ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
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WATER AND WASTEWATER MINIMIZATION IN TANNERY BY USING WATER PINCH TECHNOLOGY

CASE STUDY (ETHIO LEATHER INDUSTRY PLC (ELICO) GLOVE AND HIDE UNIT)

By

Gutama Moroda

Advisor

Dr.Ing Nurelegn Tefera

A thesis submitted to the School Of Graduate Studies of Addis Ababa University in partial fulfillment of the Degree of Master of Science in Environmental Engineering

July 2011

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ABBREVIATIONS

APHA	American Public Health Association
BOD	Biological oxygen demand
COD	Chemical oxygen Demand
ELICO	Ethio-Leather Industry PLC
HEN	Heat Exchange Network
LIDI	Leather Industries Development Institute
MEN	Mass Exchange Network
NMTB	Non-Mass Transfer-based
MTB	Mass Transfer-based
PI	Process integration
SLC	Standard Leather Chemical
SLP	Standard Leather physical
SS	Suspended solids
TDS	Total Dissolved solids
UNEP	United Nations Environment Programme
UNIDO	United Nations Industrial Development Organization
WPA	Water pinch analysis

ABSTRACT

In tanneries, the phases of conditioning and preparing the hide/skin for tanning, as well as the transportation and fixation of tanning substances are all carried out in aqueous media. Most of the steps of these processes are carried out with fresh water. This leads to the generation of high wastewater flowrates which will have to be treated due to the relatively high concentrations of pollutants. The high effluent volume requires huge investments for effluent treatment plants in order to meet the required specification for the discharge of liquid effluents to various water bodies.

In this study the total water consumption reduction of the case study tannery is investigated by using water reuse technique in some stages of the process. For the systematic design of water reuse networks, the theory of the water pinch methodology is described, which are proved to be effective in identifying water reuse opportunities. Experimental results on pilot scale are shown that the methodology is demonstrated to be successful. Water reuse reduces the load of the wastewater treatment plant as well as it reduces the costs.

During the analysis, it was tested that 100% of the effluent from de-liming discharge can be reused for presoaking and main soaking stages, reuse in bating washing-1 100% and bating washing-2 75% from bating washing-3, and the reuse of 80% of washing after shaving for tanning float. The physical and chemical parameters analyzed in the processes and for the products with reuse practice did not present any considerable difference when compared with the conventional process. This demonstrates the viability of reuse practice in tanning industry.

This study identified a potential scope of reducing both freshwater and wastewater by 44%. In turn the water reduction represents a total potential annual savings of 307200 Birr, taking into account the raw water and wastewater treatment costs, labor cost, electrical and chemical costs.

1. INTRODUCTION

Water is the most widely occurring substance in the Earth. However, 97.5% of the total water is saline and only 2.5% exist as fresh water. The greater portion of the fresh water (68.9%) is in the shape of ice and permanent snow cover in the Antarctic, the Arctic, and mountainous regions. Next 30.8% are fresh ground waters. Only 0.3% of the total amount of fresh waters on the Earth is concentrated in lakes, reservoirs, and river systems. They are most accessible for economic needs and very important for water ecosystems [1].

With the growth in environmental awareness the need to preserve natural water resources has increased. The problems of water shortage experienced nowadays have led to the need to develop strategies that enhance the development stages of the technology and management of water usage.

Agenda 21, a document developed during the United Nations Conference on Environment and Development (UNCED), held in Rio de Janeiro on June 13, 1992, was drawn up through contributions from several nations, with the goal of integrating environmental protection with economic development, mainly aimed at improved quality for human beings, thus reinforcing the concept of sustainable development. A consensus was reached on the perception of water as a limited resource of environmental and economic value. Chapter 18 of Agenda 21 highlights the need to develop new strategic relationships in water resource management, prioritizing activities that improve the integrated management of available resources [2].

The industrial activity of leather tanning is included among those that have added to environmental pollution, mainly of water bodies. Tanneries consume large amounts of water for leather production, employing toxic substances, such as chrome and sulfide, and generating effluents with high levels of contamination. The high water consumption is due to the treatment of hide in multiple aqueous steps of the process with discontinuous discharges, making this an industrial activity which generates large amount of effluents which, in turn, require significant investment and operating costs for their treatment to satisfy the emission standards required by environmental legislation [3].

In this thesis the methodologies of systematic evaluation and minimization of water resources consumption is investigated. An attempt to evaluate the needs, possibilities and possible effectiveness of such worldwide approach as “water pinch analysis” will also be made. Water pinch analysis is a technology providing a systematic approach for minimizing the use of fresh water and the discharge of effluent water without losing sight of the costs. It is a strategic tool for water management in industry. Water pinch analysis provides a formalized approach to the rational management of water. This concept has been successfully applied to a wide range of chemical process industries, with typical fresh water savings in the range of 15–40%and wastewater savings of 20–50% [4].

In its simplest form, this methodology treats a given water-using operation as a problem of mass transfer from a contaminant-rich process stream to a contaminant-lean water stream. "Contaminants" may include suspended solids, chemical oxygen demand, or other water-quality determinants that limit water reuse. Water-reuse process integration seeks to identify a pinch point, called the fresh water pinch, based on the concentration of a key contaminant. Within a given process plant, water-using operations that can tolerate contaminant levels above that concentration do not require fresh water; they can instead reuse water streams from elsewhere in the process. Analogously, plant water streams with contaminant levels below that "pinch point" do not need to be sent for disposal, but can be reused elsewhere in the plant. Using this information, system designers and retrofitters can maximize water reuse and minimize wastewater generation onsite [1].

The search for minimum water consumption derives from the fact to take into account economic criteria, therefore how much lesser the water demand in the system, minor will be the operational cost. Besides, minimizing the water consumption, the amount of wastewater to be treated and discharged is lesser, causing a little impact upon the environment [8].

1.1. Statement of the Problem

Tanning industry is one of the major consumes of water and most of the water used is discharged as a waste. The tanning process is almost wet process from which a large volume of liquid waste is almost continuously discharged throughout the working hours of the day. Tanneries use conventional systems for treatment of the mixture of all production effluents. Such an approach makes it possible to meet environmental regulations, but because of the initial investment for effluent treatment plants construction is very high and the running cost also higher with out adding any value for the end product, so that its implementation has been scarce, especially in Ethiopia.

1.2 Objectives

1.2.1 General objective

The main objective of this work is to develop method for the reduction of fresh water used and wastewater generated in tanneries with possible minimum effect to the processes and the end products.

1.2.2 Specific objectives

The specific objectives are:

- To identify the maximum water-reuse target and the minimum wastewater-generation target for leather processing operations
- To apply simple reuse with small costs and results in much cost savings both in freshwater cost and effluent handling costs.
- To compare the quality of leather produced by reuse and with out reuse of wastewater
- To reduce the amount of chemical usage in tanning industries
- To give soundable recommendation for Ethiopian leather processing industries concerning the application of water pinch technology

1.3. Scope of the Study

The scope of this research work covered the water pinch analysis for beam house operation to re-tanning operation at industrial scale. And testing the quality of leather produced with and with out reuse of water according to the water pinch analyzed. The test was done at pilot scale using testing drums of Leather Industry Development Institute.

LITERATURE REVIEW

2. Process Integration Tools for Wastewater Minimization

2.1. Process Integration

In conventional chemical process design methodologies, different units or network of units are designed individually, and then the units or network of units are linked together. Depending on the way the units are connected, the overall optimal process design may or may not be achieved. This unit-based approach can lead to operational difficulties when, as an example, the need to alter the process operating conditions arises. Moreover, local equipment failure can significantly impact the performance of the entire plant, and maintenance activities can be complicated. Furthermore, this approach can lead to a higher cost associated with a poor overall process performance, inefficient use of valuable resources, excessive waste generation, and a negative environmental impact [14].

In recent years, in 1970s a holistic approach to process design and operation has been developed. This approach, known as process integration, focuses on the unity of the overall process design and operation of all units involved within the process rather than focusing on individual units and then linking different units or network of units together. Moreover, it identifies optimal performance targets for the overall process before the detailed design of the network is developed. The design scheme that satisfies the pre-identified targets is considered to be the optimum design solution. Pre-identifying performance targets leads to a more efficient design methodology that requires less time to develop. This is particularly important, as conventional process design methodologies are time consuming and use detailed computational and iterative approaches [14, 15, 16].

This approach enabled researchers to develop systematic procedures and methodologies for sustainable development, optimal design, operational efficiency, debottlenecking, resources conservation, yield enhancement, as well as waste reduction which results in significant cost reduction for industrial facilities, and an observable benign impact on the environment. To achieve that, a set of graphical and computer-aided optimization tools are developed and utilized [16].

In a significant development in 1989, the process integration concept was extended to a new dimension by the development of the mass integration approach. **"**Mass integration can be defined as a holistic approach to the generation, separation, and routing of species and streams throughout the process. It is a systematic methodology that provides a fundamental understanding of the global flow of mass within the process, and employs it in identifying performance targets and optimizing the allocation and generation of streams and species with the objectives of enhancing yield, conserving resources, debottlenecking, mitigating environmental impact, and conserving energy [15]

The introduction of this powerful methodology and new concept in process design enabled researchers in the field to investigate numerous industrial issues and develop effective solutions for complex problems. Many techniques for water recycle and reuse networks have been reported by different researchers [15, 16].

The high demand on resources and fresh streams in chemical plants and manufacturing facilities makes it inevitable to seek effective engineering solutions to conserve resources and increase material recovery. In addition, the increasingly stringent environmental regulations and constrains on waste streams discharge, requires the chemical industry to develop technically-capable and cost effective design schemes that meet the environmental standards and maintain profitability.

Water integration methodologies are effective tools utilized to achieve this goal. A mass integration- based network synthesis provides cost effective and engineering capable solutions by answering a set of critical questions related to defining waste material streams and their optimal loads that need to be recycled, optimal allocation of the waste streams that need to be routed to the process, and what kind of arrangement need to be configured [15].

2.1.1. The water-using operations

There are two main types of water-using operations in a process plant, i.e. the mass transfer-based operation and the non-mass transfer-based operation. This will enable us to understand how the water-using processes are operated.

2.1.1.1. Mass Transfer-based Water-Using Operation

A MTB water-using operation is characterized by the preferential transfer of a species from a rich stream to water, which is being utilized as a lean stream or a mass separating agent [16]. Washing, scrubbing and extraction process are included in this category.

In the mass transfer-based type of operation, water is fed to the process continuously. At the same time, the same amount of water is continuously withdrawn, carrying a certain amount of contaminant from the process. Hence, the operation acts as water demand and water source simultaneously. A typical example of this type of operation is the normal washing process, where water (fresh or recycle water) is used to clean the process vessel or plant site. During cleaning, water is needed (as a demand) and at the same time, wastewater is generated (as a source) from the process.

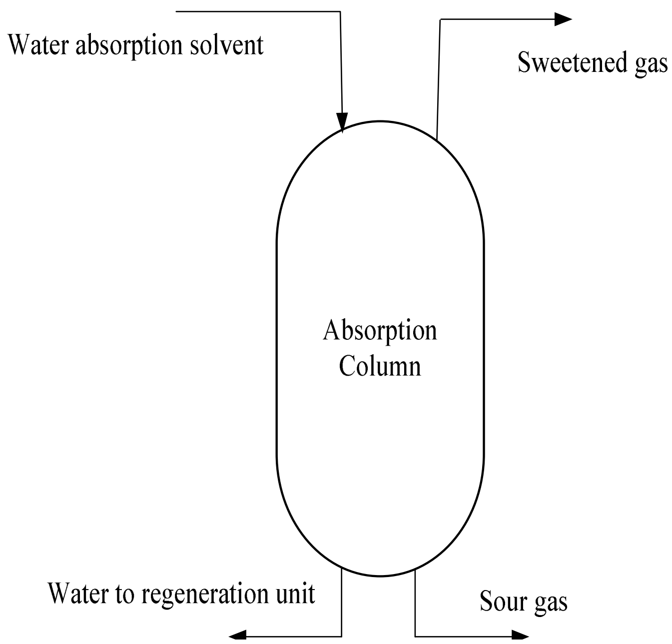

Figure 2.1. Mass transfer based using unit operations

Figure 2.1 shows water being fed into the absorptions column (as demand) and the wastewater generated (as source). Note that, the water losses from MTB water-using operation are typically assumed to be negligible and input and output flow rates assumed to be the same. This type operation is also known as fixed contaminant load problem [14-16].

2.1.1.2. Non-Mass Transfer-based Water-Using Operation

In contrast, a NMTB water-using operation covers function of water other than as a mass separating agent [11, 14]. In real system, not all water using operations can represent using MTB operations. Certain processes may have different input and output flow rates and can not be modelled as MTB. A common example includes water being fed as raw water or being withdrawn as a product or byproduct in chemical reaction. The operation in this category also covers water-using operation such as cooling towers, boilers and reactors where water being utilized as heating or cooling media, for such operations, water may exist as sources and/or demands. Therefore, the inlet and outlet flow rate for NMTB operation can have different flow rate. Note that, for the NMTB operations, water flow rate is more important than the amount of contaminants accumulated. This operation also widely known as fixed flow rate problem [11].

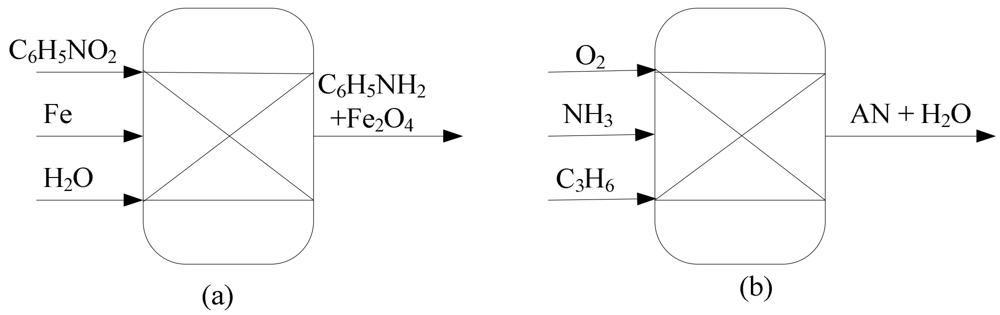

Figure 2.2. Non-mass transfer based water using operations

Figure 2.2 (a) a reactor that consumes water in aniline production (b) a react that produces water a byproduct in acylonitrile production. Figure 2.2 type of the water operation is the non-mass transfer-based model. This includes the operation where only water demand or water source occurs in the process. In these non-mass transfer-based types of water-using operations, the water flowrate is more important than the amount of contaminant being picked up from the process [13].

2.1.2. A Review on Water and Wastewater Minimization

Water is a key element for the normal functioning of many industries. It has been used in abundant quantities by chemical, petrochemical, tannery, petroleum refining, food and drink, pulp and paper and many other industries. In these industries, wastewater is generated from many sources in the process. Because of environmental impact, wastewater must be reduced to an acceptable level before being discharged. Large amounts of wastewater cause high cost for effluent treatments [9, 10].

Over the past two decades, the primary concern has always been more focused on end-of-pipe wastewater treatment. End-of-pipe solutions have been seen as the sole remedy to meet the imposed discharge limits. Later, the main concern shifted towards solutions that maximize water reuse from convectional water treatment to more sustainable water minimization activities. In the early eighties, water reuse started to become one of the active areas for water minimization activities as a means of reducing the total water requirements. This is not only saves upstream treatment of fresh water but also reduces wastewater treatment costs. Additionally, zero water discharge cycles became a desired goal for grassroots retrofit designs [7-10].

Later work concluded that it was possible to reduce the large quantities of fresh water intake and wastewater produced by industrial processes by considering the entire water network as a total water system. The authors developed a mathematical formulation and transformed it into a series of problems without inequality constraints by employing a penalty function [11]. In other work, the basic concept underlying the methodology is Mass Exchange Network (MEN) technology, which was first pioneered. They introduced the notion of MEN for the preferential transfer of a key contaminant from rich streams into lean streams [15].

Afterwards, the consideration of water minimization problem by maximizing the water reuse potential using graphical approach for targeting and manual approach to design. The authors also discovered options of regenerating wastewater even when concentration of pollutants has not reach end-of-pipe limits. Besides, they introduced the important concept of ‘water pinch’ and presented a conceptually based approach on wastewater minimization, by which the minimum fresh water utilization of a water using system can be obtained in a direct way. In general, there are a least four approaches to water minimization [20]:

a) Process changes

Process changes can reduce the inherent demand for water. For example, wet cooling towers can be changed to air coolers, or washing operations can have the number of stages increased.

b) Reuse

Water re-use is the most common technique used in water and wastewater minimization. The outlet stream from some processes can be used as an inlet stream by others. Equally, wastewater from a process can be used by the other directly, if the contaminant concentration from previous process does not disorder the next process.

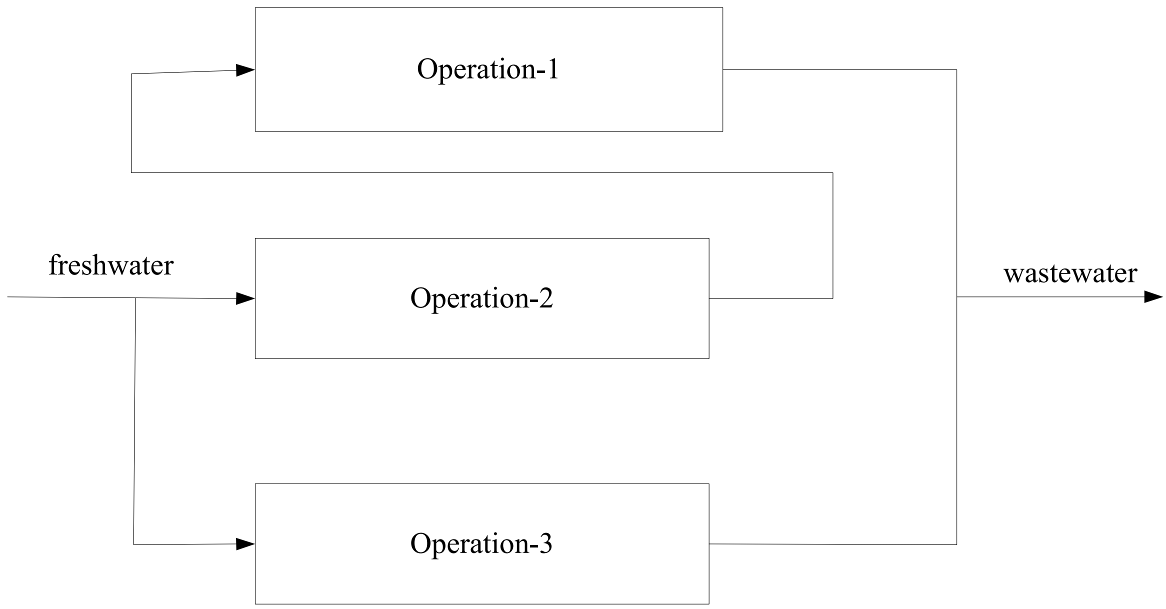

Figure 2.3. Water reuse system

Figure 2.3 shows that the discharge of water from operation-2 is partially reused in operation -1. It reduces the amount of freshwater required and wastewater generated, while it will not affect the outlet contaminant load; the outlet stream from a process does not re-enter the same process.

c) Regeneration reuse

Partial treatment can remove contaminants from wastewater which otherwise would prevent its reuse and then it can be reused in other processes (water does not re-enter processes in which it has previously been used). Examples of regeneration include pH adjustment, filtration, membrane separation, sour-water stripping and ion exchange**.** Regeneration may be done by filtration or activated carbon adsorption. Accordingly, the contaminant load of water and wastewater is reduced.

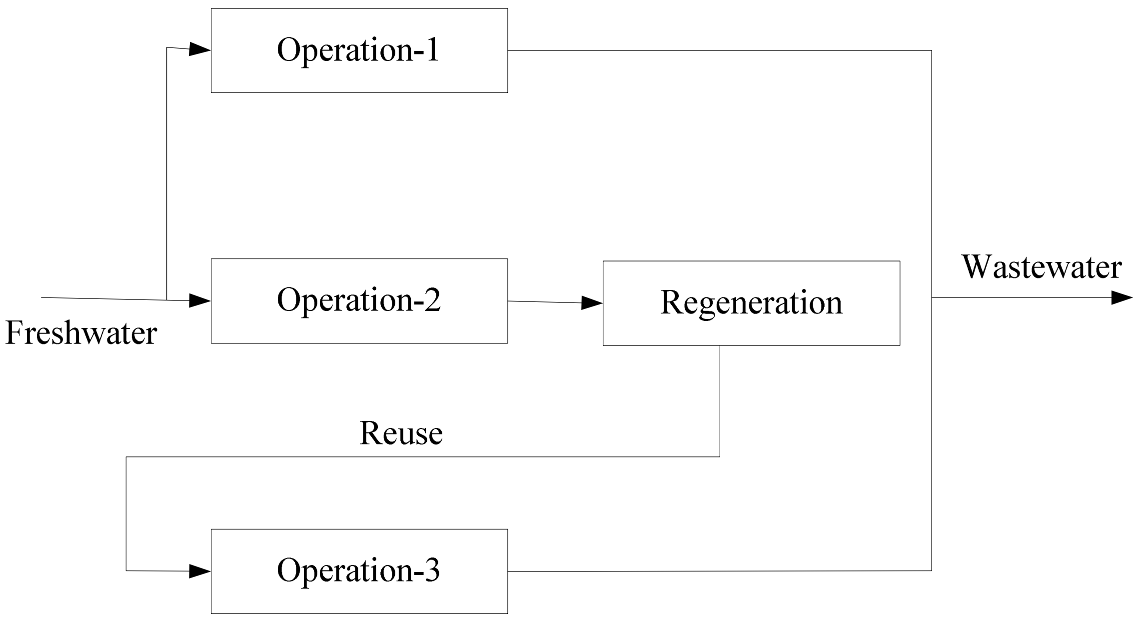

Figure 2. 4. Wastewater regeneration reuse systems

Figure 2.4 describe that wastewater discharge from operation-2 can be reused for operation-3 after partial treatment within regeneration operation.

a) Regeneration recycling

Contaminants from wastewater are partially eliminated and the wastewater is returned to the same process afterwards or operations in which it has previously been used. In this case water can re-enter processes in which it has previously been used.

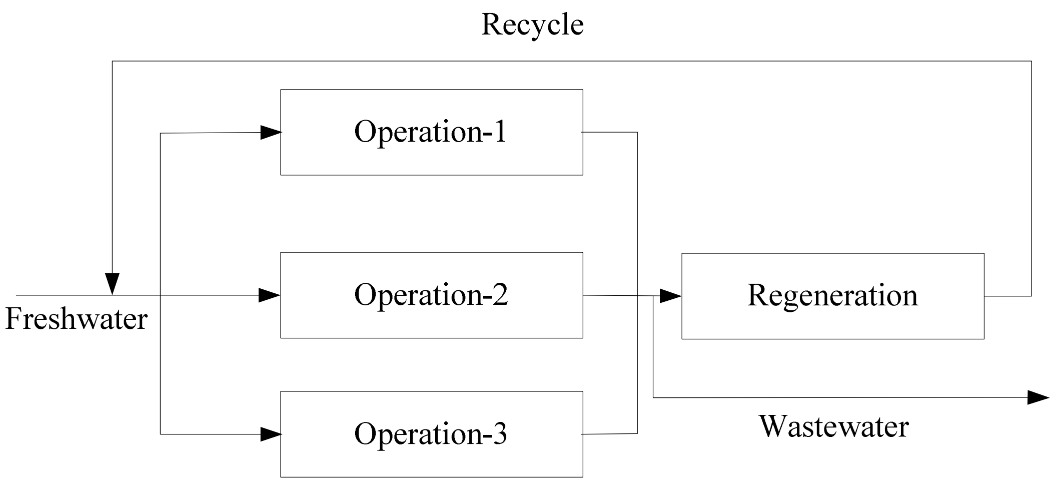

Figure 2.5. Wastewater regeneration and recycling systems

Figure 2.5 shows that wastewater discharges from operation 1, 2 and 3 can be treated and again reused processes in which it has previously been used.

2.1.2.1. Conventional Approach for Water and Wastewater Minimization

Systematic efforts have been done to increase the reuse of water on a plant wide scale and such projects have been implemented to industry for past years using conventional water reuse strategies. Conventional water reuse is often grouped according to three strategies for fresh water savings and wastewater minimization [10]:

i) Cascade reuse

Cascade reuse involves the direct water reuse with little treatment. The example of cascade reuse is storm water runoff can often be used as makeup water for cooling towers, with partial treatment.

ii) Waste minimization

Waste minimization can be obtained by reducing fresh water requirements in a process, such as by using mechanical cleaning rather than water to avoid wastewater generation.

iii) Source reduction

Source reduction is concerned with reduction of inherent need for water by a process. Counter current- rinsing stages can greatly reduce the fresh water demand for rinsing operations.

2.1.2.2. Process Integration for Water and Wastewater Minimization

The main goals of process integration *(PI)* are to integrate the use of materials and to minimize the generation of wastes. A recent development in pinch technology that deals with pollution prevention, resource recovery, and waste reduction is mass-exchange integration. In identifying water reuse and recycling opportunities a systematic technology by means of a graphical tool for analysing water networks called the water pinch diagram [20]. The water pinch diagram is used to identify key design targets such as the minimum amount of fresh water required by the studied system, the amount of water recycling and achievable reuse, and the water quality concentration bottleneck.

The process integration tools for water and wastewater minimization cover a variety of techniques, ranging between two limits [9, 11, 16]:

a. Graphical techniques based on “pinch analysis”
b. Mathematical optimisation-based approaches.

For a given water minimization problem, different solution techniques maybe required to solve the problem. Figure 2.6 illustrates the tools of process integration.

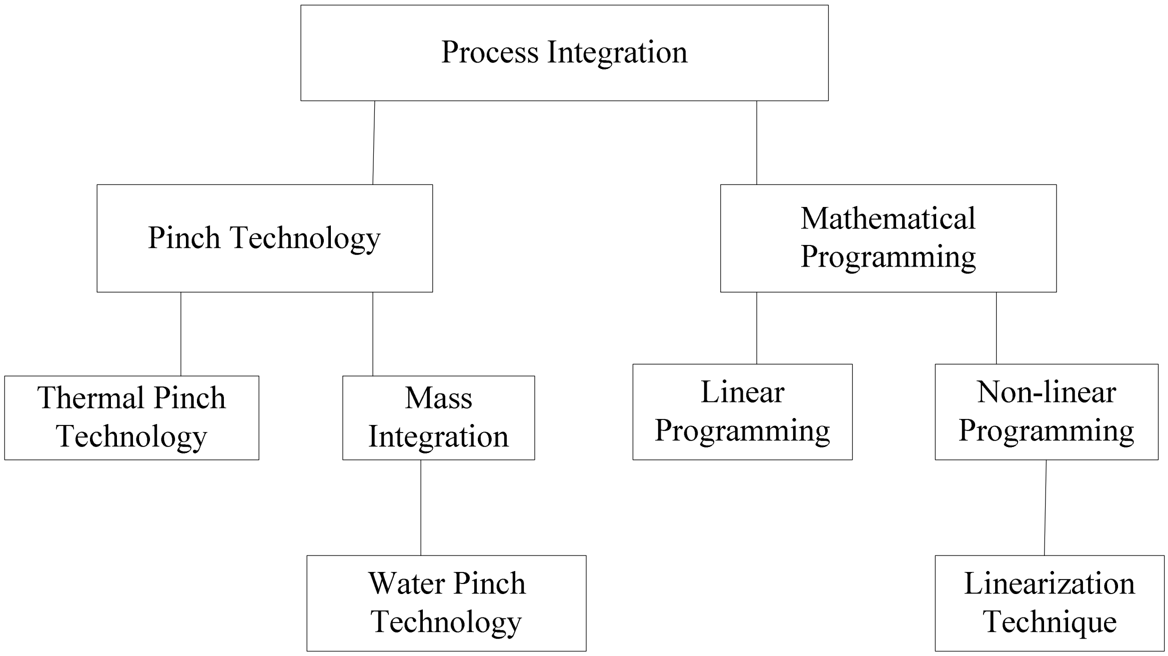

Figure 2.6. The tools of process Integration (Mann, 1999)

2.1.2.2.1. Mathematical optimization method

Design and analysis optimization methods use specialized algorithms to iteratively investigate the design space for the best values of input variables to achieve a specified goal. In many cases, optimization can be applied to everyday design problems to improve product performance/quality while simultaneously reducing manufacturing cost, weight, environmental impact, etc [11].

Although mathematical programming approach offers the advantages in handling complex water systems involving multiple contaminants, it is less popular among engineering practitioners. This is due to the difficulty to master the technique, especially the function describing it, not usually easily to obtain and little insights on water networks design. On the contrary, water pinch analysis helps in getting a physical insight of the problem through its graphical representations and simplified tableau-based calculation procedures. The two approaches are complementary where the visualization ability improves engineering understanding and the mathematical model allows the handling of complex problems [20].

Among process integration methodologies, pinch analysis is certainly the most widely used. This is due to the simplicity of its underlying concepts and, especially, to the spectacular results it has obtained in numerous projects worldwide [12].

2.1.2.2.2. Water pinch technology method

a) The pinch concept

Pinch analysis (or pinch technology) is a rigorous, structured approach was initially used for the process of heat integration for the design of heat exchange networks to transfer energy from a set of hot streams to a set of cold process streams that may be used to tackle a wide range of improvements related to process and site utility. This includes opportunities such as reducing operating costs, debottlenecking processes, improving efficiency, and reducing and planning capital investment [14].

Major reasons for the success of pinch analysis are the simplicity of the concepts behind the approach, and the impressive results it has been obtained worldwide. It analyzes a commodity, principally energy (energy pinch), hydrogen (hydrogen pinch), or water (water pinch), in terms of its quality and quantity, recognizing the fact that the cost of using that commodity will be a function of both.

In general, we are using high-value utilities in our process and rejecting waste at a lower value For example, if we consider energy, we may be burning expensive natural gas to provide the process with high temperatures heat, and are rejecting heat at low temperatures to cooling water or air. In the case of water, we feed pure water to our process and reject contaminated wastewater to treatment plants. For process gases, such as hydrogen, the expensive utility is the pure gas that is either produced on-site or imported [14].

Pinch analysis now has an established track record in energy saving, water reduction, and hydrogen system optimization. In all cases, the fundamental principle behind the approach is the ability to match individual demand for a commodity with a suitable supply. The suitability of the match depends on the quality required and the quality offered. In the context of utility management, the commodity may be heat, with its quality measured as temperature; or it may be water or hydrogen, the quality of which would be purity or pressure, for example. By maximizing the match between supplies and demands, we minimize the import of purchased utilities [12].

For example, energy pinch identifies the minimum cost of hot utility targets, as well as the projects that allow us to reach these targets in practice (or to get close to them).

When considering any pinch-type problem, whether it is related to energy, water, or process gas, the same principles apply [18]:

- Processes can be defined in terms of supplies and demands (sources and sinks) of commodities (energy, water, etc.).
- The optimal solution is achieved by appropriately matching suitable sources and sinks.
- The defining parameter in determining the suitability of matches is quality, e.g. temperature or purity.
- Inefficient transfer of resources means that the optimal solution cannot be achieved. In fact, the amount of inefficient transfer is equal to the wasteful use of imported commodities.

b) Water pinch approach

Identifying and deploying the best water reuse systems is a challenge. Modern technologies present a myriad of confusing alternatives that the engineer must consider.

Water pinch is a systematic technique for analyzing water networks and identifying projects to increase the efficient use of water in industrial processes. Advanced applications make use of advanced algorithms to identify and optimize the best water reuse, regeneration (partial treatment of process water that allows its reuse), and effluent treatment opportunities. The significance of the pinch point is that it represents the concentration level up to which fresh water must be used [18].

Water pinch may be applied to almost any industrial water system where there are users of fresh water and producers of wastewater. The technology is capable of analyzing even the most complex water systems, and has been successfully applied in a number of industrial sectors.

Significant water and wastewater reductions have been achieved by applying water pinch in various industries. Savings of 25 to 40% have been observed in the following industries: oil refining, chemicals, pulp & paper, and food & drink [1].

Of course, achieved savings greatly depend on project objectives. Good solutions that are identified with water pinch often do more than save water. They tend to reduce capital investment, recover valuable raw materials, and sometimes, recover heat.

Wang and Smith (1994) introduced a water pinch method for targeting maximum water reuse for single contaminant problems based on the construction of a composite curve of the limiting water profiles for each operation. The basic idea is that wastewater can be re-used directly in other operations when water-using operations can accept the contamination level of previous operations. The first task consists of developing a limiting water profile for each water using process operations, based on maximum inlet and outlet concentration for the water stream for each operation [18, 20].

For any aqueous process operation it is possible to construct a composite profile of water demand (sinks) and wastewater effluents (sources). For each source of water, the flow rate and the concentration of contaminant must be specified. For the demands, the required flow rates as well as the maximum admissible contaminant concentrations are required. The concentration limits are determinant in the outcome of the analysis and must be chosen carefully. Once the streams have been defined, they are ordered by increasing purity (decreasing contaminant concentration); fresh water has a purity of one [18].

The source and sink composite curves is a graphical tool for setting water recovery targets as well as for design of water recovery networks. Figure 2.7 shows such a construction, which graphically depicts the water sources and sinks in a typical process, on purity versus flow axes. Each stream is represented by a horizontal line of ordinate equal to its purity and length equal to its flow rate. The streams of the same type (demands or sources) are adjoining so that the total horizontal length of each composite profile gives the cumulative flow rates for demands and sources respectively.

The curves are drawn in such a way that they are as close together as possible (along the flow axis), subject to the constraint that the source curve must always be above the sink curve. The point of contact is called the pinch, which is a feature of the system that limits the potential for water conservation. The area of overlap (shaded) shows the scope for water reuse.

Although the targeting concept is simple, optimizing a water network involving a combination of reuse, recycling and treatment options is usually very complex, especially because one must deal with multiple contaminants. The design algorithm requires powerful mathematical programming techniques and software. The Water Pinch approach uses mathematical tools for optimization, and composite curves for graphical visualization and interpreting the results [14, 18, 20].

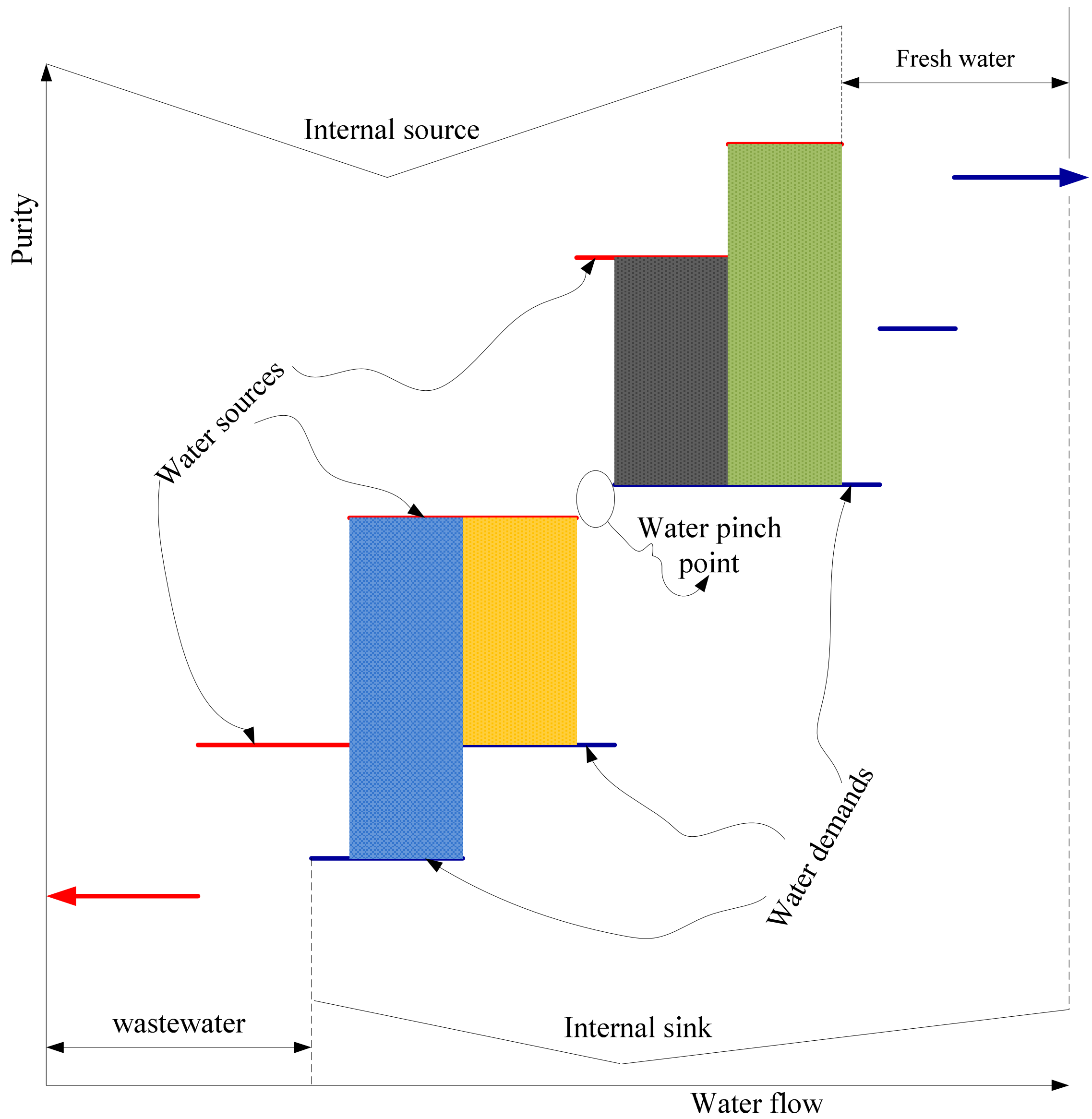

Figure 2.7. Water pinch approach basic representation

For an industrial application, water pinch methodology can be broken down into five steps [18]:

1. Find flow data. Develop a simple flowsheet model of the water system, showing where water is used (including utility services), and where (waste) water is generated. Define the appropriate data for the Water Pinch analysis, i.e. determine water ‘sources’ and ‘sinks’.

2. Find contaminant data. Select key contaminants - e.g. COD, salts, suspended solids. A key contaminant is: ’any property that prevents the direct re-use of a wastewater stream’, this might include temperature and/or acidity. Choose design concentrations – maximum allowable for sinks and minimum practical for sources. This may require input from experts in the relevant process technologies.

3. Run water pinch analysis. Carry out the water pinch analysis to determine optimum matches between sources and sinks (using software). The first round of results will probably not be a practical design, as it represents an unconstrained solution.

4. Identify pinches, examine the sensitivity plots, and relax constraints. Consider process modifications and regeneration options that may result in lower targets.

5. Review design. Examine the resulting network design. It is usually necessary at this point to evaluate the design and determine which additional contaminants should be considered, which matches should be forbidden, and which matches (if any) should be forced.

2.2. Leather Manufacturing Technology

2.2.1. Introduction

The history of leather production goes right back to prehistoric times, when primitive methods were developed for treating animal hides and skins so that they could be used for clothing to protect people from the elements [21].

It is to be assumed that the raw hides and skins were at first merely dried and preserved by smoking until with the advance of civilization, it was found that they could be made much more durable by treating them with vegetable matter containing tannin (crushed bark, wood or fruits). It was also discovered that by suspending the hides in water (controlled decomposition process) treating them with ash (liming), it was possible to remove the hairs if the "tanned" hide material was not to be used as fur but as leather.

In addition to various types of vegetable tannage (bark tannage), chamois tannage with fish oil, fat or oil is also known to have existed in ancient times and is still sometimes practiced today. White tannage with alum was presumably a later addition to the methods used by the early tanners [21-23].

The practice of dyeing (originally painting) leather with colored materials of vegetable, animal or mineral origin likewise goes back thousand of years.

From these early beginnings a craft steeped in tradition developed over the centuries. Following the introduction of chrome tannage about the end of the 19th century, this craft evolved into an industry of great economic significance which has now become established throughout the world [22].

2.2.2. Operations Involved in Leather Production

Leather processing essentially consists of series of physical and chemical operations where by the raw hide or skin of an irregularly shaped, low strength organic material that can petrify is given an almost constant thickness and such characteristics as incorruptibly, good flexibility, high tensile strength, abrasion resistance and finish with good appearance finally come out as finished leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable. The surface of hides and skins contains the hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer [21, 22, and 25].

The tannery operations can be broadly divided into four sections

- Beam House operations
- Tanning operations
- Post-tanning and
- Drying and finishing operations.

2.2.2.1. Beamhouse Operations

Before tanning the main important operations for leather manufacturing are done in beam house. Beam house operations consist of Soaking, Liming, Deliming, Bating, Pickling, Depickling and Degreasing (if necessary) etc. The operations and their objects are given bellow [23, 25]:

a) Trimming and Weighing

First of all the selected tannable hides and skins are trimmed to remove the tail, shoulder, flanks, neck and trimmable portions correctly. Then these are weighted carefully and the entire chemicals % based on these weights [26].

b) Soaking

Soaking is the first tannery operation. During curing, hides and skins lost large amount of its physiological content of water and unless the former regains this water during soaking operations, good quality leather cannot be produced. Chemicals used in soaking are 0.2 – 2.0 grams per liter sodium hydroxide, up to 1 gram per liter sodium hypochlorite and/or 0.5 – 2.0 per cent wetting agents, emulsifiers, surfactants etc. The associated wastes during soaking are chlorides, sulphates, NH3- bloods, dirts and hairs [23, 26].

The process of soaking can be classified into three stages:

- Pre-soaking (dirt soaking)-in dirt soaking, 300-400% of water is used to remove the unwanted materials
- Main soaking- the purpose of main soaking is to re-hydrated the material. In this operation, water, non-anionic wetting agent (0.2% concentrated), soda ash (0.2% concentrated) and preservatives (0.5% concentration) are used.
- Final soaking- only water is used for the washing purpose in this operation

Objects of Soaking:

1. To remove the dirt, blood and dung from the hides and skins.
2. To remove the curing salts in case of salted hides and skins.
3. To dehydrate the skins proteins.
4. To open up the contracted fibrous structure of the skins.
5. To clean off surface filth.
6. Softening the hides and skins.

c) Liming /Unhairing

Liming is a very important operation for leather manufacture. The qualities of the finished leather are largely controlled in liming process. Liming is the operation in which the soaked hides and skins are treated with 2-10 per cent milk of lime with or without the addition of sharpening agents like sulphides, cyanides, amines, markeptan etc. Unhaired hair, spills of sulphide and lime sludge is the main waste. The liquor discharged from this operation has high sulphide content and fine hairs that are responsible for high S.S, COD and BOD load.

The process of liming can be broadly classified into two parts [26]:

- Deliming- lime (8-10%) along with sodium sulphide (3%) is applied to the skin to remove hair
- Re-liming – to open up fibrours structure, lime, soda ash, caustic soda, etc., are applied.

Objects of Liming:

1. To remove the hairs, hooves, nails and other keratinous materials.
2. To remove some of the interfibrillary soluble proteins like mucins etc.
3. To swell up and to split up the fibres to the desired extent.
4. To remove the natural grease and fats.
5. To bring the collagen to a proper condition for satisfactory tannages.

d) Fleshing

Fleshing can be carried out at several stages of the process. The different fleshing operations are the following:

- green fleshing (raw fresh and chilled hides/skins)
- green fleshing (soaked -salted- hide/skins)
- lime fleshing
- Pickle fleshing.

The fleshing operation aims to remove excess connective tissue and fat from the flesh side of the hides and skins. If fresh hides are being used, green fleshing takes place before soaking. If salted hides are used, green fleshing is carried out after soaking. Lime fleshing is carried out after liming. Sheepskins can also be fleshed after pickling. Sheepskins are generally fleshed at two stages in the process, whereas hides are generally fleshed once.

There are no chemicals used for fleshing of hides and skins, other than that operators may use sawdust or an alternative to get a better grip of the slippery hides. The fleshing machines generally use water to wash away the fleshings [22, 25].

b) Splitting

Splitting can be carried out most commonly on the following substrates:

- limed pelts
- pickled pelt sheepskins
- tanned leathers
- crust leathers.

Depending on where the splitting is carried out, the use of chemicals and water in subsequent processes will be reduced, as only the required part of the hide is processed. Therefore, the earlier splitting is carried out, the fewer chemicals and the less water used to process the hides and skins. However, tanneries do not always split in the limed stage for technical reasons or the specifications of the final product.

When sheepskins are split in the pickled state to produce chamois leathers, a solution of surfactants is used on the splitting blade to increase the grip on the greasy skins, and reduce fat build up on the blade [23].

c) Deliming

After liming the unhaired and fleshed hides and skins known as pelt are taken for the next operations called deliming. The alkali present in the pelt is of two types- Free alkali & Combined alkali. The free alkalis can easily be removed by repeated washing with water or by pressing the pelt under the high pressure, but for removal of combined alkali chemical treatment is always necessary. The process is carried out by washing and by using water combined with neutralizing chemicals. Chemicals used are ammonium chloride or sulphate, 0.5– 2.0 per cent acids (lactic, formic, boric and mixtures), acidic salts, sodium bisulphite, hydrogen peroxide [22].

As a result of the reaction of this chemicals with the lime and sulphide chemicals of the pelt the most dangerous gas will evolve. This gas is hydrogen sulphide and ammonia gas. To protect employees from the exposure of this gas usually sodium bisulphate is added together with the deliming agent. However during drain of the drum either this gas may generate and make employees feel discomforts. The use of gaseous CO_2 instead of ammonium salts has been increasing [21, 26].

Objects of Deliming:

1. To remove most of the lime and alkaline materials from the pelts.
2. To reduced the swelling of the pelts.
3. Solubilization of Ca-soap.
4. To remove flesh, scud etc.
5. To adjust the PH suitable for different tannage.

g) Bating

Limed and partially delimed pelts sometimes require additional treatment known as bating, Bating is done to remove rest lime and swelling and plumping. The chemical used is often a 0.5 per cent bating material, which consists of 50 per cent wood flour (or another carrier), 30 per cent deliming agent (ammonium chloride) and 1-5 per cent pancreatic enzyme.

Objects of Bating

1. To produce smooth, fine and clean grain by enzyme action.
2. To remove some of the non-structured collagen and other proteins like albumins, globulins.
3. The scud or dirt, short hairs, greases and lime soap, dark coloured pigments and traces of epidermis are all loosened and are easily removable by scudding.
4. To allow the splitting up of collagen fibres.
5. To make the final leather soft, pliable and stretchy.

h) Degreasing

Degreasing is the process of removing fats from the skin. This is especially important in sheepskin tanneries as the fat content of their raw material is large. The process uses solvent degreasing. Solvents, which are increasingly substituted or combined with surfactants and/or enzymes, include perchloroethylene, monochlorobenzene and kerosene [23].

i) Pickling

In leather processing pickling is very important and essential operations prior to mineral tannage. The treatment of delimed or bated pelts with a solution of acid and salts is known as pickling which takes the pelts acidic condition to absorb chrome and being down the P^H for chrome fixation. The chromium salts used for chromium tanning are not soluble under alkaline conditions and will precipitate if added to high pH hides (Leather Facts 1977). The most common acids being used are sulphuric acid and formic acid. Other acids that can be used include hydrochloric acid, boric acid and other weak organic acids, e.g. acetic acid, lactic acid. The salt is used first to prevent the acid swelling of hides. Then finally acid is added so that its final PH is <1.0 [25].

Typically, acids would be added as 0.5 % – 3 % of the weight of the raw materials. Common salt is usually used in concentrations between 6 % (bovine hides) and 14 % (mainly pickled pelt skins). Alternative salts include sodium sulphate and potassium chloride.

If pickled pelt sheepskins are going to be vegetable tanned, they will firstly be de-pickled using either sodium acetate or sodium bicarbonate.

Objects of Pickling:

1. To bring the delimed and bated pelts to a required degree of acidity before chrome tannage, even vegetable tannage.
2. To reduced the P^H.
3. To modify the fiber structure.
4. To reduce the astringency of chrome tanning agents.
5. To preserve the leathers and to achieve the special effect.

2.2.2.2. Tanning Operation

In leather manufacture the most outstanding process is tanning. The process of converting the putrescible hides and skins into non-putrescible leather is called Tanning. The materials which are used for tanning are called Tannins. There is various process of tanning such as-Chrome tanning, Semi-chrome tanning, Vegetable tanning, oil tanning, Zr tanning, alum tanning, White tanning etc [26]

The following types of tannage can be used in a tannery:

Table 2.1. Types of tannage, main tanning agents, and auxiliaries

Types of tannage	Tanning agents used	Auxiliaries used
Chrome tannage	Basic sulphate complex of trivalent chrome	Salt, basifying agents, fungicide, masking agents, fatliquors, syntans, resins
Other mineral tannages	Aluminium, zirconium and titanium salts	Masking agents, basifying agents, fatliquors, syntans, resins, etc
Vegetable tannage	Polyphenolic compounds leached from vegetable material	pre-tanning agents, bleaching and sequestering agents, faliquors, formic acid syntans, resins, etc
Synthetic tannage (Resin-syntans)	Sulphonated products of phenol, cresol, naphthalene, cresylics, poly-acrilatess, melamine, resins, etc	Fixing agents, acid or alkali, fatliquors.
Aldehyde tannage	Glutaraldehyde and modified aldehydes and di-aldehydes	Alkali, bleaching agents, tanning agent carrier
Oil tannage	Cod oil and marine oils	Catalysts such as manganese, copper, or chrome, sodium bicarbonate or other alkali, aldehydes, emulsifiers.
Note: The auxiliary used vary depending on the mineral used and the type of cross link with the collagen		

For the tanning process a large variety of chemicals is necessary and only a part of these chemicals are taken up in the hides and skins. As a result, effluents are generated from tanning operations that have a low pH and carry the part of the chemicals that was not integrated. The substances released depend on the type of tanning applied. The following paragraphs discuss the consumption and releases of chrome- vegetable- and other tanning methods [21].

Tanning auxiliaries are intended to produce a desired modification of the tanning effect without developing a tanning action. Complex active and buffering substances are used for mineral tanning. Surfactant auxiliaries are added to disperse the tanning agents and accelerate the complete penetration of tannin as well as to influence the emulsion and electrolyte stability of other auxiliaries (for mineral and vegetable tanning). Sequestering agents in water treatment can combine with the hardening constituents of the water to produce more stable complexes. Fixing agents reduce souring losses of vegetable and/or syntan tannins by the formation of water insoluble compounds. These products are mainly aluminium or manganese salt, albuminious materials, usually cationic nitrogen-containing organic compounds or organic or inorganic compounds, which condense in the leather [22, 23].

i. Chrome tanning

Chrome tanned leather accounts for approximately 90 % of all the leather produced in the world. The most commonly used tanning agent is a basic chromium sulphate. Tanning is completed with a basification to bind the chromium in the leather. Chemicals used in tanning are: chrome tanning salts with in average of 14 per cent Cr (used in amounts of 8-12per cent for common processes and 5-6 per cent for low chrome processes), 1.0 per cent sodium bicarbonate (basifying agent to adjust pH), 0.5 per cent masking agent (sodium formate), and up to 0.9 per cent fungicide.

The pelt after tanning process will have nonbiodegradable nature and then called leather wet blue. Since the chrome uptake rate of the tanned leather is 70% of the input, the rest 30% will be discharged through the effluent. The discharged chrome liquor contains the poisonous pollutant chromium [21].

Objects of Tanning:

1. To convert the putrescible hides and skins into non-putrescible leather.
2. To raise the shrinkage temperature and to increase the resistance to hot water of the leather.
3. To reduce the ability to swell when wet back.
4. To increase the strength properties of leather.
5. To stabilize the leather against enzymatic degrading.

ii. Vegetable tanning

The plant extracts applied for vegetable tanning are either polyphenolic compounds (condensed vegetable tannins) or esters of glucose and gallic acid (hydrolisable vegetable tannins), which are leached (with water) from wood, barks, leaves, roots etc.

The most commonly used vegetable tannins extracts are:

- . natural quebracho

- soluble quebracho
- mimosa
- natural chestnut
- sweetened chestnut
- myrobolans
- valonia.

Three techniques of vegetable tanning can be distinguished:

- . pit tannage
- drum tannage
- pit and drum tannage.

The basic principle of pit tannage is a counter-current system, whereby the hides are first put into much used and almost exhausted liquors, and then into progressively stronger liquors to fix more tan. As these stronger liquors become denuded of tan they are "run" (pumped) down the yard and used in the earlier stages, so that as much tan as possible is used. Vegetable material (e.g. bark) can be used directly in the pits, or vegetable extracts can be used [23].

Summing and shaving

Summing and Shaving can also include in tanning operation where Summing brings leather to a uniform semi-dewatered state. The leather is passed through a summing machine that squeezes surplus water out of the leather. On the other hand, shaving is a mechanical process that controls the leather thickness. Chrome containing liquor and wet blue leather shavings and pieces are the major wastes of the summing and shaving operation, respectively [25].

2.2.2.3. Post tanning Operation

Post-tanning is s divided into four main stages: neutralization, retanning, dyeing and fat liquoring.

a. Neutralization

The process of deacidification or the excess of free or easily liberated strong acid in leather, prior to, retanning, dyeing and fat liquoring, is popularly called neutralization.

Objects of neutralization:

1. To remove the neutral salts and uncombined chromium salts from the leather.
2. Neutralization of free acid in the leather formed by the hydrolysis of the chrome complex.
3. To control the affinity of the leather for anionic materials, particularly dyestuff and anionic oil emulsions by regulating its electrostatic charge [23].

b. Re-Tanning

Mineral tanned leathers-particularly chrome or aluminum tanned leathers-are always retanned with retanning chemicals with a view to modifying the properties of the finished leather to suit modern demand.

Objects of Re-Tanning:

The retanning process can be carried out with the following objectives:

- to improve the feel and handle of the leathers
- to fill the looser and softer parts of the leather in order to produce leathers of more uniform physical properties and with more economical cutting value to the customer
- to assist in the production of corrected grain leathers
- the retanning may improve the chemical stability of the leather, particularly its resistance of alkalis and perspiration.
- to improve the wetting back property of the hides which will help the dyeing process.

A wide variety of chemicals can be used for the retannage of leather. They can generally be divided into the following categories: vegetable tanning extracts, syntans, aldehydes, mineral tanning agents and resins [22].

c. Dyeing

To colour the leather as required by the customer, this should be an even colour and should cover any grain defects. The colour should be light fast and wash fast if the finish is not covering. Typical dyestuffs are water based acid dyes. Basic and reactive dyes are less commonly used.

d. Fat liquoring

It is very important operation for leather manufacturing and it depends on the type of leather to be manufactured. Leathers must be lubricated to achieve product-specific characteristics and to re-establish the fat content lost in the previous procedures. The oils used may be of animal or vegetable origin, or might be synthetics based on mineral oils [26].

Objects of fat liquoring:

1. To improve the softness of the leather.
2. To improve the sliding properties of the leather.
3. To improve the toughness, water-repellent properties of the leather.

2.2.2.4. Drying and Finishing Operation

1) Drying

The primary purpose of drying is to remove moisture. However, at this stage, drying is more than just moisture removal. Drying is one of the most important steps in maintaining leather quality. It affects the feel, softness, area, and even color of the tanned hide/skin [22].

Drying techniques include samming, setting, centrifuging, hang drying, vacuum drying, toggle drying and paste drying. Generally samming and setting are used to reduce the moisture content mechanically before another drying technique is used to dry the leather further. After drying, the leather may be referred to as crust. Crust is a tradable intermediate product.

Air Drying - in which the skins are hung on hooks or sticks and dried by passage of air around the hides.

Staking:

Soften by separating the fibres which have become attached to each other during drying.

Toggling: in which the leather is stretched out and nailed on screen which is then placed in a dryer having constant temperature and humidity. Complete the drying to 14 % and obtain the optimum area by stretching the skin with toggles (clips).

Pasting - the wet skin is pasted on large sheets of plate glass, to which it adheres and the plates are sent through a long drying tunnel consisting of different zones of controlled temperature and humidity.

Vacuum Drying – in which the length is spread out on chrome plated polished steel surface. Heat is applied by a built in heat exchanger and the temperature is maintained by a thermostatic control of circulating hot water. This is a new technique and found extensive use in most modem tanning approaches [22].

Roto press: for ironing or embossing the surface of leather with pressure and heat producing thermoplastic flow.

2) Finishing

After the leathers are fat liquored and dyed following the tanning process, they are processed with a series of coatings on the surface in order to improve their resistance and produce appealing and uniform surface effects.

The overall objective of finishing is to enhance the appearance of the leather and to provide the performance characteristics expected of the finished leather with respect to [22, 25]:

- colour
- gloss
- handle
- flex, adhesion, rub fastness, as well as other properties including extensibility, break,light- and perspiration fastness, water vapour permeability and water resistance as required for the end use.

Generally, finishing operations can be divided into mechanical finishing processes and applying a surface coat.

Mechanical finishing processes

A wide range of mechanical finishing operations may be carried out to improve the appearance and the feel of the leather. The following list of operations includes commonly used mechanical finishing operations. However, the list is not exhaustive and many other operations exist for special leathers such as sole leathers, wool-on skins, and special effects leathers:

- conditioning (optimising the moisture content in leather for subsequent operations)
- staking (softening and stretching of leather)
- buffing/dedusting (abrading of the leather surface and removing the resulting dust from the leather surface)
- dry milling (mechanical softening)
- polishing
- Plating/embossing (flattening or printing a pattern into the leather).

These operations may be carried out before or after applying a coat, or between the application of coatings [21].

Applying a surface coat

The purposes of applying a surface coat are:

- to provide protection from contaminants (water, oil, soiling)
- to provide colour either to modify dyed colour or reinforce that provided by the dyes, to even the colour or to disguise defects
- to provide modifications to handle and gloss performance
- to provide attractive fashion or fancy effects
- to meet other customer requirements.

There is a wide range of application methods each of which has its advantages and disadvantages. A combination of methods can be used to achieve the desired effect on the finished product. In principle the following types of application methods can be distinguished:

- padding or brushing the finishing mix onto the leather surface
- spray coating, which involve spraying the finishing material with pressurised air in spray cabinets
- curtain coating, which is passing the leather through a curtain of finishing material
- roller coating, which is an application of finishing mix through a roller
- transfer coating, which is the transfer of a film/foil onto leather previously treated with an adhesive [25,26].

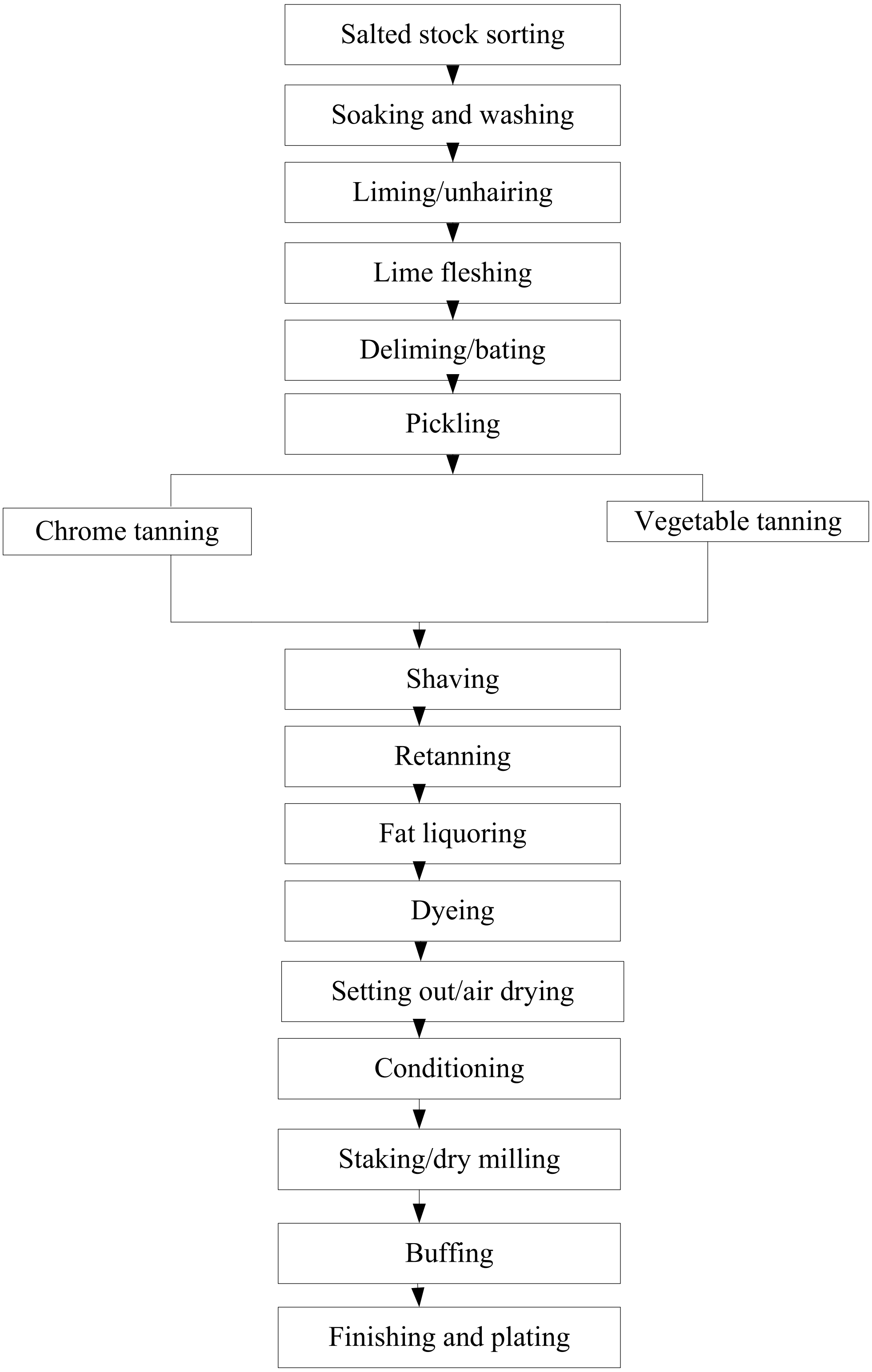

Figure 2.8. General flow diagrams of leather process steps

2.2.3. Pollution Load of Leather Processing Operations

Tannery is universally recognized as a ‘dirty’ industry, and because of this reputation very often is unpopular with the general public and even considered erroneously more dangerous than other industrial activities not having such direct and evident unpleasant impact. It must be clearly said that tannery is an unpleasant industry but not harmful and dangerous. This is well demonstrated by the fact that specific illnesses associated to the leather manufacture do not exit [2].

The leather tanning process involves an important consumption of water and generates a complex pollution consisting of a mixture of organic and inorganic substances make quite difficult and costly to treat if compare with that of other industries. Approximately 30-40 liters of water is used for processing one Kilogram of raw hide/skin into finishing leather with peak up to 60 liters per kilogram of hide/skin of processed raw material green or wet-salted weight [2, 4].

Composite untreated wastewater of hide or skin is turbid, colored, and foul smelling. It consists of acidic and alkaline liquors, chromium; sulfide; nitrogen; biochemical oxygen demand (BOD); chemical oxygen demand (COD); chloride; and high levels of fat. Suspended solids are usually half of chloride levels. Wastewater may also contain residues of pesticides used to preserve hides during transport, as well as significant levels of pathogens [24].

Significant volumes of solid wastes are produced, including trimmings, degraded hide, and hair from the beamhouse processes. The solid wastes can represent up to 70% of the wet weight of the original hides. In addition, large quantities of sludges are generated. Decaying organic material produces strong odors. Hydrogen sulfide is released during dehairing, and ammonia is released in deliming. Air quality may be further degraded by release of solvent vapors from spray application, degreasing, and finishing (for example, dye application) [6].

In general, the quantity of water usage and nature of wastewater discharge varies from process to water usage and wastewater discharge per kg of hide /skin for different process are as the Table 2.2.

Table 2.2. Averaged water consumption from beamhouse to post-tanning

Process		m^3/t raw hide/skin		
		J. Ludvík,2000	Wellinger,1993	Warner,1992
Beamhouse	Soaking Unhairing/liming Deliming/bating	7-9 9-15 7-11	6 9 5	6 9 5
	Sum	23-35	20	20
Tanning	Pickling, chrome tanning, washing after chrome tanning	3-5	3	4
	Sum	3-5	3	4
Post tanning	Neutralization,washing, retanning, dyeing, fatliquoring and cleaning	7-11	9	17
	Sum	10-16	9	17
Total amount of wastewater		36-51	32	41
Source: UBA Research project ‘Abwassereinleiter- Statistik“, Germany, 1997				

2.2.3.1. Characteristics of the Sectional Wastewater

The tanning industry has the reputation for being one of the filthiest and vile smelling of industries. Each operation in the tanning process generates certain wastes.

The primary wastes from a-tannery include wastewater from various processes, chemicals like bactericides, lime, sodium sulfide, sodium sulfhydrate, ammonium salts, enzymes, and basic chromium sulfate. Other wastes include vegetable tanning extracts, mineral acids, alum, fat liquors, acid dyes, solvent coatings, pigments, and sodium chloride. In addition, dirt, manure, fleshing, grease, residual hair, proteins, oils, unfixed tan liquors and chemicals, and leather dust may also contribute to the wastes. The wastes originating from each of the major processes are described below [2, 4, 6].

Soak and Wash

The major waste constitutes from this operation are BOD (primarily soluble proteins), suspended solids, and high concentration of dissolved solids (salt). Most of the hides/skins are usually brine-cured or green-salted, so the salt concentrations are high.

Dehairing

This operation is a major contributor to the plant effluent. Since there are two types of dehairing , namely hair-pulp and hair-save, the concentration of their wastes vary. For the hair-pulp operation, the spent dehairing liquors contain high concentrations of B0D5 (proteinaceous organic matter), sulfides, dissolved solids, and suspended solids. In the hair-save process, the waste loads are less than those for the hair-pulp process. However, the water use is much greater for machine removal and the subsequent washing of hair. The BOD from hair-save process is much lower because the proteinaceous hair does not dissolve in the dehairing solution but is loosened so that it can later be removed mechanically [28].

Bating and Pickling

Ammonium salts are usually used in the bating process. This results in large quantities of ammonium salts and some soluble proteins, suspended solids, and lime in the effluent. The primary waste constituents in the pickle liquors are acids and salts, while BOD, suspended solids, and nitrogen are found in low quantities.

Tanning

The chrome tanning process employs chromium sulfate or a chrome tanning solution as a tanning agent. This results in a large concentration of trivalent chromium in the effluent. However, the organic content of spent chrome-tan liquor including BOD and suspended solids is usually low. For non-chrome tan processes, like vegetable tan, the main constituents are BOD and color.

Retanning

Retanning employs low concentrations of chemicals. Hence, the wastewater strength is not high and the wastewater does not contribute significantly to the total waste flow.

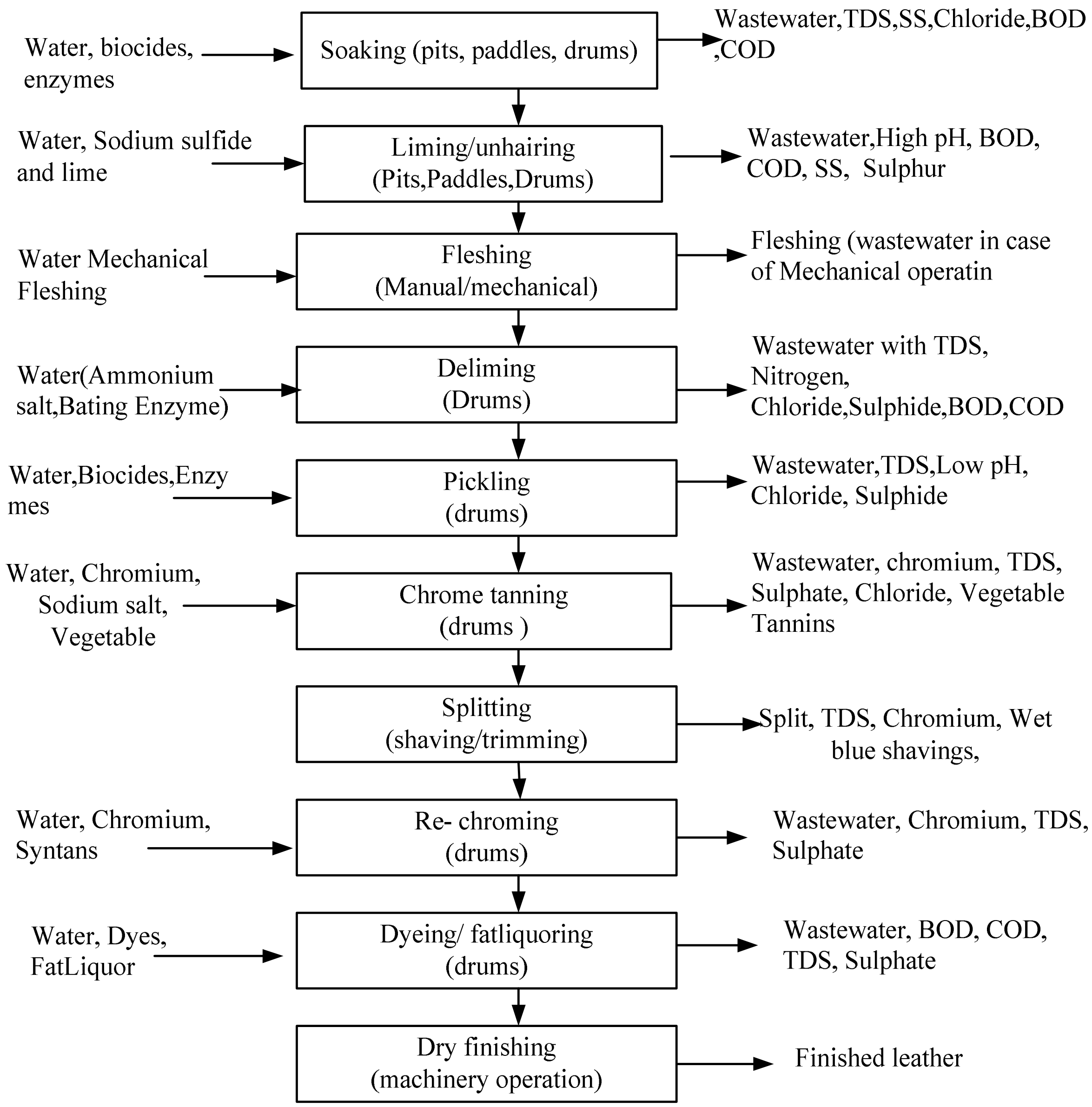

Figure 2.9. Input versus out put in tanneries

The characteristics of the sectional wastewater from the beam house operations viz. soaking, liming, deliming, are given in Table 2.3 from tanyard operations (pickling and chrome tanning) are given in Table 2.4 and for post tanning to finishing are given in Table 2.5

Table 2.3. Characteristics of effluents from beamhouse process

Parameter	Soaking	Liming	Deliming and bating
PH	7.4-7.9	10.0-12.5	8.1-9.0
Alkalinity as $CaCO_3$	600-1500	8000-15000	1000-1600
BOD	1000-1600	5000-9000	900-1500
COD	2300-3500	15000-30000	1400-3300
Cl^-	15000-21000	4000-7000	700-1200
Total solids	22000-35000	30000-45000	15000-25000
Dissolved solids	19500-29500	25000-33000	13500-22000
Suspended solids	25000-55000	5000-12000	1500-3000
S^{2-}		350-700	25-40

All values except PH are expressed in mg/l.

Table 2.4. Characteristics of effluents from tanyard process

Parameter	Pickling	Chrome tanning	Vegetable tanning
PH	2.4-3.3	3.4-4.2	3.5-4.5
Alkalinity as $CaCO_3$	500-1200	4000-5500	2000-4000
BOD	250-600	400-650	12000-18000
COD	900-2500	1800-4000	25000-35000
Cl^-	20000-35000	11000-16000	1500-3000
Total solids	45000-65000	40000-65000	55000-80000
Dissolved solids	43000-60000	38000-60000	50000-65000
Suspended solids	2000-5000	2000-5000	5000-15000
Total chromium	-	1700	3500

All values except PH are expressed in mg/l.

Table 2.5. Characteristics of liquid wastes of a post tanning process unit

Operation	Total solids	Total SS	BOD	COD	PH	Cl^-	Total chromium
Neutralization	7000-12000	1000-2000	400-1000	2000-4000	4.0-6.5	600-1800	25-50
Washing	4400	900	2400	4730	6.5	480	
Rechroming	15680	900	2000	4356	3.6	740	989.5
Basification	11080	1500	1500	4138	4.8	480	450
Fat liquoring	6980	400	700	2562	3.5	92	18

All values except PH are expressed in mg/l.

2.2.3.2. Constraints /Limiting Contaminants in Inlet and Outlet Streams

Contaminants are a species removed by a process or limiting water reuse within a system. The main contaminant in beam house processes is salt. After liming, organic material is main contaminant. After the tanning, the main residue is trivalent chromium. The acceptable limits were determined from the amounts normally used in each one of the stages of the process. The minimization of water use is theoretically possible for the set of processes that have in common the same pollutant.

If all the contaminants are considered, which usually involve many kinds of contaminants, solving the network will become complicated. As a result, the following rules are proposed to determine contaminants in the water system as stated below [4]:

- Consider contaminants that have obvious or major effects on the processes. The other contaminants will be considered as constraints after the initial network has been obtained.
- Combine the contaminants that have similar effects to reduce the number of contaminants so as to simplify the water pinch analysis. For example, if the effect of Cl^- and $SO4^{2-}$ is the salinity of water, salt can be used as a contaminant instead of Cl^- and $SO4^{2-}$ individually.

The process in tannery is divided in three groups of processes where each process groups having different main contaminants. Salt, organic material and chromium are the main contaminants [4, 27].

Process Where Salt is the Main Contaminant

The first set to be integrated is the one that presents salt (sodium chloride and ammonium sulphate) as the main contaminant. The related processes are: Pre-soaking, Soaking, Washing after soaking and deliming.

Process Where Organic Material is the Main Contaminant

After deliming and before tanning, the processes have the organic substance as the main pollutant: Bating, Washing 1, Washing 2, Washing 3 and Pickling.

Processes Where Chromium is the Main Contaminant

In the subsequent processes to the pickling (Tanning, Washing after Shaving, Wet Finishing and Retanning with chromium) chromium is the main contaminant in wastewater.

2.2.3.3 Regeneration and Reuse of Tanning Liquor

Chromium solutions are widely used in many industrial processes such as chrom plating, wood preserving, textile dyeing, pigmenting, Cr chemical production, pulp and paper industrial and tanning. The wastewater resulting from these processes contains high amount of chromium metal which is harmful for environment and human health [30-32].

Tanning process using chromium compounds is one of the most common methods for processing of hides/skines [31]. In this process about 60% - 70% of chromium reacts with the hides/skins. In the other word, about 30%- 40% of the chromium amount remains in the solid and liquid wastes (especially spent tanning solutions). Hence, the wastewater of tanning process is an important source adding Cr pollutent to the environment. In addition, the cost of the chromium metal is also important and it is possible to be recovered from the wastewater [29]. According to [30] reported that the Cr ions concentration in the tanning wastewater varies from 2500 to 8000 ppm.

When large quantities of chromium bearing floats are recovered, recycling after precipitation is another solution for chromium recovery. Precipitants that might be used include sodium carbonate, sodium hydroxide, and magnesium oxide. The difference between them is the effect they have on the precipitate: the faster the basifying reaction, which is dependent on the alkalinity and the solubility, the more voluminous, is the precipitate and the slower is the settling rate. Most of these alkalies are cheap. The highly reactive alkalies give a voluminous chromium sludge (more than 25% by volume) which makes it necessary to separate the sludge from the liquor by a filter press. Some alkaline (sodium hydroxide) make it necessary to heat the liquor in order to obtain complete chromium precipitation. The use of lime causes a simultaneous precipitation of chromium and calcium sulphate which makes the reuse of chromium problematic [29-33].

Finally two systems were considered for chrome recovery. One with sodium alkalies which need the use of filter presses and the other with magnesium oxide which, because of its low reactivity and solubility, causes the chromium to settle in a very compact way, so that separation from the liquor is merely a question of decantation of the supernatant. Dissolving the sludge can be done instantly with sufficient sulphuric acid to obtain reusable liquor. The clarified supernatant with less than 10 mg/l of chromium expressed in Cr, after chrome recovery can also be reused for first soaking float [32].

The chrome containing wastewater including wash water is screened and collected in a treatment tank. A calculated quantity of magnesium oxide is added to the liquor and stirred. During this stirring period the PH is gradually rising to the required value of about 8. After stabilization of the PH, stirring is stopped. The chromium precipitates and settles to a very compact sludge within an hour which is only about 8 to 10% by volume of the exhaust chrome liquor [30-33].

The chemical reaction of the chrome recovery is as follows:

$Cr_2(SO_4) + 3MgO + 3H_2O \leftrightarrow 2Cr(OH)_3 + MgSO_4$

$MgO + H_2S0_4 \leftrightarrow MgSO_4 + H_2O$

$2Cr(OH)_3 + 3H_2SO_4 \leftrightarrow Cr_2(SO_4) + 6H_2O$

Using recovered chrome for tanning results in wet blue that is slightly paler than conventional production. Further the re-use of precipitated chromium will lead to an increase in the neutral salts in the effluent.

2.3. Case Study: Process Description of ELICO-Gloving and Hide unit

The company has 79 years of experience on leather processing. It started to produce leather in 1924 E.C by the owner ship of Armenians in Harar. Then they dismantled the plant and installed it near Akaki river water line (i.e existing place).At that time its name was Darmar Tannery till the owner ship transferred to government control. The Tannery was nationalized following a change of government in Ethiopia. Then its name changed to Awash Tannery till it is privatized. Following a change in government and the subsequent liberalization of the economy, Awash Tannery was privatized and came under Ethio-Leather Industry PLC (ELICO) since 1989. The company uses the Akaki river water for its operation by treating it and also gets its power supply from Ethiopian electric power corporation (EEPCO). For the production of glove leathers of high quality it uses raw sheepskins. Currently the tannery produces different types of products which can be summarized by the follow flow daiagram.

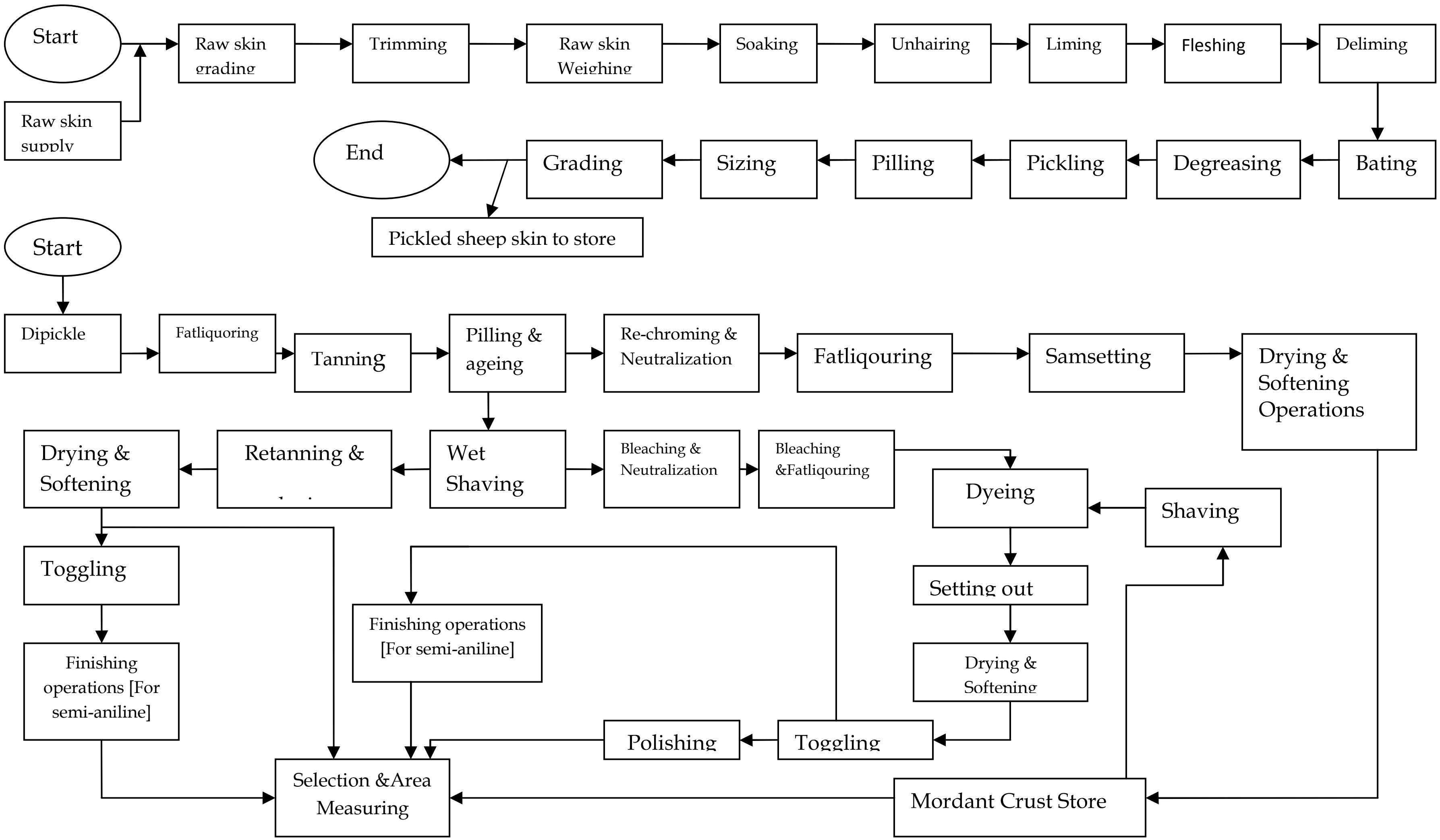

Figure 2.10. ELICO generic sheep skin process flow sheet

3. MATERIALS AND METHODS

3.1. Materials

a. Raw Material

Dry salted forty three pieces of Sheep skins were used as raw material.

b. Chemicals

The chemicals used in this research were beam house operations chemicals, tanning operations chemicals, finishing operations chemicals and Magnesium oxide.

c. Machines and Equipments

- Two testing Drums
- Model tannery equipments of Leather Development Institute such as Fleshing Machine, Trimming knife / Blade, Samming Machine, Shaving Machine, Vacuum Dryer, Toggle dryer, Hand Spray Machine, Auto spray Machine, Polishing Machine, and Embossing Machine

d. Samples of Wastewater

Samples of wastewater from Pre-soaking, Soaking, Washing after soaking, deliming, Bating, Washing 1, Washing 2, Washing 3, Pickling, Tanning, Washing after Shaving, Wet Finishing and Retanning with chromium, which were examined within the scope of the study, had been obtained at the end each process step from Ethio-Leather Industry Gloving and Hide unit (ELICO).

Since the process of tanning is batch, after finishing the process, spot samples were collected and transported to laboratory for the determination of the most important parameters as quick as possible.

e. Softwares

- Microsoft office Visio 2007 for doing water pinch analysis and drawing flow diagrams
- JMPIN version 5.0.1 for analysis of chemical and physical test result of finished leather

3.2. Methods

The following methods were employed to achieve the objective of the research.

3.2.1 Analysis of the Wastewater

In the production of glove leather different types of chemicals are used in each processing stage. As a result each process stage has its own contribution on the chemical load of the effluent. Understanding the chemical load at each stage helps to know the concentration limit required for pinch analysis. The main contaminant in beam house processes is salt. After liming, organic material is main contaminant. After the tanning, the main residue is trivalent chromium [29]. The chemical analyses of the collected wastewater from end of each process units were carried out using the following standard methods:

a) Chloride (Cl^-)

The standard used for chloride determination was according to APHA 4500 Cl^- B (Argentometric). The analysis was made for pre-soaking, soaking, soaking washing baths and deliming.

Chloride is precipitated with silver nitrate, the protein matter destroyed by boiling with concentrated nitric acid, and the excess silver nitrate determined by titration with potassium thiocyanate.

b)Sulphate ($SO4^{-2}$)

The standard used for chloride determination was APHA 4500-$SO4^{-2}$. For pre-soaking, soaking, soaking washing baths and de-liming were verified the presence and the concentration of sulphate.

Sulfate is precipitated in a hydrochloric acid (HCl) solution as barium sulfate by addition of barium chloride. The precipitation is carried out near the boiling temperature, and after a period of digestion the precipitate is filtered, washed with until free of chloride, ignited or dried, and weighted as barium sulfate.

c) Chemical oxygen demand (COD)

COD was determined according to standard method (SM) 5220-COD B, for Bating, Washing 1, Washing 2, Washing 3 and Pickling.

Most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acid. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion, the remaining unreduced potassium dichromate is titrated with ferrous ammonium sulfate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidezable matter is calculated in terms of oxygen equivalent.

d) Trivalent chromium (Cr^{+3})

The standard SLC 208 was used to determine the concentration of trivalent chromium for tanning, washing after shaving, re-chromium and re-tanning.

A suitable volume of used liquor is oxidized to hexavalent state using a procedure based on the use of perchloric acid. The resulting solution is titrated with either standard ferrous ammonium sulfate solution.

3.2.2. Water Pinch Analysis methodology

The graphic-based pinch method is applicable to the exchange of a single species. The water pinch analysis performed at industry scale for the case study. The first step consists of establishing the inventory of the demands and sources of water for process units from presoaking to re-tanning. For each source of water, the flow rate and the concentration of contaminant must be specified. For the demands, the required flow rates as well as the maximum admissible contaminant concentrations are collected from working recipes. The concentration limits of sources are determinant in the outcome of the analysis of each process units.

For water related process, construct a composite profile of water demand (sinks) and wastewater effluents (sources). The graph depicts the water sources and sinks for a typical process, contaminant load and water flow. This identifies the pinch, the point in the process that limits the potential for water conservation. The area of overlap (shaded) shows the scope for water reuse.

3.2.3. Regeneration and Reuse of Tanning Discharge for Soaking Float

In this case separating of trivalent chromium from first tanning liquor and preparing its supernatant to reuse for soaking purpose is required.

The chromium concentrated wastewater taken from tanning unit was treated by using water bath and beakers equipped with magnetic stirrer used for mixing of magnesium oxide with wastewater, with aid of electric motor, coupled with a regulator for speed controller. For separation of supernatant from sludge conical plastics were used. The basic steps and equipments used for this experiment can be summarized as showing by the following procedure.

Procedure

1. Take a sample of chrome liquor from drum and add to the beak after screening to grid of material
2. Add Magnesium oxide while stirring well slowly not less than for 50 minute until the P^H of the solution reaches 8 and control the temperature of solution at 30 ^oC.
3. When the P^H reaches switch off the stirrer and transfer the solution to the conical plastic and leave it over night settling chromium in the form of compacted sludge
4. Decant the supernatant and use it for soaking float after analyzing for chromium (if it is less than 10ppm).

3.2.4. Pilot Plant Test and Laboratory Experiments

During the experiments the first steps to prepare the working recipe in small scale. Then collect the waste water required for reuse according to the water pinch analysis result.

For the processes forty three sheep skins were divided into groups and placed in pilot drums for seven experiments. Only one experiment was convectional process which has used freshwater at all stages of the process. The three different experiments were done reusing water according to water pinch analysis result for process where salt, organic matters and trivalent chromium are the limiting contaminants. The other two experiments were done according to the combination of processes where salt and organic matters, and organic matters and trivalent chromium were the limiting contaminants. The last experiment was done by using the supernatant of chrome recovery for soaking process.

The chemical and physical quality of the semi product and finished leather was analyzed and evaluated for both convectional and reuse (the six experiments) processes.

Table 3.1. In process follow up, monitoring and measuring product

Process stage	Inspected parameter	Specification
Soaking	Hair sleep, Yes/No	No
	Baume of soak ^{0}Be	≤0.1
	pH of soak water	≥0.7
	Temp. of soak water(^{0}C)	Room Temperature
Liming	^{0}Be	26-28
	Duration of liming	Over night
	Un hair condition	Proper
	pH	12.5/13.0
De-liming	Amount of chemical added (Ok, excess, under)	Ok
	pH of de-liming liquor	≤9.3
	Temp. de-liming liquor	32-34
Pickling	P^H of pickle float	≤1.0
	Shrinkage of temp.(^{0}C)	70
	Cleanness of pelt (Ok, Not)	Ok
	Temperature of float(^{0}C)	22-25
	Weighing moisture of pickle	55-65
De-pickling	Pickle skin grading Ok/Not	Ok
	pH	6.2/6.8
Degreasing	Cleanliness of liquor Ok/Not	Ok
Tanning	Cross section testing (good tannage/ poor tannage)	Good tannage
	Chromium exhaustion Ok/No	Ok
	Dilution and addition of sodium bicarbonate(dilution ratio Ok/No)	OK
	pH	3.6/3.8
	Shrinkage temperature (^{0}C)	≥90
Shaving	Shaving effect (easy to tear or not)	Not
	Shaving chatter (present/absent)	Absent
Neutralization	Amount of chemical added (Ok, excess, under)	Ok
	Dilution and addition of sodium bicarbonate (Ok/Not)	Ok
Fat liquoring	Amount of chemicals added(ok, excess, under	Ok
	Condition of emulsification (Ok/ Not)	Ok
Dyeing	pH	3.0/3.2
	Penetration (Ok/ Not)	Ok

3.2.4.1. Chemical Analysis of Wet Blue Leather

Samples of wet blue leather were taken for both conventional process and advanced process using reused water according to pinch analysis result. The samplings of wet blue were taken according to the standard methods SLC 1 and 2. Then its chromic oxide content was analyzed using standard SLC 8.

3.2.4.2. Physical Tests of Finished Leather

Physical testing of leather indicates the quality of the finished leathers produced. The finished leather produced by convectional process and advanced processes which reuse water depending on water pinch analysis result were tested for the following physical tests for comparisons of the test results. Due to limitations of time and the availability of instrument, selected physical tests were accomplished and these tests are briefly discussed here. All samples were collected according standard methods of SLC 1 and 2.

A. Tensile strength and percent of elongation

A test piece was extended at a specified rate until the forces reach a predetermined value or until the test piece breaks according to ISO3376:2002(E) method.

Tensile strength is actually the force (N) per unit area of cross section (sq mm) required to cause a rupture to cause a rupture of the test specimen,

$$\text{Tensile strength} = \frac{\text{Breaking load (N)}}{\text{cross section area(sq mm)}}$$

Breaking load mainly depends upon the number of collagen fibers acting in the direction of applied load.

The extent of elongation of the leather specimen at the time of its breaking, while applying the tensile force, expressed as the percentage of the original length said specimen is the elongation at break. The elongation at break is taken by the difference between the initial strength and the length.

$$\%\ \text{elongation at break} = \frac{\text{final distance between the jaws} - \text{initial distance between jas}}{\text{intial distance between jaws}} x100$$

B. Ball burst test

The bursting strength in an index of the overall strength of the leather. It was tested according to ISO 3379:2005 method. This method may be used with any light leather, but it is intended more particularly for use with boot and shoe upper leather. For this test the specimens were cut from the samples by a circle type cutting dice and the specimens were placed on a lastometer being conditioned by clamp whose flesh sides were adjacent to the ball of the instrument. The increasing that is the up thrust of the ball with the pressure by handling indicates the dissension at a rate of 0.2mm/sec. And simultaneously watch the grain surface for the occurrence of a crack the ball and dissension of grain cracking and bursting wear noted.

C. Water vapour absorption

The test piece and an impermeable material are clamped over the opening of a metal container containing water for specific time according to SLP 19 test method. The water vapour absorption of the test piece was determined by the increase in mass.

D. Colour fastness

Color fastness was tested according to ISO 11640:1993(E). A specimen of the leather to be tested was subjected to the action of the agency in question either on its own or brought into contact with an accompanying material in an appropriate manner for assessing the staining. The extent of any change in the colour of the leather as well as of any change in the colour of the leather as well as of any staining of the accompanying material is assessed and expressed in fastness numbers. The degree of staining or change of color is assessed using gray scales and results quoted for dry rub or wet rub.

4. RESULT AND DISCUSSION

4.1. Water Pinch Analysis

To minimize wastewater by Single contaminant approach, it is necessary to calculate minimum water flow-rate required to reduce the contaminant concentration to an acceptable level. In this research, a graphical method named concentration composite curve has been used to determine pinch point. Therefore, it must be taken some steps. The first step is providing limiting process data table. This table includes minimum inlet and outlet flow-rates, maximum inlet and outlet concentrations.

There are many contaminants in leather processing industry. If all the contaminants are considered, which usually involve many kinds of contaminants, solving the network will become complicated. According to the leather processing units, there are three groups of processes based on the main/ limiting contaminant. The first group: presoaking, soaking, washing after soaking and de-liming are processes in which salt is the main contaminant. In the second group: bating, washing 1, 2, 3 and pickling organic materials (COD) are the main contaminants. Finally the third group in which chromium is the main contaminant consists of tanning, washing after shaving, Re-tanning with chromium and re-tanning. The water pinch analysis for each group of process is performed individually and finally the total process water saving and waste minimization is computed. In this case for each process stage water consumption was collected from case study tannery only for one batch process which uses 3500 pieces of dry sheep skin.

In the next step, construct source and sink composite curve, on purity versus flow axes. Each stream is represented by a horizontal line of ordinate equal to its purity and length equal to its flow rate. Demand or source curves are adjoining so that the total horizontal length of each composite profile gives the cumulative flow rates for demands and sources respectively.

The curves are drawn in such a way that they are as close together as possible (along the flow axis), subject to the constraint that the source curve must always be above the sink curve. The point of contact is called the pinch, which is a feature of the system that limits the potential for water conservation. The area of overlap (shaded) shows the scope for water reuse.

4.1.1. Salt as Limiting Contaminant

Table 4.1. Limiting data for salt [combine Cl- and SO4-2 salts] is the main contaminant

Process	Sink conc.(g/L)	source con.(g/L)	Water flow rate(L/batch)
Presoaking	80	107.7	7000
Main soaking	20	86.02	6000
Soaking washing	5	12.7	13000
De-liming	0	6.5	14000
Total water consumption			40000

Based on the mass balance presented in working recipe of Ethio-leather industry and laboratory analysis result, the average water consumption and contaminant concentration for processing of 3500 pieces of heavy sheep skins are shown in Table 4.1.

To make the demand composite curve, all inlet streams are drawn simultaneously. The horizontal axis shows the water flow-rate while the vertical axis indicates the contaminant mass load. The outlet streams from operations are drawn to make the source composite curve the same as inlet streams.

These two curves are drawn in a coordinated system and touch each other at one point. This point shows the potential for water reuse.

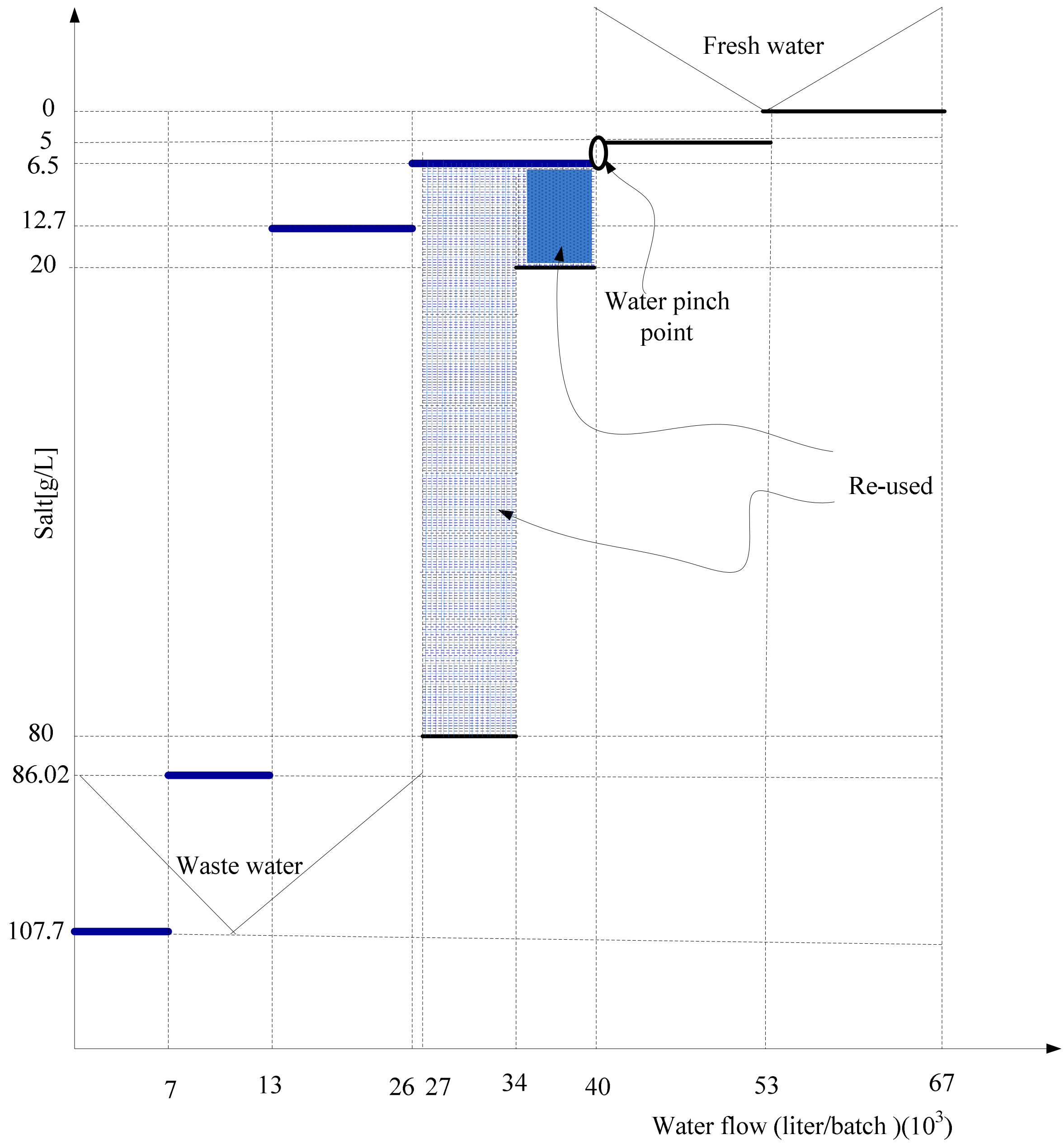

Figure 4.1. Source -sink curve of water pinch analysis for processes from presoaking to de-liming where salt is the main contaminant

As shown in the water pinch analysis Figure 4.1, de-liming discharge can be reused for pre-soaking and main soaking float. So that the amount of fresh water consumption for the processes where salt is the limiting contaminant decreases equivalent to fresh water required by presoaking and main soaking for convectional process. That means 13000 liter/batch (32.5%) of fresh water consumption or wastewater generation is saved.

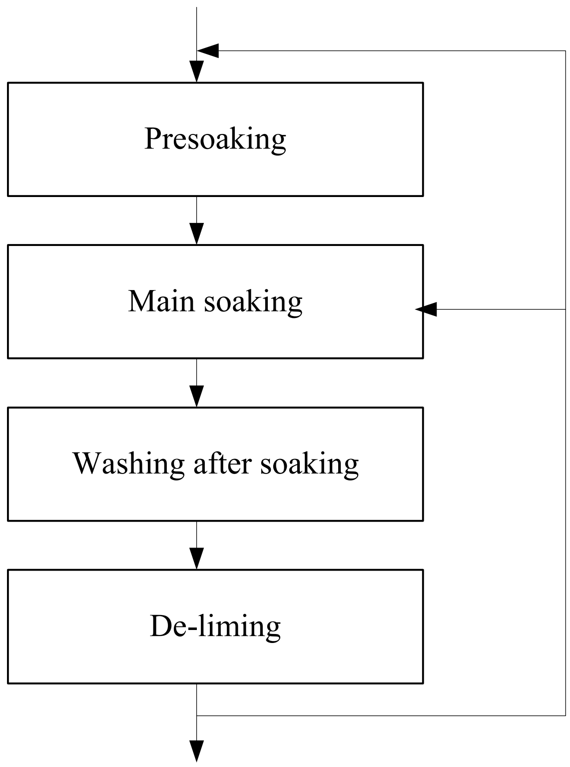

Figure 4.2. Flow diagram of leather processing when salt is the main contaminant: de- liming discharge will be reused for presoaking and main soaking processes.

4.1.2. Organic Materials as Main Contaminants

Table 4.2. Acceptable limits where organic matter is the main contaminant

Process	Sink con.(g/L)	Source con.(g/L)	Water flow(L/batch)
Bating	2	10	4000
Washing 1	2	4.2	4000
Washing 2	1.5	3	6000
Washing 3	0.5	1	6000
Pickling	0.3	1.7	4000
Total water consumption			24000

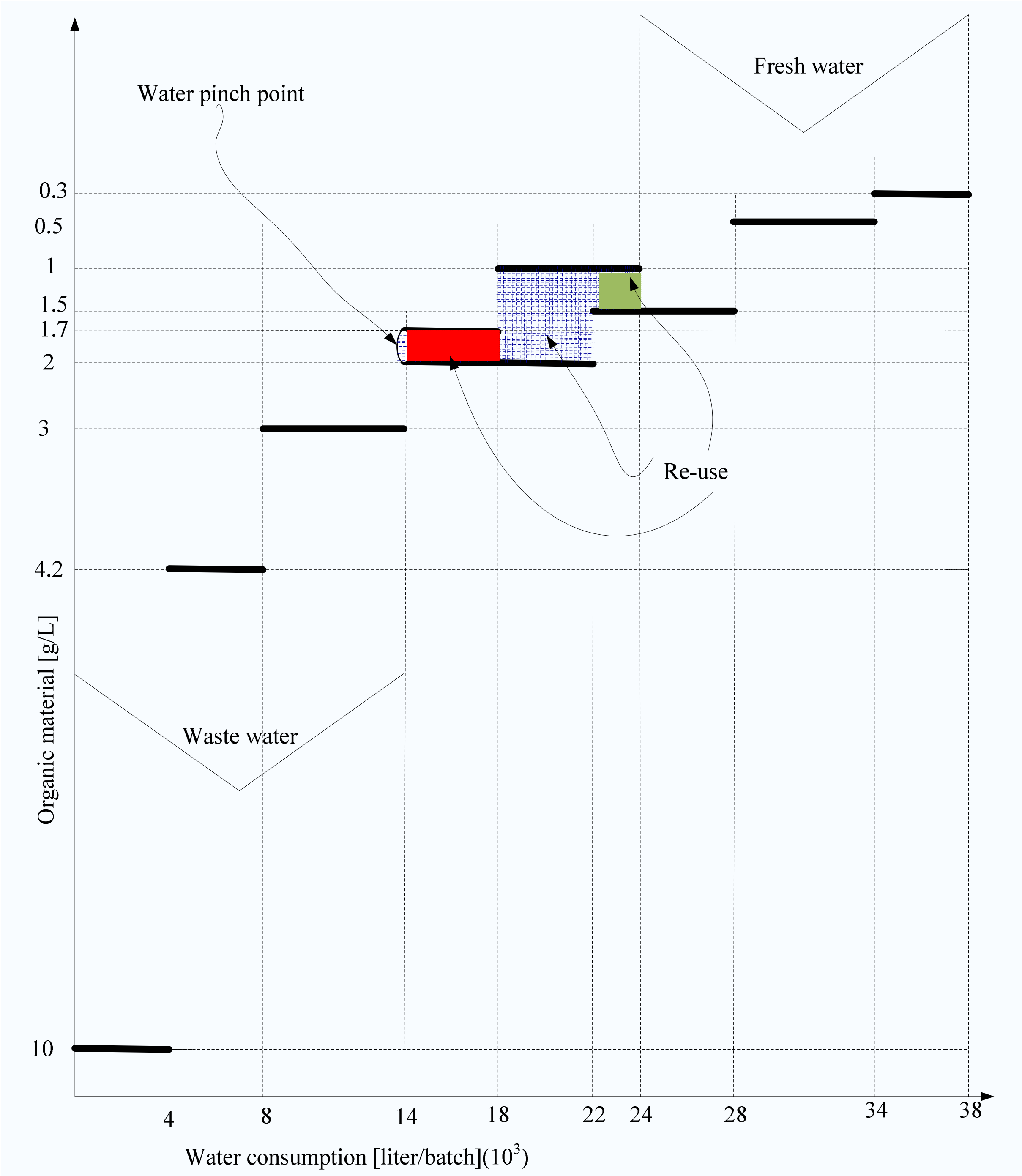

Figure 4.3. Source -sink curve of water pinch analysis for processes from bating to pickling where organic materials are the main contaminant

The above water pinch analysis result on Figures 4.3 shows that washing 3 discharges can be reused for washing 2 and washing1 float. In this case, all in all washing 1 uses washing 3 float but washing 2 uses the mixture of fresh water and washing 3 discharges by ratio of 2:1.

In addition to this the source- sink curve indicates that the pickling discharge can be reused for bating float which is not recommended because of the following reasons. The first reason is that the pickle float will be used for tanning process with out any difficulty. The other reason is the pH of pickle is 3 in averages and that of bating is around 8.5 which are by far different from each other.

Then with out including the pickle discharge the freshwater or wastewater generation saved for this water pinch analysis is 6000 liter/batch (25%).

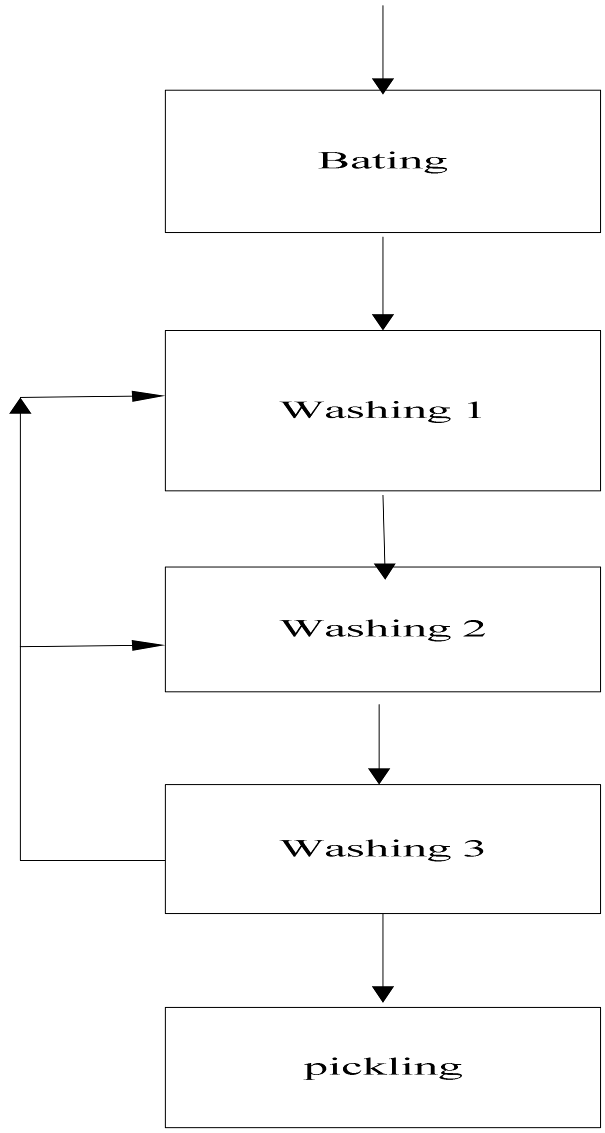

Figure 4.4. Flow diagram of leather processing when organic matter is the main contaminant: reusing wastewater from washing 3 to washing 1 and washing 2

4.1.3. Chromium as Main Contaminant

Table 4.3. Limiting data where trivalent chromium is the main contaminant

Process	Sink con.(g/L)	Source con.(g/L)	Water flow(L/batch)
Tanning	3	5.7	15000
Washing after shaving	0.1	0.5	12000
Re-chromium	1	3.3	6000
Re-tanning	0	0.3	3000
Total water consumption			36000

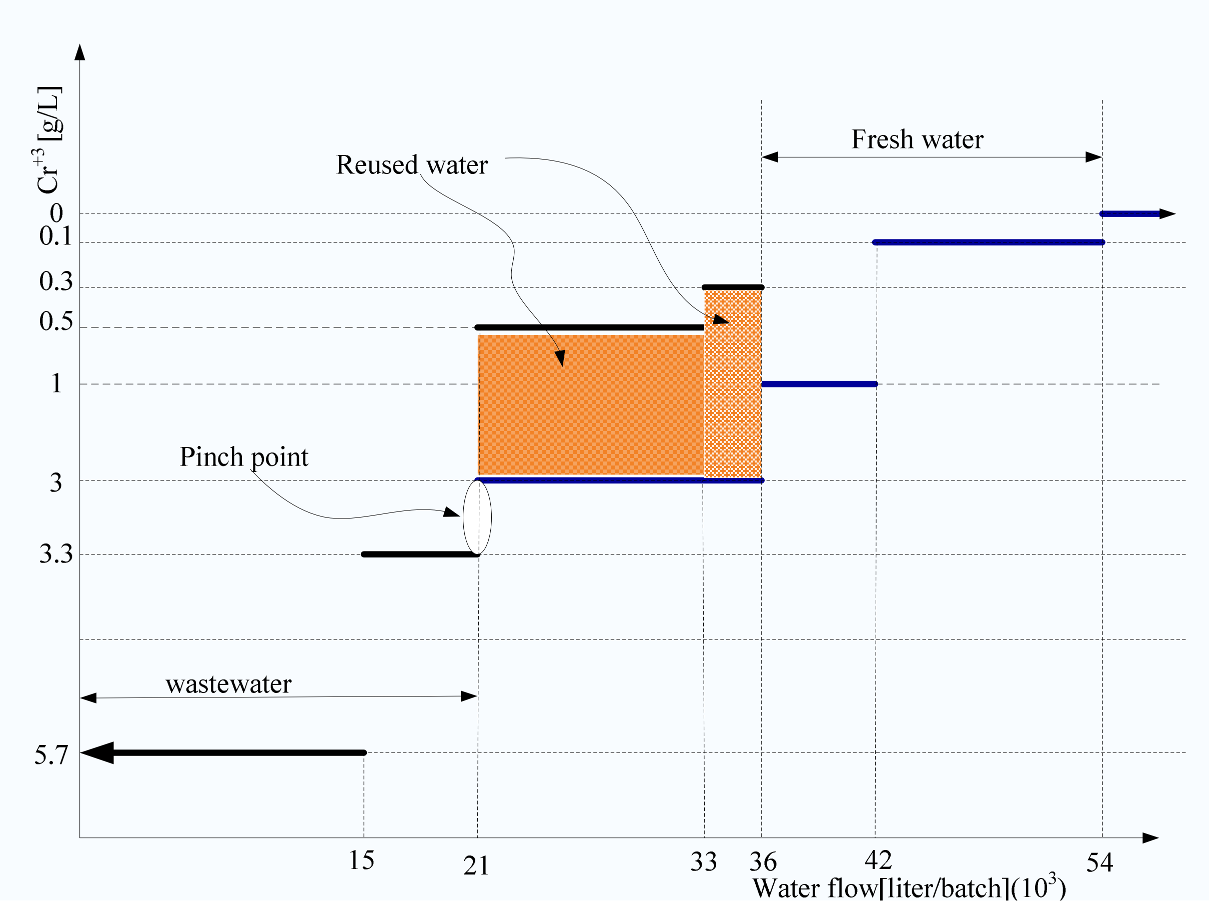

Figure 4.5. source -sink curve of water pinch analysis for processes from tanning to re-tanning where trivalent chromium is the main contaminant

Source-sink curve of water pinch analysis figure 4.5 demonstrates that washing after shaving and re-tanning discharge can be reused for tanning float. But reusing re-tanning discharge for tanning float with out treatment is not compatible interims of other contaminants rather than trivalent chromium. With out including the re-tanning discharge the amount of freshwater saved from the above source-sink curve of water pinch analysis is 12000 liter/batch (33.33%).

Table 4.4. Summery of total process freshwater saving or wastewater generation minimization in liter/batch

Process group	Freshwater consumption		Freshwater or wastewater generation saved by advanced process
	Conventional Process	Advanced process	
Processes where salt is the main contaminant	40000	27000	13000
Processes where organic material is the main cont.	24000	18000	6000
Processes chromium is the main contaminant	36000	24000	12000
Total	**100000**	**69000**	**31000**
			31%

4.1.4. Regeneration and Reuse of Tanning Discharge for Soaking Float

During this experiment, the first step was to analysis the concentration of chromium in tanning discharge so that the magnesium oxide dosing will be accordingly. The laboratory analysis result shows that the concentration of chromium before any treatment was 5g/L. After treatment with MgO 4.5g/L the supernatant was separated from the sludge and the test result show that the supernatant was 90.5% by volume and 9.7ppm of chromium concentration.

Using the supernatant for soaking float and washing after soaking, pilot scale was tested and the freshwater consumption saving including the above water pinch analysis result was increased into 44000 liter/batch which mean 44% wastewater generation minimization.

4.2. Test for Water Reuse in Pilot Scale

During the test the first step is preparing the working recipe in small scale see annex-1. This recipe was used for all processes except fresh and reuse water were according to the water pinch analysis result of each processes.

The processing types tested were:

Process 1: convectional process in which tests were carried out from pre-soaking to finishing and compare the quality of semi-finished and finished leather with other process in which water was reused at different stages according to process 2 up process 6.

Process 2: in this test, the possibility of reusing de-liming liquors in the pre- soaking and main soaking operations was verified.

Process 3: the reuse of 3^{rd} bating washing liquors for 1^{st} and 2^{nd} bating washing was tested.

Process 4: reuse of washing liquors after shaving in tanning process was tested.

Process 5: the combination of process 2 with process 4 was verified.

Process 6: the combination of process 3 and process 4 was tested.

These processes can be demonstrated by using the following flow diagram:

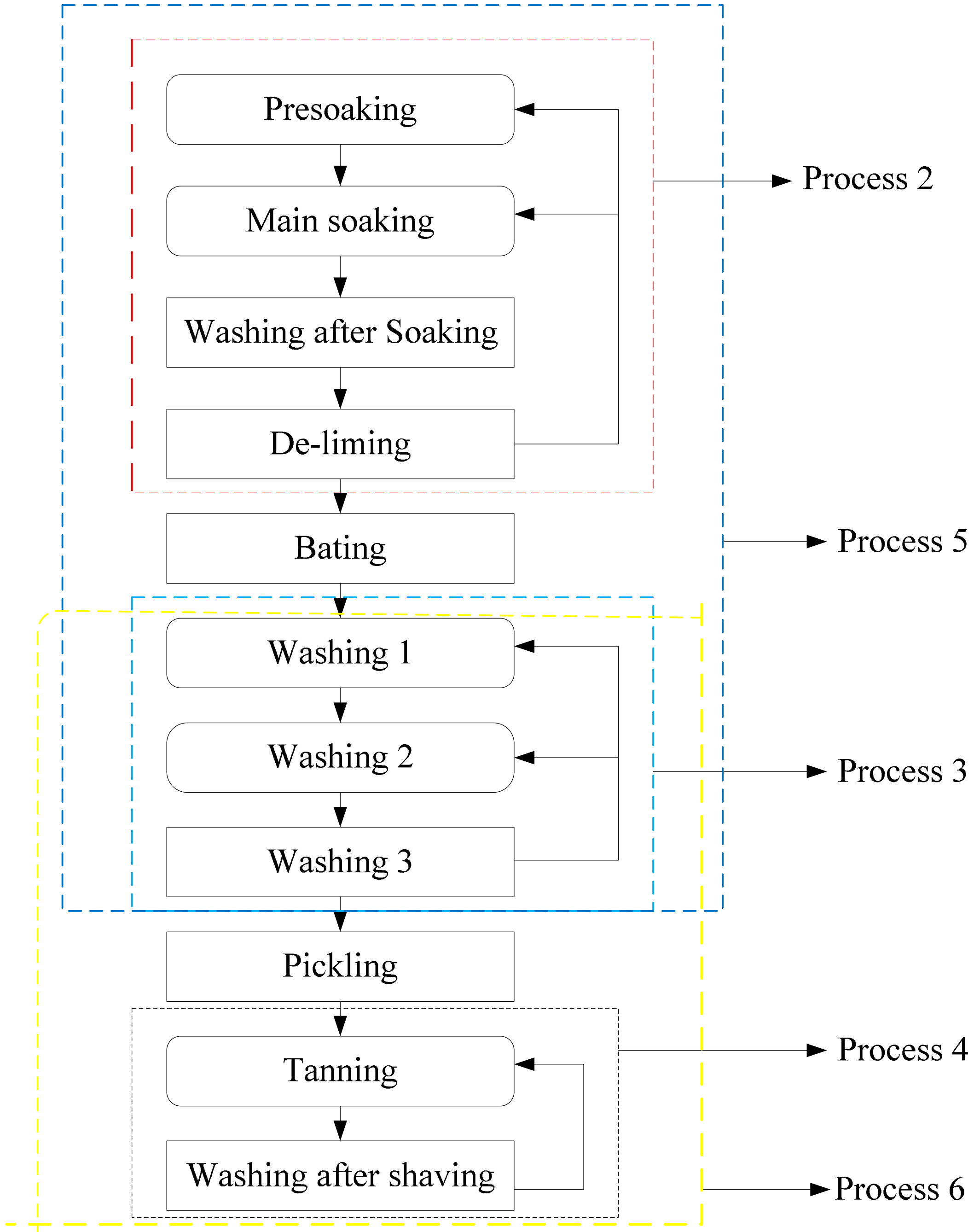

Figure 4.6. Flow chart of pilot tests on water reuse

For each of the above processes ten pieces of dry salted sheep skins were processed in testing drums. The chemical and physical quality test of semi product and finished leather produced by each type of processes were analyzed.

The results of chemical analysis of wet blue leather for each process types are given in Table 4.5.

Table 4.5. Chemical analysis of wet-blue leather for different process types

Process types	Moisture content (%)	Chromium oxide content of wet- blue leather	
		Wet base (%)	Dry base (%)
Process 1	77.8	1.29	5.8
Process 2	73.5	1.47	5.5
Process 3	76.5	1.34	5.7
Process 4	76.99	1.45	5.9
Process 5	76.91	1.24	5.6
Process 6	74.16	1.42	5.5

The chrome is the tanning agent that reacts with the collagen tissue of the dermic substances to achieve irreversible stabilization of the skin which is otherwise susceptible to deterioration. For this reason the acceptable quantity in leather according to the specifications is >3.5% dry based. The result of chromium oxide content for all processes shows in agreement with this value. But by observation (table 4.5) there is slightly difference between each process.

So that to analysis the result whether statistically different or not JMP software was used.
JMP uses an extraordinary graphical interface to display and analyze data. JMP is software for interactive statistical graphics and includes a broad range of graphical and statistical methods for data analysis.

There are a variety of methods to test differences in group means (multiple comparisons) that vary in detail about how to size the test to accommodate different kinds of multiple comparisons. Fit Y by X automatically produces the standard analysis of variance and optionally offers multiple comparison tests.

For this research to compare all pairs Tukey – Kramer mean comparison technique which compare all the mean values and give comparison grade as A, AB, B, BC, C, CD, D, etc. was used. According to this statistical testing method processes that are connected to the same letter (grade) are not statistically different.

Table 4.6. Mean comparison result of chromium oxide of wet-blue leather for different process types using Tukey-Kramer test

Process types	Mean	Grade
Process 1	3.545	A
Process 2	3.485	A
Process 3	3.520	A
Process 4	3.675	A
Process 5	3.420	A
Process 6	3.460	A

The mean comparison between convectional process and reuse processes has the same grade as it was demonstrated in table 4.6 and within the experimental error of the analysis.

The physical test results for finished leather by different process types were presented below.

Table 4.7. Tensile strength and percent of elongation of finished leather test results

Process types	Tensile strength (N/mm^2)		Percentage of elongation (%)	
	Parallel	Transverse	Parallel	Transverse
Process 1	23.92	16.61	68	74.80
Process 2	25.21	17.03	72.8	71.14
Process 3	26.18	19.57	64.7	80.34
Process 4	24.16	20.00	69.2	73.20
Process 5	20.34	19.86	71	69.50
Process 6	23.86	16.74	68.20	74.12

To analysis whether the tensile strength and percent of elongation results are statistically the same of not, JMP (Tukey- Kramer method) was used within 95% confident interval and the result showed that all means have the same grade. That means tensile strength and percent of elongations are not affected by reused water.

Table 4.8. Mean comparison result of tensile and percent of elongation by Tukey-Kramer test

Process types	Tensile strength		Percent of elongation	
	Mean	Grade	Mean	Grade
Process 1	20.265	A	71.40	A
Process 2	21.120	A	71.97	A
Process 3	22.87	A	72.52	A
Process 4	22.08	A	71.20	A
Process 5	21.10	A	70.25	A
Process 6	20.30	A	71.16	A

Table 4.9. Ball burst test result of finished leather for different process types

Process types	Distention		Load	
	Adc (mm)	Adb (mm)	Alc (N)	Alb (N)
Process 1	17.57	18.2	376.3	399.3
Process 2	16.7	17.4	326	388.7
Process 3	16.3	17.6	354.7	392.3
Process 4	18.3	18.8	387.3	401.3
Process 5	16	17.7	344.7	381.7
Process 6	17.1	16.9	368	385

Note: Adc= average distention crack

Alc= average load crack

Adb = average distention burst

Alb = average load burst

Table 4.10. Mean comparison result of Ball burst test by Tukey-Kramer method

Process types	Combination of distention crack and distention burst		Combination of load crack and load burst	
	Mean	Grade	Mean	Grade
Process 1	17.885	AB	387.8	A
Process 2	17.05	AB	357.35	A
Process 3	16.95	AB	373.50	A
Process 4	18.55	A	394.30	A
Process 5	16.85	AB	363.20	A
Process 6	17.00	B	375.50	A

According to Tukey-Kramer test result (Table 4.10) all processes have got the same grade for the combination of load crack and load burst. This indicate that load crack and load bust of the finished leather is not affected by reuse of water.

But the mean comparison result (Table 4.10) for combination of distention crack and distention burst demonstrate that process 1, 2, 3 and 5 have got the same grade AB, process 4 A and process 6 have got grade B. The variations in grade show that there are slightly statistically differences for process 4 and 6 when compared to the other process types. In general, since all grades are not less than B grade the difference are very small and can be within the analysis error indicating that ball burst test is not affected by reuse water.

Table 4.11. Test results of water absorption of finished leather for different process types

Process types	Volume/mass (%)		Volume /volume (%)	
	2hr	24hr	2hr	24hr
Process 1	346.8	382	228	260
Process 2	343	375	216.7	244.5
Process 3	333.6	361.4	226.7	234.2
Process 4	309	316	228	197
Process 5	320	278	179.5	186
Process 6	315	312	214	205

Similar to the above physical tests all pairs of process were compared by using Tukey-Kramer techniques as demonstrated by Table 4.12.

Table 4.12. Mean comparison of water absorption result by Tukey-Kramer test method

Process types	Volume/mass		Volume/volume	
	Mean	Grade	Mean	Grade
Process 1	364.4	A	244.0	A
Process 2	359	A	230.6	A
Process 3	347.5	A	230.45	A
Process 4	312.5	A	212	AB
Process 5	299	A	182.75	B
Process 6	313.5	A	209.5	AB

According to the Tukey-Kramer mean comparison test (Table 4.12) for volume/mass water all process types are graded as 'A' which indicates that there is no statistical difference between the means. But volume/volume water absorption mean comparisons (4.12) show that some products are statistically different. The difference is very close (A, AB & B) and can be within the analysis error.

Table 4.13. Color fastness test results for finished leather of different processes

Process types	Dry fastness			Wet fastness		
	Cycle	On test piece	On felt pad	Cycle	On test piece	On felt pad
Process 1	50 100 150	5 5 5	5 5 5	50	1	3/4
Process 2	50 100 150	5 5 5	5 5 5	50	1	3/4
Process 3	50 100 150	5 5 5	5 5 5	50 100	4/5 1	4/5 3/4
Process 4	50 100 150	5 5 4/5	5 5 4/5	50	¾	1
Process 5	50 100 150	5 4/5 4/5	5 4/5 4/5	50 100	4/5 3/4	¾ 1
Process 6	50 100 150	5 4/5 4/5	5 4/5 4/5	50	¾	1

The degree of staining or change of color is assessed using gray scales and results quoted for dry rub or wet rub. Color fastness test on dry bases as shown on Table 4.13 is excellent for processes 1 to 4 and very good for other processes and color fastness on wet base for all process are good in grade.

In addition to the above six processes, pilot experiment reuse of chrome recovery supernatant for soaking was tested.

The optimum conditions estimated from laboratory experiment were:

Magnesium oxide dose addition = 4. 5g/l

Temperature = 30^{o}C

Mixing period= 1hr

pH= 8. 5

For the starting, 10 liter of tanning liquor with 5 g/l chromium trivalent concentration treated and after treatment the remaining chromium concentration in supernatant was 9.7ppm and pH= 7.35 which is valid for soaking float.

Reusing the above supernatant after chromium recovery in soaking float was tested for three pieces of dry sheep skins in testing drum. The test result show that there was no change both on process and product (chromic oxide content at pickle stage was below detention limit) except the amount of soda ash used for soaking was less by 0.3% with compared to convectional process so that, the supernatant of chrome recovery can be reused for soaking with out any difficulty.

4.3. COST ANALYSIS

Waste minimization will save you money, either as extra profit or in reduced operating costs. An effluent treatment plant will cost less to run if the site produces less effluent in the first place.

Investigating where and how effluent arises, and its composition site will give you a more detailed understanding of how your process affects the operation of effluent treatment plant. However, the first stage is to take action to reduce the site's water consumption and effluent generation.

In this cost analysis fixed capital cost was not considered since most fresh water and waste water minimization is performed for processes which are operational.

Now three cost reduction factors can be considered: 1.cost reduction due to water saving, 2. cost of reduction of effluent treatment reduction and finally 3. Cost reduction due to chemical savings.

4.3.1. Cost reduction due to Freshwater Saving

The case study tannery uses ground and river water for all operations up to tanning operation and starting from tanning to the end operation the tannery uses municipal water.

Amount of fresh water consumed from October, 2010- December, 2010:

Municipal water

Consumption 21,517 m^3

Daily average consumption 717.13 m^3

Market value of the water 81,764.6 Birr (3.8 Birr/m^3)

River water

Consumption 14,034.8 m^3

Daily average consumption 467.83 m^3

Ground water

Consumption 18,748 m^3

Daily average consumption 624.93 m^3

Table 4.14. Summary of cost pretreatment and supply of ground and river water

Types of cost	Item	Quantity	Unit price	Total amount in Birr
Chemical	Aluminum sulphate	136 kg	7.24 Birr/kg	984.64
	Sodium Hypochlorite	85 kg	16.01 Birr/kg	1360.85
Subtotal				2345.49
Electricity	Pump No. 2	5665.5 kwH	0.5778Br./kwH	3273.53
	Pump No. 5	13451.2kwH	0.5778Br./kwH	7772.1
	Pump No. 6	1208kwH	0.5778Br./kwH	697.98
	Pump No. 7	6179.2kwH	0.5778Br./kwH	3570.34
	Pump No. 8	13481.6kwh	0.5778Br./kwH	7789.67
Subtotal				23103.62
Labour	Basic salary			15429.00
	Over time paid			4731.67
Subtotal				20,160.67
General total				45609.78

From Table 4.14, the cost of River and ground water 1.39 Birr/m^3. The water pinch analysis result for bemhouse operations shows that 19000 liter/batch of freshwater was saved. Including the use of chrome recovery supernatant for soaking and washing after soaking the freshwater saved is 32000 liter/batch. Daily on average the tannery processes two batch so that the total freshwater is 64m^3/day.

Fresh water saving cost in bemhouse operations = 64 m^3/day * 1.39 Birr/m^3 = 88.96 Birr/day

= 300days/year* 88.99 Birr/day

= 26688Birr/year

Fresh water saving cost in tanning operation = 24 m^3/day * 3.8 Birr/m^3

= 91.2 Birr/day

= 300days/year* 91. 2 Birr/day

= 27360 Birr/year

4.3.2. Cost for Reduction of Effluent Treatment

To treat the effluent the tannery has chemical cost, electric cost and labor cost.

Table 4.15. Chemical cost of ETP

Name of the chemicals	Price (Br./kg)	Quantity (kg)	Total amount (Birr)
Aluminum sulphate	7.24	2200	15928.00
Poy electrolyte	26.26	27	709.02
Lime powder	2.366	120	283.92
Manganese sulphate	27.49	1175	32300.75
Total			49221.69

Considering 23221.68 m^3 of effluent treated in this quarter, the chemical costs will be 2.12 Birr/m^3.

Table 4.16. Electric cost (0.5778/KWH)

Name of machines	Quantity	Power (kw)	Total working hours	KWH	Total cost (Birr)
Brush screen	2	1.5	1379:5	2069.25	1195.6
Sulphide pump	1	2.2	345:9	760.98	439.7
Chemical dosing pump	3	0.5	1127:3	563.7	325.7
Mixer dosing pumps	3	2.2	310:2	682.44	394.3
Equalization pumps	1	3.0	435:6	1306.80	755.1
Scrapper	1	0.55	291:6	160.38	92.7
Mixer on equal and sulp tank	3	15.0	38:8	582	336.3
Mixer on flocculation tank	1	3.0	435:3	1305.9	754.5
Mixer on lime milk tank	1	2.2	0:8	1.76	1.0
Mixer on sludge tank	1	2.0	672	1344	776.6
Screw pump	4	5.5	7:5	41.25	23.8
Piston pump	2	3.0	152	456	263.5
Filter pump	2	4.0	1360	5440	3143.2
Conveyer belt	2	2.2	4:3	9.46	5.5
Compressor	1	37.0	709:9	26266.30	15176.7
Total					23684.5

Considering the total amount of effluent 20196.1 m^3 treated in this month the average chemical cost will be 1.03 Birr/ m^3.

Labour cost

Considering both basic and overtime paid salary the labour cost is 0.38 Birr/m^3.

Then total running cost of the treatment = chemical cost + Electric cost + labour cost

= 2.12 +1.03 + 0.42

= 3.56 Birr/m^3

Cost of reduction of wastewater generation by 92m^3/day with the help of water pinch analysis and reuse of chrome recovery supernatant in soaking = 92m^3/day *3.56 Birr/m^3

= 327.52 Birr/day

= 300days /year*327.52 Birr/day

= 98256 birr/year

4.3.2.1. Chrome Recovery Costs

Table 4.17. Shows chemical, electrical and labor costs for chrome recovery

Types of cost	Item	Quantity	Unit price (Birr)	Total (Birr)
Chemical	Magnesium oxide	216 kg	19.7291	4261.5
	Sulphuric acid	92 kg	8.045	740.1
	Subtotal			5001.6
Electricity	Submersible pump	202*23hr	50.6	29.24
	Precipitation mixer	2.2*35hr	77	44.5
	Screw pump	1.5*0.4hr	0.6	0.35
	Dissolution mixer	2.2*16.24hr	35.73	20.6
	Fan	0.37*21.5hr	7.96	4.6
Subtotal				99.3
Labour		2	856.5	1713
General total				6813.9

Amount of 21% chrome sulphate recovered for this quarter is 108819 kg which costs 21238.5 Birr (19.5147 Birr/kg).

Net saving = 21238.5-6813.9

= 14424 Birr for the quarter which is 57696 Birr/year

4.3.3. Cost of Chemical Saving During the Reuse of Water

Amount of chrome saved when washing after shaving was used for tanning float can be estimated as follow:

Since the concentration of the waste is 0.5g/L of chrome, within 12000 liter per batch we will save 6kg of chromium which saves 6*2 * 19.5147 =234 Birr per day

= 300days/year*234 Birr per day

= 97200 Birr/year

Over all reduction cost of the tannery = freshwater saving cost+ wastewater treatment saving

Cost+ chemical saving cost in reuse and chrome recovery

= 26688 +27360 +98256+57696+97200

= 307200 Birr/ year

So that if the case study tannery implement this water pinch technology the operating cost will be reduced by 307200 Birr/ year. More ever, if all the effluent parameters meet according to the Ethiopian environmental standard the operating cost reduction will be greater.

5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

The problems of environmental damages from wastewater discharge, increasing expenditures for freshwater supply and wastewater treatment have led researcher to find several options for freshwater utility minimization especially in the tanning industries with high rates of water consumption. Pinch analysis is introduced as an option for water and wastewater minimization. The method mentioned in this study is graphical methods for pinch analysis which is easily understandable for users.

Test in pilot scale enable the leather behavior to be verified at each step of the process and an easy comparison between processes with and with out water reuse. Leathers obtained in the test with and with our water reuse has no difference both in chemical and physical tests that means their quality was unaffected with reuse of water. The reuse of the liquors from the de-liming in the presoaking and main soaking, of liquors from bating washing 3 in the bating washing 2 and 1 and of liquors from washing after shaving in the tanning operation, was found feasible.

The following conclusions can be drawn from the application of the methods discussed in this thesis to the industrial case studies:

1. There is a significant decrease in the minimum freshwater requirement of a system with the reuse and regeneration of wastewater as compared to systems without reuse. The reduction in freshwater requirement with reuse according to the pinch analysis is 31 % and including the reuse of chrome recovery supernatant in soaking, freshwater requirement or wastewater generation reduced by 44%.
2. The process of regeneration reuse gives a greater reduction in minimum freshwater requirement as compared to only reuse.
3. This result has greater potential because we only apply simple reuse with small costs and results in much cost savings both in freshwater cost and effluent treatment costs which leads to a decrease in the total annual operating cost of the system by 307200 Birr/ year.

   Thus the process of wastewater minimization through pinch analysis is a powerful tool in process integration and plays a significant role design of the conventional water reuse project, by identifying a minimum freshwater flowrate and key water reuse opportunities.

5.2. Recommendations

It is recommended that more contaminants are considered for study of water networks and reach water utility optimization based on key contaminant as well. Besides, graphical method, mathematical optimization methods and computer programming could be used to obtain results that are more exact. Clearly, water minimization through single contaminant approach was more considerable. However, results based on multiple contaminants (i.e. mathematical optimization and computer programming) approach are more precise than single contaminant.

Based on the case study result, tanneries are highly recommended to use the freshwater and wastewater minimization water pinch technique that results in the maximum environmental protection and cost reduction. Moreover for new establishment of tanneries consideration of water pinch analysis for the design of water network is recommended.

The basic message of Water Pinch analysis should be the starting point: don’t solve an End-Of-Pipe problem with an End-Of-Pipe solution. Unless you have explored the in process solutions, your End-Of-Pipe solution could be the worst solution to your problem.

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ANNEXES

Annex 1: Working recipe from soaking to tanning

COMPANY: LIDI-Leather Manufacturing Technology Directorate Wet salted Hair sheep skin soaking and liming process sheet Note: % based on wet salted Wt								
Process	Chemicals	%	Kg/Lt	Temp[^oC]	Time	Control		Remarks
						Standard	Actual	
	Load skins into drum							
Presoaking 2X	Water	To cover		RT	10’			Drain though valves while drum is running 10’
	Water	250		RT				
	Wetting agent	0.2						
	Bactericide	0.1			30’	Be^0 (0.5/0.1)		Drain
2X	Water	250		RT	10’	Be^0 (0.5/0.1)		Drain while drum is running
Main soaking	Water	250		RT				
	Soaking enzyme	0.3						
	Wetting agent	0.2			30’			
Adjust P^H	Soda	0.4/0.8			20’	P^H(9/9.5)		
	Run /stop the drum				40’/ 20’			
	Liming Auxiliary	1.0			60’			Then stop for 20’
	Drain while the drum is running							
	Water	To cover		RT	10’			Check cleanness bath, drain
	Unload pile for the skin for 30’							
Painting +de wooling	Paint the flesh side of the skin, Pile flesh to flesh and keep the pile for 3-4hrs, then un-hair completing							
	Make up float	150			RT			
	Lime powder	0.5						
	Liming auxiliary	0.5			15’			
	Add dewooling skin				20’			
	Sodium sulphide flakes	0.5			30’	S^{2-} content		
	Surfactant having degreasing power	0.1			20’			Run 10’/hr for O/N
Next day	Run in cold water drum running – valves open				10’			Un load for fleshing

Deliming – Tanning Hair Sheep Skin process sheet Note: % based on fleshed Wt								
Process	Chemicals	%	Kg/Lt	Temp[^{o}C]	Time	Control		Remarks
						Standard	Actual	
	Load fleshed skins into empty drum				10’			
Washing	Water	100		35	10’			Drain though valves while drum is running 5’
	Water	100		35	10’			Drain though valves while drum is running 10’
	Water	200		35	10’			Drain though valves while drum is running completely
	Water	80		35				
Deliming	Ammonium sulphate	1.2			20’			
	Ammonium sulphate	0.3						
	Wetting agent	0.3						
	Sodium bisulphate	0.3			30’	P^{H}(8/8.2)		Drain through valves
Bating	Water	100		35				
	Bating agent	0.25						
	Ammonium sulphate	0.20			60’			Drain completely
	Common salt	1.0						
	Degreasing agent	3			40’			Drain through valves for 20’
	Water	100		37				
	Common salt	2			20’			Drain through valves for 20’
	Water	100		37				
	Common salt	1			20’			Drain through valves for 20’
	Water	250		cold	10’			Drain completely
Pickling	Water	30		cold				
	Common salt	8			10’	Be^{0} (6.5/7.5)		
	Formic acid (1:5cold)	0.5			30’		P^{H}___	
	Sulphuric acid (1:10cold)	0.6			60’	P^{H} (2.8/3.2)		
Adjust P^{H} ifany	Anti fungus	0.1			30’			

Process	Chemicals	%	Kg/Lt	Temp[^oC]	Time	Control		Remarks
						Standard	Actual	
Tanning	Load skins into drum							
	Chrome 33% B	3			45’			
	Self basified chrome	5			120’		P^H____	
	Water	70		40	60’			
	Sod bicarbonate (1:20@33^{0}C)	0.2			20’	P^H (3.7/3.9)	P^H____	
	Sod bicarbonate (1:20@33^{0}C)	0.2			20’	P^H (3.7/3.9)	P^H____	
If necessary	Sod bicarbonate (1:20@33^{0}C)	0.2			20’	P^H (3.7/3.9)	P^H____	
	Run the drum				30’			
	Anti fungus	0.5			30’			
	Water	100		40	15’			Discharge for piling

Annex 2: Recipe for post tanning

COMPANY	LIDI			**TECHNICIAN :**
TYPE OF LEATHER	SHEEP NAPPA UPPER		**COLOUR:** NATURAL	**COMPANY :**
INPUT MATERIAL	**SIZE:**	**QUANTITY:**	**WEIGHT:**	**PH NO. :**
	GRADE:	**THICKNESS:** 0.8/0.9mm		**E- MAIL :**

Process	**%**	**Te (^OC)**	**Chemicals**	**Time**	**pH**	**Remarks**
WETTING BACK	200	30	WATER			
	0.4		ACETIC ACID			
	0.5		TRD-78E	40’		DRAIN/WASH/DRAIN
DEGREASING	50	45	WATER			
	2.5		SELESAL DLA	40’		Check:
	200	30	WATER	10’		DRAIN/WASH
RECHROMING	150	35	WATER			
	0.5		FORMINC ACID (1:10 cold)	15’		
	0.5		CATIPOL GS	15’		
	3		CHROME (33% B) }			
	2		SINTAL TAN 40 SC }			
	2.5		GENCRYL QS }	60		
	2.5		GENETAN LD	20’		
	1		FOSFOL AUT C6	15’		
BASIFICATION	0.8		SODIUM FORMATE (1:5 @30 ^{0}C)	10x10’		
	0.8		SODIUM BICARBONATE (1:10 @30 ^{0}C)	10x10x10’	3.8/4.0	L/O/N,
DAY 2			MORNING: RUN	5’		DRAIN ,
NEUTRALIZATION	200	30	WATER			
	0.8		SODIUM FORMATE (1:5 @ 30 ^{0}C)	10x10’		
	0.8		GENETAN NEUTRO A2 }			
	0.7		GENETAN LX }	30’		
	0.5		SODIUM BICARBOBATE (1:10 @ 30 ^{0}C)	10x10x10’	5/5.2	Ø (BCG):

COMPANY	LIDI				TECHNICIAN :	
TYPE OF LEATHER	SHEEP NAPPA UPPER		COLOUR: NATURAL		COMPANY :	
INPUT MATERIAL	SIZE:	QUANTITY:	WEIGHT:		PH NO. :	
	GRADE:		THICKNESS: 0.8/0.9mm		E- MAIL :	

			DRAIN/WASH/DRAIN			
RETANNING	100	45	WATER			
	1.5		SEROIL L (1:10 @ 60 ^{0}C)	20’		
	5		SINTAN SO	5’		
	5		MIMOSA			
	4		QUEBRACHO			
	2.5		GENECRYL QS	50’		
	3		RETANAL MD 80			
	2.5		SERTAN DC	60’		
	100	60	WATER			
	2		NELFILL POWDER	20’		
FATLIQOURING	2		FOSFOL 54			
	1		SEROIL L			
	0.5		SOLFIPOL OS/LA			
	1.5		CORELIN UL (1:10 @ 60 ^{0}C)			
	0.1		TRD-78E			
	0.1		PREVENTOL WB	3x10 + 30’		
	1		SERFIX D (1:3 cold)	20’		
	2.5		FORMINC ACID (1:10 cold)	3X5’ + 30’		Exhaustion=
						DARAIN WASH/PILE

Annex 3: Recipes for dyeing

COMPANY	LIDI-LEATHER MANUFATURING TECHNOLOGY DIRECRORATE				TECHNICIAN :
TYPE OF LEATHER	SHEEP NAPPA UPPER DYEING RECIPE		COLOUR:		COMPANY :
INPUT MATERIAL	SIZE:	QUANTITY:	WEIGHT:		PH NO. :
	GRADE:				E- MAIL :

Process	%	Te (^{O}C)	Chemicals		Time	Remarks
ADD	1000	35	WATER			
	0.8		SURFACTANT			
	1		AMMONIA LIQUID		120’	THEN L/O/N,
NEXT DAY DRAIN THE BATH						
ADD	100	50	WATER			
	0.5		DYE dispersing agent	paste and		
	4		DYE STUFF	dilute@60 ^{0}C	20’	
	0.5		AMMONIUM SOLUTION		60	CHECK Ø
ADD	300	60	WATER			
	4		Sulphated fatliquor			
	1		Sulphited fatliquor	mix well		
	3		Electrolyte stable fatliquor	and		
	2		Water proofing fatliquor	dilute		
	1		Treated fish oil	1:10 @ 60 ^{0}C		
	0.1		Surfactant			
	0.1		Anti fungus		3x10+30’	

COMPANY	LIDI-LEATHER MANUFATURING TECHNOLOGY DIRECROATE		**TECHNICIAN :**
TYPE OF LEATHER	SHEEP NAPPA UPPER DYEING RECIPE	**COLOUR:**	**COMPANY :**
INPUT MATERIAL	**SIZE**: **QUANTITY:**	**WEIGHT:**	**PH NO. :**
	GRADE:		**E- MAIL :**

	1		Dye fixing agent	20’	
	3		Formic acid(1:5cold)	5x5x5+30	Check exhaustion drain
ADD	100		Water		
	0.5		dye stuff(paste &dilute @)50 ^0C	20’	
	1		Formic acid (1:5 cold)	30’	
	150	45	Water	10’	Check exhaustion drain/wash/pile O/N

Annex 4: Provisional standards for discharge of effluent by Ethiopian leather tanning and finishing industries

Parameter	**Limit Value**
Temperature	40 °C
pH	6 – 9
BOD_5 at 20^0C	90% removal or 200 mg/l, whichever is less
COD	500 mg/l
Suspended solids	50 mg/l
Total ammonia (as N)	30 mg/l
Total nitrogen (as N)	80% removal or 60 mg/l, whichever is less
Total phosphorus (as P)	80% removal or 10 mg/l, whichever is less
Oils, fats, and grease	15 mg/l
Mineral oils at oil trap or interceptors	20 mg/l
Chromium (as total Cr)	2 mg/l
Chromium (as Cr VI)	0.1 mg/l
Chlorides (as Cl)	1000 mg/l
Sulphides (as S)	1 mg/l
Phenols	1 mg/l

Annex 5: Effluent analysis test result of ELICO from July/2010 to September/2010

S.R	Characteristics to be tested	Test result	
		Inlet (untreated)	Outlet treated
1	pH	7.83	7.65
2	COD (mg/L O_2)	9348.6	2593.5
3	BOD_5	-	-
4	Cr_2O_3 (mg/Rt)	0.034	0.015
5	Na_2S (mg/Kg)	0.397	0.014
6	Salinity (gm/kg)	7.56	8.43 (* 2.42)
7	Settleable matter (mL/L/)	5.54	0.132
8	Suspended matter (mL/L)	0.2	0
9	TDS (mg/L)	16321	7304.30

Remark: * salinity is expressed choride content

Annex 6: Pictures of some common machines used in leather manufacturing process:

Fleshing machine

Samming machine

Auto spray machine

shaving machine