared. Screening of materials having surfactant properties, lead to the extraction of three plant products. Their de-inking properties were evaluated and compared with each other and also with commercially available surfactants.One of them was found to have better de-inking capability.

Bleaching of the de-inked pulp for higher brightness pulp grades is discussed in Chapter IV, **Bleaching of the de-inked pulp**. A comparative study of the oxidative and reductive bleaching was discussed. Bleaching by hydrogen peroxide, sodium hydrosulphite, sodium bisulphite and FAS was dealt with. The effect of bleaching on brightness of de-inked pulp was estimated.

Chapter V, **Environmental effects of de-inking**, is an attempt to generate data regarding the major environmental effects of de-inking operations. The solid and liquid effluents were analyzed and their components were identified and estimated. Analysis of the laboratory de-inked sludge, and its ash were also done. The heating value of the sludge was estimated. X-ray diffraction data of the de-inked ash was generated to identify the mineral components. A discussion on environmental impacts of de-inking was made. The possibility of recovering the clay component as a paper filling material was also discussed.

CONCLUSION

- The present investigation has helped to gain a fundamental understanding of what is occurring in de-inking process.
- De-inking process requires careful balancing of physical and chemical conditions to produce the most effective ink removal and brightening of the de-inked fiber .
- Production of good quality de-inked pulp can be achieved by flotation de-inking.
- Under optimized conditions around 60% brightness could be obtained by flotation de-inking and a further gain of nearly 4 to 5 % by an additional bleaching stage.
- The total rejects could be limited to around 5% under the experimental conditions.
- Sodium alginate and surfactants isolated from natural products could make the process environmentally favourable.

in India this figure is much low. Technical challenges involved in greater and better utilisation of waste paper is improving the quality of these fibers to the same level as that of virgin fibers. The difficulties for countries like India will be that they will be forced to deal with an ever-decreasing quality of waste paper in the future. Therefore, in view of future raw material shortage and environmental legislation to maintain ecological balance, there is an immediate need to develop a de-inking technology which could ensure uninterrupted supply of de-inked waste paper pulp suitable for making all type of light coloured paper grades including writing and printing papers. I believe that this study is one step forward in that direction. The major companies involved in paper making, in both public and private sector, may turn some of their profits to research in this field.

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