Carbon dioxide deliming of full thickness hides

MINIMISING THE CHLORIDE/SULFATE/AMMONIUM ION CONTENT FROM DELIMING

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In World Leather May 2007, a list was given of 45 papers that had been published which addressed various aspects of salinity that arise from leather manufacture. To make the compendium as complete as possible, some papers that were still awaiting publication were also included.
This was an unusual step but, with consideration to the growing environmental pressures that tanners are facing, and to make the compendium comprehensive, it was considered right to include this material.
The following is one of the papers that was awaiting publication, and concerns the use of carbon dioxide as a proven method of reducing the total dissolved solids (TDS) content of wastewaters.
CSIRO was at the forefront in the investigation of this technology and its introduction into commercial use. When reading this paper, it should be remembered that the original report was produced in the early 1990s and, as it has only been subject to a very light edit, some minor details will have now changed. The information set down is, however, fundamental to the highly successful technology and this is probably the most informative study written on this subject.

Australian tanneries mainly delime unsplit, full-thickness hides from beef cattle. Although carbon dioxide (CO_2) deliming is now being widely used in many countries for lime-split hides, it is too slow for thick hides.

To delime unsplit hides it has been suggested that ammonium salts or polycarboxylic acids are used in conjunction with CO_2, but their use has not been well-documented. Stringent regulations for ammonia in Australian industrial effluents require deliming processes which use very little or no ammonium salt. Such processes have been developed for thick hides and have been implemented in Australian tanneries without any increase in process time.

The method of CO_2 dissolution and the choice of auxiliary depend on the processing vessels used and the effluent restrictions imposed on the particular tannery. It is possible to design a CO_2 deliming process to meet each tannery's specific requirements and the ammonium salt addition can range from zero to 1% of hide weight.

Panel 1: Deliming with reagents in combination with CO_2

Reagent	Extent of deliming* (mm)
Carbon Dioxide (only)	1.6
Ammonium chloride (0.25M)	>6.5
Ammonium chloride (0.05M)	2.7
Polycarboxylic acid (0.05M)	2.6

** Total hide thickness that was clear to phenolphthalein after 70 minutes of treatment.*

The screening tests for CO_2 deliming

To identify deliming systems with practical potential, pieces of hide (4cm diameter, average weight ~ 10g) were agitated at 35°C in solutions (15ml) of various compounds. A CO_2 atmosphere was maintained over the solution for a period of 70 minutes. After this time the hide pieces were cut in half. The freshly exposed surfaces were then treated with phenolphthalein indicator (~ 4 drops of a 1% solution in ethanol/water, 1:1) and the colour was allowed to develop. The thickness of the hide was measured, together with the thickness of the section within the hide that was pink to phenolphthalein (i.e. pH>9). The difference between these two measurements indicated the extent of deliming brought about by the particular deliming treatment.

Typical results of these tests are given in *Panel 1*, showing that CO_2 alone delimes very slowly and 0.25M ammonium chloride greatly accelerates the process. If the extent of deliming exceeded 4.5mm, the system was further investigated.

Optimised deliming with CO_2 plus ammonium salts

A process developed to reduce, but not eliminate, the use of ammonium salts in deliming is given in *Panel 2*.

Panel 2: CO_2/ammonium chloride deliming production run

Elapsed time (min)	Load weight	9060 kg
	Average green weight	27.0 kg
	Temperature	35°C (in lime wash)
	Float	0% (no added float)
	NH_4Cl	1%
	$Na_2S_2O_5$	0.3%
	Non-ionic surfactant	0.2%
0	Drum at 4 rpm	
15	CO_2 injection at 1.25 kg/min	1.0% CO_2 added over 70 min
45	Drum at 8 rpm.	
85	Cease CO_2 injection	
	Liquor pH	7.5
180	Neck cut	Clear to phenolphthalein
	Bate*	1 hour
240	Liquor pH	8.1

** If bate is added earlier, total process time can be less than 3 hours*

Depending on the tannery's requirements, ammonium sulfate can be substituted for ammonium chloride in this process. Moreover, sulfate is appropriate if land is irrigated with the tannery effluent. Sodium metabisulfite is used to control the release of hydrogen sulfide from the drum during the deliming. It is used in preference to hydrogen peroxide because of the past experience of an Australian tannery when peroxide attacked the timber of wooden drums and greatly reduced the working life of a drum.

In optimising the process, it was found that the most efficient use of CO_2 to achieve full-thickness deliming is to start with a low float—approximately 30% at 35°C—and to inject CO_2 only until the pH of the float reaches 7.5.

The rate of CO_2 injection is adjusted to achieve this pH in about 70 minutes. Bating can commence at this time or can be delayed until the hides are completely delimed. Drumming continues until deliming is complete and, at this stage, the pH of the liquor and hide is over pH 8.0 but neck cuts are clear of phenolphthalein.

Deliming time increases with average hide weight. For example, 20kg hides (neck thickness, 10mm) can be delimed and bated in 2 hours, whereas 30kg hides (neck thickness, 15mm) require 3 hours.

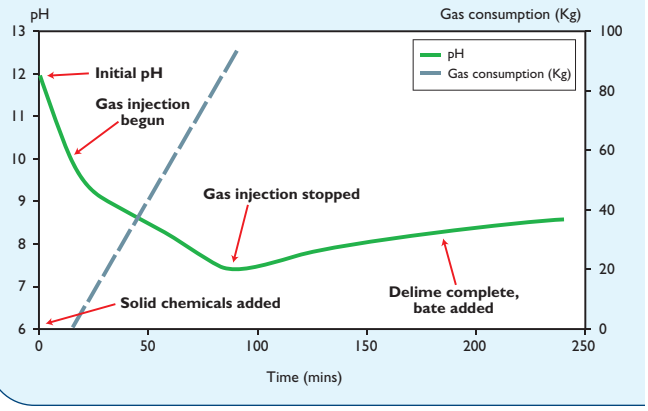
Initial drum speed is slow but during the CO_2 injection, and as the hides release water, the drum speed can be increased without causing damage to the hides.

The change in pH and the rate of addition of CO_2 gas to the tanning vessel during the course of the process, outlined in *Panel 2,* are shown in *Panel 3*.

Tanners select the bate that they consider appropriate for their process, and both pancreatic and bacterial bates have been used with good results. During bating the pH of the hide is between pH 8.0 and 8.5 and the level of dissolved salts, which could influence bating action, will differ from conventional processes. Some change in bating agent might be needed, but this is best determined by an assessment of the finished leathers.

At the time of these trials it was recommended that the pH of the deliming liquor should be reduced to below pH 7.0 during CO_2 dosing, and the hide should be delimed to pH 7.0. This was because of the possibility of precipitation of insoluble calcium salts at higher pH values.

Panel 3: Carbon dioxide gas addition and pH change during deliming



With the CO_2 deliming systems used in Australian tanneries for full thickness hides, the pH is considerably higher than 7.0—as shown in *Panel 1*—at all times. However, no problems have been observed with either precipitation of calcium salts or leather quality.

An evaluation of quality

An essential part in the development of a beamhouse process is an evaluation of how that process influences the quality of finished leathers. To this end, a number of matched side trials were conducted in which the wet blue and finished sides from various CO_2 deliming processes were compared to the corresponding sides that had undergone a conventional deliming treatment. It became obvious very early in this work that wet blue from a process that uses CO_2 is cleaner and flatter than wet blue that comes from a process which involves a conventional ammonium chloride delime.

One matched side comparison of a CO_2/ammonium chloride process with conventional deliming showed that, in the wet blue stage, all six CO_2 delimed sides were cleaner and had a less drawn grain than the matching sides. As black aniline shoe leather, the CO_2 delimed sides had significantly less growth marks and drawn grain and tended to have a tighter break than the sides from the conventional processes. The two treatments produced similar 'feel' and 'levelness' characteristics in the finished leather.

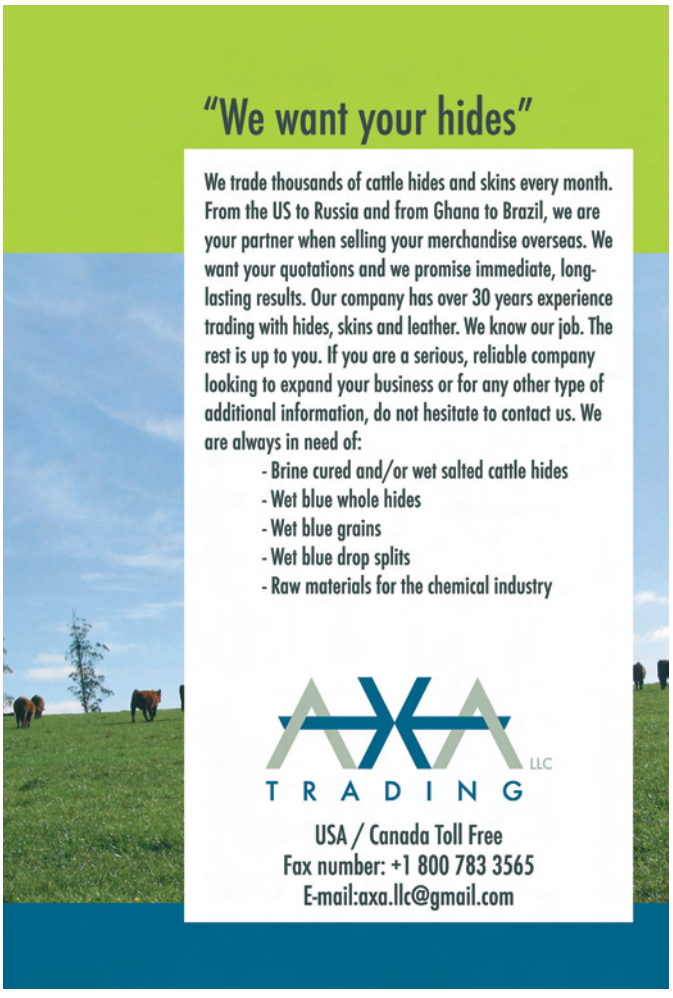
Once the processes were used in full commercial production, the improved leather quality resulting from the CO_2 deliming was confirmed.

Pickling of hides from CO_2 deliming processes

CO_2 deliming can increase the acid combining capacity of delimed hides as shown in *Panel 4*. ➤

Panel 4: Acid combining capacity of delimed hides

Deliming process	Acid combining capacity (mmol H^+/g delimed hide)
Conventional NH_4Cl	0.28
CO_2/NH_4Cl	0.38



The hides that have been delimed with CO_2 can take up more acid than hides delimed with a conventional ammonium chloride system. This occurs because calcium bicarbonate is formed during CO_2 deliming. A significant amount of the bicarbonate remains in thick hides after the delime wash and in pickling solutions it reacts with acid to liberate CO_2. The reactions are:

Deliming: $Ca(OH)_2 + 2CO_2 + Ca(HCO_3)_2$
Pickling: $Ca(HCO_3)_2 + 2H + Ca^{2+} + 2H_2O + 2CO_2$

There are two practical considerations associated with the effect of CO_2 deliming on the pickling process.

- CO_2 delimed hides may require a higher offer of acid in the pickling process to satisfy the requirements of the tanner
- Tanning drums need to be well vented to overcome any risk of pressurising the drum as the CO_2 is released during pickling

A demonstration with 17 tons of hides in a large drum with inadequate drainage resulted in excessive carry-over of lime into deliming and excessive bicarbonate into pickling. As the drum had insufficient venting, the released CO_2 built up excessive pressure in the drum.

It is recommended that breather tubes are fitted to drums and that they discharge outside the tannery building. It is of interest to note that tanners who have adopted these CO_2/ammonium chloride deliming processes have not found it necessary to increase the acid offer for pickling.

The dissolution of CO_2

An efficient CO_2 deliming is dependent on efficiently dissolving CO_2 in the deliming liquor. The method of delivering CO_2 depends on the tanning vessel. For conventional tanning drums, the gas is simply injected into the headspace through the hollow axle. For drums with a recirculation system, the gas can be injected into the recirculation loop.

Due to the low float that is used in these deliming processes, the volume of liquor that initially passes through the recirculation line is likely to be small and hence much of the gas that is injected into the loop will enter the drum undissolved. In practice this technique is essentially equivalent to hollow axle injection.

The turbulence generated by drumming provides an efficient method for the dissolution of CO_2. This was demonstrated in a trial where the dissolution of CO_2 was calculated by measuring the difference between gas outflow and gas inflow at various drum speeds. The results of this experiment are summarised in *Panel 5*.

This experiment indicates that it is an advantage to increase the drum speed as early as possible during the deliming process. However, possible abrasion to the grain layer of the hides must be considered. A compromise needs to be made between increasing speed quickly to increase gas uptake, and maintaining a low speed until the hides have sufficiently fallen to protect them from abrasion. No grain abrasion has occurred in any of the CO_2 deliming trials or in production.

The delivery of CO_2 into more open tanning vessels, such as mixers, paddles and pits requires more sophisticated dissolution techniques. In these vessels, it is necessary to recirculate a delime float through a venturi and inject the CO_2. By dissolving the gas directly into the liquor, the possibility of creating a potentially

Panel 5: Gas dissolution at various drum speeds

Drum speed (rpm)	Gas injection rate (lpm)	Gas outflow rate (lpm)	Gas consumption (lpm)
Zero	1280	1160	120
4	1280	1060	220
6	1280	800	480

hazardous CO_2-enriched atmosphere is avoided. Because the gas dissolution takes place outside the tanning vessel, higher floats may be necessary to achieve a desirable recirculation rate.

The safe use of CO_2 in tanneries

Used correctly, CO_2 is safe. However, CO_2 gas will displace oxygen from the atmosphere. This can cause an increase in breathing rate and a shortness of breath, and can result in unconsciousness. Workers should be made aware of the properties of CO_2 and must take care when drums are opened after CO_2 deliming. The drum will not have the offensive odour of an ammonia delime but it is still not safe. Furthermore, CO_2 is heavier than air and therefore nobody should be under a drum when the door is opened. The efficient use of CO_2 and its addition during the first hour of deliming minimises the amount of CO_2 in the drum at the end of the process.

The choice of an accelerated CO_2 deliming system

CO_2 is now being used in conjunction with a variety of auxiliaries to delime full thickness hides to produce improved quality leathers without an increase in process time. When selecting a CO_2 deliming process for thick hides, consideration must be given to both the effluent requirements and overall costs.

The process is of high value for minimising the levels of chloride or sulfate ions in wastewaters and there is considerable value in reducing the ammonium ion content.

At the time of these investigations the lowest cost process for unsplit hides reduced the use of ammonium salts by about 75% compared with conventional deliming. However, other processes which either do not use ammonium salts or use extremely low levels can be more cost effective due to reduced effluent treatment costs and disposal charges. For example, a process, which reduces the use of ammonium salts by 97%, can achieve total ammonia discharges of less than 500mg per kg hide processed.

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References

- *C.A.Money, JALCA, 86, 229, (1991).*
- *K.H.Munz, XXth IULTCS Congress, Philadelphia, (1989)*
- *M.Tomaselli, B.Naviglio and A.Russo, Cuoio Pelli Mat. Concianti 67, 5, (1991).*
- *M.J.Klaasse, JALCA, 85, 407, (1990).*
- *Pulp and Paper, Chemistry and Chemical Technology, 3rd ed., Vol. 1,Ed: J.P.Casey, Wiley, (1980).*
- *D. Lachenal, In: Pulp, Paper and Board, Ed: I.F.Hendry and W.J.H.Hanssens,Elsevier, (1987).*
- *J.Christner, Das Leder, 43, 203, (1992).*

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