

3003

INTRODUCING CLEANER PRODUCTION OPTIONS TO THE LEBANESE TANNING SECTOR

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MINISTRY OF THE ENVIRONMENT

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1. Introduction

1.1 General Overview

The Industrial Sector in Lebanon with its operations is a source of considerable environmental impact leading to high levels of pollution. Many of those impacts are on the health and safety of individual workers and the public. In addition, the deterioration of natural resources resulting from pollution can have a negative effect on the long-term growth potential of the country, even if immediate economic benefits may be gained by individual enterprises.

The Ministry of Environment (MoE), being aware of this serious situation, plans to ameliorate the problem by promoting environmentally sound basis for industrial operations. This includes the introduction of cleaner production options based on the best available technologies, good housekeeping, appropriate waste treatment, and adequate environmental monitoring.

To prioritize the industrial sectors according to their potential environmental impact, the Unit of Planning and Programming (UPP) at MoE has conducted a study using the Decision Support System for Industrial Pollution Control (DSS/IPC). Two hundred industrial questionnaires were collected from different industrial sectors, and thirty-four environmental reviews were conducted accordingly. The study has identified the tanning industrial sector as a primary priority because of its diverse environmental impacts. In addition to the traditional air and water pollution problems attributed to tanneries, the increased use of chemicals have led to: serious land and ground water contamination, spills and accidents involving chemical substances, solid and hazardous wastes disposal issues, waste water and sludge sophisticated treatment, and the general nuisance of odor and noise from installations have become important issues to be addressed.

As the study done by MoE, and UPP (using DSS/IPC) has identified the tanning sector as a primary priority because of its diverse environmental impacts, whose objectives were:

As a result, the Ministry of Environment has contracted Envirotech Ltd. to conduct an environmental audit on one selected tannery. The results of the audit shall be used to identify cleaner production options and promote efficient operations at both the economic and ecologic levels.

1.2 *Scope of the Study*

1.2.1 Objectives

1. To promote economically and ecologically efficient operations and encourage the dissemination of environmentally sound technologies related to the industrial sector in Lebanon.
2. To train and build the capacity of the private sector to adopt new technologies.

1.2.2 Project Outputs

1. The transfer of knowledge and environmentally sound processes will promote cleaner technologies at the local level.
2. The experience and knowledge gained by government and industrial staff at which audit took place would be used to replicate the work at other industries.

1.2.3 Methodology and Terms of Reference

The consultant submitted to MoE a detailed work plan for the implementation of the study. The workplan was prepared in consultation with the counterpart staff at the MoE along with UPP and Capacity 21 experts. The consultant selected the most polluting sector as identified by the UPP DSS study. From that sector, one 'typical facility' was selected for an environmental audit.

The contents of the workplan included the following topics:

1- Conducting detailed environmental audit:

The facility was thoroughly reviewed with respect to environmental impacts, with the ultimate aim of identifying cleaner production options.

The following aspects were considered

- General conditions of the facility (process, operation, management...)
- Raw materials and auxiliaries flow: input/output

- Storage, internal movement, handling, processing, labeling and packaging of ^{raw} materials used
- Water consumption pattern, quality and alternative sources
- Energy usage, consumption patterns, efficiency of the combustion process, losses and reuse of the heat generated
- Quantities and nature of waste, waste water and emissions to air

The environmental review gave a good overview of the status, working conditions, emissions and discharges. This led to the following evaluation stage.

2- Evaluation of cleaner production options (technical and financial):

- Optimization of production processes
- Minimization of waste at the source and pollution prevention
- Safe housekeeping practices
- Saving in raw materials and utilities
- Energy conservation
- Water conservation
- Recycling and reuse of byproducts
- Treatment of effluents and emissions
- Possible replacement of hazardous raw materials with non-hazardous materials

3- Establishing dissemination and training program:

The study will be complemented with a training workshop for the Ministry of Environment, Ministry of Industry, Lebanese Industrial Association, Industries of selected sectors, concerned NGOs and other stakeholders identified by MoE. These training programs are to expose the steps followed throughout the case study that have led to the identification of cleaner technology options.

Figure 1 illustrates the project activities.

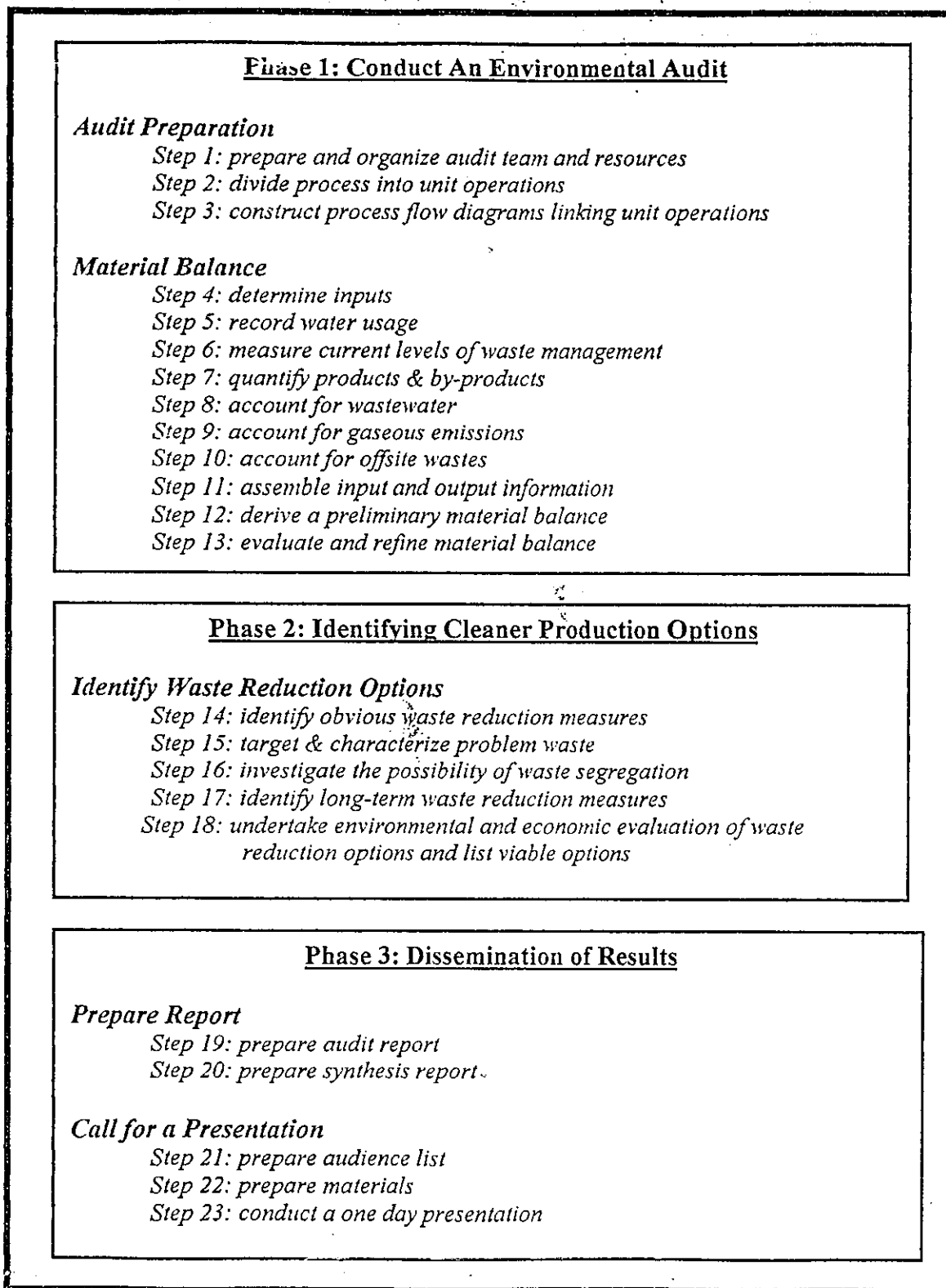


Figure 1: Illustration of the Project Activities

1.3 *The Lebanese Tanning Industry*

1.3.1 Geographical Distribution

The tanneries in Lebanon are geographically distributed in five areas:

Area A: Dora and Jounieh areas

Area B: Saida

Area C: Wadi Chahrour

Area D: Bzemmar and Machghara

Area A: Tanneries are located on the coast within or close to Beirut, for a total of 13 tanneries;

Area B: Saida producers are also located in coastal areas to the south of Beirut, for a total of 7 tanneries.

Area C: 4 tanners, including one major unit, are already located in an industrial area, namely Wadi Chahrour.

Area D: 2 individual tanners are located in separate distant mountainous areas, in Machghara and Bzemmar.

Thus the total number of active tanneries is 26 units. The surface of each, ranging between 600 m² and 13,000 m².

1.3.2 Economic Data

The present economic difficulties didn't prevent some Lebanese tanneries from replacing or updating their old equipment with some newer ones. This kept Lebanon's know-how in this field, among the best in the Middle-Eastern region. Regarding the national production, about 30 000 000 US\$ are generated annually, coming from the hides' and skins' leather production. Close to 1000 hides and 6000 skins are produced daily by all the national tanneries. These, are afterwards sold to various leather goods industries (shoes, hand-bags, belts, etc.). However, the actual recession is inhibiting the potential development of the whole sector, which lead to a complete loss of

several pre-war markets. Moreover, the repercussions of this slow down were also largely felt at the level of the leather goods industry in general. An example could be the case of the shoe industry, seeing its national yearly production decreasing from 10 to 12 million pairs, to close to 4 million pairs a year. Socially the whole leather sector plays an important role due to the hundreds of jobs it generates.

1.3.3 Production

The majority of Lebanese tanneries conduct the whole tanning process from its earliest stage (trimming, soaking) to the last (finishing), while others might stop their process at the pickling or wet-blue stages.

The national daily leather production amounts approximately to 80000 ft² divided into two general categories:

- Cow hides.
- Skins (Sheep, goat, etc.).

Cow hides constituting nearly 50% of the whole production (i.e. 40000 ft²), their price varying from 1.5 to 2.00\$ per ft². While sheep or goat leather is usually sold at a slightly lower price (1.00 to 1.25\$ per ft²).

The following table gives an estimate of the yearly production (250 working days/year).

Table 1: Estimation of Yearly Production

| | Total Daily Production In ft ² | Average Price Per ft ² | Average Daily Production In (USD) | Average Yearly Production In (USD) |
|---------------|---|-----------------------------------|-----------------------------------|------------------------------------|
| Hides | 40,000 | 1.75\$ | 70,000\$ | 17,500,000\$ |
| Skins | 40,000 | 1.12\$ | 44,800\$ | 11,200,000\$ |
| Totals | 80,000 | | 114,800\$ | 28,700,000\$ |

2. The Tanning Process

2.1 Introduction

Tanning is the process by which animal hides and skins, the by-products of the meat industry, are converted into leather. There is no single process for producing leather. Different techniques are used depending on the type of skin to be processed and the intended end use of the leather product. While the exact specifications and procedures vary considerably, especially in the re-tanning and finishing procedures, the basic processes are common to all tanning operations.

The hides and skins are usually received at the tannery in a cured form rather than raw. To reach the tannery in an acceptable condition, hides and skins are preserved by drying, salting, or chilling at abattoirs. In some cases, environmentally persistent toxic chemicals are being used for preservation purposes. In addition, hides and skins are often treated with insecticides to discourage beetle and other insect attack during storage and transportation.

In the tanning process, animal hides and skins are treated to remove hair, non-structured proteins and fats. They are then treated with chemicals, which cross-link the microscopic collagen fibers to form a stable, durable material. The chemicals used may be derived from traditional vegetable products, or prepared by industrial chemical suppliers.

The tanning process for leather production usually involves three distinct phases:

- Beamhouse (Preparation Phase)
- Tanyard (Tanning Phase)
- Finishing (including re-tanning, dyeing and surface treatment)

2.2 *Beamhouse*

The Beamhouse is a preparation stage where hides and skins are prepared for tanning by cleaning and conditioning. It's typical steps are:

2.2.1 Soaking and Rinsing

Soaking and rinsing are applied to hides and skins in pits, paddles or drums. Its objective is to remove salt and to rehydrate the skin to reverse the cure process, i.e. restore the moisture contents of the skins. By rinsing, foreign materials would be removed. Those include blood, dirt, manure and dung. Chemicals used are Sodium Hydroxide, Sulphide, Sodium Hypochlorite, wetting agents, emulsifiers, surfactants, and enzymes.

2.2.2 Liming

Liming is performed to remove the interstitial material, thus it opens up the collagen structure and "plumps" the hide. Sodium Sulphide is blended with lime to loose wool and hair or dissolves them into pulp. This step requires 8 hours in a drum and up to 7 days in a pit. Chemicals used are Calcium Hydroxide, Sodium Sulphide, Sodium Sulphydrate, caustic soda, and enzymes.

For rapid and economical subsequent processing, hides should be split after liming. But since it is technically easier to split hides in its tanned form, splitting is rarely done at this stage.

2.2.3 Fleshing

Fleshing is done to remove excess tissue from the interior of the limed hides (pelts). Hides are fleshed mechanically and the adipose tissue is removed. Fleshing machines are equipped with a rubber roller and a shaft to which spiral knives are attached leaving a clean uniform surface. In some cases fleshing is done manually. It is recommended to perform fleshing immediately after soaking so that the removed

flesh may be used as a by-product since it still doesn't contain chemicals. This known as Green Fleshing.

2.2.4 Deliming

At this stage, lime is removed from the pelt to prepare hides and skins for tanning. Pelts are then washed thoroughly with running water for a set period of time. Neutralizing chemicals are then applied. They include acids, acidic salts, Ammonium Chloride or Sulphate, Sodium Bisulphite, and Hydrogen Peroxide.

2.2.5 Bating

Bating depends on the enzymatic actions on the grains of pelts affecting the stretch of subsequent leather. The enzymatic action requires 0.5% bating agents for 30 minutes and up to 12 hours. In old times, dog dung or pigeon droppings were used instead of bating agents. Typically, the bating agents are composed of wood flour (as a carrier), Ammonium Chloride (deliming agent), and pancreatic enzymes.

2.2.6 Pickling

Pickling is the final step in the Beamhouse. Pickling is applied to achieve a low pH, thereby sterilizing the skins, ending the bating action, and improving the penetration by increasing the solubility of the tanning chemicals. Chemicals used are salts such as Sodium Chloride or sodium Sulphate, acids (Sulfuric, Hydrochloric, Acetic or Formic) and fungicides.

2.3 *Tanyard*

2.3.1 Tanning

Tanning stabilizes the collagen structure of the hides and skins, and imparts them with their basic properties. Tanning chemicals are either natural or synthetic.

1. Chrome Tanning

Chrome is the most commonly used tanning agent. Hides and skins are chrome tanned in drums for 4 to 24 hours. Chemicals used are basic trivalent Chromium Sulphate, hydrated complexes, Sodium Bicarbonate (basifying agent to adjust pH), Sodium Formate (masking agent), Phthalate or salts of Dicarboxylic acids, and fungicides.

2. Vegetable Tanning

Vegetable tanning usage is declining. It is being only used for sole and saddlery, and some specialty leathers. Vegetable tanning in drums takes 1 day and 6 weeks in pits. Substances used are commercial tanning extracts that are extracted aqueously from bark or wood of trees. The extract is often sulphitated and then spray dried or concentrated.

2.4 *Finishing*

The finishing phase includes re-tanning, dyeing, and fat liquoring to impart special properties to the leather, increase penetration of tanning solution, replenish oils in the hides and impart color to the leather.

2.4.1 Re-tanning

Re-tanning involves further processing of the stabilized collagen network when special characteristics such as perspiration resistance are required. A combination of chrome, vegetable, glutaraldehyde, or syntan agents is often used.

2.4.2 Mechanical Operations

Following tannage, certain mechanical operations are performed to level the surface of the leather. They include:

- Sammying by pressurized rollers to remove excess moisture.
- Splitting the leather into two.
- Shaving to level the surface and remove surplus material.
- Trimming to shape up the edges of the leather.

2.4.3 Surface Finishing

After drying and mechanical treatment, leather goes into its final finishing process i.e. surface treatment. The surface coatings consist of dyes or pigments dispersed in a blender, typically casein or an acrylic or polyurethane polymer, and are applied by padding, spraying or rolling. Nitrocellulose lacquer or urethane lacquer may be applied with organic solvents as top coats. Non-solvent based finishing substances is replacing aqueous solvents. Chrome VI is occasionally used for dyeing.

3. Tanneries and the Environment

3.1 Background

It is noted that environmental pollution related to tanneries in many countries is still serious as a great deal of control remains to be implemented. Typical environmental complaints expressed by the public concerning tanneries are odors and water pollution from untreated effluents. However, governmental bodies, environmental authorities and non-governmental organizations are heavily addressing other serious pollution problems. In addition to rapid environmental degradation especially on land and water, problems are mainly related to the increased use of toxic persistent synthetic chemicals such as pesticides, solvents, dyes, and finishing agents. The new chemicals used in the tanning process impart diverse negative health effects on humans. They create an occupational health hazard at the workplace leading to morbidity, injury, and even death of exposed workers.

The diverse environmental impacts of the tanneries affect many environmental parameters including surface water, land, ground water, air, and waste management systems. Chart 1 illustrates the diverse impacts on water and air and the generation of solid waste.

3.2 Impact on Surface Water

Untreated tanneries' wastewaters are often discharged into neighboring surface water bodies, namely rivers or small water canals, and eventually reach the sea. Such effluents deteriorate rapidly the physical, chemical, and biological properties of the receiving water bodies. Loads of organic matters decompose at a high rate in water giving rise to noxious odors, and depleting the dissolved oxygen in water, which is needed for its decomposition. As oxygen is vital for aquatic life, its decrease would highly affect water biodiversity and alter its existence. Animal hides and skins are usually received in a cured form at the tannery, thus carrying large amounts of salt.

After soaking and rinsing, the resulting brine solution mixes with receiving water bodies turning them saline and hard due to the presence of inorganic salts. Toxic substances from the soaking and rinsing of cured hides and skins are also released. Water consumption is a critical issue in environmental analysis of an industry and especially a tannery. Water is a sensitive environmental parameter with regards to its quality and quantity. The increased levels of environmental pollution have deteriorated water quality, thus decreasing the amounts available for consumption in an acceptable quality. With the increase in water consumption for domestic, agricultural and industrial purposes, and with the improper management of water resources, water supply is becoming insufficient in many countries and notably in Lebanon. In addition to the increase in water demand, the increase in water use in the tanning process would increase the use of chemicals, and increase wastewater loads. Consequently, the increased pollution loads needs treatment plants with larger capacities thus increasing the treatment costs.

3.3 Impact on Land

The tannery site and layout, specifically pits, lagoons, storage areas, and waste dumps may severely damage the underlying soil. This damage would alter subsequent land use for agriculture, recreation, or even building. It also accelerates soil erosion. Soil damage occurs when the pollutant load is larger than the neutralizing capacity of the soil. If the soil structure is damaged, its agricultural production capacity would decrease, and it would take a long period of time for soil to recover. Therefore, pollutant levels should be continuously monitored especially of the treated effluent is to be dispersed on land or used for crop irrigation. Dumped wastes on land would stagnate and produce noxious odors. All tanning pollutants affect soil, but the most significant are Chrome and Sodium that alters the Sodium Absorption Ratio (SAR). The substitutes of Chrome, namely Zirconium, Titanium, and Aluminum in large amounts have detrimental effect on plant growth. Land pollution would subsequently lead to groundwater pollution due to high salt content and toxic components.

3.4 Impact on Ground Water

Ground water is an important source of water supply for many communities. Its self-purification capacity is less than that of surface water as it moves slowly and is out of contact with air. Ground water contamination occurs when waste water and chemicals seep through soil from unlined ponds, pits, pipes and drains, or from dumps, spills, and direct discharge of effluents on land. Significant pollutants are Chlorides, Tannins, Sulphates, Sulphides, and all trace organic chemicals and solvents. Nitrogen in large amounts in water is a serious threat to health, especially for babies.

3.5 Impact on Air

The major characteristic of air pollution from tanneries is its noxious odor. It is due to the biological decomposition of organic materials, as well as to Sulphide emissions from wastewater. The acidification of liquids still containing Sulphides generates toxic Hydrogen Sulphide gas. With prior treatment using Hydrogen Peroxide or Sodium Bisulphite to oxidize the Sulphides, this problem would be avoided. Sources of odors from the tanning process are: Sulphide emissions from de-hairing and waste treatment; Ammonia emissions from un-hairing and de-liming liquors, and from fleshings. In the finishing operations, emissions from solvents impose a workplace health problem. If efficient technology with controlled operations is used, these emissions would be avoided. Leather dust is considered as a potential carcinogen for exposed workers. Typical air pollution contaminants such as CO, CO₂, NO_x, and SO_x are also emitted from tanneries by the use of boilers and generators.

3.6 Impact on Waste Management Systems

Solid wastes from tanneries to be disposed of in landfills create highly objectionable odors. Special linings and leachate treatment systems to control sweepings of hazardous chemicals to ground water should be installed in landfills receiving solid wastes from tanneries. Some containers of chemicals used by tanners are found in open dumps and are being re-used by people resulting in poisoning and adverse health

effects. Sludge disposal in industrial waste dumps has led to severe groundwater contamination.

Tanneries' wastewater cause encrustation of Calcium Carbonate in sewers. High Sulphides and Sulphates concentrations would increase the corrosiveness and deterioration of concrete or cement. Chrome and other toxic components interfere with the biological processes in sewage treatment plants.

3.7 Effect on Human Health

Tanneries are well recognized for their effect on human health especially on workers inside the premises of the production sites. The nature of chemicals used in the tanning process imposes occupational health hazards to exposed workers. Due to their toxicity, direct contact with industrial chemicals may cause disability, illness and death. The toxicity builds up by being frequently exposed even to minor concentrations of the chemicals. Major sources of exposure in the tanning process are vapors from degreasing and finishing solvents. As mentioned before, leather dust has been listed by the European Commission (EC) as a potential carcinogen. Exposure to pesticides is significant during their unskilled handling as well as to the handling of treated hides. The improper packaging, transport, storage, and handling of chemical leads to accidents and spills, thus creating hazards and facilitating direct exposure. The effect of the chrome substitutes in the tanning process is still not well explained. The substitutes are promoted because of their lower environmental impact and not for being safe chemicals. For instance, high levels of Aluminum in drinking water have contributed to the increase in Alheimers disease. The EC lists Titanium as a toxic substance although it is inert in its dioxide form. In some tanneries where old machinery are still used, and when workers are not using personal protection equipment, noise would also pose an occupational hazard.

3.8 *Effects of Most Significant Tanning Pollutants*

3.8.1 Chromium

The use of Chromium in the tanning industry is still a controversial issue due to its different persistence and potential toxicity with its different chemical forms. The most commonly used form in the tanning industry is the trivalent chrome, which has a lower toxicity than the hexavalent form. Trivalent chrome can be readily precipitated from solution, and its potential for conversion to more toxic forms is relatively low. The adverse effects of chrome depend on its chemical state. Diverse effects have been noted on humans, aquatic life, and terrestrial plants. This is realized due to its ability to move between media. The re-use of sludge containing Chromium for irrigation purposes is not recommended as soil damage may occur.

3.8.2 Chrome Substitutes

Chrome substitutes namely Aluminum, Zirconium, and Titanium have a lower acute toxicity than Chromium however, their long term effects on health and the environment are not well investigated. Consequently, their concentration in effluents should be kept as low as possible.

3.8.3 Hydrogen Sulfide

The use of sodium sulfide, sodium sulfhydrate, and organic sulfides for the unhairing process cause the development of hydrogen sulfide (H_2S). H_2S is a poisonous gas that has an irritating effect on the mucous membranes and may paralyze respiration cells, and eventually damages the nerves. The signs and symptoms of H_2S poisoning are inflammation of the eyes, bronchials and lungs. High concentration cause cramps, unconsciousness, and eventually death due to respiratory paralysis. In addition, H_2S forms explosive mixtures with air, therefore it is necessary to avoid ignition sources.

3.8.4 Biological Oxygen Demand (BOD)

BOD is a method of estimating the power of the effluent to reduce the oxygen content of water. Over-application of high BOD effluents on land can create anaerobic conditions in the soil. Prolonged oxygen depletion will reduce the soil microorganisms' capability to break down the organic matter in the effluent that may lead to noxious odor generation and surface and ground water pollution.

3.8.5 Chemical Oxygen Demand (COD)

COD is a method of estimating the chemical reduction power of the effluent and hence its ability to destroy any potential oxygen content of the water. High COD values causes water quality to be altered to one which is comparable to septic water quality, resulting in public health problem.

3.8.6 Total Dissolved Solids

The total dissolved solids or salinity concentration is an important water quality parameter. An increase in salinity causes an increase in the osmotic pressure of the soil solution, resulting in a reduced availability of water for plant consumption and possible retardation of plant growth. Parameters of consideration for irrigation water quality are TDS, Sodium (SAR), and Chromium. Excessive sodium in irrigation water relative to calcium and magnesium can adversely affect soil structure and reduce the rate at which water moves into and through the soil.

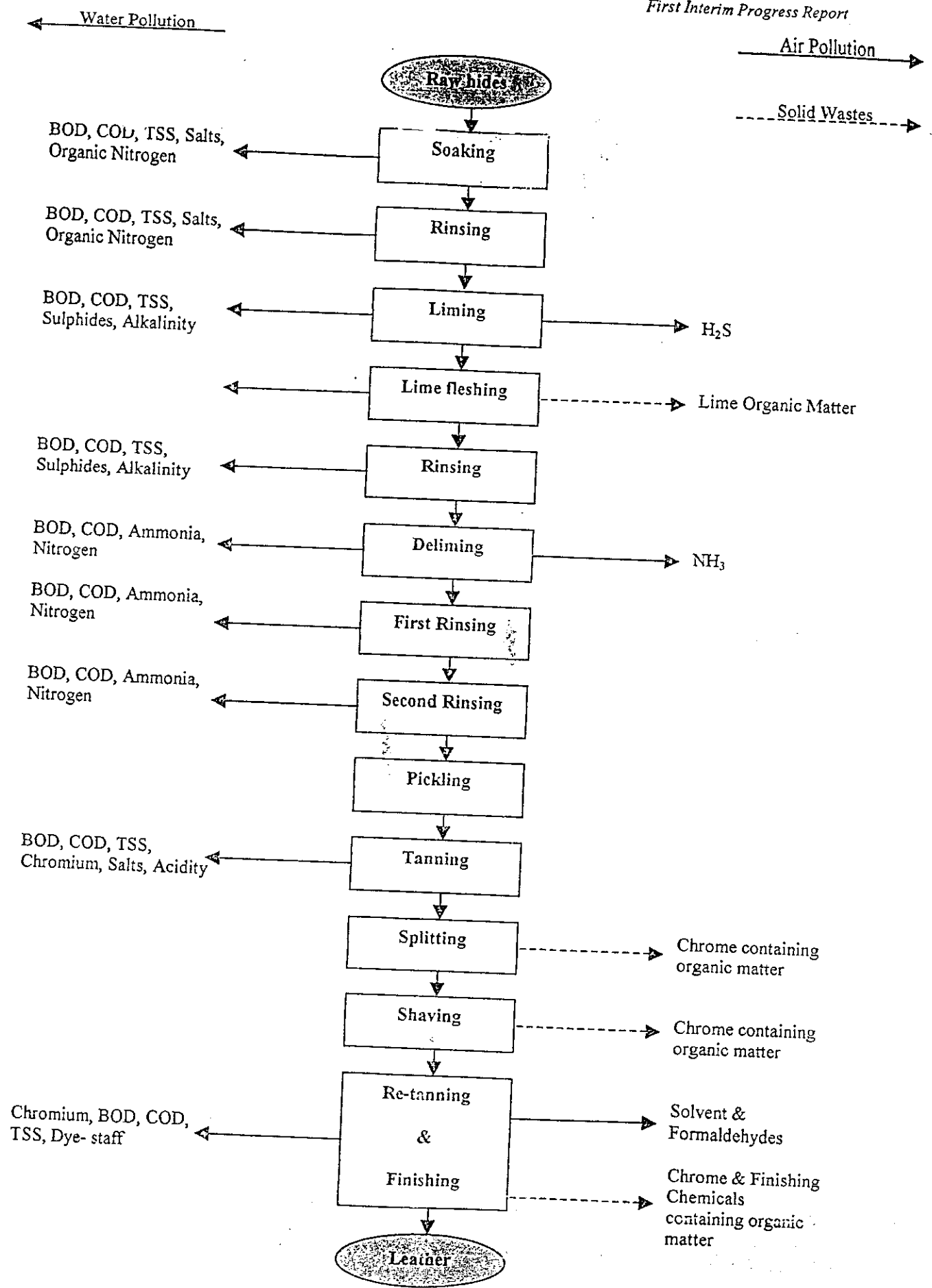


Chart 1: Resulting Impact on Various Environmental Aspects

4. Scope of the Environmental Audit

4.1 Background

An environmental audit is a systematic evaluation of a facility's operations with regard to environment, safety and health. It is part of an overall audit program, which involves the documentation, implementation, and periodic tracking and follow-up of the audit's action plan.

It is an important step in establishing an industrial environmental management program; however, it is not the first step. The process begins with a management decision to analyze and improve upon current waste management practices or to address a specific environmental problem. The audit serves as a diagnostic tool to analyze all aspects of company's operations. The motivation for initiating an environmental audit and environmental management program is based on five important criteria:

- concern for the consequences of non-compliance (enforcement action)
- the need to identify, reduce and / or contain environmental risks and liabilities
- the importance of image to consumers and to the local community
- the belief that environmental affairs should be managed like financial affairs (with control, frequent review, and an eye toward improvement)
- the belief that protecting the environment is an important part of good management practices

The primary benefit of an audit is that it ensures cost-effective compliance not only with laws, regulations and standards, but also with company policies.

It will start by the creation of an environmental audit team who will conduct thorough research, analysis and evaluation of the environmental management practices of the company. The audit is guided by detailed protocols or questionnaires designed specifically to the type of industries to be audited. The audit findings point to improvements needed in all aspects of a company's operations, including: purchasing and inventory, manufacturing processes, waste streams (air, water, and solids),

organizational management and staffing, record keeping, and internal and external communication.

Environmental audits should provide answers to the following questions raised by company managers:

- What are we doing?
- Can we do it better? In particular, are there non-regulated areas where operations can be improved to minimize the impact on the environment?
- Can we do it more cheaply?
- What more should we do?

The audit findings and recommendations form the basis of an action plan. The audit team presents the results of the assessment to senior management, both verbally and in written form, and works jointly with key decision makers in the company to develop a detailed action plan.

4.2 Audit Plan

The audit plan for the selected tannery was based on the information provided in 7 pre-prepared checklists, which are included in Appendix 1. The first checklist deals with the general overview of the facility. The second identifies the water consumption of the facility. The third deals with the conditions and capacities of water and fuel tanks of the facility. The fourth identify the industrial operations and processes involved, water consumption and waste streams from the different manufacturing processes, it also identifies qualitatively and quantitatively input raw materials and output products. It deals with equipment and machines' age, production efficiency, energy consumption, and maintenance operations of all process-related equipment. The fifth checklist provides information on all non-manufacturing equipment and processes. The sixth provides information on the storage areas of the facilities and finally the seventh checklist provides information about occupational health and safety measures practiced in the facility.

4.3 Audit Preparation

Preparation for the environmental audit, included audit team selection and development of an audit itinerary. The audit team consisted of an industrial engineer, an occupational health and safety expert, and an environmental engineer. All were responsible for auditing the systems process, the inputs and outputs, the occupational health and safety practices, etc..

4.4 Audit Performance

The environmental audit for the selected facility was initiated on September 15th, 1998. The audit was completed in about 50 man-days. Management support was obtained prior to the start of the audit, in order to be able to collect the required data and information, and for general access to facility. Once the checklists were completed, environmental monitoring and sampling of air and wastewater discharges were initiated. Samples were tested subsequently for the appropriate environmental parameters.

The audit team during their site audits encountered several difficulties. These included lack of knowledge of particular processes by some personnel, incomplete records on equipment and processes, and hazardous working conditions.

5. Environmental Monitoring Program

5.1 Introduction

The pollution loads coming out of a tannery can be divided into 3 main categories:

- Wastewater
- Air Emissions
- Solid Wastes

The objective of the environmental monitoring program is to quantify the pollution loads generated throughout the tanning process. Measurements of pollutants in the three media were conducted at every step of the process when applicable. The following sections give a detailed description of the methods used in the monitoring program.

5.2 Description of the Monitoring Program

5.2.1 Wastewater Sampling and Analysis

The sampling program adopted in the wastewater survey, was intended to ensure that representative samples were gathered from the various manufacturing processes. Thus samples were taken all through the leather tanning process, whenever wastewater was emptied from the drums. Various water quality tests were performed. Depending on the sample taken, these could include the determination of the wastewater's BOD₅, COD, pH, Ammonia, Nitrates, Phosphates, Sulphates, Chlorides, residues at 180 Celsius, Sulfides, TTS (total suspended solids) and Chromium. Furthermore a sample from the water used was tested for its hardness level.

The drums being usually rotated for a certain period of time, this allows the water and chemicals (if any) to be mixed efficiently. Thus the wastewater emptied from any process can be considered quite homogeneous, having been mixed thoroughly. Wastewater samples were collected from the rotating drum as the valves were opened to empty it. After that, a test to determine the pH level was performed directly on site.

Collected samples were placed into an isolated container, to be taken the same day to the laboratory for several or all of the above mentioned tests.

A wastewater sample representing the hole tanning process could not be collected since the different processes are not conducted simultaneously, therefore, the sample would represent only the process being conducted at the time of collection. Wastewater samples were collected from the following processes: soaking, rinsing, liming, rinsing after fleshing, de-liming, first rinse after de-liming, second rinse after de-liming, chrome tanning, colored re-tanning, and non-colored re-tanning.

5.2.2 Air Emissions

Regarding the air emissions, an apparatus was used to measure the level of CO, CO₂, O₂ remaining, NO, NO₂, NO_x, SO₂ and SO_x.

The apparatus testing hose was installed in the boiler chimney and the main generator chimney. Pollutant concentration in parts per million (ppm) was read on the spot.

5.2.3 Solid Waste Generation

The weighing of the solid wastes emanating from the whole process, was conducted at the different steps whenever it was generated in substantial quantities.

The first weighing was for the trimmings (i.e. removal of tails, feet, etc.) at the level of the salted hides before placing them in drums. The whole load of wastes from a batch of 65 hides was weighed. At the same time the weight of 10 salted and trimmed cow hides was measured.

The second step was to verify the weight of all the solid wastes resulting from the fleshing and trimming after the liming stage. The fleshing collected as well as the solid wastes trimmed were weighed respectively. Following that, the whole batch of wet hides was weighed.

The third step was determining the weight of the trimmings, once the leather has been split.

Finally we had to determine the weight of the various trimmings done at the finishing level.

6. Environmental Audit Findings for the Unit Manufacturing Processes

6.1 The Selected Facility

The audit was conducted on a facility previously reviewed by MoE for the Decision Support System for Industrial Pollution Control study. It is important to note that the selected facility is a typical medium size chromium tannery. The latter processes yearly close to 250 tones of raw hides and goat skins (80 to 20% respectively). However, due to the decreased market needs, goat skins tanning was not processed during the execution of this project. Thus, the auditing was only conducted on the tanning of cow hides.

6.2 Energy Consumption

All the machines at the tannery are operated by electricity and water is heated through steam produced in a boiler. Two generators produce electricity needed to operate the machines used in the tanning process. The main generator has a capacity of 450 KVA producing 360 kWh. Another generator is used as a stand-by, with a capacity of 220 KVA producing 176 kWh. Both generators use gas oil as a fuel and consume about 4000 liters per month. The boiler's capacity is 500Kg and is operated for 5-6 hours per day.

6.3 Water Consumption

The total water consumption measured during the audit was 112836 liters for 2754 Kg of salted hides. Thus 41 liters of water per 1 Kg of salted hides is the average water consumption in the tanning process. It is worth noting that the above mentioned figure corresponds to water consumption by the tanning process and doesn't take into account water used for housekeeping and sanitary purposes (this amount could not be measured). Worldwide, water consumption in tanneries range from less than 25l/Kg of raw hides to greater than 80l/Kg. The variation in water consumption is due to

different technologies used, and to the type of hides processed. The audited tannery depends on two sources of water, the public municipal network, and a private well. However, water quality is not monitored by the tannery's administration and consequently, no treatment techniques are used such as filters or softeners. Lab testing of the water used in different processes showed a total hardness of 150 mg/l (calcium 120mg/l, magnesium 30 mg/l, pH 7.78) equivalent to 15 German degree of hardness, ranked to be fairly hard water. Chart 2 illustrates water consumption (measured in % in reference to the initial weight of salted hides) of every step of the tanning process.

6.4 Wastewater Discharge and Treatment

Wastewater is considered as the major environmental concern in the tanning industrial sector, being characterized by their large volumes, high total organic contents, and increased concentrations of toxic chemicals. The tannery under study discharges 112169 liters of wastewater for 2754 Kg of salted hides, i.e. about 41 l/Kg. It is assumed that the amount of water absorbed by the salted hides during its processing is equal to the amount lost (the amount of wastewater resulting from housekeeping and sanitary purposes could not be calculated). The chemical characteristics of the effluents are described in section 6.8 for every step of the tanning process. The total pollution loads and its comparison with acceptable standards are discussed in section 7.

The audited tannery did not perform any treatment of its wastewater, which is directly discharged into an open sewer with its outlet in the sea. Chart 3 illustrates the % and of the wastewater generated from each step in reference to the weight of the initial salted hides.

6.5 Solid Waste Management

Solid wastes are produced at different steps of the tanning process. When cured hides are received at the tannery, they are trimmed. These trimmings (tails, feet, etc.) were collected, and weighed amounting to 180 Kg out of the 2934 Kg of hides. Thus, on the average, 0.06 Kg of trimmings are generated from every 1 Kg of hides. The



second step generating solid waste is fleshing. If green fleshing is practiced, then its solid waste would consist of fat-containing organic matter, without chemical residues, allowing it to be re-used by other industries. However, when fleshing is practiced after liming, the generated fat-containing organic matter would contain lime. The fleshing and trimmings were also collected and weighed 619 Kg out of the 3289 Kg of soaked hides, or 0.19 Kg per 1 Kg of soaked hides. Splitting produces trimmings as solid wastes and shaving after chrome-tanning produces the same type of solid waste both were collected and weighed 433 kg out of the 2163 kg of wet blue, or 0.2 kg per kg of wet blue. The waste generated at the trimming stage is constituted of limed organic matter if splitting is done after liming, and of chrome containing organic matter if it is performed after tanning. The last step generating solid waste is trimming after re-tanning and drying. The solid wastes after this step are composed of chrome and pre-finishing containing organic matter collected, they weighed 138 kg of 1730 kg of finished product, or 0.08 kg per 1 kg of finished products. In addition to solid wastes generated by the tanning process, ordinary solid wastes from housekeeping and offices are produced.

Currently, all solid wastes are disposed of in an open dump in the vicinity of the tannery. The rapid decomposition of their organic content produces noxious odors on the site and attracts vermin and rodents. The chemical residues pollute the land and may contaminate ground water. The disposal of empty containers can be problematic at uncontrolled sites as people tend to re-use them. Such containers should be rinsed out, punctured and crushed before disposal to avoid their re-use and subsequent adverse health effects. Table 2 summarizes the generation of solid waste from every step. The total weight of solid waste generated throughout the whole process is equal to 1370Kg, corresponding to 50% of the initial weight of salted hide. The resulting leather was calculated to be about 26% (716 Kg) of the initial weight of salted hide. This will justify the material balance of our audit since the water adsorption was found to be equal to 19%. The remaining 5 % correspond to the weight of lost hair and buffing dust.

Table 2: Amount of Solid Waste Generated in Different Processes.

| Process Name | Weight of Solid Waste (Kg) |
|---------------------------|----------------------------|
| Trimmings | 180 |
| Fleshing | 619 |
| Splitting & Shaving | 433 |
| Trimming After Re-Tanning | 138 |
| Total | 1370 |

6.6 Air Emission

Odor is the most prominent air pollution problem emanating from the tannery. In addition, solvent vapors and the unintentional generation of H₂S impose serious occupational health hazards. Emissions from fuel combustion in the boiler and generators are directly emitted to the atmosphere through chimneys or smokestacks, without passing through filters. Measurements of such emissions were conducted using special probes that can measure the concentrations of pollutants directly from within the smokestacks. Results are tabulated in table 3. While no national regulatory standards exist for flue gas emissions from chimneys, several benefits can be realized from these measurements. First, they can be easily used to recalibrate boiler and generator settings to match manufacturer's specifications as closely as possible. Second, they can be used in future comprehensive study of regional air pollution and comparison with ambient air standards become relevant and meaningful. Based on the audit findings, it is concluded that fuel oil should not be used in industries located beside residential areas because it originally contains high percentage of sulfur. Furthermore, short smokestacks result in higher levels of pollution. Lack or irregular maintenance operations for the generator resulted in an increase in the amount of pollutant. It was also found that regular maintenance of the boiler resulted in reduced amounts of pollution loads emitted to the atmosphere.

Table 3: Pollution Load Emanating by Existing Boiler and Generator

| Parameters | Boiler (high chimney, under periodic maintenance program) | Generator (very short chimney, lack of regular maintenance) |
|--------------------------|---|---|
| CO | 9 ppm | 168 ppm |
| CO ₂ | 2.8 % | 7 % |
| Remaining O ₂ | 17.2 % | 11.5 % |
| NO | 42 ppm | 633 ppm |
| NO ₂ | 0 ppm | 4 ppm |
| NO _x | 42 ppm | 637 ppm |
| SO ₂ | 43 ppm | 0 ppm |
| Flow Temperature | 75.3 °C | 399.8 °C |
| Ambient Temperature | 27.8 °C | 30.6 °C |
| Efficiency | 85.5 % | 66.5 % |

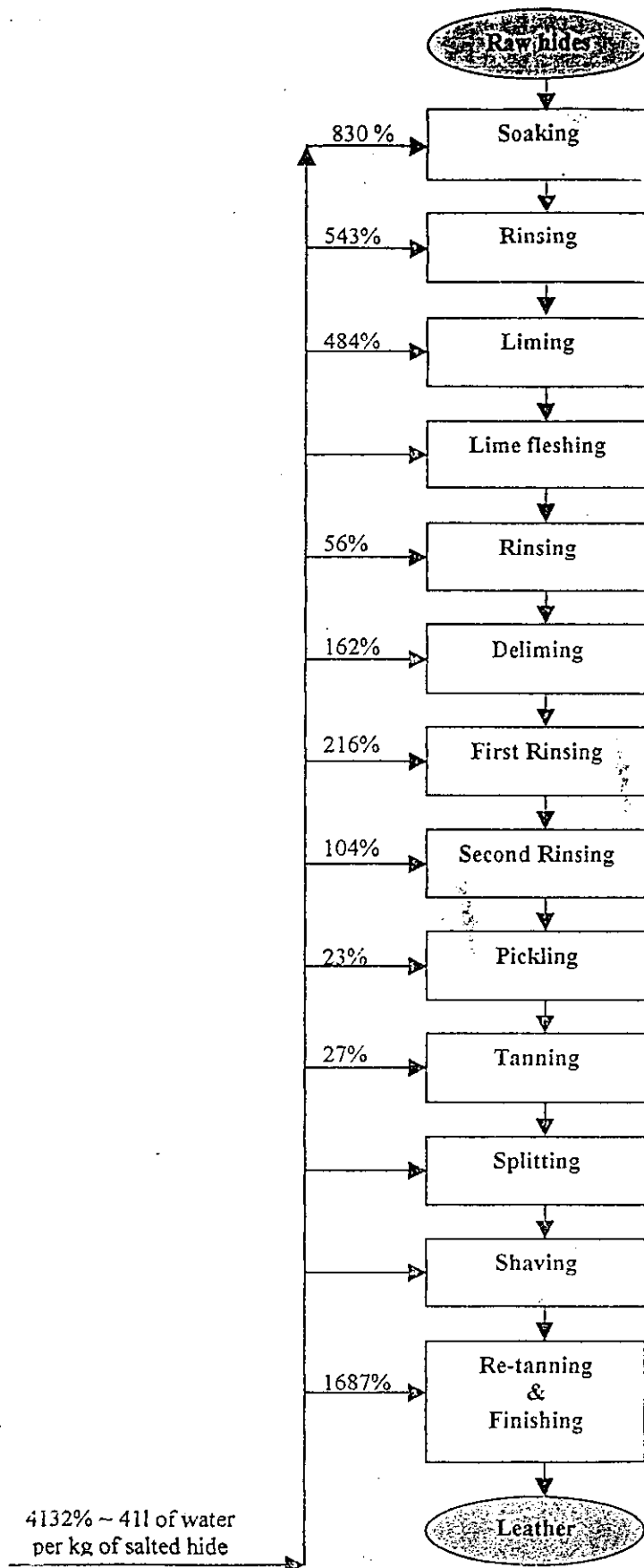


Chart 2: Water Consumption Per Process

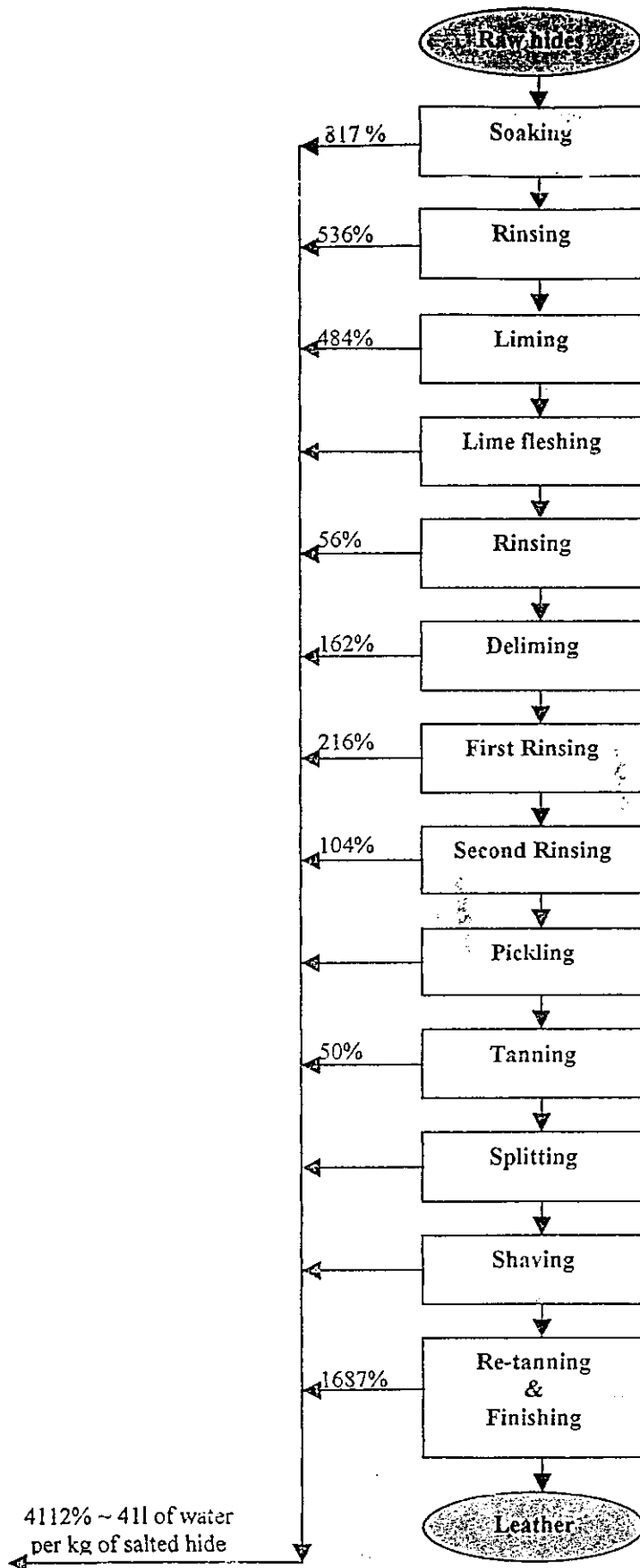


Chart 3: Wastewater Generation Per Process

6.7 Occupational Health and Safety

Many steps in the tanning process impose a hazard to exposed workers. The health effects discussed earlier from workplace exposure, could be alleviated by implementing general industrial safety regulations. International guidelines to limit the exposure to Chromium have been set by the International Labor Organization (ILO) and the United Nations Environment Program (UNEP). Threshold Limit Values (TLV) for solvent vapors are also set. Checklist #7 (Annex 1) was used to assess the occupational health and safety status at the workplace under study. The facility is not equipped with a ventilation system. Therefore, air movement and air pollutant dispersion are not controlled. Personal protection equipment (PPE) such as respirators, special clothing, and safety boots are not available at the workplace and therefore not being used by the workers. There is no adequate lighting in some areas of the tannery. This may lead to accidents and spills. Warning signs are also not installed, especially on hazardous machines such as the fleshing, splitting, shaving and sammying machines, the boiler, generators, and electric boards. Due to the limited space of the facility, hallways and stairs are narrow, machines are close to each other, and workers movement is not organized increasing the risk of accidents.. Fire fighting equipment is scarce and very old in spite of having a high risk of fire due to the presence of flammable material such as solvents, gas oil, and fuel oil. Spills in storage areas, near the boiler and generators, and the loose electric wires with the unprotected electric boards increase the risk of fire or electrocution. First aid kits are also not present in appropriate places.

All of the above mentioned observations render the workplace unsafe due to the high potential of accidents and injuries to occur. Appropriate precautionary measures and suitable organizational procedures would highly reduce exposure to chemical hazards, physical dangers, spills, accidents, and fire. Factors rendering the indoor environment hazardous contribute significantly to the outdoors environmental degradation, and to the potential adverse effects that a tannery impose on the people living in its neighborhoods.

A well planned occupational health and safety program should be tailored to individual tanneries. The program should address the following aspects:

- Continuous provision by the management and responsible authorities of safe working conditions and procedures;
- Participation of the workers in the safety program;
- Safety training and instructions;
- Reporting, investigation, and analysis of accidents and working conditions;
- Dissemination of information on hazards and risks;

Such programs are not trivial and should be implemented as soon as possible. Adverse health effects and accidents occurring to tannery workers is well documented worldwide, and occupational health and safety programs are well acknowledged in reducing such hazards.

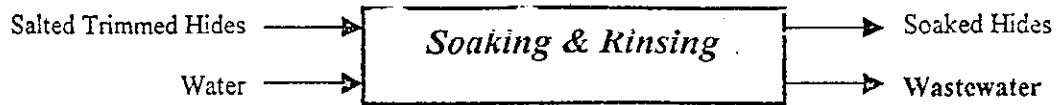
6.8 *Material Balance and Wastewater Analyses*

6.8.1 **Process: Trimming**



| Material Balance | | | |
|-------------------------|--------------------|---------------|--------------------|
| Input | Weight (Kg) | Output | Weight (Kg) |
| Salted Hides | 2934 | Trimmed Hides | 2754 |
| | | Solid Waste | 180 (6.1%) |

6.8.2 Process: Soaking and Rinsing

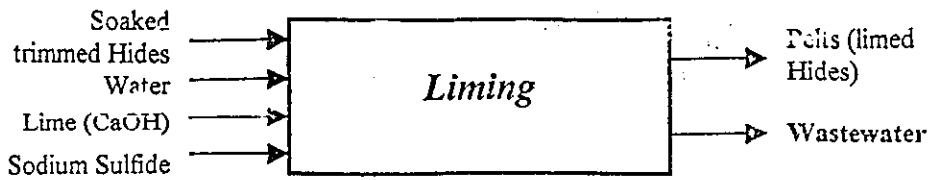


| Material Balance | | | |
|----------------------|---|--------------|----------------------------------|
| Input | Weight (Kg) | Output | Weight (Kg) |
| Salted Trimmed Hides | 2754 | Soaked Hides | 3289 (19.4% absorption of water) |
| Water | 37818 (1373%) Soaking 830% Rinsing 543% | Waste water | 37283 |

| Waste Water Analysis: Soaking | | | |
|-------------------------------|---------------------|-----------------------|-------------------------------------|
| Pollutant | Lab Analysis (mg/l) | Waste Water Loads (l) | Pollution Load g/Kg of Salted Hides |
| Ammonia | 40 | 22519 | 0.33 |
| Nitrates | 230 | | 1.88 |
| Phosphates | 26 | | 0.21 |
| Sulphates | 700 | | 5.72 |
| Chlorides | 24500 | | 200.33 |
| COD | 48000 | | 39.24 |
| BOD5 | 1700 | | 13.90 |
| Sulphides | 4.8 | | 0.04 |
| Chromium | - | | - |
| TSS | 960 | | 7.85 |

| Waste Water Analysis: Rinsing | | | |
|-------------------------------|---------------------|-----------------------|-------------------------------------|
| Pollutant | Lab Analysis (mg/l) | Waste Water Loads (l) | Pollution Load g/Kg of Salted Hides |
| Ammonia | 18 | 14764 | 0.10 |
| Nitrates | 23 | | 0.12 |
| Phosphates | 13 | | 0.07 |
| Sulphates | 570 | | 3.06 |
| Chlorides | 7600 | | 40.74 |
| COD | 2400 | | 12.87 |
| BOD5 | 2300 | | 12.33 |
| Sulphides | 4.8 | | 0.02 |
| Chromium | - | | - |
| TSS | 440 | | 2.36 |

6.8.3 Process: Liming



| Material Balance | | | |
|------------------|--------------|-------------|-------------|
| Input | Weight (Kg) | Output | Weight (Kg) |
| Hides | 3289 | Pelts | 3289 |
| Water | 13330 (484%) | Waste Water | 13330 |
| Sodium Sulphate | 64 (2.3%) | | |
| Lime | 100 (3.6%) | | |

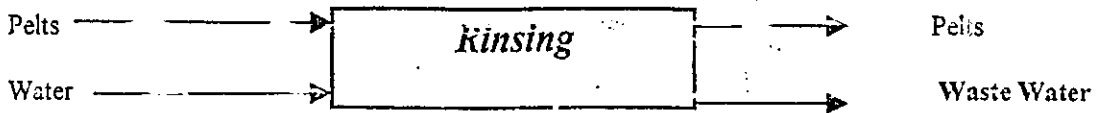
| Waste Water Analysis | | | |
|----------------------|---------------------|-----------------------|-------------------------------------|
| Pollutant | Lab Analysis (mg/l) | Waste Water Loads (l) | Pollution Load g/Kg of Salted Hides |
| Ammonia | 430 | 13330 | 2.08 |
| Nitrates | 3500 | | 16.94 |
| Phosphates | 57 | | 0.28 |
| Sulphates | 1900 | | 9.20 |
| Chlorides | 8000 | | 38.72 |
| COD | 12000 | | 58.08 |
| BOD5 | 7000 | | 33.88 |
| Sulphides | 4600 | | 22.26 |
| Chromium | - | | - |
| TSS | 28000 | | 135.53 |
| pH | 12.08 | | - |

6.8.4 Process: Fleshing and Trimming



| Material Balance | | | |
|------------------|-------------|-----------------------|-------------|
| Input | Weight (Kg) | Output | Weight (Kg) |
| Pelts | 3289 | Trimmed/Fleshed Pelts | 2670 |
| | | Solid Waste: | 619 (18.8%) |
| | | Trimmings | 159 (4.8%) |
| | | Fleshings | 460 (14%) |

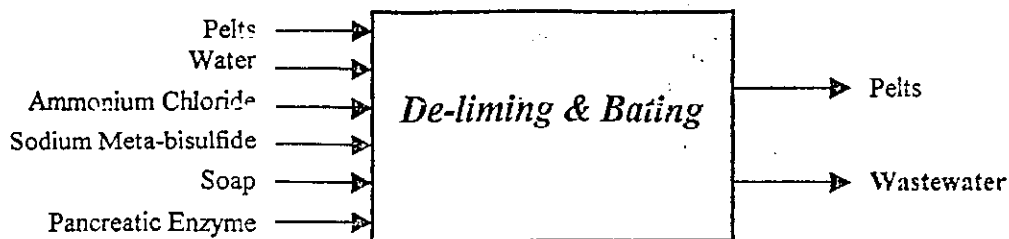
6.8.5 Process: Rinsing after Liming



| Material Balance | | | |
|------------------|-------------|-------------|-------------|
| Input | Weight (Kg) | Output | Weight (Kg) |
| Pelts | 2670 | Pelts | 2670 |
| Water | 1505 (56%) | Waste water | 1505 |

| Waste Water Analysis | | | |
|----------------------|---------------------|-----------------------|-------------------------------------|
| Pollutant | Lab Analysis (mg/l) | Waste Water Loads (l) | Pollution Load g/Kg of Salted Hides |
| Ammonia | 360 | 1505 | 0.20 |
| Nitrates | 360 | | 0.20 |
| Phosphates | 8.0 | | 0.00 |
| Sulphates | 600 | | 0.33 |
| Chlorides | 7000 | | 3.83 |
| COD | 7000 | | 3.83 |
| BOD5 | 5200 | | 2.84 |
| Sulphides | 120 | | 0.07 |
| Chromium | - | | - |
| TSS | 140 | | 0.08 |
| pH | 10.12 | | - |

6.8.6 Process: De-liming and bating



| Material Balance | | | |
|-----------------------|--------------|-------------|-------------|
| Input | Weight (Kg) | Output | Weight (Kg) |
| Pelts | 2670 | Pelts | 2370 |
| Water | 12407 (482%) | Waste water | 11775 |
| Sodium Meta-Bisulfide | 21 (0.79%) | | |
| Ammonium Chloride | 64 (2.4%) | | |
| Soap | 5.6 (0.21%) | | |
| Pancreatic Enzyme | 6.9 (0.26%) | | |

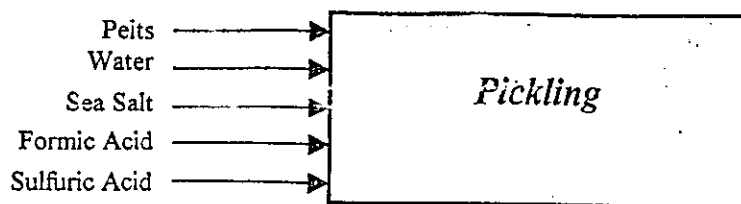
| Waste Water Analysis: Deliming and Bating | | | |
|---|---------------------|-----------------------|-------------------------------------|
| Pollutant | Lab Analysis (mg/l) | Waste Water Loads (l) | Pollution Load g/Kg of Salted Hides |
| Ammonia | 3700 | 4460 | 5.99 |
| Nitrates | 850 | | 1.38 |
| Phosphates | 77 | | 0.12 |
| Sulphates | 6800 | | 11.01 |
| Chlorides | 27000 | | 43.73 |
| COD | 8000 | | 12.96 |
| BOD5 | 4500 | | 7.29 |
| Sulphides | 2000 | | 3.24 |
| Chromium | - | | - |
| TSS | 1100 | | 1.62 |
| PH | 7.85 | | |

| Waste Water Analysis: First Rinsing | | | |
|-------------------------------------|---------------------|-----------------------|-------------------------------------|
| Pollutant | Lab Analysis (mg/l) | Waste Water Loads (l) | Pollution Load g/Kg of Salted Hides |
| Ammonia | 680 | 5928 | 1.46 |
| Nitrates | 320 | | 0.69 |
| Phosphates | 2 | | 0.00 |
| Sulphates | 600 | | 1.29 |
| Chlorides | 4500 | | 9.69 |
| COD | 3600 | | 7.75 |
| BOD5 | 2100 | | 4.52 |
| Sulphides | 210 | | 0.45 |
| Chromium | - | | - |
| TSS (mg/ml) | 90 | | 0.19 |

| Waste Water Analysis: Second Rinsing | | | |
|---|----------------------------|------------------------------|--|
| Pollutant | Lab Analysis (mg/l) | Waste Water Loads (l) | Pollution Load g/Kg of Salted Hides |
| Ammonia | 310 | 2851 | 0.32 |
| Nitrates | 260 | | 0.27 |
| Phosphates | 1 | | 0.00 |
| Sulphates | 1200 | | 1.24 |
| Chlorides | 4000 | | 4.14 |
| COD | 2600 | | 2.70 |
| BOD5 | 1800 | | 1.86 |
| Sulphides | 74 | | 0.08 |
| Chromium | - | | - |
| TSS | 60 | | 0.06 |

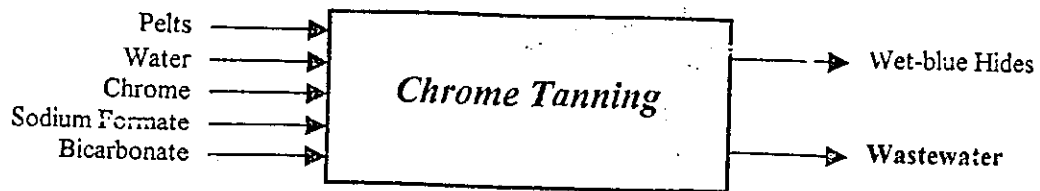
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6.8.7 Process: Pickling



| Material Balance | | | |
|------------------|-------------|--------|-------------|
| Input | Weight (Kg) | Output | Weight (Kg) |
| Pelts | 2670 | Pelts | 2670 |
| Water | 593 (23%) | | |
| Sea Salt | 179 (6.7%) | | |
| Formic Acid | 22 (0.82%) | | |
| Sulfuric Acid | 28 (1.05%) | | |
| Media pH: 3.09 | | | |

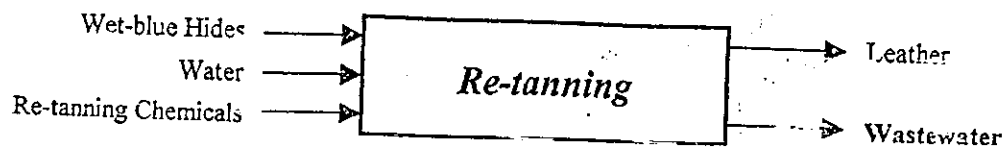
6.8.9 Process: Tanning



| Material Balance | | | |
|------------------|-------------|-------------|-------------|
| Input | Weight (Kg) | Output | Weight (Kg) |
| Pelts | 2670 | Pelts | 2670 |
| Water | 721 (27%) | Waste water | 1814 |
| Sodium Formate | 43 (1.6%) | | |
| Bicarbonates | 4 (0.16%) | | |
| Chrome | 84 (3%) | | |

| Waste Water Analysis | | | |
|----------------------|---------------------|-------------------|--|
| Pollutant | Lab Analysis (mg/l) | Waste Water Loads | Pollution Load g/Kg of Salted Hides |
| Ammonia | 95 | 1814 | 0.06 |
| Nitrates | 80 | | 0.05 |
| Phosphates | 0.5 | | 0.02 |
| Sulphates | 15000 | | 9.88 |
| Chlorides | 47000 | | 30.96 |
| COD | 8000 | | 5.27 |
| BOD5 | 3800 | | 2.50 |
| Sulphides | 210 | | 0.14 |
| Chromium | 490 | | 0.32 |
| TSS | 110 | | 0.07 |
| pH | 3.5 | | - |

6.8.10 Process: Re-tanning



| Material Balance | | | |
|------------------------------|-------------|-------------|-------------|
| Input | Weight (Kg) | Output | Weight (Kg) |
| Pelts | 2670 | Leather | 2670 |
| Water | 46460 | Waste water | 46460 |
| Buffered organic sulpho-acid | 20 (0.75%) | | |
| Acrylic Resin | 80.1(3%) | | |
| Aromatic Sulpho-acid | 80.1(3%) | | |
| Formaldehyde condensate | 53.4 (2%) | | |
| Phenol condensate | 53.4 (2%) | | |
| Aromatic Sulphoacid | 53.4 (2%) | | |
| Phenol | | | |
| Fat Liquor | 26.7 (1%) | | |

| Waste Water Analysis: Colored | | | |
|-------------------------------|---------------------|-------------------|-------------------------------------|
| Pollutant | Lab Analysis (mg/l) | Waste Water Loads | Pollution Load g/Kg of Salted Hides |
| Ammonia | 270 | | |
| Nitrates | 17 | | |
| Phosphates | 7 | | |
| Sulphates | 9200 | | |
| Chlorides | 4500 | | |
| COD | 2200 | | |
| BOD5 | 840 | | |
| Sulphides | 400 | | |
| Chromium | 1.8 | | |
| TSS | 190 | | |
| pH | | | |

| Waste Water Analysis: Non-colored | | | |
|-----------------------------------|---------------------|-------------------|--|
| Pollutant | Lab Analysis (mg/l) | Waste Water Loads | Pollution Load g/Kg of Salted Hides |
| Ammonia | 240 | 46460 | 4.05 |
| Nitrates | 4.6 | | 0.03 |
| Phosphates | 0.3 | | 0.05 |
| Sulphates | 340 | | 5.75 |
| Chlorides | 2200 | | 37.11 |
| COD | 3000 | | 50.6 |
| BOD5 | 1900 | | 32.05 |
| Sulphides | 4 | | 0.07 |
| Chromium | 2.3 | | 0.04 |
| TSS | 30 | | 0.51 |
| pH | | | |

6.9 Interpretation of Wastewater Results

The analysis of the wastewater results is presented for every pollutant throughout the tanning process. Table 4 shows a comparison of the wastewater results of the selected tannery with discharge standards for tannery wastewater for Italy and Syria. Table 5 shows the total pollution load from the selected tannery for every pollutant in grams per Kilogram of salted hides. Figures 2 through 11 show the distribution of pollutants generation from all the steps of the tanning process.

6.9.1 pH

pH levels shown on Figure 2 fall within the Italian and Syrian standards, ranging respectively from 5.5 to 9.5 and 6 to 10. However, the pH of 12.03 at the Liming process is very high rendering the solution alkaline. On the other hand, the Chrome tanning process has a pH of 3.5 which renders the solution acidic.

6.9.2 Biological Oxygen Demand (BOD)

Theoretically, traditional Soaking and Liming (unhairing) account for over 50% of the total BOD and COD loads generated in typical tannery effluents. Figure 3 indicates that more than 50% of the BOD load is generated in the early stages of the process. The fact that Soaking, Rinsing, Liming and Rinsing after Liming account for 53% of the BOD is due mainly to the high concentrations of organic matter originating from the hides. Combined together, Liming and Rinsing after De-liming account for 39% of the BOD load, results from the hair and other unwanted material that have been removed. On average, 111.17 g of BOD is generated for every Kg of salted hides processed. BOD concentrations are 6.8 times (Soaking) to 28 times (Liming) higher than the acceptable limit, set at 250mg/l (Italian). And it is 1.7 to 7 times higher than the Syrian Standards, set at 1000 mg/l.

Table 4: Comparison of Wastewater Characteristics of Different Processes With Some International Standards

| Parameter (mg/l unless other) | Soaking | Rinsing | Liming | Rinsing | De- liming & Bating | 1st Rinsing | 2nd Rinsing | Chrome Tanning | Re-tanning | Italy | Syria | India |
|-------------------------------------|---------|---------|--------|---------|---------------------------|----------------|----------------|-------------------|------------|---------|--------|---------|
| pH units | 7,6 | 7,44 | 12,08 | 10,12 | 7,85 | 7,66 | 7,3 | 3,5 | | 5,5-9,5 | 6,0-10 | 5,5-9,0 |
| BOD5 | 1700 | 2300 | 7000 | 5200 | 4500 | 2100 | 1800 | 3800 | 1900 | 250 | 1000 | 30 |
| COD | 4800 | 2400 | 12000 | 7000 | 8000 | 3600 | 2600 | 8000 | 3000 | 500 | 3000 | 250 |
| Susp. solids | 960 | 440 | 28000 | 140 | 1100 | 90 | 60 | 1100 | 30 | 40 | 500 | 100 |
| Sulphide | 4,8 | 4,8 | 4600 | 120 | 2000 | 210 | 74 | 210 | 4 | 2 | 3 | 2 |
| Chrome (III) | | | | | | | | 490 | 2,3 | 4 | 5 | 2 |
| Chloride | 24500 | 7600 | 8000 | 7000 | 27000 | 4500 | 4000 | 47000 | 2200 | 1000 | | |
| Sulphate | 700 | 570 | 1900 | 600 | 6800 | 600 | 1200 | 15000 | 340 | 150 | | 1000 |
| Ammonia | 40 | 18 | 430 | 360 | 3700 | 680 | 310 | 95 | 240 | 15 | | |

6.9.3 Chemical Oxygen Demand (COD)

Theoretically, the highest levels of COD are generated at the earliest stages of the leather tanning process. Referring to figure 4 indicating the COD levels in different processes, 50% of the total COD load is generated from Soaking, Rinsing after Soaking, Liming and Rinsing after Liming. On average 546.56g of COD are generated for every Kg of salted hides. In comparison with the Italian Standards, COD levels are 4.8 times (2nd Rinsing after De-Liming & Bating) to 24 times (Liming) higher than the acceptable limit, set at 500mg/l. However, concentration at the Rinsing after Soaking and 2nd Rinsing after De-Liming & Bating processes, are less than the Syrian standards. Other steps of the tanning process generate COD concentrations higher than 3000 mg/l.

6.9.4 Total Suspended Solids (TSS)

As shown in figure 5, the highest percentage (89%) of total suspended solids is generated from Liming operations. The high concentration of TSS is due to the high amounts of hair removed from the hides. The remaining 11% is distributed along all other processes. On average 148.27 g of TSS are generated per Kg of salted hides. Compared with the Italian Standard, set at 30 mg/l, all the steps of the tanning process, except the Re-tanning step, generate a higher concentration of TSS. During the liming stage, the concentration reaches a maximum of 700 times of the authorized Italian levels, and is as low as 0.75 times of the authorized level during re-tanning. Regarding the Syrian standards set at 500 mg/l, 5 out of 9 processing steps generate a lower concentration of TSS.

6.9.5 Sulphide

As shown in figure 6, Sulphide is found in minute quantities in the Soaking, Rinsing after Soaking and Re-tanning steps (about 0%). While 63% is generated from the Liming stage due to the high amounts of Sodium Sulphide required for this operation. On average 26.37g of Sulphide are generated from every Kg of salted hides. The

concentrations of Sulphide are higher than the acceptable limits in Italy or Syria, which are set respectively at 2 mg/l and 3 mg/l. The concentration at the Re-tanning stage is 2 times higher than the Italian Standard, and 1.33 times higher than the Syrian one. The concentrations reaches its maximum at the Liming step being 1533 times higher than Italian standards and 1150 times above the Syrian regulations.

6.9.6 Chrome

The tanning and re-tanning steps generate chrome. On average 0.36g of Chrome are generated for every Kg of salted hides. The concentration of Chrome after tanning is 123 times higher than the Italian standard and 98 times higher than the Syrian one. However, Chrome concentrations at the Re-tanning process are within standards.

6.9.7 Chlorides

The highest level of Chlorides (36%) is generated after the Chrome tanning stage, followed by the early stage of Soaking and Rinsing (25%) as shown in figure 7. The high levels are due to the amount of salt used in the Chrome tanning process as well as the salt used for the conservation of the cow hides. On average 409.25 g of Chlorides are generated from every Kg of salted hides. Compared with the Italian standards where the maximum accepted level of Chlorides is 1000 mg/l, it's concentration is 47 times at the Chrome Tanning operation, and 2.2 times at the Re-tanning stage. Chlorides limits are not included in the Syrian Standard.

6.9.8 Sulphate

Interpreting the results of figure 8 regarding the concentrations of Sulphate found in the wastewater, it can be seen that the highest percentage loads are found at the Chrome tanning stage (53%). This high concentration is due to the Chrome tanning agent containing partially, some amounts of Sulphates. On average 41.75 g of Sulphates are generated from every Kg of salted hides. According to Italian standards where the highest level of Sulphate should be set at 150 mg/l, the minimum level

recorded through the present study was 2.26 times higher (Re-tanning) than the Italian standards, and the highest was close to 100 times higher (Chrome Tanning stage) than the authorized limit.

6.9.9 Ammonia

The highest percentage of Ammonia (63%) is generated during De-Liming & Bating operations due to the Ammonia added. The remaining steps except the 1st Rinsing after De-liming & Bating have a low contribution in the generation of Ammonia (see figure 9). On average 14.59 g of Ammonia are generated from every Kg of salted hides. Italian and Syrian Standards for Ammonia are not set.

6.9.10 Phosphates

As shown in figure 10, the highest portion (42%) of phosphate is generated at the De-Liming & Bating stage, due to the amount of soap needed to react as a surfactant. On average 0.54g of Phosphates are generated from every Kg of salted hides processed. Italian and Syrian Standards for Ammonia are not set.

6.9.11 Nitrates

According to figure 11, Nitrates are mainly generated from the Liming operations. The high level of organic matter found at the Liming stage increases the concentration level of Nitrates. On average 21.61g of Nitrates are generated for every Kg of salted hides.

6.10 Projection of Pollution Loads on a National Scale

As stated in section 1.3.2, the daily production of hides by all national tanneries is close to 1000 hides. On the average, one hide weighs 34 to 37 kg thus the national production of hides in Kg is between 34000 and 37000. The audit results clearly quantified the total pollution load of every pollutant generated per kg of salted hides processed at the selected tannery. Assuming that all national tanneries use similar processing techniques as the one audited, their total pollution load would be estimated by multiplying the pollution load per one kg of salted hides by the total daily production. Table 5 shows the total pollution load resulting from the daily processing of 1000 hides.

Table 5: Total Pollution Load Resulting From the Daily Processing of 1000 Hides

| Total Pollution Loads | | | |
|------------------------------|--|--|--|
| Pollutant | Total Pollution Load of Selected Tannery (g/Kg of Salted Hides) | Total Pollution Load for a National Production Level of 34000 Kg/Day (kg/day) | Total Pollution Load for a National Production Level of 37000 Kg/Day (kg/day) |
| Ammonia | 14.59 | 496 | 540 |
| Nitrates | 21.61 | 735 | 780 |
| Phosphates | 0.54 | 18 | 20 |
| Sulphates | 41.75 | 1420 | 1545 |
| Chlorides | 409.25 | 13914 | 15142 |
| COD | 546.56 | 18583 | 20223 |
| BOD5 | 111.17 | 3778 | 4113 |
| Sulphides | 26.37 | 897 | 976 |
| Chromium | 0.36 | 12 | 13 |
| TSS | 148.27 | 5041 | 5486 |

These estimated results represent partial (processing of hides) environmental impact of the tanning sector. It is the worst case scenario since no treatment techniques neither waste reduction measures are actually practiced. The data found are to be used for tailoring an environmental management plan for the tanning sector and specifically for the design of wastewater treatment plant and cleaner production options.

Figure 2: pH of Different Wastewater Streams

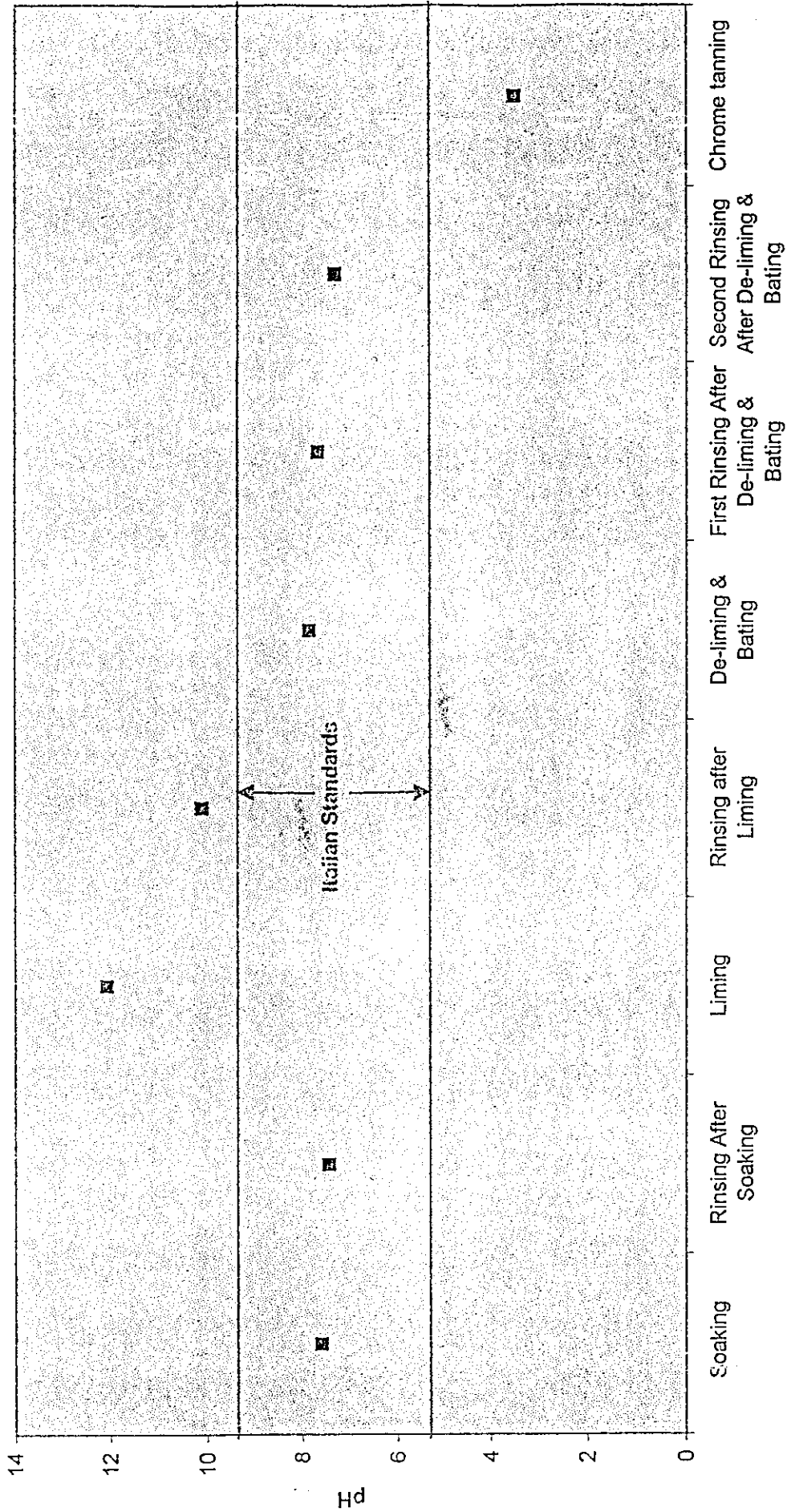


Figure 3: BOD5 In Different Processes

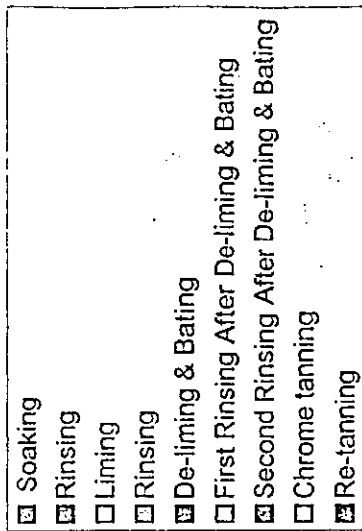
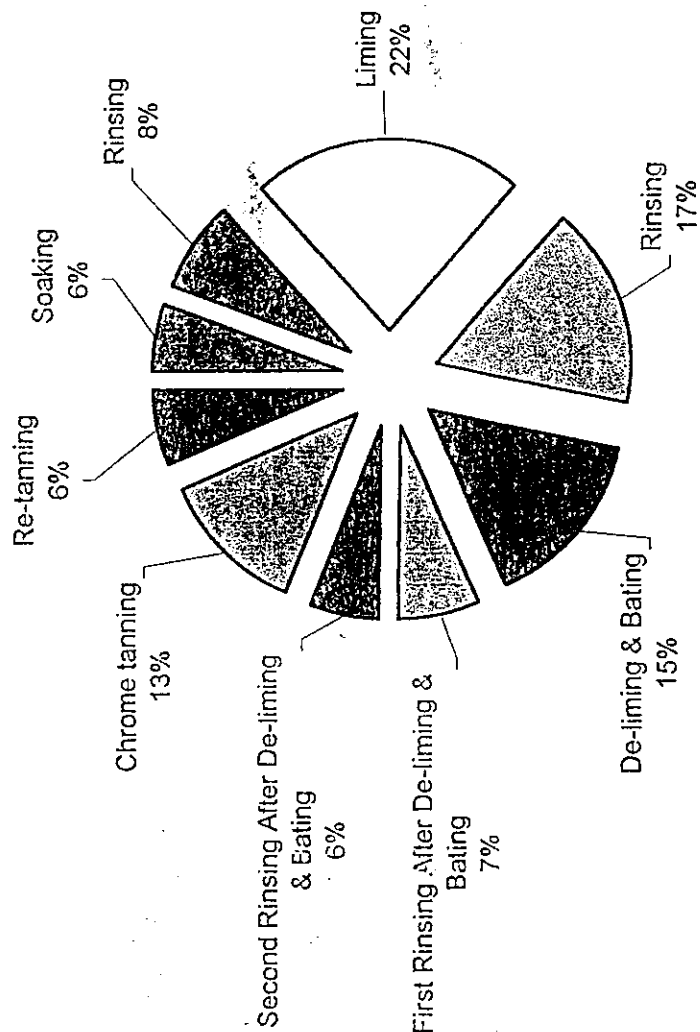


Figure 4: COD In Different Processes

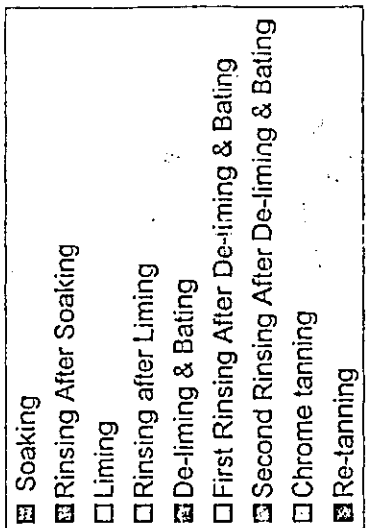
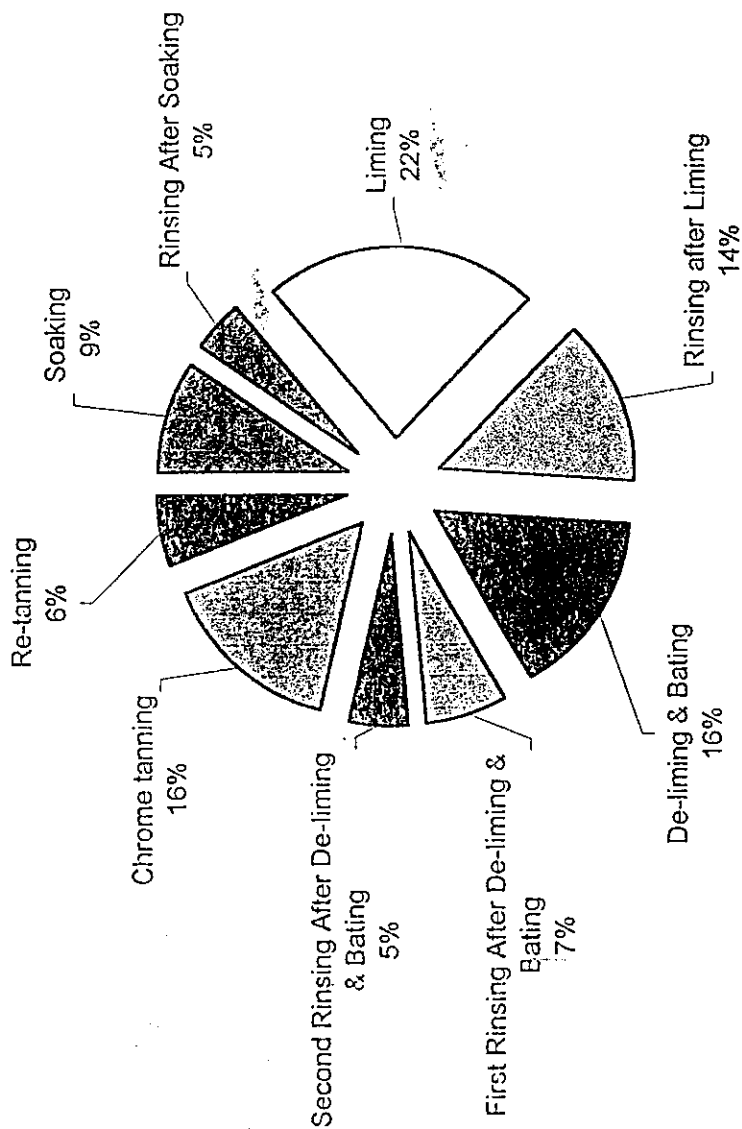
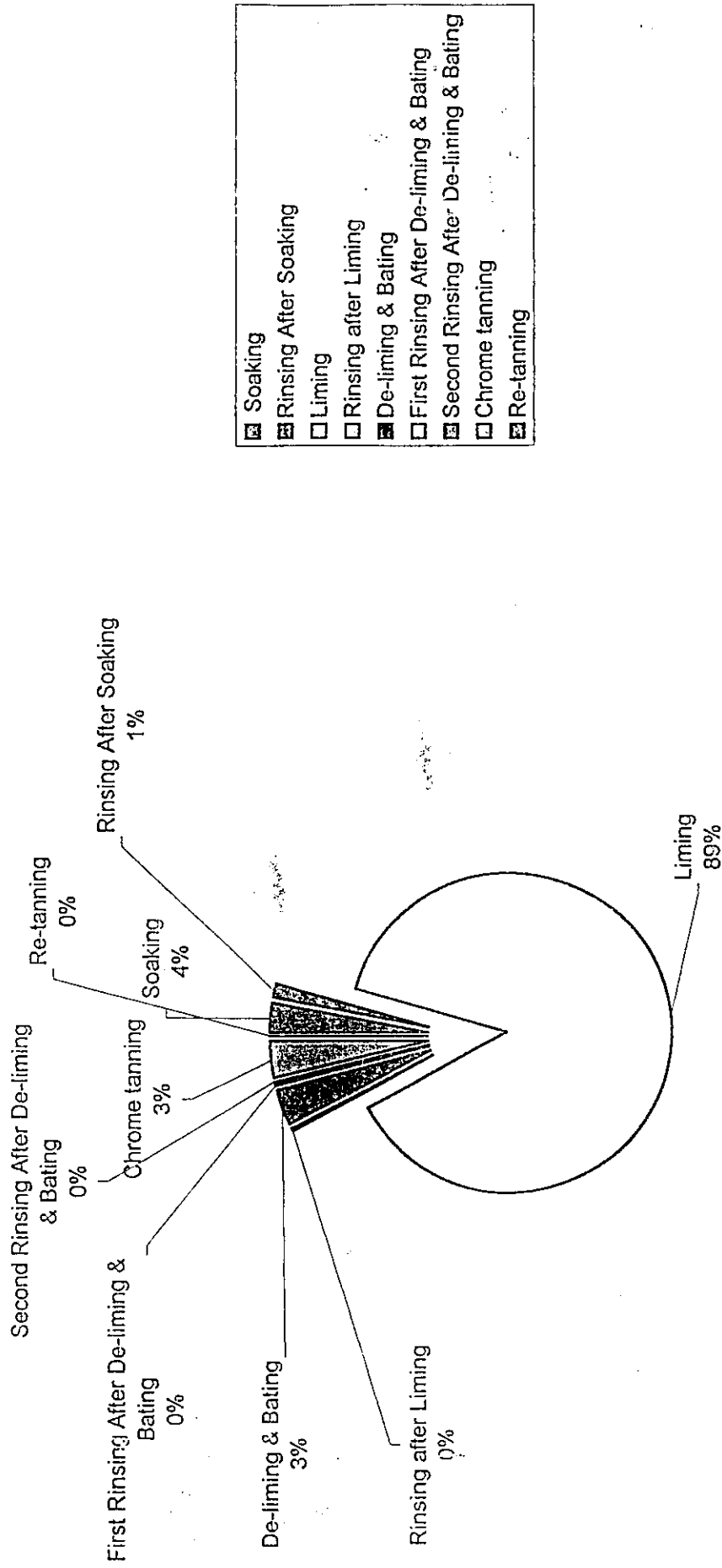


Figure 5: TSS in Different Wastewater Streams



- Soaking
- Rinsing After Soaking
- Liming
- Rinsing after Liming
- De-liming & Bating
- First Rinsing After De-liming & Bating
- Second Rinsing After De-liming & Bating
- Chrome tanning
- Re-tanning

Figure 6: Level of Sulphide in Different Wastewater Streams

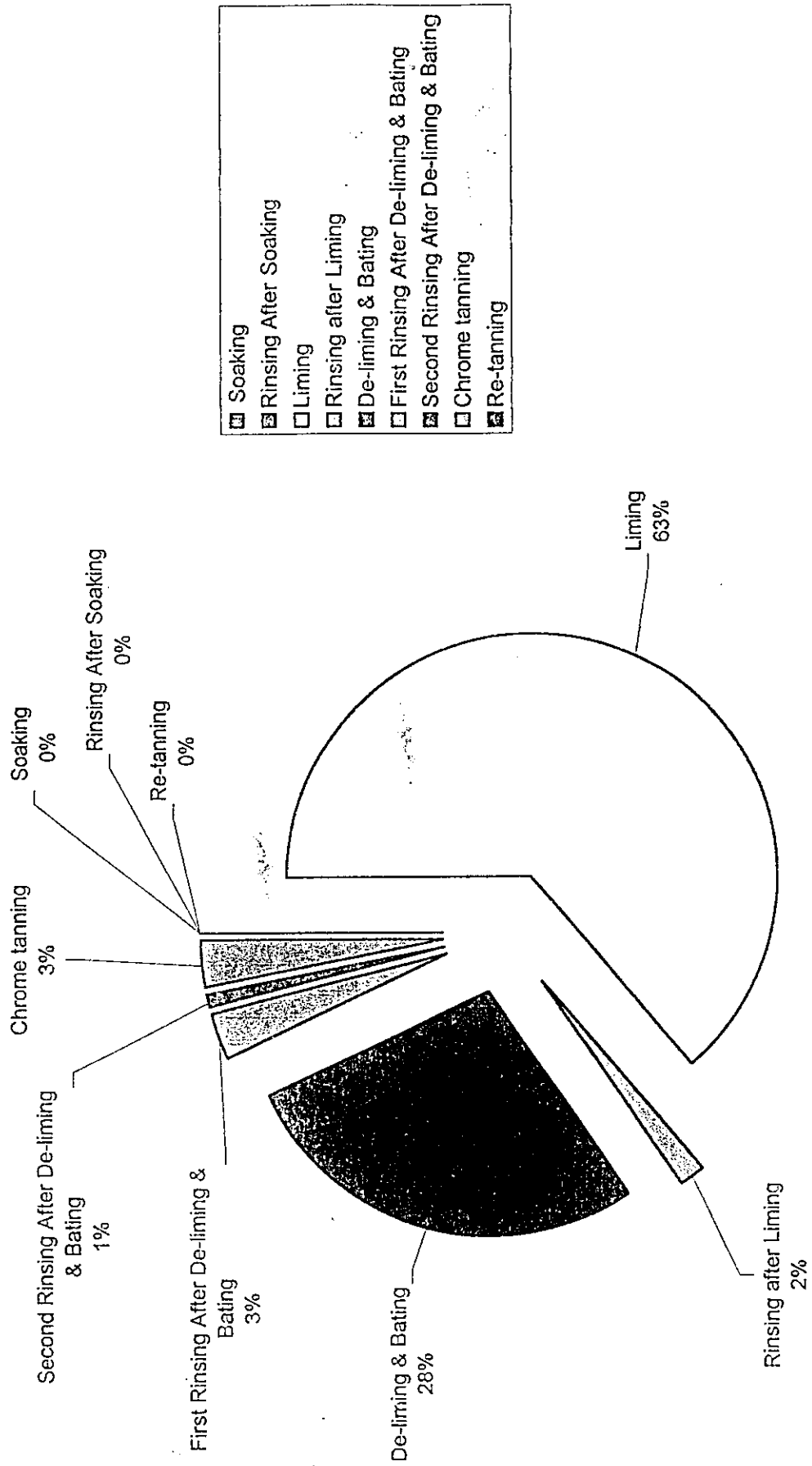


Figure 7: Chlorides in Different Wastewater Streams

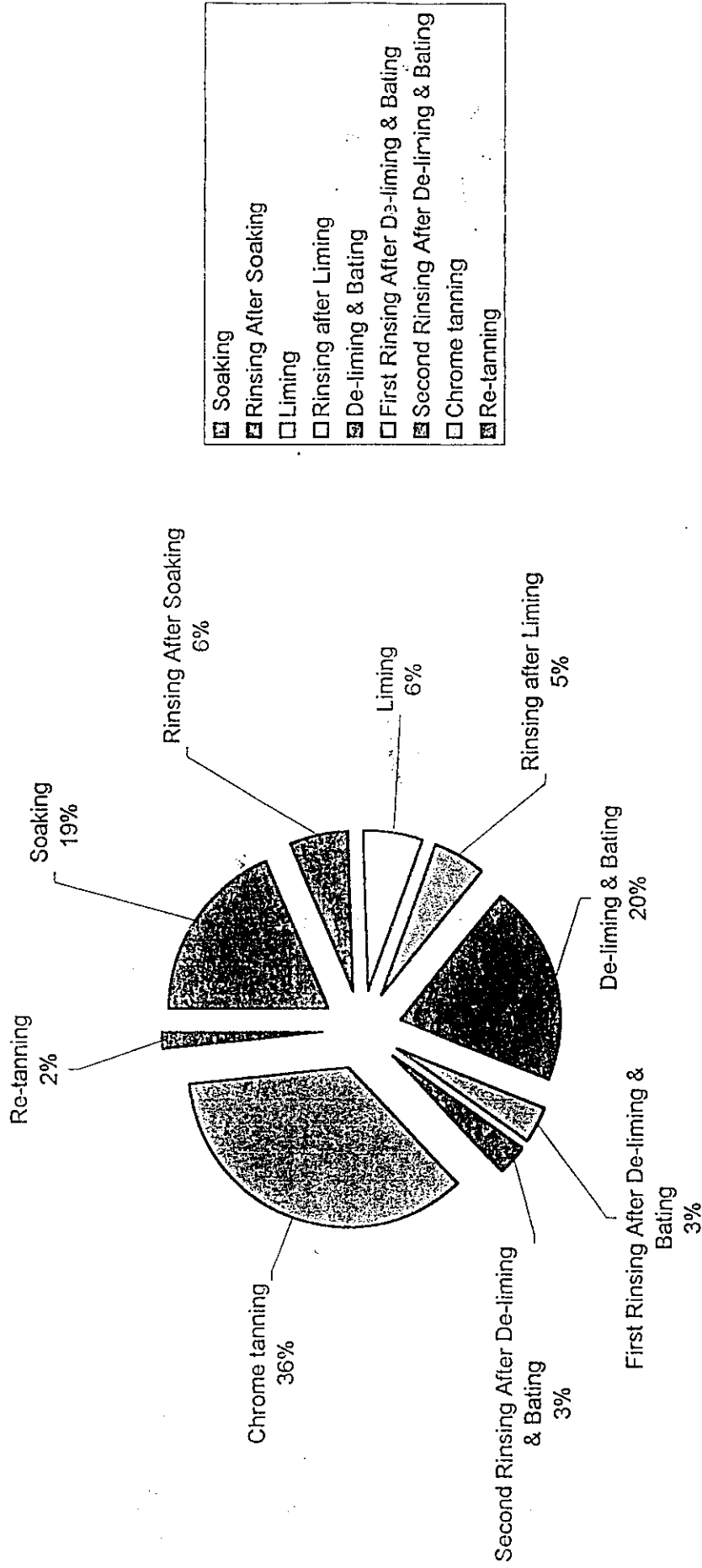
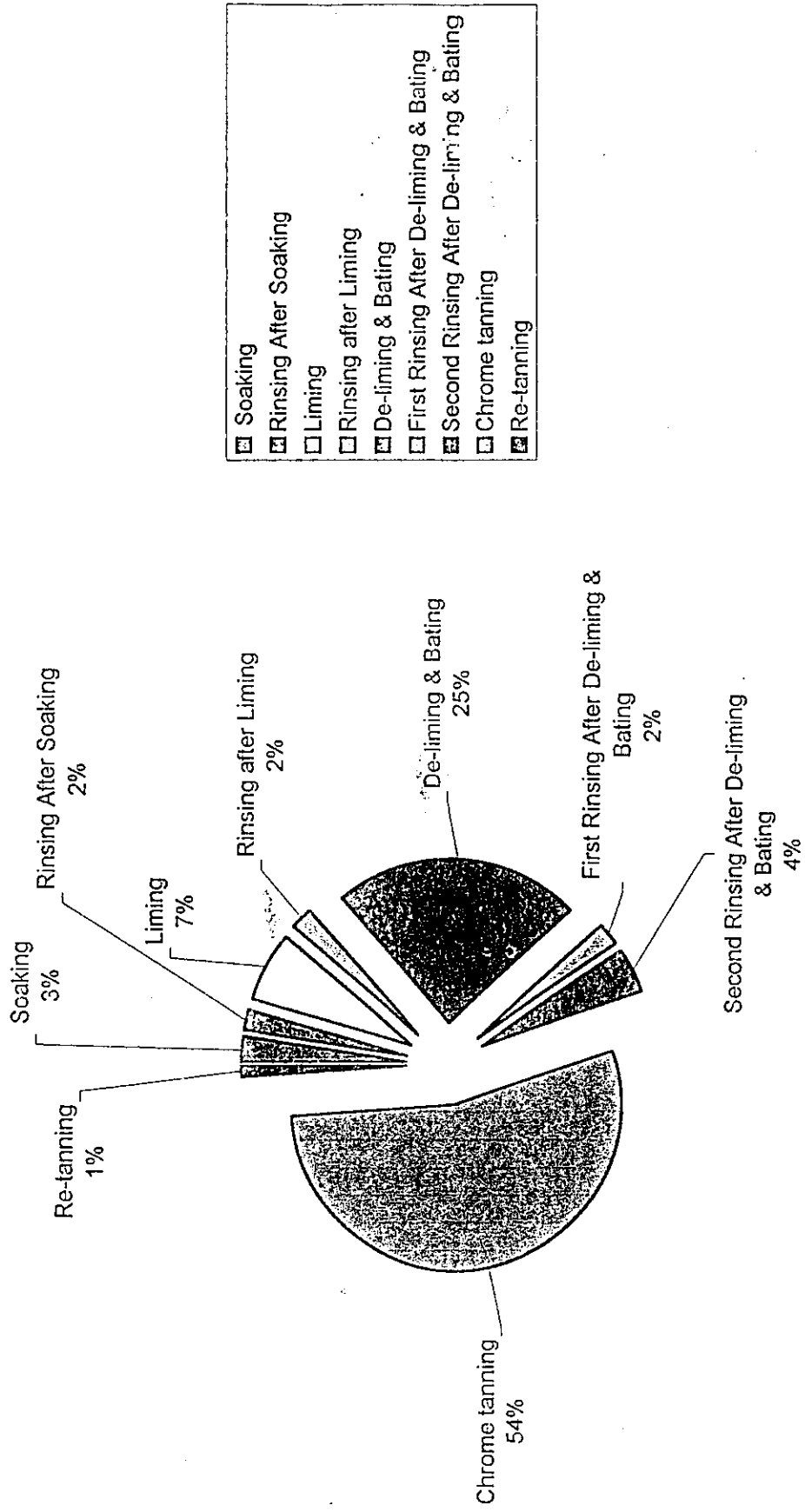
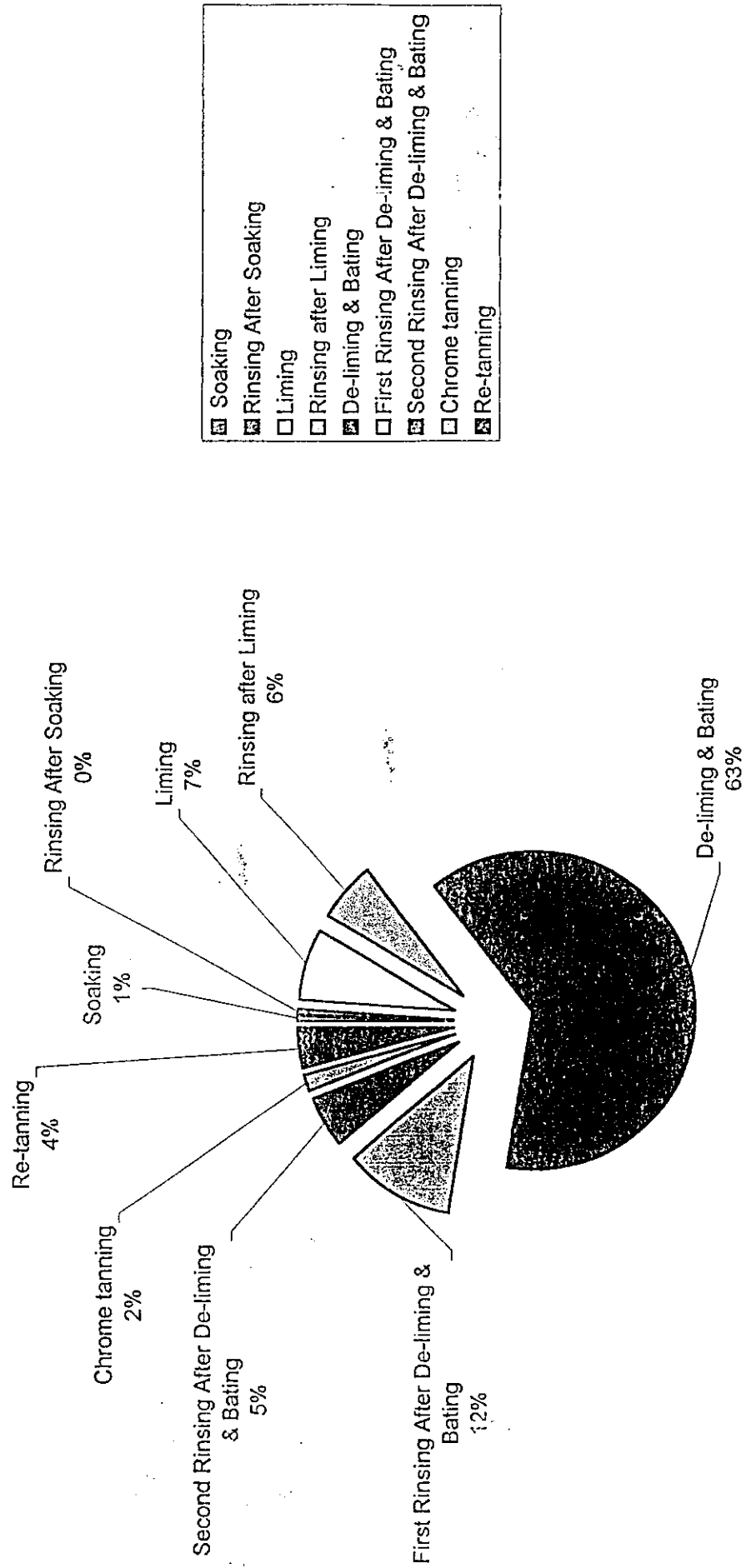


Figure 8: Sulphate in Different Wastewater Streams



- Soaking
- Rinsing After Soaking
- Liming
- Rinsing after Liming
- De-liming & Bating
- First Rinsing After De-liming & Bating
- Second Rinsing After De-liming & Bating
- Chrome tanning
- Re-tanning

Figure 9: Ammonia in Different Wastewater Streams



- Soaking
- Rinsing After Soaking
- Liming
- Rinsing after Liming
- De-liming & Bating
- First Rinsing After De-liming & Bating
- Second Rinsing After De-liming & Bating
- Chrome tanning
- Re-tanning

Figure 10: Phosphate in Different Wastewater Processes

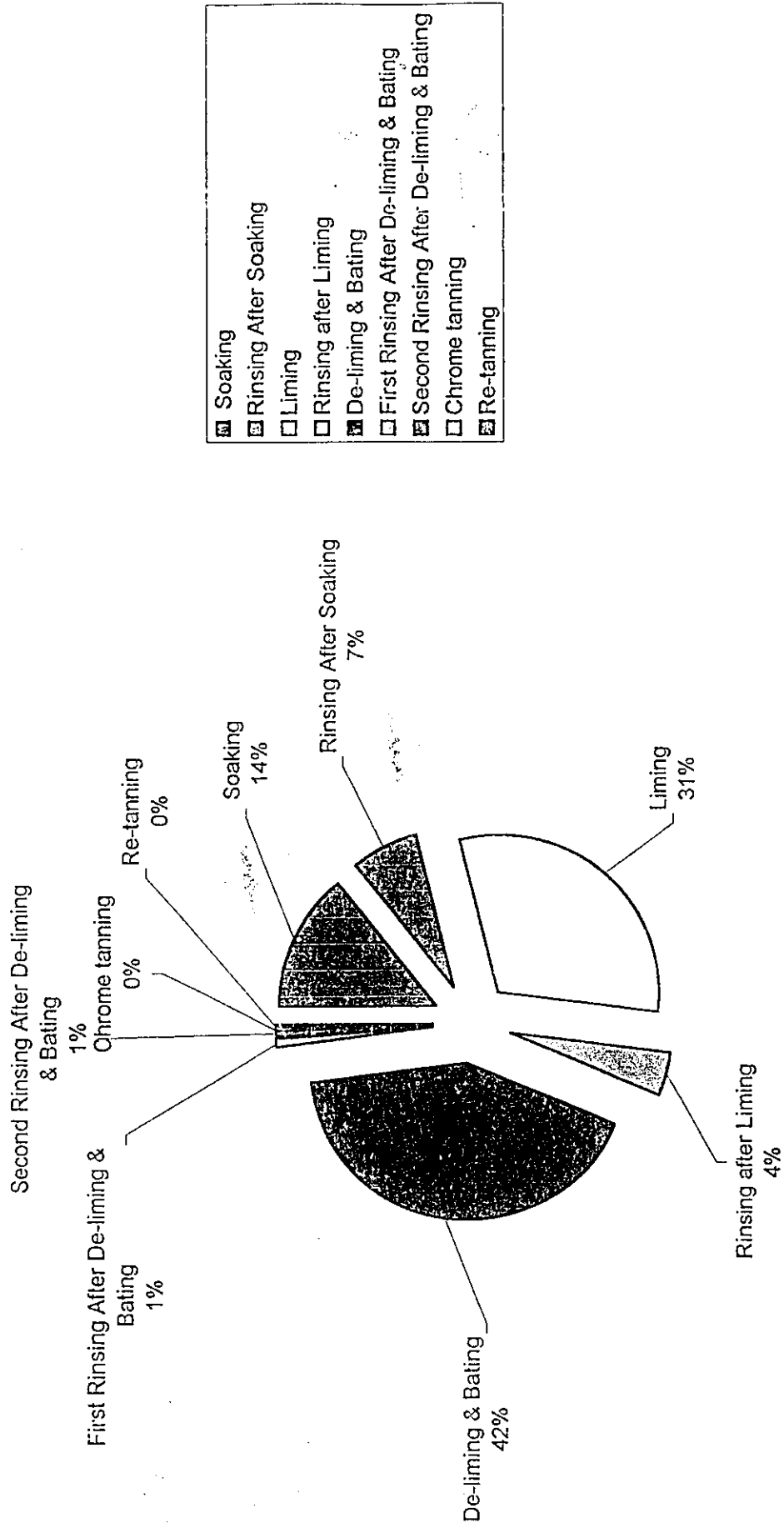
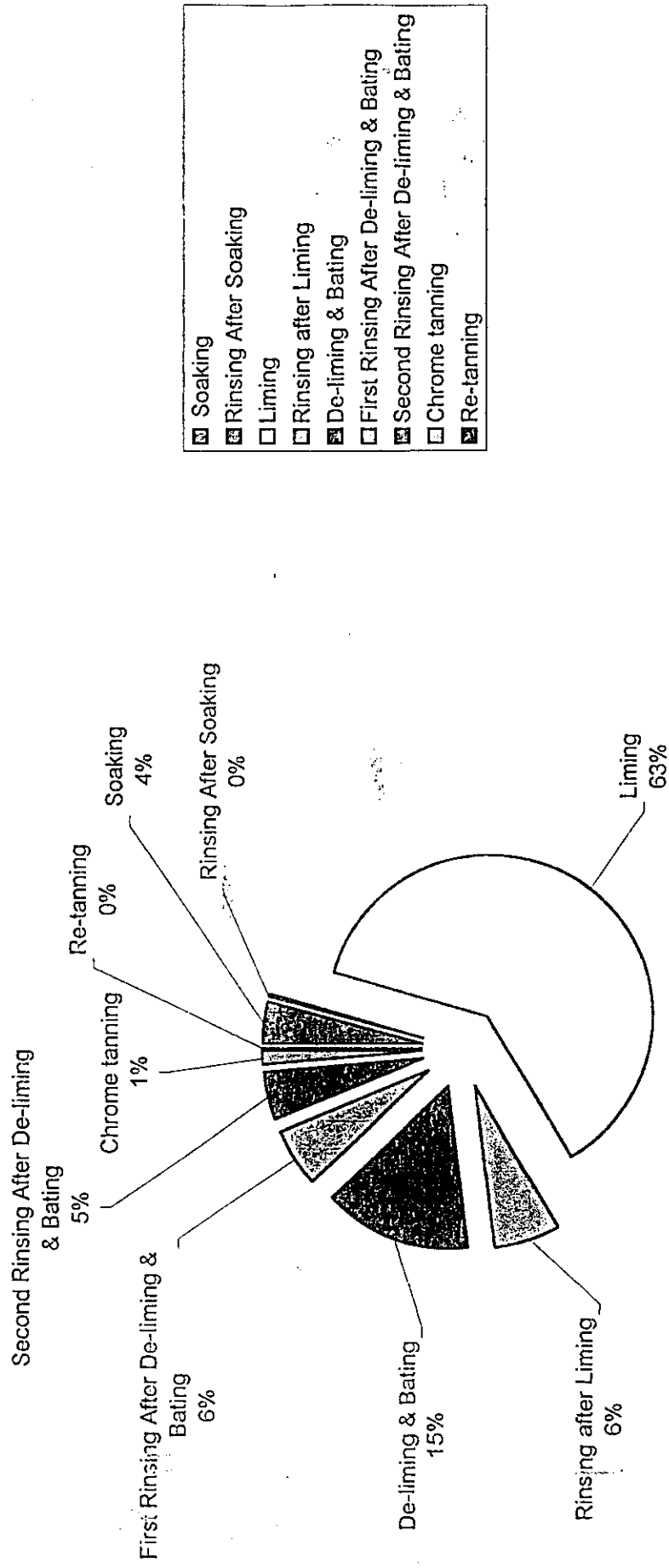


Figure 11: Nitrates in Different Wastewater Streams



- Soaking
- Rinsing After Soaking
- Liming
- Rinsing after Liming
- De-liming & Bating
- First Rinsing After De-liming & Bating
- Second Rinsing After De-liming & Bating
- Chrome tanning
- Re-tanning

APPENDIX 1: Audit Checklists

Checklist # 1: General Overview

1. Company name:
2. Address:
3. Tel:
4. Fax:
5. E-mail:
6. Contact Person:
7. Title:
8. Location (within which municipality):
9. Distance from Main Road:
10. Distance from residential area:
11. Distance from main city:
12. Distance from surface water:
13. Other interesting features:
14. Production area:
15. Total facility area:
16. # of buildings (if one building # of floors per building):
17. Is the company part of a wider corporation (making intermediate products or products for export)?

18. Total number of employees

Full time:

Part Time:

19. Production hours per week:

Per year:

20. Number of shifts per day:

21. Administration structure (draw a chart):

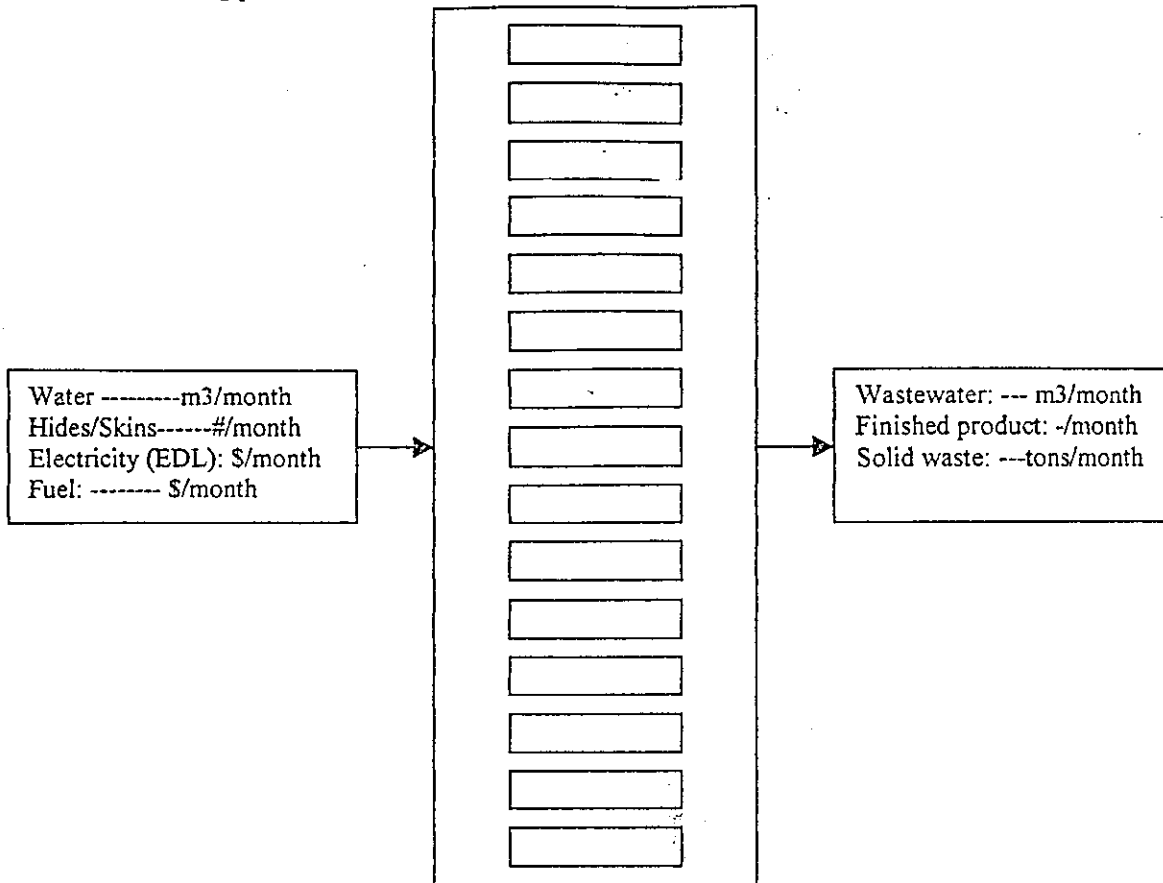
22. Site History:

23. Relation with Regulatory Authorities:

MoE:

Environmental Committee of Association of Lebanese Industrialists:

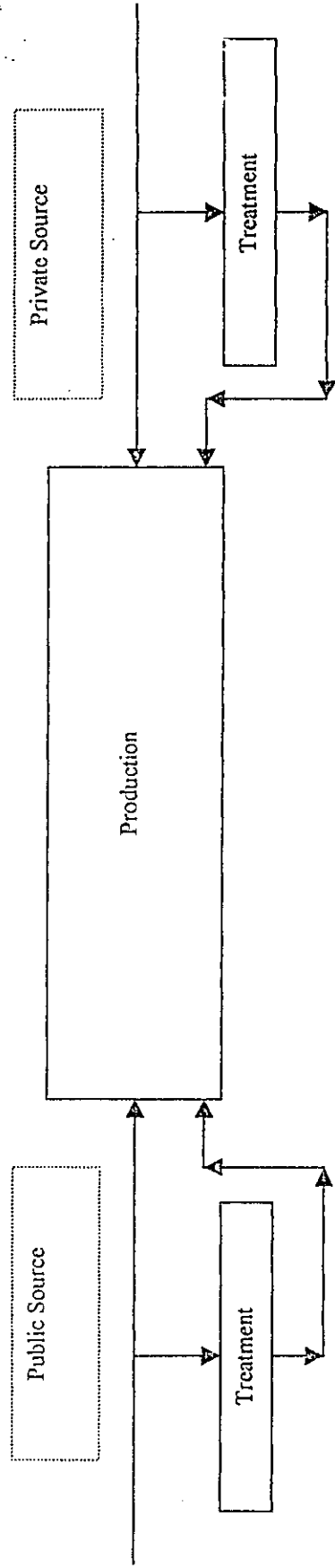
24. List all existing processes and draw the general production flow chart (box form)



25. Sketch Company's location:

Checklist # 2: Water Resources

| | Total Consumption (m ³ /day) | Quality (hardness, pH, etc.) | Purpose Sanitary vs Production (m ³ /day) | Pre-treatment (specify) | Comments & Observations |
|----------|---|------------------------------|--|-------------------------|-------------------------|
| Public | | | | | |
| Private | | | | | |
| Recycled | | | | | |
| Other: | | | | | |



Checklist # 3: Water and Fuel Tanks

Water Tanks

| Tank # | Location | Under or Above Ground | Capacity m ³ | Date of installation Was it ever under leaking tests | Purpose | Observation |
|--------|----------|--------------------------|----------------------------|--|---|-------------|
| e.g. 1 | Basement | above | 8 | 1974 no | Collect municipal water before softening | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

Fuel Tanks

| Tank # | Type of Fuel | Under or Above Ground | Capacity m ³ | Date of installation Was it ever under leaking tests | Location | Observation |
|--------|--------------|-----------------------|-------------------------|---|----------|-------------|
| e.g. 1 | Fuel # 2 | Below | 3 | 1974 no | Basement | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

Checklist # 4: Existing Processes

Process Name:

of required employees:

Batch duration:

Description:

Inputs:

| Type (raw materials, water, steam, etc.) | Quantities (Kg/batch) | Observation (nature, quality, etc.) |
|--|-----------------------|-------------------------------------|
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |

Process Flow Chart and Material Balance

Checklist # 5: Non-Manufacturing Equipment and Processes

Generators

| Generator # | Fuel Type | Consumption (ton/year) | Efficiency | Load (comparing to EDL) | Maintenance Program | Observations |
|-------------|-----------|------------------------|------------|-------------------------|---------------------|--------------|
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

Softeners

| Softener # | Theoretical Capacity (m3/day) | Actual Capacity (m3/day) | Intake (m3/day) | Regeneration Timer vs Volumetric | Amount of resins | Associate filters | Maintenance program | Observations |
|------------|-------------------------------|--------------------------|-----------------|----------------------------------|------------------|-------------------|---------------------|--------------|
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |

Boilers

| Boiler # | Type | Work rate | Steam generated | | Source | | Make up water | | Blow down | | | Discharge location | Observation |
|----------|------|-----------|-----------------|----------|----------|---------|---------------|---------|-----------|----------|---------|--------------------|-------------|
| | | | Destination | Quantity | Quantity | Quality | Quantity | Quality | Frequency | Quantity | Quality | | |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |

Others

| Name and type | Purpose | Description | Observation |
|---------------|---------|-------------|-------------|
| | | | |
| | | | |
| | | | |
| | | | |

Checklist # 6: Storage Areas

General Information

1. What is it used for?
2. Location: Extension of a section Independent Specify: -----
3. Previous accidents:

Fire Leakage Other Specify: -----
4. Are there any plans or programs to prevent or deal with accidents?
 - a. Examples:
 - b. are there workers trained in prevention or accident response:
5. What materials are stored?
 - a. Are they labeled, with indications of their type and danger?
 - b. How are the materials arranged (first in first out)?

Fire

1. Is there a smoke detector system in the ceiling?
 - a. Is there a sprinkler system in the ceiling?
 - b. Are there fire extinguishers?
 - c. Do the workers have easy access to it?
 - d. Is there any other fire fighting equipment in the section?
 - e. Are there emergency exits?
 - f. Are the workers trained to fight fires?

Ventilation

1. Is there a ventilation system?

If yes, continue:

a. Ventilation method: good average bad

b. Describe the method of ventilation:

c. Number of ventilation systems:

d. Means of ventilation: adequate inadequate

e. Required temperature in the section: ----- deg. C. ----- % humidity

2. Is there natural ventilation?

If yes, continue:

a. Windows Openings

b. Number of windows/openings

c. Size of windows/openings

Signs

1. Are there signs warning the workers of dangers?

2. Are there "no smoking" signs?

Lighting

1. Suitable Unsuitable

2. Is there electric lighting? Yes No

3. Neon total number: number not working:

4. Are windows used in lighting?

Spills

1. Does this section handle chemical materials? If yes, continue:

3. Describe is there any procedure used to avoid spillage (overfilling, packaging rupture, etc.):

4. How often you face such problems?

5. How do you deal with it?

