IDEAS ON LIMING

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Vinzenz OLIP
OeCW - Weißenstein
Karl Heinz MUNZ
VAL - Vienna

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 dyeing 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 $Ca(OH)_2$ under formation of insoluble $CaCO_3$. Sodium Sulphide hydrolyses into Na_2CO_3 and H_2S. 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 oxydize residual sulphides. Since no additional chemicals are required and H_2O_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/lit.With addition of 0,5 - 1 lit H_2O_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 O_2.Since H_2O_2 is added with little excess,smelly follower reaction will be forestalled.

2. Hairsaving Systems - Painting - After-Liming:

Aim of liming is the separation of hairs,epidermis and parts or unstructered 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 un-destroyed.

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 SCROGGIE 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 H_2S - 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,decomposits Lanthionine completely.Investigations carried out by HEIDEMANN and collegues 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 hydrolyses 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,Na_2S 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 continous 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 emptyfied,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.

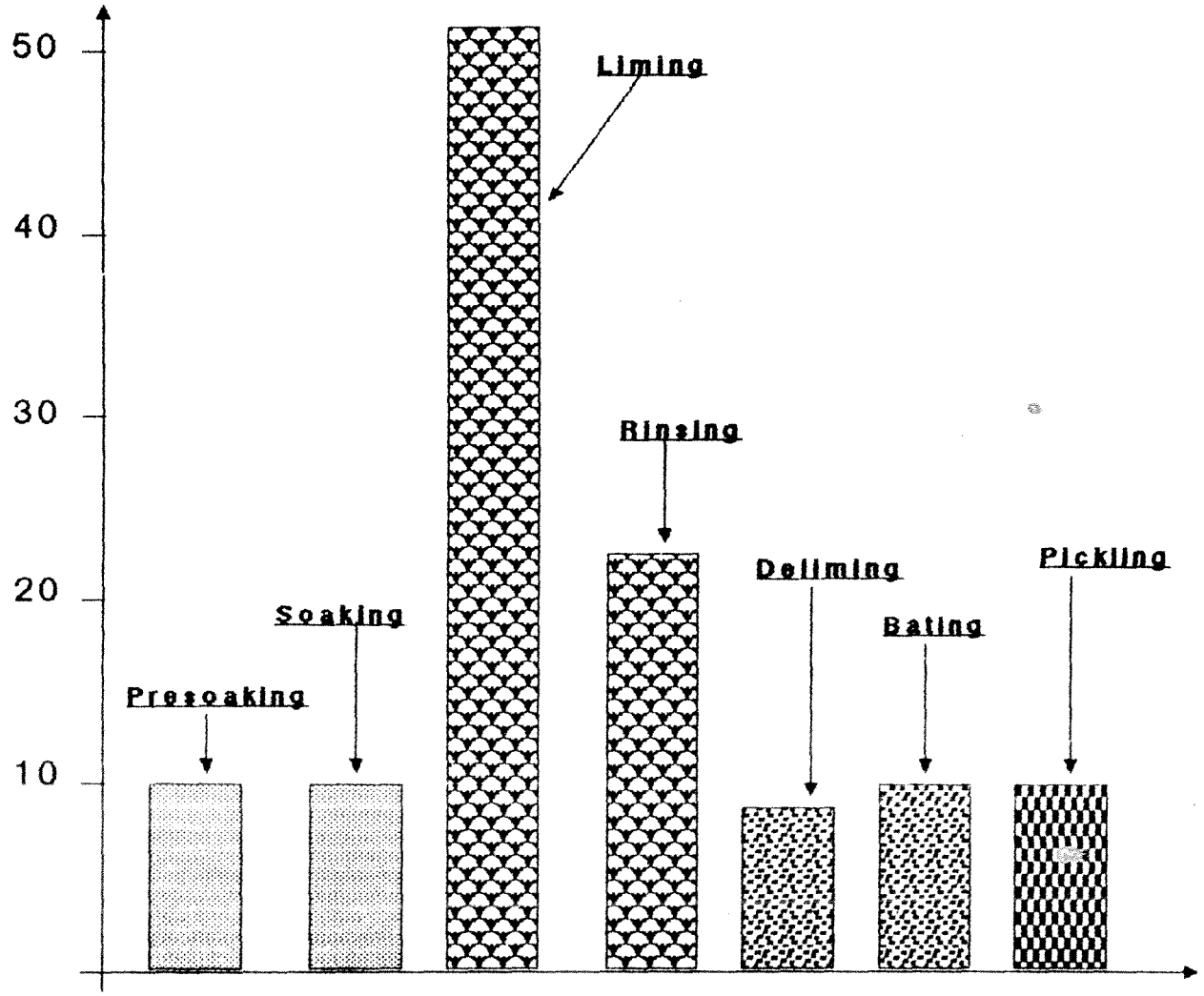
(Figures 5 + 6)

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

(Tables 1 + 2)

Common Hairburn Liming

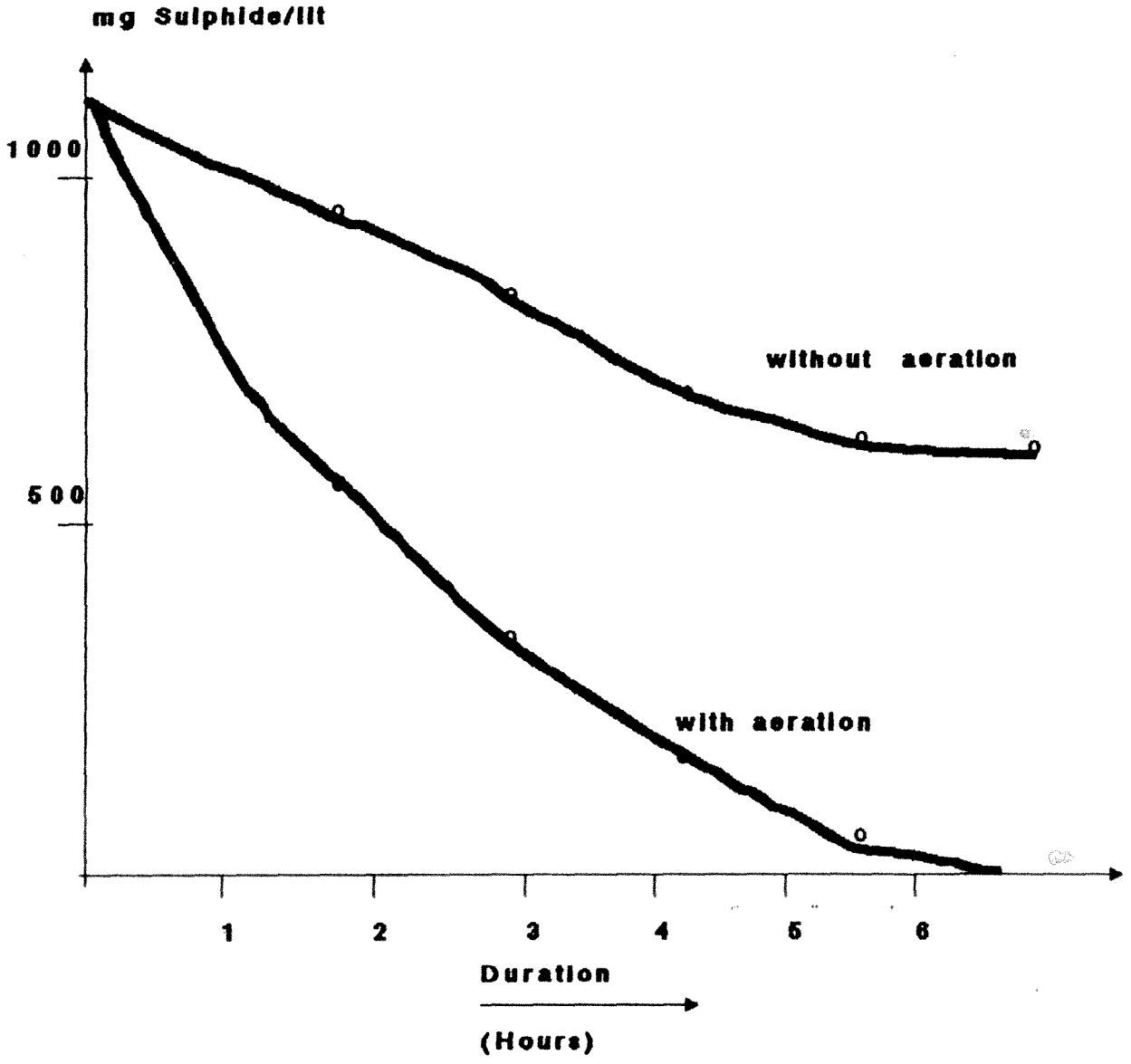
CSB (mg Oxygen/lit x 1000)
Float relation 100 %



VAL Vienna Austria		Figure 1	Ideas on Deliming 1991

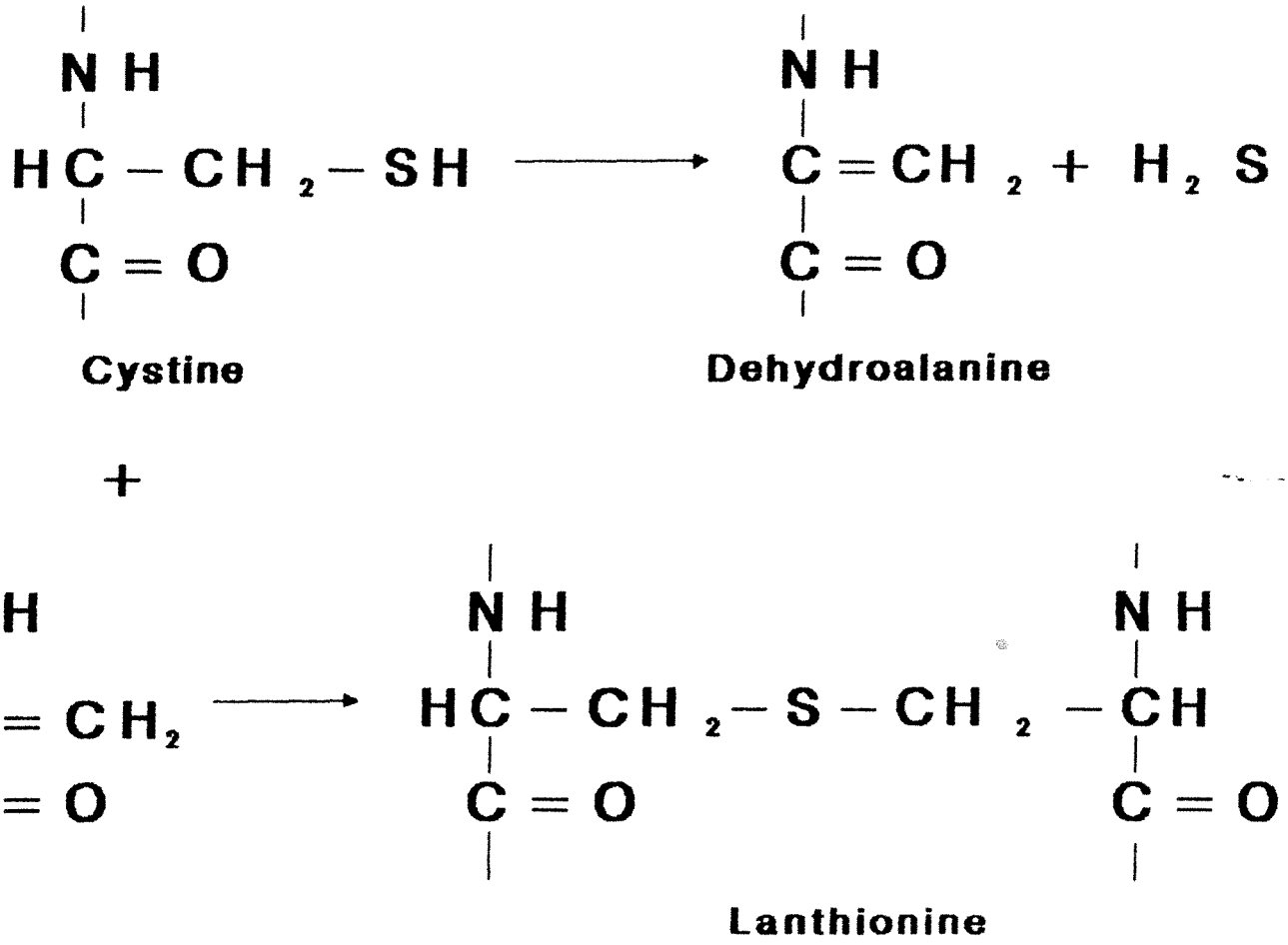
Oxydation of Lime Liquors

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



VAL Vienna Austria		Figure 2	Ideas on Deliming 1991

Formation of Lanthionine

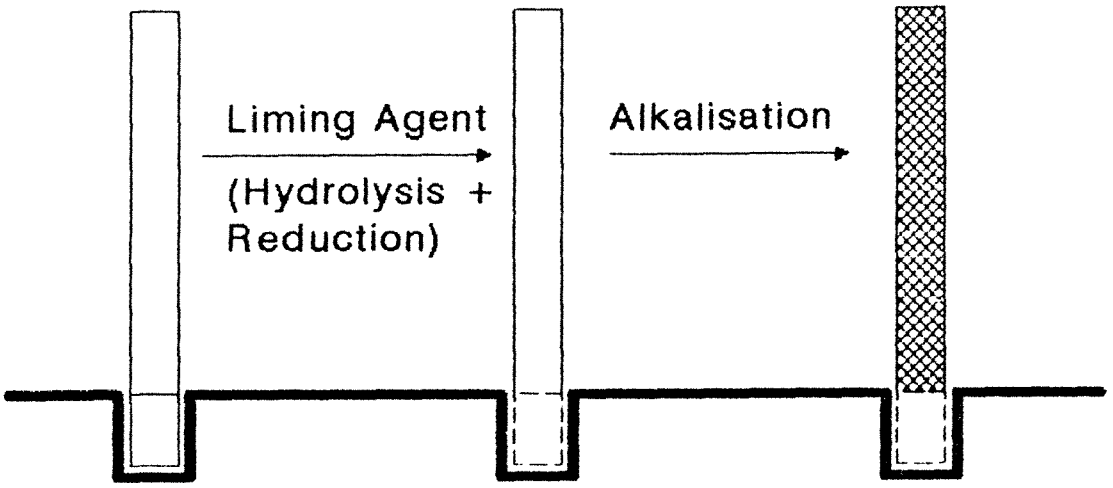


VAL Vienna Austria		Figure 3	Ideas on Deliming 1991

Scheme of Controlled Immunisation

Hairs

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



Untreated Hair

Partial Hydrolysis

with Prekeratine in Sphere of Hair Roots:

Protection against Immunisation

Immunisized Hair:

Sphere of Hair Roots (Prekeratine) protected against Immunisation

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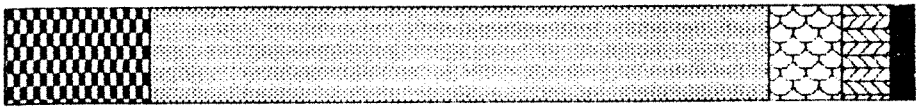
Sludge – Volume

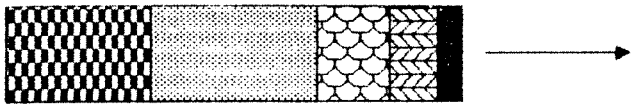
Common Liming (Hair burn)



15 % 66 % 9 % 4 %

6 %

Hairsaving Process



utilization of hairs

15 % 17 % 8 % 4 %

6 %

Hairsaving Process **(incl. separation of fibres during tannage and retannage)**

15 % 17 % 8 % 60 %

Soaking

Liming

Bating

Tanning

Retanning,Dyeing

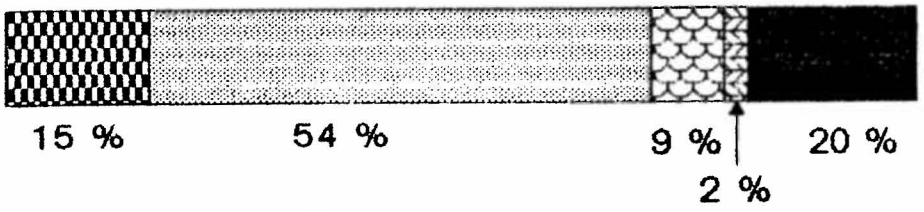
Fatliquoring

Reduction of Sludge Volume

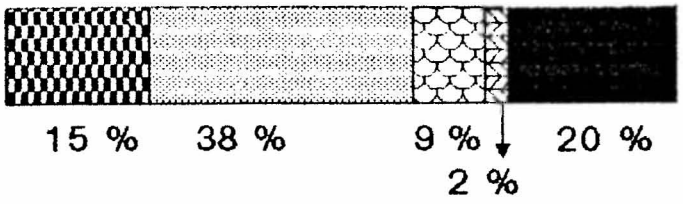
VAL Vienna Austria		Figure 5	Ideas on Deliming 1991

Influence on COD

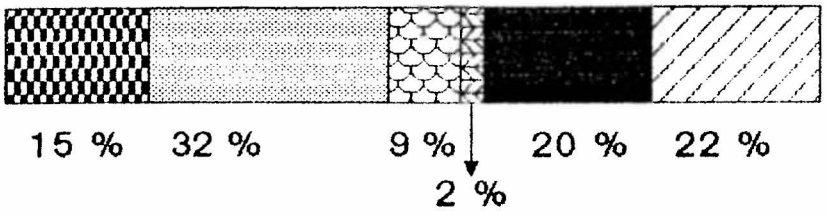
Common Liming (Hair burn)



Hairsaving Process (without Sulphoxidation)



Hairsaving Process (with Sulphoxidation)



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

VAL Vienna Austria		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