



The potential of silicates in leather production Part 1 of 4

Salt-free curing of hides and skins and reducing the salt content of tannery effluents

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Major benefits from the use of sodium silicate in leather manufacture have been researched and developed. The project - with the acronym "SILIC-SALT" - was funded under the EC programme INCO-DEV⁹. Four important sets of findings were gained from this project:

1. *Silicates can be successfully used for the long-term preservation of hides and skins, and the subsequent manufacture of commercially acceptable leathers.*
2. *Within leather processing:*
 - *Lime can be replaced by silicates within the liming and unhairing process.*
 - *An additional silicate penetration/neutralisation of pelts led to improved uptake of tanning and retannage agents, dyestuffs and fatliquoring - hence rationalised and cleaner processing.*
 - *The development of new trading commodities.*
3. *Silicates in tannery wastewaters are not detrimental to plant health. In contrast, common salt at levels normally found in tannery effluents is highly detrimental.*
4. *Information regarding silicate related chemistry, and interactions within leather manufacture at fundamental level.*

The background and the findings listed as 1 are presented in the following paper. Findings listed as 2, 3 and 4 are presented respectively as Parts 2, 3 and 4: these will be published in World Leather in April, May and June/July 2006. Each part presents the findings from that component of the investigation.

The project

The main objective of the project was to develop reliable salt-free curing methods for raw hides and skins. This was to enable a major reduction of the salt loading of tannery effluents. This is seen as critical for the survival of the many tanneries that rely upon salted hides and skins which are unable to meet legally and environmentally acceptable limits for chloride and TDS in effluent discharge. It also holds the potential for the re-use of these effluents for crop irrigation in areas suffering from severe water shortages.

The research group

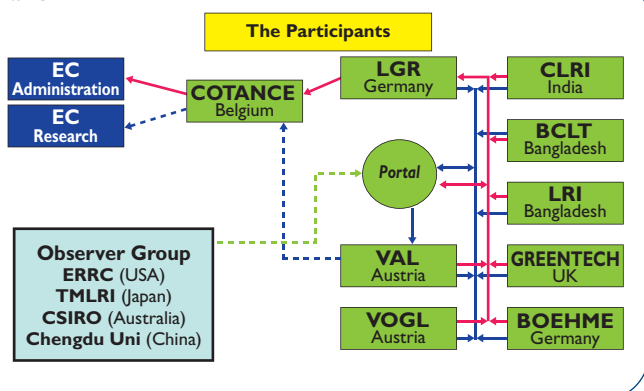
The European Union strongly supports international co-operation in research and technology development (RTD) within Europe, but also between Europe and a large number of countries in other continents. The objective of INCO-DEV⁹ projects, are mainly to develop solutions for problems in developing countries. Nevertheless, benefits for the EU also have to be evident.

In this project, institutes and companies from the EU co-operated closely with institutes from the Indian sub- ➤



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Panel 1



continent (*India and Bangladesh*). In an observer group, institutes from Australia, China, Japan and the USA had constant access to information in the project. This was mostly managed via a Knowledge Management Platform "Portal". The structure of the research group is given in *Panel 1*.

Background to the project

The leather industry and down-stream manufacture is of very high economic value to countries in Asia. However, considerable volumes of water are consumed by the tanning industry in the conversion of hides and skins into leather, and these wastewaters have a high sodium chloride or common salt content on discharge. This is mainly because of the large quantities of salt needed to preserve raw hides and skins.

Almost all of the components in these wastewaters can be removed by effluent treatment, but there is no effective way of removing common salt. Many techniques have been investigated but without practical success. With consent limits for discharge now focusing on the total dissolved solids, or the chloride content of an effluent, despite considerable investment into effluent treatment many tanneries are in danger of closure.

The presence of common salt in irrigation water can be a disaster. The structure of some soils can be changed, and a combination of toxicity and osmotic effects dramatically reduces crop yields. Moreover, in hot climates even moderate salinity in the soil will increase dramatically due to surface evaporation, percolation, and transpiration from growing plants.

Agriculture is a significant contributor to the Gross Domestic Product (GDP) in India, and provides employment to the bulk of people surpassing the contribution to other sectors. Tamil Nadu is one of the most water-starved states in India, and a large quantity of water is drawn for conventional usage in agriculture. In addition to this, the growth of traditional industries, such as tanneries and textiles which use large quantities of water, has led to rapidly depleting groundwater resources. The discharge of polluted wastewater from these traditional industries, with particularly high salinity, causes damage to soil, groundwater quality and has resulted in a decrease in the agricultural productivity year by year.

Taking these problems into account was one of the reasons for inviting the Indian and Bangladeshi Institutes to participate in this present project so as to develop feasible alternatives for tanneries on the Indian sub-continent.

Curing of raw hides and skins

Today, most hides and skins are still preserved after flying

with common salt (*NaCl*) for purposes of storage and transport. For this "hide curing", common salt at approximately 40% of the pelt weight is applied to the hides and skins, with more than half of this salt remaining within the cured raw materials. When these hides and skins are rehydrated in the initial soaking process, all of the salt is dissolved.

Various procedures, such as reverse osmosis, ultra filtration and evaporation have been tested on a small technical scale to remove salts from tannery effluents at various stages of treatment. None have been proven to be technically viable.

In the project, two different methods for salt substitution by neutralised alkali silicates were developed. Both methods enabled a reduction of the salt load of the soak liquors by more than 95%.

METHOD 1: POWDER CURING OF HIDES AND SKINS

On the Indian sub-continent a full salt replacement by neutralised alkali silicate powder has been developed. This powder method was specifically developed to meet the needs of the large number of rural slaughter slabs without any technical equipment and inadequate transport possibilities on the ➤

Panel 2: Formic acid neutralised Wasserglass powder



Panel 3: Powder application on goat skins





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Panel 4: Drum-cured bovine hide



Panel 5: Bangladeshi bovine hide, shipped to Europe



Indian sub-continent. The institutes from the Indian subcontinent prepared powdered alkali silicates by neutralisation of common Wasserglass, followed by drying by evaporation. The type of acids used for this neutralisation (*sulphuric, citric, formic, acetic acid*) and the addition of small amounts of "soft" preservatives (*boric acid, sodium meta-bisulfite*) were of minor influence. The dried powder is shown in *Panel 2*.

This silicate powder was applied to hides and skins in the same way as common curing salts. 20-25% by weight was required for bovine hides, and 15-20% for goat and sheepskins. This produced a stronger dewatering effect than experienced with salt curing. The silica cured hides finally contained 10-14% moisture, and were very stiff. A sample hide is presented in *Panel 3*.

These cured hides and skins were then exchanged between the participating institutes (*and so between different continents*) and converted into crust leather. For all of the trials, it can be stated that:

- Soaking back was performed without problems
- Neither bad odour nor any hide defects were observed
- The resulting crusts showed a satisfying appearance and feel, and were free of any grain damage, moulds or stains.

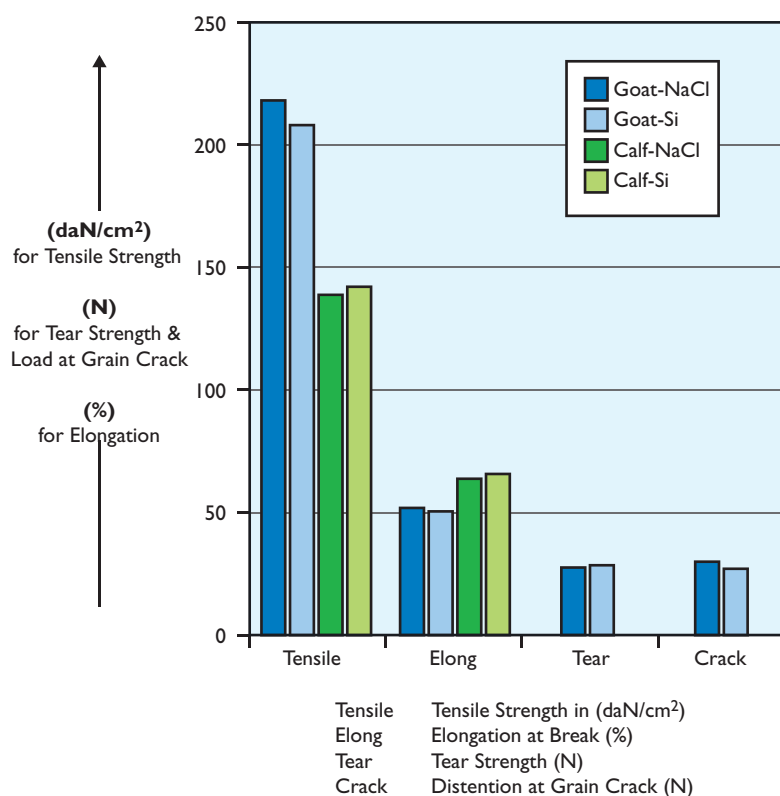
METHOD 2: DRUM CURING OF HIDES AND SKINS

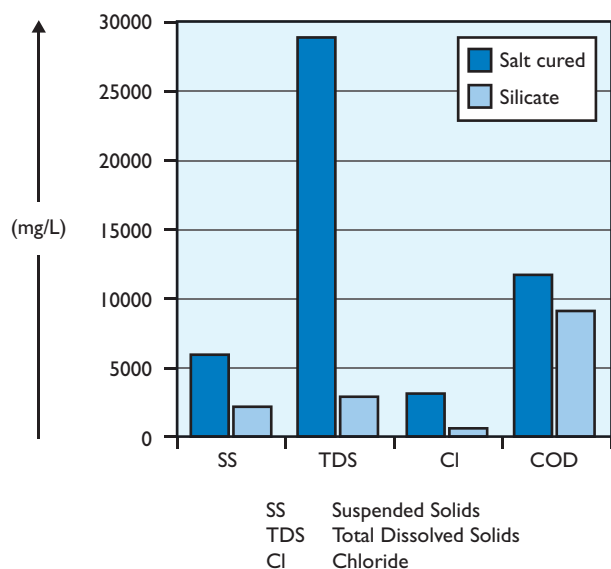
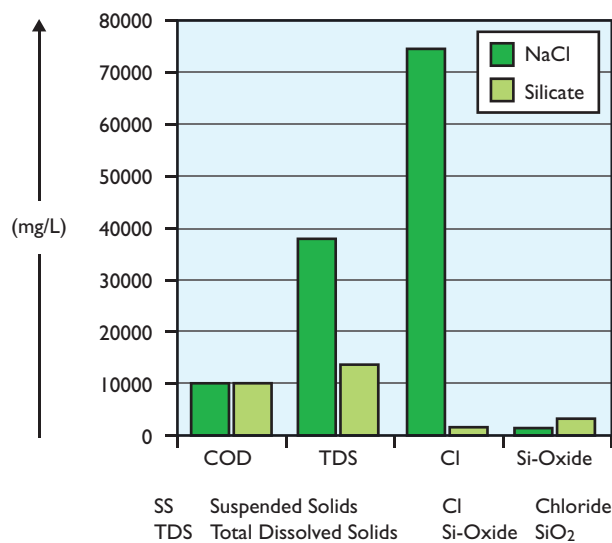
European institutes focused on drum preservation of green hides. In principle and dependent upon the type and weight, raw hides and skins were penetrated using 5-30% Wasserglass in 200-300% float. After draining and refloating, the raw materials were neutralised with organic acid (*preferably formic or citric acid*) to pH 5.5.

During horsing, strong dewatering occurred, lowering the moisture content to 10-14%. The hides were also stiff, were storable over many months, could be rewatered easily, and did not show any grain damage. A sample hide is presented in *Panel 4*.

Panel 6: Physical testing data for crust leathers from calf skins

Parameter	Salt cured skins	Silicate cured skins
Tensile Strength (daN/cm ²)	220 +/- 20	210 +/- 15
Elongation at Break (%)	50 - 55	48 - 55
Tear Strength (N)	29 +/- 3	30 +/- 5
Load at Grain Crack (N)	27 - 35	24 - 32
Distension at Grain Crack (mm)	8.5 - 10.5	8 - 10



**Panel 7: Silicate powder compared with salt preservation****Panel 8: Silicate drum cured compared with salt preservation**

The impact of silicate curing on leather quality

The hides that were exchanged intercontinentally were strongly dewatered and very stiff, and samples are shown in *Panel 5*.

Despite these characteristics, no problems with rewatering were found in any of the trials. Once soaked, these hides and skins were processed without any process adaptation. No visual or tactile changes in property were detected when compared with salted hides and skins, nor any decrease in physical testing performance. Representative performance of crust leathers from salt and silicate curing are presented in *Panel 6*.

The impact of silicate curing on soaking liquor composition

As expected, in all of the trials the Total Dissolved Solids (TDS), sodium chloride (NaCl), and chloride (Cl) content of the pre-soak and main-soak liquor was reduced tremendously. The compositions of the pre- and main soak liquors from a 20% silicate powder application, and from the equivalent salt cured hides is shown for comparison in *Panel 7*.

Similar results were obtained from hides preserved using 30% Wasserglass in a drum curing system. The comparison with salt cured hides as a control are shown in *Panel 8*.

Findings from the silicate curing component of the investigation

- Two different curing procedures were developed. For the members from the Indian sub-continent, powder application seems more feasible. This is because of the climatic conditions, and the structure and logistics of the operation of the slaughter units. For Europe, the drum method seems to be appropriate.
- Both methods led to silicate-cured raw materials. These can be stored up to several months. The silicate-cured hides and skins can be transported and exchanged both regionally and on an intercontinental basis without problems.
- Leather quality from silicate-cured raw materials is in the

same range as commonly produced leathers.

- The salt content arising from soaking silicate-cured hides and skins is less than 2% of the salt generated from soaking the equivalent materials when salt cured. Likewise, the TDS was reduced to about one third.
- The chemical costs of silicate preservation are more than double the cost of common salt. Nevertheless, the lower saline content of effluents offers potential savings in effluent treatment costs: there is evidence of improved bacterial activity within biological treatment at lower levels of salinity, opportunities for land irrigation, and a possible route to avoid closure where the maximum limits for discharge as TDS or Cl are legally enforced.
- The silicate dewatering of hides and skins is stronger than that experienced with salt curing. This reduces the weight of cured hides and skins and transport costs. The greater firmness requires more attention in handling in the initial soaking process.
- Procedures have been established for silicate-cured hides and skins as a new commodity.

Legend

- Advanced Federal Teaching and Testing Institute for Chemical Industry
- Lederinstitut Gerberschule Reutlingen
- Central Leather Research Institute
- Greentech + Associates
- Lederfabrik Vogl GmbH & Co Kg
- Bangladesh College of Leather Technology
- Leather Research Institute of Bangladesh Council for Scientific and Industrial Research
- Dr. Th. Boehme KG Chem. Fabrik GmbH
- Industrial Co-operation with Developing Countries

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