

The role of bound and free water in the liming process

In World Leather August/September 2004, observations were presented showing that if limed hides were washed at different temperatures, a warmer wash caused an increase in softness and hide relaxation, but without change in the total water content⁽¹⁾. These softening effects were linked to the glass transition temperature of collagen, also being presented in the August/September 2004 issue⁽²⁾. However, references were made to earlier investigations that address other aspects that need taking into account. Translations and detailed studies of these reports are summarised in the following paper.

Summary by A.W. Landmann

Investigations by Herfeld and associates, Lederinstitut Gerberschule Reutlingen, Germany.

Herfeld and associates carried out a series of experiments, which were published between 1963 and 1967. This followed a practical approach using three parameters to evaluate the experimental results:

% weight gain: This is the traditional parameter for the judgement of the liming, being the % increase, mainly of water held by the pelt at the end of liming, i.e.:

$$\frac{(\text{weight after liming} - \text{weight after soaking})}{\text{weight after soaking}} \times 100$$

% swelling or increase in thickness: This is closely related to the total volume swelling, i.e.:

$$\frac{(\text{final thickness} - \text{original soaked thickness})}{\text{original soaked thickness}} \times 100$$

% compression: This is a measure of the compressibility of limed pelt under applied pressure, i.e.:

$$\frac{(\text{original thickness} - \text{final thickness after increased pressure})}{\text{original thickness}} \times 100$$

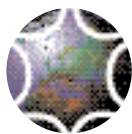
These investigations showed that pelts swell to different levels according to the pH. In addition, pelts swollen to the same percentage can show different levels of compression—hence softness and relaxation—according to the type of cation and temperature, and salt if offered to the system.

Investigations by Bienkiewicz, Leather Research Institute, Lodz, Poland

Bienkiewicz (JALCA 85, 1990,305) wrote a paper “Leather - Water: a system?” In this paper he pointed out the importance of water and the similarity in the way that water was held by the collagen in both pelt and leather. Four different mechanisms were given:

1. In the triple helix. This water is held so tightly that it cannot be determined by drying as within normal moisture determination, but can be detected and estimated by Nuclear Magnetic Resonance.
2. Water believed to be held by two hydrogen bonds. If the leather is chilled by applying dry ice this water is not available to form ice, so the leather does not harden.
3. Water weakly attached to side chains by hydrogen bonding. This may be displaced by changes in charge due to pH variations, the presence of anions/cations, or by temperature rise. This release may cause softening due to lubrication between the fibres.
4. More weakly held water which can be removed mechanically, and which is in part dependent on pH.

He describes how each mechanism is recognised and estimated, but states that researchers using alternative methods have produced findings that differ numerically and differently assign the linkages to collagen.▶



Bound and free water

According to Bienkiewicz, bound water includes mechanisms 1 & 2, but is difficult to determine. These terms are not used for Herfeld purposes, however, it is useful to bear these in mind. In this event the percentage of free water is the water that can be removed mechanically by pressure, and bound water the difference between this free water and the total moisture content as determined by drying according to the official SLTC/IUC method.

Using the Herfeld parameters, within the context of liming the bound water gives rise to swelling. This makes the pelt hard as it is held firmly by the fibre structure and is not available as a lubricant. However, the free water acts as a lubricant and provides softness and flexibility.

It can thus be recognised that swelling is related to the sum of the free and bound water, and degree of compression to free water. Accordingly, two pelts may have the same total water content, but if the ratios of free to bound water are different, then they will differ in their degree of compression and softness.

Herfeld published a series of papers in which he examined systematically the factors which can influence liming. Initially (*Paper 1*) he maintained a constant SH^- concentration but increased the alkalinity by adding equivalent amounts of sodium hydroxide and calcium hydroxide. These do not produce the same concentration of hydroxyl ions in solution due to the limited solubility of lime. He concluded that:

- The percentage weight gain did not characterise the behaviour of the pelt in liming.
- The offered alkalinity did not characterise the behaviour of the pelt in liming.
- The presence of cations was significant as Na, Ca, NH_4 , due to the very different pHs each produced at the same molar concentration.

Subsequently the effect of temperature was examined. These investigations showed that changes in swelling and compression were not parallel, and differed according to the cations involved. It is unlikely that today's tanners would use the theoretical liquors used in this research, but the work is very significant in pointing out that as temperatures rise, although the swelling may be constant, the degree of compression will increase, hence greater softening of the pelt.

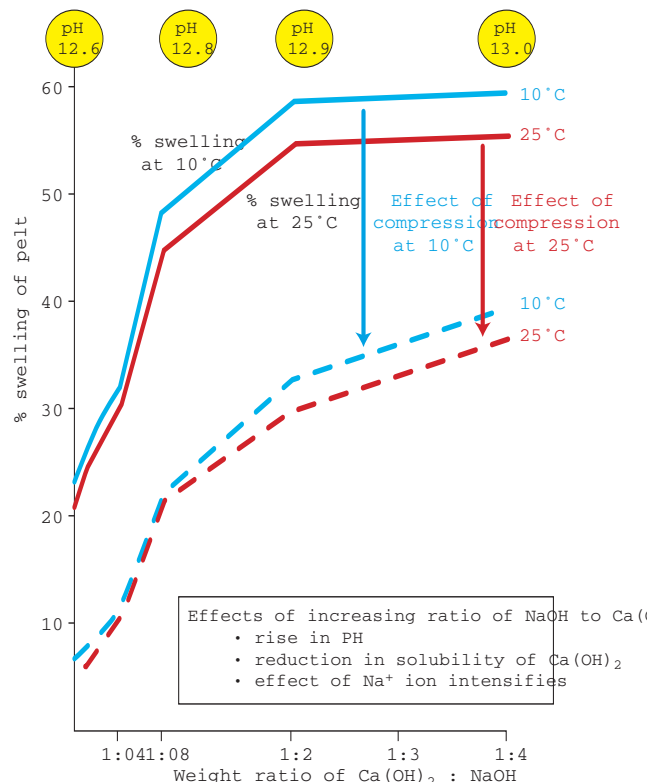
The investigations continued, using a basic lime liquor to which sharpeners were added. This was performed at two temperatures, and the results evaluated in terms of the same parameters. The conclusions at this stage were:

- The higher the final pH, the greater the swelling.
- At the same pH sodium hydroxide provides more swelling and less compression than lime-based systems.
- In mixed or binary systems where OH^- was provided by both Ca^- and NH_4^+ a reduction in swelling was observed, but a greater increase in compression when compared to Na^+ .

Finally, the whole series is summarised (*Paper 7*) and the earlier conclusions reinforced. Linkage is made to the practical importance of these findings, where apart from the hair removal, liming affects the remaining collagen hence the final leather. To relate the properties of final leather to the degree of swelling and compression in the liming process Herfeld uses the term "liming outcome", concluding that:

- A strong outcome is linked to increased softness,

Swelling and compression of pelt due to increasing ratios of $\text{NaOH} : \text{Ca}(\text{OH})_2$ at different temperatures



smoothness of grain and stretch. However, there is a danger of loose grain and increased water absorbency with empty flanks.

- When the outcome is less, the grain is finer and tighter, but the leather can be tinny with insufficient softness and less fullness.

Binary systems and the influence of salt

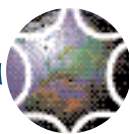
Within binary systems he concludes that:

- NaHS + ammonia is unsuitable because a final pH of 12.0 cannot be reached.
- NaOH/NaHS was also unsuitable because at low NaOH concentrations the pH was too low, and at higher NaOH concentrations the pelt became too plump.
- The traditional NHS/NaOH + $\text{Ca}(\text{OH})_2$ remained as the preferred system.

The effect of the addition of sodium chloride was also made, resulting in reduced swelling. In these investigations the degree of compression was not reduced to the same extent, and the effects are less at higher temperatures. However, addition of the salt calcium chloride actually caused an increase in swelling due to lyotropic effects, that is an uncontrolled breakdown of the collagen structure.

The Herfeld summary

- In liming, the end-pH governs both the degree of swelling and the percentage compression.
- Sodium cation gives more swelling than calcium, and in excess gives an undesirable glassy condition.
- The solubility of the calcium ion can be affected by the presence of other cations and salt.



- Both the degree of swelling and the degree of compression affects the liming outcome, which in turn is related to the characteristics of the final leather.

Regarding the final leather, the greater the “liming outcome”, the softer, smoother and more relaxed the leather. The area yield is increased, but with a loss in substance. The flanks are looser, but the water absorption is increased together with the water vapour permeability.

The smaller the “liming outcome”, the tighter the grain and firmer the flanks of the final leather. There is an accentuation of neck folds and an inclination for the leather to be tinny.

Choices have to be made between these two extremes, and to influence the swelling and the degree of compression, the following can be used:

- Variation of the ratio of lime to sulfide. The less lime and more OH^- from $\text{Na}_2\text{S}/\text{NaOH}$ at similar pH values, the greater the compression and softness.
- Change the temperature. A rise in temperature increases the degree of compression at a given level of swelling and increases the softness.

It must be understood that these investigations were based on high float situations, that is more similar to conditions found in paddle liming processes as opposed to drum systems. These findings do not take into account the effects of changes in osmotic pressure that can be introduced by increasing float levels during liming as often used in drum system. In this situation it is possible to increase the degree of swelling that might be attributed to lime, or in low float situations and in the presence of solubles, to repress swelling effects due $\text{Na}_2\text{S}/\text{NaOH}$. And in practice auxiliaries and other techniques can create similar effects.

Nevertheless, the investigations are important as they throw light on the fundamental effects that take place within liming. As a generalisation, the findings show that the swelling should be at as low a level as possible while attaining a satisfactory result in the final leather. Within this degree of swelling, releasing bound water to provide greater lubrication can raise the degree of compression. This can be achieved by increasing the lime and reducing sodium hydroxide as a source of alkali, raising the temperature, or by repressing swelling with sodium chloride although this is no longer environmentally acceptable. These changes provide a shift towards greater softness and flaccidity in liming, hence an improved leather in terms of softness, relaxation, reduced draw and neck growth.

Bienkiewicz explains the various combinations which water can bind or be released by collagen. Herfeld and his research group introduced two simple parameters as degree of swelling and degree of compression to characterise the liming process, and carefully investigated events that influenced these properties. These papers when combined show the importance of the way that water is held within the collagen structure, and the effects of change within these bondings with regard to the outcome of the liming process. ●

References

1. *Observations: Temperature related relaxation within liming and other wet processes: R P Daniels, Technical editor, World Leather, August/September 2004*
2. *The glass transition temperature of leather and its implications to the leather industry: Sujee Jeypalina, British School of Leather Technology, University College Northampton, UK, World Leather, August/September 2004.*