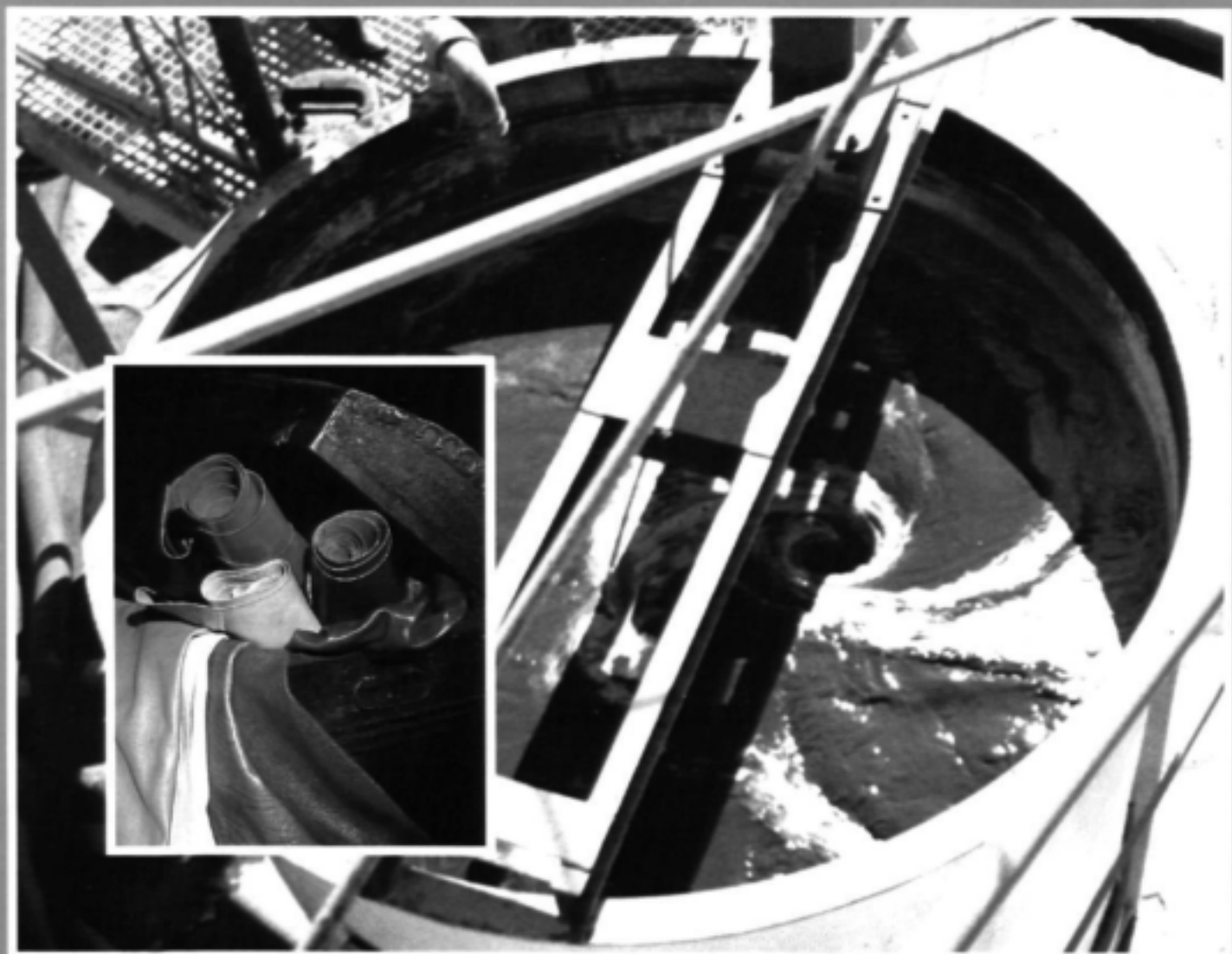


NATSURV 10

WATER AND WASTE-WATER MANAGEMENT IN THE TANNING AND LEATHER FINISHING INDUSTRY



NATSURV 10

WATER AND WASTE-WATER MANAGEMENT
IN THE
TANNING AND LEATHER FINISHING INDUSTRY

PREPARED FOR THE
WATER RESEARCH COMMISSION

BY

STEFFEN, ROBERTSON AND KIRSTEN
CONSULTING ENGINEERS

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Steffen, Robertson and Kirsten Inc
16th Floor
20 Anderson Street
JOHANNESBURG
2001

P O Box 8856
JOHANNESBURG
2000
Tel : (011) 492-1316

Available from:

Water Research Commission
P O Box 824
PRETORIA
0001
Republic of South Africa

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FOREWORD

The need for guidelines to reduce water intake and waste-water disposal by industry is of national concern in view of the scarcity of water in South Africa.

To establish norms for water intake and waste-water disposal, the Water Research Commission (WRC) in collaboration with the Department of Water Affairs (DWA), contracted Steffen, Robertson and Kirsten, a firm of consulting Engineers, to undertake the National Industrial Water and Waste-water Survey (NATSURV) of the tanning industry.

It is expected that this Guide will be of value to the tanning industry itself and to other interested parties such as municipalities, legislators, researchers and consultants in the water and waste-water fields.

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Dr O O Hart	Water Research Commission
Mr D F Sutton	Department of Water Affairs
Dr D R Cooper	LIRI
Dr S G Shuttleworth	LIRI
Mr R A Rowswell	LIRI
Mr D A Boast	LIRI
Mr G N Steenveld	Steffen, Robertson and Kirsten
Mr P Skivington	Steffen, Robertson and Kirsten.

SUMMARY

There are twenty tanneries in the Republic of South Africa, which process approximately two million hides annually. Water usage by these tanneries is approximately 600 000 m³ per annum and almost all of this becomes waste water. The range of specific water intake (SWI) for full tanning was found to be 320-744 l/hide with the average being 432 l/hide. A target SWI figure has been proposed at 432 l/hide.

The water requirement is dependent on the specific tanning process. In most cases potable domestic water is used, but some tanneries depend on good quality river water, and for selected processes purified domestic sewage effluent can be utilised where available. Furthermore, if tannery effluent is treated sufficiently, it can be blended with other water for specific applications.

The range of specific pollution load (SPL) was found to be 0,9 - 6,8 kg COD/hide with a mean of 3,7 kg COD/hide, 2,6 - 8,9 kg TDS/hide, with a mean of 7,7 kg TDS/hide, 0,5 - 1,4 kg SS/hide with a mean of 0,8 kg SS/hide and 0,01 - 0,2 kg Cr/hide with a mean of 0,1 kg Cr/hide. Target figures have been proposed of 1,0 kg COD/hide, 3,0 kg TDS/hide, 0,5 kg SS/hide and <0,01 kg Cr/hide.

Investigations have shown that the technology for economic effluent purification to river water standards does not exist, and that the systems used by tanneries depend on the requirements of the Department of Water Affairs and local authorities. Where dilution with domestic sewage and subsequent treatment by local authorities are inadequate, the alternatives are irrigation or evaporation ponds, with pre-treatment to remove sulphide and settleable solids.

A summary is given of the main systems used for waste-water and solid waste disposal and the biological and physico-chemical treatment methods investigated and reported in the "Guide to Waste Water Management in the Tanning and Fellmongering Industries" published by the Water Research Commission (No. ISBN O 908356 52 8).

Results of large-scale applications and monitoring of treatment systems are also summarised. Recent large-scale investigations in the field of effluent treatment include lime and chrome recycling and recovery of chrome, recovery of fat and grease, and anaerobic digestion.

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GLOSSARY

- 1 **Bating** - The use of enzymes (usually extracted from the pancreatic glands of pigs) to dissolve and remove some of the interfibrillary proteins of delimed hides and skins. This is in order to produce a softer leather, with a smoother grain surface.
- 2 **Chrome tanning** - The use of chromium salts (usually one-third basic chromium sulphate).
- 3 **Deliming** - Removal of lime from hides or skins using ammonium salts and/or weak acids which have soluble calcium salts.
- 4 **Drums** - Large wooden drums which are rotated at speeds suitable for the particular process.
- 5 **Epidermis** - The outer surface layer of the hide or skin which holds the hair roots. It is removed during the leather-making process.
- 6 **Fatliquoring** - Drumming an emulsion of fats and oils into the wet leather to provide lubrication and subsequent softness and flexibility.
- 7 **Fleshing** - Removal of the fleshy, fatty material situated on the insides of hides and skins.
- 8 **Filling** - Drumming process whereby substances are added to vegetable tanned leather, to create a more compact leather, eg vegetable-tanned sole leather.
- 9 **Float** - Volume of water that is present in the tanning vessel.
- 10 **Hides** - Skins of larger animals, eg cattle.
- 11 **Limeyard** - (Modern day). Area in the tannery where the hides are soaked and unhaired.
- 12 **Neutralising** - De-acidifying of chrome tanned leather from pH values of 3,5 - 3,9 to 4,2 - 5,5, depending on the type of leather being processed.

GLOSSARY (Cont)

- 13 **Paddles** - Large wooden vessels fitted with wooden paddles which are rotated to create a stirring action.
- 14 **Protein** - A complex naturally occurring organic material consisting of long interwoven chains with side chains containing acidic and basic groups.
- 15 **Retanning** - Process whereby special products (eg synthetic tannins) are applied to leather, to impart specific properties eg softness, evenness of colour, etc.
- 16 **Sammying** - A mechanical process where excess moisture is squeezed out of the hide material.
- 17 **Setting** - Mechanical operation to remove wrinkles and to flatten the leather surface.
- 18 **Settleable solids** - The solids which settle out in one hour in an Imhoff Cone, expressed as mt/t .
- 19 **SPL** - The mass of a given pollutant for a particular parameter divided by the number of hides produced (or the mass of hides produced) for the same period.
- 20 **SWI** - The water intake for a particular period divided by the number of hides produced (or the mass of hides produced) for the same period.
- 21 **Tanning** - The process whereby animal hides and skins are converted to a useful, stable product known as leather.
- 22 **Vegetable tanning** - The use of tannins from plant origin, eg mimosa.
- 23 **Wet blue** - Chrome tanned hides which have been sammyed to remove surplus moisture, but not finished, and are suitable for marketing locally or overseas. Further processing is required to produce leather.

1 INTRODUCTION

On the basis of raw material intake, the tanning industry has expanded steadily during the past 12 years, partly due to modern methods of upgrading the quality of leather processed from local hides. The principal market is the local footwear and upholstery industries.

At present there are twenty tanneries of various sizes, but the majority of the leather produced comes from tanneries situated in Central and Southern Transvaal (3), the Orange Free State (1), Natal (2), the Western Cape (3) and the Eastern Cape (4).

The tanning industry in the RSA processes in excess of 2 million hides per annum and consumes approximately 0,6 million m³ of water, most of which becomes effluent of a rather intractable nature. Solid wastes include raw hide and leather trimmings, shavings and buffing dust, fleshings and degraded hair, and sludge settled out from the liquid wastes.

There are three clearly defined stages in upper leather processing depending on the degree to which the hide is processed, namely the 'wet-blue' stage, retanning and dyeing, and the finishing stage. Traditionally tanneries carried out the full process and transformed raw hides into fully finished leather. Recent trends have seen the establishment of increasing numbers of wet-blue tanneries where the raw hides are processed only to the chrome-tanned stage. The wet-blue hides can then be stored or transported for final processing elsewhere.

The results contained in this document are based on data collected at 11 tanneries in the RSA.

The Water Research Commission has sponsored investigations on tannery effluent treatment, the results of which are described in "A Guide to Wastewater Management in the Tanning and Fellmongering Industries", and many of the recommendations arising from this research have been implemented on a large scale.

2 PROCESS RÉSUMÉ

This process résumé is not intended as a detailed description of the process.

2.1 Definition

Tanning is the process whereby hides or skins are converted into leather by the action of either chemicals or vegetable tannins.

2.2 Curing of Hides and Skins

Curing is the process which prevents the organic degradation of hides and skins from the time they are removed from the animals to the start of the tanning process. This can range from a few hours to six months.

Several types of curing are practised:

- a) Short-term cures (up to 3 weeks)
 - (i) Cooling
 - (ii) Chemical curing

- b) Long-term cures (up to 6 months)
 - (i) Drying
 - (ii) Dry salting
 - (iii) Wet salting (brining)
 - (iv) Stack salting

Where tanneries are situated close to abattoirs, the fresh or "green" hides or skins can be processed without curing. For periods longer than one day, the use of salt can be avoided by applying the chemical curing methods developed at LIRI, which assists the tanner in meeting standards for dissolved solids and conductivity. However, for the export of hides it is still necessary to use salt due to the necessity for longer storage.

2.3 The Tanning Process

2.3.1 Soaking

Hides and skins are washed in drums and paddles to remove blood and dirt and then drummed or paddled until fully rehydrated. In the case of salted hides a major proportion of the curing salt is removed. The soaking time depends on the type of cure, and an antiseptic is used, while for dry hides a soaking agent is normally added to accelerate the wetting back process.

2.3.2 Unhairing

After soaking, the hides or skins are drummed or paddled in a lime sulphide solution to remove the hair and epidermis and to open up the fibre structure for the subsequent penetration of the tanning materials. The effluent from the unhairing process has a high solids content consisting of degraded protein and hair, surplus lime and sulphides and high pH, PV and COD values.

2.3.3 Fleshing

From the unhairing drum the hides are fleshed by machine to remove fatty tissue on the flesh side. The sludge from this machine consists of fatty tissue, hair, protein matter and sulphide compounds.

2.3.4 Delime and Bate

The hides are loaded into a drum, floated in warm water and delimed with ammonium salts and/or weak acid to bring the pH value to approximately 8.5, suitable for the bating enzymes. The bating operation cleans up the grain surface of degraded material resulting from the unhairing process. The effluent contains ammonium and calcium salts and degraded protein matter.

2.3.5 Chrome Tanning

The delimed and bated hides are then pickled in a solution of sulphuric and formic acids plus sufficient sodium chloride to prevent acid swelling, followed by the addition of the chrome tanning salts. The spent liquor contains chromium and other salts which can be recycled to minimise chromium and salt in the effluent and to reduce costs. However, it is not possible to drain all the spent liquor from the drum

and the subsequent washing process gives rise to some chromium in the effluent. However, a large proportion of this chrome can be recovered economically by precipitation followed by re-acidification of the precipitate.

2.3.6 Wet blue

At this stage the hides may be washed and partially dewatered through a sammying machine, giving rise to a stable marketable product known as wet blue.

2.3.7 Neutralising and retanning

After thinning operations the wet-blue stock is loaded into a drum, washed and neutralised with a solution of mild alkali to bring the pH up to about 4.5, suitable for retanning. A wide range of retanning agents are drummed into the leather. These comprise vegetable tans, synthetic tans and synthetic polymers, the first rendering an effluent with higher oxygen demand than when using organic polymers.

2.3.8 Dyeing and fatliquoring

After retanning the drum is drained and the hides are refloated in warm water. The dye is added and drummed into the leather, followed by the addition of an emulsion of fatliquoring oil. The effluent contains spent dye-stuff and oil.

2.3.9 Samm/Setting

A comparatively small amount of effluent is generated during the mechanical samm/setting operation. This contains low concentrations of spent dye-stuff and oil.

2.3.10 Vegetable tanning

Because of the high oxygen demand of vegetable tannins, every effort is made by tanners to reduce these in the effluent. Where light-weight vegetable tanned leathers are produced a minimum of vegetable tan extract is used in a drum process, preferably with a low float in order to maximise absorption and to minimise the effluent problem. For vegetable sole leather the Liritan Sole Leather Process is used in the RSA and many other countries. The delimed hides are drummed or suspended in pits in a polymeric sodium hexametaphosphate and sulphuric acid solution which can be used repeatedly with topping up. This is followed by immersion in an initial weak tan liquor, some of which is discarded to maintain the

purity of the subsequent strong liquors circulating at a warm temperature in a series of pits. After tanning the leather is washed in a drum followed by bleaching and filling. These effluents contain spent vegetable tans.

2.3.11 Finishing

Finishing is the application of a coating or coatings to the leather surface, to impart specific effects and properties (colour, scuff resistance, etc.) Finishing processes vary according to the end-product and, if properly managed, should not produce significant quantities of effluent.

3 SUMMARY OF SURVEY RESULTS

3.1 Water Intake

The results obtained from the survey are summarized in Table 1.

TABLE 1 TYPICAL SWI FIGURES FOR THE TANNING AND LEATHER FINISHING INDUSTRIES

	Nos	Production (hides/d)		Water intake (m ³ /d)		SWI (l/hide)	
		Range	Average	Range	Average	Range	Average
Full tanneries	9	72-1300	775	25-534	303	320-744	432
Wet-blue plant	1		675		230		339
Retanning, dyeing and finishing plant	1		950		370		389

Data from game skin tanneries are not included. Only one example of a wet-blue plant and one of a retanning, dyeing and finishing plant were surveyed.

It is important to note that the range of SWI was found to be large. These variations indicate that opportunities exist for better water management in the industry.

The retanning, dyeing and finishing plant utilizes a considerable volume of water and appears to be comparable in terms of volume of water used, to a wet-blue plant. Full tanneries appear to use less water per hide than would be indicated by summing the SWI figures for the two separate process plants. Some economy of scale and more opportunity for water reuse may help to explain this.

As most tanneries seem to be operating at close to their design capacities, consideration of utilization of capacity related to water use is not particularly relevant but it should be kept in mind that a tannery not operating close to its capacity will have a higher SWI than it would have had if it did operate at its design capacity. This is probably less true for the tanning industry than for the food industry where large quantities of water are used for purposes of hygiene.

Tanneries do use water for cleaning and wash-down but less frequently than would be the case in the food industry.

There does seem to be some evidence to suggest that larger tanneries are more efficient in terms of water usage than smaller ones. For full tanneries producing more than 900 hides/d the average SWI was found to be 356 t/hide while for full tanneries producing less than 900 wet-blue hides per day, the corresponding SWI figure was 546 t/hide.

Certain economies of scale may again apply but then tighter water management is also probably practised in the larger establishments because water costs are higher and generally more staff tend to be available.

3.2 Breakdown of Water Use

Table 2 indicates how water is used in a typical tanning operation up to the wet-blue stage.

TABLE 2 WATER USE FOR WET-BLUE HIDE PROCESSING

Process stage	Water use		Typical breakdown of SWI (l/hide)
	Range	Typical	
Limeyard			
- soaking	15 - 20%	16%	54
- unhairing	7 - 12%	10%	34
- washing	10 - 25%	19%	65
- fleshing	neg	neg	-
Total limeyard	Total ranges	45%	153
Chromeyard			
- washing	16 - 64%	44%	149
- delime and bate	5 - 9%	8%	27
- pickling and chrome tanning	2 - 9%	3%	10
Total chromeyard	Total ranges	55%	186
Total process	Total ranges	100%	339

Water use in retanning, dyeing and finishing operations was found to be so variable that comparisons between operations was not sensible.

As can be seen the major water use in the wet-blue process is associated with the various washing processes (typically about 60%). These have been lumped together under the main process groupings of limeyard and chromeyard but they actually represent many separate washing operations which occur after each process stage in the tanning process. When comparing different tanneries washing is also where the greatest variation in water use occurs.

The other process stages were found to have much less variation in water use. On average the limeyard operation was responsible for about 45% and the chromeyard for about 55% of the total water use associated with wet-blue processing.

3.3 Waste Water

Most tanning operations are non-consumptive in their water use and, apart from minor evaporative losses, all water used is discharged as waste water. Generally therefore, SEV figures are slightly lower than the SWI figures for the tanning industry.

In terms of pollution load, wet-blue processing is responsible for the majority of the load discharged by a full tannery. Although certain post-chrome tanning operations generate considerable pollution loads in their own right, they are small in comparison with the much greater loads generated by wet blue processing. A typical tannery final waste water may include soil, antiseptics, fats, salt, chrome, vegetable tannins, syntans, dyes and lacquers. It will tend to be extreme in pH variations and high in TDS, SS and organic content.

When considering full tannery waste waters it must be remembered that they tend to vary greatly over relatively short periods of time. Great care must therefore be exercised when sampling tannery waste water to ensure that the samples are representative. Samples of final raw effluent have been collected and the results are summarised in Table 3.

TABLE 3 RAW WASTE-WATER QUALITY FROM THE TANNING INDUSTRY (FULL TANNERIES)

Average daily waste-water discharge (m ³)	Determinand				
	pH	COD (mg/ℓ)	TDS (mg/ℓ)	SS (mg/ℓ)	Cr (mg/ℓ)
Range 25 - 534	3,9 - 11,1	2760 - 29110	10100-23400	1250-4100	42 - 690
Average 300	8,4	9700	19600	1970	120

From these concentrations SPL figures have been calculated as indicated in Table 4

**TABLE 4 SPECIFIC POLLUTION LOADS (SPL) IN THE TANNING INDUSTRY
(FULL TANNERIES)**

Determinand					
Average daily waste-water discharge (m ³)	Average daily hide production	COD (kg/hide)	TDS (kg/hide)	SS (kg/hide)	Cr (kg/hide)
Range 25 - 534	72 - 1300	0,9 - 6,8	2,6 - 8,9	0,5 - 1,4	0,01 - 0,2
Average 300	775	3,7	7,7	0,8	0,1

As it is normally impossible to distinguish waste waters arising from wet-blue processing and retanning in a full retanning plant, the final effluent analyses for the full tanneries only are given.

The wet-blue part of the processing gives rise to the majority of the pollution load.

The post-chrome tanning operations may be responsible for generating a considerable pollution load as well, particularly as a result of retanning and dyeing operations but these are intermittent and extremely difficult to quantify on a comparative basis. Normally the pollution load from finishing operations is low compared to that arising from processing to the wet-blue stage.

As stated earlier, the limeyard and chromeyard operations, collectively described as wet-blue processing, are responsible for the major part of the pollution load discharged by the tannery. These operations can be further broken down as follows:

TABLE 5 SPECIFIC POLLUTION LOADS (SPL) FOR WET-BLUE HIDE PROCESSING

Process stage	Typical breakdown of SPL (kg/hide)			
	COD	TDS	SS	Cr
Limeyard				
- Soaking	0,22	0,31*	0,01	nil
- Unhairing	1,43	0,99*	0,52	nil
- Washing	0,50	0,73*	0,08	nil
Total limeyard	2,15	2,03*	0,61	nil
Chromeyard				
- Delime and bate	0,19	0,45	0,01	nil
- Pickling and chrome tanning	0,01	0,14	nil	0,08
- Washing	0,55	2,38	0,08	0,01
Total chromeyard	0,75	2,97	0,09	0,09
Total process	2,9	5,0*	0,7	0,09

- * Using only salt-free hides for processing. This figure would be significantly higher if salted hides were processed.

As can be seen, the limeyard operation is responsible for producing most of the COD and SS pollution load - mainly as a result of unhairing. Both limeyard and chromeyard operations produce high TDS pollution loads while the chromeyard obviously produces all of the chromium pollution load.

3.4 Solid Wastes and By-products

The main solid wastes arising from tannery operations are fatty tissue, degraded hair and other proteinaceous materials. In many tanneries tallow is recovered from the fleshing material. Major solid waste disposal problems occur with the sludges generated in leather processing. (See Section 4.5)

4 CONCLUSIONS AND RECOMMENDATIONS

4.1 Water Use

Full tanneries in South Africa have been found to have a range of SWI of between 320 and 744 t/hide . The average SWI figure was found to be 430 t/hide . A target SWI for full tanneries corresponding to the industry mean is proposed.

The water used in many tanning operations is determined according to a formula and to change this appreciably would impact on the quality of the individual product of each tannery to an unacceptable degree. The industry should rather see its responsibility as optimizing its water use particularly with regard to the reuse of water for lower-grade purposes instead of using fresh water. This sort of policy obviously requires management input in first deciding what quality of water is acceptable for each process and secondly in ensuring that the policy is followed through on a day-to-day basis.

Water use associated with washing and also in many of the retanning operations is subject to more variation between tanneries and many opportunities exist for the reuse of water and better control of fresh-water use.

Some methods of reducing water intake are listed below :

- a) ensure maximum condensate return to boilers;
- b) monitor boiler blowdown to avoid excessive blowdown losses;
- c) use of high-pressure, low-volume equipment for floor washing and other general wash-down requirements. Each hose should be fitted with a self-closing nozzle device;
- d) installation and control of water meters at all sections in the process and commitment from the tannery management to a water monitoring and management programme;
- e) improved staff training to increase awareness of water saving methods;

- f) reuse of process exhaust liquors in the same process. Reuse of chrome pickle liquors, for example, have been reported to reduce chrome and salt by approximately 15% and 66% respectively, as well as achieving significant reductions in water use and waste-water generation in the pickling/chrome tanning process.
- h) reuse of purified waste water from other sources such as treated municipal waste water. It is reported that a tannery in the RSA has successfully used treated municipal waste water in several process applications, as do many other industries.

All tanneries in South Africa should be encouraged to reuse process waste waters, eg in lime recycling and chrome recycling.

4.2 Waste Water

The range of SPL figures found for full tanneries in South Africa was 0,9 to 6,8 kg COD/hide with a mean of 3,7 kg COD/hide, 2,6 to 8,9 kg TDS/hide with a mean of 7,7 kg TDS/hide, 0,5 to 1,4 kg SS/hide with a mean of 0,8 kg SS/hide and 0,01 - 0,2 kg Cr/hide with a mean of 0,1 kg Cr/hide.

Targets for SPL are proposed in Table 6.

TABLE 6 PROPOSED TARGETS FOR UPPER LEATHER TANNERY SPECIFIC POLLUTION LOADS (SPL)

	Current mean		Proposed target	
	kg/hide	(kg/t)	kg/hide	(kg/t)
COD	2,9	(132)	1,0	(45)
TDS	5,0	(227)	3,0	(35)
SS	0,7	(32)	0,5	(23)
Cr	0,1	(4,5)	<0,1	<0,01

These targets are proposed as being reasonably achievable by industry.

In formulating a waste-water management strategy each process liquor should only be regarded as a waste water when a tannery cannot make use of it for **any** other purpose. The main options available for managing tannery waste waters are:

- a) reuse or recycle as much of the liquors and contents as possible;
- b) alter tannery processes where possible to reduce pollutants.

4.3 Altering Tannery Processes

Altering tannery processes refers mainly to changing the chemicals used currently to alternatives which achieve the same result but produce less undesirable pollution loads. Enzymatic systems for unhairing and production of wet-white rather than wet-blue hides which are based on alternative tanning salts to chrome are some of the ideas which leather industry researchers are currently examining. Alternative chrome tanning salts which maximise chrome uptake are also being developed.

4.4 Treatment of Final Tannery Waste Waters

Traditionally the tanning industry in South Africa has disposed of final waste water by discharge to facultative lagoons or evaporation ponds, by spray irrigation of settled waste water to land or by discharge to municipal sewer after on-site pre-treatment.

The Department of Water Affairs is tightening its requirements regarding disposal of waste waters to land due to soil degradation and ground-water pollution problems. Similarly, disposal to pond systems is not very favourably viewed by the authorities as sludge disposal and odour problems eventually arise in all ponding systems.

On-site pre-treatment prior to discharge to sewer, ponding systems or reuse, is therefore becoming an increasingly essential part of tannery practice. The particular system followed will depend on individual circumstances and on the eventual disposal route for the waste water.

Treatment systems can be divided into primary processes such as fat skimming, screening, waste-water balancing and gravity settling which are relatively inexpensive and simple, secondary processes such as air flotation, activated sludge treatment and biofiltration, and tertiary processes such as membrane treatment, which are costly and complex. Normally secondary and tertiary processes would be preceded by primary treatment or pre-treatment.

For greater detail on methods of treatment for final tannery waste waters, the reader is referred to the WRC publication number ISBN 0 908356 52 8 on waste-water management in the tanning and fellmongering industries.

4.5 Monitoring and Control of Waste-water Treatment Processes

Effluent quality can be significantly improved by adequate monitoring and control of waste-water treatment processes. This can lead to a notable reduction in the costs levied by local authorities for waste-water discharges.

4.6 Sludge Handling

Sludges arise mainly from unhairing operations. A typical sludge volume of about 4,3 m³ of settled sludge per 100 m³ of final waste water, excluding solids from fleshing, has been reported. Tannery sludges generally settle readily and unless this takes place under controlled conditions sludge removal and disposal become extremely labour intensive. Secondary sludges which arise as a result of chemical precipitation, particularly between alkaline un-hairing and acidic chromeyard waste waters, also need to be catered for when planning a sludge disposal system.

Sludge disposal following thickening or further processing on site normally takes the form of drying on sludge drying beds and/or removal, dumping, land-fill, composting, soil conditioning or re-sale as animal feedstock. WRC guide ISBN 0 908356 52 8 deals with this subject in much greater detail.

4.7 Process Waste-water Segregation

As mentioned above, unhairing and chromeyard waste waters combine chemically to render sludges which can be difficult to treat. These waste waters should be segregated and dealt with separately before recombining to achieve neutralization. Another example of stream segregation would be separation of low SS, neutral waste waters arising from limeyard soaking, washing and de-lime and bate operations from the highly alkaline lime-sulphide and lime wash and acidic chrome pickle and chrome wash waste waters.