ACCELERATED CARBON DIOXIDE DELIMING OF CATTLE HIDES AND SHEEPSKINS

by

KARL BERNARD FLOWERS

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ABSTRACT

To avoid environmental pressure from water authorities, specifically regarding nitrogen and sulfate limits in tannery wastewater, modifications to existing deliming processes have been made. Conventional ammonium salt deliming methods contribute to Total Kjeldahl Nitrogen values in the region of 0.5 – 1.0g/L (33-67% of total TKN). Sulfate levels are increased with the use of organic deliming and ammonium sulfate deliming to the extent of 0.9g/L (27% of total sulfate). To understand the dynamics and kinetics of carbon dioxide equilibrium, the movement of carbon dioxide into deliming water, through carbonic acid, bicarbonate and ultimately into carbonates at liming or early deliming pH was studied. It was shown in this study that effective lime removal, at optimum conditions, resulted in fully delimed pelts at highly comparable quality and times compared to conventional ammonium salt deliming.

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LIST OF ABBREVIATIONS

3-D	Three Dimensional
α_0	Gas Solubility in Water
α_t	Gas Solubility in Salt Solution
α	Bunsen Absorption Coefficient
χ^2	Chi Squared
AA	Atomic Absorption
APHA	American Public Health Association
aq	Aqueous
atm	Atmospheres
BLC	British Leather Confederation
CA	Carbonic Acidity
$Ca(HCO_3)_2$	Calcium Bicarbonate
$Ca(OH)_2$	Calcium Hydroxide (Lime)
Ca^{2+}	Calcium Ion
$CaCO_3$	Calcium Carbonate
$CaSO_4$	Calcium Sulfate
C_i	Molar Concentration of Salt *i*
CO_2	Carbon Dioxide
CO_3^{2-}	Carbonate
COD	Chemical Oxygen Demand
df	Degrees of Freedom
DO	Dissolved Oxygen
DWAF	Department of Water Affairs and Forestry
EDL	Estimates Detection Range
EIA	Environmental Impact Assessment
Eq.	Equation
g	Gas
g/L	Grams Per Litre
H	High
H^+	Hydrogen Ion

H_2CO_3	Carbonic Acid
H_2O	Water
H_2O_2	Hydrogen Peroxide
H_2S	Hydrogen Sulfide
HCO^{3-}	Bicarbonate
H_j	Ion constant
HS^-	Hydrosulfide Ion
HSO^{3-}	Hydrogen Sulfite Ion
I	Ionic Strength
I_j	Ionic Strength Contribution of Ion j
ISO	International Standards Organisation
IUC	IULTCS Chemical Test Method
IULTCS	International Union of Leather Technologists and Chemists Societies
IUP	IULTCS Physical Test Method
K_{a1}	First Ionisation Constant
K_{a2}	Second Ionisation Constant
K_{H1}	Henry Coefficient (Ideal)
K_{H2}	Henry Coefficient (Normal)
K_{sp}	Solubility Product
L	Ostwald Coefficient
l.	Liquid
L	Litres
L.	Low
L/min	Litres Per Minute
LASRA	Leather and Shoe Research Association of New Zealand
LIRI	Leather Industries Research Institute
M	Medium
m/m	Mass for Mass
mg/L	Milligrams Per Litre
mS/m	Millisiemens Per Meter
NEMA	National Environmental Management Act. No. 107 of 1998

N/mm	Newtons Per Millimetre
N/mm^2	Newtons Per Square Millimetre
Na^+	Sodium Ion
Na_2S	Sodium Sulfide
NaHS	Sodium Hydrosulfide
NaOH	Sodium Hydroxide (Caustic Soda)
NH_3	Ammonia
NH_3-N	Nitrogen as Free Ammonia
NH_4Cl	Ammonium Chloride
$(NH_4)_2SO_4$	Ammonium Sulfate
nm	Nanometers
P	Phosphate
P	Pressure
P_{CO2}	Partial Pressure of CO_2
s	Solid
S	Sulfur
SC	Specific Conductivity
SLM	SLTC Standard Method
S/m	Siemens Per Meter
S^{2-}	Sulfide Ion
$S_2O_3^{2-}$	Thiosulfate Ion
SO_4^{2-}	Sulfate Ion
SABS	South African Bureau of Standards
SATRA	Shoe and Allied Trade Research Association
SLTC	Society of Leather Technologists and Chemists
t	Temperature (°C)
T	Temperature (°C)
TDIS	Total Dissolved Inorganic Solids
TDS	Total Dissolved Solids
TKN	Total Kjeldahl Nitrogen
To	Time Zero
v/v	Volume for Volume

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CHAPTER 1

ENVIRONMENTAL CONSTRAINTS OF DELIMING IN THE TANNING INDUSTRY

Environmental issues have become an integral part of the business enterprise worldwide and most business and development sector is being forced to internalise the costs of their wastes. In South African legislation, the National Environmental Management Act of 1998 (NEMA) (DEAT, 1998) specifies that any business or activity that was regarded as having an impact on the environment should undertake an Environmental Impact Assessment (EIA). The power of the environmental lobby, 'green' tendencies of governmental policy and greater social and business awareness of pollution have increased public pressures for conformance to waste management standards. At the same time, a balance has to be struck between the needs (primary resources and other consumables) of business and the environment. This is a particular issue facing future development in the Tanning Industry (Aloy, *et al.*, 1998).

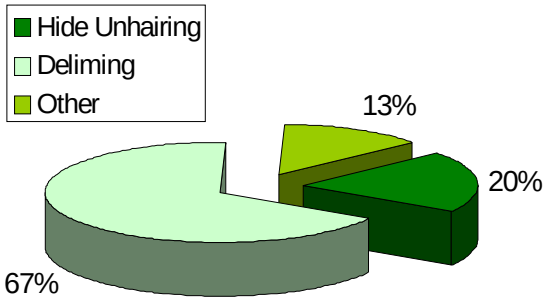
1.1 Environmental Compliance in the Tanning Industry

The environmental issues confronting modern tanneries may often determine the success or failure of a business in the leather industry. Legislation regarding disposal of tannery wastewater is increasing severely and consumers of leather demand that tanneries are environmentally compliant. The International Standards Organisation (ISO) 9000:2000 management system, and the ISO 14001:1996 environmental component, has been developed to enable the management of environmental compliance. The ISO 14001:1996 system requires that an environmental management plan is set up and audited regularly to reduce environmental impacts over a specified period. In addition, an EIA needs to be undertaken on future tannery developments and their locale (DEAT, 1998).

Among particular environmental issues that tanneries are required to meet are wastewater standards for salt, solids, pH, nitrogen, heavy metals, lipid content, sulfide levels and solid waste disposal requirements. Total Kjeldahl Nitrogen (TKN) and Total Dissolved Solids (TDS) are two factors of specific importance in South Africa, given the increasing concerns with the salinization of most of South Africa's major rivers. These parameters are very specific problems facing South Africa.

1.1.1 Total Kjeldahl Nitrogen

The TKN is comprised of several components, *viz*., free and saline ammonia, nitrate, nitrite and organic nitrogen. The TKN occurring in waste streams has to be removed by biological treatment or chemical oxidation/precipitation. The South African Department of Water Affairs and Forestry (DWAF) limits free and saline ammonia to between 0 and 1 mg/L (human consumption limit), but generally the sewer acceptance limit is 30-50 mg/L (DWAF, 1996). German legislation, namely the sixth amendment to the 1996 Wasserhaushaltgesetz, has placed the limit for free and saline ammonia into receiving water at 10mg/L (Anonymous, 1989).



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Buljan *et al*. (1999) have suggested a typical TKN composition for tannery effluent, as shown in Figure 1.1. The average discharge quoted by Thorstensen (1997) is 1 g/L - a hundred times greater than that allowed by South African and German legislation. Clearly a reduction in the use of nitrogen in deliming would have a substantial impact on reducing overall tannery wastewater TKN concentrations.

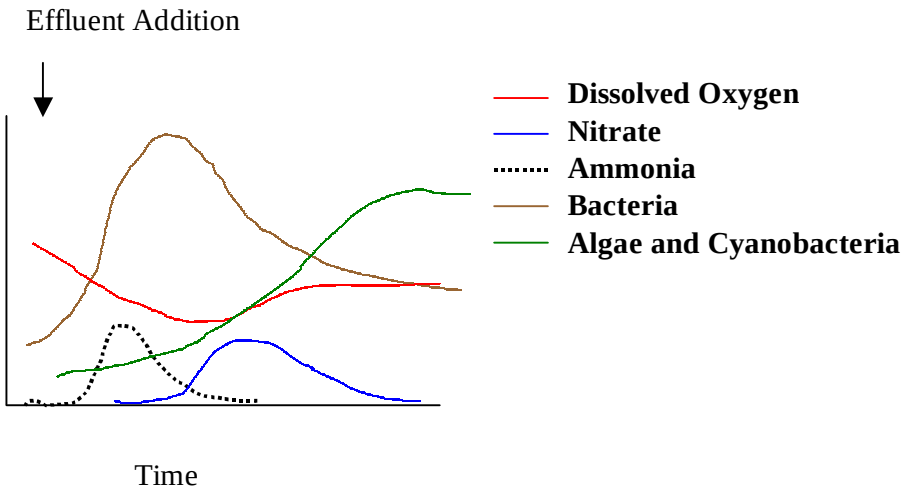

Figure 1.2 The sequence of river eutrophication due to nitrogen pollution. (Smith, 1990).

Excess nitrogen, introduced to river systems, can lead to eutrophication and a typical sequence of events has been described by Smith (1990). The nitrogen nutrient content rises above natural levels and this results in growth of nitrifying bacteria that convert ammonia to nitrite and then to nitrates. High ammonia levels give rise to a high chemical oxygen demand (COD) and a consequent decrease in dissolved oxygen (DO) in the river. The sudden increase in ammonia results in rapid growth of nitrifying bacteria as illustrated in Figure 1.2. The bloom of nitrifying bacteria results in the decrease of ammonia due to its conversion to nitrates, but they also cause an increase in overall respiration and hence a sharper decrease in dissolved oxygen (Figure 1.2). The utilization of ammonia causes increased nitrate levels, which in turn results in a peak of phytoplankton growth. The maximum photosynthetic activity takes place predominantly in the photic zone of rivers, and high biomass loads in upper levels reduces further light penetration. All dissolved oxygen that is produced by the phytoplankton is restricted to the surface and the respiration at lower levels depletes remaining dissolved oxygen. The result is a river, which is only able to sustain life in the top few centimetres. Anaerobic

conditions occur at a lower level, which results in the conversion of sulfates to sulfides and consequent odour production problems (Smith, 1990).

1.1.2 Total Dissolved Solids

Total dissolved solids (TDS) can be defined as those solids remaining in a solvent, after filtration to remove solids. The TDS includes all the material that fully dissolves within the solvent. TDS in water is classified under two categories: organic material and inorganic solids (Total Dissolved Inorganic Solids, TDIS). The TDIS in tannery wastewater derives mostly from sulfate, sulfite, chloride, phosphate, nitrate, and nitrite. Sulfate is a possible target if salt reduction in tannery wastewater is to be achieved. Rowswell *et al.* (1987) showed that conductivity is an approximation of TDS and can be used to indicate the extent of salt load or load reduction through clean technology.

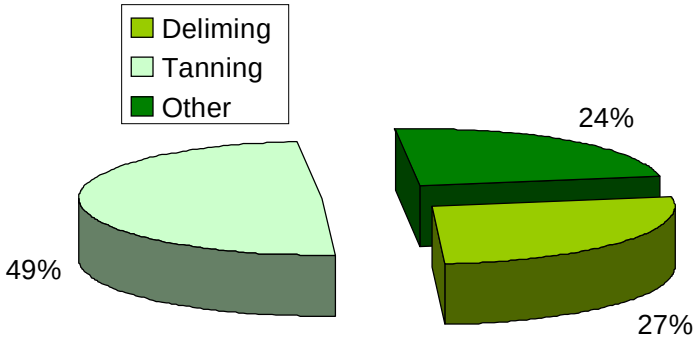

Figure 1.3 A typical total sulfate composition of total tannery effluent. (Buljan *et al.*, 1999).

DWAF limits sulfate in South Africa to between 0 and 200mg/L (human consumption limits) and 0-500mg/L (industrial limits) (DWAF, 1996). The Port Elizabeth municipality sewer acceptance limit is 1500mg/L (Anonymous, 1990) and Mastrotto *et al.* (1997) has noted the German Sewer Acceptance Limit on sulfate as 600mg/L. Thorstensen (1997) and Mastrotto *et al.* (1997) have reported an average composition of sulfate in tannery effluents of 3233mg/L, twice the accepted limit for direct disposal to sewer. Sulfate contribution from the various tannery operations is illustrated in Figure 1.3. The deliming step contributes 27% to the total sulfate with the pickle and tanning step contributing 49% and the dye-house effluent 24%. Clean technologies include

sulfuric acid-free pickles and ammonium sulfate free deliming and implementation of these strategies result in a reduction of sulfate of up to 76% (Mastrotto *et al*., 1997).

Sulfate in wastewater may be metabolised along two routes, assimilatory sulfate reduction and dissimilatory sulfate reduction. The latter is carried out by sulfate reducing bacteria under anaerobic conditions. Assimilatory sulfate reduction takes place through amino acid assimilation and upon death of the organism is carried further through desulfurylation (Brock and Madigan, 1991). Both reductions give rise to hydrogen sulfide. Acidification of sulfide compounds also gives rise to hydrogen sulfide. Hydrogen sulfide emanating from tanneries is one of the primary contributors to the poor public image of the tanning industry.

1.1.3 Deliming and Tanning

The deliming operation in the tannery is thus an area where clean technologies can make a major contribution in the reduction of TKN and TDS in tannery effluents. The study reported here has focused on the deliming process, where alternative processes could potentially result in a 67% reduction in nitrogen load and a 27% reduction in sulfate (Buljan *et al*., 1999).

1.2 The Role of Deliming

Hides (large animals) and skins (small animals) from various animal types are processed from raw to finished leather in tanneries. Various semi-processing options are available from South Africa and allow hides or skins to be exported without stringent disease control limitations.

The hides and skins undergo beamhouse operations, which include soaking, liming, deliming, and bating. Tanyard operations include pickling, tanning and basification.

The soaking stage returns the hide/skin back to its initial state (fully hydrated and flexible). The liming stage removes the hair and unwanted components. Deliming removes lime and prepares the hide/skin pH and temperature for bating. Bating removes

the interfibrillary proteins and makes the hide/skin soft. Pickling lowers the pH for the correct penetration of the tanning agents. Fixation or basification is the cross-linking of the tanning salts so that a stable leather product is obtained. Adding specific properties through retanning, adding oils in fatliquoring, and adding colour through dyeing produces what is known as crust, the dried tanned leather. Beamhouse chemicals are purely preparatory and are removed after their use. Liming and deliming are fundamentally linked and their use is vital in obtaining the 'opening up' of the hide/skin. 'Opening up' is the separation of the collagen fibres so that the correct chemical penetration and softness is produced in the end product (Sharphouse, 1994).

Liming also results in the removal of keratin, plumping of hide structure, solubilisation of glycosaminoglycans, saponification of fats and the chemical alteration of the leather collagen itself. One of the most obvious features of liming is a swollen pelt. The hide/skin swells at high pH values because of electrostatic repulsion and osmotic effects. Swelling of the pelt is at a maximum at pH 12.5. Thereafter it decreases according to the Donnan theory of membrane equilibrium (Heideman, 1993).

Osmotic swelling, has been described by Haines (1977) as essentially due to the association of large numbers of cations with ionised collagen (ionisation due to added hydroxyl groups). Lime, upon addition, yields both hydroxyl and calcium ions. The aggregation of divalent calcium ions causes an imbalance in water potential. The initial influx of water is due to the hypertonic nature of water systems associated with collagen, but later, the loss of collagen cohesion (at a pH higher than 12.8), causes swelling. The divalent nature of lime (calcium hydroxide, $Ca(OH)_2$) as opposed to monovalent caustic soda (NaOH) influences the extent of swelling. It also produces a difference in the ease with which these ions are removed. It has been shown that close linkages are formed between the calcium from lime and the collagen protein (Bowes, 1949, in Haines, 1977). Calcium has a greater solubilising influence on glycosaminoglycans, however more opening up is obtained by calcium.

1.2.1 Ammonium Sulfate Deliming

The removal of $Ca(OH)_2$ is traditionally done by ammonium salts, either ammonium chloride (NH_4Cl) or ammonium sulfate [$(NH_4)_2SO_4$]. Failure to remove lime results in the formation of lime blast. Lime blast describes the formation of calcium carbonate ($CaCO_3$) when limed material has become exposed to a carbon dioxide-rich atmosphere. The removal of calcium hydroxide involves the addition of deliming acid, which removes the lime by scavenging the hydroxyl ion associated with lime, and thereby lowers the pH (Heidemann, 1993). Monitoring of this chemical neutralisation is achieved using pH indicators. The calcium, which is weakly bonded to the collagen, is removed. It is debatable exactly how the calcium is solubilised by ammonium sulfate. Calcium sulfate is insoluble so either the calcium is retained in the skin (in which case the residual calcium determination would be detected) or some other mechanism is involved in its removal. Pilkington and O'Donnell (1997) have described the reaction for deliming with ammonium salts.

$$(NH_4)_2SO_{4(aq)} + Ca(OH)_{2(aq)} \rightarrow 2NH_{3(g)} + CaSO_{4(s)} + 2H_2O \qquad (1.1)$$

As can be seen from Equation 1.1, ammonia gas is formed. Some of this becomes volatilised in the headspace of the drum (particularly at a higher pH) and some of the gas is solubilised. The soluble gas, as well as residual ammonium ions, is a problem in effluents. Other deliming methods are currently being investigated to avoid the use of polluting ammonium chemicals.

1.2.2 Alternatives to Ammonium Sulfate

Alternatives to conventional deliming methods using ammonium salts include magnesium sulfate (Taylor *et al.*, 1988), esters (Streicher, 1988), magnesium lactate, boric acid, lactic acid, formic acid, acetic acid, mineral acids, and non-swelling organic acids (Sharphouse, 1994). Magnesium sulfate is a good replacement, but offers two additional problems. Firstly, it contains sulfate, and would still contribute to sulfate-containing effluents, and secondly the resulting quality of the pelt after deliming is below standard (particularly with regard to calcium removal). Esters delime the hide by

reacting with the alkali in the drum through an acid that is formed by the hydrolysis of the ester (Streicher, 1988). The problem with esters is, however, their price. Boric acid deliming is popular for bookbinding leathers and ostrich processing due to its superficial deliming, but has a high end-pH (pH 9.2), and it contains boron. Superficial deliming can be described as a deliming process that has culminated in a hide/skin cross section, which when tested with a pH indicator shows a high pH in the centre and low surface pH. Organic acids: lactic, formic and acetic acid all decrease the pH beyond the required pH if not carefully monitored. Dipolar non-swelling acids, such as sulfophthalic or sulfonic types, are utilised as proprietary ammonia-free chemicals, but also decrease the pH rapidly if not monitored carefully. The non-swelling acids also tend to be very superficial, have slow deliming times but bear good affinity for lime (according to Berkhofer and Carle (1992). Proprietary organic acid deliming agents cannot compete with the prices tanneries pay for ammonium salts. Mineral acids can also be used if dosed carefully and used in the presence of a buffering agent (Hein *et al.*, 1988; Boast and Horne, 1989).

The use of carbon dioxide (CO_2) gas has also been considered as an alternative to ammonium salts as a deliming agent.

1.3 CO_2 Deliming

CO_2 deliming began in the 19th century but the first documented report appeared in the 1950's when a tanner, who was pondering the effects of fermentation from the puering step, decided to try CO_2 (Ochs, 1953). He found that the quality obtained on glazed kid was comparable with traditional methods and noted "It might be mentioned here that no calcium is found in the finished leather" (Ochs, 1953). At that time the use of CO_2 was made through either pumping the gas into the bating liquid or was administered into the drum in the form of dry ice.

1.3.1 Experimental Development

The first definitive work on CO_2 deliming appeared in the Journal *Das Leder* where the authors claimed to have achieved satisfactory deliming of hides with effective removal

of calcium from the hides at an end pH of 8.5 (Munz and Toifl, 1989a). The authors claimed to have obtained a solubility of calcium bicarbonate of 1086 mg/L. Based on this, and Finnish interest three years previously by Tapio Ehder (from Viialen Nakha Oy Tannery), a deliming process was patented by a Swedish gas company, the process being dubbed 'AGA' deliming (Munz and Toifl, 1989a). The 'AGA' process used CO_2 gas pumped via the hollow axle of tanning drums into the drum headspace. Munz and Toifl (1989a) claimed to get lower levels of calcium in their leather compared to leather made using conventional ammonium sulfate deliming. The resulting leathers were claimed to be softer and had higher chromium contents. The process has also been claimed to be more cost-effective than ammonium salt deliming processes (Anonymous, 1989).

Munz and Toifl (1989b) presentated work at the International Union of Leather Technologists and Chemists Society (IULTCS) conference in Philadelphia, that noted that the chemistry for CO_2 deliming was actually quite simple and described it in Equation 1.2.

$$\mathbf{Ca(OH)_{2(aq)} + 2CO_{2(g)} \square Ca(HCO_3)_{2(aq)}} \qquad \mathbf{(1.2)}$$

Munz and Toifl (1989b) also mentioned the advantages of CO_2 in that it prevented nitrogenous pollution, clean pelts are obtained as well as better degreasing. They did, however, show that the chromium content was the same as ammonium salt delimed pelts. The ash content of upper, middle and lower hide/skin strata was lower, suggesting a lower inorganic content. There was also a four-fold reduction in nitrogen load in the effluent and a marginal increase in calcium content.

Klaasse (1990) reported results from laboratory and full-scale studies done on CO_2 deliming and indicated a further advantage, namely that CO_2 does not cause "acid shock" and "drawn grain". In addition, he claimed that CO_2 has better lime affinity than ammonium salts and is a good buffer for deliming. Klaasse (1990) also expanded the understanding of the chemistry of the process to account for the initial solubilisation of the gas and pointed out that the pH drop associated with deliming takes 10 to 20

minutes longer in CO_2 deliming. Both Munz (1989) and Klaasse (1990) noted the disadvantage of an exponentially larger hydrogen sulfide (H_2S) content. Both authors suggest the use of hydrogen peroxide to control H_2S. Klaasse (1990) pointed out additional advantages of CO_2 deliming including reduced ammonia gas in the tannery, CO_2 gas is easier to handle and automate and requires a low capital investment. H_2S gas is formed as shown in Equation 1.3 and 1.4.

$$\mathbf{Na_2S_{(s)} + 2H^+_{(aq)} \square 2Na^+_{(aq)} + S^{2-}_{(aq)} + 2H^+_{(aq)} \square H_2S_{(g)} + 2Na^+_{(aq)}} \quad \textbf{(1.3)}$$

$$\mathbf{S^{2-}_{(aq)} + 2H^+_{(aq)} \square H_2S_{(g)}} \quad \textbf{(1.4)}$$

Passman and Scrase (1991) published CO_2 deliming results, at the Leather and Shoe Research Association of New Zealand (LASRA) conference. The publication included data on the cost effectiveness of CO_2 deliming and reported the comparative costs of ammonium sulfate, ammonium chloride and boric acid use. The ammonium salts are considerably cheaper than boric acid use. The paper also included experimental work done at both laboratory-scale and production-scale. These were successful, but ran marginally longer deliming times. The wet analysis did show an interesting point however, that CO_2 gives an out-of-specification reading on total soluble protein on skins. All physical parameters were within specification. Interestingly, the effluent analysis showed a 74-fold reduction in nitrogen levels. This paper again showed the significance of H_2S problems that feature with this process.

It has been shown that Challenge Cook type vessels may be used with great success for CO_2 deliming as the gas is pumped into the re-circulation system (Anonymous, 1991). The method of injection for the first time was modified to give a rapid decrease in pH followed by a maintenance injection to keep the pH constant. It has been stated that a lower pH could have major implications by lowering enzyme activity in the bating process (Anonymous, 1991).

Munz and Weaver (1991) at the IULTCS conference in Barcelona gave a paper that for the first time compared costs for CO_2 versus ammonium salts. The comparative costs

for the entire process on sheepskins (including effluent treatment) showed that ammonium salts were about 1.4 times more expensive.

Issues surrounding the solubility of CO_2 and its effectiveness in deliming began to emerge, in that in most CO_2 experiments the optimum dissolution is better at lower temperatures (Anonymous, 1992a). However, experimental success is the opposite of that to the predicted, in that deliming is better at higher temperatures. This effect can be explained through higher diffusion of CO_2 into the skin at raised temperatures. Covington and Orsen (1992) confirmed this point by showing that changing the temperature from 15°C to 35°C could cut deliming times by half.

1.3.2 Production-Scale Application Studies

The first evidence of successful use of CO_2 at production scale came in the form of experiments run at Prodotti Biokimica SpA. In this experiment CO_2 deliming had been used at production scale at a tannery in Santa Croce (Anonymous, 1992b). Biokimica suggested the use of higher pressure to achieve better solubility. The increase in pressure would favour higher solubility due to increased CO_2 partial pressure (following Henry's Law). Deliming times varied between 40 minutes and 90 minutes, depending on split hide substance (Anonymous, 1992b). Success at production scale was confirmed by British Leather Confederation/'AGA' (BLC/AGA) experiments in 1992 when they achieved 90-minute deliming times (Anonymous, 1992c). Further experimentation in New Zealand, claimed success with CO_2 deliming at production scale with work done in a fellmongery near Manawatu River (Anonymous 1992d).

Christner (1992) claimed that CO_2 deliming did not achieve better removal of calcium compared to ammonium salts. He stated that the pH should be kept below pH 7 to prevent the formation of carbonates, which form from pH 8.2 and upward. Lampard (1993) reviewed CO_2 deliming and confirmed suggestions that hydrogen peroxide (H_2O_2) be used at 0,2% (m/m) to control H_2S via the following reaction:

$$\mathbf{S^{2-}_{(aq)} + 4H_2O_{2(l)} \rightarrow SO_4^{2-}_{(aq)} + 4H_2O} \qquad \mathbf{(1.5)}$$

Lampard (1993) reported that the leather quality was acceptable to ISO 9000: 2000 standards with acceptable chromium contents and physical properties. Purushotham *et al*. (1993) and similar review by Klaasse (1990), also reported good physical and chemical properties of CO_2 delimed leather.

White *et al*. (1993) presented work at the IULTCS conference in Brazil and again at the Society of Leather Technologists and Chemists (SLTC) – South African Section, Money *et al.* (1997) on attempts to improve the penetration of CO_2 into thick hides. This work clearly showed that thick hides could be delimed without any loss in quality using CO_2 and a small offer, 1% (m/m), of ammonium sulfate. This combination yielded an acid combining capacity of 0.38mmol H^+/g of CO_2 delimed hide, which is significantly higher than the 0.28mmol H^+/g figure for conventional ammonium deliming (White *et al.*, 1993). This means that more acid may be required in the pickling stage. Money *et al.* (1997) showed that a significant amount of CO_2 gas is formed upon pickling due to carry-over of bicarbonates, which could have serious implications in the pickling stage (Equation 1.6).

$$\mathbf{HCO_3^-{}_{(aq)} + H^+{}_{(aq)} \rightarrow H_2O + CO_{2(g)}} \qquad \textbf{(1.6)}$$

Lampard (1993) confirmed speculation that phenolphthalein was unsuitable for monitoring CO_2 deliming and that bromo-phenol blue should be used to give a better end point determination. Lampard (1994a) also suggested that an indicator which makes use of discoloration in the presence of calcium would be a better indicator of calcium removal. Lampard (1994b), on the report-back from IULTCS, Brazil, suggested the use of sodium meta-bisulfite instead of hydrogen peroxide (which may cause drum damage) to control H_2S formation.

Jackson-Moss and Horne (1994) showed that for extra heavy hides, CO_2 deliming was only possible in 190 minutes, even with the addition of 0,4% (m/m) ammonium salts. The study also showed that the effluent concentrations of ammonia were significantly improved. The study also showed a significant decrease in calcium content of the hides at pH values lower than 7.

Matheson (1995) provided many useful tips on CO_2 deliming, dealing with injection methods, which included headspace injection, re-circulation injection and vortex mixers. He also showed that various regimes could be used in CO_2 deliming, from CO_2 and ammonium salts; to CO_2, ammonium salts and organic acids; and CO_2 and organic acids. Jackson-Moss and Horne (1994) showed that organic acids significantly increased the deliming time. Matheson (1995) recommended a pulse injection technique in which CO_2 is only injected on demand, which prevents wastage of the gas. He also continued the theme of previous studies in varying the water quantity. White *et al.* (1993) suggested a low initial water quantity at low drum speeds, while Covington and Orsen (1992) suggested higher water quantities to get higher CO_2 dissolution. Matheson (1995) reported on the significance of lower enzyme activities with normal bate. Lower pH active bates can be used to overcome this problem. Matheson (1995) also supported the use of sodium meta-bisulfite at 0.5-1% (m/m) levels and suggested the use of oxygen gas to prevent H_2S formation.

To assist in the H_2S problem, Pilkington and O'Donnell (1997) reported the use of injecting hydrogen peroxide for the purposes of controlling H_2S when required. Flowers and Jackson-Moss (1997) and Flowers (1998) showed that sodium meta-bisulfite could be used for H_2S control as described in Equation 1.7.

$$\mathbf{2HS^-_{(aq)} + 4HSO_3^-{}_{(aq)} \square\ 3S_2O_3^{2-}{}_{(aq)} + 3H_2O} \qquad \mathbf{(1.7)}$$

At certain pH values, various carbonate species dominate. The type of species present at particular pH values has a dramatic influence on the rate of lime removal. As noted, lime blast forms easily from atmospheric CO_2 because the dominant ion species upon dissolving is carbonate (at pH 13). As the pH is reduced, the dominant species changes to protonated species. All CO_2 equilibrium reactions are reversible and carbonates can be converted to bicarbonates if the pH so determines. The actual chemistry of the gas itself and its behaviour in tannery solutions have not been investigated.

1.4 CO_2 Gas

1.4.1 The Gas and its Properties

CO_2 is a colourless, odourless gas, which occurs naturally at levels between 2.43 (0,024%) and 3.9 (0,039%) volumes per 10,000 volumes of air (Colt, 1984). The CO_2 tension of normal air is about 0,0003 atmospheres, thus cold oceans constantly remove CO_2 from the atmosphere while warmer portions are constantly evolving CO_2. CO_2 in the lithosphere is evolved from a number of sources, including eruptive vents and volcanoes. The major part of CO_2 comes from combustion of carbonaceous material, which through the oxidation of carbon forms CO_2 (Smith, 1990). The properties of CO_2 are presented in Table 1.1.

Table 1.1 A summary of CO_2 chemical and physical characteristics. (From Perry, 1950).

Characteristic (units)	*Value*	*Characteristic (units)*	*Value*
Melting Point ($^\circ$C)	-78.5	**Vapour Pressure (atm)**	34.4
Boiling Point ($^\circ$C)	-56.6	**Molecular Heat Capacity (cal) @0°C**	8.680
Heat of Formation (kJmol^{-1})	-393.5	**Heat of Vapourization (cal)**	83.12
Distance (C-0) (pm)	116.3	**Heat of Sublimation (g.cal/g)**	129.88
Density (g/L) @ 0°C; 1 atm	1.9769	**Heat of Fusion (g.cal/g)**	46.76
Molar Mass (g)	44.004	**Dielectric Constant (ϵ)**	1.583
Molecular Volume* (L)	22.267	**Index of Refraction (η AD)**	1.173
Molecular Diameter (m)	3.44×10^{-8}	**Sublimation (atm)**	5.2
Molecular Velocity (ms^{-1})	459.2	**Specific Gravity (SG)**	1.52
Mean Free Path (cm)	4.0×10^{-6}	**Specific Volume (L/kg) @20°C**	547
Velocity of Sound in CO_2 (ms^{-1})	258.04	**Thermal Conductivity (w/MK)@STP**	0.0146
Viscosity (poise) @20°C /1 atm	1.48×10^{4}	**Solubility in water (v/v) @ STP (%)**	76.9
Coefficient of Diffusion (cm^2/sec.)	0.164	**Mass of Gas per litre (kg)**	0.776
Triple Point ($^\circ$C)	-56.6	**Mass of Gas per m^3 (kg)**	1.839
Critical Temperature ($^\circ$C)	31		

1.4.2 The Solubility of CO_2

The values for solubility were not always agreed upon, and in particular the unit of expression of gas solubility is controversial. The Bunsen Absorption Coefficient α, one of the earliest units used, was found to be a unreliable unit due to the high variability obtained in measurements. This variability resulted from the fact that Bunsen assumed gases to be ideal and the pressures to be partial. The laws governing partiality and ideal

* **Calculated as volume of 44grams CO_2 with density at 1.976 at 0°C/atm.**

conditions are not exact in physical versus chemical determinations. As a result up to 0.7% variation in measurements can result (Markham and Kobe, 1941a).

The Ostwald coefficient of solubility *L*, excludes partiality but retains ideality. This assumption is acceptable as long as the temperature and pressure are fixed. However, this method may be inaccurate as the determination through either chemical or physical means often deviated from ideal gas conditions (Markham and Kobe, 1941b).

Henry's Law is by far the most accurate method and is expressed in the Henry Coefficient K_{H2} of normal concentrations of gas, and K_{H1} of dilute ideal solutions. Henry's law states that a gas will dissolve in water, to a certain degree, as governed by the partial pressure of that gas and the reaction of that gas with water or water's associated ions. In other words a gas lying above a liquid at a certain pressure will establish equilibrium with dissolved gas in the water. If hydration reactions or reaction with other ions uses up the gas (dissolved) then the equilibrium will shift from un-dissolved to the dissolved phase. Likewise if the gas partial pressure above the liquid increases, though possibly due to an increase in total pressure, then the effective concentration of gas above the solution will be higher which would cause more dissolution, to equalise concentrations (Markham and Kobe, 1941a; Butler, 1981). Henry's Law states that the concentration of gas in ideality will dissolve as follows (Battino and Clever, 1966):

$$\mathbf{[CO_2] = K_{H1}P_{CO2}} \qquad \textbf{(1.8)}$$

Or for real gases, which occur in most CO_2 industrial applications

$$\mathbf{[CO_2] = K_{H2}P_{CO2}} \qquad \textbf{(1.9)}$$

In aquatic systems, reported CO_2 concentrations vary from author to author. The concentration variation is due to differences in the measurement of the Henry's coefficient (K_{H2}). (Table 1.2)

Table 1.2 The dissolution constant of CO_2 as governed by Henry's law and measured as Henry's coefficient (K_{H2}), mole fraction and volume for volume (v/v) (at varying temperatures), according to various authors.

Authors	*Temperature (°C)*	*Value*
Colt, 1984	25	$10^{-1.47} - 10^{-1.7}$ (K_{H2})
Butler, 1981	25	0.001 – 0.007% (v/v)
Wilhelm *et al.*, 1977	25	6.11×10^{4} (mole fraction)
Harned and Davis, 1943	0	$10^{-1.1}$ (K_{H2})
Harned and Davis, 1943	5	$10^{-1.19}$ (K_{H2})
Harned and Davis, 1943	10	$10^{-1.27}$ (K_{H2})
Harned and Davis, 1943	15	$10^{-1.34}$ (K_{H2})
Harned and Davis, 1943	20	$10^{-1.41}$ (K_{H2})
Harned and Davis, 1943	25	$10^{-1.46}$ (K_{H2})
Harned and Davis, 1943	30	$10^{-1.51}$ (K_{H2})
Harned and Davis, 1943	35	$10^{-1.57}$ (K_{H2})
Harned and Davis, 1943	40	$10^{-1.61}$ (K_{H2})

1.4.3 The Dissociation of CO_2

Dissolved CO_2 gas undergoes a hydration reaction to form carbonic acid (H_2CO_3) as can be seen in Equation 1.10 and 1.11.

$$\mathbf{CO_{2(g)} \square CO_{2(aq)}} \qquad \textbf{(1.10)}$$

The ratio of CO_2 gas to H_2CO_3 is fixed at 99.76: 0.24 at 25°C, 1 atm, indicating that the majority of these two species lies in dissolved gas and not in the hydrated species.

$$\mathbf{CO_{2(aq)} + H_2O \square H_2CO_{3(aq)}} \qquad \textbf{(1.11)}$$

Where $k_{CO2} = 0.03s^{-1}$ (Cotton and Wilkinson, 1988)

1.4.4 The First Dissociation Constant of CO_2

The dissociation of H_2CO_3 is fairly rapid and minute quantities of this species are normally found in solution. However, the dissolution of CO_2 gas itself is rate limiting,

as can be seen by the above ratio (Moosbrugger *et al.*, 1992). In other words the dissociation of gas into bicarbonate is rapid but the dissolution of gas into carbonic acid is slower:

$$\mathbf{H_2CO_{3(aq)} \square H^+_{(aq)} + HCO_3^-{}_{(aq)}} \qquad \mathbf{(1.12)}$$

Table 1.3 The first dissociation constant (K_{a1}) for CO_2 at varying temperatures (*t*, °C) and pressures (atm), according to various authors. The pK_{a1} value illustrates the pH at which CO_2 exists as 50% H_2CO_3 and 50% HCO_3^-.

Author, Date	*t (°C)*	K_{a1}	pK_{a1}
MacInnes and Belcher, 1933	25	4.500×10^{-7}	6.346
Shedlovsky and MacInnes, 1935	0	2.613×10^{-7}	6.583
Shedlovsky and MacInnes, 1935	15	3.722×10^{-7}	6.429
Shedlovsky and MacInnes, 1935	25	4.310×10^{-7}	6.365
Shedlovsky and MacInnes, 1935	38	4.817×10^{-7}	6.317
Ellis, 1959 (1 atm)	25	4.200×10^{-7}	6.376
Ellis, 1959 (2930 atm)	25	1.670×10^{-6}	5.777
Harned and Davis, 1943	0	2.647×10^{-7}	6.577
Harned and Davis, 1943	15	3.802×10^{-7}	6.420
Harned and Davis, 1943	38	4.452×10^{-7}	6.351
Perrin, 1969 (2800 atm)	65	5.495×10^{-6}	5.260

Ellis (1959) showed that the effect of pressure on Ka_1 was quite obvious, in that as the pressure increases, the constant decreases. Ka_1 decreases because of the influence pressure has on P_{CO2}. As a consequence, more gas will be in solution at higher pressures and the carbonate equilibrium will swing toward the bicarbonate species.

From Table 1.3, various values for K_{a1} can be seen. Inaccuracy in measurement results in some of the values being unacceptable. Equation 1.13 is used to determine the first ionisation constant.

$$\mathbf{pK_{a1} = 6.572 - 0.012173}t \mathbf{+ 0.00013329}t^2 \mathbf{\ (}t \mathbf{\ in\ ^\circ C)} \qquad \mathbf{(1.13)}$$

Substitution of 25°C into Equation 1.13 gives a pK_{a1} of 6.3, which means that at pH 6.3 there is a 50% distribution between H_2CO_3 and bicarbonate (HCO_3^-) at 25°C.

1.4.5 The Second Dissociation Constant of CO_2

Most of the CO_2 in the sea is in the form of bicarbonates and its associated ions. This bicarbonate is in equilibrium with dissolved CO_2, which is regulated by the CO_2 tension of the atmosphere. Complications arise when the pH of the water is not as near neutral as those of seawater. The dissolution of CO_2 in water with a pH higher than 10 has a very rapid transition through the bicarbonate species to the carbonate species, as the CO_2 reacts with the OH^- of the alkali. The result is the formation of carbonate (CO_3^{2-}), a hydrogen free species, which readily forms insoluble compounds with certain cations, e.g., calcium carbonate ($CaCO_3$, $K_{sp} = 5 \times 10^{-9}$).

$$CO_{2(aq)} + OH^-_{(aq)} \square HCO_3^-{}_{(aq)} \quad \textbf{(slow)} \quad \textbf{(1.14)}$$

$$HCO_3^-{}_{(aq)} + OH^-_{(aq)} \square CO_3^{2-}{}_{(aq)} + H_2O \quad \textbf{(instantaneous)} \quad \textbf{(1.15)}$$

Table 1.4 The second dissociation constant (K_{a2}) for CO_2 at varying temperatures (*t*, °C), according to various authors. The pK_{a2} value illustrates the pH at which CO_2 exists as 50% HCO_3^- and 50% CO_3^{2-}

Author, Date	*t (°C)*	K_{a2}	pK_{a2}
MacInnes and Belcher, 1933	25	5.61×10^{-11}	10.251
MacInnes and Belcher, 1933	38	6.25×10^{-11}	10.204
Harned and Scholes, 1941	0	4.69×10^{-11}	10.328
McCoy, 1903*	25	6.20×10^{-11}	10.222
Stieglitz, 1905*	25	5.40×10^{-11}	10.268
Seyler and Lloyd, 1917*	25	5.30×10^{-11}	10.367
Hastings and Sendroy, 1925*	25	5.51×10^{-11}	10.259
Hastings and Sendroy, 1925*	38	6.03×10^{-11}	10.220
Perrin, 1969	0	2.29×10^{-11}	10.641
Perrin, 1969	40	6.03×10^{-11}	10.220

Harned and Scholes (1941) showed a slight correlation to the previous work of MacInnes and Belcher (1933), where using electrochemical methods, the second ionisation constant of CO_2 were measured. Table 1.4 reports the differences in K_{a2} readings from the earliest measurements to present.

* In Harned and Scholes, 1941.

The negative logarithm of K_{a2} gives values corresponding to pK_{a2}, the second ionisation constant. It is now generally accepted that the second ionisation constant is governed by the following equation:

$$\mathbf{pK_{a2} = 2909.1/T - 6.118 + 0.02272T\ (T^{\circ}K)} \qquad \mathbf{(1.16)}$$

Substitution of 25°C into Equation 1.16 gives a pK_{a2} of 10.3, which means that at pH 10.3 there is a 50% distribution between HCO_3^- and CO_3^{2-}, see Figure 1.4. The knowledge of the ionisation constants and true K_a value of H_2CO_3 allows one to compile a species diagram like that shown in Figure 1.4.

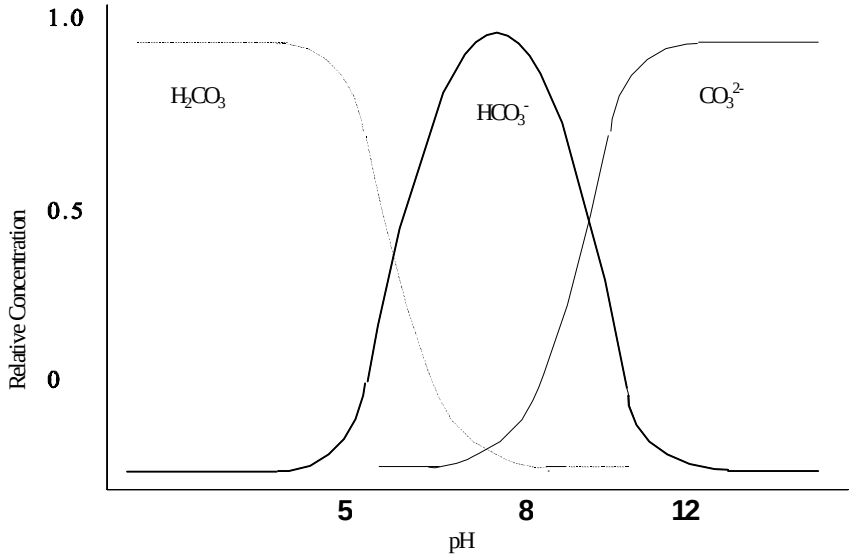

Figure 1.4 Equilibrium of the carbonate system in solutions showing relationships between H_2CO_3 and HCO_3^- and between HCO_3^- and CO_3^{2-}. Between pH 5-8 the HCO_3^- ion dominates. Above pH 10.3 the CO_3^{2-} dominates. (Adapted from Masterton *et al.*, 1986.)

1.4.6 The Effect of Salt on the Constants, K_{sp}, K_{a1} and K_{a2}

The most common effect that salts have on the constants is the "salting-out of gases" effect that electrolytes have on all gases. The effect is governed by the Sechenov equation (Eq 1.17.) In other words, the correction obtained from the ratio, α_0/α_I can be multiplied to obtain true values (Anonymous, 1979)

(1.17)

$$\log (\alpha_0/\alpha_I) = K_{s.i}\, c_i$$

where c_i is the molar concentration of the salt i and $K_{s.i}$ is a constant. α_o/α_i is the ratio of gas solubility between the gas in water compared to the gas in a salt mixture (α_i) (Schumpe *et al.*, 1982).

It is never easy to obtain the exact $K_{s.i}$ constants needed, so it has been suggested by Debye and Hückel (1923, in Albert and Serjeant, 1962) that the ionic strength equation be used:

$$I = 0.5\, \Sigma C_j z_j^2 \qquad (1.18)$$

where C_j is the molecular concentration and z is its valency.

Appendix 20 has a table showing coefficients for all relevant anions and cations taken from Schumpe *et al.* (1982). Practically one would then use the equation as follows:

$$\log (\alpha_0/\alpha_I) = \Sigma\, H_j I_j \qquad (1.19)$$

where (α_0/α_I) is the ratio of gas solubility between the gas in water compared to the gas in a salt mixture, and H_j is the ion-specific constant for a certain gas as defined by Schumpe *et al.* (1982), and I_j is the ionic strength contribution of ion j.

Barta and Bradley (1985) presented a model on gas solubilities that waives the need to determine the activity coefficient in the salting out effects, but the model has no real application due to the fact that the model is based on P-T-X data. P-T-X includes the thermodynamics of electrolyte solutions and makes the calculations tedious and complicated. Electrochemical measurements like that of Harned and Bonner (1945) are also regarded as tedious and complicated (Barta and Bradley, 1985).

1.5 Limitations of CO_2 Deliming

The CO_2 gas and its use have been generally accepted as a modern processing option and as with all tanning chemicals have advantages and disadvantages. A summary of CO_2 deliming properties is shown in Table 1.5.

Table 1.5 The advantages and disadvantages of CO_2 deliming process.

Advantages	*Disadvantages*
More cost effective than ammonium salts.	Can generate hydrogen sulfide gas due to a low operating pH.
Easily automated.	Process can be lengthy on certain pelt types.
Reduced ammonia odour.	A cryogenic effect is seen on gas lines.
A better cleaner product is obtained.	A gas risk is realised if drum pressure valves fail.
Less acid shock is possible due to a weak acid being used.	More pickle acid is required in the pickle stage.
A lower COD is obtained with this method.	A lower bate working pH can be detrimental on pH 8-active bates.
Greater dosing accuracy is possible.	The gas is not noxious for workers, but is hazardous.

Many issues surrounding CO_2 deliming can be researched, due to its relative infancy in the tanning industry. Not all of these issues were studied in this dissertation. The first major obstacle for solving some of the pressing issues is the question of slow deliming times compared to ammonium salt deliming. If a more competitive deliming time can be achieved then it could be readily accepted.

The second issue that needs to be settled is the whether the skins delimed with CO_2 are of the same quality as ammonium salt delimed skins.

1.6 Research Program

The research program reported here was formulated to address a number of questions noted here.

1.6.1 Research Objectives

Two major research objectives were identified.

1. To Improve CO_2 Deliming Rates

The rate of CO_2 deliming, compared to ammonium salt deliming, is unacceptably long and any feasible method for reducing the rate to a time comparable to that of ammonium salt deliming, would improve its acceptance in the Leather industry.

2. To Produce CO_2 Delimed Leather of High Quality

Two main quality areas of concern to tanners are that CO_2 deliming causes too much opening up of the hide/skin structure (resulting in looseness), and that there is a decrease in physical/chemical properties such as poor tensile strength, lower chromium contents, and high residual calcium values.

Potential quality improvements would need to be associated with improvements in deliming times to make the CO_2 deliming process acceptable to the tanning industry.

1.6.2 Research Hypothesis

Understanding the factors influencing CO_2 solubility in deliming solutions, will inform the optimisation of CO_2 penetration into hides/skins, and thus assist in reducing deliming times to levels comparable with conventional ammonium salt deliming.

CHAPTER 2

OPTIMAL CONDITIONS FOR CO_2 SOLUBILISATION IN DELIMING LIQUORS

2.1 Introduction

The work done by Markham and Kobe (1941a and 1941b) illustrated the solubilisation of CO_2 in laboratory solutions of distilled water. In an attempt to investigate CO_2 solubility in solutions other than distilled water, Battino and Clever (1966) and Butler (1981) quantified CO_2 solubility in solutions such as fish tank water (fresh and seawater). Very little work has been reported on CO_2 solubility in real tannery deliming liquors and little quantification of the CO_2 species in solution has been reported. Empirical studies where simple water solutions were used could have been reproduced here. It was however felt that to see exactly what CO_2 species were present, and in what quantities, in real tannery deliming liquors, after sparging with CO_2 gas, solubilisation studies using potentiometric rather than conductiometric tests should be undertaken.

2.1.1 Solubility Experiments

Solubility experiments were carried out to determine the effect that pressure (P), temperature (T), ionic strength (I) and pH have on the solubility of CO_2 in deliming liquors. The basic aim was to determine the solubility window of CO_2 in typical tannery "floats". The CO_2 'solubility window' can be defined as the conditions emerging by optimising a small group of parameters. They may be normally antagonistic, but when acting together, produce favourable conditions. Figure 2.1 shows how a 'solubility window' can be used to infer optimal conditions for further experimentation.

This simple model can be used to determine the optimal window by examining each parameter separately.

Upon further planning, it was discovered that there are two fundamental flaws. Firstly, it is not practical to examine the four parameters exclusively, as they are integrated *in situ*, and upon integration would give different effects on solubility. In other words a parameter that enhanced solubility of CO_2 could be negated by another parameter that decreased solubility. Secondly, the quality of downstream processing could be affected by a so-called ideal parameter for deliming, e.g. the optimal temperature for deliming might be say $0^{\circ}C$ which would not favour the bating process, to follow.

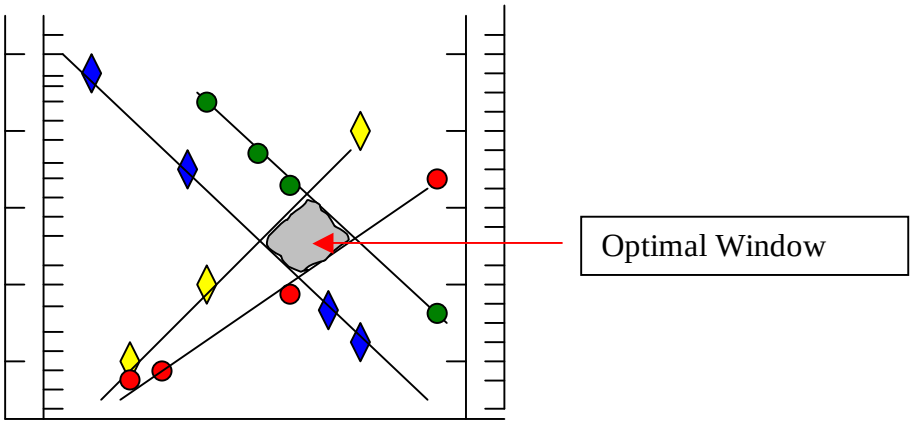

Figure 2.1 A schematic illustrating a simple model for the measurement of four parameters (two pairs are antagonistic to one another).

To overcome this type of problem a model was planned, based on a multi-factorial experiment and consequent analysis (Daniel, 1995). The different experiment runs would be performed to a multi-factored protocol and after each run the carbonate species present would then be estimated. To do this estimation of carbonate species, a number of options were evaluated.

Deffeyes (1965) suggested an algebraic and graphical method for determining carbonate species. The problem with this method was that to obtain readings the total carbonate carbon has to be measured, i.e., total carbon. The problem with total carbon measurement, particularly in pressure systems, is that the loss of CO_2 on pressure release causes incorrect results.

Loewenthal *et al.* (1986) tried to measure total alkalinity of municipal wastewater solutions by doing a simple potentiometric measurement based on principles outlined by Gran (1952). The potentiometric determination makes use of equivalence determinations to establish concentrations of carbonate species. Loewenthal *et al.* (1988) developed a computer program called Stasoft, to assist in the calculation of the carbonate species and the dosing of these species in effluent. Loewenthal *et al.* (1989) characterised the weak acid/base equilibria in wastewater and further expanded the instructions of dosing these species in Loewenthal *et al.* (1991). Moosbrugger *et al.* (1992) continued work on carbonate estimation, and later established the now recognised 4 or 5-point titration methods for carbonate species determination (Moosbrugger *et al.*, 1993a, b and c).

The carbonate species estimation utilised in this study was based on Moosbrugger *et al.* (1992) and calculations were done with the associated computer software (Stasoft). Carbonate acidity was thus expected to give a good estimation of the conditions under which the CO_2 deliming would work best.

2.2 Materials and Methods

2.2.1 Solubility Experiments

After considering the quality and quantity of information regarding the solubility, and the first and second dissociation constants measured previously (Harned and Davis, 1943; Perrin, 1969), it was deemed necessary to do tannery related measurements. All of the previous constant determinations were obtained using distilled water and parameters such as pressure, temperature, ionic strength and pH were examined individually. In the solubility experiments set out in this research, all four parameters were studied together in a variety of solutions (mainly real deliming liquors, controls of distilled water were also used), to determine solubility and subsequent CO_2 species. A series of experiments were performed consisting of the four parameters according to Table 2.1. The complete list of experiments designed are outlined in Appendix 1.

Table 2.1 The corresponding high, medium and low values for each parameter examined.

Pressure	
High	2 Atmospheres (atm)
Medium	1 atm
Low	No Pressure (slight vacuum)
Ionic Strength	
High	Saturated Salt [Specific Conductivity, SC >8 milli-Siemens per meter (mS/m)]
Medium	Tannery Strength (SC = 5m S/m)
Low	Distilled water (SC<1 mS/m)
Temperature	
High	50°C
Medium	25°C
Low	0°C
pH	
High	10
Medium	7
Low	3

All experiments, excluding where the ionic strength was 0mS/m, were carried out in deliming liquors. The deliming liquors were real liquors drawn from the Shuttleworth Experimental Tannery at the Leather Industries Research Institute (LIRI Technologies, Grahamstown, RSA), these were stored at 0°C until needed. The deliming liquors were drawn at time zero (T_0), before the addition of deliming agents, and after the hides had been drummed several times (5 minutes). This was done in order to simulate the normal conditions under which CO_2 would be pumped into the deliming drum, and a real deliming liquor was desired for relevant solubility data. The deliming liquors were analysed for sulfide, phosphate, and conductivity, as these criteria are necessary inputs into the Stasoft computer software (Moosbrugger *et al.*, 1992). Sulfide and phosphate form buffers in

solution and these buffers interfere with the carbonate buffers. The computer software, using sulfide and phosphate values, can correct for these interference effects.

2.2.1.1 Sulfide, Phosphate and Conductivity Analyses

The method used for sulfide analysis was the SLTC standard method (1998) 4/2 (SLM 4/2) and the sulfide was expressed as mg/L sulfur (S).

The method used for phosphate analysis was the IULTCS standard method (2000) 15 (IUC/15) and the phosphate was expressed as mg/L phosphate (*P*).

The effluent conductivity was measured on a Sartorius J-134 Conductivity Meter (Sartorius, Bonn) and expressed in mS/m.

2.2.2 Protocol

In order to determine the interaction between temperature, pH, pressure and ionic strength, and their collective influence on CO_2 solubility, a factorial analysis, as described by Daniel (1995) was used.

Experiments were designed using four parameters (Table 2.1), which resulted in 81 potential experiments (Appendix 1). Before the experiments were run they were statistically confounded (Daniel, 1995); i.e., if the parameter was likely to positively affect the ultimate event (enhanced solubility) it was scored a +1, if it was to negatively effect the event it was scored –1. For every experiment, each parameter was scored and an experiment total obtained. If this total was 0, -1 or +1, the experiment was not run. It was not worth running experiments which had factors which contradicted the final outcome, e.g., a high temperature would ultimately cause a pressure increase thus it was pointless to run an experiment which operated at low pressures and high temperatures simultaneously.

The four-point titration method was run according to Moosbrugger *et al.* (1992) using the apparatus as described in Figure 2.2.

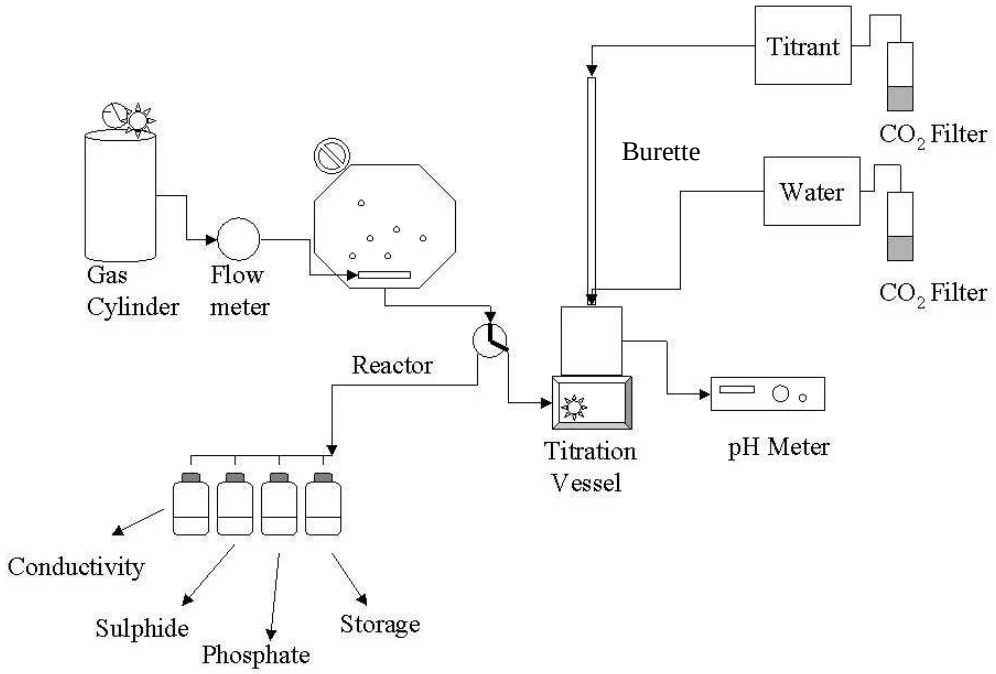

Figure 2.2 The schematic outline of the CO_2 solubility experiments

Four controls were analysed in four-point pH titrations. The controls were as follows:

1. CO_2-free distilled water at room temperature with 30 minutes sparging with CO_2
2. CO_2-free distilled water at room temperature with no sparging
3. Distilled water at room temperature with no sparging
4. Distilled water at room temperature with 30 minutes sparging with CO_2

The experiments were run, less the confounded experiments, and the titrant volumes recorded for the four pH points. The process conditions for each experiment were recorded. Liquid samples were drawn from each reaction mix and tested for sulfide, conductivity, and phosphate.

All water used in these solubility experiments was distilled water, boiled (to remove CO_2) and then stored under CO_2-free conditions in containers with soda lime CO_2 traps. The

titrants used in the experiments were standardised according to the method outlined in Moosbrugger *et al.* (1992) and the necessary corrections were built into the calculations.

The total acidity expressed as mg/L calcium carbonate was then calculated on the computer software supplied by Moosbrugger *et al.* (1992). The total carbonic acidity (mg/L) was then plotted on 3-D graphs using Excel® (Microsoft Office 2000®).

2.3 Results and Discussion.

2.3.1 Solubility Experiments

2.3.1.1 The sulfide and phosphate content

The sulfide analysis revealed that the liquor had a sulfide concentration less than 1mg/L. To emulate these low conditions, the sulfide levels were taken to be 1mg/L in the calculations. The phosphate analysis also showed a reading of less than 1 mg/L, and phosphate levels were also assumed to be 1 mg/L, for calculation purposes.

2.3.1.2 Carbonic Acidity

The results of the multi-factorial experiment are recorded graphically, which presented some difficulty in showing all the data at once. It was decided that the graphs would be expressed with two parameters constant and two parameters variable. The carbonic acidity is shown graphically in Figures 2.3 to 2.18.

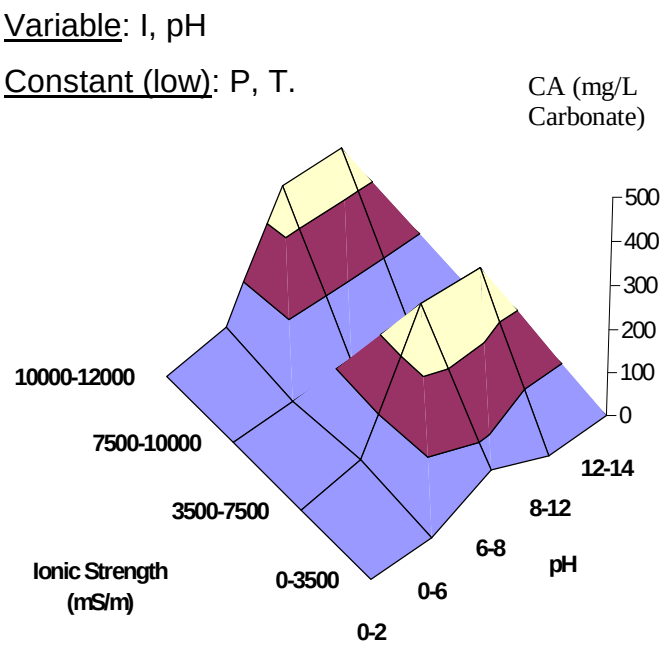

Figure 2.3 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with pressure and temperature low and constant, with ionic strength and pH variable. (Blue 0-100mg/L; maroon 100-200mg/L and yellow 200-300mg/L).

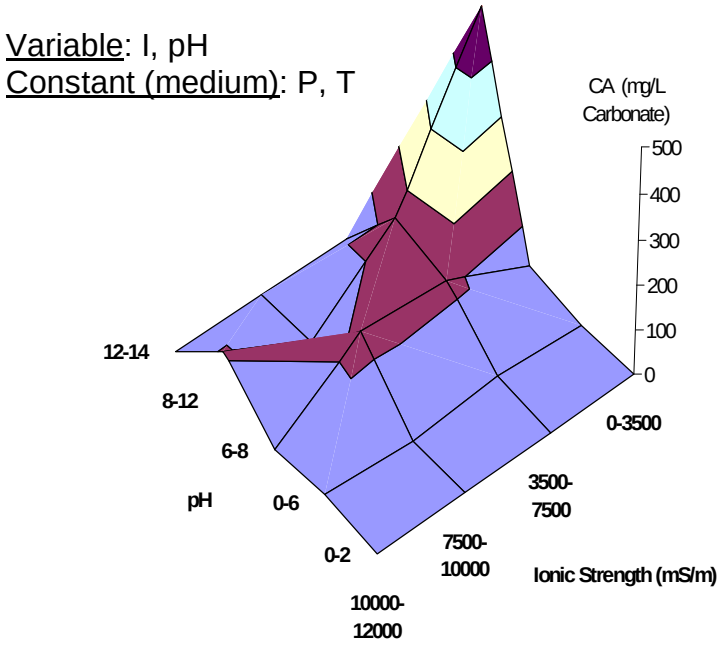

Figure 2.4 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with pressure and temperature medium and constant, with ionic strength and pH variable. (Blue 0-100mg/L; maroon 100-200mg/L; yellow 200-300mg/L; light blue 300-400mg/L and purple >500mg/L).

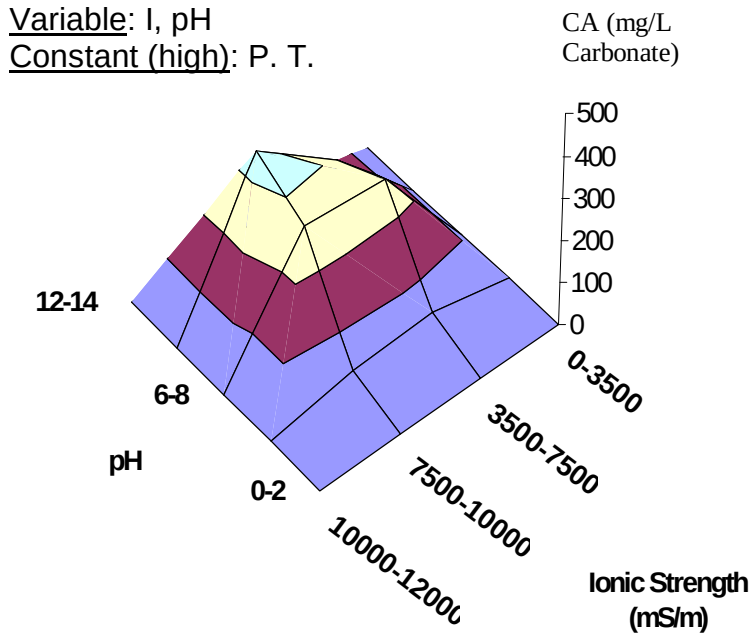

Figure 2.5 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with pressure and temperature high and constant, with ionic strength and pH variable. (Blue 0-100mg/L; maroon 100-200mg/L; yellow 200-300mg/L; and light blue 300-400mg/L).

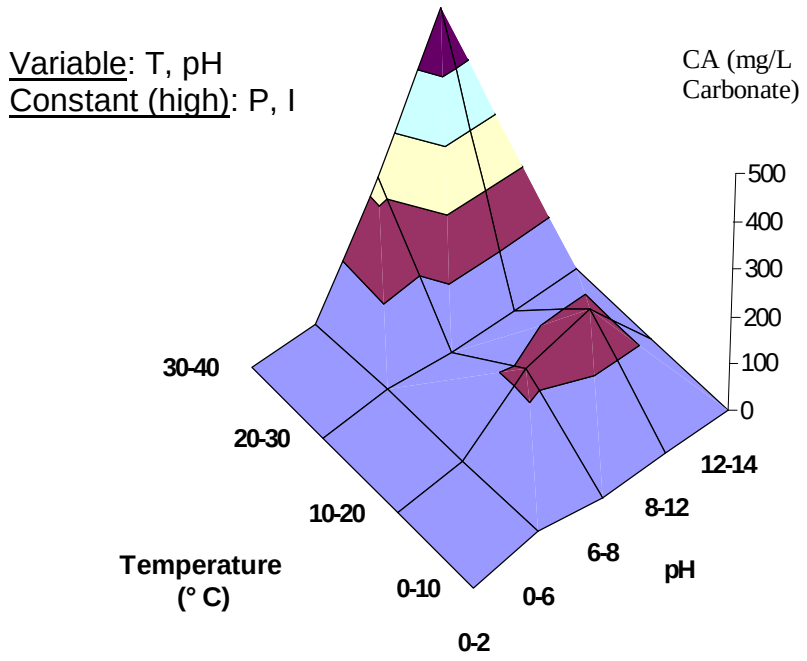

Figure 2.6 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with pressure and ionic strength high and constant, with temperature and pH variable. (Blue 0-100mg/L; maroon 100-200mg/L; yellow 200-300mg/L; light blue 300-400mg/L and purple >400mg/L).

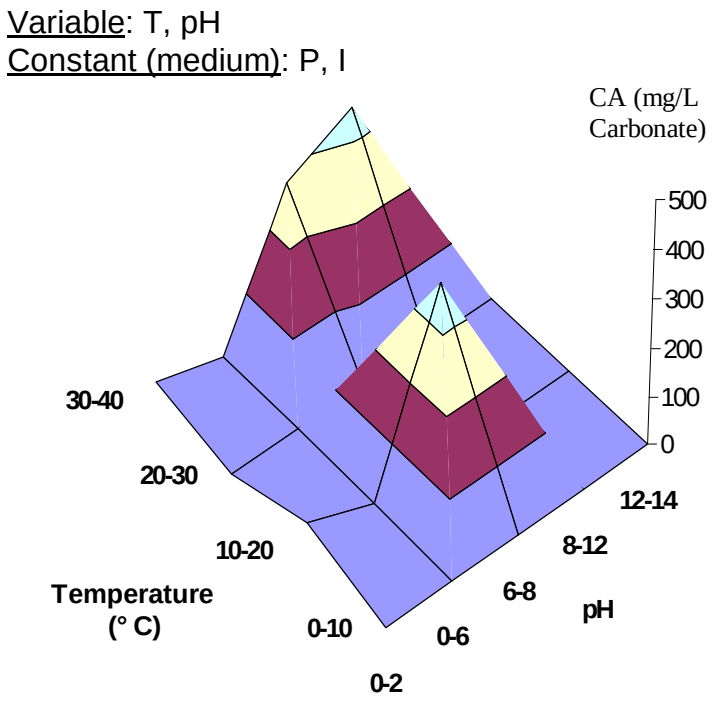

Figure 2.7 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with pressure and ionic strength medium and constant, with temperature and pH variable. (Blue 0-100mg/L; maroon 100-200mg/L; yellow 200-300mg/L; and light blue 300-400mg/L).

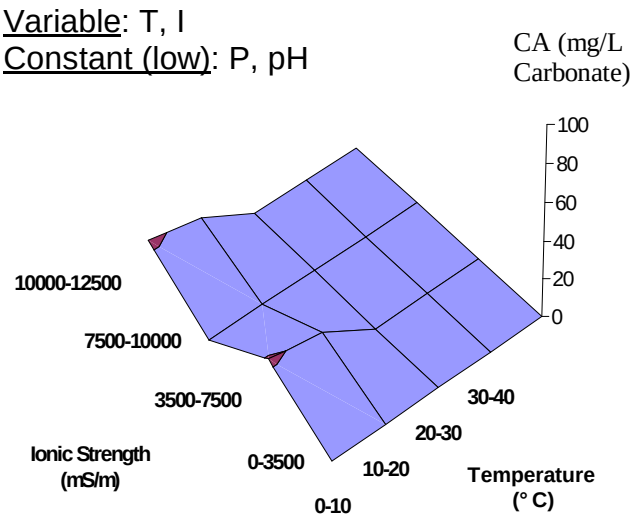

Figure 2.8 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with pressure and pH low and constant, with temperature and ionic strength variable. (Blue 0-20mg/L; and maroon >20mg/L).

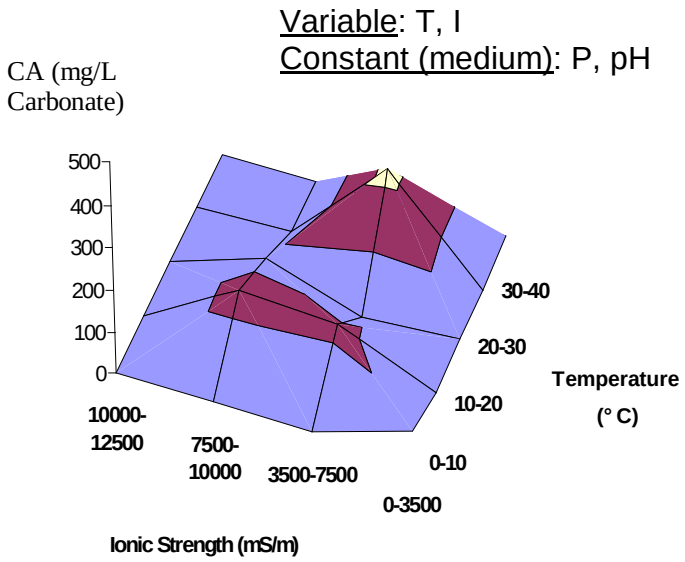

Figure 2.9 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with pressure and pH medium and constant, with temperature and ionic strength variable. (Blue 0-100mg/L; maroon 100-200mg/L and yellow 200-300mg/L).

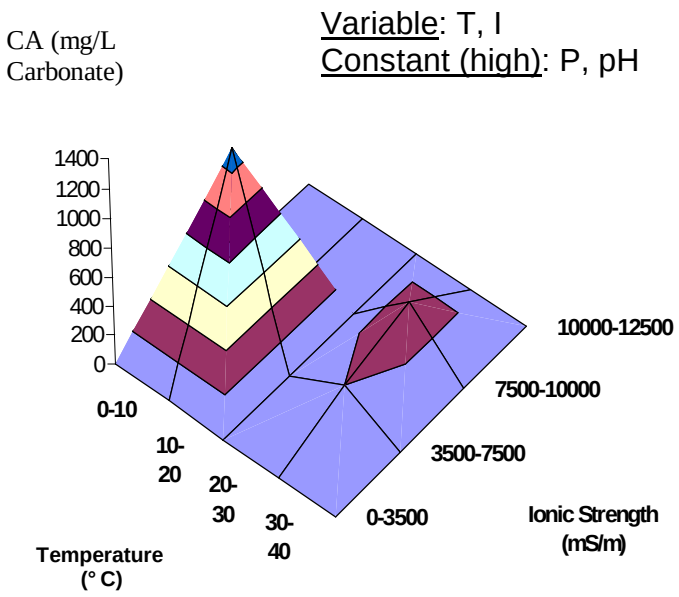

Figure 2.10 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with pressure and pH high and constant, with temperature and ionic strength variable. (Blue 0-200mg/L; maroon 200-400mg/L; yellow 400-600mg/L; light blue 600-800mg/L; purple 800-1000mg/L; orange 1000-1200mg/L and dark blue >1200mg/L).

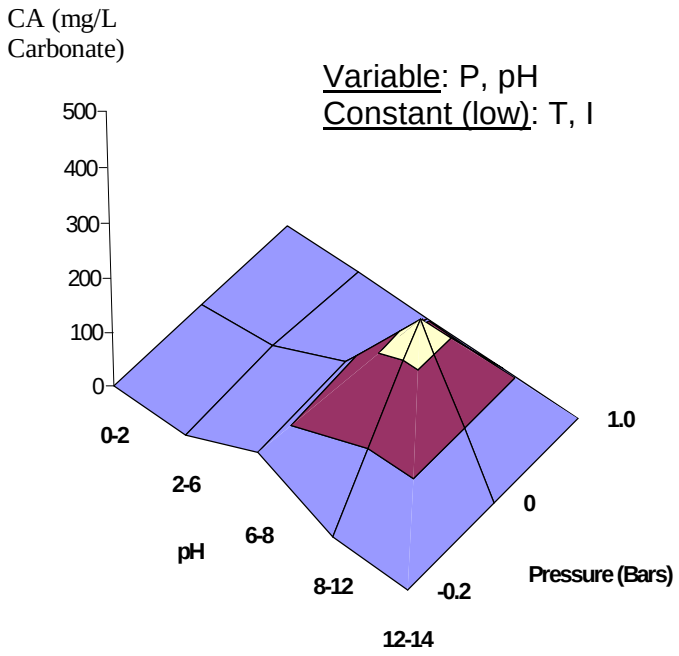

Figure 2.11 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with temperature and ionic strength low and constant, with pressure and pH variable. (Blue 0-200mg/L; maroon 200-400mg/L and yellow 400-600mg/L).

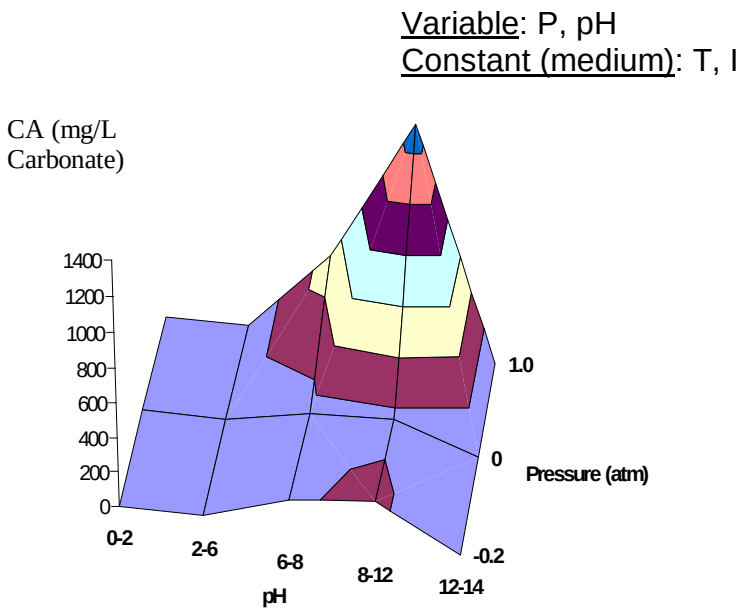

Figure 2.12 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with temperature and ionic strength medium and constant, with pressure and pH variable. (Blue 0-200mg/L; maroon 200-400mg/L; yellow 400-600mg/L; light blue 600-800mg/L; purple 800-1000mg/L; orange 1000-1200mg/L and dark blue >1200mg/L).

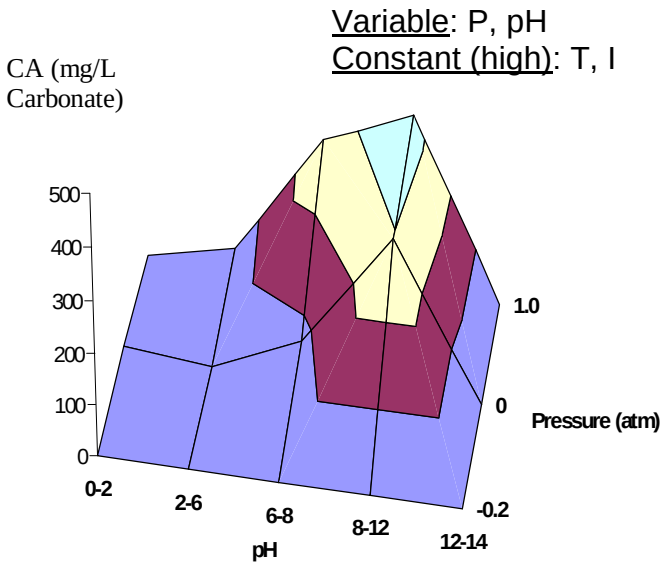

Figure 2.13 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with temperature and ionic strength high and constant, with pressure and pH variable. (Blue 0-200mg/L; maroon 200-400mg/L; yellow 400-600mg/L and light blue 600-800mg/L).

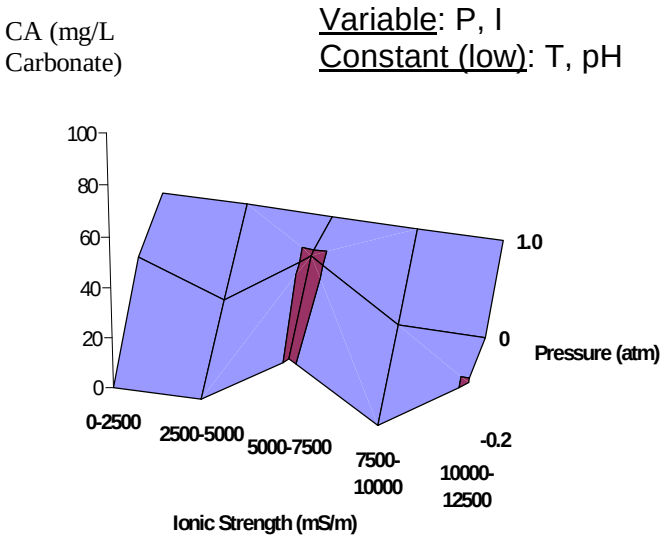

Figure 2.14 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with temperature and pH low and constant, with pressure and ionic strength variable. (Blue 0-20mg/L and maroon >20mg/L).

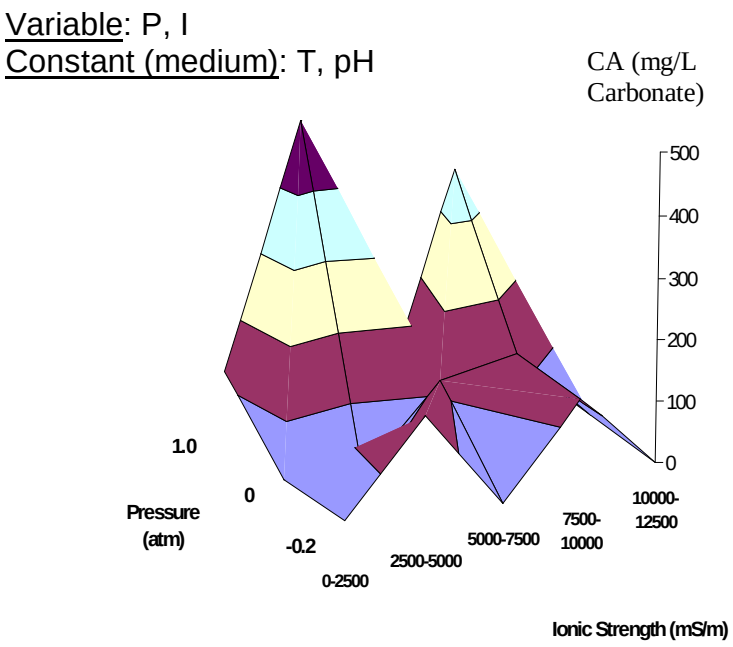

Figure 2.15 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with temperature and pH medium and constant, with pressure and ionic strength variable. (Blue 0-100mg/L; maroon 100-200mg/L; yellow 200-300mg/L; light blue 400-500mg/L and purple >500mg/L).

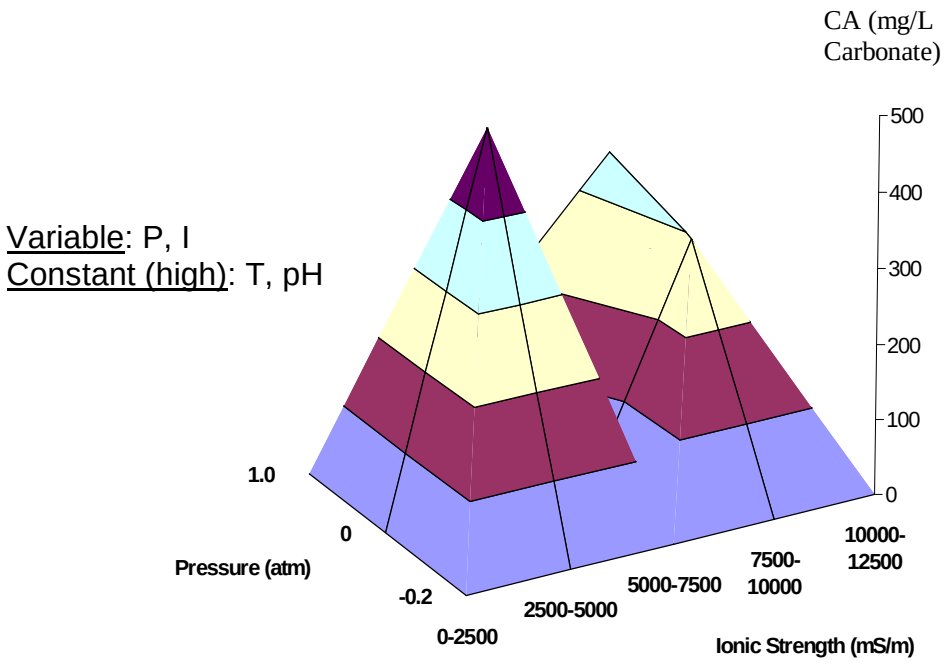

Figure 2.16 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with temperature and pH high and constant, with pressure and ionic strength variable. (Blue 0-100mg/L; maroon 100-200mg/L; yellow 200-300mg/L; light blue 300-400mg/L and purple >400mg/L).

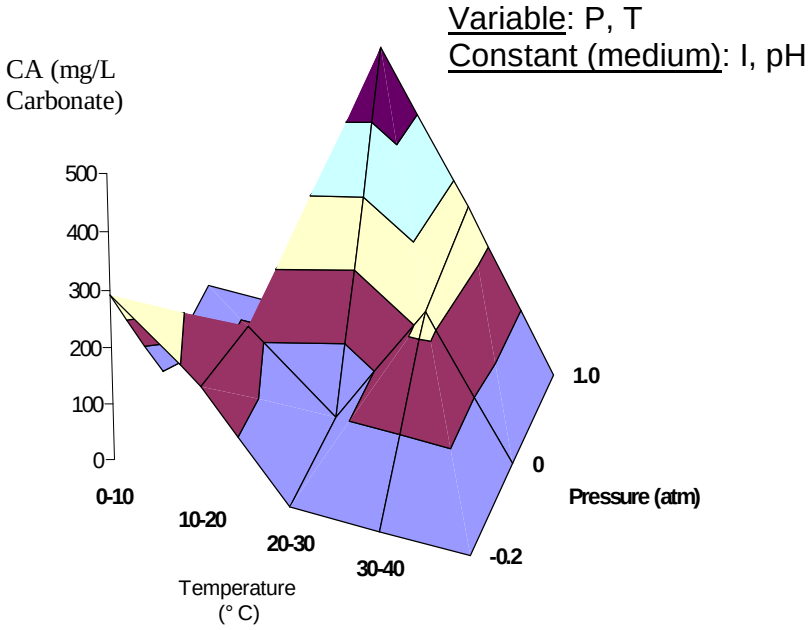

Figure 2.17 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with ionic strength and pH medium and constant, with temperature and pressure variable. (Blue 0-100mg/L; maroon 100-200mg/L; yellow 200-300mg/L; light blue 300-400mg/L and purple >400mg/L).

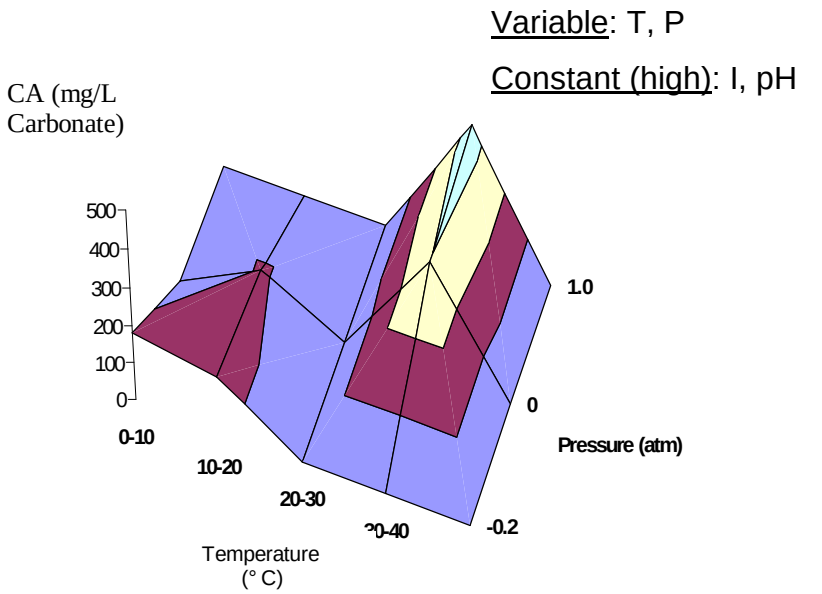

Figure 2.18 Surface graphs showing the carbonic acidity (as mg/L calcium carbonate) in experiments with ionic strength and pH high and constant, with temperature and pressure variable. (Blue 0-100mg/L; maroon 100-200mg/L; yellow 200-300mg/Land light blue >300mg/L).

From Figures 2.6 to 2.18 it can be seen that only two experiments produced highly saturated conditions. Figure 2.10 and Figure 2.12 had values of carbonic acidity (CA) of 1200mg/L and more. These experiments, after the allocated experimental time, produced conditions of gas effervescence. Super-saturation is a highly desirable condition to have during deliming and it was assumed that super-saturation would be ideal for rapid deliming. The ideal conditions for super-saturation were obtained between pH 8 and 12, 0 to 10°C, and 1 bar pressure, and ionic strength 3500 to 7500mS/m. Super-saturation would, however, not be feasible in tanning drums as super-saturated solutions are unstable in conditions where agitation occurs. Super-saturation of these would further be hindered by the fact that the pressure within the tanning drums would fluctuate, especially when the drum is opened for process checks. Agitation and rapid loss of pressure would result in the loss of the high carbonate acidity that this experiment has shown could exist.

Solutions that showed a high degree of saturation were those shown in Figures 2.4, 2.6, 2.15, 2.16 and 2.17. These experiments showed that temperatures below 15°C did not contribute to high CA values, which is contrary to every solubility experiment review. A possible explanation for this was that all papers reviewed held the solubility parameters exclusive or constant and the four vital parameters (investigated in this experiment) where never matched off against one another. From the results seen in this experiment, the importance of pH and ionic strength (in CO_2 solubility) has largely been underestimated. From Figures 2.4, 2.6, 2.15, 2.16 and 2.17 it can be seen that pH values between 8 and 12 yield CA values of 500mg/L and higher. It was our opinion that a CA value of 500mg/L and higher was favourable for rapid deliming. Ionic strengths from 3500 to7500 like those obtained in ordinary deliming “floats” seem to favour high CA values. Figure 2.4 shows that low ionic strengths of 0 to 3500 mS/m give high CA values (but only at high pH values). Low ionic strengths in deliming could never be obtained in tanning drums due to the high TDS content of limed hides and the high TDS content of the drums (due to their being used in practice in a multitude of processes, some of which the use of sodium chloride).

Another common thread emerging from these experiments showed CA values of 500mg/L and higher were obtained from working pressures of 1 bar and higher. This correlates with previous deliming work (Anonymous 1992b), where it was shown that high pressure deliming yields rapid deliming times. The high pressure and pH as well as medium ionic strengths correlate to current CO_2 solubility theory.

This experiment indicates that the most practical conditions for CO_2 deliming are 1 bar pressure, pH 7 to 12, 25°C and an ionic strength of 3.5 to 7 S/m. These conditions can be further refined in that the closer the pH was to 7, the more likely the species will be to a diprotic acidic species that, in turn, would achieve rapid deliming. In other words, a high pH of 12 would give a higher CA value, but that pH would suggest carbonate species dominance. Carbonate, as an alkaline species would not be appropriate for lime removal, as well as the risk of lime blast, being present.

2.4 Conclusions

While previously reported gas constant measurement values used classical conductance techniques (as in Harned and Scholes, 1941; Battino and Clever, 1966; Perrin, 1969), this study used *in situ* potentiometric measurements. For the first time, the four influential parameters for CO_2 solubility were varied to yield variable levels of carbonic acidity. The outcome of the determination of the optimal conditions for the solubilisation of CO_2 yields a benchmark, namely 500mg/L CA. A carbonic acidity of this level was deemed ideal and the parameters that give this are shown.

The two solutions from experiments that yielded a CA higher than 1200mg/L are impractical due to the highly saturated nature of these liquids. Super-saturated solutions would not tolerate the practical conditions of deliming.

CHAPTER 3

ACCELERATED CO_2 DELIMING: LABORATORY AND PILOT SCALE STUDIES

3.1 Introduction

From the experiments carried out in the previous chapter, it was shown for delime liquors that the solubility of CO_2 was optimal at temperature 25^{o}C, and was directly proportional to ionic strength and pressure. It was uncertain if chemical auxiliaries could also play a role. The incorporation of other weak acids e.g. formic, could also help improve the deliming time, as has been the case with the incorporation of a reduced offer of ammonium salts (Money *et al*., 1997).

The aim of this part of the study was to investigate the deliming times under the optimal conditions established above and to see which gave the best results.

3.2 Materials and Methods.

3.2.1 Protocol

Numerous process-determined factors could influence the rate of CO_2 deliming process including rotation, water quantity, pressure, simultaneous bating/bleaching, ammonium sulfate addition, pre-sparging and temperature. These would need to be determined before proceeding to larger scale trials.

Small laboratory-scale experiments were carried out on small 150g hide pieces, and delimed in a high-pressure vessel that could be tumbled. All experiments were carried out using an ammonium sulfate deliming control for comparison. The hide pieces used in these experiments came from one animal except for three pieces, which were from a lighter animal.

Combinations of process conditions investigated are outlined in Table 3.1.

Table 3.1 The process conditions varied on limed cattle hides. All experiments were carried out in a pressurised cylinder (with lid), which was then rotated (or not) on a Wacker rotation system. Other process conditions described below were carried out.

Experiment Number	*Temperature (°C)*	*Type of Deliming*	*Rotation*	*Pre-sparge*	*Water Quantity*	*Other*
1	25	CO_2	No	No	High	1 bar
2	25	CO_2	No	No	Low	1 bar
3	25	CO_2	No	15’	Low	Nil
4	25	CO_2	No	15’	Low	3% HCO_3Na
5	25	CO_2	No	15’	Low	3%, 1 bar
6	38	CO_2	No	15’	Low	3%, 1 bar, bate
7	25	CO_2	No	No	Low	Nil
8	25	CO_2	Yes	20’	Low	2%, 1 bar
9	25	CO_2	Yes	20’	Low	2%
10	25	CO_2	Yes	20’	High	2%, 1 bar
11	38	CO_2	Yes	20’	Low	2%, 1 bar, bate
12	38	CO_2	Yes	20’	Low	2%, bate
13	25	$(NH_4)_2SO_4$-light	Yes	No	Low	Nil
14	25	$(NH_4)_2SO_4$-heavy	Yes	No	Low	Nil
15	25	$(NH_4)_2SO_4$-heavy	Yes	No	High	Nil
16	25	$(NH_4)_2SO_4$-light	Yes	No	Low	Bate
17	38	$(NH_4)_2SO_4$-light	Yes	No	Low	Nil

3.2.1.1 Rotation

The reason for the presence or absence of rotation was to see whether the carbonate system was upset by agitation or not. The movement of solution may cause a super-saturated solution of CO_2 to degas. The result would be losses of carbonate species in solution, and that would mean poor deliming and consequently long deliming times. Rotation, or lack of it, with ammonium salts, would be apparent if the speed of ammonium salt penetration was improved or not.

3.2.1.2 Pre-sparge

The pre-sparge was a means of attempting to mimic ammonium salt availability, in other words if a saturated carbonate solution could be present from the beginning of the process, as was the case with ammonium salt deliming, then there was a possibility that

CO_2 deliming could be faster. A super-saturated solution has a very high proportion of soluble gas that has two possible protons for donation to a highly alkaline hide.

3.2.1.3 Water Quantity

It was unknown if a lower water quantity with a lesser total carbonate or a higher water quantity with a higher total carbonate would give faster deliming times. A higher water quantity with a higher carbonate load would reduce the mechanical action of the process and the consequent penetration rate may be reduced. The lower water quantity with higher mechanical action would not have sufficient carbonate species to effectively neutralise the alkalinity in the hide.

3.2.1.4 Bicarbonate Addition

The advantage that ammonium sulfate has over CO_2 is that the ammonium sulfate is available at T_0 during deliming, which means alkalinity neutralisation takes place from the start of the process. As with pre-sparging, the idea behind adding sodium bicarbonate was to mimic ammonium sulfate availability. From T_0 of the deliming process the carbonates will be available for neutralisation and for penetration.

3.2.1.5 Pressure

As can be seen from the CO_2 optimisation experiments, the higher the pressure the more total alkalinity there is. A super-saturated solution was quite easily obtainable from high pressures (carbonated fizzy drinks use this principle). The use of pressure will be combined with other factors to enhance deliming times.

3.2.1.6 Simultaneous bating and bleaching

Due to the very gentle nature of CO_2 deliming it has been said that the bating can be run simultaneously with the deliming (Matheson, 1995). Sufficient deliming should be allowed to ensure that the outer zones are bated while the inner zones are delimed. An additional bating time period would allow the inner zones to be bated as well. The only disadvantage of this was the over-bating potential of this regime, should deliming be extended.

Simultaneous bleaching would also assist in the control of the problematic H_2S gas. Bleaching makes use of sodium meta-bisulfite to prevent H_2S gas formation.

3.2.2 Pilot-Scale Experiments

After completion of the laboratory-scale experiments a graph could then be drawn showing comparative deliming times for all regimes. Based on the experiments that had the shortest deliming times pilot-scale experiments could then be carried out to show the effectiveness of these regimes on a larger scale. The best results were then repeated on a pilot scale in two Dose drums. Two hides were sided and matched. Two matched sides were placed into one drum and run according to the control process shown in Appendix 3.

The other two matched sides were placed in the second drum and run according to the process outlined in Appendix 4. The processes were run, pH taken at certain time intervals, along with cuts from the butt area. In order to keep a standard, the cuts were checked with phenolphthalein. A pink colour indicated a pH higher than 9 and a colourless appearance after indicator addition meant the pH was less than 9. The total thickness of the skin was measured with a Vernier calliper, as was the thickness of the coloured zones. A proportion of total thickness to colour thickness was calculated, and these proportions were then plotted in diagrams, which will be defined in this study as 'deliming maps'. The final effluents were sampled and stored at 0 $^{\circ}$C until tested. The leather was then carried on to wet blue and crusted according to the process shown in Appendix 9 and 16. Chromium percentages and shrinkage temperature samples were taken after tanning and after horsing up. The chemical and physical properties could then be measured using standard tests.

3.2.2.1 Chemical Evaluation

The chemical properties of the leather samples taken after the experiments above were tested for residual calcium, chromium content and shrinkage temperature. The effluents were analysed for nitrogen content (as free and saline ammonia) and sulfate.

- **Nitrogen**

The ammonia (NH_3) content of the effluent was analysed according to the Nessler method (method 8038) used in the Hach Company test kits for nitrogen [mg/L nitrogen as free ammonia (NH_3-N)]. The samples, after development of colour, were measured in a standard Hach Company spectrophotometer at 425 nm. The ammonia levels of the effluent were, at times, outside the estimated detection range (EDL), that is 0 to 2.5 mg/L NH_3-N, with a confidence level of $p < 0.01$. Hence, certain necessary dilutions were made and allowances for these dilutions worked into the calculations.

- **Sulfate**

The sulfate content of the effluent was analysed according to the Sulfa Ver 4 method (method 8051) used in the Hach Company test kits for sulfate (sulfate as mg/L SO_4^{2-}). The samples, after development of colour, were measured in a standard Hach Company spectrophotometer at 450 nm. The sulfate levels of the effluent were, at times, outside the EDL, that is 0 to 70 mg/L SO_4^{2-}, with a confidence level of $p < 0.01$. Hence, certain necessary dilutions were made and allowances for these dilutions worked into the calculations.

- **Chromium Content**

The chromium content of the leather was analysed after sampling leather cuts from the butt region of the sammied skins. The wet-blue was dried at 100^{o}C overnight and was analysed for chromic oxide (%, m/m) using a modified South African Bureau of Standards method 625 (SABS 625). SABS 625 method was modified to titrate with ferrous ammonium sulfate, which was standardised daily to determine normality (Anonymous, 1997).

- **Shrinkage Temperature**

The shrinkage temperatures for the wet-blue leathers were analysed on a standard meter using the IULTCS(2000) physical test method 16 (IUP/16). The samples of wet-blue were moist, sammied leathers clicked out in duplicate, parallel and perpendicular to the backbone. The shrinkage temperatures of the leathers were given to be an average of the four temperatures.

- **Residual Calcium**

Calcium tests were done on the sides prior to the wash that was done on completion of the deliming process. The residual calcium test was a modified test of the chromium test in that 0.5 g dried specimen was ashed and washed into a 250ml-Kjeldahl flask (containing glass beads). 15 ml oxidation mix (perchloric/sulfuric acid) and 15 ml concentrated nitric acid was added. The digestion mix was then boiled in a fume cupboard until the white fumes lifted off the surface of the boiling liquid.

The contents were cooled and washed into a 100ml-volumetric flask and made up to the mark. The insoluble contents of the solution were removed by filtering through Whatman No. 42 filter paper. The necessary dilutions were made and then read on a Varian Atomic Absorption (AA) Spectrophotometer using a calcium lamp. The wavelength was set at 422.7 nm with the flame width at 0.5 mm. The lamp current was set at 4 mA and the fuel mix was air and acetylene. The blank for the AA was distilled water and the spectrophotometer was calibrated with a calcium standard of 1.0-5.0 mg/L Ca^{2+}.

3.2.2.2 Physical Testing

Samples were clicked out of the butt area using standard knives and a clicking press. The samples were conditioned in the constant environment room at 20^{o}C, 65% relative humidity for 48 hours. Where necessary the sample thickness was measured using the IULTCS(2000) standard method 4 (IUP/4).

- **Lastometer**

Lastometer samples were clicked out in triplicate from the butt sampling area and tested on a Bally lastometer testing apparatus. The method used was the IULTCS(2000) standard test method 9 (IUP/9). The results for the three samples were averaged.

- **Tensile Strength**

Tensile strength and elongation at break samples were clicked out from the standard area and tested on an Instron 1122 machine (Instron, Johannesburg). The method used was the IULTCS(2000) standard test 6 (IUP/6). Duplicate samples that were clicked out, for both parallel and perpendicular directions to the backbone, were tested and the four measurements averaged.

- **Tear Strength**

Tear strength samples were clicked out from the standard area and tested on an Instron machine. The method used was the IULTCS(2000) standard test 8 (IUP/8). Duplicate samples that were clicked out, for both parallel and perpendicular directions to the backbone, were tested and the four measurements averaged.

3.3 Results and Discussions.

3.3.1 Laboratory-Scale Experiments

The laboratory-scale experiments produced a wide array of deliming times ranging from 210 minutes to 30 minutes. Generally the thinner the cattle hide the faster the deliming in both the ammonium sulfate deliming experiments and in the CO_2 deliming experiments. Figure 3.1 shows the deliming times, and as can be seen, the fastest CO_2 deliming experiment on thick hides (thickness > 15mm) was experiment number 11 with a 75 minute deliming time compared to ammonium sulfate on heavy hides at 65 minutes.

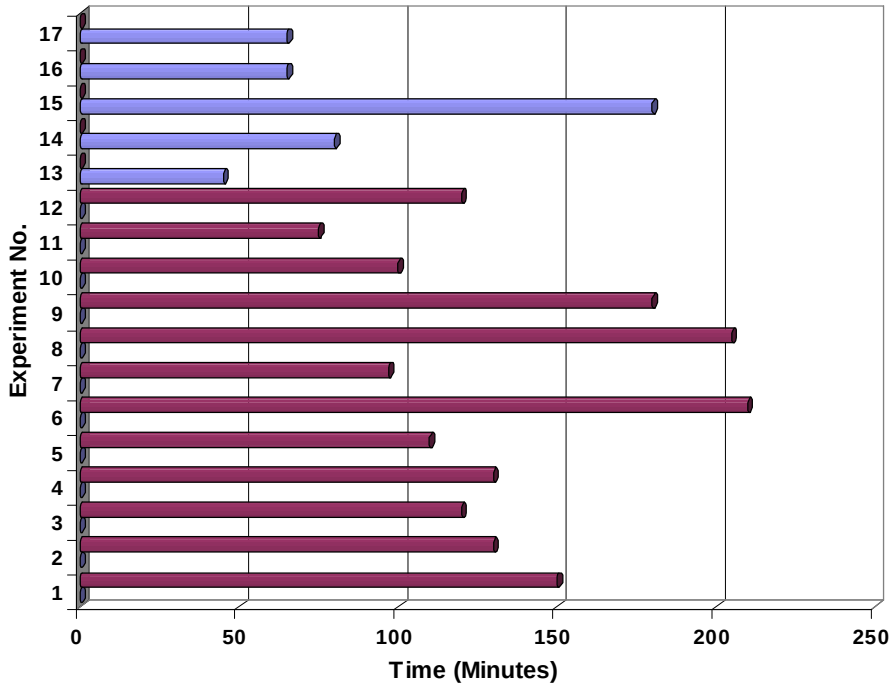

Figure 3.1 Comparative deliming times for all deliming experiments associated with the laboratory scale experiments. The blue bars show all ammonium sulfate deliming experiments and the maroon bars show the CO_2 deliming experiments. The number on the y-axis corresponds to the experimental protocol outlined in Table 3.1.

Interestingly, the ammonium sulfate experiment number 15 was an exceedingly long experiment, due to the fact that the ammonium salt was quite dilute (because it had a higher water quantity). The effect of temperature was also quite dramatic in that some of the experiments with temperatures of 38°C produced short deliming times. Experiment 6 had a long deliming time because of no rotation to assist CO_2 penetration.

None of the hides that were simultaneously bated and bleached had impaired quality. The overall deliming time of these bated experiments were exceedingly short (due to the overlap of bating and deliming for 30 minutes). The deliming had to be one third complete, proportionally, before the bating was started (as determined by delime mapping).

It was decided that the CO_2 experiment number 11 was to be repeated on a pilot-scale. The manner in which this was done is outlined in section 3.3.2.

3.3.2 Pilot-Scale Experiments

The pilot-scale experiments were also a success in that the four sides that were produced appeared in the delimed state to be of very good quality. The CO_2 delimed cattle sides as in all deliming experiments were extremely clean and had a very pleasant odour. The conventionally delimed sides had a strong ammonia smell and a grey cast. The CO_2 delimed sides had a very clean, cream colour and good softness with excellent thumbprint retention (thumbprint retention is an indicator that the bating process has removed the interfibrillary proteins, and the resulting structure is spongy). The deliming/bating waters had significantly different colour differences. The CO_2 deliming water was light brown and milky and had a sweet smell to it. The conventional deliming had a grey colour and was milky but had a pungent ammonia smell.

The analysis of effluents from the two drums is shown in Table 3.2.

Table 3.2 The effluent and hide wet chemistry measurements for both conventional (ammonium sulfate) deliming and for the CO_2 delimed hide.

Parameter	*Ammonium Sulfate*	*CO_2 Deliming*
Ammonia (mg/L NH_3-N)	32.8	9.3
Sulfate (mg/L SO_4^{2-})	124.4	63.4
Chromium Content (%)*	3.87	4.12
Calcium Content (mg/L)*	32	26
Shrinkage Temperature ($^{\circ}$C)*	103.5	105.0

The experiments were run according to the processes outlined in Appendices 3 and 4 and pH profiles obtained can be seen in Figure 3.2. The time plots were recorded and % deliming measured and plotted in Figure 3.3. The comparative deliming times are also shown in Figure 3.3. The CO_2 delimed hides, which were of a medium substance (12mm), took 135 minutes to delime plus a further 30-minute bating. The ammonium sulfate delimed hides took 95 minutes to delime but then had an additional 60-minute bating time. The overall times are also shown in Figures 3.2 and 3.3.

* Indicates those tests that were done on hide samples. All other tests were done on the effluent.

The interesting result from these graphs was firstly that the time difference between CO_2 deliming and conventional (ammonium sulfate) deliming on medium hides was minimal. Medium hides can be defined as wet-salted cattle hide with a mass between 18kg and 25kg. The pH profiles also show an interesting point in that the CO_2 delimed hides were placed into water, pre-sparged with CO_2 (the pre-sparge pH of 4.5 is not shown) but the pH of the water dropped very rapidly from pH 11.8 to pH 7.2 and then rose to 7.7 after two minutes. The pH then slowly dropped down to end up at pH 6.7. Interestingly the ammonium curve does not show such a rapid drop as mentioned in other literature (Klaasse, 1990).

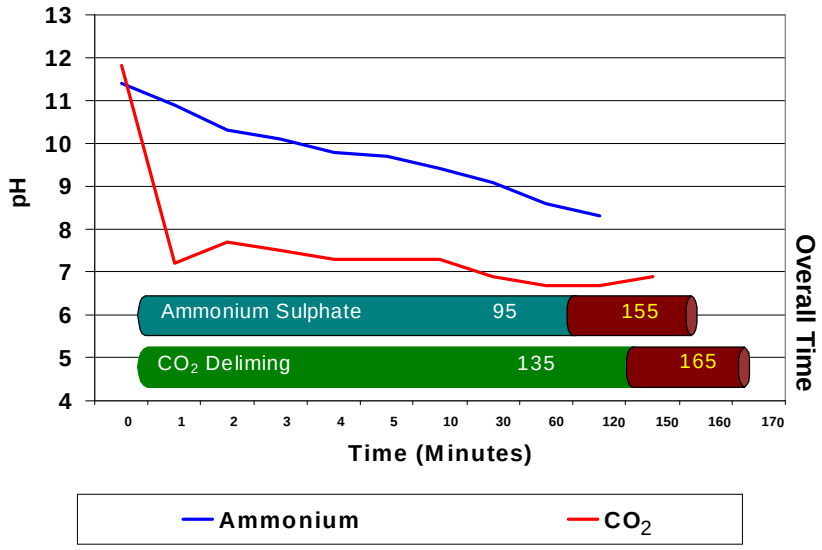

Figure 3.2 The pH profiles and overall delime times of the pilot-scale experiments of ovine material showing deliming and bating times (maroon) and ammonium sulfate (teal) and CO_2 deliming (green).

The rapid deliming times with CO_2 that can be seen in this experiment may be due to a proportional amount of CO_2 acidity, in a manner similar to ammonium sulfate acidity. The pre-sparging and sodium bicarbonate may be in slight excess but the fact remains that that a good reservoir of bicarbonate protons does drop the pH in a manner similar to ammonium salts.

From Figure 3.3, it can be seen that the speed at which lime was removed by ammonium sulfate was not mimicked by CO_2 deliming. The initial deliming was

however very similar, which was reassuring. This graph shows that CO_2 was better at deliming initially, but does slow down with time. One may find that the initial reservoir of CO_2 acidity was used up and the delivery of gas is not fast enough. A possible method in increasing delivery will be discussed later.

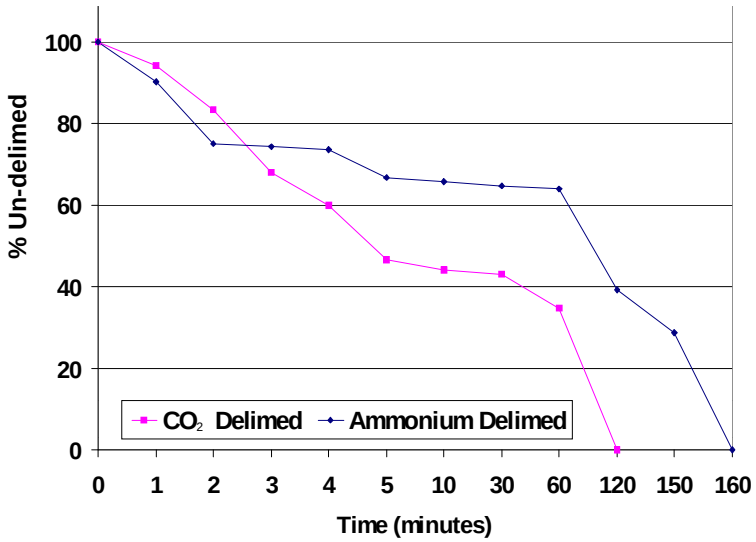

Figure 3.3 The deliming maps for pilot-scale ovine experiments shown here give the proportional lime removal over time. The first 5 minutes are very clearly shown, to closely gauge the initial deliming effect.

The CO_2 delimed wet blue leather was very blue in colour. The blue colour could be correlated to slightly higher chromium content. The final dye colour was also darker in the crusted leather as compared to the conventional delimed samples. The leather grain break was tight and the leather felt normal. The results for the physical properties can be seen in Table 3.3.

Table 3.3 The physical properties of the leather after crusting shows the physical differences between CO_2 delimed sides and ammonium sulfate delimed sides.

Parameter	***Ammonium Sulfate***	***CO_2 Delimed***
Lastometer (kg)	75	81
Tensile Strength (N/mm^2)	16.1	15.3
Tear Strength (N/mm)	68	73

There appeared to be very little difference between the experimental and control values as far as physical parameters are concerned. The leather generally seemed to be of a very good quality.

3.4 Conclusions

Small laboratory-scale experiments were carried out in a high-pressure vessel to determine whether the optimised conditions outlined in Chapter 2 could be applied to real limed hide pieces in a deliming process. Of the parameters investigated - rotation, pre-sparge, water quantity, bicarbonate addition, pressure, and simultaneous bating and bleaching – all had some influence on the deliming times, but pressure and a ready supply of carbonates (bicarbonate) gave the most impressive times.

The longest time for ammonium sulfate deliming could be as a result of gradual addition of ammonium sulfate (mimicking gradual addition of CO_2 gas). Thirty-eight degree Celsius deliming by in large produced the shortest deliming times. Experiment 6 with a lack of motion produced long times indicating the need for motion.

In the pilot-scale experiments, the CO_2 deliming of cattle sides produced very competitive results (165 minutes versus 155 minutes, CO_2 versus ammonium sulfate, respectively). Effluent parameters measured after the pilot-scale experiments showed significant reductions in ammonia and sulfate. The chromium content and shrinkage temperature of the wet-blue hides were very comparable to conventional deliming.

Physical properties of leathers from the pilot-scale experiments showed no significant deviation from the conventional deliming.

It can be concluded thus, that CO_2 deliming with bicarbonate addition and simultaneous bating/bleaching may be sufficiently rapidly operated to warrant proceeding to a semi-technical scale.

CHAPTER 4

ACCELERATED CO_2 DELIMING: SEMI-TECHNICAL SCALE STUDIES

4.1 Introduction

After obtaining the results from the optimisation experiments (Chapter 2) and the pilot experiments (Chapter 3), the deliming of sheepskin seems comparable to conventional ammonium salt deliming. Sheepskin is of a much lower substance than unsplit cattle hide. As a result the deliming times (at a pilot scale) must be equal to and must have comparable overall costs and consistent leather quality, to ammonium sulfate deliming.

Lime, specifically calcium, left in the hide results in firmer leather and sometimes the formation of calcium carbonate crystals, commonly known as lime blast or lime speckle (in sheepskin). Calcium carbonate forms from the interaction of CO_2 (in the atmosphere) with lime.

$$\mathbf{Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow CaCO_{3(s)}} \qquad \mathbf{(4.1)}$$

The calcium carbonate ions are insoluble and can crystallise with ease at the very high pH values, which may be present in the skin. The reversal of calcium carbonate to calcium bicarbonate is theoretically possible with acidification of the pelt. Acidification results in the conversion of all carbonate species to bicarbonate species. It is not clearly understood what the extent is of the damage that carbonate crystals cause to the grain enamel. Up-scale from laboratory-, to pilot-, to semi-technical-scale experimentation, aimed at determining deliming times, leather quality and levels of lime blast, is necessary. Effluent discharge levels at these scales are important if CO_2 deliming technology is to be accepted by the industry.

4.2 Materials and Methods

4.2.1 Experimental Protocol

To improve the efficiency of the deliming process a number of changes to the process could be made. It was finally decided that six of the most cost effective changes to the CO_2 deliming process would be carried out and then a semi-technical scale experiment would be run to evaluate the viability of the optimised process. The following experiments were planned:

1. Ammonium sulfate only;
2. CO_2 only;
3. CO_2 and bicarbonate;
4. CO_2 and formic acid;
5. CO_2 and calcium chelators;
6. CO_2 with simultaneous bating and bleaching.

4.2.1.1 Ovine Optimisation Experiments

Fifteen raw ovine skins, with an average limed thickness of approximately 3.0 to 4.5 mm were processed for each optimisation experiment in a wooden drum (1.5 x 1.0-m diameter). Four of the skins were selected after liming, sided, marked and matched. Two of the matched sides were delimed in a control experiment. The two matched experimental sides were added to the other eleven skins and the new weight taken. The experimental skins were then processed for deliming according to the regimes laid out above. The processes for the different regimes differed only in the deliming step. The processing up to the deliming stage is given in Appendix 2. The different deliming steps are given in Appendices 3 to 8. After the deliming steps the skins were tanned according to two types of tannage, vegetable and chromium tannage (to see the effect of CO_2 deliming on these types). The types of tannage were evaluated in two drums simultaneously (Appendices 9 and 10). The matched sides after the control and experimental processes were placed together and two of the matched pairs went for chromium tanning and two pairs went for vegetable tanning (with the other eleven skins).

The regime where ammonium sulfate was used alone did not however, have a control process and all the skins were taken through for vegetable tanned material (a fair representation of the ammonium sulfate regime was incurred, as they were the control processes for the other experiments).

The control process was similar to the experimental process, in that the skins after siding, marking and matching were put into the deliming stage as in regime one (Appendix 3). The sides were then placed together with their original pair and then tanned according to the two tannages (Appendix 9 and 10).

After the six experiments had run and the results from those experiments compared, an optimised process was run on a small scale (15 skins) to check for the efficacy of the new process (Appendix 11).

4.2.1.2 Ovine Semi-technical Scale

A production lot of 200 ovine skins was then processed according to the optimised process (Appendix 11). The 200 skins averaged 1.5 to 3.0 mm and were delimed in a 2 x 2.5m wooden drum, as if they were in normal production. The deliming time of the semi- technical experiment was then compared to the deliming time of ammonium sulfate as experienced in industry (average 45 minutes). Added to the bating time (45 minutes) the total delime/bate time in industry is on average 90 minutes. The 200 skins were then processed further using a chromium tannage process. The wet-blue skins were sampled and then crusted into undyed nappa.

4.2.1.3 Bovine Optimisation

The optimal conditions that worked for the ovine skins were adapted and tried on bovine hides. The following regime was used:

1. Split hides, bicarbonate (Appendix 12);
2. Split hides, bicarbonate and CO_2 purging (Appendix 13);
3. Unsplit hides + bicarbonate (Appendix 14);
4. Semi-technical production of split hides (Appendix 15).

The initial optimisation experiments of the hides used three hides that were lime-split at a tannery close to LIRI Technologies. The conditions that worked on split hides were then applied to unsplit hides. These conditions were then used in a semi-technical experiment using fifteen split hides. The deliming time of the semi-technical CO_2 experiment was then compared to the deliming time of ammonium sulfate as experienced in industry (average 30 minutes). Added to the bating time (30 minutes) the total delime/bate time in industry is on average 60 minutes. The 15 hides were then processed further using a chromium tannage process. The wet-blue hides were sampled and then crusted into dyed softee leather (Appendix 18).

4.2.2 Logistics of Gas Supply

Afrox Ltd. supplied the CO_2 gas used in this project in gas cylinders containing 32kg gas in the liquid form. The gas cylinders were connected in a pair manifold for the optimisation experiments. A five-cylinder manifold was used for the semi-technical scale experiment. A manifold served the purpose of ensuring a low enough draw-off rate to ensure the regulators did not freeze.

The regulators were standard CO_2/Argon type regulators with a cylinder pressure gauge and a crude flow meter gauge. The manifold led into a single half-inch oxygen hose, which led into the wooden drum through the hollow axle. The gas line was not present prior to deliming and the line was removed from the hollow axle after the experiment. The drum was well ventilated to ensure that excess pressure did not build up in the drum. The area in the immediate vicinity of the drum was well ventilated to prevent CO_2 build-up (which could be potentially hazardous).

To determine the amount of gas to be pumped into the drum the skins were weighed prior to deliming. The skin weight was then used to calculate a 2.5% (m/m) offer of gas to the skins over a fifty-minute period using Equation 4.2.

$$\frac{[g \times W] \times 0.55}{T} \times 10 \qquad (4.2)$$

Where g is the gas offer (%, m/m), W is the skin total weight in kg; T is total gas deliming time in minutes. The units were expressed as litres (L) of gas per minute

4.2.3 Delime Mapping

The progression of the deliming process was mapped using both the pH of the water and the pH of the cross-sectional area of the skin itself. The pH of the water was monitored in the same manner as the pH of the effluents (see below). Testing the pH of a leather-cut out of the butt and neck region of the skin gave the pH of the cross-sectional area. The pH indicator phenolphthalein (end point pH 8.3) was added to the cut to determine the pH gradient through the skin. The progression of the colourless front was measured using a Vernier caliper. A reference measurement (the total skin thickness) was also measured in the same locale as the front measurement. A ratio of the two measurements was then calculated and plotted over time. Deliming time plots could then be used in the generation of deliming maps.

4.2.4 Effluent Analysis

Conductivity, ammonia, sulfate and calcium levels were determined as outlined previously.

4.2.4.1 Optimisation experiments

The production effluents were sampled at different stages so that a comparison could be made between the control and the experiments. The samples were taken in every regime at the following times: after the first deliming wash, after the second deliming wash, after the deliming/bating step and after the cold wash. The effluents were analysed for the following parameters: ammonia, sulfate, pH, conductivity and chemical oxygen demand (COD). The methods used were as laid out below.

During deliming in the optimised small-scale process, samples of the effluents were taken at ten-minute intervals, to measure the levels of soluble calcium and the change in pH. The effluents from the optimised process were also analysed for sulfides.

- **Chemical oxygen demand (COD)**

The COD of the effluent was analysed according to American Public Health Authority (APHA) standard methods (APHA, 1998). COD determinations were carried out on unfiltered samples. Aliquot volumes varied according to the effluent COD but were replicated to minimise error. The determination was standardised with a duplicate blank and the normality of the ferrous ammonium sulfate was standardised on a batch-to-batch basis, daily.

4.2.4.2 Semi-technical Scale

The effluents produced were monitored in the same manner as the optimisation experiment effluents, in that pH, conductivity, ammonia, sulfate and COD were measured.

4.2.4.3 Bovine Hides

The effluents produced from the bovine processes were sampled only after the deliming stage as it was shown with the ovine experiments that there was no significant difference between the data of the pre-washes of the control and the experimental samples. The last wash was also sampled. The effluents were sampled for pH, conductivity, ammonia, sulfate and COD.

4.2.5 Wet Leather Analysis

4.2.5.1 Optimisation experiments

The semi-processed leathers were analysed for chromium content, shrinkage temperature and residual calcium content. The leathers were also examined subjectively for unusual chromium stains and unevenness. The optimised process was run on a small scale to check for efficacy and during that experiment, samples were taken at 10 minute intervals to check for calcium removal and also the total alkalinity and pH. The

chromium content, residual calcium and shrinkage temperature determinations of the leather were carried out as outlined in Chapter 3.

4.2.5.2 Semi-technical Scale

The leather produced was analysed in the same manner as the optimisation leathers in that the chromium content, shrinkage temperature and the residual calcium was analysed.

4.2.5.3 Bovine Hides

The leather produced was analysed in the same manner as the optimisation leathers in that the chromium content, shrinkage temperature and the residual calcium were analysed. All chemical tests performed, that yielded results, were analysed statistically to measure the significance between the control values and the experiment.

4.2.6 Electron Microscopy

Wet-blue leather samples from the skin experiments and the bovine experiments sampled from the butt area were examined in the Rhodes University Electron Microscopy Unit. The samples were photographed after preparation and viewing using standard techniques according to Cross (2001). The microscope used was a JSM-840 scanning electron microscope (Jeol, New Jersey) at 10kV acceleration voltage. The samples were viewed at two different magnifications (x25 and x200).

The electron micrographs were firstly examined for obvious differences. Secondly, the micrographs were randomly numbered and split into groups, namely the CO_2 delimed group and the ammonium salt delimed group. Then, blindly the individual groups were graded and subdivided into fibre opening subgroups; loose, normal and tight. 5 individuals performed blind grading. The micrograph numbers selected in those subgroups, for each person was recorded. Statistical independence for each subgroup was then analysed using a chi-squared statistical test.

4.2.7 Light Microscopy

The wet-blue skins from the optimisation experiments were sampled from the butt area and the samples stored in separate plastic bags until histological work could be carried out. The samples were orientated so that the hair follicle direction would be parallel to the plane of section. The samples were cryogenically sectioned using a microtome, into 90-micron sections. The sections were then dehydrated in an alcohol gradient (50, 70, 90 and 100%). Each alcohol step was carried out for 2 minutes. The dehydrated sections were then placed into xylene for 5 minutes. The sections were floated onto slides, orientated and mounted using a standard mountant and a cover slip.

The slides were then examined and photographed on a light microscope at 100x magnification using grey light filters and a polarising lens. The micrographs were examined to see if any looseness was apparent.

4.2.8 Crust Leather Testing

The semi-processed leathers were then crusted according to either Appendix 16, 17, 18 or Appendix 19 depending on the type of tannage. Samples were clicked out of the butt area using standard knives and a clicking press. The samples were conditioned in the constant environment room at 20^{o}C, 65% relative humidity for 48 hours. Where necessary the sample thickness was measured using the IULTCS (2000) standard method 4 (IUP 4). Physical tests carried out on the production leathers were tested as outlined in Chapter 3 for lastometer, tensile and tear strength.

4.2.8.1 Subjective Testing

The crusted leathers produced from all experiments were evaluated subjectively by LIRI Technologies' members of staff unmarked as blind samples for the following parameters: break, handle, grain cleanliness and other anomalies. The matched sides were also analysed as blind samples to evaluate the same parameters.

- **Break**

The degree of looseness of the junction between the corium minor and the corium major was evaluated to determine if there was any significance between the matched sides. All leathers were examined to determine if there was break consistency. The degree of break was assessed using the Shoe and Allied Trade Association (SATRA) break scale PM 36 (SATRA, 2001).

- **Handle**

The relative handle of the leather was evaluated to determine the firmness, fullness, degree of opening and drape in the matched sides. All leathers were examined to determine if there was handle consistency.

- **Grain cleanliness**

The surface of the leather was examined to determine the presence or absence of scud, surface stains or damage, in the matched sides. All leathers were examined for grain cleanliness.

- **Other**

The presence of any other leather anomaly was screened to determine if the CO_2 deliming process incurred any damage. Smell was often evaluated here, as it was believed that there could be a significant difference between the ammonium salt and CO_2 delimed skins/ hides.

4.3 Results and Discussion

4.3.1 General Results

4.3.1.1 Ovine Optimisation

The optimisation experiments were conducted and the difference between the deliming times, skin condition and effluent specifications noted. The matched skin experiments were carried out meticulously to ensure that direct comparisons could be made. The

ovine deliming yielded skins that, in the pelt state, showed no comparable difference between control and experimental conditions. The process times for the six experiments, although different, were however acceptable from a production point of view. The optimised conditions were then scaled up to a semi-technical level.

4.3.1.2 Semi-technical Scale

The skins produced were very acceptable from a subjective perspective. The process environment, compared to control conditions was safe and pleasant to work in. Direct feeding of the deliming chemicals into the drum was easy and efficient. Delivery of the gas to the tannery was trouble-free and relatively easy.

4.3.1.3 Bovine Experiments

The semi-technical conditions that were generated in the ovine experiments were then converted into conditions suitable for split hide deliming. The hides were delimed in a very efficient and effective manner. The control matched sides and the experimental sides were very similar except for the fact that the control pelt had a relatively strong ammoniacal smell compared to the experimental pelt. The experimental pelt was also brighter and whiter compared to the control. The success of the two bovine optimisation experiments allowed the semi-technical run of CO_2 deliming. The larger batch seemed to delime more efficiently than the laboratory and pilot scale. The increase in efficiency could have been due to the higher mechanical action present in the drum. The improvement in efficiency seen in the lime-split hides was not however matched in the unsplit hides. The unsplit hides were delimed in a manner similar to the lime-split hides in that gas purging of the headspace was performed. Gas purging was deemed to be highly successful in lime-split hides and partially successful in unsplit material.

4.3.2 Logistics of Gas Supply

One of the factors identified that could increase the efficiency of deliming was gas purging. In this instance, the scenario was equivalent to that found in the beverage industry. In this case if an atmosphere with a low partial pressure of CO_2 (air) was placed over a solution with a relatively higher partial pressure, Henry's gas law states that the CO_2 will move from the solution into the atmosphere. The injection of gas into

such a solution/system often results in poor mass transfers. In the beverage industry to ensure drinks are carbonated in an efficient manner, the injection lines are purged free of air. Hence the partial pressures for CO_2 in the atmosphere are maintained favourable for carbonation.

The cylinder manifold in parallel ensured that draw off was low per cylinder and this ensured that the regulators did not freeze up. Large tanneries requiring quantities of gas for normal production would preferably go for bulk tanks of the appropriate size. Heaters inserted on-line would ensure vaporisation did not chill the gas lines. The drum purging that was done initially places considerable strain on the delivery of gas to the drum, as the flow was relatively high, i.e. the majority of the gas offer was delivered during purging ($\geq$20 L/min.). The rest of the gas offer was delivered at a very low flow rate to maintain positive pressure inside the drum (1-2 L/min). The low flow rate during the deliming process places no demands on the gas delivery system and no freezing should occur.

The average gas usage (un-optimised) was about 3.44% (m/m). A tannery would undertake individual optimisation of gas usage and the system where the drums were purged first would ensure that gas usage was totally dependent on that individual process. The system which CO_2 deliming creates is unique. A conventional ammonium salt process would be optimised to a minimum critical level (*viz.* lower than this level) and the process would not work. CO_2 deliming would, however, pump in the specific amount of gas for that process, until deliming was completed. The quantity of gas thus would vary. Semi-technical experiments where larger quantities of skins were delimed resulted in lower gas utilisation, i.e. on average the usage was in the region of 2% (m/m, un-optimised).

Once the deliming map was known, the gas was turned off fifteen minutes before the end point. The utilisation of the gas would thus be greatly reduced. The ability to turn off gas supply but still continue with deliming would thus be another area of optimisation.

An acid taste in the mouth was present at the end of a deliming run, which suggests the presence of excess CO_2. Ventilation during deliming should therefore also be a concern for the tanner. A drum full of pelts and gas being drained ensures that the surrounding area is full of CO_2. CO_2 is heavier than air and upon draining, unused gas fills any area, if ventilation is poor.

The other noticeable gas problem was the formation of hydrogen sulfide gas in the drum headspace. High levels were detected in the optimisation experiments and allowances in process design had to be made to ensure that H_2S did not form.

The purging of drums was seen as the step forward in decreasing deliming times. Results seen in the optimisation experiments indicated that delivery up front of a percentage of gas resulted in similar deliming times to the control, being experienced. It made sense that if an initial offer of gas, comparable to an offer that was made of ammonium salts in conventional deliming, was injected, then delivery efficiencies could improve the overall efficiency.

4.3.3 Delime Mapping

4.3.3.1 Ovine Optimisation

Figure 4.1 shows the progression of the six optimisation experiments in the form of delime time plots. It can clearly be seen that the plot for CO_2 only changes at a rate considerably slower than the plot for ammonium salts only.

The ammonium salt time was completed in 45±7.3 minutes. The fastest CO_2 deliming time was CO_2 and bicarbonate (Experiment 3, see Section 4.2.1) in 60 minutes. The deliming maps were then added to a 45-minute bating time and delime maps formulated (Figure 4.2). A standard delime time denoted by a broken blue line was then drawn (Figure 4.2).

The delime time of the different options could then be compared against the standard time. Based on this and the results from the quality of effluent and leather, the process seen in Appendix 11 could then be formulated and semi-technical scale batches run. A

delime map for the semi-technical scale batch was superimposed onto Figure 4.2 to give the new CO_2 deliming method comparison.

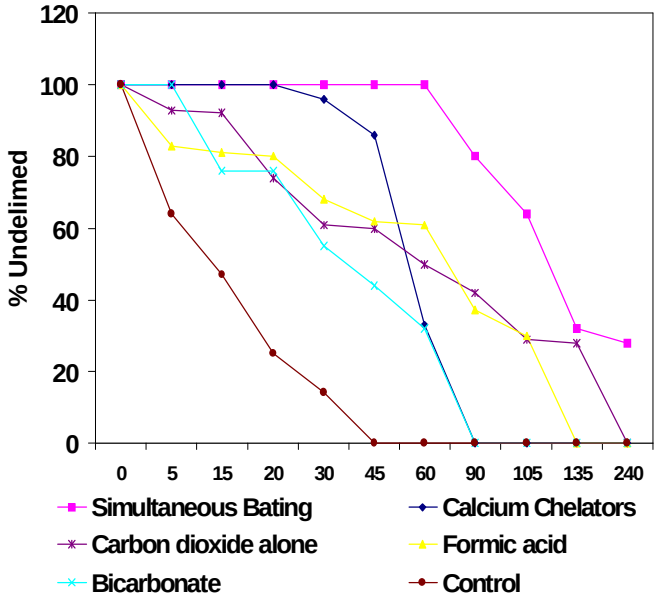

Figure 4.1 A delime map showing the progression of deliming (measured as effective removal of lime as a percentage of total thickness) over time for ovine skins. Five experimental options were compared against the control (ammonium salts).

Quite clearly the use of calcium chelators to assist CO_2 deliming was well below average. The simultaneous bleaching and bating provided a time that was above average. The mean time for all five of the optimisation experiments was 129±75 minutes, which was significantly different from the control.

4.3.3.2 Semi-technical Scale

The deliming time for the process run in Appendix 11 (semi-technical batch) was the fastest deliming time that the ovine skins had been processed using CO_2 deliming (50 minutes). The time for the semi-technical process was 10 minutes faster than the control, which was not significantly different and was considered acceptable.

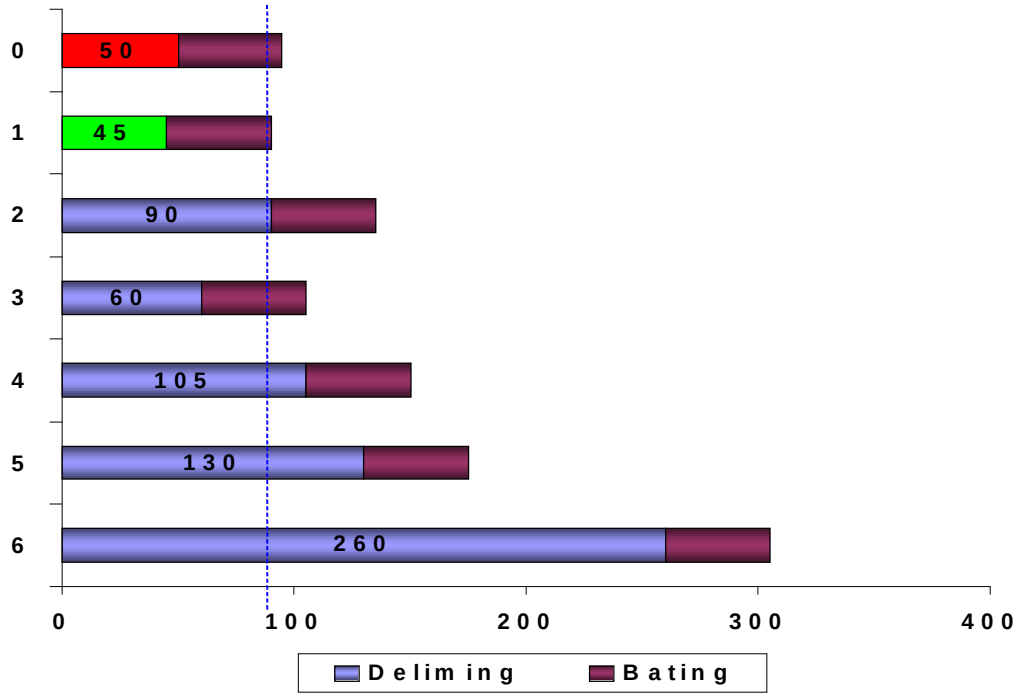

Figure 4. 2 Delime time plot of the different ovine optimisation experiments. The overall deliming times (blue or highlighted), includes 45 minutes bating (purple bar). The standard delime time - 90 minutes (blue broken line) indicates an acceptable time. Highlighted bars; 0 = red indicates the semi-technical scale batch times; 1 = green indicates the ammonium salt control. 2 = CO_2 only, 3 = CO_2 and bicarbonate, 4 = CO_2 and simultaneous bating and bleaching, 5 = CO_2 and formic acid, 6 = CO_2 and calcium chelators.

4.3.3.3 Bovine Experiments

The deliming maps generated in the bovine experiments bore very similar results to those seen in the ovine experiments (Figure 4.3). The progression of the deliming front through the cross-section of the hide was slow for CO_2 in the initial stages, but the overall cut was delimed in a time not that different from the control (about 15 minutes slower).

The rate of deliming in the semi-technical batch was very comparable to the rate of change in the control. The initial drop off in the first five minutes has been the biggest advantage of ammonium salts in previous deliming experiments conducted at LIRI Technologies. With the addition of bicarbonate and the provision of an initial gas offer, this allowed the CO_2 process to become highly competitive. The difference between purged bovine hides and non-purged hides was quite significant. Figure 4.3 shows clearly that the rate of the deliming front was much slower in non-purged runs versus purged runs.

The standard bating time of lime-split hides was taken as 30 minutes and together with this time, the delime maps could be constructed using the cut-off times from Figure 4.3. Figure 4.4 is a deliming map of the various bovine experiments. The standard time of ammonium salt deliming of lime-split hides, although technically 60 minutes, is closer to 70 minutes in industry. The mean control deliming time was however 35 ± 5 minutes

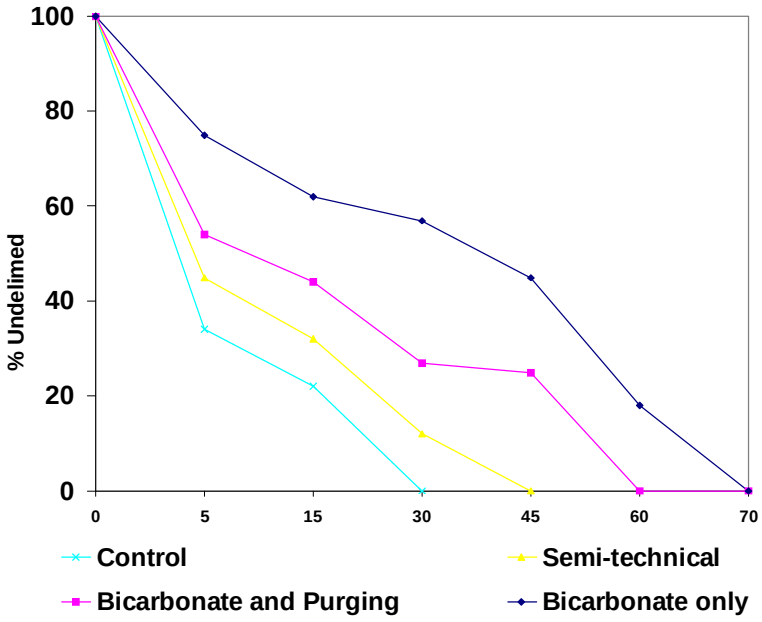

Figure 4. 3 A delime map showing the progression of bovine deliming over time (measured as effective removal of lime as a percentage of total thickness). The two experimental options (CO_2 and the option listed above) have been compared against the control (ammonium salts) and a semi-technical batch.

and the semi-technical batches' time was 35 minutes at 25% removal (when bating was commenced).

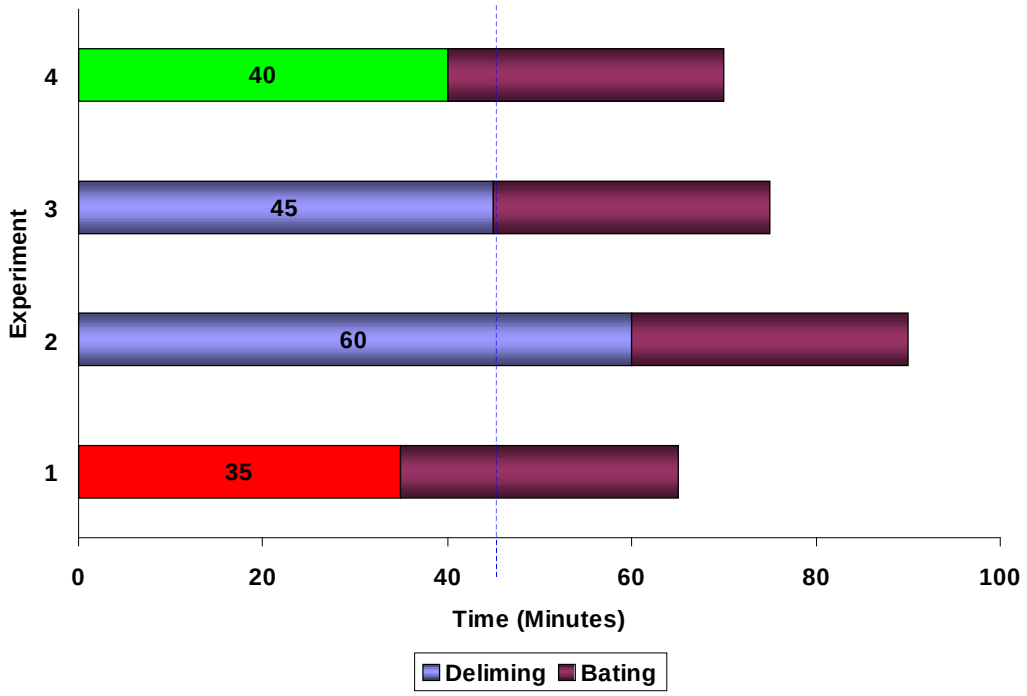

Figure 4. 4 Delime time plot of the different bovine experiments. The overall deliming times include 30 minutes bating as well (purple bar). The standard delime time (blue hashed line) indicates an acceptable time. Highlighted bars; 1= red, which indicates the semi-technical scale batch times; 2 = CO_2/ bicarbonate; 3 = CO_2/ bicarbonate/ purging. and 2= green, which indicates the ammonium salt control.

4.3.4 Effluent Analysis

4.3.4.1 pH

In the optimisation experiments, the analysis of the deliming water pH showed that there was a significant difference between conventional deliming and CO_2 deliming (Figure 4.5). The CO_2 deliming pH was a lot lower than the control.

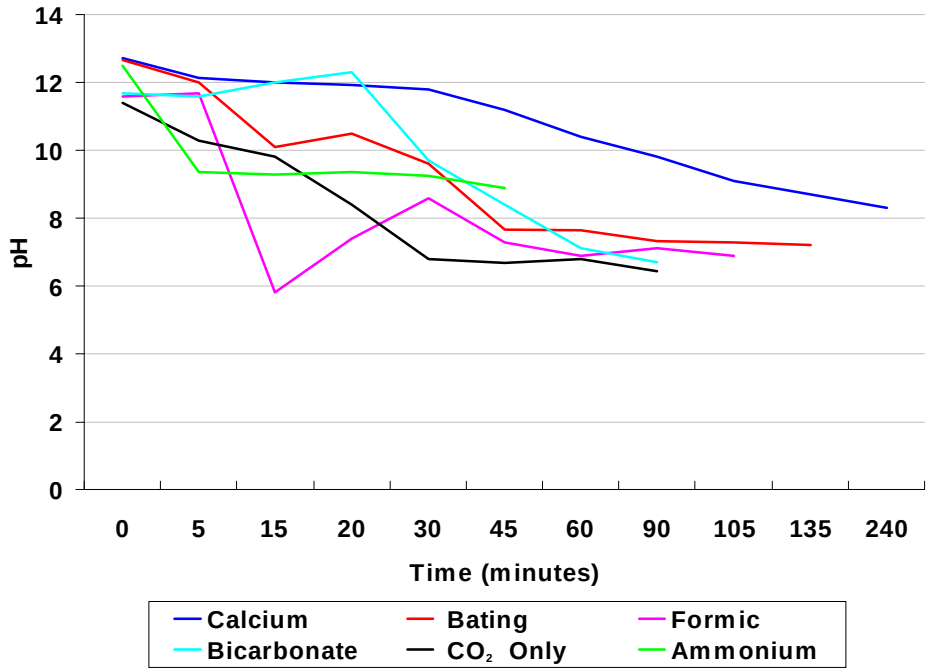

Figure 4. 5 The deliming water pH values for the various processes, where 'calcium' is the CO_2 gas and calcium chelators, 'bating' is CO_2 gas and simultaneous bating and bleaching, 'formic' is CO_2 and formic acid, 'bicarbonate' is CO_2 and bicarbonate, 'CO_2' is CO_2 gas by itself, and 'ammonium' is the ammonium salt control.

The control shows a typical deliming curve starting at pH 12.3 and ending at 8.4 with a gentle rate of decrease. The only curve that matches that rate of decrease was the simultaneous bating and bleaching and CO_2. The CO_2 gas and formic acid drops the pH very rapidly. Most of the CO_2 deliming processes end with a final pH around 7.5. The drop-off time, if CO_2 is going to be successful, has to emulate the drop-off time for the control. It was found that the semi-technical ovine and semi-technical bovine runs after optimisation did this, hence similar deliming time to conventional deliming, with the exception that the CO_2 processes end up with a lower final pH (Figure 4.6).

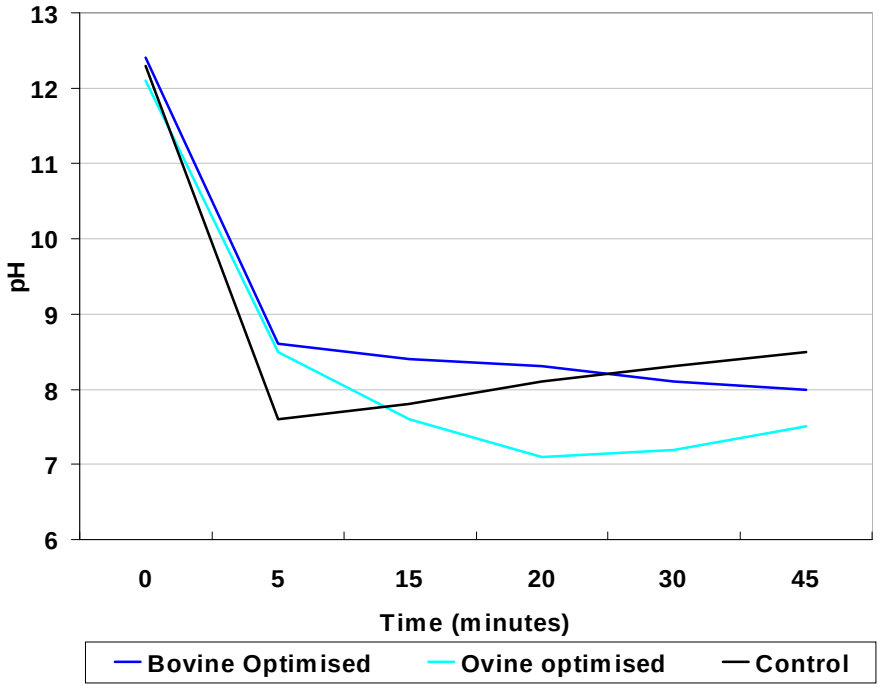

Figure 4. 6 The deliming water pH values for the various processes, where 'bovine optimised' is the lime-split hides delimed using CO_2 gas and bicarbonate, purged, on a semi-technical scale. 'Ovine optimised' is ovine material delimed using CO_2 gas and bicarbonate on a semi-technical scale. The control is the mean figures, i.e., average of the two ammonium sulfate deliming control runs for both the deliming experiments.

The drop-off rates for the optimised experiments mimicked the control drop-off and this means that on thinner material the deliming time should be the same. The lower pH value of the CO_2 experiments was more of a concern though. This has two implications, namely that the evolution of H_2S gas was higher and that a slightly different bating regime should be used (see Appendix 11). pH plays a huge role in solubility of CO_2 in that the faster the pH decreases the better the deliming. This can be explained by the fact that at a neutral pH the bicarbonate ion is present (see Figure 1.4), which ensures faster removal of lime, due to the better solubility product of the calcium bicarbonate as opposed to calcium carbonate. The diprotic carbonic acid, and monoprotic bicarbonate, present at a lower pH, also allows better proton attack of the hydroxide in lime (as opposed to carbonate, which is hydrogen free). No explanation for the lack of time decrease in formic assisted deliming can be offered.

The addition of bicarbonate to the system rapidly shifts the carbonate equilibrium to the protonated carbonate species, which can then remove lime. Purging the drum ensures that the CO_2 partial pressure facilitates a high dissolution rate of the gas being injected in the drum.

4.3.4.2 Conductivity

The conductivity results from the ovine optimisation experiments showed that there was almost a two-fold decrease in conductivity from the control (ammonium sulfate) to any of the CO_2 processes (Table 4.1).

The conductivity in the pre-washes and in the cold wash was not significantly different. The conductivity is a measure of inorganic salt content and it seems that ammonia impacts conductivity more than any other of the CO_2 experiments. Conductivity is often used as an indicator by authorities concerning compliance to effluent specifications.

Table 4.1 A comparison of the conductivity values of the various deliming waters in mS/m for the optimisation experiments.

Experiment	*Conductivity (mS/m)*
CO_2 Only	1050
CO_2 and bicarbonate	580
CO_2 and formic	730
CO_2 and simultaneous bating and bleaching	810
CO_2 and calcium chelators	840
Control	2140

The ovine semi-technical scale, the bovine optimisation and bovine semi-technical scale experiments yielded similar results for conductivity (Table 4.2). The values for the ovine experiments were, however, significantly lower than any of the bovine values. The bovine conductivity again showed the trend that the control was higher than the CO_2 delimed experiments (two and a half-fold). Sulfate impacts the conductivity in a manner significantly higher than the carbonates can. Carbonates are also easier to remove from the system than sulfate or chloride.

The conductivity value for the optimised ovine experiment (semi-technical scale) was lower than the value for other ovine experiments probably due to the larger scale.

Table 4.2 A comparison of the conductivity values in mS/m of the deliming waters for the ovine semi-technical scale (CO_2 optimised) and the bovine experiments.

Experiment	*Conductivity (mS/m)*
CO_2 Optimised (Ovine)	480
CO_2 Optimised (Bovine)[a]	790
CO_2 Optimised (Bovine)[+]	830
Control	2500

4.3.4.3 Ammonia

Table 4.3 shows all the ammonia values of the experiments, represented as mg/L NH_3–N. The ammonia value is affected in two manners, namely ammonia derived from cleaved amide groups from the hide/skin itself, or from the addition of some ammonium containing salt. In previous CO_2 experiments run elsewhere the temptation has always been to add some ammonium salts. In this project no ammonium salt was added with the CO_2 gas. Hence the seven and a half-fold reduction in ammonia levels between the control experiments and any of the CO_2 experiments.

Table 4.3 A comparison of the ammonia values of the various deliming waters in mg/L NH_3–N for all experiments.*)*

Experiment	*Ammonia (*mg/L NH_3–N)
CO_2 Only[*]	8.7
CO_2 and bicarbonate[*]	7.0
CO_2 and formic[*]	2.0
CO_2 and simultaneous bating and bleaching[*]	1.5
CO_2 and calcium chelators[*]	10.5
Semi-technical[*]	7.5
Bovine Optimisation	13.5
Semi-technical[b]	12.0
Control[++]	70.5

[a] The bovine experiment using bicarbonate and no CO_2 purging

[+] The bovine experiment using bicarbonate and CO_2 purging

[*] Ovine experiments

[b] Both bovine experiments

[++] Mean representation of bovine and ovine values. Bovine ammonia control value stood at 8050 mg/L NH_3–N.

The ammonia reduction from conventional deliming was significant, as the levels of ammonia in modern tanneries being released into effluents are high. Pressure is now being placed on tanneries to reduce values to acceptable levels. High biological oxidation demand values are synonymous with high ammonia levels (Feikes, 1988).

The high ammonia content present in drums also places the safety of drum operators at risk. Reduction in exposure limits of ammonia to workers, due to CO_2 processing, can only be advantageous. In all the CO_2 experiments the levels of ammonia were more than acceptable. Pelt odour was also very different.

4.3.4.4 Sulfate

The trends seen in ammonia reduction from the control experiments to CO_2 deliming were repeated for sulfates. Table 4.4 shows a four-fold reduction in sulfate levels between the control and any of the CO_2 deliming experiments.

Table 4.4 A comparison of the sulfate values of all deliming waters in mg/L sulfate for all experiments.

Experiment	***Sulfate (*mg/L SO_4^{2-}*)***
CO_2 Only*	50.6
CO_2 and bicarbonate*	18.0
CO_2 and formic*	47.5
CO_2 and simultaneous bating and bleaching*	20.6
CO_2 and calcium chelators*	21.0
Semi-technical*	19.6
Bovine Optimisation	41.2
Semi-technical+	38.5
Control++	208.6

Sulfate in effluents is problematic due to elevation of conductivity and the potential it has to become altered into sulfuric acid or into sulfide depending on the discharge conditions. Either option is problematic.

* Ovine experiments

+ Both bovine experiments

++ Mean representation of bovine and ovine values. Bovine sulfate control value stood at 183 mg/L SO_4^{2-}

4.3.4.5 Chemical Oxygen Demand (COD)

COD showed a drop from the control to all the CO_2 experiments (Table 4.5). The COD levels, a measure of the chemical degradability of an effluent, become lower as process shift from the ammonia salt type processing (conventional) to the use of CO_2. A three-fold reduction was seen from the control to experimental values.

Table 4.5 A comparison of the COD values of deliming effluents in mg/L COD for all experiments.

Experiment	***COD (*mg/L COD)**
CO_2 Only*	3300
CO_2 and bicarbonate*	980
CO_2 and formic*	4370
CO_2 and simultaneous bating and bleaching*	1580
CO_2 and calcium chelators*	990
Semi-technical*	1300
Bovine Optimisation	2100
Semi-technical+	2050
Control++	7800

COD values also receive contributions from auxiliaries that may be added during deliming. Acids whether organic or inorganic will increase the COD value. The propensity of tanneries to use organic deliming agents has seen the danger of a rise in effluent COD values. The organic deliming agents include sulfonic acids and other cyclic compounds. The incidence of cyclic compounds has been implicated in major increases in COD values. The danger thus exists for tanneries to opt for organic deliming agents (at a higher cost), with a major resultant increase in effluent COD levels.

* Ovine experiments

+ Both bovine experiments

++ Mean representation of bovine and ovine values. Bovine COD control value stood at 8050 mg/L COD.

4.3.4.6 Soluble Calcium

An attempt was made to see whether soluble calcium could be used as a measure of lime removal from the hide/skin. Unfortunately the method needs improvement. The results obtained were not conclusive, as the data tended to scatter. All soluble calcium measurements for the experiments resulted in 100mg/L Ca^{2+}. This does not concur with the theoretical yield expected from the limed hide. Future developments will need to include an improvement of this method.

4.3.4.7 Sulfide Content

The sulfide content of the hides/skins also yielded very inconsistent data in that no significant difference could be seen from the control to the experimental data. The mean value of sulfide levels for processing was 0.13 g/kg content in effluents. The hydrogen sulfide levels around the drums in CO_2 processes were significantly higher and typical levels will need to be measured in future experiments.

4.3.5 Wet Leather Analysis

Table 4.6 shows the data for wet leather analysis carried out for all experiments. The residual calcium and chromium content for the leathers in some CO_2 delimed pelts showed significant differences from the control. Residual calcium values were lower than those seen in ammonium salt delimed pelts. This suggests that the removal of calcium from the hide/skin in CO_2 processes was more efficient than that seen in control experiments. The higher chromium content seen in some CO_2 experiments is as yet unexplained. One possibility was that the removal of more calcium from the collagen results in more chromium attaching to anionic groups that calcium might have abandoned. The shrinkage temperatures seen in all experiments were acceptable according to international guidelines.

Table 4.6. A comparison of the wet analysis values for all the experiments.

Experiment	*Wet Analysis*				
	Moisture Content (%)	*Chromium Content (%)*	*Shrinkage Temperature (^{0}C)*	*Residual Calcium (mg/L)*	*Leather pH (After Deliming)*
CO_2 Only*	34	3.8	104.5	4.19	7.3
CO_2 and bicarbonate*	36.5	4.2	105.3	7.33	7.1
CO_2 and formic*	23.5	2.9	90.88	6.92	6.8
CO_2 and bating and bleaching*	29.5	4.3	99.1	3.38	8.0
CO_2 and calcium chelators*	33.5	4.5	109.9	3.52	7.8
Semi-technical*	36	3.6	100.9	2.50	8.2
Bovine Optimisation	32.6	4.68	103	3.07	8.4
Semi-technical+	39	3.72	105.6	4.02	8.3
Control++	31.7	3.5	102.7	10.29	8.9

4.3.6 Electron Microscopy

Very promising results were recovered in the electron micrographs from the study. The contentious issue that surrounds CO_2 deliming at present is CO_2 deliming has been said to cause looseness. For looseness to appear the junction between the corium minor and corium major would have to be damaged. This histological damage would be seen in the micrographs of CO_2 delimed wet-blue. The rest of the cross section of the pelt might also show a fair degree of openness. 100 micrographs were assessed and the micrographs showing cross sections were rated open, normal or tight. The results were then analysed using a chi-squared statistical test to see whether the looseness variable was independent of deliming method. Results showed that for the null hypothesis to exist $\chi^2 \leq 9.210$, with confidence levels at $p < 0.01$ and degrees of freedom (df) = 2. χ^2 actually resulted as 9.18, proving that from a histological point of view, looseness was an independent variable of deliming method.

* **Ovine experiments**

+ **Both bovine experiments**

++ **Mean representation of bovine and ovine values.**

Figures 4.7 to 4.15 show electron micrographs of the cross sections of all experiments. The variation in openness although not statistically different, was apparent. In most micrographs the control seemed to be unexpectedly more open. This was not substantiated statistically.

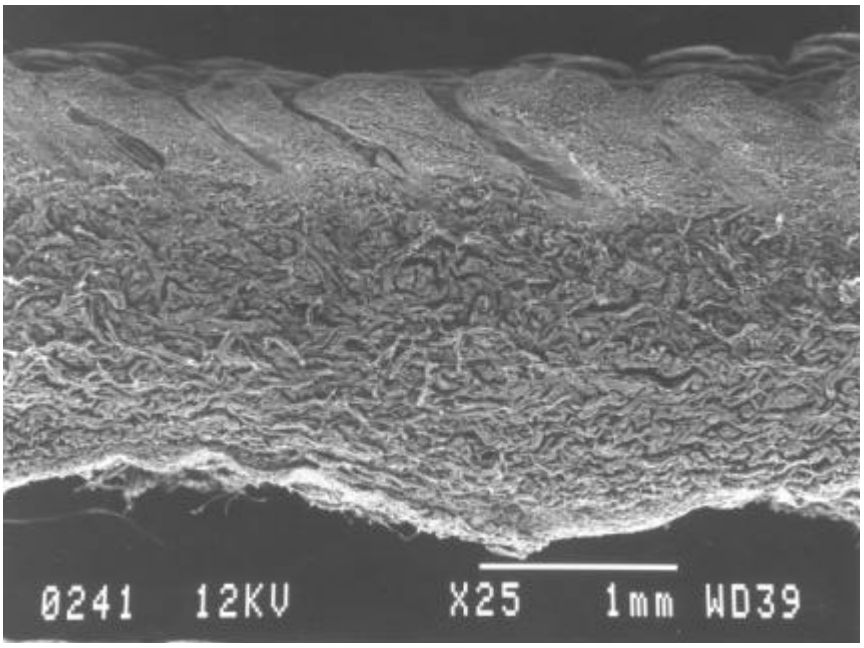

Figure 4.7 An electron micrograph of ammonium salt delimed ovine skins

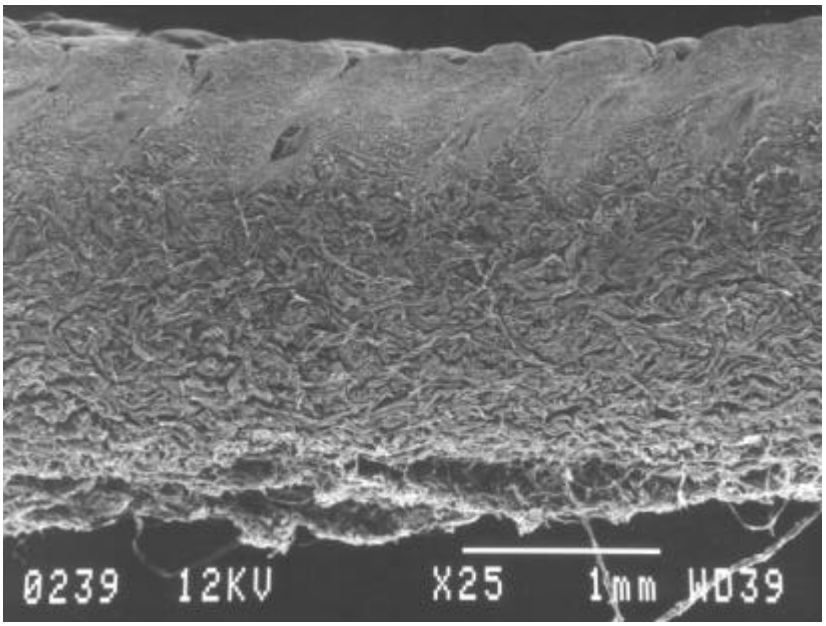

Figure 4.8 An electron micrograph of CO_2 and calcium chelator delimed ovine skins

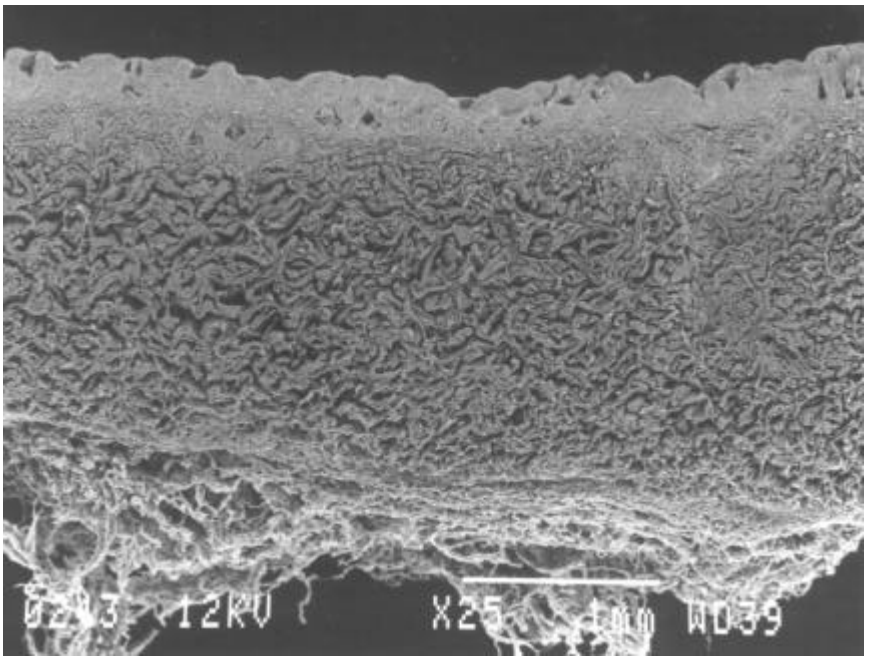

Figure 4.9 An electron micrograph of CO_2 and simultaneous bating and bleaching delimed ovine skin

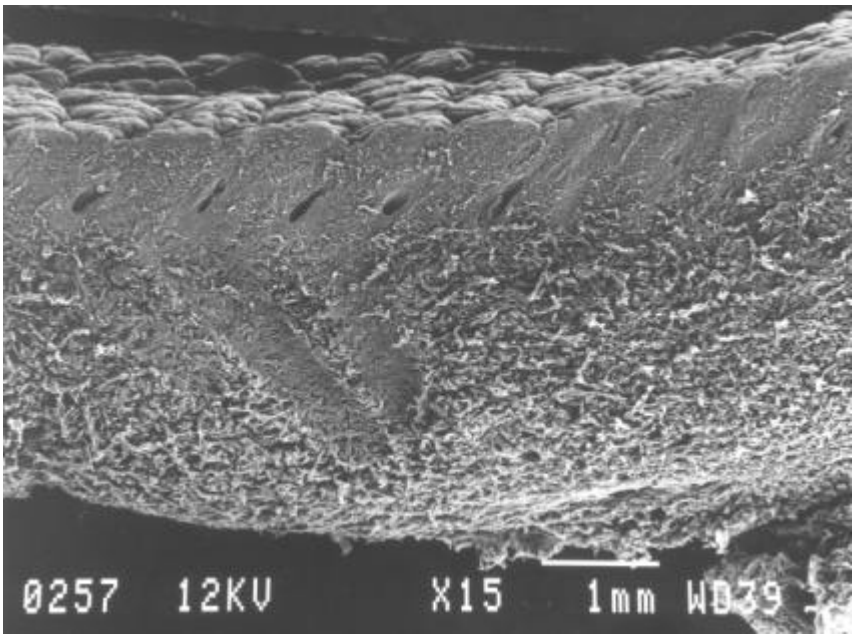

Figure 4.10 An electron micrograph of CO_2 and bicarbonate delimed ovine skin

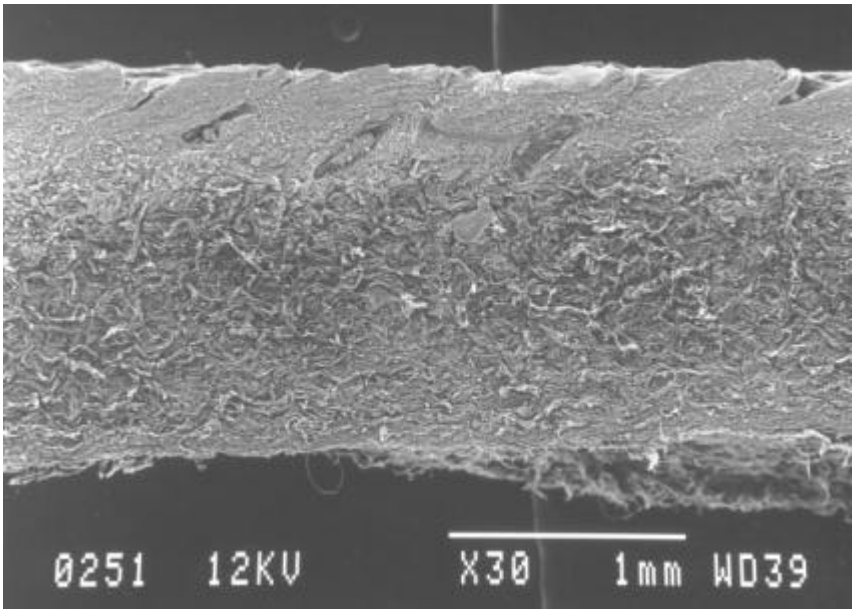

Figure 4.11 An electron micrograph of CO_2 and formic acid delimed ovine skin

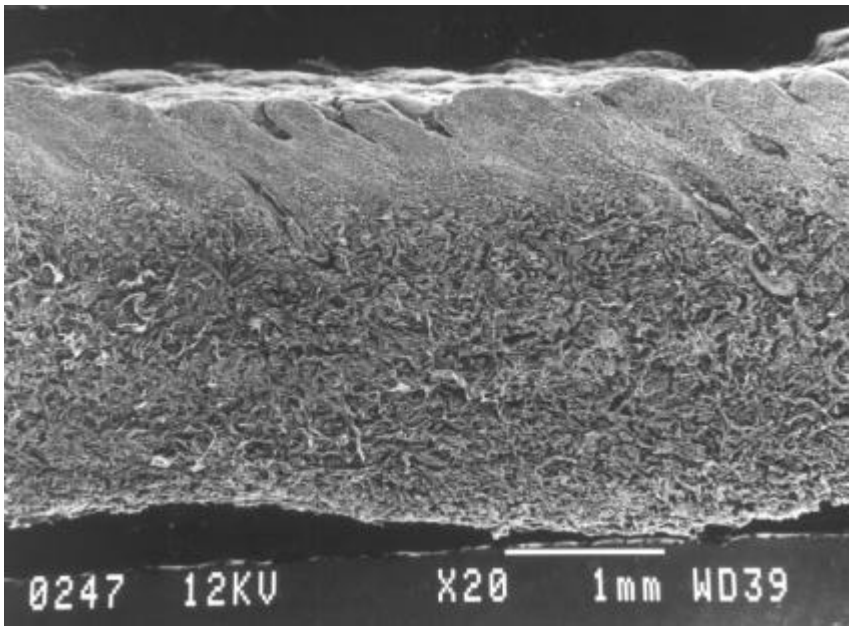

Figure 4.12 An electron micrograph of CO_2 only delimed ovine skin

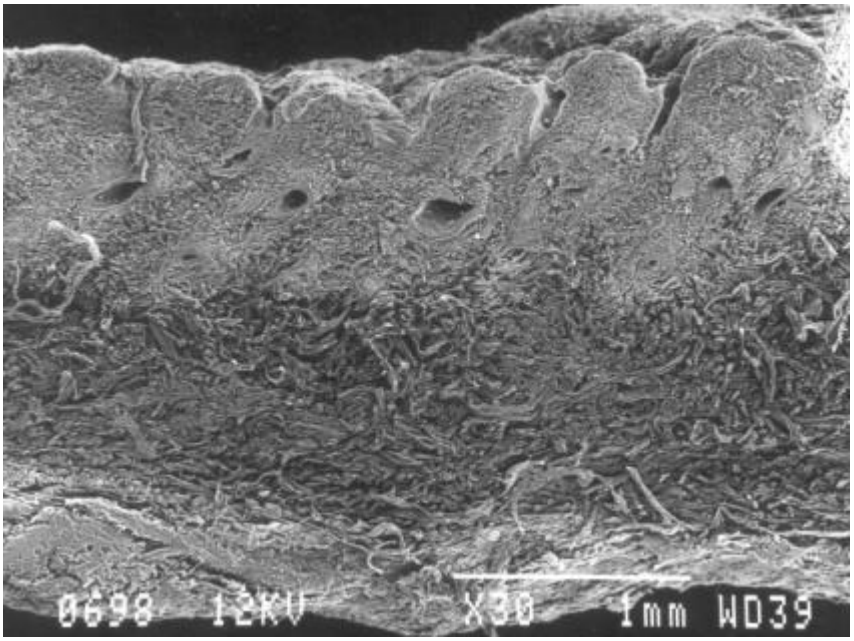

Figure 4.13 An electron micrograph of CO_2 delimed (semi-technical scale) ovine skin

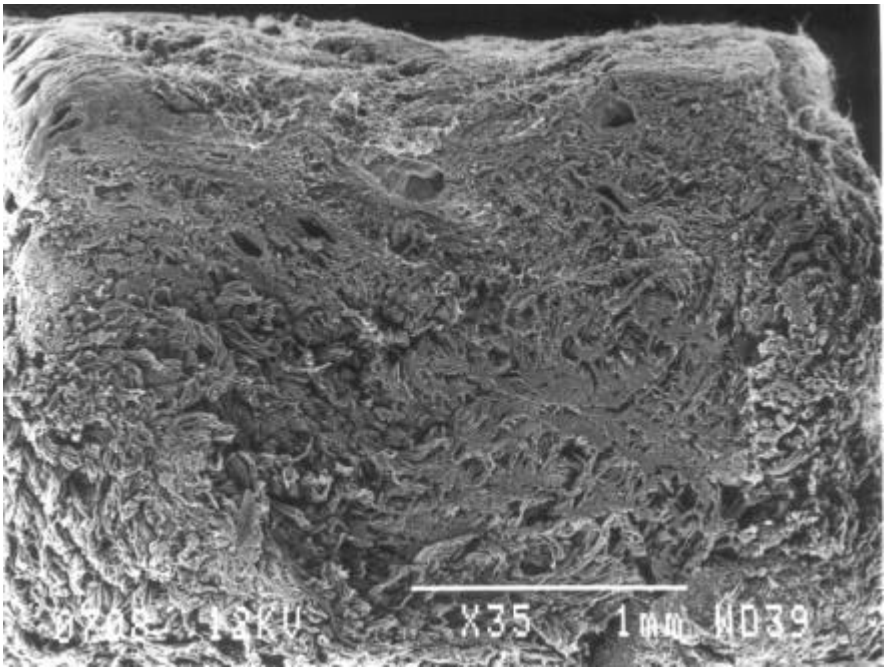

Figure 4.14 An electron micrograph of CO_2, bicarbonate delimed (with purging) bovine skin

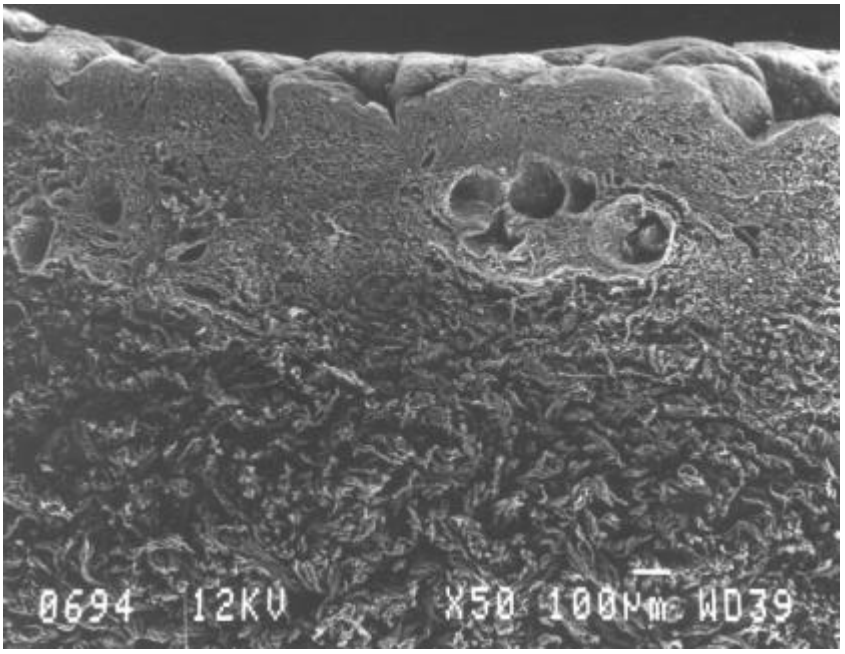

Figure 4.15 An electron micrograph of CO_2 optimised conditions delimed (semi-technical scale) bovine skin

4.3.7 Light Microscopy

The light microscopy correlated the results of the electron microscopy study in that the degree of openness was not significant from one type of deliming to the next. Figures 4.16 to 4.23 show that the fibre bundle structure of the skin appears to be normal. No visible difference was seen between the control and the other deliming methods.

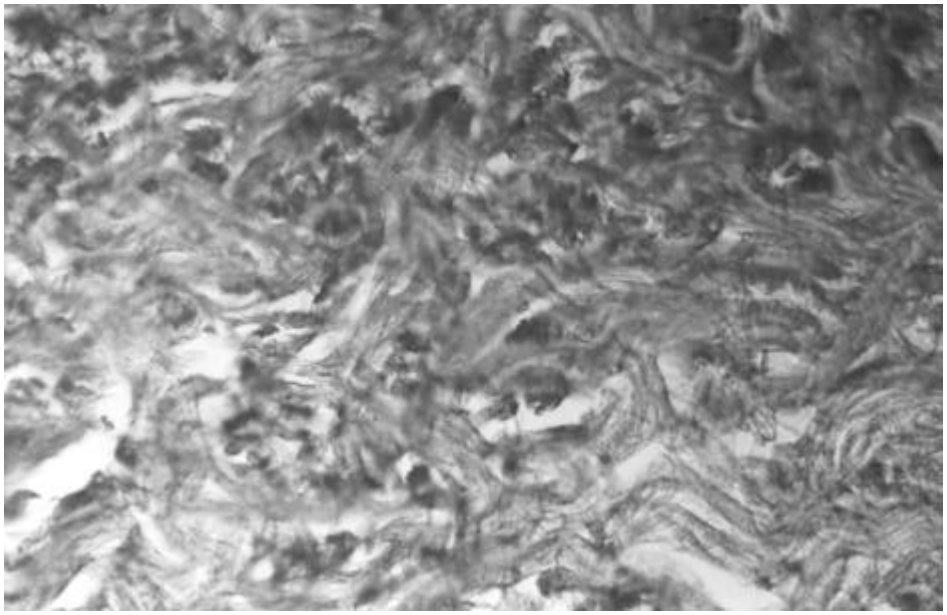

Figure 4.16 A light microscope micrograph of CO_2 only delimed ovine skin (x100)

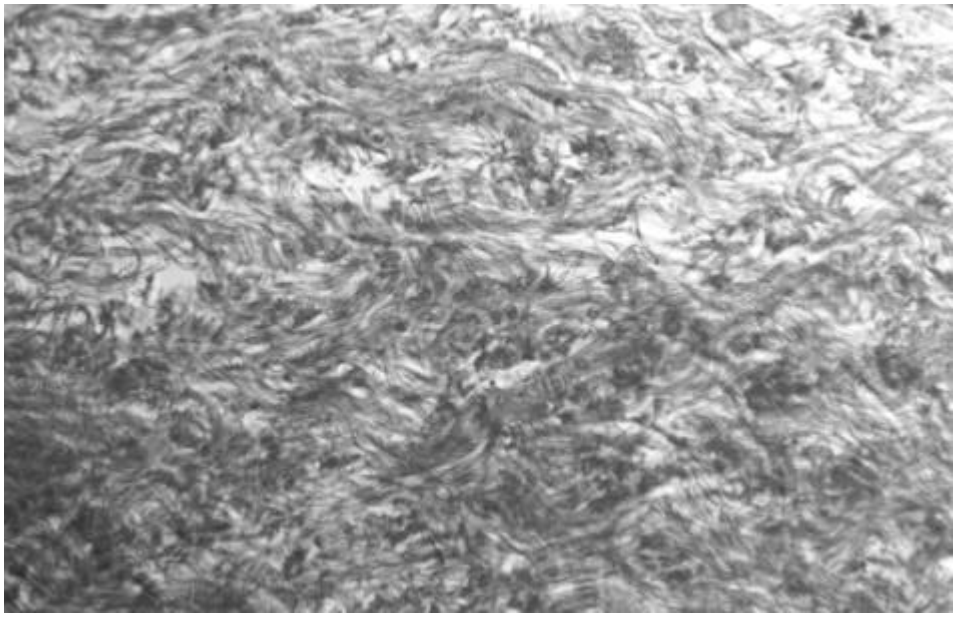

Figure 4.17 A light microscope micrograph of CO_2 and bicarbonate delimed ovine skin (x100)

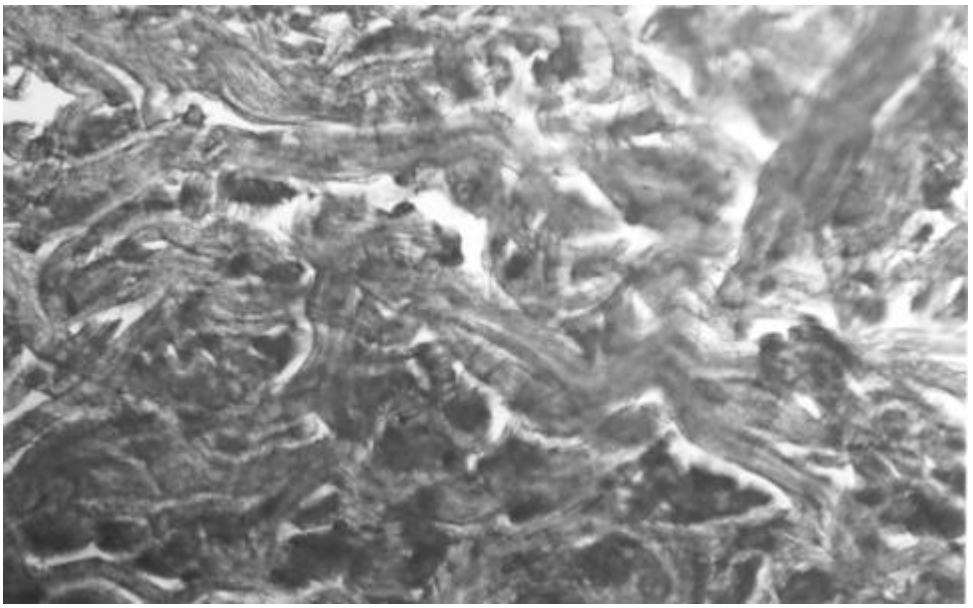

Figure 4.18 A light microscope micrograph of CO_2 and simultaneous bating and bleaching delimed ovine skin (x100)

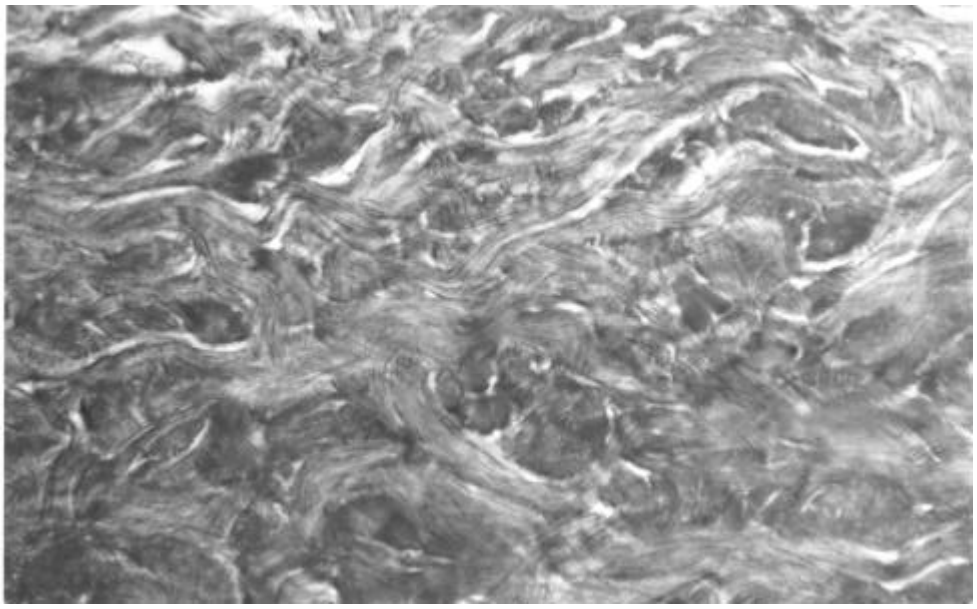

Figure 4.19 A light microscope micrograph of CO_2 and calcium chelator delimed ovine skin (x100)

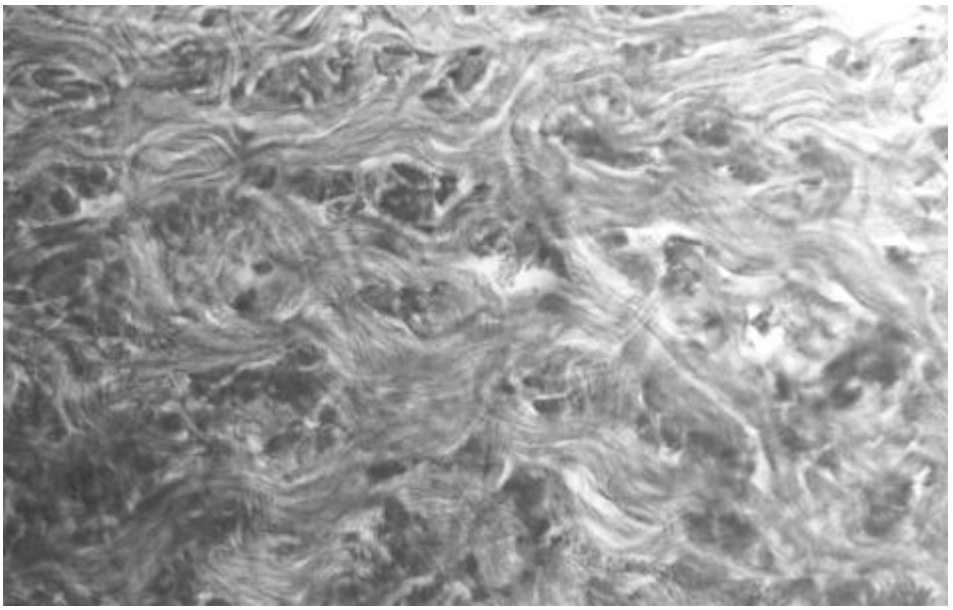

Figure 4.20 A light microscope micrograph of CO_2 and formic acid delimed ovine skin (x100)

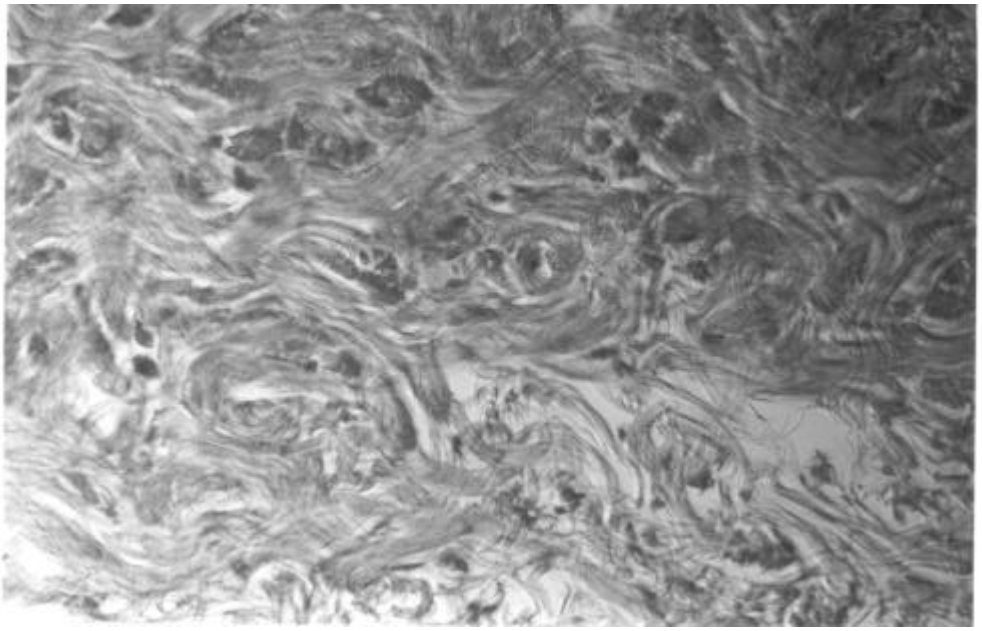

Figure 4.21 A light microscope micrograph of control delimed ovine skin (x100)

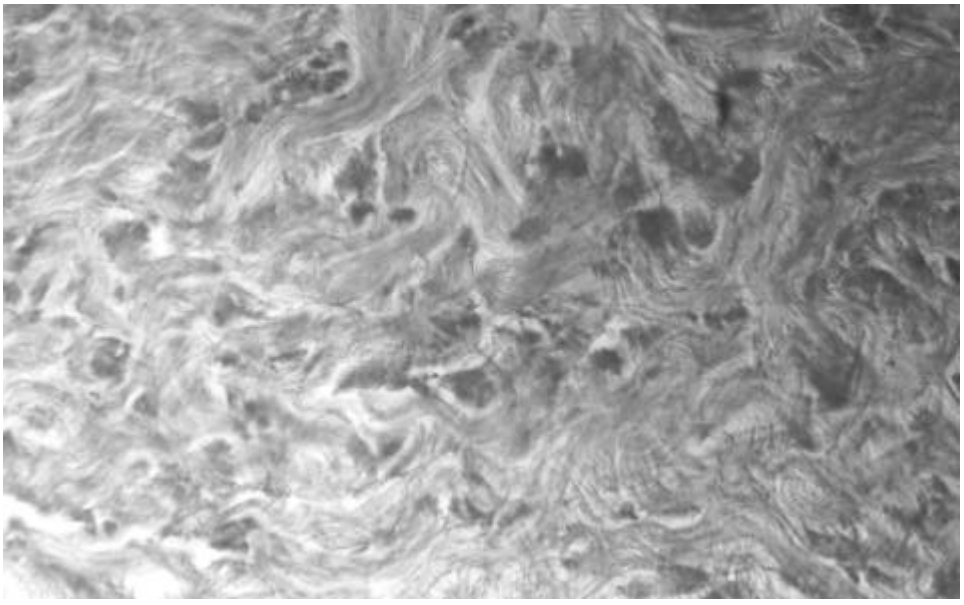

Figure 4.22 A light microscope micrograph of CO_2 optimised delimed (semi-technical scale) ovine skin (x100)

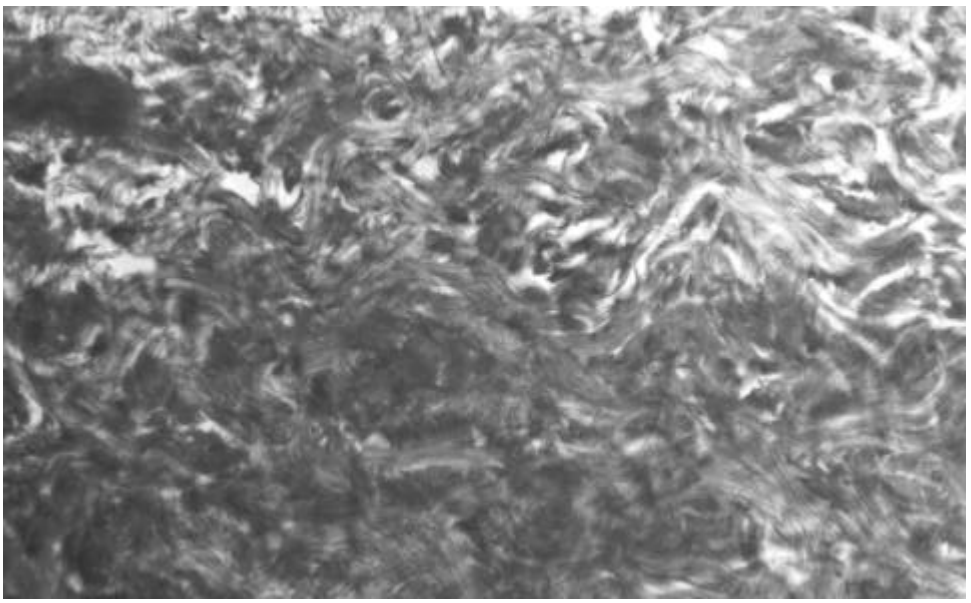

Figure 4.23 A light microscope micrograph of CO_2 optimised delimed (semi-technical scale) bovine skin (x100)

4.3.8 Crust Leather Physical Testing

Table 4.7 shows all the data for physical testing carried out for all experiments. Physical tests done on chromium-tanned leather were shown as they resulted in the most variable results. The variation between the vegetable-tanned physicals was non-existent. Values in all tests showed no significant difference. Slight variation was seen in the testing of the chromium- tanned leather but these could not be proven to be statistically different.

The physical tests of the experimental leathers show that there was no decrease in properties as one moves from ammonium salt delimed leather to CO_2 delimed leather. In some of the optimisation experiments, there was a 30daN/mm decrease in tear strength properties, but this was not repeated in the semi-technical upscale experiments. A decrease in the SATRA break scale values from pilot scale to semi-technical scale was also of little significance, as the CO_2 delimed leathers match the break of ammonium sulfate delimed leathers.

Table 4.7 A comparison of the physical analysis values for all the experiments.

Experiment	*Physical Analysis*				
	Lastometer (kg)	*Tensile Strength (daN/ mm^2)*	*Tear Strength (daN/mm)*	*Break (SATRA)*	*Grain surface*
CO_2 Only*	21.8	14.6	33.30	1	Clean
CO_2 and bicarbonate*	23.4	15.3	37.06	1	Clean
CO_2 and formic*	25.2	18.2	42.53	1	Clean
CO_2 and bating and bleaching*	26.3	13.2	39.60	1	Clean
CO_2 and calcium chelators*	22.0	15.1	32.50	1	Clean
Control*	25.5	15.3	39.89	1	Clean
Semi-technical*	23.0	15.9	44.32	1	Clean
Bovine Optimisation	41.6	12.7	65.7	2	Clean
Semi-technical+	45.0	13.1	58.2	2	Clean
Control++	38.7	12.9	64.	2	Clean

4.4 Conclusions

Of the six experimental options, experiment number 3 was the most effective, with a 60-minute CO_2 deliming time. Based on this time, a production lot of sheepskins was then processed, and yielded a CO_2 deliming time of 50 minutes. Increased mechanical action and improved gas addition allowed an improvement in time.

On the unsplit cattle hides, the CO_2 deliming time was not competitive with ammonium salt deliming (results not shown). Split cattle hides were, however, very competitive, due to addition of bicarbonate and an effective drum purging operation. In the purging process, the normal air found in drums was displaced by CO_2 gas during administration of the deliming gas offer. A CO_2-rich environment increases the partial pressure of CO_2, and facilitates rapid uptake.

Effluent analysis showed comparable pH curves for the bovine and ovine optimised experiments but a scattered range for the semi-technical experiments. Wet chemistry

* Ovine experiments

+ Both bovine experiments

++ Mean representation of bovine values.

analyses for sulfate, ammonia, COD and conductivity showed dramatic decreases in values in CO_2 deliming as opposed to conventional deliming. Other wet analyses showed no significant deviation from the conventional deliming.

Electron and light microscopy also showed no statistical deviation between the CO_2 delimed hides and the skins from conventional deliming.

Physical analyses also showed highly comparable values for lastometer, tensile strength, and tear strength.

From the evidence obtained from the semi-technical scale experiments, it was apparent that CO_2 deliming can be used on sheepskins and split cattle hides with little difference in process time and no appreciable difference in quality.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Environmental pressures have underscored the importance of a change in conventional deliming and it was evident that CO_2 deliming offers such a possible alternative. The advantages and disadvantages for CO_2 deliming can now be tabulated as follows:

Table 5.1 The advantages and disadvantages of the CO_2 deliming process as revised and based on this study.

Advantages	***Disadvantages***
More cost effective than ammonium salts.	Can generate hydrogen sulfide gas due to low operating pH values.
Less ammonia is released into wastewater as a result of CO_2 deliming.	Process can be lengthy on certain pelt types.
Less or no TDS is released into wastewater as a result of CO_2 deliming.	A cryogenic effect is seen on gas lines.
Easily automated.	A gas risk is seen if drum pressure relief valves fail.
Better calcium removal is performed during CO_2 deliming.	More pickle acid is required in the pickle stage.
Less acid shock is possible due to a weak acid being used.	A lower bate working pH can be detrimental on pH 8-active bates.
Reduced ammonia odour.	The gas is not noxious for workers, but is hazardous.
A better cleaner product is obtained. A lower COD is obtained with this method. Greater dosing accuracy is possible.	

The experiments to investigate the alleviation of some of the disadvantages of CO_2 deliming were undertaken in this study. The first stage was the determination of optimum conditions for CO_2 solubility in deliming waters. Super-saturated solutions (CA of 1200mg/L plus) were obtained (see Figures 2.10 and 2.12), and the possible use of these solutions will depend on whatever future work on extra thick cattle hides is required. A saturated solution with a CA of 500mg/L or more was required for normal deliming (see Figures 2.4, 2.11, 2.13, 2.15, and 2.17.) The optimal CO_2 solubility was obtained in deliming waters using the following conditions:

- Temperature 25°C
- Pressure 1 bar or higher
- pH 7
- Ionic Strength 3,5 to 7 S/m

After testing the optimal conditions at the laboratory-scale the deliming process had faster times. The fastest deliming experiment on a laboratory-scale was ten minutes faster in the control than in the experiment. It was shown, that if ammonium salt addition was staggered (mimicking a conventional CO_2 experiment, like that done by Jackson-Moss and Horne, 1994) then the deliming was quite long (see experiment number 15, Table 3.1). The optimal temperature for CO_2 deliming was previously 25°C, but this research showed that a process value of 38°C was better. Favourable deliming times at higher temperatures could be due to a higher diffusion coefficient through leather (which is favoured at higher temperatures). It was felt that further study in this regard could be made in an attempt obtain faster deliming times in thick cattle hides.

Simultaneously bating and bleaching gives shorter deliming times due to an overlap made with bating for 30 minutes together with deliming.

Pilot experiments at laboratory-scale showed significant reductions in discharge components of the wastewaters. The pilot experiments also showed differences on the wet-analyses of the pelts. Marginally better calcium contents and shrinkage temperatures indicate better lime removal and better chromium uptake in the presence of CO_2. The significantly reduced ammonia and sulfate levels in the wastewater can be seen in Table 3.2.

Pilot experiment times showed very similar deliming times with CO_2 delimed hides, which were of a medium substance (12mm), delimed in 135 minutes plus a further 30-

minute bating. The control hides took 95 minutes to delime but then had an additional 60-minute bating time. The overall times are also shown in Figure 3.2. The rapid deliming times with CO_2 that have been seen in this experiment may be due to a proportional amount of CO_2 acidity, in manner similar to ammonium sulfate. The pre-sparging and sodium bicarbonate may be in slight excess but the fact remains that a good reservoir of bicarbonate protons does decrease the pH in a manner similar to ammonium salts. Physical properties of experiment pelts and the crusted samples were very comparable to conventional deliming.

The semi-technical experiments confirmed what was found in the small-scale studies, but with a number of differences. The larger batch seemed to delime more efficiently than the laboratory and pilot scale. The increase in efficiency could have been due to the higher mechanical action present in the drum. Gas purging was deemed to be highly successful in lime-split hides and the possibility of increased rate of delivery seems to lie in this method.

Optimisation of gas supply needs to be investigated to ensure that the amount of gas supplied is kept to a minimum. The gas used in this research was applied in slight excess, as cost or chemical usage was not conservative. The system which CO_2 deliming creates is unique. A conventional ammonium salt process would be optimised to a minimum critical level (*viz.* lower than this level and the process would not work). CO_2 deliming would however pump in the specific amount of gas for that process, until deliming was completed. The system could even be optimised so that the gas was delivered more slowly to ensure a milder deliming, or pumped in quickly to ensure rapid but harsher deliming. The quantity of gas would therefore vary. Another area of optimisation is the ability to turn off the gas supply and still continue with the deliming process. It was also found that ventilation is a very important area of safety concern. Further work should be done to elucidate the safety guidelines for the use of this gas and the hydrogen sulfide problem associated with its use.

The control deliming times of sheepskins was completed in 45±7.3 minutes. The fastest CO_2 deliming time was CO_2 and bicarbonate - in 60 minutes (Experiment 3, see Section 4.2.1). The standard time of lime-split hide deliming, although technically 60 minutes, was closer to 70 minutes in industry. The mean control deliming time was however 35±5 minutes and the semi-technical batches' time was 35 minutes at 25% removal (when bating was commenced).

The wet-analysis of the semi-technical wastewater can be seen in Tables 4.1 to 4.5 with significant reductions in all wet-parameters. The effluent analyses of the liquors produced from all experiments are conclusive in that there are considerable reductions in problem compounds namely: sulfate (four-fold reduction), ammonia (about seven-fold reduction), conductivity (two-fold reduction) and COD (two-fold reduction). The savings in effluent charges alone should give the CO_2 process considerable cost advantages. The wet-analysis and the physical testing of the pelts and crust can be seen in Tables 4.6 and 4.7. with marginally better comparisons between control and experimental samples in the sheepskins and cattle hides. The residual calcium levels in the CO_2 delimed leather are significantly lower than that of the control which contests those results proposed by Christner (1992).

Examination of the histological differences between CO_2 delimed hides/skins and the controls revealed no statistical differences between them. The data of Passman and Scrase (1991) may be questioned where they obtained slightly lower soluble protein readings in CO_2 deliming experiments. Lower soluble protein removal in CO_2 experiments would suggest less opening up and histologically this research does not suggest this. Further investigation should be undertaken in this regard.

It is recommended that the results shown here on a semi-technical scale be proven comparable on a full production scale. The deliming of sheepskins and lime-split material was successful and should be implemented in tanneries where a semi-technical

production was performed (200 sheepskins/drum and 20 hides/drum). The results here could also be horizontally transferred into the deliming of exotic leathers.

The grease removal from pelts was not investigated in this research and a study to elucidate the full impact of calcium removal should perhaps also be investigated.

Finally, the CO_2 deliming of unsplit material could be promising but requires further study. It is recommended that a full study be financed and undertaken to improve the efficiency of unsplit material. The mechanism of improved diffusion of deliming agent into the hide as well as the osmotic de-swelling effect of ammonium salts needs to be determined. Given the considerable advantages of CO_2 deliming demonstrated in this study and the complexity of factors involved it is recommended that a full cost-benefit analysis be undertaken to compare the economic benefits of ammonium and CO_2 deliming processes.

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APPENDICES

Appendix 1

Experimental design of high order factorial analysis

H = High, M = Medium and L. = Low

	Pressure	*Temperature*	*Ionic Strength*	*pH*
1.	L.	L.	L.	L.
2.	L.	L.	L.	M
3.	L.	L.	L.	H
4.	L.	L.	M	L.
5.	L.	L.	M	M
6.	L.	L.	M	H
7.	L.	L.	H	L.
8.	L.	L.	H	M
9.	L.	L.	H	H
10.	L.	M	L.	L.
11.	L.	M	L.	M
12.	L.	M	L.	H
13.	L.	M	M	L.
14.	L.	M	M	M
15.	L.	M	M	H
16.	L.	M	H	L.
17.	L.	M	H	M
18.	L.	M	H	H
19.	L.	H	L.	L.
20.	L.	H	L.	M
21.	L.	H	L.	H
22.	L.	H	M	L.
23.	L.	H	M	M
24.	L.	H	M	H
25.	L.	H	H	L.
26.	L.	H	H	M
27.	L.	H	H	H
28.	M	L.	L.	L.
29.	M	L.	L.	M
30.	M	L.	L.	H
31.	M	L.	M	L.
32.	M	L.	M	M
33.	M	L.	M	H
34.	M	L.	H	L.
35.	M	L.	H	M
36.	M	L.	H	H
37.	M	M	L.	L.
38.	M	M	L.	M
39.	M	M	L.	H
40.	M	M	M	L.
41.	M	M	M	M
42.	M	M	M	H
43.	M	M	H	L.
44.	M	M	H	M

45.	M	M	H	H
46.	M	H	L.	L.
47.	M	H	L.	M
48.	M	H	L.	H
49.	M	H	M	L.
50.	M	H	M	M
51.	M	H	M	H
52.	M	H	H	L.
53.	M	H	H	M
54.	M	H	H	H
55.	H	L.	L.	L.
56.	H	L.	L.	M
57.	H	L.	L.	H
58.	H	L.	M	L.
59.	H	L.	M	M
60.	H	L.	M	H
61.	H	L.	H	L.
62.	H	L.	H	M
63.	H	L.	H	H
64.	H	M	L.	L.
65.	H	M	L.	M
66.	H	M	L.	H
67.	H	M	M	L.
68.	H	M	M	M
69.	H	M	M	H
70.	H	M	H	L.
71.	H	M	H	M
72.	H	M	H	H
73.	H	H	L.	L.
74.	H	H	L.	M
75.	H	H	L.	H
76.	H	H	M	L.
77.	H	H	M	M
78.	H	H	M	H
79.	H	H	H	L.
80.	H	H	H	M
81.	H	H	H	H

Appendix 2

Ovine – beamhouse up to and including reliming

Dried, dry-salted or wet-salted material
Average mass = 2,5 kg

Pre-soak	200	Water @ 25 °C	
	1 g/L	Bactericide	
	0.5 g/L	Alkali (1:10)	Stand 30' Drum 30'
			Stand 30' Drum 30'
			Drain
Soak	200	Water @ 25 °C	
	1 g/L	Bactericide	
	0.5 g/L	Alkali (1:10)	
	1 g/L	Soaking Enzyme	Drum 10' Stand 60'
			For 4 Hours
			Drain
Unhair/Lime			
	300	Water @ 28 °C	
	4	Liming agent	
	3,5	Sharpening agent	
	1 g/L	Surfactant	Drum 10' Stand 60'
			Overnight
			Drain
Wash	200	Water @ 18 °C	10'
			Drain

Lime Flesh, Flesh weight =

Relime	200	Water @ 28 °C	
	4	Liming agent	
	0.5	Surfactant	Drum 30' Stand 60'
			Drum 10' Stand 60'
			Overnight
			Drain

Appendix 3

Deliming using ammonium salts

Soaking to reliming as per Appendix 2

Wash				
	200	Water @ 38°C	10'	
			Drain	
Wash				
	200	Water @ 38°C		
	0.1	Ammonium Sulfate	10'	
			Drain	
Delime and Bate				
	30	Water from Pelts @ 35°C		
	0.2	Surfactant		
	0.5	Ammonium Sulfate		
	0.5	Bleach 2	30'	
Add	0.4	Fixing Acid (1:10)	15’	pH=8.5
Add	0.5	Bate	45'	
			Drain	
			Wash, Repeat	

Pickle as per Appendix 9

Appendix 4

CO_2 deliming

Soaking to reliming, as per Appendix 2

Wash			
	200	Water @ 38°C	10'
			Drain
Wash			
	200	Water @ 38°C	
	0.4	Bleach 1 (1:5)	10'
			Drain
Delime and Bate			
	30	Water from Pelts @ 35°C	
	0.2	Surfactant	
	0.5	Bleach 2	15'

Pump in 1.5% CO_2 gas into the head-space
Continue until deliming was 80% completed

Add	0.5	Bate	45'
			Drain
			Wash, Repeat

Pickle as per Appendix 9

Appendix 5

CO_2 deliming and calcium chelators

Soaking to reliming as per Appendix 2

Wash			
	200	Water @ 38°C	10'
			Drain
Wash			
	200	Water @ 38°C	
	0.4	Bleach 1 (1:5)	10'
			Drain
Delime and Bate			
	30	Water from Pelts @ 35°C	
	0.2	Surfactant	
	0.4	Calcium Chelators	
	0.5	Bleach 2	15'

Pump in 1.5% CO_2 gas into the head-space
Continue until deliming was 80% completed

Add	0.5	Bate	45'
			Drain
			Wash, Repeat

Pickle as per Appendix 9

Appendix 6

CO_2 deliming, simultaneous bating and bleaching

Soaking to liming, as per Appendix 2.

Wash			
	200	Water @ 38°C	10'
			Drain
Wash			
	200	Water @ 38°C	
	0.4	Bleach 1 (1:5)	10'
			Drain
Delime and Bate			
	30	Water from Pelts @ 35°C	
	0.2	Surfactant	
Add	0.8	Bleach 2	15'
Add	0.5	Bate	45’

Pump in 1.5% CO_2 gas into the head-space
Continue until deliming was 100% complete

Drain
Wash, Repeat

Pickle as per Appendix 9

Appendix 7

CO_2 deliming and formic acid

Soaking to liming, as per Appendix 2.

Wash			
	200	Water @ 38°C	10'
			Drain
Wash			
	200	Water @ 38°C	
	0.4	Bleach 1 (1:5)	10'
			Drain
Delime and Bate			
	30	Water from Pelts @ 35°C	
	0.2	Surfactant	
Add	0.8	Bleach 2	15'
Add	0.4	Formic acid (1:10)	30’

Pump in 1.5% CO_2 gas into the head-space
Continue until deliming was 80% complete

Add	0.5	Bate	45'
			Drain
			Wash, Repeat

Pickle as per Appendix 9

Appendix 8

CO_2 deliming and sodium bicarbonate

Soaking to liming, as per Appendix 2.

Wash			
	200	Water @ 38°C	10'
			Drain
Wash			
	200	Water @ 38°C	
	0.4	Bleach 1 (1:5)	10'
			Drain
Delime and Bate			
	30	Water from Pelts @ 35°C	
	0.2	Surfactant	
Add	0.4	Bleach 2	15'
Add	0.4	Sodium bicarbonate	15’

Pump in 1.5% CO_2 gas into the head-space
Continue until deliming was 80% complete

Add	0.5	Bate	45'
			Drain
			Wash, Repeat

Pickle as per Appendix 9

Appendix 9

Vegetable tannage of ovine material after deliming

Pickle/ Tan				
	20	Water @ 20 ^{o}C		
	6	Salt		
	1	Masking agent	5'	Bé = 6
Add	0.8	Pickle acid (1:10)		
	10	Conditioning agent		
	0.3	Slip agent	60'	
Add	15	Tanning agent 1		
	1	Tan oil		
	0.2	Clearing agent	120'	pH = 4.7
Add	100	Water @ 30 ^{o}C		
	0.05	Fungicide	30'	
			Drain	

Horse up overnight
Sammy-set
Partially toggle dry
Shave to clean backs or to 0.9-1.0 mm

Appendix 10

Chromium tanning of ovine material after deliming

Pickle/ Tan					
	70	Water @ 20 ^{o}C			
	6	Salt			
	0.8	Masking agent		5'	Bé = 6
Add	1.2	Pickle acid (1:10)		60’	pH = 3,0
Add	10	Chromium Tanning Salts			60’
Add	0.4	Magnesium Oxide		O/N	pH = 3,8
				Drain	
Wash					
	100	Water @ 45 ^{o}C			
	0.1	Degreaser		30’	
				Drain	

Horse up overnight
Sammy-se
Partially toggle dry
Shave to clean backs or to 0.9-1.0 mm

Appendix 11

Semi-technical process for sheepskins

Dried, dry-salted or wet-salted material
Average mass = 2,5 kg

Pre-soak			
	200	Water @ 25 °C	
	1 g/L	Bactericide	
	0.5 g/L	Alkali (1:10)	Stand 30' Drum 30'
			Stand 30' Drum 30'
			Drain
Soak			
	200	Water @ 25 °C	
	1 g/L	Bactericide	
	0.5 g/L	Alkali (1:10)	
	1 g/L	Soaking Enzyme	Drum 10' Stand 60'
			For 4 Hours
			Drain
Unhair/Lime			
	300	Water @ 28 °C	
	4	Liming agent	
	3,5	Sharpening agent	
	1 g/L	Surfactant	Drum 10' Stand 60'
			Overnight
			Drain
Wash			
	200	Water @ 18 °C	10'
			Drain

Lime Flesh, Flesh weight =

Relime			
	200	Water @ 28 °C	
	4	Liming agent	
	0.5	Surfactant	Drum 30' Stand 60'
			Drum 10' Stand 60'
			Overnight
			Drain

Wash

	200	Water @ 38°C	10'	Drain
Wash				
	200	Water @ 38°C		
	0.4	Bleach 1 (1:5)	10'	
			Drain	
Delime and bate				
	30	Water from Pelts @ 35°C		
	0.2	Surfactant		
Add	0.4	Bleach 2	5'	
Add	0.4	Sodium bicarbonate	5’	
Pump in 1.5% CO_2 gas into the head-space				
Continue until deliming was 80% complete			30’	
Bate simultaneously			pH = 7.5	
Add	0.5	Bate		
	100	Water @ 38 °C	30’	pH = 8.0
			Drain	
			Wash, Repeat	
Pickle				
	20	Water @ 20°C		
	6	Salt		
	1	Masking agent	10’	Bé = 7
Add	1.85	Pickle acid (1:10)	60’	
			Drain	
Degreasing				
	4	Degreaser	30’	
		Horse up overnight		
		Reload		
	50	Brine @ 35°C	60’	
			Drain	
Brine Wash				
	100	Brine @ 35°C		
	0.3	Degreaser	10’	
			Drain	
	100	Brine @ 35°C		
	0.3	Degreaser	10’	
			Drain, Offload	
			Flesh	
			Tan	
	100	Water @ 18°C		

	0.1	Degreaser	
	6	Salt	5’

Pre-mix and then add skins

			20’ pH = 3.0
Add	6	Chromium Tanning Salts	
	0.05	Fungicide	
	1	Fatliquor	60’ pH = 3.1

Basify

Add	0.4	Magnesium Oxide	Drum Overnight
			pH = 3.8
			Drain

Wash

	150	Water 18^{o}C	
	0.1	Degreaser	20’
			Drop

Horse up overnight
Sammy-set
Partially toggle dry
Shave to clean backs or to 0.9-1.0 mm

Appendix 12

Lime split bovine wet-blue using CO_2 with bicarbonate (for deliming)

Dried, dry-salted or wet-salted material
Average wet-salted mass = 23 kg

Static Soak				
	700	Water @ 18 °C		
	1 g/L	Bactericide		
	0.5 g/L	Alkali (1:10)	Stand Overnight	
			Drain	
Pre-soak				
	200	Water @ 25 °C		
	1 g/L	Bactericide	Drum 10'	Stand 30'
			Drum 10'	Stand 30'
			Drum 15'	
			Drain	
Soak				
	200	Water @ 25 °C		
	0.25	Enzyme Soaking Aid		
	0.75	Sharpening Aid		
	1 g/L	Soaking Aid/ Bactericide	120'	
			Drain	
Unhair/ Lime				
	30	Water @ 25 °C		
	0.2	Surfactant		
	0.75	Sharpening Aid	15'	
Add	0.72	Sharpening Aid	15'	
Add	1.5	Liming Agent		
	0.5	Sharpening Agent	15'	
Add	1.5	Liming Agent		
	0.5	Sharpening Agent	75'	
Add	50	Water @ 25 °C		
	1 g/L	Surfactant	Drum 10'	Stand 60'
			Overnight	
			Drain	
Wash	200	Water @ 18 °C	10'	
			Drain	

Lime Flesh, Split, and Split weight =

Wash

	200	Water @ 38°C		10'
			Drain	
Wash				
	200	Water @ 38°C		
	0.5	Bleach 1 (1:5)	10'	
			Drain	
De-lime and bate				
a) Using CO_2:		Experimental		
	150	Water @ 38 °C		
	0.2	Surfactant		
	0.8	Sodium bicarbonate		
	0.5	Bleach 2		
	2	CO_2 gas	45’	pH = 7.5
Add	1	Bate		
	100	Water @ 38 °C	30’	pH = 8.0
			Drain	
b) Using Ammonium salts:		Control		
	150	Water @ 38 °C		
	0.2	Surfactant		
	0.5	Bleach 2		
	3	Ammonium salts	45’	
Add	0.4	Formic acid (1:10)	30’	pH = 8.5
Add	1	Bate		
	100	Water @ 38 °C	30’	pH = 8.5
			Drain	
(resume)				
Wash	200	Water @ 18 °C	10'	
			Drain	
Pickle				
	70	Water @ 25 °C		
5 Salt				
	0.8	Masking agent	5'	Bé = 6
Add	1.6	Pickle acid (1:10)	45'	
Add	8	Chromium tanning salts		
	0.05	Fungicide		
	1.5	Fatliquor	45'	pH = 3.0
Basification				
Add	0.5	Magnesium Oxide	O/N	
Drain				
Wash	100	Water @ 25 °C	15'	
			Drain	

Horse up overnight, Sammy-set, Shave 1.1- 1.2-mm

Appendix 13

Lime split wet-blue using CO_2 with bicarbonate and purging (for deliming)

Beamhouse up to and including reliming; as in Appendix 12

Wash				
	200	Water @ 38°C	10'	
			Drain	
Wash				
	200	Water @ 38°C		
	0.5	Bleach 1 (1:5)	10'	
			Drain	
De-lime and bate				
a) Using CO_2:		Experimental		
	150	Water @ 38 °C		
	0.2	Surfactant		
	0.8	Sodium bicarbonate		
	0.5	Bleach 2	5’	
Purge the drum of air using the 2 % gas addition				
	x	CO_2 gas (as required)	45’	pH = 7.5
Add	1	Bate		
	100	Water @ 38 °C	30’	pH = 8.0
			Drain	
b) Using Ammonium salts:		Control		
	150	Water @ 38 °C		
	0.2	Surfactant		
	0.5	Bleach 2		
	3	Ammonium salts	45’	
Add	0.4	Formic acid (1:10)	30’	pH = 8.5
Add	1	Bate		
	100	Water @ 38 °C	30’	pH = 8.5
			Drain	

(resume)
Wash, Repeat and pickle as in Appendix 12

Appendix 14

Unsplit bovine wet-blue using CO_2 with bicarbonate and purging (for deliming)

Dried, dry-salted or wet-salted material
Average wet-salted mass = 30 kg

Static Soak				
	700	Water @ 18 °C		
	1 g/L	Bactericide		
	0.5 g/L	Alkali (1:10)	Stand Overnight	
			Drain	
Pre-soak				
	200	Water @ 25 °C		
	1 g/L	Bactericide	Drum 10'	Stand 30'
			Drum 10'	Stand 30'
			Drum 15'	
			Drain	
Soak				
	200	Water @ 25 °C		
	0.25	Enzyme Soaking Aid		
	0.75	Sharpening Aid		
	1 g/L	Soaking Aid/ Bactericide	120'	
			Drain	
Unhair/ Lime				
	30	Water @ 25 °C		
	0.2	Surfactant		
	0.75	Sharpening Aid	15'	
Add	0.72	Sharpening Aid	15'	
Add	1.5	Liming Agent		
	0.5	Sharpening Agent	15'	
Add	1.5	Liming Agent		
	0.5	Sharpening Agent	75'	
Add	50	Water @ 25 °C		
	1 g/L	Surfactant	Drum 10'	Stand 60'
			Overnight	
			Drain	
Wash	200	Water @ 18 °C	10'	
			Drain	

Lime Flesh, Flesh weight =

Wash			
	200	Water @ 38°C	10'

			Drain	
Wash				
	200	Water @ 38^{o}C		
	0.5	Bleach 1 (1:5)	10'	
			Drain	
De-lime and bate				
a) Using CO_2:		Experimental		
	150	Water @ 38 ^{o}C		
	0.2	Surfactant		
	0.8	Sodium bicarbonate		
	0.5	Bleach 2	5’	
Purge the drum of air using the 2 % gas addition				
	x	CO_2 gas (as required)	120’	pH = 7.5
Add	1	Bate		
	100	Water @ 38 ^{o}C	60’	pH = 8.0
			Drain	
b) Using Ammonium salts:		Control		
	150	Water @ 38 ^{o}C		
	0.2	Surfactant		
	0.5	Bleach 2		
	3	Ammonium salts	45’	
Add	0.4	Formic acid (1:10)	45’	pH = 8.5
Add	1	Bate		
	100	Water @ 38 ^{o}C	60’	pH = 8.5
			Drain	
(resume)				
Wash	200	Water @ 18 ^{o}C	10'	
			Drain	
Pickle				
	70	Water @ 25 ^{o}C		
	6	Salt		
	0.3	Slipping agent		
	1	Masking agent	10'	Bé = 6
Add	1.8	Pickle acid (1:10)	90'	pH = 4.7
Add	15	Vegetable Tanning agent		
	0.05	Fungicide		
	1.5	Fatliquor	120’	
			Drop	
Horse up overnight, Sammy-set, Split, Split Weight = Tan				
	100	Water @ 30 ^{o}C		
	25	Vegetable Tanning agent		
	0.3	Slipping agent	Drum until through	

Horse up overnight, Sammy-set, Shave

Appendix 15

Semi-technical scale- lime split, bovine wet-blue using CO2 with bicarbonate and drum purging (for deliming)

Dried, dry-salted or wet-salted material
Average wet-salted mass = 23 kg

Static Soak				
	700	Water @ 18 °C		
	1 g/L	Bactericide		
	0.5 g/L	Alkali (1:10)	Stand Overnight	
			Drain	
Pre-soak				
	200	Water @ 25 °C		
	1 g/L	Bactericide	Drum 10'	Stand 30'
			Drum 10'	Stand 30'
			Drum 15'	
			Drain	
Soak				
	200	Water @ 25 °C		
	0.25	Enzyme Soaking Aid		
	0.75	Sharpening Aid		
	1 g/L	Soaking Aid/ Bactericide	120'	
			Drain	
Unhair/ Lime				
	30	Water @ 25 °C		
	0.2	Surfactant		
	0.75	Sharpening Aid	15'	
Add	0.72	Sharpening Aid	15'	
Add	1.5	Liming Agent		
	0.5	Sharpening Agent	15'	
Add	1.5	Liming Agent		
	0.5	Sharpening Agent	75'	
Add	50	Water @ 25 °C		
	1 g/L	Surfactant	Drum 10'	Stand 60'
			Overnight	
			Drain	
Wash	200	Water @ 18 °C	10'	
			Drain	

Lime Flesh, Split, and Split weight =

Wash				
	200	Water @ 38^{o}C	10'	
			Drain	
Wash				
	200	Water @ 38^{o}C		
	0.5	Bleach 1 (1:5)	10'	
			Drain	
De-lime and bate				
	150	Water @ 38 ^{o}C		
	0.2	Surfactant		
	0.8	Sodium bicarbonate		
	0.5	Bleach 2	5’	
Purge the drum of air using the 2 % gas addition				
	x	CO_2 gas (as required)	30’	pH = 7.5
Add	1	Bate		
	100	Water @ 38 ^{o}C	30’	pH = 8.0
Wash	200	Water @ 18 ^{o}C	10'	
			Drain	
Pickle				
	70	Water @ 25 ^{o}C		
	5	Salt		
	0.8	Masking agent	5'	Bé = 6
Add	1.6	Pickle acid (1:10)	45'	
Add	8	Chromium tanning salts		
	0.05	Fungicide		
	1.5	Fatliquor	45'	pH = 3.0
Basification				
Add	0.5	Magnesium Oxide	O/N	
			Drain	
Wash	100	Water @ 25 ^{o}C	15'	
			Drain	

Horse up overnight, Sammy-set, Shave 1.1- 1.2-mm

Appendix 16

Retannage of vegetable tanned ovine skin

All weights based on damp shaved weight

Wet-back			
	400	Water @ 35 ^{o}C	10'
			Drain
Clear			
	300	Water @ 35 ^{o}C	
	1	Clearing agent	60'
			Drain
Neutralise			
	150	Water @ 38 ^{o}C	
	1.8	Neutralising agent	45'
			Drain
Wash	300	Water @ 25 ^{o}C	10'
			Drain
Retan			
	100	Water @ 25 ^{o}C	
	7	Tanning agent	
Fatliquor			
Add	150	Water @ 60 ^{o}C	
	6	Fatliquor mix (1:4)	30'
Add	0.4	Fixing acid (1:10)	15'

Horse up overnight
Set, Loosely - Toggle Dry
Condition, Mill

Appendix 17

Retannage of chromium tanned ovine skin

All weights based on damp shaved weight

Wet-back			
	400	Water @ 35 ^{o}C	10'
			Drain
Neutralise			
	150	Water @ 38 ^{o}C	
	1.8	Neutralising agent	45'
			Drain
Wash	300	Water @ 25 ^{o}C	10'
			Drain
Retan			
	100	Water @ 25 ^{o}C	
	3	Replacement syntan	
	2	Resin	30’
Dye			
Add	1	Dye	30’
Fatliquor			
Add	150	Water @ 60 ^{o}C	
	6	Fatliquor mix (1:4)	30'
Add	1	Fixing acid (1:10)	15'

Horse up overnight
Set, Loosely - Toggle Dry
Condition, Mill

Appendix 18

Retannage of chromium tanned bovine hides

All weights based on damp shaved weight

Wet-back				
		400	Water @ 35 ^{o}C	10'
				Drain
Neutralise				
		150	Water @ 38 ^{o}C	
		3	Neutralising agent	45'
				Drain
Wash		300	Water @ 25 ^{o}C	10'
				Drain
Retan				
		100	Water @ 25 ^{o}C	
		3	Replacement Syntan	
2	Resin			
		4	Wattle	45’
Fatliquor				
	Add	150	Water @ 60 ^{o}C	
		6	Fatliquor mix (1:4)	30'
	Add	1	Fixing acid (1:10)	15'

Horse up overnight
Set, Loosely - Toggle Dry
Condition, Mill

Appendix 19

Retannage of vegetable tanned bovine hides

All weights based on damp shaved weight

Clear				
	100	Water @ 35 ^{o}C		
	0.5	Oxalic		
	0.3	EDTA	20’	
			Drain	
Neutralise				
	150	Water @ 35 ^{o}C		
	1.5	Neutralising Agent	60’	
		Drain		
Retan/ Fatliquor				
	100	Water @ 45 ^{o}C		
	0.6	Vegetable Tanning Agent	20’	
Add	3	Sulfated Oil (1:4)	60’	
Add	0.3	Fixing acid (1:10)	30’	
Add	0.3	Fixing acid (1:10)	30’	pH =
			Drop	
Horse Up, Finish				

Appendix 20

Coefficients H_j (L mol^{-1}) of Cations for Eq. 8 (Adapted from Schumpe *et al.*, 1982)

Cation	*H_j (CO_2), 25°C*
H^+	-0.319
Li^+	-0.178
Na^+	-0.130
K^+	-0.196
Rb^+	-0.217
Cs^+	-0.243
NH_4^+	-0.252
Mg^{2+}	-0.078
Ca^{2+}	-0.073
Ba^{2+}	-0.064
Mn^{2+}	-0.084
Fe^{2+}	-0.078
Cu^{2+}	-0.090
Al^{3+}	-0.059
Anion	***H_j (CO_2), 25°C***
Cl^-	0.339
Br^-	0.324
J^-	0.309
NO_3^-	0.293
HSO_4^-	0.436
HSO_3^-	0.400
SO_4^{2-}	0.213
$S_2O_3^{2-}$	0.211
PO_4^{3-}	0.147 (Anonymous, 1979)