Environmental Leadership from Cradle to Grave

Dissertation

Waste Management for the Tanning Industry

Biological Treatment for Non-Chrome Containing Solid Tannery Waste

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Vorgelegt von:

Dipl.-Ing. Christian KONRAD
Matrikel-Nr.: 9135022

Betreuer

O.Univ.-Prof. Dr. Karl E. Lorber

Gutachter

O.Univ.-Prof. Dr. Karl E. Lorber
Prof. Dr. Tony Covington

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Abstract

This doctoral thesis was written within the framework of the INCO-DC project "EILT" (Reduction of Environmental Impact of Leather Tanneries). Members of the EILT working group investigated the input and output figures of 6 different tanneries (4 Chilean, 1 Ecuadorian and 1 Spanish). Based on the data which had been obtained by these input/output analyses, a flow sheet of a chromium tanning bovine hide tannery was drawn up and average consumption figures and quantities of waste water and solid waste were computed. All specific input and output figures (fresh water, chemicals, waste waters and solid wastes) are based on one ton of wet salted hide input. To reduce the dilemma of unavoidable inaccuracies, minimum and maximum figures are presented. The given ranges are practical rules of the thumb to estimate the input and output figures of a SME - tanning process.

The obtained figures are discussed and proper segregation proposed. It is suggested to segregate effluents into 4 waste water streams: low polluted, high polluted, chromium bearing and sulphide bearing waste waters. Prevention, recycling & reuse and finally treatment opportunities are discussed for the respective effluent streams.

Solid wastes might be segregated into 3 fractions: spent salt, non-chromium containing solid waste and chromium containing solid waste.

Main stress is put on the treatment of the non-chromium containing solid waste fraction, which can be up to 80% of the global solid waste that is generated at a tannery. Aerobic biological treatment (composting) is proposed as a proper treatment technology. Practical trials on reactor composting of hair residues, fleshings and thermally treated fleshings were carried out. The results are presented in this work. The main parameters - substrate, bulking material, amendments, volume ratio, aeration rate, water balance and turning frequency – were investigated and their impact on the composting process is discussed.

Finally, the product quality were analysed. Plant tolerance and the chemical composition of compost made out of hair residues, fleshings and thermally treated fleshings were investigated.

That composting is a feasible alternative to other treatment technologies under certain conditions, is discussed in the final conclusion.

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Symbols & Abbreviations

$\%_{dm}$	Percent dry matter
B	Boron
BD	Bulk Density
BOD_5	Biochemical Oxygen Demand
C/N Ratio	Ratio Carbon to Nitrogen
$Ca(OH)_2$	Calcium Hydroxide
Ca_{total}	Total Calcium
Cd	Cadmium
Cl^-	Chlorides
COD	Chemical Oxygen Demand
Cr	Chromium
Cr(III)	Trivalent Chromium
Cr(VI)	Hexavalent Chromium
Cr_2O_3	Chromium Oxide
Cu	Copper
EILT	Reduction of Environmental Impact of Leather Tanneries
EPN	Escuela Politécnica Nacional
ESADDI	Estimated Safe and Adequate Daily Dietary Intake
FAS	Free Air Space
FDA	Food and Drug Administration
H_2O	Water
H_2S	Hydrogen Sulphide
Hg	Mercury
INCO-DC	International Corporation with Developing Countries
K	Potassium
$K_{available}$	Available Potassium
K_{total}	Total Potassium
LOI	Loss of Ignition
M_{ash}	Mass of Ash
M_{dry}	Mass of Dry Substrate
M_R	Mass Ratio
M_{tara}	Mass of Pot
Mg_{total}	Total Magnesium
MUL	Montanuniversität Leoben
M_{wet}	Mass of Wet Substrate
N	Nitrogen
n.a.	not analysed
n.d.	Not detected
Na	Sodium
Na_2S	Sodium Sulphide
NaHS	Sodium Hydrogen Sulphide
NH_3	Ammonia
NH_4-N	Ammonia Nitrogen
Ni	Nickel
NO_3-N	Nitrate Nitrogen
MPN	Most Probable Number
N_{tot}	Total Nitrogen
P2	Pollution Prevention
P_{total}	Total Phosphorous
$P_{available}$	Available Phosphorous

Pb	Lead
S	Sulphur
SG	Specific Gravity
SME	Small and Medium Enterprises
SO_4^{2-}	Sulphate
SS	Suspended Solids
TIC	Total Inorganic Carbon
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
tpd	Tons per day
TS	Total Solids
TUB	Technische Universität Berlin
t_{wsH}	Ton wet salted hides
UdC	Universidad de Concepción
UdSC	Universidad de Santiago de Compostela
UFRO	Universidad de la Frontera
UNEP	United Nations Environment Program
UNIDO	United Nations Industrial Development Organisation
USEPA	United States Environmental Protection Agency
v	Varied During Operation
V_R	Volume Ratio
WC	Water Content
Zn	Zinc

1   General

1.1   Definition of the Problem and the Objective

Leather is produced by the transformation of raw animal hides - a natural renewable resource - and can be considered to be much more than merely a valuable by-product of the food industry. The raw hides are processed in various steps: cleaning, tanning and dying. Thus causing severe environmental problems, such as highly polluted waste waters, different kinds of solid and hazardous wastes and off-gases.

Forced by rigorous legal restrictions, tanneries located in industrialised countries have significantly reduced their resource consumption (fresh water and chemicals) and their generation of effluents and solid wastes. By closing recycling loops and installing sophisticated end-of-pipe technologies, they have been able to reduce their resource consumption to a minimum and comply with the strict limits concerning effluents discharge and solid waste disposal.

Unfortunately, the situation in developing countries is not at all comparable to the one in industrialised countries. Tanneries located in developing countries are responsible for considerable negative environmental impact. Most tanners are not aware of the environmental harm they cause by their activities. Ignorance seems responsible for the pollution of the environment. Per ton of wet salted hides enormous quantities of fresh water are used, and then released as effluents. These effluents are characterised by excessive BOD_5, COD, chloride, chromium and sulphide loads. Generally, waste water is discharged without any further treatment. The huge amounts of solid waste disposed of at landfills that do not correspond to minimum safety or environmental standards are another problem.

Although simple measures of "Pollution Prevention" can improve the environmental situation significantly, most tanners have no or little idea about the principles of "Pollution Prevention".

A further possibility of reducing environmental harm would be the installation of end-of-pipe technologies. Unfortunately, small and medium sized enterprises (SME) generally do not have the economic and technological resources to implement end-of-pipe technologies at their plants. On the other hand, small and medium size enterprises are predominant in the economical organisation of developing countries.

The **INCO-DC project "EILT" (Reduction of Environmental Impact of Leather Tanneries)** – funded by the European Community - wants to contribute to accelerate the process of changing the tanners´ attitude towards the environment. The members of the EILT working groups carry out **research** and **developing activities** in the areas of "**Pollution**

Prevention", chemical recycling and reuse, effluent treatment and treatment of solid waste. Their aim is to make tanners aware of the fact that on the one hand they cause significant negative environmental impact and that there are possibilities to reduce those on the other hand. (For the project description see Annex A.)

This thesis, that was written within the framework of named project, presents a **clear and coherent discussion of the material streams entering and leaving a tannery** and gives an idea about the order of magnitude of these input and output streams. Furthermore, a **proper segregation of waste water and solid waste streams** and **streams of concern** on which tanners should concentrate their resources and efforts to reduce a main part of their environmental impact, should clearly be identified.

By introducing the **principles of "Pollution Prevention"**, it can be shown that considerable savings in resource consumption and a considerable reduction of the negative environmental impact can be achieved.

By finding a proper technology for treating the non-chromium containing solid waste fraction, the global quantity of solid waste can be reduced by approximately 75 to 80%. This treatment technology has to be practicable even in developing countries by small and medium enterprises (SME). It should be shown, that **aerobic biological treatment (composting) of non-chromium containing solid tannery waste** is feasible and a real alternative to anaerobic treatment or rendering plants.

Summarising one can say, that small and medium sized tanneries located in developing countries have to be provided with tools that allow them to contribute to the protection of the environment.

1.2 Zorba the Greek

"The story focuses on the relationship of a writer and intellectual, modelled by Kazantzakis, and an uneducated man, Zorba, who drinks, works, loves and lives like a force of nature. His character has been seen as the personification of Henri Bergon´s ideas of elan vital. He doesn't care about books, his values are more experience and understanding than scholarly learning. The narrator meets Alexis Zorbas in Piraeus. He plans to reopen an abandoned mine on the island of Crete and Zorbas becomes his foreman. Kazantzakis weaves the narrator's childhood memories and thoughts against the life and teaching of Zorbas. After a series of tragedies, failures and small victories, the narrator leaves Crete, but asks Zorba to teach him to dance. "How simple and frugal a thing is happiness: a glass of wine, a roast chestnut, a wretched little brazier, the sound of the sea."" [1]

Zorba the Greek is one of the most impressive characters in literature. The Greek author Nikos Kazantzakis (1883 – 1957) wrote the autobiographical novel "Zorba, the Greek" in the year 1946. Up to the present, Zorba is a person who combines a lot of characteristic traits and virtues which seem to have become more and more lost in our modern times.
Each of us should conserve a "Zorba" in one's heart. In order not to forget him, each chapter of this doctoral thesis starts with a quotation of his thoughts and speeches.

"I remember one morning when I discovered a cocoon in the back of a tree just as a butterfly was making a hole in its case and preparing to come out. I waited awhile, but it was too long appearing and I was impatient. I bent over it and breathed on it to warm it. I warmed it as quickly as I could and the miracle began to happen before my eyes, faster than my life. The case opened; the butterfly started slowly crawling out, and I shall never forget my horror when I saw how its wings were folded back and crumpled; the wretched butterfly tried with its whole trembling body to unfold them. Bending over it, I tried to help it with my breath, in vain. I needed to be hatched out patiently and the unfolding of the wings should be a gradual process in the sun. Now it was too late. My breath had forced the butterfly to appear all crumpled, before its time. It struggled desperately and, a few seconds later, died in the palm of my hand. The little body is, I do believe, the greatest weight I have on my conscience. For I realise today that it is a mortal sin to violate the great laws of nature. We should not hurry, we should not be impatient, but we should confidently obey the eternal rhythm." (Zorba, the Greek) [2]

1.3   Introduction

The tanning of hides and skins, the process of converting animal hides into leather, has been an important (industrial) activity since early mankind. Leather is produced by the transformation of raw animal hides, a natural renewable resource which is much more than only a by-product of the food industry.

The raw hides are processed in various steps: cleaning, tanning and dying, which produce severe environmental problems, such as highly polluted wastewater, different kinds of solid and hazardous wastes and off-gases. Since millenniums, tanners have been blamed for being responsible for serious negative environmental impact. The quantities of fresh water consumed and the loads of pollutants tanneries are discharging, show that tanners are more culprits than victims. The industrial revolution, the development of the hair-burning sulphide unhairing process and the use of chromium as a tanning agent have worsened the situation.

In industrialised countries, rigorous environmental restrictions have been imposed on tanners and their activities. On the one hand such regulations protect the environment but on the other hand they make competitiveness more difficult. As a consequence, tanners in Western European countries can only survive in niche markets. That is, why the main chromium leather production can today be found in developing countries. The concentration of tanneries in certain regions and the lack of restrictive environmental laws there cause serious environmental problems.

The lack of economic resources as well as little consciousness as to environmental problems however, make a change in the near future not very likely.

This work is addressed to tanners located in developing countries. A typical chrome tanning process is modelled and streams of concern are identified. For these streams of concerns, possibilities of prevention, reduction and/or treatment are discussed. The limited economic resources of SME - tanneries are taken into consideration. Such "simple" and "cheap" methods, which can significantly reduce the negative environmental impact are presented.

In **chapter 2** a **brief overview of the tanning process** is given. The entire process of transforming skins and hides into leather is split into the individual unit steps (unit operations). Each step is explained and important information on resource consumption and environmental impact are given.

Chapter 3 deals with the principles of "Pollution Prevention" (P2). The approach of reducing the negative environmental impact of industrial processing by preventing the generation of pollutants is explained. Most measures of "Pollution Prevention" are simple and require little capital investment. Therefore this "philosophy" seems to be predestined for small and medium sized enterprises located in developing countries. An **analysis** of "**Pollution**

Prevention" and **small and medium sized enterprises (SME) located in developing countries** is given in this chapter.

Modelling the tanning process is difficult. In literature, a lot of data concerning water and chemical consumption and effluents and solid wastes generation can be found. But due to incoherent basis and lack of information the data are hardly comparable.

In **chapter 4** the **EILT model presents a chrome tanning process**. Feed stock are bovine hides with an average weight of 25 kg.

All input streams (**water and chemical consumption**) and all output streams (**waste waters and solid wastes**) are **based on 1 ton wet salted hide input (t_{wsH})**. The data was collected at **6 different tanneries** and is summarised in this chapter.

The consumption figures and the quantities of waste streams that are computed for the EILT model are average numbers developed by practical experience, as the consumption figures at different plants vary quite a lot from tannery to tannery.

After drawing up the EILT model the **material streams are discussed** and a **proper segregation** of the respective streams **is suggested**.

Approximately **75 to 80%** of the total quantity of solid wastes are **non-chromium containing fleshings, trimmings, unused split and hair residues**. Because of the high quantity, this solid waste stream is a stream of concern. Due to the organic matter of this waste a **biological treatment** is the obvious option. High capital costs and relatively sophisticated process control make **anaerobic treatment unsuitable** for small and medium scale tanneries located in developing countries. Thus, **aerobic treatment** seams to be a real alternative to anaerobic treatment.

In **chapter 5** the **principles of composting** are explained. After **characterising the substrate**, results on **windrow composting** are presented. Because of several problems, **reactor composting** might be favoured. The main **process parameters** for composting of fleshings, thermally treated fleshings and hair residues are documented and discussed.

Finally, the different **composts** that were produced are **evaluated** with regard to their chemical composition and their impact on plant growth.

Once again it must be stated that this work is addressed to small and medium sized tanneries (SME) located in developing countries. It cannot be the aim and intention of this work to show what is possible with sophisticated technologies. It is not realistic to expect that named SME-tanners have the technical and economical resources to compete with large scale tanneries. However, what can be expected by tanners is, that they become aware of the negative impact on the environment which they cause by their activities. And furthermore, it can be expected, that they concentrate their efforts on reducing the environmental harm of the main polluters leaving their plants. The streams of concern that are identified in this work and the possibilities of reducing them, should support tanners in their decision making.

2   Leather Making

In this chapter a brief discussion of the individual process steps involved in leather making will be given. For further and detailed information on tanning technology E. HEIDEMANN [3] and F. STATHER [4] are recommended. It is from these bibliographies that the main information of this chapter was taken. A good overview is also given by T.VARNALI [5].

2.1   Introduction

Tanning is the process of converting perishable animal hides into leather. Through tanning, the hides which consist of biodegradable proteins are permanently preserved. The differences between leather and un-tanned hides are:

- Leather does not get rotten after longer bouts of humidity
- In dry conditions it does not change into a hard, horny state
- Through influence from hot water it does not change to glue

Leather making, even in industrialised countries, is today still much of an industrial art or craftsmanship. Plants and equipment, capacity of production unit and end-products vary from tannery to tannery.

Leather-making is an ancient craft which has been practised by almost all cultures and civilisations, dating back some 7,000 years. The curing of animal hides has remained an essential activity from primitive to medieval times, through the industrial revolution, and on to modern day. As time has evolved, leather fabrication has seen many levels of sophistication. From the simple sun-drying of animal skins and hides by our primitive ancestors, to vegetable tanning developed by the Egyptians and Hebrews around 400 BC, through to the much-improved and highly-skilled leather–making of the Arabs in the Middle Ages, on to the wide-spread tanning practised in Europe from the 15th century onwards and, finally, to electric powered, commercialised industrial tanning performed in almost every country today.

In particular, several countries in Asia and America have, in the past few years, become important players on the international leather market as a result, primarily, of their low labour costs and rapidly developing technological capacity, as well as the growth in middle-class in these regions which has increased the size of the local market for leather products.

2.2 Steps Involved in Leather Production

Figure 1 shows a summary of a general tanning process, also indicating waste streams. Generally, the tanning process can be divided into the sections "**Beamhouse**", "**Tayard**", "**Retanning**" and "**Finishing**". Each of these sections is further divided into unit operations.

	Raw hides	
← **Water pollutants**		**Air pollutants** ┄┄► / **Solid wastes** ━━►

beamhouse

- BOD, COD, SS, TS, salt, organic N, ← **SOAKING**
- **GREEN FLESHING** → green fleshings; fat containing organic matter
- BOD, COD, SS, TS, alkalinity, sulphides, organic N, ammonia N ← **UNHAIRING LIMING** → H₂S ; Hair, lime and organic matter containing sludge
- BOD, COD, SS, TS, alkalinity, sulphides ← **LIME FLESHING** → Lime fleshings / Fat containing limed organic matter
- **LIME SPLITTING TRIMMING** → Limed split
- BOD, COD, TS, ammonia N ← **DELIMING BATING** → NH₃
- BOD, COD, TS, fats ← **DEGREASING** sheep and pig skin

tanyard

- BOD, COD, SS, chromium salt, syntans, dyes, salt, acid ← **PICKLING TANNING**
- **CHROME SPLITTING** → Chrome split (chrome containing organic matter)
- **SHAVING** → Chrome split (chrome containing organic matter)

retanning

- BOD, COD, TS, chrome and vegetable tanning chemicals, syntans, dyes, fats ← **RETANNING DYING FATLIQUORING**
- **DRYING**
- **TRIMMING** → Chrome trimmings (chrome containing organic matter)

finishing

- Finishing chemicals ← **FINISHING** → Solvents, formaldehyde

Leather

Figure 1   Unit Operations of the Tanning Process [6]

2.3 Preservation and Curing

The death of an animal causes a change in the metabolism of its body. Immediately, the process of self digestion (autolysis) starts. Autolysis is a function of temperature and salt concentration. Furthermore the organic matter is attacked by putrefactive bacteria for which autolysis products offer an excellent medium.

Therefore **curing** is necessary to protect freshly flayed hides and skins from attack by micro-organisms and to render them storable for a prolonged period.

In most developing countries hides and skins are flayed and lightly **cured with salt** at abattoirs or local hide collection centres. The commonly applied methods of salting are either incubating the hides in a vat of saturated brine or salting them dry (layer of salt and hides). The quantity of salt is about 25 – 30 % of the weight of the hides. Properly salted hides can be stored safely for several months at room temperature.

Curing often incorporates treatment with insecticides to discourage beetle and other insect attack during storage and transport. Curing fresh hides with salt causes several problems.

Encouraged by these problems, fresh hide processing was introduced in Europe and the USA several years ago. This has been done successfully by **chilling** the hides with ice, and storing them in refrigerators and transporting them in refrigerated trucks.

2.4 Beamhouse

2.4.1 Soaking

Two effects have to be achieved by soaking cured hides: **cleaning up** of the surface of the hide and **re-hydration** of the interior of the hides. Generally, hides are polluted with manure, urine and blood. Furthermore, large amounts of salt have to be removed, some of which adheres to the outside of the hide and the rest that is well penetrated in the entire cross section of the hide.

Salted hides, fresh hides and chilled hides all require several washings with fresh water under strong mechanical agitation for proper cleaning. Drums, mixers and paddles can be used and the wash float should be changed at least twice with fresh water after 30 to 60 minutes of drumming.

Full rehydration of the fibre structure is an important precondition for all beamhouse operations. Liming cannot substitute for insufficient soaking. The aim of soaking is to allow the hides to reabsorb any water which may have been lost in the previous process steps (curing, transport, storage). Furthermore, the collagen fibres and keratin cells of the hair and epidermis take up water and become more flexible.

Salted hides need about 5 hours of drum soaking while dried hides and skins may need 24 hours or even more. The water temperature should be between 10-16 °C. The water use for soaking and rinsing purpose is approximately 3 to 5 times the weight of the hides. The hide

has to reach as close as possible the state of suppleness it had when it was freshly flayed from the animal.

Soaking in the final rehydration float is currently enhanced by mechanical agitation, increased temperature and by adding chemicals – acids, alkalis, salt or enzymes. In many cases small amounts of bactericides are added. The addition of NaOH has to be made properly. The purpose is only to adjust the float to a slightly alkaline pH. The addition of too much alkali and/or poor mixing may result in hair immunisation and rapid swelling. Both shows negative impact on the leather quality. Elevated temperatures of up to 32 °C accelerate the soaking – a limit is given at 38 °C. The warmth helps to make the fibre structure more flexible. However water uptake is somewhat less than it would be at 15 °C.

2.4.2 Unhairing and Liming

Loosening and unhairing can be seen as an extension of the soaking process. The aim of **unhairing** and **liming** is to remove the hair, epidermis and to some degree the inter-fibrillary proteins, and to prepare the hide for removal of loose flesh and fat by the fleshing process. The pelt has to be freed of the epidermis and hair, including the hair roots, and the keratinous material filling the hair follicles before proceeding with the next step.

The S-S bridges of the keratin can be split by reduction or oxidation quite selectively without influencing the collagen fibre network. The keratin structure may partially break down forming a pulp or dissolving completely, leading to a clean pelt surface with the assistance of mechanical action on the hides that can suspend the hair sludge and empty the hair follicles completely.

The common unhairing agent used in the leather industry today is sodium sulphide (Na_2S). Unhairing and liming occurs simultaneously. It is generally done in a rotating vessel such as a drum or mixer in a float containing 3 to 4% lime hydrate ($Ca(OH)_2$) and 1 to 3% sodium sulphide technical grade (Na_2S).

Unhairing is done in some tanneries in paddles using an even higher float, because it is easier to drain. The combined unhairing and liming operation requires from 14 to 24 hours at room temperature to complete. The mechanical movement of the hide during the process rubs off the pulped hairs and helps to free the hair roots from deep within the hair follicle. At the same time the structure undergoes swelling and opening.
The conditions of unhairing with respect to time, temperature and concentration of sulphide and alkalinity has a strong influence on the depilation and the opening effect on the collagen fibre structure.
Enzymatic processes exist to remove the intact hair. Such processes are called "hair saving". Hair saving processes result in a cleaner grain than in the destruction, hair burn process, because the hair roots remain more or less intact and are removed in a mechanical action.

However, enzymatically unhaired hides, as a rule, have to be tanned and dyed in a different way than hides processed by other techniques.

Besides the removal of hair, the unhairing/liming has an additional effect on the hides – the swelling. Collagen behaves at low pH like a cation and at high pH like an anion. Starting at the isoelectric point, if the pH is lowered by adding acid, the carboxyl groups lose their charge, while the amino groups have become neutralised repulsive forces between the excess positive charged amino group side-chains arise. These repulsive forces are the basis of swelling in acid. In the alkaline region it is the reverse. The amino groups are neutralised by the addition of alkali and then the negatively charged carboxyl groups became predominant and create repulsive forces.

Repulsion charges are the source of swelling. Swelling in the acid range is stronger than in the alkaline range.
The extent of swelling, measured by increasing thickness and uptake of water (which means an increase in weight) depends greatly on the given structure. Hides from older animals are much more crosslinked and may swell less than a hide of a young animal under the same conditions.

Alkaline swelling in the liming step increases with increasing alkali concentration, the duration of treatment and with lowering of the temperature. The degree of swelling is only a function of alkali concentration provided that sufficient liquid for water uptake is present.
Hence the total effect of liming is that the pelt swells more at all pH values than does native hide. Forces of swelling lead to a general loss of the fibre-network and to the splitting of larger collagen fibres.

The keratin of the hair is decomposed and forms sulphur and nitrogen compounds, in conjunction with lime these compounds accelerate the breakdown of further keratin. Thus one can say the more impurities the lime liquor contains the more rapidly it unhairs. As a consequence, old spent and recycled unhairing/liming liquors are more effective than fresh ones. On the other hand the alkalinity is lower which has a negative impact on the swelling. F. STATHER [4] writes that the "art of tanning" was the knowledge of how to mix the fresh and used lime liquors. When using fresh liquors, swelling is stronger and opening weaker. While old liquors (often infected by micro-organisms) are better hair looseners.

2.4.3 Fleshing

The flesh side of the hides still have excess fat, flesh and connective tissue attached, which must now be removed prior to further drum processing. Furthermore, excess water containing salt, soluble proteins, bacteria and impurities must be squeezed away from the pelt. The pelts are individually fed through a fleshing machine consisting of a set of revolving cylinders designed to cut and scrape away the unwanted matter. During fleshing, the loose and ragged ends of the skin are removed by a hand knife. These are called trimmings.

2.4.4 Splitting

The swollen, fleshed hides are in an appropriate state for splitting into two layers to give a "grain split" and "flesh split". Unlike the original hide, the grain split is now of uniform thickness and undergoes further processing to produce leather.

The splitting of pelts in the beamhouse is today a high developed technique. The endless steel knife is held between wedge grips very tightly but still just movable. This hold fixes the knife so far that the position of the cutting edge cannot fluctuate by even a tenth of a millimetre and not be moved under lateral force. It is obvious that this adjusting needs skill. But much more difficult is the adjusting of the position of the pelt in the cutting zone due to the much weaker structure. It is very flexible and also slippery. Fixing is made by a rubber cylinder and by special intersected brass cylinder rolls.

2.4.5 Deliming, Bating and Pickling

After liming in strong alkali the alkalinity has to be reduced to neutrality. This is called **deliming**. The aims of deliming are to eliminate swelling and to remove mechanically deposited lime, chemically bound lime and capillary lime by conversion into readily soluble salts. Furthermore the pH value inside the collagen network is regulated and the bath is buffered. The fibres are separated by washing out matrix and products of protein degradation are removed from the pelt. Deliming is required because if the lime is not removed from the pelts the product will be a hard, green and inflexible leather in case of chrome tanning. Usually deliming is done by adding ammonium sulphate.

Bating is an enzymatic process which has the purpose of further loosening and peptising the fibre texture of the skin and eliminating alkali-swelling. Enzymes are biological catalysts which accelerate the reactions without being modified. They act specifically on proteins called proteases. Current enzymatic treatment employs 0.5% bating material for 30 minutes up to 12 hours, replacing the age-old process which entailed treatment with dog dung or pigeon droppings.
Temperature influences the bating effect. The rate of enzymatic reaction increases with rising temperature. Bating temperatures used in practice are approximately 30 – 37 °C.

2.5 Tanyard

2.5.1 Tanning and Pickling

Pickling invariably precedes the tanning step, because of the need to bring the acidity of the pelt to the required level. This acidity is vital for the subsequent tanning procedure. Pickling and tanning nowadays are carried out in a combined step.

The purpose of **pickling** is to acidify the pelts to a certain pH before chrome tanning and thus to reduce the astringency of the chrome tanning agents. Pickling is also used for preserving. Chemicals include 5 – 10% of common salt (sodium chloride) or sodium sulphate and 0.6 – 1.5% acid (sulphuric, hydrochloric, acetic or formic acid or mixtures).
During neutralisation of the pelts in the pickling step the pH of the collagen is shifted to the isoelectric point and the state of swelling must change.
Reversing the swelling is much more difficult, because a hide swelled in sodium hydroxide cannot be reversed by offering strong acids. Therefore weak acids or acidic salts are used. Boric acid, ammonium sulphate, sodium bisulphate and very recently sodium bicarbonate or carbon dioxide have been proven in practice. They can be offered in excess without causing acid swelling. A most important point is, that the float should be as short as possible, to obtain the highest concentration possible of the neutralising agents.

The process of **tanning** is the midpoint activity and the basis of leather-making. Tanning is the stabilisation of the collagen structure of the hide, using natural or synthetic chemicals. The stabilisation is mainly an increase in resistance against water and leads to restricted swelling. Resistance against water means, that the tanned material cannot undergo anymore changes, which are caused by an aqueous medium: putrefaction, swelling and drying up to an inflexible solid mass.
Tanning also leads to a change of the appearance and of the handle or feel of the skin or other kinds of connected tissues. The object of converting pelt into leather by tanning is to:

- Stabilise it against biological decomposition and increase its resistance to chemicals
- Raise its shrinking temperature and increase its resistance to hot water
- Reduce or eliminate its ability to swell
- Lower its density by isolating the fibres
- Reduce its deformability
- Reduce its shrinkage in volume, area and thickness
- Enhance the porosity of its fibre texture.

These effects are achieved by cross-linking the collagen chains with various tanning agents. Chromium(III) salts, Aluminium salts, Iron salts, (Glutar-) Aldehydes and vegetable tanning agents are some examples of commercially available tanning agents.

The majority of leathers today are chrome tanned. This is a consequence of the easy processing, the broad applicability and the unlimited access to chromium-tanning chemicals

and the excellent properties of the chrome tanned leather. One of its extraordinary properties is the boilfastness (a parameter characterising the thermal resistance of the leather).

Modern single-bath chrome tanning with trivalent chromium sulphate is conducted by adding commercially produced powder products to the tan drum. Chrome tanning involves:

- The application of chromium(III)sulphate (a technical product containing about 26% Cr_2O_3 of basicity 33%), using 5 - 19% which corresponds to an offer of about 1.25 – 2.5% Cr_2O_3 on pelt weight.
- An adjustment of the pH to 3.5 – 4 and an increase during tanning by basification.
- An increase in temperature up to 50 °C, but typically just over 40 °C.
- A drumming time of at least six hours.

2.5.2   Shaving

The grain leather is brought to a uniform thickness. Unevenness is removed from the back, then the pieces are grouped into batches for dying.

In the shaving process the leather is inverse to the fleshing transported into the machine. This way normally the shaving will be interrupted by lifting the rubber cylinders before the leather is full transported in the machine, and the leather is taken out, turned by hand and the second half again shaved.

2.6   Retanning

In the section **retanning**, the fibres of the leather are further crosslinked with tanning chemicals based on metal salts, syntans or vegetable based chemicals. Furthermore, the wet blue is coloured and the mechanical properties are determined.

2.6.1   Leather Dyeing

Almost all leather is dyed. With few exceptions, such as vegetable tanned leathers with a natural look, leather is artificially coloured and this visual aspect is an essential part of its aesthetic properties.

Dying of leather is the application of soluble organic dyestuffs in aqueous floats to wet leather. This leads to fixation of the dye molecules not only on the surface of the tanned fibre network but inside as well. The type of coloration of leather is completely different from the finishing operations performed in crust leather manufacturing, where insoluble dyestuffs

and/or pigments are applied together with polymeric binder substances on the surface of the dry leather.

Dyestuffs are generally synthesised organic chemical molecules of an aromatic or sometimes heterocyclic nature.

2.6.2 Fatliquoring

Next to tanning agents fat is the most important component of leather. With the exception of sole leather any kind of softer leather contains remarkable amounts (5 – 20%) of fat. Fat is the basis of the flexibility.

The fibre elements dehydrated by tanning are coated with a fat layer to give leather the desirable softness and lubrication. At the same time, fatliquoring influences the physical properties of the leather, such as extensibility, tensile strength, wetting properties, waterpersistance and permeability to air and water vapour.

Fat prevents the sticking, gluing or adhesion of fibres, which occurs though a certain fibre separation effected by tanning.

2.6.3 Drying

The two aspects of leather **drying** are: the different designs for apparatus and processes in which streaming air of varied humidity and temperature is used as carrier for water during drying and the behaviour of leather during drying and its resulting properties.

The natural state of hides and skins is the fully hydrated fibre network with a water content of about 60 to 70%. Fresh hides, when soaked, take up additional amounts of water and swell. During tanning, retanning, dyeing and fatliquoring additional substances are taken up by the fibre network in the amount equal to about half the weight of the dry protein present. But the water may be assumed to be unaffected by the presence of these substances, because of the nature of the fibre – the moisture bond remains essentially unchanged.

Different drying methods for leather are:

- Air-drying without supply of energy (hang drying)
- Air-drying with supply of energy
- Hot water drying
- Infrared drying
- Vacuum drying
- High-frequency drying

Sammying and **setting - out** are two operations which are always conducted before drying. Mechanical water removal is cheaper than removal by drying. If setting out is performed before sammying, it reverses the shrinkage of the leather, caused by drumming and leads to a smoother grain.

With the exceptions of drying by freely hanging of the leathers, all the drying methods hold the shape of the leather constant during drying in an expended state. This is the way leather is prevented from shrinking thus acquiring a smooth and wrinkle-free surface.

2.7   Leather Finishing

The purpose of **finishing** is to improve the use quality of the leather in general and to protect it from wetting and soiling, to level out patches and grain faults and to apply an artificial grain layer to split or correct grain leather. And also to modify the surface properties (shade, lustre, handle, etc.).

The finish of a leather can greatly vary mainly depending on the purpose of the leather. Hide stocks differ in the extent of grain damages. Hides with greater damages have to be corrected by buffing, which removes more or less much of the natural grain structure. They are referred to as corrected grain. Therewith the most important element of a natural look gets lost.

Leather very uneven in grain in respect to structure and coloration requires more pigments and more pigments generate thicker films thus resulting in the leather becoming more plastic-like. A so called natural feel or look is made by embossing an artificial grain and by milling and also by application of a bicolour effect.

Finishing materials may be classified into two main groups:

- **Binders** which may be waxes, proteins or synthetic polymers
- **Additives** such as pigments to give colour, or surface modifiers

There are four methods used in the leather industry to apply finishes:

- Pad coating
- Spray application
- Curtain coating
- Roller coating

3   Waste Management

3.1   Introduction

"The Congress hereby declares it to be the national policy of the United States that pollution should be prevented or reduced at the source whenever feasible, pollution that cannot be prevented should be recycled in an environmentally safe manner, whenever feasible, pollution that cannot be prevented or recycled should be treated in an environmentally safe manner whenever feasible, and disposal or other release into the environment should be employed only as a last resort and should be conducted in an environmentally safe manner." [7]

In the year 1990 the Congress of the United States defined in the United States Code / Title 42 – The Public Health and Welfare / Chapter 133 – Pollution Prevention § 13101 (b) the priorities for environmental management. This act is commonly known as the "Pollution Prevention Act of 1990".

First and highest priority is given to Pollution Prevention (P2) which equals source reduction - preventing pollution before it is created, so there is less or no need to control, treat or dispose of it.

In a memorandum released in 1992 by USEPA (United States Environmental Protection Agency) clarified the definition of "Pollution Prevention":

"Pollution Prevention" means "source reduction" and other practices that reduce or eliminate the creation of pollutants through:

- Increased efficiency in the use of raw materials, energy, water or other resources, or
- Protection of natural resources by conservation."

The term "source reduction" – the most important term in P2 – is defined in the act of Pollution Prevention from 1990. It means "... any practice which reduces the amount of any hazardous substance, pollutant or contaminant entering any waste stream or otherwise released into the environment (including fugitive emissions) prior to recycling, treatment or disposal, and reduces the hazards to public health and the environment associated with the release of such substances, pollutants or contaminants." [7]

Also some practices classified as "in-process recycling" may qualify as pollution prevention opportunities. Generally spoken for any process this means:

- The reduction of the use of water, chemicals and feedstock.
- The reduction of energy consumption
- The substitution of chemicals and / or feedstock

In the following section (section 3.2) the main principles of a modern waste management and integrated pollution control and prevention are introduced. The basic ideas are explained in a few words. This is not an in depth discussion of this topic, but a brief overview. A lot of recommendable literature concerning pollution prevention and waste management exists. For further reading the following literature is advised: [8], [9], [10] and [11].

At the end of this chapter a 19-step approach to a pollution prevention assessment is given. According to this approach, the 6 input/output analysis which are discussed in chapter 4, were carried out.

Finally, in section 3.4 the topic "Pollution Prevention and Developing Countries" is discussed. This section gives information on why the idea of Pollution Prevention has a high success potential, especially in developing countries.

A lot of literature exists, concerning the opportunities of prevention, recycling & reuse and treatment measures in the tanning industry. It was abstained to discuss these possibilities in detail, because it would be anything else but a repetition of information that is collected in other bibliographies. In the section 3.5 the most popular opportunities are listed. The following literature is highly recommended to readers who need more in depth information: [12] [13] [14] [15] [16] [17] [18] [19] [20] [21] [26] and [27]

3.2 Principles of Waste Management

"Pollution Prevention" is a part of an integrated waste management concept. Actually the most important one. Therefore, in this chapter about waste management, the main stress is put on preventing pollution. The philosophy behind "Pollution Prevention" is best described by J. FRIJNS [10] when saying: "Cleaner Production is not simply a matter of applying new technologies but requires readjustment and rethinking throughout the firm."

The new way of thinking is to develop a sensitivity for environmental pollution and to redefine pollution as an indicator of inefficiency in the production process. Inefficiency that results in wastage of resources, economic losses, poor working conditions and environmental pollution. The main reason for implementing "Pollution Prevention" in a company are the economic benefits that can be achieved.

There are a few principles that have to be seen as the base of all discussions concerning measures for reducing environmental pollution.

3.2.1 Principle 1   Waste Management Hierarchy

Figure 2   Hierarchy of Modern Waste Management

Once we are aware of the fact that a process (potentially) generates wastes (solid, liquid, gaseous and/or energy) the logical consequence must be to decide what to do with these wastes. In modern waste management the hierarchy shown in Figure 2 is accepted as the base for any discussion. When the pollution (waste) is defined as indicator of the inefficiency of the process and the objective is to minimise the inefficiency, the logical and first step is to think about prevention of the respective pollutant, or in other words, how to increase the efficiency of transforming a feedstock into a product. If prevention is not feasible, another possibility to increase efficiency is to recycle the respective material stream.

In some cases recycling is not possible or is economically not recommendable. Whereby the technical feasibility of recycling material streams can be investigated and determined under the given circumstances. An economic evaluation is much more difficult and the result depends on the factors that are taken into consideration for the calculations.
In the case that recycling cannot be recommended, the waste stream must be treated so as only potentially harmless effluent streams are released into the environment. These treatment technologies are known as "end-of-pipe" technologies.
As mentioned above, the first two approaches "prevention" and "recycling" are broadly applicable in small and middle scale industries (SME). They have their technical, economical and environmental justification. The end of pipe approach in some cases is difficult or even impossible for small and middle sized enterprises to realise. This approach refers more to large scale enterprises or public institutions.

For several types of waste even a proper treatment is not feasible. As a final solution the disposal at safe landfill areas might be taken into consideration. In developing countries the lack of such an infrastructure might be an obstacle for this approach.

Prevention   The best reduction strategy is one that keeps waste from being generated in the first place. Waste prevention may in some cases require significant changes to the process, but it provides the greatest environmental and economic rewards.

Recycling   If waste generation is not avoidable in a process, then strategies that minimise the waste to the greatest extent possible should be pursued, such as recycling and reuse.

Treatment   When waste cannot be prevented or minimised through reuse or recycling, strategies to reduce their volume or toxicity through treatment can be pursued. While end-of-pipe strategies can sometimes reduce the amount of waste, they are not as effective as preventing the waste in the first place.

Disposal   The last strategy to consider is an alternative disposal methods. Proper waste disposal is an essential component of an overall environmental management program. However, it is the last effective technique.

3.2.2   Principle 2   Generate Waste as Early as Possible

Applying the waste management hierarchy to each process unit and each waste stream, it can be shown, that most of the waste streams generated can be prevented.
However, when investigating a process there will still be waste streams which can not be avoided. An example is the fleshing step in the tanning process.

However, by carrying out the fleshing step as early as possible (green fleshing), savings in chemical consumption in subsequent process steps and savings in operation and processing costs (less weight has to be further processed) can be achieved. Generalising one can say, that waste that can not be prevented should be generated as early as possible in order to not further process a matter that is not part of the product. Early generation will lead to savings in processing cost and to a "purer" waste due to the fact that cross contamination with process chemical will be prevented.

That means: Waste that can not be avoided, should be produced as early as possible and removed from the main process.

3.2.3 Principle 3   Segregation of Waste Streams

Once having a clear idea about the waste streams generated in a plant or process, it is important to separate and segregate them into different groups for further treatment.

It should be kept in mind, not to pollute waste streams with hazardous substances from other waste streams. For instance: by separating the chromium containing effluents from the non-chromium-containing, it is not necessary to treat all the effluents in a chromium treatment plant, but only a part of them. This simple measure (not mixing effluent streams) will result in savings in capital as well as operation costs. Furthermore, the efficiency of treatment plants might be increased due to the fact that the pollutants are much more concentrated. Once mixed a segregation of the effluent streams is "not" possible anymore.

3.2.4 Principle 4   Take Measures where they are Most Effective

This principle also appears rather logical. Reducing a waste stream that represents 80% of the overall waste streams by 10% means a reduction of the overall waste streams by 8%. Reducing a waste stream that contributes with 20% to the entire waste stream by also 10% means a reduction of 2% of the total waste – 4 times less than in the first case. Pollution Prevention measures must be concentrated on the "streams of concern". These "streams of concern" have to do with quantity as well as quality (hazardous waste).

3.3   Environmental Assessment

Starting point of any discussion about measures for reducing the environmental pollution is an assessment of the prevailing situation. Such an environmental assessment can vary in detail depending on the local situation and the institution that is carrying out the audit.

However, the basic structure will always be the same. A 19 step approach that was applied for the input/output analysis that were carried out by the INCO-DC EILT working groups is presented in chapter 4. For detailed information see volume II and III of the EILT papers ([28] and [29]).

	step 1	**Preparation**
	step 2	**Unit Operations**
	step 3	**Process Flowsheet**
	step 4	**Determining Input**
	step 5	**Recording Water Usage**
	step 6	**Current Level of Waste Reuse and Recycling**
	step 7	**Determining Output**
	step 8	**Recording Waste Water**
	step 9	**Recording Gaseous Emissions**
	step 10	**Accounting for Offsite Waste**
	step 11	**Evaluation of Material Balance**
	step 12	**Refining of Material Balance**
	step 13	**Examination of Obvious Waste Reduction Options**
	step 14	**Targeting and Characterising Problem Waste**
	step 15	**Segregation of Waste Streams**
	step 16	**Developing Long-Term Waste Reduction Options**
	step 17	**Environmental and Economic Evaluation of Detected Options**
	step 19	**Developing and Implementing Actions**

Figure 3   19 Step Approach of a Pollution Prevention Assessment

First the targets and objectives of the assessment have to be defined. Than all information that is available about the plant and the concerned industry has to be gathered. By visiting the plant a flow sheet of the process is drawn up. The flow sheet consists of several levels of details. From level 0 the entire plant or process is a black box with a few input output streams which are further detailed until level x – until each unit operation is defined with the corresponding input and output streams.

According to this flow sheet, specific consumption figures for raw material, water and energy, etc. are quantified. Existing recycle loops are determined. Afterwards specific figures of generated waste are determined. Waste refers to solid, liquid and gaseous waste streams and heat as well. Besides quantifying the input and output streams of the respective process unit the current situation of the off-site waste is examined (quantities and costs).

Once having the actual data and a representative material balance, an evaluation of the data starts. Generally, after a first evaluation a number of obvious waste reduction options can be found.

In order to detect potential savings in resource consumption and savings in generated waste, extensive checklists have been elaborated. Here, just a few questions should be asked:

- What quantity of raw material is spilled during handling? Can the spillage be avoided and how?
- Is vacuum pump water recirculated?
- Is water flow controlled? Where are the main water consumers and what type of water is consumed?
- Where does the waste originate and does the waste contain valuable products?
- etc....

Further activities that have to be carried out parallel to the detection of obvious waste reduction options are a qualification and quantification of the waste streams. Where are the waste streams of concern and how are they characterised. Further a schema has to be developed on how to segregate the individual streams. According to **principle 3** – segregation of streams – the contamination of low polluted streams with heavy polluted streams must be avoided. This would result in a larger quantity of waste that requires special treatment.

The activities from step 1 to 17 can improve the environmental situation of a company significantly. For instance a reduction of emissions and waste in the range of 20–40% is reported by J. FRIJNS [10]. Savings in natural resources in the range of 5–40% can be achieved. Also the economic benefits are significant. Pay back periods for investment is reported to be less then 1 year.

Such an assessment can be expected even from entrepreneurs located in developing countries with poor infrastructure and a difficult economic situation. About the specific situation of enterprises located in developing countries see section 3.4.

Developing long term reduction options and implementing them after a technical and economical evaluation might be more difficult. Such investment requires capital and operation costs that are not likely to be available for small and medium scaled enterprises (SME) located in developing countries. But even in this advanced step of the assessment, solutions might be found that reduce the negative environmental impact of the company without weakening the competitive situation. This may be a change in technology, change in product or producing a by-product from waste streams.

3.4   Pollution Prevention and Developing Countries

In developing countries environmental pollution is an increasing problem. Small and medium scaled enterprises (SME) are seen as an important tool in the economic development of these countries. Generally it has to be stated that the main negative impact on the environment is caused by large companies and not by small scale enterprises. Due to their limited production capacity and therefore limited discharge of pollutants, they can never

cause the same environmental harm caused by a large company. But several factors exist that make it impossible to ignore the contribution of small scale enterprises to the environmental situation in a region or country.

Firstly, the **number** of small scale enterprises is an important factor. The contribution of a single company may be low or even neglectable. But due to the fact that the number of small and medium scale companies is much higher than the number of large enterprises one can not ignore this sector. Especially in developing countries, the predominant economical organisations are small and medium scaled enterprises (SME).

Secondly, small and medium scale enterprises are generally located in close **proximity to residential areas** whereas big companies are usually located away from these areas. Therefore the direct impact and effect on the population is much higher.

Large firms generally have certain safety and health standards for their plants while small scale companies lack such standards and **working conditions** are generally rather poor.

Summarising, one can say that although the small and medium scaled industry (SME) in developing countries may not be the main polluter it contributes to the bad environmental situation. Their specific pollution load (i.e. pollution load per unit product), is generally higher than the one of large companies. **Process inefficiency** proves responsible for the high specific pollution load.

The main problems are the **hazardous** and **toxic wastes** that are generated at small scale companies and not the organic pollution load of effluents or the air pollution. The negative impact on the environment and the health situation is reinforced by the fact that small scale industry is generally located in or close to **residential areas**. Proper **working conditions** are generally lacking.

An improvement of this situation generally fails due to the lack of skills, knowledge and awareness about pollution problems within the environmental sector. Further most **end of pipe technologies** as a "standard solution" for environmental problems are **inappropriate** for small scale enterprises from a **technological** and an **economical point of view**. In addition to that due to their urban location generally the **space** for the installation of treatment pants or equipment is limited.

Especially for small-scale enterprises another point that has to be taken into consideration is the fact that for the law-maker it may be difficult to detect these enterprises and control the pollution caused by them.

Taking all these problems and constraints into consideration, the concept of "Pollution Prevention" seems to be a rather promising concept to lower and control the pollution caused by small and medium size enterprises. Changing the way of thinking and overcoming the barriers is the main job of our generation.

3.5 Opportunities of Prevention, Recycling & Reuse and Treatment

In this section, a brief overview of the opportunities of prevention, recycling & reuse and finally treatment of tannery effluents and tannery wastes is given.

The tanning process is split into the individual process steps. For each unit operation, possibilities that have been investigated and are reported in literature are listed. Primary as well as secondary literature was revised and is mentioned. Especially the UNIDO provides some excellent secondary literature dealing with a proper waste management at tanneries. See for instance M.ALOY [17], J.LUDVIK [32] and D.WINTERS [38]. For practical application the overviews of several opportunities given in secondary literature is often more useful than an in-depth discussion of a single measure.

The list given in Table 1 is not complete. Further possibilities may be found as well as further literature. However, the most important and most frequent applied measures are mentioned.

It was abstained to make an evaluation of the advantages and disadvantages of the respective measurement and to give recommendations. The tanning process is a rather complex process with a lot of parameters interacting. This means that evaluations as well as recommendations are not universally valid, but have to be made for each individual tannery.

The list given in Table 1 may help tanners in gaining an overview about the existing possibilities and assist them in finding adequate literature.

Table 1   Opportunities of Prevention, Recycling & Reuse and Treatment

	Prevention	Recycling/Reuse	Treatment
Storage	▪ Green hide processing – Chilling [67] [70] ▪ Decreasing salt load by adding antiseptics [67] ▪ Substitution of salt [79] [80] [81]	▪ Shaking off by mechanical agitation [16] [67] [72] [78]	
Soaking	▪ Green hide processing – Chilling [67] ▪ Decreasing salt load by adding antiseptics [67] ▪ Shaking off in drums [67] ▪ Drums instead of paddles [56]	▪ Counter-current rinsing and washing [38]	▪ Primary and secondary treatment [38] ▪ Membrane Technology [71]
Unhairing Liming	▪ Hair immunisation [3] [16] [56] [46][49] [78] ▪ Enzymatic unhairing [38] [56] [46]	▪ Recycling of spent unhairing/liming float [38] [41] [55] [56] [67] [73] ▪ Production of NaHS [38] ▪ Ultrafiltration [38]	▪ Catalytic oxidation [38] [50] ▪ Precipitation with ferric salts [38]
Fleshing	▪ Green fleshing [3] [15] [16]		▪ Anaerobic Treatment [36] ▪ Tallow and Protein Meal Production [15]
Splitting	▪ Lime splitting [58] [67]		
Deliming Bating	▪ Substitution of ammonia [3] [32] [58] [82] ▪ Carbon dioxide deliming [16] [22] [58] [67]		▪ Primary and secondary treatment [38] ▪ Membrane Technology [71]

BEAMHOUSE

to tanyard

	Prevention	Recycling/Reuse	Treatment
Pickling Tanning	▪ High chromium exhausting additives [16] [32] [35] [38] [39] [58] [67] ▪ Law salt pickling floats [67] ▪ Chromium free tanning [38] [58] [67] [77] ▪ Optimisation of Process Parameters [35]	▪ Direct reuse of spent tanning float in subsequent cycles [15] [24] [35] [38] [39] [41] [43] [58] [67] [69] [76] ▪ Membrane Technology [71] ▪ Reuse of spent tanning float in subsequent pickling cycle [32] [38] [56] [73] ▪ Reuse of spent tanning float in subsequent retanning cycles [75] ▪ Reuse in subsequent pretanning, pickling and tanning cycle [32] ▪ Recovery of chromium by precipitation and redisolution [32] ▪ Recycling of pickling float [72] ▪ Precipitation, Incineration and Recycling [51]	▪ Chrome precipitation [35] [38] [39] [43] [45] [58] [67] [69] ▪ Dual Cell Electrolyses [75]
Sammying	▪ see tanning	▪ see tanning	
Splitting	▪ Lime slitting [3] ▪ Parameter optimisation [15]		▪ Detanning – chromium salts and hydrolysed collagen [74] ▪ Incineration [43]
Shaving	▪ Parameter optimisation [15]		▪ Detanning – chromium salts and hydrolysed collagen [74] ▪ Incineration [15] [43] ▪ LEFA production [15]

TANYARD

	Prevention	Recycling/Reuse	Treatment
from tanyard **RETANNING**	• Replacing nitrogenous compounds [32] • High exhaustion retanning, dyeing and fatliquoring [32]	• Chrome fixing in neutralisation [32]	• Chrome precipitation [32] • Separation of leather fibres and buffing dust [32]
FINISHING	• Substitution of solvent based finisher [3] [32] • Substitution of heavy metals containing pigments [32] • Improving equipment [32] [58]		
Water Savings	• Batch versus running water washes [38] • Low float techniques [38]	• Direct Reuse of waters to less critical processes [38] • Recycling of purified waste waters [73]	• Primary and secondary treatment [38] • Membrane Technology [71]

4 Modelling of the Tanning Process: EILT – model

<div align="right">

„Ich hängte die Lampe wieder an ihren Platz und
beobachtete Sorbas bei der Arbeit. Er gab sich ihr völlig
hin, hatte nichts anderes im Sinne, und wurde eins mit
der Erde, der Spitzhacke und der Kohle."

Alexis Sorbas

</div>

4.1 Introduction

Members of the INCO-DC EILT working groups investigated the input and output data of 6 different tanneries. The processes of the analysed tanneries in combination with the resource consumption figures and the figures of generated waste water and solid waste, are the base for the EILT-model. The EILT-model is the model of a small or medium scaled chromium tanning tannery (SME) located in a developing country that processes bovine hides. Resource consumption (fresh water and chemicals) is quantified for each process step. Furthermore the quantities of waste water and solid waste, that are generated by each process step, will be identified.

In a discussion of the input and output figures, a proper segregation of individual waste streams is be proposed. Streams of concern are defined. Streams of concern are streams, on which the main efforts of prevention, recycling or treatment should be concentrated (see 3.2.4). Criteria to consider a stream as a stream of concern or not, are the quantity and/or the main pollutant of the respective stream.

For the identified streams of concern, suggestions on how to prevent, recycle or treat them are made.

Data presented in this chapter can assist to the assessment of an individual tannery, but can never substitute it. A quantification of the respective input and output data has to be made. Furthermore, the prevention, recycling and treatment opportunities have to be evaluated for each individual case.

However, what can be done by this work, is to arrange the order of magnitudes, to identify streams that are streams of concern at most tanneries and to make suggestions about measures that are considered to be the most practicable ones.

4.2 Methodology and Data

The data the EILT model is based on, was collected at 6 different tanneries (see Table 2). Four tanneries are located in Chile, 1 in Spain and 1 in Ecuador. Two of the input/output analyses were carried out by the author (MUL). Four input/output analyses were carried out by the partners of the INCO-DC project. The tanneries were chosen due to their geographical location in the neighbourhood of the partner universities of the INCO-DC project. Looking at the resource consumption, the Spanish tannery is comparable to the tanneries located in South America. The only difference can be seen in the fact, that due to the legal situation, the Spanish tannery is forced to treat effluents and solid waste. The solid waste and the waste water generated at the tanneries located in South America, generally spoken, are discharged without further treatment.

Table 2   Acronyms of Universities and Corresponding Tanneries

tannery	country	date of I/O-A	University acronym	name
A	Chile	Feb – Apr 1999	**MUL**	Montanuniversität Leoben
B	Chile	Apr – May 1999	**MUL**	Montanuniversität Leoben
C	Spain	May – June 1999	**UdSC**	Universidad Santiago de Compostela
D	Ecuador	Nov 1999 – Sept 2000	**EPN**	Escuela Politécnica Nacional
E	Chile	March – Sept 2000	**UFRO**	Universidad de la Frontera
F	Chile	January – April 2001	**UdC**	Universidad de Concepción

After drawing up a process flow sheet of the respective tannery, the input and output data of the unit operations were collected. The input and output data was determined by purchasing records, formulas and direct measurement. In principle, 3 batches from each tannery were investigated and the average of the respective figures computed. When required the analyses were repeated for some figures that did not fit into the balance.
Extensive analyses of the main effluent parameters were carried out for tannery A and E.

The averaged numbers for each tannery are shown in Table 3. Basing on the process flow sheets of the 6 tanneries, a general flow sheet was drawn-up. Two main differences must be stated. Firstly, tannery A and C work with paddle technology in the beamhouse and tannery B,D,E and F carry out their beamhouse operations in drums.
Secondly, tannery A, D and F split the hides in the beamhouse, whereas tannery B,C and E perform splitting in the tanyard.
These two differences have a significant influence on the water consumption, generation of effluents and the generation of solid wastes.

According to the different process flow sheets, averages of the respective figures were calculated. Figures that were too high or too low were crossed out. However, averaging the given figures is not that easy. The standard deviation has to be expected to be between 20 and 30%. By computing minimum and maximum figures, the inaccuracy can be reduced somewhat.

**Table 3**   **Input / Output Data of the Investigated Tanneries**

	Water consumption [m³/t_wsH]						Chemical Consumption [kg/t_wsH]						Waste Water Generation [m³/t_wsH]						Solid Waste Production [kg/t_wsH]					
Tannery	A	B	C	D	E	F	A	B	C	D	E	F	A	B	C	D	E	F	A	B	C	D	E	F
Beamhouse	**21.5**	**17.4**	**28.2**	**17**	**16.9**	**13.3**	**57.1**	**93.9**	**129.6**	**38.8**	**88.4**	**88.8**	**21.2**	**16.9**	**28.2**	**16.5**	**16**	**12.9**	**545**	**396**	**200**	**310**	**219**	**618**
Soaking	9.9	6.6	8	3.9	4.4	5.5	3	10	23.8	0.15	7	9.2	9.3	6.6	8	3.6	3.2	5.1	-	-	-	-	-	-
Unhairing / Liming	6.6	4.4	16	7.7	6.1	2.7	41.5	50.4	80	30.5	54	61.5	6.6	3.8	16	7.5	6.8	2.7	-	179	-	66.7	-	180
Fleshing	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	432*	217	200	243	219	438**
Splitting	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	113	-	-	-	-	-
Deliming / Bating	5	6.4	4.2	5.4	6.4	5.1	12.6	33.5	25.8	8.2	27.4	18.1	5.3	6.5	4.2	5.4	6	5.1	-	-	-	-	-	-
Tanyard	**0.6**	**3.1**	**15.5**	**0.48**	**0.45**	**1.8**	**205.9**	**202.4**	**91.9**	**41.7**	**147.8**	**158.5**	**1.0**	**3.5**	**15.7**	**0.72**	**1.1**	**2.0**	**120**	**276**	**35**	**195**	**54**	**80**
Pickling / Tanning	0.6	3.1	15.5	0.48	0.45	1.8	205.9	202.4	91.9	41.7	147.8	158.5	0.8	3.2	15.5	0.55	1.0	1.8	-	-	-	18	-	-
Sammying	-	-	-	-	-	-	-	-	-	-	-	-	0.2	0.3	0.2	0.17	0.1	0.2	-	-	-	-	-	-
Shaving	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	112	114	35	155	17	80
Others	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	8	162	-	22	37	-
Retanning	**13.7**	**9.3**	**2.85**	**2.1**	**5.45**	**5.6**	**191**	**160**	**140**	**78.3**	**103.8**	**152.2**	**13.7**	**9.4**	**2.85**	**2.1**	**5.4**	**5.7**	**-**	**-**	**-**	**-**	**-**	**-**
Finishing	**0.2**	**-**	**0.5**	**n.a.**	**n.a.**	**n.a.**	**43.3**	**58**	**2.5**	**95.1**	**n.a.**	**n.a.**	**-**	**-**	**0.5**	**n.a.**	**n.a.**	**n.a.**	**1**	**n.a.**	**18**	**3.3**	**n.a.**	**n.a.**
Others	**21**	**29.1**	**25.5**	**n.a.**	**n.a.**	**n.a.**	**-**	**-**	**-**	**-**	**-**	**-**	**19.2**	**23.7**	**25.5**	**n.a.**	**n.a.**	**n.a.**	**-**	**50**	**n.a.**	**n.a.**	**n.a.**	**n.a.**
Boiler Feed Water	4	5.4	n.a.	n.a.	n.a.	n.a.	-	-	-	-	-	-	-	-	-	n.a.	n.a.	n.a.	-	-	-	-	-	-
Plant Wash Down	12	10	7	n.a.	n.a.	n.a.	-	-	-	-	-	-	12	10	7	n.a.	n.a.	n.a.	-	-	-	-	-	-
Machine Water	7.2	23.7	18.5	n.a.	n.a.	n.a.	-	-	-	-	-	-	7.2	23.7	18.5	n.a.	n.a.	n.a.	-	-	-	-	-	-
Global	**59.2**	**58.9**	**72.5**	**19.6**	**22.8**	**20.7**	**497.3**	**514.3**	**364**	**253.9**	**340**	**399.5**	**55.1**	**53.4**	**72.3**	**19.3**	**18.6**	**20.6**	**666**	**672**	**253**	**310**	**273**	**618**

*   Fleshings and Trimmings
**   Fleshings, Trimmings and unused Spilt

4.3 Process Flow Sheet

For this model, the tanning process was split into 5 sections. These sections are described briefly below. For more details on the process of leather production see chapter 2.
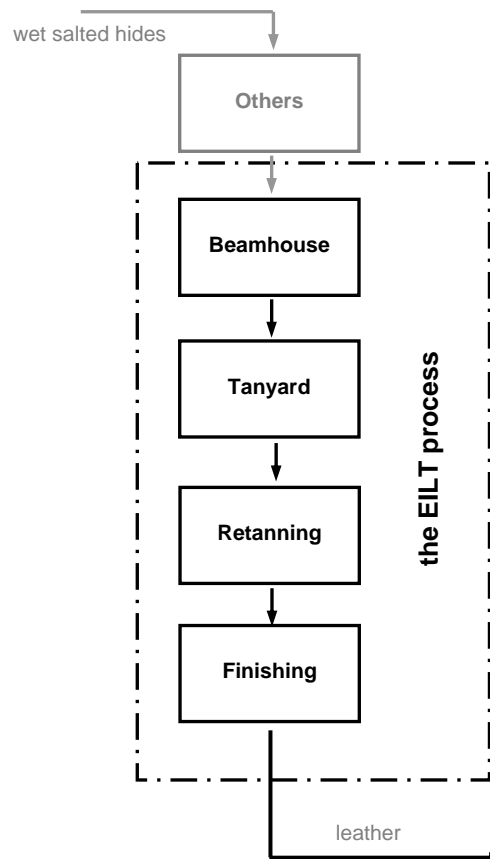
Figure 4   Generalised Flowsheet of the Tanning Process (EILT – model)

In Figure 4 the generalised flowsheet of a tanning process is shown. The 5 sections are:

- **Beamhouse**   Preparation of hides for tanning.
- **Tanning**   The transformation of pelts to wet blue.
- **Retanning**   Further tanning and determination of the leather characteristics.
- **Finishing**   Finalisation of the leather.
- **Others**   All material streams that can no be directly assigned to one of the other 4 sections.

A further section (**dressing**) may be mentioned. In this section the leather is treated mechanically in order to improve the handling properties of the final product.

Generally no resources (water, chemicals) are consumed and no wastes (solid wastes and effluents) are generated. Therefore this section is neglected in this presentation of the material streams.

The unit operations and material streams of the sections **retanning** and **finishing** depend on the product and can vary significantly even in one and the same tannery. Hence, these sections were not further split into single process units. Only overall input and output data is given for these sections.

Several material streams can not be assigned directly to one of the sections. These are for instant plant wash down water, machine water, spent salt. These streams can be found in the section "others".

The section "**beamhouse**" is further split to the single process units. In Figure 5 the schematic flowsheet is presented.
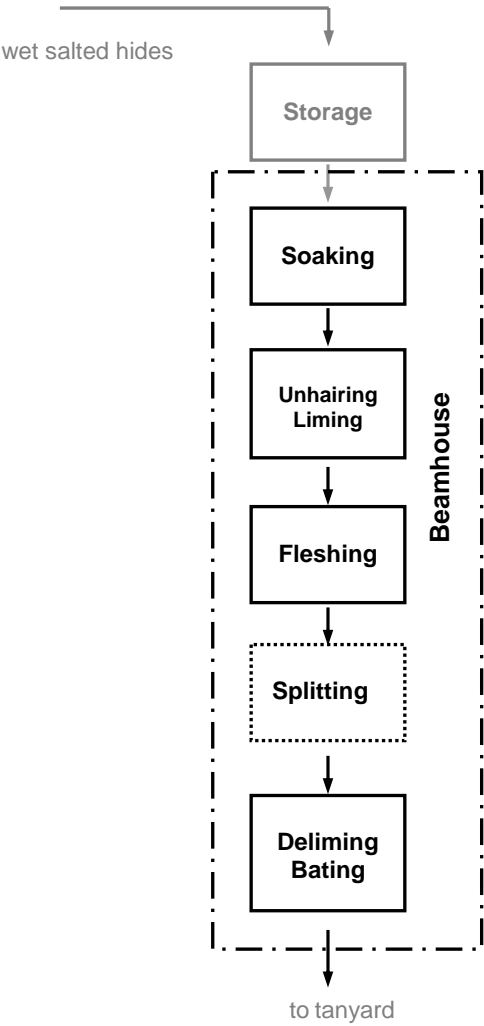
Figure 5   Schematic Flowsheet of Beamhouse Operations

The individual process units of the beamhouse section are described in chapter 2. In this place only two interesting facts should be discussed.

First, beamhouse operations can be carried out in paddles or in drums. The water consumption of latter is significantly lower than of the first one. Two (tannery A and C) of the six investigated tanneries work with paddle technology. Their water consumption in the beamhouse section is approximately 40% higher than the beamhouse water consumption of the other four tanneries.

Second, splitting can either be performed in the pelt stage or in the wet blue stage. 3 tanneries (tannery B, C and E) split the wet blue, 3 tanneries (tannery A, D and F) perform splitting in the pelt stage of the hides. Significant differences in quantity of the different solid waste fractions (chromium and non-chromium containing) are the consequence of this change in the beamhouse operations.
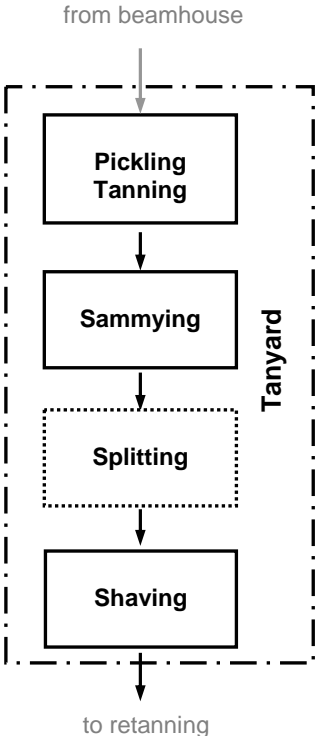
Figure 6   Schematic Flowsheet of Tanyard Operations

The unit operations of the section "tanyard" are shown in the flowsheet in Figure 6. Tanyard operations are generally performed in drums. The only difference between the tanneries is whether splitting is carried out in the beamhouse or in the tanyard section.

4.4 Material Balance

The tanning process is characterised by an excessive consumption of fresh water. In Figure 7, the global water consumption of the tanning process is shown. The figures are given in m³ water per ton of wet salted hide input.

Between 45 and 70 m³/t_{wsH} are consumed. Whether the actual consumption is in the lower or in the upper range, mainly depends on the beamhouse equipment.

In principle, one can distinguish between **process water** and **technical water**. Process water refers to water that is consumed in one of the unit operations and comes in direct contact with the product. 45 – 50% of the global water consumption is process water. Approximately 35% are consumed in the beamhouse, 1 to 5% in the tanyard, and 9 to 11% in the retanning section. The finishing section can be disregarded as a water consumer. The balance is non-process related water (technical water). This part is frequently disregarded when talking about the water consumption at tanneries.

Water Consumption of the Tanning Process
[m³/t_{wsH}]

	beamhouse	tanyard	retanning	finishing	others	total
min [m³/twsH]	15,7	0,5	5	0,3	25	46,5
max [m³/twsH]	25,4	3	6	0,3	35	69,7
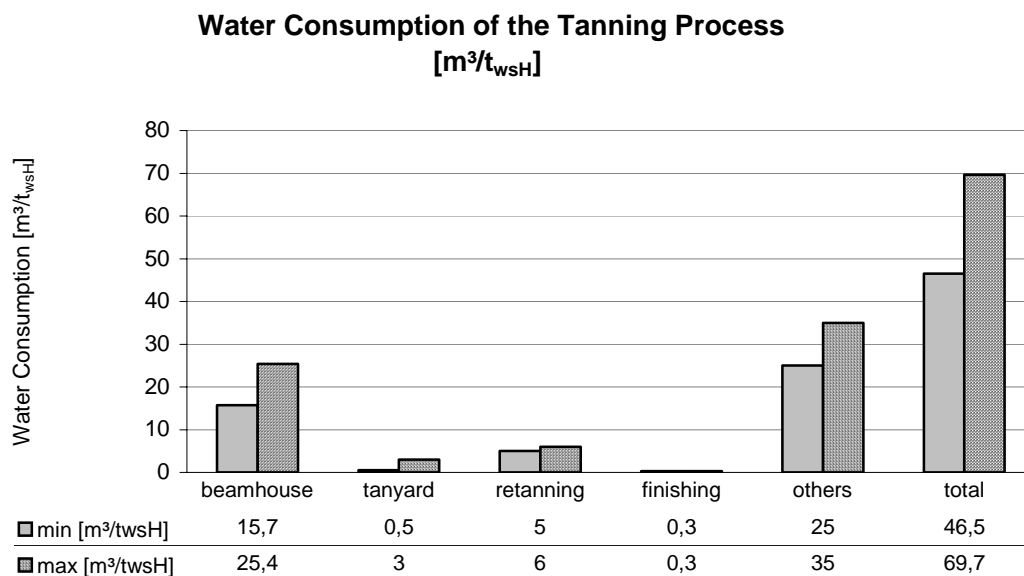
(comma is used as fraction mark)

Figure 7   Global Water Consumption of the Tanning Process

The quantity of effluent that is generated at a tannery is related to the water input. In Figure 8 the global quantity of effluents that are generated at a tannery are shown. The figures are specific figures given in m³ effluent per ton of wet salted hide.

(comma is used as fraction mark)
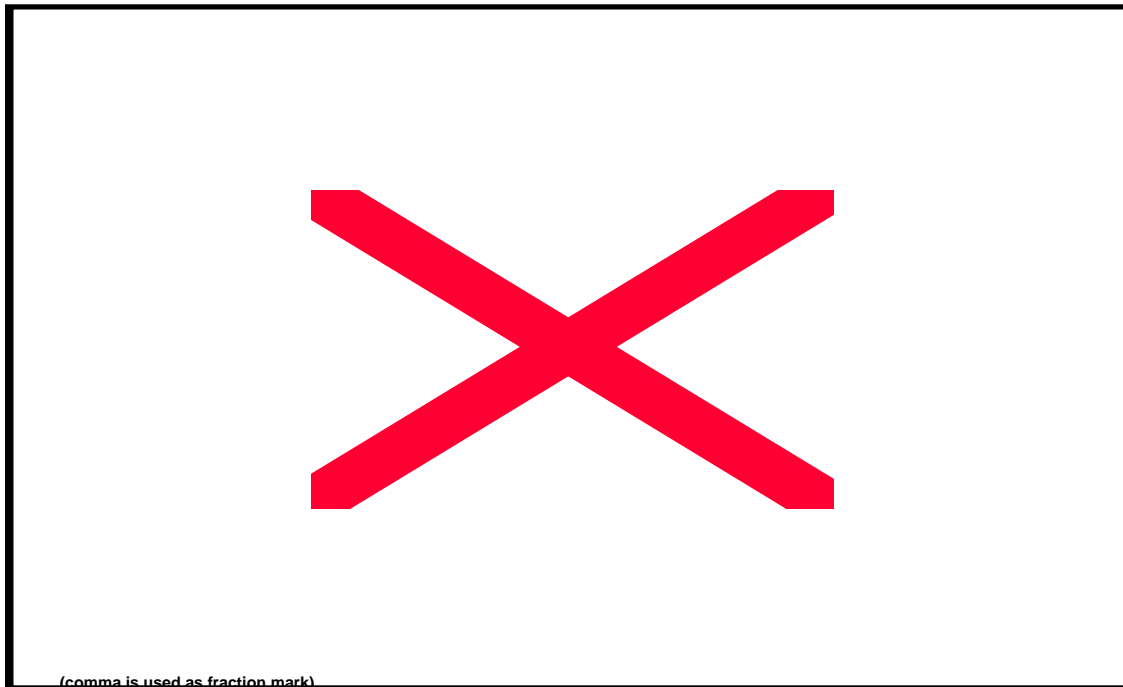
Figure 8   **Global Water Consumption of the Tanning Process**

Between 40 and 65 m³/t_{wsH} effluent is generated. In
Figure **8** the effluent streams are listed according to their origin and not according to their pollution load. A suggestion about a proper segregation will be made in the section 4.5.
Approximately 37% of the global waste water are beamhouse effluents, 2 to 5% effluents from the tanyard and 9 to 12 % are generated in the section retanning. 45 to 50% are technical, non-process related effluent. Since, in general, this water is low polluted, it is of high importance and interest when talking about closing recycling loops at a tannery.

In Table 4 the loads of the main effluent parameters that are discharged with the global tannery effluent, are shown. The figures are results from analyses obtained by members of the INCO-DC EILT working group C.BORNHARDT [30] and B.BICHLER [31]. Comments on the figures can be found in the sections of the individual effluent streams.

Table 4   Loads of Main Effluent Parameters Generated by the Tanning Process

Parameter [kg/t$_{wsH}$]	Analyses
COD	123
BOD	27
COD/BOD	4.5
Cl-	143
SO_4^{2-}	74
TKN	19
NH_3-N	5
Oil & Fat	12
Total Solids	474
Suspended Solids	53
Chromium	5
Calcium	3

To convert 1 ton of wet salted hide into leather, approximately 425 kg chemicals are required. Main chemical consumers are the retanning section (35% of global chemical consumption) and tanyard (33% of global chemical consumption). In the beamhouse approximately 19% is required. The rest of 13% is consumed in the finishing section.

(comma is used as fraction mark)
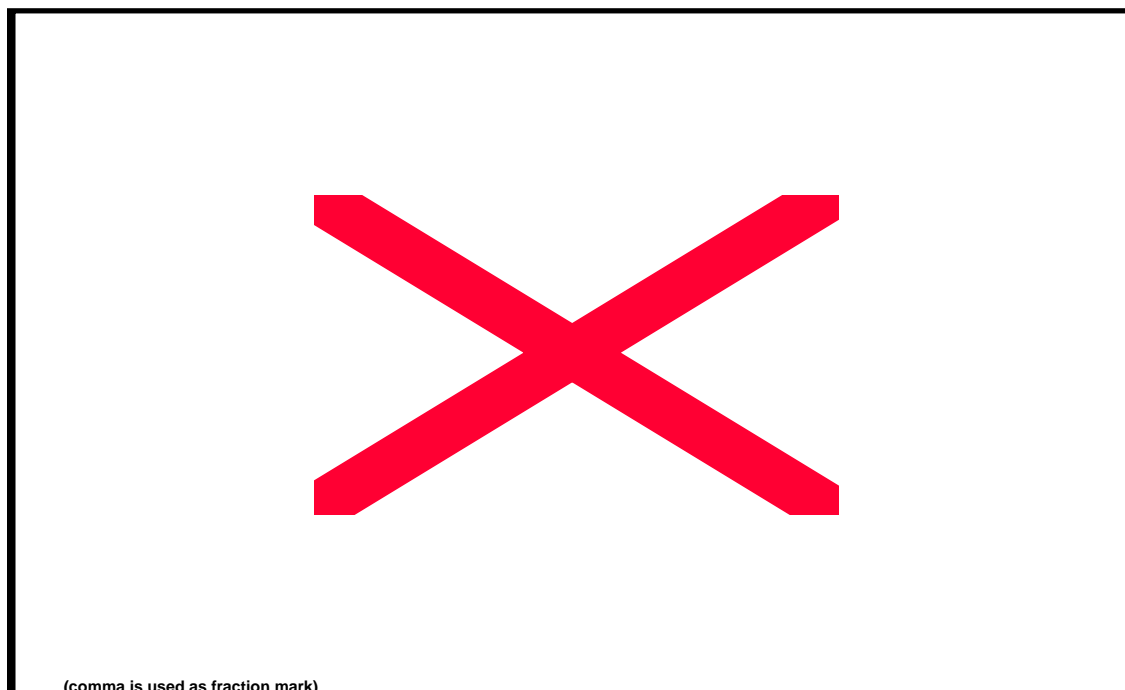
Figure 9   Global Chemical Consumption by the Tanning Process

The tanning process is characterised by the generation of a vast quantity of solid wastes. Depending on the combination of the process units (splitting in beamhouse or in the tanyard) different quantities are produced.

In principle, one can distinguish between the fraction or the place of origin. For the different fractions and a suitable segregation see section 4.5.

In Figure 10, the quantities of solid wastes are given according to their place of origin. The global solid waste generation is between 419 and 767 kg/t_{wsH}. The main part is generated in the beamhouse (approximately 75 to 80%). Between 11 and 17% are generated in the tanyard. The amount of buffing dust that is produced in the fishing section can be neglected. Finally, between 6 and 12% are spent salt from the storage facilities. Since the storage facilities are not related to the process, this type of waste is frequently disregarded.

(comma is used as fraction mark)
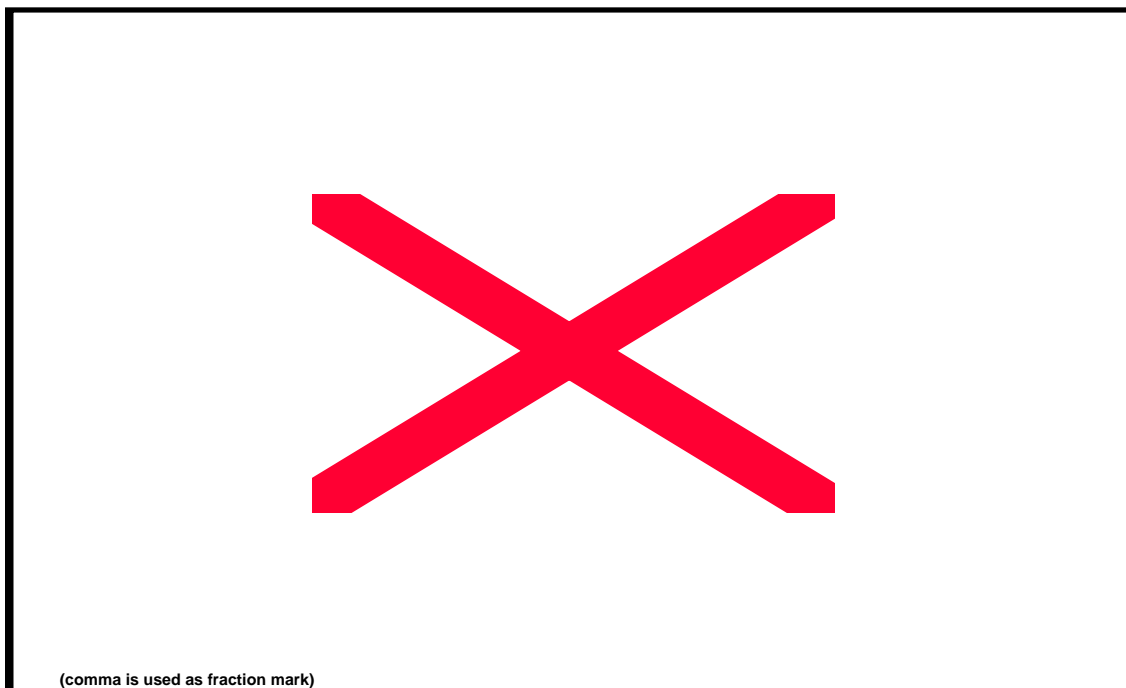
Figure 10   Global Solid Waste Generated by the Tanning Process

4.4.1   Beamhouse

In Figure 11 the consumption of fresh water in the section "beamhouse" is shown. Beamhouse operations can be performed with paddle or drum technology. Depending on the type of equipment, the water consumption varies significantly. The maximum values given in Figure 11 refer to a tannery equipped with paddles, the minimum values refer to a tannery working with drums. The deliming/bating step is generally performed in the tanning drum. Therefore no distinction between maximum and minimum consumption can be made.

Fresh Water Consumption in the Beamhouse Section
[m³/t$_{wsH}$]

	soaking	unhairing/liming	deliming/bating	total
☐ min [m³/twsH]	5,1	5,2	5,4	15,7
▨ max [m³/twsH]	9	11	5,4	25,4

(comma is used as fraction mark)
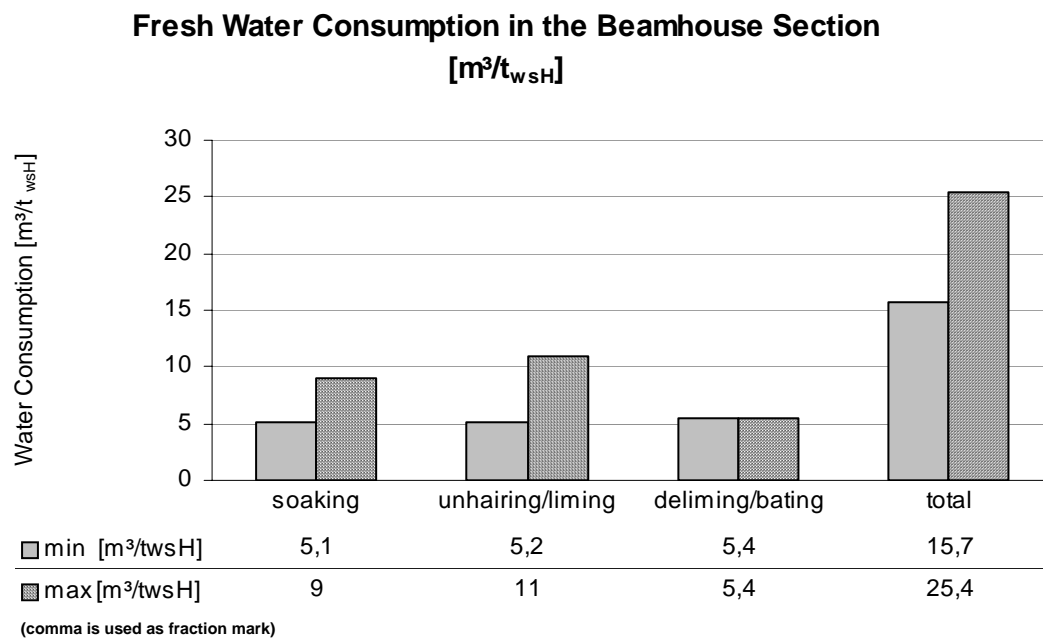
Figure 11   Water Consumption in the Section Beamhouse [m³/t$_{wsH}$]

The total quantity of fresh water that is consumed in the beamhouse is between 15.7 and 25.4 m³/t$_{wsH}$. This is 35% of the global water consumption.

The quantity of effluent that is generated in the beamhouse section corresponds to the quantity of fresh water that is consumed. Therefore the quantity of effluent is not shown in a diagram. Slight differences may be found in the section soaking, where 0.5 to 1.1 m³/t$_{wsH}$ are absorbed by the hides or spilled when the hides are discharged.

The total quantity of beamhouse effluent that can be expected is between 15.2 and 24.3 m³/t$_{wsH}$.

In the beamhouse section some of the most polluted effluents are generated. In table 4 the loads of the main effluent parameters are presented. The ranges are data that are taken from literature (J.LUDVIK [32]). The analyses are analyses carried out by members of the INCO-DC EILT working group (C.BORNHARDT et al [30], B.BICHLER [31])

Table 5   **Loads of Main Effluent Parameters Generated in the Beamhouse Section**

Parameter [kg/t_{wsH}]	Range	Analyses
COD	114 – 165	116
BOD	40 – 65	22.5
COD/BOD	2 – 3	5
Cl^-	92 – 132	126
SO_2^{4-}	12 – 30	33
TKN	10 – 15	17.8
NH_3-N	3.1 – 4.6	5
Oil & Fat	-	11.7
Solids Total	-	323.4
Suspended Solids	72 – 126	49.4
Calcium	-	3.1

Parameters where average figures and analyses do not correspond, will be discussed in the following section.

In Figure 12 the consumption of chemicals in the beamhouse section is shown. All together 78.5 kg/t_{wsH} are required. No difference between paddle and drum technology could be found. Therefore, averages were computed. However, it has to be stated, that the amount of chemicals that is consumed, strongly depends on the formula of the individual tannery and may vary significantly from the consumption figures mentioned in this work.

(comma is used as fraction mark)
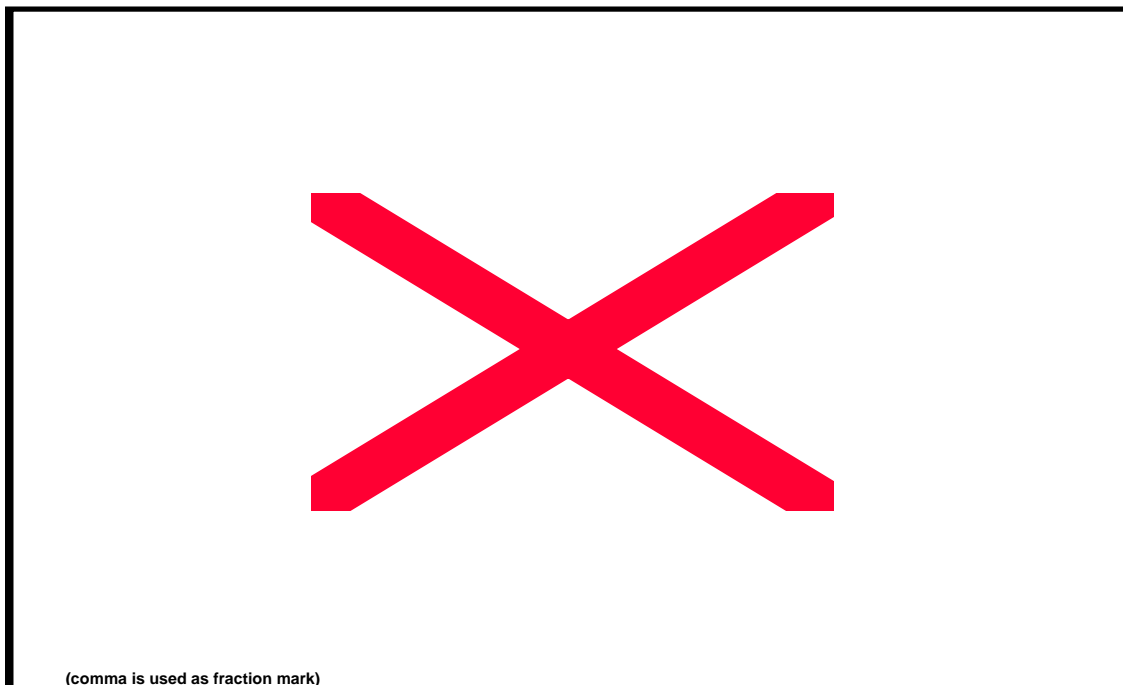
Figure 12   **Average Chemical Consumption in the Beamhouse Section [kg/t_{wsH}]**

The two main chemicals are sodium sulphide and lime (60%) for the unhairing/liming step. The remaining 40% are consumed in the soaking step and deliming/bating step.

In the beamhouse section, the main part of the global solid waste is generated (see Figure 13). Two scenarios have to be distinguished. The minimum waste scenario is a beamhouse with totally hair destroying unhairing process and without splitting. The hides are split in the wet blue stage. As a consequence, no unused split is generated in the beamhouse section and a lower amount of hair residues is separated from the effluent. The minimum quantity of waste that is generated is 322 kg/t_{wsH} (77% of the global amount of solid waste). If a partially hair destroying unhairing process is applied and the hides are split in the beamhouse, the maximum amount of solid waste will be generated. This is 585 kg/t_{wsH} or 76% of the global amount of solid waste.
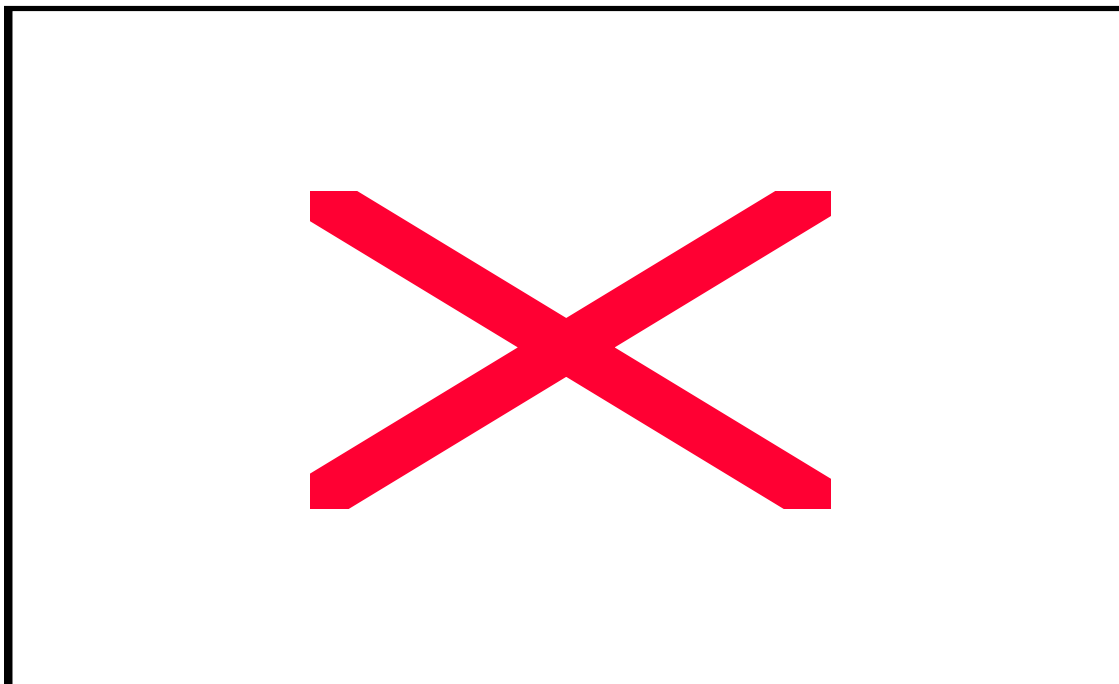
Figure 13   Solid Waste Generation in the Beamhouse Section [kg/t$_{wsH}$]

4.4.1.1   Soaking

The purpose of the soaking step is to wash and clean the wet salted hides, to wash out the salt and to re-hydrate the hides. Depending on the technology that is applied (paddle or drum), the fresh water consumption varies significantly.

The average water consumption of the 4 tanneries working with drum technology is 5.1 m³/t_{wsH}. This is 35% of the beamhouse water consumption.

Applying paddle technology results in a soaking water consumption of approximately 9 m³/t_{wsH} (average of tannery A and C). This corresponds to 37 % of the total water consumption in the beamhouse section.

The average consumption of chemicals is approximately 7 kg/t_{wsH} (approximately 9% of the total chemical consumption in the beamhouse section).This is an average and the figures of an individual tannery can vary significantly. At tannery C approximately 24 kg chemicals per ton of wet salted hides are consumed. At this tannery, soaking is already a pre-stage of unhairing (that means, alkalis are added to the soaking float). At tannery D soaking is pure washing. That means hardly any chemicals are added to the soaking float (0.15 kg/t_{wsH}). Both figures were crossed out when calculating the average chemical consumption.

The quantity of effluent that is generated during the soaking step, corresponds to the water input. It can be assumed that a certain quantity of water will be absorbed by the hides. Applying drum technology will result in 4.6 m³/t_{wsH} high polluted effluent. This is 33% of the total beamhouse effluents.
The quantity of soaking effluents that can be expected by a process working with paddles is approximately 7.9 m³/$t_{wsH.}$

The soaking step comprises of several rinsing, washing and soaking steps. The individual effluent streams are more or less polluted. In principle, talking about the soaking effluent, one refers to a mixture of these waste water streams. It can be stated, that the soaking effluent is one of the most polluted effluents that are released during the tanning process.
In Table 6 the loads of the main waste water parameters of a "typical" soaking effluent are given. The figures shown in the column "range" are taken from J. LUDVIK [32] The loads given in the column "analyses" are results obtained by the INCO-DC working group C.BORNHARDT [30].

Table 6   **Pollution Loads in Soaking Effluent**

Parameter [kg/t_{wsH}]	Range	Analyses
COD	22-23	55
BOD	7-11	11
COD/BOD	2 – 3	5
Cl$^-$	85-113	94
SO$_4^{2-}$	1-2	1.2
TKN	1 –2	3.4
NH$_3$-N	0.1-0.2	0.2
Fat&oil	-	8.6
Solids Total	-	244
Suspended Solids	11-17	18.3

The only figure that could not be confirmed is the COD load. J.LUDVIK [32] reports a range between 22 and 23 kg/t_{wsH}. The results obtained by the INCO-DC working groups are significantly higher (55 kg/t_{wsH} at tannery E and 33 kg/t_{wsH} at tannery A). A UNIDO paper [33] reports 40 kg/t_{wsH}. The differences in the COD load influences the ratio COD/BOD as well.

4.4.1.2 Unhairing/Liming

The purpose of unhairing / liming is to finish the soaking process, to destroy the hair and remove it and finally to swell the hides.

Depending on the technology, different quantities of fresh water are consumed. The average water consumption at a tannery applying drum technology is 5.2 m³/t$_{wsH}$. This is 36% of the total beamhouse consumption.

As expected, working with paddle technology will increase the water consumption of the unhairing/liming step. The average of the tanneries A and C is approximately 11 m³/t$_{wsH}$ (45% of total beamhouse effluent). However, it has to be stated that this figure may vary significantly, depending on the number of rinsing steps following unhairing/liming.

The average chemical consumption is 48 kg/t$_{wsH}$. This is the main part of the chemicals consumed in the beamhouse section (61%). The main chemicals are sodium sulphide and lime. When calculating the average chemical consumption, one figure (tannery C) was crossed out because of excessive consumption. However, the chemical consumption is the figure that is best documented at a tannery. That means that also excessive chemical consumption figures can be assumed to be correct. This shows the difficulties of modelling "the chrome tanning process".

The unhairing/liming effluent is definitively the most polluted effluent discharged by the tanning process. The quantity depends on the water input. A tannery working with drums, generated approximately 5.2 m³/t$_{wsH}$ (37% of total beamhouse effluent). A tannery applying paddle technology generated approximately 11 m³/t$_{wsH}$ (45% of total beamhouse effluent). About inaccuracies see above.

In Table 7, loads of effluent parameters are given. The figures in the column "ranges" is taken from literature [32]. The figures in column "analyses" are data from analyses made by the INCO-DC working group ([30], [31]).

Table 7   Pollution Loads of Unhairing/Liming Effluent

Parameter [kg/t$_{wsH}$]	Range	Analyses
COD	79 – 122	48
BOD	28 – 45	7.1
COD/BOD	2 – 3	6.7
Cl$^-$	5 – 15	25.8
SO$_4^{2-}$	1 – 2	0.8
S^{2-}	3.9 – 8.7	0.03
TKN	6 – 8	6.3
NH$_3$-N	0.4 – 0.5	0.3
Fat&oil	-	2.1
Solids Total	-	75
Suspended Solids	53 – 97	29.4
Calcium	-	3.1

Several figures have to be commented on. The range of the BOD_5 that is given by J.LUDVIK [32] could not be confirmed. Analyses done on tannery E and A resulted in a lower BOD load. Hence, also the ratio COD/BOD is significantly higher than the range calculated from data provided by J.LUDVIK [32].

The amount of sulphide analysed at tannery E is significantly lower that the range given in [32]. Maybe this difference can be explained by an oxidation of the sulphides in the samples from tannery E.

The total solids that can be found in the effluent are high. However, it has to be taken into consideration, that the effluents were analysed without a separation of the hair residues from the effluent stream.

Screening the unhairing/liming effluents can not be taken for granted. 3 out of the 6 tanneries that were investigated, discharge their effluents without separating. At tanneries, where this effluent stream is screened, an additional solid waste fraction is generated – the hair residues. Depending on the unhairing procedure, the amount of hair residues can vary significantly. If a completely hair destroying unhairing float is applied, approximately 65 – 70 kg/t_{wsH} solid waste can be expected (tannery D: 67 kg/t_{wsH} which is 21% of the total solid waste generated in the beamhouse section). If a partially hair destroying unhairing technique is applied, approximately 180 kg/t_{wsH} hair residues are separated by screening (31%). About the characterisation and treatment of this type of solid waste see chapter 5.

4.4.1.3 Fleshing and Splitting

The main part of the solid waste generated at a tannery are fleshings (75 – 80%). Fleshings are the part of the hides that can not be transformed into leather and therefore are removed from the swollen hides. About the characterisation of fleshings and split see chapter 5.4.

The average quantity of fleshings that are generated by the fleshing step are 220 kg/t_{wsH}. This is the average taken from 4 tanneries (tannery B, C, D and E).

If the hides are split in the pelt stage (before tanning), a certain amount of unused split will be generated. Although 3 of the investigated tanneries carry out splitting in the pelt stage, it is difficult to calculate an average quantity of unused split. Tannery A generates 113 kg/t_{wsH}. This seems to be low, particularly because the amount of fleshings and trimmings is excessive, compared to the other tanneries. Tannery D does not further process the split. That means that the total amount of split is "waste split". This can not be taken for computing an average. And finally tannery F produces 400 kg/t_{wsH} of fleshings, unused split and 38 kg of trimmings per ton of wet salted hides. From this 3 tanneries it is deduced that approximately 150 kg/t_{wsH} of unused split and 35 kg/t_{wsH} of trimmings are generated. All together in the process steps fleshing and splitting, 405 kg/t_{wsH} non-chromium containing solid waste are generated. This corresponds to 69% of the total solid waste that is generated in the beamhouse section. If splitting is carried out in the wet blue stage, the total amount of non-chromium containing solid waste in the operation steps is reduced to 255 kg/t_{wsH} (79%).

4.4.1.4   Deliming / Bating

After processing the pelts into the tanning drum, the pelts are de-limed and treated enzymatically. Approximately 23.5 kg/t_{wsH} (30% of beamhouse consumption) of chemicals are consumed. However, figures between 8 and 33 kg/t_{wsH} are reported, showing once again how difficult the calculation of average consumption figures is.

The two process steps deliming and bating are generally carried out in the same float. State of the art is the drum technology. Therefore no distinction between paddle and drum has to be made.

The average water consumption calculated by data of all 6 tanneries is 5.4 m³/t_{wsH}. These is 34% of the total beamhouse consumption or 21% when referring to paddle technology.

The quantity of waste water corresponds to the water input. 5.4 m³/t_{wsH} is a good average (36% and 22% respectively). A UNEP [6] confirms this amount, whereas a UNIIDO study [33] reports 0.5 – 1 m³/t_{wsH}. The latter can not refer to the entire deliming/bating process with all the rinsing steps, but concentrates on the deliming/bating float without rinsing steps.

Typical pollution loads of the deliming/bating effluent are given in Table 8. Ranges are taken from J.LUDVIK [32], the figures in the column "analyses" are from the work done by the INCO-DC working group. [30] [31]

Table 8   Pollutant Load of Deliming/Bating Effluent

Parameter [kg/t_{wsH}]	Range	Analyses
COD	13 – 20	13.2
BOD	5 – 9	4.4
COD/BOD	2.6 – 3.3	3
Cl^-	2 – 4	6.1
SO_4^{2-}	10 – 26	31
S^{2-}	0.2 – 0.3	0.01
TKN	3 – 5	8.1
NH_3-N	2.6 – 3.9	4.5
Fat and Oil	-	1.0
Total Solids	-	4.4
Suspended Solids	8 – 12	1.7

Once again (see section unhairing/liming), the sulphide load that were analysed by members of the INCO-DC working group is much (one order of magnitude) lower than the range given by J.LUDVIK [32].

4.4.2 Tanyard

Pickling/Tanning is the only water consuming step in the section tanyard. In Figure 14 the minimum and maximum quantities are shown. Although drum technology is the only technology that is applied in the tanyard section, consumption figures can vary significantly in the individual tanneries. As an average 1.3 m³/t_{wsH} (2-3% of global) was calculated.

(comma is used as fraction mark)
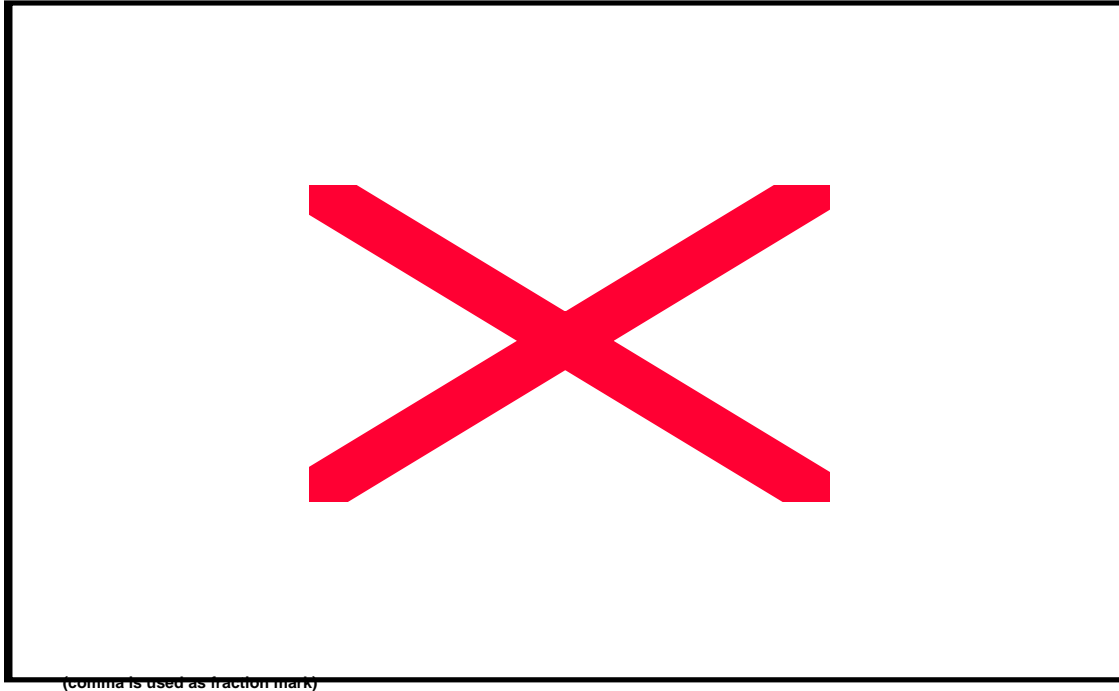
Figure 14   Minimum and Maximum Water Consumption in the Tanyard Section

The effluents generated in the beamhouse section are of high concern. The concentration of chromium may exceed 8 g/l. In general, it can be assumed that the water output exceeds the water input. However, due to the lack of proper data for this model the output was assumed to be the input plus 0.2 m³/t_{wsH} which is excess water pressed out in the sammying step.

All together this results in a total quantity of high chromium - polluted effluents of 0.7 to 3.2 m³/t_{wsH}. The average is 1.5 m³/t_{wsH}. (2-4% of global)

The loads of the main effluent parameters which can be found in the section Pickling/Tanning are shown in Table 9.

The Pickling/Tanning step is not only the only water consumer but also the only chemical consumer. The average of 140 kg/t_{wsH} are consumed in this step. Besides the retanning section, the tanyard section is one of the major chemical consumer (33% of global). The main chemicals are sodium chloride and inorganic acids for pickling purpose and chromium salts for tanning purposes.

Depending on whether splitting is carried out in the beamhouse or in the tanyard section, a different quantity of chromium - containing solid waste is generated. Splitting in the tanyard means a more uniform surface and therefore a lower amount of shavings. Unused split is

generated, but in general sold as a by-product. The average amount of chromium containing solid waste generated in the tanyard section is 45 kg/t$_{wsH}$ (11% of global).This is the minimum quantity that is generated.

If the splitting step is carried out in the beamhouse section, the amount of chromium containing shavings and trimmings will be approximately 130 kg/t$_{wsH}$ (17% of global), depending on the feedstock and the product.

4.4.2.1 Pickling / Tanning

The beamhouse operations are carried out in order to prepare the hides for tanning. The actual transformation of the perishable animal hides into leather takes place in the pickling / tanning step. This unit operation is the only water consumer in the tanyard. The average that was calculated with figures of 5 tanneries is 1.3 m³/t$_{wsH}$. This figure may vary significantly. Water consumption figures between 0.5 and 3 m³/t$_{wsH}$ are reported. Tannery C shows an excessive consumption of 15.5 m³/t$_{wsH}$ fresh water.

To determine the exact amount of fresh water consumed by the pickling/tanning step is of high importance. The quantity of effluent corresponds to the water input and is highly polluted with chromium. Approximately 1.5 m³/t$_{wsH}$ (88% of the total effluent generated in the tanyard section) of chromium bearing effluent can be expected to be generated in the pickling/tanning step.

Typical loads of main waste water parameters of the tanning effluent are shown in Table 9. The column "range" is data from literature [32], the data in the column "analyses" are analyses results obtained by the INCO-DC working group ([30], [31]).

Table 9   Pollution Loads of Pickling/Tanning Effluent

Parameter [kg/t$_{wsH}$]	Range	Analyses
COD	7 – 11	5.4
BOD	2 – 4	-
COD/BOD		-
Cl$^-$	40 – 60	11.9
SO$_4$$^{2-}$	30 – 55	22.3
S^{2-}	-	n.d.
TKN	0.6 – 0.9	0.8
NH$_3$-N	0.6 – 0.9	0.2
Solids Total	-	100
Suspended Solids	5 – 10	0.4
Chromium	2 – 5	2.8

The loads shown in the column "analyses" were calculated by multiplying the quantity of effluent with the concentration of the respective parameter. As quantity of effluent, the amount of effluent discharged by the pickling/tanning step and the sammying water was taken.

Data given in Table 9 is from tannery E effluent. BOD analyses are not available for this tannery, but are available for tannery A effluent. Approximately 9 kg/t_{wsH} BOD$_5$ were computed.

The chloride concentration seems to be low. The given range is 40 – 60 kg/t_{wsH}. In tannery E only 12 kg/t_{wsH} could be found. Assuming, that the sodium chloride that is added to the pickling float, remains in the float and is not absorbed by the pelt, a range of 40 – 60 kg/t_{wsH} seems to be more likely.

Furthermore, the load of suspended solids (0.4 kg/t_{wsH}) seems to be low compared with a range of 4 – 10 kg/t_{wsH}.

The pickling/tanning step is one of the main chemical consumer in the tanning process. Approximately 140 kg/t_{wsH} of chemicals are required. The main chemicals are NaCl and inorganic chromium(III) salts. However, depending on the formula of the respective tannery the quantity of chemicals consumed may exceed 200 kg/t_{wsH} or fall below 100 kg/t_{wsH}. It can be assumed that when splitting is carried out in the beamhouse section, the quantity of chemicals is in the lower range (see also [32]). However, this depends on the formula that is applied at the respective tannery.

4.4.2.2 Sammying

The sammying step consumes no resources. By pressing out excess water the wet blue is dried mechanically. Approximately 0.2 m³/t_{wsH} are generated. It can be assumed that this water shows the same characteristics as the effluent of the pickling/tanning step (see above).

4.4.2.3 Shaving / Splitting

Shaving of the wet blue is necessary in order to obtain a product with a uniform thickness. Depending on whether the hides were split in the beamhouse section or not, the procedure in the tanyard section is different and the amount of solid waste that is generated in the tanyard will vary.
If splitting is carried out in the beamhouse approximately 115 kg/t_{wsH} shavings can be expected. This quantity strongly depends on the quality of the feedstock (raw hides) and the product. In addition to the shavings, certain amount of trimmings are generated. Approximately 15 kg/t_{wsH} may be a good assumption.

If splitting is carried out before shaving, the quantities of solid waste will vary. Approximately 160 kg/t_{wsH} of unused split is generated. This split is generally not further processed to finished leather, but can not be called "waste" at all. Generally this split is sold as a by-product and further processed to "low quality" products.

Some shavings and trimmings are generated. The amount depends on the quality of the feedstock. An average is approximately 45 kg/t_{wsH} of shavings and trimmings. The quantity is significantly lower compared to the 130 kg/t_{wsH} that are mentioned above. This can be explained by the fact that the wet blue shows a more uniform thickness right after splitting.

Splitting in beamhouse results in a total amount of 130 kg/t_{wsH} chromium containing solid waste. Splitting in the tanyard section generates approximately 45 kg/t_{wsH} chromium containing solid waste.

In Table 10 some parameters that characterise the chromium containing solid waste "shavings" are shown ([34]). Looking at the low water content and the high chromium concentration, one can assume that the shavings are leather shavings and not wet blue shavings. Latter show a water content of 40 – 50% and a chromium oxide concentration of < 3%$_{dm}$.

Table 10   **Characterisation of Leather Shavings**

Parameter	Unit	Average
Water content	[%]	14
LOI	[%$_{dm}$]	92
TOC	[%$_{dm}$]	51
TKN	[%$_{dm}$]	13
C/N	[-]	3.9
Chromium	[%$_{dm}$]	3

4.4.2.4 Chromium Balance

Chromium is one of the key elements that is applied at a tannery. Only approximately 50% of the chromium input can be found in the product. The other 50% are discharged with the effluent. Several reasons exist, why chromium is an element of special concern.

On the one hand chromium(III) compounds are frequently confused with the toxic chromium(IV) compounds. Nowadays, at tanneries chromium(III) compounds are used exclusively. In former times, this was different. Yet, still chromium(III) is confused with chromium(IV) and (polemical) discussions concerning the environmental harm caused by tanneries exist.

On the other hand it is not completely clarified under which condition Cr(III) can be converted into C(IV) and the other way around. (For further information see Annex C)

However, fact is that chromium is a resource that should be found in the product and not in the waste streams. It is of economical interest of any tanner, to improve his chromium up-take rate.

At tannery A, the INCO-DC working group carried out chemical analyses in order to balance the chromium path of this tannery. The results are shown below.
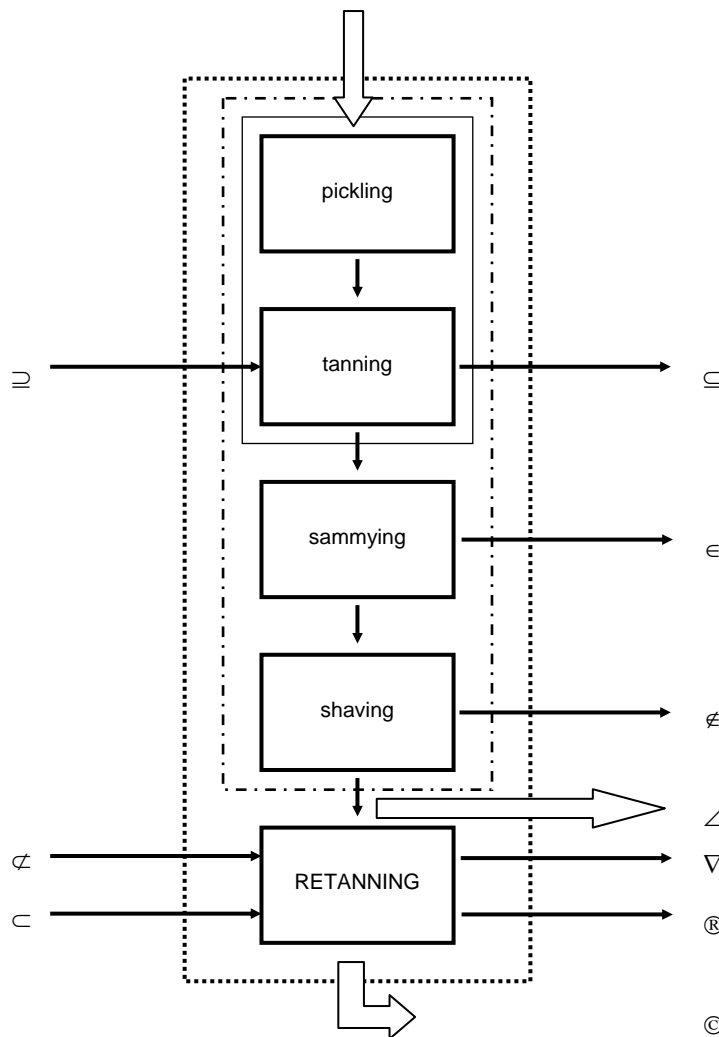
Figure 15   Schematic Flowsheet of Tannery Process Units

In Figure 15 a schematic flowsheet of the chromium sources and sinks that were identified at the tannery GACEL S.A., is presented.

The 3 main chromium input streams are named by stream 1, 2 and 3. Stream 1 is the input of chromium salts to the pickling/tanning step. Split and grain side of the hides are pickled and tanned together. After sammying, the split and the grain are separated and treated in individual batches with different formulas. Stream 2 is the input of chromium salts to the retanning step of the grain leather. And finally, stream 3 corresponds to the input of the chromium salts and the recuperated chromium to the retanning step of the split leather.

The calculations of the respective streams are shown in Table 11.

Table 11   Chromium Input to the Tanning Process at Tannery GACEL S.A.

Stream n°	Cr [kg/t_{wsH}]	Description
1	14.2	Chromium containing tanning agent. Per ton of wet salted hides 80 kg of chromium salts are used. The chromium oxide content of the product is 26%. This corresponds to a chromium input of 14.2 kg/t_{wsH}.
2	2.3	For grain leather 13 kg/t_{wsH} of chromium salt is used in the retanning section. This corresponds to 2.3 kg/t_{wsH} of chromium that is added for retanning purpose of the grain leather.
3	1	For split leather in the retanning section 0.4 kg of chrome salts are applied which corresponds to 0.07 kg/t_{wsH} Further 42.5 l of recuperated chromium are added. The chromium concentration was analysed by 22.5 g/l. The chrome input from recuperated chromium results in 0.96 kg/t_{wsH} The total chromium input for split leather is 1 kg/t_{wsH}.
input total	17.5	

Streams 4 to 10 were identified as paths through which chromium leaves the tannery. Streams 4 and 5 are effluents from the tanning and sammying step, respectively.

Streams 6 and 7 are chromium containing solid wastes (shavings) and products (industrial wet blue) that is sold in wet blue stage.

Streams 8 and 9 are effluents generated by retanning grain and split leather respectively.

And finally, stream 10 represents the chromium that leaves the tannery with the product.

The calculations of the respective streams are shown in Table 12.

Table 12   Chromium Output from the Tanning Process at Tannery GACEL S.A.

Stream n°	Cr [kg/t$_{wsH}$]	Description
4	6.2	0.77 m³/t$_{wsH}$ of effluent is discharged from the pickling/tanning step. The average chromium concentration is 8,050 mg/l (analyses of this effluent stream). This results in a total load of 6.2 kg/t$_{wsH}$ of chromium that is discharged by the effluent.
5	1.6	It is assumed that the effluent from sammying shows the same concentration as the pickling/tanning effluent [35]. The 0.2 m³/t$_{wsH}$ of sammying effluents contribute with 1.6 kg/t$_{wsH}$ to the overall chromium balance.
6	0.6	Also shavings and trimmings have to be taken into consideration when talking about chromium loss at tanneries. 120 kg/t$_{wsH}$ of shavings and trimmings with a Cr_2O_3 concentration of 1.7 %$_{dm}$ (analyses of this solid waste fraction), and a water content of approximately 55 %. This results in a total chromium load of 0.63 kg/t$_{wsH}$. Buffing dust as solid waste was neglected. Due to its low weight it has no influence on the overall chromium balance.
7	0.6	A part of the production is sold as industrial wet blue and not further processed at the tannery. The 109 [kg/t$_{wsH}$] industrial split with an average water content of 55% and a Cr_2O_3 concentration of 1.7 %$_{dm}$, corresponds to a chromium load of 0.57 kg/t$_{wsH}$
8	2.2	The effluent of the mineral retanning step contains about 1,550 mg/l of chromium (analyses of the respective effluent). With 1.4 m³/t$_{wsH}$ of effluent this results in a discharge of 2.17 kg/t$_{wsH}$ chromium.
9	0.3	206 mg/l chromium can be found in the effluent of the first neutralisation step. About 1,4 m³/t$_{wsH}$ are discharged. This results in a chromium load of 0.29 kg/t$_{wsH}$
10	6.8	Per ton wet salted hide, 253 kg grain leather and 135 kg split leather is produced. The average water content is about 15%. The average chromium oxide content on dry base is 3%$_{dm}$. All in all 6.77 kg/t$_{wsH}$ of chromium can be found in the product.
output total	**18.3**	

The global chromium input per ton of wet salted hide was computed with 17.5 kg. This figure seems to be rather reliable. On the one hand, the few input streams have an exact chromium salt input. On the other hand, the figure can be confirmed by literature ([35] for instance).

Per ton of wet salted hide 18.3 kg chromium leave the tannery. This means that the error in calculation between input and output is approximately 5%. Due to the fact that the input figure can be assumed to be correct, the error was made in the output calculations. Several inaccuracies can be found. Although the shavings and the final product were analysed in order to determine the chromium content, the results obtained of the final leather were not reliable. Hence, for these calculations, an average chromium oxide content of 3%$_{dm}$ was assumed [19].

Whether the results of 1.7%$_{dm}$ of the shavings are exact, is questionable. It is more likely, that the chromium oxide concentration of leather shavings is higher. Assuming 3%$_{dm}$ as the upper limit of the chromium concentration that can be expected, the chromium output will be 19.2 kg/t$_{wsH}$. This corresponds to an error of approximately 10% which is still in an acceptable range.

A further error may be made due to the varying water content of shavings and product. Finally, it is difficult to record all effluent streams that leave the tannery and to determine the exact concentration of chromium (rinsing for instance).

Taking all these factors into consideration, an error of 20% is an acceptable result for this balance. A further discussion of the chromium balance and distribution is given in section 4.5.

4.4.3 Retanning

During the retanning operations, the final properties of the product are determined. Depending on the type of product, the unit operations as well as the resource consumption may vary. It is not possible to calculate liable average figures for the single process units. Hence, in this thesis overall consumption figures are given. However, even such overall consumption figures are afflicted with inaccuracies.

Approximately 5 to 6 m³/t$_{wsH}$ of fresh water is consumed. Depending on the tannery, figures of up to 13.7 m³/t$_{wsH}$ are reported. But in general it can be assumed that the fresh water consumption is within the range of 5 to 6 m³/t$_{wsH}$. This corresponds to 9-11% of the global water consumption.

It can be assumed that no water up-take by the wet blue takes place in the retanning section so the quantity of effluent corresponds to the water input. The 5 to 6 m³/t$_{wsH}$ are 9-12% of the global effluent.

What must not be forgotten is the fact that most effluents released from this section are chromium bearing. Due to the low concentrations, recycling does not seem feasible.

For some parameters the effluent of the retanning section must not be neglected. This can be seen when looking at the pollutant loads shown in Table 13 ([30])

Table 13   Pollutant Load of Retanning Effluents [30]

Parameter [kg/t_{wsH}]	Average
COD	13.6
BOD	1.1
COD/BOD	12.4
Cl^-	4.9
SO_4^{2-}	19.1
S^{2-}	-
TKN	0.8
NH_3-N	0.1
Chromium	1.9
Total solids	50.5
Suspended solids	3.2

A vast variety of chemical products are used in the section retanning. Depending on the type of product, approximately 150 kg/t_{wsH} of different additives (dyes, fat liquors, tanning agents, etc...) are added. This is about 35% of the global chemical consumption. Together with the tanyard, the section retanning is a major chemical consumer at a tannery. About half of the chemicals are tanning extracts (chromium and non-chromium containing). The remaining 50% are fats, dyes, detergents and acids.

4.4.4 Finishing

Determining the resource consumption of the finishing section is difficult, even more difficult than for the retanning section. The finishing section was only investigated at two tanneries. The water consumption was low. 0.3 m³/t_{wsH} was the average figure. Compared to the other water consumers this can be neglected.
No waste water was generated. The water that was consumed, is evaporated in this section.

One of the major problems in the finishing section are the VOCs (volatile organic compounds).
In developing countries, solvent based lacquers are frequently used. Furthermore, by using old fashion equipment, a high overspray is generated. 40% overspray is an average number that is generally given in literature [32]. Determining the overspray at tannery A and B gave the following results: Tannery A showed an overspray of 60%. Tannery B's overspray was determined at 85%.

Computing an average chemical consumption is difficult. A reliable range is between 50 and 60 kg/t_{wsH} (10-15% of the global consumption). The main chemicals are binders, pigments, resins and solvents.

A minor amount of solid chromium-containing waste is generated in the buffing step. Approximately 2 kg/t_{wsH} of buffing dust has to be added to the global amount of chromium-containing solid waste.

4.4.5 Others

Most material balances concentrate only on the process itself. However, there are some figures that have to be taken into consideration.

In general, feedstock are raw salted hides. By handling these hides, spent salt is generated. The quantity was determined for tannery A. Approximately 50 kg/t_{wsH} of spent salt and trimmings are generated during the handling of the feedstock before entering the beamhouse section. This is approximately 7-12% of the global solid waste generated at tanneries, hence must it can not be neglected.

A large quantity of water is non-process related water. Three main consumer must be mentioned:

Firstly, the boiler feed water for the steam production. Approximately 5 m³/t_{wsH} of fresh water is required for steam production.

Secondly, approximately 10 m³/t_{wsH} fresh water are used as plant wash down water. Generally, tanners have no or little idea of the quantity of water that is required for washing purpose and it is quite difficult to determine this amount.

Third, major consumers are machines which require a huge amount of fresh water for a proper operation. Depending on the equipment, between 7 and 23 m³/t_{wsH} of fresh water are consumed. Major consumer are vacuum pumps, splitting machines and fleshing machines.

The actual quantity has to be determined for each individual tannery.

In this thesis 15 m³/t_{wsH} are assumed as an average. However, it has to be taken into consideration that this consumption may vary significantly from tannery to tannery.

All together 30 m³/t_{wsH} of fresh water are consumed by activities that are not directly related to the process. 30 m³/t_{wsH} are approximately 45-65% of the global water consumption and therefore have to be taken into consideration in any material balance.

It can be assumed that the 5 m³/t_{wsH} that are required for steam production, will evaporate and therefore not contribute to the generation of waste water.

That means, that from non-process related water (technical water) approximately 25 m³/t_{wsH} of low polluted effluents can be expected.

In Figure 16 the consumption of technical water (boiler feed water, plant wash down water and machine water) at a tannery is shown. Because of the difficulties in calculating an average, the amount of machine water is given within a minimum and maximum range.

Consumption of Technical Water at a Tannery
$[m^3/t_{wsH}]$

	boiler feed water	plant wash down water	machine water	total
☐ min [m³/twsH]	5	10	10	25
▨ max [m³/twsH]	5	10	20	35
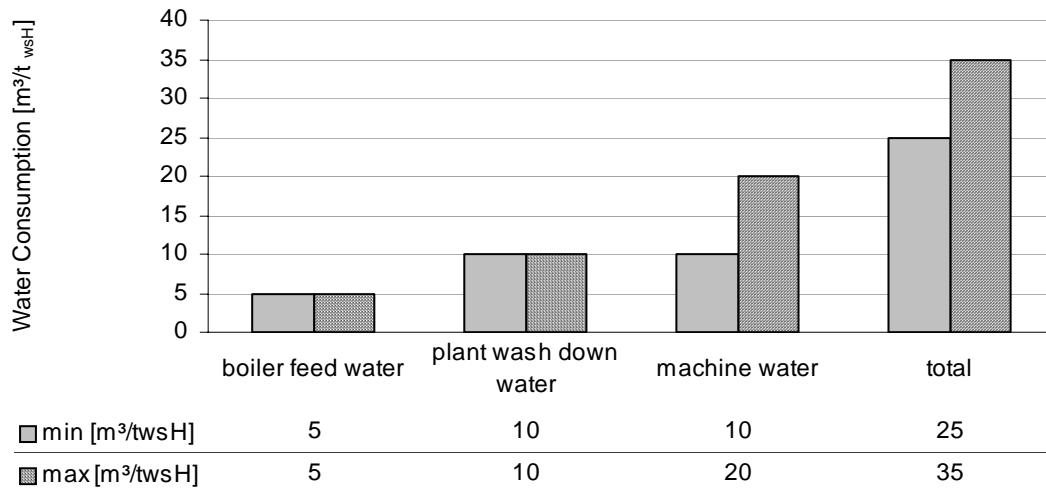
Figure 16   **Consumption of Technical Water at a Tannery**

4.5 Discussion

4.5.1 General

Developing a "universally valid, generalised" material balance of a tanning process is not a simple matter. At the most beamhouse and tanyard operations are comparable in different tanneries. However, even in these two section, depending on the feed stock (raw hides), the customs of the tanner and the equipment, the input and output figures can vary significantly. Computing average figures is difficult and standard deviations of up to 30% have to be expected.

However, by evaluating the input and output figures of several tanneries, some trends can be seen. In this thesis the dilemma of averages with a broad standard deviation is avoided by defining ranges of input and output figures. Minimum and maximum figures are defined. With this measure it was possible to split the beamhouse and tanyard section into single unit operations and to define water and chemical consumption and quantities of waste water and solid waste that are generated by this units.

It could be shown, that the equipment used in the beamhouse has significant influence on the water consumption. Carrying out soaking and unhairing/liming in paddles means an increase in the beamhouse water consumption by approximately 40%.

Obviously, this increase has significant influence on the quantity of waste water that is discharged from the beamhouse. The quantity will increase by approximately 40%, the loads however - given in kg/t_{wsH} - will remain constant.

Furthermore, it is of importance whether splitting of the hides is carried out in the beamhouse or in the tanyard. The amount of non-chromium containing solid waste is significantly lower in latter case. In addition to that, the amount of chromium containing waste can be expected to be lower. Split, that can not be further processed to leather, may be sold as low quality product. However, whether such a change in the process is feasible for the individual tannery has to be investigated from case to case.

Concerning the sections retanning and finishing it is hardly impossible to split them into single process units and to identify input and output figures. Before entering the beamhouse, the raw hides are divide into batches. In the sections beamhouse and tanyard the batches are treated together. After the shaving or splitting, the batches are split into new batches. These batches depend on the quality of the hides and the desired product. Depending on the batches, the process units and input figures of retanning and finishing section may vary in one and the same tannery. To give average input and output figures for these sections is difficult. To give averages for more than one tannery is even impossible.

Therefore in this thesis, average numbers of the total section retanning and finishing were computed. This is difficult and is afflicted with inaccuracies. However, what can be seen are trends and a percentual distribution of the input and output figures.

Further difficulties that must be mentioned, are the problems in data gathering. On the one hand in developing countries the lack of technical equipment (flow meters for instance) and the lack of proper analytical methods makes improvisation necessary. As a consequence, the accuracy of the results will suffer. On the other hand, the consciousness concerning environmental protection and sustainable usage of resources is little developed among tanners in developing countries. Only data that are of economic interest are recorded at the tannery. The support in collecting further data is small.

As a result, the input and output figures that are averaged for the EILT model are not "exact" figures, but rules of the thumb that allow tanners to estimate their resource consumption and the quantity of solid waste and waste water generated by their activity. What can be seen by this model are the order of magnitudes of the individual streams. One becomes aware of the process units that consume most resources (water and chemicals) and of the units that generate the highest quantities of solid waste and the highest polluted effluent streams. In the following discussion, the results of the previous sections are presented according to the principles of pollution prevention and a proper waste management.

4.5.2   Solid Waste

It is suggested to segregate the different solid waste fractions into 3 main groups. These groups are "**spent salt**", "**non-chromium containing waste**" and "**chromium containing waste**". In Figure 17 these 3 different solid waste streams are shown. The width of the arrows corresponds to the percentage of the respective waste stream.
Segregation of solid waste fractions at a tannery is a relatively simple matter.
In general, the fraction "spent salt" is generated by handling activities in the storage facilities. That means, it is generated at a defined location and can be collected there. The risk of cross-contamination with other solid waste fractions is low. Per ton of wet salted hide, approximately 50 kg of spent salt are generated. This corresponds to 6-12% of the global quantity of solid waste.
Additional salt can be shaken out by mechanical agitating the hides in drums. It is evident, that the quantity of solid waste will be increased by this measure. But, on the other hand, the salt fraction in the soaking effluent can be reduced by this simple measure. J.LUDVIK [32] reports a reduction of the salt load by 8 %. That means an increase of the quantity of spent salt by 7 to 9 kg/t$_{wsH}$.
It must be mentioned, that the 57 to 59 kg/t$_{wsH}$ of spent salt are not pure salt that can be reused for preservation purpose, but is highly contaminated with organic matter (dung, blood, etc...). However, tannery B uses approximately 50 kg/t$_{wsH}$ spent salt for pickling purposes (see also [67]). Bactericides are added in order to suppress bacterial growth. It can be seen that recycling spent salt in the pickling step is possible, although this procedure is not widely accepted, because the salt is considered to be "too dirty".

Salt recovery processes were developed (thermal processes), but due to the low economic value of salt, they are not applied at industrial scale [32].

The quantity of salt required for preservation purposes can be reduced by adding antiseptics (such as boric compounds, acetic acid and sodium sulphite) or bactericides. J.LUDVIK [32] reports, that the chloride load can be reduced by one half but that also the preservation efficiency will decrease.
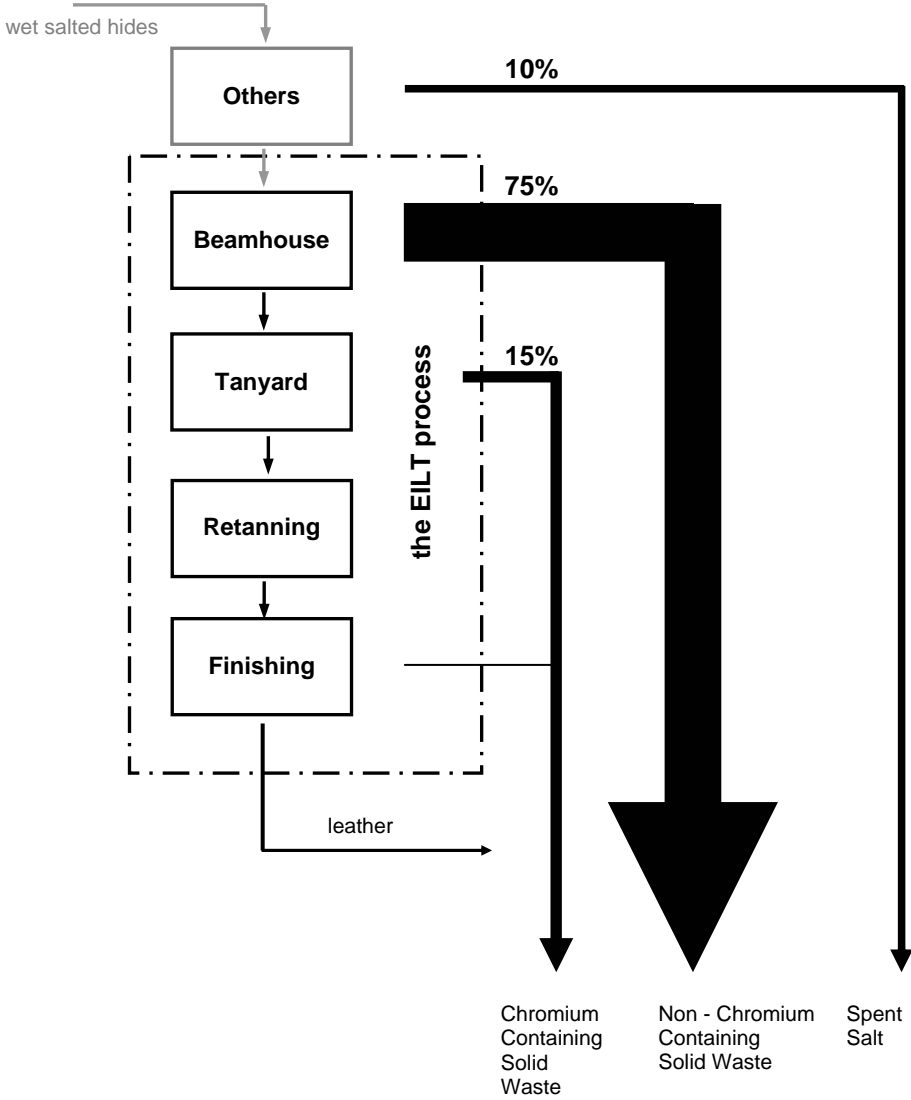

Figure 17   **Segregation of the Solid Waste Streams Generated by the Tanning Process**

According to the "philosophy" of pollution prevention, the best technology would be preservation by chilling the hides. Although, theoretically the salt load of the soaking effluent can be reduced to zero, small amounts of salt will be added to the process in order to bring some hide compounds into solution. The actual salt load of the soaking effluent can be reduced to 5 – 10 kg/t_{wsH} [32]. What will be reduced to zero is the solid waste fraction "spent salt" generated at the storage facilities. That means a reduction of the global solid waste by approximately 10%. This practice is state of the art at most tanneries in Middle Europe. However, due to the lack of infrastructure, tanners located in developing countries can not be expected to apply this technology.

The main quantity of solid waste that is generated at tanneries is **non-chromium containing waste**. 75 to 80% can be expected to correspond to this type of waste. This fraction consists of fleshings, unused split, trimmings and hair residues. To separate fleshings, unused split and trimmings is simple and cross-contamination is not likely to occur.

Separating hair residues is somewhat more difficult. Hair residues are discharged by the unhairing/liming effluent. The hair can be separated from the effluent by a screen. In practice, if a screen is available at a tannery, all effluent streams will be processed through this screen. Due to this practice, cross contamination with chromium is very likely, but has to be avoided.

By proper equipment, the generation of fleshings and trimmings can be reduced somewhat, but can never be prevented. Since the non-chromium containing fraction consists in organic matter, biological treatment seems obvious.

Due to the physical properties of the substrate, anaerobic treatment seems to be most suitable. However, M.ALOY et. al. [36] showed that this technology is feasible, but not - profitable for a tannery processing less than 40 t_{wsH} per day. Small and medium scaled tanneries (SME) located in developing countries generally process < 10 t_{wsH} per day (order of magnitude). For these enterprises, aerobic treatment of the non-chromium containing solid waste is suggested. Investigations that were carried out with this substrate are reported in chapter 5.

By treating the non-chromium containing solid waste fraction, approximately 75% of the global solid waste can be converted into a by-product.

Finally, approximately 15% of the global solid waste is chromium containing shavings, trimmings and split. When splitting is carried out in the tanyard, the quantity of chromium containing solid waste is significantly lower compared to a process, where splitting is carried out in the beamhouse. This can be explained by the fact, that unused split, that would be waste in native stage can be sold as a by product in tanned stage.

Research concerning recuperation of chromium and the production of valuable by-products from leather waste were carried out (see TOPRAK [37]). However, for tanners located at developing countries such a process seems not to be applicable. An alternative seems to be to sell chromium containing solid waste as a feedstock for LEFA production. LEFA is a leather fibre board made of leather shavings and other type of fibres. It is used in the shoe

and accessories industry. However, precondition for this solution is an existing LEFA industry. A success story can be reported from the Chilean tannery CURTAL S.A. (tannery B). They started to profitably sell their excessive quantity of wet blue waste to a LEFA production in Ecuador.

Due to the large quantity of non-chromium solid waste, main efforts must be made in a proper segregation and treatment of this fraction. Once the global waste is reduced by 75 – 80% (treatment of non-chromium containing waste fraction), one may start to work on a reduction or treatment of the remaining 20 –25%.

4.5.3   Water and Effluent Management

In Figure 18 the water streams entering and leaving a tannery are shown. The left side shows the water input into the respective sections. The strengths of the arrows represent the percentage of the global water consumption. The percentages are the averages of the minimum and maximum values given in section 4.4. One can see that the major water consumer is the section "others". Approximately 50% of the global water is consumed in this section. Main savings in water consumption can be achieved when concentrating ones efforts on this section. Second largest water consumer is the section "beamhouse". Approximately 35% of the global water input is consumed in this section.

Thus, priority should be given to measures for achieving savings in the water consumption in the section "others" or "beamhouse".

On the left side of Figure 18 the waste water streams are shown. The effluents leaving the respective process units should be segregated into 4 different waste water streams: "**Low Polluted Effluents**", "**High Polluted Effluents**", **Chromium Bearing Effluents**" and "**Sulphide Bearing Effluents**".
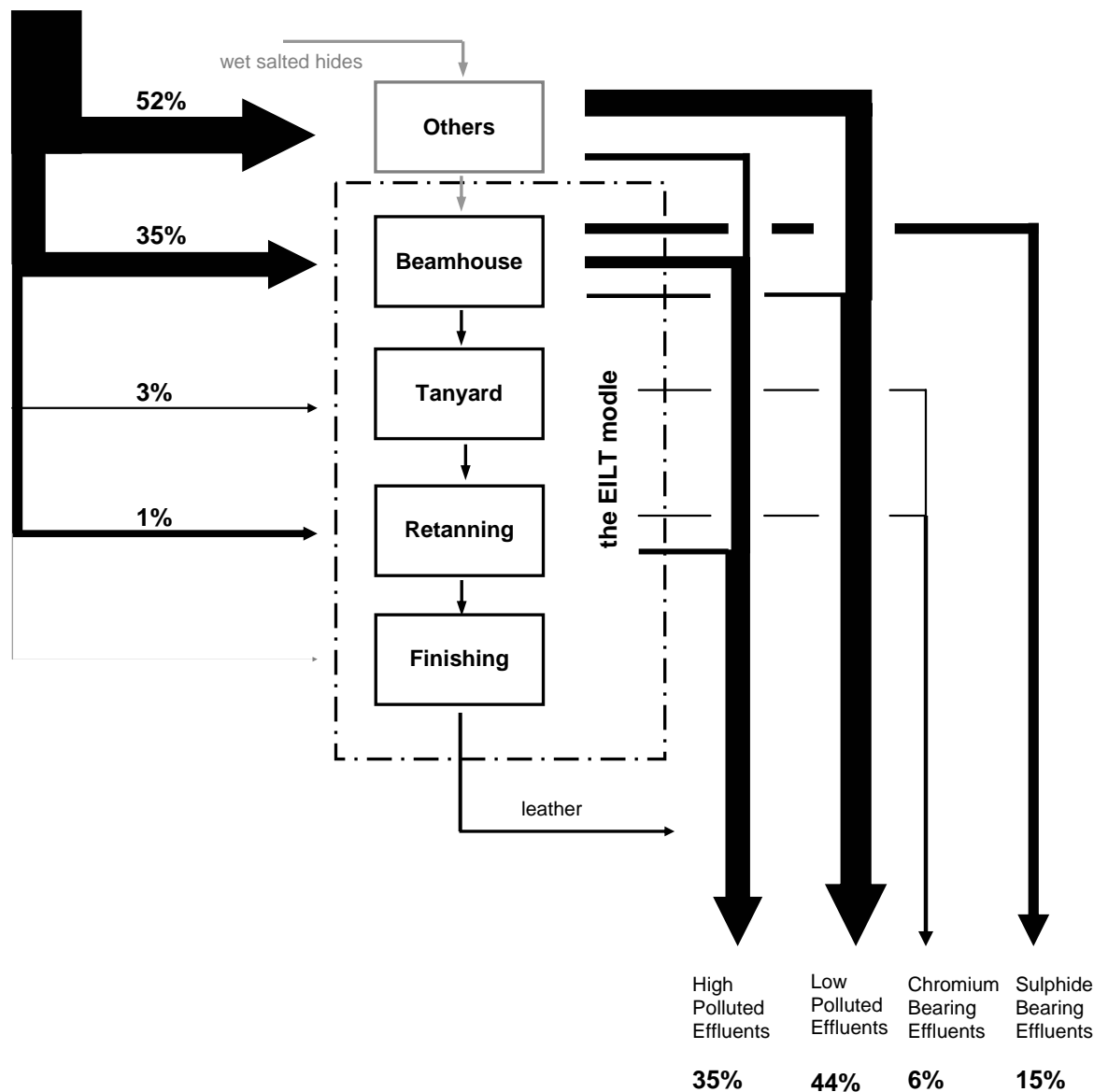
Figure 18 **Segregation of Waste Water Streams Generated by the Tanning Process**

4.5.3.1 Low Polluted Effluents

Approximately 45% of the global effluent are low polluted effluents. This is the machine water (i.e. water that is required for a proper operation of equipment). Generally, these effluents are not or slightly polluted. A direct reuse as machine water or recycling in one of the rinsing steps is possible without big efforts.

Approximately 50% of the soaking effluents is low polluted rinsing water. It could be shown by analyses made by the INCO-DC EILT working group (B.BICHLER [31]), that the majority of the pollutants are released by the actual soaking step and the washing steps. Since the rinsing steps are less polluted, one can build up a counter-current soaking operation (see D. WINTERS [38])

4.5.3.2 High Polluted Effluents

Approximately 35% of the global effluent are "high polluted effluents". These are waste water streams generated during soaking, deliming/bating and non or little chromium containing effluent streams generated in the retanning section.

In order to treat this type of effluent, primary (mechanical) and secondary (biological) treatment is indispensable. Referring to small and medium scaled tanneries (SME) located in developing countries, as a immediate measure, the primary treatment must be suggested. Biological treatment means high capital and operation costs and the implementation means long term planing.

The main problem in this type of effluent is the high chloride concentration. Loads exceeding 120 kg/t_{wsH} can be expected, which results in chloride concentrations of 5 to 10 g/l. Primary and secondary waste water treatment is ineffective in eliminating chlorides and advanced waste water treatment can generally not be expected in developing countries.

4.5.3.3 Chromium Bearing Effluents

Only 6% of the global effluent streams, but certainly a stream of concern, are the chromium bearing effluents. Besides sulphide, chromium is one of the most discussed element in the tanning industry. In Annex C, a brief overview of chromium and its compounds is given.

Various possibilities and techniques for chromium management at tanneries have been investigated and reported (see [35] [39] [40] [41] [38]).

Depending on the process approximately 40 to 50% are high chromium polluted effluents from the tanning step. The rest are low chromium polluted effluents generated by retanning operations.

The main interest of any tanner must be the highest chromium up-take rate that is possible under the given conditions. The chromium up-take rate is defined as the quantity of chromium that can be found in the leather referring to the total chromium input. In Figure 19 the results of the chromium balance computed in section 4.4.2.4 are presented.

The chromium up-take rate corresponds to the percentage of chromium that can be found in the product and in the solid waste fraction. In this case, it is approximately 44%. This is a rather bad result. On the one hand, an error may occur due to the inaccuracy of the balance. This was already discussed in section 4.4.2.4. On the other hand, at this tannery a lot of optimisation potential was identified. Hence, it is not surprising that also the process parameters of the tanning step can be improved.
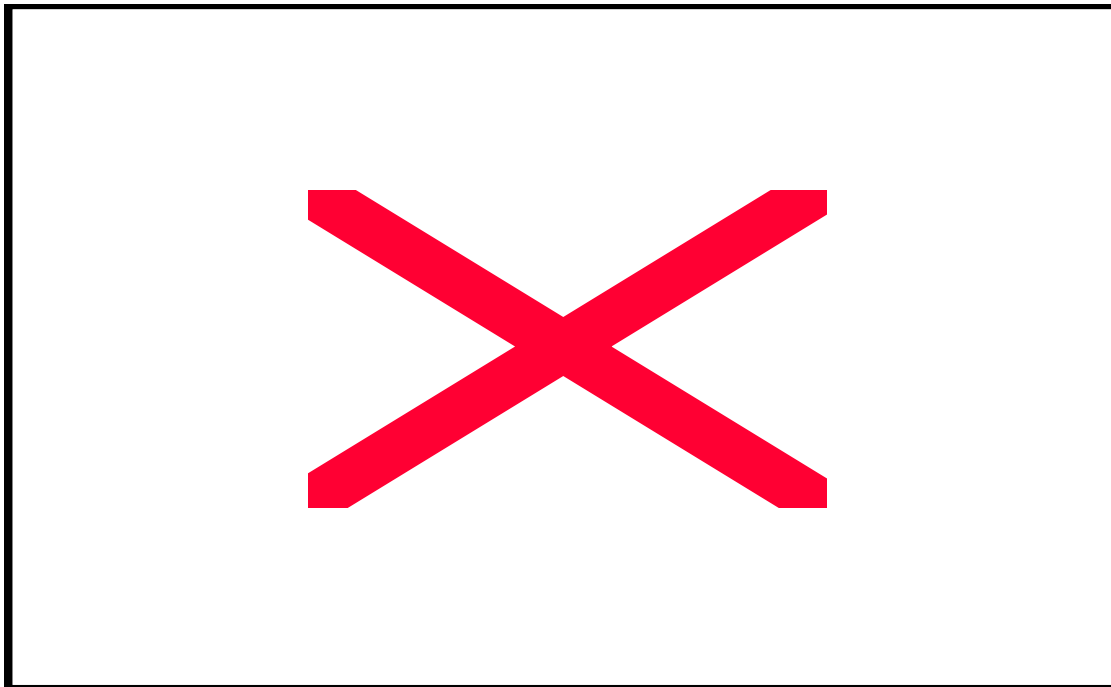
Figure 19   Percentage of Chromium Input in Product, Effluent and Solid Waste at Tannery GACEL S.A.

J.LUDVIK [35] reports, that in general, chrome uptake under typical technological conditions is of the order of 60 – 80% of the offer.

To increase the chromium up-take rate is not only a necessity from the environmental point of view, but must be of highest economic interest of any tanner. According to J.LUDVIK [35], by optimising process parameters like mechanical agitation, chrome concentration and offer, reaction time, pH and temperature, the chromium up-take rate can be increased to 80 – 90%. Recommendations that are given, are a pH between 4.0 and 4.2, float temperatures between 40 and 45°C with a slight temperature increase at the end of the tanning of the tanning step. Furthermore, a chrome offer of 1.7% combined with a high chromium concentration in the float should be provided. Finally, it is recommendable, to extend the residence time as long as possible and to use high speed drums (see [35]).

However, these are general recommendations and must be adapted to each individual case.

The chromium uptake rate may be further increased by adding high chrome exhausting additives. By optimising the parameters that are mentioned above, uptake rates of up to 95 - 98% are reported (see [35]).

Even by changing the process additives and achieving an up-take rate of >90%, in most countries the final chromium concentration in the mixed tannery effluent will exceed the discharge limits.

An alternative seems to be the direct recycling of spent tanning floats. Several possibilities of recycling schemes were proposed (see [35] [39] [38] and [43]). Common to all these

alternatives is the removal of leather fibres and other undissolved impurities by filtration and the make-up with chromium salts, prior to recycling

As to J. LUDVIK [39], direct recycling of spent tanning float when filtered shows no negative impact on the tanning process or the product quality. Problems might be caused by a volume build-up, because the pickling float is smaller than the tanning float. Furthermore the pelts contain more water than the wet blue (70 / 55%). As a consequence tanning float has to be discharged or used in the retanning step.

In an other paper, J. LUDVIK [35] reports an easily attainable recovery efficiency of 90%. By using more sophisticated collection methods - the bottleneck in most tanneries is the drainage and collection system - and with recycling techniques, an efficiency of 95 – 98% is possible. However in practise, up-take rates of <90% rather than 98% are realistic numbers.

To comply with discharge limits, for both alternatives – high chromium exhaustive additives or direct recycling of spent tanning float - further treatment of the discharged effluents is required.

This generally is done by basification and precipitation of chromium oxide sludge. By sedimentation or by a filterpress the sludge is separated from the supernatant. The overflow can be regarded as "chromium-free" and may be mixed with the remaining tannery effluents. The chromium containing sludge can either be disposed of at a landfill or re-dissolved. Latter means that by lowering the pH the chromium oxide can be converted into chromium sulphate and recycled as tanning agent. In case of a reuse of the chromium for tanning or retanning purpose, the proper basification agents are magnesium oxide, sodium hydroxide or ammonium hydroxide. As acidification agent, sulphuric acid can be used.

In case of disposal of the chromium containing sludge, the more effective calcium hydroxide may be used for basification. By adding ferric and aluminium salts, precipitation can be improved.

Comparing the alternatives of a proper chrome management gives the following picture:

Optimisation of the process parameters is a necessity for a proper chrome management at a tannery and must be the first step of any optimisation. However, by simply optimising the process parameters, discharge limits can not be kept. Further measures are required.

Each of the 3 alternatives (high-exhausting chrome tanning, direct recycling of spent float and precipitation and recycling of chromium) has advantages and disadvantages. In literature, one can find contradictory arguments about which technique is preferable. Whereas M.H.DAVIS et al [44] says the following: "It should be stressed that the method (the direct reuse) is not only useful for reducing effluent chromium concentration but has important economic and other advantages over conventional chrome tanning and even more over alternatives such as chrome precipitation/reuse or high exhaustion tanning techniques". The following words can be read in an UNIDO study "Nevertheless, recovery is considered to be the least effective of the strategies and the most effective high fixation"

The same contradictory opinions exist as to the additional costs (operation and capital). J.LUDVIK [35] writes that "costs associated with improving chrome management should be related to the particular conditions of a given tannery".

Each of the three mentioned techniques is technically feasible, yields economic advantages and lowers levels of pollution. Each tannery has to decide for itself which technique to apply. The given, particular circumstances at the respective tannery have to be taken into consideration.

An elegant solution is of course the high-exhaustion chrome tanning technique. The idea that the offered chromium should be found in the product and not in the effluent corresponds to the understanding of "Pollution Prevention". Nonetheless, chemical costs will be higher compared to the conventional tanning process. Especially the production costs for wet blue, whereas savings can be achieved in the finishing section. This means that the high exhaustion tanning alternative is economically not recommendable for a tannery that produces wet blue from wet salted hides and sells the wet blue as product [45]. The change to high chromium exhausting additives will increase the operational chemical costs by 20–36% [35]. In addition to that in some parts of the world such additives can not be purchased.

The direct recycling of the spent tanning float is the simplest alternative. Generally slight adaptation of the existing process is required. Although theoretically the recycling can be repeated indefinitely, the numbers of cycles is limited to 10 to 15 in practice [41]. S.RAJAMANI [45] even reports from only 4 - 7 cycles. The main constraints are the build-up of neutral salts and organic impurities. Furthermore a volume build-up can be observed which makes a discharge of certain quantities of chromium containing effluent necessary. Several possibilities concerning the recycling of spent floats were suggested. Tanneries have to find an individual solution.

A technology that requires little adaptation of the conventional tanning process is precipitation and reuse. Depending on the tannery and the location different types of alkali agents are of interest. For developing countries S.RAJAMANI [45] recommends precipitation with MgO with subsequent sedimentation. Besides being cost effective this process is easier to adapt then the other processes.

M.H.DAVIS et al [44] on the other hand writes "while this latter process (the precipitation & recovery) is regarded as unnecessarily costly and inconvenient for treatment of the total spent chrome liquor when it can mostly be recycled directly it may be useful for handling the relatively small volumes which cannot be recycled."

4.5.3.4 Sulphide Bearing Effluents

Approximately 15% of the global tannery waste water is sulphide bearing. Depending on the total quantity of waste water this may be between 5 and 11 m³/t_{wsH}. Sulphides are added during the unhairing/liming process. Hence, the effluents of these process steps are the main sulphide bearing effluents. Some sulphide may be found in one of the subsequent steps (deliming/bating for instance), but are of minor importance and in this thesis they are not counted as sulphide bearing effluents.

The unhairing/liming effluent is the most polluted effluent that is discharged by a tannery. Approximately 75% of the global BOD_5 and 60% of the global COD load can be found in this waste water stream. Furthermore, 55% of the global suspended solids and approximately 20% of the global total solids can be found in the unhairing/liming effluent. Finally 50% of the total nitrogen load and the main part of the sulphide load can be found.

Proper segregation of this effluent stream from the other waste water streams is required. Generally spoken, the high BOD_5, COD, SS and total solids load can not be completely prevented, but reduced by a certain level. The idea of the unhairing/liming step is, to separate the hair from the hides. As a consequence, the hair residues can be found in the effluent stream.

First, one's attention must be turned to the pollutant "sulphide". When released to the environment, sulphide shows several negative effects. First, the oxidation of sulphides requires a high quantity of oxygen. Thus the BOD_5 will increase significantly. Second, by bacterial activity, sulphides can be converted into sulphuric acid (H_2SO_4), causing serious corrosion problems in concrete sewers.

In presence of ferric salts, the sulphides react and precipitate as iron sulphide that is nearly insoluble in water and shows a dark colour and may provoke malodour.

Further problems occur when the pH drops below 9.5. The hydrogen sulphide that is formed is a gas characterised by bad odour (rotten eggs), high toxicity and deadly poison exceeding a concentration of 1,500 mg/m³. Furthermore serious corrosion problems will be caused and the efficiency of a biological waste water treatment plant is influenced negatively. Further lowering the pH will increase the concentration of H_2S. When the pH is falling below 5, no more sulphide ions will be found in the effluent.

Several suggestions to substitute, reduce or treat sulphides in the unhairing/liming float can be found in literature. (see [5] [38] [46] [47] [48] [49] [50] [32] [52] [54] and [55]).

According to the principles of pollution prevention, the first attempt must be the substitution of sulphides in the unhairing/liming process. Enzymatic unhairing techniques have been developed. Concerning efficiency of these products, contradictory information is given. On the one hand supplier of unhairing enzymes prise their product and do not mention any disadvantage. On the other hand, one can find statements like "one-site tests have yielded widely varying results that could not justify full-scale industrial use." [56]

A high level of control is required to assure the desired leather quality. Up till now, no enzyme exists that specifically targets proteins in the epidermis, hair roots and basal membrane. [46]

By enzymatic treatment also bacterial decomposition is increased. Furthermore the unhairing by enzymes is never sufficient to obtain a completely hair-free pelt. Enzymes can only be used as additives to other unhairing agents. Alkaline immunisation, alkaline swelling and sulphide treatment to eliminate ground an fine hair, are component parts of both enzymatic and other hair save unhairing processes. [46]

Savings in sulphide consumption and reductions in the pollutants loads of the effluents can be achieved by hair immunisation. The hides are treated with alkali, what leads to an immunisation of the hair. The roots of the hair remain vulnerable by the sulphides. This means, that by a subsequent treatment with sulphides, the hair roots are destroyed, the hair are loosened and can be removed by mechanical agitation.

Parameters that have main influence on this partially hair-destroying unhairing process are length of the float, lime dosage, pH, temperature, process time, intensity of mechanical agitation and hair length [46]. Disadvantages, that have to be mentioned, are risk of over-immunisation, risk of insufficient unhairing and a more complicated process.

A further opportunity of achieving savings in the consumption of sulphides, is the direct reuse of spent unhairing/liming float.

After screening and chemical make up, the spent unhairing/liming float is directly reused. As T.VARNALI [5] stated recycling of the lime float has certain advantages. Spent liming liquor become stronger in unhairing power and less alkaline. So it "has good properties for starting the liming of the next pack of hides. According to old technologists art of tanning was the knowledge how to mix the fresh and used lime liquors. In fresh liquor swelling is stronger and opening up weaker, old liquors (often infected by micro-organism) are better hair loosener." (F.STATHER [4])

Problems may occur with the increasing fat and grease content in the recycled float. If the fat and grease content influences the unhairing/liming process negatively, fat has to be removed by a hydro-cyclone for instant. Screening will reduce the fat and grease content as well. In a UNIDO paper D.WINTERS [38] reports that in developing countries the hides are supposed to contain less fat than in industrialised countries. Therefore the build-up of fat seams not to be the main problem.

What is more problematic is the build-up of organic matter, thus BOD_5. On the one hand, the quality of the leather will be influenced negatively when the BOD_5 content is too high and on the other hand, the BOD_5 of the subsequent process steps deliming/batting will increase. This means, that the problem is shifted to process steps where it is more disperse and therefore more difficult to treat. It is recommended to reject a certain quantity of spent float and to replace it by fresh water and chemicals make up.

In "Cleaner Leather Production – Prospects and Constrains" [56] on the other hand it is reported, that the enrichment of dissolved organic matter will not be higher than 3 times the

conventional concentration due to the fresh-water make up which is required anyway. But several changes to the conventional process will be required.

The recycling of spent unhairing/liming float will require a higher analytical control and is most practicable for large bovine hides [56].

Discrepancies concerning the number of recycle cycles exist. J.LUDVIK [32] reports of successful trials with 10 liming float cycles and 20 unhairing float cycles. C.CANTERA et. al. [55] on the other hand states that more than 5 recycling cycles is not possible at successful industrial scale application. A UNIDO study (D.WINTERS [38]) gives some examples of different numbers of float recycling cycles that can be found in literature. However, chemical savings of 40 – 60 % lime and 20 – 50 % sodium sulphide can be expected. [38] [56] Whereby the savings in the sodium sulphide consumption will be found in the upper range.

A further possibility to reuse the sulphide is the indirect recycling via the production of NaHS. After screening, the spent float is acidified gradually with sulphuric acid. When the pH falls below 9.5, H_2S is released with the flue. Further lowering of the pH converts the entire sulphide load into H_2S. Once a pH of 5 is reached, no sulphide will be found in the effluent, which can be released without any further sulphide treatment.

The H_2S gas is absorbed in NaOH, forming NaHS and Na_2S. A solution with 15% Na_2S can be produced. This solution can be reused as unhairing agent in the beamhouse.

However, operating such a plant is not that simple. R.H.SAYERS [57] reports several problems may occur when operating this process. Main problem is the corrosion of plant equipment. Working with the highly corrosive gas H_2S will lead to destruction of parts of the plant. Even if the critical parts are fabricated with high quality material corrosion will occur.

By acidifying the effluent proteins precipitate. This has a positive effect on the BOD_5 load of the effluent but shows negative impact on the air diffusers in the degasifier trays. They became clogged with the precipitate and have to be cleaned frequently.

Further problems that are reported, are the frequent floating of the absorber that requires sophisticated control loops and the variable air flow that is required or recommended to keep the H_2S concentration below the lower explosion limit.

Due to this problems and due to the fact that working with the extremely toxic gas H_2S is not recommended to inexperienced persons. D.WINTERS [38] recommends: „in general they may currently be assumed to be too sophisticated for tanneries in most developing countries....“

A simple treatment without any recovery of sulphides would be the oxidation of the sulphide ions. This corresponds to the classical end-off pipe technology. No savings in chemical or water consumption can be achieved, but additional costs will be caused.

However, looking at the costs, risks and disadvantages, that have to be considered with process changes and recycling plants, also the end of pipe technology is a worthwhile alternative. The UNIDO [38] states that "beamhouse recycling was not found cost beneficial and sulphide liquors were finally catalytically aerated."

By catalytic oxidation the sulphide ions are converted to sulphates by air. The elementary sulphur can be assimilated safely and easily by bacteria. Oxidation can be facilitated by catalysts. The most popular one is manganese sulphate ($MnSO_4$).

4.6 Conclusion

As a result, the following conclusions can be drawn:

Drawing-up a material balance for a chrome tanning process is not a simple matter. Factors like type and quality of the raw hides, equipment at the plant, constellation of process units, type and quality of product, customs of the tanners, etc... have significant influence on the input and output figures.
By defining ranges, that means minimum and maximum figures, it is possible to deal with all these factors. Tanners can be provided with rules of thumb to estimate their consumption figures and the quantity of waste water and solid waste they generate by their activities.
Streams of concern can be defined. Main efforts should be concentrated on the prevention, recycling or treatment of these streams of concern.

Per ton wet salted hide input, approximately **420 – 770 kg solid wastes** are generated.
The solid waste streams can be segregated into 3 different fractions – **chromium containing, non-chromium containing solid waste** and **spent salt**. Stream of concern is the fraction non-chromium containing solid waste. Between 75 and 80% of the global quantity of solid waste are fleshings, trimmings, unused spilt and hair residues. For this solid waste fraction, biological, aerobic treatment is suggested.

Although the fractions chromium-containing solid waste (15%) and spent salt (5 – 10%) are of minor importance, measures for prevention and reuse can and should be taken.

Between **46** and **67 m³/t$_{wsH}$ of fresh water** are consumed. Approximately 50% is non process related "technical water" (machine water, plant wash down water and boiler feed water). Second consumer is the section "beamhouse" (35%). Measures to reduce the overall water consumption, are most effective when they are taken in one of these two sections.

The **41 to 63 m³ of waste water** that is generated per ton wet salted hides, can be segregated into 4 different waste water streams . "**Low Polluted**", "**High Polluted**", "**Chromium Bearing**" and "**Sulphide Bearing**" effluents are distinguished.

45% of the global effluents are **low polluted effluents**. Generally spoken, these streams can be recycled without big efforts. Immediate measures can be taken to close a recycle loop for this 45%.

35% of the global effluents are **high polluted effluents**. These effluents require primary and secondary treatment. In general, this requires big economic resources and treating these

types of effluent must be seen as a matter of long-term planing. Hence, this stream was not identified as a stream of concern.

Approximately **15%** are **sulphide bearing effluent**. This 5 to 11 m³/t$_{wsH}$ are high polluted waste water generated in the unhairing/liming step. Several possibilities, how to reduce the sulphide load, exist. However, the procedure that can be recommended to SME - tanners located in developing countries is the direct recycling of the spent unhairing/liming float. The actual number of cycles has to be determined from case to case. It can be assumed, that with proper chemical make-up, at least 5 recycling steps are possible. However, a good control level in the tannery in required.

In order to eliminate the sulphides that are discharged, catalytic oxidation seems preferable.

Finally, the **6% of chromium** or **potentially chromium bearing effluents** have to be segregated from the non-chromium bearing effluents. Several opportunities of minimising the chromium consumption and chromium discharge exist.

Summarising, these alternatives for a proper chrome management at tanneries, one can state the following: First of all, an optimisation of the process parameters has to be investigated. As shown above, remarkable savings can be achieved by adjusting temperature, pH, agitation and residence time. To comply with legislative regulations further treatment is required. Direct reuse of the spent tanning float seems to be the recommendable procedure for SME – tanners located in developing countries. Retanning effluent and volume build-up from the recycling steps have to be treated separately. Precipitation and disposal of the segregated sludge seems to be the most feasible opportunity.

5 Aerobic Treatment of Non-Chromium Containing Solid Waste

„Ich war glücklich und wusste das. So lange wir ein Glück erleben, sind wir uns dessen nie so richtig bewusst. Erst wenn es uns verlassen hat und wir Rückschau halten, merken wir plötzlich – und zuweilen mit Erstaunen – wie glücklich wir waren.“

Alexis Sorbas

5.1 Introduction

Approximately 75 – 80% of the global solid waste that is generated at a tannery, is non-chromium containing waste. Depending on the process, these 75–80% correspond to 322-585 kg/t_{wsH}. Approximately 67 to 180 kg/t_{wsH} are hair residues separated from the unhairing/liming effluent. About 255 to 405 kg/t_{wsH} are fleshings, trimmings and unused split. A characterisation of the different solid waste fractions will be given in section 5.4.

Because of the organic origin of the solid waste fraction it seems reasonable to suggest a biological process as a suitable treatment technology.

As to the characterisation of the substrate, anaerobic digestion seems to be favourable. Successful industrial scale trials have been carried out. From the economical point of view the anaerobic digestion can be justified for tanneries with a capacity > 40 tons hides per day [36].

This means that the anaerobic digestion – although having several advantages compared to the aerobic digestion – is a solution for large tanneries or tannery-clusters only, but is not a solution for small to medium sized (SME) tanneries located in developing countries.

For these tanneries the second alternative of biological process – the **aerobic treatment (composting)** – was identified to be a favourable way of treating their organic solid wastes.

In section 5.2 a brief introduction to aerobic treatment (composting) is given. After explaining the methodologies and results from failed windrow composting trials (section 5.3), in section 5.5 the results of the investigations made by the INCO-DC working group are documented.

Starting point was the low-cost technology of windrow composting. This technology turned out not to be suitable for this type of substrate. Further investigations were carried out with a bench scale reactor. The different substrates which were treated are fleshings, thermally treated fleshings and hair residues. A characterisation of the different substrates is given in section 5.4. The results achieved, are documented and the process parameters that are required for a proper operation of a composting reactor are defined.

Finally, the product (compost) from the different type of substrates is tested and evaluated in section 5.5.4. In section 5.6 the results are discussed. It is shown, whether aerobic biological treatment of non-chromium containing solid tannery waste is a valid alternative to the prevalent method of disposal.

5.2 Principles of the Composting Process

The composting process can be defined as follows:

"Composting is the biological decomposition and stabilisation of organic substrates, under conditions that allow development of thermophilic temperatures as a result of biologically produced heat, to produce a final product that is stable, free of pathogens and plant seeds, and can be beneficially applied to land." (R.HAUG [59])

According to E.EPSTEIN [58], the decomposition has to take place under controlled conditions- i.e. the process has to be "managed or optimised to achieve the objectives desired." Major objectives of the composting process are:

- to decompose potentially putrescible organic matter into a stable product.
- to decompose waste into a beneficial product
- to disinfect pathogenically infected organic waste
- to bioremediate or biodegrade hazardous waste

Main **advantages** and **disadvantages** of composting are listed below

+ Municipal waste as well as biodegradable industrial and agricultural waste can be treated
+ Environmental impacts can be minimised and controlled
+ Land-savings can be achieved as alternative to landfilling
+ Waste-biomass can be transformed to a usable and beneficial product

- Odour and bioaerosol emission
- Product must be marked
- Space requirement are related to storage and market requirements

The product of the composting process – **compost** – can be defined as:

"an organic soil conditioner that has been stabilised to a humus-like product, that is free of viable human and plant pathogens and plant seeds, that does not attract insects or vectors, that can be handled and stored without nuisance and that is beneficial to the growth of plants" (R.HAUG [59])

Important is the word "humus-like". Compost is generally called "humus". But it has to be stated clearly that composting does not produce humus. Humus is the result of long-term decomposition of organic matter in soil.

The expression "... stabilised to a humus-like product,..." means that the compost is supposed to be a biologically stable product where stable is defined as "a stage in the decomposition of organic matter and as a function of biological activity". [59]
Compost also has to be maturated. Maturation means an organo-chemical condition of the compost which indicates the presence or lack of phytotoxic organic acids"

It is important to be aware of the fact that "maturity" and "stability" mean two different things.

As said above maturity is important for the lack of phytotoxic organic acids. Stability on the other hand is important for:

- not to produce **inflammatory gases**
- not to produce **CH$_4$** which contributes to the greenhouse effect
- not to produce **malodours** which are caused by gases generated under anaerobic conditions
- not to **consume nitrogen** during decomposition as some microbiological populations compete with plants for soil nitrogen. In this case plants typically exhibit chlorosis, yellowing of the leaves, indicating nitrogen deficiency.
- not to **release NH$_3$ nitrogen** during decomposition. If organic materials with low C/N ratio are added to soil, ammonia can be released which cause phytotoxicity.
- not to consume **soil – oxygen**, because the decrease in oxygen in soil can result in reduced oxygen levels or anaerobic conditions. This not only affects plant growth but also soil chemical species, heavy metal solubility and the uptake of nutrients.

The main benefits of compost on plant growth are listed as below:

- source for organic matter for proper physical soil properties (e.g. soil structure, water retention capacity; soil temperature, etc.)
- source for organic matter for proper chemical soil properties (e.g. cationic exchange capacity, soil pH, electrical conductivity, macronutrients, etc.)
- source for organic matter for proper biological soil properties (change of bacterial flora)
- improved growth of plants
- reduced plant pathogens
- nutrients (slowly released)

Contrary to popular opinion, the composting process is not simply the high-rate phase, but consists in more than just the high-temperature degradation of organic matter. A generalised flow sheet of aerobic treatment is shown in Figure 20. The other phases and process steps are often neglected by authors of composting literature and by operators of composting plants. Fact is that each step is important for the successful operation of a composting plant.
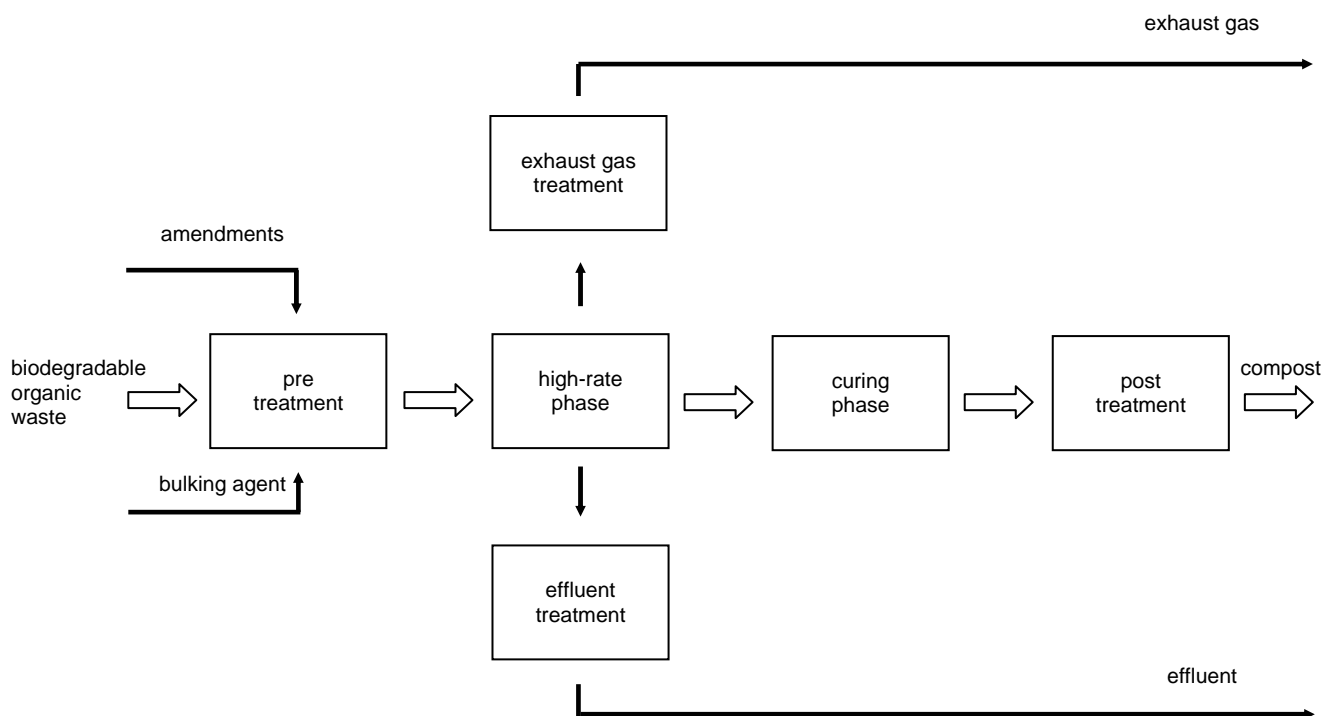
Figure 20   Generalised Process Flow Sheet of Aerobic Treatment

In the **pre-treatment** step the organic substrate is prepared for composting. This feed-conditioning can either be of physical, chemical or of thermodynamic nature or a combination of these three. Due to the fact that the pre-treatment is one of the most important steps where the composting process can be influenced by the operator, it is important to understand the different ways of how to condition the input.

As mentioned before, what is commonly understood as "composting" is the **high-rate phase**. It must not be forgotten that this step is not the entire composting process. During this phase the temperature reaches a maximum and most of the biodegradable substrate is degraded. Due to the fact that during these 2 to 3 weeks, strong odour generation and main oxygen consumption takes place, main attention was given to this step. It is important and has to be controlled carefully, but the following **curing phase** should not be considered to be less important. During the curing phase which requires about 1 – 2 months, the quality of the compost is determined.

For obtaining a marketable product, further processing like screening and packaging is necessary. These operations are combined in the **post-treatment** step. However, this step is mainly for marketing purpose and is of little relevance for the process.

Due to the generation of bad odour which can not be avoided dealing with degradation of organics, the **cleaning of the exhaust gas** is one of the most important step for public acceptance of a composting plant. In the United States several plants are reported to be closed because of not considering the exhaust air cleaning step. [58] [59]

Finally the **effluent** (leachate), highly contaminated with organic matter and characterised by a high BOD_5 concentration, has to be collected and treated before being discharged.

To gain a profound knowledge of the process of composting the following literature is recommended: E.EPSTEIN [58], R.HAUG [59]; H.HOITNIK et al [60] and A.G.R.MANSER et al [61]

5.3   Methods

In this section the equipment and technology that was applied for the biological treatment of solid tannery waste will be described.

Hence windrow composting turned out not to be recommendable, the main discoveries made by several trials will be presented in this section. Concerning reactor composting in this section only the equipment is presented. The results obtained by the reactor trials are shown in section 5.5. The fleshings were drawn from the tanneries GACEL S.A. / Chile and FERNANDO FISCHER S.A: / Chile. The trials were carried out at the premises of the UDT / Chile. (see Annex F)

Furthermore, in this section the analytical methods that were applied will be presented. Water content, loss of ignition (LOI) and CO_2 concentration have been recorded periodically by the INCO-DC working group. Further chemical analysis of the substrate and the product were carried out in chemical laboratories.

5.3.1   Equipment

5.3.1.1   Windrow Composting

In order to find a practicable solution for small and medium scaled tanneries (SME) located in developing countries, the starting point for the aerobic treatment of solid tannery waste was the low sophisticated and low cost technology of windrow composting.

Serious problems however proved that this technology is not suitable for this type of substrate. Therefore in this section only a short overview of the methods, trials and results will be given. The problems that occurred and the lessons learned will be discussed in more detail.

4 small scale windrows (l*w*h = 5*2*1 m) were erected (see Figure 21). Base was a 20 cm bark layer. In the centre of each windrow a perforated tube for forced aeration was installed.

The maximum air flow of 67 m³ per hour and windrow was supplied by a fan. This corresponds to approximately 10 m³/h m³$_{windrow}$. During the trials the air flow was not recorded. The air flow was throttled manually by opening and closing the respective valves. Daily the valve positions were readjusted according to the windrow temperature.

Water was added manually when required.
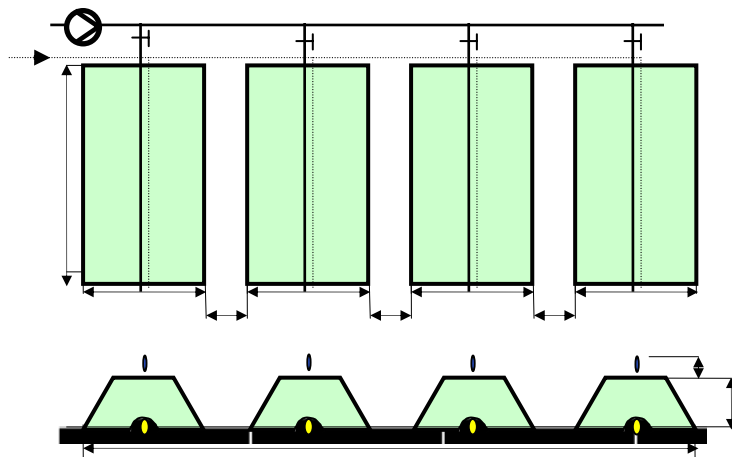
Figure 21   Drawing of Small Scale Windrows

Due to the dense, lump-like nature of the native fleshings it was obvious that composting without a bulking agent would not work. Without wood chips or bark the erection of the piles is not possible, no free airspace is available and the water content will be too high (80 – 85 %). Whether amendments are also necessary or recommendable should be shown by the different substrate mixtures of windrow 1 – 4.

Windrow 1 was erected without amendments. Bark was used as bulking material. Windrow 1 was the trial for mono-composting. 640 kg of fleshings were mixed with 640 kg of bark. Hence resulting in a mass ration of 1 kg bark per $kg_{fleshings}$, this corresponds to an volume ratio of 4 m³ bark per $m^3_{fleshings}$ (see Table 14).

Windrow 2 was erected with market waste (mainly organic matter with impurities consisting of plastics, glass and metal) as a co-substrate. Approximately 500 kg of fleshings were mixed with 400 kg of wood chips and 400 kg of organic waste. The mass ratio of 1.6 kg per $kg_{fleshings}$ corresponds to a volume ratio of 4.7 m³ per $m^3_{fleshings}$.

Table 14   Mass and Volume Ratio for Windrows 1 - 4

| Windrow #	Substrate Mixture	Mass Ratio kg/kg fleshings	Volume Ratio m³/m³ fleshings
1	Fleshings; bark	1	4
2	Fleshings; wood chips; organic waste fraction	1.6	4.7
3	Fleshings; wood chips; horse bed stable	3.5	11.8
4	Fleshings; horse bed stable	1	4.2

Windrow 3 was a mixture of fleshings, wood chips and horse bed stale. Horse bed stale actually was a mixture of approximately 80% finest wood chips and 20% horse excrements. With this windrow the influence of free air space on the windrow and therefore the composting process should be investigated. 240 kg fleshings were mixed with 700 kg wood

chips and about 140 kg horse bed stale. The mass ratio and volume ratio of 3.5 kg per kg$_{fleshings}$ and 11.8 m³ per m³$_{fleshings}$ was chosen rather high.

For windrow 4, 720 kg of fleshings were mixed with 720 kg of horse bed stable. This corresponds to a mass ratio of 1 kg of horse bed stale per kg$_{fleshings}$ and a volume ratio of about 4 m³ horse dung per m³ of fleshings.

Horse dung proofed to be quite effective. That means that the water holding capacity and the process temperatures were influenced very positively.

Making a real homogenous mixture of the substrate with amendments and bulking agent was not possible. Because of the "chewing gum" like lumps, the windrows had to be erected in layers of different substrates. (fleshings – amendments – structure material – fleshings ...) (see Picture 1). This should have significant influence on the process. It could be shown that a process temperature of higher than 70 °C is required to convert the fleshings into a white thick paste. This change in the substrate properties is necessary to decompose the fleshings.
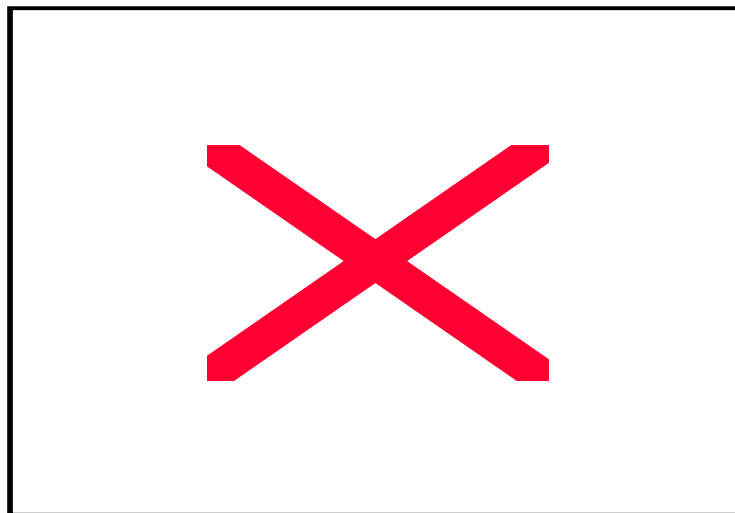
Picture 1   Erection of Windrows

The windrows were turned 4 times during the first 4 weeks of the high rate phase. After 55 days of operation the compost was separated from the bulking material by screening. Without additional air supply the compost was stored for maturation purpose for another 40 days. Weather conditions during the trial period varied – dry sunny periods as well as heavy rain showers. After a 3 months (95 days) of operation the trials were ended and the results evaluated.

Though it could be shown that it is principally possible to produce a biologically stable product, it has to be stated that the low-cost technology of windrow composting is not suitable and therefore not recommendable for treating fleshings from tanneries.

Main problems observed by windrow composting of native fleshings are:

- serious odour problems
- problems with insects
- temperature fluctuation
- influence of weather
- process control impossible
- homogenous substrate mixture difficult
- homogenous sampling difficult

The problems of temperature fluctuation and influence of weather conditions were caused by the fact that the size of the windrows were to small. Due to the lack of infrastructure the windrows had to be handled manually. The given size was the upper limit for manual handling. Constructing windrows with higher volume may reduce or eliminate these problems.

In order to guaranty hygienesation of the substrate and a complete decomposition, frequent turning of the windrows is indispensable.

Controlling the process in respect of the proper water content is difficult. Due to the high water content of the fleshings it is more or less impossible to get a uniform moisture content inside the pile. Spots that are too dry and too wet are the consequence which lead to the formation of anaerobic spots or the cease of biological activity.

After 50 days of composting still not-decomposed fleshings could be found. This was on the one hand, dried substrate that turned to a hard solid matter that could hardly be rehydrated. On the other hand, fleshings which turned to a white thick paste were found. They caused anaerobic conditions and hence a cease in aerobic microbiological activity.

The hygienesation of the substrate can not be guaranteed under these condition.

Furthermore it is nearly impossible to take homogenous and representative samples because of the in-homogenous structure of the piles.

The two most serious problems which lead to the decision that windrow composting is not suitable for composting of fleshings are odour and insects. Even if aerobic conditions are maintained during the process the formation of odorous substances can not be avoided. Decomposition of flesh generates bad odour. Furthermore this type of substrate attracts insects like flies (see Picture 2). Though this problem can be minimised by maintaining proper process conditions, it can not be eliminated. These two facts will cause serious acceptance problems in public.
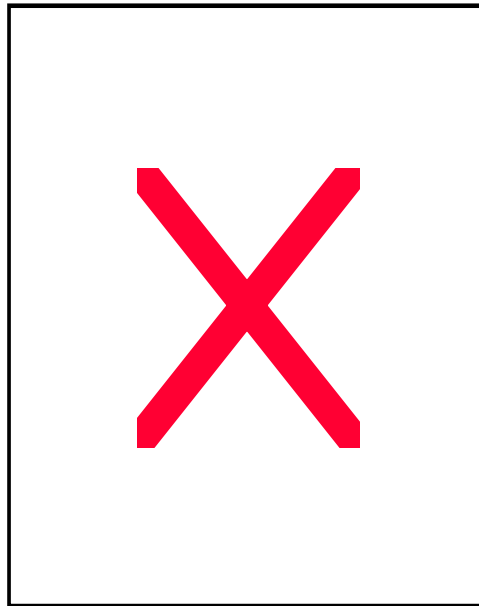
Picture 2   Problems with Insects during Windrow Composting

Although windrow composting of fleshings failed and it was decided not to continue with further trials important discoveries could be made .

In principle, composting of fleshings is possible. Furthermore it is possible to produce a product which is biologically stable and has no negative impact on plant growth. Bulking material is required, but amendments are not essentially necessary.

Problems which occur when mixing the substrate have to be solved. Furthermore it is necessary that process temperatures exceed 70 °C for several days. At this temperatures the dense lumps are converted to a thick paste that is necessary for entire decomposition. The high pH value of the fleshings is not a limiting factor. By mixing it with bulking material and amendments the pH decrease to about 10. Within the first 5 days of composting, the pH value further decreases to 7 – 8 which is near the optimum range for bacterial flora.

Due to the odour problems and problems with insects, windrow composting was stopped. Measures like covering the windrows with cured compost etc. can reduce the negative effects but never eliminate them completely.

5.3.1.2   Reactor Composting

Based on the observations made by windrow composting (see chapter 5.3.1.1), it can be stated that composting of a mixture of fleshings/bulking material is possible in principle. Main requirement is that the process is being isolated from the surrounding. That means on the one hand, that no troubles will be caused by insects and on the other hand, that the effluent and exhaust gas can be collected and treated (odour).

To comply with these requirements, a concept for reactor composting (in-vessel composting) was developed. For the schematic flow sheet see Figure 22.
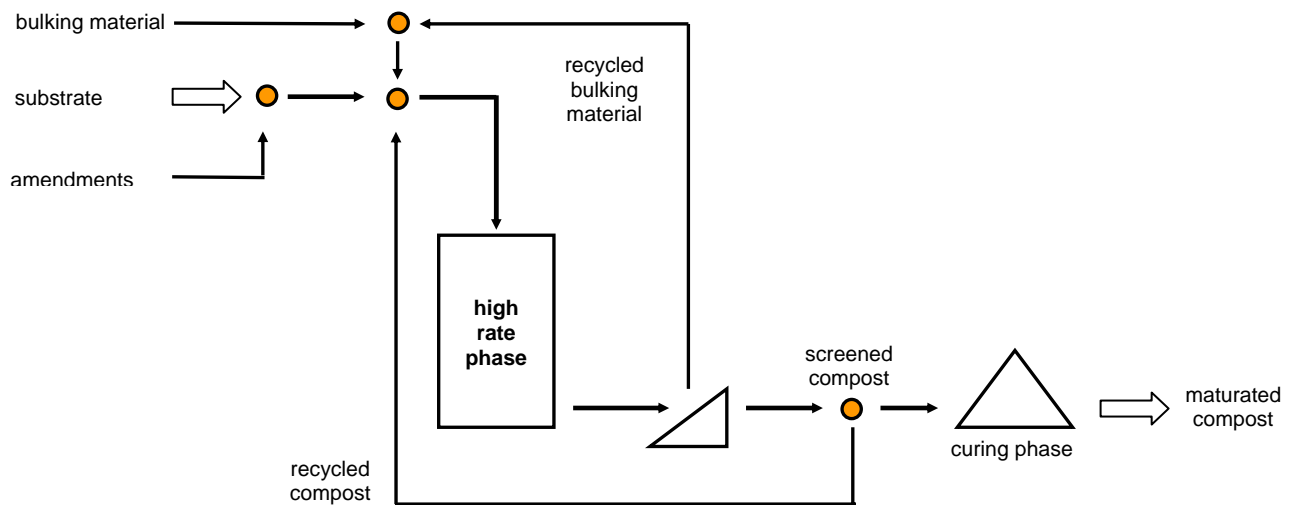
Figure 22   Schematic Flow Sheet of Composting Reactor with Substrate Path

A 600 l cylindrical reactor was designed and constructed. (For drawings and pictures see annex C). To prevent heat loss, the reactor was isolated outside. The temperature of the substrate is measured with a thermocouple in the centre of the reactor. A second reactor was constructed later. The volume of this reactor was approximately 200 l. The purpose of the trials which were carried out in this reactor was, to confirm the results obtained by the 600 l reactor. Hence, the 200 l reactor will not be described in detail.

The substrate (fleshings, fleshings thermal or hair residues) is mixed with bulking material (wood chips) and amendments (saw dust, horse bed stale and organic fraction of municipal waste). For some trials compost was recycled - mainly to decrease the water content.

The substrate mixture is charged into the reactor from the top. Residence time is between 10 to 21 days – depending on the process conditions. When the substrate is considered to be suitable for being stored on open-air for curing, the reactor is discharged at the bottom with a discharge screw.

Depending on the moisture content the substrate is screened immediately or stored on piles until the moisture content is suitable for screening. The bulking material is recycled and the raw compost stored at piles for curing purpose.

For turning during the high rate phase the reactor is discharged and charged again with the same substrate. Turning of the substrate, mixing of the substrate, as well as charging of the reactor and screening is carried out manually.

The first design of the reactor shows several disadvantages. Main problem are the discharge and turning actions. However, improvement of the reactor design was not scope of this work.
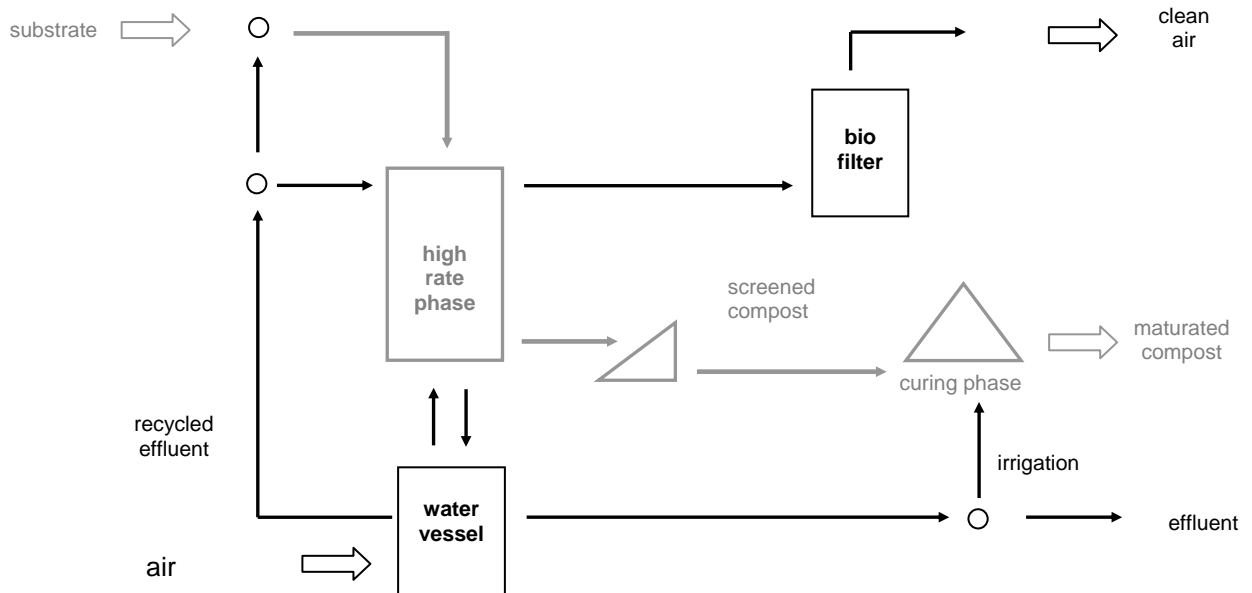
Figure 23   Schematic Flow Sheet of Composting Reactor with Air and Water Path

The air flow (see Figure 23) is provided by a compressor. The flow is controlled by a flowmeter (rotameter). During the trials the rotameter was checked twice a day. When required the air flow was adjusted manually by setting the corresponding air valve.

The air is saturated by the effluent which is collected in a water vessel. Then the saturated air is pressed counter currently through the substrate and leaves the reactor at the top. To prevent material from falling into the air duct at the bottom of the reactor, a perforated metal sheet is installed.

The waste air stream is further drawn to a biofilter where odorous compounds are eliminated. The temperature of the air stream is measured with thermocouples at the air inlet and outlet duct.

The effluent leaves the reactor at the bottom and is collected in the water vessel (see Figure 23). It can either be recycled back into the process (used to adjust the moisture content of the substrate before charging or during the process), be irrigated on the curing compost or can be treated.

5.3.2 Analytical Methods

During the trials samples were taken periodically in order to determine the water content and the loss of ignition. A silted tube served as sample taking device. When working with thermally treated fleshings and hair residues the sample taking was homogenous and representative. Concerning the treatment of native fleshings it has to be stated that homogenous sample taking was difficult. Working with this substrate made it necessary to take at least 3 samples from different parts of the reactor, to mix them and to take a homogenous sample from this substrate.

5.3.2.1 Water Content

Approximately 200 g of the sample is dried by a temperature of 105 °C for approximately 24 h. From the difference between wet weight and dry weight the moisture content of the substrate is calculated according to Equation 1.

$$WC = [(M_{wet} - M_{dry}) / (M_{dry} - M_{tara})]*100\ \%$$

Equation 1

5.3.2.2 Loss of Ignition and Total Organic Carbon

Approximately 100 g of dry sample is put into a box-type furnace and the temperature increased to 555 °C. The sample is burned up in the furnace until the weight is constant. The loss of ignition is calculated according to Equation 2.

$$LOI = [(M_{dry} - M_{ash}) / (M_{dry} - M_{tara})]*100\ \%$$

Equation 2

The organic carbon content (TOC) is calculated as shown in Equation 3. According to R.HAUG [59] this equation provides results accurate to within 2 to 10 % which is sufficiently accurate for most practical purpose.

$$TOC = LOI / 1.8$$

Equation 3

5.3.2.3 Cress Test

The cress tests were carried out according to the standard for carrying out such test (see [62]). Vegetation tests with garden cress (Lepidium sativum) are an effective and quick orientation for the plant tolerance of compost. Different mixtures of reference soil and compost were made. The content of compost was 0, 25, 50, 75 and 100%. 2 g of garden cress seeds (Lepidium sativum) were seeded per mixture. After 8 days of growth, the mass of the grown plants was determined and a yield factor calculated. This yield factor is defined by the mass of cress of the respective trial divided by the mass of cress obtained from the reference soil.

5.3.2.4 CO_2 Concentration of Waste Gas

The CO_2 concentration of the waste gas stream was measured indirectly. By subtracting the O_2 concentration of the waste gas from the O_2 concentration of the atmosphere the CO_2 concentration of the waste gas was computed. The O_2 analyser was a "Passport Oxygen Analyser". To confirm the results obtained by the oxygen analyser some measures were repeated with CO / CO_2 DRÄGER tubes.

5.3.2.5 Chemical Analyses of the Substrate

The chemical analysis of the substrate (native fleshings, fleshings thermal and hair residues) were carried out by the certified laboratories CESMEC and AQUALAQ according to standards. For the analysis see Annex D and for contacts see Annex E.

5.3.2.6 Chemical Analyses of Product

The chemical analysis of the product were carried out by a laboratory of the Universität für Bodenkultur according to the standard ÖNORM S2023. For the analysis see Annex D and for contacts see Annex E.

5.4 Characterisation of Substrate

5.4.1 Fleshings, Unused Split and Trimmings

Between 50 to 60% of the solid waste generated at a tannery are fleshings, unusable spilt and trimmings. This corresponds to a total mass of approximately 500 kg per ton wet salted hide input. Fleshings are generated in the process step "fleshing", unused split is a waste product generated in the process step "splitting". The trimmings are generated by correcting the edges of the hides. Only the epidermis can be transformed into leather. The connecting tissue, fat and rest of flesh has to be removed from the swollen hides. This removal is performed in a mechanical way with machines similar to moulding machines.

Fleshings are best described as a mud-like thick paste (see Picture 3). They are characterised by a high pH value (12.5), no porosity, zero free-air space and high water content (>80%). Trimmings and unused split show the same chemical properties as fleshings. Differences in the physical properties can be stated. Trimmings and unused split are best described as "dense, chewing-gum like lumps".
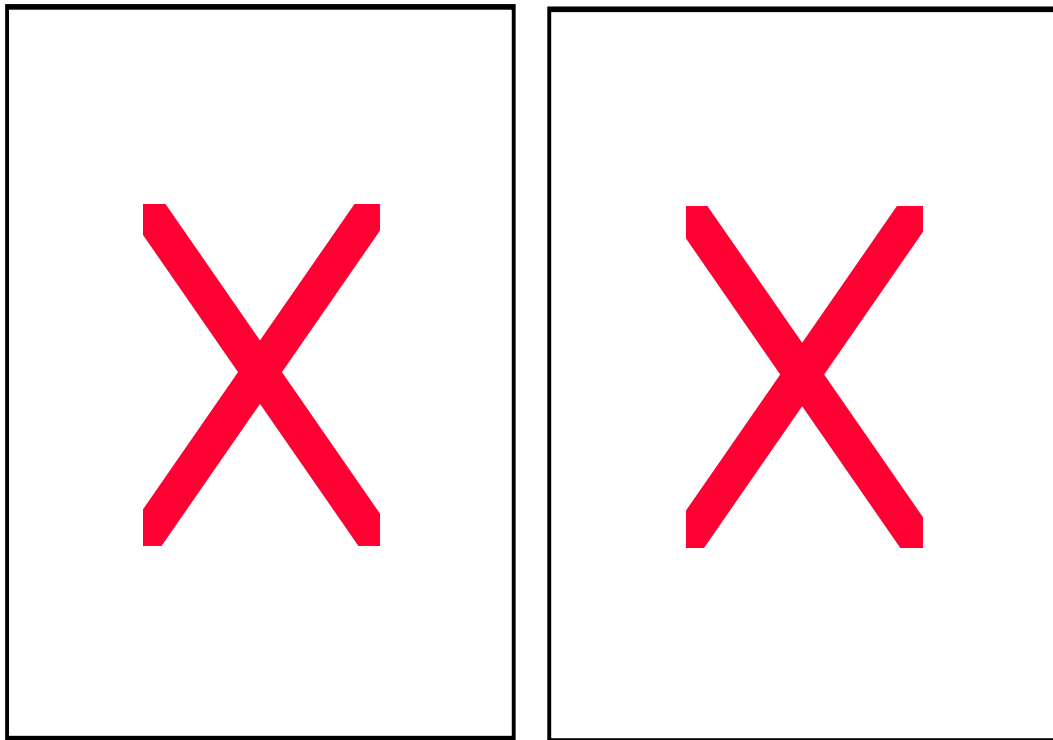
Picture 3   Fleshings and Trimmings

In Table 15 the chemical analysis of fleshings are shown. Sample 1, 2 and 3 are three different samples, the column "average" is the average of the three samples.

Table 15   **Chemical Analysis of Native Fleshings**

Parameter	Unit	Sample 1	Sample 2	Sample 3	Average
pH	-	12.5	-	12.5	**12.5**
H_2O	$\%_{wm}$	76.0	64.2	81.0	**74**
LOI	$\%_{dm}$	93.0	71.9	72.2	**79**
TOC	$\%_{dm}$	51.7	39.9	40.1	**44**
N_{total}	$\%_{dm}$	5	3.1	2.63	**3.6**
C/N	-	10.3	12.9	15.2	**12.3**
P_{total}	$mg/100g_{dm}$			0.26	**0.26**
K_{total}	$mg/100g_{dm}$			15.8	**15.8**
Ca_{total}	$\%_{dm}$			13.7	**13.7**
Cl^-	$\%_{dm}$			0.53	**0.53**
Oil & fat	$\%_{dm}$			40.8	**40.8**
Salmonella	-			n.d.	**n.d.**
Escherichia	MPN/g			< 3	**< 3**

n.d.   not detected

The analyses are representative for a hairburning - sulphide - unhairing/liming process of bovine hides. Important parameters for the composting process are the high **water content** between **70 and 80 %** and the **C/N ratio** of **10 to 15 %**. Parameters that will have influence on the product are the Ca content ($13.7\%_{dm}$) and the chloride content ($0.53\%_{dm}$). Because of the high pH (12.5) the substrate can be assumed to be sterile, i.e. free of pathogens. The analyses of Salmonella and Escherichia Colli showed negative results.

The tallow content (oil & fat) depend on the type and origin of the raw hide. For bovine hides $40\%_{dm}$ is a realistic value, but higher quantities ($50–60\%_{dm}$) are also reported (see [19]).

Depending on the raw hides and on the unhairing/liming process that is applied at the respective tannery the analysis will differ slightly (see [19]). However, for the practical trials which are described in this thesis, fleshings from 2 different tanneries were treated. It was shown that differences in the unhairing/liming process and as a consequence in the chemical analyses of the substrate show little influence on the composting process.

5.4.2   Thermally Treated Fleshings

By treating the fleshings with heat (vapour), the characteristic of the substrate can be changed significantly.

The fleshings are heated by indirect contact with vapour. The tallow is melted, separated from the residue and sold as a by-product. From 1,000 kg fleshings approximately 50 kg of fat can be recovered. This corresponds to about 5%.

The remaining protein rich substrate (thermal fleshings) is a crumbly matter with a water content of approximately 40 %. Due to this properties the substrate can be easily mixed with bulking agent or co-substrates (see Picture 4)
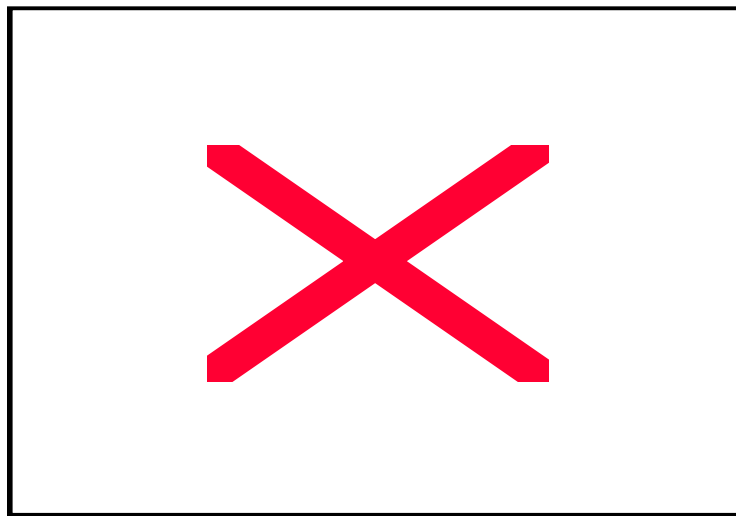
Picture 4   Fleshings after Thermal Treatment

The separation of fat and protein matter which is applied at the tannery Fernando Fischer is rather simple but ineffective. Approximately 5% of the total amount of fleshings can be recovered as fat. The remaining fat content is about 4–5% on wet base which corresponds to about 7% on dry base. In Table 16 the chemical analyses of the thermally treated fleshings are shown. 3 samples were analysed and the average of the corresponding concentrations calculated.

Although the total nitrogen content (TKN) has been analysed for three different samples and the results are comparable (average 1.5%$_{dm}$) this number definitively is not correct. Firstly, fat generally is lower in nitrogen than proteins. By separating the tallow from the protein matter it must be assumed that the nitrogen content of the thermally treated fleshings is higher than the nitrogen content of the fleshings. Looking at the prevailing analysis this is not the case. Secondly, assuming a total carbon content (TOC) of 48%$_{dm}$, what sounds realistic, a C/N ratio of 35 can be computed. This means a surplus of carbon. During the composting trials the presence of a significant amount of ammonia could be observed. Free ammonia is released when nitrogen is in excess which means a low C/N ratio. Thirdly, this low nitrogen

concentration can not be confirmed by data from literature. In a report from the German Federal Ministry for Environment, Nature Protection and Reactor Safety concerning meat and bone meat nitrogen contents between 5.8 and 10.6%$_{dm}$ are mentioned [53]. This is much more realistic and for further discussions an average nitrogen concentration of 7.8%$_{dm}$ is assumed.

As a consequence the C/N ratio of the thermally treated fleshings is reduced to 6.1.

With 11.5 the pH value is slightly lower than the pH of the initial substrate. This has no influence on the composting process.

Because of evaporation the water content of the thermally treated fleshings is reduced from 80% to 45%. This has a significant influence on the composting process. Treating fleshings produces leakage that has to be treated. Treating thermally treated fleshings on the contrary is a net water consumer.

The content of calcium (Ca^{2+}) is approximately 5% on dry base. Compared with the calcium content of the initial substrate (fleshings) which is about 14% this means that the main part of the calcium remains in the tallow which is separated from the protein matter. The same can be stated for the phosphor content which is significantly lower for the thermally treated fleshings compared to the phosphorous content of the fleshings. However, due to the low total amount of phosphorous it is not supposed to have a significant influence on the compost quality.

Table 16   **Chemical Analyses of Thermally Treated Fleshings**

Parameter	Unit	Sample 1	Sample 2	Sample 3	Average
PH	-	11.5	11.5		**11.5**
H_2O	%$_{wm}$	42.2	39.6	50	**44**
LOI	%$_{dm}$	83.7	92.7	85.3	**87.2**
TOC	%$_{dm}$	46,5	51.5	47.4	**48.4**
N_{total}	%$_{dm}$	1.2*	1.99*	1.2*	**1.5* (7.8)**
C/N	-	38.8	25.9	39.5	**34.7 (6.1)**
P_{total}	mg/100g$_{dm}$		0.08		**0.08**
K_{total}	mg/100g$_{dm}$		14.9		**14.9**
Ca_{total}	%$_{dm}$		4.56	6.6	**5.58**
Cl^-	%$_{dm}$		0.33		**0.33**
Oil & fat	%$_{dm}$		6.79		**6.79**
Salmonella	-		n.d.		**n.d.**
Escherichia	MPN/g		< 3		**<3**

*   error in analyses is assumed
n.d.   not detected

5.4.3 Unhairing Residues

Depending on the type of unhairing process, different quantities of hair residues can be separated from the unhairing/liming effluent. Approximately 250 - 300 kg/t_{wsH} from effluents of a hairsaving process, 100 to 200 kg/t_{wsH} from effluents of a partially hairburning technology and finally between 60 – 70 kg/t_{wsH} when a totally hairburning process is applied. In all three scenarios screening of the effluents of the unhairing / liming is required.
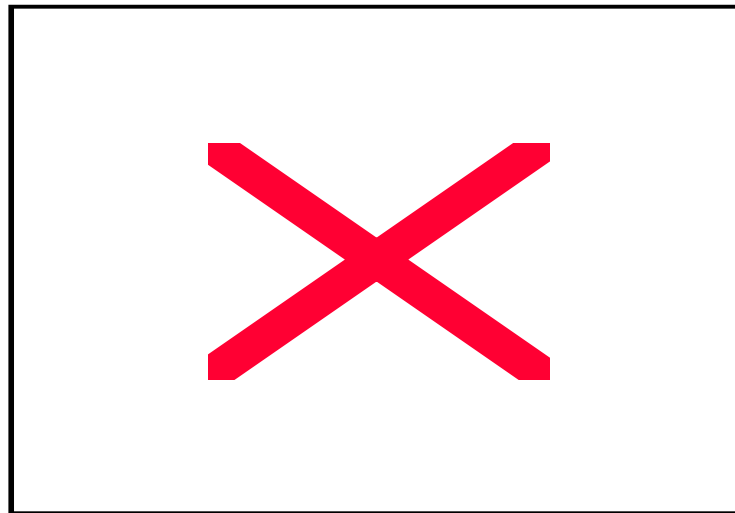
Picture 5   **Hair Residues**

The hair residues consist in hair and partially destroyed hair. They are compact balls (see Picture 5). Although the water content is approximately 80 to 85%, they do not appear wet. In Table 17 chemical analyses of two samples and the averages of these numbers are shown. The pH is approximately 12.5.

The loss of ignition (LOI) is approximately 85% which results in a calculated total organic carbon content (TOC) of 48%. The nitrogen analysis show an average of 11% on dry base. These result in a C/N ratio of 4.2.

Approximately 5.6%$_{dm}$ calcium could be found. This amount corresponds to the calcium concentration of the thermally treated fleshings. This fact confirms the results obtained from previous analysis that indicates that the calcium remains mainly in the fat.

The sulphide content in fresh hair is approximately 80 – 100 ppm. Sulphide, however, oxidises easily; within three to four hours, the sulphide content is less than 10 ppm. After a day, the sulphide has totally disappeared [46]

Table 17   Chemical Analyses of Hair Residues

Parameter	Unit	Sample 1	Sample 2	Average
pH	-	12,5		**12.5**
H_2O	$\%_{wm}$	84.2	81	**82.6**
LOI	$\%_{dm}$	86.4		**86.4**
TOC	$\%_{dm}$	48.0		**48.0**
N_{total}	$\%_{dm}$	11.4	10.8	**11.1**
C/N	-	4.2		**4.3**
P_{total}	$mg/100g_{dm}$	0.32		**0.32**
K_{total}	$mg/100g_{dm}]$	19.0		**19.0**
Ca_{total}	$\%_{dm}$	5.63	7.4	**6.5**
Cl^-	$\%_{dm}$	0.63		**0.63**
Oil & fat	$\%_{dm}$	6.3		**6.3**
Salmonella	-	n.d.		**n.d.**
Escherichia	MPN/g	< 3		**< 3**

n.d.   not detected

5.5 Trials

5.5.1 Introduction

After carrying out several trials with small-scale windrows, the low-cost and low-sophisticated technology of windrow composting was abandoned.

It could be shown, that in principle, composting is possible, but not in an open system. Serious odour- and insect problems must be expected.

A solution of these problems was seen in designing a closed composting system. A bench scale reactor was constructed. A description of this reactor is given in section 5.3.1.2. Drawings can be found in Annex C. A detailed description of the trials that were carried out in this reactor, is given in Annex F.

Process parameters were defined, which are expected to have main influence on the composting process and on the product. These parameters are:

- Substrate
- Bulking material
- Amendments
- Volume ratio
- Aeration rate
- Turning frequency
- Water consumption

In a "trial matrix" (see Table 18 in section 5.5.2) these parameters are summarised for the respective trial. In section 5.5.3 the parameters are discussed in more detail. For each substrate – fleshings, thermal fleshings and hair residues – concrete recommendations are given. However, these numbers must be seen as rule of thumb. For operating a composting plant, too many factors and interactions of them, have to be taken into consideration.

After defining the proper process parameters, the attention is concentrated on the product (see section 5.5.4). Chemical properties are analysed and plant tolerance is tested.

By gaining knowledge about the process and the product and discussing the results (section 5.6), it will be possible to give recommendations to small and medium sized (SME) tanneries located in developing countries.

5.5.2 Trial Matrix

In Table 18 the main parameters are defined for the respective trial. Trial #1 - #6 are trials with the substrate fleshings without any pre-treatment. Trial #7 - #13 are trial with fleshings that were pre-treated thermally. And finally, trial #14 – 16 are trials with the substrate hair residues. Though the process conditions for the trials with hair residues were bad (problems with the air supply system), the defined parameters are representative. Hair resides are a "good-natured" substrate, what means that without great efforts a high-quality product can be produced. Working with fleshings and thermal fleshings on the other hand, is much more difficult.

Table 18   Process Parameters of Trial #1 - #17

| Parameter		Unit	Trial															
			Fleshings						Thermal Fleshings							Hair Residues		
			#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14	#15	#16
Substrate	Fleshings	l	146	142	146	200	150	100	-	-	-	-	-	-	-	-	-	-
	Thermal fleshings	l	-	-	-	-	-	-	205	202	210	210	90	100	100	-	-	-
	Hair residues	l	-	-	-	-	-	-	-	-	-	-	-			160	150	75
Bulking material	Wood chips	l	415	415	280	200	300	210	420	200	-	147	-	-	100	170	240	120
Amendments	Saw dust	l	-	-	-	-	-	50	-	180	110	-	-	-	50	60	40	30
	Horse manure	l	-	-	165	60	60	-	-	-	-	-	-	-	-	-	-	-
	Compost	l	-	-	-	-	-	-	-	-	210	-	100	70	-	-	-	-
	Market waste	l	-	-	-	-	-	-	-	-	-	147	-	-	-	-	-	-
Volume ratio		$l/l_{substrate}$	2.8	2.9	2.8	1.4	2.6	2.6	2	1.8	1.5	1.7	1.1 v	0.7 v	1.5	1.4	1.9	2.0
Air flow		$m^3_{air}/h\ m^3_{substrate}$	2.05	2.11	2.05	1.5 v	2	v	1.46	1.48 v	5.7 v	11.7 v	6.6 v	6 v	18 v	15.4	6	3.8
Turning		-	0	2	2	0		1	0	1	3	3	2	1	1	1	1	1

v   varied

5.5.3 Parameters

5.5.3.1 Substrate

Three different types of substrates can be distinguished: fleshings, thermal fleshings and hair residues. Depending on the substrate, the composting parameters and process differ significantly. Furthermore the product "compost" shows different properties. About the chemical analyses and fertilising properties of the different products see section 5.5.4.

A crucial parameter for designing a composting process and plant is the time that is required to produce a biological stable product. In principle, the composting process can be divided into 3 phases (see Figure 24).
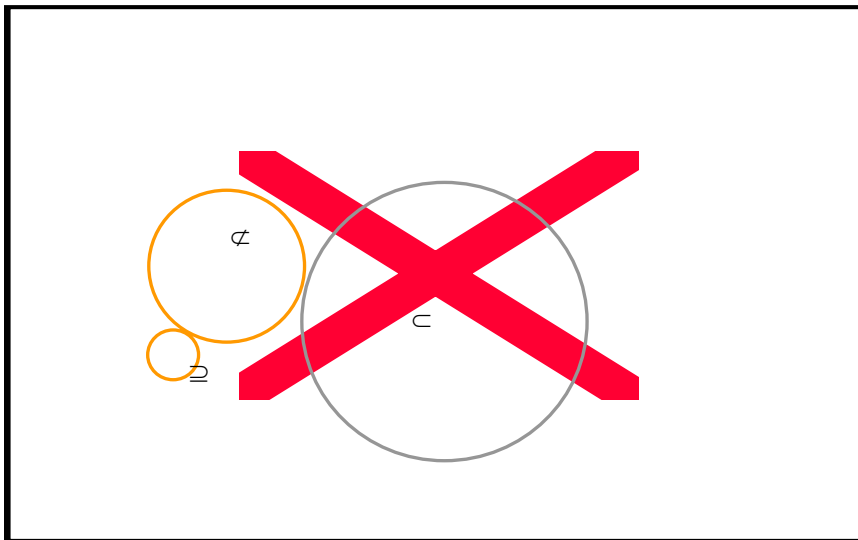
Figure 24   General Development of Temperature during the Composting Process

The two smaller circles on the left hand are marking the high rate phase – consisting of lag- ($\supseteq$) and log-phase ($\not\subset$) until thermophilic temperatures are reached. The high rate is finished when substrate temperatures decrease to approximately 40.

The lag-phase (small left circle / $\supseteq$) is the time of adaptation of the microbiological flora to the substrate. The lag-phase can be reduced by proper physical and chemical conditioning. For sterile substrate also inoculation can influence the duration of adaptation.

The log-phase (middle circle / $\not\subset$) is the phase of bacterial growth and beginning organic degradation. Due to the exothermic decomposition the temperature rise above 50 - 55°C. The mesophilic bacteria will be replaced by thermophilic ones and the substrate temperature is further increasing.   Bacterial activity is limited by 70 – 80°C which are the highest temperatures reached by composting processes.

Due to the given temperature range of thermophilic bacteria the composting process is auto-controlled. After several days (depending on the chemical composition of the substrate and the air supply) of thermophilic temperatures, process temperatures will decrease slightly until mesophilic bacteria flora is reinstalled ($\subset$).

During the following days the temperature will decrease further to about 40°C.This indicated that the high-rate phase is finished and curing phase starts.

Due to the fact that during the high-rate phase the main biological activity can be observed the first weeks of composting are accompanied by strong odour generation. For better process control the high-rate phase normally is operated in closed-vessel or reactor systems. Curing phase on the other hand normally is performed in windrow- and pile systems. This combination has turned out to be the most effective one.

In Table 19 the duration of the lag/log-phase, high rate phase and the maturation phase of the respective substrate are given. The lag/log phase is defined as the time that is required, until the bacteria are adapted to the substrate and temperatures >70°C are reached. 70°C have been defined to be a crucial temperature limit for composting fleshings. In addition to that, by exposing the substrate to temperatures >70°C it can be assumed to be free of pathogens.

The high rate phase is the phase of high temperatures and main biological decomposition. It includes the lag/log-phase. In this context, the high rate phase should be seen as the time the substrate has to be treated in a closed vessel. Although substrate temperatures may stay high, storage on open air is possible. Condition is, that no malodour is released by the substrate. In this context the maturation phase means the time from reactor discharge until a more or less plant tolerant product exists.

Table 19   **Duration of lag/log-, High Rate- and Maturation-Phase of the Respective Substrate**

Substrate [days]	lag/log Phase	High Rate Phase	Maturation Phase
Fleshings	3 – 5	14 – 21	> 60
Thermal Fleshings	2 – 3	10 – 14	30 – 45
Hair Residues	3 – 5	10 – 14	30 – 45

In Figure 25 the development of temperature, mass and volume during the high rate phase of trial #5 trial is shown. One can see that the lag-phase (time that is required by the bacteria to adapt to the substrate) is short (< 1 day). This is because of the amendment "horse bed stale" that has positive effect on the process temperature (see Figure 30). The volume of the substrate mixture was reduced by 30%. The entire reduction in volume took place during the first 5 days. The substrate mass was reduced by 30% as well. The main reduction took place during the fist 5 days. It has to be stated that this reduction is not caused by decomposition and oxidation of the substrate, but because of generation of leakage.

Unfortunately, the substrate temperature of 5 trials with fleshings was recorded only for the high rate phase. For trial #6 the temperature was recorded until the product turned into a maturated, biological stable compost. However, by this trial the influence of the aeration rate

on the process temperature has been investigated. Therefore the temperatures of the high rate phase are not representative and will not be shown here.
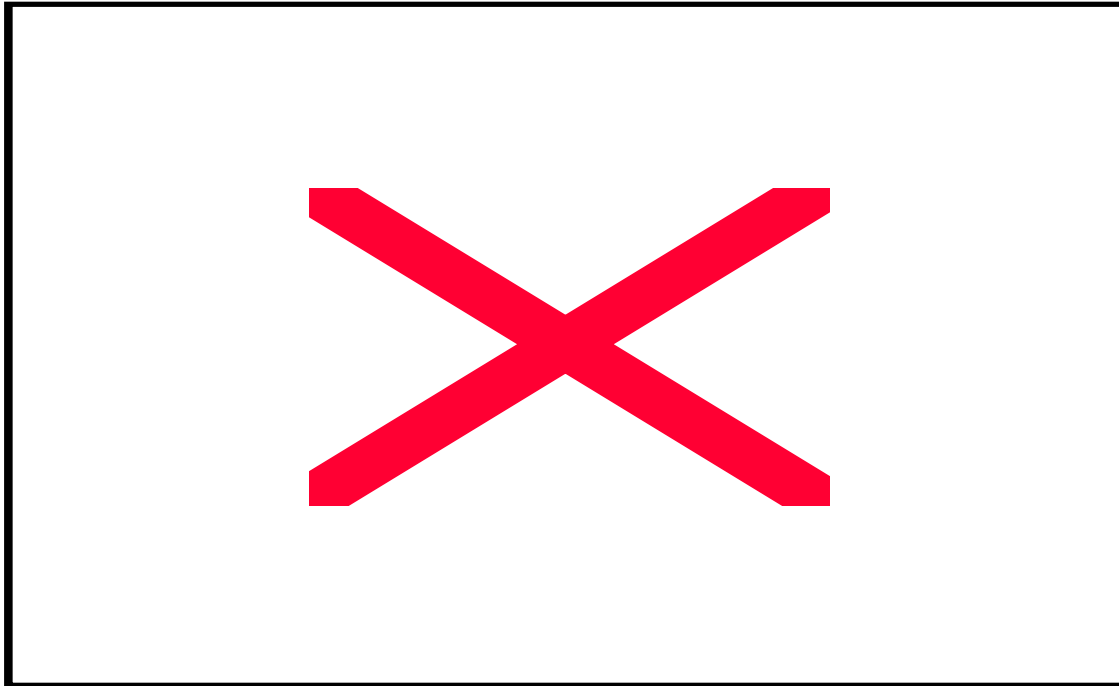

Figure 25   **Process Temperature, Mass and Volume - Development with Time (Fleshings)**

Based on the experience made with the substrate fleshing it can be assumed that the lag and log phase (time until process temperatures first exceed 70°C) of a mixture of fleshing with wood chips without horse manure is approximately 5 days. Adding horse manure will reduce this phase to 3 days.

The entire high rate phase must be assumed between 14 and 21 days. In this case, "end of the high rate phase" not necessarily means that the process temperature is < 40°C, but means that the substrate can be discharged and stored on piles without generating malodour or attracting insects.

Once discharged and stored on open air, it will take at least 30 days until the substrate temperatures decrease to ambient temperature. For the entire maturation process at least 60 days have to be calculated (see chapter 5.6)
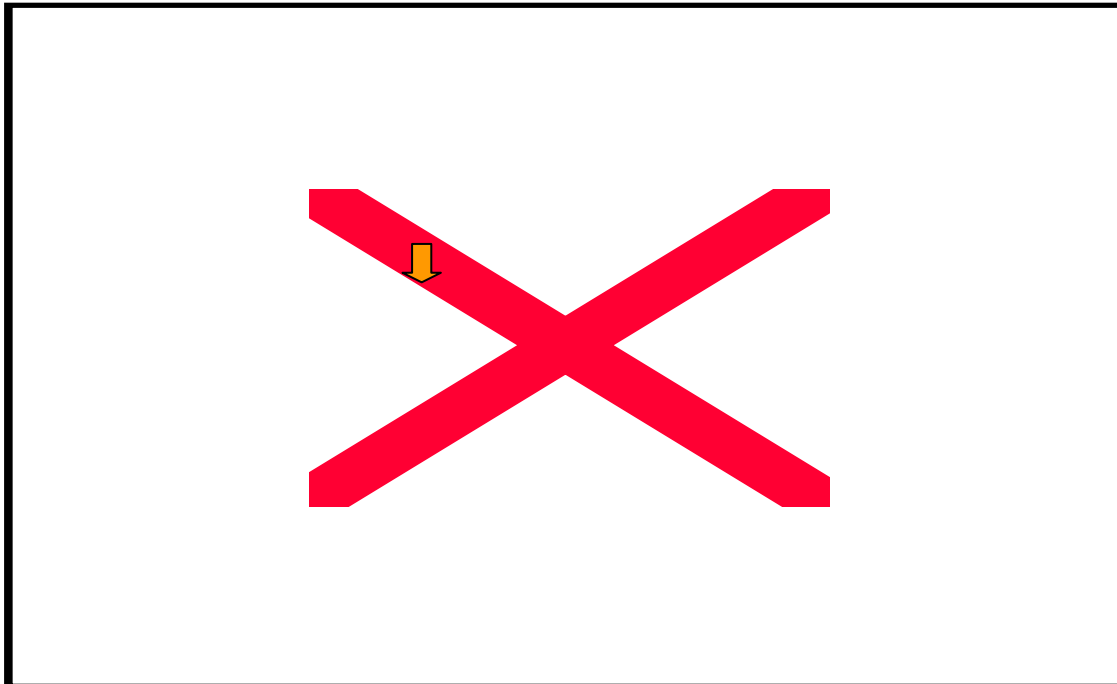
Figure 26   **Process Temperature - Development with Time (Thermal Fleshings)**

Looking at the development of the process temperature of trial #9 one can state the following (see Figure 26) The lag and log phase of thermally treated fleshings is approximately 3 days. By adding horse manure the time required by the bacteria to adapt to the substrate and to show sufficient activity to increase the process temperature to >70°C can be reduced to 2 days. The substrate of trial #9 was discharged on day 18 (see arrow in Figure 26), but from experience with this type of substrate, it can be stated that discharge is feasible after a high rate phase of 10 to 14 days. Substrate temperature still will be in the thermophilic range, but "nuisance-free" storage on windrows is possible. The reduction in volume can be expected to be between 15 and 20%. Mass reduction during the high rate phase depends on the quantity of water that is added during the process. Therefore this parameter will be discussed in chapter 5.6.

Depending on the aeration rate that was chosen during the high rate phase, the maturation phase will vary. For trial #9, it took approximately 30 days until ambient temperatures were reached. With trial #13 – an approximately 3 time higher aeration rate was adjusted – it could be shown that after 15 – 20 days ambient temperature can be reached. For the entire maturation phase approximately 30 – 45 days have to be assumed (see chapter 5.6).

In Figure 27 the temperature graph for a composting trial with a mixture of hair residues, saw dust and wood chips is shown (trial #15).

During this trial twice troubles with the air supply. Hence corrections in the temperature graph were made. On day 2 the temperature dropped to ambient due to lack of oxygen. Therefore the first two days were crossed. On day 9 the air supply system failed again. The temperature dropped to ambient. After the air supply was reinstalled again, the substrate

temperature rose to > 70°C. It can be assume that the temperature would have stayed high, under normal process conditions. Hence, in Figure 27 this temperature drop is not shown.
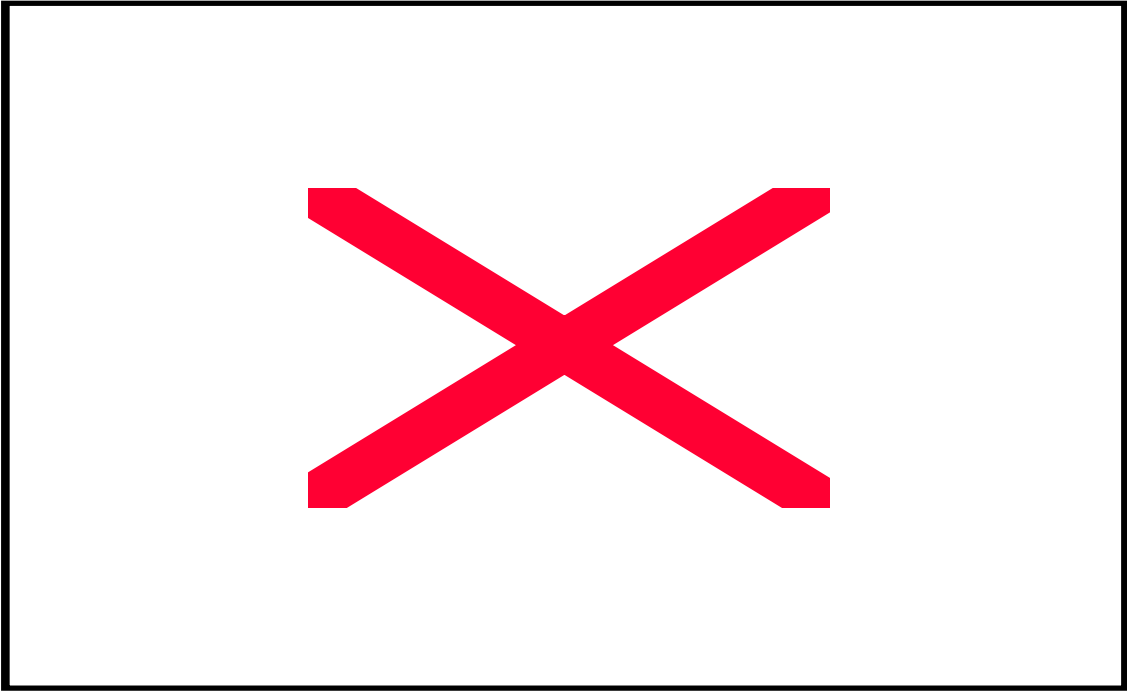
Figure 27   Process Temperature - Development with Time (Hair Residues)

Without suitable amendment (horse manure) the lag- and log phase will take about 4 to 5 days. It can be assumed that, by adding horse manure it can be reduced to 3 days. On day 21 the substrate of trial #15 was discharged and stored on open air. Operate the process for such a long time in a closed vessel is not necessary. Already after 10 days of operation the reactor can be discharged and the substrate can be stored "nuisance-free" on piles. The substrate temperature will hardly exceed mesophilic temperatures and after 30 days the temperature will be ambient. As it could be shown by the trials that were carried out with this type of substrate, independently from the duration of the high rate phase in the reactor, the total treatment time (until ambient temperature is reaches) will be about 40 days.

For a proper maturation approximately 30 to 45 days can be assumed (see also section 5.6).

5.5.3.2 Bulking Material

Composting is an aerobic biological process. That means that organic matter is decomposed by bacteria that need oxygen for their metabolism. The supply with oxygen (air) can be achieved by natural or forced aeration. In both cases the oxygen transport from the outside into the substrate must be guaranteed. Hence, a certain porosity of the substrate mixture must be given. If the main substrate lacks of sufficient porosity it can be mixed with bulking material. The main characteristics of bulking material are its porosity, a certain water holding capacity and that it is not or hardly biodegradable. Generally bulking material is mixed with the main substrate, processed through the composting process, and after separation from the compost, recycled again. Due to material losses a certain make-up with new bulking material is required. Cheap and easily available bulking materials are wood chips and bark. For the reactor trials described in this thesis, wood chips were used. In Table 20 a recommendation for the use of bulking material for the substrate "fleshings", "thermal fleshings" and "hair residues" is given.

Table 20 **Use of Bulking Material for the Respective Substrate**

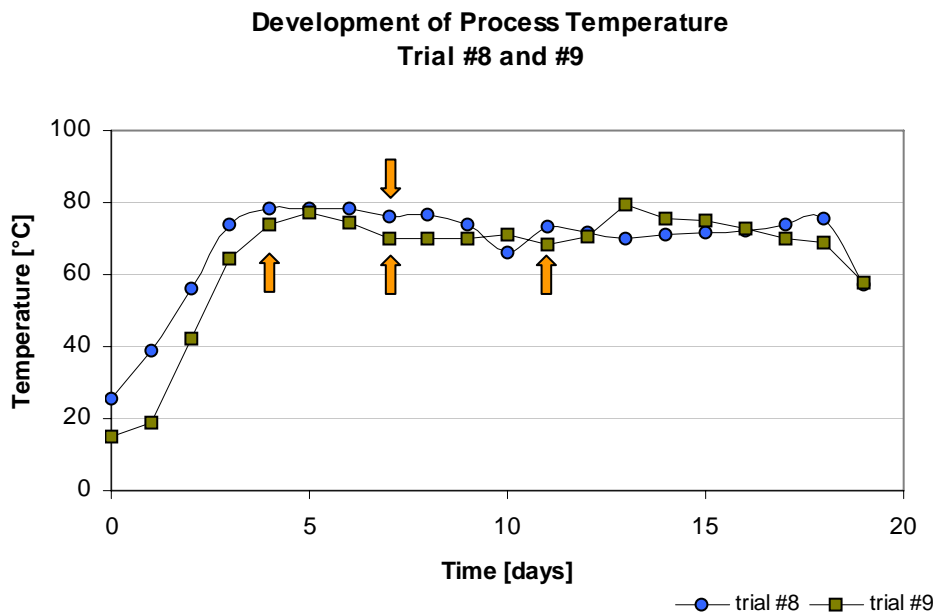| Substrate	Bulking material
Fleshings	++
Thermal Fleshings	+
Hair Residues	+

++   indispensable
+   highly recommended

Due to their dense, lump-like structure **composting of fleshings without structure material is not possible**. Even when mixed with recycled compost or saw dust, the mixture will result in a pulp with little porosity.

Thermally treated fleshings show a different structure than fleshings. They have a significant lower moisture content and are best described as a crumbly matter that can easily be mixed with bulking material and/or amendments. Composting of thermal fleshings without amendments or bulking material is not possible (see also chapter 5.5.3.4 – Volume Ratio). Substrate mixture of trial #8 is a mixture of thermal fleshings, wood chips and saw dust. Trial #9 is a substrate mixture of thermal fleshings, saw dust and compost. The process parameters of both trials are comparable. The process temperatures of both trials are shown in Figure 28.

Trial #9 – the trial without bulking material – shows a longer log–phase (time until thermophilic temperatures are reached) than the trial without bulking material. This can be explained by the fact that during trial #9 the air (oxygen) distribution and supply is worse compared to the lose substrate mixture of trial #8. After thermophilic temperatures were

reached they could be maintained only by frequent turning of the substrate – hence providing sufficient free air space (about the importance of sufficient free air space see 5.5.3.6). The arrows in Figure 28 indicate the tuning actions (discharging and recharging of the reactor). During trial #8 a single turning was sufficient, whereas during trial #9, 3 turning actions were required. The substrate compacted firmly what made the discharge of the reactor difficult.

Development of Process Temperature
Trial #8 and #9

Figure 28   Process Temperature - Development with Time (Thermal Fleshings)

No advantage could be found by omitting the bulking material "wood chips". The main disadvantage would be the increased turning frequency that would increase the operation costs.

Hence, for the substrate "thermal fleshings" the use of bulking material is highly recommended.

The trials which were carried out with the substrate "hair residues" were a mixture of hair residues, wood chips and saw dust. Because of the low porosity and the physical appearance of the substrate it was assumed that bulking material is required for a proper operation of the process. Possibly composting of hair residues works without bulking material, yet with an increased turning frequency as mentioned above.

For the substrate "hair residues" the use of bulking material is highly recommended as well.

5.5.3.3　Amendments

Amendments are organic or inorganic supplements that are mixed with the main substrate bulking material in order to improve the composting process or the final product. F.AMLINGER [52] gives a long list of possible amendments and the results that can be achieved by applying them. For the trials carried out with the solid, non-chromium containing waste fractions 4 different types of amendments were applied: Horse bed stale, market waste, saw dust and recycled compost.

In principle, it must be stated that amendments show two significant disadvantages. Additional costs in purchasing them can be expected and by processing a higher substrate mixture increased operation costs must be expected. Thus, amendments should be added only if it is absolutely necessary.

In Table 21 the impact of the investigated amendments on the composting process and the product quality is evaluated qualitatively. Finally a recommendation which amendment can or should be added, is given.

Table 21　　　　　　　　**Impact of Respective Amendment on Process and Product**

Amendment	Process	Product	Recommendation
Market Waste	o	o	-
Horse Bed Stale	++	++	++
Saw Dust	+	--	-
Recycled Compost	+	o	o

++	highly recommended
+	recommended
o	neutral
-	not recommended
-	absolutely not recommended

Market waste was the organic waste fraction collected at a local market. It consisted mainly in vegetables and fruits. Slight impurities of plastics, paper and glass could be found (< 5%). For trial #10 a mixture of thermal fleshings, wood chips and market waste was prepared. Compared to a mixture of thermal fleshings, wood chips and saw dust (trial #8), no significant advantage could be achieved. In Figure 29 the development of the process temperatures of trial # 8 and trial #10 is shown. The decrease of temperature of trial #10 around day 10 is not caused by the amendment, but by troubles with the air supply.

One difference that can be mentioned, but shows no influence on the entire process, is the fact that the lag-phase (the time that is required by the microbiological flora to adapt to the substrate and process condition) is shorter for the trial #10 (market waste) than for trial #8 (saw dust). That means that the process increases faster during the first day. This can also be seen by the CO_2 production rate.

On day 1, for trial #10 approximately 170 l_{CO2} / h m³ $_{substrate}$ are calculated. Trial #8 generated at day 1 only about 50 l_{CO2} / h m³ $_{substrate.}$ On day 3 both trials showed the same CO_2 production (approximately 220 l_{CO2} / h m³ $_{substrate}$).

An other difference that could be stated is self-evident. The volume of the substrate of trial #10 (market waste) is reduced during the high rate phase by approximately 60 %. The volume reduction of trial #8 is about 20 %. However, obviously the volume reduction is caused by the amendment market waste and not by the main substrate thermal fleshings.

Furthermore, the compost produced by trial #10 showed no advantage compared with other types of compost (see chapter 5.5.4).

The amendment "market waste" can not be recommended - neither to improve the degradation process nor to improve the product quality.

**Development of Process Temperature
Trial #8 and #10**
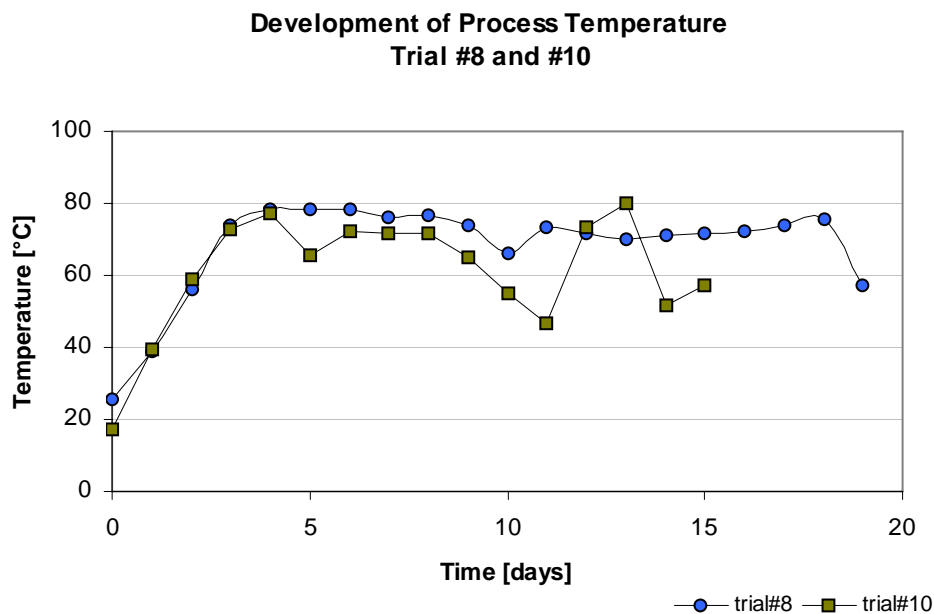
Figure 29   Development of Process Temperature with Time (Thermal Fleshings)

Horse Bed Stale is a mixture of finest wood chips (approximately 80%), horse manure and urine (approximately 20%). This type of amendment shows three main advantages.

First the wood chips are "finer" than the wood chips that are used as bulking material. They show a significant higher water holding capacity. This results in a more constant moisture content of the substrate and more uniform process temperatures (see Figure 30)
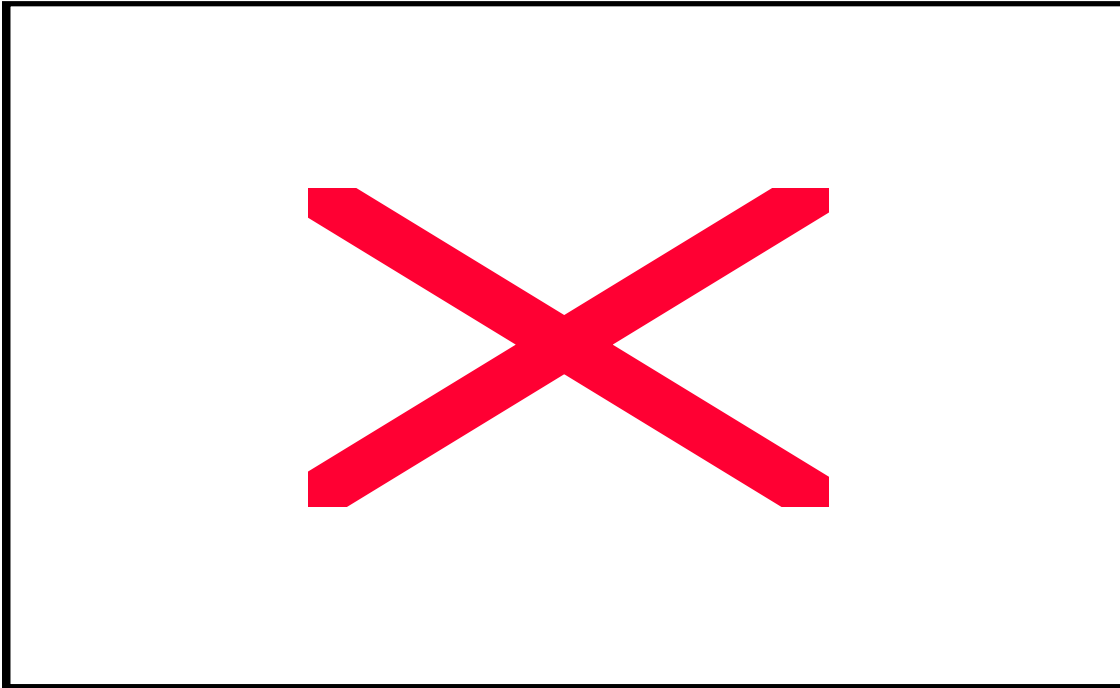
Figure 30   Process Temperature – Development with Time (Fleshings)

Second, horse manure and urine is known to generate high temperatures during biological decomposition. This can be seen in Figure 30. The substrate mixture of trial #2 is a mixture of fleshing and wood chips. The trial #3 substrate is a mixture of fleshing, wood chips (2/3 in volume) and horse bed stale (1/3 in volume). The process parameters of both trials are the same. Comparing the development of the process temperature of both trials, one can see, that the increase in temperature of trial #3 is faster than the one of trial #2 – that means that the lag and log phase (time that is required to reach thermophilic temperatures) can be reduced by 1 to 2 days by adding horse manure. In addition to that trial #3 shows higher temperatures (5 – 10 °C).

Shorter lag/log phase, higher temperatures and a more uniform process temperature lead to a better decomposition of the substrate.

Finally, the amendment "horse bed stale" shows positive impact on the fertilising properties of the compost. The chemical analyses and the plant tolerance of this product will be discussed in chapter 5.5.4.

Adding horse bed stale to the main substrates fleshings and thermal fleshings is highly recommended. Positive effects on the process as well as on the product quality can be achieved.

Saw dust is the cheapest and easiest available carbon source. Addition of carbon rich amendment is necessary when the main substrate is rich in nitrogen. In principle it can be stated that the optimum ratio carbon to nitrogen (C/N) is between 15 – 30. If the C/N ratio exceeds 30, it means that carbon is found in excess and that the composting process will last longer. Nitrogen becomes a limiting factor for the cellular syntheses and hence no new cells can be build-up. The excess carbon has to be removed by oxidation until a proper C/N range is reached.

In case of a C/N ratio that is lower than 15, nitrogen is found in excess and will be released from the system by the formation of ammonia (NH_3-gas). That does not mean that the composting process will not work at all, but means that a part of the nitrogen is released as volatilised ammonia. The loss of nitrogen means on the one hand malodour and inhibition of the microbiological activity and on the other hand a lack of nitrogen in the product, resulting in a lower product quality.

The C/N ratio of fleshings, thermal fleshings and hair residues (12.3, 6.1 and 4.2) is lower than 15. From this point of view the addition of a carbon rich amendment (saw dust) is required. On the other hand the biological decomposition of saw dust (lignin) is difficult and takes a lot of time. This is the reason why the C/N ratio of the product is high (>25). Such a high C/N ratio of the compost has negative impact on the product quality.

In Figure 31 the development of the process temperature of trial #7, #8 and #11 are compared. Trial #7 is a mixture of thermal fleshings and wood chips. The trial #8 mixture consists in thermal fleshings, wood chips (1/2 in volume) and saw dust (1/2 in volume). Process parameters of the two trials are comparable.
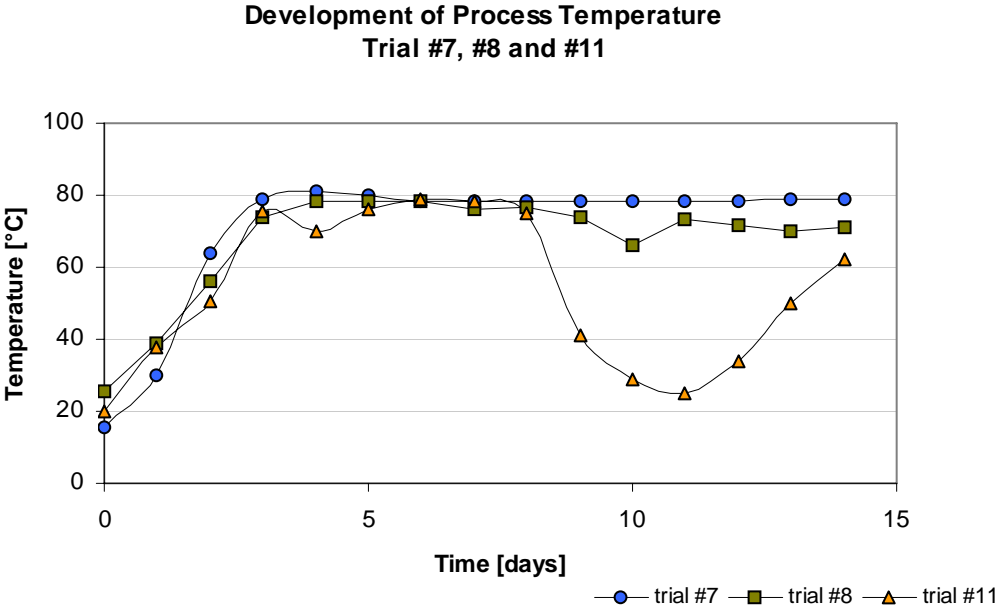
Figure 31   Process Temperature - Development with Time (Thermal Fleshings)

During the high rate phase no significant differences between the two trials can be seen. Ammonia is released in both trials but is absorbed and oxidised in the biofilter. Surprisingly, the product analysis of the composts from trial #7 and trial #8 show, that the total nitrogen content of trial #7 product (without saw dust) is higher than the one of trial #8 product (with saw dust) ($1.76\%_{dm}$: $1.29\%_{dm}$). As expected, the C/N ratio of the compost from trial #7 is significantly lower than the one of trial #8 compost (18 : 38)

As to chemical conditioning of the substrate – that means adjusting the C/N ratio – the addition of saw dust as a carbon source is not necessary. As to thermodynamic conditioning – that means adjusting the water content – the addition of a dry amendment is required. Even if it is not necessary to decrease the water content of the substrate mixture, it is indispensable to increase the water holding capacity.

An alternative to saw dust seems to be the addition of **recycled compost**. This type of amendment has the advantage that there are no additional purchasing costs. Since the recycled compost has to be processed through the plant, the operation cost is the same as for the addition of saw dust.

The main effect of the amendment "compost" is the adjustment of the moisture content and the increase of the water holding capacity. Since compost is biologically inert it will not contribute to the energy balance of the system.

In Figure 31 the development of the trial #11 process temperature with time is shown. Trial #11 is a mixture of thermal fleshings and recycled compost. The air flow of trial #11 is higher than the air flow of the other two trials. Increasing the air flow was possible because of the fact that initially the substrate mixture contained no wood chips. In this diagram on day 9 the reactor was discharged and the substrate of trial #11 stored on open air. Hence the temperature dropped for a few days.

It can be seen that there is no difference in the development of the process temperature between the three trials. From the process temperature it is the same whether no amendment, saw dust or recycled compost is added to the main substrate.

To adjust the moisture content and to improve the water holding capacity it is recommended to add recycled compost as an amendment.

5.5.3.4 Volume Ratio

The volume ratio V_R is defined by the volume of bulking material and/or amendments that is required per volume unit of substrate (fleshings, thermal fleshings or hair residues). The unit is m³/m³ $_{substrate}$. The volume ratio and the quantity of solid waste generated per day are the two most important numbers for the design of the reactor volume that influences the capital costs. Furthermore V_R is the decisive factor for the operation costs of a composting plant.

The key number V_R is a function of the physical properties of the substrate. Depending on the substrate, the water content can vary within a broad range. In literature the impression is given, that beyond the range between 40 and 60% water, composting is not possible. This is a little bit misleading. Microbiological activity will cease when the moisture content is less then 8–12% (see L.DIAZ [47]). On the other hand, C.G.GOLUEKE [42] recommends a water content for composting of saw dust and small chips between 75 and 90%. Fact is, that for most substrates biological decomposition reaches its optimum within the limits of 40 and 60%. A factor that is a function of the water content and other physical properties of the substrate as well is the "free air space" (FAS). R.HAUG [59] defines the free air space as follows:

$$FAS = 100 \times (1 - BD/SG) \times DM \qquad \textbf{Equation 4}$$

FAS	Free Air Space	[%]
BD	Bulk Density	[kg/m³]
SG	Specific Gravity	[kg/m³]
DM	Dry Matter	[%]

According to R.HAUG [59] for most substrates and most composting systems the free air space has to be approximately 30%. That means that approximately 1/3 of the total substrate volume has to be filled with air. If the free air space is significantly lower than 30% the composting process will not start.

In practice the water content and the free air space are adjusted by mixing the main substrate with bulking material and/or amendments. As a consequence for a given substrate the volume ratio is one of the main important variables by which the composting process can be influenced. In Table 22 the range of the required volume ratio for the respective substrate is shown.

Table 22   Required Volume Ratio V_R of Different Type of Substrate

Substrate	Range of Volume Ratio m³/m³$_{substrate}$
Fleshings	2.5 – 3
Thermal Fleshings	1.5 – 2
Hair Residues	1.5 – 2

Fleshings, due to their dense, lump-like characteristic and a water content between 75 and 80%, which results in a little free air space, show a high volume ratio. By carrying out several trials it could be shown that **2.5 to 3** m³ of bulking material and amendments are required per m³ of fleshings. This means, that per m³ fleshings 3.5 to 4 m³ reactor volume has to be provided.

In Figure 32 the development of the process temperature of trial #4 is shown. The initial volume ratio was 1.4 m³/m³$_{fleshings}$. On day 8, after several attempts to start the process by varying the air flow, the reactor was discharged and mixed with additional bulking material. By this change in volume ratio (from 1.4 to 2.6 m³/m³$_{fleshings}$) and water content of the mixture the process could be started.
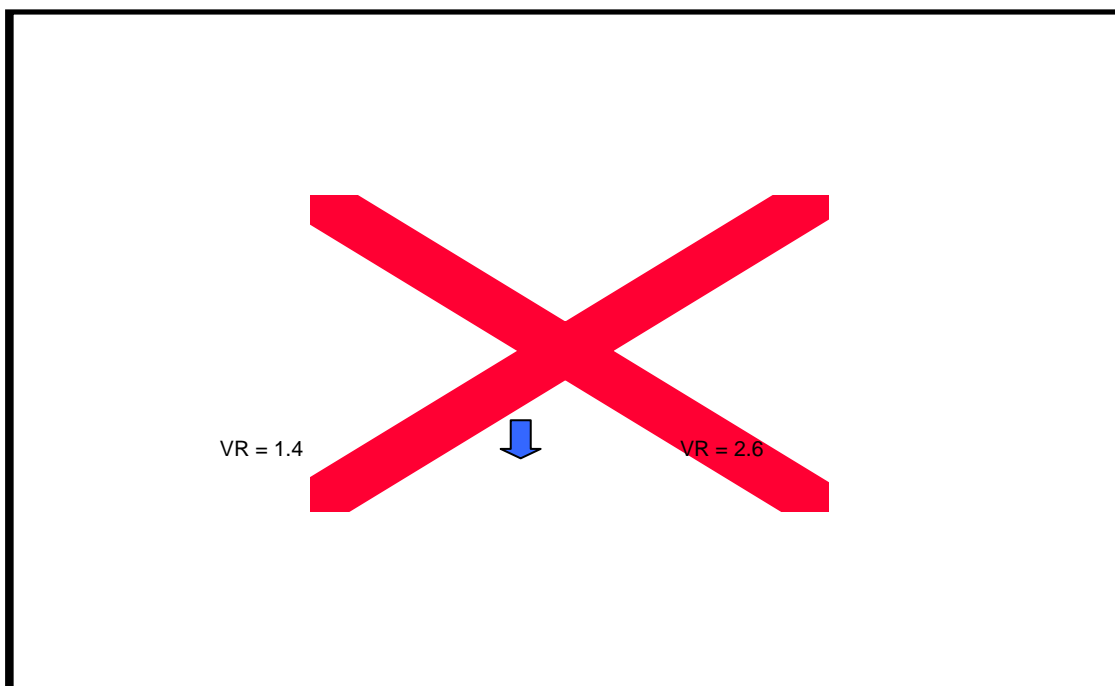
Figure 32   Development of Process Temperature by Changing the Volume Ratio (Fleshings)

Water content and physical properties of **thermally treated fleshings** are significantly different compared to the one of fleshings. Since the thermally treated fleshings are a dry (40 % water), crumbly matter the volume ratio can be reduced significantly.

In Figure 33 the process temperature of trial #12 is shown. On day 7 the volume ratio was changed from 0.7 to 1.4. On day 4 the air flow was changed. This parameter change caused a slight increase in temperature. However, on day 6 this increase in temperature stopped, which indicated that the volume ratio is too low. For thermal fleshings, an optimum range of the volume ratio between **1.5 and 2.0 m³/m³ thermal fleshings** was found.
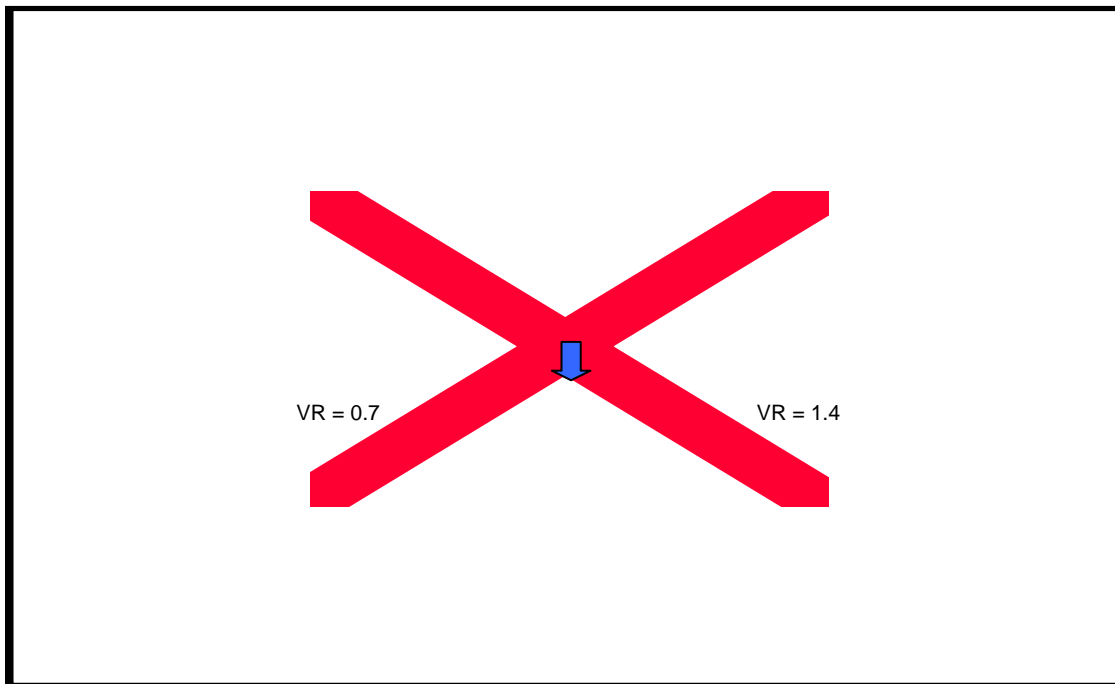
Figure 33   Development of Process Temperature by Changing the Volume Ratio (Thermal Fleshings)

The water content of **hair residues** is higher than the one for thermal fleshings. Therefore it can be expected that also the volume ratio will be higher. Actually this is the case. It could be shown that the process temperature immediately starts to increase when the volume ratio is 2.0 whereas certain delay can be expected when working with a volume ratio of 1.4.

As an optimum range of the volume ratio for a mixture hair residues with amendments and bulking material **1.5 to 2.0 m³/m³ $_{hair}$** was determined. This is the same range as given for the treatment of thermally treated fleshings. The difference between the two substrates is, that a mixture of thermally treated fleshings with a volume ratio of 1.5 will work without any problems. A mixture of hair residues with a volume ratio of 1.5 will work as well. To guarantee a trouble-free operation with the latter, a value closer to 2.0 is recommended.

5.5.3.5   Air Flow

The air flow is the only parameter to control the high rate phase during the composting process. The air supply has three main purposes. Sufficient air has to be provided to correspond to the **stoichiometric oxygen demand** to oxidise the organic matter. This term generally is the smallest one. 10 to 30 times greater may be the air demand for **moisture removal**. By increasing the air flow through a composting substrate, waste gas will leave the substrate with a temperature near process temperatures. According to the water content of saturated air the corresponding quantity of water will be removed from the substrate.

The main quantity of air is required for **heat removal**. Thermophilic temperatures (>55°C) are required at the beginning of the composting process. This is necessary to kill pathogens that may be found in the substrate. However, best decomposition of organic compounds will take place under mesophilic temperatures (35–55°C). By varying the air flow, substrate temperatures can be kept in a mesophilic range.

R.HAUG [59] gives some algorithms to calculate the required air flow rate to meet with the 3 main purposes mentioned above. However, this is of theoretic value and interesting for simulation models. For operating a composting plant, too many factor have to be taken into consideration. Hence, for practical operation of a plant, rules of thumbs and experience are of highest importance.

In Table 23 for the respective substrate the required air flow is given. The figures are not "exact" figures. They depend on the composting system, the type of amendment, moisture content, etc. However, the numbers given in Table 23 are rules of thumb that derive from the operating experience of the 600l bench scale reactor.

Table 23   Required Air Flow for the Respective Substrate

Substrate	Air Flow [m^3_{air}/$hm^3_{substrate}$]
Fleshings	6 - 15
Thermal Fleshings	15 - 35
Hair Residues	2 - 6

In Figure 34 the process temperature of trial #6 (mixture of fleshing, saw dust and wood chips) is shown with the air flow rate. To investigate the influence of the air flow on the process temperature, the flow rate was varied from 3 to 42 m^3_{air} / h $m^3_{substrate}$. What can be seen in this diagram is that the process temperature strongly depends on the air flow. There are some critical flow rates that must be designed. To start the composting process and to reach temperatures >70°C the air flow rate may not exceed 6 m^3 per hour and $m^3_{fleshings}$. Once high thermophilic process temperatures are reached the air flow can be increased but must not exceed 15 m^3 per hour and $m^3_{fleshings}$.
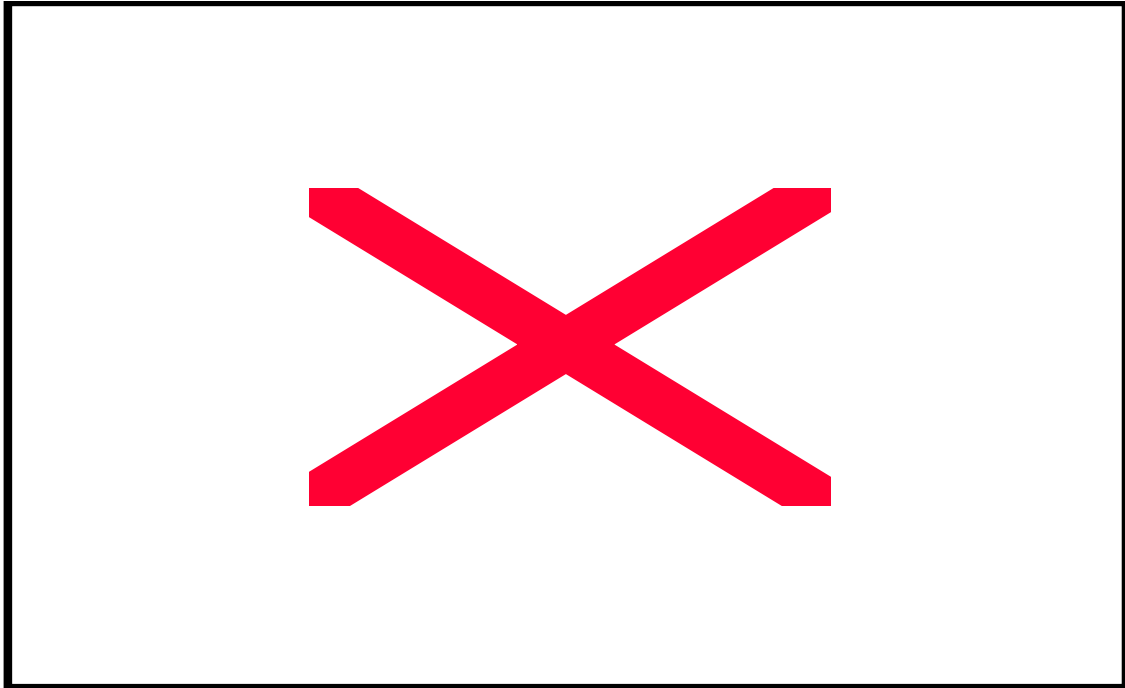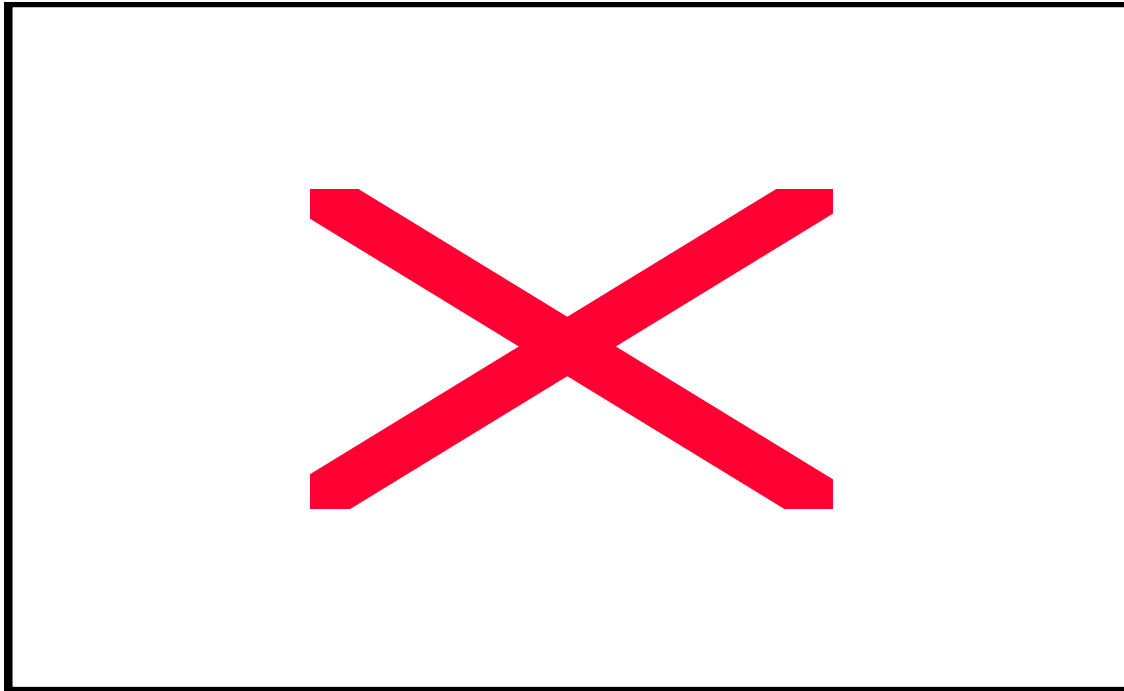
Figure 34   Development of Process Temperature by different Air Flow Rates (Fleshings)

The high volume ratio of 2.6 and the inhomogeneous mixture of fleshings, structure material and amendment sign responsible for the cooling and hence stopping of the composting process when the air flow rate exceeds these limits. Main disadvantage of such a low air flow rate is the low decomposition rate of the substrate. As it can be seen in Figure 34 after 30 days of operation still thermophilic temperatures were measured. Operating with a relative small air flow leads to a longer duration of the high rate phase and maturation phase as well.

The same investigations were made with thermally treated fleshings. In Figure 35 the influence of the air flow rate on the process temperature is shown. Starting with an air flow of approximately 15 m³ per hour and m³$_{thermal\ fleshings}$ will be the proper air flow to increase the process temperature to a thermophilic range. Once temperatures exceeding 70 °C are reached the air flow rate can be increased to approximately 35 m³$_{air}$ per hour and m³ $_{thermal\ fleshings}$. By this increase the process temperatures can be reduced to mesophilic ranges. This air flow rate is approximately 3 times higher than the one which is considered to be the upper limit for the substrate "fleshings". The explication must be seen in the different physical properties of the two substrates.

On day 15 the substrate was discharged. Hence the air flow rate in Figure 35 is zero on this day.

A high air flow has a significant influence on the duration of the high rate phase and the curing phase as well.

Figure 35   Development of Process Temperature by different Air Flow Rates (Thermal Fleshings)

The trial carried out with the substrate "hair residues" showed that a small flow rate is required to maintain proper process temperatures. In Figure 36 the development of the process temperature is shown with a varying air flow rate. Initially the air flow rate of >6 m³ per hour and m³ $_{\text{hair residues}}$ was chosen too high. The decomposition process started when the air flow rate was decreased to 2 m³/h m³ $_{\text{hair residues}}$. With 4 m³ per hour and m³ $_{\text{hair residues}}$ thermophilic temperatures can be maintained. It can be assumed that 6 m³/h m³ $_{\text{hair residues}}$ the process temperature can be kept in a mesophilic range. Although this assumption is not proven by this trial, it can be seen by the fact that the process temperature slightly increased on the first day when 6 m³/h m³ $_{\text{hair residues}}$ were adjusted.
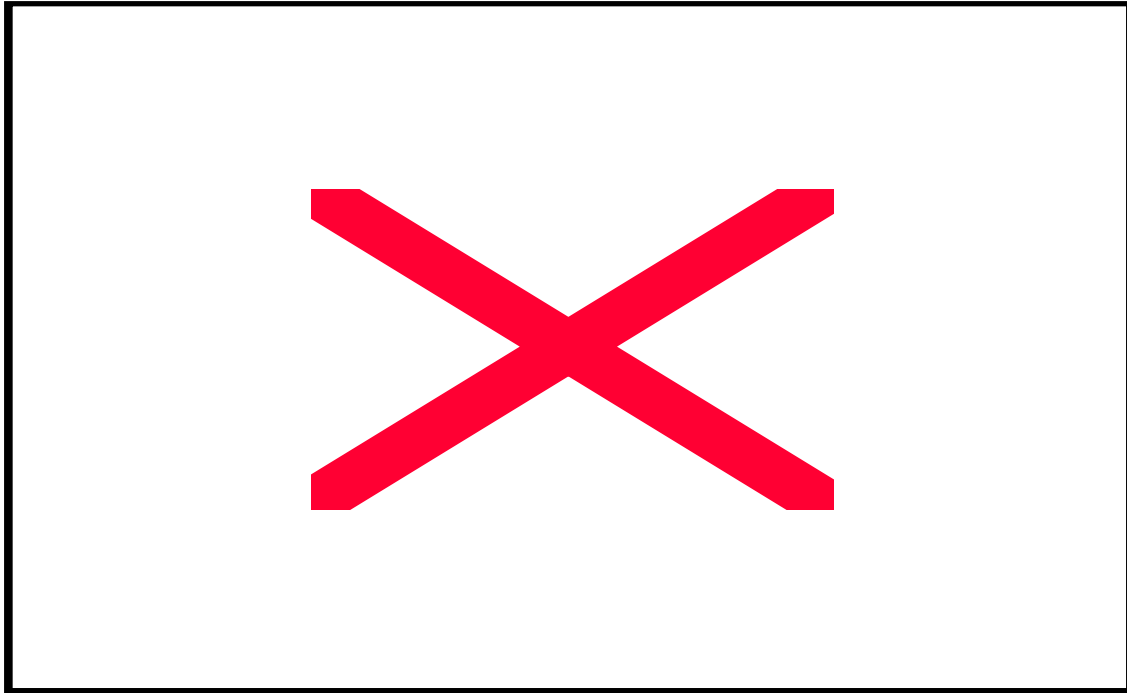
Figure 36   Development of Process Temperature by different Air Flow Rates for Trial #15

5.5.3.6   Turning Frequency

Turning and Mixing the substrate is an important factor for successful composting. Several advantages can be achieved by turning.

Firstly, the structure of the substrate is destroyed by the mechanical strain. This leads to an increase of the surface area which positively influences the biological decomposition.

Secondly, by agitating the substrate, a homogenous temperature distribution is given. By exposing each substrate particle to thermophilic temperatures, the product can be assumed to be free of pathogens.

Thirdly, turning the substrate leads to a homogenous water content in the substrate, positively influencing the composting process. For composting systems that work without forced aeration, turning is of highest importance in order to guarantee a proper oxygen supply.

Finally, the microbiological activity is stimulated by mechanical agitation of the substrate.

The main disadvantage of frequent discharging and recharging of the reactor is an increase of the operation costs of the plant. Furthermore malodour may be released during the turning procedure.

In Table 24 the number of turning actions that are recommended for the substrate fleshing, thermal fleshings and hair residues are given. These numbers are a minimum number of discharging and recharging actions. The more frequent the substrate is turned and agitated the better will be the biological decomposition. From this point of view a recommendable reactor design seems to be a horizontal flow, agitated bin. In such reactors the substrate mixture is stirred permanently during the high rate phase.

Table 24   Recommended Number of Turning Actions for the Respective Substrate

Substrate	Number of Turning Actions [-]
Fleshings	3 – 4
Thermal Fleshings	1 – 2
Hair Residues	1 – 2

For composting fleshings without pre-treatment the turning – i.e. discharging and recharging the reactor – is crucial for a successful composting process. In Figure 37 the development of the process temperature of trial #1 and trial #2 are compared.
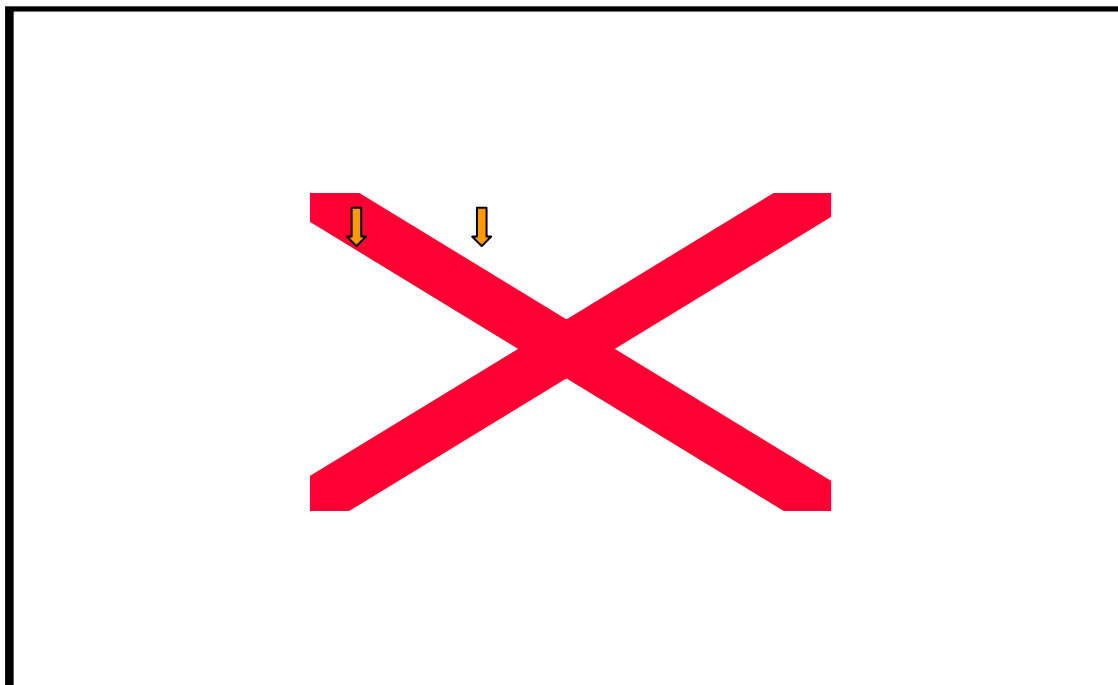
Figure 37   Development of Process Temperature with Time (Fleshings)

Trial #1 is a trial with fleshings without turning. The substrate of trial #2 was turned on day 5 and day 9 (see arrows). What can be seen in the diagram is that higher process temperatures are reached during trial #2. This is caused by a higher microbiological activity which is stimulated by turning.

What can not be seen on the diagram is that after 21 days of operation still entire fleshings were found in the substrate. By carrying out composting trials with windrows it could be shown that a temperature of >70°C is necessary to turn the fleshings into a white paste. This is considered to be necessary for biological decomposition. Unfortunately, in a reactor the temperature distribution is inhomogeneous as it is in a windrow.

The substrate temperatures in the centre are generally higher than the temperatures at the bottom, top and side of the reactor. To expose each particle to temperatures >70°C the substrate has to be turned. Furthermore by mechanical strain the structure of the fleshing is destroyed which favours the composting process.

For the substrate "**fleshings**" at **least 3 turning actions** during the high rate phase are recommended. The first turning should take place when 70°C are exceeded for the first time. This will be a few days after the start of the process (day 4). Intention of this turning is, to destroy the structure of the fleshings and to expose the entire substrate to a temperature >70°C. The following two turning actions will stimulate the microbiological activity and as a consequence accelerate the decomposition of the substrate.

Although turning is not required to destroy the structure of the substrate "**thermal fleshings**", 1 to 2 turning actions during the high rate phase have to be recommended for this substrate. Experiments with the "thermal fleshings" proved, that microbiological activity can be stimulated by mechanical agitation. In Figure 38 the CO_2 production rate of trial #8 is shown. The CO_2 production rate is defined as the volume of carbon dioxide that is generated per hour and m³ of substrate mixture. The parameter which actually was measured was the oxygen concentration of the waste gas. Taking into consideration the waste gas temperature, waste gas flow rate and the reactor volume, the CO_2 production rate was computed.

On day 6, 25 and 33 the reactor was discharged and recharged with the same substrate. On the days following the turning action (day 7, 26 and 34) a significant increase in the CO_2 production can be seen (see arrows in Figure 38).
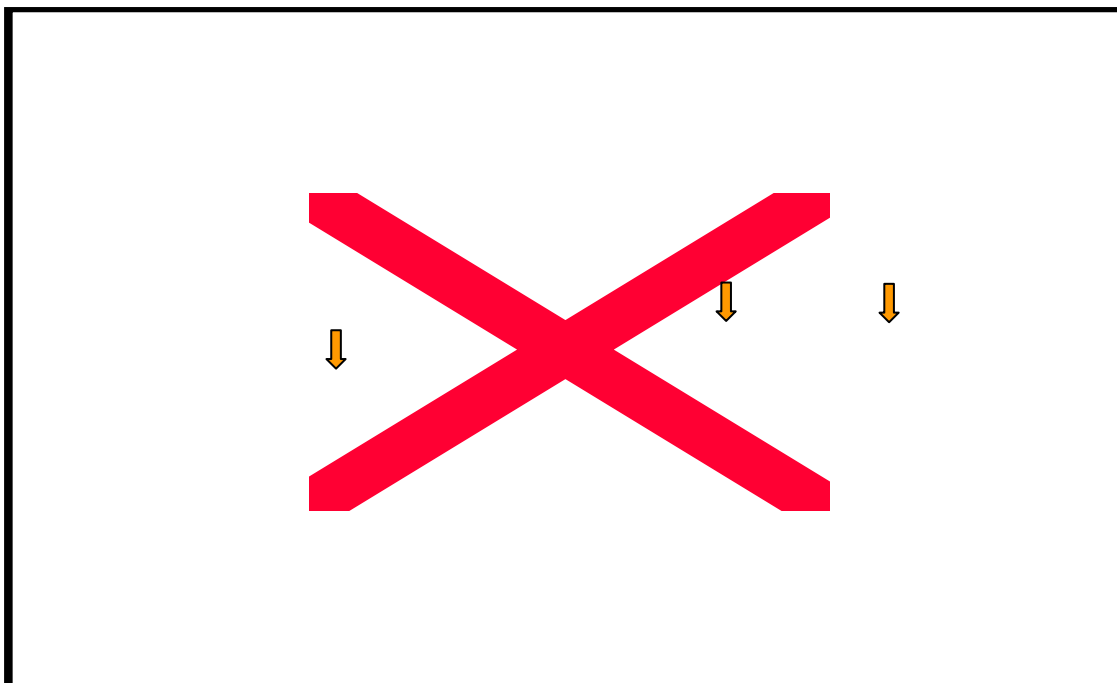

Figure 38   Carbon Dioxide Production Rate (Thermal Fleshings)

The numbers of turning actions have a significant influence on the duration of the entire composting process. The substrate of trial #7 was discharged after 3 weeks of operation. The substrate was not turned during the high rate phase and air flow adjusted to 1.46 m³ $_{air}$ / h m³ $_{substrate}$. Malodour indicated anaerobic spots in the substrate and high temperatures during the maturation phase indicated the presence of biological active substrate. After 2 months of treatment still temperatures > 40 °C were recorded.

After 2 months of treatment the substrate of trial #8 showed ambient temperature. That means that the compost of trial #8 was biologically inert. Whereas the product of trial #7 still was biologically active.

The parameters of trial #8 are comparable with the corresponding parameters of trial #7. Main differences are the turning frequency and the air flow that was increased during trial #8. For the substrate "**thermal fleshings**" at least **1 to 2 turning actions** are recommended during the high rate phase.

For the substrate "**hair residues**" the same can be stated as is stated for the thermal fleshings. **At least 1 to 2 turning** activities are recommended. However, the "hair residues" shows one peculiarity. The decomposition of the substrate is not complete. During the high rate phase the hair matter partially forms hard, dry balls that are difficult to decompose and which still can be found in the substrate after the high rate phase. Screening of the substrate separates the compost from this non-decomposed matter and wood chips. A reuse of the bulking material guarantees also the recycling of these residues. By mechanical agitation (screening and turning) these balls will be broken down and finally will be decomposed by anaerobic and aerobic processes.

5.5.3.7   Generation of Leakage and Consumption of Water

The generation of leakage is a crucial parameter for the design of a composting plant. It can be assumed that leakage leaving a compost plant is highly polluted with nitrate, ammonium, COD, BOD_5, chloride, sulphate. The actual pollution depends on substrate, composting technology and process conditions.

If leakage is generated, it has to be collected and treated. The most favourable measure that can be taken is the internal recycling. This can take place either by preconditioning (mixing with the initial substrate if this is too dry) or by irrigation during the maturation phase. Generally, compost that is stored for maturation purpose shows a certain evaporation. To maintain the proper moisture content, irrigation of water is required. Process effluents may be used for this purpose. However, it has to betaken into consideration, that problems with pathogens may occur.

If internal recycling is not possible, the effluent has to be collected and treated in a biological waste water treatment plant. For F.AMLINGER [52] this way of treating effluents makes no sense and is nothing else than a swift from an effluent problem to a sludge problem.

In Table 25 the quantities of effluent generated by treating the respective substrate is given. Working with fleshings leakage will be generated. Treating thermal fleshings is a water

consumer. And finally, the water demand that is required during the high rate phase of a process treating hair residues can be balanced by the effluent that is generated. However, in all three cases a leakage collecting system has to be installed.

Even in the two latter cases leakage will be generated, but can be irrigated during the high rate phase of the process.

Table 25   **Quantity of Effluent Generated by the Respective Substrate**

Substrate	Effluent [l/m³$_{substrate}$]	
Fleshings	300 - 350	Generated
Thermal Fleshings	300 - 400	Consumed
Hair Residues	0 - 100	Consumed

The moisture content of **fleshings** is between 75 and 80%. Mixing with bulking material and amendments may reduce the water content to 60 – 65%. These are proper conditions for the composting process, but leakage will be generated during the first days of operation. In **Figure 39** the accumulated quantity of leakage that was generated during the high rate phase of trial #5 is shown. What can be seen is that the total amount is generated during the first 6 day of operation. When thermophilic substrate temperatures are reached hardly any leakage is produced. On day 12 the leakage was recycled to the substrate. Hence the process temperature decreased on day 13. Due to the little water holding capacity of the substrate the main part of the effluent could be found in the collecting tank again. All in all 313 l effluent was generated by composting 1 m³ of fleshings.


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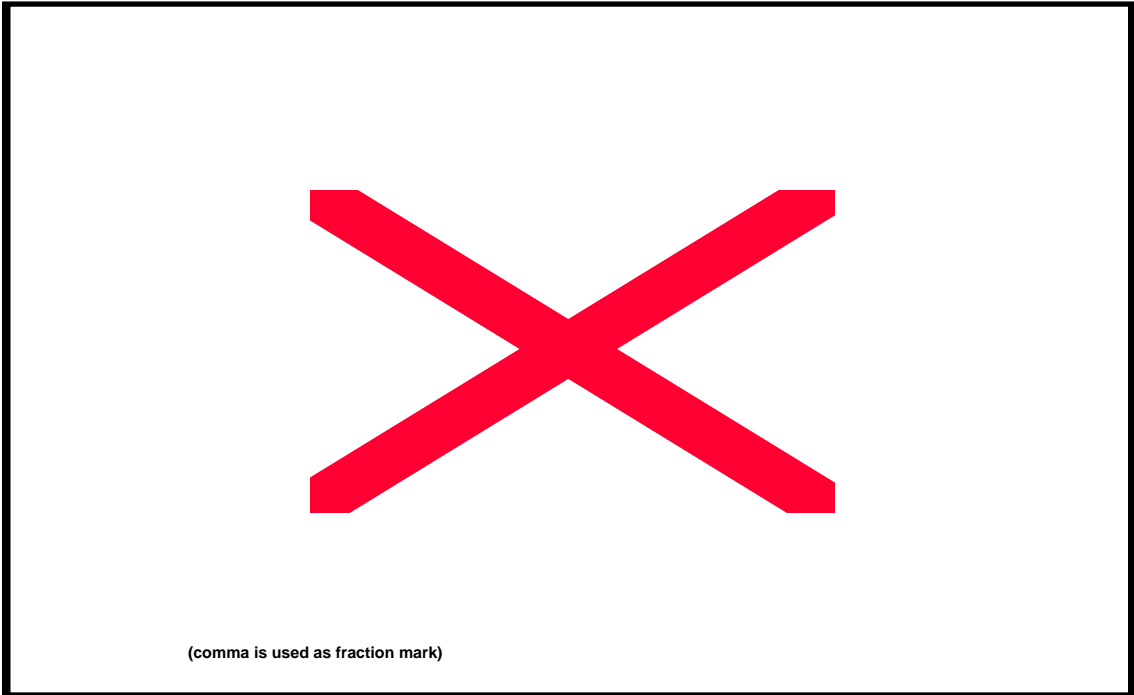
Figure 39   **Accumulated Quantity of Effluent Generated (Fleshings)**

The main parameters of this high polluted effluent are shown in Table 26. Whether the entire quantity of leakage can be irrigated during the curing phase has to be investigated.

Table 26   Parameter Concentrations of Leakage of Trial #5

Parameter	Unit	
pH	-	7 – 7.5
Conductivity	µS/cm	13,600
BOD_5	mg/l	4,453
COD	mg/l	21,258
Oil & Fat	mg/l	3,294
Cl^-	mg/l	1,769
Phosphorus total	mg/l	2
Nitrogen total	mg/l	1,401
Nitrate	mg/l	2
Sulphides	mg/l	4
Sulphates	mg/l	580

The moisture content of thermally treated fleshings is significantly lower than the one of fleshings (approximately 40 %). To the substrate mixture of thermal fleshings, amendments and bulking material approximately 100 l per ton thermal fleshings has to be added to reach an starting water content of 50 – 55%. In Figure 40 the accumulated quantity of water that was added during trial #8 is shown. Due to the high substrate temperatures and the high air flow through the substrate, the evaporation is considerable. To maintain the moisture content of the substrate between 45 and 55% approximately 900 l water were added per ton thermal fleshings. During the trial 115 l leakage per ton thermal fleshings were generated. This results in a net water consumption of 785 l/t$_{thermal\ fleshings}$.

**Accumulated Quantity of Water
Trial #8**
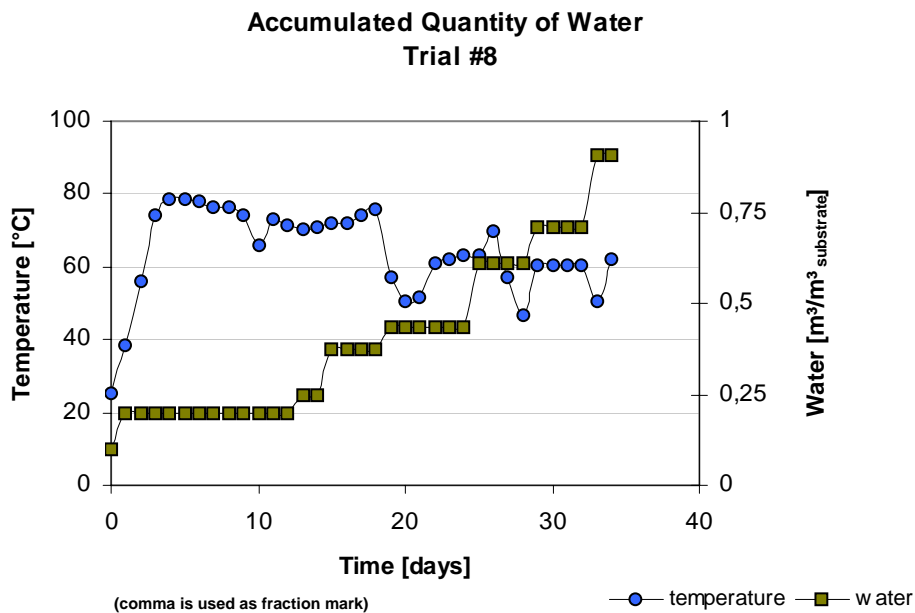
Figure 40   Accumulated Quantity of Irrigated Water (Thermal Fleshings)

This result has to be put into the right perspective. This water consumption refers to 34 days of operation. By several trial it could be shown that a discharge of the reactor is feasible after 10 to 14 days of operation. During the first 10 to 14 days between 200 and 250 l $_{water}$/t $_{thermal\ fleshings}$ were added. Subtracting the generated effluent, the net water consumption for this trial will result in 85 – 135 l/t$_{thermal\ fleshings}$ (air flow approximately 6 m³/h m³ $_{thermal\ fleshings}$)

For the treatment of thermal fleshings an air flow rate of 15 to 35 m³/h m³ $_{thermal\ fleshings}$ was recommended. It can be assumed that by increasing the air flow rate, the water consumption will increase as well. It can be assumed that the **net water consumption of the substrate thermal fleshings will be between 300 – 400 l/t$_{thermal\ fleshing}$** (depending on the moisture content of the discharged substrate).

A mixture of **hair residues**, amendments and bulking material has a starting moisture content of approximately 55 – 60%. Due to the low air flow rate that is suitable for this type of substrate, evaporation is low. That means that during the high rate phase the moisture content will stay within the limits for an optimum biological decomposition. A certain amount of leakage will be produced that can be recycled. A general assumption can be made that the water consumption and the generation of leakage are balanced. A worst case scenario would be that **100 l fresh water** have to be added to the system.
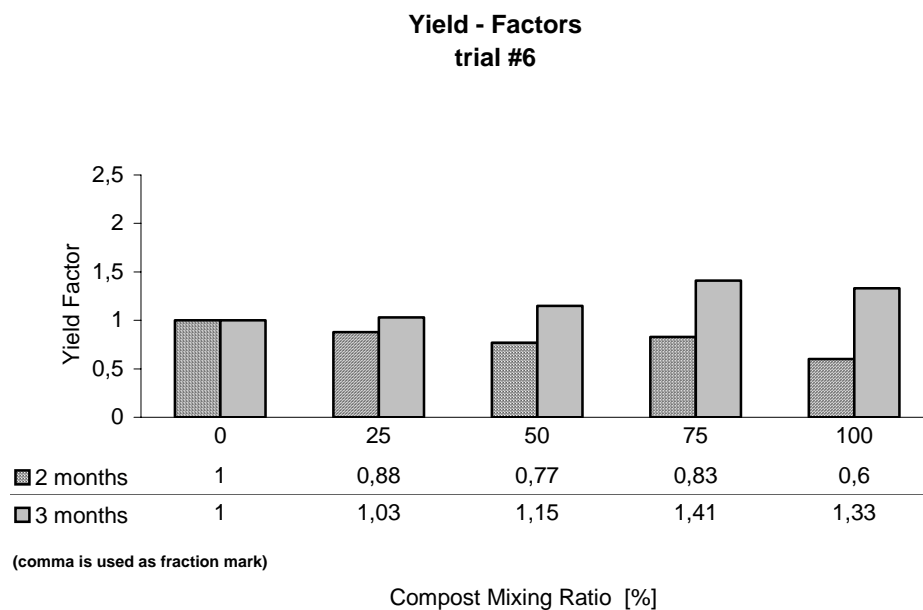
5.5.4 Product

Different types of product (compost) were obtained from the substrates fleshings, thermal fleshings and hair residues. In the previous sections the process parameters of successful composting were defined. In this section the product quality will be evaluated. On the one hand the respective compost was analysed chemically. To get a feeling for the analytical results, average concentration of a "typical" compost are given as well. [67]
On the other hand plant tolerance was determined by carrying out cress tests. For the procedures see chapter 5.3.2.3.

5.5.4.1 Compost made out of Fleshings

In
Figure **41** the yield factors of compost made out of fleshings with the amendment saw dust are shown. The cress tests were made for a 2 and a 3 months old compost. What can be seen is that a 2 months old compost shows little plant tolerance. By curing, the negative effect turns to a positive one. Mixing the standard soil with a 3 months old product increases the cress yield by the factor 1.4. It can be expected that by further curing the yield factor will further increase.

Yield - Factors
trial #6

	0	25	50	75	100
2 months	1	0,88	0,77	0,83	0,6
3 months	1	1,03	1,15	1,41	1,33

(comma is used as fraction mark)

Compost Mixing Ratio [%]

Figure 41   Yield Factors of Cress Tests for Compost Made out of Fleshings

The positive effect that can be achieved when fleshings are mixed with the amendment horse manure, can be seen in Figure 42. The yield factors are significantly higher than the corresponding yield factors for compost made out of fleshings and saw dust. Two facts sign responsible for this increase in fertilising properties. On the one hand, the first cress test with product from trial #6 was made with a 4 months old compost. It can be expected that tests with a 4 months old trial #6 compost will also show higher yield factors. On the other hand, horse manure has a positive effect on plant growth. This can be seen by the fact that the yield factors for compost made out of fleshings and horse manure are higher on the left side (lower compost concentration) whereas compost made out of fleshings and saw dust shows yield factors that are higher on the right side (higher compost concentration).

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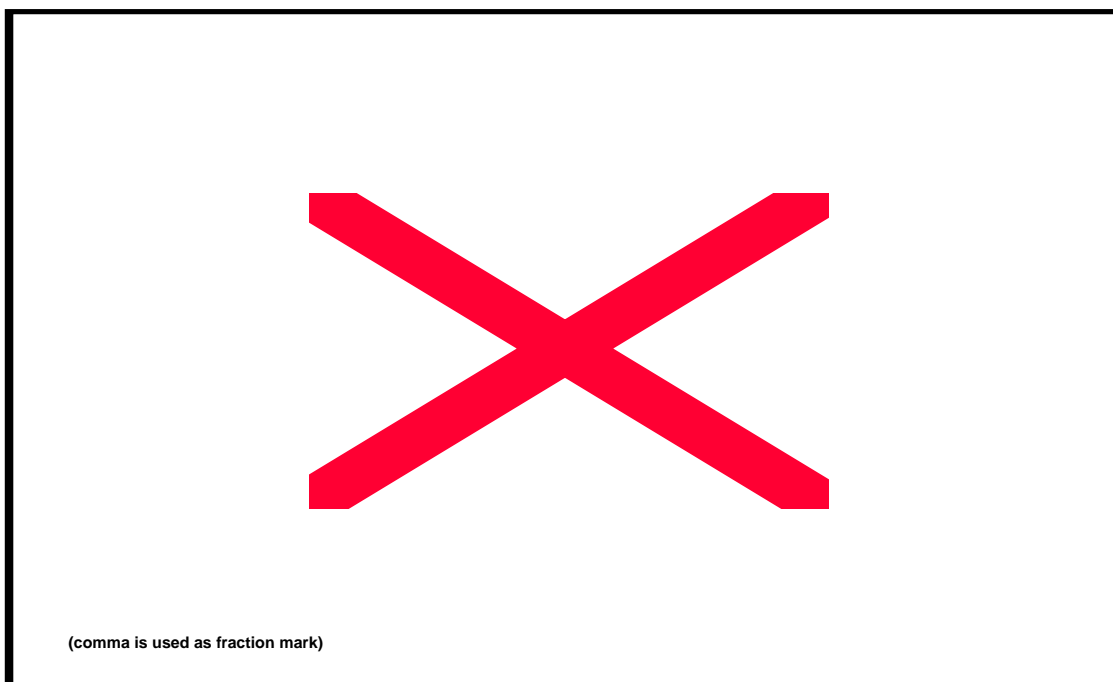
Figure 42   Yield Factors of Cress Tests for Compost Made out of Fleshings and Horse Manure

In Table 27 the chemical properties of the product of trial #5 and trial #6 are shown. The results of the chemical analyses are given in Annex E. To provide an order of magnitude to compare and evaluate the figures, average concentrations of "typical" compost are given. The data are taken from H. HOITNIK et al [60]. It has to be stated, that these figures are not limits or recommendations but "real" numbers of different compost samples.

The low water content of the sample of trial #5 is easily explained by the fact that the sample was taken after a long, dry and hot summer. Therefore, the compost that was stored on open air dried out. However, the water content has no influence on the chemical properties of the compost.

Table 27　　**Chemical Analyses of Compost Made out of Fleshings with Different Amendments**

Parameter	Unit	Trial #5 Fleshings Wood chips Saw dust	Trial #6 Fleshings Wood chips Horse manure	Reference HOITNIK [60]
pH	[-]	7.1	7.3	7.3
Conductivity	[μS/cm]	0.59	1.36	-
H_2O	[%$_{wm}$]	6.8	47.8	35.6
LOI	[%$_{dm}$]	20.3	67.8	40.6
Carbon	[%$_{dm}$]	11.4	43.5	19.6
TOC	[%$_{dm}$]	10.8	41.6	-
TIC	[%$_{dm}$]	0.6	1.9	-
N_{total}	[%$_{dm}$]	0.98	1.69	1.1
C/N	[-]	11	25	-
NH_4-N	[mg/kg$_{dm}$]	48	190	-
NO_3-N	[mg/kg$_{dm}$]	460	n.d.	-
P_{total}	[%$_{P2O5\ dm}$]	0.34	0.27	0.9
$P_{available}$	[%$_{P2O5\ dm}$]		0.05	-
Cl^-	[mg/kg$_{dm}$]	100	1,700	-
K_{total}	[%$_{K2O\ dm}$]	0.11	0.13	0.6
$K_{available}$	[%$_{K2O\ dm}$]	0.06	0.04	-
Ca_{total}	[%$_{CaO\ dm}$]	6.1	10.8	4.9
Mg_{total}	[%$_{MgO\ dm}$]	2.0	0.5	0.7
Cd	[mg/kg$_{dm}$]	0.05	0.05	5.5
Cr	[mg/kg$_{dm}$]	55	29	71.4
Cu	[mg/kg$_{dm}$]	33	17	274
Ni	[mg/kg$_{dm}$]	34	14	44.9
Pb	[mg/kg$_{dm}$]	6	6	513
Zn	[mg/kg$_{dm}$]	130	130	1,570
Hg	[mg/kg$_{dm}$]	0.12	0.13	2.4
B	[mg/kg$_{dm}$]	1.5	1.6	35.3

The loss of ignition (LOI) of 20.3% of sample of trial #5 compost indicates, that the compost is readily mineralised. It has to be stated that this number is not representative because of the age of the compost (<1year). Due of the long maturation and storage phase also the total organic carbon content is low. Negative impact on the fertilising properties of the product can be expected. The 4 and 6 months old compost of trial #5, that was used for the cress tests (see Figure 42) had a TOC content of approximately 40%.

The compost of trial #6 has a significantly higher LOI. Despite of the 67.6 %$_{dm}$ LOI and 41.6 %$_{dm}$ TOC the product can be assumed to be biologically stable. The high LOI can be explained by the amendment saw dust. Biological decomposition of wood (lignin) takes a long time. It is likely that by extending the storage period the LOI and TOC will further decrease. But this will not have any negative impact on the stored material (temperature increase of odour generation).

Compost of trial #5 shows a lower total nitrogen content than compost of trial #6 (0.96 to 1.61 $\%_{dm}$) but both are in an acceptable range for compost.

Since the carbon and nitrogen concentrations are varying also the ratio C/N differ significantly. A C/N ratio of 1, as it was calculated for compost of trial #5, is more representative for a stable compost than a C/N ratio of 26 of trial #6 compost.

However, it has to be taken into consideration, that, because of the addition of saw dust, compost that is produced of fleshing shows a high C/N ratio (see analyses in Annex E). This fact makes a C/N ratio >25 realistic. E.EPSTEIN [58] mentions that the C/N ratio can not taken as a indicator of the compost maturity. The C/N ratio is more a function of the feedstock and initial C/N ration than degree of maturity. Anyway, it must be taken into consideration that compost having an excessively high C/N ratio can lead to nitrogen deprivation for plants. Hence, suppressing plant growth.

An interesting difference between compost of trial #5 and trial #6 is the high content of nitrate - nitrogen (NO_3-N) of trial #5 compost. This is an indicator of the maturity of the compost. As shown by E.EPSTEIN [58] a high nitrate-nitrogen and a low ammonia-nitrogen content are indicators for a good and sufficient maturation of the compost. It is likely that the high nitrate-nitrogen content is caused by an initially high content of nitrogen compounds which can be assimilated by plants. These compounds are likely to be found in the horse excrements which were mixed to the substrate mixture. This might be an explication for the better cress test results of trial #5 compared to trial #6 compost.

Heavy metals of both types of compost are low and generally lower than the concentration that can be found in "typical" municipal solid waste compost.

The concentration of calcium is slightly higher than the average of "typical" compost. This can be easily explained by the fact that lime is added during the unhairing/liming process. This lime partially can be found in the fleshings and finally in the compost. Lime generally shows positive effect on plant growth.

A significant difference between compost of trial #5 and trial #6 is the chloride concentration. Trial #5 compost contains 100 mg/kg_{dm} whereas trial #6 compost contains approximately 16 times more Cl^- (1,684 mg/kg_{dm}). Looking at the results obtained by analysing the different types of compost one can state the following. The initial chloride content of trial #5 compost was comparable to the chloride content of the compost of trial #6. Since the trial #5 compost was stored during the winter (rainy season) on open air the chlorides were simply washed out.

An interesting difference between compost made out of fleshing with horse manure and compost made out of fleshing with saw dust is a high magnesium concentration of the former. The chemical analyses showed 2$\%_{dm}$ magnesium, compared to 0.5$\%_{dm}$ of compost made out of fleshings without horse manure. Latter is in the range of "conventional" compost (0.7 $\%_{dm}$).

Besides of nitrogen, potassium and phosphorous are important macro-nutrients that can be found in compost. The concentration of latter two is significantly lower than for "commercial" compost. Phosphorous is in the range of $0.3\%_{dm}$ ($0.9\%_{dm}$ for commercial compost) and approximately $0.1\%_{dm}$ potassium will be found in compost made out of fleshings. The potassium concentration of "commercial" compost is given with $0.6\%_{dm}$.

These low concentrations in macro-nutrients will have negative impact on the fertilising properties of the compost.

5.5.4.2 Compost made out of Thermal Fleshings

In Figure 43 the yield factors for compost made out of a mixture of thermally treated fleshings and saw dust is shown. The cress tests have been carried out with 2, 4 and 5 months old compost. At a glance one can see the significant difference between the yield factors of compost made out of fleshings and the yield factors of compost made out of thermally treated fleshings. Latter shows little plant tolerance or even plant intolerance. A fact that is striking is, that the older the compost got, the worse the fertilising properties became. This tendency was not expected at all. Generally, maturation improves the positive characteristics of compost. The results obtained from the investigations made on compost made of fleshings confirm this general rule. Why compost made out of thermal fleshings do not correspond, is not clear at all.



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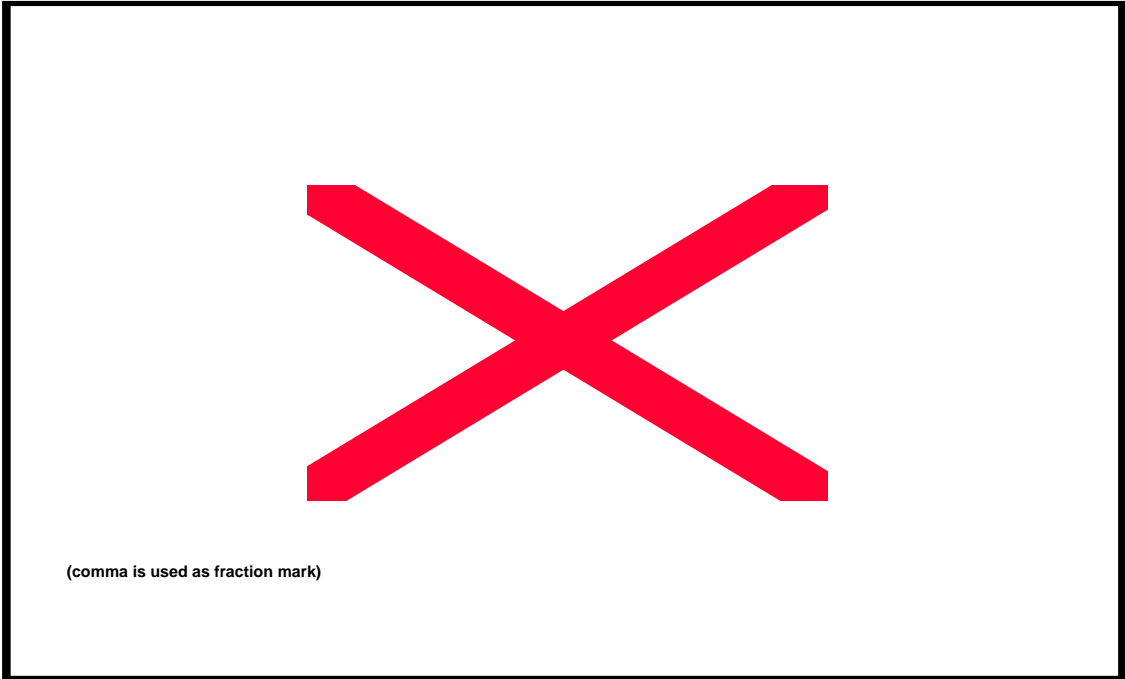
Figure 43   Yield Factors of Cress Tests for Compost Made out of Thermal Fleshings

Another astonishing result was obtained by carrying out cress tests with the compost of trial #10. Thermal fleshings were mixed with market waste and wood chips. Even if thermal fleshings can not be converted into a fertiliser, the amendment should influence the product properties positively.

In Figure 44 the yield factors of the cress tests carried out with trial #10 compost, are shown. The results are comparable to the results discussed above. This is quite surprising, too. Normally, compost made out of organic waste (vegetables and fruits) definitively shows positive effects on plant growth. The fact that this is not the case when organic matter is mixed with thermally treated fleshings, is astonishing.

Results with compost of trial #7 show that this phenomenon can not be explained by a high C/N ratio. Due to the amendment saw dust the product can be assumed to be rich in carbon. As a consequence the C/N ratio is high. A high C/N ratio may lead to nitrogen deprivation for plants. However, trial #7 compost was made out of thermal fleshings only. Hence, the C/N ratio is low (approximately 18). Non the less the yield factors hardly exceed 1.

The only reasonable explanation that can be given is the assumption, that phytotoxic compounds are formed an still are present. It can be expected, that after sufficient time of maturation, the plant tolerance will increase.

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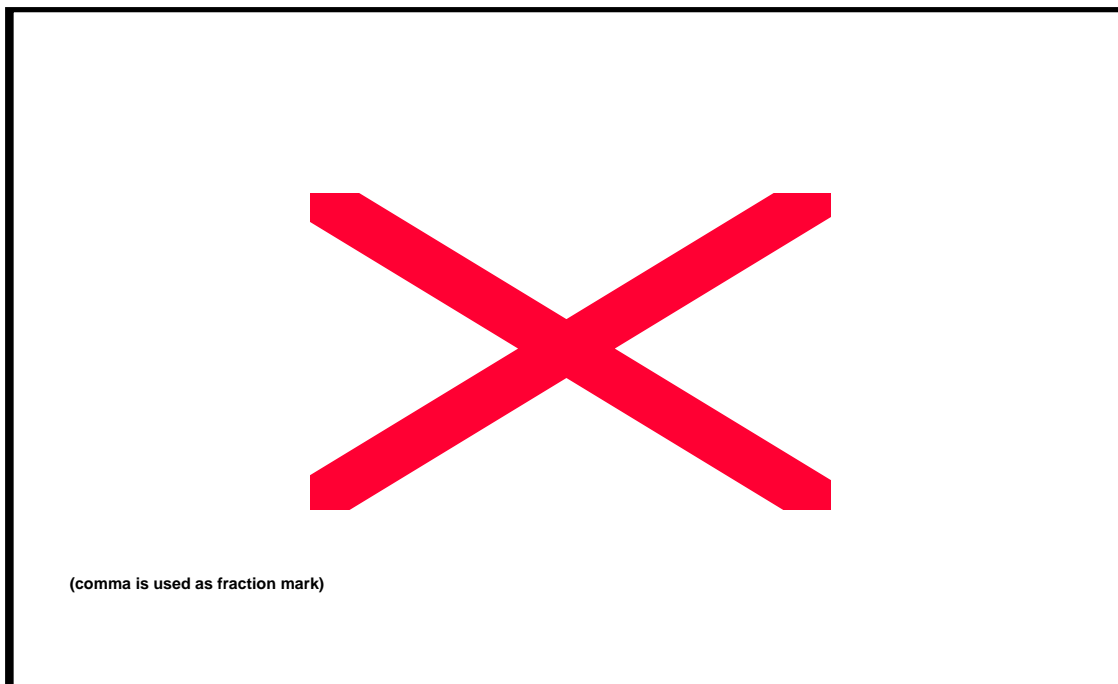
Figure 44   Yield Factors of Cress Tests for Compost Made out of Thermal Fleshings and Market Waste

However, it must be stated that the product that can be obtained by composting thermally treated fleshings can not be called compost. It is a biologically stable matter that can be stored outside without problems, but may show no or negative effect on plant growth.

In Table 28 the chemical analyses of different types of composts made out of thermally treated fleshings are shown. For comparison purpose concentrations of a "typical" compost are added.

The water content depends on the weather conditions during storage. Trial #8 and trial #9 compost were sampled after a long, sunny period. This explains the low moisture content. However, as already mentioned above, this has no influence on the product quality.

Table 28   Chemical Analyses of Compost Made out of Thermal Fleshings

Parameter	Unit	Trial #7	Trial #8	Trial #9	Trial #10	Reference
		Fleshings Chips	Fleshings Chips Saw dust	Fleshings Saw Dust Compost	Fleshings Chips Market Waste	H.HOITNIK [60]
pH	[-]	7.5	7.4	7.4	7.2	7.3
conductivity	[µS/cm]	1.31	1.15	1.32	0.93	-
H_2O	[%$_{wm}$]	31.7	7.7	9.1	35.2	35.6
LOI	[%$_{dm}$]	47.4	72.6	74.8	70.0	40.6
TOC	[%$_{dm}$]	31.5	48.9	51.6	47.2	19.6
TIC	[%$_{dm}$]	1.8	1.6	1.8	1.7	-
N_{total}	[%$_{dm}$]	1.76	1.29	1.11	1.12	1.1
C/N	[-]	18	38	46	42	-
NH_4-N	[mg/kg$_{dm}$]	155	65	45	75	-
NO_3-N	[mg/kg$_{dm}$]	5	3	n.d.	n.d.	-
						-
P_{total}	[%$_{P2O5\ dm}$]	0.36	0.30	0.18	0.27	0.9
$P_{available}$	[%$_{P2O5\ dm}$]	0.08	0.04	0.06	0.05	
Cl^-	[mg/kg$_{dm}$]	1,300	950	750	900	-
K_{total}	[%$_{K2O\ dm}$]	0.14	0.08	0.06	0.16	0.6
$K_{available}$	[%$_{K2O\ dm}$]	0.09	0.05	0.03	0.09	
Ca_{total}	[%$_{CaO\ dm}$]	9.9	8.6	8.7	9.3	4.9
Mg_{total}	[%$_{MgO\ dm}$]	1.2	0.5	0.4	0.5	0.7
Cd	[mg/kg$_{dm}$]	0.05	0.05	0.05	0.05	5.5
Cr	[mg/kg$_{dm}$]	33	31	22	26	71.4
Cu	[mg/kg$_{dm}$]	21	12	11	14	274
Ni	[mg/kg$_{dm}$]	21	15	13	12	44.9
Pb	[mg/kg$_{dm}$]	4	31	5	4	513
Zn	[mg/kg$_{dm}$]	115	95	85	100	1,570
Hg	[mg/kg$_{dm}$]	0.12	0.13	0.13	0.13	2.4
B	[mg/kg$_{dm}$]	0.5	3.9	3.6	1.0	35.3

The Loss of Ignition of the trials #8, #9 and #10 are rather high. Looking at the LOI of trial #7 compost the explanation seems rather clear. Composting thermal fleshings without amendments results in a product with a LOI of 47%$_{dm}$. Composting a mixture of thermal fleshings and amendments (saw dust, market waste) gives a product with a LOI exceeding 70%$_{dm}$. It can be assumed that the amendments are responsible for the high LOI.

As mentioned above, the loss of excess nitrogen seems not to be a problem for the product quality. A total nitrogen concentration of 1.1 – 1.2%$_{dm}$ corresponds to the nitrogen concentration of a "commercial" compost. The lowest nitrogen concentration would be

expected for compost that was made out of the substrate mixture with the lowest C/N ratio. This is the mixture of trial #6 (wood chips and thermal fleshings). Surprisingly this is not the case. Trial #6 compost shows the highest nitrogen concentration.

The C/N ratio of the different products are high (approximately 40). But as said above, this can not be the main explication why the product shows no or little fertilising properties.

As already mentioned in the section "fleshings" a lack of the macro-nutrients, potassium and phosphorous can be stated. The phosphorous concentration is in the range of $0.3\%_{dm}$ ($0.9\%_{dm}$ for commercial compost) and approximately $0.1\%_{dm}$ potassium will be found in compost made out of fleshings. The potassium concentration of "commercial" compost is given with $0.6\%_{dm}$. (see also [68])
These low concentrations in macro-nutrients will have negative impact on the fertilising properties of the compost.

Finally, as expected, the calcium concentration is high (approximately $10\%_{dm}$). It was already explained above, that this is caused by the feedstock fleshings. Though the main part of the calcium remains in the tallow, that is separated from the protein meal, the final calcium concentration in the product made out of thermal fleshings is comparable to the concentration found in compost made out of fleshings. This is explained by the different quantities of substrate that are treated per batch.

5.5.4.3 Compost made out of Hair Residues

In Figure 45 the yield factors of a 1 month and a 5 months old compost are shown. The compost is made out of hair residues and saw dust. It can be seen that compost made out of hair residues is a better fertiliser than compost made out of fleshings. After 1 month of treatment the compost shows excellent fertilising properties. After a certain time of maturation the positive effect on plant growth improves. With a 5 months old compost the plant mass can be doubled.

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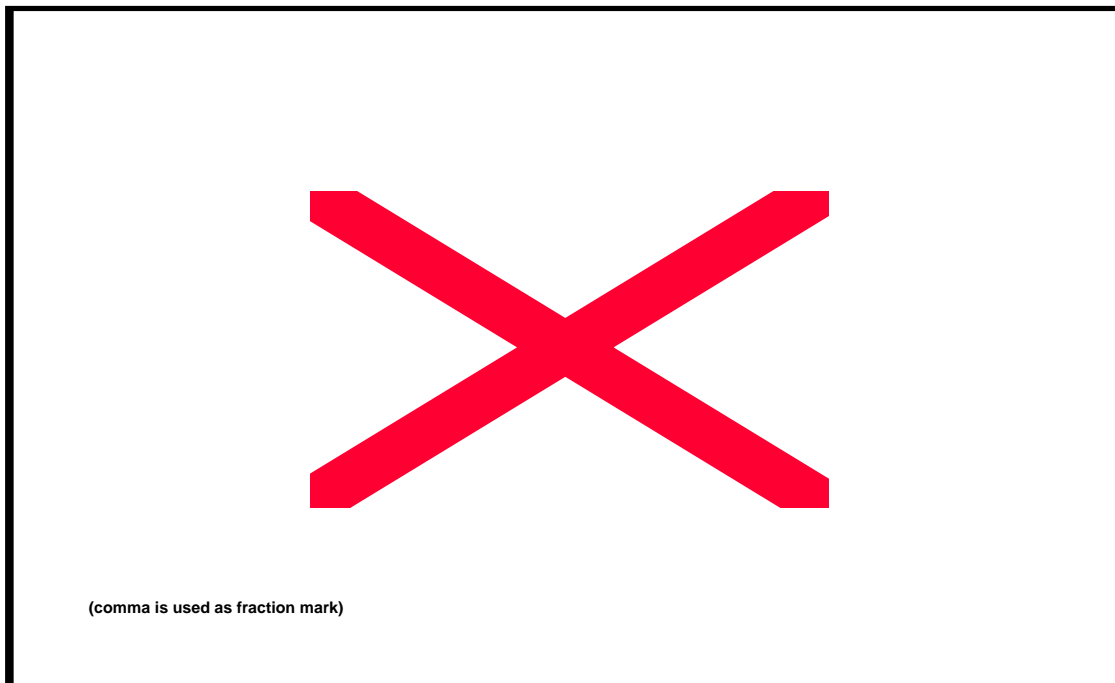
Figure 45   Yield Factors of Cress Tests for Compost Made out of Hair Residues

In Table 29 the chemical analyses of three compost samples are shown. Furthermore reference concentrations of a "typical" compost are given.

Compared to "typical" compost and the compost made out of fleshings, the total nitrogen concentration is higher for the compost made out of hair residues. This may be an explication why the plant tolerance of this product is much more higher than for the types of compost discussed above.
However, it can be assumed that the compost is not mature enough, hence NH_4-N could be detected, but no NO_3-N. A further improvement of the product quality can be expected by further maturity.

Compared to "typical" compost, the potassium and phosphorous concentrations are low. This was already discussed above. The calcium concentration on the other hand is high (see above).

Table 29　　Chemical Analyses of Compost Made out of Hair Residues

Parameter	Unit	Trial #11 Hair residues Saw dust Wood chips	Trial #13 Hair residues Saw dust Wood chips	Trial #15 Hair residues Saw dust Wood chips	Reference H.HOITNIK [60]
pH	[-]	7.4	7.4	7.6	7.3
conductivity	[µS/cm]	1.36	0.99	1.44	-
H_2O	[%$_{wm}$]	26.9	21.1	58.8	35.6
LOI	[%$_{dm}$]	66.6	68.4	50.6	40.6
TOC	[%$_{dm}$]	44.5	45.0	29.0	19.6
TIC	[%$_{dm}$]	1.8	2.4	1.0	-
N_{total}	[%$_{dm}$]	1.75	1.54	2.37	1.1
C/N	[-]	25	29	12	-
NH_4-N	[mg/kg$_{dm}$]	150	75	55	-
NO_3-N	[mg/kg$_{dm}$]	n.d.	n.d.	n.d.	-
					-
P_{total}	[%$_{P2O5\ dm}$]	0.40	0.27	0.35	0.9
$P_{available}$	[%$_{P2O5\ dm}$]	0.05	0.04	0.02	
Cl^-	[mg/kg$_{dm}$]	2,100	850	3,000	-
K_{total}	[%$_{K2O\ dm}$]	0.19	0.09	0.11	0.6
$K_{available}$	[%$_{K2O\ dm}$]	0.10	0.04	0.03	
Ca_{total}	[%$_{CaO\ dm}$]	9.9	12.3	8.4	4.9
Mg_{total}	[%$_{MgO\ dm}$]	0.6	0.5	1.2	0.7
Cd	[mg/kg$_{dm}$]	0.05	0.05	0.05	5.5
Cr	[mg/kg$_{dm}$]	28	25	1,400	71.4
Cu	[mg/kg$_{dm}$]	14	14	43	274
Ni	[mg/kg$_{dm}$]	11	11	22	44.9
Pb	[mg/kg$_{dm}$]	9	3	10	513
Zn	[mg/kg$_{dm}$]	170	180	280	1,570
Hg	[mg/kg$_{dm}$]	0.13	0.13	0.13	2.4
B	[mg/kg$_{dm}$]	0.8	0.4	2.4	35.3

Compared to the compost made out of fleshings and thermal fleshings, the chloride concentration seems high. Since the chloride concentrations of the feedstock are comparable, it is not obvious why the chloride concentration in the discussed product is that high.

One result that must be explained is the chromium concentration of the trial #15 compost. This value is that high, because the feedstock "hair residues" was contaminated with chromium bearing effluent of the tanning drum. At the tannery all effluent streams were screened by the same screen. Although it was tried to get pure substrate, cross-contamination could not be avoided totally. If a tannery composts its solid wastes, cross contamination will have to be avoided by proper separation of the individual waste streams.

5.6 Discussion

Before discussing the results presented in the previous sections, some critical comments concerning the experiments, have to be made.

Mixing of the substrate with bulking material and amendments was difficult and mostly insufficient. Proper mixing seems to have positive impact on the process H.HOITNIK [60] Working with fleshings, this inhomogeneous mixture was caused by the nature of the substrate. Even if the mixing is performed by a proper mixing device, no better results will be obtained. Mixing thermal fleshings and/or hair residues by a mechanical mixer, may optimise the process.

As a consequence of inappropriate mixing, sample taking was difficult. Representative sample taking of fleshings is hardly possible. The samples taken from substrates thermal fleshings and hair residues can be assumed to be representative. However, it is likely, that certain errors occurred also with these substrates.

The chemical analyses of the substrate were carried out in certified laboratories. Most results are reliable. An exception is the total nitrogen concentration of the thermal fleshings. The average of $1.5\%_{dm}$ must be assumed to be too low. Unfortunately, the N_{tot} concentration is important for calculating the C/N ratio, which is one of the crucial parameters of the composting process. From literature [53] a realistic figure of protein meal was assumed.

As mentioned above, the other results seem to be reliable, but have to be treated with caution.

The reactor design was a compromise between what was necessary and what was feasible. The main critical point was the discharging of the substrate by the discharging screw, that was installed at the bottom of the reactor. Each turning-step required a discharge and refill of the reactor. Due to the structure of the substrate, the material built up "bridges". Destroying these "bridges" was difficult and labour intensive. This "bottle neck" was acceptable for a bench-scale reactors, but is inadequate for a full-scale reactor. About a appropriate design see below. However, this laborious procedure had no influence on the process itself.

The process air was supplied by a compressor. Due to several failures of this compressor at the end of the trial period, a constant air supply could not be guaranteed. Connecting the air supply to the overall air supply system of the UDT did not solve this problem. During trial #15 and #16 problems with the air supply occurred. The other trials with air supply problems are not mentioned in this thesis.

Besides CO_2 concentration, the concentration of NH_4 is an important parameter of the waste gas. Latter was not measured. At the beginning no analyse instruments were available. Finally, DRÄGER tubes could be organised and measurements carried out for some trials. Due to untrustworthy data and problems with the air supply, the results are not

representative and are not presented in this thesis. However, the NH_4 concentration in the waste gas actually is a parameter that has to be investigated in more detail.

As to windrow composting, it has to be stated that this technology is not recommendable. It could be shown, that:

- Composting of a mixture of fleshings, bulking material and amendments generally is possible.
- Process Temperatures exceeding 70°C are required for proper decomposition.
- The high pH of the substrate (12.5) decreases rapidly and does not influence the process negatively.
- Severe problems with insects and other animals must be expected.
- Malodour will be generated.

However, the low cost and low sophisticated technology of windrow composting makes it interesting to tanners located in developing countries. If the sufficient space far from residential areas is available and the tanner can account for the negative impact caused by open-air composting, it may be an alternative to reactor composting. However, proper maintenance (frequent turning, proper covering with compost, leakage collecting system, etc...) has to be provided.

In close proximity to residential area windrow composting has to be refused. The only alternative seems to be reactor composting.

As to the type of substrate, the following has to be stated.

Hair residues are a "good natured" substrate. Rapid decomposition without major problems can be expected. The final product shows positive effects on plant growth. Composting of this type of substrate is highly recommended. Two facts have to be taken into consideration.

Firstly, it is advisable to separate the highest quantity of hair residues from the unhairing effluent, that is possible. This means, a hair saving or partially hair saving unhairing process has to be favoured (see chapter 4.5.3.4). On the one hand, a higher quantity of useful feedstock can be provided (up to 300 kg/t_{wsH}). On the other hand, the pollutant load of the unhairing/liming effluent will be reduced significantly.

However, whether the potential risks of changing the unhairing/liming process can be accepted, has to be decided for each individual case.

Secondly, it is crucial that unhairing effluents are not mixed with chromium bearing effluents generated at the section tanyard and retanning. After screening the unhairing/liming effluent, the hair residues have to be removed immediately. If this is not the case, cross contamination with chromium can be expected, making the organic matter unsuitable for producing a high-quality compost.

The substrate fleshings and thermal fleshings are not that "good natured". Although the properties of the compost made out of fleshings, seems to be slightly better than the properties of compost made out of thermal fleshings, reactor composting of fleshings without pre-treatment seems not to be recommendable.

Main constrain is the reactor volume. Assuming a best case scenario with a volume of 0.255 m^3/t_{wsH} fleshings and trimmings (specific gravity approximately 1) , a volume ratio of 2.5 $m^3/m^3_{fleshings}$ and a residence time (high rate phase) of 2 weeks, results in a reactor volume of 12.5 m^3 that has to be provided per ton wet salted hide that is processed at the tannery. A worst case scenario would result in reactor volume of 34 m^3/t_{wsH} (assumptions: 405 kg/t_{wsH} fleshings, volume ratio of 3 and a residence time of 21 days).

By treating the fleshings thermally, the volume can be reduced significantly. The water content of the fleshings is approximately 75%. About 40%$_{dm}$ tallow can be found. Assuming that only 50% of the tallow are separated by the thermal treatment and a water content of 40% of the thermal fleshings, the substrate volume can be reduced by the factor 2/3.

Once again a best and a worst case scenario can be computed.

For the best case scenario (255 x 0.33) m^3 thermal fleshings are treated 10 days. Volume ratio is assumed with 1.5 m^3/m^3 $_{thermal\ fleshings}$. This results in a reactor volume of 2 m^3 per ton wet salted hide input into the tannery. In the worst case scenario 5.6 m^3 reactor per ton wet salted hides that are processed at the tannery have to be provided (assumptions: 405 kg/t_{wsH} fleshings, volume ratio of 2 and a residence time of 14 days).

The required reactor space is only one fact that favours thermal pre - treatment of fleshings. Another parameter is the generation of leakage. Per m^3 substrate additional 300 to 400 l high polluted effluents are generated by the biological treatment of fleshings. Compared to the 14 to 22 m^3/t_{wsH} of high polluted effluents that are generated by the tanning process, this additional quantity is of little importance. However, it is additional effluent that is generated. Treating thermal fleshing on the other hand consumes water. Approximately 300 to 400 l are consumed per $m^3_{substrate}$. This water may be effluent that is generated at the tannery. By recycling tannery effluent in the biological treatment of thermal fleshings, the global quantity of tannery effluent is reduced insignificantly. The up to 100 l per $m^3_{substrate}$ that are consumed by treating hair residues likewise show no influence on the overall water balance.

Yet, it is a contribution to an effective and proper water management at tanneries.

It is difficult to determine the exact air flow that is required for a proper composting process. Parameters like water content, volume ratio and turning frequency, process temperature, etc. show significant influence on the m^3 of air that have to be processed hourly through the reactor. It could be shown, that certain limits are given.

Hair residues turned out to be most sensitive concerning variation of the air flow. A minimum amount of 2 m^3 air per hour and m^3 hair residues is necessary to proper operate the process. Exceeding 6 $m^3/$ h $m^3_{substrate}$ will cool down the substrate and stop the decomposition process. Treating fleshings, the minimum and maximum limits of the air flow are given by 6 and 15 $m^3/h\ m^3_{substrate}$.

The substrate "thermal fleshings" is insensitive concerning the variation of the air flow. On the contrary, it is difficult to cool the substrate and to maintain mesophilic process temperatures. As a minimum 15 m³/h m³$_{substrate}$ are recommended. The maximum flow can be assumed to be limited by 35 m³/h m³$_{substrate}$. The high air consumption seems to be caused by the physical and chemical properties of the protein meal.

A crucial factor of successful reactor composting is the turning frequency and the discharge behaviour of the substrate. The named substrates show the tendency to compact and to build-up bridges. Discharging the reactor can prove difficult. Working with a bench scale reactor, bridges may cause additional work but are no real problem. When the substrate compacts and bridges in a full-scale reactor, this can result in significant problems. In addition to that, working with "silo reactors" means, that each turning action is a discharge and recharge of the reactor. This results in odour release during the turning action.
By a proper reactor design, bridge-building and malodour release can be avoided. In addition to that, a continuous composting process can be achieved. In Figure 46 a possible design is shown.
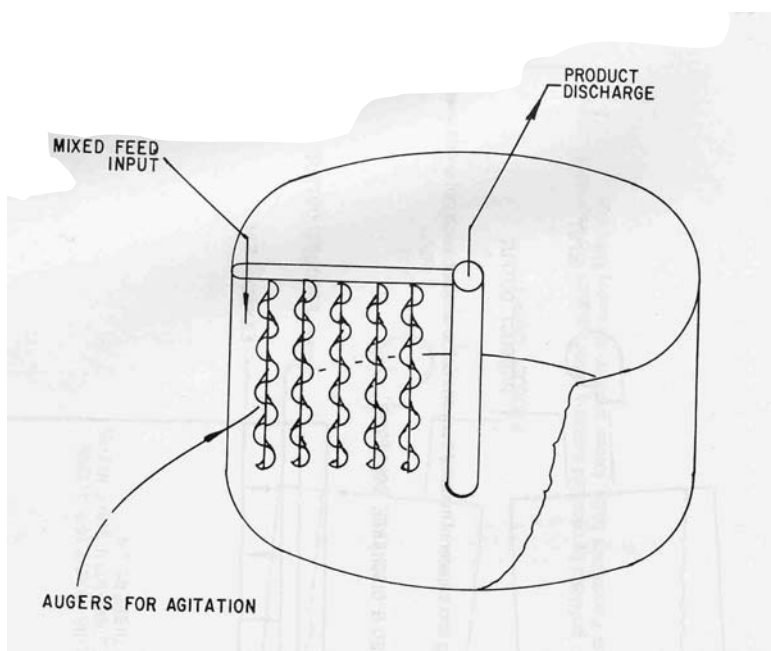
Figure 46   Possible Design of a Composting Reactor
Source: R.HAUG [59]

The rotating augers (around own axes and around the centre of the reactor) provide a permanent agitation of the substrate. Furthermore, the substrate is transported from the outside to the centre of the reactor, where the final product can be discharged. Air is introduced at the perforated bottom of the reactor and waste gas leaves the reactor at the top. It is collected and further processed through a bio-filter.

The suggested or a similar reactor design seems to be most suitable for composting solid tannery waste, yet other types of composting systems may suit as well. For an introduction to different composting systems see Annex G.

A further item that has to be discussed, is the addition of a proper amendment. In general, amendments are not absolutely required to achieve a decomposition of thermal fleshings and hair residues. The recycled structure material is "contaminated" with compost, that provides sufficient inoculation of the "sterile" substrate. To treat fleshings, amendments are indispensable for adjusting a proper water content of the substrate mixture.

Due to the low C/N ratio of the substrates (see section 5.4 - Characterisation of Substrate) the addition of carbon rich amendments is highly recommended anyway. Excess nitrogen will not be released by the waste gas, but will be fixed in the product. Saw dust is an amendment, that is easily available at any place of the world. However, saw dust has a significant disadvantage: Lignin is difficult too decompose and takes a long time. Adding saw dust to the initial substrate mixture will result in a product that is characterised by a high C/N ratio. This high C/N ratio shows negative impact on the plant growth and tolerance of the compost.

Due to the experience made, the addition of saw dust may not be recommended. Nitrogen loss seems to be more favourable, than increasing the C/N of the product. Obviously, a necessary condition is, that the waste gas is effectively cleaned in the bio-filter.

Highly recommended is the addition of horse bed stale. Horse bed stale is a mixture of horse manure, urine and coarse saw dust (chip-like). Although horse manure is also rich in nitrogen, additional carbon is added by the chips.

The addition of horse bed stale shows a positive impact on the process (water holding capacity and process temperature) and product quality as well.

Finally, the compost quality has to be discussed in a view words:

Compost made out of hair residues shows a positive effect on plant growth. With 5 months old compost, the yield of cress plants can be doubled compared to standard soil. Compost made out of hair residues is definitively a high quality fertiliser and will not further be discussed. However, as already mentioned above, crucial to produce a high-quality product is a proper separation from chromium containing waste.

Compost made out of fleshings shows a slightly better plant tolerance than compost made out of thermal fleshings. Yet, in both cases, the plant tolerance is not satisfying at all. Two facts are likely to sign responsible for the poor fertilising properties of the compost. First, due to the addition of saw dust, the C/N ratio of the compost is high (<25). In most cases it is too high for proper plant growth. The high C/N ratio is likely to decrease by further maturation.

Second, low concentration of the macro nutrients potassium and phosphorous may show negative impact on the plant growth. Due to the fact, that compost made out of hair residues also shows a low potassium and phosphorous content, latter seems to have minor impact.

As mentioned above, composting of fleshings is little feasible (reactor volume). It is preferable to pre-treat the fleshings thermally, to separate the fat and to compost the residual protein meal. The quality of the obtained compost can be improved by adding horse bed stale.

5.7   Conclusion

As a result, the following conclusions can be drawn:

Aerobic biological treatment (composting) of non-chromium containing solid tannery waste is possible. The low-cost and low-sophisticated technology of windrow composting is not recommended. A favourable process concept is a continuous, horizontal flow, agitated bin reactor design with waste gas treatment (bio-filter).

Per ton wet salted hide 67 to 180 kg hair residues can be separated from the unhairing / liming effluent. Furthermore, 255 to 405 kg fleshings, unused split and trimmings are generated. It is highly recommended to reduce the volume of latter by thermal separation of tallow and proteins. Due to a lower water content the volume can be decreased to approximately 1/3.

Thus, per ton wet salted hide input, 0.15 to 0.3 m³ non-chromium containing solid waste is generated.

Mixing with bulking material is indispensable. Amendments (saw dust, horse bed stale and/or recycled compost) are recommended. The volume ratio has to be between 1.5 and 2 m³ bulking material and/or amendments per m³ solid tannery waste. Residence time (high rate phase) is between 10 and 14 days.

These assumptions result in a total reactor volume of 3.7 to 12.6 m³ reactor per ton wet salted hide input.

Approximately 0.5 $m^3/m^3_{substrate}$ water (tannery effluent) will be consumed during the high rate phase. During the curing phase further irrigation will be required. The actual quantity depends on the climatic conditions. To obtain the proper process temperatures, the air flow has to be adjusted to 15 to 35 $m^3/h\ m^3_{substrate}$.

After 10 to 14 days in the high rate phase, the reactor can be discharged, the substrate screened and the compost stored for maturation purpose. After 40 to 50 days of maturation, the compost can me assumed to be biological "inert". However, further maturation will increase the plant tolerance and fertilising properties of the product.

It can be assumed, that the fertilising properties of compost made out of hair residues will compensate the poor fertilising properties made out of the substrate "thermal fleshings".

6   Summary

This thesis is addressed to small and medium sized tanneries (SME) located in developing countries. Members of the INCO-DC project "EILT" working groups collected input and output data at six different tanneries. 4 Chilean, 1 Spanish and 1 Ecuadorian tannery were investigated. Common to all these tanneries is, that they process bovine hides in a chromium tanning process. In this thesis, the data from the individual tanneries are collected and evaluated. A chromium tanning process of bovine hides with the corresponding average input and output figures is drawn up – the EILT model.
The tanning process can be divided into the sections

- Beamhouse
- Tanyard
- Retanning
- Finishing and
- Others.

For the first two sections - beamhouse and tanyard – a further differentiation is possible. To overcome the difficulties that arise, when the quantities of consumed water and chemicals and of generated waste waters and solid wastes are averaged, minimum and maximum quantities were calculated. All figures refer to one ton wet salted hide raw material input.

Per ton wet salted hide 46 to 70 m³ fresh water are consumed. Whether the actual water consumption is in the upper or the lower range, mainly depends on the equipment that is used in the beamhouse section (paddles or drums).
50 to 55% of the global water consumption are technical water - i.e. water that is used for steam production, plant wash down purpose and proper equipment operation (e.g. vacuum pump). This water consumer, that is pooled in the section others, frequently is neglected, when talking about the water consumption at a tannery.
Approximately 35% are consumed in the beamhouse section, 1 to 5% in the section tanyard and the balancing 9 to 11% in the retanning section.

The water output depends on the water input. Whichever is the quantity of water that is required, between 41 and 63 m^3/t_{wsH} waste water are generated. It is recommended to segregate the effluents into 4 different waste water streams:

- Low polluted effluents
- High polluted effluents
- Chromium bearing effluents and
- Sulphide bearing effluents.

Approximately 44% are low polluted effluents and can be recycled without sophisticated treatment. 35% are high polluted waste waters and have to be processed through a primary and secondary waste water treatment before they can be released to a sewage body.
6% of the global waste water are chromium bearing or at least potentially chromium bearing effluents. This 6% have to be properly separated from the other waste streams in order to prevent cross contamination. Typically, 60 to 80% of the chromium offer can be found in the wet blue. The rest is discharged by the effluents. By taking proper measures, this up-take rate can be increased to >95%. Several opportunities have been proposed. For SME-tanneries located in developing countries, the most favourable process combination seems to be direct recycling of the tanning float for several cycles. The chromium that is discharged by the reject, has to be precipitated as chromium oxide. The chromium oxide sludge should be dewatered and disposed of.
Finally, the balancing 15% of the global waste water are sulphide bearing effluents generated in the unhairing/liming step. This type of waste water is the most polluted one that is released by a tannery. It is recommendable, to separate as much hair residues as possible from the effluent, to directly recycle the spent unhairing/liming float for several batches and finally, to oxidise the sulphides to sulphates by catalytic oxidation before discharge.

Per ton of wet salted hides, approximately 423 kg chemicals are consumed. The actual quantity depends strongly on the customs of the tanner and the type of product. Major chemical consumer are the section retanning (35%) and tanyard (33%). Approximately 19% are consumed in the beamhouse and finally 13% in the finishing section. Main chemicals are sodium sulphide, lime, inorganic acids, sodium chloride and tanning salts.

Depending whether splitting is carried out in the tanyard or in the beamhouse, between 419 and 767 kg of solid waste are generated per ton wet salted hides. Segregation into three fraction is recommended:

- Spent salt
- Non-chromium containing waste
- Chromium containing waste

5 – 10% of the global solid wastes are spent salt generated at the storage facilities.

15% are chromium containing shavings, trimmings and unused spilt. The major part are non-chromium containing solid waste. Between 75 and 80% are fleshings, trimmings, unused split and hair residues, that are generated in the beamhouse section.

A proper segregation of the identified waste fraction is easy, due to the fact that each fraction has its origin in a different section.

Main efforts were put on the treatment of the non-chromium containing waste fraction. Applying a proper treatment technology will reduce the global solid waste by 80 – 75%. Because of the organic origin of the substrate, biological treatment is the obvious treatment technology. The high water content and the physical properties of the substrate suggest anaerobic treatment. From the economic point of view, **anaerobic treatment** is **not advisable** to SME-tanners. In our opinion, **aerobic treatment** (composting) is an alternative that **can be recommended to SME-tanners**.

Windrow composting - a low-cost and low sophisticated technology – is feasible but serious problems with malodour and insects must be expected.

In-vessel composting with a proper waste gas treatment (biofilter) will avoid these problems. A horizontal flow, agitated solids bed reactor is the favoured reactor design. This type of reactor will solve the compaction and "bridge building" problems. Furthermore, frequent turning will improve the decomposition of the substrate and will lead to a homogenous temperature and moisture distribution.

Thermal pre-treatment of the fleshing is highly recommended. The fleshings are heated and tallow is separated from the protein meal. The tallow is a valuable by-product and the protein-meal processed to the composting reactor. By this treatment, the volume is decreased by 2/3 and the water content is decreased from 80 to 40%. Hair residues can be composted without pre-treatment. Attention has to be paid on the avoidance of cross-contamination with chromium bearing effluents.

Mixing with bulking material is indispensable, the addition of amendments (saw dust, horse bed stale or recycled compost) is recommended, but not absolutely necessary. A volume ratio of 1.5 to 2 m³ bulking material and amendments per m³ substrate is recommended. Residence time in the composting reactor (high rate phase) is between 10 and 14 days.

Depending on the quantity of solid waste, the volume ratio and the residence time, per ton of wet salted hide that is process through a tannery, a composting reactor volume of 3.7 to 12.6m³ can be computed.

Minimum curing phase (storage at open air piles) is between 30 days for compost made out of hair residues and 40 days for compost made out of thermal fleshings.

To maintain proper moisture conditions in the reactor approximately 0.5 $m^3/m^3_{substrate}$ water is required. During the maturation phase further irrigation will be necessary. However, this depends on the prevailing climatic conditions.

Depending on the required process temperatures, the water content of the substrate and other parameters, the air flow varies significantly. Composting hair residues requires an air flow between 2 and 6 $m^3/h \ m^3_{substrate}$ during the high rate phase. The air demand for the

treatment of thermal fleshings is significantly higher. Between 15 and 35 m³/h m³$_{substrate}$ are required to maintain proper process temperatures.

The compost made out of hair residues is a high quality product with excellent fertilising properties. Compost made out of thermal fleshings shows little plant tolerance or even plant intolerance. However, the fertilising properties of the latter can be improved by adding the amendment horse manure. In addition to that, in general hair residues will be composted together with thermal fleshings, resulting in a product with an acceptable quality.

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Annexes