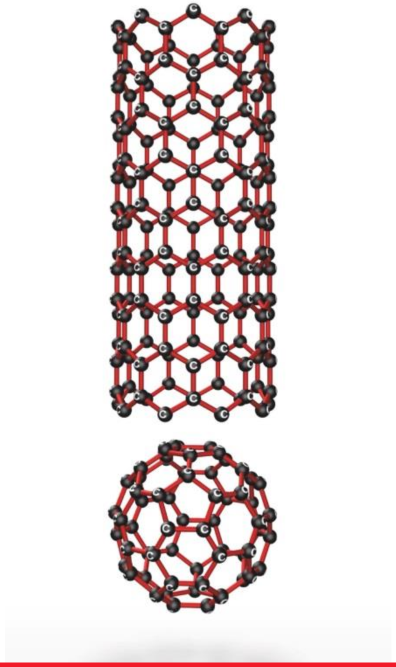


Green Beamhouse – A toolbox for cleaner Waste water

P. Rajasekaran, Christopher Henzel, Marc Hombeck

xxx

Agenda

LANXESS
Energizing Chemistry

1. Introduction
2. Green Beamhouse – Lanxess' roadmap for cleaner waste water
   a. TDS/Salt reduction: The Peltec C process
   b. COD reduction: The Peltec X-Zyme process
   c. Sludge reduction: The Peltec X-Zyme SLR process
3. Details Green Beamhouse - A Life Cycle Assessment (LCA) of the X-Zyme process

Sustainability has become one of the mega-trends – also for leather production

LANXESS
Energizing Chemistry

Sustainability = Waste water improvement

NAMAMI GANGE

"Green Beamhouse Toolbox" by Lanxess

Component	Product
Salt	Blancorol® HP, Peltec® C
COD	Peltec® X-Zyme SN / U
Sludge	Peltec® X-Zyme SLR
Sulfide	Peltec® X-Zyme U
Nitrogen	Peltec® UNF
Ammonia	Peltec® DLP / DL

Partly published: World Leather Aug/Sep 2019

Green Beamhouse –
a toolbox for improving waste water by chemical recipes

LANXESS
Energizing Chemistry

Target of lower waste in waste water can be achieved in different ways

Process-based improvements

Waste water improvements which require change of tannery processes or different mechanical processes, e.g.

- Fresh hide utilization / Brine curing CLRI
- Green fleshing
- Lime recycling
- Hair saving process
- Lime splitting

Product-based improvements

Waste water improvements which require changes of the recipe. Changes can significantly impact all relevant waste-water components, for India e.g.

- TDS
- COD
- Sludge

Green Beamhouse Toolbox

Salt Improvement: Avoidance of pickle or utilization of a low-salt pickle

LANXESS
Energizing Chemistry

General idea / theory

Origin of salt

- Largest amount of salt derives from preservation (salting) of raw-hides
- Second largest salt-addition is during pickling, ending up in the waste water

How to avoid salt

- Utilization of fresh hides
- Avoidance of pickle by switching to specific organic tanning agents (e.g. X-Tan®)
- Reduction of pickle-salt addition by utilization of Blancorol® HP

LXS product solution

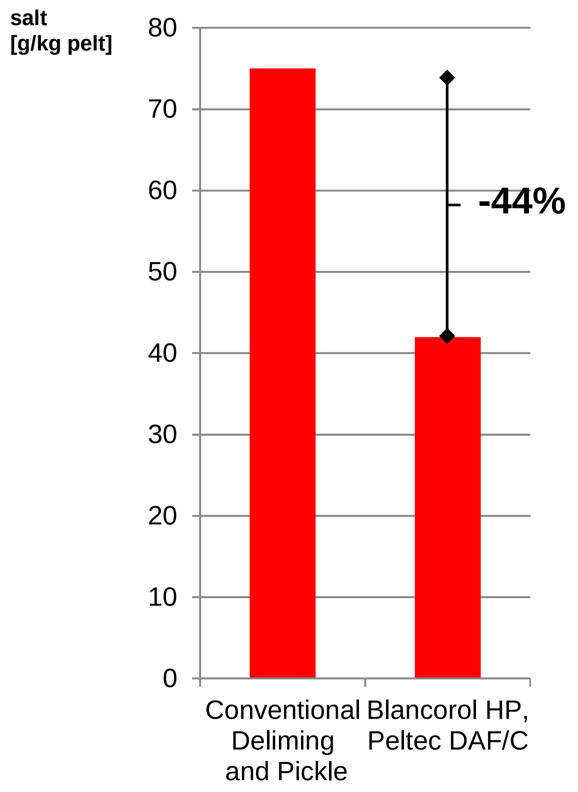
Peltec® C /DLP

- Deliming with Peltec® C or Peltec® DLP reduces salt application
- Pickling with Peltec® C combined with Blancorol® HP does not require additional salt

Blancorol® HP

- Blancorol® HP helps to reduce salt requirements to 3,8 Bé (std: 6-8 Bé) ➔ less salt in waste water
- 1.5 to 2% Blancorol® HP (fully) replaces sulfuric acid plus partly formic acid
- Blancorol® HP enables earlier chrome addition and reduces pickling time <1 hour

Impact of Peltec® C, Blancorol® HP



Low salt Deliming Process

Peltec® C and Blancorol® HP save salt and water

Application Details

- Pelt splitting recommended
- Peltec® C to be used as single deliming agent
- Bating at pH 8.5
- Best results in combination with Blancorol® HP pickle process
- No wash after deliming, only float reduction
- Float Bé of 4° required, can be adjusted with Peltec® C
- Addition of Blancorol® HP as replacement for sulfuric acid
- Application of CTS at penetration of pickle of ca. 50%,
  Gain: More time for CTS penetration

Standard vs. Peltec® C process = 70kg/t less salt

	Product	Standard process	Peltec C process	Δ - TDS	Δ - water
Deliming	water	50%	50%	x	x
	ammonia sulfate	2.5%	0%	-2.5%	
	PELTEC C	0%	1.5%	+1.5%	
	Na- bisulite	0.3%	0.3%		
	bating agent	0.4%	0.4%		
wash	water	200%	0%		-200%
Pickle	water	50%	0-20%		-30%
	NaCL	6%	0%	-6%	
	sulfuric acid	1.3%	0%		
	BLANCOROL HP	0%	1.7%		
	CTS	6%	6%		
	MgO	0.5%	0.5%		
			Savings	-7%	-230%

X- Blue Tanning, Pickle Free Tanning system

A Two Step Tanning Process with salt savings

LANXESS
Energizing Chemistry

1. X-Tan® Wet White Process

- Pelt splitting recommended
- Salt fee deliming with Peltec® DLP
- Bating at pH 8.5
- No pickle required ➔ no addition of NaCl required
- Tanning process starts at pH 8.5 and ends at pH 4.5

2. X-White Chroming Process

- Shaving of wet white
- Reduction of products/salt due to 1/3 less hide weight
- Start retannage with chrome tannage
- No pickle required ➔ no addition of NaCl required

Standard vs. X-Blue process = 35% less salt

	Product	Standard process
Deliming	water	50%
	ammonia sulfate	2.5%
	Na- bisulphite	0.3%
	bating agent	0.4%
wash	water	200%
Pickle	water	50%
	NaCl	6%
	sulfuric acid	1.3%
	CTS	6%
	MgO	0.5%
	Total Salt:	**17%**

	Product	X-Blue Process
Deliming	water	50%
	Peltec DLP	2.0%
	Na-bisulphite	0.3%
	bating agent	0.4%
wash	water	200%
X-Tan Tannage	water	50%
	X-Tan W	3%
	Tanigan HS	3%
	formic acid	1%
shaving	1/3 weight reduction	
Retannage		
Chroming	formic acid	0.5%
	CTS	6%
Neutralisation	customer	
Retannage	customer	
	Total Salt:	**11%**

COD Improvement: Removal of hide components and reduction of surfactants by enzymatic process

LANXESS
Energizing Chemistry

General idea / theory

Origin of COD

- Organic matter of raw hides which is washed out during beamhouse process
- Organic beamhouse chemicals added to the process and finally end up in waste-water as COD

How to avoid COD

- Avoidance of unnecessary hydrolysis of the hide / switching to hair saving process
- Reduction of organic chemical additives by switching to enzymatic process

LXS product solution

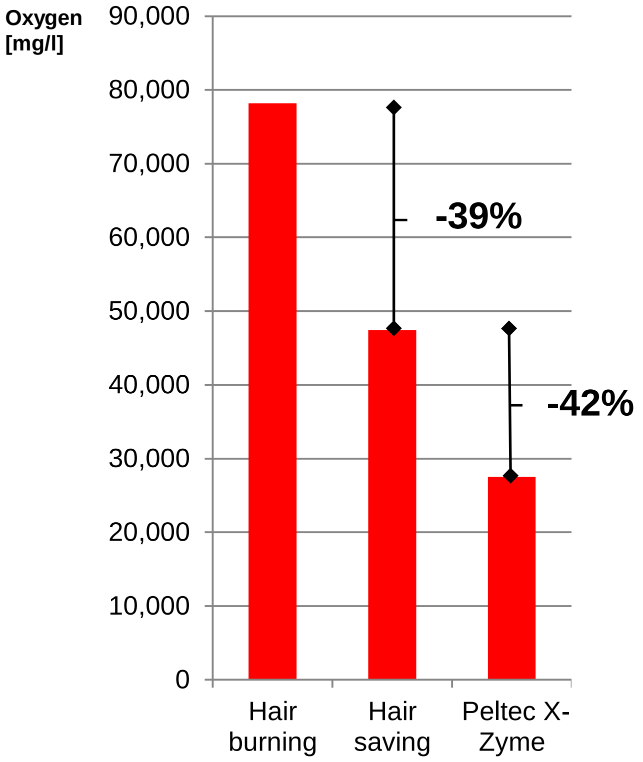
Peltec® X-Zyme SN

- Enzyme-based product ensuring the mild washing out of hyaluronic acid during soaking
- Peltec X-Zyme SN reduces other-wise required surfactants that end up as COD in waste water

Peltec® X-Zyme U

- Enzyme-based product which cleaves the hair roots forming easily filterable hair
- Subsequent hair saving process allows significant reduction of COD

Impact of Peltec® X-Zyme SN / U



COD Improvement
Peltec® X-Zyme Process

Soaking: Peltec® X-Zyme SN

Background

- Key target is removal of non-collagenous proteins
- Hyaluronic acid (HA) is locked in place by glucose amino glycans (GAGs) of dermatan sulfate proteoglycan (DSP)

Process

- Cleavage of GAGs allows easy removal of HA
- No proteolytic activity of enzyme: No damage of collagen during prolonged soaking or accidental overdosing

COD reduction

- No application of wetting agent
- Strongly reduced amount of emulsifier required
- No degreasing during soaking
- Application of Peltec® BLE-F for grease reduction

Unhairing: Peltec® X-Zyme U

Background

- No pulping of hair improves the waste water
- Reduction of lime: moderate swelling causing less wrinkles

Process

- Peltec® X-Zyme U selectively degrades basal membrane of epidermis and loosening the hair roots
- Hair loosening is achieved after ca. 45-60 min; enzymatic activity is completely stopped by pH-increase
- Addition of lime results in immunization of hair

COD reduction

- Subsequent (semi) hair-saving process with reduced amount of lime removes residual hair with moderate swelling
- Replaces application of organic sulfur compound (mercaptan), which increases the COD
- Application of lipase Peltec® BLE-F does not contribute to COD

Sludge Improvement: Removal of inorganic sludge by replacement of lime during opening up

LANXESS
Energizing Chemistry

General idea / theory

Origin of Sludge

- Organic sludge results from unhairing: hair and pulped hair plus epidermis. Furthermore it originates from dirt / dung and scrapped of sub cutis
- Inorganic sludge mainly results from hydrated lime

How to avoid Sludge

- Employment of hair saving process incl. hair filtering, green fleshing
- Replacement or reduction of lime by alternative products

LXS product solution

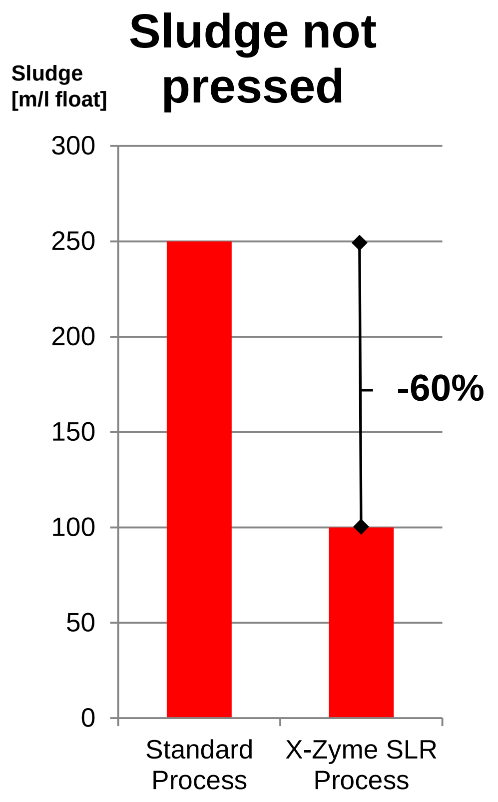
Peltec® X-Zyme SLR

- Replacement for hydrated lime
- Enzyme-based product
- Ensuring good “opening up” of collagen
- Uniform soaking

Peltec® X-Zyme U

- Enzyme based unhairing auxiliary
- Improved hair saving process with hair filtering

Impact of Peltec® X-Zyme SLR



Sludge reduction
Peltec® X-Zyme SLR process

Lime free opening up results in significant sludge reduction

Background

- Enzymatic lime free opening up of the fiber structure
- Strong selective action on dermatan sulfate proteoglycan ➔ opening up process

Process

- Opening up moved to soaking process ➔ Peltec® Zyme SLR applied in the soaking
- Small amount of lime (0.8%) added for immunization
- Reduced offer of swell regulator required due to lower alkalinity
- Reduced volume of deliming agent required due to less lime added
- Full sustainability results achieved in combination with Peltec® X-Zyme U

Sludge reduction and more advantages

- Significantly less sludge with good biodegradability achieved (ca. 40-70% reduction)
- Improved COD vs. standard X-Zyme process
- Crust with soft round handle
- Good physical properties
- Excellent waterproofing conditions

X-Zyme®Std.

X-Zyme®SLR

Green Beamhouse: Lanxess' roadmap to cleaner waste water, further investigation by LCA for X-Zyme

LANXESS
Energizing Chemistry

Summary: Reduction factors of critical waste water components

Waste water component	Product	Reduction factor
Salt	Blancorol® HP, Peltec® C	-44%
COD	Peltec® X-Zyme S, U	-42%
Sludge	Peltec® X-Zyme SLR	-60%
Sulfide	Peltec® X-Zyme U	-24%
Nitrogen	Peltec® UNF,	-20%
Ammonia	Peltec® DLP / DL	-74%

Next step: LCA X-Zyme process

- A Life Cycle Assessment (LCA) describes the impact of a complete BH-process, not of single products. It looks at all relevant compartments:
  - Fossil energy
  - Global warming
  - Eutrophication
  - Toxicity
  - Acidification
  - Photo chemical ozone formation
  - Agricultural land use
  - Fresh water use
  - Solid waste
- In comparative LCA only the differences caused by process shift are analyzed and reviewed

Comparative LCA: Peltec® X-Zyme process offers significant reduction of chemicals

LANXESS
Energizing Chemistry

Recipe-comparison between Standard- and X-Zyme process

Production step	Material	Standard process [% of hide weight]	X-Zyme process [% of hide weight}	Delta
Soaking	Surfactant	0,20%	0,10%	-0,10%
	Protease	0,50%		-0,50%
	Peltec X-Zyme S		0,12%	0,12%
	Preservative	0,15%	0,15%	0,00%
Liming	Surfactant	0,10%		-0,10%
	Thioglycolic acid	0,80%		-0,80%
	NaHS	1,00%	1,00%	0,00%
	$Ca(OH)_2$	3,00%	2,50%	-0,50%
	Na_2S	2,50%	1,00%	-1,50%
	Phosphate	0,34%	0,34%	0,00%
	Na_2CO_3		0,20%	0,20%
	Peltec X-Zyme U		0,08%	0,08%

Comparative LCA

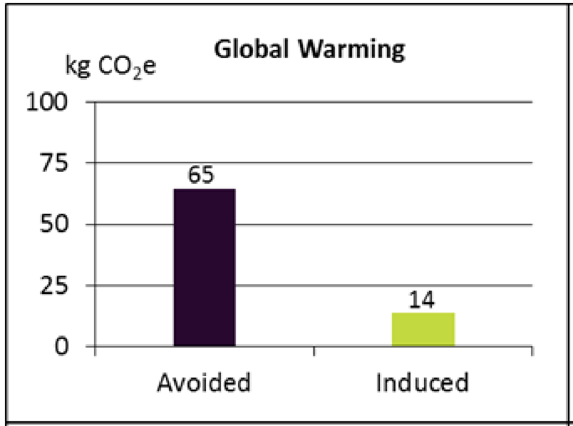
- In this example a semi hair saving (tannery std.) and a X-Zyme hair saving process were compared
- Recipes are customer specific, but principles apply to virtually all tanneries
- All values derive from full size production trials
- Both processes are suitable for upholstery and shoe-upper leather
- Net-reduction of chemicals are 30kg / ton of pelts
- Significant improvement of waste water regarding COD, BOD, sulfide

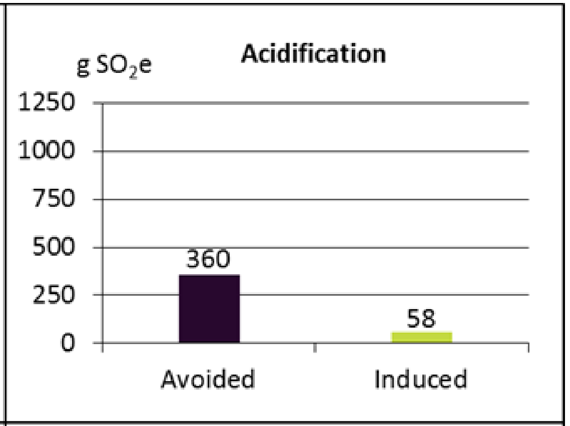
Published:
International Leather Maker Nov/Dec 2017

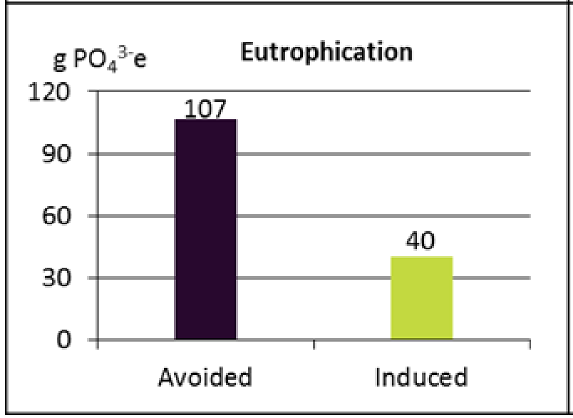
Comparative LCA: Peltec® X-Zyme process leads to beneficial results in almost all impact categories

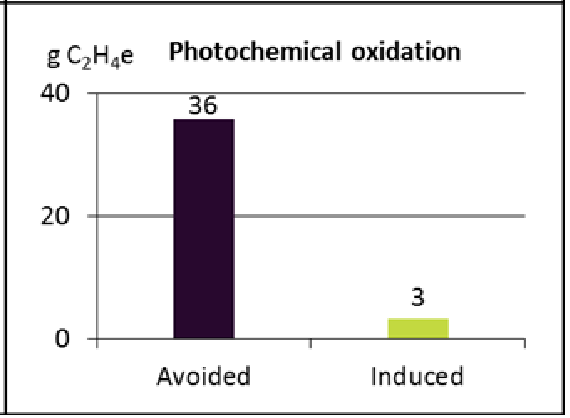
LANXESS
Energizing Chemistry

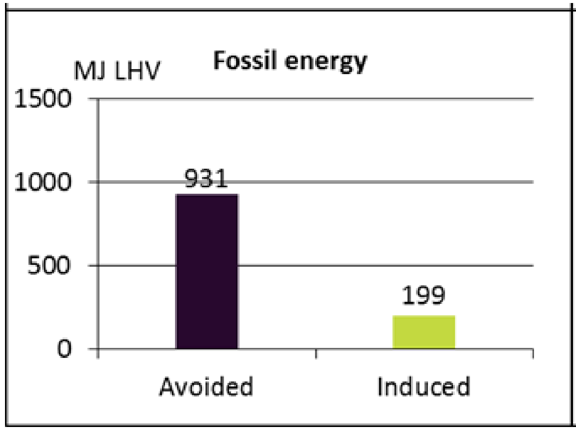
Comparison of waste water values

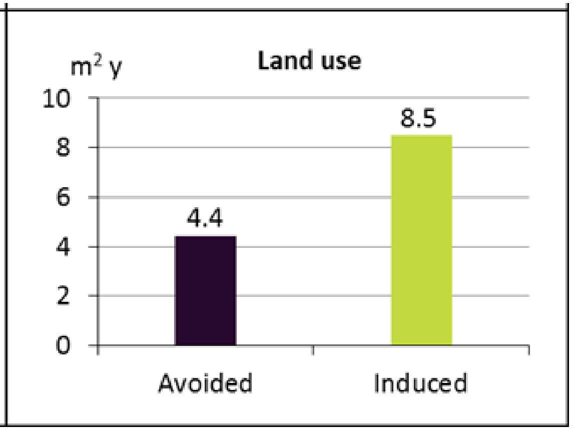












Impact category	Unit	Saved	Induced	Net
Global warming	kg CO_2 equivalents	65	14	**50**
Acidification	g SO_2 equivalents	360	58	**302**
Nutrient enrichment	g PO_4 equivalents	107	40	**66**
Photochemical ozone formation	g C_2H_4 equivalents	36	3	**32**
Energy resources	MJ lower heating value	931	199	**731**
Agricultural land use	m^2y	4.4	8.5	**-4.1**

X-Zyme process savings on global warming for 1000hide tannery: Equivalent to 122 cars / y

LANXESS
Energizing Chemistry

How to improve waste water

- Process changes (e.g. hair saving) have large effects on waste water
- Green Beamhouse offers further improvements by recipe changes
- Peltec X-Zyme process is the flagship for waste water improvements

Quality avoids waste

Sulfide Improvement: Replacing sulfide containing reduction agents by enzymatic unhairing system

General idea / theory

Origin of sulfide

- Sulfides are added for unhairing in the form of Na_2S, NaHS or mercaptans

How to avoid sulfide

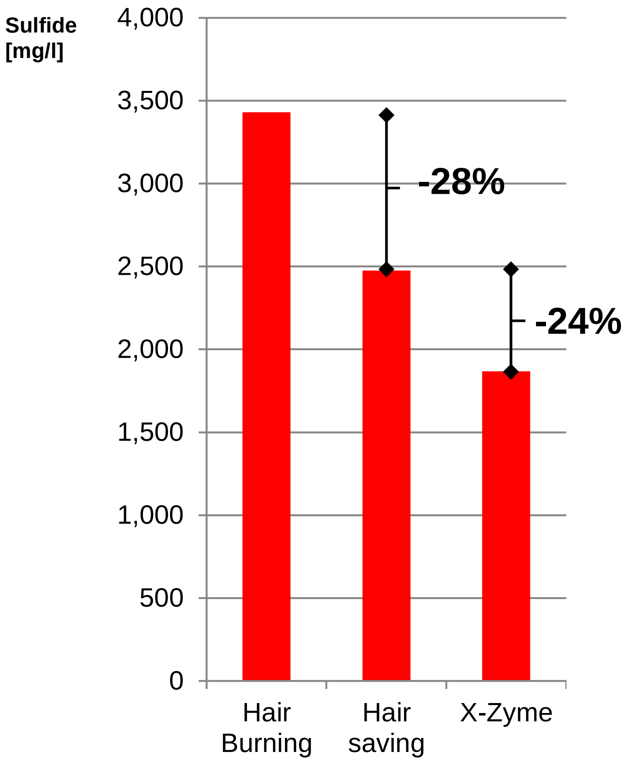
- Reduce required sulfide-volume by switching from hair burning to hair saving process
- Switching to a non-sulfide unhairing system (e.g. oxidative unhairing)
- Reduction of sulfide addition by utilizing enzymatic unhairing additives

LXS product solution

Peltec X-Zyme U

- Enzyme-based product cleaving the hair roots. Hereby partly substituting sulfide action and leading to less required sulfide
- Improved removal of hair roots leading to cleaner grain
- Pelts are reported to be flatter and smoother

Impact of Peltec X-Zyme S/U



Nitrogen Improvement: Introduction of lime recycling and utilization of amine-free swell regulators

LANXESS
Energizing Chemistry

General idea / theory

Origin of nitrogen

- Nitrogen derives from proteins of the raw hides ending up in the waste water
- Swelling regulators in liming are traditionally based on amines

How to avoid nitrogen

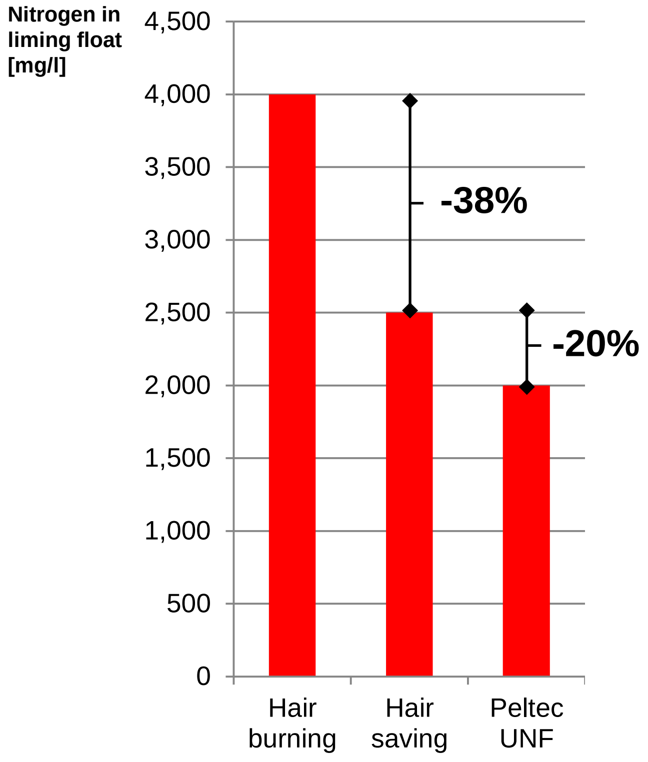
- Reduce amines from hides:
  - Liming: Switch to hair saving
  - Pickle: Shorten time and reduce temperature to avoid hydrolysis
- Introduce lime-recycling system which re-utilizes liming float including swell regulators
- Utilization of nitrogen-free swell regulators

LXS product solution

Peltec UNF

- Product is based on patent-applied nitrogen-free chemistry: No nitrogen is added to the float
- Product regulates the swelling during liming process and ensures good opening up
- No extensive plumping leads to reduced growth marks and belly draw as well as better removal of hair roods which results in clean pelts
- Cost competitive versus traditional products

Impact of Peltec X-Zyme S/U



Ammonia Improvement: Deliming with ammonia-free deliming agents

General idea / theory

Origin of ammonia

- Ammonia is added as a standard deliming agent to buffer the pelt after liming

How to avoid ammonia

- Utilization of ammonia-free deliming agents significantly reduce the nitrogen content in the waste water
- Current solutions (boric acid / dicarboxylic acids) have HSEQ-/ performance disadvantages

LXS product solution

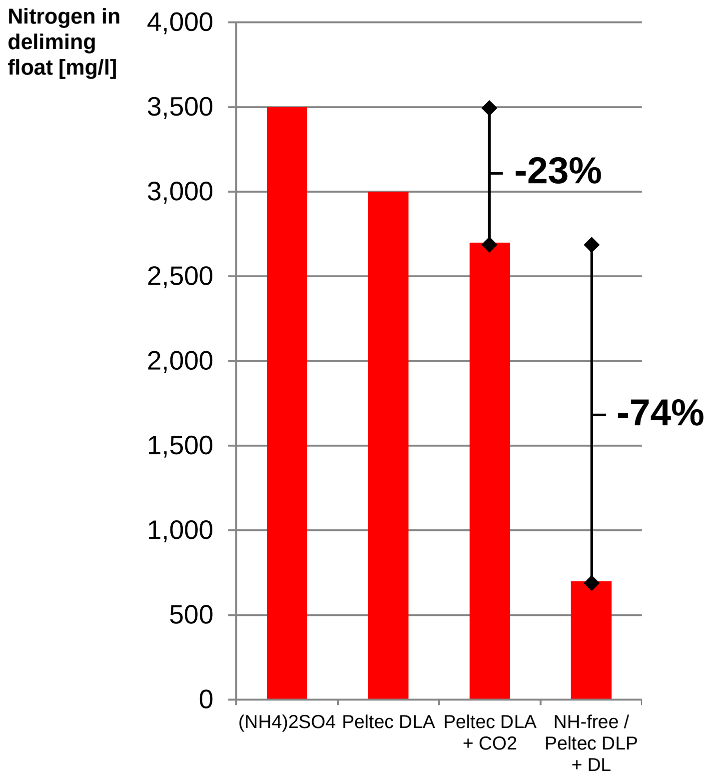
Peltec DLA

- Ammonia-reduced deliming agent which can be combined with CO_2 deliming

Peltec DLP / DL

- Products are completely free of nitrogen salts and ammonia compounds
- Peltec DLP quickly and uniformly penetrates even full substance pelts, time can be adjusted by addition of Peltec DL

Impact of Peltec X-Zyme S/U



Comparative LCA: X-Zyme process shows significant reduction of waste water values

Comparison of waste water values

- Common waste water value measurement performed on soaking and liming floats
- Hides were washed before soaking to exclude variable load of dirt attached to the hides
- Pollution of beamhouse waste water can be reduced by up to 50%

	Unit	Conventional process	X-Zyme process
BOD after soaking	kg/m3	14,9	4,7
BOD after unhairing/liming	kg/m3	23,1	12,9
COD after soaking	kg/m3	24,2	12,0
COD after unhairing/liming	kg/m3	54,0	25,5
Total nitrogen after liming	kg/m3	4,0	2,5
Sulfide after unhairing/liming	kg/m3	3,4	1,9

* Given per tonne of hides (the functional unit)

Comparative LCA: X-Zyme process savings on global warming equivalent to 122 cars / y

LANXESS
Energizing Chemistry

Environmental savings put in perspective for mid-size tannery (1000h/d)

- **Global warming:** 50kg CO_2 eq. per ton of salted hides

  => Impact mid-size tannery (1.000 hides/day) is equivalent to **122 cars/y***

- **Fossil energy:** 730 MJ LHV (lower heating value)
- **Land use:** - 4.1m^{2}y

  => 180 MJ/m2y is the gain of the additional land use.

  => This, compared to the yield achieved for bio-ethanol, outperforms the savings by **16 times****

* 142g/PKm CO_2 eq., Umwelt Bundesamt, 1,5P/Car, 20.000Km/y

** FOA of United Nations 2008: 11MJm^{2}y for bioethanol

LANXESS

Energizing Chemistry