Natsurv 10:

Water and Wastewater Management in the Tanning and Leather Finishing Industry

(Edition 2)

CD Swartz, C Jackson-Moss, RA Rowswell,
AB Mpofu, PJ Welz

WATER RESEARCH COMMISSION

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WATER AND WASTEWATER MANAGEMENT IN THE TANNING AND LEATHER FINISHING INDUSTRY: NATSURV 10 (2nd EDITION)




Report to the

Water Research Commission

by

CD Swartz[1], C Jackson-Moss[2], RA Rowswell[3], AB Mpofu[4], PJ Welz[4]

1. Chris Swartz Water Utilization Engineers
2. International School of Tanning Technology
3. Tannery Environmental Consulting Services
4. Cape Peninsula University of Technology

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Water Research Commission
Private Bag X03
Gezina, 0031

orders@wrc.org.za or download from www.wrc.org.za

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EXECUTIVE SUMMARY

BACKGROUND

In the 1980s, the Water Research Commission (WRC) and the Department of Water Affairs (now the Department of Water and Sanitation) embarked on a series of national surveys for 16 industries. These reports were referred to as NATSURV documents, focusing on the water and wastewater management of these industries. The NATSURV reports of the different industries have been well used by the sector. However, since the 1980s South Africa and its industrial sectors have either grown or in some cases shrunk considerably. The landscape has changed, and new technologies and systems have been adopted by some industries. Thus, some of the information contained in the national surveys can be considered out of date. Through the UN CEO Water Mandate, water stewardship discussions, water allocation and equity dialogues, there is also a growing awareness around water use, water security and waste production. It is therefore considered an opportune time to review the water and wastewater management practices of the different industrial sectors.

The current project is concerned with the water and wastewater management of the tannery and leather finishing industry. The first NATSURV document of this industry presented data collected during visits to 11 of the 20 tanneries in South Africa at the time. The number of tanneries and leather finishing industries had increased to 35 at the time of this research. Ten tanneries were visited, representing all the different types, categories and sizes of industry in this sector, namely, bovine, ovine and exotic hides and skins, wet blue tanning, retanning, full-house tanning and leather finishing.

AIMS

The main aims of the project were to:

- Provide a detailed overview of the tanning and leather finishing industry in South Africa, and its changes since 1980.
- Determine the water consumption and specific water consumption in the industry.
- Determine wastewater generation and typical pollutant loads.
- Provide recommendations on best practices for the tanning industry.

METHODOLOGY

A thorough search of the internet and available directories were conducted and a database compiled of tanning and leather finishing industries in South Africa. The tanneries were then contacted via e-mail and telephone calls. Information was gathered using questionnaires developed for this purpose. Of the 35 tanneries and leather finishers in the country, 10 tanneries were selected to represent different types, sizes and geographical locations. The selected tanneries were visited for personal interviews and surveys. During the visits, information and data were gathered on water usage, wastewater generation and quality, wastewater treatment processes used for treating the wastewater streams, municipal monitoring data and energy consumption figures.

BEST PRACTICES: WATER USE AND MANAGEMENT

Most tanneries visited for this study use municipal water. However, the cost of water differs from municipality to municipality. Some tanneries supplement municipal water with borehole water or storm water during the rainy season. Retanning and leather finishing tanneries consume less water than full-house tanneries because the downstream processes are less water intensive. This is one of the advantages of retanning and leather finishing tanneries, as they produce less polluted and smaller volumes of wastewater than full-house tanneries.

The range of the specific water intake (SWI) for full tanning was found to be 170-550 L/hide, compared with the 320-744 L/hide reported in the first NATSURV 10 (1989). A target SWI figure is proposed at 50-150 L/hide for wet blue process stages, 100-200 L/hide for dyehouse process stages, and 200-500 L/hide for total tanning and finishing stages.

BEST PRACTICES: WASTEWATER GENERATION AND MANAGEMENT

The effluent from tanneries contains high organic loads as measured by chemical oxygen demand (COD), and high concentrations of dissolved and suspended solids as measured by total dissolved solids (TDS) and total suspended solids (TSS). Effluent also contains varying levels of sulphates, sulphides, chlorides and chromium, which add to the pollutant load on the environment of the wastewater streams discharged. Municipalities include discharge standards for these pollutants in their trade effluent by-laws.

Beamhouse processes are the source of all non-limed and limed solid wastes such as fleshings, trimmings and waste splits. Most of the organic pollution load originates from beamhouse processes. Soak water provides most of the wastewater salinity; the remainder comes from acid salts applied to suppress pelt swelling.

The specific pollutant loads generated by the different types and categories of tanning process vary considerably for the main pollutants found in the wastewater streams (COD, TDS, TSS, sulphates, chlorides and chromium). Chapter 6 shows data on the quality of the wastewater (effluent) streams at the tanneries that were visited, data that was obtained from the tanneries themselves and data from some of the municipalities to which the tanneries discharge their final effluent. The specific pollutant loads calculated from this data are also shown, which indicate the considerable variation in ranges.

The integrated wastewater treatment systems in the tanning and leather finishing industry consist of preliminary treatment (or pretreatment), primary, secondary and tertiary treatment processes. Tanneries performing wet blue retanning and leather finishing mainly use pretreatment and primary treatment processes, whereas full-house tanneries use secondary treatment (biological treatment) as well. Some tanneries in South Africa combine all effluent streams, while others keep effluent streams from the beamhouse and tanyard separate. The latter is preferable because organic waste is the major constituent of beamhouse effluent, whereas the tanyard effluent contains high concentrations of inorganics, which could include chromium.

Cleaner production technologies are continuously being researched, developed and applied to the tanning industry. A specific focus area is the reduction of salt loadings used in the processes. A number of recent cleaner production techniques are reported in Chapter 8 of the report.

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Reference Group	Affiliation
Dr Jo Burgess (Research Manager)	Water Research Commission
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Mr D Boast	African Hide Trading
Mr S Blumberg	Cape Produce Company (Pelts)
Mr F Weideman	Cape Produce Company (Pelts)
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Mr C du Pisani	South Cape Ostrich Tanning (SCOT)
Mr E van Staden	Wettest Effluent Treatment
Mr S Woods	Woods Tanning
Mr A Woods	Woods Tanning
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Project Team:

Mr Chris Swartz, Chris Swartz Water Utilization Engineers (Project Leader)

Dr Clive Jackson-Moss, International School of Tanning Technology

Mr Roger Rowswell, Tannery Environmental Consulting Services

Dr Pamela Welz, Cape Peninsula University of Technology

Dr Seun Oyekola, Cape Peninsula University of Technology

Mr Ashton Mpofu, Cape Peninsula University of Technology

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ACRONYMS AND ABBREVIATIONS

WRC	Water Research Commission
NATSURV	National survey
FAO	Food and Agricultural Organization
pH	The measure of acidity or alkalinity of a chemical solution, from 0 to 14
NWA	National Water Act
DWS	Department of Water and Sanitation
WSA	Water Services Act
COD	Chemical oxygen demand
TDS	Total dissolved solids
TSS	Total suspended solids
SWI	Specific water intake
SWU	Specific water use
BOD	Biological oxygen demand
CAS	Conventional activated sludge
TKN	Total Kjeldahl nitrogen
HVLP	High-volume low-pressure
LIRI	Leather Industries Research Institute

GLOSSARY OF TERMS

Basic chromium sulphate – Chromium (III) hydroxide sulphate; $Cr(OH)SO_4$.

Bating – Using enzymes to dissolve and remove some of the interfibrillar proteins of delimed hides and skins to produce softer leather with a smoother grain surface.

Beamhouse/limeyard – The portion of the tannery where hides are soaked, limed, fleshed and unhaired when necessary prior to the tanning process.

Bovine – Adjective for animals from the *Bovinae* sub-family, which includes cattle and buffalo.

Brining – Curing hides by washing and soaking in a concentrated salt solution.

Chrome tanning – Using chromium salts (usually one-third basic chromium sulphate) in the tanning process.

Collagen – The principal fibrous protein in the corium of a hide of skin.

Conditioning – Softening dried leather by introducing controlled amounts of moisture.

Conventional processing – Tanning processes not modified to reduce environmental impact.

Crust leather – Leather that has simply been dried after tanning, retanning and dyeing, without further finishing.

Curing – Processes used to prevent bacteria putrefying or rotting hides and skins after they have been flayed in the slaughterhouse.

Degreasing – Removing, as far as possible, the natural grease in the skin.

Deliming – Removing lime from hides or skins using ammonium salts and/or weak acids.

Drums – Large wooden, stainless steel or polypropylene drums that are rotated at speeds suitable for a particular tanning process.

Dyeing – Imparting colour on leather by treating it with natural or synthetic dyestuff.

Epidermis – The outer surface layer of the hide or skin that holds the hair roots. It is removed during the leather-making process.

Fatliquoring – Introducing an emulsion of fats and oils into the wet leather to provide lubrication and subsequent softness and flexibility.

Fellmongery – Plant in which goatskins or sheepskins are processed to the pickled state.

Filling – Drumming process whereby substances are added to vegetable-tanned leather to create more compact leather such as vegetable-tanned sole leather.

Finishing – a) Mechanical operations, such as conditioning, staking, buffing, dry milling, polishing and plating/embossing, that improve the appearance and the feel of leather. b) Applying or fixing a surface coat to the leather.

Fleshing – Removing the fleshy, fatty material situated on the insides of hides and skins.

Fleshings – Pieces of subcutaneous tissue, fat and flesh separated from the hide during fleshing.

Float – Volume of water present in the tanning vessel.

Full-house tanning – The total tanning and finishing processes, including beamhouse, tanyard and dyehouse processes.

Grain – The outermost section of leather that is kept intact in full-grain leathers, but smoothed to some degree in corrected grain leathers.

Green fleshing – Fleshing performed prior to liming and unhairing.

Hides – Skins of larger animals such as cattle.

Horsing – Ageing of hides or skins after tanning or fatliquoring on wooden pallets or a wooden frame.

Leather – A general term for hide or skin that has been treated by tanning or another process to make it more pliable and to preserve it against decay.

Limed hide or skin – Hide or skin obtained after liming.

Lime fleshing – Fleshing performed after liming and unhairing.

Liming – Soaking in an alkali solution to prepare the skins/hides for tanning and assisting with removal of hair or wool, epidermis and subcutaneous tissue.

Limeyard – Area in the tannery where the hides are soaked and unhaired.

Mineral tanning – The tanning process where mineral salts (usually chromium, but occasionally aluminium or zirconium) are the tanning agents.

Neutralising – Deacidifying chrome-tanned leather.

Ovine – Relating to or resembling sheep.

Paddles – Large wooden vessels fitted with wooden paddles that are rotated to create a stirring action.

Pickled pelt – A skin that has been pickled.

Pickling – The acidification process that follows bating, whereby the skin or hide is immersed in brine and acid.

Protein – A complex naturally occurring organic material consisting of long interwoven chains of amino acids.

Raw hide – Untanned hide.

Retanning – Applying special products (such as synthetic tannins) to leather to impart specific properties such as softness, evenness of colour.

Rinsing/running water washes – Washing accomplished by the continuous inflow and outflow of water in a treatment apparatus.

Sammying – A mechanical process where excess moisture is squeezed out of the hide material.

Setting – Mechanical operation to remove water and wrinkles, and to flatten the surface of leather.

Settleable solids – The volume of material that settles out of a solution in a defined time period.

Shaving – The process whereby leather is mechanically trimmed to the desired thickness.

Shavings – The fragments obtained from shaving.

Soaking – The first process in the manufacture of leather, which is used to rehydrate and wash the hides or skins.

Skin – The pelt of a small animal such as a calf, pig or sheep.

Split – The non-grain fraction of a split hide.

Splitting – The horizontal splitting of hides and skins into a grain layer and, if the hide is thick enough, a flesh layer.

Syntans – Synthetic tanning agents.

Tallow – Non-edible or ‘technical’ fat.

Tanning – The process whereby animal hides and skins are converted to leather.

Tanyard – The part of the tannery where pickling, tanning and basification processes are performed.

Total Kjeldahl nitrogen – The sum of nitrogen present as organic nitrogen, ammonia and ammonium compounds measured using the Kjeldahl technique.

Trimming – Removing undesirable portions of hides and skins by cutting.

Trimmings – The residues arising from trimming hides and skins.

Upholstery leather – Leather manufactured for covering furniture or for seats of aircraft or vehicles.

Vegetable tanning – Using tannins from plant origin (such as mimosa tree extract) for tanning.

Wetting back – Rehydrating hides or skins.

Wet blue – Chrome-tanned hide that has been sammyed to remove surplus moisture. Further processing is required to produce leather.

Wet white – A hide or skin that has been limed and tanned with non-chromium agents. It remains off-white in colour and moist.

CHAPTER 1: INTRODUCTION

1.1 Background

In response to several interrelated factors, including higher costs of waste disposal, more stringent legislative requirements, and increasing environmental awareness, industries are constantly implementing more sustainable methods to reduce qualitative and quantitative industrial pollutant loads and to reuse water and waste.

Manufacturing and processing industries consume significant quantities of energy and water, and generate large volumes of wastewater. This prompted the Water Research Commission (WRC) of South Africa to commission 16 national surveys (NATSURVs) of various agricultural and non-agricultural industries (malt brewing, poultry, red meat, edible oil, sorghum malt, beer, dairy, sugar, metal finishing, soft drink, tanning/leather finishing, laundry, textile, oil and refining, and power generating), culminating in the publication of 16 separate NATSURV documents between 1986 and 2001. These documents included information about production processes, water usage, solid waste generation, and wastewater quality, quantity, and treatment practices. Significant market-related changes have taken place in many industries over the decades. Much of the information in the original NATSURV series is outdated; therefore, the WRC commissioned a new series of NATSURV documents. The previous NATSURV for the tanning and leather finishing industry (WRC TT 44/90, ISBN 0947 447 60 1) was published in 1989.

1.2 Aims, Scope and Limitations

The environmental issues facing the tannery industry are of particular concern, and wastewater discharge, air emissions, solid waste disposal, environmental pollution, and employee health and safety concerns have become increasingly important. Globally, specific discharge standards, and the occupational safety and health exposure limits are being scrutinised and adjusted. Furthermore, there is international advocacy to finding alternatives to salt curing and for cleaner production. In general, the industrialised world has adopted technologically cleaner production methods, whereas the developing world is mainly promoting waste minimisation while slowly transitioning into cleaner production.

The main objective of this NATSURV document is to stimulate water saving and pollution mitigation by serving as a comprehensive guide and benchmark tool for a number of stakeholders, including local governments, industry players, academics, researchers and engineers.

The specific aims of the survey were to:

- Provide a detailed overview of the tanning and leather finishing industry in South Africa, its changes since 1989 and its projected change(s).
- Critically evaluate and document the 'generic' industrial processes of the tanning and leather finishing industry in terms of current practice, best practice and cleaner production.
- Determine the water consumption and specific water consumption and recommend targets for use, reuse, recycling and technology adoption.
- Determine wastewater generation, and typical pollutant loads and best practice technology adoption.
- Determine local electricity, water and effluent by-laws within which these industries function, and critically evaluate if the trends and indicators are in line with water conservation demand management and environmental imperatives.
- Critically evaluate the specific industry water (including wastewater) management processes adopted and provide appropriate recommendations.

- Evaluate the industry adoption of the following concepts: cleaner production, water pinch, energy pinch, life cycle assessments, water footprints, wastewater treatment and reuse, best available technology and ISO 14 000 to name a few.
- Provide recommendations on the best practice for this industry.

CHAPTER 2: OVERVIEW OF THE TANNING AND LEATHER FINISHING INDUSTRY

2.1 Overview of the Tanning Process

The tanning industry processes hides and skins into leather. This is a chemical process that uses large quantities of water, and hence tanneries produce considerable amounts of both liquid and solid wastes. Tanneries play an important role in processing a by-product or waste from the meat industry, namely, the hides and skins. Without the tanning industry, these hides and skins would have to be disposed in landfill sites or incinerated. Tanneries therefore solve one pollution problem, but create many others during the processing of hides or skins into leather or partially processed forms of leather. This is true for most types of leather except for certain exotic skins, where the animals are farmed specifically for their skins.

'Hides' refer to the skin covering from large animals such as cows, oxen, and large game. 'Skins' refer to the skin covering of smaller animals, such as sheep, goats, ostriches, crocodiles and small game. The tanning process can be divided into three main stages (see Section 2.1.1 to Section 2.1.3), with each one of these being further sub-divided.

2.1.1 Wet blue or fellmongery processing

Wet blue or fellmongery processing involves the processing of raw hides into a product called 'wet blue'. Wet blue is a stable product that cannot rot, and is an internationally traded commodity. The production of wet blue is the most polluting of all tanning operations. Fellmongery processing refers to the conversion of raw sheepskins into pickled sheepskins.

2.1.2 Dyehouse operations

Dyehouse operations include splitting and shaving skins or hides to a defined thickness, neutralising, retanning, dyeing and fatliquoring. After dyeing, the leather is referred to as 'crust' leather. The effluent from the dyehouse pollutes less than the effluent from wet blue processing. Tanneries that carry out the crusting process usually process the crust leather further into finished leather.

2.1.3 Leather finishing

The finishing of leather involves applying a film to the leather surface to give the leather protection and durability for its intended purpose. Very little water is used in leather finishing.

It is important to note that not all tanneries carry out all processing stages as discussed in Section 2.1.1 to Section 2.1.3. It has become more common in recent times that certain tanneries will only process pickled sheepskins or wet blue, and then sell these to other facilities for further processing. This is true not only globally, but also in South Africa. This change in production has had a major impact on the effluent and solid waste produced by tanneries, as most pollution is produced when processing hides or skins up to the pickled or wet blue stage. Many developing countries process pickled skins and wet blue, and then export this semi-processed material to developed countries that have much stricter environmental regulations. Some of the newer wet blue plants have been built close to abattoirs or the source of hides, and are often a way of vertically integrating the value chain for the feedlot businesses.

More information on the tanning processes can be found in Section 3.2.

2.2 Changes in the Tanning Industry Since the Previous NATSURV

Since the last NATSURV on the tanning and leather finishing industry was published in 1989, several changes have taken place. These can be broadly outlined:

- There are fewer tanneries in South Africa.
- Wet blue plants have increased in size.
- Many small tanneries processing hair-on gameskins and taxidermists have been established.
- Many small ostrich tanneries were established, but this number has subsequently decreased.

The implementation of the Motor Industry Development Plan had a significant positive economic effect on automotive leather production. This resulted in international tanning groups establishing themselves in South Africa. Currently, there are two tanneries in South Africa that produce large quantities of automotive leather.

As a result of the deregulation of the ostrich industry, a number of smaller ostrich tanneries were established to compete with larger ostrich tanneries. Many of these have subsequently closed, or have been bought by bigger ostrich tanneries. There are three major players left tanning ostrich leather, but small quantities of ostrich leather are still processed by one or two small tanneries tanning a mixture of different leathers.

The wet blue plants in South Africa have generally increased in size, but have reduced in number. This is mainly due to the closure of wet blue plants associated with the automotive industry, and because South Africa now processes less imported hides for the automotive sector. However, some new wet blue tanneries have been established. Some feedlot operators have bought into these wet blue plants in an effort to add value to their product.

Hunting has become big business in South Africa. There are large numbers of gameskins that are tanned with the hair on or processed by taxidermists. These are too numerous to include in the NATSURV. Although these taxidermists do use water and hence produce effluent, many of the effluent streams are reused. Most of their effluent is a soaking effluent. They do not unhair the skins. It is estimated that in total they consume less water than one large tannery. Many of these small tanneries are located on farms, use their own sources of water, and discharge into ponds or evaporation dams.

2.3 Size of the Industry

2.3.1 Hide and skin production: Global and local trends

The Food and Agriculture Organization (FAO) of the United Nations regularly publishes the "World statistical compendium for raw skins and hides, leather and leather footwear". The latest version of this document (FAO, 2016) contains data from 1999 to the years 2013 and/or 2014. Unfortunately, only bovine, ovine and goat hides and skins are included in the document. Pigskins, which are produced in large numbers in Asia, are excluded, and no comprehensive data is available for ostrich, crocodile and other 'exotic' species that are important from a South African perspective. Tanning and exporting of these exotic skins and hides is a lucrative industry in South Africa. This sector of the industry has increased over the years.

As developing countries, Latin America produces 66%, Africa 60% and Asia 96% of bovine hides, sheep and lambskins, and goat and kidskins for leather (Figure 2.1). Although the developing world produces more raw hides and skins than the developed world, the developed world is a nett exporter of hides for leather, while the developing world is a nett importer.

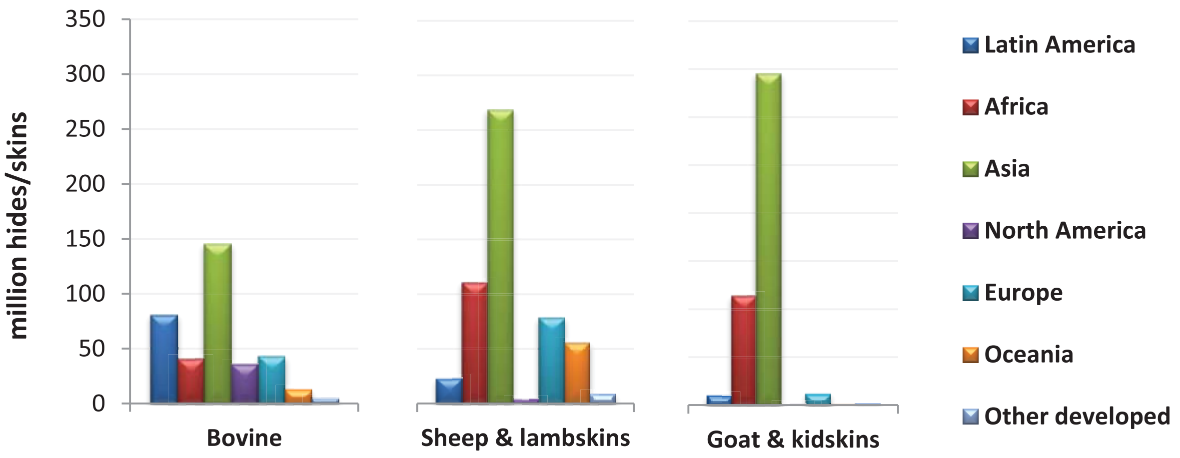

Figure 2.1: Global production of bovine, ovine and goat hides and skins in 2013 (FAO, 2016)

In 2013, South Africa accounted for 0.9% (wet salted weight) and 2.7% (dry weight) of world bovine hides and ovine skins. There has been an upward trend in the production of bovine hides in South Africa from around 2.4 million pieces in 1999/01 to 3.4 million pieces in 2014. Over the same period, the production of sheepskins has fluctuated between 8.5 and 9.0 million pieces. Unlike the developing world as a whole, South Africa is a nett exporter of hides and skins with a gross export value of US$45.5 million for bovine hides and US$172.3 for ovine skins in 2013 (FAO, 2016).

2.3.2 Leather and footwear production: Global and local trends

Although developing countries produce the largest proportion of bovine (66%) and ovine (60%) hides and skins, they produce even larger percentages of bovine 'heavy' (80%), bovine 'light' (67%), and ovine (83%) leather (Figure 2.2). Because the stringent environmental policies in many developed countries make the operation of tanneries difficult, they export the hides and skins to be converted to leather in developing countries. South Africa is anomalous as it falls into the FAO category 'other developed countries' together with Japan and Israel, and is the only African country to do so (FAO, 2016).

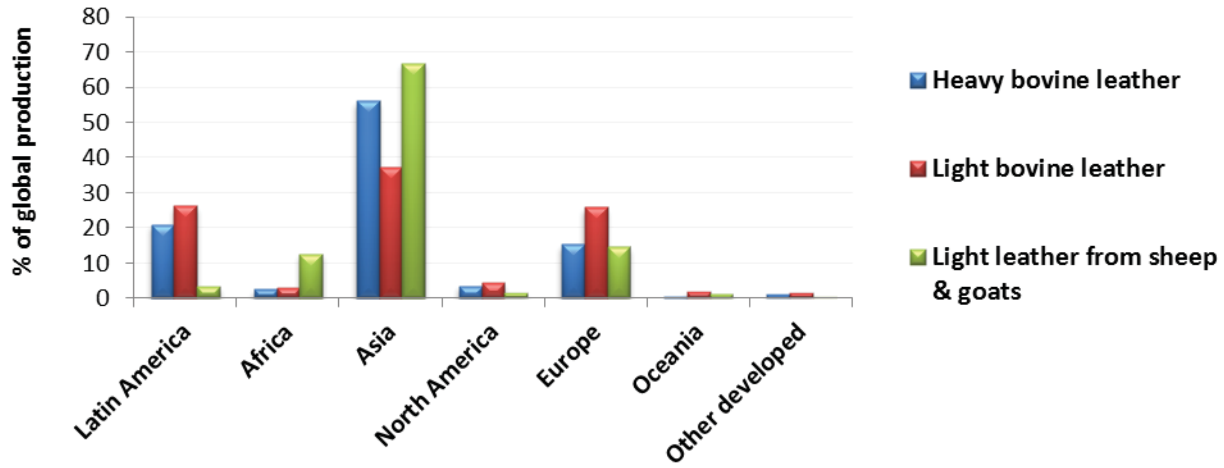

Figure 2.2: Global production of bovine, ovine and goat leather in 2013 (FAO, 2016)

In South Africa, the production of heavy leather from bovine animals has increased gradually since 1999, while the production of light leather from bovine animals has shown a slight decrease.

According to FAO data, the production of leather footwear and footwear exports in South Africa has increased significantly since 2010. Conversely, imports have decreased. The value of exports in 2013 was US$45.6 million. However, these trends are not supported by anecdotal evidence from key players at tanneries, who stated that the shoe leather industry in South Africa has declined in recent years.

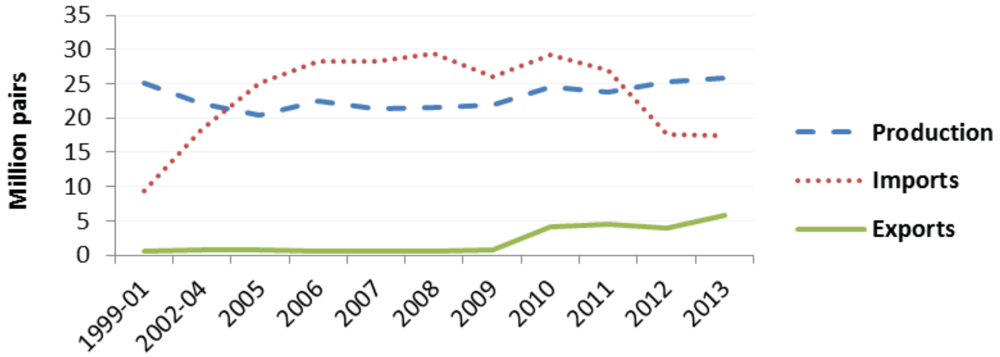

Figure 2.3: Trends in production and trade of leather footwear in South Africa (FAO, 2016)

2.3.3 South African tanneries

Table 2.1 shows the number of hides and/or skins by South African tanneries. The data in Table 2.1 is categorised according to the types of skin and/or hide and the processing methods used. The tanning processes are described in Chapter 3.

According to the data collected during the survey and discounting tanneries that process wet blue to finished leather (finishing tanneries), large- and medium-sized tanneries (≥ 100 hides/day) process approximately 10 900 to 11 400 wet blue hides, 15 000 to 17 000 pickled and 500 wool-on sheepskins, and between 1 600 and 2 150 crocodile or ostrich skins per day. Only 200 hides/day are vegetable-tanned.

Table 2.1: Size of the tanning and leather finishing industry in South Africa

Tannery	Type	Production (typical)
Wet blue and pickled skins		
Tannery 1	Wet blue and pickled sheepskins	3 500-4 000 hides/day from raw to wet blue 4 000-5 000 sheepskins/day from raw to pickled
Tannery 2	Wet blue and pickled sheepskins	2 700 hides/day from raw to wet blue 5 000 sheepskins/day from raw to pickled
Tannery 3	Wet blue and pickled sheepskins	1 800 hides/day from raw to wet blue 2 000 sheepskins/day from raw to pickled
Wet blue		
Tannery 4	Wet blue	1 300 hides/day from raw to wet blue
Tannery 5	Wet blue	1 000 hides/day from raw to wet blue
Tannery 6	Wet blue	600 hides/day from raw to wet blue
Finishing tanneries		
Automotive		
Tannery 7	Automotive upholstery	4 000 hides/day from wet blue to finished leather
Tannery 8	Automotive upholstery	4 000 hides/day from wet blue to finished leather
Shoe upper		
Tannery 9	Shoe upper leather	500 hides/day from wet blue to finished shoe upper leather

Tannery	Type	Production (typical)
Tannery 10	Shoe upper leather	350 hides/day from wet blue to finished shoe upper leather
Other		
Tannery 11	Furniture upholstery	700 hides/day from wet blue to finished leather
Tannery 12	Upholstery	300-400 hides/day from wet blue to finished leather
Tannery 13	Furniture upholstery	< 100 hides/day from wet blue to finished leather
Exotic leather		
Tannery 14	Ostrich and crocodile leather	500 ostrich skins/day from raw to finished leather 1 000 crocodile skins or small gameskins/day from raw to finished leather (crocodiles) and hair-on (gameskins)
Tannery 15	Ostrich and crocodile leather	250 ostrich skins/day from raw to finished leather 100-150 crocodile skins/day from raw to finished leather
Tannery 16	Ostrich leather	100 skins/day from raw to crust leather
Mixed production		
Tannery 17	Mixed production	< 100 hides/day
Tannery 18	Mixed production	< 50 hides/day
Tannery 19	Mixed production	< 100 hides/day
Tannery 20	Mixed production	< 50 hides/day
Tannery 21	Mixed production	< 50 hides/day
Tannery 22	Mixed production	< 50 hides/day
Tannery 23	Mixed production	< 50 hides/day
Tannery 24	Mixed production	< 50 hides/day
Tannery 25	Mixed production	< 50 hides/day
Pickled sheepskins		
Tannery 26	Pickled sheepskins	4 000-5 000 sheepskins per day from raw to pickled sheepskins
Gameskins		
Tannery 27	Hair-on gameskins	< 50 hides/day
Tannery 28	Hair-on gameskins	< 50 hides/day
Tannery 29	Hair-on gameskins	< 50 hides/day
Other		
Tannery 30	Crocodile leather	650 skins/month from raw to finished leather (< 50/day)
Tannery 31	Wool-on sheepskins	500 sheepskins/day from raw to wool-on sheepskins
Tannery 32	Hair-on hides	< 50 hides/day from raw to hair-on hides
Tannery 33	Vegetable-tanned leather	200 hides/day from raw to vegetable-tanned leather
Tannery 34	Hair-on hides	< 50 hides/day from raw to hair-on hides
Tannery 35	Suede	< 50 hides/day

Figure 2.4 shows the geographical distribution of some of the main tanneries in South Africa.

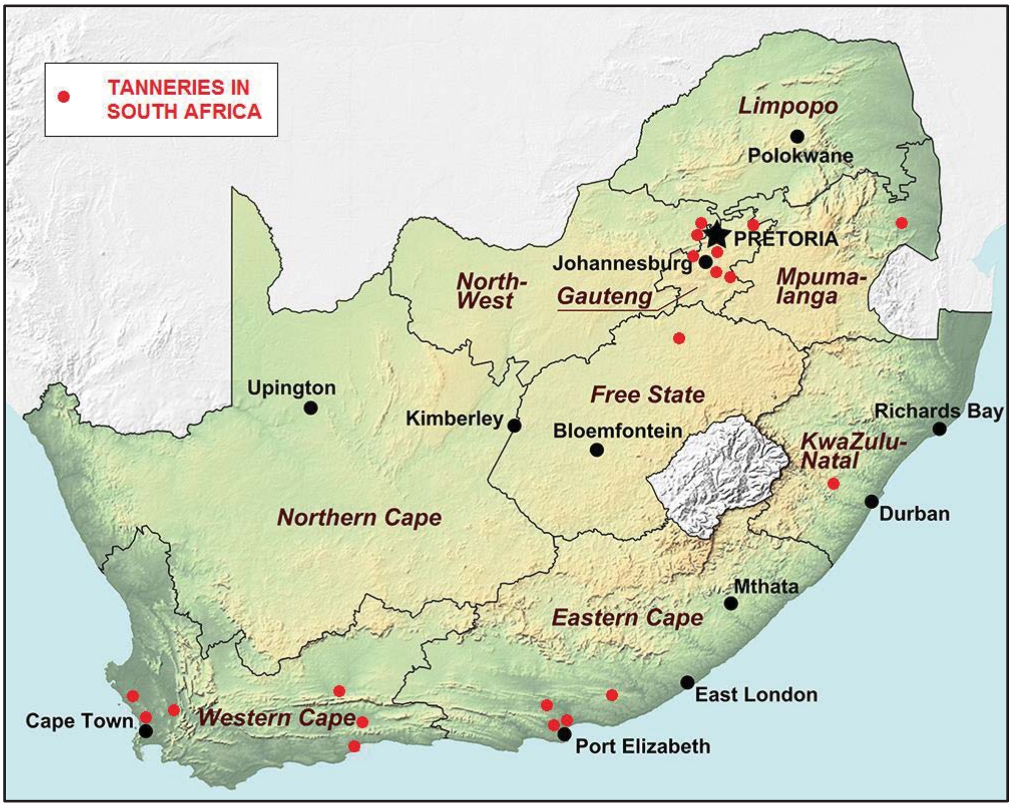

Figure 2.4: Geographical distribution of tanneries in South Africa

CHAPTER 3: TANNING AND LEATHER FINISHING PROCESSES

This chapter provides an overview of the major tanning and leather finishing processes applied in South Africa.

3.1 Categorisation of the Tanning Industry in South Africa

The main categories in the tanning industry are defined as follows:

Hides/skins:	Bovine (cattle skins)
	Ovine (sheepskins)
	Exotic (ostrich, crocodile and game)
Processes:	Wet blue (chrome tanning)
	Wet white tanning
	Vegetable tanning
	Leather finishing
Products:	Automotive upholstery
	Shoe uppers
	Furniture upholstery
	Hair-on hides
	Products from exotic skins

3.2 Tanning Processes

The main purpose of tanning and leather finishing industries is producing durable material for upholstery, and for making handbags, shoe uppers and other clothing items. Although useful by-products are generated during tanning, much of the waste is potentially toxic. In keeping with the global 'Green Economy' strategy, there are already cleaner production methods available (refer to Chapter 6 and Chapter 8). In addition, a great deal of research is being conducted worldwide into the use of 'wastes' as resources such as novel feedstocks to produce value-added products. In the future, sustainable solutions may be found to deal with tannery 'waste'.

Figure 3.1 shows the hide and skin preparation processes and subsequent tanning processes in a typical wet blue tannery, together with by-products and wastes. The figure is followed by a summarised description of each of the processes.

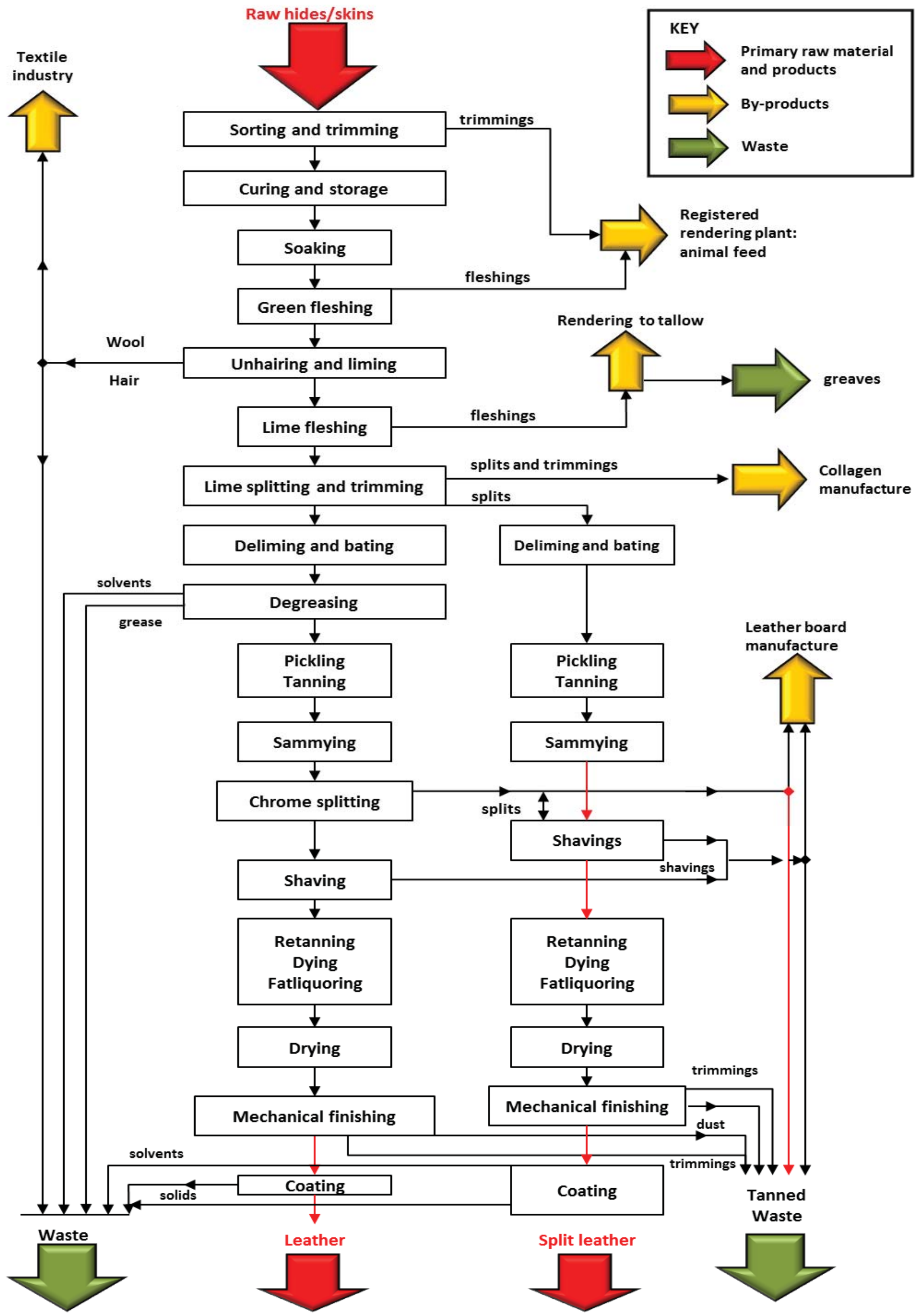

Figure 3.1: Processes, by-products and waste from wet blue tanning (adapted from European Union, 2013)

3.2.1 Hide and skin reception and storage

The reception stage consists of sorting and trimming: hides and skins are sorted into grades by size and/or weight and quality, and some of the edges (legs, tails, faces, udders, etc.) of the raw (green, chilled or chemically cured) and salted (dry salted or wet salted) hides and skins may be removed (green fleshing). If the hides are not going to be processed immediately, they may be cured (usually by salting) or chilled.

3.2.2 Process stages

The processing of raw (green, chilled or chemically cured) and salted (dry salted or wet salted) hides and skins is divided into two sections, namely, the beamhouse section (Section 3.2.2.1), and the tanyard section (Section 3.2.2.2), with a number of processes taking place in each section.

3.2.2.1 Beamhouse (or limeyard) section

Soaking

Soaking reintroduces water into the hides and skins, washes out any preservatives (usually salt), blood, manure, urine and dirt, and softens the hides and skins for subsequent processing.

Green fleshing

Fleshing is the mechanical removal of fats and flesh from the inside of hides or skins. Fleshing can be accomplished before or after liming, and there are advantages and disadvantages to each. From an environmental perspective, green fleshing is preferable as the tissue is not contaminated with chemicals, and the amount of chemicals needed for unhairing and liming are reduced. This reduces the amount of chemicals in the effluent from downstream processes.

Unhairing and liming

The liming and unhairing processes are usually carried out simultaneously. Chemicals (Table 3.1) are used to:

- Partially hydrolyse polypeptides to relax the structure of the hide or skin.
- Solublise globular proteins.
- Saponify fats.
- Swell hides.

In the case of sheepskins, the wool is recovered as a by-product by a paint unhairing process.

Lime fleshing

Lime fleshing is similar to green fleshing, but it takes place after unhairing and liming. The quality of hides from lime fleshing is typically superior to those produced using green fleshing. Lime fleshing is the method of choice in South African tanneries.

Lime splitting and trimming

Splitting is a form of trimming where the hide is mechanically divided into a grain layer and a flesh layer. This can be accomplished after liming or chromium tanning. Some trimmings may also be processed to leather (Figure 3.1). Lime splitting reduces the amount of chemicals required in downstream processes. In South Africa, splitting and shaving are usually performed after tanning.

Deliming and bating

Deliming and bating are processes that use chemicals and enzymes (Table 3.1) to:

- Remove residual chemicals and reduce the pH of the hides and skins.
- Soften the hides and skins to assist with chemical penetration in subsequent processing stages.

3.2.2.2 Tanyard section

Degreasing

Excessive amounts of grease in the hide or skin may cause non-uniform penetration of tan or dye. This causes complications with the finishing processes and creates dark and greasy patches on the finished leather. Degreasing is particularly important before chrome tanning as chromium salts can react with the greases and form insoluble chromium soaps, which are very difficult to remove.

Pickling

Pickling is a chemical (Table 3.1) process whereby:

- Acid is added to lower the pH to between 2 and 3 for better penetration of the tanning chemical.
- Salt is added to prevent the hide from swelling under acid conditions.

In the case of pickled sheepskins, the picking process preserves the skin and is the final processing step.

Tanning

Tanning is accomplished by adding tanning chemicals (Table 3.1) into a drum containing the hides for an appropriate time period. Most of the 'leather' is traded as wet blue. In the case of wet blue, the tanning agent is trivalent chrome tanning salts. In the case of wet white or metal-free leather, glutaraldehyde is used as tanning chemical. It needs to be stressed that tanneries only use trivalent chromium, CrIII, Cr^{3+} or Cr^{III}, which has been found to be non-toxic. Limits for disposal thereof have been relaxed in the European Union and North America.

Basification is the addition of a mild alkali into the tanning drum to ensure binding of the tanning chemical to the hide or skin. After tanning, a final wash is carried out to remove any unbound chemicals from the hide or skin.

Sammying

Sammying is the mechanical removal of water from the wet blue or wet white to a moisture content of approximately 50%. Drying the hides increases the effectiveness of the downstream splitting and shaving processes.

Figure 3.2: Wet blue (left) and pickled skins (right)

3.2.3 Dyehouse process stages (wet finishing and dry finishing)

Splitting and shaving

Splitting and shaving are mechanical methods used to reduce the thickness of the hide or skin to the thickness required in the final leather. Splitting after tanning is known as chrome splitting.

Washing

The skins or hides are washed in water to remove residuals from the splitting and shaving operations.

Neutralisation

Neutralisation is the raising of the pH of the wet blue or wet white to allow penetration of chemicals in subsequent process stages.

Retanning

Retanning is the introduction of different types of chemical into the wet blue or wet white that impart specific properties (such as flexibility, fullness and texture) on the final leather.

Dyeing

Dyeing is the addition of either powder or liquid dyes to give the leather the desired colour.

Fatliquoring

Fatliquoring is the addition of emulsified oils to make the leather soft and flexible.

Fixation

Fixation is the chemical binding of all the retanning chemicals, dyes and fatliquors to the leather by lowering the pH in the drum using formic acid.

Final wash

The final wash is carried out to wash out any residual unbound chemicals from the dyehouse processes.

Drying, mechanical finishing and coating

After drying, further finishing of the leather may be performed to achieve the desired product.

3.2.4 Beneficial use of tannery by-products

As shown in Table 3.1, wool and hair may be used to manufacture textiles. Fatty trimmings and fleshings from the beamhouse are typically rendered at a registered facility to make animal feed. Collagen (for example for sausage casings) may be manufactured from beamhouse splits and trimmings. In addition, leatherboard may be manufactured from tanyard splits and trimmings (UNIDO, 1991; Buljan & Král, 2015).

3.3 Chemicals and Products Used in Tanning Processes

Table 3.1 summarises the aims of applying these chemicals in the tanning and leather finishing industry.

Table 3.1: Chemicals used in various processes in the tanning industry

Process	Chemicals	Purpose
Wet blue process stages		
Soaking	Biocides, surfactants, degreasers, enzymes	Reintroduce water and washing of chemicals and dirt
Liming and unhairing	Lime, sodium sulphide, sodium hydrosulphide, caustic soda	Chemically remove hair and swell skins
Deliming and bating	Ammonium sulphate, ammonium chloride, formic acid, proteolytic enzymes	Remove lime and calcium Lower pH Soften hide
Pickling	Salt, sulphuric acid, formic acid, sodium formate, fungicide	Lower pH of the hide or skin to allow proper penetration of tanning chemicals
Tanning	Trivalent chrome tanning salts (wet blue) or glutaraldehyde (wet white)	Tanning
Basification	Magnesium oxide and sodium bicarbonate	Ensure binding of tanning chemicals to hide or skin
Dyehouse process stages		
Washing	Surfactants	Reintroduce water Soften and remove shavings, oils or greases
Neutralisation	Sodium bicarbonate, sodium formate	Increase pH to allow chemical penetration
Retanning	Syntans, resins, vegetable tannins	Give specific leatherlike properties
Dyeing	Dyestuffs	Give the desired colour
Fatliquoring	Fatliquors (emulsified oils)	Soften leather and make it flexible
Fixation	Formic acid	Lower pH to ensure chemical binding of the chemicals in the previous steps

CHAPTER 4: WASTE AND EFFLUENT DISCHARGE REGULATIONS

4.1 National Policies

The Constitution of South Africa stipulates that everyone has the right to an environment not harmful to their health or well-being. This includes the right to environmental protection for the benefit of present and future generations through reasonable legislative and other measures to prevent pollution and ecological degradation, promote conservation, and secure ecologically sustainable development and use of natural resources. These rights must be balanced with the promotion of justifiable economic and social development. Regulation that addresses these rights falls under the responsibility of the Department of Environmental Affairs. The Bill of Rights in the Constitution of the Republic of South Africa (Act 108 of 1996) enshrines the concept of sustainability. Rights regarding the environment, water, access to information, and just administrative action are specified in the Act.

These rights and other requirements are further legislated through the National Water Act (NWA), Act 36 of 1998. The NWA provides the legal basis for water management in South Africa by ensuring ecological integrity, economic growth, and social equity when managing water use. Other policies relevant to the tannery industry are the National Environmental Management Act, 1998 (Act 107 of 1998), the National Environmental Management: Waste Act, (Act 59 of 2008), and the National Environmental Management: Air Quality Act (Act 39 of 2004). Broadly speaking, these acts outline the requirements for storing and handling waste on-site, licensing requirements, establishing waste management plans, setting limits for air emissions, and setting penalties for offences.

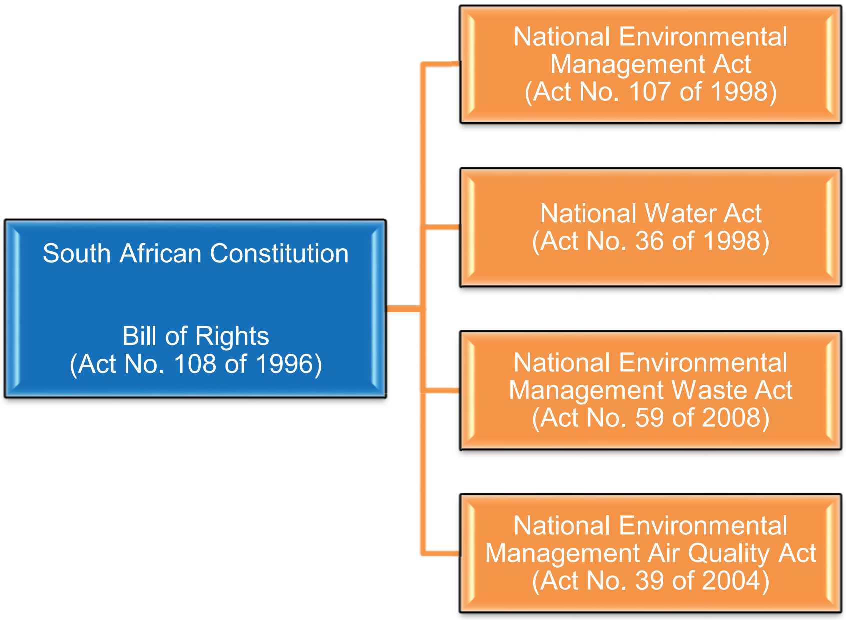

Figure 4.1: National environmental and water policies relevant to the tannery industry

The NWA introduced the concept of Integrated Water Resource Management, which provides for resource- and source-directed measures to manage the aquatic environment. Resource-directed measures aim to protect and manage the environment that receives water. Source-directed measures aim to control the impact on the receiving environment by preventing pollution, reusing water, and treating wastewater. The integration of resource- and source-directed measures forms the basis of the hierarchy of decision-making aimed at mitigating the effect of waste generation. This hierarchy is based on a precautionary approach. The order of priority for water and waste management decisions and/or actions is shown in Figure 4.2.

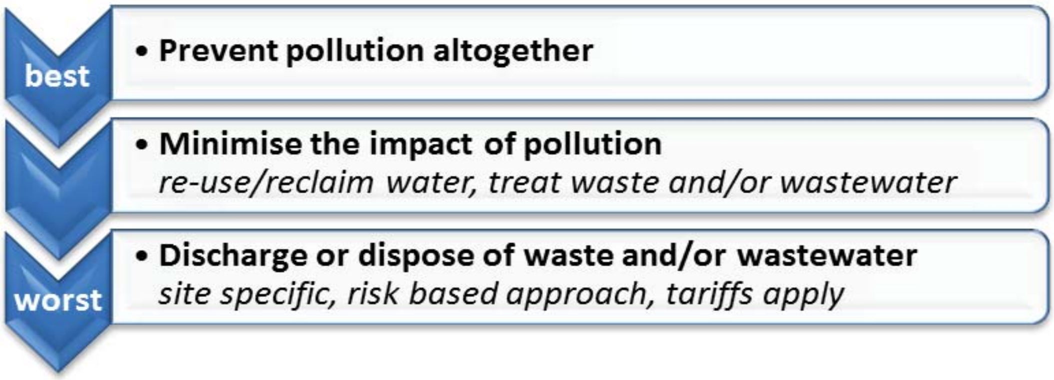

Figure 4.2: Hierarchy of decision-making intended to protect the environment

4.1.1 Water policy

The recently formed Department of Water and Sanitation (DWS), formerly the Department of Water Affairs and the Department of Water Affairs and Forestry, is the water and sanitation sector leader in South Africa. The DWS is the custodian of South Africa's water resources, and of the NWA and the Water Services Act (WSA), Act No. 108 of 1997. The DWS is also the national regulator of the water services sector.

The NWA provides the legal framework for the effective and sustainable management of water resources within South Africa. The Act aims to protect, use, develop, conserve, manage and control water resources as a whole, promoting the integrated management of water resources with the participation of all stakeholders.

The Act stipulates the requirements for, among others:

- Developing a national water strategy and catchment management agencies.
- Protecting water resources through classification.
- Setting reserves (basic human need and ecological).
- Determining resource quality objectives.
- Promoting pollution prevention.

The Act provides for penalties for non-compliance.

The WSA deals mainly with water services or potable (drinkable) water and sanitation services supplied by municipalities to households and other municipal water users. The Act contains rules about how municipalities should provide water and sanitation services. Within each municipal area, by-laws are developed that outline the water supply, as well as effluent discharge regulations and tariffs for that area (see Section 4.2).

4.1.2 Wastewater policy

Under the NWA, norms and standards for the quality of wastewater or effluent prior to discharge to sewer have been set. These consist of general and special standards and set limits for aspects such as pH, temperature, chemical oxygen demand (COD), suspended solids and metals. The test methods to be performed to determine these levels are also specified. Environmentally sensitive areas where special more stringent standards apply are listed. Any industries, or municipal or private wastewater treatment works discharging to rivers or the sea must comply with these limits. In turn, the entity operating a wastewater treatment works must set limits for industries discharging to the works such that the DWS final discharge limits can be met.

4.2 By-laws at Local Government Level

The handling and management of industrial effluent discharge creates problems for local authorities. The discharge of large volumes of industrial effluents into municipal sewerage systems, and in particular the discharge of effluents containing unwanted substances, can have a detrimental effect on the operation of the biological processes of the sewage treatment works resulting in non-compliance of the treated effluent with the NWA.

To prevent industries in a particular municipal area from discharging effluent streams that may affect public streams or the environment negatively, local authorities set requirements with which industries must comply before they discharge to the municipal sewer. In accordance with these requirements, industries need to apply for special permits to discharge effluent to the wastewater treatment works. The by-laws set limits for the quality of the effluent, as well as limits on the discharge of any specific undesirable substances. In these permits for acceptance of industrial effluent by the municipality, the maximum volume that can be discharged is indicated, as well as any special measures relating to the quality of industrial effluent for the specific industry. By virtue of these by-laws and permit systems, the local municipalities have some control over the types and quantity of industrial effluent discharged into their sewage treatment works.

The problem with the by-laws for industrial runoff is in their application, and in particular the calculation of effluent charges for certain industries carrying high loadings and/or undesirable substances to the sewer discharge. The laws can vary significantly from one municipality to another to calculate effluent charges, method and frequency of sampling, and limits placed on specific pollutants that may be discharged. These differences in by-laws and control measures not only lead to confusion with the regulatory authorities, but also by the industries they serve.

4.2.1 Industrial effluent tariffs

The calculation of industrial effluent tariffs varies significantly from one municipality to the next, depending on the cost recovery systems of the municipalities, types of industry discharging to the municipal sewer, and the receiving wastewater treatment works.

4.2.1.1 Principles in respect of industrial effluent charges to recover costs

A rational system should be used to calculate tariffs. The system should ensure that the total annual cost for the sewerage system and the wastewater treatment plant are recovered. The following are important principles relating to the preparation of industrial effluent charge calculations:

- The ‘polluter must pay’ principle contained in the NWA should apply. Industries should pay for their portion of the transportation and treatment costs for effluent disposal or dumping.
- All sewerage rates should be calculated according to the same rationale. Each local municipality should strive to formulate their tariff structure in such a way that neither a loss nor a profit is made on the wastewater treatment system.
- As is the case with water and electricity tariffs, the main objectives of sewerage tariffs are firstly to recover the full costs of providing the service, and secondly to prevent unnecessary waste and pollution.

- The rate charged for an industry must apply to the proportional costs for transport and treatment of discharge from the relevant industry. These costs include amortisation interest on capital works.
- The transport costs for the effluent should not be based on geographical location – the same unit rates for transport should apply to all.

4.3 Summary of Effluent Quality Requirements Relevant to the Tanning Industry

Table 4.1 shows the effluent quality requirements of selected municipalities with tanneries operating within their area of jurisdiction.

Table *4.1*: *Effluent standards of municipalities for water quality parameters regulated for effluents from tanneries*

Local authority/ country	pH	COD (mg/L)	o-phosphate (mg/L as P)	TSS (mg/L)	Electrical conductivity (mS/m)	Sulphate (mg/L as SO_4)	Total chromium (mg/L as Cr)	Chloride (mg/L)
South Africa								
City of Tshwane	6-10	5 000	10	2 000	300	1 800	5	100
City of Cape Town	5.5-12	5 000	25	1 000	500	1 500	10	1 500
Nelson Mandela Bay Metro	6-12	10 000	-	1 000	500	1 500	20	1 000
Ekurhuleni	6-10	5 000	50	1 000	500	1 800	20	100
Oudtshoorn	6.5-10	4 000	10	1 000	500	250	5	500
Mossel Bay	6-11	3 000	-	1 000	500	500	10	1 000
Global								
France*	6.5-8.5	2 000	-	600	-	-	-	-
Italy*	5.5-9.5	500	-	200	-	1 000	4.0	1 200
India*	5.5-9.0	-	-	100	-	1 000	2.0	-

* Buljan and Král, 2011

CHAPTER 5: WATER USE AND MANAGEMENT

5.1 Water Use in the Tannery Industry

Selected tanneries representing the different types, sizes and geographic locations in the country were visited and a survey undertaken of the volumes of water used in the preparation, tanning and finishing processes. The information was used to calculate the specific water intake (SWI).

5.2 Water Source and Consumption

During leather production, hides and skin undergo a number of successive beamhouse, tanning and finishing operations. Process water is a vital raw material used in large quantities in almost all preservation, beamhouse, tanning and finishing processes. Between 25 L and 80 L of process water is used to process 1 kg of hide (UNIDO, 1991; Covington et al., 2000; Hauber, 2000; Buljan, 2005; Buljan & Král, 2011, Buljan & Král, 2015).

Table 5.1 shows the typical volume of process water used at each processing stage by the industry at large (global data).

Table 5.1: Typical process water consumption (Ramanujam et al., 2010)

Type of process	Volume of water used per raw hide weight (L/kg)
Raw to finish	40-45
Raw to vegetable-tanned	25-30
Vegetable-tanned to finish	50-60 (per kilogram of vegetable-tanned leather)
Raw to wet blue	25-30
Wet blue to finish	20-25 (per kilogram of wet blue)
Crust to finish	10-15 (per kilogram of crust weight)

Most tanneries visited for this study use municipal water. However, the cost of water differs from municipality to municipality. Some tanneries supplement municipal water with borehole water or storm water during the rainy season. Retanning and leather finishing tanneries consume less water than full-house tanneries because the downstream processes are less water intensive. This is one of the advantages of retanning and leather finishing tanneries, as they produce less polluted and smaller volumes of wastewater than full-house tanneries.

5.3 Water Use and Water Management of the Tanneries Visited

The calculated SWI values of the 10 selected tanneries visited are given in Table 5.2. The use per process (where this information is available) for different types of tannery are given in Table 5.3.

Table 5.2: Water use and management of tanneries visited (Tanneries A1-A5)

Tannery identification	A1	A2	A3	A4	A5
Skins, hides, raw material	Exotic	Exotic	Bovine	Mostly bovine	Mostly bovine
Production process	Full-house tanning	Full-house tanning	Retanning and leather finishing	Chrome retanning, leather finishing	Chrome retanning, leather finishing
Raw water source	Municipal water	Municipal water	Municipal water	Municipal water	Municipal water (boreholes as standby)
Actual daily water consumption	~280 L per skin		~5 000 L per ton of hides	170-440 L/hide	
Water conservation measures	Recycling is currently being considered	No recycling is done at present	The process does not lend itself to recycling, mainly due to the salinity in the effluent streams	No recycling is done at present	Rainwater harvesting; recycling is not an option due to residual colour in the effluent

Table 5.3: Water use and management of tanneries visited (Tanneries A6-A10)

Tannery identification	A6	A7	A8	A9	A10
Skins, hides, raw material	Bovine	Exotic	Bovine; ovine	Bovine; ovine	Bovine; ovine
Production process	From raw to wet blue	Full house	Full house	Chrome retanning, leather finishing	Full house
Raw water source	Municipal water	Own water treatment plant to treat river water	Municipal water	Municipal water	Municipal water
Actual daily water consumption			~550 L per hide		~400 L per hide
Water conservation measures	The tannery is considering rainwater harvesting from roofs	Irrigation; recycling for secondary use	Investigating the feasibility of recycling certain effluent streams	No recycling is done at present	Currently implementing and further investigating water savings measures

Table 5.4: Typical water use in tannery production processes

Process	SWI (L/hide)		SWI (from 2016 survey) (L/hide)
	European Union, 2013	NATSURV 10, 1989	
Hide and skin reception and storage			
Curing and storage			
Wet blue process: Beamhouse (or limeyard) section			
Soaking	55-825	54	
Liming and unhairing	41.25-110	34	
Deliming and bating	~55	27	
Washing (all steps combined)		65	
Total	**151.25-990**	**180**	**270**
Wet blue process: Tanyard section			
Degreasing	Only sheepskins and pigskins		
Pickling and tanning (chrome)	27.5-82.5	10	
Draining, hosing, sammying and setting	Only wastewater		
Washing (all steps combined)	-	149	
Total	**27.5-82.5**	**159**	
Dyehouse process (wet finishing and dry finishing)			
Post-tanning	110-220		
Finishing	0-27.5		
Total	**110-247.5**	**-**	**110**
Total for all processes	**289-1 320**	**339**	**170-550**

Table 5.5 proposes specific water use (SWU) targets for tanning and leather finishing process based on available data from the literature and from surveys undertaken in this project.

Table 5.5: Proposed water use targets

Process	SWU (L/skin)
Wet blue process stages	50-150
Dyehouse process stages	100-200
Total tanning and finishing stages	200-500

CHAPTER 6: WASTEWATER GENERATION AND MANAGEMENT

6.1 Wastewater Generated in the Tannery Industry

Figure 6.1 demonstrates that international studies have shown that one ton (1 000 kg) of raw hide yields approximately 200 kg of leather plus 50 m^3 of contaminated liquid effluent, a minimum of 500 kg wet sludge and 120 kg of solids in sludge (UNIDO, 1991; European Union, 2013).

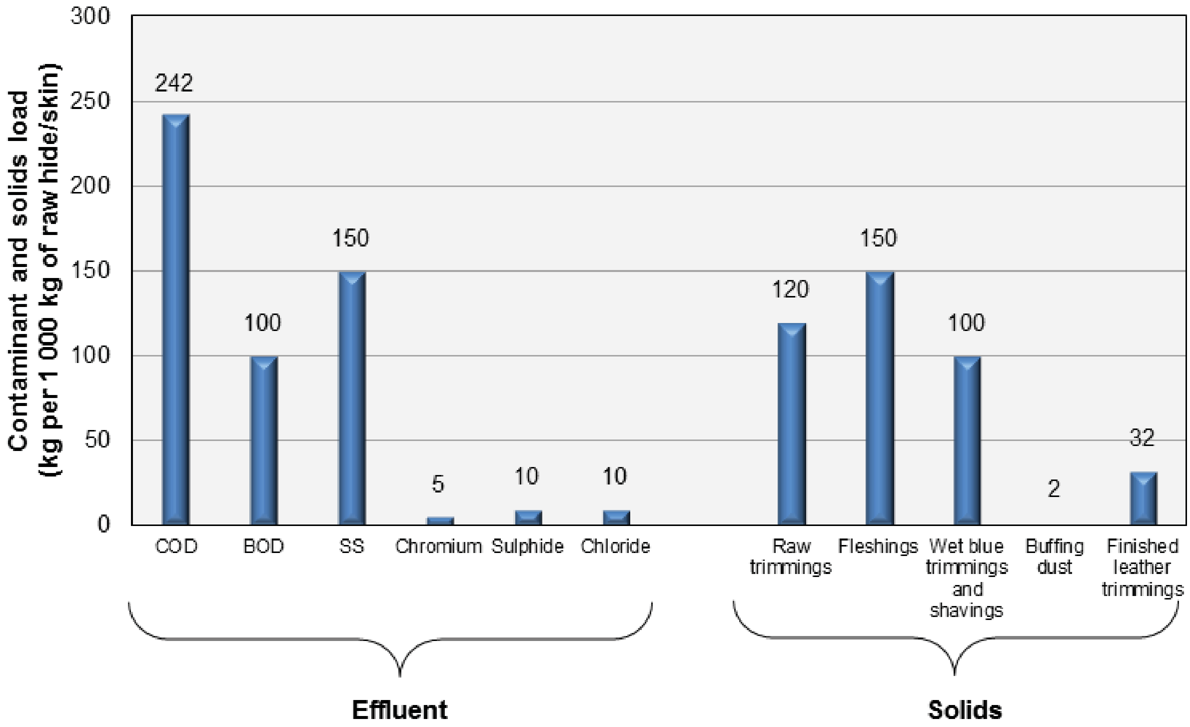

Figure 6.1: Typical solid and liquid waste generated in tanneries (European Union, 2013)

If all the various waste streams are combined, the effluent contains high concentrations of dissolved and suspended solids (SS), and organics measured as biochemical oxygen demand (BOD) and/or COD. The presence of sulphides, chlorides and chromium add to the toxicity of the effluent, and are included in most discharge standards. An interesting assessment of the toxicity of chromium can be sourced from the website of the International Union of Leather Technologists & Chemists Societies, namely, www.iultcs.org (see Appendix B).

Beamhouse processes are the source of all non-limed and limed solid wastes such as fleshings, trimmings and waste splits (UNIDO, 1991; Frendrup & Buljan, 2000; Buljan, 2012). More than 80% of the organic pollution load originates from the beamhouse processes, with approximately 70% from unhairing and liming and 10% from soak liquors (Frendrup & Buljan, 2000; Buljan, 2012). Soak water provides 60% of wastewater salinity. The remainder comes from acid salts applied to suppress pelt swelling (UNIDO, 1991; Buljan, 2012). The typical constituents in the effluent are summarised in Table 6.1. The effluent is challenging to treat, and is discussed further in Section 6.3.

Table 6.1: Typical effluent constituents from tanning and finishing processes

Processes	Typical effluent constituents
Tanning processes	
Beamhouse (limeyard) section	
Soaking	Salt, manure, blood, dirt, globular skin proteins, biocides, surfactants and degreasers.
Liming and unhairing	Decomposed hair keratin, globular skin proteins, saponified fractions of natural skin fat, sulphides, lime and caustic soda.
Fleshing	Hide fats and fleshings in the form of a solid waste.
Deliming and bating	Calcium salts, sulphide residues, organic acids, degraded proteins, residual proteolytic enzymes, ammonium sulphate and ammonium chloride.
Tanyard section	
Pickling	The water used during pickling is not emptied from the drum but is used for the tanning process.
Tanning	The water used during tanning is not emptied from the drum but is used for the basification process.
Basification	Salt, trivalent chrome (wet blue), glutaraldehyde (wet white), magnesium and sodium salts, sulphuric acid and formic acid.
Final wash	Salt, trivalent chrome (wet blue), glutaraldehyde (wet white), magnesium and sodium salts, sulphuric acid and formic acid.
Sammying	Salt, trivalent chrome (wet blue), glutaraldehyde (wet white), magnesium and sodium salts, sulphuric acid and formic acid.
Dyehouse processes	
Washing	Surfactants.
Neutralisation	Sodium salts.
Retanning	The water used during retanning is not emptied from the drum but is used for the dyeing and fatliquoring processes.
Dyeing	The water used during dyeing is not emptied from the drum but is used for the fatliquoring process.
Fatliquoring	The water used during dyeing is not emptied from the drum but is used for the fixation process.
Fixation	Residues of retanning chemicals, dyestuffs and fatliquors.

6.2 Wastewater Quality at Tanneries and Leather Finishing Industries Visited

Data on the quality of the wastewater (effluent) streams at the tanneries visited was obtained from the tanneries themselves, from some of the municipalities to which the tanneries discharge their final effluent, while samples were also taken at six of the tanneries. The data collected as well as the results of analysis are provided in Table 6.2.

Table 6.2: Wastewater quality at tanneries visited in the survey

Tannery identification		**A8; A10**	**A1, A2, A7**	**A3**	**A4, A5, A9**
Skins/hides, raw material		Bovine; ovine	Exotic	Bovine	Bovine, ovine
Production process		Full house	Full-house tanning	Leather finishing	Chrome retanning, leather finishing
pH					
Effluent quality (mg/L)	Range	6.2-12.7	3.46-9.83		8.0-8.5
Chemical oxygen demand					
Effluent quality (mg/L)	Range	880-12 091	412-4 640		
Specific pollutant load (kg/hide)	Range	1 011-1 958			
	Average	1 320		2 945	3 347-4 978
Total dissolved solids					
Effluent quality (mg/L)	Range	7 190-187 470	483-50 115		
	Average	14 839-22 244	812-7 440	3 367	4 693
Specific pollutant load (kg/hide)	Average	1.596			
Total suspended solids					
Effluent quality (mg/L)	Range	78-8 944			
	Average	839-893			1 268
Specific pollutant load (kg/hide)	Average	0.090			
Sulphates					
Effluent quality (mg/L)	Range	71-3 707	150-2 700		
	Average	867	702		2 780
Specific pollutant load (kg/hide)	Average				0.503
Chlorides					
Effluent quality (mg/L)	Range	46-24 902	1 200-6 191		
	Average	7 467-12 022	2 591	474	2-626
Specific pollutant load (kg/hide)	Range				
	Average	0.919			0.241
Total chromium					
Effluent quality (mg/L)	Range	0-141.3			
	Average	1.31-14.0			8.53-46.0
Specific pollutant load (kg/hide)	Average	0.0006			0.0027

6.3 Wastewater Treatment

6.3.1 Introduction

The integrated wastewater treatment systems in the tanning and leather finishing industry comprise preliminary treatment (or pretreatment), primary, secondary and tertiary treatment processes. However, every effluent treatment plant is site-specific. Tanneries involved in wet blue retanning and leather finishing mainly use pretreatment and primary treatment processes, whereas full-house tanneries additionally use secondary treatment (biological treatment). Some tanneries in South Africa combine all effluent streams, while others separate effluent streams from the beamhouse and tanyard. It is preferable to keep streams separate, because organic waste is the major constituent of combined effluent streams, which contains high concentrations of inorganics, including chromium. Figure 6.2 shows an example of how effluent is kept separated for primary treatment in one South African tannery.

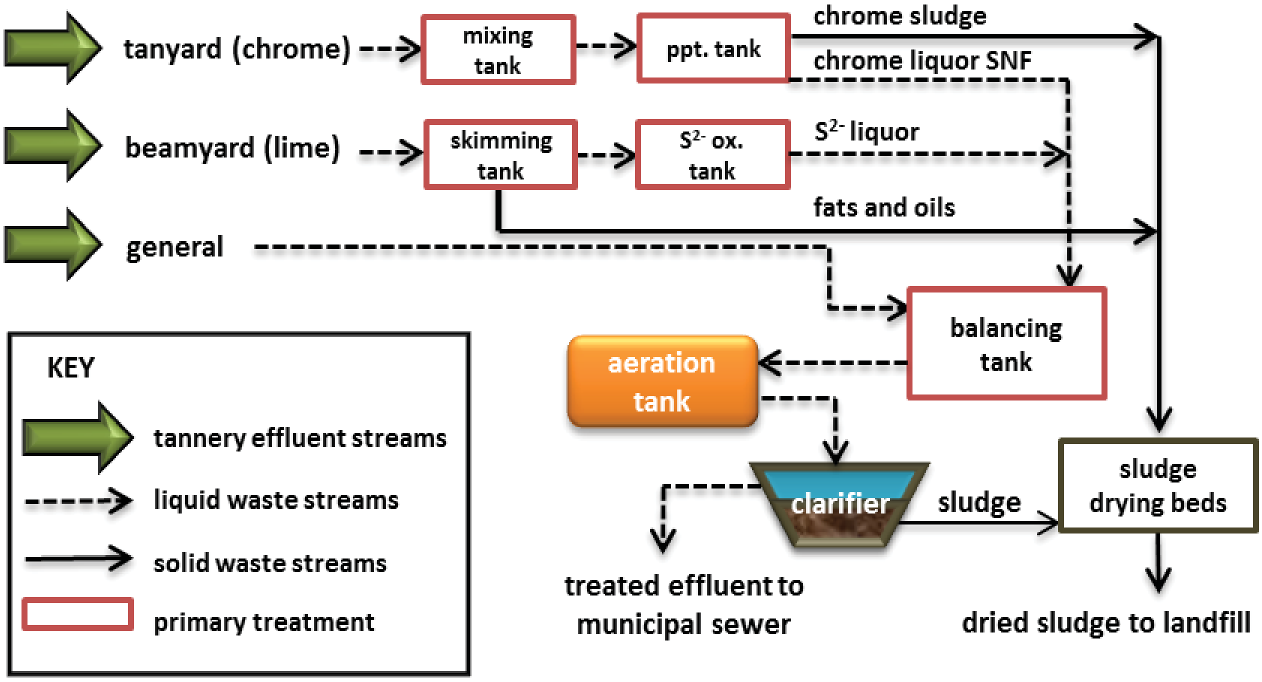

Figure 6.2: Flow diagram of conventional primary, secondary and tertiary treatment processes at a full-house tannery wastewater treatment plant where effluent streams are separated

6.3.2 Pretreatment: Screening and preliminary settling

Preliminary treatment employs mechanical screens, grit removal apparatus, distribution wells and equalisation tanks. Self-cleaning screens such as mechanical rotating screens are used to separate from 30% to 40% of suspended solids from raw waste (UNIDO, 1991). The screens generally have openings of between 3 mm and 0.5 mm and remove most of the larger solid material, including hair and other coarse material, sand and/or grit, and grease. Screening also significantly reduces the sulphide content of the effluent (UNIDO, 1991; Sahasranaman & Emmanuel, 2001; Buljan & Král, 2011). Preliminary settling of the screened effluent in grit removal chambers can separate out up to 30% COD in the form of easily settleable organic solids (UNIDO, 1991; Sahasranaman & Emmanuel, 2001).

6.3.3 Primary treatment

Primary treatment consists of physicochemical processes whereby (i) fats may be physically separated and (ii) chemical coagulants and/or flocculants are added to facilitate sedimentation of suspended solids in primary settling tanks. Coagulation is characterised by an optimum pH, and hence pH correction chemical/s are added at this stage. Primary treatment should remove the bulk of the main pollutants from the liquid waste stream/s.

Apart from removing particulate organics, primary treatment precipitates chrome and sulphides from tanyard chrome floats and beamhouse effluent, respectively (Sahasranaman & Emmanuel, 2001). It is preferable to precipitate these streams separately because neutralisation of alkaline liquors from the beamhouse causes the release of gaseous hydrogen sulphide. To prevent malodours emanating from the liquors, oxidation using a metal catalyst and aeration is often used to cause rapid precipitation of metal sulphides. However, sulphide regenerates if downstream anaerobic treatment processes are used. In such cases, direct precipitation using ferrous sulphate and ferric chloride is applied to equalised effluent, producing a large volume of dark wet sludge.

In South Africa, the chrome streams and the sulphide streams are segregated individually. The lime-sulphide waste stream undergoes sedimentation (the solids are readily settleable), after which sulphide oxidation with a catalyst (manganese sulphate) takes place. The stream is then discharged to a balancing tank. This has several benefits. The chrome liquors are precipitated with magnesium oxide giving a denser sludge, which can be reacidified with sulphuric acid to $CrSO_4$ for reuse or for drying on sludge-drying beds. The treatment process includes mixing in a mixing tank, transfer to a settling tank, drawing off the sludge for reuse or for discharge to sludge-drying beds. The supernatant, relatively chrome-free, is discharged to the effluent-balancing tank and combined with other liquors.

In all other tannery waste liquors, the streams are discharged to the balancing tank and the mixed liquors fed to the activated sludge process or aerated prior to chemical precipitation. To limit the possibility of odour nuisance, tannery waste liquors should not be allowed to become anoxic or anaerobic. The overflow from the activated sludge system goes to a clarifier where sludge is returned to the activated sludge system directly. Clarified wastewater is discharged to sewer.

Anaerobic treatment of tannery wastewater containing sulphates gives rise to odour nuisance as a result of sulphates being reduced to sulphides. Sludges (lime and spent biological sludge), once dewatered, can be used for composting or soil conditioning.

The advantage of primary settling of lime liquors to remove settleable solids over chemical precipitation of tannery wastewater is that sufficient alkalinity remains in the effluent during the activated sludge process to maintain a pH in the alkaline range (above 7.0), and prevents sludge bulking.

Chrome precipitation is achieved by the application of lime to increase the alkalinity of the liquor (to pH 8) and adding aluminium sulphate (alum) and anionic polyelectrolyte (UNIDO, 1991; Buljan & Král, 2011). Magnesium oxide is more commonly used as it results in a more compact chrome sludge. The dosage is governed by the character of the effluent and the degree of clarification required (Buljan & Král, 2011). Following precipitation, the supernatant from the beamhouse and tanyard streams is equalised in a balancing tank before secondary treatment.

6.3.4 Secondary treatment

In full-house tanneries, primary treatment is followed by aerobic or anaerobic biological treatment to further reduce the BOD. In South Africa, conventional activated sludge (CAS) systems, which are operated as completely mixed systems with extended aeration, are common. Small tanneries in South Africa also use ponds.

Anaerobic treatment is potentially an effective process for reducing the volume of sludge at comparatively lower costs and is widely used in other industries (UNIDO, 1991; Buljan & Král, 2011). The organic load is digested anaerobically and produces biogas (methane, carbon dioxide and hydrogen sulphide). However, the tanning industry has not widely adopted anaerobic technologies as they release hydrogen sulphide, which is toxic and corrosive (Buljan & Král, 2011).

6.3.5 Tertiary treatment

Following primary and/or secondary treatment, clarifiers and sand filter beds are used to separate the solids from the liquid effluent and dewatering the sludge. The sludge is left for a few days under partial aerobic conditions allowing further digestion. It is then sun-dried before disposal to landfills. Using drying beds is a cheap method that requires manual removal of the sludge from the bed when it has dried to about 30% solids content. Some retanning and leather finishing tanneries use belt filter presses. The liquid effluent from medium to large tanneries is usually discharged to municipal sewers.

6.3.6 Advanced treatment systems

These are sophisticated treatment methods that can be designed to meet specific effluent quality targets, but these methods are generally expensive and require expert operation. They include high efficiency carbon filtration, reverse osmosis, membrane filtration, ion exchange, electrodialysis and high-rate evaporation.

6.3.7 Sludge handling

In South Africa, solid waste from primary wastewater treatment and dried or filter-pressed sludge from tertiary treatment (especially from the production of wet blue) is considered to be potentially hazardous and is disposed to appropriate municipal or private landfill sites (Table 6.3). This can be costly, especially if the landfill sites are not located in close proximity to the tanneries.

Until recently, chrome sludge had to be disposed of in a toxic landfill site (Class H:h). Recent research has shown that there is no scientific evidence that Cr in Cr^{III} sludge reverts to Cr^{VI} under natural conditions and it has therefore been deregulated as far as being a potential toxic waste.

Table 6.3: Solid waste management practices of selected tanneries in South Africa

Tannery	Future plans for solid waste management
A1	Installation of an anaerobic digester to reduce sludge volume and generate biogas.
A2	Biofuel production by waste to energy companies (previously removed by such companies).
A3	No future plans.
A4	No future plans disclosed.
A5	The solids are collected in a skip. The solids have a moisture content of about 30%. Approximately two skips are taken away per month by a waste company. The tannery is investigating the possibility of incinerating the wastewater sludge for energy, but is worried about possible hexavalent chromium formation. They will therefore eliminate rechroming.

Tannery	Future plans for solid waste management
A6	The solid waste is removed by a waste company. They produce about two skips per month.
A7	No future plans disclosed.
A8	No future plans disclosed.
A9	No future plans disclosed.
A10	No future plans disclosed.

6.4 Changes in Tanning Industry Wastewater Treatment and Management Since the 1980s

There has been a move away from treating totally mixed effluent, i.e. all wastewaters were discharged into one drainage system (no segregation) and into one collection tank after screening. The streams were then treated together either by physico-chemical treatment (sedimentation or air flotation), or activated sludge, to a system where specific waste streams are segregated from the main stream. This involved redesigning and reengineering the internal drainage. In addition, two extra collection sumps had to be constructed – one for each of the specific waste streams (lime liquors and wash, and chrome tan liquors and wash). By the late 1990s, there was only one tannery using an air flotation system for treating its effluents.

The old system of combined treatment gave rise to a number of problems, such as odour nuisance as a result of sulphides (H2S), and almost neutral pH of combined liquor. Other problems included very high suspended solids from lime liquors having to be kept in suspension and aerated, effluent strength and pH balancing. Large quantities of sludge were produced with high chromium III content, which required toxic waste landfill (Class H:h) disposal.

The Leather Industries Research Institute (LIRI) in collaboration with the WRC developed a treatment system in the 1990s whereby segregation of specific wastewater streams along with their specific pretreatments addressed most of the abovementioned problems.

Although LIRI did some research in the early 1990s on treating wastewater by biological filtration, it has not been used by the industry. For biological filtration to be effective, pretreatment (screening) and primary treatment processes (settling of lime sludge and fat oil and grease removal) need to be very effective in removing problematic solids and fats that can block up the filter bed. Results from pilot plant studies indicated that this technology could be used as a secondary treatment process for tannery effluent.

Similarly, research into using microfiltration was done on tannery effluents to establish the feasibility of using ultrafiltration and reverse osmosis to remove salts from tannery effluents. It was concluded that tannery effluent needs a very effective secondary biological treatment or further tertiary treatment to remove problematic suspended solids, and soluble fats, oils and greases for microfiltration techniques to be economically viable.

Another advancement made in the 1990s was using bidim or geo-textile in the construction of sludge-drying beds. The geo-textile was set between the coarse stone underdrainage and the filter sand surface layer. This prevented the sand from permeating into the stone underdrainage and clogging up the drainage voids resulting in a longer life span for the drying beds. The drying beds were also more efficient.

There was a period when several tanneries considered lime/sulphide and chrome recycling; however, due to the stringent control required during processing and difficulties in maintaining leather standards, this practice has been discontinued by many. The survey will determine how many tanneries are still recycling. No tanneries in South Africa are using anaerobic digestion to treat wastewaters or sludge.

Regarding wastewater analyses, it is noted in the first edition that two determinants have become more of an environmental issue recently, namely, salinity or electrical conductivity, and ammonia were not included in the analyses of the final wastewaters. Both these determinants can have a significant influence on the water quality discharged by local authorities from a sewage works to a water course. Ammonia not only comes from the deliming and bating process, but also from the biological breakdown of the protein (keratin and epidermis) present in most process waste liquors. Electrical conductivity has become the more acceptable determination measuring dissolved inorganic salts in effluent in the place of total dissolved inorganic solids.

As a result of salinity in tannery effluents and the consequent water pollution, the biggest advance in combating water pollution has been moving away from processing salted hides by a number of wet blue plants. Many of the larger tanneries have resorted to processing green and/or chilled hides.

Furthermore, a number of tanneries processing gameskins have evolved. Here one should differentiate between those doing hair-on for the tourist trade and those producing leather for other purposes.

The next step is for tanneries to adopt clean technologies where many currently used process chemicals are substituted by chemicals having less impact on the environment. These include low-sulphide unhairing, hair-save, ammonia-free deliming, low-salt pickle and high uptake chrome tanning, which are more environmentally acceptable. Certain dyes and chemicals used in retanning and dyeing, especially black, had exceptionally high CODs and were replaced by more environmentally acceptable ones.

Although some research was done on treatment of tannery effluents using biological filters with plastic support media, it was concluded that biofiltration could benefit secondary treated wastewater as a tertiary treatment to lower COD, nitrogen and suspended solids content. It could also be used as a secondary treatment where a high standard of pretreatment was implemented to minimise blockages due to fats and inadequate removal of suspended solids.

Many treatment processes recommended by inexperienced consultants are not appropriate for the tanning industry as they often require a high level of process control and operator competency to achieve the desired results.

It was found that a notable improvement in the biodegradation of organics in the aerobic biological process could be achieved by adding phosphates in the form of a high phosphate content fertilizer. This also improved sludge digestion and settleability.

6.5 Summary of Wastewater Treatment Systems Most Widely Used in the Tanning and Leather Finishing Industry

The two most common secondary treatment technologies for tannery wastewater treatment in South Africa and developing countries are the CAS system with extended aeration and anaerobic ponds. Sequencing batch reactors and membrane bioreactors have also been introduced in other countries. Table 6.4 summarises the treatment processes used for treating tannery effluents streams, and describes the function and benefit of each process.

Table 6.4: Summary of tannery effluent treatment processes

Treatment Stage	Function	Benefits
Primary treatment		
Screening	To remove large particles of suspended solids	Reduces COD and suspended solids in effluent
Fat traps	To reduce fats, oils	Reduces fats and oils in effluent

Treatment Stage	Function	Benefits
Pretreatments		
Lime presettling	To remove large quantities of suspended solids consisting of pulped hair and undissolved lime	Improves sulphide oxidation and lowers catalyst requirement
Sulphide oxidation	To reduce sulphide content	Minimises odour nuisance and improves aerobic biological process
Chrome precipitation	Removes chromium from wastewater	Allows final effluent and other sludges to meets discharge and disposal limits
Secondary treatment		
Activated sludge	To break down soluble and suspended organic matter, NH_3-N and other constituents	Reduces pollution and discharge costs
Addition of phosphates to aerobic biological process	Improves breakdown of organics and process efficiency by ±30%	Reduces pollutants more efficiently
Secondary settling	Removes biomass from effluent for sludge return and reinoculation of fresh effluent with biomass	Allows effluent with minimal suspended solids and COD/BOD for discharge
Chemical precipitation	Precipitates suspended solids	Reduces COD/BOD and suspended solids
Tertiary treatment		
Biofiltration using plastic media	Reduces further soluble and suspended solids, fats and COD	Produces a high quality final effluent with low COD/BOD
Advanced treatment		
Ultrafiltration	Removes fine particles of suspended solids and soluble fats	Preparation for reverse osmosis
reverse osmosis	Removes total dissolved inorganic solids and salts (NaCl)	Preparation for reverse osmosis
Sludge dewatering		
Drying beds	Dewaters sludges by drainage and evaporation	Reduces potential odour nuisance and transport costs to landfill
Centrifuges	Separates water from solids	Reduces potential odour nuisance and transport costs to landfill
Belt presses	Separates water from solids by pressure between porous cloth	Reduces potential odour nuisance and transport costs to landfill
Pressure filter	Separates water from solids by pressure between plates	Reduces potential odour nuisance and transport costs to landfill

Table 6.5 compares the major advantages and disadvantages of each treatment process. Newer technologies, including granular activated carbon membrane bioreactors and advanced oxidation processes may gain traction in the future.

Table 6.5: Advantages and disadvantages of wastewater treatment processes used in the tanning industry

Treatment	Advantages	Disadvantages	References
CAS with extended aeration	• Activated sludge systems are widely used in South Africa. • Moderately affordable to install. • Can achieve high organic removal rates. • Continuous operation.	• Reliant on good floc formation. • Occurrence of bulking and foaming due to poor floc formation and selection of lipophilic filaments, respectively. • High operational costs for aeration. • Larger footprint than membrane bioreactor, sequencing batch reactor and upflow anaerobic sludge blanket. • Separate clarifier required for secondary settling. • Unstable to variable hydraulic and pollutant loading.	Mandal et al. (2010) Buljan and Král (2011)
Membrane bioreactor	• Products can be recovered. • Water can be reused. • No reliance on floc formation. • Small footprint. • Adjusts well to variable hydraulic and pollutant loading. • No separate clarifier required.	• Highest capital outlay for installation and operation. • Membranes prone to fouling, especially for wastewater with a high fat content. • Requires skilled operation.	Durai (2011) Faouziet et al. (2013) Jafarinejad (2016)
Sequencing batch reactor	• Decreased bulking compared with CAS. • Small footprint. • Adjusts well to variable hydraulic and pollutant loading. • No separate clarifier required for secondary settling. • Treatment cycles can be adjusted to attain complete nitrogen removal through nitrification-denitrification.	• Higher construction and operating costs than CAS. • Higher energy requirements than CAS. • Reliant on good floc formation. • Batch operation.	Singh and Srivastava (2011) Patil et al. (2013) Jafarinejad (2016)
Anaerobic ponds	• Inexpensive to install and operate. • Low energy requirements. • Low sludge production.	• Water cannot be reused. • Environmental threat due to leakage and emissions. • Difficult to desludge. • Malodorous.	Buljan and Král (2011) Goswami and Mazumder (2013)
Upflow anaerobic sludge blanket	• Low sludge production. • Biogas can be utilised for energy.	• Unstable to variable hydraulic and pollutant loading. • Methanogens sensitive to sulphides. • Long start-up periods required after shutdown.	Rajeswari et al. (2000) Goswami and Mazumder (2013) Tamilchelvan and Mohan (2013)

CHAPTER 7: ENERGY USE AND MANAGEMENT

Energy consumption in tanneries depends mainly on the following factors (European Union, 2013):

- Production methods.
- Capacity and size of equipment.
- Age and sophistication of motor controls.
- Amount of mechanical handling used to move hides and skins.
- Drying methods used.
- Heat losses from process vessels and from buildings.
- Air exchange rates to meet workplace safety conditions.
- Types of wastewater treatment on-site.
- Types of waste treatment and recovery of energy from waste on-site.

Heat losses may be mitigated by thermal insulation, but may be exacerbated by a low external temperature. A high moisture content in the air may increase the energy consumed in drying. Energy use data from one climatic zone may not be an accurate guide to what may be achieved in another.

The age and efficiency of the combustion equipment and boiler plant determine the proportion of the energy of fuel that is made available as thermal energy in the tannery. A larger central boiler may be more efficient, but if operations are dispersed on a large site, heat losses from pipework may eliminate the gains. Table 7.1 and Figure 7.1 show energy consumption by type of energy input.

Table 7.1: Consumption of thermal and electrical energy (European Union, 2013)

Energy input	Energy application	Percentage of overall consumption
Thermal energy	Drying	32-34
	Hot water	32-34
	Space heating	17-20
Electric energy	Machinery and process vessels	9-12
	Compressed air	1.5-3
	Light	1.5-3

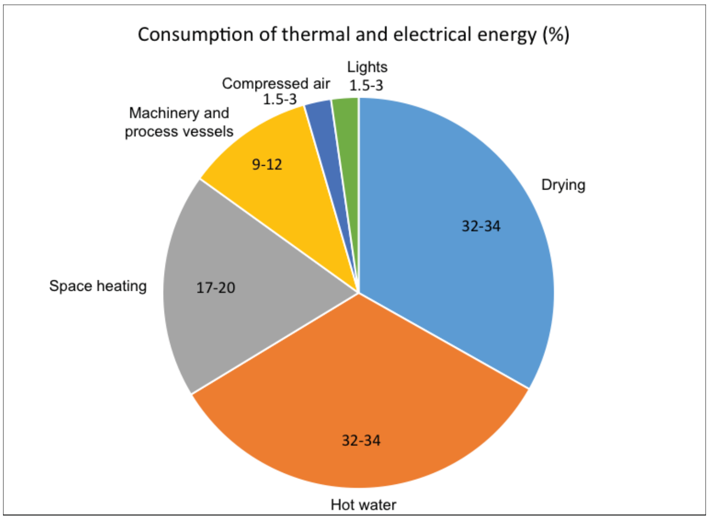

Figure 7.1: Typical energy consumption in the tannery industry (%)

It is necessary that data be compared for the same stages of the leather-making process. Ideally, energy use should be monitored and reported separately for each process stage. Most energy-efficient tanneries do so.

Where more detailed data for energy use is available, it is important that comparisons between tanneries be made on the same basis. For example, ‘effluent treatment’ may or may not include biological treatment, which can account for more than 50% of the total energy consumption in the treatment of tannery effluent.

Energy consumption figures have been obtained for the eight case study tanneries. The mode in which the figures are captured varies considerably from tannery to tannery (according to the usage per tanning or dyehouse process, or for the tannery in total). The data has been processed to obtain figures per hide or skin produced (for the different types of raw material processed).

When relating the energy consumption in the tannery to the actual production output (in terms of usage per hide or skin processed), the figures vary largely. Values calculated for those tanneries where this information was supplied ranged from 1.9-4.4 kWh per hide, while the electricity consumption at one of the exotic leather tanneries was as high as 165 kWh.

Most of the tanneries use coal-fired boilers for heating, and electricity from the local authority for the machines used in the tanning and leather finishing process. A few of the tanneries have indicated that they will be investigating the feasibility of using renewable energy in future.

CHAPTER 8: BEST PRACTICE FOR WATER USE AND WASTEWATER GENERATION IN THE TANNERY INDUSTRY

Best practice can be defined as "strategies, activities or approaches that have been shown through research and evaluation to be effective and/or efficient". The term is somewhat controversial, because some people feel that there are always ways to improve, and application of the word 'best' suggests that no further innovation is necessary. The European Union prefers the term "best available technologies". Nevertheless, best practice is an accepted term that is widely applied. The catchphrase "reduce, reuse, recycle" applies to just about all the world's resources, including water, and forms part of the best practice hierarchy (Figure 8.1).

Water use, wastewater generation and cleaner production technologies are inextricably linked, and should be considered holistically by industries seeking to become more sustainable. Reduced water consumption translates into reduced wastewater generation; reduced chemical usage or less toxic chemicals improves wastewater quality.

Adherence to best practice technologies can translate into cost savings. However, it is recognised that in some instances the adoption of best practices may result in inferior products, and a balance needs to be struck between environmental and economic issues. This is particularly relevant to the wet blue process in the tanning industry.

Figure 8.1: Best practice hierarchy – towards a sustainable future

8.1 Water Conservation and Demand Management

Reduction in water use can be achieved by decreasing the volume of water used in particular processes and/or recycling/reusing process water. Specific best available technologies to reduce the water footprint of the tanning and leather finishing industry are outlined from Section 8.2.1 to Section 8.2.5.

8.1.1 Using low floats and controlled batch washing

Water use and production costs can be reduced considerably by using low-float processing and controlled batch washing (UNIDO, 1991; Steffen, Robertson and Kirsten Consulting Engineers, 1989; Sundar et al., 2001; Buljan & Král, 2015). Low-float processing utilises 40% to 80% water on the weight of material instead of the conventional 100% to 250%, and has been shown to reduce water consumption by 20-50% (Steffen, Robertson and Kirsten Consulting Engineers, 1989; Sundar et al., 2001; Buljan & Král, 2015). However, using low floats compromises leather quality (UNIDO, 1991; Buljan & Král, 2015). Low floats cause the skins/hides, pelts or equipment (vessels) to be susceptible to wear. Dried hides and heavy leather require long floats for proper rehydration and gradual penetration of the vegetable tannins (UNIDO, 1991; Buljan & Král, 2015). High float levels are preferred by most tanners as they produce the market-desired leather qualities, particularly the fineness of grain (UNIDO, 1991; Buljan & Král, 2015).

8.1.2 Recycling wash liquors

Wash liquors from bating and neutralisation can be recycled for soaking salted or green hides. The second lime wash can be used as the basis for new lime or soak liquor. The latter is advantageous because the alkalinity of the wash liquor accelerates soaking (UNIDO, 1991; Sundar et al., 2001; Buljan & Král, 2015).

8.1.3 Processing green hides

Processing fresh or chilled skins and hides instead of salted hides theoretically eliminates the need for process water during soaking and eliminates chlorides in the ensuing effluent, although in practice, a small amount of salt is generally still added. Processing green hides is particularly applicable for tanneries that are integrated with, or close to abattoirs (Ludvik, 2000; Buljan & Král, 2015).

8.1.4 Green fleshing

If fleshing is effected before liming instead of after, water consumption and the volume of contaminated effluent are reduced. In Europe, it is estimated that green fleshing results in 10-20% reduction in process water demand (Buljan & Král, 2015). However, as with the use of low-float technology, the quality of the leather may be compromised. Therefore, green fleshing has not been widely adopted in South Africa.

8.1.5 Integrated process control systems

The processors and integrated process control systems in modern tanneries (water meters, automated valves, etc.) are designed to reduce process water and chemical usage (UNIDO, 1991; Buljan & Král, 2015; Sundar et al., 2001). Manufacturers may offset the capital outlay by expected savings in chemical and water costs (UNIDO, 1991).

8.2 Cleaner Production Techniques

One of the major environmental benefits to instituting cleaner production technologies is the improvement in wastewater quality, but water may also be saved. Table 8.1 lists the major pollutants found in the effluent of typical South African tanneries. Cleaner production technologies seek to eliminate or reduce the quantity of these chemicals generated by tanneries. A list of these technologies relevant to particular processes in the tanning industry are provided in Section 8.3.1 to Section 8.3.7, and summarised in Table 8.2.

Table 8.1: Major pollutants generated at various stages of leather production

Origin	Pollutant
Beamhouse	• Salt washed out of cured hides and skins. • High COD/solids from dissolved hair, skin proteins and process chemicals. • Sulphide used to remove the hair from hides and skins. • Ammonium ions released from the raw hide or skin and released from the process chemicals during deliming and bating.

Origin	Pollutant
Tanning	• Salt used in the pickling process. • Chrome tanning salts that are were not chemically bound to the leather.
Dyehouse	• High COD caused by incomplete exhaustion of chemicals. • Chromium salts that are extracted from the wet blue during processing. • Inorganic salts originating from chemicals and dyes. • Dyestuffs not chemically bound to the leather.
Leather finishing	• Organic solvents released from finishing auxiliaries. • Heavy metals from pigments.

8.2.1 Curing hides and skins

Recently there has been a greater international advocacy to find alternatives to salt curing of hides and skins and replace the salt pickling stage in the tanning process to significantly reduce or remove salt (NaCl) from tannery effluents. In countries such as Asia, India and Pakistan where desalination by ultrafiltration and reverse osmosis was implemented under the auspices of UNIDO, this has been a great failure due to capital cost of equipment, high running costs and the necessary requirements for brine evaporation and salt landfilling.

Alternative methods to salt curing are green hide processing, chemical curing and chilling. Hides in countries such as New Zealand, Australia and some European countries are chilled as the favoured preservation process.

Table 8.2: Material balance of salt applied in curing one ton of raw hides, with 400 kg salt applied in curing (40% on weight of raw stock) (Lampard, 2002)

Source	Amount (kg)	Percentage (%)	Ends up in
Discharge as leachate on account of dehydration during curing	60	15	Environment
Fallen during handling and transport	40	10	Environment
Fallen during handling, sorting, trimming in the tannery	15	3.75	Environment/wastewater
Removed during desalting (*)	50-80	12.5-20	Environment/wastewater
Washed out in first soaking	120-145	30-36	Wastewater
Washed out in second soaking	45-80	11.25-15	Wastewater
Carried over by hides to further operations	30-49	7.5-10	Wastewater

(*) Not all tanneries practice desalting

Chilling reduces salt by about 60% in effluent, reduces water requirement for processing and hence also reduces wastewater generated requiring treatment. Lower salinity in effluent improves oxygen uptake in aerobic processes thereby improving aeration efficiency. Processing time is shortened as only washing is required. Using a salt-free pickle would have similar advantages.

8.2.2 Unhairing and liming

8.2.2.1 Enzyme unhairing

The use of enzymes alone cannot eliminate the ground and fine hair completely and an exclusively enzyme unhairing process will never be practically possible (Frendrup & Buljan, 2000). Enzymes are therefore commonly used in combination with other unhairing agents such as alkaline immunisation, alkaline swelling and sulphide treatment to eliminate ground and fine hair (UNIDO, 1991; Frendrup & Buljan, 2000; Buljan, 2012). The latest development in this field involves the pressure injection of a proteolytic enzyme solution on the flesh side of a limed skin or hide (Buljan, 2012). Enzyme unhairing is especially attractive when good wool or hair quality has high priority (Frendrup & Buljan, 2000; Buljan, 2012). Lime liquors can be recycled and hair retained. The clear advantages of this process are reduced pollution load and chemical dosages. The organic load emanating from the beamhouse can be reduced by 60% (Frendrup & Buljan, 2000). The use of enzymes can lead to the production of leather with cleaner and finer grains and with less grain shrinkage (UNIDO, 1991; Frendrup & Buljan, 2000; Buljan, 2012). Unfortunately, enzyme preparations are rarely used by industry due to the increased cost over conventional technologies (Frendrup & Buljan, 2000; Buljan, 2012).

8.2.2.2 Use of organic sulphur compounds

There are three types of organic sulphur compound commonly used for unhairing in Europe and Asia, namely, mercaptoethanol, formamidinesulphinic acid, and a compound based on mercaptoacetic acid (UNIDO, 1991; Frendrup & Buljan, 2000; Buljan, 2012). These are strong reducing agents that have a similar mode of action to sulphides, but they are more expensive (Buljan, 2012). Their use considerably reduces the amount of sulphides in the effluent (Frendrup & Buljan, 2000; Buljan, 2012).

8.2.2.3 Hair saving methods

Sirolime process

The Sirolime process firstly uses hydrosulphide to loosen the hair, then sodium chlorate to oxidise the sulphide, and finally lime to release the hair into the bath for filtering out (Frendrup & Buljan, 2000; Buljan, 2012). The unhairing or liming liquors can be recycled and recharged into the process after filtration (UNIDO, 1991; Frendrup & Buljan, 2000; Buljan, 2012). The resultant pelt is thoroughly washed and the waste wash liquor may be used for soaking hides (UNIDO, 1991; Buljan, 2012). It has been shown that effluent sulphide use 80%, lime 93%, and COD 17% less than conventional liming (UNIDO, 1991; Frendrup & Buljan, 2000; Buljan, 2012).

Hair-save reduces COD (±50%); BOD (±50%); fat, oil and grease (±60%); and suspended solids in effluent streams. It also removes large amounts of settleable solids (hair) upfront, may obviate the need for presettling when its main function is only to remove undissolved lime. It also reduces the organic nitrogen and total Kjeldahl nitrogen (TKN) of the effluents, which on breakdown are a considerable source of ammonia nitrogen (NH_3-N) in effluents. This in turn, as the unhairing wastewaters are the largest contributor to COD, BOD and suspended solids, reduces aeration requirements considerably.

8.2.3 Deliming and bating

Replacing ammonium salts with weak organic acids (such as lactic acid, formic acid and acetic acids, esters of organic acids, magnesium lactate, and non-swelling aromatic acids) reduces the concentration of ammonia in the wastewater (UNIDO, 1991; Frendrup, 1999; Ludvik, 2000; Buljan & Král, 2015). It is also believed that less bating agent is needed for the subsequent bating process if ammonia-free compounds are used (UNIDO, 1991; Buljan & Král, 2015). However, the presence of organic acids increases the COD in the effluent (Buljan & Král, 2015).

The use of carbon dioxide (CO_2) as a deliming agent significantly reduces the concentration of ammonia, organic nitrogen and BOD in the effluent (Buljan & Král, 2015). There are some drawbacks to using this technology, including the fact that the effectiveness of deliming of thicker and unsplit hides (more than 1.5 mm) requires enhancement with a small quantity of ammonium sulphate or a salt of a polycarboxylic acid (Ludvik, 2000; Buljan & Král, 2015). In addition, the process requires precise technical control and investment in special injection piping.

A non-ammonia alternative to the conventional deliming and bating process will obviate the need for extended aeration in the aerobic biological process to oxidise NH_3-N. By implementing both hair-save and non-NH_3 deliming, significant savings are made regarding oxygen requirements for wastewater treatment.

8.2.4 Pickling

The main goal should be to avoid or significantly reduce the use of sodium chloride for pickling. There are various low- to salt-free pickling chemicals available, including non-swelling polymeric and aromatic sulphonic acids (UNIDO, 1991; Buljan & Král, 2015). However, there is a perception that they have a negative impact on chrome tanning and leather quality (Buljan & Král, 2015). Therefore, the extensive adoption of recycling the pickling and tanning floats serves as the current and best practice used by most tanneries globally (UNIDO, 1991; Buljan & Král, 2015).

8.2.5 Tanning

8.2.5.1 Process optimisation

The optimisation of chrome tanning by manipulating the mechanical action, chrome concentration, pH, temperature and reaction time improves the chrome uptake and hence reduces the chrome discharge concentrations (Covington et al., 2000; Ludvik, 2000; Buljan & Král, 2015). It has been shown that as little as 1.7% Cr_2O_3 on pelt weight at a pH of 5 can achieve a tanning efficiency of 98% (Covington et al., 2000; Buljan & Král, 2015).

8.2.5.2 High exhaustion

The high-exhaustion process is achieved by masking the chrome tanning complexes and increasing collagen reactivity. This improves chrome uptake, thereby reducing the amount of chrome required (Covington et al., 2000; Buljan & Král, 2015). Common masking ligands include oxalate, acetate, formate, dicarboxylic acids (short and long chain), polyacrylates (low molecular weight), aliphatic dicarboxylates, and syntans (UNIDO, 1991; Buljan & Král, 2015). Depending on the thickness of the pelt, chrome requirements (offer) can be reduced from a standard level of 2.0% to 1.3% (Cr_2O_3 on pelt weight), which is a 35% reduction. In addition, chrome use has been shown to increase up to 98% (conventional 65%) without affecting the quality of the leather (UNIDO, 1991; Covington et al., 2000; Buljan & Král, 2015). The discharge for high-exhaustion tanning is 4% of the offer, about one-tenth that of conventional tanning. Coupling high-exhaustion tanning with chrome reuse considerably reduces the pollution load from the tan yard (UNIDO, 1991).

8.2.5.3 Direct recycling of spent floats

Recycling of spent floats is the simplest method for reusing chrome in conventional tanning (Ludvik, 2000; Buljan & Král, 2015). Closed recycling systems reuse only spent tanning floats and sammying water for tanning in successive cycles, while other recycles are open systems that are characterised by an increase in the float volume during recycling (Ludvik, 2000; Buljan & Král, 2015). Depending on the complexity, process control efficiencies from 90-98% can be achieved (Buljan & Král, 2015). An efficiency of 90% for conventional chrome tanning is easily attainable. This reduces the chrome discharge from 2-5 kg/t to 0.1-0.25 kg/t raw hide (Ludvik, 2000). A decrease in the effluent sulphate load from 30-55 kg/t to 10-22 kg/t raw hide is attainable (Ludvik, 2000).

8.2.5.4 Chrome recovery and recycling

Chrome reuse is based on the recovery of chrome by precipitation with alkalis and redissolution with acid (Covington et al., 2000; Ludvik, 2000; Buljan & Král, 2015). Alkalis such as sodium hydroxide, sodium carbonate, and calcium hydroxide achieve rapid coagulation rates. Although precipitation with magnesium oxide is comparatively slow and the chemical is expensive, it produces a dense precipitate that does not require filtering (UNIDO, 1991; Buljan & Král, 2015). Masked chrome complexes may not precipitate easily.

Following precipitation, the spent liquor is clarified and filtered and the filter cake is dissolved in sulphuric acid (Ludvik, 2000). The basicity of the resultant solution is adjusted and the basic chromium sulphate solution produced is reused for tanning (Ludvik, 2000; Buljan & Král, 2015).

Chrome recovery and recycling can differ according to the choice of precipitating alkali, operating conditions, clarification methods, and filter cake handling and reuse (Ludvik, 2000). A decrease in chrome discharge from 2-5 kg/t to 0.1-0.25 kg/t raw hide can be achieved (Ludvik, 2000).

8.2.5.5 The use of alternative tanning agents to chrome

Alternative tanning agents include mineral salts (such as sulphates, chlorides and silicates of titanium, aluminium, iron and zirconium), vegetable tannins (such as condensable mimosa bark, quebracho wood, hydrolysable chestnut, Valonea and myrabolans), and organic compounds (such as isocyanates and aldehydes) (US Environmental Protection Agency, 1976; UNIDO, 1991; Frendrup, 1999; Covington et al., 2000; Buljan & Král, 2015).

Mineral salts

Basic mineral salts such as aluminium chloride, sodium aluminium silicate and zirconium sulphates are currently used as retanning salts when certain final characteristics are desired in leather. Ammonium titanyl sulphate and magnesium-aluminium-titanium complexes have been developed as alternatives to chromium in the primary tanning process (Frendrup, 1999; Covington et al., 2000; Buljan & Král, 2015). Zirconium and titanium salts appear to be eco-toxicologically acceptable, but the quality of the leather falls short of that produced using chrome (Frendrup, 1999; Covington et al., 2000; Buljan & Král, 2015). Although there is ongoing research to improve the iron tannage process, it currently produces leather with poor properties.

The use of masked aluminium salt as a pretannage agent produces wet white leather (UNIDO, 1991; Frendrup, 1999). However, aluminium is considered a toxic metal, and tannage is reversible (UNIDO, 1991). Pretannage with polyphosphate and sulphuric acid, such as using the South African Liritan process, has the advantages of shortened process times, and high chemical uptake that lead to low effluent pollution load (UNIDO, 1991). However, the process needs careful technical control.

Vegetable tanning

Organic (vegetable) tanning is generally applied to heavy hides to produce sole or industrial leathers (UNIDO, 1991; Frendrup, 1999; Ludvik, 2000). Developing countries use vegetable tanning on bovine hides and skins, sheep and goat skins to produce an intermediate, but marketable commodity (UNIDO, 1991). Successive pits with a progressive tannin liquor strengths from weakest to strongest are used for vegetable tanning (UNIDO, 1991; Frendrup, 1999; Ludvik, 2000; Buljan & Král, 2015). The process takes up to five weeks, depending on the character of the pelt; it can be sped up by pretanning with polyphosphate (UNIDO, 1991; Buljan & Král, 2015). In contrast to chrome tanning, vegetable tanning requires large amounts of tanning agent (typically about 40-50% on pelt weight), with an overall tannin uptake of about 50-70% of the tanning offer (Frendrup, 1999).

The effluent produced from vegetable tanning is dark and turbid, and contains a higher load of poorly biodegradable COD than chrome tanning effluent (UNIDO, 1991; Frendrup, 1999; Covington et al., 2000). In addition, neutral salts derived from extracts and pretreatments are discharged concurrently (Frendrup, 1999). However, vegetable-tanned leather is easily biodegradable and compostable as tannins are common in decaying plant materials (Frendrup, 1999).

8.2.5.6 Synthetic organic tannages

Synthetic organic tannages (syntans) are real alternatives that can compete or even outshine chrome tannage regarding leather properties and/or process technology (Frendrup, 1999; Covington et al., 2000; Buljan & Král, 2015). Syntans are sulphonated condensation products of hydroxyl-substituted aromatic compounds (phenol, cresol or naphthalene) with formaldehyde and often with amides (Buljan & Král, 2015). Although some syntans are easily biodegraded, others are recalcitrant. Those with a lower potential environmental and human health impact are available commercially, but better alternatives have yet to be developed (Frendrup, 1999; Buljan & Král, 2015).

8.2.6 Wet finishing

The implementation of advanced post-tanning methods is aimed at reducing the pollution load of chrome, sulphates, COD, suspended solids and nitrogenous compounds.

8.2.6.1 Neutralisation

The amount of neutralising salts needed should be optimised to minimise the amount that is wasted in the effluent. Post-neutralisation rinsing water should be reduced as much as possible without compromising the washing efficiency, and the pH should be properly adjusted to avoid Cr(VI) formation (Hauber, 2000; Buljan & Král, 2015). Spent floats should be screened to remove chrome-containing leather fibres (UNIDO, 1991; Buljan & Král, 2015). Commercially available special acrylic polymers with retanning effects can be used for chrome fixing during the neutralisation stage, reducing the amount of sodium and sulphate in the effluent (Ludvik, 2000).

8.2.6.2 Retanning, dyeing and fatliquoring

Optimisation of industrial wet finishing systems (retanning, dyeing and fatliquoring) is required to achieve the lowest possible COD and salt levels in the effluent. Optimised high-exhaustion retanning methods using appropriate masking agents and amounts (to avoid difficulties with the precipitation) should be implemented (UNIDO, 1991; Ludvik, 2000; Buljan & Král, 2015). The addition of amphoteric polymers improves the exhaustion of dyes and fatliquoring agents, and has been shown to reduce the COD discharged from a range of 24-40 kg/t to about 10-2 kg/t raw hide (Ludvik, 2000).

Use of biodegradable retanning agents that produce quality leather with desired properties should be prioritised as alternatives to chrome (Hauber, 2000). Retanning compounds based on urea-formaldehyde or melamine-formaldehyde resins, or amino resins should be replaced with non-nitrogenous compounds such as acrylic polymers. This may reduce the ammonia load from 0.3-0.5 kg/t to 0.1-0.2 kg/t raw hide (Ludvik, 2000). The introduction of organic chemicals and preparations with limited biodegradability, high COD values, and dyes containing toxic metals such as lead, cadmium and Cr(VI) for wet finishing should be avoided (Ludvik, 2000; Buljan & Král, 2015). Fatliquoring agents based on chlorinated paraffin, benzidine and other azo dyes (which may be reduced to carcinogenic amines) and those with oxidising properties [cause Cr(VI) formation] should also be avoided (Hauber, 2000).

8.2.7 Finishing

8.2.7.1 Water-based finishing

Water-based systems in conjunction with cross-linking agents are increasingly being favoured because of environmental concerns about organic solvents (UNIDO, 1991; Buljan & Král, 2015). However, less toxic and less volatile cross-linking agents should be used, or alternatively, self-cross-linking reactive polymers containing N-methylolamide groups (Buljan & Král, 2015). However, the drying of water-based top coats is costly (Buljan & Král, 2015) and thus organic solvents with lower health and environmental impacts may also be considered.

8.2.7.2 Improved coating techniques

Padding, curtain coating, roller coating, and spraying of leather are substantially different coating techniques suited to different types of leather article. High-volume low-pressure (HVLP) spray guns spraying with a large volume of air at low pressure should be used to reduce the loss of coating during conventional spraying considerably (Buljan & Král, 2015). However, the HVLP technique does not give completely satisfactory results for some articles, such as upper leather and garment leather (Buljan & Král, 2015).

Table 8.3: Summary of selected alternative 'best available' technologies and their environmental benefits (Jackson-Moss, personal communication)

Alternative 'clean' technologies	Environmental benefit/s
Processing of fresh hides	• Less salt in the final effluent. • Savings in water consumption.
Recycling of soak floats	• Savings in water consumption. • Savings in chemical usage.
Use of enzymatic soaking chemicals	• Less use of surfactants. • Reduced soaking times leading to less energy consumption.
Use of biodegradable surfactants	• Less chance of surfactants persisting in the environment. • Reduced impact on aquatic organisms.
Hair-save unhairing	• A 60% reduction in COD of effluent. • A 50% reduction in sulphide usage. • A 35% reduction in nitrogen content of effluent.

Alternative 'clean' technologies	Environmental benefit/s
Low-sulphide/sulphide-free unhairing	• No sulphides in effluent. • Reduced odours. • Reduced COD in effluent. • Better settling of suspended solids in effluent.
Recycling of liming floats	• Savings in water consumption. • No sulphides in final effluent. • Reduced COD in effluent.
Low ammonia deliming/CO_2 deliming	• Reduced ammonium ions in the effluent. • Less odour.
ThruBlue process	• No salt in effluent. • No sulphate ions in effluent.
Salt-free pickling process	• No salt in effluent.
Pickle recycling	• Reduced salt in effluent. • Savings in water consumption.
High-exhaustion chrome tanning	• Reduced chrome in effluent.
Chrome recycling	• Reduced chrome in effluent. • Savings in water consumption.
Chrome-free leathers	• No chrome in effluent.
High-exhaustion retanning chemicals, dyes and fatliquors	• Less COD in effluent. • Less dyestuffs in effluent.
Aqueous finishing systems	• Solvent-free air emissions.

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APPENDIX A: GLOBAL LEATHER INDUSTRY OVERVIEW

Global Leather Industry Overview: Selected Geographical Areas

Major Leather Industry Players: Asia

Country	Notes
China	• emerged as the utmost player in all sectors of the leather industry • large supply of low cost labour • highly integrated industry • innovatively the largest pigskin and pig leather supplier • reduced tax rebates and other benefits • friendly environmental legislatives
India	• strong domestic raw material base • cheap labour and domestic market • growing domestic demand (expanding middle class and automotive industry) • expected growth in the industry
Pakistan	• good local raw material supply (esp buffalo hides) and low wage cost • higher production costs • Low grade raw material imports and out dated machinery (poor quality products) • High pollution levels due to poor environmental management systems

Major Leather Industry Players: North and South America

Country	Notes
Brazil	• world's largest commercial cattle herd (14.2% of the world) • good local raw material supply • 2nd largest leather producer and 3rd largest exporter worldwide • highly integrated industry • high added value leather products • strong domestic footwear, automotive and leather (especially travel) goods production factories • only country with "Leather Law": Law No. 4.888
USA	• shortage of available supplies of hides and skins (decline in off take rates) • leading exporter of pig skins • declining domestic leather market esp footwear (cheap Chinese imports) • industry has high-tech machinery (good leather quality)

Major Leather Industry Players: Europe

Country	Notes
Italy	• tanning industry is the most internationalised sector • good raw material supply (16% of global imports) and leather products market • highly integrated industry • about 20% of the world's leather production & 25% finished leather exports • industry has built clever business models with high levels of flexibility, innovation and versatility • About 80% of tanning machinery and 50% of the footwear and leather goods manufacturing machinery • leading country in the implementation of chrome free leather tanning

Major Leather Industry Players: Africa

Country	Notes
Ethiopia	• good supply of raw material with the largest cattle population in Africa • cheap labour estimated to be ten times less than China's (Mascianà, 2015) • industry lacks skilled labour (cutting and designing) • shoe industry losing out on the market to the sophisticated Italian & Chinese shoe designs • free access to the EU and US markets • poor quality supply of skins and hides (poor animal husbandry) • cheaper utilities particularly water • Significant leather industry due to the total ban on export of skin and hides & increasing foreign investment

APPENDIX B: QUESTIONNAIRE

Questionnaire Used During Tannery Surveys

TANNING AND LEATHER FINISHING INDUSTRY QUESTIONNAIRE (CONFIDENTIAL)	NAME OF TANNERY:
1. Type, quantity and quality of products	
Which hides are used?	
What are the final products?	
What quantities are processed (per annum)?	
Is it possible to obtain long-term statistics with regard to production volumes?	
In terms of number of hides processed in South Africa, how much does this facility contribute?	
2. Seasonality	
Is the tanning process seasonal? If so, over which months does the season extend?	
3. Production processes	
Which tanning processes are used?	
Which finishing process(es) are used?	
4. Water usage	
What volume(s) and source(s) of water are employed during tanning production process? Can you provide an estimate of water usage per month, and water usage per hide/skin?	
Can you please provide a holistic cost estimate for the provision of water for the tanning process(es)? If applicable, do you know what the local municipal tariffs are?	
Are water usage targets in place? If so, to what extent are these being met?	
5. Wastewater generation and management	
What volume of wastewater is generated during each tanning process? Can you provide an estimate of the volume of wastewater generated per hide/skin processed?	
Can you provide us with historical quality data on the wastewater from each production process and the final effluent? Is it possible to collect samples for analysis?	
Is the wastewater being treated before discharge? If so, what methods are being used?	

TANNING AND LEATHER FINISHING INDUSTRY QUESTIONNAIRE (CONFIDENTIAL)	NAME OF TANNERY:
Are wastewater quality and quantity targets in place? If so, to what extent are these being met? How do the targets compare to statutory requirements?	
Is any of the wastewater being reused? If so, please give details.	
Do you think that there is scope for further beneficiation using any of the effluent streams?	
6. Solid waste/slurry generation	
What is the type and quantity of solid waste or slurry generated per hide/skin processed?	
Are any potentially toxic by-products generated?	
How is the solid waste disposed of currently?	
Do you think that there is scope for further beneficiation using any of the solid waste?	
7. Emissions	
Are gaseous emissions generated during the production processes? If so, please give details.	
Are plans in place to mitigate the production of harmful emissions?	
8. Energy usage	
What type(s) of energy are used in the tanning processes?	
How much energy is used in the tanning processes? (details or estimates).	
What is the cost (kWh) of energy used?	
Do you have plans to explore the use of alternative, green energy resources? If so, please provide details.	

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