IDEAS ON LIMING

Paper contributed to the

UNIDO EXPERT GROUP MEETING ON POLLUTION CONTROL
IN THE TANNING INDUSTRY
IN THE SOUTH-EAST ASIA REGION

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Ideas on Liming

1. Introduction:

Since liming has a big share on waste water pollution, it is worth to examine this process and to show possibilities of purification as well as avoidance technologies.

Common liming is carried out with Calcium Hydroxide ("Lime") and Sodium Sulphide. At the process hairs are chemically destroyed and dissolved, also the opening up of the hides pollute the effluents with saponified fats and fragments of proteins. Due to the contamination of effluents with these products, lime waste waters have very high oxygen demand at their biological treatment.

(Figure 1)

Spent lime liquors show alkaline reaction. When they are mixed with acid liquors from pickling and tanning, retanning and ageing, Sodium Sulphide is converted into Hydrogen Sulphide, and this poisonous gas escapes from the effluents and pollute air. This air pollution is one reason for sometimes fatal accidents in tanneries.

2. Possibilities for Treatment of Limeliquors:

In order to reduce both oxygen demand in the treatment plant as well as the formation of poisonous Hydrogen Sulphide, different methods had been developed.

a. Treatment with Fume Gases:

Carbon Dioxide from fume gases reacts with Ca(OH)\textsubscript{2} under formation of insoluble CaCO\textsubscript{3}. Sodium Sulphide hydrolyses into Na\textsubscript{2}CO\textsubscript{3} and H\textsubscript{2}S. This Hydrogen Sulphide escapes from the liquor, pollutes air and causes smell molestions. Without efficient gas scrubber is not applicable.

b. Chemical Precipitation:

In Germany precipitation with Iron Sulphate was carried out in industrial scale. At this reaction Iron Sulphide is formed, which is not easy to separate by filtering. In addition, the sludge contains remarkable amounts of Iron Hydroxyde and so the total sludge volume is increased.
Another possibility is neutralisation of the spent liquors, e.g. with used tanning liquors. When the Isoelectric Point is reached, the proteins will precipitate. To separate this precipitated sludge, high amounts of lime and iron salts are necessary in order to receive a solid filter cake.

c. Conversion of Sulphides with Air and Hydrogen Peroxide:

A promising method for desulphidation of lime liquors is the insertion of air, with Manganese salts as catalyst. Following Hydrogen Peroxide is added in order to oxidize residual sulphides. Since no additional chemicals are required and \( \text{H}_2\text{O}_2 \) is decomposed into water and oxygen, the sludge volume is not increased.

(Figure 2)

Following the graph, aeration should last 5 - 6 hours to reduce the sulphide content to less than 50 mg/l. With addition of 0.5 - 1 lit \( \text{H}_2\text{O}_2 \) (35 % age) per cbm pretreated lime liquor, the sulphide content is lowered to approx. 1 ppm.

As side-effect a fat separation occurs. Per cbm lime liquor about 3.5 kg fat can be skimmed off. So the COD is reduced from ca. 40.000 to 25.000 - 30.000 mg \( \text{O}_2 \). Since \( \text{H}_2\text{O}_2 \) is added with little excess, smellly follower reaction will be forestalled.

2. Hairsaving Systems - Painting - After-Liming:

Aim of liming is the separation of hairs, epidermis and parts of unstructured proteins from Collagen tissue. Together with hairs and parts of glue stock per ton work-in-weight about 500 kg sludge will be filter-pressed.

For sludge-conditioning Iron-salts and/or Calcium Hydroxide have to be added, so that the sludge volume will be increased additional. So the expenses for depositing these sludges are very high, and many investigations had been carried out in order to reduce the sludge volume and to save money for disposal.

The traditional hair-saving process for calf-, goat- and sheepskins is painting. Since the paint contains high amounts of Sulphide, and an after-liming is necessary in order to remove residual hairs and to complete the opening-up, the reduction on COD is only 30 - 35 % compared to a common liming. Anyway, an advantage of painting is the hairs will result nearly undestroyed.

3. Hairsaving Liming by Immunisation

In former times tanners were afraid of "Immunisation", which occurred when soaking was too alkaline and/or there was a lack of sulphides. From the chemical point of view, Immunisation is known
since long times. It is based on the formation of Lathionine. The equations are shown in

(Figure 3)

The reformation of Lanthionine into Cystein is not possible with common liming chemicals in usually concentrations. First this knowledge was used by SCROGGE in the SIROLIME - process. in order to receive nearly undestroyed hairs. Disadvantage of this process is, to apply NaHS on hides in neutral pH - range. So there is always the danger of H₂S - evolvement.

Another possibility was developed by German company ROeHM Ltd. the so called "HS - process".

Chemists of an Austrian company (OeCW) discovered, one of their auxiliaries, DEPILOR R, decomposites Lanthionine completely. Investigations carried out by HEIDEMANN and colleagues showed, hairs are much easier to immunisate than hair roots, and that pH above 12 are necessary.

So the liming agent penetrates into the sphere of hair roots and reduces or hydrolysates the prekeratines. The reducing or hydrolysing effect of the auxiliary is not adequate to destroy the Keratine in outer layers of hairs. By this treatment the hair in the root sphere will be protected against immunisation and so immunisation occurs by lime - addition only in those parts of hairs, which overtops the surface of the hides. After that small amounts of strong reducing agents, e.g. NaHS,Na₂S and/or DEPILOR, are added in order to remove hairs completely.

(Figure 4)

It is very important to remove the hairs completely. This will be supported by drum rotation. When residual hair particles will be squeezed out of the hides. With bates the residual hairs cannot be removed.

To remove the separated hairs and hair fragments from the drum, a continuous filtration can start 30 - 60 minutes after addition the last chemicals. It is also no problem to filter the hair sludge when the drum is emptied. Since hairs are immunisated in a way which protects the against dissolving.

After washing and drying the separated hairs, they can be utilized in different ways, e.g. as fertilizers, supplement for fodder or starting product for aminoacid production.

The pelts out of this process are very clean, scudfree, smooth and they show good opening - up. Due to less swelling during the liming an improvement of area - yield of 1,5 - 3 % can be expected. The process itself is very safe to handle.
Very important is the effect of this process on waste water, where a high reduction of loadings occur. The following figures show the influence on both COD and sludge volume.

(Figures 5 + 6)

Finally, two procedures are introduced, which are applied in industry.

(Tables 1 + 2)
Common Hairburn Liming

CSB (mg Oxygen/lit x 1000)
Float relation 100 %

Figure 1

VAL Vienna Austria

Figure 1
Ideas on Deliming 1991
**Oxydation of Lime Liquors**

Spent Liquor + 200 ppm Manganese - Sulphate under Rotation (in a Paddle)

![Graph showing sulphide concentration over time with and without aeration.](image)

**Figure 2**

**VAL** Vienna Austria

**Ideas on Deiling** 1991
Formation of Lanthionine

\[ \text{Cystine} \rightarrow \text{Dehydroalanine} + \]

\[ \text{Lanthionine} \]
Scheme of Controlled Immunisation

Hairs

Outer Keratine  Outer Keratine  Outer Keratine
(still intact)  (immunisized)

Liming Agent  Alkalisation
(Hydrolysis + Reduction)

Untreated Hair  Partial Hydrolysis  Immunisized Hair:
with Prekeratine in  Sphere of Hair Roots:
Sphere of Hair Roots:
Protection against  (Prekeratine) protected
Immunisation  against Immunisation

Figure 4

VAL  Vienna  Austria  Figure 4  Ideas on Deliming 1991
Sludge - Volume

Common Liming (Hair burn)

<table>
<thead>
<tr>
<th>15%</th>
<th>66%</th>
<th>9%</th>
<th>4%</th>
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<td>6%</td>
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Hairsaving Process

utilization of hairs

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<th>15%</th>
<th>17%</th>
<th>8%</th>
<th>4%</th>
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Hairsaving Process (incl. separation of fibres during tannage and retannage)

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<th>15%</th>
<th>17%</th>
<th>8%</th>
<th>60%</th>
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- Soaking
- Liming
- Bating
- Tanning
- Retanning, Dyeing
- Fatliquoring
- Reduction of Sludge Volume

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<tr>
<th>VAL</th>
<th>Vienna Austria</th>
<th>Figure 5</th>
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Influence on COD

Common Liming (Hair burn)

Hairsaving Process (without Sulphoxidation)

Hairsaving Process (with Sulphoxidation)

Soaking  Liming  Bating  Pickling + Tanning  Retanning, Dyeing  Fatliquoring  Reduction of COD

Figure 6  Ideas on Deliming 1991
Hairsaving Liming with DEPILOR

Raw Material: Cattles, Calfes

1. Soaking: as usual, + 0,3 - 0,4 % Sodium carbonat, let off

2. Hairsaving Liming

Water (25° C)................................. 70 %
Calcium Hydroxide............................. 3,0 %
  5 minutes under rotation, 25 minutes standstill
  5 minutes under rotation, 55 minutes standstill
Water (25° C)................................. 50 %
Sodium Carbonate............................ 0,3 %
Sodium Sulphide (flakes)..................... 0,8 %
  5 minutes under rotation
DEPILOR........................................ 0,7 %
  approx. 60 minutes under rotation
  Starting of filtration will be determined by visual control,
  before starting the filtration:
Water (25° C)................................. 50 %
  Filtration (approx. duration 60 minutes)
Calcium Hydroxide........................... 2,0 %
Degreaser..................................... 0,2 %
  15 minutes under rotation, then for 14 - 18 hours:
  5 minutes rotation, 55 minutes stand still

Total duration for liming: 18 - 20 hours