BLEACHING OF POSSUM FUR

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ABSTRACT

The goal of this project was to develop a process for the industrial scale bleaching of possum fur.

Research was undertaken into the bleaching of possum with regard to whiteness of final fur, damage occurring to fur and prevention of matting to fur.

A process was supplied consisting of kill, mordant, oxidative bleach, strip and reductive bleach steps. This process produced fur with a loss of around 9.5% and alkali solubility of around 70%. Improvements made to this process gave a loss of around 5% and alkali solubility of around 50%.

The main alterations made to the process were

(i) Changing the reducing agent and pH of the mordant and lengthening this stage.
(ii) Altering the temperature, time and pH of the oxidative bleach.
(iii) Shortening the strip stage
(iv) Altering the reagent system of the reductive bleach

The displacement bleaching system used was found to be successful in preventing matting of the fibre provided care is taken in transferring the wet fur for drying.

The main difficulty encountered in scaling up the laboratory process was a compression of the fur during oxidative bleaching resulting in a build up of pressure and flow problems through the fur. This is due in part to the hollow nature of possum fibre which gives it a large degree of buoyancy and the swelling of the fibres during oxidative bleaching. Changes in the surface chemistry of the fibres occurring during oxidative bleaching are also thought to play some part since these problems are not encountered with fibre which has undergone a successful oxidative bleach.

These problems were countered by using a shallower bed of fur for bleaching, reducing the flowrate through the fur and reducing the temperature of the oxidative bleach to give a more gradual bleach.

These modifications allowed the successful bleaching of a 3.5 kg batch of fur.

A larger scale pilot plant for the bleaching of 15 kg batches was constructed. An attempted run on this plant using the conditions developed in the smaller plant was unsuccessful. It was specified that the lid on the top of the plant be clamped in place however this was not undertaken as a cost and time saving measure. This then came unstuck during bleaching leading to the overflow of the vessel.

Further work is required to optimise the lower temperature oxidative bleach. With this undertaken it is recommended that the lid be clamped into place on the larger plant and the design parameters determined on the smaller plant verified before further scale-up is attempted.

A full scale plant could not be constructed within the time frame of the project.

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CHAPTER 1 LITERATURE SEARCH

1.1 INTRODUCTION

The majority of the literature on bleaching of fibres pertains to wool. Literature dealing specifically with the bleaching of fur is comparatively rare and usually specific to a particular species. The processes for bleaching of wool and fur have some similarities and the ideas mentioned in the wool papers are worthy of investigation on possum fur, as are those in papers dealing with the bleaching of other types of fur.

The purpose of the experimental work in this project is to improve upon the bleaching process currently available to Gray Fur Trading from the bleaching of whole skin furs with regards to product loss/damage, matting of fur and the cost of chemicals. When bleaching fur, or other keratinous fibres, some trade-off has to be made between "whiteness" of the product obtained and damage occurring to the product. It is the intention of Gray Fur Trading to blend the bleached fur with wool for garment manufacture. For this reason it will be necessary to obtain a significant degree of whiteness, as it is desirable that the finished product can be dyed any colour desired. The focus of the experimental work will be in obtaining this whiteness with minimum damage to the fur.

1.2 PRESENT REGIME

The following method in table 1.1 was obtained from Fur Dressers and Dyers, Dunedin, New Zealand. This method is used for the bleaching of furs on the pelt. Spinning between treatments to aid in the removal of the previous stages reagents is not feasible for loose fur since this causes matting of the fibres.

Table 1.1 Method Provided by Fur Dressers and Dyers

Stage	Reagents	Conc. (g/L)	Temp (°C)	Time (hours)
Kill	Sodium metabisulphite	11	30	3
spin				
Mordant	Ferrous Sulphate	11	40	overnight
	Ammonium Chloride	11		
	Cream of Tarter	2		
	Sodium Hydrosulphite	0.2		
	Formaldehyde	2 mL/L		
spin				
Bleach	Oxalic Acid	2	30	overnight
	Ammonium Chloride	8		
	Sodium Pyrophosphate	8		
	Hydrogen Peroxide	30 mL/L (50% w/w)		
	Soda Ash	2		
	Sodium Bicarbonate	2		
spin, wash, spin				
Strip	Oxalic Acid	8	30	2
	Ammonium Bifluoride	4		
spin, wash, spin				
Bleach	Sodium Hydrosulphite	3	30	2
spin, wash, spin				

1.3 EXPERIMENTAL CONSIDERATIONS

1.3.1 SAMPLING

The experimental work must be undertaken with a representative sample of fur so that the results obtained are applicable to industrial use. Possum fur comes in a variety of shades and the texture of the fur varies depending on the position of the fur on the possum. The fur is longest and thickest on the mid-back and decreases in length and thickness towards the belly. Longer, coarser, guard hairs are also present throughout the fur to an extent which varies depending on the genetics of the possum.

It will be necessary to obtain possum furs encompassing the range of fur shadings and fibre lengths to be used, to draw samples from. It is known that the lighter the fur the easier it is to bleach, for this reason the majority of the work will involve grey furs. The fur supplied will be homogenised so that representative samples can be drawn for processing.

1.3.2 MEASUREMENT TECHNIQUES

Whiteness can be measured by reflectance spectrometry. Various "whiteness indices" have been reported in the literature (Teasdale and Bereck 1981), (Cegarra *et al.* 1976) and these will be compared with visual appraisals of the bleached fur before an index is decided upon for use.

There are three techniques which can be applied to assess damage occurring to the fur. The loss of mass occurring during a processing step, the change in alkali solubility and a breaking strength measurement. The loss of mass during processing has been set as a specific target. This impacts directly on the profitability of the process, and the greater the mass lost from a fibre the more brittle it will be. The alkali solubility provides an indication of the scission of disulphide linkages of the keratin which is an indication of the degree of damage to the fibres (Cegarra and Gacen 1983).

1.3.3 INITIAL EXPERIMENTATION

The results given by the current process used by Gray Fur Trading will be used as a reference point for modifications made to the process. The pH of the various stages in the process will be measured since these are important process variables and are currently unknown. The Gray Fur Trading method will be undertaken using the displacement bleaching method to determine the effect this has on the matting of the fur. Initial experiments will focus on implementing the changes most likely to lead to improvements, based on a survey of the literature. This will be followed by "fine tuning" the process to find the optimum conditions for the important process variables.

1.3.4 OPTIMISATION

Due to the multi-stage nature of the bleaching process, the effects of each stage will need to be considered separately. The mordant, oxidative bleach and reductive bleach systems are thought to be primarily responsible for both the whitening of the fur and the damage occurring to the fur and so represent the main area for improvement. The kill and strip stages may possibly be eliminated from the process. The following paragraphs detail the purpose of the stages of the bleaching process and their important variables.

1.3.4.1 Kill

A kill refers to any preparatory treatment applied to the fur to make it more receptive to the mordanting and bleaching processes. This stage currently consists of a treatment with sodium metabisulphite. The effectiveness of this stage will be evaluated by comparing the bleaching and damage results when this step is excluded from the process.

1.3.4.2 Mordant

The colouring in fur is caused by the presence of melanin pigments in the fur. Eumelanin (responsible for black, dark brown and grey pigments, such as obtained in grey possum fibre) is formed by the polymerisation of the products of the enzymatic oxidation of tyrosine. The polymerisation results in a highly cross linked, highly conjugated system (Bereck 1994). Melanin does not refer to a specific compound but rather to the products of this particular process.

Stoves (1976) provides a much more detailed review of the processes responsible for eumelanin formulation and also describes the processes leading to the formation of pheomelanin (responsible for yellow and red pigments).

In a mordanted bleaching process, iron catalyses the decomposition of hydrogen peroxide leading to an enhanced bleaching process (Laxer and Whewell 1955). Iron does not bind to pheomelanin and therefore red fur is not bleached to the extent that grey fur is bleached. It is for this reason that "redneck" possums (grey possums with red fur throughout the body) are not suitable for bleaching.

Keratin is the fibrous protein which provides protective outer coatings for animals. Most notably fur, hair, wool and feathers but also external appendages such as claws, horns and nails. It is distinguished from other fibrous proteins by its high level of cysteine, which gives rise to disulphide linkages within the keratin protein.

Iron absorbed by melanin catalyses the decomposition of hydrogen peroxide via a radical mechanism (mechanism detailed in section 1.3.5.2), leading to enhanced bleaching.

The amount of iron absorbed by the melanin needs to be maximised, while the amount retained by the keratin of the fibres must be minimised, so that the attack of the aggressive hydroxyl and perhydroxyl radicals is localised as much as possible at the melanin pigments (Bereck 1985, Bereck 1994). Experiments will be undertaken where different treatments are applied to the fibres and the iron content then determined. The goal is to maximise the amount of iron absorbed by the fibres after rinsing to remove loosely bound iron (i.e. to the keratin). The efficiency of the rinsing step can be determined by analysing the iron removed by a second rinsing step and by comparison with unrinsed samples. Atomic absorption spectroscopy can be used to determine the iron content of the fibres after a digestion step as performed by Laxer and Whewell (1955). The damage occurring to the fibres can be measured by the loss of weight of the fibres and an increase in alkali solubility occurring (Cegarra and Gacen 1983).

The variables to be considered and their effect on the process are:

1.3.4.3 pH:

There will be a certain pH, thought to be at some acidic value, at which maximum absorption of ferrous iron occurs. Work by Laxer and Whewell (1955) showed differing amounts of iron absorbed by wool at different pH and similarities in the nature of the fibre suggest that this would also be the case for furs.

1.3.4.4 Temperature and time:

Increases in both these values will lead to a greater uptake of iron up to the point where maximum absorption will occur, i.e. once 'saturation' of the melanin is achieved. Too high a temperature (greater than 70-80°C) or too long an exposure period (greater than 24 hours) will not be practical for industrial applications. In all the process steps there is a strong interaction between the temperature of processing and the time required, with higher temperatures leading to lower process times.

1.3.4.5 Concentration of Iron

Reaction kinetics state that increases in iron concentration will lead to a greater rate of absorption. Bereck (1994) found that the total amount of iron absorbed by wool fibres did not increase when the concentration of ferrous iron was greater than 0.035 M. Since ferrous sulphate is not a particularly expensive reagent, concentrations could be on the higher side, provided this does not adversely impact on the adsorption of iron by the fibre keratin. Of importance is that the concentration is above that which leads to the maximum level of iron bound to the melanin.

1.3.4.6 Reducing agent

A reducing agent is necessary to prevent the oxidation of iron (II) to iron (III) since the later species will not give the selective bleaching required, as it shows similar affinity to melanin and keratin (Bereck 1994). Literature on reductive bleaching of wool has shown that the reducing agent used can damage the fibre, sulphur based reagents in particular. In the selection of the reducing agent it must be ensured that the agent does not cause excessive damage to the fibre. Two options are sodium hydrosulphite with formaldehyde as a protective agent (as per the method detailed in table 1.1) or the more expensive hypophosphorous acid (or phosphorous acid) which have been shown to cause very little fibre damage (Bereck 1985, Bereck 1994).

1.3.4.7 Rinsing

Laxer and Whewell (1955) found that ferrous iron-melanin interactions are stronger than ferrous iron-keratin interactions. Bereck (1985, 1994) found that rinsing the fibres after mordanting with a hot, dilute, hypophosphorous or phosphorous acid solution gave a selective desorption of iron from the fibre keratin. This in turn localises the attack of the peroxide radicals at the melanin minimising damage to the fibre.

1.3.5 OXIDATIVE BLEACH

The goal here is to obtain maximum bleaching with minimum damage occurring to the fibre. The important variables and their effect on the process are:

1.3.5.1 Concentration of Hydrogen Peroxide

Increasing the hydrogen peroxide concentration will increase the bleaching effect up to a point where no additional bleaching effect is obtained but degradation of the fibre continues to increase (Cegarra and Gacen 1983). Reasonably high levels will be required due to the highly pigmented nature of possum fur. The required hydrogen peroxide concentration is influenced by other process variables, most notably the pH of the oxidative bleach and also the level of mordanting.

1.3.5.2 Stabilisers and Activators and Solution pH

Of the bleaching processes surveyed, most use slightly alkaline conditions (Trollip *et al.* 1985, Arifoglu and Marmer 1990, Arifoglu *et al.* 1990, Bereck 1985, Bereck 1994, Allsop 1996, Earland and Little 1985, Stoves 1976). Gacen and Cayuela (2000) found that for the same chemical attack, wool bleached in alkaline media is whiter than that bleached in acidic media. In conventional alkaline bleaching the active species is the perhydroxyl anion generated via the following mechanism;

$$H_2O_2 + OH^- \Leftrightarrow H_2O + HO_2^-$$

With the right hand side favoured at high pH. Stabilising compounds such as sodium pyrophosphate are added to reduce the catalytic effect of the hydroxyl ion, thereby regulating the decomposition of peroxide leading to conditions that give a maximum bleaching effect with minimum fibre damage (Cegarra *et al.* 1994).

In mordanted bleaching, the main bleaching species are the hydroxyl and perhydroxyl radicals, which are released via the Haber-Weiis mechanism (Cegarra and Gacen 1983).

$$Fe^{++} + H_2O_2 \Rightarrow Fe^{+++} + {}^{\cdot}OH + OH^-$$
$$Fe^{++} + {}^{\cdot}OH \Rightarrow Fe^{+++} + OH^-$$
$$H_2O_2 + {}^{\cdot}OH \Rightarrow {}^{\cdot}O_2H + H_2O$$
$$Fe^{++} + {}^{\cdot}O_2H \Rightarrow Fe^{+++} + HO_2^-$$
$$Fe^{+++} + {}^{\cdot}O_2H \Rightarrow Fe^{++} + O_2 + H^+$$

None of these processes involve either protons or hydroxyl ions on the left hand side and since the amount of iron absorbed by the fibres will be relatively small (work by Laxer and Whewell (1955) on heavily pigmented wool showed absorption up to 1.7 mg/g), it is unclear as to how important pH is in the mordanted bleaching process. All the mordanted bleaching processes surveyed made use of alkaline oxidative bleaching conditions. The perhydroxyl ion generated in alkaline solutions reduces ferric ions to ferrous ions. This may then lead to reinitiation of the above mechanism at sites where iron is bound but the melanin has not been completely destroyed (since the ferrous iron is oxidised in the initiation process). However, the perhydroxyl radical, also generated in the above mechanism, can also reduce ferric ions to ferrous. It is known that alkaline media damages keratinous fibres and that high pH solutions of hydrogen peroxide are particularly damaging (Cegarra and Gacen 1983). For this reason it will be necessary to determine the lowest possible pH at which acceptable bleaching can be obtained. Different stabilisers are used for alkaline and acidic media. A commercial preparation Prestogen W (BASF) has been shown to be effective for acidic media, as has citric acid (Karunditu *et al.* 1994). A study by Cegarra *et al.* (1994) found a mixture of sodium pyrophosphate and ammonium oxalate or oxalic acid best suited for alkaline media, as used in the process obtained by Gray Fur Trading. Laporte Chemicals market a commercial preparation of this mixture as Stabiliser C (note: this preparation was later found to be no longer commercially available).

1.3.5.3 Temperature and Time

These variables are strongly interdependent with a higher temperature requiring a shorter bleaching time and vice versa. Studies on wool have shown that for a given temperature an optimum time exists, in that either exceeding or falling short of this temperature will lead to a lower degree of whiteness (Cegarra and Gacen 1983). The same study also shows that less damage occurs to the wool, and greater whiteness is obtained, from systems at lower temperatures and longer times. Since both wool and possum fur are keratin based fibres it would be reasonable to expect the same situation to apply. Higher temperature / shorter time systems will need to be investigated, in that they offer the possibility of reduced process times and costs.

1.3.5.4 Surfactants

Work on wool has shown the presence of sodium lauryl sulphate (SLS) to lead to a whiter, less damaged product in oxidative and reductive bleaching (Cegarra *et al.* 1983, Gacen *et al.* 1989, 1994, Gacen *et al.* 1991, Gacen *et al.* 1993). Comparisons will be made between results obtained in the presence and absence of SLS.

1.3.6 STRIP

The purpose of the strip stage is to remove iron still bound to the fibres after the oxidative bleach. It may be possible to remove this stage; work undertaken by Arifoglu and Marmer (1990) showed that ferric iron bound to wool was reduced to ferrous iron in reductive bleaching with thiourea dioxide, the ferrous iron is then easily washed away due to its lower affinity to white wool. This reduction and removal process will be investigated with sodium hydrosulphite.

1.3.7 REDUCTIVE BLEACH

After the oxidative bleach the fur will not have reached the desired shade, (due to the heavily pigmented nature of the fibre) and further treatment with reductive bleaching agents will be required. A reductive bleach is also necessary to prevent subsequent yellowing of the fibre (Allsop 1996).

The variables under consideration are basically the same as in oxidative bleaching (i.e. pH, time, temperature, concentration of reagents) but since there are different agents available the effect of some variables (e.g. pH) will differ between agents. Experimentation to find optimum conditions would need to be carried out separately for each reagent. Investigation will be limited to the two most promising reagents from the literature; Blankit IN, the stabilised hydrosulphite mixture marketed by BASF, and thiourea dioxide, formed in situ by the reaction of thiourea and residual hydrogen peroxide. Literature (Gacen *et al.* 1991, Gacen *et al.* 1994) on the bleaching of wool has given optimum pH for these reagents with and without the addition of SLS, although these may not necessarily be the case for possum fur. The difference between high temperature / shorter time and low temperature / longer time will need to be investigated. Other variables to investigate are reducing agent concentration and the effect of surfactants.

It will also be determined if the reductive bleach is effective in removing residual iron from the fur or whether it will need to be preceded by a stripping step.

1.3.8 OTHER PROCESS VARIABLES

Other variables which will need to be considered are the flow rate of solution, the degree of packing of the fur and the liquor to fur ratio. It is desired to obtain plug flow through the fur. It will also be necessary to investigate whether or not it is necessary to recirculate the solutions through the fur or whether they can be pumped in, left for the desired time, then pumped out. The packing of the fur will also need to be investigated. If the fur is packed to loosely preferential flow will occur and if the fur is too tightly packed the pressure drop through the fur will be too high, also leading to preferential flow.

The liquor ratio will also effect bleaching time with higher ratios (based on volume of solution to mass of fibre) possibly giving shorter processing times. It also has implications on the cost of the process in terms of the quantities of chemicals used per batch and on the design of full scale equipment.

1.4 OVERVIEW OF METHODS FROM LITERATURE

1.4.1 KILL

Sodium metabisulphite can be used as a reductive bleach for the bleaching of wool (Allsop 1996) so the current step will produce some modification of the fibres. In his review paper on fur dyeing Stoves (1976) states that alkalis are often applied to break down surface films of fatty matter and soften the keratin by controlled breakdown. This treatment is done primarily for the longer, coarser, protective guard hairs, which are the hardest to bleach. Given the high susceptibility of keratin to damage by alkali, care would be required with any alkali treatment. The utility of the current kill will be investigated before alternatives are trialled.

The literature surveyed so far has dealt mostly with wool. Apart from ensuring it is clean (i.e. scouring) generally no pre-treatment is given to the wool. The fur fibres must be clean before processing since this will help prevent matting. The fur is matted by foreign matter present before bleaching, such as blood and faeces, which must be removed to ensure even bleaching.

1.4.2 MORDANT

Iron (II) is the most suitable species for mordanting, due to its low cost, its good mordanting properties and the fact that relatively high levels are tolerated in effluent water (Bereck 1994). Fibres have a pH at which the absorption of iron will be maximised e.g. 3.5 for karakul wool (Bereck 1985), 4.5 for merino (Arifoglu and Marmer 1990). However, Stoves (1976) states that the amount of ferrous ion absorbed by fur increases with pH up to 6.5. This parameter will need to be determined experimentally for possum fur.

The following method was suggested by Bereck (1994) based on optimisation work he did for the mordanting of blends of black karakul and white merino wool.

Table 1.2 Mordant of Bereck (1994)

	Mordanting	Rinsing (with 0.5 mL/L hypophosphorous acid)
Iron Sulphate ($FeSO_4.7H_2O$)	10 g/L (0.036 M)	
Hypophosphorous Acid (50%)	3-4 mL/L	0.5mL/L
Formic Acid	To pH 3.0-3.5	
Temp (°C)	80	80
Time (min)	60	20

Bereck (1994) found that the presence of chelating agents impaired the selectivity of absorption leading to increased fibre damage during bleaching. The cream of tarter (potassium hydrogen tartrate) currently used, acts as a chelating agent. Frishman and Biberfeld, (1977) in their description of mordants for fur bleaching state that; “a small amount of a compound that can form a complex with ferrous iron” is added.

The reducing agent used to prevent the oxidation of iron (II) to iron (III) is also important. Arifoglu and Marmer (1990) found that wool mordanted in the presence of sodium bisulphite is bleached to a higher degree than that obtained using hypophosphorous acid, though greater fibre damage is also incurred. The conditions used were similar to Bereck (1994) except they used 1 g/L Triton X-100 as a wetting agent. Full details are included in the section on sequential bleaching systems (1.4.6). Their study was conducted in the absence of formaldehyde, which is added to cross link the fibre proteins, to partially negate the effect of the scission of disulphide linkages during oxidative bleaching. Bereck (1994) found that when formaldehyde is used with sulphur containing reducing agents, the wool obtains a yellow discolouration. He also found that less damage occurs when formaldehyde is used during hydrogen peroxide bleaching, but bleaching efficiency is reduced due to the reaction between formaldehyde and hydrogen peroxide. It was also found that formaldehyde was not necessary when hypophosphorous acid is used as a reducing agent in the mordanting procedure since the use of this reagent leads to very little damage to the fibres.

Most mordanting data found so far has dealt with bleaching of wool. Possum fur has a higher degree of pigmentation than wool and may require a higher iron concentration during mordanting. Stoves (1976) states a typical treatment for furs of 25 g/L (presumably $FeSO_4.7H_2O$), pH 6.5 for 12 to 48 hours at 25-35°C.

Laxer and Whewell (1955) have shown that iron binds more firmly to melanin than to keratin. It is necessary to conduct a rinsing step after mordanting to remove the ferrous iron which is loosely bound to the keratin, so the attack of radicals is isolated at the melanin pigment. This is not performed in the current process and therefore the iron will also be catalysing the attack of keratin. Bereck (1985) found that a hot rinse with a 0.5 mL/L hypophosphorous acid solution for 20 minutes at 80°C decreased the iron content of black wool by 59% while the iron content of melanin isolated from the wool was practically unchanged.

Ammonium chloride is also present in the current process. Cegarra and Gacen (1983) and Trotman (1968) state that ammonium sulphate is included in mordanting solutions. The mechanism by which the absorption process occurs is unknown, although it may play some part in this. The effect of ammonium salts on the mordanting process will be investigated.

1.4.3 OXIDATIVE BLEACH

It is widely accepted that hydrogen peroxide is the most suitable oxidising agent for bleaching keratinous fibres. In selecting the conditions to be used, care will have to be taken to select conditions that do not excessively damage the fur. It will be necessary to determine how far to take the oxidative bleach, considering that a reductive bleach is to follow.

Bereck (1994) suggests the following conditions for rabbit fur

Table 1.3 Oxidative Bleaching Conditions for Rabbit Fur (Bereck 1994)

Hydrogen Peroxide (35%)	20-40 mL/L
pH	8-8.5 (adjusted with ammonium hydroxide)
Temp (°C)	50-60
Time (min)	45-120
Stabiliser (sodium pryrophosphate)	10 g/L
Liquor ratio	15:1

These conditions are similar to those stated in other papers on wool bleaching i.e. slightly alkaline conditions, comparable peroxide concentration, elevated temperature (commonly 50-70 °C), and up to 3 hours contact time. The peroxide concentration in the process obtained from Gray Fur Trading is higher than any found in the literature. Higher temperature/ shorter contact time systems would be preferable from an operating perspective, if they achieve the desired bleaching with acceptable damage. Sodium pyrophosphate is commonly used as a stabilising agent, sometimes in conjunction with oxalic acid or an oxalate salt (Cegarra and Gacen 1983, Cegarra *et al.* 1994). Oxalic acid or other chelating agents are added to prevent the decomposition of peroxide in the bulk solution due to free iron, present from the mordanting procedure and also if the water supply has a significant level of iron or other heavy metals (Farr *et al.* 1992). Stabilising agents such as sodium pyrophosphate help to regulate the decomposition of peroxide by reducing the catalytic effect of the hydroxyl ion on hydrogen peroxide decomposition. The mixture of soda ash (sodium carbonate) and sodium bicarbonate would help maintain pH through a buffering action. The purpose of adding these reagents after an hour is thought to be to reduce alkali retention by the fur to prevent damage from the alkali. Acidification after bleaching should also be conducted for this reason or at least a thorough rinse (McDonald 1997).

A number of methods make use of the surfactant Sodium Lauryl Sulphate (SLS) in the wool bleaching process for both oxidative and reductive bleaching. This has lead to a whiter, less damaged product than conventional means. The surfactant protects the disulphide linkage of the keratin proteins. This is thought to be due to a net negative charge on the protein, resulting from the fixation of the anionic surfactant causing a more difficult entry of the bleaching anion. Gacen *et al.* (1993) have done work looking at various reductive bleaches in the presence of 5 g/L sodium lauryl sulphate (SLS). Allsop (1996) found that this concentration lead to foaming problems in his study of oxidative and reductive bleaches. He found that benefits are obtained from the addition of 1 g/L SLS. No studies were found making use of a surfactant in the bleaching process following a mordanting procedure. It is possible that SLS could bind to ferrous ions in the fibre through an electrostatic attraction, depending on the strength of the iron melanin interaction, hindering the approach of the HO_2^- ion. The use of this reagent is certainly worthy of investigation.

Ammonium chloride is included in the current process. The role that this plays, if any, was not found in the literature.

1.4.4 STRIP

It may be possible to remove this stage. The reductive bleaching process should convert any ferric ions present to ferrous ions, which should be easily washed away from the white fur. Arifoglu and Marmer (1990) observed that ferric staining on wool was removed during reductive bleaching with thiourea dioxide.

1.4.5 REDUCTIVE BLEACH

A variety of reducing agents have been used as reductive bleaches. Of these stabilised hydrosulphite mixtures and thiourea dioxide have received particularly good reviews. Two methods appear worthy of investigation initially. A stabilised hydrosulphite mixture Blankit IN is marketed by BASF. Gacen *et al.* (1994) suggest the following conditions for bleaching wool with stabilised hydrosulphite (i.e. Blankit IN)

Table 1.4 Reductive Bleaching Conditions for Blankit IN (Gacen *et al.* 1994)

pH	7
SLS concentration	2.5-5 g/L
Reducing Agent concentration	4-5 g/L
Temperature	55-60°C
Time	1-2 hours

This work was part of a study performed on a series of reductive bleaching agents, with and without SLS. The agents studied were sodium hydrosulphite based sulphoxylate formaldehyde formulations, non-stabilised hydrosulphite, thiourea dioxide, sodium bisulphite and stabilised hydrosulphite (i.e. Blankit IN). Of these agents, Blankit IN at the conditions given in table 1.4 gave the best results.

Arifoglu *et al.* (1990) developed a process for bleaching with thiourea dioxide where thiourea is added to the bath after the oxidative bleach and reacts with residual hydrogen peroxide to form thiourea dioxide. Care must be taken with reaction conditions in this process to ensure that thiourea dioxide is formed. Their process involves adding thiourea in a ratio of 3.2:1 ($[H_2O_2]$:[thiourea]) under acidic conditions (pH 4-5), the reaction should then be given at least 10 minutes to proceed before the pH is adjusted to 7, and bleaching begun. They followed a process for the dyeing of wool consisting of a mordanting step then sequential oxidative and reductive bleaching. This process is summarised in the section below. This process would offer time and cost savings on a large scale since the oxidative bleach is converted to the reductive bleach without changing solutions.

1.4.6 SEQUENTIAL BLEACHING TECHNIQUES

These processes are different from others surveyed in that chemicals for reductive bleaching are added without removal of the oxidative bleaching chemicals.

The following is the process developed by Arifoglu *et al.* (1990):

The mordant solution consisted of $FeSO_4.7H_2O$ (10 g/L), either hypophosphorous acid (0.2 g/L) or sodium bisulfite (2.0 g/L) as reducing agent and Triton X-100 (1.0 g/L) as wetting agent. The wool was introduced to the bath at 40°C and the temperature increased to 80°C over 20 minutes at which the wool was further mordanted for one hour. The pH of the bath was 2.87 initially, increasing to 3.45 over the course of the process.

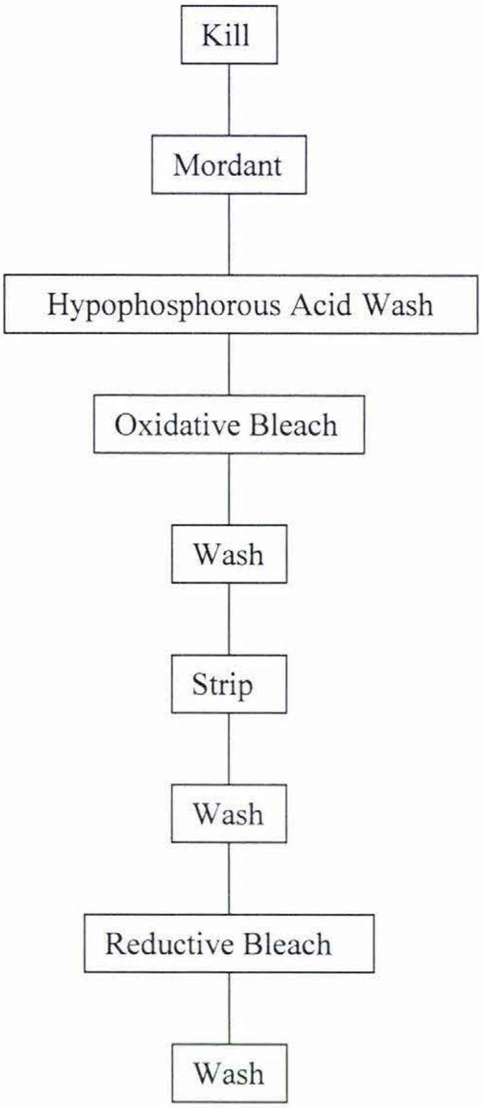
Oxidative bleaching was carried out using hydrogen peroxide (30% w/w, 20.0 mL/L) sodium pyrophosphate (10.0 g/L) and Triton X-100 (1.0 g/L). Bleaching was carried out for 90 minutes at 60°C; pH was maintained at 8.0-8.5 using liquid ammonia.

Reductive bleaching was then carried out by the previously described process for an additional 30 minutes. This process also removed staining due to the precipitation of ferric species onto the wool.

Gacen *et al.* (1991) studied the bleaching of wool with thiourea dioxide in the presence of SLS. They found that wool bleached in the presence of SLS had a higher degree of whiteness and was less damaged than that bleached without SLS. They found the optimum conditions to be; 1.5 g/L thiourea dioxide, 5 g/L SLS, 2.5 hours, 70°C, and pH 6.

An abstract was obtained from a paper (Cheng *et al.* 1999) detailing a similar process for fur. This involved bleaching in a bath containing NPS-1 (a wetting agent), sodium pyrophosphate and 20-40 g/L 30% H_2O_2 using a liquor ratio of 20-25. The bath was rotated at pH 4.5 – 6.5 for 5-12 hours. Thiourea (5-10 g/L) was then added, the bath rotated for a further 5-10 minutes before the pH was raised to 7-8 and bleaching conducted for a further 15-45 minutes.

1.5 FLOW CHART



This depicts the process as currently performed with the addition of a hypophosphorous acid wash after the mordant. This will be the first improvement examined on the process. It is likely that the presence of iron attached to the keratin will be a main contributor to the damage occurring to the fibres. An effective mordanting procedure will contribute greatly to obtaining the desired bleaching, with minimal damage to the fur. Further investigative work will need to be undertaken looking at variables such as pH and the rinsing stage.

Also of interest is the pH of the hydrogen peroxide bleach, if this is too high this step will also be contributing significantly to the damage of the fur. The reductive bleach will also be contributing to the damage, but if a commercial preparation is used, containing stabilising agents, it is likely that initially the most room for improvement is in the mordanting and oxidative bleach. Further improvement may then be obtained from the use of surfactants in the bleaching processes.

CHAPTER 2 EXPERIMENTAL TECHNIQUES

2.1 INTRODUCTION

This chapter details the experimental methodology used and provides background on experimental techniques.

2.2 BLEACHING EXPERIMENTS

2.2.1 EXPERIMENTAL SET-UP

Figure 2.1 shows the set up used in the bleaching experiments.

The solutions were held in a conical flask, which is heated initially on the hot plate then held in the water bath over the course of the experiment. The solutions are pumped upwards through the column containing the fur, by the masterflex pump, and return to the conical flask. A number 3 porous glass frit was inserted in the bottom of the column to provide distribution of flow. The top of the conical flask is covered with foil to prevent evaporative losses during the experiment.

The column and piping set-ups used have hold-ups ranging from 130 to 160 mL. This formed a significant part of the total water used.

Consider an experiment requiring 250 mL of solution. In initial experiments, the reagents would be dissolved in 250 mL H_2O, and the previously determined hold-up volume displaced from the column into a separate vessel before recirculation began. This was later modified to a procedure where the 130 mL hold up volume was factored into account when making the solution and recirculation begun immediately. If a solution had a desired volume of 250 mL the reagents would be dissolved in 120 mL and the 130 mL hold up in the column would provide the rest of the water. In the oxidative bleach, hydrogen peroxide was added in two doses, half initially and half after 10 minutes. This was done so the fur would not be exposed to too high a peroxide concentration.

Between stages of the bleaching process, such as between kill and mordant, the column was rinsed through with approximately 600 mL of water to remove any reagents from the previous stage so they could not interfere with the next stage.

The grey cardboard shown in the picture was the background for the photographs taken throughout the bleaching procedure.

2.2.2 DETERMINATION OF MIXING IN COLUMN

As previously described, the hold-up of liquid in the column resulting from rinsing between stages must be either displaced from the column or factored into account for the liquor used in the next stage.

In terms of the industrial scale plant, it would be easier to have a method where this water forms part of the liquor for the next stage, rather than switching to recirculation after draining an amount of liquor equal to the system hold-up. Any deviation from plug flow would result in a lower than desired reagent concentration. The system using the hold-up water has advantages in that less water would be used by the process and would simplify the operation of the full-scale equipment.

In order for the system where the hold-up water is mixed with each stages reagents to be feasible, it was necessary to determine the mixing dynamics of the system, so that it is certain that the fur is not exposed to excessively high levels of certain reagents. This was done experimentally.

2.2.2.1 Determination of column mixing dynamics

2.2.2.1.1 Mixing

The mixing dynamics of the column were determined by monitoring the pH of the solution vessel when a slightly alkaline solution was introduced. This solution was made of hydrosulphite and SLS, such as would be used in a reductive bleach. The initial pH of this solution was 9.61 and the column pH was 5.62. The flowrate was set at 100 mL/min.

The resultant pH time profile is shown as figure 2.2. It can be seen here that a relatively steady pH is reached after approximately ten minutes. The pH of the hydrosulphite solution decreases as it exerts its bleaching action on the fur, accounting for the slight downward trend observed on the graph.

Ten minutes was taken to be an acceptable time for mixing to occur. The lengths of the treatments are all relatively long compared with ten minutes. Of the reagents used, it is most important that the concentration of peroxide is not excessively high. For this reason peroxide was added in two doses, the second after ten minutes.

2.2.2.1.2 Temperature

Also of interest was the time it takes for the solutions to reach the desired temperature for each treatment stage.

Measurements were made at the three temperatures used in the bleaching process; 30°C, 40°C and 50°C. To obtain these temperatures the water bath was maintained at 36°C, 46°C and 62°C respectively. The solutions were initially heated to these temperatures also, except for the 50°C experiment, which was heated to 60°C. The flowrate was set at 130 mL/min. The water held up in the column ranged in temperature from 14 to 16°C. Figures 2.3 – 2.5 show the temperature time profiles obtained.

Each solution attains the desired temperature within approximately 10 minutes. This is the same time as was determined for the mixing of solutions to take place and was again taken to be an acceptable time period. Some heating was required in this ten minute period, provided by the water bath. The 30°C experiment shows a slight upward trend of a couple of degrees from 10 minutes to the end of the experiment. It was subsequently found that a bath setting of 32.5°C was necessary for a 30°C solution.

2.2.2.2 Washing effectiveness

Experiments were undertaken to determine the necessary volume of water to thoroughly rinse the column of reagents left from the previous stage.

This was conducted by thoroughly rinsing the column through with an acidic solution, then rinsing through with H_2O and measuring the pH of successive elutions.

Measurements of pH were made after 160 mL (the hold up of the column), 8 x 50 mL and 4 x 100 mL. The initial pH of the column was 1.39; the rinsing water was pH 8.23. Figures 2.6 and 2.7 show the pH of the eluting water as a function of the volume of water used and, the reduction in concentration of H^+ as a function of the system hold-ups used in washing.

The data shows a 97% reduction in the concentration of hydronium ion after 3 system hold-ups (approx. 500 mL). It was decided to use 600 mL as a standard wash volume. This did not lead to problems at any stage except between strip and reductive bleaching, when the strip was introduced, where a pH adjustment was found to be necessary. The 600-mL volume was used from chapter four onwards.

2.2.3 WHITENESS MEASUREMENT

Whiteness measurements were undertaken using a Minolta Chroma Meter CR 200, calibrated with a white plate (Y=93.8, x=0.3140, y=0.3212). Measurements were made using 4 g of fur contained within a small ring of piping (approx. 75 mm diameter by 30 mm deep). A piece of grey card was used for the background. The measurements were made in a room with no external illumination to ensure a constant background illumination. The fur samples were carded before measurement to ensure homogeneity of the fur and ten replicates averaged to give the result.

A number of possible whiteness indices were identified for use from the review papers of Teasdale and Bereck (1981) and Cegarra *et al.* (1976). These indices give a measure of "whiteness" by inserting the three tristimulus values (X, Y and Z) defined by the Commission Internationale de l'Eclairage (CIE) into a mathematical formula.

The indices trialled and their formulae are detailed below

Table 2.1 Whiteness Indices Trialled

Index	Formula
Berger	$3Z - 3X + Y$
Simple Croes	$Z - X + Y$
ASTM Whiteness	$3.387Z - 3Y$
ASTM Yellowness	$100(1.28X - 1.06Z)/Y$
Hunter	$L - 3b$
Stensby	$L + 3a - 3b$
L	$10\sqrt{Y}$
a	$17.5(1.02X - Y)/\sqrt{Y}$
b	$7(Y - 0.847Z)/\sqrt{Y}$

Stephansen	$2Z - X$
Taube	$4Z - 3Y$
Croes	$Y - 13.2Y\Delta S$
ΔS	$((\Delta V)^2 - (\Delta U)^2)^{0.5}$
ΔU	$((4X)/(X + 15Y + 3Z)) - 0.2009$
ΔV	$((6Y)/(X + 15Y + 3Z)) - 0.3073$

The indices above give similar rankings for the whiteness of the furs. The positions of certain samples may vary slightly but this is generally within the bounds of uncertainty given by the replicate measurements. Table 2.2 shows the ranking given for the first seven experiments

Table 2.2 Whiteness Indices Rankings of First Seven Experiments

Index	Experimental Number						
Ranking.	1st	2nd	3rd	4th	5th	6th	7th
Berger	1	2	7	4	5	6	3
Simple Croes	2	7	1	6	4	5	3
ASTM Whiteness	1	7	2	5	4	3	6
ASTM Yellowness	1	7	2	5	4	6	3
Hunter	1	7	2	5	4	6	3
Stensby	7	1	2	5	4	6	3
Stephansen	2	7	1	4	5	6	3
Taube	1	7	2	5	4	6	3
Croes	2	7	1	6	4	5	3

All the indices split the results into two groups. Experiments one, two and seven in one group and experiments three, four, five and six in the other. A visual examination gives the same groupings; the second group has a slight yellow tinge. A visual ranking of the furs is a somewhat subjective judgement. Different individuals gave different rankings. Figure 2.8 shows the results of the first fourteen experiments. From this it can be seen that the indices all show the same general trend. The Croes index was chosen for use in the project. It agreed with a visual appraisal of the first seven furs by the author and is representative of the general trend shown by the indices used.

Digital photographs were also taken throughout the bleaching process to allow comparison of the experiments at the various stages of the bleaching process. These were performed using the grey cardboard shown in figure 2.1 with external illumination excluded.

2.2.4 Alkali Solubility

This is a test to determine the damage occurring to the fur through bleaching, commonly applied in the wool industry.

A sample of fur is immersed in 0.1 M NaOH for one hour at 65°C. The sample is then filtered and washed exhaustively with water, then dilute acid, before drying. The alkali solubility is expressed as the percentage loss of mass resulting.
The alkali solubility of a fibre increases with the scission of disulphide links in the keratin structure (Cegarra and Gacen 1983).

2.2.5 LOSS OF MASS

For this test the samples were dried initially at 40°C. They were then left at ambient conditions until a constant mass was observed.

2.3 CONCLUSIONS

- The experimental set-up used in the experiments on the optimisation of bleaching is as described in section 2.1.
- The solutions were circulated upwards through a column of fur by a masterflex pump. Heating of the solutions was accomplished by a reservoir for the excess solution held in a water bath.
- It was found that 10 minutes is required for mixing of the solutions and for the solutions to obtain the desired temperature.
- 600 mL of water was found to provide adequate removal of the previous stages reagents before the next stage is commenced, except between the strip and reductive bleaches.
- Whiteness was measured using a Minolta Chroma colorimeter. The Croes whiteness index was decided upon for use in the project.
- Damage was assessed by the loss of mass and by alkali solubility.

Figure 2.1 Laboratory Scale Experimental Set-up

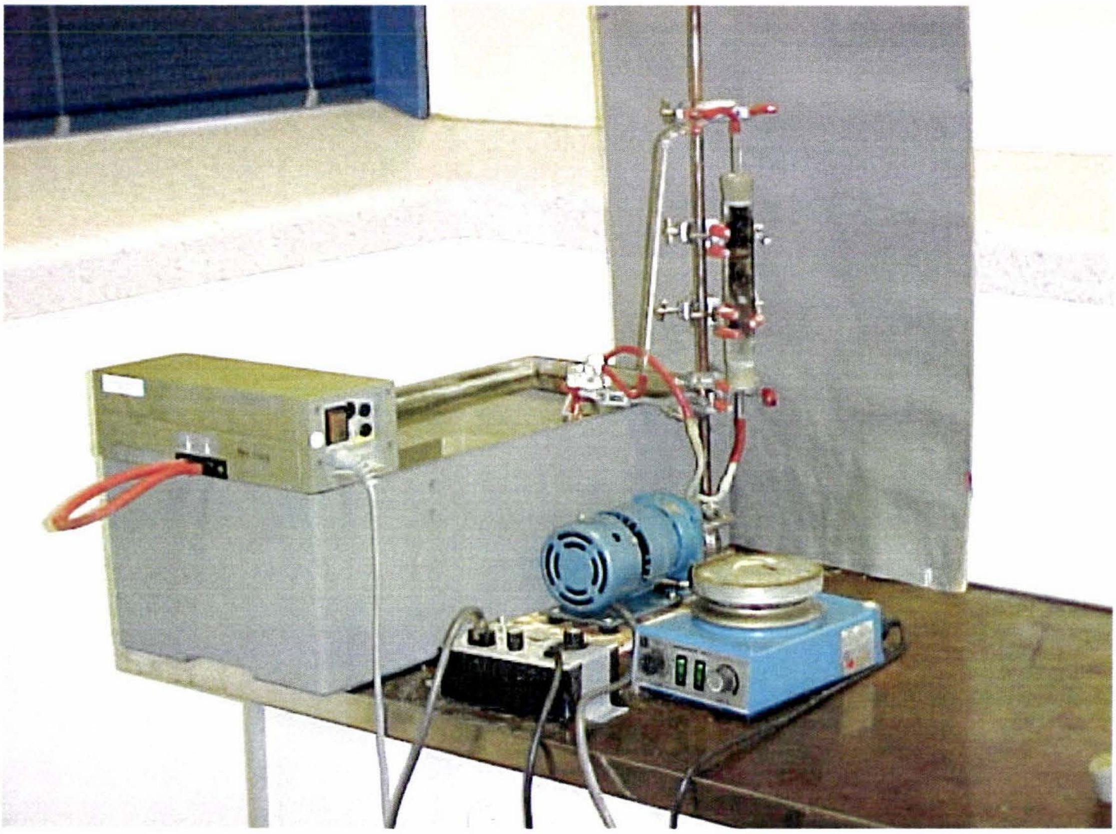


Figure 2.2

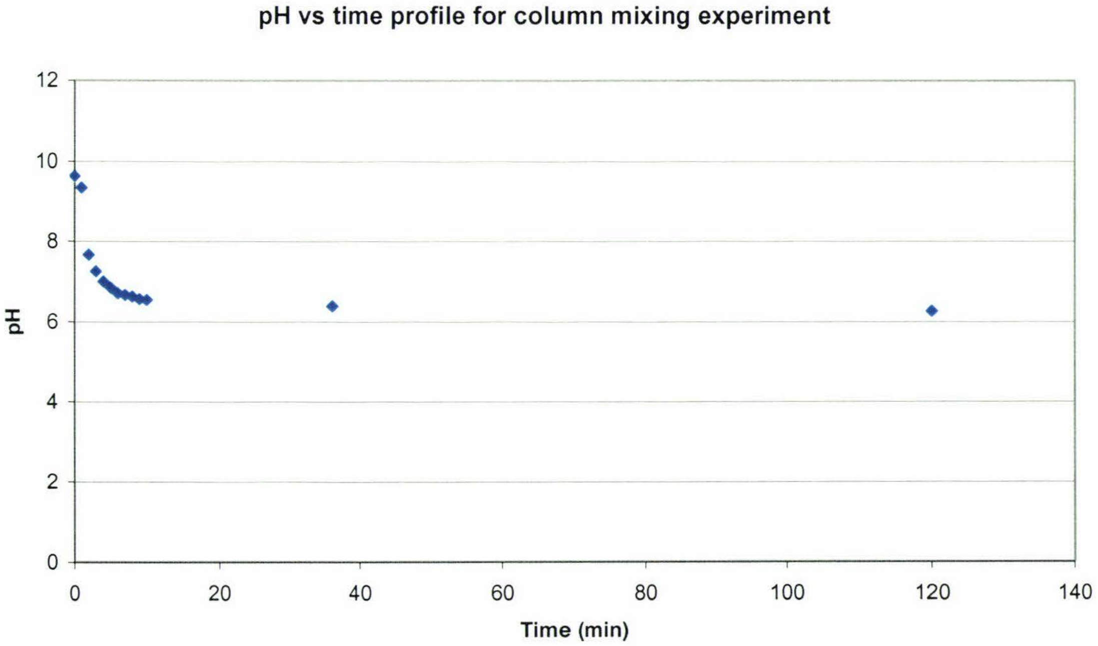


Figure 2.3

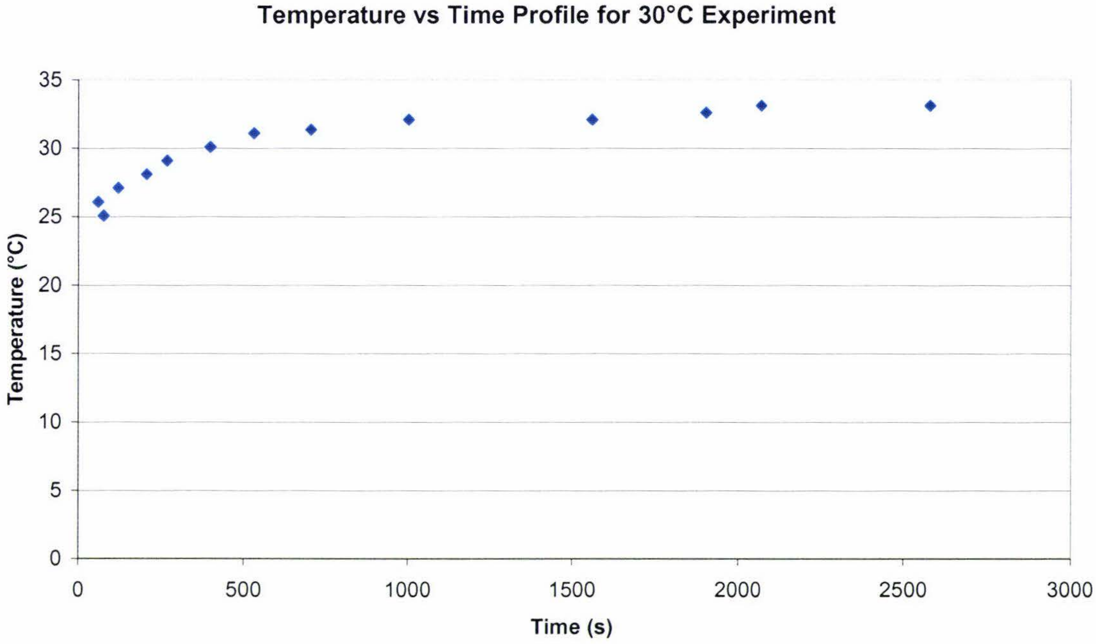


Figure 2.4

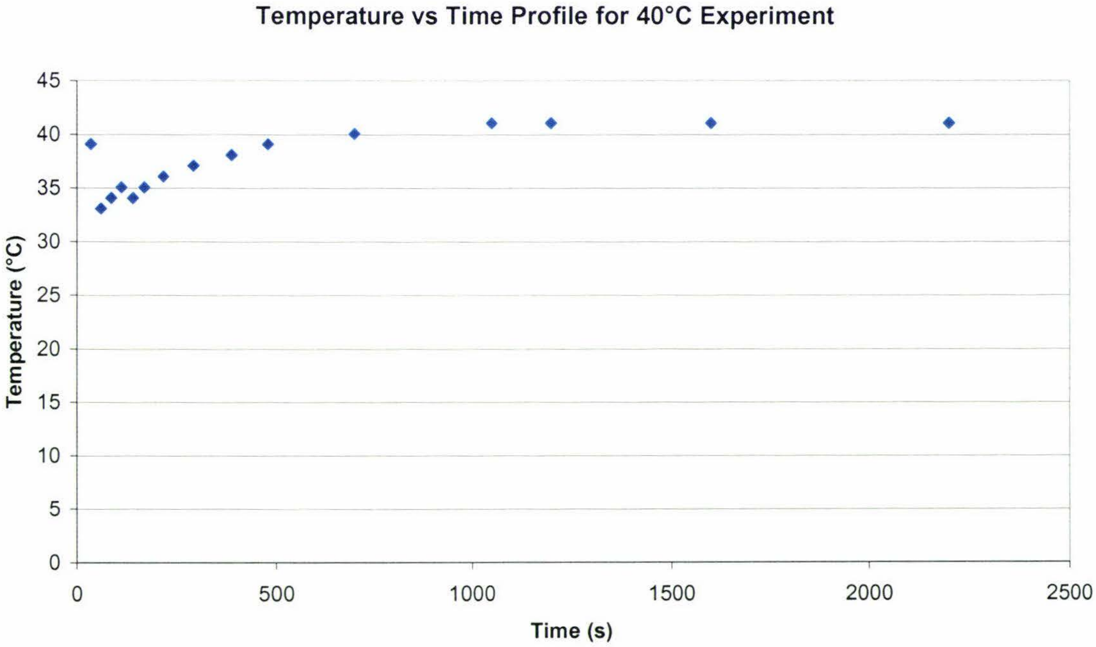


Figure 2.5

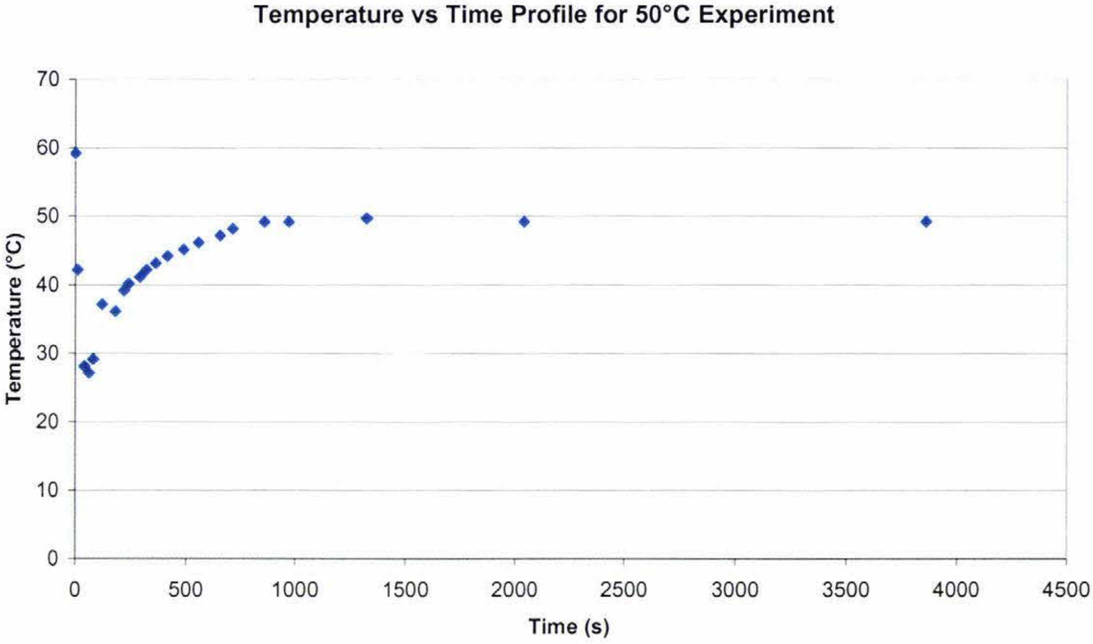


Figure 2.6

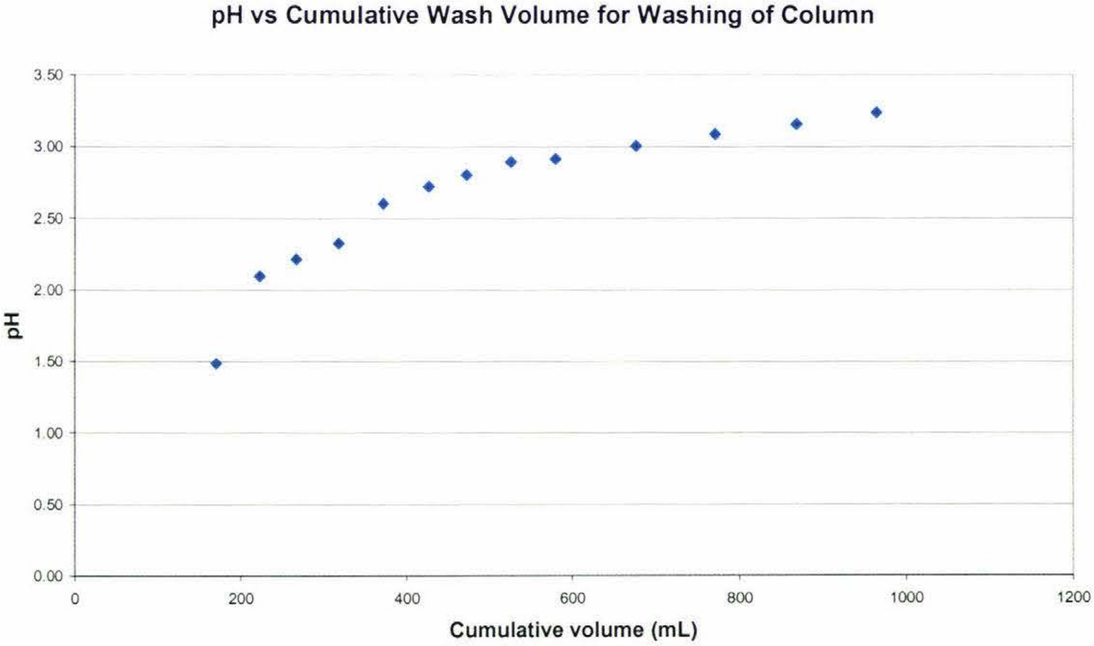


Figure 2.7

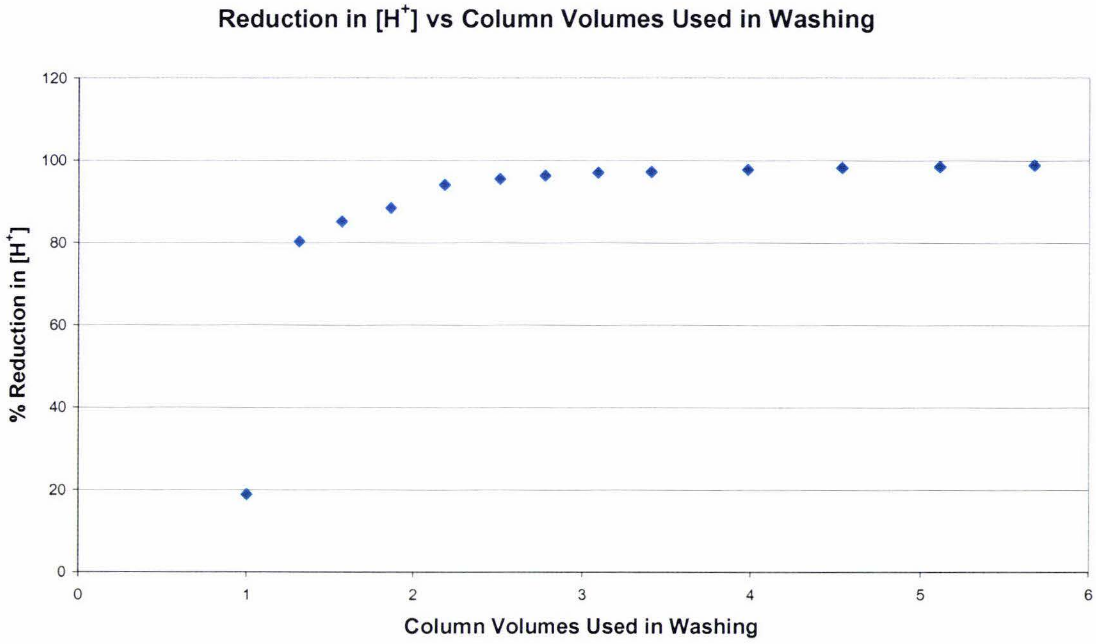
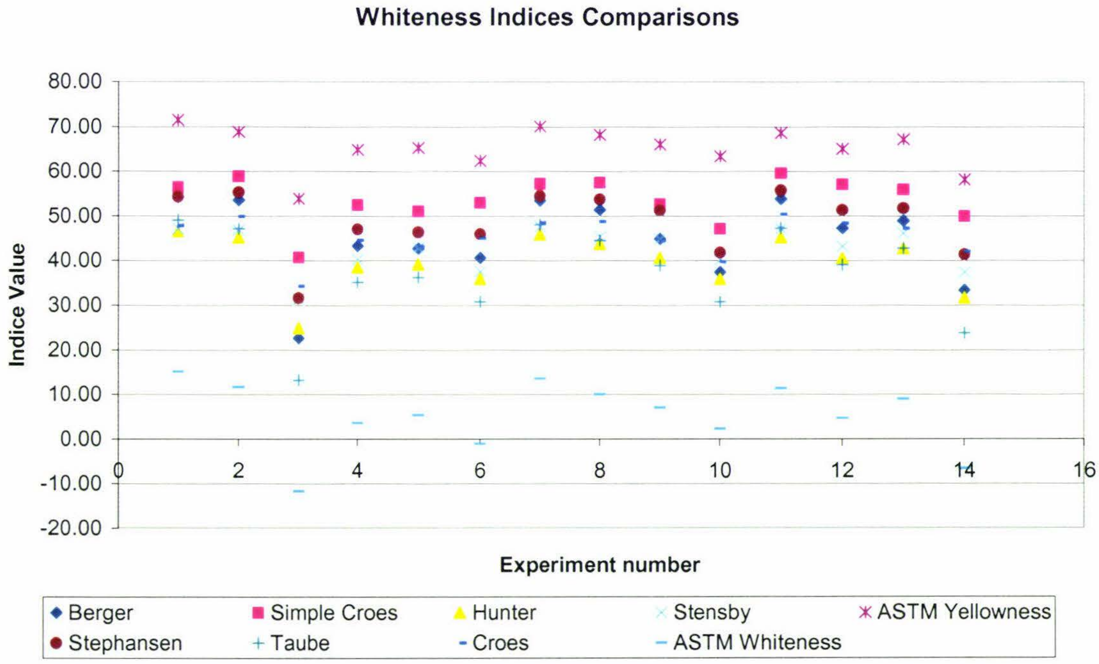


Figure 2.8



CHAPTER 3 INITIAL EXPERIMENTATION

3.1 INTRODUCTION

This chapter details the initial experimentation undertaken before the bleaching process was investigated stage by stage. This was undertaken to determine the results obtained via the method provided by Gray Fur Trading, using a displacement bleaching type system, hereafter referred to as the initial method. This involved the treatments in table 1.1, with the spin/wash procedure substituted for the rinsing methodology described in chapter 2. Of interest here was the degree of damage and the whiteness resulting and whether or not the displacement bleaching method would eliminate the matting problems encountered originally.

Experimentation undertaken to gauge the effects of the modifications obtained from the literature which appeared most likely to lead to improvements is also detailed in this section.

The fur used in these experiments was homogenised by hand, while that used in subsequent experiments was carded using two hand cards. Fur was supplied in lots which lasted around 20 experiments.

3.2 EXPERIMENTS I1 AND I2. EXPERIMENTS WITH THE METHOD OF FUR DRESSERS AND DYERS

3.2.1 OVERVIEW

These experiments were both repeats of the initial method detailed in section 1.2. The strip stage was omitted in this work on the basis of the results of Arifoglu and Marmer (1990) who observed that ferric staining on wool was removed during reductive bleaching. Overnight was taken as 15 hours for the mordant and 12 hours for the oxidative bleach. Thirty percent hydrogen peroxide was used which required 56 mL/L. The system hold-up in these experiments was 130 mL. The solutions were made up in the required volume for the use of 5g of fur at a liquor ratio of 50:1, (i.e. 250 mL) and water displaced from the column after rinsing between stages. In the first experiment 100 mL was displaced, in the second 130mL. The column was rinsed through with approximately 350 mL of water between stages. A flowrate of 30 mL/min was used. Initial attempts at wetting the fur in the columns found that the fur was not properly wetted. To counter this, the fur was rinsed through with 1.4 g/L SLS for ten minutes which was then displaced by the rinsing process. This provided adequate wetting and also served to remove any blood, faeces or other foreign matter adhering to the fur.

3.2.2 EXPERIMENTAL VARIABLES

One thing immediately evident from the literature was the importance of the pH of certain steps of the bleaching process. The following table details the pH of the steps from the original bleaching process.

Table 3.1 pH Data from the Initial Method

Stage		pH
Kill	Initial	3.85
	Final	3.75
Mordant	Initial	3.1
	Final	2.9
Oxidative Bleach	Initial	4.7
	After Carbonates	7.65
	Final	7.8
Reductive Bleach	Initial	6.5
	Final	4.5

3.2.2.1 Discussion of pH data

A discussion of the pH data collected in each stage of this experiment follows.

3.2.2.1.1 Kill

The pH used in the kill stage is what an 11 g/L metabisulphite solution will give in distilled water. The purpose of this stage is to soften the fibres to make them more receptive to subsequent treatments, rather than an actual bleaching step. For this reason, control of the pH is not critical to any bleaching treatment. The utility of the kill stage was evaluated in subsequent experimentation and is discussed in sections 3.5 and 4.2.7. No references were found in the literature detailing the use of a kill step in the bleaching of wool. It appears to be a feature unique to the bleaching furs.

3.2.2.1.2 Mordant

The pH of the mordant stage is known to be critical to the bleaching process, by effecting the amount of iron absorbed by the fibres. Various values have been quoted in the literature. Bereck (1994) states an optimum value of 3.5 for the bleaching of wool. Stoves (1976) gives a value of 6.5 for bleaching furs and Trotman (1968) states that the pH should be maintained between 5 and 6 for the mordanting of heavily pigmented animal fibres.

Clearly work was required to determine the optimum pH for the mordanting of possum fibre; this is discussed in section 4.3.

3.2.2.1.3 Oxidative Bleach

The oxidative bleach is responsible for the majority of the bleaching effect. The control of the pH of this stage is critical, too low a pH and a satisfactory bleaching effect will not be obtained, too high a pH and the fibre will be excessively damaged. Literature on the bleaching of wool states that values up to pH 9 may be used, common values are 8 to 8.5. (Bereck 1994, Arifoglu and Marmer 1992). These are at lower peroxide concentrations than that of the initial method. Subsequent work has been undertaken on the pH of the oxidative bleaching process, and is detailed in chapter five. The pH obtained from the initial method is lower than any surveyed in the literature, but the concentration of hydrogen peroxide higher.

3.2.2.1.4 Reductive Bleach

In their paper on the bleaching of wool with non-stabilised sodium hydrosulphite, with and without SLS, Gacen *et al.* (1989) found the best bleaching was obtained in the pH range 5-6. Adjustment of the pH was required during their experiments because the pH of a hydrosulphite solution decreases as its bleaching effect is exerted. The range here encompassed these values.

3.2.3 EXPERIMENTAL DISCUSSION

A graph showing the Croes whiteness index and alkali solubility for the experiments discussed in this chapter is included as figure 3.1. A graph showing loss and alkali solubility is included as figure 3.2.

3.2.3.1 Matting

The matting problems encountered in the "bucket" experiments conducted initially at Gray Fur Trading were not experienced.

Two factors contribute to the matting of the fur. The first is from the fibres rubbing against each other, either by agitation or from spinning in between stages. This was the original hypothesis for the matting of the furs and the reason why the displacement bleaching method was selected for examination. This hypothesis has been confirmed by experimentation in which a clump of fur was manually rubbed after bleaching. This fur matted whereas other fur from the same experiment not treated this way did not.

The second factor contributing to the matting of fur is the damage it sustains during bleaching. Unbleached fur, when wetted and rubbed, will matt only slightly. After an alkali solubility experiment the "fur" is basically a solid clump with no individual strands. It was also noticed over the course of the experimental work that above certain flowrates, (approx. 130 mL/min) a certain degree of compression of the fur resulted during the oxidative bleach. The fur could occupy up to 50% of its original volume. This would indicate that the surfaces of the fibres are being modified such that their tendency to repel each other is reduced. When the fibres are agitated in this condition the likelihood of matting is increased.

3.2.3.2 Whiteness and Damage.

The loss resulting from these experiments (9.6% and 9.1%) was lower than expected. In the initial work conducted by Gray Fur Trading losses of 30% had been encountered. In the Gray Fur experiments, the original method had not been followed exactly. The solutions were made at the desired temperature but no heating was conducted after this, the solutions were left to cool to ambient temperature over the course of the treatment. When a desirable level of whiteness had not been obtained after the oxidative bleach, extra peroxide was added. This is likely to have made a significant contribution to the damage occurring. Also of note is that the original method calls for only a spin after the mordant, the fibres would still be slightly damp from the ferrous sulphate solution. There is likely to have been a significant contribution to the losses from non-selective binding of iron and also free iron in solution.

The whiteness obtained in the displacement bleaching trials using the original method was of a marketable standard. The experiments had Croes whiteness indices of 47.67 and 49.74 respectively.

The second experiment has a significantly higher level of whiteness. This is attributed to the different volumes of solution displaced from the column before recirculation. In experiment one 100 mL was displaced whereas the column hold up is 130 mL. This resulted in the solutions effectively being diluted to 90% of the desired strength if an assumption of plug flow through the column is made. The higher loss in experiment one is therefore surprising. The alkali solubility results indicate similar levels of damage to the fur at 70.1 and 71.3 respectively.

The elimination of the kill stage appeared to be successful. No ferric staining was observed on the finished fur.

3.3 EXPERIMENT I3. MORDANT METHOD OF BERECK

3.3.1 OVERVIEW

This experiment involved examining the mordanting method described by Bereck (1994) and detailed in section 1.4.2. This involved mordanting for one hour at 80°C with 10 g/L $FeSO_4.7H_2O$ and 3 mL/L 50% hypophosphorous acid, followed by a rinse for 20 minutes at 80°C with 0.5 mL/L 50% hypophosphorous acid. SLS was trialled at 1.4 g/L in the oxidative and reductive bleaches. This was based on references in the literature, discussed in chapter one. All other treatments were as in experiments one and two.

The experiment was conducted using 5g of fur at a liquor ratio of 50:1. The flowrate was set at 30mL/min. The column was rinsed with 350 mL of water in between stages. The hold up volume of the column, 130mL, was displaced by the introduction of the next set of reagents.

These two modifications, i.e. the changed mordanting and bleaching with SLS, stood out in the literature as being worthy of investigation.

3.3.2 EXPERIMENTAL VARIABLES

The pH of the various stages is tabulated on the following page.

Table 3.2 pH Data Obtained with the Mordant Method of Bereck

Stage		pH
Kill	Initial	3.80
	Final	4.35
Mordant	Initial	1.5
	Final	1.7
Acid rinse	Initial	2.2
	Final	2.0
Oxidative Bleach	Initial	4.9
	After Carbonates	8.0
	Final	8.1
Reductive Bleach	Initial	6.9
	Final	5.5

The pH of the mordant step is significantly lower than in the previous experiments. Subsequent experimentation has shown the pH to be critical in the mordanting stage. The values from experiments I1 to I3 lie both side of the optimum determined.
The pH of the oxidative and reductive bleaches are slightly higher than before. This is the effect of SLS, which is slightly alkaline.

3.3.3 DISCUSSION

The bleaching obtained in this experiment was not satisfactory. This experiment performed worst in the whiteness test of any in this section at 34.12. The fur has a definite yellow colour to it. This decreased bleaching is accompanied by a substantial decrease in the damage occurring to the fur. On average there is a 42% reduction from 9.4% loss to 5.4 % loss of fur compared with experiments one and two. The alkali solubility has been more than halved from an average of 70.7 to 33.3.
It is believed that the reduced bleaching results from the changes made to the mordant. The addition of SLS was shown to lead to whiter wools and so it was expected that if it has any effect on the bleaching of fur, it would be to give whiter furs.
The mordanting procedure of Bereck (1994) calls for 10 g/L $FeSO_4.7H_2O$ and 3 – 4 mL/L 50% hypophosphorous acid with the pH adjusted to 3.0 – 3.5 with formic acid. The pH of the iron and acid solution, with the acid at 3 mL/L had a pH of 1.5. It was decided to run the experiment at an unaltered pH when this was discovered.
There are two possible explanations for this. There may have been some kind of mistake with the writing up of the paper which was not picked up before the paper was published or they have neglected to mention other chemicals present in the mordanting solution, perhaps due to commercial sensitivity. Based on pKa data, a 3 mL/L solution of hypophosphorous acid would have a pH of 2.4. The pH of ferrous sulphate solutions can also vary depending on the amount of free sulphuric acid in the salt.

What is clear is that this method of mordanting does not produce optimal results. Further work was undertaken on the use of hypophosphorous acid in mordanting due to the results of Bereck (1994) which found it to be the best of the reducing agents trialled.

3.4 EXPERIMENT I4. SUBSTITUTION OF SODIUM DITHIONITE WITH HYPOPHOSPHOROUS ACID

3.4.1 OVERVIEW

This experiment featured the substitution of sodium dithionite with hypophosphorous acid at 3.0 ml/L, in the method used in experiments I1 and I2, i.e. mordanting at 40°C for 15 hours. Formaldehyde was also excluded, based on the results of Bereck (1985) who found it to be of no benefit when the mordant featured hypophosphorous acid. SLS was again included at 1.4 g/L in the oxidative and reductive bleaches as was the acidic rinse with 0.5 mL/L hypophosphorous acid after the mordant, this time at 40°C for one hour. All other conditions were as in experiments one and two.

The experiment was undertaken using 5g of fur at a liquor ratio of 50:1. The flowrate was set at 30 mL/min. The column was rinsed with 350 mL of water in between stages. The hold up volume of the column, 130mL, was displaced by the introduction of the next set of reagents.

3.4.2 EXPERIMENTAL VARIABLES

Table 3.3 pH Data Experiment I4

Stage		pH
Kill	Initial	3.8
	Final	4.4
Mordant	Initial	1.8
	Final	2.15
Acid rinse	Initial	2.2
	Final	2.2
Oxidative Bleach	Initial	5.1
	After Carbonates	7.9
	Final	7.6
Reductive Bleach	Initial	6.9
	Final	5.35

The pH of the mordanting solution is in between that of experiments I1 and I2, and I3. Also of note is the lower pH in the oxidative bleach in this experiment.

3.4.3 DISCUSSION

A noticeable improvement in the whiteness occurred here (Croes whiteness index 43.01), although it is not as white as obtained in experiments I1 and I2. The big improvement on experiment I3 results from an improved mordanting, especially considering the lower pH oxidative bleach. The mordanting differs by the longer exposure period (at a lower temperature) and the inclusion of ammonium chloride and potassium hydrogen tartrate, leading to a higher pH. These effects were studied in more detail in later work and are discussed further in chapter four.

The loss obtained in this experiment is equal to that in experiment I3 at 5.4% although the alkali solubility is almost double at 59%. This indicates that the fur in this experiment is damaged to a greater extent, and that the loss of mass and alkali solubility will not always be directly correlated.

The alkali solubility and fur loss here is lower than in experiments one and two indicating a less damaged fur, although a decreased bleaching is also observed. On the basis of this, no conclusions can be drawn on the relative merits of the two systems.

3.5 EXPERIMENT I5. ABSENCE OF KILL STAGE

3.5.1 OVERVIEW

This experiment investigated the utility of the kill stage. All other treatments were as in experiment I4. This experiment was based on the lack of references to a kill stage found in the literature. The use of a kill step was referred to in only two papers of those surveyed dealing specifically with the bleaching of furs. It was thought that this stage should be investigated, as its elimination would provide benefits in terms of process costs and length.

3.5.2 EXPERIMENTAL VARIABLES

Table 3.4 pH Data Experiment I5

Stage		pH
Mordant	Initial	1.8
	Final	2.1
Acid rinse	Initial	2.1
	Final	2.3
Oxidative Bleach	Initial	5.1
	After Carbonates	7.6
	Final	7.45
Reductive Bleach	Initial	7.0
	Final	3.15

3.5.3 DISCUSSION

This experiment had a slightly lower whiteness index than the previous (44.41 and 43.01 respectively). A visual examination of the fur from this experiment shows the presence of a significant amount of unbleached guard hairs. These did not have a significant impact on the whiteness index, where measurements are made over an area much greater than one fibre. But they are very noticeable visually and this would lead to unsightly dark fibres in manufactured garments.

The slightly lower whiteness index is attributed to the removal of fats and lipids from the fibre making it more receptive to the subsequent treatments. The main effect appears to be making the guard hairs receptive to the subsequent treatments.

The loss and alkali solubility data is similar to the previous experiment. The loss being slightly lower at 5.0% (c.f. 5.4%), and alkali solubility slightly higher at 62.7% (c.f. 59%). It appears that in terms of the overall process, the kill step has a minimal contribution to the damage occurring, but is necessary to ensure bleaching of the guard hairs and as a preparatory treatment for the subsequent stages. Due to these results other kills were not trialled.

3.6 EXPERIMENT I6. HIGHER TEMPERATURE, SHORTER TIME, OXIDATIVE BLEACH

3.6.1 OVERVIEW

This experiment investigated the use of a higher temperature, shorter time, oxidative bleach. Oxidative bleaching was undertaken at the previously described levels of reagents, at 50°C for 95 minutes. The time period of 95 minutes was selected on the basis of a visual examination showing that bleaching had reached a similar stage as in the previous experiments.

SLS was excluded from the bleaching solutions in this experiment. The SLS had a lubricating effect on the rubber bungs used to seal the column causing them to "pop out" at elevated temperatures. All other treatments were as in experiment I4.

The experiment was conducted using 5g of fur at a liquor ratio of 50:1. This was the first experiment conducted using the method where the hold-up water is used to provide some of the liquid for the next stage, i.e. reagents were dissolved in 120 mL of water with the hold up liquor providing the other 130 mL. Hydrogen peroxide was added in two doses in the oxidative bleach to avoid exposing the fur to an excessively high peroxide concentration. One initially and one after ten minutes. Sodium carbonate and sodium bicarbonate were added to the bleaching solution after the addition of the peroxide rather than after one hour as had been the case in the lower temperature experiments

3.6.2 EXPERIMENTAL VARIABLES.

Table 3.5 pH Data Experiment I6

Stage		pH
Kill	Initial	3.8
	Final	4.4
Mordant	Initial	1.8
	Final	2.1

Acid rinse	Initial	2.2
	Final	2.0
Oxidative Bleach	Initial	7.15
	Final	6.9
Reductive Bleach	Initial	6.9
	Final	5.2

3.6.3 DISCUSSION

The pH of the oxidative bleach is lower than in the previous experiments.

This experiment differs with experiment I4 by only the different temperature/time/pH of oxidative bleaching. This experiment gave a higher whiteness index (50.91 c.f. 49.90) and a significantly lower loss and alkali solubility (4.1% & 44.0% c.f. 5.45 & 59.0%). This indicates bleaching at 50°C for 95 minutes is superior to bleaching at 30°C for twelve hours, with this particular reagent system. This does not necessarily mean that bleaching at 50°C is superior to bleaching at 30°C. Twelve hours may be longer or shorter than the optimum bleaching time at 30°C, causing a lower whiteness as detailed in chapter one.

Also of note is that the whiteness obtained is still lower than in experiments I1 and I2. The bleaching in this experiment is slightly below the desired standard. The fur has a slight yellow tinge to it. The fur could be dyed to any but the palest of colours.

The shorter bleaching time was adopted as part of the standard method in later experimental work. Significant time savings were made from this alteration.

3.7 EXPERIMENT I7. ABSENCE OF REDUCING AGENT IN THE MORDANT

3.7.1 OVERVIEW

This experiment investigated the effect of no reducing agent/ protective agent in the mordant. Neither hypophosphorous acid nor sodium dithionite/formaldehyde was included. The literature stressed the point that the use of an appropriate reducing agent was very important in the mordanting procedure. It was decided that it was worthwhile quantifying the effect of this treatment.

All other experimental parameters, e.g. flowrate, rinsing etc. were as in the previous experiment.

3.7.2 EXPERIMENTAL VARIABLES

Table 3.6 pH Data Experiment I7

Stage		pH
Kill	Initial	3.8
	Final	4.4
Mordant	Initial	2.7

	Final	2.5
Acid rinse	Initial	2.2
	Final	2.0
Oxidative Bleach	Initial	7.15
	Final	6.9
Reductive Bleach	Initial	6.9
	Final	4.0

The pH of the mordant is notably higher due to the excluded reagents.

3.7.3 DISCUSSION

A large increase in damage is observed from the previous experiment highlighting the importance of the reducing agent. Loss has increased from 4.1% to 7.2%, and alkali solubility from 44.0% to 72.3%. This increase in damage is accompanied by an increase in the whiteness index, 48.30 c.f. 44.87 in experiment six. Damage results may even have been higher if the acidic rinse was also excluded.

After this experiment, it was decided that a detailed examination of the mordant stage was required, given its bearing on the oxidative bleach.

3.8 CONCLUSIONS

- Good results were obtained using the method supplied by Gray Fur Trading. The fur was of a marketable colour and the loss within the targeted 10%. The displacement bleaching system was found to overcome the matting problems previously encountered. The elimination of the strip stage resulted in no visible ferric staining of the finished fur.
- Poor results are obtained using the mordanting method of Bereck (1994), the fur had a noticeable yellow colour. The published method must be treated with some scepticism due to the difference between the published and obtained pH values.
- Lower damage is obtained when hypophosphorous acid at 3 g/L is substituted for sodium dithionite and formaldehyde in the mordant, an acid rinse undertaken at 0.5 mL/L hypophosphorous acid, and SLS included in the bleaching solutions at 1.4 g/L. A lower bleaching effect is also observed. These were the changes identified from the literature as being most likely to lead to improvements in the process.
- The kill stage is necessary to obtain adequate bleaching of the guard hairs, and also effects the susceptibility of the bulk fibre to subsequent treatments.
- Oxidative bleaching at 50°C for 95 minutes is superior to 30°C for 12 hours with the reagent system used here.
- The inclusion of the reducing agent in the mordant is critical in preventing excessive damage to the fur.

Figure 3.1

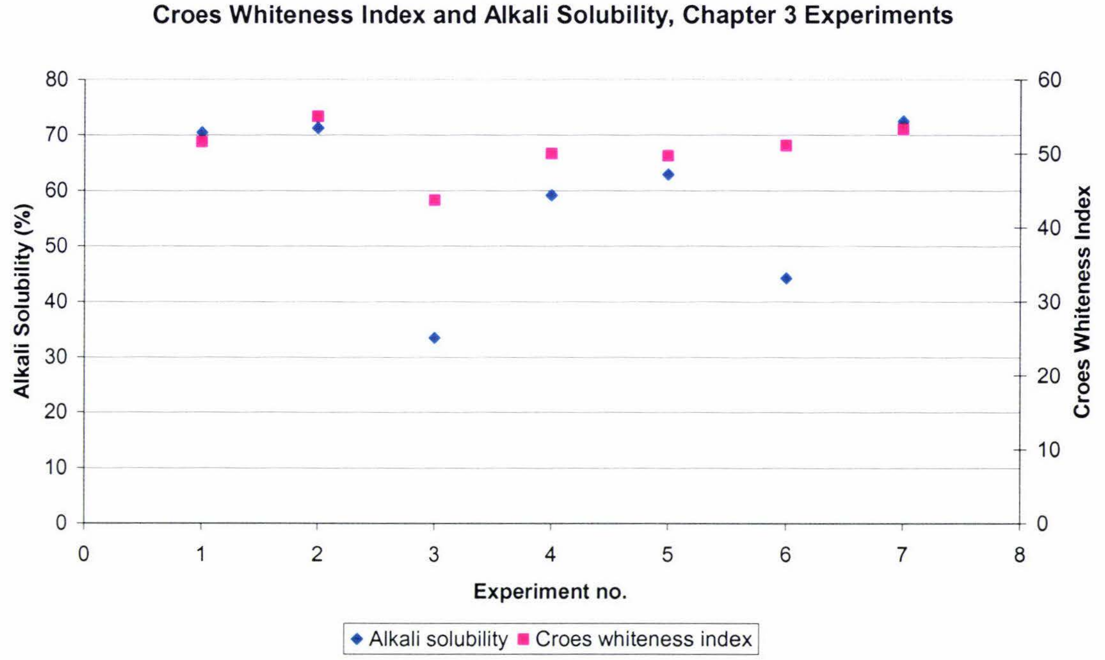
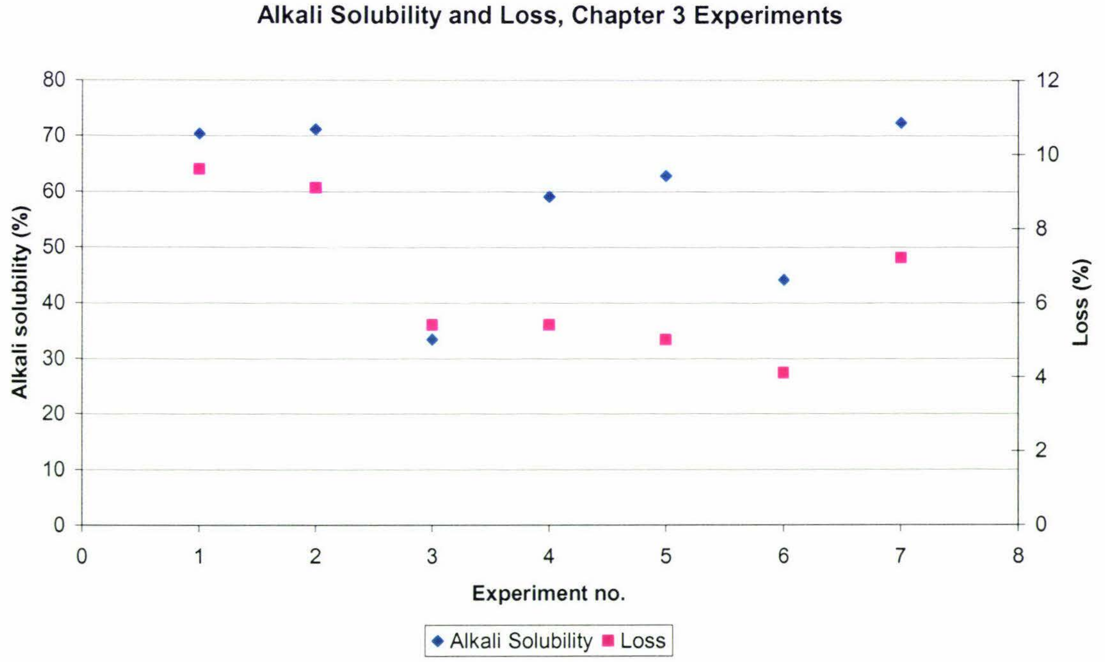


Figure 3.2



CHAPTER 4 MORDANT

4.1 INTRODUCTION

The mordanting process involves binding ferrous ions to the melanin pigments of the possum fibre to catalyse the subsequent hydrogen peroxide bleach. The mordanting procedure decided upon is made up of two separate treatments; the treatment with iron containing ferrous ions, an ammonium salt, a sequestering agent and a reducing agent and the subsequent acidic rinse with the reducing agent to remove iron bound to the keratin of the fibre.

The goal of this process is to have ferrous iron bound only to the melanin pigments. Ferrous or ferric iron will have the same effect in initiating the radical decomposition of the peroxide (although the ferric ion must first be reduced by the perhydroxyl anion to ferrous iron), however, ferric iron binds more tightly to the keratin of the fibre than ferrous. For this reason, it is preferable to use ferrous species for mordanting, to minimise the amount of iron absorbed at the fibre keratin.

The presence of ferrous species is governed by the pH of the solution and the presence of a suitable reducing agent to reduce ferric species formed.

The ammonium salt is thought to help in the absorption of the iron by the melanin pigment. The exact mechanism of this is unknown.

The experimental work on the mordant consisted of three sections. First the effects of the reagents other than iron (i.e. ammonium salt, potassium hydrogen tartrate, the reducing agent and the acid rinse the "ancillary reagents") were determined. Secondly work was undertaken on varying the pH of the mordant and thirdly the temperature and time of the mordant were varied.

4.2 EFFECTS OF THE ANCILLARY REAGENTS

4.2.1 OVERVIEW

These reagents were examined in terms of the effect their absence had, or on the effect substituting one reagent for another, had on the bleaching process. The experiments were undertaken using the initial method, as described in section 3.2, except using oxidative bleaching at 50°C for 95 minutes and omitting the strip step. An acidic rinse using 0.5 mL/L hypophosphorous acid, at 40°C for one hour, was also included after the mordant. Reagents were either eliminated or substituted using this method, as detailed in table 4.1. The following sections detail the results of these experiments.

Table 4.1 Treatments for the Ancillary Reagent Experiments

Exp. ref.	Variation
M1	Control
M2	Control
M3	Ammonium chloride and potassium hydrogen tartrate excluded
M4	Absence of ammonium salt
M5	Potassium hydrogen tartrate excluded
M6	Hydrosulphite and formaldehyde excluded
M7	Acid rinse excluded
M8	Kill excluded
M9	Ammonium sulphate vs. ammonium chloride

Figures 4.1, 4.2 and 4.3 provide an overview of the whiteness, alkali solubility and loss results obtained.

4.2.2 EXPERIMENTS M1 AND M2. CONTROL EXPERIMENTS

This experiment was conducted in duplicate. The results are summarised below.

Table 4.2 Results of the Control Experiments

	Experiment M1	Experiment M2
Fur loss (%)	7.4	7.2
Alkali solubility	60	51
Croes Whiteness	48.55	48.21

These experiments give an indication of the variation which can be expected resulting from the method used. The second experiment gave a slightly better bleaching effect than the first, with slightly lower losses and alkali solubility.

These experiments were performed using the same batch of fur, which had been carded to ensure homogeneity. Differences in the fur used can result in different bleaching effects, as subsequent work has shown.

The conditions encountered in this chapter for the oxidative and reductive bleach pH are similar to those detailed in section 3.6.2. The pH of the oxidative bleach was 7.15 – 7.20 initially falling to 7.0 – 7.1. Reductive bleach values were typically 6.5 – 6.7 falling to 4.5 – 5.5.

4.2.3 EXPERIMENT M3. ABSENCE OF POTASSIUM HYDROGEN TARTRATE AND AMMONIUM CHLORIDE

This experiment checked the mordanting in the absence of both these reagents. A lot of the mordanting procedures surveyed in the literature, for example that of Arifoglu and Marmer (1992) and that of Bereck (1994) had neither these nor similar reagents. On the basis of this it was decided to investigate if they were in fact necessary.

Of the experiments in this section, this performed poorest in the whiteness index at 39.59, the fur has on off-white grey tinge. Unbleached guard hairs are also evident.

The loss here is in between those obtained when the reagents were excluded singly at 7%, although the alkali solubility was the lowest of any observed at 38.2%.

The bleaching effect observed was clearly inferior to that when these reagents were included indicating they play a significant role in the mordanting procedure.

This experiment had the highest mordant pH of any at 3.8 but the bleaching was poor indicating a lower level of iron absorbed. The work in section 3.3 at this pH including these reagents had a greater degree of bleaching indicating one or both plays some role in the absorption of iron.

4.2.3.1 Experiment M4. Absence of ammonium salt

An experiment was undertaken excluding ammonium chloride from the method stated above. Some references were found in the literature to the use of ammonium salts in mordanting, (Cegarra and Gacen 1983; Trotman 1968) however others, such as Bereck (1994) made no mention of an ammonium salt. On the basis of this it was decided to investigate if an ammonium salt is beneficial to the mordanting procedure. Given the poor bleaching effect when both ammonium chloride and potassium hydrogen tartrate were excluded it was decided to investigate these reagents singly, in order to determine whether both these reagents were necessary.

The loss of fur in this experiment is lower (at 6.3%) than that observed in the control experiments (7.3%). A decreased bleaching effect is observed, the control whiteness index was 48.38 (average value) c.f. 41.98. This is in agreement with the hypothesis that ammonium salts play a role in the absorption of iron by the melanin pigments. The only experiments to perform worse in the whiteness indices in this section was that where both ammonium chloride and potassium hydrogen tartrate were excluded.

From this experiment it can be concluded that the addition of an ammonium salt is beneficial to the mordanting process.

4.2.4 EXPERIMENT M5. ABSENCE OF POTASSIUM HYDROGEN TARTRATE

This experiment was based on the work of Bereck (1994) who found that a chelating agent impaired the selectivity of absorption of iron leading to a more damaged fibre. It was also part of the investigation into the absence of this reagent and ammonium chloride separately.

The pH of this experiment was higher than the control experiments, 3.53 in this experiment compared with around 3 in the control experiments.

The whiteness index is very similar to that in the control experiments 47.08 c.f. 48.38 (average). The loss is higher than the control experiments at 7.8% c.f. 7.3% (average), the alkali solubility is in between that observed in the two control experiments at 57.4%. The loss and alkali solubility observed in this experiment are similar to that obtained in the section on pH manipulation for experiments at similar pH, as is the whiteness obtained. References have been found in the literature that a chelating agent aids in the mordanting procedure (Frishman and Biberfeld). When compared with the work on pH manipulation for similar pH no distinction can be made in terms of damage or whiteness.

Comparing the results of experiments M3 (potassium hydrogen tartrate and ammonium chloride excluded) and M4 (ammonium chloride excluded) a lower whiteness index is observed in the absence of potassium hydrogen tartrate. The two reagents may have some kind of synergistic effect. Potassium hydrogen tartrate was included in subsequent experimentation.

4.2.5 EXPERIMENT M6. ABSENCE OF SODIUM HYDROSULPHITE AND FORMALDEHYDE

The loss observed in this experiment is one of the lowest in this section of work at 6.5%. This was an unexpected result seeing as how the absence of the hydrosulphite will lead to a greater proportion of ferric iron, which should in turn lead to a higher loss. The alkali solubility was the highest observed, at 61.8%, which is in accordance with expectations. The loss here must be treated with some scepticism.

The whiteness observed here was the highest of this set of experiments at 50.24, but at the cost of extra damage to the fur based on the alkali solubility. Bereck (1994) found black karakul wool fibres mordanted with ferric iron gave a slightly better bleaching effect than those mordanted with ferrous iron. The fibres sustained a greater degree of damage however, due to the non-selective absorption of the ferric iron. This appears to be the case here also.

The absorption of ferric iron should be offset somewhat by the acid rinse as this should reduce the ferric iron to ferrous iron which is then easily removed from the fibre, it would be expected that the damage would be even greater if this step had not been included.

4.2.6 EXPERIMENT M7. ABSENCE OF ACID RINSE

It was expected that this experiment would lead to a more damaged fur due to a radically induced attack of the fibre keratin, resulting from iron bound to the keratin. Based on the literature (Bereck 1994) it was highly likely that this stage would be necessary in the process, this experiment was undertaken to quantify the effect of this treatment.

The loss and alkali solubility results here are the reverse of the situation obtained from the experiment dealing with the absence of formaldehyde and hydrosulphite. The loss was high, 8.5% equal highest but the alkali solubility was low, being one of several values around 50%. The alkali solubility is equal to that of the second control experiment and lower than the first. The loss is significantly higher however.

This experiment performed well in the whiteness index, the second highest at 49.30. It is clear that an increased bleaching affect is obtained when the reducing agent is excluded, or the acid rinse is excluded, both of which will lead to a greater proportion of iron attached to the keratin of the fibre and hence greater damage to the fur. The results from these two experiments are unexpected, in terms of a low loss in one case and low alkali solubility in the other. However on the basis of the high loss in one instance and high alkali solubility in the other, and the data of Bereck (1994), both these treatments were considered worthy of inclusion.

This experiment differs from those in section 3.2 (evaluation of the original method) by the 50°C, 95 minute oxidative bleach. This experiment has similar whiteness (49.30 c.f. 48.71) with lower loss (8.5% c.f. 9.4%) and lower alkali solubility (51% c.f. 70.7%) (average values used for section 3.2 experiments). This reinforces the conclusion of section 3.6.3 that bleaching at 50°C for 95 minutes is superior to 30°C for 12 hours.

4.2.7 EXPERIMENT M8. ABSENCE OF THE KILL STAGE

A repeat of the experiment detailed in section 3.5. This experiment had the third lowest whiteness index in this section at 44.31, around for units lower than the control experiments. A visual examination of the fur shows the presence of unbleached guard hair again. The kill step softens the fibres and removes lipids from the surface, to make them more susceptible to the following treatments.

This experiment reinforces the need for the kill step in the bleaching process. The decrease in bleaching of the bulk of the fur is more pronounced in this experiment than experiment I5. The fur in these experiments may have had a greater degree of oils etc. on it leading to the decreased bleaching in the absence of the kill.

The alkali solubility in this experiment is quite low at 49% but the loss is higher than expected at 8.5%, higher than the control experiments. The treatment with sodium metabisulphite will lead to some damage of the fur so it was unexpected that this experiment would have a lower alkali solubility.

4.2.7.1 Experiment M9. Ammonium chloride vs. ammonium sulphate

This experiment was conducted because the use of a sulphate salt is beneficial in terms of the prevention of localised corrosion in the stainless steel plant equipment. Although the material selected for use in the plant (316SS) is able to withstand the conditions being used, it is still prudent to use the least corrosive conditions possible.

This experiment was undertaken at Gray Fur Trading in Hokitika. A higher temperature (50°C) mordant was used. Commercial reagents (obtained from Redox Chemicals Ltd.) were used except in the cases of hypophosphorous acid (used instead of hydrosulphite and formaldehyde at 3g/L) and ammonium sulphate, which were reagent grade

Both experiments had equimolar amounts of ammonium ion. Ammonium sulphate was also used in the oxidative bleach in the sulphate experiment, again at equimolar amounts.

Visual examination of the two bleached furs shows a clear increase in the bleaching effect when ammonium sulphate is used. The mordant pH was higher in the experiment using ammonium sulphate, 2.02 c.f. 1.83 for ammonium chloride. It is likely that the increased pH is the cause of the increased bleaching observed, this is discussed in further detail in section 4.3.

The use of ammonium sulphate in the oxidative bleach had little effect on the pH of this stage, 7.02 c.f. 7.04. Therefore, the increased bleaching observed can be attributed to the increased pH of the mordant, with all other treatments being held equal, unless the sulphate anion aids in the oxidative bleaching, or aids directly in the absorption of iron in the mordant, which it almost certainly does not. No information to this effect was found in the literature.

The sulphate experiment has a slightly lower yield; the loss was 6.8% in this experiment and 6.1% in the chloride experiment. The better bleaching and subsequent higher damage is attributable to the higher pH obtained by the use of ammonium sulphate. The counter ion is thought to play no role in the absorption of iron by the fibres other than by the pH effect it provides.

4.3 PH OPTIMISATION

4.3.1 OVERVIEW

This work concerns the pH at which the mordanting process is undertaken. Different information in the literature is quoted on the optimum pH for mordanting procedures, as detailed in chapter one. It was necessary to determine an optimum pH for use in the bleaching of possum fibre.

Initial work was carried out using either hydrochloric acid or sodium hydroxide to manipulate the pH of the mordant solution. The pH of these solutions was found to change considerably over the course of the mordanting step. Since this step was left overnight, the pH could not be monitored at regular intervals, and also for the sake of comparison it was necessary to have pH as constant as possible over the course of the mordant. For this reason experiments were then undertaken using the mordanting chemicals in buffer solutions. Two buffer systems were identified as suitable for use; a glycine/HCl buffer over the pH range 2.0 – 2.4, and an acetic acid/sodium acetate buffer over the range 2.6 – 3.85. No evidence was observed of any interaction between these reagents and the mordanting chemicals. In particular, the literature (CRC Handbook of Chemistry and Physics, Langes Handbook of Chemistry) showed no evidence of any interaction between these species and iron, nor was any observed experimentally. Of concern was the formation of salts/complexes with the buffering chemicals, altering the effectiveness of the mordant process.

The experiments in this section were undertaken using hypophosphorous acid at 3.0 mL/L in place of sodium dithionite/formaldehyde, followed by a one hour rinse at 40°C with 0.5mL/L hypophosphorous acid. Oxidative bleaching was again carried out at 50°C for 95 minutes, with the strip stage omitted. All other treatments are as in the initial method.

The mordant procedure was assessed by taking the experiments through the oxidative and reductive bleaching procedure and measuring the whiteness and damage. It was initially thought that atomic absorption spectroscopy would be used to measure the level of iron in the fibres. This was abandoned when it was realised that it could not distinguish between desirable ferrous species and undesirable ferric species, so the experiments were taken through to completion to evaluate the effect of the mordant. No method was found in the literature capable of isolating iron from the fur without altering its oxidation state, to allow the use of other measurement techniques.

4.3.2 RESULTS

Table 4.2 details the pH values obtained and the buffer system used. The pH value quoted is the average of the value after 20 minutes of recirculation and the final value, typically these values would differ by 0.2 units.

Table 4.3 Data for pH Manipulation Experiments.

Exp. ref.	pH	buffer	Loss	Alkali solubility	Croes whiteness
M10	1.4	HCl	4.5	26.5	35.13
M11	1.825	HCl	5.9	40.0	42.70
M12	2.1	NaOH	6.3	48.0	42.43
M13	2.1	Gly/HCl	6.1	46.1	47.49
M14	2.1	Gly/HCl	6.3	45.2	42.20
M15	2.125	Gly/HCl	7.2	54.5	44.74
M16	2.15	Gly/HCl	6.7	67.0	51.07
M17	2.25	Gly/HCl	6.4	45.6	47.94
M18	2.375	Gly/HCl	6.1	42.2	46.32
M19	2.4	Gly/HCl	6.4	57.8	51.22
M20	2.6	HAc/NaAc	7.6	42.0	45.86
M21	2.65	HAc/NaAc	8.6	61.3	49.05
M22	2.8	HAc/NaAc	7.5	54.4	50.81
M23	3.125	HAc/NaAc	7.1	49.0	50.92
M24	3.325	HAc/NaAc	9.0	58.3	50.60
M25	3.325	HAc/NaAc	8.7	73.5	47.66
M26	3.575	HAc/NaAc	9.4	73.8	46.99
M27	3.775	HAc/NaAc	10.4	79.8	47.07
M28	3.85	HAc/NaAc	9.4	73.5	46.57

This information is illustrated graphically on figures 4.4 to 4.6

This data shows a clear increase in fur loss and alkali solubility as pH increases, and consequently a strong correlation between alkali solubility and losses. This is likely to be a result of an increased proportion of iron being present in the ferric form as pH increases. The oxidation of iron by dissolved oxygen is a pH dependent process, increasing at higher pH. The proportion of hypophosphorous acid used may not be enough to fully counter this effect at higher values of pH. It was observed that the higher the pH of the mordanting solution, the greater the rust colour present Given the lack of interaction between iron and the buffering chemicals, and that all other experimental variables were held constant, this indicates a higher presence of ferric species. The neutralisation of the hypophosphorous acid at higher values of pH is not of concern since hypophosphorous salts are also powerful reducing agents.

Also of note is that the whiteness obtained starts to decrease at higher pH values, from about 3.25 onwards, whereas the loss and alkali solubility both increase in a linear fashion with increased mordant pH. Figures 4.4 and 4.5 show Croes whiteness index vs. pH and alkali solubility. Both show a maximum with the whiteness obtained decreasing at higher values. This indicates that once the fur is attacked past a certain stage the whiteness obtained starts to decrease with further degradation of the fibre keratin being the only result. This is an effect analogous to the decrease in whiteness of bleached wool when bleached for longer than the optimum time observed by Cegarra and Gacen (1983). This could perhaps be countered by a process in which a mordant at higher pH is used with a shorter oxidative bleach. However, the presence of ferric iron is still likely to lead to less selective bleaching. It may not be possible to remove enough melanin to obtain a satisfactory bleaching without causing significant damage to the fibre. The data obtained in this section indicates that the lower the pH of the mordant, the lower the damage resulting to the fibre.

The results of some experiments around pH 2.25 have good whiteness while the loss and alkali solubility at these values is still relatively low. The pH of the solutions of mordanting chemicals without pH buffering is 2.0. This is at the lower end of the range at which good bleaching was observed. This offers the opportunity to develop mordanting conditions in which the pH of the solution does not need to be altered, by manipulating the temperature and time of the mordanting process. This is beneficial in terms of the industrial process, pH adjustment is a time consuming process in a two vessel system and it is easy to overshoot the desired value.

4.4 COMPARISON OF HYPOPHOSPHOROUS ACID AND SODIUM DITHIONITE / FORMALDEHYDE MORDANTS

The two control experiments detailed in section 4.2.2 using the sodium dithionite/ formaldehyde mordant had average pH values of 2.8 and 2.9. The results of this and the hypophosphorous acid experiment at pH 2.8 are reproduced below. These experiments were identical except for the differing mordants.

Table 4.4 Comparison of Hypophosphorous Acid and Sodium Dithionite / Formaldehyde for Similar pH.

	M22	M1	M2
Fur loss (%)	7.5	7.4	7.2
Alkali solubility	54.4	60	51
Croes Whiteness	50.92	48.55	48.21

As can be seen the damage results are similar, while a better whiteness is obtained with the use of hypophosphorous acid. Hypophosphorous acid was selected for further work on the basis of this and since it gave the desired pH without manipulation.

4.5 TEMPERATURE AND TIME

This section deals with the work on manipulating the temperature and time of the mordant process.

4.5.1 EXPERIMENTS M29 AND M30. EXTENDED MORDANTING TIME

Following the work on the manipulation of the pH of the mordant two experiments were conducted using the mordanting reagents without pH adjustment (pH 2 – 2.05) using an extended time. Experiments were conducted at 19.5 hours (M29) and 24 hours (M30); all other treatments were as in the section on pH manipulation.

Figure 4.7 shows the whiteness indices and loss results of these two experiments superimposed on the data from the pH manipulation section. The data is summarised below

Table 4.5 Results of Experiments M29 and M30

	M29	M30
Fur loss (%)	5.1	5.0
Alkali solubility (%)	51.8	50.5
Croes whiteness	52.10	50.98

From this it can be seen that the extended time is clearly beneficial to the subsequent bleaching. The whiteness obtained is as high as at any pH while a lower loss was observed than for experiments at a similar pH. The 19.5-hour experiment has the higher loss and higher whiteness. The alkali solubilities are very similar to those obtained in the buffer systems around this pH indicating the extra mordanting time has little if any effect on damage while causing a significant increase in whiteness.

In terms of the industrial process it was thought at this stage the mordant step would be left overnight, giving a time frame of about 15 hours. Experimentation was then conducted dealing with a higher temperature mordant.

4.5.2 HIGHER TEMPERATURE MORDANT

An experiment was conducted in Hokitika using the same mordant as that for the pH manipulation section except the mordanting was conducted at approximately 50°C. This experiment was conducted using the commercial reagents in Hokitika, which had previously been obtained from Redox chemicals, with the exception of the hypophosphorous acid, which was of reagent grade.

The bleaching effect obtained was not as good as that resulting from the previous experiments dealing with an extended mordanting time. This is thought to be an effect of the different grade reagents used, tap water was also used instead of reverse osmosis purified water.

The mordant pH obtained with the commercial reagents was 1.8 c.f. 2.0 previously. The pH of the oxidative bleach was also lower, 6.4 c.f. 7.15. It was decided that a comparison needed to be made with the same oxidative bleach pH which lead to the next section on the oxidative bleach.

The loss obtained here, 6.1% is higher than that from the previous experiments but not excessively high and within the target of 10%.

4.6 CONCLUSIONS

- The use of ammonium chloride and potassium hydrogen tartrate was found to be beneficial to the bleaching process. A decreased bleaching effect is observed when they are excluded.
- Hypophosphorous acid was found to be the better reducing agent for use in the mordant, giving a higher whiteness for similar damage at similar pH compared with the sodium dithionite / formaldehyde system. A post mordant rinse with hypophosphorous acid also prevents damage to the fibres.
- The utility of the kill stage was confirmed. It is postulated it is of particular use when the fur has a high degree of oils and lipids etc. present.
- In experimentation on the mordant pH, the bleaching effect was found to decrease at pH below about 2 and above about 3.25. The damage occurring to the fur increases with increasing pH.
- It was found that an extended mordant at pH 2 gave the best results. Whiteness was as good as obtained at any pH at 51 – 52 whilst damage was at an acceptable level with alkali solubility around 50% and loss around 5%. The following table details the mordant conditions for these results.

Table 4.6

Stage	Reagents	Conc. (g/L)	Temp (°C)	Time (hours)
Mordant	Ferrous Sulphate	11	40	19-24
	Ammonium Chloride	11		
	Cream of Tarter	2		
	Hypophosphorous acid	3 mL/L		
Rinse	Hypophosphorous acid	0.5 mL/L	40	1

- The use of ammonium chloride is preferable to that of ammonium sulphate since this will give a lower pH and hence lower damage. This reagent will not be a problem unless the equipment is left to dry out when wet with the mordant solution. This should not occur since the mordant is followed immediately by a rinse to remove the residual reagents from this stage, as is necessary after all stages of the process.

Figure 4.1

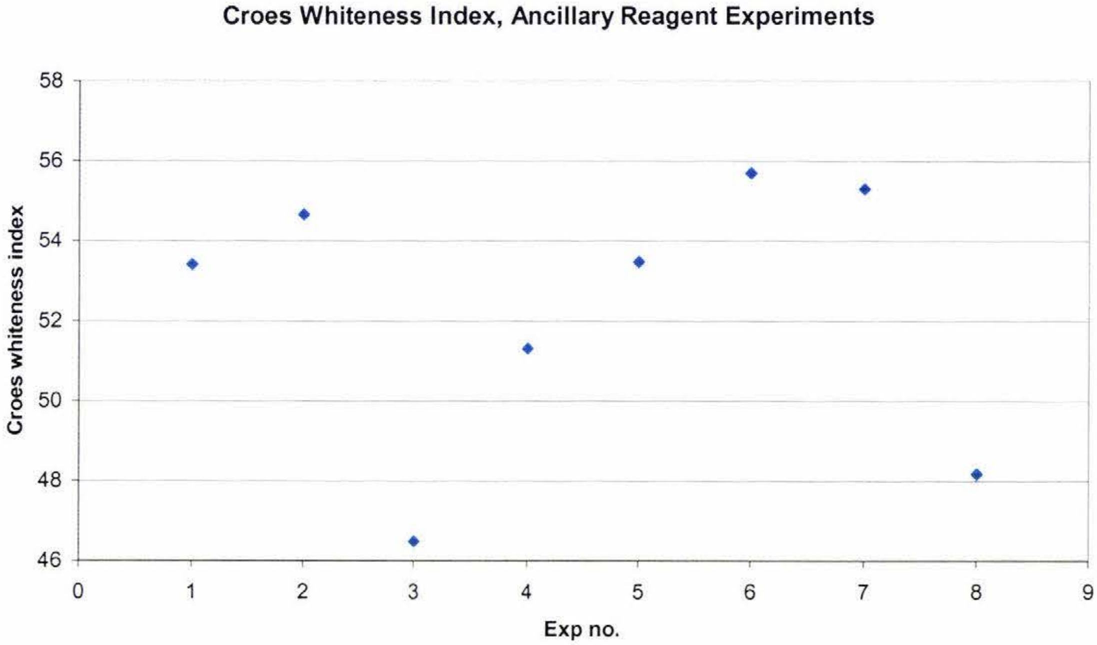


Figure 4.2

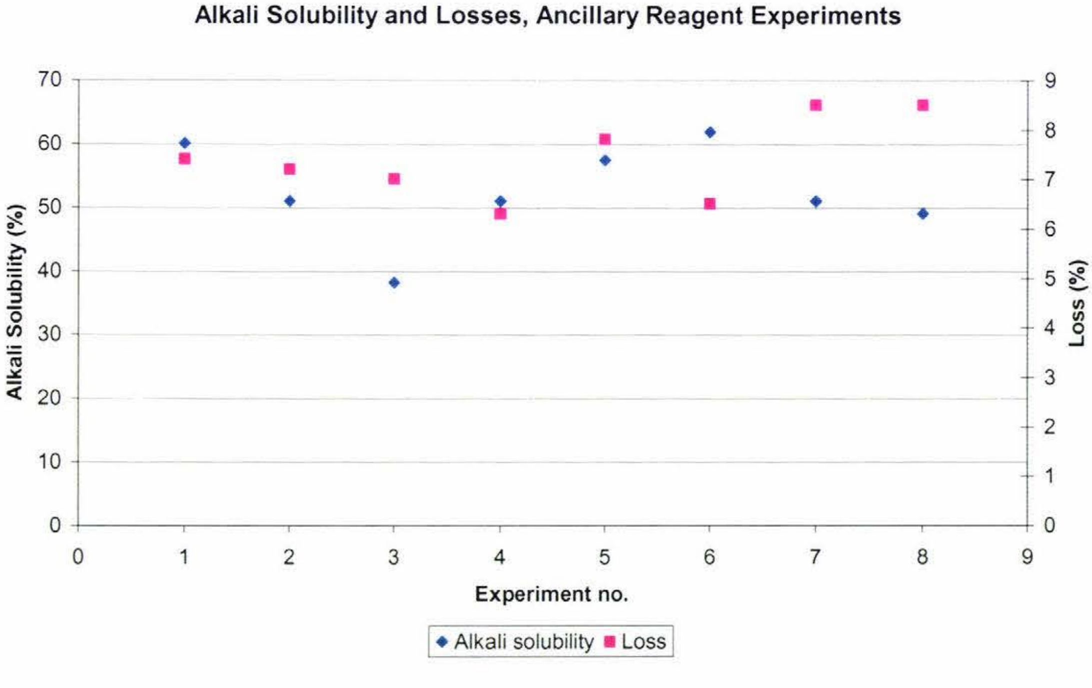


Figure 4.3

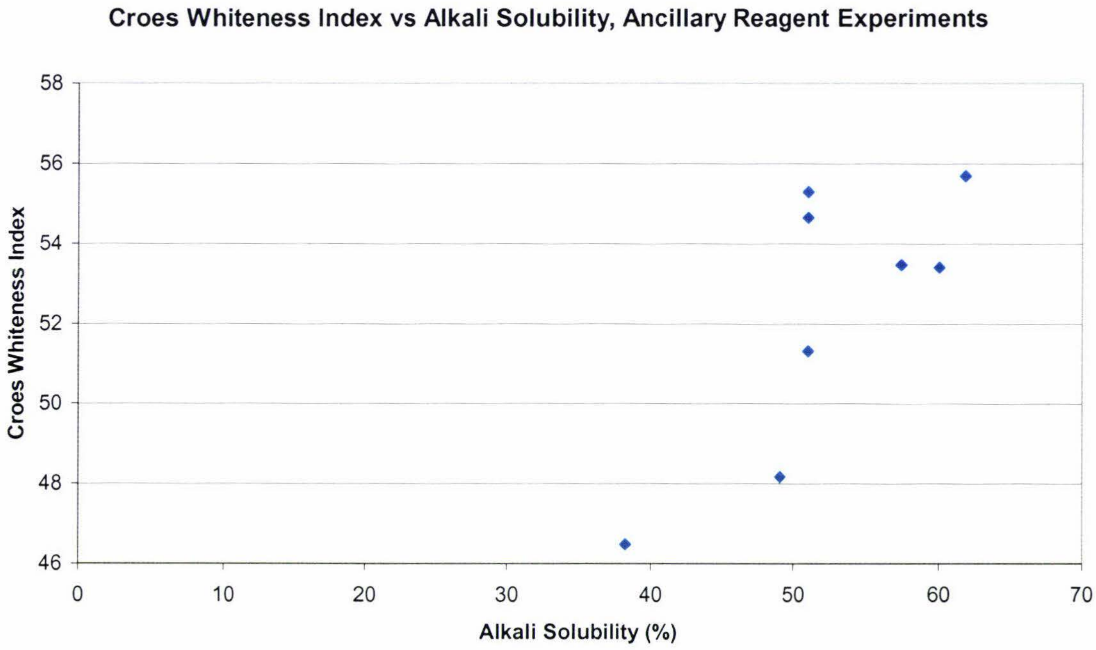


Figure 4.4

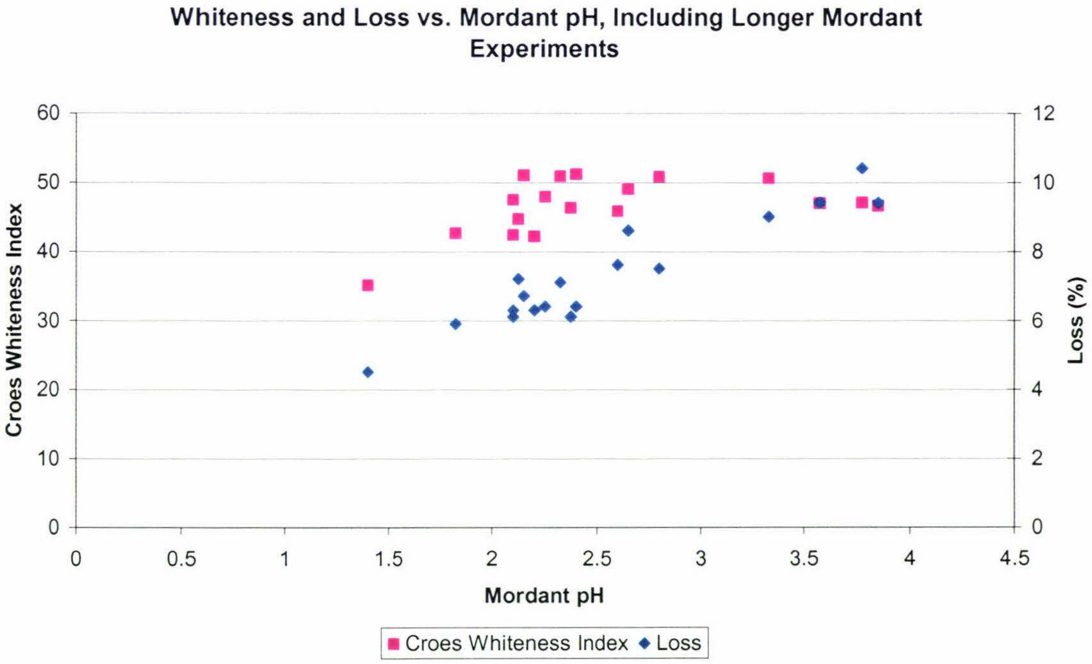


Figure 4.5

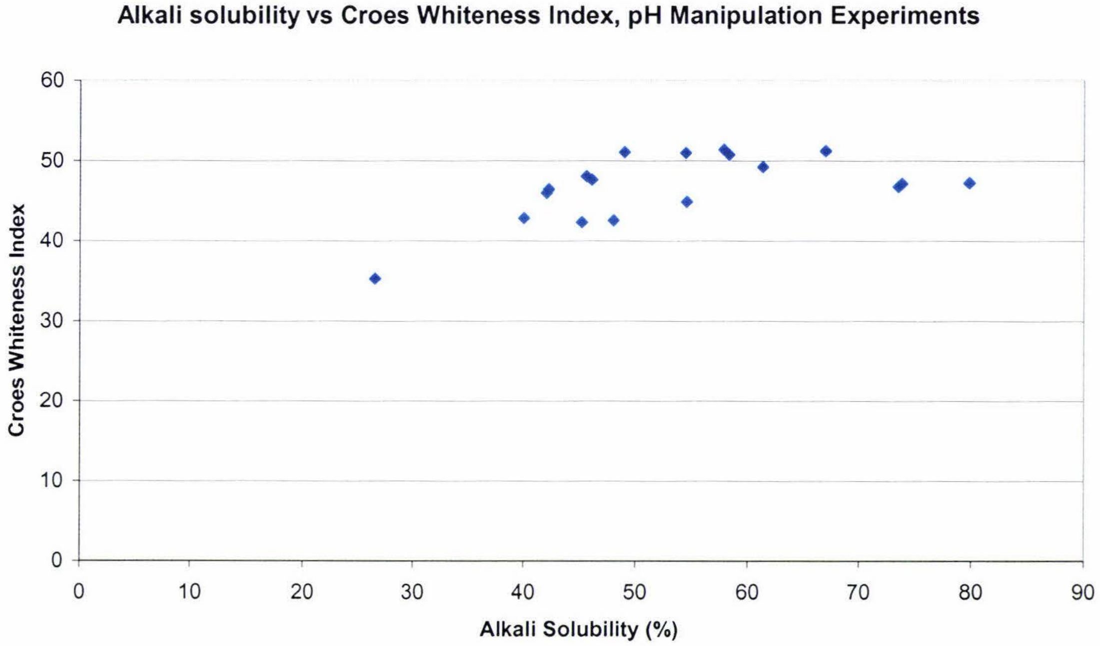


Figure 4.6

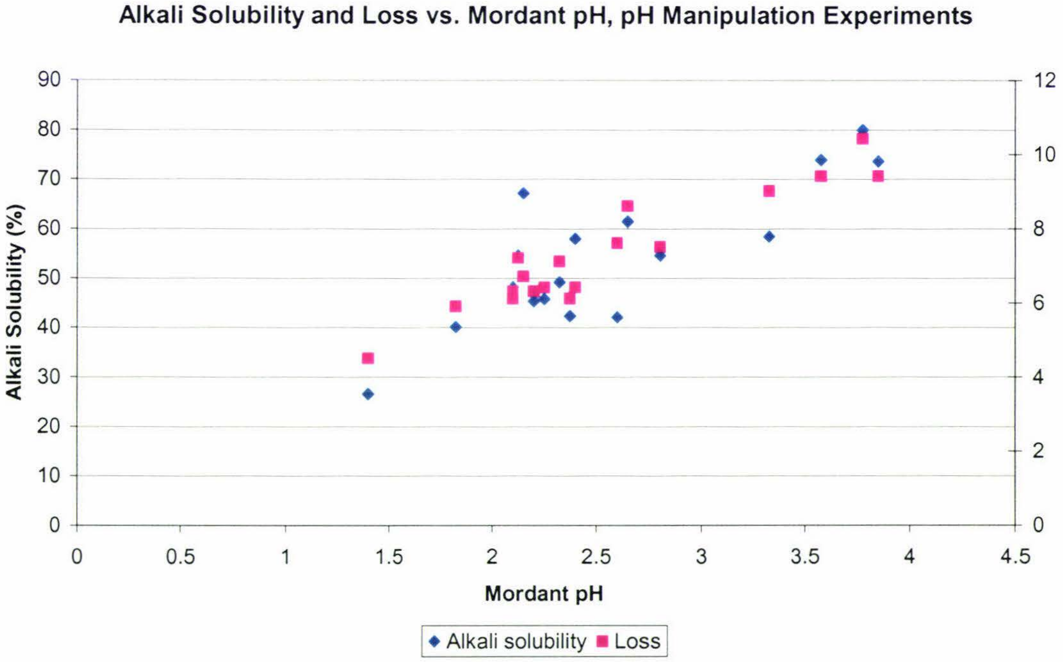
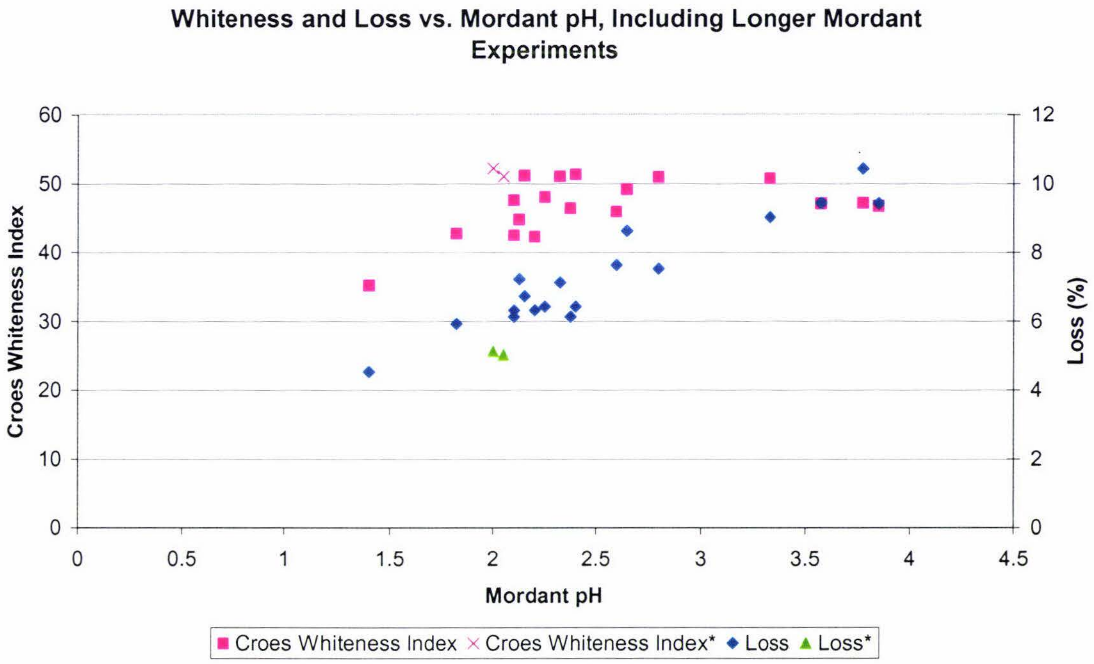


Figure 4.7


Whiteness and Loss vs. Mordant pH, Including Longer Mordant Experiments
Croes Whiteness Index
60
50
40
30
20
10
0
12
10
8
6
4
2
0
Loss (%)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
Mordant pH
■ Croes Whiteness Index × Croes Whiteness Index* ◆ Loss ▲ Loss*

CHAPTER 5 OXIDATIVE BLEACH

5.1 INTRODUCTION

The oxidative bleach is the stage responsible for the majority of the bleaching.

The bleaching results from the combination of two bleaching mechanisms. Firstly there is the bleaching from the iron induced radical decomposition of the peroxide, resulting from iron present from the mordanting stage. Secondly, there is the "conventional" bleaching resulting from the presence of the perhydroxyl ion in an alkaline peroxide solution.

The literature has shown the bleaching of keratinous fibres by hydrogen peroxide solutions to be very much a pH dependent process. Bleaching processes have been developed for wool in both acidic and alkaline media but based on the colour removal required for heavily pigmented fibres, "the only efficient way to decompose and decolourise melanin is a treatment with oxidising agents in alkaline media" (Bereck 1994).

Whilst the bleaching efficiency increases with solution pH, so does the damage occurring to the fibres. An optimum pH needed to be determined giving minimum fibre damage with the desired level of bleaching.

The pH of the solutions used in oxidative bleaching was manipulated by the addition of sodium carbonate and sodium bicarbonate. These are the reagents used in the original process. They offer the advantages of allowing relatively fine manipulation of pH, avoiding "overshooting" the desired pH and are also relatively cheap reagents.

The experimental work in this section was undertaken at Gray Fur Trading in Hokitika, and the whiteness meter was not available. This meant that samples had to be compared by eye and by taking digital photos of the bleached fur under identical lighting conditions. It also means that there is no whiteness index data for this section.

The mordant process used in the experimentation on oxidative bleaching is detailed in the following table. This system gives a pH of 1.8 – 2.0.

Table 5.1 Mordant Used in Oxidative Bleaching Experimentation

Reagents	Conc. (g/L)	Temp (°C)	Time
Ferrous Sulphate	11	50	15 hours
Ammonium Chloride	11		
Cream of Tarter	2		
Hypophosphorous Acid (50%)	3 mL/L		

The wet and wash and kill stages were undertaken as in the previous stages. A rinse with 0.5 mL/L hypophosphorous acid at 50°C for one hour was undertaken after the ferrous sulphate treatment. Reductive bleaching was undertaken using 3 g/L sodium dithionite. Unless otherwise stated, all other treatments were as per the work on the manipulation of mordant pH.

5.2 INITIAL EXPERIMENTATION ON PH MANIPULATION

5.2.1 INTRODUCTION

The experiments in this section trialled different pH bleaching systems by varying the level at which sodium carbonate and sodium bicarbonate were added to the oxidative bleach.

The experiments used 10g of fur at a liquor ratio of 30:1 and a flowrate of 130 mL/min. The carbonate/bicarbonate was added after 10 minutes of bleaching. The hydrogen peroxide was added in two doses, the second after five minutes, in this work.

The initial experimentation into the manipulation of the pH of the oxidative bleach was carried out for 95 minutes at 50°C.

5.2.2 INITIAL EXPERIMENTATION

The following table gives the relevant information for these experiments. The strip stage was included in experiment five; this is discussed in detail in section 6.2.

Table 5.2 Results of Experiments O1 to O6

Exp.	Level Carb/ bicarb (g/L)	pH initial	pH final	Average pH	Loss (%)	Alkali Sol (%)
O1	2.0	7.06	6.47	6.77	5.4	72.8
O2	2.5	7.21	6.76	6.99	5.6	77.2
O3	3.0	7.46	6.96	7.21	5.4	82.8
O4	3.5	7.34	7.26	7.30	5.9	68.3
O5	4.0	7.40	7.22	7.31	7.9	72.5
O6	4.0	7.55	7.35	7.4	5.4	68.6

Immediately noticeable from the table is that experiments O4 and O5 do not give a proportional increase in pH on the first three; and a significant difference is observed between experiments O5 and O6, which featured the same level of carbonate/bicarbonate. All the preceding steps were equal. Variations in the pH obtained from the addition of the same amount of carbonate/bicarbonate have been observed throughout the course of the experimental work. Careful adjustment of this variable will be necessary on large scale.

The losses resulting are all very similar except experiment 5, which is considerably higher. It is thought that some of the fur must have been lost in a transfer.

Photos of these experiments, taken after the oxidative bleach, are included in section 5.7 as experiments O1 to O6. These photos show that a similar level of oxidative bleaching was obtained in all cases. This similar level of bleaching was also evident in the finished fur, except in the case of experiment O5, which is improved slightly by the inclusion of the strip (discussed in detail in chapter six). From this it can be concluded that bleaching over an average pH range of approximately 6.8 to 7.3 (very close to neutral solutions) produces comparable levels of whiteness at 95 minutes total time. From the literature it can be taken as given that a higher pH will lead to an increased bleaching effect. The effect over this narrow range at close to neutral solutions must be slight in that it was not noticed by eye.

In all but one case the loss data obtained was very similar. In the first three experiments an upward trend in alkali solubility was observed, however differences in alkali solubility are observed between runs at higher carbonate/bicarbonate loadings, with the two 4 g/L experiments having slightly lower measurements than the 2 g/L experiment. Given the similarities in the bleaching obtained observed in the above experiments, an experiment was conducted at a lower pH to see if comparable whiteness can be obtained with less damage occurring, detailed in the following section.

5.2.3 FURTHER PH EXPERIMENTATION

5.2.3.1 Introduction

These experiments investigated the lowest pH which could be used successfully at 30 mL/L H_2O_2 and 50°C.

The experiments were undertaken using 10g fur at a liquor ratio of 20:1. The pH was adjusted with 2 g/L of sodium carbonate/bicarbonate. The flowrate was set at 130 mL/min.

5.2.3.2 Results

The following table gives the pH data of the experiments.

Table 5.3 pH data for Experiments O7 and O8

Experiment	Initial pH	Final pH	Average pH
O7	7.01	6.35	6.68
O8	6.84	6.18	6.51

Photos of the experiments after oxidative bleaching are shown in section 5.7.

Experiment O8 has undergone significantly less bleaching, although the difference in pH is only small. Experiment O7 shows a similar level of bleaching as experiment O1 and the others in section 5.2, it has a very similar pH profile to experiment O1. The pH conditions used in experiment O7 represent the lower limit of pH to obtain a successful oxidative bleach, at this particular temperature and peroxide concentration.

The damage results are given in the following table.

Table 5.4 Damage Results for Experiments O7 and O8

Experiment	Loss (%)	Alkali solubility (%)
O7	5.4	68.6
O8	4.8	61.0

The loss and alkali solubility in experiment O7 are similar to those in experiment O1, the slightly lower pH of experiment O1 is concordant with the slightly lower pH of this experiment. The damage in experiment O8 is lower, attributed to the lower pH of bleaching.

From these results, it would appear that the conditions described in experiment O7 give the lower limit of pH for bleaching at 50°C and 30mL/L 50% H_2O_2. A very distinct difference is observed between experiments O7 and O8 given the slight difference in pH.

Figures 5.1 and 5.2 show pH vs. alkali solubility and pH vs. loss for the experiments in this section respectively. As can be seen the loss is relatively flat (with the exception of the outlier experiment five) while the alkali solubility decreases beyond pH 7.2.

5.3 LOWER PH/EXTENDED TIME BLEACHING

5.3.1 INTRODUCTION

This experiment investigated the use of an oxidative bleach at a lower pH with an extended bleaching time. The experiment was run using 12g of fur at a liquor ratio of 20:1 and a flowrate of 130 mL/min.

5.3.2 RESULTS

The following table gives the pH profile of the experiment.

Table 5.5 Oxidative Bleaching pH Profile, Experiment O9

Time (min)	pH
10	6.92
24	5.97
45	5.95
120	5.94

The ten minute measurement was made after the carbonate/bicarbonate had been added to the flask serving as the solution reservoir but before introduction to the column. The majority of the bleaching was done at around pH 6. This experiment featured the carbonate/bicarbonate at 2 g/L. Comparison with experiment O1 in section 5.2 shows a much lower pH was obtained in this experiment reinforcing the need for a measured addition of the pH altering reagents to obtain a desired pH.

A photo of the fur after the oxidative bleach is shown in the section 5.7 as experiment O9. An examination of the photo shows that this experiment is not as white as those from the previously described experiments. Over the last 30 minutes of oxidative bleaching the fur did not appear to be getting any whiter so oxidative bleaching was stopped at this point. The finished fur is noticeably less bleached than in the experiments in section 5.2. In particular, this experiment should be compared with experiments O1 and O7 (also at 2g/L). These experiments produced a good whiteness whereas this one did not, even with the longer bleach. The fact that this experiment did not appear to be whitening appreciably at the end indicates that the pH is too low for the desired bleaching to be obtained.

The following table details the damage results of this experiment.

Table 5.6 Damage Results, Experiment O9

Loss (%)	Alkali solubility (%)
5.2	66.0

These results are similar to those in section 5.2, the alkali solubility is at the lower end of the results obtained there. The rate of attack of the keratin must be less effected by the drop in bleaching pH than the rate of attack of the melanin, leading to comparable levels of damage due to the longer bleaching time used, but a decreased bleaching effect. These results indicate that a minimum pH exists for desirable bleaching and minimal damage, regardless of the time of exposure. This is in agreement with the results of Gacen and Cayuela (2000) quoted in section 1.3.5.2 who found that for the same chemical attack, wool bleached in alkaline media is whiter than that bleached in acidic media.

This experiment, and the previous two, highlights the importance of pH in a mordanted bleaching process. This result was expected since all the mordanted bleaching processes surveyed made use of an alkaline peroxide bleach. The exact mechanism of mordanted bleaching is unknown, but it appears pH plays an important role in it. The perhydroxyl radical will be generated in greater proportions in alkaline media and it may be that this is a more aggressive bleaching species than the hydroxyl radical.

5.4 LOWER PEROXIDE CONCENTRATION

5.4.1 INTRODUCTION

After the experimentation on manipulation of pH, the next variable identified for investigation was the peroxide concentration. This experiment made use of 20 mL/L 50% H_2O_2. Twelve grams of fur at a liquor ratio of 20:1 were used. The pH was adjusted with 4 g/L sodium carbonate/bicarbonate. The flowrate was set at 130 mL/min.

5.4.2 RESULTS

The following table details the pH profile of the experiment.

Table 5.7 Oxidative Bleaching pH Profile, Experiment O10

Time (min)	pH
24	7.45
45	7.36
140	7.26

These pH results are at the higher end of the range determined for adequate bleaching at 30 mL/L 50% H_2O_2. It was thought that the higher pH may somewhat offset the lower peroxide concentration by providing a greater concentration of the perhydroxyl anion. The longer time was given so that an adequate bleaching effect could be obtained. Examination of the photo of the fur from this experiment, given as experiment O10 shows a decreased level of bleaching compared with the experiments in section 5.2. The finished fur has a yellow tinge, not of a marketable colour the bleaching was not as successful as obtained in the work in section 5.2. The following table details the results of the experiment.

Table 5.8 Damage Results, Experiment O10

Loss (%)	Alkali solubility (%)
4.6	76.5

The loss is lower than had been previously obtained, however the alkali solubility is at the higher end. A longer bleaching time would be necessary at this peroxide concentration, which would lead to further damage of the fur. Given that the damage results in this experiment are already comparable to those in section 5.2 it was concluded that the original peroxide concentration was superior.

5.5 PRESENCE OF SLS

5.5.1 INTRODUCTION

A lot of work has been done on the use of sodium lauryl sulphate (SLS) in the bleaching of wool. This work is detailed in chapter one. This experiment examined the presence of this species in the oxidative bleach at 1.4 g/L and the higher temperature conditions. This concentration is quite low when compared to the majority of work; however Allsop (1996) found benefits were obtained when SLS was included in peroxide systems (on wool) at concentrations of 1 g/L. The lower concentration had the advantage of helping to prevent the rubber seals in the columns from slipping out over the course of the experiment. The experiment featured 10g of fur at a liquor ratio of 20:1. The pH was adjusted with 2 g/L of sodium carbonate/bicarbonate. The flowrate was set at 130mL/min.

5.5.2 RESULTS

The following table details the results of the experiment

Table 5.9 Results of Experiment O11

pH initial	pH final	Average pH	Loss (%)	Alkali Sol (%)
7.00	6.82	6.91	5.0	79.4

A photo showing this experiment after oxidative bleaching is shown in section 5.7 as experiment O11. It can be seen that this experiment reached a similar level of whiteness as the experiments in section 5.2. The final fur also shows similar results.

Examination of the above results shows SLS does not have a significant impact on the whiteness or damage occurring to the fur at this concentration. The results here are comparable to those in section 5.2 in both instances, with loss at the lower end and alkali solubility at the higher. Given the results obtained in the literature, it was thought that the presence of SLS would have a beneficial effect on the bleaching. It may be that the concentration was too low to give a noticeable effect. Further work was tried at higher concentrations but the seals could not be kept in the columns at this concentration. Further work was also conducted at 1.4 g/L but again the seals would not stay in the column.

Given the favourable reviews given to bleaching with SLS in the literature it was decided higher concentrations should be trialled in the pilot scale work.

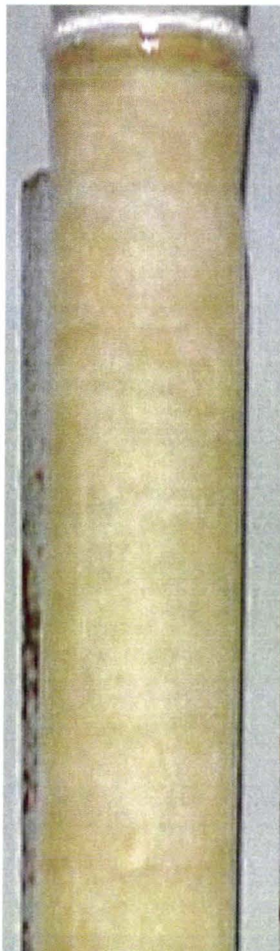
5.6 CONCLUSIONS

- Similar levels of bleaching are observed over an average pH range of 6.8 to 7.3 at 50°C, with the reagent system detailed in this chapter.
- The loss of fur occurring over the pH range 6.8 – 7.3 was relatively constant, alkali solubility was found to increase with pH then decrease above pH 7.2.
- An initial pH of around 7.0 is required for an adequate oxidative bleach using 30 mL/L 50% hydrogen peroxide at 50°C for 95 minutes. Bleaching at lower pH (around pH 6) than this did not give a satisfactory whiteness even with extended bleaching times, although the damage occurring was similar to that in the range 6.8 – 7.3 given the extended bleaching time.
- Bleaching with lower peroxide concentrations (20 mL/L 50% hydrogen peroxide as opposed to 30 mL/L) were found to give poorer bleaching for comparable levels of damage.
- SLS at 1.4 g/L was found to have no noticeable effect on bleaching or damage.
- The original reagent system was decided upon for use in subsequent experimentation. The length of the oxidative bleach was decided to be the main factor worthy of further investigation in tandem with the degree and system of reductive bleaching.

5.7 PHOTOS

Experiment O1 Experiment O2 Experiment O3 Experiment O4

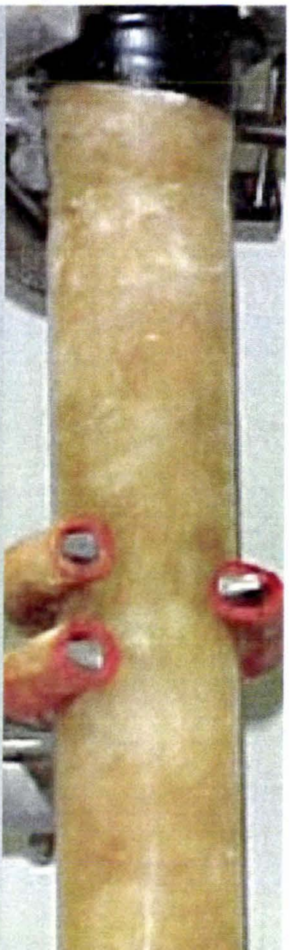
Experiment O5

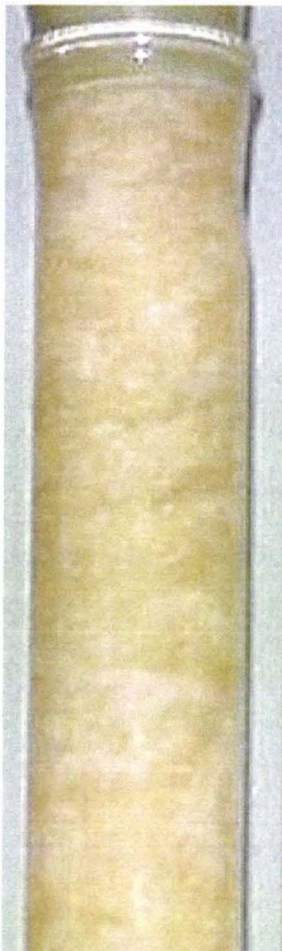


Experiment O6

Experiment O7

Experiment O8




Experiment O9


Experiment O10

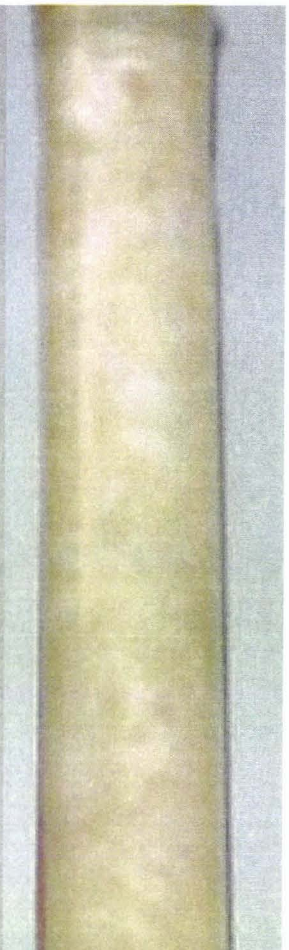

Experiment O11

Figure 5.1

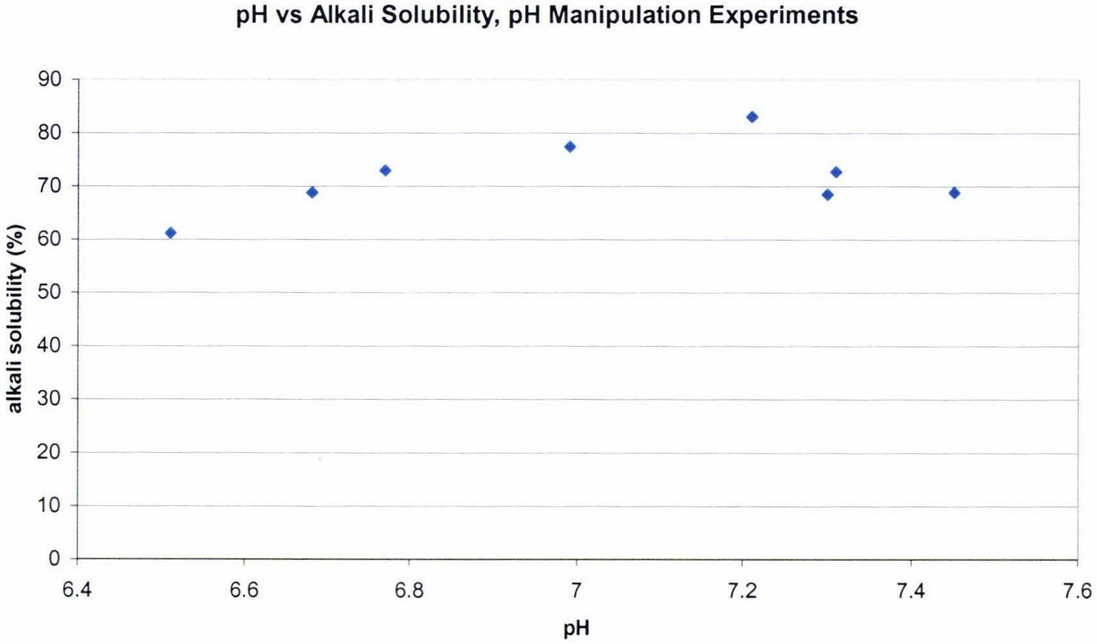
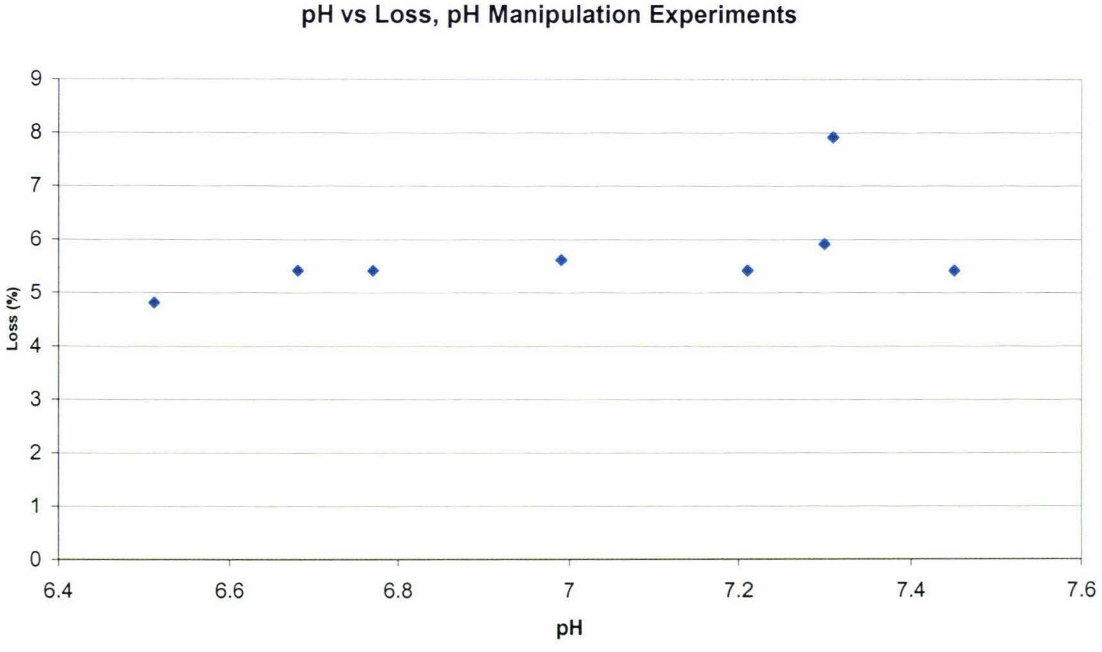


Figure 5.2



CHAPTER 6 STRIP

6.1 INTRODUCTION

The purpose of the strip stage is to remove iron bound to the fur, present from the mordanting process, after the oxidative bleach. Any iron present after oxidative bleaching will be in the ferric state giving the fur a rusty discolouration.

References were found in the literature that state that reductive bleaching with thiourea dioxide will reduce any ferric species present to ferrous ions which are easily removed from the bleached fibre (Arifoglu and Marmer 1990). On the basis of this, the strip stage was eliminated from initial experimentation and the work in chapter four, where reductive bleaching was undertaken using sodium hydrosulphite. The results obtained in this work indicated that a good whiteness can be obtained without the strip stage.

Later work showed that the inclusion of this step was beneficial to the bleaching process. This chapter details the experimentation undertaken on the strip stage.

6.2 INITIAL INVESTIGATION

6.2.1 INTRODUCTION

It was noticed that some of the experiments in which the strip stage was eliminated appeared to darken over time. It was postulated that this could be due to the presence of iron in the fur, which, over time, was oxidised to ferric iron. An experiment was conducted on one of these furs by carrying out the strip stage on the finished fur. Visually this showed a slight improvement on the previous colour. This was very slight however, and did not show through in photos taken of the experiment.

The strip stage (as detailed in section 1.2) was then carried out in one of the experiments dealing with the manipulation of the pH of the oxidative bleach, experiment O5 in chapter five. Photos S1 and S2 in section 6.6 show this experiment after the oxidative bleach and strip stages respectively. As can be seen from these photos an improvement in the colour of the fur is observed resulting from the removal of residual iron in the strip stage.

Photo S3 shows this experiment after the reductive bleach. Photo S4 shows experiment O4 from chapter 5 after the oxidative bleach. This experiment featured the carbonate/ bicarbonate level at 3.5 g/L, with no strip stage, whereas experiment O5 had 4 g/L. The two experiments show similar whiteness after the oxidative bleach. Photo five shows experiment O4 after the reductive bleach. The following observations are made:

- Experiment O5 shows little improvement in whiteness after reductive bleaching
- There is a noticeable improvement in the whiteness of experiment O4 after reductive bleaching.
- Both experiments have similar whiteness after reductive bleaching, with experiment O5 being slightly whiter

Clearly, the strip stage has a beneficial effect on the overall bleaching process. The lack of improvement in the fur from reductive bleaching in experiment O5 was found to be a pH effect resulting from the low pH of the hold-up liquor in the column after rinsing. After the standard rinsing procedure the pH of the column was found to be around 2.3. This then impacts on the pH of the reductive bleach, leading to a bleach at around pH 3.0. This is not a problem when the strip stage is omitted due to the approximately neutral pH of the oxidative bleach. This phenomenon is discussed further in the following chapter on reductive bleaching.

The following table repeats the damage information from these experiments.

Table 6.1 Damage Results for Experiments O4 and O5

Exp.	Level Carb/ bicarb (g/L)	pH initial	pH final	Average pH	Loss (%)	Alkali Sol (%)
O4	3.5	7.34	7.26	7.30	5.9	68.3
O5	4.0	7.40	7.22	7.31	7.9	72.5

The alkali solubility is slightly higher in the experiment featuring the strip; although only slightly so. The loss is significantly higher but it is thought to be due to fur being lost in a transfer.

The strip stage serves as the post oxidative bleach acidification discussed in section 1.4.3. On the above results this would appear to have no effect on the damage occurring in this particular process. It should be noted that of all the bleaching literature surveyed, this was the only reference found to this pre and post oxidative bleach acidification. The mordant and rinse stages are both acidic, and even if no strip was undertaken the oxidative bleach is only very slightly alkaline.

6.3 STRIP POSITION

6.3.1 INTRODUCTION

This experiment examined the effect of having the strip before the reductive bleach (experiment S1) and after the reductive bleach (experiment S2). If the strip could be undertaken after the reductive bleach the reductive bleach pH problem could be eliminated.

6.3.2 RESULTS

These two experiments were conducted with the same conditions except varying the position of the strip stage. Both experiments featured 10g fur at a 20:1 liquor ratio. The pH was adjusted with 2 g/L sodium carbonate/bicarbonate. The flowrate was 130 mL/min.

The following table details the pH of the oxidative bleach.

Table 6.2 Oxidative Bleach pH Conditions for Experiments S1 and S2

Experiment	Initial pH	Final pH	Average pH
S1	7.12	6.33	6.73
S2	7.06	6.33	6.70

The two experiments had very similar pH, which lead to the same degree of oxidative bleaching being obtained.

Photos of the fur at the completion of the experiments are shown as photos S6 (exp S1) and S7 (exp S2). The experiment for the strip first shows superior bleaching. This is more evident in the dry fur. Of note is that this was performed with a lower pH reductive bleach. The strip first experiment had a pH of 6.60 initially falling to 3.34, the strip second experiment 6.54 falling to 4.84. Closer monitoring of the pH of the reductive bleach was carried out in subsequent work, discussed in chapter seven. On the basis of results detailed there it is likely that the pH drop was quite rapid in experiment S1 but more gradual in experiment S2, i.e. the majority of reductive bleaching occurred at pH values of around 3.34 in experiment S1. Work by Gacen (1989) has shown that bleaching increases with increased pH for solutions of hydrosulphite. Therefore, if the position of the strip stage was unimportant, the strip second experiment should have had the better whiteness, due to the higher pH bleaching. Clearly, the strip is best situated after the oxidative bleach. Trotman (1968) states that the contact of hydrosulphite with iron or copper can lead to the formation of their sulphides which causes a greyish discolouration which is extremely difficult to remove. This could be the reason for the decreased bleaching observed but experiment S2 is more of a yellow colour than grey. The question of why a grey discolouration was not observed on previous work when the strip stage was not undertaken is also raised.

The following table details the damage results of these experiments

Table 6.3 Damage Results for Experiments S1 and S2

Strip position	Loss (%)	Alkali solubility (%)
Before ox bleach	5.5	67.4
After ox bleach	5.3	64.4

These results are comparable with other work dealing with similar mordanting and bleaching conditions and indicate no significant difference in damage was obtained from varying the strip position, or from its inclusion.

6.4 LENGTH OF STRIP STAGE

6.4.1 INTRODUCTION

It was observed that the majority of the colour change occurs quite rapidly in the strip stage, no improvement was observed after one hour. This indicates that the bulk of the iron is removed quite rapidly. An investigation was undertaken into whether or not this stage could be shortened.

6.4.2 RESULTS

This was the experiment described in section 7.5.2 using the darker fur. The pH was adjusted with 4 g/L of the carbonate/bicarbonate. The flowrate was 100 ml/min and the liquor ratio 20:1.

Photos S8 to S10 show the experiment after the oxidative bleach, the strip and the reductive bleach respectively.

Examination of photos S8 and S9 shows the typical improvement in whiteness resulting from the removal of residual iron. Photo S10 then shows an improvement from reductive bleaching. This experiment featured adjustment of the pH in between the strip and reductive bleaching as discussed in chapter seven, leading to better bleaching. No grey discolouration was observed. From these results it can be concluded that the strip stage can be shortened to one hour.

6.5 CONCLUSIONS

- The strip stage is beneficial to the overall bleaching process by removing any residual iron present on the fur and has little effect on the damage occurring to the fur.
- The strip is best situated between the oxidative and reductive bleaches.
- The strip stage is highly acidic and without pH adjustment in between the strip and reductive bleach stages, a lower pH reductive bleach is encountered, and a decreased bleaching effect obtained.
- The following conditions are recommended for the strip stage

Table 6.4

Reagent	Concentration (g/L)	Temperature (°C)	Time (hours)
Ammonium Bifluoride	8	30	1
Oxalic Acid	4		

6.6 PHOTOS

Photo S1

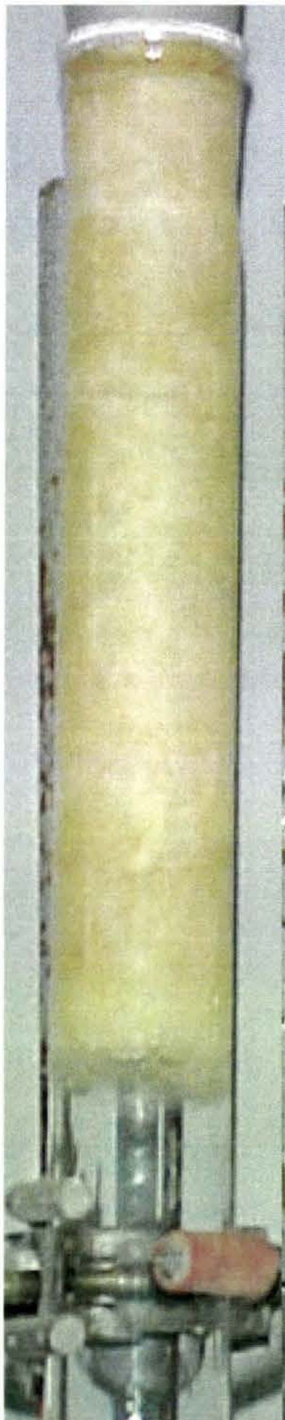


Photo S2

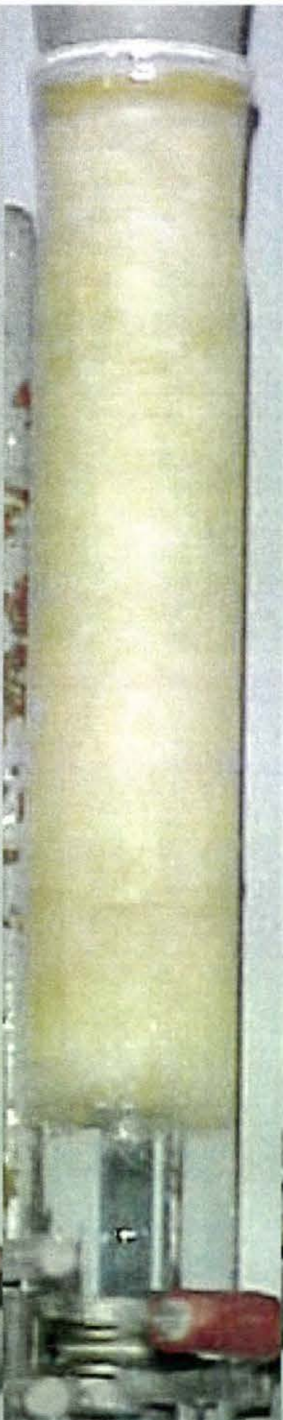


Photo S3

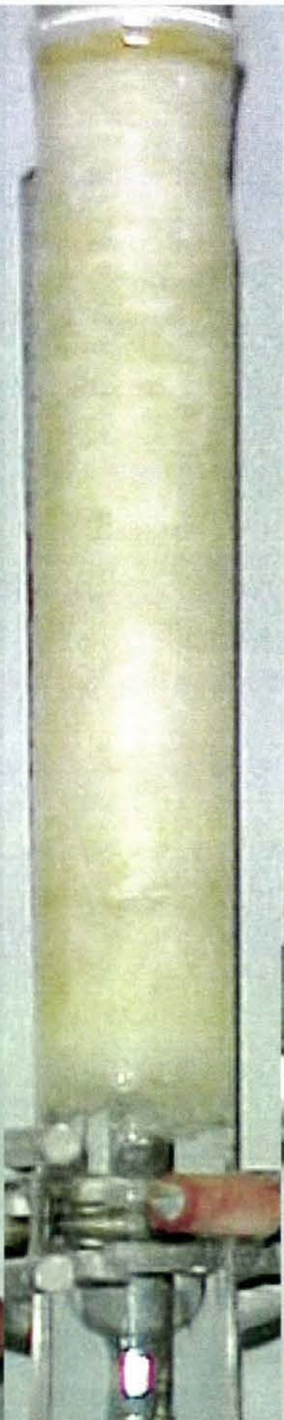


Photo S4

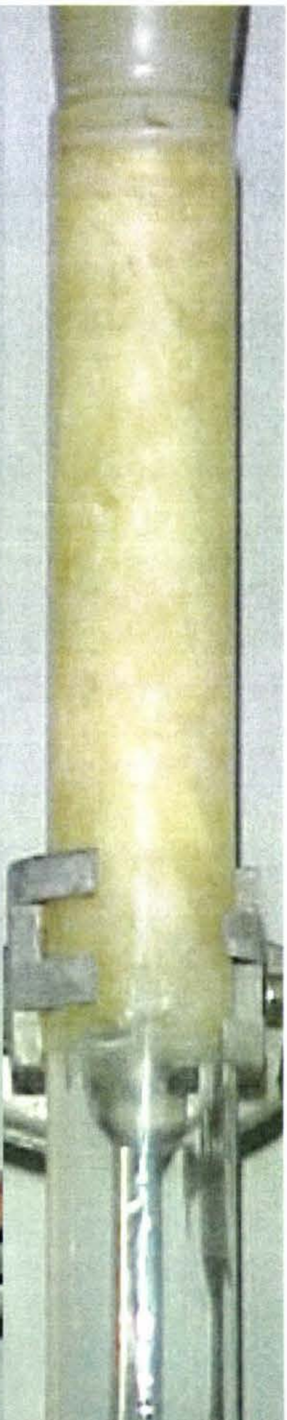


Photo S5

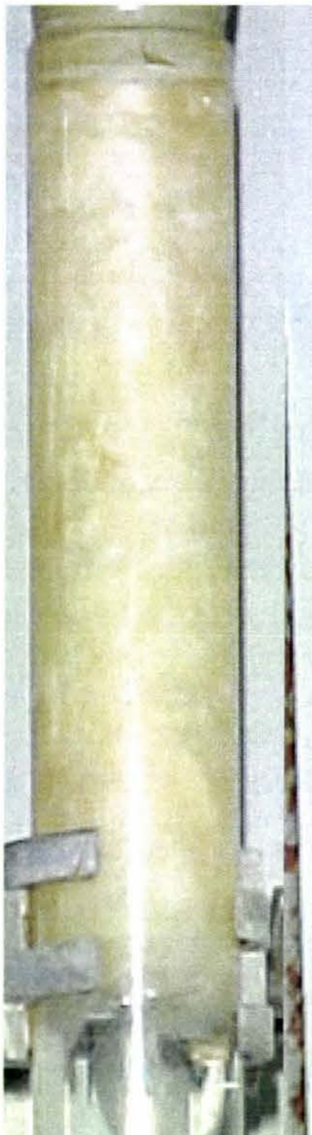


Photo S6

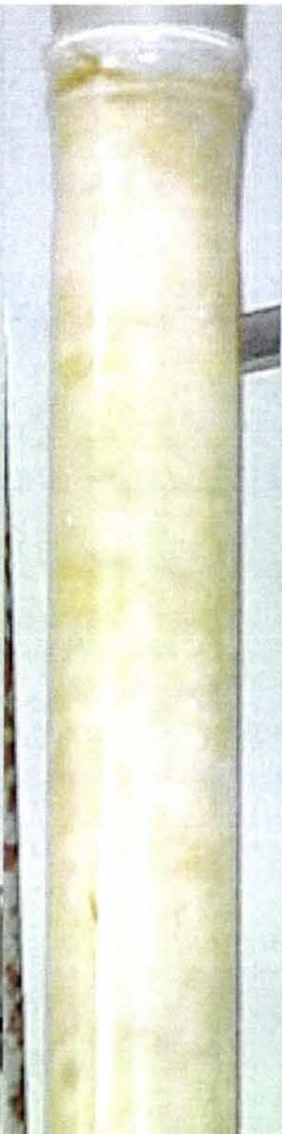


Photo S7

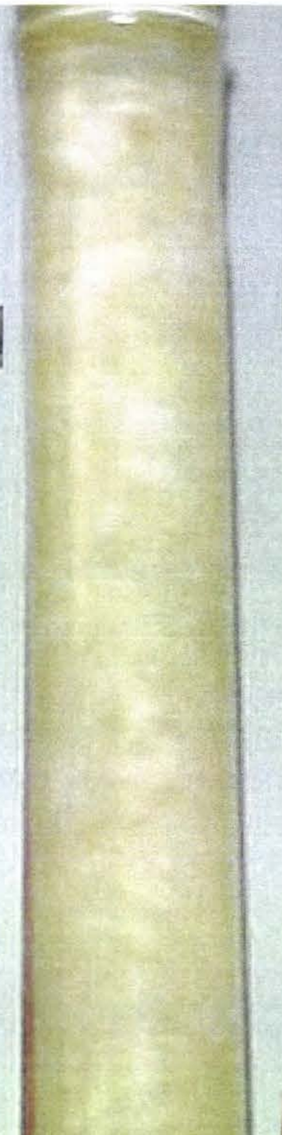


Photo S8

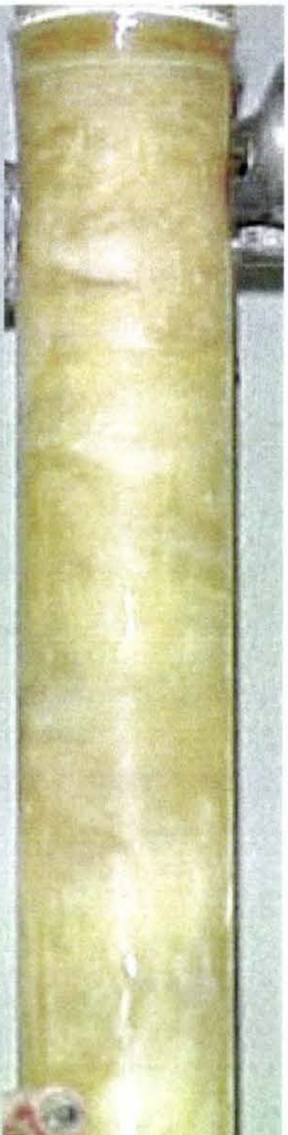


Photo S9

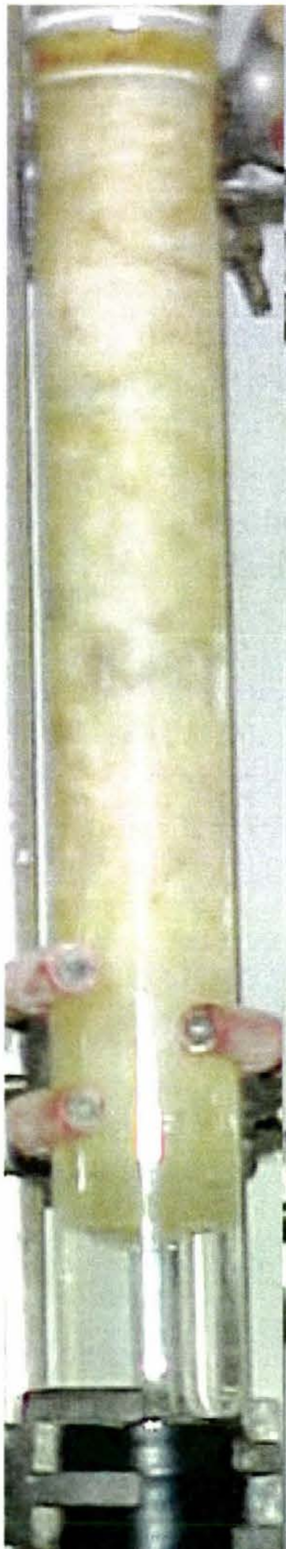
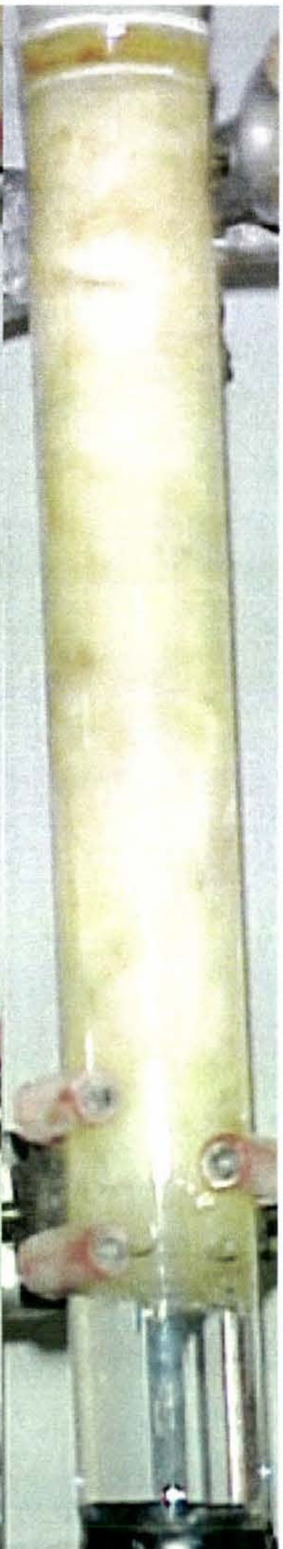


Photo S10



CHAPTER 7 REDUCTIVE BLEACH

7.1 INTRODUCTION

The reductive bleach provides the final bleaching effect. While the majority of the bleaching is completed during the oxidative bleach, this stage provides a "polish" to the bleaching to produce a good whiteness in the finished product. A reductive bleach is also necessary to ensure that the fur does not yellow over time, which may ruin any pale shades to which it has been dyed (Allsop 1996).

In the initial method the fur was bleached using non-stabilised hydrosulphite. Stabilised hydrosulphite mixtures are available which contain chemicals to regulate the breakdown of the hydrosulphite (usually sodium pyrophosphate) and sequestering agents to bind metals present in the solution to prevent the formation of their sulphides, which can cause a discolourisation of the fur.

The reductive bleach was the last stage to be investigated. Some of this work was conducted in tandem with the work on oxidative bleaching.

7.2 REDUCTIVE BLEACHING WITH THE INITIAL CONDITIONS

7.2.1 INTRODUCTION

In work dealing with the mordant and oxidative bleaches, reductive bleaching was undertaken at 3 g/L for two hours at 30°C with sodium hydrosulphite, as per the method obtained from Gray Fur Trading. The strip stage was excluded in this experimentation. Photos R1 to R4 (overleaf) give examples of the typical whitening occurring in these conditions. These photos are taken from work dealing with the manipulation of the mordant pH (bleaching parameters detailed in section 4.3.1). The whitening effect of these reductive bleaching conditions is slight. The pH conditions encountered in this work are similar to those reported in previously, i.e. 6.5 falling to around 4.5 over the course of bleaching.

Gacen *et al.* (1989) observed that whiteness obtained from non-stabilised hydrosulphite is independent of hydrosulphite concentrations from 2-8 g/L in the absence of SLS, and from 3.5 g/L in the presence of SLS, for the bleaching of wool.

Photo R1

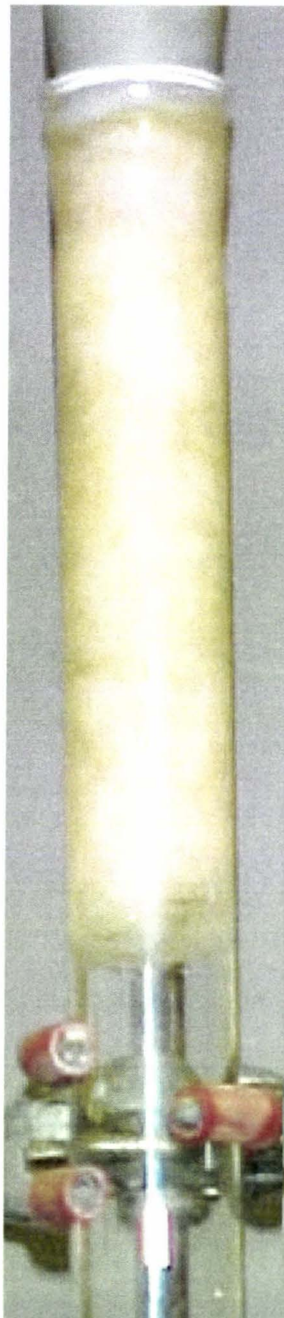


Photo R2

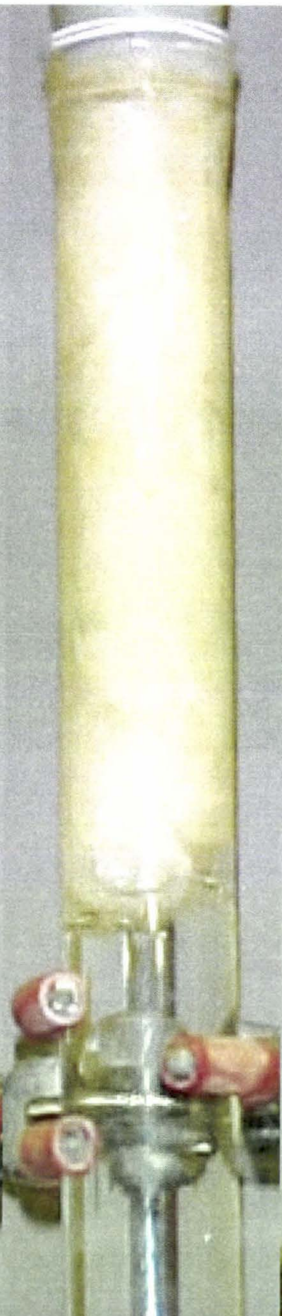
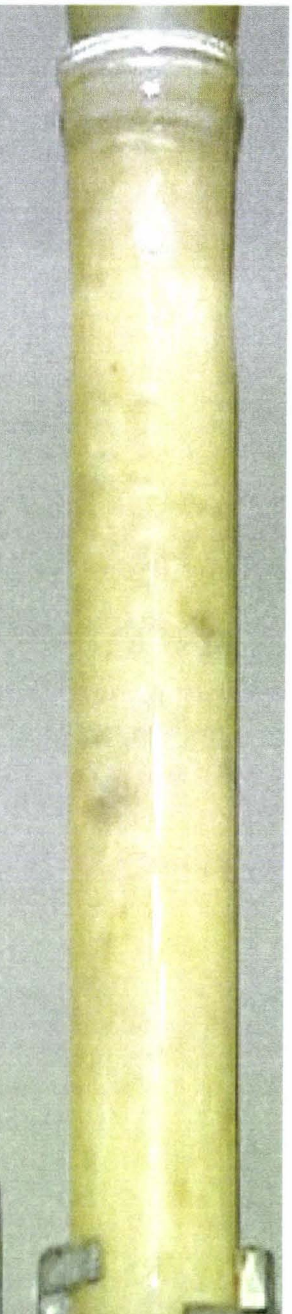


Photo R3

Photo R4



7.3 INTRODUCTION OF THE STRIP STAGE

7.3.1 INTRODUCTION

After the introduction of the strip stage it was noticed that some reductive bleaching solutions became very cloudy during bleaching from the formation of a precipitate and a decreased bleaching effect was obtained.

This effect is attributed to the formation of elemental sulphur from the breakdown of the hydrosulphite. The hydrosulphite ion decomposes in solution to give thiosulphate and hydrogensulphite ions. Thiosulphate can further decompose to give hydrogensulphite and elemental sulphur under acidic conditions. Acidification of a 3 g/L hydrosulphite solution to pH 3.2 saw the formation of the sulphur precipitate.

In some experiments this precipitate disappeared over the course of the bleaching, while in others it did not. Series one in figure 7.1 shows a typical pH profile of an experiment in which the precipitate was encountered. The precipitate was first noticed at about 7.5 minutes and was very strong by ten minutes. No reduction in the level of the precipitate occurred over the experiment. Although this phenomenon is definitely linked to pH, some other factor must also contribute. Series two in figure one shows another experiment without pH adjustment after the strip stage. Only a very faint precipitate was observed around the 30 minute mark, which disappeared by 35 minutes.

At the pH values shown in series two the precipitate should have formed, based on past observations. Another experiment in which a strong precipitate was observed had a pH which stabilised at around 3.2, which is higher than that shown in series two. The reason why the precipitate forms in some cases but not others is unknown.

The formation of this precipitate leads to a decreased bleaching effect. Photos R5 and R6 show experiment T3 from chapter eight after the strip and reductive bleaches respectively (the experiment giving series one in figure 7.1). This experiment showed a very strong precipitate throughout the reductive bleach. Photos R7 and R8 show experiment T4 from chapter eight after the strip and reductive bleaches respectively (the experiment giving series two in figure 7.1). This showed a faint precipitate at 30-35 minutes of reductive bleaching. Both these experiments used non-stabilised hydrosulphite at 3 g/L.

As can be seen from the photos, a greater degree of bleaching is obtained in the absence of the precipitate. Both experiments have very similar pH profiles so this can not be attributed to a pH effect. The comparison of damage results is not applicable in this case due to differences in preceding experimental variables but the reduced bleaching effect obtained in the presence of the precipitate is noted.

Photo R5

Photo R6

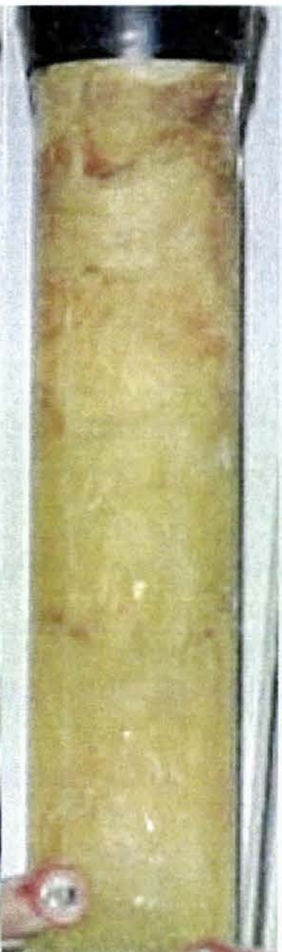


Photo R7

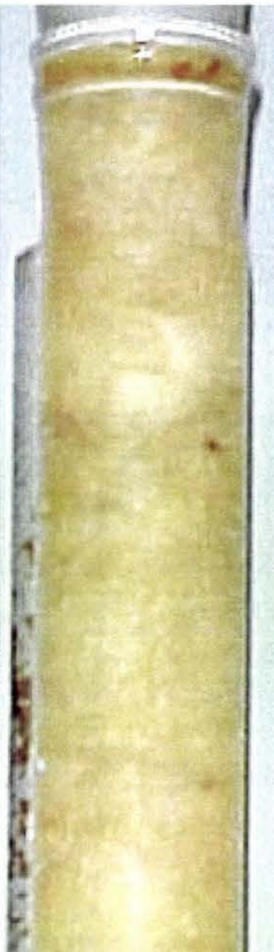
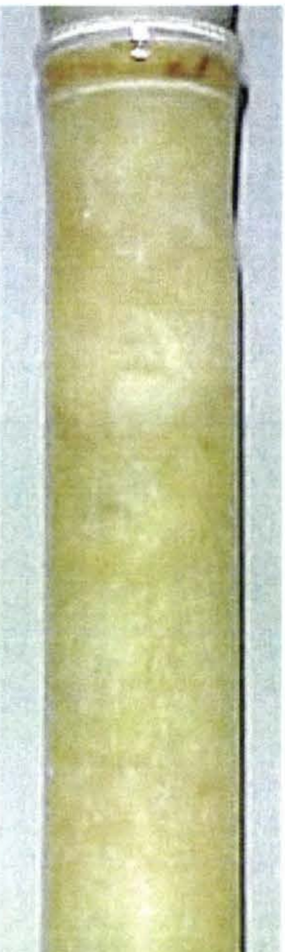


Photo R8



7.4 PH ADJUSTMENT

7.4.1 INTRODUCTION

As discussed in section 6.2, very little whitening of the fur occurs when no pH adjustment is made between the strip and reductive bleaching stages, which leads to a reductive bleach at pH values of around three.

In order to counter the problem resulting from the low pH hold-up liquor in the column after the strip, a pH adjustment had to be introduced between the strip and reductive bleaching stages. Rinsing of the column alone with large quantities of water was not enough to sufficiently raise the pH of the column so that reductive bleaching could be performed at the desired initial pH of 6.5-6.0. Rinsing the columns with 1.5 L of water (2.5 times the standard amount) was found to raise the pH to 3.7 from an initial value of 1.8. This was not sufficient for a successful reductive bleach. The use of large volumes of water in the full-scale process is not desirable, as vast quantities of water would be required to bring the pH to the desired value of around 6.0.

The pH adjustment process decided upon uses 25 % sodium carbonate on 150 mL of water recirculating through the column (giving a total volume of 280 - 310 mL). To adjust the pH of the column from values typically around 3.0 to 6.5 requires approximately 3 mL of the sodium carbonate solution. Values in the range of 2.6 to 3.1 mL were used. The pH was measured after a steady pH was reached in the vessel holding the water. The sodium carbonate solution has to be added in small doses to avoid raising the pH to levels which could damage the fur.

This process is time consuming and takes up to one hour. This effectively constitutes another stage to the bleaching process.

It was realised at this stage that the process described in chapter one for sequential bleaching techniques whereby left over hydrogen peroxide is converted to thiourea dioxide would not be feasible in the displacement bleaching method. The thiourea process requires the oxidative bleaching solution pH to be brought back to acidic values, thiourea added in a 3.2:1 thiourea to peroxide molar ratio, and the pH then bought back to neutral after ten minutes for bleaching to occur. This process is not suited to two vessel systems due to the time consuming nature of the pH adjustment process and the difficulty in ensuring the right level of thiourea when it can only be added to one vessel, with changing thiourea and hydrogen peroxide concentrations.

7.5 REDUCTIVE BLEACHING WITH PH ADJUSTMENT

7.5.1 INTRODUCTION

This section details the experiments in which reductive bleaching was undertaken after the pH adjustment process. It also details work in which the degree of oxidative bleaching, necessary before reductive bleaching, was investigated.

7.5.2 EXPERIMENTS R1 AND R2. COMPARISON OF THE BLEACHING OF LIGHTER AND DARKER GREY FURS

7.5.2.1 Introduction

This section details two experiments in which the lightest and darkest shades of grey fur was bleached. This was done so that the variations likely depending on the fur used could be gauged. Mordanting was undertaken involving the standard method using hypophosphorous acid, detailed in section 4.5.2.

7.5.2.2 Oxidative bleaching

Figure 7.2 shows the pH-time profile of the oxidative bleach for these two experiments. Oxidative bleaching was undertaken at 50°C with the same reagent system as previously used.

Experiment R1 refers to the experiment on the lighter fur which had a pH of 7.2 and was run for 95 minutes total (72 minutes after second pH adjustment, 2 x 2g/L added). Experiment R2 refers to the darker fur which was run in the range 7.2- 7.1 for a total of 120 minutes (97 after second pH adjustment, 2 x 2g/L added). The data to generate these figures is included as appendix 7.1. In these tables, measurements were made immediately prior to the addition of the sodium carbonate / sodium bicarbonate, when such an addition is shown. For the purposes of comparison, and in the generation of the graphs, it has been assumed that the solution was at the higher pH from the time of addition, in these experiments and those detailed subsequently in the chapter.

7.5.2.3 Reductive bleaching

Reductive bleaching was undertaken using the Blankit IN formulation at 3 g/L. The following table details the pH conditions resulting from the experiments. The initial pH measurements were made before recirculation of the solutions began.

Table 7.1 Reductive Bleaching Data for Experiments R1 and R2

Time (minutes)	pH experiment R1	pH experiment R2
0	9.12	9.27
18	5.50	6.41
120	3.88	5.78

Photos of the fur after the strip and reductive bleaches respectively are included as photos R9 and R10 (experiment R1) and R11 and R12 (experiment R2). As can be seen very little whitening occurred in reductive bleaching in experiment R1. Experiment R2 shows a noticeable improvement. This is due to the higher pH in experiment two. The pH of the solutions will fall during reductive bleaching. Experiment one had a column pH of 5.39 before introduction of the solution, experiment two 5.79. On the basis of this, a solution pH of about 5.8 is needed to avoid this effect being too pronounced. The pH was adjusted to at least 6 in subsequent work. The experiments gave the following damage results.

Table 7.2 Damage Results for Experiments R1 and R2

Experiment	Loss (%)	Alkali solubility
R1	3.9	66.0
R2	6.2	78.4

The two finished experiments show very good whiteness, better than the results in section 5.2, the lighter fur (R1) is better than the darker (R2). As would be expected, the darker fur was much more damaged than the lighter fur, due to the harsher bleaching conditions. The lighter fur only required 72 minutes at the final pH at which the majority of bleaching occurred. The darker fur had 97 minutes, although this would have been longer if the seal in the column had not come out, to obtain the same whiteness as in the lighter fur experiment. The lower level of oxidative bleaching was partially offset by a higher pH reductive bleach giving better reductive bleaching, although the fur is still bleached to a lesser extent.

This experiment served to illustrate the differences that can be obtained due to variations in the fur. On an industrial scale the fur bleached will be a mixture of shades. In an optimal time length process, the lightest fur would be slightly over-bleached and the darkest slightly under-bleached. This underbleached fur should not be so noticeable when the fur is carded, and is unavoidable given the decreased whiteness and increased damage obtained when the fur is bleached for longer than the optimum time.

Trotman (1968) states that stabilised hydrosulphite formulations are generally two parts hydrosulphite to one part sodium pyrophosphate. In this case the hydrosulphite concentration would be actually 2 g/L, when 3 g/L is used. It was decided to increase the concentration to 4 g/L for subsequent experimentation. This is the optimum concentration determined by Gacen *et al.* (1994). They also recommended SLS at 2.5 g/L. It was included at 1.4 g/L to avoid problems with sealing the columns.

Photo R9

Photo R10

Photo R11

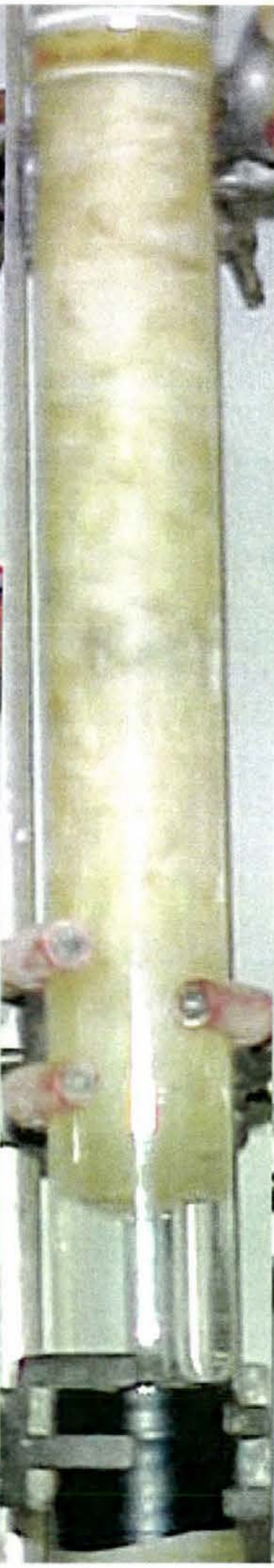
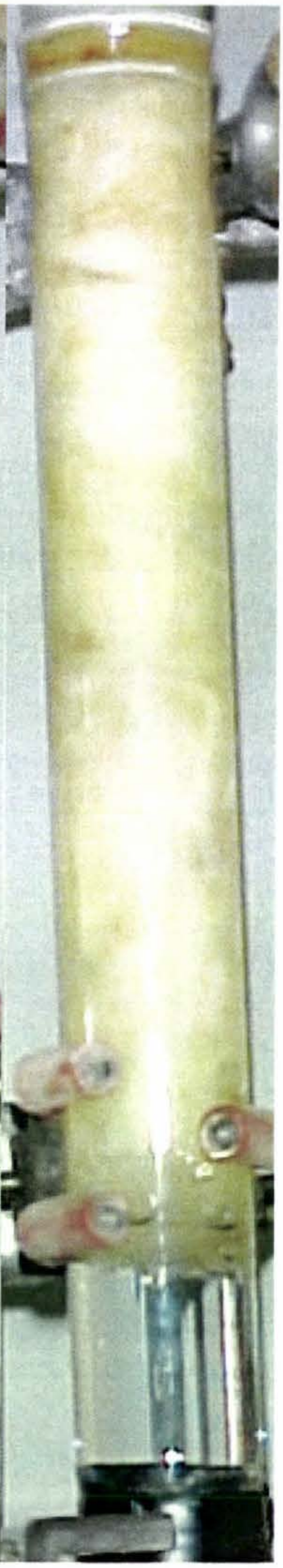


Photo R12



7.6 DETERMINATION OF THE LENGTH OF OXIDATIVE BLEACH NECESSARY BEFORE REDUCTIVE BLEACHING

7.6.1 INTRODUCTION

The following experiments all varied the length of oxidative bleaching. Reductive bleaching was carried out in all instances with Blankit IN at 4 g/L for 120 minutes. Experiments R3 and R5 both featured SLS at 1.4 g/L, which was inadvertently excluded in experiment R4. The mordant was as described in section 5.2 with experiments R4 and R5 using phosphorous acid instead of hypophosphorous acid at equimolar concentrations (1.85 g/L phosphorous acid). The acid rinse was undertaken using phosphorous acid at 0.45 g/L in experiments R4 and R5.

7.6.2 RESULTS

Figure 7.3 shows the pH-time profile for the oxidative bleaching in these experiments. The addition of carbonate/bicarbonate was made/begun after 10 minutes in all cases. Experiment R3 featured two additions at 2 g/L of the carbonate/bicarbonate mixture, the second after fifteen minutes giving a pH range of 7.21 to 7.60 over 70 minutes after the final addition. Bleaching was undertaken for 85 minutes in total. The pH was observed to rise after the final pH adjustment in this experiment, but remained relatively steady in experiments R4 and R5.

Experiment R4 had one addition at 4 g/L giving a pH range of 7.14 - 7.25, after the adjustment. Bleaching was undertaken for 70 minutes in total, with 60 minutes after the pH adjustment.

Experiment R5 also had one addition at 4 g/L, giving an increase in pH to 6.95 by 14 minutes and 7.14 by 30, rising to 7.20 over a total of 90 minutes, with 80 minutes after the pH adjustment.

Figure 7.4 shows the pH-time profile of reductive bleaching in these experiments. All experiments gave similar profiles, with experiment 3 having a slightly higher pH. It is difficult to obtain identical pH profiles due to the two vessel nature of the pH adjustment process undertaken prior to the reductive bleach. In their work with stabilised hydrosulphite mixtures, Gacen *et al.* (1994) observed a difference of one Berger unit (another whiteness index detailed in chapter two) between pH six and seven. The data used to generate figures 7.3 and 7.4 is included as appendices 7.2 – 7.4 respectively. The following table details the damage results of the experiments

Table 7.3 Damage Results for Experiments R3 – R5.

	Experiment R3	Experiment R4	Experiment R5
Loss (%)	6.1	4.7	4.9
Alkali Solubility (%)	79.0	38.8	46.5

The results of each experiment are discussed below.

7.6.3 EXPERIMENT R3

Photos R13 and R14 show this experiment after the strip and reductive bleaches respectively. An improved reductive bleaching was obtained on the previous experiments; there is quite a glare on photo fourteen which makes comparison difficult here. The final fur has a whiteness similar to the darker fur in the previous experiment. These damage results are quite high, given that only 70 minutes of bleaching were undertaken following the final pH adjustment. The pH of the oxidative bleach is higher than the necessary value determined in section 5.2. Comparison with experiment R1 which was oxidatively bleached for 72 minutes after the final pH adjustment shows greater damage obtained here. The higher pH of the oxidative bleach will contribute to this, as will the higher concentration of Blankit IN.

The pH and time used in this experiment were deemed to be sub-optimal due to the high alkali solubility result.

7.6.4 EXPERIMENT R4

Photos R15 and R16 show this experiment after the strip and reductive bleach stages respectively. The final whiteness obtained in this experiment is not as good as was obtained in experiment three. The oxidative bleach was shorter than necessary to obtain a satisfactory whiteness. The final fur is not the desired colour, the longer hairs are not well bleached which would limit the colours this fur could be dyed.

This pH is within the range determined in section 5.2, albeit toward the higher end. Bleaching was undertaken for 60 minutes after the pH adjustment. Immediately noticeable is the very much lower alkali solubility in this experiment. This experiment featured oxidative bleaching for 60 minutes after the final pH adjustment, 10 minutes shorter than that of experiment R3. The alkali solubilities are markedly different however, 38.8 c.f. 79.0. The pH of the oxidative bleach was lower in this experiment but the majority of the effect is attributed to the use of phosphorous acid in the mordant, which gave far superior results to those experienced with hypophosphorous acid. The rusty discolouration apparent in the mordanting with hypophosphorous acid is completely absent when phosphorous acid is used. Ferric iron appears to have been eliminated. Oxidative bleaching was observed to be much more rapid in experiments using a phosphorous acid mordant. This was why this experiment was stopped after 70 minutes; the oxidative bleach appeared to have reached the desired level from a visual examination. This was subsequently found not to be the case.

Phosphorous acid is slightly weaker than hypophosphorous and mordant pH values of 2.1 – 2.25 were encountered in its use. It was substituted for hypophosphorous acid since the technical grade necessary for large scale work is not available in Australasia, and Bereck (1985; 1994) found these two reagents to give very similar results. As it was, phosphorous acid (technical) would have to be imported from Australia. This will require careful inventory planning so that purchases can be made to coincide with dangerous goods shipments to avoid excessive shipping costs. A sample was obtained from Taranaki nuchem, who import it by the container for use in a fungicide spray.

7.6.5 EXPERIMENT R5

Photos of the experiment after the strip and reductive bleach are included as photos R17 and R18. The results here are an improvement on the previous experiment, comparable to those in experiment R3. From this it can be concluded 60 minutes at the higher pH in experiment R3 was sufficient for good oxidative bleaching, and 80 at the range determined in section 5.2 (i.e. as in this experiment). The higher pH leads to increased damage so the range in this experiment is preferable. In pilot scale work, detailed in chapter nine, a solution of the carbonate/bicarbonate is added, with pH monitoring, to ensure the desired value is reached.

A slight increase in the damage was obtained compared with experiment R4, as would be expected due to the longer oxidative bleach. However it is still much lower than the work using hypophosphorous acid in the mordant.

The whiteness and damage results are both very good in this experiment. Discussions with Woolyarns (a potential customer) revealed that 50% was an acceptable value of alkali solubility for bleached possum fur. Levels of around 30% are commonly obtained for bleached wool, which due to its initial colour is much easier to bleach.

Apart from the longer oxidative bleach this experiment differs from experiment R4 by a decrease in the concentration of iron. It was discovered that the ferrous sulphate at Gray Fur Trading was the monohydrate, not the heptahydrate as assumed. The heptahydrate was used in the experimental work at Massey and the iron concentration was cut back to this value

From these results it can also be concluded that the higher concentration of iron inadvertently used previously has not resulted in enhanced mordanting. This is in agreement with the results of Bereck (1994) who found that the degree of uptake of iron by the fur did not increase when the iron concentration was greater than 0.035 M; the concentration used in this experiment is 0.036 M.

The question arises, why is such a large difference is observed between the phosphorous and hypophosphorous acid. A salient point is the absence of the rust colouration in the phosphorous acid experiments, indicating a low proportion of ferric species, at both iron concentrations. This would lead to a more selective bleaching. Equimolar concentrations of acid were used, and of the two hypophosphorous acid is the stronger reducing agent.

Photo R13

Photo R14

Photo R15

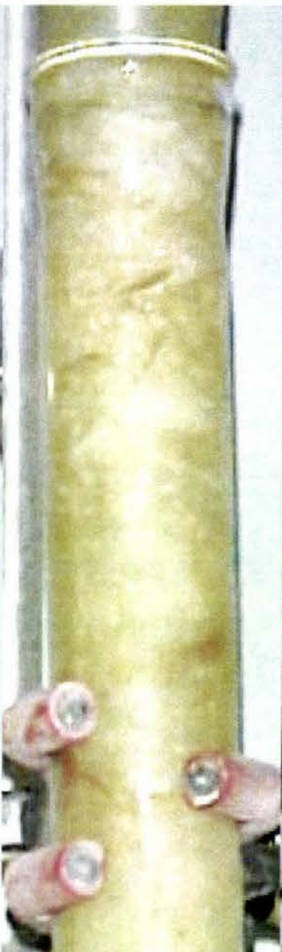


Photo R16

Photo R17

Photo R18

7.7 COMMENTS ON THE LENGTH OF REDUCTIVE BLEACHING

7.7.1 INTRODUCTION

The results of two experiments on the bleaching of tail fur are discussed here. Reductive bleaching was again undertaken using Blankit IN at 4 g/L and SLS at 1.5 g/L in both instances. The reductive bleach was extended to three hours in one instance and reduced to 90 minutes in the other.

7.7.2 RESULTS

Figure 7.5 shows the pH time profile of the reductive bleach for these experiments. As can be seen both experiments have very similar profiles.

Photos R19 and R20 show the fur after the strip and reductive bleaches respectively for the 3 hour experiment and R21 and R22 for the 1.5 hour experiment. There is a noticeable difference in the bleaching obtained for the two experiments. This is in conflict with the results of Gacen *et al.* (1994) who found that the majority of bleaching occurred in the first 1.5 hours, with very little bleaching between 1.5 and 2.5 hours. It must be noted that their work dealt with wool however, which may be susceptible to a greater rate of initial bleaching than possum fur, and also that their work was not preceded by an oxidative bleach.

This gives the possibility of either shortening or lengthening the reductive bleach if more or less bleaching than expected is obtained in the oxidative bleach. It must be noted that the reductive bleach only provides a "polish" to provide the final whiteness. A particularly poor oxidative bleach can not be rectified in the reductive bleach.

7.8 CONCLUSIONS

- The best oxidative bleaching is obtained using Blankit IN at 4 g/L and initial pH values of 6-6.5
- Best results are obtained using around 80 minutes oxidative bleaching at 50°C and 30mL/L H_2O_2, at pH 7.2 preceding the stated reductive bleaching conditions.
- The degree of bleaching obtained with the initial conditions of 3 g/L non-stabilised hydrosulphite, at 30°C for two hours is slight.
- When the strip stage was introduced, a much lower pH reductive bleach was encountered. This lead to the formation of a sulphur precipitate in some instances, and a decreased bleaching effect is observed.
- To counter this, a pH adjustment after the strip stage is necessary in the displacement bleaching method. This was achieved by a careful addition of a 25% sodium carbonate solution to the hold-up water present after rinsing to remove the reagents from the strip stage. The pH must be adjusted to at least six to obtain a satisfactory reductive bleach.

- In the bleaching of large batches of fur, some variation in the colour of the finished fur will be encountered, this is unavoidable if one wishes to obtain minimal damage to the fur. If a high white is required, it may be necessary to sort the lighter fur for processing.
- Phosphorous acid was found to cause markedly lower damage than hypophosphorous acid for a similar bleaching effect.
- The length of the reductive bleach can be altered to some extent depending on the degree of oxidative bleaching obtained, to correct for slight deviations from the oxidative bleaching expected.
- The following conditions were developed for trial in the pilot plant, which were found to give an alkali solubility of around 50% and a loss of around 5%.

Table 7.4 Conditions for use in Pilot Plant

Stage	Reagents	Conc. (g/L)	Temp (°C)	Time (hours)
Kill	Sodium metabisulphite	11	30	3
Mordant	Ferrous Sulphate	6.7	50	15
	Ammonium Chloride	11		
	Cream of Tarter	2		
	Phosphorous acid	1.85		
Rinse	Phosphorous acid	0.45	50	1
Bleach	Oxalic Acid	2	50	80 minutes after pH adjustment
	Ammonium Chloride	8		
	Sodium Pyrophosphate	8		
	Hydrogen Peroxide	30 mL/L (50% w/w)		
	Soda Ash	To pH 7.2		
	Sodium Bicarbonate			
Strip	Oxalic Acid	8	30	1
	Ammonium Bifluoride	4		
Bleach	Sodium Hydrosulphite	4	30	2
	Sodium Lauryl Sulphate	1.4		

Photo R19

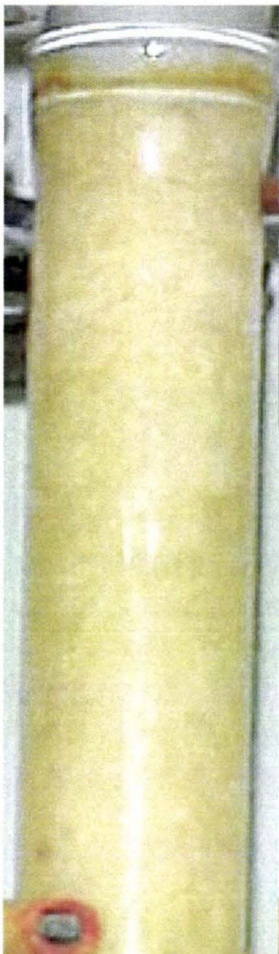


Photo R20

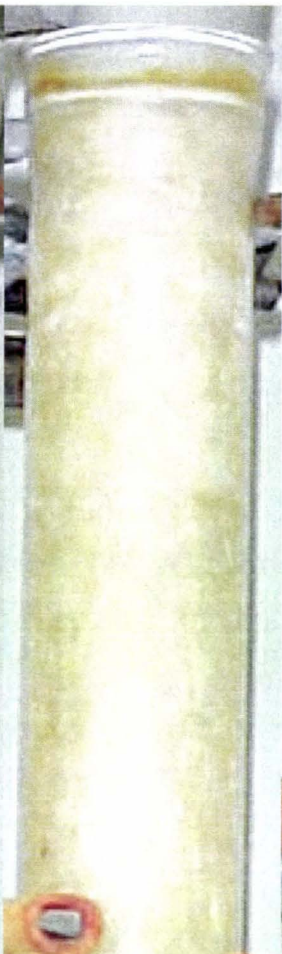


Photo R21

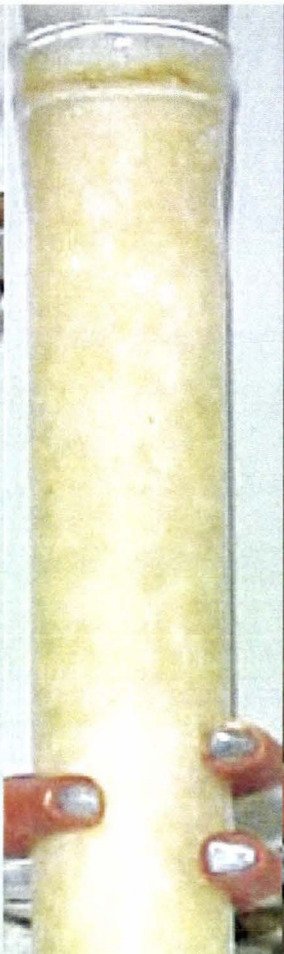


Photo R22

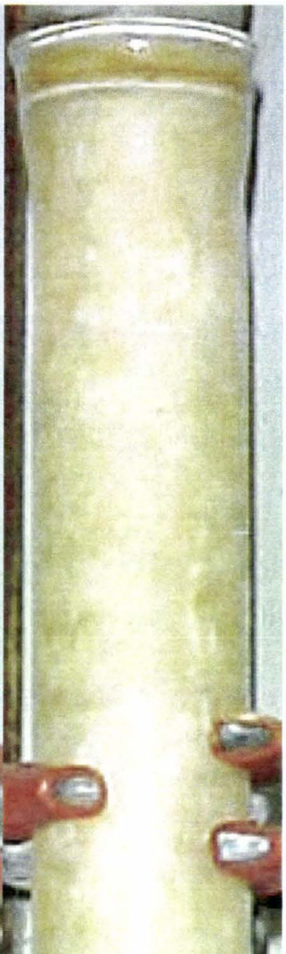


Figure 7.1

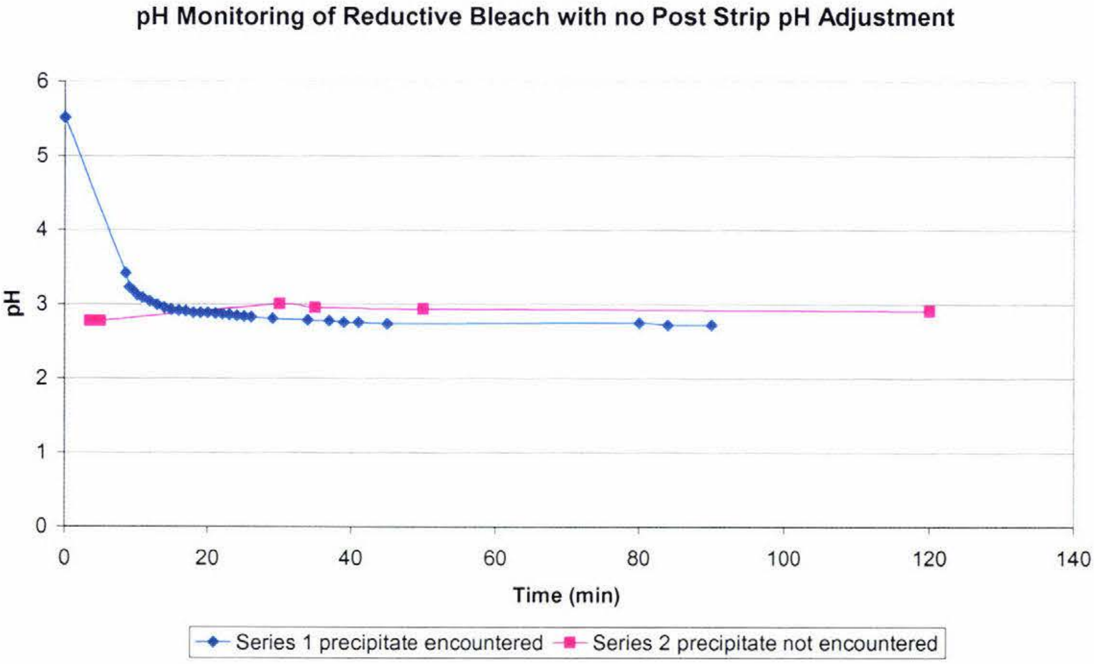


Figure 7.2

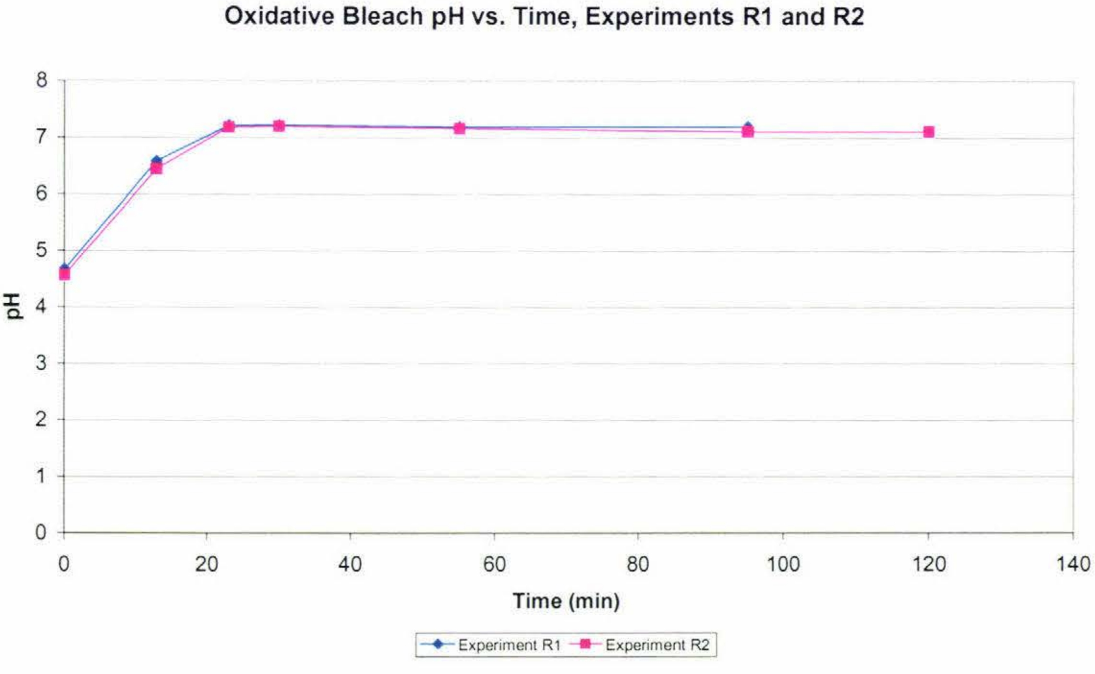


Figure 7.3

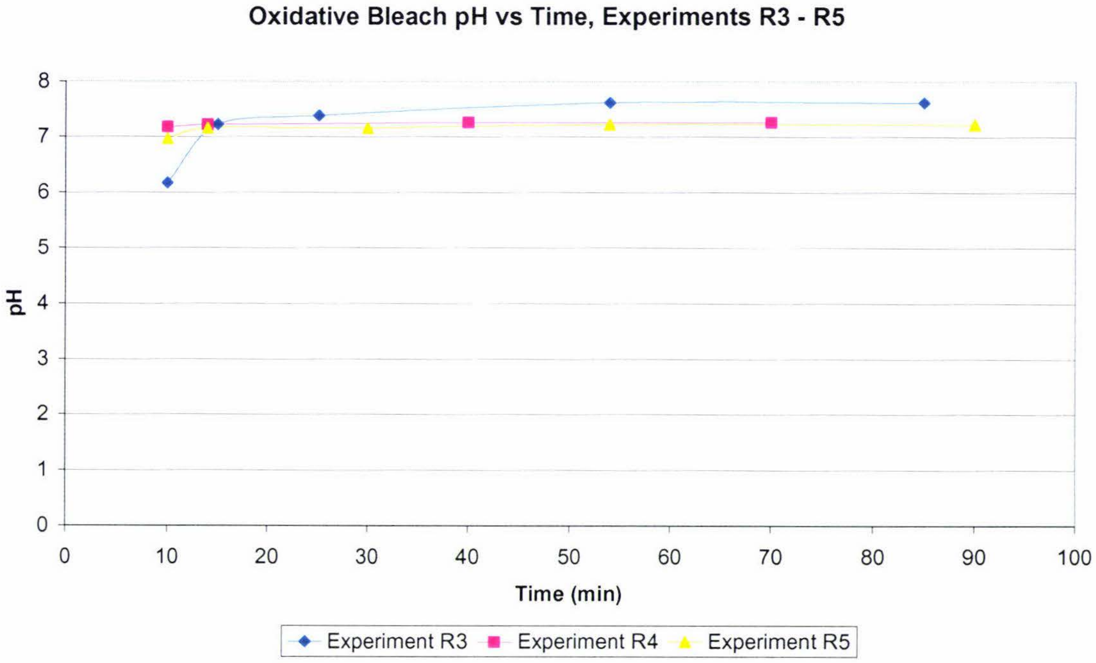


Figure 7.4

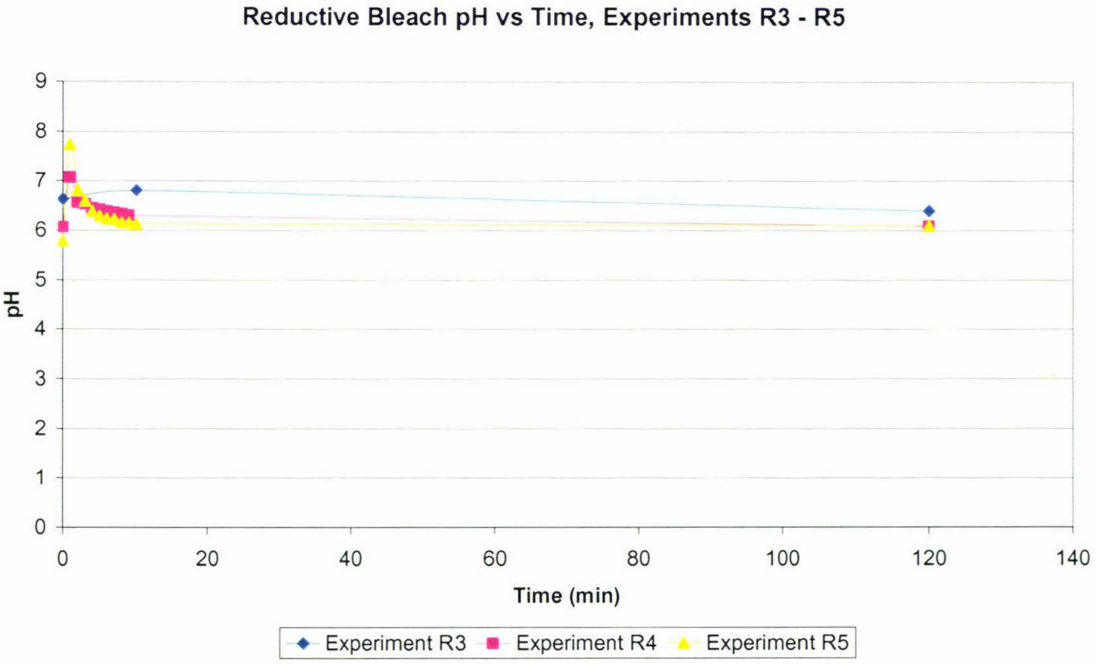
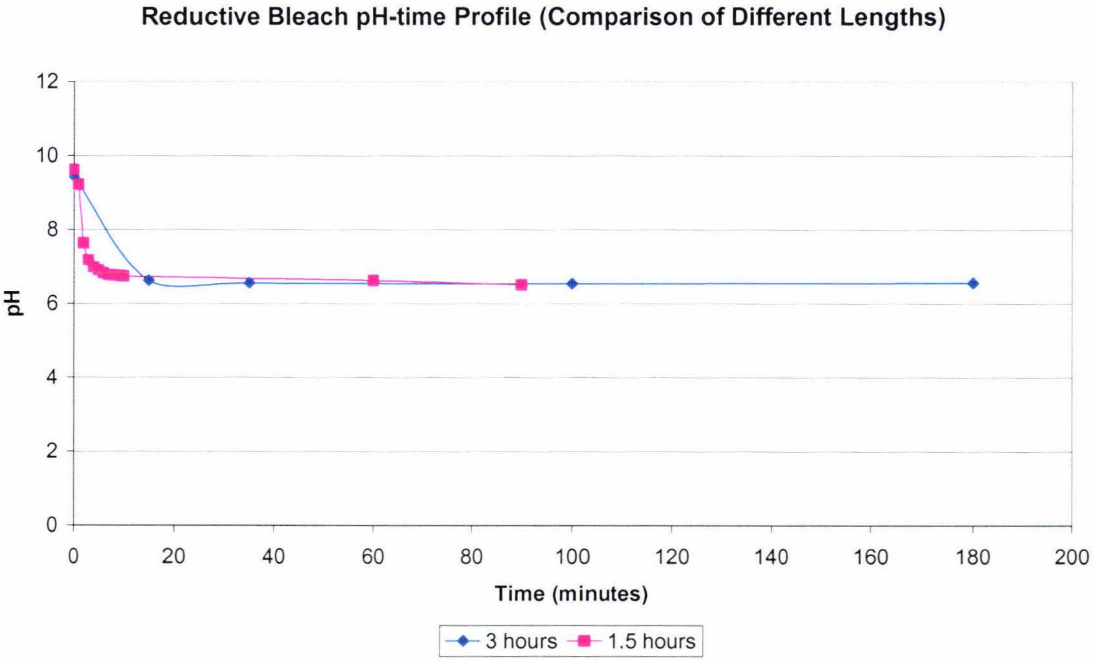


Figure 7.5


Reductive Bleach pH-time Profile (Comparison of Different Lengths)
pH
12
10
8
6
4
2
0
0
20
40
60
80
100
120
140
160
180
200
Time (minutes)
3 hours
1.5 hours

7.9 APPENDICES

Appendix 7.1

Oxidative Bleach pH Profile

Time (minutes)	Level Carb/ bicarb (g/L)	pH lighter fur (experiment R1)	pH darker fur (experiment R2)
13	0	4.65	4.55
23	2	6.57	6.43
30	4	7.20	7.17
55	4	7.21	7.19
95 (lighter fur stopped)	4	7.18	7.15
120 (darker fur stopped)	4		7.10

Reductive Bleach pH Profile

Time (minutes)	pH experiment R1	pH experiment R2
0	9.12	9.27
18	5.50	6.41
120	3.88	5.78

Appendix 7.2

Oxidative Bleach pH Profile for Experiment R3

Time (minutes)	Level $Na_2CO_3NaHCO_3$ (g/L)	pH
10	0	3.88
15	2	6.16
25	4	7.21
54	4	7.37
85	4	7.60

Reductive Bleach pH Profile for Experiment R3

Time (minutes)	pH
0	9.44
10	6.80
120	6.39

Appendix 7.3

Oxidative Bleach pH Profile for Experiment R4

Time (minutes)	Level $Na_2CO_3NaHCO_3$ (g/L)	pH
10	0	4.27
14	4	7.17

40	4	7.21
70	4	7.25

Reductive Bleach pH Profile for Experiment R4

Time (pH)	pH
0	8.63
1	7.07
2	6.56
3	6.53
4	6.45
5	6.42
6	6.39
7	6.36
8	6.34
9	6.31
120	6.08

Appendix 7.4

Oxidative Bleach pH Profile for Experiment R5

Time (minutes)	Level $Na_2CO_3NaHCO_3$ (g/L)	pH
10	0	4.74
14	4	6.95
30	4	7.14
54	4	7.14
90	4	7.20

Reductive Bleach pH Profile for Experiment R5

Time (minutes)	pH
0	9.42
1	7.73
2	6.81
3	6.60
4	6.38
5	6.29
6	6.23
7	6.22
8	6.16
9	6.15
10	6.13
120	6.10

CHAPTER 8 BLEACHING OF TAIL FUR

8.1 INTRODUCTION

The fur on the tail of the brush tailed possum is coarser and longer than the fur from the body. It is also much stronger than the normal fur, and of an almost black colour, regardless of the colouring of the body of the possum. At present it is not used for anything, the tails were discarded before this project. It had been noticed that the tail fur from bleached skins often turned out quite white. It was thought that if this fur could be bleached this resource could be utilised by Gray Fur Trading. It is thought the fur will have use in such applications as tramping socks, where a stronger fibre is required. Discussions with customers revealed that there was a market for bleached possum tail fur so an investigation into the bleaching of tail fur was undertaken.

The experimental work in this section was undertaken at Gray Fur Trading in Hokitika. This work was carried out in parallel with the other experimental work and the treatments applied based on that work.

8.2 EXPERIMENT T1

8.2.1 BLEACHING REGIME

This experiment was conducted after the optimisation of the mordant stage and during the work on oxidative and reductive bleaching. The treatments used are detailed in table 8.1. These are the same conditions as in the 4 g/L carbonate/bicarbonate experiments in section 5.2. Subsequent experiments are detailed by their differences from this regime. The experiment was conducted using 10 g of fur at a liquor ratio of 30:1. The flowrate was set at 130 mL/min. Unless otherwise stated, the pH adjustment was made after 10 minutes.

Table 8.1 Conditions for Experiment T1

Stage	Reagents	Conc. (g/L)	Temp (°C)	Time
Wet & wash	Sodium Lauryl Sulphate	1.5	Ambient	15 minutes
Kill	Sodium metabisulphite	11	30	3 hours
Mordant	Ferrous Sulphate	11	50	15 hours
	Ammonium Chloride	11		
	Cream of Tarter	2		
	Hypophosphorous Acid (50%)	3 mL/L		
Rinse	Hypophosphorous Acid (50%)	0.5 mL/L	50	One hour
Bleach	Oxalic Acid	2	50	95 minutes
	Ammonium Chloride	8		
	Sodium Pyrophosphate	8		
	Hydrogen Peroxide	30 mL/L (50% w/w)		
	Sodium Carbonate	4		
	Sodium Bicarbonate	4		
Strip	Oxalic Acid	8	30	2
	Ammonium Bifluoride	4		
Bleach	Sodium Hydrosulphite	3	30	2

8.2.2 RESULTS

The following table details the results of this experiment

Table 8.2 Results of Experiment T1

Initial pH	Final pH	Average pH	Loss (%)	Alkali Solubility (%)
7.47	7.29	7.38	9.1	75.4

The reductive bleach was performed without the pH adjustment step, having an initial pH of 7.04 (before introduction to the column) falling to 3.28 at the end of the experiment.

Examination of the photos, taken after the strip and reductive bleaching stages, shown in sections 8.11 & 8.12 as photos T1a and T1b respectively, show a good whiteness was obtained after the oxidative bleach, and a substantial improvement in the reductive bleach. This is surprising given the low pH of the reductive bleach. It was later discovered that the fur in this experiment had come from a young possum, which is much easier to bleach. All other work in this chapter, except experiment T4, dealt with mature possums. Subsequent work discovered that mature possum tails are much more difficult to bleach.

The photos are included after the strip stage in this chapter so that discolouration from iron is removed allowing a better evaluation of the oxidative bleaching, since all experiments in this chapter featured the strip.

This fur showed a very promising whiteness, being slightly less bleached than grey fur using the same conditions. It could still be dyed all but the palest of colours. Due to the likely uses of the fur in socks etc. this is unlikely to be a problem, in that pale pastel shades are unlikely to be required.

The tail fur is softened somewhat by the bleaching process, increasing its appeal for use in textiles.

The loss is quite high in this experiment at 9.1 %. The experiments dealing with tail fur all have high losses. Experiment O6 from chapter 5, which had a very similar pH profile, had a loss of 5.4% and alkali solubility of 68.6%, both lower than encountered here. Apart from the strip (which has been shown to make little contribution to damage of the fur) being included in this experiment the experiments had identical treatments.

8.3 EXPERIMENT T2

8.3.1 INTRODUCTION

Following the success of experiment T1 it was decided to investigate bleaching at a lower pH to give lower damage to the fur.

This experiment was conducted with the level of carbonate/bicarbonate at 2 g/L. SLS was included in the oxidative and reductive bleaches at 1.4 g/L, one of the few successful instances of the inclusion of this reagent. All other treatments were as in experiment one.

8.3.2 RESULTS

The following table details the results of the experiment.

Table 8.3 Results of Experiment T2

Initial pH	Final pH	Average pH	Loss (%)	Alkali Solubility (%)
6.61	6.21	6.41	6.4	79.6

Photos of the experiment after the strip and reductive bleaching stages are shown in sections 8.11 & 8.12 as photos T2a and T2b respectively.

The bleaching obtained in this experiment was very unsatisfactory. The pH obtained here was lower than expected; work on grey fur had given average values of about 6.75, although the value is within the variance previously observed. The oxidative bleach in this experiment was run for 95 minutes. Work on grey fur had shown the pH encountered here to be too low for a decent bleaching to be obtained. When it became apparent that this was also the case for tail fur, oxidative bleaching was stopped. Examination of the photos of this fur, shows a large difference in the whiteness obtained compared with the previous experiment. Clearly, on the basis of this, the pH was too low for a decent bleaching to be obtained. The bleaching effect is worse than obtained at similar pH values for grey fur.

The loss and alkali solubility in this experiment are surprisingly high given the moderate bleaching conditions used. This experiment should be compared with experiment O8 from chapter 5, which had a very similar pH profile during oxidative bleaching. The two experiments differ by the inclusion of SLS in the bleaches, which was shown to have no effect on the damage occurring to gray fur at this concentration. Experiment O8 had a loss of 4.8% and 61.0% alkali solubility c.f. 6.4% and 79.6% for this experiment. This, combined with the comparison of experiments O6 and T1 in 8.2.2 indicates that the tail fur is more susceptible to damage than body fur. The bleached fur is still noticeably stronger than bleached body fur however when manually broken.

8.4 EXPERIMENT T3

8.4.1 INTRODUCTION

Given the large difference in bleaching obtained in experiments one and two it was decided to run an experiment at a midpoint carbonate/bicarbonate level of 3 g/L. All other details were as in experiment one. This was expected to give a slightly alkaline value expected to be around 7.2, based on work in chapter five.

8.4.2 RESULTS

The following table details the results of the experiment.

Table 8.4 Results of Experiment T3

Initial pH	Final pH	Average pH	Loss (%)	Alkali Solubility (%)
7.48	6.91	7.20	7.3	79.4

Photos of the experiment after the strip and reductive bleaching stages are shown in sections 8.11 & 8.12 as photos T3a and T3b respectively.

While the fur in this experiment was an improvement on the previous experiment it was still of a very poor colour, certainly not of a marketable colour. Examination of the photos from this experiment shows an improvement on the previous experiment but still a large decrease in bleaching when compared with experiment T1.

This result was very surprising given the very slight difference in average pH of 0.18 compared with experiment T1. This is attributed to differences in maturity of the possums, although this was not realised at this point.

The oxidative bleaching in this experiment is much greater than the previous experiment. The pH was within the range determined in chapter five but below it in experiment T2, this difference was shown to be critical in experiments O7 and O8. The loss in this experiment has increased compared to that in experiment two although the alkali solubilities are similar, and both very high.

8.5 EXPERIMENT T4

8.5.1 INTRODUCTION

This experiment was one conducted in anticipation of possible pilot scale work using a stock dyer at Quality Yarns in Milton. They were not prepared to leave their boiler on overnight meaning that the mordant stage could not be heated overnight. Experiments were conducted in which the mordant was heated to 66°C, in this case for 3.5 hours, then left unheated overnight for 15 hours, during which the temperature dropped to 17°C. This experiment featured 10 g of fur at a liquor ratio of 22:1 and the sodium carbonate/bicarbonate level at 4 g/L The flowrate was reduced to 100 mL/min in this experiment. All other treatments were as in experiment one

8.5.2 RESULTS

The following table details the results

Table 8.5 Results of Experiment T4

Initial pH	Final pH	Average pH	Loss (%)	Alkali Solubility (%)
6.90	7.29	7.05	8.0	79.4

Photos of the experiment after the strip and reductive bleaching stages are shown in sections 8.11 & 8.12 as photos T4a and T4b respectively.

Experiments on grey fur using this process showed a comparable level of bleaching to those using the standard mordanting process. On the basis of this it would seem that similar levels of mordanting are obtained. The fur in this experiment is a considerable improvement on experiment T3, although still off-white

Given the lower pH (7.05) in this experiment, compared to that of experiment three (7.20) it is thought that the fur in this experiment must have came from an immature possum, which are much easier to bleach.

Direct comparisons between this experiment and the others in this section are difficult, however, due to the altered mordant process.

All possum tails appear to be basically the same colour. In the experiments to this stage samples had been withdrawn from the same bag in which the fur had not been homogenised. This fur was then carded for subsequent experiments.

8.6 EXPERIMENT T5

8.6.1 INTRODUCTION

In this experiment the carbonate/bicarbonate was added after one hour of oxidative bleaching. The rationale behind this was that a shorter alkaline bleach might be necessary, leading to less damage of the fur. Although this goes against the previously quoted findings of Gacen and Cayuela (2000), their work involved non-mordanted wool. At the initial pH, bleaching should proceed almost entirely by the radical mechanism, possibly leading to less damage to the fur.

The experiment was conducted using 13g of fur at a liquor ratio of 20:1. The flowrate was set at 100 mL/min.

This was the first experiment to feature a pH adjustment of the hold-up liquor between the strip and reductive bleaching stages. This was achieved by the addition of a 25% sodium carbonate solution, as detailed in chapter seven.

The strip stage was shortened to one hour in this and all subsequent experiments, as detailed in chapter six.

The pH-time profiles for oxidative and reductive bleaching for experiments T5 to T8 are included as figures 8.1 and 8.2 respectively. The data used to generate these graphs is included as appendices 8.1 to 8.4. These four experiments have been grouped together. It was realised at this stage that significantly harsher conditions than those used for grey fur would be required and these experiments detail this work.

8.6.2 RESULTS

The carbonate/bicarbonate was added in three doses of 2 g/L. The third addition was made at 80 minutes because the pH had not reached a desired level after the second dose. A higher pH was used to give an improved oxidative bleach. A final pH of 7.61 was achieved and bleaching undertaken for a total of 165 minutes.

Reductive bleaching was undertaken using the blankit IN formulation at 4g/L. The reductive bleach pH fell from 6.75 to 6.52 over the course of the experiment.

The following table details the damage results of the experiment

Table 8.6 Damage Results for Experiment T5

Loss (%)	Alkali solubility (%)
8.1	84.5

The fur in this experiment was a noticeable improvement on experiments T2 and T3, attributable to the higher pH oxidative bleach, and comparable to that in experiment T1, although the alkali solubility is significantly higher. The disk containing these photos was damaged so they cannot be included. The fur still had a yellow tinge to it though. Considering the very dark colour of the tail fibre initially it may not be possible to get the whites obtained with grey fur. Further experimental work was conducted to investigate how good a whiteness could be obtained.

The loss obtained in this experiment is higher than experiments T2 and T3. The alkali solubility has increased, to a very high value, due to the harsher bleaching conditions used. The fur is still stronger than the bleached body fur by hand breaking tests.

8.7 EXPERIMENT T6

8.7.1 INTRODUCTION

This experiment featured further work on increasing the harshness of the oxidative bleach. The initial one hour acidic bleach was eliminated. The experiment used 15g fur at a liquor ratio of 20:1 and a flowrate of 100 mL/min. SLS was included in the reductive bleach at 1.4 g/L.

The experiment again used 6 g/L of the sodium carbonate/bicarbonate in the oxidative bleach. This gave a final pH of 7.61, very similar to the previous experiment; the bleach was run for 150 minutes in this instance (115 after the final adjustment). The oxidative bleach was run until what appeared to be a superior whiteness than in the previous experiment had been obtained.

The reductive bleach pH was 6.64 after 10 minutes falling to 6.15 at the end of bleaching.

8.7.2 RESULTS

The following table gives the damage results of the experiment.

Table 8.7 Damage Results Experiment T6

Loss (%)	Alkali solubility (%)
7.0	83.5

Photos of the experiment after the strip and reductive bleaching stages are shown in sections 8.11 & 8.12 as photos T6a and T6b respectively.

The loss here was lower than experiment T5 and the alkali solubility very similar. The end bleaching obtained is very similar. The loss is surprisingly low compared with the other experiments in this section. Given the similar bleaching obtained in this experiment (with the longer alkaline bleach) and experiment five no benefit is observed from the one hour acidic bleaching.

8.8 EXPERIMENT T7

8.8.1 INTRODUCTION

This experiment was a continuation of experiment T6 and basically an all out attempt to obtain as good a whiteness as possible. It featured a higher pH oxidative bleach than had previously been used and for a longer time. The pH was adjusted to around 8.05 and ran for three hours (158 minutes after the final adjustment). The reductive bleach was also extended to three hours.

This experiment featured phosphorous acid in place of hypophosphorous acid in the mordanting and rinsing steps. The mordant was also run slightly longer than previously at 19.5 hours. Phosphorous acid was used at 1.85 g/L in the mordant and 0.45 g/L in the rinse, giving equimolar acid concentrations.

SLS was included in the reductive bleach at 1.4 g/L. Blankit IN was used at 4g/L. The reductive bleach pH was 6.60 falling to 6.53 over the course of the experiment.

8.8.2 RESULTS

The following table details the damage results of the experiment.

Table 8.8 Damage Results for Experiment T7

Loss (%)	Alkali solubility (%)
10.2	76.7

Photos of the experiment after the strip and reductive bleaching stages are shown in sections 8.11 & 8.12 as photos T7a and T7b respectively.

The fur in this experiment is very similar to that obtained in experiment T6. If anything it was in fact less bleached. There was no appreciable difference obtained by the harsher bleaching conditions. An optimum whiteness may exist using conditions somewhere between those above and those of experiment T6. The harsher conditions have resulted in only an increased loss of fur. The alkali solubility is marginally lower in this experiment than experiment T6, despite the harsher conditions. It must also be noted the phosphorous acid mordant was used in this experiment. A large reduction in alkali solubility was observed with the use of this reagent in work on body fur. It is likely that the fur would have been even more damaged had the hypophosphorous mordant been used.

8.9 EXPERIMENT T8

8.9.1 INTRODUCTION

In this experiment no reducing agent was included in the mordant. This gave good whiteness in an experiment on grey fur and seeing very harsh conditions were required to get good whites with tail fur, the results with this system were investigated.

8.9.2 RESULTS

The pH of the mordant was higher in this experiment due to the absence of the reducing agent, at 3.0; the acid rinse step was also excluded, giving a greater proportion of iron on the fibres.

Oxidative bleaching was undertaken for 120 minutes. Reductive bleaching was undertaken for only 90 minutes, the pH was 6.60 after 10 minutes falling to a final value of 6.48.

The following table details the damage results of the experiment.

Table 8.9 Damage Results for Experiment T8

Loss (%)	Alkali Solubility (%)
14.2	85.0

Photos of the experiment after the strip and reductive bleaching stages are shown in sections 8.11 & 8.12 as photos T8a and T8b respectively.
The whiteness obtained is similar to experiment T7, and therefore not as good as had been obtained, with a much greater degree of damage indicated by the loss and alkali solubility data. On the basis of this, it was decided that this method is not suitable to industrial application.

8.10 CONCLUSIONS

The following conditions were found to give the best whiteness in the bleaching of mature possum tail fur.

Table 8.10

Stage	Reagents	Conc. (g/L)	Temp (°C)	Time
Wet & wash	Sodium Lauryl Sulphate	1.5	Ambient	15 minutes
Kill	Sodium metabisulphite	11	30	3 hours
Mordant	Ferrous Sulphate	11	50	15 hours
	Ammonium Chloride	11		
	Cream of Tarter	2		
	Phosphorous Acid	1.85		
Rinse	Phosphorous Acid	0.45	50	One hour
Bleach	Oxalic Acid	2	50	
	Ammonium Chloride	8		
	Sodium Pyrophosphate	8		
	Hydrogen Peroxide	30 mL/L (50% w/w)		
Strip	Oxalic Acid	8	30	1
	Ammonium Bifluoride	4		
Bleach	Blankit IN	4	30	2
	SLS	1.4		

- The best bleaching was obtained using the above method with sodium carbonate and sodium bicarbonate added to a level of approximately 6 g/L in the oxidative bleach, to bring the pH to 7.6. 115 minutes of bleaching are required after this.

- Although not trialled on tail fur, experimentation on grey fur has shown that the level of ferrous sulphate monohydrate can be cut back to 6.7 g/L.
- The pH of the system needs to be adjusted to a value of at least 5.8 (6.0 was used as a target), between the strip and reductive bleaches
- The tail fur of younger possums is much easier to bleach. If the fur from these possums is separated for use, the pH of oxidative bleaching needs to be raised to about 7.4 with bleaching undertaken for 85 minutes after this adjustment is made. The rate at which the "bleaching difficulty" increases with possum age has not been determined however.
- The alkali solubilities obtained in the experiments on tail fur are all outside the range that would normally be acceptable. Bearing in mind the greater strength of tail fibres, and the intended uses of this fibre, it must be determined if this fibre is suitable for further processing.
- Tail fur is harder to bleach and more susceptible to damage than grey fur, although being naturally stronger than body fur.

8.11 POST STRIP PHOTOS

Photo T1a

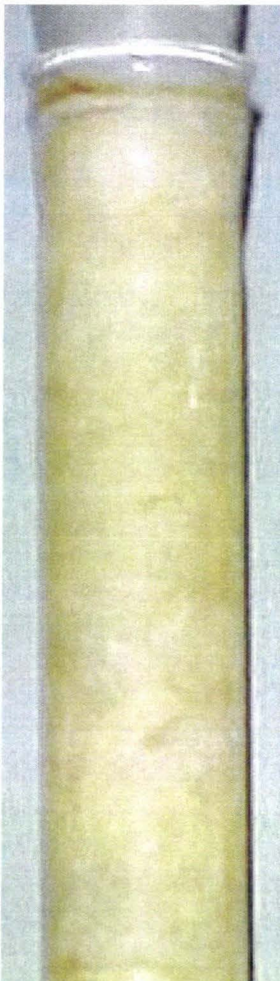


Photo T2a

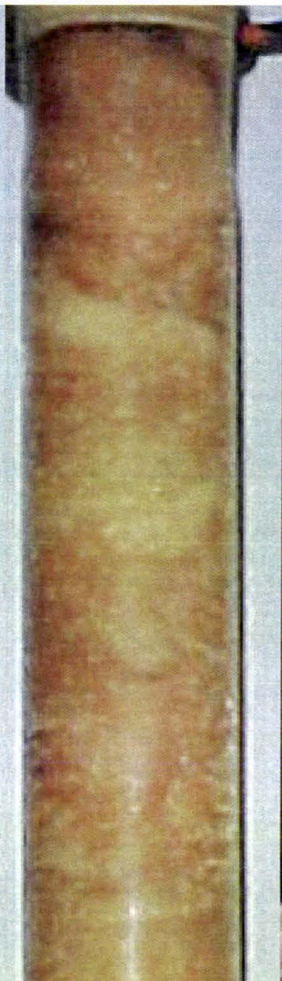


Photo T3a

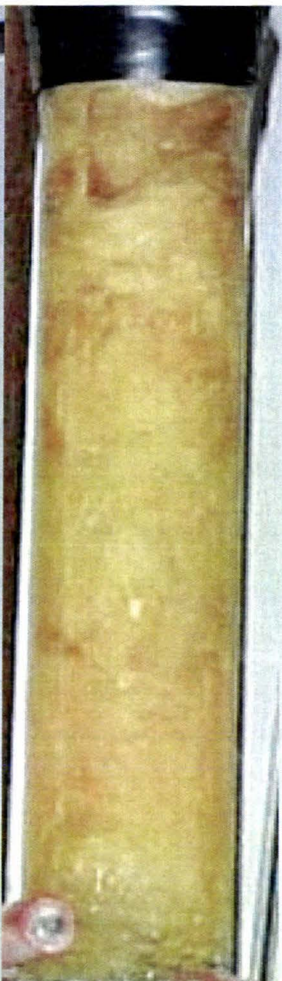


Photo T4a

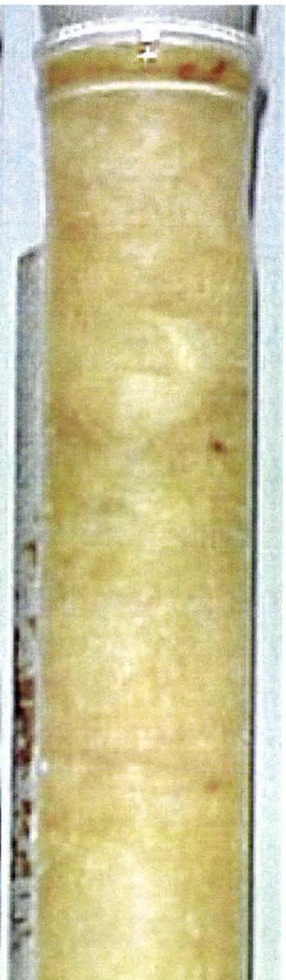


Photo T6a

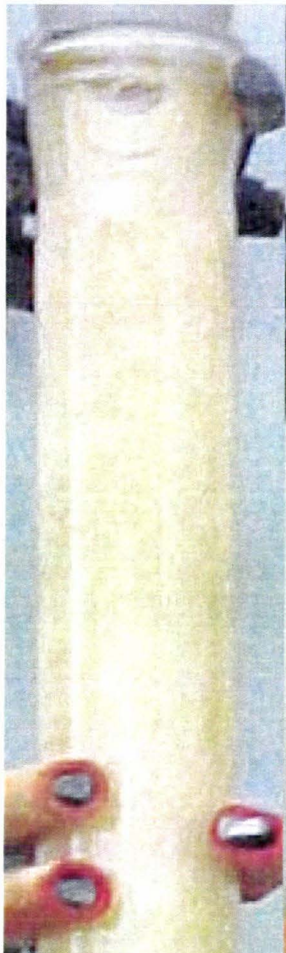


Photo T7a

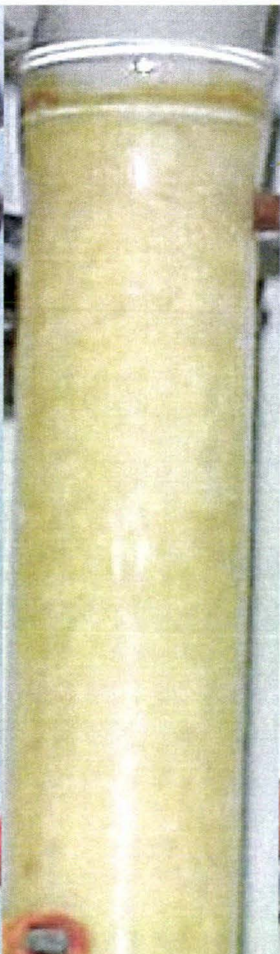
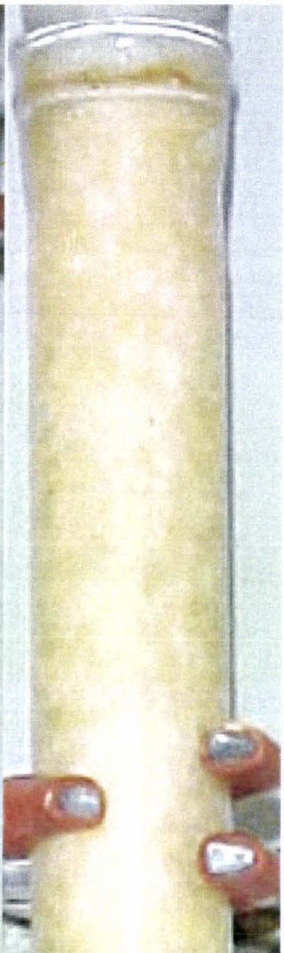


Photo T8a



8.12 POST-REDUCTIVE BLEACH PHOTOS

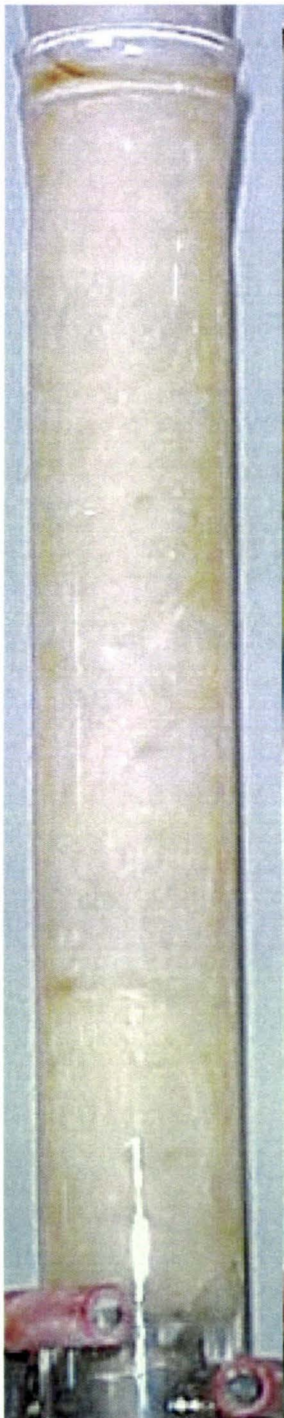


Photo T1b


Photo T2b


Photo T3b

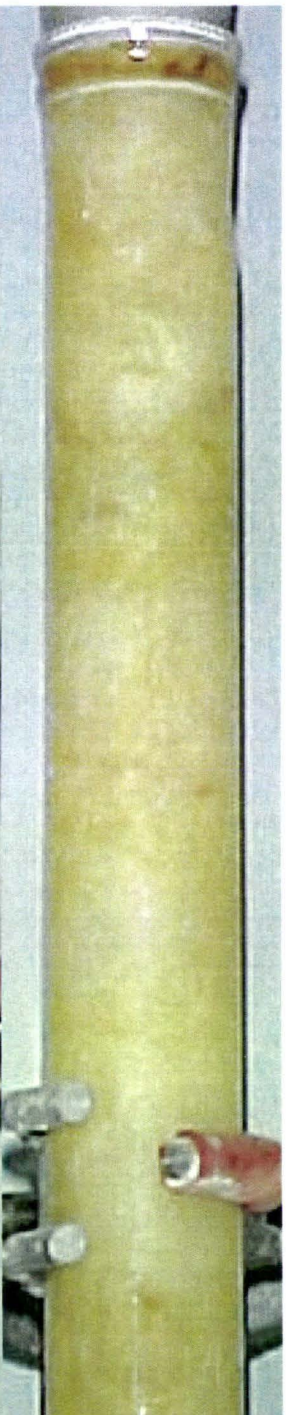


Photo T4b

Photo T6b

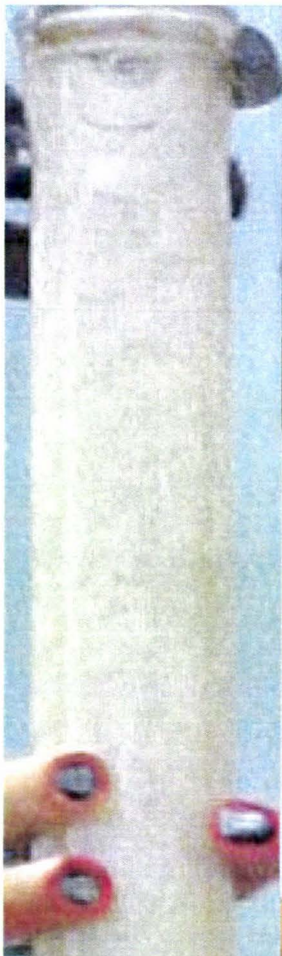


Photo T7b

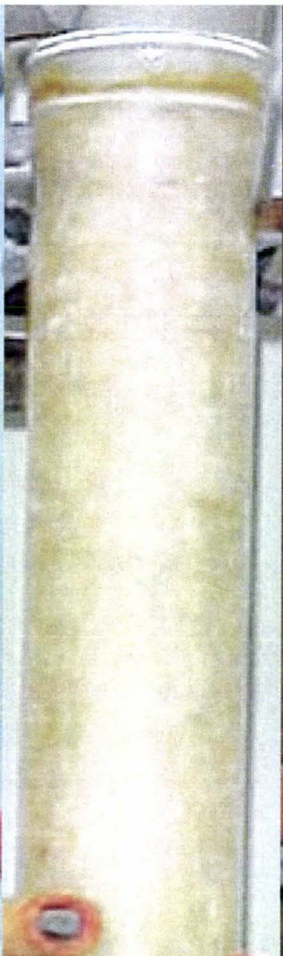


Photo T8b

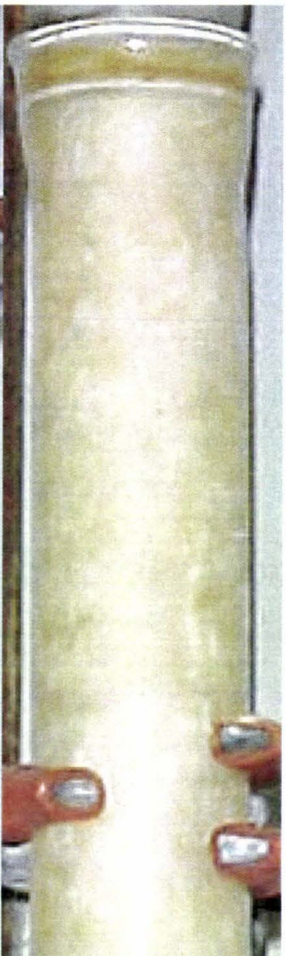


Figure 8.1

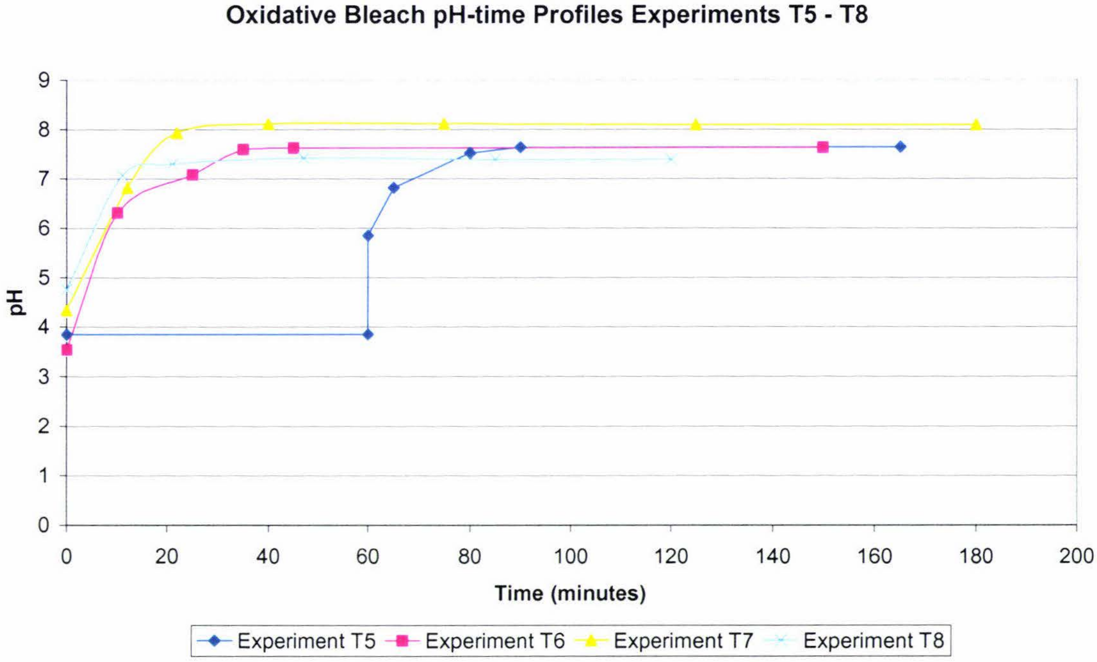
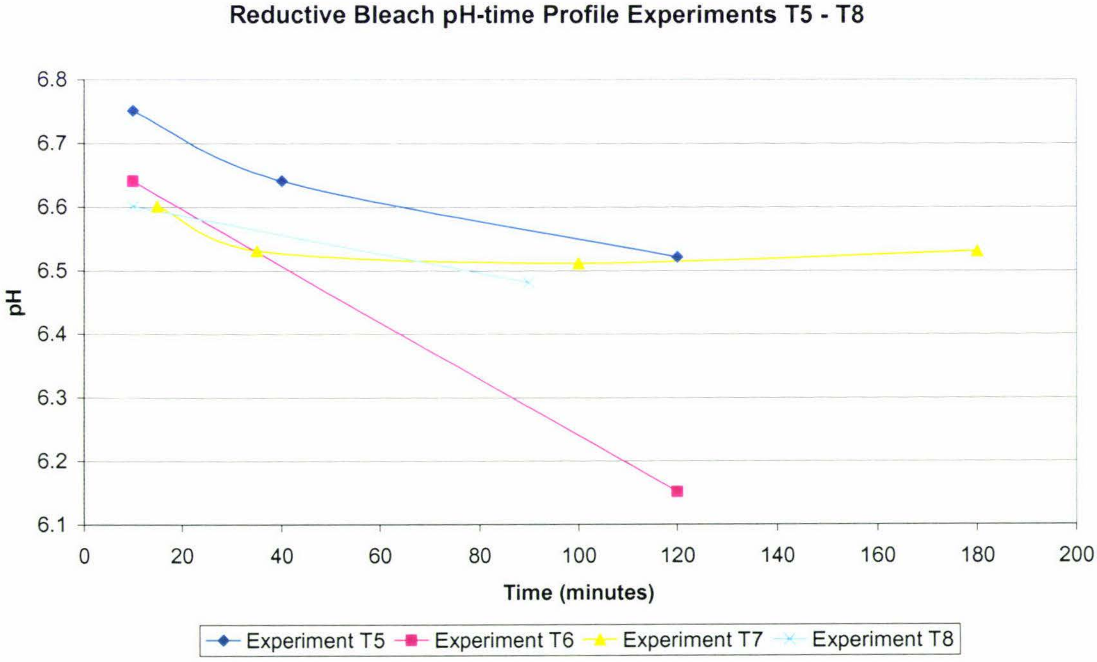


Figure 8.2



8.13 APPENDICES

Appendix 8.1 pH Data Experiment T5

Oxidative Bleach

Time (minutes)	Level $Na_2CO_3NaHCO_3$ (g/L)	pH
60	0	3.83
65	2	5.83
80	4	6.79
90	6	7.50
165 (end of bleaching)	6	7.61

Reductive Bleach

Time (minutes)	pH
10	6.75
40	6.64
120	6.52

Appendix 8.2 pH Data Experiment T6

Oxidative Bleach

Time (minutes)	Level $Na_2CO_3NaHCO_3$ (g/L)	pH
10	0	3.52
25	2	6.29
35	4	7.06
45	6	7.57
150 (end of bleaching)	6	7.60

Reductive Bleach

Time (minutes)	pH
10	6.64
120	6.15

Appendix 8.3 pH Data Experiment T7

Oxidative Bleach

Time (minutes)	Level $Na_2CO_3NaHCO_3$ (g/L)	pH
12	0	4.32
22	4	6.79
40	8	7.90
75	8	8.08
125	8	8.08
180 (end of bleaching)	8	8.06

Reductive Bleach

Time (minutes)	pH
15	6.60
35	6.53
100	6.51
180	6.53

Appendix 8.4 pH Data Experiment T8

Oxidative Bleach

Time (minutes)	Level $Na_2CO_3NaHCO_3$ (g/L)	pH
11	0	4.74
21	4	7.04
47	4	7.27
85	4	7.39
120 (end of bleaching)	4	7.36

Reductive Bleach

Time (minutes)	pH
10	6.60
90	6.48

CHAPTER 9 PILOT PLANT

9.1 INTRODUCTION

Pilot plant work was undertaken in order to identify and solve any scale-up problems likely to arise in full-scale industrial application of the bleaching process derived.

This was undertaken in two parts.

Firstly trials were undertaken at the Wool Research Organisation of New Zealand (WRONZ), on a stock dyer used for pilot scale work. Secondly, a pilot plant was built at Gray Fur Trading in Hokitika.

9.2 WORK AT WRONZ

9.2.1 INTRODUCTION

Two bleaching trials were undertaken at WRONZ over the week 13-17 November 2000. The first was on 4 kg of tail fur (at a 22.5:1 liquor ratio) and the second on 4.5 kg of grey fur (at a 20:1 liquor ratio).

This work was undertaken to investigate if the bleaching process developed could be undertaken on larger scale stock dyers. Excess capacity could then be purchased off a knitting mill saving the cost and time of building a plant.

The work was carried out on an A.P.C 4.5 kg capacity stock/package dyer manufactured by Farra bros. Dunedin under licence to Longclose Engineering U.K., using a shimaden pneumatic/electronic pump controller.

A stock dyer is a one vessel system making use of a cylindrical housing in which the fur is held between plates, in a larger open topped vessel. Solutions are alternately pumped upwards and downwards through the fur.

9.2.2 BLEACHING OF TAIL FUR

This was the first experiment undertaken at WRONZ. The method used in this experiment is detailed in the following table.

Table 9.1 Bleaching Regime for Pilot Plant Work at WRONZ

Stage	Reagents	Conc. (g/L)	Temp (°C)	Time (hours)
Kill	Sodium metabisulphite	11	30	3
Mordant	Ferrous Sulphate	11	50	15
	Ammonium Chloride	11		
	Cream of Tarter	2		
	Hypophosphorous acid	3 mL/L		
Rinse	Hypophosphorous acid	0.5 mL/L	50	1
Bleach	Oxalic Acid	2	50	95
	Ammonium Chloride	8		
	Sodium Pyrophosphate	8		
	Hydrogen Peroxide	30 mL/L (50% w/w)		
	Soda Ash	4		
	Sodium Bicarbonate	4		
	Sodium Lauryl Sulphate	2.5		
Strip	Oxalic Acid	8	30	2
	Ammonium Bifluoride	4		
Bleach	Sodium Hydrosulphite	3	30	2
	Sodium Lauryl Sulphate	1.4		

The stages before oxidative bleaching were undertaken successfully. The rinsing procedure, to remove the previous stages reagents, had to be modified for the stock dyer. The solution from the previous stage was drained from the tank and the tank refilled and allowed to overflow for 10 minutes, the tank was then drained before refilling for the next stage. This provided the necessary removal of the previous stages reagents. This procedure was adequate for this scale; however, it would be troublesome on a larger scale stock dyer. After the oxidative bleach the solution could not drain through the fur at any significant rate. The solution had to be manually tipped out using beakers. This was due to the fur being compressed into a very shallow bed preventing gravity flow.

A significant foaming problem was encountered during the oxidative bleach. This was initially thought to be due to the presence of SLS. SLS was included at 2.5 g/L because good results were quoted in the literature from the use of this reagent, but it could not be successfully trialled in laboratory work. Allsop (1996) in his study on the use of SLS in bleaching systems experienced problems at 5 g/L but not at 1 g/L. The initial hypothesis was that our midpoint value also caused this foaming. However, when SLS was excluded in the run on grey fur, foaming also resulted. This foam was attributed to the neutralisation of the acidic solution with sodium bicarbonate, leading to the evolution of carbon dioxide. SLS was not included in the oxidative bleach for any of the subsequent pilot plant work because it increases the tendency of the fibres to compact, exacerbating flow problems through the fur.

Another problem encountered in the oxidative bleach was overflow of the stock dyer, effectively leading to a lower liquor ratio for this stage. This was due to the evolution of carbon dioxide, from the neutralisation of the acidic solution with sodium bicarbonate, causing expansion of the liquor. It is estimated that between five and ten litres was lost due to this. The overflow occurred mainly when the pump switched directions to pump downwards through the bed of fur from pumping up through the fur. The pump was set to pump upwards only through the fur on the run with grey fur, largely eliminating this problem. Approximately 2-3 litres were lost in the grey fur run.

Neither bleaching experiment was successful, the bleaching obtained was vastly inferior to that obtained in the laboratory scale work using the same conditions, and certainly not marketable. This is thought to be a combination of two factors. Firstly, the overflow of the vessels would have lead to a decreased bleaching effect due to a decreased amount of peroxide. However, the effect of this may not necessarily be significant. The liquor ratio had been cut back successfully from 50:1 to 20:1, further reduction may be possible. Especially in the grey fur experiment, where a relatively small amount of solution was lost, the effect would not be particularly great. The loss of 2-3 litres would lead to an effective liquor ratio of 19:1.

The major problem was attributed to uneven flow through the fur. The flowrate is known to have been too high, leading to compression of the fur and subsequent channelling. This could be seen from a visual examination of the fur. There were areas which were quite well bleached, comparable to laboratory work, whilst others appeared to have barely seen the bleaching solutions, and areas of preferential flow were seen when unpacking the dyer. The compression of the fur is exacerbated by the heavy stainless steel plate, which sits on top of the fur bed to keep the fur in place. During the downward pumping cycle the weight of the plate serves to further compress the fur. The tail fur in particular was very poorly bleached; this is due in part to the fact that the tail fur bleaching process had not been optimised at this stage. The issue of possum maturity had not yet been discovered. However, the deficiencies of the use of a stock dyer for bleaching possum fur were shown up in the trial using grey fur. Firstly, the flowrate used was too great, leading to compression and subsequent uneven flow through the fur. Secondly, the vessel volume was insufficient to prevent overflow of the vessel, due to expansion of the oxidative bleaching solution, resulting from the evolution of carbon dioxide.

It is possible that both these problems could be overcome with a purpose designed stock dyer. A lower flowrate, possibly using only flow up through the bed of fur could alleviate the compression problem. Allowing extra volume for the expansion of the peroxide solution, or a lower temperature to reduce the rate of evolution of gaseous species, should eliminate the overflow problem. Subsequent work has shown that without a support structure only a shallow bed of fur can be bleached. It is likely that only small batches of fur could be bleached in a stock dyer set-up without encountering flow distribution problems.

The required information for this design was not known at this point however and a pilot plant was built in Hokitika at Gray Fur Trading. A one vessel system, if feasible, would offer advantages in the pH adjustment stages. Adjustment of pH in a two vessel system is quite a time consuming process.

9.3 HOKITIKA PILOT PLANT

9.3.1 INTRODUCTION

Due to the unsatisfactory results obtained at WRONZ it was decided to build a pilot plant based on the displacement bleaching used in the experimental work. The reasoning behind this was that the flow through the fur could be controlled to try to avoid the compression problems which occurred in the stock dyer.

The plant was designed for 5 kg batches of fur. A scale needed to be chosen which was large enough to bring to light any scale up issues which may arise. Laboratory scale work had already proven that the bleaching regime used was capable of providing the required level of bleaching. It would therefore follow that the main consideration in a successful scale up is ensuring the replication of the conditions of laboratory work. Therefore a scale needed to be used which would bring to light any factors which would cause the fur to be unevenly exposed to the bleaching solutions, and to determine that the temperature and concentrations used can be accurately replicated. Based on laboratory work it was known that 5 kg of fur could be packed into a volume of between 55 and 70 litres for bleaching. This was slightly larger than the mass used at WRONZ, which had given flow problems. Sixty five litre tanks were available for use and these formed the basis of the plant. Two hundred litre drums were also available for use but the five kilogram scale was opted for to minimise costs resulting from any unsuccessful pilot plant runs.

The following equipment was needed for the construction of the pilot plant.

- Two tanks. One to hold the fur and the other as a reservoir for bleaching solutions
- A pump to circulate the solutions
- A means of heating the solutions

- A distributor plate to ensure even flow through the fur bed.
- A screen to prevent fur flowing out through the top of the fur tank
- Pipework and valves to connect the equipment
- Insulation to minimise heat losses from the system

9.3.2 EQUIPMENT SELECTION

9.3.2.1 Tanks

In order to minimise the costs of the pilot plant it was decided to use plastic materials for the tanks and pipework. Two 65 L HDPE plastic drums, commonly used for transporting chemicals, were selected for both the tank to hold the bed of fur ("the fur tank") and for the tank to hold the bleaching solution ("the liquor tank"). The tanks needed to have a combined volume in excess of 100 L for 5 kg of fur at a liquor ratio of 20:1.

To ensure the plastic could withstand the reagents used they were exposed to solutions of the chemicals for a period of 3 days. No deterioration of the plastic was evident from a visual examination.

A photograph of the pilot plant set-up is included as figure 9.2. The fur tank is on the right. Solutions are pumped from the liquor tank, through the flow tube heating element, and up through the fur tank returning to the liquor tank.

9.3.2.2 Pump

Again of importance was that the pump was made of materials resistant to the bleaching solutions.

The head that the pump would be pumping against was unknown before the pilot plant work was undertaken. The scale up was based on the same superficial velocity through the fur as was used in the laboratory work. On the combination of these two factors it was decided that a positive displacement type pump would be used, to give a relatively constant flowrate irrespective of the head it was pumping against.

A local pump supplier (Keenan farm maintenance) had a Flynn milk pump available for use capable of giving the flowrates required. This pump was rented for the course of the pilot plant work. A small amount of abrasive material is present in the ferrous sulphate used, which could lead to attrition problems in the pump. This problem was countered by dissolving the ferrous sulphate and letting the abrasive material settle out before decanting into the liquor tank.

9.3.2.3 Heating

Two options were available for use here. Firstly, coils could be inserted into the liquor tank to provide the heating. Alternatively, a flow tube, containing the heating element in a tubular sheath, could be inserted between the liquor and fur tanks.

The flow tube was the more expensive option but was selected because it provided the following advantages.

- The flow tube would allow the liquor tank to be fully sealed. This is important to minimise evaporative losses during the mordant stage in particular which was left overnight at 50°C.
- With a flow tube the level of the liquor tank is unimportant. This left the option available of bleaching smaller batches of fur, if this was desired, without modification to the fur tank.
- Easier manual agitation of the liquor vessel, during pH adjustments, could be achieved with the flow tube.
- A support would have to be built for coils in the tank to prevent them melting the tank
- The supplier for the flow tube quoted a shorter delivery time (although it was a week and a half late).

The design of the flow tube is shown in figure 9.3.

9.3.2.4 Distributor plate

The distributor plate was fitted into the bottom of the fur tank. Its purpose is to provide a pressure drop sufficient to ensure that the flow through the tank is as close to plug flow as possible, ensuring that the fur is evenly exposed to the bleaching solutions.

In the laboratory experiments a piece of no. 3 sintered glass was used in the bottom of the columns to achieve this. Initially it was thought a piece of porous plastic could be used. Inquiries revealed that porous plastic wasn't stocked by any New Zealand suppliers; it would have to be imported from Australia. It was also quite expensive, a sheet costing around $2000.

It was decided that a suitable piece of equipment could be made from readily available materials. The bottom of another of the 65 litre drums used for the liquor and fur tanks was removed, at approximately 25 mm from the bottom. Holes were drilled through it and it was filled with pieces of shade cloth, as used in greenhouses and nurseries. The compatibility of the shade cloth was checked by immersion tests. The lid from another tank was removed, cut to the appropriate size, holes drilled through it then it was glued to the top of the previously described tank bottom. The distributor plate was held in place, in the bottom of the fur tank, by type 304 stainless steel self tapping screws inserted through the side of the fur vessel.

A photo showing the distributor plate in place is included as figure 9.4

9.3.2.5 Screen

The screen at the top of the fur tank was constructed by taking the lid of another tank and fixing this to the lid of the fur tank with self tapping 304 SS screws. Holes were then drilled through the lid to allow flow through the tank.

The screen is shown in figure 9.5.

9.3.2.6 Piping

Type two PVC piping was used for all the piping in the plant.

9.3.2.7 Insulation

Sections of an old foam rubber carpet were attached to the vessels and piping where possible.

9.3.3 PILOT PLANT TRIALS

9.3.3.1 Introduction

The design was based on a scale up using the same superficial velocity through the fur as used in the laboratory work, giving a flowrate of 15 L/min.

Between stages the drain valves at the bottom of both tanks were opened and the system drained of solution. The system was then washed through with 100L of water to remove reagents from the previous stage. Approximately 2.1 kg of water is retained by each kilo of fur, which must be accounted for when determining the water requirements of the next stage.

9.3.3.2 Initial experimentation

Before a pilot plant run was undertaken, the heat losses occurring throughout the system were investigated. This was done so that it could be determined what setting on the flow tube thermostat corresponded to a particular temperature exiting the fur vessel. This also served as a check on the accuracy of the thermostat.

In the course of this experimentation it became apparent that the flowrate being used was too high, leading to compression of the fur and a build-up of pressure on the lid of the fur vessel, causing it to leak. The flowrate was halved to 7.5 L/min, which gave the same problem, with a slower onset. The flowrate was then reduced to 5 L/min which eliminated this problem. This gave a threefold decrease in the superficial velocity used compared with laboratory work. This compression and overflow problem turned out to be the main scale-up issue encountered.

It was found that setting the thermostat dial to 31°C gave an average exit temperature from the fur vessel of 30°C, and a setting of 57°C gave an average exit temperature of 50°C. On/off control was observed at about 1.5 degrees each side.

9.3.3.3 Pilot Plant Trial One

The following table details the treatments intended for this trial.

Table 9.2 Bleaching Regime for Pilot Plant Run One

Stage	Reagents	Conc. (g/L)	Temp (°C)	Time (hours)
Kill	Sodium metabisulphite	11	30	3
Mordant	Ferrous Sulphate	6.7	50	15
	Ammonium Chloride	11		
	Cream of Tarter	2		
	Phosphorous acid	1.85		
Rinse	Phosphorous acid	0.45	50	1
Bleach	Oxalic Acid	2	50	?
	Ammonium Chloride	8		
	Sodium Pyrophosphate	8		
	Hydrogen Peroxide	30 mL/L (50% w/w)		
	Soda Ash	To pH 7.2		
	Sodium Bicarbonate			
Strip	Oxalic Acid	8	30	1
	Ammonium Bifluoride	4		
Bleach	Sodium Hydrosulphite	4	30	2
	Sodium Lauryl Sulphate	1.4		

Problems were encountered with this trial, and it was not successfully completed.

The kill stage was completed without trouble. In the higher temperature mordant step problems were encountered with the overflow from the fur vessel. This was countered by reducing the flow rate back to 3.5 L/min, the lowest possible flowrate with the pump used. This allowed the mordant step to be successfully completed.

The pH adjustment process in the oxidative bleach work was a much more gradual process in the pilot plant. The carbonate/bicarbonate mixture was dissolved in five litres of water (taken into account as part of the total liquor volume) which was then added in portions with monitoring of the pH to ensure values greater than 7.2 were not obtained in the liquor vessel. The time the oxidative bleach would be run for was not known at the beginning of the trial. It was not known exactly how long the pH adjustment process would take. The optimised method from laboratory experiments used 80 minutes after the pH had been adjusted to 7.2. This would need to be shortened if a greater degree of bleaching occurred during the pH adjustment, compared with laboratory work. This would be the case with the longer adjustment process; the new bleaching time would need to be determined experimentally. Monitoring of the fur was to be conducted to prevent over bleaching. The pump could be stopped and the lid of the fur tank removed to check the fur.

The pH adjustment process could not be completed because the overflow problems were again encountered.

The question arises, why does this compression and subsequent overflow problem arise only in the oxidative bleach? The oxidative bleach causes the liberation of significant quantities of gas. This could be observed in the glass columns used in laboratory work and bubbles could be heard in the fur vessel in the pilot plant. Initially it was thought that the solution expansion resulting from the liberation of this gas could be responsible for a build up of pressure leading to compression of the fur and subsequent overflow of the fur vessel. The majority of the gas is due to carbon dioxide from sodium bicarbonate, some will be oxygen produced in the reactions detailed in section 1.3.5.2, and oxygen can be generated by the following reaction;

$$2HO_2^- \Rightarrow 2OH^- + O_2$$

Although this reaction is minimised by the sodium pyrophosphate used (Cegarra and Gacen 1983)

As the fur was partially bleached at this stage and it was desired to obtain a finished product, the oxidative bleaching step was repeated at a peroxide concentration of 10 mL/L (50% H_2O_2) at 50°C. The fur only required a mild bleaching to complete oxidative bleaching. An extended bleach at a lower peroxide concentration was thought to be sufficient to achieve this, with minimal additional damage to the fur. The overflow problems were again encountered.

Examination of the plate at the top of the fur vessel showed that it had been bent inwards somewhat. It was thought that in operation the plate could be bent backwards so that it came into contact with the pipework to the liquor vessel. This would mean that liquor could only flow through the holes directly below the pipe causing a large pressure drop and hence the compression and overflow problems.

The following modifications were made to the plate to eliminate this. The rim from a smaller tank was inserted in the plate, providing a circular support of about half the diameter of the lid. Self tapping screws were also inserted through the plate into the lid around the exiting pipe. These two adjustments provided the plate with extra support so that it could not be bent inwards. Extra holes were also drilled to allow a greater flow through the lid.

Following these modifications a third oxidative bleaching step was undertaken. This was run for a total time of 95 minutes with 30mL/L 50% H_2O_2 at 50°C with the addition of sodium carbonate/bicarbonate to a level of 4 g/L giving a pH of 7.3. The overflow problems were not encountered, leading to the conclusion that the overflow problem was due to restricted flow though the top of the vessel. It was therefore decided to run this experiment again to obtain a product without stoppages to the process. The strip and reductive bleaches were run in this experiment but the final product was extremely damaged due to the three attempts at oxidative bleaching. The loss was 12.4% and the alkali solubility could not be measured due to problems filtering the sample but would be close to 100%. The fur was also significantly matted. This is in agreement with the hypothesis that fur matting is influenced by the damage occurring to it, matting was not encountered in successful pilot plant work.

9.3.3.4 Pilot Plant Run Two

This experiment was a repeat of the first pilot plant run, detailed in table 9.2.
The kill and mordant stages were completed successfully but the compression and overflow problems were again experienced in the oxidative bleach.
The previously described flow problems had been countered leaving the conclusion that the pressure build up and subsequent overflow problems are not the result of design faults. Also, the conditions used in the oxidative bleach here (50°C, 95 min) had been used in the previous run on the third attempt at bleaching without the overflow problem. Therefore there must be some factor present in oxidative bleaching, which is present in a much lesser form after the fur has been oxidatively bleached. Changes in the chemistry of the fibres which occur as the bleaching process is undertaken must lead to the compaction and overflow problems, since both water and the oxidative bleach solution can be pumped through the bleached fur.
The scission of the disulphide linkages in the fibre keratin will cause the fibres to swell. Due to the hollow nature of the fibres they are less dense than water and consequently will float. When the fibres expand during oxidative bleaching the increase in fibre volume is taken up in the area no greater previously occupied by the fibres, they cannot expand downwards into the vessel. As a result, a decreased path and subsequent increased pressure drop is observed through the fur.
The fur was also observed to be compressed during oxidative bleaching in the glass laboratory columns. This may be due to an increased buoyancy of the less dense swollen fibres. However, since solutions can be pumped through the bleached fibres at conditions which would cause overflow during the oxidative bleach, some other factor must also contribute to the phenomenon.
A detailed study of the fibres during bleaching may provide some answers to this scale-up issue, or at least verify or eliminate this reasoning.
At this stage it was thought that a further reduced flowrate might eliminate the overflow problems. Work with ambient temperature solutions had proven successful at 5 L/min but when heated to 50°C the flowrate had to be reduced to 3.5 L/min. It was thought that a further reduction in flowrate might compensate for the pressure increase due to the liberation of oxygen and thus eliminate the overflow in the oxidative bleach.
A recycle loop was put around the pump to allow further reduction of the flowrate, as shown in figure 9.1.

9.3.3.5 Pilot Plant Run Three

This run featured the same treatments as runs one and two with the use of a lower flowrate in the oxidative bleach.

Another unsuccessful run, with the lower flowrate only resulting in a slower onset of the overflow problems. At the start of oxidative bleaching the flowrate was set at 1.7 L/min (half the previous value). This decreased over the course of the oxidative bleaching to 350 mL/min as the pressure drop through the fur bed built up, causing a greater flow through the recycle loop. This value results in a 35 times reduction in superficial velocity from the laboratory work resulting in a superficial velocity to 60 micrometers per second, a very low flowrate indeed.

This reduction in flow rate was such that the process became unfeasible. The pH adjustment process was still not completed after 88 minutes when the overflow problems were encountered. At this flowrate it would take 60 minutes to flow through a bed of fur 22 cm deep, roughly the depth used. The result of this is that the fur at the bottom of the fur vessel would be bleached well before the fur at the top. It would be impossible to obtain a uniform batch of fur in the pilot plant let alone on a larger scale where it was hoped to have a deeper bed of fur.

From results quoted in chapter seven it was thought that six minutes, as encountered at the previous flowrate, would be an acceptable time difference between the base and top of the fur.

This experiment also proves that the build up of pressure leading to the overflow of the vessel is not a flowrate induced phenomenon. A flowrate of 60 micrometers per second is not going to generate any significant pressure by itself, as indeed is the higher rate of 600 micrometers per second. Compression of the fur during oxidative bleaching was observed in laboratory experiments, leading to the fur occupying half to two-thirds of its original volume, depending on the flowrate used.

The next pilot plant trial involved using only 3.5 kilograms of fur and the temperature of the oxidative bleach was reduced to 30°C. It was thought a shorter bed of fur may limit the pressure drop to workable levels. A lower temperature was used in that a more gradual bleach will cause a more gradual modification of the fibres hopefully alleviating the compression problem somewhat.

9.3.3.6 Pilot Plant Run Four

Apart from the previously stated alterations this experiment was run as in experiments one and two. The oxidative bleach was run with no definite time period in mind, bleaching was to be stopped when the fur had reached the required shade.

This was the first successful pilot plant run and resulted in approximately 3.3 kilos of bleached fur.

The following table details the treatments used in the run.

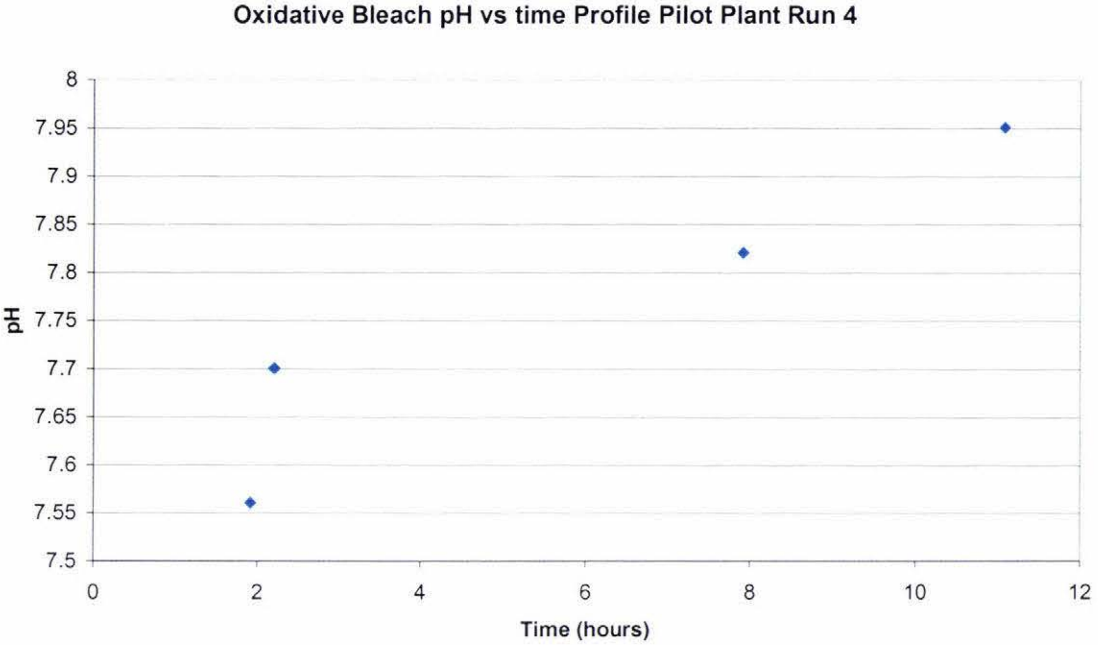
Table 9.3 Bleaching Regime for Pilot Plant Run Four

Stage	Reagents	Conc. (g/L)	Temp (°C)	Time (hours)
Kill	Sodium metabisulphite	11	30	3
Mordant	Ferrous Sulphate (monohydrate)	6.7	50	15
	Ammonium Chloride	11		
	Cream of Tarter	2		
	Phosphorous acid	1.85		
Rinse	Phosphorous acid	0.45	50	1
Bleach	Oxalic Acid	2	30	
	Ammonium Chloride	8		
	Sodium Pyrophosphate	8		
	Hydrogen Peroxide	30 mL/L (50% w/w)		
Strip	Oxalic Acid	8	30	1
	Ammonium Bifluoride	4		
Bleach	Sodium Hydrosulphite	4	30	2
	Sodium Lauryl Sulphate	1.4		

For the pH adjustment, sodium carbonate and sodium bicarbonate (280 grams, equivalent to 4 g/L) were dissolved in four litres of water, which was added portion-wise to the bleaching solution, with monitoring of the pH. This solution was not enough to reach the desired pH of 7.5. Very little work had been done dealing with oxidative bleaching at 30°C. In the interests of making time savings on the process, the majority of the experimental work was undertaken at 50°C, and it was envisaged that this would be the case in large scale work also, given the acceptable results obtained at 50°C. The work that was done at 30°C had featured pH values of close to 8. The decision to use 7.5 was made somewhat arbitrarily. Reductions in the pH had been made at 50°C and it was thought that this would now be the case given improvements made in the mordant. In the absence of any information a "hunch value" of 7.5 was decided upon. After the addition of the carbonate/bicarbonate solution the pH of the solution in the liquor vessel was 7.4 and that returning from the fur vessel 6.78. The desired pH had not been obtained and so another carbonate/bicarbonate solution was made of which 1.06 kg was added giving a carbonate/bicarbonate level of 5.0 g/L. The pH adjustment was begun after one hour of acidic bleaching and took 40 minutes.

The total bleaching time was eleven hours and five minutes. An upward trend in pH was observed over the course of bleaching after the final addition of carbonate/bicarbonate. The following graph details that trend.

Figure 9.1



The pH was observed to decrease during bleaching in the work conducted at 50°C. The hydroxyl ion is formed in the radical initiation mechanisms detailed in section 9.3.3.4. Hydrogen peroxide itself is weakly acidic. This trend may be due to the relative differences in rate of the radical formation and the hydrogen peroxide – hydroxyl ion acid base equilibrium at 30 and 50°C. The pH increase shown here corresponds to an increase in hydroxyl ion concentration of 8.72×10^{-7} M, a very small change. However this is significant in terms of the damage resulting to the fur.

The strip stage was run successfully and the pH adjustment process between strip and reductive bleach stages undertaken. This required monitoring of the pH during a portion-wise addition, as in the oxidative bleach. The buffering capability of the acidic water after rinsing, following the strip stage, is much less than in the oxidative bleach, consequently there is a greater danger of overshooting the desired pH during the adjustment process, leading to damage of the fur from alkaline solutions. For example 50 mL of the 25% sodium carbonate was enough to raise the vessel pH from 4.06 to 8.10. Subsequent adjustments used only about 10 mL, which were added when the vessel pH fell below 6.4-6.5. The pH adjustment process was not performed fully in this run. When the pH returning from the fur vessel reached 5.8 the system was drained and washed. The pH of the reductive bleaching solution was observed to start falling in this run, indicating the pH adjustment was not properly completed. The pH was adjusted with the same solution used for the post strip pH adjustment. The following table details the pH of the reductive bleach. A * indicates an adjustment of the pH was made

Table 9.4 Reductive Bleaching Data Pilot Plant Run Four

Time (minutes)	pH in liquor vessel	pH return from fur vessel
15*	4.0	
20	6.1	
32	5.24	5.90
50*	5.06	5.55
70	6.07	6.22
107	6.05	6.11

The bleaching was done mostly below the desired pH range from chapter seven of 6-6.5. The pH adjustment process needs to be properly completed to ensure adjustments are not necessary in the reductive bleach.

The run resulted in a loss of fur of 5.4% and the alkali solubility was 76.0%. The fur has a Croes Whiteness index of 46.44. The fur was of a good whiteness, but the alkali solubility is unacceptably high. The alkali solubility is significantly higher in this experiment than in the last of the laboratory work before the pilot plant. This is attributed to the non-optimised oxidative bleach used for this work. The damage results could have been better if run for a shorter time. It is difficult to judge when exactly to stop oxidative bleaching by eye considering the rust discolouration and the reductive bleach to follow. The author had also been up most of the night monitoring the pH and checking for compaction which may have influenced his judgement. Further work undertaken on bleaching at 30°C is described in section 9.3.5.

9.3.4 BED DEPTH AND PRESSURE DROP

The previous experiment proved that the displacement bleaching method could be successfully applied on a larger scale. It was decided that more investigation needed to be undertaken into the phenomenon of the compression of the fur leading to the build-up of pressure and overflow of the fur vessel.

Experiments were undertaken measuring the bed depth and pressure drop through the bed for various amounts of fur at different temperatures and flowrates. Figures 9.6 and 9.7 show pressure drop and bed depth through the fur vessel as functions of solution temperature. The pressure drop was measured by an open tube manometer, which can be seen to the right of figure 9.2.

The pressure drop through the fur was shown to increase with bed depth and flowrate and decrease with temperature. The bed depth decreases with increasing temperature. The results collected did not show a particular bed depth or flow rate above which the pressure keeps building up leading to the overflow of the fur vessel. The previous bleaching runs had given some idea of the allowable bed depth and flowrate. However, the measurements with straight water did not help to pin point the maximum allowable flowrate/ bed depth. For example, the pressure was stable at a flowrate of 6.8 L/min at

50°C, conditions which had caused the overflow during a previous mordanting stage. Unfortunately, the only way to determine the allowable bed depth and flow rate is through a trial and error process. The problem stage, the oxidative bleach, is not run until approximately 24 hours into the process. It was known at this stage that a flowrate of 3.5 L/min using 3.5 kg of fur (a packing of 36 kg per square metre of horizontal cross section) and oxidative bleaching at 30°C was allowable. A further pilot plant trial undertaken using 4.5 kg (47 kg/m^2) and the same flowrate proved unsuccessful. The optimum packing must lie between 36 and 47 kg/m^2, with this particular set of oxidative bleaching conditions. For future design purposes the figure of 36 kg/m^2 is recommended.

The pressure drop through the empty fur vessel was measured at 1.0 kPa at a flowrate of 6.3 L/min. This includes the distributor plate, the screen at the top and a sudden enlargement and sudden contraction at the inlet and outlet. Due to the low superficial velocity used in the plant (6×10^{-4} m/s) only a very low pressure drop was obtained through the distributor plate. In fact, a distributor plate may not even be necessary at such low flowrates. In the construction of a plant to bleach say, 100 kg, which would require a vessel 1.9 m in diameter a larger pressure drop, or other flow distribution system, is likely to be necessary. The geometry of the tank will also effect the pressure drop required. A vessel with a cone shaped base would serve to even out the flow perhaps eliminating the need for a distributor plate. The fur itself serves to even out flow and at the flowrates currently used very little is needed in the way of a distributor plate.

The possibility of having some kind of support network in the fur vessel to prevent the compaction problem is worthy of investigation. This would need to be such that the large volumes of fur can be packed and unpacked relatively easily. Laboratory work, in which a high degree of wall support is encountered due to the low diameter of the columns, was successful at higher temperatures and higher flowrates. The possibility of using the more practical conditions developed in the laboratory exists if an adequate support structure can be developed.

The problem is at what diameter the wall support becomes negligible. This is likely to be no more than a few times the average fibre length. Packing and unpacking around such a support network would not be practical on a large scale.

Another possibility is having a series of beds interspersed by plates so that large diameter vessels are not required and higher flowrates can be used. Further work will be required on what flowrates are acceptable with particular bed depths. The issue of how one would keep removable plates fixed in place, so that they span the whole vessel diameter, to prevent preferential flow up the sides of the vessel, and the movement of fur between layers, is also non-trivial.

9.3.5 OXIDATIVE BLEACHING AT 30°C

9.3.5.1 Introduction

Four experiments were undertaken at Massey University dealing with oxidative bleaching at 30°C over a 15 hour period. This time period was used since it would allow the oxidative bleach to be left overnight which fits well with the process timing. Investigation was undertaken into the pH of the oxidative bleach to find a level which would allow acceptable results over the time period in question.
The experimental methodology was as detailed in table 9.6 except the mordant was undertaken at 50°C for 15 hours due to time constraints.

9.3.5.2 Results

Figure 9.8 shows the pH profile of each experiment over the course of oxidative bleach, again the upward trend in pH over the course of oxidative bleaching is observed.
Figure 9.9 shows the pH profile of each experiment over the course of reductive bleach. The sodium carbonate/bicarbonate was added portion wise to the bleaching solutions to obtain the desired pH. The following table details the levels of sodium carbonate/ sodium bicarbonate and results obtained.

Table 9.5 Results of Experiments PP1 – PP4

	Reagent level	Croes whiteness	Loss (%)	Alkali sol (%)
Experiment PP1:	4.5 g/L	46.25	4.4	74
Experiment PP2:	5 g/L	42.33	5.1	70
Experiment PP3:	5.5 g/L	44.59	6.1	71
Experiment PP4:	4 g/L	41.35	4.2	70

The experiments here while having a low loss all have unacceptably high alkali solubility. The whiteness here is below that of results obtained in chapter 4 and not as good as encountered in work in chapters five and seven. Experiment PP1, which has the best whiteness, was of a marketable colour. This experiment did not feature the highest pH; it rose from a value of 7.3 to 7.8 over the course of the fifteen hour bleach. The high damage indicates that the experiments have been bleached longer than the optimum time. The results quoted by Cegarra and Gacen (1983) state that this would have caused the whiteness to decrease from that which would have been obtained at the optimum time. The fact that the pH values on each side of this experiment gave a lower whiteness indicates that this pH is close to the optimum for 30°C using 30 mL/L 50% hydrogen peroxide. The use of shorter bleaching times at this pH range and temperature would be worthy of further investigation. This then removes the possibility of oxidative bleaching over an overnight time-frame. In order to have a 15 hour bleach the use of even lower temperature is necessary. The optimum pH for this may not be as determined here however and this parameter would need to be investigated. It would be desirable to use the 19.5 – 24 hour, 40°C mordant for this, if time permitted.

9.3.6 FURTHER COMMENTS

With the oxidative bleach now run overnight at 30°C, or lower, depending on the results of further work, the time frame of the bleaching process now changes. The temperature of the mordant stage should also be reduced. Two experiments discussed in chapter four featured the mordant with no pH adjustment (pH 2.0) at 40°C for 19.5 and 24 hours. These two experiments gave very good results in terms of whiteness and damage. If the kill stage is begun at the beginning or close to it of day one, it will be possible to run the mordant in the 19 – 24 hour time frame before conducting the acid rinse and putting the oxidative bleach on over the next night. This leaves a bit of leeway in that if workers have other pressing tasks the mordant time can safely be extended, given the very similar results in these two experiments. The six minute passage through the fur bed now becomes irrelevant with lower temperature oxidative bleaching at 30°C. The effect of the longer mordant with phosphorous acid would also need to be determined.

The following set of conditions is now recommended for the bleaching of possum fur, with the temperature and time to be determined.

The rinsing process between stages has been lengthened considerably from the reduction in flowrate. An alternative arrangement, in which water is pumped into the fur vessel then allowed to drain away, should be investigated. A vacuum pump would be necessary once gravity flow has stopped to remove as much water as possible. This method was tried with gravity flow but found to offer no advantage on the previously described method.

Table 9.6 Recommended Bleaching Regime

Stage	Reagents	Conc. (g/L)	Temp (°C)	Time (hours)
Kill	Sodium metabisulphite	11	30	3
Mordant	Ferrous Sulphate	6.7	40	19-24
	Ammonium Chloride	11		
	Cream of Tarter	2		
	Phosphorous acid	1.85		
Rinse	Phosphorous acid	0.45	50	1
Bleach	Oxalic Acid	2	To be determined	To be determined.
	Ammonium Chloride	8		
	Sodium Pyrophosphate	8		
	Hydrogen Peroxide	30 mL/L (50% w/w)		
	Soda Ash	To a pH to be determined		
	Sodium Bicarbonate			
Strip	Oxalic Acid	8	30	1
	Ammonium Bifluoride	4		
Bleach	Sodium Hydrosulphite	4	30	2
	Sodium Lauryl Sulphate	1.4		

9.4 OPPORTUNITIES FOR FURTHER DEVELOPMENT

Once the design parameters of packing at 36 kg/m^2 and flow at 6 x 10^{-4} m/s had been determined a larger scale facility was built. Due to time constraints at this stage tanks could only be sourced to give a plant capable of bleaching 15 kg of fur, giving essentially a larger scale pilot plant. The design was a larger scale version of the previous system. This consisted of two tanks, a fur vessel of 300 L capacity and a jacketed liquor vessel of 1000 L capacity. Hot water for the process was provided by the factory hot water cylinder and process heating from the vessel jacket. An Onga chemical pump was used with a constriction provided by a partially closed ball valve to provide the desired flowrate. Type two PVC pipe was again used for the piping. A perforated 316 stainless steel plate in combination with a 316 stainless steel mesh plate was used for the distributor plate and a further mesh plate for the screen at the top.

It had been stated that this screen should be attached to a lid, which is then clamped onto the top of the vessel to provide the necessary support. The construction of this plant was finished after the author left Hokitika and this was not done as a cost and time saving measure. The top screen was held in place by forcing it down into the tank where it became wedged. The pH adjustment process was nearly complete (7.3 towards a target of 7.4) when it was forced out of place. The bleach was being undertaken with the method of table 9.6 using 36 kg/m² and 6 x 10^{-4} m/s superficial velocity. The wedged lid provided little support, however the neutralisation process had been largely completed. If a clamped lid arrangement, such as in the smaller pilot plant had been used, which would provide much greater support, the run would likely have been successfully completed. This must of course be verified before further scale-up is attempted.

In order for the process to be commercially viable a batch size of 100 kg is necessary. The main issue likely to arise on a 100 kg scale, assuming no problems with the 36 kg/m² packing, is one of flow distribution. This problem is somewhat minimised by the very low flowrate used in the bleaching process but a better distribution system will be needed. It is thought that a conical manifold in combination with some kind of perforated barrier will be adequate to achieve this. Two perforated plates, with the holes aligned so there is not a free path through both plates, should provide very good flow distribution, at the flowrate used.

The pump and heating elements from the current plant are suitable for a 100 kg scale. One larger tank is required, with distribution system and cover, for the fur tank. An extra hot water cylinder would be required to provide hot water. An agitator could be of use in the liquor tank for pH adjustment stages. The current liquor tank and pump could be used in the larger system.

The following capital outlay would be required for the construction of a full scale plant.

- A vessel to hold the fur bed with flow distribution system
- A hot water cylinder or boiler to provide hot water for the process.
- Associated piping and valving and a screen for the top of the fur vessel

9.5 CONCLUSIONS

- A pilot plant was built based on the displacement bleaching method and with some modification of the process a successful run was undertaken with 3.5 kg of fur using a superficial velocity of 6×10^{-4} m/s and a fur packing of 36 kg/m².
- Significant difficulties were encountered with scale-up of the laboratory process. These difficulties were compression of the fur and a subsequent build up of pressure and overflow of the bleaching vessel.
- To counter these, the superficial velocity had to be cut back to 0.6 mm/s from a desired value of 2.6 mm/s giving a flowrate of 3.5 L/min; and the temperature of the oxidative bleach reduced to 30°C.

- The optimum conditions for oxidative bleaching at 30°C have not been determined. Some work towards this is detailed in the body of this chapter. The following conditions are recommended with work on the oxidative bleach required, it may be practical to further reduce the temperature of the oxidative bleach so this stage can be run overnight.

Table 9.6 Recommended Bleaching Regime

Stage	Reagents	Conc. (g/L)	Temp (°C)	Time (hours)
Kill	Sodium metabisulphite	11	30	3
Mordant	Ferrous Sulphate	6.7	40	19-24
	Ammonium Chloride	11		
	Cream of Tarter	2		
	Phosphorous acid	1.85		
Rinse	Phosphorous acid	0.45	50	1
Bleach	Oxalic Acid	2	To be determined	To be determined.
	Ammonium Chloride	8		
	Sodium Pyrophosphate	8		
	Hydrogen Peroxide	30 mL/L (50% w/w)		
	Soda Ash	To a pH to be determined		
	Sodium Bicarbonate			
Strip	Oxalic Acid	8	30	1
	Ammonium Bifluoride	4		
Bleach	Sodium Hydrosulphite	4	30	2
	Sodium Lauryl Sulphate	1.4		

- A larger scale (15kg) pilot plant was built but the trial run on this proved unsuccessful. A clamped lid and screen should be put in place on the 15 kg plant and the parameters of a superficial velocity of 6×10^{-4} m/s, and a fur packing of 36 kg/m², be verified to allow their use for future design.
- Further work into alternative bleaching vessel designs, to provide more practical process parameters, and fur rinsing procedures is warranted. In particular some kind of support structure to alleviate the pressure build-up during oxidative bleaching and

the investigation of enhancing the draining of the fur tank with vacuum should be investigated.

- A study into the surface chemistry of the fibres during oxidative bleaching should be considered to try to pinpoint any further changes to the bleaching process to alleviate the compression problem.

9.6 PILOT PLANT CHAPTER FIGURES

Figure 9.2 Small Scale Pilot Plant

Figure 9.3 Flow Tube Design

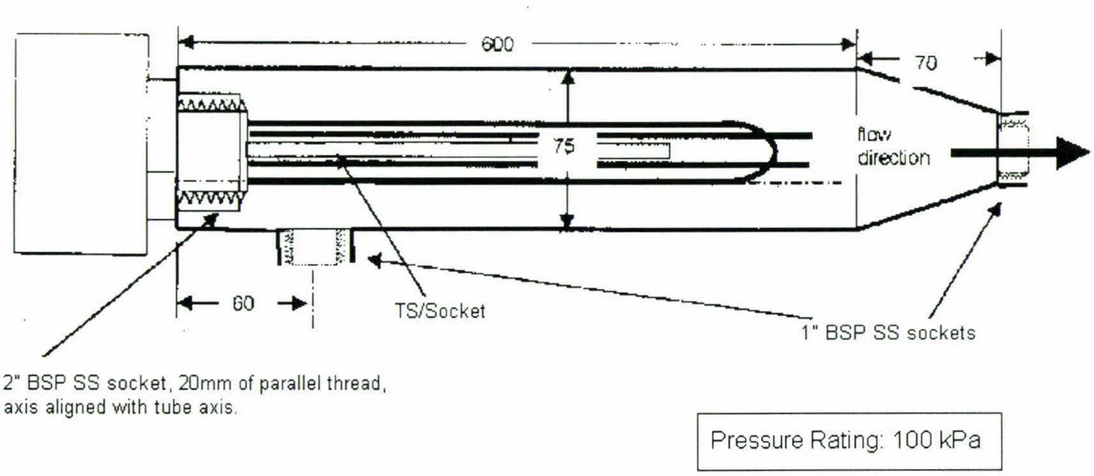


Figure 9.4 Distributor Plate

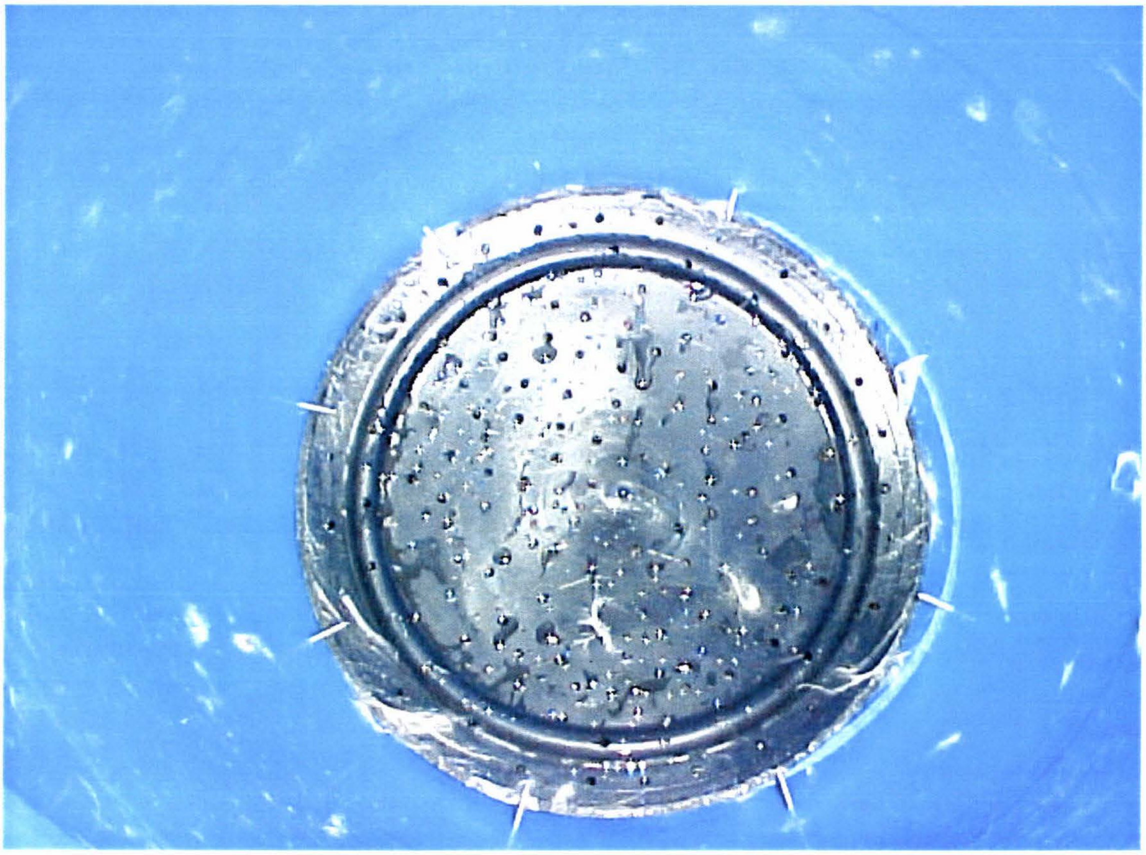


Figure 9.5 Fur Screen at top of Fur Tank

Figure 9.6

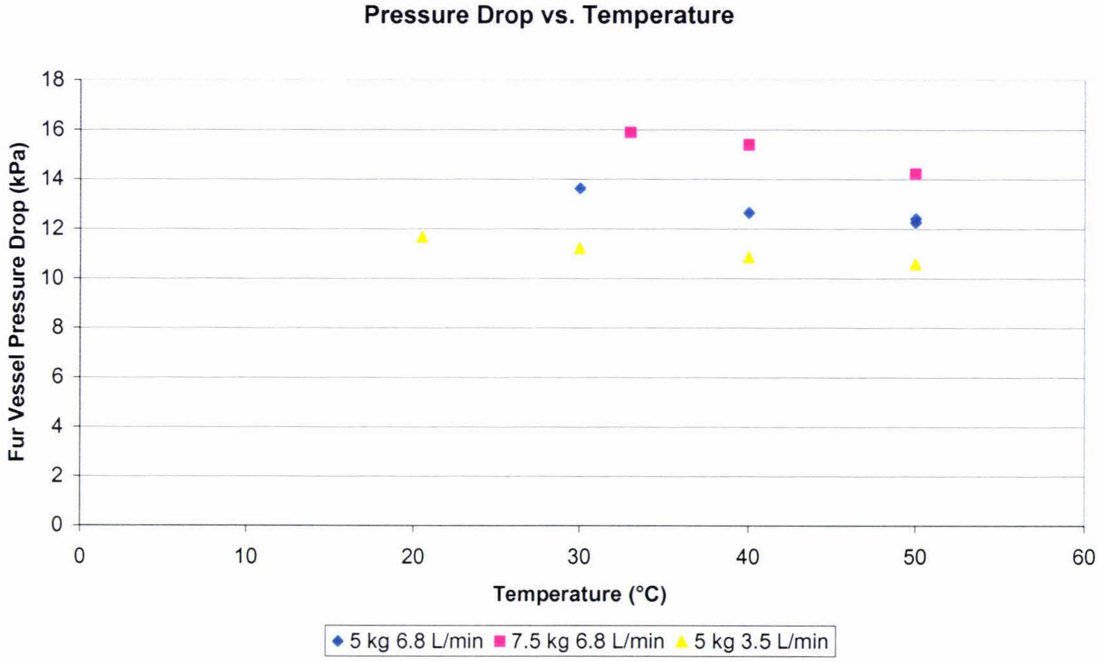


Figure 9.7

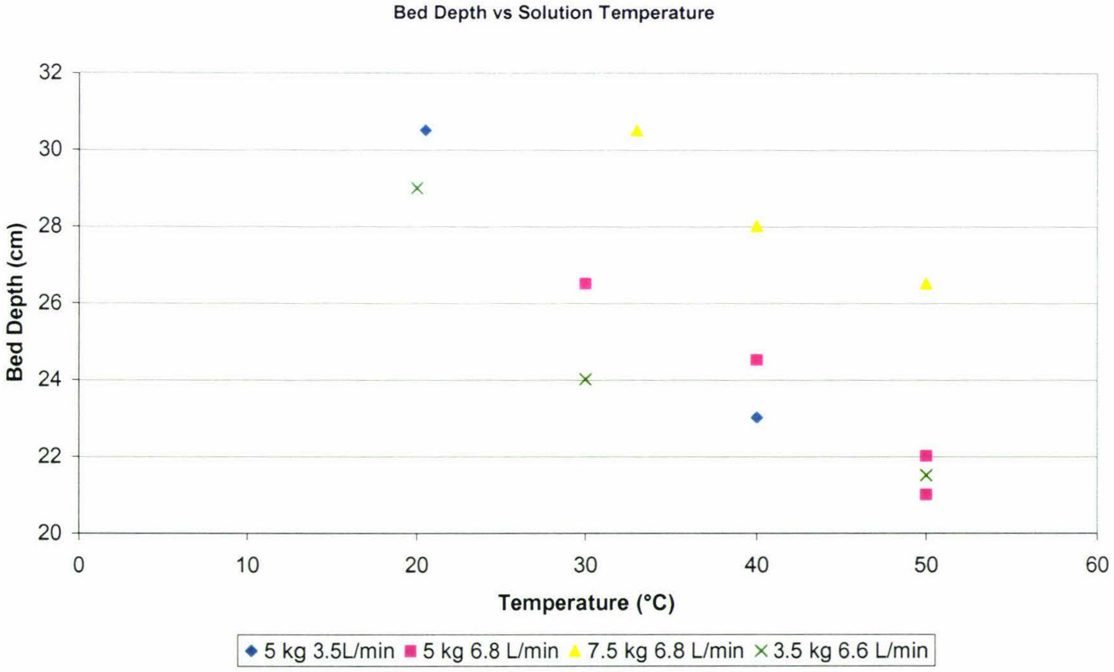


Figure 9.8

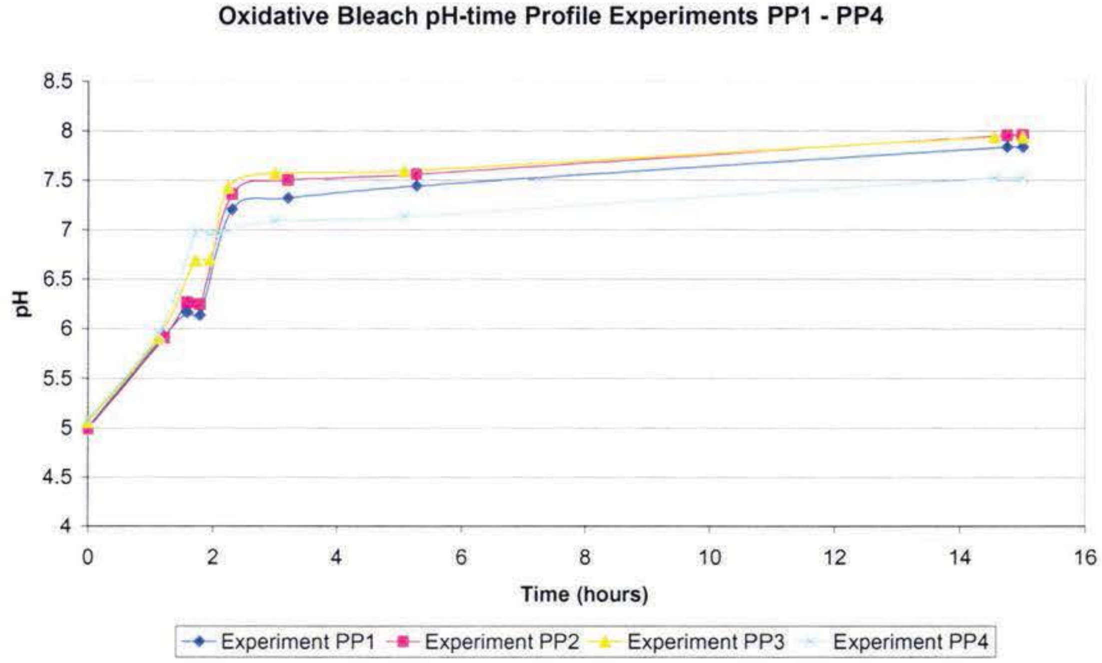
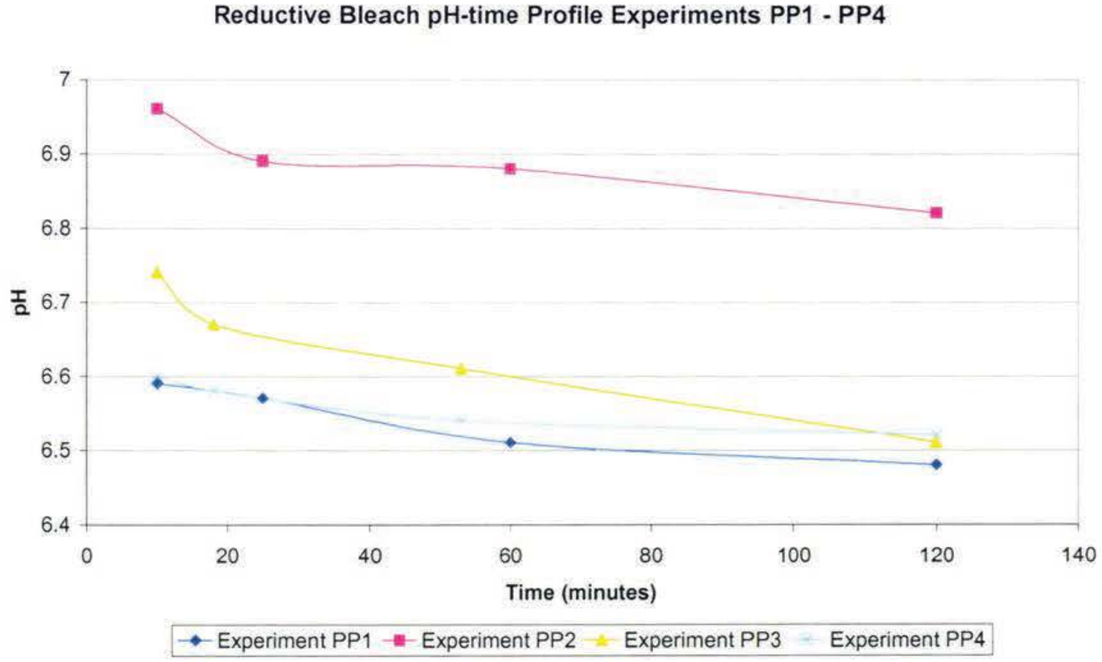


Figure 9.9



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