



Salinity-related issues in India ^(Legend 1, 2)

DEVELOPMENTS TOWARDS ZERO LIQUID DISCHARGE AND THE REDUCTION OF SALINITY

In India there are nearly 3,000 tanneries, although only around 2,000 are in regular operation. They process 700,000 tons of hides and skins per year, with an average water discharge of about 100,000 m³ per day. There are more than 200 individual effluent treatment plants, and 18 common effluent treatment plants (CETP).

Salinity in tannery effluents, measured as Total Dissolved Solids (TDS), is a critical problem in many countries, but particularly in India. About 60% of the tanning industry is in the state of Tamil Nadu, where the disposal of treated effluent with high TDS from landlocked tanning clusters remains one of the serious unresolved problems.

In accordance with the Erode Court Ruling of 2005, all tanneries in the state not discharging to a CETP must meet 2,100 ppm TDS, or install a Reverse Osmosis (RO) system by the end of 2007. CETPs must meet this limit or have zero effluent discharge, which will also require the installation of RO. This means that all tannery effluents in the state will require RO, and all of the saline concentrates will be solar evaporated.

The environmentally secure disposal of liquid wastes generated from tanneries in a sustainable way is a serious problem in India and many other developing countries. In addition, the need for the recovery of water from tannery effluents is increasing. This is because of the fast depletion of water resources, a severe shortage of quality water for drinking and green development, and the management of Total Dissolved Solids (mainly sodium chloride).

To address these issues, investigations have taken place and demonstration plants set up, and a review of the situation is given.

Water recovery and the management of Total Dissolved Solids (TDS)

Conventional effluent treatment systems adopted by the global tanning industry are designed to reduce mainly Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), sulfides, suspended solids, and chromium. They do not address the Total Dissolved Solids (TDS), which are mainly caused by common salt or sodium chloride. Due to the inherent water quality of tannery wastewaters, most of the treatment plants are unable to meet the TDS level of 2,100 mg/l as prescribed by India for treated effluent before discharge into inland lakes and streams, or for the irrigation of agricultural land. There are three options for tackling the TDS problem:

- **Dilution with domestic sewage:** This is after the tannery effluents have undergone conventional treatment in systems similar to those being followed in Italy, the USA, and Kanpur in India. This is not an option in many tannery clusters due to the absence of domestic wastewater collection.
- **Marine discharge:** This option is only feasible when tanneries or tanning clusters are located near coastal areas, such as Istanbul, Izmir, some parts of Europe, and Kolkata in India. For landlocked tanners this is not an option.
- **Membrane systems coupled with evaporation:** This

involves the use of membrane filtration to recover quality water for re-use. This involves tertiary treatment before membrane treatment, and leaves part of the water as a concentrated salt-water solution for evaporation.

To recover water and manage the TDS problem, the wastewater needs initial treatment by:

- Adopting conventional primary and secondary biological treatment (or alternative systems) to reduce the COD, BOD, suspended solids and chromium.
- Tertiary treatment—including low pressure membrane filtration.
- The application of Reverse Osmosis (RO).
- It is noted that it is possible to use membrane bioreactors to replace conventional biological treatment, clarification and sophisticated tertiary treatment methods.

By adopting membrane technology such as RO, good quality water can be recovered from treated effluent. About 75-80% of the water can be re-used, leaving 20-25% of the reject with a high TDS concentration. This must then be addressed with evaporation, using methods such as forced evaporation.

More than 50 RO systems are in operation in Tamil Nadu tanneries, and the CETPs also plan to implement RO systems. The objective is to achieve zero discharge of liquid with financial support from the Government of India. Based on the most recent experiences of pilot/commercial scale membrane systems for the recovery of water from treated effluents, a full-scale system is being implemented at a new CETP in Tamil Nadu to treat 2,400 m³/day.

Salinity reduction in tannery effluent

Tanneries in Erode processing hides from wet blue to finished leather have found that the use of permeate (recovered water following RO treatment of treated tannery effluents) provides considerable chemical savings in dyes and other expensive chemicals. This is the result of the low TDS and the good quality of the recovered water. These savings have offset costs. ➤



SALINITY-RELATED ISSUES IN INDIA

In wet blue plants most of the ROs are not yet fully operational, and there will be no cost savings. It is also likely that there will be problems with the fouling of RO membranes in these units. This is less likely where goatskins are processed as paint unhairing systems are used for hair recovery.

An audit has found that most Erode tanneries have inadequate systems for solar evaporation of waste liquors, including RO reject, and any improvement of the system will be another major expense.

In general no disposal options are available for the recovered dry salt following evaporation. These will therefore pile up at tanneries or elsewhere, and during the monsoon season it is likely that they will be dispersed into the environment.

At present, the main focus appears to be on zero discharge rather than TDS and salt reduction measures. However, both are intertwined.

Four major investigations have taken place^(Legend 2) to reduce the use of common salt in both raw hide and skin preservation and processing.

1] Hide and skin preservation

LOW SALT PRESERVATION OF GOATSKINS

To reduce TDS, Indian goatskins can be salted unopened with only 20% salt on the skin weight. This will reduce salt use 3- to 4-fold, with few salt crystals on the skin and little salt waste.

An additive is required with the salt for good preservation, and it is best that this additive is pre-mixed with the salt. It will also be most important that the wet skins are drained well before salting.

Industrial trials up to July 2005 found that the addition of 2% magnesium oxide provided satisfactory results. But, during the summer, major problems occurred with sticking, and this made the opening up of skins very difficult.

Good results were achieved using 20% common salt and 2% sodium carbonate, where skins were held in hot conditions for more than three weeks. These skins were moister than control skins, but they were well preserved and could be opened easily. Trials are now underway with 20% salt, 1% sodium carbonate and 1% magnesium oxide.

Skins preserved using low salt techniques will not require machine desalting or the disposal of the residual salt. In addition, the soak liquors will contain less salt.

2] Hide chilling

The elimination of salt would have the greatest impact on reducing TDS. In practice, it is possible that chilling can save up to 500 kg of salt per 1 tonne of hides. At present this is destined for discharge or disposal as solid waste.

Chilling in chillers or with ice has been widely used in Australia for many years. These chilled hides are normally kept for a few days, but some are kept for up to one week at low temperatures. If Indian hides and skins are available in large numbers within a relatively short distance from a tanning centre, chilling could be feasible. So far three industrial trials have taken place using a mobile chilling unit, and trials carried out by largest hide tannery in Erode (KKSK) have produced impressive results.

For the system to work in India, the following are needed:

- Quick delivery of hides to collection centres.
- Blast chillers with generators and storage areas at collection points.
- Insulated and air conditioned trucks for transport.
- Chilled storage area for holding hides at tanneries before processing.

Panel I

Salts in wet blue production^(Legend 3)

Process		% on Hide Weight	
		% Salt	% Sodium
Soak	Salted hides	14	5.6
Lime	1% NaHS (70%)	1	0.3
	1.5% Na ₂ S (60%)	1.5 [0.75]	0.55 [0.27]
	2.5% Ca(OH) ₂	2.5 [2.25]	
Delime	1% CO ₂		
	1% (NH ₄) ₂ SO ₄	1	
	0.5% Na ₂ S ₂ O ₅	0.5	0.1
Pickle	6% Salt	6 (2)	2.5 (0.8)
	1% Formic acid	1 (0.75)	
	1% Sulfuric acid	1	
Chrome tannage	8% Chrome powder	8 (6) or 7 (5)	0.8 (0.5)
	0.7% MgO	0.7	

Figures in brackets [] are achieved with lime liquor recycling

Figures in brackets () are achieved with efficient chrome liquor recycling

3] Pickle liquor recycling

It is possible to continuously recycle pickle liquors for many cycles without loss of quality by the following method:

- Collect pickle liquors and screen to remove coarse solids.
- Add acid to pH 3.5. It is important to acidify soon after collection to prevent bacterial growth and odour. The normal amount of sulfuric acid at 98% strength can be added to the pickle liquor.
- Mix well.
- Allow the liquor to cool to normal temperatures.
- Settle. Fine calcium sulfate precipitates. This does not cause a problem, and can be removed periodically.
- Add salt to give a reading of at least 7°Be.

When tanners first investigate this technology it is recommended that 10 trials are run initially and this can then be gradually increased.

4] Direct chrome liquor recycling (DCLR)

DCLR has been used for many years in Australia to reduce both sodium chloride and chrome powder, which contains up to 30% sodium sulfate.

In practice, spent chrome liquors are used for the subsequent pickle after acidification to pH<1.0.

As there is an excess of chrome liquor, these are precipitated, the chrome regenerated and re-used.

The greatest savings in salt use are made if:

- The spent chrome liquor is collected from the drum undiluted.
- The diluted liquors following washing are precipitated.

It is important to note that total precipitation of all spent chrome liquors and washings result in far higher TDS levels and good practice, as indicated, allows indefinite re-use of the chrome liquor.



THE PREPARATION OF PICKLE LIQUORS AND WET BLUE MANUFACTURE

The following details have been found important in practice:

- The recovered chrome liquor is screened and the grease skimmed if necessary.
- The liquor must be acidified before re-use in the next pack of delimed goods. When the liquor is acidified, calcium sulfate is precipitated and emulsified grease 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. If necessary cooling systems should be used.

The following is a typical process for wet blue production:

- Delime and wash.
- Drain well, leaving no float.
- Add 2-3% salt. It is vital that the Specific Gravity (SG) is sufficient to control swelling to the same degree as in normal tannery practice.
- Add 1% sodium formate.
- Drum for 10 minutes.
- Add 45% acidified recycled pickle while drumming continuously. Check pH, SG/Barkometer, temperature.
- Drum as usual for pickle. Check pH, SG/Barkometer and adjust if necessary.
- Add 5.5% chrome powder.
- Running times, fungicide addition, basification and checks as normal.

- Drain and collect the spent liquor for recycling.
- Minimum wash, with collection for precipitation and regeneration.
- Unload.

The value of these four techniques is that salt use is reduced and, proportionately, the problems of salt recovery and disposal are reduced. It is another example of where cleaner processing is better than end-of-pipe-treatment. Changes in these areas could make zero discharge from some tanneries feasible. 

Legend

This paper is a combination of two papers presented at LERIG 2007:

- 1) *Development in wastewater treatment and management in Indian Leather Industry under zero liquid discharge concepts: S.Rajamani, Chairman IUE Commission of IULTCS and Technical Advisor, Central Leather Research Institute.*
- 2) *Salinity reduction in tannery effluent: T.Ramasami⁽ⁱ⁾, N.K.Chandra Babu⁽ⁱⁱ⁾, C.Muralidharan⁽ⁱⁱ⁾, J.Ragave Rao⁽ⁱⁱ⁾, P.Saravanan⁽ⁱⁱ⁾, and Catherine A.Money⁽ⁱⁱⁱ⁾.*
⁽ⁱ⁾Secretary, Department of Science and Technology, New Delhi, India:
⁽ⁱⁱ⁾Central Leather Research Institute, Chennai, India:
⁽ⁱⁱⁱ⁾CSIRO, Australia.
- 3) *The values set down in Panel 1 are extracted from Clean Technology Challenges - Part 2: Catherine A.Money, CSIRO Leather Research Centre, XXV IULTCS India, 1999.*



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USA / Canada Toll Free
 Fax number: +1 800 783 3565
 E-mail: axa.llc@gmail.com