SALINITY REDUCTION IN TANNERY EFFLUENT

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Introduction

Salinity in tannery effluents, measured as TDS (Total Dissolved Solids), is a critical problem in many countries, particularly India and Australia. About 60% of Indian tanning occurs in Tamil Nadu where there is a discharge limit for TDS of 2100 mg/L. The Pollution Control Board has insisted that some tanneries install Reverse Osmosis but this does not solve the salt problem. The aim of a joint CLRI-CSIRO-ACIAR project is to develop and apply industrially viable systems to eliminate or significantly reduce salt use in hide and skin preservation and processing.

The four major components of the project are:

- reduced salt in curing
- short term preservation with chemicals or chilling
- pickle liquor recycling
  - in vegetable tanning (India)
  - woolskin processing (Australia)
- Direct Chrome Liquor Recycling (DCLR)

In Australia, some tanneries have significantly lowered the total amount of salt discharged mainly by processing green rather than salted hides and by directly recycling chrome tanning liquors (DCLR). At the same time, water use has been greatly reduced. Short-term preservation with chilling or chemicals is used to facilitate green processing. Because sodium chloride levels are low, these tanneries are able to sustainably use the effluent for irrigation even though the TDS can be over 10,000 mg/L. Many components of the TDS are beneficial but the application rate must be monitored.

In India, goat skins are salted with 50-100% salt by weight and hides with 40-50%. In Tamil Nadu, soak liquors from the soaking of salted skins are required to be evaporated in solar pans but this is usually inefficient and little salt is removed from the site. Used salt removed from skins before processing is also an environmental problem. UNIDO has already implemented some systems to reduce the amount of salt discharged in tannery effluents. Low salt systems with additives have been investigated in the current project with encouraging results and chilling of hides and skins is also being trialled in India.

Australian woolskins are available only seasonally and they are salted then tanned throughout the year. Low salt systems with additives have been investigated for woolskins which do not require prolonged storage.

Tannery process improvements which have the greatest impact on TDS reduction are pickle recycle and DCLR.

Low Salt Preservation

Drying and dry-salting of goatskins has been investigated but it is unlikely that they will be adopted for skin preservation in India. Many short-term preservation systems have also been investigated but are not suitable for the rigorous Indian conditions. Low salt systems with additives have given promising results and are being trialled commercially. They could
reduce salt use 3 to 4 fold which will be a significant reduction. Now that skins are not bought by weight, the weight of salt used does not affect the skin price.

It is feasible for the first handlers of Indian goat skins to salt unopened skins by rubbing salt on the flesh side as usual but with about 20% salt by weight rather than 80% salt. It will be most important that wet skins are drained well before salting. The skins will then be turned hair out. The scrotum will remain on the skins and must be well salted. Collection centres, often already controlled or influenced by tanners, could apply additives as necessary to preserve the skins for 7 to 28 days as required. It is also possible that the additive is mixed with the salt prior to application. This low salt system could reduce salt use 3 to 4 fold and there will be little excess salt on the skins and little solid salt waste. Evaporation of soak liquors will be required, as is the case at present. As waste salt will be significantly reduced, all the evaporated salt should be able to be re-used or used as a fertiliser for coconut palms.

The choice of additives is critical and health, toxicity and environmental effects must be considered. It appears to be advisable not to use boron or zinc compounds or sodium fluoride for preservation in India. It is unlikely that the Indian Environmental Charter which excludes the use of boron compounds will be changed. The concentration of zinc and boron in Indian tanning centres could lead to build-up of damaging levels in soils. A large range of chemicals has been investigated as salt additives for low salt preservation of skins. Trials show that provided there is 20% salt on skin weight, insect infestation is controlled. Laboratory trials have indicated the most suitable additive to be magnesium oxide. Sodium carbonate could also be used but for hand application, magnesium oxide is preferable. The alkaline treatments have not caused any unhairing problems due to immunisation. Good preservation for one month is also achieved with 20% salt plus 0.5% naphthalene but health and environmental issues must be considered.

Industry trials using 20% salt and 2% magnesium oxide on skin weight have produced high quality leathers after storage for a month. Even transport from Delhi and storage in Tamil Nadu during hot summer conditions did not cause grain damage. It was found to be advantageous to extend the soaking time to 18 hours and use a soaking enzyme to ensure that the leather quality is comparable with leathers from conventionally salted skins.

Australian companies are collaborating in commercial trials of flat salting woolskins with low salt levels and have compared several additives and produced good quality finished woolskins. The salt application equipment has been modified to enable the low salt application. It has been found that low salt preservation using sodium fluoride and boric acid as additives could reduce salt use 7 fold. These additives have been used for many years in Australia. The storage time required for the skins will determine the salt reduction achieved.

**Chilling**

Elimination of salt for hide and skin preservation would have the greatest impact on reducing TDS. Chilling in chillers or with ice has been widely used in Australia for many years\(^1\). Chilled hides are usually kept for only a few days but some are kept for over a week at low temperatures. Chilling was thought to be too difficult for Indian conditions but it now appears it may be viable for some hides and skins. If hides and skins are available in large numbers in a region within a relatively short drive from a tanning centre, chilling could be feasible.

Chilling is increasingly being used for food storage and transport in India and CLRI has completed hide trials and costings which are very encouraging. Chillers rather than ice are considered to be best for India. A mobile chilling unit designed for industry trials and demonstrations will initially be used for chilling hides in Kerala and transportation to Erode. Ultimately insulated trucks will be used for transport. Some Indian tanners consider that chilling could overcome their salinity problems.
Pickle Liquor Recycling

An Australian collaborating woolskin tanner has recycled commercial pickle liquors for more than 250 cycles. Previously, pickle liquors were discarded after 20 uses for no particular reason. The recycle liquor reached a steady state after cycle 11 with respect to pH, titratable acid and total nitrogen. The pH and total acidity (formic plus sulphuric) at the end of cycles is given in Figure 1. No liquor clarification has been necessary and leather properties are at least as good as standard production. A modified DCLR for woolskins has been used successfully for more than 150 cycles. This system does not give greater overall TDS reduction than the two stage pickle and tannage recycle but does reduce labour costs. The tanner is satisfied with the commercial acceptance of skins from both recycling systems. Trials of pickle liquor recycling have also been successful at Indian tanneries producing vegetable tanned goat leathers with no difference in the quality of the leathers.

![Figure 1: Car seat cover pickle conditions](image)

**Direct Chrome Liquor Recycling**

DCLR has been used for many years in Australia and reduces the use of both sodium chloride and chrome powder, which contains up to 30% sodium sulfate. Spent chrome liquors are used for the subsequent pickle after acidification to pH<1. Excess chrome liquors are precipitated and the chrome reused as illustrated in Figure 2. The greatest savings in salt use are made if the spent chrome liquor from the drum is collected undiluted for recycle and diluted liquors are precipitated. Good practice allows indefinite re-use of the chrome liquor. Total chrome precipitation from all spent chrome liquors results in far higher TDS levels.
**Figure 2:** Direct Chrome Liquor Recycling and Reuse of Excess Chrome Liquors.

**Preparation of Pickle Liquor**
- The recovered chrome liquor is screened and grease is skimmed if necessary.
- The liquor must be acidified before it is reused for the next pack of delimed hides. The usual amount of 98% sulphuric acid is all added direct to the pickle tank. The pH is <1 and this prevents chrome staining. At this low pH, the chromium species present are of low molecular weight and rapidly penetrate the hide.\(^7\)
- When the liquor is acidified, calcium sulphate precipitates and emulsified grease is released. Both can be removed periodically but do not cause a problem in the process.
- The acidification should be done early to allow time for the liquor to cool. Cooling systems can be used.

**Typical recycle process**
- Delime wash
- Drain well
  - 2% Salt (it is vital that the SG is sufficient to control swelling to the same degree as in the normal tannery process)
  - 1% Sodium formate,
- Drum 10 minutes
  - Add 45% acidified recycle pickle while drumming continuously, check pH, SG/Barko, Temperature
- Drum as for usual pickle, check pH, SG/Barko, adjust if necessary.
  - 5.5% chrome powder
- Usual drumming, fungicide addition, basification and checks
- Unload with little washing

Following laboratory investigations, successful commercial trials have been undertaken in India. It has been found that it is critical that the drum is rotating during the addition of the acidified pickle to the drum. Otherwise drawn grain caused by acid burn can occur. Also, the pickle tank should be covered to avoid fumes.
Conclusion

Technology for TDS reduction has been developed and demonstrated. However, to achieve significant TDS reductions in India, there will need to be considerable uptake of low-salt preservation of skins and chilling of hides. The proposed low-salt preservation will entail little change for first handlers of skins but greater care will be required to ensure even salt application. There will be resistance to change. One possibility that may bring about change: the tanner could pay more for skins with less salt and good preservation and less for skins with excess salt.

The costs associated with chilling will be considerable and it is generally accepted that those who gain from the development should bear the cost. It is a possibility that the Government may provide loans which industry would repay. Costs and benefits first need to be determined.

The collaborating tanners will be the champions of the new technologies. Once a technology is proven to them, they will adopt the new systems and others are expected to follow.

References